

Radiationless Transitions and Molecular Quantum Beats

JOSHUA JORTNER AND R. STEPHEN BERRY

Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, Illinois

(Received 19 October 1967)

Radiationless transitions in isolated molecules are examined from the point of view of the breakdown of the Born–Oppenheimer approximation and the nature of the decay of coherently excited states. The problem of intramolecular vibronic coupling between zero-order Born–Oppenheimer states in an isolated molecule seems amenable now to a new approach both in terms of interpretation and of experimental investigation. We have classified molecules exhibiting vibronic mixing into two extreme cases, which we call the resonant case and the statistical case, characterized by low and high densities of molecular eigenstates, respectively. We have then considered the coherent excitation of these states and derived general expressions for photon counting rates and for the integrated intensity. Quantum beat signals can be investigated to analyze close-lying molecular eigenstates in the resonance limit. In the statistical limit the interference effects within a manifold of close-lying states are manifested by a radiationless decay process. An analysis of the radiationless decay times and the quantum yields is given.

The existence of radiationless intramolecular electronic relaxation processes in isolated molecules in the gas phase is now a well-established fact for large molecules like tetracene¹ and anthracene,² for molecules of intermediate size like benzene,³ and even for small molecules like sulfur dioxide.⁴ The nature of the interactions governing the radiationless transitions was considered by Robinson and Frosch⁵ and by Ross, Hunt, and McCoy.⁶ Recently Bixon and Jortner⁷ considered the problem of radiationless transitions in an isolated molecule from the point of view of the breakdown of the Born–Oppenheimer approximation. In a sufficiently large molecule, whose density ρ of vibronic states is high enough to exceed the reciprocal of the vibronic coupling term V between the zero-order Born–Oppenheimer states, considerable configuration mixing occurs. The static problem⁷ is similar to the situation encountered in the study of the Jahn–Teller and pseudo-Jahn–Teller effect.⁸ A different aspect of the intramolecular interelectronic level mixing in small molecules is manifested by the anomalously long radiative lifetimes of the first singlet states of NO₂, SO₂, and CS₂.⁹

In essence the situation is this: We presume we know a set of vibronic state functions $\{\phi_j\}$ derived from calculations carried out in the Born–Oppenheimer approximation. The nuclear kinetic-energy operator generates a coupling among these states. If a zero-order state ϕ_i couples strongly enough with a sufficiently

dense manifold of states ϕ_j , quasidegenerate with ϕ_i , the zero-order Born–Oppenheimer states are insufficient to describe the molecular spectral properties, in the sense that the functions ϕ_i turn out to give a good representation of the observable properties, especially spectral properties, of the molecules. The nuclear kinetic-energy operator Θ_N^2 has been shown to be the key operator inducing so-called radiationless transitions in large molecules.^{5,7,10} Naturally, other operators may modify the mixing; for example, in the case of mixing of states of different multiplicity, the spin–orbit coupling operator is also required.

The static problem of configuration mixing via Θ_N^2 occurs both in large and in small molecules. Let us focus for the moment on the small molecules. In an extreme case of a continuum of vibronic states, the phenomenon takes the form of predissociation,¹¹ which is closely analogous to the process of radiationless transitions in large molecules; the density of vibronic states ϕ_j in the manifold of one electronic state is overwhelmingly greater than the density in the second Born–Oppenheimer manifold ϕ_i , while ϕ_i carries the overwhelming part of the oscillator strength connected with the molecular ground state. Alternatively, in small molecules, ϕ_i and ϕ_j may have comparable densities of vibronic states, and may or may not have similar excitation probabilities. This situation is then distinctly different from that encountered in the cases of radiationless transitions in large molecules and of predissociation.

The problem of intramolecular radiationless coupling among vibronic states seems amenable now to a new approach both in terms of interpretation and of experimental investigation. In what follows we would like to describe how one can meaningfully classify molecules exhibiting vibronic mixing into two extreme cases which we shall refer to as the “resonant case” and the “statistical case.” We shall demonstrate how one can distin-

¹ R. Williams and G. J. Goldsmith, *J. Chem. Phys.* **39**, 2008 (1963).

² P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1949), p. 271.

³ G. B. Kistiakowsky and C. S. Parmenter, *J. Chem. Phys.* **42**, 2942 (1965).

⁴ K. F. Greenough and A. B. F. Duncan, *J. Am. Chem. Soc.* **83**, 555 (1961).

⁵ G. W. Robinson and R. P. Frosch, *J. Chem. Phys.* **38**, 1187 (1963).

⁶ G. R. Hunt, E. F. McCoy, and I. G. Ross, *Australian J. Chem.* **15**, 591 (1962).

⁷ M. Bixon and J. Jortner, *J. Chem. Phys.* **48**, 715 (1968).

⁸ See, for example, H. C. Longuet-Higgins, V. Öpik, M. H. L. Pryce, and R. A. Sack, *Proc. Roy. Soc. (London)* **A244**, 1 (1958).

⁹ A. E. Douglas, *J. Chem. Phys.* **45**, 1007 (1966).

¹⁰ S. H. Lin, *J. Chem. Phys.* **44**, 3759 (1966).

¹¹ R. A. Harris, *J. Chem. Phys.* **39**, 978 (1963).

guish between the two by their behavior in a quantum-beating experiment, and how one can apply the quantum beat signals to analyze the molecular states, particularly in the resonant case. In the statistical limit the interference effects between close lying states are manifested by the radiationless intramolecular decay process. Finally we shall analyze the statistical case to show how the radiationless mixing affects the lifetimes and quantum yields of luminescence.

I. THE STATIC PROBLEM

Let us begin by examining the problem of the mixing of the Born-Oppenheimer zero-order vibronic states. Let a molecule be excited from its ground state Φ_0 to a member of the set of the eigenfunctions of the molecular Hamiltonian, Φ_K , which is adequately represented as a superposition of Born-Oppenheimer vibronic states ϕ_j :

$$\Phi_K = \sum_j \phi_j (\phi_j | \Phi_K). \quad (1)$$

The mixing amplitudes $(\phi_j | \Phi_K)$ are in general obtained by diagonalization of the matrix $(j | \Theta_{N^2} | k)$. In the limiting case when the energy gaps between the zero-order states $\epsilon_k - \epsilon_j$ exceed $(j | \Theta_{N^2} | k)$, one obtains to second order

$$(k | K) \cong 1 \quad (2)$$

and

$$(j | K) = (j | \Theta_{N^2} | k) / (\epsilon_k - \epsilon_j), \quad j \neq k. \quad (3)$$

Again, suppose that a single zero-order vibronic state carries the bulk of the transition amplitude for optical excitation, i.e.,

$$|(\Phi_0 | \mu_e | \phi_i) | \gg |(\Phi_0 | \mu_e | \phi_j) |, \quad j \neq i. \quad (4)$$

