

PREPARATION AND DECAY OF EXCITED MOLECULAR STATES

JOSHUA JORTNER and SHAUL MUKAMEL

Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel

Abstract. This paper reviews the current state of the art of theoretical understanding of the radiationless decay channels in electronically excited states of polyatomic molecules.

1. Introductory Comments

The theoretical chemist dines and wines well at the theoretical physicist's table. The borderline between theoretical physics and quantum chemistry is fuzzy and not well defined. The theoretical techniques employed are identical, only the goals and the nature of the specific questions often differ. The theory of relaxation phenomena in excited electronic states of polyatomic molecules, which is the subject matter of the present paper, draws heavily on work performed in the fields of radiation theory, collision theory, nuclear reactions and even elementary particle physics. This is not surprising as the decaying electronically excited states of a molecular system are amenable to theoretical descriptions in terms of compound states or resonances. Thus, there is a set of general features common to a wide class of physical systems. The decay characteristics of metastable states in atomic, molecular, solid state, nuclear and elementary particle physics should be described in terms of a unified theoretical picture.

Let us now attempt to specify and classify the field of non-radiative transitions. From the experimentalist's point of view, radiationless processes involve any 'transition' between the 'states' (i.e. electronic, vibrational, rotational) of a system (i.e. an atom, a molecule or a solid) which do not involve absorption or emission of radiation. These processes encompass a wide class of phenomena, which can be classified in the following manner:

- A. Atoms: (A1) Atomic autoionization [1]
- B. Molecules: (B1) Molecular autoionization [2]
 - (B2) Predissociation [2]
 - (B3) Thermally induced predissociation
 - (B4) Electronic relaxation between different states of a large molecule. Internal conversion and intersystem crossing [3-15]
 - (B5) Vibrational relaxation [16]
 - (B6) Photochemical rearrangements [17-19]
- C. Solids: (C1) Thermal ionization of impurities [20]
 - (C2) Thermal electron capture [20]
 - (C3) Electronic relaxation in impurity states
 - (C4) Electronic energy transfer [21-23]
 - (C5) Autoionization of metastable excitons [24]
 - (C6) Electronic relaxation of exciton states [24]

- D. Solutions: (D1) Thermal electron transfer [25]
(D2) Electronic energy transfer [21]
(D3) Dynamics of electron localization [26].

From the theoretician's point of view, this broad definition is fraught with difficulties, involving some hidden assumptions and pitfalls. First, and most important, the concept of a 'state of the system' has to be specified. Obviously, if we specify the Hamiltonian of the system in terms of the molecular Hamiltonian, all time dependent transitions between the stationary states of this molecular Hamiltonian are radiative in nature [27]. Thus, in order to exhibit nonradiative evolution, the system has to be 'prepared' by some experiment, via optical, electron impact, thermal or collisional excitation in a nonstationary state of the system's Hamiltonian. The resulting 'metastable state' will subsequently exhibit time evolution, where some of its decay channels may be nonradiative in nature. Second, the radiative decay channels (which involve a change in the occupation of the photon field) and the nonradiative decay channels (which conserve the number of photons) in an excited state cannot be separated. A large bulk of physical information now available [28-33] originates from optical studies of optical line shapes, radiative decay characteristics of electronically excited states and quantum yield measurements. A complete theoretical understanding of radiationless processes in excited electronic states of molecules should emerge from the proper description of their radiative decay.

The relevant relaxation processes in excited molecular states can be classified as follows:

- (a) Radiative decay.
- (b) Direct decomposition, i.e. photodissociation and photoionization.
- (c) Indirect decomposition, i.e. predissociation and autoionization.
- (d) Nonradiative electronic relaxation in excited states of large molecules.
- (e) Vibrational relaxation.
- (f) Unimolecular photochemical rearrangement reactions.

These processes, listed above, provide the main decay channels which can be encountered in excited electronic states. Processes (a)-(c) which obviously occur in an 'isolated', collision-free, molecule are not expected to be modified by an external medium. Process (d) occurs in an isolated large molecule which corresponds to the 'statistical limit', while it may be induced by medium perturbations in a small molecule. Process (e) exclusively originates from medium perturbations. Processes of type (f) are very complex and may involve a combination of processes (b)-(d).

We would like to discuss some of the results of recent work [34-68] regarding the fate of electronically excited molecular states, in an attempt to provide a unified picture for the interplay between the various basic decay channels which involve radiative decay, direct and indirect decomposition, electronic and vibrational relaxation.

2. Experimental Observables

From the experimentalist's point of view, the following spectroscopic information is

of fundamental importance for the elucidation of the decay characteristics of excited molecular states:

(1) Decay characteristics of electronically excited state. The most detailed information originates from the time and energy resolved pattern of excited electronic states. In the simplest common case, the decay pattern is exponential and the excited state is characterized by a single lifetime. More complex decay patterns which involve a superposition of exponentials were also recorded. Finally, the decay may (in principle) exhibit an oscillatory behavior, which originates from interference between closely spaced discrete levels. This phenomenon of quantum beats which is well known in level crossing atomic spectroscopy, was not yet conclusively established in large molecules.

(2) Cross sections for photon scattering from molecules. These involve both elastic photon scattering to the ground electronic-vibrational state and resonance Raman scattering to the ground electronic configuration. We shall refer to these processes as 'resonance fluorescence'.

(3) Optical absorption line shapes.

(4) Cross sections for photodissociation for molecules undergoing direct photodecomposition.

(5) Quantum yields for resonance fluorescence.

(6) Quantum yields for photodissociation.

These experimental observables fall into two different categories. In general, two classes of experiments which will be referred to as 'short excitation' and 'long excitation' processes can be utilized to extract physical information concerning the decay of electronically excited states of large molecules. When the temporal duration of the exciting photon field is short relative to the reciprocal width of the molecular resonance, it is feasible to separate the excitation and the decay processes and to consider the decay pattern of the metastable state. This experimental approach involves a 'short excitation' process. The study of the decay pattern of an 'initially' excited state corresponds to such a 'short excitation' experiment. On the other hand, when the exciting photon field is characterized by a high energy resolution, being switched on for long periods (relative to the decay time) the excitation and the decay processes cannot be separated and one has to consider resonance scattering from large molecules within the framework of a single quantum-mechanical process. Such 'long excitation' experiments involve the determination of optical line shapes, cross sections for resonance fluorescence, for intramolecular electronic relaxation and for photodissociation. Emission quantum yields can be obtained both from 'short time' excitation experiments (by the integration of the decay curve) or from 'long time' experiments (which yield the energy dependence of the quantum yield). In the special case of an isolated resonance, the information regarding the resonance width, its decay time and the corresponding energy independent quantum yield obtained from 'long time' excitation experiments should be identical to that obtained from a 'short time' excitation. However, for more complex physical situations one cannot get away by considering just the resonance width. When interference effects between resonances are exhibited,

the decay curve in the 'short excitation' experiment is nonexponential, the quantum yield is energy-dependent, and the information obtained from 'short time' and 'long time' experiments is complementary but not identical.

In the discussion of 'short time' and 'long time' experiments, we have focused attention on the nature of the optical excitation process. One can subsequently consider two extreme types of photon detection. Broad band detection which admits all emitted photons and narrow band detection which spans a narrow energy region. It is important to note that the detection process is independent of the excitation mode. Both detection methods are useful for specific purposes.

3. Models for Relaxation of Electronically Excited States

During the past few years several theoretical models for the decay characteristics of excited states were developed and solved at various levels of sophistication. These models provide a schematic description of the energy levels of a zero-order Hamiltonian which should also include the radiation field, while the residual interactions couple the zero-order states. Clearly, the choice of the basis set is merely a matter of convenience and does not affect any observable quantities. Let us consider the conventional dissection of the molecular Hamiltonian, H , for a molecular system including the radiation field,

$$\begin{aligned} H &= H_M + H_{\text{rad}} + H_{\text{int}}, \\ H_M &= H_{MO} + H_V, \end{aligned} \quad (3.1)$$

where the molecular Hamiltonian, H_M , consists of H_{MO} , the zero-order molecular Hamiltonian and H_V which corresponds to the nonadiabatic intramolecular interaction which involves the interstate coupling via nuclear kinetic energy or spin orbit coupling. There has been lately a lively controversy regarding the nature of these interactions [52-53, 69-77]. We shall avoid a detailed discussion of this problem and just point out, at the risk of triviality, that any untruncated complete molecular zero order basis set is adequate for the specification of H_M . It was recently emphasized [52-53, 74, 77] that the Born-Oppenheimer (BO) basis set is superior to the crude adiabatic basis set as it minimizes off-resonance coupling terms between different electronic configurations. Thus the utilization of the BO basis set (i.e. $H_{MO} = H_{BO}$) and the identification of H_V with the breakdown of the BO approximation provides the ideological basis for the basic model systems for electronic relaxation which usually involve a two-electronic level system for the excited state. To complete the definitions in Equation (3.1), H_{rad} is the Hamiltonian for the free electromagnetic field, while H_{int} is the radiation-matter interaction term.

The electronically excited eigenstates of H_{MO} will be labelled as follows: (1) Discrete levels $|s\rangle$, $|r\rangle$, etc. which correspond to low lying vibronic components of excited electronic configurations. (2) A manifold of levels $\{|I\rangle\}$ corresponding to a lower electronic configuration and which are quasidegenerate to the $|s\rangle$ (and/or to the $|r\rangle$) level. The levels of types (1) and (2) are sufficient for the description of electronic

relaxation. For direct and indirect photodissociation we have to consider in addition: (3) an intramolecular dissociative continuum $\{|I\rangle\}$. The electronic ground state of the system will be labelled by the vibronic components $|gv\rangle$ where $v=0$ refers to the vibrationless level while $v\neq 0$ represents excited vibronic components. Note that for the low lying ground state $|gv\rangle$ can be considered as eigenfunctions of H_0 as well as of $H_0 + H_V$, as off-resonance nonadiabatic corrections for these states are negligible. The eigenfunctions of H_{rad} will be given by the zero photon state $|\text{vac}\rangle$ and by one-photon states $|\mathbf{k}\mathbf{e}\rangle$ where \mathbf{k} and \mathbf{e} are the wave vector and the polarization vector of a photon, respectively.

A possible choice of the zero-order Hamiltonian, being often used is

$$\begin{aligned} H_0 &= H_{MO} + H_{\text{rad}} \equiv H - V, \\ V &= H_V + H_{\text{int}}. \end{aligned} \quad (3.2)$$

The eigenstates of H_0 consists of zero-photon states $|s, \text{vac}\rangle$, $|r, \text{vac}\rangle$, $\{|l, \text{vac}\rangle\}$ etc., and of one-photon states $|g\nu, \mathbf{k}\mathbf{e}\rangle$.

It is important to emphasize that the separation of the Hamiltonian as expressed by Equation (3.1) is by no means unique and this can be accomplished in a variety of ways. Another useful approach is to adopt the molecular eigenstates basis $|n\rangle$, which diagonalizes the total electronic Hamiltonian H_M [7, 34] whereupon

$$\begin{aligned} H_0 &= H_M + H_{\text{rad}}, \\ V &= H - H_0 = H_{\text{int}}. \end{aligned} \quad (3.2a)$$

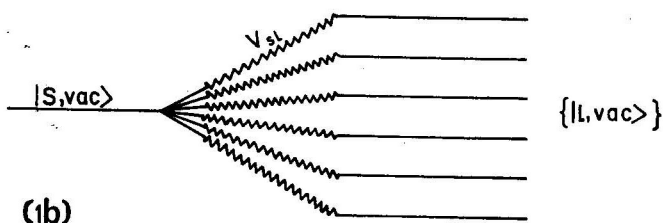
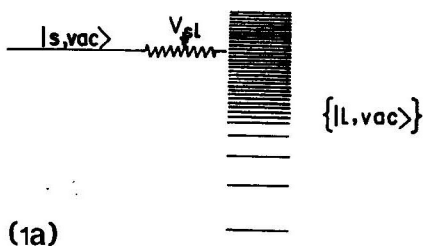
The eigenstates of H_0 consist now of the one-photon states $|g\nu, \mathbf{k}\mathbf{e}\rangle$ and the zero-photon states $|n, \text{vac}\rangle$. The hierarchy of basis sets useful for the description of decay channels in excited molecular states is summarized in Table I.

It should be noted that we have neglected the contribution of multiphoton states of the radiation field such as $|g\nu, \mathbf{k}\mathbf{e}, \mathbf{k}'\mathbf{e}'\rangle$, however, in general (at least for conventional excitation sources), the contribution of such states is negligibly small. We shall now proceed to portray the energy level diagrams for the excited states of the relevant physical systems.

In figure 1a we present a highly idealized level scheme which provides a universal model for radiationless transitions in a large 'isolates' molecule [7, 34, 78]. A zero-order vibronic level $|s\rangle$ of a higher electronic state, which carries all the oscillator strength from the ground state, is quasidegenerate with an intramolecular manifold $\{|l\rangle\}$ of bound levels which correspond to a lower electronic state. The $\{|l\rangle\}$ manifold is devoid of oscillator strength. In the case of a large molecule when the energy gap between the electronic origins of $|s\rangle$ and the $\{|l\rangle\}$ states is reasonably large (~ 1 eV) we have large densities of $\{|l\rangle\}$ states which are quasidegenerate with $|s\rangle$. The $|s\rangle$ state plays a special central role as it is optically accessible from the ground state. This situation is analogous to a 'doorway state' in nuclear scattering where a single excitation can be reached via the incident channel [81-82]. This physical system will not exhibit a truly intramolecular nonradiative relaxation but rather a Poincaré cycle [34]. For the limiting case of a large density of states, the recurrence time, t_r , for

TABLE I
Hierarchy of basis sets for description of electronic relaxation processes

Basis set	Major properties	Applicability
$ x\rangle$	Diagonalizes H (with zero- and one-photon states)	Proofs of general theorems for the properties of the decay amplitudes
$ j, \text{vac}\rangle$	a. Radiative decay provides the only dissipative channel b. Defined in \hat{P} subspace c. Diagonalizes H_{eff} d. Nonorthogonal e. Specifies independently decaying levels	Time evolution of discrete electronically excited states
$ J, \text{vac}\rangle$	a. System characterized by two parallel decay channels, radiative and nonradiative b. (e) as for $ j, \text{vac}\rangle$	Parallel radiative and nonradiative decay of excited states
$ n, \text{vac}\rangle$	Diagonalizes H_M	Radiative decay of small molecules and intermediate-type states of large molecules
Born-Oppenheimer basis	a. Diagonalizes $H_{MO} = H_{BO}$ b. Off-resonance interactions with higher excited states are negligible	Description of the statistical limit



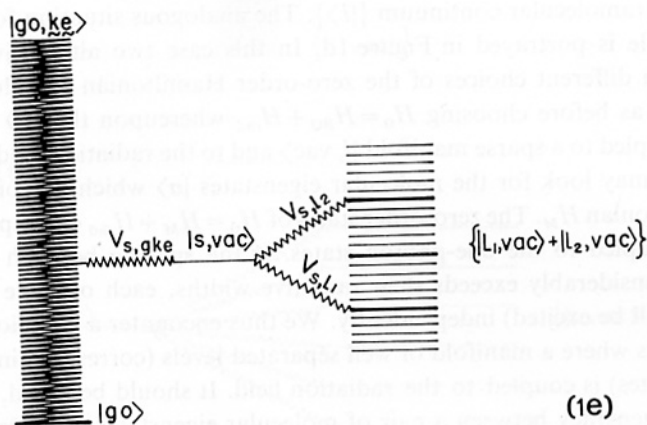
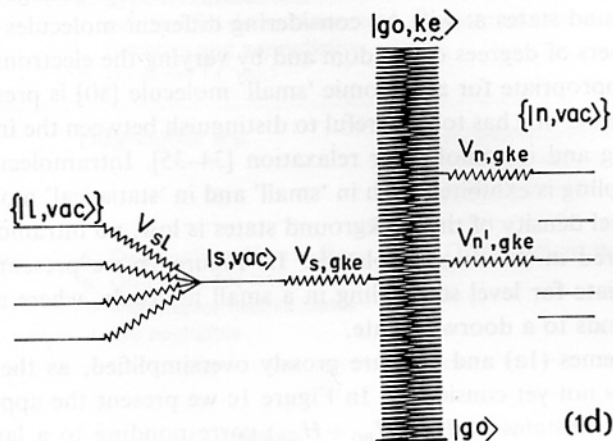
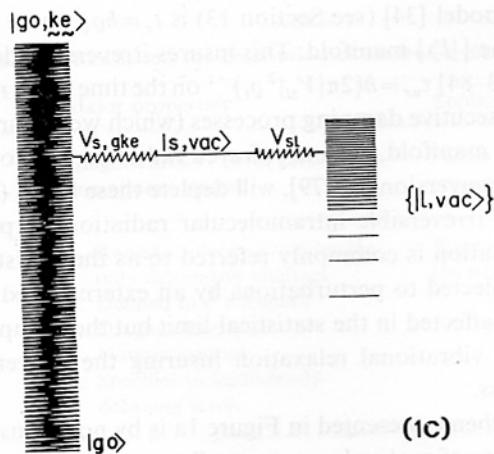
Figs. 1a-b. Useful molecular decay models. — (a) Interstate coupling and nonradiative decay in an isolated large (statistical) molecule. (b) Interstate coupling in a small molecule.

the simple Bixon–Jortner model [34] (see Section 13) is $t_r = \hbar \varrho_I$ where ϱ_I corresponds to the density of states in the $\{|I\rangle\}$ manifold. This insures irreversible decay characterized by the decay time [34, 83–84] $\tau_{nr} = \hbar(2\pi|V_{sl}|^2 \varrho_I)^{-1}$ on the time scale, t , of interest, i.e. $\tau_{nr} \lesssim t \ll t_r$. Subsequent consecutive damping processes (which were disregarded in this simple scheme) of the $\{|I\rangle\}$ manifold, such as infrared radiation [34], or photon emission in the case of internal conversion [41, 79], will deplete these levels (see Section 13) insuring the occurrence of irreversible intramolecular radiationless processes in an isolated molecule. This situation is commonly referred to as the statistical limit [35]. If the large molecule is subjected to perturbations by an external medium [4, 64–65] the decay lifetime τ_{nr} is not affected in the statistical limit but the occupied $\{|I\rangle\}$ levels will be again depleted via vibrational relaxation insuring the irreversibility of the electronic relaxation process.

The basic energy levels scheme presented in Figure 1a is by no means restricted to a large molecule. The flexibility of molecular systems allows us to change the density of the $\{|I\rangle\}$ background states at will, by considering different molecules characterized by different numbers of degrees of freedom and by varying the electronic energy gap. A level scheme appropriate for a triatomic ‘small’ molecule [80] is presented in Figure 1b. In this context one has to be careful to distinguish between the implications of interstate coupling and intramolecular relaxation [34–35]. Intramolecular interstate nonadiabatic coupling is exhibited both in ‘small’ and in ‘statistical’ molecules. However, when the level density of the background states is low, no intramolecular relaxation is encountered in the small molecule. In Figure 1b we present the physical situation appropriate for level scrambling in a small molecule, where again a single $|s\rangle$ state corresponds to a doorway state.

The simple schemes (1a) and (1b) are grossly oversimplified, as the effect of the radiation field was not yet considered. In Figure 1c we present the appropriate level scheme (for the eigenstates of $H_0 = H_{BO} + H_{rad}$) corresponding to a large molecule. Now the doorway state $|s\rangle$ is simultaneously coupled to the radiation field $\{|g, \mathbf{k}\epsilon\rangle\}$ and to the intramolecular continuum $\{|I\rangle\}$. The analogous situation for the case of a small molecule is portrayed in Figure 1d. In this case two alternative descriptions which rest on different choices of the zero-order Hamiltonian are illuminating. We may proceed as before choosing $H_0 = H_{BO} + H_{rad}$ whereupon the BO doorway state $|s, \text{vac}\rangle$ is coupled to a sparse manifold $|l, \text{vac}\rangle$ and to the radiation field. Alternatively [40–41], one may look for the molecular eigenstates $|n\rangle$ which diagonalize the electronic Hamiltonian H_M . The zero-order states of $H_0 = H_M + H_{rad}$ correspond to $|n, \text{vac}\rangle$ which are coupled to the one-photon states. If the spacing between the molecular eigenstates considerably exceeds their radiative widths, each of these $|n\rangle$ levels will decay (and will be excited) independently. We thus encounter a situation occurring in atomic physics where a manifold of well separated levels (corresponding to the molecular eigenstates) is coupled to the radiation field. It should be noted, however, that accidental degeneracy between a pair of molecular eigenstates may result in interference effects which will exhibit quantum beats [38] in the radiative decay.

