On the theory of time resolved near-resonance light scattering*

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Time resolved resonance and near-resonance light scattering is analyzed by means of Green's operator formalism. We study the process of a photon wavepacket colliding with and scattered from a given molecule. Two decay components similar to those observed by Williams, Rousseau, and Dworetsky are obtained under appropriate conditions. Unlike other recent treatments of this problem, the light pulse is not treated as a pure quantum state (minimum uncertainty wavepacket) but rather as a mixture having characteristic time and energy profiles. It is shown that the nature of the light pulse may strongly influence the ratio of the short time to the long time decay intensities.

I. INTRODUCTION

The experimental observation of time resolved resonance and near-resonance fluorescence from molecular iodine[1] has triggered some theoretical work on this topic.[2,3] As opposed to more common problems in time resolved spectroscopy, the Williams, Rousseau, Dworetsky (WRD)[1] experiment provides a rare example of a study where the preparation (excitation) process cannot be separated from the following decay (emission) process in a simple way. Therefore, this experiment cannot be approximated as a "short time" experiment (in which the molecule is assumed to be initially in its excited state and the consecutive decay is described) or as a "long time" experiment (where initially and finally the molecule is in the ground electronic state and the formalism of time-independent scattering theory is employed to extract cross sections for light adsorption and scattering)[4] but has to be treated as a time-dependent collision process where the molecular ground state and the incoming photon constitute an initial state whose time evolution is explored.[5] This approach is used in Refs. 2 and 3; Ref. 2b takes into account the additional effects of collision broadening of the light scattering process. The following assumptions are common to these works:

(1) The photon intensity is small enough to allow the characterization of the initial state by a linear combination of one photon state multiplied by the molecular ground state.

(2) The photon field is initially in a pure quantum state, also referred to as a minimum uncertainty wave packet: its characteristic decay time and its energy spread are related by a simple Fourier transform (or alternatively by an equality sign in the Heisenberg uncertainty principle). More explicitly, the unperturbed initial state of the radiation field is assumed to be a wave packet of the form[6]

$$\psi_R(0) = \int dE\, A(E) |E\rangle \,, \tag{1}$$

where $|E\rangle$ is an eigenstate of H_R (the Hamiltonian of the free radiation field) with energy E, and $|A(E)|^2$ is some function centered around the energy $E - E_0$ with width $\frac{1}{2}\gamma$. The temporal evolution of this state[7]

$$|\langle \psi_R(0)| e^{-iHt} |\psi_R(0)\rangle|^2 = \left| \int dE\, e^{-iEt} |A(E)|^2 \right|^2 \tag{2}$$

has a characteristic decay time $1/\gamma$.

With assumption (1) and (2), a light pulse with a given local temporal evolution or a given frequency profile is almost fully characterized. [We hedge with the word "almost" since we are given $|A(E)|^2$ or its Fourier transform and not $A(E)$. The models for $A(E)$ or $\hat{A}(t) \equiv \int e^{iEt} A(E)\, dE$ employed in Refs. 2 and 3 as well as in the present paper thus involve an additional assumption about the phase. This is not expected to cause any difficulty as long as we are not looking for interference effects.] However, it is clear that taking the light pulse as a minimum uncertainty wavepacket for one photon casts a severe restriction on the system since we lose one parameter (because the time evolution and the frequency spread are described by the same parameter γ) and also lose any possibility of discussing stimulated light scattering. The study of more complicated initial states of the radiation field involves a many body problem of considerable intricacy. An attempt to solve it exactly is pointless at present, since we lack sufficient knowledge on the exact structure and statistics of commonly applied light pulses. Our purpose in this paper is to demonstrate by the use of greatly simplified models that the inclusion of these details may modify the theoretical predictions in an important way. As a preliminary, in Sec. II we study the one photon model[2,3] because we will need the concepts introduced there. In addition, we believe that we give a clearer derivation.

