radicals with unlike g tensors. A direct, approximate solution of the Zeeman$+$dipolar Hamiltonian is used. The high-temperature, large-field, and small $\Delta\omega/\bar{\omega}$ approximations are introduced, but arbitrary ratios of the dipolar coupling ω_d among unlike radicals to $\Delta\omega$ are permitted. The approximations for solving the many-body problem were tested by several model calculations and the line shift was shown to be insensitive to the approximations. The dipolar line shifts and linewidths agree with results obtained by the moment method in the limits $\Delta\omega \ll \omega_d$ and $\Delta\omega \gg \omega_d$.

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Radiative Decay of Polyatomic Molecules

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In this paper we present a quantum-mechanical treatment of the radiative decay of polyatomic molecules. The decay of a manifold of closely spaced coupled levels is handled by applying the Green's function formalism for the transition probability, where the matrix elements are displayed in an energy representation which involves either the Born–Oppenheimer or the molecular eigenstate basis set. General criteria are obtained for the occurrence of an irreversible intramolecular electronic relaxation process. The features of radiationless transitions in large, medium-sized, and small molecules are elucidated, deriving general expressions for the radiative decay times and for the fluorescence quantum yields. Some possibilities for studying radiative interference effects in intersystem crossing are explored. A general theoretical demonstration of the occurrence of long radiative lifetimes of small molecules is presented.

I. INTRODUCTION

All the direct physical information now available concerning electronic relaxation processes in large and medium-sized molecules comes from the experimental studies of molecular luminescence.[1,2] The radiative decay of an excited state of a polyatomic molecule cannot be handled by the conventional theory for the radiative decay of a single excited level. It is now well established that in excited electronic states of polyatomic molecules the Born–Oppenheimer (BO) separability conditions for electronic and nuclear motion break down in view of intramolecular vibronic (and spin–orbit, etc.) coupling between any zero-order vibronic level and a manifold of vibronic levels which correspond to a lower electronic configuration.[2–12] These vibronic (and other) coupling effects between BO levels are manifested in the shortening of the radiative lifetimes of large molecules[1] and in the observation of anomalously long radiative lifetimes of small (triatomic) molecules.[12] Obviously a satisfactory and complete theory of the radiative decay of a polyatomic molecule should involve a proper description of the decay of a manifold of a large number of closely spaced levels. The features of so-called radiationless transitions in large molecules should emerge from a unified theory of the radiative decay.

The basic conceptual framework for the understanding of intramolecular vibronic coupling in polyatomic molecules and in solids was provided by the early work of Franck and Sponer[3a] and by Kubo[3b] who have pointed out that the nuclear kinetic-energy term in the molecular Hamiltonian leads to the mixing of zero-order Born–Oppenheimer states. Since then extensive work was performed on the problem of "radiationless transitions" in large molecules by considering the vibronic (spin–orbit, etc.) coupling matrix elements which couple the zero-order Born–Oppenheimer states.[3–9] These studies rest on the assumption that an excited metastable state of a large molecule is prepared in a nonstationary Born–Oppenheimer state, which *subsequently* decays into a dense manifold of Born–Oppenheimer levels corresponding to another electronic configuration. These authors[3–9] considered the intramolecular decay as a simple rate process, with the rate constant given by the Fermi "golden rule," without providing any justification for the validity of this

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approach. In this context two qualitative contradictory statements were recently made: Kistiakowsky and Paramenter[13] claimed that the experimental observation of a radiationless transition in the isolated benzene molecule "contradicts the laws of quantum mechanics," while Robinson[9] argues that in large molecules the density of vibronic states is sufficiently large so that they can act as an effective dissipative quasicontinuum. Recently an alternative approach to this problem was presented, in which the molecular eigenstates of the molecular Hamiltonian were constructed as a superposition of zero-order Born–Oppenheimer states.[10,11,14] Using a simple model (equal level spacing) for the energy-level structure in the excited states, this approach established a proper criterion for the irreversibility of the radiationless transition process in an isolated large molecule.[10] This model also provided physical insight into the way in which the oscillator strength, carried by a simple zeroth-order BO component, is spread out over the manifold of molecular eigenstates, making them active in emission (and in absorption).[10,11,14,15] A discussion of the small molecule limit was also given for this model. However, it is still desirable to obtain these results in a model independent manner, to provide better criteria as to when the small and large molecule limits occur, and to discuss other phenomena such as internal conversion.

When radiative decay processes are considered, the molecular eigenstates are no longer proper eigenstates of the total Hamiltonian:

$$H=H_{el}+H_r+H_{\mathrm{int}}, \tag{1}$$

where

$$H_{el}=H_{\mathrm{BO}}+H_v. \tag{2}$$

The molecular Hamiltonian H_{el} consists of the Born–Oppenheimer term H_{BO} and an intramolecular perturbation H_v, which consists of vibronic coupling terms, spin–orbit coupling interactions, etc. H_r is the Hamiltonian corresponding to the free radiation field, and H_{int} is the radiation–matter interaction term. The time evolution of a nonstationary excited state of the system can be described either in terms of the eigenstates of H_{BO} (the BO basis set) or of H_{el} (the molecular eigenstates basis). Obviously the choice of the basis set is merely a matter of convenience and does not affect any observable quantities. The purpose of this paper is to present a general scheme for the decay of a manifold of closely spaced levels. Relying heavily on the work of Goldberger and Watson[16] and of Mower,[17] we focus our attention on the Green's function formalism for the transition probability. Rather than repeating their derivations, only the relevant equations are presented, but an attempt is made to explain their salient physical features. The matrix elements of the Green's function are displayed in an unperturbed energy representation for a manifold of coupled levels. The coupling may consist of radiative interactions, or vibronic interactions (etc.), or of both. Such a description is directly applicable to the study of the radiative decay of polyatomic molecules. In this context we demonstrate that under different limiting conditions for the molecular level spacings, different basis sets are recommended as being simpler in practice. Finally the unified theory is applied for several cases of physical interest.

II. THE RADIATIVE DECAY OF CLOSELY SPACED LEVELS

In discussing radiationless transitions we are usually interested in the situation where the molecule has a ground state ϕ_0 which can be safely taken as an eigenfunction of both H_{BO} and H_{el} since $\langle\phi_0 \mid H_v \mid \phi_0\rangle\approx 0$. The electronically excited states of interest consist of an excited singlet BO state ϕ_s, which carries oscillator strength to ϕ_0, and a manifold of excited BO states $\{\phi_l\}$, which correspond to a lower electronic configuration, which are quasidegenerate with ϕ_s, and which do not carry oscillator strength to the ground state. The system is prepared by optical excitation at time $t=0$ in a nonstationary state of H, so that the molecule is in some electronically excited state, which may or may not be an eigenfunction of H_{el} (the latter case corresponds to the usual definition of a "stationary state" in the absence of the radiation field), and no photons are present. The initial excited molecular state $\Psi_m(0)$ can be always expressed as a superposition of either the molecular eigenstates $\{\psi_n\}$ or the BO states $\{\phi_s, \phi_l\}$, and all physical properties are of course independent of this choice. Thus the initial excited state of the system is

$$\begin{aligned}\Psi(0)=\Psi_m(0) \mid \mathrm{vac}\rangle &= \sum_n a_n(0) \mid \psi_n; \mathrm{vac}\rangle \\ &\equiv b_s(0) \mid \phi_s; \mathrm{vac}\rangle + \sum_{l\neq s} b_l(0) \mid \phi_l; \mathrm{vac}\rangle, \end{aligned} \tag{3}$$

where $\mid\mathrm{vac}\rangle$ is the zero photon state. In many cases of physical interest the initial excited state of the system can be visualized to be prepared by a coherent excitation by a short light pulse or by a chaotic broad-band source, whereupon $a_n(0)=\langle\phi_s \mid \psi_n\rangle$. The completeness of the molecular basis set for the excited states and the fact that ϕ_s is the only state which carries oscillator strength immediately implies that in this case $\Psi(0)=\mid\phi_s; \mathrm{vac}\rangle$. When narrow-band excitation is used, the $\{b_l(0)\}$ are not necessarily nonzero, and their contributions to the radiative decay should be also con-

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sidered. Thus, the initial state of the system is given in the general form (3). The details of the $\{a_n(0)\}$ or the $\{b_l(0)\}$ can be determined in a given situation by calculating the probability amplitudes for excitation to a nonstationary state. (These are quite simply related to those for the decay of such a nonstationary state.)

