ELECTRONIC RELAXATION PROCESSES IN LARGE MOLECULES

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ABSTRACT

In this paper, we review recent progress in the theory of non-radiative decay processes in polyatomic molecules. This review has been subdivided into the following sections:

I. Introduction
II. Brief comments on compound states
III. Intramolecular coupling
IV. Molecular eigenstates
V. Diffuseness and interference effects in the electron spectra of large molecules
VI. Intramolecular non-radiative decay
VII. Irreversible intramolecular decay in the statistical limit
VIII. The coupling between radiative and non-radiative processes in large molecules
IX. Conclusions

I. INTRODUCTION

RADIATIONLESS processes in excited electronic states of large molecules can be classified as follows:

(a) Radiationless decomposition[1]:
    (a1) Molecular predissociation.
    (a2) Molecular autoionization.
(b) Intramolecular relaxation[2]:
    (b1) Electronic relaxation processes which involve transitions between different electronic states in a large molecule (e.g. internal conversion and intersystem crossing.)
    (b2) Unimolecular photochemical rearrangement reactions in excited electronic states of large molecules such as *cis–trans* isomerization or electrocyclic reactions.

From the historical point of view it has been known since 1888 that many organic molecules exhibit a strong afterglow (or rather phosphorescence) when excited by ultra-violet light: this emission occurs invariably at lower

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* This work was supported in part by the National Aeronautics and Space Administration and by the Air Force Office of Scientific Research and has benefited from the support of Materials Research by the Advanced Research Projects Agency of The University of Chicago.

frequencies than the fluorescence (if any) of the compound[3]. These observations were followed in 1933 by the phenomenological description of the three level system by Jablonski[4]. The modern focus on the importance and generality of intramolecular relaxation processes was emphasized by the work of Lewis and co-workers and by Kasha[5].

Extensive experimental data are available on electronic relaxation processes in polyatomic molecules imbedded in a dense medium (e.g. solution, rigid glasses, mixed crystals)[2]. These studies resulted in several important generalizations which can be summarized in terms of the Kasha rules, the 'shortening' of the radiative lifetimes of large molecules[2a, b], the Robinson–Frosch energy gap law[6] and the (energy gap dependent) deuterium isotope effect[6–8].

Although most of the available experimental results concern systems of molecules whose states are coupled to an environment sufficient experimental data are now available to demonstrate conclusively that radiationless transitions occur in an 'isolated' low density gas phase large molecule. The relevant evidence[9–15] is based on the absence of resonance fluorescence from the second excited singlet state of anthracene, tetracene and naphthalene, the 'shortening' of the radiative lifetimes of the first singlet states of anthracene and perylene, and on fluorescence quantum yield measurements for benzene in the limit of low pressures. These results demonstrate that radiationless transitions in large molecules involve an intramolecular relaxation process.

I would like to discuss some questions that come up whenever one thinks of measuring and analysing experimental radiative decay times and optical line shape data in polyatomic molecules and how these quantities relate to fundamental intramolecular electronic relaxation processes.

II. BRIEF COMMENTS ON COMPOUND STATES

How does a relaxation process take place in a microscopic system? Three major points have to be amplified in this context:

(a) The description of the decaying state.

(b) The preparation of the metastable non-stationary state.

(c) The relation between the decay time and the optical line shapes.

Suppose that the system under consideration is described by the Hamiltonian

$$H = H_0 + V \tag{II.1}$$

where H_0 is a 'convenient' zero order Hamiltonian (e.g. independent particles Hamiltonian in the case of autoionization[16], of the Born–Oppenheimer Hamiltonian in the case of predissociation[17–19]), while V is a perturbation term which includes whatever we have left out of H_0. The zero order eigenstates of H_0 are now partitioned into two sets: a (dynamic) sparse subset which is characterized by a small number of discrete levels ϕ_1, ϕ_2 and a dissipative part ϕ_E which is characterized by a continuous spectrum. As the zero order states of the two subsystems are degenerate extensive 'configuration interaction' is induced by the (small) interaction term V which couples the dynamic and the dissipative part. An atom or molecule in a stationary state cannot make transitions to the other states which are induced by the 'small terms in the molecular Hamiltonian' (i.e. V in equation II.1). Obviously all time dependent transitions between stationary states are radiative in nature. However, this conclusion does not apply when the molecular system is prepared by some experiment in a non-stationary state of the system's Hamiltonian. To obtain the physical information concerning the relaxation process it will be convenient to proceed as follows[16, 19].

(a) The *molecular eigenstates* ψ_E of the system are constructed (e.g. the eigenstates of H in the absence of the radiation field) as a time independent superposition of the zero order states. For convenience we shall consider only a single state ϕ_1 in the dynamic subset, so that

$$\psi_E = a(E)\,\phi_1 + \int b_{E'}(E)\,\phi_{E'}\,\rho(E')\,\mathrm{d}E' \tag{II.2}$$

where $\rho(E')$ is the density of states in the zero order continuum, and $a(E)$ and $\{b_{E'}(E)\}$ correspond to expansion coefficients. Note that the eigenstates ψ_E form a continuous spectrum.

(b) *The resonance width* $\Gamma(E)$ is given for a single resonance by the Fermi Golden Rule

$$\Gamma(E) = 2\pi\,|\langle\phi_1\,|V|\,\psi_E\rangle|^2\,\rho(E). \tag{II.3}$$

For the case of a dissipative continuum one expects a slowly varying function of the energy in the vicinity of the $E = E_1$ which is the energy of the zero order state ϕ_1.

(c) *The Breit Wigner formula.* The amplitude square of the zero order state ϕ_1 is given by the distribution

$$|a(E)|^2 = (\Gamma/2)/[(E - E_1 - \gamma_1)^2 + (\Gamma/2)^2] \tag{II.4}$$

where γ_1 is a level shift. Thus the effect of configuration interaction is to dilute' the discrete state ϕ_1 through a manifold of stationary states. The profile of the distribution is a Lorentzian characterized by the width

$$\Delta = \Gamma \tag{II.5}$$

(d) *The transition matrix element* of the transition operator $\hat{T}$ for optical (or other type) excitation from the ground state ϕ_0 is determined by

$$\langle\phi_0|\hat{T}|\psi_E\rangle = a(E)\langle\phi_0|\hat{T}|\phi_1\rangle + \int b_{E'}(E)\langle\phi_0|\hat{T}|\phi_{E'}\rangle \times \rho(E')\,\mathrm{d}E' \tag{II.6}$$

(e) *The line shape* $A(E)$ for optical excitation will be determined by the square of the transition matrix element

$$A(E) \propto < \phi_0|\hat{T}|\psi_E\rangle|^2 \tag{II.7}$$

(f) *Lorentzian line shapes.* The absorption profile will be Lorentzian only provided that the continuum does not carry oscillator strength, i.e. $\langle\phi_0|T|\phi_{E'}\rangle = 0$ for all $\phi_{E'}$. Then

$$A(E) \propto |a(E)|^2 = 1/(1 + \varepsilon^2) \tag{II.8}$$

where the reduced energy parameter ε is

$$\varepsilon = E - E_1 - \gamma_1/(\Gamma/2) \tag{II.9}$$

(g) *Fano type line shapes.* In the general case when the continuum does carry oscillator strength from the ground state interference effects in absorption will be observed arising from the contributions of $\langle\phi_0|\hat{T}|\phi_1\rangle$ and $\langle\phi_0|\hat{T}|\phi_{E'}\rangle$ which will interfere with opposite phases on the two sides of the resonance. The line shape function will then be

$$A(E) \propto (q + \varepsilon)^2/(1 + \varepsilon^2) \tag{II.10}$$

where the line profile index q is determined by the ratio transition moments for the discrete state and for the continuum.

$$q \approx \frac{\langle\phi_0|\hat{T}|\phi_1\rangle}{\langle\phi_0|\hat{T}|\phi_E\rangle\langle\phi_E|V|\phi_1\rangle\,\rho(E)} \tag{II.11}$$

Note that equation II.10 is reduced to the Lorentzian form II.8 provided that $q \to \infty$. This situation will be realized when: (1) the coupling between the zero order states is negligible, (2) when the oscillator strength of the background absorption is negligibly small relative to the intensity carried by ϕ_1.

(h) *A compound state* of the system will be described as a time dependent superposition of time independent zero order states. The choice of the basis set is merely a matter of convenience. One possible choice of the basis set involves the stationary states of H or alternatively the basis set of H_0 may be used. Let $p(E)$ correspond to the excitation amplitude of ψ_E, then two alternative forms for the time dependent excited state can be immediately written:

$$\Psi(t) = \int p(E)\psi_E \exp(-iEt/\hbar)\rho(E)\,\mathrm{d}E$$
$$\equiv A(t)\phi_1 + \int B_E(t)\phi_E\rho(E)\,\mathrm{d}E \tag{II.12}$$

It should be noted that the compound state involves an admixture of zero order discrete and continuum states.

(i) *The time evolution* of the amplitude of the discrete state can then be given

$$P(t) = |\langle\phi_1|\Psi(t)\rangle|^2 = |\int p(E)a(E)\exp(-iEt/\hbar)\rho(E)\,\mathrm{d}E|^2 \equiv |A(t)|^2 \tag{II.13}$$

Thus the decay law is determined by an energy distribution function. It should be noted that unlike the line shapes which are definitely experimental observables, the quantity $P(t)$ may not always be amenable to experimental observation.

(1) Decay of state 'prepared' initially in ϕ_1

The $|A(0)|^2 = 1$ or $p(E) = a(E)$; provided that $\Gamma(E)$ is a slowly varying function of the energy an exponential decay law results

$$P(t) \propto \exp(-\Gamma t/\hbar) \tag{II.14}$$

The half lifetime is just $\hbar/\Gamma$ and the simple decay law is related to the width of the amplitude distribution $|a(E)|^2$. This is again a 'theoretical exercise' which not always will be realized in a real life experiment.

The foregoing arguments are general, leading to the conclusion that there is a set of features common to all compound states of a wide class of systems. The shapes of resonances encountered in nuclear, atomic, molecular and solid state physics are nearly the same and the decay rates of many different kinds of metastable states have the same functional form.

For radiationless decomposition processes the dissipative channel is well defined (e.g. a dissociative continuum for the case of predissociation and an ionization continuum for autoionization). The details of the relaxation process (e.g. decay times and line shapes) will be determined by the coupling matrix elements, the transition moments and the line profile index. At first sight it may appear that there is an apparent basic difference between radiationless decomposition and intramolecular relaxation as in the latter case *a 'true' dissipative continuum is not involved* In this context several statements were made concerning non-radiative intramolecular relaxation processes. It was stated by Herzberg[20] in 1966: 'The mechanism of (internal) conversion is not well understood as yet but is presumably connected with strong perturbations between the two states involved'. At about the same time Kistiakowsky and Parmenter[13] stated that their experimental observation of a radiationless transition in the isolated benzene molecule 'may be incompatible with the laws of quantum mechanics'. The questions that come up in relation to intramolecular relaxation processes in large molecules can be summarized as follows:

(a) What is the nature of the intramolecular coupling? In this context it is important to notice that the existence of intramolecular coupling is not sufficient to lead to a relaxation process.

(b) Do radiationless transitions take place in an isolated molecule and under what conditions can we consider a legitimate intramolecular relaxation process in a large molecule?

(c) What is the nature of the intramolecular dissipative channel? In the theory of radiationless transitions it will be of primary importance to consider the decay into a quasicontinuum and to establish the recurrence time for this process.

(d) What are the criteria for irreversibility of an intramolecular relaxation process?

(e) What are the implications of intramolecular coupling and a background quasicontinuum of states concerning intensity distribution in optical absorption?

