Coherent optical interaction of a multilevel system with fluctuating laser fields

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The effect of stochastic laser phase fluctuations on nonlinear optical phenomena are investigated within the phase-diffusion model. Averaged equations of motion are derived in the limit of infinitely short correlation times and the results are applied to multiphoton absorption and to four-wave mixing. The effect of the stochastic phase fluctuations is shown to be equivalent to a T_2 dephasing process, and a procedure is described for the inclusion of this equivalence in many nonlinear-optical problems. When a given mode contributes n photons to a multiphoton absorption process, its contribution to the width of the multiphoton transition is n^2 times its own stochastic width. When correlated lasers are used as the excitation sources in four-wave-mixing experiments, (new) stochastic-fluctuation-induced extra resonances in four-wave mixing (SFIER4) will be observed, in complete analogy to the extra resonances induced by collisions [pressure-induced extra resonances in form-wave mixing (PIER4)].

I. INTRODUCTION

The interaction of multilevel atomic and molecular systems with coherent light was extensively investigated theoretically and experimentally during the last few years.[1–4] The lasers currently utilized for the nonlinear excitation of atoms and molecules are by no means ideal, i.e., single-frequency amplitude and phase stabilized sources; and the dynamics of the excitation may be affected by the phase and amplitude fluctuations of the electromagnetic fields. In order to describe these fluctuations, a stochastic description for the relevant parameters has been invoked.[5–16] In this context, Haken[5] and Cohen-Tannoudji[6] considered a laser beam which is characterized by a stabilized amplitude and a fluctuating phase. The fluctuation phase has been assumed to obey the Langevin equation and to be driven by a fluctuating force which is assumed to have a zero mean. As is discussed by these authors, this is a reasonable description for a single-mode dye laser operating far from its threshold. Since the gain bandwidth of the dye is considerably larger than the laser linewidth, one may separate the time scales of the very fast fluctuations of the phase and the "slow" phase-diffusion time.

The phase-diffusion model (PDM) has been applied to the description of the fluorescence spectrum of a saturated two-level atom,[6] to multiphoton transitions,[15,16] to the dynamics of three-photon ionization,[9,10,17–19] and to multiphoton excitation of molecular multilevel systems.[14,17] These studies of ionization and excitation in multilevel systems provided novel information concerning the extrinsic erosion of phase coherence effects in multiphoton excitation within a sparse level structure of collisionless molecules.[13,14,20,21]

Coherent nonlinear optical phenomena in fluctuating laser fields are of considerable current interest. In this context, the problem of coherent wave mixing should be investigated in detail, as it may suggest ways to test the predictions and applicability of the phase-diffusion model. In a four-wave-mixing experiment, three input fields interact with a multilevel system to generate a fourth coherent beam which is emitted at well-defined frequency and direction. The general formalism for treating coherent nonlinear optical interactions is well developed. The perturbative expansion in ascending order of nonlinear susceptibilities, as established more than 20 years ago,[22,23] has proven itself as a very powerful tool, and a good basis for the treatment of most such problems. More recently, diagrammatic derivations of the higher-order susceptibilities have also proven useful.[23–29]

In all these treatments, molecular relaxation processes are included phenomenologically, in much the same way they have been included in NMR.[30] The problem of laser linewidth is usually ignored, or if considered, is discussed only in a general phenomenological way.[31] More recently, the proper phenomenological treatment of collisional relaxation, either by perturbative expansion or diagrammatic treatment of the density matrix, led to the observation of a new family of effects[32,33] that was termed PIER4 (pressure-induced extra resonances in four-wave mixing). Such dephasing-induced phenomena have also been seen in molecular crystals at low temperatures, where dephasing was induced by lattice phonons.[34] A significant step towards the elucidation of the effects of fluctuating laser fields on PIER4 was undertaken by Agarwal *et al.*,[35–37] who had considered the influence of laser fluctuations on pressure-induced resonances.

In this paper we consider a multilevel (molecular) system driven by several laser fields, which are characterized by fluctuating phases. The equations of motion are solved for the PDM. The results are utilized to study the effect of laser phase fluctuations on multiphoton absorption and

on four-wave mixing. In the case of n-photon absorption, the stochastic contribution to the linewidth induced by a single laser is n^2 times the width of the laser itself, in accord with the analysis of Mollow[15] and Agrawal.[16] For four-wave mixing we predict the possibility of observing extra resonances, which are induced by the stochastic fluctuations in the laser field. These new extra resonances bear a close analogy to the PIER4, being amenable to experimental observation even in the absence of collision or other (molecular) dephasing processes.

II. THEORY

In this section the interaction of an electromagnetic field (consisting of several modes) and a multilevel molecular system is considered. The treatment is semiclassical, where the molecular level system is quantized, and the electromagnetic (EM) field is treated classically. The effect of the phase of each mode is discussed explicitly within the semiclassical description.

