

Lifetimes for resonance fluorescence and near resonance Raman scattering

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In this paper we present a quantum mechanical treatment of time resolved resonant and near resonant light scattering from a molecular system. The time resolved decay pattern is characterized by just two types of lifetimes, those specifying the molecular system and those characterizing the light pulse, while the off resonance energy parameter affects the total intensity and, in some cases, the relative intensities of the different decay components. The theoretical results for the "isolated" molecule are confronted with the recent experimental data of Williams, Rousseau, and Dworetzky [Phys. Rev. Lett. **32**, 196 (1974)] for resonance and near resonance photon scattering from I_2 . Finally, we present a general scheme for handling photon scattering from a multilevel molecular system.

I. INTRODUCTION

In conventional resonance fluorescence studies, when the energy of the incoming photon coincides with an atomic or a molecular transition energy, the observed radiative decay pattern is determined by the total homogeneous width of the excited state.¹⁻⁵ When the excitation energy is moved away from the molecular resonance, the time resolved decay pattern contains an additional very short component, which was assigned to a "Raman-like" process. The transition from resonance, fluorescence (RF) to near resonance Raman scattering (NRRS)⁶ while changing the mean frequency of the pulse, raises some interesting questions regarding the proper interpretation of such time resolved photon scattering experiments, which were reported just very recently.⁵ In the present paper, we provide a quantum-mechanical treatment of this problem. We conclude that the time resolved decay pattern for scattering of a photon wave packet from an atomic or a molecular system is characterized by just two types of lifetimes (or rather energy parameters): those specifying the energy levels of the molecular system and those associated with the light pulse. No new lifetimes enter into the decay pattern while the (mean) pulse frequency is tuned away from a molecular resonance. The transition from RF to NRRS is manifested only by changes in the total intensity and in the relative intensities of the above-mentioned different components. Finally, we would like to emphasize that energy-time uncertainty type arguments can be recast in terms of the time delay matrix for photon scattering,⁷ which is expressed in terms of a weighted average over the two types of the characteristic lifetimes, and does not result in any new observable decay times.

Section II is devoted to the study of the simplest possible system, that of a time resolved decay of a single molecular resonance which corresponds to a bound molecular state. In Sec. III we present several explicit results for the transition from RF to NRRS using different shapes for the light pulse. In Sec. IV we provide a brief discussion of the lifetime matrix and its relevance to photon scattering experiments. Finally, in Sec. V we extend the theory to handle photon scattering for any

general molecular level structure of bound molecular states.

II. TIME RESOLVED PHOTON SCATTERING

In order to consider a typical scattering experiment of a light pulse from a molecular system we shall consider separately the description of the time profile of the photon wave packet and the relevant molecular decay function.

Weak light pulses can be described in terms of a wave packet of one photon states²⁻⁴

$$\psi_p = \sum_{\mathbf{k}} A_{\mathbf{k}} |\mathbf{k}\rangle = \int \frac{d^3\mathbf{k}}{\sqrt{k}} A_{\mathbf{k}} |\mathbf{k}\rangle, \quad (\text{II. 1})$$

where \mathbf{k} is the photon wave vector, k corresponds to the photon energy,⁸ and $|\mathbf{k}\rangle$ labels the one photon state subjected to the normalization condition $\langle \mathbf{k} | \mathbf{k}' \rangle = k \delta(\mathbf{k} - \mathbf{k}')$. For the sake of convenience we shall omit the label for the photon polarization in $|\mathbf{k}\rangle$.

The photon density per unit volume at the time t is given by⁹

$$\rho(x, y, z, t) = \frac{1}{(2\pi)^3} |\bar{\varphi}(\mathbf{Q})|^2, \quad (\text{II. 2})$$

where

$$\bar{\varphi}(\mathbf{Q}) = \int d^3\mathbf{k} \exp(-i\mathbf{k} \cdot \mathbf{Q}) A_{\mathbf{k}} \quad (\text{II. 3})$$

and $\mathbf{K} = (k, k_x, k_y, k_z)$, $\mathbf{Q} = (ct, x, y, z)$ represent the energy-momentum and the time-space four vectors, respectively. For a light pulse travelling along the x axis, Eqs. (II. 1)–(II. 3) take the simple form

$$\psi_p = \sum_k A_k |k\rangle = \int \frac{dk}{\sqrt{k}} A_k |k\rangle, \quad (\text{II. 1a})$$

$$\rho(x, t) = \frac{1}{2\pi} |\bar{\varphi}(x + ct)|^2, \quad (\text{II. 2a})$$

$$\bar{\varphi}(\mathbf{Q}) = \bar{\varphi}(x + ct) = \int dk A_k \exp[-ik(x + ct)]. \quad (\text{II. 3a})$$

Thus the four vector $\mathbf{Q} = \mathbf{x} + ct$ reduces to a scalar while

$(1/2\pi)|\bar{\varphi}(x+ct)|^2$ corresponds to the time dependent spatial profile of the pulse. Let us now define the Fourier transform of the wave packet amplitudes

$$\begin{aligned}\bar{\varphi}(t) &= \int dk A_k \exp(-ikt), \\ A_k &= \frac{1}{2\pi} \int dt \bar{\varphi}(t) \exp(ikt).\end{aligned}\quad (\text{II. 4})$$

