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Theory of Radiationless Transitions in an Isolated Molecule

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A treatment of radiationless transitions in an isolated molecule is considered using a Green's-function formalism. Molecular eigenstates are constructed by superposition of quasidegenerate Born–Oppenheimer states, considering the mixing of one and two discrete zero-order BO states(s) with a manifold of quasicontinuum BO states, which correspond to another electronic configuration. The nature of inhomogeneous line broadening and the time evolution of the excited states are considered. The radiative decay following a coherent excitation process is treated in detail. The various features and anomalies observed in the decay times of medium-size and large molecules can be properly accounted for.

I. INTRODUCTION

Studies of aromatic compounds have revealed that in complex molecules, even when isolated, nonradiative decay of an excited state may compete very efficiently with radiative decay of the same state. For example, excitation of anthracene to the second singlet state leads to fluorescence from the vibrationally excited first-singlet state, not from the second singlet state.[1] A second interesting example is benzene which, even in the free molecule limit, undergoes intersystem crossing.[2] That is, excitation of benzene to the first singlet state leads to a finite yield of benzene in the lowest triplet state. These and many other facts have been known for some time, but it is only recently that an understanding of the processes observed has begun to develop.

The electronic states of a molecule are usually classified in the representation derived from the Born–Oppenheimer (BO) approximation. It was demonstrated by Franck and Sponer and by Kubo[3] that the nuclear kinetic-energy terms can induce radiationless transitions between zero-order BO states. Robinson and Frosch, Lin, and Siebrand[4] have presented analyses of internal conversion and of intersystem crossing starting from the assumption that the initial and the final states are well-defined BO states. Now, it is well known that the BO approximation is valid only if the energy difference between the BO states is large relative to the vibronic matrix elements connecting these states. When there are near-degenerate or degenerate zero-order vibronic states belonging to different electronic configurations the BO approximation fails completely. The breakdown of the BO approximation in such circumstances is well known as the Jahn Teller, the Pseudo-Jahn Teller, and the Renner effects.

Provided that the BO states generate a complete set of functions, the eigenstates of the molecular Hamiltonian may be represented as a superposition of BO states. This procedure, which was used by Bixon and Jortner,[5] will be adopted in the present paper. It differs from the Robinson–Frosch–Lin–Siebrand treatment in that we do not regard the BO states as good zero-order approximations to the excited states of the molecule. It is just the very breakdown of the BO approximation which plays the central role in the theory of radiationless transitions presented here.

In the present paper general-perturbation theoretic methods are applied to the study of the coupling of one or more zero-order states (which are connected to the ground state by finite transition moments) with a dense manifold of zero-order vibronic states belonging to a second electronic configuration (which have vanishing transition moments to the ground state). A detailed examination of the time evolution of the excited states is presented. We have chosen to use a Green's function formalism because of the generality of this method. The general techniques have been applied by Harris[6] to the study of predissociation. Our analysis is an extension and generalization of the work of Bixon and Jortner. The analysis presented herein may be shown to be completely equivalent to the configuration–interaction approach of Fano.[7] Indeed, at several points we shall compare our predictions with those of Fano and of Mies and Krauss.[8] A different point of view from that presented herein was adopted by Jortner and Berry.[9] These investigators consider the nature of intramolecular vibronic coupling and the decay of coherently excited states as an example of a quantum-beat experiment. Two extreme cases were considered: the resonant limit and the statistical limit characterized by small and large densities of molecular eigenstates, respectively. Quantum-beat signals between closely spaced eigenstates should be observed in a radiative decay process in the resonance limit. In small molecules, e.g., SO_2, the radiative lifetime is much longer than predicted from the known integrated absorption curve. In the statistical limit, intramolecular interference effects,

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[1] W. V. Gruzinskii and N. A. Borisevitch, Opt. Spectrosc. **15**, 246 (1963) [Opt. Spektrosk. **15**, 457 (1963)].

[2] G. B. Kistiakowsky and C. S. Parmenter, J. Chem. Phys. **42**, 2942 (1965).

[3] J. Franck and H. Sponer, Gott. Nachr. **1928**, 241; R. Kubo, Phys. Rev. **86**, 929 (1952).

[4] G. W. Robinson and R. P. Frosch. J. Chem. Phys. **37**, 1962 (1962); **38**, 1187 (1963). Also, S. H. Lin, *ibid.* **44**, 3759 (1966); and W. Siebrand, *ibid.* **46**, 440 (1967).

[5] M. Bison and J. Jortner, J. Chem. Phys. **48**, 715 (1968).

[6] R. A. Harris, J. Chem. Phys. **39**, 978 (1963).

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

[8] F. H. Mies and M. Krauss, J. Chem. Phys. **45**, 4455 (1966).

[9] J. Jortner and R. S. Berry, J. Chem. Phys. **48**, 2757 (1968).

which were considered by Jortner and Berry using a simple step-function approximation for the line shape, lead to a radiationless decay and to a reduction of the quantum yield. In the present work we generalize the treatment of the radiative decay of coherently excited molecular eigenstates by taking into account the proper line-shape function for the inhomogenously broadened band.

The principal results of the theory of radiationless transitions presented herein are the following:

(a) It is predicted that under certain circumstances the rate of decay of a BO component of an excited state cannot be described in terms of a simple single exponential form. (See *Note added in proof*, Sec. VI.)

(b) The line shape corresponding to the radiative decay of an excited molecule is shown to correspond to a case of inhomogeneous broadening.

(c) The lifetime against radiative decay of an excited BO component in resonance with a dense manifold of BO components is lengthened by the dilution accompanying the mixing of states. This increase of the lifetime, which depends on the level spacing in the dense manifold, may be very large. Such effects have been observed with small molecules, e.g., SO_2.[10]

(d) The lifetime against radiative decay depends on the state to which the molecule is excited.

(e) In the case that transitions from the ground state to a discrete BO state are allowed, but to the continuum are not allowed, the absorption line shape is predicted to be Lorentzian unless the level shift and linewidth are energy dependent. In the latter case the absorption line shape is an asymmetric Lorentzian.

(f) The quantum yield of fluorescence depends on both the nonradiative lifetime and certain features of the energy spectrum of the dense quasicontinuum of BO states. In cases of interest the usual relationship between quantum yield and lifetime is recovered.[11]

(g) Radiationless transitions in an isolated molecule can be described as an intramolecular interference phenomenon.

This paper is primarily devoted to describing the theory of radiationless transitions in isolated molecules, but one numerical example is considered for illustrative purposes, i.e., in the last section we discuss radiationless transitions in anthracene.

II. GENERAL COMMENTS

In this paper we discuss the properties of an excited free molecule in interaction with the radiation field. Our analysis is based on establishing a relationship between approximate Born–Oppenheimer states and the exact molecular eigenstates. To begin we represent the molecular Hamiltonian of an isolated molecule in the form

$$H=-\sum_N (\hbar^2/2M_N)\nabla_N^2-\sum_i (\hbar^2/2m)\nabla_i^2 -\sum_i\sum_N (Z_Ne^2/r_{iN})+\sum_{i>j} (e^2/r_{ij}) +\sum_{N>M} (Z_NZ_Me^2/r_{NM}), \quad (1)$$

where M_N and Z_Ne denote the mass and charge of the Nth nucleus of the molecule, m the mass of the electron, and r_{ij}, r_{iN}, r_{NM} the distance between two electrons, between electron i and nucleus N, and between two nuclei, respectively. In the Born–Oppenheimer approximation the nuclei move in an effective potential generated by the electron distribution, while the electron distribution is a function of the nuclear positions. The BO wavefunctions are the well-known products

$$\psi_{as}^{\mathrm{BO}}(\{\mathbf{r}\},\{\mathbf{R}\})=\phi_a(\{\mathbf{r}\},\{\mathbf{R}\})\chi_{as}(\{\mathbf{R}\}), \quad (2)$$

where ϕ_a $(\{\mathbf{r}\}, \{\mathbf{R}\})$ is the electronic wavefunction corresponding to the stationary nuclear configuration $\{\mathbf{R}\}$ and $\chi_{as}(\{\mathbf{R}\})$ is the nuclear vibrational wavefunction corresponding to the electronic state a. As should be obvious, we have denoted by $\{\mathbf{r}\}$ and $\{\mathbf{R}\}$ the complete sets of electronic and nuclear coordinates of the molecule. Clearly, the product states defined in Eq. (2) will be good approximations to the eigenstates of H [defined in Eq. (1)] only if the off-diagonal elements of H in the basis defined by Eq. (2) are small relative to the separation of vibronic levels. By direct computation one finds[12]

$$\begin{aligned}\langle\psi_{as}^{\mathrm{BO}}\mid H\mid\psi_{ai}^{\mathrm{BO}}\rangle&=\langle\chi_{as}\mid -\sum_N(\hbar^2/2M_N)\nabla_N^2\\&\quad+\sum_{N>M}(Z_NZ_Me^2/r_{NM})+E_a(\{\mathbf{R}\})\\&\quad+\langle\phi_a\mid-\sum_N(\hbar^2/2M_N)\nabla_N^2\mid\phi_a\rangle\mid\chi_{ai}\rangle\\&=\langle\psi_{as}^{\mathrm{BO}}\mid H^{\mathrm{BO}}\mid\psi_{ai}^{\mathrm{BO}}\rangle\\&=E_{as}\delta_{si} \qquad (3)\end{aligned}$$

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[10] A. E. Douglas, J. Chem. Phys. **45**, 1007 (1966) and references therein.

