

Angular distribution of photofragments along a Fano profile

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For incident linearly polarized light and randomly oriented molecules, the angular distribution of photofragments has a dipolar pattern. It will be shown that along a Fano profile, the resonance, interference, and continuum terms have different β parameters, each of which will be discussed in a form directly related to an experiment.

I. INTRODUCTION

Recently, the angular distribution of photodissociated fragments has been investigated along the Fano profile of a well-resolved rotational predissociated line [1]. The theoretical studies of angular distribution of photofragments refer to direct dissociations of a well-defined continuum [2–5]. The predissociation case had been considered formally by Mukamel and Jortner [6] and applied in the case of broadband excitation for which predissociated rotational lines are not resolved [7]. They noted that their equations could apply to a Fano profile [8] and might be of experimental interest but did not go further.

According to Fano's approach [8], the total absorption cross section for a line profile can be decomposed into a part due to the continuum, a part due to the resonance line, and a third part with a dispersion shape due to the interference between the two channels, resulting in an asymmetrical well-known profile. The differential cross section for directional photodissociation can be decomposed in the same way. We will show below that each of the contributing terms has a specific angular distribution. For molecules that are initially randomly oriented and for incident linearly polarized light, these distributions have a dipolar behavior characterized by a β parameter:

$$\begin{aligned} \frac{d\sigma}{dk} = & (\sigma_{\text{cont}}/4\pi)[1 + \beta_{\text{cont}}P_2(\cos\theta)] \\ & + (\sigma_{\text{res}}/4\pi)[1 + \beta_{\text{res}}P_2(\cos\Theta)] \\ & + (\sigma_{\text{int}}/4\pi)[1 + \beta_{\text{int}}P_2(\cos\Theta)] \end{aligned} \quad (1)$$

where $P_2(\cos\Theta)$ is the second Legendre polynomial:

$$P_2 = \frac{1}{2}(3 \cos^2\Theta - 1). \quad (2)$$

The aim of this paper is to verify Eq. (1) and to calculate the β parameters, which will provide expressions easily related to experiments.

The Fano formalism may be considered as somewhat dated but is much easier to use for experimentalists than more powerful formalisms like multichannel quantum-defect theory (MQDT) which may be applied to the problem [9].

II. GENERAL FORMALISM

Let us consider the dissociation of a diatomic molecule characterized by three electronic states: the initial bound state $|i\rangle$, an excited bound state $|r\rangle$, and a dissociative state $|d\rangle$.

The total dissociation cross section is given by [8,10]

$$\begin{aligned} \sigma = (8\pi^3/\lambda) \sum_{J', M_i} & \left| \langle i | \mathbf{e}_\lambda \cdot \mathbf{M} | d \rangle \frac{E - E_{J'}}{E - E_{J'} + i\Gamma_{J'}/2} \right. \\ & + \langle i | \mathbf{e}_\lambda \cdot \mathbf{M} | r \rangle \\ & \left. \times \langle r | H | d \rangle / (E - E_{J'} + i\Gamma_{J'}/2) \right|^2 \\ & \times \rho_{M_i} / (2J_i + 1) \end{aligned} \quad (3)$$

where the unperturbed continuum $|d\rangle$ state is assumed energy normalized. Let λ be the wavelength of the incident photon, \mathbf{e}_λ its polarization vector, \mathbf{M} the dipole moment operator, H the coupling Hamiltonian, E_J the energy of the bound excited level, and Γ_J its width. The cross sections for the various initial M_i substates have to be considered with their individual probabilities ρ_{M_i} , as well as the contributions from the various rotational transitions. The first energy factor comes from the phase shift due to the coupling of the resonance state [8].

In Eq. (3), the molecular states are described in the usual Born-Oppenheimer basis set:

$$\begin{aligned} \Psi_{v, J, M, \Omega} = & \varphi_\Omega(\mathbf{r}, R)(1/R)\chi_{vJ\Omega}(R) \\ & \times [(2J+1)/4\pi]^{1/2} D_{M\Omega}^{J*}(\varphi, \theta, 0) \end{aligned} \quad (4)$$

where \mathbf{r} represents the electronic coordinates, and R , θ , and φ the polar coordinates of the internuclear axis with respect to the laboratory-fixed frame. $D_{M\Omega}^J$ is the Wigner rotation matrix element [11]. The vibrational quantum number v is replaced by ϵ for the dissociating state. The notation corresponds to Hund's case (a); for Hund's case (b) $J = N$ and $\Omega = \Lambda$.

