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Detector integrated angular distribution: Chemisorption-site geometry, axial-recoil photofragmentation, and molecular-beam orientation

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The seemingly diverse problems of chemisorption site geometry, orientation of species in molecular beams, and the axial recoil of molecular photofragments can be analyzed by means of the dependence of photoexcitation on target orientation. Expressions are derived for this orientation dependence in terms of the electric-dipole excitation amplitudes of the target. For cylindrically symmetric targets a particularly simple single-parameter distribution $1+\beta_T P_2(\cos\theta_T)$ is obtained, analogous to the Yang-theorem result $1+\beta_D P_2(\cos\theta_D)$ familiar from random-molecule photoelectron angular distributions (T denotes target, D denotes detector). For targets of arbitrary symmetry the distribution has a maximum harmonic dependence of second order and is completely characterized by at most eight parameters in addition to the overall cross section. The special utility of elliptically polarized light is also discussed.

In principle the geometry of an oriented species (e.g., molecules adsorbed on a surface, or aligned in a molecular beam) can be determined from the angular distribution of electrons photoionized from it by comparing the observed distribution with a calculated one. This comparison will be more or less complicated depending on the inherent complexity of the distribution itself and on alterations to that distribution due to, e.g., substrate bonding and backscattering for a chemisorbed target, interaction-region geometry for a molecular beam. We have sought to identify the type of photoionization experiment which is best suited to the determination of target orientation, in terms of low-order angular dependence, minimal experimental complication, and lack of extraneous information.

In a given photoionization experiment the orientation of the target, or the (electron-) detection direction, or both, may be resolved. (By "resolved" we mean "measured" in the quantum-mechanical sense; in particular, an unresolved quantity must be treated theoretically as completely random.) Clearly, the most detailed information is available in the experiment which resolves both, either by measuring the angular distribution of electrons from a fixed target (for alternative target orientations), or by measuring as a function of target orientation the photocurrent at a fixed detector (for alternative detector-light orientations). Both of these "fully resolved" processes have been explored in prototype calculations (see below). The predicted distributions are beautifully rich in structure and detail. However, for the purposes of determining the geometry of an oriented species (the geometry of a molecule on a surface or the population of its rotational sublevels in a molecular beam), both of these techniques yield much superfluous information which is due to the relative orientations of the light source and detector alone. We show here that, *if one is interested in target orientation only, then the simplest approach is to measure the total photocurrent, e.g., at a collecting sphere surrounding the target orientation.* The resulting integrated detector angular distribution (IDAD) has two simplifying key features: (i) all interference vanishes between ionization amplitudes with alternative orbital momenta l and momentum projections m, in contrast with photoelectron angular distributions, and (ii) the maximum harmonic dependence is second order, so that the distribution can be completely characterized experimentally with relative ease, even for targets of arbitrary symmetry. Further, and of particular significance to chemisorption studies, the IDAD is necessarily impervious to the effects of elastic scattering of ejected electrons from any substrate. Indeed, the experiment may be performed equivalently by measuring photoabsorption alone; ionization is not even required. This approach may be especially appropriate to the study of gas-phase orientation in molecular beams, etc. For cylindrically symmetric targets, a particularly simple $1+\beta_T P_2(\cos\theta_T)$ single-parameter distribution results (T denotes target; see below), analogous to the Yang-theorem result $1+\beta_D P_2(\cos\theta_D)$ for random molecule-photoelectron angular distributions (D denotes detector; see below).

To make things clearer we have found it helpful to cast the present study in the broader context of the alternative possible photoionization angular distribution studies. We begin with the basic cross-section expression[1]

$$\frac{d^2\sigma}{d\hat{R}_T d\Omega_D} = \sum_{K=0}^{2l_{\max}+2} \sum_{M=-K}^{K} \sum_{K_e=0}^{2l_{\max}} \sum_{M_e^\gamma=-K_e}^{K_e} C^{m_p}_{KM,K_eM_e^\gamma} Y_{K_eM_e^\gamma}(\Omega_D) D^K_{M,-M_e^\gamma}(\hat{R}_T), \tag{1}$$

where

$$\begin{aligned} C^{m_p}_{KM,K_eM_e^\gamma} = 4\pi^2\alpha h\nu \sum_{\substack{lm m_\gamma \\ l'm'm'_\gamma}} & (-1)^{m+m'_\gamma-m_p-M_e^\gamma}[(2l'+1)(2l+1)/4\pi]^{1/2} i^{(l'-l)} \exp[i(\sigma_l-\sigma'_l)] \\ & \times D^{(-)\Gamma_0 *}_{l'm'm'_\gamma} D^{(-)\Gamma_0}_{lmm_\gamma}(lm,l'-m'|K_eM_e)(l0,l'0|K_e0)(2K_e+1)^{-1/2} \\ & \times \sum_{K_\gamma} (1m_\gamma, 1-m'_\gamma|K_\gamma M_\gamma)(1m_p,1-m_p|K_\gamma 0) \\ & \times (K_e-M_e, K_\gamma M_\gamma|KM)(K_e-M_e^\gamma, K_\gamma 0|K-M_e^\gamma); \end{aligned} \tag{2}$$

this is doubly differential in target orientation $\hat{R}_T$, specified by the set of Euler angles[2] $\{\alpha,\beta,\gamma\}$ of the rotations which carry the laboratory (light) frame into the target frame, and in the photoelectron ejection direction along the solid angle $\Omega_D=(\theta_D,\phi_D)$ of the detector. Photoionization dynamics determine the coefficients $C^{m_p}_{KM,K_eM_e^\gamma}$ through ingoing-wave normalized electric-dipole transition amplitudes $D^{(-)\Gamma_0}_{lmm_\gamma}$ [defined below, Eq. (7)]. The harmonic composition is limited by the dipole character of the interaction (2×1) and the maximum orbital momentum $l_{\max}$ of the ejected electron $(2l_{\max})$. Within this context we can identify four classes of experiments, summarized in Table I:

a. Fixed-target angular distribution (FTAD). The orientation $\hat{R}_T$ of the target is held fixed and the

