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Intermediate level structure in highly excited electronic states of large molecules

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In this paper we consider the radiative decay of excited electronic states of a large molecule which correspond to the dense intermediate level spacing situation, encountered for the second excited singlet state of some aromatic hydrocarbons, which is separated from the first excited singlet state by a small (3000 to 4000 cm^{-1}) electronic energy gap. Intramolecular interstate coupling and the interaction with the radiation field were handled by a self-consistent extension of the Wigner–Weisskopf approximation. We were able to derive a general expression for the time and energy resolved decay spectrum of a highly excited state of a large molecule, which yields information concerning the decay pattern, for the fluorescence lifetime(s) and for the corresponding quantum yields, in different spectral regions. Weak and strong coupling limits can be distinguished and defined in terms of the magnitude of the non-adiabatic interstate coupling terms relative to the spacing and the width of the zero states. In the intermediate level spacing in a large molecule, the radiative decay of the excited state should be considered in terms of the decay of a finite set of coupled levels and intramolecular relaxation between these states does not occur in the 'isolated' molecule. Resonance fluorescence is amenable to experimental observation from the second excited singlet state of a large molecule which corresponds to this intermediate case. The weak and strong coupling situations can be experimentally distinguished on the basis of energy resolved lifetime measurements. General criteria have been provided for the observation of quantum interference effects in the radiative decay for different coupling schemes. The present theoretical results provide a proper interpretation of some recent experimental data concerning the radiative decay of the second excited state of some aromatic molecules (3,4-benzpyrene and naphthalene).

1. INTRODUCTION

Recent theoretical work (Robinson & Frosch 1964; Lin & Bersohn 1968; Siebrand 1966, 1967*a*, *b*; Siebrand & Williams 1967; Henry & Kasha 1968; Robinson 1967; Burland & Robinson 1969; Bixon & Jortner 1968; Jortner & Berry 1968) on intramolecular coupling and electronic relaxation in the polyatomic molecules focused attention on the statistical limit and on the small molecule case. The most fashionable model involved a single zero order Born–Oppenheimer state ϕ_s coupled to a manifold $\{\phi_l\}$ which corresponds to a lower electronic configuration (Bixon & Jortner 1968). One common feature of the characteristics of the radiative decay of strongly coupled excited states of small molecules and of the excited states of large molecules, which correspond to the statistical limit, is the absence of interference effects in the radiative decay. The statistical limit is characterized by a smooth exponential decay (Bixon & Jortner 1969*a*; Freed & Jortner 1969; Rhodes

1969), while in the sparse level distribution in diatomic and in triatomic molecules most of the molecular eigenstates are well separated relative to their radiative widths and interference effects will not be exhibited (Bixon & Jortner 1969*b*). Accidental degeneracy of a pair of molecular eigenstates may, of course, be encountered (Franken 1961; Bixon, Jortner & Dothan 1969; Rose & Corovillano 1961; Podgoretskii & Khrustalev 1964).

A potentially interesting physical situation involves the so-called 'dense intermediate case' (Bixon & Jortner 1969*b*), whereupon a small electronic energy gap exists between two electronic states of a large molecule. It was previously noted that the 'coarse graining' procedure disregarding the details of the variation of the interstate coupling terms and the level distribution in the $\{\phi_l\}$ manifold is no longer justified (Jortner 1969). In this intermediate case one has to consider details of the level distribution and the individual coupling terms for the effectively coupled levels in the $\{\phi_l\}$ manifold. The physical situation is closely related to the problem of intermediate structure in nuclear reactions (Feschbach, Kerman & Lemmar 1967). When the density of nuclear excitations is low, fine structure is exhibited in the nuclear scattering process. Several interesting effects may be exhibited in this case.

(*a*) *Intermediate structure in the optical absorption spectrum*

The second excited singlet state of the naphthalene molecule, which is separated by about 3500 cm^{-1} from the origin of the first excited singlet, when studied in a low-temperature mixed crystal exhibits a large number of sharp lines (McClure 1954; Wessel & McClure 1970). This fine structure is sensitive to the nature of the host crystal (which affects the electronic energy gap) and to the isotropic composition of the guest molecule. This complex spectrum exhibits the strongly coupled levels in the $\{\phi_l\}$ manifold which borrow most of the oscillator strength of the ϕ_s state and which are sparse enough to be optically resolved. The resulting complex structure due to the strongly coupled levels bears a close analogy to the complex spectrum revealed by the lower excited singlet states of triatomic molecules which are characterized by strong interstate coupling with a sparse manifold (Bixon & Jortner 1969*b*; Douglas 1967; Douglas & Huber 1965; Redford & Broida 1963).

(*b*) *Features of the radiative decay*

In analogy with the small molecule case we may encounter the phenomenon of lengthening the radiative lifetimes in an excited state of a large molecule provided that the molecular eigenstates will be well separated relative to their radiative widths and provided that the intramolecular coupling is strong. If a pair (or a small number) of such levels are closely spaced, radiative interference effects (quantum beats) will be exhibited.

In the present paper the theory of intramolecular coupling and radiative decay of polyatomic molecules is extended in an attempt to resolve these problems. Since this paper is primarily intended to provide impetus for experimental work on the radiative decay of the second excited singlet state of some large molecules a conscientious attempt is made to employ simple mathematical techniques based on the self consistent extension of the Wigner–Weisskopf procedure (Bixon *et al.* 1969). When radiative level shifts are neglected the resulting equations for the physically observable quantities coincide with the theoretical results based on the more elaborate Green function method (Freed & Jortner 1969).

2. COUPLING AND DECAY IN THE SECOND EXCITED SINGLET STATE

We shall consider the direct physical information which is obtained from monitoring the fluorescence emission resulting from optical excitation into the so called second excited singlet state of an 'isolated' large molecule. The total hamiltonian of the system

$$H = H_{\mathrm{el}} + H_R + H_{\mathrm{int}} = H_{\mathrm{B.O.}} + H_v + H_R + H_{\mathrm{int}} \tag{2.1}$$

consists of the molecular hamiltonian H_{el} (which can be decomposed into the Born–Oppenheimer hamiltonian, $H_{\mathrm{B.O.}}$ and an intermolecular perturbation term H_v), the radiation field hamiltonian H_R, and the radiation matter interaction term H_{int}. The features of the problem of the simultaneous radiative and non-radiative decay of the second excited singlet state of a large molecule can be specified as follows:

(*a*) A zero-order vibronic level, ϕ_s of $H_{\mathrm{B.O.}}$ which corresponds to the S_2 singlet state, is accessible by optical excitation from the lowest vibronic component of the ground electronic state, ϕ_0^0. The zero-order eigenstate of $H_{\mathrm{B.O.}} + H_R$ which will be denoted by $|\phi_s; \mathrm{vac}\rangle$ (where $|\mathrm{vac}\rangle$ corresponds to the 'empty' electromagnetic field) can decay radiatively to ϕ_0^0 and to other totally symmetric vibronic components of the ground state, ϕ_0^w (where $w = 0, 1, \ldots$ refers to a totally symmetric optically active vibration). These final zero-order states of $H_{\mathrm{B.O.}} + H_R$ will be characterized by $|\phi_0^w; \boldsymbol{k}, \boldsymbol{e}\rangle$, where $|\boldsymbol{k}, \boldsymbol{e}\rangle$ represents a single phonon state characterized by energy $E = \hbar|\boldsymbol{k}|$ and polarization $\boldsymbol{e}$. The coupling with the radiative field is given by the matrix elements

$$V_{s,owr} = \langle \phi_s; \mathrm{vac}\, | H_{\mathrm{int}} |\, \phi_0^w; \boldsymbol{k}, \boldsymbol{e} \rangle \tag{2.2}$$

(from now on we shall denote by the index r a photon state $|\boldsymbol{k}, \boldsymbol{e}\rangle$).

(*b*) A manifold of zero-order Born–Oppenheimer vibronic states $\{\phi_l\}$ of the S_1 electronic configuration are coupled to ϕ_s by non-adiabatic interactions, the coupling terms being

$$V_{sl} = \langle \phi_s | H_v |\, \phi_l \rangle \equiv \langle \phi_s; \mathrm{vac}\, | H_v |\, \phi_l; \mathrm{vac} \rangle. \tag{2.3}$$

Effective intramolecular coupling will be manifested only provided that the vibrational part of the ϕ_l vibronic wavefunctions contains a single promoting mode (Lin 1966; Lin & Bersohn 1968), whereupon in general the manifold ϕ_l corresponds to a subset of the vibronic states of the S_1 electronic configuration. This conclusion is based on the following plausible assumptions:

(1) The promoting modes are non-totally symmetric (which is correct in the realistic case when the S_1 and S_2 electronic states correspond to non-degenerate

states of different symmetry). (2) The projections of the molecular potential surface on the promoting coordinates do not suffer any distortions or shifts between the electronic states S_1 and S_2. (3) The harmonic approximation (Freed & Jortner 1970; Jortner 1969) is taken for granted.

(*c*) Any zero-order state in the $\{\phi_l\}$ manifold is radiatively coupled to high vibrational levels ϕ_0^{lw} of the ground electronic state. It is important to notice that in view of the symmetry restrictions on the vibrational part of $\{\phi_l\}$ (which has to contain a promoting mode), each of the final states ϕ_0^{lw} have to be characterized by the same vibrational symmetry as the corresponding ϕ_l excited level (and can then further contain some w totally symmetric optically active modes). The radiative coupling matrix elements are

$$V_{l,olwr} = \langle \phi_l; \mathrm{vac}\, |H_{\mathrm{int}}|\, \phi_0^{lw}; \boldsymbol{k}, \boldsymbol{e}\rangle. \tag{2.4}$$

(*d*) Each of the ϕ_l states is coupled to a manifold of zero order states $\{\phi_T^l\}$ which correspond to some vibronic levels of the lower triplet(s) and possibly to the ground state

$$V_{l,Tl} = \langle \phi_l |H_v|\, \phi_T^l\rangle. \tag{2.5}$$

In a similar manner the ϕ_s state is coupled to the manifold $\{\phi_T^s\}$ via

$$V_{s,Ts} = \langle \phi_s |H_v|\, \phi_T^s\rangle. \tag{2.6}$$

Again, in view of the propensity rules for intramolecular coupling, it is reasonable to expect that each subset $\{\phi_T^l\}$ and the subset $\{\phi_T^s\}$ are different. Finally, we assume that the $\{\phi_T\}$ zero-order states do not carry oscillator strength to the ground state and are inactive in electronic transitions (they may decay in isolated molecules by infrared emission, or by strongly spin forbidden emission from the triplet to the ground state).