II. MINIMUM UNCERTAINTY PACKETS OF ONE PHOTON STATES

Our system is composed of a single molecule[8] imbedded in the radiation field. The Hamiltonian is

$$H = H_0 + V + H_R + H_{\rm int} \,; \tag{3}$$

H_0 is a zero order molecular Hamiltonian which is composed of a ground state $|g\rangle$, a discrete optically active excited state $|s\rangle$, and a continuous manifold of excited states $\{|l\rangle\}$ of zero oscillator strength. The intramolecular correction to H_0, denoted V, couples $|s\rangle$ to $\{|l\rangle\}$ and induces a radiationless decay $|s\rangle \rightarrow \{|l\rangle\}$ which we

take to correspond to the statistical limit. Note that (a) Neglecting other discrete excited states $|s'\rangle$ is a good approximation under the WRD excitation condition as long as we are not too far off resonance; otherwise the coupling of $|g\rangle$ to other excited states has to be taken into account[3]; (b) The continuous manifold $\{|l\rangle\}$ corresponds in the WRD case (iodine molecule) to lower dissociative states $[O_g^+(^3\pi),\ 1_u(^1\pi),\ O_u^-(^3\pi)]$ whose coupling to $|s\rangle$ $[BO_u^+(^3\pi)]$ is small.[9] In this case V may be neglected, but its inclusion in the present model does not involve any additional difficulty. H_R is the Hamiltonian of the radiation field, which in second quantization with neglect of the energy of the vacuum takes the form

$$H_R = \sum_{\mathbf{k}\sigma} \omega_k (a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma}) , \tag{4}$$

where ω_k is the frequency of a photon of wavenumber $\mathbf{k}$. The symbol σ denotes the polarization and $a^\dagger_{\mathbf{k}\sigma}$, $a_{\mathbf{k}\sigma}$ are creation and annihilation operators, respectively, for a photon of wavenumber $\mathbf{k}$ and polarization σ. Finally, $H_{\rm int}$ is the molecule–field interaction which in the dipole approximation takes the form

$$H_{\rm int} = a \sum_{\mathbf{k}\sigma} \sqrt{\frac{\omega_k}{L^3}} (a_{\mathbf{k}\sigma} - a^\dagger_{\mathbf{k}\sigma}) (\mathbf{e}_{\mathbf{k}\sigma} \cdot \boldsymbol{\mu}) ; \tag{5}$$

a involves numerical constants which are unimportant for our purpose. L^3 is the normalization volume of the field; $\mathbf{e}_{\mathbf{k}\sigma}$ the polarization vector of the photon $(\mathbf{k})$; and $\boldsymbol{\mu}$ the molecular dipole operator which is assumed to couple $|g\rangle$ to $|s\rangle$. Since the orientation of the molecule is assumed to be random, and since we are interested in the total scattering, the summation and average over the photon polarization establishes another multiplicative numerical constant which is unimportant for our study and is therefore suppressed. Note that in Eq. (5) the center of molecular mass is taken as the origin of spatial coordinates $\rho = 0$; otherwise $a_{\mathbf{k}}$ and $a^\dagger_{\mathbf{k}}$ should be replaced by $a_{\mathbf{k}} e^{i\mathbf{k}\cdot\rho}$ and $a^\dagger_{\mathbf{k}} e^{-i\mathbf{k}\cdot\rho}$.

A. Initial state

For the initial state of the system we choose an eigenstate of $H_0 + H_R$, with the molecule in its ground state centered at the origin and the field in a wave packet of one photon state centered around some point x_0 on the x axis and moving toward the origin. To build such a wave packet we first define the field operators

$$\psi(x) = L^{-1/2} \sum_k a_k \exp[i(k - k_0)x], \tag{6a}$$

$$\psi^\dagger(x) = L^{-1/2} \sum_k a^\dagger_k \exp[-i(k - k_0)x] \tag{6b}$$

which annihilate and create a photon on the plane x; k denotes a wave vector in the x direction. The initial state of the field is now taken as

$$|i\rangle = \int dx A(x - x_0) \psi^\dagger(x) |0\rangle , \tag{7}$$

where $|0\rangle$ is the vacuum state of the radiation field and $A(x - x_0)$ is some function of x centered with a given width symmetrically around x_0. Defining the function $A(k)$ as