TABLE I. Photoionization angular dependence.[a]

Distribution	Characteristics	General form	Harmonic dependence
FTAD[b–d]	$\hat{R}_T$ fixed Ω_D varied	$d\sigma(\hat{R}_T)/d\Omega_D\|_{m_p} = \sum_{K_eM_e^\gamma} A^{m_p}_{K_eM_e^\gamma}(\hat{R}_T) Y_{K_eM_e^\gamma}(\Omega_D)$	$0\le K_e\le 2l_{\max}$ $-K_e\le M_e^\gamma\le K_e$
FDAD[d,e]	Ω_D fixed $\hat{R}_T$ varied	$d\sigma(\Omega_D)/d\hat{R}_T\|_{m_p} = \sum_{KMM_e^\gamma} B^{m_p}_{KMM_e^\gamma}(\Omega_D) D^K_{M,-M_e^\gamma}(\hat{R}_T)$	$0\le K\le 2l_{\max}+2$ $-K\le M\le K$ $-2l_{\max}\le M_e^\gamma\le 2l_{\max}$
ITAD[f]	$\hat{R}_T$ unresolved Ω_D varied	$d\sigma/d\Omega_D\|_0 = (\sigma/4\pi)[1+\beta_D P_2(\cos\theta_D)]$	$K=0,2$ $M=0$
IDAD[g]	Ω_D unresolved $\hat{R}_T$ varied	$d\sigma/d\Omega_T\|_{m_p} = \sum_{KM} Z^{m_p}_{KM} Y_{KM}(\Omega_T)$	$0\le K\le 2$ $-K\le M\le K$

[a] For all distributions elliptical polarization is represented by a linear combination of the considered distributions for left and right circular polarizations plus an interference term; see text. In Ref. 1, $\hat{R}_\gamma=\hat{R}_T$ and $\hat{k}_e^\gamma=\Omega_D$.

[b] Ω_D is the laboratory-frame ejection direction which is defined in terms of the target-frame ejection direction by

$$Y_{lm}(\Omega_D)=\sum_{m'} Y_{lm'}(\hat{k}_e) D^l_{m'm}(\hat{R}_T).$$

[c] $A^{m_p}_{K_eM_e^\gamma}(\hat{R}_T) \equiv \sum_{KM} C^{m_p}_{KM,K_eM_e^\gamma} D^K_{M,-M_e^\gamma}(\hat{R}_T)$; see Eq. (2).

[d] For a cylindrically symmetric target the first rotation, through α_γ, of the set $\hat{R}_\gamma$ is about the symmetry axis of the target and therefore moot; in this case the rotation matrix element is proportional to the spherical harmonic $Y_{KM}(\beta,\alpha)$, where β,α are angles in the set $R=\{\alpha,\beta,0\}=\hat{R}_\gamma^{-1}$, the transformation which carries the laboratory frame to coincidence with the target frame (Ref. 5).

[e] $B^{m_p}_{KMM_e^\gamma}(\Omega_D) \equiv \sum_{K_e} C^{m_p}_{KM,K_eM_e^\gamma} Y_{K_eM_e^\gamma}(\Omega_D)$; see Eq. (2).

[f] For $m_p=\pm 1$, $\beta_D \rightarrow -\frac{1}{2}\beta_D$.

[g] Replacement $\hat{R}_T \rightarrow \Omega_T$ possible in the absence of elliptical polarization; see text.

variation of photocurrent is measured as a function of detector orientations Ω_D. Davenport[3] predicted the first FTAD for valence-shell ionization of CO with He I 584-Å resonance radiation for orientations $\hat{R}_T$ parallel and perpendicular to the electric vector of the light. Other workers[4] have extended this work to treat K-shell ionization over the range 0–5 Ry electron kinetic energy.

b. Fixed-detector angular distribution (FDAD). The detector orientation Ω_D is held fixed and the photocurrent is measured as a function of target orientations $\hat{R}_T$. This arrangement is appropriate to photoelectron spectrometers with fixed light-detector geometry (typically set at 90°) but with the ability to rotate a mounted chemisorption substrate. In anticipation of such studies, the FDAD for K-shell ionization of CO has been calculated for a range of detector orientations.[5]

c. Integrated-target angular distribution (ITAD). The net photocurrent for all target orientations $\hat{R}_T$ along the direction Ω_D is measured. This corresponds, e.g., to the usual gas-phase (random-target) photoelectron-angular-distribution experiment. The distribution is obtained by integration of Eq. (1) over $\hat{R}_T$. The result (for nonchiral targets[6]) is

$$\frac{d\sigma}{d\Omega_D}=\frac{\sigma}{4\pi}[1+\beta_D P_2(\cos\theta_D)]\,, \tag{3}$$

where σ is the integrated cross section, θ_D is measured from the electric vector of the light, and the single asymmetry parameter β_D completely characterizes the distribution. This simple result is a consequence of the dipole character and well-defined parity of the ionizing interaction,[7] and is altogether independent of the dynamical details of the process. Quite general expressions for β_D are available.[8]

d. Integrated-detector angular distribution (IDAD). As described above and the topic of this report, the net interaction with the target (for all detection directions if ionization occurs) is measured as a function of orientation $\hat{R}_T$. The distribution is obtained by integration of Eq. (1) over Ω_D. The result is of the form

$$\frac{d\sigma}{d\Omega_T}=\sum_{K=0}^{2}\sum_{M=0}^{K}\mathrm{Re}[Z_{KM}Y_{KM}(\Omega_T)]\,. \tag{4}$$

