Nonimpact unified theory of four-wave mixing and two-photon processes

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A microscopic correlation-function theory for coherent, parametric, four-photon processes (four-wave mixing) and for single-absorber two-photon processes (two-photon absorption, Raman, and fluorescence spectra) is developed. Both types of experimental observables are expressed in terms of four-point correlation functions of the dipole operator. The latter are then evaluated semiclassically or within the factorization approximation in which they are expressed in terms of ordinary single-photon line-shape functions. The common results of the Bloch equations are shown to be the outcome of two successive approximations: the factorization approximation and the impact limit whereby the single-photon line-shape functions are taken to be Lorentzian. Effects of fluctuations in the radiation fields are easily incorporated within the present approach.

I. INTRODUCTION

Studies of nonlinear optical phenomena such as four-wave mixing[1-8] or two-photon absorption, Raman, and fluorescence spectroscopy[9-12] provide a very sensitive means for the measurement of spectral line shapes. The common theoretical model which applies to these studies consists of a few-level system (the "absorber") which interacts with an electromagnetic field and with an external bath consisting of many degress of freedom. The bath usually causes relaxation and the absorber-bath interaction influences significantly the time evolution of the absorber. The conventional theoretical tool in these studies, which was applied with remarkable success for numerous different experimental situations, is the multilevel Bloch equations.[13-15] In these equations the radiation field is treated classically and the effects of the bath are incorporated by the addition of phenomenological level relaxation (T_1) and dephasing (T_2) rates into the Liouville equation for the isolated absorber plus field. The classical treatment of the radiation field is justified in many cases[16,17] and is usually equivalent to the fully quantum-mechanical "dressed-atom" approach[18,19] with the exception of phenomena such as spontaneous emission.[20] The phenomenological treatment of the relaxation poses several serious fundamental problems. A direct consequence of this treatment is that an ordinary line shape is predicted to have a simple Lorentzian form. Moreover, all few-photon and multiphoton cross sections are given as sums of products of Lorentzian complex amplitudes. This simplicity which provides a very convenient way for back of the envelope interpretation of experiments, is obviously at the expense of rigor, and is often in disagreement with experimental facts. A few examples are the following. (1) It is well established both experimentally and theoretically that no ordinary line shape is Lorentzian in its far wings, which means that even if the simple Bloch equations hold for small detunings, they will fail in the wings.[21] Deviations from a Lorentzian form will be significant whenever the detuning is comparable with the inverse correlation time of the bath (e.g., duration of a collision in pressure broadening, the inverse of a typical phonon frequency in crystals, etc.). The detailed study and analysis of spectral line shapes in the wings may yield microscopic information regarding the dynamical interactions in the system, provided an adequate theory is available. (2) Precise measurements of spectral line shapes near the line center show asymmetries which reflect the finite duration of atomic collisions and are in contradiction to the simple Lorentzian form, even in cases where the latter is most likely to hold.[22,23] (3) Single-photon line shapes are often adequately evaluated in the static limit where the deviations from a Lorentzian behavior are very significant.[21,24] (4) In multiphoton processes, there are dephasing-induced effects such as the collisional redistribution in resonance Raman[9-11] and two-photon absorption[12] or the collision-induced resonances in four-wave mixing[7,8] [the so-called PIER4 (pressure-induced extra resonance) or its solid-state analog DICE (dephasing-induced coherent emission) signals]. In these cases, the magnitude of the effect itself (and not just its behavior in the wings) depends on the behavior in the wings of some line shapes. As a result, these effects provide a convenient and a sensitive way to study line shapes at large detunings[25] where the Lorentzian form fails. For resonance Raman in a three-level system, there is a coherent and an incoherent (redistribution) component of the scattered radiation. The theoretical treatment based on the Bloch equations[26] predicts that the ratio of these two components is independent on the detuning of the exciting radiation. This is in contrast with reality, since the redistribution component actually vanishes much faster than the coherent component as the detuning is increased.[10] In this paper, we shall develop a microscopic theory for four-wave-mixing (4 WM) line shapes. Four-wave mixing is one of the most sensitive spectroscopic tools available at present. The 4 WM is a parametric (i.e., many-absorber) macroscopic four-photon process in which three electromagnetic fields (ω_1, ω_2, and ω_3) are interacting simultaneously with a sample and a fourth field (ω_4) is being coherently generated and detected (Fig. 1). The

fourth field is subject to phase-matching conditions and has a sharp frequency and spatial profiles $\sim\delta(\omega_4+\omega_2-\omega_1-\omega_3)\delta(\vec{k}_4+\vec{k}_2-\vec{k}_1-\vec{k}_3)$, $\vec{k}_i$ being the wave vector of the ith field. The basic quantity which is usually used in 4WM studies is the nonlinear susceptibility $\chi^{(3)}$ which was evaluated by Bloembergen[1] using the Bloch equations. The signal intensity in a 4WM experiment [Eq. (27)] is proportional to the absolute magnitude square of $\chi^{(3)}$, i.e.,

$$S_{4\mathrm{WM}}(-\omega_4,\omega_1,-\omega_2,\omega_3)\alpha\,|\,\chi^{(3)}(-\omega_4,\omega_1,-\omega_2,\omega_3)\,|^2\,. \tag{1}$$

Equation (1) holds since the 4WM is a coherent parametric process. Therefore, we may calculate an amplitude for the process ($\chi^{(3)}$), average it over the bath, and then square it to get $S_{4\mathrm{WM}}$. Using a microscopic description, the cross section for an n-photon process is usually expressed in terms of a $2n$ time-correlation function of the dipole operator.[27] Therefore, the rigorous calculation of $S_{4\mathrm{WM}}$ (a four-photon process) requires the evaluation of an eight—time-correlation function. However, since we are actually calculating a thermally averaged *amplitude* for this coherent processes, the calculation involves only a four-point correlation function. It is our purpose in this paper to develop a microscopic theory for $S_{4\mathrm{WM}}$. To that end we shall express $\chi^{(3)}$ in terms of four-point correlation functions and then derive microscopic expressions for the latter quantities. This is done in two degrees of sophistication. We first make use of the *factorization approximation* which enables us to write the cross section for any multiphoton process as a product of single-photon complex line-shape functions. The problem of ordinary (single-photon) absorption line shapes has been treated in the literature by numerous methods (cluster expansion, perturbation theory, semiclassical methods, stochastic approaches, etc.) and is well understood.[21,27] By now there exists the unified theory of spectral line shapes which enables us to calculate them microscopically. Using the factorization approximation, we can then make use of the enormous progress made in the theoretical treatment of the latter quantities and provide simple easily calculable expressions for $\chi^{(3)}$. We further show that the conventional results of the Bloch equations are obtained if in addition to the factorization we further assume that the single-photon line shapes are simply Lorentzian (the impact limit). The Bloch equations are therefore equivalent to the factorization together with the impact approximations. By relaxing the impact and retaining just the factorization approximation, we are able to generalize Bloembergen's expression for $\chi^{(3)}$ in a straightforward way. The second method for the calculation of the four—time-correlation functions is *semiclassical* and utilizes the cumulant expansion. Both methods interpolate between the impact and the static limits. With this we conclude our discussion of four-wave-mixing experiments. We note, however, that the cross sections for two-photon processes (two-photon absorption, fluorescence, or Raman spectra) of a single absorber (in a bath) are also given by a four-point correlation function.[27] In this case, since these are nonparametric processes, we average the *cross section* (and not the *amplitude)* over the bath and this is why we need a four-point correlation function for a two-photon process. We therefore show later how the cross section for two-photon processes is actually probing virtually the same microscopic quantity as a 4WM experiment (of course with a different sensitivity, and each experiment may be probing better different features of this correlation function). The plan of this paper is as follows. In Sec. II, we review nonlinear reponse theory and derive a compact expression for nonlinear susceptibilities [Eq. (14c) or (21)]. In Sec. III, we specialize to 4WM and present the diagrams as well as explicit expressions for $\chi^{(3)}$ in terms of appropriate four-point correlation functions. In Sec. IV, we evaluate the latter using the factorization approximation and in Sec. V, we present the more rigorous semiclassical calculation of the four-point correlation functions. Finally, in Sec. VI, we consider two-photon processes and show how both steady-state and transient experiments are actually probing the same correlation functions which appear in 4WM. The present theory is valid for a general type of bath which causes dephasing and it may be collisions, density fluctuations in liquids, electron-phonon coupling, phase fluctuations of the radiation field, etc.[27]

II. SURVEY OF NONLINEAR RESPONSE THEORY

In this section, we shall briefly review nonlinear response theory in order to introduce the formal tools and the notation to be used throughout this paper.[1,2,27]

We consider a system driven by a time-dependent classical field. The Hamiltonian for the perturbed system is given by

$$H=H_0+\tilde{V}(t)\,. \tag{2}$$

The Liouville equation for the density matrix ρ is

$$\frac{d\rho}{dt}=-iL\rho=-i[L_0+\tilde{\mathscr{V}}(t)]\rho\,, \tag{3}$$

where

$$L_0\equiv[H_0,\ ]\,, \tag{4a}$$

$$L\equiv[H,\ ]\,, \tag{4b}$$

and

$$\tilde{\mathscr{V}}(t)\equiv[\tilde{V}(t),\ ] \tag{4c}$$

are Liouville-space (tetradic) operators.

