Resonance Fluorescence from Large Molecules

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In this paper we apply the $T$ matrix formalism of scattering theory to derive general expressions for the absorption cross sections, the cross sections for resonance fluorescence and the emission quantum yields from large molecules in the statistical limit. In the simple case of an isolated molecular resonance both the absorption line shape and the photon scattering cross section exhibit a Lorentzian distribution on the photon energy, the emission quantum yields are distributed among the ground state vibronic levels according to their radiative widths and, most important, the emission quantum yields are independent of the photon energy and of the spectral width of the exciting light. We were able to derive general expressions for the resonance scattering from a pair of overlapping resonances, including radiative corrections to infinite order. The absorption cross section does not vanish in the region of destructive interference but assumes a finite value which depends on the radiative widths. A sharp maximum in the partial and in the total emission quantum yields is exhibited in the destructive interference regions. This general scheme was applied to a pair of zero order discrete states, one of which is optically active, which interact with an optically inactive quasicontinuum. The energy dependent quantum yield depends on the total width of the radiatively impotent state and may exhibit a minimum. We have demonstrated that when interference effects are involved the decay characteristics of this system will differ for coherent and for narrow band excitation. The general formalism was utilized to derive approximate relations for the resonance fluorescence cross sections and for the quantum yield in the case of a Fano absorption line shape which are valid away from the interference region. Finally, we have applied the general theoretical scheme to the case of the direct photodissociation spectrum of molecules. We have demonstrated that a finite energy dependent emission quantum yield will be observed when a molecule is optically pumped into a dissociative continuum.

I. INTRODUCTION

There has been extensive theoretical activity aimed towards the elucidation of intramolecular radiationless transitions in large molecules.4 In general, two classes of experiments which will be referred to as “short excitation” and “long excitation” processes can be utilized to extract direct physical information concerning the decay of electronically excited states of large molecules which correspond to the statistical limit.7 When the temporal duration of the exciting photon field is short relative to the reciprocal width of the molecular resonance, it is feasible to separate the excitation and the decay processes and to consider the decay pattern to the metastable state. This approach concerning a “short excitation” process has been very popular.4a,5b On the other hand, when the exciting photon field is characterized by a high energy resolution, being switched on for long periods (relative to the decay time) the excitation and the decay processes cannot be separated and one has to consider resonance scattering from large molecules within the framework of a single quantum mechanical process. Such “long excitation” experiments involve the determination of optical line shapes,7b,9 cross sections for resonance fluorescence9 and emission quantum yields. The physical information concerning the resonance width, originating from “short excitation” and “long excitation” experiments, should be equivalent. However, when interference effects are exhibited one cannot get away by considering just the widths of the resonances.

In this paper we present the result of a theoretical study of resonance fluorescence from large molecules which correspond to the statistical limit. We shall derive the cross sections for resonance fluorescence utilizing some general results of scattering theory. These results combined with the optical line shape formula will yield general expressions for the quantum yield. We shall further explore the general features of the cross sections for resonance fluorescence and the quantum yield in the case of a single molecular resonance, a resonance originating from coupling to an optically active quasicontinuum and an optical line shape resulting from interference between resonances. We shall focus attention on the nature of the physical information which can be extracted from “long excitation” processes in large molecules.

II. APPLICATION OF SCATTERING THEORY

Scattering theory provides a powerful tool for the understanding of the interaction of a molecular system with the radiation field which is responsible for the absorption line shape and resonance scattering. As we are interested in “long excitation” experimental observables one can consider a “collision process” between a monochromatic wave train and the “isolated” molecule within the framework of the Lippman Schwinger equation expressed in terms of the $T$ matrix formalism.11 Rather than rehash this general treatment we shall proceed to apply it directly to the problem at hand. Consider the conventional dissection of the total Hamiltonian for the system including the radiation field

$$H = H_0 + H_R + H_v + H_{\text{int}}$$

$$= H_0 + H_R + V,$$  \hspace{1cm} (II.1)

where $H_0$ is the zero order molecular Hamiltonian, $H_v$ is the intramolecular nonadiabatic perturbation, $H_R$ is
the Hamiltonian for the free electromagnetic field, while $H_{\text{int}}$ is the matter–radiation interaction term. The electronically excited eigenstates of $H_0$ are labelled as $|s\rangle$, $|r\rangle$, etc. for the discrete optically active levels, and as $|l\rangle$ for the dissipative intramolecular quasi-continuum. The electronic ground state of the system will be labeled by the vibronic components $|g, v_g\rangle$, where $v_g=0$ refers to the vibrationless level while $v_g \neq 0$ represents excited vibronic levels. Note that for the low lying ground states $|g, v_g\rangle$ can be considered as eigenfunctions of $H_0$ as well as of $H_0+H_{\text{int}}$, as off-resonance nonadiabatic corrections for these states are negligible. The eigenfunctions of $H_{\text{R}}$ will be given by the zero photon state $|\text{vac}\rangle$ and by one photon states $|\mathbf{k}, e\rangle$ where $\mathbf{k}$ and $\mathbf{e}$ are the wave vector and the polarization vector of a photon, respectively. At the distant past, the molecule is in the state $|a\rangle=|g, v_g; k, e\rangle$ characterized by the energy $E_a$. The final states resulting from photon scattering will be denoted by $|b\rangle=|g, v_g; k_f, e_f\rangle$ characterized by the energy $E_b$. The probability for the transition $|a\rangle \rightarrow |b\rangle$ is given by

$$W_{ab}=(2\pi\hbar)^{-1}T_{ab}^{-1}B(E_b-E_a), \quad (1.2)$$

where the $T$ matrix (the reaction operator) is defined by

$$T=V+V(E_a-H+i\eta)^{-1}V \quad (1.3)$$

with $\eta \to 0^+$ and $V=H_0+H_{\text{int}}$. Equations (1.2) and (1.3) are the generalization of Fermi’s golden rule, where the delta function insures energy conservation. The physically meaningful concept involved in Eq. (1.2) is a transition to a group of final states within the energy interval $dE_b$, so that when this equation is integrated over the final states one gets the familiar density of states $\rho_0$ in the final expression. The cross section for the process $a \rightarrow b$, $\sigma(a \rightarrow b)$, is obtained by dividing the transition probability by the photon flux $F=c/Q$ where $c$ is the velocity of light and $Q$ represents the volume of the system

$$\sigma(a \rightarrow b)=(2\pi\hbar)^{-1} T_{ab}^{-1} B(E_b-E_a). \quad (1.4)$$

The second general result we require is the rate of disappearance $W_{ab}$ of the initial state $|a\rangle$, which is given by the optical theorem of scattering theory,11

$$W_{ab}=-(2\hbar)^{-1} \text{Im}(T_{ab}), \quad (1.5)$$

while the absorption cross section $\sigma_a$ is given by dividing by the flux

$$\sigma_a=-(2\pi\hbar)^{-1} \text{Im}(T_{ab}). \quad (1.6)$$

We can immediately apply these results by setting for the initial energy $E_a=E_g^0+H+i\eta$ the energy of the ground state vibrationless level and $E=hc$ is the incident photon energy, whereupon the absorption cross section is obtained from (1.6) in the form

$$\sigma_a(E)=-\frac{1}{2} \sum_{g, e_f} \sigma(g, o_g; \mathbf{k}, \mathbf{e}) \times T(g, o_g; \mathbf{k}, \mathbf{e}) \quad (1.7)$$

Consider now the cross section for resonance fluorescence. We focus attention on the photon scattering process $|g, o_g; \mathbf{k}, \mathbf{e}\rangle \rightarrow |g, o_g; \mathbf{k}, \mathbf{e}\rangle$, which takes place between the initial state characterized by the energy $E_g^0+E=E_g^0+k\hbar c$ and the final states characterized by the energy $E_f+E_f=E_f^0+k\hbar c$, where by $E_f^0$ we denote the energy of the state $|g, v_f\rangle$ and where the emitted photon which is characterized by the polarization $\mathbf{e}_f$ and momentum $\mathbf{k}_f$ is scattered into the spherical angle $\Omega_{k_f} \rightarrow \Omega_{k_f} + d\Omega_{k_f}$. Equation (1.4) results in

$$\sigma(g, o_g; \mathbf{k}, \mathbf{e}) = (2\pi\hbar^2/\hbar)^2 \sum_{g, o_g; \mathbf{k}, \mathbf{e}_f} \langle g, v_g; \mathbf{k}, \mathbf{e}_f | \mathbf{T} | g, v_g; \mathbf{k}, \mathbf{e} \rangle^2, \quad (1.8)$$

where the density of final states in the radiator field is

$$\rho_f=[k_f/(2\pi\hbar^2 c)]^2, \quad (1.9)$$

where one has to take $k_f=c-E_f^0-E_{g}^0-kc$ to insure energy conservation. The resonance scattering cross section $\sigma_R(v_g; E)$ into the final molecular state $|g, v_g\rangle$ will be obtained by summing up Eq. (1.8) over all final spatial directions and polarization directions. This scattering cross section depends on the energy $E=hc$ of the initial photon, and as we consider a sample of randomly oriented (noninteracting) molecules, we are not interested in polarization measurements and shall also average over the initial polarization directions $\mathbf{e}$, resulting in

$$\sigma_R(v_g; E)=\frac{1}{2} \sum_{g, \mathbf{e}_f} \delta(E_g^0+E-E_f^0) \times T(g, v_g; \mathbf{k}, \mathbf{e}_f) \quad (1.10)$$

The total cross section for resonance fluorescence is obtained by monitoring all the emitted photons resulting from scattering into all the final molecular states $|g, v_g\rangle$, where

$$\sigma_R(E) = \sum_{v_g} \sigma_R(v_g; E). \quad (1.11)$$

The (energy dependent) quantum yield resulting from absorption of a photon of energy $E$ leading to the molecular state $|g, v_g\rangle$ is given by the ratio of the resonance scattering cross section [Eq. (1.10)] and the absorption cross section [Eq. (1.7)]

$$Y(v_g; E) = \frac{\sigma_R(v_g; E)}{\sigma_a(E)}. \quad (1.12)$$

If the ground state energy levels are well spaced the different channels can be resolved.

Finally the total quantum yield for emission is given by

$$Y(E) = \sum_{v_g} Y(v_g; E) = \frac{\sigma_R(E)}{\sigma_a(E)}. \quad (1.13)$$

To conclude this formal discussion the following points are in order:

(a) The general expressions for the absorption cross sections, for the resonance fluorescence cross sections
and for the emission quantum yields in the “statistical” molecular case will involve as “open channels” not only the radiation continuum but also the intramolecular quasicontinuum \{ | l \} which for all practical purposes can be considered as an “open” decay channel. In this case the unitarity relations for the scattering matrix do not imply that the sum \( \sum_{k'} \sum_{\nu} \sum_{\sigma} \langle g, o_{\sigma}; k, e \rightarrow g, \nu_{\nu}; k_{\nu}, e_{\nu} \rangle = 1 \) is equal to unity as intramolecular decay channels have to be considered. The formulation of the absorption cross section is similar to that given by Shore\(^{12}\) for the case of atomic autoionization. The formulas for resonance fluorescence derived herein are new.

(b) The present formulation of the cross sections and of the quantum yields is more general than previous attempts\(^{1-8}\) which were based on the “decay of prepared states”. When the time is sharply defined one cannot, of course, consider the probing of the structure of the resonances by monitoring the energy dependence of the quantum yield. For this purpose the energy of the incident photons has to be sharply defined. As we shall demonstrate in Sec. III this problem is immaterial for the Bixon–Jortner\(^4\) basic model, however, once interference effects with background absorption or between resonances are important the energy dependence of the relevant cross sections and of the quantum yields becomes crucial.

(c) The general expressions for the physical observables obtained herein are invariant under different choices of the zero order molecular Hamiltonian \( H_{0} \) and of the intramolecular perturbation \( H_{e} \). Thus any untruncated and complete molecular zero order basis set is adequate for describing the physical properties of the system. As was previously pointed out\(^6\) the Born–Oppenheimer basis set is superior to the crude adiabatic basis as the former basis set minimizes off resonance coupling terms between different electronic configurations.

III. A SINGLE MOLECULAR RESONANCE

We shall now apply the general results obtained above to the simple model system characterized by the following features: (a) A single molecular excited zero order state \(| s \rangle \) carries oscillator strength from the molecular ground state \(| g, o_{\sigma}; k, e \rangle \); (b) the zero order quasicontinuum \{ | l \} \) is optically inactive; (c) the quasicontinuum is quasidegenerate with \(| s \rangle \) and is coupled to it by \( H_{e} \); (d) the ground molecular levels \(| g, \nu_{\nu} \rangle \) are coupled to excited states only by \( H_{\text{int}} \); (e) other “optically active” excited states \(| r \rangle \) are well separated from \(| s \rangle \) relative to their widths; (f) off-resonance coupling with \(| s \rangle \) and \(| r \rangle \) is negligible.

