PHYSICAL REVIEW A, VOLUME 62, 052702

Chiralities in double photoionization of rotating linear molecules

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(Received 30 December 1999; revised manuscript received 25 May 2000; published 11 October 2000)

In this paper we investigate the existence and study the properties of linear dichroism and of circular dichroism in a linear, achiral molecule through a process in which absorption of a single photon results in the simultaneous ejection of two electrons. The two dichroic effects are found to provide complementary information about molecular double photoionization and possess very different properties. Dependence of such chiralities on nuclear rotation has properly been studied by using parity-adapted states to represent the target molecule and its doubly charged residual photoion. The discussion presented is independent of any dynamical models. Both magnitude and behavior of the linear as well as circular dichroisms have phenomenologically been calculated for double photoionization in a σ_g^2 shell of a $D_{\infty h}$ molecule rotating in its ${}^1\Sigma_g^+$ electronic state.

PACS number(s): 32.80.Fb, 33.55.Ad

I. INTRODUCTION

Increasing emphasis is being placed on experimental studies of those processes that involve simultaneous ejection of two electrons following the absorption of a single photon by a linear molecular target in general and diatomics [1–7] in particular. This double photoionization (DPI), firstly, is the most direct manifestation of electron-electron correlation [1–5]: The two electrons ejected in a single step share between themselves not only the energy of the absorbed photon in excess to the potential for double ionization of the target, but also the spin-orbit interaction present in the continuum of each of the two freed electrons [8]. These aspects of DPI have been investigated in several experiments [1–5] by measuring spin-unresolved, integrated, and/or angular photocurrents of one or both of the two electrons ejected from the simplest possible molecules like H_2, D_2, etc. In a recent experiment, Dorner *et al.* [5] have measured a DPI cross section when the molecular axis is aligned parallel or perpendicular to the polarization axis of the ionizing radiation.

Secondly, due to Coulomb repulsion between atomic ions, the potential energy of a dication (i.e., doubly charged positive ion) of a diatomic molecule is always greater than its dissociation energy [5–7,9]. Consequently, dictations of diatomic molecules are inherently unstable against their dissociation [5–7,9]. Hall *et al.* [6] have probed the DPI of O_2 using threshold photoelectrons coincidence (TPEsCO) spectroscopy and studied vibrational structure of the shortlived ${O_2}^{2+}$ ground state; whereas, Penent *et al.* [7] have combined TPEsCO spectroscopy with ion time-of-flight spectroscopy and the coincidence technique for studying dissociation dynamics of state-selected doubly charged ions of CO, i.e., CO^{2+}.

Thus DPI is now being increasingly used to study spectroscopy of both neutral linear molecules and of their dications with photoelectrons. Recent advances [10,11] in measuring integrated and/or angular photocurrents arising from the production of singly charged diatomic ions in different rotational states of ${H_2}^+$,${N_2}^+$,NO^+,${O_2}^+$, etc., which have a relatively small moment of inertia, suggest that it should, in principle, be possible to perform in a not too distant future rotationally resolved studies of such processes that involve DPI of at least those linear molecules [10,11] whose high resolution electron spectra for single photoionization (SPI) have already been observed. Such experiments, whose theoretical aspects have recently been developed by us [12], will provide an opportunity to simultaneously study electron-electron correlation in molecules as well as high-resolution spectroscopy of these targets and of their dications. Such spectra will, in addition, reveal how and to what extent the nuclear rotation and electron correlation influence each other in a molecule.

Another dimension to the studies of DPI was added by the recent theoretical predictions that energy and angular distributions of two simultaneously ejected electrons strongly depend upon the helicity of the photon absorbed in an atom [13,14] or a molecule [15]. This prediction has since been experimentally verified in atomic [16–19] as well as molecular [20] DPI. The dependence of the angular distribution on the helicity of the absorbed radiation means that, in a given direction, a different photocurrent is produced by right and left circularly polarized light. This phenomenon has come to be known as circular dichroism (CD). It, being the difference of two measurements, provides a more sensitive test for the states of the target, photoelectrons, and of residual dication. Another advantage in studying CD is that it is much easier to calculate theoretically than the complete angular distribution as the former involves a smaller number of parameters (usually one) than those present in the later. This advantage, in other words, also means that CD measurements cannot provide the full information needed to completely specify the DPI of an atom or molecule. Neither the theoretical [15] study of CD for molecules belonging to one of the 32 point groups nor that performed [20] experimentally for D_2 takes rotation of the nuclei of the target into account. The target molecule in both of these references [15,20] was unpolarized as well as unoriented.

Another observable, analogous to CD, is the linear dichroism (LD). It is the difference between the two angular distributions of photoelectrons, each produced by the absorption of a single photon which is linearly polarized (LP) along two

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1050-2947/2000/62(5)/052702(13)/$15.00

mutually perpendicular directions. LD has so far been studied in the SPI of oriented molecules [21,22] and of polarized atoms [23–26], in the DPI of unpolarized atoms [18], and of unpolarized as well as unoriented ‘‘rotationless’’ D_2 [20].

In this paper we present the first discussion of LD and CD in DPI of a rotating linear molecule. In Sec. II we derive a general mathematical expression for LD and discuss its hitherto unknown properties in the present context. An expression for CD in the DPI of a rotating linear molecule is obtained in Sec. III. Therein, it is shown that its properties are very different from those of LD discussed in Sec. II. We further show in Sec. III that CD and LD provide complementary information on DPI determining two completely different sets of dynamical parameters. Section IV contains the results of our phenomenological calculations of both LD and CD for the DPI in the σ_g^2 shell of a $D_{\infty h}$ molecule in its ${}^1\Sigma_g^+$ state. Conclusions of this study are presented in Sec. V.

II. THEORY

The spin-unresolved DPI of interest to us in this paper can schematically be represented as

$$h\upsilon_r(|\vec{l}_r|=1,m_r)+AB(J_0M_0p_0) \rightarrow AB^{++}(J_fM_fp_f)+e_1(\vec{k}_1)+e_2(\vec{k}_2). \qquad (1)$$

Here AB^{++} is the doubly charged, residual photoion of the molecule *AB*. Both *AB* and AB^{++} belong to the same point group which can be [27] either $C_{\infty v}$ or $D_{\infty h}$. The absorbed photon has angular momentum $|\vec{l}_r|=1$ in the electric dipole ($E1$) approximation, and energy $E_r=h\upsilon_r$. The parameter m_r in Eq. (1) specifies the state of polarization of the incident electromagnetic radiation: $m_r=+1,0,-1$ for the right circular polarization (RCP), linear polarization (LP), and left circular polarization (LCP), respectively. An unpolarized (UP) beam will be represented by an even mixture of RCP and LCP radiations. Further in Eq. (1), $|J_0M_0p_0\rangle$ and $|J_fM_fp_f\rangle$ are the bound states of *AB* with energy E_0 and of AB^{++} possessing energy E_f, respectively. M_0 and M_f are the respective projections of the total angular momenta $\vec{J}_0$ of *AB* and $\vec{J}_f$ of AB^{++} along the space quantization axis. $|J_0M_0p_0\rangle$ has the parity [27,28] p_0, while p_f is that of the state $|J_fM_fp_f\rangle$. The propagation vectors $\vec{k}_1$ (k_1,θ_1,ϕ_1) and $\vec{k}_2$ (k_2,θ_2,ϕ_2) of the photoelectrons e_1 and e_2 are, respectively, defined in Fig. 1 in the photon-fixed coordinate system, say $OX_pY_pZ_p$ with its origin O at the center of mass of the target *AB*. The two photoelectrons e_1 and e_2 equally share between themselves the energy of the absorbed photon in excess to the potential for double ionization of *AB*, i.e., $\varepsilon_1+\varepsilon_2=h\upsilon_r-(E_f-E_0)$. Here $\varepsilon_1=\hbar^2k_1^2/2m$ and $\varepsilon_2=\hbar^2k_2^2/2m$ are the energies of the photoelectrons e_1 and e_2, respectively. Although we do not analyze spins of either of the ejected electrons, the two, nevertheless, share [8] also the spin-orbit interaction present in the continuum of each of them.

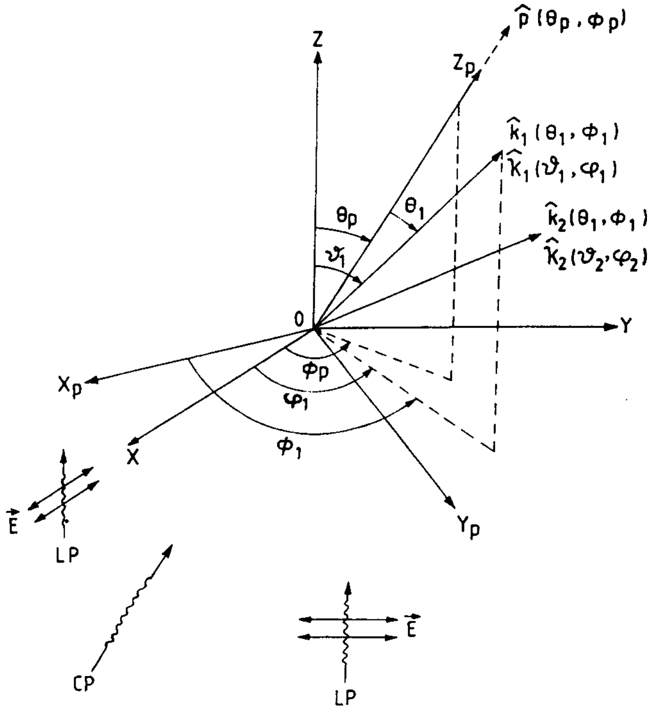

FIG. 1. Space- (or laboratory-) and photon-fixed coordinate systems *OXYZ* and $OX_pY_pZ_p$, respectively.

