Transient nonlinear optical phenomena in exciton-phonon systems

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Propagation of a light pulse in the bulk and hole bleaching in the absorption spectrum from a film of polydiacetylene-toluene sulfonate are investigated in the transient regime. This polymer is treated as an example of an exciton-phonon coupling system with only two phonon modes dominating the coupling. For the propagation, we use the Maxwell wave equation to express the field in terms of the polarization density, which is found microscopically from a set of optical Bloch-like equations in the semiclassical approximation. Phonon-mediated phenomena predicted in this work include the photon echo in a solid and bistable behavior of both the absorption coefficient and refraction index. The absorption spectrum is calculated for a thin film of an exciton-phonon system under a strong pump field and a weak probe field from the optical Bloch-like equations only. Phonon-mediated bleaching of holes is obtained in good agreement with experiments.

I. INTRODUCTION

In the study of nonlinear optical properties of solids, it is sometimes useful to describe the solid by a simple model of electron-phonon coupling systems, provided that there are only a limited number of phonon modes coupled strongly to the electronic system. To name just a few examples, we note that interesting results are found by assuming the coupling to be between vibrational modes localized near impurities in solids and the electronic transition of the impurity atom,[1] or between the localized phonon modes and the electron-hole system instead of the impurity atom in solids.[2] The vibrational modes of the bond connecting admolecules to a solid surface have been studied theoretically[3] and experimentally,[4] and their coupling to the electronic transition in solids has also been studied.[5] It has been found in many polymers that only a few phonon modes along the stretch of bonds composing the backbone couple strongly with excitons in the system.[6]

In recent years, we have found many interesting phenomena in the nonlinear optical response of polymers by considering the polymer as an exciton-phonon coupling system. Phonon-mediated optical bistabilities[7–9] with novel behavior are found with or without external feedback from the cavity or a solid surface nearby. Exciton-phonon coupling is also found to be responsible for the splitting of the optical susceptibility of polymers.[10] Very recently, we have investigated the coupling of an impurity electron with a localized phonon mode and calculated the resonance fluorescence spectrum of the impurity atom.[11] Novel structures are found at the sideband peaks, and we have shown that the hole and antihole are direct results of the electron-phonon interaction.

In this paper, we study the propagation of a light pulse in an exciton-phonon coupling system and the transient nonlinear optical response of this system. Light pulses propagating in a near-resonant medium can produce a number of interesting phenomena, most of which have their origin in the transient response of the medium to coherent pulsed excitations. Hence one of the most interesting subjects in physics is the coherent transient interaction between materials and optical fields. Studies of transient and propagational optical effects are of particular importance to the development of coherent optical spectroscopy as well as fast-response nonlinear optical materials. We choose polydiacetylene-toluene sulfonate (PTS) as our medium in this study because it is a typical material with only a few phonon modes coupling strongly with excitons.[6,12]

II. LIGHT-PULSE PROPAGATION IN THE MATERIAL

It is well known that when light propagates in a material it induces polarizations which, in turn, modify the field of the propagating light. To treat the problem, we first express the field in terms of the polarization density from the Maxwell wave equation in which the polarization of the medium acts as the source. The polarization is then expressed in terms of microscopic quantities characterizing the exciton and phonons in the material. These elementary excitations are treated as damped harmonic oscillators, and the light field is regarded as the driving force. Thus, both the field and polarization can

be determined by solving the set of all these coupled equations.

In general, the wave equation for the electric field in an isotropic medium is

$$\left[\nabla^2-\frac{n_0^2}{c^2}\frac{\partial^2}{\partial t^2}\right]\mathbf{E}(\mathbf{r},t)=\frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{P}(\mathbf{r},t)\ , \tag{1a}$$

where $\mathbf{E}(\mathbf{r},t)$ is the electric field of the light, and $\mathbf{P}(\mathbf{r},t)$ is the polarization density of the medium which represents the dipole moment density of excitons. This polarization P is excited by the electric field only and thus has the same direction of the vector E. We may take the direction of propagation as the x direction and consider this electric field to be of the plane-wave type with no transverse variance. Assuming a linear polarization of this field, we can write the wave equation in a one-dimensional form as[13]

$$\left[\frac{\partial^2}{\partial x^2}-\frac{n_0^2}{c^2}\frac{\partial^2}{\partial t^2}\right]\mathrm{E}(x,t)=\frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2}P(x,t)\ . \tag{1b}$$

