INTERFERENCE EFFECTS IN DIRECTIONAL PHOTODISSOCIATION

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We present a scattering formalism for the problem of the angular distribution of the products in the photofragmentation of diatomics, in a process where both the (zero order) bound excited level and the dissociative continuum carry oscillator strength from the ground state.

Recent theoretical and experimental studies have elucidated the nature of the angular distribution of the photodissociation products of diatomics using plane polarized light [1–6]. A semiclassical model for retarded photodissociation was provided by Jonah [3], while the present authors have considered the partial erosion of angular anisotropy in a predissociation process [6]. In this note we present a study of the angular distribution in the photofragmentation of diatomics which involve interference between direct photodissociation and predissociation.

The level scheme advanced by Fano for the study of optical line shapes in autoionization and predissociation [7], was employed. We consider a three electronic level system of a diatomic: a bound ground electronic state |g⟩, an excited bound electronic state |s⟩, and a dissociative state |d⟩. Interference between potential and resonance scattering originates from radiative coupling of |g⟩ both to |s⟩ and to |d⟩. The eigenstates of the two bound electronic states are

\[ |\alpha M⟩ = r^{-1} \psi_{\alpha}(q,r) x_{\alpha}(q) (2J+1)/4\pi)^{1/2} D_{M\lambda\alpha}^{J}(\varphi, \theta, 0), \quad \alpha = g, s; \]  

(1)

\( \Lambda, \nu \) and \( J M \) represent the quantum numbers related to the total electronic angular momentum, the vibrational and the rotational motions of the nuclei, respectively. \( q \) are the electronic coordinates while \( r, \theta, \varphi \) correspond to the polar coordinates of the internuclear axis. \( \psi_{\alpha} \) is the electronic wavefunction, \( x_{\alpha} \) is the vibrational wavefunction and \( D_{M\lambda\alpha}^{J} \) is the Wigner rotation matrix [8]. The continuous eigenstates of the dissociative state, |\( d \rangle \) are chosen to satisfy the appropriate boundary conditions [5], exhibiting an asymptotic behaviour of a plane wave in an arbitrary \( \vec{k} \) direction plus an outgoing spherical wave, so that

\[ \langle K | = (K\epsilon)^{-1} \psi_{e}(q,r) \sum_{J M'} (2J'+1)\nu' \exp(-i\delta_{J'}) x_{e}^{(d)}(K\epsilon) D_{M'\lambda\alpha}^{J}(\varphi, \theta, 0) D_{M\lambda\alpha}^{J'}(\Phi, \Theta, 0). \]  

(2)

\( x_{e}^{(d)}(K\epsilon) \) is the solution of the radial equation for the |\( d \rangle \) state, characterized by kinetic energy, \( \epsilon \), momentum \( \hbar \vec{K} \) and normalized as \( \sin(K\epsilon - \frac{1}{2} \pi J + \delta_{J}) \) at asymptotically large \( K\epsilon \) values. \( \delta_{J} \) is the phase shift and \( \Phi, \Theta \) are the polar coordinates of \( K \). The states (1) and (2) correspond to the eigenstates of the Born–Oppenheimer Hamiltonian \( H_{BO} \).

The free radiation field \( H_{rad} \) is characterized by the zero photon state \( |vac \rangle \), and one photon states \( |ke \rangle \) where \( \vec{k} \) and \( e \) stand for the photon wavevector and polarization, respectively. Since we are interested in photodissociation using plane polarized light we can choose the \( x \) direction along \( e \) and omit \( e \) from the notation for the photon state.

The total Hamiltonian for the system is \( H = H_{0} + H_{v} + H_{int} \) where the zero order Hamiltonian is \( H_{0} = H_{BO} + H_{rad} \).
being characterized by the relevant eigenstates \(|guJM,k\rangle\), \(|su'J'M',\text{vac}\rangle\) and \(|K,\text{vac}\rangle\). \(H_q\) is the intramolecular coupling and \(H_{\text{int}}\) is the radiation—matter interaction term. The matrix elements of the electromagnetic interaction between the bound states are

\[
\langle su'J'M',\text{vac}|H_{\text{int}}|s\Omega JM,k\rangle = R^{(s)\Omega}_{J} \xi(J'M'\Lambda_d, J\Lambda_g),
\]

\[
R^{(s)\Omega}_{J} = \int dr \chi^{(s)\Omega}_{J}(r) \mu_d(r) \chi^{(s)\Omega}_{J}(r),
\]

\[
\mu_d(r) = \int \psi_e^{(s)}(q,r) \sum_i e q_i \psi_e^{(s)}(q,r) dq,
\]

\[
\xi(J'M'\Lambda_d, J\Lambda_g) = (4\pi)^{-1/2} \beta [(2J+1)(2J'+1)]^{1/2} \int d\Omega D_{J'M'}^{J'}(\varphi \theta 0) D_{\Lambda_d}^{\Lambda_g}(\varphi \theta 0) D_{\Lambda_g}^{\Lambda_d}(\varphi \theta 0),
\]

where \(\mu = \sum_i e q_i\) is the electronic transition moment operator and \(\beta\) is a numerical constant. Eqs. (3a) and (3b) represent the conventional Franck–Condon radial integral, while (3c) gives the angular integral which implies the well known selection rules \(J' = J, J \pm 1\) and \(M' = M\). \(\Lambda_d = |\Lambda_2 - \Lambda_g|\) is zero for parallel transitions and unity for perpendicular transitions.

