

Theory of molecular photofragmentation

Shaul Mukamel* and Joshua Jortner

*Department of Chemistry, Tel-Aviv University, Tel Aviv, Israel
and Applied Optics Department, Soreq Nuclear Research Centre, Yavne, Israel
(Received 3 November 1975)*

In this paper we advance a unified theoretical scheme for the description of direct photodissociation and predissociation of polyatomic molecules. In the case of direct photodissociation we consider energy-resolved variables, i.e., the cross sections for photon absorption, for elastic and inelastic photon scattering, and for the populations of different dissociative channels. For predissociation we consider both time-resolved and energy-resolved experimental observables. The various cross sections relevant for the description of a direct photodissociation process were formally expressed by introducing a distorted wave basis to specify the eigenvalues of the nuclear states on the dissociative potential surface and advancing a general wave operator which is completely defined within the dissociative potential surface. Explicit expressions for the cross sections were derived with a proper account for radiative coupling effects. Utilizing projection operator techniques we have demonstrated that to a low (second) order in radiative interactions, which constitute an excellent approximation to the problem at hand, the photodissociation process is isomorphous with a coherent superposition of full collision processes on the electronically excited nuclear potential surface. Similar theoretical techniques are utilized for the study of energy-resolved and time-resolved observables in predissociation. Subsequently, we have invoked a set of systematic approximations to reduce the formal expression to a tractable form. The Heitler K matrix formalism is utilized, and the introduction of the first-order approximation for the K matrix results in explicit expressions for the time- and energy-resolved observables in photofragmentation, where the cross sections are expressed in terms of products of an initial coupling matrix, the wave operator matrix, and a radiative interference matrix. This formalism is then adopted for the special case of linear photofragmentation of triatomics. Analytical, quantum mechanical expressions for the experimental observables and, in particular, for the vibrational energy distribution of the photofragments were derived for a linear triatomic, where the interfragment repulsion is exponential and the diatomic fragment is characterized by a harmonic potential. The effects of intercontinuum coupling on the vibrational energy distribution in the predissociation of XCN ($X = \text{H, Cl, Br, and I}$) molecules in the energy range $\sim 6.5\text{--}10.5$ eV were investigated.

I. INTRODUCTORY REMARKS

The advent of new radiation sources, such as lasers, vacuum ultraviolet lamps, and synchrotron radiation, combined with spectroscopic detection methods and molecular-beam techniques, made it possible to probe some interesting new features of direct photodissociation (DP) and predissociation (PR) of polyatomic molecules.¹⁻⁸ Experimental studies in this field have unfolded the nature of the internal energy distribution^{1,2,5,6,8} and the angular distribution^{2,3,7} of the photofragmentation products. Related information originates from the vibrational-energy distribution of the fragments resulting from collisional dissociative reactions between an electronically excited atom and a ground-state triatomic molecule^{9,10} and from collisionally induced electronic-to-vibrational energy transfer between an excited atom and a ground-state diatomic molecule.¹¹ There has been recently a considerable theoretical effort directed towards the elucidation of the dynamics of molecular photofragmentation.¹²⁻³⁰ The following problems are relevant in this context:

(a) What is the proper theoretical description of the optical excitation process which results in photofragmentation? In most theoretical studies of molecular photodissociation, the effects of the optical excitation were disregarded and one has started with the dynamic problem on the final potential surface.

(b) What are the effects of intrafragment structure on the photofragmentation dynamics? One has to consider the effects of the configurational changes and frequency changes in the polyatomic radicals resulting

from photofragmentation, relative to the bound molecule. The latter corresponds to the ground electronic state in the case of DP or to a metastable electronically-vibrationally excited (zero order) state in the case of PR. These effects may be accounted for in terms of the multidimensional Franck-Condon factors for the optical transition, incorporating both the bound modes of the fragments as well as the dissociative mode.

(c) What is the role of interfragment coupling on the dynamics of photofragmentation? These effects stem from interactions between final dissociative channels.

(d) What is the nature of the vibrational-energy distribution of the photofragmentation products? The intrafragment structure will determine the coupling between the dissociative exit channels and the ground state for the case of DP, where the coupling is radiative, or with a bound electronically excited state in the case of PR, where the coupling corresponds to nonadiabatic intramolecular interactions. The interfragment coupling connects different decay channels. Thus, both effects have to be simultaneously considered.

(e) What is the nature of the rotational energy distribution of the photofragments?

Concerning point (a), we note that time-resolved (TR) excitation experiments, where the excitation and subsequent decay processes can be separated are practical only for the case of PR. In the case of DP the time scale for the dissociation process is determined by the Fourier transform of the absorption line shape function. The structureless, bell-shaped, molecular absorption

bands originating from DP are broad, being characterized by a typical width of $10^3 \sim 10^4 \text{ cm}^{-1}$, which correspond to ultrafast decay times of $\sim 10^{-14} \text{ sec}$, whereupon time-resolved optical experiments are currently not practical. Thus, DP has to be described in terms of energy-resolved (ER) observables, such as cross sections and quantum yields, for the population of final exit channels. Predissociation processes are amenable to experimental study both in terms of the above (energy-resolved) cross sections or, alternatively, via the short excitation experiments involving decay of metastable states. Regarding the role of intrafragment structure [point (b)], it was recently suggested by Simons and Tasker,²⁹ Berry,³⁰ and Band and Freed²⁷ that Franck-Condon overlap factors, which determine the transition amplitudes to the various dissociative channels determine the vibrational-translational energy of the photofragments. Regarding the effects of interfragment coupling [point (c)], Wilson and his colleagues^{15,2} have advanced the "half-collision" picture which was later subjected to some numerical calculations by Shapiro and Levine,¹⁷ while the present authors have proposed a physical picture which rests on a sequential decay model involving multiple coupled continua.^{24,25} Most treatments emphasize exclusively either the intrafragment coupling or, alternatively, the interfragment dynamics, although we have recently provided a phenomenological model which incorporates both effects.²⁵ The dichotomy between these two physical effects which determine the vibrational distribution of the photofragmentation products [point (d)] cannot be currently bridged on the basis of the available experimental data, and a theoretical reexamination of the problem is desirable. Our previous study²⁵ of the final vibrational-energy distribution in the photofragmentation of a linear triatomic molecule, which is determined by "initial" coupling to different dissociative continua together with intercontinuum coupling, contains the essential physical ingredient required for a coherent description of the problem. However, we did not provide explicit expressions for the interfragment coupling between adjacent continua. Finally, from the point of view of general methodology, it is important to notice that the collinear photofragmentation models, which are analogous to the popular approach to reactive scattering in collinear chemical reactions,³¹ are adequate just for vibrational-energy redistribution. In order to account for the rotational energy redistribution [point (e)], as well as for angular distribution, one can either adopt statistical models assuming that all degrees of freedom are sufficiently scrambled to insure a significant population of all exit channels or, preferably, a complete quantum-mechanical description of angular momentum coupling in photofragmentation of polyatomics should be advanced.

The present paper provides a theoretical scheme for the description of DP and PR processes of polyatomic molecules. In Sec. II we define the various cross sections in a DP experiment and express them in terms of a distorted wave operator F_1 , completely defined within the dissociative-potential surface. Utilizing projection operator techniques we show that to low or-

der in radiative interactions, which constitutes a very good approximation, one can describe the photodissociation process as a coherent superposition of full collisions on the dissociative potential surface, thus establishing the formal relation between photofragmentation and collision theory. In Sec. IV we express the experimental observables in TR and ER, PR experiments in terms of the F_1 matrix of Sec. II and the formal similarity between PR and DP processes is demonstrated. In order to reduce the formal treatment to a tractable form we subsequently consider in Sec. V the Heitler relation for the reaction operator (K). We show how the first order K matrix can be applied to reduce the problem at hand to the inversion of a finite-size, on-the-energy-shell matrix, resulting in explicit expressions for the distribution of the products. This formalism is applied in Sec. VI to the special case of linear photofragmentation of triatomics. The role of intercontinuum coupling in photofragmentation of triatomics is explored, and compared with the experimental results of Mele and Okabe⁵ on the photodissociation of XCN molecules.

II. A MODEL HAMILTONIAN FOR PHOTOFRAGMENTATION

Consider a polyatomic molecule RA, undergoing photofragmentation into the fragments R and A. We assume that only two electronic molecular states may be considered in the description of DP, while three electronic states are involved in PR. The total Hamiltonian for DP can be written in the form

$$H = |g_e\rangle H_{\text{BO}}^{(g)} \langle g_e| + |d_e\rangle H_{\text{BO}}^{(d)} \langle d_e| + H_r + H_{\text{int}} \quad (\text{II. 1})$$

while for predissociation we have

$$H = |g_e\rangle H_{\text{BO}}^{(g)} \langle g_e| + |s_e\rangle H_{\text{BO}}^{(s)} \langle s_e| + |d_e\rangle H_{\text{BO}}^{(d)} \langle d_e| + H_r + H_{\text{int}} + H_v \quad (\text{II. 2})$$

The following notation is used in Eqs. (II. 1) and (II. 2):

$|j_e \alpha\rangle \equiv |j_e\rangle |j \alpha\rangle$ is a Born-Oppenheimer state of the molecule represented in terms of the product of electronic $|j_e\rangle$ and nuclear $|j \alpha\rangle$ states; $\epsilon_{j \alpha}$ —energy of the $|j_e \alpha\rangle$ state where j and α correspond to all electronic and nuclear quantum numbers, respectively.

$H_{\text{BO}} = \sum_j |j_e\rangle H_{\text{BO}}^{(j)} \langle j_e|$ is the total Born-Oppenheimer molecular Hamiltonian.

$H_{\text{BO}}^{(j)} = \sum_\alpha |j \alpha\rangle \epsilon_{j \alpha} \langle j \alpha|$ is the Born-Oppenheimer Hamiltonian of the j th electronic state. $H_{\text{BO}}^{(j)}$ acts on the nuclear coordinate space. $j = g, d, s$.

$|g_e\rangle$ is the electronic ground state.

$|d_e\rangle$ is an electronically excited dissociative state.

$|s_e\rangle$ is a bound, electronically excited state.

H_v is the nonadiabatic intramolecular coupling (i. e., nuclear kinetic energy and spin-orbit interaction).

H_r is the Hamiltonian of the free radiation field.

H_{int} is the molecule-radiation field interaction.

The various parts of the total Hamiltonian, as well as the corresponding eigenstates, are defined in Table I.

TABLE I. Definitions of Hamiltonian and coupling terms for photofragmentation.

Term	Definition	Eigenstates	Eigenvalues	Remarks
$H_{\text{BO}}^{(g)}$	Ground state BO Hamiltonian	$ g_e v_g\rangle = g_e\rangle g v_g\rangle$	$E_{g v_g}$	v_g denotes all the internal quantum numbers. Eigenfunctions $\langle Q_g g v_g \rangle$ are products of H.O. wavefunctions and rotational parts.
$H_{\text{BO}}^{(s)}$	Excited (discrete) state BO Hamiltonian	$ s_e v_s\rangle = s_e\rangle s v_s\rangle$	$E_{s v_s}$	v_s denotes all internal quantum numbers. Eigenfunctions $\langle Q_s s v_s \rangle$ are products of H.O. wavefunctions and rotational parts.
$H_{\text{BO}}^{(d)}$	BO Hamiltonian for the dissociative state	Wavefunction is a complicated superposition of all available channels (usually not known).		Nuclear coordinates are chosen as Q_R internal coordinates of R , Q_A internal coordinates of A , Q_{RA} interfragment vector,
$\hat{H}_{\text{BO}}^{(d)}$	asymptotic form of $H_{\text{BO}}^{(d)}$ when $Q_{RA} \rightarrow \infty$	$ d_e \gamma_A \gamma_R l\rangle$		γ_A internal quantum numbers of A , γ_R internal quantum numbers of R , l relative momentum of fragments.
$V_d(Q_R, Q_A, Q_{RA}) \equiv H_{\text{BO}}^{(d)} - \hat{H}_{\text{BO}}^{(d)} = V_0 + V_1$	interfragment interaction			We assume that the $ d_e\rangle$ electronic state has no bound states, otherwise V_d would have included additional terms.
V_0	Elastic part of V_d (i.e., the part of V_d which does not cause internal excitation)			
				$V_0 = \sum_{v_d, l, l'} d v_d l\rangle \langle d v_d l V_d d v_d l' \rangle \langle d v_d l' $
V_1	Inelastic part of V_d			
				$V_1 = \sum_{v_d \neq v_d', l, l'} d v_d l\rangle \langle d v_d l V_d d v_d' l' \rangle \langle d v_d' l' $
$\bar{H}_{\text{BO}}^{(d)} = \hat{H}_{\text{BO}}^{(d)} + V_0$	Distorted wave (DW) Hamiltonian, taking care for elastic scattering of A on R	$ d v_d l^{\pm}\rangle = d v_d l\rangle + (E - \hat{H}_{\text{BO}}^{(d)} \pm i\eta)^{-1} V_0 d v_d l^{\pm}\rangle$		The $+$ ($-$) signs pertain to the asymptotic behavior of an incident beam + an outgoing (incoming) spherical wave.
		$ d_e v_d l^{\pm}\rangle \equiv d_e\rangle d v_d l^{\pm}\rangle$		
H_r	Hamiltonian for the free radiation field	$ \text{vac}\rangle$ vacuum state $ k\rangle$ one photon state with wave vector k		We do not specify explicitly the photon polarization ϵ but when needed it will be specified. We are not interested in high field effects (saturation, etc.) so we do not consider multiphoton states.
$\langle d_e v_d l^{\pm}, \text{vac} H_{\text{int}} g_e v_g, k \rangle = D_{dg}^{(\text{int})} \text{FC}_{dg}(v_d l^{\pm}, v_g)$	Radiative interaction matrix element between $ g_e\rangle$ and $ d_e\rangle$.			$D_{dg}^{(\text{int})}$ is an electronic transition moment.
$\text{FC}_{dg}(v_d l^{\pm}, v_g) \equiv \langle d v_d l^{\pm} g v_g \rangle$	Franck-Condon overlap factor.			
$\langle s_e v_s, \text{vac} H_{\text{int}} g_e v_g, k \rangle = D_{sg}^{(\text{int})} \text{FC}_{sg}(v_s, v_g)$	radiative interaction matrix element between $ s_e\rangle$ and $ g_e\rangle$			$D_{sg}^{(\text{int})}$ is an electronic transition moment.
$\text{FC}_{sg}(v_s, v_g) \equiv \langle s v_s g v_g \rangle$	Franck-Condon overlap factor.			