$$A(k) = L^{-1/2} e^{ikx_0} \int dx A(x) e^{-ikx} , \tag{8}$$

we see that the initial state of the field is

$$|i\rangle = \sum_k A(k - k_0) e^{-ikx_0} a^\dagger_k |0\rangle . \tag{9}$$

The state $|i\rangle$ describes a planar wave packet of one photon state centered around x_0 in position space and around k_0 in wavenumber space; the normalization condition is

$$\int dx |A(x)|^2 = \sum_k |A(k)|^2 = 1 . \tag{10}$$

Now define

$$x_0 = c t_0 , \tag{11}$$

where c is the light velocity, so that t_0 is the time in which the wave packet at x_0 reaches the molecule (located at the origin). Also use the dispersion relation for the photon field

$$\omega = kc \tag{12}$$

to recast Eq. (9) in the form

$$|i\rangle = \int d\omega B(\omega - \omega_0) e^{-i\omega t_0} |\omega\rangle , \tag{13}$$

where

$$|\omega\rangle = a^\dagger_{k=\omega/c} |0\rangle \tag{14}$$

and where $B(\omega - \omega_0) = \rho(\omega) A[1/c(\omega - \omega_0)]$ and $\int d\omega |B(\omega)|^2 = 1$. The density of states $\rho(\omega)$ may be approximated by a constant $\rho(\omega_0)$ if the width of the envelope function $B(\omega)$ is small.

The initial state of the system is now taken to be $|ig\rangle$, a direct product of the ground molecular state and the radiation pulse state of Eq. (13).

B. Temporal evolution

In the absence of molecule–field interaction, the time evolution of the radiation pulse is given by

$$\exp[-iH_R t] |i\rangle = \sum_k A(k - k_0) \exp[-ik(x_0 + ct)] a^\dagger_k |0\rangle , \tag{15}$$

which describes a pulse of constant spatial shape and constant energy profile moving with velocity c in the positive x direction. We thus choose x_0 to be negative to allow for a collision between the molecule and the wave packet. Since $|s\rangle$ is the only molecular state which is coupled radiatively to $|g\rangle$, the total scattering (or fluorescence) intensity at time t is proportional to the population of the state $|s\rangle$, which is given by $|C_s(t)|^2$ with

$$C_s(t) = \langle s0 | \exp(-iHt) | gi \rangle . \tag{16}$$

As before, the symbol 0 denotes the vacuum state of the radiation field.

The rest of the calculations are identical to those given in Refs. 2 and 3, and we give here only a brief outline. Equations (13) and (16) yield

$$C_s(t) = \int d\omega B(\omega - \omega_0) e^{-i\omega t_0} \langle s\,0 | e^{-iHt} | g\omega \rangle . \tag{17}$$

The matrix element in (17) is easily evaluated for the present model by standard Green's function technique, and we get in the limit $t_0 \to -\infty$

$$e^{-\omega t_0}\langle s0|e^{-iHt}|g\omega\rangle \propto \frac{\mu_{sg}}{\omega - E_s + \frac{1}{2}i\Gamma}\, e^{i\omega t} \tag{18}$$

and

$$C_s(t) = \int d\omega\, B(\omega-\omega_0)\frac{\mu_{sg}}{\omega - E_s + \frac{1}{2}i\Gamma}\, e^{i\omega t}\,. \tag{19}$$

Here we have defined $\mu_{sg} = \langle s|\mu|g\rangle$; E_s is the (shifted) energy of the state s, and Γ is its total width. There are two contributions to Γ, a radiative one due to the coupling of $|s\rangle$ to the radiation field, and a nonradiative one due to the coupling to the manifold $\{|l\rangle\}$. In Eqs. (18) and (19) we have assumed that the slowly varying factor $\sqrt{\omega}$ [see Eq. (5)] can be replaced by a constant and put into the proportionality constant. Since the radiation pulse is often characterized by its time rather than its frequency profile, we may replace Eq. (19) by

