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Rotationally state-selected and oriented molecules: Photoelectron spectroscopy and chirality of C_{3V} molecules

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Abstract. This paper reports a theoretical study of photoionization in a gaseous C_{3v} molecule prepared in a single $|JKM\rangle$ rotational state of its ground electronic motion by an electrostatic hexapole field and oriented in space by the subsequent application of a weak homogeneous electric field **E**. Markedly different cross-sections are calculated for electrons ejected from $13a_1^2$ orbital of a CH_3I molecule by electromagnetic radiation plane polarized parallel and perpendicular to **E**. These photocurrents change further in different manners with rotational states of CH_3I. In accord with the experimental observation by Kaesdorf *et al.* [Phys. Rev. Lett. **54,** 885 (1985)], we also find a pronounced asymmetry in the photocurrents emitted in directions along and opposite to **E**. This forward – backward asymmetry, which very strongly depends upon the rotational state $|JKM\rangle$ of the molecule, is however more pronounced in parallel than in perpendicular experimental geometry. Both circular as well as linear dichroisms have also been studied, but neither of these shows any forward-backward asymmetry in the present application.

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1 Introduction

It is now very well known [1] that molecules in a beam prepared by the sequential applications of an electrostatic hexapole field and of an orienting (weak and homogeneous) electric field **E** are not only in a pure rotational state of their ground electronic motion, but also oriented [2] in space in their gas phase. A single-photon ionization experiment performed on such beams brings to the study of photoelectron spectroscopy (PES) the ability to probe photoionization dynamics of a single rotational quantum state of the target molecule. This ability completely eliminates the need to deconvolute the contributions to ionization over a rotational population distribution in the ground electronic level, which must otherwise be included in the usual single photon gas phase experiments. (The much simple method of pulsed seeded expansion has also been used [3,4] to prepare many diatomics predominately in a single rotational state, the rotational ground state. The $(m+n)$ resonance enhanced multiphoton ionization (REMPI) [5], on the other hand, provides ability for photoionization from an isolated, single rovibrational level only of an excited electronic state.) Secondly, molecules prepared by electrostatic hexapole field techniques [1] are oriented [2] as well in space in their gas phase. Studies of ionization of oriented molecules by absorbing a single photon have been known [6–13] to be potentially a richer source of information on photoionization dynamics than those performed on molecules which have a random orientation in space.

Thus, angle-resolved photoelectron spectroscopy (ARPES) caused by the absorption of a single photon in molecules oriented in space in a pure rotational state of their ground electronic motion provides an opportunity to study simultaneously the effects of gaseous molecular orientation and of its nuclear rotation on electron emission, provided the photocurrent is resolved in its energy with respect to the rotational states of the target [14,15]. Such processes are relevant also to studies [16] in molecular reaction dynamics and chemical reactivity which are currently of great interest. Furthermore, ARPES can be used [14,15] as one of the possible alternatives to photodissociation to determine orientational distribution function [17,18] of rotationally state selected and oriented molecules.

In contrast to the tetrahedral molecules like CCl_4 considered in the paper I [14], the symmetric top polar molecules CY_3X (where X is a halogen (F, Cl, Br, I) and Y is a H, F, or methyl), belonging to the C_{3v} point group, have very successfully been state selected and oriented using electrostatic hexapole field techniques [1] in several gas-gas [19–21], gas-surface [22], and electron-molecule [23,24], collision experiments. Probably, the first single-photon ARPES experiment on ionization in $2e$ orbital of a CH_3I molecule, prepared by a hexapole type apparatus, was performed by Kaesdorf *et al.* [25]. This

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experiment showed that there is a pronounced asymmetry in photocurrent depending upon whether electrons are emitted parallel or antiparallel to the axis of CH_3I. However, photoionization of an oriented CH_3I studied in reference [25] was in a non-quantum-state-specific manner. That is, the photocurrent measured by Kaesdorf *et al.* [25] was produced by ionizing molecules in a continuous beam of CH_3I with a relatively high rotational temperature prepared in different $|JKM\rangle$ state mixtures at different voltages of their hexapoles. But a pure $|JKM\rangle$ rotational state of CH_3I and of other polar symmetric top molecules has since been prepared by employing, instead, colder pulsed beams and long hexapole rods (see, for example, Refs. [1, 20], *etc.*). The recent advances [26] in the techniques of high resolution electron spectroscopy have, in principle, made it possible to measure photocurrents arising from ionization of a molecule in its different rotational states. By an example of photoionization in $13a_1^2$ orbital of a state selected and oriented CH_3I, we show, among other things, in this paper that the asymmetry observed by Kaesdorf *et al.* [25] should strongly depend on the rotational state of the target at the time of photoabsorption. Moreover, this dependence of the forward-backward asymmetry in the angular photocurrent on a $|JKM\rangle$ state is different in different experimental geometries. The present study therefore suggests that energy- and angle-resolved photoelectron spectroscopy of a state selected and oriented C_{3v} molecule can be used to determine its $|JKM\rangle$ rotational level as well as orientation of the molecular axis in space.

Earlier, several workers had proposed various methods for the determination of the orientation of the axis of a C_{3v} molecule in space. For example, Bernstein and coworkers [1,17,27] measured up-down asymmetry in the fragments produced in photodissociation of oriented and state-selected alkali halides; Novakoski and McClelland [28] have used an electrostatic hexapole field for detecting orientation of CF_3H desorbed from Ag surface; Leahy *et al.* [29] have related the form of the photoelectron angular distribution following $(1 + 1')$-REMPI to the orientation of the symmetry axis of a C_{3v} molecule; Kasai *et al.* [23] have observed effects of molecular orientation on indirect ionization of CH_3Cl by electron impact. The theoretical suggestion made by Kohl and Shipsey [30] to measure orientation by electron scattering has been experimentally realized by Bowering and coworkers [24]. Recently, Powis *et al.* [12] have performed theoretical studies of photoionization in some of the C_{3v} molecules, *e.g.*, CF_3I, CH_3I, and CF_3Cl. In order to relate the results to photoelectron-photoion coincidence experiments, Powis and coworkers [12] have considered the target molecules in their calculations to be fixed in space.

Two new physical phenomena which have currently been found to be useful for studying oriented molecules or polarized atomic as well as molecular targets through their photoionization are circular and linear dichroisms. Circular dichroism (CD) is known to be the difference in the effects produced by the absorption of left circularly polarized (LCP) and right circularly polarized (RCP) photons; whereas, the difference in the effects arising due to the absorption of electromagnetic radiation which are linearly polarized (LP) in two mutually perpendicular directions is called linear dichroism (LD). Originally, circular dichroism in angular distribution of photoelectron (CDAD) was first theoretically studied [31] and then experimentally measured [32] for molecules fixed in space. It was later shown by us [14,15] to exist in the photoionization of even state selected and oriented molecules. Molecular targets fixed in space have been shown [33] to exhibit also linear dichroism in the angular distribution of their photoelectrons (LDAD).

In this paper we show that both CDAD and LDAD not only are described by expressions which are considerably simpler compared to that needed to study angular distribution of photoelectrons, but also provide complementary information on photoionization of state-selected and oriented molecules. However, unlike the photoelectron angular distribution, neither of these exhibits any forward-backward asymmetry in the photocurrent. In fact, in the present application we find that each of CDAD and LDAD vanishes identically in directions parallel or opposite to the axis of CH_3I. But in directions other than these two, both CDAD and LDAD strongly depend upon the state $|JKM\rangle$ and also on the experimental geometry.

The general theory [14] for photoelectron spectroscopy of state-selected and oriental molecules is briefly reviewed in Section 2. The next section describes also the linear dichroism in photoionization of state-selected and oriented molecules. Hitherto [14,15,33], it has not been studied for molecules prepared by an electrostatic hexapole field. In the Section 3 we first describe, in short, a theoretical framework [15] for performing a semi-empirical study of photoionization in a_1 orbital of a state-selected and oriented C_{3v} molecule. This framework utilizes [15] just two observables measured in a typical gas phase experiment on photoionization of randomly oriented molecules. Results of the application of this framework to photoionization in $13a_1^2$ orbital of CH_3I prepared by an electrostatic hexapole field are presented in the Section 3.1. Unlike in reference [15], the rotational states of the residual CH_3I^+ are not taken into account in this paper. But, both the forward-backward asymmetry and the linear dichroism, not studied elsewhere [14,15], have been calculated in the application presented in the Section 3.1. The final Section 4 discusses the conclusions of this work.

2 Theory for photoionization of state selected and oriented molecule

We have developed in reference [14] a theory for ARPES of a symmetric top molecule (say, $\mathcal{M}$) belonging to one of the 32 point groups. The target $\mathcal{M}$ was taken to be oriented in space in a single $|JKM\rangle$ rotational state of its ground electronic motion using [1] electrostatic hexapole field followed by a weak, homogeneous electric field $\mathbf{E}$. (See Fig. 1 for the meaning of the quantum numbers J, K, and M.) In this section of the present communication we briefly discuss the important properties of the relevant formulae derived in reference [14].

$$\chi'_{L_r}(JKM;\hat{\mathbf{p}};\mathbf{k}) = \mathcal{K}\sum_{\substack{L_T\neq 0\\ LM}}^{2J}\sum_{\substack{lm\lambda_r\\ l'm'\lambda'_r}} (-1)^{L+m+\lambda'_r}\sqrt{(2L+1)(2L+2)}$$
$$\times \begin{pmatrix} l & l' & L\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l & l' & L\\ -m & m' & M\end{pmatrix}\begin{pmatrix} 1 & 1 & L_r\\ -\lambda_r & \lambda'_r & M\end{pmatrix}\begin{pmatrix} L & L_r & L_T\\ M & -M & 0\end{pmatrix}\mathcal{Y}^{LL_r}_{L_T0}(\hat{\mathbf{p}},\mathbf{k})d_{lm}(\lambda_r)d^*_{l'm'}(\lambda'_r)\overline{P}_{L_T}. \qquad (4d)$$