A multimode electromagnetic field, which is emitted by several uncorrelated laser sources, is given by

$$E(t)=\sum_{\alpha}E_{\alpha}(t)\exp\{-i[\omega_{\alpha}t+\phi_{\alpha}(t)]\}+\text{c.c.}\ , \tag{2.1}$$

where $E_{\alpha}(t)$ denotes the generally time-dependent field amplitude, ω_{α} is the mean frequency, and $\phi_{\alpha}(t)$ is the fluctuating phase of the αth mode. The phases $\{\phi_{\alpha}\}$ and the assumptions involved in their inclusion will be discussed in detail. Throughout this calculation, the slowly varying amplitude approximation will be assumed, namely, the rate of change of the amplitude $E_{\alpha}(t)$ is slow compared to all the relevant time scales of the problem and the amplitude may be assumed constant.

The molecular level structure is specified in terms of the N eigenkets $\{|k\rangle\}$ of the molecular Hamiltonian H_m, with corresponding energies $\{E_k\}$. The radiation-molecule interaction is electric dipolar

$$H_{\text{int}}=\boldsymbol{\mu}\cdot\mathbf{E}(t)\ , \tag{2.2}$$

where $\boldsymbol{\mu}$ is the molecular dipole moment operator. The equation of motion of the molecular density matrix ρ is given by

$$i\hbar\dot{\rho}=[H,\rho]-\frac{i\hbar}{2}(\bar{\Gamma}\rho+\rho\bar{\Gamma})\ . \tag{2.3}$$

$H=H_m+H_{\text{int}}$ denotes the full Hamiltonian of the system and $\bar{\Gamma}$ is a phenomenological decay operator having the elements

$$\bar{\Gamma}_{kl}=\Gamma_k\delta_{kl}+\Gamma_{kl}^{\text{pd}}\ . \tag{2.4}$$

The diagonal contribution, Γ_k is the nonadiabatic decay rate (e.g., due to spontaneous emission from level $|k\rangle$) whereas Γ_{kl}^{pd} is the rate of proper dephasing of the element ρ_{kl} of the density matrix, which may be caused by such physical processes as collisions in a fluid or interactions with the lattice in a solid. This form of phenomenological relaxation rates can be justified whenever the spectral distributions of the random perturbations are broad enough so that the typical correlation time is very short compared to other relevant time scales of the molecular dynamics.

In the case of a gaseous sample, this limit implies an infinitely short collision, or the impact approximation. For a collision of duration τ_D, this approximation is valid for detunings $\Delta\omega$ such that $\Delta\omega\,\tau_D\ll 1$, and under these conditions the molecule "forgets" its own coherent information immediately after the collision.

Electromagnetic fields with fluctuating phases have been discussed by several authors.[5–9,13,14] A single-mode dye laser may be described by one mode of the radiation field as written above. It is assumed that the phases $\{\phi_{\alpha}\}$ obey separate equations of motion, and in the irreversible Wiener-Levy limit[7] their rates of change $\{\dot{\phi}_{\alpha}\}$ are characterized by narrow correlation functions. A useful form involves the exponential correlation function

$$\langle\dot{\phi}_{\alpha}(t)\dot{\phi}_{\beta}(t-\tau)\rangle=a_{\alpha}\gamma_{\alpha}\exp(-\gamma_{\alpha}|\tau|)\delta_{\alpha\beta}\ , \tag{2.5}$$

where γ_{α}^{-1} is a typical time for change of the fluctuating force which derives the time-development of the phase and a_{α} is the slow phase-diffusion width. The term $\delta_{\alpha\beta}$ assures the uncorrelation of the various modes. As is discussed by Cohen-Tannoudji,[6] this description is adequate for a dye laser operating high above threshold. In order to solve Eq. (2.3), we define a transformation to the rotating frame, setting

$$\tilde{\rho}_{kl}=\rho_{kl}\exp\left[i\sum_{\alpha}\lambda_{kl}^{\alpha}(\omega_{\alpha}t+\phi_{\alpha})\right]\ , \tag{2.6}$$

where λ_{kl}^{α} is an integer which counts the number of photons of the αth mode which participate in the molecular $|k\rangle\rightleftarrows|l\rangle$ transition. This transformation is useful for resonant cases, where a particular combination of frequencies is nearly resonant with a transition. Note that the frequency of the rotating frame includes the random phases of the modes involved.

In a similar manner, define the corresponding detunings,

$$\Delta_{kl}=(E_k-E_l)/\hbar-\sum_{\alpha}\lambda_{kl}^{\alpha}\omega_{\alpha}\ , \tag{2.7}$$

where now, for reasons to become clear later, the phases have been left out.

