Theory of the angular distribution of photoelectrons ejected from optically active molecules and molecular negative ions*

Burke Ritchie[†]

Argonne National Laboratory, Argonne, Illinois 60439

It is shown that the angular distribution of photoelectrons ejected on absorption of left or right circularly polarized light by a mixture of randomly oriented dextrorotatory and levorotatory optical isomers behaves as $A \pm B\cos\theta + C\cos^2\theta$, where θ is the angle between the photoelectron momentum and photon direction of incidence and $\pm B\cos\theta$ is introduced by the presence of unequal numbers of each isomer. All coefficients of $\cos^n\theta$ are of order α, and analysis shows that B can be as large as A and C.

It is usually considered[1,2] that the angular distributions

$$I(\theta) = \sum_L b_L P_L(\cos\theta) \qquad (1)$$

of photoelectrons ejected by unpolarized atomic or molecular targets contain only even orders of P_L, regardless of the polarization of the photon. This belief, which restricts the experimental parameters available for analysis of the target atoms or molecules, depends on the assumption that the reaction is dominated by incident photons of a single parity; in practice, this means electric-dipole photons which have odd parity. More specifically, the electric-dipole photon has unit angular momentum. This means that the squared modulus of the amplitude, from which Eq. (1) is derived, can be characterized by total angular momenta L whose magnitudes occur in the interval $0 \le L \le 2$. The terms corresponding to $L = 1$ (as we shall see in the ensuing analysis) disappear unless three conditions are met simultaneously: (i) that the angle of ejection be defined such that it is measured from the polar axis normal to the plane containing the polarization vector of the photon, which, in practice, can mean circular polarization with the angle of ejection defined as the angle between the momentum of the photoelectron $\hbar\vec{k}$ and the direction of incidence of the photon; (ii) that the eigenstates of the target system be states of indefinite parity; and (iii) that the symmetry of the target system be low enough such that the effective potential in which the photoelectron moves shows an inequivalence as a function of azimuthal angle, resulting, in turn, in an inequivalence of wave functions for positive and negative values of azimuthal quantum numbers.

Circular polarization and conditions (ii) and (iii) are the same conditions necessary and sufficient for the existence of optical activity in discrete absorption,[3] i.e., the optical rotatory dispersion and circular dichroism exhibited by "chiral" molecules. Condition (ii) must obtain for the existence of the microscopic terms responsible for these phenomena when the molecule is oriented in space; however, condition (iii) must obtain for these terms not to vanish by cancellation when the intensity is averaged over all molecular orientations appropriate for an experiment involving a sample of randomly oriented molecules. The angular distributions characteristic of the terms responsible for optical activity (terms due to electric-dipole–magnetic-dipole interference) and of other terms depending on higher multipoles of the photon will be analyzed in a later paper.

Thus, the belief that b_1 of Eq. (1) disappears also depends on the assumption that the target atoms or molecules are in a statistical state which is symmetric under space inversion. For this to be true, it is sufficient that (a) each target atom or molecule is in an eigenstate of definite parity, but not necessarily all in the same parity state or (b) for each target atom of molecule not in a parity eigenstate, as in a dextrorotatory (D-isomer) sugar molecule, there is another in the corresponding space inverted eigenstate, as in a levorotatory (L-isomer) sugar molecule. Assumption (a) is used in most discussions of photoelectron angular distributions, but some form of assumptions (a) and (b) is always used[4,5] to prove that $b_L = 0$ for odd L.

The purpose of this paper is to point out that these assumptions fail for chiral molecules when the sample has a preponderance of one chirality, and therefore some new experimental parameters become available in principle. In practice, the most useful case is the parameter b_1 for circularly polarized light in the electric-dipole approximation. Since the vanishing of b_1 requires space-inversion symmetry and does not follow from any rotation invariance alone, that coefficient can be expected to be significant whenever the electric-

dipole matrix element depends significantly on the chiral structure of the molecule. The $L=1$ term should also exist for the angular distribution of molecular fragments produced on photodissociation of chiral molecules in which the chirality is not destroyed by the bond cleavage. We shall present this analysis in a later paper.