Equation (II.7) is directly applicable bearing in mind that the ground state \(| g, o_{\sigma}; k, e \rangle \) is coupled only by \( H_{\text{int}} \) to other molecular states. Thus we get

\[
\sigma_{\alpha}(E) = -\frac{(2Q/\hbar c)}{|g, o_{\sigma}; k, e | H_{\text{int}} | s + \text{vac} \rangle |^{2} \times \Im \langle s; \text{vac} | (E_{\text{vac}} + E - H + i\eta)^{-1} | s; \text{vac} \rangle. \]  

The diagonal matrix element of the Green’s function is well known, being given by

\[
\langle s; \text{vac} | (E_{\text{vac}} + E - H + i\eta)^{-1} | s; \text{vac} \rangle = (E_{\text{vac}} + E - E_{s} - D_{s} + i\hbar \Gamma_{s})^{-1}. \]  

\( D \) is a level shift term which will be incorporated into the energy \( E_{s} \) of the zero state \(| s \rangle \) setting \( E_{s} = E_{s} + D_{s} \). The total width \( \Gamma_{s} \) of the zero order state \(| s; \text{vac} \rangle \) includes the contribution of the radiative decay into the channels \(| b \rangle \) = \(| g, \nu_{\nu}; k_{\nu}, e_{\nu} \rangle \) and the contribution of the intramolecular decay into the quasicontinuum \{ | l; \text{vac} \rangle \). This width can be defined in general in terms of the level shift operator,\(^{11}\)

\[
\hat{R}(E) = V + (1 - P)(E - H_{\text{int}}) \theta(1 - P)V, \]  

where \( V = H_{s} + H_{\text{int}} \) and \( P = | s \rangle \langle s | \).

The partial width due to the intramolecular decay \( \Gamma_{s}^{I} \), and due to the radiative decay into the ground state vibronic levels \( \Gamma_{s}^{R} \), \( \nu = \nu_{\nu} = 0, 1, \cdots \), can now be defined in terms of the level shift operators

\[
\Gamma_{s}^{I}(E) = 2\pi \sum_{l} | \langle s; \text{vac} | \hat{R}(E) | l; \text{vac} \rangle |^{2} \theta(E_{s} - E_{l}), \]  

and

\[
\Gamma_{s}^{R}(E) = 2\pi \sum_{\nu} | \int d\Omega_{\nu} | \langle s; \text{vac} | \hat{R}(E) | g, \nu_{\nu} ; k_{\nu}, e_{\nu} \rangle \rho_{\nu}^{s} |^{2}, \]  

where \( \rho_{\nu}^{s} \) is given by (II.9) and where \( k_{\nu} = (E + E_{s} - E_{\nu})/\epsilon \). The radiative width (which is always a slowly varying function of the energy in the vicinity of \( E \approx E_{s} \)) can for our purposes be displayed in terms of first order perturbation theory, resulting in

\[
\Gamma_{s}^{R} = 2\pi \sum_{\nu} | \int d\Omega_{\nu} \rho_{\nu}^{s} | \langle s; \text{vac} | H_{\text{int}} | g, \nu_{\nu} ; k_{\nu}, e_{\nu} \rangle |^{2}, \]  

where we have utilized Eq. (II.9) and performed the summation over the spatial angles and the polarization directions. Turning now our attention to the non radiative width \( \Gamma_{s}^{I} \), we can assert that in the statistical limit the function (II.4) is slowly varying with energy.\(^{12}\) Provided that restriction (e) is fulfilled (which is the case for the adiabatic basis), we can apply Fermi’s golden rule resulting in

\[
\Gamma_{s}^{I} = 2\pi \sum_{l} | \langle s | H_{e} | l \rangle |^{2} \theta(E_{s} - E_{l}). \]  

Now the total width \(|\Gamma_{s}^{I} + \Gamma_{s}^{R}|\) is given by

\[
\Gamma_{s} = \Gamma_{s}^{I} + \Gamma_{s}^{R} \]  

with the total radiative width \( \Gamma_{s}^{R} = \sum_{\nu} \Gamma_{s}^{R} \).

Equations (III.1) and (III.2) lead to the simple
Lorentzian line shape

\[ \sigma_A(E) = (Q/\hbar c) | \langle g, o_\phi; k, e | H_{int} | s; vac \rangle |^2 \times | \Gamma_s/[(E-E_{sp})^2 + (\frac{1}{2}\Gamma_s)^2] |, \]  

where we have set \( E_{sp} = E_o - E_{sp} \).

The matrix element in (III.7) can be displayed in terms of the radiative width \( \Gamma^o_s \) of the state \( s \) due to its decay into the vibrationless level \( | g, o_\phi \rangle \). Utilizing Eq. (III.5') we have

\[ | \langle g, o_\phi; k, e | H_{int} | s; vac \rangle |^2 = (\pi \hbar^2 c/2k^2Q) \Gamma^o_s \]  

(III.8)

\[ | \langle g, o_\phi; k_f, e_f | T | g, o_\phi; k_f, e_f | H_{int} | s; vac \rangle | E-E_{sp} + \frac{1}{2}i\Gamma_s \rangle \langle s; vac | H_{int} | g, o_\phi; k, e \rangle \] (III.10)

whereupon

\[ | \langle g, o_\phi; k_f, e_f | T | g, o_\phi; k, e \rangle |^2 = | \langle g, o_\phi; k_f, e_f | H_{int} | s; vac \rangle |^2 | \langle s; vac | H_{int} | g, o_\phi; k, e \rangle |^2/[(E-E_{sp})^2 + (\frac{1}{2}\Gamma_s)^2] \]  

(III.10')

Now utilizing Eqs. (II.8)–(II.11) and (III.10) we obtain the following expression for resonance scattering into the \( | g, o_\phi \rangle \) vibronic state:

\[ \sigma_R(v_o; E) = \frac{\pi \hbar^2 / (2\pi\hbar)^2}{(Q^2/c^2) \sum_{e_f} j dW_{f} | \langle g, o_\phi; k_f, e_f | H_{int} | s; vac \rangle |^2} \times \sum_o | \langle s; vac | H_{int} | g, o_\phi; k, e \rangle |^2 / [(E-E_{sp})^2 + (\frac{1}{2}\Gamma_s)^2]^{-1} \]  

(III.11)

Making use of Eqs. (III.5) and (III.8) we get

\[ \sigma_R(v_o; E) = \frac{1}{2} \pi (\hbar/k)^2 \Gamma^o_s \Gamma_s^o / [(E-E_{sp})^2 + (\frac{1}{2}\Gamma_s)^2] \]  

(III.12)

while the total cross section for resonance scattering Eq. (II.11) is

\[ \sigma_R(E) = \frac{1}{2} \pi (\hbar/k)^2 \Gamma^o_s \Gamma_s^o / [(E-E_{sp})^2 + (\frac{1}{2}\Gamma_s)^2] \]  

(III.13)

Equations (III.9), (III.12), and (III.13) together with (III.6) provide us with the general results for the cross sections originating from a single molecular resonance.

The quantum yields for emission given by Eqs. (II.12) and (II.13) are now readily obtained in the form

\[ Y(v; E) = \Gamma_s^o / \Gamma_s^o + (\Gamma_s^o + \Gamma_s^R) \]  

(III.14a)

\[ Y(E) = \Gamma_s^R / \Gamma_s^o + (\Gamma_s^o + \Gamma_s^R) \]  

(III.14b)

These results are well known,\(^8\) however, to the best of our knowledge, they were not previously derived for a “long excitation” type experiment.

We thus conclude that for the case of a single molecular resonance: (1) Both the absorption line shape and the cross section for resonance fluorescence exhibit a Lorentzian dependence on the photon energy \( E = \hbar \omega \).

(2) The emission yields are distributed among the ground state vibronic levels according to their widths.

(3) The emission quantum yields are independent of the photon energy, or of the spectral width of the exciting light. (4) From (3) we assert that the emission quantum yield is thus equal to the yield obtained in a “short excitation” experiment which was previously studied.

The present general treatment of a “long excitation” optical experiment clearly demonstrates that in the case of a single molecular resonance it will be useless to probe the structure of this resonance by narrow band excitation. This problem has been raised in the literature\(^9\) and cannot be settled definitely by considering the decay of initially excited states. Freed\(^1a\) has reached a similar conclusion concerning the energy dependence of the quantum yield by considering the decay resulting from monochromatic excitation, which is suddenly terminated. Freed concludes\(^1a\) that for a single molecular resonance the resulting decay is then equivalent to that of the initially prepared \( | s; vac \rangle \) state. It is not clear whether Freed’s procedure of terminating the radiation field is consistent with the theoretical requirements for a “long excitation” experiment.

We would like to point out that the present treatment pertains to a long time monochromatic excitation experiment. One may, of course, perform long time experiments utilizing broad band excitation sources. Such experiments were discussed by Rhodes\(^1b,1c\) and by us.\(^1d\)

For the case of a single resonance where the line shape is Lorentzian the details of the “preparation” of the
excited state are relatively simple. When more complex physical resonances are encountered and interference effects with background continuum or between resonance are exhibited, the present theoretical methods based on “long time” excitation processes will prove to be very powerful.

IV. INTERFERENCE BETWEEN TWO RESONANCES

When the linewidth of a molecular resonance exceeds 100 cm⁻¹ serious deviations from the ideal Lorentzian line shape are expected due to the breakdown of some of the assumptions listed in Sec. III. In what follows we shall discuss the case in which assumption (e) of Sec. III, namely that |s⟩ is an isolated resonance, does not hold. We shall consider the cross sections for absorption and for resonance fluorescence for a system characterized by two excited discrete zero order states |s, νs⟩ and |r, νr⟩ interacting with an optically inactive quasi-continuum where the widths of the resonances are comparable to or even exceed their spacing.

As in the previous simple case of an isolated resonance (Sec. III) we shall first evaluate the diagonal and the off diagonal elements of the scattering matrix \( T \) given by Eq. (II.3), which we shall rewrite in the form

\[
T(E) = V + V G(E) V,
\]

where the Green’s function \( G(E) \) has the form

\[
G(E) = (E_0^+ + E - H + i\eta)^{-1},
\]

with \( E_0 = E_0^+ + E = E_0^+ + kc \)

is the initial energy of the system. We are interested in the matrix elements

\[
T_{sa} = \langle b \mid T \mid a \rangle = \langle g, \nu_g; k_f, \nu_f \mid T \mid g, \nu_g; k, \nu \rangle
\]

and

\[
T_{ba} = \langle a \mid T \mid a \rangle = \langle g, \nu_g; k, \nu \mid T \mid g, \nu_g; k, \nu \rangle.
\]

As before, the first term of \( T \) (the interaction \( V \)) does not contribute so that the matrix elements in Eqs. (IV.4) and (IV.5) may be conveniently expanded in the form

\[
T_{ba} = \langle b \mid V \mid s \rangle G_{sa} \langle s \mid V \mid a \rangle + \langle b \mid V \mid r \rangle G_{sa} \langle r \mid V \mid a \rangle
\]

+ \langle b \mid V \mid s \rangle G_{sr} \langle r \mid V \mid a \rangle + \langle b \mid V \mid r \rangle G_{sr} \langle s \mid V \mid a \rangle.
\]

To avoid complicated notations |s⟩ and |r⟩ will stand for |s, νs⟩ and |r, νr⟩ as long as we do not need to specify explicitly the vibrational parts of these states. It is taken for granted that these are vacuum field states. We shall also use \( V \) as the interaction potential throughout the present discussion, keeping in mind that

\[
\langle a \mid V \mid s \rangle = \langle a \mid H_{\text{int}} \mid s \rangle; \quad \langle a \mid V \mid r \rangle = \langle a \mid H_{\text{int}} \mid r \rangle,
\]

\[
\langle b \mid V \mid s \rangle = \langle b \mid H_{\text{int}} \mid s \rangle; \quad \langle b \mid V \mid r \rangle = \langle b \mid H_{\text{int}} \mid r \rangle,
\]

\[
\langle t \mid V \mid s \rangle = \langle t \mid H_s \mid s \rangle; \quad \langle t \mid V \mid r \rangle = \langle t \mid H_s \mid r \rangle,
\]

\[
\langle s \mid V \mid r \rangle = \langle s \mid H_s \mid r \rangle.
\]

To proceed we shall evaluate the matrix elements of the Green’s operator \( G_{sa}, G_{sr}, G_{as}, \) and \( G_{rs} \) which appear in Eq. (IV.6). Utilizing the Dyson equation we have

\[
G = G_0 + G_0 V G_0 = G_0 + G V G_0,
\]

where

\[
G_0 = (E_0 - H_0 + i\eta)^{-1}; \quad \eta \rightarrow 0^+.
\]

