

Photoelectron spectroscopic studies of polyatomic molecules: Angular momentum transfer and parity unfavoredness

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The angular distribution of electrons ejected in photoionization of nonlinear molecules is resolved into contributions with different angular momentum transfer $l_i = l - l_r$. It is found that, unlike for atomic and linear molecular targets, the photoionization amplitude needs to be characterized not only by a value of l_i but also by its associated projection $|m_i| \leq l_i$. Expressions for ionization amplitudes, cross sections, and asymmetry parameters corresponding to parity-favored and parity-unfavored transitions have been derived. Of the p and d partial waves, which were recently shown to be necessary and sufficient for representing the continuum t_2 orbital of the ejected electron in order to study the hitherto observed angle-resolved photoelectron spectrum of the a_1 orbital in certain T_d molecules, all the amplitudes corresponding to parity-unfavored transitions associated with $l = 1$ are found to vanish identically, while for the d wave both parity-favored and parity-unfavored values of l_i make nonzero contributions. The ratio $\bar{\delta}$ of the parity-unfavored to parity-favored cross sections has been deduced from the experimental measurements as a function of photon energy from ionization threshold to higher values. The analysis reveals that the variations observed in the angular distribution asymmetry as a function of photoelectron energy for ionization in the $4a_1$ orbital of CF_4 , $6a_1$ orbital of CCl_4 , and $7a_1$ orbital of SiCl_4 are due primarily to the dynamical ratio $\bar{\delta}$, because the averaged asymmetry $\langle \bar{\beta}_f \rangle$ for parity-favored transitions always stays close to two and varies little with photon energy.

I. INTRODUCTION

The role of angular momentum transfer has been stressed in the angular distribution of photoelectrons,¹ of scattered particles,² and recently³ in photofragment alignment and orientation. Here the cross section resolves into an incoherent sum of terms for each of the alternative values of the angular momentum transferred during the process under study. The allowed values of the angular momentum transfer in photoionization are $l_i = l - l_r$, where l is the angular momentum of the ejected electron and l_r [$=1$ for electric dipole ($E1$) processes] is the angular momentum of the incident radiation.

Such an angular momentum decomposition has been discussed⁴ to have four main features. Probably the most important¹⁻⁶ one among them is that the anisotropy between the colliding particles or photofragments is analyzed in terms of a new set of continuum amplitudes characterized by the alternative values of the angular momentum transfer. This property holds for photofragmentation in both atomic⁶ and linear^{1,3,5} molecular targets where "reduced" amplitudes are independent of the projection m_i associated with l_i .

It has recently been shown⁷ that if such an analysis is carried out for photoionization in nonlinear molecules, the reduced amplitudes depend not only on l_i but also on its projection $|m_i| \leq l_i$. Therefore the number of such amplitudes now needed is much greater than those three (or one for $l=0$) present in the case of atomic and linear systems. These amplitudes and the subsequent expressions for parity-favored and parity-unfavored com-

ponents of the cross-section ($\bar{\sigma}$) and asymmetry parameter ($\bar{\beta}$) are derived in Sec. II of this paper. $\bar{\beta}$ has been further expressed as a function of $\bar{\delta}$ which is the ratio of the parity-unfavored to parity-favored cross sections recently introduced by Greene and Zare⁸ in the context of photofragment alignment and orientation in diatomic molecules. This section also shows that a selection rule for parity-unfavored transitions in linear molecules is no longer applicable for nonlinear systems.

Recent⁹ analysis of angle-resolved photoelectron spectrum (ARPES) of the a_1 orbital in certain T_d molecules (e.g., CF_4 , CCl_4 , SiCl_4 , etc.) has revealed that it is necessary, and probably sufficient, to represent the continuum t_2 orbital of the photoelectron by p ($l=1$) and d ($l=2$) partial waves only. Contributions of both of these values of l to parity-favored and parity-unfavored transitions are calculated in Sec. III. Variation of the dynamical ratio $\bar{\delta}$ has too been studied in this section as a function of energy of the ionizing radiation. Section IV contains the conclusions of this paper.

II. THEORY

If one formulates the theory for photoionization in nonlinear molecular systems and introduces the angular momentum transfer l_i by recoupling the angular momenta, it can be shown⁷ that the photoelectron angular distribution averaged over all random orientations of the target is given by

$$\frac{d\bar{\sigma}}{d\Omega} = \frac{3}{4} (-1)^{m_r} \left[\frac{e^2}{\alpha E_r} \right]^2 \sum_{l, l', l_t, m_t} (-1)^{l_t} (2l_t + 1) \sqrt{(2l + 1)(2l' + 1)} d_l(l_t, m_t) d_l^*(l_t, m_t) \sum_L (2L + 1) \times \begin{Bmatrix} l & l' & L \\ 0 & 0 & 0 \end{Bmatrix} \begin{Bmatrix} 1 & 1 & L \\ m_r & -m_r & 0 \end{Bmatrix} \begin{Bmatrix} l & 1 & l_t \\ 1 & l' & L \end{Bmatrix} P_L(\cos\theta), \quad (1)$$

where e is the electronic charge, α is the dimensionless fine-structure constant, E_r is the energy of the ionizing radiation whose state of polarization is specified by m_r , [=0 for linear, +1 (-1) for left (right) circular polarization].