The BO discrete states corresponding to $H_{\text{BO}}^{(g)}$ and $H_{\text{BO}}^{(s)}$ are usually well defined. As for $H_{\text{BO}}^{(d)}$, its true eigenstates are complicated scattering wavefunctions involving all the available channels. So we define in Table I two kinds of zero-order Hamiltonians: $\hat{H}_{\text{BO}}^{(d)}$ corresponding to the separated fragments, and a distorted-wave^{32,33} Hamiltonian $\bar{H}_{\text{BO}}^{(d)}$ whose eigenstates are the solutions of the approximate elastic scattering problem of A on R.

Our zeroth-order molecular basis set consists of the BO states belonging to $|g_e\rangle$ and $|s_e\rangle$ (i. e., eigenstates of $|g_e\rangle H_{\text{BO}}^{(g)} \langle g_e|$ and $|s_e\rangle H_{\text{BO}}^{(s)} \langle s_e|$, respectively) and the DW states $|d_e v_d l\rangle$ which are eigenstates of $|d_e\rangle \bar{H}_{\text{BO}}^{(d)} \langle d_e|$. The Hamiltonian (II. 2) contains three interaction terms having off-diagonal elements in our zeroth-order basis set: V_1 , H_{int} , and H_v . The V_1 term (the inelastic part of the interfragment potential) will be discussed later in detail. At this stage, let us just specify explicitly the other off-diagonal terms. The radiative coupling matrix elements may be factorized within the Condon approximation into a product of an electronic transition moment and a Franck-Condon overlap factor (see Table I). In the case of PR we have to consider also the matrix element of H_{v1} , $\langle d_e v_d l | H_v | s_e v_s \rangle$. When the electronic configurations $|s_e\rangle$ and $|d_e\rangle$ correspond to different spin states, $H_v = H_{so}$ is the spin-orbit coupling operator, whereas when nonradiative coupling between the same spin states $|s_e\rangle$ and $|d_e\rangle$ is considered, the interaction is due to the nuclear kinetic energy term T_N . In both cases the matrix element of H_v may be described approximately in terms of appropriate Franck-Condon factors.

III. CROSS SECTIONS FOR DIRECT PHOTODISSOCIATION AND RELATION WITH SCATTERING THEORY

The half-collision concept has been introduced by Wilson *et al.*¹⁵ for the description of the dissociative dynamics. The idea is that the dissociating system is initially prepared as a wave packet localized in the interaction region of a dissociative potential surface, and the evolution of this state leads to the dissociation. The term half-collision stems from the fact that the system is initially already in the interaction region and undergoes only the "second half" of a usual collision process. As performing TR direct photodissociation is not practical at present (see Sec. I), we shall adopt here the complementary approach and consider ER experiments in order to examine whether the observables of such experiments may be expressed in terms of collision theory. The results of ER experiments may be expressed in terms of the relevant cross sections, i. e., $\sigma_d^{v_g \rightarrow v_d}(E)$ —cross section for dissociation in the v_d channel, $\sigma_r^{v_g \rightarrow v_g'}(E)$ —cross section for photon scattering into the v_g' channel (the scattering may be elastic if $v_g = v_g'$ or inelastic) and, finally, we have the total absorption cross section (the line shape) $\sigma_a^{v_g}(E)$. The cross section for photodissociation per unit solid angle Ω_d into the intramolecular continuum $|d_e v_d l, \text{vac}\rangle$ is given in terms of the transition (T) matrix^{32,33}

$$\begin{aligned} & \langle d_e v_d l, \text{vac} | T | g_e v_g, \mathbf{k} e \rangle \rightarrow | d_e v_d, \text{vac} \rangle \\ & = (2\pi L^3 / \hbar c) | \langle d_e v_d l, \text{vac} | T | g_e v_g, \mathbf{k} e \rangle |^2 \rho_d(E), \quad (\text{III. 1}) \end{aligned}$$

where L^3 is the volume of the box and $\rho_d(E)$ is the density of states in the dissociative continuum. We shall define also an integrated dissociation cross section by summing up Eq. (III. 1) over the momenta of the final states and averaging over the initial photon polarization and propagation directions, resulting in $\sigma_d^{v_g \rightarrow v_d}(E)$ —the photodissociation cross section into channel v_d

$$\sigma_d^{v_g \rightarrow v_d}(E) = \left\langle \int d\Omega_d \frac{d\sigma_d^{v_g \rightarrow v_d}}{d\Omega_d} (|g_e v_g, \mathbf{k} e\rangle - |d_e v_d l, \text{vac}\rangle) \right\rangle. \quad (\text{III. 2})$$

The differential photon scattering cross section (per unit solid angle Ω' of k' photons) is given by

$$\begin{aligned} & \langle d\sigma_r / d\Omega' (|g_e v_g, \mathbf{k} e\rangle - |g_e v_g', \mathbf{k}' e'\rangle) \\ & = (2\pi L^3 / \hbar c) | \langle g_e v_g', \mathbf{k}' e' | T | g_e v_g, \mathbf{k} e \rangle |^2 \rho_r'(k'). \quad (\text{III. 3}) \end{aligned}$$

Here $\rho_r'(k')$ is the density of final photon states

$$\rho_r'(k') = k'^2 L^3 / (2\pi)^3 \hbar c. \quad (\text{III. 4})$$

The photon scattering cross section $\sigma_r^{v_g \rightarrow v_g'}(E)$ into the final molecular state $|v_g'\rangle$ will be obtained by summing up Eq. (III. 6) over all final spatial directions and polarization directions

$$\sigma_r^{v_g \rightarrow v_g'}(E) = \left\langle \int_{\Omega'} d\Omega' \langle d\sigma_r / d\Omega' (|g_e v_g, \mathbf{k} e\rangle - |g_e v_g', \mathbf{k}' e'\rangle) \right\rangle, \quad (\text{III. 5})$$

where $\langle \rangle$ denotes averaging over initial molecular orientations with respect to the photon polarization. Finally, the photon absorption cross section is now given by

$$\sigma_a^{v_g}(E) = - (2L^3 / \hbar c) \text{Im} \langle g_e v_g, \mathbf{k} e | H_{\text{int}} G(E) H_{\text{int}} | g_e v_g, \mathbf{k} e \rangle. \quad (\text{III. 6})$$

The quantum yields for the various channels, when the incident field has an intensity distribution $W(E)$, are

$$Y_{\alpha}^{v_g \rightarrow \beta} = \int dE W(E) \sigma_{\alpha}^{v_g \rightarrow \beta} / \int dE W(E) \sigma_a^{v_g}(E). \quad (\text{III. 7})$$

Substituting $\alpha = r$, $\beta = v_g'$ results in photon scattering yields, whereas substituting $\alpha = d$, $\beta = v_d$ results in photodissociation yields. The relevant T matrix elements appearing in Eqs. (III. 1), (III. 3), and (III. 6) will now be evaluated utilizing projector-operator techniques.^{34,35} For the treatment of a DP process we shall partition our Hilbert space as follows:

$$\hat{P} = \sum_{v_g, \mathbf{k}} |g_e v_g, \mathbf{k}\rangle \langle g_e v_g, \mathbf{k}| \quad (\text{III. 8a})$$

and

$$\hat{Q} = \sum_{v_d, l} |d_e v_d l, \text{vac}\rangle \langle d_e v_d l, \text{vac}|. \quad (\text{III. 8b})$$

The cross sections for photon scattering (absorption) and for photodissociation are given in terms of the matrix elements of $\hat{P} T \hat{P}$ and $\hat{Q} T \hat{P}$, respectively. In Appendix A it is shown that these matrix elements may be written in the form

$$\begin{aligned} & \langle d_e v_d l, \text{vac} | \hat{Q} T \hat{P} | g_e v_g, k \rangle \\ & = \sum_{v_g'} \langle d_e v_d l, \text{vac} | \hat{Q} R \hat{P} | g_e v_g', \mathbf{k} \rangle \langle v_g' | \Phi^{-1} | v_g \rangle \quad (\text{III. 9}) \end{aligned}$$

and

$$\langle g_e v'_g, \mathbf{k}' | \hat{P}T\hat{P} | g_e v_g, \mathbf{k} \rangle \\ = \sum_{v'_g} \langle g_e v'_g, \mathbf{k}' | \hat{P}R\hat{P} | g_e v''_g, \mathbf{k} \rangle \langle v''_g | \Phi^{-1} | v_g \rangle, \quad (\text{III. 10})$$

where R [Eq. (A4)] is the level-shift operator, whereas Φ is an $m \times m$ matrix, m being the number of open radiative channels in the ground state, i. e., the number of $|g_e v_g\rangle$ states. The Φ matrix accounts for high order radiative transitions between the P and Q subspaces, and provides an interference between the various radiative channels. We have estimated elsewhere^{36,37} the order of magnitude of Φ for a diatomic molecule, which is characterized by a single dissociative channel. We have established that $\Phi \approx 1 + O(10^{-7})$, so that for all practical purposes Φ may be replaced by a unit matrix. This amounts to treating the problem to lowest order in H_{int} (i. e., first order for dissociation expressed in terms of $\hat{Q}T\hat{P}$ and second order for photon scattering determined by $\hat{P}T\hat{P}$). The rough estimate of the effect of radiative coupling is valid also for polyatomic molecules since it is based on orders of magnitude considerations of the radiation-matter interaction. In Sec. V we shall provide explicit expressions for the matrix elements of Φ for a simplified molecular model, which will further confirm this conclusion. We thus conclude that to low order in radiative interaction we have the compact results

$$\hat{Q}T\hat{P} \approx \hat{Q}R\hat{P}, \quad (\text{III. 11a})$$

$$\hat{P}T\hat{P} \approx \hat{P}R\hat{P}. \quad (\text{III. 11b})$$

We are now in a position to investigate the concept of half-collision in energy-resolved experiments. Operating with $\hat{Q}R\hat{P}$,

$$\hat{Q}R\hat{P} = \hat{Q}V\hat{P} + \hat{Q}R\hat{Q}G_0\hat{Q}V\hat{P}, \quad (\text{III. 12})$$

on a state $|g_e v_g, \mathbf{k}\rangle$ results in

$$\hat{Q}R\hat{P} | g_e v_g, \mathbf{k} \rangle = \hat{Q}H_{\text{int}}\hat{P} | g_e v_g, \mathbf{k} \rangle + \hat{Q}R\hat{Q} \cdot \sum_{v_d 1} | d_e v_d 1 \rangle \\ \times (E - E_{v_d 1} + i\eta)^{-1} \langle d_e v_d 1 | H_{\text{int}} | g_e v_g, \mathbf{k} \rangle, \quad (\text{III. 13})$$

where we have explicitly introduced a complete set of \hat{Q} states.

The first term in Eq. (III. 13) is a direct coupling term, while the second term consists of the operator $\hat{Q}R\hat{Q}$ acting on a wave packet defined on the excited electronic surface. Note that $\hat{Q}R\hat{Q}$ is actually the transition (T) matrix on the upper excited electronic surface, when we ignore any interaction with the ground state. The second term in Eq. (III. 13) thus represents a superposition of full collisions on the dissociative potential surface. This superposition forms a well-defined wave packet at the interaction region (since $|g_e v_g, \mathbf{k}\rangle$ is strongly localized in this region), and this wave packet undergoes the second half of a usual collision process. We have thus provided the theoretical justification for treating photodissociation as a half-collision on the single potential surface which corresponds to the excited electronic state.

The following conclusions concerning half-collisions

can be drawn at this stage:

(1) The half-collision is a meaningful concept for ER measurements and in view of Eq. (III. 13) it can be represented as a well-defined superposition of full collision processes on the excited electronic surface.

(2) This superposition yields an appropriate wave packet located at the interaction region at time $t=0$.

(3) The final distribution amplitudes are sums of the direct coupling plus the contribution of the half-collision.

(4) Numerical solution of the S matrix on the dissociative surface together with Eq. (III. 13) will result in the photodissociation cross sections. We have thus established the connection between photodissociation processes and the general framework of scattering calculations. Previous attempts³⁸ to establish the connection are, in our opinion, incomplete.

(5) It is important to notice that in spite of the fact that in ER scattering there is no "preparation" of states in the usual sense, we can still treat the system in terms of a collision of a wave packet of virtual states.

