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Angular Distribution of Molecular Photoelectrons*

John C. Tully,[†] R. Stephen Berry, and Bryan J. Dalton[‡]

Department of Chemistry and The James Franck Institute, University of Chicago, Chicago, Illinois 60637

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The nonrelativistic differential cross sections for photo-ionization of molecules are derived and are worked out in detail for systems with random orientation. The more important contributions due to electric dipole, electric quadrupole, magnetic dipole, and two-photon (nonresonant) absorption have been included. Processes such as vibrationally induced auto-ionization have been discussed. The significance of these results with regard to the design and interpretation of photo-ionization experiments is also considered. The angular distribution of photoelectrons from H_2 is calculated as an example.

I. INTRODUCTION

The angular distribution of photoelectrons emitted by a randomly oriented set of molecules is, in general, correlated with the polarization and propagation directions of the incident light. Recent measurements of angular distributions of molecular photoelectrons[1] have demonstrated the usefulness of such measurements in obtaining information about initial states of some systems.

It has been well established that *atomic* photoionization, in the electric dipole approximation, yields an angular distribution of the form $\tilde\alpha + \tilde\beta \times \cos^2\theta$, where θ is measured from the polarization direction of incident linearly polarized light.[2] Reference 2 also states that "Averaging over the rotational orientations of molecules also gives this form." In this paper we derive expressions for the nonrelativistic differential cross sections for photo-ionization of randomly oriented diatomic molecules, giving explicit equations for the coefficients $\tilde\alpha$ and $\tilde\beta$ in terms of the transition matrix elements. The more important contributions due to electric dipole, electric quadrupole, magnetic dipole and two-photon (nonresonant) absorption have been included. The pure electric dipole contribution is the largest for normal photon intensi-

ties. Interference contributions from the next-higher multipoles may affect the differential photo-ionization cross section by a few percent. Processes such as vibrationally induced auto-ionization have also been considered. The resulting expressions indicate the types of information one might be able to obtain from photoelectron angular-distribution measurements and may be helpful in the design of future experiments.

In nuclear physics, problems involving the correlation between directions and polarizations of various radiations are quite common. As a result, the development of formalisms for treating these processes has been very extensive.[3] Although certain nuclei share with molecules the feature of being nonspherical, the method of handling angular distributions from aspheric targets differs in the two cases. In the case of a molecule, the period of rotation is generally long compared with the time scale of the various photoelectronic processes. Consequently we can treat photoejection from a single molecule as if it occurred with the molecule oriented in a fixed direction in space. We may then average the angular distribution over molecular orientations in the sample. In the case of nuclei, the radiative lifetimes are long compared with rotation periods so

that the calculation of the angular distribution (of photonucleons) must be handled differently. Molecular cases for which the period of rotation is comparable to the time scale of various photoelectronic processes are not treated here, and would involve including the molecular rotational wave functions and taking an appropriate temperature average.

The development that follows is basically an application of the standard procedures for treating angular-correlation problems that are outlined in Ref. 3c. In Sec. II we present the formalism in which we describe single-photon photoionization (or photodetachment). We include a detailed discussion of the forms of the wave functions that serve as initial and final states in the transition. We present these wave functions in a form sufficiently general to allow the final results to have a wide range of applicability. In particular, we do *not* assume that the internuclear distance is fixed, that outgoing channels are uncoupled, or that the electronic wave functions are calculated in some approximate scheme such as Hartree-Fock. We *do*

invoke the Born-Oppenheimer approximation for evaluating the radiative transition matrix elements, we treat rotation as discussed above, and for simplicity we assume that either Hund's coupling case (a) or (b) applies. In Part C of Sec. II we derive expressions for the electric-dipole, electric-quadrupole, and magnetic-dipole matrix elements between the initial and final wave functions. In Sec. III we extend the treatment to account for two-photon processes, and in Sec. IV we present final expressions for the differential cross section of photoelectrons from a collection of randomly oriented molecules. Finally in Sec. V, various implications of these expressions are discussed. As an illustration, in Appendix B we show that for certain molecules the angular distribution of photoelectrons would be expected to be distinctly different either from that of the related atomic system or from that calculated by assuming the molecular rotation period to be fast compared with the photoelectronic process. We include in this Appendix a calculation of the differential cross section for photo-ionization of H_2.

II. PROCEDURE

A. Expression for Cross Section

Consider electromagnetic radiation of frequency $\nu = \omega/2\pi$ incident on a diatomic molecule in some initial state i. If $h\nu$ is greater than some ionization potential $I_{i\Gamma}$ of the state i, then ionization can take place. Neglecting multiphoton processes, we have

$$\hbar^2 k_\Gamma{}^2/2m = h\nu - I_{i\Gamma} , \tag{2.1}$$

where Γ is the channel index which designates the electronic, vibrational, and spin states of the residual core, as well as the spin state of the outgoing electron. $\hbar^2 k_\Gamma{}^2/2m$ is the energy of the ejected electron at infinite separation in the Γ channel.

We define two coordinate systems, a laboratory system and a molecule-fixed system. We take the laboratory x axis as the propagation direction of the incident radiation and the laboratory z axis as its polarization direction. The axis of the linear molecule defines the z' axis of the molecular system. Angles and other coordinates measured with respect to the molecular frame will be primed; those with respect to the laboratory frame unprimed. Spherical harmonics $Y_{jm}(\theta', \Phi')$ written in terms of angles in the molecular system can be expressed as linear combinations of spherical harmonics involving the corresponding angles in the laboratory system:

$$Y_{jm}(\theta', \varphi') = \sum_{m'=-j}^{j} D_{m'm}{}^j(\alpha, \beta, \gamma) Y_{jm'}(\theta, \varphi) , \tag{2.2}$$

where $D_{m'm}{}^j(\alpha, \beta, \gamma)$ is the usual rotation matrix, as defined by Rose.[4] The orientation of the molecular axes relative to the laboratory axes is given by Euler angles α, β, and γ also according to Rose's convention.

Assume that during the entire photoelectronic process, each molecule is in a fixed orientation with respect to the laboratory frame, defined by $\vec{\beta} \equiv (\alpha, \beta, \gamma)$. Assume that the Born-Oppenheimer approximation can be used for calculating all radiative transition matrix elements. Finally, assume that either Hund's coupling case (a) or (b) is applicable.