The fluorescence intensity of the system under *conventional conditions* following a narrow-band excitation is usually taken as

$$F = |(\Phi_0 | \mu_e | \phi_i) |^2 \sum_{\{K\}} |(\phi_i | \Phi_K) |^2, \quad (5)$$

where the sum over the limited set $\{K\}$ is taken only over the narrow excitation range. If the density of the Born-Oppenheimer states is sufficiently large, so that the number of vibronic states Φ_K is large, and if the vibronic interaction is sufficiently strong, so that ϕ_i is spread out among a large number of stationary states Φ_K , then the fluorescence probability factor F is considerably smaller than $|(\Phi_0 | \mu_e | \phi_i) |^2$. In this case, the intensity is spread over a moderately wide spectral region, and a narrow-band excitation reduces drastically the fluorescence intensity, relative to what one would infer from a pure Born-Oppenheimer state. This reduction occurs entire as an intramolecular phenomenon. The situation encountered here is analogous to inhomogeneous broadening. This limiting case will be referred to as the "statistical case." The foregoing is essentially a statement, from a slightly different point of view, of the analysis of Bixon and Jortner.⁷ In particular it was

demonstrated⁷ that the intramolecular coupling leads to the broadening of the excited state, which gives a Lorentzian line shape. Although the situation involves a discrete state ϕ_i interacting with a quasicontinuum of ϕ_j states no Fano-type line asymmetries and anti-resonances¹² are encountered. This is because the oscillator strength from the ground state to the quasicontinuum state is very small; this in turn is due to the very small Franck-Condon factors and sometimes to spin selection rules.

On the other hand, the states mixing in a small molecule, with only a few degrees of freedom, can only reduce the fluorescence rate by a modest amount [at the most by a factor of $1/n$, where n is the (small) number of nearly degenerate states] below that predicted for the Born-Oppenheimer state ϕ_i . We shall refer to this limit of low density of states as the resonant case. In this case one must introduce an external relaxation mechanism, e.g., collision processes, to play the role of the manifold of quasicontinuum states which appear in the statistical case. The effect of an external relaxation process in the resonant case will be manifested by the population of energy levels in the ϕ_j manifold which are not able to mix effectively with ϕ_i via Θ_{N^2} . Furthermore, the rates of population of these states and their dependence on the nature of the colliding species will generally follow the gross features of vibrational relaxation processes. The low excited states of the SO_2 molecules provide a good example of this situation. We now argue that the statistical and resonant cases can be distinguished by the following criteria:

(a) The requirement for statistical mixing is determined by the size of the average energy normalized coupling parameter $\bar{\rho}\bar{V}$ where $\bar{\rho}$ is the mean density of vibronic states and \bar{V} is a typical off-diagonal perturbation matrix element $(\phi_i | \Theta_{N^2} | \phi_j)$. The requirement for statistical mixing is⁷

$$\bar{\rho}\bar{V} \gg 1. \quad (6)$$

In this limit the linewidth is given⁷ by $2\Delta = \pi\bar{\rho}\bar{V}^2$.

(b) Inhomogeneous line broadening occurs only in the statistical case and is not encountered in the resonance case.

(c) Intermolecular relaxation occurs in the statistical case in the absence of an external perturbation, while a vibrational relaxation process is a prerequisite for relaxation in the resonance case.

The requirement for statistical mixing represents the situation of the decay of a resonance state into a quasicontinuum. The situation is formally the same as that for the decay of a resonance state into a true continuum, as encountered in α decay of nuclei, atomic and molecular autoionization, molecular predissociation, and radiative decay. In all these cases a resonant state of the compound system decays into a true or a quasi-

¹² U. Fano, Phys. Rev. **124**, 1866 (1961).

continuum, the choice depending solely on what boundary conditions are applied at large distances from the compound system. Statistical radiationless transitions fall in the same category, with the dense manifold of states playing the role of the quasicontinuum, provided that criterion (6) is met.

On the other hand the resonance case is analogous to configuration interaction between closely spaced states. Thus in the absence of an external perturbation which leads to a relaxation process, the resonant case does not involve an intramolecular decay process. Rather, this situation is manifested in the breakdown of the Born-Oppenheimer approximation, leading to the distribution of the properties of the zero-order Born-Oppenheimer states (such as the oscillator strength) among the observable mixed stationary states.

II. THE COUPLING PARAMETERS

We now proceed to a quantitative development of $\bar{\rho}\bar{V}$. The density of states at energy E can be approximated by the semiclassical expression in the harmonic approximation¹³:

$$\rho = [E^{n-1}/(n-1)!] (\prod_i h\nu_i)^{-1} \{1 + [h \sum_i (\frac{1}{2}\nu_i)/E]\}^{n-1}, \tag{7}$$

where n is the number of the vibrational degrees of freedom, characterized by the eigenfrequencies ν_i . Anharmonicity effects will only increase $\bar{\rho}$. If we take ρ from (7) we assume that all states couple effectively. The product $\bar{\rho}\bar{V}$ really represents the density of states each weighted by its coupling coefficient.⁷

The coupling element \bar{V} calls for close attention because its general properties depend very much on the case under consideration. In general we write the zero-order functions in the form

$$\phi_i = \psi_\alpha \prod_{j=1}^n \chi_{\alpha j}(z_j), \tag{8}$$

where ψ_α is the electronic wavefunction in the Born-Oppenheimer approximation and $\chi_{\alpha j}(\nu_j)$ are the vibrational wavefunctions in the ν th vibrational state of the j th mode for a molecule in the electronic state α .

The perturbation operator Θ_N^2 can be expressed as a sum over the kinetic energies corresponding to the normal modes

$$\Theta_N^2 = \sum_k \theta_k^2, \tag{9}$$

where

$$\theta_k^2 = -\frac{1}{2} (d^2/d\mathbf{q}_k^2) \tag{10}$$

with \mathbf{q}_k being the k th mass-weighted normal coordinate in atomic units. Thus a typical coupling matrix element is

$$\bar{V} = \sum_k (\psi_\alpha \prod_{j=1}^n \chi_{\alpha j} | \theta_k^2 | \psi_\beta \prod_{j=1}^n \chi_{\beta j}). \tag{11}$$

Bearing in mind that θ_k is a differential operator and the electronic states ψ_α and ψ_β are orthogonal one gets

$$\begin{aligned} \bar{V} = & - \sum_k \frac{1}{2} (\prod_j \chi_{\alpha j} \langle \psi_\alpha | d^2/d\mathbf{q}^2 | \psi_\beta \rangle \prod_j \chi_{\beta j}) \\ & - \sum_k (\prod_j \chi_{\alpha j} \langle \psi_\alpha | d/d\mathbf{q} | \psi_\beta \rangle \cdot d/d\mathbf{q} \prod_j \chi_{\beta j}). \end{aligned} \tag{12}$$

This result is identical with the equation obtained using a variational expansion method for the molecular eigenstates.^{7,10}

In the most complex situation, the equilibrium geometries of the states α and β are very different, so that the vibrational wavefunction $\chi_{\alpha j}$ and $\chi_{\beta j}$ considerably differ from each other. In this case one cannot simplify Eq. (12) in any systematic way. However we can make successive approximations for successively simpler cases. If the electronic wavefunctions change character only slowly with nuclear displacements, then the first term in Eq. (12) can be neglected. It was first demonstrated by Bloch and Bradbury¹⁴ for diatomics, that in many situations the ratio of the first to the second term is comparable to the ratio of the vibrational amplitude to the intermolecular distance. However this argument must be applied with great caution for small molecules either if the electronic wavefunction changes or if the excited state involves the molecule far from the ground-state equilibrium configuration. Good examples of such cases are associative or Penning ionization.¹⁵