For directional photodissociation, it is more appropriate to consider dissociative wave functions which at infinity behave like an outgoing plane wave moving in the \mathbf{k} direction with respect to the laboratory-fixed frame:

$$|k, d\rangle = (4\pi)^{1/2} \sum_{J', M'} (2J' + 1)^{1/2} i^{J'} \exp(-i\delta_{J'\Omega_d}) \times \Psi_{\epsilon, J', M', \Omega_d} D_{M', \Omega_d}^{J'}(\phi, \Theta, 0) \quad (5)$$

where ϕ and Θ are the two polar angles defining the \mathbf{k}

direction, and the factor $\delta_{J'\Omega_d}$ is the phase shift of the vibrational part of the dissociative wave function, which has the asymptotic form at $R \rightarrow \infty$:

$$\chi_{\epsilon, J', \Omega_d} \rightarrow (2\mu/\pi\hbar^2 k)^{1/2} \sin(kR + \delta_{J'\Omega_d} - \frac{1}{2}\pi J') \quad (6)$$

The differential cross section for photodissociation into a solid angle $dk = \sin\Theta d\Theta d\phi$ around the \mathbf{k} direction, according to Ref. [6] and taking into account the phase shift due to the coupling is given by

$$\frac{d\sigma}{dk} = \frac{2\pi^2}{\lambda} \sum_{M_i, J', \Omega_d = \pm|\Omega_d|} |\langle i | \mathbf{e}_\lambda \cdot \mathbf{M} | k, d \rangle \langle E - E_{J'} \rangle / (E - E_{J'} + i\Gamma_{J'}/2) + \langle i | \mathbf{e}_\lambda \cdot \mathbf{M} | r \rangle \langle r | H | k, d \rangle / (E - E_{J'} + i\Gamma_{J'}/2)|^2 \rho_{M_i} / (2J_i + 1) \quad (7a)$$

with

$$\langle i | \mathbf{e}_\lambda \cdot \mathbf{M} | k, d \rangle = \sum_{J', M'} \langle i | \mathbf{e}_\lambda \cdot \mathbf{M} | d \rangle (4\pi)^{1/2} (2J' + 1)^{1/2} i^{J'} \exp(-i\delta_{J'\Omega_d}) D_{M', \Omega_d}^{J'}(\phi, \Theta, 0) \quad (7b)$$

The polarization vector e_λ is expressed in spatial components:

$$e_0 = \mathbf{e}_\lambda \cdot \mathbf{z} \quad \text{and} \quad e_{\pm 1} = \mp 2^{1/2} (\mathbf{e}_\lambda \cdot \mathbf{x} \pm i \mathbf{e}_\lambda \cdot \mathbf{y}) \quad (8)$$

and the dipole matrix element is equal to [5]

$$\begin{aligned} \langle i | \mathbf{e}_\lambda \cdot \mathbf{M} | d \rangle = & \sum_{q=0, \pm 1} (-1)^q e_{-q} [(2J' + 1)(2J_i + 1)/2]^{1/2} (-1)^{2J_i + M_i - \Omega_d} \begin{bmatrix} J' & 1 & J_i \\ -M' & q & M_i \end{bmatrix} \\ & \times \sum_{p=0, \pm 1} \left[\langle \chi_{\epsilon J' \Omega_d} | M_p(R) | \chi_{v_i J_i \Omega_i} \rangle \begin{bmatrix} J' & 1 & J_i \\ -\Omega_d & p & \Omega_i \end{bmatrix} \right. \\ & \left. + (-1)^{P_i} \langle \chi_{\epsilon J' \Omega_d} | M_p(R) | \chi_{i J_i - \Omega_i} \rangle \begin{bmatrix} J' & 1 & J_i \\ -\Omega_d & p & -\Omega_i \end{bmatrix} \right] \quad (9) \end{aligned}$$

where the terms in large parentheses are $3j$ symbols. The definite parity P_i of the bound state $|i\rangle$ has been taken into account. For an incident light linearly polarized along the z direction, e_0 is the only nonzero component whereas $e_{\pm 1}$ describes circularly polarized light propagating along the z direction. According to the symmetry rules of the $3j$ coefficients, the summation over p reduces to one term except when one of the states is a Σ state (in such a case only the normalization factor differs).

