Learning about non-Markovian effects by degenerate four-wave-mixing processes

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I analyze the conditions for the correctness of the formula proposed by Lavoine and Villaeys [Phys. Rev. Lett. **67**, 2780 (1991)] for learning about the non-Markovian effects by degenerate four-wave-mixing processes. I show that this dependence does not provide information about non-Markovian relaxation dynamics for the case of the inhomogeneously broadened transition. Such information can be obtained by the modification of a three-pulse four-wave-mixing experiment.

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In a recent interesting Letter, Lavoine and Villaeys [1] have analyzed the influence of non-Markovian effects in a three-pulse time-dependent four-wave-mixing experiment. In this experiment [Fig. 1(a)], pump pulses propagate in the directions $\mathbf{k}_1$ and $\mathbf{k}_2$ and induce a grating in a medium. The dependence of the grating efficiency on the delay time τ between pulses $\mathbf{k}_1$ and $\mathbf{k}_2$ is recorded using the scattering of the probing pulse $\mathbf{k}_3$, delayed by a fixed time T with respect to pulse $\mathbf{k}_2$. Authors [1] have shown that the energy of the diffracted light can be expressed as a square of the relaxation function $g(\tau)$ [2–4],

$$I(\tau)\sim|g(\tau)|^2 , \tag{1}$$

when the medium is excited by very short pulses. Their calculation does not make assumptions about the analytical form of $g(\tau)$. For this reason it is possible to consider result (1) as general, and this result is interesting from the point of view of learning about the dynamics of the bath.

In this Brief Report, I first define more precisely the conditions of the correctness of Eq. (1). Then I show that this dependence does not provide information about non-Markovian relaxation dynamics for the case of the inhomogeneously broadened transition (slow modulation limit). Such information can be obtained by the modification of a three-pulse four-wave-mixing experiment [5].

Previously a similar study [6] was conducted for the case of the Gaussian modulation of an optical transition frequency. I considered a two-level system ($E_2>E_1$), subjected to the action of radiation and a random stationary adiabatic perturbation $W(t)$, which gives rise to relaxation in the system. I suppose that the quantity $\mu(t)=\hbar^{-1}[W_{22}(t)-W_{11}(t)]$, which describes a stochastic modulation of an optical transition frequency, is a Gaussian random process with the correlation function $K(t)=\langle\mu(0)\mu(t)\rangle$. Contrary to Ref. [1], I did not make any assumptions about the rates of the time evolutions of the coherences and the populations.

I obtained the following formula for the energy of the diffracted light [Ref. [6], Eq. (10)] for the case of the Gauss-Markov modulation when the correlation function has an exponential form $K(t)=a^2\exp(-|t|/\tau_c)$, a is the amplitude of modulation, and τ_c is the correlation time of the interaction with the surrounding bath:

$$I(\tau)\sim|g(\tau)|^2\exp(q)q^{-2p^2}\gamma(2p^2,q) , \tag{2}$$

where

$$q=2p^2\{1+\exp(-T/\tau_c)[1-\exp(-\tau/\tau_c)]\} , \tag{3}$$

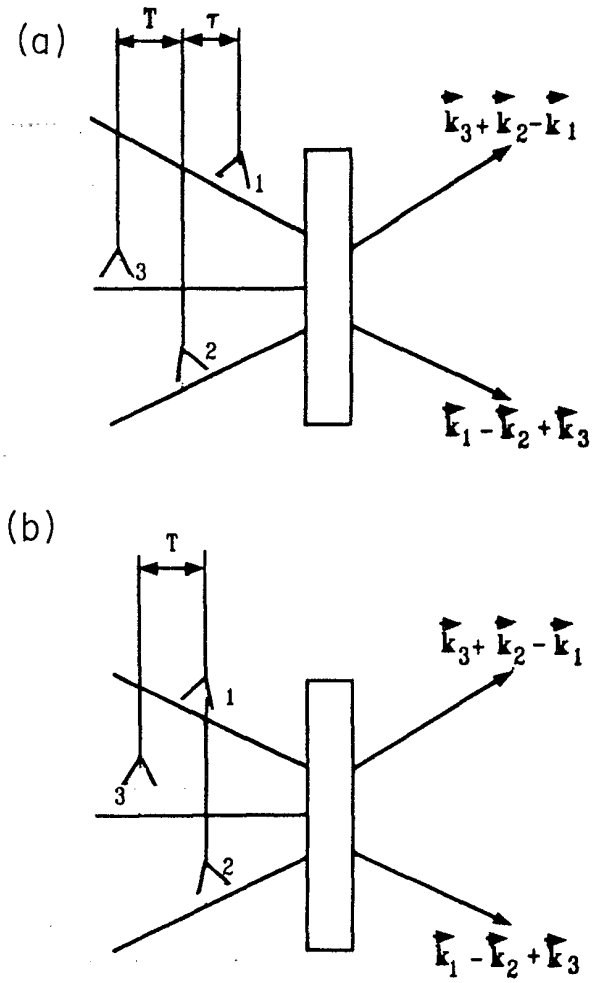

FIG. 1. Geometry for three-pulse time-delayed four-wave-mixing experiments: (a) grating on the basis of a polarization (τ variable, T = const); (b) population grating ($\tau=0$, T variable).