The refraction index n_0 of the medium is assumed to be unity throughout this paper. The electric field can be written as

$$\mathrm{E}(x,t)=E(x,t)e^{i(\omega t-kx)}+\text{c.c.}\ , \tag{2a}$$

and consequently, the polarization density takes the form

$$P(x,t)=\mathcal{P}(x,t)e^{i(\omega t-kx)}+\text{c.c.}\ , \tag{2b}$$

where E and $\mathcal{P}$ are the amplitudes, ω the frequency, and k the wave vector of the field. Since the envelope of the field varies slowly on the scale of the carrier wave, we have $\omega E\gg\dot{E}$, $kE\gg\nabla E$, $\omega\mathcal{P}\gg\dot{\mathcal{P}}$, and $k\mathcal{P}\gg\nabla\mathcal{P}$. Inserting Eqs. (2) into (1b), we obtain

$$(k^2-k_0^2)E=4\pi k_0^2\mathrm{Re}\mathcal{P}\ , \tag{3a}$$

$$k\frac{\partial E}{\partial x}+\frac{k_0}{c}\frac{\partial E}{\partial t}=2\pi k_0^2\mathrm{Im}\mathcal{P}\ , \tag{3b}$$

where $k_0=\omega/c$. Two more equations are needed to determine the complex amplitudes completely. In what follows, we attempt to find the polarization density from microscopic considerations. A set of optical Bloch-like equations is obtained to find $\mathcal{P}$ in terms of the field, and Eqs. (3) then determine E from $\mathcal{P}$.

By modeling both the exciton and phonons as damped oscillators, we write the Hamiltonian for the medium as

$$H=H_0+V\ , \tag{4a}$$

$$H_0=(\omega_x-i\gamma_x)a^\dagger a+\sum_i(\omega_i-i\gamma_i)b_i^\dagger b_i+\sum_i\lambda_i a^\dagger a(b_i^\dagger+b_i)\ , \tag{4b}$$

$$V=-[\mu a^\dagger E^{(+)}(x,t)+\text{h.c.}]\ , \tag{4c}$$

where we have used the rotating-wave approximation[14] (RWA), which is valid as long as the field is nearly on-resonance with the excitonic transition.[15]

The operators $a^\dagger$ (a) and $b_i^\dagger$ (b_i) stand for the creation (annihilation) operators for the exciton and the ith phonon mode with corresponding frequencies ω_x and ω_i and decay rates γ_x and γ_i, respectively. The exciton-phonon coupling constant is λ_i, and the exciton dipole matrix element is μ. $E^{(+)}(x,t)$ is the positive frequency part of the field $E(x,t)$ defined by (2a). For PTS as our medium, we only have to include the two phonon modes coupled most strongly to excitons.[6,7,12]

Since we are not interested in any quantity that is sensitive to the quantum number counting, we neglect quantum fluctuations and deal with the mean values of the relevant operators. Thus we define

$$u=\mathrm{Re}\langle a\rangle\ , \tag{5a}$$

$$v=\mathrm{Im}\langle a\rangle\ , \tag{5b}$$

$$q_i=\mathrm{Re}\langle b_i\rangle\ , \tag{6a}$$

$$w_i=\mathrm{Im}\langle b_i\rangle\ . \tag{6b}$$

With the non-Hermitian Hamiltonian (4), we find equations of motion for these mean values from the quantum Liouville equation for dissipating systems.[16] The essential elements of the theory are outlined in the Appendix.

In the rotating frame, $\langle a\rangle$ is replaced by $\langle a\rangle e^{-i\omega t}$, and the equations of motion are

$$\dot{u}=\Delta v+2\sum_{i=1}^{2}\lambda_i q_i v-\gamma_x u\ , \tag{7a}$$

$$\dot{v}=-\Delta u-2\sum_{i=1}^{2}\lambda_i q_i u-\gamma_x v+\Omega\ , \tag{7b}$$

$$\dot{q}_i=-\gamma_i q_i+\omega_i w_i \tag{7c}$$

$$\dot{w}_i=-\gamma_i w_i-\omega_i q_i-\lambda_i(u^2+v^2)\ , \tag{7d}$$

where we have defined the Rabi frequency $\Omega=\mu E$ and detuning $\Delta=\omega_x-\omega$, and have made use of Eq. (2a). As the polarization density in the rotating frame is given by[13,15]

$$\mathcal{P}=N\mu\langle a^\dagger\rangle\ , \tag{8}$$

where N denotes the exciton density, Eqs. (3) and (7) form the closed set of equations from which the problem of light propagation can be solved. In terms of u, v, and Ω, Eqs. (3) become

$$(k^2-k_0^2)\Omega=4\pi k_0^2 N|\mu|^2 u\ , \tag{9a}$$

$$k\frac{\partial\Omega}{\partial x}+\frac{k_0}{c}\frac{\partial\Omega}{\partial t}=-2\pi k_0^2 N|\mu|^2 v\ . \tag{9b}$$

Evidently the set of coupled equations (7) and (9) cannot be solved analytically. Assuming that there is no exciton and phonon initially, we consider for simplicity a square pulse of the initial laser field in our numerical solution. In the case of light with square pulses interacting with a two-level atom at resonance, a pulse of area π just "inverts" the atom.