[11] The usual definition of the quantum yield implies that the decay is exponential. When this is not true, a new definition must be adopted. On the scale of one decade of time we predict only small deviations from exponential decay, hence the statement made.

[12] In Eqs. (3) and (4), the brackets involving ϕ's imply integration over the electronic coordinates $\{\mathbf{r}\}$ only. The ∇_n^2 operators do not act outside the brackets. Note also that

$$\Big[-\sum_i(\hbar^2/2m)\nabla_i^2-\sum_i\sum_n(Z_ne^2/r_{in})+\sum_{i>j}(e^2/r_{ij})\Big]\phi_a(\{\mathbf{r}\},\{\mathbf{R}\}) =E_a(\{\mathbf{R}\})\phi_a(\{\mathbf{r}\},\{\mathbf{R}\})$$

$$H^{\mathrm{BO}}=-\sum_N(\hbar^2/2M_N)\nabla_N^2+\sum\sum_{N>M}(Z_NZ_Me^2/r_{NM})+\sum_a\mid\phi_a\rangle(E_a(\{\mathbf{R}\}) +\langle\phi_a\mid-\sum_N(\hbar^2/2M_N)\nabla_N^2\mid\phi_a\rangle)\langle\phi_a\mid.$$

The ∇_N^2 in the first term acts only on $\chi_{as}(\{\mathbf{R}\})$.

and

$$\langle\psi_{as}{}^{\mathrm{BO}}\mid H\mid\psi_{bi}{}^{\mathrm{BO}}\rangle=\langle\chi_{as}\mid\langle\phi_a\mid-\sum_N(\hbar^2/2M_N)\nabla_N{}^2\mid\phi_b\rangle$$

$$+\langle\phi_a\mid-2\sum_N(\hbar^2/2M_N)\nabla_N\mid\phi_b\rangle\cdot\nabla_N\mid\chi_{bi}\rangle$$

$$=\langle\psi_{as}{}^{\mathrm{BO}}\mid V\mid\psi_{bi}{}^{\mathrm{BO}}\rangle. \qquad (4)$$

In Eq. (3) $E_a(\{\mathbf{R}\})$ is the electronic energy corresponding to the nuclear configuration $\{\mathbf{R}\}$, while in Eq. (4) V is defined as the difference between H and H^{BO} [defined in (3)]. Examination of the matrix element displayed in Eq. (4) shows that it is proportional to the reciprocal of the energy separation between the BO vibronic states. Thus, when any given BO vibronic level s is degenerate or quasidegenerate with one or more other BO levels $\{i\}$ the Born–Oppenheimer approximation breaks down, and the BO states must be combined (mixed) in order to obtain an appropriate wavefunction.

To proceed we assume that the BO states form a complete orthonormal set such that

$$\sum_i\sum_r\mid ir\rangle\langle ir\mid+\sum_r\int d\epsilon\mid\epsilon r\rangle\langle\epsilon r\mid=1. \qquad (5)$$

We shall also assume that the true eigenstates of the total Hamiltonian H form a complete orthonormal set,

$$\sum_n\sum_p\mid np\rangle\langle np\mid+\sum_p\int dE\mid E_p\rangle\langle E_p\mid=1. \qquad (6)$$

In Eqs. (5) and (6) we have used i and n to label the energy and r and p to label all other parameters necessary to describe the states of the molecule. We shall use, in all that follows, ir to refer to BO states and np to refer to exact molecular eigenstates.

Let z be a complex variable in the energy plane. Then the Green's functions corresponding to H^{BO} and H are, respectively,

$$G_{\mathrm{BO}}(z)=(z-H^{\mathrm{BO}})^{-1}, \qquad (7)$$

$$G(z)=(z-H)^{-1}. \qquad (8)$$

From the definitions of G_{BO} and G, it follows that

$$\lim_{\delta\to0}[\langle i\mid G(x-i\delta)\mid i\rangle-\langle i\mid G(x+i\delta)\mid i\rangle]$$

$$=\lim_{\delta\to0}\Big(\sum\mid\langle i\mid n\rangle\mid^2[(x-i\delta-E_n)^{-1}-(x+i\delta-E_n)^{-1}]$$

$$+\int_{E_{\min}}^{\infty}dE\mid\langle i\mid E\rangle\mid^2[(x-i\delta-E)^{-1}-(x+i\delta-E)^{-1}]\Big), \qquad (9)$$

where $x>E_{\min}$ in the integral term and i refers to a BO state. Thus the form displayed in (9) is related to the probability of finding a component $\mid i\rangle$ of H^{BO} in a state $\mid x\rangle$ of H in the energy region between x and $x+dx$. Indeed,

$$W_i(x)dx=\mid\langle i\mid x\rangle\mid^2dx, \qquad (10)$$

which we evaluate by noting that the first term on the right-hand side of (9) makes no contribution because the E_n's define a discrete set, and that there exists a formal relationship of the form

$$\lim_{\delta\to0}(x\pm i\delta)^{-1}=P(x)^{-1}\mp i\pi\delta(x) \qquad (11)$$

with $P(x)^{-1}$ the principal part of $(x)^{-1}$. The result is

$$W_i(x)dx=(2\pi i)^{-1}\lim_{\delta\to0}[\langle i\mid G(x-i\delta)\mid i\rangle$$

$$-\langle i\mid G(x+i\delta)\mid i\rangle]dx. \qquad (12)$$

In the case of scattering theory the choices $\pm i\delta$ with $\delta>0$ correspond to outgoing and incoming spherical waves, respectively. The coefficient of the delta function is compatible with the wavefunction having as its asymptotic form a phase-shifted sinusoidal function. With this normalization the Green's function method should lead to results identical with those obtained from the Fano theory of configuration–interaction, provided that the matrix elements satisfy the same block diagonalization (partial prediagonalization) conditions in both cases.

III. COUPLING BETWEEN ONE DISCRETE STATE AND A QUASICONTINUUM

We now consider the special case of one discrete Born–Oppenheimer state in resonance with a quasicontinuum of other BO states. Let the ground-state energy be taken as zero, and let E_{as} be the energy of the BO state ψ_{as}. Further, let the quasicontinuum be a manifold of BO states, $\{\psi_{bi}\}$. Our principal assumption will be that transitions from the ground state to ψ_{as} carry oscillator strength, but that transitions from the ground state to the manifold $\{\psi_{bi}\}$ carry no oscillator strength. If the state ψ_{as} is singlet, and the manifold $\{\psi_{bi}\}$ is triplet, spin-selection rules are adequate to make this assumption an accurate approximation. If the manifold $\{\psi_{bi}\}$ is singlet, and the lowest BO vibronic levels of $\{\psi_{bi}\}$ and ψ_{as} are well separated in energy, the Franck–Condon factors for excitation of states of $\{\psi_{bi}\}$ degenerate or nearly degenerate with ψ_{as} are so small that the assumption used is a very good approximation. Although spin-selection rules are adequate to insure that the oscillator strengths of singlet–triplet transitions are small, the finite spin–orbit coupling leads to mixing of states of different multiplicity. Of course, mixing between states of the same multiplicity is spin allowed. Thus, when ψ_{as} is in resonance with the manifold $\{\psi_{bi}\}$ it is to be expected that there is extensive state mixing. It is important to reiterate that a consequence of the overlapping of ψ_{as} and the $\{\psi_{bi}\}$ is the breakdown of the BO description, so that a proper description of the states of the molecule must replace the BO approximation.