From Eqs. (II. 4) and (II. 3a) we conclude that $\bar{\varphi}(t) = \bar{\varphi}(x=0, t)$ whereupon $(2\pi)^{-1}|\bar{\varphi}(t)|^2$ provides us with the photon density at $x=0$. It is proper to refer to $\bar{\varphi}(t)$ as the field amplitude. Thus from Eq. (II. 4) we conclude that the light pulse can be characterized by its amplitudes $\{A_k\}$ or alternatively by the field amplitude function. The general features of the light pulse can be further described by two types of parameters: (1) an energy parameter \bar{k} defining the mean energy; (2) characteristic times which specify the pulse duration and its characteristic rise and fall times. To introduce the energetic parameter \bar{k} it is convenient to recast Eq. (II. 4) in the form

$$\varphi(t) = \int dk \exp[i(\bar{k}-k)t] A_k = \bar{\varphi}(t) \exp(i\bar{k}t), \quad (\text{II. 5})$$

so that $\varphi(t)$ is determined by the pulse characteristic times. For our discussion we shall specify two such parameters: (1) The pulse duration T ; (2) the characteristic rise and fall time of the pulse τ_p . The latter is typically appreciably shorter than T . The definition of τ_p implies an exponential decay (and buildup) of the pulse. Other decay modes could be used, however, this is not essential.

We shall now consider the simplest molecular system which consists of two discrete levels, a ground state $|g\rangle$ and an excited state $|s\rangle$. The eigenstates of the zero order Hamiltonian (consisting of the molecular and the radiation field Hamiltonians) are $|g, \mathbf{k}\rangle$ and $|s, \text{vac}\rangle$. The $|s\rangle$ level is characterized by a total radiative width Γ which corresponds to a lifetime $\tau_s = \Gamma^{-1}$. Denoting the ground state energy by $E_g = 0$ the single molecular resonance is characterized by the energy $\bar{E}_s = E_s + D_s$, where the level shift D_s is usually negligibly small. The off resonance energy parameter is

$$\Delta = \bar{k} - \bar{E}_s \quad (\text{II. 6})$$

To explore the consequences of the interaction of the molecular system with the radiation field, we define the probability $P_s(t)$ for finding the system at time t in the zero photon state $|s, \text{vac}\rangle$, which is expressed in terms of a convolution of the field amplitude and a molecular decay amplitude⁴

$$P_s(t) = |V_{sg}|^2 \left| \int_0^t d\tau \bar{\varphi}(t-\tau) C_{ss}(\tau) \right|^2, \quad (\text{II. 7})$$

where V_{sg} is the electromagnetic coupling matrix element between $|g, \mathbf{k}\rangle$ and $|s, \text{vac}\rangle$, so that $\Gamma = 2\pi |V_{sg}|^2 \rho_r(\bar{k})$, where $\rho_r(\bar{k})$ denotes the density of the states in the radiation field at the vicinity of the energy \bar{k} . $C_{ss}(t)$ is the decay amplitude which corresponds to the Fourier transform of the matrix element of the Green's function. For the present case we have

$$\begin{aligned}C_{ss}(t) &= (2\pi i)^{-1} \int_{-\infty}^{\infty} dE \exp(-iEt) \left(E - E_s - D_s + \frac{i}{2}\Gamma \right)^{-1} \\ &= \exp(-i\bar{E}_s t) \exp(-\Gamma/2t).\end{aligned}\quad (\text{II. 8})$$

Making use of Eqs. (II. 5)–(II. 8) the probability function (II. 7) takes the form

$$P_s(t) = |V_{sg}|^2 |\phi_s(t)|^2, \quad (\text{II. 9})$$

where

$$\phi_s(t) = \int_0^t d\tau \varphi(\tau) \exp[-(\Gamma/2)(t-\tau)] \exp(-i\Delta t). \quad (\text{II. 9a})$$

The experimental photon counting rate has now to be carefully defined. In general, the experimentalist is interested in monitoring all the outgoing photons except those corresponding to the original light pulse (II. 1a) (i.e., except those photons having the same spatial direction and polarization as the original pulse). The photon counting rate $F(t)$ is expressed in terms of the time derivative of the probability function for finding the system in any state $|g, \mathbf{k}'\rangle$, where $\mathbf{k}' \neq \mathbf{k}$ in Eq. (II. 1a). A straightforward extension of our previous study⁴ results in

$$F(t) = \Gamma P_s(t) = \Gamma |V_{sg}|^2 |\phi_s(t)|^2, \quad (\text{II. 10})$$

where we have utilized Eq. (II. 9). The integral $\phi_s(t)$ which determines the experimental photon counting rate is determined by the four parameters: the molecular decay width Γ , the off resonance energy Δ , and the characteristic times specifying the light pulse $\tau_p = \gamma^{-1}$, and T .

It is important to notice that Eq. (II. 10) is valid within the framework of two assumptions, concerning a weak electromagnetic field and the usual conditions for exponential decay³ which is usually the case provided that $\Gamma \ll E_s$. We shall now proceed to explore the time resolved decay pattern for some typical pulse profiles.