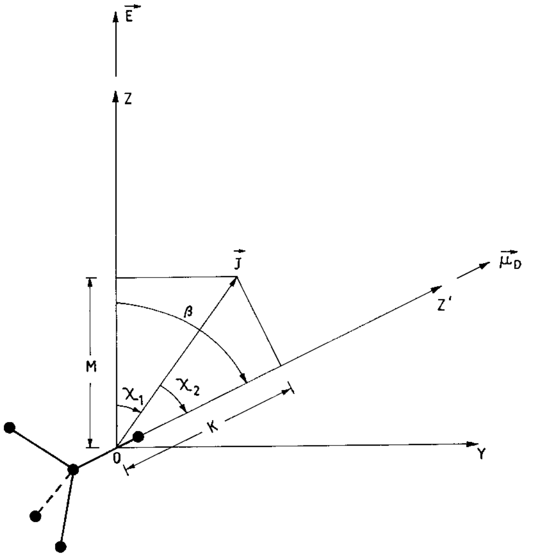

Fig. 1. $OXYZ$ is the space (or laboratory)-fixed frame of reference. Its polar axis is along the weak, homogeneous, orienting electric field $\mathbf{E}$ and defines the space-fixed quantization direction. The permanent electric dipole moment $\boldsymbol{\mu}_D$ of a symmetric top is along the OZ' axis and forms the body (or molecule)-fixed quantization direction. The center of mass of the molecule is at O. OZ' is also the polar axis of a molecule-fixed coordinate system ($OX'Y'Z'$, not shown in this figure) which is concentric with $OXYZ$. The rotational state $|JKM\rangle$ of a symmetric top is represented in these two frames of reference by the total angular momentum vector $\mathbf{J}$ of magnitude $|\mathbf{J}|\hbar = \sqrt{J(J+1)}\hbar$. $\mathbf{J}$ uniformly rotates about the OZ axis at a constant inclination χ_1 such that its projection $M = \mathbf{J}\cdot\hat{\mathbf{O}}Z = \sqrt{J(J+1)}\cos\chi_1$ represents space quantization of the $|JKM\rangle$ state. The spinning of the symmetric top about its own axis (OZ') generates angular momentum $K\hbar$ such that OZ', in turn, processes about $\mathbf{J}$ at a constant angle χ_2 given by $K = \mathbf{J}\cdot\hat{\mathbf{O}}Z' = \sqrt{J(J+1)}\cos\chi_2$. The quantum number K thus describes the quantization of $\mathbf{J}$ in molecule-fixed frame of reference. The angle β at which the OZ' axis of the symmetric top revolves about $\mathbf{E}$ on account of the torque $\boldsymbol{\mu}_D\times\mathbf{E}$ experienced by it is such that $|\chi_1-\chi_2|\leq\beta\leq\chi_1+\chi_2$.

Differential cross-section for ionization of a state-selected and oriented molecule $\mathcal{M}$ in electric dipole ($E1$) approximation is given by equation (I.19) [14]. That expression can be written in the following form

$$\frac{d^2\sigma(m_r;JKM)}{d\hat{\mathbf{p}}d\hat{\mathbf{k}}} = \frac{d^2\overline{\sigma}(m_r)}{d\hat{\mathbf{p}}d\hat{\mathbf{k}}} + \sigma(m_r;JKM;\hat{\mathbf{p}};\mathbf{k}). \qquad (1)$$

The quantity m_r used in equation (1) and elsewhere in this paper specifies the state of polarization of the absorbed radiation: $m_r = 0$ for LP, $m_r = +1$ for RCP, and $m_r = -1$ for LCP. An unpolarized (UP) electromagnetic wave is treated to be an even mixture of RCP and LCP radiation. The unit vector $\hat{\mathbf{p}}(\theta_p,\phi_p)$ specifies the direction of propagation of UP, RCP, and LCP photon beams. A LP radiation, on the other hand, is considered to be polarized along $\hat{\mathbf{p}}$. The spherical angles (θ_p,ϕ_p) are measured with respect to the space-fixed frame of reference $OXYZ$, shown and explained in Figure 1. The direction of departure $\hat{\mathbf{k}}(k,\theta_k,\phi_k)$ of a photoelectron ejected with kinetic energy $\varepsilon = \hbar^2k^2/2m$ is also specified with respect to the space-frame.

Further in equation (1)

$$\frac{d^2\overline{\sigma}(m_r)}{d\hat{\mathbf{p}}d\hat{\mathbf{k}}} = \frac{\overline{\sigma}}{4\pi}\left[1+\frac{1}{2}(2-3m_r^2)\overline{\beta}P_2(\hat{\mathbf{p}}\hat{\mathbf{k}})\right] \qquad (2)$$

is the usual [34] angular photocurrent measured in a typical ionization experiment on unoriented gas phase molecules. (It describes also the photoionization of a $|000\rangle$ rotational state which can not be oriented [1].) Here, $P_L(x)$ is the Legendre polynomial [35] of order L, $\overline{\sigma}$ is the detection-integrated photoionization cross-section, and $\overline{\beta}$ is the angular asymmetry parameter. Explicit expressions for $\overline{\sigma}$ and $\overline{\beta}$ in terms of the $E1$ photoionization amplitudes (5) are readily obtained either by comparing (1) and (I.19), or directly from reference [36].

In order to understand the reasons for the presence of the second term $\sigma(m_r;(JKM;\hat{\mathbf{p}};\mathbf{k}))$ in (1), let us first write it in the following form

$$\begin{aligned}\sigma(m_r;(JKM;\hat{\mathbf{p}};\mathbf{k})) &= \chi_0(JKM;\hat{\mathbf{k}})\\ &+\frac{1}{2}m_r\chi_1(JKM;\hat{\mathbf{p}};\mathbf{k})\\ &+\frac{1}{2}(2-3m_r^2)\chi_2(JKM;\hat{\mathbf{p}};\mathbf{k}). \qquad (3)\end{aligned}$$

Here (χ_0,χ_1,χ_2) are three independent parameters given by

$$\chi_0(JKM;\hat{\mathbf{k}}) = -\frac{1}{\sqrt{3}}\chi'_0(JKM;\hat{\mathbf{k}}) \qquad (4a)$$

$$\chi_1(JKM;\hat{\mathbf{p}};\mathbf{k}) = -\sqrt{2}\chi'_1(JKM;\hat{\mathbf{p}};\mathbf{k}) \qquad (4b)$$

$$\chi_2(JKM;\hat{\mathbf{p}};\mathbf{k}) = \sqrt{\frac{2}{3}}\chi'_2(JKM;\hat{\mathbf{p}};\mathbf{k}) \qquad (4c)$$

with

See equation (4d) above

and

$$d_{lm}(\lambda_r) = (-i)^l e^{i\sigma_l}\sqrt{2l+1}\sum_{p\tau h} b^{p\tau}_{hlm} d^{p\tau}_{hl}(\lambda_r). \qquad (5)$$

In expression (4d), the constant $\mathcal{K} = 3\pi(e^2/\alpha_0 E_r)^2$, with α_0 the dimensionless fine structure constant and E_r the energy of the ionizing radiation; $\mathcal{Y}$'s are the bipolar harmonics [37]; the Legendre moment $\overline{P}_{L_T}$ defined, for example, in equation (I.7) is the expectation value of the Legendre polynomial P_{L_T} between the states $|JKM\rangle$ of a molecule $\mathcal{M}$ rotating like a symmetric top. Further, equation (5) above is identical to equation (3b) in reference [15]. The detailed descriptions given therein [15] of the $E1$ amplitude $d^{p\tau}_{hl}(\lambda_r)$ and of other quantities present in equation (5) are applicable also in the present paper.

It is obvious from the occurrence of the moments $\overline{P}_{L_T}$ in (4d), that the second term in (1) depends upon the rotational state $|JKM\rangle \neq |000\rangle$ of $\mathcal{M}$. It, thus, represents the contribution to the angular photocurrent arising due to the orientation of $\mathcal{M}$ in space in a single $|JKM\rangle$ state of its ground electronic motion. Hence the additional information gained in photoionization of state selected and oriented molecules is contained in $\sigma(m_r; JKM; \hat{\mathbf{p}}; \mathbf{k})$. It is evident from (3) that this information is completely characterized by three independent parameters (χ_0, χ_1, χ_2). Each of these parameters depends, in addition to the photoionization dynamics and the rotational state $|JKM\rangle$, on the experimental geometry *via* the photoelectron propagation and photon vectors $\hat{\mathbf{k}}$ and $\hat{\mathbf{p}}$, respectively. In contrast, the differential cross-section (2) for photoionization in unoriented molecules requires only two dynamical parameter ($\overline{\sigma}$ and $\overline{\beta}$) which depend neither on the experimental geometry nor on the quantum numbers J, K, and M. In conclusion, the angular photocurrent produced in ionization in $E1$ approximation of a state-selected and oriented molecule is completely determined by the five independent parameters $(\overline{\sigma}, \overline{\beta}, \chi_0, \chi_1, \chi_2)$.

On integrating expression (1) over $\hat{\mathbf{k}}$, one obtains the detection-integrated cross-section

$$\frac{d\sigma(m_r; JKM)}{d\theta_p} = \overline{\sigma} + \sigma(m_r; JKM; \theta_p) \qquad (6)$$

for the same process. The contribution to the cross-section (6) due to orientation of $\mathcal{M}$ in a single $|JKM\rangle$ rotational state is given by

$$\begin{aligned}\sigma(m_r; JKM; \theta_p) = {} & \frac{1}{2} m_r \sigma^{(1)}(JKM)\cos\theta_p \\ & + \frac{1}{2}(2 - 3m_r)\sigma^{(2)}(JKM) P_2(\cos\theta_p)\end{aligned} \qquad (7)$$

with

$$\sigma^{(1)}(JKM) = \mathcal{K}\overline{P}_1 \sum_{\substack{p\tau h\\ l\lambda_r}} \lambda_r \left|d^{p\tau}_{hl}(\lambda_r)\right|^2 \qquad (8a)$$

and

$$\sigma^{(2)}(JKM) = \frac{1}{3}\mathcal{K}\overline{P}_2 \sum_{\substack{p\tau h\\ l\lambda_r}} (2 - 3\lambda_r^2)\left|d^{p\tau}_{hl}(\lambda_r)\right|^2. \qquad (8b)$$

Thus, only three $(\overline{\sigma}, \sigma^{(1)}, \sigma^{(2)})$ parameters, rather than five, $(\overline{\sigma}, \overline{\beta}, \chi_0, \chi_1, \chi_2)$ present in the angular distribution (1), are sufficient to characterize the integrated cross-section (6). Moreover, unlike the geometry-dependent parameters (χ_0, χ_1, χ_2) present in (3), $\sigma^{(1)}$ and $\sigma^{(2)}$ no longer contain any of the directions $\hat{\mathbf{p}}$ and $\hat{\mathbf{k}}$. The $|JKM\rangle$ dependence of $\sigma^{(1)}$ and $\sigma^{(2)}$ arises due only to the Legendre moments of order one and two (*i.e.* $\overline{P}_1$ and $\overline{P}_2$ in Eqs. (8)), respectively; whereas, each of χ_0, χ_1, and χ_2 in (3) can have Legendre moments of order upto $2J$. The integrated cross-section (6) is, of course, independent of the propagation direction $\hat{\mathbf{k}}$ of the photoelectron, does involve $(m_r, \hat{\mathbf{p}})$ characteristics of the absorbed radiation, but has cylindrical symmetry about $\mathbf{E}$.