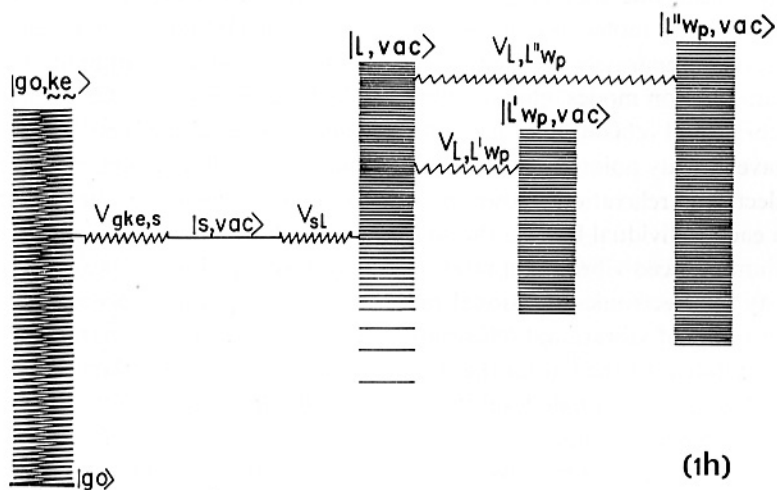
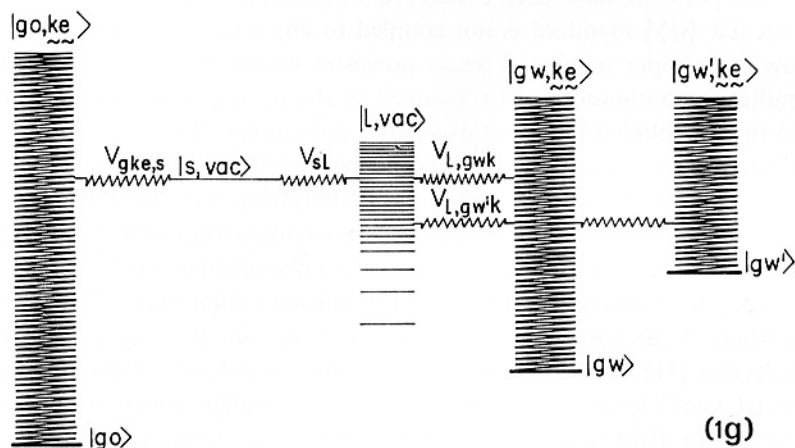
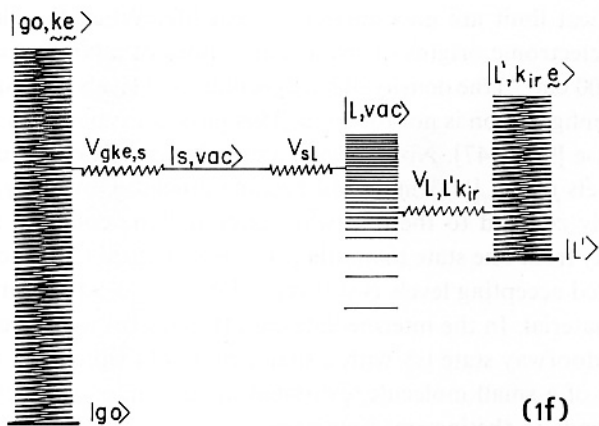
As it is common in physical problems, situations intermediate between the small



Figs. 1c-e. (c) Radiative and interstate coupling in a statistical large molecule. (d) Radiative coupling in a small molecule. (e) Intermediate level structure in a large molecule.

molecule and the statistical limit are encountered in real life. When the electronic energy gap between the electronic origins of two excited states of a large molecule is relatively small ($2000\text{--}3000\text{ cm}^{-1}$) the density of background $\{|I\rangle\}$ levels corresponding to the lower electronic configuration is not too high. This physical situation is referred to as the intermediate case [9–10, 47]. Now in such a case the details of the coupling strengths for various levels in the $\{|I\rangle\}$ manifold become crucial. Obviously, not all these levels are effectively coupled to the doorway state, and the coupling strength $(H_V)_{sI}$ varies substantially from one state to another. In the statistical limit the density of these effectively coupled accepting levels is still very high and the variation of their coupling strength is immaterial. In the intermediate case (Figure 1e) we expect simultaneous coupling of the doorway state $|s\rangle$ with a sparse manifold which will result in the decay characteristics of a small molecule, exhibited by an excited state of a large molecule which corresponds to the intermediate case.

Up to this point we have been concerned with simple coupling schemes where the intramolecular $\{|I\rangle\}$ manifold is not coupled to any additional decay channels. We have now to consider sequential decay processes where the doorway state (coupled to the radiative continuum) is also coupled to the (sparse or dense) $\{|I\rangle\}$ manifold, which in turn is coupled to a final dissipative continuum. We shall consider first the physical situation where each of the intermediate $\{|I\rangle\}$ levels is coupled to a different final continuum, and will thus exhibit non-interfering sequential decay. Relevant physical processes in this category are: (a) Sequential decay of the $\{|I\rangle\}$ quasicontinuum in an isolated statistical molecule due to infrared emission [34, 85]. Thus each of the $|I, \text{vac}\rangle$ levels is coupled to a separate radiative continuum $|I', \mathbf{k}_r, \mathbf{e}\rangle$ (see Figure 1f), where $|\mathbf{k}_r, \mathbf{e}\rangle$ correspond to an infrared photon. (b) Internal conversion in large molecules [51]. In the case of internal conversion from a highly excited singlet state the $\{|I, \text{vac}\rangle\}$ levels are electronically excited singlets, which are in turn radiatively coupled to highly excited (nontotally symmetric) vibrational levels $|g_\omega, \mathbf{k}'\mathbf{e}'\rangle$ of the ground electronic state (Figure 1g). (c) Vibrational relaxation of the $\{|I\rangle\}$ manifold of a statistical molecule embedded in a medium [64] (Figure 1h). In this case each $|I, \text{vac}\rangle$ level is separately coupled to a $|I'_{(\omega_p)}, \text{vac}\rangle$ continuum containing a collection of medium phonon modes, characterized by the frequencies $\{\omega_p\}$. (d) Sequential electronic-vibrational relaxation of a small molecule in a dense medium [65] (Figure 1i). As we have already pointed out, an isolated small molecule does not exhibit intramolecular electronic relaxation. However, when such a molecule is embedded in a dense medium each individual level in the sparse manifold $|I', \text{vac}\rangle$ can subsequently decay via medium-induced vibrational relaxation to a lower level $|I'_{(\omega_p)}, \text{vac}\rangle$ thus providing a pathway for electronic-vibrational radiationless process. This process can be envisioned in terms of vibrational relaxation of the molecular eigenstates, which are well separated relative to their total (i.e. radiative and vibrational) relaxation widths. (e) Sequential decay via a single level [50]. This is a model system where strong coupling is exhibited between the doorway state $|s, \text{vac}\rangle$ and one of the $|I, \text{vac}\rangle$ levels (Figure 1j). The special $|I\rangle$ level is subsequently coupled to an internal continuum due to vibrational relaxation. Such a physical situation is encountered when an excited state of a

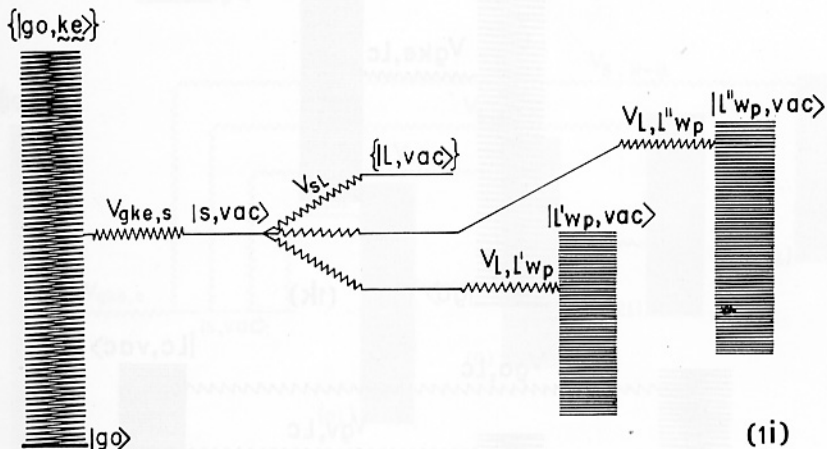


Figs. 1f-h. (f) Sequential decay of intramolecular continuum by IR emission. (g) Internal conversion. (h) Vibrational relaxation in the intramolecular manifold due to medium perturbation.

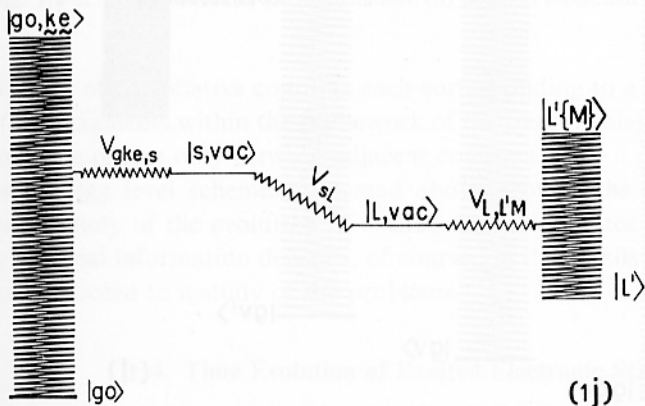
large molecule, which corresponds to the intermediate case previously described in Figure 1e is subjected to medium induced collisional perturbation [50]. In this case of nearly degenerate two discrete levels interference effects in the decay process will be exhibited.

Finally we have to consider sequential decay processes involving interference where all the intermediate states $\{|I\rangle\}$ are coupled to the same continuum. The simplest example (Figure 1k) involves the coupling between a radiative ($g, \mathbf{k}e$) and the non-radiative dissociative continuum $\{|I\rangle\}$ which provides the simplest case of direct photodissociation.

This state of affairs corresponds to 'elastic' photon scattering from and into a single radiative continuum. We can easily extend this picture taking into account (Figure 1l) the role of other radiative channels $|gv, \mathbf{k}e\rangle$ corresponding to the vibrationally excited ground state levels. This system will now exhibit both elastic (Rayleigh-



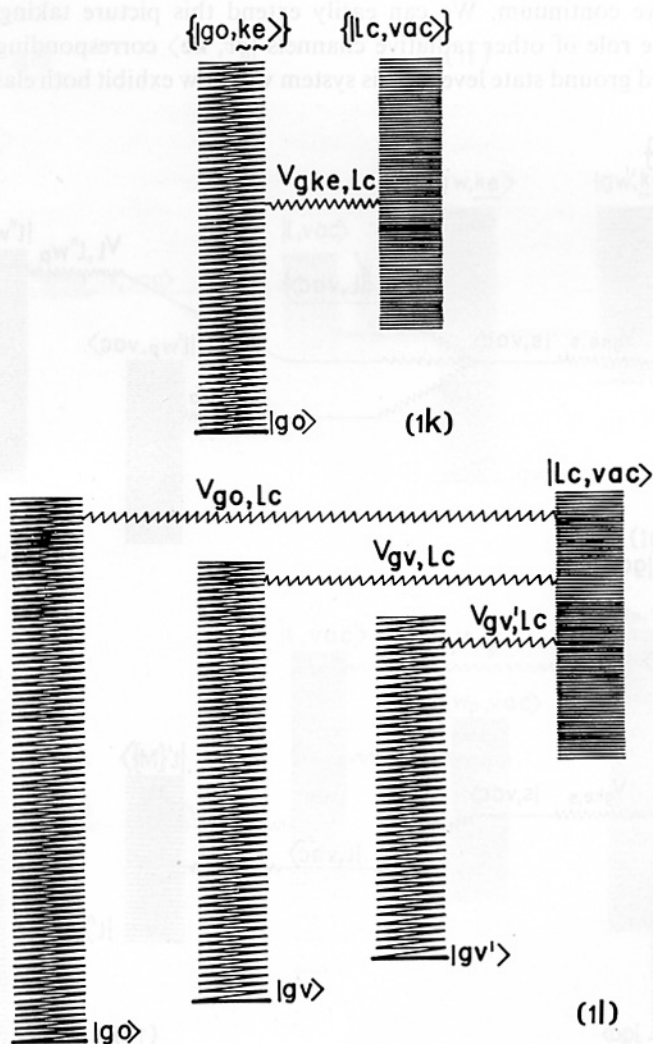
(i)



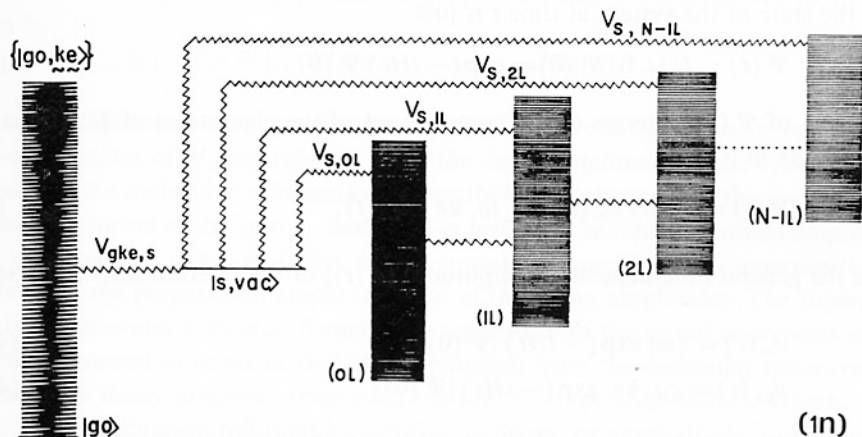
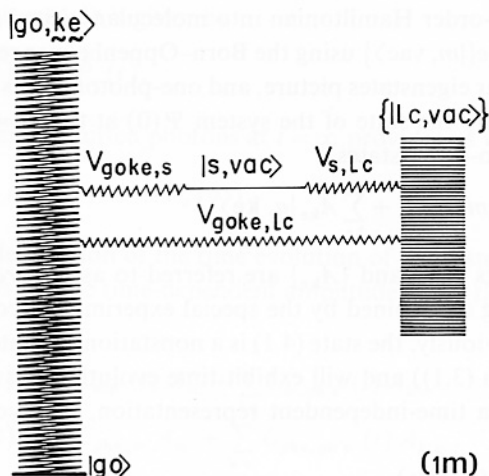
(j)

Figs. 1i-j. (i) Electronic-vibrational relaxation of a small molecule in a medium. (j) Sequential and parallel decay of two discrete levels.

type) and Raman scattering [86]. Another interesting situation involves indirect photodissociation where a discrete excited state is involved being in turn coupled to a dissociative continuum [68]. This situation prevails for molecular predissociation. When the dissociative continuum is devoid of oscillator strength (Figure 1m with $V_{g_0, \mathbf{k}e}; t_{c, \text{vac}} = 0$;) we have a situation which bears close analogy to radiationless transitions in the statistical limit (Figure 1c). An interesting state of affairs is encountered when the dissociative continuum is radiatively coupled (Figure 1m) to $|g_0, \mathbf{k}e\rangle$ where interference effects will be exhibited. Finally, we consider direct and indirect photofragmentations of large polyatomic molecules. Here one has to consider (Fig-



Figs. 1k-l. (k) Direct photodissociation. (l) Coupling of dissociative continuum with a manifold of radiative continua.



Figs. 1m-n. (m) Molecular predissociation. (n) Indirect molecular photofragmentation.

ure 1n) a set of dissociative continua each corresponding to a given vibrational state $|v_f\rangle$ of the fragments within the framework of the (reasonable) harmonic approximation coupling occurs only between adjacent continua.

These energy level schemes presented above provide the starting point for the theoretical study of the evolution of excited molecular states. The nature of the resulting physical information depends, of course, on the details of the experiment. We shall now proceed to a study of the problems.

4. Time Evolution of Excited Electronic States

We shall now consider excitation and decay processes in a general system consisting of an isolated single molecule and the radiation field. We shall segregate the eigen-

states of the system's zero-order Hamiltonian into molecular excited states, $|m, \text{vac}\rangle$, i.e. $|s, \text{vac}\rangle$, $\{|l, \text{vac}\rangle\}$ etc., $\varepsilon\{|m, \text{vac}\rangle\}$ using the Born–Oppenheimer representation, or $|n, \text{vac}\rangle$ using the molecular eigenstates picture, and one-photon states $|g, \mathbf{ke}\rangle$. In most general terms we can specify the state of the system $\Psi(0)$ at time $t=0$ in terms of a superposition of these zero-order states

$$\Psi(0) = \sum_m A_m |m, \text{vac}\rangle + \sum_{\mathbf{ke}} A_{\mathbf{ke}} |g, \mathbf{ke}\rangle. \quad (4.1)$$

The two sets of coefficients $\{A_m\}$ and $\{A_{\mathbf{ke}}\}$ are referred to as the *preparation amplitudes* for the system, being determined by the special experimental conditions, which were not yet specified. Obviously, the state (4.1) is a nonstationary state of the system's Hamiltonian H (Equation (3.1)) and will exhibit time evolution. As we have chosen the Hamiltonian (3.1) in a time-independent representation, the evolution operator is simply

$$U(t, 0) = \exp(-iHt). \quad (4.2)$$

Thus the state of the system at time t is just

$$\Psi(t) = U(t, 0) \Psi(0) = \exp(-iHt) \Psi(0). \quad (4.3)$$

Expansion of $\Psi(t)$ in terms of the complete set of the eigenstates of H_0 (Equation (3.2)) results in

$$\Psi(t) = \sum_m |m\rangle d_m(t) + \sum_{\mathbf{ke}} |g, \mathbf{ke}\rangle d_{\mathbf{ke}}(t), \quad (4.4)$$

where the general time-dependent amplitudes $\{d(t)\}$ of the relevant zero-order states are

$$d_m(t) = \langle m | \exp(-iHt) | \Psi(0) \rangle, \quad (4.5a)$$

$$d_{\mathbf{ke}}(t) = \langle g, \mathbf{ke} | \exp(-iHt) | \Psi(0) \rangle. \quad (4.5b)$$

The probability p_e of the system to be in any excited state at time t is given by

$$P_e(t) = \sum_m |\langle m, \text{vac} | \Psi(t) \rangle|^2 = \sum_m |d_m(t)|^2, \quad (4.6)$$

while the probability of the system to be found in any one-photon ground electronic state is

$$P_g(t) = \sum_{\mathbf{ke}} |\langle g, \mathbf{ke} | \Psi(t) \rangle|^2 = \sum_{\mathbf{ke}} |d_{\mathbf{ke}}(t)|^2. \quad (4.7)$$

The normalization condition for $\Psi(t)$ implies the conservation law

$$P_e(t) + P_g(t) = 1 \quad (4.8)$$

for all t . Finally, to bring this general treatment down to earth we have to relate these results to some experimental observables. The photon counting rate which monitors the number of photons emitted per unit time is just

$$\dot{P}_g(t) = dP_g/dt, \quad (4.9)$$

which by Equation (4.8) is given by

$$\dot{P}_g(t) = -\dot{P}_e(t). \quad (4.9a)$$

The total number of emitted photons at $t = \infty$ provides us with the quantum yield, Y ,

$$Y = P_g(\infty) = 1 - P_e(\infty). \quad (4.10)$$

This general description of the time evolution of the system results in very cumbersome expressions for the time-dependent amplitudes $\{d(t)\}$ which are explicitly given in the form:

$$\begin{aligned} d_m(t) &= \sum_{m'} C_{mm'}(t) A_{m'} + \sum_{\mathbf{k}\mathbf{e}} C_{m, g\mathbf{k}'\mathbf{e}'}(t) A_{\mathbf{k}'\mathbf{e}'}, \\ d_{\mathbf{k}\mathbf{e}}(t) &= \sum_{m'} C_{g\mathbf{k}\mathbf{e}, m'} A_{m'} + \sum_{\mathbf{k}'\mathbf{e}'} C_{g\mathbf{k}\mathbf{e}, g\mathbf{k}'\mathbf{e}'}(t) A_{\mathbf{k}'\mathbf{e}'}, \end{aligned} \quad (4.11)$$

where the time-dependent amplitudes $C_{\alpha\beta}(t)$ with α and $\beta \equiv |m, \text{vac}\rangle$ or $|g, \mathbf{k}\mathbf{e}\rangle$ are given by

$$C_{\alpha\beta}(t) = \langle \alpha | U(t, 0) | \beta \rangle \equiv \langle \alpha | \exp(-iHt) | \beta \rangle. \quad (4.12)$$

The (time-dependent) matrix elements $C_{\alpha\beta}(t)$ of the evolution operator between the zero-order states of H_0 are referred to as the *decay amplitudes* of the system. These include all the molecular information about the decay channels of the system. Thus the time evolution of the system, described in terms of the time-dependent amplitudes $\{d(t)\}$ (Equations (4.4) and (4.5)), can be completely specified by a superposition of products of the preparation amplitudes and of the decay amplitudes. The superposition (4.11) provides a mental, formal type separation of the initial conditions of the system (expressed in terms of the $\{A\}$ amplitudes) from the molecular radiative and nonradiative decay processes (expressed via the $\{C\}$ -type amplitudes). Whether one can consider excitation followed by subsequent decay, or alternatively a single quantum photon scattering process depends on the specific experimental conditions. However, it should be realized that the formalism developed up to this point is applicable both for 'short excitation' and for 'long excitation' experiments. From the point of view of the formal theory we can now proceed to consider separately the decay amplitudes and the preparation amplitudes. The former are invariant with respect to the nature of the optical excitation, while the specification of the latter will determine the nature of the excitation process.

5. Formal Expressions for the Decay Amplitudes

When the evaluation of the decay amplitudes is involved it is more convenient and practical to express the matrix elements of the evolution operator in terms of the Fourier transform of the Green operator [87-90]

$$G(E) = (E - H + i\eta)^{-1}, \quad (5.1)$$

where $\eta \rightarrow 0^+$. Thus all integrations over (5.1) will be performed over a contour which runs from $-\infty$ to ∞ just above the real E axis. Let us introduce at this point complete set of eigenfunctions $|\chi\rangle$ of the total Hamiltonian H . We realize that these can be determined in real life only for simple systems, but for the present general argument their detailed form is immaterial. Thus this basis set satisfies the Schrödinger equation

$$H|\chi\rangle = E_\chi|\chi\rangle \quad (5.2)$$

and the completeness condition

$$\sum_\chi |\chi\rangle \langle\chi| = 1. \quad (5.3)$$

We now write down immediately the time evolution operator (Equation (4.2)) and the Green operator (Equation (5.1)) in terms of their spectral representations

$$\exp(-iHt) = \sum_\chi |\chi\rangle \exp(-iE_\chi t) \langle\chi| \quad (5.4)$$

and

$$G(E) = \sum_\chi \frac{|\chi\rangle \langle\chi|}{E - E_\chi + i\eta}. \quad (5.5)$$

We note that expressions (5.4) and (5.5) are not valid for any arbitrary basis set, but just for the special basis set $|\chi\rangle$. Utilizing Equations (5.4) and (5.5) we can formally recast the time evolution operator in terms of the Fourier transform of the Green's function

$$\exp(-iHt) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \exp(-iEt) G(E) dE, \quad (5.6)$$

where the conventional methods of residue integration have been utilized. Finally, utilizing the formal representation (5.6) the decay amplitudes (4.12) are explicitly expressed in the form

$$C_{\alpha\beta}(t) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} G_{\alpha\beta}(E) \exp(-iEt) dE \quad (5.7)$$

of

$$G_{\alpha\beta}(E) \equiv \langle\alpha| G(E) |\beta\rangle, \quad (5.7a)$$

i.e. the matrix elements of the Green's function between the zero-order states. Thus the evaluation of the decay amplitudes boils down to the evaluation of the matrix elements of the Green's function.