Following conventional time dependent perturbation theory the compound state of the decaying system at time t can be represented in the general form

$$\left.\begin{aligned} \psi(t) &= C_s(t)|\phi_s; \mathrm{vac}\rangle + \sum_l C_l(t)|\phi_l; \mathrm{vac}\rangle + \mathscr{L}(t), \\ \text{where}\qquad \mathscr{L}(t) &= \sum_l\sum_T C_{Tl}(t)|\phi_T^l; \mathrm{vac}\rangle + \sum_T C_{Ts}(t)|\phi_T^s; \mathrm{vac}\rangle \\ &\quad + \sum_r\sum_w C_{owr}(t)|\phi_0^w; R\rangle + \sum_r\sum_w\sum_l C_{olwr}|\phi_0^{lw}; R\rangle. \end{aligned}\right\} \tag{2.7}$$

The first two terms in equation (2.7) represent the time evolution of the zero-order vibronic levels corresponding to the second and to the first singlet, the third and fourth terms represent the coupling of those vibronic components to the lower triplet (and to the ground state) while the last two terms correspond to the radiative decay of the ϕ_s state and of the $\{\phi_l\}$ manifold. One should note in passing that we have chosen to work with the Born–Oppenheimer approximation, however, any other complete basis set could have been employed. The solution of (2.7) is, of course, subjected to the initial conditions determined by the nature of the initially 'prepared' state. To bring the problem into a tractable form the following simplifying and physically feasible assumptions are introduced:

(1) The transition moment to the ϕ_s state from the ground electronic state greatly exceeds the corresponding transition moments to the $\{\phi_l\}$ manifold. This assertion

is justified as each state in the $\{\phi_l\}$ manifold is expected to contain a non-totally symmetric vibration, so that those states will not be accessible to optical excitation from the ground state. Furthermore, we shall be interested in molecular systems where the integrated oscillator strength of the second singlet state exceeds that of the lower lying singlet by one to two orders of magnitude.

(2) The radiative damping matrix of the $\{\phi_l\}$ manifold is diagonal in the Born–Oppenheimer basis. The radiative damping matrix for each decay channel $|\phi_0^{lw}; R\rangle$ is defined by (Freed & Jortner 1969; Bixon *et al.* 1969).

$$\Gamma_{ll'}^{lw} = 2\pi\sum_e\int \mathrm{d}\Omega_k\langle\phi_l; \mathrm{vac}\,|H_{\mathrm{int}}|\,\phi_0^{lw}; \boldsymbol{k}, \boldsymbol{e}\rangle\,\langle\phi_0^{lw}; \boldsymbol{k}, \boldsymbol{e}|H_{\mathrm{int}}|\,\phi_{l'}; \mathrm{vac}\rangle\,\rho_k, \tag{2.8}$$

where $\sum_e\int \mathrm{d}\Omega_k$ represents summation over all polarization directions and integration over all spatial directions of the emitted radiation. ρ_k is the density of phonon states. Now, as the close lying levels in the zero-order manifold $\{\phi_l\}$ have different symmetries each of them will decay into its own radiative continuum, which involves a different highly lying vibronic level corresponding to the ground electronic state. We can thus define the partial radiative width of each ϕ_l state for the radiative decay into the ϕ_0^{lw} state

$$\Gamma_{ll'}^{lw} = \Gamma_l^w\,\delta_{ll'}, \tag{2.9}$$

where

$$\Gamma_l^w = 2\pi\sum_e\int \mathrm{d}\Omega_k|V_{l,\,olwr}|^2\rho_k. \tag{2.10}$$

The total radiative width of the ϕ_l state is

$$\Gamma_l = \sum_w \Gamma_l^w. \tag{2.11}$$

The radiative decay of the ϕ_s state to the final states ϕ_0^w does not interfere with the radiative decay of the $\{\phi_l\}$ levels, and we can thus assert that the only non-vanishing matrix elements of the radiative decay matrix for the s state involve the (diagonal) partial widths

$$\Gamma_s^w = 2\pi\sum_e\int \mathrm{d}\Omega_k|V_{s,\,owr}|^2\rho_k, \tag{2.12}$$

while the total radiative width of the s state is

$$\Gamma_s = \sum_w \Gamma_s^w. \tag{2.13}$$

(3) The triplet manifolds $\{\phi_T^l\}$ and $\{\phi_T^s\}$ correspond to the statistical limit and can be considered as dissipative channels. In a manner completely analogous to the radiative decay we can define the non-radiative decay matrices

$$\Delta_{ii'} = 2\pi\langle\phi_i|H_v|\,\phi_T^i\rangle\,\langle\phi_T^i|H_v|\,\phi_{i'}\rangle\,\rho_{Ti}, \tag{2.14}$$

where $i = s$ and $\{l\}$, and ρ_{Ti} is the density of states in the $\{\phi_T^i\}$ manifold.

On the basis of symmetry arguments discussed above we can assert that each of the states ϕ_s and ϕ_l decays into its own quasicontinuum, whereupon the non-radiative decay matrix is diagonal, the diagonal terms being characterized by the non-radiative widths

$$\Delta_l = 2\pi|V_{l,\,Tl}|^2\rho_{Tl}, \tag{2.15}$$

$$\Delta_s = 2\pi|V_{s,\,Ts}|^2\rho_{Ts}. \tag{2.16}$$

The observation that in the B.O. representation 'direct' interference effects are negligible both for radiative and non-radiative decay of the $\{\phi_l\}$ manifold make it possible to extract pertinent physical information from (2.7). This aspect was not clearly realized in previous work leading to some cumbersome equations which can now be recast in a physically transparent form.

The application of the Wigner–Weisskopf approximation (Bixon *et al.* 1969), extended to include the radiative and the non-radiative widths of the $\{l\}$ levels yields the following set of coupled differential equations for the amplitudes $C_i(t)$; $i = s, \{l\}$:

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{bmatrix} C_s(t) \\ C_1(t) \\ C_2(t) \\ \vdots \\ C_n(t) \end{bmatrix}$$

$$= -\mathrm{i}\begin{bmatrix} E_s - \tfrac{1}{2}\mathrm{i}(\Gamma_s + \Delta_s) & V_{s1} & \cdots & V_{sn} \\ V_{1s} & E_1 - \tfrac{1}{2}\mathrm{i}(\Gamma_1 + \Delta_1) & & \mathbf{0} \\ \vdots & \mathbf{0} & \ddots & \\ V_{ns} & \cdots & & E_n - \tfrac{1}{2}\mathrm{i}(\Gamma_n + \Delta_n) \end{bmatrix}\begin{bmatrix} C_s(t) \\ C_1(t) \\ C_2(t) \\ \vdots \\ C_n(t) \end{bmatrix} \qquad (2.17)$$

or in abbreviated form

$$\mathrm{i}\,\mathrm{d}\boldsymbol{C}(t)/\mathrm{d}t = (\boldsymbol{H}_{\mathrm{el}} - \tfrac{1}{2}\mathrm{i}\boldsymbol{\Gamma} - \tfrac{1}{2}\mathrm{i}\boldsymbol{\Delta})\,\boldsymbol{C}(t), \qquad (2.17a)$$

where $\boldsymbol{C}(t)$ is the column vector of the amplitudes, $\boldsymbol{\Gamma}$ is the diagonal radiative damping matrix whose diagonal terms are (2.11) and (2.13) while $\boldsymbol{\Delta}$ corresponds to the diagonal non-radiative damping matrix ((2.15) and (2.16)). The initial conditions (see assumption (1)) are

$$\boldsymbol{C}(0) = \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}. \qquad (2.18)$$

All the physical information concerning the decay of the system is contained in the coefficients $\boldsymbol{C}(t)$. If the details of the zero order level spacings are known, (2.17) can be diagonalized by complex orthogonal (non-unitary) transformation.

$$\boldsymbol{S}(\boldsymbol{H}_{\mathrm{el}} - \tfrac{1}{2}\mathrm{i}\boldsymbol{\Gamma} - \tfrac{1}{2}\mathrm{i}\boldsymbol{\Delta})\,\boldsymbol{S}^{-1} = \boldsymbol{\Lambda}, \qquad (2.19)$$

where $\boldsymbol{\Lambda}$ is the complex eigenvalue matrix, the real and imaginary parts of the eigenvalues correspond to the energy levels and the 'decay times' of these levels. Obviously, as the complex matrix is non-diagonal we cannot assert that each state decays independently. The amplitudes can now be displayed in the general form

$$\boldsymbol{C}(t) = \boldsymbol{S}^{-1}\exp(i\boldsymbol{\Lambda}t)\,\boldsymbol{S}\boldsymbol{C}(0). \qquad (2.20)$$