The contribution $\sigma(m_r; JKM; \theta_p)$ due to orientation of the molecule to the cross-section (6) vanishes identically for ionization by LP or UP radiation with $\theta_p = 54.7°$, *i.e.* the magic angle θ_m. Equation (6) then directly gives $\overline{\sigma}$. *Thus, one can measure the integrated photocurrent produced in ionization of an unoriented molecule by performing experiments on state-selected and oriented molecules as well. Such measurements should be very useful in calibrating the difficult apparatus of a hexapole field arrangement combined with a high resolution electron spectrometer.*

Once $\sigma^{(1)}$ and $\sigma^{(2)}$ are measured, one can determine, using the respective equations (8a) and (8b), the Legendre moments $\overline{P}_1$ and $\overline{P}_2$. According to equation (I.7), $\overline{P}_1 = \langle\cos\beta\rangle$, *i.e.*, the mean degree of orientation of the molecular axis about the weak and homogeneous orienting field $\mathbf{E}$ (see Fig. 1); $\overline{P}_2 = \frac{1}{2}\langle 3\cos^2\beta - 1\rangle$ measures the alignment of the rotational probability distribution of the molecule. Although, $\overline{\sigma}$ will remain same, both $\sigma^{(1)}$ and $\sigma^{(2)}$ will be different for different $|JKM\rangle$ states of $\mathcal{M}$ selected by the hexapole field.

Circular dichroism in the integrated photocurrent (CDIP) [31] produced in the ionization of a state-selected and oriented molecule is obtained from equations (6) and (7) to be

$$\begin{aligned}\frac{d\sigma_{CD}(JKM)}{d\theta_p} \equiv {} & \frac{d\sigma(m_r = +1; JKM)}{d\theta_p} \\ & - \frac{d\sigma(m_r = -1; JKM)}{d\theta_p} \\ = {} & \sigma^{(1)}(JKM)\cos\theta_p.\end{aligned} \qquad (9)$$

Thus only a single $[\sigma^{(1)}(JKM)]$, out of the three $[\overline{\sigma}, \sigma^{(1)}(JKM)$ and $\sigma^{(2)}(JKM)]$, parameters is sufficient to determine CDIP (9). As $\sigma^{(1)}$ determines a part of the contribution (7) to the photoionization cross-section (6) which arises due to orientation of the molecules in a single $|JKM\rangle$ state, CDIP obviously does not exist for ionization in unoriented molecules. Moreover, CDIP even for

$$\sigma_{LD}(JKM;\mathbf{k}) = \chi_2(JKM;\hat{\mathbf{p}};\mathbf{k})\,\big|_{\hat{\mathbf{p}}\|\hat{\mathbf{y}}} - \chi_2(JKM;\hat{\mathbf{p}};\mathbf{k})\big|_{\hat{\mathbf{p}}\|\hat{\mathbf{x}}} \tag{14a}$$

$$= -\frac{\mathcal{K}}{4\pi}\sqrt{5}\sum_{\substack{L_T\neq 0\\ LM}}\sum_{\substack{lm\lambda r\\ l'm'\lambda'_r}}(-1)^{m+\lambda_r}(2L+1)(2L_T+1)\sqrt{(L-M)!(L+M)!}\begin{pmatrix} l & l' & L\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l & l' & L\\ -m & m' & M\end{pmatrix}$$
$$\times\begin{pmatrix} 1 & 1 & L_r\\ \lambda_r & -\lambda'_r & -M\end{pmatrix}\begin{pmatrix} L & 2 & L_r\\ M & -M & 0\end{pmatrix}\begin{pmatrix} L & 2 & L_r\\ 2 & -2 & 0\end{pmatrix}P_L^2(\cos\theta_k)[e^{2i\phi_k}+(-1)^{L+L_T}e^{-2i\phi_k}]d_{lm}(\lambda_r)d^*_{l'm'}(\lambda'_r)\overline{P}_{L_T} \tag{14b}$$

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oriented molecules vanishes identically if the CP radiation is incident perpendicular to the orientating field **E** (*i.e.*, $\theta_p = \pi/2$ in Fig. 1), otherwise it has cylindrical symmetry about **E**. A single measurement of $\dfrac{d\sigma_{CD}(JKM)}{d\theta_p}$ is sufficient to extract the Legendre moment $\overline{P}_1$, *i.e.*, the mean degree of molecular orientation about **E**.

Equations (1), (2) and (3) show that

$$\frac{d^2\sigma_{CD}(JKM)}{d\hat{\mathbf{p}}d\hat{\mathbf{k}}} \equiv \frac{d^2\sigma_{CD}(m_r=+1,JKM)}{d\hat{\mathbf{p}}d\hat{\mathbf{k}}} - \frac{d^2\sigma_{CD}(m_r=-1;JKM)}{d\hat{\mathbf{p}}d\hat{\mathbf{k}}} = \chi_1(JKM;\hat{\mathbf{p}};\mathbf{k}) \tag{10}$$

is the CDAD for photonionization in rotationally state-selected and oriented molecules. Here too we find that, unlike the specification of $\dfrac{d^2\sigma(m_r;JKM)}{d\hat{\mathbf{p}}d\hat{\mathbf{k}}}$ in equation (1) which requires five parameters, only a single parameter χ_1 is sufficient to determine the CDAD (10). Thus studies of dichroic effects in the integrated as well as in the angular photocurrent produced in ionization of state-selected and oriented molecules are much simpler than those of the corresponding cross-sections and give us direct information on both photoionization dynamics and orientational distribution function.

In order to study LD in the present paper, let us take two mutually perpendicular directions for linear polarization of the ionizing radiation to be along the X- and Y-axes of the space fixed coordinate system $OXYZ$ shown in the Figure 1 (*i.e.*, $\hat{\mathbf{p}}(\frac{\pi}{2},0)$ and $\hat{\mathbf{p}}(\frac{\pi}{2},\frac{\pi}{2})$, respectively). Then linear dichroism in the integrated photocurrent (LDIP) [33] is obtained from equations (6) and (7) to be

$$\sigma_{LD}(JKM) \equiv \frac{d\sigma(m_r=0;JKM)}{d\hat{\mathbf{p}}(\frac{\pi}{2},\frac{\pi}{2})} - \frac{d\sigma(m_r=0;JKM)}{d\hat{\mathbf{p}}(\frac{\pi}{2},0)} = 0 \tag{11}$$

Thus unlike CDIP (9), LDIP does not exist in the photoionization of even state-selected and oriented molecules. The LDAD, on the other hand,

$$\frac{d\sigma_{LD}(JKM)}{d\hat{\mathbf{k}}} \equiv \frac{d^2\sigma(m_r=0;JKM)}{d\hat{\mathbf{p}}(\frac{\pi}{2},\frac{\pi}{2})d\hat{\mathbf{k}}} - \frac{d^2\sigma(m_r=0;JKM)}{d\hat{\mathbf{p}}(\frac{\pi}{2},0)d\hat{\mathbf{k}}} = \frac{d\overline{\sigma}_{LD}}{d\hat{\mathbf{k}}} + \sigma_{LD}(JKM;\hat{\mathbf{k}}) \tag{12}$$

is obtained from equation (1). Here

$$\frac{d\sigma_{LD}}{d\hat{\mathbf{k}}} = -\frac{3}{8\pi}\overline{\sigma}\overline{\beta}\sin^2\theta_k\cos 2\phi_k = -\frac{1}{4\pi}\mathcal{K}\sqrt{\frac{15}{2}}\sin^2\theta_k\cos 2\phi_k \times\sum_{\substack{ll'\lambda_r\lambda'_r\\ mm'M}}(-1)^{m+\lambda_r}\begin{pmatrix} l & l' & 2\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l & l' & 2\\ m & -m' & M\end{pmatrix}\times\begin{pmatrix} 1 & 1 & 2\\ \lambda_r & -\lambda'_r & -M\end{pmatrix}d_{lm}(\lambda_r)d^*_{l'm'}(\lambda'_r) \tag{13}$$

is the LDAD for ionization in randomly oriented molecules, *i.e.*, for molecules which are oriented in $|000\rangle$ rotational state. Expression (13) is identical to that derived in reference [33]. Further in (12),

See equations (14a) and (14b) above

is the contribution to LDAD due to orientation of the molecule in the rotational state $|JKM\rangle \neq |000\rangle$. It depends upon the state $|JKM\rangle$ being photoionized as well as on the direction of propagation $\hat{\mathbf{k}}$ of the photoelectron. Thus, unlike CDAD (10) which is due only to the orientation of the molecule in space, the LDAD (12) is the sum of the LDAD for unoriented molecules [33] and an additional contribution due to orientation of the molecule. Consequently, while a single parameter χ_1 (Eq. (4b)) determines the CDAD (10), three parameters $\overline{\sigma}, \overline{\beta}$ and χ_2 (Eqs. (13) and (14a)) are needed for a complete specification of the LDAD (12). Thus CDAD and LDAD provide complementary information on photoinization of state-selected and oriented molecules.

