PHYSICAL REVIEW A VOLUME 14, NUMBER 1 JULY 1976

Theory of the angular distribution for ejection of photoelectrons from optically active molecules and molecular negative ions. II*

Burke Ritchie†
Argonne National Laboratory, Argonne, Illinois 60439
(Received 2 June 1975)

Formulas are presented for the angular distribution of photoelectrons produced on absorption of circularly polarized photons by randomly oriented, optically active (chiral) molecules or molecular negative ions. Results are presented to order α^3. The results for nonchiral molecules can be recovered by setting the appropriate coefficients equal to zero. These findings suggest measurement of the angular distribution difference for absorption of left and right circularly polarized photons, whose leading term behaves as $2B_e\cos\theta$, where B_e is a coefficient appropriate for the electric dipole ($E1$) process and θ is the angle between the direction of the emerging beam of photoelectrons and the direction of incidence of the photon beam. The integrated cross-section difference behaves as $8\pi(A_m + C_m/3)$, where these coefficients are appropriate for the electric-dipole, magnetic-dipole ($E1M1$) interference; this term is responsible for the circular dichroism of the molecule in the region of continuous absorption.

I. INTRODUCTION

In a previous paper[1] (I), a general expression was derived for the electric-dipole ($E1$) angular distribution of photoelectrons ejected from unpolarized molecules or molecular negative ions on the absorption of linearly or circularly polarized photons. The reader is referred to this paper for the details of the theoretical formulation (electron-molecule "fixed-nuclei" theory[2]) and mathematical development to be used in the present paper. It was shown that the angular distribution behaves as $A_e \pm B_e\cos\theta + C_e\cos^2\theta$ on absorption of left (+) or right (−) circularly polarized photons by optically active (chiral) molecules, where the term $\pm B_e\cos\theta$ is introduced by the presence of unequal numbers of D (dextrorotatory) and L (levorotatory) optical isomers and θ is the angle between the direction of the emerging beam of photoelectrons and the direction of incidence of the photon beam.

In this paper we wish to derive expressions for the angular distributions produced on absorption of circularly polarized photons by unpolarized target molecules or molecular negative ions due to the interference between different partial waves of the photon, namely the electric-dipole, magnetic-dipole ($E1M1$) and electric-dipole, electric-quadrupole ($E1E2$) interference terms. We show that new terms[3] exist also in these angular distributions if the molecule is optically active. We find that the integrated cross-section difference for absorption of left and right circularly polarized photons behaves as $8\pi(A_m + \frac{1}{3}C_m)$. This term is responsible for the circular dichroism of the optically active molecule in the region of continuous absorption. In another previous paper[4] the angular distribution difference was calculated for nonchiral, definite-parity eigenstate, *oriented* molecules. This difference vanishes on averaging the angular distribution difference over all molecular orientations unless the molecule is chiral. The nonvanishing of the absorption coefficient difference for chiral molecules is well known[5,6] in discrete absorption, and this phenomenon, the circular dichroism or "optical activity" in the region of discrete absorption, has been one of the principal means of physical characterization of this class of molecules. From I and this paper, we wish to emphasize that this measurement can be extended into the region of continuous absorption, where the leading term of the angular distribution difference behaves as $2B_e\cos\theta$ and the integrated cross-section difference behaves as $8\pi(A_m + \frac{1}{3}C_m)$, providing new experimental parameters with which to characterize the $E1$ and $E1M1$ processes, respectively.

II. THEORY

The general expression for the angular distribution[1,7] is given by

$$\frac{d\sigma_{L,R}}{d\Omega} = \frac{d\sigma_{L,R}^{(E1)}}{d\Omega} + \frac{d\sigma_{L,R}^{(E1M1)}}{d\Omega} + \frac{d\sigma_{L,R}^{(E1E2)}}{d\Omega} + O(\alpha^3 a_0^2)\,, \tag{1a}$$

$$\frac{d\sigma_{L,R}^{(E1)}}{d\Omega} = \frac{\alpha a_0^2}{2\pi} E_p k \left|\langle\psi_{\vec{k}}^{(-)}\right|\hat{p}_{L,R}\cdot\vec{r}\left|\psi_i\rangle\right|^2 , \tag{1b}$$