Assuming that at time $t\to-\infty$, $\rho(-\infty)$ is an equilibrium distribution of H_0, i.e.,

$$L_0\rho(-\infty)=0\,, \tag{5}$$

we may write the formal expression for the time-dependent density matrix $\rho(t)$ as follows:

$$\rho(t)=U(t,-\infty)\rho(-\infty)\equiv\rho^{(0)}+\rho^{(1)}+\rho^{(2)}+\cdots\,. \tag{6}$$

Here, U is the propagator,

$$U(t,-\infty)=1-i\int_{-\infty}^{t}d\tau\, G_0(t-\tau)\tilde{\mathscr{V}}(\tau)+(-i)^2\int_{-\infty}^{t}d\tau_1\int_{-\infty}^{\tau_1}d\tau_2 G_0(t-\tau_1)\tilde{\mathscr{V}}(\tau_1)G_0(\tau_1-\tau_2)\tilde{\mathscr{V}}(\tau_2)+\cdots\ , \tag{7}$$

where

$$G_0(\tau)=\exp(-iL_0\tau)\ . \tag{8}$$

$\rho^{(j)}$ is the term in the expansion [Eq. (6)] that is to jth order in $\tilde{\mathscr{V}}$. We shall now assume that the external field is a superposition of a few monochromatic fields, i.e.,

$$\tilde{V}(t)=V\{[E_1\exp(-i\omega_1 t)+E_2\exp(-i\omega_2 t)+\cdots]+\text{c.c.}\}\ . \tag{9}$$

Here E_j is the amplitude of the jth field and V is the dipole operator of the material system. Making use of the trivial identity

$$\exp(-i\omega_j\tau)=\exp(-i\omega_j t)\exp[-i\omega_j(\tau-t)] \tag{10}$$

and substituting it in Eqs. (6) and (7), we get

$$\rho^{(0)}(t)=\rho(-\infty)\ , \tag{11a}$$

$$\rho^{(1)}(t)=E_1\exp(-i\omega_1 t)G_0(\omega_1)\mathscr{V}\rho(-\infty)\ , \tag{11b}$$

$$\rho^{(2)}(t)=E_1\exp(-i\omega_1 t)E_2\exp(-i\omega_2 t)\times G(\omega_1+\omega_2)\mathscr{V}G(\omega_1)\mathscr{V}\rho(-\infty)\ , \tag{11c}$$

etc., where $\mathscr{V}\equiv[V,\ ]$ and

$$G_0(\omega)\equiv\frac{1}{\omega-L_0+i\epsilon},\quad \epsilon\to 0\ . \tag{12}$$

In Eqs. (11) we should also include positive frequency terms obtained by the substitution $\omega_j\to-\omega_j$. Moreover, $\rho^{(n)}$ should contain a sum over all possible permutations of the n frequencies $\omega_1,\ldots,\omega_n$. This corresponds to the fact that the interactions with the various fields may occur in all possible sequences in time. For brevity, we did not write these terms explicitly here.

The expectation value of the dynamical variable B at time t will now be given by

$$\langle B(t)\rangle\equiv\mathrm{Tr}[B\rho(t)]\equiv\sum_k\chi^{(k)}(-\omega_p,\omega_1,\omega_2,\ldots,\omega_k)E_1\exp(-i\omega_1 t)E_2\exp(-i\omega_2 t)\cdots E_k\exp(-i\omega_k t)\ , \tag{13}$$

where

$$\omega_p=\omega_1+\omega_2+\cdots+\omega_k\ . \tag{13'}$$

The index ω_p in the definition of $\chi^{(k)}$ means that we select the component of B oscillating at this frequency [Eq. (13')]. Using Eqs. (11) and (13) $\chi^{(k)}$ are given by

$$\chi^{(1)}=\langle\langle B\mid G(\omega_1)\mathscr{V}\mid\rho(-\infty)\rangle\rangle\ , \tag{14a}$$

$$\chi^{(2)}=\sum_{P(\omega_1,\omega_2)}\langle\langle B\mid G(\omega_1+\omega_2)\mathscr{V}G(\omega_1)\mathscr{V}\mid\rho(-\infty)\rangle\rangle\ , \tag{14b}$$

$$\vdots$$

$$\chi^{(n)}=\sum_{P(\omega_1,\omega_2,\ldots,\omega_n)}\langle\langle B\mid G(\omega_1+\omega_2+\cdots+\omega_n)\mathscr{V}G(\omega_1+\cdots+\omega_{n-1})\mathscr{V}\cdots G(\omega_1)\mathscr{V}\mid\rho(-\infty)\rangle\rangle\ , \tag{14c}$$

where we have introduced a notation for a tetradic "matrix element"

$$\langle\langle B\mid\mathscr{V}\mid A\rangle\rangle\equiv\mathrm{Tr}(B^\dagger\mathscr{V}A)\ . \tag{15}$$

Equation (14c) is our basic formal relation to be used later. Alternatively, we may rewrite it in the time domain:

$$\chi^{(n)}(-\omega_p,\omega_1,\ldots,\omega_n)=(-i)^n\sum_{P(\omega_1,\omega_2,\ldots,\omega_n)}\int_0^\infty dt_1\int_0^{t_1}dt_2\cdots\int_0^{t_{n-1}}dt_n\exp(i\omega_1 t_1+i\omega_2 t_2+\cdots+i\omega_n t_n)\times\langle\langle B\mid G_0(t_n)\mathscr{V}G_0(t_{n-1}-t_n)\mathscr{V}G_0(t_{n-2}-t_{n-1})\mathscr{V}\times\cdots G_0(t_1-t_2)\mathscr{V}\mid\rho(-\infty)\rangle\rangle\ . \tag{16}$$

It should be noted that when the polarizations of the various fields are explicitly included, $\chi^{(3)}$ becomes a tensorial quantity. For the sake of simplifying the presentation we did not introduce here the tensorial notation. This can be done, however, without major difficulty.[1,2]

We are now in a position to rewrite Eq. (16) in terms of appropriate correlation functions. To that end let us specify more precisely our Hamiltonian H_0. We assume that we have a few-level system with levels $|\nu\rangle=|a\rangle$, $|b\rangle$, $|c\rangle$, etc., interacting with a bath. The total Hamiltonian is written as

$$H_0=\sum_{\nu=a,b,c,\ldots}|\nu\rangle[\epsilon_\nu-\tfrac{1}{2}i\gamma_\nu+F_\nu(Q_B)]\langle\nu| \ . \tag{17}$$

Here, ϵ_ν and γ_ν are the energy and inverse lifetime of the level ν. $F_\nu(Q_B)$ is an adiabatic Hamiltonian describing the bath degrees of freedom (Q_B) interacting with our n-level system in the state ν. For the sake of the present development, we do not need to specify F_ν any further. The only restriction here is that F_ν is adiabatic (i.e., diagonal in the system states). All inelastic interactions are included in γ_ν. Owing to our phenomenological treatment of the level lifetimes γ_ν, H_0 contains an anti-Hermitian part ($\frac{1}{2}i\gamma_\nu$). It is therefore convenient to split H_0 as follows:

$$H_0\equiv H_s+H' \ , \tag{18}$$

where H' is Hermitian. A simple choice for the partitioning (18) is

$$H_s=\sum_\nu|\nu\rangle(\epsilon_\nu-\tfrac{1}{2}i\gamma_\nu)\langle\nu| \ , \tag{18'}$$

$$H'=\sum_\nu|\nu\rangle F_\nu(Q_B)\langle\nu| \tag{18''}$$

with the corresponding Liouville operators

$$L_s=[H_s,\ ] \ , \tag{19a}$$

$$L'=[H',\ ] \ . \tag{19b}$$

Note that H_s and H' commute, i.e.,

$$[H_s,H']=0 \ . \tag{20}$$

We can then write

$$\chi^{(n)}=(-i)^n\sum_{P(\omega_1,\omega_2,\ldots,\omega_n)}\int_0^\infty dt_1\int_0^{t_1}dt_2\cdots\int_0^{t_{n-1}}dt_n\exp(i\omega_1t_1+i\omega_2t_2+\cdots+i\omega_nt_n)$$
$$\times\langle\langle B(t_1)|\ G_s(t_n)\mathscr{V}(t_1-t_n)G_s(t_{n-1}-t_n)\mathscr{V}(t_1-t_{n-1})$$
$$\times\cdots\mathscr{V}(t_1-t_2)G_s(t_1-t_2)\mathscr{V}(0)|\,aa\rangle\rangle \ , \tag{21}$$

where

$$B(\tau)=\exp(iH'\tau)B\exp(-iH'\tau) \ , \tag{21'}$$

$$\mathscr{V}(\tau)=\exp(iL'\tau)\mathscr{V}\exp(-iL'\tau) \ , \tag{21''}$$

and

$$G_s(\tau)=\exp(-iL_s\tau) \ . \tag{21'''}$$

It is important that L' is Hermitian so that the non-Hermitian parts of L_0 are included in L_s. $G_s(\tau)$ is a simple operator given by

$$\langle\langle\nu\mu|\,G_s(\tau)\,|\nu'\mu'\rangle\rangle=\delta_{\nu\nu'}\delta_{\mu\mu'}\exp(-\gamma_{\nu\mu}\tau),\quad \gamma_{\nu\mu}\equiv\tfrac{1}{2}(\gamma_\nu+\gamma_\mu)+i(\epsilon_\nu-\epsilon_\mu) \ . \tag{22}$$

Upon changing the integration variables

$$\tau_1=t_1,\quad \tau_2=t_1-t_n,\quad \tau_3=t_1-t_{n-1},\quad \ldots,\quad \tau_n=t_1-t_2 \ , \tag{23}$$

we finally get

$$\chi^{(n)}=(-i)^n\sum_{P(\omega_1,\omega_2,\ldots,\omega_n)}\int_0^\infty d\tau_1\int_0^{\tau_1}d\tau_2\cdots\int_0^{\tau_{n-1}}d\tau_n\exp[\,i\omega_1\tau_1+i\omega_2(\tau_1-\tau_n)+i\omega_3(\tau_1-\tau_{n-1})$$
$$+\cdots+i\omega_n(\tau_1-\tau_2)]$$
$$\times\langle\langle B(\tau_1)|\ G_s(\tau_1-\tau_2)\mathscr{V}(\tau_2)G_s(\tau_2-\tau_3)\mathscr{V}(\tau_3)$$
$$\times\cdots\mathscr{V}(\tau_n)G_s(\tau_n)\mathscr{V}(0)|\,\rho(-\infty)\rangle\rangle \ . \tag{24}$$

When Eq. (24) is evaluated explicitly, the G_s terms simply contribute phase and damping factors [Eq. (22)] whereas the $\mathscr{V}$ terms when applied in all possible ways (from left to right) will result in a linear combintaion of correlation functions of the dipole operator. Equations (7), (14), and (24) are the general formal relations which will be used in the following sections to calculate $\chi^{(3)}$ and the cross sections for two-photon processes.