These general expressions for the decay amplitudes have many attractive features. From the point of view of general methodology, as we are dealing with a large number of levels, such general approach is most useful. From the point of view of mathematical convenience these expressions are quite easy to evaluate. In particular it is a

simple matter to relate the matrix elements of $G(E) = (E - H + i\eta)^{-1}$ to those of the corresponding Green's function for the 'unperturbed' zero-order system $G^0(E) = (E - H_0 + i\eta)^{-1}$, where $H_0 = H - V$, via the Dyson operator identity [87]

$$G(E) = G^0(E) + G^0(E)VG(E) = G^0(E) + G(E)VG^0(E).$$

Some more formal and powerful techniques for the evaluation of the relevant matrix elements of the Green's function are available. We note that these matrix elements $G_{\alpha\beta}(E)$ are of three types: (1) $\langle g, \mathbf{ke} | G(E) | m, \text{vac} \rangle$, (2) $\langle m, \text{vac} | G(E) \times | m', \text{vac} \rangle$, and (3) $\langle g, \mathbf{ke} | G(E) | g\mathbf{k}'e' \rangle$. We shall now partition the Hilbert space as follows [88-90]:

$$\hat{P} = \sum_m |m, \text{vac}\rangle \langle m, \text{vac}|, \quad (5.8)$$

$$\hat{Q} = \sum_{\mathbf{ke}} |g, \mathbf{ke}\rangle \langle g, \mathbf{ke}|, \quad (5.9)$$

where the subspace \hat{P} contains the excited zero-photon levels while the subspace \hat{Q} contains the one-photon zero-order states. Provided that we disregard the contribution of zero photon ground state and multiphoton excited states, which will yield only off-resonance terms, the completeness condition requires that

$$\hat{P} + \hat{Q} = 1. \quad (5.10)$$

We immediately notice that the matrix elements of type (1) combine the \hat{Q} subspace with the \hat{P} subspace, while the matrix elements of type (2) combine the \hat{P} subspace with itself.

Thus, in view of the orthogonality of the subspaces \hat{P} and \hat{Q} , evaluation of matrix elements of type (1), (2) and (3) requires the operators $\hat{Q}G\hat{P}$ and $\hat{P}G\hat{P}$ and $\hat{Q}G\hat{Q}$, respectively. The explicit forms for these operators are [88-90]

$$\hat{Q}G(E)\hat{P} = (E - \hat{Q}H_0\hat{Q} + i\eta)^{-1} \hat{Q}R(E)\hat{P}(E - H_0 - \hat{P}R(E)\hat{P})^{-1}, \quad (5.11)$$

$$\hat{P}G(E)\hat{P} = (E - \hat{P}H_0\hat{P} - \hat{P}R(E)\hat{P})^{-1} \hat{P}, \quad (5.12)$$

$$\begin{aligned} \hat{Q}G(E)\hat{Q} &= \hat{Q}(E - \hat{Q}H\hat{Q} + i\eta)^{-1} + \\ &+ \hat{Q}(E - \hat{Q}H\hat{Q} + i\eta)^{-1} V\hat{P}G(E)\hat{P}V(E - \hat{Q}H\hat{Q} + i\eta)^{-1} \hat{Q}. \end{aligned} \quad (5.13)$$

Being expressed in terms of the level shift operator

$$R(E) = V + V\hat{Q}(E - \hat{Q}H\hat{Q})^{-1} \hat{Q}V. \quad (5.14)$$

It is important to notice that the level shift operator consists of two contributions; a direct coupling, V , and a relaxation contribution.

These general formal expressions are of great value both for practical evaluation of the matrix elements and, more important, also for the choice of the most convenient basis set to describe the decay of the system. To conclude this exposition of the math-

emational methods we would like to point out that the partitioning (5.8) and (5.9) is again not unique, as it is common for many intermediate steps in the formal theory. For some specific systems it will be convenient (see Section 10) to adopt an alternative partitioning procedure, retaining in subspace \hat{P} just the discrete excited molecular states and throwing into subspace \hat{Q} both the radiative continuum and the molecular (zero-photon) continua (or quasicontinua).

From the physical point of view the Green's function method is indeed very clear and transparent (at least after one has crossed a psychological barrier and became acquainted with these techniques). We have noted that the poles of the Green's function in the $|\chi\rangle$ representation (see Equation (5.5)) provide us with the energy spectrum of the system. It is important to note that in this case the poles $E = E_x$ are located on the real E axis, thus the system in an eigenstate of H is characterized by a real energy and does not exhibit a decay.

When we consider the matrix elements of $G(E)$ between the eigenstates of H_0 the poles of $G(E)$ will have imaginary parts of the form $E = E_e - \frac{1}{2}i\Gamma_e$. In general a large number of poles can be exhibited, whose imaginary components Γ_e provide the contributions to the decay rate of the nonstationary state.

6. Time Evolution Resulting from Wave-Packet Excitation

We have now to provide a physically realistic model for the excitation process. The most natural way to excite the system is to switch on a photon wave packet at the time $t=0$, and then utilize the techniques of Section 3 to follow the time evolution of the system. It is important to note that by this general experiment we have not necessarily 'prepared' the system in an initial metastable decaying state, and that this formulation is general, and can be used both for 'short excitation' and for 'long excitation' experiments, as well as for intermediate excitation conditions.

Let us regress for a moment and consider some properties of a photon wave packet. The molecular system is now absent so that $H = H_{\text{rad}}$. A general representation of a photon wave packet is

$$\sum_{n_1, n_2, \dots} a_{n_1 n_2 \dots} \prod_i |n_i, \mathbf{k}_i \mathbf{e}_i\rangle, \quad (6.1)$$

where n_i is the population number of the photon state $|\mathbf{k}_i \mathbf{e}_i\rangle$ which is characterized by the energy $\varepsilon_i = k_i$ (where in this section we shall use the sloppy units $\hbar = c = 1$).

For moderately weak fields $n_i = 0$ or 1 for all i , under these conditions we may consider an initial state of the field $\Psi_p(t=0)$ consisting of a wave packet of one-photon states [90]

$$\Psi_p(0) = \sum_{\mathbf{k}} a_{\mathbf{k}} |\mathbf{k}\mathbf{e}\rangle, \quad (6.2)$$

where $a_{\mathbf{k}}$ is the initial amplitude of the state $|\mathbf{k}\mathbf{e}\rangle$, while the summation $\sum_{\mathbf{k}}$ represents integration over photon energies, over spatial directions and summation over all

polarization directions. In what follows we shall use fixed propagation and polarization directions and sum only over the photon energies. The time evolution of the wave packet (in the absence of the molecular system) is

$$\Psi_p(t) = \exp(-iHt) |\Psi(0)\rangle = \sum_k a_k \exp(-ikt) |k\mathbf{e}\rangle. \quad (6.3)$$

It will be useful to define at this point the Fourier transform, $\varphi(t)$ of the wave-packet amplitudes

$$\varphi(t) = \sum_k a_k \exp(-ikt), \quad (6.4)$$

which from (6.3) is just

$$\varphi(t) = \sum_{k'} \langle k'\mathbf{e} | \Psi_p(t) \rangle. \quad (6.5)$$

We shall refer to $\varphi(t)$ as the time-dependent field amplitude. The time evolution of the wave packet is expressed by the function

$$F(t) = |\langle \Psi_p(0) | \Psi_p(t) \rangle|^2 = \sum_k |a_k|^2 \exp(-ikt), \quad (6.6)$$

which just corresponds to the Fourier transform of $|a_k|^2$. The power spectrum $|a_k|^2$ of the photon wave packet is the (inverse) Fourier transform of $F(t)$

$$|a_k|^2 = \frac{1}{2\pi} \int_0^{\infty} dt \exp(ikt) F(t). \quad (6.7)$$

We shall now present a specific example of a photon wave packet which will be subsequently utilized in the study of molecular excitation processes. Consider a wave packet whose amplitudes are given in terms of a coherent Lorentzian distribution [90]

$$a_k = \frac{A_N}{k - \bar{k} + \frac{1}{2}i\gamma_p}, \quad (6.8)$$

where \bar{k} is the center of the distribution, γ_p its width and A_N is a normalization factor. It must be stressed that this choice (6.8) of the energy spread of the wave packet is by no means unique, and will be used for the sake of mathematical convenience. Other shapes (i.e. Gaussian) can be used leading to similar results. The field amplitude for the Lorentzian wave packet is (see Equation (6.4))

$$\varphi(t) = \begin{cases} 2\pi i A_N \exp(-i\bar{k}t - \frac{1}{2}\gamma_p t) & t > 0 \\ 0 & t < 0 \end{cases} \quad (6.9)$$

while the time evolution of the wave packet (expressed in terms of the Fourier transform of the power spectrum, Equation (6.6)) exhibits a simple exponential decay

$$F(t) = \frac{2\pi |A_N|^2}{\gamma_p} \exp[-\gamma_p |t|]. \quad (6.10)$$

It will be useful at this stage to consider two limiting extreme situations for (6.8).

(a) An ideal 'long time' excitation experiment is characterized by a narrow wave packet

$$a_{\mathbf{k}} = \delta(\mathbf{k} - \bar{\mathbf{k}}) \quad (6.11)$$

and consequently

$$|\varphi(t)| = 1, \quad (6.12)$$

In this case the photon wave packet is well defined in energy. Note that this definition is general and does not depend on the specific form (6.8).

(b) When 'short time' excitation conditions are considered we require that $\varphi(t) \propto \delta(t)$ and consequently $a_{\mathbf{k}} = \text{const}$. This limit may be obtained by choosing $A_N = \frac{1}{2}i\gamma_p$ in (6.8) and taking large γ_p values, i.e. $\gamma_p \rightarrow \infty$. Then for the relevant values of \mathbf{k} $|\mathbf{k} - \bar{\mathbf{k}}| \ll \gamma_p$ and thus $a_{\mathbf{k}} \rightarrow 1$.

We note in passing that for different purposes we have to choose different normalization conditions for the initial photon wave packet. If we want to obtain the long time case (a) as a limiting form of a Lorentzian wave-packet excitation we should normalize the excitation amplitudes

$$\sum_{\mathbf{k}} a_{\mathbf{k}} = 1 \quad (6.13)$$

and then set $\gamma_p \rightarrow 0$. For case (b) $\varphi(t)$ should be normalized to a constant, (see Section 8)

$$\int_0^{\infty} \varphi(\tau) d\tau = \text{const}. \quad (6.14)$$

In order to follow the general time evolution of the system it is often convenient to normalize as the power spectrum, i.e.

$$\sum_{\mathbf{k}} |a_{\mathbf{k}}|^2 = 1. \quad (6.15)$$

This latter normalization is adopted later on in this chapter.

We now return to the physical situation of interest and insert back the molecule in the system. At the time $t=0$ the photon wave packet is introduced so that the initial state of the system is

$$\Psi(0) = \sum_{\mathbf{k}} a_{\mathbf{k}} |g, \mathbf{k}\mathbf{e}\rangle. \quad (6.16)$$

This representation of the initial conditions is much more simple and physically transparent than the general expression (4.1) where we have now set for the preparation amplitudes $A_{\mathbf{k}\mathbf{e}} = a_{\mathbf{k}}$ and $A_m = 0$. The time evolution of the system is now obtained from Equation (4.3) in the explicit form

$$\Psi(t) = \sum_{\mathbf{k}} \sum_m |m, \text{vac}\rangle C_{m, g\mathbf{k}\mathbf{e}}(t) a_{\mathbf{k}} + \sum_{\mathbf{k}} \sum_{\mathbf{k}'\mathbf{e}'} |g, \mathbf{k}'\mathbf{e}'\rangle C_{g\mathbf{k}'\mathbf{e}', g\mathbf{k}\mathbf{e}}(t) a_{\mathbf{k}}. \quad (6.16a)$$

We can now immediately project out from (6.16a) either the vacuum states $|m, \text{vac}\rangle$ or the one-photon state $|g, \mathbf{k}'\mathbf{e}'\rangle$. Thus the probability (4.6) for finding the system in any excited zero-photon state at time t is

$$P_e(t) = \sum_m \left| \sum_{\mathbf{k}} C_{m, g\mathbf{k}\mathbf{e}}(t) a_{\mathbf{k}} \right|^2. \quad (6.17)$$

While the probability for finding the system at a time t in any one-photon ground electronic state is (Equation (4.7)):

$$P_g(t) = \sum_{\mathbf{k}'} \left| \sum_{\mathbf{k}} C_{g\mathbf{k}'\mathbf{e}', g\mathbf{k}\mathbf{e}}(t) a_{\mathbf{k}} \right|^2, \quad (6.18)$$

which obviously satisfies the conservation law $P_e(t) + P_g(t) = 1$ for all t . One can ask and answer at this stage some other more detailed and specific questions, such as what is the probability of the population of a subset of the $|m, \text{vac}\rangle$ levels, which correspond to some specific zero-order molecular states, or what is the population of a subset of the one-photon states (i.e. characterized by certain energies, or certain spatial or polarization directions). The general theoretical scheme presented above is able to answer all such questions, however, for the sake of presentation of the general arguments such extensions are not necessary. Let us reflect at this stage what are the 'hidden approximations' in our treatment. First, we have considered only a single electronic ground state. Second, a wave packet consisting only of one-photon states was considered to interact with the system. Third, we are averaging over photons spatial and polarization directions. These approximations can be indeed easily relaxed which will just result in more complex expressions which will not affect the general argument.

Thus Equations (6.17) and (6.18) provide us with all the pertinent general information regarding the experimentally observable time evolution of the system. The probability and rate of photon emission is expressed in terms of products of the preparation amplitudes, now given in terms of the wave packet amplitudes and the decay amplitudes which we had considered in detail in Section 5. We are now in a position to provide exact criteria for the applicability of the concept of 'decay of an initially excited state' and its range of validity, and also to specify the general conditions for 'short excitation' and 'long excitation' experiments.

7. Time Dependence of the Population of the Excited States

We shall now proceed to derive explicit theoretical expressions for the probability function $P_e(t)$. For this purpose we have to utilize the formalism outlined in Section 5 for the evaluation of the decay amplitudes of the system. We have chosen to calculate the function $P_e(t)$ (Equation (4.6)) rather than $P_g(t)$ (Equation (4.7)) although the latter is really related to experimental observables. The reason for that is simply mathematical convenience, as the decay amplitudes (or rather the corresponding matrix elements of the Green's function) of the form $C_{m, g\mathbf{k}\mathbf{e}}(t)$ are somewhat easier to evaluate than the $C_{g'\mathbf{k}'\mathbf{e}', g\mathbf{k}\mathbf{e}}(t)$ amplitudes. In any case, once we have evaluated $P_e(t)$ we

have $P_g(t)$ from the basic conservation relation (4.8). We shall now consider two relevant physical situations. First, the simplest case where only a single excited level carries oscillator strength from the ground state. This is a common state of affairs for many interesting molecular systems which were discussed in Section 2. Second, we shall focus attention on the general case when an arbitrary number of discrete $|m, \text{vac}\rangle$ levels are radiatively connected to the $|g, \mathbf{ke}\rangle$ radiative continuum.

When a single molecular level, say $|s, \text{vac}\rangle$, acts as a doorway state we can set for the radiative coupling matrix elements

$$\langle g, \mathbf{ke} | V | m, \text{vac} \rangle = (H_{\text{int}})_{g\mathbf{ke}, s} \delta_{s, m} \equiv V_{g\mathbf{ke}, s} \delta_{s, m}, \quad (7.1)$$

To evaluate the matrix elements of the Green's function which determine the decay amplitudes $C_{s, g\mathbf{ke}}$ and $C_{m, g\mathbf{ke}} (m \neq s)$ in Equations (6.17), (6.18), we make use of the Dyson Equation (5.7) and get

$$G_{s, g\mathbf{ke}}(E) = G_{ss}(E) V_{s, g\mathbf{ke}} \frac{1}{E - E_g - k + i\eta}, \quad (7.2)$$

$$G_{m, g\mathbf{ke}}(E) = G_{ms}(E) V_{s, g\mathbf{ke}} \frac{1}{E - E_g - k + i\eta}, \quad (7.3)$$

where E_g is the energy of the electronic ground state $|g\rangle$, which can be taken as $E_g = 0$. The form for the matrix elements (7.2) and (7.3) is very convenient, as we shall be able now to relate the probability function $P_e(t)$ to the decay amplitudes $C_{ss}(t)$ and $C_{ms}(t)$ combining only the excited states. These decay amplitudes now take the form

$$C_{m, g\mathbf{ke}}(t) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} dE \exp(-iEt) G_{ms}(E^+) \frac{1}{E - k + i\eta} V_{s, g\mathbf{ke}}, \quad (7.4)$$

for all $|m\rangle$ including $|s\rangle$. Invoking the customary assumption that the radiative coupling matrix elements (7.1) exhibit a weak energy dependence we have

$$C_{m, g\mathbf{ke}}(t) = \frac{1}{2\pi i} V_{s, g\mathbf{ke}} \exp(-ikt) \int dE G_{ms}(E) \frac{\exp[-i(E-k)t]}{E - k + i\eta}. \quad (7.4a)$$

Now making use of the trivial identity

$$\frac{\exp[-i(E-k)t]}{E - k} = (-i) \int_0^t \exp[-i(E-k)\tau] d\tau + \frac{1}{E - k}, \quad (7.4b)$$

and utilizing again the basic definition (7.4) we get

$$2\pi i C_{m, g\mathbf{ke}}(t) = -i V_{s, g\mathbf{ke}} \exp(-ikt) \times \\ \times \int_{-\infty}^{\infty} dE \int_0^t d\tau \exp[-i(E-k)\tau] G_{ms}(E) + C_{m, g\mathbf{ke}}(0).$$

As by definition $C_{m, g\mathbf{ke}}(0) = 0$ we get the final result for the decay amplitude

$$C_{m, g\mathbf{ke}}(t) = -iV_{s, g\mathbf{ke}} \exp(-ikt) \int_0^t d\tau \exp(ik\tau) C_{ms}(\tau). \quad (7.5)$$

Now utilizing Equation (6.17) for $P_e(t)$ and the definition (6.4) for the (time-dependent) field amplitudes we obtain

$$P_e(t) = |V_{s, g\mathbf{ke}}|^2 \sum_m \left| \int_0^t \varphi(t-\tau) C_{ms}(\tau) d\tau \right|^2. \quad (7.6)$$

Equation (7.6) provides us with the final general result for the time dependence of the population of all the excited electronic states, for the simple case of a single doorway state. It is important to realize at this stage that the decay characteristics are determined by the convolution of the decay amplitudes $C_{ms}(t)$ (combining the doorway state with the other excited states) and the field amplitudes.

It is a simple matter to generalize this result for the case of an arbitrary number of optically active excited states whereupon $\langle m, \text{vac} | H_{\text{int}} | g, \mathbf{ke} \rangle \equiv V_{m, g\mathbf{ke}} \neq 0$; for several (or even for all) $|m\rangle$ states. In order to calculate the relevant decay amplitudes we need the matrix elements $G_{m, g\mathbf{ke}}(E)$ which by the Dyson equation take the explicit form

$$G_{m, g\mathbf{ke}}(E) = \sum_{m'} \langle m, \text{vac} | G(E) | m', \text{vac} \rangle \cdot \langle m', \text{vac} | H_{\text{int}} | g, \mathbf{ke} \rangle \frac{1}{E - k + i\eta}. \quad (7.7)$$

We can now define a *generalized doorway states* $|N\rangle$ by the relation

$$|N, \text{vac}\rangle = \frac{1}{\gamma_N} \sum_m |m, \text{vac}\rangle \langle m, \text{vac} | H_{\text{int}} | g, \mathbf{ke} \rangle, \quad (7.8)$$

where

$$\gamma_N^2 = \sum_{m'} \langle g, \mathbf{ke} | H_{\text{int}} | m', \text{vac} \rangle \langle m', \text{vac} | H_{\text{int}} | g, \mathbf{ke} \rangle. \quad (7.9)$$

The definition (7.8) implies a very simple physical interpretation. The generalized doorway state is just a superposition of the excited molecular states each weighted by its coupling strength with the electronic ground-state-radiative continuum $|g, \mathbf{ke}\rangle$. In the special case of the single doorway state

$$|N, \text{vac}\rangle = |s, \text{vac}\rangle. \quad (7.10)$$

The concept of the generalized doorway state was previously invoked by Nitzan and Jortner [60, 62] using first order perturbation theory. They wrote $|N\rangle = \sum_m |m\rangle \mu_{gm}$ where μ is the transition moment operator. Definition (7.8) is more general. Finally, it is worthwhile noting that the generalized doorway state (7.8) can be expressed in terms of the projection operators (5.8) and (5.9) whereupon $|N, \text{vac}\rangle = (1/\gamma_N) \hat{P} H_{\text{int}} \times$

$\times |g, \mathbf{ke}\rangle$. As $\hat{Q}H_{\text{int}}\hat{Q}=0$, then in view of the completeness condition (5.10), one gets the compact form

$$|N, \text{vac}\rangle = \frac{1}{\gamma_N} H_{\text{int}} |g, \mathbf{ke}\rangle, \quad (7.8a)$$

$$|\gamma_N|^2 = \langle g, \mathbf{ke} | H_{\text{int}}^2 |g, \mathbf{ke}\rangle. \quad (7.9a)$$

This definition is very useful being independent of the basis set used to specify the excited states in the \hat{P} subspace.

Returning now to the evaluation of the decay amplitudes in the general case, Equation (7.7) for the matrix elements of the Green's function now takes the form

$$G_{m, g\mathbf{ke}}(E) = \gamma_N G_{m, N}(E) \frac{1}{E - k + i\eta}. \quad (7.11)$$

It is apparent that Equation (7.11) provides us with a generalization of the simple relations (7.2) and (7.3) as in the case of a single doorway state Equation (7.10) applies.

