

Some anisotropy effects in molecular photoejection spectroscopy

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In this paper we present a theoretical study of the angular distribution of the fragments in the predissociation of diatomics. We have utilized scattering theory and the effective Hamiltonian approach to derive general expressions for the differential cross section and for the angular anisotropy under different excitation conditions.

I. INTRODUCTORY COMMENTS

Interest in the basic mechanisms of molecular photodissociation and predissociation has recently been revived by a number of new experimental observations such as (a) molecular alignment by selective photodissociation,¹ (b) spectroscopic studies by vibrational and rotational distribution of a diatomic fragment which results from a direct or indirect photodissociation of a triatomic molecule,² (c) laser action accomplished by preparing a vibrationally inverted molecule via photodissociation of a polyatomic,³ and (d) studies of the angular distribution and the velocity distribution of the photofragments.^{4,5} Photodissociation and predissociation of diatomic (or quasidiatomic) molecules provide one of the simplest examples of a nonradiative decomposition (or decay) process of an excited molecular state which is amenable to a detailed theoretical study.^{6,7,8,9} The problem of the angular distribution of molecular photodissociation products achieved by the action of plane polarized light has recently been elucidated by the beautiful experimental work of Jonah, Chandra, and Bersohn⁴ and of Busch and Wilson.⁵ The theoretical foundations for the understanding of photodissociation dynamics have been provided by Zare⁷ and by Bersohn and Lin.⁸ In these studies of direct photodissociation, an instantaneous dissociation process was correctly assumed. It was pointed out by Busch and Wilson⁵ and by Jonah⁶ that the anisotropy in the spatial distribution of products would be eroded were the molecule to rotate before dissociation. A semiclassical picture for a photodissociation process characterized by a finite delay time was provided by Jonah.⁶ The nature of anisotropic direct and "delayed" photodissociation bears a close analogy to the problem of angular correlation in nuclear physics^{10a} and to atomic angular correlation spectroscopy.^{10b}

The problem of angular distribution in a delayed photodissociation process requires the explicit introduction of rotational effects for the description of a nonradiative molecular decay process. In the most recent literature on the theory of intramolecular coupling and nonradiative processes such as the theory of radiative decay of small molecules and electronic relaxation in large molecules,¹¹ the role of rotational effects was usually ignored. This is justified, as the intramolecular cou-

pling between different electronic or vibrational states conserves the angular momentum and consequently also the rotational quantum numbers, provided that vibrational-rotational coupling in polyatomics can be disregarded. From the experimental point of view, the work of Parmenter and Schuh¹² on resonance fluorescence from the first singlet state of benzene has demonstrated that internal conversion in this "large" molecule is not sensitive to rotational effects. Concerning small molecules, we would like to mention the large variation of the interstate coupling between discrete levels in some diatomics with the rotational level.^{13a} This effect can be easily understood in terms of the modification of the energy gap between rotational states which are characterized by the same rotational quantum numbers and which correspond to different electronic configurations. This effect originates just from the change in the rotational constants between the two electronic states. More interesting are predissociating states of some diatomics (i. e., the $A^2\Sigma^+$ of OD) which exhibit a marked dependence of the predissociation width on the rotational state.^{13b} Finally, in the study of photoejection dynamics, the role of rotational effects is, of course, crucial, as has already been demonstrated in Zare's quantum mechanical treatment of direct photodissociation⁷ and in Jonah's semiclassical treatment of delayed photodissociation.⁶

While the direct photodissociation problem is well understood, further studies of the delayed photodissociation are of interest. In this paper, we utilize theoretical techniques developed by us for nonradiative molecular decay processes,¹⁴ to provide a complete quantum mechanical treatment of the anisotropy of products in the predissociation of diatomic molecules.

We were able to obtain explicit results both for "short time" excitation mode, where the exciting photon field spans a broad energy range, and for "long time" excitation characterized by high energy resolution. Selection of specific rotational states is possible, of course, only in the latter case. The predissociation lifetime enters into the theory in a self-consistent, natural way and determines the angular distribution of the products. The direct photodissociation problem treated by Zare⁷ is obtained as a limiting case of our results. Jonah's results⁶ hold in the case of predissociation in the "short excitation" limit.

II. A FORMAL TREATMENT OF PREDISSOCIATION

We shall now provide some general expressions for the directional predissociation process. The most convenient approach involves the calculation of the cross section for scattering from the one photon ground molecular state to the dissociative continuum. This energy dependent cross section can subsequently be integrated over the photon wavepacket, resulting in the angular distribution under different excitation conditions.

We consider electronic dissociation of a diatomic molecule, which is characterized by three electronic states: the bound ground state $|g_e\rangle$, an excited bound state $|s_e\rangle$, and a dissociative state $|d_e\rangle$. The discrete singlet molecular states that correspond to $|g_e\rangle$ and $|s_e\rangle$ are

$$|gvJM\rangle = \frac{1}{r} \psi_e^{(g)}(\mathbf{q}, \mathbf{r}) \chi_{vJ}^{(g)}(r) \sqrt{\frac{2J+1}{4\pi}} D_{M\Lambda}^J(\varphi, \theta, 0), \quad (\text{II. 1})$$

$$|sv'J'M'\rangle = \frac{1}{r} \psi_e^{(s)}(\mathbf{q}, \mathbf{r}) \chi_{v'J'}^{(s)}(r) \sqrt{\frac{2J'+1}{4\pi}} D_{M'\Lambda'}^{J'}(\varphi, \theta, 0),$$

where \mathbf{q} are the electronic coordinates, while r , θ , and φ represent the polar coordinates of the internuclear axis with respect to the laboratory-fixed frame. $\psi_e^{(g)}$ and $\chi_{vJ}^{(g)}$ ($\alpha = g, s$) correspond to the electronic and the vibrational wavefunctions, respectively, while $D_{M\Lambda}^J(\varphi, \theta, 0)$ is the Wigner rotation matrix.¹⁵ $\Lambda = 0$ and 1 for $^1\Sigma$ and $^1\Pi$ states, respectively.

The dissociative state wavefunctions can be represented in terms of a complete set of states

$$|d\epsilon J''M''\rangle = \frac{1}{Kr} \psi_e^{(d)}(\mathbf{q}, \mathbf{r}) \chi_{\epsilon J''}^{(d)}(Kr) \sqrt{\frac{2J''+1}{4\pi}} D_{M''\Lambda''}^{J''}(\varphi, \theta, 0), \quad (\text{II. 2})$$

each characterized by the relative kinetic energy $\epsilon = \hbar^2 K^2 / 2\mu$ and a definite angular momentum ($J''M''$). The continuum nuclear wavefunctions $\chi_{\epsilon J''}^{(d)}$ behave asymptotically as

$$\chi_{\epsilon J''}^{(d)}(Kr) = \sin(Kr - \frac{\pi}{2} J'' + \delta_{J''}). \quad (\text{II. 3})$$

$\psi_e^{(d)}$ is the electronic wavefunction, $\chi_{\epsilon J''}^{(d)}$ is the solution of the radial (nuclear) equation, and $\delta_{J''}$ is the phase shift. For the present study, it is more convenient to take a linear combination of the (degenerate) states (II. 2), satisfying the appropriate boundary conditions for our experiment (i.e., an incoming spherical wave plus a plane wave in an arbitrary \mathbf{K} direction). \mathbf{K} represents the propagation vector pointing along the final recoil direction of the fragments. The polar angles of \mathbf{K} with respect to the space fixed coordinate system (xyz) are denoted by Φ and Θ . The wavefunction corresponding to $|\mathbf{K}\rangle$ is

$$|\mathbf{K}\rangle = \frac{1}{Kr} \psi_e^{(d)*}(\mathbf{q}, \mathbf{r}) \sum_{J'} (2J'+1)(i)^{J'} \exp(-i\delta_{J'}) \otimes \chi_{\epsilon J'}^{(d)}(Kr) D_{\Lambda\Lambda'}^{J'}(\hat{\mathbf{K}}, \hat{\mathbf{r}}), \quad (\text{II. 4})$$

