Time Evolution of Excited Molecular States

SHAUL MUKAMEL †

JOSHUA JORTNER

Department of Chemistry
Tel Aviv University
Tel Aviv, Israel

† *Present address* Department of Chemistry, University of California, Berkeley, California 94720.

I. Prologue

The level structure of electronically excited states of a polyatomic molecule is generally very complex and may include discrete molecular states, intramolecular dissipative quasicontinua (Bixon and Jortner, 1968; Robinson, 1967), and dissociative continua (Herzberg, 1966). The complete understanding of intramolecular excited state dynamics in large molecules requires the elucidation of the time dependence of the molecular system interacting with the electromagnetic field. Early treatments of time-resolved experiments studied the nature of an "initially prepared" state in large molecules, considering only the role of the intramolecular, nonradiative decay channel (Bixon and Jortner, 1968; Jortner and Berry, 1968; Rhodes, 1969; Chock *et al.*, 1969), while subsequent studies have considered the time evolution of the molecular system after the termination of the exciting pulse (Freed, 1970; Rhodes, 1971, 1974). On the other hand, energy-resolved experimental observables such as optical lineshapes and cross sections for photon scattering and for intramolecular decay were treated by studying photon scattering by a molecule within the framework of the Lippman–Schwinger formalism (Goldberger and Watson, 1964; Shore, 1967; Nitzan and Jortner, 1972). One can handle both "time-resolved" and "energy-resolved" experiments by considering the time evolution of a molecular system interacting with a photon wave packet (Kroll, 1964; Cohen Tannoudji, 1968; Jortner and Mukamel, 1974). The fundamental problems encountered in the field of intramolecular dynamics in electronically excited states of large molecules, commonly referred to as intramolecular radiationless processes (Henry and Kasha, 1968; Jortner *et al.*, 1969; Schlag *et al.*, 1971; Freed, 1972; Robinson, 1973; Jortner and Mukamel, 1974), are intimately related to the general areas of resonance Raman spectroscopy (Huber, 1969; Omont *et al.*, 1972; Shen, 1974) and to the nature of the "transition" from resonance fluorescence to near-resonance Raman scattering from molecules (Friedman and Hochstrasser, 1974; Williams *et al.*, 1974; Mukamel and Jortner, 1975; Mukamel *et al.*, 1975; Berg *et al.*, 1974; Metiu *et al.*, 1975; Hilborn, 1975).

The general theoretical techniques for handling time-resolved and energy-resolved experimental observables in all those areas are identical, and only the specific questions sometimes differ. In the field of resonance Raman spectroscopy and light scattering from molecules one is interested intrinsically in the time and energy-resolved profiles of the scattered radiation. In the study of radiationless transitions one would like to entangle the time- and energy-resolved photon scattering data to obtain pertinent infor-

mation regarding the various intramolecular decay channels in a large molecule. A complete theoretical treatment of these interesting problems is desirable. We have considered the problem of time- and energy-resolved photon scattering from large molecules (Jortner and Mukamel, 1974). Friedman and Hochstrasser (1974) have utilized scattering theory to derive an expression for time-dependent scattering of a Lorentzian photon wave packet from a molecular level, which is in agreement with one of our special results (Mukamel and Jortner, 1975). Berg et al. (1974), Metiu et al. (1975), and the present authors (Mukamel et al., 1975) have advanced a general treatment of time-resolved photon scattering from a single molecular resonance. In the present review we advance a theoretical framework for the treatment of the optical excitation of a general molecular system, which is characterized by an arbitrarily complex molecular level structure. A uniform formalism bridging time-resolved and energy-resolved experimental observables will be advanced by considering the time evolution of a molecular system interacting with a photon wave packet. General excitation conditions by weak optical sources are amenable to a detailed study by this formalism. Application of the theory will be presented subsequently to handle photon scattering from several physical models for molecular level structure in excited electronic states of polyatomic molecules.

II. Quantum Mechanical Treatment of a Light Pulse

A classical description of the electromagnetic field and of light pulses has often been adopted in connection with laser theory (Haken, 1970) and linear response phenomena (Ben-Reuven, 1975). We shall utilize a quantum mechanical approach (Kroll, 1964; Cohen Tannoudji, 1968) in which spontaneous emission is inherently incorporated without any semiempirical assumptions.

Consider a large optical cavity with the field modes $\mathbf{k}$; k denotes the photon wave vector, while for the sake of brevity we shall suppress the photon polarization vector $\mathbf{e}$. We have a complete set of field states $\{|n_k\rangle\} = \Pi_i |n_i\rangle$, which are characterized by n_i photons in the ith mode. A general state of the electromagnetic field may be represented as a linear superposition of these $\{|n_k\rangle\}$ states. Weak fields are characterized by a small number of photons in each mode and can be represented as a wave packet of one-photon states (Kroll, 1964; Cohen Tannoudji, 1968)

$$\psi = \int d^3k A_k |\mathbf{k}\rangle \tag{1}$$

where $_i\mathbf{k}$ denotes a state of the field having one photon $\mathbf{k}$ and zero photons in all other modes. $A_{\mathbf{k}}$ are the wave-packet amplitudes and $k = |\mathbf{k}|$. The wave packet (1) satisfies the normalization condition

$$\int d^3k\,|A_{\mathbf{k}}|^2 = 1 \tag{1a}$$

(throughout this paper we shall use the units $h = c = 1$). It should be emphasized that although Eq. (1) is directly applicable for weak fields it may be used for an adequate description of any linear response phenomena even for strong fields

Let us now digress on the properties of the photon wave packet (1). The one-photon states $_i\mathbf{k}$ are normalized as

$$\langle\mathbf{k}|\mathbf{k}'\rangle = \delta(\mathbf{k} - \mathbf{k}') \tag{2}$$

We define the vectors $\mathbf{Q}$ and $\mathbf{K}$ as follows

$$\mathbf{Q} = \begin{pmatrix} t \\ x \\ y \\ z \end{pmatrix} \qquad \mathbf{K} = \begin{pmatrix} k \\ k_x \\ k_y \\ k_z \end{pmatrix} \tag{3}$$

$\mathbf{Q}$ represents a general space-time point, whereas $\mathbf{K}$ consists of the photon energy k and momentum $\mathbf{k} = (k_x, k_y, k_z)$. The scalar product $\mathbf{K} \cdot \mathbf{Q}$ is

$$\mathbf{K} \cdot \mathbf{Q} = kt + \mathbf{k} \cdot \mathbf{q} \tag{4}$$

where $\mathbf{q} = (x, y, z)$ is the position vector. The photon density I per unit volume at the space point $\mathbf{q}$ and at $t = 0$ is given by

$$I(\mathbf{q}) = \langle\psi|\hat{N}(\mathbf{q})|\psi\rangle \tag{5}$$

where $\hat{N}(q)$ is the photon density operator (Schweber, 1961; Glauber, 1969)

$$\hat{N}(\mathbf{q}) = \phi^+(\mathbf{q})\phi(\mathbf{q}) \tag{6}$$

and

$$\phi(\mathbf{q}) = (2\pi)^{-3/2} \sum_{\bullet} \int d^3k \, \exp(-i\mathbf{k} \cdot \mathbf{q})a_{\mathbf{k}} \tag{7}$$

corresponds to the Fourier transform of the photon annihilation operator $a_{\mathbf{k}}$. For the free electromagnetic field we have

$$\psi(t) = \sum_{\bullet} \int d^3k \, \exp(-ikt)A_{\mathbf{k}}|\mathbf{k}\rangle \tag{8}$$

and the photon density at a general space-time point $\mathbf{Q}$ is given by

$$I(\mathbf{Q}) = \langle\psi(t)|\hat{N}(\mathbf{q})|\psi(t)\rangle \tag{9}$$

Provided that the energy spread Δk of the photon wave packet is much smaller than its mean energy $\bar{k}$, the energy density $W(\mathbf{Q})$ of the field is proportional to $I(\mathbf{Q})$, and is given by

$$W(\mathbf{Q}) = \bar{k}I(\mathbf{Q}) \tag{10}$$

Thus, apart from a normalization constant, the field energy density is given by Eq. (9). Substitution of Eq. (8) in (9) results in

$$I(\mathbf{Q}) = (2\pi)^{-3} \sum_{\bullet} \sum_{\bullet} \iint d^3k \, d^3k'$$

$$\times \exp[-i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{q}] A_{\mathbf{k}} A_{\mathbf{k}'}^* \exp[i(k - k')t] \tag{11}$$

Defining the Fourier transform of the photon wave-packet amplitudes

$$\varphi(\mathbf{Q}) = \sum_{\bullet} \int d^3k \, \exp(-i\mathbf{K} \cdot \mathbf{Q}) A_{\mathbf{k}} \tag{12}$$

and

$$\sum_{\bullet} A_{\mathbf{k}} = (2\pi)^{-3} \int d^3q \, \varphi(0, \mathbf{q}) \exp(i\mathbf{k} \cdot \mathbf{q}) \tag{13}$$

we finally obtain a transparent result for the energy density

$$I(\mathbf{Q}) = (2\pi)^{-3} |\varphi(\mathbf{Q})|^2 \tag{14}$$

The normalization of $I(\mathbf{Q})$ follows from Eq. (1a),

$$\int d^3q \, I(\mathbf{Q}) = (2\pi)^{-3} \int d^3q \, |\varphi(\mathbf{Q})|^2$$

$$= \sum_{\bullet} \int d^3k \, |A_{\mathbf{k}}|^2 = 1 \tag{15}$$

which implies a straightforward conservation law for the number of photons in the free field.

Consider now a special case of a light pulse traveling along the x axis. Equations (1), (12), and (13) are reduced to

$$\psi = \int dk \, A_k |k\rangle \tag{16}$$

$$\varphi(t) = \int dk \, A_k \exp(-ikt) \tag{17}$$

$$A_k = (2\pi)^{-1} \int dt \, \varphi(t) \exp(ikt) \tag{18}$$

In this case q is actually a scalar $q = x + t$. The photon density at q is given by

$$I(x + t) = (2\pi)^{-1}|\varphi(x + t)|^2 \tag{19}$$

Thus $|\varphi|^2$ provides us with the spatial and time profile of the pulse.

We have thus presented an adequate way to describe a minimal wave packet satisfying the uncertainty relation $\Delta E \Delta t \sim 1$. A more general treatment of weak fields can be carried out by treating the light pulse in terms of a density matrix of one-photon states

$$\rho(0) = \int\int |k\rangle \rho_{kk'} \langle k'| \, dk \, dk' \tag{20}$$

and the pulse intensity is now

$$I(Q) = \mathrm{Tr}[\rho(t) \cdot \hat{N}(\mathbf{q})] \tag{21}$$

Our minimal wave packet (16) is characterized by the off-diagonal elements $\rho_{kk'} = A_k A_{k'}^*$, however, in real life the light pulse is not necessarily minimal and $\rho_{kk'}$ may be represented in terms of any function. Since for a given light source we usually do not know the exact state or density matrix of the field we shall proceed using Eqs. (16) and (19), and bearing in mind that whenever we have a product of the form $\varphi(\tau)^*\varphi(\tau')$ it should be replaced by the appropriate correlation function (Glauber, 1969; Loudon, 1973) $\langle \varphi^*(\tau)\varphi(\tau')\rangle$.

III. General Theory of Photon Counting

The total Hamiltonian for a molecule interacting with the radiation field is given by

$$H = H_0 + V \tag{22}$$

where

$$H_0 = H_m^0 + H_v + H_r \tag{22a}$$

and

$$V = H_{\mathrm{int}} \tag{22b}$$

Here H_m^0 is some zeroth-order molecular Hamiltonian and H_v is an intramolecular coupling term. The exact molecular Hamiltonian is $H_m = H_m^0 + H_v$. H_r is the Hamiltonian for the free radiation field and H_{int} is the radiation–matter interaction term. The eigenstates of H_r were introduced

in Section II, and we shall consider throughout this review only the one-photon $|k\rangle$ and the vacuum $|vac\rangle$ states. The molecular level scheme (i.e., the spectrum of H_m^0) is taken to consist of several electronic states: $|g\rangle$ (the ground state) and $|s\rangle$, $|r\rangle$ (excited electronic states), etc. Each of these states contains a manifold of vibrational-rotational states. Denoting the collection of nuclear quantum numbers by v, we have for the spectrum of H_0: $|gv, vac\rangle$, $|gv, k\rangle$, $|sv, vac\rangle$, $|sv, k\rangle$, etc. Since usually the energy gap between $|g\rangle$ and $|s\rangle$ is sufficiently large so that off-resonant interactions do not contribute appreciably to the time evolution, we shall consider only one-photon states of the $|gv, k\rangle$ type and vacuum excited electronic states $|sv, vac\rangle$, $|rv, vac\rangle$, etc., and neglect the contribution of states such as $|gv, vac\rangle$ or $|sv, k\rangle$. This approach is equivalent to the rotating wave approximation (Louisell, 1964). The basic 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.

We can now proceed to treat the photon counting problem. Consider a small target of isolated molecules in the gas phase at low pressure located at the origin of a Cartesian coordinate system. A photon wave packet [Eq. (16)] traveling along the x axis is being scattered from the target, and we are monitoring the photon scattering rate using a point photodetector which is located at a spatial point A, characterized by the polar coordinates (R, Θ, Φ). The photodetector measures all photons having the propagation direction (Θ, P). Choosing as our detector an ideal photomultiplier tube characterized by an infinite time resolution (and no energy resolution), the photoelectric current (i.e., the photon counting rate) is generally given by (Louisell, 1964)

$$I(Q) = \alpha\langle\psi(t)|\hat{N}(\Omega, R)|\psi(t)\rangle \qquad (23)$$

where α is determined by the efficiency of the detector and by the geometry of our system, and $\hat{N}(\Omega, R)$ is the photon density operator at point A. Utilizing Eqs. (6) and (7) we have for the photon density operator

$$\hat{N}(\Omega, R) = (2\pi)^{-3} \sum \iint dk\, dk' k^2 k'^2$$
$$\times \exp[-i(k - k')R]a_k^+ a_k \qquad (24)$$