III. A CORRELATION-FUNCTION EXPRESSION FOR FOUR-WAVE MIXING

We shall now focus on four-wave-mixing experiments. In these experiments, we have three external electromagnetic fields (ω_1, ω_2, and ω_3) interacting simultaneously with a macroscopic sample, and a fourth field (ω_4) is being generated by the process shown in Fig. 1. The conventional procedure for the calculation of the gain in the ω_4 field[1,2,6,28] consists of calculating the macroscopic polarization, which is the expectation value of the dipole operator at steady state [$B=V$ in Eq. (24)], which oscillates at frequency $\omega_4=\omega_1+\omega_3-\omega_2$,

$$P(\omega_4)=\chi^{(3)}(-\omega_4,\omega_1,-\omega_2,\omega_3)E_1E_2E_3\exp(-i\omega_1 t+i\omega_2 t-i\omega_3 t)\ . \tag{25}$$

This polarization is then used as a source in Maxwell's equations and generates a field with frequency ω_4 and wave vector $\vec{k}_4=\vec{k}_1+\vec{k}_3-\vec{k}_2$. We therefore have [using Eq. (14c)]

$$\chi^{(3)}(-\omega_4,\omega_1,-\omega_2,\omega_3)=\sum_{P(\omega_1,-\omega_2,\omega_3)}\sum_a \langle\langle V\,|\,G(\omega_1-\omega_2+\omega_3)\mathscr{V}G(\omega_1-\omega_2)\mathscr{V}G(\omega_1)\mathscr{V}\,|\,aa\rangle\rangle\bar{P}(a)\ . \tag{26a}$$

Alternatively, in the time domain [Eq. (24)], we have

$$\chi^{(3)}(-\omega_4,\omega_1,-\omega_2,\omega_3)=(-i)^3\sum_{P(\omega_1,-\omega_2,\omega_3)}\sum_a\int_0^\infty d\tau_1\int_0^{\tau_1}d\tau_2\int_0^{\tau_2}d\tau_3\exp[i\omega_1\tau_1-i\omega_2(\tau_1-\tau_3)+i\omega_3(\tau_1-\tau_2)]$$
$$\times\langle\langle V(\tau_1)\,|\,G_s(\tau_1-\tau_2)\mathscr{V}(\tau_2)G_s(\tau_2-\tau_3)$$
$$\times\mathscr{V}(\tau_3)G_s(\tau_3)\mathscr{V}(0)\,|\,aa\rangle\rangle\bar{P}(a)\ . \tag{26b}$$

We have taken $B=V$ in Eqs. (14c) and (24). In addition, we took

$$\rho(-\infty)=\sum_a\bar{P}(a)\,|\,aa\rangle\rangle\ , \tag{26c}$$

where $\bar{P}(a)$ is the population of level $|a\rangle$ at thermal equilibrium, in the absence of any radiation field. The intensity of the 4WM signal may be obtained by substituting the polarization [Eq. (25)] as a source in Maxwell's equations and solving for the ω_4 field. Within the slowly varying amplitude approximation this results in[1-3,6]

$$S_{4\mathrm{WM}}=\frac{2\pi\omega_4^2 l^2}{n(\omega_4)c^2}\,|P(\omega_4)|^2 \times\frac{\sin^2[(\vec{k}_1+\vec{k}_3-\vec{k}_2-\vec{k}_4)\cdot\vec{l}/2]}{[(\vec{k}_1+\vec{k}_3-\vec{k}_2-\vec{k}_4)\cdot\vec{l}/2]^2}\ . \tag{27}$$

Here n is the index of refraction, c is the velocity of light, and l is the length of the sample.

A pictorial representation of Eq. (26) is given in Fig. 2. Each bond denotes a radiative coupling $\mathscr{V}$. Since $\mathscr{V}$ is a commutator, it can act either from the right (horizontal lines) or from the left (vertical lines). Figure 2 is an efficient bookkeeping device which keeps track of the eight different three-bond pathways relevant for $\chi^{(3)}$. In each pathway, the first bond which starts at $|aa\rangle\rangle$ comes first in time, etc. [Eq. (26b)]. We note that in general for $\chi^{(n)}$ there will be 2^n, n-bond pathways. In addition to this, the fields ω_1, $-\omega_2$, and ω_3 can be applied in all possible sequences. We therefore have $3!=6$ permutations of the fields. Altogether, we have $6\times8=48$ terms (for $\chi^{(n)}$ we shall have $2^n n!$ terms).[1,2,6,28]

Let us consider now the eight pathways in detail. The first pathway is the one in which $\mathscr{V}$ operates always from the right, and ends up in $|ad\rangle\rangle$. We denote this path by (RRR). The second pathway is the one in which $\mathscr{V}$ operates first from the left and then twice from the right. It ends up in $|dc\rangle\rangle$ and will be denoted (RRL), etc. We shall now list our eight pathways. The first set of parentheses in each line in Eq. (28) denotes the left-right choice of the path. Note that there is a minus sign associated with each R (commutator acting from the right). The second set of parentheses denotes the points (Fig. 2) through which it passes, and then comes its contribution to Eq. (26b). Note that all the pathways end up along the broken line in Fig. 2:

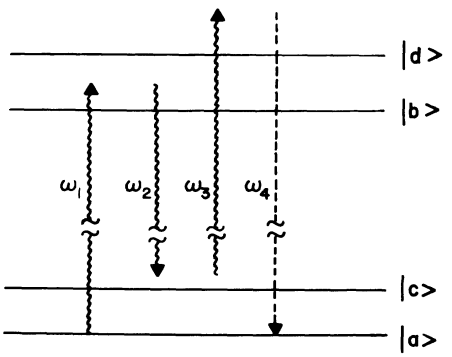

FIG. 1. Energy-level scheme and mode frequencies for four-wave mixing.

$$
\begin{array}{lll}
\text{(i)} & (RRR), & (ad,ac,ab,aa), \quad F(0,\tau_3,\tau_2,\tau_1)\exp[-\gamma_{ab}\tau_3-\gamma_{ac}(\tau_2-\tau_3)-\gamma_{ad}(\tau_1-\tau_2)], \\
\text{(ii)} & (RRL), & (dc,db,da,aa), \quad F(\tau_3,\tau_2,\tau_1,0)\exp[-\gamma_{da}\tau_3-\gamma_{db}(\tau_2-\tau_3)-\gamma_{dc}(\tau_1-\tau_2)], \\
\text{(iii)} & (RLR), & (dc,db,ab,aa), \quad F(0,\tau_2,\tau_1,\tau_3)\exp[-\gamma_{ab}\tau_3-\gamma_{db}(\tau_2-\tau_3)-\gamma_{dc}(\tau_1-\tau_2)], \\
\text{(iv)} & (LRR), & (dc,ac,ab,aa), \quad F(0,\tau_3,\tau_1,\tau_2)\exp[-\gamma_{ab}\tau_3-\gamma_{ac}(\tau_2-\tau_3)-\gamma_{dc}(\tau_1-\tau_2)], \\
\text{(v)} & (LLL), & (ba,ca,da,aa), \quad F(\tau_1,\tau_2,\tau_3,0)\exp[-\gamma_{da}\tau_3-\gamma_{ca}(\tau_2-\tau_3)-\gamma_{ba}(\tau_1-\tau_2)], \\
\text{(vi)} & (LLR), & (cb,db,ab,aa), \quad F(0,\tau_1,\tau_2,\tau_3)\exp[-\gamma_{ab}\tau_3-\gamma_{db}(\tau_2-\tau_3)-\gamma_{cb}(\tau_1-\tau_2)], \\
\text{(vii)} & (LRL), & (cb,db,da,aa), \quad F(\tau_3,\tau_1,\tau_2,0)\exp[-\gamma_{da}\tau_3-\gamma_{db}(\tau_2-\tau_3)-\gamma_{cb}(\tau_1-\tau_2)], \\
\text{(viii)} & (RLL), & (cb,ca,da,aa), \quad F(\tau_2,\tau_1,\tau_3,0)\exp[-\gamma_{da}\tau_3-\gamma_{ca}(\tau_2-\tau_3)-\gamma_{cb}(\tau_1-\tau_2)],
\end{array}
\tag{28}
$$

where

$$F(\tau_1,\tau_2,\tau_3,\tau_4)\equiv\langle V_{ab}(\tau_1)V_{bc}(\tau_2)V_{cd}(\tau_3)V_{da}(\tau_4)\rangle\ , \tag{29}$$