III. DECAY OF A SINGLE MOLECULAR RESONANCE

In order to elucidate the effects of the various pulse parameters on the decay pattern, let us first consider a square pulse of the form:

$$\begin{aligned}\varphi(\tau) &= 1 \quad 0 < \tau < T \\ &= 0 \quad \tau > T\end{aligned}\quad (\text{III. 1})$$

whose energy profile is

$$\begin{aligned}A_k &= (2\pi)^{-1} \int_0^T d\tau \varphi(\tau) \exp[i(k-\bar{k})\tau] \\ &= \frac{1}{2\pi} \frac{\exp[i(k-\bar{k})T] - 1}{i(k-\bar{k})} \\ &= \frac{1}{2\pi} \left[\frac{\sin(k-\bar{k})T}{k-\bar{k}} - \frac{2\sin^2[\frac{1}{2}(k-\bar{k})T]}{i(k-\bar{k})} \right].\end{aligned}\quad (\text{III. 2})$$

Utilizing Eq. (II. 9a) we obtain

$$\begin{aligned}\phi_s(t) &= i \frac{\exp(-i\Delta t) - \exp(-\frac{1}{2}\Gamma t)}{\Delta + i\frac{1}{2}\Gamma}; \quad t \leq T \\ &= i e^{-1/2\Gamma(t-T)} \frac{\exp(-i\Delta T) - \exp(-\frac{1}{2}\Gamma T)}{\Delta + i\frac{1}{2}\Gamma}; \quad t \geq T\end{aligned}\quad (\text{III. 3})$$

which gives for the decay pattern

$$F(t) = \Gamma |V_{sr}|^2 \frac{1 + \exp(-\Gamma t) - 2\exp(-\frac{1}{2}\Gamma t)\cos\Delta t}{\Delta^2 + \frac{1}{4}\Gamma^2}; \quad t \leq T$$

$$= \Gamma |V_{sr}|^2 \frac{1 + \exp(-\Gamma T) - 2\exp(-\frac{1}{2}\Gamma T)\cos\Delta T}{\Delta^2 + \frac{1}{4}\Gamma^2} \times \exp[-\Gamma(t-T)]; \quad t \geq T. \quad (\text{III. 4})$$

For the square pulse excitation we thus have the following features:

- (1) The only characteristic decay time is Γ^{-1} , since the pulse is turned on and off instantaneously.
- (2) Δ enters as an oscillatory contribution, originating from an interference type "ringing" effect, characteristic of a "two level" system.¹⁰
- (3) When Δ increases the intensity of the whole decay pattern decreases, and the total yield exhibits a Lorentzian dependence on Δ .

As a second characteristic pulse, let us take a Lorentzian time profile

$$\varphi(\tau) = 0; \quad \tau < 0$$

$$= \exp(-\frac{1}{2}\gamma\tau); \quad \tau > 0 \quad (\text{III. 5})$$

whose energy spectrum is

$$A_k = (i/2\pi)[k - \bar{k} + (i/2)\gamma]^{-1}. \quad (\text{III. 6})$$

In this case $\phi_s(t)$, Eq. (II. 9a), is given by

$$\phi_s(t) = \int_0^t d\tau \exp\left(-\frac{\gamma}{2}\tau\right) \exp\left[-\frac{\Gamma}{2}(t-\tau)\right] \exp(-i\Delta\tau)$$

$$= i \exp(-i\Delta t) \frac{\exp(-\frac{1}{2}\gamma t) - \exp(i\Delta t)\exp(-\frac{1}{2}\Gamma t)}{\Delta - (i/2)(\gamma - \Gamma)} \quad (\text{III. 7})$$

$$F(t) = \Gamma |V_{sr}|^2 \frac{\exp(-\gamma t) + \exp(-\Gamma t) - 2\exp[-\frac{1}{2}(\Gamma + \gamma)t]\cos\Delta t}{\Delta^2 + \frac{1}{4}(\gamma - \Gamma)^2}. \quad (\text{III. 8})$$

From this result we conclude that for a Lorentzian pulse:

(1) the time resolved decay involves two characteristic lifetimes: γ^{-1} and Γ^{-1} , which characterize the pulse and the molecular system, respectively.

(2) The common situation in time resolved experiments is $\gamma \gg \Gamma$ which means that the duration of the light pulse is short relative to the molecular lifetime. In such cases, Eq. (III. 8) yields a short time component, $F^{(1)}(t)$ following the light pulse and a long time component, $F^{(2)}(t)$, where

$$F^{(1)}(t) \propto \exp(-\gamma t) - 2\cos\Delta t \exp[-\frac{1}{2}(\Gamma + \gamma)t]; \quad 0 < t \sim \gamma^{-1} \quad (\text{III. 9})$$

$$F^{(2)}(t) \propto \exp(-\Gamma t); \quad t \gg \gamma^{-1}. \quad (\text{III. 10})$$

(3) the intensity ratio of these two components (III. 9) and (III. 10) is practically independent of Δ , apart from an oscillatory contribution, originating from interference effects.

(4) The dependence of the total intensity on Δ is a Lorentzian whose width is $|\gamma - \Gamma|$, which under the condition of "short pulse termination" is equal to γ .