(f) Under what conditions can the intramolecular decay be considered as a simple rate process with the rate constant being given by Fermi's 'Golden Rule'?

(g) What are the consequences of the coupling between radiative and non-radiative decay processes in a large molecule?

III. INTRAMOLECULAR COUPLING

The nature of the intramolecular coupling responsible for radiationless transitions was elucidated many years ago by Franck and Sponer[21] and by Teller[22] who pointed out that the nuclear kinetic energy operator provides the major interaction term which is responsible for the occurrence of radiationless processes in large molecules. Naturally, other intramolecular interaction terms may modify the mixing. Thus, for example, spin–orbit interactions have to be included in the case of mixing of quasi degenerate vibronic components which correspond to two electronic states of different multiplicity.

The electronic states of a molecule are conventionally classified within the framework of the Born–Oppenheimer approximation to separate electronic and nuclear motion. Let us focus our attention on the conventional Born–Oppenheimer (BO) adiabatic approximation for the two level system presented in *Figure 1.*

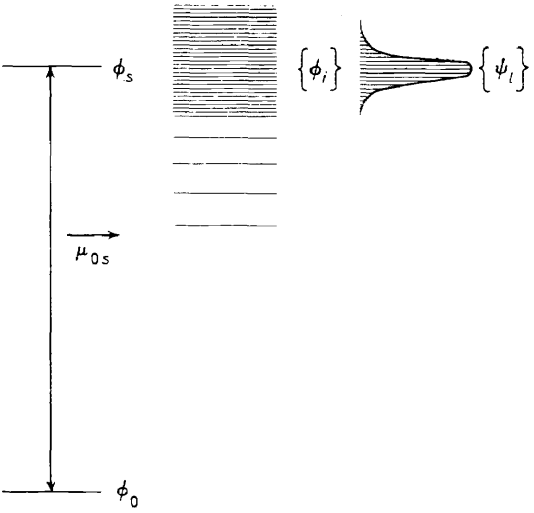

Figure 1. Energy levels scheme for a large molecule.

The higher excited electronic state, s, is characterized by the zero order BO levels $\phi_{s\alpha}(\boldsymbol{r}, \boldsymbol{Q})$ which are coarsely spaced, each of which is coupled to the dense quasicontinuum of vibronic levels $\phi_{l\beta}(\boldsymbol{r}, \boldsymbol{Q})$. These functions are usually approximated in the form:

$$\begin{aligned}\phi_{s\alpha}(\boldsymbol{r}, \boldsymbol{Q}) &= \Theta_s(\boldsymbol{r}, \boldsymbol{Q})\chi_{s\alpha}(\boldsymbol{Q})\\ \phi_{l\beta}(\boldsymbol{r}, \boldsymbol{Q}) &= \Theta_l(\boldsymbol{r}, \boldsymbol{Q})\chi_{l\beta}(\boldsymbol{Q})\end{aligned} \tag{III.1}$$

where $\boldsymbol{r}$ represents the electronic coordinates, while $\boldsymbol{Q} \equiv Q_1, Q_2, \ldots Q_k \ldots$ (III.1) correspond to the nuclear coordinates. Θ and χ represent electronic and vibration wavefunctions. The potential surfaces in the two electronic states will be denoted by $E_s(Q)$ and $E_1(Q)$ while the energies of the vibronic components will be represented by $E_{s\alpha}$ and $E_{l\beta}$, respectively.

As is well known, the BO representation is diagonal within a single electronic manifold while (hopefully small) matrix elements connect different electronic states. These off diagonal matrix elements are given in the general form:

$$v_{s\alpha,\,l\beta} = \tfrac{1}{2} \sum_k \int \mathrm{d}\boldsymbol{Q}\chi_{s\alpha}(\boldsymbol{Q}) \left\langle \Theta_s(\boldsymbol{q},\boldsymbol{Q}) \left| \frac{\partial^2}{\partial Q_k^2} \right| \Theta_l(\boldsymbol{q},\boldsymbol{Q}) \right\rangle \chi_{l\beta}(\boldsymbol{Q})$$

$$- \sum_k \int \mathrm{d}\boldsymbol{Q}\chi_{s\alpha}(\boldsymbol{Q}) \left\langle \Theta_s(\boldsymbol{q},\boldsymbol{Q}) \left| \frac{\partial}{\partial Q_k} \right| \Theta_l(\boldsymbol{q},\boldsymbol{Q}) \frac{\partial}{\partial Q_k} \chi_{l\beta}(\boldsymbol{Q}) \right\rangle \quad \text{(III.2)}$$

The electronic matrix elements appearing in III.2 can be expressed in the exact form:

$$J_{sl}^k = \left\langle \Theta_s(\boldsymbol{q},\boldsymbol{Q}) \left| \frac{\partial}{\partial Q_k} \right| \Theta_l(\boldsymbol{q},\boldsymbol{Q}) \right\rangle \quad \text{(III.3a)}$$

$$= \frac{\langle \Theta_s(\boldsymbol{q},\boldsymbol{Q}) | \partial U(\boldsymbol{q},\boldsymbol{Q})/\partial Q_k | \Theta_l(\boldsymbol{q},\boldsymbol{Q}) \rangle}{E_s(\boldsymbol{Q}) - E_l(\boldsymbol{Q})} \quad \text{(III.3b)}$$

where $U(\boldsymbol{q},\boldsymbol{Q})$ corresponds to the molecular potential energy term.

The breakdown of the BO approximation will be encountered under the following circumstances:

(a) Strong interaction between degenerate or quasidegenerate electronic origins. This situation corresponds to the Jahn Teller and Renner coupling in molecules.

(b) Intersection of potential surfaces. The electronic matrix element III.3 is a rapidly varying function of the nuclear coordinates, whereupon near the intersection (where $E_s(\boldsymbol{Q}) - E_l(\boldsymbol{Q}) = 0$) a new representation of the vibronic wavefunctions has to be found in a manner analogous to the treatment of the Jahn Teller problem. Such situations which involve a large configurational change between two electronic states will be encountered in the field of organic photochemistry.

(c) Case of near degeneracy. Now we encounter a small configurational change between two electronic states. The electronic integral J_{sl}^k is a slowly varying function of $\boldsymbol{Q}$ and we expect that $J_{sl}^k \propto \Delta E^{-1}$, where $\Delta E = E_{s0} - E_{l0}$ corresponding to the electronic energy gap between the origins of the two electronic states. ΔE is appreciable and the $v_{s\alpha,\,l\beta}$ terms are small not only in view of the energy denominator but rather as they involve extremely small[6, 23–26] Franck–Condon vibrational overlap terms. However, the smallness of the v terms does not ensure the validity of the BO approximation. The adiabatic approximation is expected to hold only provided the energy difference between the zero order vibronic states is large relative to the coupling matrix element III.2 so that

$$|E_{s\alpha} - E_{l\beta}| \gg |v_{s\alpha,\,l\beta}| \quad \text{(III.4)}$$

When a situation of near degeneracy is encountered we expect the BO approximation to break down even provided that the v terms are small.

Let us now consider the behaviour of the excited electronic levels of a complex molecule (*Figure 1*). The zero order vibronic level ϕ_s of a higher excited state is quasidegenerate with a manifold $\{\phi_l\}$ of vibronic levels which correspond to the lower excited electron states and to the ground state. The density of vibronic states of these lower configurations is determined by two factors:

(a) the number of vibrational degrees of freedom,

(b) the energy gap between the zeroth vibronic levels of the two electronic states.

The density of vibronic states at energy ΔE above the origin of an electronic state can be approximated by the semiclassical expression in the harmonic approximation[27]

$$\rho = \frac{\Delta E^{n-1}}{(n-1)!} \prod_{i=1}^{n} (h\nu_i)^{-1} \left(1 + \tfrac{1}{2}h \sum_i \nu_i/\Delta E\right)^{-1} \qquad \text{(III.5)}$$

where n is the number of the vibrational degrees of freedom, characterized by the frequencies ν_i. To obtain some feeling for the order of magnitude of the density of these background states we have displayed in *Table 1* estimates of the vibrational density of levels in a hypothetical polyatomic molecule characterized by an energy gap of 1eV, while in *Table 2* we have assembled some data for real physical systems. Obviously in view of the overwhelmingly large densities of vibronic states encountered in large molecules we expect that even small coupling matrix elements (equation III.2) will lead to appreciable level mixing. Under these common situations when a discrete zero order level is quasidegenerate with a background manifold of vibronic states the Born–Oppenheimer separability conditions break down. Thus, in general, the excited electronic states of large molecules cannot be considered as 'pure' BO states.

Table 1. Density of vibrational states in a series of hypothetical polyatomic molecules where all $\nu_i = 1000\ \text{cm}^{-1}$ and $\Delta E = 1\,\text{eV}$

No. of atoms	3	4	5	6	10
ρ cm	0·06	4	50	400	4×10^5

Table 2. Densities of vibronic states in some aromatic hydrocarbons

System	*Lower state*	*Upper state*	ΔE cm^{-1}	ρ cm
Anthracene	$^3B_{2u}$	$^1B_{2u}$	12000	5×10^{10}
Naphthalene	$^1A_{1g}$	$^3B_{2u}$	20000	8×10^{15}
Azulene	$^1A_1$	$^1B_1$	14000	10^{11}
Benzene	$^3B_{1u}$	$^1B_{2u}$	8400	8×10^4

Two final comments should be made at this point concerning our book keeping. (a) We have considered only vibronic levels. Mixing of different rotational levels in the isolated molecule is unnecessary as the zero order Hamiltonian is chosen to conserve angular momentum. (b) Spin selection rules are not strict in view of the fact that when the density of states is exceedingly large the small spin–orbit coupling terms cannot be left out.

One has to distinguish very carefully between the consequences of intramolecular coupling and intramolecular relaxation. In particular it should be borne in mind that the coupling can be exhibited while relaxation does not occur. We shall therefore attack the problem in two steps which will be analogous to the general problem of relaxation already considered: (a) The molecular eigenstates of the system will be constructed[28–30, 2a]; (b) The conditions for irreversible decay will then be established[30–32].

IV. MOLECULAR EIGENSTATES

A proper representation of the molecular eigenstates ψ_n can be obtained from a superposition of zero order Born–Oppenheimer states.

$$\psi_n = a_s^n \phi_s + \sum_l b_l^n \phi_l \tag{IV.1}$$

The Hamiltonian is given by

$$H_{el} = H_{BO} + H_V \tag{IV.2}$$

where H_{BO} corresponds to the Born–Oppenheimer Hamiltonian while H_V contains the nuclear kinetic energy, spin–orbit coupling etc. ϕ_s and $\{p_l\}$ are eigenstates of H_{BO}. Notice how the near degeneracy of levels in a large molecule resembles the situation encountered in the treatment of the pseudo Jahn Teller effect. However, in the present case the coupling between many quasidegenerate zero order states must be considered rather than that between only a few states. The configuration interaction scheme[28] employed herein is similar to the treatments employed many years ago by Rice[17] in the study of predissociation, and by Fano[16] in the study of autoionization. However, it should be stressed that unlike the cases of autoionization and predissociation, in the present case the dense manifold of states is discrete.

