Resonance fluorescence involving optically active continua

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(Received 16 August 1973)

In this paper we utilize the T matrix formalism of scattering theory for the study of the cross sections specifying optical absorption, resonance fluorescence elastic photon scattering, resonance Raman scattering, and photodissociation for molecules undergoing direct photodissociation or predissociation into a continuum, which carries oscillator strength from the ground state. We have demonstrated that for the special case of radiative interactions with a single molecular continuum explicit expressions can be derived for the Green's function and for the reaction operator, incorporating radiative interactions with one photon states to infinite order. From the complete solution for elastic photon scattering from a dissociative continuum we conclude that the direct radiative corrections are of the order of the "radiative Lamb shift" for the continuum states, and are negligible. The elastic photon scattering cross sections can be expressed in terms of a complex Hilbert transform of the Franck–Condon transition density, while the absolute photon scattering quantum yield is $\sim 10^{-7}$. This treatment has been extended for the study of resonance Raman scattering from a dissociative continuum, where the scattering cross sections can be expressed in terms of absolute squares of complex Hilbert transforms of the product of two Franck–Condon vibrational overlaps for bound-continuum transitions. No selection rules for the final vibrational state are exhibited. Finally, we have derived a general solution for photon scattering for a discrete molecular level coupled to an optically active dissociative continuum. The absorption cross section is finite at the interference dip, being determined by the interference function for the continuum states. The quantum yield for resonance fluorescence exhibits a sharp maximum reaching a value of unity at the interference dip where the quantum yield for dissociation vanishes.

I. INTRODUCTION

Molecular photofragmentation processes proceeding via direct photodissociation or by predissociation are amenable to a theoretical description in terms of quantum scattering theory, which has been thoroughly applied to nuclear reactions, atomic collision processes and also to photon-induced processes such as autoionization and intramolecular electronic relaxation. For these "long time" optical excitation experiments where the exciting photon field is characterized by a high resolution, the excitation and decay process cannot be separated and one has to consider resonance scattering of photons from molecules within the framework of a single quantum mechanical process. The physically relevant observables in direct photodissociation and in indirect photofragmentation (i. e., predissociation) experiments are the cross sections for absorption, for fluorescence, and for fragmentation, whose ratios result in the relevant quantum yields.

In molecular photon scattering processes, the theoretican's goal is to relate scattering amplitudes to matrix elements of radiative and intramolecular coupling. The description of indirect processes such as predissociation rests on the partitioning of the basis states into two classes which involve: (o) open and (c) closed channels. The open channels can be further subdivided into two types: (o1) one-photon states involving the ground molecular electronic level and (o2) zero-photon states involving the dissociative fragments. The initial state is contained entirely within (o1). It was recently demonstrated[1] that the general problem can be solved for a finite number of (c) states provided that the radiative coupling between (o1) and (o2) is negligible.

When the zero-photon continuum states carry oscillator strength from the ground state we encounter the Fano problem which was solved for the lineshapes and for the scattering cross sections incorporating radiative interactions only to first order.[2] In the case of photon scattering by a system which is characterized by a discrete ground state and an optically active dissociative continuum, we have to focus attention on photon scattering between (o1) and (o2) where the system does contain only open channels. Nitzan and Jortner[3] attempted to handle this problem to low order in the radiative interactions and to the best of our knowledge, a general solution has not yet been provided.

In this paper we present the results of a theoretical study of optical absorption cross sections, resonance fluorescence scattering cross sections, and photodissociation cross sections for molecules undergoing direct photodissociation or predissociation into an optically active continuum. We were able to derive general expressions for the absorption and for the photon scattering cross sections including radiative interactions to infinite order, taking into account zero and one photon states. These theoretical results are of interest because of the following reasons:

(1) In the study of predissociation in a molecular system which involves an optically active dissociative continuum one encounters interference effects between resonance and potential scattering. In Fano's classical treatment of this problem[2] the absorption cross section, which is equal to the sum of all scattering cross sections to the open channels, vanishes at the reduced energy which equals the negative value of the line profile index. As in the case of two overlapping resonances[3] we expect

that when radiative interactions will be properly included the absorption cross section will be small but finite at this energy. It is interesting to inquire how the interference effects modify the individual scattering cross section to the dissociative continuum and for resonance scattering of photons. The energy dependence of the quantum yield will provide a dramatic behavior near the finite "dip" in the line shape, which may be amenable to experimental detection.

(2) Regarding direct optical photodissociation of diatomic and polyatomic molecules it is interesting to inquire whether resonance fluroescence, which is equivalent to resonance Raman scattering, can be observed when a molecule is pumped into the dissociative continuum. From the experimental point of view, it was demonstrated that such a resonance fluorescence (which we identify with resonance Raman scattering) is exhibited for photodissociative molecular continua. It is interesting to provide a complete theoretical study of this effect and to establish the absolute magnitude of the emission quantum yield and its energy dependence.

Our treatment rests on the application of the T matrix formalism of scattering theory. The present approach provides a generalization of the problem of sequential decay which involves intercontinuum interference effects. It was recently demonstrated[4] that the matrix elements of the Green's function for the case of a discrete state decaying into coupled continua and the T matrix for scattering between one continuum and a set of coupled continua can be explicitly evaluated for a simple model system which involves constant coupling between adjacent unbound continua. We shall demonstrate that a general solution which includes the energy dependence of the intercontinuum coupling, and the effect of continua bound below, can be derived for two problems: (1) scattering from a radiative continuum into an open dissociative channel, which is just the problem of direct photodissociation, and (2) scattering from a radiative continuum into a superposition of a discrete level and an open dissociative channel, which directly pertains to the problem of predissociation with an optically active continuum.

II. PHOTON SCATTERING FORMALISM

We consider the conventional form of the total Hamiltonian H for the system including the radiation field

$$H = H_0 + V, \qquad \text{(II. 1)}$$

$$H_0 = H_{BO} + H_R, \qquad \text{(II. 1a)}$$

$$V = H_{int} + H_V, \qquad \text{(II. 1b)}$$

where H_{BO} is the (zero order) molecular Born–Oppenheimer Hamiltonian, H_V is the intramolecular nonadiabatic coupling, H_R is the Hamiltonian for the free electromagnetic field, while H_{int} is the matter-radiation interaction term. The ground electronic state $|g_e\rangle$, of the molecule is specified in terms of the discrete vibronic levels $|g_e v\rangle$, where v corresponds to the vibrational level. These discrete states $|g_e v\rangle$ can be considered as eignefunctions of H_0 as well as of $H_0 + V$. The excited states of H_0 can include in general discrete

levels which we shall label as $|s_e\rangle$, $|r_e\rangle \cdots$ etc., and continuous levels $\{|l_e\rangle\}$, which for the present discussion correspond to a dissociative state. The eigenfunctions of H_R will be taken as zero photon states, $|vac\rangle$, and one photon states $|ke\rangle$, where k and e represent the wavevector and the polarization vector of a photon, respectively. The eigenstates of H_0 are labeled as follows: $|g_e o, ke\rangle$ and $|g_e v, k'e'\rangle$ for the ground electronic state while for excited electronic states we have $|s_e, vac\rangle$ for discrete states and $|l_e, vac\rangle$ for continuum states. In Fig. 1 we portray the relevant eigenstates of H_0 for direct photodissociation and for predissociation together with the relevant coupling via V [Eq. (II.1)].

We shall describe a collision process between a monochromatic wave train characterized by the energy $E = \hbar c k$ and the molecule in terms of the T matrix formalism. We are interested in the evaluation of the scattering cross sections for the following processes:

(1) Photon scattering cross sections $\sigma_r(g_e o, ke \to g_e v, k'e')$, $(v = 0, 1, \ldots)$. The cross section $\sigma_r(g_e o, ke \to g_e o, k'e')$ corresponds to "elastic" scattering while $\sigma_r(g_e o, ke \to g_e v, k'e')(v \neq 0)$ determines the Raman scattering.

(2) Dissociation cross sections $\sigma_d(g_e o, ke \to l_e, vac)$.

(3) Photon absorption cross section $\sigma_d(E)$, determined at the photon energy $E = \hbar k c$.

Application of scattering theory leads to the following expressions for the cross sections[3,5]:
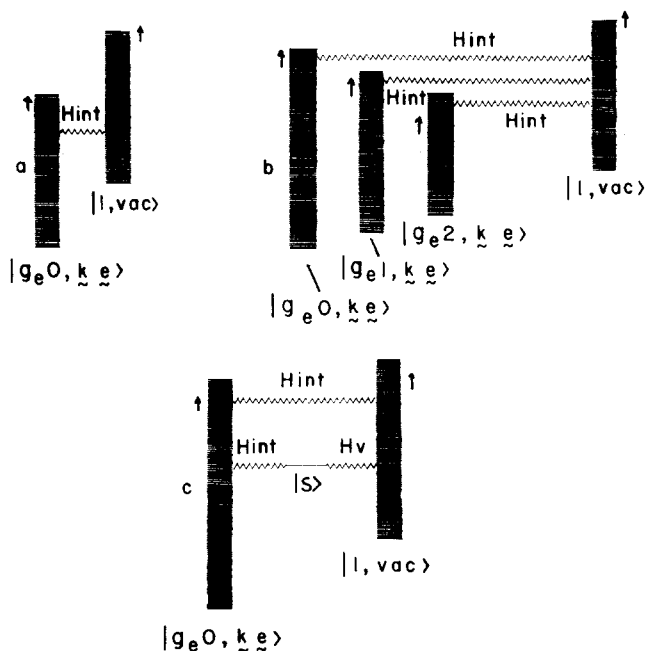

FIG. 1. Coupling schemes for models involving an optically active continuum. (a) Direct photodissociation involving one radiative and one dissociative continua. (b) Direct photodissociation including various vibrational channels of the ground state (c) Predissociation where the internal continuum carries oscillator strength

$$\sigma_r(g_e o, \mathbf{ke} \to g_e v, \mathbf{k'e'}) = (2\pi Q/\hbar c)\, | \langle g_e o, \mathbf{ke} \,|\, T(E) \,|\, g_e v, \mathbf{k'e'} \rangle |^2$$

$$\otimes \delta(\overline{E}_{g o} + \hbar k c - \overline{E}_{g v} - \hbar k' c), \qquad \text{(II. 2)}$$

$$\sigma_d(g_e o, \mathbf{ke} \to l_e, \mathrm{vac}) = (2\pi Q/\hbar c)\, | \langle g_e o, \mathbf{ke} \,|\, T(E) \,|\, l_e, \mathrm{vac} \rangle |^2$$

$$\otimes \delta(\overline{E}_g + \hbar k c - E_l), \qquad \text{(II. 3)}$$

$$\sigma_a(g_e o, \mathbf{ke}) = -(2Q/\hbar c)\mathrm{Im}\, \langle g_e o, \mathbf{ke} \,|\, T(E) \,|\, g_e o, \mathbf{ke} \rangle. \qquad \text{(II. 4)}$$

The T matrix (the reaction operator) is defined by

$$T(E) = V + VG(E)V, \qquad \text{(II. 5)}$$

where the Green's operator is

$$(E - H + i\eta)^{-1} = (E^+ - H)^{-1}; \quad \eta \to 0^+, \qquad \text{(II. 6)}$$

where $E^+ = E + i\eta$.

In Eqs. (II. 2)–(II. 4) the initial energy is $\overline{E}_{g o} + \hbar k c$ while the energy of the final state is $\overline{E}_{g v} + \hbar k' c$, where $\overline{E}_{g o}$ and $\overline{E}_{g v}$ correspond to the energies of the molecular states $|\, g_e o \rangle$ and $|\, g_e v \rangle$, respectively, and we can choose the origin of energy as $\overline{E}_{g o} = 0$. Q is the volume of the system, c represents the velocity of light, and E_l is the energy of the $|\, l_e, \mathrm{vac} \rangle$ state. Finally, V in Eq. (II. 5) is defined in terms of Eq. (II. 1).