Neglecting relativistic effects, we can find the angular distribution of electrons emitted by molecules with various orientations $\vec{\beta}$ following closely the treatment of Bethe and Salpeter for atoms.[5] Let $\hbar \vec{k}_\Gamma$ be a possible momentum of the electron consistent with Eq. (2.1). Let $G_{\Gamma\vec{\beta}}(\Omega)$ denote the matrix element

$$G_{\Gamma\vec{\beta}}(\Omega) = \int u^*_{\Gamma \vec{k}_\Gamma \vec{\beta}}(\vec{r}_1, \ldots, \vec{r}_N; R) \sum_{j=1}^{N} e^{ikx_j} \frac{\partial u_i(\vec{r}_1, \ldots, \vec{r}_N)}{\partial z_j} d\tau . \tag{2.3}$$

$G_{\Gamma\vec{\beta}}$ is a function of the angle Ω of $\vec{k}_\Gamma$ in the laboratory system; $\vec{r}_j$ is the position vector of the jth electron. The integral extends over the configuration space of all the electrons, and over the internuclear-distance coordinate R. The function u_i is the electronic and vibrational part of the initial (bound) wave function of the molecule in state i, and u_Γ (the subscripts $\vec{k}_\Gamma$ and β are understood) is the continuum function, which is taken to be a plane wave plus ingoing spherical waves[6]; i. e., it is an eigenstate of the molecular electronic and vibrational (BO) Hamiltonian, antisymmetric with respect to interchange of any two electronic coordinates, and with an asymptotic form (as $r_N \to \infty$) given by

$$u_{\Gamma\vec{k}_\Gamma\vec{\beta}} \sim [k_\Gamma/(2\pi)^3]^{1/2}\,\Phi_{\Gamma\vec{\beta}}(\vec{r}_1,\ldots,\vec{r}_{N-1};R)\exp[i\vec{k}_\Gamma\cdot\vec{r}_N - i\zeta_\Gamma\,\ln(k_\Gamma r_N + \vec{k}_\Gamma\cdot\vec{r}_N)]$$

$$+ \sum_{\Gamma'}[k_{\Gamma'}/(2\pi)^3]^{1/2}\,\Phi_{\Gamma'\vec{\beta}}(\vec{r}_1,\ldots,\vec{r}_{N-1};R)f_{\Gamma'\vec{\beta}}^{-}(\theta_N,\varphi_N)r_N^{-1}\exp[-ik_{\Gamma'}r_N + i\zeta_{\Gamma'}\,\ln(2k_{\Gamma'}r_N)]. \quad (2.4)$$

Here $f_{\Gamma'\vec{\beta}}^{-}(\theta_N,\varphi_N)$ is the scattering amplitude of the Γ' channel for a molecule with orientation $\vec{\beta}$, $k_\Gamma\zeta_\Gamma$ is the net charge of the residual core, and $\Phi_{\Gamma\vec{\beta}}(r_1,\ldots,r_{N-1};R)$ is the electronic and vibrational wave function of the channel Γ core. For simplicity of notation we have absorbed into $\Phi_{\Gamma\vec{\beta}}$ the spin wave function of the outgoing electron in this channel; u_i and the $\Phi_{\Gamma\vec{\beta}}$ are assumed normalized to unity and u_Γ is normalized per unit energy interval.

The differential cross section for photoelectrons in the Γ channel from molecules with a particular orientation $\vec{\beta}$, for which k_Γ lies within the solid angle Ω, is then given by[5]

$$\sigma_{\Gamma\vec{\beta}}(\Omega)d\Omega = d\Omega\,(2\pi e^2\hbar^2/m^2 c\nu)|\,G_{\Gamma\vec{\beta}}(\Omega)|^2, \quad (2.5)$$

where the incident light is plane polarized along the z axis and propagates along the x axis.

The differential cross section in the Γ channel for an ensemble of molecules with various orientations is obtained by averaging $\sigma_{\Gamma\vec{\beta}}(\Omega)$ over $\vec{\beta}$:

$$\sigma_\Gamma(\Omega)d\Omega = (8\pi^2)^{-1}d\Omega\int\sigma_{\Gamma\vec{\beta}}(\Omega)\rho(\vec{\beta})\sin\beta\,d\alpha\,d\beta\,d\gamma; \quad (2.6)$$

$\rho(\vec{\beta})$ is the distribution function for molecular orientation, which we shall assume is unity for most of the following discussion.

Expression (2.6) is the basic angular-distribution formula for an ensemble of arbitrarily oriented molecules, in the approximation that molecular rotation is slow. To apply it to a specific situation, one merely expresses $\rho(\vec{\beta})$ as one knows it from experimental conditions; e.g., $\rho(\vec{\beta}) = 1$ for random orientation and $|Y_J^M(\beta,\alpha)|^2$ for a system in the J, M state.

Finally, the core state of the Γ channel has a definite magnetic quantum number M_Γ. For $|M_\Gamma| \ne 0$, degenerate with the state corresponding to M_Γ is the state with magnetic quantum number $-M_\Gamma$. If we let Γ^+ and Γ^- denote the channels whose core magnetic quantum numbers are M_Γ and $-M_\Gamma$, respectively, then we have $k_{\Gamma^+} = k_{\Gamma^-}$ and the usual experiments cannot distinguish between these two channels. If our initial ensemble of molecules is not M_i selected, we would have equal numbers of the degenerate initial states i and i' with magnetic quantum numbers M_i and $-M_i$. With these considerations, our final expression for the differential cross section in the Γ channel is

$$\bar\sigma_\Gamma(\Omega) = [2(1+\delta_{M_\Gamma})]^{-1}[(\sigma_{\Gamma^+})_{M_i} + (\sigma_{\Gamma^-})_{M_i} + (\sigma_{\Gamma^+})_{-M_i} + (\sigma_{\Gamma^-})_{-M_i}]. \quad (2.7)$$

In addition to averaging over $\pm M_i$ and summing over $\pm M_\Gamma$, one should average over-all initial states i' and sum over-all channels Γ' for which the ionization potentials $I_{i'\Gamma'}$ are equal or nearly equal to $I_{i\Gamma}$, if more than one channel is available.

We now wish to calculate $G_{\Gamma\vec{\beta}}(\Omega)$ as a function of the laboratory angle Ω and the parameter $\vec{\beta}$. In Eq. (2.3), u_i, the bound-state wave function, is most naturally expressed in terms of angles θ_j', φ_j' referring to the molecule-fixed system. The free function u_Γ refers to the direction Ω of k_Γ in which we want to measure flux, and, hence, to the laboratory angles θ_j, φ_j. The operators due to the radiation field, $\exp(ik_\Gamma x_j)(\partial/\partial z_j)$, are, of course, also in the laboratory system. Our procedure at this point is to express the latter and u_Γ in terms of the molecule-fixed electronic coordinates θ_j', φ_j', involving as parameters the Euler angles α, β, and γ and the angles θ,φ of k_Γ with respect to the laboratory frame. We may then integrate over the electronic coordinates θ_j', φ_j' to form $G_{\Gamma\vec{\beta}}(\Omega)$, substitute into Eq. (2.5) to find $\sigma_{\Gamma\vec{\beta}}(\Omega)$, obtain $\sigma_\Gamma(\Omega)$ by integrating over the Euler angles α, β, and γ according to Eq. (2.6), and finally obtain $\bar\sigma_\Gamma(\Omega)$ from Eq. (2.7).