Here, Λ corresponds to the electronic angular momentum of $|d_e\rangle$, and $\hat{\mathbf{K}}$ and $\hat{\mathbf{r}}$ are the unit vectors along the

propagation and the position directions, respectively. Making use of some standard relations for the Wigner rotation matrices,¹⁵ Eq. (II. 4) takes the form

$$|\mathbf{K}\rangle = \frac{1}{Kr} \psi_e^{(d)*}(\mathbf{q}, \mathbf{r}) \sum_{J'} (2J'+1)(i)^{J'} \exp(-i\delta_{J'}) \otimes \chi_{\epsilon J'}^{(d)}(Kr) D_{M'\Lambda'}^{J'}(\varphi, \theta, 0) D_{M\Lambda}^{J'}(\Phi, \Theta, 0). \quad (\text{II. 5})$$

The molecular states (II. 1) and (II. 5) correspond to the eigenstates of the zero order molecular Hamiltonian H_M^0 . The total Hamiltonian is $H = H_M^0 + H_V + H_{\text{rad}} + H_{\text{int}}$. We shall separate the Hamiltonian into two parts $H = H_0 + V$, where $H_0 = H_M^0 + H_{\text{rad}}$ and $V = H_V + H_{\text{int}}$. H_V is the intramolecular coupling term, H_{rad} the free radiation field Hamiltonian, and H_{int} is the radiation-matter interaction term. To specify the eigenstates of H_0 , we now consider the free radiation field. For weak photon fields, the eigenstates of H_{rad} are the zero photon state $|\text{vac}\rangle$ and the one photon states $|\mathbf{k}, \mathbf{e}\rangle$, where \mathbf{k} is the photon wavevector and \mathbf{e} its polarization vector. Since we are interested in predissociation induced by a plane polarized light, we shall choose a single polarization direction \mathbf{e} along the laboratory z axis and from now on the one photon states will be labeled by $|\mathbf{k}\rangle$. The relevant eigenstates of H_0 are one photon states $|i\rangle = |gvJM, \mathbf{k}\rangle$ and two types of zero photon states $|\bar{s}\rangle = |svJM, \text{vac}\rangle$ and $|f\rangle = |\mathbf{K}, \text{vac}\rangle$. We note in passing that off-resonance contributions will be neglected. The states $|i\rangle$ are coupled by H_{int} to $|\bar{s}\rangle$, which in turn is coupled by H_V to the continuum states $|f\rangle$. In the present treatment, the coupling between the radiative continuum $|i\rangle$ and the molecular dissociative continuum $|f\rangle$ is not considered, which is justified for many cases of physical interest.¹¹

Application of scattering theory¹⁶ results in a general expression for the scattering cross section from the continuum state $|i\rangle = |gvJM, \mathbf{k}\rangle$, characterized by the energy $E_i = E_{gvJM} + E$, with $E = \hbar kc$, to the continuum state $|f\rangle = |\mathbf{K}, \text{vac}\rangle$ characterized by the energy E_f . The differential scattering cross section $\sigma(\Theta, \Phi, E)$ depends explicitly on the photon energy $E = \hbar kc$ and on the polar angles Φ, Θ and is expressed in the form

$$\sigma(\Theta, \Phi, E) = \frac{2\pi}{\hbar c} \sum_f |\langle f | T(E) | i \rangle|^2 \delta(E_i - E_f), \quad (\text{II. 6})$$

where $T(E)$ is the reaction matrix

$$T(E) = V + VG^+(E)V, \quad (\text{II. 7})$$

$$G^+(E) = (E - H + i\eta)^{-1}, \quad \eta \rightarrow 0^+,$$

$G^+(E)$ is the Green's function, H the total Hamiltonian, and $V = H_{\text{int}} + H_V$.

We now segregate the Hilbert space into two parts,

$$\hat{P} = \sum_v \sum_{JM} |svJM, \text{vac}\rangle \langle svJM, \text{vac}|, \\ \hat{Q} = \sum_v \sum_{JM} \sum_{\mathbf{k}} |gvJM, \mathbf{k}\rangle \langle gvJM, \mathbf{k}| + \sum_{\mathbf{K}} |\mathbf{K}, \text{vac}\rangle \langle \mathbf{K}, \text{vac}|, \\ \hat{P} + \hat{Q} = 1, \quad (\text{II. 8})$$

where the subspace \hat{P} contains discrete states, while \hat{Q}

spans all the continuum states of our system. We now note that the coupling terms H_V and H_{int} couple only states in different subspaces, i. e., $\hat{P}V\hat{P} = \hat{Q}V\hat{Q} = 0$ so that

$$V = H_V + H_{int} = \hat{P}V\hat{Q} + \hat{Q}V\hat{P}. \quad (\text{II. 9})$$

In order to express the matrix element on the rhs of Eq. (II. 6), we make use of the operator $\hat{Q}T(E)\hat{Q}$, which is now given in the form

$$\hat{Q}T(E)\hat{Q} = \hat{Q}V\hat{P}G(E)\hat{P}V\hat{Q}. \quad (\text{II. 10})$$

Finally, the operator $\hat{P}G(E)\hat{P}$ in Eq. (II. 10) can be expressed in terms of the effective Hamiltonian formalism^{17,14}

$$\begin{aligned} \hat{P}G(E)\hat{P} &= (E - \hat{P}H_{eff}\hat{P})^{-1}\hat{P}, \\ \hat{P}H_{eff}\hat{P} &= \hat{P}(H - V)\hat{P} + \hat{P}R(E)\hat{P}, \\ R(E) &= V + V\hat{Q}(E - H_0 - \hat{Q}V\hat{Q})^{-1}\hat{Q}V. \end{aligned} \quad (\text{II. 11})$$

H_{eff} is the effective Hamiltonian, while $R(E)$ corresponds to the level shift operator. Thus, Eqs. (II. 6), (II. 10), and (II. 11) provide us with the final formal expression for the differential scattering cross sections into the dissociative continuum. These cross sections are obtained for a well defined photon energy E . In an actual experiment, the exciting light source is not necessarily monochromatic. Excitation of the system by a photon wavepacket $\sum_k A_k |k\rangle$, where $A_k \equiv A(E)$ correspond to the amplitudes of the one photon states (all characterized by the same polarization and propagation direction) will result in an angular distribution $W(\Theta, \Phi) d\Omega$ which can be expressed in terms of the integral of σ over the power spectrum of the pulse

$$W(\Theta, \Phi) = \int dE |A(E)|^2 \sigma(\Theta, \Phi, E). \quad (\text{II. 12})$$

We note in passing that for a monochromatic excitation (i. e., long time excitation), $|A(E')|^2 = \delta(E - E')$ and $W(\Theta, \Phi) = \sigma(\Theta, \Phi, E)$, while for a broad pulse, we have $W(\Theta, \Phi) = \int dE \sigma(\Theta, \Phi, E)$.

$$\Gamma(svJM, svJ'M') = 2\pi \langle svJM, \text{vac} | H_V | d\epsilon JM, \text{vac} \rangle \rho_d \langle d\epsilon JM, \text{vac} | H_V | svJ'M' \rangle$$

$$+ 2\pi \sum_{J''M'', \nu_g, \mathbf{k}} \langle svJM, \text{vac} | H_{int} | g\nu_g J''M'', \mathbf{k} \rangle \rho_r \langle g\nu_g J''M'', \mathbf{k} | H_{int} | svJ'M', \text{vac} \rangle, \quad (\text{III. 2})$$

where ρ_d and ρ_r correspond to the densities of states in the dissociative continuum and in the radiation field, respectively, at the energy E above the ground state $|g0JM\rangle$ level. The intermediate states $(d\epsilon JM, \text{vac})$ and $|g\nu_g J''M'', \mathbf{k}\rangle$ are taken on the energy shell. We are now in need of the matrix elements in Eq. (III. 2).

