

# Molecular Radiationless Processes

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## 1. PROLOGUE

In this review we shall be concerned with nonreactive electronic relaxation phenomena in electronically excited states of polyatomic molecules. In general, the level structure of such states is complex and may include discrete levels, dense manifolds of discrete states and dissociative continua. A coherent picture of the dynamic processes in excited states of large molecules requires the elucidation of the time evolution of the molecular system interacting with the electromagnetic field. It should be borne in mind that the radiative decay channel provides just one route for the decay of electronically excited states and the goal of the theory is to extract the physical information concerning the various decay channels which involve radiative decay, electronic (nonreactive) relaxation and direct and indirect photodecomposition processes.

From the experimentalist's point of view, there are currently powerful tools available to monitor the various decay channels of electronically excited molecular states. The available spectroscopic and chemical information can be classified as follows:

1. Decay characteristics of electronically excited states. The following decay modes may be exhibited:

- 1a. A single lifetime (pure exponential decay);
- 1b. Superposition of exponentials;
- 1c. Oscillatory "quantum beats" originating from interference between closely spaced levels.

2. Time evolution of the population of excited states other than those accessible by optical excitation.

3. Cross sections for elastic and inelastic "Raman-type" photon scattering (which will be referred to as "resonance fluorescence").
4. Photon absorption cross sections.
5. Cross sections for the population of intramolecular and dissociative decay channels.
6. Quantum yields for "resonance fluorescence."
7. Quantum yields for the population of the intramolecular decay channels.

These experimental observables fall into two different limiting categories, which pertain to time-resolved "short excitation" and energy-resolved "long excitation" experiments. The information which stems from both types of experiments is complementary but not identical. When the pulse duration is short relative to the relevant reciprocal widths of the molecular resonances (i.e., the molecular "lifetimes"), the excitation and the subsequent decay can be separated and one considers the problem of the decay of a metastable state. Thus for the limiting situation of "short excitation" experiments, we encounter a "memory erosion" effect of the excited molecule with respect to the details of its excitation process. In this case, energy resolution is sacrificed for the sake of time resolution. On the other hand, when the exciting photon field is characterized by high energy resolution, information concerning the time resolution is eroded. In such "long excitation" experiments, the excitation and the decay process cannot be separated and have to be handled within the framework of a single quantum-mechanical process.

In general, observables 1 and 2 correspond to "short excitation" conditions, observables 3-5 are conventionally obtained from "long excitation" experiments, while quantum yields (observables 6 and 7) can be derived both from "short" and "long" excitation experiments. It should be borne in mind that this segregation of excitation modes reflects only on limiting cases, and intermediate excitation conditions (Williams et al., 1974) followed by time-resolved experimental detection are expected to provide useful additional information concerning the nature of the molecular level structure, and in addition can also utilize the molecule to probe some of the characteristics of the exciting light pulse.

Early treatments of "short time" excitation experiments (Bixon and Jortner, 1968; Jortner and Berry, 1968; Rhodes, 1969) studied the decay of an "initially prepared" metastable state, while subsequent studies (Freed, 1970; Rhodes, 1971) focused attention on the time-evolution of the molecular system after the sudden termination of a light pulse. In this context many variations on the theme of time dependent quantum mechanics were utilized, the most general method involving the Green's function technique (Goldberger and Watson, 1964; Cohen Tannoudji, 1966, 1967; Mower, 1966; Harris, 1963; Chock et al., 1968; Freed and Jortner, 1969; Jortner and Mukamel, 1974). On the other hand, "long excitation" experimental observables were treated by studies of photon scattering from molecules utilizing

the Lippman-Schwinger formalism (Shore, 1967; Nitzan and Jortner, 1972; Jortner and Mukamel, 1974). A general formalism bridging the "short" and "long" excitation approach was provided (Cohen Tannoudji, 1966, 1967; Jortner and Mukamel, 1974) by the study of the time evolution of a molecular system interacting with a photon wavepacket, starting at the distant past and considering the state of the total system (i.e., the molecule plus the radiation field) at the distant future. Intermediate type excitation conditions are amenable to a detailed study by this formalism (Mukamel and Jortner, 1975*a, b*; Mukamel et al., 1975). We shall now proceed to advance this formalism of time-resolved photon scattering from large molecules and subsequently apply these results for the description of non-reactive scattering phenomena in excited states of large molecules.

## 2. METHODOLOGY

Consider the general problem of the rise and fall of excited molecular states of large molecules in the presence of the radiation field. The system is specified in terms of the time independent Hamiltonian

$$H = H_m + H_{\text{rad}} + H_{\text{int}}$$

$$H_m = H_{m0} + H_v \quad (2.1)$$

which is decomposed into the following contributions:  $H_m$ , the molecular Hamiltonian;  $H_{m0}$ , the zero-order molecular Hamiltonian;  $H_v$ , the intramolecular, non-adiabatic coupling;  $H_{\text{rad}}$ , the Hamiltonian for the free electromagnetic field;  $H_{\text{int}}$ , the radiation-matter interaction term.

There are variety of possibilities for the specification of the zero-order molecular Hamiltonian  $H_{m0}$ . These involve the adiabatic Hamiltonian (Born and Huang, 1956), the crude adiabatic Hamiltonian (Longuet Higgins, 1961), the diabatic Hamiltonian (Smith, 1969), etc. We shall not dwell on this problem here. It is however worthwhile to point out that current studies of excited state dynamics of polyatomics are still restricted to simple model systems, characterized by a small number of electronic configurations. Such truncated basis sets can be adequately handled by the utilization of the Born-Oppenheimer adiabatic basis as eigenstates of  $H_{m0}$ , which minimizes off-resonance interactions, whereupon  $H_v$  corresponds to nuclear kinetic energy and spin-orbit coupling terms.

The eigenstates of the subparts of the Hamiltonian (2.1) are summarized in the following list:

Hamiltonian	Eigenstates
$H_m$	$ g\rangle = \text{ground state}$
$H_{m0}$	$ g\rangle = \text{ground state}$ $ s\rangle = \text{discrete excited state}$ $\{ l\rangle\} = \text{manifold of excited states quasi-degenerate with }  s\rangle$
$H_{rad}$	$ k\rangle = \text{one photon states}$ $ \text{vac}\rangle = \text{zero photon state}$
$H_0 \equiv H_{m0} - H_{rad}$	$ s, \text{vac}\rangle, \{ l, \text{vac}\rangle\}$ $ g, k\rangle$

The total Hamiltonian is

$$H = H_0 + V$$

$$V = H_r + H_{int} \quad (2.1a)$$

The ground molecular state  $|g\rangle$  (for the sake of simplicity we shall disregard its vibrational structure, a kind of omission which can be easily amended) is considered to be well-separated from the excited manifold, so that the off-resonance molecular coupling terms  $\langle s|H_r|g\rangle$  and  $\langle l|H_v|g\rangle$  can be safely disregarded, whereupon  $|g\rangle$  can be considered as an eigenstate of both  $H_m$  and  $H_{m0}$ . The density of states in the background manifold  $\{|l\rangle\}$  can be varied at will for different systems. In Fig. 1 we display the statistical limit, characterized by a large density  $\rho_l$  of background states  $\{|l\rangle\}$ , the small molecule case specified by a coarse density of states, and the interesting case of intermediate level structure in large molecules characterized by a small electronic energy gap. Concerning the eigenstates of  $H_{rad}$  we specialize in weak light pulses (see Sec. 3) considering only the zero-photon state  $|\text{vac}\rangle$  and the one photon states  $|k\rangle$ , characterized by the photon wavevector  $\mathbf{k}$ . Furthermore, we shall invoke the rotating wave approximation (Cohen Tannoudji, 1966), neglecting the contribution of the off-resonance eigenstates  $|s, \mathbf{k}\rangle$ ,  $\{|l, \mathbf{k}\rangle\}$  and  $|g, \text{vac}\rangle$  to  $H_0$ .

Turning now to the radiative coupling term  $H_{int}$ , we have to distinguish between two cases. When the incident  $|g, \mathbf{k}\rangle$  channel is directly coupled to the final intramolecular channels, we have a direct scattering process. However, in many cases of physical interest, only the discrete  $|s\rangle$  state is directly radiatively coupled to the ground state. In such cases, the scattering process is indirect and the state  $|s\rangle$  serves as a *doorway state* (see Sec. 5) which is formed by the excitation and subsequently decays into one of the open final channels. The level schemes of Fig. 1 can be now utilized to provide a complete description of both the decay of metastable molecular states and of photon scattering by an "isolated", collision-free, molecule. The nature of the specific experiment depends on the characteristics of the light pulse, which has now to be specified.

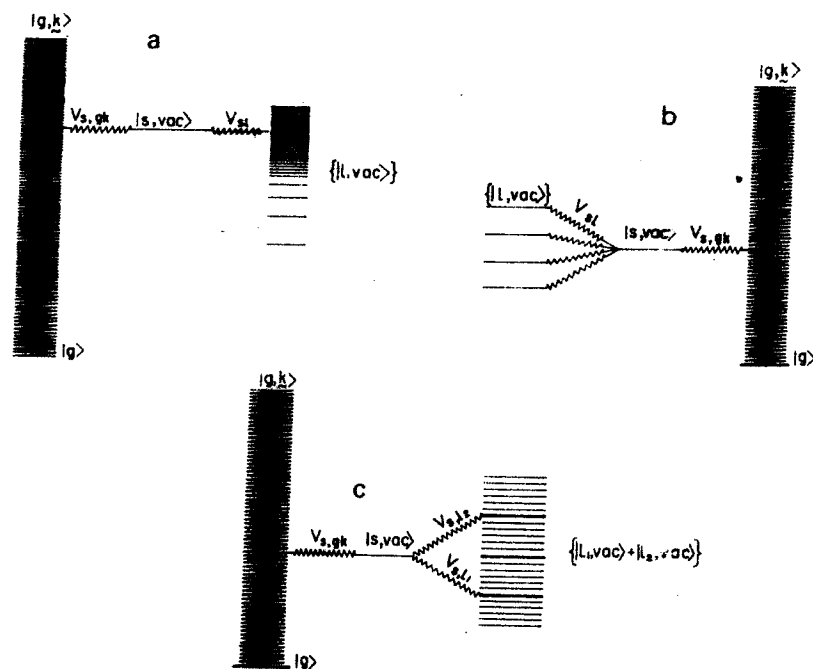


FIGURE 1. Typical radiative and interstate coupling schemes in molecules: (a) A statistical large molecule; (b) A small molecule; (c) Intermediate level structure in a large molecule.