The model I would like to discuss is grossly over-simplified but transparent. First we assume that the levels in the $\{\phi_1\}$ manifold are equally spaced with spacing ρ^{-1}. This is not too bad. However, the second assumption is rather serious. We shall assume that all the coupling terms are equal and set $v_{sl} = \langle \phi_s | H_{el} | \phi_1 \rangle = v$. This immediately leads to a simple eigenvalue problem

$$\begin{pmatrix} E_s - E & v & v & \cdots \\ v & E_1 - E & 0 & \cdots \\ v & 0 & E_2 - E & \cdots \\ \vdots & \vdots & \vdots & \end{pmatrix} \begin{pmatrix} a_s \\ b_1 \\ b_2 \\ \vdots \end{pmatrix} = 0 \tag{IV.3}$$

The solutions for the energies E_n of the molecular eigenstates (III.1) can be obtained from the equation

$$E_s - E_n - \pi v^2 \rho \operatorname{cotg} [\pi \rho (E_s - E_n)] = 0 \tag{IV.4}$$

which can be solved numerically. The expansion coefficients representing the weights of the zero order states ϕ_s in the molecular eigenstate ψ_n are given by

$$|a_s^n|^2 = v^2/\{(E_n - E_s)^2 + v^2 + (\pi v^2 \rho)^2\} \tag{IV.5}$$

Two points have to be made here. (a) The choice of the BO basis set to describe the molecular eigenstates is arbitrary but extremely useful. In principle all the eigenstates of H_0 have to be included in equation IV.1. In the BO representation the admixture of higher excited states (whose electronic origin is located above ϕ_s) will be very small. On the other hand, had we chosen a poor zero order representation which involves electronic wavefunctions at a fixed nuclear configuration (the 'crude adiabatic approximation')[34] the admixture of these higher states which are not quasidegenerate with ϕ_s would have become important.

(b) The zero order BO state ϕ_s plays a special role as this state carries oscillator strength from the ground state while the manifold $\{\phi_l\}$ is devoid of oscillator strength. Thus the intensity distribution in absorption will be determined by $|a_s^n|^2$.

The following comments should be made at this point concerning the square of the expansion coefficient IV.5:

(a) The distribution is Lorentzian.

(b) The width Δ of the distribution is given by the dominant term in the denominator which is either v^2 or $(\pi v^2 \rho)^2$.

(c) The condition for strong interstate coupling is

$$v\rho \gg 1 \tag{IV.6}$$

This condition implies, of course, that Δ is determined by $v^2\rho$ rather than by v itself. Inequality IV.6 will be valid provided that one of the following situations is realized:

(c1) Strong interaction with a sparse manifold or alternatively (c2) Relatively weak coupling with a dense manifold. Condition (c1) or (c2) implies that the width of the distribution will be determined by the simple relation

$$\Delta = \pi v^2 \rho \tag{IV.7}$$

(d) The criterion IV.7 for strong mixing is just equivalent to the breakdown of the BO approximation (equation III.1).

When the strong electronic coupling condition applies the intensity (in absorption) of the zero order states ϕ_s is distributed among a manifold of molecular eigenstates. Two cases have to be considered.

(1) *Coarsely spaced molecular eigenstates.* The levels are well separated relative to their radiative and inhomogeneous widths (c1). The individual transitions $\phi_0 \rightarrow \psi_n$ can then be resolved and the corresponding transition moments will be given by

$$|\langle\phi_0|\boldsymbol{\mu}|\psi_n\rangle|^2 = |a_s^n|^2 |\langle\phi_0|\boldsymbol{\mu}|\phi_s\rangle|^2 \tag{IV.8}$$

Thus the intensity is distributed over a coarsely spaced well resolved manifold of states.

(2) *The statistical limit.* The molecular eigenstates are densely spaced relative to their radiative widths and inequality IV.6 is valid. Now, we cannot expect to resolve individual levels in the optical spectrum. The following implications are evident:

(2a) The line shape in absorption is:

$$A(E) \propto \rho |a_s^n|^2 = \frac{v^2 \rho}{(E - E_s)^2 + (\pi v^2 \rho)^2} \tag{IV.9}$$

(2b) The absorption line shape is Lorentzian, the half line width being given by (IV.7).

(2c) The Lorentzian line shape is due to the fact that the background continuum does not carry oscillator strength.

(2d) The situation in this case is completely analogous to the Lorentzian distribution of amplitudes and the line shape obtained for a single resonance which results from the interaction with a 'real' continuum (see section II). Thus the dense quasicontinuum acts as an effective continuum.

This situation will be referred to as *The Statistical Limit.*

To conclude this discussion it is interesting to point out that the description presented herein of the strong interstate coupling in molecules bears a close resemblance to the problem of intermediate structure in nuclear reactions[35]. In the latter case compound states of the nucleus are constructed as a superposition of a single excitation and more complex excitations in a manner completely analogous to equation IV.1. The single excitation which can be reached via the incident channel is referred to as a 'doorway state' and is formally analogous to the BO state ϕ_s in the molecular case.

V. DIFFUSENESS AND INTERFERENCE EFFECTS IN THE ELECTRONIC SPECTRA OF LARGE MOLECULES

We shall now consider the implications of the effects of intramolecular interstate coupling in molecules for the understanding of the intensity distribution in absorption.

(a) *Strongly coupled sparse manifold.* Singlet excited states of small molecules such as SO_2, NO_2 or CS_2 are quasidegenerate with a relatively low density of vibronic states belonging to the lower triplet state and the ground state. However, because of favourable Franck–Condon vibrational overlap factors (due to changes in the molecular geometry in the excited states) the vibronic coupling terms are quite large. Thus, we expect that $v\rho > 1$. The occurrence of vibronic coupling in moderately small molecules implies the redistribution of the intensity of the zero order component ϕ_s, and this redistribution induces the appearance of many new lines (corresponding to all the molecular eigenstates ψ_n) into the spectrum. A situation of this type probably explains the high resolution spectrum of NO_2, where a large number of irregularly spaced lines is observed. The general conclusions cited concur with those of Douglas[36].

(b) *The statistical limit.* The breakdown of the BO approximation in the statistical limit results in line broadening which arises from a differential distribution of intensity among a large number of closely spaced molecular eigenstates. This 'diffuseness' of the spectral lines occurs as an intramolecular phenomenon.

What are the experimental implications of this result for spectroscopic studies of large molecules?

(a) *Intravalence excitations.* Intramolecular coupling with a dense vibronic manifold leads to broadening of higher excited states arising from intravalence excitations in large molecules. To assess the role of intramolecular coupling on the line broadening, 'trivial' broadening effects have to be eliminated. In the elegant work of Ross *et al.*[37] the following 'irrelevant' broadening mechanisms in the gas phase spectra of large molecules were considered: (a) Doppler width, (b) Rotational broadening, (c) Spectral congestion, (d) Photodissociation, (e) Non-radiative decompositions (autoionization and predissociation).

In solid state spectra of molecules trapped in low temperature matrices effects (a), (b) and (c) are missing; however, the following additional sources of broadening have to be taken into account: (f) Phonon broadening, which can be eliminated by utilization of Spolski matrices for the observation of zero phonon lines, (g) Vibrational relaxation of higher vibronic components, (h) Site splittings. Ross *et al.* have systematically demonstrated that no trivial mechanism can explain the diffuseness of higher intravalence excitations in the gas phase. To demonstrate this phenomenon of line broadening we display in *Figures 2* and *3* the absorption spectra for the first and second singlet states of the benzene molecule in an annealed krypton matrix at 20°K as reported by Katz *et al.* The excessive broadening of the second transition $[\Delta(^1B_{1u}) \approx 300\ \mathrm{cm}^{-1}]$ relative to the small broadening in the first singlet

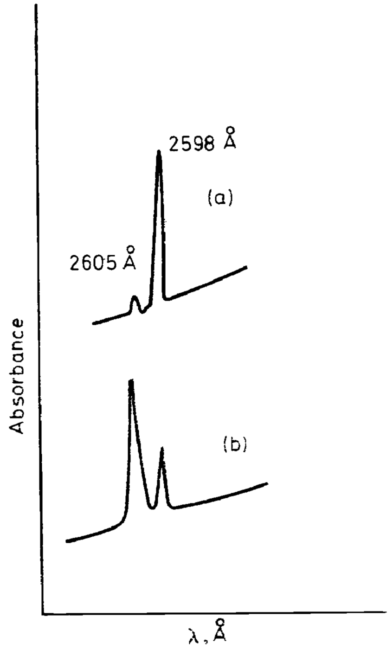

Figure 2. The false origin of the first $^1A_{1g} \rightarrow {}^1B_{2u}$ transition of the benzene molecule in K_{12} matrix at 20°K. Upper curve: annealed matrix deposited at 40°K and measured at 20°K. Lower curve: unannealed matrix deposited and measured at 20°K. The two lines correspond to site splitting. [Data reproduced from B. Katz, M. Brith, B. Sharf and J. Jortner, *J. Chem. Phys.* 52, 88 (1970).]

state [$\Delta(^1B_{2u}) \approx 20$ cm^{-1} which arises from trivial broadening effects] demonstrates the behaviour encountered in the statistical limit.

(c) *Extravalence excitations.* The situation with respect to line broadening is radically different when extravalence excitations, such as transitions to molecular Rydberg states in large molecules are considered. In the gas phase, these absorption lines corresponding to the Rydberg levels are quite sharp[39].

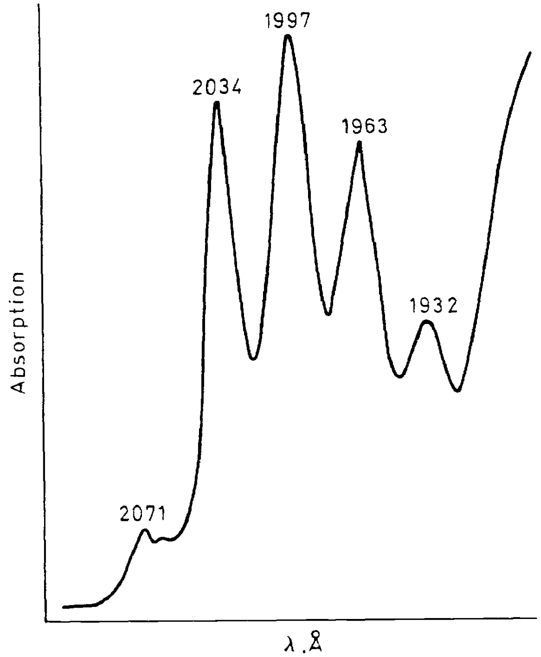

Figure 3. The second transition $^1A_{1g} \rightarrow {}^1B_{1u}$ of the benzene molecule in an annealed krypton matrix at 20°K. [Data reproduced from B. Katz, M. Brith, B. Sharf and J. Jortner, *J. Chem. Phys.* **52**, 88 (1970).]

Thus, for example, the line widths of the 3R Rydberg states of benzene are of the order of a few cm^{-1}, i.e. about one to two orders of magnitude lower than the line widths of the $\pi \rightarrow \pi^*$ $^1A_{1g} \rightarrow {}^1E_{1u}$ transition. The situation is reminiscent of relatively weak vibronic coupling in these Rydberg states. This observation can be easily rationalized by noting that the vibronic coupling terms involve one electron operator of the form $\sum_k \partial v/\partial Q_k$ where v is the molecular coulomb potential energy while $\{Q_k\}$ corresponds to the nuclear coordinates (see section IV). Hence the coupling between the large radius Rydberg orbital and the ground state orbital via the $\partial v/\partial Q_k$ terms is expected to be relatively weak.

(d) *Interference between resonances.* Even when the background quasi-continuum does not carry intensity, interesting effects are expected to be encountered when the widths of several Lorentzians (e.g. several vibrational components in a given electronic state) exceed their spacings. Under these circumstances, we cannot limit ourselves to a single resonance as interference effects between resonances are expected to be encountered[31]. No definite experimental evidence for this effect in molecular spectra is at present available.

