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Optical Nonlinearity in Coupled Exciton-Phonon Systems Near Metal Surfaces

by

X. Li, D. L. Lin and Thomas F. George

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Departments of Chemistry and Physics
Washington State University
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Optical Nonlinearity in Coupled Exciton-Phonon Systems Near Metal Surfaces

X. Li and D. L. Lin

Department of Physics and Astronomy
State University of New York at Buffalo
Buffalo, New York 14260

Thomas F. George

Departments of Chemistry and Physics
Washington State University
Pullman, Washington 99164

Abstract

Surface effect on optical bistability and pump-probe processes for coupled exciton-phonon systems are studied theoretically. When a laser beam is directed on an exciton-phonon coupling system inside an optical cavity, the cavity field intensity is investigated as a function of the driving field intensity for various distances between the sample and a metallic surface representing one of the mirrors of the cavity. It is found that the direction of switch of the optical bistability can be controlled by adjusting the distance from the surface. For a strong laser pump field and a weak probe field directed on this system located, the pump-field-induced absorption spectrum is investigated for different distances between this sample and the metal surface. It is found that the position and line shape of the spectrum are significantly changed due to the presence of the surface.



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1. Introduction

The investigation of optical properties of molecular systems near a solid surface has been of great interest from both the fundamental and practical points of view¹⁻⁴. The study of an atom or a molecule adsorbed on a solid surface has attracted much attention in the past, both theoretically and experimentally. Exciton-phonon coupling systems such as organic semiconductors have been considered⁵ very recently instead of single molecular systems located near an ideal metal surface. Surface-induced optical bistability has been discovered, and its nature and origin investigated.

In this paper we study the effects of the metal surface on optical nonlinearity of an exciton-phonon system for two different processes of laser-matter interactions. For the first process, we consider optical bistability of a linear chain of polydiacetylene-toluene-sulfonate (PTS) located inside an optical cavity and oriented parallel to the metal surface of the mirrors. For the second process, we consider the pump-field-induced absorption spectrum for a PTS chain located near a metal surface and parallel to it. The sample is irradiated by a pump field and a probe (test) field.

1. Optical bistability

We now consider in this section a PTS chain inside an optical cavity. The chain is embedded in a non-absorbing material of dielectric constant ϵ_1 and is oriented parallel to the reflecting metallic mirrors that constitute the cavity. The dielectric function of the mirror is

$$\epsilon_2(\omega) = 1 - \frac{\omega_{pl}^2}{\omega(\omega + i\Gamma)} \quad , \quad (1)$$

where ω_{pl} is the plasma frequency and Γ the damping rate. Our purpose is to investigate how the optical bistability behavior is influenced by the presence of the metallic surface of one of the mirrors if the polymer is placed at a distance d smaller than the excitonic wavelength. When an incident laser beam is directed into the cavity, excitons are excited in PTS and act as emitting dipoles. The emitted light is reflected by the surface, and

the reflected light interacts in turn with the emitting excitons and changes their response to the incident light. At the same time, the excitons couple with phonon modes in PTS, which play the role of mediation in the photon-exciton interaction⁶.

We model the excitons, phonon modes and cavity field as damped oscillators and assume a dissipative interaction between the exciton and surface-reflected field³. The problem is then treated by means of Dekker's quantization procedure for dissipative systems⁷. In this model, the system is described by the non-Hermitian Hamiltonian

$$H = (\Omega - i\kappa)a^\dagger a + (\omega_x - i\gamma_x)c^\dagger c + \sum_i (\omega_i - i\gamma_i)b_i^\dagger b_i + \sum_i \lambda_i c^\dagger c (b_i^\dagger + b_i) + ig(a^\dagger c - c^\dagger a) + i(a^\dagger E_0 e^{-i\omega_0 t} - a E^* e^{i\omega_0 t}) - \mu^* c^\dagger E_R. \quad (2)$$

Here $a^\dagger$ (a), $b_i^\dagger$ (b_i) and $c^\dagger$ (c) stand for the creation (annihilation) operators for the cavity field, the i -th phonon mode and the exciton with corresponding frequencies Ω , ω_i and ω_x , respectively, κ , γ_x and γ_i are the damping rates for the cavity field, exciton and i -th phonon mode, respectively; λ_i is the coupling constant for the i -th phonon mode interacting with the exciton; and g is the exciton-cavity field coupling constant. The frequency and amplitude of the coherent driving field are denoted by ω_0 and E_0 , respectively. The dipole moment of the emitting exciton is represented by $p = \mu a$, with μ as its matrix element. E_R stands for the reflected field at the position of the dipole; it is proportional to p and hence can be written as $E_R = E_r c$, where E_r is a c -number. As we shall see later, E_r is in general a complex quantity, so that the interaction is dissipative⁸.