### 3. PHOTON WAVEPACKETS

We are using a quantum-mechanical description of the radiation field which has some advantages over the classical description. First, spontaneous emission is inherently incorporated into this formalism, without any additional semiempirical assumptions. Second, such an approach can be extended to account for the detailed features of the photon statistics (Glauber, 1964) in the incident and for the emitted photon fields. We shall confine ourselves to weak fields which are characterized by a small number (one or zero) of photons in each field mode and can be represented as a wavepacket of one-photon states (Kroll, 1964; Cohen Tannoudji, 1966, 1967). The (unperturbed) state of the radiation field at  $t = 0$  is then

$$\psi_p(0) = \int d\mathbf{k} A_{\mathbf{k}} |\mathbf{k}\rangle \quad (3.1)$$

where  $|\mathbf{k}\rangle$  is an eigenstate of  $H_{\text{rad}}$ ,

$$H_{\text{rad}} |\mathbf{k}\rangle = k |\mathbf{k}\rangle \quad (3.2)$$

being characterized by one photon with momentum  $\mathbf{k}$  and energy  $k = |\mathbf{k}|$  (we are using the units  $\hbar = c = 1$ ). The one-photon states are normalized

$$\langle \mathbf{k} | \mathbf{k}' \rangle = \delta(\mathbf{k} - \mathbf{k}') \quad (3.3)$$

and the wavepacket amplitudes  $A_{\mathbf{k}}$  satisfy the normalization condition

$$\int d\mathbf{k} |A_{\mathbf{k}}|^2 = 1 \quad (3.4)$$

The time evolution of the free one-photon wavepacket (3.1) is given by

$$|\psi_p(t)\rangle = \exp(-iH_{\text{rad}}t) |\psi_p(0)\rangle = \int d\mathbf{k} A_{\mathbf{k}} \exp(-ikt) |\mathbf{k}\rangle, \quad -\infty < t < \infty \quad (3.5)$$

The spatial and temporal evolution of the pulse is thus completely specified in terms of the amplitudes  $A_{\mathbf{k}}$ . Note, however, that the experimental spectrum of the pulse results in  $|A_{\mathbf{k}}|^2$  and the exact determination of the phases of the field amplitudes  $A_{\mathbf{k}}$  is not an easy task.

We consider now the special case, which is of interest to us, that of a light pulse traveling in the  $x$  direction, whereupon  $\mathbf{k} = (k, 0, 0)$ . The photon wavepacket (3.5) now takes the form

$$|\psi_p(t)\rangle = \int dk A_k \exp(-ikt) |k\rangle \quad (3.6)$$

We can now express the photon density  $I(t)$  at  $x = 0$  and time  $t$  in the transparent form

$$I(t) = (2\pi)^{-1} |\varphi(t)|^2 \quad (3.7)$$

where

$$\varphi(t) \equiv \int dk A_k \exp(-ikt) \quad (3.8)$$

It is thus appropriate to refer to  $\varphi(t)$ , Eq. (3.8), as the field amplitude.

This formalism provides us with an adequate theoretical framework for describing a minimum-uncertainty wavepacket of one-photon states, which satisfies the relation  $\Delta E \Delta t \simeq 1$ , with  $\Delta E$  and  $\Delta t$  being the pulse energy spread and time duration, respectively. A more general treatment of weak fields can be conducted by treating the pulse in terms of a density matrix of one-photon states, given at zero time by

$$\rho_p(0) = \iint |k\rangle \rho_{kk'} \langle k'| dk dk' \quad (3.9)$$

The matrix elements  $\rho_{kk'}$  may take a variety of different forms. Only mode-locked laser pulses (under appropriate experimental conditions) are of the minimum-uncertainty type. In view of our current ignorance of the detailed features of light sources, i.e., the form of the pulse density matrix used in actual experiments, we shall continue using the minimum uncertainty wavepackets, Eq. (3.6) (i.e., substituting  $\rho_{kk'} = A_k A_k^*$  in (3.9)). We bear in mind, however, that whenever we encounter a product of the form  $\varphi^*(\tau) \varphi(\tau')$ , it has to be replaced by the appropriate correlation function (Glauber, 1964)

$$D(\tau, \tau') = \langle \varphi^*(\tau) \varphi(\tau') \rangle \quad (3.10)$$

for the light pulse.

#### 4. INTERACTION OF AN ISOLATED MOLECULE WITH A PHOTON WAVEPACKET

Consider now excitation and decay processes in a system consisting of a sample of "isolated" molecules and the radiation field. We assume that the molecules (all being in the ground state  $|g\rangle$ ) are located at the origin of a cartesian coordinate system. The photon wavepacket (3.6) is traveling along the  $x$  axis and, in the absence of interaction with the molecular sample, it arrives at the origin at  $t \approx 0$ . Physically, we expect that at sufficiently early times  $t$  ( $t \rightarrow -\infty$ ), the molecular system does not interact with the pulse (as the photon wavepacket is far from the origin) and the asymptotic behavior of the system (molecules + the radiation field) is represented by

$$|\psi(t)\rangle \xrightarrow{t \rightarrow -\infty} |\psi_0(t)\rangle \equiv \exp(-iH_0 t) |\psi_0(0)\rangle \quad (4.1)$$

where  $\psi_0(0)$  is the wavefunction the system would have at  $t = 0$  in the absence of  $H_{int}$ , i.e.,

$$|\psi_0(0)\rangle = \int dk A_k |g, k\rangle \quad (4.2)$$

and

$$H_0 = H - H_{int} \quad (4.3)$$

Eq. (4.1) thus contains the boundary conditions for our photon-scattering problem.

Turning now to the experimental observables, we can write for the probability of finding the system in any excited state  $|m, \text{vac}\rangle \in |s, \text{vac}\rangle, \{|l, \text{vac}\rangle\}$  at time  $t$

$$P_e(t) = \sum_m |\langle m, \text{vac} | \psi(t) \rangle|^2 \quad (4.4)$$

while the probability for finding the system in any one-photon ground electronic state  $|g, \mathbf{k}\rangle$  is

$$P_g(t) = \sum_{\mathbf{k}} |\langle g, \mathbf{k} | \psi(t) \rangle|^2 \quad (4.5)$$

( $\sum_{\mathbf{k}}$  in (4.5) denotes integration over all photon directions and energies followed by a summation over photon polarizations). Conservation of probability expressed in terms of the normalization condition for  $\psi(t)$ , implies that

$$P_e(t) + P_g(t) = 1 \quad (4.6)$$

for all  $t$ .

The experimentalist engaged in photon-counting experiments is not interested in the total number of photons,  $dP_g/dt$ , emitted from the system per unit time, as these include also the photons corresponding to the exciting light pulse, and the experimentalist takes great pains to eliminate this background radiation. The experimentally relevant photon counting rate,  $I(t)$ , for all the outgoing photons, excluding those corresponding to the original exciting pulse may be easily accomplished by excluding from the summation in (4.5) all the photons  $|\mathbf{k}\rangle$  having the same propagation and polarization directions as the exciting pulse. Thus

$$I(t) = \left\langle \frac{d}{dt} \sum_{\mathbf{k} \neq \mathbf{k}_0} |\langle g, \mathbf{k} | \psi(t) \rangle|^2 \right\rangle \quad (4.7)$$

where the brackets  $\langle \dots \rangle$  denote averaging over molecular orientations with respect to the incident-photon polarization direction.

To proceed, we require manageable mathematical expressions for the projections of  $\psi(t)$  appearing in Eqs. (4.4), (4.5) and (4.7). Making use of our boundary conditions (4.1), we obtain

$$\begin{aligned} \langle \alpha | \psi(t) \rangle &= \int dk C_{\alpha, gk}(t - t') A_k \exp(-ikt'), t' \rightarrow -\infty \\ |\alpha\rangle &= |g, \mathbf{k}\rangle, |m, \text{vac}\rangle \end{aligned} \quad (4.8)$$

The time-dependent amplitudes

$$C_{\alpha\beta}(t) = \langle \alpha | \exp(-iHt) | \beta \rangle \quad (4.9)$$

with  $|\alpha\rangle, |\beta\rangle = |g, \mathbf{k}\rangle$  or  $|m, \text{vac}\rangle$  are just the matrix elements of the time-evolution operator between the eigenstates of the zero-order hamiltonian  $H_0$ . We shall refer to these amplitudes as the decay amplitudes of the molecular system, as they incorporate all the information concerning the molecular (radiative and nonradiative) decay channels.



A convenient way to evaluate the decay amplitudes rests on the Green's function method (Goldberger and Watson, 1964; Cohen Tannoudji, 1966, 1967; Mower 1966; Freed and Jortner, 1969; Jortner and Mukamel, 1974). Defining the retarded Green's operator

$$G(E) = (E - H + i\eta)^{-1}, \quad \eta \rightarrow 0^+ \quad (4.10)$$

and utilizing the conventional methods of residue integration, one can formally recast the time-evolution operator in terms of the Fourier transform of the retarded Green's operator

$$-\theta(t) \exp(-iHt) = (2\pi i)^{-1} \int_{-\infty}^{\infty} dE \exp(-iEt) G(E) \quad (4.11)$$

where  $\theta(t)$  is the Heavyside step-function.

Thus the decay amplitudes (4.9) can be finally expressed in terms of the Fourier transform

$$\begin{aligned} \theta(t) C_{\alpha\beta}(t) &= -(2\pi i)^{-1} \int_{-\infty}^{\infty} dE \exp(-iEt) G_{\alpha\beta}(E) \\ G_{\alpha\beta}(E) &\equiv \langle \alpha | G(E) | \beta \rangle \end{aligned} \quad (4.12)$$

of the appropriate matrix elements of the Green's function. Utilizing Eqs. (4.1) and (4.10)–(4.12), we can rewrite Eq. (4.8) in a form independent of  $t'$ :

$$\langle \alpha | \psi(t) \rangle = \langle \alpha | \psi_0(t) \rangle + \sum_{\beta} \int dE \exp(-iEt) G_{\alpha\beta}(E) A(E) \langle \beta | H_{int} | g, E \rangle \quad (4.13)$$

where  $|g, E\rangle$  is equivalent to  $|g, k\rangle$  ( $E = k\hbar C$ ).