After a time t has evolved, the state of the system is completely determined by the Hamiltonian (1), so that

$$\Psi(t)=\exp(-iHt)\Psi(0), \tag{4}$$

where the units $\hbar=c=1$ are used. Now, just as $\Psi(0)$ could be expanded in $\{\phi\}$ or in $\{\psi\}$, $\Psi(t)$ can be expanded in either of these basis sets provided that we include the possibility of spontaneous emission by allowing $\Psi(t)$ to also contain the one-photon ground state $\phi_{\mathbf{k},\mathbf{e}}=|\phi_0,\mathbf{k},\mathbf{e}\rangle$, $\mathbf{k}$ and $\mathbf{e}$ are the wavevector and the polarization vector of the emitted photon, respectively. Using the alternative descriptions displayed in Eq. (3), the decay process can be described as the radiative decay of $\{\psi_n\}$, or alternatively but equivalently, as the radiative decay of $\{\phi_s, \phi_l\}$. The probability $P_{\mathbf{k},\mathbf{e}}(t)$ of finding the system in the state $\phi_{\mathbf{k},\mathbf{e}}$ at time t is defined by

$$\begin{aligned}P_{\mathbf{k},\mathbf{e}}(t)&=|\langle\phi_{\mathbf{k},\mathbf{e}}\mid\Psi(t)\rangle|^2\\&=|\langle\phi_{\mathbf{k},\mathbf{e}}\mid\exp(-iHt)\mid\Psi(0)\rangle|^2.\end{aligned} \tag{5}$$

Using (3), Eq. (5) can be displayed in two equivalent forms:

$$P_{\mathbf{k},\mathbf{e}}(t)=\sum_{j,j'=s,\{l\}}\langle\phi_{\mathbf{k},\mathbf{e}}\mid\exp(-iHt)\mid\phi_j\mathrm{vac}\rangle b_j(0)\langle\phi_{\mathbf{k},\mathbf{e}}\mid\exp(-iHt)\mid\phi_{j'},\mathrm{vac}\rangle^* b_{j'}^*(0) \tag{6a}$$

$$=\sum_{nn'}\langle\phi_{\mathbf{k},\mathbf{e}}\mid\exp(-iHt)\mid\psi_n\mathrm{vac}\rangle a_n(0)\langle\phi_{\mathbf{k},\mathbf{e}}\mid\exp(-iHt)\mid\psi_{n'}\mathrm{vac}\rangle^* a_{n'}^*(0). \tag{6b}$$

It should be noted that in (6a) and (6b) there is the possibility of interference between the different states, $\{\phi_s, \phi_l\}$ and $\{\psi_n\}$, respectively, as many of them may be located close together and may be strongly coupled. It is a well-known fact in quantum theory that, when the possibility of interference between states exists, simple rate theories based on the Pauli master equation become invalid. For the case of broad-band excitation, the coefficients may simply be taken as $b_j(0)=\delta_{js}$ while $a_n(0)=\langle\psi_n\mid\phi_s\rangle$.

In discussing the phenomenon of radiative decay, it is customary to introduce the radiative lifetime of states. By virtue of (6) it is convenient to introduce the lifetime in a manner which accounts for some types of interference effects. The damping matrix $\mathbf{\Gamma}$ is a generalization of the Fermi "golden-rule" transition rates. Let $\Gamma_{\alpha\alpha'}(E)$ be defined for some set of zero-photon excited molecular states $\{\alpha\}$ (either $\{\psi\}$ or $\{\phi\}$, etc.):

$$\begin{aligned}\Gamma_{\alpha\alpha'}(E)=2\sum_{\mathbf{e}}\int d\Omega_{\mathbf{k}}\langle\alpha\mid H_{\mathrm{int}}\mid\phi_0,\mathbf{k},\mathbf{e}\rangle\\\times\langle\phi_0,\mathbf{k},\mathbf{e}\mid H_{\mathrm{int}}\mid\alpha'\rangle\rho_p(E-E_0),\end{aligned} \tag{7}$$

where $\sum_{\mathbf{e}} d\Omega_{\mathbf{k}}$ corresponds to the integration over all propagation directions in $\mathbf{k}$ space and summation over all polarization directions. E_0 is the energy of ϕ_0, E is an energy parameter whose value of interest is E_0+k, and $\rho_p(E-E_0)$ is the density of photon states of energy $E-E_0$ [usually $\rho_p(k)$]. The diagonal elements of $\Gamma_{\alpha\alpha}(E_\alpha)$ give the Fermi "golden-rule" transition rates out of the molecular states α whose energies are E_α. $\mathbf{\Gamma}(E)$ is in general nondiagonal,[18] as can be seen from our simple example below. The nonzero matrix elements of H in the BO basis are given by

$$\langle\phi_{\mathbf{ke}}\mid H\mid\phi_{\mathbf{k'e'}}\rangle=(E_0+k)\delta_{\mathbf{kk'}}\delta_{\mathbf{ee'}}, \tag{8a}$$

$$\langle\phi_s\mid H\mid\phi_l\rangle=\langle\phi_s\mid H_v\mid\phi_l\rangle=v_{sl}, \tag{8b}$$

$$\langle\phi_{\mathbf{ke}}\mid H\mid\phi_s\rangle=\langle\phi_{\mathbf{ke}}\mid H_{\mathrm{int}}\mid\phi_s\rangle=W_{\mathbf{ke}}, \tag{8c}$$

$$\langle\phi_s\mid H\mid\phi_s\rangle=E_s, \tag{8d}$$

$$\langle\phi_l\mid H\mid\phi_{l'}\rangle=E_l\delta_{ll'}. \tag{8e}$$

In this basis set it is easily verified that

$$\Gamma_{ss}\equiv\Gamma_s\neq0, \tag{9a}$$

$$\Gamma_{sl}=\Gamma_{ll'}=0,\quad \text{all}\quad l,l', \tag{9b}$$

and hence $\mathbf{\Gamma}$ is diagonal in this basis. However, if we diagonalize H_e [i.e., (8b), (8d), (8e)], the $\mathbf{\Gamma}$ of (9) undergoes a unitary transformation and is no longer diagonal. It is well known[17] [Mower, Eq. (34)] that if

$$\Gamma_{\alpha\alpha'}\gtrsim|E_\alpha-E_{\alpha'}-(i/2)(\Gamma_{\alpha\alpha}-\Gamma_{\alpha'\alpha'})|, \tag{10}$$

the two states α and α' do not decay independently, i.e., are not characterized by simple exponential decay. For the above case, in the $\{\psi_n\}$ basis set for $E_l\approx E_{l'}$, when

$$\Gamma_{nn'}\gtrsim\tfrac{1}{2}|\Gamma_{nn}-\Gamma_{n'n'}|\neq0, \tag{11}$$

the states ψ_n and $\psi_{n'}$ do not have simple exponential decays. When the density of the BO states $\{\phi_l\}$ is high, there are many ψ_n satisfying (11). Bixon *et al.*[19] have discussed the fact that in this case the cross terms in (6b) contribute in a manner which is well understood as the phenomena of level crossing.[18] It might be

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tempting to look for a set of excited molecular states which have simple exponential decays. Freed[20] has shown that such a set of states can be provided by the set $\{\chi_j\}$ which diagonalizes the effective Hamiltonian:

$$\mathbf{H}_{\mathrm{eff}}=\mathbf{H}_{\mathrm{el}}-i\mathbf{\Gamma}/2. \tag{12}$$

This effective Hamiltonian can be displayed either in the $\{\phi_s, \phi_l\}$ representation or in the $\{\psi_n\}$ manifold. However, it is not always necessary to evaluate the $\{\chi_j\}$ set. It should be noted however that the transformation $\mathbf{S}$ which diagonalized $\mathbf{H}_{\mathrm{eff}}$ via

$$\mathbf{S}\mathbf{H}_{\mathrm{eff}}\mathbf{S}^{-1}=\mathbf{\Lambda}, \tag{13}$$

where $\mathbf{\Lambda}$ is diagonal, is a complex orthogonal matrix. The real and imaginary parts of the eigenvalues $\mathbf{\Lambda}$ give the energies E_j and $-\frac{1}{2}\tau_j^{-1}$, respectively, where τ_j are the "lifetimes" of the states. However, even if the $\{\chi_j\}$ are used in (6b) instead of the $\{\psi_n\}$, the decay may not just be a superposition of exponentials since we still have the possibility of the cross terms (level-crossing terms) contributing.

Equations (5) and (6) correspond to a discussion of the radiative decay of closely coupled states, where the coupling may be due to vibronic coupling [Eq. (8b)] or to level-crossing terms in (6b), etc. The general theory of the decay of closely coupled levels has been given by Mower[17] using the techniques described by Goldberger and Watson.[16] Rather than giving a complete rehash of their formulas, the relevant ones are summarized, and an attempt is made to give the salient qualitative features of their physical content.