The intramolecular coupling matrix elements can be written in the form

$$\langle \mathbf{K} | H_V | svJM \rangle = \sqrt{4\pi(2J+1)} R_J^{(ds)} D_{M\Lambda}^J(\Phi, \Theta, 0) \delta_{\Lambda_s, \Lambda}, \quad (\text{III. 3})$$

where

We shall now proceed to the calculation of the predissociation cross section for our molecular model.

III. DIRECTIONAL PREDISSOCIATION OF A SINGLE VIBRONIC LEVEL

We shall now derive explicit expressions for photon scattering from the ground vibronic one photon state $|g0JM, \mathbf{k}\rangle$ to the dissociative continuum, considering a single vibronic level $|sv\rangle$ which belongs to the electronic configuration $|s_e\rangle$. This is justified provided the spacings between the origins of adjacent vibronic levels considerably exceed all the relevant radiative and nonradiative widths of the $|svJM, \text{vac}\rangle$ states. This is the general rule, although exceptions may be encountered, such as in some vibrational levels of the BO_u^+ state of Se_2 .¹⁸ From now on, we consider a single vibronic level and take a diagonal matrix for the level shift operator [Eq. (II. 11)]. When the widths of the vibronic levels exceed their spacings, the level shift matrix should contain all the relevant coupled vibronic levels as it should be prediagonalized in order to obtain the independently decaying levels^{14,17} of the system. For the evaluation of the reaction operator (II.10) using (II. 11), we recall that $\hat{P}G\hat{P}$ can be written in terms of the spectral resolution of the states which diagonalize the effective Hamiltonian

$$H_{eff} = H_0 + \Delta - \frac{1}{2}i\Gamma, \quad (\text{III. 1})$$

where Δ is the level shift and Γ corresponds to the level width matrix. H_{eff} will be represented in terms of the eigenstates $|svJM\rangle$ of H_0 , which are characterized by a well defined angular momentum.

In subsequent manipulations, we shall ignore the level shift matrix Δ . Since we actually consider an almost diagonal level shift matrix (see below), Δ just modifies the energy levels and we have to replace the energy E_{svJM} by $E_{svJM} + \Delta(svJM, svJM)$. We can thus treat E_{svJM} as the modified energy, and from now on we shall not explicitly write the level shift terms.

The level width matrix $\Gamma(i, j) \equiv \Gamma_{ij}$, is

$$R_J^{(ds)} = \frac{1}{K} (i)^J \exp(-i\delta_J) \int dr \chi_{eJ}^{(d)}(Kr) \nu_{ds}(r) \chi_{vJ}^{(s)}(r) dr \quad (\text{III. 4})$$

and

$$\nu_{ds}(r) = \int \psi_e^{*(d)}(\mathbf{q}, r) H_V \psi_e^{(s)}(\mathbf{q}, r) d\mathbf{q}. \quad (\text{III. 5})$$

In the derivation of (III. 3) we have used the fact that the intramolecular coupling conserves the angular momentum. The radiative interaction matrix elements may be written as

$$\begin{aligned} \langle svJ'M', \text{vac} | H_{int} | g0JM, \mathbf{k} \rangle &= \beta \langle svJ'M', \text{vac} | \mu \cdot \mathbf{e} | g0JM, \mathbf{k} \rangle \\ &= \xi (J'M'\Lambda_{ss}, JMA_s) R_J^{(sr)} \end{aligned} \quad (\text{III. 6})$$

where β is a numerical constant, μ the transition dipole moment, and $\mu \cdot e$ its projection on the z axis. The auxiliary functions in Eq. (III. 6) involve the radial part

$$R_{J'}^{(s)} = \int \chi_{\nu'}^{(s)*}(r) \mu_{s\nu'}(r) \chi_{0J}^{(s)}(r) dr, \quad (\text{III. 7})$$

$$\mu_{s\nu'}(r) = \int \psi_e^{(s)*}(\mathbf{q}, \mathbf{r}) \sum_i e \mathbf{q}_i \psi_e^{(s)}(\mathbf{q}, \mathbf{r}) d\mathbf{q},$$

and the angular contribution

$$\xi(J' M' \Lambda_s, J M \Lambda_r) = (4\pi)^{-1} \beta \sqrt{(2J+1)(2J'+1)} \\ \otimes \int D_{M' \Lambda_s}^{J'}(\varphi \theta 0) D_{0 \Lambda}^J(\varphi \theta 0) D_{M \Lambda_r}^J(\varphi \theta 0) d\Omega, \quad (\text{III. 8})$$

where

$$\lambda = |\Lambda_r - \Lambda_s|.$$

$$\Gamma(svJM, sv(J+2)M) = 2\pi \langle svJM, \text{vac} | H_{\text{int}} | g0(J+1)M, \mathbf{k} \rangle \langle g0(J+1)M, \mathbf{k} | H_{\text{int}} | sv(J+2)M, \text{vac} \rangle \rho_r \quad (\text{III. 10a})$$

and

$$\Gamma(svJM, sv(J-2)M) = 2\pi \langle svJM, \text{vac} | H_{\text{int}} | g0(J-1)M, \mathbf{k} \rangle \langle g0(J-1)M, \mathbf{k} | H_{\text{int}} | sv(J-2)M, \text{vac} \rangle \rho_r. \quad (\text{III. 10b})$$

Although, strictly speaking, the decay matrix is non-diagonal and the effective Hamiltonian (III. 1) has to be diagonalized, this cumbersome procedure is unnecessary. The off-diagonal matrix elements [Eq. (III. 10)] of the decay matrix are of the order of the radiative widths, that is, $\sim 10^{-2} \text{ cm}^{-1}$. These terms are typically much smaller than the spacings between the adjacent diagonal matrix elements of H_0 , i.e., the separation of rotational levels, and thus radiative interference effects can be disregarded. $\hat{P}H_{\text{eff}}\hat{P}$ [Eq. (III. 1)] can be considered to be diagonal in the $|svJM\rangle$ basis, which provides an adequate description for the independently decaying levels of the system. Under these circumstances, $\hat{P}G\hat{P}$ [Eq. (II. 11)], assumes the simple form

$$\hat{P}G(E)\hat{P} = \sum_{J'M'} \frac{|SvJ'M'\rangle \langle SvJ'M'|}{E - E_{J'} + \frac{1}{2}i\Gamma_{J'}}, \quad (\text{III. 11})$$

where $E_{J'}$ is the energy of the $|svJ'M'\rangle$ state, and $\Gamma_{J'}$ is given by Eq. (III. 9). The width $\Gamma_{J'}$ consists of a non-radiative width and a radiative width. Utilizing Eqs. (II. 10) and (III. 11), the matrix elements of the reaction operator in the $|svJM\rangle$ basis take the form

$$\langle \mathbf{K}, \text{vac} | T(E) | g0JM, \mathbf{k} \rangle \\ = \sum_{J'M'} \frac{\langle \mathbf{K} | H_V | SvJ'M' \rangle \langle SvJ'M' | H_{\text{int}} | g0JM, \mathbf{k} \rangle}{E - E_{J'} + \frac{1}{2}i\Gamma_{J'}} \quad (\text{III. 12})$$