The second dipole matrix element of Eq. (7) can be written in a way similar to Eq. (9), taking into account the definite parity of both $|i\rangle$ and $|r\rangle$ states.

We consider the case of an isolated rotational predissociated level J'_r , which means that

$$|E_{J'} - E_{J'_r}| \gg \Gamma_{J'} \quad \text{for} \quad J' \neq J'_r.$$

The energy denominator of Eq. (7) is resonant here only for $J' = J'_r$ and Eq. (7) can be written explicitly, taking into account the parity of the states (E_r will be used instead of $E_{J'_r}$ and Γ_r instead of $\Gamma_{J'_r}$ for the sake of simplicity):

$$\begin{aligned}
\frac{d\sigma}{dk} = & (2\pi^2/\lambda) \sum_{M_i, \Omega_d = \pm|\Omega_d|} \frac{1}{2} \rho_{M_i} \sum_{J'_1} \left\{ (2J'_1 + 1) \begin{bmatrix} J'_1 & 1 & J_i \\ -M_i & 0 & M_i \end{bmatrix} \right. \\
& \times \begin{bmatrix} \tilde{M}_{\epsilon J'_1} \begin{bmatrix} J'_1 & 1 & J_i \\ -\Omega_d & p & \Omega_i \end{bmatrix} \\
& \left. + (-1)^{\Omega_r - \Omega_d} M_r \tilde{V}_r \delta(J_r, J'_1) \begin{bmatrix} J'_1 & 1 & J_i \\ -\Omega_r & p' & \Omega_i \end{bmatrix} / (E - E_r + i\Gamma_r/2) \right\} \\
& \times \sum_{J'_2} \left\{ (2J'_2 + 1) \begin{bmatrix} J'_2 & 1 & J_i \\ -M_i & 0 & M_i \end{bmatrix} \right. \\
& \times \begin{bmatrix} \tilde{M}_{\epsilon J'_2}^* \begin{bmatrix} J'_2 & 1 & J_i \\ -\Omega_d & p & \Omega_i \end{bmatrix} \\
& \left. + (-1)^{\Omega_r - \Omega_d} M_r^* \tilde{V}_r^* \delta(J_r, J'_2) \begin{bmatrix} J'_2 & 1 & J_i \\ -\Omega_r & p' & \Omega_i \end{bmatrix} / (E - E_r - i\Gamma_r/2) \right\} \\
& \times D_{M_i, \Omega_d}^{J'_1}(\phi, \Theta, 0) D_{M_i, \Omega_d}^{J'_2*}(\phi, \Theta, 0) . \tag{10}
\end{aligned}$$

The following reduced notations have been used:

$$\begin{aligned}
M_r &= \langle \chi_{v, J_i, \Omega_i} | M_p(R) | \chi_{v, J_r, \Omega_r} \rangle , \\
\tilde{V}_r &= i^{J'_r} \exp(-i\delta_{J'_r, \Omega_d}) \langle r | H | d \rangle \tag{11a}
\end{aligned}$$

with

$$\Gamma_r = 2\pi |\tilde{V}_r|^2 .$$

For $J' = J'_r$ according to Fano's approach [8], the phase shift due to the coupling with the resonance state has already been taken into account and $\delta_{J'_r}$ is the unperturbed phase. The dipole matrix element of the continuum perturbed by the coupling is

$$\tilde{M}_{\epsilon J'_r} = (E - E_r) / (E - E_r + i\Gamma_r/2) i^{J'_r} \exp(-i\delta_{J'_r}) \langle \chi_{v, J_i, \Omega_i} | M_p(R) | \chi_{\epsilon J'_r, \Omega_d} \rangle . \tag{11b}$$

Far from the resonance energy, the perturbed value tends toward the unperturbed value. The perturbation of the phase of the continuum explains the dip in the Fano profile with $Q=0$. It reduced to $\tilde{M}_{\epsilon J'} = i^{J'} \exp(-i\delta_{J', \Omega_d}) \langle \chi_{v, J_i, \Omega_i} | M_q(R) | \chi_{\epsilon J', \Omega_d} \rangle$ for $J' \neq J'_r$ as $\Gamma_{J'} \ll |E_{J'} - E_{J'_r}|$.