Utilizing Equation (7.11) we can immediately obtain a general expression for the corresponding decay amplitudes following the same methods as applied for the derivation of Equations (7.5) from (7.4). Thus we get

$$C_{m, g\mathbf{ke}}(t) = -i\gamma_N \exp(-ikt) \int_0^t d\tau \exp(ik\tau) C_{mN}(\tau), \quad (7.12)$$

while the population of the excited state is obtained from Equations (6.17), (6.4) and (7.12) in the form

$$P_e(t) = |\gamma_N|^2 \sum_m \left| \int_0^t d\tau \varphi(t-\tau) C_{mN}(\tau) \right|^2, \quad (7.13)$$

where for the sake of clarity we redefine the relevant decay amplitudes

$$\begin{aligned} C_{m, N}(t) &= \langle m, \text{vac} | U(t, 0) |N, \text{vac}\rangle = \\ &= \frac{1}{2\pi i} \int dE \exp(-iEt) \langle m, \text{vac} | G(E) |N, \text{vac}\rangle. \end{aligned} \quad (7.14)$$

Equations (7.13) and (7.14) provide us with the desirable general result for the time evolution of an excited state consisting of an arbitrary (dense or sparse) level structure and where an arbitrary number of these levels carry oscillator strength from the ground state. This general form (7.13) implies that the time evolution $P_e(t)$ is determined by a sum of amplitudes squared, where each amplitude is determined by the convolution of the (time-dependent) field amplitude and the decay amplitude, which combines the generalized doorway state with the various (zero-order) molecular states. We are able now to discuss the general features of both 'long time' and 'short time' excitation experiments as limiting cases of Equation (7.13).

We shall start with the short excitations. This will be conducted in two stages. First, we shall provide a rigorous definition of an 'initially prepared' state of a physical system (see Section 8). Subsequently, by introducing the concept of 'independently decaying states' (Section 9) we shall be able to provide explicit expressions for the time evolution of a system consisting of any number of closely spaced levels at an arbitrary excitation time scale. This will be accomplished in Section 9.

8. An 'Initially Prepared' Doorway State

The understanding of the nature of the 'initially prepared' optically excited state is crucial for the understanding of any short excitation decay experiment when one wants to formulate the precise conditions for validity of the separation of the excitation and decay processes. Early treatments of this problem [34, 83-84] considered the radiative excitation process to lowest order and accounted for the nonradiative decay occurring during the excitation process. These formulations of the excitation and nonradiative decay process were provided by considering the time evolution of excited molecular eigenstates utilizing the time evolution of the density matrix. The original treatments [34, 83-84] were grossly oversimplified as they disregarded the radiative decay channel. Rhodes [91] has demonstrated how to handle the excitation and both radiative and nonradiative decay using the density matrix formalism and how to follow the time evolution after the termination of the pulse. He has shown [91] that for long excitation times the density matrix assumes a partially diagonal form, however [60], this does not affect the decay characteristics in the statistical limit. In this context Freed [79] has treated the excitation-decay process by starting from the system at $t=0$ in the state $|g, \mathbf{ke}\rangle$ and subsequently terminating the photon field after an arbitrary time. $\Psi(t=0)$ in his formalism is precisely defined in energy and thus this approach is adequate to long time excitations rather than for short excitation experiments. An unsatisfactory feature common to all these treatments mentioned above involves the termination of the exciting pulse after an arbitrary time. A way out of this difficulty is using a delta function excitation in time and treating this preparation process to low order [9, 35-36]. This approach is basically valid for model systems, although it is esthetically unattractive. The present approach adopted herein provides a self-consistent general solution to the problem of 'preparation' of metastable decaying states.

It should be borne in mind that the definition of an 'initially excited' state is essentially a theoretical problem. However, the nature of the time resolved decay pattern experimentally observed in a short time experiment requires this definition. In order to provide a meaningful definition for this concept two basic conditions have to be satisfied: (a) A single state has to be defined which is radiatively coupled to and carrying all the oscillator strength from the ground state. (b) The duration of the exciting pulse is appreciably shorter than all the (radiative and nonradiative) 'decay times' of the excited states. This second condition will be considered in two stages. First we shall consider excitation by a 'white' pulse containing all frequencies. This leads to an

unrealistic state of affairs, as obviously the system contains also other excited states, so that such a pulse will excite all states including those which are of no interest to the experimentalist. We shall thus have to provide a more precise definition of the decay times for a complicated molecular system.

We consider first the idealized system which involves a small number (say, two) of excited electronic configurations and these constitute the entire energy spectrum of excited states. Obviously this system can involve an arbitrary number of vibronic levels corresponding to these two electronic configurations. This idealized system is now excited by a light pulse which contains all frequencies, thus the Lorentzian pulse (6.8) takes the limiting form $a_{\mathbf{k}} = \text{const.}$ for all \mathbf{k} while the field amplitude is given by $\varphi(t) = \phi \cdot \delta(t)$ where ϕ is a normalization factor to be determined later. This delta excitation function obviously satisfies condition (b). Thus the time evolution of a general excited state (Equation (7.13)) takes now the simple form

$$P_e(t) = |\gamma_N|^2 |\phi|^2 \sum_m |C_{mN}(t)|^2, \quad (8.1)$$

while for the special case of a single doorway state we have

$$P_e(t) = |\gamma_N|^2 |\phi|^2 \sum_m |C_{ms}(t)|^2. \quad (8.1a)$$

Equation (8.1) provides a proper specification of an 'initially prepared' state. From these results we conclude that

(a) Under the extreme conditions of broad band excitation, the time evolution of the excited states is equivalent to preparing the $\phi \gamma_N |N, \text{vac}\rangle$ state at $t=0$ and this initial state exhibits time evolution. Choosing $\phi = 1/\gamma_N$ we obtain the normalized state $|N, \text{vac}\rangle$ at $t=0$.

(b) Under these extreme excitation conditions the time evolution of the system is solely determined by the decay amplitudes, and provides only information concerning the molecular decay characteristics.

(c) In this case, the time-dependent amplitudes (4.5) are $d_m(t) = C_{m,N}(t)$ and $d_{\mathbf{k}e}(t) = C_{g\mathbf{k}e,N}(t)$. Utilizing the basic definitions (4.6) and (4.7) and the conservation law (4.8), the population probability of the ground one photon states is now

$$P_g(t) = \sum_{\mathbf{k}e} |C_{g\mathbf{k}e,N}(t)|^2, \quad (8.2)$$

or for the special case of a single doorway state

$$P_g(t) = \sum_{\mathbf{k}e} |C_{g\mathbf{k}e,s}(t)|^2. \quad (8.2a)$$

(d) It will be useful to provide an alternative expression for the population of the ground state (Equation (8.2)), expressing it in terms of the diagonal decay amplitudes $C_{NN}(t)$ (or of $C_{ss}(t)$ for a single doorway state). We shall thus be able to relate the photon counting rate to the probability of the survival of the 'initially prepared' excited state at time t . Let us consider first the simple situation of the single doorway state.

In analogy with (7.5) we have

$$C_{g\mathbf{k}e, s}(t) = -iV_{g\mathbf{k}e, s} \exp(-ikt) \int_0^t d\tau \exp(ik\tau) C_{ss}(\tau). \quad (8.3)$$

Inserting this result into Equation (8.2a) results in

$$P_g(t) = \sum_{\mathbf{k}e} |V_{g\mathbf{k}e, s}|^2 \int_0^t d\tau \int_0^t d\tau' \exp(ik(\tau - \tau')) C_{ss}(\tau) C_{ss}^*(\tau'). \quad (8.4)$$

The summation in Equation (7.4) implies after averaging on polarization directions

$$\sum_{\mathbf{k}e} \rightarrow \int \varrho_r(E) dk, \quad (8.5)$$

where $\varrho_r(E)$ is the density of photon states at the energy $E=k$. We shall further define the radiative width of the $|s\rangle$ state by the common relation

$$\Gamma_s(E) = 2\pi |V_{g\mathbf{k}e, s}|^2 \varrho_r(E). \quad (8.6)$$

Assuming that it is a slowly varying function of the energy around $E=E_s$ and we set $\Gamma_s(E) = \Gamma_s(E_s) = \Gamma_s$. Equation (8.4) takes the form

$$\begin{aligned} P_g(t) &= \frac{\Gamma_s}{2\pi} \int_0^t d\tau \int_0^t d\tau' \int_0^\infty dk \exp(ik(\tau - \tau')) C_{ss}^*(\tau) C_{ss}(\tau') = \\ &= \Gamma_s \int_0^t d\tau |C_{ss}(\tau)|^2, \end{aligned} \quad (8.7)$$

and the photon counting rate for a single doorway state is just

$$\dot{P}_g(t) = \Gamma_s |C_{ss}(t)|^2. \quad (8.7a)$$

Equation (8.7a) was previously derived using the Wigner-Weisskopf method [39, 47].

Turning now to the case of the generalized doorway state we utilize the basic definitions (7.8) to write

$$\gamma_N C_{g\mathbf{k}e, N}(t) = \sum_m C_{g\mathbf{k}e, m}(t) V_{m, g\mathbf{k}e}, \quad (8.8)$$

and from Equation (7.11) we have

$$iC_{g\mathbf{k}e, m}(t) = \gamma_N \exp(-ikt) \int_0^t d\tau \exp(ik\tau) C_{Nm}(\tau). \quad (8.9)$$

Thus

$$\begin{aligned}
 P_g(t) &= \sum_{\mathbf{k}\mathbf{e}} \left| \sum_m \int_0^t d\tau \exp(ik\tau) C_{Nm}(\tau) V_{m,g\mathbf{k}\mathbf{e}} \right|^2 = \\
 &= |\gamma_N|^2 \sum_{\mathbf{k}\mathbf{e}} \left| \int_0^t d\tau \exp(ik\tau) C_{NN}(\tau) \right|^2.
 \end{aligned} \tag{8.10}$$

Making use of Equation (8.5) and performing the integration over k we get

$$P_g(t) = \Gamma_N^{(\text{rad})} \int_0^t |C_{NN}(\tau)|^2 d\tau \tag{8.11}$$

and

$$\dot{P}_g(t) = \Gamma_N^{(\text{rad})} |C_{NN}(t)|^2. \tag{8.11a}$$

In the derivation of (8.10), (8.11) we have neglected the weak \mathbf{k} dependence of γ_N and we have defined

$$\Gamma_N^{(\text{rad})} = 2\pi |\gamma_N|^2 \varrho_r, \tag{8.11b}$$

and ϱ_r is the density of the radiation field states around the relevant energy. In analogy with (8.7) we see that $\Gamma_N^{(\text{rad})}$ is the radiative width of the $|N\rangle$ state. The simple-compact form of Equation (8.11) should not mislead us, as this expression involves a large number of cross terms. These concise expressions ((8.7 and (8.11)) will be invoked again to relate the decay rate of the system (i.e. photon counting rate) to optical absorption line shape (see Section 17).

Up to this point we have been concerned with a single ground molecular state $|g\rangle$. Any real molecule is characterized by a vibrational manifold $\{|gv\rangle\}$ (where $v=0, 1, \dots$ correspond to the collection of vibrational quantum numbers) in the ground state and for certain applications we have to consider radiative decay processes to different radiative continua $\{|gv, \mathbf{k}\mathbf{e}\rangle\}$ ($v=0, 1, \dots$). For the case of a single molecular resonance in a large molecule (see Section 13) this extension is of little interest. However, in the case of internal conversion [47, 51] from a highly excited singlet state (see Figure 1g) the $|l, \text{vac}\rangle$ states are radiatively coupled to $|gv, \mathbf{k}\mathbf{e}\rangle$ levels characterized by high v values, and such an extension of the theory is pertinent. The initially excited doorway state is now

$$|N_0, \text{vac}\rangle = \frac{1}{\gamma_{N_0}} H_{\text{int}} |g_0, \mathbf{k}\mathbf{e}\rangle. \tag{8.12}$$

We can subsequently define a whole set of discrete states

$$|N_v, \text{vac}\rangle = \frac{1}{\gamma_{N_v}} H_{\text{int}} |gv, \mathbf{k}\mathbf{e}\rangle, \tag{8.13}$$

where

$$|\gamma_{Nv}|^2 = \langle gv, \mathbf{ke} | H_{\text{int}} \cdot H_{\text{int}} | gv, \mathbf{ke} \rangle. \quad (8.14)$$

In the ideal short time experiment, where the $|N_0\rangle$ state is initially excited, the probability $P_g^v(t)$ for population of the $|gv\rangle$ ground state level at time t is given by

$$P_g^v(t) = \Gamma_{Nv}^{(\text{rad})} \int_0^t |C_{Nv, N_0}(\tau)|^2 d\tau, \quad (8.15)$$

where

$$\Gamma_{Nv}^{(\text{rad})} = 2\pi |\gamma_{Nv}|^2 \rho_r. \quad (8.16)$$

The different radiative decay channels to different v states (or groups of v states) can be separated experimentally by monitoring the energy resolved decay spectrum. We have to distinguish at this point between the doorway state $|N_0\rangle$ and the 'escaping' states $|N_v\rangle$ (all v). In the simplest case there is only a single escape state $|N_0\rangle$. In more complicated situations there is a whole manifold of scape states. Under the latter circumstances the decay probabilities $P_g^v(t)$ will be characterized by a different time dependence for different v values.

We were able to obtain a general formal picture for the decay of an initially excited state prepared by a delta function field excitation amplitudes. These general results are not entirely satisfactory because of two reasons. First, the expressions obtained for the general time evolution of the system and for the case of the decay of initially prepared state are formal. To account for any real life situation we have to provide explicit expressions for the decay amplitudes. Second, the description of the excitation process is suitable only for the model system consisting of two electronic configurations. When the experimentalist will hit a real molecule by an extremely broad pulse including all frequencies, he will excite a multitude of electronic states, and the experimentally monitored photon counting rate will not be very informative. One has to find some weaker conditions than the delta function excitation to specify the decay of the excited states. We have stated in condition (b) that the pulse duration should not exceed the relevant 'decay times' of the system. We have thus to provide a proper description of these characteristic decay times, or rather decay widths, of the general molecular system. For a bunch of closely spaced levels the resulting decay pattern is complex, exhibiting several decay times and/or oscillatory interference terms. Subsequently we shall be able to define a short time experiment by the condition that the width of the wave packet exceeds all these characteristic widths. We now proceed to provide the necessary parameters which determine the molecular decay amplitudes.

9. An Effective Hamiltonian for Independently Radiatively Decaying Levels

In order to apply the general theory outlined above we shall introduce and explore an effective Hamiltonian which specifies the time evolution of the excited molecular states in the presence of the radiation field. The use of such effective Hamiltonians is

common in fields such as magnetic resonance, where in handling relaxation problems one considers the time evolution of a small part of the system. In our problem we shall consider the time evolution of the subpart $\{|m, \text{vac}\rangle\}$ consisting of all discrete zero photon electronically excited states.

Radiationless transitions in a hypothetical system, in the absence of radiative decay, can be adequately described in terms of the molecular eigenstates which diagonalize the electronic Hamiltonian H_M . However, for a real physical system of closely spaced levels, the molecular eigenstates lose their general physical utility. Adopting the generalized Wigner-Weisskopf approximation, Bixon *et al.* [38] have demonstrated that the time evolution of the excited molecular states can be described in terms of an effective Hamiltonian. The same argument was provided by Freed and Jortner [41] in terms of the Green's function formalism.

The definition of the effective Hamiltonian for the excited states rests on the following observations:

(1) The Hilbert space is partitioned into the subspaces \hat{P} and \hat{Q} (see Equations (5.8)–(5.10)).

(2) The general time evolution of the excited states Equation (7.13) or Equation (7.6), is determined by decay amplitudes combining levels in the \hat{P} subspace.

(3) Thus, the evaluation of the relevant decay amplitudes requires the matrix elements of $\hat{P}G\hat{P}$ between excited states.

(4) The operator $\hat{P}G\hat{P}$ (Equation (5.12)) will be rewritten in the form

$$\hat{P}G(E)\hat{P} = \hat{P}(E - H_{\text{eff}} + i\eta)^{-1}\hat{P}, \quad (9.1)$$

where the effective Hamiltonian in the \hat{P} subspace is

$$H_{\text{eff}} = \hat{P}(H_0 + R)\hat{P}. \quad (9.2)$$

(5) The evolution operator in the \hat{P} subspace can be formally represented utilizing Equation (5.6)

$$\hat{P}U(t, 0)\hat{P} = \int_{-\infty}^{+\infty} dE \exp(-iEt) \hat{P}G(E)\hat{P}. \quad (9.3)$$

Now, making use of (9.2) we get

$$\begin{aligned} \hat{P}U(t, 0)\hat{P} &= \int_{-\infty}^{+\infty} dE \hat{P} \frac{\exp(-iEt)}{E - H_{\text{eff}} + i\eta} \hat{P} = \exp[-i\hat{P}(H_0 + R)\hat{P}t] \hat{P} = \\ &= \hat{P} \exp[-iH_{\text{eff}}t] \hat{P}. \end{aligned} \quad (9.3a)$$

(6) A set of states $\{|j, \text{vac}\rangle\}$ defined in the \hat{P} subspace which diagonalize the effective Hamiltonian can be then used for the spectral representation of $\hat{P}G\hat{P}$ and of the evolution operator (9.3a) in the \hat{P} subspace.

Let us now proceed to explore the general form of the effective Hamiltonian (9.1).

Utilizing the definition of the level shift operator (Equation (5.13)) we have

$$H_{\text{eff}} = \hat{P} \left(H + V \hat{Q} \frac{1}{E - \hat{Q} H \hat{Q} + i\eta} \hat{Q} V \right) \hat{P}. \quad (9.4)$$

As $\hat{P} (H_{\text{rad}} + H_{\text{int}}) \hat{P} = 0$ and $\hat{P} V \hat{Q} = \hat{P} H_{\text{int}} \hat{Q}$ we obtain the formal result

$$H_{\text{eff}} = \hat{P} \left(H_M + H_{\text{int}} \hat{Q} \frac{1}{E - \hat{Q} H \hat{Q}} \hat{Q} H_{\text{int}} \right) \hat{P}. \quad (9.5)$$

The effective Hamiltonian can be thus recast in the matrix form

$$H_{\text{eff}} = H_M + \Delta - \frac{1}{2} i \Gamma, \quad (9.6)$$

where it is understood that H_{eff} combines only $|m, \text{vac}\rangle$ states in the \hat{P} subspace. The explicit forms for the level shift matrix Δ and for the decay matrix Γ are obtained from the relaxation contribution of the level shift operator Equation (5.14) to Equation (9.5).

$$\begin{aligned} \Delta(E) - \frac{i}{2} \Gamma(E) &= \sum_{\mathbf{g}\mathbf{e}} \frac{H_{\text{int}} |g, \mathbf{k}\mathbf{e}\rangle \langle g, \mathbf{k}\mathbf{e}| H_{\text{int}}}{E - E_g - k + i\eta} = \\ &= \sum_{\mathbf{e}} \int \frac{H_{\text{int}} |g\mathbf{k}\mathbf{e}\rangle \langle g\mathbf{k}\mathbf{e}| H_{\text{int}}}{E - k + i\eta} \varrho_r(k) d\mathbf{k}, \end{aligned} \quad (9.7)$$

where we have applied Equation (8.5) and set $E_g = 0$. Utilizing the well-known relation

$$\int \frac{f(k)}{E - k + i\eta} dk = PP \int \frac{f(k)}{E - k} - i\pi f(E), \quad (9.8)$$

where PP represents the Cauchy principal part of the integral, we obtain

$$\Delta(E) = PP \sum_{\mathbf{e}} \int \frac{H_{\text{int}} |g\mathbf{k}\mathbf{e}\rangle \langle g\mathbf{k}\mathbf{e}| H_{\text{int}}}{E - k} \varrho(\mathbf{k}) d\mathbf{k}, \quad (9.9)$$

$$\Gamma(E) = 2\pi \sum_{\mathbf{e}} \int d\Omega H_{\text{int}} |g\mathbf{k}\mathbf{e}\rangle \varrho_r(E) \langle g\mathbf{k}\mathbf{e}| H_{\text{int}}. \quad (9.10)$$

The matrix elements of the level shift matrix are

$$\Delta_{mm'} = PP \sum_{\mathbf{e}} \int \frac{\langle m, \text{vac}| H_{\text{int}} |g, \mathbf{k}\mathbf{e}\rangle \langle g, \mathbf{k}\mathbf{e}| H_{\text{int}} |m', \text{vac}\rangle \varrho_r(k)}{E - k} d\mathbf{k}. \quad (9.11)$$

This is a generalization of the concept of the ordinary level shift of a single resonance (i.e. single level interacting with a continuum). The elements of the (real) level shift matrix (9.9) diverge when the integration over k is performed to infinity, as $\varrho_r(k) \propto k^2$. This well-known difficulty [92] of quantum electrodynamics is resolved by a renormalization procedure as is done in the theory of the Lamb shift. The diagonal and off-diagonal matrix elements of Δ are expected to be of the order of [86] $\Delta \sim L^H/n$ where

$L^H \sim 10^{-2} \text{ cm}^{-1}$ is the hydrogenic Lamb shift, and n is the number of effectively coupled levels. Then Δ varies from 10^{-2} cm^{-1} for a small number of coupled levels to 10^{-6} cm^{-1} for a dense distribution. These terms will result in shifts of the (real part) of H_{eff} and they are of minor practical interest.