Since we are mainly interested in the relation between intensities of the cavity field and input field, we may take a semiclassical approach by neglecting all quantum fluctuations⁸. Thus, instead of the operators a , b_i , c and $c^\dagger c$, we are dealing with their mean values $\alpha = \langle a \rangle$, $\beta_i = \langle b_i \rangle$, $\eta = \langle c \rangle$ and $n = \langle c^\dagger c \rangle$. With these mean values defined as classical variables, the corresponding equations of motion can be obtained from Eq. (2) as follows^{3,4,9}:

$$\dot{\alpha} = -(i\Delta_1 + \kappa)\alpha + g\eta + E_0 , \quad (3a)$$

$$\dot{\beta}_i = -(i\omega_i + \gamma_i)\beta_i - i\lambda_i n , \quad (3b)$$

$$\dot{\eta} = -(i\Delta_2 + \gamma_t)\eta - i \sum_i \lambda_i (\beta_i + \beta_i^*)\eta - g\alpha , \quad (3c)$$

$$\dot{n} = -g(\alpha\eta^* + \alpha^*\eta) - 2\gamma_t n , \quad (3d)$$

where we have defined the detunings $\Delta_1 = \Omega - \omega_0$ and $\Delta_2 = \omega_x - \omega_0 + \omega_s$, and $\gamma_t = \gamma_x + \gamma_s$.

The surface effect on the exciton is reflected in the surface- induced frequency shift

$$\omega_s = |\mu|^2 \text{Re}\left(\frac{E_r}{\mu}\right) \quad (4a)$$

and the decay rate

$$\gamma_s = |\mu|^2 \text{Im}\left(\frac{E_r}{\mu}\right) . \quad (4b)$$

The reflected electric field E_r in the dipole direction can be found by a classical approach. We take the oscillating dipole moment to be located at a distance d from the surface of a semi-infinite metal. From electromagnetic field theory, we find in a straightforward manner that

$$E_r = -i \frac{3}{2\mu^*} \int_0^\infty du u^3 R_{\parallel} \exp(2i\mu_1 x) / \sqrt{1-u^2} , \quad (5)$$

which has been expressed in the unit of $\gamma_x = \frac{2}{3}\sqrt{\epsilon_1}|\mu|^2 k_0^3$. From now on and throughout this paper, all quantities with t^{-1} dimension will be expressed in γ_x . In the derivation of Eq. (5), we have assumed that the dipole is perpendicular to the surface. Here we have also defined $k_0 = \omega_x/c$, $x = \sqrt{\epsilon_1}k_0 d$ and

$$R_{\parallel} = \frac{\epsilon_1 \mu_2 - \epsilon_2 \mu_1}{\epsilon_1 \mu_2 + \epsilon_2 \mu_1} , \quad (6a)$$

$$\mu_l = \sqrt{\epsilon_l(\epsilon_1 - \mu^2)} , \quad l = 1, 2. \quad (6b)$$

If we introduce a dimensionless input field intensity $I_{in} = g^2|E_0|^2/(k\gamma_x)^2$, we find from Eqs. (3) that the mean exciton number n satisfies the cubic equation

$$\lambda_p^2[1 + (\Delta_1/\kappa)^2]n^3 + 2\lambda_p[\Delta_1(g^2 - \Delta_1\Delta_2)/\kappa^2 - \Delta_2]n^2 + \{[1 + \gamma_s + (g^2 - \Delta_1\Delta_2)/\kappa]^2 + [\Delta_2 + (1 + \gamma_s)\Delta_1/\kappa]^2\}n - I_{in} = 0 . \quad (7)$$

