we indicate schematically the changes in orbital energy with molecular expansion, resulting in thermal luminescence at somewhat longer wavelengths than the optical absorption. On the extreme right are shown the various dissociation limits estimated by comparison with similar molecules.

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Long Radiative Lifetimes of Small Molecules

Mordechai Bixon* and Joshua Jortner†
Department of Chemistry, Tel Aviv University, Tel Aviv, Israel

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In this paper, we apply a theory of electronic relaxation in polyatomic molecules for the study of the anomalously long radiative lifetimes of NO_2, CS_2, and SO_2. We have classified medium-size molecules which exhibit intramolecular vibronic coupling into two intermediate cases, which we call the sparse intermediate case and the dense intermediate case, characterized by low and high spacing of the vibronic levels relative to the radiative width. The radiative decay in the sparse intermediate case was considered in detail, taking advantage of the coarse level spacing and the extremely short intramolecular recurrence time encountered in this case. From our model calculations, we conclude that:

(a) in the sparse case, the radiative decay rate is characterized by a superposition of slowly varying exponentials;
(b) the mean radiative lifetime is expressed as a radiative lifetime calculated from the integrated oscillator strength and "diluted" by the number of states within the half-width of the manifold of coupled levels;
(c) no intramolecular electronic relaxation processes are encountered in this case;
(d) a qualitative interpretation of the complex molecular spectra is provided.

I. INTRODUCTION

It has been experimentally demonstrated that the first spin allowed excited states of NO_2, SO_2, and CS_2 exhibit anomalously long radiative lifetimes,[1–4] which are considerably longer lifetimes than those expected on the basis of the integrated oscillator strength.[1] Furthermore, it was observed that the absorption spectra of these molecules are very complex,[5] consisting of a large number of lines which could not be classified as corresponding to the usual system of vibrational–rotational manifold of a single electronic state. It was suggested by Douglas[1] that these peculiarities are reminiscent of intramolecular vibronic coupling in these molecules which result in the redistribution of the intensity of a zero-order Born–Oppenheimer state (corresponding to the excited singlet) among a large number of zero-order levels which are quasidegenerate with this former level, and which do not carry oscillator strength. In the present paper, we provide a theoretical formulation of Douglas' suggestion.[1] The treatment presented herein is based on a theory of electronic relaxation in polyatomic molecules[6] recently developed by us.

The basic conceptual framework for the understanding of electronic relaxation processes in polyatomic molecules and in solids was provided by the early work of Franck and Sponer[7] and of Kubo,[8] who have pointed out that the nuclear kinetic-energy terms in the molecular Hamiltonian lead to the mixing of zero-order Born–Oppenheimer states. Since then, several authors[9–13] have investigated the problem of radiationless transition in large molecules by considering the vibronic matrix elements which couple the zero-order

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* Present address: Institute for Fluid Dynamics and Applied Mathematics, University of Maryland, College Park, Md. 20740.

† Also at Department of Chemistry and the James Franck Institute, The University of Chicago, Chicago, Ill. 60637.

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vibronic states in a polyatomic molecule. We have recently demonstrated[14] how to construct the molecular eigenstates of the electronic Hamiltonian[15] in an isolated polyatomic molecule. Intramolecular vibronic interactions result in significant level mixing and in redistribution of intensity in large- and medium-sized molecules. Previous calculations,[14,16] based on a simple model system, established criteria for inhomogeneous line broadening and led to a definition of a recurrence time for the occurrence of intramolecular radiationless transition in a large molecule. The situation is, of course, radically different in the case of medium-sized molecules on which we focus our attention in the present work. In this case, intramolecular vibronic coupling may still be effective; however, intramolecular radiationless transitions will not occur in the isolated molecule.

It will be useful at this point to consider the classification scheme recently proposed for molecules[16] which exhibit intramolecular vibronic coupling according to their efficiency with respect to intramolecular electronic relaxation, the effect of the medium on the relaxation process, and the behavior of the molecule in a quantum-beat experiment.[17]