3 Application: Photoionization in a_1 orbital of a C_{3v} molecule

The group theoretical methods show that for an allowed $E1$ process the continuum orbital of an electron ejected from the a_1 bound orbital of a C_{3v} molecule should transform according to either non-degenerate A_1 or doubly degenerate E IR of this point group. (Hereafter, these orbitals and the corresponding electrons will always be represented by εa_1 and εe, respectively.) In the present study we, therefore, need $E1$ amplitudes for each of the photoionizing transitions $a_1^2 \to a_1^1 \varepsilon a_1$ and $a_1^2 \to a_1^1 \varepsilon e$, *i.e.*, $d_{hl}^{a_1}(\lambda_r)$ (omitting the superscript τ as its value is always one in this case) and $d_{hl}^{e\tau}(\lambda_r)$ (with $\tau = 1$ and 2), respectively. It has already been shown in reference [15] that due to the group theoretical considerations and the relationship (12a) obtained therein [15] among $d_{hl}^{e\tau}(\lambda_r)$ (with $\tau = 1$, 2 and $\lambda_r = \pm 1$), the number of independent transition moments for each set of the subscripts (hl) needed to represent photoelectron in the εa_1 and εe continuum orbitals reduces to two, namely $d_{hl}^{e}(0)$ and $d_{hl}^{e}(1)$.

An analysis [15] of the ARPES observed in reference [38] for $E1$ ionization in the $13a_1^2$ orbital of randomly oriented gaseous CH_3I has shown that in order to reproduce the experimentally measured values of both the $\overline{\sigma}$ and $\overline{\beta}$ in the angular distribution (2) of electrons ejected in photoionization of unoriented targets over the whole range of photon energies, starting from threshold to higher values, considered by Carlson *et al.* [38] in their experiment, it was necessary to represent the photoelectron in its continuum εa_1 and εe orbitals by $s(l = 0)$ - and $p(l = 1)$ - partial waves, respectively. In the present work as well, we therefore represent the outgoing $E1$ electron by these two partial waves only, *i.e.*, consider the respective amplitudes $d_{h_0}^{a_1}(0)$ and $d_{hl}^{e}(1)$ only. Following further the discussion given in reference [15], the independent transition amplitudes used in the present study are $d_{10}^{a_1}(0)$ and $d_{11}^{e}(1)$, *i.e.*, one each for the respective $a_1^2 \to a_1^1 \varepsilon a_1$ and $a_1^2 \to a_1^1 \varepsilon e$ bound-free transitions in a C_{3v} molecules. The magnitudes

$$|d_{10}^{a_1}(0)|^2 = \frac{3\overline{\sigma}}{7\mathcal{K}}(7 - 5\overline{\beta})$$

and (15)

$$|d_{11}^{e}(1)|^2 = \frac{15\overline{\sigma}}{28\mathcal{K}}\overline{\beta}$$

of both of these matrix elements are extracted [15] from the experimentally measured values of $\overline{\sigma}$ and $\overline{\beta}$ present in equation (2). If α_0 and α_1 are the phases of these two $E1$ amplitudes, then

$$d_{10}^{a_1}(0) = |d_{10}^{a_1}(0)|\, e^{i\alpha_0}$$

and (16a)

$$d_{11}^{e}(1) = |d_{11}^{e}(1)|\, e^{i\alpha_1}.$$

In the remaining discussion we will also need to use the phase

$$\delta = (\sigma_0 + \alpha_0) - (\sigma_1 + \alpha_1). \qquad (16b)$$

Here σ_0 and σ_1 are the Coulomb phases (defined, for example, in Ref. [39]) for s- and p-partial waves of the photoelectron, respectively.

3.1 Results: Photoionization in $13a_1^2$ orbital of CH_3I

In this sub-section, we present our results of the calculations performed using the framework developed in Section 2 in this paper. The specific example considered by us is photoionization in $13a_1^2$ orbital of a gaseous CH_3I molecule prepared [1] in a single $|JKM\rangle$ rotational state of its ground electronic motion by electrostatic hexapole field and subsequently oriented in space using the weak and homogeneous field $\mathbf{E}$. The information about photoionization dynamics needed in the expressions given in the Section 2 is obtained from equations (15) and (16). Because we do not do any dynamical calculations in this paper, the experimentally measured values of $(\overline{\sigma}, \overline{\beta})$ needed in the probabilities (15) are therefore used. Approximations [15], briefly described at the beginning of this section and employed in the derivation of equation (15), should preferably be used for photon energies close to threshold to ionization of $13a_1^2$ orbital of CH_3I so that the energy of the escaping electron is small. In our study, we have used the minimum photon energy ($E_r = 16$ eV) measurements reported by Carlson *et al.* [38] corresponding to $\overline{\sigma} = 15.5$ Mb and $\overline{\beta} = 0.28$ in the angular distribution (2) of photoelectrons departing with energy 3.5 eV from the $13a_1^2$ orbital of a CH_3I molecule. The only energy dependent quantity now left to be known is the phase δ, defined in equation (16b), which is treated as a parameter in this paper. Also, we have, herein, considered $1 \le J \le 4$ appropriate for low-temperature beams. Furthermore, the two experimental geometries used in this paper are those in which the vector $\hat{\mathbf{p}}(\theta_p, \phi_p)$ is parallel (*i.e.*, $\theta_p = 0, \phi_p$) and perpendicular (*i.e.*, $\theta_p = \frac{\pi}{2}, \phi_p$) to the weak and homogeneous orienting field $\mathbf{E}$, taken to be along the OZ axis in Figure 1. For LP ionizing radiation, this means that the electric vector is either along or perpendicular to $\mathbf{E}$. If, on the other hand, ionization is caused by the absorption of a CP or UP photon, it is taken to be incident, according to the two geometries considered by us, either along the Z-direction or in the X-Y plane.

3.1.1 Integrated and differential cross-sections

According to equations (6) and (7), a complete specification of the detection integrated photocurrent produced in the ionization of a state-selected and oriented molecule requires a knowledge of the parameters $\overline{\sigma}, \sigma^{(1)}(JKM)$, and $\sigma^{(2)}(JKM)$. On specializing expressions for these parameters to the approximations described in this section, we obtain

$$\overline{\sigma} = \frac{\mathcal{K}}{3}\left(|d_{10}^{a_1}(0)|^2 + 4\,|d_{11}^{e}(1)|^2\right), \qquad (17)$$

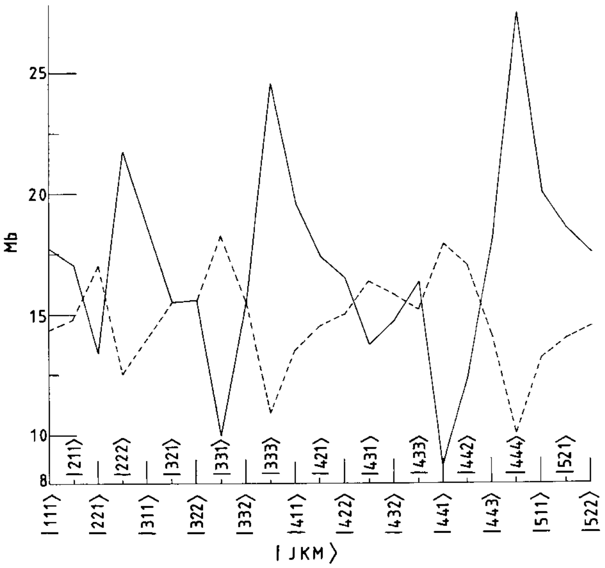

Fig. 2. The integrated cross-sections for photoionization in $13a_1^2$ orbital of CH$_3$I oriented in space in a single $|JKM\rangle$ rotational state. The electric vector in the LP beam of ionizing radiation is either parallel or perpendicular to the space-fixed quantization **E** direction. These cross-sections are calculated by using in equation (19) the values of $\overline{\sigma}$ and $\overline{\beta}$ measured by Carlson *et al.* [38] for photoelectron energy $\varepsilon = 3.5$ eV. $\sigma^{\|}(0; JKM)$: (——); $\sigma^{\perp}(0; JKM)$: (– – –).

$$\sigma^{(1)}(JKM) = 0$$

and (18)

$$\sigma^{(2)}(JKM) = \frac{2}{3}\mathcal{K}\left(|d^{a_1}_{10}(0)|^2 + 2\,|d^{e}_{11}(1)|^2\right)\overline{P}_2.$$

Thus, while $\sigma^{(1)}$ vanishes identically, $\overline{\sigma}$ as well as $\sigma^{(2)}$ are independent of the phase (16) and completely determined by the magnitudes (15) of the transition probabilities. In view of equations (7) and (18), the contribution $\sigma(m_r; JKM; \theta_p)$ to the integrated cross-section (6) due to orientation of a C_{3v} molecule in a single $|JKM\rangle$ state is now given by $\sigma^{(2)}(JKM)$ only. On combining equations (6, 7, 17, 18), and then using the probabilities (15) we find the desired quantity

$$\frac{d\sigma(m_r; JKM)}{d\theta_p} = \overline{\sigma} + (2 - 3m_r^2) \times (1 - \frac{15}{14}\overline{\beta})\overline{\sigma}\,\overline{P}_2 P_2(\cos\theta_p). \tag{19}$$

The second term on the right hand side of this equation is $\sigma(m_r; JKM; \theta_p)$ defined in equation (7). This contribution obviously vanishes if the ionization radiation has $\theta_p = \theta_m$. In this way one can determine $\overline{\sigma}$ even by performing an experiment on photoionization in a_1^2 orbital of state-selected and oriented C_{3v} molecules. With known values of $(\overline{\sigma}, \overline{\beta})$, a single measurement of (19) will directly give the Legendre moment $\overline{P}_2$, *i.e.*, the first alignment parameter $\langle P_2(\cos\beta)\rangle$ of the rotational state distribution.