All that is required in (5) in order to evaluate the total transition probability are matrix elements of $\exp(-iHt)$ between the states $\phi_{\mathbf{k}e}$ and $\Psi(0)$, where $\Psi(0)$ may be expressed in any one of a number of equivalent basis sets as in (6). However, $\exp(-iHt)$ is in a rather unwieldy form, and it turns out to be much simpler to look at the (imaginary) Laplace transform of its matrix elements, i.e., the matrix elements of the resolvent or Green's function,

$$G(E)=(E-H)^{-1}. \tag{14}$$

One reason why it is so convenient to work in terms of $G(E)$ is that the "energies" and "lifetimes" of the excited molecular states can be determined by finding the poles of $G(E)$ for $E=E_\alpha-i\Gamma_\alpha/2$. [Actually, $G(E)$ is analytic for all E not on the branch cut $E>E_0$, and the poles of $G(E)$, which are situated on the second Riemann sheet, determine the position and width of the metastable excited states.]

Explicity,

$$\exp(-iHt)=(2\pi i)^{-1}\int_C dE\,\exp(-iEt)G(E), \tag{15}$$

or

$$\langle\phi_{\mathbf{k}e}\,|\,\exp(-iHt)\,|\,\alpha\rangle=(2\pi i)^{-1}\int_C\langle\phi_{\mathbf{k}e}\,|\,G(E)\,|\,\alpha\rangle \times\exp(-iEt)dE, \tag{16}$$

where the contour C runs from $+\infty$ to $-\infty$ above all singularities of $G(E)$, i.e., above the real axis. If $\langle\phi_{\mathbf{k}e}\,|\,G(E)\,|\,\alpha\rangle$ has a set of complex poles $E_j-i\Gamma_j(E)/2$, where $\{\Gamma_j(E)\}$ are "smooth" functions of E for $E\approx E_0+k$, these poles in (16) give to lowest order (neglecting branch-cut contributions)

$$\sum_j\frac{\langle\phi_{\mathbf{k}e}\,|\,H_{\mathrm{int}}\,|\,j\rangle\exp[-i(E_0+k)t]\{1-\exp[-i(E_j-\frac{1}{2}i\Gamma_j-E_0-k)t]\}\langle j\,|\,\alpha\rangle}{E_0+k-E_j+\frac{1}{2}i\Gamma_j}. \tag{17}$$

This is a sum of decaying exponentials with differing lifetimes if there are more than one different value of $\Gamma_j\equiv\Gamma_j(E_0+k)$. It turns out that (17), in general, can contain more than one exponential decay when the closely lying states $\{\alpha\}$ are coupled, via say H_v, or have off-diagonal components of $\mathbf{\Gamma}(E)$ in this basis set. It is possible to insure that each state in the set $\{\alpha\}$ has a single decay with $\Gamma_{\alpha\alpha}$ if we choose our basis set as that which diagonalizes (12), provided our initial basis set is large enough so that $\Gamma_{\alpha\alpha}(E)$ is very slowly varying for $E\approx(E_0+k)$. (See examples in next sections.)

There are two major choices of basis sets which correspond to evaluating (5) with $\{\phi_s, \phi_l\}$ or $\{\psi\}$, and these are discussed in Secs. III and IV, respectively, along with their range of validity (or simplicity). In Secs. III and IV, physical processes are discussed which can be described in a form in which "interference effects" are absent, and hence, the results could also be obtained by simple rate equations since the conditions for the validity of the Pauli master equation are met. However, Secs. V and VI discuss physical processes in which "strong coupling" or "interference effects" can play an interesting role.

III. THE BO BASIS SET

For simplicity we consider in this section the classic case of broad-band excitation for which $\Psi(0)$ is $|\,\phi_s, \mathrm{vac}\rangle$. It is convenient to separate this state from all others by defining its projection operator

$$P=|\,\phi_s, \mathrm{vac}\rangle\langle\phi_s, \mathrm{vac}\,| \tag{18}$$

and the projection operator on to all other states

$$Q=1-P. \tag{19}$$

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[20] K. F. Freed (unpublished).

In order to evaluate $P_{\mathbf{k}e}(t)$ in (5), attention is initially focused on the relevant matrix element of $G(E)$, defined by (15), which determines the transition energies, their widths (or lifetimes), and their oscillator strengths. The matrix element of interest is simply

$$\langle\phi_{\mathbf{k}e} \mid G(E) \mid \phi_s, \mathrm{vac}\rangle \equiv \langle\phi_{\mathbf{k}e} \mid QG(E)P \mid \phi_s\, \mathrm{vac}\rangle \qquad (20)$$

by the definition of P and Q. If we define our zeroth-order Hamiltonian for this basis

$$K = H_{\mathrm{BO}} + H_r, \qquad (21a)$$

then the perturbation is

$$V = H_v + H_{\mathrm{int}}. \qquad (21b)$$

As given by Mower,[17]

$$QG(E)P = (E-QKQ)^{-1}QR(E)P[E-PKP-PR(E)P]^{-1}, \qquad (22a)$$

where

$$R(E) = V + VQ(E-QHQ)^{-1}QV \qquad (22b)$$

is the level shift operator. Then, neglecting level shifts (or incorporating them in E_s, etc.), one gets to lowest order

$$\langle\phi_{\mathbf{k},e} \mid QG(E)P \mid \phi_s, \mathrm{vac}\rangle = (E-E_0-k)^{-1} \times \langle\phi_{\mathbf{k}e} \mid H_{\mathrm{int}} \mid \phi_s, \mathrm{vac}\rangle[E-E_s+\tfrac{1}{2}i\Gamma_s(E)+\tfrac{1}{2}i\Delta(E)]^{-1}, \qquad (23)$$

where since as discussed in (9), $\mathbf{\Gamma}$ is diagonal in this basis, so $\Gamma_s(E)$ is the radiative width of ϕ_s as defined in (7) for $\alpha=\alpha'=|\phi_s, \mathrm{vac}\rangle$. $\Delta(E)$ is the width of $|\phi_s, \mathrm{vac}\rangle$ due to the vibronic coupling (8b) with the BO manifold $\{\phi_l\}$ and is given by (neglecting level shifts)

$$\Delta(E) = 2\sum \frac{|\langle\phi_s \mid H_v \mid \phi_l\rangle|^2}{(E-E_l)^2+[\tfrac{1}{2}\Gamma_l(E)]^2}\,\tfrac{1}{2}(\Gamma_l) = 2\sum_l \frac{(\tfrac{1}{2}\Gamma_l)\;|v_{sl}|^2}{(E-E_l)^2+[\tfrac{1}{2}\Gamma_l(E)]^2}, \qquad (24)$$

where the states $\{\phi_l\}$ $(l\neq s)$ have been allowed to to have very small widths due to highly forbidden radiative transitions. Addition of contributions to Γ_l may arise from intermolecular perturbations, e.g., collisions. In an isolated molecule Γ_l may be often taken as $\Gamma_l(E)\rightarrow 0^+$. At first sight it may seem that (23) has a single complex pole for

$$E \approx E_s - \tfrac{1}{2}[i\Gamma_s(E_s)] - \tfrac{1}{2}[i\Delta(E_s)]. \qquad (25)$$

However, as Mower has shown[17] (25) is the only complex pole *provided that* $\Gamma_s(E)+\Delta(E)$ *is a smooth function of* E *for* $E\approx E_s\approx E_0+k$. *If these widths are not smooth, there are more poles in* (23), *and hence, according to* (17) *more than one exponential decay time.* As is well known, $\Gamma_s(E)$ is a very smooth function of E in the appropriate region; however, $\Delta(E)$ may not be.