Next, let us consider the compound pulse whose time

profile consists of a sharp rise followed by a constant part and an exponential decay,

$$\varphi(\tau) = 0; \quad \tau < 0$$

$$= 1; \quad 0 < \tau < T$$

$$= \exp[-\frac{1}{2}\gamma(\tau - T)]; \quad \tau > T. \quad (\text{III. 11})$$

The time evolution of the molecule interacting with this pulse is readily expressed, making use of Eqs. (III. 3) and (III. 7),

$$\phi_s(t) = \phi_s^{(1)}(t) + \phi_s^{(2)}(t - T)\exp(-i\Delta T), \quad (\text{III. 12})$$

where $\phi_s^{(1)}$ is given by Eq. (III. 3) whereas $\phi_s^{(2)}$ is given by Eq. (III. 7). Equation (III. 12) can be now expressed in the explicit form:

$$\phi_s(t) = 0; \quad t < 0$$

$$= i \frac{\exp(-i\Delta t) - \exp(-\frac{1}{2}\Gamma t)}{\Delta + i\frac{1}{2}\Gamma}; \quad 0 < t < T$$

$$= i \exp\left[-\frac{\Gamma}{2}(t - T)\right] \frac{\exp(-i\Delta T) - \exp(-\frac{1}{2}\Gamma T)}{\Delta + i\frac{1}{2}\Gamma}$$

$$+ i \exp(-i\Delta t) \frac{\exp[-\frac{1}{2}\gamma(t - T)] - \exp[(i\Delta - \frac{1}{2}\Gamma)(t - T)]}{\Delta - \frac{1}{2}i(\gamma - \Gamma)}; \quad t > T. \quad (\text{III. 13})$$

For $t > T$ we may rearrange Eq. (III. 13) to give

$$\phi_s(t) = i \exp(-i\Delta t)$$

$$\times \{A_p \exp[-\frac{1}{2}\gamma(t - T)] - \exp[i\Delta(t - T)]\}$$

$$\times A_s \exp[-\frac{1}{2}\Gamma(t - T)]\}, \quad (\text{III. 14})$$

where

$$A_p = [\Delta - \frac{1}{2}i(\gamma - \Gamma)]^{-1} \quad (\text{III. 14a})$$

and

$$A_s = \frac{1}{\Delta - \frac{1}{2}i(\gamma - \Gamma)} - \frac{1 - \exp(i\Delta T)\exp(-\frac{1}{2}\Gamma T)}{\Delta + i\frac{1}{2}\Gamma}. \quad (\text{III. 14b})$$

The photon counting rate is obtained from Eqs. (II. 10) and (III. 14) in the form

$$F(t) = \Gamma |V_{sr}|^2 \{ |A_p|^2 \exp[-\gamma(t - T)] + |A_s|^2 \exp[-\Gamma(t - T)]$$

$$- 2 \operatorname{Re}\{A_p^* A_s \exp[i\Delta(t - T)] \exp[-\frac{1}{2}(\gamma + \Gamma)(t - T)]\}. \quad (\text{III. 15})$$

For the compound pulse (III. 11) we have the following features:

(1) the first and second time dependent contributions to the decay pattern are determined by the pulse decay time and by the molecular decay time, respectively, while the third contribution involves an interference term. The decay pattern is determined by the two lifetimes γ^{-1} and Γ^{-1} , in complete analogy with the case of the Lorentzian pulse [Eq. (III. 8)].

(2) Provided that $\gamma > \Gamma$ two decay components are exhibited for $t > T$. The second term in Eq. (III. 15) represents the long, fluorescence decay contribution, while the other two terms correspond to the short components, which are determined by the decay time of the pulse. The intensity ratio of the long molecular decay component to the total emission intensity at $t = T$ is

$$R = |A_s|^2 / |\phi_s(T)|^2. \quad (\text{III. 16})$$

We note that $R=1$ implies that no short decay component is resolved, while for $R \rightarrow 0$ we expect an intense short decay component followed by a weak long decay component.

(3) At resonance ($\Delta = 0$) we have

$$R = \{1 + [\Gamma/(\gamma - \Gamma)][1 - \exp(-\frac{1}{2}\Gamma T)]^{-1}\}^2. \quad (\text{III. 17a})$$

If T is long enough (i. e., $\Gamma T > 0.1$) and $\gamma \gg \Gamma$ we get

$$R \approx 1 + (2\Gamma/\gamma)[1 - \exp(-\Gamma T)] \quad (\text{III. 17b})$$

which implies that $R = 1 + O(\Gamma/\gamma)$ and we actually observe only the molecular decay time Γ^{-1} .

(4) For the extreme off resonance situation when $\Delta \gg \gamma > \Gamma$ Eq. (III. 14) results in $A_s \approx \exp[i(\Delta - \Gamma/2)T]/\Delta + O(\gamma/\Delta^2) + O(\Gamma/\Delta^2)$, whereas $\phi_s(T) \approx (i/\Delta)[\exp(-i\Delta T) - \exp(-\Gamma T/2)]$ so that $|\phi_s(T)|^2$ is approximately equal to $\Delta^{-2}[1 + \exp(-\Gamma T) - 2 \cos(\Delta T) \exp(-\Gamma T/2)]$. It should be borne in mind that the decay pattern should be averaged over the Doppler width of the line shape. If T is long compared to β^{-1} , where β is the Doppler width, the third oscillatory term in $|\phi_s(T)|^2$ will average out to zero. Thus we obtain

$$R \approx \exp(-\Gamma T) / [1 + \exp(-\Gamma T)] \quad (\text{III. 18})$$

and the ratio of the two decay components assumes a constant value independent of Δ .