The true molecular eigenstates in the energy region corresponding to overlap of BO states can be represented as the superposition

$$\Psi_n \equiv |\, n \rangle = a_s^n \,|\, s \rangle + \sum_i b_i^n \,|\, i \rangle, \qquad (13)$$

where $\psi_{as} \equiv |\, s \rangle = \psi_s$, $\psi_{bi} \equiv |\, i \rangle = \psi_i$, and we have assumed that no other BO states ψ_{at} are close to $|\, s \rangle$ in the energy region of interest. The state $|\, s \rangle$ must, therefore, be close to the bottom of its BO nuclear vibrational potential-energy surface. Now, all the states used in (13) are discrete, so that (12) cannot be directly used to calculate the probability of finding the BO component $|\, s \rangle$ in the true molecular state $|\, n \rangle$,[13] i.e., $|\, \langle n \,|\, s \rangle \,|^2$. If the states $|\, i \rangle$ are very dense we may approximate this quasicontinuous set of states by a continuum, so that (12) may become applicable,

$$\sum_i |\, \psi_i \rangle \langle \psi_i \,| = \int |\, \psi^i(\epsilon) \rangle \rho_i(\epsilon) \langle \psi^i(\epsilon) \,|\, d\epsilon, \qquad (14)$$

$$\sum_n |\, \Psi_n \rangle \langle \Psi_n \,| = \int |\, \Psi^n(E) \rangle \rho_n(E) \langle \Psi^n(E) \,|\, dE, \qquad (15)$$

where the energy densities $\rho_i(\epsilon)$ and $\rho_n(\epsilon)$ are defined by

$$\rho_i(\epsilon) = \sum_i \delta(\epsilon - \epsilon_i),$$

$$\rho_n(E) = \sum_n \delta(E - E_n). \qquad (16)$$

We now replace (16) by a Lorentzian function (to be explained later). As a result of this replacement the discrete sums (14) and (15) become continuous, and from (12)

$$\lim_{\delta\to 0}[\langle s \,|\, G(E_n - i\delta) \,|\, s \rangle - \langle s \,|\, G(E_n + i\delta) \,|\, s \rangle]$$

$$= \lim_{\delta\to 0} \int |\, \langle s \,|\, \Psi^n(E) \rangle \,|^2 \rho_n(E) \times [(E_n - i\delta - E)^{-1} - (E_n + i\delta - E)^{-1}]$$

$$= |\, \langle s \,|\, \Psi_n(E) \rangle \,|^2 2\pi i \rho_n(E_n) \qquad (17)$$

and of course,

$$\Psi^n(E_n) \equiv \Psi_n.$$

Defining the projection operator[6]

$$P = |\, s \rangle \langle s \,| \qquad (18)$$

and

$$\langle s \,|\, F(x \pm i\delta) \,|\, s \rangle = \gamma_1^s(x) \mp i\pi\gamma_2^s(x) \qquad (19)$$

and using (17), we find for the coefficient a_s^n of the BO state $|\, s \rangle$ in $|\, n \rangle$

$$|\, a_s^n \,|^2 = |\, \langle s \,|\, \Psi^n(E_n) \rangle \,|^2$$

$$= [2\pi i \rho_n(E_n)]^{-1} \{[E_n - E_s + i\delta - \langle s \,|\, F(E_n + i\delta) \,|\, s \rangle]^{-1} - [E_n - E_s - i\delta - \langle s \,|\, F(E_n - i\delta) \,|\, s \rangle]^{-1}\} \qquad (20)$$

or

$$|\, a_s^n \,|^2 = [\rho_n(E_n)]^{-1} \{\gamma_2^s / [(E_n - E_s - \gamma_1^s)^2 + \pi^2(\gamma_2^s)^2]\}, \qquad (21)$$

where $E_s \equiv E_{as}$ introduced earlier. Using the completeness relation

$$1 = |\, s \rangle \langle s \,| + \sum_i |\, i \rangle \langle i \,|, \qquad (22)$$

which is valid in the energy region under study, we find

$$\langle s \,|\, F(E_n + i\delta) \,|\, s \rangle = \langle s \,|\, V \,|\, s \rangle + \sum_i \{ |\, \langle \psi_i \,|\, V \,|\, s \rangle \,|^2 / [E_n + i\delta - E_i] \}$$

$$= \langle s \,|\, V \,|\, s \rangle + P \int d\epsilon \rho_i(\epsilon) \times [\, |\, \langle \psi^i(\epsilon) \,|\, V \,|\, s \rangle \,|^2 / (E_n - \epsilon)]$$

$$- i\pi \rho_i(E_n) \,|\, \langle \psi^i(E_n) \,|\, V \,|\, s \rangle \,|^2. \qquad (23)$$

Of course, using the defined BO states,

$$\langle \psi_i \,|\, V \,|\, \psi_j \rangle \equiv \langle \psi_{bi} \,|\, B \,|\, \psi_{bj} \rangle \approx 0 \qquad (24)$$

as displayed in (3). Also

$$\langle \psi_{as} \,|\, V \,|\, \psi_{as} \rangle \equiv \langle s \,|\, V \,|\, s \rangle = 0. \qquad (25)$$

Thus, the level shift is just

$$\gamma_1^s = P \int d\epsilon \rho_i(\epsilon) \frac{|\, \langle \psi^i(\epsilon) \,|\, V \,|\, s \rangle \,|^2}{E_n - \epsilon} \qquad (26)$$

and the linewidth is proportional to

$$\gamma_2^s = \rho_i(E_n) \,|\, \langle \psi^i(E_n) \,|\, V \,|\, s \rangle \,|^2. \qquad (27)$$

In (27) it is satisfactory to approximate $\psi^i(E_n)$ by the BO state with energy closest to E_n.

We have already noted that we intend to replace Eqs. (16) by Lorentzian functions. Thus far in the argument we have used no particular form for $\rho_i(\epsilon)$ or $\rho_n(E)$, except that for (17) *et. seq.* to be valid these

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[13] This is because the discrete part gives zero contribution in Eq. (9). The broadening due to collision, etc., is neglected in our low density limit.

functions must be continuous, i.e., they cannot be delta functions. We now introduce the specific form

$$\rho_n(E_n)=(\pi)^{-1}\sum_m \lim_{\epsilon_m\to 0_+} \{\epsilon_m/[(E_n-E_m)^2+\epsilon_m{}^2]\} \quad (28)$$

and assume that $\epsilon_m \to 0_+$, which is the energy spacing between adjacent levels. Note that we do not allow ϵ_m to become zero. In what follows we shall let all $\epsilon_m=\epsilon_n=$constant. Then

$$\rho_n(E_n)=(\pi\epsilon_n)^{-1}[1+2\sum_{m=1}^{N}(m^2+1)^{-1}] \quad (29)$$

with the factor two arising from the addition of contributions from above and below E_n. Now, let $N\to\infty$ as an approximation. In this limit[14]

$$\begin{aligned}\rho_n(E_n)&=(\pi\epsilon_n)^{-1}(1+2\{\tfrac{1}{2}\pi[\coth\pi+(\pi)^{-1}]-1\})\\ &=(\epsilon_n)^{-1}\coth\pi\\ &\approx(\epsilon_n)^{-1}, \end{aligned} \quad (30)$$

which is consistent with the assumption that ϵ_n corresponds to the energy separation between the adjacent true molecular states. We find, by a similar argument,

$$\rho_i(E_n)\approx(\epsilon_i)^{-1} \quad (31)$$

at the energy nearest to E_n. It is important to remark that the interpretation of ϵ_n as the width of the state is unphysical because an intrinsic statewidth (implying intrinsic diffusion of states) in an isolated system is not compatible with the uncertainty principle. The use of a summation over a large number of states allows us to interpret ϵ_n as the energy separation between states.

There is no restriction on the magnitudes of ϵ_i and ϵ_n, except that they must be infinitesimally small on the energy scale of interest. The breakdown of the BO approximation ensures the condition

$$\gamma_2{}^s \gg |\langle\psi^i(E_n)\mid V\mid s\rangle| \quad (32)$$

whereupon

$$|\langle\psi^i(E_n)\mid V\mid s\rangle|/\epsilon_i=v/\epsilon\gg 1 \quad (33)$$

and finally

$$|a_s{}^n|^2=(\epsilon_n/\epsilon_i)\{V^2/[(E_n-E_s-\gamma_1{}^s)^2+\pi^2(v^2/\epsilon)^2]\}. \quad (34)$$

Clearly, ϵ_n and ϵ_i are of the same order of magnitude. If the ratio (ϵ_n/ϵ_i) is replaced by unity (34) becomes identical with the expression for the mixing coefficient previously derived by Bixon and Jortner. Notice that (34) is more general than the latter's result in that v need not be assumed constant. The assumption that v is constant will be used in the later sections of this paper when the damping is approximated by a constant.