The above formulation requires the introduction⁷ of two coordinate systems whose origins coincide with the center of mass of the molecule. One of these two is the photon (or laboratory) frame of reference. Its polar axis is the direction of incidence (electric vector) for unpolarized (linearly polarized) light and the angle θ in (1) is measured with respect to this axis. The second coordinate system is the usual molecule frame of reference. Here the axis of the highest symmetry in the target is the polar (also called the molecular) axis. These two frames of reference are related by appropriate Euler angles.⁷

The reduced photoionization amplitude used in expression (1) is defined in I to be

$$d_l(l_t, m_t) = (-i)^{l_t} e^{i\sigma_l} \sum_{p, \mu, h, m, \lambda_r} (-1)^m \begin{Bmatrix} 1 & l & l_t \\ \lambda_r & -m & m_t \end{Bmatrix} \times b_{hlm}^{p\mu} d_{hl}^{p\mu}(\lambda_r). \quad (2)$$

Here $\sigma_l = \arg(l + 1 + i\eta)$, with

$$\eta k = -\mu_e \left[\sum_{i=1}^N Z_i - (n_e - 1) \right] \frac{e^2}{\hbar^2},$$

is the Coulomb phase of a photoelectron of reduced mass μ_e and wave number k escaping from the field of a molecule consisting of $(n_e - 1)$ electrons and N atoms with their atomic numbers Z_i . Further, the coefficients $b_{hlm}^{p\mu}$ are needed^{10,11} to linearly combine the spherical harmonics Y_l^m in order to form angular basis functions which transform according to the p th irreducible representation (IR) of dimensionality μ of the molecular point symmetry group. The subscript h distinguishes between different basis of an IR belonging to the same l . Finally, $d_{hl}^{p\mu}(\lambda_r)$ are the transition amplitudes⁷ for photoionization in electric dipole ($E1$) approximation. It has already been discussed elsewhere⁷ that m , λ_r , and m_t are the respective projections of l , l_r , and of l_t along the molecular axis (say, Oz').

Equations (1) and (2) can be readily simplified to the forms suitable for linear systems, where the molecular axis is along the line joining all the nuclei and $b_{hlm}^{p\mu} = 1$ always. In such cases the continuum orbital of the photoelectron as well as its IR and dimensionality will all be specified by the projection m of the orbital angular

momentum l along the molecular axis. The reduced amplitude (2) will therefore become

$$d_l(l_t, m_t) = (-i)^{l_t} e^{i\sigma_l} \sum_{m, \lambda_r} (-1)^m \begin{Bmatrix} 1 & l & l_t \\ \lambda_r & -m & m_t \end{Bmatrix} d_{lm}(\lambda_r).$$

The subscript h on the dipole amplitude $d_{hl}^{p\mu}(\lambda_r)$ in the above relation is not needed for linear molecules. The component of the orbital angular momentum along the molecular axis (i.e., the axial angular momentum) is a good quantum number for these systems. Therefore $m_t = m - \lambda_r$ is a conserved quantity and should be equal¹² to the difference $\Lambda - \Lambda'$, where Λ and Λ' are, respectively, the axial angular momenta of the pre- and post-photoionization electronic states of the target. The sum over m_t in the angular distribution (1) therefore collapses to a single term corresponding to $m_t = \Lambda - \Lambda'$. The expressions for reduced amplitude and angular distribution for photoionization in linear systems have been derived earlier by many workers.^{1,5,12,13}

An electron in a nonlinear molecule, unlike in linear targets, does not in general move in an axially symmetric nuclear field. The Hamiltonian of such systems does not therefore commute with the L_z component of the orbital angular momentum \mathbf{L} along the polar axis of the molecule frame. Because the eigenvalue of L_z is not now a conserved quantity, Λ and Λ' are therefore not defined for nonlinear targets. Also, the projection m_t of the angular momentum transfer l_t along the molecular axis is not conserved and, consequently, can take all values commensurate with the $3-j$ symbol present in Eq. (2). Thus, unlike the case of linear molecules discussed above, m_t , for photoionization in nonlinear systems is not restricted to a single value $\Lambda - \Lambda'$. Hence the reduced amplitude (2) for photoionization in such targets can no longer be characterized merely by a value l_t of the angular momentum transfer. Instead, one now needs to use, in addition to l_t , also all values of its associated projection on the molecular axis given by $|m_t| \leq l_t$.

Consequently, the total number of reduced amplitudes to be considered in the present case for a given value of the orbital angular momentum l of the photoelectron will not be three (one) corresponding to $l_t = l - 1$, l , and $l + 1$ ($l_t = 1$ for $l = 0$). Their number, on the other hand, is equal to

$$\sum_{l_t=l-1}^{l+1} (2l_t + 1) = 6l + 3.$$

However, the geometrical function

$$G(l_r=1, m_r, l_l', l_t, \theta) = \frac{1}{4\pi} (-1)^{m_r+l_t} (2l_t+1) \sqrt{(2l+1)(2l'+1)} \\ \times \sum_L (2L+1) \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 & L \\ m_r & -m_r & 0 \end{pmatrix} \begin{pmatrix} l & 1 & l_t \\ 1 & l' & L \end{pmatrix} P_l(\cos\theta)$$

present in the angular distribution (1) is still the same as obtained earlier by Fano and Dill¹ for an $E1$ process in atoms and linear molecules. This is a consequence¹⁴ of the conservation of parity and angular momentum in photoionization and also of random orientation of the target. The parity-favored and parity-unfavored transitions will therefore again be specified by those values of the angular momentum transfer which have already been determined.¹⁵ Parity-unfavored transitions are those¹⁶ for which angular distribution of the escaping particle vanishes in the forward and backward directions. Dill and Fano¹⁵ pointed out that for such transitions in $E1$ photoionization processes $l_t+l+1=\text{odd}$. With this requirement, the parity-favored transitions will naturally correspond to $l_t=l\pm 1$.