According to condition (iii) above, the symmetry of the molecule must be low enough such that an effective potential in which an electron moves shows an inequivalence as a function of the azimuthal angle. In other words, $V(r, \theta, \varphi)$ $\neq V(r, \theta, -\varphi)$, where the polar axis in the coordinate system in which the potential surface is defined is taken along the highest-order rotational axis of the point group to which the molecule belongs, in this case C_1. Physically, the absorption of a left or right circularly polarized photon will selectively populate a single fine-structure level of an oriented molecule according to the selection rule $m_f = m_0 \pm 1$, respectively, where m_f and m_0 are the azimuthal quantum numbers for the final and initial states, respectively. For random orientations of the molecule an equal mixture of the fine-structure levels is populated. As long as m_f or m_0 levels are equivalent as a result of the condition $V(r, \theta, \varphi) = V(r, \theta, -\varphi)$, then terms linear in $\cos\theta$ cancel on the summation over all possible azimuthal quantum numbers which occur in the expression for the angular distribution. However, if the magnetic sublevels, which are mixed by a molecular field of symmetry so low, are inequivalent for m_f and/or m_0 equal to plus and minus values, then a "memory" of the population of a single level in the *oriented* molecule will remain in the *unoriented* molecule. This "memory," as we shall see, occurs in the matrix elements as a result of different radial amplitudes in the two cases, and *incomplete* cancellation occurs in the summation. Thus, the term linear in $\cos\theta$ survives, and has a "sense" or sign depending on the left or right circular polarization of the photon and on the left or right handedness of the molecule. Each "enantiomer" of a pair of "optical isomers" will show the opposite sense, and the terms linear in $\cos\theta$ will cancel for the angular distribution for a pair of optical isomers, the simplest "racemic" mixture.

Let us construct a potential surface for an electron moving in the field of a chiral molecule or molecular ion. It has the form

$$V(r, \theta, \varphi) \sim V_0(r, \theta) + V_{1c}(r, \theta)\cos\varphi$$
$$+ V_{1s}(r, \theta)\sin\varphi + \cdots , \quad (2)$$

where $V_{1s}(r, \theta) = 0$ for a nonchiral molecule. The terms in the potential behaving as $\cos\varphi$ and $\sin\varphi$ will cause admixtures of terms of identical form

in the wave function calculated in the potential; hence the wave function for an electron moving in this field will also be of the form

$$\psi \sim \varphi_0(r, \theta) + \varphi_{1c}(r, \theta)\cos\varphi + \varphi_{1s}(r, \theta)\sin\varphi + \cdots .$$
$$(3)$$

If the wave function is recast in the form of a spherical partial wave expansion

$$\psi \sim \sum_{lm} \varphi_{lm}(r)Y_{lm}(\theta, \varphi) , \quad (4)$$

then it is easy to show (within a phase factor) that the radial wave functions for $l=1$, $m=+1$, and $m=-1$ behave as

$$\varphi_{1+1} \sim \varphi_{1c} + i\varphi_{1s} , \quad (5a)$$

$$\varphi_{1-1} \sim \varphi_{1c} - i\varphi_{1s} , \quad (5b)$$

respectively. The phase factor must be chosen, on physical grounds, such that $\varphi_{1+1} = \varphi_{1-1}$ when $\varphi_{1s} = 0$, which occurs when $V_{1s}(\theta, \varphi) = 0$ in the limit of nonchiral molecules. The presence of the φ_{1s} components causes an addition rather than a cancellation of terms linear in $\cos\theta$ on summation over the azimuthal quantum numbers. The sign of V_{1s} in Eq. (1) is taken to be that for a single handedness, say left handedness. For a molecule of the opposite handedness, then $V_{1s} \rightarrow -V_{1s}$, φ_{1s} $\rightarrow -\varphi_{1s}$, $\varphi_{1+1} \rightarrow \varphi_{1+1}^*$, and $\varphi_{1-1} \rightarrow \varphi_{1-1}^*$.