If the $\{\phi_l\}$ manifold is very dense, i.e., a continuum, then in (24) we may replace $\sum_l \rightarrow \int dE_l \rho_l(E_l)$, where $\rho_l(E_l)$ is the density of the $\{\phi_l\}$ states at energy E, and $v_{sl}\rightarrow v_{sl}(E_l)$. Taking the limit $\Gamma_l(E)\rightarrow 0^+$, (24) becomes

$$\Delta(E) = 2\pi\,|v_{sl}(E)|^2\rho_l(E), \qquad (26)$$

and since $\rho_l(E)$ and $v_{sl}(E)$ can often be taken to be slowly varying in large molecules (see Sec. VI for another case) for $E\approx E_s$, in the dense manifold case (the statistical limit) there is indeed only a single complex pole. Thus, using (17), (5) becomes[16]

$$P_{\mathbf{k},e}(t) = \frac{|\langle\phi_{\mathbf{k}e} \mid H_{\mathrm{int}} \mid \phi_s \mathrm{vac}\rangle|^2}{(E_0+k-E_s)^2+\tfrac{1}{4}[\Gamma_s(E_s)+\Delta(E_s)]^2} \times \{1-2\exp[-\tfrac{1}{2}(\Gamma_s+\Delta)t]\cos(E_0+k-E_s)t + \exp[-(\Gamma_s+\Delta)t]\}. \qquad (27)$$

Integrating over all frequencies and $\Omega_{\mathbf{k}e}$, Eq. (27) gives finally[16]

$$P(t) = \{\Gamma_s(E_s)/[\Gamma_s(E_s)+\Delta(E_s)]\} \times (1-\exp\{-[\Gamma_s(E_s)+\Delta(E_s)]t\}), \qquad (28)$$

describing a single decaying state with inverse lifetime $\Gamma_s+\Delta$ and quantum yield $P(\infty)=\Gamma_s/(\Gamma_s+\Delta)$. This result is known already,[15] however the present derivation is more general and physically transparent. It is important to notice that the conventional interpretation[5–9] of excitation to ϕ_s followed in time by intersystem crossing is in principle invalid in a quantum-mechanical sense since the radiationless transition is not an independent isolated process, but results in a natural way from the unified treatment of the radiative decay. Equation (28) results from the excitation to a resonance which is due to a state which is coupled to two different continua. Just as the photon continuum allows for irreversible radiative decay, the states $\{\phi_l\}$ act as an effective continuum which enable irreversible decay into this manifold. We could have defined the probability P_t of finding the molecule in the $\{\phi_l\}$ manifold at time t (which in the case of a triplet manifold we could in principle measure by ESR). In this case we would have obtained

$$P_t(t) = [\Delta/(\Gamma_s+\Delta)]\{1-\exp[-(\Gamma_s+\Delta)t]\}. \qquad (29a)$$

Note that

$$1-P_t(t)-P(t) = \exp[-(\Gamma_s+\Delta)t] \qquad (29b)$$

is the probability that the molecule is in its initial state $|\phi_s, \mathrm{vac}\rangle$.

When the BO manifold $\{\phi_l\}$ is no longer a continuum, i.e., $|E_l-E_{l'}| \gtrsim \tfrac{1}{2}[\Gamma_l(E)+\Gamma_{l'}(E)]$, and $\Delta(E)$ is no longer a smooth function of E in the range of interest, then according to (17), the situation corresponds to the decay of a number of closely coupled levels, i.e., nearby and possibly overlapping resonances. In this case it is convenient to choose an initial basis set for the excited vibronic states (i.e., spanned by a projection operator P) which is large enough to describe a set of excited levels. This is considered in the next section, where the $\{\psi_n\}$ basis set is used.

IV. THE MOLECULAR EIGENSTATES

The molecular eigenstates $\{\psi_n\}$ are isolated by defining their projection operator

$$P=\sum_n |\psi_n, \mathrm{vac}\rangle\langle\psi_n, \mathrm{vac}| \tag{30}$$

and the projection operator on to all other states

$$Q=1-P. \tag{31}$$

The matrix elements of interest are now

$$\langle\phi_{\mathrm{ke}}|G(E)|\psi_n, \mathrm{vac}\rangle\equiv\langle\phi_{\mathrm{ke}}|QG(E)P|\psi_n, \mathrm{vac}\rangle. \tag{32}$$

Letting

$$K=H_{el}+H_r, \tag{33a}$$

$$V=H_{\mathrm{int}}, \tag{33b}$$

$QG(E)P$ is again given by (22a) and (22b). However, now

$$\langle\phi_{\mathrm{ke}}|QR(E)P|\psi_n, \mathrm{vac}\rangle\cong\langle\phi_{\mathrm{ke}}|H_{\mathrm{int}}|\psi_n, \mathrm{vac}\rangle$$

$$=\langle\phi_{\mathrm{ke}}|H_{\mathrm{int}}|\phi_s, \mathrm{vac}\rangle\langle\phi_s|\psi_n\rangle \tag{34}$$

and

$$PRP\cong-(i/2)P\mathbf{\Gamma}(E)P, \tag{35}$$

where $P\mathbf{\Gamma}(E)P$ is the radiative damping matrix in the $\{\psi_n\}$ basis which is nondiagonal as discussed after Eq. (9). Using (34) and (35) into (22) gives

$$\langle\phi_{\mathrm{ke}}|QG(E)P\cong(E-E_0-k)^{-1}$$

$$\times\langle\phi_{\mathrm{ke}}|H_{\mathrm{int}}P[E-PKP+(i/2)P\Gamma(E)P]^{-1}. \tag{36}$$

Since $PKP=\sum_n|\psi_n, \mathrm{vac}\rangle E_n\langle\psi_n, \mathrm{vac}|$, where E_n are the energies of the molecular states ψ_n, the last term in (36) is the inverse of a nondiagonal matrix. However, we see that it would be diagonalized by the $\{\chi_j\}$ basis corresponding to H_{eff} of (12), proving that assertion.

Thus, we see that a proper definition of the absorption coefficient, which includes any interactions amond the excited states via H_v or off-diagonal parts of $\mathbf{\Gamma}$, is given by

$$A(\omega)\alpha-\mathrm{ImTr}[\boldsymbol{\mu}(\omega-H_{\mathrm{eff}})^{-1}\boldsymbol{\mu}\rho(0)], \tag{37}$$

where $\boldsymbol{\mu}$ is the dipole operation and $\rho(0)$ is the thermal-density matrix for the ground electronic state.

We should note that since $\mathbf{\Gamma}(E)$ is a radiative damping matrix, each of its matrix elements can be considered to be smooth functions of E in the range of interest. [In isolated molecules, if $\Gamma_s(E)\gg\sum_l\Gamma_l(E)$, the sum of the (usually) small widths of the $\{\phi_l\}$ manifold, then $\mathbf{\Gamma}(E)$ is $\Gamma_s(E)$ times a matrix quadratic in the E-independent coefficients for the transformation between the $\{\phi_l\}$ and $\{\psi_n\}$ basis sets, thus establishing the smoothness of the elements of $\mathbf{\Gamma}(E)$.]

In the case that the molecular eigenstates $\{\psi_n\}$ are very sparse in the sense that

$$E_n-E_{n'}\gg\Gamma_{nn'}, \tag{38a}$$

the off-diagonal parts of $\mathbf{\Gamma}(E)$ can be safely neglected. Furthermore, in this case, if

$$|E_n-E_{n'}|\gg\tfrac{1}{2}(\Gamma_{nn}+\Gamma_{n'n'}), \tag{38b}$$

the level-crossing-type interference terms in (6b) for $l\neq l'$ are negligible, and the molecular levels represent independently decaying states (and for narrow-band absorption, independently absorbing states) with energies E_n, widths Γ_{nn}, and oscillator strengths $\alpha|W_{\mathrm{ke}}|^2|\langle\phi_s|\psi_n\rangle|^2$. Since the trace of a matrix is an invariant, $\mathrm{Tr}\mathbf{\Gamma}$ in $\{\phi\}$ basis $=\mathrm{Tr}\mathbf{\Gamma}$ in $\{\psi\}$ basis, or

$$\Gamma_s=\sum_n\Gamma_{nn}, \tag{39}$$

so

$$\Gamma_{nn}<\Gamma_s, \qquad \text{for all } n. \tag{40a}$$

Since the lifetime of the molecular eigenstates

$$\tau_n=1/\Gamma_{nn}>1/\Gamma_s=\tau_s, \tag{40b}$$

we have the explanation for the anomalously long lifetimes of the small triatomic molecules observed by Douglas.[12]

In discussing the decay of these states, the $\{a_n(0)\}$ in Eq. (6b) must contain information about the details of the excitation process since it is possible to excite only one or a few of the levels using narrow-band excitation. More precisely, if some $a_n(0)\neq0$, making use of Eq. (6b) and again taking advantage of the restrictions (38a) and (38b), we obtain the simple result

$$P(t)=\sum_n|a_n(0)|^2[1-\exp(-\Gamma_{nn}t)]. \tag{41}$$

Hence the decay of the system is represented in terms of independent contributions from the molecular eigenstates.

In the limit that some of the states $\{\psi_n\}$ violate conditions (38a) and (38b), these levels exhibit level-anticrossing-type interference.[18,21] As shown by Bixon and Jortner[15] when the $\{\psi_n\}$ form a continuum, the result (28) is of course still obtained for broad-band excitation even though the $\{\psi_n\}$ interfere with each other. However, the approach in Sec. III is simpler in this case, and also enables a discussion on the range of validity of that formula.