The decay of the system can be experimentally monitored by following the emitted fluorescence in different spectral regions which can be described in terms of radiative transitions to the final states $|\phi_0^w; \boldsymbol{k}, \boldsymbol{e}\rangle$ and $|\phi_0^{lw}; \boldsymbol{k}, \boldsymbol{e}\rangle$. The emitted radiation is monitored by a photon counting apparatus which is characterized by equal sensitivity over the whole spectral range and which admits all photons in the range $\{\boldsymbol{k}, \boldsymbol{e}\}$ (under real life situation the experimentally measured photon flux has to be corrected for the spectral response of the measuring equipment). The integrated photon counting rate $P^{\{k,e\}}(t)$ is determined by the total probabilities for radiative decay of the state $\psi(t)$ (equation (2.7)) and is given in the form

$$P^{\{k,e\}}(t) = \sum_{\{k,e\}} \sum_{w} |\langle\psi(t)|\, \phi_0^w; \boldsymbol{k}, \boldsymbol{e}\rangle|^2 + \sum_{\{k,e\}} \sum_{l,\,w} |\langle\psi(t)|\, \phi_0^{lw}; \boldsymbol{k}, \boldsymbol{e}\rangle|^2, \tag{2.21}$$

which are related to the partial radiative transition probabilities of the zero order excited states $|\phi_s; \text{vac}\rangle$ and $|\phi_l; \text{vac}\rangle$. The summation $\sum_{\{k,e\}}$ in (2.21) implies restricted summations over the states in the energy range ΔE admitted by the photon counter $|\hbar k + E_{ow} - E_s| \leqslant \Delta E$ and $|\hbar k + E_{lw} - E_l| \leqslant \Delta E$ where $\hbar|k|$ is located in the region $\hbar k \ldots \hbar(k + \Delta k) = E \ldots E + \Delta E$. For the sake of simplicity let us assume that all polarization directions are admitted by the photon counter. Furthermore, let us assume that the spectral resolution of the photon counter is sufficiently poor so that it passes all radiation in an energy range ΔE which is much wider than the radiative and non-radiative widths of the zero-order states, i.e. $\Delta E \geqslant \varGamma_s^w$, $\varGamma_l^{lw}$, $\varDelta_s$, $\varDelta_l$ for all l and w. This assumption enables us to replace the restricted summation over photon energy and the unrestricted summation over final molecular states by a restricted summation over final states accompanied by an unrestricted summation over photon energies. Making use of (2.18) to (2.23) we have

$$|\langle\psi(t)|\, \phi_0^w; \boldsymbol{k}, \boldsymbol{e}\rangle|^2 = |V_{owr,s}|^2 \int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2\, C_s^*(t_1)\, C_s(t_2) \exp\left[\mathrm{i}E_{owr,s}(t_1 - t_2)\right],$$

$$|\langle\psi(t)|\, \phi_0^{lw}; \boldsymbol{k}, \boldsymbol{e}\rangle|^2 = |V_{olwr,l}|^2 \int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2\, C_l^*(t_1)\, C_l(t_2) \exp\left[\mathrm{i}E_{olwr,l}(t_1 - t_2)\right],$$

where $E_{ij} = E_i - E_j$.

Integration over the energy region ΔE followed by summation over all polarization directions results in the following form for the total decay probability $P^{\Delta E}(t)$ in the energy range ΔE

$$P^{\Delta E}(t) = \sum_{w}^{|E_s - E_{ow} - E| \leqslant \Delta E} \varGamma_s^w \int_0^t \mathrm{d}t' |C_s(t')|^2 + \sum_{l} \sum_{lw}^{|E_l - E_{lw} - E| \leqslant \Delta E} \varGamma_l^w \int_0^t \mathrm{d}t' |C_l(t')|^2. \tag{2.23}$$

The sums in (2.23) are taken over the energy region ΔE. The differential counting rate $\mathrm{d}P^{\Delta E}/\mathrm{d}t$ in the energy region ΔE is obviously given by

$$\dot{P}^{\Delta E}(t) = \sum_{w}^{|E_s - E_{ow} - E| \leqslant \Delta E} \varGamma_s^w |C_s(t)|^2 + \sum_{l} \sum_{lw}^{|E_l - E_{lw} - E| \leqslant \Delta E} \varGamma_l^w |C_l(t)|^2. \tag{2.24}$$

Finally, the differential photon counting rate integrated over the whole energy region is given by

$$\dot{P}(t) = \varGamma_s |C_s(t)|^2 + \sum_{l} \varGamma_l |C_l(t)|^2. \tag{2.25}$$

The integrated quantum yield, Y, for total emission is given in the form

$$Y = \int_0^\infty \mathrm{d}t' \, \dot{P}(t') = \Gamma_s \int_0^\infty \mathrm{d}t' |C_s(t')|^2 + \sum_l \Gamma_l \int_0^\infty |C_l(t')|^2 \, \mathrm{d}t'. \tag{2.26}$$

A restricted form of the two last equations (when $\Gamma_l = 0$ for all l) has been previously utilized by Bixon & Jortner (1969*b*). From these results we conclude that:

(*a*) The expressions derived herein for the total decay probability (equation (2.23)) and for the differential counting rate (equation (2.26)) in the energy range ΔE involve a generalization of the line shape formulas (for absorption or emission processes) which were extensively used in solid state physics (Lax 1952; Huang & Rhys 1951; Kubo & Toyozawa 1955), except that we now display the time resolved spectrum.

(*b*) The general expressions for spectral resolved total radiative decay probability and the differential counting rate are determined by two types of terms: (1) The partial radiative widths Γ_s^w and Γ_l^w which are determined by the appropriate Franck–Condon factors and the time-independent energy distribution of the intensity in the radiative decay of the $\{\phi_l\}$ and ϕ_s states. (2) The time-dependent amplitudes squared $|C_s(t)|^2$ and $\{|C_l(t)|^2\}$ which are determined by all the radiative and non-radiative widths Γ_s^w, Γ_l^w, Δ_s^w and Δ_l^w.

(*c*) In general the decay pattern in any spectral region is not purely exponential, as the time-dependent factors in (2.26) may reveal oscillatory behaviour under certain conditions which will be specified later.

(*d*) The spectrally resolved differential counting rate consists of two contributions which can be described (in the particular representation) as due to the radiative decay of ϕ_s and of $\{\phi_l\}$. The physically observable $\dot{P}^{\Delta E}(t)$ contains contributions in the energy regions $|E_s - E_{ow}|$ and $|E_l - E_{lw}|$ (for all l) which in principle can overlap. The relative contributions are determined in each energy range by the appropriate Franck–Condon factors. The radiative decay of the zero order ϕ_s state will occur to the manifold $\phi_0^0, \phi_0^1, \phi_0^2, \ldots$ (see figure 2). Obviously, the highest energy corresponds to $E_s - E_{0,0}$. The states $\{\phi_l\}$ are combined radiatively to the following final states (see figure 2):

(1) $\phi_0^{l\,w=0}$ which corresponds to the same occupation of vibrational modes in the ground state as in the excited states. Each of the energies $E_l - E_{o,lw=0}$ overlaps the 0–0 band of the S_1–S_0 transition.

(2) The manifold $\phi_0^{l\,w=0}$ can be shifted to higher energies by one (or more) totally symmetric vibrational frequencies. These manifolds $\phi_0^{l\,w=1}$, $\phi_0^{l\,w=2}$, etc., will contain the same number of levels as the $\phi_0^{l\,w=0}$ manifold and will combine radiatively with the states $\{\phi_l\}$ contributing to emissions at lower energies than that corresponding to $\phi_0^{l\,w=0}$.

(3) If some of the zero-order levels in the excited $\{\phi_l\}$ manifold contain one (or more) totally symmetric vibrations they can decay to ground-state levels which are located below $\phi_0^{l\,w=0}$. We have thus ground-state manifolds $\phi_0^{l\,w=-1}$, $\phi_0^{l\,w=-2}$, etc. (see figure 2) characterized by a number of levels which is lower than (or at most,

equal to) the number of levels in $\phi_0^{l\,w=0}$, which combine radiatively with $\{\phi_l\}$ and thus contribute to the emission at energies higher than $|E_l - E_{o,lw=0}|$.

(*e*) As all the states in the $\{\phi_l\}$ manifold contain one quantum of a non-totally symmetric promoting mode, we may expect that there will always be an energy gap $\hbar\omega_{\mathrm{p}}$ (where ω_{p} is the frequency of the promoting mode) which separates the contributions to the emission $\phi_s \rightarrow \phi_0^{0w}$ and $\{\phi_l\} \rightarrow \{\phi_0^{lw}\}$. In the energy region

$$\Delta E = |E_s - E_{0,0}| - |E_s - E_{0,0} - \hbar\omega_{\mathrm{p}}|$$

the contribution to the spectrally resolved emission will originate only from the ϕ_s state and will be given by

$$\dot{P}^{\Delta E}(t) = \Gamma_s^{w=0}|C_s(t)|^2$$

at energies lower than $|E_s - E_{0,0} - \hbar\omega_{\mathrm{p}}|$, in principle, the superposition (2.36) will be observed.

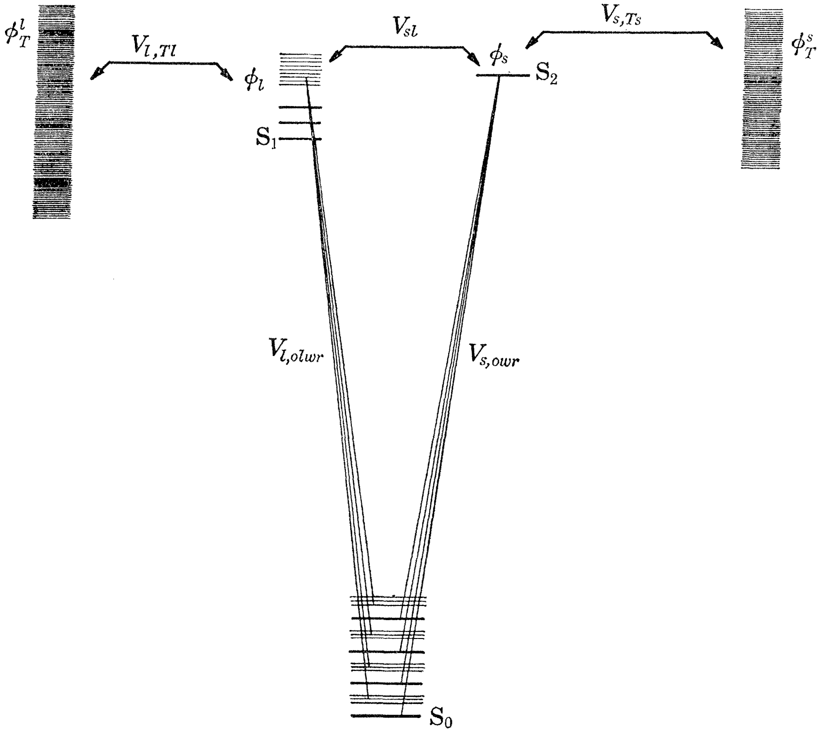

FIGURE 1. Coupling scheme for higher excited states of a large molecule.