We may now define the total cross section for photon scattering (resulting in the molecular state $|\, g_e v \rangle$) by summing Eq. (II. 2) over final photon states (i. e., energy, spatial direction, and polarization) followed by averaging over molecular orientations. This procedure results in the averaged cross section for scattering of a photon of energy $E = \hbar k c$ resulting in a photon of energy $E' = \hbar k c - \overline{E}_{g v}$

$$\sigma_r^v(E) = \Big\langle \sum_{e'} \int d^3k'\, \sigma_r(g_e o, \mathbf{ke} \to g_e v, \mathbf{k'e'})\, \rho_r'(E') \Big\rangle, \qquad \text{(II. 2a)}$$

where $\langle\,\rangle$ denotes averaging over all molecular orientations and ρ_r' is the density of photon states per unit volume

$$\rho_r'\, dE = [Q/(2\pi)^3]\, dE. \qquad \text{(II. 7)}$$

In a similar manner we may define the spatially averaged dissociation cross section

$$\sigma_d(E) = \langle \sigma_d(g_e o, \mathbf{ke} \to l_e, \mathrm{vac}) \rangle \qquad \text{(II. 3a)}$$

and the averaged absorption cross section is

$$\sigma_a(E) = \langle \sigma_a(g_e o, \mathbf{ke}) \rangle. \qquad \text{(II. 4a)}$$

The unitarity relations[5] for the scattering matrix result in the optical theorem

$$-\mathrm{Im}\, T_{aa} = (1/\pi) \sum_b \sigma(a \to b) \qquad \text{(II. 8)}$$

which leads to the conservation law

$$\sigma_a(E) = \sum_v \sigma_r^v(E) + \sigma_d(E). \qquad \text{(II. 9)}$$

Finally, we can define the quantum yields for photon scattering into $|\, g_e v \rangle$ by

$$Y_r^v(E) = \sigma_r^v(E)/\sigma_a(E) \qquad \text{(II. 10)}$$

the total emission quantum yield

$$Y_r(E) = \sum_v Y_r^v(E) \qquad \text{(II. 11)}$$

and the quantum yield for photodissociation

$$Y_d(E) = \sigma_d(E)/\sigma_a(E). \qquad \text{(II. 12)}$$

Equations (II. 2)–(II. 5) together with (II. 2a)–(II. 4a) and Eqs. (II. 10)–(II. 12) contain all of the relevant physical information regarding the "long time" excitation experiments. The physical observables are expressed in terms of the matrix elements of the T matrix, which in turn can be recast in terms of the matrix elements of the perturbation and of the Green's function. The evaluation of the intercontinuum matrix elements of the Green's function was previously accomplished only for simple model systems involving constant, energy independent, coupling between two continua.[4] We would like to point out that when the coupling between two continua (say, $\{|\, m \rangle\}$ and $\{|\, n \rangle\}$) can be factorized as a product of two independent functions, each determined by the energetics of one continuum only, i. e.,

$$\langle n \,|\, V \,|\, m \rangle \equiv V_{nm} = V_1(n) V_2(m) \qquad \text{(II. 13)}$$

general explicit expressions can be obtained for the matrix elements of the Green's function. The intercontinuum coupling for the problems at hand (see Fig. 1) involves radiative interactions between the continua $|\, g_e v, \mathbf{ke} \rangle$ and $|\, l_e, \mathrm{vac} \rangle$. These coupling terms can be factored out into a product of separate contributions from the two continua.[6] This can be easily demonstrated by considering the explicit form of (II. 1).

$$H_{\mathrm{int}} = -(e\hbar/m)\Big[\sum_{\mathbf{ke}} \Big(\frac{2\pi}{Q\hbar c k}\Big)^{1/2} \Big(a_{\mathbf{ke}} \sum_j (\mathbf{p}_j \cdot \mathbf{e}) \exp(i\mathbf{k r}_j) + \mathrm{c.\,c.} \Big) \Big], \qquad \text{(II. 14)}$$

where $a_{\mathbf{ke}}$ is the $\mathbf{ke}$ photon annihilation operator and $\mathbf{p}_j$ and $\mathbf{r}_j$ correspond to the j electron momentum and to the j electron coordinates, respectively.

The zero order molecular wavefunctions in the Born–Oppenheimer approximation are

$$|\, g_e v \rangle = \varphi_g(\mathbf{r}, \mathbf{R}) \chi_v(\mathbf{R})$$

$$|\, l_e \rangle = \varphi_l(\mathbf{r}, \mathbf{R}) \chi_l(\mathbf{R}, E_l) \qquad \text{(II. 15)}$$

where φ and χ refer to the electronic and nuclear wavefunctions. Thus in the dipole approximation one gets

$$\langle l_e, \mathrm{vac} \,|\, H_{\mathrm{int}} \,|\, g_e v, \mathbf{ke} \rangle = \beta' h(\mathbf{k}) \langle \varphi_l \chi_l \,|\, \mathbf{p} \cdot \mathbf{e} \,|\, \varphi_g \chi_v \rangle, \qquad \text{(II. 16)}$$

where

$$\beta' = -(e\hbar/m)(2\pi/Q\hbar c)^{1/2}, \qquad \text{(II. 17)}$$

$$h(k) = 1/\sqrt{k}, \qquad \text{(II. 18)}$$

and $\mathbf{p} = \sum_j \mathbf{p}_j$ is the electronic momentum operator. Invoking the Condon approximation we may further factor out Eq. (II. 16) in the form

$$\langle l_e, \mathrm{vac} \,|\, H_{\mathrm{int}} \,|\, g_e v, \mathbf{ke} \rangle = \beta_{e(\mathbf{k})} h(k) f_v(E_l), \qquad \text{(II. 19)}$$

where

$$f_v(E_l) = \langle \chi_l \,|\, \chi_v \rangle \qquad \text{(II. 20)}$$

is the Franck–Condon overlap integral. The coefficient $\beta_{e(\mathbf{k})}$ in Eq. (II. 19) which is given by

$$\beta_{e(\mathbf{k})} = \beta' \langle \varphi_l \,|\, \mathbf{p} \cdot \mathbf{e} \,|\, \varphi_g \rangle \qquad \text{(II. 21)}$$

depends explicitely on the molecular orientations with respect to the photon polarization vector. When spher-

ical averaging and summation over polarization directions is performed we can (see Sec. III) replace $\beta_{e\,(\mathbf{k})}$ by a constant for a given electronic transition.

Thus Eq. (III.19) can be factorized into a product of a function $h(k)$ which is solely determined by the energy levels in the photon continuum, the Franck–Condon vibrational overlap $f_v(E_l)$ which exclusively depends on the energy levels in the dissociative continuum and a "nonseparable" contribution $\beta_{e\,(\mathbf{k})}$ which is determined by the molecular orientation with respect to e. The last factor does not depend on the energy levels of the two continua, and we shall demonstrate in (Sec. III) that for the interaction (II.19) an exact solution can be obtained for the matrix elements of the Green's function and for the T matrix as is the case for the general interaction of the form (II.13). The solution for the coupling between a radiative and a dissociative continuum (where some other discrete molecular states can be also present) can be derived in two entirely equivalent ways. One can calculate the matrix elements of the Green's function using the level shift operator. This will be done in Secs. III and IV for the problem of photon scattering from a dissociative continuum. Alternatively, we may seek a direct solution for the matrix elements of the T matrix. This approach will be adopted in Sec. V for the Fano problem.

III. ELASTIC PHOTON SCATTERING FROM A DISSOCIATIVE CONTINUUM

We shall now consider the simplest realistic example for direct photodissociation. The eigenstates of the molecular Hamiltonian, which in this case can be taken as either H_{BO}, neglecting the mixing by H_v, or as $H_{BO} + H_v$, are taken to consist of a single discrete ground state $|g_e o\rangle$ and the continuum $|l_e\rangle$. The photon scattering process

$$|g_e o, \mathbf{ke}\rangle \to |g_e o, \mathbf{k'e'}\rangle \qquad (\text{III.1})$$

involves $V = H_{\text{int}}$, so that $H_0 = H - H_{\text{int}}$.

We shall now proceed to the calculation of the matrix elements of the T matrix. To simplify the notation, we shall denote

$$|g\rangle \equiv |g_e o, \mathbf{ke}\rangle, \quad |g'\rangle \equiv |g_e o, \mathbf{k'e'}\rangle$$

and $|l_e \text{vac}\rangle \equiv |l\rangle$. Thus, the sums over one photon states are $\sum_{\mathbf{k}}\sum_{e} \equiv \sum_{g}$ and those over zero photon molecular states will be designated by $\sum_{l}$. The relevant matrix elements of the reaction operator [Eq. (II.5)] which determine the cross sections (II.2)–(II.4) are:

$$\langle g_e o, \mathbf{k'e'}| T(E)|g_e o, \mathbf{ke}\rangle \equiv T_{g'g} = \sum_{l}\sum_{l'} V_{g'l'} G_{l'l} V_{lg}, \qquad (\text{III.2})$$

$$\langle l_e, \text{vac}| T(E)|g_e o, \mathbf{ke}\rangle \equiv T_{lg} = V_{lg} + \sum_{g'}\sum_{l'} V_{lg'} G_{g'l'} V_{l'g}. \qquad (\text{III.3})$$

Thus the matrix elements $T_{g'g}$ and T_{lg} are determined by $G_{l'l}$ and by $G_{g'l'}$, respectively. The matrix elements of the Green's function can be expressed in terms of the level shift operator[7]

$$R = V + V\hat{Q}(E - \hat{Q}H\hat{Q})^{-1}\hat{Q}V, \qquad (\text{III.4})$$

where the projection operator $\hat{Q}$ over the $|g_e 0, \mathbf{ke}\rangle$ sub-

space

$$\hat{Q} = \sum_{\mathbf{k}e} |g_e o, \mathbf{ke}\rangle\langle \mathbf{ke}, g_e o | \equiv \sum_{g} |g\rangle\langle g | \qquad (\text{III.5a})$$

is complementary to

$$\hat{P} = \sum_{l} |l_e, \text{vac}\rangle\langle l_e, \text{vac}| \equiv \sum_{l} |l\rangle\langle l| \qquad (\text{III.5b})$$

so that using this partitioning $\hat{P} + \hat{Q} = 1$. The total Hamiltonian is prediagonalized within each subspace $\hat{P}$ and $\hat{Q}$. A cursory examination of the operator identities[7]

$$\hat{P}G\hat{P} = \hat{P}G_0\hat{P} + \hat{P}G^0\hat{P}R\hat{P}G\hat{P} \qquad (\text{III.6})$$

$$\hat{Q}G\hat{P} = (E^+ - \hat{Q}H_0\hat{Q})^{-1}\hat{Q}R\hat{P}(E^+ - H_0 - \hat{P}R\hat{P})^{-1}, \qquad (\text{III.7})$$

where $G_0 = (E^+ - H_0)^{-1}$, reveals that $G_{l'l}$ [which determines $T_{g'g}$ via Eq. (III.2)] can be expressed in terms of $R_{l'l}$ while the matrix elements $G_{g'l}$ [which determine T_{lg} via Eq. (III.3)] are given in terms of R_{gl}. These matrix elements of the level shift operator are

$$R_{l'l} \equiv \langle l' | R | l\rangle = \sum_{g} \frac{\langle l' | V | g\rangle\langle g | V | l\rangle}{E^+ - E_g}, \qquad (\text{III.8})$$

where $E_g = \hbar k c$, and

$$R_{gl} \equiv \langle g | R | l\rangle = \langle g | V | l\rangle. \qquad (\text{III.8a})$$

Up to this point the results are general and formal. We now utilize the explicit form of the radiative coupling matrix elements [Eq. (II.19)] for V_{gl} and proceed to the evaluation of the Green's function. To calculate $G_{l'l}$ we recast Eq. (III.8) in the form

$$R_{l'l} = |\beta|^2 f_0(E_{l'}) f_0^*(E_l) A^g, \qquad (\text{III.8b})$$

where $|\beta|^2$ is an averaged value of $\beta_{e\,(\mathbf{k})}$ which is given by

$$|\beta|^2 \equiv \tfrac{2}{3} |\beta'|^2 |\langle\varphi_l| \mathbf{p}| \varphi_g\rangle|^2. \qquad (\text{III.8c})$$

This averaged value is obtained (see Appendix A) by spatial integration and summation over polarization directions of (III.8). The (complex) level shift function of the zero photon states $|l_e, \text{vac}\rangle$ is

$$A^g(E) = \sum_{\mathbf{k}} [|h(k)|^2/(E^+ - k\hbar c)]. \qquad (\text{III.9})$$

From Eqs. (III.6) and (III.8b) we get

$$G_{l'l} = [\delta(E_l - E_{l'})/(E^+ - E_{l'})] + |\beta|^2 A^g [f_0(E_{l'})/(E^+ - E_{l'})]a_l, \qquad (\text{III.10})$$

where

$$a_l = \sum_{l''} f_0^*(E_{l''}) G_{l''l}. \qquad (\text{III.11})$$

An explicit solution for the auxiliary function (III.11) can be readily obtained by multiplying Eq. (III.10) by $f_0^*(E_{l'})$ followed by summation over l', resulting in

$$a_l = [f_0^*(E_l)/(E^+ - E_l)] + |\beta|^2 A^g A^l a_l, \qquad (\text{III.12})$$

where the (complex) level shift function of the one photon states $|g\rangle$ is

$$A^l(E) = \sum_{l'} [|f_0(E_{l'})|^2/(E^+ - E_{l'})]. \qquad (\text{III.13})$$

From Eqs. (III.10) and (III.12) we obtain

$$G_{l'l}(E) = \frac{\delta(E_l - E_{l'})}{E^+ - E_{l'}} + \frac{|\beta|^2 A^g(E) f_0(E_{l'}) f_0^*(E_l)}{(E^+ - E_{l'})(E^+ - E_l)[1 - |\beta|^2 A^g(E)A^l(E)]}. \qquad (\text{III.14})$$

To evaluate G_{gl} we make use of Eqs. (III. 7) and (III. 8a), which results in

$$G_{gl}(E) = (E^+ - E_g)^{-1} \sum_{l'} V_{gl'} G_{l'l} \qquad (III.15)$$

and from Eqs. (III. 14) and (III. 15) we get

$$G_{gl}(E) = \left[\frac{V_{gl}}{1 - |\beta|^2 |A^g(E)A^l(E)} \right] \left[\frac{1}{(E^+ - E_g)(E^+ - E_l)} \right] . \qquad (III.16)$$

Finally, we can utilize Eqs. (III. 14) and (III. 16) to express the matrix elements of the T matrix [Eqs. (III. 2) and (III. 3)] in the explicit form

$$T_{g'g} = \frac{\beta_e \beta_{e'}^* h(E'/\hbar c) h(E/\hbar c) A^l(E)}{1 - |\beta|^2 A^g(E)A^l(E)} , \qquad (III.17)$$

$$T_{lg} = \frac{\beta_e f_0(E_l) h(E/\hbar c)}{1 - |\beta|^2 A^g(E)A^l(E)} . \qquad (III.18)$$