Another significant difference from the case of atoms and linear molecules is that both the integrated cross section

$$\bar{\sigma} = \sum_{l_t, m_t} \bar{\sigma}(l_t, m_t) \quad (3)$$

and the angular distribution

$$\frac{d\bar{\sigma}}{d\Omega} = \sum_{l_t, m_t} \frac{d\bar{\sigma}(l_t, m_t)}{d\Omega} \\ = \sum_{l_t, m_t} \frac{\bar{\sigma}(l_t, m_t)}{4\pi} [1 + \bar{\beta}(l_t, m_t) P_2(\cos\theta)] \quad (4)$$

of electrons ejected in photoionization of nonlinear molecular targets are incoherent superposition of terms for different l_t, m_t . On combining Eqs. (3) and (4) one obtains the well-known expression¹⁴

$$\bar{\sigma}_f(l_t, m_t) \bar{\beta}_f(l_t, m_t) = \frac{K}{3} \{ (l_t-1) |d_{l_t-1}(l_t, m_t)|^2 + (l_t+2) |d_{l_t+1}(l_t, m_t)|^2 \\ - 6\sqrt{l_t(l_t+1)} \text{Re}[d_{l_t-1}(l_t, m_t) d_{l_t+1}^*(l_t, m_t)] \} \quad (10a)$$

and, similar to photoionization in atomic and linear targets,^{4,6,15}

$$\bar{\beta}_u(l_t, m_t) = -1 \quad (10b)$$

for all possible values of l_t, m_t .

Although the above relations, which have been arrived at by assuming that the incident light is linearly polarized [i.e., $m_r=0$ in Eq. (1)], are similar to those obtained earlier by Dill and Fano¹⁵ and by Dill^{4,6} for atoms and linear molecules, Eqs. (3)–(10) differ from the earlier results^{4,6,15} in an important respect, namely, the six quantities $\bar{\sigma}_f(l_t, m_t)$, $\bar{\sigma}_u(l_t, m_t)$, $\bar{\sigma}(l_t, m_t)$, $\bar{\beta}_f(l_t, m_t)$, $\bar{\beta}_u(l_t, m_t)$, and $\bar{\beta}(l_t, m_t)$ used in addition to the reduced amplitude $d_l(l_t, m_t)$, are now characterized by both l_t and m_t .

One can readily show from Eq. (2) that the reduced amplitudes

$$\frac{d\bar{\sigma}}{d\Omega} = \frac{\bar{\sigma}}{4\pi} [1 + \bar{\beta} P_2(\cos\theta)] \quad (5)$$

for photoelectron angular distribution averaged over all orientations of the target. The asymmetry parameter in (5) is given by

$$\bar{\beta} = \frac{1}{\bar{\sigma}} \sum_{l_t, m_t} \bar{\sigma}(l_t, m_t) \bar{\beta}(l_t, m_t). \quad (6)$$

In Eqs. (3), (4), and (6)

$$\bar{\sigma}(l_t, m_t) = \bar{\sigma}_f(l_t, m_t) + \bar{\sigma}_u(l_t, m_t), \quad (7)$$

where

$$\bar{\sigma}_f(l_t, m_t) = \frac{K}{3} (2l_t+1) [|d_{l_t-1}(l_t, m_t)|^2 \\ + |d_{l_t+1}(l_t, m_t)|^2] \quad (8a)$$

and

$$\bar{\sigma}_u(l_t, m_t) = (K/3)(2l_t+1) |d_l(l_t, m_t)|^2, \quad (8b)$$

with $K=3\pi(e^2/\alpha E_r)^2$, are the respective contributions of the parity-favored and parity-unfavored values of l_t to the integrated photoionization cross section $\bar{\sigma}(l_t, m_t)$. Further, the asymmetry parameter for each value of l_t, m_t in Eqs. (4) and (6) can readily be shown to be

$$\bar{\sigma}(l_t, m_t) \bar{\beta}(l_t, m_t) = \bar{\sigma}_f(l_t, m_t) \bar{\beta}_f(l_t, m_t) \\ + \bar{\sigma}_u(l_t, m_t) \bar{\beta}_u(l_t, m_t), \quad (9)$$

where

$$d_{l,+1}(l_t, m_t) = i^{l_t+1} e^{i\sigma_{l_t+1}} [(2l_t+1)(2l_t+2)(2l_t+3)]^{-1/2} \\ \times \sum_{p,\mu,h} [\sqrt{(l_t-m_t+1)(l_t-m_t+2)} b_{hl_t+1, m_t-1}^{p\mu} d_{hl_t+1}^{p\mu}(-1) + \sqrt{2(l_t-m_t+1)(l_t+m_t+1)} b_{hl_t+1, m_t}^{p\mu} d_{hl_t+1}^{p\mu}(0) \\ + \sqrt{(l_t+m_t+1)(l_t+m_t+2)} b_{hl_t+1, m_t+1}^{p\mu} d_{hl_t+1}^{p\mu}(1)] \quad (11a)$$

and

$$d_{l,-1}(l_t, m_t) = i^{l_t-1} e^{i\sigma_{l_t-1}} [(2l_t-1)2l_t(2l_t+1)]^{-1/2} \\ \times \sum_{p,\mu,h} [\sqrt{(l_t+m_t-1)(l_t+m_t)} b_{hl_t-1, m_t-1}^{p\mu} d_{hl_t-1}^{p\mu}(-1) - \sqrt{2(l_t-m_t)(l_t+m_t)} b_{hl_t-1, m_t}^{p\mu} d_{hl_t-1}^{p\mu}(0) \\ + \sqrt{(l_t-m_t-1)(l_t-m_t)} b_{hl_t-1, m_t+1}^{p\mu} d_{hl_t-1}^{p\mu}(1)] \quad (11b)$$

are for parity-favored values $l_t = l - 1$ and $l_t = l + 1$, respectively. The parity-unfavored amplitude for $l_t = l$, on the other hand, is given by

$$d_l(l_t, m_t) = -i^{l_t} e^{i\sigma_{l_t}} [(l_t+1)2l_t(2l_t+1)]^{-1/2} \\ \times \sum_{p,\mu,h} [\sqrt{(l_t-m_t+1)(l_t+m_t)} b_{hl_t, m_t-1}^{p\mu} d_{hl_t}^{p\mu}(-1) + \sqrt{2} m_t b_{hl_t, m_t}^{p\mu} d_{hl_t}^{p\mu}(0) \\ - \sqrt{(l_t-m_t)(l_t+m_t+1)} b_{hl_t, m_t+1}^{p\mu} d_{hl_t}^{p\mu}(1)] \quad (12)$$