To understand this, let us start with the Hamiltonian in the RWA for the interactions of a two-level atom with a classical electric field,

$$H=\omega_{ab}\sigma_z-(\mu E_2 e^{-i\omega_2 t}\sigma_+ +\mu^* E_2^* e^{i\omega_2 t}\sigma_-)\ . \tag{10}$$

Here ω_{ab} is the transition frequency between the two levels $|a\rangle$ and $|b\rangle$; μ is the dipole moment element of the atom; E_2 and ω_2 are the amplitude and frequency of the field, respectively; and the spin operators are $\sigma_{\pm}=\sigma_x \pm i\sigma_y$, where σ_x, σ_y, and σ_z are the Pauli matrices. Suppose that the atom is initially in its lower level $|b\rangle$. The state vector for this atom can be written as

$$|\psi(t)\rangle = C_a(t)|a\rangle + C_b(t)|b\rangle \ , \tag{11}$$

where $C_a(0)=0$ and $C_b(0)=1$. By using the Schrödinger equation $i\dot{\psi}=H\psi$ and the orthonormality of the states $|a\rangle$ and $|b\rangle$, we find from Eqs. (10) and (11) the probabilities for the atom to be in its two levels,

$$P_a(t)=\sin^2\left[\frac{\mu E_2}{2}t\right] \quad \text{(upper level)} \ , \tag{12a}$$

$$P_b(t)=\cos^2\left[\frac{\mu E_2}{2}t\right] \quad \text{(lower level)} \ , \tag{12b}$$

where we have assumed the resonance interaction, or $\omega_{ab}=\omega_2$. Evidently, at time $t=\pi/\mu E_2$ the atom has completed the transition to the upper level $|a\rangle$, i.e., $P_a(\pi/\mu E_2)=1$ and $P_b(\pi/\mu E_2)=0$. In other words, the atom is "inverted." A "pulse" characterized by this value of μE_2 for an interval of t is sometimes called a π pulse because $\mu E_2 t=\pi$. Similarly, when a square pulse of light interacts with an exciton as in the present case, our numerical calculation indicates that a pulse of area 1.77 excites an exciton in the system. Thus, a π pulse means in this paper a pulse of area 1.77. By the same token, an $n\pi$ pulse means a pulse of area $1.77n$. For convenience we fix the duration of the pulse to be 1.77 throughout this paper and change the area by varying the value of E. Here and throughout this paper, we adopt γ_x ($=0.05$ eV) as the energy unit, γ_x^{-1} as the time unit, and 10^4 Å as the length unit. The parameters employed in our numerical work are $\omega_x=40$, $N|\mu|^2=1/2\pi, \omega_1=5.16, \lambda_1=2, \omega_2=3.68, \lambda_2=1.66, \gamma_1=\gamma_2=0.04$.

Figure 1 shows the propagation of a 6π pulse at a distance x inside the material under consideration. For the sake of comparison, we also plot dashed lines representing results for the hypothetical case in which the existence of phonon modes is completely ignored. At short distances as in Fig. 1(a) for $x=0.05$, it is seen that a square 6π pulse evolves into several groups. The first three are shown in the figure. Each consists of three narrow pulses and occupies a time interval of roughly 1.77. This is a complicated phenomenon of photon echoes. A group of pulses passing a point in the material at which the initial pulse is located is followed by several sets of pulses. On the other hand, if there are no phonon modes present in the material, there is no echo. It is, therefore, clear that the novel phenomenon is phonon mediated.

As the pulse propagates deeper inside the material, all the peaks become smaller because of the strong absorption, and the interesting phenomenon gradually disappears. The situation at $x=5.0$ is depicted in Fig. 1(b). The evolution of a π pulse at different distances in the material is shown in Fig. 2. The difference between results for cases with and without phonon modes diminishes quickly as x increases, and the two lines coincide almost entirely for $x>5$.

It is noted that in every case we have studied it always takes some time for the phonon effects to show up. In other words, the solid lines do not deviate from the corresponding dashed lines right away at $t=0$ because there is initially no phonon in the system, and phonon modes are excited only indirectly via excitons. At large distances, the strong absorption effect greatly reduces the pulse intensity, so that no exciton and hence no phonon can be excited. For the zero π pulse, our calculations show no phonon influence at all, indicating the importance of the pulse power in the phonon creation process.