We have recently shown [12] that the correlation function (CF) for the energy-, angle-, and rotationally resolved process (1) can be written in the following form:

$$\frac{d^3\sigma(m_r)}{d\varepsilon_1 d\hat{k}_1 d\hat{k}_2}=\sum_{\substack{l_1l_2l_p\\ l_1'l_2'l_p'}}\sum_{\substack{s_pJ_p\\ l_t}} G(1m_r;(l_1l_2)l_p;(l_1'l_2')l_p';l_t;\hat{k}_1;\hat{k}_2) \times d_{(l_1l_2)l_p}(s_p;J_p;l_t)\,d^*_{(l_1'l_2')l_p'}(s_p;J_p;l_t). \qquad (2)$$

In this expression,

$$\begin{aligned} G(1m_r;(l_1l_2)l_p;(l_1'l_2')l_p';l_t;\hat{k}_1;\hat{k}_2) &= (-1)^{l_1+l_2+l_p'+l_t+m_r}\frac{\mathcal{K}}{4\pi}(2l_t+1) \\ &\quad\times\begin{pmatrix}1 & 1 & L_r\\ m_r & -m_r & 0\end{pmatrix}\begin{Bmatrix}1 & 1 & L_r\\ l_p & l_p' & l_t\end{Bmatrix} \\ &\quad\times\sum_{\substack{L_1L_2\\ L_r}}(-1)^{L_r}\sqrt{(2L_1+1)(2L_2+1)(2L_r+1)} \\ &\quad\times\begin{pmatrix}l_1 & l_1' & L_1\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_2 & l_2' & L_2\\ 0 & 0 & 0\end{pmatrix} \\ &\quad\times\begin{Bmatrix}l_1 & l_1' & L_1\\ l_2 & l_2' & L_2\\ l_p & l_p' & L_r\end{Bmatrix}\mathcal{Y}^{L_1L_2}_{L_r0}(\hat{k}_1;\hat{k}_2) \end{aligned} \qquad (3a)$$

is the geometrical factor and

$$d_{(l_1 l_2)l_p}(s_p;J_p;l_t) \equiv \langle J_f p_f;(l_1 l_2)l_p;s_p;J_p|F(l_t)|J_0 p_0;1\rangle \tag{3b}$$

is the dynamical amplitude. Equations (2), (3a), and (3b), which correspond [12] to the respective Eqs. (I.25), (I.15), and (I.26), are equally applicable to the description of *AB* and AB^{++} in Eq. (1) in Hund's case [27] (a) or (b). Whereas the geometrical factor (3a) is the same in both of these Hund's coupling schemes, the dynamical amplitude (3b) is, however, given by Eqs. [(I.11),(I.12)] for case (a) and by Eqs. [(I.21),(I.22)] for case (b). We have not reproduced those [12] long expressions for $d_{(l_1 l_2)l_p}(s_p;J_p;l_t)$ herein as they are not relevant to the present discussion. Similarly, detailed descriptions of the explicit forms of the parity-adapted states $|J_0 M_0 p_0\rangle$ of *AB* and $|J_f M_f p_f\rangle$ of AB^{++}, given and used in Ref. [12] in the derivation of expressions (I.11), (I.12), (I.21), and (I.22) will not be needed in this paper. Further in Eq. (3a), coefficient [12] $\mathcal{K}=3\pi(e^2/\alpha_0 E_r)^2$, where α_0 is the dimensionless fine-structure constant and $\mathcal{Y}$'s are bipolar harmonics [29].

Similar to most of the other studies performed hitherto on single and/or double photoionization of free and unpolarized atoms and molecules, the derivation of the geometrical factor (3a) is based on the well-known experimental configuration that the photon frame of reference $OX_pY_pZ_p$ is also the concentric, space-fixed coordinate system *OXYZ* (whose polar *OZ* axis is the space quantization axis). The polar (OZ_p) axis of the photon frame is defined by the state of polarization of the radiation incident in Eq. (1). For example [12], the OZ_p axis is taken to be parallel to the electric vector of the LP ($m_r=0$) ionizing electromagnetic wave, whereas the direction of incidence of RCP, LCP, or UP radiation defines this axis. However, if one is interested in studying the chiral properties of atoms and molecules, specifically the LD, in photoionization, then the photon frame $OX_pY_pZ_p$ is not the most convenient choice for a space-fixed coordinate system. In Fig. 1 in the present paper we, therefore, consider the space-fixed coordinate system *OXYZ* to be different from, but concentric with, the photon frame $OX_pY_pZ_p$. A rotation by the Euler angles [30] $\omega_p(\phi_p,\theta_p,\gamma_p)$ puts the *OXYZ* in coincidence with the photon-frame coordinate system $OX_pY_pZ_p$. The projection M_0 of the total angular momentum $\vec{J}_0$ of *AB* in the state $|J_0 M_0 p_0\rangle$ and that of M_f of the total angular momentum $\vec{J}_f$ of AB^{++} in the state $|J_f M_f p_f\rangle$ are now defined with respect to the quantization axis *OZ*. Let us take $\vec{\kappa}_1$ $(k_1,\vartheta_1,\varphi_1)$ and $\vec{\kappa}_2$ $(k_2,\vartheta_2,\varphi_2)$ to be the propagation vectors (see Fig. 1) of photoelectrons e_1 and e_2, respectively, in the *OXYZ* coordinate system.

In order to express the geometrical factor occurring in Eq. (2) with respect to our new (i.e., *OXYZ*) coordinate system, we need to write the bipolar harmonics present in expression (3a) in terms of the propagation vectors $\vec{\kappa}_1$ and $\vec{\kappa}_2$. This is readily done by using the inverse of the relation (2) given on page 87 in Ref. [29]. We, therefore, have

$$Y_{L_1}^{M_L}(\hat{k}_1)=\sum_{M_1}\mathcal{D}_{M_L M_1}^{L_1 *}(\omega_p)Y_{L_1}^{M_1}(\hat{\kappa}_1) \tag{4}$$

and a similar relation for $Y_{L_2}^{M_L}(\hat{k}_2)$. Here $\mathcal{D}$'s are the rotational harmonics [30]. We now substitute Eq. (4) in the expression for bipolar harmonics present in Eq. (3a). The resulting expression for the geometrical factor can be simplified by using the Clebsch-Gordon series [30] in $3j$ symbols for combining the two rotational harmonics and the orthonormality of $3j$ symbols. The final form of the CF (2) specified with respect to the *OXYZ* coordinate system can be written as

$$\begin{aligned}\frac{d^3\sigma(m_r)}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}&=(-1)^{m_r}\sqrt{4\pi}\\&\times\sum_{\substack{L_r M_r\\L_1 L_2}}(-1)^{L_r+M_r}\begin{pmatrix}1&1&L_r\\m_r&-m_r&0\end{pmatrix}\\&\times\gamma_{L_1L_2}(L_r;\varepsilon_1\varepsilon_2)\mathcal{Y}_{L_r,-M_r}^{L_1\,L_2}(\hat{\kappa}_1,\hat{\kappa}_2)Y_{L_r}^{M_r}(\hat{p})\end{aligned} \tag{5a}$$

with

$$\begin{aligned}\gamma_{L_1L_2}(L_r;\varepsilon_1\varepsilon_2)&=\frac{\mathcal{K}}{4\pi}\sqrt{(2L_1+1)(2L_2+1)}\\&\times\sum_{\substack{l_1\,l_2\,l_p\\l_1'\,l_2'\,l_p'}}\sum_{\substack{s_pJ_p\\l_t}}(-1)^{l_1+l_2+l_p'+l_t}(2l_t+1)\\&\times\begin{pmatrix}l_1&l_1'&L_1\\0&0&0\end{pmatrix}\begin{pmatrix}l_2&l_2'&L_2\\0&0&0\end{pmatrix}\\&\times\begin{Bmatrix}1&1&L_r\\l_p&l_p'&l_t\end{Bmatrix}\begin{Bmatrix}l_1&l_1'&L_1\\l_2&l_2'&L_2\\l_p&l_p'&L_r\end{Bmatrix}\\&\times d_{(l_1l_2)l_p}(s_p;J_p;l_t)d^*_{(l_1'l_2')l_p'}(s_p;J_p;l_t)\end{aligned} \tag{5b}$$

and $\hat{p}(\theta_p,\phi_p)$, in Fig. 1, is the unit vector in the direction of the OZ_p axis with respect to the *OXYZ* coordinate system. Obviously, in the special case when photon frame $OX_pY_pZ_p$ coincides with the space frame *OXYZ* (i.e., $\theta_p=0$), CF (5) becomes identical to that given by Eq. (2). In the CF (5), while the total number of allowed values for L_1 and L_2 are $(2l_1+1)$ and $(2l_2+1)$, respectively, L_r can take only three values (i.e., $L_r=0-2$). Thus, complete specification of the CF (5) requires a knowledge of three sets of dynamical parameters, namely, $\gamma_{L_1L_2}(0;\varepsilon_1\varepsilon_2)$, $\gamma_{L_1L_2}(1;\varepsilon_1\varepsilon_2)$, and $\gamma_{L_1L_2}(2;\varepsilon_1\varepsilon_2)$.

According to the selection rule (I.13c), the dynamical amplitudes $d_{(l_1l_2)l_p}(s_p;J_p;l_t)$ and $d_{(l_1'l_2')l_p'}(s_p;J_p;l_t)$ present in Eq. (5b) will vanish unless each of $l_1+l_2+J_0-J_f+p_0+p_f$ and $l_1'+l_2'+J_0-J_f+p_0+p_f$ is even. Since both [12] J_0-J_f and p_0+p_f are always integers, we must therefore have $l_1+l_2+l_1'+l_2'=$even. A combination of this requirement with the well-known properties [30] (i.e., $l_1+l_1'+L_1=\text{even}$ and $l_2+l_2'+L_2=\text{even}$) of the first two 3-j symbols occurring in Eq. (5b) immediately gives that $L_1+L_2=\text{even}$. This parity of L_1+L_2 can be used to readily derive following relevant properties of the bipolar harmonics [29]

$$\mathcal{Y}^{L_1\,L_2}_{L_r,-M_r}(\hat{\kappa}_1,\hat{\kappa}_2)=(-1)^{M_r}\sqrt{2L_r+1}\times\sum_{M_1M_2}\begin{pmatrix}L_1 & L_2 & L_r\\ M_1 & M_2 & M_r\end{pmatrix}\times Y^{M_1}_{L_1}(\hat{\kappa}_1)Y^{M_2}_{L_2}(\hat{\kappa}_2) \tag{6}$$

present in the angular distribution (5a),

$$\text{(i)}\quad \mathcal{Y}^{L_1\,L_2 *}_{L_r,-M_r}(\hat{\kappa}_1,\hat{\kappa}_2)=(-1)^{L_r+M_r}\mathcal{Y}^{L_1L_2}_{L_rM_r}(\hat{\kappa}_1,\hat{\kappa}_2). \tag{7a}$$

