RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 30, NUMBER 10 15 NOVEMBER 1984

Non-Markovian effect in transient optical parametric phenomena in an exciton-phonon system

Masaki Aihara
Department of Physics, Faculty of Liberal Arts, Yamaguchi University, Yamaguchi 753, Japan
(Received 14 June 1984)

The theoretical study on the non-Markovian effect in the exciton-phonon system associated with the transient optical parametric phenomena is presented. It is found that there arises the oscillatory nonlinear-optical response due to the virtual-exciton relaxation caused by LA and LO phonons. The oscillation due to LA phonons is much slower than that for the localized–electron-phonon system, which makes its observation much more possible.

With the advent of the transient nonlinear spectroscopic techniques using pulsed lasers, it becomes possible to observe directly in the time domain the dynamical behavior of the extremely fast relaxation phenomena in condensed phases.[1,2] Recently, the present author pointed out that, in the extremely short-time region comparable to the reservoir correlation time, the conventional theories using the constant relaxation rates are no longer valid, and predicted that the transient nonlinear-optical response exhibits the characteristic time variation inherent in the non-Markovian nature of condensed phases.[3] However, in this work only the localized excitation was concerned, so the characteristic features inherent in condensed phases were not fully taken into consideration.

The exciton-coherence effect associated with the transient grating experiments were theoretically investigated by Wong and Kenkre;[4,5] these works are interesting and related to the non-Markovian problems in a sense that the time dependence of the energy-transfer rate is considered. In these works, however, the non-Markovian effect associated with the exciton-phonon interaction is not considered; that is, the time dependence of the exciton relaxation rate due to phonons is disregarded.

In this Rapid Communication, we present the theoretical study on the transient non-Markovian optical parametric phenomena in an exciton-phonon system, from a fully microscopic viewpoint of the exciton-phonon interaction. It is found that there appears an oscillatory behavior with characteristic frequency $\omega_c = Mu^2/2h$ (M is the total exciton mass, u is the LA phonon velocity, and h is the Planck constant) in the transient nonlinear-optical response. It is also found that in polar semiconductors there also appears, in a much shorter time region, a strong oscillation with the LO-phonon period. These oscillations cannot simply be interpreted as quantum beat, but as the non-Markovian effect where the time dependence of the transverse relaxation rates plays the essential role. To be concrete, they are attributed to the relaxation of the virtual exciton with a frequency different from that for the real exciton, by the order of the inverse of the observation time. In contrast to the case of the localized–electron-phonon system, the translational motion of an exciton and the momentum conservation in the exciton-phonon interaction play important roles. Especially, with respect to the exciton-LA-phonon interaction, the translational motion of an exciton significantly reduces the above-mentioned characteristic frequency ω_c in the transient nonlinear-optical response, so it becomes much easier to observe the non-Markovian effect in an exciton-phonon system than in a localized–electron-phonon system, if temperature is low enough to be able to neglect the effect due to exciton relaxation assisted by the LO-phonon absorption.

According to the general formulation of the transient nonlinear optics, the time-integrated intensity of the signal radiation for the transient parametric process caused by the two–short-pulse excitation, is expressed, as a function of a pulse interval τ_s by[3]

$$I(\tau_s)=\int_{t_s}^{\infty} dt \exp\{-2[2S(t-\tau_s)+2S(\tau_s)-S(t)]\} , \tag{1}$$

where the unimportant multiplicative factor is omitted. In Eq. (1), $S(t)$ is the second cumulant defined by

$$S(t)=\int_0^t dt_1 \Gamma(t_1) . \tag{2}$$

Here $\Gamma(t_1)$ is the time-dependent exciton damping rate (in other words, the inverse of the time-dependent transverse relaxation time of exciton[6]); its lowest order is expressed, with the units of $h/2\pi=1$, by

$$\Gamma(t_1)=\int_0^{t_1} dt_2 \mathrm{Re}[\langle V(t_2)V(0)\rangle] = \sum_{\eta}\sum_{\vec{q}} V_{\eta}^2(\vec{q})\left[[1+N(\vec{q})]\frac{\sin[\epsilon(0)-\epsilon(\vec{q})-\omega_{\eta}(\vec{q})]t_1}{\epsilon(0)-\epsilon(\vec{q})-\omega_{\eta}(\vec{q})}+N(\vec{q})\frac{\sin[\epsilon(0)-\epsilon(\vec{q})+\omega_{\eta}(\vec{q})]t_1}{\epsilon(0)-\epsilon(\vec{q})+\omega_{\eta}(\vec{q})}\right] . \tag{3}$$