$$V(\tau)\equiv\exp(iH'\tau)V\exp(-iH'\tau)\ . \tag{30}$$

Upon substituting Eq. (28) in Eq. (26b) we finally get

$$
\begin{aligned}
\chi^{(3)}(-\omega_4,\omega_1,-\omega_2,\omega_3)
&= \sum_{a,b,c,d}\bar{P}(a)\sum_{P(\omega_1,-\omega_2,\omega_3)}\int_0^\infty d\tau_1\int_0^{\tau_1}d\tau_2\int_0^{\tau_2}d\tau_3\exp[i\omega_1\tau_1+i\omega_2(\tau_1-\tau_3)+i\omega_3(\tau_1-\tau_2)] \\
&\times\{\,-F(0,\tau_3,\tau_2,\tau_1)\exp[-\gamma_{ab}\tau_3-\gamma_{ac}(\tau_2-\tau_3)-\gamma_{ad}(\tau_1-\tau_2)] \\
&\quad +F(\tau_3,\tau_2,\tau_1,0)\exp[-\gamma_{da}\tau_3-\gamma_{db}(\tau_2-\tau_3)-\gamma_{dc}(\tau_1-\tau_2)] \\
&\quad +F(0,\tau_2,\tau_1,\tau_3)\exp[-\gamma_{ab}\tau_3-\gamma_{db}(\tau_2-\tau_3)-\gamma_{dc}(\tau_1-\tau_2)] \\
&\quad +F(0,\tau_3,\tau_1,\tau_2)\exp[-\gamma_{ab}\tau_3-\gamma_{ac}(\tau_2-\tau_3)-\gamma_{dc}(\tau_1-\tau_2)]\}-\text{c.c.})\ .
\end{aligned}
\tag{31}
$$

The following points should now be noted.

(1) In Eq. (31) we have written explicitly only pathways (i)—(iv). Pathways (v)—(viii) are obtained from the first four paths by reversing all time arguments and interchanging b and d. Since Eq. (31) includes a summation over all possible b and d states, their contribution is simply the complex conjugate of the former, as indicated in Eq. (31).

(2) The expression is *averaged* over the initial thermal distribution of $|a\rangle$, $\bar{P}(a)$ and *summed* over all possible b,c,d states.

(3) $\sum_{P(\omega_1,-\omega_2,\omega_3)}$ means that after calculating the eight pathways, we have to allow for the $3!=6$ permutations of the three frequencies. This will make $6\times8=48$ terms altogether. (In general, for $\chi^{(n)}$ we have $2^n n!$ terms corresponding to the 2^n pathways and $n!$ permutations of the fields.)

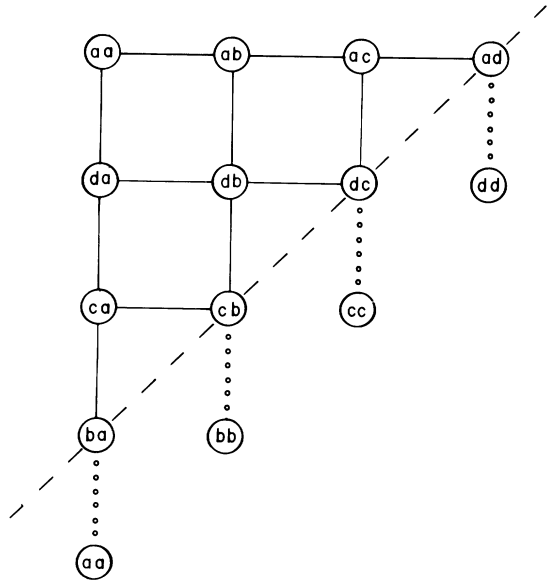

FIG. 2. Pictorial representation of the possible pathways for four-wave mixing [Eq. (26)]. Solid lines denote radiative coupling $\mathscr{V}$. Horizontal (vertical) lines represent action of $\mathscr{V}$ from the right (left). Starting at aa, after three perturbations, the system finds itself along the dashed line. Open circles represent the last V which acts from the left. At the end of four perturbations, the system is in a diagonal state (aa, bb, cc, or dd). Number of three-bond pathways leading to ad, ba, dc, and cb is 1, 1, 3, and 3, respectively. Altogether, there are therefore eight pathways. In each pathway one perturbation has to be V_1, another V_2, and the third V_3. There are $3!=6$ possible permutations of these fields. Altogether, Eq. (31) contains $6\times8=48$ terms.

IV. FACTORIZATION APPROXIMATION

As is clearly evident from Sec. III, the microscopic evaluation of $\chi^{(3)}$ is quite tedious. It involves the calculation of the four-point correlation function $F(\tau_1,\tau_2,\tau_3,\tau_4)$ followed by a triple integration. While a semiclassical microscopic evaluation of F will be carried out in Sec. V, we shall consider here a much simpler and often very useful approximation for $\chi^{(3)}$—the *factorization approximation*. This approximation was developed recently for multiphoton process in general[27] and was successfully applied to a variety of line-shape problems. It enables us to express the

cross section for an arbitrary multiphoton process in terms of ordinary single-photon line-shape functions, which are readily calculable. A detailed discussion and analysis of this approximation was made recently.[27] Using projection-operator techniques it was shown that the factorization is the first term in a systematic expansion of the multiple time-correlation functions.[27,29] In the impact limit (short correlation time of the bath) the factorization is exact. For nonimpact line shapes the factorization amounts to treating the correlations between the system and the bath in an approximate way.

The factorization proceeds as follows. When we evaluate $\chi^{(3)}$ we have to average the entire right-hand side of Eq. (26) over the states of the bath, i.e.,

$$\chi^{(3)}(-\omega_4,\omega_1,-\omega_2,\omega_3)=\sum_{P(\omega_1,-\omega_2,\omega_3)}\sum_a \langle\langle V \mid G(\omega_1-\omega_2+\omega_3)\mathscr{V}G(\omega_1-\omega_2)\mathscr{V}G(\omega_1)\mathscr{V} \mid aa\rangle\rangle_{\rm av}\bar{P}(a)\ , \tag{32}$$

where the bold brackets stand for the average over the bath. Within the factorization approximation we replace this by the product of averaged Green's functions:

$$\begin{aligned}\chi^{(3)} &\cong \sum_{P(\omega_1,-\omega_2,\omega_3)}\sum_a \langle\langle V \mid \bar{G}(\omega_1-\omega_2+\omega_3)\mathscr{V}\bar{G}(\omega_1-\omega_2)\mathscr{V}\bar{G}(\omega_1)\mathscr{V} \mid aa\rangle\rangle\bar{P}(a) \\ &= \sum_{P(\omega_1,-\omega_2,\omega_3)}\sum_{\nu,a}\langle\langle \nu\nu \mid V\bar{G}(\omega_1-\omega_2+\omega_3)\mathscr{V}\bar{G}(\omega_1-\omega_2)\mathscr{V}\bar{G}(\omega_1)\mathscr{V} \mid aa\rangle\rangle\bar{P}(a)\ ,\end{aligned} \tag{33}$$

where the bar stands for the average over the bath. The second equality is simply the definition of a trace. Each $G_{\nu\mu}$ is a complex generalized line-shape function for the $\nu\mu$ transition, i.e.,

$$I_{\nu\mu}(\omega)\equiv\bar{G}_{\nu\mu}(\omega)=-i\int_0^\infty d\tau\exp(i\omega\tau)\exp[-i\omega_{\nu\mu}\tau-\tfrac{1}{2}(\gamma_\nu+\gamma_\mu)\tau-g_{\nu\mu}(\tau)]\ . \tag{34}$$

Here γ_ν,γ_μ are the inverse lifetimes of the ν and μ levels, $\omega_{\nu\mu}\equiv\epsilon_\nu-\epsilon_\mu$ is the frequency of the $\nu\mu$ transition, and $g_{\nu\mu}(\tau)$ is the line-broadening function which may be evaluated in numerous ways.[27] We note that $I_{\nu\mu}$ satisfies the Kramers-Kronig relations

$$I'_{\nu\mu}=\frac{-1}{\pi}\mathrm{P}\int_{-\infty}^{\infty}d\omega'\frac{I''_{\nu\mu}(\omega')}{\omega'-\omega}\ , \tag{35}$$

where

$$I_{\nu\mu}(\omega)\equiv I'_{\nu\mu}-iI''_{\nu\mu} \tag{36}$$

and $I''_{\nu\mu}$ is the ordinary absorption line shape between levels ν and μ. Within the factorization approximation, each of the eight pathways contributes a simple product of three $\bar{G}$'s. We thus get

$$\begin{aligned}\chi^{(3)}(-\omega_4,\omega_1,-\omega_2,\omega_3) &= \sum_{a,b,c,d}\bar{P}(a)\sum_{P(\omega_1,-\omega_2,\omega_3)}[-I_{ad}(\omega_1-\omega_2+\omega_3)I_{ac}(\omega_1-\omega_2)I_{ab}(\omega_1)+I_{dc}(\omega_1-\omega_2+\omega_3)I_{db}(\omega_1-\omega_2)I_{da}(\omega_1) \\ &\quad +I_{dc}(\omega_1-\omega_2+\omega_3)I_{db}(\omega_1-\omega_2)I_{ab}(\omega_1)+I_{dc}(\omega_1-\omega_2+\omega_3)I_{ac}(\omega_1-\omega_2)I_{ab}(\omega_1) \\ &\quad +I_{ba}(\omega_1-\omega_2+\omega_3)I_{ca}(\omega_1-\omega_2)I_{da}(\omega_1)-I_{cb}(\omega_1-\omega_2+\omega_3)I_{db}(\omega_1-\omega_2)I_{ab}(\omega_1) \\ &\quad -I_{cb}(\omega_1-\omega_2+\omega_3)I_{db}(\omega_1-\omega_2)I_{da}(\omega_1)-I_{cb}(\omega_1-\omega_2+\omega_3)I_{ca}(\omega_1-\omega_2)I_{da}(\omega_1)]\ .\end{aligned} \tag{37}$$