$$\frac{d\sigma_{L,R}^{(E1M1)}}{d\Omega}=\frac{(\alpha a_0)^2}{2\pi}E_p k\,\mathrm{Im}[\langle\psi_{\vec{k}}^{(-)}|\hat{\rho}_{L,R}\cdot\vec{r}|\psi_i\rangle^*\langle\psi_{\vec{k}}^{(-)}|\vec{l}\cdot i(\hat{k}_p\times\hat{\rho}_{L,R})|\psi_i\rangle]\,, \tag{1c}$$

$$\frac{d\sigma_{L,R}^{(E1E2)}}{d\Omega}=-\frac{(\alpha a_0)^2}{2\pi}E_p^2 k\,\mathrm{Im}[\langle\psi_{\vec{k}}^{(-)}|\hat{\rho}_{L,R}\cdot\vec{r}|\psi_i\rangle^*\langle\psi_{\vec{k}}^{(-)}|(\hat{\rho}_{L,R}\cdot\vec{r})(\hat{k}_p\cdot\vec{r})|\psi_i\rangle]\,. \tag{1d}$$

The quantities are defined as follows: α is the fine-structure constant, a_0 the Bohr radius, E_p the energy of the photon in atomic units, k the velocity of the photoelectron in atomic units, $\psi_{\vec{k}}^{(-)}$ the wave function of the final system, normalized to satisfy incoming boundary conditions, ψ_i the wave function for the initial system, $\vec{r}$ the summation over the positions of all electrons of the system, $\vec{l}$ the summation over the angular momenta of all electrons of the system, $\hat{k}_p$ a unit vector in the direction of propagation of the photon, and $\hat{\rho}_{L,R}$ the unit vector in the direction of polarization of the photon.

Upon taking the partial-wave expansion of the continuum wave functions in Eqs. (1a)–(1d) and averaging over molecular orientations,[1,2] we obtain

$$\frac{d\sigma_{L,R}^{(E1)}}{d\Omega}=\frac{8\pi}{3}\,\alpha a_0^2 E_p k\sum\langle\psi_i|rY_{1\mu_1}^*|\psi_{\lambda_j\mu_j}^{(-)}\rangle\langle\psi_{l_jm_j}^{(-)}|rY_{1m_1}|\psi_i\rangle\,\Phi_1(\lambda_j\mu_jl_jm_j1\mu_11m_1L;\theta)\,, \tag{2a}$$

$$\Phi_1=(-1)^{(m_1+m_j+1)}(2L+1)(2l_j+1)^{1/2}(2\lambda_j+1)^{1/2}\begin{pmatrix} l_j & \lambda_j & L\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}1 & 1 & L\\ \pm1 & \mp1 & 0\end{pmatrix}$$
$$\times\begin{pmatrix} l_j & \lambda_j & L\\ m_j & -\mu_j & -(m_j-\mu_j)\end{pmatrix}\begin{pmatrix}1 & 1 & L\\ m_1 & -\mu_1 & -(m_j-\mu_j)\end{pmatrix}P_L(\cos\theta)\,, \tag{2b}$$

$$\frac{d\sigma_{L,R}^{(E1M1)}}{d\Omega}=\mp\left(\frac{8\pi}{3}\right)^{1/2}(\alpha a_0)^2E_pk\,\mathrm{Im}\sum\langle\psi_i|rY_{1\mu_1}^*|\psi_{\lambda_j\mu_j}^{(-)}\rangle\langle\psi_{l_jm_j}^{(-)}|l_{m_1}|\psi_i\rangle[(1-\delta_{0m_1})(1-2\delta_{-1m_1})]$$
$$\times\Phi_1(\lambda_j\mu_jl_jm_j1\mu_11m_1L;\theta)\,, \tag{2c}$$

$$\frac{d\sigma_{L,R}^{(E1E2)}}{d\Omega}=2\left(\frac{4\pi}{3}\right)^{3/2}(\alpha a_0)^2E_p^2k\,\mathrm{Im}\sum\langle\psi_i|rY_{1\mu_1}^*|\psi_{\lambda_j\mu_j}^{(-)}\rangle\langle\psi_{l_jm_j}^{(-)}|r^2Y_{1m_1}Y_{1m_2}|\psi_i\rangle(-1)^{m_1+m_2}(2\kappa+1)$$
$$\times\begin{pmatrix}1 & 1 & \kappa\\ \pm1 & 0 & \mp1\end{pmatrix}\begin{pmatrix}1 & 1 & \kappa\\ m_1 & m_2 & -(m_1+m_2)\end{pmatrix}\Phi_2(\lambda_j\mu_jl_jm_j1\mu_1\kappa(m_1+m_2)L;\theta)\,, \tag{2d}$$