Assuming that the matrix element of  $H_{int}$  in (4.13) is weakly dependent on  $E$  in the energy range of the wavepacket ( $\Delta k$  around  $\bar{k}$ ), we can rewrite (4.13) in the form

$$\langle \alpha | \psi(t) \rangle = \langle \alpha | \psi_0(t) \rangle + i \sum_{\beta} \langle \beta | H_{int} | g, \bar{k} \rangle \int_{-\infty}^t d\tau C_{\alpha\beta}(t - \tau) \varphi(\tau) \quad (4.14)$$

The first term in (4.13) and (4.14) does not contribute to our desired projections (4.4), (4.5), (4.7), as it corresponds to one-photon states belonging to the exciting pulse. Substitution of (4.14) (or (4.13)) in (4.4), (4.5) and (4.7) thus results in

$$P_e(t) = \sum_m \left| \sum_{m'} \langle m' | H_{int} | g, \bar{k} \rangle \int_{-\infty}^t d\tau C_{mm'}(t - \tau) \varphi(\tau) \right|^2 \quad (4.15)$$

$$P_g(t) = \sum_{k''} \left| \sum_m \langle m | H_{int} | g, \bar{k} \rangle \int_{-\infty}^t d\tau C_{gk'',m}(t - \tau) \varphi(\tau) \right|^2 \quad (4.16)$$

and

$$I(t) = \left\langle \frac{d}{dt} \left( \sum_{\mathbf{k}' \neq \mathbf{k}} \left| \sum_m \langle m | H_{int} | g, \mathbf{k} \rangle \int_{-\infty}^t d\tau C_{gk'm}(t - \tau) \varphi(\tau) \right|^2 \right) \right\rangle \quad (4.17)$$

From the physical point of view, this general formal approach is attractive as we are dealing with a large number of levels, a problem which calls for the utilization of many-body techniques. To establish the relation between this formal treatment and the simple well-known concepts of stationary and metastable states formulated in terms of conventional time-dependent perturbation theory, let us first utilize the (unknown) eigenstates  $|\chi\rangle$ , with energies  $E_\chi$ , of the total Hamiltonian  $H$  for the system. The Green's function is diagonal in this representation, i.e.,

$$G_{\chi\chi'} = (E - E_\chi + i\eta)^{-1} \delta_{\chi\chi'}, \quad \eta \rightarrow 0^+ \quad (4.18)$$

and its poles are located on the real axis. Thus the system in an eigenstate  $|\chi\rangle$  is characterized by a real energy and does not exhibit any decay process. On the other hand, the matrix element of  $G(E)$  between (zero-order) states of  $H_0$  will be characterized by complex poles of the form  $E_j - \frac{1}{2}i\Gamma_j$ . The imaginary components  $\Gamma_j$  will determine the decay rate of the metastable states. From the mathematical point, the matrix elements  $G_{\alpha\beta}(E)$  are quite easy to evaluate by the utilization of the Dyson equation (Goldberger and Watson, 1964) and by the application of projection operators in the Hilbert space (Mower, 1966; Cohen Tannoudji, 1966, 1967). We shall not dwell on these methods here, but rather proceed to expose some physical results.

## 5. DOORWAY STATES

It has been often inquired: "What is the nature of the state accessible by optical excitation?" There is no unique answer to this question for a given molecular system, as in time-resolved experiments, the molecular decay mode is influenced by the nature of the exciting light pulse. In this section we shall treat time-resolved photon scattering experiments from molecules characterized by an arbitrarily complex level-structure. (The molecular level-scheme may include discrete states, intramolecular quasicontinua and true (dissociative) continua). The photon-counting rate will be expressed in terms of a "doorway state" which appears naturally in the treatment of preparation and decay problems.

Doorway states have long been used in nuclear physics for the interpretation of scattering cross sections (energy-resolved observables) (Feshbach et al., 1967). Only recently the notion of "doorway states" was utilized to handle molecular problems (Nitzan and Jortner, 1972; Jortner and Mukamel, 1974, 1975; Mukamel and Jortner, 1957b). The doorway state  $|N, \text{vac}\rangle$  is the superposition of excited molecular states,

each weighted by its radiative coupling with the ground state,

$$|N, \text{vac}\rangle = \gamma_N^{-1} \sum_m |m, \text{vac}\rangle \langle m, \text{vac} | H_{\text{int}} | g, \mathbf{k} \rangle \quad (5.1)$$

$$\gamma_N^2 = \sum_m |\langle g, \mathbf{k} | H_{\text{int}} | m, \text{vac} \rangle|^2 \quad (5.2)$$

where  $\gamma_N$  is the appropriate normalization constant and  $\sum_m$  stands for summation over the discrete excited states and an integration over the continuous part of the spectrum. It should be noted that the definition of the doorway state is independent of the choice of the particular one-photon state  $|\mathbf{k}\rangle$  in Eqs. (5.1) and (5.2) provided all the states  $\{|m\rangle\}$  have transition moments parallel to  $|g\rangle$  (Mukamel and Jortner, 1975b). We shall hereafter assume in (5.1) and (5.2) a photon  $|\mathbf{k}\rangle$  polarized along this common transition moment.

The experimental counting rate from the molecule (4.7) is then

$$I(t) = \Gamma_N^* P_N(t) \quad (5.3)$$

where  $\Gamma_N^*$  is the radiative width of the doorway state (Mukamel and Jortner, 1975b),

$$\Gamma_N^* = \frac{4}{3} \gamma_N^2 k^2 \quad (5.4)$$

and  $P_N(t)$  is the probability of finding the system in the doorway state at time  $t$ ,

$$P_N(t) = |\langle N, \text{vac} | \psi(t) \rangle|^2 \quad (5.5)$$

Utilizing (5.1) with (5.2), (5.5) and (4.14) we may write

$$P_N(t) = \frac{1}{3} \gamma_N^2 \left| \int_{-\infty}^t d\tau \varphi(\tau) C_{NN}(t - \tau) \right|^2 \quad (5.6)$$

where

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

and

$$G_{NN}(E) = \langle N, \text{vac} | G(E) | N, \text{vac} \rangle \quad (5.8)$$

The following comments are now in order:

1. The photon counting rate from a general molecular level structure is expressed in terms of a convolution of the pulse field amplitude  $\varphi(t)$  and the molecular decay amplitude  $C_{NN}(t)$ .

2. All the molecular information is incorporated in  $C_{NN}(t)$ .
3. The optical excitation mode is determined by  $\varphi(t)$ .
4. Changing the optical excitation conditions, i.e., utilizing different forms of the field amplitude, will lead to different decay patterns in the photon counting experiment. However, the basic molecular information is always incorporated in the molecular decay amplitude. One can use different pulse shapes to extract  $C_{NN}(t)$ , or alternatively use the molecule for probing the pulse.
5. The probability (5.6) and consequently the photon counting rate  $I(t) \propto P_N(t)$  can be recast in an alternative form, in terms of the field amplitudes. Utilizing Eq. (4.13)

$$P_N(t) = \frac{1}{3} \gamma_N^2 \left| \int_{-\infty}^{\infty} dE A(E) G_{NN}(E) \exp(-iEt) \right|^2 \quad (5.9)$$

where we have specified the photon wavepacket amplitudes  $A(E) \equiv A_k$  in terms of their energies.

6. For the limiting case of a coherent excitation by an ultrashort light pulse.  $A(E) = \text{constant}$  or  $\varphi(t - \tau) = \delta(t - \tau)$  and we obtain from Eqs. (5.3) and (5.6) or (5.9)

$$I(t) = \frac{1}{3} \Gamma_N^r \gamma_N^2 |C_{NN}(t)|^2 \quad (5.10)$$

7. Up to this point we have been concerned with the properties of a minimum-uncertainty pulse. The extension to more realistic light pulses follows the discussion presented in Sec. 3. Eq. (5.6) should simply be replaced by

$$P_N(t) = \frac{1}{3} \gamma_N^2 \left| \int_{-\infty}^t \int_{-\infty}^t d\tau d\tau' D(\tau, \tau') C_{NN}^*(t - \tau) C_{NN}(t - \tau') \right|^2 \quad (5.11)$$

8. The results obtained herein are to second order in the applied field and hence are valid for weak light pulses. Spontaneous emission, however, is properly incorporated in a non-perturbative way.

## 6. TIME-RESOLVED PHOTON SCATTERING FROM A SINGLE RESONANCE

To provide a simple and physically relevant application for the formalism of the preceding section, let us consider now photon scattering from a single molecular resonance (a state of affairs common for the radiative decay of bound and pre-dissociating states). The energy-level scheme is presented in Fig. 2a, which shows a single discrete excited state  $|s\rangle$  coupled to the radiative continuum characterized by the density of states  $\rho_r$ ;  $|s\rangle$  can also be coupled to an intramolecular continuum

$\{|c\rangle\}$  characterized by the density of states  $\rho_c$  in the vicinity of the energy  $E = E_s$ . The intrinsic optical molecular lineshape  $\mathcal{L}(E)$  (see Sec. 7) is a Lorentzian peaked at the energy  $\bar{E}_s = E_s + \Delta_s$ , where  $\Delta_s$  is a (small) level shift, and characterized by the width

$$\begin{aligned}\Gamma_s &= \Gamma_s^r + \Gamma_s^c \\ \Gamma_s^r &= 2\pi |V_{s,r}|^2 \rho_r \\ \Gamma_s^c &= 2\pi |V_{s,c}|^2 \rho_c\end{aligned}\quad (6.1)$$

consisting of the sum of a radiative  $\Gamma_s^r$  and a nonradiative  $\Gamma_s^c$  contributions.

The decay amplitude of the doorway state  $|s\rangle$  is

$$C_{ss}(\tau) = \exp(-i\bar{E}_s\tau) \exp(-\Gamma_s\tau/2) \quad (6.2)$$

while the photon counting rate is now obtained from Eqs. (5.3), (5.6) and (6.2):

$$I(t) = \frac{1}{3} \Gamma_s^r |V_{s,r}|^2 \left| \int_{-\infty}^t \varphi(\tau) \exp[-i\bar{E}_s(t-\tau)] \exp[-\Gamma_s(t-\tau)/2] d\tau \right|^2 \quad (6.3)$$

This result can be utilized to analyze the experimental observations of the continuous transition between time-resolved resonance fluorescence and near-resonance photon scattering, reported by Williams, Rousseau and Dworetzky (1974). These authors have performed scattering of a light pulse of a tunable laser from a single rotovibrational level of the  $B^2\Pi$  state of molecular iodine and have recently triggered a lot of theoretical activity (Mukamel and Jortner, 1975a; Mukamel et al., 1975; Berg et al., 1974; Metiu et al., 1975). The basic idea of the experiment of Williams et al. (1974) is presented in Fig. 2b. The time-resolved decay (i.e., time-resolved photon scattering) is determined as a function of the energy increment

$$\Delta = |\bar{E}_s - k| \quad (6.4)$$

The exciting light pulse is characterized (Fig. 2c) by the amplitude

$$\begin{aligned}\varphi(t) &= \exp(\gamma_1 t/2) \exp(-ikt), \quad t < 0 \\ \varphi(t) &= \exp(-ikt), \quad 0 < t < T \\ \varphi(t) &= \exp[-\gamma_2(t-T)/2] \exp(-ikt), \quad t > T\end{aligned}\quad (6.5)$$

where  $\gamma_i^{-1}$  with  $i = 1$  and  $2$  correspond to the pulse rise and decay times respectively, while  $T$  denotes the pulse duration. The additional parameter which enters the game is the Doppler width.

