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Angular Distribution and Intensity in Molecular Photoelectron Spectroscopy I. General Theory for Diatomic Molecules

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Angular distribution and intensity in molecular photoelectron spectroscopy

I. General theory for diatomic molecules

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A theory of the angular distribution of photoelectrons ejected with a given energy from diatomic molecules is presented. The differential cross-section σ_Ω is of the form

$$\sigma_\Omega = \frac{\sigma_{\text{total}}}{4\pi}[1+\beta P_2(\cos\Theta)]$$

where σ_{total} is the total cross-section, β an anisotropy parameter and Θ the angle between the polarization vector of the incident light and the direction of the photoelectron. Expressions for σ_{total} and β in terms of internal transition dipole moments are obtained for transitions between individual rotational states of the molecule and ion, for either of Hund's cases (*a*) or (*b*). The formulae have been developed for central-field bases for the eigenstates of the electron before and after ionization. When rotational structure in the photoelectron spectrum is unresolved the angular distribution is independent of the choice of Hund's case.

1. INTRODUCTION

Molecular photoelectron spectroscopy (Al-Joboury & Turner 1963) has become a source of extensive data on molecular ionization potentials, orbital energies and Franck–Condon factors in ionization (Turner 1968*a*, *b*). Experiments on the angular distribution of photoelectrons ejected from molecules (Berkowitz & Ehrhardt 1966; Berkowitz, Ehrhardt & Tekaat 1967) suggest that the angular distribution may be useful as a source of information regarding the symmetry of the molecular orbital from which photoelectrons of a given energy are ejected. This information would supplement that available from band shapes and Franck–Condon factors (Al-Joboury & Turner 1963; Frost, McDowell & Vroom 1967). Also, Berry (1966) suggested that a study of the angular distribution of photoelectrons might be useful in determining those photon energies at which autoionization is important if the angular distribution of autoionized electrons is different from that for directly ionized electrons. Again, such information would supplement that available from Franck–Condon factors (Natalis & Collin 1968).

For atoms, the theory of the angular distribution of photoelectrons is well established (Bethe & Salpeter 1957). Recent calculations (Cooper & Zare 1968) for electrons photodetached from H^-, C^-, and O^- are in approximate agreement with experiment (Hall & Siegel 1968).

The theory of the angular distribution for molecules is more complex than that for light atoms, since:

(i) The molecular orbitals are not eigenfunctions of the orbital angular momentum operator l^2, due to the absence of spherical symmetry.

(ii) The bound orbital, from which the photoelectron is ejected, is quantized on the molecular axis, while the continuum function of the ejected electron is more readily referred to space-fixed axes, and

(iii) There may be transfer of angular momentum between electronic and rotational motion, as considered by Cohen & Fano (1966).

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This paper describes a general theory for diatomic molecules. Very recently another paper on this problem has been published (Tully, Berry & Dalton 1968), and its treatment is similar to ours in some respects. However, our theory treats molecular rotation explicitly, so that it is applicable to transitions between individual rotational levels; different angular distributions are found according to whether rotational structure is resolved or not. In this connexion we note that Turner (1968*c*) suggested that rotational fine structure in molecular photoelectron spectroscopy should be resolved in favourable cases. In addition, we employ a single-centre expansion for the bound orbital from which the photoelectron is ejected; this permits the reduction of the problem to purely radial integrals, and the expression of the result in a form analogous to that obtained for atoms by Cooper & Zare (1968).

2. General considerations

Consider the photoionization of a diatomic molecule by plane-polarized light of frequency ν resulting in the ejection of a photoelectron into an element of solid angle $\mathrm{d}\Omega$. The kinetic energy of the photoelectron is $E = h\nu - I$, where I is an ionization potential of the molecule. We assume that the energy of the incident photon is such that autoionization processes ejecting electrons with kinetic energy E are negligible. If this is so, the predominant ionization mechanism in the energy range used for molecular photoelectron spectroscopy is an electric-dipole transition from an intial molecular state $|g\rangle$ to a final state $|f_k\rangle = |f_{\mathrm{ion}};\, \boldsymbol{k}m_\sigma\rangle$ representing the bound state of the ionized molecule and the continuum state of a photoelectron having momentum $\hbar\boldsymbol{k}$ in the asymptotic limit of large r, and spin m_σ quantized along the space-fixed z axis. We neglect the electric quadrupole, magnetic dipole and two-photon processes considered by Tully *et al.* (1968); these are expected to be negligible under the normal experimental conditions of molecular photoelectron spectroscopy.

For an isotropic gas, the differential cross-section for ejection of an electron with energy E into the element of solid angle $\mathrm{d}\Omega$ is then (cf. Bethe & Salpeter 1957)

$$\sigma_\Omega = \frac{8\pi^3 e^2 \nu}{c n_g} \sum_{\substack{\text{degenerate}\\ \text{states}}} |\langle f_k| \sum_i z_i |g\rangle|^2, \tag{1}$$

where z is the direction of polarization of the incident light and n_g the total statistical weight of the initial state. The inner summation extends over all electrons i and the outer over all degenerate states of both molecule and ion, as well as over the photoelectron spin m_σ.