(e) *Intermediate structure.* Electronic states of large molecules which are characterized by a small electronic energy gap reveal some interesting structures in optical absorption. Thus the second singlet excited state of the naphthalene molecule (*Figure 4*) which is separated by about 3000 cm^{-1} from the first singlet exhibits some relatively sharp lines superimposed on a diffuse background[40]. This fine-structure is sensitive to the nature of the host crystal (which affects the energy gap) and to the isotopic composition of the molecule. Now, it is obvious that in real life not all the states in the $\{\phi_l\}$ manifold couple to the Q_s with the same strength. In the statistical limit this problem is of minor importance; however, in the present intermediate case these strongly coupled levels will borrow most of the oscillator strength and will be resolved in the spectrum.

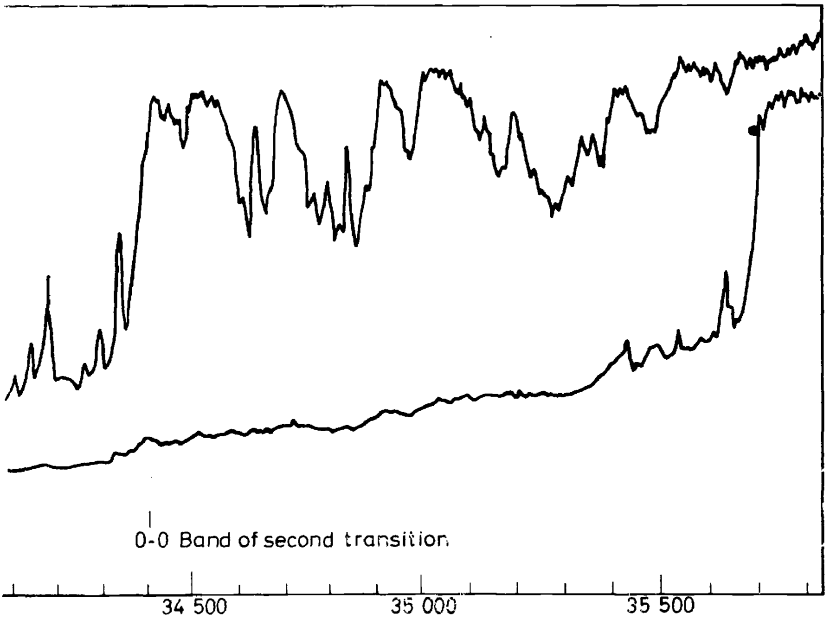

Figure 4. The second ${}^1A_{1g} \rightarrow {}^1B_{2u}$ transition of naphthalene in a durene matrix. [Data reproduced from D. S. McClure, *J. Chem. Phys.* **22**, 1968 (1954).] The fine structure on the O—O band near 34550 cm^{-1} is attributed to intermediate structure.

(f) *Interference with background absorption.* Up to this point we have considered only an isolated resonance. In this case, the 'background' states $\{\phi_l\}$ do not carry oscillator strength so that no Fano-type interference effects are expected to be revealed in the optical spectrum. An interesting relevant situation is encountered when Rydberg levels overlap an inhomogeneously broadened $\pi \rightarrow \pi^*$ transition. Such a situation prevails for the 2*R* Rydberg state of benzene which in the gas phase is quasidegenerate with the ${}^1A_{1g} \rightarrow {}^1E_{1u}$ $\pi \rightarrow \pi^*$ transition[41]. In the case of the naphthalene molecule, the $n = 5$ to $n = 13$ Rydberg levels overlap a medium intensity ($f \sim 0{\cdot}1$) transition located near 62000 cm^{-1}. The gas phase optical spectrum of naphthalene as reported recently by Angus, Christ and Morris reveals several sharp anti-resonances (*Figure 5*). Morris and Jortner discussed the nature of the interference effects which give rise to this unique behaviour in the optical spectrum of an isolated large molecule[42] between resonance and potential scattering.

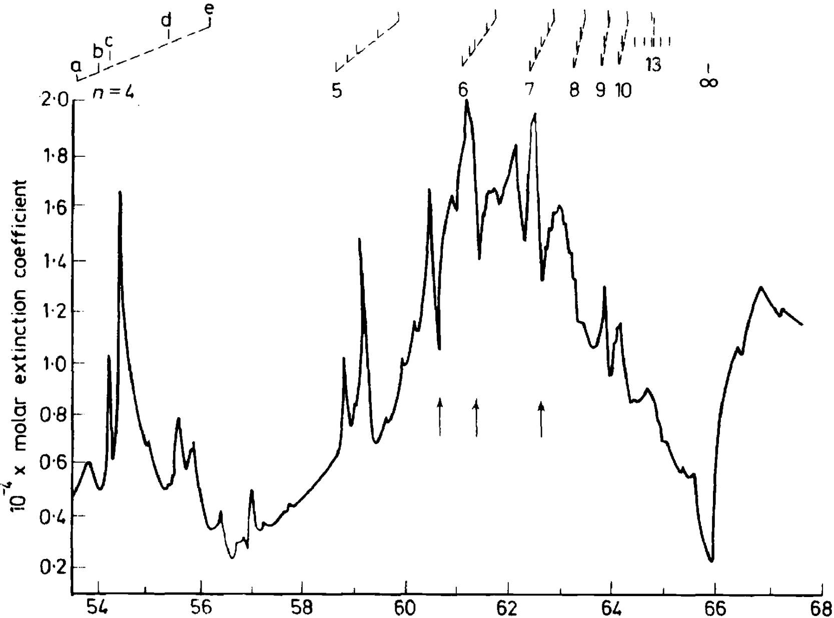

Figure 5. The vacuum u.v. absorption spectrum of the naphthalene molecule in the gas phase as reported by Angus, Christ, and Morris (*Austral. J. Chem.* In press). a, b, c, d, e refer to Rydberg absorption bands of series characterized by different quantum defects and formed with increasing values of the principal quantum number (n). The positions of some of the more obvious anti-resonances are indicated by the vertical arrows (↑).

In essence, the situation is this: assume that we know a set of zero order Born–Oppenheimer states which consists of the following vibronic wavefunctions:

(a) A small set $\{\phi_s\}$, $s = 1, 2 \ldots$, of the vibronic components of a highly excited $\pi \rightarrow \pi^*$ state which carry oscillator strength from the ground state.

(b) A Rydberg ϕ_R which also carries oscillator strength from the ground state.

(c) A dense manifold of states $\{\phi_l\}$, corresponding to all lower electronic configurations, which are quasidegenerate with $\{\phi_s\}$ and with ϕ_R. These $\{\phi_l\}$ states do not carry oscillator strength from the ground state.

The optical properties of the system can now be elucidated by considering the molecular eigenstates Ψ_n of the system which consist of the superposition

$$\Psi_n = \sum_s a_s^n \phi_s + a_R^n \phi_R + \sum_l b_l^n \phi_l \tag{V.1}$$

The off-diagonal matrix elements of the molecular Hamiltonian, H_{el}, in the Born–Oppenheimer representation are:

$$\begin{aligned} \langle \phi_s | H_{el} | \phi_R \rangle &= v_{sR} \\ \langle \phi_s | H_{el} | \phi_l \rangle &= v_{sl} \\ \langle \phi_R | H_{el} | \phi_l \rangle &= v_{Rl} \end{aligned} \tag{V.2}$$

From the experimental observation of the narrow line widths of Rydberg states we can safely assume $v_{sl} \gg v_{Rl}$ for all l and $v_{sR} \sim v_{sl}$. The problem can then be handled by the application of the Fano configuration interactions scheme, as the quasicontinuum $\{\phi_l\}$ is dense enough to act as a real continuum. An effective continuum $\{\psi_j\}$ which carries oscillator strength from the ground state is formed by a superposition of $\{\phi_s\}$ and $\{\phi_l\}$. Then the Rydberg state ϕ_R is coupled to $\{\psi_j\}$. The situation is now completely analogous to the Fano type line shape discussed in section II.

The molecular eigenstates are then given in the form

$$\Psi_n = A_R^n \phi_R + \sum_j B_j^n \psi_j \tag{V.3}$$

while the relevant coupling term is $v_j = \langle \phi_R | H_{el} | \psi_j \rangle$. The line shape function $A(E)$ is given by (see section II)

$$A(E) \propto \frac{(q + \varepsilon)^2}{1 + \varepsilon^2} |\langle \phi_0 | \boldsymbol{\mu} | \psi_j(E) \rangle|^2 \tag{V.4}$$

where $\langle \phi_0 | \boldsymbol{\mu} | \psi_j(\varepsilon) \rangle$ is the dipole matrix element connecting the ground state ϕ_0 with the quasicontinuum states ψ_j near E. The reduced energy parameter, ε, is

$$\varepsilon = (E - E_R - \gamma_1)/\tfrac{1}{2}\Gamma_n \tag{V.5}$$

where γ_1 corresponds to the level shift and Γ_R is the resonance width of ϕ_R due to coupling to the quasicontinuum $\{\psi_j\}$. The line profile index, q, is determined by the relative oscillator amplitudes of the states Ψ_n and ψ_j

$$q = \langle \phi_0 | \boldsymbol{\mu} | \Psi_n \rangle / \pi v_j \rho_j \langle \phi_0 | \boldsymbol{\mu} | \psi_j \rangle \tag{V.6}$$

From qualitative arguments we can assert that $v_{si} \sim v_{sR}$. The following comments should now be made.

(1) Provided that the ratio of the transient moments

$$\langle \phi_0 | \boldsymbol{\mu} | \Psi_n \rangle / \langle \phi_0 | \boldsymbol{\mu} | \psi_j \rangle$$

is of the order of 1 to 10, the absolute value of the line profile index is expected to be of the order of unity and interference effects in absorption are expected to be revealed.

(2) A cursory examination of the Rydberg spectrum of naphthalene (*Figure 5*) reveals that antiresonances in absorption are observed in the

region where $\langle\phi_0|\boldsymbol{\mu}|\psi_j\rangle$ is large (i.e. strong background absorption), as expected on the basis of Fano's theory.

(3) The experimental observation of interference effects in the optical spectrum of a large molecule provides direct experimental evidence for the role of the vibronic quasicontinuum in interstate coupling and in intramolecular relaxation processes.