In the interesting intermediate case where the BO

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[21] See, for example, R. L. Kelly, Phys. Rev. **147**, 376 (1966).

states $\{\phi_l\}$ do not form a continuum, i.e., $\Delta(E)$ is not smooth, but (38a) and/or (38b) may be violated for some states, the $\{\chi_j\}$ basis suggested by Freed[20] may be convenient, and some level-crossing-type interference could be present. Again, in order to discuss the fluorescence characteristics, it is necessary to more carefully specify the excitation process and the details of the energy-level structure.

V. RADIATIVE DECAY IN INTERNAL CONVERSION

It can usually be safely assumed that the BO states $\{\phi_l\}$ do not carry oscillator strength to the ground state ϕ_0, in view of spin selection rules (when the $\{\phi_l\}$ manifold is a triplet) or because of vanishingly small Franck–Condon vibrational overlap factor (when this manifold is a singlet). However when the BO states $\{\phi\ \}$ are singlets, they do carry oscillator strength to some high vibrational levels of the ground electronic state ϕ_0^v. We now face a situation where both ϕ_s and $\{\phi_l\}$ carry oscillator strength. Under these circumstances the radiative decay of the $\{\phi_l\}$ manifold has to be taken into account. Since we are interested here in the case that $\{\phi_l\}$ effectively form a continuum, the initial state is taken as $|\phi_s, \text{vac}\rangle$, resulting from broad-band excitation.

Using the techniques of Sec. III, since emission may also occur to ϕ_0^v, matrix elements of

$$\langle\phi_{\mathbf{ke}}^v | G(E) | \phi_s, \text{vac}\rangle = \langle\phi_{\mathbf{k},\mathbf{e}}^v | QG(E)P | \phi_s, \text{vac}\rangle \quad (42)$$

must also be considered. $\phi_{\mathbf{ke}}^v = |\phi_0^v, \mathbf{k}, \mathbf{e}\rangle$ and P is again given as in Eq. (18). For the case in which the $\{\phi_l\}$ effectively form a continuum,

$$\Delta(E) = 2\int \frac{dE_l\, |v_{sl}(E_l)|^2(\tfrac{1}{2}\Gamma_l)\rho_l(E_l)}{(E-E_l)^2+[\tfrac{1}{2}\Gamma_l(E)]^2}, \quad (43)$$

where ρ_l is again the density of BO states $\{\phi_l\}$ and $\Gamma_l(E)$ are their radiative widths due to spontaneous emission, which are now nonnegligible and are given by

$$\Gamma_l(E) = 2\pi \sum_{\mathbf{e}} \int d\Omega_{\mathbf{k}}\, |\langle\phi_{\mathbf{ke}}^v | H_{\text{int}} | \phi_l\rangle|^2 \rho_p(E-E_0^v),$$

and it has been assumed that the damping matrix $\Gamma_{ll'}$ is diagonal in the $\{\phi_l\}$ basis. A sum over v is implied when more than one vibronic component ϕ_0^v can contribute. $\Delta(E)$, $\Gamma_l(E)$, and $\Gamma_s(E)$ as defined in Sec. III can all be considered to be smooth functions of E.

As in Sec. III the matrix element (42) can be written as

$$(E-E_0^v-k)^{-1}\langle\phi_{\mathbf{ke}}^v | QR(E)P | \phi_s, \text{vac}\rangle \times\{E-E_s+(i/2)[\Gamma_s(E)+\Delta(E)]\}^{-1}. \quad (44)$$

But now since the $\{\phi_l\}$ carry oscillator strength,

$$\langle\phi_{\mathbf{ke}}^v | H_{\text{int}} | \phi_l, \text{vac}\rangle = W_{\mathbf{ke}}^v(1-\delta_{v0}), \quad (45\text{a})$$

$$\langle\phi_{\mathbf{ke}}^v | H_{\text{int}} | \phi_s, \text{vac}\rangle = W_{\mathbf{ke}}^0\delta_{v0}, \quad (45\text{b})$$

the matrix elements of $QR(E)P$ can describe emission to both ϕ_0^v and ϕ_0:

$$\langle\phi_{\mathbf{ke}}^v | QR(E)P | \phi_s, \text{vac}\rangle = W_{\mathbf{ke}}^0\delta_{v0} + \sum_l (W_{ke}^v v_{ls}(1-\delta_{v0})/\{E-E_l-[\tfrac{1}{2}i\Gamma_l(E)]\}), \quad (46)$$

where $v_{ls} = \langle\phi_l | H | \phi_s\rangle$. When (46) is substituted into (44), the first term is of identical form to (23), but the second term has two complex poles. The result of the contour integration (neglecting the contribution from the branch cut) is

$$\langle\phi_{\mathbf{ke}} | \exp(-iHt) | \phi_s, \text{vac}\rangle = \frac{W_{\mathbf{ke}}^0 \exp[-i(E_0+k)t](1-\exp\{-i[E_s-E_0-k-i\tfrac{1}{2}(\Gamma_s+\Delta)]t\})}{[E_0+k-E_s+(i/2)(\Gamma_s+\Delta)]}, \quad (47\text{a})$$

$$\langle\phi_{\mathbf{ke}}^v | \exp(-iHt) | \phi_s, \text{vac}\rangle = \sum_l \frac{W_{\mathbf{ke}}^v v_{ls} \exp[-i(E_0+k)t]}{E_s-E_l+(i/2)(\Gamma_l-\Gamma_s-\Delta)} \times\left(\frac{1-\exp\{-i[(E_s-E_0^v-k-(i/2)(\Gamma_s+\Delta)]t\}}{E_0^v+k-E_s+(i/2)(\Gamma_s+\Delta)} - \frac{1-\exp\{-i[E_l-E_0^v-k-\tfrac{1}{2}i\Gamma_l]t\}}{E_0^v+k-E_l+i\tfrac{1}{2}\Gamma_l}\right), \quad (47\text{b})$$

where Γ_s, Δ, and Γ_l can all be taken as, e.g., $\Gamma(E_0+k)$ in (47a) and $\Gamma(E_0^v+k)$ in (47b). The two fluorescence probabilities are obtained by taking the absolute value squared, integrating over all frequencies k, all $\Omega_{\mathbf{k}}$, and $\mathbf{e}$, giving finally

$$P_0(t) = [\Gamma_s/(\Gamma_s+\Delta)]\{1-\exp[-(\Gamma_s+\Delta)t]\}, \quad (48\text{a})$$

$$P_v(t) = \frac{\{1-\exp[-(\Gamma_s+\Delta)t]\}}{\Gamma_s+\Delta} \sum_l |\langle\psi_l | \phi_s\rangle|^2\Gamma_l + \sum_l |\langle\psi_l | \phi_s\rangle|^2 \times[1-\exp(-\Gamma_l t)] + 2\sum_l \Gamma_l |\langle\psi_l | \phi_s\rangle|^2 \,\text{Re}\left(\frac{1-\exp\{-[\tfrac{1}{2}(\Gamma_s+\Delta+\Gamma_l)+i(E_l-E_s)]t\}}{\tfrac{1}{2}(\Gamma_s+\Delta+\Gamma_l)+i(E_l-E_s)}\right), \quad (48\text{b})$$

where (again ignoring level shifts)

$$|\langle\psi_l\,|\,\phi_s\rangle|^2=v_{ls}^2/[(E_s-E_l)^2+\tfrac{1}{4}(\Gamma_s+\Delta-\Gamma_l)^2] \tag{48c}$$

is the component of ϕ_s in the molecular eigenstate ψ_l. In intermediate-case molecules (discussed in Sec. VI), the $\sum_l$ in (48b) would (with slight alterations in that formula) be understood to be a sum over the few "strongly coupled resonances," and an integral over the remaining quasicontinuum. For simplicity, since the more general case can be inferred from Sec. VI, we consider the extreme statistical limit where $\sum_l\rightarrow\int dE_l\rho_l(E_l)$, etc. If we make the simple approximation that Γ_l is a constant,

$$P_v(t)=\frac{\{1-\exp[-(\Gamma_s+\Delta)t]\}\Delta\Gamma_l}{(\Gamma_s+\Delta)(\Gamma_s+\Delta-\Gamma_l)}+\frac{\Delta[1-\exp(-\Gamma_lt)]}{(\Gamma_s+\Delta-\Gamma_l)}+\frac{2[1-\exp[-(\Gamma_s+\Delta)t]\}\Gamma_l\Delta}{(\Gamma_s+\Delta-\Gamma_l)^2}. \tag{49}$$