The following experimental observations were reported.

1. For the case of resonance excitation, i.e., when  $\Delta \leq \beta$ , only a long, molecular, decay component,  $\exp(-\Gamma_s t)$  is exhibited for  $t > T$ .

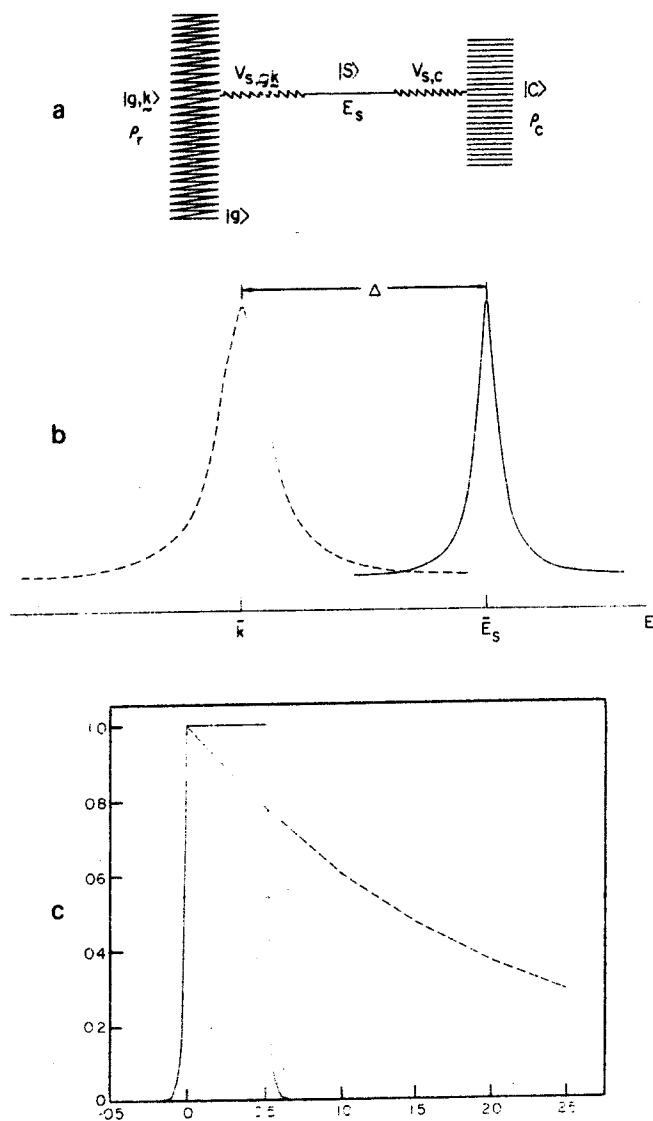


FIGURE 2. (a) Energy-level scheme for photon scattering from an isolated resonance. (b) Energy profile for near resonance photon scattering experiment: solid curve, line-shape  $\mathcal{L}(E)$  of the isolated resonance (a Lorentzian around  $E_s$ , with width  $\Gamma_s$ ); broken curve, power spectrum  $|A(E)|^2$  of the light pulse around  $\bar{k}$  which may assume an arbitrary form. (c) Molecular decay amplitude  $|C_{ss}(t)|$  and pulse field amplitude  $|\varphi(t)|$  in a time-resolved photon scattering experiment from an isolated resonance: broken curve  $|C_{ss}(t)|$  from Eq. (6.2); solid curve,  $|\varphi(t)|$  from Eq. (6.5).

2. When the off-resonance energy increment is large, i.e.,  $\Delta > \beta > \gamma_i > \Gamma_s \sim T^{-1}$ , two decay components with lifetimes  $\gamma_2^{-1}$  and  $\Gamma_s^{-1}$  are exhibited. The experimental photon counting rate  $F(\Delta, t)$  for  $t > T$  is

$$F(\Delta, t) \approx I_p(t) + I_m(t) \quad (6.6)$$

with

$$I_p(t) = I_p^0 \exp[-\gamma_2(t - T)] \quad (6.7a)$$

$$I_m(t) = I_m^0 \exp[-\Gamma_s(t - T)] \quad (6.7b)$$

$I_p(t)$  and  $I_m(t)$  denote the components corresponding to near-resonance Raman scattering from the molecule and to molecular resonance-fluorescence, respectively.

3. At moderately low pressures of  $I_2$  (0.03 torr), the intensity ratio

$$R = I_m^0/(I_p^0 + I_m^0) = I_m^0/F(\Delta, T) \quad (6.8)$$

is a slowly decreasing function of  $\Delta$ , becoming practically constant for large values of  $\Delta$ .

4. Increasing the pressure to 0.25 torr results in a dramatic enhancement of the long-lived molecular component relative to the total intensity (i.e.,  $R$  increases).

Utilizing Eq. (6.3) for the photon counting rate from a single molecule, which depends on  $\Delta$  and will be now denoted by  $I(\Delta, t)$ , we now have to account for the Doppler broadening. The experimentally observable decay pattern of a single molecule,  $F(\Delta, t)$ , is obtained by convoluting  $I(\Delta, t)$  with the Gaussian distribution

$$f(\Delta) = (\pi\beta^2)^{-1/2} \exp(-\Delta^2/\beta^2) \quad (6.9)$$

so that

$$F(\Delta, t) = \int_{-\infty}^{\infty} f(\Delta - \Delta') I(\Delta', t) d\Delta' \quad (6.10)$$

In Fig. 3 we present numerical results for  $F(\Delta, t)$  using the pulse shape (6.5) and substituting typical parameters corresponding to the experimental situation (Williams et al., 1974), i.e.,  $\gamma_1/\Gamma_s = \gamma_2/\Gamma_s = 100$ ,  $\Gamma_s T = 0.5$  and  $\beta/\Gamma_s = 500$  (in the experiment,  $\Gamma_s^{-1} = 10^{-6}$  sec). Our calculations reveal the following features:

1. For the resonance situation, i.e.,  $\Delta \lesssim \beta$ , only the long molecular decay component is exhibited.
2. Moving away from resonance, when  $\Delta > 2\beta$ , both short and long decay components appear.
3. Increasing  $\Delta$  results in a decrease of the total intensity. For the extreme off-resonance situation we have

$$F(\Delta, T) \propto \Delta^{-2} \quad (6.11)$$

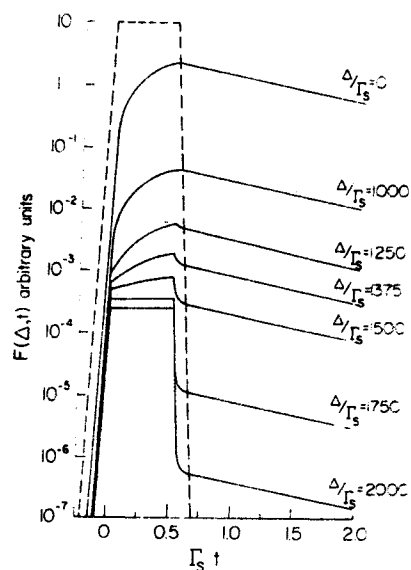


FIGURE 3. Time resolution of the photon counting rate  $F(\Delta, t)$  (Eq. (6.10)) (in arbitrary units) for the pulse (6.5) for various values of the off-resonance energy  $\Delta$ . The Doppler width (in units of the resonance radiative width) is  $\beta/\Gamma_s = 500$ ; the rise and fall times of the pulse are  $\gamma_1/\Gamma_s = \gamma_2/\Gamma_s = 100$ ; the inverse duration of the pulse is  $T^{-1}/\Gamma_s = 2$ . The dotted line is proportional to the time-resolved pulse intensity.

4. The intensity of the molecular decay component for the off-resonance situation decreases as

$$I_m(\Delta, T) \propto \Delta^{-4} \quad (6.12)$$

5. The only typical lifetimes (or decay modes) which determine the time-resolved decay pattern for resonance fluorescence and for near-resonance Raman scattering are that characterizing the pulse decay and that specifying the molecular lifetime. The off-resonance energy does not appear as an additional lifetime, rather it just determines the total emission intensity via Eq. (6.11) and the relative intensity  $R$  of the long component (6.12) at off-resonance.

6. The intensity ratio  $R$  for the off-resonance situation in the isolated molecule assumes the limiting form

$$R \propto \Delta^{-2} \quad (6.13)$$

The general features 1–5 are compatible with the experimental results of Williams et al. (1974). It is important to emphasize that the time-resolved decay pattern depends crucially on the pulse shape. Thus, for example, for the case of a pulse charac-



terized by a rectangular function for  $\varphi(t)$  ( $\gamma_1, \gamma_2 \rightarrow \infty$ ) only the molecular component will be exhibited, while for the realistic pulse shape (6.5) both decay components are revealed.

It is, however, apparent from our calculations (see Fig. 3) that the theoretical prediction 6 for the isolated molecule, i.e.,  $R \propto \Delta^{-2}$  for the extreme off-resonance situation is at variance with the "low" pressure data of Williams et al. (1974). Together with Ben-Reuven (Mukamel, Ben-Reuven and Jortner, 1975), we have concluded that collisional effects are of considerable importance under 0.03 torr of  $I_2$ , and have advanced a theory of time-resolved photon scattering by collisionally-perturbed molecules. It has been noted that pressure broadening effects cannot be elucidated by a naive extension of the results for the isolated molecule by simply modifying the molecular decay width  $\Gamma$ , by an addition of a pressure-dependent term. The photon-counting rate under collisional perturbations involves both  $T_1$  (level relaxation) and  $T_2$  (line broadening) contributions. The latter incorporate interference effects between the lower and the upper states, due to phase shifts (Ben-Reuven, 1975), which cannot be expressed in terms of additive contributions of the individual levels.