The eight terms in Eq. (37) correspond to the eight pathways (i)—(viii), respectively. In the *impact* limit,[21,24,27,30] $g(\tau)$ is linear in time:

$$g_{\nu\mu}(\tau)=\hat{\Gamma}_{\nu\mu}\mid\tau\mid\ , \tag{38}$$

and we get

$$I_{\nu\mu}(\omega)=\frac{1}{\omega-\omega_{\nu\mu}+i(\frac{1}{2}\gamma_\nu+\frac{1}{2}\gamma_\mu+\hat{\Gamma}_{\nu\mu})}\ . \tag{39}$$

Upon the substitution of Eq. (39) in Eq. (37) we finally get Bloembergen's expression for $\chi^{(3)}$.[1(b)] In other words, the general expression of $\chi^{(3)}$ [Eq. (26)] reduces to Bloembergen's expression which is based on the Bloch equations when two approximations are made: (1) factorization [Eq. (33)], and (2) the impact limit [Eq. (39)]. Equation (37) allows us a simple generalization in which we invoke the factorization, but not the impact approximation. The result is an expression involving only ordinary line-shape functions $I_{\nu\mu}(\omega)$ [Eq. (34)]. It should be noted that the imaginary part of $I_{\nu\mu}$,$I''_{\nu\mu}$, [Eq. (36)] is simply the absorption line shape for the $\nu\mu$ transition and may be evaluated using one of the many standard techniques developed for single-photon line shapes.[21,27] $I''_{\nu\mu}$ (and $I_{\nu\mu}$) may then be evaluated using the Kramers-Kronig relations [Eq. (35)].

V. WEAK-COUPLING SEMICLASSICAL EVALUATION OF THE FOUR-POINT CORRELATION FUNCTION

We shall now develop a more rigorous expression for the four-point correlation function $F(\tau_1,\tau_2,\tau_3,\tau_4)$ [Eq. (29)]. The natural thing to do is to use the cluster expansion and to get an expression to the lowest order in perturber density (pressure). This was done recently for the case $b=d$ which appears in fluorescence[27] and may be easily done here as well. The problem is that the resulting final expression is quite complicated and difficult to use. We shall, therefore, adopt a simplified method which yields a much more transparent result. This will be done by going to the semiclassical limit and making a weak-coupling approximation. The semiclassical limit is achieved as follows. We first make the (reasonable) assumption that the dipole operator depends weakly on the bath coordinates, and get

$$V_{ab}(\tau)=\mu_{ab}\exp(iH_a\tau)\exp(-iH_b\tau)$$
$$=\mu_{ab}\exp_+\left[-i\int_0^\tau d\tau_1 U_{ba}(\tau_1)\right] . \tag{40}$$

Here $\exp_+$ is the positive-time–ordered exponential and

$$U_{ba}\equiv H_b-H_a . \tag{41}$$

In the classical limit we replace $\exp_+$ by an ordinary exponential and treat $U_{ba}(\tau)$ as an ordinary function of time (not an operator) denoted $-\delta\omega_{ab}(\tau)$. We then have

$$V_{ab}(\tau)\underset{\text{classical limit}}{\longrightarrow}\mu_{ab}\exp\left[i\int_0^\tau d\tau_1\delta\omega_{ab}(\tau_1)\right] . \tag{42}$$

Similar expressions are written for V_{bc}, V_{cd}, and V_{da}. Upon substituting them in Eq. (29), we get

$$F(\tau_1,\tau_2,\tau_3,\tau_4)=\mu_{ab}\mu_{bc}\mu_{cd}\mu_{da}\left\langle\exp\left[i\left[\int_0^{\tau_1}d\tau\,\delta\omega_{ab}(\tau)+\int_0^{\tau_2}d\tau\,\delta\omega_{bc}(\tau)+\int_0^{\tau_3}d\tau\,\delta\omega_{cd}(\tau)+\int_0^{\tau_4}d\tau\,\delta\omega_{da}(\tau)\right]\right]\right\rangle . \tag{43}$$

To proceed further, let us define

$$g_{\alpha\beta}(\tau)\equiv\int_0^\tau d\tau_1\int_0^{\tau_1}d\tau_2\langle\delta\omega_{\alpha\beta}(\tau_2)\delta\omega_{\alpha\beta}(0)\rangle=\int_0^\tau d\tau_1(\tau-\tau_1)\langle\delta\omega_{\alpha\beta}(\tau_1)\delta\omega_{\alpha\beta}(0)\rangle , \tag{44}$$

$$\tilde{\Psi}_{\alpha\beta,\gamma\delta}(\tau_1,\tau_2)\equiv\delta\omega_{\alpha\beta}(\tau_1)\delta\omega_{\gamma\delta}(\tau_2) , \tag{45}$$

$$\Psi_{\alpha\beta,\gamma\delta}(\tau_1,\tau_2)\equiv\int_0^{\tau_1}dt_1\int_0^{\tau_2}dt_2\tilde{\Psi}_{\alpha\beta,\gamma\delta}(t_1,t_2) . \tag{46}$$

Without loss of generality, we can always shift $\omega_{\alpha\beta}$ so that

$$\langle\delta\omega_{\alpha\beta}\rangle=0 . \tag{47}$$

Upon expanding Eq. (43) to second order in $\delta\omega$ and making use of the definitions (44)–(47), we get

$$F(\tau_1,\tau_2,\tau_2,\tau_3)\cong 1-g_{ab}(\tau_1)-g_{bc}(\tau_2)-g_{cd}(\tau_3)-g_{da}(\tau_4)-\Psi_{ab,bc}(\tau_1,\tau_2)-\Psi_{bc,cd}(\tau_2,\tau_3)$$
$$-\Psi_{cd,da}(\tau_3,\tau_4)-\Psi_{da,ab}(\tau_4,\tau_1)-\Psi_{ab,cd}(\tau_1,\tau_3)-\Psi_{bc,da}(\tau_2,\tau_4) . \tag{48}$$

Since

$$\delta\omega_{\alpha\gamma}=\delta\omega_{\alpha\beta}+\delta\omega_{\beta\gamma} , \tag{49}$$

we have

$$\tilde{\Psi}_{\alpha\beta,\beta\gamma}(\tau_1,\tau_2)=\tfrac{1}{2}[\tilde{\Psi}_{\alpha\gamma,\alpha\gamma}(\tau_1,\tau_2)-\tilde{\Psi}_{\alpha\beta,\alpha\beta}(\tau_1,\tau_2)$$
$$-\tilde{\Psi}_{\beta\gamma,\beta\gamma}(\tau_1,\tau_2)] . \tag{50}$$

Using Eqs. (45) and (46) and Fig. 3, we get

$$\Psi_{\alpha\beta,\alpha\beta}(\tau_1,\tau_2)=\int_0^{\tau_1}dt_1\int_0^{\tau_2}dt_2\tilde{\Psi}_{\alpha\beta,\alpha\beta}(t_1,t_2)$$
$$=g_{\alpha\beta}(\tau_1)+g_{\alpha\beta}(\tau_2)-g_{\alpha\beta}(\tau_1-\tau_2) . \tag{51}$$

Equations (50) and (51) can be used to express the $\Psi_{ab,bc}$, $\Psi_{bc,cd}$, $\Psi_{cd,da}$, and $\Psi_{da,ab}$ terms in Eq. (48) in terms of $g_{\alpha\beta}$. The last two Ψ's in Eq. (48) ($\Psi_{ab,cd}$ and $\Psi_{bc,da}$) may be evaluated by using the identity

$$\tilde{\Psi}_{\alpha\beta,\gamma\delta}(t_1,t_2)=[\delta\omega_{\alpha\gamma}(t_1)+\delta\omega_{\gamma\beta}(t_1)]\delta\omega_{\gamma\delta}(t_2)$$
$$=\tilde{\Psi}_{\alpha\gamma,\gamma\delta}(t_1,t_2)-\tilde{\Psi}_{\beta\gamma,\gamma\delta}(t_1,t_2) . \tag{52}$$

Equation (52) together with Eqs. (50) and (51) may also be used to express $\Psi_{ab,cd}$ and $\Psi_{bc,da}$ in terms of $g_{\alpha\beta}$. The final step in the evaluation of F will be to use the cumulant expansion which amounts to exponentiating the expansion (48) and results in

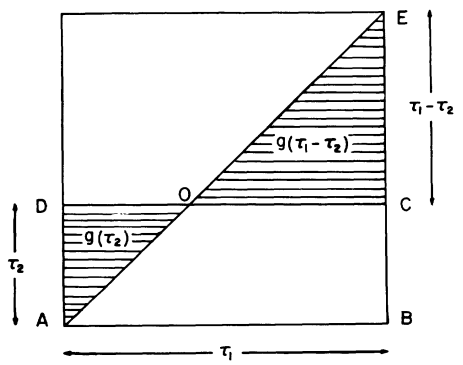

FIG. 3. Pictorial representation of Eq. (51). $\Psi(\tau_1,\tau_2)$, $g(\tau_1)$, $g(\tau_2)$, and $g(\tau_1-\tau_2)$ are obtained by integrating $\tilde{\Psi}$ over the following regions: $\frac{1}{2}$–*ABCD*, *ABE*, *ADO*, and *EOC*, respectively. *ABCD* region is a sum of *ABE* and *ADO* minus *EOC*. This results in Eq. (51).