We will now give a mathematical demonstration of the preceding statements and present the results of a model calculation. The general expression for the differential cross section is

$$\frac{d\sigma^{(p)}}{d\Omega} = \frac{\alpha a_0^2}{2\pi} |\langle \psi^{(-)}(\vec{r}, \vec{k})|\hat{\rho}_p \cdot \vec{r}|\psi_i(\vec{r})\rangle|^2 E_p k , \quad (6)$$

where α is the fine-structure constant, a_0 is the Bohr radius, and, in atomic units, E_p and k are the photon energy and photoelectron velocity, respectively. The functions ψ_i and $\psi^{(-)}$ are the initial and final eigenstates of the system, the $(-)$ superscript designating normalization to satisfy incoming boundary conditions. First, we specify the form of the unit vector of polarization of the photon $\hat{\rho}_p$

$$\hat{\rho}_p \cdot \vec{r} = (\tfrac{4}{3}\pi)^{1/2} r \sum_{m_1} Y_{1m_1}(\theta_r, \varphi_r)D_{pm_1}^{(1)*}(\alpha\beta\gamma)(1 - 2\delta_{1p}) , \quad (7)$$

where we have used the addition theorem for spherical harmonics[6] and the transformation equation[6]

$$Y_{1m_1}^*(\theta_j, \varphi_j) = \sum_p Y_{1p}^*(\theta_p, \varphi_p)D_{pm_1}^{(1)*}(\alpha\beta\gamma) \quad (8)$$

for relating spherical harmonics defined in the

molecule-fixed frame (left-hand side) to those defined in the laboratory frame (right-hand side), where $D_{mm'}^{(l)}$, are the rotational matrices, whose arguments are the Euler angles. The index p takes on a single value corresponding to a fixed polarization of the photon, ± 1 for left or right circular polarization, respectively, in the plane normal to the direction of incidence, taken to be along the polar axis in the laboratory frame, or 0 for linear polarization along the polar axis, where the direction of incidence in this case must be taken along x or y in the laboratory frame. The angles θ_r, φ_r specify the direction of $\vec{r}$ in the molecule-fixed frame, and the angles θ_j, φ_j and θ_p, φ_p specify the directions of the unit vectors associated with $\hat{p}_p$ in the molecule-fixed and laboratory frames, respectively. The latter set take on a single set of values for each polarization according to the geometrical definitions just given.

Next we consider the forms of the bound and continuum wave functions in Eq. (6). In general, these will be Slater determinants, appropriate for a many-electron system. However, we will restrict the discussion to a one-electron picture. This simplification will not affect the general validity of our results, which depend in part on the details of the motion of the photoelectron in a potential field of the form given by Eq. (2), which in an actual calculation would be constructed within the framework of fixed-nuclei theory.[7,8] The form of $\psi^{(-)}$ is

$$\psi^{(-)} = 4\pi \sum u_{l_i l_j m_i m_j}^{(-)}(r) Y_{l_i m_i}(\theta_r, \varphi_r) Y_{l_j m_j}^*(\theta, \varphi)$$

$$\times D_{m_j' m_j}^{(l_j)*}(\alpha\beta\gamma), \tag{9}$$

where θ, φ specify the direction of the beam of ejected electrons in the laboratory frame (also defined as the direction of $\hbar\vec{k}$, the momentum of the ejected electron). This wave function (within a phase factor) is the transform of Eq. (2.2) of Ref. 8 on the application of the operation of time reversal[9] to the latter function; hence the wave function obtained on application of the time-reversal operation to Eq. (9) (or its complex conjugate) would be appropriate to describe a beam of incident electrons in a scattering experiment. The factor 4π normalizes the result such that the partial-wave-resolved plane wave is recoverable in the limit of zero potential. We note that the angles θ, φ and θ_k, φ_k, the latter of which specify the direction of the emerging beam in the molecule-fixed frame, are arbitrary with respect to the axis of quantization for the molecular eigenstates, as they must be for experiments involving randomly oriented molecules. The form given by Eq. (9) is appropriate for the calculation of the continuum wave function in the single-center approximation.[7,8] We note, however, that we can cast the theory in more general form if we perform the summation over $l_i m_i$ and write

$$\psi^{(-)} = 4\pi \sum \psi_{l_j m_j}^{(-)}(\vec{r}) Y_{l_j m_j}^*(\theta, \varphi) D_{m_j' m_j}^{(l_j)*}(\alpha\beta\gamma), \tag{10}$$

which is just the partial-wave resolution of $\psi^{(-)}(\vec{r}, \vec{k})$ with respect to $\vec{k}$. This form makes it clear that the validity of the results do not depend on the method used to calculate the wave functions.