Of crucial importance is the damping matrix (9.11) which is explicitly given in the form

$$\Gamma_{mm'} = 2\pi \sum_{\mathbf{e}} \int d\Omega \langle m, \text{vac} | H_{\text{int}} | g, \mathbf{ke} \rangle \langle g, \mathbf{ke} | H_{\text{int}} | m', \text{vac} \rangle \varrho_{\mathbf{e}}. \quad (9.12)$$

The following features of the damping matrix should be noted:

- (a) Γ provides a generalization of the Fermi golden rule. For the decay of a single resonance, the resonance width (or the reciprocal decay time) is given by Γ_{mm} .
- (b) Γ is, in general, nondiagonal.
- (c) Γ is Hermitian.
- (d) Γ is a slowly varying function of the energy in the range of interest.
- (e) The offdiagonal matrix elements of Γ represent coupling between the $|m, \text{vac}\rangle$ states via the one-photon states,

$$|m, \text{vac}\rangle \rightarrow |g, \mathbf{ke}\rangle \rightarrow |m', \text{vac}\rangle.$$

These off-diagonal contributions will be important only in the case of near degeneracy when these terms are comparable to the energy spacing between the energy levels, i.e.

$$\Gamma_{mm'} \sim |E_m - E_{m'}|. \quad (9.13)$$

To be more specific let us now provide some simple examples for the effective Hamiltonian (9.6) in different representations, neglecting the (small) contribution of the level shift matrix. Consider first the Born–Oppenheimer basis $|s\rangle$ and $\{|I\rangle\} E|m\rangle$ where $|s\rangle$ is the single doorway state. Then the effective Hamiltonian is

$$H_{\text{eff}} = \begin{pmatrix} E_s - \frac{1}{2}i\Gamma_s & (H_v)_{st} & (H_v)_{st'} \dots \\ (H_v)_{ts} & E_t & 0 \dots \\ (H_v)_{t's} & 0 & E_{t'} \dots \end{pmatrix}, \quad (9.14)$$

so that the electronic Hamiltonian is off-diagonal, while the damping matrix is diagonal, with a single finite diagonal term given by (7.7). In the molecular eigenstates representation $\{|n\rangle\} E\{|m\rangle\}$ where the molecular eigenstates $\{|n\rangle\}$ are characterized by the energies E_1, E_2, \dots, E_n etc. The effective Hamiltonian assumes the form

$$H_{\text{eff}} = \begin{pmatrix} E_1 - \frac{1}{2}i\Gamma_{11} & -\frac{1}{2}i\Gamma_{12} & \dots \\ -\frac{1}{2}i\Gamma_{21} & E_2 - \frac{1}{2}i\Gamma_{22} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix}. \quad (9.15)$$

Thus the electronic Hamiltonian is diagonal, but we pay the price by having an off-diagonal damping matrix.

We shall now proceed to explore the general properties of the effective Hamiltonian (9.6):

(1) The effective Hamiltonian is nonhermitian. This can be rationalized by noting that we consider only a subspace of the Hilbert space consisting of the (discrete) zero-photon manifold. In fact, from the basic definition (9.6) and from the hermitian property of Γ we conclude that H_{eff} is in general a sum of a Hermitian matrix H_M and an antihermitian matrix, $-\frac{1}{2}i\Gamma$.

(2) When the effective Hamiltonian is nondiagonal within a given basis of zero-photon states, these states cannot be considered to decay independently, in view of the appearance of off-diagonal terms in H_{eff} . Thus the evolution operator (9.3a) in the \hat{P} subspace will contain such off-diagonal contributions.

(3) One can find, in principle, for the general case and in practice for simple model systems, a basis of zero-photon states $\{|j, \text{vac}\rangle\}$ which diagonalize the effective Hamiltonian. This basis set is obtained by the transformation:

$$\begin{pmatrix} |j_1, \text{vac}\rangle \\ |j_2, \text{vac}\rangle \\ \vdots \end{pmatrix} = D \begin{pmatrix} |m_1, \text{vac}\rangle \\ |m_2, \text{vac}\rangle \\ \vdots \end{pmatrix}. \quad (9.16)$$

(4) The effective Hamiltonian is diagonalized by the transformation

$$D H_{\text{eff}} D^{-1} = A, \quad (9.17)$$

where A is diagonal, $A_{ij} = A_{ii}\delta_{ij}$. As H_{eff} is a sum of Hermitian matrix H_M and an antihermitian matrix $-\frac{1}{2}i\Gamma$, D is nonunitary matrix. When we use a basis set $|m\rangle$ of real functions, H_{eff} is a complex symmetric matrix and it can be always diagonalized using an orthogonal (nonunitary) transformation matrix D .

(5) The matrix elements of the diagonal matrix A (9.17) are in general complex

$$A_{jj'} = (E_j - \frac{1}{2}i\Gamma_j) \delta_{jj'}. \quad (9.18)$$

(6) The effective Hamiltonian matrix in the $|j, \text{vac}\rangle$ representation is not given by the usual scheme suitable for orthogonal basis sets, i.e.

$$A_{jj'} \neq \langle j, \text{vac} | H_{\text{eff}} | j', \text{vac} \rangle = (E_{j'} - \frac{1}{2}i\Gamma_{j'}) \cdot \langle j, \text{vac} | j', \text{vac} \rangle. \quad (9.19)$$

(7) The new basis set $|j, \text{vac}\rangle$ which diagonalizes H_{eff} is characterized by complex energies $E_j - \frac{1}{2}i\Gamma_j$. It is natural to assign the real part of (9.19) to the energies of these states, i.e. $\text{Re } A_{jj} = E_j$ while the imaginary parts $\text{Im } A_{jj} = \frac{1}{2}\Gamma_j$ corresponds to the characteristic widths of the system in the presence of the radiation field.

(8) The diagonal sum rule applies to the transformation (9.17). Thus

$$\text{Re} [\text{Tr } A] = \text{Re} [\text{Tr } H_{\text{eff}}] = \text{Tr} [H_M], \quad (9.20)$$

$$\text{Im} [\text{Tr } A] = \text{Im} [\text{Tr } H_{\text{eff}}] = -\frac{1}{2} [\text{Tr } \Gamma]. \quad (9.21)$$

Equation (9.20) implies that

$$\sum_j E_j = \sum_m E_m, \quad (9.22)$$

which is the conventional diagonal sum rule, whereupon the sum of the real energies

of the $|j, \text{vac}\rangle$ states is equal to the sum of the energies of any other basis states $|m, \text{vac}\rangle$. From Equation (9.21) we have the more interesting result

$$\sum_j \Gamma_j = \sum_m \Gamma_{mm}. \quad (9.23)$$

Thus the sum of the widths of the $|j, \text{vac}\rangle$ states is equal to the sum of the diagonal elements of the (nondiagonal) Γ matrix in any $|m, \text{vac}\rangle$ representation.

(9) The $|j, \text{vac}\rangle$ basis set is *not* orthogonal. This is a consequence of the antihermitian property of $\frac{1}{2}i\Gamma$ which causes the non-unitarity of D .

(10) In order to expand \hat{P} in terms of diagonalized projections we shall now define the complementary basis set $|\bar{j}, \text{vac}\rangle$ by the relation:

$$\begin{pmatrix} |\bar{j}_1, \text{vac}\rangle \\ |\bar{j}_2, \text{vac}\rangle \\ \vdots \end{pmatrix} = (D^{-1})^\dagger \begin{pmatrix} |m_1, \text{vac}\rangle \\ |m_2, \text{vac}\rangle \\ \vdots \end{pmatrix}. \quad (9.24a)$$

In the special case when the $|m, \text{vac}\rangle$ basis set has a real representation the transformation is orthogonal, i.e. $D^{-1} = \tilde{D}$, and we get

$$(D^{-1})^\dagger = D^*, \quad (9.24b)$$

so that in this special case $|\bar{j}, \text{vac}\rangle = |j^*, \text{vac}\rangle$.

We can write for the general case

$$\hat{P} = \sum_j |j, \text{vac}\rangle \langle \bar{j}, \text{vac}|, \quad (9.25)$$

where $|\bar{j}, \text{vac}\rangle$ are obtained from the transformation (9.24). This relation is the consequence of the orthogonality of $\{|j\rangle\}$ and $\{|\bar{j}\rangle\}$, i.e.

$$\langle \bar{j}, \text{vac} | j', \text{vac}\rangle = \delta_{jj'}.$$

Finally we can derive a form of \hat{P} in terms of the $|j, \text{vac}\rangle$ basis. From Equations (9.24) and (9.25) we get

$$|j, \text{vac}\rangle = \sum_{j'} [(D^{-1})^\dagger D^{-1}]_{jj'} |j', \text{vac}\rangle \quad (9.26)$$

and

$$\hat{P} = \sum_{jj'} |j', \text{vac}\rangle [(D^{-1})^\dagger D^{-1}]_{jj'}^* \langle j', \text{vac}|. \quad (9.27)$$

In the special case when we use a real basis set,

$$\begin{aligned} (D^{-1})^{\dagger*} &= D, \\ (D^{-1})^* &= D^\dagger \end{aligned} \quad (9.28)$$

and we get

$$\hat{P} = \sum_{jj'} |j, \text{vac}\rangle (DD^\dagger)_{jj'} \langle j', \text{vac}|. \quad (9.29)$$

(11) We shall now explore the most important feature of the basis sets. The time

evolution operator (Equation (9.3a)) is

$$\begin{aligned}\hat{P}U(t, 0)\hat{P} &= \hat{P} \exp(-iH_{\text{eff}}t)\hat{P} = \sum_j |j, \text{vac}\rangle \exp[-iA_{jj}t] \langle j, \text{vac}| = \\ &= \sum_j |j, \text{vac}\rangle \exp[-iE_jt - \frac{1}{2}\Gamma_j t] \langle j, \text{vac}|.\end{aligned}\quad (9.30)$$

This general result implies that the decay amplitudes combining any pair of $|m, \text{vac}\rangle$ states will be expressed as a superposition of terms of the form $\exp[-\frac{1}{2}\Gamma_j t - iE_j t]$, i.e. a sum of independently decaying exponentials. Thus the basis set $|j, \text{vac}\rangle$ can be considered as the set of *independently decaying levels* characterizing the molecular system.

(12) To conclude this formal discussion we shall recast the Green's function in the \hat{P} subspace in the spectral representation of the independently decaying levels $|j, \text{vac}\rangle$. Making use of Equations (9.1), (9.19) and (9.25) we get

$$\hat{P}G(E)\hat{P} = \sum_j \frac{|j\rangle \langle j|}{E - E_j + \frac{1}{2}i\Gamma_j}, \quad (9.31)$$

which is of course nothing but the inverse Fourier transform of (9.30). Equation (9.31) will be useful in the study of optical lineshapes of a system with a large number of closely spaced levels (see Section 17).

10. Theoret' 1 Results for Time Evolution of Excited Molecular States

We are now able to provide explicit expressions for the general time evolution of an excited molecular state. The decay amplitude (7.14) which describes the time evolution of the excited state with the aid of (9.30) takes the form

$$C_{mN}(\tau) = \sum_j \langle m, \text{vac} | j, \text{vac}\rangle \exp[-iE_j\tau - \frac{1}{2}\Gamma_j\tau] \langle j, \text{vac} | N, \text{vac}\rangle. \quad (10.1)$$

Thus Equation (7.13) is

$$\begin{aligned}P_e(t) &= |\gamma_N|^2 \sum_m \left| \int_0^t d\tau \varphi(t-\tau) \sum_j \langle m, \text{vac} | j, \text{vac}\rangle \cdot \exp[-iE_j\tau - \frac{1}{2}\Gamma_j\tau] \times \right. \\ &\quad \left. \times \langle j, \text{vac} | N, \text{vac}\rangle \right|^2.\end{aligned}\quad (10.2)$$

We now note that $\hat{Q}|j, \text{vac}\rangle = 0$ for each $|j, \text{vac}\rangle$ whereupon Equation (10.2) can be further simplified and recast to include only matrix elements of the $|N, \text{vac}\rangle$ state and the $|j, \text{vac}\rangle$ basis

$$\begin{aligned}P_e(t) &= \int_0^t d\tau \int_0^t d\tau' \varphi(t-r) \varphi^*(t-\tau') \cdot \sum_{jj'} A_{jj'} \exp[-iE_j\tau - \frac{1}{2}\Gamma_j\tau] \times \\ &\quad \times \exp[iE_{j'}\tau' - \frac{1}{2}\Gamma_{j'}\tau'],\end{aligned}\quad (10.3)$$

where

$$A_{j'j} = \langle N | j', \text{vac} \rangle \langle j', \text{vac} | j, \text{vac} \rangle \langle \bar{j}, \text{vac} | N, \text{vac} \rangle \cdot |\gamma_N|^2. \quad (10.4a)$$

Utilizing the general formal definition (7.8a) of the doorway state we can express the coefficients $A_{j'j}$, in (10.3) in terms of the radiative coupling matrix elements with the ground state

$$A_{j'j} = \langle g, \mathbf{ke} | H_{\text{int}} | j', \text{vac} \rangle \langle j', \text{vac} | j, \text{vac} \rangle \langle \bar{j}, \text{vac} | H_{\text{int}} | g, \mathbf{ke} \rangle. \quad (10.4b)$$

Equation (10.3) may be rewritten in the following manner:

$$P_e(t) = \sum_{j'j} A_{j'j} F_{j'}^{p*}(t) F_j^p(t) = \sum_j A_{jj} |F_j^p(t)|^2 + 2\text{Re} \sum_{j'>j} A_{j'j} F_{j'}^{p*}(t) F_j^p(t), \quad (10.5)$$

where

$$F_j^p(t) = \int_0^t dr \varphi(t-\tau) \exp(-iE_j\tau) \exp(-\frac{1}{2}\Gamma_j\tau). \quad (10.6)$$

We note that $\varphi(\tau)=0$; and $C_{jj}(\tau)=0$ for $\tau<0$. Thus the integral (10.6) can be rewritten as $\int_{-\infty}^{\infty} d\tau \varphi(t-\tau) C_{jj}(\tau)$. Utilizing the convolution theorem for Fourier transforms we get

$$F_j^p(t) = -i \int_{-\infty}^{\infty} dE \exp(-iEt) G_{jj}(E) a_k(E). \quad (10.7)$$

To bring Equation (10.3) into a more tractable form let us utilize the Lorentzian photon wave packet (6.8) $a_k = A_N / (k - k + \frac{1}{2}i\gamma_p)$ for optical excitation. Thus we obtain

$$F_j^p(t) = 2\pi A_N \frac{\exp[-iE_j t] \exp[-\frac{1}{2}\Gamma_j t] - \exp[-i\bar{k}t] \exp[-\frac{1}{2}\gamma_p t]}{\bar{k} - E_j + \frac{1}{2}i(\Gamma_j - \gamma_p)}, \quad (10.8)$$

and the photon counting rate is

$$\dot{P}_g(t) = -\frac{d}{dt} \left[\sum_j \sum_{j'} A_{j'j} F_{j'}^{p*}(t) F_j(t) \right]. \quad (10.9)$$

Equations (10.5), (10.8) together with the definition (10.4) provide us with the desired general results concerning the time evolution of the excited state. From these results we can immediately draw some general conclusions for the time evolution of a system of closely spaced levels:

(a) The time evolution of the excited states is expressed in terms of cross products of the functions $F_j^p(t)$. It is important to notice that the matrix $A_{j'j}$ (Equation (10.4)) is not diagonal in view of the nonorthogonality of the basis set $|j, \text{vac}\rangle$.

(b) Each of the functions $F_j^p(t)$ incorporates dual information. It contains the molecular energies E_j and widths Γ_j of the independently decaying levels, together with relevant energy parameters \bar{k} and γ_p which characterize the energy maximum and the width of the exciting pulse.

(c) The time-independent denominators of F_j^p provide the attenuation factor for absorption of the pulse energy by the $|j, \text{vac}\rangle$ level.

(d) In the *mathematical* limit $t \rightarrow \infty$, $F_j^p(t) \rightarrow 0$ for all j irrespective of the relation between γ_p and $\{\Gamma_j\}$. This implies that $P_e(\infty) = 0$. Thus for a physical system characterized by a *discrete* spectrum of excited states the total photon emission yield at $t = \infty$ will be unity, i.e. $P_g(\infty) = 1$. It is important to stress at this point that the procedure which led to the definition of the $|j, \text{vac}\rangle$ basis and the derivation of Equation (10.4) considered a discrete molecular spectrum. When the spectrum of H_{BO} (when the Born–Oppenheimer molecular basis is employed) or of H_M (when the molecular eigenstates are used) contains continuum states we should not incorporate them in the \hat{P} subspace. Under these more complicated circumstances we have to include the zero photon continuum molecular states in the \hat{Q} subspace while the \hat{P} subspace will contain only discrete levels. Under these conditions the probability of the system to be in the (extended) \hat{Q} space at $t = \infty$ will be still unity, however, the photon emission yield at $t = \infty$ may be lower than unity due to the branching between the radiative channels and the nonradiative continuum channels. It should be finally pointed out that these results do by no means contradict the idea of electronic relaxation (internal conversion or intersystem crossing) in an isolated molecule, where the concept of the statistical limit rests on the notion of (a) practical irreversibility at a time scale short relative to the (exceedingly long) Poincaré recurrence time and (b) the occurrence of sequential decay processes in the dense intramolecular manifold.

(e) In the limit of high energy resolution of the exciting pulse, $\gamma_p \ll \Gamma_j$ and the contribution to the $F_j^p(t)$ functions originating from the molecular lifetimes Γ_j will be masked out by the long decay time of the pulse. Under these circumstances the time resolved photon counting rate will not result in any relevant information regarding the ‘molecular’ widths. This situation corresponds to the ‘long time’ excitation experiment.

(f) In the limit of a broad excitation pulse we encounter the ‘short excitation’ experiment and the time resolved decay pattern provides us with pertinent information regarding the molecular decay widths.

11. ‘Initially Prepared’ Decaying State, Revisited

As we have already pointed out in Section 8 the description of an ‘initially prepared’ decaying state excited by a delta function field amplitude (6.16) has to be modified. We can now provide a less stringent realistic condition for the ‘preparation’ process by requiring that the energetic spread γ_p of the photon wave packet considerably exceeds the characteristic widths Γ_j for all the independently decaying levels, i.e.

$$\gamma_p \gg \Gamma_j \quad (11.1)$$

for all j . Under these circumstances the functions (10.8) take the form

$$F_j^p(t) = -2\pi A_N \frac{\exp[-iE_j t] \exp[-\frac{1}{2}\Gamma_j t]}{E_j - \bar{k} + \frac{1}{2}i\gamma_p} \quad (11.2)$$

Using Equations (10.4) and (11.2) the time evolution of the excited states resulting from the realistic 'short time' excitation experiment can be now written as follows

$$P_e(t) = \sum_j \frac{\bar{A}_{jj}}{(E_j - \bar{k})^2 + (\frac{1}{2}\gamma_p)^2} \exp(-\Gamma_j t) + 2\text{Re} \sum_{j < j'} \frac{\bar{A}_{j'j} \exp[i(E_{j'} - E_j)t - \frac{1}{2}(\Gamma_j + \Gamma_{j'})t]}{[E_j - \bar{k} + \frac{1}{2}i\gamma_p][E_{j'} - \bar{k} - \frac{1}{2}i\gamma_p]}, \quad (11.3)$$

where we have defined

$$\bar{A}_{j'j} = 4\pi^2 |A_N|^2 A_{j'j} = 4\pi^2 |A_N|^2 \langle N, \text{vac} | j', \text{vac} \rangle \times \langle j', \text{vac} | j, \text{vac} \rangle \langle j, \text{vac} | N, \text{vac} \rangle |\gamma_N|^2. \quad (11.3a)$$

Separating the mixed coefficients Equation (11.3) into their real and imaginary parts

$$\frac{\bar{A}_{j'j}}{[E_j - \bar{k} + \frac{1}{2}i\gamma_p][E_{j'} - \bar{k} - \frac{1}{2}i\gamma_p]} \equiv R_{j'j} \exp[i\varphi_{j'j}] \quad (11.3b)$$

we get

$$P_e(t) = \sum_j \frac{\bar{A}_{jj} \exp[-\Gamma_j t]}{(E_j - \bar{k})^2 + \frac{1}{4}\gamma_p^2} + 2 \sum_{j < j'} R_{j'j} \exp[-\frac{1}{2}(\Gamma_j + \Gamma_{j'})t] \cos[(E_{j'} - E_j)t + \varphi_{j'j}]. \quad (11.3c)$$

This result provides us with the proper description of the time evolution of the discrete excited states resulting from a realistic short time excitation.

Thus the time evolution of the excited state is solely determined by the molecular parameters E_j and Γ_j . This result differs from that obtained in Section 8 for the extremely broad excitation condition (i.e. $\gamma_p \rightarrow \infty$) only by the introduction of the time-independent numerical factors $[(E_j - \bar{k}) + \frac{1}{2}i\gamma_p]^{-1}$ in the denominators of all the terms in Equation (11.3). These attenuation factors account for the absorption strength of the exciting pulse by the various independently decaying levels $|j, \text{vac}\rangle$.

We can now introduce a second condition for the pulse width

$$\gamma_p \gg |E_j - \bar{k}| \quad (11.4)$$

for all E_j which implies that the pulse width exceeds the energy spread of $|j, \text{vac}\rangle$. When both conditions (11.1) and (11.4) are simultaneously satisfied we get

$$P_e(t) = \frac{4}{\gamma_p^2} \sum_{j, j'} \bar{A}_{j'j} \exp[i(E_{j'} - E_j)t - \frac{1}{2}(\Gamma_j + \Gamma_{j'})t], \quad (11.5)$$

which corresponds to the extremely broad excitation condition. Thus Equation (11.1) provides the necessary condition for a realistic broad band excitation. This condition is useful for the study of a sparse distribution of strongly coupled levels as is the case

for interstate coupling in small molecules. The combination of conditions (11.1) and (11.4) provides us with the circumstances equivalent to a delta function excitation in time, which are useful for the study of systems of closely spaced levels, i.e. a dense level structure in the excited states of large molecules.

The time evolution, Equation (11.3), consists of two contributions: (a) a sum of decaying exponentials; (b) a sum of cross terms, which contain oscillatory contributions for the time evolution of the excited states. These oscillatory terms characterized by the periods $\hbar(E_{j'} - E_j)^{-1}$ may lead to the observation of quantum beats in the radiative decay.