Figure 2 shows the cross-section (19) as a function of the rotational states $|JKM\rangle$ for ionization in $13a_1^2$ orbital of state-selected and oriented CH$_3$I by LP radiation ($m_r = 0$) in parallel (*i.e.*, $[d\sigma(0; JKM))/d\theta_p]_{\theta_p=0} \equiv \sigma^{\|}(0; JKM)$) and perpendicular (*i.e.*; $[d\sigma(0; JKM)/d\theta_p]_{\theta_p=\frac{\pi}{2}} \equiv \sigma^{\perp}(0; JKM)$) geometries. We see that, while the cross-section $\overline{\sigma}$ for ionization of unoriented CH$_3$I provides a constant background, both $\sigma^{\|}(0; JKM)$ and $\sigma^{\perp}(0; JKM)$ are not only different from each other, but also change in different manners with the states $|JKM\rangle$. For example, while $\sigma^{\|}$ is maximum for photoionization in the $|JJJ\rangle$ state for a given rotational quantum number J, $\sigma^{\perp}$ has its minimum value for photoionization in this head *versus* tail orientation of CH$_3$I. On the other hand $\sigma^{\|}$ and $\sigma^{\perp}$ become, respectively, minimum and maximum for photoelectron emission from the $|JJ1\rangle$ state which corresponds to broad side orientation of CH$_3$I in the weak, homogeneous field **E**.

In an experimental arrangement in which $\sigma^{\|}(0; JJJ)$ is measured, both the electric vector in the LP ionizating radiation and the molecular axis are along **E** (see Fig. 1). But in experiments measuring $\sigma^{\perp}(0; JJJ)$, while the electric vector of the ionizing radiation becomes perpendicular to **E**, the molecular axis is still in the direction of **E**. On the other hand, experimental configurations appropriate for the measurements of $\sigma^{\|}(0; JJ1)$ and $\sigma^{\perp}(0; JJ1)$ consist of the electric vector in the LP incident photon beam parallel and perpendicular to **E**, respectively; whereas CH$_3$I is in a broad side orientation with its axis making the largest possible angle ($\leq 90°$) with the space-fixed quantization direction **E** (see Fig. 1).

In view of the discussions presented in the two preceding paragraphs, one can easily conclude that the integrated cross-section for photoionization in $13a_1^2$ orbital of a state selected and oriented molecule is larger when the electric field vector in the LP radiation is parallel to the axis of the molecule oriented in space compared to when the two are mutually perpendicular. Moreover, this cross-section further increases when both the electric field vector in LP light and the molecular axis point in the direction of **E**.

In order to calculate the angular photocurrent produced in ionization of a state selected and oriented C_{3v} molecule, we first specialize relations (4) to the approximations at the beginning of this section. This immediately gives

$$\chi_0(JKM; \mathbf{k}) = \frac{\mathcal{K}}{6\pi}\,|d^{e}_{11}(1)|^2\,\overline{P}_2 P_2(\cos\theta_k), \tag{20a}$$

$$\chi_1(JKM; \hat{\mathbf{p}}; \mathbf{k}) = \frac{\mathcal{K}}{\pi}\sqrt{\frac{3}{2}}\,|d^{a_1}_{10}(0)|\,|d^{e}_{11}(1)| \times \overline{P}_1 \cos\delta \sin\theta_k \sin\theta_p \sin(\phi_k - \phi_p), \tag{20b}$$

$$\chi_2(JKM;\hat{\mathbf{p}};\mathbf{k}) = 2\frac{\mathcal{K}}{\pi}\left\{\frac{1}{12}\left|d_{10}^{a_1}(0)\right|^2\overline{P}_2 P_2(\cos\theta_p)\right.$$

$$+\left[\frac{1}{28}(5\overline{P}_2+\frac{3}{5}\overline{P}_4)\sin^2\theta_p\sin^2\theta_k\cos(\phi_p-\phi_k)\right.$$

$$-\frac{1}{7}\left(\frac{5}{8}\overline{P}_2+\frac{3}{5}\overline{P}_4\right)\sin 2\theta_p\sin 2\theta_k\cos(\phi_p-\phi_k)$$

$$-\frac{1}{7}\left(\frac{5}{3}\overline{P}_2+\frac{6}{5}\overline{P}_4\right)P_2(\cos\theta_p)P_2(\cos\theta_k)$$

$$\left.\left.-\frac{1}{6}P_2(\cos\theta_p)\overline{P}_2\right]\left|d_{11}^{e}(1)\right|^2\right\}. \qquad (20c)$$

These three parameters completely determine, according to equation (3), the contribution $\sigma(m_r;JKM;\hat{\mathbf{p}};\mathbf{k})$ to the angular photocurrent (1) due to orientation of a C_{3v} molecule in its $|JKM\rangle$ state.

Let us use the probabilities (15) in (20) and then substitute the resulting expression for the parameters χ_0,χ_1 and χ_2 in (3). Next we add to the subsequent $\sigma(m_r;JKM;\hat{\mathbf{p}};\mathbf{k})$ the usual differential cross-section (2) for photoionization in unoriented molecules. The final expression thus obtained for angular photo-current ejected from a_1^2 orbital in ionization of a state-selection and oriented C_{3v} molecule is then specialized to the parallel and perpendicular geometries. All these operations give

$$\frac{d^2\sigma(m_r=0;JKM)}{d\hat{\mathbf{p}}(\theta_p=0,\phi_p)d\hat{\mathbf{k}}} \equiv \frac{d\sigma^{\parallel}(0;JKM)}{d\hat{\mathbf{k}}}$$

$$= \frac{d\sigma^{\parallel}(0)}{d\hat{\mathbf{k}}} + \sigma^{\parallel}(0;JKM;\hat{\mathbf{k}}), \qquad (21a)$$

where

$$\frac{d\sigma^{\parallel}(0)}{d\hat{\mathbf{k}}} \equiv \frac{\overline{\sigma}}{4\pi}(1+\overline{\beta}P_2(\cos\theta_k) \qquad (21b)$$

and

$$\sigma^{\parallel}(0;JKM;\hat{\mathbf{k}}) = \frac{\overline{\sigma}}{28\pi}\left\{\left[14-\frac{5}{14}(25+51\cos^2\theta_k)\overline{\beta}\right]\overline{P}_2\right.$$

$$+\frac{36}{7}P_2(\cos\theta_k)\overline{P}_4+6\sqrt{\frac{6}{5}(7-5\overline{\beta})\overline{\beta}}$$

$$\left.\times(\overline{P}_1-\overline{P}_3)\cos\theta_k\sin\delta\right\}. \qquad (21c)$$

Similarly

$$\frac{d^2\sigma(m_r=0;JKM)}{d\hat{\mathbf{p}}(\theta_p=\frac{\pi}{2},\phi_p)d\hat{\mathbf{k}}} \equiv \frac{d\sigma^{\perp}(0;JKM)}{d\hat{\mathbf{k}}}$$

$$= \frac{d\sigma^{\perp}(0)}{d\hat{\mathbf{k}}} + \sigma^{\perp}(0;JKM;\hat{\mathbf{k}}) \qquad (22a)$$

with

$$\frac{d\sigma^{\perp}(0)}{d\hat{\mathbf{k}}} = \frac{\overline{\sigma}}{4\pi}\left\{1+\overline{\beta}\left[P_2(\cos\theta_k)\right.\right.$$

$$\left.\left.+3\sin^2\theta_k\cos 2(\phi_k-\phi_p)\right]\right\} \qquad (22b)$$

and

$$\sigma^{\perp}(0;JKM;\hat{\mathbf{k}}) = -\frac{\overline{\sigma}}{28\pi}\left\{7\overline{P}_2-\left[13+6\cos^2\theta_k\right.\right.$$

$$+\frac{1}{14}(147+150\overline{P}_2+18\overline{P}_4)\sin^2\theta_k\cos 2(\phi_k-\phi_p)$$

$$\left.+(7-\frac{50}{7}\overline{P}_2+\frac{1}{5}\overline{P}_4)P_2(\cos\theta_k)\right]\bar{\beta}$$

$$\left.-3\sqrt{\frac{6}{5}(7-5\overline{\beta})\overline{\beta}}(\overline{P}_1-\overline{P}_2)\cos\theta_k\sin\delta\right\}. \qquad (22c)$$

Expressions (21) and (22) have interesting properties: Firstly, Legendre moments of order upto four ($\overline{P}_0=1$, $\overline{P}_1,\overline{P}_2,\overline{P}_3$ and $\overline{P}_4$) contribute to these cross-sections; secondly, the phase angle δ, defined in equation (16) for the transition moments $d_{10}^{a_1}$ and $d_{11}^{e}(1)$, is also present in both (21c) and (22c); thirdly, (22) contain also the azimuthal angles ϕ_p and ϕ_k of the photon vector $\hat{\mathbf{p}}$ and the propagation vector $\hat{\mathbf{k}}$, respectively. In contrast, the integrated cross-section (19) has only a single Legendre moment $\overline{P}_2$, does not involve δ, and is also independent of ϕ_p. Thus, the angular, rather than the integrated, photocurrent gives more detailed information on photoionization dynamics as well as on the orientational distribution function of rotationally state selected and oriented molecules. Moreover, the differential cross-section (2) for ionization in unoriented molecules does not contain any Legendre moments $\overline{P}_n$. In addition, as a result of the approximations used in calculating the present results, (2) is independent also of the phase δ. Therefore, differential cross-section for ionization of state-selected and oriented molecules is a greater source of information compared to that of unoriented molecules. One can easily extract the phase angle δ from a single measurement of either $d\sigma^{\parallel}(0;JKM)/d\hat{\mathbf{k}}$ or $d\sigma^{\perp}(0;JKM)/d\hat{\mathbf{k}}$ for ionization by absorbing a LP photon in a_1 orbital of a C_{3v} molecule oriented in space in one of its $|JKM\rangle$ rotational state.

The angular distributions calculated from equations (21) and (22) for photoionization by LP light in $13a_1^2$ orbital of state-selected and oriented CH_3I are labeled in the respective Figures 3 and 4 by the rotational state $|JKM\rangle$. These correspond to taking $\delta=\frac{\pi}{2}$ and $\phi_k=\phi_p$ in (21) and (22). Both of these cross-sections are presented as polar plots where the angle θ_k is that between the electric field $\mathbf{E}$ and the propagation vector $\hat{\mathbf{k}}(\theta_k,\phi_k)$ of the photoelectrons. The radius of each plot in Figure 3 is $d\sigma^{\parallel}(0;JKM)/d\hat{\mathbf{k}}$; whereas, in Figure 4 it is $d\sigma^{\perp}(0;JKM)/d\hat{\mathbf{k}}$.