After discussing the general framework for handling photodissociation problems, let us consider in more detail how evaluation of the various cross sections is really made. We have shown that the problem of distribution of products is actually equivalent to a coherent superposition of full collisions on the excited electronic surface, which may be handled using the appropriate transition matrix $\hat{Q}R\hat{Q}$. As was already noted in Sec. II, it is convenient to handle the inelastic collisions problem by means of the DW basis set (see Table I). Using this basis we shall be able to treat the elastic part of the potential (V_0) rigorously and obtain an exact result for the contribution of the inelastic part (V_1) which can be subsequently simplified by various systematic approximation procedures. In this section we present the exact formalism, while the approximate methods will be given in Sec. V. We shall now apply the formula of scattering by two potentials^{32,33} to rewrite the matrix elements of $\hat{Q}R\hat{P}$ in the form^{35,37}

$$\langle d_e v_d 1, \text{vac} | \hat{Q}R\hat{P} | g_e v_g, \mathbf{k} \rangle \\ = \sum_{v'_d 1'} \langle d v'_d 1' | \hat{Q}F_1\hat{Q} | d v'_d 1' \rangle \langle d_e v'_d 1' | H_{\text{int}} | g_e v_g, \mathbf{k} \rangle, \quad (\text{III. 14})$$

where

$$\hat{Q}F_1\hat{Q} = \hat{Q} + \hat{Q}V_1\hat{Q}(E - H_0 - V_0 - V_1)^{-1}\hat{Q}, \quad (\text{III. 15})$$

satisfying the integral equations

$$\hat{Q}F_1\hat{Q} = \hat{Q} + \hat{Q}V_1\hat{Q}(E - H_0 - V_0)^{-1}\hat{Q}F_1\hat{Q} \quad (\text{III. 16a})$$

and

$$\hat{Q}F_1\hat{Q} = \hat{Q} + \hat{Q}F_1\hat{Q}V_1\hat{Q}(E - H_0 - V_0)^{-1} \quad (\text{III. 16b})$$

and $|d v_d 1\rangle$ are the incoming solutions of the elastic scattering problem given in Table I. Note that Eq. (III. 15) is a version of the Lippman-Schwinger equation.³² We have thus expressed the $\hat{Q}T\hat{P}$ matrix elements in terms of the DW solutions of the excited, dissociative, electronic state. Substituting Eq. (III. 16) in Eq. (III. 14) results in

$$\langle d_e v_d \mathbf{l}, \text{vac} | \hat{Q}R\hat{P} | g_e v_g, \mathbf{k} \rangle = \langle d_e v_d \mathbf{l}^-, \text{vac} | H_{\text{int}} | g_e v_g, \mathbf{k} \rangle + \sum_{v_d' \mathbf{l}'} \langle d v_d' \mathbf{l}^-, \text{vac} | \hat{Q}R_1 \hat{Q} | d v_d' \mathbf{l}'^-, \text{vac} \rangle (E - E_{v_d' \mathbf{l}'^-} + i\eta)^{-1} \langle d_e v_d' \mathbf{l}', \text{vac} | H_{\text{int}} | g_e v_g, \mathbf{k} \rangle, \quad (\text{III. 17})$$

where

$$\hat{Q}R_1 \hat{Q} = \hat{Q}F_1 \hat{Q}V_1 \hat{Q} \quad (\text{III. 18})$$

is an operator whose matrix elements in the DW basis give the inelastic scattering amplitudes within Q [see Eq. (III. 21)]. Equation (III. 17) is the distorted wave-form of Eq. (III. 13).

$$\langle g_e v_g', \mathbf{k}' | \hat{P}T\hat{P} | g_e v_g, \mathbf{k} \rangle = \langle g_e v_g', \mathbf{k}' | \hat{P}H_{\text{int}} \hat{Q}G_0 \hat{Q}F_1 \hat{Q}H_{\text{int}} \hat{P} | g_e v_g, \mathbf{k} \rangle = \sum_{v_d' \mathbf{l}'} \langle g_e v_g' \mathbf{k}' | H_{\text{int}} | d_e v_d' \mathbf{l}'^- \rangle \frac{1}{E - E_{v_d' \mathbf{l}'^-}} \langle d v_d' \mathbf{l} | \hat{Q}F_1 \hat{Q} | d v_d' \mathbf{l}'^- \rangle \langle d_e v_d' \mathbf{l}'^- | H_{\text{int}} | g_e v_g, \mathbf{k} \rangle. \quad (\text{III. 20})$$

For the sake of completeness let us also recall the formula for the scattering amplitudes within the $|d_e\rangle$ surface, i. e.,^{32,33}

$$\langle d v_d' \mathbf{l}' | \hat{Q}R\hat{Q} | d v_d \mathbf{l} \rangle = \langle d v_d' \mathbf{l}' | \hat{Q}V_0 \hat{Q} | d v_d \mathbf{l}^* \rangle + \langle d v_d' \mathbf{l}'^- | \hat{Q}R_1 \hat{Q} | d v_d \mathbf{l}^* \rangle, \quad (\text{III. 21})$$

where the first term represents the elastic scattering, whereas the second is responsible for the scattering due to V_1 in the presence of V_0 , and contributes to the inelastic and elastic cross sections. $\hat{Q}R_1 \hat{Q}$ was already defined in Eq. (III. 18). This completes the formal procedure for providing explicit expressions for the matrix elements which determine the relevant cross sections for the photodissociation problem.

IV. ENERGY PARTITIONING IN PREDISSOCIATION

The level scheme and Hamiltonian of a molecule undergoing predissociation were described in Sec. II. As before, we utilize the projection-operators technique and partition the Hilbert space by the projections \hat{P} and $\hat{Q} = \hat{Q}_g + \hat{Q}_d$, where \hat{P} projects into the states $|s_e \beta, \text{vac}\rangle$, \hat{Q}_g includes the states $|g_e v_g, \mathbf{k}\rangle$, whereas \hat{Q}_d includes the dissociative states $|d_e v_d \mathbf{l}\rangle$.

As in the case of direct photodissociation, an ER experiment is completely specified in terms of the cross sections for dissociation (σ_d), photon scattering (σ_r), and absorption (σ_a). We now assume that (i) H_{int} couples $|g_e\rangle$ with $|s_e\rangle$, whereas H_v couples $|s_e\rangle$ with $|d_e\rangle$. This assumption implies that there is no direct scattering between $|g_e\rangle$ and $|d_e\rangle$, and it strictly holds in many cases of physical interest. (ii) The P space consists of a single discrete state $|s\rangle$. The various cross sections (III. 1), (III. 3), and (III. 6) now assume the form (see Appendix B)

$$\frac{d\sigma_d}{d\Omega_d} (|g_e v_g, \mathbf{k}\rangle \rightarrow |d_e v_d \mathbf{l}, \text{vac}\rangle) = \frac{2\pi L^3}{\hbar c} |\langle d_e v_d \mathbf{l}, 1 | \hat{Q}_d R^{(d)} \hat{P} | s_e, \text{vac}\rangle|^2 \times |\langle s_e, \text{vac} | H_{\text{int}} | g_e v_g, \mathbf{k}\rangle|^2 \frac{1}{(E - E_s - D_s)^2 + \frac{1}{4}\Gamma_s^2}, \quad (\text{IV. 1})$$

In a similar way, we have for $\hat{P}T\hat{P}$, utilizing Eq. (III. 11),

$$\hat{P}T\hat{P} = \hat{P}R\hat{P} = \hat{P}H_{\text{int}} \hat{Q} (E - H_0 - V_0 - V_1)^{-1} \hat{Q}H_{\text{int}} \hat{P}. \quad (\text{III. 19})$$

We now make use of the Dyson equation and the definition (III. 15) to get

$$\frac{d\sigma_r}{d\Omega'} (|g_e v_g, \mathbf{k}\rangle \rightarrow |g_e v_g', \mathbf{k}'\rangle) = \frac{2\pi L^3}{\hbar c} |\langle g_e v_g', \mathbf{k}' | H_{\text{int}} | s_e, \text{vac}\rangle \times \langle s_e, \text{vac} | H_{\text{int}} | g_e v_g, \mathbf{k}\rangle|^2 \frac{1}{(E - E_s - D_s)^2 + \frac{1}{4}\Gamma_s^2}, \quad (\text{IV. 2})$$

and finally,

$$\sigma_a(E) = \frac{L^3}{\hbar c} \frac{|\langle g_e v_g, \mathbf{k} | H_{\text{int}} | s_e, \text{vac}\rangle|^2 \Gamma_s}{(E - E_s - D_s)^2 + \frac{1}{4}\Gamma_s^2}. \quad (\text{IV. 3})$$

Here E_s is the zeroth order energy of $|s\rangle$, whereas D_s and Γ_s are the level shift and width of $|s, \text{vac}\rangle$. We note that the partitioning among products is determined by $\hat{Q}_d R^{(d)} \hat{P}$, in analogy with the direct dissociation where it was determined by $\hat{Q}R\hat{P}$, except that R , Eq. (A4), is replaced in the case of the predissociation by $R^{(d)}$, Eq. (B5), a level shift operator due to dissociative states. All the manipulations performed in Sec. III with $\hat{Q}R\hat{P}$ also apply here. In particular, we can make use of the DW basis set to rewrite the matrix element of $\hat{Q}_d R^{(d)} \hat{P}$, and Eq. (IV. 1) may be recast in the form³⁷

$$\frac{d\sigma_d^{v_g' v_d}}{d\Omega_d} (E) = \frac{2\pi L^3}{\hbar c} |\langle d_e v_d \mathbf{l}^- | \hat{Q}_d F_1^{(d)} \hat{Q}_d H_v \hat{P} | s_e, \text{vac}\rangle|^2 \times |\langle s_e, \text{vac} | H_{\text{int}} | g_e v_g, \mathbf{k}\rangle|^2 \frac{1}{(E - E_s - D_s)^2 + \frac{1}{4}\Gamma_s^2}. \quad (\text{IV. 1a})$$

Turning now to TR experiments we inquire what is the probability $P_s(t)$ of the system to be found at time t in the $|s\rangle$ state, in the $|d_e v_d \mathbf{l}\rangle$ dissociative state (with any l) [$P_{v_d}(t)$], and to emit a photon into the $|g_e v_g, \mathbf{k}\rangle$ state (with any \mathbf{k}) [$P_{v_g}(t)$]. These quantities may be written in the form³⁷

$$P_s(t) = \exp(-\Gamma_s t), \quad (\text{IV. 4})$$

$$P_{v_d}(t) = \frac{2\pi}{\Gamma_s} |\langle d_e v_d \mathbf{l} | \hat{Q}_d R^{(d)} \hat{P} | s_e \rangle|^2 [1 - \exp(-\Gamma_s t)], \quad (\text{IV. 5})$$

$$P_{v_g}(t) = \frac{2\pi}{\Gamma_s} |\langle g_e v_g, \mathbf{k} | \hat{Q}_g R^{(g)} \hat{P} | s_e \rangle|^2 [1 - \exp(-\Gamma_s t)], \quad (\text{IV. 6})$$

where $R^{(d)}$, $R^{(g)}$, and Γ_s are defined in Appendix B.

Assuming that the radiative channels are not coupled

among themselves, i. e., $\hat{Q}_g V \hat{Q}_g = 0$, which is physically reasonable, we have

$$\langle g_e v_g, \mathbf{k} | \hat{Q}_g R^{(g)} \hat{P} | s_e, \text{vac} \rangle = \langle g_e v_g, \mathbf{k} | H_{\text{int}} | s_e, \text{vac} \rangle. \quad (\text{IV. 7})$$

Regarding the relative populations of the dissociative states, we note that as in the ER case they are determined by $\hat{Q}_d R^{(d)} \hat{P}$, whose matrix elements may be written utilizing the DW basis

$$\begin{aligned} \langle d_e v_d \mathbf{l}, \text{vac} | \hat{Q}_d R^{(d)} \hat{P} | s_e, \text{vac} \rangle \\ = \langle d_e v_d \mathbf{l}^- | \hat{Q}_d F_1^{(d)} \hat{Q}_d H_v \hat{P} | s_e, \text{vac} \rangle. \end{aligned} \quad (\text{IV. 8})$$

The various quantum yields are obtained from Eqs. (IV. 5) and (IV. 6) as $Y_g^{v_g} = P_{v_d}(\infty)$ and $Y_g^{v_g} = P_{v_g}(\infty)$.

In concluding the present treatment of TR and ER observables in predissociation we note that, utilizing the formal expressions [Eq. (A5)], we can easily relax assumptions (i) and (ii), invoked here merely for the sake of simplicity. Relaxing assumption (i) will result in interference terms between direct and resonant scattering.^{36,37} Relaxing assumption (ii) is trivial in view of the effective Hamiltonian formalism^{34,35,37,39} and the general expression for $\hat{P}G\hat{P}$ in terms of the independently decaying levels.^{37,39} Inserting this expression into Eqs. (B4) and (B6) will result in the generalized T matrix elements for an arbitrarily complex P space.

V. APPLICATION OF THE REACTION (K) MATRIX FORMALISM TO THE PHOTODISSOCIATION OF POLYATOMIC MOLECULES

In this section we shall utilize the Heitler (K) matrix^{32,33} to present a simplified scheme for evaluating the various T matrix elements involved in the photodissociation of polyatomic molecules, Eqs. (III. 9) and (III. 10). The results will be expressed in terms of a F_1 $n \times n$ matrix (where n is the number of open dissociative channels). The F_1 matrix Eq. (III. 16) is obtained by the inversion of an $n \times n$ coupling matrix. The set of cross sections thus obtained satisfies the optical theorem and enables us to evaluate the quantum yields for the various processes. It will be explicitly demonstrated that $\Phi^{-1} = 1 + O(10^{-7})$ and its contribution is thus negligible.

We have already introduced in Table I the partitioning of the V_d interaction into elastic and inelastic parts (V_0 and V_1 , respectively), where V_1 is responsible for the vibrational excitation. An important feature of this dissection is that it enables us to treat V_0 rigorously (by finding the DW basis set) and take account for V_1 in an appropriate manner. One possible approximate scheme involves the replacement of $\hat{Q}R_1\hat{Q}$ [Eq. (III. 21)] by $\hat{Q}V_1\hat{Q}$, resulting in the well-known distorted wave approximation (DWA).^{32,33} In this work we shall adopt a different method based on Heitler's reaction matrix (the K matrix),^{32,33} defined as

$$K = V + VPP[1/(E - H_0)]K, \quad (\text{V. 1})$$

where PP denotes the Cauchy Principle part of the integral. It can be easily shown that the T matrix [Eq. (A3)] may be expanded in terms of K as

$$T = K - i\pi T\delta(E - H_0)K. \quad (\text{V. 2})$$

For any Hermitian K matrix, Eq. (V. 2) results in a unitary S matrix.