The photoelectron may be considered to be removed from a molecular orbital quantized along the molecular axis, and it is convenient to expand the continuum orbital $|\boldsymbol{k}\rangle$ in terms of functions quantized along this axis. The state $|\boldsymbol{k}\rangle$ depends on the orientation of the molecule with respect to the direction of $\boldsymbol{k}$, but we make the simplifying assumption that $|\boldsymbol{k}\rangle$ is an energy eigenfunction for a central potential, since the dominant contribution to the transition matrix elements in (1) is expected to come from regions far enough from the nucleus for this approximation to be reasonable. Then $|\boldsymbol{k}\rangle$ is axially symmetric about the direction of observation and can be expanded in partial waves (Bethe & Salpeter 1957; Messiah 1961):

$$|\boldsymbol{k}\rangle = (4\pi)^{-1} \sum_\lambda i^\lambda (2\lambda+1)\, R_\lambda(r)\, P_\lambda(\boldsymbol{k}\,.\,\boldsymbol{r}/kr), \tag{2}$$

where $\boldsymbol{r}$ is the position vector of the photoelectron with respect to the centre of mass of the ion (see § 7), P_λ is a Legendre polynomial and R_λ a function of r, normalized to $\delta(E-E')$ in atomic units. For photodetachment, the electron moves in a potential which falls off faster than r^{-1}, so that in the asymptotic limit of large r, equation (2) becomes a plane wave plus a spherical wave. For photoionization from a neutral molecule or positive ion, the potential is asymptotically coulombic, and both plane and spherical waves are modified by logarithmic phase factors, but the asymptotic limit of the current density is unaltered (Messiah 1961). In either case, the $R_\lambda(r)$ must be chosen so that the spherical wave is ingoing, since $|\boldsymbol{k}\rangle$ represents a final state (Breit & Bethe 1954).

Using the spherical harmonic addition theorem to expand $P_\lambda(\boldsymbol{k}\,.\,\boldsymbol{r}/kr)$ in terms of spherical harmonics $Y_{\lambda m_\lambda}(\theta, \phi)$ quantized along the space-fixed z axis,

$$|\boldsymbol{k}\rangle = \sum_\lambda i^\lambda R_\lambda(r) \sum_{m_\lambda} Y^*_{\lambda m_\lambda}(\Theta, \Phi)\, Y_{\lambda m_\lambda}(\theta, \phi) = \sum_{\lambda, m_\lambda} |E\lambda m_\lambda\rangle\, Y^*_{\lambda m_\lambda}(\Theta, \Phi), \tag{3}$$

where (Θ, Φ) and (θ, ϕ) are the polar and azimuthal angles of $\boldsymbol{k}$ and $\boldsymbol{r}$ with respect to the z axis. The states $|E\lambda m_\lambda\rangle$ will be expanded later in terms of states quantized along the molecular axis. The differential cross-section now becomes

$$\sigma_\Omega = \frac{8\pi^3 e^2 \nu}{c n_g} \sum_{\substack{\text{degenerate}\\ \text{states}}} \sum_{\lambda, \bar{\lambda}, m_\lambda} \langle f_{\text{ion}};\, E\lambda m_\lambda m_\sigma | \sum_i z_i | g\rangle \langle f_{\text{ion}};\, E\bar{\lambda} m_\lambda m_\sigma | \sum_i z_i | g\rangle^* Y_{\lambda m_\lambda}(\Theta, \Phi)\, Y^*_{\bar{\lambda} m_\lambda}(\Theta, \Phi), \tag{4}$$

since σ_Ω must be real. The product of spherical harmonics may be expanded as a sum of Legendre polynomials to give

$$\begin{aligned}\sigma_\Omega = \frac{2\pi^2 e^2 \nu}{c n_g} \sum_L (2L+1)\, P_L(\cos\Theta) \sum_{\lambda, \bar{\lambda}} (2\lambda+1)^{\frac{1}{2}}\, (2\bar{\lambda}+1)^{\frac{1}{2}} \begin{pmatrix} \lambda & \bar{\lambda} & L \\ 0 & 0 & 0 \end{pmatrix} \\ \times \sum_{\substack{m_\lambda, \text{degenerate}\\ \text{states}}} (-1)^{-m_\lambda} \begin{pmatrix} \lambda & \bar{\lambda} & L \\ m_\lambda & -m_\lambda & 0 \end{pmatrix} \langle f_{\text{ion}};\, E\lambda m_\lambda m_\sigma | \sum_i z_i | g\rangle \langle f_{\text{ion}};\, E\bar{\lambda} m_\lambda m_\sigma | \sum_i z_i | g\rangle^*,\end{aligned} \tag{5}$$

where quantities of the form $\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ are symmetrized vector-coupling coefficients or $3j$-symbols (Edmonds 1960).

It will be shown that (5) reduces to the form

$$\sigma_\Omega = \sigma_{\text{total}} (4\pi)^{-1} [1 + \beta P_2(\cos\Theta)] \tag{6}$$

for plane-polarized light. For unpolarized light

$$\sigma_\Omega = \sigma_{\text{total}} (4\pi)^{-1} [1 - \tfrac{1}{2}\beta P_2(\cos\Theta_\chi)], \tag{7}$$

where Θ_χ is measured from the axis of propagation of the incident light. The case of partial polarization has been considered by Samson (1969).

For a given degree of polarization, the angular distribution of photoelectrons then depends only on the *anisotropy parameter* β. The form (6) is to be expected from general considerations provided that, as we have assumed, all degenerate initial states are equally populated (Bethe & Salpeter 1957; Cooper & Zare 1968). In order to reduce (5) to this form and evaluate β, however, the sums over degenerate states must be evaluated explicitly.