The level scheme for collisional and radiative coupling is portrayed in Fig. 4. We now consider a manifold  $|si\rangle$  of excited (presumably rotational) states. The relaxation processes are specified in terms of the  $T_1$  and  $T_2$  damping matrices for which we have considered the following simple model (Mukamel et al., 1975):

$$\begin{aligned} (\Gamma_1^c)_{ii} &= \Gamma_1' & (\text{damping}) \\ (\Gamma_1^c)_{ij} &= -\Gamma_1'', \quad i \neq j & (\text{cross relaxation}) \end{aligned} \quad (6.14)$$

for  $T_1$  processes, and

$$(\Gamma_2^c)_{ij} = \Gamma_2 \delta_{ij} \quad (6.15)$$

for  $T_2$  processes.

The matrices  $\Gamma_1$  and  $\Gamma_2$  are defined in the Liouville space (Ben-Reuven, 1975) and the indexes  $i, j$  in Eqs. (6.14) and (6.15) refer to  $|si\ si\rangle$  and  $|si\ gk\rangle$ , respectively.

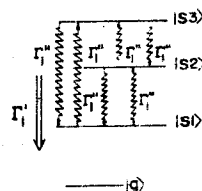


FIGURE 4. Level-scheme and damping matrices for a collisionally perturbed molecule (Eqs. (6.14), (6.15)).

in the double-bracket notation (Baranger, 1958). The  $T_1$  matrix, Eq. (6.14), is characterized by an eigenvector

$$\begin{pmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{pmatrix}$$
 having the eigenvalue

$$\Gamma_1 = \Gamma_1 - (n - 1)\Gamma_1'' \quad (6.16)$$

where  $n$  is the number of the relevant excited  $|si\rangle$  levels. In the case of no collisional relaxation from the excited electronic configuration  $\Gamma_1 = \Gamma_1$ . The  $T_2$  matrix (6.15) is characterized by the diagonal elements

$$\Gamma_2 = \frac{1}{2}\Gamma_1' + \Gamma_2' \quad (6.17)$$

where  $\Gamma_2'$  involves the contribution of the proper  $T_2$  processes (Ben-Reuven, 1975).

The calculation of the photon counting rate under collisional perturbations provides an example of the use of tetradic Green's functions in Liouville space (Zwanzig, 1961; Fano, 1963). Under reasonable and realistic assumptions, the photon counting rate is expressed in terms of a convolution of  $F(\Delta, t)$  from (6.10) with a Lorentzian profile

$$C(\Delta) = (\hat{\Gamma}/\pi)/(\Delta^2 + \hat{\Gamma}^2) \quad (6.18)$$

$$\hat{\Gamma} = \frac{1}{2}(n - 1)\Gamma_1'' + \Gamma_2' \quad (6.19)$$

which incorporates purely collisional effects due to interstate cross relaxation ( $\Gamma_1''$ ) and "proper"  $T_2$  processes ( $\Gamma_2'$ ) resulting from phase-changing collisions. Thus the photon counting rate from the collisionally perturbed molecule assumes the final form

$$\langle F(\Delta, t) \rangle = \int_{-\infty}^{\infty} d\Delta' \int_{-\infty}^{\infty} d\Delta'' I(\Delta', t) (\pi\beta^2)^{-1/2} \otimes \exp[-(\Delta' - \Delta'')^2/\beta^2] \frac{(\Gamma/\pi)}{(\Delta - \Delta'')^2 + \Gamma^2} = I * f * C \quad (6.20)$$

The physical features of the photon scattering problem are now clear. The short-decay component originates from a photon scattering process, which has to be handled within the framework of a single quantum mechanical process, while the resonance fluorescence, long lived component originates from the decay of metastable states, where the excitation and the subsequent decay can be segregated. Different Fourier components of the exciting optical pulse contribute to the (separable) "resonant scattering" and to the (inseparable) direct-scattering processes. At zero pressure, those Fourier components of the pulse which are close to resonance excite

the long decay components, while other Fourier components of the pulse are directly scattered. The mathematical implication of our results is made obvious by considering the asymptotic form of the convolution integral (6.20). In the isolated molecule  $I_m(T) \propto \Delta^{-4}$  and convoluting this result with the pressure broadening Lorentzian term (6.18) we obtain the asymptotic form for the long molecular component from the collisionally perturbed molecule of the form  $\propto \Delta^{-2}$  for finite  $\hat{\Gamma}$ . On the other hand,  $F(\Delta, T) \propto \Delta^{-2}$  in the isolated molecule and convolution with the Lorentzian (6.18) does not alter the asymptotic behaviour  $\langle F(\Delta, t) \rangle \propto \Delta^{-2}$ .  $R$  is thus independent of  $\Delta$  under the conditions of collisional perturbations. These considerations are fully borne out by the results of the numerical calculations based on Eq. (6.20) which are portrayed in Fig. 5. We note that a small collisional perturbation, i.e.,  $\hat{\Gamma}/\Gamma_s \approx 0.01$ , goes a far way resulting in the asymptotic form for  $R$  which is practically independent of  $\Delta$ . This interesting feature stems from the Lorentzian shape of the collisional contribution to the line shape and from the basic rule that the asymptotic behaviour of a convolution is governed by the weaker decreasing function. Thus under the conditions of off-resonance situation, pressure broadening effects result in a dominating contribution to  $I_m(\Delta, t)$  from the vicinity of  $\Delta = 0$ , i.e., from near-resonance. As the collisionally broadened Lorentzian line spans a larger fraction of the Fourier components of the pulse, the contribution to two-stage scattering

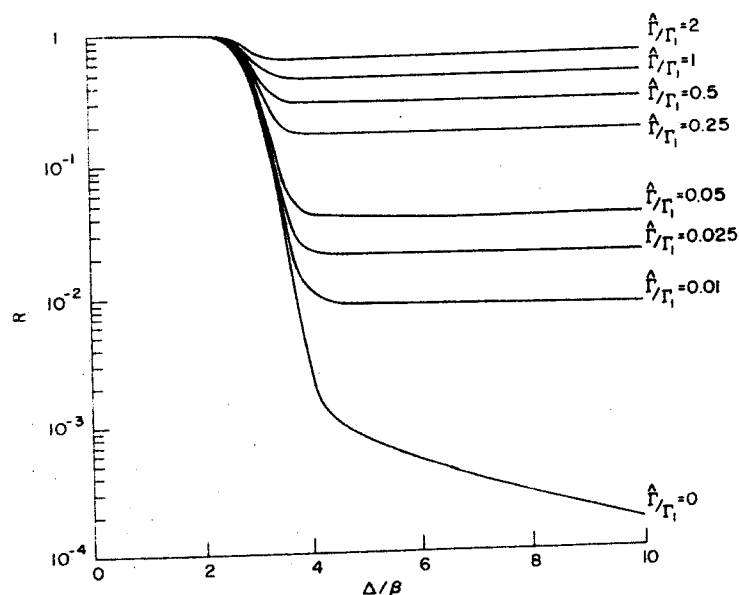


FIGURE 5. The intensity ratio  $R$  between the slowly-decaying component and the total photon-counting rate evaluated at  $t = T$  as a function of the off-resonance parameter  $\Delta$ , at different values of the collision-broadening rate  $\hat{\Gamma}$ . Other parameters as in Fig. 3.

due to the decay of metastable states is enhanced, in comparison with the contribution of direct scattering. Thus, Mukamel et al. (1975) have considered collisional perturbations as exerting "memory erosion" effect on the molecule, increasing the contribution to the time-resolved decay from molecules which have lost their memory with regard to the time-profile of the light pulse.

We have dwelt on the subject of time-resolved photon scattering from a single resonance, which can be coupled by collisional perturbations to other states, well separated from it. We shall now turn to the general solution of the more interesting problem of time-resolved photon scattering from a manifold of densely spaced molecular states.

## 7. THE EFFECTIVE HAMILTONIAN AND TIME-RESOLVED PHOTON SCATTERING

In Sec. 5 we have presented general formal expressions for the counting rate in time-resolved photon scattering experiments from molecules with an arbitrarily complex level-scheme. We shall now proceed to provide explicit formal expressions for the photon counting from the quite general level scheme presented in Fig. 6. This level scheme consists of some bound states which are radiatively coupled to the ground state and may be also coupled to intramolecular continua, or to other decay channels which do not carry oscillator strength from the ground state. We recall that the photon counting rate is determined by the projection of  $|N\rangle$  on  $\psi(t)$  (Eqs. (5.5)–(5.8)). Thus even if we had a complete information on  $\psi(t)$ , a large part of it would be redundant, as we only require the subpart of  $\psi(t)$  given by the projection

$$|N, \text{vac}\rangle \langle N, \text{vac}| \quad (7.1)$$

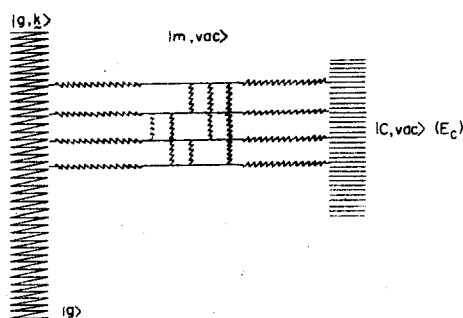


FIGURE 6. A general molecular level scheme consisting of a group of closely spaced discrete levels radiatively coupled to the ground state, which may also be coupled to intramolecular channels.

In other words, we can limit ourselves to the time evolution of a (small) subpart of the Hilbert space spanned by the discrete states  $|m, \text{vac}\rangle$ . This leads us to a formulation of an effective Hamiltonian which specifies the time evolution of the relevant subsystem in the presence of the radiation field and other intramolecular decay channels. (Jortner and Mukamel, 1974, 1975; Mukamel and Jortner, 1974b).

Being guided by Eq. (5.1), we partition the total Hilbert space by the use of the following projection operators:

$$\begin{aligned}\hat{P} &= \sum_m |m, \text{vac}\rangle \langle m, \text{vac}| \\ \hat{Q} &= \sum_{\mathbf{k}} |g, \mathbf{k}\rangle \langle g, \mathbf{k}| + \sum_c |c\rangle \langle c| \\ \hat{P} + \hat{Q} &= 1\end{aligned}\quad (7.2)$$

Following this formal approach, Eqs. (5.3) and (5.8) take the form

$$I(t) = \Gamma_N |\langle N, \text{vac} | \hat{P} \psi(t) \rangle|^2 \quad (7.3)$$

and

$$G_{NN}(E) = \langle N, \text{vac} | \hat{P} G(E) \hat{P} | N, \text{vac} \rangle \quad (7.4)$$

Thus the relevant physical information is embedded in the projection  $\hat{P}G\hat{P}$ . Alternatively, working in the time rather than in the energy domain we may state that we require the projection  $\hat{P} \exp(-iHt) \hat{P}$  of the time-evolution operator to specify the time evolution in the relevant subpart of the Hilbert space.

