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Optical Nutation in Polymers Irradiated by Ultrashort Laser Pulses

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Optical nutation in polymers irradiated by ultrashort laser pulses

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Abstract

The transient behavior of the optical susceptibility of polydiacetylene induced by an ultrafast pump field is investigated. Within a two-level model which includes phonon effects phenomenologically, an analytical expression for the nonlinear susceptibility is obtained. In addition to spectral hole burning, the novel phenomenon of optical nutation is found. Both this nutation and the shape of the hole depend sensitively on the detuning between the exciton frequency and the sum of the pump field and the phonon mode frequencies. The electronic state and phonon-mediated optical Stark blue shift are also found in this model. The results are in qualitative agreement with experiments and indicate that the steady-state approximation is reliable only when the pulse of the pump field is longer than several exciton lifetimes.

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I. Introduction

Coherent transient interactions between materials and optical fields are one of the most interesting subjects in physics. Investigations of transient optical effects have become very important in the development of coherent optical spectroscopy and fast response nonlinear optical materials. Such studies cover such a wide spectrum of subjects and materials as photon echo, free induction decay and optical nutation in gaseous materials,[1-5] ultrafast dynamical blue shift of the exciton resonance accompanied by strong bleaching in quantum wells in heterostructure semiconductors,[6-9] nonlinear optical response of excitons[10,11] and large susceptibilities[12,13] in polymers, optical nutation in direct-gap bulk semiconductors,[14,15] and so forth.

A nonlinear optical material can be defined as one whose optical properties change when light shines upon it. In recent years, the study of coherent nonlinear optical processes produced by the excitation of semiconductors in the transparent region well below the absorption edge[6-9] has been extended to polymers.[10,11] When the frequency of the laser beam falling on semiconductors is tuned below the exciton resonance, it is known that virtual excitons are generated. These excitons interact with photons in exactly the same way as real excitons.[7,9-11] Such excitonic effects can be explored more naturally by probing the susceptibility[9] and looking for transient changes that persist as long as the excitation. The imaginary part of the susceptibility is usually examined via the absorption spectrum, and its real part is explored by measuring the index of refraction, provided that the sample is strongly excited well below the conduction band edge.

It is well known that polymers exhibit large nonlinear optical susceptibilities. In comparison with other materials, polymers have the added advantage of having extremely fast ground-state recovery times, which is why

they attract much attention for their potential applications in future generations of signal processing devices. Polydiacetylene (PDA) may be a good candidate for such considerations because of its large $\chi^{(3)}$ and small transmission loss α which can be reduced to as low as[16] $\alpha < 1$ db/cm. Thus the material possesses a fairly large ratio $\chi^{(3)}/\alpha$, which is usually the measure of the usefulness of a material employed in switching devices. Besides, PDA is easier to use in the construction of waveguides.[17] In spite of the considerable amount of research carried out so far, however, the mechanism that governs its nonlinear optical response is still not well understood, although tremendous progress has made it ripe for further examination.

In this paper, we study the transient behavior of the induced optical susceptibility of polymers due to irradiation by an ultrashort pulse of a pump laser field. We take, as an example, polydiacetylene-toluene sulfanate (PTS) which is irradiated by a strong pump laser and a weak probing laser. The two lasers may have pulse duration of femtoseconds to picoseconds. For the PTS system we adopt the two-level model[4,6,15] to describe its ground-state and virtual exciton state. The lifetime of the exciton and the mediating effects of the phonon are introduced phenomenologically. We use the perturbation technique to find the differential nonlinear susceptibility by solving analytically to all orders in the pump field and to first order in the test field.

II. Two-level model

The two electronic states of PTS are denoted by $|+>$ and $|->$. We assume a dipole transition and define the dipole operators

$$S^- = |-><+| \qquad\qquad (1a)$$

$$S^+ = |+\rangle\langle-| \quad , \tag{1b}$$

with the inversion operator given by

$$S^z = \frac{1}{2} \left(|+\rangle\langle+| - |-\rangle\langle-|\right) \quad . \tag{1c}$$