We have replaced $\hat{R}_T$ by the target solid angle $\Omega_T=(\theta_T,\phi_T)\equiv(\beta,\gamma)$ since, because of the cylindrical symmetry of the dipole interaction (i.e., in the absence of elliptical polarization), the first Euler angle α is dynamically moot. Expressions are obtained below for the dynamical coefficients Z_{KM}. For cylindrically symmetric nonchiral[6] targets, all Z_{KM} vanish except $Z_{00}=\sigma/4\pi$ and $Z_{20}=\sigma\beta_T/4\pi$, so that the IDAD takes the particularly simple form

$$\frac{d\sigma}{d\Omega_T}=\frac{\sigma}{4\pi}[1+\beta_T P_2(\cos\theta_T)]\,, \tag{5}$$

analogous to the ITAD (3).

Both the FTAD and FDAD are generally very richly structured because of the coherent superposition of the anisotropies in the response of the target to the light and in the distribution pattern of ejected electrons. The IDAD is substantially simpler because of the elimination of any such coherence and indeed of any dependence on ejection anisotropy whatsoever. (The ITAD, of course, contains no information on target orientation.) The IDAD measures directly and exclusively the dependence of the target response on the orientation Ω_T with respect to the light. As such the IDAD is conceptually and experimentally the most direct probe of target orientation.

The general formula for the FTAD and FDAD in the form of Eq. (1) derives from Eq. (15) of Ref. 1,

$$\begin{aligned}\left.\frac{d^2\sigma}{d\hat{R}_\gamma d\hat{k}_e}\right|_{m_p}=4\pi^2\alpha h\nu&\sum_{\substack{lm m_\gamma\\ l'm'm'_\gamma}}(-1)^{m'+m_\gamma'-m_p}\left(\frac{(2l'+1)(2l+1)}{4\pi}\right)^{1/2}i^{(l'-l)}e^{i(\sigma_l-\sigma_{l'})}\\&\times D^{(-)\Gamma_0^*}_{l'm'm_\gamma'}(k_e)D^{(-)\Gamma_0}_{lmm_\gamma}(k_e)\sum_{K_e}(lm,l'-m'|K_eM_e)(l0,l'0|K_e0)(2K_e+1)^{-1/2}\\&\times Y_{K_eM_e}(\hat{k}_e)\sum_{K_\gamma}(1m_\gamma,1-m_\gamma'|K_\gamma M_\gamma)(1m_p,1-m_p|K_\gamma 0)\,D^{K_\gamma}_{M_\gamma 0}(R)\,.\end{aligned} \tag{6}$$

Here α is the fine-structure constant, σ_l is the Coulomb phase $\arg\Gamma(l+1-i/k_e)$, and $D^{K_\gamma}_{M_\gamma 0}(\hat{R}_\gamma)$ is the rotation matrix element whose argument $\hat{R}_\gamma$ is the set of Euler angles $\{\alpha_\gamma,\beta_\gamma,\gamma_\gamma\}$ which transforms the target-frame coordinate system into the laboratory-frame system. The choice of the target-frame coordinate system is arbitrary, although it must be the same as that in which the dipole transition amplitudes are defined. The laboratory coordinate system is characterized by a single z direction (assuming no elliptical polarization; see below), taken either as the axis of polarization for linearly polarized light (polarization quantum number $m_p=0$), or as the propagation direction for circular or natural polarization ($m_p=\pm 1$ for left- or right-circular polarization, positive or negative helicity, respectively; natural polarization may be represented by an incoherent sum of left and right circular polarizations). All the dynamics are contained in the target-frame amplitudes

$$D^{(-)\Gamma_0}_{lmm_\gamma}(k_e)=\left(\frac{4\pi}{3}\right)^{1/2}\int d\vec{\mathrm{r}}\,\Psi^{(-)*}_{lm}(k_e,\vec{\mathrm{r}})\times rY_{1m_\gamma}(\hat{r})\Psi_{\Gamma_0}(\vec{\mathrm{r}}) \tag{7}$$

for electric-dipole transition from the initial state $\Psi_{\Gamma_0}(\vec{\mathrm{r}})$ to the ingoing-wave-normalized continuum state $\Psi^{(-)}_{lm}(k_e,\vec{\mathrm{r}})$ of electron kinetic energy k_e^2. The set of polar angles $\hat{k}_e=(\theta_e,\phi_e)$ specifies the electron ejection direction in the molecule-frame coordinate system. [Since these angles will be integrated over, there is no need here to express them in terms of laboratory-frame angles $\Omega_D=(\theta_D,\phi_D)$, as would be required to obtain Eq. (1); see Eq. (23) of Ref. 1.] All dependence on ejection direction is found in the spherical harmonic $Y_{K_eM_e}(\hat{k}_e)$; the contribution to the integral over $\hat{k}_e$ is zero except for $K_e=M_e=0$, i.e.,

$$\int d\hat{k}_e Y_{K_eM_e}(\hat{k}_e)=(4\pi)^{1/2}\delta_{K_e0}\delta_{M_e0}. \tag{8}$$