It has been shown elsewhere (Mower, 1966; Cohen Tannoudji, 1966, 1967; Jortner and Mukamel, 1974, 1975) that the Green's function and the time-evolution operator in the  $P$  subspace can be expressed in terms of an effective Hamiltonian

$$H_{\text{eff}} = \hat{P}(H_0 + R)\hat{P} \quad (7.5)$$

where  $H_0$  is the zero order Hamiltonian (2.1a) and  $R$  is the level-shift operator

$$R = V + V\hat{Q}(E - \hat{Q}H\hat{Q})^{-1}\hat{Q}V \quad (7.6)$$

The latter consists of two contributions, a direct coupling term and a relaxation contribution.

The appropriate projections on the Green's function and the time-evolution

operator result in the simple-looking expressions

$$\hat{P}G(E)\hat{P} = \hat{P}(E - H_{\text{eff}})^{-1}\hat{P} \quad (7.7a)$$

$$\hat{P}\exp(-iHt)\hat{P} = \hat{P}\exp(-iH_{\text{eff}}t)\hat{P} \quad (7.7b)$$

Thus all the relevant information is contained in the effective Hamiltonian  $H_{\text{eff}}$  which can be recast in matrix form

$$H_{\text{eff}} = H_m + \Delta - \frac{1}{2}i\Gamma \quad (7.8)$$

where  $H_m$  is the molecular Hamiltonian,  $\Delta$  is a level-shift matrix, and  $\Gamma$  is the decay matrix, both matrices originating from the coupling of the discrete states with the radiative and the nonradiative continua. We have split the two individual contributions originating from the radiative coupling and from the coupling to the intramolecular continuum  $\{|c\rangle\}$  as follows:

$$\begin{aligned} (\Delta)_{mm'} &= (\Delta^r)_{mm'} + (\Delta^c)_{mm'} \\ (\Delta^r)_{mm'} &= PP \sum_{\mathbf{k}} \frac{\langle m, \text{vac} | H_{\text{int}} | g, \mathbf{k} \rangle \langle g, \mathbf{k} | H_{\text{int}} | m', \text{vac} \rangle}{E - k} \\ (\Delta^c)_{mm'} &= PP \sum_c \frac{\langle m, \text{vac} | H_v | c, \text{vac} \rangle \langle c, \text{vac} | H_v | m', \text{vac} \rangle}{E - E_c} \end{aligned} \quad (7.9)$$

where  $PP$  stands for a principal part of an integral and

$$\begin{aligned} (\Gamma)_{mm'} &= (\Gamma^r)_{mm'} + (\Gamma^c)_{mm'} \\ (\Gamma^r)_{mm'} &= 2\pi \langle m, \text{vac} | H_{\text{int}} | g, \mathbf{k} \rangle \rho_r(k) \langle g, \mathbf{k} | H_{\text{int}} | m', \text{vac} \rangle \\ (\Gamma^c)_{mm'} &= 2\pi \langle m, \text{vac} | H_v | c, \text{vac} \rangle \rho_c \langle c, \text{vac} | H_v | m', \text{vac} \rangle \end{aligned} \quad (7.10)$$

Here  $\rho_r(k)$  and  $\rho_c$  denote the density of states in the photon field and in the intramolecular continuum, respectively.

The level-shift and the damping matrices provide a generalization of these (scalar) quantities for the case of a single resonance. It is important to notice that, in principle, both the level-shift and the damping matrix are energy dependent. Concerning the level-shift matrix, we can quite safely disregard the (divergent) radiative contributions  $\Delta_{mm}^r$ , which can be handled by the renormalization theory adopted in the study of the Lamb shift (Schweber, 1961). The level-shift contributions  $\Delta_{mm}^c$  may be of importance in modifying the energy levels.

The properties of the relaxation matrix  $\Gamma$  are the following:

1. It provides a generalization of Fermi's Golden Rule for a multilevel system.
2. It is, in general, non-diagonal.

3. The off-diagonal terms represent indirect coupling between the discrete states via the continuum states.

4. The off-diagonal contributions are of importance only in the case of near-degeneracy, i.e.,  $\Gamma_{mm'} \sim |E_m - E_m|$

5.  $\Gamma$  is Hermitian

6. Usually it is safe to assume that  $\Gamma$  is a weakly varying function of energy in the relevant range. (An exception exists when we have a resonance too close to some threshold (Goldberger and Watson, 1964).)

We now turn to the features of the effective Hamiltonian which can be summarized as follows:

1.  $H_{\text{eff}}$  is non-Hermitian.

2. In general,  $H_{\text{eff}}$  is not diagonalized by the eigenstates of  $H_m$ .

3.  $H_{\text{eff}}$  can be diagonalized by the transformation

$$\mathbf{D}H_{\text{eff}}\mathbf{D}^{-1} = \Lambda$$

$$\Lambda_{ij} = \Lambda_{jj}\delta_{ij} = E_j - \frac{1}{2}i\Gamma_j \quad (7.11)$$

4. The transformation matrix  $\mathbf{D}$  is non-unitary. When the eigenfunctions corresponding to  $|m, \text{vac}\rangle$  are real,  $H_{\text{eff}}$  is complex symmetric while  $\mathbf{D}$  is an orthogonal matrix.

5. The basis of zero-photon states  $|j, \text{vac}\rangle$  diagonalizes  $H_{\text{eff}}$  via the transformation

$$|j, \text{vac}\rangle = \sum_m D_{jm} |m, \text{vac}\rangle \quad (7.12)$$

(accidental degeneracies are disregarded in our discussion).

6. The  $|j, \text{vac}\rangle$  basis is non-orthogonal.

7. One can define a complementary basis  $|j, \text{vac}\rangle$  via the transformation

$$|j, \text{vac}\rangle = \sum_m [(D^{-1})^\dagger]_{jm} |m, \text{vac}\rangle \quad (7.13)$$

In the special case 4, the wavefunction corresponding to  $|j\rangle$  is the complex conjugate of the wavefunction corresponding to  $|j, \text{vac}\rangle$ .

The projection operator into the  $P$  space may be written as

$$\hat{P} = \sum_j |j, \text{vac}\rangle \langle j, \text{vac}| \quad (7.14)$$

This relation is a consequence of the orthonormality of  $|j, \text{vac}\rangle$  and  $|j, \text{vac}\rangle$ .

8. The diagonal sum rule applies to the transformation (7.11), whereupon

$$\sum_m (E_m + \Delta_{mm}) = \sum_j E_j \quad (7.15)$$

$$\sum_m \Gamma_{mm} = \sum_j \Gamma_j$$

9. The Green's function and the time evolution operator in the  $P$  space are

$$\hat{P}G(E)\hat{P} = \sum_j \frac{|j, \text{vac}\rangle \langle j, \text{vac}|}{E - E_j + (i/2)\Gamma_j} \quad (7.16)$$

and

$$\hat{P} \exp(-iH_{\text{eff}}t) \hat{P} = \sum_j |j, \text{vac}\rangle \exp[-iE_j t - \frac{1}{2}\Gamma_j t] \langle j, \text{vac}|. \quad (7.17)$$

A final important conclusion emerging from the last formal result is that the molecular decay amplitudes (see section IV) combining any pair of zero-order  $|m, \text{vac}\rangle$  states can be expressed as a superposition of exponential functions  $\exp[-iE_j t - \frac{1}{2}\Gamma_j t]$ . It is thus proper to refer to the basis set  $|j, \text{vac}\rangle$  as the *independently decaying levels* of the molecular system.

At this stage we can combine Eqs. (5.3)–(5.8) together with (7.3), (7.4) and (7.17) to derive the following expression for the photon counting rate from a manifold of discrete optically active levels:

$$I(t) = \frac{1}{3} \gamma_N^2 \Gamma_N \left\{ \sum_j \sum_{j'} A_j^* A_{j'} F_{j'}^*(t) F_j(t) \exp[-i(E_j - E_{j'})t] \right\} \quad (7.18)$$

$$A_j = \langle N, \text{vac} | j, \text{vac} \rangle \langle j, \text{vac} | N, \text{vac} \rangle \quad (7.19a)$$

$$F_j(t) = \int_{-\infty}^t d\tau \varphi(\tau) \exp(iE_j \tau) \exp[-\frac{1}{2}\Gamma_j(t - \tau)] \quad (7.19b)$$

Some general conclusions are immediately apparent:

1. The photon counting rate is determined by the cross products of terms consisting of the coefficients  $A_j$  and time dependent amplitudes  $F_j$ .
2. The coefficients  $A_j$  constitute the residues of the Green's function (7.16).
3. The time-dependent coefficients  $F_j(t)$  contain information concerning the light pulse and the decay modes of the independently decaying levels.

To provide the background for the discussion of time-resolved experiments under intermediate excitation conditions, let us consider excitation by a Lorentzian wavepacket so that  $\varphi(t) = \theta(t) \exp(-ik t) \exp(-\frac{1}{2}\gamma_p t)$ , where  $\gamma_p$  corresponds to the reciprocal decay time of the pulse (Cohen Tannoudji, 1966; Jortner and Mukamel, 1974, 1975). Eq. (7.19) takes the form

$$F_j(t) = i \frac{\exp[-i(\bar{k} - E_j)t] \exp(-\frac{1}{2}\gamma_p t) - \exp(-\frac{1}{2}\Gamma_j t)}{\bar{k} - E_j + (i/2)(\Gamma_j - \gamma_p)} \quad (7.20)$$

As the pulse width  $\gamma_p$  can be varied at will, we shall now consider two physical situations pertaining to short-excitation experiments:



7.1. The case of energy-weighted excitation. Provided that

$$\gamma_p \gg \Gamma_j \quad \text{for all } j \quad (7.21)$$

the photon counting rate is

$$I(t) = \frac{1}{3} \gamma_p^2 \Gamma_N \left\{ \sum_j \frac{|A_j|^2 \exp(-\Gamma_j t)}{(E_j - \bar{k})^2 + \frac{1}{4} \gamma_p^2} + \sum_{j \neq j'} \frac{A_j^* A_{j'}}{(E_j - \bar{k} + (i/2) \gamma_p)(E_{j'} - \bar{k} - (i/2) \gamma_p)} \otimes \otimes \exp[i(E_{j'} - E_j)t] \exp[-(\Gamma_j + \Gamma_{j'})t/2] \right\} \quad (7.22)$$

In this case, each component is weighted by the attenuation factors in the denominator which account for the different absorption strengths of the exciting pulse by the independently decaying levels. It is interesting to explore the behavior of Eq. (7.22) in different time domains. Consider first short times after the excitation, i.e.,

$$\gamma_p^{-1} \lesssim t \ll \Gamma_j^{-1} \quad (7.23)$$

whereupon the exponential functions  $\exp(-\Gamma_j t)$  can be set equal to unity and Eq. (7.22) takes the form of the Fourier sum

$$I_0(t) \propto \left| \sum_j \frac{A_j \exp(-iE_j t)}{E_j - \bar{k} + (i/2) \gamma_p} \right|^2 \quad (7.24)$$

The time evolution is determined by the pulse widths  $\gamma_p$  and by the "spreading width"  $\Gamma_d$  (i.e., the energy spread of distribution of the  $|j\rangle$  states). As an example consider a Lorentzian distribution  $A_j$ , i.e.,

$$A_j = (E_j - E_0 + (i/2) \Gamma_d)^{-1} \quad (7.25)$$

Such distribution is known in nuclear physics as the "giant resonance" model (Lane 1969) and was recently discussed in connection with molecular problems (Voltz, 1974).