We now proceed to derive a general expression for the wave function of the system $\psi(t)$, at time t, using the Green's function method (Goldberger and Watson, 1964). For the sake of simplicity we consider first a system
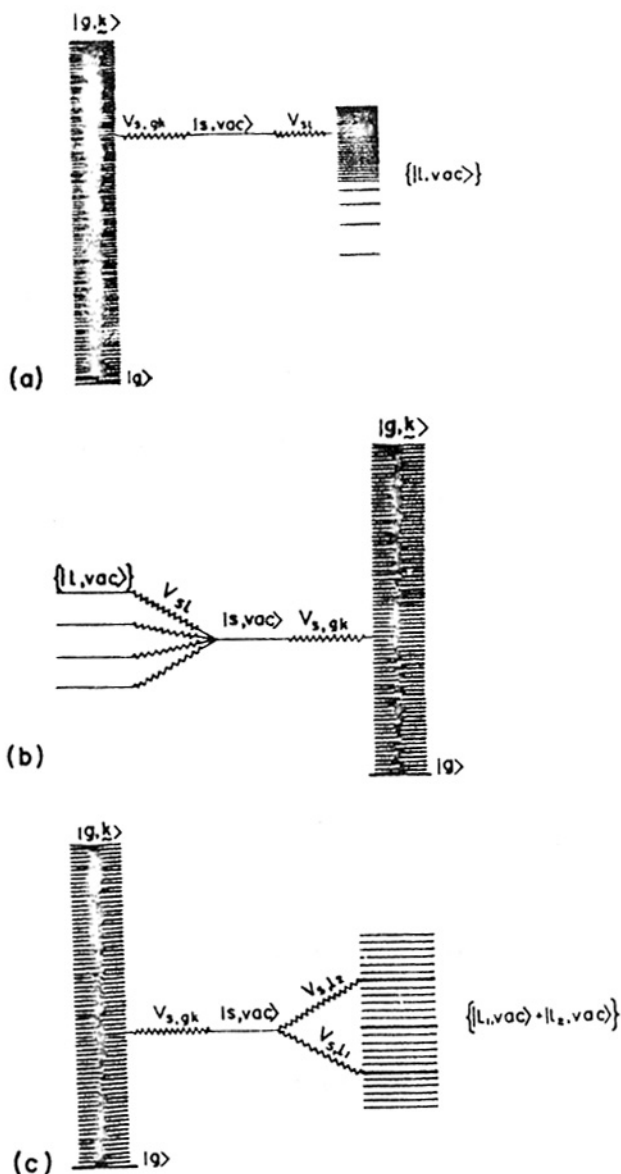
Fig. 1. Basic level schemes for radiative and interstate coupling in polyatomic molecules. (a) A statistical large molecule. (b) a small molecule, and (c) intermediate level structure in a large molecule.

characterized by a single ground state $|g\rangle$. Let

$$\psi_0(0) = \int dk A_k |g, k\rangle \tag{25}$$

be the wave function of a hypothetical system at $t = 0$ in the absence of H_{int}. In the Appendix it is shown that

$$\psi(t) = \psi_0(t) + (2\pi i)^{-1} \int dE \exp(-iEt)$$

$$\times G(E)H_{int}(G_0(E) - G_0^+(E))\psi_0(0) \tag{26}$$

where $G(E)$ is the Green's operator

$$G(E) = (E - H + i\eta)^{-1}; \qquad \eta \to 0^+ \tag{26a}$$

and

$$G_0(E) = (E - H_0 + i\eta)^{-1}; \qquad \eta \to 0^+ \tag{26b}$$

Using Eqs. (25) and (26) we get

$$\psi(t) = \psi_0(t) - \int dE \exp(-iEt)G(E)H_{int}A(E)|g, E\rangle \tag{27}$$

where $A(E) \equiv A_k$, $|g, E\rangle \equiv |g, k\rangle$ and k is a photon belonging to the exciting pulse, which is characterized by the energy E. The experimentalist engaged in photon counting experiments takes great pains to eliminate the "stray light" which involves the photons corresponding to the exciting light pulse. The experimentally relevant photon counting rate, excluding those photons, $|k\rangle \equiv |E\rangle$, of the original exciting pulse may be obtained from Eqs. (23) and (27) excluding the contribution of ψ_0 to Eq. (27). This is apparent since ψ_0 pertains only to those photons which have the same propagation (and polarization) directions of the original exciting pulse, and which are not monitored in the actual photon counting experiment. Equations (23) and (27) result in

$$I(R, \Theta, \Phi, t) = \frac{\alpha}{(2\pi)^3} \sum_e \sum_{e'} \int\int dE\, dE' \int\int dk\, dk'$$

$$\times k^2 k'^2 \exp[-i(E - E')t] \exp[i(k - k')R]$$

$$\times A(E)A^*(E')\langle g, E'|H_{int}G^+(E')|g, k'\rangle$$

$$\times \langle g, k|G(E)H_{int}|g, E\rangle \tag{28}$$

which can be rearranged to yield

$$I(R, \Theta, \Phi, t) = \frac{\alpha}{(2\pi)^3} \sum_e |\phi|^2 \tag{29}$$

where

$$\phi = \iint dE \, dk k^2 A(E) \langle g, k | G(E) H_{int} | g, E \rangle$$

$$\times \exp(-iEt) \exp(iER) \tag{30}$$

It should be borne in mind that the $|E\rangle$ photons are all traveling along the x axis, whereas the k' photons are traveling in the direction $\Omega = (\Theta, \Phi)$.

We now introduce an additional assumption regarding molecular rotation. Since we are not interested at present in the angular distribution of the emitted photons, we shall treat the rotations semiclassically, assuming first that the molecular direction is fixed in space so that its transition dipole is oriented along the z axis. The final expression for the photon counting rate will be obtained subsequently by properly averaging Eq. (29) over the exciting photon propagation and polarization directions and integrating over all the propagation directions of the photons. The final expression for the photon counting rate is

$$I(t) = \alpha \iint d\Phi d \cos \Theta \langle I(R, \Theta, \Phi, t) \rangle \tag{31}$$

where the $\langle \cdots \rangle$ stands for averaging over molecular orientations. Using Eqs. (29)–(31) we finally get for the spatially averaged photon counting rate

$$I(t) = (\alpha/9\pi^2) |\phi|^2 \tag{32}$$

Equation (32) together with Eq. (31) constitute a formal result for the photon counting rate from a general level structure in the excited manifold, while the molecular system is characterized by a single ground state $|g\rangle$. The latter simplification may be easily relaxed by considering a ground state vibronic manifold $\{|gv\rangle\}$. In analogy with Eq. (30), the general expression for the photon counting rate (at zero temperature) is now given by

$$I(R, \Theta, \Phi, t) = \frac{\alpha}{(2\pi)^3} \sum_v \sum_e |\phi_v|^2 \tag{33}$$

where

$$\phi_v = \iint dE \, dk k^2 A(E) \langle gv, k | G(E) H_{int} | g_0, E \rangle \exp(-iEt) \tag{34}$$

and the spherical averaging finally results in the photon counting rate

$$I(t) = \frac{\alpha}{9\pi^2} \sum_v |\phi_v|^2 \tag{35}$$

Equations (34) and (35) provide us with a formal result for a general molecular level structure, which is valid for weak fields within the framework of the rotating-wave approximation. We now proceed to derive explicit theoretical expressions for level structures of increasing complexity.

IV. The Two-Level System

We shall first consider the application of the general formalism to the simple case of a two-level system, so that the molecular Hamiltonian H_m has just two discrete eigenstates, the ground state $|g\rangle$ and an excited state $|s\rangle$. Although these results are already known, we believe that a systematic derivation is of some interest, particularly in relation to the general problem of an arbitrarily complex level structure which will be considered in Section V.

The photon counting rate can now be obtained from Eqs. (30) and (32). Making use of the Dyson equation we cast the matrix element appearing on the integrand of Eq. (30) in the form

$$\langle g, k | G(E)H_{int} | g, E \rangle = |\gamma|^2 (E - k + i\eta)^{-1} G_{ss}(E) \tag{36}$$

where

$$\gamma = \langle g, \bar{k} | H_{int} | s, \text{vac} \rangle \tag{37}$$

In the derivation of Eq. (37) we made use of the weak k dependence of the electromagnetic interaction in the relevant k domain. This is valid provided $\Delta k \ll \bar{k}$, where Δk is the energy range of the incident and of the emitted photons, and $\bar{k}$ is the mean excitation energy. Substituting Eq. (36) in Eq. (30) and performing the k integration we get

$$\phi = 2\pi i |\gamma|^2 |\bar{k}|^2 \int_{-\infty}^{\infty} dE \exp[-iE(t - R)] G_{ss}(E) A(E) \tag{38}$$

The $(t - R)$ factor in Eq. (38) originates from time delay due to the location of our detector, and hereafter we can set $R = 0$. Equation (38) provides an explicit result for the photon counting rate from a two-level system in terms of an integral of the product of the diagonal matrix element $G_{ss}(E)$ of the Green's function [Eq. (26a)], and the photon wave-packet amplitude. Equation (38) can be alternatively written in the form of a convolution integral in the time domain

$$\phi = 2\pi |\gamma|^2 |\bar{k}|^2 \int_{-\infty}^{t} d\tau C_{ss}(t - \tau) \wp(\tau) \tag{39}$$

where the Fourier transform of the Green's function

$$C_{si}(t) = (2\pi i)^{-1} \int_{-\infty}^{\infty} dE \exp(-iEt)G_{ss}(E) \tag{40}$$

constitutes the molecular decay amplitude for this system.

Equations (38) or (39) together with Eq. (32) constitute our final result. To gain further physical insight we shall now relate the photon counting rate to the probability, $P_s(t)$, for finding the system in the excited $|s\rangle$ state. Utilizing Eq. (27) it can be immediately shown that

$$P_s(t) \equiv |\langle s, \text{vac}|\psi(t)\rangle|^2 = \tfrac{1}{2}(\pi|\gamma\bar{k}^2|)^{-2}|\phi|^2 \tag{41}$$

we have thus demonstrated the well-known proportionality between the photon counting rate and $P_s(t)$.

Our final result for a two-level system can be recast in the form

$$I(t) = \Gamma P_s(t) \tag{42}$$

where

$$\Gamma = 4\alpha/3 |\gamma|^2 |\bar{k}|^4 \tag{43}$$

is proportional to the (spherically averaged) width of the excited state and

$$P_s(t) = \frac{|\gamma|^2}{3} \int_{-\infty}^{t} d\tau \int_{-\infty}^{t} d\tau' C_{ss}(t - \tau)C_{ss}(t - \tau')\langle\varphi(\tau)\varphi^*(\tau')\rangle \tag{44}$$

Here we have explicitly introduced the field correlation function following the discussion of Section II.

V. Doorway States and Photon Scattering from a General Molecular Level Scheme

We now address ourselves to the derivation of explicit theoretical expressions for time-resolved photon scattering from a molecule characterized by an arbitrary (complex) level structure in the excited electronic states. The general molecular level structure consists of a ground state $|g\rangle$ with the various vibronic levels $|gv\rangle$ and, in addition, a variety of electronically excited states including discrete states, intramolecular quasicontinua, and true (dissociative) continua. A convenient way of handling the time evolution of a system characterized by such general level schemes rests on the use of projection operators (Mower, 1966; Feschbach *et al.*, 1967), which enable us to concentrate on the time evolution of a small subpart of the Hilbert space, spanned by those states which exhibit the most significant contribu-

tion to the photon scattering process, and treat the rest of the levels in a less rigorous way. The essential step in applying projection operators is to partition the Hilbert space into two or more subspaces. For the purpose of treating photon scattering experiments we can define a Q subspace spanned by the $|gv, k\rangle$ states (all v and k) and a P subspace containing the rest of the states. In addition, we shall make use of partitioning the P subspace into two parts: $P = P_d + P'$, where P_d contains all the zero-order states directly coupled by H_{int} to the Q space. It should be emphasized that this segregation is by no means unique, and other choices may be adopted when dealing with specific molecular states. The Q space can contain, for example, some intramolecular decay channels not coupled directly with $|g\rangle$. For the sake of our present general discussion, the dissection introduced above is found to be most convenient. Denoting the projection operators for the P_d, P', and Q spaces by $\hat{P}_d$, $\hat{P}'$, and $\hat{Q}$, respectively, we have $\hat{P} + \hat{Q} = 1$, where $\hat{P} = \hat{P}_d + \hat{P}'$, and the coupling V [Eq. (22)], can be written as

$$V = \hat{P}_d H_{int} \hat{Q} + \hat{Q} H_{int} \hat{P}_d \tag{45}$$

The photon counting rate from the molecule is now formally given in terms of Eqs. (34) and (35). We proceed to consider the matrix element appearing in the integrand of Eq. (34). Making use of Eq. (45) this matrix element may be cast in the form:

$$\langle gv, k | G(E) H_{int} | g_0, E \rangle = \langle gv, k | \hat{Q} G(E) \hat{P} H_{int} | g_0, E \rangle \tag{46}$$

We now utilize the formal expression for the projection $\hat{Q} G \hat{P}$ (Mower, 1966)

$$\hat{Q} G \hat{P} = \hat{Q}(E - H_0 - \hat{Q} V \hat{Q})^{-1} \hat{Q} H_{int} \hat{P} G \hat{P} \tag{47}$$

where

$$\hat{P} G \hat{P} = (E - H_0 - \hat{P} R \hat{P})^{-1} \hat{P} \tag{48}$$

and R is the level shift operator:

$$R = V + V \hat{Q}(E - H_0 - \hat{Q} V \hat{Q}) \hat{Q} V \tag{49}$$

Using Eqs. (46) and (47) and bearing in mind that $\hat{Q} V \hat{Q} = 0$, whereupon $(E - H_0 - \hat{Q} V \hat{Q})^{-1} \hat{Q}$ is diagonal in our representation, we get

$\langle gv, k | G(E) H_{int} | g_0, E \rangle$

$$= (E - k - E_{gv} + i\eta)^{-1}$$
$$\times \langle gv, \bar{k} | H_{int} \hat{P}_d G(E) \hat{P}_d H_{int} | g_0, \bar{k} \rangle (e \cdot \hat{z}) \tag{50}$$

where E_{gv} is the energy of the $|gv\rangle$ state.

The matrix element (50) can be visualized as a matrix element of the Green's function between generalized states of the form $\hat{P}_d H_{int} | gv, \bar{k} \rangle$. At

this stage we introduce the basic concept of molecular doorway states. This notion has long been used in nuclear physics for the interpretation of scattering cross sections (Feschbach, 1974; Mahaux, 1973) (i.e., energy resolved experiments) and was recently introduced (Jortner and Mukamel, 1974, 1975) for the study of intramolecular dynamics. A molecular doorway state $|N_v\rangle$ is defined as the superposition of all excited molecular states, $|\xi\rangle$, each weighted by its radiative coupling strength with the vibronic ground state level $|gv\rangle$

$$|N_v, \text{vac}\rangle = \gamma_v^{-1} H_{\text{int}} |gv, \bar{k}\rangle$$

$$= \gamma_v^{-1} \sum_\xi |\xi, \text{vac}\rangle \langle \xi, \text{vac}| H_{\text{int}} |gv, \bar{k}\rangle \tag{51}$$

where

$$\gamma_v^2 = \sum_\xi |\langle gv, \bar{k}| H_{\text{int}} |\xi, \text{vac}\rangle|^2$$

$$= \langle gv, \bar{k}| H_{\text{int}}^2 |gv, \bar{k}\rangle \tag{52}$$

is an appropriate normalization constant that corresponds to the radiative width of the doorway state. As the (discrete and/or continuum) states $\{|\xi\rangle\}$ span the P_d subspace, we note that

$$\hat{P}_d |N_v, \text{vac}\rangle = |N_v, \text{vac}\rangle = \gamma_v^{-1} \hat{P}_d H_{\text{int}} |gv, \bar{k}\rangle \tag{53}$$

We would like to emphasize that Eq. (51) provides a definition of a set of doorway states $\{|N_v\rangle\}$, each corresponding to a certain vibronic level of the ground electronic state. The definition of doorway states presented herein is more general than that previously used (Jortner and Mukamel, 1974, 1975) where only a single doorway state was considered. The present general formalism involving a (discrete) set of $|N_v\rangle$ states is necessary for the description of several cases of physical interest, e.g., inelastic photon scattering from a dissociative continuum (Section XI) and for time-resolved photon scattering from a discrete complex molecular level structure where the origins of two electronic configurations are nearly degenerate and both are radiatively coupled to the ground state. In many cases of physical interest, when a single excited state carries all oscillator strength from the ground state (Bixon and Jortner, 1968) the concept of a single doorway state is sufficient. We have assumed that all the states in the P_d subspace have the same direction of the transition moment to the ground state. This assumption implies that the definition (51) is independent on the direction of $\bar{k}$. The extension of the present formalism to the case of a more general P_d subspace, allowing for variations in the direction of the transition moment, may be carried out. The photon averaging will then be more elaborate and will include interference terms. It should be noted, however, that this assumption

is strictly valid within the framework of the Condon approximation when all excited states belong to the same electronic configuration (Mukamel and Jortner, 1974a, b).