B. Expression for Final State

For a specific orientation of the molecule, wave functions $\psi_{\Gamma lm}(\vec{r}_1,\ldots,\vec{r}_{N-1},\vec{r}_N;R)$ can be found which are everywhere solutions of the molecular electronic and vibrational Hamiltonian, and in the asymptotic region $r_N \to \infty$ behave like

$$\psi_{\Gamma l m}(\vec{r}_1, \ldots, \vec{r}_{N-1}, \vec{r}; R) \sim k_\Gamma^{-1/2} \Phi_{\Gamma\beta}(\vec{r}_1, \ldots, \vec{r}_{N-1}; R) r^{-1} \exp[i(k_\Gamma r - \tfrac{1}{2} l\pi - \zeta_\Gamma \ln 2kr + \eta_l)] Y_{lm}(\theta', \varphi')$$

$$- \sum_{\Gamma' l' m'} \{ S^\dagger_{\Gamma\Gamma', lm, l'm'} k_{\Gamma'}^{-1/2} \Phi_{\Gamma'\beta}(\vec{r}_1, \ldots, \vec{r}_{N-1}; R) r^{-1} \exp[-i(k_{\Gamma'} r - \tfrac{1}{2} l\pi - \zeta_{\Gamma'} \ln 2kr + \eta_l)] Y_{l'm'}(\theta', \varphi'),$$

$$(2.8)$$

where we have dropped the subscript N. The matrix $S^\dagger$ is the adjoint of the scattering matrix in the angular momentum representation; $\eta_l = \arg \Gamma(l+1+i\zeta)$, the Coulomb phase shift. Equation (2.8) is quite general in that it does not assume that final-state channels are decoupled. For photodetachment, the form (2.8) would be the same but we would have $\zeta_\Gamma = \eta_l = 0$. It should be noted that $\psi_{\Gamma l m}(\vec{r}_1, \ldots, \vec{r}_N, R)$ is written in terms of molecular coordinates, and in all regions of space is an eigenstate of the component of angular momentum along the molecular z' axis, with eigenvalue $(M_\Gamma + m)$.

To obtain the final-state wave function u_Γ with the asymptotic form (2.4), we form a linear combination of the $\psi_{\Gamma l m}$ with coefficients $a_{lm}^{\vec{\beta}}(\vec{k}_\Gamma)$ that depend on the molecular orientation and the direction of $\vec{k}_\Gamma$:

$$u_{\Gamma \vec{k}_\Gamma \vec{\beta}} = \sum_{l,m} a_{lm}^{\vec{\beta}}(\vec{k}_\Gamma) \psi_{\Gamma l m}(\vec{r}_1, \ldots, \vec{r}_N; R). \qquad (2.9)$$

We now wish to obtain the required form of these coefficients. Expanding the plane-wave term of (2.4) not in the usual laboratory angles but in the molecular angles, we find

$$\exp[i\vec{k}_\Gamma \cdot \vec{r} - i\zeta_\Gamma \ln(k_\Gamma r + \vec{k}_\Gamma \cdot \vec{r})] + \psi_s^*$$

$$= \frac{4\pi}{k_\Gamma r} \sum_{lm} i^l e^{i\eta_l} F_l(\zeta_\Gamma; k_\Gamma r) Y_{lm}^*(\theta_k', \varphi_k') Y_{lm}(\theta', \varphi'), \qquad (2.10)$$

where $F_l(\zeta; kr)$ is a regular Coulomb function,[7] and θ_k', φ_k' give the direction of $\vec{k}_\Gamma$ in the molecular frame; ψ_s^*, which is defined in Ref. 7, contains only incoming terms. Expression (2.9) for u_Γ must equal expression (2.4). Since the asymptotic form as $r \to \infty$ of F_l in Eq. (2.10) is

$$F_l(\zeta_\Gamma; k_\Gamma r) \sim \sin(k_\Gamma r - \zeta_\Gamma \ln 2k_\Gamma r - \tfrac{1}{2} l\pi + \eta_l), \qquad (2.11)$$

we can equate coefficients of $\exp i(k_\Gamma r - \zeta_\Gamma \ln 2k_\Gamma r)$ in Eqs. (2.9) and (2.4) in the asymptotic region to find $a_{lm}^{\vec{\beta}}(\vec{k}_\Gamma)$:

$$a_{lm}^{\vec{\beta}}(\vec{k}_\Gamma) = i - (2\pi)^{-\frac{1}{2}} i^l e^{-i\eta l} Y_{lm}^*(\theta_k', \varphi_k'). \qquad (2.12)$$

Finally, we can express $a_{lm}^{\vec{\beta}}(\vec{k}_\Gamma)$ in the laboratory system by using Eq. (2.2):

$$a_{lm}^{\vec{\beta}}(\vec{k}_\Gamma) = -i(2\pi)^{-\frac{1}{2}} i^l e^{-i\eta l} \sum_{m'=-l}^{l} D_{m'm}^{l*}(\alpha, \beta, \gamma) Y_{lm'}^*(\theta, \varphi). \qquad (2.13)$$

θ, φ gives the direction of the electron momentum $\vec{k}_\Gamma$ in the laboratory frame. Equation (2.13) with Eqs. (2.8) and (2.9) gives us the desired expression for u_Γ.

C. Multipole Expansion

Since the exponent kx_j in Eq. (2.3) is small, we may use the usual multipole expansion and retain only the electric-dipole, electric-quadrupole, and magnetic-dipole terms. Thus we write $G_{\Gamma\vec{\beta}}$ of Eq. (2.3) as

$$G_{\Gamma\vec{\beta}} \cong G_{\Gamma\vec{\beta}}^{E1} + G_{\Gamma\vec{\beta}}^{E2} + G_{\Gamma\vec{\beta}}^{M1}, \qquad (2.14)$$

where $E1$, $E2$, and $M1$ refer to electric dipole, electric quadrupole, and magnetic dipole, respectively; i.e.,[8]

$$G_{\Gamma\vec{\beta}}^{E1} = (2\pi m \nu/\hbar) \int u_{\Gamma \vec{k}_\Gamma \vec{\beta}}^* \sum_j z_j u_i d\tau, \qquad (2.15a)$$

$$G_{\Gamma\vec{\beta}}^{E2} = (2\pi^2 i m \nu^2/c\hbar) \int u_{\Gamma \vec{k}_\Gamma \vec{\beta}}^* \sum_j x_j z_j u_i d\tau, \qquad (2.15b)$$

$$G_{\Gamma \vec{k}_\Gamma \vec{\beta}} = (\pi \nu/c) \int u_{\Gamma \vec{k}_\Gamma \vec{\beta}}^* (K_y + 2S_y) u_i d\tau. \qquad (2.15c)$$