The choice of $\{\lambda_{kl}^{\alpha}\}$ is arbitrary in the general case, but is obvious for resonant transitions, and for exact "on-resonance" conditions the corresponding detunings vanish. In this rotating frame the explicit equation of motion [Eq. (2.3)] becomes

$$\frac{d}{dt}\tilde{\rho}_{kl}=-i\Delta_{kl}\tilde{\rho}_{kl}+i\sum_{\alpha}\lambda_{kl}^{\alpha}\dot{\phi}_{\alpha}(t)\tilde{\rho}_{kl}$$
$$-i\sum_{j\,(\neq k)}\mu_{kj}\tilde{\rho}_{jl}\sum_{\alpha}E_{\alpha}\left[\exp\left[-i\sum_{\beta}(\lambda_{jk}^{\beta}+\delta_{\alpha\beta})(\omega_{\beta}t+\phi_{\beta}\right]+\exp\left[-i\sum_{\beta}(\lambda_{jk}^{\beta}-\delta_{\alpha\beta})(\omega_{\beta}t+\phi_{\beta})\right]\right]$$
$$+i\sum_{j\,(\neq l)}\mu_{jl}\tilde{\rho}_{kj}\sum_{\alpha}E_{\alpha}\left[\exp\left[-i\sum_{\beta}(\lambda_{lj}^{\beta}+\delta_{\alpha\beta})(\omega_{\beta}t+\phi_{\beta})\right]+\exp\left[-i\sum_{\beta}(\lambda_{lj}^{\beta}-\delta_{\alpha\beta})(\omega_{\beta}t+\phi_{\beta})\right]\right]$$
$$-\left[\frac{\Gamma_k+\Gamma_l}{2}+\Gamma_{kl}^{\mathrm{pd}}\right]\tilde{\rho}_{kl}\ . \tag{2.8}$$

In Eq. (2.8), the first two terms come from taking time derivatives and from the transformation into the rotating frame, the two sums are the detailed expressions for the commutator $[H,\rho]$, and the last term is the relaxation.

So far the semiclassical approximation for the EM field and the dipolar interaction were utilized. We invoke now the rotating-wave approximation (RWA) and out of all the exponential terms only the dc terms survive, whereas the highly oscillatory terms are averaged to zero. Consequently, the sole terms $\mu_{kj}\tilde{\rho}_{jl}E_{\alpha}$ which survive are those which multiply the exponential products which contain the terms

$$\lambda_{jk}^{\alpha}\pm 1=0\ ,$$
$$\lambda_{jk}^{\beta}=0,\quad \beta\neq\alpha\ . \tag{2.9}$$

The first condition is derived from terms containing the $\pm\delta_{\alpha\beta}$ contributions. In this case the αth mode induces a single-photon transition between the levels $|j\rangle$ and $|k\rangle$ and the set $\{E_{\beta}\}$ $(\beta\neq\alpha)$ does not induce this transition. The RWA actually takes into consideration only single-photon connected transitions.

The stochastic contribution due to the fluctuating phases is diagonal in the sense that the rate of change of $\tilde{\rho}_{kl}$ is connected by this stochastic term only to $\tilde{\rho}_{kl}$ itself:

$$\left[\frac{d}{dt}\tilde{\rho}_{kl}(t)\right]_{\text{stochastic}}=i\left[\sum_{\alpha}\lambda_{kl}^{\alpha}\dot{\phi}_{\alpha}(t)\right]\tilde{\rho}_{kl}(t)\ . \tag{2.10}$$

If the possibility of absorption into a virtual state followed by immediate reemission induced by the same field is ignored (since this is a higher-order process), one is left with $\lambda_{kk}^{\alpha}=0$, namely, the diagonal elements of the density matrix $\{\tilde{\rho}_{kk}\}$ are not influenced directly by the fluctuating phases.

In order to proceed it is convenient[13] to arrange the elements of the density matrix in an N^2-dimensional column vector $\underline{X}$. The transposed vector $(X^{\dagger})$ being

$$X^{\dagger}=(\tilde{\rho}_{11},\tilde{\rho}_{12},\ldots,\tilde{\rho}_{1N},\tilde{\rho}_{21},\tilde{\rho}_{22},\ldots,\tilde{\rho}_{2N},\ldots,\tilde{\rho}_{NN})\ . \tag{2.11}$$

With this arrangement the dynamics of the density matrix is expressed in a dyadic, rather than in a tetradic, form:

$$\frac{d}{dt}X(t)=\underline{L}(t)X(t)\ . \tag{2.12}$$

The dyadic Liouville operator is divided into two parts:

$$\underline{L}(t)=\underline{L}_0+\underline{L}_1(t)\ . \tag{2.13}$$

The matrix $\underline{L}_0$ is the time-independent nonstochastic contribution and $\underline{L}_1$ is the time-dependent stochastic contribution due to the rates of change of the fluctuating phases. Both matrices $\underline{L}_0$ and $\underline{L}_1$ are obtained from the tetradic equation of motion [Eq. (2.8)] (which is reduced in the RWA to the simpler form), according to the arrangement of the elements of the density matrix in the vector $X(t)$ [Eq. (2.11)]. The stochastic term $\underline{L}_1$ is written in terms of the corresponding contributions of the various laser modes

$$\underline{L}_1=i\sum_{\alpha}\underline{L}_1^{\alpha}\dot{\phi}_{\alpha}(t)\ . \tag{2.14}$$