It should be noted that the form of Eq. (V. 2) is a special case of a general class of exponential approximations to the S matrix,⁴⁰ all leading to a unitary S matrix.

At this stage we shall introduce an approximate form of the K matrix for the evaluation of F_1 , Eq. (III. 16), which determines all the relevant cross sections. Consider first the inelastic scattering matrix within Q , i. e., $\hat{Q}R_1\hat{Q}$ [Eq. (III. 21)]. In analogy with Eq. (V. 2) we may write

$$\hat{Q}R_1\hat{Q} = K - i\pi\hat{Q}R_1\hat{Q}\delta(E - \hat{Q}H_0\hat{Q} - \hat{Q}V_0\hat{Q})K, \quad (\text{V. 3})$$

where

$$\hat{Q}K\hat{Q} = \hat{Q}V_1\hat{Q} + \hat{Q}V_1\hat{Q}PP(E - H)^{-1}\hat{Q}V_1\hat{Q}. \quad (\text{V. 4})$$

Expanding K to first order in V_1 , i. e., substituting $K = V_1$ in Eq. (V. 3) results in

$$\hat{Q}R_1\hat{Q} = \hat{Q}\bar{F}_1\hat{Q}V_1\hat{Q}, \quad (\text{V. 5})$$

where

$$\hat{Q}\bar{F}_1\hat{Q} = \hat{Q} - i\pi\hat{Q}\bar{F}_1\hat{Q}V_1\hat{Q}\delta(E - H_0 - \hat{Q}V_0\hat{Q}), \quad (\text{V. 6})$$

which is an "on the energy shell" approximation to Eq. (III. 16b). Next, utilizing Eq. (III. 14) we can now write the first order K matrix approximation (FOK) to the matrix elements of $\hat{Q}R\hat{P}$

$$\langle d_e v_d \mathbf{l}, \text{vac} | \hat{Q}R\hat{P} | g_e v_g, \mathbf{k} \rangle = \langle d_e v_d \mathbf{l}^-, \text{vac} | \hat{Q}\bar{F}_1\hat{Q}\hat{H}_{\text{int}}\hat{P} | g_e v_g, \mathbf{k} \rangle. \quad (\text{V. 7})$$

Finally, $\hat{P}R\hat{P}$ [Eq. (III. 20)] will be given to the same degree of approximation by

$$\begin{aligned} \hat{P}R\hat{P} &= \hat{P}H_{\text{int}}\hat{Q}F_1\hat{Q}(E - H_0 - \hat{Q}V_0\hat{Q})^{-1}\hat{Q}H_{\text{int}}\hat{P} \\ &\simeq -i\pi\hat{P}H_{\text{int}}\hat{Q}\bar{F}_1\hat{Q}\delta(E - H_0 - \hat{Q}V_0\hat{Q})\hat{Q}H_{\text{int}}\hat{P}. \end{aligned} \quad (\text{V. 8})$$

These approximate relations to first order in the K matrix (FOK) have several advantages. Firstly, the integral equation (V. 6) is defined on the energy shell, which appreciably simplifies its solution. Secondly, the cross sections obtained from Eqs. (V. 5), (V. 7), and (V. 8) are usually better than those obtained by simple DWA, as the present procedure includes certain interaction terms (on the energy shell) to infinite order in V_1 . Finally, as we have seen, the S matrix thus obtained is unitary.

Equation (III. 11) together with Eqs. (V. 6), (V. 7), and (V. 8) constitute a solution to the general photodissociation problem within the framework of the first order approximation to the K matrix. We invoke now the most drastic approximation involved in our work, specializing to the case of linear photodissociation, i. e., we consider a collinear model for the dissociation process (say along the breaking bond). In this case l (the relative momentum of the fragments) is a scalar. We note in passing that, alternatively, we could have assumed a three-dimensional model with isotropic interfragment coupling. This assumption immediately implies energy normalization of the distorted waves, i. e.,

$$\langle dv_d' \mathbf{l}'^- | dv_d \mathbf{l}^- \rangle = \delta_{v_d v_d'} \delta(E_1 - E_1'). \quad (\text{V. 9})$$

In Table II we define the relevant interactions, wave

TABLE II. Matrices for one dimensional photodissociation problem.^a

Matrix	Definition	Dimension
\hat{V}_1	$\hat{V}_1(E)_{v_d'v_d} = \langle dv_d l'^- V_1 dv_d l^- \rangle$	$n \times n$
\hat{F}_1	$\hat{F}_1(E) = \hat{I} - i\pi\hat{V}_1(E)\hat{F}_1(E) = \hat{I} - i\pi\hat{V}_1(E)\hat{F}_1(E)$ or alternatively: $\hat{F}_1(E) = (\hat{I} + i\pi\hat{V}_1(E))^{-1}$ (\hat{I} is the unit matrix).	$n \times n$
\hat{W}	$(\hat{W}(E))_{v_d'v_d} = \left(\frac{2L^3}{3\hbar c \lambda^2}\right)^{1/2} \langle d_e v_d l^-, \text{vac} H_{\text{int}} g_e v_d, k \rangle$ (λ is the wavelength of the k proton $\lambda = \frac{2\pi}{k}$).	$n \times n$
\hat{R}_1	$(\hat{R}_1(E))_{v_d'v_d} = \langle dv_d l'^- \hat{Q}R_1\hat{Q} dv_d l^- \rangle = \hat{F}_1 \cdot \hat{V}_1$ (Note that in our collinear model $ dv_d l'^- \rangle = dv_d l^- \rangle$).	$n \times n$
\hat{R}_2	$(\hat{R}_2(E))_{v_d'v_d} = \langle dv_d l, \text{vac} \hat{Q}R_2\hat{Q} g_e v_d, k \rangle$ $\hat{R}_2(E) = \left(\frac{3\hbar c \lambda_i^2}{2L^3}\right)^{1/2} \hat{F}_1(E)\hat{W}(E)$ (λ_i is the wavelength of the incident photon).	$m \times n$
\hat{R}_3	$R_3(E)_{v_d'v_d} = \langle g v_d', k' \hat{P}R_3\hat{P} g v_d, k \rangle$ $= \frac{-3i\pi\hbar c \lambda_i \lambda'}{2L^3} \hat{W}^\dagger \hat{F}_1 \hat{W}$ (λ' is the wavelength of k' ($\lambda' = \frac{2\pi}{k'}$)).	$m \times m$
\hat{N}	$\hat{N} = \pi^2 \hat{W}^\dagger \hat{F}_1 \hat{W}$	$m \times m$
$\hat{\Phi}$	$\hat{\Phi} = \hat{I} + \hat{N}$	$m \times m$

^aNote that the \hat{V}_1 , \hat{F}_1 , \hat{W} , $\hat{\Phi}$, and \hat{N} matrices are dimensionless.

operator, and level-shift matrices required for expressing the experimental observables for linear photodissociation within the framework of the FOK approximation. All these matrices are defined on the energy shell (i. e., the energies of the bra and ket states are the same). In the definition of the interference matrix \hat{N} we have ignored the real part of A^e [Eq. (A9)]. This is just a Heitler-matrix type approximation for the radiative interaction. We have thus provided explicit expressions for the relevant transition matrices $\hat{Q}T\hat{P}$, $\hat{P}T\hat{P}$ in terms of the \hat{F}_1 matrix [which in turn can be evaluated by inverting an $n \times n$ matrix (see Table II)]

$$\hat{Q}\hat{T}\hat{P} = (3\hbar c \lambda^2 / 2L^3)^{1/2} \hat{F}_1 \hat{W} (\hat{I} + \hat{N})^{-1}, \quad (\text{V. 10a})$$

$$\hat{P}\hat{T}\hat{P} = - (3i\pi\hbar c \lambda^2 / 2L^3) \hat{W}^\dagger \hat{F}_1 \hat{W} (\hat{I} + \hat{N})^{-1}. \quad (\text{V. 10b})$$

In addition, we have an expression for $\hat{Q}R_1\hat{Q}$ [Eq. (III. 21)] which provides the solution to the inelastic, full collision problem on the dissociative electronic surface

$$\hat{Q}R_1\hat{Q} = \hat{F}_1 \hat{V}_1. \quad (\text{V. 10c})$$

The photodissociation cross section is now obtained by substituting Eqs. (V. 10a) in (III. 1), and utilizing Eq. (III. 2),

$$\sigma_{g'v_d'}^{v_d}(E) = \pi\lambda^2 \left| \left[\hat{F}_1 \hat{W} (\hat{I} + \hat{N})^{-1} \right]_{v_d'v_d} \right|^2. \quad (\text{V. 11})$$

Making use of Eq. (V. 10b), we obtain for the photon scattering cross section, Eqs. (III. 3) and (III. 5),

$$\sigma_{g'v_d'}^{v_d'}(E) = \pi\lambda^2 \left| \left[\pi \hat{W}^\dagger \hat{F}_1 \hat{W} (\hat{I} + \hat{N})^{-1} \right]_{v_d'v_d} \right|^2, \quad (\text{V. 12})$$

and the photon-absorption cross section [Eq. (III. 6)] is given by

$$\sigma_d^{v_d'}(E) = \pi\lambda^2 \text{Re} \left[\hat{W}^\dagger \hat{F}_1 \hat{W} (\hat{I} + \hat{N})^{-1} \right]_{v_d'v_d}, \quad (\text{V. 13})$$

where we again made use of Eq. (V. 10b).

The ratios between these cross sections [Eq. (III. 7)] result in the relevant quantum yields. Equations (V. 11)–(V. 13) are direct extensions of previous results³⁶ to include several dissociative channels (via \hat{F}_1) and several radiative channels [via $(\hat{I} + \hat{N})^{-1}$]. Let us now consider a special case where we have only one open radiative channel. In this case \hat{N} is just a number and \hat{W} is a vector. The photon scattering quantum yield becomes

$$Y_r = \frac{|\pi \hat{W}^\dagger \hat{F}_1 \hat{W}|^2}{|\pi \hat{W}^\dagger \hat{F}_1 \hat{W}|^2 + R_e \hat{W}^\dagger \hat{F}_1 \hat{W}}, \quad (\text{V. 14a})$$

the photodissociation quantum yield for channel v_d is

$$Y_d^{v_d'v_d} = \frac{|(\hat{F}_1 \hat{W})_{v_d}|^2}{|\pi \hat{W}^\dagger \hat{F}_1 \hat{W}|^2 + R_e \hat{W}^\dagger \hat{F}_1 \hat{W}}, \quad (\text{V. 14b})$$

and the total dissociation quantum yield is

$$Y_d = \sum_{v_d'} Y_d^{v_d'v_d} = \frac{\hat{W}^\dagger \hat{F}_1 \hat{F}_1 \hat{W}}{|\pi \hat{W}^\dagger \hat{F}_1 \hat{W}|^2 + R_e \hat{W}^\dagger \hat{F}_1 \hat{W}}. \quad (\text{V. 15})$$

The optical theorem^{32,33} results in the relation

$$\hat{W}^\dagger \hat{F}_1 \hat{F}_1 \hat{W} = R_e \hat{W}^\dagger \hat{F}_1 \hat{W}. \quad (\text{V. 16})$$

Finally, we note that the \hat{F}_1 wave operator matrix determines also the energy partitioning in predissociation. Defining an n dimensional vector \hat{U}

$$U_{v_d}(E) = \langle d_e v_d l^- | H_v | s_e \rangle, \quad (\text{V. 17})$$

then the matrix corresponding to $\hat{Q}R^{(d)}\hat{P}$ [Eq. (B5)] ($\hat{R}^{(d)}$) is given by

$$\hat{R}^{(d)} = \hat{F}_1 \cdot \hat{U}. \quad (\text{V. 18})$$

This matrix appears in the expressions for the photodissociation cross sections [Eq. (IV. 1)] and in the dissociation rates [Eq. (IV. 5)]. Making use of Eq. (V. 18), the dissociative width of $|s\rangle$, $\Gamma_s^{(d)}$ assumes the form

$$\Gamma_s^{(d)} = 2\pi \hat{U}^\dagger \hat{F}_1 \hat{U}. \quad (\text{V. 18a})$$

Conservation of probability requires

$$\sum_{v_d} P_{v_d}(\infty) + \sum_{v_d'} P_{v_d'}(\infty) = 1. \quad (\text{V. 19})$$

Substituting Eqs. (V. 18) and (V. 19) into Eqs. (IV. 5) and (IV. 6) gives

$$2\pi \hat{U}^\dagger \hat{F}_1 \hat{F}_1 \hat{U} + \Gamma_s^{(r)} = 2\pi \text{Re} \hat{U}^\dagger \hat{F}_1 \hat{U} + \Gamma_s^{(r)}, \quad (\text{V. 20})$$

i. e.,

$$\hat{U}^\dagger \hat{F}_1 \hat{F}_1 \hat{U} = \text{Re} \hat{U}^\dagger \hat{F}_1 \hat{U}, \quad (\text{V. 20a})$$

which is analogous to Eq. (V. 16).