In Eq. (2.15c), K_y and S_y are the laboratory y components of the electronic orbital angular momentum and the spin angular momentum in units of $\hbar$, respectively. The S_y term arises due to a more correct version of Eq. (2.5) which allows for spin. We now express the operators z_j, $x_j z_j$ and $(K_y + 2S_y)$ in molecular coordinates. Using the inverse of Eq. (2.2) we have

$$z = (\tfrac{4}{3}\pi)^{1/2}\, r\, Y_{10}(\theta,\varphi) = (\tfrac{4}{3}\pi)^{1/2}\, r \sum_{m''=-1}^{1} Y_{1m''}(\theta',\varphi') D^{1*}_{0m''}(\alpha,\beta,\gamma)\,, \tag{2.16a}$$

$$xz = \tfrac{1}{3}\sqrt{8}\,\pi r^2 Y_{10}(\theta,\varphi)[Y_{1,-1}(\theta,\varphi) - Y_{11}(\theta,\varphi)] = \tfrac{1}{3}\sqrt{8}\,\pi r^2 \sum_{m''=-1}^{1}\sum_{m'''=-1}^{1} D^{1*}_{0m''}(\vec{\beta})\,[D^{1*}_{-1m'''}(\vec{\beta})$$

$$- D^{1*}_{1m'''}(\vec{\beta})]\,Y_{1m''}(\theta',\varphi')Y_{1m'''}(\theta',\varphi')\,, \tag{2.16b}$$

and

$$[K_y + 2S_y] = (i/\sqrt{2})\sum_{m''}[D^{1*}_{-1m''} + D^{1*}_{1m''}][K_{m''} + 2S_{m''}]\,. \tag{2.16c}$$

$K_{m''}$ and $S_{m''}$ are the angular-momentum operators in terms of molecular angles. Using Eqs. (2.8), (2.9), and (2.13) for u_Γ and substituting (2.16a), (2.16b), and (2.16c) into (2.15a), (2.15b), and (2.15c), respectively, we arrive at final expressions for $G_{\Gamma\vec{\beta}}$

$$G_{\Gamma\vec{\beta}}^{E1} = \sum_{l,m,m'} A_{lmM_\Gamma M_i} D^{l}_{m'm}(\vec{\beta}) D^{1*}_{0,m+M_\Gamma-M_i}(\vec{\beta}) Y_{lm'}(\theta,\varphi)\,, \tag{2.17a}$$

$$G_{\Gamma\vec{\beta}}^{E2} = \sum_{l,m,m',m''} Q_{lmm''M_\Gamma M_i} D^{l}_{m'm}(\vec{\beta}) D^{1*}_{0m''}(\vec{\beta})[D^{1*}_{-1,m+M_\Gamma-M_i-m''}(\vec{\beta})$$

$$- D^{1*}_{1,m+M_\Gamma-M_i-m''}(\vec{\beta})]\,Y_{lm'}(\theta,\varphi)\,, \tag{2.17b}$$

$$G_{\Gamma\vec{\beta}}^{M1} = \sum_{lmm'} M_{lmM_\Gamma M_i} D^{l}_{m'm}(\vec{\beta})[D^{1*}_{1,m+M_\Gamma-M_i}(\vec{\beta}) + D^{1*}_{-1,m+M_\Gamma-M_i}(\vec{\beta})]\,Y_{lm'}(\theta,\varphi)\,, \tag{2.17c}$$

where we have defined

$$A_{lmM_\Gamma M_i} = (2\pi m\nu/\hbar)[i(\tfrac{2}{3})^{\frac{1}{2}}(i)^{-l}\exp(i\eta_l)]\,d_{lmM_\Gamma M_i}\,, \tag{2.18a}$$

$$Q_{lmm''M_\Gamma M_i} = (2\pi^2 im\nu^2/c\hbar)[i\tfrac{2}{3}\sqrt{\pi}\,(i)^{-l}\exp(i\eta_l)]\,q_{lmm''M_\Gamma M_i}\,, \tag{2.18b}$$

and $$M_{lmM_\Gamma M_i} = -(\pi\nu/c)[(2\sqrt{\pi})^{-1}(i)^{-l}\exp(i\eta_l)]\,s_{lmM_\Gamma M_i}\,. \tag{2.18c}$$

Here $\underline{d}$, $\underline{q}$ and $\underline{s}$ are the molecular-transition dipole, quadrupole, and magnetic-dipole matrices, respectively; i.e.,

$$d_{lmM_\Gamma M_i} \equiv (\sum_j \int r_j \psi_{\Gamma lm}^* Y_{1m''}(\theta_j',\varphi_j')u_i\,d\tau)_{m''=m+M_\Gamma-M_i}\,, \tag{2.19a}$$

$$q_{lmm''M_\Gamma M_i} \equiv (\sum_j \int r_j^2 \psi_{\Gamma lm}^* Y_{1m''}(\theta_j',\varphi_j')Y_{1m'''}(\theta_j',\varphi_j')u_i\,d\tau)_{m'''=m+M_\Gamma-M_i-m''}\,, \tag{2.19b}$$

$$s_{lmM_\Gamma M_i} \equiv (\int \psi_{\Gamma lm}^*(K_{m''}+2S_{m''})u_i\,d\tau)_{m''=m+M_\Gamma-M_i}\,. \tag{2.19c}$$

Again, the integrations are over the configuration space of all electrons and over the internuclear coordinate R. We have eliminated one summation in each of Eqs. (2.17) by making use of selection rules on M in the integrals (2.19). These selection rules appear as a result of our initial assumption that Hund's coupling case (a) or (b) is applicable.

Furthermore, as a result of the reflection symmetry of a diatomic molecule we can show that

$$A_{lmM_\Gamma M_i}Q^*_{\lambda\mu\mu''M_\Gamma M_i} = A_{l-m-M_\Gamma-M_i}Q^*_{\lambda-\mu-\mu''-M_\Gamma-M_i}\,, \tag{2.20a}$$

$$A_{lmM_\Gamma M_i}{}^{M*}_{\lambda\mu M_\Gamma M_i} = -A_{l-m-M_\Gamma - M_i}{}^{M*}_{\lambda - \mu - M_\Gamma - M_i} \quad . \tag{2.20b}$$

Since the $\psi_{\Gamma lm}$ as defined by Eq. (2.8) are complex, the matrices of Eqs. (2.19) are in inconvenient forms for numerical calculations. We may express $\psi_{\Gamma lm}$ in terms of more convenient (real) standing-wave solutions $\tilde{\psi}_{\Gamma lm}$ using the relation[9]

$$\psi_{\Gamma lm} = i \sum_{\Gamma'l'm'} (\underline{1} - i\underline{R})^{-1}_{\Gamma\Gamma'll'mm'} \tilde{\psi}_{\Gamma'l'm'} \quad , \tag{2.21}$$

where the matrices $\underline{R}$ and $\underline{S}$ are related by

$$R_{\Gamma\Gamma'll'mm'} = i[(\underline{1} - \underline{S})/(\underline{1} + \underline{S})]_{\Gamma\Gamma'll'mm'} \quad . \tag{2.22}$$

The standing waves $\tilde{\psi}_{\Gamma lm}$ are eigenfunctions of the molecular electronic and vibrational Hamiltonian satisfying (as $r \to \infty$) the boundary conditions

$$\tilde{\psi}_{\Gamma lm} \sim k_\Gamma^{-1/2} \Phi_{\Gamma\vec{\beta}}(\vec{r}_1, \ldots, \vec{r}_{N-1}; R) r^{-1} \sin(k_\Gamma r - \tfrac{1}{2}l\pi - \zeta_\Gamma \ln 2k_\Gamma r + \eta_l) Y_{lm}(\theta', \varphi')$$

$$+ \sum_{\Gamma'l'm'} R_{\Gamma\Gamma'll'mm'} k_{\Gamma'}^{-1/2} \Phi_{\Gamma'\vec{\beta}}(\vec{r}_1, \ldots, \vec{r}_{N-1}; R) r^{-1} \cos(k_\Gamma r - \tfrac{1}{2}l'\pi$$

$$- \zeta_{\Gamma'} \ln 2k_\Gamma r + \eta_{l'}) Y_{l'm'}(\theta', \varphi') \quad . \tag{2.23}$$

Substitution of Eq. (2.21) into Eqs. (2.19) results in an expression for the matrix elements which is better suited for calculations.