For an 'oriented' sample of molecules in which degenerate states are unequally populated, as for example in a molecular beam experiment, a more complex angular distribution can be obtained, as shown by Lin (1968) for the hydrogen atom. A more complex distribution may also result due to electric quadrupole or magnetic dipole terms (Tully *et al.* 1968), but these should be significant only at very high energies. We consider here only electric dipole transitions in an isotropic gas, for which (6) is valid.

Either the molecule or the ion, or both, must have a net spin, so it is necessary to consider the way in which the spin angular momentum is coupled to the orbital and rotational angular momenta. The two most common modes of coupling are Hund's cases (*a*) and (*b*) (Herzberg 1950); case (*b*) is the simpler to treat here. We consider first transitions between individual rotational levels when both the molecule and the ion can be described as Hund's case (*b*) (§§ 3 and 4), and then average over rotational levels to obtain a result applicable if rotational structure is not resolved (§ 5). We then consider the modification of the theory required if the molecule and/or the ion conform to Hund's case (*a*) (§ 6), and finally discuss briefly the radial integrals in the theory (§ 7).

3. THEORY FOR TRANSITIONS BETWEEN INDIVIDUAL HUND'S CASE (*b*) ROTATIONAL LEVELS

In Hund's case (*b*) the spin is weakly coupled to the resultant of the orbital (if any) and rotational angular momenta, and the spin is quantized along a space-fixed axis. This description is specially suitable for, say, $^2\Sigma \leftarrow {}^1\Sigma$ ionization.

We neglect small interactions due to spin-rotation coupling, as well as those involved in Λ-type doubling (Herzberg 1950), and describe the molecular and ionic states by quantum numbers n, Λ, K, M_K, S, M_S, where Λ is the component of orbital angular momentum along the molecular axis. K is the resultant of orbital and rotational angular momenta, S is the total spin, M_K and M_S are the components of K and S along the space-fixed z axis, and n represents the other quantum numbers required to define the state. The explicit form of (5) in this case is

$$\sigma_\Omega = \frac{2\pi^2 e^2 \nu}{c(2K''+1)\,(2S''+1)} \sum_L (2L+1)\, P_L(\cos\Theta) \sum_{\lambda,\bar{\lambda}} (2\lambda+1)^{\frac{1}{2}}\,(2\bar{\lambda}+1)^{\frac{1}{2}} \begin{pmatrix} \lambda & \bar{\lambda} & L \\ 0 & 0 & 0 \end{pmatrix}$$
$$\times \sum_{\substack{m_\lambda,\, M''_K,\, M'_K \\ m_\sigma,\, M''_S,\, M'_S}} (-1)^{-m_\lambda} \begin{pmatrix} \lambda & \bar{\lambda} & L \\ m_\lambda & -m_\lambda & 0 \end{pmatrix} \langle n'\Lambda' K' M'_K S' M'_S;\, E\lambda m_\lambda m_\sigma | \sum_i z_i \,| n''\Lambda'' K'' M''_K S'' M''_S \rangle$$
$$\times \langle n'\Lambda' K' M'_K S' M'_S;\, E\bar{\lambda} m_\lambda m_\sigma | \sum_i z_i \,| n''\Lambda'' K'' M''_K S'' M''_S \rangle^*, \quad (8)$$

where single primes refer to ionic, and double primes to molecular, quantum numbers.

The spin quantum numbers can be eliminated immediately from (8), since the sum over M'_S and m_σ is equivalent to a sum over the total spin S_T of the final system (ion plus electron) and its z component M_T. The sum over S_T, M_T and M''_S is $(2S''+1)$ times the term for which

$$S_T = M_T = M''_S = S''.$$

We now reduce the matrix elements in (8) to integrals over 'internal' coordinates, defined with respect to axes fixed in the molecule. The continuum functions of the photoelectron are expanded:

$$|E\lambda m_\lambda\rangle = \sum_{m'_\lambda} |E\lambda m'_\lambda\rangle\, \mathscr{D}^{(\lambda)}_{m'_\lambda m_\lambda}(\omega), \quad (9)$$

where $|E\lambda m'_\lambda\rangle$ is a state with orbital angular momentum component m'_λ along the molecular axis, ω indicates the Euler angles describing the molecular orientation, and the '$\mathscr{D}$-function', $\mathscr{D}^{(\lambda)}_{m'_\lambda m_\lambda}(\omega)$, is a matrix element of the appropriate rotation operator (Edmonds 1960). Similarly, the electric dipole operator for the ith electron is

$$-ez_i = -(\tfrac{4}{3}\pi)^{\frac{1}{2}}\, er_i\, Y_{10}(\theta_i, \phi_i) = -(\tfrac{4}{3}\pi)^{\frac{1}{2}}\, er_i \sum_{m'} Y_{1m'}(\theta'_i, \phi'_i)\, \mathscr{D}^{(1)}_{m'0}(\omega), \quad (10)$$

where m' is an angular momentum component along the molecular axis and r_i, θ'_i, ϕ'_i are polar coordinates referred to the molecular frame.