$$C_s(t) \propto \mu_{sg}\exp(-iE_s t - \tfrac{1}{2}\Gamma t) \times \int_{-t}^{\infty} dt'\hat{B}(-t')\exp[-i(E_s-\omega_0)t' - \tfrac{1}{2}\Gamma t']\,, \tag{20}$$

where

$$\hat{B}(t) = \int_{-\infty}^{\infty} e^{-i\omega t}B(\omega)\,d\omega \tag{21}$$

characterizes the time profile of the free pulse. With a given function $B(t)$, $C_s(t)$ and $|C_s(t)|^2$ may be calculated. To account for molecular motion, $|C_s(t)|^2$ has to be averaged over a Gaussian (Doppler) distribution of energies E_s. Mukamel, Jortner, and Ben Reuven have further shown[20] that when collisions between the light absorbing molecule and inert molecules are taken into account, an additional average over a Lorentzian distribution of E_s has to be performed.

We conclude this section by pointing out again that the radiation field is described in this model by a pure quantum state, Eq. (13), given as a linear combination of one photon states. This is a minimum uncertainty wave packet whose time and energy profiles are related by a simple Fourier transform, Eq. (21).

III. MIXED SINGLE PHOTON STATES PACKETS

In general, it is not possible to describe a given light pulse as a pure quantum state of one photon. The macroscopic characteristics of the pulse, its time structure, its energy profile, and its intensity need to be described in terms of many possible pure and mixed quantum states. Two obvious generalizations of the model described in the previous section are (a) generalization to a pulse of n photons

$$|i\rangle = \int dx[A(x-x_0)\psi^{\dagger}(x)]^n|0\rangle\,, \tag{22}$$

which describes a wave packet of the same characteristics as Eq. (7) only with n photons; (b) generalization to a mixed state for one photon described by the diagonal density operator

$$\rho = \int d\omega_0 C(\omega_0-\omega_\mu)|i,\omega_0\rangle\langle i,\omega_0|\,, \tag{23}$$

where $C(\omega)$ is a function distributed around ω_0 with

$$\int d\omega C(\omega) = 1\,, \tag{24}$$

and where $|i,\omega_0\rangle$ is a one photon wave packet described by Eq. (13); the index ω_0 is added for better characterization.

In this section we study the implications of excitation by a pulse described by Eq. (23). This is an incoherent combination of wave packets, each given by Eq. (13). The wave packet (13) has a frequency profile given by $B(\omega-\omega_0)$ which is a function centered around ω_0 with a given width γ_c. Its time profile is characterized by the Fourier transform of B [Eq. (21)]. This is a planar wave packet which at time 0 is distributed in space around $x_0 = t_0/c$ and is moving at later times with velocity c towards the molecule at the origin. The density operator ρ (Eq. 23) describes a combination of such packets. Each has the same location (at any time) and shape but with a frequency profile centered around a different ω_0 with a weight function $C(\omega_0-\omega_M)$. This leads to a new frequency profile centered around ω_M with a total width of the order

$$\gamma_M \sim \gamma_c + \gamma_0\,. \tag{25}$$

However, the local lifetime of the pulse remains as before $\sim(\gamma_0)^{-1}$ (see Appendix A). We thus have

$$\gamma_M(\gamma_c)^{-1} > 1, \tag{26}$$

which characterizes a pulse of larger than minimum uncertainty.

To calculate the time evolution of the total scattered light intensity we have to evaluate

$$\langle|C_s(t)|^2\rangle = \mathrm{Tr}(|s0\rangle\langle s0|\rho(t)) = \langle s0|\rho(t)|s0\rangle\,, \tag{27}$$

where ρ is now the density operator of the full system given at time zero by

$$\rho(t=0) = \int d\omega_0 C(\omega_0-\omega_M)|i,\omega_0;g\rangle\langle i,\omega_0;g| \tag{28}$$

and where the time evolution is now due to the full system Hamiltonian, Eq. (3). Since $\rho(t=0)$ is diagonal in the representation of possible initial pure states, the evaluation of Eq. (27) involves just a simple extension of the treatment of Sec. II and leads to the results of Sec. II averaged over the distribution $C(\omega_0-\omega_M)$,

$$\langle|C_s(t)|^2\rangle_{\omega_M} = \int d\omega_0 C(\omega_0-\omega_M) \times\langle s0|e^{-iHt}|i\omega_0;g\rangle\langle i,\omega_0;g|e^{iHt}|s0\rangle\,, \tag{29a}$$

where $C_s(t,\omega_0)$ is given by Eq. (20).