III. TWO-PHOTON IONIZATION

By starting with Eq. (2.3), which is derived by treating the interaction of the electron with the radiation field as a small perturbation, we have ignored the possibility of multiphoton processes. These may be included in a straightforward way. The transition probability for two-photon absorption from an initial state u_i to a final state u_f is given by[10]

$$W_{i \to f} = c | T_{\Gamma\vec{\beta}}(\Omega)|^2 \quad , \tag{3.1}$$

where c is a proportionality constant. For ω much further than a linewidth from the frequency ω_N of any electric dipole-allowed transition from the initial state i

$$T_{\Gamma\vec{\beta}}(\Omega) = \sum_n \frac{\omega_n(2\omega - \omega_n)}{\omega_n - \omega} \sum_{j,j'} \int u_f^* z_j u_n d\tau \int u_n^* z_{j'} u_i d\tau \quad , \tag{3.2}$$

with $\omega_n = E_n - E_0$ and $\omega = 2\pi\nu$. We have assumed the light is monochromatic and have used the electric-dipole approximation for the two integrals in Eq. (3.1). Usually only a very few intermediate states need be included in this summation. The wave functions u_n of the intermediate states are conveniently described in the molecular system, and Eqs. (2.8), (2.9), and (2.13) are again appropriate to describe the final continuum function. Using Eq. (2.16a) for z_j, we have

$$T_{\Gamma\vec{\beta}} = \sum_n \frac{\omega_n(2\omega - \omega_n)}{\omega_n - \omega} \sum_{lmm'} P_{lmnM_\Gamma M_i} D^l_{m'm}(\vec{\beta}) D^{1*}_{0, M_n - M_i}(\vec{\beta}) D^{1*}_{0, m + M_\Gamma - M_n}(\vec{\beta}) Y_{lm'}(\theta, \varphi) \quad , \tag{3.3}$$

where

$$P_{lmnM_\Gamma M_i} \equiv \tfrac{4}{3}\pi d_{ni}' d_{nlmM_\Gamma} i(-i)^l (2\pi)^{-\frac{1}{2}} \exp(i\eta_l) , \tag{3.4}$$

and

$$d_{ni}' \equiv [\sum_j \int r_j u_n^* Y_{1m'''}(\theta_j', \varphi_j') u_i d\tau]_{m''' = M_n - M_i} , \tag{3.5}$$

$$d_{nlmM_\Gamma} \equiv [\sum_j \int r_j \psi_{\Gamma lm}^* Y_{1m''}(\theta_j', \varphi_j') u_n d\tau]_{m'' = M_\Gamma + m - M_i} \quad . \tag{3.6}$$

Again we have made use of selection rules on the m.

IV. RESULTS

We now find an expression for $\sigma_{\Gamma\vec{\beta}}(\Omega)$ by substituting Eqs. (2.15) into Eq. (2.5). Assuming that we have a collection of randomly oriented molecules so that $\rho(\vec{\beta})$ may be set equal to unity, we obtain the differential cross section $\sigma_\Gamma(\Omega)$ from Eq. (2.6). After some algebraic manipulation, which is illustrated in Appendix A for the electric-dipole term $\sigma_\Gamma{}^{E1\cdot E1}$, the general expression for the cross section (2.6) takes the form

$$\sigma_\Gamma = \sigma_\Gamma{}^{E1\cdot E1} + \sigma_\Gamma{}^{E1\cdot E2} + \sigma_\Gamma{}^{E1\cdot M1} + \cdots , \tag{4.1}$$

where

$$\sigma_\Gamma{}^{E1\cdot E1}(\Omega) = A_{00} + A_{20}P_2{}^0(\cos\theta) , \tag{4.2a}$$

$$\sigma_\Gamma{}^{E1\cdot E2}(\Omega) = (B_{11}+B_{11}{}^*)P_1{}^1(\cos\theta)\cos\varphi + (B_{31}+B_{31}{}^*)P_3{}^1(\cos\theta)\cos\varphi , \tag{4.2b}$$

$$\sigma_\Gamma{}^{E1\cdot M1}(\Omega) = [C_{11}+C_{11}{}^*]\,P_1{}^1(\cos\theta)\cos\varphi . \tag{4.2c}$$

The $P_l{}^m$ are associated Legendre polynomials. The angles are measured relative to the laboratory system; i.e., θ is measured from the polarization direction of the light.

$$A_{\xi 0} = \frac{2\pi e^2\hbar^2}{m^2 c\nu}\sum_{l\lambda m\mu}A_{lmM_\Gamma M_i}A^*_{\lambda\mu M_\Gamma M_i}(-1)^{M_\Gamma+M_i}\frac{[(2l+1)(2\lambda+1)]^{1/2}}{4\pi(2\xi+1)}$$

$$\times C(11\xi\,|M_i-m-M_\Gamma,\mu+M_\Gamma-M_i)C(11\xi\,|00)C(\lambda l\xi\,|\mu-m)C(\lambda l\xi\,|00), \tag{4.3a}$$

$$B_{\xi 1} = \frac{2\pi e^2\hbar^2}{m^2 c\nu}\sum_{lm\lambda\mu\mu''}A_{lmM_\Gamma M_i}Q^*_{\lambda\mu\mu''M_\Gamma M_i}(-1)^{M_\Gamma+M_i}\frac{[(2l+1)(2\lambda+1)]^{1/2}}{2\pi(2\xi+1)}\left(\frac{(\xi-1)!}{(\xi+1)!}\right)^{1/2}$$

$$\times \sum_{J=0,2}C(\lambda l\xi\,|\mu,-m)C(11J\,|00)C(11J\,|\mu'',-m+M_i-M_\Gamma)$$

$$\times \; C(1J\xi\,|\mu+M_\Gamma-M_i-\mu'',\mu''-m-M_\Gamma+M_i)C(1J\xi\,|10)C(\lambda l\xi\,|00), \tag{4.3b}$$

$$C_{\xi 1} = \frac{2\pi e^2\hbar^2}{m^2 c\nu}\sum_{l\lambda m\mu}A_{lmM_\Gamma M_i}M^*_{\lambda\mu M_\Gamma M_i}(-1)^{M_\Gamma+M_i+1}\frac{[(2l+1)(2\lambda+1)]^{1/2}}{2\pi(2\xi+1)}\left(\frac{(\xi-1)!}{(\xi+1)!}\right)^{1/2}$$

$$\times C(\lambda l\xi\,|00)C(\lambda l\xi\,|\mu,-m)C(11\xi\,|\mu+M_\Gamma-M_i,-m-M_\Gamma+M_i)C(11\xi\,|10). \tag{4.3c}$$

The $C(j_1 j_2 J|m_1 m_2)$ are Clebsch-Gordan coefficients.