According to Ref. [11], the product of the Wigner matrix elements of Eq. (10) reduces to

$$D_{M_i, \Omega_d}^{J'_1}(\phi, \Theta, 0) D_{M_i, \Omega_d}^{J'_2*}(\phi, \Theta, 0) = \sum_j (-1)^{M_i - \Omega_d} P_j(\cos\Theta) (2j+1) \begin{bmatrix} J'_1 & J'_2 & j \\ \Omega_d & -\Omega_d & 0 \end{bmatrix} \begin{bmatrix} J'_1 & J'_2 & j \\ M_i & -M_i & 0 \end{bmatrix} . \tag{12}$$

P_j denotes the Legendre polynomial of j th order. Then from Eq. (12), the differential cross section of Eq. (10) can be easily analyzed in terms of Legendre polynomials.

Equation (10) includes a summation over j which leads to the angular distribution, and summations over J'_1, J'_2, M_i , and Ω_d . The last summation over Ω_d just compensates for the $\frac{1}{2}$ factor [in Eq. (10)] due to the symmetrization of the bound wave function. For linearly polarized light ($q=0$), the summation over M_i gives a simple expression if all the M_i sublevels are equally populated, i.e., if

$$\rho_{M_i} = 1$$

which means that the molecules are initially randomly oriented:

$$\sum_{M_i} (-1)^{M_i - \Omega_d} \begin{bmatrix} J'_1 & 1 & J_i \\ -M_i & 0 & M_i \end{bmatrix} \begin{bmatrix} J'_2 & 1 & J_i \\ -M_i & 0 & M_i \end{bmatrix} \begin{bmatrix} J'_1 & J'_2 & j \\ M_i & -M_i & 0 \end{bmatrix} = (-1)^{J'_1 + J'_2 + J_i - \Omega_d} \begin{bmatrix} 1 & 1 & j \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 1 & 1 & j \\ J'_1 & J'_2 & J_i \end{bmatrix} \tag{13}$$

with a $6j$ coefficient. The above expression will not be zero if the j variable is equal to 0 or 2, according to the $3j$

coefficient properties [11]. The $j=0$ value, with P_0 , corresponds to the isotropic part of the differential cross section, whereas the $j=2$ value leads to the $P_2(\cos\Theta)$ expected contribution. It is important to notice that if the ρ_{M_i} coefficients are not all equal to 1, Eq. (13) is much more complicated, with j values from 0 to maybe $2J_i+4$, all even for linearly polarized light, odd and even for circularly polarized light.

The differential cross section takes the form

$$\begin{aligned} \frac{d\sigma}{dk} = & (2\pi^2/\lambda) \sum_{J'_1} (2J'_1+1) \left[\tilde{M}_{\epsilon J'_1} \begin{bmatrix} J'_1 & 1 & J_i \\ -\Omega_d & p & \Omega_i \end{bmatrix} + (-1)^{\Omega_r - \Omega_d} M_r \tilde{V}_r \delta(J_r J'_1) \begin{bmatrix} J'_1 & 1 & J_i \\ -\Omega_r & p' & \Omega_i \end{bmatrix} \right] / (E - E_r + i\Gamma_r/2) \\ & \times \sum_{J'_2} (2J'_2+1) \left[\tilde{M}_{\epsilon J'_2} \begin{bmatrix} J'_2 & 1 & J_i \\ -\Omega_d & p & \Omega_i \end{bmatrix} \right. \\ & \quad \left. + (-1)^{\Omega_r - \Omega_d} M_r^* \tilde{V}_r^* \delta(J_r J'_2) \begin{bmatrix} J'_2 & 1 & J_i \\ -\Omega_r & p' & \Omega_i \end{bmatrix} \right] / (E - E_r - i\Gamma_r/2) \\ & \times \sum_j (-1)^{J'_1 + J'_2 + J_i - \Omega_d} (2j+1) \begin{bmatrix} 1 & 1 & j \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} J'_1 & J'_2 & j \\ \Omega_d & -\Omega_d & 0 \end{bmatrix} \\ & \times \begin{bmatrix} 1 & 1 & j \\ J'_1 & J'_2 & J_i \end{bmatrix} P_j(\cos\Theta) \end{aligned} \quad (14)$$

from which one can easily separate the contribution from the continuum in $\tilde{M}_\epsilon \tilde{M}_\epsilon^*$, the resonant term in $M_r M_r^*$, and the crossed term or interference contribution. We will study each of these in the following section.