A. The Statistical Limit

The density of vibronic states is extremely high, so that the average vibronic-coupling matrix element v appreciably exceeds the mean spacing, $\epsilon=\rho^{-1}$ (where ρ is the density of states), between these levels, so that

$$v\rho\gg 1. \tag{1}$$

In this limit, inhomogeneous broadening occurs entirely as an intramolecular phenomenon. Intramolecular relaxation occurs on the time scale

$$t\ll\hbar\rho, \tag{2}$$

which defines a recurrence time $\hbar\rho$ for the occurrence of the relaxation process. Equation (2) also implies[6] that the radiative width Γ of the zero-order state which carries oscillator strength exceeds the mean level spacing so that

$$\Gamma\gg\epsilon. \tag{3}$$

Large organic molecules (e.g., naphthalene, anthracene, tetracene) fall in this catetory.[13,14,16]

B. The Resonance Limit

When the energy levels are coarsely spaced, a small number of degenerate or quasidegenerate zero-order levels may be split by the intrinsic or by external perturbations. Provided that $\epsilon\sim\Gamma$, the only decay channel of the coherently excited system (in the absence of external perturbation) will involve a radiative decay process which will exhibit a beat spectrum. Typical examples for this case involve level crossing and level anticrossing in atoms and in diatomic molecules.[18a]

The intramolecular vibronic-coupling matrix elements in a diatomic molecule may considerably exceed the radiative widths of the molecular levels. A small (e.g., diatomic) molecule may reveal the effects of strong vibronic perturbations between pairs of levels, while the interference effects in the radiative decay are not encountered. In this case, we expect that $\Gamma\gg\epsilon$ while $v\epsilon\sim 1$. We shall refer to this situation as a coarse level spacing. A typical molecule in this group is CN, in which $^2\Sigma$–$^2\Pi$ mixing occurs.[18b] The matrix elements connecting the $^2\Sigma$ and $^2\Pi$ states of CN are of the order of 1 cm^{-1}, so that those Born–Oppenheimer states which are separated by 1 cm^{-1} will exhibit large perturbations.[18b]

As it usually happens in nature, intermediate cases are encountered and these are of considerable interest. It would be useful to consider two categories.

C. The Dense Intermediate Case

The molecular eigenstates are not sufficiently dense so that Relations (1)–(3) are replaced by

$$v\rho\sim 1, \tag{1'}$$

$$t\sim\hbar\rho, \tag{2'}$$

and

$$\epsilon\sim\Gamma. \tag{3'}$$

It was suspected[13] that $^1B_{2u}\rightarrow{}^3B_{1u}$ coupling in the benzene molecule may correspond to this case. These considerations are based on an order-of-magnitude estimate of the parameter $v\rho$, (without taking into account the vibronic manifold corresponding to the ground electronic state). Recent experimental data[19] indicate that the decay of the $^1B_{2u}$ state of benzene corresponds to the statistical limit.

D. The Sparse Intermediate Case

The density of vibronic states is rather small, while the vibronic-coupling matrix elements are rather large,

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due to favorable Franck–Condon vibrational overlap factors. Under these circumstances, we may expect that

$$v\rho > 1. \tag{1''}$$

The experimental time scale t (for the fluorescence detection) considerably exceeds the recurrence time so that

$$t \gg \hbar\rho, \tag{2''}$$

while the coarse spacing of levels exceeds the radiative bandwidth

$$\Gamma \ll \epsilon. \tag{3''}$$

The first excited singlet states of SO_2, NO_2, and CS_2 are expected to fall in this category. The density of vibronic states (corresponding to the ground state and to the first triplet state), which are quasidegenerate with the excited singlet, is, of course, rather low, being of the order of one state per energy interval of one wavenumber. These nonlinear molecules are characterized by different bond angles in the ground and excited states,[20] resulting in a large vibrational-overlap Franck–Condon factor. Thus, Eq. ($1''$) is expected to hold in this case so that extensive level mixing still takes place.

II. THE RADIATIVE-DECAY PROBLEM

We shall now turn our attention to the theoretical study of the radiative decay of molecules which correspond to the sparse intermediate case. To this end, we consider the radiative decay of a molecule for which $v\rho > 1$, which corresponds both to the statistical limit[6] and to the sparse intermediate case.

The complete Hamiltonian for the system, composed of the molecule and the radiation field, is given by

$$H = H_{el} + H_{\text{rad}} + H_{\text{int}} \tag{4}$$

and

$$H_{el} = H_{\text{BO}} + H_v. \tag{5}$$

The molecular Hamiltonian H_{el} consists of the Born–Oppenheimer Hamiltonian H_{BO} and an intramolecular perturbation term H_v which consists of vibronic coupling, spin–orbit interactions, etc. The nuclear kinetic-energy operator dominates the coupling,[7–15] although in the case of states of different multiplicity the spin–orbit interaction has to be also included. H_{rad} is the Hamiltonian corresponding to the free radiation field and H_{int} is the radiation–matter interaction term.