Denoting by \( \{ \mid m \} \) the states in the radiative continua and making use of Eq. (IV.8), we may expand the various matrix elements of the Green’s operator in the form

\[
G_{sa} = G_{sa} V_0 (Z - E_0)^{-1} + \sum_l G_{sl} V_{ls} (Z - E_l)^{-1} + \sum_m G_{sm} V_{mr} (Z - E_m)^{-1},
\]

\[
G_{sa} = (Z - E_0)^{-1} V_{rs} G_{as} + \sum_l (Z - E_l)^{-1} V_{rt} G_{ts} + \sum_m (Z - E_m)^{-1} V_{rm} G_{mr},
\]

\[
G_{rt} = (Z - E_l)^{-1} V_{ls} G_{rs} + (Z - E_l)^{-1} V_{lt} G_{ts},
\]

\[
G_{ms} = G_{ms} V_{sm} (Z - E_m)^{-1} + G_{mr} V_{sm} (Z - E_m)^{-1},
\]

\[
G_{me} = (Z - E_m)^{-1} V_{ms} G_{me} + (Z - E_m)^{-1} V_{me} G_{me},
\]

\[
G_{es} = (Z - E_s)^{-1} (Z - E_e)^{-1} \sum_l V_{er} G_{ls} + (Z - E_e)^{-1} \sum_m V_{em} G_{mr} + (Z - E_e)^{-1} V_{re} G_{re},
\]

\[
G_{tr} = (Z - E_l)^{-1} V_{ls} G_{re} + (Z - E_l)^{-1} V_{lt} G_{re},
\]

\[
G_{mt} = (Z - E_m)^{-1} V_{ms} G_{re} + (Z - E_m)^{-1} V_{me} G_{re},
\]

\[
G_{re} = (Z - E_e)^{-1} (Z - E_e)^{-1} \sum_l V_{re} G_{ls} + (Z - E_e)^{-1} \sum_m V_{re} G_{mr},
\]

\[
G_{rt} = (Z - E_l)^{-1} V_{ls} G_{re} + (Z - E_l)^{-1} V_{lt} G_{re},
\]

\[
G_{ms} = G_{ms} V_{ms} (Z - E_m)^{-1} + G_{mr} V_{ms} (Z - E_m)^{-1},
\]

\[
G_{me} = (Z - E_m)^{-1} V_{ms} G_{me} + (Z - E_m)^{-1} V_{me} G_{me},
\]

\[
G_{es} = (Z - E_s)^{-1} (Z - E_e)^{-1} \sum_l V_{re} G_{ls} + (Z - E_e)^{-1} \sum_m V_{em} G_{mr} + (Z - E_e)^{-1} V_{re} G_{re},
\]

\[
G_{tr} = (Z - E_l)^{-1} V_{ls} G_{re} + (Z - E_l)^{-1} V_{lt} G_{re},
\]

\[
G_{mt} = (Z - E_m)^{-1} V_{ms} G_{re} + (Z - E_m)^{-1} V_{me} G_{re},
\]

\[
G_{re} = (Z - E_e)^{-1} (Z - E_e)^{-1} \sum_l V_{re} G_{ls} + (Z - E_e)^{-1} \sum_m V_{re} G_{mr},
\]

where

\[
Z = E_0 + i\eta.
\]
RESONANCE FLUORESCENCE FROM LARGE MOLECULES

Utilizing Eqs. (IV.10a)–(IV.10j) the desired matrix elements of the Green's operator are

\[ G_{ss} = \left[ E_n - \vec{E}_r + \frac{1}{2}(i) \Gamma_r - \frac{1}{2}(V_{rs} + \alpha - i\beta) \right] \left( V_{rs} + \alpha - i\beta \right)^{-1}, \]

\[ G_{sr} = \left( \langle V_{sr} + \alpha - i\beta \rangle \right) \left( [E_n - \vec{E}_r + \frac{1}{2}(i) \Gamma_r] \right) G_{ss}, \]

\[ G_{rs} = \left( \langle V_{sr} + \alpha - i\beta \rangle \right) \left( [E_n - \vec{E}_r + \frac{1}{2}(i) \Gamma_r] \right) G_{sr}, \]

\[ G_{rr} = \left( \langle E_n - \vec{E}_r + \frac{1}{2}(i) \Gamma_r \rangle \right) \left( [E_n - \vec{E}_r + \frac{1}{2}(i) \Gamma_r] \right) G_{ss}, \]

where, as usual, \((PP\) denotes the principal part) and

\[ \vec{E}_n = E_n + PP \sum_l \left[ \frac{1}{(E_n - E_l)} \right] + PP \sum_m \left[ \frac{1}{(E_n - E_m)} \right], \]

\[ \Gamma_n = \Gamma_n^L + \Gamma_n^M, \]

\[ \Gamma_n^K = 2\pi \sum_l |V_{nl}|^2 \delta(E_n - E_l), \]

\[ \Gamma_n^M = 2\pi \sum_m |V_{nm}|^2 \delta(E_n - E_m), \]

with \( n = r, s \), and where we have further defined the auxiliary functions

\[ \alpha = \alpha^M + \alpha^L; \]

\[ \beta = \beta^M + \beta^L, \]

\[ \alpha^K = PP \sum_k \left[ \langle V_{rk}V_{ks} \rangle \delta(E_n - E_k) \right], \]

\[ \beta^K = \pi \sum_k \langle V_{rk}V_{ks} \rangle \delta(E_n - E_k), \]

where \( K = L, M \) and \( k = l, m \). Note that \( \Gamma_n^M \) and \( \Gamma_n^M \) are identical with the radiative widths \( \Gamma_n^R \) and \( \Gamma_n^s \), respectively.

Defining now

\[ V_{sr} + \alpha = \gamma, \]

\[ V_{ns} + \alpha = \gamma, \]

we may replace \( V_{sr} + \alpha - i\beta \) by \( \gamma - i\beta \) and \( V_{ns} + \alpha - i\beta \) by \( \gamma - i\beta \) anywhere in Eqs. (IV.11)–(IV.13).

Throughout this discussion we shall assume that products of the form \( V_{rk}V_{ks} \) are real (which is true for the \( H_{inl} \) portion of \( V \), and also for the \( H \) contribution in the case of internal conversion). Then we set

\[ \alpha^K* = \alpha^K; \]

\[ \beta^K* = \beta^K \]

\( K = L, M \),

\[ V_{sr} = V_{rs}, \]

so that

\[ \gamma = \gamma*; \]

\[ \beta = \beta*, \]

and Eqs. (IV.11)–(IV.13) take the somewhat simpler form

\[ G_{ss} = (E_n - \vec{E}_r + \frac{1}{2}(i) \Gamma_r - (\gamma - i\beta) / (E_n - \vec{E}_r + \frac{1}{2}(i) \Gamma_r))^{-1}, \]

\[ G_{ss} = G_{rr} = (\gamma - i\beta / (E_n - \vec{E}_r + \frac{1}{2}(i) \Gamma_r) G_{ss}. \]

Equations (IV.11'), (IV.12'), and (IV.14) may now be inserted into Eq. (IV.6) to yield an explicit form of the \( T \) matrix elements. The procedure is straightforward. Making use of the definitions

\[ \langle k | \langle V | \langle s | V | a \rangle = \langle g, v_{s}; k_f, e_f | V | s; \text{vac} \rangle \langle s; \text{vac} | V | g, o_{g}; k, e \rangle \]

\[ = A_f(v_{g}), \]

\[ \langle k | \langle V | \langle r | V | a \rangle = \langle g, v_{r}; k_f, e_f | V | r; \text{vac} \rangle \langle r; \text{vac} | V | g, o_{g}; k, e \rangle \]

\[ = B_f(v_{g}), \]

\[ \langle k | \langle V | \langle r | V | a \rangle + \langle k | \langle V | \langle r | V | a \rangle = \langle g, v_{s}; k_f, e_f | V | s; \text{vac} \rangle \langle s; \text{vac} | V | g, o_{g}; k, e \rangle \]

\[ + \langle g, v_{r}; k_f, e_f | V | r; \text{vac} \rangle \langle r; \text{vac} | V | g, o_{g}; k, e \rangle \]

\[ = C_f(v_{g}), \]
and also
\begin{align*}
\langle a | V | s \rangle \langle s | V | a \rangle &= A_0, \\
\langle a | V | r \rangle \langle r | V | a \rangle &= B_0, \\
\langle a | V | s \rangle \langle r | V | a \rangle + \langle a | V | r \rangle \langle s | V | a \rangle &= 2 \langle a | V | s \rangle \langle r | V | a \rangle = C_0.
\end{align*}

The relevant matrix elements can be recast in the form
\begin{align}
T_{0a} &= X_f/Z, \\
T_{aa} &= X_0/Z,
\end{align}

where
\begin{align}
Z &= (E - E_{s0})(E - E_{e0}) - \frac{1}{2} (\Gamma_r \Gamma_r) + \beta \gamma + \frac{i}{2} [\Gamma_r (E - E_{s0}) - \Gamma_s (E - E_{e0}) + 4 \gamma \beta], \\
X_f(v_e) &= A_f(E - E_{e0}) + B_f(E - E_{e0}) + C_f \gamma + \frac{1}{2} i (A_f \Gamma_r + B_f \Gamma_s - 2 C_f \beta),
\end{align}

and
\begin{align}
X_0 &= \frac{E_e - E_{e0}}{E_e - E_{e0}}, \\
E_{e0} &= \frac{E_e - E_{e0}}{E_e - E_{e0}}.
\end{align}

The explicit expressions for the absorption cross section and for the scattering cross sections may be now easily obtained by applying Eqs. (11.6) and (11.10) and utilizing Eqs. (IV.28)-(IV.30), resulting in
\begin{align}
\sigma_a(E) &= \frac{1}{2} \pi \hbar^2 \left[ \frac{A_0(E - E_{e0}) + B_0(E - E_{e0}) + C_0 \gamma}{[\Gamma_r (E - E_{s0}) + \Gamma_s (E - E_{e0}) + 4 \gamma \beta]} \right] \\
&\quad \times \left[ E - E_{e0} - \frac{1}{2} (\Gamma_r \Gamma_r) + \beta \gamma + \frac{i}{2} [\Gamma_r (E - E_{s0}) - \Gamma_s (E - E_{e0}) + 4 \gamma \beta] \right]^{-1},
\end{align}

and
\begin{align}
\sigma_s(v_s; E) &= \frac{1}{2} \pi \hbar^2 \left[ \frac{A_f(E - E_{e0}) + B_f(E - E_{e0}) + C_f \gamma}{[\Gamma_r (E - E_{s0}) + \Gamma_s (E - E_{e0}) + 4 \gamma \beta]} \right] \\
&\quad \times \left[ E - E_{e0} - \frac{1}{2} (\Gamma_r \Gamma_r) + \beta \gamma + \frac{i}{2} [\Gamma_r (E - E_{s0}) - \Gamma_s (E - E_{e0}) + 4 \gamma \beta] \right]^{-1},
\end{align}

while the partial quantum yield is
\begin{align}
\gamma(v_s; E) &= \frac{1}{2} \pi \hbar^2 \left[ \frac{C_0(E - E_{e0}) + B_0(E - E_{e0}) + C_0 \gamma}{[\Gamma_r (E - E_{e0}) + \Gamma_s (E - E_{e0}) + 4 \gamma \beta]} \right] \\
&\quad \times \left[ E - E_{e0} - \frac{1}{2} (\Gamma_r \Gamma_r) + \beta \gamma + \frac{i}{2} [\Gamma_r (E - E_{s0}) - \Gamma_s (E - E_{e0}) + 4 \gamma \beta] \right]^{-1}.
\end{align}

Equation (IV.32), for the energy dependence of the absorption cross section, is a generalization of previous treatments of the linear shape of overlapping resonances\textsuperscript{7,8} where the radiative widths were neglected. A well-known feature of the earlier approximations is that the absorption cross section vanishes at some energy (located either inside or outside the energy range spanned by \( E_{s0} \) and \( E_{e0} \)) due to destructive interference effects. Now, let us state, at the risk of triviality, that if \( \sigma_a(E) = 0 \) at a certain energy \( E \), the quantum yield will be infinite (and a basic conservation law is violated) unless \( \sigma_s(v_s; E) = 0 \) at the same energy. Equation (IV.33) implies that the scattering cross section will vanish provided that the following two relations are satisfied:
\begin{align}
A_f(E - E_{e0}) + B_f(E - E_{e0}) + C_f \gamma &= 0, \\
A_f \Gamma_r + B_f \Gamma_s - 2 C_f \beta &= 0.
\end{align}

Note that condition (IV.35b) does not depend on the energy. We thus conclude that in general \( \sigma_s(v_s; E) \neq 0 \) for all \( E \). In order to avoid the unphysical divergence of the quantum yield, we must conclude that when the effects of radiative interactions are properly included, then (a) the absorption cross sections, are finite for all \( E \), and (b), the vanishing of \( \sigma_a(E) \), is determined by two conditions identical to (IV.35).