Substitution of Eqs. (7) and (10) into Eq. (6) and performance of the average of the result over the Euler angles[7,8] yield the result

$$\frac{d\sigma^{(p)}}{d\Omega} = \frac{8}{3}\pi\alpha a_0^2 E_p k \sum \langle \psi_i | r Y_{1\mu_1}^* | \psi_{\lambda_j \mu_j}^{(-)}\rangle \langle \psi_{l_j m_j}^{(-)} | r Y_{1m_1} | \psi_i\rangle \Phi(p; \lambda_j\mu_j l_j m_j 1\mu_1 1m_1 L; \theta), \tag{11a}$$

$$\Phi(p; \lambda_j\mu_j l_j m_j 1\mu_1 1m_1 L; \theta) = (-1)^{p+m_1+m_j}(2L+1)(2l_j+1)^{1/2}(2\lambda_j+1)^{1/2}$$

$$\times \begin{pmatrix} l_j & \lambda_j & L \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 1 & 1 & L \\ p & -p & 0 \end{pmatrix}\begin{pmatrix} l_j & \lambda_j & L \\ m_j & -\mu_j & -(m_j-\mu_j) \end{pmatrix}\begin{pmatrix} 1 & 1 & L \\ m_1 & -\mu_1 & -(m_j-\mu_j) \end{pmatrix} P_L(\cos\theta). \tag{11b}$$

In deriving Eqs. (11) we have made consecutive use of two sum rules[10] to perform the summations over m_j', which casts the angular distribution in the form given by Fano and Dill,[2,11] and over j, a total angular momentum quantum number[2] defined as $\vec{j} = \vec{l}_j + \vec{1}$, respectively.

The following selection rules are readily apparent from the conditions for the existence of the 3-j symbols. According to the second 3-j symbol,

$0 \le L \le 2$. Also for $p = 0$, L cannot be odd by the rule that $1 + 1 + L$ be even. These conditions imply Yang's theorem[5] that the angular distribution behaves as $A + C\cos^2\theta$ for a linearly polarized photon and unpolarized target. For $p = \pm 1$, however, L can be odd, and

$$\begin{pmatrix} 1 & 1 & L \\ 1 & -1 & 0 \end{pmatrix} = (-1)^L \begin{pmatrix} 1 & 1 & L \\ -1 & 1 & 0 \end{pmatrix}. \tag{12}$$

According to the first 3-j symbol, however, l_j + λ_j + L must be even. If L is odd, the l_j and λ_j must be of opposite parity for this 3-j symbol to exist. This condition restricts the existence of terms linear in $\cos\theta$, for a single set of values of the azimuthal quantum numbers, to molecules whose states have indefinite parity (i.e., all values of the set λ_i, l_i are allowed) as a result of the absence of a center or plane of symmetry with respect to inversion or reflection of the coordinates, respectively.

These terms linear in $\cos\theta$ cancel, however, when the summation is performed over all possible values of the azimuthal quantum numbers, unless the molecule is chiral, a constraint in addition to the existence of states of indefinite parity. This statement can be proved by inspection of the fourth 3-j symbol. When L is odd, the symbol will vanish for $m_1 = \mu_1 = 0$ and will change sign by the rule

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

(13)

on summation over all allowed values of the set $\mu_j m_j \mu_1 m_1$ such that complete cancellation results. This cancellation would not occur if the matrix elements in Eq. (11b) were inequivalent for positive and negative values of the set $\mu_1 m_1$. Such an inequivalence occurs only in chiral or optically active molecules, as discussed previously. Hence the angular distribution behaves as $A \pm B \cos\theta$ + $C \cos^2\theta$ in this special case.

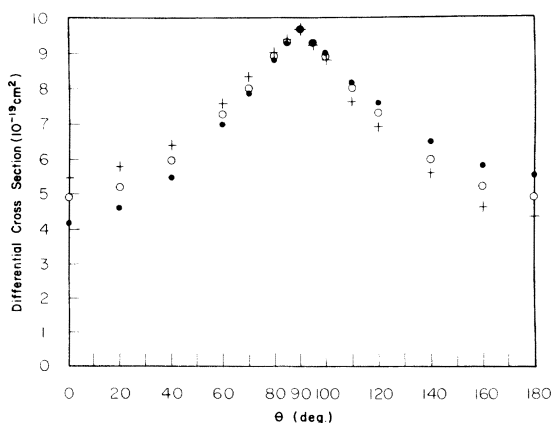We present the results of a model calculation in Fig. 1. This is a one-electron calculation for the