III. RESULTS

A. The resonant contribution

Because of the resonant denominator, the resonant contribution has no summation over J' and reduces to

$$\begin{aligned} \left[\frac{d\sigma}{dk} \right]_{\text{res}} = & (2\pi^2/\lambda) \{ |M_r|^2 |\tilde{V}_r|^2 / [(E - E_r)^2 + \Gamma_r^2/4] \} (2J'_r + 1)^2 \begin{bmatrix} J'_r & 1 & J_i \\ -\Omega_r & p' & \Omega_i \end{bmatrix}^2 \\ & \times \sum_j (-1)^{2J'_r + J_i - \Omega_d} (2j+1) \begin{bmatrix} 1 & 1 & j \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} J'_r & J'_r & j \\ \Omega_d & -\Omega_d & 0 \end{bmatrix} \begin{bmatrix} 1 & 1 & j \\ J'_r & J'_r & J_i \end{bmatrix} P_j(\cos\Theta). \end{aligned} \quad (15)$$

Using the explicit forms of the $3j$ and $6j$ coefficients from Ref. [12], one obtains

$$\left[\frac{d\sigma}{dk} \right]_{\text{res}} = (\sigma_{\text{res}}/4\pi) [1 + \beta_{\text{res}} P_2(\cos\Theta)] \quad (16)$$

with

$$\beta_{\text{res}} = \begin{cases} \frac{J_i(J_i-1) - 3\Omega_d^2}{J_i(2J_i+1)} & \text{for a } P(J_i) \text{ line} \\ -\frac{J_i(J_i+1) - 3\Omega_d^2}{J_i(J_i+1)} & \text{for a } Q(J_i) \text{ line} \\ \frac{(J_i+1)(J_i+2) - 3\Omega_d^2}{(J_i+1)(2J_i+1)} & \text{for an } R(J_i) \text{ line.} \end{cases} \quad (17)$$

From these values one can see that no information can be obtained about the predissociated state or the nature of the coupling, since it depends only on the rotational line and the Ω value of the continuum state.

The other part,

$$\sigma_{\text{res}} = (8\pi^3/\lambda) (2J_r+1) \begin{bmatrix} J'_r & 1 & J_i \\ -\Omega_r & p' & \Omega_i \end{bmatrix}^2 \frac{1}{3} |M_r|^2 |\tilde{V}_r|^2 / [(E - E_r)^2 + \Gamma_r^2/4] \quad (18)$$

is really the resonance part of the total photodissociation cross section of Eq. (3).

B. The interference term

From Eq. (14), this term is

$$\begin{aligned}
 \left[\frac{d\sigma}{dk} \right]_{\text{int}} &= (2\pi^2/\lambda) \sum_j (2j+1) (-1)^{J_i - \Omega_r} (2J'_r + 1) \begin{bmatrix} J'_r & 1 & J_i \\ -\Omega_r & p' & \Omega_i \end{bmatrix} \begin{bmatrix} 1 & 1 & j \\ 0 & 0 & 0 \end{bmatrix} P_j(\cos\Theta) \\
 &\times \left[\sum_{J'_1} (-1)^{J'_1 + J_r} (2J'_1 + 1) \begin{bmatrix} J'_1 & 1 & J_i \\ -\Omega_d & p & \Omega_i \end{bmatrix} \begin{bmatrix} J'_1 & J'_r & j \\ \Omega_d & -\Omega_d & 0 \end{bmatrix} \begin{bmatrix} 1 & 1 & j \\ J'_1 & J'_r & J_i \end{bmatrix} \right. \\
 &\quad \times \tilde{M}_{\epsilon J'_1} M_r^* \tilde{V}_r^* / (E - E_r - i\Gamma_r/2) \\
 &\quad + \sum_{J'_2} (-1)^{J'_2 + J_r} (2J'_2 + 1) \begin{bmatrix} J'_2 & 1 & J_i \\ -\Omega_d & p & \Omega_i \end{bmatrix} \begin{bmatrix} J'_2 & J'_r & j \\ \Omega_d & -\Omega_d & 0 \end{bmatrix} \\
 &\quad \left. \times \begin{bmatrix} 1 & 1 & j \\ J'_2 & J'_r & J_i \end{bmatrix} \tilde{M}_{\epsilon J'_2} M_r \tilde{V}_r / (E - E_r + i\Gamma_r/2) \right]. \tag{19}
 \end{aligned}$$