When we consider the excitation of the system by a single pulse, disregarding more sophisticated techniques such as double resonance methods, the experimental information regarding the decay features originates from the photon counting rate. When only condition (11.1) is satisfied we get from Equation (11.3) for the realistic short time excitation experiment:

$$\begin{aligned} \dot{P}_g(t) = -\dot{P}_e(t) = & \sum_j \frac{\bar{A}_{jj}\Gamma_j \exp(-\Gamma_j t)}{(E_j - \bar{k})^2 + (\frac{1}{2}\gamma_p)^2} + \\ & + \sum_{j \neq j'} \frac{\bar{A}_{j'j} \left[i(E_{j'} - E_j) - \frac{\Gamma_j + \Gamma_{j'}}{2} \right]}{[E_j - \bar{k} + \frac{1}{2}i\gamma_p][E_{j'} - \bar{k} - \frac{1}{2}i\gamma_p]} \times \\ & \times \exp[i(E_{j'} - E_j)t] \exp[-\frac{1}{2}(\Gamma_j + \Gamma_{j'})t]. \end{aligned} \quad (11.6)$$

Now, for a system of densely spaced excited levels, we can invoke the additional condition (11.4) whereupon Equation (11.6) is simplified to read

$$\begin{aligned} \dot{P}_g(t) = \frac{4}{\gamma_p^2} \sum_{jj'} \bar{A}_{j'j} \left[\frac{1}{2}(\Gamma_j + \Gamma_{j'}) + i(E_{j'} - E_j) \right] \times \\ \times \exp[i(E_{j'} - E_j)t] \exp[-\frac{1}{2}(\Gamma_j + \Gamma_{j'})t], \end{aligned} \quad (11.7)$$

where the coefficients $\bar{A}_{j'j}$ are given by (10.4) and (11.3a). Equation (11.7) could have been alternatively derived from the expression (8.11a) utilizing the form of the evolution operator (9.30) in the $|j\rangle$ representation

$$\begin{aligned} \dot{P}_g(t) = 2\pi |\gamma_N|^2 \varrho_r |C_{NN}(t)|^2 = \\ = \sum_j \sum_{j'} B_{j'j} \exp[-i(E_j - E_{j'})t - \frac{1}{2}(\Gamma_j + \Gamma_{j'})t], \end{aligned} \quad (11.8)$$

where

$$B_{j'j} = 2\pi |\gamma_N|^2 \varrho_r \langle N | j \rangle \langle j | N \rangle \langle N | j' \rangle \langle j' | N \rangle. \quad (11.9)$$

In the short excitation limit we choose $A_N = i\gamma_p/4\pi\gamma_N$ (in order to obtain $\varphi(t) = (1/\gamma_N)\delta(t)$, see Section 8). Hence, the equivalence of Equations (11.7) and (11.8) implies that

$$\hat{A}_{j'j} = \hat{B}_{j'j}, \quad (11.10)$$

where

$$\hat{A}_{j'j} = \langle j' | j \rangle [i(E_j - E_{j'}) + \frac{1}{2}(\Gamma_j + \Gamma_{j'})] \quad (11.10a)$$

and

$$\hat{B}_{j'j} = \langle N | j \rangle \langle j' | N \rangle 2\pi |\gamma_N|^2 \varrho_r. \quad (11.10b)$$

This equality (11.10) can be easily proved by utilizing the general properties of H_{eff} . We have

$$\hat{A}_{j'j} = i[\langle j' | H_{\text{eff}} | j \rangle - \langle j^* | H_{\text{eff}}^* | j'^* \rangle]. \quad (11.11)$$

Separating H_{eff} into Hermitian and an antihermitian parts i.e. $H_{\text{eff}} = H_M - (i/2)\Gamma$, where H_M and Γ are obviously Hermitian, we get

$$\hat{A}_{j'j} = i[\langle j' | H_M - i\Gamma | j \rangle - \langle j^* | H_M + i\Gamma | j'^* \rangle] = 2\langle j' | \Gamma | j \rangle. \quad (11.11a)$$

Using the definition of Γ (Equation (9.10)), we get from (11.11a)

$$\hat{A}_{j'j} = 2\pi |\gamma_N|^2 \varrho_N \langle j' | N \rangle \langle N | j \rangle = \hat{B}_{j'j}. \quad (11.12)$$

We note in passing that the equivalence of Equations (11.7) and (11.8) implies that for the extreme case of short time excitation, the generalized doorway state obeys the relation

$$\dot{P}_g(t) = \frac{d}{dt} [\langle N(t) | N(t) \rangle] = 2\pi |\gamma_N|^2 \varrho_r |\langle N(0) | N(t) \rangle|^2. \quad (11.13)$$

From these results we conclude that the radiative decay rate of a system of discrete excited levels exhibits the following features:

(a) The photon counting rate can be in general recast in terms of linear superposition of a sum of direct exponentials and of a sum of oscillatory terms.

(b) The feasibility of the observation of the oscillatory pattern of the decay is crucially determined by the nature of the physical system.

(c) When the spacings between the $|j\rangle$ levels considerably exceed their radiative widths, i.e. $\Gamma_j, \Gamma_{j'} \ll |E_j - E_{j'}|$ for all $|j\rangle$ and $|j'\rangle$ the oscillatory term will exhibit extremely fast oscillations on the time scale Γ_j^{-1} or $\Gamma_{j'}^{-1}$ which will average out to zero. Thus for a system of coarsely spaced $|j\rangle$ levels no oscillatory contributions to the decay in (11.6) or (11.7) will be exhibited and the radiative decay rate will be determined by the first sum in (11.6), i.e. a linear superposition of decaying exponentials. This situation prevails for strong coupling between a sparse distribution of levels in a small molecule.

(d) Consider now the opposite extreme case of a dense level distribution with a single (zero-order) $|s\rangle$ level acting as a doorway state, as is the situation in a large isolated statistical molecule. In this case there is a large number of cross terms in Equation (11.6) or rather in (11.7). These oscillatory terms will lead to a destructive interference effect resulting in shortening of the radiative decay time on the experimentally relevant time scale (see Section 13).

(e) Interference effects, i.e. quantum beats in the radiative decay of an isolated

molecule can be experimentally observed only for a system characterized by a small number of closely spaced $|j, \text{vac}\rangle$ levels, where $\Gamma_{j'}$, $\Gamma_j \sim |E_{j'} - E_j|$. This situation requires effective coupling between a small number of zero order molecular levels corresponding to two electronic configurations. In real life it may be possible [47] to observe quantum beats in the decay of an excited state of a large molecule which corresponds to the intermediate level structure (see Figure 1e and discussion in Section 15).

(f) From the point of view of general methodology it is important to notice that the oscillatory terms which may result in observable quantum beats are exhibited both in the probability for population of the excited state, $P_e(t)$, and of the ground state, $P_g(t)$. Thus the phenomenon of quantum beats in the radiative decay rate originates from the oscillations of the system between its electronically excited zero-photon levels. An attempt was made [93] to consider 'recurrence oscillations' in the excited state as distinguished from quantum beats in the radiative decay. The general treatment presented herein demonstrates that such a distinction is not acceptable.

12. Parallel Decay of Metastable States

We have demonstrated in Section 10 that for a discrete spectrum of zero-order excited states (which result in a discrete manifold $|j, \text{vac}\rangle$), $P_e(t) \rightarrow 0$ and $P_g(t) \rightarrow 1$, in the mathematical limit $t \rightarrow \infty$, whereupon the quantum yield for emission at $t = \infty$ is unity and no discrete excited levels are populated at the distant future. The situation is drastically different when the excited molecular states contain a continuum $|l_c, \text{vac}\rangle$ characterized by the density of states ρ_c , for example, a dissociative intramolecular continuum in the case of predissociation. We shall consider now the simplest physical common situation where the radiative continuum $|g, \mathbf{ke}\rangle$ and the molecular zero photon continuum $|l_c, \text{vac}\rangle$ are not directly coupled, i.e.

$$\langle g, \mathbf{ke} | V | l_c, \text{vac} \rangle = 0. \quad (12.1)$$

We shall partition the Hilbert space as follows: the \hat{P} subspace will contain the discrete zero photon excited states, as before

$$\hat{P} = \sum_m |m, \text{vac}\rangle \langle m, \text{vac}|, \quad (12.2)$$

while the \hat{Q} subspace will contain the two continua, that is

$$\begin{aligned} \hat{Q} &= \hat{Q}_r + \hat{Q}_l, \\ \hat{Q}_r &= \sum_{\mathbf{ke}} |g, \mathbf{ke}\rangle \langle g, \mathbf{ke}|, \\ \hat{Q}_l &= \sum_{l_c} |l_c, \text{vac}\rangle \langle l_c, \text{vac}|. \end{aligned} \quad (12.3)$$

Under the conditions of short-time excitation satisfying conditions (11.1) and (11.4) together with (12.1) the initially excited state is still $|N, \text{vac}\rangle$ (Equation (7.8)) the time evolution of the discrete levels is given by (8.1) while the rate of photon counting is (8.11a). For most practical purposes we can consider the decay amplitudes which

combine only the (discrete) states in the \hat{P} subspace. Now the relevant coupling matrix elements combining the \hat{P} and \hat{Q} subspaces are $\langle g, \mathbf{ke} | H_{\text{int}} | m, \text{vac} \rangle$ and $\langle l_c, \text{vac} | H_v | m, \text{vac} \rangle$. We can again define a generalized effective Hamiltonian for the \hat{P} subspace which will incorporate the effects of both radiative decay into $|g, \mathbf{ke}\rangle$ and nonradiative decay into the dissipative continuum $|l_c, \text{vac}\rangle$. Equation (9.4) is still applicable however now the dissipative part of the level shift operator includes two contributions for parallel decay:

$$H_{\text{eff}} = \hat{P} \left(H_M + H_{\text{int}} \hat{Q}_r \frac{1}{E - \hat{Q}_r H \hat{Q}_r} \hat{Q}_r H_{\text{int}} + H_v \hat{Q}_l \frac{1}{E - \hat{Q}_l H \hat{Q}_l} \hat{Q}_l H_v \right) \hat{P}. \quad (12.4)$$

Thus the effective Hamiltonian takes the explicit form, which is a generalization of (9.6)

$$H_{\text{eff}} = \hat{P} (H_M + \delta - \frac{1}{2}i\gamma) \hat{P}, \quad (12.5)$$

where δ and γ are the generalized level shift and decay matrices, now given in the explicit form

$$\begin{aligned} \delta_{mm'} = & PP \sum_{\mathbf{e}} \int d\mathbf{k} \frac{\langle m, \text{vac} | H_{\text{int}} | g, \mathbf{ke} \rangle \langle g, \mathbf{ke} | H_{\text{int}} | m', \text{vac} \rangle}{E - k} \varrho_r(\mathbf{k}) + \\ & + PP \int dE_l \frac{\langle m, \text{vac} | H_v | l_c, \text{vac} \rangle \langle l_c, \text{vac} | H_v | m', \text{vac} \rangle \varrho_c(E_l)}{E - E_{l_c}} \end{aligned} \quad (12.6)$$

and

$$\begin{aligned} \gamma_{mm'} = & 2\pi \sum_{\mathbf{e}} \int d\Omega \langle m, \text{vac} | H_{\text{int}} | g, \mathbf{ke} \rangle \langle g, \mathbf{ke} | H_{\text{int}} | m, \text{vac} \rangle \varrho_r + \\ & + 2\pi \langle m, \text{vac} | H_v | l_c, \text{vac} \rangle \langle l_c, \text{vac} | H_v | m', \text{vac} \rangle \varrho_c. \end{aligned} \quad (12.7)$$

We can proceed as in Section 9 to find the basis set $|J, \text{vac}\rangle$ which diagonalizes the effective Hamiltonian (12.5), i.e.

$$(H_{\text{eff}})_{JJ'} = (E_J - \frac{1}{2}i\gamma_J) \delta_{JJ'}, \quad (12.8a)$$

while for the complementary basis set $|\bar{J}, \text{vac}\rangle$ we have

$$(H_{\text{eff}}^*)_{JJ'} = (E_J + \frac{1}{2}i\gamma_J) \delta_{JJ'}. \quad (12.8b)$$

Now the decay widths of the independently decaying levels $|J, \text{vac}\rangle$ contain both radiative and nonradiative contributions. Finally, the evolution operator in the \hat{P} subspace is

$$\hat{P}U(t, 0)\hat{P} = \sum_J |J, \text{vac}\rangle \exp[-iE_J t - \frac{1}{2}\gamma_J t] \langle \bar{J}, \text{vac} |. \quad (12.9)$$

It is a simple matter to extend the formalism presented in Sections 10 and 11 to include the role of the additional decay channel. To obtain the time evolution of the discrete states one has just to replace E_j by E_j and the radiative widths Γ_j by the total widths γ_j in Equations (10.3)–(10.6) for the general excitation and in Equations (11.3)–(11.7)

for the 'short time' excitation. It is important to realize that $P_e(t)$ represents the time-dependent population of the excited discrete states and not of all excited states, so that $\dot{P}_g(t) \neq -\dot{P}_e(t)$ but rather $\dot{P}_g(t) = -\dot{P}_e(t) - \dot{P}_c(t)$ where $P_c(t)$ is the occupation probability of the $\{|l_c\rangle\}$ continuum. To gain some insight into the nature of the modification introduced by the presence of additional intramolecular decay channels let us write the photon counting rate for the excitation which satisfies both conditions (11.1) and (11.4). From Equations (8.11) and (10.9) we have

$$\dot{P}_g(t) = \sum_J \sum_{J'} B_{J,J'} \exp[i(E_{J'} - E_J)t] \exp[-\frac{1}{2}(\gamma_J + \gamma_{J'})t], \quad (12.10)$$

where

$$B_{J,J'} = \langle N | J \rangle \langle J | N \rangle \langle N | J' \rangle \langle J' | N \rangle \cdot 2\pi |\gamma_N|^2 \rho_r. \quad (12.11)$$

From these results we conclude that for the simplest case of parallel radiative and nonradiative decay:

(a) The time-dependent decay pattern is determined by the total widths γ_J of the independently decaying states. When the effective Hamiltonian (12.4) is nondiagonal these total widths have to be obtained from the general procedure outlined herein.

(b) Interference effects in the time evolution and in the photon counting rate of a system consisting of a small number of discrete coupled zero order excited states undergoing parallel decay may be exhibited. Quantum beats will be observed provided that the spacings between the small number of $|J, \text{vac}\rangle$ levels are comparable to their total widths, i.e.

$$\gamma_J, \gamma_{J'} \sim |E_J - E_{J'}|$$

for all J and J' . Quantum beats will not be observed for (1) a dense manifold of a large number of levels; (2) for extremely broadened levels manifold where

$$\gamma_J, \gamma_{J'} \gg |E_J - E_{J'}|.$$

(c) For a system of a small number of levels undergoing parallel decay it may be possible to vary continuously the γ_J widths via external perturbations and consequently modify the decay into the nonradiative relaxation channel [50]. Then interference effects will be exhibited for a narrow range of γ_J values.

(d) The total emission yield at $t = \infty$ can be obtained by integrating Equation (12.10), which results in the occupation probability of the radiative continuum in the distant future.

$$P_g(\infty) = \sum_J \sum_{J'} \frac{B_{J,J'}}{i(E_J - E_{J'}) + \frac{1}{2}(\gamma_J + \gamma_{J'})}. \quad (12.12)$$

As for $t=0$ the initially excited $|N, \text{vac}\rangle$ state is normalized to unity thus $P_g(\infty)$ represents the emission quantum yield. The yield for decaying into the nonradiative continuum is

$$P_c(\infty) = 1 - P_g(\infty). \quad (12.13)$$

To lay the foundation for the discussion of the statistical limit we shall consider the simplest situation where a single level $|s, \text{vac}\rangle$ exhibits parallel decay into a radiative and a nonradiative continua. Now $\hat{P} = |s, \text{vac}\rangle \langle s, \text{vac}|$ while \hat{Q} is given by (12.3). There is a single state in the $|J, \text{vac}\rangle$ manifold, i.e. $|J, \text{vac}\rangle \equiv |s, \text{vac}\rangle$. The time evolution of the excited state under the general conditions of wave-packet excitation is obtained from Equation (7.13) in the form

$$P_e(t) = |\gamma_N|^2 \left| \int_0^t \varphi(t-\tau) C_{ss}(\tau) d\tau \right|^2. \quad (12.14)$$

$C_{ss}(\tau)$ is the Fourier transform of

$$G_{ss}(E) = \frac{1}{E - E_s + \frac{1}{2}i\gamma_s}, \quad (12.15)$$

where the total width of the $|s, \text{vac}\rangle$ state is the sum of the radiative and nonradiative widths

$$\gamma_s = \Gamma_s + \Gamma_s^c \quad (12.16a)$$

$$\Gamma_s^c = 2\pi |\langle s, \text{vac} | H_v | c, \text{vac} \rangle|^2 \rho_c, \quad (12.16b)$$

so that

$$C_{ss}(\tau) = \exp[-iE_s\tau - \frac{1}{2}\gamma_s\tau]. \quad (12.17)$$

Thus we get

$$P_e(t) = 4\pi^2 |A_N|^2 |\gamma_N|^2 \times \frac{\exp(-\gamma_s t) + \exp(-\gamma_p t) - 2 \exp(-\frac{1}{2}(\gamma_s + \gamma_p)t) \cos(E_s - \bar{k})t}{(E_s - \bar{k})^2 + \frac{1}{4}(\gamma_p - \gamma_s)^2}. \quad (12.18)$$

From this result we conclude that (1) the only molecular information originating from the time evolution of this system is the resonance width γ_s . Excitation characterized by different wave-packet widths (i.e. different excitation times) will not result in new information. (2) The trigonometric factor $\cos(E_s - \bar{k})t$ in (12.18) represents a 'ringing effect' between the field and the molecular system. (3) When $\gamma_p \gg \gamma_s$ we encounter the 'short excitation' condition,

$$P_e(t) \propto \exp(-\gamma_s t).$$

When both conditions (11.1) and (11.4) are obeyed the photon counting rate contains a single exponential decay

$$\dot{P}_g(t) = \Gamma_s \exp(-\gamma_s t). \quad (12.19)$$

Finally, the emission quantum yield is just the branching ratio between the radiative and the total width,

$$Y = \Gamma_s / \gamma_s = \Gamma_s / (\Gamma_s + \Gamma_s^c). \quad (12.20)$$

13. The Statistical Limit

When the background density of the vibronic levels in a large molecule is exceedingly high (see Figures 1a, c) one should enquire under what circumstances this intramolecular quasicontinuum can act as a practical decay channel. This question is central for understanding of electronic relaxation (i.e. internal conversion and intersystem crossing) in an isolated large molecule. This interesting problem imposes some conceptual difficulties. We have demonstrated that for a general discrete spectrum of the excited states the probability of the system to be in a discrete excited state is zero at $t = \infty$. Only when the system contains a real continuum the emission quantum yield is smaller than unity at $t = \infty$, i.e. the intramolecular continuum acts as a legitimate dissipative channel. However, we should note that the distinction between a 'real' (dissociative or ionization) continuum and an intramolecular dense quasicontinuum is not physical, as one can convert any 'real' continuum into a quasicontinuum by enclosing the system in a box. The experimental observables are not affected by the mathematical boundary conditions imposed on the system. We should now enquire what conditions should a quasicontinuum satisfy, to act, for all practical purposes, as a dissipative continuum [34, 78, 84].

Bixon and Jortner [34] have introduced the notion of practical irreversibility for the simple model of Figure 1a. In the absence of radiative decay the molecular eigenstates are adequate for the spectral representation of the Green's function,

$$G^+(E) = \sum_n \frac{|n\rangle \langle n|}{E^+ + E_n}, \quad (13.1)$$

so that the time evolution of the doorway state $|s\rangle$ is

$$\begin{aligned} \langle s|U(t, 0)|s\rangle &= \int_{-\infty}^{+\infty} \exp(-iEt) G_{ss}(E) dE = \\ &= \sum_n \int dE \exp(-iEt) \frac{\langle s|n\rangle \langle n|s\rangle}{E - E_n + i\eta} = \\ &= \sum_n |\langle s|n\rangle|^2 \exp(-iE_n t). \end{aligned} \quad (13.2)$$

Thus the time evolution is described in terms of a Fourier sum which exhibits an oscillatory behavior. It was demonstrated that for the simple model system characterized by equal $\{|l\rangle\}$ level spacing ($1/\varrho_l$) and constant V_{sl} coupling, the Fourier sum (13.2) exhibits an exponential decay on a time scale, t , which satisfies the condition

$$t \ll t_r = h\varrho_l. \quad (13.3)$$

Thus Equation (13.3) establishes the time scale for the occurrence of an effective relaxation into a quasicontinuum. t_r corresponds to the recurrence time for the intramo-

molecular nonradiative decay. This definition introduces the notion of a Poincaré recurrence cycle for the decay process. For excited states of large molecules characterized by a large electronic energy gap, $\hbar\omega_l$ is exceedingly long compared to all relevant decay times.

In real life an 'isolated' large molecule cannot wait long enough to pass a Poincaré cycle. Under any realistic experimental conditions in the laboratory the population of the $\{|I\rangle\}$ manifold will be relaxed due to 'trivial' quenching processes such as wall collisions or kinetic collisions. Finally, it is important to realize that even an isolated large molecule in the outer space, in the absence of 'trivial' quenching mechanisms, will not exhibit a Poincaré cycle. We have focused attention just on the simple level scheme 1a or 1c. In a real molecule the $\{|I\rangle\}$ manifold will exhibit subsequent decay mechanisms such as: (a) Infrared emission to lower vibrational levels [34] as was indeed already observed by Drent and Kommandeur [85]. (b) Radiative decay to the highly vibrationally excited ground state levels in the case of internal conversion [41, 79] between high excited states. Thus, strictly speaking, all electronic relaxation processes in a large molecule involve noninterfering sequential decay (see qualitative discussion in Section 3). It is a simple matter to provide the time evolution for the physical systems portrayed in Figures 1f, g. The theory of noninterfering sequential decay for such level schemes was provided by Freed, Nitzan and Jortner [41, 64]. For a doorway state $|s, \text{vac}\rangle$ coupled in parallel to the radiative continuum $|g, \mathbf{k}\epsilon\rangle$ and to a quasi-continuum $|l, \text{vac}\rangle$, which in turn is coupled to a continuum $\{|c, \text{vac}\rangle\}$ one gets [64]

$$G_{ss}(E) = [E - E_s - \Delta_s - \Delta_s^{nr} + \frac{1}{2}i(\Gamma_s + \Gamma_s^{nr}(E))]^{-1}, \quad (13.4)$$

where Δ_s is the radiative level shift, Δ_s^{nr} is a nonradiative level shift function

$$\Delta_s^{nr} = \sum_l \frac{2(E - \tilde{E}_l) |V_{sl}|^2}{(E - \tilde{E}_l)^2 + \frac{1}{4}\Gamma_l^2} \quad (13.5a)$$

and

$$\tilde{E}_l = E_l + p p \sum_{lc} \frac{|V_{l,lc}|^2}{E - E_{lc}}. \quad (13.5b)$$

Γ_s is the radiative width of the doorway state while finally, and most important

$$\Gamma_s^{nr}(E) = \sum_l \frac{\Gamma_l |V_{sl}|^2}{(E - \tilde{E}_l)^2 + \frac{1}{4}\Gamma_l^2}, \quad (13.6)$$

where the width Γ_l of each $\{|I\rangle\}$ level due to its coupling with the $\{|c\rangle\}$ continuum is

$$\Gamma_l = 2\pi |V_{l,lc}|^2 \rho_{lc}(E_l). \quad (13.7)$$

The time evolution of a general system specified in terms of (13.4) may be very complex, as the Green's function may be characterized by a large number of poles. When the widths of the $\{|I\rangle\}$ levels considerably exceed their spacing, i.e.

$$\Gamma_l \gg |E_l - E_{l\pm 1}| \simeq \omega_l^{-1}. \quad (13.8)$$

The function $\Gamma_s^{nr}(E)$ (Equation (13.6)) is weakly varying with energy and can be considered to be constant. Only under these circumstances G_{ss} has a single pole at

$$E = E_s + A_s + A_s^{nr} - \frac{1}{2}i(\Gamma_s + \Gamma_s^{nr}), \quad (13.9)$$

and the time evolution of the excited states is characterized by the total width

$$\gamma_s = \Gamma_s + \Gamma_s^{nr}. \quad (13.10)$$

Conditions (13.3) and (13.8) provide us with the physical basis for the definition of the statistical limit in a large molecule. Each of these relations yields an independent necessary and sufficient condition for treating the intramolecular quasicontinuum as a legitimate dissipative continuum.