Equations (III. 17) and (III. 18) together with the definitions (II. 19), (II. 17), (II. 18), and (II. 21) can be immediately applied for the calculation of the (spatially and polarization averaged) scattering cross sections (II. 2a)–(II. 4a).[8] As we consider elastic photon scatting, we can set $k = k'$ (i.e., $E = E'$). It will also be useful to recast the proportionality factor in Eqs. (II. 2)–(II. 4) [and (II. 2a)–(II. 4a)] in the form

$$2Q/\hbar c = \rho_r(E)\lambda^2 = \rho_r(E')\lambda'^2 , \qquad (III.19)$$

where $\lambda = 2\pi/k$ (or $\lambda' = 2\pi/k'$) corresponds to the wavelength of the photon, and where

$$\rho_r(E) = \int \rho_r' \, d^3 \hat{k} = 4\pi Q k^2/(2\pi)^3 \hbar c \qquad (III.19b)$$

corresponds to the spatially integrated density of states

per unit energy in the ratiation field. In Eq. (III.19b), $\hat{k}$ is a unit vector in the k direction. The cross sections (II. 2a)–(II. 4a) take the form

$$\sigma_r(E) = \frac{\pi\lambda^2}{2} \frac{|\beta|^4 |h(E/\hbar c)|^4 |A^l(E)|^2 \rho_r^2(E)}{|1 - |\beta|^2 A^g(E)A^l(E)|^2} , \qquad (III.20a)$$

$$\sigma_d(E) = \frac{\pi\lambda^2}{2} \frac{|\beta|^2 |f_0(E)|^2 |h(E/\hbar c)|^2}{|1 - |\beta|^2 A^g(E)A^l(E)|^2} \rho_l(E)\rho_r(E), \qquad (III.20b)$$

$$\sigma_a(E) = -\frac{\lambda^2}{2} \beta |^2| h(E/\hbar c)|^2 \rho_r(E) \, \mathrm{Im} \, \frac{A^l(E)}{1 - |\beta|^2 A^g(E)A^l(E)} , \qquad (III.20c)$$

where $\rho_l(E)$ corresponds to the density of states in the dissociative continuum at the energy E. To express Eq. (III. 20) in a more transparent form we now separate the functions $A^g(E)$ and $A^l(E)$ into their real and imaginary parts

$$A^g(E) = \alpha^g(E) - i\pi\rho_r(E) |h(E/\hbar c)|^2 , \qquad (III.21)$$

where

$$\alpha^g(E) = pp \int \frac{|h(E'/\hbar c)|^2 \rho_r(E')}{E - E'} dE' \qquad (III.22)$$

and

$$A^l(E) = \alpha^l(E) - i\pi\rho_l(E) |f_0(E)|^2 , \qquad (III.23)$$

where

$$\alpha^l(E) = pp \int \frac{|f_0(E_l)|^2 \rho_l(E_l) dE_l}{E - E_l} . \qquad (III.24)$$

PP in Eqs. (III. 22) and (III. 24) corresponds to the principal part of the integral. The cross sections (III. 20) take the final form

$$\sigma_a(E) = \frac{\lambda^2}{2} \frac{|\beta|^2 |h(E/\hbar c)|^2 [\pi(1 + N'(E)) |f_0(E)|^2 \rho_l(E) + \alpha^l(E)\delta(E)]\rho_r(E)}{(1 + N'(E))^2 + \delta^2(E)} ,$$

$$\sigma_r(E) = \frac{\pi\lambda^2}{2} \frac{|\beta|^4 |h(E/\hbar c)|^4 |\alpha^l(E) - i\pi |f_0(E)|^2 \rho_l(E)|^2 \rho_r^2(E)}{(1 + N'(E))^2 + \delta^2(E)} , \qquad (III.25)$$

$$\sigma_d(E) = \frac{\pi\lambda^2}{2} \frac{|\beta|^2 |f_0(E)|^2 |h(E/\hbar c)|^2 \rho_l(E)\rho_r(E)}{(1 + N'(E))^2 + \delta^2(E)} ,$$

where we have defined

$$N'(E) = |\beta|^2 [\pi^2 |h(E/\hbar c)|^2 |f_0(E)|^2 \rho_r(E)\rho_l(E) - \alpha^g(E)\alpha^l(E)] \qquad (III.26)$$

and

$$\delta(E) = \pi |\beta|^2 [|f_0(E)|^2 \rho_l(E)\alpha^g(E) + |h(E/\hbar c)|^2 \rho_r(E)\alpha^l(E)] . \qquad (III.27)$$

The quantum yields for resonance scattering [Eq. (II. 10)] and for photodissociation are given from (III. 25) in the form

$$Y_r^0(E) = \frac{\pi |\beta|^2 |h(E/\hbar c)|^2 \rho_r(E)| \alpha^l(E) - i\pi |f_0(E)|^2 \rho_l(E)|^2}{\pi(1 + N'(E)) |f_0(E)|^2 \rho_l(E) + \delta(E)\alpha^l(E)} \qquad (III.28)$$

$$Y_d(E) = \frac{\pi |f_0(E)|^2 \rho_l(E)}{\pi(1 + N'(E)) |f_0(E)|^2 \rho_l(E) + \alpha^l(E)\delta(E)} .$$

We note in passing that Eq. (III. 25) and Eq. (III. 28) obey, of course, the conservation laws

$$\sigma_a(E) = \sigma_r(E) + \sigma_d(E) \qquad (III.29a)$$

and

$$Y_r^0 + Y_d = 1 . \qquad (III.29b)$$

Equations (III. 25) and (III. 28) provide the general solution for resonance photon scattering from a dissociative continuum, where radiative interactions (with one photon states) have been incorporated to infinite order. Thus interference effects between the continuum states are included to infinite order. The only hidden approximation involves the neglect of one photon states $|l_e, \mathbf{ke}\rangle$ and zero photon states $|g_e 0, \text{vac}\rangle$. However incorporating these states in the eigenstates of $H_0 = H - H_{int}$ will lead to "off-resonance" interactions which are of minor importance. To reduce our results into a manageable form we shall proceed at two levels of sophistication. First, a crude approximation will be invoked to obtain order of magnitude estimates for the cross sections

neglecting the real part of the level shifts. Second, we shall provide a reliable estimate for the physical quantities from a detailed consideration of the level shifts.

For the sake of a crude order of magnitude estimates we neglect the (real) level shifts (III.22) and (III.24) setting $\alpha^l \simeq 0$ and $\alpha^f \simeq 0$. This approximation is somewhat more general than the common assumption of energy independent coupling between two unbound continua. In this case we get

$$\sigma_a(E) \simeq \frac{\lambda^2}{2\pi} \frac{N(E)}{1 + N(E)} \;,$$

$$\sigma_r(E) \simeq \frac{\lambda^2}{2\pi} \frac{N(E)^2}{[1 + N(E)]^2} \;, \tag{III.30}$$

$$\sigma_d(E) = \frac{\lambda^2}{2\pi} \frac{N(E)}{[1 + N(E)]^2} \;,$$

where

$$N(E) = \pi^2 |\beta|^2 |f_0(E)|^2 |h(E/\hbar c)|^2 \rho_l(E)\rho_r(E)$$
$$= 2\pi^2 \langle |V_{lg}|^2 \rangle \rho_l(E)\rho_r(E) \;. \tag{III.31}$$

The parameter N corresponds to the product of the "radiative width" of the $|l_g, \text{vac}\rangle$ states and the density of states. An analogous interference function was previously encountered in the study of sequential decay involving two coupled continua or quasicontinua.[4] From the approximate relations (III.30) we can readily obtain an estimate for N from experimental absorption cross sections for molecular photodissociation, which are typically $\sigma_a \simeq 10^{-17}$ cm^2 for diatomic. Hence taking $\lambda = 2000$ Å results in $N \simeq \sigma_a/\lambda^2 = 10^{-7}$, $\sigma_a \sim \lambda^2 N$, $\sigma_r \sim \lambda^2 N^2$, and $\sigma_d \sim \lambda^2 N$. Thus the quantum yield for resonance scattering $Y_r^0 \sim N \sim 10^{-7}$ which concurs with the estimate of Nitzan and Jortner.[3]

In order to derive a more complete and reliable theoretical expression for the cross sections we have to estimate the level shifts in detail. We consider first the (complex) level shift term A^l [Eq. (III.13)], and its real part α^l [Eq. (III.24)], which originate from virtual coupling of one photon states $|g_e o, \mathbf{k}e\rangle$ via zero photon states $|l_g, \text{vac}\rangle$. Utilizing the molecular wavefunctions in the Born–Oppenheimer approximation in [Eqs. (II.15)]. We get

$$\alpha^l(E) = PP \int dE_l \left[|\langle \chi_0 | \chi_l \rangle|^2 \rho_l(E_l)/(E - E_l) \right] \tag{III.32}$$

$$\text{Im}A^l = |\langle \chi_0 | \chi_l \rangle|^2 \rho_l \;. \tag{III.33}$$

We may conclude that except for exceptional energy values where $\alpha^l = 0$ (i.e., at the maximum of a symmetric distribution ImA^l) we have $\alpha^l \simeq$ ImA^l and consequently the level shift α^l cannot be neglected in the evaluation of the cross sections.

The complex Lamb shift function $A^f(E)$ [Eq. (III.9)] and its real part $\alpha^f(E)$ originate from virtual transitions between any zero photon state $|l_e, \text{vac}\rangle$ and itself via one photon states $|g_e o, \mathbf{k}\rangle$, which is identical with the second order coupling which yields the radiative level shift. Performing the integration $\sum_k \to \int \rho_r d^3\mathbf{k}$ over (III.9) and utilizing (III.19) we have

$$A^f(E_l) = \frac{Q}{2\pi^2} \int_0^\infty \frac{k\,dk}{E^+ - k\hbar c} \;. \tag{III.34}$$

This integral diverges linearly resulting in an infinite level shift α^f. In Appendix B we apply the elementary theory of the Lamb shift, performing mass renormalization and performing the integration up to the limit $K = mc^2/\hbar c$. Subsequently the renormalized level shift function should be taken in the form:

$$A^{f\,\text{renormalized}} \xrightarrow{} \frac{4\pi Q}{(2\pi)^3} \frac{E_l}{(\hbar c)^2} \int_0^K \frac{\hbar c\,dk}{E_l - k\hbar c} = \frac{Q}{2\pi^2(\hbar c)^2} E_l \left[\ln\left|\frac{\hbar K c}{E_l}\right| + i\pi \right] \tag{III.35}$$

which has the common form obtained in the theory of the hydrogen Lamb shift,[9a] ΔE_L^H. In Appendix B we present a reasonable, order of magnitude estimate of the parameters N' and δ which results in

$$|N'| \sim |\delta| \simeq \Delta E_L^H / W \;, \tag{III.36}$$

where W corresponds to the width of the absorption band.[9b] Taking $\Delta E_L^H \simeq 3 \times 10^{-2}$ cm^{-1} and $W \simeq 10^4$ cm^{-1} we obtain

$$|N'| \sim |\delta| \sim 10^{-6} \ll 1 \;. \tag{III.37}$$

Condition (III.37) results in a considerable simplification of Eqs. (III.25) for the cross sections, where we can safely neglect N' and δ in the denominators and N' and $\delta\alpha^l$ in the numerator for $\sigma_a(E)$. We thus obtain

$$\sigma_a(E) = \frac{\pi\lambda^2}{2} |\beta|^2 |h(E/\hbar c)|^2 |f_0(E)|^2 \rho_l(E)\rho_r(E)[1 + O(N')] \;, \tag{III.38}$$

$$\sigma_r(E) = \frac{\pi\lambda^2}{2} |\beta|^4 |h(E/\hbar c)|^4 \rho_r^2(E) |\alpha^l(E) - i\pi| f_0(E)|^2 \rho_l(E)|^2$$
$$\times [(1 + O(N')] \;, \tag{III.39}$$

$$\sigma_d(E) = \frac{\pi\lambda^2}{2} |\beta|^2 |h(E/\hbar c)|^2 |f_0(E)|^2 \rho_l(E)\rho_r(E)[1 + O(N')] \;, \tag{III.40}$$

where in view of (III.37) the terms $O(N')$ in (III.38), (III.39), and (III.40) are negligible. From Eqs. (III.19b), (II.15), (II.16), (III.33), and (III.38), the absorption cross section takes the conventional form

$$\sigma_a(E) = \frac{4\pi^2 e^2}{3m^2 c^2 k} |\langle \varphi_g | \mathbf{p} | \varphi_l \rangle|^2 |\langle \chi_0 | \chi_l(E_l)\rangle|^2 \rho_l(E) \;. \tag{III.41}$$

Finally it will be useful to relate the photon scattering cross section and the photodissociation cross section to the absorption cross section. Eqs. (III.39) and (III.40) can be rewritten in terms of Eq. (III.41) in the final form:

$$\sigma_r(E) = \frac{1}{(2\pi)^3(\hbar c)^2} \left| \int \frac{E'\sigma_a(E')\,dE'}{E^+ - E'} \right|^2 [1 + O(N')] \tag{III.42}$$

$$\sigma_a(E) = \sigma_d(E)[1 + O(N')] \;. \tag{III.43}$$

Finally the quantum yield (III.28) for resonance elastic scattering is

$$Y_r^0(E) = \frac{|\int E'\sigma_a(E')\,dE'/(E^+ - E')|^2}{(2\pi)^3(\hbar c)^2 \sigma_a(E)} \;. \tag{III.44}$$

From these results we conclude that

(a) The photon scattering cross section (III.42) and the corresponding quantum yield (III.44) are determined by the (complex) Hilbert transform of the line shape function. This conclusion was reached before by Nitzan and Jortner[3] on the basis of a somewhat complicated

low order perturbation treatment. Our results were recast in a somewhat more transparent form.