$\{\underline{L}_1^{\alpha}\}$ are time-dependent diagonal matrices, each one is obtained from the corresponding tetradic matrices, which are related to the αth mode, as given in Eq. (2.10) for the stochastic contribution to the rate of change of $\tilde{\rho}_{kl}$.

The stochastic equation of motion, Eq. (2.12), is averaged over the ensemble of various phases, in order to obtain an explicit expression for the equation of motion of the averaged (over the fluctuating phases) elements of the density matrix. Thus, an "effective" equation of motion is obtained:

$$\frac{d}{dt}\langle X(t)\rangle=\underline{L}_{\text{eff}}\langle X(t)\rangle\ . \tag{2.15}$$

In the cumulant expansion method, which rests on a second-order cumulant series,[38] the effective propagator is given by

$$\underline{L}_{\text{eff}}(t)=\underline{L}_0+\int_0^t d\tau\langle\langle\underline{L}_1(t)\exp(\underline{L}_0\tau)\underline{L}_1(t-\tau)\exp(-\underline{L}_0\tau)\rangle\rangle\ , \tag{2.16}$$

where $\langle\langle\ \rangle\rangle$ denotes the cumulant average. This procedure is justified when the correlation times τ_c of the fluctuating phases are short enough. In this case,[13] the relative errors increase according to τ_c^2.

Since the fluctuating phases of the various laser modes are not correlated, Eq. (2.2), $\underline{L}_{\text{eff}}$ reduces to

$$\underline{L}_{\text{eff}}=\underline{L}_0-\sum_{\alpha}\int_0^t d\tau\,\underline{L}_1^{\alpha}\exp(\underline{L}_0\tau)\underline{L}_1^{\alpha}\exp(-\underline{L}_0\tau)\times\langle\dot{\phi}_{\alpha}(t)\dot{\phi}_{\alpha}(t-\tau)\rangle\ . \tag{2.17}$$

Consequently, the various modes contribute separately to the effective propagator. All the cross mode-mode terms drop out due to the noncorrelation of the various laser modes.

Since $[\underline{L}_1^{\alpha},\underline{L}_0]\neq 0$, there is no simple expression for the operator integral. In Appendix A an explicit expression for $\underline{L}_{\text{eff}}$ is obtained for the case where an exponential correlation function, Eq. (2.2), is used for $\{\dot{\phi}_\alpha(t)\}$. When the width γ_α is set to infinity, the correlation function Eq. (2.2) becomes a δ function:

$$\langle \dot{\phi}_\alpha(t)\dot{\phi}_\alpha(t-\tau)\rangle = 2a_\alpha\delta(\tau) . \tag{2.18}$$

In this limit the effective propagator, Eq. (2.17), becomes

$$\underline{L}_{\text{eff}} = \underline{L}_0 - \sum_\alpha a_\alpha(\underline{L}_1^{\alpha})^2 . \tag{2.19}$$

Equations (2.17) and (2.19) are the main result of this work. Equation (2.16) is a convolution integral applicable in the general case. In many practical cases simplifying assumptions (i.e., impact approximation) are made regarding the correlation time, and Eq. (2.19) is the result for infinitely short correlations. In this case the effect of laser phase fluctuations may be analyzed directly, and the results of such analysis are given in the next sections.

III. MULTIPHOTON LINE SHAPE

The result of Sec. II is an effective equation of motion (2.15) with an effective propagator. For an extremely short phase correlation time, this propagator was shown to be of the form (2.19). Thus L_{eff} is "diagonal" in the sense that each element of the vector X (an element of the density matrix) decays at a rate proportional to its value, where the rate is given by a deterministic rate $\underline{L}_0$, and a stochastic contribution

$$a_{kl} = \sum_\alpha a_\alpha(\lambda_{kl}^{\alpha})^2 . \tag{3.1}$$

λ_{kl}^{α} is the number of photons of the αth mode which participate in the $|k\rangle \rightleftarrows |l\rangle$ transition. The present definition of a_{kl} is a generalization of the result obtained previously for a two-level system and a single radiation mode.[13,14]

As explained above, only off-diagonal elements of the density matrix $\{\tilde{\rho}_{kl}\}$ are affected by this decay and it can clearly be seen that this decay is exponential. Thus, a_{kl} is equivalent to a transverse dephasing process like T_2. The rate a_{kl} is a sum of uncorrelated contributions, each one being a correlated contribution of a single mode. This partial correlation is manifested by the term $(\lambda_{kl}^{\alpha})^2$, which results from the fact that all the photons of the αth mode are completely correlated.