IV. COUPLING BETWEEN TWO DISCRETE STATES AND A QUASICONTINUUM

Consider two BO states, $|s\rangle$ and $|s'\rangle$, with energies E_s and $E_{s'}$, respectively. Let $|s\rangle$ and $|s'\rangle$ have the same multiplicity. We now consider the coupling of $|s\rangle$ and $|s'\rangle$ to a quasicontinuum of states $\{|i\rangle\}$, with energies $\{E_i\}$, which may have the same or different multiplicity. Equation (17) remains valid, but (20) is modified because the projection operator (18) becomes in the present case

$$P=|s\rangle\langle s|+|s'\rangle\langle s'|, \quad (35)$$

$$1-P=\sum_i |i\rangle\langle i|; \quad (36)$$

one then finds

$$\begin{aligned}\langle s\mid G^{\pm}\mid s\rangle=[x\pm i\delta-E_s-\langle s\mid F^{\pm}\mid s\rangle\\ -\langle s\mid F^{\pm}\mid s'\rangle\langle s'\mid F^{\pm}\mid s\rangle\\ \times(x\pm i\delta-E_{s'}-\langle s'\mid F^{\pm}\mid s'\rangle)^{-1}]^{-1}.\end{aligned} \quad (37)$$

In (37) we have used the definition $G(x\pm i\delta)\equiv G^{\pm}$. A similar expression is obtained for $\langle s'\mid G^{\pm}\mid s'\rangle$ merely by interchanging s and s'. The off-diagonal element $\langle s\mid G^{\pm}\mid s'\rangle$ is found to be

$$\begin{aligned}\langle s\mid G^{\pm}\mid s'\rangle=\langle s\mid F^{\pm}\mid s'\rangle[(x\pm i\delta-E_s-\langle s\mid F^{\pm}\mid s\rangle)\\ \times(x\pm i\delta-E_{s'}-\langle s'\mid F^{\pm}\mid s'\rangle)\\ -\langle s\mid F^{\pm}\mid s'\rangle\langle s'\mid F^{\pm}\mid s\rangle]^{-1}\end{aligned} \quad (38)$$

and $\langle s'\mid G^{\pm}\mid s\rangle$ is obtained merely by interchanging s and s'. Proceeding as in Sec. III we now decompose the matrix elements of F into real and imaginary parts:

$$\begin{aligned}\langle s\mid F(E_n\pm i\delta)\mid s\rangle&=\gamma_1{}^s\mp i\pi\gamma_2{}^s\\ &=P\int\frac{\rho_i(\epsilon)\mid\langle\psi^i(\epsilon)\mid V\mid s\rangle\mid^2}{E_n-\epsilon}d\epsilon\\ &\mp i\pi\rho_i(E_n)\mid\langle\psi^i(E_n)\mid V\mid s\rangle\mid^2,\end{aligned} \quad (39)$$

$$\begin{aligned}\langle s'\mid F(E_n\pm i\delta)\mid s'\rangle&=\gamma_1{}^{s'}\mp i\pi\gamma_2{}^{s'}\\ &=P\int\frac{\rho_i(\epsilon)\mid\langle\psi^i(\epsilon)\mid V\mid s'\rangle\mid^2}{E_n-\epsilon}d\epsilon\\ &\mp i\pi\rho_i(E_n)\mid\langle\psi^i(E_n)\mid V\mid s'\rangle\mid^2,\end{aligned} \quad (40)$$

$$\begin{aligned}&\langle s\mid F(E_n\pm i\delta)\mid s'\rangle\\ &=\langle s'\mid F(E_n\pm i\delta)\mid s\rangle=\gamma_1\mp i\pi\gamma_2\\ &=P\int\frac{\rho_i(\epsilon)\langle s\mid V\mid\psi^i(\epsilon)\rangle\langle\psi^i(\epsilon)\mid V\mid s'\rangle}{E_n-\epsilon}d\epsilon\\ &\mp i\pi\rho_i(E_n)\langle s\mid V\mid\psi^i(E_n)\rangle\langle\psi^i(E_n)\mid V\mid s'\rangle.\end{aligned} \quad (41)$$

In obtaining Eqs. (39)–(41) it has been assumed that

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[14] V. Mangulis, *Handbook of Series for Scientists and Engineers* (Academic Press Inc., New York, 1965), p. 79.

the functions $|i\rangle$, $|s\rangle$, and $|s'\rangle$ are real, and that V is Hermitian. Note also that

$$\langle s|F^{\pm}|s'\rangle\langle s'|F^{\pm}|s\rangle=(\langle s|F^{\pm}|s'\rangle)^2 \neq |\langle s|F^{\pm}|s'\rangle|^2. \tag{42}$$

Of course, just as in Sec. III, the energy densities ρ_i and ρ_n must be taken to be continuous. We use the same representation as in Sec. III, so that again $\rho_i(E_n)=\rho_n(E_n)=\epsilon^{-1}$. Using Eqs. (37), (39), (41), together with Eq. (9), we find for the coefficient a_s^n,

$$\begin{aligned}|a_s^n|^2&=[2\pi i\rho_n(E_n)]^{-1}(\{E_n-E_s-\gamma_1^s-i\pi\gamma_2^s-[(\gamma_1+i\pi\gamma_2)^2/(E_n-E_{s'}-\gamma_1^{s'}-i\pi\gamma_2^{s'})]\}^{-1}\\&\qquad-\{E_n-E_s-\gamma_1^s+i\pi\gamma_2^s-[(\gamma_1-i\pi\gamma_2)^2/(E_n-E_{s'}-\gamma_1^{s'}+i\pi\gamma_2^{s'})]\}^{-1})\\&=[\rho_n(E_n)]^{-1}\{\gamma_2^s[(E_n-E_{s'}-\gamma_1^{s'})^2+\pi^2(\gamma_2^{s'})^2]+\gamma_1\gamma_2(E_n-E_{s'}-\gamma_1^{s'})+\gamma_2^{s'}(\gamma_1^2-\pi^2\gamma_2^2)\}\\&\qquad\times\{[(E_n-E_s-\gamma_1^s)^2+\pi^2(\gamma_2^s)^2][(E_n-E_{s'}-\gamma_1^{s'})^2+\pi^2(\gamma_2^{s'})^2]+(\gamma_1^2+\pi^2\gamma_2^2)^2\\&\qquad-2[(E_n-E_s-\gamma_1^s)(E_n-E_{s'}-\gamma_1^{s'})-\pi^2\gamma_2^s\gamma_2^{s'}](\gamma_1^2-\pi^2\gamma_2^2)\\&\qquad+4\pi^2\gamma_1\gamma_2[(E_n-E_s-\gamma_1^s)\gamma_2^{s'}+(E_n-E_{s'}-\gamma_1^{s'})\gamma_2^s]\}^{-1}.\end{aligned} \tag{43}$$

In the limit that the energy shifts γ_1, γ_1^s, $\gamma_1^{s'}$ are negligibly small, and if we set $\gamma_2\approx\gamma_2^s\approx\gamma_2^{s'}$, then

$$|a_s^n|^2=[\rho_n(E_n)]^{-1}\left\{\frac{(E_n-E_s)^2\pi\gamma_2^s}{(E_n-E_s)^2(E_n-E_{s'})^2+(E_n-E_s)^2\pi^2(\gamma_2^{s'})^2+(E_n-E_{s'})^2\pi^2(\gamma_2^s)^2+2(E_n-E_s)(E_n-E_{s'})\pi^2\gamma_2^s\gamma_2^{s'}}\right\}, \tag{44}$$

which is identical with the result obtained by Mies and Krauss[8] from the Fano configuration–interaction approach.

We close this section with the remark that the Green's function method and the Fano theory are sensibly equivalent, except that the Green's function theory does not require any prediagonalization of matrix elements to block form. If there are transitions from the ground state to the background continuum, our theory predicts antiresonances just as does the Fano theory. To actually calculate the antiresonant line shape, prediagonalization of the matrix elements of the Green's function must be carried out, just as in the Fano theory.

V. THE TIME EVOLUTION OF EXCITED STATES

With the analyses of Secs. II–IV we have prepared the background for a discussion of the time evolution of states undergoing radiationless transitions. For the present the radiative transition is ignored. The simultaneous influence of radiative and radiationless transitions on the time evolution of a state is considered in Sec. VII.

It is convenient to start by displaying the total Hamiltonian in the form

$$H_T(t)=H+H_1(t), \tag{45}$$

$$H=H^{\mathrm{BO}}+V, \tag{46}$$

and $H_1(t)$ is the perturbation (to be specified later). To first order we find for the equation of evolution

$$[i\hbar(\partial/\partial t)-H]\psi_1(t)=H_1(t)\psi_0(t), \tag{47}$$

where

$$\psi(t)=\psi_0(t)+\psi_1(t) \tag{48}$$

and

$$H\psi_0(t)=i\hbar(\partial/\partial t)\psi_0(t)$$

$$\psi_0(t)=|\psi_0\rangle\exp(-iE_0t/\hbar). \tag{49}$$

It is well known that $\psi(t)$ can be expressed in the form

$$\psi(t)=\psi_0(t)+(2\pi)^{-1}\int_{-\infty}^{\infty}d\omega\exp(-i\omega t)(\hbar\omega+i\delta-H)^{-1}\tilde{H}_1(\omega)|\psi_0\rangle \tag{50}$$

where $\tilde{H}_1(\omega)$ is the Fourier transform of $H_1(t)$. We now must identify $H_1(t)$. We shall assume that the perturbation is an electromagnetic pulse of the form

$$H_1(t)=\mu E'\delta(t), \tag{51}$$

where μ is the dipole moment in the direction of E' and E' has the dimension of electric field multiplied by time. The Fourier transform of $H_1(t)$ is just

$$\tilde{H}_1(\omega)=\mu E'. \tag{52}$$

We now consider again the cases discussed separately in Secs. III and IV.