In the case of the localized electron-phonon system,[3] $V(t)$ in Eq. (3) represents the energy change of the excited state due to phonons, but in the case of the exciton-phonon system $V(t)$ represents the scattering of zero-momentum exciton by phonons. The second line of Eq. (3) is obtained from the correlation function for $V(t)$ similar to Eq. (36) of Ref. 3 for which the phonon propagator $\exp(\mp ie_k t)$ is replaced by $\exp\{i[\mp\omega_{\eta}(q)+\epsilon(0)-\epsilon(q)]t\}$, in order to take into consideration the center-of-mass motion of an exciton. Here η takes LA- and LO-phonon modes, $V_{\eta}(\vec{q})$ is the matrix element for the exciton-phonon coupling with momentum transfer $\vec{q}$ (see Ref. 7), $N(\vec{q})$ is the Bose-

Einstein distribution function for an exciton, $\epsilon(\vec{q})$ is the exciton energy, and $\omega_\eta(\vec{q})$ is the phonon energy. We have assumed that the matter dimension is much smaller than the exciting-pulse length, and that the exciton-phonon interaction is small enough to be able to be terminated up to the second cumulant. It is important to remark that in the present problem the relevant system is the exciton with zero momentum, which is directly coupled with a photon, and both excitons with other momentums and the phonon system play the role of the reservoir; in the first line of Eq. (3), the average $\langle \cdots \rangle$ has been made over the initial distribution of the reservoir.

In the following, we present the numerical results for A_1 exciton of CdS, as a typical example. For simplicity, only $1S$ exciton is considered. In Fig. 1, we show the time dependence of the exciton damping rate $\Gamma(t)$; we clearly find the oscillatory behavior. This means that Γ should not be regarded merely as constant except in the long-time limit much larger than this oscillation period. In other words, the transverse relaxation time $T_2(=\Gamma^{-1})$ periodically varies with time. This phenomenon is closely related to the energy dependence of the self-energy of the relevant system, which plays an essential role in the formation of the Raman-like component in the resonant light scattering spectrum[8] and also in the unification of the resonant–Rayleigh-type optical mixing and the resonant coherent anti-Stokes Raman scattering.[9] In the present transient problem where the dynamical behavior of the system is of interest, the concept of the time-dependent exciton damping rate is more appropriate to describe the non-Markovian property.

We are now in a position to consider what determines the oscillation period in Fig. 1. As stated before, the non-Markovian effect is caused by the memory effect of the reservoir in the short-time region which is comparable to the reservoir correlation time τ_c. An equivalent statement in the present case is that this effect is due to virtual zero-momentum exciton with an energy range of the order of the inverse of the observation time. The parabola in the insert in Fig. 1 is the exciton dispersion curve, and the slope of dashed lines is associated with the magnitude of the sound velocity. As is shown in this figure, a virtual exciton (A) with energy larger than $Mu^2/2$ is scattered to the real exciton states by emitting or absorbing a phonon. The virtual exciton (B), especially with energy $Mu^2/2$, plays the predominant role because of the large final density of states for this process. The oscillation in Fig. 1 corresponds to this virtual-exciton energy. For the present example, this oscillation period is about 43 psec, which is much longer than the period in the case of a localized electron, so the observation of the non-Markovian effect in an exciton-phonon system is quite within the bounds of possibility.

The numerical result for the integrated signal intensity expressed by Eq. (1) is shown in Fig. 2(a); we observe the deviation from simple exponential decay, which reflects the

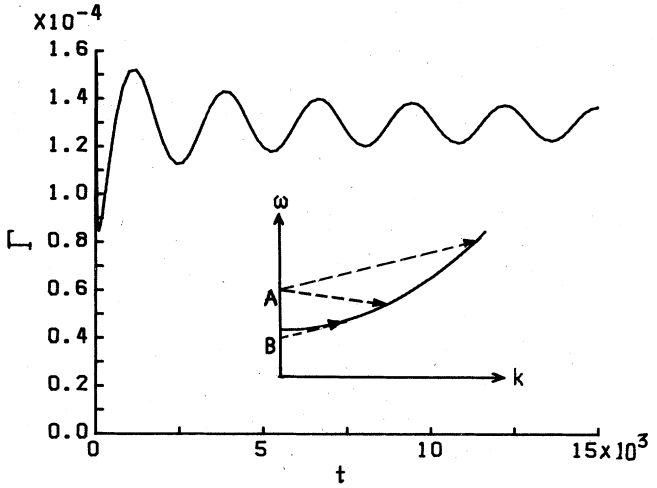

FIG. 1. The time dependence of the exciton damping rate Γ. The abscissa is normalized by the inverse of the LO-phonon angular frequency ω_{LO} which is about 17 fsec for the present example. The ordinate is normalized by ω_{LO}. The temperature is set at $kT/\omega_{LO}=0.02$. The hyperbola in the inserted figure represents the exciton dispersion curve, and the slope of dashed lines is associated with the LA-phonon velocity. The oscillatory behavior is due to LA phonons.