Thus, harmonics (6) with $M_r=0$ is pure real or imaginary according to $L_r=\text{even}$ or odd, respectively.

$$\text{(ii)}\quad \mathcal{Y}^{L_1\,L_2}_{L_r,-M_r}(-\hat{\kappa}_1,-\hat{\kappa}_2)=\mathcal{Y}^{L_1\,L_2}_{L_r,-M_r}(\hat{\kappa}_1,\hat{\kappa}_2). \tag{7b}$$

That is, bipolar harmonics (6) always have even parity.

$$\text{(iii)}\quad \mathcal{Y}^{L_1\,L_2}_{L_r,-M_r}(\hat{\kappa}_2,\hat{\kappa}_1)=(-1)^{L_r}\mathcal{Y}^{L_2\,L_1}_{L_r,-M_r}(\hat{\kappa}_1,\hat{\kappa}_2). \tag{7c}$$

This implies bipolar harmonics $\mathcal{Y}^{L\,L}_{L_r,-M_r}(\hat{\kappa},\hat{\kappa})=0$ always for an odd L_r.

$$\begin{aligned}\text{(iv)}\quad &\mathcal{Y}^{L_1\,L_2}_{L_r,-M_r}(\vartheta_1,\varphi_1;\vartheta_2,\varphi_1+n\pi)\\ &=(-1)^{M_r}\sqrt{2L_r+1}\\ &\quad\times\sum_{M_1M_2}(-1)^{nM_2}e^{-iM_r\varphi_1}\begin{pmatrix}L_1 & L_2 & L_r\\ M_1 & M_2 & M_r\end{pmatrix}\\ &\quad\times\mathcal{L}^{M_1}_{L_1}(\cos\vartheta_1)\mathcal{L}^{M_2}_{L_2}(\cos\vartheta_2)\end{aligned} \tag{7d}$$

with

$$\mathcal{L}^m_l(\cos\vartheta)=(-1)^m\sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}}P^m_l(\cos\vartheta)$$

such that $\mathcal{L}^{-m}_l(\cos\vartheta)=(-1)^{-m}\mathcal{L}^m_l(\cos\vartheta)$. Here $P^m_l(\cos\vartheta)$ is the associated Legendre polynomial [30]. Thus Eq. (7d), where n is an integer, gives us a bipolar harmonics for the special case when $\hat{\kappa}_1(\vartheta_1,\varphi_1)$ and $\hat{\kappa}_2(\vartheta_2,\varphi_2=\varphi_1+n\pi)$ lie in a plane which contains the polar OZ axis of the space frame (see Fig. 1). This is pure real for $\hat{\kappa}_1$ in any direction but $M_r=0$, or $\hat{\kappa}_1$ in the X-Z plane (i.e., $\varphi_1=0$ or π) for all permitted values of M_r or $\hat{\kappa}_1$ in the Y-Z plane (i.e., $\varphi_1=\pi/2$ or $3\pi/2$) for M_r even; on the other hand, Eq. (7d) becomes pure imaginary if $\hat{\kappa}_1$ is in the Y-Z plane and M_r is odd. In the remaining cases, it is complex. An important corollary to Eq. (7d) is when $\hat{\kappa}_2\|-\hat{\kappa}_1=-\hat{\kappa}(\vartheta,\varphi)$ [i.e., $\hat{\kappa}_1$ and $\hat{\kappa}_2$ are in the opposite directions with $\theta_2=\pi-\vartheta$, $\varphi_2=\varphi+\pi$]. In this special case

$$\begin{aligned}\mathcal{Y}^{L_1\,L_2}_{L_r,-M_r}(\hat{\kappa}_1,\hat{\kappa}_2)&=\mathcal{Y}^{L_1\,L_2}_{L_r,-M_r}(\hat{\kappa},-\hat{\kappa})\\ &=(-1)^{L_2}\mathcal{Y}^{L_1\,L_2}_{L_r,-M_r}(\hat{\kappa},\hat{\kappa})\\ &=(-1)^{L_2+M_r}\sqrt{\frac{(2L_1+1)(2L_2+1)}{4\pi}}\\ &\quad\times\begin{pmatrix}L_1 & L_2 & L_r\\ 0 & 0 & 0\end{pmatrix}Y^{M_r}_{L_r}(\hat{\kappa}).\end{aligned} \tag{7e}$$

Thus, the bipolar harmonics (6) in a collinear geometry may exist if L_r is even. In this case, it simply becomes a multiple of the spherical harmonics $Y^{M_r}_{L_r}(\hat{\kappa})$.

(v) Let us integrate Eq. (6) over one of the directions, say $\hat{\kappa}_2$. This yields

$$\int\mathcal{Y}^{L_1\,L_2}_{L_r,-M_r}(\hat{\kappa}_1,\hat{\kappa}_2)d\hat{\kappa}_2=(-1)^{L_r}\sqrt{4\pi}\,\delta_{L_1L_r}\delta_{0L_2}Y^{-M_r}_{L_r}(\hat{\kappa}_1); \tag{7f}$$

consequently,

$$\int\mathcal{Y}^{L_1\,L_2}_{L_r,-M_r}(\hat{\kappa}_1,\hat{\kappa}_2)d\hat{\kappa}_2\,d\hat{\kappa}_1=4\pi\delta_{0L_1}\delta_{0L_2}\delta_{0L_r}\delta_{0M_r}. \tag{7g}$$

A. Linear dichroism in double photoionization

In order to obtain an expression for LD in the space frame, we consider two LP beams of ionizing radiation, one each with its electric vector along the OX (i.e., $\theta_p=\pi/2$, $\phi_p=0$) and OY (i.e., $\theta_p=\pi/2$, $\phi_p=\pi/2$) axes. LD is then given by

$$\begin{aligned}\frac{d^3\sigma^{\text{LD}}}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}&=\left.\frac{d^3\sigma(m_r=0)}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}\right|_{OX}-\left.\frac{d^3\sigma(m_r=0)}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}\right|_{OY}\\ &=2\sum_{L_1L_2}\mathcal{R}[\mathcal{Y}^{L_1L_2}_{2\,2}(\hat{\kappa}_1,\hat{\kappa}_2)]\gamma_{L_1L_2}(2;\varepsilon_1\varepsilon_2).\end{aligned} \tag{8}$$

In arriving at the last result we have used the CF (5a) and the property (7a) of bipolar harmonics, in addition to making some other simplifications. Expression (8) obviously corresponds to an experimented geometry in which each of the two photon beams, LP along mutually perpendicular directions, are incident along the polar OZ axis of the space frame (see Fig. 1).

The LD (8) is thus completely determined by only the last [i.e., $\gamma_{L_1L_2}(2;\varepsilon_1\varepsilon_2)$] of the three sets of dynamical parameters needed for the complete specification of CF (5). No information about the remaining two parameters can be extracted from Eq. (8). Thus, although the calculation of LD is, at least theoretically, much easier than that of the angular photocurrent (5a) for the DPI, however, the process of taking difference involved in the evaluation of LD wipes out some information about the CF (5) of the DPI (1). One can readily deduce the following properties of the LD (8).

(i) The requirement for the LD to be an observable demands that the coefficients $\gamma_{L_1L_2}(2;\varepsilon_1\varepsilon_2)$ must be pure real.

(ii) Property (7c) combined with the requirement that the LD (8) should remain invariant under the exchange of two photoelectrons means that

$$\gamma_{L_1L_2}(2;\varepsilon_2\varepsilon_1)=\gamma_{L_2L_1}(2;\varepsilon_1\varepsilon_2).$$

Thus of the three dynamical parameters (corresponding to $L_2=L_1,\ L_1\pm 2$) that contribute to Eq. (8), none of $\gamma_{L_1L_2}(2;\varepsilon_2\varepsilon_1)$ is necessarily zero for two photoelectrons ejected with equal energy $\varepsilon_1=\varepsilon_2=\varepsilon$ (say). Therefore, LD (8) may exist even for that DPI (1) wherein both electrons move out from the molecule *AB* with equal energies.

(iii) LD in a coplanar geometry which contains two photoelectrons and the *OZ* axis of the space frame (i.e., the direction of propagation of two photon beams in the space frame) in a single plane is obtained by substituting Eq. (7d) in Eq. (8), i.e.,

$$\frac{d^3\sigma^{\mathrm{LD}}}{d\varepsilon_1 d\vartheta_1 d\varphi_1 d\vartheta_2}=2\sqrt{5}\cos 2\varphi_1\sum_{\substack{L_1\,L_2\\M_1\,M_2}}(-1)^{nM_2}\times\begin{pmatrix}L_1 & L_2 & 2\\ M_1 & M_2 & -2\end{pmatrix}\mathcal{L}_{L_1}^{M_1}(\cos\vartheta_1)\times\mathcal{L}_{L_2}^{M_2}(\cos\vartheta_2)\,\gamma_{L_1L_2}(2;\varepsilon_1\varepsilon_2). \qquad (9a)$$

This expression is not zero in general. It, however, obviously vanishes when the angle between the *Z-X* plane and the plane that contains two photoelectrons is given by $\varphi_1=(2m+1)\pi/4$ with $m=0-3$. Thus LD in the DPI may exist even in a coplanar experimental arrangement. But, the LD in this setup will identically vanish if this plane bisects the angle between two LP beams of electromagnetic waves with their electric field vectors in the *X* and *Y* directions.

(iv) In order to obtain LD in a collinear setup when two photoelectrons are moving, say, in opposite directions, we substitute Eq. (7e) in Eq. (8). This yields

$$\frac{d^2\sigma^{\mathrm{LD}}}{d\varepsilon_1 d\hat{\kappa}}=\frac{1}{4\pi}\sqrt{\frac{15}{2}}\sin^2\vartheta\cos 2\varphi\times\sum_{L_1L_2}(-1)^{L_2}\sqrt{(2L_1+1)(2L_2+1)}\times\begin{pmatrix}L_1 & L_2 & 2\\ 0 & 0 & 0\end{pmatrix}\gamma_{L_1L_2}(2;\varepsilon_1\varepsilon_2). \qquad (9b)$$

This expression is not necessarily zero. It, however, vanishes identically if the line joining the two photoelectrons has a direction defined by the spherical angles ($\vartheta=0$ or π,φ) or $[\vartheta,\varphi=(2m+1)\pi/4]$, i.e., the two photoelectrons are ejected either parallel to the polar axis or along a line which makes an angle $\varphi=(2m+1)\pi/4$ with the *Z-X* plane.