The most remarkable feature of the Figures 3 and 4 is the dependence of the photocurrents on the directions $\hat{\mathbf{p}}$ and $\hat{\mathbf{k}}$, and on the rotational state $|JKM\rangle$ of CH_3I. While $d\sigma^{\parallel}(0;JKM)/d\hat{\mathbf{k}}$ tends to elongate in the forward ($\theta_k=0°$) and backward ($\theta_k=180°$) directions, $d\sigma^{\perp}(0;JKM)/d\hat{\mathbf{k}}$ is usually largest for $\theta_k=90°$. The other interesting feature of these cross-sections is that $d\sigma^{\parallel}(0;JKM)/d\hat{\mathbf{k}}$ changes somewhat more than

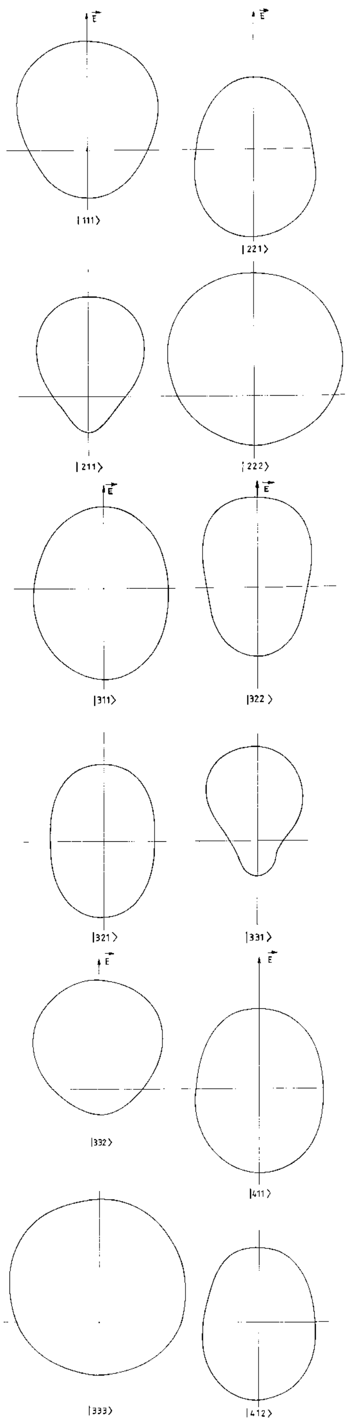

Fig. 3. Polar plots of the differential cross-section $d\sigma^{\parallel}(0; JKM)/d\hat{\mathbf{k}}$ (in Mb/Sr^{-1}) for photoionization in $13a_1^2$ orbital of CH$_3$I oriented in space in a $|JKM\rangle$ state of its ground electronic motion. The electric field vector in the LP beam of ionizing radiation is parallel to the space-fixed quantization direction **E**. The vertical direction $\theta_k = 0°$, *i.e.*, along **E**. Radius in each plot is the angular photocurrent in the direction θ_k. (All plots are not drawn to the same scale). These cross-section are calculated for $m_r = 0$, $\delta = 90°$, and using in equation (21) the values of $\overline{\sigma}$ and $\overline{\beta}$ measured by Carlson *et al.* [38] for photoelectron energy $\varepsilon = 3.5$ eV.

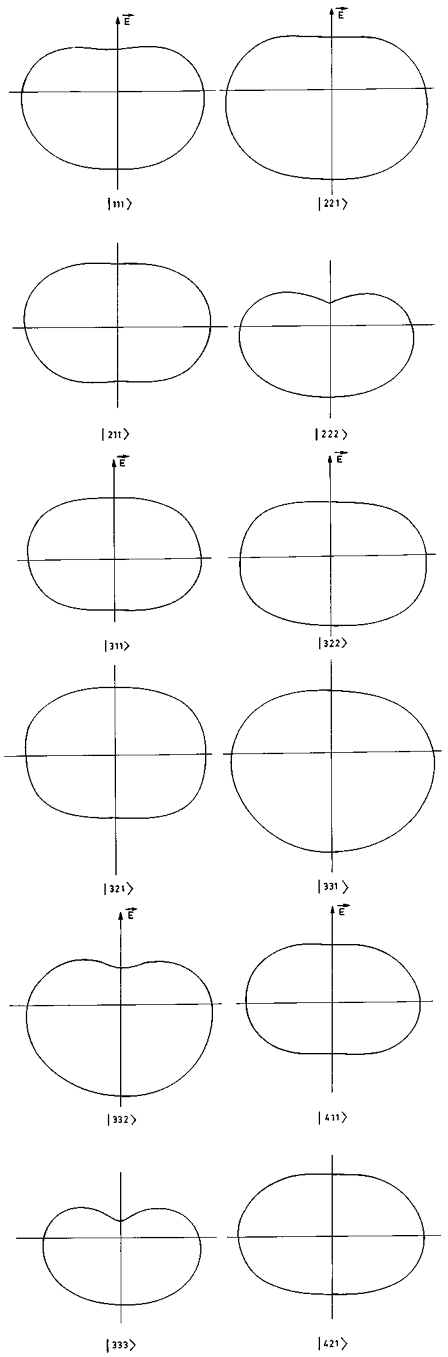

Fig. 4. Same as Figure 3, but for electric vector in the LP beam of ionizing radiation perpendicular to the space-fixed quantization direction **E**. That is, this figure contains $d\sigma^{\perp}(0; JKM)/d\hat{\mathbf{k}}$ (in Mb/Sr^{-1}). These angular photocurrents are calculated for $\phi_k = \phi_p$ in equation (22).

$d\sigma^{\perp}(0; JKM)/d\hat{\mathbf{k}}$ in both shape and size with the $|JKM\rangle$ state of the oriented CH$_3$I.

Kaesdorf *et al.* [25] in their experiment on ionization in $2e$ orbital of CH$_3$I oriented using electrostatic hexapole field techniques [1], have measured the ratio I$^-$/I$^+$ of photoelectrons emitted parallel and antiparallel to the molecular axis as a function of the voltage V_0 in hexapole. The desired cross-sections were measured for a given V_0 by keeping the electron spectrometer fixed but changing the polarity of electrodes which produce the orienting (weak and homogeneous) field $\mathbf{E}$ (see Fig. 1 in Ref. [25]). The same photoelectron intensities I_0 and I_π will, however, be obtained for a given V_0 if one keeps $\mathbf{E}$ (both in magnitude and direction) fixed, but puts the spectrometer in the forward ($\theta_k = 0°$) and backward ($\theta_k = 180°$) directions of electron emission, respectively. As mentioned in the introduction to this paper, Kaesdorf *et al.* [25] had prepared different $|JKM\rangle$ state mixtures at different voltages V_0 of their hexapole. Consequently, the ratio $\mathrm{I}^-/\mathrm{I}^+$ measured in reference [25] was non-quantum state-specific. These measurements [25], nevertheless, showed that the asymmetry $\mathrm{I}^-/\mathrm{I}^+$ was quite pronounced and varied with the voltage V_0 applied to electrodes in a hexapole apparatus.

If we take the ionization radiation to be LP with its electric vector parallel and perpendicular to $\mathbf{E}$, then the two asymmetries obtained from the respective equations (21) and (22) are:

$$\frac{I_0^{\parallel}}{I_\pi^{\parallel}}(JKM) \equiv \frac{\dfrac{d\sigma^{\parallel}(0;JKM)}{d\hat{\mathbf{k}}(\theta_k = 0, \phi_k)}}{\dfrac{d\sigma^{\parallel}(0;JKM)}{d\hat{\mathbf{k}}(\theta_k = \pi, \phi_k)}} \tag{23a}$$

and

$$\frac{I_0^{\perp}}{I_\pi^{\perp}}(JKM) \equiv \frac{\dfrac{d\sigma^{\perp}(0;JKM)}{d\hat{\mathbf{k}}(\theta_k = 0, \phi_k)}}{\dfrac{d\sigma^{\perp}(0;JKM)}{d\hat{\mathbf{k}}(\theta_k = \pi, \phi_k)}} \cdot \tag{23b}$$

Figure 5 contains the asymmetries (23a) and (23b) calculated for the example being considered in this paper. One notices from this figure that I_0/I_π varies significantly with the states $|JKM\rangle$ as well as with the two experimental geometries of equation (23). On the other hand, one can readily verify from equation (2) that $I_0^{\parallel}/I_\pi^{\parallel} = 1 = I_0^{\perp}/I_\pi^{\perp}$, *i.e.*, no forward-backward asymmetry exists in photocurrent, emitted from unoriented molecules.

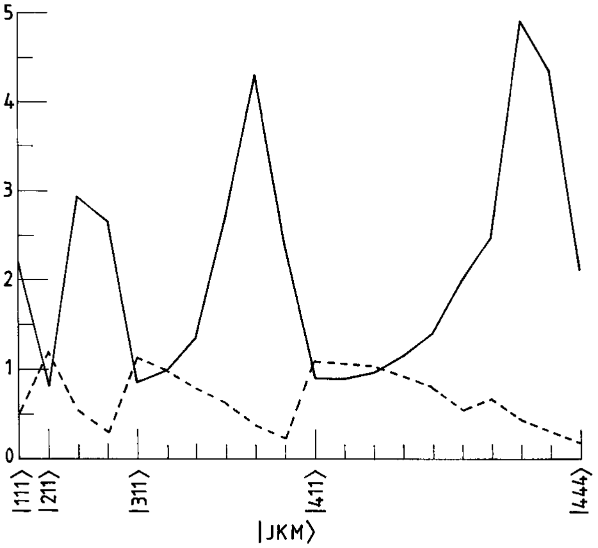

Fig. 5. Asymmetry $\frac{I_0}{I_\pi}(JKM)$ of photocurrent emitted parallel and antiparallel to the orienting field $\mathbf{E}$, for ionization in $13a_1^2$ orbital of CH$_3$I oriented in space in a single $|JKM\rangle$ rotational state. The electric field vector in the LP beam of ionizing radiation is either parallel or perpendicular to $\mathbf{E}$. This asymmetry is calculated by using in equation (23) the values of $\overline{\sigma}$ and $\overline{\beta}$ measured by Carlson *et al.* [38] for photoelectron energy $\varepsilon = 3.5$ eV. $\frac{I_0^{\parallel}}{I_\pi^{\parallel}}(JKM)$ (Eq. (23a)): (——); $\frac{I_0^{\perp}}{I_\pi^{\perp}}(JKM)$ (Eq. (23b)): (– – – –).