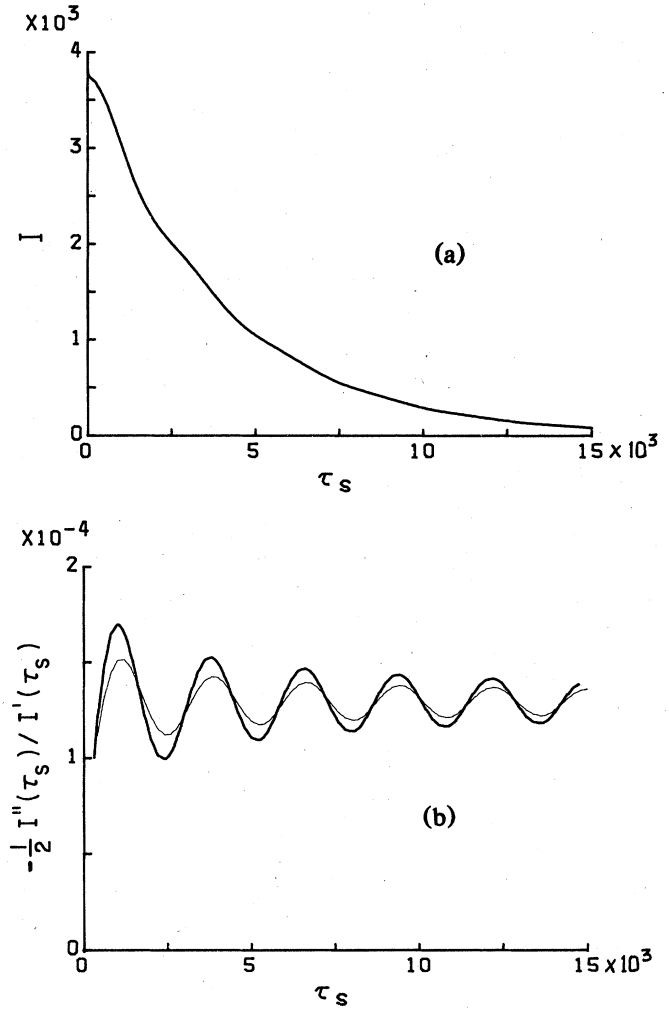

FIG. 2. (a) The dependence of the integrated signal intensity I on exciting-pulse separation τ_s. The abscissa is normalized by the inverse of the LO-phonon angular frequency ω_{LO}. The temperature is set at $kT/\omega_{LO}=0.02$. The oscillatory behavior is due to LA phonons. (b) The display of $-\frac{1}{2}I''(\tau_s)/I'(\tau_s)$ as a function of exciting-pulse separation τ_s. The ordinate is normalized by ω_{LO}. The thin solid curve is the same as the curve in Fig. 1.

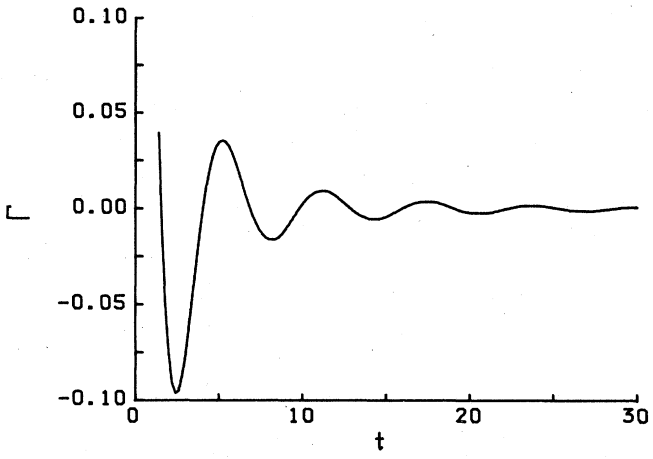

FIG. 3. The time dependence of the exciton damping rate Γ. The abscissa is normalized by the inverse of the LO-phonon angular frequency ω_{LO}. The ordinate is normalized by ω_{LO}. The temperature is set at $kT/\omega_{LO}=0.02$. The oscillatory behavior is due to LO phonons.