We have not given the final form for the angular distribution, obtained from (4.2) by taking the mean of the cross sections associated with molecules initially with magnetic quantum numbers $+M_i$ and $-M_i$, and summing over final-core quantum numbers $+M_\Gamma$ and $-M_\Gamma$, as in Eq. (2.6). Using the symmetry relationships (2.20), this step results in the $\xi=2$ terms in $\bar\sigma_\Gamma{}^{E1\cdot E2}$ and $\bar\sigma_\Gamma{}^{E1\cdot M1}$ summing to zero. For this reason we have not included the $\xi=2$ terms in (4.2b) and (4.2c), although strictly they do occur.

Both the electric-quadrupole and magnetic-dipole matrix elements, Eqs. (2.17b) and (2.17c), are of order v/c smaller than the electric-dipole matrix element (2.17a), where v is the velocity of the outgoing electron and c is the velocity of light. We have included the cross sections $\sigma_\Gamma{}^{E1\cdot E2}$ and $\sigma_\Gamma{}^{E1\cdot M1}$ which are linear in these matrix elements. The cross sections $\sigma_\Gamma{}^{E2\cdot E2}$, $\sigma_\Gamma{}^{M1\cdot M1}$, and $\sigma_\Gamma{}^{E2\cdot M1}$ have been neglected, since these terms are of order v^2/c^2 and therefore of the same order as relativistic effects which we neglected from the start.

For a two-photon process, the transition probability becomes

$$W_\Gamma(\Omega)\propto D_0 + D_2 P_2(\cos\theta) + D_4 P_4(\cos\theta) , \tag{4.4}$$

where

$$D_\xi = \sum_{nn'}\left(\frac{\omega_n(2\omega-\omega_n)}{\omega_n-\omega}\right)\left(\frac{\omega_{n'}(2\omega-\omega_{n'})}{\omega_{n'}-\omega}\right)\sum_{l\lambda m\mu}P_{lmnM_\Gamma M_i}P_{\lambda\mu n'M_\Gamma M_i}(-1)^{M_\Gamma+M_i}$$

$$\times \sum_{J=0,2} \sum_{J'=0,2} \frac{[(2l+1)(2\lambda+1)]^{1/2}}{4\pi(2\xi+1)} C(\lambda l\xi|\mu,-m)C(11J|00)C(11J'|00)C(\lambda l\xi|00)$$

$$\times C(11J|M_{n'}-M_i,M_i-M_n)C(11J'|\mu+M_\Gamma-M_{n'},M_{n'}-m-M_\Gamma)C(J'J\xi|\mu+M_n-M_{n'}-m,M_{n'}-M_n)$$

$$\times C(J'J\xi|00). \tag{4.5}$$

V. DISCUSSION

The electric dipole term $\sigma_\Gamma{}^{E1\cdot E1}$ given by Eq. (4.2a) is the dominant contribution to the cross section. For randomly oriented molecules, just as for atoms, the angular distribution of photoelectrons resulting from this term is of the form $\tilde{\alpha}+\tilde{\beta}\cos^2\theta$. Therefore in this approximation the only information that can be obtained from angular-distribution measurements of photoelectrons of a given energy is the magnitude of the two constants $\tilde{\alpha}$ and $\tilde{\beta}$, or equivalently, A_{00} and A_{20} of Eq. (4.2a). Inclusion of the higher-multipole terms given by Eqs. (4.2b) and (4.2c) results in a more complicated θ dependence as well as a φ dependence. These additional terms, which depend on electric-quadrupole and magnetic-dipole matrix elements, should be small, but if observable they might provide additional information. Unless one is interested in these higher-multipole effects or in using a molecular ensemble with a nonrandom distribution, there appears to be no reason for designing an apparatus which is capable of analyzing complicated angular dependences; two relatively large detectors should suffice to determine $\tilde{\alpha}$ and $\tilde{\beta}$.

The phenomenological forms (4a–4c) could have been obtained by an alternative procedure: One could have expanded the wave functions and expressed the transition moments in *laboratory* coordinates rather than in molecular coordinates. Such a procedure has the advantage that one obtains expressions (4a–4c) in a slightly less cumbersome way than we did. However it has the considerable disadvantage that the coefficients are not easily related to the microscopic transition moments that one can calculate from accurate electronic wave functions. We chose the longer procedure for our derivation in order to obtain explicit and readily calculable expressions for the coefficients.

Since in molecular processes a large number of elements of the electric-dipole matrix d in Eq. (2.19a) are often important, knowing the values of the two parameters $\tilde{\alpha}$ and $\tilde{\beta}$ will in general not be sufficient to determine matrix elements or even to indicate which might be important. Nevertheless, in certain cases such as the one discussed in Appendix B, knowledge of $\tilde{\alpha}$ and $\tilde{\beta}$ might be very informative. In cases where more information is sought, experiments with M_i-selected or otherwise partially oriented molecules ($\rho(\tilde{\beta})\neq 1$) might be considered.

Auto-ionization often plays an important or even dominant role in the photo-ionization of molecules.[11] Electronically induced auto-ionization such as the type occurring in atomic systems has been taken into account in the formalism of the preceding sections. This is a result of the form of the final

state, Eqs. (2.8) and (2.9), which allows for coupling between channels. But auto-ionization involving a breakdown of the Born-Oppenheimer approximation cannot be treated within the present framework. To extend the theory to include such processes in a way consistent with the scheme outlined in Ref. 11 would be a straightforward task. However, it can be seen from the preceding development that any process such as auto-ionization which can be described as photoexcitation to a "bound" intermediate state followed by some sort of internal conversion to a continuum state,[12] will not change the analytic form of the angular distribution given by Eqs. (4.2). Nevertheless, in many cases, from the absolute or relative magnitudes of the coefficients $\tilde{\alpha}$ and $\tilde{\beta}$ one might be able to infer the importance of auto-ionization and even information about the lifetimes of the intermediate states involved. That this might be so can be seen from the specific example discussed in Appendix B.