In order to evaluate this matrix element of T which appears in Eq. (II. 6), we shall utilize the explicit form of $|\mathbf{K}, \text{vac}\rangle$ [Eq. (II. 5)] together with the coupling matrix elements [Eqs. (III. 3)–(III. 9)] and Eq. (4. 62) of Rose.¹⁵ Straightforward algebraic manipulations lead to the result

$$\langle \mathbf{K}, \text{vac} | T(E) | g0JM, \mathbf{k} \rangle \\ = \sum_{J'} \frac{(2J+1)^{1/2} R_{J'} A_{J'} D_{M \Lambda}^{J'}(\Phi \theta 0)}{E - E_{J'} + \frac{1}{2}i\Gamma_{J'}} \quad (\text{III. 13})$$

In the case of parallel (e.g., $^1\Sigma - ^1\Sigma$) transitions in diatomic $\lambda = 0$, while for perpendicular transitions (e.g., $^1\Sigma - ^1\Pi$), $\lambda = 1$. The integral in Eq. (III. 8) yields the conventional selection rules $M = M'$ and $J = J' \pm 1$. Making use of Eqs. (III. 3)–(III. 8), the decay matrix (III. 2) takes the form

$$\Gamma_J = \Gamma(svJM, svJM) \\ = 2\pi |\langle svJM | H_V | dEJM \rangle|^2 \rho_d \\ + 2\pi |\langle svJM, \text{vac} | H_{\text{int}} | g0(J+1)M, \mathbf{k} \rangle|^2 \rho_r \\ + 2\pi |\langle svJM, \text{vac} | H_{\text{int}} | g0(J-1)M, \mathbf{k} \rangle|^2 \rho_r \quad (\text{III. 9})$$

for the diagonal matrix elements, while the only non-vanishing off-diagonal matrix elements are

where

$$R_{J'} = \sqrt{4\pi} \beta R_{J'}^{(ds)} R_{J'}^{(sr)} \quad (\text{III. 14})$$

and

$$A_{J'} = C(J1J' | M0) C(J1J' | 0\lambda). \quad (\text{III. 15})$$

Here $C(J_1 J_2 J_3 | M_1 M_2)$ are the Clebsch–Gordan coefficients.¹⁵ We notice that $A_{J'}$ vanishes unless $J' = J$ or $J' = J \pm 1$.

We now consider a molecule in the $|g0JM\rangle$ state. The cross section for dissociation in the $\hat{\mathbf{K}}$ direction is¹⁹

$$\sigma_{JM}(\Theta, E) = \frac{(2\pi)^2}{\hbar c} |\langle \mathbf{K} | T(E) | g0JM, \mathbf{k} \rangle|^2 \rho_d \quad (\text{III. 16})$$

To obtain a cross section observable in a real life experiment, we have to proceed in three steps. First, we average σ_{JM} [Eq. (III. 16)] over the $(2J+1)M$ values. The averaged cross section for photodissociation of a single ground state J level is given by

$$\sigma_J(\Theta, E) = (2J+1)^{-1} \sum_{M=-J}^J \sigma_{JM}(\Theta, E). \quad (\text{III. 17})$$

This averaging corresponds classically to averaging over the initial molecular orientations. Second, we have to consider the spectral distribution of the exciting light and utilize Eq. (II. 12) to obtain the angular distribution for dissociation $W_J(\Theta)$ from a single J level in the form

$$W_J(\Theta) = \int dE |A(E)|^2 \sigma_J(\Theta, E). \quad (\text{III. 18})$$

Third, a thermal averaging over the initial distribution has to be performed, resulting in the final result

$$\langle W(\Theta) \rangle = \frac{1}{Z} \sum_J (2J+1) W_J(\Theta) \exp(-\beta E_J), \quad (\text{III. 19})$$

where $Z = \sum_J (2J+1) \exp(-\beta E_J)$ is the rotational parti-

tion function and $\beta = (k_B T)^{-1}$. k_B is Boltzmann's constant and T is the absolute temperature.

We shall now provide a general expression for

$$\sigma_J(\Theta, E) = \frac{(2\pi)^2}{\hbar c} \rho_d \sum_{J', J''=J, J\pm 1} \frac{R_{J'} R_{J''}^*}{(E - E_{J'} + \frac{1}{2}i\Gamma_{J'}) (E - E_{J''} - \frac{1}{2}i\Gamma_{J''})} \eta_{J' J''}^{J \Lambda} \quad (\text{III. 20})$$

where

$$\eta_{J' J''}^{J \Lambda} = (-1)^{\Lambda+J'+1} \sqrt{(2J'+1)(2J''+1)} C(J1J'|0\lambda) C(J1J''|0\lambda) \otimes \sum_{\bar{J}=0,2} W(1J\bar{J}J''|J'1) C(11\bar{J}|00) C(J'J''\bar{J}|\Lambda-\Lambda) D_{00}^{\bar{J}} \quad (\text{III. 21})$$

$W(abcd|ef)$ is the Racah coefficient.¹⁵

Equations (III.20) and (III.21) together with Eqs. (III.18) and (III.19) provide us with the general quantum mechanical expressions for the angular distribution of the predissociation products, which incorporates both the effects of the relative kinetic energy of the recoiling atoms and the effects of rotations. From now on, we shall be mainly interested in the common situation

$\sigma_J(\Theta, E)$ [Eq. (III.17)], utilizing Eqs. (III.13) and (III.16). The mathematical details are given in Appendix A. The final result for the scattering cross section from a single ground state J level is

where predissociation takes place well above the onset of the $|d_e\rangle$ dissociative state, whereupon ϵ exceeds the mean rotational energy, i.e., $\epsilon \gg k_B T$. Under these circumstances, we can utilize the common "axial recoil" approximation,⁷ i.e., that the nuclear radial wave functions $\chi_{v'J'}^{(u)}$, $\chi_{v''J''}^{(s)}$, and $\chi_{v''J''}^{(d)}$ exhibit a weak J dependence and consequently $\Gamma_{J'}$ [Eq. (III.9)] and $R_{J'}$ [Eq. (III.14)] are assumed to be independent of J' for a narrow J' range ($J' = J, J \pm 1$). Within the axial recoil approximation, Eq. (III.20) takes the form

$$\sigma_J(\Theta, E) = \frac{(2\pi)^2}{\hbar c} \rho_d |R_J|^2 \otimes \sum_{J', J''=J, J\pm 1} \frac{(E - E_{J'}) (E - E_{J''}) + \frac{1}{4}\Gamma_{J'}^2}{[(E - E_{J'})^2 + \frac{1}{4}\Gamma_{J'}^2][(E - E_{J''})^2 + \frac{1}{4}\Gamma_{J''}^2]} \eta_{J' J''}^{J \Lambda} \quad (\text{III. 22})$$

It is easy to demonstrate how Eq. (III.22) reduces to Zare's result⁷ for direct photodissociation. For this purpose, we require Γ_J to be large compared to $|E_{J'} - E_{J''}|$, where $J', J'' = J, J \pm 1$. To provide a reasonable estimate of the energy difference $|E_{J'} - E_{J''}|$, we recall that thermal averaging over ground state population will lead to optically accessible J states in the range of $\langle J \rangle \sim (k_B T/B)^{1/2}$ so that $|E_{J'} - E_{J''}| \sim 2\sqrt{Bk_B T}$. We thus require that $\Gamma_J \gg \sqrt{Bk_B T}$. Under these circumstances, Eq. (III.22) takes the form

$$\sigma_J(\Theta, E) = \frac{(2\pi)^2}{\hbar c} |R_J|^2 \rho_d \frac{1}{(E - E_J)^2 + (\Gamma_J^2/4)} \times \sum_{J', J''=J, J\pm 1} \eta_{J' J''}^{J \Lambda} \quad (\text{III. 23})$$

The sum on the rhs of Eq. (III.23) is evaluated in Appendix B, resulting in

$$\sigma_J(\Theta, E) \propto |D_{0\lambda}^1(\Phi, \Theta, 0)|^2,$$

resulting in a $\sigma_J''(\Theta, E) \propto \cos^2\Theta$ angular distribution for parallel transitions, and a $\sigma_J^{\perp}(\Theta, E) \propto \sin^2\Theta$ angular distribution for perpendicular transitions. The same distribution could have been obtained by neglecting off the energy shell contributions to $\sigma_J(\Theta, E)$, i.e., taking $\Gamma_J \gg |E - E_{J'}|, |E - E_{J''}|$ in Eq. (III.22).