Utilizing the compound pulse (III. 11) two interesting features of the time resolved photon scattering pattern emerge. First, two decay components are exhibited and second, in the extreme limiting case of off resonance the ratio R is independent of Δ . A cursory examination of our results may indicate that the second feature does provide an adequate physical interpretation for the recent experimental observation of Williams *et al.*⁵ for photon scattering from the $B^3\Pi$ state of I_2 . They reported⁵ that when moving away from resonance, the relative intensity of the "long lived" molecular component ceases to decrease relative to that of the short decay component. It is, however, important to realize that the compound pulse (III. 11) is characterized by one unphysical feature, which is its infinitely fast rise time. This will contribute a broad energetic spread of the pulse amplitudes A_k , whereupon the absorption line in the isolated molecule will span an appreciable fraction of the Fourier components of the pulse even when Δ is large. This unphysical feature will be removed once we allow for a proper rise time of the pulse.

To provide a realistic calculation we consider a pulse specified by the following parameters: the pulse rise time γ_1^{-1} , the pulse duration T , and the pulse fall time γ_2^{-1} . The pulse time profile is taken in the form

$$\begin{aligned} \varphi(\tau) &= \exp(\gamma_1 \tau / 2) & \tau < 0 \\ \varphi(\tau) &= 1 & 0 < \tau < T \\ \varphi(\tau) &= \exp[-\gamma_2(\tau - T) / 2] & \tau > T \end{aligned} \quad (\text{III. 19})$$

The pulse profile presented by Williams *et al.*⁵ is quite faithfully represented by Eq. (III. 19) with $\gamma_1 \approx \gamma_2$. Equation (II. 9a) can be now expressed in the explicit form

$$\begin{aligned} \phi_s(t) &= \frac{i \exp(-i\Delta t) \exp(\gamma_1 t / 2)}{\Delta + i(\gamma_1 + \Gamma) / 2}, & t < 0, \\ &= \frac{i \exp(-\Gamma t)}{\Delta + i(\Gamma + \gamma_1) / 2} + \frac{i[\exp(-i\Delta t) - \exp(-\Gamma t / 2)]}{\Delta + i\Gamma / 2}, & 0 < t < T, \\ &= i \exp(-i\Delta t) \{A_p \exp[-\frac{\gamma_2(t-T)}{2}] \\ &\quad - A_s \exp[i\Delta(t-T)] \exp[-\frac{\Gamma(t-T)}{2}]\}, & t > T, \end{aligned} \quad (\text{III. 20})$$

where we have defined the auxiliary parameters

$$\begin{aligned} A_p &= [\Delta + \frac{1}{2}i(\Gamma - \gamma_2)]^{-1}, \\ A_s &= [\Delta + \frac{1}{2}i(\Gamma - \gamma_2)]^{-1} - [\Delta + \frac{1}{2}i\Gamma]^{-1} \\ &\quad + \exp(-\Gamma T / 2) \exp(i\Delta T) \{[\Delta + \frac{1}{2}i\Gamma]^{-1} - [\Delta + \frac{1}{2}i(\Gamma + \gamma_1)]^{-1}\}, \end{aligned} \quad (\text{III. 21})$$

The photon counting rate, in the absence of Doppler broadening for $t > T$ is now

$$\begin{aligned} F(t) &= \Gamma |V_{sg}|^2 (|A_s|^2 \exp[-\Gamma(t-T)] \\ &\quad + |A_p|^2 \exp[-\gamma_2(t-T)] \\ &\quad - 2 \text{Re}\{A_p^* A_s \exp[i\Delta(t-T)]\} \exp[-\frac{1}{2}(\gamma_2 + \Gamma)(t-T)] \}. \end{aligned} \quad (\text{III. 22})$$

For the realistic pulse shape, Eq. (III. 19), we have the following features:

(1) Two decay components are exhibited, determined again by the molecular decay time and by the pulse decay time, respectively. These are given by the first and the second term of Eq. (III. 22).

(2) The third term in Eq. (III. 22) provides, as usually, an interference type contribution. For a realistic situation when $\Gamma \ll \gamma_2$ this term is dominated by the pulse decay time.

(3) The relative contribution of the long time decay component, Eq. (III. 16) is given by

$$R = \frac{|A_s|^2}{|A_s|^2 + |A_p|^2 - 2 \text{Re}\{A_s^* A_p\}} \quad (\text{III. 23})$$

together with Eq. (III. 21).

(4) At resonance $\Delta = 0$ and $R \approx 1$ whereupon only the molecular decay appears.

(5) Far off resonance when $\Delta \gg \Gamma, \gamma_1, \gamma_2$

$$R \approx \frac{1}{4\Delta^2} [\gamma_2^2 + \gamma_1^2 \exp(-\Gamma T) - 2 \cos(\Delta T) \gamma_1 \gamma_2 \exp(-\Gamma T / 2)] \quad \Delta \rightarrow \infty \quad (\text{III. 24})$$

which for $\Gamma T < 1$ is of the order

$$R \approx \frac{\gamma_1^2 + \gamma_2^2}{4\Delta^2}; \quad \Gamma T < 1, \quad \Delta \rightarrow \infty \quad (\text{III. 24a})$$

Thus in the off resonance limit $R \rightarrow 0$ as Δ^{-2} .