$$\Phi_2=(-1)^{m_1+m_j+1}(2L+1)(2l_j+1)^{1/2}(2\lambda_j+1)^{1/2}\begin{pmatrix} l_j & \lambda_j & L\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\kappa & 1 & L\\ \pm1 & \mp1 & 0\end{pmatrix}$$
$$\times\begin{pmatrix} l_j & \lambda_j & L\\ m_j & -\mu_j & -(m_j-\mu_j)\end{pmatrix}\begin{pmatrix}\kappa & 1 & L\\ (m_1+m_2) & -\mu_1 & -(m_j-\mu_j)\end{pmatrix}P_L(\cos\theta)\,, \tag{2e}$$

where the upper or lower sign is taken for left or right circular polarization, respectively. The expression for the $E1$ process has been presented previously.[1] The quantities are defined as follows. The angle of ejection, θ, is defined as the angle between $\hbar\vec{k}$ and $\hbar\vec{k}_p$, the momenta of the photoelectron and photon, respectively. The set of angular momentum quantum numbers, $\lambda_j\mu_jl_jm_j$, corresponds to the angular momenta, $\hbar\vec{\lambda}_j$ and $\hbar\vec{l}_j$ of the photoelectron. These are "channel" momenta corresponding to partial waves which resolve $\psi^{(-)}(\vec{r},\vec{k})$ with respect to $\vec{k}$ [see Eq. (10) of I]. Further partial-wave analysis of the continuum wave functions of Eqs. (2a)–(2e) will generate another set of quantum numbers, $\lambda_i\mu_il_im_i$, corresponding to the angular momenta, $\hbar\vec{\lambda}_i$ and $\hbar\vec{l}_i$, and characterizing partial waves which resolve $\psi^{(-)}(\vec{r},\vec{k})$ with respect to $\vec{r}$ [see Eq. (9) of I]. L is the total angular momentum quantum number, $\vec{L}=\vec{l}_j+\vec{\lambda}_j$. The operator l_{m_1} stands for l_+, the raising operator, for $m_1=+1$, and stands for l_-, the lowering operator, when $m_1=-1$. The value $m_1=0$ is excluded because l_z is a diagonal operator. The bras and kets are understood to stand for Slater determinantal wave functions, and the superscript $(-)$ means that the wave function for the final state has been normalized to satisfy incoming boundary conditions. In deriving Eqs. (2a)–(2e) we have made consecutive use[1] of two sum rules[8] to perform the summations: over m_j', which casts the $E1$ angular distribution in the form given by Fano and Dill[9,10]; and over j, a total-angular-momentum quantum number,[9] defined as $\vec{j}=\vec{l}_j+\vec{l}$. [However, as stated above, the chiral effect for the $E1$ term was first derived in I from analysis of the form of the angular distribution given by Eqs. (2a) and (2b).]

We note that the $E1M1$ term given by Eq. (2c) has a sign ($\mp$) appropriate for left ($-$) or right ($+$) circular polarization, while the $E1$ and $E1E2$ terms have a single sign appropriate for either polarization. This behavior arises from the fact that the unit vector in Eq. (1c), $i(\hat{k}_p \times \hat{\rho}_{L,R})$, which is in the direction of the magnetic field associated with the radiation, has a sign ($\pm$) appropriate for left ($+$) or right ($-$) circular polarization, since $\hat{\rho}_{L,R}$ is defined as $(\hat{i} \pm i\hat{j})/\sqrt{2}$; thus the directions of the magnetic fields associated with photons of either polarization are antiparallel.