For $m_t = 0$, this simplifies to

$$d_l(l_t, 0) = i^{l_t} e^{i\sigma_{l_t}} [2(2l_t+1)]^{-1/2} \sum_{p,\mu,h} [b_{hl_t, 1}^{p\mu} d_{hl_t}^{p\mu}(1) - b_{hl_t, -1}^{p\mu} d_{hl_t}^{p\mu}(-1)] \quad (13)$$

It is obvious that none of the reduced amplitudes (11)–(13) will necessarily be zero. Therefore there does not seem to be any general criterion which can be used to find out those parity-favored and/or parity-unfavored amplitudes which vanish identically in photoionization of nonlinear molecules. But in the case of linear targets, there is a well-known selection rule for nonzero parity-unfavored amplitudes. There the necessary condition is that either the change in the axial angular momentum of the molecule should be different from zero^{12(a)} or the interaction of the motion of the photoelectron with the rotation of the nuclei in the residual target be taken into account.⁵ This latter kind of interaction is known^{5,17} to give rise to rotationally induced autoionization (or rotational preionization) in linear systems.

Equation (6) can be written in the following alternative form:

$$\bar{\beta} = \frac{\bar{\sigma}_f}{\bar{\sigma}_f + \bar{\sigma}_u} \frac{\sum_{l_t, m_t} \bar{\sigma}_f(l_t, m_t) \bar{\beta}_f(l_t, m_t)}{\bar{\sigma}_f} - \frac{\bar{\sigma}_u}{\bar{\sigma}_f + \bar{\sigma}_u} \quad (14)$$

where

$$\bar{\sigma}_{f,u} = \sum_{l_t, m_t} \bar{\sigma}_{f,u}(l_t, m_t) \quad (15)$$

by substituting Eqs. (9) and (10b), and combining (3) with (7). If we define the asymmetry parameter averaged over all parity-favored transitions (i.e., averaged parity-favored asymmetry parameter) by

$$\langle \bar{\beta}_f \rangle = \frac{1}{\bar{\sigma}_f} \sum_{l_t, m_t} \bar{\sigma}_f(l_t, m_t) \bar{\beta}_f(l_t, m_t) \quad (16)$$

and use the dynamical ratio⁸

$$\bar{\delta} = \bar{\sigma}_u / \bar{\sigma}_f \quad (17)$$

of the parity-unfavored ($l_t = l$) to the parity-favored ($l_t = l \pm 1$) contributions to the total photoionization cross section, Eq. (14) becomes

$$\bar{\beta} = \frac{1}{1 + \bar{\delta}} (\langle \bar{\beta}_f \rangle - \bar{\delta}) \quad (18)$$

Such partitioning of $\bar{\beta}$ will facilitate, in Sec. III, the interpretation of experimental data according to the contributions of various partial waves to parity-favored and parity-unfavored transitions and will subsequently help in revealing the cause of its variation with energy of the ionizing radiation from threshold to higher values.

III. APPLICATION

Let us consider, as an example, photoionization in the a_1 orbital of T_d molecules. The appropriate dipole amplitudes one needs to consider on the right-hand side of

Eq. (2) are shown⁹ to have the following relationships among themselves:

$$\begin{aligned} d_l^{\mu=1}(0) &= d_l^{\mu=2}(0) = d_l^{\mu=3}(-1) = d_l^{\mu=3}(1) = 0, \\ d_l^{\mu=1}(-1) &= -d_l^{\mu=1}(1) = \frac{1}{\sqrt{2}} d_l^{\mu=3}(0), \\ d_l^{\mu=2}(-1) &= d_l^{\mu=2}(1). \end{aligned} \quad (19)$$

A further simplification

$$d_l^{\mu=2}(1) = -\frac{1}{\sqrt{2}} d_l^{\mu=3}(0) \quad (20)$$

is obtained⁹ if the $l_i=0$ term is only taken into account in the a_1 orbital of the target. The two respective amplitudes $d_1^{\mu=3}(0)$ and $d_2^{\mu=3}(0)$, needed when the photoelectron in the continuum t_2 orbital is represented by p and d partial waves can be the goal of a particular calculational study to obtain d 's from *ab initio* methods. It has also been shown in II that

$$\begin{aligned} |d_1^{\mu=3}(0)|^2 &= \frac{7\bar{\sigma}}{20K} \left(\frac{6}{7} + \bar{\beta} \right), \\ |d_2^{\mu=3}(0)|^2 &= \frac{7\bar{\sigma}}{20K} (2 - \bar{\beta}). \end{aligned} \quad (21)$$

The $\bar{\beta}$ measured for photoionization in the a_1 orbital of all the T_d molecules studied¹⁸⁻²¹ so far is much greater than $-\frac{6}{7}$. The only three such targets known to us for whom both $\bar{\sigma}$ and $\bar{\beta}$ have been measured as a function of photon energy for ionization in some of their orbitals are CCl_4 ,¹⁸ CF_4 ,¹⁹ and SiCl_4 .²¹ It has, therefore, been possible to extract the p - and d -wave probabilities in Eq. (21) for⁹ ionization in the $4a_1$ orbital of CF_4 and the $6a_1$ orbital of CCl_4 from the ARPES taken by Carlson *et al.*¹⁹ and Carlson *et al.*,¹⁸ respectively, and also for²² the $7a_1$ orbital of SiCl_4 from the recently measured ARPES by Carlson *et al.*²¹