For a gas of noninteracting molecules, Eq. (29) has to be further averaged over a Gaussian Doppler distribution of excitation energies which yields

$$\langle\langle |C_s(t)|^2 \rangle\rangle = \frac{2}{\sqrt{\pi\beta^2}} \int_{-\infty}^{\infty} \exp\left[-\frac{4(\omega_M' - \omega_M)^2}{\beta^2}\right] \langle |C_S(t)|^2 \rangle_{\omega_M} d\omega_M \tag{29b}$$

where β is the Doppler width. It was shown[2b] that if collision broadening is important, it will lead to an additional averaging over a Lorentzian distribution.

We have performed numerical computations based on Eq. (29) for the case where $C(\omega)$ is a Lorentzian,

$$C(\omega_0 - \omega_M) = \frac{\gamma_c}{\pi} \frac{1}{(\omega_0 - \omega_M)^2 + \gamma_c^2} \tag{30}$$

and where the time profile is given by

$$\hat{B}(t) = \begin{cases} \exp[\gamma_c(t+b)] & t \leq -b \\ 1 & -b \leq t \leq b \\ \exp[-\gamma_c(t-b)] & t \geq b\,. \end{cases} \tag{31}$$

$2b$ is the duration of constant intensity (100 nsec in the WRD experiment). Since extensive computational results on a similar model have been recently reported by Mukamel, Jortner, and Ben Reuven[2b] (where an average over a Lorentzian distribution is performed to account for collisional broadening), we do not give any computational details here. The characteristic behavior is shown in Fig. 1. When the excitation is far enough from resonance and when the width γ_0 is not too large, the fluorescence exhibits short and long components: the short lifetime is characterized by the lifetime of the light pulse γ_c^{-1}, while the long time corresponds to the decay of the level $|s\rangle$, Γ^{-1}. The oscillations appearing in some of the graphs have a small amplitude and will be smeared out when Doppler broadening is taken into account. They will not be seen experimentally. The following points are now in order:

(1) Equation (29) describes the time dependence of the population of the optically active molecular excited state $|s\rangle$ at all times following the situation in which a planar pulse of light characterized by the density operator (23) is formed at an infinite distance from the molecule and starts moving towards the molecule The total intensity of the light scattered by the molecule is proportional at each time to this quantity.

(2) The new feature of the result, Eq. (29), relative to previous results is the mutual independence of the time [characterized by the distribution function $B(\omega)$] and energy [characterized by both $B(\omega)$ and $C(\omega)$] profiles. This reflects the independence of shutter and filter in an experimental setup. When a pulse is really of minimum uncertainty, we set $C(\omega) = \delta(\omega)$, and this leads to the results of Sec. II.