Utilizing the definition (51) and (52) of the doorway state and ignoring the weak k dependence of the electromagnetic coupling matrix elements we can recast Eq. (50) in the transparent form:

$$\langle gv, k | G(E)H_{\text{int}} | g_0, E \rangle = \frac{\bar{\imath}_v \bar{\imath}_0}{E - k - E_{gv} + i\eta} (\mathbf{e} \cdot \hat{z}) \tag{54}$$

This result is analogous to Eq. (36) previously obtained for a two-level system. Using Eq. (54) together with Eqs. (34) and (35) we can now proceed along the same lines as in Section IV and get the total photon counting rate. The calculation is straightforward leading to the result

$$\phi_v = 2\pi i \bar{\imath}_v^2 |\bar{k}|^2 \int_{-\infty}^{\infty} dE \, \exp(-iEt) G_{N_v, N_0}(E) A(E)$$

$$= 2\pi \bar{\imath}_v^2 |\bar{k}|^2 \int_{-\infty}^{t} d\tau \, C_{N_v, N_0}(t - \tau) \varphi(\tau) \tag{55}$$

where

$$C_{N_v, N_0}(t) = -(2\pi i)^{-1} \int_{-\infty}^{\infty} dE \, \exp(-iEt) G_{N_v, N_0}(E) \tag{56}$$

is the (generalized) molecular decay amplitude.

We can now relate the photon counting rate, Eqs. (35) and (32) to the probabilities, $P_{N_v}(t)$, for finding the system in each of the $|N_v, \text{vac}\rangle$ doorway states at time t,

$$P_{N_v}(t) \equiv |\langle N_v, \text{vac} | \psi(t) \rangle|^2$$

$$= \frac{\bar{\imath}_0^2}{3} \int_{-\infty}^{t} \int_{-\infty}^{t} d\tau \, d\tau' C_{N_v N_0}(t - \tau) C^*_{N_v N_0}(t - \tau')$$

$$\times \langle \varphi(\tau) \varphi^*(\tau') \rangle \tag{57}$$

The photon counting rate is recast in the final form

$$I(t) = \sum_v I_v(t) \tag{58}$$

where

$$I_v(t) = \Gamma_{N_v} P_{N_v}(t) \tag{59}$$

and

$$\Gamma_{N_v} = (4\alpha/3) \bar{\imath}_v^2 |\bar{k}|^4 \tag{60}$$

The formal results [Eqs. (57)–(60)] derived in this section enable us to provide a transparent description of the features of any time-resolved photon scattering experiment from molecules characterized by an arbitrarily complex level structure. To do so, we conceptually divide the molecular Hilbert space into two parts, Q and P. The Q subspace contains the initial and final radiative channels $|gv\rangle$ which usually constitute isolated discrete states. Our photon detection is performed within the Q subspace, as the population of the $|gv, k\rangle$ states is monitored, as is evident from Eq. (35). The complementary P subspace contains all the electronically excited states and in general has a complex level structure. In the case of an isolated resonance (Section IV) the photon counting rate $I(t)$ is proportional to the population of the resonance state $P_s(t)$ [Eq. (42)]. In the general case of a multichannel photon scattering from a complex P space of excited levels we can attribute to each $|gv\rangle$ ground vibronic state, a corresponding doorway state $|N_v\rangle$ which is entirely contained within the P space, and the rate of emission into the vth channel is proportional to the population of this particular doorway state. The photon emission rate into the vth channel $I_v(t) \propto P_{N_v}(t) \equiv |\langle N_v | \psi(t)\rangle|^2$ is proportional to the occupation probability of the doorway state $|N_v\rangle$ for this channel. The following dynamical picture of the photon scattering experiment now emerges. We assume that the molecule is initially in the $|g_0\rangle$ state. Due to the interaction with the photon field it enters the "black box" of P states through the doorway state $|N_0\rangle$. Since $|N_0\rangle$ is not an eigenstate of the total Hamiltonian, it undergoes a (nontrivial) time evolution. We can specify what is happening within the P subspace only by monitoring the population of the $|N_v, \text{vac}\rangle$ states, through which the system escapes into the various v final channels where it is amenable to optical detection. The $\{|N_v\rangle\}$ ($v \neq 0$) states thus serve as exit (or "escape") doorway states.

From the point of view of general methodology it is important to point out that the total photon counting rate [Eq. (58)], is expressed in terms of additive contributions from the final $|gv\rangle$ decay channels. Provided that the energy spread of the exciting pulse is lower than the energy difference between adjacent vibronic levels in the $|gv\rangle$ ground state manifold, the partial photon counting rates $I_v(t)$ to different final states are amenable to experimental observation.

We now consider some special situation where the physical system is characterized by a single doorway state. The general expression (57)–(59) for the photon counting rate reduces to a simple form in three cases:

1. The two level-scheme, discussed in Section IV, is of considerable interest for the understanding of photon scattering from a single vibrational–rotational level of a small (e.g., diatomic) molecule (Williams *et al.*, 1974; Rousseau *et al.*, 1975).

2. A single state $|s\rangle$ in the excited (complex) manifold carries oscillator strength from the ground state. This is a common situation in excited electronic states of large molecules (Bixon and Jortner, 1968). The subspace P_d contains a single state $|s\rangle$, whereupon the manifold of doorway states [Eq. (51)], is given in the form $|N_v, \text{vac}\rangle \equiv |s, \text{vac}\rangle$ for all v, being independent of v. The system is, in fact, characterized by a single doorway state $|s\rangle$, which is active in absorption and in emission. The partial photon counting rates [Eq. (59)], are

$$I_v(t) = (4\alpha/3)|\bar{k}|^4 |\langle gv, k|H_{\text{int}}|s, \text{vac}\rangle|^2 P_s(t) \qquad (61)$$

Thus, the time evolution is identical in all the exit channels $|gv\rangle$. Making use of the Condon approximation we immediately obtain $I_v(t)/I_{v'}(t) = M(gv; s)/M(gv'; s)$, where $M(gv; s)$ is the square of the vibrational overlap integral between $|gv\rangle$ and $|s\rangle$. Making use of the sum rule $\sum_v M(gv, s) = 1$, Eq. (58) results in

$$I(t) = (4\alpha/3)|\bar{k}|^4 |\mu_{gs}|^2 P_s(t) \qquad (62)$$

μ_{gs} being the electronic transition dipole between $|g\rangle$ and $|s\rangle$.

The total and the partial photon counting rates are determined by the occupation probability of the single doorway state $|s\rangle$.

3. The molecular spectrum is characterized by a single state $|g_0\rangle$ in the electronic ground state manifold. This hypothetical case is of some interest for the elucidation of the relation between the photon counting rate and the absorption line shape, which will be discussed in Section VII. There is a single doorway state

$$|N_0, \text{vac}\rangle = \gamma_0^{-1} \sum_\xi |\xi, \text{vac}\rangle\langle\xi, \text{vac}|H_{\text{int}}|g_0, \bar{k}\rangle \qquad (51a)$$

where the states $|\xi, \text{vac}\rangle$ span the P_d subspace. The photon counting rate is

$$I(t) = I_0(t) = \Gamma_{N_0} P_{N_0}(t) \qquad (59a)$$

and only elastic photon scattering prevails. These results are valid for any complex level structure in the excited electronic state.

We conclude this discussion of the general theory of photon counting and the following comments are in order:

i. The doorway states are superpositions of the excited molecular states $\{|\xi\rangle\}$ each weighed by its radiative coupling strength with $|gv, \bar{k}\rangle$. Invoking the Condon approximation for the radiative matrix elements, each $|\xi\rangle$ in the expansion of $|N_v\rangle$ is weighed by the Franck–Condon vibrational overlap factor $M(gv; \xi)$ between $|\xi\rangle$ and $|gv\rangle$.

ii. The various $\{|N_v\rangle\}$ states are not necessarily orthogonal.

iii. The doorway states $\{|N_v\rangle\}$ are discrete as long as the corresponding

$\{|gv\rangle\}$ states are discrete, even if the subspace P_d contains intramolecular continua.

 ' *iv.* The picture of photon scattering presented herein rests on the separability of the electromagnetic interaction (i.e., the matrix elements of H_{int} are separable in the molecular variables and in the field variables). Actually, the separability is not complete since the interaction matrix element contains also a nonseparable angular part; but this is easily handled here using a semiclassical picture for molecular rotations.

 v. Our semiclassical treatment of rotations is not essential and we could use a purely quantum mechanical formulation (Mukamel and Jortner, 1974a,b). In such a case each $|gvJM\rangle$ state would have its own doorway state $H_{int}|gvJM, \bar{k}\rangle$ (here JM are the rotational quantum numbers) and Eq. (58) should be written in the form

$$I = \sum_v \langle\langle I_v(t)\rangle\rangle \tag{63}$$

where $\langle\langle\cdots\rangle\rangle$ denotes summation over M and averaging over the thermal J distribution in the ground state. Since we usually do not expect the couplings (and the photon counting rate) to vary crucially with changing J, it is natural to invoke the semiclassical approach, thus reducing appreciably the number of doorway states without essentially affecting the physical results.

 vi. Note that the expression for the photon counting rate [Eqs. (57)–(59)] includes a convolution of a field and molecular correlation functions. In an idealized photon counting experiment we take

$$\langle\varphi(\tau)\varphi^*(\tau')\rangle = \delta(\tau - \tau')\delta(\tau) \tag{64}$$

resulting in

$$I_v(t)\alpha|C_{N_vN_0}(t)|^2 \tag{65}$$

The excitation mode specified in terms of Eq. (64) is often referred to as a "coherent short excitation." In this case we can assert that at time $t = 0$ we have "initially" prepared the $|N\rangle$ state, and the interpretation of the experimental decay pattern is considerably simplified. The meaning of condition (64) is that the pulse duration and the pulse correlation time are much shorter than all the intrinsic molecular decay times. An exact definition of the molecular decay times will be presented in Sections X and XI for specific molecular level schemes.

 vii. Explicit calculation of $I_v(t)$, Eq. (58) requires the evaluation of the molecular correlation matrix $G_{N_vN_0}(E)$. Since this matrix is entirely confined within the P_d subspace we can use the formal indentities [in analogy with Eqs. (48) and (49)] (Mower, 1966)

$$\hat{P}_d G \hat{P}_d = (E - H_0 - \hat{P}_d \bar{R} \hat{P}_d)^{-1}\hat{P}_d \tag{66}$$

where

$$\bar{R} = V + V\hat{Q}_d(E - H_0 - \hat{Q}_d V \hat{Q}_d)^{-1}\hat{Q}_d V \tag{67}$$

and

$$\hat{Q}_d = 1 \qquad \hat{P}_d = \hat{Q} + \hat{P}' \tag{68}$$

This matrix has the dimensionality of the P_d space and determines the time evolution of the system within the P_d subspace. $P_d G P_d$ may be recast in the form $(E - H_{eff})^{-1} \hat{P}_d$, where $H_{eff} \equiv H_0 + \hat{P}_d R \hat{P}_d$ is the *effective Hamiltonian* for the time evolution within P_d. Effective Hamiltonians will be further discussed in Sections IX–XI. The matrix elements of $\hat{P}_d G \hat{P}_d$ may be now evaluated by a perturbative expansion in $\hat{Q}_d V \hat{Q}_d$ or, alternatively, by a continued fraction expansion. Defining a $P_d^{(2)}$ subspace as a subspace of Q_d containing the states directly coupled to the P_d subspace we have

$$\hat{P}_d R \hat{P}_d = \hat{P}_d V \hat{P}_d + \hat{P}_d V \hat{P}_d^{(2)}$$
$$\times (E - H_0 - \hat{Q}_d V \hat{Q}_d)^{-1} \hat{P}_d^{(2)} V \hat{P}_d \tag{69}$$

Utilizing the same derivations which lead to (48) and (49) we can write (Cohen Tannoudji, 1968; Mower, 1966)

$$\hat{P}_d^{(2)}(E - H_0 - \hat{Q}_d V \hat{Q}_d)^{-1} \hat{P}_d^{(2)} = (E - H_0 - \hat{P}_d^{(2)} R^{(2)} \hat{P}_d^{(2)})^{-1} \hat{P}_d^{(2)} \tag{70}$$

Here $R^{(2)}$ is analogous to R [Eq. (49)], where $\hat{Q}$ is replaced by $\hat{Q}_d^{(2)} = \hat{Q}_d - \hat{P}_d$. We can continue the process of reducing our Q space in the same way, thus obtaining a continued fraction expansion of $\hat{P}_d G \hat{P}_d$.

viii. Equations (57)–(59) may be also derived by defining the photon counting rate in terms of the time derivative of the probability for finding the molecular system in any one photon state, see, i.e., Jortner and Mukamel (1974, 1975).

$$I(t) = \alpha' \frac{d}{dt} \sum_v \int dk' |\langle gv, k' | \psi(t) \rangle|^2 \tag{71}$$

where the integration over k' excludes photons having the same propagation and polarization directions as the original light pulse. α' is a proportionality constant. Equation (71) together with (27) and (54) results in

$$I(t) = \frac{\alpha'}{4\pi^2} \frac{d}{dt} \sum_v \int dk' \left| \int dE \exp(-iEt) \right.$$
$$\left. \times \langle gv, k' | \hat{Q} G \hat{P} H_{int} | g_0, E \rangle A(E) \right|^2$$
$$= \frac{\alpha' \gamma_0^2 \gamma_v^2}{4\pi^2} \frac{d}{dt} \sum_v \iint dE\, dE'\, A(E) A^*(E)$$
$$\times G_{N_v N_0}(E) G_{N_v N_0}^*(E')$$
$$\times \int d^3k' \frac{\exp[-i(E-E')t]}{(E - E_{gv} - k' + i\eta)(E' - E_{gv} - k' - i\eta)} \tag{72}$$

We can now perform the k' integration $\int d^3k' = 2\pi \int k'^2 \, dk' d(\cos \Theta')$ which results in

$$\frac{d}{dt} 4\pi \int \frac{k'^2 \, dk' \exp[-i(E - E')t]}{(E - E_{gv} - k' + i\eta)(E' - E_{gv} - k' - i\eta)}$$

$$= 8\pi^2(E' - E_{gv})^2 \exp[-i(E - E')t] \tag{73}$$

Substitution of (73) in (72) and neglecting the slow variation of E^2 in the energy range of interest, we finally get Eqs. (57)–(59).