The zero–order states are taken as the eigenstates of the Hamiltonian

$$H_0 = H_{\text{BO}} + H_{\text{rad}}. \tag{6}$$

They include the vibronic state $\varphi_s \equiv |\varphi_s; vac\rangle$, which is the zero-order approximation to the excited state, and the vibronic manifold $\varphi_i \equiv |\varphi_i; vac\rangle$, which represent the vibrationally excited states of lower electronic states, while $|vac\rangle$ corresponds to a zero-photon radiation field. The final zero-order states of the system are $\varphi_E = |\phi_0; \mathbf{k}, \mathbf{e}\rangle$, where ϕ_0 corresponds to the molecular ground state and $|\mathbf{k}, \mathbf{e}\rangle$ represents a one-photon state. These final states are normalized per unit energy interval.

The matrix elements of the Hamiltonian between the zero-order states are taken to be

$$\begin{aligned} \langle\varphi_s | H | \varphi_i\rangle &= v, & \langle\varphi_s | H | \varphi_s\rangle &= E_s \\ \langle\varphi_i | H | \varphi_j\rangle &= E_i\delta_{ij}, & \langle\varphi_E | H | \varphi_{E'}\rangle &= E\delta(E-E') \\ \langle\varphi_s | H | \varphi_E\rangle &= W, & \langle\varphi_i | H | \varphi_E\rangle &= 0, \end{aligned} \tag{7}$$

where it is assumed that only the state φ_s carried oscillator strength and that W is independent of E, and v is independent of i. To simplify the treatment further, it is also assumed that the states $\{\varphi_i\}$ are uniformly spaced with the separation $\epsilon = \rho^{-1}$.

The diagonalization of the Hamiltonian is carried out in two stages. The first stage involves the diagonalization of the molecular problem which results in the following excited molecular eigenstates[14]:

$$\psi_n = \alpha_s^n \varphi_s + \sum_i \beta_i^n \varphi_i \tag{8}$$

with energies E_n. The mixing coefficients are given in the form[14]

$$|\alpha_s^n|^2 = v^2[(E_n - E_s)^2 + v^2 + (\pi v^2/\epsilon)^2]^{-1}. \tag{9}$$

The mixing with the radiation field results in the following (time-independent) eigenfunctions[6]:

$$\psi_E = \sum_n a_n(E)\psi_n + \int dE' C_{E'}(E)\varphi_{E'}, \tag{10}$$

where

$$a_n(E) = [\alpha_s^n W/(E - E_n)]\{Z^2(E)/[\pi^2 + Z^2(E)]\}, \tag{11}$$

and

$$Z(E) = \{\sum_n [|\alpha_s^n W|^2/(E - E_n)]\}^{-1}. \tag{12}$$

The excited state resulting from the optical excitation by a short light pulse[6,16] is given (bearing in mind that only the state φ_s carries oscillator strength) by the following expression:

$$\Psi(t=0) = \int dE \sum_n \alpha_s^n a_n(E)\psi_E. \tag{13}$$

The time development of this excited state is simply obtained by incorporating the phase development of these eigenstates

$$\Psi(t) = \sum_n \alpha_s^n \int dE a_n(E)\psi_E \exp\left(-\frac{i}{\hbar}Et\right). \tag{14}$$

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The fluorescence rate is given by

$$\dot{P}(t)=(2\pi/\hbar)\ |\langle\phi_0|T|\Psi(t)\rangle|^2\rho_k =(\Gamma/\hbar)\ |A_s(t)|^2, \tag{15}$$

where $\Gamma/\hbar$ is the radiative decay probability of the zero-order state φ_s; T corresponds to the transition operator; ρ_k is the density of states in the radiation field; and $A_s(t)=\langle\varphi_s|\Psi(t)\rangle$ is the amplitude of the state φ_s in the excited state $\Psi(t)$ at time t. This amplitude can be displayed in the form[6]

$$A_s(t)=\frac{2}{\pi\Gamma}\int\frac{\exp(-iE_st/\hbar)\exp(-iEt/\hbar)dE}{1+(16/\Delta^2\Gamma^2)[E^2+(\Delta^2/4)]^2[(2E/\Delta)\operatorname{cotgh}(\pi\Delta/2\epsilon)+\operatorname{cotg}(\pi E/\epsilon)]^{-2}}, \tag{16}$$

where Δ is given by

$$\Delta=2\pi v^2\rho, \tag{17}$$

which corresponds to the nonradiative half-width of the distribution of lines.