VI. VIBRATIONAL-ENERGY DISTRIBUTION IN THE PHOTODISSOCIATION OF A LINEAR TRIATOMIC MOLECULE

We shall now consider the linear photodissociation of a triatomic molecule ABC resulting in the diatomic fragment BC and the atom A. The repulsive inter-fragment interaction term V_d is assumed to prevail between adjacent atoms, i. e.,

$$V_d = V_{AB}(R_{AB}), \quad (\text{VI. 1})$$

where R_{AB} (and R_{BC}) are the internuclear distances, V_{AB} is repulsive, and the BC molecule is assumed to be harmonic. Making use of the reduced coordinates⁴¹

$$y = [(\mu_{BC} \chi)^{1/2} / \hbar]^{1/2} (R_{BC} - \bar{R}_{BC}), \quad (\text{VI. 2a})$$

$$x = [(\mu_{BC} \chi)^{1/2} / \hbar]^{1/2} \left[\frac{M_B + M_C}{M_C} \bar{x} - \bar{R}_{BC} \right], \quad (\text{VI. 2b})$$

and of the reduced mass parameter

$$m = M_A M_C / (M_A + M_B + M_C) M_B, \quad (\text{VI. 2c})$$

the nuclear Hamiltonian (Table I) in the dissociative state (in units of the oscillator quanta $\hbar\omega$) assumes the form

$$H_{BO}^{(d)} = -\frac{1}{2m} \frac{\partial^2}{\partial x^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} + \frac{1}{2} y^2 + V_d(x-y), \quad (\text{VI. 3})$$

where $V_d(x-y)$ is a repulsive term. In Eqs. (VI. 2) χ , \bar{R}_{BC} and μ_{BC} are the BC oscillator force constant, equilibrium distance, and reduced mass, respectively. R_{BC} is the BC distance and \bar{x} is the distance of A from the center of mass of the BC molecule. Note that Eq. (VI. 3) is mathematically equivalent to the Schrödinger equation of a particle of mass m colliding with a harmonic oscillator of unit mass.

Let us now take an exponential repulsive potential

$$V_d(x-y) = C \exp[-\alpha(x-y)] \quad (\text{VI. 4})$$

which to first order in the oscillator coordinate becomes

$$V_d \approx C \exp(-\alpha x)(1 + \alpha y) \equiv V_0 + V_1, \quad (\text{VI. 5})$$

where

$$V_0 = C \exp(-\alpha x) \quad (\text{VI. 5a})$$

$$V_1 = V_0 \alpha y. \quad (\text{VI. 5b})$$

V_0 is the elastic part of the potential (does not couple different oscillator states), whereas V_1 couples oscillator states differing by one quantum (see Table I). In terms of the oscillator creation and annihilation operators (a^\dagger and a , respectively) we may write

$$V_1 = (C\alpha/\sqrt{2}) \exp(-\alpha x)(a + a^\dagger). \quad (\text{VI. 6})$$

Jackson and Mott⁴² have solved the full collision problem represented by the Hamiltonian (VI. 3) and (VI. 4) in the DWA. The solutions are products of the harmonic oscillator wavefunction $X_v(y)$ (where v is the vibrational quantum number) and a continuous part $\Psi_{l_v}(x)$, which up to a normalization factor is equal to a modified Bessel function. l_v denotes the relative momentum of the fragment in the v th channel. Denoting the total (dimensionless) energy of the system (relative to the zero of the potential) by ϵ we have

$$l_v = [2m(\epsilon - v - \frac{1}{2})]^{1/2} \equiv (2m\epsilon_v)^{1/2}. \quad (\text{VI. 7})$$

It will be convenient to introduce also a reduced wave vector,

$$q_v = 2l_v/\alpha. \quad (\text{VI. 7a})$$

Adopting an energy normalization for $\Psi_{l_v}(x)$, i. e.,

$$\langle \Psi_{l_v} | \Psi_{l_v'} \rangle = \delta(\epsilon_v - \epsilon_{v'}), \quad (\text{VI. 8})$$

we require the following asymptotic behavior

$$\Psi_{l_v}(x) \xrightarrow{x \rightarrow \infty} \left(\frac{2m}{\pi l_v} \right)^{1/2} \cos(l_v x + \phi). \quad (\text{VI. 9})$$

The dimensionless coupling matrix elements of Eq. (VI. 5b) in the DW representation $\{|v q_v\rangle\} \equiv \{\chi_v(y)\psi_{l_v}(x)\}$ now assume the form

$$\langle v' q_{v'} | V_1 | v q_v \rangle = g_v \delta_{v, v'-1} + g_{v'} \delta_{v, v'+1}, \quad (\text{VI. 10})$$

where

$$g_v = \alpha[(v+1)/2]^{1/2} I(q_v, q_{v'}) \quad (\text{VI. 10a})$$

and

$$I(q_v, q_{v'}) = \int_{-\infty}^{+\infty} dx \exp(-\alpha x) \Psi_{l_v}(x) \Psi_{l_{v'}}(x) \\ = \frac{1}{8} \frac{(\sinh \pi q_{v'} \sinh \pi q_v)^{1/2}}{\sinh \frac{1}{2} \pi (q_v + q_{v'})} \frac{q_{v'}^2 - q_v^2}{\sinh \frac{1}{2} \pi (q_{v'} - q_v)} \quad (\text{VI. 11})$$

Let us consider now another possible partitioning of the Hamiltonian, utilizing the relative coordinate system⁴³

$$z = x - y, \\ y' = y, \quad (\text{VI. 12})$$

in terms of which $H_{BO}^{(d)}$ assumes the form

$$H_{BO}^{(d)} = -\frac{1}{2} \left(1 + \frac{1}{m} \right) \frac{\partial^2}{\partial z^2} - \frac{1}{2} \frac{\partial^2}{\partial y'^2} + \frac{\partial^2}{\partial y' \partial z} + \frac{1}{2} y'^2 + V_d(z). \quad (\text{VI. 13})$$

We notice that in this coordinate system the potential is vibrationally adiabatic, whereas the kinetic energy couples different vibrational states; this is exactly the reverse situation than in Eq. (VI. 3) where the kinetic energy was separable in terms of x and y and the interaction potential provided the nonadiabatic coupling. The interaction V_d (Table I) is now

$$V_d = V_0 + V_1, \quad (\text{VI. 14})$$

where

$$V_0 = C \exp(-\alpha z) \quad (\text{VI. 14a})$$

and

$$V_1 = \partial^2 / \partial y' \partial z. \quad (\text{VI. 14b})$$

We notice that the distorted waves for this partitioning are the same as for the previous partitioning [Eq. (VI. 5)] except that the coordinate x is replaced by z . A favorable property of the inelastic potential V_1 [Eq. (VI. 14b)] is that it couples only states of the oscillator differing by one quantum $\Delta v = \pm 1$. (In the previous partitioning this was obtained as a result of linearizing the potential in the oscillator coordinate.) Thus, one may think that it is preferable to use the coupling g_v obtained from this partitioning and improve the results of the model. However, it should be noted that the interaction potential [Eq. (VI. 14b)] does not vanish at infinity (as $z \rightarrow \infty$), as is the common situation in scattering theory, and so the wavefunctions ψ_{l_v}' have a wrong asymptotic behavior

$$\psi_{l_v}'(z) \propto \cos(l_v z + \phi) \quad (\text{VI. 15})$$

rather than

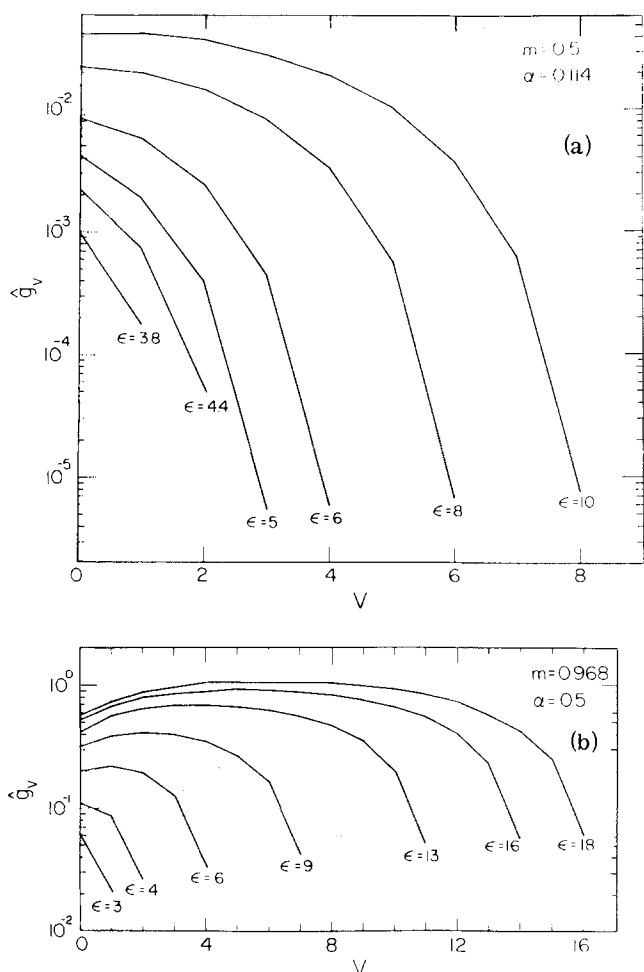


FIG. 1. Intercontinuum coupling strength \hat{g}_v [Eq. (VI.16)] for various ϵ values: (a) α , m taken from Secret and Johnson⁴¹; (b) α , m corresponding to ICN (see Fig. 3).

$$\psi_{1v}(x) \propto \cos(l_v x + \phi'), \quad (\text{VI. 15a})$$

given by Eq. (VI. 9). This point has been investigated⁴⁴ recently by using a renormalization procedure⁴⁵ based on an appropriate shifting of the energy of the continuum states. The result is that the renormalized coupling is given by Eq. (VI. 10) with g_v replaced by \hat{g}_v , where

$$\hat{g}_v = (1+m)^{-1}g_v \quad (\text{VI. 16})$$

and $I(q_v, q_{v'})$ is given by Eq. (VI. 11).

At high energies $q_v + q_{v'}$, we have the limiting form of \hat{g}_v ,

$$\hat{g}_v \rightarrow \left(\frac{v+1}{2}\right)^{1/2} \frac{m}{(1+m) \sinh \frac{4\pi m}{\alpha^2(q_v + q_{v'})}}, \quad (\text{VI. 17a})$$

and if in addition $q_v + q_{v'} \gg 4\pi m/\alpha^2$, we have

$$\hat{g}_v \rightarrow \left(\frac{v+1}{2}\right)^{1/2} \frac{(q_v + q_{v'})\alpha}{4\pi(1+m)}. \quad (\text{VI. 17b})$$

At low energies $q_v + q_{v'} \ll 1$ and we get

$$\hat{g}_v \rightarrow \left(\frac{v+1}{2}\right)^{1/2} \frac{m}{1+m} \frac{2(q_v q_{v'})^{1/2}}{\alpha(q_v + q_{v'}) \sinh \frac{4\pi m}{\alpha^2(q_v + q_{v'})}}, \quad (\text{VI. 17c})$$

which when $q_v + q_{v'} \ll 4\pi m/\alpha^2$ assumes the form

$$\hat{g}_v \rightarrow \left(\frac{v+1}{2}\right)^{1/2} \frac{m}{1+m} \frac{4(q_v q_{v'})^{1/2}}{\alpha(q_v + q_{v'})} \exp\left[-\frac{4\pi m}{\alpha^2(q_v + q_{v'})}\right]. \quad (\text{VI. 17d})$$

In order to obtain an insight into the variation of the coupling strength over the entire energy domain, we plot in Fig. 1 \hat{g}_v as a function of v for several values of ϵ and m . The explicit evaluation of the \hat{F}_1 matrix for a coupling of the form (VI. 10) was given elsewhere.^{37, 44b} The result is

$$\hat{F}_1(v, v') = \begin{cases} \frac{Q_v \bar{Q}_{v'}}{Q_n} \prod_{j=v}^{v'-1} (-i\pi g_j), & v' > v, \\ \frac{Q_{v'} \bar{Q}_v}{Q_n} \prod_{j=v'}^{v-1} (-i\pi g_j^*), & v' < v, \\ \frac{Q_v \bar{Q}_v}{Q_n}, & v = v', \end{cases} \quad (\text{VI. 18})$$

where Q_v and \bar{Q}_v are polynomials in the interference parameters N_j ($N_j \equiv \pi^2 |g_j|^2$) and n is the number of open dissociative channels. The polynomials $Q_{v'}$ and $\bar{Q}_{v'}$ are defined in terms of the recurrence relations

$$Q_0 = Q_1 = 1, \quad (\text{VI. 18a})$$

$$Q_{j+1} = Q_j + \hat{N}_{j-1} Q_{j-1}, \quad j = 1, 2, \dots,$$

and

$$\bar{Q}_{n-1} = \bar{Q}_{n-2} = 1, \quad j = n-2, n-3, \dots, \quad (\text{VI. 18b})$$

$$\bar{Q}_{j-1} = \bar{Q}_j + \hat{N}_j \bar{Q}_{j+1}.$$

The \hat{F}_1 matrix provides us with the transition amplitudes within the Q space, i. e., $F_1(v, v')$ is the amplitude of the system to escape in the v th channel if it had entered in the v' channel. The $\prod_j (-i\pi g_j)$ term is the lowest order transition amplitude (i. e., direct transition between adjacent continua from v' to v), whereas the polynomial factor which has the property^{37, 44(b)} $0 < (Q_v \bar{Q}_{v'}/Q_n) \leq 1$ is a retardation factor. This factor is equal to unity when the continua are not coupled, when $g_v = 0$, and $F(v, v') = \delta_{vv'}$. The explicit expression for \hat{F}_1 , when substituted in Eqs. (V. 11)–(V. 13) will result in all the cross sections involved in our problem.