Next, if the molecule has approximately the same equilibrium geometry in the states α and β , and if it is never very far from this geometry, one can factor out the electronic matrix elements to obtain

$$\begin{aligned} V \approx & - \langle \psi_\alpha | \frac{1}{2} \sum_k d^2/d\mathbf{q}_k^2 | \psi_\beta \rangle \langle \prod_j \chi_{\alpha j} | \prod_{j'} \chi_{\beta j'} \rangle \\ & - \sum_k \langle \psi_\alpha | d/d\mathbf{q}_k | \psi_\beta \rangle \langle \prod_j \chi_{\alpha j} | d/d\mathbf{q}_k | \prod_{j'} \chi_{\beta j'} \rangle. \end{aligned} \tag{13}$$

If the states α and β are similar not only in their equilibrium geometries but in their potential surfaces as well, a considerable simplification of the vibrational integrals in Eq. (13) takes place. In this case the normal modes of the state α and β are very similar. In this limiting case we can further factor out Eq. (13) to get

$$\begin{aligned} V \approx & - \sum_k \langle \psi_\alpha | d^2/d\mathbf{q}_k^2 | \psi_\beta \rangle - \sum_k \langle \psi_\alpha | d/d\mathbf{q}_k | \psi_\beta \rangle \\ & \cdot \langle \chi_{\alpha k}(v_{\alpha k}) | d/d\mathbf{q}_k | \chi_{\beta k}(v_{\beta k}) \rangle \prod_{i \neq k} \delta_{v_{\alpha i}, v_{\beta i}}. \end{aligned} \tag{14}$$

III. APPROXIMATE SELECTION RULES

We have used the constraint that the vibrational functions are orthonormal, being independent of the electronic state,

$$\langle \chi_{\alpha i}(v_{\alpha i}) | \chi_{\beta j}(v_{\beta j}) \rangle = \delta_{v_{\alpha i}, v_{\beta i}} \tag{15}$$

¹³ P. C. Haarhoff, Mol. Phys. 7, 101 (1963).

¹⁴ F. Bloch and N. E. Bradbury, Phys. Rev. 48, 689 (1935).

¹⁵ R. S. Berry, J. Chem. Phys. 45, 1228 (1966).

to obtain Eq. (14). This equation provides us with two pieces of information about radiationless mixing among states, which we can formulate as the first and the second propensity rules. First, mixing will occur primarily between pairs of vibronic states having the same number of quanta in all vibrational states but one, so that only one normal mode will change its quantum state. Second, in the mode that does change its energy, a change of one quantum is much more probable than the change of two quanta, which in turn is more probable than the change of three quanta, etc.

The second of these rules has been previously introduced by one of us¹⁵ as a "propensity rule" for autoionization of diatomics. Our first rule, stated above, is also a propensity rule, rather than a true selection rule, because the states α and β cannot be expected to have identical potential surfaces. Consequently, the orthogonality and factoring simplifications are only approximate. An immediate conclusion of these approximate selection rules is that a large molecule in the statistical limit will exhibit faster radiationless transition rates in higher excited vibronic states of the zero-order manifold ϕ_i . This conclusion was recently reached on the basis of numerical calculations.¹⁶

IV. ROUGH NUMERICAL ESTIMATES

Following the foregoing analysis we now examine three representative cases: a statistical case (anthracene), an intermediate case (benzene), and a resonant case (SO_2). For anthracene $\Delta E(^1B_{2u}-^3B_{2u}) = 12\,000\text{ cm}^{-1}$; there are 66 vibrational degrees of freedom, with frequencies of $\sim 10^3\text{ cm}^{-1}$, the level density $\rho \approx 5 \times 10^{10}$ levels per cm^{-1} .⁷ From the experimental intersystem crossing rate $\tau^{-1} = 2\pi\hbar^{-1}\rho$, $V^2 = 5 \times 10^{-9}\text{ sec}^{-1}$,¹⁷ we infer that⁷ $V = 6 \times 10^{-7}\text{ cm}^{-1}$, so that $V\rho = 3 \times 10^4$, which means that anthracene is clearly a statistical case.

For benzene, the energy gap ($^1B_{2u}-^3B_{1u}$) is 8400 cm^{-1} . The level density of the triplet in the region of the vibrationless state of the $^1B_{2u}$ is 8×10^4 levels per cm^{-1} and the intersystem crossing rate is $\sim 10^6\text{ sec}^{-1}$,³ from which we infer that $V = 1.5 \times 10^{-5}\text{ cm}^{-1}$ and $V\rho = 1.5$. This means that benzene molecules might be expected to show different lifetimes for different lines in its gas-phase fluorescence, due to different amounts of singlet-triplet mixing. This intermediate case behavior is of course nicely consonant with the findings of Parmenter and Kistiakowsky³—that the fluorescence yield at low pressures is less than unity, and that the lowest triplet is present in an irradiated gas sample, even at low densities.

Finally we examine SO_2 .⁴ The energy gap between the lowest excited singlet 1B_1 and the lowest triplet 3B_1 is approximately 4000 cm^{-1} .⁴ The triplet-level density in the vicinity of the vibrationless state of the singlet is 1.5×10^{-2} levels per cm^{-1} . Obviously, because

this is another singlet-triplet coupling case, the value of V is not expected to exceed 10 cm^{-1} and is probably much smaller. Therefore the $^1B_1-^3B_1$ coupling in SO_2 is clearly a case for which $V\rho \ll 1$ and must be treated as a resonant case.

Note that all three of the foregoing examples involve singlet-triplet mixing, so that their coupling matrix elements V must contain a spin-orbit coupling factor as well as a matrix element of Θ_N^2 . The spin-orbit factor will be given roughly by the square of the ratio of the oscillator strengths for singlet and triplet transition $(f_{\text{triplet}}/f_{\text{singlet}})^{1/2}$, or about $10^{-3}-10^{-4}$ for hydrocarbons, and for SO_2 , about 10^{-2} . We therefore can expect the benzene singlet manifolds to interact according to the statistical limit, since all the numerical factors except V are comparable to those for the $^1B_{2u}-^3B_{1u}$ mixing. The coupling element for the two singlets must differ from that for triplet-singlet coupling primarily by the absence of a spin-orbit factor. This is consistent with the "broad lines" observed in the gas-phase absorption of the $^1B_{1u}$ state in benzene.

We can likewise expect singlet-singlet couplings in triatomics containing a moderately heavy atom—i.e., molecules like SO_2 —to be intermediate cases, although small vibrational overlaps could turn them back into resonant cases. Experimental evidence⁴ from the irradiation of the second excited singlet state of SO_2 makes this look like an intermediate case; the irradiation leads to the same fluorescence one obtains when one irradiates in the first excited singlet state.