To explore further the general decay features of the system under off resonance conditions ($\Delta \gg \Gamma$), we write an alternative expression for $\phi_s(t)$ [Eq. (II. 9a)] in the form

$$\phi_s(t) = -i \int dE A(E) G_{ss}(E) \exp[-i(E - \bar{E}_s)t], \quad (\text{III. 25})$$

where

$$G_{ss}(E) = (E - \bar{E}_s + \frac{1}{2}i\Gamma)^{-1} \quad (\text{III. 26})$$

and where we have replaced the pulse amplitudes A_k by $A(E)$. When Δ is much larger than the characteristic widths Γ and $\gamma = 1/\tau_p$, the major contribution to the Fourier integral (III. 25) are obtained at the energies \bar{k} and \bar{E}_s and we get the approximate relation

$$\phi_s(t) \approx 2\pi A(\bar{E}_s) \exp(-\frac{1}{2}\Gamma t) - iG_{ss}(\bar{k}) \exp(-i\Delta t) \varphi(t). \quad (\text{III. 27})$$

We thus have two decay components: the first has the time profile of $|s\rangle$ whereas the second has the time profile of the pulse. The relative contribution of these two components depends on the asymptotic behavior of $G_{ss}(E)$ and $A(E)$. We can use Eq. (III. 27) to regain our previous results for different pulse profiles in the off resonance limit.

The most important conclusion originating from the present results is that the only typical lifetimes which determine the time resolved decay pattern for RF and NRRS involve the pulse and the molecular lifetimes. The off resonance energy contributes only to an interference "ringing type" term, in all cases it affects the total emission intensity while in some cases (e.g., our compound pulse) it determines the relative ratio between the short and the long time components.

To compare the theoretical results with a real life situation the effect of Doppler broadening and other possible broadening effects, i.e., originating from hyperfine interactions have to be included. We shall focus attention on a low pressure molecular system disregard-

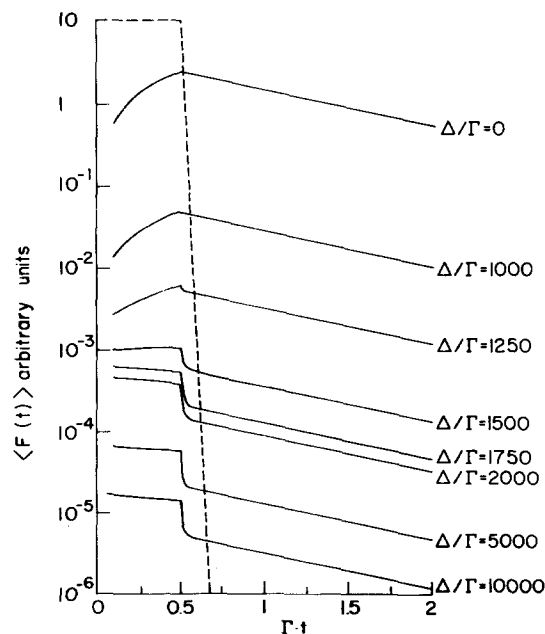


FIG. 1. Model calculations for the time resolved decay pattern for the composite pulse [Eq. (III. 11)] and including the effects of Doppler broadening. The photon counting rate $\langle F(t) \rangle$ is displayed for various values of Δ/Γ . The following typical parameters were employed: $\gamma/\Gamma = 100$, $\Gamma T = 0.5$, and $\beta/\Gamma = 500$. The dashed line represents the time profile $|\varphi(t)|^2$ of the pulse.

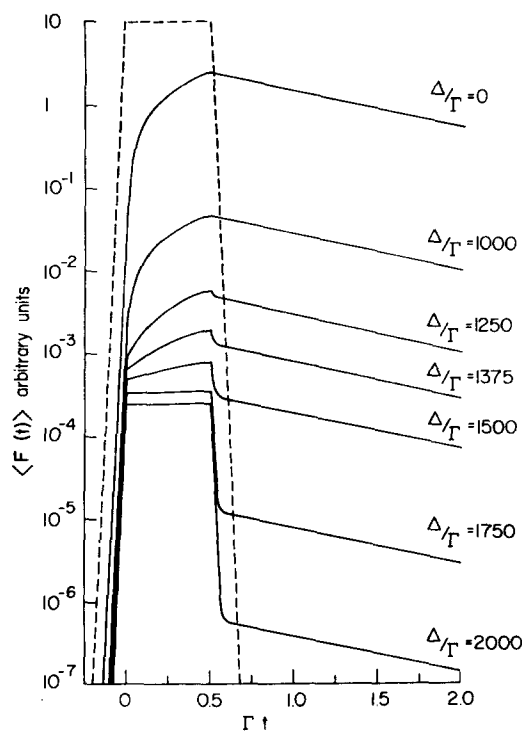


FIG. 2. Model calculations for the time resolved decay pattern for the realistic pulse shape [Eq. (III. 19)]. The parameters γ/Γ , ΓT , and β/Γ are the same as in Fig. 1. The dashed line represents the time profile $|\varphi(t)|^2$ of the pulse.

ing for the time being the interesting effects of pressure broadening, and considering Doppler broadening only. The experimental decay pattern $\langle F(t) \rangle$ is given by averaging $F(t)$ [Eq. (II. 10)] over the proper Gaussian distribution.

$$f(\Delta') = (1/\sqrt{\pi\beta^2}) \exp[-(\Delta' - \Delta)^2/\beta^2]. \quad (\text{III. 28})$$

Δ is the mean off resonance energy so that

$$\langle F(t) \rangle = \int_{-\infty}^{+\infty} f(\Delta') F(t) d\Delta'. \quad (\text{III. 29})$$

[$F(t)$ is a function of the off resonance parameter Δ' .]