The allowed parity-favored values in the present case are 0,2 and 1,3 while parity-unfavored values are 1 and 2 corresponding, respectively, to $l=1$ and $l=2$ orbital angular momentum of the escaping electron. Using the relations (19), we find that the parity-favored reduced amplitudes

$$d_1(0,0) = -ie^{i\sigma_1}(2/3)^{1/2} [d_1^{\mu=2}(1) - \sqrt{2}d_1^{\mu=3}(0)] \quad (22)$$

for $l=1$ and

$$d_2(1,-1) = d_2(1,0) = d_2(1,1) = 0 \quad (23)$$

for $l=2$ are obtained from Eq. (11a). Equation (11b) gives

$$\begin{aligned} d_1(2,-1) &= d_1(2,1) = 0, \\ d_1(2,-2) &= d_1(2,2) = \sqrt{3/2} d_1(2,0) \\ &= -i \frac{e^{i\sigma_1}}{2\sqrt{5}} [\sqrt{2}d_1^{\mu=2}(1) + d_1^{\mu=3}(0)] \end{aligned} \quad (24)$$

and

$$\begin{aligned} d_2(3,-3) &= d_2(3,-1) = d_2(3,0) \\ &= d_2(3,1) = d_2(3,3) = 0, \\ d_2(3,-2) &= -d_2(3,2) \\ &= -\frac{e^{i\sigma_2}}{\sqrt{21}} [d_2^{\mu=2}(1) + \sqrt{2}d_2^{\mu=3}(0)] \end{aligned} \quad (25)$$

for $l=1$ and $l=2$, respectively. Similarly, the following parity-unfavored amplitudes can be calculated from Eq. (12):

$$d_1(1,-1) = d_1(1,0) = d_1(1,1) = 0 \quad (26)$$

for $l=1$ and

$$\begin{aligned} d_2(2,-1) &= d_2(2,1) = 0, \\ d_2(2,-2) &= d_2(2,2) = -\frac{1}{\sqrt{6}} d_2(2,0) \\ &= -\frac{e^{i\sigma_2}}{2\sqrt{15}} [\sqrt{2}d_2^{\mu=2}(1) - d_2^{\mu=3}(0)] \end{aligned} \quad (27)$$

for $l=2$.

It is obvious from Eqs. (22)–(25) that for the parity-favored transition $l_i=l-1$, all three amplitudes associated with d wave vanish identically; but both p and d waves have some of their amplitudes nonzero for $l_i=l+1$. Equations (26) and (27), on the other hand, reveal that among the parity-unfavored reduced amplitudes, only three of the five associated with $l_i=l=2$ (i.e., d wave) are nonzero, while all those corresponding to p partial wave (i.e., $l_i=l=1$) vanish.

Substitution of the amplitudes (22)–(27) in Eqs. (8a) and (8b) gives the respective contributions of the parity-favored and parity-unfavored transition to photoionization cross section for various values of l_i, m_i as follows:

$$\begin{aligned} \bar{\sigma}_f(0,0) &= \frac{K}{3} |d_1(0,0)|^2, \\ \bar{\sigma}_f(1,-1) &= \bar{\sigma}_f(1,0) = \bar{\sigma}_f(1,1) = 0, \\ \bar{\sigma}_f(2,-1) &= \bar{\sigma}_f(2,1) = 0, \\ \bar{\sigma}_f(2,-2) &= \bar{\sigma}_f(2,2) = \frac{3}{2} \bar{\sigma}_f(2,0) \\ &= \frac{5}{2} K |d_1(2,0)|^2, \\ \bar{\sigma}_f(3,-3) &= \bar{\sigma}_f(3,-1) = \bar{\sigma}_f(3,0) \\ &= \bar{\sigma}_f(3,1) = \bar{\sigma}_f(3,3) = 0, \\ \bar{\sigma}_f(3,-2) &= \bar{\sigma}_f(3,2) = \frac{7}{3} K |d_2(3,2)|^2, \end{aligned} \quad (28)$$

and

$$\begin{aligned} \bar{\sigma}_u(1,-1) &= \bar{\sigma}_u(1,0) = \bar{\sigma}_u(1,1) = 0, \\ \bar{\sigma}_u(2,-1) &= \bar{\sigma}_u(2,1) = 0, \\ \bar{\sigma}_u(2,-2) &= \bar{\sigma}_u(2,2) = \frac{1}{6} \bar{\sigma}_u(2,0) \\ &= \frac{5}{18} K |d_2(2,0)|^2. \end{aligned} \quad (29)$$

The cross-section

$$\bar{\sigma}_f = \frac{2K}{3} \begin{cases} |d_1^{\mu=2}(1)|^2 + |d_1^{\mu=3}(0)|^2 & \text{for } l=1, \\ |d_1^{\mu=2}(1)|^2 + |d_1^{\mu=3}(0)|^2 + \frac{1}{3}(|d_2^{\mu=2}(1)|^2 + 2|d_2^{\mu=3}(0)|^2 + 2\sqrt{2}\text{Re}\{d_2^{\mu=2}(1)[d_2^{\mu=3}(0)]^*\}) & \text{for } l=1,2, \end{cases} \quad (30)$$

for parity-favored transitions is obtained by combining (28) with (15). On the other hand, if (29) is substituted in (15), one gets

$$\bar{\sigma}_u = \frac{2K}{9} \begin{cases} 0 & \text{for } l=1, \\ 2|d_2^{\mu=2}(1)|^2 + |d_2^{\mu=3}(0)|^2 - 2\sqrt{2}\text{Re}\{d_2^{\mu=2}(1)[d_2^{\mu=3}(0)]^*\} & \text{for } l=1,2, \end{cases} \quad (31)$$

for parity-unfavored transitions. We thus have from the last equation that the p wave in the continuum t_2 orbital of the photoelectron makes no contribution to the parity-unfavored cross section.