A careful examination of a_{kl} reveals the interesting result that if a given radiation mode has contributed n photons to the kl transition, its contribution to the dephasing rate of this transition is n^2a_0. Expressed in even simpler terms, if a two-photon transition is induced by two uncorrelated lasers, the stochastic contribution to the observed width is the sum of the individual contributions, but if only one laser has been used, the width is four times the individual width. This conclusion concurs with the prediction of Mollow[15] and with the subsequent treatment of Agarwal.[16]

An intuitive analogy to this result may be drawn from the theory of superradiance.[39] For an inverted system, all the n dipoles which constitute the giant dipole moment are aligned (correlated), and the decay (radiation) rate is proportional to n^2. In the other limit, of nearly equal populations, the dipole moments are not aligned (correlated) and the radiation rate is proportional to n.

The explicit prediction that the stochastic contribution to the width of two- (multi-) photon transition induced by one laser is 4 (n^2) times the stochastic contribution of the laser width itself, was very recently confirmed in the beautiful experimental work of Elliot *et al.*[40] which was published after this work had been completed.

IV. FOUR-WAVE MIXING AND EXTRA RESONANCES

The third-order susceptibility $\chi^{(3)}$ is the lowest nonvanishing nonlinear susceptibility for free atoms and molecules, or for any other medium with center of inversion symmetry, and thus, the study of four-wave mixing has become the mainstream of nonlinear (NL) optics.

A very satisfactory approach to the treatment of four-wave mixing (FWM) has been a perturbative solution of Eq. (2.3). Such a solution has been derived by explicit iterative integration (for a particular Fourier component) of the relevant density matrix element[22,23] or directly by the use of double-sided Feynman diagrams,[24–29] and both approaches yield the same result.[41] Following the detailed derivation of Bloembergen and Shen,[23] one notices immediately that relaxation processes are included phenomenologically by introducing $1/T_2$ and $1/T_1$ terms. Moreover, these terms are included in each step of the perturbative expansion. The inclusion of a phenomenological decay rate is an implicit integration over the (fast) interaction with the degrees of freedom of the thermal bath. Strictly speaking, the detailed interaction with the bath should be written down explicitly, and averages should be performed only at the end of the calculation. The full Hamiltonian of the interaction with the bath is not known, nor is it relevant for our application, but since its time scale is known, a very significant simplification occurs. For infinitely short correlation time of these interactions, one obtains exponential decay constants, and one may average at each step of the iterative solution. This procedure has been justified in NMR (Ref. 30) and verified under many experimental conditions both in NMR and in coherent optics. In what follows we will refer to collisions as the dephasing mechanism, but the same applies to other processes like interaction with lattice phonons. Thus, as long as the collision time τ_D is short compared to all other time scales in the problem, the impact approximation is valid. The typical time scale is the inverse of the Rabi frequency

$$\Omega \equiv [(\Delta\omega)^2+(\kappa E)^2]^{1/2} ,$$

where $\Delta\omega$ is the detuning, $\kappa = 2\mu/\hbar$ is the strength of the coupling, and E is the electric field amplitude. The explicit condition for the impact approximation ($\Omega\tau_D \ll 1$)

sets an upper limit on strong fields or on large detunings, but it has supplied a very useful framework for the discussion of most problems in NL optics.

Recently, this phenomenological description was carried even further, and collision-induced interferences between terms of the NL susceptibility have been observed.[32,33] Even within the impact approximation collisions can destroy destructive interferences between terms (diagrams) of the NL susceptibility, leading to (pressure-induced) extra resonances between equally populated ground states and "unpopulated" excited states. If two or more terms (diagrams) interfere in such a way that certain frequency dependences are not observable, the presence of dephasing may remove this interference allowing the appearance of such resonances. Observations in Na vapor[32,33] and in molecular crystals[34] have verified the existence and nature of these extra resonances.

It should be reemphasized that these extra resonances can be derived only if each one of the 48 terms (diagrams) in the full expression for the susceptibility is averaged separately, namely, if the collisions are assumed infinitely short. The experimental observation of these effects provides an *a posteriori* justification for the validity of the separate averaging procedure.

In analogy with collisions, phase fluctuations may play the same role of destroying the interference between different terms (diagrams). The assumption of an infinitely short (δ-function) correlation time for the laser phase fluctuations leads to separate averaging of the different terms of the susceptibility, and thus to the cancellation of destructive interferences in exactly the same way as for collisions.