Results of numerical calculations of $\langle F(t) \rangle$ using the compound pulse [Eq. (III. 11)] and the realistic pulse shape [Eq. (III. 19)] are presented in Figs. 1 and 2. These results exhibit the following general features:

(1) The effects of the Doppler broadening have a pronounced influence on the decay pattern. When $\beta \gg \Gamma$ the decay pattern corresponds to a resonance excitation as long as $\Delta \leq \beta$. Under these conditions, only the long decay component is observed. When $\Delta > \beta$ both the short and the long components are exhibited and we obtain the off resonance situation.

(2) The oscillatory interference contribution is smeared out due to averaging over Δ .

(3) The total intensity $\langle F(t) \rangle$, for each t , decreases with increasing Δ .

(4) The contribution of the fast (Raman-like) component relative to the long, fluorescent type, component

increases with increasing Δ .

The general features (1)–(4) are exhibited for both the compound pulse (III. 11) and the realistic pulse (III. 19). The compound pulse does, however, exhibit one unphysical feature, which originates from its infinitely fast rise time. When Δ increases (i.e., $\Delta \gg \beta$) the intensity ratio $\langle R \rangle = \langle |A_s|^2 \rangle / \langle F(T) \rangle$ for (III. 11) assumes the limiting form (III. 18) which is independent of Δ . On the other hand, for the pulse shape (III. 19), the intensity ratio $\langle R \rangle$ is found to decrease as Δ^{-2} , for the off resonance situation, as is evident from Fig. 2. For the comparison of our results with a real life situation the realistic pulse shape (III. 19), which faithfully reproduces the experimental pulse employed by Williams *et al.*,⁵ has to be used.

IV. RELATION TO THE LIFETIME MATRIX

We have demonstrated that the off resonance energy parameter Δ^{-1} does not enter as an observable lifetime in the time resolved decay process. For certain pulse profiles the molecular decay component (Γ) decreases relative to the pulse component (γ), with increasing Δ . However, this is not a fundamental feature originating from the time-energy uncertainty principle,⁵ as we can consider certain realistic pulse profiles [e.g., (III. 5)] for which the ratio of the two components is independent of Δ (apart from the interference oscillatory contribution). We can, however, demonstrate that Δ^{-1} is associated with the lifetime matrix of scattering theory.

The lifetime matrix $Q(E)^{7,11}$ gives the time delay in a scattering experiment due to the interaction between the beam and the target. Usually, a particle beam is considered, but we can also handle the scattering of a photon wave packet by the same formalism. The Q matrix refers to a typical "long time" experiment^{12,4} where a monochromatic beam is scattered at steady state.

$$Q(E) = \hbar \frac{d}{dE} \eta, \quad (IV. 1)$$

where η is the phase shift. For a scattering from a single resonance we have

$$\eta = 2\delta = 2\delta_0 + 2 \arctan[\Gamma / (\bar{E}_s - E)] \quad (IV. 2)$$

which gives for $Q(E)$

$$Q(E) = 2\Gamma \hbar / (E - E_s)^2 + \Gamma^2. \quad (IV. 3)$$

For a monochromatic photon beam with energy \bar{E}_s we get $Q(E) = 2\hbar/\Gamma$ which is just twice the lifetime of the resonant molecule state. Appropriate averaging over energies around the resonances gives^{7b}

$$Q = \hbar/\Gamma. \quad (IV. 4)$$

Far off resonance, if we assume that the wave packet width is much smaller than Δ (the energy difference between \bar{E}_s and the center of the wave packet \bar{k}) we have

$$Q = \frac{2\hbar}{\Gamma + \Delta^2/\Gamma}. \quad (IV. 5)$$

We have thus established the relation between Δ and the lifetime matrix. In general, the time delay $\langle t \rangle$ in the scattering experiment is obtained by averaging $Q(E)$ over the (phonon) scattering cross section $\sigma(E)$ and the wave

packet amplitudes $A(E)$,

$$\langle t \rangle \propto \int Q(E) \sigma(E) |A(E)|^2 dE. \quad (IV. 6)$$

However, this delay time does not yield the time resolved decay components, but rather results in the difference between the weighted average of the characteristic decay lifetimes and the pulse time. The averaging depends explicitly on Δ .

To elucidate the physical features of our results we note that different Fourier components of the exciting pulse contribute to resonant scattering, which is characterized by the molecular lifetime, and to direct scattering, which should be considered as a single quantum mechanical process. Only the Fourier components of the pulse which are close to resonance, excite the long molecular decay component, while other Fourier components are directly scattered. When a realistic pulse shape Eq. (III. 19), is employed, the population of "metastable states," excited near resonance decreases as Δ^{-4} while their relative contribution decreases as Δ^{-2} for large Δ .