(*f*) The emission in the energy range ΔE discussed in (*f*) can be considered as true resonance fluorescence of a large molecule.

(*g*) When the energy gap (Englman & Jortner 1970) between the electronic origins of the two electronic states S_2 and S_1 is large (relative to intramolecular frequencies) there will be negligible overlap between the energy regions $|E_s - E_{o,w}|$ where the Γ_s^w widths are large and the energy range $E_l - E_{o,lw}$ where the Γ_l^w terms are appreciable, whereupon the contributions of the zero-order states ϕ_s and ϕ_l in these energy regions will be experimentally separable. One will then encounter two well separated decay patterns. (This situation will be realized under the circumstances when the manifold ϕ_l is dense (owing to the large energy gap) and acts as a dissipative quasicontinuum.)

The partial radiative widths appearing in (2.10) and (2.12) can be extracted from the analysis of the optical absorption spectrum of the isolated large molecule (the effects of sequence congestion should not worry us, as they just lead to intensity spread). All the pertinent physical information is now contained in the coefficients $C_s(t)$ and $\{|C_l(t)|^2\}$. We shall now focus attention on the case where the manifold $\{\phi_l\}$ is not sufficiently dense so that we cannot consider it to act as a dissipative quasicontinuum for the decay of ϕ_s, however, interstate coupling exists. This situation corresponds to intermediate level structure in a large molecule.

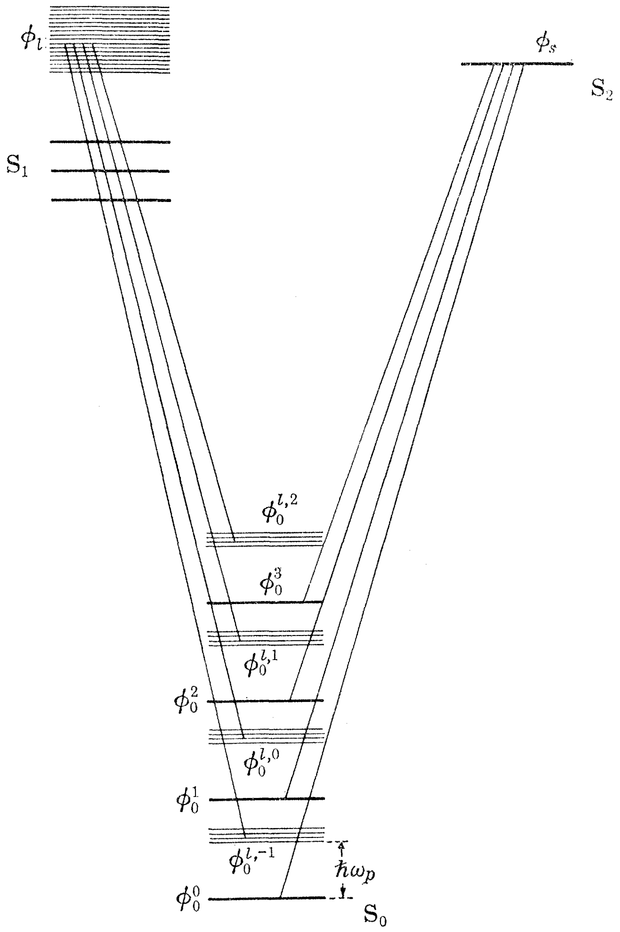

FIGURE 2. A schematic representation of the radiative decay pattern of the second excited singlet state of a large molecule expressed in terms of zero order Born–Oppenheimer states. For notation, see text.

3. THE INTERMEDIATE CASE

On the basis of vibronic coupling theory one can assert that not all the states in the $\{\phi_l\}$ manifold will couple to ϕ_s with the same efficiency. In the intermediate case (see § 1) when the level density in the $\{\phi_l\}$ manifold is relatively low the nature of the levels in the $\{\phi_l\}$ manifold which couple effectively with ϕ_s is of crucial importance. Freed & Jortner (1969) have provided a qualitative discussion of this situation. We shall now represent this small number of effectively coupled levels in the $\{\phi_l\}$ manifold by a single zero-order ϕ_l, and utilize the general treatment of § 2. The decay matrix for this model system can be represented in the form

$$\boldsymbol{A} = \begin{bmatrix} E_s - \tfrac{1}{2}\mathrm{i}\gamma_s & V_{sl} \\ V_{ls} & E_l - \tfrac{1}{2}\mathrm{i}\gamma_l \end{bmatrix} \tag{3.1}$$

where

$$\gamma_s = \Gamma_s + \Delta_s, \tag{3.2}$$

$$\gamma_l = \Gamma_l + \Delta_l, \tag{3.3}$$

corresponding to the sums of the total radiative and non-radiative widths of the two states. It should be noticed that (3.1) represents a generalization of the level anticrossing problem which is now extended to include additional non-radiative decay channels of the two zero-order states. A similar problem has been recently considered by Gamurar, Perlin & Tsukerblat (1969) in the study of energy transfer between impurity states in solids.

The solutions of the eigenvalue equation take the simple form

$$\lambda_{1,2} = -\tfrac{1}{2}\{\Delta E + \tfrac{1}{2}\mathrm{i}(\gamma_s + \gamma_l) \mp \surd([\Delta E + \tfrac{1}{2}\mathrm{i}(\gamma_l - \gamma_s)]^2 + 4|V_{sl}|^2)\}, \tag{3.4}$$

where

$$\Delta E = E_s - E_l. \tag{3.4a}$$

It will be convenient to separate the complex energies (3.4) into their real and imaginary parts:

$$\lambda_{1,2} = \beta_{1,2} - \tfrac{1}{2}\mathrm{i}\gamma_{1,2}. \tag{3.5}$$

Making use of (2.26) and (2.27) and the initial condition (2.25) one gets

$$C_s(t) = -\frac{1}{\lambda_1 - \lambda_2}[(-\lambda_1 - \Delta E - \tfrac{1}{2}\mathrm{i}\gamma_l)\exp(-\mathrm{i}\lambda_1 t) - (-\lambda_2 - \Delta E - \tfrac{1}{2}\mathrm{i}\gamma_l)\exp(-\mathrm{i}\lambda_2 t)], \tag{3.6}$$

$$C_l(t) = \frac{V_{sl}}{\lambda_1 - \lambda_2}[\exp(-\mathrm{i}\lambda_1 t) - \exp(-\mathrm{i}\lambda_2 t)]. \tag{3.7}$$

The general expressions for the two separate contributions to the radiative decay probability (2.37) take the form

$$|C_s(t)|^2 = \{(a^2 + b^2)\,\mathrm{e}^{-\gamma_1 t} + (c^2 + d^2)\mathrm{e}^{-\gamma_2 t} - 2\mathrm{Re}\,[(a + \mathrm{i}b)\,(c - \mathrm{i}d)\exp\{-\tfrac{1}{2}(\gamma_1 + \gamma_2)\,t\} \times \exp\{-\mathrm{i}(\beta_1 - \beta_2)\,t\}]\}\,[(\beta_1 - \beta_2)^2 + \{\tfrac{1}{2}(\gamma_1 - \gamma_2)\}^2]^{-1}, \tag{3.8}$$

$$|C_l(t)|^2 = |V_{ls}|^2\,[\exp(-\gamma_1 t) + \exp(-\gamma_2 t) - 2\exp(-\tfrac{1}{2}(\gamma_1 + \gamma_2)\,t)\cos((\beta_1 - \beta_2)\,t)] \times [(\beta_1 - \beta_2)^2 + \{\tfrac{1}{2}(\gamma_1 - \gamma_2)\}^2]^{-1}, \tag{3.9}$$

where we have defined the following auxiliary quantities:

$$\left.\begin{aligned} a &= -\beta_1-\Delta E, \\ b &= \tfrac{1}{2}(\gamma_1-\gamma_l), \\ c &= -\beta_2-\Delta E, \\ d &= \tfrac{1}{2}(\gamma_2-\gamma_l). \end{aligned}\right\} \tag{3.10}$$

From these general results we conclude that:

(*a*) In view of the initial condition (2.25) the radiative decay of the excited state corresponds to a decay scheme where ϕ_s decays into a radiative and non-radiative continuum and is also coupled to an 'intermediate' level ϕ_l which in turn again decays into different radiative and non-radiative continuum.

(*b*) The relative quantum efficiency for the contribution of the radiative decay of the ϕ_l state is given by a 'perturbation-like' contribution $|V_{sl}|^2/|\lambda_1-\lambda_2|$ and is determined by the coupling strength and by the spacing between the complex eigenvalues of the decay matrix.

(*c*) Interference effects are exhibited in principle in both contributions $|C_s(t)|^2$ and $|C_l(t)|^2$. The conditions for experimental detection of these interference effects in time resolved radiative decay can be formulated as follows:

(1) The 'level spacing' of the states which diagonalize the decay matrix is comparable to the sum of the total (radiative and non-radiative) widths:

$$|\beta_2-\beta_1| \approx \tfrac{1}{2}(\gamma_1+\gamma_2) = \tfrac{1}{2}(\gamma_s+\gamma_l). \tag{3.11}$$

The last equality arising from the applicability of the diagonal sum rule to the (complex) decay matrix.

(2) The relative contributions of the pre-exponential terms of the interference contributions in (3.8) are comparable, i.e.

$$\mathrm{Re}\,(a+\mathrm{i}b)\,(c-\mathrm{i}d) \approx (a^2+b^2),\ (c^2+d^2). \tag{3.12}$$

(3) The oscillation frequency (here $|\beta_1-\beta_2|$) is sufficiently small in comparison with $1/\Delta t$ where Δt is the experimental time resolution of the system.

The results obtained for the simple model system can be considerably simplified for some limiting cases which are pertinent for the understanding of the physical effects expected in the intermediate case.