For a single virtual exciton and a single phonon mode, we can write the free Hamiltonian as

$$H_o = \hbar\omega_x S^z + \hbar\omega_i b_i^\dagger b_i \quad , \tag{2a}$$

where $b_i^\dagger$ (b_i) creates (annihilates) a phonon in mode i with frequency ω_i, and ω_x is the exciton frequency.[11] For the interaction Hamiltonian we consider that each virtual exciton interacts with both a strong pump field of amplitude E_p and frequency ω_p and a weak test field of amplitude E_t and frequency ω_t. Since the test field is very weak, we assume the mediating effects of the phonons on the dipole transition to be induced only by the pump field, as shown in Fig. 1. Therefore, we can write the interaction Hamiltonian in both the rotating-wave approximation and the interaction representation as

$$H_{Pi} = -\frac{1}{2} \lambda E_p e^{i\Delta_{p_i} t} b_i^\dagger S^- + \text{h.c.} \tag{2b}$$

for the interaction between the pump field and the PTS, and

$$H_t = -\frac{1}{2} \mu E_t e^{i\Delta_t t} S^- + \text{h.c.} \tag{2c}$$

for the interaction between the test field and the PTS, where $\Delta_{p_i} = \omega_p + \omega_i - \omega_x$, $\Delta_t = \omega_t - \omega_x$, μ is the dipole matrix element, and λ is a coupling constant proportional to the transition dipole moment μ. Here we have neglected the momentum dependence of virtual excitons[11,15] and the damping effect of the phonons. This Hamiltonian uses dipole or projection operators to describe the dipole transition between the ground state and the excitonic state of the material by external fields. It is different from that of Ref. 11, where creation and annihilation operators were used for virtual excitons.

For simplicity, we assume that each phonon mode has only two states, $|1\rangle$ and $|0\rangle$, and that the two and higher-phonon effects are negligible. The initial condition we consider here is that the system electronically is in its ground state with no virtual exciton present, while the phonon mode is in its excited state $|1\rangle$. We define $C_{i\pm}(t)$ as the probability amplitude of the state $|\pm\rangle$ when there is the i-th phonon mode only, of which the time derivative $\dot{C}_{i\pm}$ is composed of three parts: pump field-induced part $\dot{C}^p_{i\pm}$, test field-induced part $\dot{C}^t_{i\pm}$, and damping part $\dot{C}^d_{i\pm}$. By using the Schrödinger equation and the interaction Hamiltonians (2), we obtain[14,15]

$$\dot{C}^{p,t}_{i+}(t) = i\Omega^*_{p,t} e^{-i\Delta_{p_i,t}t} C_{i-} \quad , \tag{3a}$$

$$\dot{C}^{p,t}_{i-}(t) = i\Omega_{p,t} e^{i\Delta_{p_i,t}t} C_{i+} \quad , \tag{3b}$$

where in deriving the equation for $\dot{C}^t_\pm$ we have neglected the phonon effects and have defined $\Omega_p = \lambda E_p/2\hbar$ and $\Omega_t = \mu E_t/2\hbar$. Then we may write the damping part phenomenologically[14,15] as

$$\dot{C}^d_{i+}(t) = -\gamma C_{i+} \tag{4a}$$

$$\dot{C}^d_{i-}(t) = 0 \quad , \tag{4b}$$

where γ is the damping rate describing the short lifetime of the virtual exciton. Therefore, from $\dot{C}_{i\pm} = \dot{C}^P_{i\pm} + \dot{C}^t_{i\pm} + \dot{C}^d_{i\pm}$ we have the following equations for $C_{i\pm}$:

$$\dot{C}_{i+}(t) = i\Omega^*_p e^{-i\Delta_{p_i}t} C_- + i\Omega^*_t e^{-i\Delta_t t} C_{i-} - \gamma C_{i+} \tag{5a}$$

$$\dot{C}_{i-}(t) = i\Omega_p e^{i\Delta_{p_i}t} C_{i+} + i\Omega_t e^{i\Delta_t t} C_{i+} \quad . \tag{5b}$$

Since the test field is in most cases much weaker than the pump field, we can safely apply perturbtaion theory to solve (5). The zeroth-order equations are obtained by setting $E_t = 0$ in (5), namely,

$$\dot{C}^o_{i+} = i\Omega^*_p e^{-i\Delta_{p_i}t} C^o_{i-} - \gamma C^o_{i+} \tag{6a}$$

$$\dot{C}^o_{i-} = i\Omega_p e^{i\Delta_{p_i}t} C^o_{i+} \quad . \tag{6b}$$

In what follows, we assume for simplicity $\mu = \mu^*$, $\lambda = \lambda^*$ and $\Omega_{p,t} = \Omega^*_{p,t}$. With the initial conditions $C^o_{i+}(0) = 0$ and $C^o_{i-}(0) = 1$, we find the solutions

$$C^o_{i+} = \frac{i\Omega_p}{\Omega_i} \sin\Omega_i t \, \exp[-(i\Delta_{p_i} + \gamma)t/2] \tag{7a}$$

$$C_{i-}^{o} = (\cos\Omega t + \frac{\gamma - i\Delta_{p_i}}{2\Omega_i} \sin\Omega_i t)\, e^{(i\Delta_{p_i} - \gamma)t/2} \quad , \qquad (7b)$$

where we have defined the complex Rabi frequency

$$\Omega_i = \frac{1}{2}[(\Delta_{p_i} + i\gamma)^2 + 4\Omega_p^2]^{\frac{1}{2}} \quad . \qquad (8)$$