(v) Integration of Eq. (8) over the photoelectron propagation directions $\hat{\kappa}_1$ and $\hat{\kappa}_2$ and the subsequent use of the property (7g) immediately shows that LD does not exist in the integrated photocurrent produced in a DPI experiment.

(vi) In order to see as to what happens to LD in a noncoincident experiment on the DPI, i.e., when one (say, e_1) of the two photoelectrons is only observed, let us integrate Eq. (8) over $\hat{\kappa}_2$. An application of the property (7f) gives

$$\frac{d^2\sigma^{\mathrm{LD}}}{d\varepsilon_1 d\hat{\kappa}_1}=\int\frac{d^3\sigma^{\mathrm{LD}}}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}d\hat{\kappa}_2=\sqrt{\frac{15}{2}}\gamma_{20}(2;\varepsilon_1,\varepsilon_2)\sin^2\vartheta_1\cos 2\varphi_1. \qquad (10a)$$

After substituting (5b), we can write

$$\frac{d^2\sigma^{\mathrm{LD}}}{d\varepsilon_1 d\hat{\kappa}_1}=\frac{3}{8\pi}\left(\frac{d\sigma}{d\varepsilon_1}\right)\beta_1\sin^2\vartheta_1\cos 2\varphi_1, \qquad (10b)$$

where the integrated cross section $(d\sigma/d\varepsilon_1)$ and the parameter β_1 are defined in Eqs. (I. 32) applicable to a noncoincident DPI experiment [see also Eq. (18)]. The result (10b) is formally identical to that first derived in Ref. [21] for the SPI of molecules with a random orientation in space and without taking the rotation of their nuclei into account. A comparison of Eq. (9b) with the above expression shows that the angular dependence of LD when both photoelectrons are observed in a collinear experimental geometry is identical to that in a noncoincident DPI. The former contains the spherical angles of the line joining two photoelectrons, whereas those of the single detected photoelectrons are present in the latter. Both sets of spherical angles are, however, referred to the space frame, i.e., the *OXYZ* coordinate system in Fig. 1. The ratio (for $\vartheta_1=\vartheta,\ \varphi_1=\varphi$)

$$\frac{d^2\sigma^{\mathrm{LD}}}{d\varepsilon_1 d\hat{\kappa}}\Bigg/\frac{d^2\sigma^{\mathrm{LD}}}{d\varepsilon_1 d\hat{\kappa}_1}=\sqrt{\frac{10}{3}}\left(\beta_1\frac{d\sigma}{d\varepsilon_1}\right)^{-1}\sum_{L_1L_2}(-1)^{L_2}\times\sqrt{(2L_1+1)(2L_2+1)}\times\begin{pmatrix}L_1 & L_2 & 2\\ 0 & 0 & 0\end{pmatrix}\gamma_{L_1L_2}(2;\varepsilon_1\varepsilon_2) \qquad (11)$$

of two LD's is, therefore, isotropic and is completely determined by the dynamical terms. Noncoincident DPI experiments are easier to perform compared to those in which both photoelectrons are observed simultaneously. Expression (11) provides a simple method to determine the other if one of the two is known. As this ratio of the two LD's is totally isotropic, they can be measured in any one of the convenient directions.

B. Circular dichroism in double photoionization

CD in the DPI of a rotating linear molecule is obtained from Eq. (5a) to be

$$\frac{d^3\sigma^{\mathrm{CD}}}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}=\frac{d^3\sigma(m_r=+1)}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}-\frac{d^3\sigma(m_r=-1)}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}$$
$$=2\left(\frac{2\pi}{3}\right)^{1/2}\sum_{\substack{L_1L_2\\M_r}}(-1)^{M_r}\mathcal{Y}^{L_1\,L_2}_{1,-M_r}$$
$$\times(\hat{\kappa}_1,\hat{\kappa}_2)Y_1^{M_r}(\hat{p})\gamma_{L_1L_2}(1;\varepsilon_1\varepsilon_2). \quad (12)$$

On comparing this expression with that given in Eq. (8), we find that CD and LD are determined by entirely different dynamical parameters, namely, $\gamma_{L_1L_2}(1;\varepsilon_1\varepsilon_2)$ and $\gamma_{L_1L_2}(2;\varepsilon_1\varepsilon_2)$, respectively. Thus, LD and CD provide complimentary information on the DPI of a rotating linear molecule. Although, similar to LD, theoretical calculation of CD is easier as well; the information on the DPI lost during the determination of either of the two observables (CD and LD) is, however, completely different in each case.

The bipolar harmonics $\mathcal{Y}^{L_1\,L_2}_{1,-M_r}(\hat{\kappa}_1,\hat{\kappa}_2)$ in Eq. (6) contains a 3-*j* symbol, whereas a 9-*j* symbol, among others, is present in the dynamical coefficient $\gamma_{L_1L_2}(1;\varepsilon_1\varepsilon_2)$ [see Eq. (5b)]. Whenever the triangular condition $\Delta(L_1,L_2,1)$ is not satisfied, both of these symbols will vanish. Further, it has already been shown in this paper that L_1+L_2 is always even in the DPI of a rotating linear molecule. Simultaneous satisfaction of these two requirements imposes the condition that, out of the three allowed values of $L_2(=L_1,L_1\pm1)$, the CD (12) may exist only for $L_2=L_1=L$ (say). Using this and some other simplifications, along with the relation (7a), CD (12) reduces to

$$\frac{d^3\sigma^{\mathrm{CD}}}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}=\sum_L\,\{\sqrt{2}\mathcal{Y}^{LL}_{10}(\hat{\kappa}_1,\hat{\kappa}_2)\cos\theta_p-i2\,\mathrm{Im}$$
$$\times[\mathcal{Y}^{LL}_{11}(\hat{\kappa}_1,\hat{\kappa}_2)e^{-i\phi_p}]\sin\theta_p\}\gamma_{LL}(1;\varepsilon_1\varepsilon_2). \quad (13)$$

This expression provides CD for an experimental geometry in which the CP ionizing radiation is incident along a direction specified by the spherical angles (θ_p,ϕ_p) in the space frame *OXYZ* (see Fig. 1). The form of relation (13) is obviously different from those derived in Refs. [13–15]. However, as soon as we specialize it to the case $\theta_p=0$, CD (13) becomes formally identical to those given in [13–15]. This general expression for CD in the DPI of rotating linear molecules can readily be shown to possess the following properties.

(i) The first interesting feature of Eq. (13) is that it always vanishes whenever

$$\tan\theta_p=-\frac{i}{\sqrt{2}}\,\frac{\Sigma_L\mathcal{Y}^{LL}_{10}(\hat{\kappa}_1,\hat{\kappa}_2)\gamma_{LL}(1;\varepsilon_1\varepsilon_2)}{\Sigma_L\,\mathrm{Im}[\mathcal{Y}^{LL}_{11}(\hat{\kappa}_1,\hat{\kappa}_2)e^{-i\phi_p}]\gamma_{LL}(1;\varepsilon_1\varepsilon_2)}. \quad (14)$$

Here θ_p is the angle between the direction of incidence of the CP ionizing radiation and the polar axis of the *OXYZ* space-frame (see Fig. 1). Equation (14) gives a general result which includes both the directions of propagation of ejected photoelectrons e_1 and e_2 as well as the dynamics of DPI. This is a geometrical condition for CD to become identically zero and, to the best of our knowledge, has not hitherto been reported in the literature [13–20]. Conversely, it [i.e., Eq. (14)] can readily be implemented to determine the degree of CP of the incident radiation. However, no such condition was found for the LD analyzed in Sec. II A.

(ii) According to (7a), $\mathcal{Y}^{11}_{10}$ is pure imaginary. Consequently, the geometrical part [contained in the curly brackets on the right-hand side of Eq. (13)] of CD is pure imaginary. This, in turn, implies that the dynamical coefficient $\gamma_{LL}(1;\varepsilon_1\varepsilon_2)$ is pure imaginary as well. But, the corresponding parameter $\gamma_{L_1L_2}(2;\varepsilon_1\varepsilon_2)$ responsible for the existence of LD (8) in the angular distribution of two photoelectrons e_1 and e_2 has already been shown to be pure real in this paper

(iii) The invariance of CD (13) under exchange of two photoelectrons combined with the condition (7c) means that $\gamma_{LL}(1;\varepsilon\varepsilon)=0$. Thus, when two electrons in the DPI of a rotating linear molecule are ejected with equal energies, CD vanishes identically. This is a dynamical condition for the nonexistence of CD. But, according to the discussion presented in Sec. III A there is no such condition applicable to LD.

(iv) It is obvious from Eq. (7d) that when e_1, e_2, and the *OZ* axis are in a single plane, $\mathcal{Y}^{LL}_{10}(\hat{\kappa}_1,\hat{\kappa}_2)$ becomes pure real. Therefore, the first term, present in Eq. (13), will not contribute. Hence, the CD in this configuration is given by

$$\frac{d^3\sigma^{\mathrm{CD}}}{d\varepsilon_1 d\vartheta_1 d\varphi_1 d\vartheta_2}=i2\sqrt{3}\sin\theta_p\sin(\varphi_1-\phi_p)$$
$$\times\sum_{\substack{L\\M_1M_2}}(-1)^{nM_2}\begin{pmatrix}L & L & 1\\ M_1 & M_2 & -1\end{pmatrix}$$
$$\times\mathcal{L}_L^{M_1}(\cos\vartheta_1)\mathcal{L}_L^{M_2}(\cos\vartheta_2)\gamma_{LL}(1;\varepsilon_1\varepsilon_2). \quad (15)$$

This expression does not necessarily vanish unless $\theta_p=0,\pi$ or $\varphi_1-\phi_p=m\pi$ with m an integer. These two, apparently different, conditions geometrically mean one and the same thing. Namely, whenever $\theta_p=0,\pi$ and/or $\varphi_1-\phi_p=m\pi$, with $\varphi_2=\varphi_1+n\pi$, the propagation direction of the CP radiation lies in the same plane which contains both of the photoelectrons and the *OZ* axis. In conclusion, whenever $\hat{\kappa}_1$ and $\hat{\kappa}_2$ and the *OZ* axis are in a single plane, CD (15) may exist as long this plane does not contain the vector $\hat{p}$; otherwise, i.e., in a coplanar geometry (i.e., when $\hat{\kappa}_1\hat{\kappa}_2$, the *OZ* axis and $\hat{p}$ are in the same plane), it is identically zero. This behavior of CD is very different from that found for LD in Sec. II A of the present paper.

