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Circular dichroism in photoionization of oriented nonlinear molecules

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It is shown that the angular distribution of $E1$ photoelectrons from oriented nonlinear molecules exhibits circular dichroism. The study, based upon a general expression that is obtained by taking full account of the transformation properties of the point-symmetry group of the target, reveals that, unlike the case of fixed linear molecules, (i) it may arise even if there is only a single photoelectron continuum, (ii) all terms, interference or otherwise, in $-L \leq M(=m-m') \leq L$ with L both even and odd contribute, and (iii) there are in general no restrictions on the experimental arrangement for it to be observable in nonlinear systems. This discussion has been illustrated by ionization in the $6a_1$ orbital in an oriented CCl_4 molecule.

It has already been demonstrated[1,2] that the angular distribution of electrons ejected by interaction of light with oriented linear molecules in the electric dipole ($E1$) approximation depends upon whether the incident radiation is left or right circularly polarized. This circular dichroism in photoelectron angular distribution (CDAD) appears even in the absence of any spin-orbit interactions.[1,2] In this Rapid Communication, we show that the CDAD, under the similar conditions, also exists in nonlinear molecules. But the reasons for its presence in such targets are different from those[2] for linear molecules. In particular, all terms, interference ($m \neq m'$) or otherwise ($m = m'$), with $|m-m'| \leq 2l_>$, where $l_>$ is the angular momentum of the highest partial wave used to represent the photoelectron, contribute to this phenomena in nonlinear targets. Such terms may arise both from a single continuum or from interaction between more than one continua available to the departing electron. Furthermore, dichroism in nonlinear molecules is, in general, observable even in those photon-propagation electron-detection configurations where it strictly vanishes[2] for linear oriented systems. As an example, CDAD for the $6a_1$ orbital in an isolated fixed CCl_4 molecule has been presented and compared with other photoelectron angular distributions (PEAD's).

The present discussion uses a recently developed theory[3] for angular distribution of electrons ejected in photoionization of oriented polyatomic molecules. The ionization amplitude in this formulation was shown[3] to reduce, by taking full advantage of the molecular symmetry properties, to a sum of terms characterized by the irreducible representations (irrep's) of the point group of the $(e+M^+)$ system, where M^+ is the residual molecular ion of the target M. This treatment is applicable to photoionization in all molecular (both linear and nonlinear) systems with their symmetry elements described by one of the 32 point groups. Our approach, therefore, not only presents a single unified theory for the physical process, but it also directly gives, in addition to other things,[3,4] the contributions made to the photoionization by each of the possible continua which belongs to one or the other of the irrep's of the molecular point group and is allowed by the $E1$ selection rules.

On the other hand, in a recent paper, Charepkov and Kuznetsov[5] have tried to generalize their expression for angle- and spin-resolved photoelectron spectroscopy in oriented linear molecules to nonlinear targets possessing some specific symmetry elements. This approach will probably not be easy to use because it does not take into account the point-group properties which may be present in a complicated nonlinear system to be studied. Furthermore, their treatment, although it helped Cherepkov and Kuznetsov[5] to predict the existence of CDAD in oriented molecules of relatively low symmetry even in the absence of any spin-orbit interactions, could not reveal the above-mentioned important and interesting properties which are very different from those[2] of CDAD in linear targets, but are possessed by the CDAD in oriented nonlinear molecules.

The PEAD for ionization in an oriented polyatomic molecule can be written as[3]

$$\frac{d^2\sigma(m_r)}{d\omega\, d\hat{\mathbf{k}}} = (-1)^{m_r} K \sum_{L,M} A_{LM}(\omega, m_r, \hat{k}) Y_L^M(\hat{\mathbf{k}}) , \tag{1}$$

where K contains energy E_r of the ionizing radiation and the variable m_r specifies the state of polarization of the incident radiation in the laboratory (photon)-fixed frame of reference. The polar axis of this coordinate system is taken to be along the direction of incidence of the photon beam. The propagation vector $\mathbf{k}(k,\theta,\phi)$ of the photoelectron in (1) is, on the other hand, referred to the molecule-fixed frame whose polar axis is the axis of the highest symmetry in the target. These two frames of reference are related[3] by the Euler angles $\omega = \alpha\beta\gamma$. The CDAD, defined by[1,2]