V. BEAT SPECTROSCOPY

We shall now derive the general expression for luminescence emission rate. We shall demonstrate how one can analyze the amplitudes and frequencies of the interference oscillations (beats) to obtain information concerning the coupling matrix elements and the location of the levels. We are dealing here with a phenomenon associated with very closely spaced levels. It has been known for a long time that the spectral properties of a system with closely spaced levels are far more interesting than Eq. (5) suggests.¹⁸⁻²⁰ That equation is based on the explicit assumption that all the emitting levels are uncorrelated, whereas in practice one can obtain a great deal of information about the close-lying states by preparing them with a coherent excitation.

For example, level-crossing spectroscopy and the oscillatory decay of fluorescence (beat spectroscopy) both arise from interference between coherently excited close-lying states.

The same kind of interference phenomena can be expected in molecular spectra when mixing occurs between close vibronic zero-order states corresponding to different Born-Oppenheimer manifolds. In this case the

¹⁸ G. Breit, Rev. Mod. Phys. 5, 91 (1933).

¹⁹ M. Podgoretskii and O. Khurstalev, Soviet Phys.—Usp., 6, 682 (1964).

²⁰ J. Dodd, R. Kaul, and D. Warrington, Proc. Phys. Soc. (London) 84, 176 (1964).

¹⁶ D. L. Dexter and W. B. Fowler, J. Chem. Phys. 47, 1379 (1967).

¹⁷ R. E. Kellog, J. Chem. Phys. 44, 411 (1966).

mixed states $\Phi_J, \Phi_K \dots$ all contain some contribution of a light pulse with duration Δt , shorter than the inverse of the separation ν of the levels $\Phi_J, \Phi_K \dots$. Then these levels are essentially excited simultaneously and their decay will reveal mutual interference.

The general problem of the decay of metastable states was presented in detail by Goldberger and Watson.²¹ This formalism was recently applied by Kelley²² in the study of level interference following electron impact. In what follows we shall examine the general problem of molecular beat spectroscopy within the framework of the Goldberger-Watson formulation,²¹ with a generalized delta function excitation. This excitation, for example, may be a light pulse or an electron collision.

We start with the system in the ground state Φ_0 . At time $t=0$ an excitation process is applied. This excitation process introduces a time-dependent perturbation $T(t)$ for a duration τ . An excited nonstationary state is produced which can be represented as a superposition

$$\Psi(\tau) = \sum_n |\Phi_n\rangle \int_0^\tau \exp\left(\frac{i}{\hbar} (E_n - E_0)t'\right) \langle \Phi_n | T | \Phi_0 \rangle dt' \quad (16)$$

We now assume that the duration of the perturbation is short on the time scale of the decay of the excited state, so that it can be taken as a delta function $T(t) = T\delta(t)$, where T is a time-independent coupling operator. In the case of optical excitation T is proportional to the electric moment operator. The excited state can be displayed now as a time-dependent superposition of eigenstates of the molecular Hamiltonian, each of which is a time-independent superposition of Born-Oppenheimer basis function ϕ_j :

$$\Psi(\tau) = \sum_L \Phi_L T_{L0}, \quad (17)$$

where

$$T_{L0} = (\Phi_L | T | \Phi_0). \quad (18)$$

Using expansion (1) we write

$$T_{L0} = \sum_j (\Phi_L | \phi_j) T_{j0}. \quad (19)$$

To describe the decay process of the state (17) we shall consider the Hamiltonian

$$\hat{H} = H_0 + H_R + V_R, \quad (20)$$

where H_0 is the molecular Hamiltonian, H_R the Hamiltonian for the free electromagnetic field, and V_R is the usual $(\mathbf{p} \cdot \mathbf{A} + A^2)$ matter-radiation interaction term. The time evolution operator for the system is

$$\hat{U}(t) = \exp(-i\hat{H}t) \quad (21)$$

so that the wavefunction of the decaying state at time t ($t \gg \tau$) is displayed in the form

$$\Psi(t) = \sum_L T_{L0} \exp(-i\hat{H}t) | \Phi_L; \text{vac} \rangle, \quad (22)$$

where $| \Phi_L; \text{vac} \rangle = \Phi_L | \text{vac} \rangle$ and corresponds to the vacuum state of the electromagnetic field. Limiting our attention to one-photon decay process, the ground state of the system is $| \phi_0; \mathbf{k}, \mathbf{e} \rangle$, where \mathbf{k} is the photon angular frequency and \mathbf{e} its polarization vector. Note that Φ_L and Φ_0 are eigenstates of H_0 . On the other hand $| \text{vac} \rangle$ and $| \mathbf{k}, \mathbf{e} \rangle$ are zero-photon and one-photon eigenstates of H_R , respectively. The radiation field is quantized in a box of volume V_0 so that these eigenstates are discrete. The transition probability from the excited decay state to the ground state accompanied by the emission of a photon \mathbf{k}, \mathbf{e} is given by $| \langle \Psi(t) | \Phi_0; \mathbf{k}, \mathbf{e} \rangle |^2$.

Consider now the experimental situation. The radiative transition is monitored by a photon counting apparatus, admitting all photons in the range $\{k, e\}$ and being characterized by equal sensitivity over the whole admittance spectral range. Under these conditions the integrated photon counting rate is given in the form

$$P(t) = \sum_{\{\mathbf{k}, \mathbf{e}\}} | \langle \Psi(t) | \Phi_0; \mathbf{k}, \mathbf{e} \rangle |^2. \quad (23)$$

We now display the integrated emission rate as a sum of a normal term $P_1(t)$ and an interference term $P_2(t)$, so that

$$P(t) = P_1(t) + P_2(t), \quad (24)$$

and from Eqs. (22) and (23) we obtain

$$P_1(t) = \sum_{\{\mathbf{k}, \mathbf{e}\}} \sum_L | T_{L0} |^2 | \langle \Phi_0; \mathbf{k}, \mathbf{e} | \exp(-i\hat{H}t) | \Phi_L; \text{vac} \rangle |^2 \quad (25)$$

and

$$P_2(t) = 2 \text{Re} \sum_{\{\mathbf{k}, \mathbf{e}\}} \sum_{L < M} T_{L0} T_{M0}^* \times \langle \Phi_0; \mathbf{k}, \mathbf{e} | \exp(-i\hat{H}t) | \Phi_L; \text{vac} \rangle \times \langle \Phi_0; \mathbf{k}, \mathbf{e} | \exp(-i\hat{H}t) | \Phi_M; \text{vac} \rangle^*. \quad (26)$$