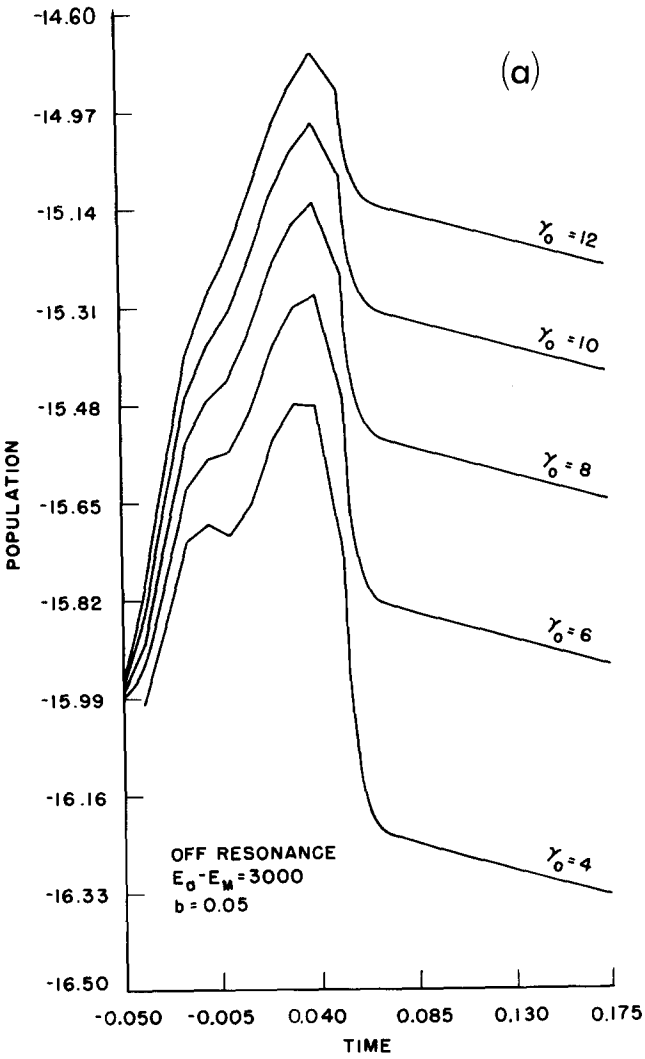
(3) Laser pulses are sometimes, to a good approximation, of the minimum uncertainty type, in which case $\gamma_c \gg \gamma_0$ and $\gamma_M \simeq \gamma_c$. However, even in such cases the influence of a small nonzero γ_0 can lead to nontrivial consequences. Consider for example the WRD experiment. Here γ_c^{-1} is the rise time of the laser pulse ($\sim 3 \times 10^{-9}$ sec) and corresponds to a width of $\sim 2\times10^{-3}$ cm^{-1}, while the long decay time of the fluorescence ($\sim 1\times10^{-6}$ sec) corresponds to a width of $\Gamma \sim 5\times10^{-6}$ cm^{-1}. Now, for the case in which the distribution $C(\omega_0 - \omega_M)$ [Eq. (23)] is the Lorentzian [Eq. (30)], numerical computations show[2b] that even for γ_0 as small as $\sim 1\times10^{-7}$ cm^{-1}, an average over this distribution leads to a qualitative change in the theoretical prediction. In this case $\gamma_0/\gamma_c \sim 10^{-4}$ and we see that a mixed character of a tenth of a percent is sufficient to cause a measurable effect. Explicitly, the consideration of γ_0 makes the dependence of the ratio of intensities of the long and short decay components a weak function of the off-resonance energy, $\Delta = E_s - \omega_M$, in the range $\Delta = 2500\,\Gamma \sim 5000\,\Gamma$ as experimentally observed, rather than the Δ^2 behavior predicted for the case $\gamma_0 = 0$.