To demonstrate these points we shall apply a simpler version of our model invoking an additional assumption that the radiative interactions of the states \( s \) and \( r \) are equal, i.e., \( \langle a | V | s \rangle = \langle a | V | r \rangle \) and \( \langle b | V | s \rangle = \langle b | V | r \rangle \). For this simplified case one has
\begin{align}
A_0 &= B_0 = \frac{1}{2} C_0, \\
A_f &= B_f = \frac{1}{2} C_f
\end{align}

so that the conditions (IV.35) for the vanishing of the scattering cross section become
\begin{align}
2(E + \gamma - E_{e0} - E_{s0}) &= 0, \\
\Gamma_r + \Gamma_s - 4 \beta &= 0,
\end{align}

while straightforward manipulations of the numerator
of Eq. (IV.32) result in the following condition for the vanishing of the absorption cross section
\[
\left(\frac{1}{2} \Gamma_r - \beta^b \Gamma_r \right) \left( \Gamma_r + \frac{1}{2} \Gamma_r - 2\beta \right) + \left[ \frac{1}{2} \Gamma_r (E + \gamma - E_{eg})^2 + \frac{1}{2} \Gamma_r (E + \gamma - E_{eg})^2 \right] + 2\beta (E + \gamma - E_{eg}) (E + \gamma - E_{eg}) = 0.
\] (IV.38)

In Appendix A we demonstrate that the two terms on the rhs of the last equation may not be negative, which implies that Eq. (IV.38) can be satisfied only provided that both terms will simultaneously vanish. We further show in Appendix A that the requirement for the first term in (IV.38) to vanish is \( \Gamma_r = \Gamma_r = 2\beta \), and inserting this relation into the second term we end up with the two conditions (IV.37). The inclusion of the radiative interaction to infinite order is essential for this result. If radiative widths are neglected the identity \( \beta^b = \frac{1}{2} \Gamma_r \Gamma_r \) (see Appendix A) insures automatically the vanishing of the first term on the rhs of Eq. (IV.38) so that we are left with only a single energy condition for the vanishing of the absorption cross section while for the vanishing of the scattering cross section we still have to satisfy the two conditions (IV.37a) and (IV.37b). As the radiative contributions to the (energy independent) conditions (IV.35b) and (IV.37b) are small relative to the nonradiative widths, it is reasonable to assert that the energy conditions (IV.35a) or (IV.37a) specify the minima in the absorption cross section and in the scattering cross section, while the quantum yields remain finite and smaller than unity. Numerical calculations reported in Sec. V justify these tentative conclusions.

V. INTERFERENCE BETWEEN RESONANCES IN A HARMONIC MOLECULE

We shall now consider a simple model of an harmonic molecule characterized by identical displaced potential surfaces. The radiative interactions are governed by the appropriate Franck–Condon factors. The total radiative widths \( \Gamma_r^R = \Gamma_r^M \) and \( \Gamma_r^R = \Gamma_r^M \) and also the mixed width \( \beta^R = \beta^M \), may be evaluated in terms of the electronic–radiative matrix elements \( U \) [Eq. (B5)]. The details of the calculations are outlined in Appendices B and C. For the useful case where \( s \) and \( r \) correspond to the same electronic configuration, we were able to derive the following explicit expressions for the radiative widths:
\[
\Gamma_r^R = [16\pi Q/(2\pi hc)^2] U^2 J_{r,s},
\]
(V.1)
\[
\Gamma_r^R = [16\pi Q/(2\pi hc)^2] U^2 J_{r,s},
\]
(V.2)
\[
\beta^R = [8\pi Q/(2\pi hc)^2] U J_{r,s},
\]
(V.3)
where the matrix elements \( J_{r,s} \) are given by Eq. (C.6). In particular for the diagonal terms: \( u = v \) we get
\[
J_{r,s} = E - \hbar \omega (v + 1),
\]
(V.4)
while if \( v = u - 1 \), we obtain
\[
J_{r,v+1} = - (\hbar \omega \Delta/\sqrt{2}) (v + 1)^{1/2},
\]
(V.5)
where \( \Delta \) is the displacement of the origins of the potential surfaces normalized by the zero energy displacement.

General expressions for the nonradiative widths \( \Gamma_r^L \), \( \Gamma_r^L \) and the mixed nonradiative width \( \beta^L \) may also be evaluated for this model. The results obtained are:
\[
\Gamma_r^L = \hbar^{-1} \int_{-\infty}^{\infty} J_{r,s}^L (t) dt,
\]
(V.6a)
\[
\Gamma_r^L = \hbar^{-1} \int_{-\infty}^{\infty} J_{r,s}^L (t) dt,
\]
(V.6b)
\[
\beta^L = \hbar^{-1} \int_{-\infty}^{\infty} J_{r,s}^L (t) dt,
\]
(V.6c)
where the matrix elements \( J_{r,s}^L (t) \) are given by
\[
J_{r,s}^L (t) = \sum_k \tilde{C}_r \tilde{C}_s \delta_{\omega t} \exp [-i (E_r - E_r) (t/\hbar)]
\]
\[
\times \left[ (v_r + 1) \exp (i \omega t) + v_r \exp (-i \omega t) \right] \prod \tilde{g}_{\omega t} (t),
\]
(V.7)
where \( \tilde{C}_r \) and \( \tilde{C}_s \) are electronic coupling matrix elements (in our case \( r = s \)) and where \( r \) and \( s \) are assumed to be characterized by equal occupation numbers \( v_r \) of the promoting modes \( \omega \) (otherwise they will not be coupled to the same nonradiative quasicontinuum \{ \{ l \} \}). \( E_r \) is the pure electronic origin of the manifold \( l \). \( \mu \) is the general mode index and \( g_{\omega t} (t) \) is given by
\[
g_{\omega t} (t) = \exp \left[-\frac{1}{2} (\Delta_{rs}^2 + \Delta_{ss}^2) - \frac{1}{2} \Delta_{ss} \Delta_{ss} \exp (i \omega t) \right]
\]
\[
\times \left[ (v_r + 1) \exp (i \omega t) + v_r \exp (-i \omega t) \right] \prod \tilde{g}_{\omega t} (t),
\]
(V.7)
in which \( \Delta_{rs} \) and \( \Delta_{ss} \) denote the displacements of the potential surfaces which correspond to the \( r \) and \( s \) states relative to the \( l \) potential surface (here of course \( \Delta_{ss} = \Delta_{rr} \), \( v_{rs} \) and \( v_{ss} \) are occupation numbers of the mode \( \mu \) in the \( r \) and \( s \) states and
\[
\lambda_{rs}^\mu (+) = (1/\sqrt{2}) (\Delta_{rr} - \Delta_{ss} \exp (-i \omega t)),
\]
(V.9)
The nonradiative widths may now be calculated utilizing Eqs. (V.6)–(V.9). However in the present discussion we shall regard the nonradiative widths as constant numbers, and shall introduce them as parameters of the theory. Equations (IV.28)–(IV.34) can be now utilized to yield explicit expressions for \( \sigma_r (E) \), \( \sigma_r (v_{rs}; E) \), and for \( \sigma_r (v_{rs}; E) \).

Finally it is of interest to evaluate the total cross section for fluorescence, by summing up the contributions due to all final | \( g \); \( v_g \) | molecular levels. The
procedure is outlined in Appendix D, the final result is
\[
\sigma_R(E) = \sum_{\nu_e} \sigma_R(\nu_e; E) = \left[ 2Q^2/\pi(\hbar c)^4 \right] (X^T/Z),
\]
where \( Z \) is given by Eq. (1V.29) and \( X^T \) is
\[
X^T = \sum_{\nu_e} E^2(\nu_e) \left| X_f(\nu_e) \right|^2
\]
with
\[
E_f(\nu_e) = E + E_e - E_{\nu_e} = E - \hbar \omega \nu_e
\]
the energy of the emitted photon. \( X^T \) is evaluated in Appendix D and can be expressed in the form
\[
X^T = \left( \frac{U^A}{E} \right) \left[ (X_a^2 + X_b^2) J_{\nu_e, \nu_e} + (X_e^2 + X_f^2) J_{\nu_e, \nu_e} \right]
+ 2(\bar{X}_a X_a + \bar{X}_b X_b) J_{\nu_e, \nu_e},
\]
where
\[
X_a = \frac{1}{2} \left( \langle \sigma_e | \nu_e \rangle \Gamma_{\nu_e} - 2 \langle \sigma_e | \nu_e \rangle \beta \right),
\]
\[
X_b = \langle \sigma_e | \nu_e \rangle (E - E_{\nu_e}) + \langle \sigma_e | \nu_e \rangle \gamma,
\]
\[
X_e = \frac{1}{2} \left( \langle \sigma_e | \nu_e \rangle \Gamma_{\nu_e} - 2 \langle \sigma_e | \nu_e \rangle \beta \right),
\]
\[
X_f = \langle \sigma_e | \nu_e \rangle (E - E_{\nu_e}) + \langle \sigma_e | \nu_e \rangle \gamma.
\]
The same procedure leads also to an expression for the total quantum yield which is simply given by
\[
Y(E) = \sigma_R(E)/\sigma_0(E).
\]
In Fig. 1 we display some typical results of numerical calculations for the absorption and emission cross sections, and for the emission quantum yields. Figure 1 represents linear plots which are of experimental interest. For these model calculations \( g^0 \) has been chosen to be the vibrationless level of the ground electronic state while \( g^0 \) was taken as the first excited totally symmetric vibrational state of the ground state electronic manifold (i.e., \( \nu = 1 \)). | \( s \rangle \) and | \( r \rangle \) were chosen to be the zero and the first totally symmetric excited vibrational levels of an excited electronic state whose potential surface is displaced relative to that of the ground electronic state by an amount \( \Delta \), which may be positive or negative. The nonradiative width of the states | \( s \rangle \) and | \( r \rangle \) were assumed to be independent on the energy and were assigned values of 500 and 100 cm\(^{-1}\) in different cases. The radiative widths were calculated according to Eqs. (V.1)–(V.3) choosing the electronic matrix.
and quantum yields are multiplied by the following numerical factors: (a) $\sigma_a(E)$ ($\times 10^8$), $\sigma_B(E)$ ($\times 2 \times 10^9$), $\sigma_B(E)$ ($\times 10^9$), (b) Same factors as in Fig. 1(a) for $\sigma_a$, $\sigma_B(E)$ and $\sigma_B$, $\gamma(E)$ ($\times 10^9$), (c) and (d) $\sigma_a(E)$ ($\times 10^8$), $\sigma_B(E)$ ($\times 5 \times 10^8$), $\sigma_b(E)$ ($\times 10^8$), (e) $\sigma_a(E)$ ($\times 10^8$), $\sigma_B(E)$ ($\times 5 \times 10^8$), $\sigma_B(E)$ ($\times 2 \times 10^8$), (f) Same factors as in Fig. 1(c) for $\sigma_a$, $\sigma_B(E)$ and $\sigma_B$, $\gamma(E)$ ($\times 10^9$), (g) and (h) $\sigma_a(E)$ ($\times 10^8$), $\sigma_B(E)$ ($\times 5 \times 10^8$), $\sigma_B(E)$ ($\times 2 \times 10^8$).

Element $U$ so that $\Gamma, E \sim 10^{-4}$ cm$^{-1}$. The electronic energy gap was taken to be 20000 cm$^{-1}$ while the molecular frequency was chose as 1000 cm$^{-1}$ in both electronic states. The parameter $\Delta$ takes the (normalized) values $\pm 0.2$ and $\pm 0.8$. The numerical results obtained [Figs. 1 and 2] lead to the following conclusions:

1. As expected interference between the two resonances affects the absorption line shape. In contrast to the simplified model previously employed where higher order radiative contributions were neglected, the absorption cross section does not vanish in the region of destructive interference, but assumes a very small value depending on the radiative widths of the resonances.

2. Depending on the sign of $\Delta$ we encounter destructive interference in the absorption and in the emission cross sections either inside or outside the energy region located between the absorption (or emission) peaks. A similar effect is obtained by changing the sign of $\beta$, as may be seen from Eqs. (IV.32) and (IV.33). When destructive interference occurs in one of the above mentioned energy regions, constructive interference is encountered in the other region.

The dependence of the interference effects on the sign of the displacement is of interest. This effect originates from the dependence of the cross sections [Eqs. (IV.32) and (IV.33)] on the relative signs of the radiative coupling matrix elements $\langle a | V | s \rangle$ and $\langle a | V | r \rangle$ (or $\langle b | V | s \rangle$ and $\langle b | V | r \rangle$). These matrix elements depend on the relative signs of the corresponding vibrational overlap factors, which in turn are determined by the sign of $\Delta$. We have recently discussed this effect for simplified model where the contribution of the radiative widths to the interference effects is neglected.