In the statistical limit (where a single inhomogeneously broadened Lorentzian-shaped line results), Eqs. (2) and (3) are also satisfied. Then the Fourier transform in Eq. (16) can be evaluated[6] resulting in a simple exponential decay, e.g., $|A_s(t)|^2=\exp[-(\Delta+\Gamma/\hbar)t]$

III. THE SPARSE INTERMEDIATE CASE

In the sparse intermediate case, Eq. (1″)-(3″) imply that $\Delta>\epsilon\gg\Gamma$, and therefore two simplifications can be introduced at this point. In the first place, we can set $\coth(\pi\Delta/2\epsilon)\approx1$ in Eq. (16). Furthermore, we notice that the argument of the Fourier integral [Eq. (16)] is characterized by very small numerical values, except around the points where $E=n\epsilon$ with $n=0, \pm1, \pm2$, etc., where the function $\operatorname{cotg}(\pi E/\epsilon)$ diverges. Near these "critical" points the cotangent function may be approximated by

$$\cot(\pi E/\epsilon)\approx\epsilon/\pi(E-n\epsilon);\qquad n=0,\pm1,\pm2,\cdots. \tag{18}$$

One can then express the amplitude $A_s(t)$ as a sum of integrals whose arguments are functions centered around the points $E=n\epsilon$:

$$A_s(t)=\frac{2}{\pi\Gamma}\exp\left(-\frac{iE_st}{\hbar}\right)\sum_n\exp\left(-\frac{i\epsilon nt}{\hbar}\right)\int_{-\infty}^{\infty}\frac{\exp[-(i/\hbar)Et]dE}{1+(16/\Delta^2\Gamma^2)[(n\epsilon)^2+\frac{1}{4}\Delta^2]^2(\pi E/\epsilon)^2}. \tag{19}$$

This equation can be rearranged as follows:

$$A_s(t)=\frac{2\exp[-(i/\hbar)E_st]}{\pi\Gamma}\frac{\epsilon^2\Delta^2\Gamma^2}{16\pi^2}\sum_n\exp\left(-\frac{i}{\hbar}\epsilon nt\right)[(n\epsilon)^2+\tfrac{1}{4}\Delta^2]^{-1}\int_{-\infty}^{\infty}\frac{\exp[-(i/\hbar)Et]dE}{(\epsilon^2\Delta^2\Gamma^2/16\pi^2)[(n\epsilon)^2+\frac{1}{4}\Delta^2]^{-2}+E^2}. \tag{20}$$

The integrals appearing in Eq. (20) correspond to Fourier transforms of Lorentzians, so that the following expression results:

$$A_s(t)=\left(\frac{2\exp[-(i/\hbar)E_st]}{\pi\Gamma}\right)\tfrac{1}{4}(\epsilon\Delta\Gamma)\sum_n\exp\left(-\frac{i}{\hbar}n\epsilon t\right)[(n\epsilon)^2+\tfrac{1}{4}\Delta^2]^{-1}\exp\{-(\epsilon\Delta\Gamma/4\pi\hbar)[(n\epsilon)^2+\tfrac{1}{4}\Delta^2]^{-1}t\}. \tag{21}$$

The fluorescence rate is now evaluated from Eqs. (15) and (21):

$$\dot{P}(t)=\frac{\epsilon^2\Delta^2\Gamma}{4\pi^2\hbar}\sum_n\sum_m\exp\left(-\frac{i}{\hbar}(n-m)\epsilon t\right)[(n\epsilon)^2+\tfrac{1}{4}\Delta^2]^{-1}[(m\epsilon)^2+\tfrac{1}{4}\Delta^2]^{-1}$$
$$\times\exp(-(\epsilon\Delta\Gamma/4\pi\hbar)\{[(n\epsilon)^2+\tfrac{1}{4}\Delta^2]^{-1}+[(m\epsilon)^2+\tfrac{1}{4}\Delta^2]^{-1}\}t), \tag{22}$$

or alternatively, using Eqs. (9) and (17) we get

$$\dot{P}(t)=(\Gamma/\hbar)\sum_n\sum_m\exp[-(i/\hbar)(n-m)\epsilon t]\ |\alpha_s^n|^2\ |\alpha_s^m|^2\exp[-(\Gamma/2\hbar)(|\alpha_s^n|^2+|\alpha_s^m|^2)t]. \tag{22′}$$