IV. BROAD-BAND OPTICAL EXCITATION

We now consider the applications of our general results to the extreme broad band excitation limit, where the molecular ensemble is excited by a light source that contains all frequencies. The angular distribution for predissociation from a single vibronic level is now given by Eq. (III.18) in terms of the integrated cross section:

$$W_J(\Theta) = \int dE \sigma_J(\Theta, E) \quad (\text{IV. 1})$$

Making use of Eq. (III.20), we get the general result for this mode of excitation,

$$W_J(\Theta) = \frac{(2\pi)^2}{\hbar c} \rho_d \sum_{J', J''=J, J\pm 1} \frac{2\pi i R_{J'} R_{J''}^*}{E_{J''} - E_{J'} + \frac{1}{2}i(\Gamma_{J'} + \Gamma_{J''})} \eta_{J' J''}^{J \Lambda} \quad (\text{IV. 2})$$

In the derivation of Eq. (IV.2), we used the fact that $R_{J'}$ is a slowly varying function of the energy over the energy range Γ_J . $R_{J'}$ in Eq. (IV.2) is taken at the energy $E_{J''}$.

At this stage, we again invoke the axial recoil approximation; thus, Eq. (IV.2) results in the expression

$$W_J(\Theta) = \frac{(2\pi)^2}{\hbar c} \rho_d \frac{2\pi}{\Gamma_J} |R_J|^2 \times$$

$$\times \left[\sum_{J'} \eta_{J',J'}^{J\Lambda} + 2 \sum_{\substack{J',J'' \\ J'' > J'}} \frac{\Gamma_J^2}{(E_{J''} - E_{J'})^2 + \Gamma_J^2} \eta_{J',J''}^{J\Lambda} \right], \quad (IV. 3)$$

which can be brought into the alternative form

$$W_J(\Theta) = \frac{2\pi}{\hbar c} \frac{2\pi}{\Gamma_J} |R_J|^2 \times \left[\sum_{J',J''} \eta_{J',J''}^{J\Lambda} - 2 \sum_{J'' > J'} \frac{(E_{J''} - E_{J'})^2}{(E_{J''} - E_{J'})^2 + \Gamma_J^2} \eta_{J',J''}^{J\Lambda} \right]. \quad (IV. 4)$$

The first sum on the rhs of Eq. (IV. 4) is given by Eq. (B4) in Appendix B. To evaluate the coefficients $\eta_{J',J''}^{J\Lambda}$ ($J' \neq J''$) in the second sum, we make use of Eqs. (A4) and (A5) in Appendix A, bearing in mind that $C(J'J''0|\Lambda - \Lambda)$ vanishes for $J' \neq J''$. Thus, we get

$$\begin{aligned} \eta_{J',J''}^{J\Lambda} &= \bar{\eta}_{J',J''}^{J\Lambda} P_2(\cos\Theta); \quad J' \neq J'', \\ \bar{\eta}_{J',J''}^{J\Lambda} &= C(J'J''2|\Lambda - \Lambda) C(J1J'|0\Lambda) \\ &\quad \times C(J1J''|0\Lambda) C(112|00) \\ &\quad \times (-1)^{\Lambda+J'+1} [(2J'+1)(2J''+1)]^{1/2} W(1J2J''|J'1). \end{aligned} \quad (IV. 5)$$

Making use of Eqs. (B4) and (IV. 5), we obtain the transparent result

$$W_J(\Theta) = \frac{(2\pi)^3}{\hbar c \Gamma_J} \rho_d |R_J|^2 [|D_{0\Lambda}^{\Lambda}(\Phi, \Theta, 0)|^2 \alpha_J P_2(\cos\Theta)], \quad (IV. 6)$$

where

$$\alpha_J = 2 \sum_{\substack{J',J''=J,J\pm 1 \\ J'' > J'}} \frac{\delta_{J',J''}^2}{1 + \delta_{J',J''}^2} \bar{\eta}_{J',J''}^{J\Lambda} \quad (IV. 7)$$

and $\delta_{J',J''} = |E_{J'} - E_{J''}|/\Gamma_J$ is proportional to the ratio between the molecular lifetime Γ_J^{-1} and the mean rota-

tional period at the J level, $|E_{J'} - E_{J''}|^{-1}$, where $J', J'' = J, J \pm 1$. Equation (IV. 6) contains two contributions. The first term involves the anisotropy for "instant predissociation" being proportional to $\cos^2\Theta$ for a parallel transition ($\lambda=0$) and proportional to $\sin^2\Theta$ for a perpendicular ($\lambda=1$) transition. The dynamical information concerning the system is incorporated in the α_J parameter, Eq. (IV. 7), of the second term in Eq. (IV. 6). The magnitude of this second contribution which partially erodes the anisotropy in predissociation is determined by the ratio $\delta_{J',J''}$, when $\delta_{J',J''} \gg 1$ the second term has maximal influence on the distribution, whereas when $\delta_{J',J''} \rightarrow 0$, this term vanishes and the distribution is governed by the "instantaneous" term.

It is a straightforward matter to evaluate the coefficients $\eta_{J',J''}^{J\Lambda}$, Eqs. (III. 21) and (IV. 5), which can be used to evaluate σ_J [Eqs. (III. 20) and (III. 22)] or the angular distribution (IV. 6) for the broad band excitation limit.

To compare our results with Jonah's treatment,⁶ we consider a special case of $^1\Sigma \rightarrow ^1\Sigma$ predissociation, where all three $|g_e\rangle$, $|s_e\rangle$, and $|d_e\rangle$ electronic configurations correspond to a $^1\Sigma$ state. We now have to evaluate the $\eta_{J',J''}^{J\Lambda}$ coefficients for $J'J'' = J \pm 1$. After some algebraic manipulations, we get

$$\begin{aligned} \eta_{J+1,J+1}^{J0} &= \frac{1}{3} \left[\frac{J+1}{2J+1} + \frac{(J+1)(J+2)}{(2J+1)^2} P_2(\cos\Theta) \right], \\ \eta_{J-1,J-1}^{J0} &= \frac{1}{3} \left[\frac{J}{2J+1} + \frac{J(J-1)}{(2J+1)^2} P_2(\cos\Theta) \right], \\ \eta_{J+1,J-1}^{J0} &= \frac{J(J+1)}{(2J+1)^2} P_2(\cos\Theta). \end{aligned} \quad (IV. 8)$$

The general cross section, Eq. (III. 20), is given by

$$\begin{aligned} \sigma_J(\Theta, E) &= \frac{(2\pi)^3}{\hbar} \rho_d \left[\frac{|R_{J+1}|^2}{(E - E_{J+1})^2 + \frac{1}{4}\Gamma_{J+1}^2} \eta_{J+1,J+1}^{J0} + \frac{|R_{J-1}|^2}{(E - E_{J-1})^2 + \frac{1}{4}\Gamma_{J-1}^2} \eta_{J-1,J-1}^{J0} \right. \\ &\quad \left. + 2 \operatorname{Re} \frac{R_{J+1} R_{J-1}^*}{(E - E_{J+1} + \frac{1}{2}i\Gamma_{J+1})(E - E_{J-1} - \frac{1}{2}i\Gamma_{J-1})} \eta_{J+1,J-1}^{J0} \right]. \end{aligned} \quad (IV. 9)$$

While the angular distribution in the short excitation limit, adopting the axial recoil approximation [Eq. (IV. 6)], takes the form

$$W_J(\Theta) = \frac{(2\pi)^3}{\hbar} \frac{2\pi}{\Gamma_J} |R_J|^2 \left[\cos^2\Theta - 2 \frac{J(J+1)}{(2J+1)^2} \frac{\xi_J^2}{1 + \xi_J^2} P_2(\cos\Theta) \right], \quad (IV. 10)$$

where B is the rotational constant of the molecule, i.e., $E_J = BJ(J+1)$ and $\xi_J = 2B(2J+1)/\Gamma_J$.