Here the parameter $p=a\tau_c$ characterizes a kind of stochastic modulation ($p\gg1$ corresponds to the slow modulation that results in an inhomogeneous broadening of the optical transition; $p\ll1$ corresponds to the fast modulation that results in a homogeneous broadening of the optical transition); $g(\tau)=\exp[-\int_0^\tau(\tau-t)K(t)dt]$ is the relaxation function; $\gamma(b,z)$ is the incomplete gamma function [7]. Equations (2) and (3) reduce to Eq. (1) only for $T\gg\tau_c$. That is to say, the delay time T of the probe pulse must be much larger than the correlation time. The lack of the signal dependence on the ratio T/τ_c in Eq. (1) is connected apparently with neglecting the influence of bath fluctuations on populations in [1] due to the assumption that the time evolution of the coherences is much faster than that of the populations. This must be the case within the slow modulation limit ($p^2\gg1$) (see below and Refs. [5,8]). However, in general, it is not the case.

Further, in the slow modulation limit (inhomogeneously broadened transition) the dependence $I(\tau)$ for $T\gg\tau_c$ is the following [Ref. [6], Eq. (17)]: $I(\tau)\sim\exp(-a^2\tau^2)$. That is to say, in this case, formula (1) does not provide information about the correlation time of the interaction with the surrounding bath.

This result is not astonishing. Really, it is well known that the relaxation function $g(\tau)$ is the Fourier transformation of the absorption spectrum [4]. In the case of the slow modulation this spectrum reflects directly the distribution of the modulation with the modulation amplitude a. Both the width of the absorption spectrum (in the frequency domain) and the width of the relaxation function (in the time domain) will be about a, and the response of the system is dynamic and coherent [4]. Thus, in the slow modulation limit, the relaxation function $g(\tau)$ does not provide additional information with respect to the absorption spectrum.

The possibility of the correlation time measurements in the slow modulation limit ($p^2\gg1$) is based on the time evolution of an inhomogeneously broadened optical transition [5,8]. This problem was investigated in Ref. [5] by considering coherent optical effects (a photon echo) in such a system. It has been demonstrated that the following times are typical for the time evolution of the system investigated:

$$a^{-1}<T'\ll\tau_c\ ,$$

where a^{-1} plays the role of the reversible dephasing time of an optical transition, $T'\equiv(\tau_c a^{-2})^{1/3}=\tau_c p^{-2/3}$ plays the role of the irreversible dephasing time, and the correlation time τ_c plays the role of the relaxation time of populations. Thus, if one wants to measure the correlation time τ_c in the slow modulation limit, one ought to use the population grating [Fig. 1(b)] instead of the grating on the basis of a polarization [Fig. 1(a)]. The latter corresponds to the three-pulse echo experiment. Therefore it has been proposed in Ref. [5] to modify the three-pulse method in the slow modulation limit such that $\tau=0$ and $T=$var. In this case the pump pulses $\mathbf{k}_1$ and $\mathbf{k}_2$ form both the grating on the basis of a polarization and the population grating. The polarization grating attenuates for the time $\sim T'$. Therefore, if pulse durations $t_p>T'>a^{-1}$ (and naturally, $T\sim t_p>T'$), only the population grating preserves, and the probing pulse $\mathbf{k}_3$, delayed by the time T, allows one to measure the population grating relaxation, i.e., time τ_c.

For this case the dependence $I(T)$ is determined by Eqs. (11) and (16) of Ref. [5], obtained for the case of a strongly broadened vibronic transition. For simplicity we shall write this dependence here only for the partial case of the strictly resonance excitation of the absorption band and large Stokes shift of the absorption and emission spectra:

$$I(\tau=0,T)\sim[1-\psi^2(T)]^{-1}\ , \tag{4}$$

where $\psi(t)\equiv K(t)/K(0)$ is the normalized correlation function of the interaction with the surrounding bath [for the case of Gauss-Markov modulation $\psi(t)=\exp(-|t|/\tau_c)$]. Thus the dependence $I(T)$ allows one to determine the correlation time τ_c of the frequency fluctuations for the case of the inhomogeneously broadened transition.

It is necessary to note that Eqs. (2) and (3) do not reduce to Eq. (4) for $\tau=0$, since Eq. (4) has been obtained for the case of the excitation by pulses of durations $t_p<\tau_c$ and $t_p\gg T'\equiv(\tau_c/a^2)^{1/3}>a^{-1}$ [5], and Eqs. (1)–(3) are correct for pulses $t_p\ll a^{-1/2},\tau_c$.

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[1] J. P. Lavoine and A. A. Villaeys, Phys. Rev. Lett. **67**, 2780 (1991).

[2] The function $g(\tau)$ in Ref. [1] is determined by the memory kernel for the dynamics of the system [see Eqs. (18) and (19), Ref. [1]]. Using Eq. (19), Ref. [1], one can show that $g(\tau)$ is the characteristic function of the resonance absorption spectrum $J(\omega-\omega_{21})$ and is expressed by $g(\tau)=\int_{-\infty}^{\infty}J(\omega')\exp(i\omega'\tau)d\omega'$, where ω_{21} is the frequency of the corresponding transition $1\rightarrow2$. It is well known that the characteristic function is the relaxation function that describes the relaxation of the response of a system after removal of the outer disturbance [3,4]. Therefore I call $g(\tau)$ by the relaxation function because such a definition is more general.

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