FIG. 1. Angular distribution of photoelectrons. Open circles, $A + C \cos^2\theta$; solid circles, $A + B \cos\theta + C \cos^2\theta$, appropriate for left circular polarization; plus signs, $A - B \cos\theta + C \cos^2\theta$, appropriate for right circular polarization.

photoionization of a molecule of ionization potential $\frac{1}{2}$ a.u., where the potential field is assumed to have the form given by Eq. (2) and the continuum wave function has the form given by Eq. (3) (for simplicity the bound molecular orbital has the form appropriate for a potential having no dependence on the azimuthal quantum number). We adopt single-center expansions for both bound and continuum [see Eq. (9)] wave functions, truncating the bound orbital expansion after $l_0 = 1$, assuming equal strength of the $l_0 = 0$ and $l_0 = 1$ radial components, and ignoring the effect of nonorthogonality between the bound and continuum functions (see Ref. 11 for the inclusion of this effect in the angular distribution). In addition, we truncate the continuum wave expansion after $l_i = 1$ and assume that $l_j = l_i$ and $m_j = m_i$, i.e., we ignore single-center partial-wave coupling. Also, we use Coulombic waves calculated in a potential of unit strength and Slater-type orbitals (STO's with Slater exponential parameters equal to unity) for the single-center radial components of the continuum and bound wave functions, respectively, allowing us to calculate the radial matrix elements in analytic form.[12] Thus, this cross section corresponds physically to one-half that for photoionization of a closed-shell two-electron molecule, calculated in a Flannery-Öpik-type model.[11,13] The use of the form for the wave function given by Eq. (3) mimics an m_i dependence in the radial matrix elements (Coulombic results are independent of m_i), where we have taken $\varphi_s = \varphi_c$. For a photoelectron velocity of $k = 0.1$ a.u. we calculate the following values (in units of 10^{-19} cm^2) for A, B, and C: $A = 9.771$, $B = -0.646$, and $C = -4.885$. We note from the selection rule $l_j + \lambda_j + L$ odd for $L = 1$, requiring that l_j and λ_j have opposite parity, that it is the $l_0 = 0$, $\lambda_0 = 1$ cross term arising from the bound orbital expansion, corresponding to interference between the processes $l_0 = 0 \rightarrow l_i = 1$ and $\lambda_0 = 1 \rightarrow \lambda_i = 0$, from which the entire $L = 1$ contribution arises in this model. This gives us valuable insight into structural information available in this term, not available in the angular distributions for ordinary nonchiral molecules; namely, for nonchiral molecules contributions from the cross terms corresponding to radial components of *opposite* parity belonging to the bound orbital can occur only if l_j and λ_j have the *same* parity (since otherwise the $L = 1$ term will disappear by cancellation), meaning that only radial continuum waves *nondiagonal* in l_j and l_i (and λ_j and λ_i) can contribute since, if l_0 and λ_0 have opposite parity, so too must l_i and λ_i by the selection rules for the existence of the electric-dipole matrix elements. Contributions from nondiagonal waves have been found to be smaller than those from diagonal waves.[14]

We have checked this result by setting $\varphi_s = 0$, recovering the ordinary form, $A + C \cos^2 \theta$. We note that $C = -A$ for the $l_0 = 0$ contribution in this model, giving the familiar $\sin^2 \theta$ dependence for ejection from an s orbital.

An important consequence of the existence of terms linear in $\cos \theta$ is the possibility of performing an experiment in which the angular distribution difference for absorption of left and right circularly polarized photons is measured. This difference behaves as $2B \cos \theta$. Finally, the sum of the angular distributions for absorption of left and right circularly polarized photons behaves as $2(A + C \cos^2 \theta)$. This form is recovered also for the absorption of photons of either polarization by a pair of molecules of opposite handedness, the simplest "racemic" mixture or unpolarized system, in agreement with Yang's theorem[5] for unpolarized photon and target.

*Work performed under the auspices of the U. S. Energy Research and Development Administration.
†Present address: Department of Chemistry, University of Alabama, University, Alabama 35486.
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