$$F(\tau_1,\tau_2,\tau_3,\tau_4)=\mu_{ab}\mu_{bc}\mu_{cd}\mu_{da}$$
$$\times\exp\{-\tfrac{1}{2}[\,g_{ab}(\tau_1-\tau_2)+g_{ab}(\tau_1-\tau_4)-g_{ab}(\tau_2-\tau_4)-g_{ac}(\tau_1-\tau_2)-g_{ac}(\tau_3-\tau_4)$$
$$+g_{ac}(\tau_1-\tau_3)+g_{ac}(\tau_2-\tau_4)+g_{ad}(\tau_3-\tau_4)+g_{ad}(\tau_1-\tau_4)-g_{ad}(\tau_1-\tau_3)+g_{bc}(\tau_1-\tau_2)$$
$$+g_{bc}(\tau_2-\tau_3)-g_{bc}(\tau_1-\tau_3)-g_{bd}(\tau_2-\tau_3)-g_{bd}(\tau_1-\tau_4)+g_{bd}(\tau_1-\tau_3)+g_{bd}(\tau_2-\tau_4)$$
$$+g_{cd}(\tau_2-\tau_3)+g_{cd}(\tau_3-\tau_4)-g_{cd}(\tau_2-\tau_4)]\}\ . \tag{53}$$

Equation (53) is our final result for F within the semiclassical and perturbative (second order in $\delta\omega$) approximation. Together with Eq. (31) it provides a microscopic expression for $\chi^{(3)}$.

We note that in order to calculate F we need to know the line broadening associated with all possible pairs of levels: *ab*, *ac*, *ad*, *bc*, *bd*, and *cd*, regardless of whether they are radiatively coupled or not. In the impact limit, we set

$$g_{\nu\mu}(\tau)=\hat{\Gamma}_{\nu\mu}\,|\,\tau|\ , \tag{54}$$

where $\hat{\Gamma}_{\nu\mu}$ is the proper dephasing rate of the $\nu\mu$ transition. Upon substituting Eqs. (54) and (53) and then back in Eq. (31) we recover Eq. (37) together with (39). In general, however, the factorization is not rigorous and $\chi^{(3)}$ as given by Eqs. (53) and (31) is more complicated than Eq. (37).

Finally, we note that Eq. (53) is the exact solution of the stochastic Gaussian random modulation model of Kubo[24] which asssume $\delta\omega_{\alpha\beta}$ to be a Gaussian random process. The present derivation shows that in reality it corresponds to the semiclassical and the weak-coupling approximations.

VI. CORRELATION-FUNCTION EXPRESSION FOR TWO-PHOTON PROCESSES

It was already mentioned in the Introduction that the cross section for nonparametric single-absorber two-photon processes is also given by a correlation function very similar to $F(\tau_1,\tau_2,\tau_3,\tau_4)$ [Eq. (29)]. In this section, we shall derive explicit expressions both for time-resolved and frequency-resolved two-photon processes using F. This will show the intimate relation which exists on a microscopic level between these two types of experiments. We consider a three-level absorber which undergoes a two-photon process with two fields ω_L and ω_s. We shall treat in a unified way a Raman process [Fig. 4(a)] and a two-photon absorption (TPA) [Fig. 4(b)]. In a Raman process, energy is being absorbed from ω_L and emitted to ω_s. In a TPA energy is being absorbed from both fields. (In order to treat the Raman process classically we have to assume that we put in two fields. The result is, however, the same as obtained from the quantum dressed-atom picture with no external ω_s field present.)

We further assume that the ω_L field is near resonance with the *ab* transition (ω_{ab}) and ω_s with ω_{bc}. We therefore modify slightly $\tilde{V}(t)$ [Eq. (9)] and write it in the rotating-wave approximation (RWA)

$$\tilde{V}(t)=[\,\mu_{ab}E_L\exp(i\omega_L t)\,|\,a\rangle\langle b\,|$$
$$+\mu_{bc}E_s\exp(i\omega_s t)\,|\,b\rangle\langle c\,|\,]+\text{c.c.} \tag{55}$$

Equation (55) automatically chooses the right (near-resonant) frequency with the right sign for each transition in a TPA. We shall further introduce the following definitions. For TPA,

$$\bar{E}_a=\epsilon_a+\omega_L+\omega_s,\quad \bar{E}_b=\epsilon_b+\omega_s\ , \tag{56}$$

and

$$\bar{E}_c=\epsilon_c\ .$$

For a Raman process, we define

$$\bar{E}_a=\epsilon_a+\omega_L,\quad \bar{E}_b=\epsilon_b,\quad \bar{E}_c=\epsilon_c+\omega_s\ . \tag{57}$$

We shall define the detuning parameters (Fig. 4)

$$\Delta_L=\bar{E}_a-\bar{E}_b=\omega_L-\omega_{ba}\ ,$$
$$\Delta_s=\bar{E}_c-\bar{E}_b=\begin{cases}\omega_s-\omega_{bc}, & \text{(Raman)}\\ \omega_{cb}-\omega_s & \text{(TPA)}\ .\end{cases} \tag{58}$$

The different definition of Δ_s [Eq. (58)] is the only difference between the theories of Raman and TPA. From now on we shall consider TPA but all the results of this section apply to Raman spectroscopy as well.

Our experimental observable is the rate of change of the population in level c which is the same as the photon absorption (or emission) rate in the mode ω_s. If we define

$$B\equiv\frac{d}{dt}\,|\,cc\,\rangle\!\rangle=i\mathscr{V}\,|\,cc\,\rangle\!\rangle \tag{59}$$

then the desired rate of the two-photon process will be

$$\hat{I}(t,\Delta_L,\Delta_s)\equiv\langle B\rangle=-i\langle\langle\,cc\,|\,\mathscr{V}\,|\,\rho(t)\rangle\!\rangle\ . \tag{60}$$

We shall consider now several cases.

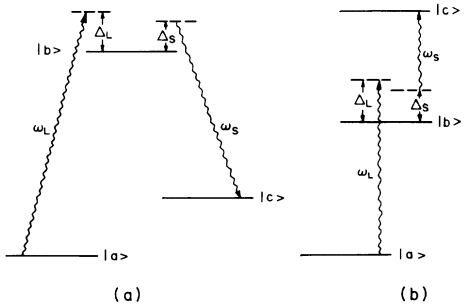

FIG. 4. Two-photon processes in a three-level system ($|\,a\rangle$, $|\,b\rangle$, and $|\,c\rangle$) interacting with two modes of the radiation field with frequencies ω_L and ω_s. Corresponding frequency detunings are denoted by Δ_L and Δ_s. (a) A resonance Raman process. (b) Two-photon absorption.

A. Steady-state experiments

At steady state, we may use Eqs. (59), (60), and (6) and (7). We then get[31]

$$\hat{I}(\Delta_L,\Delta_s)=(-i)^4\int_0^\infty d\tau_1\int_0^{\tau_1}d\tau_2\int_0^{\tau_2}d\tau_3\langle\langle cc\,|\,\mathscr{V}(\tau_1)G_s(\tau_1-\tau_2)\mathscr{V}(\tau_2)G_s(\tau_2-\tau_3)\mathscr{V}(\tau_3)G_s(\tau_3)\mathscr{V}(0)\,|\,aa\rangle\rangle\ . \tag{61}$$

Since we are in the RWA, it is more convenient to include the field frequencies in $G_s(\tau)$. We therefore modify Eq. (22) and define

$$\langle\langle\nu\mu\,|\,G_s(\tau)\,|\,\nu'\mu'\rangle\rangle=\exp[-i(\bar{E}_\nu-\bar{E}_\mu)\tau-\tfrac{1}{2}(\gamma_\nu+\gamma_\mu)\tau]\delta_{\nu\nu'}\delta_{\mu\mu'}\ , \tag{62}$$

where $\bar{E}_\nu$, $\bar{E}_\mu$ were defined in Eqs. (56) and (57).

A simple inspection of Fig. 5 shows that there are three different pathways (plus their complex conjugates) which lead from $|aa\rangle\rangle$ to $|cc\rangle\rangle$ in fourth order and contribute to $\hat{I}(\Delta_L,\Delta_s)$. Adopting the same notation introduced in Eq. (28), we have

$$\begin{array}{lll}\text{(i)} & (RLLR),\ (cc,cb,bb,ab,aa), & F(0,\tau_1,\tau_2,\tau_3)\phi(\tau_1,\tau_2,\tau_3),\\ \text{(ii)} & (LRLR),\ (cc,bc,bb,ab,aa), & F(0,\tau_2,\tau_1,\tau_3)\phi(\tau_2,\tau_1,\tau_3),\\ \text{(iii)} & (LLRR),\ (cc,bc,ac,ab,aa), & F(0,\tau_3,\tau_1,\tau_2)\phi(\tau_3,\tau_1,\tau_2),\end{array} \tag{63}$$

where

$$F(\tau_1,\tau_2,\tau_3,\tau_4)\equiv\langle V_{ab}(\tau_1)V_{bc}(\tau_2)V_{cb}(\tau_3)V_{ba}(\tau_4)\rangle \tag{64}$$

and

$$\phi(\tau_1,\tau_2,\tau_3)=\exp[-i\Delta_L\tau_3-i\Delta_s(\tau_1-\tau_2)-\tfrac{1}{2}\gamma_a\tau_3-\tfrac{1}{2}\gamma_b(\tau_1+\tau_2-\tau_3)-\tfrac{1}{2}\gamma_c\,|\,\tau_1-\tau_2\,|\,]\ . \tag{65}$$