The normalized eigenfunctions of a symmetric top also involve the $\mathscr{D}$-functions (Edmonds 1960), so that in the Born–Oppenheimer approximation,

$$|n\Lambda K M_K S M_S\rangle = [(2K+1)/8\pi^2]^{\frac{1}{2}}\,|n\Lambda S M_S\rangle\,\mathscr{D}^{(K)}_{\Lambda M_K}(\omega) \tag{11}$$

for both molecular and ionic states. The matrix elements in (8) now become, on dropping spin quantum numbers,

$$\begin{aligned}\langle n'\Lambda'K'M_K';\,E\lambda m_\lambda|\sum_i z_i\,|n''\Lambda''K''M_K''\rangle \\ = \left[\frac{(2K''+1)\,(2K'+1)}{48\pi^3}\right]^{\frac{1}{2}} \sum_{m_\lambda',\,m'} a^{n'\Lambda'}_{n''\Lambda''}(m';\,E\lambda m_\lambda') \int \mathrm{d}\omega\,\mathscr{D}^{(K')*}_{\Lambda'M_K'}(\omega)\,\mathscr{D}^{(\lambda)*}_{m_\lambda' m_\lambda}(\omega)\,\mathscr{D}^{(1)}_{m'0}(\omega)\,\mathscr{D}^{(K'')}_{\Lambda''M_K''}(\omega),\end{aligned} \tag{12}$$

where the 'internal' transition moment

$$a^{n'\Lambda'}_{n''\Lambda''}(m';\,E\lambda m_\lambda') = \langle n'\Lambda';\,E\lambda m_\lambda'|\sum_i r_i Y_{1m'}(\theta_i',\phi_i')\,|n''\Lambda''\rangle. \tag{13}$$

The integral over orientation is evaluated by expanding the product of two of the $\mathscr{D}$ functions and using the integral (Edmonds 1960) for a product of three $\mathscr{D}$ functions:

$$\begin{aligned}\int \mathrm{d}\omega\,\mathscr{D}^{(K')*}_{\Lambda'M_K'}(\omega)\,\mathscr{D}^{(\lambda)*}_{m_\lambda' m_\lambda}(\omega)\,\mathscr{D}^{(1)}_{m'0}(\omega)\,\mathscr{D}^{(K'')}_{\Lambda''M_K''}(\omega) \\ = 8\pi^2(-1)^{\Lambda'-M_K'-m'}\sum_j (2j+1) \\ \times\begin{pmatrix}\lambda & 1 & j\\ -m_\lambda' & m' & -\Delta\Lambda\end{pmatrix}\begin{pmatrix}\lambda & 1 & j\\ -m_\lambda & 0 & m_\lambda\end{pmatrix}\begin{pmatrix}K' & j & K''\\ -\Lambda' & \Delta\Lambda & \Lambda''\end{pmatrix}\begin{pmatrix}K' & j & K''\\ -M_K' & -m_\lambda & M_K''\end{pmatrix},\end{aligned} \tag{14}$$

where $\Delta\Lambda = \Lambda'-\Lambda''$, and j is a dummy variable ranging from $|\lambda-1|$ to $\lambda+1$. From (8), (12) and (14) the differential cross-section is

$$\begin{aligned}\sigma_\Omega = \frac{8\pi^3e^2\nu}{3c}\sum_L (2L+1)\,P_L(\cos\Theta)\sum_{\lambda,\,\bar{\lambda},\,j}(2j+1)\,(2\lambda+1)^{\frac{1}{2}}\,(2\bar{\lambda}+1)^{\frac{1}{2}}\begin{pmatrix}\lambda & \bar{\lambda} & L\\ 0 & 0 & 0\end{pmatrix} \\ \times Q^{\Lambda'K'}_{\Lambda''K''}(j)\,A^{n'\Lambda'}_{n''\Lambda''}(E\lambda j)\,A^{n'\Lambda'}_{n''\Lambda''}(E\bar{\lambda}j)^*\sum_{m_\lambda}(-1)^{-m_\lambda} \\ \times\begin{pmatrix}\lambda & \bar{\lambda} & L\\ m_\lambda & -m_\lambda & 0\end{pmatrix}\begin{pmatrix}\lambda & 1 & j\\ -m_\lambda & 0 & m_\lambda\end{pmatrix}\begin{pmatrix}\bar{\lambda} & 1 & j\\ -m_\lambda & 0 & m_\lambda\end{pmatrix},\end{aligned} \tag{15}$$

where we have made use of an orthogonality relation for $3j$-symbols and defined

$$Q^{\Lambda'K'}_{\Lambda''K''}(j) = (2K'+1)\begin{pmatrix}K' & j & K''\\ -\Lambda' & \Delta\Lambda & \Lambda''\end{pmatrix}^2 \tag{16}$$

and

$$A^{n'\Lambda'}_{n''\Lambda''}(E\lambda j) = \sum_{m',\,m_\lambda'}(-1)^{-m'}\,a^{n'\Lambda'}_{n''\Lambda''}(m';\,E\lambda m_\lambda')\begin{pmatrix}\lambda & 1 & j\\ -m_\lambda' & m' & -\Delta\Lambda\end{pmatrix}. \tag{17}$$

The factor $Q^{\Lambda'K'}_{\Lambda''K''}(j)$ contains the dependence on rotational quantum numbers. It will be shown later (§ 6) that only this factor depends on the assumption of Hund's case (*b*) states, so we shall write it simply as $Q(j)$ and evaluate it for Hund's case (*a*) states later.