When the pulse duration is longer than the lifetime of both phonons and excitons, the amplitude of the light field is approximately constant. Hence, it is possible to apply the steady-state results of the optical Bloch-like equations (7). The standard algebraic procedure[7–9] then leads to the exciton variables

$$u=(\Delta-\lambda_p n)\Omega/[(\Delta-\lambda_p n)^2+\gamma_x^2] \ , \tag{13a}$$

$$v=\gamma_x\Omega/[(\Delta-\lambda_p n)^2+\gamma_x^2] \ , \tag{13b}$$

where $n=u^2+v^2$ is the mean number of excitons deter-

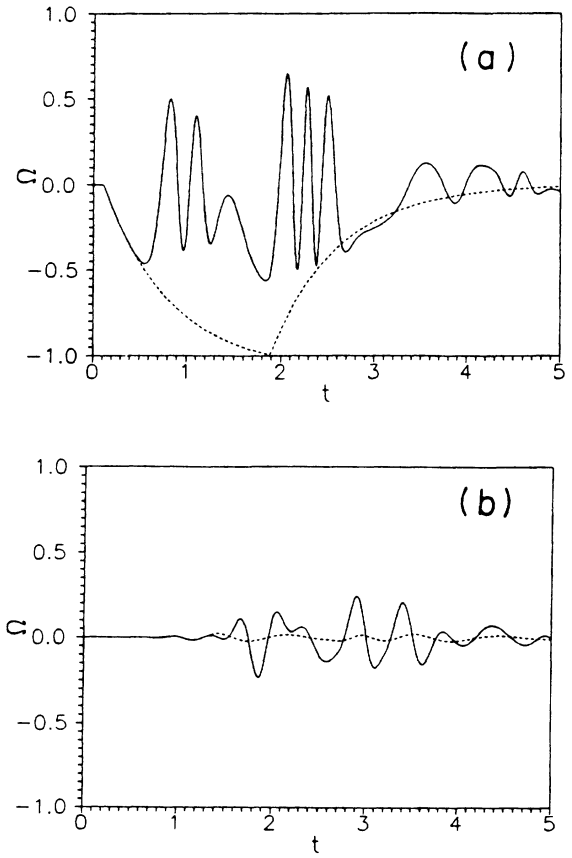

FIG. 1. Time evolution of an on-resonance 6π laser pulse propagating in PTS with $\lambda_i \neq 0$ (solid lines) and $\lambda_i=0$ (dashed lines) (a) $x=0.05$, (b) $x=5.0$.

mined by

$$\lambda_p^2 n^3 - 2\Delta\lambda_p n^2 + (\Delta^2+\gamma_x^2)n - |\Omega|^2 = 0 \tag{13c}$$

and

$$\lambda_p = 2\sum_{i=1}^{2} \lambda_i^2 \omega_i/(\omega_i^2+\gamma_i^2) \ . \tag{13d}$$

The third-order algebraic equation (13c) may have three distinct roots for n, implying the possible existence of bistable behavior for u, v, and n. It is such bistable behavior that results in novel phenomena of nonlinear nature. As $\partial\Omega/\partial t = 0$ in the present case, we have from Eqs. (9b) and (13b)

$$\frac{\partial}{\partial x} I = -\alpha I \ , \tag{14}$$

with $I = \Omega^2$, and the absorption coefficient

$$\alpha = 4\pi N|\mu|^2(k_0^2/k)\gamma_x/[(\Delta-\lambda_p n)^2+\gamma_x^2] \ . \tag{15}$$

The index of refraction follows directly from Eqs. (9a) and (13a),

$$n_r^2 = 1 + 4\pi N|\mu|^2(\Delta-\lambda_p n)/[(\Delta-\lambda_p n)^2+\gamma_x^2] \ . \tag{16}$$

In Figs. 3 and 4, we plot the absorption coefficient and refractive index, respectively, as functions of the intensity I. The bistable behavior is clearly seen in parts (b) of these plots. The bistability loop for the absorption in Fig. 3(b) is like the normal one, while it is an inverted loop in Fig. 4(b) for the refraction index. These bistabilities are apparent results of the nonlinear interaction between the light and virtual excitons with the mediation of phonon modes. In the case of light interaction with real excitons, $\Delta = 0$ and no phonon mediation is needed. Results shown in Figs. 3(a) and 4(a) do not show any feature of bistability. On the other hand, the absorption becomes saturated for sufficiently strong excitation, no matter if the exciton is real or virtual.