3. The most striking effect encountered for this model system is the occurrence of a sharp maximum in the partial and in the total quantum yields in the vicinity of the dip in the absorption cross section. From the mathematical point of view this effect originates from the observation that in the vicinity of this "dip" the absorption cross section decreases more
VI. THE ROLE OF A RADIATIVELY IMPOTENT STATE

We shall now consider a special case of the general problem discussed in Sec. IV, whereupon the zero order state \( |r \rangle \) does not carry oscillator strength from the ground state. The physical situation where a pair of zero order discrete states are mutually coupled and interact with several optically inactive quascontinua, while one of these discrete states is characterized by a vanishingly small oscillator strength, is of considerable interest for the understanding of intermediate coupling cases in large molecules.\(^{14}\) The general results [Eqs. (IV.32)–(IV.34)] are now simplified by taking

\[
B_0 = C_0 = C_r = B_r = 0, \quad \Gamma_r = 0, \quad \beta = \beta^2, \quad \Gamma_r \Gamma_r - \beta^2 + \gamma^2 \quad (E - E_{eq})^2
\]

Inserting Eqs. (VI.1)–(VI.4) into Eqs. (IV.32)–(IV.34), we obtain

\[
\sigma_a(E) = \frac{2A_0}{\hbar \omega_c} \left[ \Gamma_r \Gamma_r - \beta^2 + \gamma^2 \right] \left[ \frac{1}{2} \Gamma_r \right] \left[ (E - E_{eq})^2 + \Gamma_r \right] \left[ \frac{1}{4} \right] \left[ \frac{1}{2} \Gamma_r \right] \left[ (E - E_{eq})^2 + \Gamma_r \right] \left[ \frac{1}{4} \right] \left[ \frac{1}{2} \Gamma_r \right] \left[ (E - E_{eq})^2 + \Gamma_r \right] \left[ \frac{1}{4} \right] \left[ \frac{1}{2} \Gamma_r \right]
\]

\[
Y(v_s; E) = \frac{2Qk_e^2}{\pi \hbar c A_0} \left[ (E - E_{eq})^2 + \left( \frac{1}{2} \Gamma_r \right)^2 \right] \left[ (E - E_{eq})^2 + \left( \frac{1}{2} \Gamma_r \right)^2 \right] \left[ (E - E_{eq})^2 + \left( \frac{1}{2} \Gamma_r \right)^2 \right]
\]

Now, making use of Eqs. (IV.26a) and (IV.27a), we note that \( A_r \) and \( A_0 \) may be expressed in terms of the partial radiative widths of the state \( s \) in the forms

\[
A_r = \Gamma_r \left[ (2\pi \hbar c)^{1/4} / 16\pi^2 Q E_r E_r \right], \quad | A_r |^2 = \Gamma_r \Gamma_r \left[ (2\pi \hbar c)^{1/4} / 16\pi^2 Q E_r E_r \right].
\]
Inserting Eqs. (VI.8) and (VI.9) into Eqs. (VI.5)–(VI.7), we obtain

\[
\sigma_\sigma(E) = \frac{1}{2} \frac{h^2}{k} \Gamma_s \left[ \frac{\Gamma_s + \frac{4\gamma\beta}{E - E_{gg}}}{(E_{gg} - E)^2} \Gamma_r \right] \times \left[ \left( E - E_{gg} - \frac{\Gamma_s \Gamma_r - \beta^2 + \gamma^2}{E - E_{gg}} \right)^2 + \frac{1}{4} \left( \frac{\Gamma_s + \Gamma_r}{E - E_{gg}} \frac{E - E_{gg}}{E - E_{gg}} + \frac{4\gamma\beta}{E - E_{gg}} \right)^2 \right]^{-1},
\]

(VI.10)

\[
\sigma_R(v_o; E) = \frac{1}{2} \frac{h^2}{k} \Gamma_s \Gamma_r \left[ 1 + \left( \frac{\Gamma_r}{E - E_{gg}} \right)^2 \right] \times \left[ \left( E - E_{gg} - \frac{\Gamma_s \Gamma_r - \beta^2 + \gamma^2}{E - E_{gg}} \right)^2 + \frac{1}{4} \left( \frac{\Gamma_s + \Gamma_r}{E - E_{gg}} \frac{E - E_{gg}}{E - E_{gg}} + \frac{4\gamma\beta}{E - E_{gg}} \right)^2 \right]^{-1},
\]

(VI.11)

\[
Y(v_o; E) = \Gamma_s \left[ (E - E_{gg})^2 + (\frac{\Gamma_s}{E - E_{gg}})^2 \right] \left[ (E - E_{gg})^2 \Gamma_r + (E - E_{gg}) \Gamma_r + (\frac{\Gamma_s}{E - E_{gg}})^2 \right]^{-1}
\]

(VI.12)

By summing up the partial quantum yields we get the total fluorescence quantum yield in the form

\[
Y(E) = \Gamma_r \left[ (E - E_{gg})^2 + (\frac{\Gamma_r}{E - E_{gg}})^2 \right] \left[ (E - E_{gg})^2 \Gamma_s + (E - E_{gg}) \Gamma_s + (\frac{\Gamma_s}{E - E_{gg}})^2 \right]^{-1}
\]

(VI.13)

In a similar way the total cross section for resonance fluorescence may be obtained from Eq. (VI.11) by replacing \( \Gamma_r \) by \( \Gamma_r^R \). We note at this point that the results Eqs. (VI.10)–(VI.13) are readily seen to reduce to the single resonance expressions of Sec. II when the contribution of the state \( r \) vanishes, e.g., when \( E - E_{gg} \to \infty \), or when \( \gamma \), \( \beta \), and \( \Gamma_r \) are set equal to zero.

The general model discussed herein can be applied to account for interference phenomena in the radiative decay of the first excited singlet state of the biacetyl molecule. Calculations were previously performed\(^{14b}\) using a formalism which corresponds to a short time excitation experiment, invoking the assumption that at time \( t = 0 \) the pure quantum state \( | s \rangle \) has been populated. The model applied was a simpler version of the present model which assumed that the states \( | s \rangle \) and \( | r \rangle \) are not coupled to the same continuum so that \( \Gamma_{sr} \) vanishes. On the other hand, the interaction \( V_{sr} \) was taken to be different from zero, so that \( | \gamma | = | V_{sr} | \).

In this case Eq. (VI.13) is

\[
Y(E) = \Gamma_r \left[ (E - E_{gg})^2 + (\frac{\Gamma_r}{E - E_{gg}})^2 \right] \left[ (E - E_{gg})^2 \Gamma_s + (E - E_{gg}) \Gamma_s + (\frac{\Gamma_s}{E - E_{gg}})^2 \right]^{-1}
\]

(VI.14)

Alternatively we can recast the quantum yield in the final form

\[
Y(E) = \left( \frac{\Gamma_r^R}{\Gamma_r} \right) \left( 1 + \left| \frac{V_{sr}}{\Gamma_r} \right|^2 \right)^{-1} \left( \frac{\Gamma_s}{(E - E_{gg})^2 + (\frac{\Gamma_s}{E - E_{gg}})^2} \right)^{-1}
\]

(VI.15)

**Fig. 3.** Total emission quantum yield as a function of \( \Gamma_r \) for broad pulse (coherent) excitation (- - -) and for long time narrow bandwidth excitation: (---). \( E \) for the second case is taken to be equal to \( E_o \). The molecular parameters employed are identical to those employed in Ref. 14(b), namely \( \Gamma_r^R = 1.0 \times 10^6 \text{ cm}^{-1}, | V_{sr} | = 1.0 \times 10^4 \text{ cm}^{-1} \), and \( \Gamma_s = 1.0 \times 10^4 \text{ cm}^{-1} \) for case II.**

The following comments are now in order:

(a) Equation (VI.15) corresponds to a narrow band excitation and thus the quantum yield exhibits energy dependence.

(b) The quantum yield will take the limiting (energy independent) value \( Y \to \Gamma_r^R/\Gamma_r \) under the following conditions: (b1) \( \Gamma_r = 0 \), (b2) \( \Gamma_r \to \infty \), (b3) \( V_{sr} = 0 \) and (b4) \( E - E_{gg} \to \infty \). The conditions (b1), (b2), and (b4) exhibit the limiting cases where the problem at hand reduces to the simple case of an isolated resonance \( | \gamma | \). The condition (b4) is in fact of minor experimental interest as in this energy range \( \sigma_\sigma(E) \to 0 \).

(c) When externally induced vibrational relaxation is considered it can be speculated\(^{14b}\) that \( \Gamma_r \) linearly depends on pressure. In this case we can consider the dependence of the quantum yield on the width \( \Gamma_r \) for a constant excitation energy \( E \). The quantum yield will exhibit a minimum when \( \Gamma_r = | E - E_{gg} | \).

(d) For the widths \( \Gamma_r \), which satisfy the condition
the quantum yield takes the form
\[
Y(E) = \frac{\Gamma_r^R}{\Gamma_r + \left[ | V_{sr} |^2 / (E - E_{re})^2 \right] \Gamma_r}. \tag{VI.16}
\]
Now provided that \( \Gamma_r \) is linearly dependent on the pressure, Eq. (VI.16) is the quantum mechanical analog of the Stern Volmer relation for the case of narrow band excitation.

We have considered the decay characteristics of a pair of coupled discrete zero order states one of which is optically active, studied by narrow band and long time optical excitation. These results for the quantum yield are of course different from those previously obtained for a short time coherent excitation of the zero order \( | s \rangle \) state. It should be noted that for the coherent excitation case the quantum yield is of course energy independent and the relevant energy parameter is the separation of the zero order states \( | E_{re} - E_{re} | \). While in the present experiment the quantum yield is energy dependent. The general structure of the quantum yield expression for the short time excitation [Ref. 14b, Eq. (9)], and for the long time excitation [Eq. (VI.15)] is different. The results of numerical model calculations for this system are displayed in Figs. 2 and 3. In Fig. 3 we present some numerical results comparing the dependence of the quantum yield on \( \Gamma_r \) for short time and for long time narrow bandwidth excitation experiments. The general functional behavior of the quantum yield on \( \Gamma_r \) is similar in both cases, however, the two physical situations differ in quantitative details. The experimental results of Drendt and Kommandeur are not detailed enough to distinguish between these cases. Careful monitoring of the decay of bisacetyl and similar systems by a narrow band CW dye laser will provide interesting experimental information concerning the difference between coherent and narrow band excitation. These results provide the first complete example pertaining to the interesting problem of how does the "preparation" of the excited optical state affect its decay characteristics.

\section*{VII. INTERFERENCE WITH BACKGROUND ABSORPTION}

We have previously demonstrated that when the two electronic level system \( | s \rangle \) and \( | l \rangle \) is employed within the framework of the adiabatic representations the quasicontinuum \( | l \rangle \) does carry oscillator strength from the ground state. As the transition moment for the \( | g_0 \rangle \rightarrow | l \rangle \) transition is proportional to the transition moment \( | g_0 \rangle \rightarrow | s \rangle \), a simple Fano type line shape will result. We shall now consider the cross sections for absorption and for resonance fluorescence for a system characterized by an excited discrete state interacting with a quasicontinuum when the latter is optically active. This model still implies that the spacing between resonances exceeds their widths. A further, physically reasonable assumption which we shall impose is that the nonradiative width of the resonance considerably exceeds its radiative width.

The cross section for absorption is now given by Eq. (II.7) in the explicit form
\[
\sigma_a(E) = -(2Q/\hbar c) \text{Im} \{ \langle g, o_g | k, e | H_{\text{int}} | s; \text{vac} \rangle \\
\times G_{st}(s; \text{vac} | H_{\text{int}} | g, o_g | k, e) \\
+ \sum_i (g, o_g | k, e | H_{\text{int}} | l; \text{vac} \rangle \\
\times G_{st}(s; \text{vac} | H_{\text{int}} | g, o_g | k, e) \\
+ \sum_i (g, o_g | k, e | H_{\text{int}} | s; \text{vac} \rangle \\
\times G_{st}(s; \text{vac} | H_{\text{int}} | g, o_g | k, e) \\
+ \sum_{i, \nu} (g, o_g | k, e | H_{\text{int}} | l; \text{vac} \rangle \\
\times G_{st}(s; \text{vac} | H_{\text{int}} | g, o_g | k, e) \}, \tag{VII.1}
\]
where we have defined
\[
G_{ij} = \langle i; \text{vac} | (E_0 + E - H + i\eta)^{-1} | j; \text{vac} \rangle, \quad i, j = s, \{ l \}. \tag{VII.2}
\]
At this stage we shall invoke the assumption that the radiative widths are negligible compared to the nonradiative intramolecular width due to \( s \rightarrow l \) coupling via \( H_s \). This assumption is not necessary; however, the general treatment of the problem including the contribution of radiative coupling to the matrix elements (III.2) is very cumbersome, as the radiative damping matrix is nondiagonal. As has been demonstrated in section V these radiative contributions are of minor importance except for energies close to the dip which originates from destructive interference in the absorption cross section. It is thus expected that our approximation will result in the correct general behavior of the absorption and emission cross sections except that the calculated quantum yield will exhibit an unphysical divergence near the interference dip.