When condition (13.3) is satisfied and the widths Γ_l are very small (originating from infrared decay, as will be the case for intersystem crossing) we can set $\Gamma_l \rightarrow 0$ (in (13.6)) whereupon

$$\Gamma_s^{nr} = 2\pi \sum_l |V_{sl}|^2 \delta(E_s - \tilde{E}_l) \cong 2\pi \langle |V_{sl}|^2 \rho_l \rangle, \quad (13.11)$$

which is the conventional expression for the nonradiative decay probability into a continuum [34] (note that the manifold of the delta functions, which enters as a book-keeping device, has to be extremely dense). When only condition (13.8) is satisfied, as may be the case for internal conversion (or for electronic-vibrational relaxation of a small molecule in a medium) Equation (13.6) has to be used.

We have established the physical criteria for treating intramolecular quasicontinuum as a dissipative intramolecular channel. In the statistical limit we can factor the Hilbert space as follows

$$\hat{P} = |s\rangle \langle s| \quad (13.12)$$

for the discrete subspace and

$$\hat{Q} = \sum_{\mathbf{ke}} |g, \mathbf{ke}\rangle \langle g, \mathbf{ke}| + \sum_l |l, \text{vac}\rangle \langle l, \text{vac}| \quad (13.13)$$

for the continuous part. The physical situation is that of parallel decay of a single discrete level into two noninteracting channels. Using the results of Section 11 we notice that in this case it is easy to satisfy the condition (11.1). When also condition (11.4) is obeyed we have for the photon counting rate

$$\dot{P}_g(t) = \Gamma_s \exp(-\gamma_s t), \quad (13.14)$$

where γ_s is given by (12.16) and for the quantum yield

$$Y = \frac{\Gamma_s}{\Gamma_s + \Gamma_s^{nr}}. \quad (13.15)$$

The major experimental characteristics of the statistical limit can be summarized as follows:

(1) Shortening of the radiative decay time. As $\gamma_s > \Gamma_s$ the experimental radiative decay time is shorter than expected on the basis of the integrated oscillator strength, which yields Γ_s .

(2) The decay resulting from short time excitation is a pure exponential.

(3) Reduction of the emission quantum yield, i.e. $Y < 1$. That implies that for any practical purpose the intramolecular quasicontinuum acts as a continuum.

(4) An inert medium will not in general modify the decay characteristics of a statistical molecule. Medium-induced vibrational relaxation will introduce a new contribution to the widths Γ_l . When $\Gamma_s^{rr}(E)$ is already a slowly varying function of the energy in the isolated molecule, this additional sequential decay is of minor importance.

(5) As the physical situation in the statistical limit is equivalent to that of a single discrete level exhibiting parallel decay into two continua, the only pertinent information is the resonance width γ_s . We cannot give new information about the decay characteristics of the system by changing the energetic width γ_p (or the duration) of the exciting photon wave packet.

14 Interstate Coupling in Small Molecules

In the small molecule limit [40–41] the interstate coupling matrix elements V_{st} between the Born–Oppenheimer states are large while the density of states in the background manifold is low (see Figures 1b, d). The $\{|I\rangle\}$ levels are coarsely spaced, relative to their radiative widths. The sparse $\{|I\rangle\}$ manifold cannot act as a dissipative channel (in the isolated molecule) and we are encountered with the problem of the radiative decay of a set of discrete coupled levels, i.e. $|s, \text{vac}\rangle$ and $\{|I, \text{vac}\rangle\}$. In this case the molecular eigenstates basis, $|n, \text{vac}\rangle$ which diagonalizes H_M , is of great utility. The level distribution of $|n, \text{vac}\rangle$ is sufficiently sparse so that in the absence of accidental degeneracies we expect the off-diagonal matrix elements of the radiative decay matrix to be negligible compared to the level spacings, i.e.

$$\Gamma_{mn'} \ll |E_n - E_{n'}|. \quad (14.1)$$

So that H_{eff} in the $|n, \text{vac}\rangle$ representation (Section 3) is diagonal. Under these circumstances the molecular eigenstates are expected to provide a good description of the independently decaying levels $|j, \text{vac}\rangle$ (see Section 9). The corresponding complex energies are

$$(H_{\text{eff}})_{nn'} = (E_n - \frac{1}{2}i\gamma_n) \delta_{nn'}, \quad (14.2)$$

where the radiative widths of the molecular eigenstates are

$$\Gamma_n = \Gamma_s |\langle s, \text{vac} | n, \text{vac} \rangle|^2, \quad (14.3)$$

and Γ_s is the radiative width of the 'doorway state' (Section 7). We note in passing that for accidental degeneracies we have to diagonalize H_{eff} for these states. In this interference effects may be exhibited.

In view of the diagonal sum rule (9.23)

$$\Gamma_s = \sum_n \Gamma_n, \quad (14.4)$$

thus $\Gamma_n \ll \Gamma_s$ for all n . The overlap factors $|\langle s, \text{vac} | n, \text{vac} \rangle|^{-2}$ are of the order of the number of effectively coupled levels in the $\{|I\rangle\}$ manifold. We have thus provided an explanation for the anomalously long radiative decay times (as compared to what is expected on the basis of the integrated oscillator strength) of small molecules, reported by Douglas [80] (see Table II). The occurrence of interstate coupling in small molecules which results from the distribution of the absorption intensity of the doorway state and the dilution of its decay time among the molecular eigenstates, each of which is active in absorption and in emission. We also note that in this case of a discrete molecular spectrum we expect that $Y=1$.

TABLE II
Long radiative lifetimes of small molecules^a

Molecule	Transition	τ (exp.) sec	τ (integrated f) sec
NO ₂	¹ B ₂ - ¹ A ₁ 4300 Å	44 × 10 ⁻⁶	0.3 × 10 ⁻⁶
SO ₂	¹ B ₁ - ¹ A ₁ 3000 Å	42 × 10 ⁻⁶	0.2 × 10 ⁻⁶
CS ₂	¹ Σ- ¹ Σ ¹ Π- ¹ Π 3200 Å	15 × 10 ⁻⁶	3 × 10 ⁻⁶

^a Experimental results for τ (exp.) from Douglas [80].

The detailed decay mode is determined by the pulse characteristics. We can easily satisfy condition (11.1) but not condition (11.4) in view of the large energy spread of the $|n\rangle$ levels. The decay law will now be (see Equation (11.6))

$$\dot{P}_g(t) \propto \sum_n \frac{\Gamma_n}{(\bar{k} - E_n)^2 + (\frac{1}{2}\gamma_p)^2} \exp(-\Gamma_n t). \quad (14.5)$$

Thus the decay mode is in general a superposition of exponentials. The constant coefficients in (14.5) just express the absorption strength of the wavepacket by the individual molecular eigenstates.

To conclude this discussion we would like to emphasize that as the small molecule case corresponds essentially to excitation and decay from the molecular eigenstates it is meaningless to consider nonradiative relaxation from $|s\rangle$ to $\{|I\rangle\}$ in the isolated small molecule. Only when such a small molecule is embedded in a medium, electronic-medium induced vibrational relaxation may result in non-radiative relaxation of the doorway state [65] (see Figure 1i).

15. Intermediate Level Structure

The statistical and the small molecule limits represent well defined, observable physical cases. Another potentially interesting situation involves the intermediate case when a small electronic energy gap exists between two electronic states of a large molecule [47]. It should be noted that now it is unjustified to use 'coarse graining' procedures employed in the statistical limit, which disregards the details of the variation of the inter-state coupling terms and the level distribution in the background $\{|I\rangle\}$ manifold. These features have to be considered in detail for the intermediate case. The physical situation is closely related to the problem of intermediate structure in nuclear reactions [82] where the density of nuclear excitations is low and fine structure is exhibited in the nuclear scattering process.

As in the statistical limit, we can consider a single doorway state $|s, \text{vac}\rangle$ (see Figure 1e). In view of simple symmetry arguments, not all the states in the $\{|I\rangle\}$ manifold are coupled to $|s\rangle$ with the same efficiency. When the total density of the former states is relatively low, for small electronic energy gaps, say 10^3 – 10^4 cm^{-1} [9], only few of these levels will be effectively coupled to $|s\rangle$. We shall partition the $\{|I\rangle\}$ manifold into a small subset $\{|I_a\rangle\}$ of effectively coupled levels and another subset $\{|I_b\rangle\}$ which contains the majority of the levels, which are weakly coupled to $|s\rangle$. The $\{|I_b\rangle\}$ manifold may be considered as a statistical dissipative channel which leads to irreversible intramolecular decay on the relevant time scale. We should also incorporate in principle, other intramolecular statistical decay channels which correspond to dense vibronic manifold of even lower electronic configurations $|c, \text{vac}\rangle$ and of the ground state. This is a simple extension which was previously considered.

The subset of discrete states in the Born–Oppenheimer representation corresponds to the projection operator

$$\hat{P} = |s, \text{vac}\rangle \langle s, \text{vac}| + \sum_{I_a} |I_a\rangle \langle I_a| \quad (15.1)$$

and the projection into the remainder of the Hilbert space is

$$\hat{Q} = \sum_{I_b} |I_b\rangle \langle I_b| + \sum_c |c, \text{vac}\rangle \langle c, \text{vac}| + \sum_{\mathbf{ke}} |g, \mathbf{ke}\rangle \langle g, \mathbf{ke}|. \quad (15.2)$$

The states in \hat{P} constitute a sparse manifold of discrete levels, which bears a close analogy to the small molecule case, apart from the possibility of accidental degeneracies. We can now write the effective Hamiltonian $H_{\text{eff}} = \hat{P}H_0\hat{P} + \hat{P}\hat{R}\hat{P}$ for (15.1). Subsequently, it will be convenient to find the molecular eigenstates which diagonalize $\hat{P}H_M\hat{P}$.

The effective Hamiltonian Equation (9.4) is then

$$(H_{\text{eff}})_{nn'} = E_n \delta_{nn'} - \frac{1}{2} i \gamma_{nn'}, \quad (15.4)$$

where

$$\gamma_{nn'} = \Gamma_{nn'} + \Gamma_{nn'}^{nr}, \quad (15.5)$$

$$\Gamma_{nn'} = 2\pi \sum_{\mathbf{e}} \int d\Omega \langle n, \text{vac}| H_{\text{int}} |g, \mathbf{ke}\rangle \langle g, \mathbf{ke}| H_{\text{int}} |n', \text{vac}\rangle \varrho_{\mathbf{e}} \quad (15.6)$$

$$\Gamma_{nn'}^{nr} = 2\pi \langle n, \text{vac} | H_v | l_b, \text{vac} \rangle \langle l_b, \text{vac} | H_v | n' \rangle \varrho_{l_b} + 2\pi \langle n, \text{vac} | H_v | c, \text{vac} \rangle \langle c, \text{vac} | H_v | n', \text{vac} \rangle \varrho_c, \quad (15.7)$$

where ϱ_{l_b} and ϱ_c correspond to the densities of states in the intramolecular $\{|l_b\rangle\}$ and $\{|c\rangle\}$ manifolds. Radiative and non-radiative level shifts were neglected in (15.4). The physical situation corresponds to a parallel decay of a discrete manifold into radiative and nonradiative continua.

Two cases of increasing complexity will be considered:

(1) The molecular eigenstates in \hat{P} are well separated relative to their total widths, i.e.

$$\gamma_{nn'} \ll |E_n - E_{n'}| \quad (15.8)$$

for all n and n' . The situation is equivalent to that encountered in the small molecule case. The effective Hamiltonian is diagonal in the $|n, \text{vac}\rangle$ representation and the characteristic decay widths of the independently decaying levels are

$$\gamma_{nn'} = |\langle s, \text{vac} | n, \text{vac} \rangle|^2 (\Gamma_s + \Gamma_s^{nr}), \quad (15.9)$$

where the radiative width Γ_s and nonradiative widths Γ_s^{nr} of the doorway state are obtained from (15.6) and (15.7) by replacing both n and n' by s .

The photon counting rate resulting from an excitation by a Lorentzian pulse is given by

$$\dot{P}_g(t) \propto \sum_n \frac{\gamma_{nn}}{(E_n - \bar{k})^2 + (\frac{1}{2}\gamma_p)^2} \exp(-\gamma_{nn}t), \quad (15.10)$$

which is analogous to Equation (11.6) except that the radiative widths Γ_n are replaced by the total widths γ_{nn} .

As $|\langle s, \text{vac} | n, \text{vac} \rangle| \ll 1$ for all n then provided that $\Gamma_s^{nr} \sim \Gamma_s$ we expect that $\gamma_{nn} < \gamma_s$. The experimental decay width of the excited states $|n, \text{vac}\rangle$ now accessible by optical excitation will be reduced relative to the radiative width of the zero-order state obtained from the integrated oscillator strength. We expect a lengthening of the radiative decay times of a large molecule which corresponds to the intermediate case [47].

(2) When some of the molecular eigenstates in \hat{P} are closely spaced relative to their total widths interference effects will be exhibited in the radiative decay [47]. The effective Hamiltonian (15.4) has to be diagonalized resulting in the $|j, \text{vac}\rangle$ states. The rate of radiative decay will be given by Equation (11.6).

The following experimental and theoretical features of the intermediate case have to be considered:

(a) Lengthening of the radiative decay times relative to those estimated from the integrated oscillator strength. Thus a state of a large molecule which corresponds to the intermediate level structure will exhibit the decay characteristics of a small molecule. This theoretical prediction was experimentally confirmed by Pertzepis *et al.* [95-97] (see Table III).

TABLE III
Anomalously long radiative decay times of some excited electronic states
of large molecules^a

Molecule	Transition	Energy gap cm ⁻¹	τ (exp.) sec	τ (integrated f) sec
3, 4-Benzopyrene	$S_2 \rightarrow S_0$	3800 ($S_2 - S_1$)	7×10^{-8}	1×10^{-8}
Naphthalene	$S_2 \rightarrow S_0$	3500 ($S_2 - S_1$)	4×10^{-8}	1×10^{-8}
Benzophenone	$S_1 \rightarrow S_0$	3000 ($S_1 - T_1$)	1×10^{-5}	1×10^{-6}

^a Data from [95-97].

(b) The time resolved decay mode in case (1) above may exhibit a superposition of exponential decays (see Equation (15.10)) and vary with the mean excitation energy (if the exciting pulse sufficiently broad, i.e. $\gamma_p \gg \gamma_{nm}$).

(c) The $\{|I_a\rangle\}$ manifold is nondissipative. The strong interstate coupling between $|s\rangle$ and $\{|I_a\rangle\}$ does not provide a pathway for electronic relaxation in the isolated molecule.

(d) When the molecule is perturbed by an external medium a new relaxation channel is added to the $|s\rangle$ state: $|s\rangle \rightarrow \{|I_a\rangle\} \rightarrow \{|I_m\rangle\}$. Consecutive relaxation will occur as collisions or phonon coupling provide a vibrational relaxation decay channel. To provide a verification of these conclusions we note that the $|s\rangle$ state of the benzophenone molecule which is separated by 2800 cm^{-1} from T_1 and which does not exhibit fluorescence in solution [98] fluoresces in the low pressure gas phase [97].

16. 'Long Time' Excitation Experimental Observables

Up to this point we have been concerned with the interesting physical information which can be extracted from 'short time' excitation experiments exploring the conditions for and the consequences of separation between the preparation and the decay processes. The time has come to consider the second extreme situation of a 'long time' excitation where one has to consider photon scattering from large molecules as a single quantum-mechanical process. The exciting photon field can be now characterized by high energy resolution and we shall proceed to study the relevant cross sections (see Section 2) resulting from scattering of photons having the energy $E = hck$. We shall first follow the work of Nitzan and Jortner [62] and focus attention on the physical information which can be extracted from such 'long excitation' processes in a large molecule where the only nonradiative decay channel involves an intramolecular statistical quasicontinuum.

Scattering theory provides a powerful tool for the understanding of the interaction of a molecular system with the radiation field which is responsible for the absorption

line shape and photon scattering processes. Nitzan and Jortner [62] proposed that 'long excitation' experimental observables pertaining to electronic relaxation in large molecules can be handled by considering a 'collision process' between a monochromatic wave train and the 'isolated' molecule within the framework of the Lippman-Schwinger equation, expressed in terms of the T matrix formalism, as was previously done for atomic autoionization [99]. At the distant past, the molecule is in the continuum state $|a\rangle = |g_0, \mathbf{k}_e\rangle$ characterized by the energy E_a . The final (continuum) states resulting from photon scattering will be denoted by $|b\rangle = |g\nu, \mathbf{k}_f \mathbf{e}_f\rangle$ characterized by the energy E_b . Let us define [92] the transition probability per unit time from a continuum state $|a\rangle$ to a continuum state $|b\rangle$ as the increase (per unit time) of the probability that a system initially in the state $|a\rangle$ is found at time t to be in the state $|b\rangle$, i.e.

$$W_{ba} = \lim_{t_0 \rightarrow -\infty} \frac{d}{dt} |\langle b| U(t_0, t) |a\rangle|^2. \quad (16.1)$$

The probability W_{ba} is independent of t . To prove that assertion we quote here a result of scattering theory [92]

$$W_{ba} = \frac{2}{\hbar} \delta(b - a) \text{Im } T_{aa} + \frac{2\pi}{\hbar} \delta(E_b - E_a) |T_{ba}|^2, \quad (16.2)$$

where the T matrix (the reaction operator) is defined by

$$T = V + VG(E^+)V. \quad (16.3)$$

Here we use the notation

$$E^+ = E + i\eta, \quad \eta \rightarrow 0^+ \quad (16.3a)$$

with $V = H_V + H_{int}$. Equations (16.1) and (16.2) are the generalization of Fermi's golden rule, where the delta function insures energy conservation. The physically meaningful concept involved in Equation (16.1) is a transition to a group of final states within the energy interval dE_b , so that when this equation is integrated over the final states one gets the familiar density of states ρ_b in the final expression. The cross section for the process $a \rightarrow b$, $\sigma(a \rightarrow b)$, is obtained by dividing the transition probability by the photon flux $F = c/Q$, where c is the velocity of light and Q represents the volume, and we use box normalization for the radiation field. Thus, the cross section is:

$$\sigma(a \rightarrow b) = \frac{2\pi Q}{\hbar c} |T_{ba}|^2 \delta(E_b - E_a). \quad (16.4)$$

The second general result we require is the rate of disappearance, W_a , of the initial state $|a\rangle$, which is given by the optical theorem of scattering theory

$$W_a = \frac{d}{dt} |\langle a| U(t_0, t) |a\rangle|^2 = -\frac{2}{\hbar} \text{Im}(T_{aa}), \quad (16.5)$$

while the absorption cross section σ_a is given again by dividing (16.5) by the flux

$$\sigma_a = -\frac{2Q}{\hbar c} \text{Im } T_{aa}. \quad (16.6)$$

We can immediately apply these results by setting for the initial energy $E_a = E(|g_0, \mathbf{k}\mathbf{e}\rangle) = E_{g_0} + E$ where E_{g_0} is the energy of the ground state vibrationless level and $E = \hbar\omega$ is the incident photon energy, whereupon the absorption cross section is obtained from (16.6) in the form

$$\begin{aligned} \sigma_a(E) &= -\frac{2Q}{\hbar c} \text{Im} \langle g_0, \mathbf{k}\mathbf{e} | T | g_0, \mathbf{k}\mathbf{e} \rangle = \\ &= -\frac{2Q}{\hbar c} \text{Im} \langle g_0, \mathbf{k}\mathbf{e} | V G(E^+) V | g_0, \mathbf{k}\mathbf{e} \rangle. \end{aligned} \quad (16.6a)$$

Strictly speaking Equation (16.6) represents the absorption cross section at zero temperature. At finite temperatures a proper thermal average has to be performed.