In order to calculate $\bar{\sigma}_f$ and $\bar{\sigma}_u$ within the approximation discussed at the beginning of this section, one merely needs to substitute two relations (20) and (21) in each of the Eqs. (30) and (31) which, respectively, give

$$\bar{\sigma}_f = \begin{cases} K |d_1^{\mu=3}(0)|^2 = \bar{\sigma} & \text{for } l=1, \\ K(|d_1^{\mu=3}(0)|^2 + \frac{1}{9}|d_2^{\mu=3}(0)|^2) = \frac{\bar{\sigma}}{45}(17+14\bar{\beta}) & \text{for } l=1,2 \end{cases} \quad (32)$$

and

$$\bar{\sigma}_u = \begin{cases} 0 & \text{for } l=1, \\ \frac{8}{9}K |d_2^{\mu=3}(0)|^2 = \frac{14}{45}\bar{\sigma}(2-\bar{\beta}) & \text{for } l=1,2, \end{cases} \quad (33)$$

so that $\bar{\sigma}_f + \bar{\sigma}_u = \bar{\sigma}$ always. From known values of both $\bar{\sigma}$ and $\bar{\beta}$ one can readily obtain the contributions of parity-favored as well as parity-unfavored transitions to

the photoionization cross section.

Similarly, the parity-favored components

$$\begin{aligned} \bar{\beta}_f(0,0) &= 2, \\ \bar{\beta}_f(1,m_l) &= 1, \quad |m_l| \leq 1 \\ \bar{\beta}_f(2,m_l) &= \frac{1}{5}, \quad |m_l| \leq 2 \\ \bar{\beta}_f(3,m_l) &= \frac{2}{7}, \quad |m_l| \leq 3 \end{aligned} \quad (34)$$

of the asymmetry are readily obtained by substituting Eqs. (22)–(25) and (28) in (10a). The parity-unfavored asymmetry parameter, on the other hand, has already been shown in Eq. (10b) to be always equal to -1 for all values of l, m_l .

The averaged parity-favored asymmetry parameter $\langle \bar{\beta}_f \rangle$ can be obtained in two ways. If one wants to use the reduced amplitudes (22)–(25), one will then need to substitute Eq. (10a) in the numerator and Eqs. (15) and (8a) in the denominator of Eq. (16). Alternatively, it can be obtained by using the parity-favored cross section (30) and its components (28) along with those of the asymmetry parameter (34) in the definition (16). These finally give

$$\langle \bar{\beta}_f \rangle = \frac{2}{3} \begin{cases} \frac{\frac{6}{5}|d_1^{\mu=2}(1)|^2 + \frac{21}{10}|d_1^{\mu=3}(0)|^2 - (9\sqrt{2}/5)\text{Re}\{d_1^{\mu=2}(1)[d_1^{\mu=3}(0)]^*\}}{|d_1^{\mu=2}(1)|^2 + |d_1^{\mu=3}(0)|^2} & \text{for } l=1, \\ \left[\frac{\frac{6}{5}|d_1^{\mu=2}(1)|^2 + \frac{21}{10}|d_1^{\mu=3}(0)|^2 - (9\sqrt{2}/5)\text{Re}\{d_1^{\mu=2}(1)[d_1^{\mu=3}(0)]^*\}}{+ \frac{1}{7}(|d_2^{\mu=2}(1)|^2 + 2|d_2^{\mu=3}(0)|^2 + 2\sqrt{2}\text{Re}\{d_2^{\mu=2}(1)[d_2^{\mu=3}(0)]^*\})} \right] \\ \times [|d_1^{\mu=2}(1)|^2 + |d_1^{\mu=3}(0)|^2 + \frac{1}{3}(|d_2^{\mu=2}(1)|^2 + 2|d_2^{\mu=3}(0)|^2 + 2\sqrt{2}\text{Re}\{d_2^{\mu=2}(1)[d_2^{\mu=3}(0)]^*\})]^{-1} & \text{for } l=1,2. \end{cases} \quad (35)$$

Similarly, an expression for the dynamical ratio $\bar{\delta}$ in terms of the dipole amplitudes can be found by substituting in Eq. (17) either the cross sections (30) and (31) or Eq. (15) along with (8) and the reduced amplitudes (22)–(27).

$$\bar{\delta} = \begin{cases} 0 & \text{for } l=1, \\ (2|d_2^{\mu=2}(1)|^2 + |d_2^{\mu=3}(0)|^2 - 2\sqrt{2}\text{Re}\{d_2^{\mu=2}(1)[d_2^{\mu=3}(0)]^*\}) \\ \times (3[|d_1^{\mu=2}(1)|^2 + |d_1^{\mu=3}(0)|^2] + |d_2^{\mu=2}(1)|^2 + 2|d_2^{\mu=3}(0)|^2 + 2\sqrt{2}\text{Re}\{d_2^{\mu=2}(1)[d_2^{\mu=3}(0)]^*\})^{-1} & \text{for } l=1,2. \end{cases} \quad (36)$$

The result $\bar{\delta}=0$ for $l=1$ is in conformity with the observation made earlier that the parity-unfavored cross section $\bar{\sigma}_u$ is zero when the ejected electron in photoionization in the a_1 orbital of T_d molecules is being represented by only p wave. According to Eq. (18), $\bar{\beta}$ in such cases becomes exactly equal to $\langle\bar{\beta}_f\rangle$ which is given by the first of Eqs. (25).