VI. INTRAMOLECULAR NON-RADIATIVE DECAY

We now study some of the consequences of statistical mixing, and consider the time development of coherently excited states. The molecule in the ground state is subjected to a radiative perturbation, which in the dipole approximation is

$$H'(t) = \boldsymbol{\mu}\cdot\boldsymbol{\varepsilon}\delta(t) \qquad \text{(VI.1)}$$

where $\boldsymbol{\varepsilon}$ is the electric field acting on the molecule. For simplicity we have used a delta function excitation. The excited state at time $t = 0$ can be described in terms of a superposition of molecular eigenstates

$$\Psi_{(t=0)} = \sum_n \mu_{0n}\psi_n \qquad \text{(VI.2)}$$

where μ_{0n} is the transition dipole moment to the molecular eigenstate ψ_n, which can be displayed in the form

$$\mu_{0n} = a_s^n\mu_{s0} \qquad \text{(VI.3)}$$

The wavefunction at time t is given by

$$\Psi(t) = \sum_n \mu_{0n}\psi_n \exp(-iE_nt/\hbar) \qquad \text{(VI.4)}$$

Consider now the time development of the amplitude of the zero order state ϕ_s in the excited state which is given by

$$P(t) = |\langle\phi_s|\Psi(t)\rangle|^2 = (\mu_{0s}^2/\hbar^2)\,|s(t)|^2 \qquad \text{(VI.5)}$$

In the kernel $S(t)$ is

$$S(t) = \sum_n |a_s^n|^2 \exp(-iE_nt/\hbar) \qquad \text{(VI.6)}$$

so that the relaxation rate will be determined by the Fourier transform of the line shape function $|a_s^n|^2$. Under the limiting conditions

$$v\rho \gg 1 \qquad \text{(VI.7)}$$

$$t \ll \hbar\rho \qquad \text{(VI.8)}$$

The relaxation process is exponential

$$P(t) \propto \exp(-t/\tau_{nr}) \qquad \text{(VI.9)}$$

where the non-radiative decay time is given by the Fermi Golden Rule

$$\tau_{nr} = \hbar/2\pi v^2\rho \qquad \text{(VI.10)}$$

Up to this point we have considered the relaxation process within the framework of a simple model system. A more general treatment can easily be performed, which as in the case of the absorption coefficient (section V) will lead to a more general criterion for the validity of the statistical limit. Consider again the alternative representation of $\Psi(t)$ in terms of the BO basis set. Making use of the orthonormality properties of the expansion coefficients a_s^n and b_l^n in equation IV.1, the initial state VI.2 can then be represented in the form

$$\Psi_{(t=0)} = \mu_{0s}\phi_s \tag{VI.11}$$

The time evolution of the excited state can now be displayed as the time dependent superposition

$$\Psi(t) = A(t)\phi_s + \sum_l B_l(t)\,\phi_l \tag{VI.12}$$

Making use of conventional time dependent perturbation theory results in the equation of motion for the amplitude $A(t)$

$$\begin{aligned} \hbar^2\dot{A}(t) &= -\int_0^t \mathrm{d}t' A(t') \sum_l |v_{sl}|^2 \exp\left[i(E_l - E_s)(t - t')/\hbar\right] \\ &= -2\pi \iint \mathrm{d}E\,\mathrm{d}t' A(t') \sum_l |v_{sl}|^2 \exp\left[i(E - E_s)(t - t')/\hbar\right]\, \delta(E - E_l) \\ &= -\iint \mathrm{d}E\,\mathrm{d}t' A(t')\,\Delta(E) \exp\left[i(E - E_s)(t - t')/\hbar\right] \end{aligned} \tag{VI.13}$$

where

$$\Delta(E) = 2\pi \sum_l |v_{sl}|^2\, \delta(E - E_l) \tag{VI.14}$$

In the statistical limit $\Delta(E)$ is the slowly varying function of the energy[33,43] and thus we set it to be a constant $\Delta = \Delta(E)$. The expression for $\Delta(E)$ in the statistical limit is just the half line width IV.7. One now immediately obtains the exponential decay law

$$|A(t)|^2 = |A(0)|^2 \exp(-t/\tau_{nr}) \tag{VI.15}$$

VII. IRREVERSIBLE INTRAMOLECULAR DECAY IN THE STATISTICAL LIMIT

When the background density of vibronic states in a large molecule is extremely high this manifold is expected to act as an effective continuum with respect to line broadening and to intramolecular relaxation. The general criteria obtained for the statistical limit can be summarized as follows:

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

$$t \ll \hbar\rho \tag{VII.2}$$

$$\Delta(E) = 2\pi \sum_l |v_{sl}|^2\, \delta(E - E_l) \tag{VII.3}$$

is smooth.

It should be borne in mind that while conditions VII.1 and VII.2 were obtained for a simple model system, equation VII.3 is general and model independent. The simple model calculations provide us with physical insight concerning the general features of the non-radiative decay process which can be summarized as follows:

(a) Equation VII.1 provides a necessary condition for line broadening and for the occurrence of intramolecular non-radiative decay; however, this energetic condition is by no means sufficient.

(b) The relation VII.2 establishes the time scale for the occurrence of the non-radiative decay. In fact $t_R = \hbar\rho$ corresponds to the recurrence time for the decay of the zero order level ϕ_s into the quasicontinuum. For times longer than t_R, the amplitude of ϕ_s in $\Psi(t)$ will increase towards its initial value. However, for large molecules these recurrence times considerably exceed the time scale of any experiment.

(c) The definition of the recurrence time introduces the notion of irreversibility of the intramolecular radiationless process. This recurrence time introduces a Pioncaré cycle for the irreversible process. An intramolecular radiationless process in the limit of a sufficiently large density of vibronic levels corresponds to an irreversible process on a time scale which is shorter than $\hbar\rho$

Table 3. Parameters descriptive of radiationless transitions in large molecules

System	τ_{nr} sec	v cm^{-1}	ρ cm	$v\rho$	$\hbar\rho$ sec
Anthracene ${}^1B_{2u}$–${}^3B_{2u}$ $E = 12000$ cm^{-1}	5×10^{-9}	6×10^{-7}	5×10^{10}	3×10^{10}	0·25
Naphthalene ${}^3B_{2u}$–${}^1A_{1g}$ $E = 20000$ cm^{-1}	2	10^{-14}	8×10^{15}	80	4×10^4
Azulene ${}^1B_1$–${}^1A_1$ $E = 14000$ cm^{-1}	6×10^{-11}	2×10^{-5}	10^{11}	2×10^6	0·5
Benzene ${}^1B_{2u}$–${}^3B_{1u}$	10^{-6}	$1{\cdot}5 \times 10^{-5}$	8×10^4	1·5	4×10^{-7}

(d) Electronic relaxation in large molecules (see *Table 3*) obeys the restrictions VII.1 and VII.2. Thus these can be considered as legitimate intramolecular relaxation phenomena.

Obviously the simple relations VII.1 and VII.2 are gross oversimplifications based on a 'coarse graining' procedure. Let us consider now a real physical system where the necessary and sufficient condition for irreversible non-radiative decay is given by the 'smoothness' of $\Delta(E)$ (equation VII.3). This restriction is more general and enables us to ascertain the salient features of the intramolecular decay in a large molecule. We note that a 'hidden assumption' involved in the simple model calculations implies that the zero states $\{\phi_l\}$ have zero widths. If these levels are characterized by finite widths

$\{\Gamma_l\}$ then the resonance width should be altered by replacing each delta function in the sum VII.3 by a Lorentzian[33, 43]

$$\Delta(E) = \sum_l \frac{(\Gamma_l/2)\,|v_{sl}|^2}{(E - E_l)^2 + (\Gamma_l/2)^2} = I_m \sum_l \frac{|v_{sl}|^2}{(E - E_l) + i\Gamma_l/2}$$

Obviously when $\Gamma_l \to 0^+$ we regenerate equation VII.3. In order to consider an upper limit t_m for the decay process, Freed[43] adds an imaginary part $i\hbar/t_m$ to the energy E so that

$$E \to E + i\hbar/t_m \tag{VII.4}$$

Such a trick is common in scattering theory and amounts to describing the decay process in terms of a (complex) Green's function $G(E + i\hbar/t_m)$. Usually one sets $\hbar/t_m \to 0^+$; however, as pointed out by Freed[43], this is not really necessary, as the introduction of the imaginary factor introduces a term of the form $\exp\,(-\,t/t_m)$ in the decay process and thus erases all the behaviour of the system for long times, e.g. $t \gg t_m$.

The general form of the resonance width is then

$$\Delta(E) = \sum_l \frac{|v_{sl}|^2 \left(\dfrac{\Gamma_l}{2} + \dfrac{\hbar}{t_m}\right)}{(E - E_l)^2 + \left(\dfrac{\Gamma_l}{2} + \dfrac{\hbar}{t_m}\right)^2} \tag{VII.5}$$

This result exhibits a superposition of generalized Lorentzians, each characterized by the strength $|v_{sl}|^2$ and by the width $(\frac{1}{2}\Gamma_l + \hbar/t_m)$.

A general condition for the smoothness of $\Delta(E)$ is that the widths of successive Lorentzians considerably exceed their spacings. Stated mathematically

$$\Gamma_l/2 + \hbar/t_m \gg E_{l+1} - E_l \sim \hbar/\rho \tag{VII.6}$$

Hence the general condition for irreversibility will be displayed in the form

$$\rho^{-1} \ll \hbar/t_m + \tfrac{1}{2}\Gamma_l \tag{VII.7}$$

The following cases should now be considered.

(a) Intersystem crossing in the lowest triplet in an isolated molecule. In this case the line widths Γ_l are negligibly small, as the levels $\{\phi_l\}$ do not carry oscillator strength to the ground state or to any of its vibronic components. Setting $\Gamma_l \to \mathrm{O}^+$ one immediately obtains the simple relation VII.2.

(b) Internal conversion in an isolated molecule. Now the dense manifold is connected by non-vanishing radiative coupling terms to high vibronic levels of the ground state. This is, of course, the reason for the observation of fluorescence radiation from the second (and any higher) singlet to high vibrational levels of the ground state. Hence $\Gamma_l > 0$. Two pertinent cases have to be considered:

(a) A large energy gap between two excited states of the same multiplicity. Thus for example the first $(^1B_{2u})$ and the second $(^1B_{3u}^+)$ singlet excited states of anthracene are separated by $\Delta E = 15000\ \mathrm{cm}^{-1}$. In this case we expect that

$$\Gamma_l \gg \rho^{-1} \tag{VII.8}$$

and the function $\Delta(E)$ is smooth on any time scale as we can set $t_m \to \infty$.

(b2) A small energy gap between two states of the same multiplicity. A good example in this category involves the $^1B_{2u}$ and the $^1B_{3u}$ excited states of the naphthalene molecule where the energy gap is $\Delta E = 3400\ \mathrm{cm}^{-1}$. In this case $\rho^{-1} \sim 10^{-3}\ \mathrm{cm}^{-1}$. Now $\rho^{-1} \gg \Gamma_l$ and again the condition $t_m \ll \hbar\rho$ has to be applied for the decay of the $^1B_{2u}$ state.

(c) Internal conversion and intersystem crossing in a medium. Getting away from the isolated molecule and considering for a moment the medium effects at low temperatures, we note that now Γ_l has a substantial contribution (10^{-2} to $10^{-1}\ \mathrm{cm}^{-1}$) due to vibrational relaxation. Hence the condition $\Gamma_l \gg \rho^{-1}$ is usually satisfied. We can neglect t_m^{-1} with respect to Γ_l and the decay process is irreversible for long times. Obviously, molecular states which correspond to intermediate cases in the low pressure gas phase will reveal irreversible decay when embedded in a medium.

To summarize this discussion, the following relations are of interest:

(a) For the case of intersystem crossing

$$\tau_{\mathrm{rad}}(l) \gg \hbar\rho \gg t_m \gg \tau_{\mathrm{rad}}(s)$$

(b1) For internal conversion (large energy gap)

$$\infty \leftarrow t_m \gg \hbar\rho \gg \tau_{\mathrm{rad}}(l) \sim \tau_{\mathrm{rad}}(s)$$

(b2) For internal conversion (small energy gap)

$$\tau_{\mathrm{rad}}(s) \sim \tau_{\mathrm{rad}}(l) \gg \hbar\rho \gg t_m$$

(c) For a molecule in a dense medium

$$\infty \leftarrow t_m \gg \hbar\rho \gg \tau_{\mathrm{rad}}(s) \gtrsim \tau_{v,r}(l)$$

where τ_{rad} and $\tau_{v,r}$ correspond to lifetimes due to radiative decay and to vibrational relaxation, respectively.

VIII. THE COUPLING BETWEEN RADIATIVE AND NON-RADIATIVE PROCESSES IN LARGE MOLECULES

A large bulk of physical information now available concerning intramolecular coupling and electronic relaxation in polyatomic molecules comes from lifetimes of molecular luminescence. Clearly, a complete theoretical description of the radiationless transition process should emerge from the description of the radiative decay. It should be recalled that we are now considering a phenomenon associated with the decay of a manifold of a large number of closely spaced levels (e.g. the molecular eigenstates).