Invoking this approximation for the calculation of Eq. (III.2) we utilize the (approximate) relation
\[
(E_0 + E - H + i\eta)^{-1} = (E_0 + E - H_0 + i\eta)^{-1} \\
+ (E_0 + E - H_0 + i\eta)^{-1}H_s(E_0 + E - H + i\eta)^{-1}, \tag{VII.3}
\]
which immediately leads to the results
\[
G_{st} = G_{st}(H_s)_{st}(E - E_{10} + i\eta)^{-1},
\]
\[
G_{st} = (E - E_{10} + i\eta)^{-1}(H_s)_{st}G_{st},
\]
\[
G_{st} = \left[ \delta_{st} / (E - E_{10} + i\eta) \right] \\
+ (E - E_{10} + i\eta)^{-1}(H_s)_{st}G_{st}(H_s)_{st}(E - E_{10} + i\eta)^{-1},
\]
\[
G_{st} = (E - E_{10} + i\eta)^{-1}, \tag{VII.4}
\]
where \( E_{10} = E_1 - E_{0g}, \ E_{0g} = E_0 - E_{0g} \), and the width is
\[
\Gamma_r^R = 2\pi \sum_i | \langle s | H_s | l \rangle |^2 (E_i - E_0), \text{ as before.}
\]
From Eqs. (VII.1)–(VII.4) the absorption cross section...
section is
\[ \sigma_a(E) = - \frac{(2Q/\hbar c)}{E} \times \text{Im} \left\{ \sum_i \left[ \langle g, o_i; k, e | H_{\text{int}} | l; \text{vac} \rangle |^{2} / (E - E_{1g} + i\eta) \right] \right. \]
\[ + G_{\text{int}} \langle g, o_i; k, e | H_{\text{int}} | s; \text{vac} \rangle + \alpha - i\beta \]
\[ \times \langle \langle s; \text{vac} | H_{\text{int}} | g, o_i; k, e \rangle + \alpha^* - i\beta^* \rangle, \]  
(VII.5)
where, in this section,
\[ \alpha = \text{PP} \sum_i \langle g, o_i; k, e | H_{\text{int}} | l; \text{vac} \rangle \langle l; \text{vac} | H_{\text{int}} | s; \text{vac} \rangle E - E_{1g} \]  
(VII.6a)
\[ \beta = \pi \sum_i \langle g, o_i; k, e | H_{\text{int}} | l; \text{vac} \rangle \times \langle l; \text{vac} | H_{\text{int}} | s; \text{vac} \rangle \delta(E - E_{1g}) \]  
(VII.6b)
In the statistical limit, the summations over the index \( l \) represent integrals over the density of states \( \rho_l \) in the \( \{ l \} \) manifold. \( \text{PP} \) represents the principle part of such an integral, \( \alpha \) and \( \beta \) represent again “mixed type” level shift and widths terms. It is also worthwhile to note that now
\[ | \beta |^2 = \frac{2\pi \Gamma_{r}^L}{\hbar} \sum_i \langle g, o_i; k, e | H_{\text{int}} | l; \text{vac} \rangle |^{2} \delta(E - E_{1g}). \]  
(VII.7)
Defining now the Fano reduced energy \( \epsilon \) and the line shape index \( q \), in the conventional form
\[ \epsilon = (E - E_{1g}) / \frac{2}{\hbar} \Gamma_{r}^L, \]  
(VII.8a)
\[ q = \frac{\langle g, o_i; k, e | H_{\text{int}} | s; \text{vac} \rangle + \alpha}{\beta}, \]  
(VII.8b)
we note that \( q \) is real for internal conversion between nondegenerate states. Thus Eqs. (VII.4)–(VII.7) result in the familiar expression
\[ \sigma_a(E) = \frac{(2Q/\hbar c)}{E} \times \text{Im} \left\{ \sum_i \langle g, o_i; k, e | H_{\text{int}} | l; \text{vac} \rangle |^{2} / (E - E_{1g}) \right\} \times (\epsilon + q)^2 / (1 + \epsilon)^2. \]  
(VII.9)
We shall define the radiative decay width \( \Gamma_{r}^* \) resulting from the spontaneous decay of \( \{ l; \text{vac} \} \) to \( \langle g, o_i; k_f, e_f \rangle \), utilizing the same procedure which leads to Eq. (III.5) :
\[ \Gamma_{r}^* = \left[ \frac{16\pi^2 k^3 Q}{(2\pi \hbar)^5} \right] \langle \langle l; \text{vac} | H_{\text{int}} | g, o_i; k_f, e_f \rangle |^{2}. \]  
(VII.10)
The absorption cross (VII.9) can be rewritten in the form
\[ \sigma_a(E) = \pi^2 (\hbar/k)^2 \sum_i \Gamma_{r}^L \delta(E_{1g} - E) [\epsilon + q]^2 / (1 + \epsilon)^2]. \]  
(VII.11)
It should be noted that (1) we have neglected the radiative contribution to \( \Gamma_{s}. \) (2) \( q \) is assumed to be real. (3) The directions of the interfering transitions in the dipole approximation are equal. (4) When \( q \rightarrow \infty \) Eqs. (VII.7) and (VII.11) result in the simple case (III.9), only that \( \Gamma_{s} = \Gamma_{r}^s + \Gamma_{r}^L \) is replaced by \( \Gamma_{r}^L. \)
We shall now consider the cross section for resonance fluorescence utilizing Eqs. (II.8)–(II.11). The off-diagonal matrix elements of the \( T \) matrix are
\[ I(v_o; E) = \langle g, o_i; k, e | T | g, v_o; k_f, e_f \rangle = \langle g, o_i; k, e | H_{\text{int}} | s; \text{vac} \rangle G_{\text{int}}(s; \text{vac} | H_{\text{int}} | g, v_o; k_f, e_f) \]
\[ + \sum_i \langle g, o_i; k, e | H_{\text{int}} | l; \text{vac} \rangle G_{\text{int}}(l; \text{vac} | H_{\text{int}} | g, v_o; k_f, e_f) \]
\[ + \sum_i \langle g, o_i; k, e | H_{\text{int}} | l; \text{vac} \rangle G_{\text{int}}(l; \text{vac} | H_{\text{int}} | g, v_o; k_f, e_f) \]
\[ + \sum_i \sum_{\eta} \langle g, o_i; k, e | H_{\text{int}} | l; \text{vac} \rangle \delta(E - E_{1g}), \]  
(VII.12)
which have, of course, identical structures to the diagonal element \( T_{ss} \), Eq. (VII.1). Invoking again the assumption that the radiative widths are negligible relative to the nonradiative width we shall utilize Eqs. (VII.4) for the matrix elements of the Green’s function. It will be convenient at this stage to define the auxiliary functions:
\[ B(v_o; E) = \text{PP} \sum_i \left[ \langle g, o_i; k, e | H_{\text{int}} | l; \text{vac} \rangle \langle l; \text{vac} | H_{\text{int}} | g, v_o; k_f, e_f \rangle / (E - E_{1g}) \right] \]  
(VII.13a)
\[ C(v_o; E) = \pi \sum_i \langle g, o_i; k, e | H_{\text{int}} | l; \text{vac} \rangle \langle l; \text{vac} | H_{\text{int}} | g, v_o; k_f, e_f \rangle \times \delta(E - E_{1g}), \]  
(VII.13b)
and
\[ \gamma(v_o; E) = \text{PP} \sum_i \left[ \langle s; \text{vac} | H_{\text{int}} | l; \text{vac} \rangle \langle l; \text{vac} | H_{\text{int}} | g, v_o; k_f, e_f \rangle / (E - E_{1g}) \right] \]  
(VII.14a)
\[ \delta(v_o; E) = \pi \sum_i \langle s; \text{vac} | H_{\text{int}} | l; \text{vac} \rangle \langle l; \text{vac} | H_{\text{int}} | g, v_o; k_f, e_f \rangle \delta(E - E_{1g}). \]  
(VII.14b)
Utilizing Eqs. (VII.6), (VII.13), and (VII.14), Eq. (VII.12) takes the form
\[ I(v_o; E) = B(v_o; E) - iC(v_o; E) + G_{\text{int}}(\langle g, o_i; k, e | H_{\text{int}} | s; \text{vac} \rangle + \alpha - i\beta \]
\[ \times \langle s; \text{vac} | H_{\text{int}} | g, v_o; k_f, e_f \rangle + \gamma(v_o; E) - i\delta(v_o; E)) \right]. \]  
(VII.15)
Defining two line index parameters,

\[ q = (\langle g, o_s; k, e | H_{\text{int}} | s; \text{vac} \rangle + \alpha) / \beta, \]  

\[ \hat{q} = [\langle s; \text{vac} | H_{\text{int}} | g, v_s; k_j, e_{j*} \rangle + \gamma(v_s; E)] / \delta(v_s; E), \]  

and utilizing (VII.4), Eq. (VII.15) takes the form

\[ I(v_s; E) = B(v_s; E) - iC(v_s; E) + \left[ \beta \delta(v_s; E) / \frac{1}{2} \Gamma_T \right] [(q-i)/(q+i)] \]  

where \( q \) and \( \hat{q} \) are real.

It can now be easily shown that

\[ \beta \delta = \frac{1}{2} \Gamma_T C(v_s; E) \]  

so that when the level shift term \( V(v_s; E) \) is disregarded, Eq. (VII.17) becomes

\[ I(v_s; E) = C(v_s; E) \left[ -\epsilon + q \hat{q} - i(q+\hat{q}) \right] / (\epsilon+i) \]  

The relevant term in Eq. (II.4) is now

\[ \left| I(v_s; E) \right|^2 = \left| C(v_s; E) \right|^2 \left[ \left| q \right|^2 + \left| q \right|^2 + \left| \hat{q} \right|^2 + 2q \hat{q} + 2(\epsilon+q+\hat{q}) \right] / (1+\epsilon^2) \]  

The cross section for resonance scattering is now obtained from Eqs. (II.10) and (VII.20):

\[ \sigma_R(v_s; E) = (\pi Q / h\epsilon) \sum_n \sum_{\alpha \beta} \int dQ_{\alpha \beta} \rho_f \left| C(v_s; E) \right|^2 \times \left[ \left| q \right|^2 + \left| q \right|^2 + \left| \hat{q} \right|^2 + 2q \hat{q} + 2(\epsilon+q+\hat{q}) \right] / (1+\epsilon^2) \]  

where Eq. (VII.13b) yields

\[ \left| C(v_s; E) \right|^2 = \pi \sum_l \left| \langle g, o_s; k, e | H_{\text{int}} | l; \text{vac} \rangle \right|^2 \times \Gamma_{\text{res}}^2 (E-E_{1g}) \times \pi \sum_l \left| \langle l; \text{vac} | H_{\text{int}} | g, v_s; k_j, e_{j*} \rangle \right|^2 \]  

Utilizing Eq. (VII.10) and (VII.22), Eq. (VII.21) is recast in the final form

\[ \sigma_R(v_s; E) = \pi (\hbar / k)^2 \sum_l \Gamma_{\text{res}}^2 (E_{1g} - E) \times \Gamma_{\text{res}}^2 (E_{1g} - E) \times \left[ \left| q \right|^2 + \left| q \right|^2 + \left| \hat{q} \right|^2 + 2q \hat{q} + 2(\epsilon+q+\hat{q}) \right] / (1+\epsilon^2) \]  

Now the quantum yield for resonance scattering into \( g, v_s \) [Eq. (II.12)] is given from (VII.11) and (VII.23) by

\[ Y(v_s; E) = \sum_l \Gamma_{\text{res}}^2 (E_{1g} - E) \times \left[ \left| q \right|^2 + \left| q \right|^2 + \left| \hat{q} \right|^2 + 2q \hat{q} + 2(\epsilon+q+\hat{q}) \right] / (\epsilon+q)^2 \]

\[ = \sum_l \Gamma_{\text{res}}^2 (E_{1g} - E) \left[ 1 + (\epsilon+q)^2 + 2(\epsilon+q)^2 / (\epsilon+q)^2 \right] \]  

Equations (VII.11), (VII.23), and (VII.24) summarize the features of the energy dependence of the absorption and the scattering cross sections and the quantum yield. These results are valid in the energy range where the contribution of the radiative widths can be disregarded. It is thus not surprising that these results exhibit a reasonable behavior in the limit \( \epsilon \to \infty \) where only the background continuum contributes to the quantum yield. On the other hand the divergence of the quantum yield at \( \epsilon = -q \) is unphysical, and can be amended (in principle) by incorporating the role of radiative corrections as done for the case of overlapping resonances (Sec. IV). From the results obtained in Sec. IV we can assert that the role of these radiative corrections in the present case will be important in the energy region from \( E = (-q-0.1) \) to \( E = (-q+0.1) \) [where the reduced energy scale (VII.8a) has been used]. Our expressions [Eqs. (VII.11), (VII.23), and (VII.24)] are valid outside this energy region.