To derive the thermally averaged distribution, Eq. (III. 19), for a broad-band excitation of a $^1\Sigma \rightarrow ^1\Sigma$ predissociation process, we define the thermal averages

$$\gamma_1 = \left\langle \frac{|R_J|^2}{\Gamma_J} \right\rangle = \frac{1}{Z} \sum_J (2J+1) \frac{|R_J|^2}{\Gamma_J} \exp(-\beta E_J)$$

and

$$\gamma_2 = \frac{3}{Z} \sum_J \frac{|R_J|^2}{\Gamma_J} \frac{4B^2(J+1)(2J+1)}{4B^2(2J+1)^2 + \Gamma_J^2} \exp(-\beta E_J). \quad (IV. 11)$$

Equation (IV. 10) now yields the thermally averaged distribution

$$\langle W(\Theta) \rangle = \frac{(2\pi)^3 \gamma_1}{3\hbar c} \rho_d [1 + 2b P_2(\cos\Theta)], \quad (IV. 12)$$

where

$$b = \frac{\gamma_1 - \gamma_2}{\gamma_1}. \quad (IV. 13)$$

Equation (IV. 12) provides a slight generalization of Jonah's results⁶ for a $^1\Sigma \rightarrow ^1\Sigma$ "retarded dissociation." Jonah's semiclassical treatment did not include thermal averaging of the $|R_J|^2/\Gamma_J$ terms, which are not expected to be constant over a broad J range.^{13a}

It is easily demonstrated that Eq. (IV. 12) provides

the correct limiting cases. In the case of fast predissociation $\Gamma_J \gg \langle B(J+1) \rangle \approx \sqrt{Bk_B T}$, then $\gamma_2/\gamma_1 \rightarrow 0$ and $b \rightarrow 1$, so that

$$\langle W(\Theta) \rangle = \frac{(2\pi)^3}{\hbar c} \rho_d \left\langle \frac{|R_J|^2}{\Gamma_J} \right\rangle \cos^2 \Theta, \quad (\text{IV. 14})$$

while for the limit of slow predissociation $\Gamma_J \ll \sqrt{K_B T B}$, $\gamma_2/\gamma_1 = \frac{3}{4}$, $b = \frac{1}{4}$, and therefore

$$\langle W(\Theta) \rangle = \frac{(2\pi)^3}{\hbar c} \rho_d \left\langle \frac{|R_J|^2}{\Gamma_J} \right\rangle^{\frac{1}{4}} (1 + \cos^2 \Theta). \quad (\text{IV. 15})$$

This limiting angular dependence has previously been derived.⁶

V. TIME-DEPENDENT APPROACH TO DIRECTIONAL PREDISSOCIATION

We have obtained the final distribution of the predissociation products in terms of averages over the relevant cross sections. The latter were derived by the application of the T matrix. This approach considers the molecular system as a "black box," in the sense that no information is obtained regarding the time evolution of the system. An alternative attitude to the problem of directional predissociation can be based on the time-dependent approach. In this section, we shall provide a formulation of the time resolved angular distribution, which in the limit of $t \rightarrow \infty$ reduces to the scattering formalism of Secs. II-IV. This time-dependent approach is of interest, as it elucidates the nature of the semi-classical approximations.⁶

In the time-dependent approach, we begin with a photon wave packet characterized by the amplitudes A_k , interacting with a ground state in a well-defined angular momentum eigenstate. The wavefunction of the system at $t=0$ is^{20,14}

$$|\psi(0)\rangle = \sum_k A_k |g 0JM, \mathbf{k}\rangle. \quad (\text{V. 1})$$

Utilizing the partitioning of our Hilbert space [Eq. (II. 8)] and the Green's function [Eq. (II. 11)], one can follow the time evolution of the system in terms of the pulse and the molecular characteristics. It can be shown¹⁴ that in the extreme short time excitation limit (i. e., a white photon wave packet of short duration), the system is "prepared" at $t=0$ in the doorway state

$$\begin{aligned} \psi(0) &= |N\rangle, \\ |N\rangle &= \hat{P} H_{\text{int}} |g 0JM, \mathbf{k}\rangle \\ &= \sum_{J'} |sJ'M\rangle \langle sJ'M | H_{\text{int}} |g 0JM, \mathbf{k}\rangle. \end{aligned} \quad (\text{V. 2})$$

The time evolution of $|N\rangle$ is given by

$$|N(t)\rangle = \frac{1}{2\pi i} \int_{-\infty}^{+\infty} dE \exp(-iEt) G^*(E) |N\rangle. \quad (\text{V. 3})$$

Since we are interested in the angular distribution of the dissociation products, we should consider the projection of $|\mathbf{K}\rangle$ (II. 5) on (V. 3),

$$\langle \mathbf{K} | N(t) \rangle = (2\pi i)^{-1} \int_{-\infty}^{+\infty} dE \langle \mathbf{K} | \hat{Q} G^*(E) \hat{P} | N \rangle \exp(-iEt). \quad (\text{V. 4})$$

The operator $\hat{Q} G^*(E) \hat{P}$ is given by¹⁷

$$\hat{Q} G^*(E) \hat{P} = (E - H_0 - \hat{Q} V \hat{Q})^{-1} \hat{Q} V \hat{P} G \hat{P}. \quad (\text{V. 5})$$

Utilizing Eqs. (V. 5), (III. 3), (III. 6), and (III. 11), Eq. (V. 4) assumes the form

$$\begin{aligned} \langle \mathbf{K} | N(t) \rangle &= \sum_{J'} R_{J'}^{(ds)} R_{J'}^{(sg)} A_{J'} D_{M\Lambda}^{J'}(\Phi, \Theta, 0) \sqrt{2J+1} \\ &\times \int_{-\infty}^{+\infty} dE \exp(-iEt) \frac{1}{(E - K + i\eta)(E - E_{J'} + \frac{1}{2}i\Gamma_{J'})}. \end{aligned} \quad (\text{V. 6a})$$

Performing the integration and introducing the definition $F_{J'}(t)$, we get

$$\langle \mathbf{K} | N(t) \rangle = \sum_{J'} R_{J'}^{(ds)} R_{J'}^{(sg)} A_{J'} \sqrt{2J+1} F_{J'}(t) D_{M\Lambda}^{J'}(\Phi, \Theta, 0), \quad (\text{V. 6b})$$

where

$$F_{J'}(t) = \frac{\exp(-iKt) - \exp(-iE_{J'}t - \frac{1}{2}\Gamma_{J'}t)}{K - E_{J'} + \frac{1}{2}i\Gamma_{J'}}. \quad (\text{V. 7})$$

The time-dependent angular distribution is given by

$$W_J(\Theta, t) = \frac{1}{2J+1} \sum_M \int d\mathbf{k} |\langle \mathbf{K} | N(t) \rangle|^2, \quad (\text{V. 8})$$

where the integration is performed over the energies and not over spatial directions. Equations (V. 6) and (V. 8) result in

$$W_J(\Theta, t) = \sum_{J', J''=J, J \pm 1} R_{J'} R_{J''} \eta_{J', J''}^{\Lambda} \phi_{J', J''}(t), \quad (\text{V. 9})$$

where

$$\phi_{J', J''}(t) = \int d\mathbf{k} F_{J'}(\mathbf{k}, t) F_{J''}^*(\mathbf{k}, t). \quad (\text{V. 10})$$