The decay probability to the lowest vibronic component of the ground state is determined by the branching ratio $\Gamma_s/(\Gamma_s+\Delta)$ and by the lifetime $(\Gamma_s+\Delta)^{-1}$. These results are identical with those obtained in Sec. III, as also in the present case of internal conversion the manifold $\{\phi_l\}$ does not carry oscillator strength to the lowest vibronic state. The fluorescence probability to the higher vibronic levels [Eqs. (48b) and (49)] consists of three contributions which involve two "direct-decay" terms and an interference term: (a) The first term in Eq. (49) describes an initial decay rate (for $t\rightarrow0$) which is proportional to Γ_l. For long times this term exhibits a fast decay with a lifetime of $(\Gamma_s+\Delta)^{-1}$, which arises from the fact that a molecular eigenstate ψ_s, which is primarily ϕ_s and has a width $\Gamma_s+\Delta$, contains some $\{\phi_l\}$. For this long-time scale the contribution from this term is negligible, as under common circumstances for internal conversion between excited singlet states $\Gamma_s\ll\Delta$ and $\Gamma_l\ll\Delta$, so that the contribution of this term to the fluorescence is expected to be of the order of $\Gamma_l/\Delta\ll1$. (b) The second term in Eqs. (48b) and (49) corresponds to the "direct" radiative decay of the manifold $\{\phi_l\}$ which is determined by the lifetimes $\{\Gamma_l\}$. It is important to notice that the initial rate $(dP_v/dt)_{t=0}$ arising from the terms (a) and (b) is proportional to Γ_l, while for longer times the (b) term dominates the "direct" decay. Hence the joint contribution from the "direct"-decay terms will be always determined by the lifetimes Γ_l of the $\{\phi_l\}$ states. (c) The third contribution to the decay probability [Eq. (49)] arises from level-crossing terms which in the statistical limit gives a small contribution that is similar in form to (a). The radiative decay of the manifold $\{\phi_l\}$ will exhibit interference effects in the more general and interesting intermediate case which is discussed in Sec. VI.

Some interesting conclusions emerge from the present preliminary and admittedly oversimplified description of the radiative decay of a second-excited singlet state of a large molecule. The resonance fluorescence is expected to be very weak in view of the small branching ratio $\Gamma_s/(\Gamma_s+\Delta)\ll10^{-4}$, but when this fluorescence will be experimentally detected, the decay will exhibit ordinary exponential behavior. The fluorescence yield to the highly vibrationally excited ground state is close to unity, *and thus the fluorescence appears to arise from the first singlet.* Of course, any "intersystem crossing" to triplet states has been neglected and would have to be included when appropriate. We now turn our attention to the radiative decay to the higher vibronic components of the ground state, which do roughly but not exactly overlap the fluorescence spectrum from the first excited singlet state. This decay is expected to reveal interference effects between the closely spaced states $\{\phi_l\}$. The detailed features of this interesting new effect are of course determined by the details of the excitation process (i.e., narrow vs broad-band excitation).

VI. INTERMEDIATE-LEVEL DENSITY AND VIBRATIONAL RELAXATION IN THE $\{\phi_l\}$ MANIFOLD

It was pointed out in Sec. III that the "smoothness" of the function $\Delta(E)$ [Eq. (24)] provides a proper criterion for the existence of an effective continuum which gives rise to an irreversible intramolecular decay. In the statistical limit the density of vibronic levels in the manifold $\{\phi_l\}$ is sufficiently large so that $\Delta(E)$ [Eq. (26)] is independent of the widths $\{\Gamma_l\}$ of the states in the manifold $\{\phi_l\}$. If we invoke the usual assumption that the states $\{\phi_l\}$ do not carry oscillator strength the widths $\{\Gamma_l\}$ are very small $(\Gamma_l\rightarrow0^+)$ in the isolated molecule, while coupling of the molecule with an external medium would provide an additional nonzero contribution to these widths. Now, it is well known that not all the states in the manifold $\{\phi_l\}$ couple to ϕ_s with the same efficiency. This problem is of minor importance for the statistical case; however, for somewhat smaller molecules (or when the splitting between two different electronic states is small) the level density is lower, and the nature of these strongly coupled levels in the manifold $\{\phi_l\}$ should be considered. We shall refer to such systems as intermediate cases. In this case the relevant matrix elements of the Green's function may be characterized by more than a single complex pole, and the behavior of the intermediate case molecule will be influenced by external perturbation.

It is convenient at this point to consider $\{\phi_l\}$ to consist of two sets: a weakly coupled continuum $\{\phi_{l'}\}$, and a few discrete levels $\{\phi_t\}$ which are strongly coupled to ϕ_s, so that $v_{sl'} \ll v_{st}$ for all l' and t. For simplicity we represent the "strongly coupled" subset $\{\phi_t\}$ by a single "effective" level ϕ_t. Furthermore we again consider broad-band excitation and assume that $\Psi(0) = |\phi_s; \text{vac}\rangle$. Consider a strongly coupled single resonance so that $|v_{st}| > |E_s - E_t| \sim \Delta_s \sim \Gamma_s$. Attention is focused on two limiting cases whereupon the width of the strongly coupled level is appreciably smaller than the coupling term, e.g., $|v_{st}| \gg \Gamma_t$ (a narrow resonance), or alternatively this width exceeds the coupling term, e.g., $|v_{st}| \ll \Gamma_t$ (a broad resonance). From Eqs. (20)–(22) in the general case of a single coupled resonance:

$$\langle\phi_{\mathrm{k,e}} | G(E) | \phi_s; \text{vac}\rangle = (E - E_0 + k)^{-1} W_{\mathrm{ke}} (E - E_s + (i/2)[\Gamma_s(E) + \Delta_s(E)] - \{|v_{st}|^2 / [E - E_t + \tfrac{1}{2} i \Gamma_t(E)]\})^{-1}, \quad (50)$$

where Γ_s is the radiative lifetime of $\phi_s (\Gamma_s = 2\pi\rho_k \int |W_{\mathrm{ke}}|^2)$ and $\Delta_s = 2\pi |v_{sl'}|^2 \rho_{l'}$ is the width due to the coupling of ϕ_s with the effective continuum $\{\phi_{l'}\}$. In the isolated molecule $\Gamma_t = 2\pi |v_{tl'}|^2 \rho_{l'}$ is the width of ϕ_t due to coupling with the effective continuum $\{\phi_{l'}\}$. If $\{\phi_{l'}\}$ and ϕ_t are BO functions corresponding to the same electronic configuration, then $v_{l't} = 0$. However the manifold $\{\phi_{l'}\}$ may include also vibronic components corresponding to other electronic configurations such as the ground electronic state. In this case $v_{l't}$ is nonzero, but nevertheless very small. Thus in the isolated molecule we expect Γ_t to correspond to a narrow resonance. When external perturbations are exerted we expect Γ_t to increase substantially due to external vibrational relaxation. We shall return later to this point. Now, both Δ_s and Γ_t are expected to be smooth functions of E. The matrix element of the Green's function (50) now has two complex poles located at the energies:

$$E_{\pm} = \tfrac{1}{2}(E_s + E_t - (i/2)(\Gamma + \Gamma_t) \pm \{[E_s - E_t - (i/2)(\Gamma - \Gamma_t)]^2 + 4|v_{st}|^2\}^{1/2}), \quad (51)$$

where $\Gamma = \Gamma_s + \Delta_s$. Thus we can write

$$\langle\phi_{\mathrm{ke}} | G(E) | \phi_s; \text{vac}\rangle = (E - E_0 - k)^{-1} W_{\mathrm{ke}} [E - E_t + (i/2)\Gamma_t](E - E_+)^{-1}(E - E_-)^{-1}. \quad (52)$$

Equations (51) and (52) result in

$$\langle\phi_{\mathrm{ke}} | \exp(-iHt) | \phi_s; \text{vac}\rangle = \frac{W_{\mathrm{ke}}}{E_+ - E_-} \left(\frac{\exp[-i(E_0 + k)t][E_+ - E_t + (i/2)\Gamma_t]}{E_0 + k - E_+} \{1 - \exp[-i(E_+ - E_0 - k)t]\} \right.$$
$$\left. - \frac{\exp[-i(E_0 + k)t][E_- - E_t + (i/2)\Gamma_t]}{E_0 + k - E_-} \{1 - \exp[-i(E_- - E_0 - k)t]\} \right), \quad (53)$$

and the fluorescence probability can be displayed in the form

$$P = \sum_{\mathrm{e}} \int d^3k \, |\langle\phi_{ke} | \exp(-iHt) | \phi_s \text{vac}\rangle|^2$$
$$= \frac{\Gamma_s}{(\Delta E)^2 + \frac{1}{4}(\Gamma_+ - \Gamma_-)^2} \left[\frac{(E_+{}^0 - E_t)^2 + [(\Gamma_+ - \Gamma_t)^2/4]}{\Gamma_+} [1 - \exp(-\Gamma_+ t)] + \frac{(E_-{}^0 - E_t)^2 + (\Gamma_- - \Gamma_t)^2/4}{\Gamma_-} \right.$$
$$\left. \times [1 - \exp(-\Gamma_- t)] + 2\,\mathrm{Re} \left(\frac{[E_+ - E_t + (i/2)\Gamma_t][E_-^* - E_t - (i/2)\Gamma_t]}{i(E_+ - E_-^*)} \{1 - \exp[i(E_-^* - E_+)t]\} \right) \right], \quad (54)$$

where $E_{\pm} = E_{\pm}{}^0 - (i/2)\Gamma_{\pm}$ and $\Delta E = E_+{}^0 - E_-{}^0$.