III. SYMMETRY ANALYSIS AND DISCUSSION

The symmetry properties of the $E1$ term have been previously analyzed,[1] and the reader is referred to that paper for a complete discussion. The symmetry properties of the $E1M1$ term can be similarly analyzed. A special problem associated with this term, however, is the choice of phase for the matrix elements of the angular momentum operator l_{m_1} (please see Ref. 4, Sec. II B). The phase must be chosen from physical considerations. In the case of oriented molecules[4] the phase is chosen such that the E1M1 interference exists for bound-bound transitions for molecules of arbitrary symmetry. This result is then analytically continued into the region of continuous absorption, where the dependence on the phases of the radial wave functions unambiguously emerges. Physically, absorption of a left or right circularly polarized photon populates a single fine-structure level in the oriented system according to the selection rule $m_f = m_0 \pm 1$, respectively, where m_f and m_0 are the final and initial azimuthal quantum numbers, respectively. The direction of the magnetic field associated with one polarization of the photon is antiparallel to that associated with the other polarization such that the "senses" or signs of the interferences are opposed for both polarizations; hence the difference cross section for absorption of a left and right circularly polarized photon by an oriented system must exist.[4] In an unoriented system, on the other hand, an equal mixture of fine-structure levels are populated, and the same physical consideration (namely, that the directions of the magnetic fields associated with the population of levels having positive azimuthal quantum numbers is antiparallel to that associated with the population of levels having negative azimuthal quantum numbers) demands that the phase of the magnetic dipole matrix element be chosen such that the $E1M1$ interference vanishes for bound-bound transitions for molecules of arbitrary symmetry by cancellation of the terms for positive and negative quantum numbers. There is incomplete cancellation, then, only when there is an inequivalence in the radial matrix elements for positive and negative quantum numbers, i.e., the presence of molecular chirality. This result can then be analytically continued into the region of continuous absorption, giving the well-known result[3] of a term behaving as $B_m \cos\theta$ for nonchiral molecules, for light of either polarization. This choice of phase is according to

$$\langle jm\pm 1 | lY_{1m_1} | jm\rangle = \mp(3/8\pi)^{1/2}[(1-\delta_{0m_1})][(1-2\delta_{-1m_1})] \times \langle jm\pm 1 | l_{m_1} | jm\rangle , \tag{3a}$$

$$\langle jm\pm 1 | l_{\pm} | jm\rangle = [(j\pm m+1)(j\mp m)]^{1/2} , \tag{3b}$$

in agreement with that chosen for the circular dichroism is discrete absorption.[5,6] The sign of the matrix element is still arbitary because, as discussed by Condon,[5] the $E1M1$ interference is a pseudoscalar and not a true invariant.

The symmetry properties of the $E1M1$ interference are readily apparent from inspection of Eqs. (2b) and (2c). First, since the $E1$ term causes a change in parity, according to $\Delta l = \pm 1$, and the $M1$ term no change in parity, according to $\Delta l = 0$, l_j and λ_j will have opposite parity for molecules having states of definite parity. Thus, for the first 3-j symbol to exist, L must be odd. The range of values for L is $0 \le L \le 2$; thus only $L=1$ is possible. According to fourth 3-j symbol,

$$\begin{pmatrix} 1 & 1 & L \\ m_1 & -\mu_1 & -(m_j-\mu_j) \end{pmatrix} = (-1)^L \begin{pmatrix} 1 & 1 & L \\ -m_1 & \mu_1 & (m_j-\mu_j) \end{pmatrix} . \tag{4}$$

This property, combined with the choice of phase for the magnetic dipole matrix element, insures that this term exists for light of either polarization. According to the second 3-j symbol,

$$\begin{pmatrix} 1 & 1 & L \\ 1 & -1 & 0 \end{pmatrix} = (-1)^L \begin{pmatrix} 1 & 1 & L \\ -1 & 1 & 0 \end{pmatrix} \tag{5}$$

where the left- or right-hand sides occur for left or right circular polarization. This property, combined with the choice of sign multiplying Eq. (2c) for left or right circular polarization, respectively, insures that the sign of the interference must be the *same* for light of both polarizations.

On the other hand, if the molecular states have indefinite parity, then l_j and λ_j can have the same parity, and L can be even. Then Eq. (4) and the choice of phase for the matrix elements tell us that complete cancellation occurs for the absorption of a photon of either polarization unless the molecule possesses chirality. Finally, Eq. (5) and the signs multiplying Eq. (2c) tell us that the signs of these interferences for even L must be different for light of either polarization. Thus the angular distribution for the $E1M1$ interference behaves as $\pm A_m + B_m \cos\theta \pm C_m \cos^2\theta$, where $A_m = C_m = 0$ in the limit of nonchiral molecules.