From Eqs. (V. 7) and (V. 10), we get

$$\phi_{J', J''}(t) = i \frac{1 - \exp[-i(E_{J'} - E_{J''})t] \exp[-\frac{1}{2}(\Gamma_{J'} + \Gamma_{J''})t]}{E_{J'} - E_{J''} + \frac{1}{2}i(\Gamma_{J'} + \Gamma_{J''})}. \quad (\text{V. 11})$$

Finally, we consider the counting rate of the predissociation products at (Θ, t) , which is given by the time derivative of the probability function (V. 9), so that

$$\frac{d}{dt} W_J(\Theta, t) = \sum_{J', J''=J, J \pm 1} R_{J'} R_{J''} \eta_{J', J''}^{\Lambda} \dot{\phi}_{J', J''}(t), \quad (\text{V. 12})$$

where

$$\dot{\phi}_{J', J''}(t) = \exp[-i(E_{J'} - E_{J''})t] \exp[-\frac{1}{2}(\Gamma_{J'} + \Gamma_{J''})t]. \quad (\text{V. 13})$$

Equations (V. 9) and (V. 12) together with (V. 11) and (V. 13) provide the exact formulation of the time evolution of a $|g 0JM\rangle$ molecular ground state interacting with the radiation field. To gain some further physical insight, let us invoke the axial recoil approximation; Eq. (V. 12) reduces to

$$\begin{aligned} \frac{d}{dt} W(\Theta, t) &= |R_J|^2 e^{-\Gamma_J t} \\ &\left[\sum_{J'=J, J \pm 1} \eta_{J', J'}^{\Lambda} + 2 \sum_{\substack{J', J''=J, J \pm 1 \\ J' > J''}} \eta_{J', J''}^{\Lambda} \cos(E_{J'} - E_{J''})t \right], \end{aligned} \quad (\text{V. 12}')$$

consisting of a direct scattering term and an interference term. When the energy ratio

$$\langle \delta \rangle = \sqrt{Bk_B T / \Gamma_J}$$

is small, the contribution of the second term in (V.12') is time independent at the relevant time scale (a few Γ_J values) and the time-dependent angular distribution is given by $\exp(-\Gamma_J t) |D_{00}^A(\Phi, \Theta, 0)|^2$. On the other hand, when $\langle \delta \rangle$ is large, interference type oscillatory contributions result in a partial erosion of the anisotropy.

These remarks are of academic interest only, as it is practically impossible to monitor the time evolution of the dissociation products on the time scale of the predissociation process, i. e., \hbar/Γ_J . More important, we note that in the limit $t \rightarrow \infty$ $\phi_{J,J''}(t)$, Eq. (V.11) takes the form

$$\phi_{J,J''}(\infty) = \frac{2\pi i}{E_{J''} - E_J + \frac{1}{2}i(\Gamma_{J'} + \Gamma_{J''})}, \quad (\text{V.14})$$

whereupon $W_J(\Theta, \infty) = W_J(\Theta)$ and Eq. (V.9) reduces to our previous result, Eq. (IV.2), which was obtained using scattering theory.

To compare the present quantum mechanical approach with Jonah's original treatment,⁶ all that is necessary is to assume that the fragments recoil along the molecular axis. Thus, the semiclassical probability for recoil in the Ω spatial direction is obtained from $|N(t)\rangle$, Eq. (V.3), expressed in the Ω representation that is

$$\frac{d}{dt} W_J(\Theta, t) \propto |\langle \Omega | \hat{P} | N(t) \rangle|^2. \quad (\text{V.15})$$

Such a treatment results in Eq. (V.12') and automatically introduces the axial recoil approximation.

VI. CONCLUDING REMARKS

We have provided a general quantum mechanical treatment for the problem of angular anisotropy in the predissociation of diatomics. From the point of view of general methodology, it is important to emphasize that no delay effects are observed in direct photodissociation, which, for all practical purposes (i. e., on a time scale larger than the inverse width of the bell shaped absorption line shape), can be considered to be instantaneous. The delay time for predissociation which was previously introduced in an *ad hoc* way,⁸ originates in a self-consistent manner from our study of predissociation. Our theory reduces to the original results of Zare⁷ for the case of direct photodissociation when we set the width Γ_J to be large. The same limiting result can be obtained by solving the problem of angular distribution in predissociation of a molecule where both the discrete excited state and the dissociative continuum carry oscillator strength from the ground state.²¹ When the coupling between the discrete state and the continuum is switched off, the direct photodissociation result is, of course, recovered. The extension of the present system for the Fano problem²² may be of some experimental interest in view of the recent observation of interference effects in the absorption line shapes for the predissociating Rydberg states of the H_2 molecule.²³

The results of Busch and Wilson,⁵ Jonah,⁶ and the present detailed treatment demonstrate that for the case of instantaneous direct photodissociation (or fast pre-

dissociation), the distribution of the products is determined by the initial distribution of the absorbing molecules. Slow predissociation does not erode all the anisotropy effects, although these are obviously reduced. Thus, for example, in a ${}^1\Sigma^-1\Sigma$ predissociation, the angular distribution is changed from $\cos^2\Theta$ for large value of $\langle \delta \rangle = \Gamma_J / (Bk_B T)^{1/2}$ to $(1 + \cos^2\Theta)$ for small value of $\langle \delta \rangle$. It can easily be shown that for a plane rotator, the product distribution will become isotropic in the limit of large $\langle \delta \rangle$. However, for a three-dimensional rotor, the dissociation process retains some of the information regarding its initial orientation even on a time scale long relative to the rotational period. This result can be rationalized in terms of two independent rotational modes of a three-dimensional rotor; one giving an isotropic distribution, while the other resulting in an anisotropic contribution.

There is a set of unified general features characterizing the angular distribution of photofragments in molecular photodissociation and predissociation, the angular distribution of electrons in atomic and molecular photoionization,^{10b} as well as angular correlations in nuclear decay.^{10a} The most general expression for the angular distribution, $I(\Theta)$, resulting from dipole induced one photon processes with an isotropic ensemble as a target, is of the form¹⁰

$$I(\Theta) = a(E) + b(E)P_2(\cos\Theta). \quad (\text{VI.1})$$

The general results [Eqs. (III.20) and (III.21)] for the case of predissociation derived herein are of this form, as the angular dependence of the cross section is determined by the parameters $\eta_{J',J''}^A$ which just contain the rotation matrices $D_{00}^0 \equiv P_0(\cos\Theta)$ and $D_{00}^2 \equiv P_2(\cos\Theta)$.