Consider now the cross section for resonance fluorescence. We focus attention on the photon scattering process $|g_0, \mathbf{k}\mathbf{e}\rangle \rightarrow |g\nu, \mathbf{k}_f\mathbf{e}_f\rangle$, which takes place between the initial state $|g_0, \mathbf{k}\mathbf{e}\rangle$ characterized by the energy $E_{g_0} + E = E_{g_0} + \hbar\omega$ and the final states $|g\nu, \mathbf{k}_f\mathbf{e}_f\rangle$ characterized by the energy $E_{g\nu} + E_f = E_{g\nu} + \hbar\omega_f$ (where by $E_{g\nu}$ we denote the energy of the state $|g\nu\rangle$ and where the emitted photon which is characterized by the polarization \mathbf{e}_f and momentum \mathbf{k}_f is scattered into the spherical angle $\Omega_{\mathbf{k}_f} - (\Omega_{\mathbf{k}_f} + d\Omega_{\mathbf{k}_f})$). Equation (16.4) results in

$$\begin{aligned} \sigma(g_0, \mathbf{k}\mathbf{e} \rightarrow g\nu, \mathbf{k}_f\mathbf{e}_f) &= \frac{2\pi Q}{\hbar c} \times \\ &\times \delta(E_{g\nu} + E_f - E_{g_0} - E) |\langle g\nu, \mathbf{k}_f\mathbf{e}_f | T | g_0, \mathbf{k}\mathbf{e} \rangle|^2. \end{aligned} \quad (16.7)$$

The density of final states in the radiation field is

$$\rho_r(k_f) = \frac{4\pi k_f^2 Q}{(2\pi)^3}, \quad (16.8)$$

and one has to take $k_f c = E_{g\nu} - E_{g_0} - \hbar\omega$ to insure energy conservation. The resonance scattering cross section $\sigma_r^v(E)$ into the final molecular state $|g\nu\rangle$ will be obtained by summing up Equation (16.7) over all final spatial directions and polarization directions. This scattering cross section depends on the energy E of the initial photon. We consider a sample of randomly oriented (noninteracting) molecules, and provided that we are not interested in polarization measurements, then averaging over the initial polarization directions \mathbf{e} , results in

$$\sigma_r^v(E) = \left\langle \sum_{\mathbf{e}_f} \int d\Omega_{\mathbf{k}_f} \sigma(g_0, \mathbf{k}\mathbf{e} \rightarrow g\nu, \mathbf{k}_f\mathbf{e}_f) \right\rangle, \quad (16.9)$$

where $\langle \rangle$ denotes averaging over molecular orientations with respect to photon polarization.

The total cross section for resonance fluorescence is obtained by monitoring all the emitted photons resulting from scattering into all the final molecular states $|gv\rangle$

$$\sigma_r(E) = \sum_v \sigma_r^v(E). \quad (16.10)$$

In a similar manner we can define a cross section $\sigma_{nr}(E)$ for effective scattering into the quasicontinuum $\{|I, \text{vac}\rangle\}$, which we consider to be an operational continuum. This is given by

$$\sigma_{nr}(E) = \left(\frac{2\pi Q}{\hbar c}\right) |\langle go, \mathbf{k}e | T(E) |I, \text{vac}\rangle|^2 \varrho_I(E). \quad (16.11)$$

The unitarity relations for the scattering matrix result in the optical theorem [99]

$$-\frac{1}{\pi} \text{Im } T_{aa} = \sum_{\text{all } b} |T_{ba}|^2 \delta(E_a - E_b), \quad (16.12)$$

which leads to the conservation law

$$\sigma_a(E) = \sum_v \sigma_r^v(E) + \sigma_{nr}(E). \quad (16.13)$$

The (energy-dependent) quantum yield resulting from absorption of a photon of energy E leading to the molecular state $|gv\rangle$ is given by the ratio of the resonance scattering cross section Equation (16.9) and the absorption cross section Equation (16.6)

$$Y^v(E) = \sigma_r^v(E)/\sigma_a(E). \quad (16.14)$$

If the ground state energy levels are well spaced the different channels can be resolved.

Finally, the total quantum yield for emission is given by

$$Y(E) = \sum_v Y^v(E) = \sigma_r(E)/\sigma_a(E). \quad (16.15)$$

In a similar way the quantum yield for electronic relaxation in a statistical molecule is

$$Y_{nr}(E) = \sigma_{nr}(E)/\sigma_a(E), \quad (16.16)$$

and Equation (16.13) implies that

$$Y(E) + Y_{nr}(E) = 1. \quad (16.17)$$

The general expressions for the absorption cross sections, for the resonance fluorescence cross sections and for the emission quantum yields in the 'statistical' molecular case will involve as 'open channels' not only the radiation continuum but also the intramolecular quasicontinuum $\{|I\rangle\}$ which for all practical purposes can be considered as an 'open' decay channel. In this case the unitarity relations for the scattering matrix do not imply that $Y(E)$ is equal to unity as intramolecular decay channels have to be considered, as is evident from Equation (16.13).

17. Relation between 'Short Excitation' and 'Long Excitation' Experiments

At first sight it may appear to the uninitiated reader that there is no direct relation between the theoretical treatment based on the time evolution of the molecular system resulting from wave-packet excitation (Sections 6-7) and the study of photon scattering exposed in Section 16. We have now to establish the connection between observables obtained under 'short time' and 'long time' excitation conditions. This treatment will result in a general useful definition of the emission quantum yields and to a new insight into the physical interpretation of the absorption line-shape function.

The reaction matrix, T , containing all the relevant information regarding 'long time' experiments can be obtained from time-dependent scattering formalism by taking appropriate limits for the evolution operator from the distant past to the far future. Formally, we can define the scattering matrix S [92]:

$$S = \lim_{\substack{t'' \rightarrow -\infty \\ t' \rightarrow +\infty}} U^I(t'', t'), \quad (17.1)$$

where the evolution operator $U^I(t'', t')$ in the interaction representation is

$$U^I(t'', t') = \exp(iH_0 t'') U(t'', t') \exp(-iH_0 t'). \quad (17.2)$$

The S and T matrices are related by [99]

$$S = I - 2\pi i \delta(E_i - E_f) T, \quad (17.3)$$

when I is the unity matrix.

In the description of time evolution of excited states we have utilized the evolution operator $U(t, 0)$. However, as $U(t'', t') = U(t'' - t', 0)$, we can use the equivalent expression

$$U(t, 0) = U(\frac{1}{2}t, -\frac{1}{2}t). \quad (17.4)$$

Thus the scattering matrix (17.1) can be obtained by a single rather than a double limiting process [90]

$$S = \lim_{t \rightarrow \infty} U^I(\frac{1}{2}t, -\frac{1}{2}t). \quad (17.5)$$

Making use of (17.4) we have

$$S = \lim_{t \rightarrow \infty} U^I(t, 0) \quad (17.6)$$

or making use of the relation (5.6) we get a relation between the S matrix and the Green's function

$$S = \frac{1}{2\pi i} \lim_{t \rightarrow \infty} \exp(iH_0 t) \int_{-\infty}^{\infty} dE G(E^+) \exp(-iEt). \quad (17.7)$$

This relation enables us to consider the relation between the decay of a 'prepared'

state at the finite time $t=0$ and photon scattering, while the conventional formulation would have required a state of affairs where the excited states is 'prepared' at $t = -\infty$ whereas one could not utilize the Green's function formalism to describe its time evolution. Equations (17.7) and (17.3) establish the formal connection between 'long' and 'short' excitation experiments.

The quantum yield (Section 16) in a given exit channel is defined in a general way as the number of photons or molecules scattered into that channel divided by the number of absorbed photons. The system contains as effective exit channels, the radiative continua $|gv, \mathbf{k}_f \mathbf{e}_f\rangle$ and the intramolecular quasicontinuum.

We proceed to calculate the probability for finding the system in the exit channels at $t = \infty$. Taking the initial state (6.2) and utilizing the form (17.7) for the S matrix we have

$$\begin{aligned} \Psi(\infty) = S\Psi(0) = & \sum_{\mathbf{k}_f \mathbf{e}_f} \sum_v \sum_k |gv, \mathbf{k}_f \mathbf{e}_f\rangle \langle gv, \mathbf{k}_f \mathbf{e}_f| S |go, \mathbf{ke}\rangle a_k + \\ & + \sum_l \sum_k |l, \text{vac}\rangle \langle l, \text{vac}| S |go, \mathbf{ke}\rangle a_k + \\ & + \sum_m \sum_k |m, \text{vac}\rangle \langle m, \text{vac}| S |go, \mathbf{ke}\rangle a_k. \end{aligned} \quad (17.8)$$

The probability of the system decaying radiatively into the final states $\{|gv, \mathbf{k}_f \mathbf{e}_f\rangle\}$ resulting in the molecular ground state $|gv\rangle$ at $t = \infty$ is

$$P_g^v(\infty) = \sum_{\mathbf{k}_f \mathbf{e}_f} \left| \sum_k a_k \langle gv, \mathbf{k}_f \mathbf{e}_f| S |go, \mathbf{ke}\rangle \right|^2. \quad (17.9)$$

Making use of Equation (17.3) (and performing spatial integration and summation over polarization directions as in Section 16) we get

$$P_g^v(\infty) = 4\pi^2 \sum_{\mathbf{k}_f \mathbf{e}_f} \sum_k |a_k|^2 |\langle gv, \mathbf{k}_f \mathbf{e}_f| T |go, \mathbf{ke}\rangle|^2 \delta(E - k). \quad (17.10)$$

In an analogous manner we obtain the probability for the population of the quasi-continuum at $t = \infty$

$$P_l(\infty) = 4\pi^2 \sum_l \sum_k |a_k|^2 |\langle l, \text{vac}| T |go, \mathbf{ke}\rangle|^2 \delta(E - E_l). \quad (17.11)$$

Thus the quantum yield for emission into $|gv\rangle$ is

$$Y^v = P_g^v(\infty) / \left(\sum_v P_g^v(\infty) + P_l(\infty) \right), \quad (17.12)$$

and the total emission quantum yield

$$Y = \sum_v Y^v. \quad (17.12a)$$

The denominator of Equation (17.12) represents just the total probability of populating all the decay channels, which is just the probability of photon absorption.

From Equations (17.11) and (17.10) we have

$$P_l(\infty) + \sum_v P_g^v(\infty) = 4\pi^2 \sum_k |a_k|^2 \left[\sum_{\mathbf{k}_f \mathbf{e}_f} |\langle g v, \mathbf{k}_f \mathbf{e}_f | T | g 0, \mathbf{k} \rangle|^2 \delta(E - k_f) + \sum_l |\langle l, \text{vac} | T | g 0, \mathbf{k} \rangle|^2 \delta(E - E_l) \right]. \quad (17.13)$$

Making use of the optical theorem (Equation (16.12)) we obtain

$$P_l(\infty) + \sum P_g^v(\infty) = - \sum_k |a_k|^2 \text{Im} \langle g 0, \mathbf{k} | T | g 0, \mathbf{k} \rangle \cdot 4\pi. \quad (17.13a)$$

The emission quantum yields (17.12a) and (17.12) can be recast with the help of Equations (16.6), (16.7), (16.9) and (17.12a) into the final form

$$Y^v = \frac{\sum_k |a_k|^2 \sigma_r^v(E)}{\sum_k |a_k|^2 \sigma_a(E)} = \frac{\int_0^\infty |a(E)|^2 \sigma_r^v(E) dE}{\int_0^\infty |a(E)|^2 \sigma_a(E) dE} \quad (17.14)$$

and

$$Y = \frac{\int_0^\infty |a(E)|^2 \sigma_r(E) dE}{\int_0^\infty |a(E)|^2 \sigma_a(E) dE}. \quad (17.15)$$

In a similar way the yield for nonradiative decay is

$$Y_{nr}(E) = \frac{\int |a(E)|^2 \sigma_{nr}(E) dE}{\int |a(E)|^2 \sigma_a(E) dE}, \quad (17.16)$$

where we have set $a_k \equiv a(E)$.

Equations (17.14)–(17.16) constitute the general expressions for the quantum yields, which can be expressed as the ratio of integrals involving the products of the relevant cross sections and the power spectrum of the exciting light pulse. These results are valid for all excitation conditions. Although for short time experiments one can evaluate $P_g(\infty)$ directly, the present method is more general and useful. From these results we conclude that:

(a) The quantum yields are determined in general by both the characteristics of the molecular system, expressed in terms of the cross sections $\sigma_r^v(E)$, $\sigma_{nr}(E)$ and $\sigma_a(E)$ and by the features of the source.

(b) Regarding the source characteristics we notice that the quantum yields are determined by the power spectrum of the source, $|a(E)|^2$, the only relevant feature is the energetic spread. Unlike the time-resolved decay pattern which is determined by the excitation amplitudes (Equation (7.13)) and thus possibly by phases of the radiation field, the quantum yields are just determined by the energetic spread of the pulse.

(c) In the 'long excitation' limit $|a_k|^2$ is sharply peaked around \bar{k} and $\sigma_r^v(E)$ and $\sigma_a(E)$ vary slowly in the range where the power spectrum is finite. Then the quantum yields are obtained in terms of Equations (16.14)–(16.15).

(d) For the 'short excitation' limit $|a_k|^2$ is a slowly varying function of the energy, thus the emission quantum yields become

$$Y^v = \int_0^\infty \sigma_r^v(E) dE \bigg/ \int_0^\infty \sigma_a(E) dE. \quad (17.17)$$

(e) Only in the long excitation and short excitation limits the quantum yields are solely determined by the molecular parameters.

(f) Only when both cross sections $\sigma_r^v(E)$ and $\sigma_a(E)$ exhibit the same dependence on the energy, E , the quantum yields will be independent of the pulse width being identical for long and for short excitation conditions as well as for intermediate situations. This situation is encountered in the simple case of a single molecular resonance where both cross sections are characterized by a Lorentzian energy dependence.

(g) In general, when interference effects are exhibited, the quantum yield differs for different energy conditions. Nitzan and Jortner [62, 50] have demonstrated this effect for the case of two overlapping resonances, which was applied to provide the only available interpretation for the decay characteristics of the S_1 state of biacetyl.

To pursue further the relation between short excitation and long excitation experiments we shall establish the relation between the scattering cross sections $\sigma_r^v(E)$ and $\sigma_a(E)$ and the independently decaying discrete molecular states (see Sections 9–12). As we are interested in parallel coupling of the discrete levels $|m, \text{vac}\rangle$ to radiative and nonradiative channels we shall consider the effective Hamiltonian H_{eff} (Equation (12.4)) characterized by the eigenstates $|J, \text{vac}\rangle$. The cross sections are determined by matrix elements of T involving one-photon states, so that $V = H_{\text{int}}$, which combines only states within the \hat{Q} and \hat{P} subspaces (see Equation (12.4)). Furthermore, we have just to evaluate the matrix elements of $H_{\text{int}} \hat{P} G \hat{P} H_{\text{int}}$ between one-photon states. Thus we get, apart from irrelevant numerical factors,

$$\sigma_r^v(E) \propto \left| \sum_J \frac{\langle gv, \mathbf{k}_f \mathbf{e}_f | H_{\text{int}} | J, \text{vac} \rangle \langle J, \text{vac} | H_{\text{int}} | go, \mathbf{ke} \rangle}{E - E_J + \frac{1}{2} i \gamma_J} \right|^2 \times \\ \times \varrho_r(k_f) \delta(E_{g_0} - E_{g_v} + \hbar k c - \hbar k_f c), \quad (17.18)$$

$$\sigma_a(E) \propto \sum_J \text{Im} \frac{\langle go, \mathbf{ke} | H_{\text{int}} | J, \text{vac} \rangle \langle J, \text{vac} | H_{\text{int}} | go, \mathbf{ke} \rangle}{E - E_J + \frac{1}{2} i \gamma_J}, \quad (17.19)$$

where γ_J are the total widths of the independently decaying states. These results exhibit some interesting features. The photon scattering cross section $\sigma_r^v(E)$ will definitely involve interference effects provided that $|E_J - E_{J'}| < \gamma_J, \gamma_{J'}$. This is the analogue for long-time experiments of the quantum beats expected under these circumstances for short-time excitation experiments. The expression for the absorption cross section reveals formally a superposition of Lorentzians. This feature should not mislead us, as one has to bear in mind that the states $|J, \text{vac}\rangle$ and their complementary states $|\bar{J}, \text{vac}\rangle$ are characterized by complex expansion coefficients of $|m, \text{vac}\rangle$, whereupon the single sum (17.19) will exhibit interference effects of the absorption line shape for closely spaced (relative to γ_J) levels.

Finally we shall consider some features of the optical absorption line shape. The basic form (16.6a) for $\sigma_a(E)$ and the definition of the generalized doorway states $|N, \text{vac}\rangle$ (Equation (7.8)) imply that

$$\sigma_a(E) = - \left(\frac{2Q}{\hbar c} \right) |\gamma_N|^2 \text{Im} \langle N, \text{vac} | G(E^+) | N, \text{vac} \rangle. \quad (17.20)$$

The decay rate of the 'initially prepared' doorway state $|N\rangle$ in the short excitation limit (Equation (8.11a)), as monitored by the photon counting rate is

$$\dot{P}_g(t) = 2\pi |\gamma_N|^2 \varrho_r \left| \frac{1}{2\pi i} \int_{-\infty}^{+\infty} dE \exp(-iEt) \langle N, \text{vac} | G(E^+) | N, \text{vac} \rangle \right|^2. \quad (17.21)$$

Making use of the dispersion relation [87]

$$\langle N, \text{vac} | G(E^+) | N, \text{vac} \rangle = - \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\text{Im} \langle N, \text{vac} | G(E') | N, \text{vac} \rangle dE'}{E' - E - i\eta} \quad (17.22)$$

we get for $t > 0$

$$\begin{aligned} \frac{1}{2\pi i} \int_{-\infty}^{\infty} dE \langle N, \text{vac} | G(E^+) | N, \text{vac} \rangle \exp(-iEt) &= \\ &= \frac{1}{2\pi i} \frac{1}{\pi} \int_{-\infty}^{\infty} dE \int_{-\infty}^{\infty} dE' \frac{\text{Im} \langle N, \text{vac} | G(E') | N, \text{vac} \rangle}{E - E' + i\eta} \exp(-iEt) = \\ &= \frac{1}{\pi} \int_{-\infty}^{\infty} dE' \text{Im} \langle N, \text{vac} | G(E') | N, \text{vac} \rangle \exp(-iE't). \quad (17.23) \end{aligned}$$

Equations (17.20)–(17.23) result in

$$\dot{P}_g(t) = \frac{2}{\pi} \left(\frac{\hbar c}{2Q} \right)^2 \frac{Q_r}{|\gamma_N|^2} \left| \int_{-\infty}^{\infty} dE \exp(-iEt) \sigma_a(E) \right|^2. \quad (17.24)$$

The same result can be obtained by taking the Fourier transform of $\sigma_a(E)$ expressed in the $|J, \text{vac}\rangle$ representation, Equation (17.19).

Equation (17.24) provides us with a general result relating the decay rate of any excited state to the Fourier transform of the absorption line-shape function. This result was often derived and utilized for the simple case of a single resonance, where the lineshape is Lorentzian and the decay rate being exponential. The present discussion provides a proof which is valid for any level structure in the excited state.

18. Concluding Remarks

In this paper we have presented a unified theoretical scheme for the description of the diverse decay channels of excited electronic states of polyatomic molecules. We have focused attention on the dissipative channels in small, intermediate type and large molecules, bearing in mind that the same techniques utilized for electronic relaxation are applicable for direct and indirect photodissociation. We have made a conscientious attempt to focus attention on general theoretical schemes, rather than on specific applications, as many of the latter were already published.

Many applications of the theory were aimed towards the understanding of the decay characteristics in the statistical limit. As pointed out by Lin and Bersohn [100] and subsequently by Englman, Freed and Jortner [43–44], the nonradiative widths (13.6) can be considered as multiphonon processes displaying the transition probability as a Fourier transform of a generating function. Explicit solutions for a harmonic molecule were provided, which are amenable to numerical calculations and to analytic approximations. Two limiting cases were considered. The strong electron–phonon coupling limit, which corresponds to the Teller model [101] for crossing of potential surfaces and which reduces at high temperatures to an activated rate equation. The weak electron–phonon coupling situation which corresponds to most cases of internal conversion and intersystem crossing exhibits the energy gap law [43, 102] and the well-known deuterium isotope effect [103]. These calculations pertain to a ‘harmonic’ model molecule, and obviously unharmonicity corrections are important from the quantitative point of view. Unfortunately, in spite of recent efforts by Fisher *et al.* [104] there is no satisfactory way for handling unharmonicity corrections. This can be handled by displaying the Fourier integral in terms of a convolution, factoring out a small number of strongly unharmonic modes. These studies rested on the evaluation of the thermally averaged transition probability. An interesting related problem involves the optical selection studies [48, 54] where the nonradiative decay of a single zero-order vibronic level with excess vibrational energy above the electronic origin is considered.

The elegant Feynman operator technique can be applied for this problem, although brute force methods [105] resulted in somewhat more detailed information. Unfortunately, for molecules larger than the benzene molecule, sequence congestion effects [58] are important, so that the isolated molecule preserves the memory of the ground state Boltzmann population in the excited states, and a single vibronic level cannot be excited. Finally, when a molecule is externally perturbed, coupling between electronic and vibrational relaxation may be exhibited. Such processes are of cardinal importance for the understanding of some experimental results of picosecond spectroscopy [98] for ultrafast electronic relaxation in solution.

The statistical limit is well understood, and many of the theoretical results concur with experimental observations. The situation is different for the theory of interference effects in the radiative decay of large molecules, where the experimental information is meager. Three classes of interference effects can be distinguished:

(1) Interference between a small number of closely spaced levels (see Sections [14–15]). In spite of extensive experimental effort no conclusive evidence was yet obtained for the occurrence of this effect in excited states of large molecules which correspond to the intermediate case [95–97]. It is possible that spectroscopic sequence congestion effects mask this interesting feature of the decay.

(2) Interference between a zero-order discrete state and a dissociative continuum both of which are coupled to the radiative field. This problem originally solved by Fano [1] for $\sigma_a(E)$, may be of considerable interest for some molecular predissociation processes. We have recently derived [86] a general solution for the absorption, photon scattering and dissociation cross sections for the Fano problem incorporating radiative interactions to infinite order and elucidating the nature of interference effects between resonance and potential scattering.

(3) Interference between continua. The problem of sequential decay with interference was recently handled utilizing simple model systems [67]. We have recently provided a complete general solution for the coupling between the radiative continuum and a dissociative continuum [86]. This problem is central for the theoretical study of molecular photodissociation processes.

From the foregoing discussion of interference effects it is evident that classes (2) and (3) are relevant for a profound theoretical understanding of a variety of processes such as the dynamics of direct photofragmentation and indirect predissociation in large molecules. The same theoretical techniques are also directly applicable to the study of inverse radiative processes such as radiative recombination and inverse predissociation.

We hope that the present unified approach to the decay of excited states will be of general applicability for the elucidation of a variety of interesting photophysical processes.

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