The real part of the Rabi frequency is given by

$$\Omega_R = [(\sqrt{x^2 + y^2} + x)/8]^{\frac{1}{2}} \quad , \qquad (9a)$$

which determines the oscillation frequency, and the imaginary part by

$$\Omega_I = -[(\sqrt{x^2 + y^2} - x)/8]^{\frac{1}{2}} \quad , \qquad (9b)$$

which determines the envelope of the oscillation. In (9) we have defined $x = \Delta_{p_i}^2 + 4\Omega_p^2 - \gamma^2$ and $y = 2\Delta_{p_i}\gamma$, with $\Delta_{p_i} < 0$.

The solutions up to first-order perturbation can be obtained by inserting the zeroth-order solutions (7) into the right-hand side of (5). The results are

$$C_{i\pm}(t) = C_{i\pm}^{o}(t) + \delta C_{i\pm}(t) + A_{i\pm} \qquad (10)$$

$$\delta C_{i-} = \frac{\Omega_t \Omega_p}{\Omega_i} \frac{\exp[i\Delta_t t - \frac{1}{2}(i\Delta_{p_i} + \gamma)t]}{[\frac{1}{2}(i\Delta_{p_i} + \gamma) - i\Delta_t]^2 + \Omega_i^2}$$

$$\times \; [(\tfrac{1}{2}(i\Delta_{p_i} + \gamma) - i\Delta_t)\; \sin\Omega_i t + \Omega_i \cos\Omega_i t] \tag{11a}$$

$$\delta C_{i+} = \frac{i\Omega_t}{2\Omega_i} \frac{\exp[-i\Delta_t t + \tfrac{1}{2}(i\Delta_{p_i} - \gamma)t]}{[i\Delta_t - \tfrac{1}{2}(i\Delta_{p_i} - \gamma)]^2 + \Omega_i^2}$$

$$\times \; \{[(\Delta_{p_i} + i\gamma)^2 + 2\Omega_p^2 + i\Delta_t(i\Delta_{p_i} - \gamma)]\; \sin\Omega_i t$$

$$- \; 2\Omega_i[i(\Delta_t - \Delta_{p_i}) + \gamma]\cos\Omega_i t\} \quad . \tag{11b}$$

The integration constants $A_{i\pm}$ in (10) are determined by the initial conditions.

The expectation value of the dipole moment of a virtual exciton is

$$\mu_i(t) = \mu\langle S_i^-(t)\rangle\, e^{-i\omega_x t} = \mu C_{i-}^* C_{i+}\, e^{-i\omega_x t}$$

$$= \mu(C_{i-}^{o*} + \delta C_{i-}^* + A_{i-}^*)(C_{i+}^o + \delta C_{i+} + A_{i+})\, e^{-i\omega_x t} \quad . \tag{12}$$

It is evident that the dipole moment induced by the test beam is given by

$$\delta\mu_i(t) = \mu(C_{i-}^o{}^* \delta C_{i+} + C_{i+}^o \delta C_{i-}^*)e^{-i\omega_x t} \quad . \tag{13}$$

Therefore, the nonlinear optical susceptibility experienced by the test beam is simply

$$\chi_i = n_i \delta\mu_i(t)/(E_t e^{-i\omega_t t})$$

$$= in_i \frac{|\mu|^2}{2\hbar} e^{-\gamma t} \left(\frac{1}{2\Omega_i z_1^i} \left[\cos\Omega_i^* t + i \frac{\Delta_{p_i} - i\gamma}{2\Omega_i^*} \sin\Omega_i^* t\right]\right.$$

$$\times \left[((\Delta_{p_i} + i\gamma)^2 + 2\Omega_p^2 - \Delta_t(\Delta_{p_i} + i\gamma)) \sin\Omega_i t\right.$$

$$\left. - 2\Omega_i(i(\Delta_t - \Delta_{p_i}) + \gamma) \cos\Omega_i t\right]$$

$$\left. - \frac{\Omega_p^2}{|\Omega_i|^2 z_2^i} \sin\Omega_i t[(\frac{1}{2}(i\Delta_{p_i} - \gamma) - i\Delta_t) \sin\Omega_i^* t + \Omega_i^* \cos\Omega_i^* t])\right) \quad , \quad (14)$$

where

$$z_1^i = [\frac{1}{2}(i\Delta_{p_i} - \gamma) - i\Delta_t]^2 + \Omega_i^2 \qquad (15a)$$

$$z_2^i = [\frac{1}{2}(i\Delta_{p_i} - \gamma) - i\Delta_t]^2 + \Omega_i^{*2} \quad . \qquad (15b)$$