VII. NUMERICAL SOLUTIONS FOR THE ROLE OF INTERCONTINUUM COUPLING IN LINEAR PHOTOFRAGMENTATION AND IN COLLINEAR COLLISIONS

In the preceding section we have provided an analytical, quantum mechanical expression for the cross sections for photon absorption, photon scattering, and photofragmentation into different vibrational channels of a linear triatomic, where the interfragment repulsion is exponential and the diatomic fragment is characterized by a harmonic potential. To consider the vibrational energy distribution in photofragmentation, we make use of Eq. (V. 11) with one channel feeding the dissociative states, so that the coupling matrix \hat{W} (Table II) for DP and U [Eq. (V. 17)] for predissociation is a vector. The wave operator \hat{F}_1 is given (in both cases) in terms of Eq. (VI. 18). The probability for finding the product BC molecule in the vibrational state

v_d , starting from an initial vibrational state v_i ($v_i = v_g$ for DP and $v_i = v_s$ for PR) will be denoted by $P(v_i, v_d, E)$. This probability is proportional to $\sigma_d^{v_i-v_d}$ [Eq. (III. 1) for DP and Eq. (IV. 1) for PR]. Thus, the vibrational distribution of the diatomic molecule is

$$P(v_i, v_d; E) = \left| \int_{\bar{v}_d} F_1(v_d, \bar{v}_d) A(\bar{v}_d, v_i) \right|^2, \quad (\text{VII. 1})$$

where the wave operator \hat{F}_1 , Eq. (VI. 18), depends on the molecular parameters α and m and on the number n of open dissociative channels (or the translational energy ϵ above threshold). $A(\bar{v}_d, v_i)$ is the initial coupling matrix

$$A(\bar{v}_d, v_i) \equiv W(\bar{v}_d, v_g) \quad (\text{VII. 2a})$$

for DP and

$$A(\bar{v}_d, v_i) \equiv U(\bar{v}_d, v_s) \quad (\text{VII. 2b})$$

for PR. A is nothing but the vector of the multidimensional (generalized) Franck-Condon vibrational overlap factors given in Sec. II.

Equation (VII. 1) constitutes a general analytical solution for the product distribution in the photofragmentation of a model system. It contains the two essential ingredients involved in our problem. First, the direct initial coupling to the dissociative channels are expressed in terms of the Franck-Condon factors. Second, the intercontinuum coupling effects are recast in terms of the approximate form for the wave operator \hat{F}_1 which is given within the framework of the FOK approximation.

One new feature of the global model advanced herein is the recipe for the systematic evaluation of the intercontinuum coupling terms. The following approximations for \hat{F}_1 were utilized in this context:

- (i) FODWA is the first-order distorted wave solution,⁴² i. e., $F_1 = V_1$.
- (ii) FODWN is a normalized version of (i) using relative coordinates where we take $V_1 \rightarrow V_1/(1+m)$ [see Eq. (VI. 16)].
- (iii) FOKL is the first-order K matrix, using the linearized coupling [Eq. (VI. 10a)].
- (iv) FOKRC is the first-order K matrix using relative coordinates. The coupling terms \hat{g}_j are given by Eq. (VI. 16).

Before presenting our numerical results for the role of the intercontinuum coupling in photofragmentation problems it is crucial to assess the accuracy of the approximate schemes involved in the evaluation of \hat{F}_1 . To do so we have considered the simpler case of a full collinear collision of an atom and a harmonic oscillator. This is a key problem in molecular scattering theory and was extensively studied in the literature.⁴⁶ An exact numerical solution of the transition probabilities was obtained by Secrest and Johnson⁴¹ and may be used as a check. In our approximate treatment, the transition matrix (V. 5) is given by

$$\hat{R}_1 = \hat{F}_1 \hat{V}_1. \quad (\text{VII. 3})$$

Utilizing Eq. (V. 11) we can rewrite Eq. (VII. 3) in the form

$$\hat{R}_1 = (i\pi)^{-1} (\hat{I} - \hat{F}_1). \quad (\text{VII. 4})$$

Substitution of Eq. (VII. 4) into the S matrix^{32,33} results in the transition probabilities (per collision) from channel v' to v , $P_{vv'}$, i. e.,

$$P_{vv'} = |S_{vv'}|^2 = |\delta_{vv'} - 2\hat{F}_1(v, v')|^2, \quad (\text{VII. 5})$$

the F_1 matrix [Eq. (VI. 18)] is determined by the coupling factors g_v [Eq. (VI. 10a)] or \hat{g}_v [Eq. (VI. 16)] (and by the interference parameters N_v), which in turn are functions of the intrinsic parameters of the problem m , α , and ϵ . Extensive numerical results for the scattering problem were presented elsewhere.⁴⁴ The main conclusions from these recent studies of approximations (i)-(iv) for the full collinear problem are:

- (1) The results of the first-order transition probabilities using the relative coordinates (ii) are comparable in accuracy to the results of the adiabatic approximation.⁴⁴
- (2) At low transition probabilities (small α , low energy) the FODWA is sufficient and both K matrix approximations coincide. However, at high transition probabilities (large α , high energy) the K matrix treatments are much better than the first-order approximations FODWA and FODWN.
- (3) Usually the FOKRC approximation is better than FOKL.
- (4) For multiquantum transitions where the first-order approximations completely fail, the K matrix results agree fairly well with the exact calculations and here also the FOKRC is superior to FOKL.

In conclusion, we note that as a by-product of this work⁴⁴ an analytical, quantum mechanical expression for the transition probabilities in the collinear collision of an atom and a harmonic oscillator was provided. We can now proceed with confidence to the study of the role of intercontinuum coupling in photofragmentation using the same approximation schemes.

Consider the photofragmentation of triatomic cyanide molecules XCN, which under vacuum ultraviolet irradiation yield the CN radical in the $B^2\Sigma$ excited state. The compounds studied by Mele and Okabe⁵ are ICN, BrCN, ClCN, and HCN. The following information is required for the application of Eq. (VII. 1) to the theoretical study of the vibrational energy distribution:

- (1) Does the photofragmentation proceed via DP or by PR?
- (2) Once point (1) is established, one has to evaluate the components of the coupling vector A , Eq. (VII. 2). For the case of DP one can take $v_g = 0$, while for predissociation v_s depends on the (metastable) vibrational state of the $|s_g\rangle$ manifold which is accessible by optical excitation.
- (3) The calculation of the wave operator \hat{F}_1 requires the molecular parameters n (number of coupled channels on the energy shell), m [the reduced mass, Eq. (VI. 2c)],

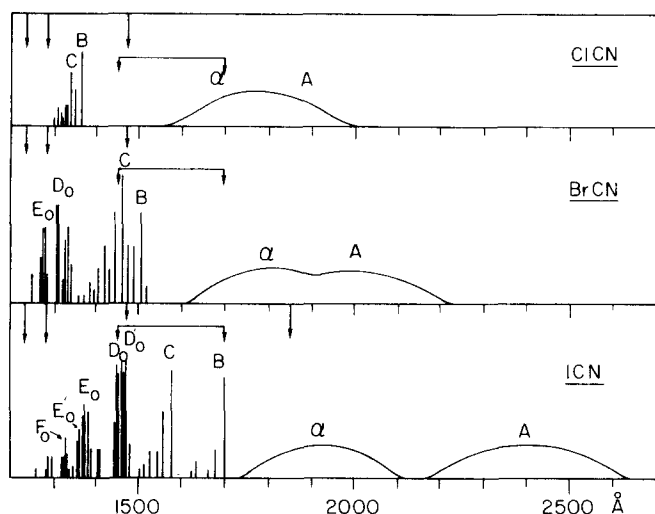


FIG. 2. Absorption spectra of halocyanides.⁴⁹ Arrows mark excitation energies used by Mele and Okabe.⁵

and α [the exponent of the repulsive potential, Eq. (VI. 4)].

Regarding the first point, it is apparent from the absorption spectra⁴⁷ presented in Fig. 2 together with the energetic data summarized in Table III that all the photofragmentation experiments of Mele and Okabe on ICN, BrCN, and possibly HCN in the range 7.2–10.6 eV result in PR from Rydberg type states, while for ClCN both DP (in the α continuum) at 7.2 and 8.5 eV and PR from Rydberg states at higher energies are exhibited. Furthermore, we note that the predissociating states of the halogen XCN (X=I, Br, and Cl) molecules are linear, so that our model is strictly applicable. On the other hand, the low excited states of HCN are bent and it is questionable whether the linear model does apply. We now consider point (2), noting that in the majority of cases photofragmentation of XCN molecules in the energy range experimentally studied proceeds via predissociation. Thus, the identity of the $|s_e v_s\rangle$ metastable state(s) from which the predissociation takes place is unknown. One can, of course, invoke the somewhat naive and unjustified assumption that predissociation always takes place from the $|s_e v_s = 0\rangle$ electronic origin. But even then the calculation of the multidimensional Franck–Condon factors will be fraught with difficulties as the spectroscopic constants (i. e., frequencies) for the metastable excited states are not completely known. As we are interested here in assessing the effects of the intercontinuum coupling, we assume (somewhat naively) that direct coupling occurs to the $|d_e, v_d = 0\rangle$ state. Some support for this assumption stems from our previous model calculations which demonstrate that when substantial initial coupling occurs to higher $|d_e v_d\rangle$ states, the vibrational distribution peaks around that v_d value, which is incompatible with the experimental data. We thus take for our model calculations

$$A(\bar{v}_d, v_i) = \delta_{\bar{v}_d=0, v_i=0}, \quad (\text{VII. 6})$$

whereupon Eq. (VII. 1) takes the simple form

$$P_{v_d} \equiv P(v_i, v_d, E) = |\hat{F}_1(v_d, 0)|^2. \quad (\text{VII. 7})$$

Consider now the molecular parameters pertinent to point (3). m is determined by the atomic masses. The number n of effectively coupled continua was estimated from the excess electronic energy (E_e) above the dissociation threshold (E_t), i. e., $n = (E_e - E_t)/\omega_{\text{CN}}$, where ω_{CN} is the vibrational frequency of the CN $B^2\Sigma$ radical (see Table III). Finally, we have to estimate the repulsive parameter α , which is not accurately known. This quantity can be approximated by the method suggested by Herzfeld⁴⁸ and by Secrest and Johnson⁴¹ and is taken in the form

$$\alpha = L^{-1} \frac{M_C}{M_B + M_C} \left(\frac{\hbar}{\mu_{\text{BC}} \chi^{1/2}} \right)^{1/2}, \quad (\text{VII. 8})$$

where L is the range of the repulsive potential. Holdy, Klotz, and Wilson¹⁵ provide the value $L = 0.16 \text{ \AA}$ for the I–CN exponential repulsive potential. A reasonable universal estimate ($L \approx 0.2 \text{ \AA}$) was used by Secrest and Johnson for a variety of systems. The latter estimate results in $\alpha = 0.13$ for the XCN molecules. In Figs. 3–5 we provide the results of numerical calculations of the vibrational distribution [Eq. (VII. 7)] for X=I, Br, and Cl for a broad range of α values together with the experimental data.⁵ From these results we conclude that for the halocyanogen photofragmentation, the interpretation of the experimental data solely in terms of intercontinuum coupling effects requires very high values of α . The optimal values of the repulsive parameter α for ICN, ClCN, and BrCN are about $\alpha = 0.5$ in all cases. This value of α is considerably higher than our rough estimate (0.13) and we cannot provide any justification for such a high value of α . We tentatively conclude that in the predissociation of ClCN, BrCN, and ICN the role of Franck–Condon vibrational overlap factors is important for the determination of the vibrational partitioning. This conclusion for those special molecules concurs with the recent proposals of Simons and Tasker²⁹ and of Band and

TABLE III. Energetic and structural data for photofragmentation of XCN compounds.^{5,49}

Molecule	m	Excitation Energy E_e (eV)	n	Photofragmentation mechanism
ICN	0.9677	6.7	2	DP
		7.2–8.5	6	PR
		8.4, 9.5	9	PR
		10, 10.6	16	PR
BrCN	0.8797	7.2–8.5	4–5	PR+DP
		8.4, 9.5	7	PR
		10, 10.6	14	PR
ClCN	0.6726	7.2–8.5	4–5	DP
		8.4, 9.5	5	PR
		10, 10.6	12	PR
HCN	0.4349	8.4	1	
		8.4, 9.5	5	
		10, 10.6	8	

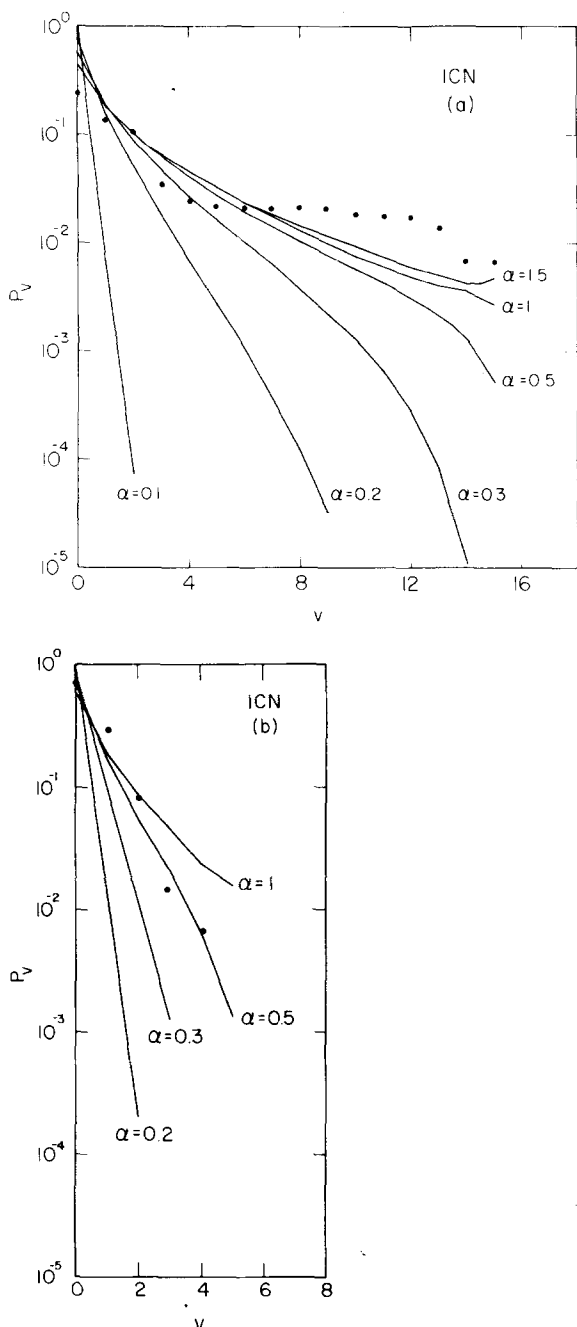


FIG. 3. Comparison of the FOKRC model [Eq. (VII.7)] for various values of α , with experimental results (marked by black dots) for ICN⁵: (a) $\lambda=1165, 1236 \text{ \AA}$. Averaged distribution for $n=16$ and $n=17$; (b) $\lambda=1450\text{--}1700 \text{ \AA}$, $n=7$.