Performing the integration yields

$$\begin{aligned}\left.\frac{d\sigma}{d\hat{R}_\gamma}\right|_{m_p}&=\int d\hat{k}_e\left.\left(\frac{d^2\sigma}{d\hat{k}_e d\hat{R}_\gamma}\right)\right|_{m_p}\\&=(4\pi)^{1/2}4\pi^2\alpha h\nu\sum_{\substack{lmm_\gamma\\l'm'm'_\gamma}}(-1)^{m'+m'_\gamma-m_p}\left(\frac{(2l'+1)(2l+1)}{4\pi}\right)^{1/2}\\&\qquad\times i^{(l'-l)}e^{i(\sigma_l-\sigma_{l'})}D^{(-)\Gamma_0^*}_{l'm'm'_\gamma}D^{(-)\Gamma_0}_{lmm_\gamma}(lm,l'-m'|00)(l0,l'0|00)\\&\qquad\times\sum_{K_\gamma}(1m_\gamma,1-m'_\gamma|K_\gamma M_\gamma)(1m_p,1-m_p|K_\gamma 0)D^{K_\gamma}_{M_\gamma 0}(\hat{R}_\gamma).\end{aligned} \tag{9}$$

This leads immediately to the selections $l=l', m=m'$ by triangular conditions on the Clebsch-Gordan coefficients; all interference vanishes between ionization amplitudes with alternative values of the angular momentum or its projection. The zero index on the rotation matrix element

$$\begin{aligned}D^{K_\gamma}_{M_\gamma 0}(\hat{R}_\gamma)&=D^{K_\gamma}_{M_\gamma 0}(\alpha_\gamma,\beta_\gamma,0)\\&=\left(\frac{4\pi}{2K_\gamma+1}\right)^{1/2}Y^*_{K_\gamma M_\gamma}(\beta_\gamma,\alpha_\gamma)\end{aligned} \tag{10}$$

reflects the cylindrical symmetry of the dipole interaction. Substituting Eq. (10) and replacing the simpler Clebsch-Gordan coefficients with their algebraic forms[9] in Eq. (9), we obtain

$$\begin{aligned}\left.\frac{d\sigma}{d\hat{R}_\gamma}\right|_{m_p}&=(4\pi)^{1/2}4\pi^2\alpha h\nu\sum_{lm}\sum_{m_\gamma m'_\gamma}(-1)^{m'_\gamma-m_p}D^{(-)\Gamma_0^*}_{lmm'_\gamma}D^{(-)\Gamma_0}_{lmm_\gamma}\\&\qquad\times\sum_{K_\gamma}(1m_\gamma,1-m'_\gamma|K_\gamma M_\gamma)(1m_p,1-m_p|K_\gamma 0)(2K_\gamma+1)^{-1/2}Y^*_{K_\gamma M_\gamma}(\beta_\gamma,\alpha_\gamma).\end{aligned} \tag{11}$$

The angles $(\beta_\gamma,\alpha_\gamma)$ are equivalent to the polar angles of the laboratory z axis in the target frame. The harmonic in these angles is related to the harmonic in the polar angles of the target in the laboratory frame by

$$\begin{aligned}Y^*_{K_\gamma M_\gamma}(\beta_\gamma,\alpha_\gamma)&=(-1)^{M_\gamma}Y_{K_\gamma M_\gamma}(\beta,\gamma)\\&\equiv(-1)^{M_\gamma}Y_{K_\gamma M_\gamma}(\theta_T,\phi_T),\end{aligned} \tag{12}$$

as derived in the Appendix. Making the replacements $K_\gamma\to K$ and $M_\gamma\to M$, we may cast Eq. (11) in the form of Eq. (4), i.e.,

$$\left.\frac{d\sigma}{d\Omega_T}\right|_{m_p}=\frac{\pi\alpha h\nu}{3}\sum_{K=0}^{2}\sum_{M=0}^{K}\mathrm{Re}[Z^{m_p}_{KM}\bar{Y}_{KM}(\theta_T,\phi_T)]. \tag{13}$$

Here we have replaced $d\hat{R}_\gamma$ by $(4\pi)^{-1}d\Omega_T$ (see Appendix), since there is no dependence on the third Euler angle γ_γ, and for convenience we use unnormalized spherical harmonics $\bar{Y}_{KM}=[4\pi/(2K+1)]^{1/2}\times Y_{KM}$. The limit $K\leq 2$ is given by triangular conditions in Eq. (11). As a consequence of the fact that the cross section is real, the sum over $m_\gamma<m'_\gamma$ in Eq. (11) is the complex conjugate of the sum over $m_\gamma>m'_\gamma$. Therefore taking only $m_\gamma\geq m'_\gamma$ (giving $M=M_\gamma=m_\gamma-m'_\gamma\geq 0$), this sum can be expressed in terms of real parts as in Eq. (13), with the factor $(2-\delta_{m_\gamma m'_\gamma})=(2-\delta_{M0})$ to ensure that the $m_\gamma=m'_\gamma$ terms are counted only once. Thus, the coefficients $Z^{m_p}_{KM}$ here differ from those in Eq. (4) by the factor $[4\pi/(2K+1)]^{1/2}(\frac{1}{3}\pi\alpha h\nu)(2-\delta_{M0})$ and are given by