The summation over m_λ may be evaluated using the identity (Edmonds 1960)

$$\begin{aligned}\sum_{\mu_1,\,\mu_2,\,\mu_3}(-1)^{l_1+l_2+l_3+\mu_1+\mu_2+\mu_3}\begin{pmatrix}j_1 & l_2 & l_3\\ m_1 & \mu_2 & -\mu_3\end{pmatrix}\begin{pmatrix}l_1 & j_2 & l_3\\ -\mu_1 & m_2 & \mu_3\end{pmatrix}\begin{pmatrix}l_1 & l_2 & j_3\\ \mu_1 & -\mu_2 & m_3\end{pmatrix} \\ = \begin{pmatrix}j_1 & j_2 & j_3\\ m_1 & m_2 & m_3\end{pmatrix}\begin{Bmatrix}j_1 & j_2 & j_3\\ l_1 & l_2 & l_3\end{Bmatrix},\end{aligned} \tag{18}$$

where the expression in curly brackets is a $6j$-symbol. The differential cross-section then becomes

$$\sigma_{\Omega} = \frac{8\pi^3 e^2 \nu}{3c} \sum_{L} (2L+1)\, P_L(\cos\Theta) \begin{pmatrix} L & 1 & 1 \\ 0 & 0 & 0 \end{pmatrix} \sum_{\lambda,\bar{\lambda}} (2\lambda+1)^{\frac{1}{2}} (2\bar{\lambda}+1)^{\frac{1}{2}} \begin{pmatrix} \lambda & \bar{\lambda} & L \\ 0 & 0 & 0 \end{pmatrix}$$
$$\times \sum_{j} (-1)^{-j} (2j+1)\, Q(j) \begin{Bmatrix} L & 1 & 1 \\ j & \bar{\lambda} & \lambda \end{Bmatrix} A^{n'\Lambda'}_{n''\Lambda''}(E\lambda j)\, A^{n'\Lambda'}_{n''\Lambda''}(E\bar{\lambda} j)^{*}. \tag{19}$$

It is now clear that the differential cross-section has the form of (6), since the $3j$-symbol $\begin{pmatrix} L & 1 & 1 \\ 0 & 0 & 0 \end{pmatrix}$ is non-zero only for $L = 0, 2$. Evaluation of all non-zero $3j$- and $6j$-symbols (Edmonds 1960) leads to

$$\sigma_{\text{total}} = \frac{32\pi^4 e^2 \nu}{9c} \sum_{\lambda=0}^{\infty} \sum_{j=|\lambda-1|}^{\lambda+1} (2j+1)\, Q(j)\, |A^{n'\Lambda'}_{n''\Lambda''}(E\lambda j)|^2, \tag{20}$$

$$\beta\sigma_{\text{total}} = \frac{32\pi^4 e^2 \nu}{9c} \sum_{\lambda=1}^{\infty} [\lambda Q(\lambda+1)\, |A^{n'\Lambda'}_{n''\Lambda''}(E\lambda\, \lambda+1)|^2 - (2\lambda+1)\, Q(\lambda) |A^{n'\Lambda'}_{n''\Lambda''}(E\lambda\lambda)|^2$$
$$+ (\lambda+1)\, Q(\lambda-1)\, |A^{n'\Lambda'}_{n''\Lambda''}(E\lambda\lambda-1)|^2 - 6[\lambda(\lambda+1)]^{\frac{1}{2}}$$
$$\times Q(\lambda)\, \mathrm{Re}\{A^{n'\Lambda'}_{n''\Lambda''}(E\lambda-1\lambda)\, A^{n'\Lambda'}_{n''\Lambda''}(E\lambda+1\lambda)^{*}\}]. \tag{21}$$

4. EVALUATION OF INTERNAL MATRIX ELEMENTS IN ORBITAL APPROXIMATION

We now consider an orbital picture of a vertical ionization process, and assume first of all that the molecular electronic wave function is given by the Hartree–Fock approximation as a linear combination of the minimum number of Slater determinants consistent with the assumed spin quantum numbers. For a ground-state multiplet, the state with $M''_S = S''$ is a single determinant with $2S''$ odd electrons. We also assume that the photoelectron is removed from a definite orbital, leaving an ion in which the other orbitals are not affected by the ionization process. This is Koopmans's (1933) approximation, which leads to the identity of vertical ionization potentials and Hartree–Fock orbital energies.

The integral over electronic coordinates in the internal matrix elements defined by (13) is then an integral of a sum of one-electron operators taken between determinantal wavefunctions differing in one spin-orbital only, and may be reduced to a one-electron integral (Parr 1964; Slater 1960). We find that

$$a^{n'\Lambda'}_{n''\Lambda''}(m'; E\lambda m'_{\lambda}) = q_{\text{vib}}\, k_{\text{spin}} \int \mathrm{d}\boldsymbol{r}\, u^{*}_{E\lambda m'_{\lambda}}\, r Y_{1m'}(\theta', \phi')\, u_{n,-\Delta\Lambda}, \tag{22}$$

where the first orbital is a continuum function, and the second with angular momentum component $-\Delta\Lambda$ along the molecular axis is the orbital from which the photoelectron is ejected. The factor q_{vib} is a vibrational overlap integral (q^2_{vib} is a Franck–Condon factor) due to integration over the internuclear coordinate, and k_{spin} depends on S'' and S' and allows for the fact that the final state of the ionized system with $M'_T = S'_T = S''$ is not in general a single Slater determinant.