The radiative coupling between the ground state and the dissociative state is

\[
\langle K|H_{\text{int}}|s\Omega JM,k\rangle = \sum_{J'M'} R^{(d)s}_{J'J} \xi(J'M'\Lambda_d, J\Lambda_g) D_{J'M'}^{J'}(\Phi, \Theta, 0),
\]

where

\[
R^{(d)s}_{J'J} = K^{-1} i^{J'} \exp(-i\delta_{J'}) \int \chi^{(d)s}_{J}(Kr) \mu_{dq}(r) \chi^{(s)\Omega}_{J}(r) dr,
\]

and

\[
\xi(J'M'\Lambda_d, J\Lambda_g) = (2J'+1) \xi(J'M'\Lambda_d, J\Lambda_g) [(2J'+1)4\pi]^{1/2}.
\]

\(\mu_{dq}(r)\) is given by eq. (3b) by replacing the index \(s\) by \(d\). The intramolecular coupling \(H_q\) (responsible for the predissociation) conserves angular momentum and the resonance coupling matrix elements are

\[
\langle K|H_q|s\Omega JM\rangle = [4\pi(2J+1)]^{1/2} R^{(d)s}_{J} D_{\Lambda_g}^{J}(\Phi, \Theta, 0) \delta_{\Lambda_d, \Lambda_g},
\]

\[
R^{(d)s}_{J} = K^{-1} i^{J} \exp(-i\delta_{J}) \int \chi^{(d)s*}_{J}(Kr) \nu_{dq}(r) \chi^{(s)\Omega}_{J}(r) dr,
\]

\[
\nu_{dq}(r) = \int \psi_e^{(d)s*}(q,r) H_q \psi_e^{(s)}(q,r) dq.
\]

To evaluate the angular distribution in a “long time” experiment we consider first the scattering cross sections from the initial one photon continuum state \(|i\rangle \equiv |s\Omega JM,k\rangle\) to the final dissociative continuum channel \(|f\rangle \equiv |K,\text{vac}\rangle\) which is given in terms of the reaction matrix \(T(E)\) [9]

\[
a_{i-f} = (2\pi/\hbar c) \sum_f \langle K,\text{vac}|T(E)|s\Omega JM,k\rangle^2 \rho_d,
\]

where \(\rho_d\) is the density of states in the final channel, \(c\) is the velocity of light and \(\hbar\) is Planck’s constant. To calculate the matrix elements of \(T(E)\) we partition our Hilbert space in the following manner:

\[
\hat{P} = |s,\text{vac}\rangle \langle s,\text{vac}|, \quad \hat{Q} = \hat{Q}_i + \hat{Q}_f = 1 - \hat{P},
\]

\[
\hat{Q}_i = \sum_{uJM,k} |guJM,k\rangle \langle guJM,k|, \quad \hat{Q}_f = \sum_K |K,\text{vac}\rangle \langle K,\text{vac}|.
\]
The reaction matrix may be written as:

$$T(E) = \hat{R}(E) + \hat{R}(E) \hat{P}G(E) \hat{P} \hat{R}(E),$$

(8)

where $\hat{R}$ is the level shift operator [10, 11], $G(E)$ is the Green function of the system which in the $\hat{P}$ subspace takes the form

$$\hat{P}G\hat{P} = (E - H_0 - \hat{P}H_0\hat{P})^{-1}.$$

(9)

The first term in eq. (8) may be regarded as a non-resonant part whereas the second is the resonant part of $T$. To evaluate $\langle f | T(E) | i \rangle$ one needs the operator $\hat{Q}_f T \hat{Q}_i$.