3.1. *The weak coupling limit*

The off-diagonal elements of the decay matrix (3.1) are smaller than the spacing between the (complex) diagonal elements, so that

$$|V_{sl}| \ll |(E_s-E_l)-\tfrac{1}{2}\mathrm{i}(\gamma_s-\gamma_l)|, \tag{3.13}$$

whereupon ordinary perturbation treatment is applicable. Expanding (3.4) up to the first power in $|V_{sl}|^2/|\Delta E-\frac{1}{2}\mathrm{i}(\gamma_s-\gamma_l)|^2$ leads to the following results in this limit:

$$\beta_1 = \frac{|V_{sl}|^2\,\Delta E}{\Delta E^2+\{\frac{1}{2}(\gamma_l-\gamma_s)\}^2}, \tag{3.14a}$$

$$\beta_2 = -\Delta E-\frac{|V_{sl}|^2\,\Delta E}{\Delta E^2+\{\frac{1}{2}(\gamma_l-\gamma_s)\}^2} \tag{3.14b}$$

(measured from E_s), and

$$\gamma_1 = \gamma_s + \frac{2|V_{sl}|^2\,\tfrac{1}{2}(\gamma_l-\gamma_s)}{\Delta E^2+\{\tfrac{1}{2}(\gamma_l-\gamma_s)\}^2}, \tag{3.15a}$$

$$\gamma_2 = \gamma_l - \frac{2|V_{sl}|^2\,\tfrac{1}{2}(\gamma_l-\gamma_s)}{\Delta E^2+\{\tfrac{1}{2}(\gamma_l-\gamma_s)\}^2}, \tag{3.15b}$$

while the auxiliary functions (3.10) now take the form

$$\left.\begin{aligned} a &= -\frac{|V_{sl}|^2\,\Delta E}{\Delta E^2+(\tfrac{1}{2}(\gamma_l-\gamma_s))^2}-\Delta E,\\ b &= \tfrac{1}{2}(\gamma_s-\gamma_l)-\frac{|V_{sl}|^2\,\tfrac{1}{2}(\gamma_l-\gamma_s)}{\Delta E^2+\{\tfrac{1}{2}(\gamma_l-\gamma_s)\}^2},\\ c &= \frac{|V_{sl}|^2\,\Delta E}{\Delta E^2+\{\tfrac{1}{2}(\gamma_l-\gamma_s)\}^2},\\ d &= -\frac{|V_{sl}|^2\,\tfrac{1}{2}(\gamma_l-\gamma_s)}{\Delta E^2+\{\tfrac{1}{2}(\gamma_l-\gamma_s)\}^2}. \end{aligned}\right\} \tag{3.16}$$

Finally, the contributions to the decay pattern are given by

$$\begin{aligned} |C_s(t)|^2 \approx{}& \exp[-(\gamma_s+(\gamma_l-\gamma_s)\,V)\,t]+V^2\exp[-(\gamma_l-(\gamma_l-\gamma_s)\,V)\,t]\\ &+2V\exp\{-\tfrac{1}{2}(\gamma_l+\gamma_s)\,t\}\cos[(\Delta E+2V\Delta E)\,t], \end{aligned} \tag{3.17a}$$

$$\begin{aligned} |C_l(t)|^2 \approx{}& V\{\exp[-(\gamma_s+(\gamma_l-\gamma_s)\,V)\,t]+\exp[-(\gamma_l-(\gamma_l-\gamma_s)\,V)\,t]\\ &-2\exp\{-\tfrac{1}{2}(\gamma_l+\gamma_s)\,t\}\cos[(\Delta E+2V\Delta E)\,t]\}, \end{aligned} \tag{3.17b}$$

where

$$V = \frac{|V_{ls}|^2}{\Delta E^2+\{\tfrac{1}{2}(\gamma_l-\gamma_s)\}^2}. \tag{3.18}$$

In these last expressions we have omitted some small terms (relative to unity).

From these results we conclude that:

(*a*) In the weak coupling limit the 'lifetimes' γ_1 and γ_2 are not modified appreciably relative to the total widths of the zero states γ_s and γ_l, the correction terms being of the order $V(\gamma_l-\gamma_s)$.

(*b*) In an isolated molecule where the second singlet excited state corresponds to the intermediate weakly coupled situation we expect that $\gamma_s > \gamma_l$ as the radiative contribution to γ_s is larger than to γ_l while the non-radiative widths are comparable whereupon $\gamma_1 \approx \gamma_s(1-V)$ while $\gamma_2 \approx \gamma_l(1-V)+V\gamma_s$ so that the effect of intramolecular coupling results in a slight lengthening of the lifetime γ_1^{-1} and shortening of the lifetime γ_2^{-1} relative to the zero-order lifetimes γ_s^{-1} and γ_l^{-1}, respectively.

(*c*) Lifetimes and decay patterns will differ in different spectral regions.

(*d*) If interference effects will be observable (see (*f*)) they will be manifested in the energy regions where the contribution of the $|C_l(t)|^2$ term is appreciable.

(*e*) The relative contribution of the two terms (3.17) to the time and energy integrated spectral distribution (2.36) will be of the order of $V(\Gamma_l/\gamma_l)/(\Gamma_s/\gamma_s)$. As $V \ll 1$ in this limit we expect, of course, that most of the intensity in emission will be located in the energy region where the partial widths Γ_s^w are large.

(*f*) The necessary condition for observation of interference effects in this limit (for the regions where the contribution of $|C_s(t)|^2$ to (2.37) is small) is determined by

$$\Delta E \approx \tfrac{1}{2}(\gamma_s+\gamma_l). \tag{3.19}$$

It should be noted that the general condition (3.14) for the applicability of the weak coupling limit does not necessarily contradict the restriction (3.19).

(*g*) Consider now the case of a weakly coupled narrow resonances whereupon $\Delta E \gg |\gamma_s-\gamma_l|$ and (3.14) are simultaneously satisfied. In this case $V = |V_{sl}|^2/\Delta E^2$ corresponds to the ordinary first-order perturbation expression. Beats can be observed only provided that $\gamma_s \approx \gamma_l$ as $\gamma_s+\gamma_l$ can then be comparable to ΔE.

(*h*) Consider now the case of a weakly coupled broad resonance so that

$$\Delta E \ll |\gamma_s-\gamma_l|.$$

In this case $V = 4|V_{sl}|^2/(\gamma_s-\gamma_l)^2$. Now (3.19) can be satisfied and quantum beats can be observed provided that there is a spectral energy region where only $|C_l(t)|^2$ provides major contribution to the decay.

(*i*) It is important to notice that the non-radiative decay contributions to γ_s and to γ_l (due to other decay channels) enhance the possibility of the observation of quantum beats. Unfortunately when the broadening becomes excessively large (as is the case for a molecule in a medium) the partial quantum yield for these emission channels becomes very small. Furthermore the two level picture breaks down.

3.2. *The strong coupling limit*

The off diagonal matrix elements of the decay matrix (3.1) considerably exceed the spacing between the (complex) zero-order levels, whereupon

$$|V_{sl}| \gg |E_s-E_l-\tfrac{1}{2}\mathrm{i}(\gamma_s-\gamma_l)|. \tag{3.20}$$

The roots of (3.4) now take the form

$$\lambda_{1,2} = -\tfrac{1}{2}\Delta E-\tfrac{1}{4}\mathrm{i}(\gamma_s+\gamma_l) \pm |V_{sl}|, \tag{3.21}$$

so that $\beta_1 = -\tfrac{1}{2}\Delta E+V_{sl};\quad \beta_2 = -\tfrac{1}{2}\Delta E-V_{sl};\quad \gamma_1 = \gamma_2 = \tfrac{1}{2}(\gamma_s+\gamma_l),$

while the auxiliary functions (3.10) take the form

$$a = -\tfrac{1}{2}\Delta E-|V_{sl}| \approx -|V_{sl}|;\quad C = -\tfrac{1}{2}\Delta E+|V_{sl}| \approx |V_{sl}|;$$
$$b = d = \tfrac{1}{2}(\gamma_s-\gamma_l) \ll V_{sl}.$$

The contributions to the decay pattern can be recasted to the first order in the form

$$|C_s(t)|^2 = \tfrac{1}{2}[\exp\{-\tfrac{1}{2}(\gamma_s+\gamma_l)\,t\}+\exp\{-\tfrac{1}{2}(\gamma_s+\gamma_l)\,t\}\cos(2V_{sl}t)], \tag{3.22}$$
$$|C_l(t)|^2 = \tfrac{1}{2}[\exp\{-\tfrac{1}{2}(\gamma_s+\gamma_l)\,t\}-\exp\{-\tfrac{1}{2}(\gamma_s+\gamma_l)\,t\}\cos(2V_{sl}t)]. \tag{3.23}$$

From these results we conclude that for a strongly coupled two-level system:

(*a*) In the strong coupling limit we cannot assign unique parentage to the states which diagonalize the decay matrix, as corresponding to either 'perturbed' ϕ_s and ϕ_l zero-order levels, as these states are extensively scrambled.

(*b*) The direct decay times γ_1 and γ_2 are equal, and the sum of the total widths of the zero-order states is partitioned between the states which diagonalize the decay matrix.

(*c*) When the major contribution to γ_1 and γ_2 arises from radiative decay, then for the second excited singlet state of a large molecule it is safe to assert that $\Gamma_s > \Gamma_l$, whereupon the direct decay terms γ_1 and γ_2 will both be smaller than Γ_s. Under these circumstances, the time resolved radiative decay envelope (which may include beats) will be characterized by a lifetime which is *longer* than what might be expected on the basis of the integrated oscillator strength of the second singlet state. This behaviour is reminiscent of the radiative decay of triatomic molecules, and provides an analogue of the Douglas effect (Douglas 1967; Heicken 1963; Greenough & Duncan 1964) in a large molecule which corresponds to the intermediate case.

(*d*) The time resolved radiative decay spectrum (2.36) will be characterized by similar direct decay times in both energy regions where either the $|C_s(t)|^2$ term or the $|C_l(t)|^2$ term provides a major contribution to the radiative decay.

(*e*) The relative intensities arising from the two contributions to the time and energy integrated spectral distribution (2.37) are now of the order of Γ_l/Γ_s.