At the same time, the cavity field intensity $I_{cav} = |\alpha|^2/\gamma_x^2$ can be expressed in terms of the input field intensity I_{in} as

$$I_{cav} = \frac{(1 + \gamma_s)^2 + (\Delta_2 - \lambda_p n)^2}{[1 + \gamma_s + g^2/\kappa - \Delta_1(\Delta_2 - \lambda_p n)/\kappa]^2 + [\Delta_1(1 + \gamma_s)/\kappa + \Delta_2 - \lambda_p n]^2} I_{in} , \quad (8)$$

where we have defined $\lambda_p = 2 \sum_i \lambda_i^2/\omega_i$. Equation (7) is solved numerically, and the solutions are used to study the tristability of the cavity field intensity in Eq. (8) under various conditions. When the incident field frequency is on resonance with both the cavity field and the excitonic transition, the occurrence of optical bistability depends on the location of the chain in the cavity. If the chain is far away from the mirror surfaces of the cavity, Eq. (7) has only one physical solution and there is no optical bistability. If the PTS chain is near a mirror surface or if d is smaller than the excitonic wavelength, Eq. (7) may possess three real solutions, and it is possible to find optical bistability in the cavity. As discussed in Ref. 5, this surface-induced bistability is caused by both the frequency shift ω_s and the width change γ_s of the excitonic transition due to the surface. If the distance becomes too small or $x \ll 1$, the surface absorption becomes so strong that the lifetime of the exciton is too short to interact strongly and nonlinearly with the phonon modes. Consequently, there can no longer be bistability. Off resonance, the behavior depends very much on the sign of the detuning. When $\Delta_1 > 0$, the optical bistability is expressed in a normal hysteresis loop, and the presence of a surface can not change this nature. However, a nearby surface can affect the threshold input intensity and the contrast of the hysteresis loop. When $\Delta_1 < 0$, optical bistability can usually be found with the inverted hysteresis loop, even if the sample is far away from the surface. In the presence of a nearby surface,

our calculations show a completely new phenomenon, namely that the two cavity field intensities cross each other as the driving field intensity changes. In our numerical work, we have included all four phonon modes that couple most strongly to the excitons^{6,9,10}. These modes are characterized by the parameters $\omega_1 = 5.16$, $\lambda_1 = 2$; $\omega_2 = 3.68$, $\lambda_2 = 1.66$; $\omega_3 = 2.98$, $\lambda_3 = 0.46$; $\omega_4 = 2.36$, $\lambda_4 = 0.48$. Some of the results for $\Delta_1 < 0$ are plotted in Fig. 1 in which we demonstrate the change of the bistability nature by varying the distance from the surface only. Figure 1(a) shows no bistability because of the small distance. As mentioned above, the strong absorption by the surface prevents the exciton from interacting with phonon modes nonlinearly. There can not be optical bistability for any Δ_1 . In Fig. 1(b), we find the interesting new phenomenon where the two output states cross each other, forming a peculiar 8-shaped loop. The cavity field changes the normal bistability as the driving field intensity increases, but follows the inverted loop as I_{in} decreases. The hysteresis loop becomes a triangle in Fig. 1(c) at the distance $x = 2.0$. After this point, the loop becomes inverted and stays that way as the distance increases further. As discussed in Ref. 9 in more detail, in an optical cavity, the real part of the optical response of PTS or the dispersion part plays a more important role than the absorption part because the refractive index is changed by the excitons which are excited by the input field. Our numerical computations indicate that the major contribution to the bistability comes from the exciton energy shift induced by the surface. This is in contrast to the case discussed in Ref. 5, where the absorptive bistability is caused by reduced vacuum fluctuations.