To reduce the result to radial integrals, the bound orbital in (22) may be expanded in terms of central field functions (cf. §7):

$$u_{n,-\Delta\Lambda} = \sum_{l=|\Delta\Lambda|}^{\infty} C_{nl} R_{nl}(r)\, Y_{l,-\Delta\Lambda}(\theta', \phi'), \tag{23}$$

where $R_{nl}(r)$ is normalized. The continuum function in (22) is a central-field orbital in our approximation, and evaluation of the angular integrals leads to

$$a^{n'\Lambda'}_{n''\Lambda''}(m'; E\lambda m'_{\lambda}) = \mathrm{i}^{-\lambda}(-1)^{-m'_{\lambda}} \left[\frac{3(2\lambda+1)}{4\pi}\right]^{\frac{1}{2}} q_{\text{vib}}\, k_{\text{spin}} \sum_{l=|\Delta\Lambda|}^{\infty} C_{nl} F^{E\lambda}_{nl} (2l+1)^{\frac{1}{2}}$$
$$\times \begin{pmatrix} \lambda & 1 & l \\ -m'_{\lambda} & m' & -\Delta\Lambda \end{pmatrix} \begin{pmatrix} \lambda & 1 & l \\ 0 & 0 & 0 \end{pmatrix}, \tag{24}$$

where we have defined a *radial transition integral*

$$F_{nl}^{E\lambda} = \int_0^\infty r^2\,\mathrm{d}r\,R_\lambda^*(r)\,rR_{nl}(r). \tag{25}$$

Substituting (24) into (17) and inserting the result into (20), (21) leads to the total cross-section

$$\sigma_{\text{total}} = \frac{8\pi^3e^2\nu q_{\text{vib}}^2k_{\text{spin}}^2}{3c}\sum_{l=|\Delta\Lambda|}^{\infty}(2l+1)^{-1}\,Q(l)\,|C_{nl}|^2\,[l\,|F_{nl}^{E,l-1}|^2+(l+1)\,|F_{nl}^{E,l+1}|^2], \tag{26}$$

and the anisotropy parameter

$$\beta = \frac{\sum\limits_{l=|\Delta\Lambda|}^{\infty}|C_{nl}|^2\,Q(l)\,(2l+1)^{-2}\,[l(l-1)\,|F_{nl}^{E,l-1}|^2+(l+1)\,(l+2)\,|F_{nl}^{E,l+1}|^2-6l(l+1)\,\mathrm{Re}\,(F_{nl}^{E,l-1}F_{nl}^{E,l+1*})]}{\sum\limits_{l=|\Delta\Lambda|}^{\infty}|C_{nl}|^2\,Q(l)\,(2l+1)^{-1}\,[l\,|F_{nl}^{E,l-1}|^2+(l+1)\,|F_{nl}^{E,l+1}|^2]}. \tag{27}$$

For Hund's case (*b*), the factor $Q(l)$ is given by (16).

5. AVERAGING OVER ROTATIONAL LEVELS

The above calculation refers to transitions between individual rotational levels. This is essential for the interpretation of experiments in which rotational structure is resolved. In such experiments the terms corresponding to different l values could be separated. Also, (26) can be used as the starting-point for a theory of the shape of rotational profiles. However, rotational fine structure has not yet been resolved in molecular photoelectron spectroscopy, although this should become possible (Turner 1968*c*). To make the present theory directly applicable to experiments in which rotational structure is not resolved, it is necessary to average the differential cross-section over rotational levels of the molecule, and sum over the levels of the ion. The result is the same as that obtained by evaluating the cross-section for a particular direction of the molecular axis, and then averaging over all possible directions, as in the work of Tully *et al.* (1968).

We now denote the differential cross-section relating to individual rotational levels by $\sigma_\Omega(K'\leftarrow K'')$. Then for an initial Boltzmann population, the differential cross-section for photoionization from all rotational levels of a given molecular vibrational state to all rotational levels of a given ionic vibrational state is

$$\sigma_\Omega = (2S''+1)\,Z^{-1}\sum_{K''=\Lambda''}^{\infty}(2K''+1)\,g(K'')\,\mathrm{e}^{-E''_{\text{rot}}/kT}\sum_{K'=\Lambda'}^{\infty}\sigma_\Omega(K'\leftarrow K''), \tag{28}$$

where Z is a partition function of the molecule, $g(K'')$ is a statistical weight to allow for nuclear spin symmetry ($=1$ for heteronuclear diatomics), and E''_{rot} is the rotational energy of the initial state.

The differential cross-section still has the form of (6), with the total cross-section and anisotropy parameter given by (26) and (27) except that now

$$Q(l) = (2S''+1)\,Z^{-1}\sum_{K''=\Lambda''}^{\infty}(2K''+1)\,g(K'')\,\mathrm{e}^{-E''_{\text{rot}}/kT}\sum_{K'=\Lambda'}^{\infty}Q(l,K'\leftarrow K''), \tag{29}$$

with $Q(l, K' \leftarrow K'')$ given by (16). The summation over K' yields unity because of an orthogonality relation for $3j$-symbols, so $Q(l) = 1$, and the anisotropy parameter becomes

$$\beta = \frac{\sum\limits_{l=|\Delta\Lambda|}^{\infty} |C_{nl}|^2 (2l+1)^{-2}[l(l-1)\,|F_{nl}^{E,l-1}|^2 + (l+1)\,(l+2)\,|F_{nl}^{E,l+1}|^2 - 6l(l+1)\,\mathrm{Re}\,(F_{nl}^{E,l-1} F_{nl}^{E,l+1*})]}{\sum\limits_{l=|\Delta\Lambda|}^{\infty} |C_{nl}|^2 (2l+1)^{-1}[l\,|F_{nl}^{E,l-1}|^2 + (l+1)\,|F_{nl}^{E,l+1}|^2]}. \tag{30}$$

If the orbital from which the photoelectron is ejected were an angular momentum eigenfunction, so that only a single value of l is involved, (30) would reduce to a form equivalent to that suitable for atoms (Cooper & Zare 1968). For molecules this would not be a good approximation in most cases. For example, Berkowitz *et al.* (1967) found a virtually isotropic distribution of photoelectrons from the σ_g orbitals of N_2 and CO (the subscript g being an approximate label for the latter), indicating that the non-spherical components of the orbital contribute significantly to the anisotropy parameter. For N_2, this has been confirmed by Samson (1970).