VI. General Expressions for Emission Quantum Yields

In time-resolved experiments, when we distinguish (by proper energy resolution) between the various final channels for photon scattering, one can define the partial quantum yield Y_v for the channel v, as the number of photons scattered to the state $|gv\rangle$, divided by the total number of absorbed photons. If no intramolecular decay channels are considered, then the number of absorbed photons is equal to the total number of scattered photons, and $\sum_v Y_v = 1$. In general, the photon emission rate into the vth channel is given by $I_v(t)$, and we expect the following relation to hold:

$$Y_v = \frac{\int_{-\infty}^{\infty} dt I_v(t)}{\sum_{v'} \int_{-\infty}^{\infty} dt I_{v'}(t)} = \frac{\int_{-\infty}^{\infty} dt I_v(t)}{\int_{-\infty}^{\infty} dt I(t)} \tag{74}$$

Equation (74) constitutes a definition of Y_v in terms of integrals over time-resolved observables. An alternative approach to this problem is to express these yields in terms of integrals over energy-resolved observables. Using the definition of the scattering (S) and the transition (T) matrices (Goldberger and Watson, 1964), it was shown that for the scattering photon wave packet characterized by the amplitudes $A(E)$, the partial quantum yields are (Jortner and Mukamel, 1975)

$$Y_v = \frac{\int \sigma_v(E) |A(E)|^2 \, dE}{\int \sigma_a(E) |A(E)|^2 \, dE} = \frac{\int \sigma_v(E) |A(E)|^2 \, dE}{\sum_{v'} \int \sigma_{v'}(E) |A(E)|^2 \, dE} \tag{75}$$

where $\sigma_v(E)$ is the photon scattering cross-section into the channel v, while $\sigma_a(E)$ denotes the photon absorption cross-section. We shall now demonstrate the equivalence of Eqs. (74) and (75). Equation (75) can be alternatively written in the form (Jortner and Mukamel, 1975)

$$Y_v = \frac{\int dE |A(E)|^2 |\langle gv, k | T(E) | g_0, E\rangle|^2}{\sum_{v'} \int dE |A(E)|^2 |\langle gv, k | T(E) | g_0, E\rangle|^2} \tag{76}$$

where $T(E)$ is the transition matrix

$$T = V + VG(E)V \tag{77}$$

and the k photon satisfies energy conservation $E_{gv} - E_{g0} + k = E$, where E_{gv}, E_{g0} are the energies of the $|gv\rangle$ and $|g_0\rangle$ states, respectively. Using the relation

$$\langle gv, k' | T(E) | g_0, k \rangle = \gamma_v \gamma_0 G_{N_v N_0}(E) \tag{78}$$

we establish a basic identity between the time integral of the (time-resolved) variable $I_v(t)$ and the energy integral of the (energy-resolved) cross section $\sigma_v(E)$,

$$\int dE |A(E)|^2 \sigma_v(E) \propto \int dE |A(E)|^2 |\langle gv, k | T(E) | g_0, E \rangle|^2$$

$$= \gamma_v^2 \gamma_0^2 \int_{-\infty}^{\infty} dt \left| \int dE\, G_{N_v N_0}(E) A(E) \exp(-iEt) \right|^2$$

$$= \frac{\gamma_v^2 \gamma_0^2}{4\pi^2} \int_{-\infty}^{t} dt \left| \int_{-\infty}^{t} d\tau\, C_{N_v N_0}(t - \tau) \varphi(\tau) \right|^2$$

$$\propto \int_{-\infty}^{\infty} dt\, I_v(t) \tag{79}$$

Substituting Eq. (79) in (76) results in Eq. (74). The equivalence of Eqs. (74) and (75) establishes an important relation between the time-resolved observables $I_v(t)$ and $I(t)$ and the energy-resolved cross-sections $\sigma_a(E)$ and $\sigma_v(E)$.

VII. Comments on the Relation between Time-Resolved Observables and the Optical Absorption Lineshape

We now pursue further relations between time-resolved and energy-resolved experimental observables and consider the connection between the photon counting rate and the optical absorption lineshape. It was often stated in papers on the theory of molecular radiationless transitions that the decay mode is expressed in terms of the Fourier transform of the lineshape function (Bixon and Jortner, 1968; Chock et al., 1969; Robinson, 1973; Robinson and Langhoff, 1974). It is well known from linear-response theory (Kubo, 1959) that the optical lineshape is expressed in terms of a Fourier transform of a (molecular) correlation function. However, this general result does not establish the above-mentioned relation between $I(t)$ and the lineshape function. We shall now attempt to elucidate the general features of this interesting problem.

The photon counting rate [Eq. (58)] is determined in terms of squares of convolution integrals which involve the molecular decay amplitudes $C_{N_v, N_0}(t)$ [Eq. (56)], i.e., the molecular correlation matrix. For a general molecular level structure we require both the diagonal term $C_{N_0, N_0}(t)$ as well as all the off-diagonal terms connecting $|N_0\rangle$ with $|N_v\rangle$ ($v \neq 0$) to specify completely the time evolution. The diagonal decay amplitude $C_{N_0, N_0}(t)$, appearing in $I_0(t)$, which determines the elastic photon scattering mode, may be directly obtained from the (intrinsic) absorption cross-section $\sigma_a(E)$. The latter energy-resolved observable is given (apart from irrelevant proportionality constants) at zero temperature by (Chock *et al.*, 1969; Jortner *et al.*, 1969; Jortner and Mukamel, 1974; Robinson, 1973)

$$\sigma_a(E) = |\gamma_0|^2 \, \text{Im} \, G_{N_0 N_0}(E) \tag{80}$$

Making use of the dispersion relation (Goldberger and Watson, 1964) for the Green's operation

$$G(E) = -\frac{1}{\pi} \int_{-\infty}^{\infty} dE' \frac{\text{Im} \, G(E')}{E' - E - i\eta} \tag{81}$$

and applying it to $G_{N_0 N_0}(E)$ we get for Eq. (74),

$$C_{N_0 N_0}(t) = \theta(t) \int dE \exp(-iEt)\sigma_a(E) \tag{82}$$

where $\theta(t)$ is the Heaviside step function. From Eq. (82) it is apparent that $\sigma_a(E)$ is expressed in terms of a Fourier transform of a molecular correlation function as implied by linear response theory.

From Eqs. (57), (59), and (82) we obtain an explicit expression for the partial photon counting rate $I_0(t)$ to the $v = 0$ channel, which is valid for any general level structure

$$I_0(t) \propto f(t) \tag{83}$$

where

$$f(t) = \left| \int_{-\infty}^{t} d\tau \varphi(\tau) \int_{-\infty}^{\infty} dE' \sigma_a(E') \exp[iE'(t - \tau)] \right|^2 \tag{84}$$

From this result we conclude that, in principle, the measurement of the energy-resolved variable $\sigma_a(E)$ provides complete information concerning time-resolved elastic photon scattering to the incident channel. One should note, however, that for a general level structure the lineshape data do not provide us with the partial photon counting rates $I_v(t)$ ($v \neq 0$) for inelastic photon scattering, nor with the total photon counting rate. From the (thermally averaged) absorption cross-section at finite temperatures

$$\langle \sigma_a(E) \rangle_T = \frac{\text{Tr}\{e^{-\beta H} |\gamma_v|^2 \, \text{Im} \, G_{N_v, N_v}(E)\}}{\text{Tr}\{e^{-\beta H}\}} \tag{85}$$

$\beta = (kT)^{-1}$, we can extract (by analyzing the optical spectrum at several temperatures), the values of the absorption cross sections $|\gamma_e|^2 \, \text{Im} \, G_{N_v,N_v}$ from different initial $|gv\rangle$ levels. However, the values of $\text{Im} \, G_{N_v,N_v}$ together with the dispersion relation (81) will result only in the diagonal decay ampli-tudes $C_{N_v,N_v}(t)$, while what is required to specify the time evolution are the off-diagonal terms $C_{N_0,N_e}(t)$, which cannot be extracted from the lineshape data. Partial information concerning these off-diagonal terms may be ob-tained from the measurements of the (energy-resolved) photon scattering cross sections $\sigma_v(E)$ into the vth channel. From previous results [see Eq. (76)] we have (Nitzan and Jortner, 1972; Mukamel and Jortner, 1974a, b) $\sigma_v(E) \propto |\langle gv, k|T(E)|g_0, E\rangle|^2$ and making use of Eq. (78) we then get $\sigma_v(E) \propto |G_{N_v,N_0}(E)|^2$. While the measurements of $\sigma_v(E)$ results in $|G_{N_v,N_0}(E)|^2$ this is insufficient to determine $C_{N_v,N_0}(t)$ or $|C_{N_v,N_0}(t)|^2$. Thus the information extracted from photon scattering cross sections does not incorporate all the phase information required for the determination of the time evolution. On the other hand, this phase information is redundant for the determination of quantum yields, discussed in Section VI. We thus con-clude that for a general level structure, unique relations between time-resolved and energy-resolved observables for inelastic photon scattering exist only for the integrated quantities, i.e., the quantum yields, and not for the local quantities in the energy or in the time domains.

A unique relation between the absorption lineshape and *all* the partial photon counting rates [as well as with $I(t)$] does hold for special physical cases whenever the molecular system is characterized by a single doorway state. Such situations were considered in Section V. The cases of a two-level system (case 1) and of the hypothetical system characterized by a single ground state (case 3) are trivial in this context since only elastic photon scattering prevails and $I(t) = I_0(t)$ [Eq. (83)]. When a single state $|s\rangle$ in the (complex) excited manifold carries oscillator strength from the ground elec-tronic state (case 2) then the partial photon counting rates $I_v(t)$ for all v as well as $I(t)$ are proportional to the population probability $P_s(t)$, which (apart from irrelevant proportionality constants) is given by

$$P_s(t) \propto f(t) \tag{86}$$

where $f(t)$ is presented by Eq. (84).

The following general conclusions now emerge:

1. For a general level structure, $\sigma_a(E)$ determines just the elastic photon counting rate but is insufficient to determine the inelastic contributions to time-resolved photon counting.

2. For the special and physically relevant case of a system characterized by a single doorway state, Eq. (86), together with Eqs. (61) and (62), provide a general relation between all the partial (and the total) photon counting rates and the Fourier transform of $\sigma_a(E)$.

3. For the special case of a broad-band excitation [see Eq. (64)] of a system characterized by a single doorway state, the commonly quoted relation between $I(t)$ and the Fourier transform of $\sigma_a(E)$ does hold. The formalism presented herein provides us with a general framework for handling time-resolved photon scattering. The problem reduces to the evaluation of the decay amplitudes (i.e., the molecular correlation functions) $C_{v_r v_0}(t)$ between $|N_0\rangle$ and all other doorway states. These correlation functions depend on the detailed molecular level structure and incorporate all the relevant physical information concerning the molecular dynamics that we can extract from experiment.

VIII. Photon Scattering from a Single Molecular Resonance and Effects of Collisional Perturbations

To provide a transparent and relevant application of the formalism outlined in the preceding section, we now consider the "transition" from resonance fluorescence to near-resonance Raman scattering in a time-resolved experiment involving photon scattering from a molecular resonance. The energy levels scheme for a single resonance coupled to a radiative continuum and a dissociative (i.e., predissociative) channel is displayed in Fig. 2. The intrinsic optical molecular lineshape $L(E)$, is a Lorentzian peaked at the energy $\bar{E}_s = E_s + \Delta_s$, where Δ_s is a (small) level shift, and is characterized by the width

$$\Gamma_s = \Gamma_s^r + \Gamma_s^c$$
$$\Gamma_s^r = 2\pi |V_{s,gk}|^2 \rho_r \qquad (87)$$
$$\Gamma_s^c = 2\pi |V_{s,c}|^2 \rho_c$$

consisting of the sum of a radiative Γ_s^r and a nonradiative Γ_s^c contributions.
The decay amplitude of the doorway state $|s\rangle$ is

$$C_{ss}(t) = \exp(-i\bar{E}_s t) \exp(-\Gamma_s t/2) \qquad (88)$$

While the photon counting rate is now

$$I(t) = \tfrac{1}{2}\Gamma_s^r |V_{s,gk}|^2 \left| \int_{-\infty}^{t} \varphi(\tau) \exp[-i\bar{E}_s(t-\tau)] \exp[-\Gamma_s(t-\tau)/2] \, d\tau \right|^2 \quad (89)$$

Williams et al. (1974) have studied scattering of a light pulse of a tunable laser from a single rotovibrational level of the $B^3\Pi$ state of molecular iodine. The basic idea of the experiment of Williams et al. is presented in Fig. 2b.
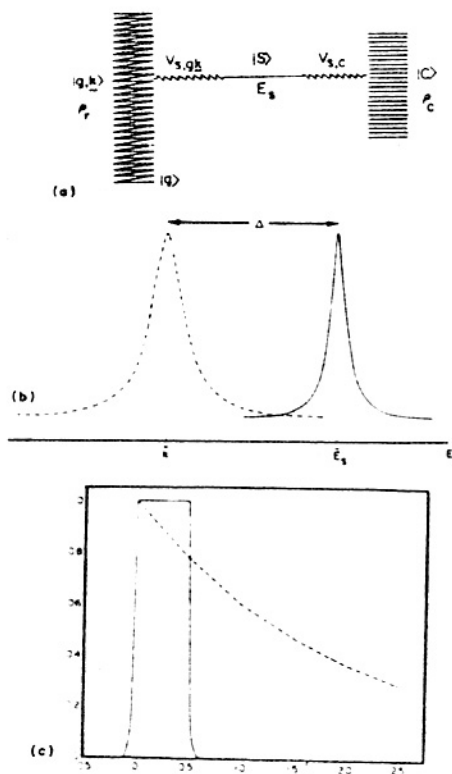
Fig. 2 (a) Energy level scheme for photon scattering from a single isolated resonance. (b) Energy profile for a near resonance photon scattering experiment. (———) $L(E)$, lineshape of the isolated resonance (a Lorentzian around $\bar{E}_s$ with width Γ_s). (- - -) $|A(E)|^2$, power spectrum of the light 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. (- - -) $C_{ss}(t)$ [Eq. (88)]. (———) $\varphi(t)$ [Eq. (91)].

The time-resolved photon scattering is determined as a function of the energy increment

$$\Delta = |\bar{E}_s - \bar{k}| \tag{90}$$

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

$$\varphi(t) = \exp(\gamma_1 t/2)\exp(-i\bar{k}t) \qquad t < 0$$

$$\varphi(t) = \exp(-i\bar{k}t) \qquad\qquad 0 < t < T \tag{91}$$

$$\varphi(t) = \exp[-\gamma_2(t-T)/2]\exp(-i\bar{k}t) \qquad t > T$$

where γ_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 that enters into the game is the Doppler width. The following experimental observations were reported.

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

2. When the off resonance energy increment is large, i.e., $\Delta > \beta > \gamma_i > \Gamma_s \sim T^{-1}$, two decay components, characterized by the lifetimes γ_2^{-1} and Γ_s^{-1} are exhibited. The experimental photon counting rate $[F(\Delta, t)]$ for $t > T$ is,

$$F(\Delta, t) \approx I_p(t) + I_m(t) \tag{92}$$

with

$$I_p(t) = I_p^0 \exp[-\gamma_2(t - T)] \tag{93a}$$

$$I_m(t) = I_m^0 \exp[-\Gamma_s(t - T)] \tag{93b}$$

$I_p(t)$ 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

$$R = I_m^0/(I_p^0 + I_m^0) = I_m^0/F(\Delta, T) \tag{94}$$

is a slowly decreasing function of Δ, becoming practically constant for large values of Δ.