(v) It is obvious from Eq. (7e) that both of the bipolar harmonics $\mathcal{Y}^{LL}_{10}(\hat{\kappa}_1,\hat{\kappa}_2)$ and $\mathcal{Y}^{LL}_{11}(\hat{\kappa}_1,\hat{\kappa}_2)$ in Eq. (13) are zero for $\hat{\kappa}_2\|\pm\hat{\kappa}_1$. Thus, unlike LD (9b), CD in the DPI of a rotating linear molecule is always zero if two photoelectrons are observed in the same or opposite directions.

(vi) CD in a noncoincident DPI of a rotating linear molecule is obtained by integrating Eq. (13) over the propagation direction of the unobserved photoelectron, say, e_2. Use of the property (7f) immediately shows that CD does not exist in noncoincident DPI. This behavior of CD is opposite to that of LD. However, neither LD nor CD exists in the integrated cross section for DPI of a rotating linear molecule.

Let us briefly compare these properties of CD in the DPI of a rotating linear molecule with those discovered earlier for the same process in an atom [13] and in a ''rotationless'' molecule [15] belonging to one of the 32 point groups. Properties (ii), (iii), (v), and (vi) found herein are identical to those discovered in Ref. [13] for atoms and in Ref. [15] for a $C_{\infty v}$ or $D_{\infty h}$ molecule in the absence of rotation. As far as property (iv) is concerned, its first part is showing the existence of CD in an experiment performed by observing an electron pair in a plane which contains the polar *OZ* axis, but not the CP ionizing photon beam, has been discussed in neither of the Refs. [13] and [15]. However, its second part concerning the disappearance of CD in a coplanar experimental geometry (containing the *OZ* axis and the three vectors $\hat{\kappa}_1, \hat{\kappa}_2, \hat{p}$ in one plane) is in complete agreement with that arrived at by Klar *et al.* [13] and by Chandra [15] for the DPI of atomic and of rotationless linear molecular targets, respectively. Property (i) has not been discussed in either Refs. [13] or [15].

The present discussion shows that inclusion of nuclear dynamics has not altered the basic properties of CD in the DPI of a linear molecule. Nuclear rotation must certainly affect the magnitude of CD so that dichroic effects will be different for different rotational transitions accompanying the DPI of a linear molecule. Our phenomenological results presented in Sec. III confirm this view.

Lastly, in their study of CD in the SPI of oriented molecules, Westphal *et al.* [31] have argued that experimentally it is more convenient to measure normalized CD. Correspondingly, Cherepkov *et al.* [23] also have defined normalized LD in their theoretical study of the SPI of polarized atoms. But those definitions of normalized LD [23] and of CD [31] are, probably, not very suitable if one wants to compare magnitudes and other aspects of the behavior of these two phenomena in the same process of the SPI or DPI taking place in the same atomic or molecular target. In order to compare the properties of LD and CD in our present study of the DPI of a rotating linear molecule, we, unlike in Refs. [23] and [31], divide each by the integrated photocurrent emitted from the target in its DPI. This facilitates a direct comparison of the magnitudes of LD and CD by making each a ratio to the same quantity. Secondly, as the integrated photocurrent for the DPI is independent of all angles as well as of the state of polarization of the absorbed radiation, one will also be able to compare immediately the angular distribution of two photoelectrons ejected simultaneously in each of the two processes of LD and CD. Moreover, integrated photocurrent has readily been measured in several experiments on the DPI [1–7]. In this paper the normalized LD and CD are, therefore, defined as

$$\frac{d^3\sigma_n^{\mathrm{LD}}}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2} \equiv \frac{d^3\sigma^{\mathrm{LD}}}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}\left(\frac{d\sigma}{d\varepsilon_1}\right)^{-1} \tag{16}$$

and

$$\frac{d^3\sigma_n^{\mathrm{CD}}}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2} \equiv \frac{d^3\sigma^{\mathrm{CD}}}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}\left(\frac{d\sigma}{d\varepsilon_1}\right)^{-1}, \tag{17}$$

respectively. In these definitions,

$$\frac{d\sigma}{d\varepsilon_1} = \frac{1}{3}\mathcal{K}\sum_{\substack{l_1 l_2 \\ l_p s_p}}\sum_{l_t J_p}(2l_t+1)[(2l_1+1)(2l_2+1) \times(2l_p+1)]^{-1}|d_{(l_1 l_2)l_p}(S_p;J_p;l_t)|^2 \tag{18}$$

is the integrated photocurrent (I. 32b) ejected in the DPI of a rotating linear molecule. It has already been introduced in Eqs. (10b) and (11) of the present communication.

III. APPLICATION

In this section we present some generic results on CD and LD applicable to the DPI of all those rotating molecules that belong to the $D_{\infty h}$ point group and possess a closed-shell electronic configuration giving rise to the $^1\Sigma_g^+$ state. One of the simplest, most common, and very widely studied molecules for several different processes is $(1\sigma_g^2\, 1\sigma_u^2\, 2\sigma_g^2\, 2\sigma_u^2\, 1\pi_u^4\, 3\sigma_g^2\ {}^1\Sigma_g^+)N_2$. (Its angle- and rotationally resolved photoelectron spectroscopy has recently been studied by Ohrwall *et al.* [11b] for the SPI of the $3\sigma_g^2$ shell.) Let us assume that both electrons come out from the outermost $3\sigma_g^2$ shell of N_2. Then both the target and its doubly charged residual photoion $(1\sigma_g^2\, 1\sigma_u^2\, 2\sigma_g^2\, 2\sigma_u^2\, 1\pi_u^4\, 3\sigma_g^0)$ $N_2{}^{2+}$ are in their $^1\Sigma_g^+$ electronic states with $(\Lambda_0, S_0, p_0 = 0)$ and $(\Lambda_f, S_f, p_f = 0)$, respectively. Under these conditions, the dynamics of both of these species can appropriately be described [27] in Hund's coupling scheme (b). One then readily finds that [12] that $s_p = 0$, $J_0 = N_0$, $J_f = N_f$ in (2) in the present application. It has already been shown by us in Ref. [12] that, in the DPI process under consideration, $l_1 + l_2 =$ odd and one has a transition from an even rotational state of N_2 to an even rotational state of $N_2{}^{2+}$, or between odd rotational states of these two species.

Let us represent each of the two photoelectrons in the continuum by *s*, *p*, and *d* partial waves. Then the permitted [12] combinations of (l_1, l_2) in the present example are $(l_1, l_2) = (0,1)$, $(1,0)$, $(1,2)$, and $(2,1)$. One also finds [12] that $l_t = 0$, 2, and 4 for $d_{(l_1 l_2)l_p}$ $(s_p = 0; N_f; l_t)$ do not vanish trivially. Consequently, one needs to consider only the following reduced amplitudes [12]:

$$\begin{aligned}
d_{(01)1}(0;N_f;0)&=(-1)^{N_f}g_1(\varepsilon_2)I(\varepsilon_10)\,\delta_{N_0N_{f,l}},\\
d_{(01)1}(0;N_f;2)&=\sqrt{\frac{2(2N_f+1)}{5}}\begin{pmatrix}N_0 & N_f & 2\\ 0 & 0 & 0\end{pmatrix}f(\varepsilon_2)I(\varepsilon_10),\\
d_{(12)1}(0;N_f;0)&=(-1)^{N_f}\sqrt{\frac{2}{5}}f(\varepsilon_1)I(\varepsilon_22)\,\delta_{N_0N_f},\\
d_{(12)1}(0;N_f;2)&=\frac{1}{5}\sqrt{2N_f+1}\begin{pmatrix}N_0 & N_f & 2\\ 0 & 0 & 0\end{pmatrix}g_2(\varepsilon_1)I(\varepsilon_22),\\
d_{(12)3}(0;N_f;2)&=\frac{1}{5}\sqrt{2N_f+1}\begin{pmatrix}N_0 & N_f & 2\\ 0 & 0 & 0\end{pmatrix}g_3(\varepsilon_1)I(\varepsilon_22),\\
d_{(12)3}(0;N_f;4)&=2\sqrt{\frac{2N_f+1}{15}}\begin{pmatrix}N_0 & N_f & 4\\ 0 & 0 & 0\end{pmatrix}f(\varepsilon_1)I(\varepsilon_22),
\end{aligned}\tag{19}$$

in the present example. The reduced matrix elements for $(l_1,l_2)=(1,0)$ and (2,1) are obtained by interchanging ε_1 and ε_2 in the expressions (19) that contain d's for $(l_1,l_2)=(0,1)$ and (1,2). In relations (19), we have defined [12]

$$\begin{aligned}
f(\varepsilon_i)&=I_d(\varepsilon_i11)-I_d(\varepsilon_i10),\\
g_1(\varepsilon_i)&=I_d(\varepsilon_i10)+2I_d(\varepsilon_i11),\\
g_2(\varepsilon_i)&=2I_d(\varepsilon_i10)+I_d(\varepsilon_i11),\\
g_3(\varepsilon_i)&=3I_d(\varepsilon_i10)+4I_d(\varepsilon_i11).
\end{aligned}\tag{20}$$

Here I_d's are the dipole integrals (I.63b). For the values of $l_t=0$, 2, and 4, three possible transitions from the N_0th rotational state of N_2 to the N_fth rotational state of N_2^{2+} in an $E1$ DPI are $\Delta N=N_f-N_0=0,\pm 2,\pm 4$. With the help of the reduced $E1$ amplitudes (19), one can study for each of these three rotational transitions both LD as well as CD for the DPI in the σ_g^2 shell of a $D_{\infty h}$ molecule in its ${}^1\Sigma_g^+$ electronic state. It can be done in any geometry or experimental arrangement. In the following we report our model generic results for a general experimental geometry.