The index of refraction depends very much on the detuning. When $\Delta < 0$ or the pulse light frequency is higher

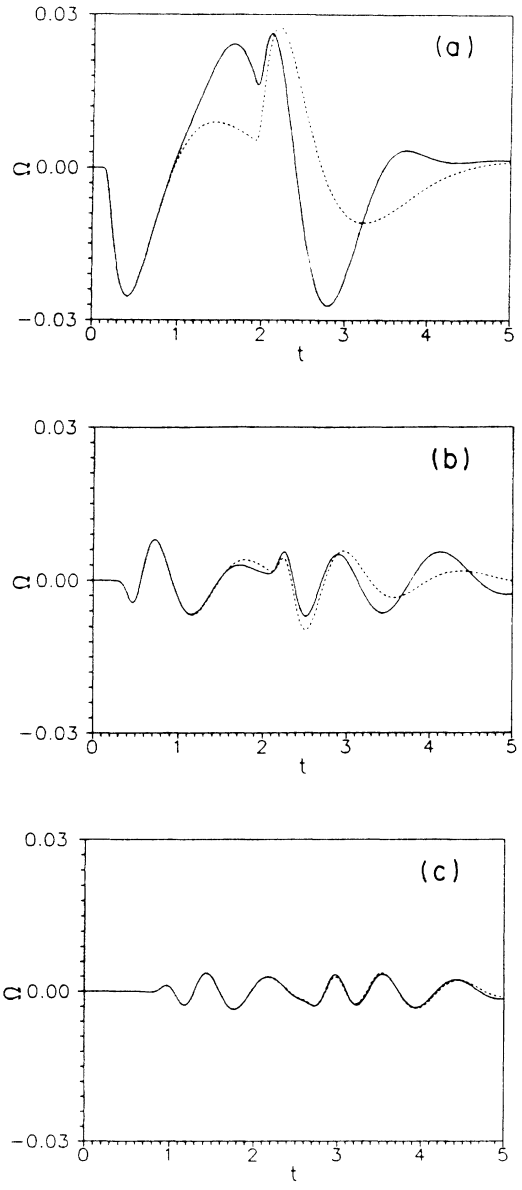

FIG. 2. Time evolution of an on-resonance π pulse propagating in PTS with $\lambda_i \neq 0$ (solid lines) and $\lambda_i = 0$ (dashed lines). (a) $x = 0.5$, (b) $x = 2.0$, (c) $x = 5.0$.

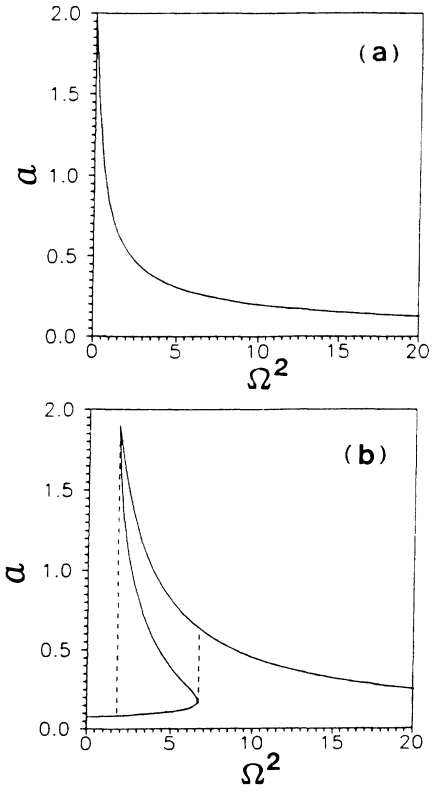

FIG. 3. Absorption coefficient vs intensity of the laser field of constant amplitude, where α is in the unit of k_0^2/k. (a) $\Delta = 0$, (b) $\Delta = 5$.

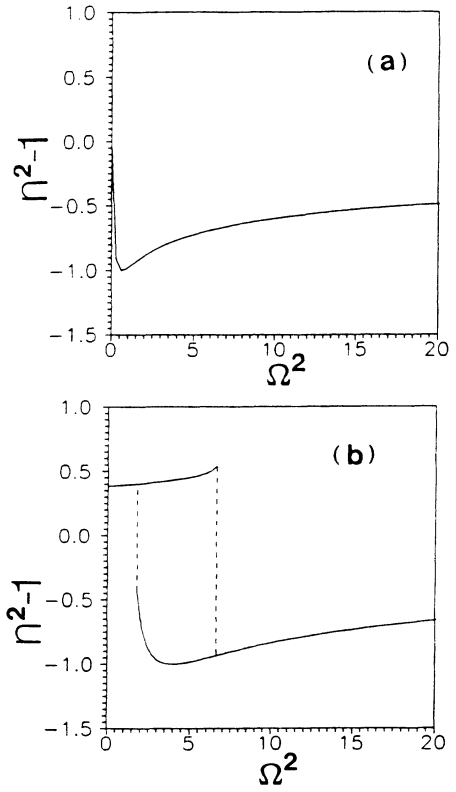

FIG. 4. Index of refraction vs intensity of the laser field of constant amplitude. (a) $\Delta=0$, (b) $\Delta=5$.

than that of the exciton, $n_r<1$ and hence the wave velocity in the material is always greater than c, the velocity of light in vacuum. When $\Delta>0$, virtual excitons are excited and coupled to phonon modes. The refraction index may be larger or smaller than unity depending upon the intensity of the light field. If the field is strong enough to excite a number of excitons so that $\lambda_p n>\Delta$, then $n_r<1$. Otherwise, $\Delta>\lambda_p n$ and $n_r>1$, resulting a propagation velocity in the material smaller than c.