4. Increasing the pressure to 0.25 torr results in a dramatic enhancement of the long-lived molecular component relative to the total intensity. For $\Delta = 1.7$ GHz, R increases from 0.14 at $p = 0.03$ to $R = 0.44$ at $p = 0.25$ torr (Rousseau *et al.*, 1975).

Utilizing Eq. (89) for the photon counting rate from a single molecule, which depends on Δ and will now be denoted by $I(\Delta, t)$, we subsequently 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

$$f(\Delta) = (\pi\beta^2)^{-1/2} \exp(-\Delta^2/\beta^2) \tag{95}$$

so that

$$F(\Delta, t) = \int_{-\infty}^{\infty} f(\Delta - \Delta')I(\Delta', t) \, d\Delta' \tag{96}$$

In Fig. 3 we present numerical results for $F(\Delta, t)$ using the pulse shape (78) and substituting typical parameters corresponding roughly to the experimental situation; the dependence of R on Δ is presented in Fig. 4. Our
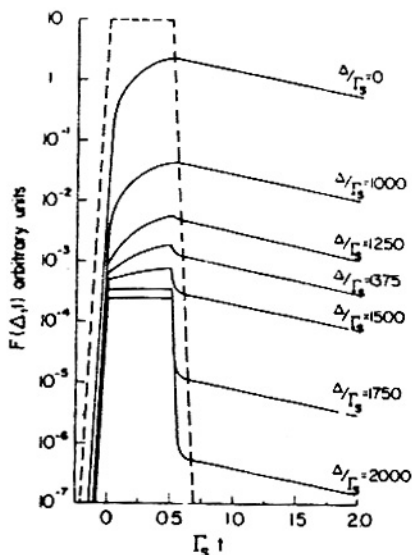
Fig. 3. The time resolution of the photon counting rate $F(\Delta, t)$ [Eq. (96)] (in arbitrary units) for the pulse (91) for various values of the off-resonance energy Δ, the Doppler width (in units of the resonance radiative width) is $\beta/\Gamma_s = 500$; the rise and fall times of the pulse are $\gamma_1/\Gamma_s = \gamma_2/\Gamma_s = 100$; the inverse duration of the pulse is $T^{-1}/\Gamma_s = 2$. The dotted line is proportional to the pulse time-resolved intensity.
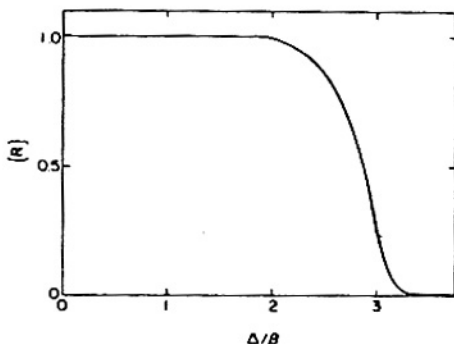

Fig. 4. The dependence of the fractional intensity ratio $\{R\}$ of the long decay component on the off-resonance energy Δ at zero pressure. $\Gamma_s = 0.4 \times 10^6 \text{ sec}^{-1}$, $\beta = 1.7 \times 10^9 \text{ sec}^{-1}$, $\gamma_1 = \gamma_2 = 3.3 \times 10^8 \text{ sec}^{-1}$, and $T = 100$ nsec.

calculations reveal the following features:

 i. For the resonance situations, i.e., $\Delta \lesssim \beta$, only the long molecular decay component is exhibited.

 ii. Moving away from resonance, when $\Delta > 2\beta$, both short and long decay components appear.

iii. Increasing Δ results in a decrease of the total intensity. For the extreme off-resonance situation

$$F(\Delta, T) \propto \Delta^{-2} \tag{97}$$

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

$$I_m(\Delta, T) \propto \Delta^{-4} \tag{98}$$

v. The only typical lifetimes (or decay modes) that determine the time-resolved decay pattern for resonance fluorescence and for near-resonance Raman scattering are those characterizing the pulse decay and those specifying the molecular lifetimes. The off-resonance energy does not appear as an additional lifetime; rather it just determines the total emission intensity via Eq. (97), and the relative intensity R of the long component (98) at off-resonance.

vi. The intensity ratio R for the off-resonance situation in the isolated molecule assumes the limiting form (Fig. 4)

$$R \propto \Delta^{-2} \tag{99}$$

The general features *i–v* are compatible with the experimental results of Williams *et al.* It is apparent, however, from our calculations (Figs. 3 and 4) that the theoretical prediction *vi* for the isolated molecule, i.e., $R \propto \Delta^{-2}$ for the extreme off-resonance situation is in variance with the "low" pressure data of Williams *et al.* (1974). Mukamel *et al.* (1975, 1976) have concluded that under 0.03 torr pressure of I_2, collisional effects are of considerable importance, and they have advanced a theory of time-resolved photon scattering by collisionally perturbed molecules. It was 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 Γ_s 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. In the present context the following collisional effects have to be considered:

(a) Collisionally induced predissociation characterized by a width Γ_1^{cp} (T_1 process);
(b) Vibrational–rotational cross-relaxation specified by widths Γ_1^x (T_2 process);
(c) Interference effects between the lower and the upper electronic states due to phase shifts (T_2 process), contributing a width Γ_2^{ps}.

The level scheme for simultaneous collisional and radiative coupling is portrayed in Fig. 5. The photon counting rate $\langle F(t) \rangle$ is expressed in terms of
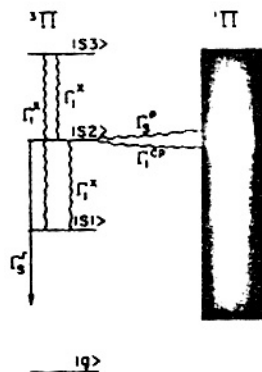
Fig. 5. Energy level scheme for spontaneous and collisionally induced damping processes in I_2.

a triple convolution

$$\langle F(t)\rangle = \int_{-\infty}^{\infty} d\Delta' \int_{-\infty}^{\infty} d\Delta'' I(\Delta', t) f(\Delta' - \Delta'') C(\Delta' - \Delta) \qquad (100)$$

where I is given by Eq. (76) with Γ_s replaced by the total decay width $\Gamma_s + \Gamma_1^{sp}$, and f corresponds to the Gaussian–Doppler function (95), while the collisional-Lorentzian term is

$$C(\Delta) = \frac{(\hat{\Gamma}/2\pi)}{\Delta^2 + \hat{\Gamma}^2} \qquad (101)$$

$$\hat{\Gamma} = \Gamma_2^{gs} + \tfrac{1}{2}(n-1)\Gamma_1^x \qquad (102)$$

The latter incorporates only intrastate cross-relaxation and phase shifts. Regarding the general features of the time-resolved photon scattering, we note that the short decay component $I_p(t)$ originates from a direct quantum mechanical scattering, while the molecular "component" $I_m(t)$ arises from the decay of a collisionally perturbed molecular state, where excitation and subsequent decay can be separated. Collisional effects are twofold. First, they provide a contribution Γ_1^{sp} to Γ_1 modifying the decay time of $I_m(t)$. Second, the width $\hat{\Gamma}$ of the Lorentzian function (102) spans a large fraction of the Fourier components of the pulse near resonance, resulting in a dramatic pressure-induced enhancement of the intensity ratio $\{R\}$, as evident from Fig. 6. We also note from Fig. 6 that for off-resonance $\{R\}$ is practically independent of Δ, in accord with experiment. Finally, we note (Fig. 7 and Table 1) that the present theory provides a quantitative account of the recent experimental data of Rousseau et al. (1975).
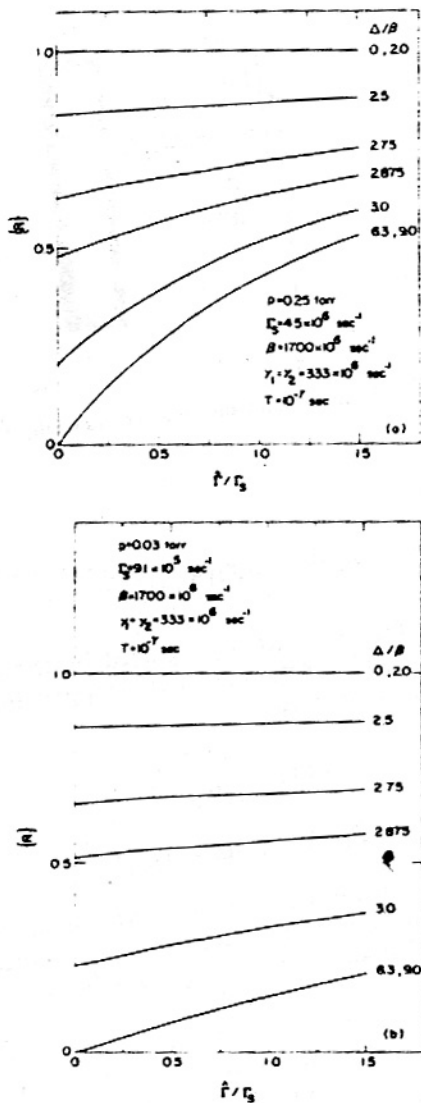
Fig. 6. The intensity ratio $\{R\}$ between the slowly decaying component and the total photon-counting rate, evaluated at $t = T$, as a function of the off-resonance parameter Δ, at different values of the collision-broadening rate $\bar{\Gamma}$. (a) $p = 0.25$ torr, Γ, $= 4.5 \times 10^6 \text{sec}^{-1}$. (b) $p = 0.03$ torr, Γ, $= 9 \times 10^5 \text{sec}^{-1}$: other parameters, same as in Fig. 4.
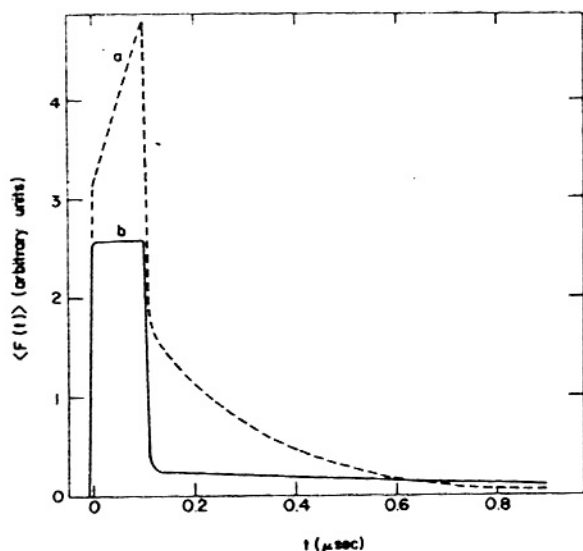
Fig. 7. Simulation of the experimental results of Rousseau *et al.* (1975) for time-resolved light scattering from I_2. Curve a $p = 0.25$ torr, $\Gamma_s = 4.5 \times 10^6$ sec^{-1}, $\hat{\Gamma} = 4 \times 10^6$ sec^{-1}; curve b $p = 0.03$ torr, $\Gamma_s = 9 \times 10^5$ sec^{-1}, $\hat{\Gamma} = 4.8 \times 10^5$ sec^{-1}.

TABLE 1

DECAY RATES Γ_s AND $\hat{\Gamma}$ AND THE FRACTIONAL INTENSITY $\{R\}$ OF THE LONG DECAY COMPONENT AT $t = T$ FOR TIME-RESOLVED PHOTON SCATTERING FROM I_2 AT 5145 Å[a]

	$p = 0$	$p = 0.03$ torr	$p = 0.25$ torr
Γ_s from self-quenching data[b]	4.2×10^5 sec^{-1}	9.0×10^5 sec^{-1}	4.5×10^6 sec^{-1}
Γ_s direct measurement[c]	—	$> 5 \times 10^5$ sec^{-1}	3.3×10^6 sec^{-1}
$\hat{\Gamma}$	0	4.8×10^5 sec^{-1}	4.0×10^6 sec^{-1} spectroscopic data[c]
$\{R\}$ (experiment)[c]	—	0.14	0.45
$\{R\}$ (theory)[d]	5×10^{-4}	0.08	0.38

[a] The off-resonance energy is $\Delta = 17$ GHz and the Doppler width is $\beta = 1.7 \times 10^5$ sec^{-1}, while the pulse parameters are $\gamma_1 = \gamma_2 = 3.3 \times 10^8$ sec^{-1} and $T = 100$ nsec.

[b] Chutjian *et al.* (1967).

[c] Rousseau *et al.* (1975).

[d] Mukamel *et al.* (1975).

IX. The Effective Hamiltonian and Independently Decaying Levels

We now proceed to provide explicit formal expressions for the photon counting from the quite general level scheme of densely spaced molecular states presented in Fig. 8. This level scheme consists of some bound states
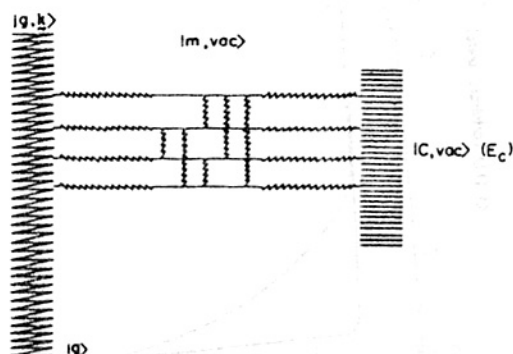

Fig. 8. A general molecular level scheme consisting of a group of closely spaced discrete levels radiatively coupled to the ground state which may be coupled also to intramolecular channels.

which are radiatively coupled to the ground state and which also may be coupled to intramolecular continua or to other decay channels that do not carry oscillator strength from the ground state. We recall that the photon counting rate is determined by the projection of $|N_v\rangle$ on $\Psi(t)$ [Eqs. (58)–(60)]. Thus even if we had a complete information on $\Psi(t)$, a large part of it is redundant, since we only require the subpart of $\Psi(t)$ given by the projection

$$\sum_v |N_v \text{ vac}\rangle\langle N_v \text{ vac}| \tag{103}$$

In other words, we can limit ourselves to handle 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 that specifies the time evolution of the relevant subsystem in the presence of the radiation field and other intramolecular decay channels.