We should note in passing that Eq. (22′) is equivalent to Eq. (45) in the work of Jortner and Berry.[16] To proceed, Eq. (22) can be rearranged to yield

$$\dot{P}(t)=(\epsilon^2\Delta^2\Gamma/4\pi^2\hbar)\sum_{n\leq m}\sum(2-\delta_{nm})\cos[(n-m)(\epsilon t/\hbar)][(n\epsilon)^2+\tfrac{1}{4}\Delta^2]^{-1}[(m\epsilon)^2+\tfrac{1}{4}\Delta^2]^{-1}$$
$$\times\exp(-(\epsilon\Delta\Gamma/4\pi\hbar)\{[(n\epsilon)^2+\tfrac{1}{4}\Delta^2]^{-1}+[(m\epsilon)^2+\tfrac{1}{4}\Delta^2]^{-1}\}t). \tag{23}$$

The resulting fluorescence rate is characterized by two contributions: exponential decay terms (which correspond to the case $n=m$) and interference terms. Thus, the fluorescence rate will exhibit a quasioscillatory behavior with periods of the order of the recurrence time $\hbar/\epsilon$, which in the sparse intermediate case corresponds to $\hbar/\epsilon\sim10^{-12}$ sec. This recurrence time is appreciably shorter than the experimental time resolution for fluorescence detection. We, thus, expect that the photon counter (employed in this experiment) will measure an average fluorescence rate where the oscillatory behavior will be smared out. Let the experimental time resolution be $\Delta t\gg\hbar/\epsilon$, so that we may average $P(t)$ over time intervals of the length Δt:

$$\langle\dot{P}(t)\rangle_{\mathrm{Av}}=(\Delta t)^{-1}\int_{t-(\Delta t/2)}^{t+(\Delta t/2)}\dot{P}(t')dt'. \tag{24}$$

A cursory examination of Eq. (23) reveals that the only part of $\dot{P}(t)$ which appreciably changes during the time interval Δt involves the function $\cos[(n-m)\epsilon t/\hbar]$, while the exponential function varies slowly on this time scale. We may thus average only over the trigonometric function, and to a good approximation we get

$$(\Delta t)^{-1}\int_{t-(\Delta t/2)}^{t+(\Delta t/2)}\cos\left[(n-m)\frac{\epsilon t'}{\hbar}\right]dt'\approx\delta_{nm}, \tag{25}$$

so that the interference terms in Eqs. (22) and (23) can be disregarded in this case. The following expression now is obtained for the average rate of fluorescence decay:

$$\dot{P}(t)=(\epsilon^2\Delta^2\Gamma/4\pi^2\hbar)\sum_n[(n\epsilon)^2+\tfrac{1}{4}\Delta^2]^{-2}\exp\{-(\epsilon\Delta\Gamma/2\pi\hbar)[(n\epsilon)^2+\tfrac{1}{4}\Delta^2]^{-1}t\}. \tag{26}$$

To recast this result into a more physically transparent form, let us define the (approximate) number N of states within the half-width of the inhomogeneously broadened manifold of levels

$$N=\Delta/2\epsilon=\pi v^2\rho^2. \tag{27}$$

Equation (26) can be now displayed in the form

$$\langle\dot{P}(t)\rangle_{\mathrm{Av}}=\frac{\Gamma}{\hbar^2\pi^2N^2}\sum_n\left[1+\left(\frac{n}{N}\right)^2\right]^{-2}\exp\left(-\frac{\Gamma t}{\pi\hbar N[1+(n/N)^2]}\right). \tag{28}$$

An important consistency check involves the determination of the quantum yield. The integrated fluorescence yield measured up to the time τ after the excitation is easily obtained by integrating Eq. (26):

$$Y(\tau)=\int_0^\tau\langle\dot{P}(t)\rangle_{\mathrm{Av}}dt=\left(\frac{\epsilon^2\Delta^2\Gamma}{4\pi\hbar}\right)\left(\frac{2\pi\hbar}{\Delta\Gamma\epsilon}\right)\sum_n[(n\epsilon)^2+\tfrac{1}{4}\Delta^2]^{-1}\left\{1-\exp\left[-\frac{\epsilon\Delta\Gamma}{2\pi\hbar}((n\epsilon)^2+\tfrac{1}{4}\Delta^2)^{-1}\tau\right]\right\}, \tag{29}$$

where τ is large relative to the average decay times (e.g., $\tau\rightarrow\infty$), the result in the following express for the quantum yield Y:

$$Y=Y(\infty)=(\epsilon\Delta/2\pi)\sum_n[(n\epsilon)^2+\tfrac{1}{4}\Delta^2]^{-1}=\sum_n|\alpha_s^n|^2=1. \tag{30}$$