**VIII. linewidths and resonance fluorescence in the case of an optically active continuum**

The concept of molecular eigenstates (which diagonalize the "exact" molecular Hamiltonian) played a central role in the understanding of molecular electronic relaxation process. However, it often happens that the treatment of general problems concerning resonance fluorescence and emission quantum yields is simplified by the utilization of another basis set. This is the case when a basis set can be chosen where only a single (or a small number of) zero order state(s) will carry oscillator strength from the ground state. It may happen that the only relevant physical information pertains to the "exact" molecular eigenstates of the system (or to a reasonable approximation to these states). The formulation of the optical line shape and the quantum yield problem must rest in this case on the molecular basis set. We have then to deal with photon scattering by a system which is characterized by a discrete ground state and an optically active continuum. A good physical example for such a system involves the direct optical photodissociation spectrum.
of diatomic and polyatomic molecules. In the case of predissociation it is self-evident that resonance fluorescence involving a metastable state can be legitimately considered and handled by the theoretical methods described in the present work. On the other hand, it is interesting to inquire whether resonance fluorescence will be observed when a molecule is optically pumped into a dissociative continuum. In the case of direct photodissociation the definition of a metastable state is fraught with conceptual difficulties, as we cannot define a zero order bound state, as in the case of predissociation. However, it is quite easy to demonstrate the existence of a finite quantum yield for resonance fluorescence. This quantum yield will be very low ($\sim 10^{-7}$) however with the utilization of high power laser sources this yield will be amenable to experimental observation.

When the physical properties of excited molecular states are interrogated by a long time experiment one can always define in a formal manner an “optically active state” $|s\rangle$ which carries the entire oscillator strength from the ground state, in the form

$$
|s\rangle = \sum_j |j\rangle \langle j | \mu | g\rangle / (\sum_j |j\rangle \langle j | \mu | g\rangle)^{1/2},
$$

where $\{ |j\rangle \}$ is the optically active continuum, $|g\rangle = |g, o_g, k, e\rangle$ is the ground electronic-vibrational state and $\mu$ is the transition moment. Note that the $|s\rangle$ state now carries all the oscillator strength from the ground state. The only restriction on the validity of this formal definition is that the optically accessible excited states $\{ |j\rangle \}$ (characterized by energies $E_j$ and density of states $\rho_j$) are confined to a limited energy region in the sense that $\rho_j |\langle j | \mu | g\rangle|^2$ decreases to zero faster than $E_j^{-1}$ outside this region. If the energy range of optically active excited states is bound according to the definition presented above, the sum specifying the $|s\rangle$ state converges and its definition is unique.

We shall now attempt to utilize the general formula of the resonance fluorescence problem employing the molecular basis $\{ |j\rangle \}$. A rather serious approximation involved in this approach is that high order radiative interactions are not included. However, we have demonstrated in Sec. V and VII that this approach is justified provided that in the relevant energy region distinctive interference effects can be disregarded. In the case of optical photodissociation we expect this approximation to be valid.

Turning now to the general formalism outlined in the previous section we are interested in the matrix elements of the $T$ operator:

$$
T_{ba} = \sum_j \sum_{j'} \langle b | V | j\rangle G_{j'j} \langle j | V | a\rangle = \sum_j \left[ \langle b | V | j\rangle \langle j | V | a\rangle / (E_a - E_j + i\eta) \right],
$$

where $|a\rangle = |g, o_a, k, e\rangle$ and $|b\rangle = |g, o_b, k, e\rangle$ represent single photon states. $|j\rangle = |j, \nu, \nu_c\rangle$ corresponds to an excited molecular eigenstates. When radiative interactions in $G$ are neglected it becomes diagonal in this molecular basis. Finally, $V$ corresponds just to the radiative interaction $H_{int}$, as the present basis set is diagonalized with respect to $H_{int}$.

For the line shape we now have $(E_a = E_b + E)$,

$$
\sigma_a(E) = -4Q/\hbar c \Im \langle a | V(E_a - H + i\eta) - V | a\rangle = (2\pi/\hbar c) \int dE_{i} \rho_i |\langle a | V | j\rangle|^2 \delta(E_a - E_i) = (2\pi/\hbar c) \sum_j |\langle a | V | j\rangle|^2 \rho_i (E_i = E_a).
$$

(VIII.2)

This is the trivial solution for the line shape of a photodissociation spectrum. In order to evaluate the scattering cross section we utilize Eqs. (II.10) and (VIII.1) which yield

$$
\sigma_B(o_g, E) = 2\pi (Qk_f/\hbar c)^2 \left| T_{ab} \right|^2
$$

$$
\times \left\{ \sum_j \left[ \right. \left| \langle b | V | j\rangle \langle j | V | a\rangle / (E_a - E_j + i\eta) \right] \right\}^2.
$$

(VIII.3)

In order to obtain a general formal expression for the cross sections and quantum yields we shall define the auxiliary functions,

$$
\tilde{F}(E) = -i \tilde{G}(E) = -i \int dE' \tilde{G}(E') = \sum_j \left[ \langle b | V | j\rangle \langle j | V | a\rangle / (E_a - E_j + i\eta) \right],
$$

where

$$
\tilde{F}(E) = PP \sum_j \left[ \langle b | V | j\rangle \langle j | V | a\rangle / (E_a - E_j) \right],
$$

$$
\tilde{G}(E) = \pi \sum_j \langle b | V | j\rangle \langle j | V | a\rangle \delta(E_a - E_j) = \pi \langle b | V | j\rangle \langle j | V | a\rangle \delta_{E_j = E_a}
$$

(VIII.5a)

(VIII.5b)

which are related by the dispersion relation

$$
\tilde{F}(E) = \pi^{-1} PP \left[ \tilde{G}(E') dE' / (E - E') \right].
$$

(VIII.5c)

In terms of these functions we get

$$
\sigma_a(o_g, E) = 2\pi (Qk_f/\hbar c)^2 \left[ \left| \tilde{F}(E) \right|^2 + \left| \tilde{G}(E) \right|^2 \right].
$$

(VIII.6)

Note that for the case of resonance scattering into the $|g, o_s\rangle$ molecular state, $|a\rangle$ and $|b\rangle$ are identical, and in this case we have

$$
\sigma_a(E) = (2Q/\hbar c) \tilde{G}(E),
$$

(VIII.7)
while the quantum yield takes the form

$$Y(o_2; E) = \sigma_2(o_2; E)/\sigma_a(E) = (\pi Qk^2/\hbar^2c) [\tilde{G}(E)^2 + \tilde{F}(E)^2]/\tilde{G}(E),$$

(VIII.8)

where we have assumed that $G$ and $F$ are real.

It will be useful at this stage to recast these general results in terms of the states $|s\rangle$ and $|s'\rangle$ which are coupled by $V$ to $|a\rangle$ and to $|b\rangle$, respectively. Defining,

$$|s\rangle = V |a\rangle/(\langle a | VV | a\rangle)^{1/2}$$

$$= \sum_j |j\rangle \langle j | V | a\rangle/\langle \sum_j |a\rangle \langle j | V \rangle \langle j | V | a\rangle \rangle^{1/2}$$

(VIII.9a)

and

$$|s'\rangle = V |b\rangle/\langle b \rangle \langle VV | b\rangle \rangle^{1/2}$$

$$= \sum_j |j\rangle \langle j | V | b\rangle/\langle \sum_j \langle b \rangle \langle j | V \rangle \langle j | V | b\rangle \rangle^{1/2},$$

(VIII.9b)

we rewrite Eqs. (VIII.2) and (VIII.3) in the form

$$\sigma_a(E) = (2\pi Q/\hbar c) \langle a | V | s\rangle^2 \langle j | s \rangle \delta_{p_j | E_a = E_s}$$

(VIII.10a)

and

$$\sigma_B(o_2; E) = 2\pi Qk^2/\hbar^2c |dE|L(E_j) (E_a - E_j + i\eta)^{-1} \eta/L(E_a),$$

(VIII.10b)

In the case of resonance fluorescence to $g, o_2$ we have again $|a\rangle = |b\rangle$ and the quantum yield takes the simple form

$$Y(o_2; E) = \sigma_2(o_2; E)/\sigma_a(E) = \gamma^R \left[ \int dE_j L(E_j) (E_a - E_j + i\eta)^{-1} \eta/L(E_a) \right],$$

(VIII.11)

where

$$\gamma^R = (Qk^2/\hbar^2c) \langle a | V | s\rangle^2,$$

(VIII.12a)

while

$$L(E_j) = \langle s | j \rangle \delta_{p_j} \quad L(E_a) = L(E_j) \delta_{E_a = E_s}.$$

(VIII.12b)

The width $\gamma^R$ represents the pure radiative width of the "zero order state" (or rather the wave packet) $|s\rangle$.

$L(E_j)$ is the (normalized) absorption line shape. Equation (VIII.11) implies that the quantum yield for resonance fluorescence is determined by the Hilbert transform of the line shape function. This general statement pertaining to a "long time experiment" is complementary to the well known result that the decay pattern in a "short time experiment" is determined by the Fourier transform of the line shape.

In order to gain further physical insight into the nature of these general expressions consider the case of photodissociation when the explicit representation of the molecular wavefunctions in the Born–Oppenheimer approximation, i.e., $|g, o_2\rangle = \phi_2(\mathbf{r}, \mathbf{R}) \chi_o(\mathbf{R})$ and $|j\rangle = \phi_j(\mathbf{r}, \mathbf{R}) \chi_j(\mathbf{R})$, where $\phi$ and $\chi$ refer to electronic and nuclear wavefunctions, respectively. Invoking the Condon approximation for the calculation of the width $\gamma^R$ (VIII.12a) this width is determined by the matrix element $\langle \phi_s | \mu | \phi_j \rangle$ i.e., corresponding to the total radiative width of the electronic state $j$. Thus a reasonable approximation for $\gamma^R$ can be obtained from the integrated oscillator strength for bound-continuum absorption.

Equation (VIII.11) provides us with a manageable theoretical expression for the quantum yield of resonance fluorescence from an optically active continuum. This expression is valid provided that $L(E_j)$ tends sufficiently rapidly to zero when $E_j$ goes to $\pm \infty$, and provided that high order radiative corrections can be disregarded. As a check on this result we note that for a Lorentzian distribution, characterized by a width $\Gamma$, the integral (III.11) can be evaluated by the method of residues, and by the utilization of Eq. (III.8) for $\gamma^R$ we regain Eq. (III.14a) for the energy independent quantum yield for this simple case of a Lorentzian resonance. For any other form of the line shape (such as a Gaussian which provides a reasonable approximation for the case of photodissociation) the quantum yield will be energy dependent. From the point of view of the experimentalist a rough order of magnitude of the resonance fluorescence quantum yield (which is strictly valid only for the case of a Lorentzian distribution) is given by the ratio $Y \sim \gamma^R/\Gamma$, where $\gamma^R \sim 10^{-3}$ cm$^{-1}$ and the total width of the distribution is $\Gamma \sim 10^4$ cm$^{-1}$, thus $Y \sim 10^{-4}$. This low yield can be experimentally detected.

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APPENDIX A: EVALUATION OF THE TERMS APPEARING IN EQ. (IV.38)

Starting from

$$\beta = \pi \left[ \sum_i V_{ri} V_{id} \delta (E_a - E_i) + \sum_m V_{rm} V_{md} \delta (E_a - E_m) \right],$$

(A1)
we obtain
\[ \beta = \pi \left[ \sum \sum V_{v_i} V_{v_i'} V_{v_i} \delta(E_a-E_i) \delta(E_a-E_i') + \sum \sum V_{v_m} V_{v_m'} V_{v_m} \delta(E_a-E_m) \delta(E_a-E_m') \right] + 2 \sum \sum V_{v_i} V_{v_i} V_{v_m} \delta(E_a-E_i) \delta(E_a-E_m) \]
\[ = \pi \sum \sum V_{v_i} \delta(E_a-E_i) \sum V_{v_i} \delta(E_a-E_i') + \sum \sum V_{v_m} \delta(E_a-E_i) \sum V_{v_m} \delta(E_a-E_m) + 2 \sum V_{v_i} V_{v_i} \delta(E_a-E_i) \sum V_{v_m} \delta(E_a-E_m) \] (A2)

Utilizing now the expressions for \( \Gamma_s \) and \( \Gamma_r \),
\[ \Gamma_s = 2\pi \left[ \sum \sum V_{v_i} \delta(E_a-E_i) + \sum \sum V_{v_m} \delta(E_a-E_m) \right] \]
(3) \[ \Gamma_r = 2\pi \left[ \sum \sum V_{v_i} \delta(E_a-E_i) + \sum \sum V_{v_m} \delta(E_a-E_m) \right] \]
(A4)

and invoking the assumption that
\[ |V_{v_m}| = |V_{v_m'}| \]
(A5)

we easily obtain
\[ \frac{1}{2} (\Gamma_s, \Gamma_r) - \beta = \pi \sum \sum V_{v_m} \delta(E_a-E_m) \sum \sum (V_{v_i} \pm V_{v_i'}) \delta(E_a-E_i) \]
(A6)

which is clearly nonnegative. Also
\[ \frac{1}{2} \Gamma_s + \frac{1}{2} \Gamma_r - 2\beta = \pi \sum \sum (V_{v_i} - V_{v_r}) \delta(E_a-E_i) + \sum \sum (V_{v_m} - V_{v_m}) \delta(E_a-E_m) \]
(A7)

which is again nonnegative. Note that this conclusion [Eq. (A7)] does not depend on the assumption (A5). The first term in Eq. (IV.38) is thus nonnegative, and if \( V_{v_m} = V_{v_m} \), the condition for its vanishing is \( V_{v_i} = V_{v_r} \) which implies \( \Gamma_s = \Gamma_r = 2\beta \).