It will be interesting to confront these theoretical results with a real life situation and to study experimentally the angular distribution in molecular predissociation of a single molecule by varying some of the following parameters: (a) Excitation energy into different vibrational (rotational) levels. For the case of intersection of potential curves on the attractive branch of the bound state (Mulliken's case C^+), the predissociation widths $\Gamma_{v,J}$ exhibit a fluctuating pattern with changing the vibrational quantum number v , while for intersection on the repulsive branch of the bound state (Mulliken's case C^-), a smooth variation of the widths $\Gamma_{v,J}$ is exhibited by changing v .²⁴⁻²⁷ In suitable predissociating systems, one can thus vary the parameters $\langle \delta \rangle \approx (Bk_B T)^{1/2} / \Gamma_{v,J}$ passing from the slow decay limit to the fast decay situation; (b) In certain cases, external magnetic fields can enhance the predissociation rate,²⁸ thus providing an alternative way for passing to the fast dissociation limit; (c) Temperature changes will, of course, modify the angular distribution under the common excitation conditions, when individual rotational states are not selected. Let us now consider several specific examples, which demonstrate that in many common cases the predissociation decay rates are low relative to the rotational period. In the case of predissociation from the $B^3\Pi(0_0^+)$ state of I_2 , the predissociation rates are in the range $3 \times 10^5 - 3 \times 10^6 \text{ sec}^{-1}$, whereupon $\Gamma \approx 1.5 \times 10^{-6} - 5 \times 10^{-6} \text{ cm}^{-1}$. The rotational constant being $B = 0.029 \text{ cm}^{-1}$, so that $(Bk_B T)^{1/2} = 2.4 \text{ cm}^{-1}$ at room temperature, whereupon

$\langle \delta \rangle \sim 10^6$ and the slow photofragmentation limit prevails. In the case of predissociation from the $B^3\Sigma_u^-$ state of O_2 , the predissociation linewidth fluctuate for different v values in the range²⁵ 0.1–5.0 cm^{-1} , while $B = 1.5 \text{ cm}^{-1}$, and $(Bk_B T)^{1/2} = 17 \text{ cm}^{-1}$ (at 300 °K), thus $\langle \delta_v \rangle$ varies in the range 15–0.3. Some modification of the angular distribution will be exhibited when different vibronic manifolds are optically selected; however, even for the broadest vibronic levels, the situation will still be close to the slow dissociation limit. Another interesting case in this category involves predissociation from the $B0_u^+$ state of Se_2 . Theoretical studies^{18b} indicate that the resonance widths for different vibronic manifolds vary in the range 0.01 cm^{-1} to 200 cm^{-1} . From²⁶ $B = 0.01 \text{ cm}^{-1}$, we have $(Bk_B T)^{1/2} = 2.4 \text{ cm}^{-1}$ at 900 °K. Thus $\langle \delta_v \rangle$ varies from 0.01 to 250 for different v values spanning the whole domain from slow dissociation to extremely fast photofragmentation. It should be noted, however, that some of the details of the present theory have to be modified to handle this latter case properly. First, we have to consider the rotational states and the intramolecular coupling for Hund's case (c), while the present treatment strictly applies to Hund's case (a). Second, and more interesting, for the broad resonances in Se_2 we cannot get away with the treatment of the independent decay of a single vibronic level, as the spacing between vibronic states²⁶ ($\hbar\omega \approx 360 \text{ cm}^{-1}$) is of the order of their widths^{18b} ($\Gamma \approx 200 \text{ cm}^{-1}$). The theory has to be extended to account for this interesting situation.

APPENDIX A: EVALUATION OF THE CROSS SECTION FOR PHOTODISSOCIATION FOR A SINGLE GROUND STATE J LEVEL

Equation (III. 16) can be written with the help of Eq. (III. 13) in the explicit form

$$\sigma_{JM}(\Theta, E) = \frac{(2\pi)^2}{\hbar c} (2J+1) \rho_d \otimes \sum_{J', J''=J, J \pm 1} \frac{R_{J'} R_{J''}^* A_{J'} A_{J''} D_{M\Lambda}^J(\Phi, \Theta, 0) D_{M\Lambda}^{J''*}(\Phi, \Theta, 0)}{(E - E_{J'} + \frac{1}{2}i\Gamma_{J'}) (E - E_{J''} - \frac{1}{2}i\Gamma_{J''})} \quad (\text{A1})$$

Using Rose's Eqs. (4. 22) and (4. 25),¹⁵ we have for the products of the Wigner rotation matrices

$$D_{M\Lambda}^{J'} D_{M\Lambda}^{J''*} = (-1)^{M-\Lambda} D_{M\Lambda}^{J'} D_{M\Lambda}^{J''} = \sum_{\bar{J}} c(J' J'' \bar{J} | M - M) c(J' J'' \bar{J} | \Lambda - \Lambda) D_{00}^{\bar{J}} \quad (\text{A2})$$

We can now obtain $\sigma_J(\Theta, E)$ [Eq. (III. 17)] by summing Eq. (A1) over M to give

$$\sigma_J(\Theta, E) = \frac{1}{2J+1} \sum_M \sigma_{JM}(\Theta, E) = \frac{(2\pi)^2}{\hbar c} \rho_d \sum_{J', J''=J, J \pm 1} \frac{R_{J'} R_{J''}^*}{(E - E_{J'} + \frac{1}{2}i\Gamma_{J'}) (E - E_{J''} - \frac{1}{2}i\Gamma_{J''})} \eta_{J' J''}^{J\Lambda} \quad (\text{A3})$$

where

$$\eta_{J' J''}^{J\Lambda} = \sum_{\bar{J}} \alpha_{\bar{J}} c(J' J'' \bar{J} | \Lambda - \Lambda) c(J1J' | 0\Lambda) c(J1J'' | 0\Lambda) D_{00}^{\bar{J}} \quad (\text{A4})$$

and

$$\alpha_{\bar{J}} = \sum_M (-1)^{M-\Lambda} c(J' J'' \bar{J} | M - M) c(J1J' | 0\Lambda) c(J1J'' | 0\Lambda) \quad (\text{A5})$$

Making use of the well-known properties of the Clebsch Gordan coefficients (Rose,¹⁵ Chap. 3), we have

$$\alpha_{\bar{J}} = \sum_M (-1)^{M-\Lambda} c(J' J'' \bar{J} | M - M) c(1J J' | 0M) (-1)^{J+J'+1} \times c(J J'' 1 | M - M) (-1)^{J+M} \sqrt{\frac{2J''+1}{3}} \quad (\text{A6})$$

In this form, we can use Rose's Eq. (6. 5b) to get

$$\alpha_{\bar{J}} = (-1)^{\Lambda+J'+1} \sqrt{(2J'+1)(2J''+1)} W(1J J J'' | J' 1) \otimes c(11\bar{J} | 00), \quad (\text{A7})$$

where $W(abcd : ef)$ is the Racah coefficient.¹⁵

The factors $C(J1J' | 0\Lambda)$, $C(J1J'' | 0\Lambda)$ do not vanish only when J' , $J'' = J, J \pm 1$ (for $\Lambda = 0$, only if $J', J'' = J \pm 1$). The coefficient $C(11\bar{J} | 00)$ requires $\bar{J} = 0$ or 2. Equation (III. 20) is obtained from Eqs. (A3)–(A7).

APPENDIX B: SOME ALGEBRAIC MANIPULATIONS

From Eqs. (A1) and (A3), we have

$$\sum_{J', J''=J, J \pm 1} \eta_{J' J''}^{J\Lambda} = \sum_M \sum_{J', J''} A_{J'} A_{J''} D_{M\Lambda}^{J'}(\Phi, \Theta, 0) D_{M\Lambda}^{J''*}(\Phi, \Theta, 0) = \sum_M \left| \sum_{J'} A_{J'} D_{M\Lambda}^{J'}(\Phi, \Theta, 0) \right|^2 \quad (\text{B1})$$

Using Rose's¹⁵ Eq. (4. 25), we get

$$\sum_{J', J''} \eta_{J' J''}^{J\Lambda} = \sum_M |D_{M0}^J(\Phi, \Theta, 0) D_{0\Lambda}^1(\Phi, \Theta, 0)|^2; \quad (\text{B2})$$

since

$$\sum_M |D_{M0}^J(\Phi, \Theta, 0)|^2 = 1, \quad (\text{B3})$$

we finally obtain

$$\sum_{J', J''} \eta_{J' J''}^{J\Lambda} = |D_{0\Lambda}^1(\Phi, \Theta, 0)|^2 \quad (\text{B4})$$

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