We have introduced in (14) the optically-induced transient virtual exciton density n_i which is taken to be proportional to the probability of virtual exciton state,[18]

$$n_i = n_s C_{i+}^o C_{i+}^{o*} = n_s \frac{\Omega_p^2}{|\Omega_i|^2} |\sin\Omega_i t|^2 \exp(-\gamma t) \quad , \qquad (16)$$

where we have assumed that all the virtual excitons are induced by the pump field E_p, since those induced by the weaker probe field are much less likely, and n_s is the saturation density of the virtual excitons. In this paper we only consider the two phonon modes coupling most strongly to the exciton,[19] so that we have the nonlinear susceptibility

$$\chi_t = \sum_{i=1}^{2} \chi_i \; .$$ (17)

The transient behavior of the nonlinear optical susceptibility χ_t is calculated numerically as a function of time and the frequencies ω_p and ω_t. The results are presented and discussed in the next section.

III. Results and discussion

In our numerical study, we have used the unit $\hbar = 1$. Other parameters are chosen as[10,11,20] $\omega_1 = 0.184$ eV, $\omega_2 = 0.258$ eV, $\gamma = 0.02$ eV, $\frac{1}{e}|\mu|^2 n_s = \frac{1}{40\pi}$ eV, $\Omega_p = 5 \times 10^{-4}$ eV and $\omega_x = 1.978$ eV. The real and imaginary parts of χ_t are computed separately. Figure 2 shows snapshots at different instants of time of the variation of χ_t with the pump detuning. The variation with time for fixed detuning is shown in Fig. 3. Figure 4 shows snapshots at different instants of time of the imaginary part of χ_t when the resonance condition is satisfied, i.e., $\omega_x = \omega_p + \omega_2$.

It is clearly seen from Fig. 2 that both the differential absorption and refraction are direct effects of the virtual excitons induced by the pump field. The mediating role played by the phonon is substantial when the duration of the pump pulse is long enough (see the two peaks of the imaginary part, where $\omega_x = \omega_p + \omega_i$). This is in agreement with the experimental results

of Ref. 11. However, when the duration of the pump pulse is short, e.g., less than the lifetime of the virtual exciton, the peak structure of the imaginary part is not clear, i.e., we cannot see evident optical phonon-mediated effects. It should be noted at this point that the present results are different from those reported in Ref. 21 in which steady-state susceptibilities are calculated in the three-level two-field model without phonon effects.

Optical nutation can be observed in polymers in the ultrashort time regime when virtual excitons are generated by a pump field tuned below the exciton resonance. This situation can be seen from Fig. 3. However, when the sum of the pump field frequency and one of the phonon frequencies is on resonance with the exciton frequency, the Rabi oscillation amplitude becomes smaller. This reflects the fact that the optical phonon plays a crucial role in the optical nutation of PTS. It is also clearly shown that sometimes the oscillation centers of $Im\chi_t$ change with time. This is quite different from nutation phenomena predicted in Refs. 14 and 15 for semiconductors where the oscillation amplitude decreases monotonically like damped oscillators.

From Fig. 4, we can see the transient behavior of the spectral hole burning, which also needs sufficient long duration of the pump pulse to have an effect. The hole is close to the exciton resonance, and there is a deeper hole when $\omega_x - \omega_p + \omega_i$. This indicates that there is energy transfer from the pump field to the test field via optical phonons and virtual excitons, also in qualitative agreement with experiments.[10,11]

Since it takes time for the pump field to build up enough virtual excitons and since the virtual excitons are short-lived, their effects are appreciable and stable most of the time during the pulse (on the order of picoseconds). The respon   me can be anywhere between 20 - 200 femtoseconds

according to our calculation. Both the absorption and refraction parts show up almost right away and taper off rather slowly after reaching their peaks. So, for longer excitation time of the pump field, say, several times of the exciton lifetime, the steady-state method may be reliable.