Interference effects in the decay of closely spaced atomic or molecular states are intimately related to the fundamental principles of quantum theory and have been known for many years. The depolarization of resonance radiation associated with the crossing of Zeeman levels at zero magnetic field was discovered by Hanle[44] in 1928, and has been used to determine the lifetimes of excited atomic states (see *Figure* 6). The level crossing technique[46–50], which is of more recent vintage, utilizes interference effects in the resonance fluorescence between two levels which are split in zero magnetic field by fine and hyperfine interactions, and which cross because of the application of an external magnetic field. When the two levels are closer in energy than their radiative widths, spatial interference in resonant scattering can be observed, provided that the two levels are connected to the ground state by allowed dipole transitions. The two levels may be prevented from crossing by the presence of a small perturbation which couples the zero order states, so that these levels will then repel each other. Although crossing does not occur in this situation (called level anti-crossing), it is still possible to observe changes in the resonance fluorescence intensity resulting from interference effects between the levels. The physical situation encountered in the cases of level crossing and anti-crossing is analogous to the phenomena observed in a classical double slit interference pattern, where the same photon can be shared between the two slits. It should be noted that in the double slit experiment the total light intensity is, of course, conserved and the separation of the slits leads only to the modification of the distribution of the light intensity. Thus, in the level crossing experiment only the angular distribution of the re-emitted radiation is modified, while the total scattered intensity is unaffected.

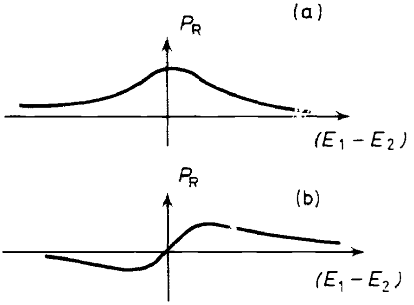

Figure 6 (top). Schematic representation of fluoresence depolarization [*Proc. Phys. Soc.* **92**, 797 (1967)] in a level crossing experiment. P_R represents the partial fluorescence yields while E_1–E_2 corresponds to the levels spacing: (a) A Lorentzian yield curve; (b) A dispersion yield curve.

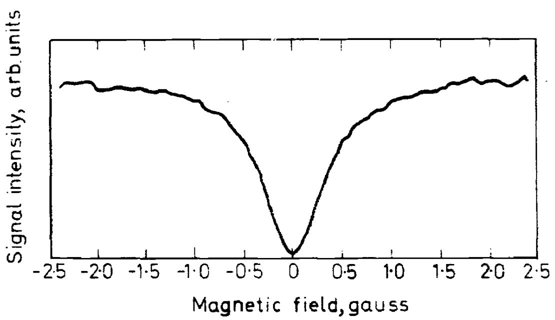

Figure 6 (bottom). Experimental results for the level crossing in NO. Figure reproduced from D. R. C. Crosley and R. N. Zare, *Phys. Rev. Letters*. **18**, 942 (1967).

A closely related phenomenon to that described is the observation of quantum beats[51–53] in the radiative decay of a set of coherently excited states (see *Figure 7*). Since transitions to the ground state can take place via two or more channels, interference effects may be observed.

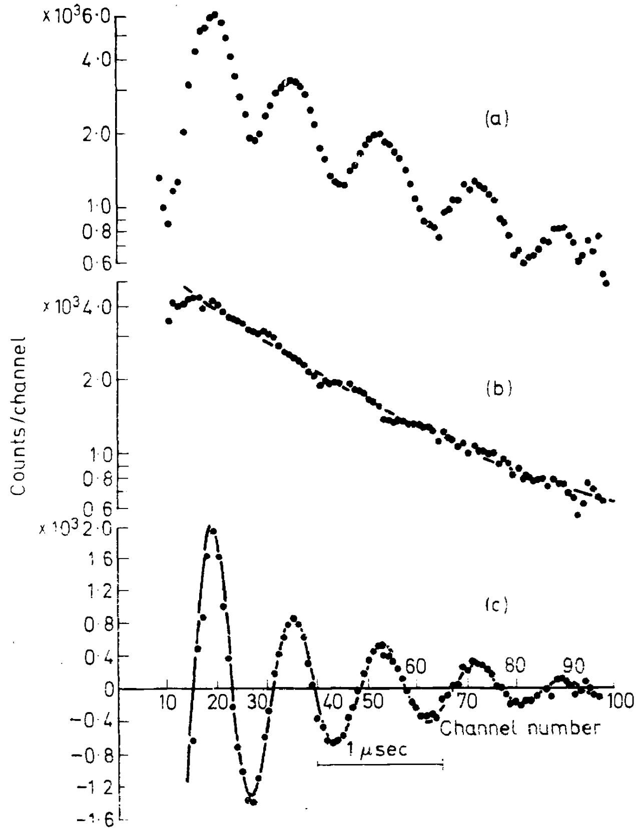

Figure 7. The fluorescence decay of cadmium vapour in a magnetic field. (a) Experimental data exhibiting the phenomenon of quantum beats; (b) The exponentially decaying component; (c) The decaying modulated component (This figure is reproduced from the work of J. N. Dodd, W. J. Sandle and D. Zisserman, *Proc. Phys. Soc.* **92**, 797 (1967).

Consider, now, the experimental conditions required for the observation of quantum beats. The resolving power of the photon counting apparatus must be inadequate to resolve the two transitions, because the resolution process involves the separation of the two channels, thus eliminating the possibility of interference. Of course, energy resolution is only possible provided that the spacing between the levels exceeds their radiative widths. It is interesting to ask whether in some cases the two channels can be identified by an alternative method which does not involve energy resolution[30]. The quantum beat signals reported in the literature involve the interference between two ($m = 1$ and $m = -1$) Zeeman components split by a magnetic field. In this case the two decay channels are characterized by different angular polarizations (e.g. photon angular momentum), since the $m = 1$ and the $m = -1$ levels decay by the emission of right hand and left hand circular polarized radiation, respectively. Thus, in principle, one can distinguish experimentally between the two decay channels by inserting a quarter wavelength plate and a polarizer in front of the photon counter. We shall refer[30] to the case of two (or more) decay channels which can be identified by a method which does not involve energy resolution as a system of *distinguishable levels.* On the other hand, one often encounters the case wherein a number of decaying levels emit photons with the same polarization. As an example, consider the degenerate zero order BO singlet and triplet states of a small molecule. The molecular eigenstates contain equal mixtures of singlet and triplet components and are split by the spin–orbit interaction. The decay channels, which now all have the same polarization, cannot be separated by a method similar to that described above for the Zeeman levels. We shall refer to this case as a system of *indistinguishable levels.*

The theoretical framework for the description of level crossing experiments mentioned is provided by the Breit formula[45]. Using the language of time dependent perturbation theory, it is usually assumed that the states involved are eigenfunctions of a molecular Hamiltonian and that they may be damped by coupling to the radiation field. In the conventional theory it is also assumed that the damping matrix is diagonal, and each state decays with its own lifetime so that the damping of each excited state can be accounted for by the inclusion of an independent exponential decay factor in the amplitude of each state. This assumption simply involves an *ad hoc* generalization of the Wigner–Weisskopf[54] exponential decay law to the case of a number of closely spaced levels.

It was pointed out by Bixon, Jortner and Dothan[30] that the treatment presented above of the level crossing experiment is applicable only to the description of the decay of a manifold of distinguishable levels. The assumed independent decay of each level is not valid when the levels concerned are indistinguishable.

In general, optical interference experiments cannot be treated by displaying the damping matrix in diagonal form[30, 55], because the *ad hoc* assumption of diagonality can be shown to violate a basic conservation law, whereupon the molecule will act as a 'photon sink' or a 'photon source'. The general treatment based on the correct non-diagonal form of the damping matrix led to the following conclusions:

(a) In a system of distinguishable levels the observation of quantum beats requires that the photon counting procedure shall cover only a limited solid angle. Interference effects are observed only for partial transition probabilities. The spatial integration over all angles and polarizations results in the vanishing of the interference terms.

(b) On the other hand, for a system of indistinguishable levels the quantum beats also appear in the total integrated emission rate.

We shall now consider a simplified version of the theory of the radiative decay of polyatomic molecules[29–33]. One pedantic comment should be made at this point concerning the molecular eigenstates representation. When radiative decay processes are considered the molecular eigenstates are no longer proper eigenstates of the Hamiltonian

$$H = H_{el} + H_r + H_{int.} \tag{VIII.1}$$

As before, the molecular Hamiltonian, H_{el}, consists of the BO term H_{BO} and an intramolecular perturbation H_v (vibronic, spin orbit, etc.). H_r is the Hamiltonian corresponding to the free radiation field while H_{int} is the radiation–matter interaction term. The time evolution of a non-stationary state of the system can be described either in terms of the eigenstates of H_{BO} (the BO basis set) or of H_{el} (the molecular eigenstates basis). Obviously, the choice of the basis set is merely a matter of convenience and thus does not affect any observable quantities. The questions that have to be answered by a complete study of the radiative decay of a polyatomic molecule are as follows:

(a) Are simple kinetic schemes, as applied for years by the experimentalist, adequate?

(b) When will interference effects be observed in the radiative decay?

(c) How can details of the decay process (e.g. quantum yields and experimental radiative lifetimes) be elucidated?

In order to handle the radiative decay of a large molecule, consider the initial excited state at time $t = 0$ which is a non-stationary state of H, and no photons are present. The initial excited molecular state $\Psi_m(0)$ can always be expressed as a superposition of either the molecular eigenstates $\{\psi_n\}$ or the BO states ϕ_s, $\{\phi_l\}$. The initial state of the system is

$$\begin{aligned}\Psi(0) &= \Psi_m(0)\,|vac\rangle \\ &= \sum_n a_n(0)\,|\psi_r; vac\rangle \\ &= b_s(0)\,|\phi_s; vac\rangle + \sum_{l \neq s} b_l(0)\,|\phi_l; vac\rangle\end{aligned} \tag{VIII.2}$$

where $|vac\rangle$ is the zero photon state. In many cases of physical interest the initial excited state of the system can be visualized to be prepared by a coherent excitation by a short light pulse or by a chaotic broad band source whereupon

$$\begin{aligned}a_n(0) &= \langle\phi_s|\psi_n\rangle \\ b_l(0) &= \delta_{ls}\end{aligned} \tag{VIII.3}$$

Obviously, the completeness of the molecular eigenstates basis and the fact that ϕ_s is the only state which carries oscillator strength immediately imply that in this case

$$\Psi(0) = \sum_n \langle\phi_s|\psi_n\rangle|\psi_n; vac\rangle \equiv |\phi_s; vac\rangle \tag{VIII.4}$$

We now proceed to provide a simple description of the decay process. A more elaborate treatment was recently provided by Freed and Jortner. The final states of the system consist of one photon ground state $\phi_{\boldsymbol{k},\boldsymbol{e}} = |\phi_0\ \boldsymbol{k}, \boldsymbol{e})$ where ϕ_0 is the ground electronic state while $\boldsymbol{k}$ and $\boldsymbol{e}$ correspond to the wave vector and the polarization vector of the emitted photon. The time dependent state of the system is given by

$$\begin{aligned}\Psi(t) &= \sum_n a_n(t)\,|\psi_r; vac\rangle + \sum_k \sum_e C_{ke}(t)\,|\phi_0; \boldsymbol{k}, \boldsymbol{e}\rangle \\ &\equiv b_s(t)\,|\phi_s; vac\rangle + \sum_{l \neq s} b_l(t)\,|\phi_l; vac\rangle \\ &\qquad + \sum_k \sum_e d_{ke}(t)\,|\phi_0; \boldsymbol{k}, \boldsymbol{e}\rangle \qquad \text{(VIII.5)}\end{aligned}$$

with the initial conditions given by equations VIII.3 and $C_{\boldsymbol{k},\boldsymbol{e}}(0) = d_{\boldsymbol{k},\boldsymbol{e}}(0) = 0$ for all $\boldsymbol{k}$ and $\boldsymbol{e}$. The probability $A_s(t)$ for the decay of the system is given by

$$A_s(t) = |\langle \Psi(0)|\Psi(t)\rangle|^2 \qquad \text{(VIII.6)}$$

Making use of the initial conditions VIII.3 we get for the decay rate of the excited state, which corresponds to the total number of photons emitted per unit time,

$$\dot{Q}(t) = \frac{\Gamma_s}{\hbar}|A_s(t)|^2 = \frac{\Gamma_s}{\hbar}|\sum_n a_n(t)\,a_n(0)|^2 \equiv \frac{\Gamma_s}{\hbar}|b_s(t)|^2 \qquad \text{(VIII.7)}$$

where Γ_s is the radiative width of the zero order state ϕ_s. Equation VIII.7 reveals the following features of the decay process:

(a) When the BO basis set is employed we have to focus our attention on the decay channels of the zero order state ϕ_s.