Next we analyze the $E1E2$ term. As for the $E1M1$ term, for molecular states of definite parity, l_j and λ_j must have opposite parity, since the existence of the $E1$ term requires a change of parity, according to $\Delta l = \pm 1$, and the existence of the $E2$ term requires no change in parity, according to $\Delta l = 0$ or $\Delta l = \pm 2$. Then by the first 3-j symbol in Eq. (2e), L must be odd. By the triangular condition, κ is restricted to the range of values $0 \leq \kappa \leq 2$, where $\vec{\kappa}$ is a total photon angular momentum for the $E2$ term, according to $\vec{\kappa} = \vec{1} + \vec{1}$. Because of the transverse nature (direction of propagation perpendicular to the polarization) of the photon, $\kappa = 0$ is eliminated. This elimination occurs in the conditions for the existence of the first 3-j symbol in Eq. (2d) or the second 3-j symbol in Eq. (2e). If $\kappa = 1$, $\kappa + 1 + L$ is odd for L odd, and according to the relation

$$\begin{pmatrix} \kappa & 1 & L \\ (m_1+m_2) & -\mu_1 & -(m_j-\mu_j) \end{pmatrix} = (-1)^{\kappa+1+L} \begin{pmatrix} \kappa & 1 & L \\ -(m_1+m_2) & \mu_1 & (m_j-\mu_j) \end{pmatrix} \qquad (6)$$

cancellation would result on the summation over all allowed azimuthal quantum numbers. This restricts κ to 2. By the triangular condition, $|\kappa - 1| \leq L \leq \kappa + 1$; thus terms linear and cubic in $\cos\theta$ are possible.[3] For molecular states of indefinite parity, l_j and λ_j can have the same parity, and L can be even. Then for $\kappa = 1$, $\kappa + 1 + L$ is even, and according to Eq. (6) constructive interference results. According to the triangular condition, $L = 0$ is possible when $\kappa = 1$, giving an isotropic term in the angular distribution. Also $\kappa = 1$, $L = 2$ is possible, giving terms isotropic and quadratic on $\cos\theta$. Further, when $\kappa = 1$ and $L = 1$ or when $\kappa = 2$ and $L = 2$, $\kappa + 1 + L$ is odd, and according to Eq. (6) cancellation results unless there is molecular chirality.

Thus, the presence of molecular states of indefinite parity introduces two new terms, isotropic and quadratic in $\cos\theta$; and molecular chirality introduces three new terms, isotropic, linear, and quadratic in $\cos\theta$. The $E1E2$ angular distribution thus behaves as

$$A_q \mp C'_q/3 + (B_q \pm B'_q)\cos\theta + (C_q \pm C'_q)\cos^2\theta + D_q \cos^3\theta\ ,$$

where $B'_q = C'_q = 0$ in the limit of nonchiral molecules, and $A_q = C_q = 0$ in the presence of molecular eigenstates of definite parity. We note that the structure of the $E1E2$ interference is more complicated owing to the existence of two states of the photon corresponding to $\kappa = 1$ and $\kappa = 2$, respectively.

---

*Work performed under the auspices of the U. S. Energy Research and Development Administration.

†Summer visitor. Permanent address: Dept. of Chemistry, Univ. of Alabama, University, Al. 35486.

[1] B. Ritchie, Phys. Rev. A 13, 1411 (1976).

[2] A. Temkin and K. V. Vasavada, Phys. Rev. 160, 109 (1967); A. Temkin, K. V. Vasavada, E. S. Chang, and A. Silver, *ibid.* 186, 57 (1969).

[3] For a cogent analysis of the angular distributions for nonchiral definite-parity eigenstate targets, see M. Peshkin, Adv. Chem. Phys. 18, 1 (1970).

[4] B. Ritchie, Phys. Rev. A 12, 567 (1975).

[5] E. U. Condon, Rev. Mod. Phys. 9, 432 (1937).

[6] E. U. Condon, W. Altar, and H. Eyring, J. Chem. Phys. 5, 753 (1937).

[7] J. C. Tully, R. S. Berry, and B. J. Dalton, Phys. Rev. 176, 95 (1968).

[8] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University, Princeton, 1957), p. 95, Eqs. (6.2.8) and (6.2.6).

[9] U. Fano and D. Dill, Phys. Rev. A 6, 185 (1972).

[10] B. Ritchie, J. Chem. Phys. 61, 3279 (1974); see Ref. 11 of I.