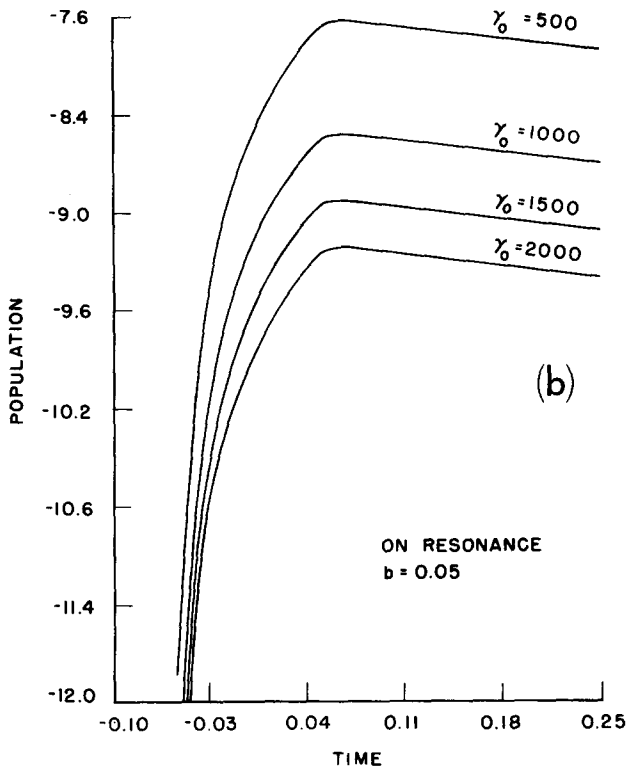
However, Mukamel, Jortner, and Ben Reuven[2b] also showed that distributions $C(\omega)$ which decreases as a function of ω more rapidly than Δ^{-4} have relatively little effect on the calculated quantities, and in particular do not modify the ratio of intensities of the long and short decay components in the way the Lorentzian distribution, Eq. (30), does. In general, one should expect that different experimental conditions will be characterized by different distributions $C(\omega)$, and hence knowledge of that distribution of the incident photon is necessary for understanding some of the finer details of the subsequent relaxation process.

IV. CONCLUSION

This paper has provided a simple extension of recent work[2,3] on resonant and near-resonant scattering of light pulses. This extension allows for a description based on mixed states of one photon pulses, also referred to as larger than minimum uncertainty pulses. The results for the present model are obtained as averages of the previous results over the distribution which characterizes the density matrix of the light pulse. Physically the present model allows for independent time and energy profiles of the light pulse, while in the earlier models[2,3] these were related to each other by a simple Fourier transform. Our modification may have observable consequences even for a very small mixed nature of the light pulse. This should be kept in mind, especially when one tries to estimate the cross section for phase changing oollisions from results of experiments[2b] such as those of WRD. The reliability of such estimates is uncertain as long as the nature of the light pulse is not exactly known. We have shown that a Lorentzian width of the distribution function $C(\omega)$, Eq. (30), of 0.1% of the total pulsewidth in the WRD experiment would lead to essentially the same observation that Mukamel, Jortner, and Ben Reuven[2b] attribute to collision broadening.

The model discussion by us (like that treated in Sec. II and in Refs. 2 and 3) is only one of many possible models compatible with our present knowledge of the structure of light pulses. The correct statistics of the pulse might play an important role in the outcome of a given experiment. Especially, the intensity of the pulse might have a nontrivial influence on some measurements like the ratio of the short and long life intensities, which may happen because for strong pulses the excited molecular state interacts during the lifetime of the short component with a nonvacuum radiation field. To check