(b) The energy dependence of the scattering cross section and of the quantum yield can be explicitly obtained in the form

$$\sigma_r(E) = \frac{2}{\pi \lambda^2} \left[\left| PP \int \frac{E' \sigma_a(E')}{(E-E')} dE' \right|^2 \cdot E^{-2} + \pi^2 \left| \sigma_a(E) \right|^2 \right] \quad \text{(III.45)}$$

$$Y_r(E) = \frac{2}{\pi \lambda^2} \left[\frac{E^{-2}}{\sigma_a(E)} \left| PP \int \frac{E' \sigma_a(E') dE'}{(E-E')} \right|^2 + \pi^2 \sigma_a(E) \right] \quad . \quad \text{(III.46)}$$

Thus from the known experimental bell shape function of the photodissociation spectrum one can evaluate the scattering cross section. As on order of magnitude estimates we can take

$$\sigma_r(E) \sim \left(\frac{\sigma_a(E)}{\lambda} \right)^2 \sim \left(\frac{10^{-17}}{10^{-5}} \right)^2 \sim 10^{-24} \text{ cm}^2$$

and

$$Y_r(E) \sim \sigma_a(E)/\lambda^2 \sim 10^{-7} \quad .$$

(c) Thus resonance fluorescence from a dissociative continuum is amenable to experimental detection.

(d) The numerical relation (III.37) provides us with the ideological justification for neglecting high order radiative interaction in the calculation of the cross section $\sigma_a(E)$, $\sigma_r(E)$, and $\sigma_d(E)$. Thus the overwhelming contribution to the photon scattering processes involves the single path $|g_e o, \text{ke}\rangle \rightarrow |l_e, \text{vac}\rangle \rightarrow |g_e o, \text{k}'\text{e}'\rangle$ and higher order photon multiple scattering processes can be disregarded. This result is of considerable practical value for the theoretical treatment of inelastic, Raman type scattering from a dissociative continuum, where a number of radiative continua $|g_e v, \text{ke}\rangle$ should be considered. On the basis of the complete solution of the elastic scattering problem, the Raman scattering problem can be now easily handled by treating radiative interactions to low order.

IV. RAMAN SCATTERING FROM A DISSOCIATIVE CONTINUUM

We shall now extend the treatment of photon scattering from a dissociative molecular continuum to include the role of the vibrational levels of the ground state and consider inelastic Raman type photon scattering to final channels $|g_e v, \text{ke}\rangle$ (all v). The physical situation is that portrayed in Fig. 1 where the eigenstates of H_0 are now $|g_e v, \text{ke}\rangle$ ($v = 0, 1, 2, \ldots$) and $|l_e, \text{vac}\rangle$. To avoid unnecessary complications we assume that the molecular system is in the distant past in the $|g_e o\rangle$ state. This restriction will be removed later. We then consider the photon scattering processes

$$| g_e o, \text{ke}\rangle \rightarrow | g_e v, \text{k}'\text{e}'\rangle \quad \text{(IV.1)}$$

to all the vibrational levels of the ground state. The perturbation is again $V = H_{\text{int}}$.

In view of the results obtained in Sec. III we can safely neglect the role of high order radiative interactions. We shall consider only single scattering events

$|g_e o, \text{ke}\rangle \rightarrow |l_e, \text{vac}\rangle \rightarrow |g_e v, \text{k}'\text{e}'\rangle$, while multiple photon scattering processes will be disregarded. The T matrix can be expanded in a perturbation series

$$T = V + VG^0 V + VG^0 VG^0 V + VG^0 VG^0 VG^0 V + \cdots , \quad \text{(IV.2)}$$

where only even terms in V contribute to photon scattering. The second term on the rhs of Eq. (IV.2) involves a single scattering path while higher terms in V represent multiple scattering. In order to calculate the relevant cross sections up to the order $1 + O(N')$ [the magnitude of N' is estimated in (III.37)], it is sufficient to take

$$T \simeq V + VG^0 V \quad . \quad \text{(IV.2a)}$$

The calculation of the matrix elements of (IV.2a) is straightforward, resulting in

$$\langle g_e v, \text{k}'\text{e}' | T | g_e 0, \text{ke} \rangle$$
$$= \sum_l \frac{\langle g_e v, \text{k}'\text{e}' | V | l \rangle \langle l | V | g_e o, \text{ke} \rangle}{E^+ - E_l} \quad \text{(IV.3)}$$

$$\langle l_e, \text{vac} | T | g_e o, \text{ke} \rangle = \langle l_e, \text{vac} | V | g_e o, \text{ke} \rangle \quad . \quad \text{(IV.4)}$$

Making use of Eqs. (II.15) and (II.16) for the radiative coupling matrix elements we obtain

$$\langle g_e v, \text{k}'\text{e}' | T | g_e o, \text{ke} \rangle = \beta_e \beta_{e'}^* h(k) h(k')$$
$$\times \sum_l \frac{f_v^*(E_l) f_0(E_l)}{E^+ - E_l} \quad \text{(IV.5)}$$

$$\langle l, \text{vac} | T | g o, \text{ke} \rangle = \beta h(k) f_0(E_l) \quad . \quad \text{(IV.6)}$$

The cross sections (II.2a)–(II.4a) take the form

$$\sigma_a(E) = \frac{\pi \lambda^2}{2} | \beta |^2 | h(E/\hbar c) |^2 | f_0(E_l) |^2 \rho_l(E) \rho_r(E) , \quad \text{(IV.7)}$$

$$\sigma_d(E) = \frac{\pi \lambda^2}{2} | \beta |^2 | h(E/\hbar c) |^2 | f_0(E_l) |^2 \rho_l(E) \rho_r(E) , \quad \text{(IV.8)}$$

$$\sigma_r^v(E) = \frac{\pi \lambda^2}{2} | \beta |^4 | h(E/\hbar c) |^4 \rho_r^2(E)$$
$$\times \left| \int \frac{f_v^*(E_l) f_0(E_l) \rho_l(E_l) dE_l}{E^+ - E_l} \right|^2$$
$$= \frac{\lambda^4}{8\pi} | \beta |^4 \rho_r^2(E) \left[\left| PP \int \frac{f_0(E_l) f_v^*(E_l) \rho_l dE_l}{E^+ - E_l} \right|^2 \right.$$
$$\left. + \left| \pi f_0(E) f_v^*(E) \rho_l(E) \right|^2 \right] \quad . \quad \text{(IV.9)}$$

These results are, of course, valid to order $(1 + O(N'))$. It is an easy matter to extend the treatment (see Appendix C) to include the radiative corrections up to the order $O(N'^2)$. This result is of minor importance for the interaction between a radiative and a purely dissociative continuum considered herein. However, when we consider photon scattering from a discrete state plus a dissociative continuum (see Sec. V) the correction $O(N')$ is crucial near the interference dip.

Returning to Eqs. (IV.7)–(IV.9) we expect that conservation law (II.8) is obeyed up to

$$\sigma_a(E) = [\sigma_d(E) + \sum_v \sigma_r^v(E)](1 + O(N')) \quad . \quad \text{(IV.10)}$$

Equations (IV.7) and (IV.8) are identical up to $O(N')$ to those obtained for the elastic scattering case [Eqs. (III.25)], as expected. Our new result involves the Raman scattering cross section (IV.9) to different vi-

brational levels $|g_e v\rangle$ of the ground electronic state. From Eq. (II. 20) it is evident that $f_v(E_l)$ is equal to the vibrational overlap Franck–Condon nuclear integral $\langle \chi_v | \chi_l(E)\rangle$. Thus the Raman scattering cross sections are determined by the (complex) Hilbert transforms of the product of the Franck–Condon integrals $\langle \chi_0 | \chi_l(E_l)\rangle$ $\langle \chi_l(E_l) | \chi_v \rangle$. Finally we can relate these scattering cross sections to the absorption cross sections (from $|g_e o\rangle$),

$$\sigma_r^v = \frac{1}{(2\pi)^3 (\hbar c)^2} \left| \int \frac{E' \sigma_a(E')[f_v(E')/f_0(E')]^* dE'}{E^+ - E'} \right|^2$$

$$= (2/\pi\lambda^2) \left[\left| pp \int \frac{E' \sigma_a(E')[f_v(E')/f_0(E')]^* dE'}{E - E'} \right|^2 E^{-2} \right.$$

$$\left. + \pi^2 \left| \sigma_a(E) f_v(E)/f_0(E) \right|^2 \right]. \qquad \text{(IV.11)}$$

The emission quantum yields are just given by

$$Y^v(E) = (2/\pi\lambda^2) \left\{ [1/E^2 \sigma_a(E)] \right.$$

$$\times pp \left| \int \frac{E' \sigma_a(E')[f_v(E')/f_0(E')]^* dE'}{E - E'} \right|^2$$

$$\left. + \pi^2 \sigma_a(E) \left| f_v(E)/f_0(E) \right|^2 \right\}. \qquad \text{(IV.12)}$$

The functional dependence of the Raman scattering from a dissociative continuum was recently derived by Berjot, Jacon, and Bernard[10] and by Williams and Rousseau[11] within low order in the radiative interactions. We believe that the present derivation, which rests on the results of the complete analysis of the simple model system of Sec. III, is more transparent. In order to apply these results to a real life situation we have to consider again the hidden approximations involved in the present treatment.

(1) The two electronic level system $|g_e\rangle$ and $|l_e\rangle$ has to be extended to include all excited states. It is a simple matter to include the off resonance contributions of other molecular levels in the calculation of the matrix elements of T [Eq. (IV.2a)]. This off-resonance term will involve only a small correction to the scattering cross section, and the major contribution originates from the continuum states.

(2) The situation is more complex when resonance photon scattering occurs from two overlapping dissociative continua which correspond to different electronic configurations. To quote a specific and relevant example, in the case of I_2 the $^3\pi_u$ continuum (which corresponds to the continuum levels of an attractive potential curve) overlaps the $^1\pi_u$ dissociative continuum (which originates from a purely repulsive potential curve.[12,13] We assert that even in the simple case when non adiabatic coupling between the two cintinua is negligible, the scattering cross section does not involve an additive contribution from the two continua, but rather involves "interference type" contributions from the two continua. Denoting the parameters of the two continua by the indices (a) and (b), respectively, the scattering cross section is

$$\sigma_r^v(E) = \frac{\pi\lambda^2}{2} \left| h(E/\hbar c) \right|^4 \rho_r^2(E)$$

$$\times \left| |\beta_a|^2 \int \frac{f_0^{(a)}(E_l) f_v^{*(a)}(E_l) \rho_l^{(a)}(E_l) dE_l}{E^+ - E_l} \right.$$

$$\left. + |\beta_b|^2 \int \frac{f_0^{(b)}(E_l) f_v^{*(b)}(E_l) \rho_l^{(b)}(E_l) dE_l}{E^+ - E_l} \right|^2. \qquad \text{(IV.13)}$$

Separation of the integrals in Eq. (IV.11) into their real and imaginary parts and evaluation of their square modulus will result in mixed contributions from the two continua. This straightforward extension of the theory will have to be applied for a quantitative study of specific systems.

(3) As in Sec. III we have disregarded two-photon states such as $|l_e, ke, k'e'\rangle$ single scattering contribution via two-photon states of the form $|g_e o, ke\rangle$ $\rightarrow |l_e, kek'e'\rangle \rightarrow |g_e v, k'e'\rangle$ will result in an additional contribution to T [Eq. (IV.2a)]. However, these are high order contributions which are expected to be small. The role of higher (three-photon etc.) states is also negligibly small.

(4) We have assumed that the thermal population of the higher vibrational components of the ground state is small. The extension of the formalism to handle a real life situation is trivial, as one has just to perform a Boltzmann type average (of the initial states $|g_e v\rangle$) over the cross sections $\sigma_r^v(E)$.

We thus conclude that Eqs. (IV.10) and (IV.11) provide a satisfactory theory of Raman scattering from a single dissociative continuum. As the scattering cross sections are determined by the (complex) Hilbert transform of the product of the vibrational overlap factors for the bound-continuum transition, there are no selection rules for the final vibrational state reached by resonance Raman scattering from a continuum. To provide a visual demonstration of this result we portray in Figs. 2 and 3 the results of a simple numerical calculation of photon scattering from a "diatomic molecule" characterized by a harmonic ground state and a linear repulsive excited state, when the Franck–Condon overlap factors were estimated by the reflection method. The details of the calculation are outlined in Appendix D. The vibrational distribution of the final $|g_e v\rangle$ states exhibits a marked dependence on the reduced energy parameter ϵ (see Appendix D), where ϵ corresponds to the maximum of the (Gaussian) absorption line shape from $v = 0$, while the corresponding absorption half-linewidth is $\epsilon_{1/2} = 0.83$. As is evident from Figs. 2 and 3 the two individual contributions to σ_r [Eqs. (IV.9)] fluctuate wildly with changing v, while their sum is a smooth function of the final vibrational state. From Fig. 3 it is apparent that for $\epsilon \lesssim 2\epsilon_{1/2}$ a long vibrational progression is expected to be revealed, while for $\epsilon\rangle 2\epsilon_{1/2}$ the intensity of the higher overtones is diminished. Thus, in many cases of interest one expects a long vibrational progression in the Raman spectrum. The appearance of a large number of overtones in the resonance Raman spectrum from the dissociative continuum of I_2 was indeed experimentally observed.[14]