A. Coupling between One Discrete State and a Quasicontinuum

We proceed by expanding (50) in the basis of the BO states $|s\rangle$ and $\{|i\rangle\}$, in the energy region of interest.

We assume that

$$\mu_{i0}=\langle i\mid\mu\mid 0\rangle=0,$$

$$\mu_{s0}=\langle s\mid\mu\mid 0\rangle\neq 0. \tag{53}$$

In terms of the matrix elements of the dipole moment (50) may be represented as

$$\psi(t)=\psi_0(t)+(2\pi)^{-1}\int_{-\infty}^{\infty}d\omega E'\exp(-i\omega t)$$

$$\times\{\mid s\rangle\langle s\mid G^+\mid s\rangle\langle s\mid\mu\mid\psi_0\rangle+\sum_i\mid i\rangle\langle i\mid G^+\mid s\rangle\langle s\mid\mu\mid\psi_0\rangle\}. \tag{54}$$

We shall now assume that an adequate approximation to the true ground state $\mid\psi_0\rangle$ is given by the BO ground state, $\mid\psi_0^{\mathrm{BO}}\rangle$. The ground-state energy, E_0, is taken to be zero. Thus,

$$\psi_0(t)\approx\psi_0^{\mathrm{BO}}\exp(-iE_0t/\hbar)=\psi_0^{\mathrm{BO}}. \tag{55}$$

$\psi(t)$ can now be shown to be

$$\psi(t)=\psi_0(t)+(2\pi)^{-1}\int_{-\infty}^{\infty}d\omega E'\exp(-i\omega t)$$

$$\times\left\{\frac{\mu_{s0}}{\hbar\omega+i\delta-E_s-\langle s\mid F(\hbar\omega+i\delta)\mid s\rangle}\times\left[\mid s\rangle+\sum_i\mid i\rangle\frac{\langle i\mid F(\hbar\omega+i\delta)\mid s\rangle}{\hbar\omega+i\delta-E_i}\right]\right\}. \tag{56}$$

What is the probability of finding the BO component $\mid s\rangle$ in $\psi(t)$ as a function of time? This probability, which we denote $W_s(t)$, is

$$W_s(t)=\mid\langle s\mid\psi(t)\rangle\mid^2$$

$$=(4\pi)^{-1}\mid\mu_{s0}\mid^2E'^2$$

$$\times\left|\int_{-\infty}^{\infty}d\omega\frac{\exp(-i\omega t)}{\hbar\omega+i\delta-E_s-\langle s\mid F(\hbar\omega+i\delta)\mid s\rangle}\right|^2. \tag{57}$$

We now introduce into Eqs. (19) and (23) for $\langle s\mid F^+\mid s\rangle$ and assume that $\gamma_1^s(\omega)$ and $\gamma_2^s(\omega)$ are constant with respect to ω. The result is

$$W_s(t)=(\mid\mu_{s0}\mid^2/\hbar^2)E'^2\exp(-2\pi\gamma_2^st)$$

$$=(\mid\mu_{s0}\mid^2/\hbar^2)E'^2\exp(-t/\tau_{nr}), \tag{58}$$

where

$$\tau_{nr}=(2\pi\gamma_2^s)^{-1}$$

$$=\epsilon\hbar/2\pi v^2 \tag{59}$$

is the nonradiative decay lifetime. Equation (58), which describes an exponential decay of the BO component $\mid s\rangle$ in $\psi(t)$, is in agreement with the description obtained from a simple kinetic equation.

B. Coupling between Two Discrete States and a Quasicontinuum

We consider now that there are transitions possible from the ground state to two BO states, $\mid s\rangle$ and $\mid s'\rangle$, each of which overlaps the quasicontinuum of BO states $\{\mid i\rangle\}$. As before, we assume

$$\mu_{s0}=\langle s\mid\mu\mid 0\rangle\neq 0,$$

$$\mu_{s'0}=\langle s'\mid\mu\mid 0\rangle\neq 0,$$

$$\mu_{i0}=\langle i\mid\mu\mid 0\rangle=0. \tag{60}$$

Proceeding as in Sec. IV, we expand (50) in terms of the BO states $\mid s\rangle$, $\mid s'\rangle$, and $\{\mid i\rangle\}$. The result is

$$\psi(t)=\psi_0(t)+(2\pi)^{-1}\int_{-\infty}^{\infty}d\omega\exp(-i\omega t)E'[\mid s\rangle(\langle s\mid G^+\mid s\rangle\mu_{s0}+\langle s\mid G^+\mid s'\rangle\mu_{s'0})$$

$$+\mid s'\rangle(\langle s'\mid G^+\mid s\rangle\mu_{s0}+\langle s'\mid G^+\mid s'\rangle\mu_{s'0})+\sum_i\mid i\rangle(\langle i\mid G^+\mid s\rangle\mu_{s0}+\langle i\mid G^+\mid s'\rangle\mu_{s'0})], \tag{61}$$

where the delta function pulse is used as the perturbation. After use of Eqs. (37) and (38) we find for the BO component $\mid s\rangle$ in $\psi(t)$ the result

$$\mid\langle s\mid\psi(t)\rangle\mid^2=(4\pi^2)^{-1}\left|\int_{-\infty}^{\infty}d\omega\exp(-i\omega t)E'\right.$$

$$\left.\times\left[\frac{\mu_{s0}(\hbar\omega+i\delta-E_{s'}-\langle s'\mid F(\hbar\omega+i\delta)\mid s'\rangle)+\mu_{s'0}\langle s\mid F(\hbar\omega+i\delta)\mid s'\rangle}{(\hbar\omega+i\delta-E_s-\langle s\mid F(\hbar\omega+i\delta)\mid s\rangle)(\hbar\omega+i\delta-E_{s'}-\langle s'\mid F(\hbar\omega+i\delta)\mid s'\rangle)-(\langle s\mid F(\hbar\omega+i\delta)\mid s'\rangle)^2}\right]\right|^2 \tag{62}$$

and Eqs. (39)–(41) define the several matrix elements of $F(\hbar\omega+i\delta)$.

It is evident that

$$\mid\langle s\mid V\mid\psi^i(\hbar\omega)\rangle\mid^2+\mid\langle s'\mid V\mid\psi^i(\hbar\omega)\rangle\mid\geq 2\langle s\mid V\mid\psi^i(\hbar\omega)\rangle\langle\psi^i(\hbar\omega)\mid V\mid s'\rangle \tag{63}$$

so that

$$\gamma_1^s+\gamma_2^s\geq 2\gamma_2, \tag{64}$$

a result we shall use later [see Eq. (72)].

To evaluate W_s it is necessary to evaluate a complicated integral. The notation is simplified if we use the new variables

$$\begin{aligned} a&=E_s+\gamma_1^s,\\ b&=\pi\gamma_2^s,\\ c&=E_{s'}+\gamma_1^{s'},\\ d&=\pi\gamma_2^{s'},\\ e&=\gamma_1,\\ f&=\pi\gamma_2. \end{aligned} \tag{65}$$

In the new notation

$$\begin{aligned} W_s&=|\langle s|\psi(t)\rangle|^2\\ &=\frac{E'^2}{4\pi^2}\left|\int_{-\infty}^{\infty}d\omega\exp(-i\omega t)\left\{\frac{\mu_{s0}[\hbar\omega-(c-id)]+\mu_{s'0}(e-if)}{[\hbar\omega-(a-ib)][\hbar\omega-(c-id)]-(e-if)^2}\right\}\right|^2. \end{aligned} \tag{66}$$

The integrand of (66) has two simple poles at

$$\hbar\omega=\tfrac{1}{2}\big((a+c)-i(b+d)\pm\{[(a-c)-i(b-d)]^2+4(e-if)^2\}^{1/2}\big) \tag{67}$$

so that

$$\begin{aligned} W_s=(E'^2/\hbar^2)\,|\,(\cdots)^{-1/2}\big(&\exp\{-\tfrac{1}{2}(it)[(a+c)-i(b+d)+(\cdots)^{1/2}]\}(\mu_{s0}\tfrac{1}{2}[(a-c)-i(b-d)+(\cdots)^{1/2}]+\mu_{s'0}(e-if)\\ &-\exp\{-\tfrac{1}{2}(it)[(a+c)-i(b+d)-(\cdots)^{1/2}]\}(\mu_{s0}\tfrac{1}{2}[(a-c)-i(b-d)-(\cdots)^{1/2}]+\mu_{s'0}(e-if)\big)\,|^2. \end{aligned} \tag{68}$$