Freed.²⁷ We, however, differ from these authors regarding important details and maintain that at present the calculation of these factors for predissociation, as is the case here, is fraught with considerable difficulties and cannot be considered as reliable.

Finally, we turn to the case of the HCN molecule, which is linear in its ground state but bent in its lowest excited states.⁴⁹ Despite this, it is tempting to examine qualitatively this system in the light of the present model in the hope that the vibrational distribution is not appreciably affected by the bending. Figure 6 shows the fit of our model [Eq. (VII.7)] to the experimental

results for HCN. Best agreement with the experimental data is accomplished for the value $\alpha=0.25$, which is quite reasonable and corresponds to an interaction range of $L=0.1 \text{ \AA}$. It thus appears that for the HCN photofragmentation the role of intercontinuum coupling is important in determining the dynamics of predissociation. This conclusion differs from that of Band and Freed,²⁷ who attribute the vibrational distribution solely to the initial coupling via Franck-Condon terms. In view of the reasonable fit of the HCN data with our

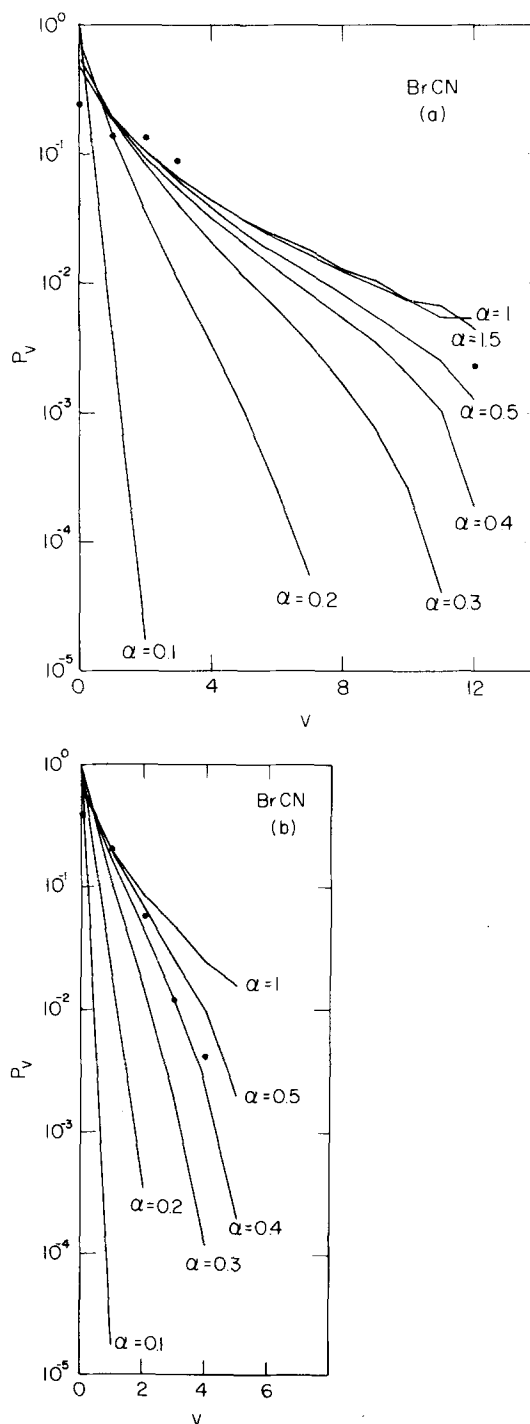


FIG. 4. Comparison of our FOKRC model [Eq. (VII.7)] with experimental results (marked by black dots) for BrCN.⁵ (a) $\lambda=1165, 1236 \text{ \AA}$, $n=14$; (b) $\lambda=1295, 1470 \text{ \AA}$, $n=7$.

model using a physically acceptable value of α , we can provide an estimate of the deuterium isotope effect on the vibrational distribution. Using the same value of L (and α) for DCN as for HCN we now predict the vibrational distribution in DCN with the same excess energy ϵ . This prediction is shown in Fig. 7 and we expect the vibrational distribution in the photofragmentation of DCN to be narrower than that of HCN.

The global model presented herein incorporates all

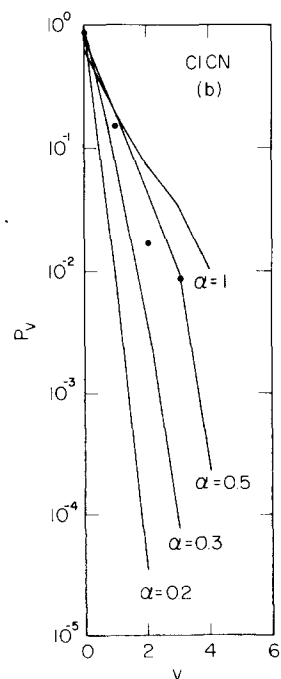
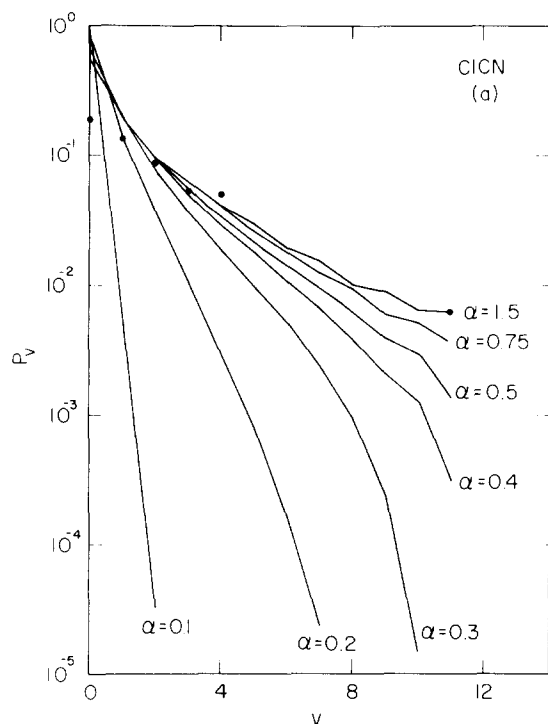


FIG. 5. Comparison of our FOKRC model [Eq. (VII.7)] with experimental results (marked by black dots) for ClCN⁵: (a) $\lambda=1165, 1236 \text{ \AA}$, $n=12$ (results of $v=10, 11$ are averaged on $n=12$ and $n=13$); (b) $\lambda=1295, 1470 \text{ \AA}$, $n=5$.

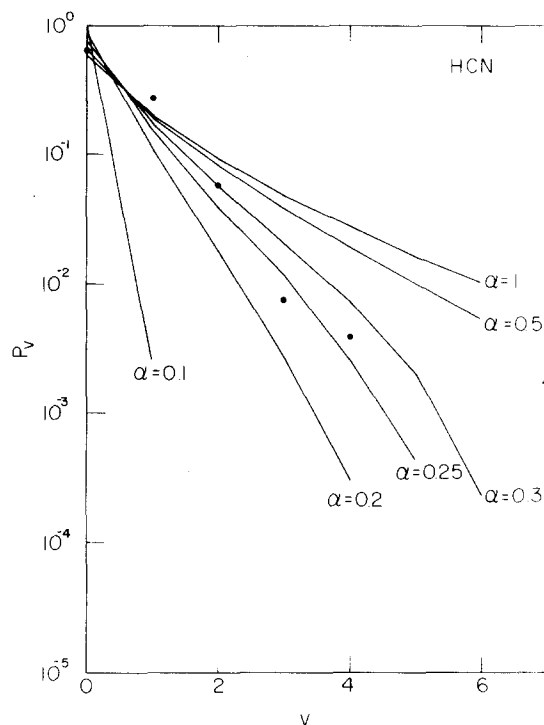


FIG. 6. Comparison of our FOKRC model [Eq. (VII.7)] with experimental results (marked by black dots) for HCN⁵: $\lambda=1165, 1236 \text{ \AA}$, $n=8$.

the physical features of the vibrational energy partitioning for the linear photofragmentation problem. Once the spectroscopic data concerning the nature or molecular constants of the relevant predissociating states will become available, the coupling matrix U will be

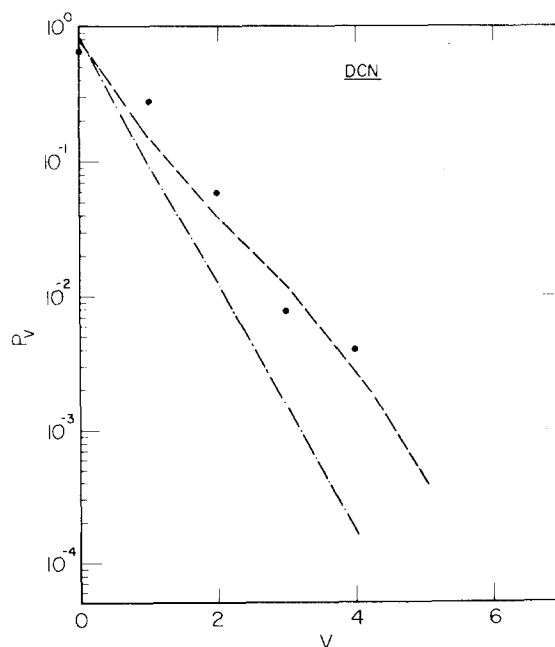


FIG. 7. Predicted distribution of products for DCN (---) $m=0.8379$, $\alpha=0.25$, $n=8$. For comparison we present also the experimental (●) and theoretical (—) distribution for HCN (see Fig. 6).

amenable to calculation and the model will be subjected to a rigorous test. A complete solution of the problem of distribution of products in photofragmentation will require the analysis of the three-dimensional case. In this context we believe that our theoretical results regarding the connection between photofragmentation and scattering theory are of interest.

APPENDIX A. SOME FORMAL MANIPULATIONS FOR DIRECT PHOTODISSOCIATIONS

The Hamiltonian in DP [Eq. II.1] may be partitioned into $H_0 + V$, where

$$V = H_{\text{int}} + V_d, \quad (\text{A1})$$

$$H_0 \equiv H - V.$$

Using the projection operators [Eq. (III.8)] and since $V_d \hat{P} = 0$, we may write for the T matrix³²

$$T\hat{P} = V\hat{P} + V G V \hat{P}, \quad (\text{A2})$$

which may be recast in the form

$$T\hat{P} = R\hat{P} + T\hat{P}G_0 P R \hat{P}, \quad (\text{A3})$$

where $G_0 = (E - H_0 + i\eta)$ and R is the level-shift operator

$$R = V + V\hat{Q}(E - H_0 - \hat{Q}V\hat{Q})^{-1}\hat{Q}V. \quad (\text{A4})$$

Since in our case $VP = QH_{\text{int}}P$, we can

$$(\hat{Q} + V G \hat{Q}) \hat{Q} H_{\text{int}} \hat{P} (\hat{P} - \hat{P} G_0 P R \hat{P}) = R \hat{P}. \quad (\text{A5})$$

Suppose now that our molecular orientation is fixed in space so that its transition moment for the $|g_e\rangle \rightarrow |d_e\rangle$ transition lies along the z axis. We also take a photon k whose polarization is along z . Considering a matrix element of Eq. (A3) between $|g_e v_e \mathbf{k}\rangle$ and any other state $|\alpha\rangle$ (belonging either to \hat{P} or to \hat{Q}), and bearing Eq. (A5) in mind we may write

$$\langle \alpha | T\hat{P} | g_e v_e \mathbf{k} \rangle = \sum_{v'_e} \langle \alpha | R\hat{P} | g_e v'_e \mathbf{k} \rangle \langle v'_e | \Phi^{-1} | v_e \rangle, \quad (\text{A6})$$

where $\cos\theta = \hat{\mathbf{k}} \cdot \hat{\mathbf{k}}'$ and we have defined a matrix Φ , $m \times m$, where m is the number of open radiative channels in the ground state

$$\langle v'_e | \Phi | v_e \rangle = \sum_{\mathbf{k}} \sqrt{\frac{k'}{k}} \cos\theta' \langle g_e v'_e \mathbf{k}' | \hat{P} - \hat{P} G_0 P R \hat{P} | g_e v_e \mathbf{k} \rangle. \quad (\text{A7})$$

The Φ matrix elements [Eq. (A7)] may be rewritten in the form

$$\Phi_{v'_e v_e} = \delta_{v'_e v_e} - \frac{1}{3} A^e (E - E_{v'_e}) \langle g_e v'_e \mathbf{k}' | \hat{P} R \hat{P} | g_e v_e \mathbf{k} \rangle, \quad (\text{A8})$$

where

$$A^e (E - E_{v'_e}) = \left(\frac{L}{2\pi}\right)^3 \int \frac{4\pi k dk}{E - E_{v'_e} - k + i\eta} \quad (\text{A9})$$

and $E_{v'_e} + k$ is the energy of the $|g_e v'_e \mathbf{k}\rangle$ state. Substituting the relevant α values in Eq. (A6) results in Eqs. (III.9) and (III.10).