J'_1 and J'_2 play similar roles and using the symmetry properties of the $3j$ and $6j$ coefficients [11] Eq. (19) reduces to

$$\begin{aligned}
 \left[\frac{d\sigma}{dk} \right]_{\text{int}} &= (2\pi^2/\lambda) \sum_{j, J'} (-1)^{J' + J'_r + J_i - \Omega_r} (2j+1) (2J'+1) (2J'_r+1) \begin{bmatrix} 1 & 1 & j \\ 0 & 0 & 0 \end{bmatrix} P_j \begin{bmatrix} J'_r & 1 & J_i \\ -\Omega_r & p' & \Omega_i \end{bmatrix} \\
 &\times \begin{bmatrix} J' & 1 & J_i \\ -\Omega_d & p & \Omega_i \end{bmatrix} \begin{bmatrix} J' & J'_r & j \\ \Omega_d & -\Omega_d & 0 \end{bmatrix} \begin{bmatrix} 1 & 1 & j \\ J' & J'_r & J_i \end{bmatrix} \\
 &\times [\tilde{M}_{\epsilon J'} M_r^* \tilde{V}_r^* / (E - E_r - i\Gamma_r/2) + \tilde{M}_{\epsilon J'}^* M_r \tilde{V}_r / (E - E_r + i\Gamma_r/2)]. \tag{20}
 \end{aligned}$$

According to Fano's approach [8], the phase shift due to the coupling with the resonance state has already been taken into account in Eqs. (3) and (7) and the unperturbed phase $\delta_{j'}$ must be used instead.

Far from threshold, the dissociation occurs in a time much shorter than the rotational time, and the molecule cannot rotate before breaking: this is the axial recoil approximation. In quantum mechanics the axial recoil approximation means that the $\tilde{M}_{\epsilon J'}$ matrix elements do not depend on J' (or very slightly), which implies

$$i^{J'} \exp(-i\delta_{j'\Omega}) \simeq 1 \tag{21}$$

and

$$M_{\epsilon J'} \simeq M_{\epsilon} \simeq M_{\epsilon J'_r} \tag{22}$$

for all values of J' . This approximation is generally valid, and greatly simplifies the expressions. We will use it throughout this part of the paper.

In axial recoil approximation Eq. (20) can be written

$$\begin{aligned}
 \left[\frac{d\sigma}{dk} \right]_{\text{int}} &= (2\pi^2/\lambda) \sum_j (2j+1) \begin{bmatrix} 1 & 1 & j \\ 0 & 0 & 0 \end{bmatrix} P_j(\cos\theta) (-1)^{J'_r - \Omega_r} (2J'_r + 1) \begin{bmatrix} J'_r & 1 & J_i \\ -\Omega_r & p' & \Omega_i \end{bmatrix} \\
 &\quad \times 2M_{\epsilon} M_r V_r / [(E - E_r)^2 + \Gamma_r^2/4] \\
 &\quad \times \sum_{J'} (2J'+1) \begin{bmatrix} J' & 1 & J_i \\ -\Omega_d & p & \Omega_i \end{bmatrix} \begin{bmatrix} J' & J'_r & j \\ \Omega_d & -\Omega_d & 0 \end{bmatrix} \begin{bmatrix} 1' & 1 & j \\ J' & J'_r & J_i \end{bmatrix} (-1)^{J' + J_i}. \tag{23}
 \end{aligned}$$

The summation over J' is straightforward [13] giving, for Eq. (23),

$$\begin{aligned}
 \left[\frac{d\sigma}{dk} \right]_{\text{int}} &= (2\pi^2/\lambda) \sum_j (2j+1) \begin{bmatrix} 1 & 1 & j \\ 0 & 0 & 0 \end{bmatrix} P_j(\cos\theta) (-1)^{J'_r - \Omega_r} (2J'_r + 1) \begin{bmatrix} J'_r & 1 & J_i \\ -\Omega_r & p' & \Omega_i \end{bmatrix} \\
 &\quad \times 2M_{\epsilon} M_r V_r / [(E - E_r)^2 + \Gamma_r^2/4] (-1)^{J_i - \Omega_i - 1} \begin{bmatrix} j & 1 & 1 \\ 0 & p & -p \end{bmatrix} \begin{bmatrix} J'_r & 1 & J_i \\ -\Omega_d & p & \Omega_i \end{bmatrix}. \tag{24}
 \end{aligned}$$