On the basis of our previous study of radiative interactions in the Fano problem [12], we can safely treat the problem to first order in $H_{\text{int}}$, whereupon eq. (8) results in

$$\hat{Q}_f T(E) \hat{Q}_i = \hat{Q}_f H_{\text{int}} \hat{Q}_i + \hat{Q}_f H_{\text{int}} \hat{P}G(E) \hat{P}H_{\text{int}} \hat{Q}_i.$$

(10)

Let us now consider a single isolated vibronic level $|sJ'M\rangle$. This level has a manifold of rotational states $|J'M\rangle$ each characterized by an energy $E_J$ and a width $\Gamma_J = -2 \text{Im} \langle sJ'M|\hat{P}H_0\hat{P}|sJ'M\rangle$. We assume that the level shift operator is diagonal in this basis set and that the energies $E_J$ contain the real part of the level shift operator [6]. Utilizing eqs. (3)–(5) and (8)–(10) we get

$$\langle K, \text{vac} | T(E) | g0JM, k \rangle = \sum_J (2J+1)^{1/2} \frac{R_{J'J}^{(d)} D^*_M \lambda_{J'0}(\Theta, \Phi, 0)}{E - E_J + \frac{1}{2} \Gamma_J} + \sum_J (2J+1)^{1/2} \frac{R_{J'J}^{(s)} A^{(d)}_{J'} D^*_M \lambda_{J'0}(\Theta, \Phi, 0)}{E - E_J + \frac{1}{2} \Gamma_J},$$

(11)

where

$$A^{(d)}_{J'0} = C(J1J'|J0) C(J1J'|0) \lambda_{J'0},$$

(11a)

and

$$R_{J'J} = (4\pi)^{1/2} \beta R_{J'J}^{(d)} R_{J'J}^{(s)}.$$  

(11b)

The cross section $\sigma_{JM}(\Theta, \Phi, E)$ for $|i\rangle \rightarrow |f\rangle$ scattering of photons with energy $E_i = \hbar \omega$ from a molecule in the $|g0JM\rangle$ state can now be obtained from eqs. (6) and (11). In the common case where the initial angular distribution of the ground state molecules is isotropic, we have to average the cross section over the available $M$ values, resulting in the cross section for a single $J$ level

$$\sigma_J(\Theta, \Phi, E) = (2J+1)^{-1} \sum_M \sigma_{JM}(\Theta, \Phi, E).$$

(12)

This averaging may be performed using the properties of the Wigner rotation matrices and Racah algebra [8]. After some algebraic manipulations we get

$$\sigma_J(\Theta, \Phi, E) = \frac{2\pi^2}{\hbar c} \rho_J \left[ \sum_{J',J''} R^{(d)}_{J'J} R^{(s)}_{J''J} \eta_{J'J''} \right]$$

$$+ \sum_{J',J''} R^{(d)}_{J'J} R^{(s)}_{J''J} \frac{R^{(d)}_{J'J''}}{E-E_J+i\Gamma_J} \frac{R^{(s)}_{J''J}}{E-E_J-i\Gamma_J} \eta_{J'J''}.$$  

(13)

where

$$\eta_{J'J''} = \frac{\langle f_J \rangle^2}{\langle f_{J''} \rangle^2} \langle f_J \rangle^2.$$  

Since the angular distribution is independent on $\Phi$ we can integrate $\sigma_J(\Theta, \Phi, E)$ over $\Phi$ resulting in $\sigma_J(\Theta, E) = \int d\Phi \sigma_J(\Theta, \Phi, E) = 2\eta_{J'J''} \sigma_J(\Theta, E).$  

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\[ \eta^{(g, g)}_{J J'} = \sum_{J=0,2} \alpha_J \mathcal{C}(J J'' J | J) \mathcal{C}(J J' | 0) \mathcal{C}(J J'' | 0) \mathcal{D}_{10}^J(\Phi, \Theta, 0) ; \]
\[ \lambda_\rho = |\Lambda_\rho - \Lambda_s| ; \alpha = d, s ; \beta = d, s \]
\[ \alpha_J = \sum_M (-1)^{M-\Lambda} \mathcal{C}(J J'' J | M - M) \mathcal{C}(J J' | M 0) C(J J' | M 0) \]
\[ = (-1)^{\Lambda+J+1} [(2J'+1)(2J''+1)]^{1/2} W(1 J J'' | J' 1) C(1 J J | 0 0) , \]
where \( \mathcal{C}(J J'' J | M M') \) is the Clebsch–Gordan coefficient and \( W(abcd|ef) \) is the Racah coefficient [8].