$$\frac{d^2\sigma_{CD}}{d\omega\, d\hat{\mathbf{k}}} = \frac{d^2\sigma(m_r=+1)}{d\omega\, d\hat{\mathbf{k}}} - \frac{d^2\sigma(m_r=-1)}{d\omega\, d\hat{\mathbf{k}}} ,$$

becomes[6]

$$\frac{d^2\sigma_{\mathrm{CD}}}{d\omega\, d\hat{\mathbf{k}}} = K\sqrt{2}\sum_{L=0}^{2l_>}\sum_{M=-L}^{L}\sum_{\substack{p,\mu,h,l,m,\lambda_r\\ p',\mu',h',l',m',\lambda_r'}}(-i)^{l-l'}e^{i(\sigma_l-\sigma_{l'})}(-1)^{m-\lambda_r'}[(2l+1)(2l'+1)(2L+1)]^{1/2}$$
$$\times\begin{pmatrix} l & l' & L\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l & l' & L\\ -m & m' & M\end{pmatrix}\begin{pmatrix} 1 & 1 & 1\\ -\lambda_r & \lambda_r' & \lambda_r-\lambda_r'\end{pmatrix}$$
$$\times b^{p\mu}_{hlm}b^{p'\mu'*}_{h'l'm'}d^{p\mu}_{hl}(\lambda_r)d^{p'\mu'*}_{h'l'}(\lambda_r')Y^M_L(\hat{\mathbf{k}})Y_1^{\lambda_r-\lambda_r'}(\beta\gamma)\,. \tag{2}$$

Here, $l_> = \max(l,l')$ and the coefficients $b^{p\mu}_{hlm}$ are needed[7] to linearly combine the spherical harmonics to form the basis angular functions [or generalized harmonics (GH)] which belong to the pth irrep of dimensionality μ of the molecular point group. The subscript h on b's distinguishes between different GH of an irrep belonging to the same l. Finally, $d^{p\mu}_{hl}(\lambda_r)$ with $\lambda_r = 0$ and ± 1 are the $E1$ photoionization amplitudes.[3]

It is obvious from the second 3-j symbol that all the terms with $|m-m'| \le 2l_>$ will be present in the expression (2). The CDAD in the oriented nonlinear molecules is, therefore, due not only to the interference terms $0 < |m-m'| \le 2l_>$ (i.e., $m \ne m'$), but also includes those contributions for which $m = m'$. In the oriented linear molecules we have, on the other hand, two additional requirements:[2] $m+\lambda_r = m'+\lambda_r'$ and $d_{lm}(\lambda_r) = d_{l,-m}(-\lambda_r)$. [The superscripts (subscripts) $p\mu$ (h) are not needed and $b^{p\mu}_{hlm} = 1$ always, for such systems.[4]] These impose the condition[2] that for linear targets $M = m - m' = \lambda_r' - \lambda_r = \pm 1$ only.

Unlike in the case of linear systems, the projection m of l along the molecular axis is not a good quantum number for nonlinear systems. A GH of order l in the wave function of such targets may thus contain[3] all possible values of $|m| \le l$. This means that, while in the CDAD of a linear molecule, each $|m|$ corresponds to a different continuum orbital of the outgoing electron; a single photoelectron continuum represented by a given p in the expression (2) for nonlinear targets may have, on the other hand, several values of $|m| \le l$.

Consequently, CDAD in the oriented linear molecules arises[2] only as a result of interferences between degenerate continuum channels with $\Delta m = \pm 1$. But the oriented nonlinear molecules will probably always exhibit this phenomena no matter if there is a single $(p = p' = 1)$ continuum or more than one $(p,p' > 1)$ continua for the departing electron available in the expression (2). Secondly, it includes contributions due to interference $(m \ne m')$ and all other terms $(m = m')$ for which $0 \le |m-m'| \le 2l_>$. Both a single photoelectron continuum and interaction between two continua $(p \ne p')$ may give rise to such terms.