3. Pump-Probe Process

In this section we consider two laser beams directed on a chain of PTS embedded in a medium with dielectric constant ϵ_1 and located at a distance d from a metal surface with the dielectric function characterized by Eq. (1). In the same way as the above section, the excitons and phonons are modeled as damped oscillators. The Hamiltonian is

$$H = (\omega_x - i\gamma_x)c^\dagger c + (\omega - i\gamma)b^\dagger b + \lambda c^\dagger c(b^\dagger + b) - [\mu c(E_p^* e^{i\omega_p t} + E_t^* e^{i\omega_t t}) + h.c.] - \mu^* c^\dagger E_R, \quad (9)$$

where E_p (E_t) and ω_p (ω_t) are the amplitude and the frequency of the pump (probe) field, and we have only included one phonon mode coupling most strongly to the excitons. The subscripts of b , γ and λ have therefore been dropped. Following a similar procedure as in Refs.5 and 11, we find the nonlinear susceptibility χ_t to first order in E_t and all orders in E_p as

$$\chi_t = n_0 |\mu|^2 \sum_{i=1}^3 p^i, \quad (10)$$

where n_0 is the density of the excitons and

$$p^i = (n_i / \sum_{i=1}^3 n^i) \frac{Y + Z}{Y^2 - \Sigma^2 - Z^2}, \quad (11)$$

with $Y = \Delta_p + \omega_s - \lambda_x n^i + \Sigma$, $Z = \Delta_t + i(1 + \gamma_s)$, $\Sigma = \frac{2\lambda^2 \omega n^i}{\Delta_t^2 + i\gamma\Delta_t - \omega^2}$, $\lambda_x = \frac{2\lambda^2 \omega}{\omega^2 + \gamma^2}$, $\Delta_p = \omega_x - \omega_p$ and $\Delta_t = \omega_t - \omega_p$. The superscript i is used to denote the i -th root of the cubic equation with respect to the exciton number n :

$$\lambda_x^2 n^3 - 2(\Delta_p + \omega_s)\lambda_x n^2 + [(\Delta_p + \omega_s)^2 + (1 + \gamma_s)^2]n - |\mu E_p|^2 = 0. \quad (12)$$

Therefore the nonlinear susceptibility induced by the pump field $\Delta\chi_t$ is the difference between the χ_t with and without the presence of the pump field namely,

$$\Delta\chi_t = \chi_t|_{E_p \neq 0} - \chi_t|_{E_p = 0}. \quad (13)$$

Figure 2 shows some of our numerical results calculated from Eq.(11) where we have used $\Delta_p = 6$, $\omega = 5.16$, $\gamma = 0.04$, $|\mu E_p| = 0.2$, and $\lambda = 2$. For Figs. 2 (a) and (b) we have chosen the distances x such that the radiative lifetime is prolonged due to the presence of the metal surface. In this case the spectrum of $\Delta\chi_t$ has three structures, of which the two

sidebands are located at $\omega_t - \omega_p = \pm\omega$. Evidently they result from the interaction between the beat component of the two incident field and the phonon. Because this interaction is mediated by the excitons, such interesting phenomenon becomes appreciable only when the lifetime of the excitons is long enough. For Fig.2(c), the vacuum field fluctuation is not reduced (so the lifetime of the excitons is not prolonged), so that there are no such sidebands. In addition, we have also found that the position of the dispersion-like structure in the spectrum of $\Delta\chi_t$ depends on the distance between the PTS chain and the metal surface, and so does the width of the peak or the hole. This is due to the fact that the presence of the surface changes both the lifetime and the frequency of the excitons, and similar to Refs. 1,3 and 4, this change depends on the distance of the excitons away from the surface.

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Figure Captions

1. Cavity field intensity I_{cav} vs the incident field intensity I_{in} for various distances x between this system and the metal surface when $\Delta_1 = -0.25$, $\omega_x/\omega_{pl} = 0.8$, $\Delta_2 = 6$, and $g^2/k = 0.5$. (a) $x = 0.5$, (b) $x = 1.25$, (c) $x = 2.0$, (d) $x = \infty$.
2. Pump field induced absorptive part of the susceptibility vs frequency of the test field when $\Delta_p = 6.0$, and $\omega_x/\omega_{pl} = 0.8$. (a) $x = 0.5$, (b) $x = 0.75$, (c) $x = \infty$.