In both parallel (Eq. (23a)) as well as perpendicular (Eq. (23b)) configurations, I_0/I_π for some $|JKM\rangle$ states is very different from unity; whereas, for others, it is almost equal to one. Rotational states for which it is noticeably different from one have, in general $\frac{I_0^{\parallel}}{I_\pi^{\parallel}}(JKM) > 1$ and $\frac{I_0^{\perp}}{I_\pi^{\perp}}(JKM) < 1$. This, in other words, means that the photocurrent emitted parallel or antiparallel to $\mathbf{E}$ is larger depending upon whether the electric vector in the LP ionizing radiation is along or perpendicular $\mathbf{E}$, respectively. In addition, we also find from Figure 5 that the rotational state for which $\frac{I_0^{\parallel}}{I_\pi^{\parallel}}(JKM)$ is largest (> 1) for a given J is one of $|J, K = J, M \neq J\rangle$; whereas $\frac{I_0^{\perp}}{I_\pi^{\perp}}(JKM)$ has smallest value (< 1) for any given J when $K = M = J$. According to the Figure 1, the axis of CH$_3$I molecules in $|JJJ\rangle$ state is always oriented along the quantization direction $\mathbf{E}$; but in the $|J, K = J, M \neq J\rangle$ states, on the other hand, although the molecular axis coincides with $\mathbf{J}$, it is not parallel to $\mathbf{E}$. As pointed out by Kasedorf *et al.* [25], asymmetries I_0/I_π can be used to determine both the $|JKM\rangle$ rotational state and orientation of a CH$_3$I molecule prepared by the hexapole field techniques [1].

3.1.2 Circular dichroism (CD)

It has already been shown in this paper that, in view of (18), there is no CDIP (9) in the present example. According to equation (10), the CDAD is directly obtained from the single parameter $\chi_1(JKM; \hat{\mathbf{p}}; \mathbf{k})$ given in equation (20b). When the circularly polarized (CP) ionization radiation is made to be incident along $\mathbf{E}$, CDAD calculated from equations (10) and (20b) is again found to vanish identically. But on taking the CP photon beam to be incident on the molecular target perpendicular to **E**, CDAD, given by

$$\frac{d^2\sigma_{CD}(JKM)}{d\hat{\mathbf{p}}(\theta_p=\frac{\pi}{2},\phi_p)d\hat{\mathbf{k}}} \equiv \frac{d\sigma^{\perp}_{CD}(JKM)}{d\hat{\mathbf{k}}} = \frac{3}{14\pi}\sqrt{\frac{15}{2}(7-5\overline{\beta})\overline{\beta}}\,\overline{\sigma}\,\overline{P}_1\sin\theta_k \times\sin(\phi_k-\phi_p)\cos\delta, \tag{24}$$

is found to exist. It contains a single Legendre moment $\overline{P}_1$ only, always has a $\sin\theta_k$ distribution, and depends on the phase (16) of the transition moments as well as on the azimuthal angles ϕ_k and ϕ_p. For all $|JKM\rangle$ states of an oriented CH_3I molecule, CD (24) will always vanish parallel ($\theta_k = 0°$) or antiparallel ($\theta_k = 180°$) to **E**, or in the plane defined by $|\phi_k - \phi_p| = n\pi$ with $n = 0{-}2$ (*i.e.*, which contains **E**, photoelectron as well as photon beam). Furthermore, while CDAD (24) does not obviously exhibit any forward-backward asymmetry with respect to the photoelectrons emitted parallel or antiparallel to **E**, it however has an asymmetry of $-\tan\phi_p$ for photoelectrons going out of the a_1 orbital of a state selected and oriented C_{3v} molecule in the X-Z and Y-Z planes of the space fixed frame of reference, *i.e.*,

$$\frac{\dfrac{d\sigma^{\perp}_{CD}(JKM)}{d\hat{\mathbf{k}}(\theta_k,\phi_k=0°)}}{\dfrac{d\sigma^{\perp}{}_{CD}(JKM)}{d\hat{\mathbf{k}}(\theta_k,\phi_k=\frac{\pi}{2})}} \equiv \frac{(\sigma^{\perp}_{CD})_{x-z}}{(\sigma^{\perp}_{CD})_{y-z}} = -\tan\phi_p. \tag{25a}$$

similarly,

$$\frac{\dfrac{d^2\sigma_{CD}(JKM)}{d\hat{\mathbf{p}}(\theta_p=\frac{\pi}{2},\phi_p=0)d\hat{\mathbf{k}}}}{\dfrac{d^2\sigma_{CD}(JKM)}{d\hat{\mathbf{p}}(\theta_p=\frac{\pi}{2},\phi_p=\frac{\pi}{2})d\hat{\mathbf{k}}}} \equiv \frac{(\sigma^{\perp}_{CD})_{\hat{\mathbf{x}}}}{(\sigma^{\perp}_{CD})_{\hat{\mathbf{y}}}} = -\tan\phi_k, \tag{25b}$$

That is, CDAD has an asymmetry of $-\tan\phi_k$ for photoelectrons ejected by the absorption of CP light incident along the OX- and OY-axes of this space frame.

Figure 6 shows CD calculated from equation (24) for the example in photoionization being considered in this paper. It is obtained by taking $\delta = 0°$ and $\phi_k - \phi_p = 90°$. The dichroic effects for ionization in a given rotational state in this case are always maximum when both CP ionizing radiation and photoelectrons are moving perpendicular to **E**. The other interesting thing about the CDAD (24) shown in Figure 6 is that, for a given values of J and θ_k, it is always minimum and maximum for photoionization in $13a_1^2$ orbital of CH_3I molecule oriented in space in $|J11\rangle$ and $|JJJ\rangle$ rotational states of its ground electronic motion, respectively. Even for other $|JKM\rangle$ states with $K = M$, CDAD (24) is always found to increase for photoionization from $K = M = 1$ to $K = M = J$ state for each of the J and θ_k values considered in Figure 6. The axis of a symmetric top molecule in its $|JKM\rangle$ state with $K = M$ is known [17,18] to be along the space quantization direction, with a maximum possible alignment along **E** being in $|JJJ\rangle$ state. The behaviour of the CDAD (24) shown in Figure 6 and discussed above, then obviously means that dichroic effect in photoionization in $13a_1^2$ orbital of a state-selected and oriented CH_3I is maximum when the direction of incidence of the CP ionizing radiation and of photoelectron detection are both perpendicular to **E** and the axis of the target molecule is aligned as much along **E** as possible. Furthermore, a single measurement of (24) will give us $\overline{P}_1$, *i.e.*, the mean degree of orientation $\langle\cos\beta\rangle$ of the axis of CH_3I with respect to **E** in Figure 1.

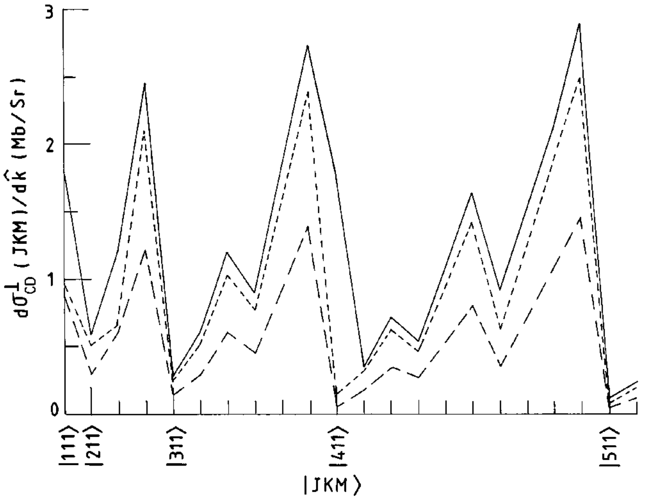

Fig. 6. CDAD for photoionization in $13a_1^2$ orbital of CH_3I oriented in space in a single $|JKM\rangle$ state. The CP ionizing radiation is incident perpendicular to the space fixed quantization direction **E**. This CD is calculated by using in equation (24) $\delta = 0°$, $\phi_k - \phi_p = 90°$, the values of $\overline{\sigma}$ and $\overline{\beta}$ measured by Carlson *et al.* [38] for photon energy $\varepsilon = 3.5$ eV. $\theta_k = 30°$: (— — —); $\theta_k = 60°$: (- - - -); $\theta_k = 90°$: (——).