We shall now prove that the second term in Eq. (IV.38)
\[ F(E) \equiv \frac{1}{2} \Gamma_s (E+\gamma-E_{\gamma})^2 + \frac{1}{2} \Gamma_r (E+\gamma-E_{\gamma})^2 + 2\beta (E+\gamma-E_{\gamma}) (E+\gamma-E_{\gamma}) \]
(A8)

is also nonnegative. In terms of the dimensionless parameter
\[ d = (E+\gamma-E_{\gamma}) / (E+\gamma-E_{\gamma}) \]
(A9)

Eq. (A8) takes the form
\[ F(E) = (E+\gamma-E_{\gamma})^2 (\frac{1}{2} \Gamma_s d^2 + \frac{1}{2} \Gamma_r + 2\beta d) \]
(A10)

Utilizing Eqs. (A1), (A3), and (A4), the second factor on the rhs of Eq. (A10) takes the form
\[ \frac{1}{2} \Gamma_s d^2 + 2\beta d + \frac{1}{2} \Gamma_r = \pi \sum \sum (dV_{v_i} + V_{v_r}) \delta(E_a-E_i) + \sum \sum (dV_{v_m} + V_{v_m}) \delta(E_a-E_m) \]
(A11)

which implies that for any \( d \) the function \( F(E) \) is nonnegative.

**APPENDIX B: RADIATIVE WIDTHS OF EXCITED VIBRIONIC LEVELS OF A MOLECULE CHARACTERIZED BY DISPLACED POTENTIAL SURFACES**

Generally the relevant excited vibrionic states of a symmetric molecule, particularly those which correspond to an allowed electronic transition, are characterized by a single excited totally symmetric vibrational mode while the rest remain unexcited. This feature of the excitation process enables us to consider a simple one frequency model. The total radiative width of the excited vibrionic level \( \gamma \) may thus be written in the form
\[ \Gamma_s^s(E) = \Gamma_s^m(E) = 2\pi \sum \sum \sum \sum \gamma_{v_i} \gamma_{v_i'} |\langle v_i | \phi_i | v_i' \rangle|^2 \left[ E+E_{\gamma} - (E_{\gamma}+E_{\gamma}) \right] \]
(B1)

which is identical to Eq. (IV.18), only that the vibrational contents \( \gamma_{v_i} \) of the excited vibrionic state \( \gamma \) is written specifically, the sum over \( m \) is replaced by \( \sum \gamma v \sum \gamma_{v_i} \), where \( \sum \gamma_{v_i} \) represents a sum over all final photon states (i.e., an integration over \( k_f \) and over spatial direction and a summation over the possible final polarizations), and finally \( E_a \) and \( E_m \) are replaced by \( E+\gamma_{\gamma} \) and \( E_{\gamma}+E_{\gamma} \), respectively, where \( E \) and \( E_{\gamma} \) are the initial and final photon energies.

We now perform the summation over the photon states in the usual form:
\[ \sum \sum \sum \sum \sum \gamma_{v_i} \gamma_{v_i'} \left| \langle v_i | \phi_i | v_i' \rangle \right|^2 \left[ E+E_{\gamma} - (E_{\gamma}+E_{\gamma}) \right] = \sum \sum \sum \sum \gamma_{v_i} \gamma_{v_i'} |\langle v_i | \phi_i | v_i' \rangle|^2 \left[ (E+\gamma_{\gamma} - (E_{\gamma}+E_{\gamma}) \right] \]
(B2)
This expression depends on the final photon energy $E_f$ through the energy dependence of the photon density of states:

$$\rho(E_f) = \frac{8\pi E_f^2 Q}{(2\pi \hbar c)^3}$$  \hspace{1cm} (B3)

and also through the energy dependence of the radiative matrix element which may be written in the form

$$| \langle s; vac | H_{\text{int}} | g; k_f, e_f \rangle |^2 = U^2/E_f,$$  \hspace{1cm} (B4)

where $U$ is independent on the photon energy. (Note that $U$ is linearly dependent on the electronic energy gap $E_{g\rightarrow e_f}$. However, it does not change with the excess vibrational energy of the emitting state.) Utilizing Eqs. (B1)–(B4), we obtain the total radiative width of the state $| s, v_s \rangle$ in the form

$$\Gamma_s^{R}(E) = \left[ \frac{16\pi^3 Q U^2}{(2\pi \hbar c)^3} \right] \sum_{v_g} | \langle v_s | v_g \rangle |^2 (E - \hbar \omega_{v_g}).$$  \hspace{1cm} (B5)

The summation over $v_g$ may be evaluated by introducing the energy factor into the matrix element and replacing $\hbar \omega_{v_g}$ by the operator $\hbar \omega a^+ a$, where $a^+$ and $a$ are the ladder operators for the ground electronic state harmonic oscillator.

$$\Gamma_s^{R}(E) = \left[ \frac{16\pi^3 Q U^2}{(2\pi \hbar c)^3} \right] \sum_{v_g} \langle v_s | E - \hbar \omega a^+ a | v_g \rangle / \langle v_s | v_g \rangle$$

$$= \left[ \frac{16\pi^3 Q}{(2\pi \hbar c)^3} \right] \langle v_s | E - \hbar \omega a^+ a | v_g \rangle U^2.$$  \hspace{1cm} (B6)

Utilizing exactly the same procedure, we obtain

$$\Gamma_r^{R}(E) = \left[ \frac{16\pi^3 Q}{(2\pi \hbar c)^3} \right] \langle v_r | E - \hbar \omega a^+ a | v_r \rangle U^2,$$  \hspace{1cm} (B7)

$$\beta^{R}(E) = \beta^{m}(E) = \left[ \frac{8\pi^3 Q}{(2\pi \hbar c)^3} \right] \langle v_r | E - \hbar \omega a^+ a | v_r \rangle U^2.$$  \hspace{1cm} (B8)

Equations (B7) and (B8) are written for the useful case where $| s, v_s \rangle$ and $| r, v_r \rangle$ belong to the same electronic manifold so that the electronic integral $U$ do not change in going to $\Gamma_s^{R}$ and $\beta^{R}$. The matrix elements appearing in Eqs. (B6)–(B8) are evaluated in Appendix C (again for the case where $s$ and $r$ belong to the same electronic manifold). Inserting Eq. (C6) into Eqs. (B6)–(B8), we readily obtain Eqs. (V.1)–(V.3).

**APPENDIX C: EVALUATION OF MATRIX ELEMENTS (B6)–(B8)**

Here we shall evaluate matrix elements of the form $\langle v | E - \hbar \omega a^+ a | u \rangle$, where $| v \rangle$ and $| u \rangle$ are harmonic oscillator eigenstates defined for a potential surface which is displaced relative to that potential surface for which the operators $a$ and $a^+$ are defined. These states are most easily cast as

$$| u \rangle = (u!)^{-1/2} \exp(i \Delta) (a^+)^u | 0 \rangle,$$

$$\langle v | = (v!)^{-1/2} \langle 0 | a^v \exp(-i \Delta)$$  \hspace{1cm} (C1)

in terms of the reduced momentum operator

$$\hat{p} = (i/\sqrt{2}) (a^+ - a),$$  \hspace{1cm} (C2)

where $\Delta$ is the relative displacement of the origins of the potential surfaces. The desired matrix element now takes the form

$$J_{v,u} = \left[ \frac{\hbar \omega}{(v! u!)^{1/2}} \right] \langle 0 | a^u \exp(-i \Delta) [E/\hbar \omega - a^+ a] \exp(i \Delta) (a^+)^v | 0 \rangle.$$  \hspace{1cm} (C3)

Utilizing now the transformation relations

$$\exp(-i \Delta) a^+ \exp(i \Delta) = a^+ + (\Delta/\sqrt{2})$$

$$\exp(-i \Delta) a \exp(i \Delta) = a + (\Delta/\sqrt{2})$$

we get,

$$J_{v,u} = \left[ \frac{\hbar \omega}{(v! u!)^{1/2}} \right] \langle 0 | a^u [E/\hbar \omega - a^+ a - (\Delta/\sqrt{2}) (a^+ + a) - \frac{1}{2} \Delta^2] (a^+)^v | 0 \rangle.$$  \hspace{1cm} (C5)

Applying some simple properties of the creation and annihilation operators, Eq. (C5) takes the final form

$$J_{v,u} = [E - \hbar \omega (\nu + \frac{1}{2} \Delta^2)] \delta_{v,u} - \langle \hbar \omega \Delta/\sqrt{2} \rangle \left[ \frac{(v)!}{\nu! (v-\nu)!} \right] \left( \nu + \frac{1}{2} \right) \delta_{v,u+1} + \left( v + 1 \right) \delta_{v,u-1}.$$  \hspace{1cm} (C6)
APPENDIX D: THE TOTAL CROSS SECTION FOR RESONANCE FLUORESCENCE IN THE CASE OF TWO OVERLAPPING RESONANCES

Here we shall evaluate the sum

\[ X^T = \sum_{v_o} |X_f(v_o)|^2 (E - \hbar \omega p)^2. \]  

(D1)

where Eq. (IV.30)

\[ |X_f(v_o)|^2 = \left[ A_f (E - E_{r_o}) + B_f (E - E_{s_o}) + C_f \Gamma \right]^2 + 4 \left[ A_f \Gamma_r + B_f \Gamma_s - 2 C_f \beta \right]^2. \]  

(D2)

In terms of \( X^T \), the total cross section of resonance fluorescence is given by

\[ \sigma_R(E) = \sum_{v_o} \sigma_R(v_o; E) = \left[ 2 Q^2 / \pi (\hbar c)^2 \right] (X^T/Z), \]  

(D3)

as is easily asserted by utilizing Eq. (IV.33). \( Z \) is defined by Eq. (IV.29). To perform the summation in (D1) we shall make use of the following forms of the coefficients \( A_f, B_f, \) and \( C_f \):

\[ A_f = \langle v_s | v_o \rangle \langle v_o | v_r \rangle \left[ U^2 / \left( E - \hbar \omega p \right) \right]^{1/2}, \]  

(D4)

\[ B_f = \langle v_r | v_o \rangle \langle v_o | v_r \rangle \left[ U^2 / \left( E - \hbar \omega p \right) \right]^{1/2}, \]  

(D5)

\[ C_f = \langle v_o | v_o \rangle \langle v_o | v_r \rangle + \langle v_o | v_r \rangle \langle v_r | v_o \rangle \left[ U^2 / \left( E - \hbar \omega p \right) \right]^{1/2}, \]  

(D6)

where \( U \) is defined by Eq. (B4) and where we have assumed that the states \( r \) and \( s \) correspond to the same electronic manifold. Inserting Eqs. (D4)–(D6) into Eq. (D2), we obtain, after some algebra,

\[ |X_f(v_o)|^2 = \left[ U^4 / \left( E - \hbar \omega p \right) \right] \left[ (X_s^2 + X_t^2) \langle v_o | v_o \rangle \langle v_o | v_o \rangle + (X_o^2 + X_o^2) \langle v_o | v_o \rangle \langle v_o | v_o \rangle + 2 (X_o X_c + X_o X_c) \langle v_o | v_o \rangle \langle v_o | v_o \rangle \right], \]  

(D7)

where \( X_s, X_t, X_o, \) and \( X_d \) are defined by Eqs. (V.14)–(V.17). Utilizing now the closure relation, Eq. (D1) may be recast in the form

\[ X^T = \left( U^4 / E \right) \left[ (X_s^2 + X_t^2) \langle v_o | (E - \hbar \omega a)^2 \rangle \langle v_o | (E - \hbar \omega a)^2 \rangle + (X_o^2 + X_o^2) \langle v_o | (E - \hbar \omega a)^2 \rangle \langle v_o | (E - \hbar \omega a)^2 \rangle + 2 (X_o X_c + X_o X_c) \langle v_o | (E - \hbar \omega a)^2 \rangle \langle v_o | (E - \hbar \omega a)^2 \rangle \right], \]  

(D8)

where the creation and annihilation operators are defined for the \( g \) potential surface as in Appendices B and C. The matrix elements encountered here were evaluated in Appendix C. Equation (D8) is now identical to Eq. (V.13), where \( J_{s,s}, J_{s,s}, \) and \( J_{s,s} \) are defined by Eqs. (V.4) and (V.5).

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