If use is made of relation (20), the expressions (35) and (36) for $\langle\bar{\beta}_f\rangle$ and $\bar{\delta}$, respectively, reduce to the following simple forms:

$$\langle\bar{\beta}_f\rangle = 2 \begin{cases} 1 & \text{for } l=1, \\ \frac{|d_1^{\mu=3}(0)|^2 + \frac{1}{63}|d_2^{\mu=3}(0)|^2}{|d_1^{\mu=3}(0)|^2 + \frac{1}{9}|d_2^{\mu=3}(0)|^2} & \text{for } l=1,2 \end{cases} \quad (37)$$

and

$$\bar{\delta} = \begin{cases} 0 & \text{for } l=1, \\ \frac{8}{9} \frac{|d_2^{\mu=3}(0)|^2}{|d_1^{\mu=3}(0)|^2 + \frac{1}{9}|d_2^{\mu=3}(0)|^2} & \text{for } l=1,2 \end{cases} \quad (38)$$

Substituting the amplitudes (21) in Eqs. (37) and (38), we finally obtain

$$\langle\bar{\beta}_f\rangle = \begin{cases} 2 & \text{for } l=1, \\ \frac{\frac{28}{31} + \bar{\beta}}{\frac{31}{14} + \bar{\beta}} & \text{for } l=1,2 \end{cases} \quad (39)$$

and

$$\bar{\delta} = \begin{cases} 0 & \text{for } l=1, \\ \frac{2 - \bar{\beta}}{\frac{17}{14} + \bar{\beta}} & \text{for } l=1,2. \end{cases} \quad (40)$$

The $\langle\bar{\beta}_f\rangle$ calculated from Eq. (39) and $\bar{\delta}$ from (40) as a function of photon energy using the asymmetry parameter measured by Carlson *et al.* for ionization in the $4a_1$ orbital of CF_4 ,¹⁹ $6a_1$ orbital of CCl_4 ,¹⁸ and $7a_1$ orbital of SiCl_4 ,²¹ are shown in Figs. 1–3, respectively. These figures also contain, along with $\bar{\beta}_u = -1$, the pure p -wave values $\langle\bar{\beta}_f\rangle = 2$ and $\bar{\delta} = 0$ for all photon energies considered here. It is therefore obvious from Eqs. (18), (39), and (40) that if one represents the ejected electron by only $l=1$ partial wave, the resulting asymmetry parameter is independent of the energy of the ionizing radiation⁹ with $\bar{\beta} = 2$ arising completely from the parity-favored angular momentum transfer $l_t = l - 1$ [see Eq. (34)]. Further, Eqs. (32) and (33) tell us that the integrated photoionization cross section in this case is exactly equal to that of the parity-favored transitions.

The three accompanying figures also point out that when both p and d waves are included in the continuum

t_2 orbital of the photoelectron, both $\langle\bar{\beta}_f\rangle$ and $\bar{\delta}$, and hence $\bar{\beta}$, vary with photon energy. Parity-favored as well as parity-unfavored transitions make nonzero contributions for d wave with $l_t = l + 1 = 3$ and $l_t = l = 2$, respectively [see the reduced amplitudes (22)–(27)]. Therefore the observed variation in the asymmetry parameter $\bar{\beta}$ with photon energy for ionization in the a_1 orbital of CF_4 , CCl_4 , and SiCl_4 is due to the presence of nonvanishing parity-favored and parity-unfavored contributions associated with $l=2$ orbital angular momentum of the ejected electron. This represents the dynamical difference between the p and d waves in the t_2 continuum orbital of the photoelectron.

The other interesting thing which needs to be considered is that although δ varies rapidly over the whole range of photon energy considered in the three figures when both $l=1$ and 2 are included in the continuum orbital, $\langle\bar{\beta}_f\rangle$ stays close to two and varies little in Figs. 2 and 3 at all energies and in Fig. 1 at higher energies of the ionizing radiation. This feature clearly indicates that as far as variations in $\bar{\beta}$ at higher photon energies are concerned they are due primarily to contributions of the parity-unfavored transitions $l_t = l = 2$ contained in the

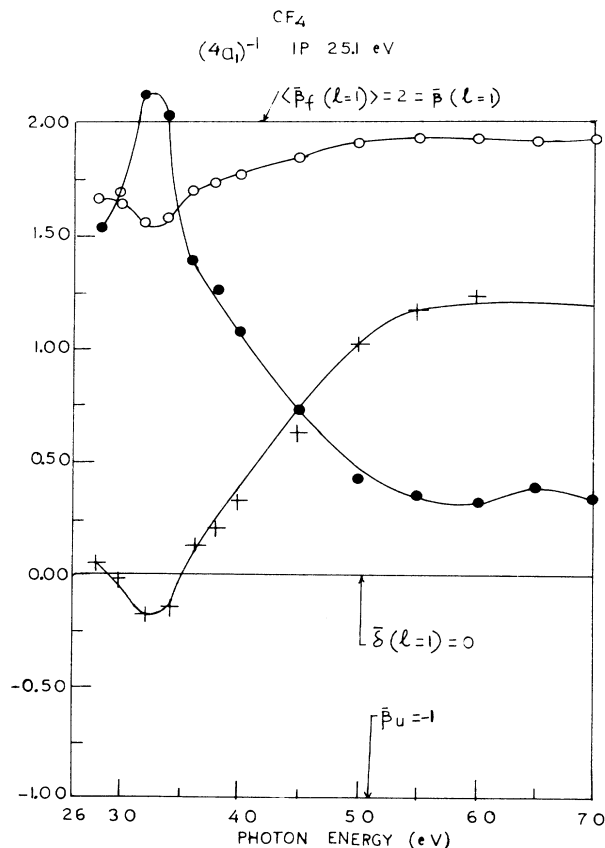


FIG. 1. Variation of $\bar{\beta}$, $\bar{\delta}$, $\bar{\beta}_u$, and $\langle\bar{\beta}_f\rangle$ with photon energy for ionization in the $4a_1$ orbital of CF_4 . Experimental values of $\bar{\beta}$ measured by Carlson *et al.* (Ref. 19), +; $\langle\bar{\beta}_f\rangle$ calculated from Eq. (39) for $l=1$ and 2 , \circ ; $\bar{\delta}$ calculated from Eq. (40) for $l=1$ and 2 , \bullet .