We now rewrite W_s in the form

$$\begin{aligned} (A^2+B^2)^{1/4}\exp[\tfrac{1}{2}i\arctan(-B/A)]&=(A^2+B^2)^{1/4}\{\cos[\tfrac{1}{2}\arctan(-B/A)]+i\sin[\tfrac{1}{2}\arctan(-B/A)]\}\\ &=\frac{(A^2+B^2)^{1/4}}{\sqrt{2}}\left[\left(\left|1+\frac{A}{(A^2+B^2)^{1/2}}\right|\right)^{1/2}\pm i\left(\left|1-\frac{A}{(A^2+B^2)^{1/2}}\right|\right)^{1/2}\right] \end{aligned} \tag{69}$$

where the positive sign is chosen if $B<0$, and the negative sign if $B>0$. The quantities A and B are defined by

$$\begin{aligned} A&=(a-c)^2-(b-d)^2+4e^2-4f^2,\\ B&=2[(a-c)(b-d)+4ef]. \end{aligned} \tag{70}$$

To calculate $W_{s'}$ we need only interchange s and s', a and c, and b and d.

Equations (68) and (69) are much too complicated to permit easy interpretation. There are, however, two limiting cases of interest in which W_s assumes simple forms.

(i) Suppose that $a\approx c$ and $b\approx d$. In this case the two BO levels $|s\rangle$ and $|s'\rangle$ are very close and have about the same lifetime.

Then

$$\begin{aligned} W_s&=(E'^2/4\hbar^2)\,|\exp[-i\tfrac{1}{2}t(a+c+2e)-\tfrac{1}{2}t(b+d+2f)](\mu_{s0}+\mu_{s'0})\\ &\qquad-\exp[-i\tfrac{1}{2}t(a+c-2e)-\tfrac{1}{2}t(b+d-2f)](\mu_{s'0}-\mu_{s0})\,|^2,\\ &=(E'^2/4\hbar^2)\exp[-t(b+d)][\,|\mu_{s0}+\mu_{s'0}|^2\exp(-2ft)+|\mu_{s'0}-\mu_{s0}|^2\exp(2ft)-(|\mu_{s'0}|^2-|\mu_{s0}|^2)2\cos(et)],\\ &=(E'^2/4\hbar^2)\exp[-\pi t(\gamma_2^s+\gamma_2^{s'})][\,|\mu_{s0}+\mu_{s'0}|^2\exp(-2\pi\gamma_2 t)+|\mu_{s'0}-\mu_{s0}|^2\exp(2\pi\gamma_2 t)\\ &\qquad-(|u_{s'0}|^2-|\mu_{s0}|^2)2\cos\gamma_1 t]. \end{aligned} \tag{71}$$

The total probability of decay in this case is then just

$$W_s+W_{s'}=(E'^2/2\hbar^2)\exp[-\pi t(\gamma_2^s+\gamma_2^{s'})][\,|\mu_{s0}+\mu_{s'0}|^2\exp(-2\pi\gamma_2 t)+|\mu_{s'0}-\mu_{s0}|^2\exp(2\pi\gamma_2 t)]. \tag{72}$$

Note that the decay rate is not a simple exponential form. Indeed, because of the positive exponential term in the brackets the decay rate is less than might have been expected and the decay rate decreases as time increases. The calculation of Mies and Krauss[8] leads to the same conclusion.

(ii) Suppose that $a \gg c$ and $b \approx d$. In this case the two BO levels are far apart, but have comparable lifetimes. We find that

$$\{[(a-c)-i(b-d)]^2-4(e-if)^2\}^{1/2} \to a-c$$

and

$$W_s=(E'^2/\hbar^2)\left|\frac{\exp[-ita-\frac{1}{2}t(b+d)]\mu_{s0}(a-c)}{(a-c)}\right.$$

$$\left.+\text{small term}\right|^2$$

$$=(E'^2/\hbar^2)\,|\mu_{s0}|^2\exp[-\pi t(\gamma_2{}^s+\gamma_2{}^{s'})]. \tag{73}$$

The total probability of finding either $|s\rangle$ or $|s'\rangle$ in $\psi(t)$ is, thus,

$$W_s+W_{s'}=(E'^2/\hbar^2)(|\mu_{s0}|^2+|\mu_{s'0}|^2)$$

$$\times\exp[-\pi t(\gamma_2{}^s+\gamma_2{}^{s'})], \tag{74}$$

which has the form of a simple exponential decay. Equation (74) is, again, in agreement with the calculations of Mies and Krauss. We conclude that a simple exponential decay is an adequate description of the time dependence of W_s provided that all the resonance levels undergoing transitions are sufficiently far apart (relative to their width).

VI. TIME EVOLUTION WITH COUPLED RADIATIVE AND RADIATIONLESS DECAYS

Note added in proof: The results obtained in this section are based on the assumption that each level decays with its own natural lifetime, independently of the other levels except for interference arising from phase coherence. More recent work (Bixon and Jortner, unpublished data) shows that when the only radiative components of a set of levels all have the same parentage and are thereby indistinguishable, the level decays are not independent. The consequence is that, in the statistical limit, contrary to the results obtained with our assumption, the radiative decay is exponential.

In this section we consider the nature of the emission from an isolated excited molecule in which both radiative and radiationless decay are possible. We suppose that the molecule is excited to a state $\Psi(t)$ at time $t=0$ by application of a delta function light pulse, $H_1(t)=H'\delta(t)$. The radiative decay of the state $\Psi(0)$ is then determined by counting the photons emitted.

Because the state $\Psi(t)$ is prepared by exciting the molecule from the ground-state, first-order perturbation theory gives

$$\Psi(t)=-\frac{i}{\hbar}\int_0^t d\tau\exp\left(i\frac{H}{\hbar}(\tau-t)\right)H_1(\tau)$$

$$\times\exp\left(-i\frac{H_T}{\hbar}\right)|0\rangle, \tag{75}$$

where H is the Hamiltonian of the isolated molecule. If we set $H_1(\tau)=H'\delta(\tau)$ and multiply (75) by $\sum_n|n\rangle\langle n|$ we find

$$\Psi(t)=-(i/\hbar)\sum_n|n\rangle\exp(-iE_nt/\hbar)\langle n|H'|0\rangle. \tag{76}$$

The reader is reminded that the states $|n\rangle$ are the true molecular eigenstates. From (76) we find for the initial state

$$\Psi(0)=-(i/\hbar)\sum_n|n\rangle\langle n|H'|0\rangle. \tag{77}$$

The decay of $\Psi(0)$ to the ground state is determined by the amplitude

$$|\langle 0,\mathbf{k},\hat{e}|U(t)|\Psi(0),\text{vac}\rangle|^2$$

where $\mathbf{k}$, $\hat{e}$ refer to the wave vector and polarization of the emitted photon and $U(t)$ is the time-evolution operator. We restrict attention to the case of single photon emission. We also assume that the excited state $\Psi(0)$ is sufficiently close (in energy) to the ground state that radiative decay to the ground state dominates over radiative decay to any other states.

The total Hamiltonian of the system molecule plus radiation field is

$$H_T=H+H_{\text{field}}+H_{\text{int}}. \tag{78}$$

In terms of H_T, the probability that one photon of any polarization $\hat{e}$ and wave vector $\mathbf{k}$ is emitted during decay to the ground state is

$$\langle P(t)\rangle=\sum_{k,\hat{e}}|\langle 0,\mathbf{k},\hat{e}|U(t)|\Psi(0),\text{vac}\rangle|^2$$

$$=\sum_{k,e}(1/\hbar^2)\{\sum_n|\langle n|H'|0\rangle^2|\langle 0,\mathbf{k},\hat{e}|\exp(-iH_Tt/\hbar)|n,\text{vac}\rangle|^2+2\,\text{Re}\sum_{n>n'}\langle 0|H'|n\rangle\langle n'|H'|0\rangle$$

$$\times\langle 0,\mathbf{k},\hat{e}|\exp(-iH_Tt/\hbar)|n,\text{vac}\rangle\langle 0,\mathbf{k},\hat{e}|\exp(-iH_Tt/\hbar)|n',\text{vac}\rangle^*\}. \tag{79}$$