Next we consider the matrix elements of $\exp(-i\hat{H}t)$. Following the analysis of Goldberger and Watson²¹ in the case of dipole-allowed transitions these matrix elements are given in the form

$$\langle \Phi_0; \mathbf{k}, \mathbf{e} | \exp(-i\hat{H}t) | \Phi_L; \text{vac} \rangle = - \left(\frac{2\pi e^2}{V_0 k} \right)^{1/2} \left\langle \Phi_0 \left| \frac{\mathbf{e} \cdot \mathbf{P}}{m} \right| \Phi_L \right\rangle \exp[-i(\omega_0 + k)t] \times \left(\frac{1 - \exp[i(k + \omega_0 - \omega_L + \frac{1}{2}i\Gamma_L)t]}{k + \omega_0 - \omega_L + \frac{1}{2}\Gamma_L} \right), \quad (27)$$

where $\omega_L = E_L/\hbar$, and \mathbf{P} is the total electron momentum operator, and Γ_L is the natural linewidth. The latter quantity can be expressed as a sum of partial widths

$$\Gamma_L = \sum_{M, \omega_M < \omega_L} \sum_e \Gamma_L^e(M), \quad (28)$$

where

$$\Gamma_L^e(M) = \frac{e^2(\omega_L - \omega_M)}{2\pi} \int \left| \left\langle \Phi_L \left| \frac{\mathbf{e} \cdot \mathbf{P}}{m} \right| \Phi_M \right\rangle \right|^2 d\Omega_k; \quad (29)$$

²¹ M. Goldberger and K. Watson, *Collision Theory* (John Wiley & Sons, Inc., New York, 1964), p. 451.

²² R. L. Kelley, *Phys. Rev.* **147**, 376 (1966).

the integration is carried out over a solid angle in the k space. Making use of these results and changing the sum over $\{k\}$ into an integral we obtain

$$P_1(t) = \sum_L |T_{L0}|^2 \int_{\{k\}} d\Omega_k \sum_{\{e\}} \frac{e^2}{4\pi^2} \left| \left\langle \Phi_0 \left| \frac{\mathbf{e} \cdot \mathbf{P}}{m} \right| \Phi_L \right\rangle \right|^2 \int k dk \left| \frac{1 - \exp[i(k + \omega_0 - \omega_L + \frac{1}{2}i\Gamma_L)t]}{k + \omega_0 - \omega_L + \frac{1}{2}i\Gamma_L} \right|^2 \quad (30)$$

and

$$P_2(t) = 2 \operatorname{Re} \sum_{L < M} T_{L0} T_{M0}^* \int_{\{k\}} d\Omega_k \sum_{\{e\}} \frac{e^2}{4\pi^2} \left\langle \Phi_0 \left| \frac{\mathbf{e} \cdot \mathbf{P}}{m} \right| \Phi_L \right\rangle \left\langle \Phi_0 \left| \frac{\mathbf{e} \cdot \mathbf{P}}{m} \right| \Phi_M \right\rangle^* \\ \times \int_{\{k\}} k dk \left(\frac{1 - \exp[i(k + \omega_0 - \omega_L + \frac{1}{2}i\Gamma_L)t]}{k + \omega_0 - \omega_L + \frac{1}{2}i\Gamma_L} \right) \left(\frac{1 - \exp[i(k + \omega_0 - \omega_M + \frac{1}{2}i\Gamma_M)t]}{k + \omega_0 - \omega_M + \frac{1}{2}i\Gamma_M} \right)^* \quad (31)$$

We now replace $\int_{\{k\}} k dk$ by

$$(\omega_L - \omega_0) \int_{-\infty}^{\infty} dk,$$

which implies that the photon counting system passes all radiation with the frequency $(\omega_L - \omega_0)$ in a frequency range much wider than Γ_L . We now define an interference width for states L and M

$$\Gamma_{ML} = \frac{e^2}{2\pi} \left[\frac{1}{2}(E_L + E_M) - E_0 \right] \int d\Omega_k \sum_{\{e\}} \left\langle \Phi_0 \left| \frac{\mathbf{e} \cdot \mathbf{P}}{m} \right| \Phi_L \right\rangle \left\langle \Phi_0 \left| \frac{\mathbf{e} \cdot \mathbf{P}}{m} \right| \Phi_M \right\rangle^* \quad (32)$$

The diagonal elements of the matrix Γ_{ML} are obtained from the definition (29) in the form

$$\Gamma_{LL} = \sum_{\{e\}} \Gamma_L^e(0). \quad (33)$$

Then we can finally express the integrated emission rates in the form

$$P_1(t) = \sum_L |T_{L0}|^2 (\Gamma_{LL}/\Gamma_L) [1 - \exp(-\Gamma_L t)] \quad (34)$$

and

$$P_2(t) = -2 \operatorname{Im} \sum_{L < M} T_{L0} T_{M0}^* \\ \times \{ \Gamma_{ML} / [\omega_M - \omega_L + \frac{1}{2}i(\Gamma_L + \Gamma_M)] \} \\ + \{ 1 - \exp[i(\omega_M - \omega_L)t] \exp[-\frac{1}{2}(\Gamma_L + \Gamma_M)t] \}. \quad (35)$$

The fluorescence rate is given in the form

$$dP/dt = (dP_1/dt) + (dP_2/dt), \quad (36)$$

where

$$dP_1/dt = \sum_L |T_{L0}|^2 \Gamma_{LL} \exp(-\Gamma_L t) \quad (36a)$$

and

$$dP_2/dt = 2 \operatorname{Re} \sum_{L < M} T_{L0} T_{M0}^* \Gamma_{ML} \\ \times \exp[i(\omega_M - \omega_L)t] \exp\{-[(\Gamma_M + \Gamma_L)t/2]\}. \quad (36b)$$

The general structure of Eq. (36) represents two components: the first is a sum of exponential decays each with its own lifetime Γ_L . Under conditions of incoherent steady-state illumination this sum corresponds to the expression in Eq. (5) because, under such conditions the sinusoidal second term averages to zero. The second

term in Eq. (36) represents interference effects between each pair of levels. Each term in the interference part adds a frequency component $(\omega_M - \omega_L)$ superimposed on the smooth exponential envelope.

Consider now the resonance limit, when a small number of eigenstates is involved. In this limit a true quantum beat spectrum is obtained. Let us see first how to extract information from the amplitude of the modulation. Let Φ_1 and Φ_2 be two eigenstates of the molecular Hamiltonian; each consists of vibronically coupled zero-order states, a lowest excited singlet state ϕ_s and a triplet state ϕ_t . This simple situation allows us to reduce Eq. (36) to the interaction of one pair of states and to drop the Born-Oppenheimer triplet contribution to the matrix elements.