Using explicit expressions for the $3j$ coefficients with j , one obtains

$$\left(\frac{d\sigma}{dk}\right)_{\text{int}} = (2\pi^2/\lambda)(-1)^{J'_r - \Omega_r + \Omega_d + J_i + 1} (2J'_r + 1) \begin{bmatrix} J'_r & 1 & J_i \\ -\Omega_r & p' & \Omega_i \end{bmatrix} \begin{bmatrix} J'_r & 1 & J_i \\ -\Omega_d & p & \Omega_i \end{bmatrix} \\ \times \frac{2}{3} M_\epsilon M_r V_r / [(E - E_r)^2 + \Gamma_r^2/4] \{1 + [2 - 3(\Omega_d - \Omega_i)^2] P_2(\cos\Theta)\}, \quad (25)$$

which is easy to identify with

$$\left(\frac{d\sigma}{dk}\right)_{\text{int}} = (\sigma_{\text{int}}/4\pi) [1 + \beta_{\text{int}} P_2(\cos\Theta)] \quad (26)$$

with $\beta_{\text{int}} = 2$ for a parallel transition and -1 for a perpendicular one. This is the value obtained for the unperturbed continuum in the axial recoil limit [2,3]. We can remark that for a parallel transition to the continuum $\beta_{\text{int}} = 2$, then at 90° the continuum term is zero; the interference contribution has to be zero as well and thus the angular dependence of the interference term has to be the same as that of the continuum one.

C. The continuum contribution

In the axial recoil approximation this contribution is equal to

$$\left(\frac{d\sigma}{dk}\right)_{\text{cont}} = (2\pi^2/\lambda) \sum_j (2j+1) \begin{bmatrix} 1 & 1 & j \\ 0 & 0 & 0 \end{bmatrix} P_j(\cos\theta) \\ \times \sum_{J'_1, J'_2} \begin{bmatrix} J'_1 & 1 & J_i \\ -\Omega_d & p & \Omega_i \end{bmatrix} \begin{bmatrix} J'_2 & 1 & J_i \\ -\Omega_d & p & \Omega_i \end{bmatrix} \begin{bmatrix} J'_1 & J'_2 & j \\ \Omega_d & -\Omega_d & 0 \end{bmatrix} \begin{bmatrix} 1 & 1 & j \\ J'_1 & J'_2 & J_i \end{bmatrix} \\ \times (-1)^{J'_1 + J'_2 + J_i - \Omega_d} (2J'_1 + 1)(2J'_2 + 1) M_\epsilon^2 \left[1 - \frac{i\Gamma_r/2\delta(J'_1 J'_r)}{E - E_r + i\Gamma_r/2}\right] \\ \times \left[1 + \frac{i\Gamma/2\delta(J'_r J'_2)}{E - E_r - i\Gamma_r/2}\right] \quad (27)$$

using Eqs. (21) and (22), which can be decomposed again into parts: one nonresonant (the unperturbed continuum) and one resonant due to the perturbation. In the resonant contribution, the dispersive part is proportional to

$$(i\Gamma_r/2)(E - E_r) [\delta(J'_2 J_r) - \delta(J'_1 J_r)] / [(E - E_r)^2 + \Gamma_r^2/4]. \quad (28)$$

As noted previously J'_1 and J'_2 play symmetrical roles, and the above expression when summed over J'_1 and J'_2 gives zero. The other resonant contribution is proportional to

$$[-\delta(J'_1 J'_r) - \delta(J'_2 J'_r) + \delta(J'_1 J'_r) \delta(J'_2 J'_r)] (\Gamma_r^2/4) / [(E - E_r)^2 + \Gamma_r^2/4]. \quad (29)$$