(*f*) The splitting of the levels which diagonalize the decay matrix is $2V_{sl}$ so that the magnitude of the strength of the perturbation relative to the total widths $\gamma_1 = \gamma_2$ determines whether interference effects will be exhibited in the decay spectrum. The condition for the observation of a beat spectrum is now

$$2V_{sl} \approx \tfrac{1}{2}(\gamma_s + \gamma_l). \tag{3.24}$$

This situation can be realized only provided that the zero-order levels are nearly degenerate (i.e. $\Delta E \approx 0$) and characterized by about equal total widths (i.e. $\gamma_s \sim \gamma_l$) which in turn exceed the coupling strength, so that (3.24) is satisfied.

4. GENERAL COMMENTS ON THE DENSE INTERMEDIATE CASE

Up to this point we have been concerned with a simple exactly soluble two-level model system. In real life we expect that in the second excited state of a large molecule there is a number of levels in the $\{\phi_l\}$ manifold which are effectively coupled to ϕ_s. An exact solution of the general problem (2.7*a*) cannot be provided in view of our ignorance of the details of the level distribution and their widths, however, we can now be guided by the results of the foregoing treatment to get some insight into the nature of the physical situation which prevails in the intermediate case. Let the $n+1$ zero order Born–Oppenheimer levels be characterized by the energies $E_s, \{E_2, E_3, \ldots, E_{n+1}\}$ and by the total widths $\gamma_s, \{\gamma_2, \gamma_3, \ldots, \gamma_{n+4}\}$. The resulting $n+1$ complex eigenvalues $\lambda^k = \beta^k - \tfrac{1}{2}\mathrm{i}\gamma^k$ of the decay matrix obey the following rules:

(*a*) The diagonal sum rule is obeyed for both the real and imaginary parts of the eigenvalues:

$$\sum_{k=1}^{n+1} \beta^k = E_s + \sum_{l=2}^{n+1} E_l, \tag{4.1}$$

$$\gamma_t = \sum_{k=1}^{n+1} \gamma^k = \gamma_s + \sum_{l=2}^{n+1} \gamma_l. \tag{4.2}$$

(*b*) The quantum mechanical separation theorem is expected to hold for the real part of each eigenvalue of the decay matrix, whereupon each new eigenvalue β^k, is located between a pair of zero-order (real) energies of the Born–Oppenheimer states.

(*c*) Interference contributions to the radiative decay may be amenable to experimental observation provided that of any pair of 'new' states, say i and j

$$|\beta^i-\beta^j| \approx \tfrac{1}{2}(\gamma^i-\gamma^j). \tag{4.3}$$

We shall now consider separately the weak and strong coupling situation.

The weak coupling limit can be easily defined by the relations $|V_{sl}| \ll |E_s-E_l|$, $|\gamma_s-\gamma_l|$; for all l. In this situation the 'new' energy levels β^k and their widths γ^k are only slightly modified relative to the corresponding zero-order levels. One can thus assign a definite parentage to each of the 'new' levels. Application of conventional perturbation theory to the diagonalization problem (2.26) leads to the following results for the eigenvalues to second order:

$$\lambda^1 = X_s+\sum_l \frac{|V_{sl}|^2}{X_s-X_l}, \tag{4.4a}$$

$$\lambda^j = X_l+\frac{|V_{sl}|^2}{X_l-X_s} \quad (j=l=2,3,\ldots,n+1); \tag{4.4b}$$

where

$$X_i = E_i-\tfrac{1}{2}\mathrm{i}\gamma_i \quad (i = s \text{ and } l).$$

Thus, for example for the modified s state we get

$$\beta^1 = E_s+\sum_l \frac{|V_{sl}|^2(E_s-E_l)}{(E_s-E_l)^2+\{\tfrac{1}{2}(\gamma_s-\gamma_l)\}^2} \tag{4.5a}$$

and

$$\gamma^1 = \gamma_s+\sum_l \frac{|V_{sl}|^2(\gamma_l-\gamma_s)}{(E_s-E_l)^2+\{\tfrac{1}{2}(\gamma_s-\gamma_l)\}^2}. \tag{4.5b}$$

Suffering just a slight shift and slight decrease of the direct decay time of this state relative to the zero-order state. The energies and widths of the states originating from $\{\phi_l\}$ will be modified in a similar manner, so that $\beta^k \approx E_k$ and $\gamma^k \approx \gamma_k$ for the n states of $\{\phi_l\}$ parentage.

The S matrix of (2.26) is, to the first order

$$\mathbf{S} = \begin{pmatrix} 1 & \dfrac{V_{s1}}{X_1-X_s} & \cdots & \dfrac{V_{sn}}{X_n-X_s} \\ \dfrac{V_{1s}}{X_s-X_1} & 1 & & 0 \\ \vdots & & \ddots & \\ \dfrac{V_{ns}}{X_s-X_n} & 0 & & 1 \end{pmatrix} \tag{4.6}$$

so that we can evaluate $C_s(t)$ and $C_l(t)$ in a straightforward manner.

The contribution to the time-resolved decay from the $|C_s(t)|^2$ term will be roughly of the form

$$\Gamma_s|C_s(t)|^2 \approx \Gamma_s\left(\mathrm{e}^{-\gamma^1 t}+\sum_l \frac{|V_{sl}|^2\,\mathrm{e}^{-\gamma^l t}}{(E_s-E_l)^2+\{\tfrac{1}{2}(\gamma_s-\gamma_l)\}^2}+\text{interference terms}\right),$$

so that in the spectral region where this contribution dominates, the decay time will be non-exponential and a major contribution will be characterized by the short decay time $(\gamma^1)^{-1}$. On the other hand, in the spectral region where the contribution from the radiative decay of the $\{\phi_l\}$ states dominates one expects the time-resolved decay patterns to be

$$\sum_l \Gamma_l |C_l(t)|^2 \approx \sum_l \left[\frac{|V_{sl}|^2 \Gamma_l}{(E_s-E_l)^2+\{\frac{1}{2}(\gamma_s-\gamma_l)\}^2}(\mathrm{e}^{-\gamma^1 t}+\mathrm{e}^{-\gamma^l t})+\text{interference terms}\right],$$

so that again non-exponential decay may be expected in this energy region. The relative contributions of the $\{|C_l(t)|^2\}$ and of the $|C_s(t)|^2$ terms to the total energy and times integrated emission spectrum is of the form

$$\sum_l (\Gamma_l/\Gamma_s) \times |V_{sl}|^2/[(E_s-E_l)^2+\{\tfrac{1}{2}(\gamma_s-\gamma_l)\}^2]$$

and is expected to be relatively small. Finally interference effects will be exhibited provided that for a pair (or small number) of levels $|E_i-E_j| \sim \frac{1}{2}(\gamma_i+\gamma_j)$.

Focusing our attention now on the strong coupling limit within a manifold of $n+1$ 'strongly coupled' levels, one should notice that some care has to be exercised in specifying the strong coupling situation for a multilevel system. The naïve extension of the level situation will be to assume that $|V_{sl}| \gg |E_s-E_l|$, $|\gamma_s-\gamma_l|$; for each l. In this case it can be easily demonstrated that the $(n+1)$ eigenvalues of the damping matrix (2.26) have the following features: $n-1$ levels will each be characterized by the widths γ_l as the original $\{\phi_l\}$ zero-order states, while two states will be characterized by equal widths of $\frac{1}{2}(\gamma_s+\gamma_l)$. Obviously this straightforward extension of the definition of strong coupling for a two-level system is inadequate to handle the strongly coupled multilevel situation, as in a real molecular system some of the levels in the sparse $\{\phi_l\}$ manifold which are nearly degenerate to ϕ_s are strongly coupled to it, while other ϕ_l levels simultaneously exhibit intermediate or weak coupling relative to their separation from the ϕ_s level. Thus a physically realistic model for the 'strongly coupled' multilevel system involves the assumption

$$|V_{sl}| \gg |E_l-E_{l'}|, \tag{4.7}$$

where ϕ_l and $\phi_{l'}$ are two adjacent levels in the l manifold. This problem is completely analogous to the strong interstate coupling in a triatomic molecule previously considered (Bixon & Jortner 1969*b*; Freed & Jortner 1969). In the strong coupling situation the $n+1$ levels are strongly scrambled whereupon we cannot assign a definite parentage (in terms of the zero-order states ϕ_s and $\{\phi_l\}$) to the states which diagonalize the decay matrix. In this case it will be useful to employ the molecular eigenstates (Bixon & Jortner 1968) zero-order basis set $\{\psi_i\}$ $(i = 1 \dots n+1)$, defined by the unitary transformation

$$\psi_i = a_i^s \phi_s + \sum_l b_i^l \phi_l, \tag{4.8}$$

each state ψ_i is characterized by the energy ϵ_i. The time evolution of the compound state (2.7) can be now displayed in the alternative form

$$\psi(t) = \sum_i d_i(t)\, \psi_i(t) + \mathscr{L}(t). \tag{4.9}$$

Invoking again the Wigner–Weisskopf approximation, the vector $\boldsymbol{d}$ of the coefficients $\{d_i\}$ obeys the relation

$$\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}d(t) = \begin{pmatrix} \epsilon_1 - \frac{1}{2}\mathrm{i}g_1 & -\frac{1}{2}\mathrm{i}g_{1,2} & \cdots \\ -\frac{1}{2}\mathrm{i}g_{2,1} & \epsilon_2 - \frac{1}{2}\mathrm{i}g_2 & \\ \vdots & & \ddots \end{pmatrix} d(t), \tag{4.10}$$

with the initial conditions $d_i(0) \propto a_i^s$.