A. Linear dichroism

(i) Noncoincident DPI

It has been shown in Sec. II A of this paper that LD may exist even in the noncoincident DPI of a rotating linear molecule. It is given by Eq. (10) when only one (say, e_1) of the two ejected photoelectrons is observed. Both the integrated cross section $(d\sigma/d\varepsilon_1)$ and parameter β_1 needed in the expression (10b) have already been obtained by us in Ref. [12] for the current example of DPI. Those values can readily be used in Eq. (10b) and one can study LD in noncoincident DPI. The LD thus obtained will carry a signature of electron-electron correlation in molecules. Therefore, a comparison of the LD in a noncoincident DPI with that obtained in the SPI will provide direct observable effects of correlations which can readily be calculated theoretically and measured experimentally.

(ii) Coincident DPI

We specialize the general expression (8) for LD to the example described in this section and obtain the following results:

(a) $N_0\rightarrow N_f=N_0$ ($\Delta N=0$, with $N_0,N_f=0$). It is obvious that in the rotational transition $N_0=0\rightarrow N_f=0$, only the first and the third of the transition amplitudes (19) will contribute [32] to the unnormalized LD (8). The second, fourth, and fifth of the $E1$ amplitudes (19) will make additional contributions to the LD in rotationally elastic ($\Delta N=0$) DPI if $N_0\geqslant 1$; similarly, the last $[d_{(12)3}(0;N_f;4)]$ of the d's in Eq. (19) will participate in a $N_0\rightarrow N_f=N_0\geqslant 2$ transition.

Let us calculate the normalized LD (16) for the present example of DPI by representing two photoelectrons by $(l_1,l_2)=(0,1)$ and (1,0) partial waves. For rotationally elastic ($\Delta N=0$) DPI with $N_0=0$ we find that

$$\frac{d^3\sigma_n^{\mathrm{LD}}}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}=\frac{3}{16\pi^2}\times\frac{A(\hat{\kappa}_1)\rho_0^2+2B(\hat{\kappa}_1,\hat{\kappa}_2)\rho_0\cos\alpha_0+A(\hat{\kappa}_2)}{1+\rho_0^2}.\tag{21a}$$

Here we have defined

$$\rho_0e^{i\alpha_0}=\frac{d_{(10)1}(0;N_f;0)}{d_{(01)1}(0;N_f;0)}=\frac{g_1(\varepsilon_1)I(\varepsilon_20)}{g_1(\varepsilon_2)I(\varepsilon_10)}=\frac{[I_d(\varepsilon_110)+2I_d(\varepsilon_111)]I(\varepsilon_20)}{[I_d(\varepsilon_210)+2I_d(\varepsilon_211)]I(\varepsilon_10)}\tag{21b}$$

with

$$A(\hat{\kappa}_i)=\sin^2\vartheta_i\cos 2\varphi_i\quad\text{for } i=1 \text{ and } 2,\tag{22a}$$

$$B(\hat{\kappa}_1,\hat{\kappa}_2)=\sin\vartheta_1\sin\vartheta_2\cos(\varphi_1+\varphi_2). \tag{22b}$$

Definitions (19) and (20) have been used in arriving at Eq. (21). On taking $\rho_0=0$, i.e., *p*-wave dipole integrals $I_d(\varepsilon_1 11)=-I_d(\varepsilon_1 10)/2$ for the photoelectrons e_1, or the overlap integral $I(\varepsilon_2 0)=0$ for the photoelectron e_2, one finds from Eq. (21a)

$$\frac{d^3\sigma_n^{\mathrm{LD}}}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}=\frac{3}{16\pi^2}A(\hat{\kappa}_2). \tag{23a}$$

Similarly, we further obtain from Eq. (21b) that

$$\frac{d^3\sigma_n^{\mathrm{LD}}}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}=\frac{3}{16\pi^2}A(\hat{\kappa}_1), \tag{23b}$$

for $\rho_0=\infty$, i.e., the *p*-wave dipole integrals $I_d(\varepsilon_2 11)=-I_d(\varepsilon_2 10)/2$ and/or the overlap integral $I(\varepsilon_1 0)=0$ for the photoelectrons e_2 and e_1, respectively. Consequently, for the present example of the DPI, the magnitude of the normalized LD in the *s* and *p* partial waves approximations is always given by

$$\left|\frac{d\sigma_n^{\mathrm{LD}}}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}\right|\leqslant\frac{3}{16\pi^2}.$$

Thus, the maximum magnitude of the LD in the present example of the DPI is about 2% that of the integrated cross section for this process.

(b) $N_0\rightarrow N_f=N_0\pm 2$. In our present example, the differential cross section for the DPI accompanied with this rotationally inelastic transition will be determined by four [i.e., 2nd, 4th–6th] of the dipole amplitudes (19). The resulting expression [32] is very long and complicated. This expression [32] is, however, considerably simplified by representing each of the photoelectrons e_1 and e_2 by *s* and *p* waves. In this case only the terms that contain $E1$ amplitudes $d_{(01)1}(0;N_f;2)$ and $d_{(10)1}(0;N_f;2)$ contribute.

The normalized LD (16) for $\Delta N=\pm 2$ transitions then becomes

$$\frac{d^3\sigma_n^{\mathrm{LD}}}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}=\frac{3}{160\pi^2}\,\frac{A(\hat{\kappa}_1)\rho_2^2+2B(\hat{\kappa}_1,\hat{\kappa}_2)\rho_2\cos\alpha_2+A(\hat{\kappa}_2)}{1+\rho_2^2}. \tag{24a}$$

Here

$$\rho_2 e^{i\alpha_2}=\frac{d_{(10)1}(0;N_f;2)}{d_{(01)1}(0;N_f;2)}=\frac{f(\varepsilon_1)I(\varepsilon_2 0)}{f(\varepsilon_2)I(\varepsilon_1 0)}=\frac{[I_d(\varepsilon_1 11)-I_d(\varepsilon_1 10)]I(\varepsilon_2 0)}{[I_d(\varepsilon_2 11)-I_d(\varepsilon_2 10)]I(\varepsilon_1 0)}, \tag{24b}$$

whereas the coefficients *A*’s and *B*’s have already been defined in Eqs. (22). Relations (24) are obtained with the help of Eqs. (19) and (20).

In the present example of the DPI both the numerator and denominator in the normalized LD (16) depend on the quantum numbers N_0 and N_f only through the factor $(2N_f+1)\begin{pmatrix} N_0 & N_f & 2\\ 0 & 0 & 0\end{pmatrix}^2$ for a $\Delta N=\pm 2$ transition in the *s* and *p* partial waves approximation. Consequently, the normalized LD (24) becomes independent of rotational states for the $\Delta N=\pm 2$ transitions.

On taking $\rho_2=0$, i.e., the *p* wave dipole integrals for the electron e_1, $I_d(\varepsilon_1 11)=I_d(\varepsilon_1 10)$, or the overlap integral $I(\varepsilon_2 0)=0$ for the photoelectron e_2, one finds

$$\frac{d^3\sigma_n^{\mathrm{LD}}}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}=\frac{3}{160\pi^2}A(\hat{\kappa}_2). \tag{25a}$$

We further obtain from Eq. (24) that

$$\frac{d^3\sigma_n^{\mathrm{LD}}}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}=\frac{3}{160\pi^2}A(\hat{\kappa}_1). \tag{25b}$$

for $\rho_2=\infty$, i.e., either the overlap integral $I(\varepsilon_1 0)=0$ or the *p* wave dipole integrals $I_d(\varepsilon_2 11)=I_d(\varepsilon_2 10)$ for the photoelectrons e_1 and e_2, respectively. A comparison of Eqs. (23) and (25) readily shows that, within the present approximations, LD in the DPI with $\Delta N=\pm 2$ transitions has a magnitude which is about one-tenth of that with $\Delta N=0$ transition. Consequently, the largest possible magnitude of the former in our present example is about 0.2%, i.e., about 0.002 times the magnitude of the integrated cross section. Thus the dichroic effect in the DPI caused by the absorption of LP light are weaker for rotationally inelastic transitions $N_0\rightarrow N_f=N_0\pm 2$ than for the elastic $N_0=0\rightarrow N_f=0$ transition.

(c) $N_0\rightarrow N_f=N_0\pm 4$ The DPI for this rotationally resolved transition is determined by the last of the dipole amplitudes (19). The corresponding expression depends [32] upon the rotational quantum numbers N_0 of *AB* and N_f of AB^{++} only through the factor $(2N_f+1)\begin{pmatrix} N_0 & N_f & 4\\ 0 & 0 & 0\end{pmatrix}^2$. However, when we divide it by $(d\sigma/d\varepsilon_1)$ in order to obtain the normalized LD for $\Delta N=\pm 4$ rotational transitions, this factor is canceled. The remaining expression can be written as

$$\frac{d^3\sigma_n^{\mathrm{LD}}}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}=\frac{35}{4\pi^2}\,\frac{A'(\hat{\kappa}_1,\hat{\kappa}_2)\rho_4^2+2B'(\hat{\kappa}_1,\hat{\kappa}_2)\rho_4\cos\alpha_4+A'(\hat{\kappa}_2,\hat{\kappa}_1)}{1+\rho_4^2}. \tag{26a}$$

with

$$\rho_4 e^{i\alpha_4}=\frac{d_{(21)3}(0;N_f;4)}{d_{(12)3}(0;N_f;4)}=\frac{f(\varepsilon_2)I(\varepsilon_1 2)}{f(\varepsilon_1)I(\varepsilon_2 2)}=\frac{[I_d(\varepsilon_2 11)-I_d(\varepsilon_2 10)]I(\varepsilon_1 2)}{[I_d(\varepsilon_1 11)-I_d(\varepsilon_1 10)]I(\varepsilon_2 2)}, \tag{26b}$$