Furthermore, for a photoelectron in the X-Y plane, $Y^M_L(\pi/2,\phi) = 0$ if either L is even and M is odd or vice versa. Because of the first 3-j symbol, L in (2) has to be either even or odd according to whether l,l' have the same or opposite parities. Usually, in the wave functions of nonlinear molecules, GH corresponding to both even and odd l are present.[3] L can therefore be even as well as an odd positive integer, along with $-L \le M(=m-m') \le L$, in (2). Hence, CDAD will in general be nonzero in a plane perpendicular to the axis of a fixed nonlinear molecule. This conclusion again is different from that arrived at by Dubs, Dixit, and McKoy[2] for ionization in oriented D_∞ molecules where CDAD vanishes in a plane perpendicular to the molecular axis.

In order to see what happens to the CDAD in nonlinear molecules when the direction of incidence of light, the molecular axis, and the vector $\mathbf{k}$ are in the same plane (i.e., in a coplanar experimental configuration), let us specialize expression (2) to the situation when the polar axis of the photon frame is coincident with that of the molecule frame. This can be done either by taking $\beta = 0$ in (2) or by using the results derived elsewhere.[8] We then have

$$\frac{d^2\sigma_{\mathrm{CD}}}{d\omega(\beta=0)\, d\hat{\mathbf{k}}} = K\sqrt{6}\sum_{L=0}^{2l_>}\sum_{M=-L}^{L}\sum_{\substack{p,\mu,h,l,m,\lambda_r\\ p',\mu',h',l',m'}}(-i)^{l-l'}e^{i(\sigma_l-\sigma_{l'})}(-1)^{m-\lambda_r}\left[\frac{(2l+1)(2l'+1)(2L+1)}{4\pi}\right]^{1/2}$$
$$\times\begin{pmatrix} l & l' & L\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l & l' & L\\ -m & m' & M\end{pmatrix}\begin{pmatrix} 1 & 1 & 1\\ -\lambda_r & \lambda_r & 0\end{pmatrix}b^{p\mu}_{hlm}$$
$$\times b^{p'\mu'*}_{h'l'm'}d^{p\mu}_{hl}(\lambda_r)d^{p'\mu'*}_{h'l'}(\lambda_r)Y^M_L(\hat{\mathbf{k}})\,. \tag{3}$$

This expression, for all propagation directions $\hat{\mathbf{k}}(\theta,\phi)$, corresponds to a coplanar experimental arrangement. It is obvious that the CDAD (3) will not necessarily be zero for any values of the angles (θ,ϕ). This result that CDAD for fixed nonlinear molecules exists even in a coplanar configuration, has also been arrived at by Cherepkov and Kuznetsov[5] by a different method. On the other hand, application of the conditions mentioned after Eq. (2) causes CDAD (3) to vanish identically for oriented linear molecules.[2]

Let us consider, as an example, photoionization in $6a_1$ orbital of an isolated fixed $\mathrm{CCl_4}$ molecule. The only continuum channel available[4] to the departing electron in this case is the one which belongs to the t_2 irrep of the T_d

point group of the target molecule. [This means, $p=p'=1$ in Eqs. (2) and (3) in this case.] PEAD's for the process $6a_1 \rightarrow kt_2$ in the freely rotating[4] as well as in the oriented[8] CCl_4 have already been studied by us. It can be shown either from the results derived earlier[8] or directly from the general expression (3) that, if the first[3] $l_i=0$ term is only taken into account in the bound a_1 orbital and the photoelectron is represented by $p(l=1)$ and $d(l=2)$waves [i.e., $l,l'=1,2$ and consequently,[3] $h=h'=1$ in (3)], the CDAD in a coplanar configuration is given by[6]

$$\frac{d^2\sigma_{CD}}{d\omega(\beta=0)d\hat{\mathbf{k}}} = \frac{3K}{\pi\sqrt{5}}\,|d_1^{\mu=3}(0)|\,|d_2^{\mu=3}(0)| \times [P_1(\cos\theta)-P_3(\cos\theta)]\sin\delta\,, \qquad (4)$$

where P_L is the Lth order Ledendre polynomial. By substituting $|d_1^{\mu=3}(0)|$ and $|d_2^{\mu=3}(0)|$ from Ref. 4 for the respective p- and d-wave ionization probabilities, angular distribution (4) becomes

$$\frac{d^2\sigma_{CD}}{d\omega(\beta=0)d\hat{\mathbf{k}}} = \frac{21\bar{\sigma}}{8\pi\sqrt{35}}(12+8\bar{\beta}-7\bar{\beta}^2)^{1/2} \times \sin^2\theta\cos\theta\sin\delta\,. \qquad (5)$$