This result may be further simplified by adopting the axial recoil approximation [5, 6] which rests on the fact that the vibrational wavefunctions depend only slowly on \( J' \) for a small \( J' = J, J \pm 1 \). Thus we may replace \( R_{J J}^{(d g)} \) and \( R_{J J}^{(d g)} \) by \( R_{J J} \) and \( R_{J J}^{(d g)} \), respectively. Eq. (13) thus assumes the form
\[ \sigma_J(\Theta, E) = (4\pi^2/\hbar c) \rho_d \left[ |R_{J J}^{(d g)}|^2 |D_{0\lambda}\rangle(\Phi, \Theta, 0)|^2 \right. \]
\[ + |R_{J J}|^2 \sum_{J', J''=J \pm 1} \frac{(E-E_J)(E-E_J')}{2(1+4\Gamma_J^2)} \left[ (E-E_J)^2 + 4\Gamma_J^2 \right] \eta^{(d g)}_{J J'} \]
\[ \left. \sum_{J'', J''=J \pm 1} \frac{(E-E_J)(E-E_J')}{2(1+4\Gamma_J^2)} \eta^{(d g)}_{J J''} \right] , \]
Eqs. (13) and (16) provide us with the general result for the directional anisotropic photofragmentation under the conditions of monochromatic excitation of a single ground state \(|\nu\rangle\) level. The angular distribution under these circumstances is determined by three contributions, the first term on the r.h.s. of these equations involves the contribution of direct photodissociation, the second term corresponds to the resonant predissociation process while the third term is an interference contribution between direct photodissociation and resonant predissociation. To compare these results with a real life situation two further steps should be taken: (A) To account for the energy spread of the exciting pulse the cross sections should be averaged over the power spectrum \(|A(E)|^2\), where \( A(E) \) represents the amplitudes of the photon wavepacket [13]. The directional photofragmentation probability is
\[ W_J(\Theta) = \int dE|A(E)|^2 \sigma_J(\Theta, E) . \]
(B) \( W_J(\Theta) \) should be thermally averaged over the ground state initial \( J \) distribution.

Under the extreme conditions of broad band (or "short time") excitation \(|A(E)|^2 = 1 \) for all \( E \) so that \( W_J(\Theta) = \int dE\sigma_J(\Theta, E) \) and we obtain from eqs. (13) and (14)
\[ W_J(\Theta) = (4\pi^2/\hbar c) \rho_d \left[ \int dE |R_{J J}^{(d g)}(E)|^2 |D_{0\lambda}\rangle(\Phi, \Theta, 0)|^2 \right. \]
\[ + |R_{J J}|^2 \left( 2\pi/\Gamma_J \right) \left[ |D_{0\lambda}\rangle(\Phi, \Theta, 0)|^2 - 2 \sum_{J', J''=J \pm 1} \frac{(E_J - E_J')^2}{(E_J - E_J')^2 + 4\Gamma_J^2} \eta^{(d g)}_{J J'} P_2(\cos \Theta) \right] \],
where \( P_2(\cos \Theta) \) is a Legendre polynomial and
\[ \eta^{(d g)}_{J J'} = C(J J'' J | J) \mathcal{C}(J J' | 0) C(J J'' | 0) \mathcal{D}_{10}^J(\Phi, \Theta, 0) ; \]
\[ \alpha_J = \sum_M (-1)^{M-\Lambda} \mathcal{C}(J J'' J | M-M) \mathcal{C}(J J' | M 0) C(J J' | M 0) \]
\[ = (-1)^{\Lambda+J+1} [(2J'+1)(2J''+1)]^{1/2} W(1 J J'' | J' 1) C(1 J J | 0 0) . \]
We notice in passing that for the extreme case of broad-band excitation the contribution of the interference term [i.e., the third term on the r.h.s. of eq. (16)] vanishes.

To complete the presentation of the formal results let us consider the simplest case of a \( ^1\Sigma-^1\Sigma-^1\Sigma \) photofragmentation process, i.e., \( \Lambda_g = \Lambda_s = \Lambda_d = 0 \). Eq. (17) takes the form
\[ W_J(\Theta) = (4\pi^2/3\hbar c) \rho_d (F_1 + F_2) \]
Two concluding remarks should be made. First, our general results eqs. (13) and (16), together with the anisotropic distribution for broad band excitation [eq. (17)] and its special version (20), reduce under proper limiting conditions to the special results previously derived in this field [3, 5, 6]. When the resonance intramolecular coupling is switched off \( R^{dd}_{j} = 0 \) [see eq. (5)] only the first term survives in eqs. (13) and (16) and our results reduce to the case of direct photodissociation studied by Zare [5]. When the direct radiative coupling to the continuum states vanishes \( R^{(dd)}_{j} = 0 \) [see eq. (4)] only the second term in eqs. (13) and (16) is nonzero and the formalism reduces to the case of predissociation of a single resonance originally considered by Jonah within the framework of a semiclassical model [3] and recently studied by us [6]. Second, we would like to emphasize that the general form of the angular distribution in the photofragmentation process, i.e., \( a(E) + b(E) \cos \Theta \), for which eq. (19) provides a special example, is independent of the details (i.e., level structure and couplings) of the problem. This general form of the anisotropy is a direct consequence of the dipolar radiative interaction inherent in our problem. Such general relations, just depending on the order of the multipole of the electromagnetic coupling, are well known in nuclear physics [14] and in the field of atomic angular correlation spectroscopy [15].

References