III. ABSORPTION SPECTRUM

To study the absorption, we consider a slab of PTS material with thickness far smaller than the light wavelength.[12] The absorptive part of the optical susceptibility is prepared by the pump field and then monitored by the probe field. Since the propagation has no effect on the material at a distance much shorter than the wavelength, we only have to solve the optical Bloch-like equations.[12,16] The Hamiltonian in this case is the same as Eqs. (4), except for the probe field which interacts with the exciton as the pump field does. Thus we replace Eq. (4c) by

$$V=-[\mu a^{\dagger}(E_p e^{-i\omega_p t}+E_t e^{-i\omega_t t})+\text{h.c.}] , \tag{4c'}$$

where E_p (E_t) stands for the amplitude of the pump (probe) field with frequency ω_p (ω_t). In the rotating frame of the pump field, it is easily shown that the probe field changes only the first two of the equations of motion, namely

$$\dot{u}=\Delta_x v+2\sum_{i=1}^{2}\lambda_i q_i v-\gamma_x u+\Omega_t\sin(\Delta_t t) , \tag{7a'}$$

$$\dot{v}\equiv-\Delta_x u-2\sum_{i=1}^{2}\lambda_i q_i u-\gamma_x v+\Omega_p+\Omega_t\cos(\Delta_t t) , \tag{7b'}$$

where we have defined the detunings $\Delta_t=\omega_t-\omega_p$, $\Delta_x=\omega_x-\omega_p$, and the Rabi frequencies $\Omega_{p,t}=\mu E_{p,t}$. As E_t is much weaker than E_p, we treat it as a small perturbation and write the solutions as $u=u_0+\delta u$, $v=v_0+\delta v$, $q_i=q_{i0}+\delta q_i$, and $w_i=w_{i0}+\delta w_i$.

Substituting into Eqs. (7), we have the unperturbed equations of motion

$$\dot{u}_0=\Delta_x v_0+2\sum_{i=1}^{2}\lambda_i q_{i0}v_0-\gamma_x u_0 , \tag{17a}$$

$$\dot{v}_0=-\Delta_x u_0-2\sum_{i=1}^{2}\lambda_i q_{i0}u_0-\gamma_x v_0+\Omega_p , \tag{17b}$$

$$\dot{q}_{i0}=-\gamma_i q_{i0}+\omega_i w_{i0} , \tag{17c}$$

$$\dot{w}_{i0}=-\gamma_i w_{i0}-\omega_i q_{i0}-\lambda_i(u_0^2+v_0^2) , \tag{17d}$$

and to first order in the perturbation,

$$\delta\dot{u}=\Delta_x\delta v+2\sum_{i=1}^{2}\lambda_i(q_{i0}\delta v+v_0\delta q_i)-\gamma_x\delta u+\Omega_t\sin(\Delta_t t) , \tag{18a}$$

$$\delta\dot{v}=-\Delta_x\delta v-2\sum_{i=1}^{2}\lambda_i(q_{i0}\delta u+u_0\delta q_{i0})-\gamma_x\delta v+\Omega_t\cos(\Delta_t t) , \tag{18b}$$

$$\delta\dot{q}_i=-\gamma_i\delta q_i+\omega_i\delta w_i , \tag{18c}$$

$$\delta\dot{w}_i=-\gamma_i\delta w_i-\omega_i\delta q_i-2\lambda_i(u_0\delta u+v_0\delta v) . \tag{18d}$$

First-order corrections $\delta\eta$ ($\eta=u,v,q_i,w_i$) due to the weak probe field are known from numerical analysis[16] to be oscillating around their unperturbed values with the frequency Δ_t. Thus we have

$$\delta\eta=\delta\eta_+ e^{-i\Delta_t t}+\delta\eta_+^* e^{i\Delta_t t} . \tag{19}$$

The absorptive part of the optical susceptibility experienced by the probe field is given by[17]

$$\chi_i=N\mu^2\delta v_+/\Omega_t . \tag{20}$$

Differential transmission rates are usually measured in pump-probe experiments, and the differential absorptive part of the optical susceptibility dominates in these processes when the film is thin compared to the wavelengths.[12] We are interested in the absorptive part of the susceptibility that is induced solely by the pump field, that is,

$$\Delta(\text{Im}\chi_i)=\text{Im}\chi_i|_{\Omega_p\neq 0}-\text{Im}\chi_i|_{\Omega_p=0} . \tag{21}$$