Here, $\bar{\sigma}$ is the partial integrated cross section and $\bar{\beta}$ is the asymmetry parameter for the desired transition in unoriented CCl_4 $\delta=\sigma_2-\sigma_1+\alpha_2-\alpha_1$ with α_1,α_2 the

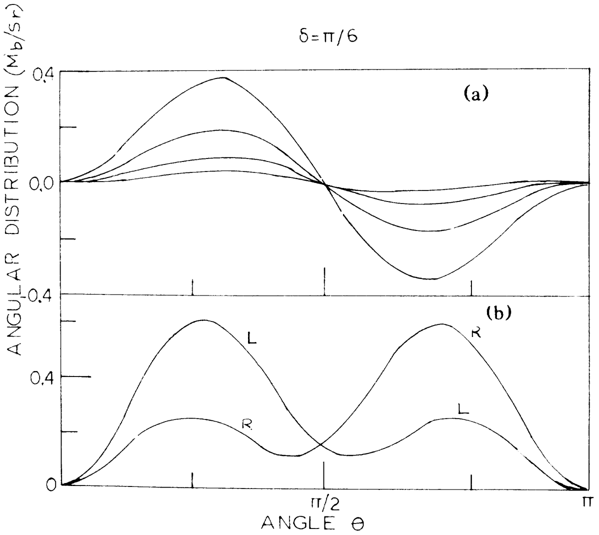

FIG. 1. (a) CDAD for ionization in the $6a_1$ orbital of an oriented CCl_4 molecule for a coplanar experimental configuration with $\delta=\pi/6$ in expression (5). These distributions, starting from the top curve, are at $E_r=23$, 25, 30, and 35 eV, respectively. The angle θ of the photoelectron propagation vector is in the molecule-fixed frame of reference. (b) The PEAD for ionization by the left (L curve) and right (R curve) circularly polarized light at $E_r=23$ eV. The phase δ, polar angle θ, and the experimental arrangement are the same as in (a).

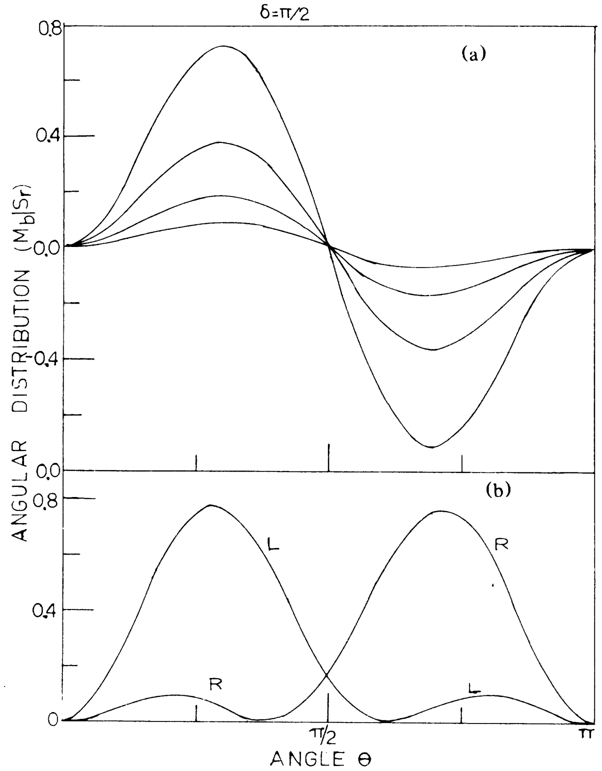

FIG. 2. Same as Fig. 1, but for $\delta=\pi/2$.