Being guided by Eq. (103), we partition the total Hilbert space by the use of the following projection operators

$$\hat{P} = \sum_m |m, \text{vac}\rangle\langle m, \text{vac}|$$

$$\hat{Q} = \sum_v \sum_k |gv, \mathbf{k}\rangle\langle gv, \mathbf{k}| + \sum_c |c\rangle\langle c|$$

$$\hat{P} + \hat{Q} = 1 \tag{104}$$

Following this formal approach, Eqs. (58)–(60) take the form

$$I_v(t) = \Gamma_{N_v}^r |\langle N, \text{vac} | \hat{P} \Psi(t) \rangle|^2 \tag{105}$$

and

$$G_{N_v N_v}(E) = \langle N, \text{vac} | \hat{P} G(E) \hat{P} | N, \text{vac} \rangle \tag{106}$$

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 in Section V that the Green's function and the evolution operator within the P subspace can be expressed in terms of the effective Hamiltonian

$$H_{\text{eff}} = \hat{P}(H_0 + R)\hat{P} \tag{107}$$

i.e.,

$$\hat{P} G(E) \hat{P} = \hat{P}(E - H_{\text{eff}})^{-1} \hat{P} \tag{108}$$

or

$$\hat{P} \exp(-iHt)\hat{P} = \hat{P} \exp(-iH_{\text{eff}}t)\hat{P} \tag{109}$$

where H_0 is the zero-order Hamiltonian and R is the level-shift operator [Eq. (49)]

The effective Hamiltonian can be recast in a matrix form

$$H_{\text{eff}} = H_m + \Delta - (i/2)\Gamma \tag{110}$$

where H_m is the molecular Hamiltonian, Δ is a level-shift matrix, while Γ is the decay matrix both 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 $\{|c\rangle\}$ intramolecular continuum as follows:

$$(\Delta)_{mm'} = (\Delta^r)_{mm'} + (\Delta^c)_{mm'}$$

$$(\Delta^r)_{mm'} = \text{PP} \sum_k \frac{\langle m, \text{vac} | H_{\text{int}} | g, k \rangle \langle g, k | H_{\text{int}} | m', \text{vac} \rangle}{E - k}$$

$$(\Delta^c)_{mm'} = \text{PP} \sum_c \frac{\langle m, \text{vac} | H_v | c, \text{vac} \rangle \langle c, \text{vac} | H_v | m', \text{vac} \rangle}{E - E_c} \tag{111}$$

where PP stands for a principal part of an integral and

$$(\Gamma)_{mm'} = (\Gamma^r)_{mm'} + (\Gamma^c)_{mm'}$$

$$(\Gamma^r)_{mm'} = 2\pi \langle m, \text{vac} | H_{\text{int}} | g, k \rangle \rho_r(k) \langle g, k | H_{\text{int}} | m', \text{vac} \rangle$$

$$(\Gamma^c)_{mm'} = 2\pi \langle m, \text{vac} | H_v | c, \text{vac} \rangle \rho_c \langle c, \text{vac} | H_v | m', \text{vac} \rangle \tag{112}$$

Here $\rho_r(k)$ and ρ_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 $\Delta^r_{mm'}$, which can be handled by the renormalization theory adopted in the study of the Lamb shift (Schweber, 1961). The level-shift contributions Δ^c_{mm}, may be of importance in modifying the energy levels.

The properties of the relaxation matrix Γ are as follows.

1. It provides a generalization of Fermi's golden rule for a multilevel system.

2. It is, in general, nondiagonal.

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. Γ is Hermitian.

6. Usually it is safe to assume that Γ 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_{eff} is non-Hermitian.

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

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

$$DH_{eff}D^{-1} = \Lambda \tag{113}$$

$$\Lambda_{ij} = \Lambda_{jj}\delta_{ij} = (E_j - (i/2)\Gamma_j)\,\delta_{ij}$$

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

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

$$|j, \text{vac}\rangle = \sum_m D_{jm}|m, \text{vac}\rangle \tag{114}$$

(Accidental degeneracies are disregarded in our discussion.)

6. The $|j, \text{vac}\rangle$ basis is nonorthogonal.

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

$$|\bar{j}, \text{vac}\rangle = \sum_m [(D^{-1})^+]_{jm} |m, \text{vac}\rangle \tag{115}$$

In the special case (4), the wave functions corresponding to $|j\rangle$ are the complex conjugate of the wave function corresponding to $|\bar{j}\rangle$.

The projection operator into the P space may be written as

$$P = \sum_j |j, \text{vac}\rangle\langle\bar{j}, \text{vac}| \tag{116}$$

This relation is a consequence of the orthonormality of $|j, \text{vac}\rangle$ and $|\bar{j}, \text{vac}\rangle$, i.e., $\langle j|\bar{j}'\rangle = \delta_{jj'}$.

8. The diagonal sum rule applies to the transformation (113) whereupon

$$\sum_m (E_m + \Delta_{mm}) = \sum_j E_j \tag{117}$$

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

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

$$\hat{P}G(E)\hat{P} = \sum_j \frac{|j, \text{vac}\rangle\langle\bar{j}, \text{vac}|}{E - E_j + (i/2)\Gamma_j} \tag{118}$$

and

$$\hat{P} \exp(-iH_{\text{eff}}t)\hat{P} = \sum_j |j, \text{vac}\rangle \exp\left(-iE_j t - \frac{1}{2}\Gamma_j t\right) \langle\bar{j}, \text{vac}| \tag{119}$$

A final important conclusion is emerging from the last formal result that the molecular decay amplitudes combining any pair of zero-order $|m, \text{vac}\rangle$ states can be expressed as a superposition of exponential functions

$$\exp[-iE_j t - (\Gamma_j/2)t]$$

It is thus proper to refer to the basis set $|j, \text{vac}\rangle$ as the *independently decaying levels* of the molecular system. The doorway states (and any other state defined within the P subspace) may be then expanded in the form

$$|N_v\rangle = \sum_j |j\rangle\langle\bar{j}|N_v\rangle \tag{120}$$

and the decay amplitudes are

$$C_{N_v N_{v'}}(t) = \sum_j \exp[-(iE_j - \tfrac{1}{2}\Gamma_j)t]\langle N_v|j\rangle\langle\bar{j}|N_{v'}\rangle \tag{121}$$

Utilizing Eq. (121) the population probability of the $|N_v\rangle$ state Eq. (115) assumes the form

$$P_{N_v}(t) = \gamma_v^2 \sum_j \sum_{j'} A_j^v A_{j'}^{v*} \langle F_{j'}^*(t)F_j(t)\rangle \tag{122}$$

with the coefficients

$$A_j^v = \langle N_v | j \rangle \langle \bar{j} | N_0 \rangle \tag{123}$$

the time-dependent amplitudes

$$F_j(t) = \int_{-\infty}^t d\tau \varphi(\tau) \exp[(-iE_j - \tfrac{1}{2}\Gamma_j)(t - \tau)] \tag{124}$$

and the correlated time-dependent amplitudes

$$\langle F_{j'}^*(t)F_j(t)\rangle = \int_{-\infty}^t \int_{-\infty}^t d\tau \, d\tau' \exp[(-iE_j - \tfrac{1}{2}\Gamma_j)(t - \tau)]$$
$$\times \exp[(iE_{j'} - \tfrac{1}{2}\Gamma_{j'})(t - \tau')]\langle \varphi^*(\tau')\varphi(\tau)\rangle \tag{125}$$

Equations (122)–(125) together with Eqs. (59)–(60) provide us with the general theory of photon scattering from any molecular level structure.

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.

3. The time-dependent coefficients $F_j(t)$ contain information concerning the light pulse and the decay modes of the independently decaying levels.

X. Time-Resolved Photon Scattering from Large Molecules

To provide the background for the discussion of time-resolved experiments under intermediate excitation conditions, let us consider excitation by a Lorentzian wave packet so that $\varphi(t) = \theta(t) \exp(-i\bar{k}t) \exp(-\gamma_p t/2)$, where γ_p corresponds to the reciprocal decay time of the pulse. Equation (124) takes the form

$$F_j(t) = i \frac{\exp[-i(\bar{k} - E_j)t] \exp(-(\gamma_p/2)t) - \exp(-(\Gamma_j/2)t)}{\bar{k} - E_j + (i/2)(\Gamma_j - \gamma_p)} \tag{126}$$

Since the pulse width γ_p can be varied at will, we shall now consider two physical situations pertaining to short excitation experiments.

A. Energy-Weighted Excitation

Provided that

$$\gamma_p \gg \Gamma_j \quad \text{all} \quad j \tag{127}$$

the photon counting rate is

$$I(t) = \tfrac{1}{2}\gamma_N^2 \Gamma_N \left| \sum_j \frac{|A_j|^2 \exp(-\Gamma_j t)}{(E_j - \bar{k})^2 + \tfrac{1}{4}\gamma_p^2} \right.$$

$$+ \sum_{j \neq j'} \frac{A_{j'}^* A_j}{(E_j - \bar{k} + (i/2)\gamma_p)(E_{j'} - \bar{k} - (i/2)\gamma_p)}$$

$$\left. \times \exp[i(E_{j'} - E_j] \exp[-(\Gamma_j + \Gamma_{j'})t/2] \right| \tag{128}$$

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. (128) in different time domains. Consider first short times after the excitation, i.e.,

$$\gamma_p^{-1} \lesssim t \ll \Gamma_j^{-1} \tag{129}$$

whereupon the exponential functions $\exp(-\Gamma_j t)$ can be set equal to unity and Eq. (128) takes the form of the Fourier sum

$$I_0(t) \propto \left| \sum_j \frac{A_j \exp(-iE_j t)}{E_j - \bar{k} + (i/2)\gamma_p} \right|^2 \tag{130}$$

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

$$A_j = (E_j - E_0 + (i/2)\Gamma_d)^{-1} \tag{131}$$

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 [Eq. (130)] for $t < \rho_j$ (where ρ_j is the average density of the $|j\rangle$ states) assumes the form

$$I_0(t) \propto \left| \frac{\exp(iE_0 t - \tfrac{1}{2}\Gamma_d t) - \exp(i\bar{k}t - \tfrac{1}{2}\gamma_p t)}{(E_0 - \bar{k}) + (i/2)(\gamma_p - \Gamma_d)} \right|^2 \tag{132}$$

Consider now another time domain where $t \sim \Gamma_j^{-1} \gg \gamma_p^{-1}$. The photon counting rate [Eq. (130)] consists of two contributions, a direct decay term

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

1. Energy Weighted Excitation of a Coarse Distribution

When the spacings between the $|j\rangle$ levels considerably exceed their widths, i.e.,

$$\Gamma_j, \Gamma_{j'} \ll |E_j - E_{j'}| \tag{133}$$

the oscillatory terms will exhibit fast oscillators on the relevant time scale $\sim \Gamma_j^{-1}$ and the second term on the right-hand side of Eq. (128) vanishes. The decay rate is

$$I(t) = \tfrac{1}{2}\gamma_N^2 \Gamma_N \sum_j \frac{|A_j|^2 \exp(-\Gamma_j t)}{(E_j - k)^2 + \tfrac{1}{4}\gamma_p^2} \tag{134}$$

being determined by a sum of exponentials.

2. Energy Weighted Excitation of a Moderately Dense Distribution

Now there are a large number of cross terms in Eq. (128). 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 again exhibit the decay mode given by Eq. (134).

From the point of view of the experimentalist, the decay mode (134) 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 implies that the following conditions pertaining to the molecular level scheme have to be satisfied

$$\Gamma_j < \rho_j^{-1} \qquad \Gamma_j < \Gamma_d \tag{135}$$

while concerning the pulse width we require that $\gamma_p < \Gamma_d$ together with Eq. (127) are obeyed. These two molecular conditions (135) are definitely satisfied for the case of interstate coupling in small molecules (Douglas, 1966; Bixon and Jortner, 1969). They are also realized (under proper excitation conditions) for the intermediate case, that of a small energy gap in a large molecule (Freed and Jortner, 1969; Jortner and Mukamel, 1974). In real life such systems (see Fig. 1) are characterized by a single doorway state $|s\rangle$, where Γ_s can be determined from the integrated oscillator strength, which is now spread among a large number of levels, all of which are active in

absorption and emission. In the low-lying electronic configuration of a triatomic the total width Γ_s of the doorway state is $\Gamma_s = \Gamma_s^r$, while the sum rule (117) implies that

$$\Gamma_s = \sum_j \Gamma_j \tag{136}$$

whereupon for level scrambling in a triatomic

$$\Gamma_s \simeq \Gamma_s^r / D \tag{137}$$

where $D \gg 1$ is the dilution factor. Equation (137) provides the theoretical basis for the Douglas effect (1966), i.e., long radiative decay times of triatomics, relative to what is expected on the basis of the integrated oscillator strength. In the case of a small energy gap in a large molecule $\Gamma_s = \Gamma_s^r + \Gamma_s^{nr}$, where the width Γ_s^{nr} originates from coupling of the doorway state to other intramolecular decay channels, the most common case being electronic relaxation to lower levels and in particular to the ground state. From Eq. (136) we now have

$$\Gamma_j \simeq \frac{\Gamma_s}{D} = \frac{\Gamma_s^r + \Gamma_s^{nr}}{D} \tag{137a}$$

where $D \gg 1$ again corresponds to a dilution factor. It is important to realize that the dilution effect due to interstate mixing of a doorway state with a sparse manifold involves not only the radiative component but also the nonradiative width.

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

B. Broad-Band Excitation

To handle the excitation by a "white" light pulse, we require that

$$\gamma_p \gg \Gamma_j \tag{138}$$

and

$$\gamma_p \gg |E_j - \bar{k}| \tag{139}$$

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

$$\gamma_p \gg \Gamma_d \tag{140}$$

The photon counting rate now assumes the simple form

$$I(t) = \frac{4\gamma_N^2 \Gamma_N}{3\gamma_p^2} \sum_{jj'} A_j A_{j'}^* \exp\left[-\frac{\Gamma_j + \Gamma_{j'}}{2} t + i(E_{j'} - E_j)t \right] \tag{141}$$

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. (130) assumes the form

$$I_0(t) \propto \left| \sum_j A_j \exp(-iE_j t) \right|^2 \qquad (142)$$

The instant time evolution following such excitation is determined just by the energy spread Γ_d. For a Lorentzian distribution of the coefficients A_j (131) we get the familiar decay mode

$$I_0(t) \propto \exp(-\Gamma_d t) \qquad (143)$$

This decay mode will be exhibited on the time scale

$$t < \rho_j^{-1} \qquad (144)$$

which is the Bixon–Jortner (1968) recurrence relation. This result is applicable, in principle, to any level structure, subjected to the conditions that the excitation mode will satisfy relations (138) and (139), and (144) is obeyed. The "white" excitation conditions cannot be accomplished in real life for the small molecule, but can be realized for the statistical limit (Jortner et al., 1969) and possibly for some intermediate cases. From the physical point of view Eq. (143) implies that the oscillatory terms in the photon counting rate in a large molecule result in shortening of the radiative decay time. The reciprocal lifetime on this short timescale is roughly given by the average (Bixon and Jortner, 1968) $\Gamma_d = 2\pi V_{sl}^2 \rho_l$ for a single doorway state $|s\rangle$ coupled to an $\{|l\rangle\}$ manifold.

Without alluding to any specific calculations we can conclude that for the general case of a discrete (complex) spectrum in the excited state, the only decay modes that can be exhibited in the time-resolved experiment are: (a) The real molecular decay times Γ_j^{-1} exhibited under all excitation conditions. (b) A short decay mode $\sim \Gamma_d^{-1}$ which monitors the inverse of the energetic spread of the eigenstates of H_{eff} and which is realized under the conditions of a coherent short excitation. (c) Decay modes characteristic of the fall time of the pulse, which provide "adiabatic following" type contributions to the time evolution (Courtens, 1972).