In order to be specific, three diagrams in the NL susceptibility will be considered in detail and combined to show the new form of the "correction terms." There are 48 different diagrams for the different ordering of terms in the general expression for the third-order susceptibility. For input beams at $\omega_a,\omega_b,\omega_c$ which produce an output at ω_p ($\omega_p=\omega_a+\omega_b-\omega_c$), one obtains

$$\chi^{(3)}(-\omega_p,\omega_a,\omega_b,-\omega_c)=\frac{NL}{6\hbar^3}\sum_{g,k,t,j}(R_{gk}R_{kt}R_{tj}R_{jg}\rho^{(0)}_{gg}A)$$
$$\text{(sum of 48 "terms")} \quad (4.1)$$

where N is the number of molecules, L is the interaction length, and A is the sum of 48 terms resulting from the corresponding diagrams. R is the dipole moment operator connecting the corresponding levels, and the sum is over all intermediate levels. The derivation has been given by several authors;[24,42] we will follow the notation of Ref. 41.

In previous derivations complex molecular frequencies have been used, namely ω_{lm} is complex

$$\omega_{lm}\equiv(E_l-E_m)/\hbar-i\Gamma_{lm}\ , \quad (4.2)$$

leading to a compact notation.

In the present calculation, based on the results of Sec. II, we introduce complex frequencies for the lasers themselves, where the imaginary part is the averaged contribution of the phase fluctuations. Thus we use the complex frequencies

$$\begin{aligned}\omega_a&\equiv\bar{\omega}_a-ia_a\ ,\\ \omega_b&\equiv\bar{\omega}_b-ia_b\ ,\\ \omega_c&\equiv\bar{\omega}_c-ia_c\ ,\\ \omega_p&\equiv\bar{\omega}_p-ia_p\ ,\end{aligned} \quad (4.3)$$

where $\bar{\omega}=\mathrm{Re}\omega$. In addition, define the width involved in multiphoton transitions a_{ab},a_{ac},a_{bc} corresponding to two-photon resonances $(\omega_a+\omega_b),(\omega_a-\omega_c),(\omega_b-\omega_c)$, and a_p corresponding to the $(\omega_a+\omega_b-\omega_c)$ transition. A crucial observation to make at this point is that for *uncorrelated lasers*

$$\begin{aligned}a_{ab}&=a_a+a_b\ ,\\ a_{bc}&=a_b+a_c\ ,\\ a_{ac}&=a_a+a_c\ ,\\ a_p&=a_a+a_b+a_c\ ,\end{aligned} \quad (4.4)$$

but for correlated lasers these relations do not hold, and they are replaced in accordance with Eq. (2.19).

Consider, as an example, the three diagrams in Fig. 1. These are lines 16, 17, and 18 in Ref. 41, with the laser frequencies now being written as complex quantities where appropriate. Following Bloembergen, Lotem, and Lynch[42] this triplet is now combined to a single expression which may be written as $(1+K)$ where K is a "correction term" vanishing under certain circumstances. $\beta\gamma\mu\alpha$ stands for the order of the polarization components of the individual laser beams.

Thus, with the new complex laser frequency notation, the sum of three diagrams is

$$\frac{1}{[\omega_{tg}-(\bar{\omega}_b-\bar{\omega}_c)-ia_{bc}](\omega_{kg}-\omega_b)}\times\frac{\beta\gamma\mu\alpha[1+K((\omega_b-\omega_c),(\omega_a+\omega_b))]}{(\omega^*_{jg}+\omega^*_a)}\ , \quad (4.5)$$

where the correction term is given by

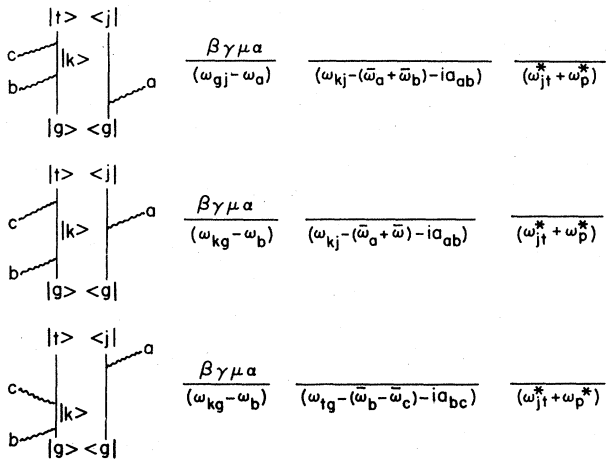

FIG. 1. Diagrams for three different time orderings of terms for the third-order susceptibility. Taken from Ref. 41.