(b) When the molecular eigenstates basis is used the decay rate contains a contribution from interference effects between closely spaced levels.

Equation VIII.5 provides us with a proper description of the time dependent compound state of the system which is presented as a superposition of time independent zero order states. In order to elucidate the features of the decay process we have to establish the equations of motion for the coefficients $\{a_n(t)\}$ or $\{b_s(t), b_l(t)\}$. This can be accomplished by the following methods:

(a) A self-consistent extension of the Wigner–Weisskopf method[54] to account for the decay of a large number of levels[30].

(b) The 'unitary relations' method employed in the field of elementary particles physics[56, 57] which is based on general conservation rules[30].

(c) The Fano configuration interaction method[16] whereupon the radiation field provides a dissipative continuum[30, 31].

(d) The Green's function method adapted to the decay of a large number of metastable levels[33].

All these methods lead to the following result: let the time dependent compound state be given in the general form

$$\Psi(t) = \sum_j \alpha_j(t)\,|\chi_j; vac\rangle + \sum_k \sum_e \beta_{k,e}(t)\,|\phi_{k,e}\rangle \qquad \text{(VIII.8)}$$

where the set χ_j is any general complete set (molecular eigenstates, BO basis or other). If we define the row vector

$$\boldsymbol{\alpha}(t) = \begin{pmatrix}\alpha_1(t)\\ \alpha_2(t)\\ \vdots\end{pmatrix} \qquad \text{(VIII.9)}$$

the equation of motion is

$$i(\mathrm{d}/\mathrm{d}t)\,\boldsymbol{\alpha}(t) = \boldsymbol{H}_{eff}\boldsymbol{\alpha}(t) \qquad \text{(VIII.10)}$$

$$\boldsymbol{H}_{eff} = \boldsymbol{H}_{el} - \tfrac{1}{2}i\boldsymbol{\Gamma} \qquad \text{(VIII.11)}$$

where $\boldsymbol{\Gamma}$ corresponds to the damping matrix. In discussing phenomena of radiative decay it is customary to introduce the radiative lifetimes of states. The damping matrix $\boldsymbol{\Gamma}$ is defined for some (arbitrary) set of zero photon excited states in the form

$$\Gamma_{jj'} = 2\pi/\hbar \sum_{e} \int \mathrm{d}\Omega_k \, \langle \chi_j; vac \,|H_{int}|\, \phi_{k,e} \rangle \times \langle \phi_{k,e} \,|H_{int}|\, \chi_j; vac \rangle \, \rho_k \quad \text{(VIII.12)}$$

where

$$\sum \int \mathrm{d}\Omega_k$$

corresponds to the integration over all propagation directions in the k space and summation over all polarization directions of the emitted photon. ρ_k is the density of photon states. Thus equations VIII.10 and VIII.12 provide us with the general decay law for a manifold of closely spaced levels. The following comments are now in order:

(a) The damping matrix provides a generalization of the Fermi 'Golden Rule' transition rates.

(b) The damping matrix $\boldsymbol{\Gamma}$ is in general non-diagonal.

(c) The matrix $\boldsymbol{H}_{eff}$ which determines the decay is non-hermitian (or rather antihermitian). This observation can be rationalized by noting that equation VIII.10 factors out only a finite number of (zero photon) states of the system instead of considering the infinite number of states which characterize the Hamiltonian VIII.1.

(d) When a non-diagonal representation of $\boldsymbol{H}_{eff}$ is employed (which is usual) the states $|\chi_j; vac\rangle$ do not decay independently, e.g. they cannot be characterised by simple exponential decays. This is so provided that the off-diagonal terms of the damping matrix are large, so that

$$\Gamma_{jj'} \gtrsim |E_j - E_{j'} - \tfrac{1}{2}i(\Gamma_{jj} - \Gamma_{j'j'})| \quad \text{(VIII.13)}$$

This effect is known in level crossing, where the decaying states are indistinguishable (e.g. characterized by the same symmetry).

(e) In principle, one can find a set of zero photon states characterized by exponential decay, provided that $\boldsymbol{H}_{eff}$ is diagonalized by a complex orthogonal matrix $\boldsymbol{S}$, so that

$$\boldsymbol{S}\boldsymbol{H}_{eff}\boldsymbol{S}^{-1} = \boldsymbol{\Lambda} \quad \text{(VIII.14)}$$

The real and imaginary parts of the diagonal matrix $\boldsymbol{\Lambda}$ provide us with the energies and lifetimes respectively of the states for which $\boldsymbol{H}_{eff}$ is diagonal.

(f) In the BO basis $\{\phi_s, \phi^l\}$ the effective Hamiltonian is

$$\begin{pmatrix} (E_s - \tfrac{1}{2}i\Gamma_s) & v_{s1} & v_{s2} & \cdots \\ v_{s1} & E_1 & 0 & \cdots \\ v_{s2} & 0 & E_2 & \cdots \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{pmatrix} \quad \text{(VIII.15)}$$

so that $\boldsymbol{H}_{el}$ is off-diagonal while the damping matrix is diagonal.

(g) For the molecular eigenstate $\{\psi_n\}$ basis the effective Hamiltonian is given in the form

$$\begin{pmatrix} E_1 - \frac{1}{2}i\Gamma_{11} & -\frac{1}{2}i\Gamma_{12} & \cdots \\ -\frac{1}{2}i\Gamma_{21} & E_2 - \frac{1}{2}i\Gamma_{22} & \cdots \\ . & . & \\ . & . & \\ . & . & \end{pmatrix} \qquad \text{(VIII.16)}$$

Now H_{el} is diagonalized; however, we pay the price by having the damping matrix in a non-diagonal representation.

Table 4. Long radiative lifetimes of small molecules

Molecule	*Transition*	$\tau_{(\text{expt})}$ sec	$\tau_{(\text{integrated } f)}$ sec
NO_2	$^1B_2$–$^1A_1$ 4300 Å	44×10^{-6}	$0{\cdot}3 \times 10^{-6}$
SO_2	3000 Å $^1B_1$–$^1A_1$	42×10^{-6}	$0{\cdot}2 \times 10^{-6}$
CS_2	3200 Å $^1\Sigma$–$^1\Sigma$ $^1\Pi$–$^1\Sigma$	15×10^{-6}	3×10^{-6}

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

This general formalism can be immediately applied for the following cases:

(a) Long radiative lifetimes of triatomic molecules (see *Table 4*). Under these circumstances the levels in the $\{\phi_l\}$ manifold are coarsely spaced, considerably exceeding the radiative widths of the molecular eigenstates. Application of the molecular eigenstates basis implies that for the off-diagonal elements of the damping matrix

$$\Gamma_{nn1} \leqslant |E_n - E_{n'} - \tfrac{1}{2}i(\Gamma_{nn} - \Gamma_{n'n'})| \qquad \text{(VIII.17)}$$

so that these off-diagonal terms are negligible. Thus in this limit we get

$$(H_{eff})_{nn'} = (E_n - \tfrac{1}{2}i\Gamma_n)\,\delta_{nn'} \qquad \text{(VIII.18)}$$

where Γ_n is the radiative width of the molecular eigenstate ψ_n so that

$$\Gamma_n \equiv \Gamma_{nn} = \Gamma_s\,|\langle\psi_n|\phi_s\rangle|^2 = \Gamma_n\,|a_s^n|^2 \qquad \text{(VIII.19)}$$

where the coefficient a_s^n is given by equation IV.1.

The decay law is given by a sum of exponentials

$$\dot{Q}(t) = \sum_n |a_n(0)|^2 \exp(-\Gamma_n t/\hbar) \qquad \text{(VIII.20)}$$

Since $|a_s^n|^2 < 1$ we have from equation VIII.19

$$\Gamma_n < \Gamma_s \quad \text{for all } n \qquad \text{(VIII.21)}$$

We thus have the explanation for the anomalously long radiative lifetimes of small molecules[30]. The occurrence of vibronic coupling in triatomic molecules implies the redistribution of intensity of the zero order component ϕ_s and the 'dilution' of the decay times of the molecular eigenstates each of which now decays independently.

(b) Short radiative lifetimes of large molecules (see *Figure 8*). In the statistical limit the decay law is

$$\dot{Q}(t) = (\Gamma_s/\hbar)\exp(-\{(\Gamma_s + \Delta)/\hbar\}\, t) \qquad \text{(VIII.22)}$$

Thus the radiative decay in the statistical limit is exponential and the experimental radiative decay time consists of independent contributions from non-radiative and radiative components.

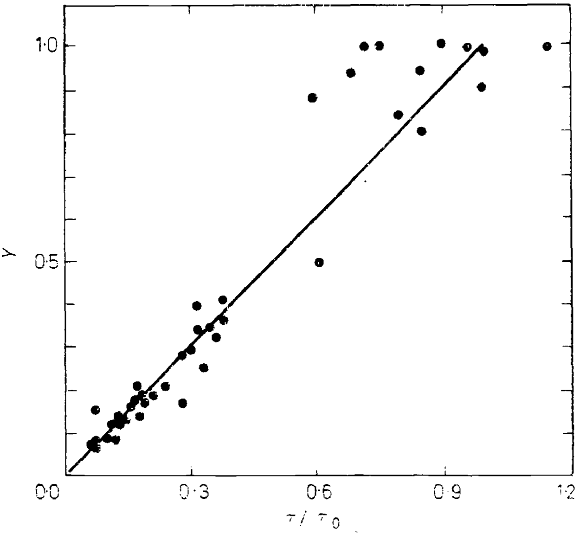

Figure 8. Experimental radiative decay times and fluorescence quantum yields for aromatic molecules in inert solvents. [Data from: (a) I. B. Berlman, *Handbook of Fluorescence Spectra*, Wiley: New York (1965): (b) Strickler and Berg, *J. Chem. Phys.* **37**, 814 (1962).]

The quantum yield determined on a time scale appreciably shorter than the recurrence time is given in the form

$$Y = \Gamma_s/(\Gamma_s + \Delta) \qquad \text{(VIII.23)}$$

This result does not imply that the large molecule acts as a photon trap, but rather that only a fraction Y of photons will be emitted on the time scale $t \ll \hbar\rho$ or, stated more generally, on the time scale $t \ll t_m$ (see section VII).