$$Z^{m_p}_{KM}=3(1m_p,1-m_p|K0)(-1)^{m_p}\sum_{lm}\sum_{m_\gamma\geq m'_\gamma}(-1)^{m_\gamma}D^{(-)\Gamma_0^*}_{lmm'_\gamma}D^{(-)\Gamma_0}_{lmm}(1m_\gamma,1-m'_\gamma|KM)(2-\delta_{M0}),\qquad(14)$$

where the factor 3 arises because each of the Clebsch-Gordan coefficients in Eq. (14) when evaluated for $K=0$ contributes a factor $(3)^{-1/2}$. The explicit expressions for these coefficients in terms of dipole amplitudes labeled by l, m, and m_γ are

$$\begin{aligned}
Z^{m_p}_{00}&=\sum_{lmm_\gamma}|D^{(-)\Gamma_0}_{lmm_\gamma}|^2,\\
Z^{m_p}_{10}&=\frac{3m_p}{2}\sum_{lmm_\gamma}m_\gamma|D^{(-)\Gamma_0}_{lmm_\gamma}|^2,\\
Z^{m_p}_{11}&=3\sqrt{2}m_p\sum_{lmm_\gamma}D^{(-)\Gamma_0}_{lmm_\gamma}\;D^{(-)\Gamma_0^*}_{lmm_\gamma-1},\\
Z^{m_p}_{20}&=\frac{3m_p^2-2}{2}\sum_{lmm_\gamma}(3m_\gamma^2-2)|D^{(-)\Gamma_0}_{lmm_\gamma}|^2,\\
Z^{m_p}_{21}&=(3m_p^2-2)\sqrt{3}\sum_{lmm_\gamma}(2m_\gamma-1)D^{(-)\Gamma_0}_{lmm_\gamma}D^{(-)\Gamma_0^*}_{lmm_\gamma-1},\\
Z^{m_p}_{22}&=(3m_p^2-2)\sqrt{6}\sum_{lm}D^{(-)\Gamma_0}_{lm1}D^{(-)\Gamma_0^*}_{lm-1}.
\end{aligned}\qquad(15)$$

The definitions of the $Z^{m_p}_{KM}$ make use of the fact that m_γ and m'_γ, the projections of the dipole interaction along the target z axis, are restricted to the values -1, 0, $+1$, i.e., $D^{(-)\Gamma_0}_{lmm_\gamma}=0$ otherwise. Of the six coefficients defined in Eq. (15), only those for which $M\neq 0$ have an imaginary part. Denoting the real and imaginary parts of these three coefficients as Z^c_{KM} and Z^s_{KM}, respectively, and substituting explicit forms for the unnormalized harmonics $\overline{Y}_{KM}$, we express the IDAD in the form most suitable for fitting to experiment

$$\begin{aligned}
\left.\frac{d\sigma}{d\Omega_T}\right|_{m_p}=\frac{\pi\alpha h\nu}{3}\{&Z_{00}+Z_{10}\cos\theta_T+Z_{20}\tfrac{1}{2}(3\cos^2\theta_T-1)\\
&-[\sqrt{\tfrac{1}{2}}(Z^c_{11}\cos\phi_T-Z^s_{11}\sin\phi_T)+\sqrt{\tfrac{3}{2}}(Z^c_{21}\cos\phi_T-Z^s_{21}\sin\phi_T)\cos\theta_T]\sin\theta_T\\
&+\sqrt{\tfrac{3}{8}}(Z^c_{22}\cos2\phi_T-Z^s_{22}\sin2\phi_T)\sin^2\theta_T\}.
\end{aligned}\qquad(16)$$

Only the first term contributes to the integrated cross section

$$\begin{aligned}
\sigma&=\int d\Omega_T\left(\frac{d\sigma}{d\Omega_T}\right)=\frac{\pi\alpha h\nu}{3}Z_{00}(4\pi)\\
&=\frac{4\pi^2\alpha h\nu}{3}\sum_{lmm_\gamma}|D^{(-)\Gamma_0}_{lmm_\gamma}|^2.
\end{aligned}\qquad(17)$$

Thus, once the value of the integrated cross section σ is fixed, the shape of the distribution is characterized by the remaining eight parameters; or five in the case of linear polarization, $m_p=0$, since the $K=1$ terms vanish, or for natural polarization, since the incoherent sum of left- and right-circular polarizations, $m_p=\pm 1$, gives zero net contribution from the $K=1$ terms.

Equations (15) and (16), then, are the key results of this study. In order to apply them to the determination of molecular orientation on a surface, one would first specify an (arbitrary) target-frame coordinate system attached to the surface, and then seek to determine the orientation of the molecule within that frame. Unfortunately the orientation cannot be inferred directly from the measured distribution: The dependence upon the orientation of the molecule in the target frame is contained implicitly in the dipole transition amplitudes, and in practice there are many more than nine of these at best; thus a simultaneous solution for the dipole amplitudes is impossible. Instead we may proceed in reverse and, guided by intuition, compute the distributions resulting from alternative probable orientations until the observed distribution is reproduced.