It should be noted that pathways (i) and (ii) represent processes where a population ($|bb\rangle\rangle$) is created in the intermediate state on the way from $|aa\rangle\rangle$ to $|cc\rangle\rangle$. Pathway (iii), on the other hand, represents a direct photon scattering process in which a two-quantum coherence $|ac\rangle\rangle$ is being generated instead.[27,28,30] Using Eqs. (61) and (63) we finally get[27]

$$\begin{aligned}\hat{I}(\Delta_L,\Delta_s)=\mu_L^2\mu_s^2\int_0^\infty d\tau_1\int_0^{\tau_1}d\tau_2\int_0^{\tau_2}d\tau_3\{[\,&\phi(\tau_1,\tau_2,\tau_3)F(0,\tau_1,\tau_2,\tau_3)+\phi(\tau_2,\tau_1,\tau_3)F(0,\tau_2,\tau_1,\tau_3)\\&+\phi(\tau_3,\tau_1,\tau_2)F(0,\tau_3,\tau_1,\tau_2)]+\text{c.c.}\}\ ,\end{aligned} \tag{66}$$

where $\mu_L=|\mu_{ab}|$ and $\mu_s=|\mu_{bc}|$. Equation (66) is the most general expression for a stationary two-photon process. It is given in terms of a four–time-correlation function very similar to the one which appears in 4WM (the only difference being that here we have only three levels and $b=d$). Let us consider now several special cases.

1. Factorization approximation

Here, we use Eq. (7) and average each Green's function separately, resulting in

$$\hat{I}(\Delta_L,\Delta_s)=(-i)^4\int_0^\infty d\tau_1\int_0^{\tau_1}d\tau_2\int_0^{\tau_2}d\tau_3\langle\langle cc\,|\,\tilde{\mathscr{V}}(\tau_1)\bar{G}_0(\tau_1-\tau_2)\tilde{\mathscr{V}}(\tau_2)\bar{G}_0(\tau_2-\tau_3)\tilde{\mathscr{V}}(\tau_3)\bar{G}_0(\tau_3)\tilde{\mathscr{V}}(0)\,|\,aa\rangle\rangle\ . \tag{67}$$

Equation (67) allows us to express $\hat{I}(\Delta_L,\Delta_s)$ in terms of the single-photon line-shape functions $I_{\nu\mu}(\omega)$ [Eq. (34)]. It will be convenient to change slightly the notation and define[27]

$$\begin{aligned}I_{\nu\mu}(\Delta)&\equiv-i\int_0^\infty d\tau\exp[-i\Delta\tau-\tfrac{1}{2}(\gamma_\nu+\gamma_\mu)\tau-g_{\nu\mu}(\tau)]\\&\equiv I'_{\nu\mu}-iI''_{\nu\mu}\ .\end{aligned} \tag{68a}$$

Using Eqs. (67) and (68a) we finally get[27]

$$\hat{I}(\Delta_L,\Delta_s)=2\mu_L^2\mu_s^2\left[\frac{2}{\gamma_b}I''_{ab}(\Delta_L)I''_{cb}(\Delta_s)+\text{Im}[I^*_{ac}(\Delta_L-\Delta_s)I_{cb}(\Delta_s)I^*_{ab}(\Delta_L)]\right]\ . \tag{68b}$$

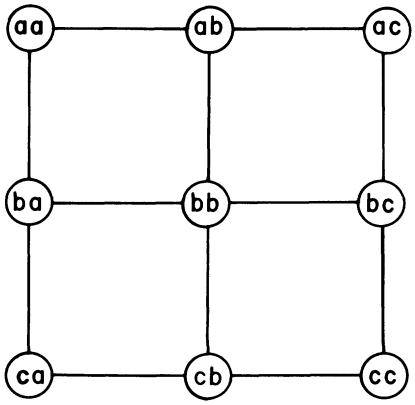

FIG. 5. Pathways in Liouville space which contribute to two-photon spectra. There are three pathways (plus their three complex-conjugate pathways) which lead from *aa* to *cc* in fourth order. These correspond to the terms (i), (ii), and (iii) in Eq. (63).

2. Impact limit

The impact limit for the single-photon line shapes was discussed in detail previously. Basically, it results in substituting the simple Lorentzian amplitude [Eq. (39)] for the single-photon line shapes $I_{\nu\mu}$. Upon the substitution of Eqs. (39) in Eq. (68), we finally get[31-33]

$$\hat{I}(\Delta_L,\Delta_s)=\frac{2\mu_L^2\mu_s^2}{\Delta_L^2+\Gamma_{ab}^2}\left[\pi\delta(\Delta_s-\Delta_L)+\frac{2\hat{\Gamma}_{ab}}{\gamma_b}\frac{\Gamma_{bc}}{\Delta_s^2+\Gamma_{bc}^2}\right], \tag{69}$$

where for the sake of simplicity we have also taken

$$\gamma_a=\gamma_c=0 . \tag{70}$$

We recall that in this case

$$\Gamma_{ab}=\tfrac{1}{2}\gamma_b+\hat{\Gamma}_{ab} ,$$
$$\Gamma_{bc}=\tfrac{1}{2}\gamma_b+\hat{\Gamma}_{ac} . \tag{71}$$

The first term in the square brackets in Eq. (69) is a direct scattering (Raman) component whereas the second is the redistribution. Note that the intergrated ratio of these components is simply $2\hat{\Gamma}_{ab}/\gamma_b$ and is independent of Δ_L. Experimentally however, this ratio goes to zero as Δ_L increases.[10] This is a limitation of an impact limit. Equations (66) or (68), however, show the correct dependence on Δ_L.[27]

3. Weak-coupling semiclassical limit

This is the special case of Eq. (53) with $b=d$. It can be written in a simpler way by defining

$$\hat{g}_{\nu\mu}(\tau_1,\tau_2,\tau_3,\tau_4)\equiv\tfrac{1}{2}[g_{\nu\mu}(\tau_1-\tau_2)+g_{\nu\mu}(\tau_3-\tau_4)-g_{\nu\mu}(\tau_2-\tau_4)-g_{\nu\mu}(\tau_1-\tau_3)] . \tag{72}$$

We then get

$$F(\tau_1,\tau_2,\tau_3,\tau_4)=\exp[-g_{ab}(\tau_1-\tau_4)-g_{bc}(\tau_2-\tau_3)-\hat{g}_{ab}(\tau_1,\tau_2,\tau_3,\tau_4)-\hat{g}_{bc}(\tau_1,\tau_2,\tau_3,\tau_4)+\hat{g}_{ac}(\tau_1,\tau_2,\tau_3,\tau_4)] . \tag{73}$$

Equation (73) together with Eq. (66) is the general semiclassical weak-coupling expression for steady-state two-photon processes.[27,31]

4. Effects of fluctuations in the radiation fields

If the amplitude or the phase of the radiation field E_i is fluctuating (incoherence in the field[34,35]) we can very easily incorporate this into our Eq. (66). All we have to do is set

$$F(\tau_1,\tau_2,\tau_3,\tau_4)\rightarrow\langle E_L(\tau_1)E_L(\tau_4)\rangle\langle E_s(\tau_2)E_s(\tau_3)\rangle F(\tau_1,\tau_2,\tau_3,\tau_4) , \tag{74}$$

i.e., we should simply multiply F by the appropriate correlation functions of the field. (Note that V_L acts at times τ_1 and τ_4 and V_s acts at times τ_2 and τ_3.) In the case of Raman or fluorescence processes, E_s is not fluctuating. By using the dressed-atom picture, we see that E_s comes from coupling with vacuum modes of the radiation field. In this case, we should multiply F by $\langle(E_L(\tau_1)E_L(\tau_4)\rangle$ only. If the field correlation functions $\langle E_i(\tau)E_i(\tau')\rangle$ are exponential in $\tau-\tau'$ this simply amounts to the addition of another dephasing process to the problem.

B. Time-resolved experiments

In the case of time and frequency resolution, we define $\langle dP_c/dt\rangle$ using Eqs. (6), (7), and (57), and we get

$$\hat{I}(t,\Delta_L,\Delta_s)=(-i)^4\int_{-\infty}^{t}d\tau_1\int_{-\infty}^{\tau_1}d\tau_2\int_{-\infty}^{\tau_2}d\tau_3\langle\langle cc\,|\,\mathscr{V}(t)G_0(t-\tau_1)\mathscr{V}(\tau_1)G_0(\tau_1-\tau_2)\mathscr{V}(\tau_2)G_0(\tau_2-\tau_3)\mathscr{V}(\tau_3)\,|\,aa\rangle\rangle . \tag{75}$$

The bookkeeping is as before except that the amplitudes of the external fields are time dependent $E_L=E_L(\tau)$, $E_s=E_s(\tau)$. The time dependence represents the envelope of an external pulse. It can also come from fluctuations in the fields. Proceeding along the same steps that led to Eq. (66) we get in this case

$$\begin{aligned}\hat{I}(t,\Delta_L,\Delta_s)=(-i)^4\int_{-\infty}^{t}d\tau_1\int_{-\infty}^{\tau_1}d\tau_2\int_{-\infty}^{\tau_2}d\tau_3 F(0,t-\tau_3,\tau_1-\tau_3,\tau_2-\tau_3)\phi(t-\tau_3,\tau_1-\tau_3,\tau_2-\tau_3)\\ \times\langle E_L(\tau_2)E_L(\tau_3)\rangle\langle E_s(t)E_s(\tau_1)\rangle\\ +F(0,\tau_1-\tau_3,t-\tau_3,\tau_2-\tau_3)\phi(\tau_1-\tau_3,t-\tau_3,\tau_2-\tau_3)\langle E_L(\tau_2)E_L(\tau_3)\rangle\langle E_s(t)E_s(\tau_1)\rangle\\ +F(0,\tau_2-\tau_3,t-\tau_3,\tau_1-\tau_3)\phi(\tau_2-\tau_3,t-\tau_3,\tau_1-\tau_3)\langle E_L(\tau_1)E_L(\tau_3)\rangle\langle E_s(\tau_2)E_s(t)\rangle .\end{aligned} \tag{76}$$

We thus see that the same four-point correlation function enters also in the calculation of the time-resolved experiments. In the case of a Raman process (spontaneous emission), we should simply put $E_s=1$ in Eq. (76).