$$\begin{aligned} A'(\hat{\kappa}_1,\hat{\kappa}_2)=\frac{3}{2^6\times 5^2\times 7^3}\biggl\{ & 2^3\times 7^2 A(\hat{\kappa}_1)+2^4\times 5\times 7A(\hat{\kappa}_2)+5\times 7\sin^2\vartheta_1\sin^4\vartheta_2\cos 2(\varphi_1-2\varphi_2) \\ & +\frac{5\times 7}{\sqrt{3}}\sin 2\vartheta_1\sin 2\vartheta_2\sin^2\vartheta_2\cos(\varphi_1-3\varphi_2)+\frac{2^2\times 5}{3}P_2(\cos\vartheta_1)(7\cos^2\vartheta_2-1)\sin^2\vartheta_2 \\ & \times\cos^2\varphi_2+2(35\cos^4\vartheta_2-30\cos^2\vartheta_2+3)\sin^2\vartheta_1\cos^2\varphi_1-2\times 5(7\cos^2\vartheta_2-3)\sin 2\vartheta_1 \\ & \times\sin 2\vartheta_2\cos(\varphi_1+\varphi_2)+2^5\times 5\sqrt{2}[\sin^2\vartheta_1\cos 2\vartheta_1 P_2(\cos\vartheta_2)+\sin^2\vartheta_2\cos 2\vartheta_2 P_2 \\ & \times(\cos\vartheta_1)-\tfrac{1}{4}\sin 2\vartheta_1\sin 2\vartheta_2\cos(\varphi_1+\varphi_2)]\biggr\}, \end{aligned} \tag{26c}$$

and

$$\begin{aligned} B'(\hat{\kappa}_1,\hat{\kappa}_2)=\frac{3^2}{2^7\times 5^2\times 7^2}\biggl\{\biggl[& \frac{2^4}{3\times 5\times 7}B(\hat{\kappa}_1,\hat{\kappa}_2)-\frac{2\times 3}{5}\sqrt{\tfrac{7}{2}}(5\cos^2\vartheta_1-1)(5\cos^2\vartheta_2-1) \\ & \times\sin\vartheta_1\sin\vartheta_2\cos(\varphi_1+\varphi_2)-\frac{2^4\times 7}{5\times 11}(5\cos^2\vartheta_1-1)\sin\vartheta_1\sin\vartheta_2\cos(\varphi_1+\varphi_2) \\ & +\frac{2^4\times 7}{11}\sin\vartheta_1\sin^3\vartheta_2\cos(\phi_1-3\phi_2)-\frac{2^4\times 7}{11}\cos\vartheta_1\sin\vartheta_2\sin 2\vartheta_2\cos 2\vartheta_2 \\ & +\sqrt{\tfrac{7}{2}}(5\cos^2\vartheta_2-1)\sin^3\vartheta_2\sin\vartheta_2\cos(3\varphi_1-\varphi_2)+\sqrt[2]{\tfrac{7}{2}}(3\cos^2\vartheta_2+2\cos\vartheta_2-3) \\ & \times\sin\vartheta_1\sin 2\vartheta\cos\vartheta_2\cos 2\vartheta_1\biggr]+(1\rightleftharpoons 2)\biggr\}. \end{aligned} \tag{26d}$$

In this last relation (26d), $(1\rightleftharpoons 2)$ represents terms obtained by interchanging 1 and 2 in the square brackets.

The normalized LD given by Eqs. (26) is independent of the rotational states N_0 and N_f involved in the rotational transitions $\Delta N=\pm 4$. On taking $\rho_4=0$, i.e., the p-wave dipole integrals $I_d(\varepsilon_2 11)=I_d(\varepsilon_2 10)$ for electron e_2, or the overlap integral $I(\varepsilon_1 2)=0$ for the photoelectron e_1, expression (26a) reduces to

$$\frac{d^3\sigma_n^{\mathrm{LD}}}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}=\frac{35}{4\pi^2}A'(\hat{\kappa}_2,\hat{\kappa}_1). \tag{27a}$$

If, on the other hand, p-wave dipole integrals for the electrons e_1 are equal, i.e., $I_d(\varepsilon_2 11)=I_d(\varepsilon_2 10)$, or the overlap integral $I(\varepsilon_2 2)=0$ for the electron e_2, then Eq. (26b) shows that $\rho_4=\infty$. In this case, Eq. (26a) simplifies to

$$\frac{d^3\sigma_n^{\mathrm{LD}}}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}=\frac{35}{4\pi^2}A'(\hat{\kappa}_1,\hat{\kappa}_2). \tag{27b}$$

Both $A'(\hat{\kappa}_1,\hat{\kappa}_2)$ and $A'(\hat{\kappa}_2,\hat{\kappa}_1)$ are obtained from Eq. (26c) by interchanging 1 and 2. Therefore, we always have

$$\left|\frac{d^3\sigma_n^{\mathrm{LD}}}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}\right|\leqslant\frac{35}{4\pi^2}|A'(\hat{\kappa}_2,\hat{\kappa}_1)|.$$

B. Circular dichroism

(i) Noncoincident DPI

It has already been shown in Sec. II B of this paper that CD does not exist in the detection of only one of the two photoelectrons ejected in the DPI of a rotating linear molecule.

(ii) Coincident DPI

Unless stated otherwise, the following CD in the angular distribution of photoelectrons has been calculated for the most common [13–15] geometry, i.e., direction of incidence of the CP ionizing radiation is along the polar axis of the space frame (see Fig. 1). The corresponding expression is obtained by taking $\theta_p=0$ in Eq. (13). This, in other words, means that in the following discussion the photoelectrons' propagation directions $(\hat{\kappa}_1,\hat{\kappa}_2)$ and $(\hat{k}_1,\hat{k}_2)$, defined (see Fig. 1) with respect to the space frame and photon frame, respectively, become identical.

(a) $N_0\to N_f=N_0$ ($\Delta N=0$ with $N_0,N_f=0$). For this rotationally elastic transition, we have calculated [32] an unnormalized CD by taking s, p, and d partial waves into account. On dividing that expression [32] by the integrated cross section (18), one obtains the normalized CD for the $N_0=0\to N_f=0$ transition. In order to compare its magnitude with that of LD obtained in Eq. (21a), we consider only the s and p partial waves. This gives

$$\frac{d^3\sigma_n^{\mathrm{CD}}}{d\varepsilon_1 d\hat{k}_1 d\hat{k}_2} = -\frac{3}{8\pi^2}\frac{\rho_0 \sin\alpha_0}{1+\rho_0^2} a(\hat{k}_1,\hat{k}_2) \tag{28a}$$

with

$$a(\hat{k}_1,\hat{k}_2) = \sin\theta_1 \sin\theta_2 \sin(\phi_1-\phi_2), \tag{28b}$$

where ρ_0 and α_0 are defined by Eq. (21b). The structure of Eq. (28a) is very different from that of Eq. (21a). Firstly, unlike normalized LD (21a), Eq. (28) always vanishes for $\rho_0=0$ or ∞, or when either of the two photoelectrons is observed in a direction which is either the same or opposite (i.e., θ_1 and/or $\theta_2=0$ or π) to that of the direction of propagation of the CP wave, and also for $|\phi_1-\phi_2|=m\pi$. Expression (28a) will have its maximum absolute value for $\rho_0=1$ and $\alpha_0=(m\pm\frac{1}{2})\pi$, where m is an integer. Therefore

$$\left|\frac{d^3\sigma^{\mathrm{CD}}}{d\varepsilon_1 d\hat{k}_1 d\hat{k}_2}\right|_{\max} = \frac{3}{16\pi^2}\frac{d\sigma}{d\varepsilon_1}. \tag{29a}$$

We find from Eq. (21b) that $\rho_0=1$ for

$$\left|\frac{I(\varepsilon_1 0)}{I(\varepsilon_2 0)}\right| = \left|\frac{I_d(\varepsilon_1 10)+2I_d(\varepsilon_1 11)}{I_d(\varepsilon_2 10)+2I_d(\varepsilon_2 11)}\right|. \tag{29b}$$

That is the absolute value of the ratio of the overlap integrals for photoelectrons e_1 and e_2 must be equal to the ratio (29b) of their respective dipole integrals. On comparing it with Eq. (23), we find that the maximum magnitude of each of LD and CD for the $N_0=0\rightarrow N_f=0$ rotational transition in the DPI of a rotating linear molecule is of the same order and is equal to about 0.02 times the integrated cross section for the DPI. However, while LD becomes maximum for $\rho_0=0$ or ∞, CD vanishes for each of these value of ρ_0 and acquires it maximum values for $\rho_0=1$.

One of the other important differences in the behavior of LD [Eqs. (21a)] and CD [Eq. (28a)] is LD depends upon the cosine of the difference α_0 between the phases of the photoionization amplitudes $d_{(10)1}(0;N_f;0)$ and $d_{(01)1}(0;N_f;0)$, whereas CD involves sine of this angle. Thus measurement of both LD and CD can give us absolute phases of the ionization amplitudes.

(b) $N_0\rightarrow N_f=N_0\pm 2$. The CD for this rotationally inelastic transition has been calculated [32] using *s*, *p*, and *d* partial waves. For a $N_0=0\rightarrow N_f=2$ or vice versa transition, CD has rotational dependence [32] only through the factor

$$(2N_f+1)\begin{pmatrix} N_0 & N_f & 2 \\ 0 & 0 & 0 \end{pmatrix}^2,$$

but for a general $\Delta N=\pm 2$ transition, with neither N_0 nor N_f equal to zero, the additional terms containing the factor

$$(2N_f+1)\begin{pmatrix} N_0 & N_f & 4 \\ 0 & 0 & 0 \end{pmatrix}^2$$

will also be present as well [32]. The normalized CD within the *s* and *p* partial-waves approximation is given by

$$\frac{d^3\sigma_n^{\mathrm{CD}}}{d\varepsilon_1 d\hat{k}_1 d\hat{k}_2} = \frac{3}{16\pi^2}\frac{\rho_2 \sin\alpha_2}{1+\rho_2^2} a(\hat{k}_1,\hat{k}_2), \tag{30a}$$

where (ρ_2,α_2) are defined by Eq. (24b) and a is the same as introduced in Eq. (28b). The behavior of Eq. (30a) is identical to that of $d^3\sigma_n^{\mathrm{CD}}/d\varepsilon_1 d\hat{k}_1 d\hat{k}_2$ for the $N_0=0\rightarrow N_f=0$ transition in Eq. (28a), but the magnitude of the former is half of that of the later. Also, Eq. (30a) is independent of the rotational states N_0 and N_f involved in the $\Delta N=\pm 2$ transition in the DPI. Expression (30a) also shows that the maximum magnitude of $d^3\sigma_n^{\mathrm{CD}}/d\varepsilon_1 d\hat{k}_1 d\hat{k}_2$ is about five times greater than that of $d^3\sigma_n^{\mathrm{LD}}/d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2$ [Eq. (25)] for the rotational transition $\Delta N=\pm 2$. For the former to acquire its maximum magnitude one should have, in addition to $\alpha_2=(n\pm\frac{1}{2})\pi$, $\rho_2=1$, i.e.,

$$\left|\frac{I(\varepsilon_1 0)}{I(\varepsilon_2 0)}\right| = \left|\frac{I_d(\varepsilon_1 10)-I_d(\varepsilon_1 11)}{I_d(\varepsilon_2 10)-I_d(\varepsilon_2 11)}\right|, \tag{30b}$$

whereas the magnitude of the latter will be maximum when $\rho_2=0$ or $\rho_2=\infty$. The other properties of Eq. (30a) are identical to those discussed for CD in the DPI with $N_0=0\rightarrow N_f=0$ rotational transition.