When the dipole transition moment is dominant,[15]

$$\langle 0,\mathbf{k},\hat{e}|\exp(-iH_Tt/\hbar)|n,\text{vac}\rangle=-[(2\pi e^2\hbar^2c)/V_0k]^{1/2}\langle 0|(\hat{e}\cdot\mathbf{P}/mc)|n\rangle\exp[-i(E_0/\hbar+kc)t]$$

$$\times\frac{1-\exp\{i[\hbar kc-(E_n-E_0)+(i\Gamma_n/2)]t/\hbar\}}{\hbar kc-(E_n-E_0)+(i\Gamma_n/2)}, \tag{80}$$

where k is the wavenumber ($k=|\mathbf{k}|$) of the photon, $\mathbf{P}$ the total momentum operator, E_n and E_0 are the

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[15] See, e.g., M. L. Goldberger and K. M. Watson, *Collision Theory* (John Wiley & Sons, Inc., New York, 1964), p. 464. Also see R. L. Kelly, Phys. Rev. **147**, 376 (1966).

energies of $|n\rangle$ and $|0\rangle$, respectively, and V_0 is the volume of the box in which the electromagnetic field is quantized. Finally, the natural linewidth Γ_n is given by

$$\Gamma_n=(e^2/2\pi\hbar c^3)(E_n-E_0)\int d\Omega_k\sum_e |\langle 0|(\hat{e}\cdot\mathbf{P}/mc)|n\rangle|^2. \tag{81}$$

As is usual in problems of this sort we change the sum over wave vectors, $\sum_{\mathbf{k}}$ to an integration by the formula

$$\sum_{\mathbf{k}}\rightarrow\frac{V_0}{(2\pi)^3}\int k^2dkd\Omega_k,$$

where $d\Omega_k$ is the solid angle. We now assume that the monochromator used in the experiment passes all radiation with frequency in the vicinity of E_n in a bandpass much larger than Γ_n. In that case $\int kdk$ may be replaced by $\int(E_n/\hbar c)dk$. Using these replacements (79) gives

$$\begin{aligned}\langle P(t)\rangle=&\sum_n\frac{|\langle 0|H'|n\rangle|^2}{\hbar^2}[1-\exp(-\Gamma_nt/\hbar)]\\&-2\,\mathrm{Im}\sum_{n>n'}\frac{\langle 0|H'|n'\rangle\langle n|H'|0\rangle}{\hbar^2}\\&\times\frac{\Gamma_{nn'}}{E_n-E_{n'}+i(\Gamma_n+\Gamma_{n'})/2}\\&\times\{1-\exp[i(E_n-E_{n'})t/\hbar]\exp[-\tfrac{1}{2}(\Gamma_n+\Gamma_{n'})t/\hbar]\}.\end{aligned} \tag{82}$$

If we differentiate $\langle P(t)\rangle$ with respect to t there is obtained the rate of photon counting. This is

$$\begin{aligned}(d\langle P(t)\rangle)/dt=&(\hbar^2)^{-1}\{\sum_n|\langle 0|H'|n\rangle|^2(\Gamma_n/\hbar)\\&\times\exp(-\Gamma_nt/\hbar)+2\,\mathrm{Re}\sum_{n>n'}\langle 0|H'|n'\rangle\langle n|H'|0\rangle\Gamma_{nn'}\\&\times\exp[i(E_n-E_{n'})t/\hbar]\exp[-\tfrac{1}{2}(\Gamma_n+\Gamma_{n'})t/\hbar]\},\end{aligned} \tag{83}$$

where

$$\begin{aligned}\Gamma_{nn'}=&\frac{e^2}{2\pi\hbar^2c^2}[\tfrac{1}{2}(E_n+E_{n'})-E_0]\int d\Omega_k\\&\times\sum\left\langle 0\left|\frac{\hat{e}\cdot\mathbf{P}}{mc}\right|n\right\rangle^*\left\langle 0\left|\frac{\hat{e}\cdot\mathbf{P}}{mc}\right|n'\right\rangle.\end{aligned} \tag{84}$$

Explicit evaluation of $(d\langle P(t)\rangle/dt)$ is achieved by expressing the states $|n\rangle$ and $|n'\rangle$ in terms of the BO states $|s\rangle$ and $|i\rangle$, which overlap in the energy region of interest. We assume that radiative decay can only occur from $|s\rangle$ to $|0\rangle$. Thus, $\langle n|H'|0\rangle$ may be replaced by $a_s^n\langle s|H'|0\rangle$. Following the analysis of Bixon and Jortner, assuming all wavefunctions to be real, and setting $E_0=0$, we write (henceforth $a_n\equiv a_s^n$)

$$a_n^2=[(\pi v/\epsilon)^2+(\epsilon/v)^2n^2]^{-1}, \tag{85}$$

where n is an integer corresponding to the state $|n\rangle$. That is, n is defined by

$$E_n=E_s+n\epsilon,\qquad n=0,\pm1,\pm2,\cdots. \tag{86}$$

v will be assumed to be constant[5] [see Eq. (33)]. Substitution of (85) and (86) into (81) and (84) and defining

$$\Gamma_s\equiv\frac{e^2}{2\pi\hbar^2c^3}E_s\int d\Omega_k\sum_{\hat{e}}\left|\left\langle 0\left|\frac{\hat{e}\cdot\mathbf{P}}{mc}\right|s\right\rangle\right|^2, \tag{87}$$

$$A\equiv\frac{e^2}{2\pi\hbar^2c^3}\int d\Omega_k\sum_{\hat{e}}\left|\left\langle 0\left|\frac{\hat{e}\cdot\mathbf{P}}{mc}\right|s\right\rangle\right|^2, \tag{88}$$

we find

$$\Gamma_n=(n\epsilon A+\Gamma_s)a_n^2=\frac{n\epsilon A+\Gamma_s}{(\pi v/\epsilon)^2+(\epsilon/v)^2n^2}, \tag{89}$$

$$\begin{aligned}\Gamma_{nn'}&=[\tfrac{1}{2}(n+n')\epsilon A+\Gamma_s]a_na_{n'}\\&=[\tfrac{1}{2}(n+n')\epsilon A+\Gamma_s]\\&\quad\times\{[(\pi v/\epsilon)^2+(\epsilon/v)^2n^2][(\pi v/\epsilon)^2+(\epsilon/v)^2n^2]\}^{-1/2}.\end{aligned} \tag{90}$$

It is interesting that

$$A\approx e^2E_sf_{s0}/4\pi mc^3\hbar\lesssim(e^2/\hbar c)^3f_{s0}, \tag{91}$$

where $e^2/\hbar c\equiv\alpha=1/137$ and f_{s0} is the oscillator strength. The rate of photon counting now assumes the form

$$\begin{aligned}\frac{d\langle P(t)\rangle}{dt}=&\frac{1}{\hbar^3}\mathrm{Re}\sum_{n,n'}|\langle s|H'|0\rangle|^2\frac{\tfrac{1}{2}\epsilon A(n+n')+\Gamma_s}{(B+Cn^2)(B+Cn'^2)}\\&\times\exp\left[\frac{i(n-n')\epsilon t}{\hbar}\right]\exp\left(-\frac{t}{2\hbar}\right)\left\{\frac{A\epsilon n+\Gamma_s}{B+Cn^2}+\frac{A\epsilon n'+\Gamma_s}{B+Cn'^2}\right\},\end{aligned} \tag{92}$$

where

$$\begin{aligned}B&\equiv(\pi v/\epsilon)^2\gg1,\\C&\equiv(\epsilon/v)^2\ll1.\end{aligned} \tag{93}$$

To evaluate (92) we can replace the summation by an integration provided that $\epsilon t/\hbar\ll1$. With negligible error the domain of integration can be extended to $\pm\infty$. Furthermore, we neglect $A\epsilon n$ relative to Γ_s. This approximation is valid because the excitation energy considerably exceeds the linewidth, so that $E_s\gg n\epsilon$. With these operations carried out,

$$\begin{aligned}\frac{d\langle P(t)\rangle}{dt}=&\frac{|\langle s|H'|0\rangle|^2}{\hbar^3}\mathrm{Re}\int_{-\infty}^{\infty}\int dndn'\Gamma_s\\&\times\frac{\exp[i(n-n')\epsilon t/\hbar]}{(B+Cn^2)(B+Cn'^2)}\\&\times\exp\left(-\frac{t\Gamma_s}{2\hbar}\right)[(B+Cn^2)^{-1}+(B+Cn'^2)^{-1}]\\=&\frac{|\langle s|H'|0\rangle|^2}{\hbar^3}\Gamma_s\left(4\left\{\int_0^{\infty}dn(B+Cn^2)^{-1}\right.\right.\\&\left.\left.\times\cos\left(\frac{n\epsilon t}{\hbar}\right)\exp\left[-\frac{\Gamma_st}{2\hbar}(B+Cn^2)^{-1}\right\}^2\right]\right)\\=&(|\langle s|H'|0\rangle|^2/\hbar^3)\Gamma_sI.\end{aligned} \tag{94}$$

The remaining step is, of course, the evaluation of the integral in Eq. (94). The reader should note that the integral is similar to that encountered in the theory of diffraction from a slit. We have not found an exact quadrature possible and have, therefore, considered the following approximations:

(a) Let a_n^2 be replaced by a step function of height B^{-1} and width $2(B/C)^{1/2}$. This corresponds to replacing the true bell shape a_n^2 by a rectangular distribution of the same width at half-height. With this replacement (94) may be integrated to give

$$\frac{d\langle P(t)\rangle}{dt}=\frac{|\langle s\,|\,H'\,|\,0\rangle|^2}{\hbar^3}\times\exp\left(-\frac{\Gamma_s t\epsilon^2}{\pi^2v^2\hbar}\right)\Gamma_s\frac{4}{\pi^2}\frac{\sin^2[(t/2)\tau_{nr}]}{[(t/2)\tau_{nr}]^2},\tag{95}$$

where

$$\tau_{nr}\equiv\epsilon\hbar/2\pi v^2$$

as in (59) is the lifetime against nonradiative decay. Note that the rate of decay resembles the diffraction pattern from a rectangular slit modulated by an exponential decay. (See note after Sec. VI.)