Consider now the case of a narrow resonance when the coupling matrix element v_{st} exceeds both the widths and the spacings of the levels E_s and E_t:

$$|v_{st}| > |E_s - E_t - (i/2)(\Gamma - \Gamma_t)|. \quad (55)$$

Under these circumstances

$$E_{\pm} = \tfrac{1}{2}(E_s + E_t) \pm |v_{st}| - (i/2)[\tfrac{1}{2}(\Gamma + \Gamma_t) \pm \tfrac{1}{2}(E_s - E_t)(\Gamma - \Gamma_t)/|v_{st}|] + \cdots, \quad (56)$$

so that the energy levels are

$$E_{\pm}{}^0 \approx \tfrac{1}{2}(E_s + E_t) \pm |v_{st}| \quad (57)$$

and the corresponding widths are given by

$$\Gamma_{\pm} = \tfrac{1}{2}(\Gamma + \Gamma_t) \pm \tfrac{1}{2}(E_s - E_t)(\Gamma - \Gamma_t)/|v_{st}|. \quad (58)$$

The fluorescence decay is now given by

$$P(t)\approx\frac{\Gamma_s}{4\Gamma_+}[1-\exp(-\Gamma_+t)]+\frac{\Gamma_s}{4\Gamma_-}[1-\exp(-\Gamma_-t)]-2\,\mathrm{Re}\left(\frac{\Gamma_s}{4}\frac{1-(i/2)(\Gamma_t/|v_{st}|)}{\frac{1}{2}(\Gamma+\Gamma_t)+2i|v_{st}|}\times(1-\exp\{-[\tfrac{1}{2}(\Gamma+\Gamma_t)-2i|v_{st}|]t\})\right).\quad(59)$$

Thus in the general case of a strongly coupled narrow resonance the decay consists of two "direct" terms characterized by the lifetimes Γ_+ and Γ_- and an interference term which would be the same order of magnitude as the direct term when $|v_{st}|\sim|E_s-E_t-(i/2)(\Gamma-\Gamma_t)|$. The situation is reminescent of level anticrossing when a small number of resonances are encountered. Under the extreme conditions when $|v_{st}|\gg|E_s-E_t|$ and $|v_{st}|\gg|\Gamma-\Gamma_t|$, we may set Γ_+ and Γ_- to be about equal, i.e., $\Gamma_+\approx\Gamma_-\approx\frac{1}{2}(\Gamma_t+\Gamma)$. The dominating contribution to the fluorescence yield now arises from direct-decay terms, while the interference term is of the order of $\Gamma_s\Gamma/|v_{st}|^2$ and can be safely neglected. For weaker coupling (smaller $|v_{st}|$) these interference terms are nonnegligible, and the more general formula (54) must be used. We then obtain the simple approximate result

$$P(t)\approx[\Gamma_s/(\Gamma+\Gamma_t)]\{1-\exp-[\tfrac{1}{2}(\Gamma+\Gamma_t)]t\}.\quad(60)$$

We may thus conclude that an addition of a single strongly coupled narrow resonance to the smooth quasicontinuum results in an (approximate) exponential decay mode characterized by the lifetime $2(\Gamma_s+\Delta_s+\Gamma_t)^{-1}$. It should be noted that the addition of a narrow strongly coupled resonances affects the lifetime in quite a complex manner. The lifetime, relative to $(\Gamma_s+\Delta_s)^{-1}$, is lengthened by a numerical factor which is of the order of the number of strongly coupled levels, while the inclusion of Γ_t (or rather $\sum_t\Gamma_t$ where the sum is taken over the small number of strongly coupled states) leads to shortening of the lifetime relative to the reference value mentioned above. Finally we should note that the branching ratio for a single narrow ϕ_s, ϕ_t is of the approximate form $\Gamma_s/(\Gamma_s+\Delta_s+\Gamma_t)$, as it includes contributions from both the decay modes Γ_+ and Γ_-. In the case of a finite set of strongly coupled narrow levels, the set $\{\phi_s,\phi_t\}$ behaves just as a small molecule which may exhibit level-anticrossing effects. Note that total width

$$\Gamma_s+\Delta_s+\sum_{t=1}\Gamma_t\equiv\Gamma_{\mathrm{tot}}$$

is partitioned between the N levels resulting in lifetimes $\alpha_j\Gamma_{\mathrm{tot}}^{-1}$, where

$$\sum_{j=1}^{n}\alpha_j=1,$$

and the individual branching ratios are $\alpha_j'\Gamma_s/\Gamma_{\mathrm{tot}}$. The total fluorescence yield will probably be of the order $\Gamma_s/\Gamma_{\mathrm{tot}}$.

We now turn our attention to the case of a broad strongly coupled resonance characterized by the width Γ_t^b so that $\Gamma_t^b\gg|v_{st}|\gg\Delta_s\sim\Gamma_s\sim|E_s-E_t|$. Under these limiting conditions the energy levels are

$$E_+\approx E_s-(i/2)[\Gamma+(4|v_{st}|^2/\Gamma_t^b)],\quad(61a)$$

$$E_-\approx E_t-(i/2)[\Gamma_t^b-(4|v_{st}|^2/\Gamma_t^b)],\quad(61b)$$

$$\Delta E\approx E_s-E_t,\quad(61c)$$

$$\Gamma_+\approx\Gamma+(4|v_{st}|^2/\Gamma_t^b),\quad(61d)$$

$$\Gamma_-\approx\Gamma_t^b.\quad(61e)$$

The damping of the state located at E_s is characterized by a width $\Gamma_s+\Delta_s+(4|v_{st}|^2/\Gamma_t^b)$ so that the strongly coupled broad level adds an additional contribution to the width of the resonance which looks like an additional contribution from the continuum of states $\{\phi_l\}$ for which the effective "density of states" is $(2/\pi)(|v_{st}|^2/\Gamma_t^b|v_{sl}|^2)$. The fluorescence yield is now given in the approximate form

$$P(t)\approx\frac{\Gamma_s}{\Gamma_+}[1-\exp(-\Gamma_+t)]+\frac{\Gamma_s}{\Gamma_t^b}[1-\exp(-\Gamma_t^bt]+\frac{4\Gamma_s}{\Gamma+\Gamma_t^b}\{1-\exp[-(\Gamma+\Gamma_t^b)t]\cos(E_s-E_t)t\}.\quad(62)$$

The contributions from the second direct-decay term and from the third interference term in Eq. (62) are of the order of Γ_s/Γ_t^b and are thus expected to be small. Thus the following approximate relation is obtained

$$P(t)\approx\frac{\Gamma_s}{[\Gamma+(4|v_{st}|^2/\Gamma_t^b)]}\times\left\{1-\exp\left[-\left(\Gamma+\frac{4|v_{st}|^2}{\Gamma_t^b}\right)t\right]\right\}.\quad(63)$$

This result implies that a superposition of a broad strongly coupled resonance to a smooth quasicontinuum results in the approximate branching ratio $\Gamma_s[\Gamma_s+\Delta_s+(4|v_{st}|^2/\Gamma_t^b)]^{-1}$ and in the decay time $[\Gamma_s+\Delta_s+(4|v_{st}|^2/\Gamma_t^b)]^{-1}$. Again, if a small finite number of strongly coupled states has to be considered, the decay time is expected to be of the approximate form $[\Gamma_s+\Delta_s+\sum_t 4|v_{st}|^2/\Gamma_t^b]^{-1}$, and hence, the $\{\phi_t\}$ now behave as if they were part of the continuum of vibronic BO states. In the present case, unlike the situation encountered in the case of a narrow strongly coupled resonance, a shortening of the decay time, relative to $(\Gamma_s+\Delta_s)^{-1}$, is encountered.