$$K=\frac{1}{\omega_{jt}^{*}+\omega_{p}^{*}}\left\{i(\Gamma_{jg}-\Gamma_{jt}+\Gamma_{tg})+i(a_a+a_{bc}-a_p)\right.$$
$$+[i(\Gamma_{jg}+\Gamma_{kg}-\Gamma_{kj})+i(a_a+a_b-a_{ab})]$$
$$\left.\times\frac{\omega_{tg}-(\bar{\omega}_b-\bar{\omega}_c)-ia_{bc}}{\omega_{kj}-(\bar{\omega}_a+\bar{\omega}_b)-ia_{ab}}\right\} \quad (4.6)$$

with similar expressions for the other diagrams. The correction term K may be written as the sum of two parts

$$K=K_{\rm coll}+K_{\rm stoch}\ , \quad (4.7)$$

where

$$K_{\rm coll}=\frac{1}{\omega_{jt}^{*}+\omega_{p}^{*}}\left\{i(\Gamma_{jg}-\Gamma_{jt}+\Gamma_{tg})\right.$$
$$+i(\Gamma_{jg}+\Gamma_{kg}-\Gamma_{kj})$$
$$\left.\times\frac{\omega_{tg}-(\bar{\omega}_b-\bar{\omega}_c)-ia_{bc}}{\omega_{kj}-(\bar{\omega}_a+\bar{\omega}_b)-ia_{ab})}\right\} \quad (4.8)$$

and

$$K_{\rm stoch}=\frac{1}{\omega_{jt}^{*}+\omega_{p}^{*}}\left\{i(a_a+a_{bc}-a_p)\right.$$
$$+i(a_a+a_b-a_{ab})$$
$$\left.\times\frac{\omega_{tg}-(\bar{\omega}_b-\bar{\omega}_c)-ia_{bc}}{\omega_{kj}-(\bar{\omega}_a+\bar{\omega}_b)-ia_{ab}}\right\}. \quad (4.9)$$

As has been discussed in great detail[32,33,42] in the context of PIER4, in the absence of proper dephasing

$$\Gamma_{jg}-\Gamma_{jt}-\Gamma_{tg}=0\ ,$$
$$\Gamma_{jg}+\Gamma_{kg}-\Gamma_{kj}=0\ , \quad (4.10)$$

and the collisional contribution ($K_{\rm coll}$) to the extra resonance vanishes.

The appearance of the laser stochastic contribution to the extra resonance ($K_{\rm stoch}$) constitutes the major result of our analysis. When laser fluctuations are included, the following conclusion is reached: For uncorrelated lasers relations (4.4) hold and $K_{\rm stoch}$, the stochastic contribution to the correction term, vanishes. Thus relations (4.4) for the laser fluctuation play the same role as Eq. (4.10) for collision. *If the lasers are correlated (e.g., the frequencies ω_a and ω_b are identical and derived from the same laser), the stochastic contribution $K_{\rm stoch}$ to the correction term does not vanish, and a stochastic-fluctuation-induced extra resonance in four-wave mixing (SFIER4) may be observed.*

The characteristics of the SFIER4 are as follows.

(1) It constitutes a coherent signal generated at the difference frequency ($\omega_a+\omega_b-\omega_c$).

(2) The appearance of the induced resonance is conditional upon the existence of field fluctuations, and it will vanish for nonfluctuating or uncorrelated laser fields, according to Eq. (4.4).

(3) The amplitude of the induced resonance is proportional to the clustered stochastic width ($a_a+a_b-a_{ab}$), Eq. (4.9).

(4) The contributions of laser fluctuations and collisional dephasing to four-wave mixing are distinct and independent. The SFIER4 exists even in the limit of zero pressure.

(5) The features of the SFIER4 are independent of but analogous to the PIER4,[32,33] appearing at the same energy, with the clustered stochastic laser width replacing the collisional dephasing rate.

From the point of view of general methodology we would like to emphasize that the SFIER4 advanced by us is distinct from the field-induced resonance considered by Agrawal and Kunasz.[35] The Agrawal-Kunasz resonance is predicted to be located at the atomic frequency, not contributing to the usual four-wave mixing. It satisfies different phase matching conditions, and exhibits a pressure dependence. The Agrawal and Kunasz resonance arises from a different term in the explicit expression for the third order susceptibility, and is not an "extra" resonance in the same sense as the PIER4 or SFIER4 are. In particular, the analysis of Agrawal and Cooper[36] and of Agrawal and Kunasz[37] predicts that no resonance will exist at the frequency $2\omega_1-\omega_2$ in the absence of collisions. Our result is different. For *correlated* laser fields we predict the existence of an extra resonance, according to Eqs. (4.4)–(4.10). The basic difference between the present analysis and the previous approach[36,37] originates from the incorporation of correlation effects between the laser fields, which is explicit in our model. This inclusion of correlation effects constitutes a central feature of our analysis and provides a necessary condition for the appearance of the SFIER4. In addition to the appearance of an extra resonance, our approach leads to an additional quantitative feature. When correlation effects between the laser fields were disregarded, Agarwal and Cooper[36] predicted that the linewidths of the two lasers simply add to the width Γ_0 of a resonance. We predict the existence of a clustered stochastic width, which replaces the collisional dephasing width. The crucial role of correlation effects when applied to the closely related problem of two-photon absorption, is corroborated by the recent experiments of Elliott *et al.*[40]