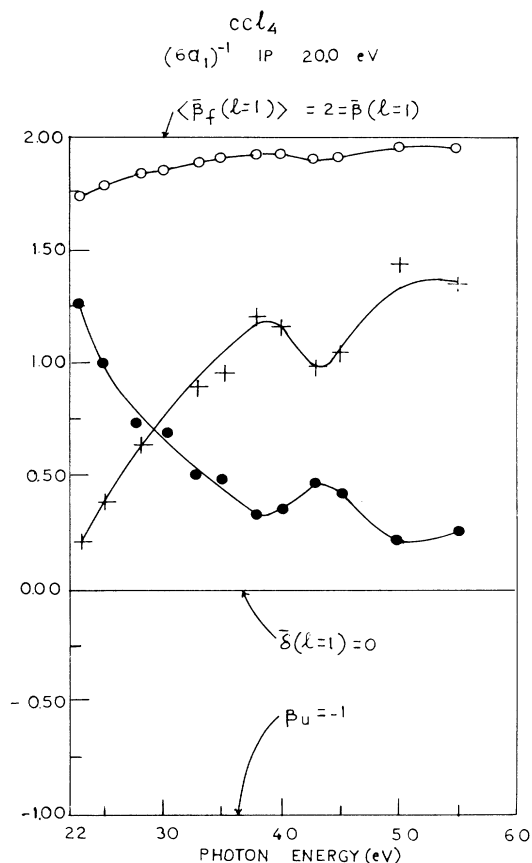


FIG. 2. Same as Fig. 1 but for photoionization in the $6a_1$ orbital of CCl_4 . The experimental values of $\bar{\beta}$ are taken from Carlson *et al.* (Ref. 18).

cross-section ratio $\bar{\delta}$. The parity-favored transitions for both partial waves vary little even close to threshold at least for ionization in the $6a_1$ orbital of CCl_4 and the $7a_1$ orbital of $SiCl_4$. But in the case of ionization in the $4a_1$ orbital of CF_4 , there is a significant departure of $\langle \bar{\beta}_f \rangle$ in Fig. 1 from its pure- p wave value of two, accompanied with a very rapid variation, at photon energies close to threshold.

The present analysis also reveals that the contribution to cross section of the parity-favored transitions is always greater than that of the parity-unfavored transitions (i.e., $\bar{\delta} < 1$) except for photoelectron energies less than 16 and 5 eV in Figs. 1 and 2, respectively. In the former case, $\bar{\delta}$ has exceeded not only $\langle \bar{\beta}_f \rangle$ at photon energies between approximately 29 to 35 eV where experimentally measured $\bar{\beta}$ is negative, it has even become greater than two indicating that the parity-unfavored cross section for this range of energy of the ionizing ra-

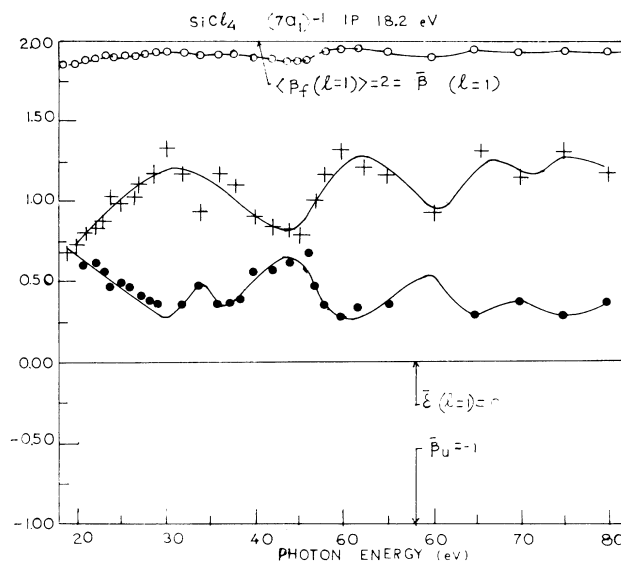


FIG. 3. Same as Fig. 1 but for photoionization in the $7a_1$ orbital of $SiCl_4$. The experimental values of $\bar{\beta}$ are taken from Carlson *et al.* (Ref. 21).

diation is more than twice that of the parity-favored transitions.

IV. CONCLUSION

This paper formulates a theory for photoionization in nonlinear molecules in terms of angular momentum transfer and parity-favored and parity-unfavored transitions. It is shown that the present theory is different from that for linear systems because the projection of the orbital angular momentum along the molecular axis in nonlinear targets is not a conserved quantum number. The theory has been applied to photoionization in the a_1 orbital of certain T_d molecules. The cross-section ratio $\bar{\delta}$, which is a quantitative specification of the parity-favored and parity-unfavored path ways, has been calculated. The asymmetry parameter has been expressed as a function of $\bar{\delta}$ which shows that the variations as a function of photon energy in the experimentally measured $\bar{\beta}$ for ionization in the $4a_1$ orbital of CF_4 , the $6a_1$ orbital of CCl_4 , and the $1a_1$ orbital of $SiCl_4$ are due primarily to the contributions of parity-unfavored transitions to the cross-section ratio $\bar{\delta}$.

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