Tully *et al.* (1968) calculated the angular distribution of photoelectrons ejected from H_2 (including only contributions from the p-component ($l = 1$) of the continuum state. They have neglected the interference terms which were found to be large for atoms (Cooper & Zare 1968); this may be responsible for the fact that their calculated angular distribution is approximately $\cos^2\Theta$ ($\beta = 2$) in contrast to the experimental results for the σ_g orbitals of N_2 and CO (no results have been published for H_2).

6. THEORY FOR HUND'S CASE (*a*)

The theory for Hund's case (*b*) states can be extended to Hund's case (*a*) states; we obtain different angular distributions for transitions between individual rotational levels, but the same distribution as for case (*b*) if rotational structure is not resolved.

In Hund's case (*a*) the spin is strongly coupled to the molecular axis. This description is specially suitable for, say, ${}^2\Pi \leftarrow {}^1\Sigma$ ionization. States can be described by quantum numbers n, Λ, S, Σ, Ω, J and M, where Σ is the component of spin along the molecular axis, $\Omega = \Lambda + \Sigma$, and M is the component of J along the space-fixed z axis. The other quantum numbers have the same meaning as for Hund's case (*b*). The rotational wave function of either the molecule or the ion is now that of a symmetric top with half-integral angular momentum. Also, when transforming the photoelectron state, the spin function as well as the orbital function must be transformed to a new basis quantized on the molecular axis, since now the molecular and ionic spins are quantized along this axis.

For Hund's case (*a*), therefore, the matrix element analogous to that given by (12) is

$$\begin{aligned}\langle n'\Lambda'S'\Sigma'\Omega'J'M';\, E\lambda m_\lambda m_\sigma \,|\, \sum_i z_i \,|n''\Lambda''S''\Sigma''\Omega''J''M''\rangle \\ = \left[\frac{(2J''+1)\,(2J'+1)}{48\pi^3}\right]^{\frac{1}{2}} \sum_{m',\,m'_\lambda,\,m'_\sigma} \langle n'\Lambda'S'\Sigma'\Omega';\, E\lambda m'_\lambda m'_\sigma|\, \sum_i r_i Y_{1m'}(\theta'_i, \phi'_i)\,|n''\Lambda''S''\Sigma''\Omega''\rangle \\ \times \int \mathrm{d}\omega\, \mathscr{D}^{(J')*}_{\Omega'M'}(\omega)\, \mathscr{D}^{(\lambda)*}_{m'_\lambda m_\lambda}(\omega)\, \mathscr{D}^{(\frac{1}{2})*}_{m'_\sigma m_\sigma}(\omega)\, \mathscr{D}^{(1)}_{m'0}(\omega)\, \mathscr{D}^{(J'')}_{\Omega''M''}(\omega).\end{aligned} \tag{31}$$

The internal matrix element is related to that defined in (13) by

$$\langle n'\Lambda'S'\Sigma'\Omega';\, E\lambda m'_\lambda m'_\sigma|\, \sum_i r_i Y_{1m'}(\theta'_i, \phi'_i)\,|n''\Lambda''S''\Sigma''\Omega''\rangle = a^{n'\Lambda'}_{n''\Lambda''}(m';\, E\lambda m'_\lambda)\, \langle S'\,\Sigma'\tfrac{1}{2}m'_\sigma \,|\, S'\tfrac{1}{2}S''\Sigma''\rangle, \tag{32}$$

where the second factor is a vector-coupling coefficient. The integral over orientation has the value

$$\int \mathrm{d}\omega\, \mathscr{D}^{(J')*}_{\Omega' M'}(\omega)\, \mathscr{D}^{(\lambda)*}_{m'_\lambda m_\lambda}(\omega)\, \mathscr{D}^{(\frac{1}{2})*}_{m'_\sigma m_\sigma}(\omega)\, \mathscr{D}^{(1)}_{m' 0}(\omega)\, \mathscr{D}^{(J'')}_{\Omega'' M''}(\omega)$$
$$= 8\pi^2(-1)^{\Omega'-M'+m'_\lambda-m_\lambda} \sum_j (2j+1) \begin{pmatrix} \lambda & 1 & j \\ -m'_\lambda & m' & -\Delta\Lambda \end{pmatrix} \begin{pmatrix} \lambda & 1 & j \\ -m_\lambda & 0 & m_\lambda \end{pmatrix}$$
$$\times \sum_\chi (2\chi+1) \begin{pmatrix} j & \frac{1}{2} & \chi \\ \Delta\Lambda & \Delta\Sigma & -\Delta\Omega \end{pmatrix} \begin{pmatrix} j & \frac{1}{2} & \chi \\ -m_\lambda & -m_\sigma & m_\lambda+m_\sigma \end{pmatrix}$$
$$\times \begin{pmatrix} J' & \chi & J'' \\ -\Omega' & \Delta\Omega & \Omega'' \end{pmatrix} \begin{pmatrix} J' & \chi & J'' \\ -M' & -m_\lambda-m_\sigma & M'' \end{pmatrix}, \tag{33}$$

where χ is a dummy variable taking the values $j \pm \frac{1}{2}$. Evaluation of the differential cross-section leads again to (15), but now with