IV. DISCUSSION

From the results obtained herein, we conclude that:

(a) The sparse intermediate case involves a manifold of molecular eigenstates which are well separated relative to their radiative widths. Hence interference effects in the radiative decay of the coarsely spaced levels are not expected to be revealed in this case. Thus the sparse intermediate case corresponds to the physical situation whereupon each radiatively decaying state (e.g., each decay channel) can be characterized by its own lifetime. It can be thus inferred that in this case the damping matrix[21] is diagonal. It is therefore not surprising that our result for the intermediate sparse case [Eq. (22′)] is identical with Eq. (45) in the work of Jortner and Berry.[16] In that early work,[16] it was implicitly assumed that the decay of the amplitude of each molecular eigenstate, say ψ_n, can be described by an independent radiative lifetime which is given by $\hbar\Gamma^{-1}|\alpha_s^n|^{-2}$. From subsequent work,[6,21] it is evident that in the resonance limit, in the statistical limit, and in the intermediate dense case, the radiative decay of the manifold of indistinguishable levels[21] had to be described in terms of a nondiagonal damping matrix. Hence, the Jortner–Berry[16] treatment is applicable only for the sparse intermediate case. The agreement encountered in the latter case between the present results (which are based on the Fano method) and those of the

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[21] M. Bixon, J. Jortner, and Y. Dothan (unpublished data).

TABLE I. General features of the decay of molecular levels.

Physical property	Resonance limit	Coarse distribution	Sparse intermediate case	Dense intermediate case	Statistical limit
Number of states $N=v^2\rho^2$ or v^2/ϵ^2 [a,b]	···	$N\sim1$	$N>1$	$N\sim1$	$N\gg1$
Level separation relative to radiative width	$\epsilon\sim\Gamma$	$\epsilon\gg\Gamma$	$\rho^{-1}\gg\Gamma$	$\rho^{-1}\sim\Gamma$	$\rho^{-1}\ll\Gamma$
Line shape	Natural radiative+ conventional broadening	Natural radiative+ conventional broadening	Well-separated lines	No observable effect	Lorentzian line shape $\Delta=\pi v^2\rho$
Time scale t relative to recurrence time	$t\sim\hbar/\epsilon$	$t\gg\hbar/\epsilon$	$t\gg\hbar\rho$	$t\sim\hbar\rho$	$t\ll\hbar\rho$
Mode of decay	Beat spectrum	Normal exponential decay	Sum of (slowly varying) exponentials	Oscillatory (beats) (?)	Exponential
Mean radiative decay time[c]	···	$\tau_e\sim\hbar/\Gamma$	$\tau_e\sim N\hbar/\Gamma$	$\tau_e\sim\hbar/\Gamma$	$\tau_e=\hbar/(\Delta+\Gamma)$
Experimental fluorescence quantum yield[d]	$Y=1$	$Y=1$	$Y=1$	$Y=1$	$Y=[\Gamma\Delta/(\Gamma+\Delta)]<1$
Features of relaxation	External	External	External	External	Intramolecular $\tau_{NR}=\hbar/\Delta$
Examples	Level crossing Level anticrossing	CN	SO_2, NO_2, CS_2	?	Naphthalene Anthracene Tetracene

[a] In the resonance limit, we shall just consider two levels with spacing ϵ. The number of states N is, of course, meaningless in this limit.

[b] In the case of a coarse distribution, we consider a pair of levels with spacing ϵ, where $v\epsilon\sim1$.

[c] In the case of oscillatory decay which exhibits quantum beats, a proper definition of the radiative decay time cannot be provided.

[d] The quantum yield in the statistical limit is measured on a time scale shorter than the recurrence time.

previous treatment[16] (which rest on the time evolution operator technique) provides a consistency check for the general treatment presented herein. It is gratifying that our general formalism for the radiative deday of molecules [Eqs. (15) and (16)] is applicable for all cases of physical interest.