V. CONCLUSIONS

We have examined the effects of laser field fluctuations on coherent nonlinear optical phenomena, with an emphasis on multiphoton absorption and on four-wave mixing. We have shown that within the framework of the phase-diffusion model fast laser phase fluctuations provide a direct stochastic dephasing contribution to the absorption coefficient and to the third-order susceptibility. For multiphoton absorption, we utilize our scheme to demonstrate that if a given radiation field mode has contributed n photons to a certain transition, its contribution to the dephasing rate is n^2 times the stochastic width of the laser itself.[15,16] For four-wave mixing the laser stochastic widths are incorporated in the correction term for the third-order susceptibility. For a system interrogated

by correlated lasers we expect the appearance of a new stochastic-fluctuation-induced extra resonance in four-wave mixing. The novel aspect of our treatment involves the separation of effects of molecular dephasing and field fluctuations on coherent phenomena. These theoretical predictions are amenable to experimental observation. The very recent interrogation of two-photon absorption[40] provides an important test for the validity and applicability of the PDM. The observation of the SFIER4 will yield novel information on extrinsic laser-field-induced interference effects, providing a firm experimental basis for the analogy between interferences induced by collisions and by stochastic field fluctuations.

Our general results for the equivalence of the dephasing due to the laser phase fluctuations with conventional "T_2-type" mechanisms, is applicable to other experimental observables in the area of nonlinear optics. Several pertinent examples are saturation in a two-level system, traveling-wave amplification, and stimulated Raman oscillations. In all these cases the extrinsic stochastic contributions to the dephasing widths have to be incorporated.

Our treatment, which provides an analysis of laser field fluctuations in nonlinear optical phenomena, rests on the PDM. The extension of the PDM to more refined pictures for the laser phase fluctuations, going beyond simple stochastic models for these phenomena, will be of considerable interest.

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APPENDIX: EFFECTIVE PROPAGATOR FOR EXPONENTIAL CORRELATION FUNCTION

The general expression for the effective propagator, Eq. (2.17), is expanded in a matrix form and the exponential correlation function, Eq. (2.2), is used. The operator $\underline{L}_0$ is diagonalized by the matrix U,

$$\underline{L}_0 = UDU^{-1} , \tag{A1}$$

where D is a diagonal matrix

$$D_{kl} = D_k \delta_{kl} . \tag{A2}$$

The (k,l) element of the product $\underline{L}'_\alpha = \underline{L}^\alpha_1 \times \exp(\underline{L}_0 \tau) \underline{L}^\alpha_1 \exp(-\underline{L}_0 \tau)$ which appears in the integrand of $\underline{L}_{\text{eff}}$ is given by

$$(\underline{L}'_\alpha)_{kl} = \sum_{j,r} G^\alpha_{kl}(j,r) \exp[(D_r - D_j)\tau] , \tag{A3}$$

where

$$G^\alpha_{kl}(j,r) = \sum_{i,m,n} (\underline{L}^\alpha_1)_{ki} (U)_{ij} (U^{-1})_{jm} (\underline{L}^\alpha_1)_{mn} (U)_{nr} (U^{-1})_{rl} . \tag{A4}$$

Using the exponential correlation function, Eq. (2.2), the (k,l) element of the effective propagator is given by

$$(\underline{L}_{\text{eff}})_{kl} = (\underline{L}_0)_{kl} - \sum_\alpha \sum_{j,r} G_k(j,r) \frac{1-\exp[-(\gamma_\alpha - D_r + D_j)t]}{\gamma_\alpha - D_r + D_j} a_\alpha \gamma_\alpha . \tag{A5}$$

Ignoring the transient effects of the short duration of the order of $\{\gamma_\alpha^{-1}\}$ this matrix element becomes time independent:

$$(\underline{L}_{\text{eff}})_{kl} = (\underline{L}_0)_{kl} - \sum_\alpha a_\alpha \gamma_\alpha \sum_{j,r} \frac{G^\alpha_{kl}(j,r)}{\gamma_\alpha + D_j - D_r} . \tag{A6}$$

In the extreme limit, where $\gamma_\alpha \gg \{D_j\}$, which is practically equivalent to referring to the exponential correlation function Eq. (2.2) as to a δ function Eq. (2.18), the more general form, Eq. (A6), of the effective propagator reduces to the simpler form, Eq. (2.19). This is a consequence of the fact that

$$\sum_{j,r} G^\alpha_{kl}(j,r) = ((L^\alpha_1)^2)_{kl} \tag{A7}$$

which is obtained by using the definition of G^α, Eq. (A4).

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