The non-diagonal g matrix of the widths of the states (4.8) can now be expressed in terms of the widths γ_s and γ_l in the form

$$\begin{aligned} g_i &= |a_s^i|^2\gamma_s + \sum_l |b_l^i|^2\gamma_l \\ &\approx |a_s^i|^2\gamma_s + \langle\gamma_l\rangle(1-|a_s^i|^2), \end{aligned} \tag{4.11}$$

$$g_{i,j} = a_s^{i*}a_s^j\gamma_s + \sum_l b_l^{i*}b_l^j\gamma_l \approx |a_s^i|^2\gamma_s, \tag{4.12}$$

where $\langle\gamma_l\rangle$ is a mean decay width of a state in the $\{\phi_l\}$ manifold. Now it was demonstrated by Bixon & Jortner (1969*b*) that condition (4.7) implies that $|a_s^i|^2 = 1/n$, where the number of strongly coupled levels is $n \approx \pi\langle v\rangle^2/\langle\epsilon\rangle^2$, $\langle v\rangle$ being the mean coupling term and $\langle\epsilon\rangle$ the mean spacing of levels in the $\{\phi_l\}$ manifold. One can then expect that the diagonal matrix elements (4.11) will all be roughly comparable, being of the order

$$g_i \approx \frac{\gamma_t}{n} = \frac{\gamma_s}{n} + \langle\gamma_l\rangle. \tag{4.13}$$

Now, provided that the spacing between adjacent (complex) energy levels in the $\{\psi_i\}$ manifold exceeds the off diagonal matrix elements $g_{i,j}$, i.e.

$$g_{i,j} \ll |(\epsilon_i - \epsilon_j) + i(g_i - g_j)|,$$

the reciprocal lifetimes of the decaying states will be approximately

$$\gamma^k = g_k = \frac{\gamma_s}{n} + \langle\gamma_l\rangle \tag{4.14}$$

for all k. Obviously, variations of the order 2–4 might be expected for different γ^k values, depending on the fine details of the coupling terms and level spacing.

In order to gain some further semiquantitative understanding of the emission spectrum it will be useful to reconsider the representation in terms of zero order Born–Oppenheimer states. This can be easily accomplished provided that (4.14) holds. The general relations (2.7) and (4.9) then imply

$$\left.\begin{aligned} C_s(t) &= \sum_i |a_s^i|^2 \exp(-\mathrm{i}\epsilon_i t - \tfrac{1}{2}g_i t), \\ C_l(t) &= \sum_i a_s^{i*}b_l^i \exp(-\mathrm{i}\epsilon_i t - \tfrac{1}{2}g_i t). \end{aligned}\right\} \tag{4.15}$$

The contributions of the $|C_s(t)|^2$ term and *each* of the $|C_l(t)|^2$ terms to the time resolved decay will now involve identical time dependence and will be just scaled by the corresponding radiative widths of the zero-order states, whereupon

$$\Gamma_s|C_s(t)|^2 \approx (\Gamma_s/n)(\mathrm{e}^{-\gamma^k t} + \ldots) \quad \text{and} \quad \Gamma_l|C_l(t)|^2 = (\Gamma_l/n)(\mathrm{e}^{-\gamma^k t} + \ldots).$$

The short decay time of the zero-order state ϕ_s now 'diluted' between $n+1$ levels. The decay times in the two different spectral regions which are dominated by the contribution of the terms $\Gamma_s|C_s(t)|^2$ or $\Gamma_l|C_l(t)|^2$ are now expected to be comparable. The relative contribution to the time and energy integrated emission spectrum in the two energy regions will be roughly of the form

$$R = \sum_l \Gamma_l/\Gamma_s \approx n\langle\Gamma_l\rangle/\Gamma_s.$$

The situation is more complicated when some of the off diagonal g_{ij} terms in (4.10) are comparable to the level spacing $|\epsilon_i - \epsilon_j|$ and then interference effects will be exhibited in the radiative decay. In view of the applicability of the separability theorem we can assess that in the strong coupling limit the condition for the observation of quantum beats is

$$\tfrac{1}{2}(\gamma^i + \gamma^j) \approx \tfrac{1}{2}(g_i + g_j) \approx |\epsilon_i - \epsilon_j|$$

for any pair i and j.

5. DISCUSSION

In this paper we have been concerned with the radiative decay of an excited electronic state of an 'isolated' large molecule which corresponds to the dense intermediate case. From the experimentalist's point of view, the relevant physical systems which will exhibit the behaviour characteristic of the intermediate case in large molecules, will involve the second excited singlet states of some aromatic hydrocarbons, where the electronic energy gap between the first and the second excited singlet states is small, such as the naphthalene molecule and the acene aromatic series where the spacing between the electronic origins of the S_1, $\propto$ type and the S_2, p type, states is 3000 to 4000 cm^{-1}. Other physically interesting states in this category involve the lowest excited singlet states of some ketones such as benzophenone (Rentzepis 1970) or biacetyl (Drent & Kommandeur 1971) which are separated by 2000 to 3000 cm^{-1} from the lowest excited triplet state. The latter case is somewhat simpler as we can set $\Gamma_l = 0$.

We have been able to derive a number of theoretical results which can be directly applied to characterize the experimental features of the radiative decay of the second excited singlet state of a large molecule which corresponds to the interesting intermediate case. In order to cover all the pertinent experimental situations we have also provided elsewhere (Nitzan, Jortner & Rentzepis 1972) a solution for the less interesting statistical limit in inter-system crossing. The general expressions derived herein for the time and frequency resolved decay spectrum of a large molecule yield direct information concerning the decay pattern in different spectral regions, in particular we are able to state whether the decay is purely exponential, a superposition of exponentials, and under what circumstances the radiative decay will exhibit quantum beats. As the absorption spectrum in the intermediate case can be adequately specified and characterized in terms of zero order Born–Oppenheimer states, it is extremely useful to define two separate spectral regions of the radiative decay spectrum: the *s* region characterized solely by the contribution of

TABLE 1. FEATURES OF RADIATIVE DECAY OF THE SECO

physical situation	features of decay in s region	lifetime(s) in s region	features of decay in l region	lifetime(s) i l region
intermediate weak coupling $V_{sl} \ll \lvert E_s - E_l \rvert$ $V_{sl} \ll \lvert \gamma_s - \gamma_l \rvert$	non-exponential $\exp\{-\gamma_s t\} + n\langle V_l\rangle \times \exp\{-\langle\gamma_l\rangle t\}$	γ_s^{-1} (major contribution) $\langle\gamma_l\rangle^{-1}$ (minor contribution)	non-exponential $\exp\{-\gamma_s t\} + \exp\{-\langle\gamma_l\rangle t\}$	γ_s^{-1} $\langle\gamma_l\rangle^{-1}$
intermediate strong coupling $V_{sl} \gg \lvert E_l - E_{l+1} \rvert$	roughly exponential $\exp\{-(\gamma_s/n + \langle\gamma_l\rangle)\, t\}$	$\left(\dfrac{\gamma_s}{n} + \langle\gamma_l\rangle\right)^{-1}$	roughly exponential $\exp\{-(\gamma_s/n + \langle\gamma_l\rangle)\, t\}$	$\left(\dfrac{\gamma_s}{n} + \langle\gamma_l\rangle\right)$
statistical limit $\sum\limits_l \to \int \rho_l \mathrm{d}E_l$	pure exponential $\exp\{-(\gamma_s + \Delta_{sl})\, t\}$	$(\gamma_s + \Delta_{sl})^{-1}$	consecutive $\exp\{-\langle\gamma_l\rangle t\} - \exp\{-(\gamma_s + \Delta_{sl})\, t\}$	long times $\langle\gamma_l\rangle$

Definitions: $\gamma_l = \Gamma_l + \Delta_l \quad V_l = \dfrac{|V_{sl}|^2}{(E_s - E_l)^2 + (\gamma_s - \gamma_l)^2} \ll 1$ in weak coupling

$\gamma_s = \Gamma_s + \Delta_s \quad \langle\ \rangle$ average value over l manifold

the $\Gamma_s|C_s(t)|^2$ term (see (3.36)) and the l region where the $\Gamma_l|C_l(t)|^2$ terms dominate. The decay patterns and the decay lifetimes can be different in these two regions. Finally, important complementary information can be extracted from the relative quantum yields in these two spectral regions. The main results of the present theoretical study are summarized in table 1. The experimental implications of these results can be summarized as follows:

(*a*) In the intermediate situation intramolecular non-radiative electronic relaxation does not occur between the coupled ϕ_s level and the $\{\phi_l\}$ manifold in the isolated molecule. The radiative decay of the second excited singlet state of a large molecule which is close to the first excited singlet should be considered in terms of a decay of a finite set of coupled levels.

(*b*) Resonance fluorescence is amenable to experimental observation in the radiative decay of the second excited singlet state of a large molecule which corresponds to the intermediate case. The resonance fluorescence is expected to be exhibited in the s spectral region. Both in the weak and in the strong coupling limits which correspond to the intermediate case, the relative resonance fluorescence yield in the s region is proportional to the reciprocal of the number, n, of effectively coupled levels. On the other hand, in the statistical limit, the relative quantum yield for emission in the s region is expected to be negligibly small.

(*c*) The weak and strong intermediate coupling cases can be experimentally distinguished on the basis of energy resolved lifetime measurements in the s and l spectral regions, and by comparing these experimental decay times with the 'pure'

CITED SINGLET STATE OF LARGE MOLECULES

uantum yield in s region	quantum yield in l region	relative quantum yields in l and s region $R = Y_l/Y_s$	possibility of observing quantum beats
$\approx \dfrac{\Gamma_s}{\gamma_s}$	$Y_l \approx n\langle V_l\rangle \left(\dfrac{1}{\gamma_s}+\dfrac{1}{\gamma_l}\right)$	$R = \dfrac{n\langle V_l\rangle\langle \Gamma_l\rangle}{\Gamma_s}$	in l region
$\approx \dfrac{\Gamma_s}{n(\gamma_s/n+\langle\gamma_l\rangle)}$	$Y_l = \dfrac{\langle\Gamma_l\rangle}{\gamma_s/n+\langle\gamma_l\rangle}$	$R = \dfrac{n\langle\Gamma_l\rangle}{\Gamma_s}$	both in s and l regions
$= \dfrac{\Gamma_s}{\Gamma_s+\Delta_{sl}}$	$Y_l = \dfrac{\Gamma_s\Delta_{sl}}{(\gamma_s+\Delta_{sl})\langle\gamma_l\rangle}$	$R = \dfrac{\Gamma_l\Delta_{sl}}{\Gamma_s\langle\gamma_l\rangle}$	none

radiative widths Γ_s (for the S_2 state) and Γ_l (for the S_1 state) obtained from the integrated oscillator strength. In the weak coupling limit the decay time in the S region is expected to be close to γ_s^{-1}, being shorter than the pure radiative lifetime Γ_s^{-1}. On the other hand, in the strong coupling situation the experimental decay time $(\gamma_s/n + \langle\gamma_l\rangle)^{-1}$ in the s region is appreciably lengthened relative to the reciprocal radiative width γ_s^{-1} of the S_2 state. Complementary information can be obtained from the decay pattern in the l region which is non-exponential, containing equal contributions from a short lifetime component γ_s^{-1} and a long lifetime component $\langle\gamma_l\rangle^{-1}$.