For a target with cylindrical symmetry about its z axis a further simplification results, since m and m' are conserved for cylindrical symmetry, and therfore,

$$m=m_\gamma+m_0,\qquad(18a)$$

$$m'=m'_\gamma+m_0,\qquad(18b)$$

where m_0 is the projection of the initial-state angular momentum. Equation (9) then restricts $M_\gamma=m_\gamma-m'_\gamma=m-m_0-m'+m_0=m-m'=0$, i.e., $m_\gamma=m'_\gamma$ and all nondiagonal terms in m_γ vanish in Eq. (15), leaving only those terms in Eq. (13) for which $M=0$:

$$\left.\frac{d\sigma}{d\Omega_T}\right|_{m_p}=\frac{\pi\alpha h\nu}{3}\sum_{K=0}^{2} Z_{K0}^{m_p}P_K(\cos\theta_T), \tag{19}$$

where the unnormalized spherical harmonics with zero projection are just the Legendre polynomials $P_K(\cos\theta_T)$. The odd term still vanishes with linearly or naturally polarized light, but also if $m_0=0$ (i.e., Σ-state photoionization), because $D_{l\,-m}^{(-)\Gamma_0}=D_{l\,+m}^{(-)\Gamma_0}$ for a cylindrically symmetric target and the terms with opposite signs in the summation over m in $Z_{10}^{m_p}$ cancel one another. For either of these cases the distribution takes the form of Eq. (5),

$$\begin{aligned}\left.\frac{d\sigma}{d\Omega_T}\right|_{m_p}&=\frac{\pi\alpha h\nu}{3}\sum_{K=0,2} Z_{K0}^{m_p}P_K(\cos\theta_T)\\&=\frac{\sigma}{4\pi}\left[1+\beta_T P_2(\cos\theta_T)\right],\end{aligned} \tag{20}$$

where the asymmetry parameter is given by

$$\beta_T=\frac{Z_{20}^{m_p}}{Z_{00}^{m_p}}=\left(\frac{3m_p^2-2}{2}\right)\sum_{lm}\left|D_{lm\,m-m_0}^{(-)\Gamma_0}\right|^2\left[3(m-m_0)^2-2\right]\Big/\sum_{lm}\left|D_{lm\,m-m_0}^{(-)\Gamma_0}\right|^2. \tag{21}$$

Equations (16) and (20) give the IDAD for a target of general symmetry and cylindrical symmetry, respectively, for linearly and circularly polarized light, and for naturally polarized light (which may be expressed as the incoherent sum of left- and right-circular polarizations). One further generalization which can be made is the treatment of elliptical polarization, which may be expressed as the weighted *coherent* sum of left- and right-circular polarizations; indeed linear and circular polarizations are limiting cases of elliptical polarization with eccentricity 1 and 0, respectively. The doubly differential cross section (6) is an expansion of the expression[1]

$$\left.\frac{d^2\sigma}{d\hat{R}_\gamma d\hat{k}_e}\right|_{m_p}=4\pi^2\alpha h\nu\left|\langle\Psi^{(-)}(\vec{k}_e,\vec{r})\,|\,\xi_{m_p}(\hat{R}_\gamma)\,|\,\Psi_{\Gamma_0}(\vec{r})\rangle\right|^2, \tag{22}$$

where the dipole operator is

$$\xi_{m_p}(\hat{R}_\gamma)=\left(\frac{4\pi}{3}\right)^{1/2}(1-2\delta_{1m_p})r\sum_{m_\gamma}Y_{1m_\gamma}(\hat{r})D^1_{m_\gamma m_p}(\hat{R}_\gamma)\,. \tag{23}$$

The treatment of elliptical polarization then consists of replacing the operator in Eq. (22) with a linear combination of the left- and right-circular polarization operators,

$$\xi^e_{m_p}(\hat{R}_\gamma)=\sin\epsilon\;\xi_{+1}(\hat{R}_\gamma)+\cos\epsilon\;\xi_{-1}(\hat{R}_\gamma), \tag{24}$$

where the superscript e denotes elliptical polarization and the weighting factors are given in terms of an angle ϵ to preserve normalization. The subscript m_p still labels the operator because it may be defined in such a way that the helicity of the elliptical polarization is given by the sign of $m_p[|m_p|=1$ only now]. Forming the squared modulus, as in Eq. (22), three terms result:

$$\begin{aligned}\left.\frac{d^2\sigma}{d\hat{R}_\gamma d\hat{k}_e}\right|_{m_p}=4\pi^2\alpha h\nu\{&\sin^2\epsilon\,|\langle\Psi^{(-)}|\,\xi_{+1}(\hat{R}_\gamma)\,|\Psi_{\Gamma_0}\rangle|^2+\cos^2\epsilon\,|\langle\Psi^{(-)}|\,\xi_{-1}(\hat{R}_\gamma)\,|\Psi_{\Gamma_0}\rangle|^2\\&+\sin2\epsilon\,\mathrm{Re}[\langle\Psi^{(-)}|\,\xi_{+1}(\hat{R}_\gamma)\,|\Psi_{\Gamma_0}\rangle\langle\Psi_{\Gamma_0}|\,\xi_{-1}(\hat{R}_\gamma)\,|\Psi^{(-)}\rangle]\}.\end{aligned} \tag{25}$$