In this case, the initial time evolution (7.24) for  $t < \rho_j$  (where  $\rho_j$  is the average density of the  $|j\rangle$  states) assumes the form

$$I_0(t) \propto \left| \frac{\exp(iE_0 t - \frac{1}{2} \Gamma_d t) - \exp(i\bar{k}t - \frac{1}{2} \gamma_p t)}{(E_0 - \bar{k}) + \frac{1}{2} i(\gamma_p - \Gamma_d)} \right|^2 \quad (7.26)$$

Consider now another time domain where  $t \sim \Gamma_j^{-1} \gg \gamma_p^{-1}$ . The photon counting rate (7.22) consists of two contributions, a direct decay term and an interference

term. Regarding the interesting interference terms, two limiting situations will be now considered:

7.1.1. *Energy-weighted excitation of a coarse distribution.* When the spacings between the  $|j\rangle$  levels considerably exceed their widths, i.e.,

$$\Gamma_j, \Gamma_j \ll |E_j - E_j| \quad (7.27)$$

the oscillatory terms will exhibit fast oscillations on the relevant time scale  $\sim \Gamma_j^{-1}$ , and the second term on the r.h.s of Eq. (7.22) vanishes. The decay rate is

$$I(t) = \frac{1}{3} \gamma_p^2 \Gamma_N^2 \sum_j \frac{|A_j|^2 \exp(-\Gamma_j t)}{(E_j - \bar{k})^2 + \frac{1}{4} \gamma_p^2} \quad (7.28)$$

being determined by a sum of exponentials.

7.1.2. *Energy-weighted excitation of a moderately dense distribution.* Now there is a large number of cross-terms in Eq. (7.22). The independently decaying levels are, of course, not equally spaced in real life (in contrast to simple models (Bixon and Jortner, 1968)), whereupon destructive interference effects between randomly spaced levels will result in the vanishing of the interference terms on the time scale  $t > (E_j - E_j)^{-1}$ . Thus on the time scale  $\rho_j < t \sim \Gamma_j^{-1}$  the dense level structure will exhibit again the decay mode given by Eq. (7.28).

From the point of view of the experimentalist, the decay mode (7.28) following energy-weighted excitation can be observed provided that the following set of relations is realized  $\Gamma_d^{-1} < \gamma_p^{-1} \sim \Gamma_j^{-1} > \rho_j$ , which imply that the following conditions pertaining the molecular level scheme have to be satisfied:

$$\Gamma_j < \rho_j^{-1} \quad (7.29)$$

$$\Gamma_j < \Gamma_d \quad (7.30)$$

Concerning the pulse width we require that  $\gamma_p < \Gamma_d$  together with Eq. (7.21). These two molecular conditions (7.29) and (7.30) are definitely satisfied for the case of inter-state coupling in small molecules (Douglas, 1966; Bixon and Jortner, 1969; Freed and Jortner, 1969; Jortner and Mukamel, 1974). They may also be realized (under proper excitation conditions) for the intermediate case, that of a small energy gap in a large molecule (Freed and Jortner, 1969; Nitzan et al., 1971; Jortner and Mukamel, 1974). From the foregoing discussion we note that no direct information can be deduced from these energy-filtered experiments concerning time-resolved decay in the statistical limit (Jortner and Berry, 1968; Robinson, 1967; Freed and Jortner, 1969; Jortner and Mukamel, 1974, 1975) where a dense manifold of background (bound)  $\{|I\rangle\}$  (zero-order) states acts as an effective dissipative quasi-continuum. This is not surprising, as we recall from the treatment of Sec. 4 that as long as  $\gamma_p$  is smaller than the width of a single resonance, no time-resolved information

can be obtained concerning the molecular parameters which govern the decay of the resonance.

We now proceed to consider the time evolution following a second type of excitation mode.

**7.2. The case of a coherent excitation.** To handle the excitation by a "white" light pulse, we require that

$$\Gamma_p \gg \Gamma_j \quad (7.31)$$

and

$$\gamma_p \gg |E_j - \bar{k}| \quad (7.32)$$

Thus the pulse widths exceed the energy spread of the excited level distribution, that is

$$\gamma_p \gg \Gamma_d \quad (7.33)$$

The photon counting rate now assumes the simple form

$$I(t) = \frac{4\gamma_N^2 \Gamma_N}{3\gamma_p^2} \sum_{jj'} A^j A_j^{*} \exp \left[ -\frac{\Gamma_j + \Gamma_{j'}}{2} t + i(E_{j'} - E_j) t \right] \quad (7.34)$$

We can now obtain significant molecular information for certain level structures in the short-time domain  $\gamma_p^{-1} \lesssim t \ll \Gamma_j^{-1}$ , whereupon Eq. (7.34) assumes the form

$$I_0(t) \propto \left| \sum_j A_j \exp(-iE_j t) \right|^2 \quad (7.35)$$

The instant time evolution following coherent excitation is simply determined by the energy-spread  $\Gamma_d$ . For a Lorentzian distribution of the coefficients  $A_j$  (7.25), we get the familiar decay mode

$$I_0(t) \propto \exp(-\Gamma_d t) \quad (7.36)$$

This decay mode will be exhibited on the time-scale

$$t < \rho_j^{-1} \quad (7.37)$$

which is the Bixon-Jortner recurrence relation (1968).

This result is applicable, in principle, to any level structure, subject to the conditions that the excitation mode satisfies relations (7.31), (7.32) and that Eq. (7.37) is obeyed. The coherent excitation conditions cannot be accomplished in real life for the small molecule, but can be realized for the statistical limit and possibly for some intermediate cases. From the physical point of view, Eq. (7.36) implies that the oscillatory terms in the photon counting rate in a large molecule result in a shortening of the

radiative decay time. The reciprocal lifetime on this short timescale is roughly given by the average  $\Gamma_d = (2\pi \langle V_{si}^2 \rho_i \rangle)$  for a single doorway state  $|s\rangle$  coupled to a  $\{|l\rangle\}$  manifold (Bixon and Jortner, 1968).

In the statistical limit,  $\Gamma_d$  is the only observable decay time. This leads to the well-known results concerning exponential (to a good approximation) decay mode. "shortening" of the experimental decay time (i.e.,  $\Gamma_d > \Gamma_s'$ ) compared to that estimated from the Einstein relations for the integrated oscillator strength, decrease of the emission quantum yield below unity, and insensitivity of the decay time  $\Gamma_d^{-1}$  to external perturbations by an inert medium. To answer the question under what conditions no other decay modes exist except the  $\Gamma_d^{-1}$  exhibited in the decay pattern of a polyatomic molecule, we have to bear in mind that the widths  $\Gamma_j$  incorporate all sequential-decay processes of the states of the  $\{|l\rangle\}$  intermediate manifold. Such sequential-decay phenomena may involve infrared decay, optical decay in the case of internal conversion from highly excited levels, and collisional perturbation. A complete theory of sequential decay (Nitzan and Jortner, 1973; Jortner and Mukamel, 1974; Mukamel and Jortner, 1974*a, b*) was developed and we shall not dwell on it here. For the sake of the present discussion it is sufficient to note that the magnitude of the widths  $\Gamma_j$  of the independently decaying levels (relative to  $\Gamma_d$  and to  $\rho_j^{-1}$ ) will determine the long-time behavior of the decay pattern. On the time scale exceeding the recurrence time,  $t > \rho_j$ , the interference terms in Eq. (7.34) vanish, resulting in

$$I(t) \propto \sum_j |A_j|^2 \exp(-\Gamma_j t). \quad (7.38)$$

Usually (Nitzan, Rentzepis and Jortner, 1972; Jortner and Mukamel, 1974)  $\Gamma_j \ll \Gamma_s'$  and a dilution effect of the lifetimes will be exhibited in the intermediate (or large) molecule on the time scale  $\tau_p^{-1} < \Gamma_d^{-1} \ll t \sim \Gamma_j^{-1}$ , provided that this decay mode is amenable to experimental observation. Thus the conditions for observing the asymptotic behavior (7.38) are again given by Eqs. (7.29) and (7.30), being identical for the case of coherent excitation to that of energy-weighted excitation.

We have already argued that coherent excitation conditions prevail only for the statistical limit and for the intermediate case, so that we do not have to discuss interstate coupling in small molecules in the present context. In the statistical limit  $\rho_j$  is expected to be overwhelmingly large, whereupon any contribution to  $\Gamma_j$  from sequential-decay processes will result in the condition

$$\Gamma_j > \rho_j^{-1} \quad (7.39)$$

violating condition (7.29). Thus relation (7.39) provides the basic condition for the applicability of the statistical limit, when the background dense levels are sufficiently broadened, relative to their spacing, to provide an intramolecular dissipative channel.

We finally turn to the interesting case of intermediate level structure in large molecules where "coarse graining" procedures regarding the background  $\{|l\rangle\}$  levels are not applicable. In this case one can observe two decay components, the short decay  $\exp(-\Gamma_d t)$  on the time scale  $t < \rho_j^{-1}, \Gamma_j^{-1}$  and the long component which is a sum of exponentials on the time scale  $t \gtrsim \rho_j^{-1}, \Gamma_j^{-1}$  provided that  $\Gamma_j < \rho_j^{-1}$  and  $\Gamma_j < \Gamma_d$ . Such state of affairs can be realized for a large molecule characterized by a small energy gap, whereupon  $\rho_j \sim 10^3 \text{ cm}$ , while  $\Gamma_j \ll 10^{-3} \text{ cm}^{-1}$ , i.e., the background states correspond to a triplet manifold, or to a singlet state whose transitions to lower-lying levels are symmetry forbidden. For the sake of general methodology, it is important to emphasize that the observation of two decay components cannot be described in terms of a reversible kinetic scheme as proposed by Lahmani et al. (1974), where the initially excited state  $|s\rangle$  decays to the  $\{|l\rangle\}$  manifold, which subsequently undergoes a reversible process back to  $|s\rangle$ . It is well known that the Pauli master equation, which provides the ideological basis for kinetic schemes, breaks down when interference effects are exhibited, as in the situation for the intermediate level structure, whereupon conventional kinetic picture is inapplicable.