3.1.3 Linear dichroism

We know from equation (11) that LDIP for ionization in any state-selected and oriented molecules is always zero. In order to obtain LDAD, we first substitute the amplitudes (15) and (16) in (20c) and then the subsequent expression obtained for the parameter χ_2 is used in equation (14a). This will give us the expression for $\sigma_{LD}(JKM;\mathbf{k})$ (*i.e.*, the contribution to LDAD due to orientation of the molecule). On adding to this $\sigma_{LD}(JKM;\mathbf{k})$ the usual state independent part (13) arising from unoriented molecules, we finally find from equation (12)

$$\frac{d\sigma_{LD}(JKM)}{d\hat{\mathbf{k}}} = -\frac{15}{56\pi}\left(\frac{7}{5}+\frac{10}{7}\overline{P}_2+\frac{6}{35}\overline{P}_4\right) \times\overline{\sigma}\overline{\beta}\sin^2\theta_k\cos 2\phi_k. \tag{26}$$

Many important differences between the CDAD (24) and the LDAD (26) are obvious. For example, in contrast to a single odd Legendre moment $\overline{P}_1$ present in (24), LDAD (26) contains first three even Legendre moments $\overline{P}_0(=1)$,

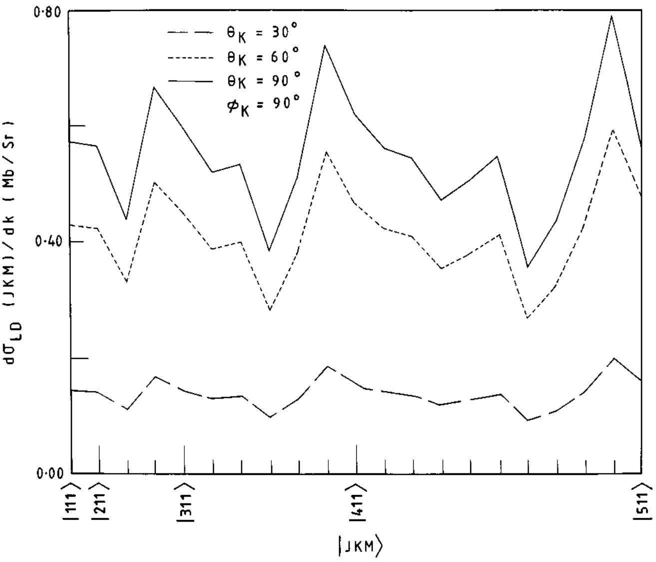

Fig. 7. LDAD for photoionization in $13a_1^2$ orbital of CH$_3$I oriented in space in a single $|JKM\rangle$ state. The electric vector in the LP ionizing radiation is perpendicular to the space-fixed quantization direction **E**. This LDAD is calculated using in equation (26) $\phi_k = \frac{\pi}{2}$ and the values of $\overline{\sigma}$ and $\overline{\beta}$ measured by Carlson *et al.* [38] for photon energy $\varepsilon = 3.5$ eV. $\theta_k = 30°$: (— — —); $\theta_k = 60°$: (- - - -); $\theta_k = 90°$: (——).

$\overline{P}_2$, and $\overline{P}_4$. Thus, while CDAD (24) determines orientation of the molecule axis, LDAD (26) provides information about the alignment of the rotational probability distribution of the molecule. Unlike (24), (26) is independent of the phase δ defined in equation (16). In addition CDAD and LDAD have two entirely different kind of dependence on the photoelectron propagation direction $\hat{\mathbf{k}}(\theta_k, \phi_k)$.

However, similar to CDAD, LDAD too does not possesses any forward-backward asymmetry in the photocurrent. In fact neither of these exists in the forward $[\hat{\mathbf{k}}(\theta_k = 0, \phi_k)]$ as well as in the backward $[\hat{\mathbf{k}}(\theta_k = \pi, \phi_k)]$ directions. In addition, there is no LDAD if photoelectron is ejected in a plane defined by the azimuthal angle $\phi_k = (2n+1)\pi/4$. For a given $|JKM\rangle$ rotational state and values of $\overline{\sigma}$ and of $\overline{\beta}$, LDAD (26) will have same magnitude for electron moving in the $X-Z$ or $Y-Z$ plane of the space-fixed frame shown in Figure 1.

Figure 7 contains LDAD calculated from (26) for ionization in $13a_1^2$ orbital of state-selected and oriented CH$_3$I. These results correspond to $\phi_k = \frac{\pi}{2}$ for three different values of the polar angle θ_k. We see that for the same value of $\sin\theta_k$ and of $\sin^2\theta_k$, for the magnitude of $\sin(\phi_k - \phi_p)$ in (24) same as that of $\cos 2\phi_k$, LDAD is almost one-third of CDAD for a given $|JKM\rangle$. In any direction **k**, both CDAD and LDAD have their maximum magnitudes for head *versus* tail orientation of CH$_3$I, *i.e.*, in $|JJJ\rangle$ state for a given J. But two rotational state, $|JKM\rangle$ for which CDAD and LDAD are minimum are different for the same J. For example, CDAD has its minimum magnitude when CH$_3$I is oriented in $|J11\rangle$ state; whereas the minimum magnitude for LDAD occurs for ionization in $|JJ1\rangle$ state, *i.e.*, when CH$_3$I has a broad side orientation.

4 Conclusion

This paper shows that ARPES of molecules oriented in space in a single rotational $|JKM\rangle$ state of their ground electronic motion is completely characterized by seven independent dynamical parameters. Two of these are the well known $\overline{\sigma}$ and $\overline{\beta}$ which completely characterize the angular distribution of $E1$ photoelectrons ejected from a randomly oriented molecule. Neither of these depend on the experimental geometry or on the state $|JKM\rangle$. The other two $(\sigma^{(1)}, \sigma^{(2)})$, however, involve the state $|JKM\rangle$ but are geometry independent. The remaining three parameters (χ_0, χ_1, χ_2) contain the rotational state $|JKM\rangle$ as well as experimental geometry. These seven parameters are sufficient to study not only the integrated and differential cross-sections for photoionization, but also circular and linear dichroisms in state selected and oriented molecules.

The approximations developed by us in reference [15] and described briefly herein are such that they can be used to obtain, without doing any dynamical calculations, semi-empirical qualitative results for photoionization in a_1 orbital of any state-selected and oriented C_{3v} molecule. The only two quantities needed to perform such model calculations are $\overline{\sigma}$ and $\overline{\beta}$. Such semi-empirical results provide also a useful preliminary check on sophisticated *ab-initio* calculations.

Both integrated and differential cross-sections for photoionization in $13a_1^2$ orbital of CH$_3$I have been calculated. These show marked variation with respect to the rotational state of the molecule as well as to the experimental configuration. We also find a pronounced asymmetry in the photocurrent emitted parallel and antiparallel to the orienting field. This asymmetry too varies significantly with the two above mentioned factors. Such asymmetries are useful in extracting information about the rotational state as well as orientation of the molecule focussed by a electrostatic hexapole field apparatus.

The other interesting result obtained from the present study is that the integrated cross-section for photoionization by light LP along the magic angle with respect to **E**, or by RCP/LCP/UP radiation incident at the magic angle, is totally independent of the rotational state selected by the hexapole electrostatic field and has a value equal to the total photocurrent measured in a typical experiment on ionization of randomly oriented gaseous molecules whose rotation has not been taken into account. This property should be helpful in calibrating the complicated apparatus used in studying angle-resolved photoelectron spectroscopy of state-selected and oriented molecules.

Expressions for photocurrents emitted from such molecules are quite complicated. However, these are considerably simplified if one considers the difference between two photocurrents produced by the absorption of light of two different polarizations in the same experimental geometry, or of the same polarization in two different configurations. Such a difference calculated for RCP and LCP light shows that it has much simple analytical structure and varies sharply with respect to the phases of the $E1$ transition moments. Therefore, one can, readily extract information about photoionization dynamics by measuring CDAD. However, as it depends in the present example upon a single Legendre moment (*i.e.*, $\overline{P}_1$), CDAD may not give complete information about the orientation distribution function of a state selected and oriented molecule. But the difference in angular photocurrents ejected by the absorption of radiation polarized linearly in two mutually perpendicular directions, *i.e.* LDAD, has a behaviour which is entirely different from that of CDAD. For example, although it too possesses a simple analytical structure, LDAD is independent of the phase of $E1$ transition moments and contains in the present application, Legendre moments of even order upto four. Thus CDAD and LDAD provide, to some extent, complimentary information about photoionization dynamics and about the orientational distribution function of the molecule. However, neither of the two produces any forward-backward asymmetry in the photocurrent. A single measurement of CDAD is sufficient to extract the phases of the ionization amplitudes as well as the mean degree of orientation of the molecular axis about the weak and external homogeneous electric field $\mathbf{E}$.

In order to take energy dependent effects and final state interactions properly into account in a more accurate application of the exact theory [14], one needs to do dynamical calculations including both correlation effects and other short-range interactions, in addition to representing the photoelectron by higher than p-partial wave. But such *ab-initio* calculations for complex non-linear molecular targets like CH_3I will probably be quite arduous. However, the basic behaviour of the cross-sections with respect to the energy of the ejected electron as well as to the various variables mentioned in the preceding paragraphs, which an exhaustive and accurate calculation of $E1$ ionization amplitudes for CH_3I is likely to give, will probably be the same as brought out by the present qualitative analysis, at least in those cases which do not involve the phase δ, *i.e.*, $d\sigma(m_r; JKM)/d\theta_p$ and $d\sigma_{LD}(0; JKM)/d\hat{\mathbf{k}}$ given by equations (19) and (26), respectively. It will primarily be so because the magnitudes (15) of the transition moments used in this work, exactly reproduce the energy dependent behaviour of both $\overline{\sigma}$ and $\overline{\beta}$ measured by Carlson *et al.* [38] over the whole range of photon energies considered in their experiments on photoionization in unoriented CH_3I. A single measurement of the differential cross-section $d^2\sigma(0; JKM)/d\hat{\mathbf{p}}d\hat{\mathbf{k}}$. (Eq. (21) or Eq. (22)), of the ratio (23), or of CDAD (24), on the other hand, will directly give us the phase δ, which has been left as a parameter in these equations.

Nevertheless, any non-empirical calculations, however difficult they may for $E1$ photoionization in state-selected and oriented molecules, are highly desirable. It has already been mentioned in the Section 1 of this paper that Powis [12] has performed, using the phenomenological MS-X_α method [40,41], calculations for photoionization in several molecular targets belonging to the C_{3v} point group. Among those [12], the one reported in reference [12] was for ionization in $2e$ orbital of a CH_3I molecule. Although, it [12] is just the case which was also studied in the experiment of Kaesdorf *et al.* [25], the CH_3I molecule by Powis was however taken to be fixed-in-space. Consequently, unlike the semi-empirical study performed in the present communication, none of the calculations reported in references [12] describe photoionization of a state-selected and oriented molecule.

Molecules belonging to the C_{3v} point group are usually heavy and, consequently, have small separation between their rotational energy levels. But lighter linear molecules like NO (Ref. [22]) and, recently, OH (Ref. [42]), have also been state-selected and oriented in space using electrostatic hexapole field methods. All such molecules belong to the $C_{\infty v}$ point group. Their rotationally resolved photoelectron spectra have successfully been observed in several high resolution gas phase experiments [26] on unoriented targets. The theoretical frame work developed in the Section 2 in this paper is general as well as exact and can be readily used to study ARPES of such linear molecules which can be oriented in space in a single rotational state of their ground electronic motion [22,42].

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