V. INTERFERENCE OF A DISCRETE STATE WITH AN OPTICALLY ACTIVE DISSOCIATIVE CONTINUUM

We shall now consider the cross sections for absorption, resonance fluorescence and photodissociation for a system characterized by a discrete excited state in-
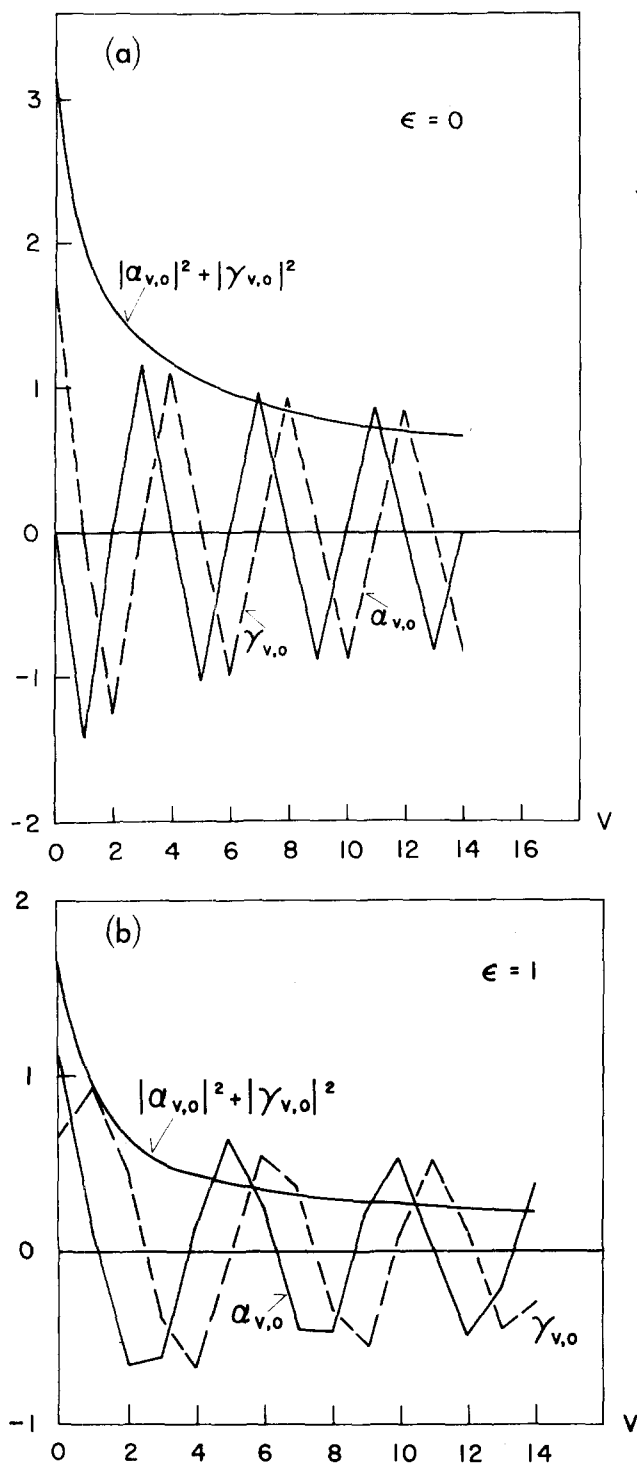
of molecular predissociation and this formalism is also directly applicable for autoionization and for some cases of electronic relaxation to an intramolecular quasicontinuum.[3] The last case is of lesser experimental interest, as the quasicontinuum does not carry appreciable oscillator strength from the ground state. The absorption cross sections were originally handled in the classical work of Fano[2] who has demonstrated the role of interference between resonance and potential scattering which results in a dip of $\sigma_a(E)$. Fano has incorporated radiative interactions to low order, so that $\sigma_a(E_d) = 0$ at the dip energy E_d. Nitzan and Jortner have treated the cross sections for resonance fluorescence in the Fano problem, again within low order perutrbation theory for radiative interactions.[3] As realized by these authors such an approach is invalid for energies close to the interference dip, where the approximate quantum yield will exhibit an unphysical divergence. We shall now present a general treatment of this problem including radiative interactions between one photon and zero photon states to infinite order. This problem is of intrinsic theoretical interest, as we shall be able to ellucidate the nature of interference in the Fano model system. From the experimental point of view the present results are relevant to establish the nature of the additional information which will result from resonance photon scattering experiments from some predissociating molecular systems.

FIG. 2. Raman scattering cross sections from a dissociative continuum characterized by a Gaussian absorption line shape. Plots of the relative populations of the final $|g_e v\rangle$ molecular states which are given by

$$|A_{v,0}(\epsilon)|^2 = |\alpha_{v,0}(\epsilon)|^2 + |\gamma_{v,0}(\epsilon)|^2$$

and expressed as a function of the reduced energy parameter ϵ. The details of the calculation are given in Appendix D. (a) $\epsilon = 0$, (b) $\epsilon = 1$.

teracting with a molecular dissociative continuum via nonadiabatic intramolecular coupling. The molecular continuum carries oscillator strength from the ground state. This physical situation prevails for some cases
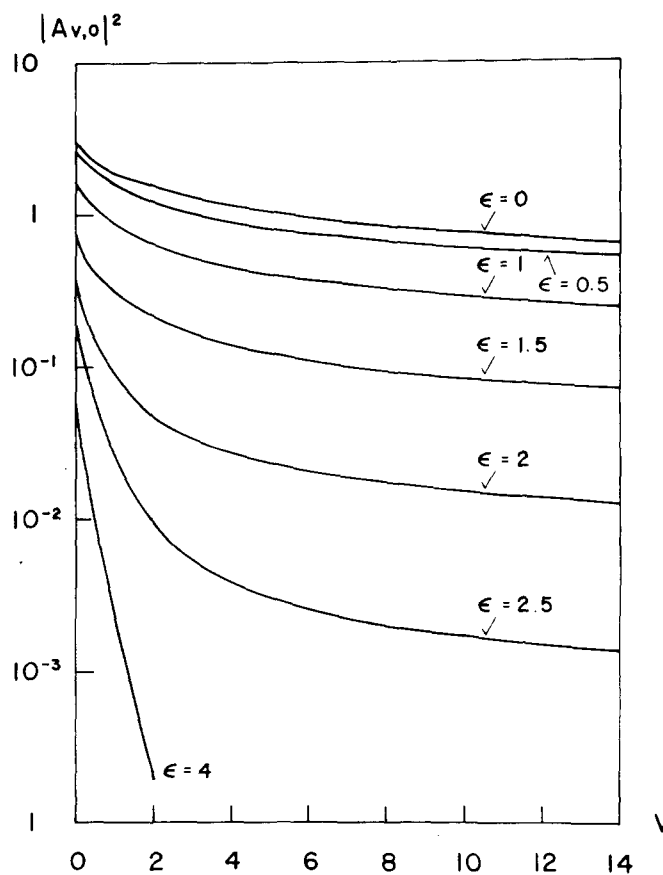

FIG. 3. Plots of the Raman intensities for scattering from a dissociative continuum (see Appendix D). Plots are given for various values of the reduced energy parameter ϵ.

The physical system considered herein is portrayed in Fig. 1(c). The eigenstates of the zero order Hamiltonian $H_0 = H_{BO} + H_{rad}$ [Eq. (II.1a)] are $|g\rangle \equiv |g_e0, \text{ke}\rangle$; $|s\rangle \equiv |s_e, \text{vac}\rangle$ and $|l\rangle \equiv |l_e, \text{vac}\rangle$. The zero order energies are $E_g = E_{ge} + \hbar kc$, $E_s = E_{se}$ and $E_l = E_{l_e}$. The perturbation is $V = H_{int} + H_V$. The radiative coupling matrix elements can be rewritten utilizing Eqs. (II.15) and (II.19) in the form

$$V_{gl} = \langle g_e0, \text{ke}|H_{int}|l_e, \text{vac}\rangle = \beta^*_{e(k)}h(k)f_0^*(E_l) \qquad (V.1)$$

and

$$V_{gs} = \langle g_e0, \text{ke}|H_{int}|s_e, \text{vac}\rangle = \alpha_{e(k)}h(k) \equiv \overline{\alpha}h(k)\cos\theta, \qquad (V.2)$$

where

$$\alpha_{e(k)} = (e\hbar/m)(2\pi/Q\hbar c)^{1/2}\langle g_e0|\mathbf{p}\cdot\mathbf{e}|s_e\rangle \equiv \overline{\alpha}\cos\theta \qquad (V.2a)$$

θ is the angle between $\mathbf{e}$ and the transition moment. The nonadiabatic coupling terms

$$V_{ls} \equiv \langle l_e|H_v|s_e\rangle \qquad (V.3)$$

vary only with the states $|l_e\rangle$.

The energy level system for this problem [Fig. 1(c)] is analogous to that previously considered for sequential decay involving a pair of coupled continua, which was solved invoking simplifying assumptions of constant coupling between unbounded continua.[4] In view of the special form of the matrix elements (V.1)–(V.3) where the separate energetic contribution of the two continua can be factorized, we are able to provide a general solution to the problem. We shall now demonstrate that explicit general expressions can be obtained for the matrix elements of the T matrix which determine the cross sections.

Utilizing an alternative form of Eq. (II.5):

$$T = V + VG_0T . \qquad (V.4)$$

The matrix elements of the operator combining the eigenstates of H_0 are

$$T_{g'g} = \langle g_e'0, \text{k'e'}|T|g_e0, \text{ke}\rangle = \frac{V_{g's}}{E - E_s}T_{sg}$$
$$+ \sum_l V_{g'l}(E^+ - E_l)^{-1}T_{lg} , \qquad (V.5)$$

$$T_{lg} \equiv \langle l_e, \text{vac}|T|g_e0, \text{ke}\rangle = V_{lg} + V_{ls}(E - E_s)^{-1}T_{sg}$$
$$+ \sum_{g'} V_{lg'}(E^+ - E_{g'})^{-1}T_{g'g} , \qquad (V.6)$$

$$T_{sg} \equiv \langle s_e, \text{vac}|T|g_e0, \text{ke}\rangle = V_{sg} + \sum_l V_{sl}(E^+ - E_l)^{-1}T_{lg}$$
$$+ \sum_{g'} V_{sg'}(E^+ - E_{g'})^{-1}T_{g'g} . \qquad (V.7)$$

The relevant matrix elements which determine the cross sections (II.2)–(II.4) can be recast utilizing Eqs. (V.2)–(V.4) together with the definition $\beta_{e(k)} \equiv \beta_e = \overline{\beta}\cos\theta$,

$$T_{g'g} = [V_{g's}/(E - E_s)]T_{sg} + \beta^*_{e}h(E/\hbar c)a^l \qquad (V.8)$$

$$T_{lg} = V_{lg} + [V_{ls}/(E - E_s)]T_{sg} + \overline{\beta}\,f_0(E_l)a^g , \qquad (V.9)$$

where we have defined

$$a^l \equiv a^l(E) = \sum_l [f_0^*(E_l)/(E^+ - E_l)]T_{lg} \qquad (V.10)$$

and

$$a^g \equiv a^g(E) = \sum_{g'} \frac{h(E_{g'}'/\hbar c)}{E^+ - E_{g'}}T_{g'g}\cos\theta . \qquad (V.11)$$

We have now to find algebraic equations for a^g, a^l, and T_{sg}. To express these equations in a transparent form we shall utilize the definitions of the (complex) level shifts A^g [Eq. (III.9)], A^l [Eq. (III.13)] and further define the (complex) level shift functions originating from intramolecular coupling

$$A^s(E) = \sum_l [|V_{sl}|^2/(E^+ - E_l)] \qquad (V.12)$$

and the "mixed" level shift function

$$A^{ls}(E) = \sum_l [V_{ls}f_0^*(E_l)/(E^+ - E_l)] \qquad (V.13)$$

and

$$\tilde{A}^{ls}(E) = \sum_l [V_{ls}^*f_0(E_l)/(E^+ - E_l)] \qquad (V.13a)$$

Multiplication of Eq. (V.8) by $h(k')/(E^+ - E_{g'})\cos\theta$ followed by summation over the $|g'\rangle$ photon continuum results in

$$a^g - \tfrac{2}{3}\overline{\beta}^*A^ga^l - [2\overline{\alpha}/3(E - E_s)]A^gT_{sg} = 0; \qquad (V.14)$$

In a similar manner multiplying Eq. (V.9) by $f_0^*(E_l)/(E^+ - E_l)$ and summing over the $\{|l\rangle\}$ states yields

$$\overline{\beta}A^la^g - a^l + [A^{ls}/(E - E_s)]T_{sg} = -\beta_e h(k)A^l . \qquad (V.15)$$

Then from Eqs. (V.6) and (V.7) we obtain

$$(\overline{\beta}\tilde{A}^{ls} + \overline{\alpha}^*)a^g + T_{sg}[A^s(E - E_s)^{-1} - 1]$$
$$= -\beta_e h(k)\tilde{A}^{ls} - V_{sg} \qquad (V.16)$$

Equations (V.14)–(V.16) can now be solved for the weighted sums $a^l(E)$ and $a^g(E)$ and for T_{sg}, resulting in

$$T_{sg} = \frac{[V_{sg} + \beta_e\tilde{A}^{ls}h(k)](E - E_s)}{E - E_s - A^s - A^g} \qquad (V.17a)$$

$$A^g = (\tfrac{2}{3})A^g \frac{(\overline{\alpha} + \overline{\beta}^*A^{ls})(\overline{\alpha}^* + \overline{\beta}\tilde{A}^{ls})}{1 - |\beta|^2A^lA^g} \qquad (V.17b)$$

$$a^g = \frac{|\beta|^2A^lh(k)\cos\theta + (\tfrac{2}{3})(\overline{\alpha} + \overline{\beta}^*A^{ls})T_{sg}(E - E_s)^{-1}}{1 - |\beta|^2A^lA^g}A^g \qquad (V17c)$$

$$a^l = \frac{\beta_e h(k)A^l + [A^{ls} + (\tfrac{2}{3})\overline{\alpha}\overline{\beta}A^gA^l]T_{sg}(E - E_s)^{-1}}{1 - |\beta|^2A^lA^g} \qquad (V.17d)$$

Finally, the matrix elements (V.8) and (V.9) take the form

$$T_{g'g} = \frac{\beta_e\beta_e^*h(k)h(k')A^l(E - E_s - A^s) + [V_{g's} + \beta_e h(k')A^{ls}][V_{sg} + \beta_e h(k)\tilde{A}^{ls}]}{(1 - |\beta|^2A^lA^g)(E - E_s - A^s - A^g)} \qquad (V.18)$$

$$T_{lg} = \frac{V_{ls}(V_{sg} + \beta_e h(k)\tilde{A}^{ls}) + (E - E_s - A^s)V_{lg}}{(1 - |\beta|^2A^lA^g)(E - E_s - A^s - A^g)} \qquad (V.19)$$