The fact that only the two parameters $\tilde{\alpha}$ and $\tilde{\beta}$ govern the angular distribution still leaves open two important possibilities for obtaining information from angular-distribution measurements. We must keep in mind that $\tilde{\alpha}$ and $\tilde{\beta}$ are functions of both the frequency of the incident light ω, and of the kinetic energy of the outgoing electron; i.e., $\tilde{\alpha}=\tilde{\alpha}(\omega,k_\Gamma{}^2)$ and $\tilde{\beta}=\tilde{\beta}(\omega,k_\Gamma{}^2)$. The dependences of some angular distributions on $k_\Gamma{}^2$, the final electron energy, have been studied[1]; one can sort out various final channels with such measurements. One may also expect to see variations in $\tilde{\alpha}(\omega,k_\Gamma{}^2)$ and $\tilde{\beta}(\omega,k_\Gamma{}^2)$ with ω. In particular, when ω coincides with the excitation frequency for an auto-ionizing state, one can expect $\tilde{\alpha}$ and $\tilde{\beta}$ to be dominated or at least strongly affected by the nature of the final state in the autoionizing channel. This dominance may be detectable in measurements that count all photoelectrons entering given solid angles, but it will surely be detectable in measurements that energy analyze the photoelectrons. Thus, for example, one could extend the experiments of Doolittle and Schoen[13] on H_2 photo-ionization by using polarized incident light and two collectors, one centered at $\theta=0°$ and one centered at $\theta=90°$. The measurements of energy-analyzed photocurrents already reported[13] show that the total photoelectron current has a very sharp maximum when the incident light wavelength corresponds to the excitation energy of an auto-ionizing level and when the energy-selected electrons have energies corresponding to excitation of the vibrational state $v'=1$ of the $H_2{}^+$ product. We may expect electrons in this same energy band excited by the same line, to have angular-distribution parameters $\tilde{\alpha}$ and $\tilde{\beta}$ different from those of electrons excited by the same spectral line but with different energy, and

from those excited by light of a different frequency, whatever their energy.

From Eq. (4.4) we see that for a two-photon process in the electric-dipole approximation, we can describe the angular distribution of photoelectrons by $\tilde{\alpha} + \tilde{\beta}\cos^2\theta + \tilde{\gamma}\cos^4\theta$; i.e., we can obtain 3 parameters from angular-distribution measurements. This is true for atoms as well as for randomly oriented molecules. Here as in the case of single-photon ionization, angular-distribution measurements cannot provide complete information about the molecular processes involved, but some important information might be obtained. For example, suppose that an intermediate state n had an excitation frequency ω_n near the frequency ω of the incident light. Then the possibility of near-resonant two-photon ionization arises. If the ionization is truly a coherent two-photon process, then the angular distribution

of photoelectrons is given by (4.4) and (4.5). If, on the other hand, the intermediate state behaves like a real state, then the distribution must be that of (4.2a) and (4.3a), with the "initial" state taken as the state n; i.e., the coefficient $\tilde{\gamma}$ of the $\cos^4\theta$ term would be zero. Partial coherence in the intermediate state n would be reflected in an angular distribution somewhere between these two extremes. Thus one has a method which, in principle, can give the degree of coherence in an intermediate state from the form of the angular dependence of products.

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APPENDIX A: DERIVATION OF EQ. (4.2a)

Using Eq. (2.17a) in Eq. (2.5), and substituting into Eq. (2.6), we obtain

$$\sigma_\Gamma^{E1\cdot E1}(\Omega) = \frac{2\pi e^2\hbar^2}{m^2 c\nu} \sum_{l\lambda m\mu m'\mu'} A_{lmM_\Gamma M_i} A^*_{\lambda\mu M_\Gamma M_i} Y_{lm'}(\theta,\varphi) Y_{\lambda\mu'}{}^*(\theta,\varphi)$$

$$\times (1/8\pi^2)\int D^l_{m'm} D^{1*}_{0,m+M_\Gamma - M_i} D^{\lambda*}_{\mu'\mu} D^1_{0,\mu+M_\Gamma - M_i} \sin\beta\, d\alpha\, d\beta\, d\gamma. \tag{A1}$$

Making use of the relations[4]

$$D_{\mu_1 m_1}{}^{*J_1} = (-1)^{\mu_1 - m_1} D_{-\mu_1 - m_1}{}^{J_1} \tag{A2}$$

and $D_{\mu_1 m_1}{}^{J_1} D_{\mu_2 m_2}{}^{J_2} = \sum_J C(J_1 J_2 J \mid \mu_1 \mu_2) C(J_1 J_2 J \mid m_1 m_2) D_{\mu_1+\mu_2, m_1+m_2}^J \tag{A3}$

we obtain

$$\sigma_\Gamma^{E1\cdot E1} = \frac{2\pi e^2\hbar^2}{m^2 c\nu} \sum_{l\lambda m\mu m'\mu'} A_{lmM_\Gamma M_i} A^*_{\lambda\mu M_\Gamma M_i} Y_{lm'}(\theta,\varphi) Y_{\lambda\mu'}{}^*(\theta,\varphi)(-1)^{\mu'+M_i+M_\Gamma}$$

$$\times \sum_{J_1=0}^{2} \sum_{J=|l-\lambda|}^{l+\lambda} C(11J_1 \mid M_i - m - M_\Gamma, \mu + M_\Gamma - M_i) C(11J_1 \mid 00) C(l\lambda J \mid m, -\mu)$$

$$\times C(l\lambda J \mid m', -\mu')(1/8\pi^2)\int D_{0,m-\mu}^{J_1*} D_{m'-\mu',m-\mu}^J \sin\beta\, d\alpha\, d\beta\, d\gamma. \tag{A4}$$

Applying the orthogonality of the rotation functions

$$\int D_{\mu_1 m_1}^{J_1*} D_{\mu_2 m_2}^{J_2} \sin\beta\, d\alpha\, d\beta\, d\gamma = (8\pi^2/2J_2 + 1)\delta_{\mu_1\mu_2}\delta_{m_1 m_2}\delta_{J_1 J_2} \tag{A5}$$

we obtain

$$\sigma_\Gamma^{E1\cdot E1} = \frac{2\pi e^2\hbar^2}{m^2 c\nu} \sum_{l\lambda m\mu} A_{lmM_\Gamma M_i} A^*_{\lambda\mu M_\Gamma M_i} (-1)^{M_\Gamma + M_i} \sum_{J=0}^{2} \frac{1}{2J+1}$$

$$\times C(11J \mid M_i - m - M_\Gamma, \mu + M_\Gamma - M_i) C(11J \mid 00) C(l\lambda J \mid m, -\mu)$$

$$\times \left\{ \sum_{m'} (-1)^{m'} C(l\lambda J \mid m', -m') Y_{lm'}(\theta,\varphi) Y_{lm'}{}^*(\theta,\varphi) \right\}. \tag{A6}$$

But the final sum over m' is equal to

$$\{[(2l+1)(2\lambda+1)]^{1/2}/4\pi\}\, C(l\lambda J \,|\, 00)P_j\,(\cos\theta)\,.$$

Moreover, the Clebsch-Gordan coefficient $C(11J\,|\,00)$ vanishes except when $J=0$ or 2. Therefore our final expression is

$$\sigma_\Gamma^{E1\,\circ\,E1}(\Omega)=\frac{2\pi e^2\hbar^2}{m^2cv}\sum_{l\lambda m\mu}(-1)^{M_\Gamma+M_i}[(2l+1)(2\lambda+1)]^{1/2}A_{lmM_\Gamma M_i}A^*_{\lambda\mu M_\Gamma M_i}\sum_{J=0,2}\frac{1}{4\pi(2J+1)}$$

$$\times C(11J\,|\,M_i-m-M_\Gamma,\,\mu+M_\Gamma-M_i)C(11J\,|\,00)C(l\lambda J\,|\,m,-\mu)C(l\lambda J\,|\,00)P_j\,(\cos\theta)\,. \qquad\text{(A7)}$$

This is easily seen to be equivalent to Eqs. (4.2a) and (4.3a).