This theoretical result for the "isolated" molecule is in variance with the low pressure (0.025 torr) experimental results of Williams *et al.*⁵ It thus appears that under their experimental conditions collisional perturbations have already a dominating role in determining the decay pattern.

V. INTERACTION OF A LIGHT PULSE WITH A MANIFOLD OF MOLECULAR RESONANCES

The treatment of the previous sections may be extended to include an arbitrary number of molecular resonances. The treatment of the radiative decay of a manifold of molecular levels rests on the effective Hamiltonian formalism.^{2,4,10,13} Let us assume that instead of a single $|s\rangle$ resonance we have a set of n excited molecular levels $\{|m\rangle\}$ coupled radiatively to the ground state $|g\rangle$ and can be also coupled among themselves. The effective Hamiltonian, defined within the subspace \hat{P} spanned by the $\{|m\rangle\}$ levels may be diagonalized by a symmetric (nonunitary) transformation resulting in a set $\{|j\rangle\}$ of independently decaying levels characterized by the complex energies $E_j - i\frac{1}{2}\Gamma_j$.^{4,10,13} It is also useful at this stage to define the set of the corresponding complex conjugate states $\{|\bar{j}\rangle\}$. We thus have for the projection operator of the zero photon states

$$\hat{P} = \sum_m |m, \text{vac}\rangle \langle m, \text{vac}| = \sum_j |j, \text{vac}\rangle \langle \bar{j}, \text{vac}| \quad (V. 1)$$

and the projection of the time evolution operator, $U(t, 0)$, within \hat{P} is given by

$$\hat{P}U(t, 0)\hat{P} = \sum_j |j\rangle \exp\left[\left(-iE_j - \frac{\Gamma_j}{2}\right)t\right] \langle \bar{j}|. \quad (V. 2)$$

We now define the general doorway state $|N, \text{vac}\rangle$ carrying all the oscillator strength from the ground state⁴

$$|N, \text{vac}\rangle = \frac{1}{\gamma_N} H_{\text{int}} |g, k\rangle = \frac{1}{\gamma_N} \hat{P} H_{\text{int}} |g, k\rangle, \quad (V. 3)$$

where $|\text{vac}\rangle$ and $|k\rangle$ are zero and the one photon states

of the electromagnetic field, H_{int} is the electromagnetic interaction and the width γ_N is given by

$$|\gamma_N|^2 = \langle g, k | H_{\text{int}} \cdot H_{\text{int}} | g, k \rangle. \quad (\text{V. 4})$$

The radiative width of $|N\rangle$, Γ_N , is

$$\Gamma_N = 2\pi |\gamma_N|^2 \rho_r, \quad (\text{V. 5})$$

where ρ_r is the density of states of the electromagnetic field at some average k value. The photon counting rate is^{4,14}

$$F(t) = \Gamma_N \sum_j \sum_{j'} A_j A_{j'}^* f_{j'}^*(t) f_j(t), \quad (\text{V. 6})$$

where

$$A_j = \langle N | j \rangle \langle \bar{j} | N \rangle \quad (\text{V. 7a})$$

and

$$f_j(t) = \int_0^t d\tau \varphi(t-\tau) \exp[-i\bar{k}(t-\tau)] \exp\left[-\left(iE_j + \frac{\Gamma_j}{2}\right)\tau\right] \quad (\text{V. 7b})$$

$$= \exp(-iE_j t) \int_0^t d\tau \varphi(\tau) \exp(-i\Delta_j \tau) \exp\left[-\frac{\Gamma_j}{2}(t-\tau)\right], \quad (\text{V. 8})$$

where

$$\Delta_j = \bar{k} - E_j.$$

Equations (V. 6)–(V. 8) provide us with a general solution for the radiative decay problem of a molecule characterized by a complex excited state level structure. The decay pattern is now determined by the set of molecular lifetimes $\{\Gamma_j^{-1}\}$, by the characteristic times specifying the pulse profile, and by the set of off resonance energies $\{\Delta_j\}$. These general results can be utilized for specific systems interacting with a variety of light pulses. Without alluding to any specific calculations we can conclude that as in the case of a single resonance the only lifetimes which will determine the decay mode will be $(\Gamma_j)^{-1}$ and the lifetimes characterizing the pulse decay, while the off resonance energies will again just contribute to the relative total yields. We hope that the results presented herein elucidate the nature of the "transition" from RF to NRRS.

Note added in proof: There has recently been considerable activity in this interesting field. Friedman and Hochstrasser [J. M. Friedman and R. M. Hochstrasser, *Chem. Phys.* **6**, 155 (1974)] have treated one of our cases and derived Eq. (III. 8) of the present paper for the Lorentzian time profile of a light pulse. Berg,

Langhoff, and Robinson [J. O. Berg, C. A. Langhoff, and G. W. Robinson, *Chem. Phys. Lett.* **29**, 305 (1974)] have treated the problem of time resolved scattering utilizing a formalism similar to that of Ref. 4 and of the present paper.

The main conclusion of Berg *et al.* that "there is no exponentially decaying component which depends on the frequency difference between the exciting pulse and the resonance" concurs with our analysis. The present work bears a family resemblance, but is distinct in some respects from all of these.

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