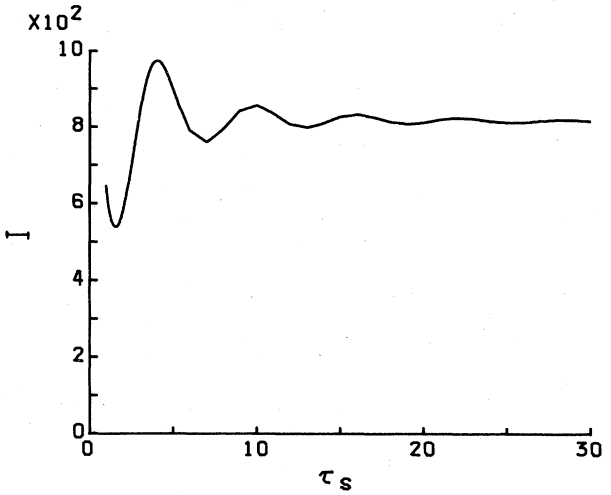

FIG. 4. The dependence of the integrated signal intensity I on exciting-pulse separation τ_s. The abscissa is normalized by the inverse of the LO-phonon angular frequency ω_{LO}. The temperature is set at $kT/\omega_{LO}=0.02$. The oscillatory behavior is due to LO phonons.

oscillatory time dependence of the exciton damping rate shown in Fig. 1. To see this oscillation more clearly, we show $-\frac{1}{2}I''(\tau_s)/I'(\tau_s)$ in Fig. 2(b). It should be noted that this curve is similar to that of the time dependence of the exciton damping rate Γ shown in Fig. 1. This is because, in the case that the exciton-phonon interaction is not very strong, the integrated intensity given by Eq. (1) is approximated by

$$I(\tau_s)\sim\int_{\tau_s}^{\infty}dt\exp\left[-2\int_0^t dt_1\Gamma(t_1)\right] . \quad (4)$$

It is important to remark that the abscissa in Fig. 2 is not t but τ_s, so we can obtain information on the time dependence of the exciton damping rate without measuring directly the time dependence of the signal intensity. This is the distinctive advantage of the transient parametric effect over the usual linear method using only a single pulse. We should also remark that in Fig. 2(b) the oscillation is stronger than that in Fig. 1; this difference is due to the fact that in Eq. (1) the reservoir correlation between the different time segments separated by two excitation pulses, is taken into consideration.

In the much shorter time region where the inverse of its time scale is comparable to the LO-phonon energy, we observe the non-Markovian effect due to LO phonons. The exciton damping rate Γ and the integrated signal intensity $I(\tau_s)$ are shown in Figs. 3 and 4, respectively. From Fig. 3, we observe that Γ oscillates very strongly with the LO-phonon oscillation period (0.11 psec for the present example), and takes even negative values. This implies that in the ultrashort-time scale comparable to the LO-phonon oscillation period, Γ no longer has the meaning of the relaxation rate. This strong non-Markovian character is caused by the strong Fröhlich-type exciton–LO-phonon interaction. From Fig. 4, we observe the strong oscillation in $I(\tau_s)$ reflecting the time dependence of Γ shown in Fig. 3. In contrast to the case of the localized-electron-phonon system in which the decay of the oscillation is mainly associated with the width of the phonon density of states, the decay of the oscillation in the present case is associated with the recoil motion of an exciton.

In conclusion, we investigated the transient non-Markovian behavior in the exciton-phonon system associated with the two-pulse optical parametric effect. The results are attributed to the dynamical behavior of the virtual-exciton relaxation caused by LA and LO phonons. The effect due to the finiteness of the excitation pulse duration and the polariton effect will be presented in a forthcoming paper.

[1] *Picosecond Phenomena III,* edited by K. B. Eisenthal, R. M. Hochstrasser, W. Kaiser, and A. Laubereau (Springer-Verlag, Berlin, 1982).
[2] Y. Masumoto, S. Shionoya, and T. Takagahara, Phys. Rev. Lett. **51**, 923 (1983).
[3] M. Aihara, Phys. Rev. B **25**, 53 (1982).
[4] Y. M. Wong and V. M. Kenkre, Phys. Rev. B **22**, 3072 (1980).
[5] V. M. Kenkre, Phys. Lett. **82A**, 100 (1981).
[6] M. Tokuyama and H. Mori, Prog. Theor. Phys. **55**, 411 (1976); F. Shibata, J. Phys. Soc. Jpn. **44**, 1435 (1978).
[7] Y. Toyozawa, Prog. Theor. Phys. **20**, 53 (1958).
[8] A. Kotani and Y. Toyozawa, J. Phys. Soc. Jpn. **41**, 1699 (1976).
[9] M. Aihara, Phys. Rev. B **27**, 5904 (1983).