(b) In the sparse intermediate case, the fluorescence rate is expressed as a sum of exponentials with decay times τ_e of the order of $\tau_e \sim \hbar N/\Gamma$. Taking $N \sim 100$ as a rough order-of-magnitude estimate, then the major contribution to the sum (28) will arise from terms where $(n/N) \lesssim 1$. A nonexponential decay is expected, characterized by a continuous distribution of lifetimes which are approximately in the range $\hbar N/\Gamma - 2\hbar N/\Gamma$. A zero-order approximation for the decay law is $\dot{P}(t) \sim (\Gamma/\hbar N) \exp(-\Gamma t/\hbar N)$. The radiative decay time in this limit is characterized by a longer radiative lifetime than that expected on the basis of the integrated oscillator strength (which is just $\hbar/\Gamma$). The "dilution factor" for the radiative lifetime is approximately given by the factor N.

(c) As the final expression [Eq. (28)] for the radiative decay rate does not involve interference terms, the same result is expected to hold also when the excitation process is not coherent.

(d) From the spectroscopic point of view, the occurrence of efficient intramolecular vibronic coupling in the sparse intermediate case implies the redistribution of the intensity of the zero-order component φ_s which induces the appearance of many new, well-resolved lines (which correspond to all the molecular eigenstates ψ_n in the optical spectrum).

(e) Quantum yield measurements performed on the gas at low pressures, where the average time between collisions is long compared to the decay time τ_e, will result in a fluorescence quantum yield of unity. In the sparse intermediate case, the recurrence time is exceedingly short, so that nonradiative intramolecular electronic relaxation processes will not be observed. At higher pressures, intermolecular electronic relaxation processes may take place.

In order to elucidate the implications of our theoretical treatment, one should now inquire whether the first excited singlet states of SO_2, NO_2, and CS_2 [1] can be indeed classified as corresponding to the sparse intermediate case. Rough order-of-magnitude estimates will be useful in this respect. From the known ground-state vibrational frequencies, one can estimate the density of vibronic levels using Haarhoff's method[22] (or similar techniques). These results can be then combined with the experimental "dilution factor" N to estimate the mean value of the vibronic-coupling term v. In the case of NO_2, the estimated density of vibronic levels which correspond to the ground electronic state at the energy of 23000 cm^{-1} is about $\rho \sim 0.3$ cm. The experimental radiative lifetime leads to the estimate $N \approx 100$ for the dilution factor. Hence one gets $\Delta \sim N\rho^{-1}$, or $\Delta \sim 300$ cm^{-1}, so that $v \sim 10$ cm^{-1}. This vibronic-coupling matrix element is of the expected order of magnitude.[6] According to this qualitative analysis, the absorption spectrum should consist of ~100 absorption lines distributed over an energy interval of ~300 cm^{-1}. It is difficult to verify this conclusion experimentally as in view of angular-momentum conservation rules our arguments apply only for a single rotational state. The actual spectrum reveals, of course, a large number of different rotational transitions, so it is impossible at present to identify the homogeneously broadened manifolds which correspond to a single rotational state. Besides, according to our simple model,[14,6] the intensity of these lines is expected to behave regularly, as they correspond to a Lorentzian distribution. In real life, the parameter v is not constant, being dependent on the nature of the vibronic states, which in turn are not uniformly distributed. Real calculations of vibronic matrix elements are, at present, a difficult task because of our ignorance of important features of molecular geometry and of the anharmonicity constants of the highly excited vibronic levels in the ground state of these polyatomic molecules.

These comments conclude our discussion of intermediate sparse case of vibronic coupling. The resonance[16,21] and the statistical limit[6,14] were previously treated. Finally, the intermediate dense limit should be briefly considered. Although a theoretical treatment of this case was not yet carried out, it is expected that in this case the radiative decay will exhibit an oscillatory behavior as the manifold of the radiatively decaying eigenstates will now reveal interference effects and the recurrence time is now of the order of $\hbar/\Gamma$. Unlike the statistical limit and the sparse intermediate case, spectroscopic evidence derived from the intensity distribution in absorption spectrum cannot be used in the dense intermediate case. In summary, we display in Table I the characteristic features of the radiative decay of small, medium-size, and large molecules. We hope that these theoretical results will stimulate further experimental activity in this interesting field.

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[22] P. C. Haarhoff, Mol. Phys. 7, 101 (1963).