In addition, we have also found that increasing the intensity of the pump field leads to a deeper and wider hole in the absorption spectrum, which is qualitatively in agreement with the steady-state results of Ref. 11. What seems to be more interesting is that we find a blue shift of 0.005 eV in our calculation. This represents joint effects of both the phonon-induced optical Stark shift and the electronic state optical Stark shift. Such effects have been observed in a recent experiment[20] in which the differential transmission of polydiacetylene-toluene sulfanate has been measured by means of coherent inverse Raman spectroscopy. It is demonstrated in Ref. 20 that this ac Stark effect is important in the determination of the nonlinear optical response of PTS even in the small signal limit. The effect is reproduced theoretically in Ref. 20 by including an extra term to modify the exciton resonance frequency in the simple model of Schmitt-Rink et al.[11] However, we need not do so, and the treatment in both Refs. 11 and 20 assumes a steady-state solution while the experimental conditions are more transient-like.

Acknowledgments

References

1. R. G. Brewer and R. L. Shoemaker, Phys. Rev. Lett. $\underline{27}$, 631 (1971).

2. S. L. McCall and E. L. Hahn, Phys. Rev. A $\underline{2}$, 861 (1970).

3. R. G. Brewer, in Nonlinear Optics, ed. by P. G. Harper and B. S. Wherett (Academic, London, 1977), p. 307 ff.

4. L. Allen and J. H. Eberly, Optical Resonance and Two-level Atoms (Wiley, New York, 1975).

5. Y. R. Shen, The Principles of Nonlinear Optics (Wiley, New York, 1984).

6. A. Mysyrowicz, D. Hulin, A. Antonetti, A. Migns, W. T. Masselink and H. Morkoc, Phys. Rev. Lett. $\underline{56}$, 2748 (1986).

7. S. Schmitt-Rink and D. S. Chemla, Phys. Rev. Lett. $\underline{57}$, 2752 (1986).

8. A. Von Lenman, D. S. Chemla, J. E. Zucker and J. P. Heritage, Opt. Lett. $\underline{11}$, 609 (1986).

9. D. S. Chemla, D. A. B. Miller and S. Schmitt-Rink, in Optical Nonlinearities and Instabilities in Semiconductors, ed. by H. Haug (Academic, New York, 1988), p. 83 ff.

10. B. I. Greene, J. Orenstein, R. R. Millard and L. R. Williams, Chem. Phys. Lett. $\underline{139}$, 381 (1987); Phys. Rev. Lett. $\underline{58}$, 2750 (1987).

11. B. I. Green, J. F. Mueller, J. Orenstein, D. H. Rapkine, S. Schmitt-Rink and M. Thakur, Phys. Rev. Lett. $\underline{61}$, 325 (1988).

12. See, for example, Nonlinear Optical Properties of Organic Molecules and Crystals, ed. by D. S. Chemla and J. Zyss (Academic, New York, 1987).

13. G. M. Carter, Y. J. Chen and S. K. Tripathy, Appl. Phys. Lett. $\underline{43}$, 891 (1983).

14. P. Sen and P. K. Sen, IEEE J. Quantum Electron. $\underline{QE23}$, 2033 (1987).

15. K. Singh, P. Sen and P. K. Sen, IEEE J. Quantum Electron. $\underline{QE25}$, 67 (1989).

16. P. D. Townsend, G. L. Baker, N. E. Schlotter and S. Etemad, Synth. Met. 28, D633 (1989).

17. M. Thakur, Y. Shani, G. C. Chi and K. O'Brian, Synth. Met. 28, D595 (1989).

18. C. H. B. Cruz, J. P. Gordon, P. C. Becker, R. L. Fork and C. V. Shank, IEEE J. Quantum Electron. QE24, 261 (1986).

19. See D. N. Batchelder in Polydiacetylenes, ed. by D. Bloor and R. R. Chance (Martinus Nijhoff, Dordrecht, The Netherlands, 1985), p. 187 ff.

20. G. J. Blanchard, J. P. Heritage, A. C. Von Lehmen, G. L. Baker and S. Etemad, Bull. Am. Phys. Soc. 34, 452 (1989).

21. S. Saikan, N. Hashimoto, T. Kushida and K. Namba, J. Chem. Phys. 82, 5409 (1985).

Figure captions

1. Two-level model representing the excitonic state $|+>$ and ground state $|->$. The virtual excitons are induced by a strong pump field with frequency ω_p. Each transitions is mediated by a single phonon of frequency ω_i, such that $\omega_p + \omega_i = \omega_x$ on resonance.

2. Snapshots of the real (curve 1) and imaginary (c rve 2) parts of the nonlinear susceptibility versus pump detuning at various times for $\omega_t = \omega_x$: (a) $t = 25$ (eV)$^{-1}$, (b) $t = 100$ (eV)$^{-1}$, (c) $t = 500$ (eV)$^{-1}$, (d) $t = 3500$ (eV)$^{-1}$.