(*d*) Complementary information concerning the assignment of an intermediate level spacing in a large molecule to the strong or to the weak coupling situation can be obtained from quantum yield data. In the intermediate weak coupling limit the quantum yield for emission in the s region should exceed the quantum yield in the l region, (as $\langle V_l\rangle \ll 1$, see table 1). On the other hand, for the strong coupling situation we may expect that $R = Y_l/Y_s \geqslant 1$.

(*e*) On the basis of general physical arguments we may expect that in real life the radiative decay of the second excited singlet state of a large molecule which corresponds to the intermediate case will reveal the features of the strong coupling situation. As the S_2–S_1 electronic energy gap is small the interstate coupling matrix elements are large, in view of large Franck–Condon factors between the vibronic states. We may thus expect that a small number of vibronic levels in the S_1 vibronic manifold will then be strongly coupled. Obviously, a larger number of other vibronic states in the S_1 manifold will be simultaneously weakly coupled to S_2, so that both the strong and the weak coupling situation may prevail within the same molecule, however, in the intermediate case the effects of strong coupling will be much more dramatic. We may thus conclude that the intermediate level structure in a large molecule corresponds to the small molecule limit (Bixon & Jortner 1969*b*; Douglas 1967) occurring within a large molecule.

(*f*) The number n of effectively strongly coupled levels to the second excited singlet state of a large molecule which is lying closely to the first singlet can be obtained from the quantum yield ratio $R = n\langle \Gamma_l \rangle / \Gamma_s$ (see table 1).

(*g*) Interference effects in the radiative decay of the second excited state which corresponds to the intermediate strong coupling case will be exhibited provided that the widths of two or more states which diagonalize the decay matrix (2.26) (in the Born–Oppenheimer representation) or (4.10) (in the molecular eigenstates basis), exceed their spacing. It should be noted that as the total number, n, of 'strongly coupled' zero-order states in the $\{\phi_l\}$ manifold is quite large and may be of the order of $n \approx 10$ to 100 (as is the case in some triatomic molecules). Very accurate experimental data will be required to detect the interference effects between a small number of levels corresponding to some of the $n+1$ states which diagonalize the decay matrix. It is still an open question whether this interesting effect will be amenable to experimental observation. Finally, it should be stressed that one should be very careful in distinguishing between 'model dependent' and 'physically observable' interference effects. Obviously, the choice of zero-order basis set for the description of the decaying state is arbitrary and is just a matter of convenience. On the basis of physical arguments we have asserted that the radiative and nonradiative decay of each of the zero order Born–Oppenheimer states in the $\{\phi_l\}$ manifold are independent. A different choice of the basis set (say the molecular eigenstates basis) yields off diagonal damping terms. However, these are just intellectual exercises providing a pictorial description of the zero-order basis, while in real life the only relevant situation involves the spacing and widths of the eigenstates of the decay matrix, and the initial conditions specifying the preparation of the decaying state.

How can these theoretical conclusions be reconciled with the available experimental data? In this context, it will be very useful to obtain experimental studies of the energy resolved decay times and energy distribution originating from fluorescence excitation into the second excited singlet state of a large molecule corresponding to the intermediate case. Recently, Geldof, Rettschnick & Hoytink (1969) have reported 'anomalous' fluorescence from the second excited singlet state of pyrene and 3,4-benzpyrene in the low-pressure gas phase, both of these molecules being characterized by a small S_2–S_1 energy gap and are thus expected to correspond to the intermediate case. Very recently, Wannier, Rentzepis & Jortner (1971) monitored the fluorescence of 3,4-benzpyrene in the low-pressure gas phase excited into the second excited singlet state by the second harmonic of a ruby mode locked laser (at 28 800 cm^{-1}). The spectral distribution obtained (figure 3) is consistent with the original results of Geldof *et al.* (1969). For 3,4-benzpyrene the experimental ratio of the fluorescence yield in the l and s regions is $R \simeq 10$, whereupon making use of the theoretical strong coupling relation $R = n\langle \Gamma_l \rangle / \Gamma_s$ and taking $\langle \Gamma_l \rangle / \Gamma_s = 0.1$

from the ratio of the oscillator strength of the α and p bands we get $n \simeq 100$ for the number of strongly coupled levels. The energy resolved decay lifetimes of 3,4-benzpyrene in the *s* and *l* regions (figure 3) vary very mildly from the *s* region (360 to 380 nm) to the *l* region (> 385 nm). In particular it should be noted that the radiative lifetime in the *s* region which corresponds to 'resonance fluorescence' from the second excited singlet state is appreciably longer (by about a numerical factor of about 5) than expected on the basis of the integrated oscillator strength.

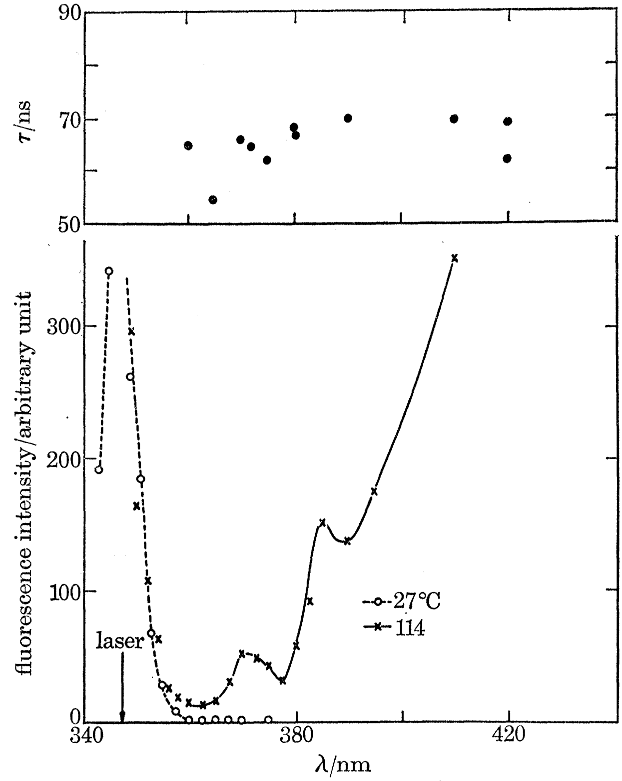

FIGURE 3. Energy and time resolved decay spectrum of 3,4-benzpyrene in the low-pressure gas phase ($p \simeq 0.1$ Torr (10 Pa)) excited by the second harmonic of the ruby laser. The room temperature (27 °C) curve provides a measurement of the scattered light.

These experimental results are in complete agreement with the theoretical predictions for the strong coupling situation.

Another interesting system in this category involves the second excited singlet state of the naphthalene molecule. Watts & Strickler (1966) have reported the absence of resonance fluorescence from the second excited singlet state of the naphthalene molecule in the low-pressure gas phase monitored by conventional methods. Recently Wannier *et al.* (1971) have demonstrated that when the naphthalene molecule is excited to the second excited singlet state by the fourth harmonic of the neodymium laser ($\lambda = 264.5$ nm) weak fluorescence is observed in the spectral region 270 to 300 nm (see figure 4). In this case the ratio of the fluorescence yields in the l and s region is $R \simeq 30$ while the decay times again are practically identical in the s and in the l regions (see figure 4). This situation corresponds to simultaneous contributions of strong coupling with a small number of levels ($n \simeq 10$–100) and weak coupling with a large number of levels, however, the effects of strong coupling seems again to dominate the decay patterns of the second excited singlet state of

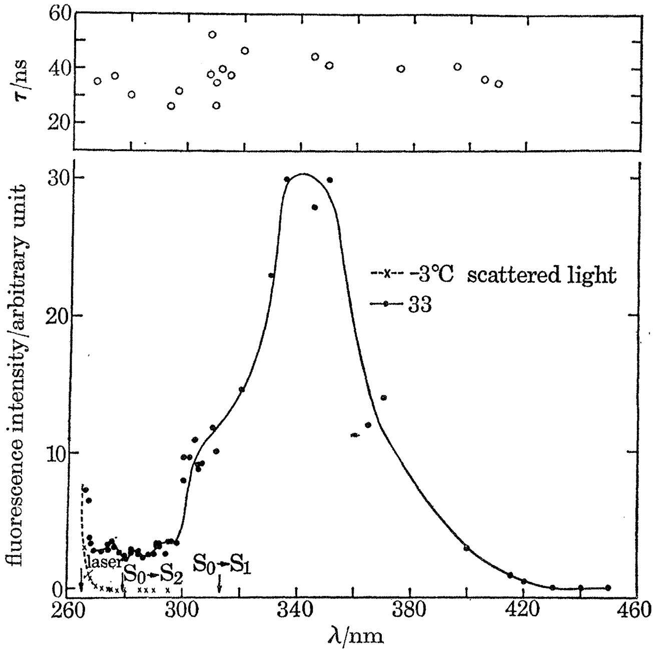

FIGURE 4. Energy and time resolved decay spectrum of naphthalene in the low-pressure gas phase ($p \simeq$ Torr (20 Pa)) excited by the fourth harmonic of Nd^{3+} laser. The data at − 3 °C provide a measurement of the scattered light. The electronic origins of the two lowest excited singlet states are indicated by arrows.

the naphthalene molecule, which exhibits resonance fluorescence characterized by an anomalously long decay time. A full report of the experimental results will be published elsewhere.

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