At this point we are able to provide a qualitative description of medium effects on the decay of excited states of molecules which correspond to an intermediate case when the medium is "inert" in the sense that it produces negligible level shifts. When such a molecule is isolated in the gas phase, one can safely assume that the widths Γ_t of the strongly coupled state correspond to narrow resonances. However when this molecule is subjected to external perturbations (i.e., collisions in the gas phase or in solution) the major contribution to the widths of the strongly coupled states which arises from molecular vibrational relaxation has to be included.[22,23] A reasonable order-of-magnitude estimate of Γ_t^b obtained from vibrational-relaxation data in a dense medium is $\Gamma_t^b\sim0.1\ \text{cm}^{-1}-1\ \text{cm}^{-1}$. Hence, an externally perturbed intermediate molecule can be described in terms of strongly coupled broad resonances.

The occurrence of a set of strongly coupled levels $\{\phi_t\}$, is very reminiscent of the discussion of small molecules in Sec. IV. Again only one BO component carries oscillator strength, but now all of the states $\{\phi_t\}$ may have final widths. The result is that sums of the widths of these states in the isolated molecule will probably not exceed the width of the single broad resonance which is encountered when the molecule is perturbed by an "inert" medium since we expect that $\Gamma_t\lesssim4|v_{st}|^2/\Gamma_t^b$. However, in the free molecule, since this width is shared between a few closely spaced resonances, each of their lifetimes is longer than in the presence of the medium. The observed result is then a longer lifetime in the intermediate-case molecule than in the medium. A cursory examination of the fluorescence quantum yields indicates that

$$\frac{\Gamma_s}{\Gamma_s+\Delta_s+4|v_{st}|^2/\Gamma_t^b}<\frac{\Gamma_s}{\Gamma_s+\Delta_s+\sum_t\Gamma_t},$$

so we expect the fluorescence quantum yield of an intermediate case molecule to decrease in a medium.[24]

The experimental implications of this analysis provide a qualitative interpretation for the radiative decay of intermediate-case molecules. The ${}^1B_{2u}$ state of the benzene molecule reveals different branching ratios under different experimental conditions.[13,24,25] In the gas phase at the low-pressure limit the fluorescence quantum yield is $P(\infty)=0.32$ which drops to $P(\infty)=0.2$[13] at high pressures, while in an organic solvent the value $P(\infty)=0.09$ [26] was reported. Such a behavior is expected when a small number of strongly coupled levels are present. (A similar result could, of course, occur in the statistical limit when solvent shifts vary greatly for different electronic states.) In a large molecule, which corresponds to the statistical limit, a physically meaningful distinction can no longer be made between weakly coupled and (a large number of) strongly coupled states in the manifold $\{\phi_l\}$. When the number of strongly coupled states becomes large, they have to be directly included in $\Delta(E)$, and the final result for the narrow radiative width will be independent of the widths $\{\Gamma_t\}$. The coupling of a large statistical limit molecule with an "inert" medium is expected to exhibit a negligible effect on the decay process. Indeed, in a large molecule such as anthracene the lifetime of the first excited singlet state and the fluorescence quantum yield is identical in the gas phase and in an organic solvent.[27]

This discussion, although quite qualitative, does provide some insight into what is meant by the smoothness of $\Delta(E)$. If matrix elements of $G(E)$ have poles at $E_j-(i/2)\Gamma_j$, where $|v_{sj}|\ll|E_s-E_j|$, $|\Gamma_s-\Gamma_j|$, then this pole behaves as part of an effective continuum which gives rise to relaxation. In the opposite limit where $|v_{sj}|\gg|E_s-E_j|$, $|\Gamma_s-\Gamma_j|$, the set of states $\{\phi_s, \phi_j\}$ may behave as a small set of strongly coupled states, which is analogous to the small-molecule limit, except that now we have $\Gamma_j\simeq\Gamma_s$. For $|v_{sj}|\sim|E_s-E_j|$, $|\Gamma_s-\Gamma_j|$, interference terms can become important.

VII. CONCLUSIONS

In the present work we have presented a general quantum-mechanical treatment of the radiative decay of polyatomic molecules. It is evident that as both intramolecular vibronic (spin–orbit, etc.) interactions and coupling with the radiation field have to be simultaneously accounted for, the decaying excited states of a polyatomic molecule should be described in terms of resonance (or compound) states similar to formulations used in the theory of nuclear reactions,[28] scattering,[16] predissociation,[29] and photoionization.[30]

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[22] W. Siebrand, Fourth Molecular Crystals Symposium, THT Emschede, Holland, July 1968, p. 80 (unpublished).

[23] The external medium can also add another width to the state due to collisional quenching of this state. This effect is trivial and will just lead to vibrational relaxation. However, this quenching rate should not differ significantly in the intermediate case and statistical limit.

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[28] See, for example, M. A. Preston *Physics of the Nucleus* (Addison-Wesley Publ. Co., Inc., London, 1962).

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[30] U. Fano, Phys. Rev. **124**, 1866 (1961).

This feature of excited molecular states has been recently realized;[11,14] however, the present treatment handles the decay problem without relying on any simplified model systems, as was done in previous work on this subject.[10,11,14,15] The description of this decaying resonance state in terms of the BO basis or the molecular eigenstate basis does not reflect in any way on the nature of the physical description since either (complete) set can be legitimately employed. In choosing a particular basis set, the form of the electronic Hamiltonian and of the damping matrix in that representation have to be considered. In the case of broad-band excitation of a large molecule which corresponds to the statistical limit, the BO basis set is more suitable, while in the case of a small (say, triatomic) molecule which corresponds to the sparse case, the molecular eigenstate basis is more convenient. We hope that these general comments will remove some confusion which existed in the literature concerning the choice of the "proper" basis set for the description of the decaying excited states of polyatomic molecules.

In this paper we have attempted to show that the mathematical techniques that have had such great success in the fields of scattering theory, nuclear-reaction theory, predissociation, etc., can also be valuable in understanding radiationless processes in polyatomic molecules. The Green's function techniques, aside from being simple to use, *are completely general and very physical in nature*. As such, a few simple examples encountered in radiationless processes are discussed:

(1) The well-known result for intersystem crossing in the statistical limit is shown to arise simply from the presence of a single zeroth-order state which is coupled to both radiative and vibronic continua.

(2) The anomalously long lifetimes observed by Douglas in small (triatomic) molecules are seen to arise from the mixing of discrete zeroth-order vibronic states, only one of which carries oscillator strength.

(3) Internal conversion can also be discussed in terms of this formalism, and interesting features such as interference phenomena can be described. (These interference effects merit further theoretical and experimental work.)

(4) A discussion can also be given of cases intermediate between the sparse and statistical limits, which may shed some light on the effects of the external medium on the observed fluorescence yields of these molecules.

In keeping with our broad purpose of demonstrating the wide utility of the Green's function methods to radiationless processes as well as explaining some of the observed physical phenomena, the discussions are not meant to be complete. Specifically, the details of the excitation process are not treated in complete generality, but are chosen as a matter of convenience and simplicity in each case. A broad-band excitation mode was considered in the case of a large molecule. A discussion of the narrow-band excitation was given; however, the explicit solution was not provided. This extension is straightforward, but can be rather cumbersome. In the case of a sparse level distribution, the narrow-band excitation is trivial and was considered in Sec. IV.

The main handicap in the quantitative application of the theory is the lack of any detailed information on the coupling parameters v_{sl}, the widths Γ_l, and the density of states in the manifold $\{\phi_l\}$. It is important to notice that contributions to $\{\phi_l\}$ arise from all the electronic states located below ϕ_s. Some attempts were made in the past to reverse the order of the analysis and to use the experimental decay times coupled with rough estimates of the (total) density of states to make estimates of the (mean) coupling parameters v_{sl}. The results of the present work suggest some further experimental methods to monitor the nature of level distribution and the coupling parameters. Interference effects may be observed in the radiative decay in internal conversion in isolated intermediate-case molecules and will possibly resolve the question of what is the number of effectively strongly coupled states in the manifold $\{\phi_l\}$. Experimental work on intermediate-case isolated molecules will result in nonexponential decay times which will elucidate the nature of the strongly coupled levels. Another technique to probe the nature of the level distribution in the $\{\phi_l\}$ manifold in isolated intermediate case molecules will involve studies of fluorescence decay from the first singlet in a strong magnetic field. The triplet manifold $\{\phi_l\}$ will be then considerably modified (due to Zeeman splitting of each level), so that the number of the strongly coupled narrow resonances may be altered. Finally, from the studies of the decay of intermediate molecules under external perturbations, complementary information may be obtained on the nature of the intramolecular coupling parameters and on vibrational relaxation times in a dense medium.

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