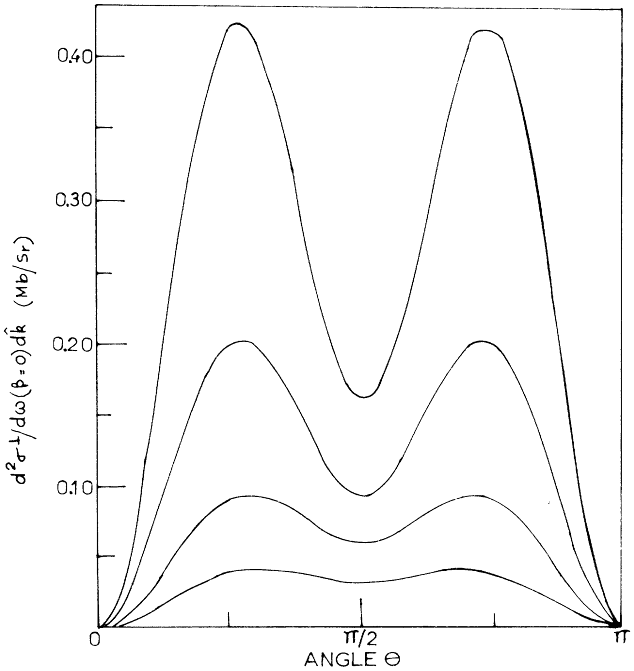

FIG. 3. Photoelectron angular distribution for ionization in $6a_1$ orbital of oriented CCl_4 with electric vector perpendicular to the molecular axis. These distributions, starting from the top curve, are at $E_r=23$, 25, 30, 35 eV respectively, and are independent of the phase δ (Ref. 8).

respective phases[6,8] of the p- and d-wave dipole-matrix elements, and σ_1,σ_2 the corresponding Coulomb phases.[3]

It is obvious from the relation (4) that if the electron ejected by photoionization in $6a_1$ orbital of an oriented CCl_4 is represented by p and d waves, only the terms with $M=m-m'=0$ and $L=\text{odd}(1,3)$ make nonvanishing contributions to the CDAD in (3). The angular distribution (4) [or (5)] is, therefore, independent of the azimuthal angle ϕ. Consequently, the photoelectron collection plane may have any orientation with respect to the X-Z plane of the molecule-fixed frame. Expression (5) further shows that for the present example, the CDAD in a coplanar experimental configuration is, in general, nonzero except when the electron detector is either along (i.e., $\theta=0,\pi$) or perpendicular (i.e., $\theta=\pi/2$) to the molecular axis.

CDAD for $\delta=\pi/6$ and $\pi/2$ are shown in Figs. 1(a) and 2(a), respectively, at each of the four $E_r=23$, 25, 30, and 35 eV. The (b) part of these figures contains the PEAD's for ionization by left and right circularly polarized light at $E_r=23$ eV.[6] The $\bar{\sigma}$ and β measured by Carlson *et al.*[9] were used in the calculations of both the CDAD from the expression (5) and that of PEAD's,[6] while δ is left as a parameter. For comparison, the PEAD for the same process $6a_1 \rightarrow kt_2$ is also shown in Fig. 3 with electric vector of the incident light perpendicular to the molecular axis in the fixed CCl_4. This distribution is defined by

$$\frac{d^2\sigma\perp}{d\omega(\beta=0)d\hat{k}}=\frac{1}{2}\left\{\frac{d^2\sigma(m_r=+1)}{d\omega(\beta=0)d\hat{k}}+\frac{d^2\sigma(m_r=-1)}{d\omega(\beta=0)d\hat{k}}\right\}$$

and has already been calculated by us.[8]

All of the cross sections shown in Figs. 1-3 have one or the other form of symmetry about $\theta=\pi/2$. Although the values of CDAD and of PEAD's both for left and right circularly polarized light in Figs. 1 and 2 strongly depend upon the phase δ, but $d^2\sigma^{\perp}/d\omega(\beta=0)d\hat{k}$ was found[8] to be independent of this angle. Therefore, a single measurement of CDAD in a coplanar experimental configuration in any direction other than $\theta=0$, $\pi/2$, and π will directly give the phase δ. Figures 1 and 2 also show that all three angular distributions are almost of the same order of magnitude for a given value of E_r.

This example thus demonstrates that the oriented nonlinear molecules also exhibit the CDAD in the $E1$ approximation in the absence of any spin-orbit interactions. In addition, it shows properties of CDAD that are brought out in this Communication for nonlinear systems, but are different from those[2] for linear targets. The CDAD spectra may be useful in studying those molecules whose axes are fixed in space along a direction by, e.g., adsorption on to a surface in their solid phase.

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