APPENDIX B: AN EXAMPLE

Consider the case of photoejection of an electron from an $s\sigma$ orbital of a homonuclear diatomic molecule; e.g., photo-ionization of the ground state of H_2. Let us assume that we are interested in energies low enough so that only channels which leave the molecule ion in its lowest electronic state are involved, and there are no competing auto-ionizing processes. Let us further assume that this orbital is sufficiently spherical so that only orbitals of symmetry $p\sigma$ or $p\pi$ have non-negligible dipole matrix elements with the initial state. Then substituting Eq. (4.3a) with $l=\lambda=1$ into Eq. (4.2a), we find

$$\sigma_\Gamma(\Omega)=\tilde\alpha+\tilde\beta\cos^2\theta\,, \qquad\text{(B1)}$$

where

$$\tilde\alpha=A[\,|d_{10}|^2-2\,\mathrm{Re}(d_{10}{}^*d_{11})+|d_{11}|^2] \qquad\text{(B2)}$$

and

$$\tilde\beta=A[2\,|d_{10}|^2+6\,\mathrm{Re}(d_{10}{}^*d_{11})+7\,|d_{11}|^2]\,. \qquad\text{(B3)}$$

A is a constant which can be determined from (4.3a). d_{10} and d_{11} are the electric-dipole matrix elements, Eq. (2.19a), between the initial $s\sigma$ orbital and the $p\sigma$ and $p\pi$ continuum functions, respectively, and we have used the relation $d_{11}=d_{1,-1}$ for a diatomic molecule. For an atom, $d_{11}=d_{10}$ so that from (B2) we have the well-known result $\tilde\alpha=0$. For a nonspherical molecule this is not true. In fact, our assumption that the electron leaves in either a $p\sigma$ or $p\pi$ wave allows us to determine both d_{10} and d_{11} experimentally by measuring $\tilde\alpha$ and $\tilde\beta$. Even in cases where other matrix elements cannot be neglected, the extent to which $\tilde\alpha$ is nonvanishing is a direct measure of l spoiling in the molecule. If an auto-ionization process such as excitation to a vibrationally excited ($p\sigma$ or $p\pi$) Rydberg level followed by a vibrationally induced "transition" to the continuum (s, p, or d wave) were important, then the change in approximate l selection rules would produce a nonzero $\tilde\alpha$. In fact, if this auto-ionizing process were dominant and if the life of the metastable Rydberg state were long compared with the rotational relaxation time in the gas, we would expect the electrons to be ejected isotropically and $\tilde\alpha$ would become very much greater than $\tilde\beta$. Studying the dependence of $\tilde\alpha$ and $\tilde\beta$ on electron velocity in such a case, one might obtain information about the relative importance of competing processes and about the effect of nonspherical terms in the molecular potential.

The total photo-ionization cross section for H_2 has been calculated by Flannery and Öpik.[14] They use the Weinbaum function to approximate the initial electronic state and take the final state to be an $H_2{}^+$ ion in its ground state and a free electron moving in a field of 2 point charges of half-elementary charge each. The distance between the point charges is chosen such that their quadrupole moment equals that of the residual $H_2{}^+$ ion. They find that only those final states for which the ejected electron is in a $p\sigma$ or $p\pi$ orbital give appreciable contributions to the total cross section. The contributions from the $f\sigma$ and $f\pi$ final states are entirely negligible. If we make the slightly more questionable assumption that the f orbitals do not contribute appreciably to the differential cross section, then we can estimate the angular distribution of photoelectrons from H_2 as a function of energy, using the electronic matrix elements M_z and $M_\pm$ obtained from Ref. 14. Since these are matrix elements involving standing waves, we also need values for the $p\sigma$ and $p\pi$ phase shifts to use in Eq. (2.21). We have used the values calculated by Temkin and Vasavada by their method of "polarized single-center orbitals."[15] We find that

$$\sigma(\Omega)=\frac{\sigma_{\text{tot}}}{4\pi(\tilde\alpha/\tilde\beta+\tfrac{1}{3})}\!\left(\frac{\tilde\alpha}{\tilde\beta}+\cos^2\theta\right)\,, \qquad\text{(B4)}$$

where σ_{tot} and $\tilde\alpha/\tilde\beta$ are given in Table I. In Ref. 15 the phase shifts were calculated for an internuclear distance $R=2.0$ a.u. instead of $R=1.4$ a.u. As a result, we expect our values of $\tilde\alpha/\tilde\beta$ to be slightly too large. Also, we have neglected auto-ionization so that we cannot expect our results to agree with experiment in the low-energy region. Nevertheless, this calculation can serve as an indication of the magnitude of the effect that l spoiling has on the angular distribution of molecular photoelectrons. From the values of $\tilde\alpha/\tilde\beta$ in Table I we see that for H_2, a molecule in which l spoiling is known to be small, this effect can be expected to be considerably larger than the effects due to electric-quadrupole and magnetic-dipole radiation. Therefore simply fitting the two coefficients $\tilde\alpha$ and $\tilde\beta$ to fit the experimental angular distribution and analyzing the results in the dipole approximation might provide valuable information about the nonspherical nature of molecules.

TABLE I. Values of $\tilde{\alpha}/\tilde{\beta}$ and σ_{tot} in Eq. (B4), computed using the electronic matrix elements M_z and $M_\pm$ from Ref. 14, and phase shifts δ_{10} and δ_{11} from Ref. 15.

k^2 (Ry)	M_z	$M_\pm$	δ_{10}	δ_{11}	$\tilde{\alpha}/\tilde{\beta}$	σ_{tot} $(10^{-18}\,cm^2)$
0.0	1.851	1.571	0.493	−0.308	0.051	13.6
0.4	1.134	1.025	0.495	−0.286	0.046	7.33
0.8	0.758	0.723	0.504	−0.257	0.042	4.37
1.2	0.538	0.544	0.503	−0.228	0.038	2.86
1.6	0.401	0.426	0.493	−0.206	0.034	1.98
2.0	0.306	0.349	0.475	−0.191	0.031	1.46

[a]Matrix elements taken from Ref. 14 for $R = 1.4$ a.u.
[b]Phase shifts taken from Ref. 15 for $R = 2.0$ a.u.

The experimental results for photo-ionization of H_2 have not yet yielded reliable values for $\tilde{\alpha}/\tilde{\beta}$.[1,16] It seems reasonable to expect that direct comparison of experimental and theoretical values of this function, both for H_2 and for other diatomics for which theoretical values are presently unavailable, can be made in the near future.

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