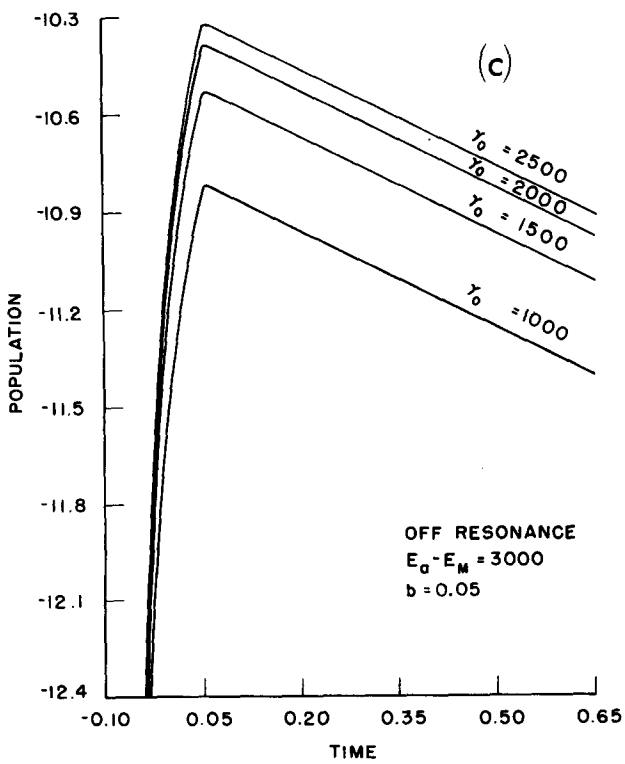


FIG. 1. The population of the level $|s\rangle$ given in a logarithmic scale and arbitrary units, as a function of time. All parameters are given in units of 2Γ (frequency) and $(2\Gamma)^{-1}$(time). For I_2, Γ is of the order 10^6 sec^{-1}; γ_c^{-1} is the rise time of the pulse defined by (31) and is taken to be 1500; b is the duration of the pulse [Eq. (31)]; γ_0 is the width of the Lorentzian $B(\omega)$ appearing in (21); Γ is the line width (natural + radiationless) of the line s; $E_a - \omega_n$ is the off-resonance parameter. 1(a) Represents the off-resonance population for relatively small γ_0. Two decay times are present as in WRD; 1(b) is the on-resonance population; 1(c) is the off-resonance population at large γ_0. Only one time scale is present in this case.

the consequence of this, models which include pulses like Eq. (22) should be treated.

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APPENDIX A

Here we compare the local time evolution of the pure packet given by Eq. (13) or Eq. (9) and the mixed packet described by Eq. (23). The density of photons at some point, say the origin $x=0$ at time t, is given by the expectation value of the operator $\psi^\dagger(0)\psi(0)$ at this time. For the state (9) we get

$$|\langle i|e^{iH_R t}\psi^\dagger(0)\psi(0)e^{-iH_R t}|i\rangle|^2 \propto \left|\sum_k\sum_{k'}\sum_{k_1}\sum_{k_2}A(k-k_0)A^*(k'-k_0)e^{-i(k-k')x_0}\langle 0|a_{k'}e^{i\omega_{k'}t}a_{k_1}^\dagger a_{k_2}e^{-i\omega_k t}a_k^\dagger|0\rangle\right|^2$$
$$= \left|\sum_k\sum_{k'}A(k-k_0)A^*(k'-k_0)\exp[-i(k-k')(x_0+ct)]\right|^2$$
$$= \left|\sum_k A(k-k_0)\exp[-ikc(t_0+t)]\right|^2 = \left|\int d\omega B(\omega-\omega_0)\exp[-i\omega(t_0+t)]\right|^2, \tag{A1}$$

while the time evolution of Eq. (23) leads to

$$\mathrm{Tr}(\psi^\dagger(x)\psi(x)\rho(t)) \propto \int d\omega_0(\omega_0-\omega_M)\sum_k\sum_{k'}\sum_{k_1}\sum_{k_2}A(k-k_0)A^*(k'-k_0)\exp[-i(k-k')(x_0+ct)]\,\mathrm{Tr}[a_{k_1}^\dagger a_{k_2}a_k^\dagger|0\rangle\langle 0|a_{k'}]$$
$$= \int d\omega_0 c(\omega_0-\omega_M)\sum_k\sum_{k'}\sum_{k_1}\sum_{k_2}A(k-k_0)A^*(k'-k_0)\exp[-i(k-k')(x_0+ct)]\,\delta_{k_1k'}\delta_{k_2k}$$
$$= \int d\omega_0 c(\omega_0-\omega_M)\left|\sum_k A(k-k_0)\exp[-i\omega(t_0+t)]\right|^2$$
$$= \int d\omega_0 c(\omega_0-\omega_M)\left|\int d\omega B(\omega-\omega_0)\exp[-i\omega(t_0+t)]\right|^2. \tag{A2}$$

The quantity within the absolute value does not depend on ω_0, and from $\int d\omega_0 C(\omega_0-\omega_M)=1$ we get Eq. (A1), as before. Both wave packets are thus characterized by the same temporal behavior.

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[6]We neglect here the dependence on spatial coordinates which will be taken into account later.

[7]Throughout this paper the energy is in units of $\hbar$.

[8]We neglect intermolecular interactions and assume that the size l of the molecular sample is small enough so that l/c is much smaller than the shortest time scale of the experiment (3×10^{-9} sec in the WRD experiment which implies $l \ll 90$ cm).

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