Now let

$$\Phi_1 = \lambda\phi_s + \mu\phi_t, \\ \Phi_2 = \mu\phi_s - \lambda\phi_t, \quad (37)$$

where $\lambda = (y + \Delta/2y)^{1/2}$ and $\mu = (y - \Delta/2y)^{1/2}$, Δ is the splitting of the zero-order states, and $y = (4V^2 + \Delta^2)^{1/2}$. Now we can set $T_{10} = \lambda T_{0S}$ and $T_{20} = \mu T_{0S}$. Furthermore in this simple case $\Gamma_{11} = \Gamma_1 \cong \lambda^2 \Gamma_S$, $\Gamma_{22} = \Gamma_2 \cong \mu^2 \Gamma_S$, and $\Gamma_{12} = \lambda\mu \Gamma_S$. From Eq. (36) we get

$$dP/dt = \lambda^4 \Gamma_S |T_{0S}|^2 \exp(-\lambda \Gamma_S t) \\ + \mu^4 \Gamma_S |T_{0S}|^2 \exp(-\mu \Gamma_S t) \\ + 2\lambda^2 \mu^2 |T_{0S}|^2 \Gamma_S \exp\{-[(\lambda + \mu) \Gamma_S t/2]\} \cos(\omega_1 - \omega_2)t. \quad (38)$$

It is important to note that one must retain the exact eigenfrequencies ω_1 and ω_2 of the molecular Hamiltonian. The amplitude of the modulation relative to the normal

terms is

$$R = \frac{2\lambda^2(1-\lambda^2) \exp\{-[(\lambda+\mu)\Gamma_{st}/2]\}}{\lambda^4 \exp(-\lambda\Gamma_{st}) + (1-\lambda^2)^2 \exp(-\mu\Gamma_{st})}. \quad (39)$$

This result provides a direct measure of the square of the projections of the singlet Born-Oppenheimer states on the mixed states. Finally it is important to notice that in this simple case the oscillations would start at a maximum since $\Gamma_S |T_{0S}|^2 > 0$. In more complex cases the beats between the states L and M can start either at maximum or minimum depending on the sign of the product $\text{Re}T_{L0}T_{M0}^*\Gamma_{LM}$.

Now let us extract information from the frequency behavior of the modulation; here one obtains the spacing of each pair of levels. To demonstrate this point we take the Fourier transform of Eq. (36) to get the result

$$F(\omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} dt \exp(i\omega t) \frac{dP}{dt} \\ = \sum_L \frac{|T_{L0}|^2 \Gamma_{LL} \Gamma_L}{\omega^2 + \Gamma_L^2} \\ + 2 \text{Re} \sum_{L < M} \frac{T_{L0} T_{M0}^* \Gamma_{ML} [(\Gamma_M + \Gamma_L)/2]}{(\omega + \omega_L - \omega_M)^2 + [(\Gamma_M + \Gamma_L)/2]^2}. \quad (40)$$

Hence the power spectrum $F(\omega)$ is a sum of Lorentzians; each of the levels contributes its term centered about $\omega=0$, and each pair of levels contributes a displaced maximum at $\omega = |\omega_L - \omega_M|$. So long as the level spacing $\omega_L - \omega_{L\pm 1}$ is comparable to or smaller than the radiative width Γ_i , the beats will be slow enough to be observable. So long as the differences in pair separations, $|\omega_L - \omega_{L\pm 1}|$ and $|\omega_M - \omega_{M\pm 1}|$ are greater than the radiative width, one can determine separately the individual pair separations.

Thus for a small number of molecular eigenstates the positions of the Fourier components will give the level spacing, the relative peak intensities will give the information concerning the ratio of the matrix elements, and the widths will provide the sums of radiative lifetimes $\Gamma_L + \Gamma_M$. This is the most useful way for analyzing the results of a molecular beat experiment. This information will make possible the location and identification of close-lying states in the resonance limit.

VI. INTERFERENCE EFFECTS IN THE STATISTICAL LIMIT

We now turn our attention to a transition of a multi-level system exhibiting the statistical behavior. The

$$dP_2/dt = \text{Re} \sum_{L \neq L'} \sum |a_i^{L'}|^2 |a_i^L|^2 |T_{i0}|^2 \Gamma_i \exp[i(E_L - E_{L'})t] \exp[-(\Gamma_i/2)(|a_i^L|^2 + |a_i^{L'}|^2)t]. \quad (43)$$

We now assume that the levels E_L are equally spaced and set $(E_L - E_{L'}) = (L - L')/\rho$. We can now simplify this result by removing the restriction $L \neq L'$ in the summation and write

$$dP_2/dt = \left\{ \text{Re} \sum_L \sum_{L'} |a_i^{L'}|^2 |a_i^L|^2 |T_{i0}|^2 \exp[i(L - L')t/\hbar\rho] \exp[-(\Gamma_i/2)(|a_i^L|^2 + |a_i^{L'}|^2)t] \right. \\ \left. - \sum_L |a_i^L|^4 |T_{i0}|^2 \exp(-|a_i^L|^2 \Gamma_i t) \right\}. \quad (44)$$

eigenstates of the molecular Hamiltonian are

$$\Phi_L = a_i^L \phi_i + \sum_{j \neq i} a_j^L \phi_j.$$

At the time the excitation is applied, all states are coherently excited. What will happen to the direct decay term dP_1/dt ? To consider this problem we make the following assumptions, similar to those employed by Bixon and Jortner⁷: (1) The T matrix elements are real. (2) The only nonvanishing transition matrix element is T_{0i} , so that $T_{0j} = 0$ for $j \neq i$. (3) There are no other zero-order states ϕ_k located below ϕ_i for which $T_{ki} \neq 0$, so that $\Gamma_{LL} = \Gamma_L$ for all L . (4) The linewidth $2\Delta = \pi V^2 \rho$ is small relative to the excitation energies $\hbar(\omega_L - \omega_0)$ for all L . Using these reasonable assumptions we can get $T_{L0} = a_i^L T_{i0}$ and $\Gamma_L = \Gamma_{LL} = |a_i^L|^2 \Gamma_i$. Hence we obtain

$$dP_1/dt \cong \sum_L |a_i^L|^4 |T_{i0}|^2 \Gamma_i \exp(-|a_i^L|^2 \Gamma_i t). \quad (41)$$

For the sake of a rough estimate let us now assume that the average spacing of the levels Φ_j is ρ^{-1} so that within the linewidth there are $n = \pi V^2 \rho^2$ states. Furthermore we assume that for the energies $-\Delta \leq E_L - \epsilon_i \leq \Delta$, $|a_i^L|^2 \cong n^{-1}$, and is zero otherwise. This assumption is equivalent to replacing the Lorentzian line shape⁷ by a step function of the width 2Δ . Then we can write

$$dP_1/dt \cong n |T_{i0}|^2 (-1/n)^2 \Gamma_i \exp(-\Gamma_i t/n) \\ = |T_{i0}|^2 (\Gamma_i/n) \exp[-(\Gamma_i/n)t]. \quad (42)$$

A cursory examination of Eq. (42) reveals a rather peculiar behavior of the term dP_1/dt : The direct contribution to the decay process leads to an exponential term characterized by a mean lifetime of n/Γ_i which is lower than the radiative lifetime *with no reference to any nonradiative process*. Anomalously long radiative lifetimes were observed for small molecules in the resonance limit.⁹ However in the statistical limit such a result for the total differential emission rate contradicts both experience and intuition. This apparent discrepancy can be removed immediately if we consider the contribution of the interference term dP_2/dt . It can now be demonstrated easily that the interference contains this information. We write dP_2/dt so that it consists of two contributions: one exactly cancelling the contribution of the direct term and a second part determining the total decay rate. Using the same reasonable approximations applied for the derivation of Eq. (41) we recast Eq. (36b) in the form