3. Real (curve 1) and imaginary (curve 2) parts of χ_t versus time for $\omega_t = \omega_x$: (a) $\omega_p = 1.6$ eV; (b) $\omega_p = 1.72$ eV.

4. Snapshots of the imaginary part of the susceptibility versus probe frequency when $\omega_p = 1.72$ eV: (a) $t = 25$ (eV)$^{-1}$, (b) $t = 500$ (eV)$^{-1}$, (c) $t = 3500$ (eV)$^{-1}$.
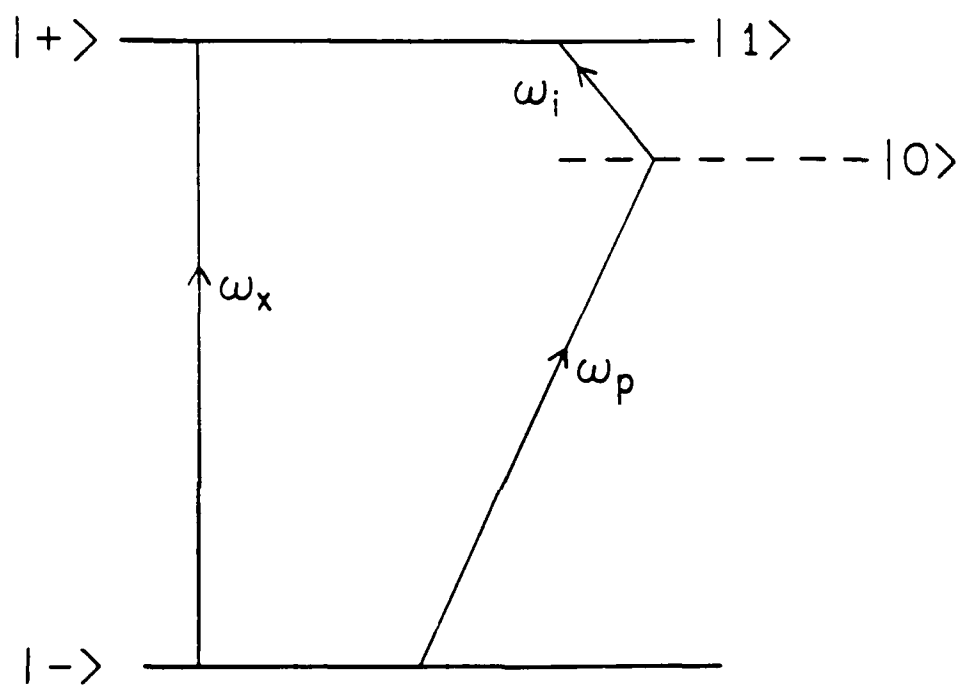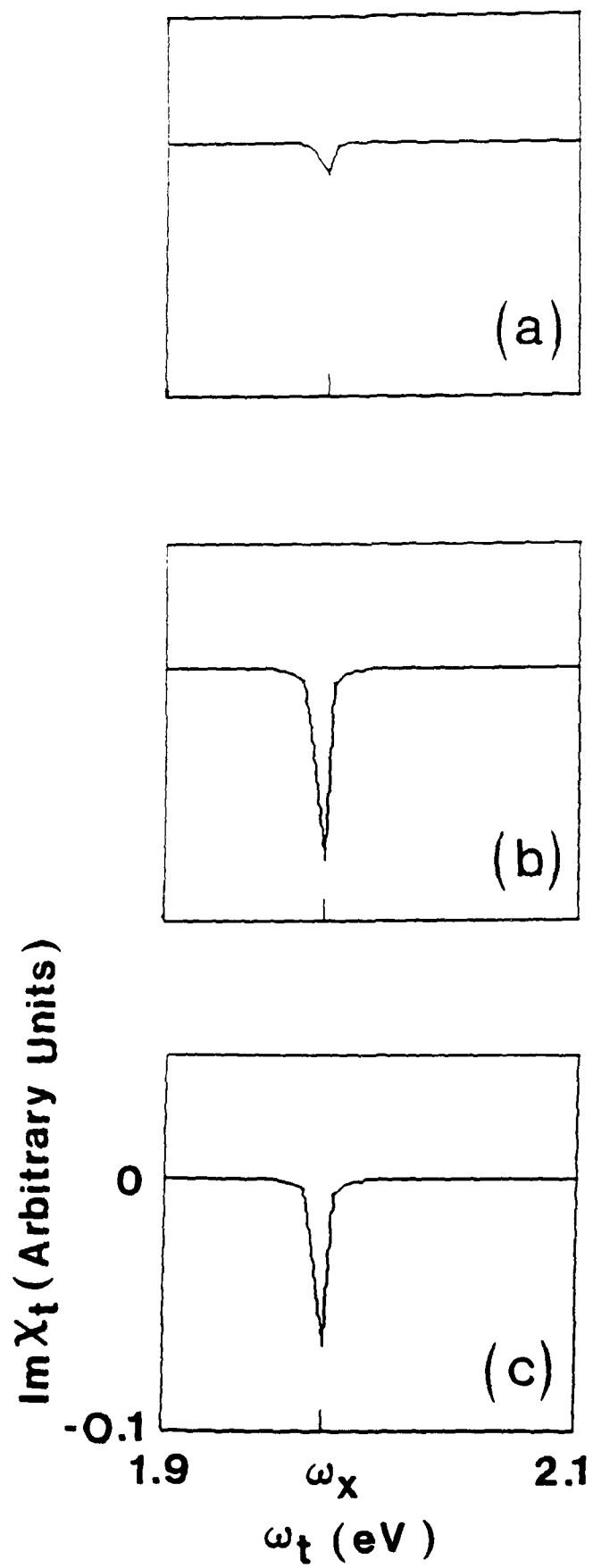
Fig. 1