(c) $N_0\rightarrow N_f=N_0\pm 4$. According to our earlier discussion, only the last of the dipole amplitudes (19) contribute to this rotationally inelastic transition accompanying the DPI considered by us in the present example. For known values of the rotational quantum numbers N_0 and N_f, this [32] CD is proportional to

$$(2N_f+1)\begin{pmatrix} N_0 & N_f & 4 \\ 0 & 0 & 0 \end{pmatrix}^2.$$

The normalized CD

$$\frac{d^3\sigma^{\mathrm{CD}}}{d\varepsilon_1 d\hat{k}_1 d\hat{k}_2} = \frac{9}{40\pi^2}\frac{\rho_4 \sin\alpha_4}{1+\rho_4^2} a'(\hat{k}_1,\hat{k}_2) \tag{31a}$$

is independent of the states N_0 and N_f involved in the rotational transitions $\Delta N=\pm 4$. Here

$$\begin{aligned} a'(\hat{k}_1,\hat{k}_2) = {} & [1+(5\cos^2\theta_1-1)(5\cos^2\theta_2-1) \\ & +\tfrac{5}{2}\sin 2\theta_1 \sin 2\theta_2 \cos(\phi_1-\phi_2) \\ & +\tfrac{5}{4}\sin^2\theta_1 \sin^2\theta_2 \sin 3(\phi_1-\phi_2)/ \\ & \sin(\phi_1-\phi_2)]a(\hat{k}_1,\hat{k}_2), \end{aligned} \tag{31b}$$

with (ρ_4,α_4) defined by Eq. (26b) and $a(\hat{k}_1,\hat{k}_2)$ given by Eq. (28b). Similar to the CD's (28a) and (30a) for the DPI with $\Delta N=0$ and $\Delta N=\pm 2$ transitions, respectively, we find that the dynamical part $[\rho_4 \sin\alpha/(1+\rho_4^2)]$ of the current CD (31a) also depends upon the sine of the difference in the phases of $d_{(12)3}(0;N_f;4)$ and $d_{(21)3}(0;N_f;4)$, vanishes for $\rho_4=0$ or ∞, but has its maximum magnitude of one-half for $\rho_4=1$. Thus

$$\left|\frac{d^3\sigma^{\mathrm{CD}}}{d\varepsilon_1 d\hat{k}_1 d\hat{k}_2}\right|_{\max}=\frac{9}{80\pi^2}\frac{d\sigma}{d\varepsilon_1}|a'(\hat{k}_1,\hat{k}_2)|_{\max} \tag{32a}$$

for $\alpha_4=(n\pm\frac{1}{2})\pi$ and

$$\left|\frac{I(\varepsilon_1 2)}{I(\varepsilon_2 2)}\right|=\left|\frac{I_d(\varepsilon_1 10)-I_d(\varepsilon_1 11)}{I_d(\varepsilon_2 10)-I_d(\varepsilon_2 11)}\right|. \tag{32b}$$

(iii) Before closing this discussion on the calculation of LD and CD for the present example, let us also briefly consider the results obtained from Eq. (14). It has already been mentioned elsewhere in this paper that θ_p, given by Eq. (14), is the direction of incidence of the CP ionizing radiation, with respect to the polar axis of the space frame, for which CD in the DPI becomes zero. If we represent by s and p waves the pair of photoelectrons ejected in the DPI from the σ_g^2 shells of a $D_{\infty h}$ molecule in its ${}^1\Sigma_g^+$ electronic state, we find that θ_p, obtained from Eq. (14), becomes independent of the dynamics of photoionization and the same for $\Delta N=0$ as well as $\Delta N=\pm 2$ rotational transitions. It is then given by

$$\tan\theta_p=\frac{\sin(\varphi_1-\varphi_2)}{\cot\vartheta_2\sin(\varphi_1-\phi_p)-\cot\vartheta_1\sin(\varphi_2-\phi_p)}. \tag{33}$$

Here one needs to remember that the propagation vectors $\hat{\kappa}_1(\vartheta_1,\varphi_1)$ and $\hat{\kappa}_2(\vartheta_2,\varphi_2)$ of the photoelectrons e_1 and e_2, respectively, are referred to the space frame which is different from the photon frame (see Fig. 1). Some of the noncoplanar (i.e., OZ axis, $\hat{p}$, $\hat{\kappa}_1$ and $\hat{\kappa}_2$ not in a single plane) geometries in which CD vanishes are

$$\hat{p}\left(\theta_p=\frac{\pi}{2}-\frac{\varphi_2}{2},\phi_p=\frac{\pi}{2}\right),\ \ \hat{\kappa}_1\left(\vartheta_1=\frac{\pi}{4},\varphi_1=0\right),$$

$$\hat{\kappa}_2\left(\vartheta_2=\frac{\pi}{4},\varphi_2\right),\ \ \hat{p}\left(\theta_p=\frac{1}{2}\varphi_2,\phi_p=\frac{\pi}{2}\right),$$

$$\hat{\kappa}_1\left(\vartheta_1=\frac{\pi}{4},\varphi_1=\pi\right),\ \ \hat{\kappa}_2\left(\vartheta_2=\frac{\pi}{4},\varphi_2\right),$$

$$\hat{p}\left(\theta_p=\frac{\pi}{4};\phi_p=\varphi_2\right),\ \ \hat{\kappa}_1\left(\vartheta_1=\frac{\pi}{2},\varphi_1\right),\ \ \hat{\kappa}_2\left(\vartheta_2=\frac{\pi}{4},\varphi_2\right).$$

Similarly, one can show, again from Eq. (14), that there are noncoplanar experimental setups in which CD in the DPI with $\Delta N=\pm 4$ also becomes zero.

(iv) Finally, if we substitute the $E1$ matrix elements (19) in (5b), we see that both LD (8) and CD (12) will depend on N_0 and N_f through

$$(2N_f+1)\begin{pmatrix} N_0 & N_f & l_t \\ 0 & 0 & 0 \end{pmatrix}^2$$

for allowed values of the pair (l_1,l_2). The sum of this expression over N_f is well known [30] to be unity. The resulting expression for $\Sigma_{N_f}\gamma_{L_1L_2}(L_r;\varepsilon_1\varepsilon_2)$ will become independent also of the initial rotational level N_0. Therefore rotationally unresolved, normalized LD and CD are

$$\frac{d^3\overline{\sigma}_n^{\mathrm{LD}}}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}=\sum_{N_f}\frac{d^3\sigma^{\mathrm{LD}}}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}\Bigg/\frac{d\overline{\sigma}}{d\varepsilon_1}$$

and

$$\frac{d^3\overline{\sigma}_n^{\mathrm{CD}}}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}=\sum_{N_f}\frac{d^3\sigma^{\mathrm{CD}}}{d\varepsilon_1 d\hat{\kappa}_1 d\hat{\kappa}_2}\Bigg/\frac{d\overline{\sigma}}{d\varepsilon_1},$$

respectively. Here $d\overline{\sigma}/d\varepsilon_1=\Sigma_{N_f}(d\sigma/d\varepsilon_1)$ is the rotationally unresolved integrated photocurrent emitted in the DPI with $d\sigma/d\varepsilon_1$ given by Eq. (18).

IV. CONCLUSIONS

This paper presents the first study of LD and CD in the DPI of linear molecules by taking the rotation of their nuclei properly into account. Our analysis shows that these two observables provide complementary information on the DPI. LD and CD are separately determined by two different dynamical parameters. While the single parameter that contributes to LD is pure real, the one responsible for the existence of CD is pure imaginary. Although the calculation of each is simpler, a knowledge of both is necessary for the complete specification of the DPI of a given target.

In certain respects, LD and CD are found to have opposite properties. For example, the condition that CD in the DPI of rotating linear molecules does not exist if the two simultaneously ejected electrons have equal energies and/or are observed in a plane which contains a CP beam of ionizing radiation, the polar axis of the space frame and both photoelectrons, does not apply to LD; although CD vanishes in noncoincident DPI, LD may exist. The angular dependence of LD in noncoincident DPI is found to be identical to that of a single photoionization or in a coincident DPI when both electrons are observed in a straight line. The other, hitherto unknown, results obtained from the present analysis are that one can determine from the expressions derived herein the directions of incidence of the CP electromagnetic wave when the CD will vanish in other than coplanar geometries for photoelectrons observed with unequal energies and also the experimental arrangements in which the LD does not exist in the DPI. A comparison of the magnitudes of LD and/or CD in the DPI with different rotational transitions has been found to be greatly facilitated if they are all normalized with respect to the integrated photocurrent ejected in the DPI.

The analysis developed herein has been applied to a generic example of the DPI in a σ_g^2 shell of a $D_{\infty h}$ molecule (e.g., N_2) in its ${}^1\Sigma_g^+$ electronic state. We find that the maximum magnitude of each one of the normalized LD and CD decreases as one goes from $\Delta N=0$ to $\Delta N=\pm 2$ transitions. Also the maximum magnitude of the normalized LD is either smaller or equal to that of CD for the same rotational transition.

In view of the large similarities between the properties of CD in the DPI of atoms and of rotating linear molecules discussed after Sec. II B (vi), it is natural to expect that most of the properties of LD and, hitherto unfamiliar, properties of

CD predicted in this paper should also be present in the linear and circular chiralities in the DPI of atoms and of rotationless molecules belonging to the $C_{\infty v}$ or $D_{\infty h}$ point groups. The necessary theoretical expressions for these two cases can readily be developed along the lines used in the present communication.

ACKNOWLEDGMENTS

This work was supported by the Department of Science and Technology, India, under Grant No. SP/S2/L04/95. One of us (S.S.) is thankful to the Council of Scientific and Industrial Research, India, for financial support.

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