To conclude this discussion of the statistical limit we should notice that two legitimate complementary descriptions of the decay of an excited state of a large molecule can be given:

(1) Interference effects between a large number of closely spaced zero order levels (e.g. the molecular eigenstates) give rise to the shortening of the radiative lifetime.

(2) The excited state corresponds to a resonance which is coupled to two different continua. Just as the photon continuum allows for irreversible radiative decay, the $\{\phi_l\}$ manifold acts as a second dissipative channel.

To conclude this discussion we shall briefly consider the general features of radiative decay of polyatomic molecules.

Intramolecular coupling, intramolecular relaxation and no observable radiative interference effects are expected in the following cases:

(a) *Intramolecular radiationless decomposition.* In the well understood cases of predissociation and autoionization we encounter a conventional relaxation phenomenon. Line broadening is observed and the branching ratio for fluorescence is lower than unity. Obviously, the reduction of emission is a much more sensitive criterion for radiationless decomposition than line broadening.

(b) *The statistical limit.* In large molecules the dense quasi-continuum can be considered for all practical purposes as an effective decay channel. Line broadening and intramolecular relaxation effects are exhibited in this limit.

Intramolecular coupling will be exhibited while no intramolecular relaxation and no radiative interference effects will be observed in the following cases:

(c) *Accidental degeneracy* of two levels corresponding to different electronic terms in a diatomic molecule. A small molecule may exhibit the effects of strong vibronic perturbations between pairs of accidentally degenerate levels. These perturbations considerably exceed the radiative width. A complex spectrum results which is sensitive to external fields; however, no radiative interference effects will be exhibited. A typical example involves $^2\Sigma - ^2\Pi$ mixing in the CN molecule[58].

(d) *Sparse intermediate case.* The density of vibronic states in the $\{\phi_l\}$ manifold is rather small ($\rho_{\sim}$/cm); however, the coupling matrix elements are large. The situation corresponds to the coarse strongly coupled distribution discussed in section IV. These small molecules will exhibit a long radiative lifetime[35].

Finally we have to consider the circumstances whereupon radiative interference effects will (or may) be observed:

(e) *The resonance limit.* A pair of levels which we split by intrinsic or external perturbations and which are spaced within their radiative widths will exhibit quantum beats in the radiative decay.

(f) *The dense intermediate case.* A small electronic energy gap in a large molecule (e.g. the second excited singlet state of naphthalene and pyrene which are separated by 3000 cm^{-1} from the first singlet). In this case one has to consider separately the weak and strong coupled levels in the vibronic manifold $\{\phi_l\}$. Under these circumstances the width of the zero order state is shared between several closely spaced resonances. Several interesting effects can be now encountered for the radiative decay resulting from intersystem crossing in the isolated molecule which corresponds to this situation. Emission will take place from the highly excited vibronic component of the lowest singlet to high vibronic components of the ground state (see *Figure 9*). The following effects may be observable[33]:

(1) 'Lengthening' of the radiative lifetime of some strongly coupled components.

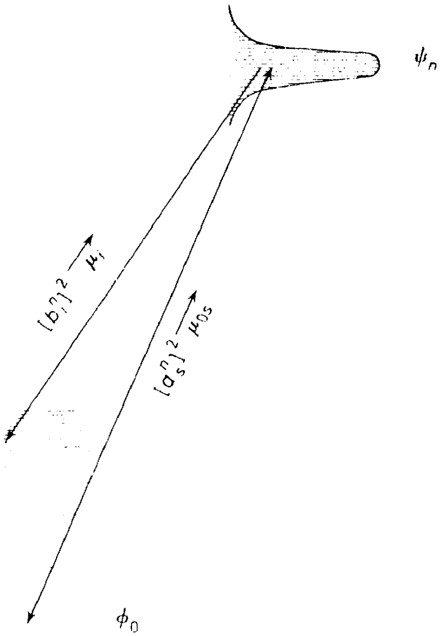

Figure 9. Schematic representation of radiative decay of a large molecule resulting from inter-system crossing.

Table 5. Experimental phenomena related to intramolecular coupling and relaxation in molecules

Classification	(a) *Radiationless decomposition predissociation autoionization*	(b) *Sparse level distribution*	(c) *Dense intermediate case*	(d) *Statistical limit*
System	*Small and large molecules*	(a) $^2\Pi$–$^2\Sigma$ *coupling in* CN (b) SO_2, NO_2, CS_2	*Small gap in large molecules*	*Large gap in large molecules case* (c) *in solution*
Experimental methods	(1), 2, (3), 6	1, 2, 3, 4, 5	1, 2, 3, 4, (5)	1, 2, 3, 4, 6
Intramolecular interstate coupling	+	+	+	+
Radiative interference	–	–	(+ ?)	–
Intramolecular relaxation	+	–	(+ ?)	+

Experimental methods:
(1) Decay times
(2) Line shapes or intensity distribution in absorption
(3) Fluorescence yields
(4) Fluorescence spectra
(5) External fields
(6) Population of final state.

Table 6. General features of the decay of molecular levels

Physical property	*Resonance limit*	*Sparse intermediate case*	*Dense intermediate case*	*Statistical limit*
No. of states $N = \Delta/2\varepsilon = \pi V^2\rho^2$	—	$N > 1$	$N \sim 1$	$N \gg 1$
Level separation relative to radiation width	$\varepsilon \sim \Gamma_s$	$\rho^{-1} \gg \Gamma_s$	$\rho^{-1} \sim \Gamma_s$	$\rho^{-1} \ll \Gamma_s$
Line shape	*Natural radiative + conventional broadening*	*Intensity distribution, well separated lines*	*Intermediate structure*	*Lorentzian line shape*
Time scale t relative to recurrence time	$t \sim \hbar/\varepsilon$	$t \gg \hbar\rho$	$t \sim \hbar\rho$	$\Delta = \pi V^2\rho$ $t \ll \hbar\rho$
Mode of decay	*Beat spectrum*	*Sum of (slowly varying) exponentials*	*Oscillatory (beats)* (?)	*Exponential*
Mean radiative decay time	—	$\tau_e \sim N\hbar/\Gamma_s$	$\tau_e \sim \hbar/\Gamma_s$ (?)	$\tau_e = \hbar/(\Delta + \Gamma_s)$
Experimental fluorescence quantum yield	$Y = 1$	$Y = 1$	$Y = 1$	$Y = \Gamma_s/(\Gamma_s + \Delta)$
Features of relaxation	*External*	*External*	*External*	*Intramolecular* $\tau_{NR} = \hbar/\Delta$
Examples	*Level crossing* *Level anticrossing*	SO_2, NO_2, CS_2	?	*Anthracene* *Tetracene*

(2) A possible observation of quantum beats due to interference between a small number of closely spaced levels.

(3) Non-exponential decay due to 'smearing out' of the interference effects, when the number of the strongly coupled levels is too large (but insufficient for the validity of the statistical limit).

(4) Effects of external fields on the level mixing and the decay characteristics.

(5) All these phenomena will be erased when the molecule is embedded in a dense medium in view of external vibrational relaxation effects.

In summary, we have presented in *Table 5* the experimental phenomena related to intramolecular coupling and intramolecular relaxation while *Table 6* presents some of the characteristic features of the radiative decay of small, medium sized and large molecules.

IX. CONCLUSIONS

We have attempted to outline a unified and consistent theoretical framework within which the multitude of intramolecular electronic relaxation phenomena can be interpreted. In summarizing the contributions of the unified theory we shall distinguish between the following categories of theoretical results:

(a) Questions concerning methodology:

(a1) The decaying excited states in a polyatomic molecule should be described in terms of *resonance (or compound) states* similar to the theory of nuclear reactions, scattering and radiationless decomposition.

(a2) Criteria for *irreversibility of the non-radiative decay* in an isolated large molecule were established. The description of electronic relaxation in the statistical limit is completely analogous to other legitimate relaxation processes such as predissociation or autoionization. When a resonant state of the compound system decays into a dissipative channel, then the description of this channel in terms of a continuum or a quasi-continuum depends solely on the boundary conditions applied at large distances from the compound system. Thus if you enclose a preionizing molecule in a large box the dissipative channel will involve a quasicontinuum, which is sufficiently dense to warrant a relaxation process characterized by a long recurrence time. The same situation applied to statistical electronic relaxation in large molecules.

(a3) *Classification of non-radiative processes.* In this context it is important to distinguish between intramolecular vibronic coupling and relaxation phenomena. Preionization and predissociation in small molecules as well as electronic relaxation in large molecules which correspond to the statistical limit do exhibit irreversible intramolecular relaxation.

On the other hand in small and medium sized molecules intramolecular vibronic and spin orbit coupling can be involved but intramolecular relaxation will not take place in the isolated molecule. When a few such levels are located within their radiative width, level crossing and level anticrossing phenomena will be observed. This category should be referred to as the resonance limit.

The intramolecular coupling terms can exceed, of course, the radiative width. One can therefore encounter a coarse distribution of levels which are still coupled vibronically or by spin orbit interactions. At this point one must introduce the criterion of comparing the level spacing with the radiative width. Intramolecular coupling phenomena but not radiative interference effects are exhibited in the $^2\Sigma$–$^2\Pi$ coupling in CN and also in the anomalous fluorescence lifetimes of some triatomic molecules.

Naturally intermediate cases are also encountered in medium sized and in large molecules for specific pairs of electronic energy levels when the energy gap is small.

(b) Interpretation of available experimental data

(b1) *Intensity distribution* for a strongly coupled coarse manifold will lead to a large number of well resolved lines. When the density of the background levels increases, intermediate structure in the absorption spectrum will be observed.

(b2) *Statistical broadening.* In large molecules line broadening manifests an intramolecular relaxation phenomenon. The difference between line broadening of intravalence and extravalence excitations in the statistical limit can be adequately rationalized.

(b3) *Interference effects in absorption.* When the background quasi-continuum carries oscillator strength Fano-type interference effects in absorption will be exhibited in the isolated molecule.

(b4) *The decay times and quantum yields* in the statistical limit can be legitimately handled by the Fermi Golden Rule.

(b5) *Long radiative lifetimes of triatomic molecules.* A proper theoretical interpretation of the Douglas effect was obtained.

(c) Theoretical predictions

(c1) *Intermediate structure in absorption spectrum*, the effects of isotope substitution, host crystal, etc., on the absorption spectrum of states corresponding to the intermediate dense case should be studied.

(c2) *Antiresonances in absorption.* Rydberg series in large molecules (other than naphthalene) should interfere with intravalence excitations leading to further evidence concerning intramolecular interference in the optical spectra.

(c3) *Radiative interference effects.* In the dense intermediate case exhibited by a small electronic energy gap in a large molecule vibronic coupling effects will lead not only to intermediate structure in absorption but also to non-exponential radiative decay and possibly to quantum beats.

(c4) *Level probing.* Application of external fields will affect the decay characteristics of small and medium sized molecules.

(c5) *Radiationless transitions and photochemistry.* There exists a relation between photochemical processes and radiationless transitions. In fact unimolecular rearrangement processes in excited electron states are radiationless transitions and when large molecules are considered these again correspond to the statistical limit. However, one must be particularly careful in interpreting photochemical rearrangement reactions with the same formalism as that of non-radiative transitions in large molecules since the former involve large configurational changes. Non-radiative transition theory must be extended to take this case into account; the underlying philosophy and basic ideas are the same. It should also be noted that ideas concerning resonances also apply to dissociation reactions in excited electronic states.

My interest in the problems discussed herein has been continuously stimulated by rewarding collaboration with Dr M. Bixon, Dr R. S. Berry, D. R. Englman, Dr Y. Dothan and Dr K. Freed. They have materially contributed to our understanding of the subject matter treated.

I am grateful to Professor U. Fano for some most helpful discussions.

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