Within the factorization approximation, we have in this case

$$\hat{I}(t,\Delta_L,\Delta_s)=(-i)^4\int_{-\infty}^{t}d\tau_1\int_{-\infty}^{\tau_1}d\tau_2\int_{-\infty}^{\tau_2}d\tau_3 I_{cb}(t-\tau_1)I_{bb}(\tau_1-\tau_2)I_{ab}(\tau_2-\tau_3)\langle E_L(\tau_2)E_L(\tau_3)\rangle\langle E_s(t)E_s(\tau_1)\rangle$$
$$+I_{bc}(t-\tau_1)I_{bb}(\tau_1-\tau_2)I_{ab}(\tau_2-\tau_3)\langle E_L(\tau_2)E_L(\tau_3)\rangle\langle E_s(t)E_s(\tau_1)\rangle$$
$$+I_{bc}(t-\tau_1)I_{ac}(\tau_1-\tau_2)I_{ab}(\tau_2-\tau_3)\langle E_L(\tau_1)E_L(\tau_3)\rangle\langle E_s(t)E_s(\tau_2)\rangle\ , \tag{77}$$

where

$$I_{\nu\mu}(\tau)=\exp[-i(\bar{E}_\nu-\bar{E}_\mu)\tau-\tfrac{1}{2}(\gamma_\nu+\gamma_\mu)\tau-g_{\nu\mu}(\tau)]\ . \tag{78}$$

In the semiclassical weak-coupling limit, we substitute Eq. (53) in Eq. (76). Finally, we note that $\hat{I}(t,\Delta_L,\Delta_s)$ as defined in Eq. (75) is not an observable quantity since it corresponds to an unrealistic measurement with infinite temporal and frequency resolution, which violates the energy-time uncertainty relation. Any realistic detector will contain a finite temporal and spectral resolution and these should be convoluted with $\hat{I}(t,\Delta_L,\Delta_s)$ to get the actual result of a particular measurement.[36]

VII. CONCLUDING REMARKS

In this paper, we have shown that coherent $2n$-photon processes and incoherent n-photon processes are both probing a similar $2n$-time-correlation function of the dipole operator. The reason is that in a coherent process we calculate an ensemble averaged *amplitude* whereas in an incoherent process we average the *cross section* (amplitude square) over the ensemble. We specialized in $n=2$ and looked at the following processes: (1) four-wave mixing in steady state, (2) two-photon processes in steady state, and (3) time-resolved two-photon processes. We have provided explicit expressions for all the observables in these experiments in terms of essentially the same four-point correlation function $F(\tau_1,\tau_2,\tau_3,\tau_4)$. A semiclassical approximation for F was developed. In addition, we have derived the factorization approximation which expresses these observables in terms of products of ordinary single-photon lineshape functions. In all cases, our results reduce to the conventional expressions of the Bloch equation if we invoke the factorization approximation and the impact limit whereby we replace each single-photon line shape by a simple Lorentzian. Effects of fluctuations in the radiation field (amplitude, phase, or both) are easily incorporated in the present approach. Our result for $\chi^{(3)}$ in the factorization approximation [Eq. (37)] is of particular interest since it provides a simple and a straightforward generalization to the well-known expressions of Bloembergen *et al.*[1(b)] which are valid in the impact limit.

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[1](a) N. Bloembergen, *Nonlinear Optics* (Benjamin, New York, 1965); (b) N. Bloembergen, H. Lotem, and R. T. Lynch, Indian J. Pure Appl. Phys. 16, 151 (1978).

[2]P. N. Butcher, *Nonlinear Optical Phenomena* (Ohio University Press, Athens, Ohio, 1965).

[3]D. C. Hanna, M. A. Yuratich, and D. Cotter, *Nonlinear Optics of Free Atoms and Molecules* (Springer, New York, 1979); *Laser Spectroscopy IV,* edited by H. Walther and H. W. Rothe (Springer, New York, 1979).

[4]S. A. J. Druet and J. P. E. Taran, Prog. Quantum Electron. 7, 1 (1981); R. J. Hall and A. C. Eckbreth, in *Laser Applications,* edited by R. K. Erf (Academic, New York, 1981).

[5]J. O. Bjarnason, B. S. Hudson, and H. C. Andersen, J. Chem. Phys. 70, 4130 (1979).

[6]M. D. Levenson, *Introduction to Nonlinear Laser Spectroscopy* (Academic, New York, 1982).

[7]Y. Prior, A. R. Bogdan, M. Dagenais, and N. Bloembergen, Phys. Rev. Lett. 46, 111 (1981); A. R. Bogdan, M. W. Downer, and N. Bloembergen, Phys. Rev. A 24, 623 (1981).

[8]J. R. Andrews, R. M. Hochstrasser, and H. P. Tromsdorff, Chem. Phys. 62, 87 (1981).

[9]P. F. Williams, D. L. Rousseau, and S. H. Dworetsky, Phys. Rev. Lett. 32, 196 (1974); D. L. Rousseau, G. D. Patterson, and P. F. Williams, *ibid.* 34, 1306 (1975); D. L. Rousseau and P. F. Williams, J. Chem. Phys. 64, 3519 (1976).

[10]J. L. Carlsten and A. Szoke, Phys. Rev. Lett. 36, 667 (1976); J. Phys. B 9, L231 (1976); J. L. Carlsten, A. Szoke, and M. G. Raymer, Phys. Rev. A 15, 1029 (1977); E. Courtens and A. Szoke, *ibid.* 15, 1588 (1978).

[11]R. M. Hochstrasser and C. A. Nyi, J. Chem. Phys. 70, 1112 (1979).

[12]P. R. Liao, J. E. Bjorkholm, and P. R. Berman, Phys. Rev. A 20, 1489 (1979).

[13]A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961).

[14]R. G. Brewer and E. L. Hahn, Phys. Rev. A 8, 464 (1973); 11, 1641 (1975).

[15]L. Allen and J. H. Eberly, *Optical Resonance and Two-Level Atoms* (Wiley, New York, 1975).

[16]J. H. Shirley, Phys. Rev. 138, B979 (1965).

[17]P. W. Milonni, Phys. Rep. 25, 1 (1976).

[18]C. Cohen-Tannoudji, in *Frontiers in Laser Spectroscopy,* edited

by R. Balian, S. Haroche, and S. Liberman (North-Holland, Amsterdam, 1977), Vol. 1, p. 1.
[19]S. Haroche, Ann. Phys. (Paris) 6, 189 (1971); 6, 327 (1971).
[20]C. R. Stroud and E. T. Jaynes, Phys. Rev. A 1, 106 (1970).
[21]R. G. Breene, Jr., *The Shift and Shape of Spectral Lines* (Pergamon, New York, 1961); *Theories of Spectral Line Shapes* (Wiley, New York, 1981).
[22]J. F. Kielkopf and N. F. Allard, J. Phys. B 13, 709 (1980).
[23]R. E. Walkup, A. Spielfieldel, and D. E. Pritchard, Phys. Rev. Lett. 45, 986 (1980).
[24]R. Kubo, in *Fluctuation Relaxation and Resonance in Magnetic Systems,* edited by D. Ter-Haar (Oliver and Boyd, Edinburgh, 1962); Adv. Chem. Phys. 15, 101 (1969).
[25]V. Mizrahi, Y. Prior, and S. Mukamel, Opt. Lett. 8, 145 (1983).
[26]D. L. Huber, Phys. Rev. 158, 843 (1967); 170, 418 (1968); 178, 93 (1969).
[27]S. Mukamel, Phys. Rep. 93, 1 (1982).
[28]P. D. Maker and R. W. Terhune, Phys. Rev. 137, A801 (1965).
[29]Y. Rabin, D. Grimbert, and S. Mukamel, Phys. Rev. A 26, 271 (1982); S. Mukamel, D. Grimbert, and Y. Rabin, *ibid.* 26, 341 (1982).
[30]P. R. Berman, in *Advances in Atomic and Molecular Physics,* edited by D. R. Bates and B. Bederson (Academic, New York, 1977), Vol. 13, p. 57.
[31]S. Mukamel, J. Chem. Phys. 71, 2884 (1979).
[32]D. L. Huber, Phys. Rev. 158, 843 (1967); 170, 418 (1968); 178, 93 (1969).
[33]L. S. Vasilenko, V. P. Chebataev, and A. V. Shishaev, Zh. Eksp. Teor. Fiz. Piz'ma Red. 12, 161 (1970) [JETP Lett. 12, 113 (1970)].
[34]A. T. Georges and P. Lambropoulos, Phys. Rev. A 20, 991 (1979).
[35]L. Mandel and H. J. Kimble, in *Multiphoton Processes,* edited by J. H. Eberly and P. Lambropoulos (Wiley, New York, 1978), p. 119.
[36]J. H. Eberly and K. Wodkiewicz, J. Opt. Soc. Am. 67, 1252 (1977).