The term in $\delta(J'_1 J'_r) \delta(J'_2 J'_r)$ is similar to the resonant term whereas the others are similar to the interference term. All calculations done, it reduces to

$$\left(\frac{d\sigma}{dk}\right)_{\text{cont}} = (2\pi^2/\lambda) \frac{1}{3} |M_\epsilon|^2 \{1 + [2 - 3(\Omega_d - \Omega_i)^2] P_2(\cos\Theta)\} \\ - (2\pi^2/\lambda) \frac{1}{3} |M_\epsilon|^2 (2J'_r + 1) \begin{bmatrix} J'_r & 1 & J_i \\ -\Omega_d & p & \Omega_i \end{bmatrix}^2 (1 + \{2[2 - 3(\Omega_d - \Omega_i)^2] - \beta_r\} P_2(\cos\Theta)) / [(E - E_r)^2 + \Gamma_r^2/4]. \quad (30)$$

This means that the continuum is decomposed into the unperturbed part and the dip (observable for a Fano parameter $Q=0$, i.e., $M_r=0$) has a composite signature dependent on both transitions.

The right summation over $\pm\Omega_i$ and $\pm\Omega_d$ leads to $2|M_\epsilon|^2$ instead of $|M_\epsilon|^2$ in the case of a $^1\Sigma \rightarrow ^1\Pi$ transition.

IV. CONCLUSION

We have described precisely the angular distribution of photodissociation fragments along a Fano profile. We carefully took into account the well-defined parity of the bound levels, the possible degeneracy of the continuum, and the Fano dip due to the perturbation of the discrete

state. We showed that the dipolar form of the angular distribution was true only for randomly oriented molecules excited by linearly polarized light.

Nearby a resonance, the experimental photodissociation cross section was put in the form [1]

$$\frac{d\sigma(E, \theta)}{d\Omega} = A(\theta)[(E - E_r)^2 + \Gamma_r^2/4] + B(\theta)(E - E_r)/[(E - E_r)^2 + \Gamma_r^2/4] + C(\theta) \quad (31)$$

from the energy variations (resonant, dispersion shaped, and constant). Then to compare the theoretical values to experimental ones, it is more convenient to gather the resonant part of the continuum with the resonance signal.

Letting σ_{cont} be the total cross section of the unperturbed continuum far from the resonance, interactive ($J' = J_r'$) and noninteractive ($J' \neq J_r'$), and letting Q be the usual Fano parameter, the differential photodissociation cross section can be written

$$\frac{d\sigma}{dk} = \sigma_{\text{cont}}[1 + \beta_{\text{cont}}P_2(\cos\theta)] + \sigma_{\text{int}}[1 + \beta_{\text{int}}P_2(\cos\Theta)] + \tilde{\sigma}_{\text{res}}[1 + \tilde{\beta}_{\text{res}}P_2(\cos\theta)] \quad (32)$$

with

$$\begin{aligned} \beta_{\text{int}} = \beta_{\text{cont}} &= 2 - 3(\Omega_d - \Omega_i)^2, \\ \tilde{\sigma}_{\text{res}} &= \sigma_{\text{res}}(Q^2 - 1)/Q^2, \\ \tilde{\beta}_{\text{res}} &= [\beta_{\text{res}}(Q^2 + 1) - 2\beta_{\text{cont}}]/(Q^2 - 1), \end{aligned} \quad (33)$$

and

$$\beta_{\text{res}} = \begin{cases} \frac{J_i(J_i - 1) - 3\Omega_d^2}{J_i(2J_i + 1)} & \text{for a } P(J_i) \text{ line} \\ -\frac{J_i(J_i + 1) - 3\Omega_d^2}{J_i(J_i + 1)} & \text{for a } Q(J_i) \text{ line} \\ \frac{(J_i + 1)(J_i + 2) - 3\Omega_d^2}{(J_i + 1)(2J_i + 1)} & \text{for an } R(J_i) \text{ line} \end{cases} \quad (34)$$

which is valid in the axial recoil limit (i.e., for dissociation energy much larger than the continuum rotational energy) for incident linearly polarized light and for molecules initially randomly oriented.

The β_{int} , β_{cont} , and $\tilde{\beta}_{\text{res}}$ values can be directly compared to the experimental parameters.

The "interference" term observed in Ref. [1] corresponding to the dispersive part of the photodissociation variations with E presents clearly a $\cos\theta$ behavior in agreement with the theoretical $\beta_{\text{int}} = 2$ value (in this case $\Omega_d = \Omega_i = 1$).

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