Thus, the cross section for elliptical polarization may be expressed as the incoherent sum of left- and right-circular polarizations, with weights $\sin^2\epsilon$ and $\cos^2\epsilon$, respectively, plus a crossterm weighted by $\sin2\epsilon$ which represents their coherent superposition. The matrix elements in the first two terms in Eq. (25) are just the same as for the pure left- and right-circular polarization cross sections; only the weighting is different. All the interference is contained in the crossterm. The extension of this result to the IDAD for elliptical polarization is direct: Integration of Eq. (25) over detection directions $\hat{k}_e$ gives simply a weighted sum of the IDAD's for left and right circular polarizations and the analogous detector-integrated crossterm. Denoting this interference term by $dX/d\hat{R}_\gamma$ we may write

$$\begin{aligned}\left.\frac{d\sigma}{d\hat{R}_\gamma}\right|_{m_p}=&\left.\frac{\sin^2\epsilon\,d\sigma}{d\hat{R}_\gamma}\right|_{m_p=1}+\left.\frac{\cos^2\epsilon\,d\sigma}{d\hat{R}_\gamma}\right|_{m_p=-1}\\&+\left.\frac{\sin2\epsilon\,\mathrm{Re}dX}{d\hat{R}_\gamma}\right|_{m_p},\end{aligned} \tag{26}$$

and its contribution to the IDAD can be shown[10] to have the general form

$$\begin{aligned}\left.\frac{dX}{d\hat{R}_\gamma}\right|_{m_p}\propto\sum_{lm}\sum_{m_\gamma m_\gamma'}&D_{lmm_\gamma'}^{(-)\Gamma_0^*}D_{lmm_\gamma}^{(-)\Gamma_0}(-1)^{m_\gamma'}\\&\times(1m_\gamma,1-m_\gamma'\,|\,2m_\gamma-m_\gamma')\\&\times D^2_{m_\gamma-m_\gamma',2}(\hat{R}_\gamma),\end{aligned} \tag{27}$$

where the constant of proportionality is $\exp(2i\delta)$ and specifies the angle δ between the major axis of the ellipse in the xy plane and the x axis.[10] This interference contribution has two important features. First, it depends on all three Euler angles in the set $\hat{R}_\gamma$ since elliptical polarization destroys the cylindrical symmetry of the dipole interaction (e.g., the magnitude of the interaction will depend upon whether, say, a linear molecule is aligned along the major or minor axis of the ellipse). Second, the interference term makes no net contribution to the integrated cross section σ. This intuitively obvious result is demonstrated by integrating Eq. (27) over all target orientations $\hat{R}_\gamma$: The integral of the rotation matrix element over $\hat{R}_\gamma$ is zero unless all its indices are zero, and therefore the net contribution of the crossterm to the overall cross section is $X=0$.

Apart from its utility in describing accurately the radiation from a true source which has an elliptical component of greater or lesser magnitude (we have in mind particularly synchrotron radiation[11]), the use of elliptical polarization allows the resolution of the third target orientation angle $\gamma_\gamma = \alpha$. With linearly or circularly polarized light, the IDAD allows the specification of target geometry only to within a rotation about the symmetry axis of the light. Furthermore, elliptical polarization allows some manipulation of the features of the resulting distribution. Considering the IDAD (16) as a sum of the integrated cross section $(\frac{1}{3}\pi\alpha h\nu)Z_{00} = \sigma$ and periodic perturbations due to the $K=1,2$ terms it is seen from the definitions (15) that the $K=2$ terms have twice the magnitude for linear polarization ($m_p=0$) as for circular polarization ($m_p=\pm 1$), but at the expense of the $K=1$ terms, which vanish for linear polarization. By using the intermediate elliptical polarization (which may be as well, if not as conveniently, represented as a coherent sum of linear and circular polarizations), the distribution may be "tuned" to give maximum structure by changing the degree of elliptical polarization.

DISCUSSION

Because of its simple form and the fact that it depends only on the relative orientations of target and radiation source, the IDAD seems preferable to either the FDAD or FTAD for the determination of site geometry in adsorbed species. Yet, it is not possible to infer directly the orientation of a molecule on a surface from the measurement of this distribution without first making some dynamical assumptions about the adsorption interaction itself; either that it is weak enough that the distribution is dominated by the shape of the "isolated molecule" distribution, so that the orientation can be obtained by comparison with the calculated free-molecule distributions, or that it is known (or assumed) beforehand, so that calculations accounting for the appropriate site geometry may be performed and then compared to experiment. Nonetheless, these are restrictions to which the doubly differential FTAD and FDAD are even more sensitive because of the choice of a particular detection direction, and if one is interested in target orientation alone they are unnecessarily complicated.

There is a case in which an oriented target may be considered to be isolated in space—in a molecular beam at sufficiently low pressure that the interactions with other particles in the beam are negligible. Since the IDAD measures differential cross section as a function of target orientation alone, the photocurrent needs not even to be measured, rather the distribution can be characterized directly by absorption of light as a function of source-beam orientation, and in fact this type of experiment does not require ionization at all. Alternatively, if the photoabsorption accesses a repulsive molecular state, and dissociation is rapid compared to molecular rotation (axial-recoil limit[12]), then the angular distribution of the photofragments gives the IDAD directly. This has been applied recently by Dehmer and Dill[13] to the analysis of $H_2 \rightarrow H + H^+ + e^-$ photofragmentation. Deviations from the axial-recoil limit may be included by the treatment of the target as being in a definite rotational state, i.e., no longer can a particular orientation be assumed, but rather the target will span a distribution of orientations determined by the rotational state distributions.

APPENDIX

The following relations[2] will be used in the manipulations in this Appendix:

(i) The set of Euler angles defining a rotational transformation is related to the set defining the inverse transformation as

$$\hat{R} \equiv \{\alpha, \beta, \gamma\}, \tag{A1a}$$

$$\hat{R}^{-1} = \{-\gamma, -\beta, -\alpha\}. \tag{A1b}$$

(ii) The rotation matrix element with second m index and third Euler angle zero is related to a spherical harmonic in the remaining two angles:

$$D^j_{m0}(\alpha, \beta, 0) = [4\pi/(2j+1)]^{1/2} Y^*_{jm}(\beta, \alpha), \tag{A2}$$

where now (β, α) are equivalent to the usual polar angles.