$$Q(j) = (2J'+1)\,(2S''+1) \begin{pmatrix} S' & \frac{1}{2} & S'' \\ \Sigma' & -\Delta\Sigma & -\Sigma'' \end{pmatrix}^2$$
$$\times \sum_\chi (2\chi+1) \begin{pmatrix} j & \frac{1}{2} & \chi \\ \Delta\Lambda & \Delta\Sigma & -\Delta\Omega \end{pmatrix}^2 \begin{pmatrix} J' & \chi & J'' \\ -\Omega' & \Delta\Omega & \Omega'' \end{pmatrix}^2, \tag{34}$$

where $\Delta\Sigma = \Sigma' - \Sigma''$ and $\Delta\Omega = \Omega' - \Omega''$. The factor $Q(j)$ contains the dependence on spin and rotational quantum numbers. The derivation of (26) and (27) in the orbital approximation is the same as that for Hund's case (*b*), and the total cross-section and anisotropy parameter are given by the same formulae, except that $Q(l)$ is given by (34).

The average and sum over rotational levels, using (29) with K replaced by J throughout, leads to:

$$Q(l) = (2S''+1) \begin{pmatrix} S' & \frac{1}{2} & S'' \\ \Sigma' & -\Delta\Sigma & -\Sigma'' \end{pmatrix}^2. \tag{35}$$

This is independent of l, so the anisotropy parameter is the same as for Hund's case (*b*) when rotational structure is not resolved. It may be seen that in this case the angular distribution is the same for all components of a spin multiplet.

If neither the molecule nor the ion is in a singlet state, as for NO and O_2, it may be necessary to treat one as Hund's case (*a*) and the other as Hund's case (*b*). The calculation is similar to that when both are Hund's case (*a*), except that two of the three spins in each matrix element are now quantized along the space-fixed z axis so that in evaluating the matrix elements, it is best to transform the third spin (that of the case (*a*) state) to a basis quantized along this axis.

We again obtain (26) and (27) but with a different $Q(l)$. For transitions between individual rotational levels, for (*a*) ← (*b*)

$$Q(l) = (2J'+1)\,(2S'+1)^{-1} \sum_\chi (2\chi+1) \begin{pmatrix} l & S' & \chi \\ \Delta\Lambda & \Sigma' & \Lambda''-\Omega' \end{pmatrix}^2 \begin{pmatrix} J' & \chi & K'' \\ -\Omega' & \Omega'-\Lambda'' & \Lambda'' \end{pmatrix}^2. \tag{36}$$

and for (*b*) ← (*a*)

$$Q(l) = (2K'+1) \sum_\chi (2\chi+1) \begin{pmatrix} l & S'' & \chi \\ -\Delta\Lambda & \Sigma'' & \Lambda'-\Omega'' \end{pmatrix}^2 \begin{pmatrix} K' & \chi & J'' \\ -\Lambda' & \Lambda'-\Omega'' & \Omega'' \end{pmatrix}^2. \tag{37}$$

After averaging over rotational levels, we obtain for (*a*) ← (*b*)

$$Q(l) = (2S'+1)^{-1}, \tag{38}$$

and for (*b*) ← (*a*)

$$Q(l) = 1. \tag{39}$$

Again these factors are independent of l, so equation (30) for the anisotropy parameter holds in all cases when rotational structure is not resolved.

7. RADIAL INTEGRALS

In order to evaluate the total ionization cross-section and anisotropy parameter, the radial transition integrals are required. The $R_{nl}(r)$ are found by resolution of the bound molecular orbital, from which the photoelectron is ejected, into its angular momentum components, as in (23). This resolution is known already for some molecules from single-centre molecular orbital calculations (Bishop 1967; Hayes & Parr 1967).

Continuum eigenfunctions are not available for most molecules so that it is necessary to use some approximate scheme. For photoionization from a neutral or positively charged molecule, the potential of the ion is coulombic at large r, so that the continuum function asymptotically approaches a linear combination of regular and irregular coulomb functions of appropriate energy (Messiah 1961). Close to the nuclei, the potential is not coulombic, but we expect the coulomb approximation (Bates & Damgaard 1949; Seaton 1958; Peach 1967) to be reasonable and the effect on the transition integral of departure from spherical symmetry to be small. Plane-wave final states are not likely to be useful in this theory, since they lead to an incorrect angular distribution even for atomic p-electrons in the high-energy limit (Bethe & Salpeter 1957).

For a heteronuclear diatomic a problem arises since the centre of the molecule is not uniquely defined. The natural origin for the central-field functions in the present theory is the centre of mass, since this is the only point in the molecule which remains fixed in space as the molecule rotates. The continuum eigenfunction, however, is determined by the potential of the ion, and therefore is most closely approximated by an energy eigenfunction for a central potential when the origin is the centre of charge of the ion. We infer that the present theory is most accurate for ionization to states whose centre of charge is close to the centre of mass.

For photodetachment (from negative ions) the potential of the final neutral molecule falls off faster than a coulomb potential, so the continuum function asymptotically approaches a free-particle wave function. The Robinson–Geltman (1967) potential has been found useful in calculations of the angular distribution of electrons photodetached from atoms (Cooper & Zare 1968).

8. CONCLUSIONS

We have derived expressions for the anisotropy parameter of the angular distribution of photoelectrons ejected from molecules, both for transitions between individual rotational levels and when rotational structure is not resolved. Detailed calculations to determine the important contributions to the anisotropy parameter for orbitals of various symmetries are now in progress.

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