Fig. 2
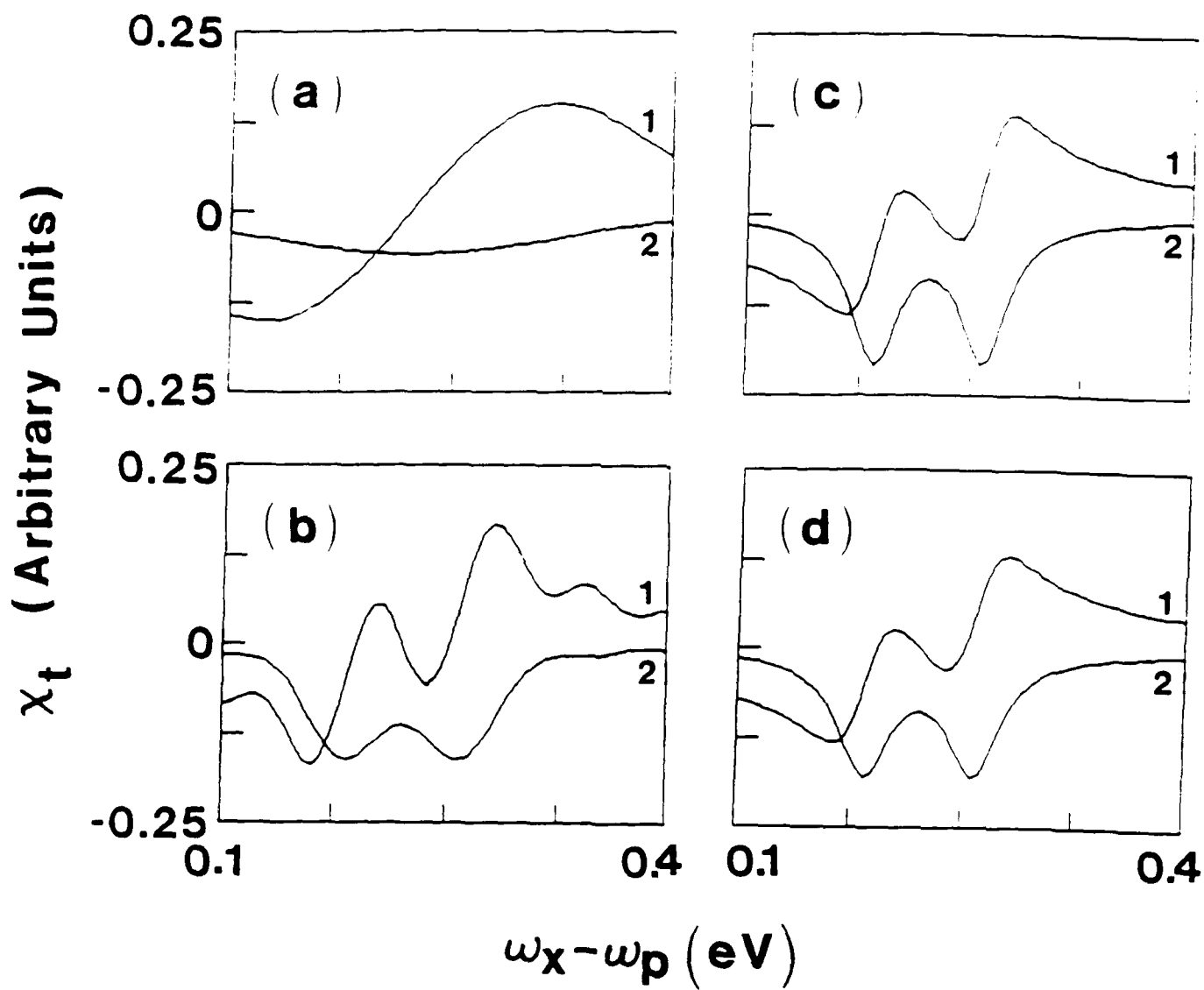
FIG. 3
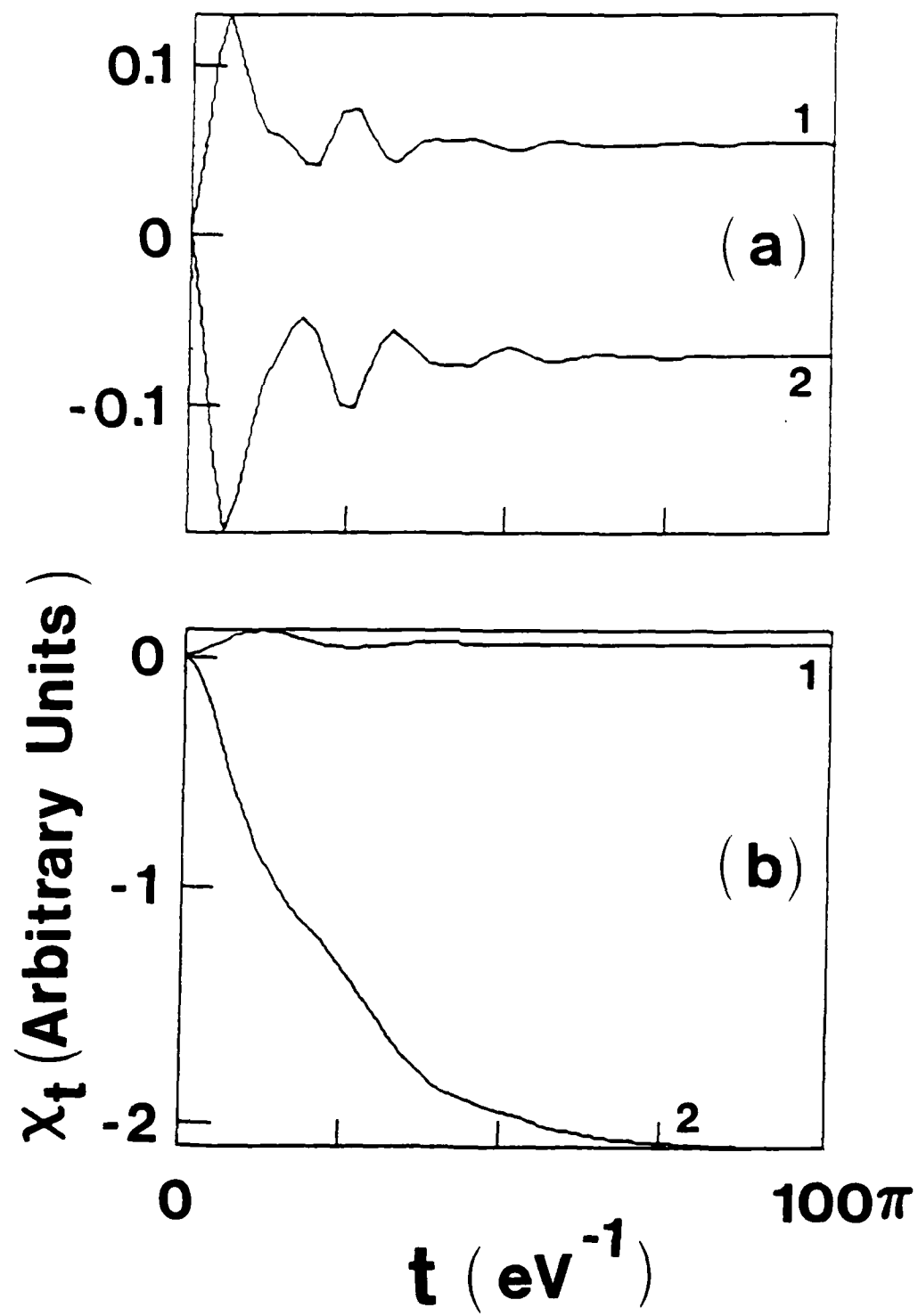
Fig. 4

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9