(iii) The following definition of the spherical harmonic $Y_{lm}(\theta, \phi)$ is used:

$$Y_{lm}(\theta,\phi)=\left[\frac{2l+1}{4\pi}\,\frac{(l-m)!}{(l+m)!}\right]^{1/2}(1/2^l l!)e^{im\phi}(-\sin\theta)^m \times[d/d\cos\theta]^{l+m}(\cos^2\theta-1)^l. \tag{A3}$$

(iv) The orthogonality relation between rotation matrix elements is

$$\int d\hat{R}\,D^{j_1 *}_{\mu_1 m_1}(\hat{R})D^{j_2}_{\mu_2 m_2}(\hat{R})=\frac{8\pi^2}{2j_1+1}\,\delta_{\mu_1\mu_2}\delta_{m_1 m_2}\delta_{j_1 j_2}. \tag{A4}$$

The orientation of the target in the doubly differential cross section (6) is specified by $\hat{R}_\gamma \equiv\{\alpha_\gamma,\beta_\gamma,\gamma_\gamma\}$, the set of Euler angles which carries the target-frame coordinate system into coincidence with the laboratory-frame system. The laboratory-, or photon-frame z axis is taken as the polarization axis for linear polarization axis for linear polarization and the propagation direction for circular polarization, and the frame is therefore cylindrically symmetric about z. Thus, the final Euler rotation, through γ_γ about this axis, is moot and γ_γ may be set equal to zero. If we define the inverse of this transformation as $\hat{R}\equiv\{\alpha,\beta,\gamma\}$, then by Eqs. (A1),

$$\hat{R}_\gamma\equiv\{\alpha_\gamma,\beta_\gamma,\gamma_\gamma\}=\{\alpha_\gamma,\beta_\gamma,0\}, \tag{A5}$$

$$\hat{R}\equiv\{\alpha,\beta,\gamma\}=\hat{R}_\gamma^{-1}=\{0,-\beta_\gamma,-\alpha_\gamma\}, \tag{A6}$$

and we identify $\alpha=0$, $\beta=-\beta_\gamma$, $\gamma=-\alpha_\gamma$. The relation (A2) is applied to the rotation matrix element $D^{K_\gamma}_{M_\gamma 0}(\hat{R}_\gamma)$ in Eq. (5):

$$D^{K_\gamma}_{M_\gamma 0}(\hat{R}_\gamma)=[4\pi/(2K_\gamma+1)]^{1/2}Y^*_{K_\gamma M_\gamma}(\beta_\gamma,\alpha_\gamma), \tag{A7}$$

where $(\beta_\gamma,\alpha_\gamma)$ is equivalent to the set of polar angles of the laboratory $\hat{z}$ direction in the target frame. The harmonic can be expressed in terms of the harmonic in the laboratory frame polar angles of the target by the relationship (A6) and the identifications following:

$$Y^*_{K_\gamma M_\gamma}(\beta_\gamma,\alpha_\gamma)=Y^*_{K_\gamma M_\gamma}(-\beta,-\gamma). \tag{A8}$$

But $Y_{K_\gamma M_\gamma}(-\beta,-\gamma)$ can be related to $Y_{K_\gamma M_\gamma}(\beta,\gamma)$ by explicit substitution into the defining relation (A3):

$$\begin{aligned}Y_{K_\gamma M_\gamma}(-\beta,-\gamma)&=\left(\frac{2K_\gamma+1}{4\pi}\,\frac{(K_\gamma-M_\gamma)!}{(K_\gamma+M_\gamma)!}\right)^{1/2}\\&\quad\times\frac{1}{2^{K_\gamma}K_\gamma!}\,e^{-iM_\gamma\gamma}\,[(-1)(-\sin\beta)]^{M_\gamma}\\&\quad\times\left(\frac{d}{d\cos\beta}\right)^{K_\gamma+M_\gamma}(\cos^2\beta-1)^{K_\gamma}.\\&=(-1)^{M_\gamma}Y^*_{K_\gamma M_\gamma}(\beta,\gamma),\end{aligned} \tag{A9}$$

which leads directly to the relationship in Eq. (12). Using relationship (12) we may rewrite Eq. (11) as

$$\frac{d\sigma}{d\hat{R}}=(4\pi)^{1/2}4\pi^2\alpha h\nu\sum_{lm}\sum_{m_\gamma m'_\gamma}(-1)^{m'_\gamma-m_p}D^{(-)\Gamma}_{lmm'_\gamma p}{}^{*}D^{(-)\Gamma}_{lmm_\gamma 0} \times\sum_{K_\gamma}(1m_\gamma,1-m'_\gamma|K_\gamma M_\gamma)(1m_p,1-m_p|K_\gamma 0)(2K_\gamma+1)^{-1/2}(-1)^{M_\gamma}Y_{K_\gamma M_\gamma}(\beta,\gamma). \tag{A10}$$

The elements of solid Euler angle and solid polar angle are

$$d\hat{R}\equiv(8\pi^2)^{-1}d\alpha\,\sin\beta\,d\beta\,d\gamma, \tag{A11}$$

$$d\Omega\equiv\sin\beta\,d\beta\,d\gamma. \tag{A12}$$

Carrying out the integration over α gives 2π. We can therefore write for Eq. (A10),

$$\frac{d\sigma}{d\hat{R}}=\left(\frac{2\pi}{8\pi^2}\right)\frac{d\sigma}{d\Omega}=(4\pi)^{-1}\frac{d\sigma}{d\Omega}. \tag{A13}$$

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