The absorption cross section can be expressed from (II.4) and (V.18) in the general form:

$$\sigma_a(E) = -(2Q/\hbar c)\mathrm{Im}\, T_{gg} \ . \tag{II4.a}$$

To recast these general results in a more familiar form we now separate the complex level shifts (III.9), (III.13), (V.12), and (V.13) into their real and imaginary parts

$$A^{(j)} = \mathrm{Re}(A^j) - i\mathrm{Im}(A^j)\ ; \quad j \equiv g, l, s\ , \ (ls) \tag{V.20}$$

and define the Fano reduced energy ϵ and line profile index q in the conventional form

$$\epsilon = [E - E_s - \mathrm{Re}(A^s)]/\mathrm{Im}(A^s) \tag{V.21a}$$

$$q = [\alpha + \beta \mathrm{Re}(A^{ls})]/\beta \mathrm{Im}(A^{ls}) \ . \tag{V.21b}$$

We further assume that q is real and that the interfering bound–bound and bound–continuum transitions are characterized by parallel dipole moments. The matrix elements $T_{g'g}$ [Eq. (V.18)] which determine the absorption and the photon scattering cross sections can be rewritten in terms of a linear superposition of resonance continuum and bound state scattering.

$$T_{g'g} = T^0_{g'g}\left[1 + I_m A^l (A^l)^{-1}(9-i)^2(\epsilon+i)^{-1}\right]\mathfrak{F} \tag{V.22}$$

where

$$T^0_{g'g} = \frac{\beta_e \beta_{e'}^* h(E'/\hbar c)h(E/\hbar c)A^l(E)}{1 - |\beta|^2 A^l(E)A^g(E)} \ . \tag{V.23}$$

represents the T matrix for scattering from an optically active continuum (in the absence of the $|s_e\rangle$ state) which is of course identical with Eq. (III.17); while

$$\mathfrak{F} = \left[| -|\beta|^2 A^g \mathrm{Im}A^l(|-|\beta|^2 A^g A^l)^{-1}(9-i)^2(\epsilon+i)^{-1}\right]^{-1} \tag{V.24}$$

constitutes of the radiative correction to the bound state scattering term. We note in passing that when radiative interactions are incorporated only to first order, Eq. (V.22) will result in the well known Fano equations[2] for $\sigma_a(E)$ and for the expression derived by Nitzan and Jortner[3] for $\sigma_r(E)$.

Equations (V.22)–(V.24) together with the basic definitions (II.2)–(II.4) result in general expressions for the absorption and for the resonance fluorescence cross sections including radiative interactions and incorporating the energy dependence of the absorption cross section to the zero order continuum states. The resulting expressions obtained by straightforward algebraic manipulations are cumbersome and not very informative. They will become useful for numerical applications for specific systems when detailed experimental results for a predissociating state coupled to an optically active continuum will become available. We shall thus consider a somewhat simplified model system neglecting the real parts of the radiative level shift A^g and the real part of the continuum level shift A^l. From the analysis presented in Sec. III we can conclude that the radiative Lamb shift can always be neglected. Neglecting the molecular continuum level shift Re A^l eliminates some of the fine details of the energy dependence of the cross

sections. As we are interested in the behavior of the cross sections in a narrow energy region this approximation is reasonable. Setting Re $A^g = 0$ and Re $A^l = 0$ in Eqs. (V.18) and (V.19) and utilizing Eqs. (II.2)–(II.4) we obtain after simple algebraic manipulations

$$\sigma_a(E) = \frac{\lambda^2}{2\pi}\ \frac{N(E)}{1+N(E)}\ \frac{q^2\Delta + (\epsilon+r)(\epsilon+2q)}{(\epsilon+r)^2 + \Delta^2}\ , \tag{V.25}$$

$$\sigma_r(E) = \frac{\lambda^2}{2\pi}\ \frac{N^2(E)}{(1+N(E))^2}\left(\frac{q^4 + (\epsilon+2q)^2}{(\epsilon+r)^2+\Delta^2}\right), \tag{V.26}$$

$$\sigma_d(E) = \frac{\lambda^2}{2\pi}\ \frac{N(E)}{(1+N(E))^2}\left(\frac{(q+\epsilon)^2}{(\epsilon+r)^2+\Delta^2}\right), \tag{V.27}$$

where $N(E)$ is the (first order) transition density to the continuum given by (III.31), and where we have defined two auxiliary parameters

$$\gamma = 2qN/(1+N) \tag{V.28a}$$

and

$$\Delta = (Nq^2+1)/(1+N) \ . \tag{V.28b}$$

Equations (V.25)–(V.27) together with the definitions (V.21a), (V.21b), and (V.28) constitute our final results for the Fano problem. In Figs. 4 and 5 we present some typical forms for the energy dependence of the cross sections and the fluorescence quantum yield. From these results it is apparent that:

(1) When the level shifts Re(A^g) and Re(A^l) are neglected, the relevant cross sections are expressed in terms of a product of the corresponding cross section for a dissociative (or ionization) continuum [Eqs. (III.30)] and a correction function which contains the interference effects.

(2) The cross sections obey the conservation law $\sigma_a(E) = \sigma_r(E) + \sigma_d(E)$ for all E, which provides just a convenient consistency check.

(3) To study the features of the absorption line shape we define

$$\epsilon' = (\epsilon+r)/\Delta$$

$$Q = q/\Delta(1+N) = q/(Nq^2+1) \ . \tag{V.29}$$

Now Eq. (V.25) assumes the form

$$\sigma_a(\epsilon') = \frac{\lambda^2}{2\pi}\ \frac{N(\epsilon')}{1+N(\epsilon')}\left[\frac{(\epsilon'+Q)^2+\chi}{1+\epsilon'^2}\right], \tag{V.30}$$

where

$$\chi = \frac{q^2}{\Delta} - \frac{q^2}{\Delta^2(1+N)^2} = \frac{N^2q^2 + N(1+q^2)}{(1+N)(Nq^2+1)} > 0 \ ;$$

Thus the absorption cross section does not vanish over the entire energy range, for any value of q and $N \neq 0$.

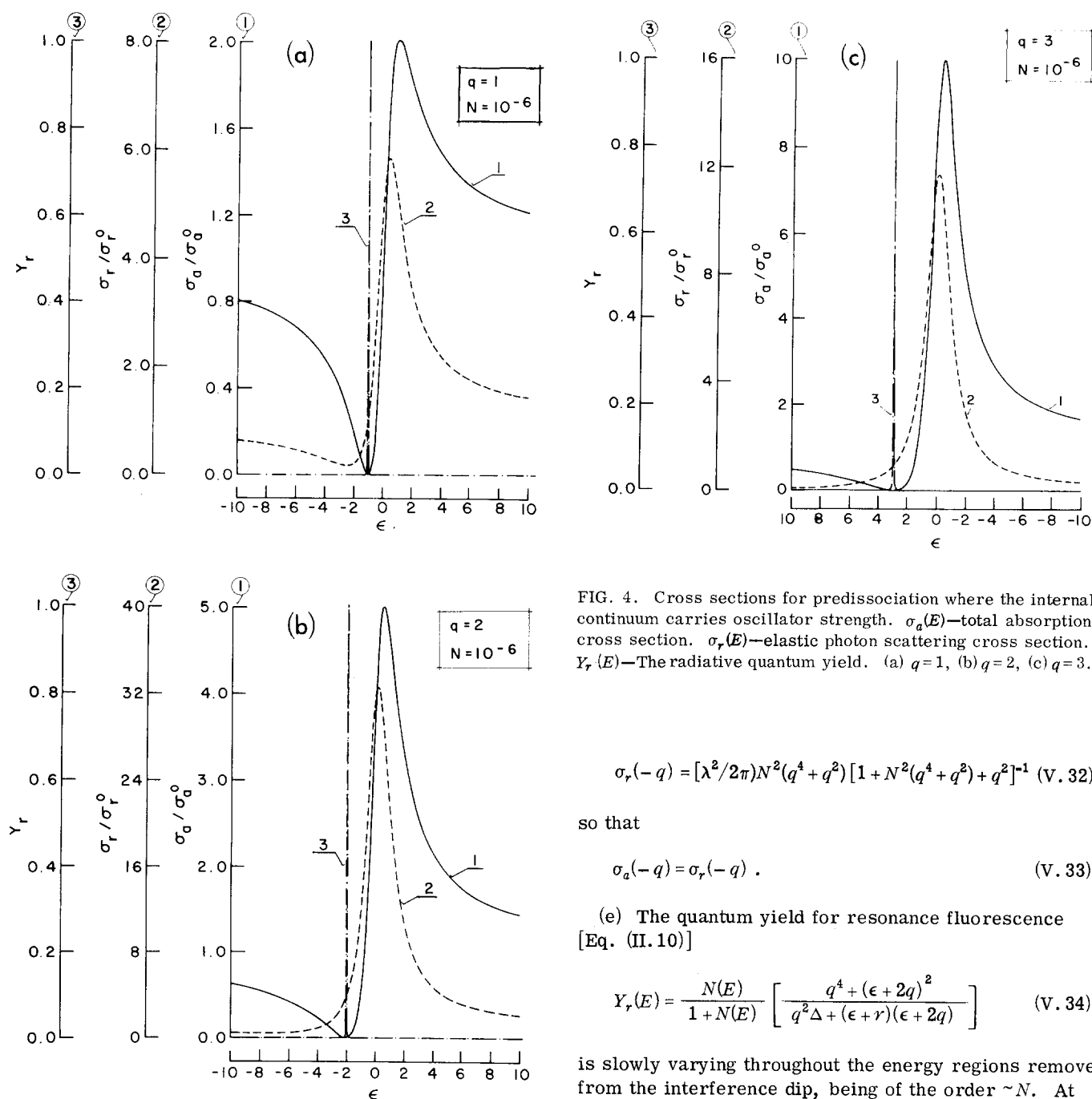To study the behavior of σ_a near the interference dip we recast (V.25) in an alternative form

FIG. 4. Cross sections for predissociation where the internal continuum carries oscillator strength. $\sigma_a(E)$—total absorption cross section. $\sigma_r(E)$—elastic photon scattering cross section. $Y_r(E)$—The radiative quantum yield. (a) $q=1$, (b) $q=2$, (c) $q=3$.

$$\sigma_r(-q) = [\lambda^2/2\pi)N^2(q^4+q^2)[1+N^2(q^4+q^2)+q^2]^{-1} \quad (V.32)$$

so that

$$\sigma_a(-q) = \sigma_r(-q) . \quad (V.33)$$

(e) The quantum yield for resonance fluorescence [Eq. (II.10)]

$$Y_r(E) = \frac{N(E)}{1+N(E)} \left[\frac{q^4+(\epsilon+2q)^2}{q^2\Delta+(\epsilon+r)(\epsilon+2q)} \right] \quad (V.34)$$

is slowly varying throughout the energy regions removed from the interference dip, being of the order $\sim N$. At $\epsilon = -q, Y(-q) = 1$ as is evident from Eq. (V.33). We thus expect the occurrence of a sharp maximum in the quantum yield rising from $Y_r = N$ to $Y_r = 1$ in the vicinity of the dip. The half widths of $Y_r(E)$ curve near $\epsilon = -q$ is $2|q|\sqrt{1+q^2} \sqrt{N}$. This is evident from Fig. 5. A similar maximum in the region of destructive interference was obtained from the numerical calculations of Nitzan and Jortner for the case of two overlapping resonances.[3] From the physical point of view this effect originates from the fact that at the interference dip the cross sections and quantum yield for dissociation vanish identically [see section (f)]. This interesting effect provides a new experimental criterion for the identification of interference effects. With the advent of tunable high energy lasers such effects may become amenable to experimental observation. This will be extremely difficult to get in view of the low absorption cross section in the vicinity of the interference dip.

$$\sigma_a(E) = \frac{\lambda^2}{2\pi} \left(\frac{N}{1+N} \right) \left[\frac{(q+\epsilon)^2 + [N/(1+N)](q^4+3q^2+2q\epsilon)}{(\epsilon+r)^2+\Delta^2} \right]$$
$$V.25a)$$

which at $q = -\epsilon$ is just

$$\sigma_a(-q) = [\lambda^2/2\pi)N^2(q^4+q^2)[1+N^2(q^4+q^2)+q^2]^{-1} \quad (V.31)$$

We note that $\sigma_a(-q) \sim \lambda^2 N^2$ being reduced by a factor of $N \sim 10^{-6}$ at the interference dip.[15]

(d) The photon scattering cross section is of the order of $\sim \lambda^2 N^2$ throughout the whole energy region (see Figs. 4 and 5). At the interference dip Eq. (V.26) yields
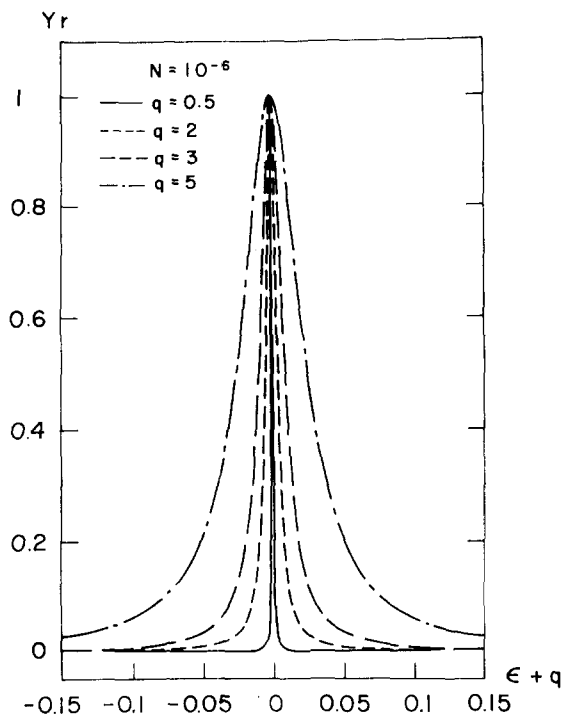
FIG. 5. Dependence of $\gamma_r(\epsilon)$ for predissociation where the internal continuum carries oscillator strengths near the interference dip. The different curves refer to various q values (0.5, 2, 3, 5).