Fig. 1

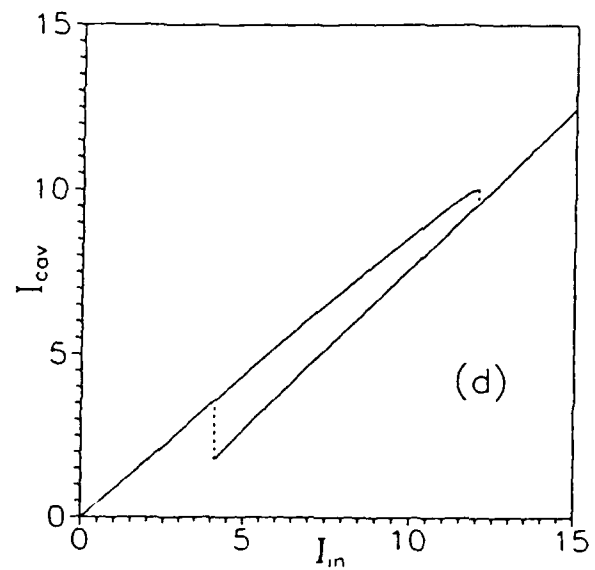
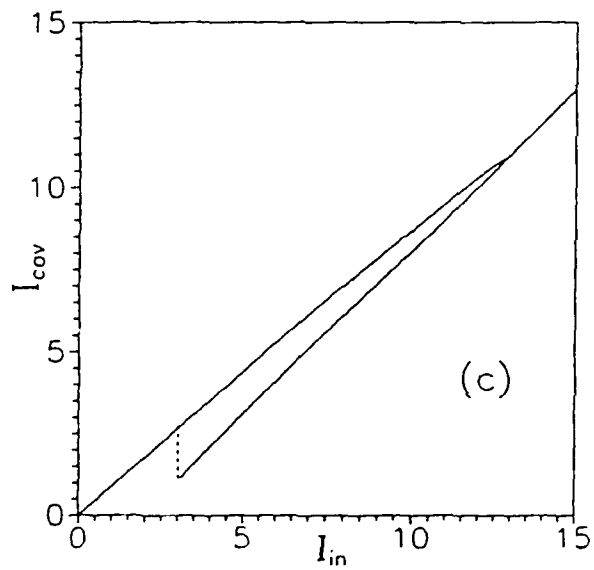
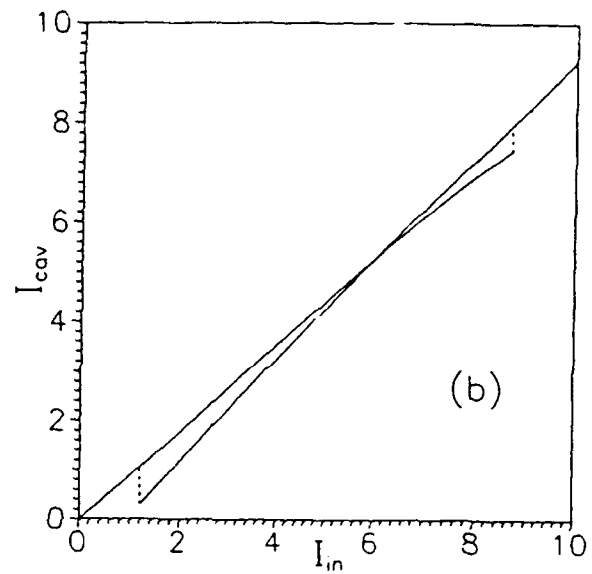
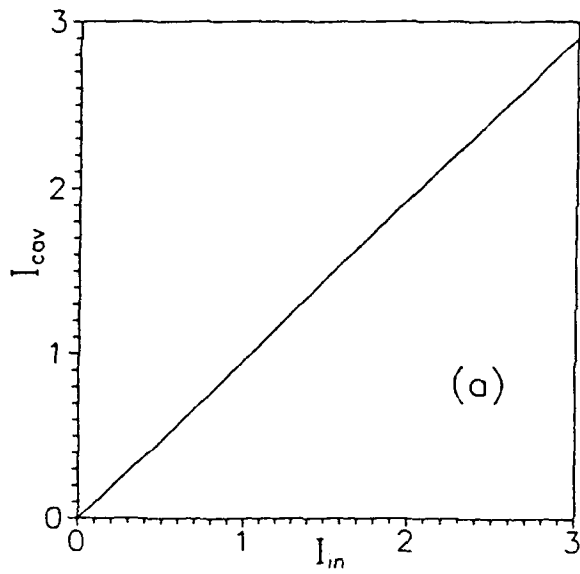


Fig. 2