The calculation is carried out numerically. All the exciton and phonon parameters are the same as before, and

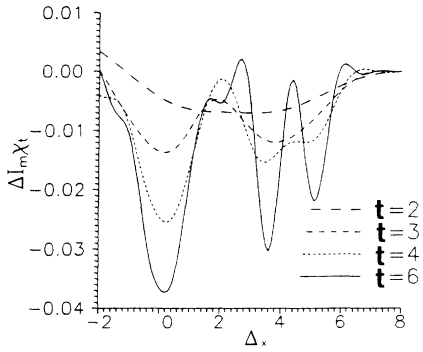

FIG. 5. Absorption part of the optical susceptibility induced by the pump field alone as a function of the detuning Δ_x at various time instants. Other parameters are $\omega_t=\omega_x=40$ and $\Omega_p=0.2$.

the units for energy and time are once more γ_x and γ_x^{-1}. Ω_t is assumed to be two orders of magnitude smaller than Ω_p, although our results are actually independent of Ω_t. The initial conditions are such that all variables start from zero.

To study the effect of the pump detuning Δ_x on the hole burning, we calculate Eq. (20) for $\omega_t=\omega_x$. The results are plotted in Fig. 5 as functions of Δ_x for various instants in time. It is observed that a hole shapes up at $t=2$ and splits into two wide components at $t=3$. At $t=6$, three sharper holes are burned in the absorption spectrum at $\omega_p=\omega_x$, $\omega_x-\omega_1$, and $\omega_x-\omega_2$, respectively, indicating clearly the phonon-mediated bleaching. That the bleaching seems to be absent at early times is understandable, because it takes time to excite enough excitons and phonons in the material.

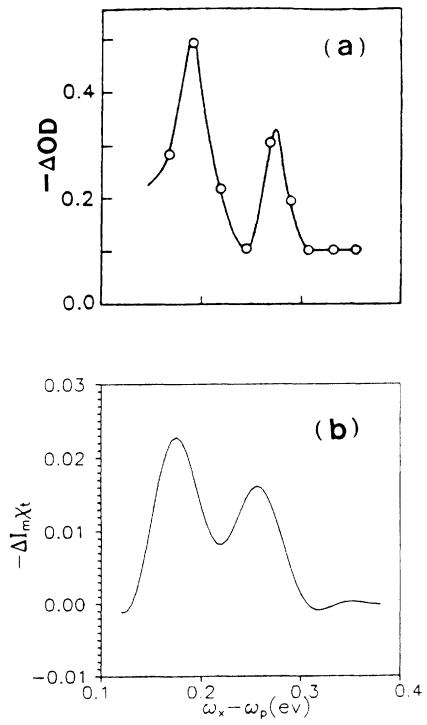

FIG. 6. (a) Differential optical density measured as a function of Δ_t from Ref. 12. (b) Absorption part of the differential susceptibility calculated from the present theory for $t=5$, $\omega_t=\omega_x$, and $\Omega_p=0.2$.

It is interesting to see how the present calculation is borne out by experiments. Figure 6(a) shows experimental data,[12] and our theoretical results for $t=5$ are shown in Fig. 6(b), where the hole at $\omega_x=\omega_p$ is not plotted as there are no data available. Good agreement is observed in these figures. In addition, we have found that the hole depths increase with increasing pump field intensity. The bleaching due to the real exciton saturation at $\omega_p=\omega_x$ is stronger than that due to virtual excitons with phonon mediation. It is also learned from our calculation that for similar coupling strength the hole bleaching is stronger if the phonon frequency is lower.

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APPENDIX

The classical one-dimensional damped harmonic oscillator of unit mass is normally described by the equations of motion of its real Cartesian coordinates x and momentum p, that is

$$\dot{x}=p \ , \tag{A1}$$

$$\dot{p}=-2\gamma p-\Omega_d^2 x \ , \tag{A2}$$

where 2γ is the damping constant and Ω_d the free oscillator frequency. For $\gamma<\Omega_d$, we can introduce a complex formal coordinate[16]

$$q=[p+(\gamma-i\omega_d)x]/\sqrt{\omega_d} \ , \tag{A3}$$

where $\omega_d=[\Omega_d^2-\gamma^2]^{1/2}$. From Eqs. (A1) and (A2), we find that q obeys the equation of motion

$$\dot{q}=-\gamma q-i\omega_d q \ . \tag{A4}$$

It can be shown that Eq. (A4) follows from the Lagrangian[16]