APPENDIX B. T MATRIX ELEMENTS IN PREDISSOCIATION

We wish to have explicit expressions for the T matrix elements relevant for predissociation.

Utilizing assumption (i) (Sec. IV) and the general expression for the T matrix,³² we see that

$$\hat{Q}_e T \hat{Q}_e = \hat{Q}_e H_{\text{int}} G \hat{P} H_{\text{int}} \hat{Q}_e, \quad (\text{B1a})$$

whereas

$$\hat{Q}_d T \hat{Q}_e = \hat{Q}_d (V_d + H_v) G \hat{P} H_{\text{int}} \hat{Q}_e. \quad (\text{B1b})$$

Since $(H_v + V_d)\hat{Q}_e = 0$, we can recast Eqs. (B1a) and (B1b) in terms of the symmetric T matrix [Eq. (A2)], where V is now

$$V = V_d + H_v + H_{\text{int}}. \quad (\text{B2})$$

We can now use the formal relation (A3) and obtain for the relevant T matrix elements

$$\begin{aligned} \langle d_e v_d \mathbf{l}, \text{vac} | \hat{Q}_d T \hat{Q}_e | g_e v_e \mathbf{k} \rangle \\ = \langle d_e v_d \mathbf{l}, \text{vac} | \hat{Q}_d R^{(d)} \hat{P} H_{\text{int}} \hat{Q}_e | g_e v_e \mathbf{k} \rangle, \end{aligned} \quad (\text{B3})$$

and

$$\begin{aligned} \langle g_e v'_e \mathbf{k}' | \hat{Q}_e T \hat{Q}_e | g_e v_e \mathbf{k} \rangle \\ = \langle g_e v'_e \mathbf{k}' | \hat{Q}_e H_{\text{int}} \hat{P} G \hat{P} H_{\text{int}} \hat{Q}_e | g_e v_e \mathbf{k} \rangle, \end{aligned} \quad (\text{B4})$$

where $R^{(d)}$ is a level shift operator due to the dissociative states, i. e.,

$$R^{(d)} = V + V\hat{Q}_d(E - H_0 - \hat{Q}_d V \hat{Q}_d)^{-1}\hat{Q}_d V, \quad (\text{B5})$$

and V is given by Eq. (B2).

Consider now the dissociation T matrix elements (B3). As was done in Sec. III, they may be rewritten in terms of a DW basis set (Table I) diagonalizing the $\{|dv_d \mathbf{l}\rangle$ states with respect to the elastic part of V_d (i. e., V_0)

$$\begin{aligned} \langle d_e v_d \mathbf{l}, \text{vac} | \hat{Q}_d T \hat{Q}_e | g_e v_e \mathbf{k} \rangle \\ = \langle d_e v_d \mathbf{l}^- | \hat{Q}_d F_1^{(d)} \hat{Q}_d H_v \hat{P} G \hat{P} H_{\text{int}} | g_e v_e \mathbf{k} \rangle. \end{aligned} \quad (\text{B6})$$

$\hat{Q}_d F_1^{(d)} \hat{Q}_d$ is defined in terms of the inelastic part of $V_d(V_1)$, i. e.,

$$\hat{Q}_d F_1^{(d)} \hat{Q}_d = \hat{Q}_d + \hat{Q}_d V_1 \hat{Q}_d (E - H_0 - V_0)^{-1} \hat{Q}_d F_1^{(d)} \hat{Q}_d. \quad (\text{B7})$$

Equation (B7) is analogous to Eq. (III.16).

Invoking now assumption (ii) of Sec. IV, we have

$$\hat{P} G \hat{P} = \frac{|s_e, \text{vac}\rangle \langle s_e, \text{vac}|}{E - E_s - D_s + \frac{1}{2}\Gamma_s}. \quad (\text{B8})$$

Defining a second level-shift operator, this time due to the interaction with the photon continua,

$$R^{(e)} = V + V\hat{Q}_e(E - H_0 - \hat{Q}_e V \hat{Q}_e)^{-1}\hat{Q}_e V, \quad (\text{B9})$$

we can write formal expressions for D_s and Γ_s ,

$$D_s(E) = \text{Re}\langle s | \hat{P} R(E) \hat{P} | s \rangle \equiv D_s^{(r)} + D_s^{(d)} \quad (\text{B10a})$$

and

$$\Gamma_s = -2 \text{Im}\langle s | \hat{P} R(E) \hat{P} | s \rangle \equiv \Gamma_s^{(r)} + \Gamma_s^{(d)}, \quad (\text{B10b})$$

where

$$R(E) = R^{(d)}(E) + R^{(e)}(E), \quad (\text{B11})$$

and $D_s^{(\alpha)}$, $\Gamma_s^{(\alpha)}$ are the appropriate matrix elements of $R^{(\alpha)}$ $\alpha = r, d$.

Equation (B4), (B6), and (B8) result in Eqs. (IV.1)–(IV.3).

- *Present address: 6-234, Department of Chemistry, M.I.T., Cambridge, Mass. 02139.
- ¹(a) N. Basco, J. E. Nicholas, and G. W. Norrish, *Proc. R. Soc. (London) Ser. A* **268**, 291 (1962); **272**, 147 (1963); (b) T. Carrington, *J. Chem. Phys.* **41**, 2012 (1964); (c) R. C. Mitchell and J. P. Simons, *Discuss. Faraday Soc.* **44**, 208 (1967).
 - ²(a) G. E. Busch, R. T. Mahoney, R. I. Morse, and K. R. Wilson, *J. Chem. Phys.* **51**, 837 (1969); (b) K. R. Wilson, in *Chemistry of the excited states* edited by J. N. Pitts, Jr. (Gordon and Breach, New York, 1970); (c) G. E. Busch and K. R. Wilson, *J. Chem. Phys.* **56**, 3655 (1972); (d) **56**, 3638 (1972).
 - ³(a) J. Solomon, *J. Chem. Phys.* **47**, 889 (1967); (b) R. Bersohn and S. H. Lin, *Adv. Chem. Phys.* **16**, 80 (1969); (c) J. Solomon, C. Jonah, P. Chandra, and R. Bersohn, *J. Chem. Phys.* **55**, 1908 (1971); (d) C. Jonah, P. Chandra, and R. Bersohn, *J. Chem. Phys.* **55**, 1903 (1971); (e) C. Jonah, *ibid.* **55**, 1915 (1971); (f) R. Bersohn, *Isr. J. Chem.* **11**, 675 (1973); (g) M. Dzvonik, S. Yang, and R. Bersohn, *J. Chem. Phys.* **61**, 4408 (1974); (h) S. C. Yang and R. Bersohn, *ibid.* **61**, 4400 (1974).
 - ⁴(a) N. V. Karlov, Yu. N. Petrov, A. M. Prokhorov, and O. M. Stel'makh, *JETP Lett.* **11**, 135 (1970); (b) N. V. Karlov, Yu. B. Konev, and A. M. Prokhorov, *ibid.* **14**, 117 (1971).
 - ⁵A. Mele and H. Okabe, *J. Chem. Phys.* **51**, 4798 (1969).
 - ⁶(a) E. S. Yeung and C. Bradley Moore, *J. Am. Chem. Soc.* **93**, 2059 (1971); (b) E. S. Yeung and C. Bradley Moore, *J. Chem. Phys.* **58**, 3988 (1973).
 - ⁷(a) R. N. Zare and D. R. Herschbach, *Proc. IEEE* **51**, 173 (1963); (b) R. N. Zare, *Mol. Photochem.* **4**, 1 (1972).
 - ⁸L. C. Lee and D. L. Judge, *Can J. Phys.* **51**, 378 (1973).
 - ⁹J. A. Coxon, D. W. Setser, and W. H. Duerer, *J. Chem. Phys.* **58**, 2244 (1973).
 - ¹⁰T. Urisu and K. Kuchitsu, (a) *Chem. Lett.* **1**, 813 (1972); (b) *Chem. Phys. Lett.* **18**, 337 (1973); (c) *J. Photochem.* **2**, 409 (1973).
 - ¹¹(a) G. Karl, P. Kruss, and J. C. Polanyi, *J. Chem. Phys.* **46**, 224 (1967); (b) H. Heydtmann, J. C. Polanyi, and T. Taguchi, *Appl. Opt.* **10**, 1755 (1971).
 - ¹²J. N. Murrell and J. M. Taylor, *Mol. Phys.* **16**, 609 (1969).
 - ¹³R. J. Campbell and E. W. Schlag, *J. Am. Chem. Soc.* **89**, 5103 (1967).
 - ¹⁴A. S. Dickenson and R. B. Bernstein, *Mol. Phys.* **18**, 305 (1970).
 - ¹⁵K. E. Holdy, L. C. Klotz, and K. R. Wilson, *J. Chem. Phys.* **52**, 4588 (1970).
 - ¹⁶V. G. Plotnikov, *Opt. Spectrosc. (USSR)* **29**, 453 (1970).
 - ¹⁷M. Shapiro and R. D. Levine, *Chem. Phys. Lett.* **5**, 499 (1970).
 - ¹⁸O. S. Ramsay and M. S. Child, *Mol. Phys.* **22**, 263 (1971).
 - ¹⁹K. G. Kay and S. A. Rice, *J. Chem. Phys.* **57**, 3041 (1972).
 - ²⁰R. A. Van Santen, *Chem. Phys. Lett.* **15**, 621 (1972).
 - ²¹K. G. Kay and S. A. Rice, *J. Chem. Phys.* **58**, 4852 (1973).
 - ²²B. L. Borovich, V. Ya. Karpob, N. I. Kozlov, and Yu. Yu. Soilov, *Sov. Phys. JETP* **37**, 616 (1973).
 - ²³J. A. Beswick, *J. Phys. (Paris)* **34**, 813 (1973).
 - ²⁴S. Mukamel and J. Jortner, *Mol. Phys.* **27**, 1543 (1974).
 - ²⁵S. Mukamel and J. Jortner, *J. Chem. Phys.* **60**, 4760 (1974).
 - ²⁶K. G. Kay, *J. Chem. Phys.* **60**, 2370 (1974).
 - ²⁷Y. Band and K. F. Freed, *Chem. Phys. Lett.* **28**, 328 (1974).
 - ²⁸E. S. Yeung and C. Bradley Moore, *J. Chem. Phys.* **60**, 2139 (1974).
 - ²⁹J. P. Simons and P. W. Tasker, *Mol. Phys.* **26**, 1267 (1973); **27**, 1691 (1974).
 - ³⁰M. J. Berry, *Chem. Phys. Lett.* **29**, 329 (1974).
 - ³¹R. D. Levine, in *MTP International Review of Science*, edited by W. Byers Brown (Butterworths, London, 1972), Vol. 1, p. 229.
 - ³²M. L. Goldberger and R. M. Watson, *Collision Theory* (Wiley, New York, 1964).
 - ³³L. S. Rodberg and R. M. Thaler, *Introduction to the quantum theory of scattering* (Academic, New York, 1966).
 - ³⁴(a) L. Mower, *Phys. Rev.* **142**, 799 (1966); (b) **165**, 145 (1968).
 - ³⁵C. Cohen Tannoudji, in *Introduction de l'Electronique Quantique Cours de l'Association Vandoire de Recherches en Physique* Saas Fee (1968).
 - ³⁶S. Mukamel and J. Jortner, *J. Chem. Phys.* **61**, 227 (1974).
 - ³⁷S. Mukamel, thesis, Tel-Aviv University, 1975.
 - ³⁸M. Shapiro, *Isr. J. Chem.* **11**, 691 (1973).
 - ³⁹(a) J. Jortner and S. Mukamel, in *The World of Quantum Chemistry* edited by R. Daudel and B. Pullman (Reidel, Holland, 1973); (b) J. Jortner and S. Mukamel in *MPT International Review of Science*, edited by A. D. Buckingham (Butterworths, London, 1975), Ser. 2, Vol. 1.
 - ⁴⁰(a) R. D. Levine, *J. Phys. B* **2**, 839 (1969); (b) R. D. Levine, *Mol. Phys.* **22**, 497 (1971).
 - ⁴¹D. Secrest and B. R. Johnson, *J. Chem. Phys.* **45**, 4556 (1966).
 - ⁴²J. M. Jackson and N. F. Mott, *Proc. R. Soc. (London) Ser. A* **137**, 703 (1932).
 - ⁴³N. Rosen, *J. Chem. Phys.* **1**, 319 (1933).
 - ⁴⁴(a) O. Atabek, J. A. Beswick, and R. Lefebvre, *Chem. Phys. Lett.* **32**, 28 (1975); (b) O. Atabek, J. A. Beswick, R. Lefebvre, S. Mukamel, and J. Jortner, *Mol. Phys.* **31**, 1 (1976).
 - ⁴⁵L. Van Hove, *Physica* **22**, 345 (1955).
 - ⁴⁶(a) D. Rapp and T. Kassal, *Chem. Rev.* **69**, 61 (1969); (b) J. H. Weare and E. Thiele, *J. Chem. Phys.* **48**, 513 (1968); (c) E. Thiele and J. H. Weare, *ibid.* **48**, 513 (1968); (d) F. E. Heidrich, K. R. Wilson, and D. Rapp, *J. Chem. Phys.* **54**, 3885 (1971).
 - ⁴⁷G. W. King and A. W. Richardson, *J. Mol. Spectrosc.* **21**, 339, 353 (1966).
 - ⁴⁸K. F. Herzfeld, "Relaxation phenomena in gases," in *Thermodynamics and Physics in Matter* (Princeton University, Princeton, 1955).
 - ⁴⁹(a) G. Herzberg and K. K. Innes, *Can. J. Phys.* **35**, 842 (1957); (b) G. Herzberg, *Electronic Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1966).