The second contribution to the interference term (44) is just $-dP_1/dt$. Hence from (36a) we get for the total differential emission rate

$$dP/dt = \text{Re} |T_{i0}|^2 \sum_L \sum_{L'} |a_i^L|^2 |a_i^{L'}|^2 \exp[i(L-L')t/\hbar\rho] \exp[-(\Gamma_i/2)(|a_i^L|^2 + |a_i^{L'}|^2)t]. \quad (45)$$

Now defining $y = t/\hbar\rho$, $F(L) = |a_i^L|^2$, and $\alpha = \Gamma_i t/2$, we can display the general result in terms of a Fourier series

$$dP/dt = |T_{i0}|^2 \Gamma_i [f(y, \alpha)]^2, \quad (45a)$$

where

$$f(y, \alpha) = \sum_{L=-\infty}^{\infty} F(L) \exp[-\alpha F(L)] \cos(Ly). \quad (46)$$

In the statistical limit $y \ll 1$. This limiting condition was previously applied by Bixon and Jortner⁷ to establish a time scale for the intramolecular decay process. Then the f function (46) is reduced to a Fourier integral

$$f(y, \alpha) = \int_{-\infty}^{\infty} dz F(z) \exp[-\alpha F(z)] \cos(yz). \quad (46a)$$

Replacing the sum (46) by the integral (46a) introduces irreversibility by pushing the recurrence times to infinity. The integral approximation is not necessary at this stage; the summation could still be carried out exactly and analytically. However, the integral will be useful for computing quantum yields (Eq. 50, below).

To simplify the mathematical treatment we again use the step function approximation (instead of the exact Lorentzian shape) for the line shape, as applied before for the derivation of Eq. (42). In this case $-n/2 \leq L$, $L' \leq n/2$. Thus we get

$$dP/dt \cong \Gamma_i/n^2 |T_{i0}|^2 \exp[-(\Gamma_i t/n)] \times \sum_L \sum_{L'} \exp[i(L-L')t/\hbar\rho]. \quad (47)$$

Applying again the limiting condition⁷ $\hbar\rho \gg t$, the double summation in Eq. (47) can be replaced by an integration leading to the result:

$$\sum_L \sum_{L'} \exp\left(\frac{i(L-L')t}{\hbar\rho}\right) = \left[\int_{-n/2}^{n/2} \exp\left(\frac{izt}{\hbar\rho}\right) dz \right]^2 = (2\hbar\rho/t)^2 \sin^2(nt/2\hbar\rho). \quad (47a)$$

We can define an intramolecular radiationless decay time τ_{NR}

$$\tau_{NR}^{-1} = n/2\hbar\rho, \quad (48)$$

which apart from a numerical factor is just the formal result of Fermi's golden rule. This intramolecular relaxation rate determines the radiationless decay.

We now display Eq. (45) in the form

$$\frac{dP}{dt} = \Gamma_i |T_{i0}|^2 \exp\left(-\frac{\Gamma_i t}{n}\right) \left[\frac{\sin(t/\tau_{NR})}{(t/\tau_{NR})} \right]^2. \quad (49)$$

The integrated number of photons detected, $P(\infty)$, is given by

$$P(\infty) = \Gamma_i |T_{i0}|^2 \int_0^{\infty} \exp\left(-\frac{\Gamma_i t}{n}\right) \left[\frac{\sin(t/\tau_{NR})}{(t/\tau_{NR})} \right]^2 dt \quad (50)$$

so that in our approximation the integrated yield is²³

$$P(\infty) = n |T_{i0}|^2 [\xi^{-1} \arctg(2\xi) - (4\xi^2)^{-1} \ln(1+4\xi^2)], \quad (51)$$

where

$$\xi = n/\Gamma_i \tau_{NR}. \quad (52)$$

We can now consider the quantum yield for the integrated fluorescence emission. The frequency-integrated absorbed cross section P_E (i.e., the number of photons absorbed per unit incident flux) for our system is given in the form

$$P_E = |T_{i0}|^2. \quad (53)$$

The quantum yield Y is given by

$$Y = P(\infty)/P_E. \quad (54)$$

From Eqs. (51) and (53) we get the general result

$$Y = (n/\xi) \arctg(2\xi) - (n/y\xi^2) \ln(1+y\xi^2). \quad (55)$$

In the statistical limit we expect that $\xi \gg 1$ and one obtains

$$P(\infty) = n\pi |T_{i0}|^2/2\xi = (\pi/2) |T_{i0}|^2 \tau_{NR} \Gamma_i, \quad (56)$$

and the quantum yield is then

$$Y = \tau_{NR} \Gamma_i, \quad (57)$$

where the numerical factor $\pi/2$ has been disregarded.

From the results obtained herein we reach the following conclusions:

(a) The pure radiative component in the decay rate [Eq. (48)] is "diluted" in view of the appearance of the factor Γ_i/n in the role of the effective reciprocal lifetime of each individual molecular eigenstate. This is the consequence of the static mixing of zero-order levels and the redistribution of the oscillator strength within the inhomogeneously broadened band. This level dilution effect in the case of small molecules, i.e., SO_2 , NO_2 , and CS_2 leads to an anomalously long radiative lifetime⁹ in the resonance limit.

²³ I. S. Gradshteyn and I. W. Ryzhik, *Table of Integrals, Series and Products* (Academic Press Inc., New York, 1965), p. 490.

(b) In the statistical limit the beat spectrum disappears. The interference effects between the large number of densely spaced levels are manifested by the appearance of an intramolecular decay process characterized by a nonradiative lifetime τ_{NR} , resulting in the reduction of the quantum yield. A radiationless transition in the statistical limit can be called level crossing^{21,22} in the limit of a large number of quasidegenerate molecular eigenstates, constructed from zero-order states of which only one carries oscillator strength.

(c) The parameter ξ which determines the quantum yield provides us with an additional criterion for the statistical limit. We expect that $Y < 1$ for $\xi > 1$. Using Eq. (48) we obtain

$$\hbar\Gamma_i/n^2 < \rho^{-1} \quad (58)$$

so that we expect that the statistical limit will be encountered when the mean spacing between the molecular eigenstates is appreciably smaller than the radiation width. Note that in the case of the resonance limit the condition for the observation of beats between two states is $\hbar\Gamma \approx \epsilon_L - \epsilon_{L'}$. The physical reasoning behind Eq. (58) is the following: There are now $M(M-1)/2 \sim n^2$ pairs of levels in the system, with the mean separation of ρ^{-1} . The recurrence time in a quantum beat experiment, the period necessary for the system to complete one oscillation, is $\hbar\rho/n^2$. If this period is shorter than the reciprocal radiative time Γ_i , no beat spectrum will be observed, but instead a fast decay process (on the time scale of τ_{NR}) will take place.

(d) In the extreme limit of an infinite density of states, i.e., $\rho \rightarrow \infty$, then $\tau_{NR} \rightarrow 0$ as $\hbar/V^2\rho$ so $dP/dt \rightarrow 0$ and $Y \rightarrow 0$. This situation is of course encountered in the case of fast predissociation.