In the statistical limit, Γ_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, reduction of the emission quantum yield from unity and insensitivity of the decay time Γ_d^{-1} to external perturbations by an inert medium. To answer the question "under what conditions there are no other decay modes except Γ_d^{-1} exhibited in the decay pattern of a polyatomic

molecule?" we have to bear in mind that the widths Γ_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 perturbations. A complete theory of sequential decay was developed (Nitzan and Jortner, 1973), 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 Γ_j of the independently decaying levels (relative to Γ_d and to ρ_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. (141) vanish, resulting in

$$I(t) \propto \sum_j |A_j|^2 \exp(-\Gamma_j t) \tag{145}$$

Usually (Jortner and Mukamel, 1974; Nitzan et al., 1972) $\Gamma_j \ll \Gamma$, and a dilution effect of the lifetimes will be exhibited in the intermediate (or large) molecule on the time scale $\gamma_p^{-1} < \Gamma_d^{-1} \ll t \sim \Gamma_j^{-1}$, provided that this decay mode is amenable to experimental observation. Thus the conditions for observing the asymptotic behavior [Eq. (145)] are again given by Eqs. (137) and (137a), being identical for the case of coherent excitation to that of energy weighted excitation.

We have already argued that white 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 ρ_j is expected to be overwhelmingly large, whereupon any contribution to Γ_j from sequential decay processes will result in the condition

$$\Gamma_j > \rho_j^{-1} \tag{146}$$

violating condition (137). Thus relation (146) 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 $t < \rho_j^{-1}$, Γ_j^{-1} and the long component which is a sum of exponentials on the time scale $t \gtrsim \rho_j^{-1}$, Γ_j^{-1} provided that $\Gamma_j < \rho_j^{-1}$ and $\Gamma_j < \Gamma_d$. Such a state of affairs can be realized for a large molecule characterized by a small energy gap, whereupon $\rho_j \sim 10^3$ cm, while $\Gamma_j \ll 10^{-3}$ 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 method-

ology 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 (Zwanzig, 1961), which provides the ideological basis for kinetic schemes, breaks down when interference effects are exhibited, as is the situation for the intermediate level structure, whereupon the conventional kinetic picture is inapplicable.

XI. Photon Scattering from a Dissociative Continuum

There has been considerable experimental (Fouche and Chang, 1972; Holzer *et al.*, 1970; Kiefer and Bernstein, 1972a,b) and theoretical (Jacon *et al.*, 1971a,b; Berjot *et al.*, 1971a,b; Mukamel and Jortner, 1974b) interest in photon scattering from a dissociative molecular continuum. Such a molecular continuum can be smooth, as is the case for direct photodissociation of diatomics and triatomics (Herzberg, 1966), or structured, as is expected for the case of predissociation into a continuum which carries oscillator strength from the ground state (Fano, 1961). The theory of energy-resolved observables, i.e., photon scattering cross sections, photofragmentation cross sections, and lineshapes is well known for diatomics (Jacon *et al.*, 1971a,b; Mukamel and Jortner, 1974b) and was also worked out for polyatomics (Mukamel and Jortner, 1976). We shall address ourselves to the problem of time-resolved photon scattering from dissociative molecular states.

A. The Dissociative Continuum

We now consider the gross features of time-resolved photon scattering from a molecular dissociative continuum. The molecular level scheme consists of a bound ground electronic state having vibronic levels $\{|gv\rangle\}$ and an excited dissociative state $\{|dl\rangle\}$ with l denoting the relative translational energy of the dissociating fragments. The radiative coupling matrix elements within the Condon approximation are given by (Mukamel and Jortner, 1974b)

$$\langle dl, \text{vac} | H_{\text{int}} | gv, \mathbf{k} \rangle = \beta k^{-1/2} f_v(E_l) \tag{147}$$

where $f_v(E_l)$ is the nuclear Franck–Condon overlap integral between $|gv\rangle$ and the dissociative continuum, and β is a constant. The photon k is taken to be polarized along the direction of the transition moment between $|g\rangle$ and

$|d\rangle$. The (discrete) doorway states are now superpositions of the continuum states:

$$|N_v\rangle = \gamma_v^{-1} \int dE_l \rho_l |dl, \text{vac}\rangle\langle dl, \text{vac}|H_{int}|gv, \bar{k}\rangle \tag{148}$$

where ρ_l is the density of states in the dissociative continuum, and

$$\gamma_v^2 = \int dE_l \rho_l |\langle dl, \text{vac}|H_{int}|gv, \bar{k}\rangle|^2 \tag{149}$$

corresponds to a radiative width of the $|gv\rangle$ state. The molecular Green's function is (Mukamel and Jortner, 1974b) to second order in H_{int}:

$$G_{N_v N_0}(E) = \frac{\beta^2}{k} \int dE_l \frac{f_v^*(E_l)f_0(E_l)}{E - E_l + i\eta} \rho_l(E_l)$$

$$= \frac{\beta^2}{k}\left[-i\pi f_v^*(E)f_0(E)\rho_l(E) + \text{PP} \int dE_l \right.$$

$$\left. \times \frac{f_v^*(E_l)f_0(E_l)}{E - E_l + i\eta} \rho_l(E_l) \right] \tag{150}$$

with PP denoting the Cauchy principal part of the integral. Equation (150) is valid up to corrections of the order 10^{-6}–10^{-7} (Mukamel and Jortner, 1974b). Performing a Fourier transform of Eq. (150) we get for the molecular decay amplitude

$$C_{N_v N_0}(t) = \theta(t) \int dE f_v^*(E)f_0(E)\rho_l(E)$$

$$\times \exp(-iEt) \tag{151}$$

This result can be recast in an alternative form. Utilizing the definition

$$\Omega_v(t) = \int \exp(-iE_l t)f_v(E_l)(\rho_l(E_l))^{1/2} \beta\bar{k}^{-1/2} dE_l \tag{152}$$

we get

$$C_{N_v N_0}(t) = \theta(t) \int_{-\infty}^{\infty} d\tau \Omega_v(t - \tau)\Omega_0(\tau) \tag{153}$$

It is apparent from Eq. (151) that the molecular decay amplitudes behave like the Fourier components of the generalized Franck–Condon factor $f_v^*(E)f_0(E)$.

The decay amplitude $C_{N_0 N_0}(t)$ [Eq. (151)] which determines the elastic photon scattering from the dissociative continuum is determined by the Fourier transform of $|f_0(E)|^2$, i.e., the optical lineshape function at zero

temperature, in accord with the general discussion of Section VII. We note in passing that as $\sigma_a(E) \propto |f_0(E)|^2$ for dissociative continua is quasi-Gaussian, the above-mentioned decay amplitude is not exponential. Usually the half linewidth of $\sigma_a(E)$ is of the order of $\Delta \simeq 10^3 - 10^4$ cm^{-1} so we expect that $C_{N_0 N_0}(t)$ (and the other decay amplitudes) in Eq. (151) will decay on the time scale of $\Delta^{-1} \simeq 10^{-14}$-$10^{-15}$ sec, which is the "duration" of the photodissociation process from the point of view of the experimentalist. At the risk of triviality we mention that a time-resolved photon counting experiment on a photodissociating system requires a light source where the decay time of $\varphi(\tau)$ is shorter than or comparable to Δ^{-1}, which is at present impractical in the optical region.

From the point of view of general methodology we wish to note that as the partial photon counting rates to all the final $|gv\rangle$ channels are determined by the Fourier transforms of the products $f_0(E) f_v^*(E)$, these quantities for inelastic scattering ($v \neq 0$) cannot be obtained from absorption spectroscopy which just yields the "diagonal" terms $|f_v(E)|^2$. This analysis of a special model system concurs with the general discussion of Section VII.

B. Interference between a Discrete State and a Dissociative Continuum

Finally, we focus attention on the Fano (1961) level scheme, which consists of a single ground state $|g\rangle$ coupled radiatively to a discrete state $|s\rangle$ and to a dissociative continuum $\{|dl\rangle\}$, while $|s\rangle$ is coupled to $\{|dl\rangle\}$ via nonadiabatic intramolecular coupling H_v. The relevant matrix elements are

$$\langle dl, \text{vac}|H_{\text{int}}|g, k\rangle = V_{gd}(E_l) \tag{154a}$$

$$\langle s, \text{vac}|H_{\text{int}}|g, k\rangle = V_{sg}(E_q) \tag{154b}$$

$$\langle dl, \text{vac}|H_v|s, \text{vac}\rangle = V_{ds}(E_l) \tag{154c}$$

The system is characterized by a single doorway state

$$|N, \text{vac}\rangle = \gamma^{-1}\left[V_{sg}|s\rangle + \int dE_l \rho_l V_{dg}(E_l)|dl\rangle\right] \tag{155}$$

where

$$\gamma^2 = |\langle s, \text{vac}|H_{\text{int}}|g, \bar{k}\rangle|^2$$
$$+ \int dE_l \rho_l(E_l)|\langle dl|H_{\text{int}}|g, \bar{k}\rangle|^2 \tag{156}$$

The detailed calculation of the T-matrix elements have been carried out elsewhere (Mukamel and Jortner, 1974b), resulting in the following expres-

sions for the Green's function $G_{NN}(E)$:

$$G_{NN}(E) = \gamma^{-2} \left\{ A^l(E) + \frac{(V_{gs} + A^{ls}(E))(V_{sg} + \bar{A}^{ls}(E))}{E - E_s + (i/2)\Gamma_s} \right\} \tag{157}$$

defined in terms of the following Hilbert transforms:

$$A^l(E) = \int dE_l \frac{|V_{dg}(E_l)|^2}{E - E_l + i\eta} \rho(E_l) \tag{158a}$$

$$A^{ls}(E) = \int dE_l \frac{V_{gd}(E_l)V_{ds}(E_l)}{E - E_l + i\eta} \rho(E_l) \tag{158b}$$

and

$$\bar{A}^{ls}(E) = \int dE_l \frac{V^*_{dg}(E_l)V^*_{ds}(E_l)}{E - E_l + i\eta} \rho(E_l) \tag{158c}$$

Equation (157) is valid to second order in H_{int}, being accurate up to the order of $\sim 10^{-6} - 10^{-7}$.

For the purpose of evaluating the molecular decay amplitudes it is convenient to define the following auxiliary functions:

$$\Omega_{dg}(t) = \int dE_l V_{dg}(E_l)[\rho(E_l)]^{1/2} \exp(-iE_l t) \tag{159}$$

$$\Omega_{ds}(t) = \int dE_l V_{ds}(E_l)[\rho(E_l)]^{1/2} \exp(-iE_l t) \tag{159a}$$

$$\Omega_s(t) = (2\pi i)^{-1} \int dE \exp(-iEt) \left(E - E_s + \frac{i}{2}\Gamma_s \right)^{-1}$$
$$= \theta(t) \exp[(-iE_s - \tfrac{1}{2}\Gamma_s)t] \tag{159b}$$

We can now express the Fourier transform of A^l, A^{ls}, and $\bar{A}^{ls}$ [Eqs. (158a)–(158c)] in terms of these functions as follows:

$$\int dE A^l(E) \exp(-iEt) = 2\pi i \theta(t)$$

$$\times \int dE_l |V_{dg}(E_l)|^2 \rho(E_l) \exp(-iE_l t)$$

$$= i\theta(t) \int_{-\infty}^{\infty} d\tau \Omega_{dg}(t-\tau)\Omega^*_{dg}(-\tau)$$

$$\equiv i\theta(t)a^l(t) \tag{160}$$

$$\int dE A^{ls}(E) \exp(-iEt) = \theta(t) 2\pi i$$

$$\times \int dE_i V_{dg}(E_i) V_{ds}(E_i) \rho(E_i) \exp(-iE_i t)$$

$$= i\theta(t) \int_{-\infty}^{\infty} d\tau \Omega_{ds}(t - \tau) \Omega_{dg}^*(-\tau)$$

$$\equiv i\theta(t) a^{ls}(t) \tag{161}$$

$$\int dE \tilde{A}^{ls}(E) \exp(-iEt) = i\theta(t) a^{ls*}(t) \tag{162}$$

Following straightforward algebraic manipulations, the molecular decay amplitude assumes the form

$$C_{NN}(t) = \gamma^{-2} \theta(t) \left\{ |V_{sg}|^2 \int dE_i \exp(-iE_i t) \Omega_s(t) \right.$$

$$+ \int dE_i \exp(-iE_i t) |V_{dg}(E_i)|^2$$

$$+ \frac{i}{2\pi} \int_0^t d\tau [V_{sg} a^{ls}(t - \tau) + V_{gs} a^{ls*}(-t + \tau)] \Omega_s(\tau)$$

$$- \frac{1}{(2\pi)^2} \int_0^t d\tau \int_0^t d\tau' a^{ls}(t - \tau) a^{ls*}(-\tau + \tau') \Omega_s(\tau') \right\} \tag{163}$$

The molecular decay amplitude (163) consists of four contributions: the first term is just the decay of a single discrete state (see Section (VIII)), the second term corresponds to the contribution from the dissociative continuum discussed in Section (XI.A), while the last two terms represent interference contributions. The decay mode in this case corresponds to the Fourier transform of the Green's function which is given by the imaginary part of Eq. (157), which constitutes a slight generalization of Fano's lineshape formula (Fano, 1961).

XII. Epilogue

We have advanced a general theoretical framework for the treatment of time-resolved photon scattering from a single molecule which is characterized by an arbitrarily complex level structure. Utilizing a quantum mechanical description of light pulses in terms of wave packets of one-photon states, the results are valid for weak fields, within the framework of the rotating-wave approximation. The latter approximation is valid also for strong fields, as in the case of the well-known Rabi (1936) two-level problem. Thus, the present treatment is of general applicability for (a) a general level-structure, (b) a collision-free molecule, and (c) excitation by weak electromagnetic fields. Concerning point (a) the formulation of intramolecular dynamics as inferred from time-resolved and energy-resolved photon scattering provides a laboratory tool for the elucidation of the diverse and interesting decay modes which were observed in electronically excited states of polyatomic molecules. It should be noted, however, that we have focused attention on intramolecular coupling and relaxation between different (zero-order) electronic configurations. The interesting problem of intramolecular vibrational relaxation within a single electronic configuration (Fischer, 1972; Nitzan and Jortner, 1972; Nordholm and Rice, 1974) was not considered. This problem is of considerable interest regarding chemical activation, unimolecular processes, mass spectrometry (Lee et al., 1972), infrared chemiluminescence (Moehlmann et al., 1974), optical selection studies (Rice, 1975), relaxation of large molecules in molecular beams (Sander et al., 1976), and molecular photofragmentation in intense laser fields (Bloembergen, 1975; Mukamel and Jortner, 1976).

Concerning collisional perturbations, point (b), the theory was quite fully developed (Mukamel et al., 1975) for the simple case of a single resonance. For the interesting case of a complex level structure, general conclusions were drawn regarding the insensitivity of excited states, which correspond to the statistical limit, to collisional perturbations (Jortner and Mukamel, 1974, 1975). The pronounced effects of collisions in the intermediate level structure require a complete study. A first step in that direction was undertaken by Freed (1976).

Finally, it will be interesting to consider point (c) regarding the behavior of complex molecules in intense electromagnetic fields. The problems of excitation modes and intramolecular dynamics in intense laser fields are of considerable interest in relation to molecular photofragmentation and isotope separation in intense laser fields (Ambartsumyan et al., 1975a,b,c; Robinson et al., 1975; Lyman et al. (1975); Bloembergen, 1975; Mukamel and

Jortner, 1976). The theoretical understanding of these problems is still in embryonic stages and will open new horizons to the elucidation of new and exciting molecular phenomena.