$$L=\frac{i}{2}(q^*\dot{q}-q\dot{q}^*)-(\omega_d-i\gamma)q^*q \ , \tag{A5}$$

from which the canonical momentum π conjugate to q is defined as

$$\pi=\frac{\partial L}{\partial \dot{q}}-\frac{i}{2}q^* \ . \tag{A6}$$

Consider a dissipative system described by the classical complex Hamiltonian

$$H=H_0+i\Gamma \ . \tag{A7}$$

The generalized equation of motion for an arbitrary func-

tion $F(\pi,q)$ can be written as[16]

$$\dot{F}=\{F,H_0\}_-+i\{F,\Gamma\}_+ , \tag{A8}$$

where the symbols $\{\ \}_\pm$ stand for Poisson and anti-Poisson brackets defined by

$$\{u,v\}_\pm=\frac{\partial u}{\partial q}\frac{\partial v}{\partial \pi}\pm\frac{\partial v}{\partial q}\frac{\partial u}{\partial \pi} . \tag{A9}$$

It can be shown from the fundamental Poisson bracket $\{q,\pi\}_-=1$ that[18]

$$\begin{aligned}\{q,F\}_-&=\frac{\partial}{\partial \pi}F ,\\ \{\pi,F\}_-&=-\frac{\partial}{\partial q}F .\end{aligned} \tag{A10}$$

Hamilton's equations of motion are then

$$\begin{aligned}\dot{q}&=\frac{\partial H}{\partial \pi} ,\\ \dot{\pi}&=-\frac{\partial H^*}{\partial q} .\end{aligned} \tag{A11}$$

The classical density function ρ satisfies the equation of continuity

$$\frac{\partial \rho}{\partial t}+\frac{\partial}{\partial q}(\dot{q}\rho)+\frac{\partial}{\partial \pi}(\rho\dot{\pi})=0 . \tag{A12}$$

For a quantized system, the Poisson brackets are replaced by the corresponding commutators. Thus Eqs. (A10) become

$$\begin{aligned}[q,F]&=i\hbar\frac{\partial}{\partial \pi}F ,\\ [\pi,F]&=-i\hbar\frac{\partial}{\partial q}F .\end{aligned} \tag{A13}$$

Taking the function F to be the Hamiltonian, we find after a little algebra that Eq. (A12) becomes

$$\dot{\rho}=-\hbar^{-2}[\pi,[q,H]\rho]+\hbar^{-2}[\rho[H^\dagger,\pi],q] , \tag{A14}$$

which is the quantum Liouville equation. In a similar fashion, we obtain in the k-dimensional phase space

$$\dot{\rho}=-\frac{1}{\hbar^2}\sum_{j=1}^{k}\{[\pi_j,[q_j,H]\rho]+[\rho[H^\dagger,\pi_j],q_j]\} . \tag{A15}$$

In this paper, both the exciton and phonon modes are taken as damped oscillators. If we choose $\hbar=1$ and set $k=i+1$, we find that Eq. (A14) reduces to

$$\begin{aligned}\dot{\rho}=&-i[a^\dagger,[a,H]\rho]+i[\rho[H^\dagger,a^\dagger],a]\\ &-i\sum_i\{[b_i^\dagger,[b_i,H]\rho]+i[\rho[H^\dagger,b_i^\dagger],b_i]\} ,\end{aligned} \tag{A16}$$

where we have made use of the definitions $a=q/\sqrt{2}$, $a^\dagger=-i\sqrt{2}\pi$, $b_i=q_{i+1}/\sqrt{2}$, and $b_i^\dagger=-i\sqrt{2}\pi_{i+1}$. Equation (A16) is the basis on which the equation of motion for the mean value $\langle A\rangle$ of any quantity A is derived. In other words, $\langle \dot{A}\rangle=\mathrm{Tr}(A\dot{\rho})$, and Eqs. (7a)–(7d) are obtained exactly this way.

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[14] The exciton-field coupling is described by the interaction Hamiltonian

$$V=-[\mu(a+a^\dagger)E^{(+)}(x,t)+\text{h.c.}]$$

which, in the interaction picture, takes the form

$$V_I=e^{i\omega_x a^\dagger a t}Ve^{-i\omega_x a^\dagger a t} .$$

The rotating-wave approximation refers to the case in which we keep only terms with the phases of the excitonic and radiation waves rotating together, $[\exp(-i\omega_x t)]^*$ and $\exp(-i\omega t)$. Under the RWA, we have

$$V_I=-\mu[a^\dagger e^{i\omega_x t}E^{(+)}(x,t)+ae^{-i\omega_x t}E^{(-)}(x,t)] ,$$

and then its expression in the Schrödinger picture becomes

$$V=-\mu[a^\dagger E^{(+)}(x,t)+aE^{(-)}(x,t)] .$$

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