(f) The photodissociation cross section σ_d (V. 27) vanishes at $\epsilon = -q$ (up to the order $O(N'^2)$).[16] This is the real physical significance of interference between resonance and potential scattering.

VI. CONCLUDING REMARKS

The present theoretical study of absorption, resonance fluorescence, and photodissociation cross sections provide a general theoretical framework for the treatment of coupled radiative and intramolecular continua. The techniques developed herein to handle this interesting problem rest on factorization of the inter-continuum coupling into a product of separate contributions from the two continua. Subsequently, by the utilization of the Dyson equation for the Green's function or the mathematically equivalent identity for the T matrix we were able to provide a solution for the decay (or scattering) problem involving two continua. Such techniques are applicable at present for radiative interactions only, where the factorization procedure (II. 19) is valid. For intramolecular non adiabatic coupling[1] such a separation is inapplicable and at present the problem of coupled intramolecular dissociative continua (originating from different vibrational states of fragments from a polyatomic molecule) were handled by approximate model system.[4b] We have limited ourselves in the present paper to the study of a system involving a single dissociation continuum. At a lower level of sophistication, by invoking some simplifying assumptions such as constant coupling between intramolecular dissociative continua the photodissociation and predissociation of a polyatomic molecule can be handled by

similar techniques. In that case, additional interesting information involves the vibrational distribution of the fragments.

The present results are relevant for elucidation of the nature of resonance fluorescence and Raman scattering from a dissociative continuum and from predissociating states of small molecules, where the molecular continuum is optically active. The same techniques are directly applicable to the theoretical study of inverse radiative processes, such as radiative recombination and inverse dissociation. We hope that the present approach based on photon scattering from molecules will be of considerable general applicability for the elucidation of a variety of interesting photophysical processes.

ACKNOWLEDGMENT

APPENDIX A: EVALUATION OF THE MATRIX ELEMENTS OF THE LEVEL SHIFT OPERATOR

We consider the matrix element (III. 8)

$$R_{l'l} = \langle l' | R | l \rangle = \sum_g \frac{\langle l' | V | g \rangle \langle g | V | l \rangle}{E - E_g} . \tag{A1}$$

Utilizing Eqs. (II. 15)–(II. 21) we have

$$R_{l'l} = f_0(E_{l'}) f_0^*(E_l) \, | \beta' |^2 \int d\mathbf{k} \, | h(k) |^2$$

$$\times \frac{Q}{(2\pi)^3} \sum_e \frac{| \langle \varphi_l | \mathbf{p} \cdot \mathbf{e} | \varphi_g \rangle |^2}{E^+ - \hbar k c} . \tag{A2}$$

We shall now utilize the identity

$$\sum_{e(k)} | \mathbf{p} \cdot \mathbf{e}(k) |^2 = | \mathbf{p} |^2 - (\mathbf{p} \cdot \hat{\mathbf{k}})^2 , \tag{A3}$$

where $\hat{\mathbf{k}}$ is a unit vector in the k direction. Equation (A2) assumes the form

$$R_{l'l} = f_0(E_{l'}) f_0^*(E_l) \, | \beta' |^2 \frac{Q}{(2\pi)^3} \int | h(k) |^2$$

$$\times \frac{k^2 dk \sin\theta d\theta d\varphi [\langle \varphi_l | \mathbf{p} | \varphi_g \rangle|^2 - |\langle \varphi_l | \mathbf{p} \cdot \hat{\mathbf{k}} | \varphi_g \rangle|^2]}{E^+ - \hbar k c}$$

$$= f_0(E_{l'}) f_0^*(E_l) \, | \beta' |^2 | \langle \varphi_l | \mathbf{p} | \varphi_g \rangle |^2$$

$$\frac{Q}{(2\pi)^3} \int \frac{k \sin\theta (1 - \cos^2\theta) \, d\theta d\varphi dk}{E^+ - \hbar k c} . \tag{A4}$$

Equation (A4) can be written in the form

$$R_{l'l} = | \beta |^2 f_0(E_{l'}) f_0^*(E_l) A^\epsilon(E) , \tag{A5}$$

where

$$| \beta |^2 = \tfrac{2}{3} | \beta' |^2 | \langle \varphi_l | \mathbf{p} | \varphi_g \rangle |^2 \tag{A6}$$

and

$$A^\epsilon = \frac{Q}{(2\pi)^3} \int [4\pi k^2 | h(k) |^2 dk / (E^+ - \hbar k c)] . \tag{A7}$$

APPENDIX B: THE MASS RENORMALIZATION PROBLEM

Our expression for the various cross sections in the photodissociation problem (Sec. III) contain the integral (III-34) which diverges linearly and yields an infinite level shift due to the interaction of the molecular system with the radiation field. This problem is handled using the mass renormalization technique.[9a] We consider a molecular or atomic system and denote by $\{|n\rangle\}$ the spectrum of the "bare" molecular system which does not interact with the radiation field. The level shift of a state, $|m\rangle \in \{|n\rangle\}$ due to its interaction with the radiation field is given by $\langle m, \text{vac}|R|m, \text{vac}\rangle$, where R is the level shift operator [Eq. (III.4)] and the $\hat{p}$ subspace contains only the $|m, \text{vac}\rangle$ level. Using the explicit form of H_{int} (II.14) we may express its matrix elements in the same way as was done in (II.16) and (II.19) replacing $f_v(E_l)$ by $f_n(m)$ and thus we get

$$\langle m, \text{vac}|R|m, \text{vac}\rangle = \frac{4\pi Q}{(2\pi)^3}|\beta|^2 \sum_n |f_n(m)|^2$$
$$\times \int_0^\infty \frac{k\,dk}{E_m - E_n - k\hbar c} \quad , \qquad \text{(B1)}$$

We now write

$$\frac{-k\hbar c}{E_m - E_n - k\hbar c} = 1 - \frac{E_m - E_n}{E_m - E_n - k\hbar c} \qquad \text{(B2)}$$

and so

$$\langle m, \text{vac}|R|m, \text{vac}\rangle = -\frac{4\pi Q}{(2\pi)^3}\frac{|\beta|^2}{\hbar c}\sum_n |f_n(m)|^2$$
$$\times \left[\int_0^\infty dk - (E_m - E_n)\int_0^\infty \frac{dk}{E_m - E_n - k\hbar c}\right] \qquad \text{(B3)}$$

performing the renormalization it turns out that the first integral is just the level shift for the "dressed" free electron and we obtain

$$\langle m, \text{vac}|R|m, \text{vac}\rangle \rightarrow \frac{4\pi Q}{(2\pi)^3}\frac{|\beta|^2}{\hbar c}\sum_n |f_n(m)|^2(E_m - E_n)$$
$$\times \int_0^K \frac{dk}{E_m^+ - E_n - k\hbar c} \quad . \qquad \text{(B4)}$$

Performing the summation over e and subsequent averaging over polarization orientations results in[9a]

$$\Delta E^{(m)} = -\frac{2\alpha}{3\pi c^2}\sum_n |\langle m|\hat{V}|n\rangle|^2(E_m - E_n)$$
$$\times \left[\ln\left|\frac{K\hbar c}{E_m - E_n}\right| + i\pi\right] , \qquad \text{(B5)}$$

where $\hat{V}$ is the velocity operator $\hat{V} = \mathbf{p}/m$ and α is the fine structure constant. Now defining,

$$E_m - E_n = k_0^{(mn)}\hbar c \qquad \text{(B6)}$$

we get

$$\Delta E^{(m)} = -\frac{2\alpha}{3\pi c^2}\sum_n |\langle n|\hat{V}|m\rangle|^2\hbar c\, k_0^{(mn)}$$
$$\times \left[\ln\left|\frac{K}{k_0^{(mn)}}\right| + i\pi\right] \quad . \qquad \text{(B7)}$$

This is the expression for the hydrogenic Lamb shift.

Since the same type of integral A^g appears in our theory of line shape of a continuum we assume that renormalization of this problem will give actually the same "renormalized integral" (this assumption is not rigorous but is clearly good for an order of magnitude estimates of our corrections) we thus assume that

$$-\int\frac{dk\,k\,\hbar c}{E_l - E_g - k\hbar c} \rightarrow k_0^{(lg)}\left(\ln\left|\frac{K}{k_0^{(lg)}}\right| + i\pi\right) \qquad \text{(B8)}$$

and so [see Eqs. (III.26) and (III.27)]

$$N' + i\delta = -|\beta|^2 A^l A^g = \frac{e^2}{m^2}\frac{2\pi}{Q\hbar c}\hbar^2\int dE_l\,\rho_l\frac{|\langle g|p|l\rangle|^2}{E^+ - E_l}$$
$$\times \int\frac{dk\,k}{E^+ - E_g - k\hbar c}\otimes\frac{4\pi Q}{(2\pi)^3} \quad . \qquad \text{(B9)}$$

For a Lorentzian distribution of $|\langle g|\hat{V}|l\rangle|^2$ {i.e., $\langle g|\hat{V}|l\rangle|^2\propto[(E_l - \bar{E}_l)^2 + \frac{1}{4}\gamma^2]^{-1}$} we get

$$\int dE_l\,\rho_l\frac{|\langle g|\hat{V}|l\rangle|^2}{E^+ - E_l} = \pi|\langle g|\hat{V}|E\rangle|^2\rho_l(E)\left(\frac{E - \bar{E}_l}{\frac{1}{2}\gamma} - i\right) \qquad \text{(B10)}$$

and Eq. (B9) assumes the form

$$N' + i\delta = \frac{8\alpha}{3c^2}\pi|\langle g|\hat{V}|E\rangle|^2\rho_l(E)(E_l - E_g)$$
$$\times \left(\frac{E_l - \bar{E}_l}{\frac{1}{2}\gamma} - i\right)\left(\ln\left|\frac{K}{k_0^{(lg)}}\right| + i\pi\right) . \qquad \text{(B11)}$$

Denoting the hydrogen Lamb shift[9a] by α_H and a typical energy spacing $(E_n - E_m)$, whose average contribution to α_H is $\bar{k}_H\hbar c$, we get

$$N' + i\delta = \alpha_H\frac{k_0^{(lg)}}{\bar{k}_H}\frac{d\sigma(E)/dE}{\sigma_H(E)}(a + ib) , \qquad \text{(B12)}$$

where a and b are of the order of unity

$$a = \frac{E_l - \bar{E}_l}{\frac{1}{2}\gamma} + \frac{\pi}{\ln|K/k_0^{lg}|} , $$

$$b = \frac{\pi}{\ln|K/k_0^{lg}|}\cdot\frac{E_l - \bar{E}_l}{\frac{1}{2}\gamma} - 1 . \qquad \text{(B13)}$$

$d\sigma/dE$ is the differential scattering cross section from our continuum whereas σ_H is the hydrogenic cross section, $\bar{k}_H$ is the mean k contributing to the Lamb shift. Thus for an order of magnitude estimate we have

$$|N'|\simeq|\delta|\sim\alpha_H\frac{k_0^{(lg)}}{\bar{k}_A}\frac{d\sigma/dE}{\sigma_H} \quad . \qquad \text{(B14)}$$

Integrating over the continuum molecular band which is characterized by a width Δ we get

$$|N'|\cdot\Delta = \alpha_H\frac{k_0^{(lg)}}{\bar{k}_H}\frac{\sigma_T}{\sigma_H} , \qquad \text{(B15)}$$

where

$$\sigma_T = \int dE\,[d\sigma(E)/dE] \qquad \text{(B16)}$$

assuming

$$k_0^{(lg)}\approx\bar{k}_H \qquad \text{(B17)}$$

and

$$\sigma_T\approx\sigma_H$$

we finally get

$$|N'| \simeq \alpha_H/\Delta \ . \tag{B18}$$

This result was used in Sec. III.

APPENDIX C: RAMAN SCATTERING FROM AN OPTICALLY ACTIVE CONTINUUM

In Sec. IV we have presented a solution for resonance Raman scattering from a dissociative continuum to zero order in the radiative interaction terms N' and δ [see Eqs. (IV-7), (IV-8), and (IV-9)]. It is of some interest to provide a systematic extension of this treatment to any order in the radiative interactions. We shall now demonstrate that the level shift operator for this problem [see Fig. 1(b)] can be evaluated to infinite order and can be then subsequently utilized for the systematic evaluation of the matrix elements of the Green's function and of the T matrix. Our Hibert space is partitioned as follows:

$$\hat{Q} = \sum_{\mathbf{k},\mathbf{e}} \sum_v |g_e v, \mathbf{ke}\rangle\langle g_e v, \mathbf{ke}| \ ,$$

$$\hat{P} = \sum_l |l_e, \text{vac}\rangle\langle l_e, \text{vac}| \ , \tag{C1}$$

$$\hat{P} + \hat{Q} = 1 \ .$$

Making use of the formal definition

$$\hat{P}R\hat{P} = \hat{P}V\hat{P} + \hat{P}V\hat{Q}(E - H_0 - \hat{Q}V\hat{Q})^{-1}\hat{Q}V\hat{P} \tag{C2}$$

and representing the radiative interaction in the form

$$\langle l_e, \text{vac} |V|g_e v, \mathbf{ke}\rangle \equiv V_{l,gv\mathbf{ke}} = \beta_{\mathbf{e}(\mathbf{k})}f_v(E_l)h(k) \tag{C3}$$

$$R_{l'l} = |\beta|^2 \sum_v f_v(E_{l'}) f_v^*(E_l) A^g(E - E_v) \ , \tag{C4}$$

where

$$A^g(E - E_v) = \sum_{\mathbf{k},\mathbf{e}} \frac{|h(k)|^2}{E - E_v - \hbar kc} \tag{C5}$$

and E_v corresponds to the energy of the molecular level $|g_e v\rangle$. Note that Eq. (C4) is general.