Appendix

The Time-Dependent Wave Functions

Let $\psi(t')$ be the wave function of the system at a given time t'. Then, for any time t we have

$$\psi(t) = \exp[-iH(t - t')]\psi(t') \tag{A1}$$

which for $t > t'$ can be rewritten in the form:

$$\psi(t) = -(2\pi i)^{-1} \int dE \exp[-iE(t - t')]G(E)\psi(t') \tag{A2}$$

where $G(E)$ is the retarded Green's function of the system

$$G(E) = (E - H + i\eta)^{-1} \qquad \eta \to 0^+ \tag{A3}$$

We construct a state of the radiation field $\psi_r(0)$ in the form of a wave packet of eigenstates of H_r traveling along the x axis and arriving at the origin at $t \approx 0$ in the absence of the interaction with the molecular system.

We expect that at sufficiently early times t' the system is not subjected to the interaction H_{int} since the photon wave packet is far from the origin, so that

$$\psi(t') \simeq \exp(-iH_0 t')\psi_0(0) \qquad t' \overset{\bullet}{\to} -\infty \tag{A4}$$

where $\psi_0(0)$ is the wave function the total system would have at $t = 0$ in the absence of H_{int}.

$$\psi_0(0) = \psi_r(0)\psi_m \tag{A5}$$

ψ_m is the initial molecular wave function (usually an eigenstate of H_m).

Equation (A4) thus contains the boundary conditions for our problem. Substitution of (A4) in (A2) yields

$$\psi(t) = -(2\pi i)^{-1} \int dE \exp[-iE(t - t')]G(E) \exp(-iH_0 t')\psi_0(0) \tag{A6}$$

Making use of the Dyson equation

$$G = G_0 + G_0 H_{\text{int}} G \tag{A7}$$

where

$$G_0 = (E - H_0 + i\eta)^{-1} \tag{A8}$$

results in

$$\psi(t) = \psi_0(t) - (2\pi i)^{-1} \int dE \exp(-iEt)GH_{int}$$

$$\times \frac{\exp[i(E - H_0)t']}{E - H_0 + i\eta} \psi_0(0) \tag{A9}$$

Here $\psi_0(t) = \exp(-iH_0 t)\psi_0(0)$ is the hypothetical wave function of our system at time t in the absence of H_{int}. We now make use of the identity;

$$\frac{\exp[i(E - H_0)t']}{E - H_0 + i\eta} = -i \int_{-\infty}^{\infty} \theta(\tau - t') d\tau$$

$$\times \exp[i(E - H_0 + i\eta)\tau] \xrightarrow{t' \to -\infty} -2\pi i$$

$$\times \delta(E - H_0) = G_0 - G_0^+ \tag{A10}$$

and Eq. (A9) results in

$$\psi(t) = \psi_0(t) + (2\pi i)^{-1} \int dE \exp(-iEt)$$

$$\times GH_{int}(G_0 - G_0^+)\psi_0(0) \tag{A11}$$

References

Ambartsumyan, R. V., Letokhov, V. S., Ryabov, E. A., and Chekalin, N. V. (1975a). *JETP Lett.* (*Engl. Transl.*) **20**, 273.

Ambartsumyan, R. V., Gorkhov, Yu.A., Letokhov, V. S., and Makarov, G. N. (1975b). *JETP Lett.* (*Engl. Transl.*) **21**, 171.

Ambartsumyan, R. V., Chekalin, N. V., Letokhov, V. S., and Ryabov, E. A. (1975c). *Chem. Phys. Lett.* **36**, 301.

Ben-Reuven, A. (1975). *Adv. Chem. Phys.* **33**, 235.

Berg, J. O., Langhoff, C. A., and Robinson, G. W. (1974). *Chem. Phys. Lett.* **29**, 305.

Berjot, M., Jacon, M., and Bernard, L. (1971a). *Opt. Commun.* **4**, 117.

Berjot, M., Jacon, M., and Bernard, L. (1971b). *Opt. Commun.* **4**, 246.

Bixon, M., and Jortner, J. (1968). *J. Chem. Phys.* **48**, 715.

Bixon, M., and Jortner, J. (1969). *J. Chem. Phys.* **50**, 3284.

Bloembergen, N. (1975). *Opt. Commun.* **15**, 416.

Chock, D., Jortner, J., and Rice, S. A. (1969). *J. Chem. Phys.* **49**, 610.

Cohen Tannoudji, C. (1968). *In* "Introduction a l'Electronique Quantique, Cours de l'Association Vandoire des Recherches en Physique," p. 92. Saas Fee.

Courtens, E. (1972). *In* "Laser Handbook" (F. T. Arecchi and E. O. Schultz, eds.), p. 1259. North-Holland Publ., Amsterdam.

where

$$G_0 = (E - H_0 + i\eta)^{-1} \qquad \text{(A8)}$$

results in

$$\psi(t) = \psi_0(t) - (2\pi i)^{-1} \int dE \exp(-iEt) G H_{\text{int}}$$

$$\times \frac{\exp[i(E - H_0)t']}{E - H_0 + i\eta} \psi_0(0) \qquad \text{(A9)}$$

Here $\psi_0(t) = \exp(-iH_0 t)\psi_0(0)$ is the hypothetical wave function of our system at time t in the absence of H_{int}. We now make use of the identity;

$$\frac{\exp[i(E - H_0)t']}{E - H_0 + i\eta} = -i \int_{-\infty}^{\infty} \theta(\tau - t') \, d\tau$$

$$\times \exp[i(E - H_0 + i\eta)\tau] \xrightarrow{t \to -\infty} -2\pi i$$

$$\times \delta(E - H_0) = G_0 - G_0^+ \qquad \text{(A10)}$$

and Eq. (A9) results in

$$\psi(t) = \psi_0(t) + (2\pi i)^{-1} \int dE \exp(-iEt)$$

$$\times G H_{\text{int}}(G_0 - G_0^+)\psi_0(0) \qquad \text{(A11)}$$

References

Ambartsumyan, R. V., Letokhov, V. S., Ryabov, E. A., and Chekalin, N. V. (1975a). *JETP Lett.* (Engl. Transl.) **20**, 273.

Ambartsumyan, R. V., Gorkhov, Yu.A., Letokhov, V. S., and Makarov, G. N. (1975b). *JETP Lett.* (Engl. Transl.) **21**, 171.

Ambartsumyan, R. V., Chekalin, N. V., Letokhov, V. S., and Ryabov, E. A. (1975c). *Chem. Phys. Lett.* **36**, 301.

Ben-Reuven, A. (1975). *Adv. Chem. Phys.* **33**, 235.

Berg, J. O., Langhoff, C. A., and Robinson, G. W. (1974). *Chem. Phys. Lett.* **29**, 305.

Berjot, M., Jacon, M., and Bernard, L. (1971a). *Opt. Commun.* **4**, 117.

Berjot, M., Jacon, M., and Bernard, L. (1971b). *Opt. Commun.* **4**, 246.

Bixon, M., and Jortner, J. (1968). *J. Chem. Phys.* **48**, 715.

Bixon, M., and Jortner, J. (1969). *J. Chem. Phys.* **50**, 3284.

Bloembergen, N. (1975). *Opt. Commun.* **15**, 416.

Chock, D., Jortner, J., and Rice, S. A. (1969). *J. Chem. Phys.* **49**, 610.

Cohen Tannoudji, C. (1968). *In* "Introduction a l'Electronique Quantique, Cours de l'Association Vandoire des Recherches en Physique," p. 92. Saas Fee.

Courtens, E. (1972). *In* "Laser Handbook" (F. T. Arecchi and E. O. Schultz, eds.), p. 1259. North-Holland Publ., Amsterdam.

Chutjian, A. (1969). *J. Chem. Phys.* **51**, 5414.
Chutjian, A., Link, J. L., and Brewer, L. (1967). *J. Chem. Phys.* **46**, 2666.
Douglas, A. E. (1966) *J. Chem. Phys.* **45**, 1007.
Fano, U. (1961). *Phys. Rev.* **124**, 1866.
Feschbach, H. (1974). *Rev. Mod. Phys.* **46**, 1.
Feschbach, H., Kerman, A. K., and Lemmer, R. H. (1967). *Ann. Phys. (N.Y.)* **41**, 230.
Fischer, S. F. (1972) *Chem. Phys. Lett.* **17**, 25.
Fouche, D. G., and Chang, R. K. (1972) *Phys. Rev. Lett.* **29**, 536.
Freed, K. F. (1970). *J. Chem. Phys.* **52**, 1345.
Freed, K. F. (1972). *Top. Curr. Chem.* **31**, 105.
Freed, K. F. (1976). *J. Chem. Phys.* **64**, 1604.
Freed, K. F., and Jortner, J. (1969). *J. Chem. Phys.* **50**, 2916.
Friedman, J. M., and Hochstrasser, R. M. (1974). *Chem. Phys.* **6**, 155.
Glauber, R. (1969). *Proc. Int. Sch. Phys. "Enrico Fermi"* **11**, 11.
Goldberger, M. L., and Watson, R. M. (1964). "Collision Theory." Wiley, New York.
Haken, H. (1970). *In* "Handbuch der Physik" (S. Flügge, ed.), Vol. 25, Part IIC, p. 1. Springer-Verlag, Berlin and New York.
Henry, B. R., and Kasha, M. (1968). *Annu. Rev. Phys. Chem.* **19**, 161.
Herzberg, G. (1966). "Electronic Spectra of Polyatomic Molecules." Van Nostrand-Reinhold, Princeton, New Jersey.
Hilborn, R. C. (1975). *Chem. Phys. Lett.* **32**, 76.
Holzer, W., Murphy, W. F., and Bernstein, H. J. (1970). *J. Chem. Phys.* **52**, 399.
Huber, D. L. (1969). *Phys. Rev.* **93**, 178.
Jacon, M., Berjot, M., and Bernard, L. (1971a). *C.R. Hebd. Seances Acad. Sci. Ser. B* **273**, 595.
Jacon, M., Berjot, M., and Bernard, L. (1971b). *C.R. Hebd. Seances Acad. Sci. Ser. B* **273**, 956.
Jortner, J., and Berry, R. S. (1968). *J. Chem. Phys.* **48**, 2757.
Jortner, J., and Mukamel, S. (1974). *In* "The World of Quantum Chemistry" (R. Daudel and B. Pullman, eds.), p. 205. Reidel Publ., Dordrecht, Netherlands.
Jortner, J., and Mukamel, S. (1975). *Phys. Chem., Ser. Two* **13**, 327.
Jortner, J., Rice, S. A., and Hochstrasser, R. M. (1969). *Adv. Photochem.* **7**, 149.
Kiefer, W., and Bernstein, H. J. (1972a). *J. Mol. Spectrosc.* **43**, 366.
Kiefer, W., and Bernstein, H. J. (1972b). *J. Chem. Phys.* **57**, 3017.
Kroll, N. M. (1964). *In* "Quantum Optics and Electronics" (C. De Witt, A. Blandin, and C. Cohen Tannoudji, eds.), p. 3. Gordon & Breach, New York.
Kubo, R. (1959). *Lect. Theor. Phys.* **1**, 181.
Lahmani, F., Tramer, A., and Tric, C. (1974). *J. Chem. Phys.* **60**, 4431..
Lane, A. M. (1969). *In* "Isospin in Nuclear Physics" (D. H. Wilkinson, ed.), p. 509. North-Holland Publ., Amsterdam.
Lee, A., Le Roy, R., Herman, F., Wolfgang, R., and Tully, J. C. (1972). *Chem. Phys. Lett.* **12**, 569.
Loudon, R. (1973). "The Quantum Theory of Light." Oxford Univ. Press (Clarendon), London and New York.
Louisell, W. H. (1964). "Radiation and Noise in Quantum Electronics," Chapter 7. McGraw-Hill, New York.
Lyman, J. L., Jensen, R. J., Rink, J., Robinson, C. P., and Rockwood, S. D. (1975). *Appl. Phys. Lett.* **27**, 87.
Mahaux, C. (1973). *Annu. Rev. Nucl. Sci.* **23**, 193.
Metiu, H., Ross, J., and Nitzan, A. (1975). *J. Chem. Phys.* **63**, 1289.
Moehlmann, J. G., Gleaves, J. T., Hudgens, J. W., and McDonald, J. D. (1974). *J. Chem. Phys.* **60**, 2040.
Mower, L. (1966). *Phys. Rev.* **142**, 799.

Mukamel, S., and Jortner, J. (1974a). *J. Chem. Phys.* **61**, 227.

Mukamel, S., and Jortner, J. (1974b). *J. Chem. Phys.* **61**, 436.

Mukamel, S., and Jortner, J. (1975). *J. Chem. Phys.* **62**, 3609.

Mukamel, S., and Jortner, J. (1976). *J. Chem. Phys.* **65**, 5204.

Mukamel, S., Ben-Reuven, A., and Jortner, J. (1975). *Phys. Rev.* A **12**, 947.

Mukamel, S., Ben-Reuven, A., and Jortner, J. (1976). *J. Chem. Phys.* **64**, 3971.

Nitzan, A., and Jortner, J. (1972). *J. Chem. Phys.* **57**, 2870.

Nitzan, A., and Jortner, J. (1973). *Theor. Chim. Acta* **30**, 217.

Nitzan, A., Rentzepis, P. M., and Jortner, J. (1972). *Mol. Phys.* **22**, 585.

Nordholm, S., and Rice, S. A. (1974). *J. Chem. Phys.* **61**, 203.

Omont, A., Smith, E. W., and Cooper, J. (1972). *Astrophys. J.* **175**, 185.

Rabi, I. I. (1936). *Phys. Rev.* **51**, 652.

Rhodes, W. (1969). *J. Chem. Phys.* **50**, 2885.

Rhodes, W. (1971). *Chem. Phys. Lett.* **11**, 179.

Rhodes, W. (1974). *Chem. Phys.* **4**, 259.

Rice, S. A. (1975). *In* "Excited States" (E. C. Lim, ed.), Vol. 2, p. 111. Academic Press, New York.

Robinson, C. P. (1975). *Proc. Laser Spectrosc. Conf., 2nd*, Megève, p. 275.

Robinson, G. W. (1967). *J. Chem. Phys.* **47**, 1967.

Robinson, G. W. (1973). *In* "Excited States" (E. C. Lim, ed.), Vol. 1, p. 1. Academic Press, New York.

Robinson, G. W., and Langhoff, C. A. (1974). *Chem. Phys.* **1**, 1.

Rousseau, D. L., Patterson, G. D., and Williams, P. F. (1975). *Phys. Rev. Lett.* **34**, 1306.

Sander, R. K., Soep, B., and Zare, R. N. (1976). *J. Chem. Phys.* **64**, 1242.

Schlag, E. W., Schneider, S., and Fischer, S. F. (1971). *Annu. Rev. Phys. Chem.* **22**, 465.

Schweber, S. S. (1961). "An Introduction to Relativistic Quantum Field Theory." Harper, New York.

Shen, Y. R. (1974). *Phys. Rev.* B **9**, 622.

Shore, B. W. (1967). *Rev. Mod. Phys.* **39**, 439.

Voltz, R. (1974). *Org. Mol. Photophys.* **2**, 217.

Williams, P. F., Rousseau, D. L., and Dworetsky, S. H. (1974). *Phys. Rev. Lett.* **32**, 196.

Zwanzig, R. (1961). *Lect. Theor. Phys.* **3**, 106.