(e) The quantum yield in the statistical limit [Eq. (57)] reproduces the conventional empirical expression for the fluorescence quantum yields. It is interesting to note that Y contains the conventional undiluted radiative lifetime, as determined from the integrated absorption intensity. In the extreme limit of appreciable line broadening, our result can be expressed in terms of the linewidth 2Δ (equal to n/ρ in our model) which under the present conditions is dominated by the nonradiative decay. The (low) quantum yield can be then expressed in the form $Y \approx \hbar\Gamma_i/2\Delta$. In a typical case like that of the first excited singlet state of azulene $Y \sim 10^{-4}$. This system can be excited by a giant pulsed ruby laser.²⁴

On the other hand in the resonant limit of low ρ , simple manipulations of Eq. (47) lead to the result $Y = 1$, as expected.

(f) It was customary to represent the experimental decay times τ_{ex} , determined by photon counting methods, in terms of the sum of a radiative and nonradiative contribution $1/\tau_{ex} = \Gamma_i + 1/\tau_{NR}$, where Γ_i was obtained again from the integrated absorption coefficient. The observation of the "dilution of the radiative lifetime"

opens some interesting questions concerning the adequacy of this conventional interpretation. Equation (49) suggests that one should write $1/\tau_{ex} = (\Gamma_i/n) + (1/\tau_{NR})$. It should be pointed out however that our present results are approximate (being based on the primitive step function for the line shape) and an exact solution of the problem has to be still carried out.

(g) Specifically because of the "square line shape" approximation, the nonradiative component of the decay arising from intramolecular radiationless transition in the statistical limit was expressed in the form

$$\left[\frac{\sin(t/\tau_{NR})}{(t/\tau_{NR})} \right]^2,$$

rather than be $\exp(-t/\tau_{NR})$. For a more exact treatment, we might have used a more realistic shape, e.g., a Lorentzian. However we have been unable to solve the integral of $f(y, \alpha)$ [Eq. (46a)] in an analytic form. A similar difficulty is encountered in classical optics²⁵ in the solution of Fraunhofer diffraction by a bell-shaped slit. The physical situation is however quite properly reflected by this simplified analysis, as the radiationless decay mode is approximated by a fast-decaying curve characterized by a mean lifetime of the order of τ_{NR} . We shall return later to this point.

VII. DISCUSSION

We shall now review the hidden approximations involved in our treatment. We have treated an isolated molecule in the gas phase. We have assumed that the set of zero-order Born-Oppenheimer states is complete and can be used for the construction of proper molecular eigenstates. We have considered only quasidegenerate zero-order states in the mixing of states. We have also assumed that the ground-state wavefunction is a pure Born-Oppenheimer state. The first assumption, though never proved, is the basis for all studies of molecular dynamics. The second and third assumptions can be justified as the basis of simple perturbation theory arguments. These considerations apply, of course, to the construction of molecular Hamiltonian eigenstates both in the statistical and in the resonance limits.

In considering the excitation and the radiative decay processes of an isolated molecule, we have considered a two-step process, involving excitation followed by a subsequent decay. The salient feature of the two-step process is that a crude approximation for the excitation mechanism is sufficient because of the dominant role of the decay. The delta function approximation for the excitation mechanism deserves some further comments. The two-step mechanism employed by us requires that in the statistical limit the excitation time τ be shorter than the nonradiative decay time, so that

²⁴ A. D. Albrecht (private communication).

²⁵ M. Born and E. Wolf, *Principles of Optics* (Pergamon Press, Inc., New York, 1959).

$\tau \ll \tau_{NR} \cong \hbar \rho / n$. On the other hand the application of Eq. (16) in the derivation of the excitation cross section implies that a coherent excitation of the states takes place provided that $\tau \ll (\omega_L - \omega_{L'})^{-1} \sim \hbar / \Delta \sim \hbar \rho / n$. Hence these two restrictions are self-consistent.

In this context it is important to consider the excitation process by a conventional light source,⁷ where the amplitudes and the phases of the field are subjected to random fluctuations, which are determined by the width $\delta\nu$ of the spectral band.²⁵ In this case the excitation matrix element can be expressed in terms of the autocorrelation function of the field.⁷ The autocorrelation function differs from zero for time intervals shorter than the reciprocal width of the exciting source. In the case when $\delta\nu \gg \Delta$, that is the spectral width of the exciting source exceeds the inhomogeneously broadened linewidth, the field correlation function can be expressed in terms of a delta function and the two-step excitation mechanism is applicable. This result was previously demonstrated⁷ in a simpler case when radiative decay of the excited state was not explicitly considered.

The expression (57) for the quantum yield in the statistical limit ($\xi \gg 1$) might be construed as a paradox insofar as the molecules appear to trap a fraction $1 - Y$ of the photons absorbed. This results from the assumption that only one zero-order Born–Oppenheimer function ϕ_i carries oscillator strength. The proper interpretation of Eq. (55) is actually this: Only a fraction Y of the absorbed photons can be re-emitted by action of the oscillator strength of the zero-order state ϕ_i . In a real system, the fraction $1 - Y$ is emitted on the far longer time scale determined by the small oscillator strength of all the other zero-order Born–Oppenheimer states. Such a situation is indeed encountered in the emission from the vibrationally excited levels of the first excited singlet induced by absorption into the second excited singlet state of naphthalene and anthracene.

Finally we should point out that we have assumed only a single ground state Φ_0 to which the system may return. It is straightforward to extend the analysis to include the vibrationally excited states in the ground-state manifold. These states must be considered ex-

plicitly for any detailed interpretation of spin-allowed internal conversion processes for which “converse” fluorescence is observed, such as inverse predissociation.

The distinction between the resonance and the statistical limits of static intramolecular coupling is of great assistance in describing intramolecular and intermolecular relaxation processes, and interference effects between closely spaced levels. In the resonance limit, exciting a group of states coherently will lead to quantum beat effects between molecular levels, which will provide useful information on molecular eigenstates. In the statistical limit interference effects between a large number of closely spaced levels results in a nonradiative decay process. We have considered the problem from the point of view of the experimentalist, who usually obtains the information about the so-called radiationless transition by monitoring the rate of the radiative decay by a photon counter. The phenomenon of intramolecular radiationless transitions can be considered as an interference effect between a large number of decay channels.

In this context it is interesting to make a final comment concerning a classical analog of the rate equation (45a). The function $f(y, \alpha)$ [Eq. (46a)] which determines the decay in the statistical limit is nothing but a generalization of the classical Fraunhofer diffraction integral²⁵ to the case of diffraction by a nonuniform slit characterized by a varying intensity distribution. It is therefore not surprising that the step function approximation for the line shape used in Sec. VI leads to a functional dependence of the form $(\sin x/x)^2$ which is just analogous to the diffraction pattern from a rectangular aperture. The classical analog to the intramolecular radiationless transition in the statistical limit is a diffraction pattern produced by a Lorentzian slit.

ACKNOWLEDGMENTS

We are grateful to Professor S. A. Rice, Dr. I. McLaughlin, and Mr. D. Chock for helpful discussions. This research was supported by the U.S. Air Force Office of Scientific Research (J. J.) and by the National Science Foundation (R. S. B.).