The general expression for $\hat{P}G\hat{P}$ is

$$\hat{P}G\hat{P} = \hat{P}G_0\hat{P} + \hat{P}G^0\hat{P}R\hat{P}G\hat{P} \tag{C6}$$

which yields, using Eqs. (C1)-(C5):

$$G_{l'l} = \frac{\delta(E_l - E_{l'})}{E - E_{l'}} + \frac{1}{E - E_{l'}}$$

$$\times |\beta|^2 \sum_{v,\bar{l}} f_v(E_{l'}) f_v^*(E_{\bar{l}}) A^g(E - v\hbar\omega) G_{\bar{l}l} \ . \tag{C7}$$

This is an infinite set of coupled integral equations for $G_{l'l}$.

We now expand (C6) in powers of $\hat{P}R\hat{P}$ and get

$$\hat{P}G\hat{P} \simeq \hat{P}G^0\hat{P} + \hat{P}G^0\hat{P}R\hat{P}G^0\hat{P} \tag{C8}$$

which results in an immediate explicit expression for $G_{l'l}$

$$G_{l'l} = \frac{\delta(E_l - E_{l'})}{E - E_{l'}} + \frac{|\beta|^2}{E - E_{l'}} \sum_v f_v(E_{l'}) f_v^*(E_l)$$

$$\times \frac{1}{E - E_l} A^g(E - v\hbar\omega) \ . \tag{C9}$$

Using this form for $G_{l'l}$ we can find the T matrix element for the photon scattering processes:

$$\langle g_e v, \mathbf{k'e'}| T |g_e 0, \mathbf{ke}\rangle = \sum_{l'l} V_{v\mathbf{k'e'},l'} G_{l'l} V_{l,0\mathbf{ke}} \tag{C10}$$

which may be written in the following manner:

$$\langle g_e v, \mathbf{k'e'}| T |g_e 0, \mathbf{ke}\rangle = \beta^*_{\mathbf{e'}(\mathbf{k})} \beta_{\mathbf{e}(\mathbf{k})} h(k')h(k)$$

$$\otimes A_{v,0}(E) \left[1 + |\beta|^2 \sum_s \frac{A_{v,s}(E)}{A_{v,0}(E)}\right.$$

$$\left.\otimes A_{s,0}(E) A^g(E - s\hbar\omega)\right] \tag{C11}$$

where we have defined the auxiliary functions

$$A_{v,s}(E) = \sum_l \frac{f_v^*(E_l) f_s(E_l)}{E^+ - E_l} \ . \qquad s = 0,1,\dots \tag{C12}$$

The s summation in Eq. (C11) is over all the possible vibrational states of the exit channel.

Defining

$$-|\beta|^2 A_{s,0} A^g(E - s\hbar\omega) = N'_s + i\delta_s \tag{C13}$$

we get

$$\langle g_e v, \mathbf{k'e'}| T |g_e 0, \mathbf{ke}\rangle = \beta^*_{\mathbf{e'}(\mathbf{k'})}\beta_{\mathbf{e}(\mathbf{k})} h(k')h(k) A_{v,0}$$

$$\otimes \left[1 - \sum_s \frac{A_{v,s}}{A_{v,0}} (N'_s + i\delta_s)\right] \tag{C14}$$

The second matrix element of T which is required for evaluating the various cross sections of our problem is $\langle l_e, \text{vac}| T |g_e 0, \mathbf{ke}\rangle$ which may be expressed in terms of $\langle g_e v, \mathbf{ke}|G| l_e, \text{vac}\rangle$, i.e., $\hat{Q}G\hat{P}$. The formal expression for $\hat{Q}G\hat{P}$ is

$$\hat{Q}G\hat{P} = (E - \hat{Q}H_0\hat{Q})^{-1} \hat{Q}R\hat{P} (E - H_0 - \hat{P}R\hat{P})^{-1} \tag{C15}$$

since $\langle g_e v, \mathbf{ke}|R| l_e, \text{vac}\rangle = V_{v\mathbf{ke},l}$ we may write

$$G_{v\mathbf{ke},l} \equiv \langle g_e v, \mathbf{ke}| G | l_e, \text{vac}\rangle$$

$$= \sum_{l'} \frac{1}{E - v\hbar\omega - k\hbar c} V_{v\mathbf{ke},l'} G_{q'l} \ . \tag{C16}$$

Using (C9) and (C16) we obtain

$$G_{v\mathbf{ke},l} = \frac{\beta^*_{\mathbf{e}(\mathbf{k})} h(k) f_v^*(E_l)}{(E - v\hbar\omega - \hbar kc)(E - E_l)}$$

$$+ \frac{\beta^*_{\mathbf{e}(\mathbf{k})} h(k)|\beta|^2}{(E - v\hbar\omega - k\hbar c)(E - E_l)}$$

$$\otimes \sum_s A_{v,s} f_s^*(E_l) A^g(E - s\hbar\omega) \ . \tag{C17}$$

From Eq. (C17) we can now obtain the following expression for $T_{l,0\mathbf{k}}$

$$T_{l,0\mathbf{k}} = V_{l,0\mathbf{k}} + \sum_{v\mathbf{k'}l'} V_{l,v\mathbf{k'}} G_{v\mathbf{k'}l'} V_{l',0\mathbf{k}} \tag{C18}$$

which yields after some algebraic manipulations

$$T_{l,0\mathbf{k}} = \beta_{\mathbf{e}(\mathbf{k})} f_0(E_l) h(k) \left[1 - \sum_v (N'_v + i\delta_v) \frac{f_v(E_l)}{f_0(E_l)}\right.$$

$$\left.\otimes \left(1 - \sum_s \frac{A_{v,s}}{A_{v,0}} (N'_s + i\delta_s)\right)\right] \ . \tag{C19}$$

We are now in the position to evaluate the various cross sections: $\sigma_a(E)$, $\sigma_r^v(E)$, and $\sigma_d(E)$ using Eqs. (II.2),

(II. 3), (II. 4), (II. 2a), (II. 3a), and (II. 4a) and our expressions for the T matrix elements (C14) and (C19).

We get

$$\sigma_a(E) = - \, | \, \beta \, |^2 \, | \, h(E/\hbar c) \, |^2 \, \rho_r(E)(\lambda^2/2)$$

$$\otimes \left[\mathrm{Im} A_{0,0} - \sum_s (\mathrm{Re} A_{0,s}) \, \delta_s - \sum_s (\mathrm{Im} A_{0,s}) N_s' \right],$$

$$\tag{C20}$$

$$\sigma_r^v(E) = \frac{\pi \lambda^2}{2} \, | \, \beta \, |^4 \, | \, h(E/\hbar c) \, |^4 \, \rho_r^2(E)$$

$$\otimes \left| A_{v,0} - \sum_s A_{v,s}(N_s' + i \delta_s) \right|^2,$$

$$\tag{C21}$$

$$\sigma_d(E) = \frac{\pi \lambda^2}{2} \, \rho_r(E) \rho_l(E) \, | \, \beta \, |^2 \, | \, h(k) \, |^2$$

$$\otimes \left| f_0(E_l) - \sum_v (N_v', + i \delta_v) \, f_v(E_l) \right.$$

$$\times \left[1 - \sum_s \frac{A_{v,s}}{A_{v,0}} (N_s' + i \delta_s) \right] \Bigg|^2.$$

$$\tag{C22}$$

Neglecting all the terms containing N_k' or δ_k, then expressions (C20)–(C22) are reduced to (IV. 7)–(IV. 9).

If $| \, f_0(E_e) \, | > | \, f_v(E_e)(N_v' + i \delta_v) \, | \quad v = 0, 1, \ldots$

then all the corrections introduced here are of the form $[1 + O(N') + O(\delta')]$ which are negligible small. However if $\mathrm{Im} A_{0,0}[\text{or } f_0(E_l)]$ vanish at some energy as is the case for the Fano problem (Sec. V) then the corrections of the order of $O(N')$ become important.

APPENDIX D: RESONANCE RAMAN INTENSITIES FROM A SINGLE DISSOCIATIVE CONTINUUM

As we have shown in Sec. IV the cross section for resonance Raman scattering $\sigma_r(0ke \rightarrow vk'e')$ is proportional to $|A_{v,0}|^2$ where

$$A_{v,0}(E) = \int_{\eta \rightarrow 0^+} dE_l \rho_l \frac{f_v^*(E_l) f_0(E_l)}{E - E_l + i\eta}$$

$$= \alpha_{v,0}(E) - i\pi \rho_l f_v^*(E) f_0(E) \tag{D1}$$

and

$$\alpha_{v,0} = PP \int dE_l \rho_l \frac{f_v^*(E_l) f_0(E_l)}{E - E_l}. \tag{D2}$$

In order to have a qualitative understanding of the behavior of this distribution we have solved this integral numerically for a simple molecular model.

Our assumptions are:

(1) We have a diatomic molecule with a Harmonic ground state whose potential function is

$$W_g(Q) = \tfrac{1}{2}(Q^2 - 1), \tag{D3}$$

where Q is the reduced oscillator coordinate

$$Q = \sqrt{M\omega/\hbar} \, (q - q_0). \tag{D4}$$

q is the internuclear distance, q_0 is the equilibrium separation distance, and M is the oscillator mass. The energy is measured in $(\hbar w)$ units and the zeroth vibrational level is chosen as the energy zero.

(2) The repulsive electronic state has a linear poten-

tial function with slope k

$$W_l(Q) = kQ + A. \tag{D5}$$

(3) The Franck–Condon factors are evaluated by the "reflection method", i.e.,

$$f_v(E_l) \simeq \chi_v[(E_l - A)/k], \tag{D6}$$

where the continuum wavefunctions are energy normalized (i.e., $\rho_l = 1$) and χ_v is the Harmonic oscillator wave wavefunction

$$\chi_v(Q) = (\sqrt{\pi} \, 2^v v!)^{-1/2} e^{-1/2Q^2} H_v(Q) \tag{D7}$$

and H_v is a Hermite polynomial. Using (D1) and (D6) we obtain

$$A_{v,0} = \int_{-\infty}^{\infty} \frac{\psi_v[(E_l - A)/k] \psi_0[(E_l - A)/k]}{E^+ - E_l} \, dE_l, \tag{D8}$$

which may be rearranged in the following manner:

$$A_{v,0}(\epsilon) = \alpha_{v,0}(\epsilon) + i \gamma_{v,0}(\epsilon), \tag{D9}$$

where

$$\alpha_{v,0}(\epsilon) = -pp \int_{-\infty}^{\infty} dz \, \frac{\psi_v(\epsilon + z)\psi_0(\epsilon + z)}{z}$$

$$\gamma_{v,0}(\epsilon) = \pi \psi_v(\epsilon)\psi_0(\epsilon), \tag{D10}$$

where $\epsilon = (E - A)/k$ is our new reduced energy parameter. Note that ϵ corresponds just to the reduced coordinates Q [Eq. (D4)] at which absorption occurs from $v = 0$.

We thus have

$$| A_{v,0}(\epsilon) |^2 = | \alpha_{v,0}(\epsilon) |^2 + | \gamma_{v,0}(\epsilon) |^2 \tag{D11}$$

and also

$$| A_{v,0}(-\epsilon) |^2 = | A_{v,0}(\epsilon) |^2. \tag{D12}$$

Numerical calculations were performed for (D1) in the approximation (D11) for various values of ϵ. The transition energy in each case corresponds to $E = A + k\epsilon$ and the band maximum is located at $E_{\max} \simeq A$. The absorption line shape from $v = 0$ within a reasonable good approximation corresponds to $\sigma_a(\epsilon) \propto e^{-Q2} = e^{-\epsilon 2}$ so that the half-linewidth is $(\ln 2)^{1/2} \approx 0.83$.

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[6] Actually, the separation is not complete due to the fact that the interaction depends upon the molecular orientations with respect to the photon polarization vector. However, spatial averaging over molecular orientations and polarization directions will result in a separable interaction.
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$\sigma_a \propto \cos^2\theta$, $\sigma_d \propto \cos^2\theta$ and $\sigma_r \propto \cos^2\theta\cos^2\theta'$, where θ and θ' are the polar angles of the e and e' polarization vectors, and the electronic transition momentum is directed along the z axis. Averaging over θ we replace $\langle\cos^2\theta\rangle = \frac{1}{3}$. Summing σ_r over all possible e' values is carried out as in Appendix A. $|\beta|^2$ which appears in Eq. (III.20) is defined in Appendix A.

[9](a) S. S. Schweber, *An Introduction to Relativistic Quantum Field Theory* (Row, New York, 1961). (b) The expression

$$\sum_l \left[|\langle g|V|l\rangle|^2/(E^+ - E_l)\right] = |\beta_e|^2 h(E/\hbar c)A^l(E)$$

may be viewed as a "nonradiative Lamb shift" of the one photon state $|g_e, \mathbf{k}e\rangle$ arising from its interaction with the intramolecular continuum.

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[15]The case of $q = 0$ is not physical once the principal part is incorporated in the definition (V.21).

[16]As we have neglected the level shifts $R_e A^s$ and $R_e A^1$, the photodissociation cross section vanishes up to the order $O(N'^2)$ This can be shown from the results of Appendix C [Eq. (C 22)] for $f_0(E_l)$. For any practical application we can take $\sigma_d = 0$ at at the interference dip.