(b) Let a_n^2 be replaced by a triangular function of height B^{-1}, i.e.,

$$a_n^2=B^{-1}[1+\tfrac{1}{2}(C/B)^{1/2}n]\quad\text{for}\quad n\leq0,$$
$$a_n^2=B^{-1}[1-\tfrac{1}{2}(C/B)^{1/2}n]\quad\text{for}\quad n\geq0.\tag{96}$$

It is then found that

$$\frac{d\langle P(t)\rangle}{dt}=\frac{|\langle s\,|\,H'\,|\,0\rangle|^2}{\hbar^3}\exp\left(-\frac{\Gamma_s t\epsilon^2}{\pi^2v^2\hbar}\right)\Gamma_s\frac{4}{\pi^2}\times\left(\frac{1-\exp(\Gamma_s t\epsilon^2/2\pi^2v^2\hbar)\cos(t/\tau_{nr})}{t^2/2\tau_{nr}^2}\right)^2,\tag{97}$$

which again resembles a diffraction pattern modulated by an exponential decay.

(c) We write, for the case that a_n^2 has a bell shape, the approximation

$$\int^{\infty}dn(B+Cn^2)^{-1}\cos\left(\frac{n\epsilon t}{\hbar}\right)\exp\left[-\frac{\Gamma_s t}{2\hbar}(B+Cn^2)^{-1}\right]$$
$$=\exp\left(-\frac{\Gamma_s t}{2B\hbar}\right)\int_0^{\infty}dn(B+Cn^2)^{-1}\times\exp\left[\left(-\frac{\Gamma_s t}{2\hbar}\right)[(B+Cn^2)^{-1}-B^{-1}]\right]\cos\frac{n\epsilon t}{\hbar}$$
$$\approx\exp\left(-\frac{\Gamma_s t}{2B\hbar}\right)\int_0^{\infty}dn(B+Cn^2)^{-1}\cos\frac{n\epsilon t}{\hbar}$$
$$=\exp(-\Gamma_s t/2B\hbar)(\pi/2C)z^{-1/2}\exp(-yz^{1/2})$$
$$=\tfrac{1}{2}\exp(-\Gamma_s t/2B\hbar)\exp(-t/2\tau_{nr})\tag{98}$$

and therefore

$$\frac{d\langle P(t)\rangle}{dt}=\frac{|\langle s\,|\,H'\,|\,0\rangle|^2}{\hbar^3}\Gamma_s\exp\left[-\left(\frac{\Gamma_s\epsilon^2}{\pi^2v^2\hbar}+\tau_{nr}^{-1}\right)t\right].\tag{99}$$

In (97) we have set

$$y=\epsilon t/\hbar,$$
$$z=B/C,$$
$$yz^{1/2}=(t/2\tau_{nr}).$$

Approximation (c) is valid only if $\epsilon t/\hbar\ll1$, and $\Gamma_s t/\hbar B\ll1$ depending on which restriction on t is more stringent. In general, the former restriction appears to be dominant, for molecules in the statistical limit. A good approximation to this is $\epsilon tB/\hbar\approx1$. This will serve as a validity criteria for the approximation (c). In this limit

$$\exp[-(\Gamma_s t/2\hbar)(B+Cn^2)^{-1}]\approx1$$

for both small n and large n. Although the approximation leading to a simple exponential decay is useful it cannot be correct everywhere. Equation (99) does account for the anomaly in the radiative decay rate (because of the factor $\epsilon^2/\pi v^2$ in the exponential and for the fact that the rate of the radiationless transition overtakes the rate of radiative transition when both occur simultaneously. For longer times the rate of decay is not a simple exponential form.

As our last topic we consider the quantum yield of fluorescence. To calculate the quantum yield we need the total number of photons emitted, i.e., $\langle P(\infty)\rangle$. We therefore integrate the expression for $d\langle P(t)\rangle/dt$ using approximation (c) to find

$$\langle P(\infty)\rangle=\frac{|\langle s\,|\,H'\,|\,0\rangle|^2}{\hbar^3}\Gamma_s\int_0^{\infty}\exp\left(-\frac{\Gamma_s t}{\hbar B}-\frac{t}{\tau_{nr}}\right)dt$$
$$=(|\langle s\,|\,H'\,|\,0\rangle|^2/\hbar^2)[\tau_{nr}B/(\tau_{nr}+\tau_r B)]$$
$$=(|\langle s\,|\,H'\,|\,0\rangle|^2/\hbar^2)\phi,\tag{100}$$

where $\tau_{nr}\equiv\epsilon\hbar/2\pi v^2$ and $\tau_r\equiv\hbar/\Gamma_s$ is the uncorrected radiative lifetime. Since $B=(\pi v/\epsilon)^2$ is very much larger than unity, and $\tau_{nr}\lesssim\tau_r$ in general, we find

$$\langle P(\infty)\rangle\simeq(|\langle s\,|\,H'\,|\,0\rangle|^2/\hbar^2)(\tau_{nr}/\tau_r)\tag{101}$$

or

$$\phi=\tau_{nr}/\tau_r\tag{102}$$

as given by elementary kinetic arguments. Notice that (100) and hence (101) is valid only if the exponential decay law (98) holds. Since the numerical calculation shows that this is not so at large t, (100) and (101) can only be treated as a very crude approximation.

VII. DISCUSSION

We have already commented extensively on the formalism used in the course of the analysis, so that this concluding section will deal with only a few points of interest. We note that:

(a) The treatment of the breakdown of the BO approximation presented herein is very general and does not depend on any explicit assumptions about level spacing in the statistical limit. Our analysis is philosophically different from the Robinson–Frosch–Lin–Siebrand theory in that we focus attention on the properties of the true molecular eigenstates. The advantage of the present approach is that it permits explicit description of the time evolution of an arbitrary BO component of an exact eigenstate, of the absorption line shape, of the radiative decay from the molecular state, and of the coupling between radiative and nonradiative decay processes.

(b) It is a direct prediction of our theory that the mixing of BO states in the true molecular eigenstate leads to a lengthening of the radiative lifetime of each molecular eigenstate. This phenomenon is noticeable in triatomic molecules which have large enough coupling constants to make up for the intrinsic low density of states. It has been reported for the case of SO_2, CS_2, and NO_2.[10] The interpretation given by Douglas is thus explicitly verified.

(c) The nonradiative component of the decay of a molecular state can be thought of as arising from the interference between the many coherently excited states within the inhomogeneously broadened line. The inhomogeneous line broadening itself arises from the differential distribution of a single BO component amongst the many components of the dense BO manifold, which all together constitute the representation of the exact molecular eigenstate.

(d) Although it is customary to assume that the radiative and nonradiative decay modes are independent, and that the observed decay process can be separated into two components, Eq. (99) shows clearly that the radiative decay time is altered by the existence of inhomogeneous broadening of the line. That is, the radiative decay time depends on the number of states within the half-linewidth. The correct relationship between the observed decay time (τ_{obs}), the nonradiative decay time, and the apparent radiative decay time (determined from the oscillator strength) is

$$1/\tau_{\text{obs}} = (1/B\tau_r) + (1/\tau_{nr})$$

in the limit where t is small (in general, of the order of the nonradiative decay time).

(e) If the widths of two states exceed their separation, as can occur in the case of two low-lying vibrational components of a second higher excited-singlet state, the decay rate becomes nonexponential. Perhaps the use of picosecond laser pulses will provide a means of directly testing this prediction.

We close by remarking that our description of the decay of excited molecular states implies that such states are best thought of as resonant states of a compound system analogous with the resonant states which are encountered in autoionization, predissociation, and photochemical unimolecular processes.

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