## 8. ENERGY-RESOLVED EXPERIMENTAL OBSERVABLES

We now proceed to discuss "long time" (energy resolved), experiments where no restrictions are imposed on the energy resolution of the photon field. Scattering theory provides a powerful tool for the understanding of the interaction of molecules with the radiation field which is responsible for the absorption line shape and for photon scattering processes (elastic, inelastic and reactive). Energy-resolved experimental observables 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 (the transition operator) defined by

$$T = V' + V'G(E)V \quad (8.1)$$

(Goldberger and Watson, 1964; Shore, 1967).

The definition of  $V$  and  $V'$  depends on the boundary conditions for the scattering process. In our case, where a photon is being scattered from a molecule initially in the ground state  $|g\rangle$  and where  $|g\rangle$  is an eigenstate of  $H_{m0}$  and of  $H_m$  (see Sec. 2), we can take (Mukamel and Jortner, 1974b; Mukamel, 1975)

$$V = V' = H_{int} + H_v \quad (8.1a)$$

Let us first consider nonreactive photon scattering. At the distant past, the molecule is in the continuum state  $|a\rangle \equiv |g0, \mathbf{k}\rangle$  characterized by the energy  $E_a$ . The final (continuum) states resulting from photon scattering will be denoted by  $|b\rangle =$

$|gv, \mathbf{k}_f\rangle$  characterized by the energy  $E_b$ . (Here  $r$  denotes a collection of nuclear quantum numbers).

The cross section  $\sigma(a \rightarrow b)$  for the transition  $a \rightarrow b$  to a group of final states in the energy interval  $dE_b$  is obtained by dividing the transition probability by the photon flux  $F = c/L^3$ , where  $c$  is the velocity of light and  $L^3$  represents the volume, and we use box normalization for the radiation field. Thus we have

$$\sigma(a \rightarrow b) = \frac{2\pi L^3}{\hbar c} |T_{ba}|^2 \delta(E_a - E_b) \quad (8.2)$$

The rate of disappearance  $W_a$  of the initial state  $a$  is given by

$$W_a = -\frac{2}{\hbar} I_m(T_{aa}) \quad (8.3)$$

while the absorption cross section  $\sigma_a$  (at zero temperature) is obtained again by dividing through by the flux:

$$\sigma_a = -\frac{2L^3}{\hbar c} I_m(T_{aa}) \quad (8.4)$$

We can immediately apply these results by setting for the initial energy  $E_i = E(|g0, \mathbf{k}\rangle) = E_{g0} + E$ , where  $E_{g0}$  is the energy of the ground-state vibrationless level and  $E = \hbar c k$  is the incident-photon energy, the absorption cross section is then obtained from Eq. (8.4) in the form

$$\sigma_a(E) = -\frac{2L^3}{\hbar c} I_m \langle g0, \mathbf{k} | V G(E) V | g0, \mathbf{k} \rangle \quad (8.5)$$

Consider now the cross section for the photon scattering process  $|g0, \mathbf{k}\rangle \rightarrow |gv, \mathbf{k}_f\rangle$ , which takes place between the initial state  $|g0, \mathbf{k}\rangle$  characterized by the energy  $E_{g0} + \hbar c k$  and the final states  $|gv, \mathbf{k}_f\rangle$  characterized by the energy  $E_{gr} + \hbar c k_f$ :

$$\sigma(g0, \mathbf{k} \rightarrow gv, \mathbf{k}_f) = \frac{2\pi L^3}{\hbar c} |\langle gv, \mathbf{k}_f | V G(E) V | g0, \mathbf{k} \rangle|^2 \rho_r(k_f) \quad (8.6)$$

where

$$\rho_r(k_f) = \frac{L^3 k_f^2}{(2\pi)^3 \hbar c} \quad (8.6a)$$

Our final expression for the photon scattering cross section  $\sigma_r^v(E)$  into the molecular state  $|gv\rangle$  may be recast in the form

$$\sigma_r^v(E) = \left\langle \sum_{\mathbf{e}_f} \int d\Omega_f \sigma(g0, \mathbf{k} \rightarrow gv, \mathbf{k}_f) \right\rangle \quad (8.7)$$

Eq. (8.7) includes integration of (8.6) over the final spatial photon directions ( $\int d\Omega_f$ ), summation over the final photon polarization directions ( $\sum_{e_f}$ ) and averaging over the initial molecular orientations with respect to the photon polarization ( $\langle \dots \rangle$ ). The total cross section for resonance fluorescence is obtained by monitoring all the emitted photons resulting from scattering into all the final molecular states  $|gv\rangle$ .

$$\sigma_r(E) = \sum_r \sigma_r^r(E) \quad (8.8)$$

In a similar manner we can define a cross section  $\sigma_{nr}^\alpha(E)$  for effective scattering into the quasicontinuum  $\{|xl, \text{vac}\rangle\}$ , which we consider to be an operational continuum. (Here  $\alpha$  denotes the collection of quantum numbers defining the nonradiative channel, whereas  $l$  is a continuous intrachannel quantum number.) Thus.

$$\sigma_{nr}^\alpha(E) = \frac{2\pi L^3}{hc} |\langle xl, \text{vac} | T(E) | g0, \mathbf{k} \rangle|^2 \rho_l^\alpha(E) \quad (8.9)$$

The unitarity relations for the scattering matrix result in the optical theorem of scattering theory (Goldberger and Watson, 1964);

$$-\frac{1}{\pi} I_m T_{aa} = \sum_{\text{all } b} |T_{ba}|^2 \delta(E_a - E_b) \quad (8.10)$$

which leads to the conservation law

$$\sigma_a(E) = \sum_r \sigma_r^v(E) + \sum_x \sigma_{nr}^\alpha(E) \quad (8.11)$$

The (energy-dependent) quantum yield for 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 (8.7) and the absorption cross section (8.8),  $Y_r^v(E) = \sigma_r^v(E)/\sigma_a(E)$ . If the ground-state energy levels are well-spaced, the different channels can be resolved. Finally, the total quantum yield for photon emission is given by  $Y_r(E) = \sum_r Y_r^v(E) = \sigma_r(E)/\sigma_a(E)$ . In a similar way, the quantum yield for electronic relaxation in a statistical molecule (or for predissociation) is  $Y_{nr}(E) = \sum_x Y_{nr}^\alpha(E)$ , where  $Y_{nr}^\alpha(E) = \sigma_{nr}^\alpha(E)/\sigma_a(E)$ .

Eq. (8.11) now implies that  $Y_r(E) + Y_{nr}(E) = 1$ . 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 quasicontinua  $\{|xl\rangle\}$  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  $Y_r(E)$  is equal to unity as intramolecular decay channels have to be considered.

We have recently established the relation between the theoretical treatment of in time evolution of the molecular system resulting from wave packet excitation in "short time" excitation experiments and the study of photon scattering cross sections involved in "long time" excitation conditions (Jortner and Mukamel, 1974). This was accomplished by pursuing the general relations between the transition  $T$  matrix and the (photon) scattering matrix  $S$ . This formalism leads to general useful results for the quantum yields expressed in terms of the pulse amplitudes  $A_k \equiv A(E)$  and the relevant cross sections

$$Y_r^v = \frac{\int dE |A(E)|^2 \sigma_r^v(E)}{\int dE |A(E)|^2 \sigma_a(E)} \quad (8.12)$$

$$Y_{nr}^z = \frac{\int dE |A(E)|^2 \sigma_{nr}^z(E)}{\int dE |A(E)|^2 \sigma_a(E)} \quad (8.13)$$

These results are valid for all excitation conditions. We note that, in general, the quantum yields are determined by the power spectrum of the source (i.e.,  $|A(E)|^2$ ), and the only relevant information required concerning the excitation source involves its energetic spread and not the phases of the radiation field. In the "long time" excitation limit  $|A(E)|^2$  is sharply peaked around  $\bar{E}$  and the quantum yields are given in terms of the ratios of the cross sections at this particular energy. In the extreme case of short excitation conditions  $|A(E)|^2$  is a slowly varying function of the energy and the quantum yields reduce to the ratio of the integrals over the cross sections. In these two limits the quantum yields are solely determined by the molecular parameters and not by the characteristics of the source. In general, the quantum yields are different under different excitation conditions. Only when both cross sections  $\sigma_r^v(E)$  and  $\sigma_a(E)$  exhibit the same energy dependence will  $Y_r^v$  be independent of the pulse characteristics under all excitation conditions. This situation is encountered only in the special, but useful, case of a single molecular resonance, when both cross sections exhibit a Lorentzian energy dependence.

Finally, let us consider the general relation between the photon counting rate and the optical lineshape. Making use of the definition for the lineshape, Eq. (8.8), and bearing in mind that the basic definition of the doorway state, Eq. (5.1), implies that  $|N, \text{vac}\rangle = \gamma_N^{-1} H_{\text{int}} |g, \mathbf{k}\rangle$ , we get

$$\sigma_a(E) = -\frac{2L^3}{3\hbar c} |\gamma_N|^2 I_m G_{NN}(E) \quad (8.14)$$



Making use of the dispersion relation (Goldberger and Watson, 1964)

$$G_{NN}(E) = -\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{I_m G_{NN}(E')}{E' - E - i\eta} dE' \quad (8.15)$$

implies that the photon counting rate is given by

$$I(t) = \frac{3\Gamma_N^r}{|\gamma_N|^2} \left( \frac{\hbar c}{2\pi L^3} \right)^2 \left| \int_{-\infty}^t \varphi(\tau) d\tau \int_{-\infty}^x dE' \sigma_a(E') \exp[-iE'(t - \tau)] \right|^2 \quad (8.16)$$

This result constitutes a generalization of the well-known theorem that under coherent excitation conditions the decay mode is given in terms of the Fourier transform of the lineshape function. Eq. (8.16) is valid for general optical excitation conditions and for any level structure in the excited state of a polyatomic molecule.

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