Phonon-Mediated Optical Nonlinearity in Polydiacetylene

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We have studied the nonlinear optical response of the quasi-1D semiconductor polydiacetylene-toluene sulfonate under ultrashort optical pulse excitation. The effect of the excitation is to "burn a hole" in the exciton line. The line shape of the hole depends sensitively on the pump frequency, ω_p, and its magnitude peaks when $\omega_p = \omega_x - \omega_o$, where ω_o and ω_x are the phonon and exciton frequencies. We discuss these results with a model in which optical nonlinearity results from phonon-mediated interactions between virtual excitons.

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Organic molecules and polymers have long been known to exhibit large values of the third-order susceptibility, $\chi^{(3)}$.[1] However, in spite of many investigations, the mechanisms governing the nonlinear optical response of these materials are not well understood. Recently, tremendous progress in two related areas has made this problem ripe for further examination. Intense study of polyacetylene and related materials has led to a more complete understanding of the ground state and elementary excitations of conjugated polymer chains,[2] while studies of quasi-2D inorganic semiconductors, notably GaAs-AlGaAs multiple-quantum-well structures (MQWS), have highlighted the importance of reduced dimensionality for optical nonlinearity.[3]

In this work we have extended the experimental and theoretical approach recently applied in MQWS to quasi-1D polydiacetylene-toluene sulfonate (PTS), with unusual and novel results. The approach examines in detail the change in the elementary-excitation spectrum of a semiconductor due to the presence of a population of photogenerated excitons.[3-5] This change in the elementary-excitation spectrum is due to anharmonic interactions between excitons and photons, and among the excitons themselves.[3,5] The dominant interaction results from the fact that excitons are composite bosons made from fermions which obey the exclusion principle. This interaction, referred to as the phase-space filling (PSF) effect, predicts a reduction in exciton oscillator strength (bleaching) under resonant photoexcitation, in agreement with observation.[3,6,7] When the frequency of the photoexcitation is tuned below the exciton resonance, then virtual, as opposed to real, excitons are generated. An important unifying concept is that the nonlinear optical response is still due to the same anharmonic interactions, i.e., virtual excitons interact just as real ones do.[3,5,7] This concept, applied to nonresonant experiments in MQWS, has explained the bleaching and blue shift of the exciton line (i.e., the optical Stark effect), as well as the dependence of both effects on pump frequency.[3,5]

The extension of this approach to PTS is clearly desirable, particularly since PTS is an excellent realization of a 1D semiconductor. An experimental difficulty in the past has been that, because of the enormous strength of the exciton absorption in PTS, extremely thin samples ($\simeq$100 Å) are required for optical transmission studies. Recently, a process for the growth of single-crystal films has been developed.[8] The thin films used in this work are $\simeq$200 Å in thickness. Their optical absorption is dominated by a peak at $\omega_x \simeq 2$ eV of width $2\gamma_x \simeq 100$ meV ($\hbar = 1$), consistent with results obtained previously by Kramers-Kronig analysis of bulk crystal reflectivity.[9]

Pump and probe measurements were performed with these samples, by utilization of a 10-Hz amplified CPM dye laser system described previously.[10] Laser pulses roughly 70 fs FWHM centered at 625 nm were used to generate white-light continuum pulses. 10-nm spectral sections of these pulses were further amplified in a single stage and utilized as a variable-wavelength excitation source. As a probe source, broadband continuum light was compressed with a diffraction grating pair, thereby minimizing the effects of temporal dispersion on our measurements. Frequency mixing of the pump pulse with different frequency components of the compressed probe pulse indicated an essentially chirp-free probe pulse in the spectral region 500–700 nm.

In our measurements we monitored the differential optical density, ΔOD [the optical density (OD) is $-\ln T$, where T is the sample transmissivity], throughout the region of exciton absorption as the pump was tuned through and below resonance. As previously reported, the ground-state recovery time after resonant excitation is $\simeq$2 ps.[10,11] As the pump frequency is lowered, the recovery time becomes progressively shorter, reaching the resolution limit at $\omega_p \simeq 1.9$ eV. This indicates that below this energy the optical nonlinearities are dominated by virtual excitons.

The top panel in Fig. 1 shows the optical density of a $\simeq$200-Å single-crystal film, with electric field along the chain axis, in the region of the exciton resonance. The middle and lower panels show the differential optical density for nonresonant and resonant excitation, respec-

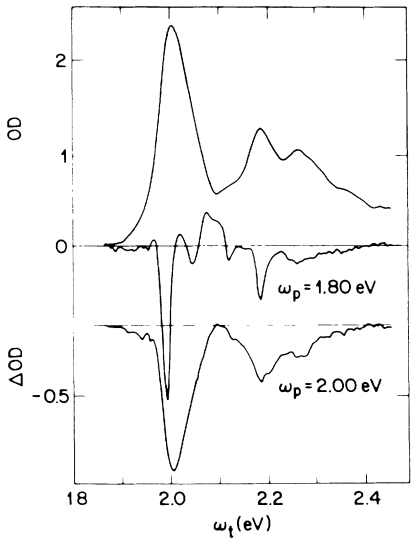

FIG. 1. Optical density of a ≃200-Å polydiacetylene-toluene sulfonate film (top). Differential optical density for 1.8-eV excitation (middle) and 2-eV excitation (bottom).

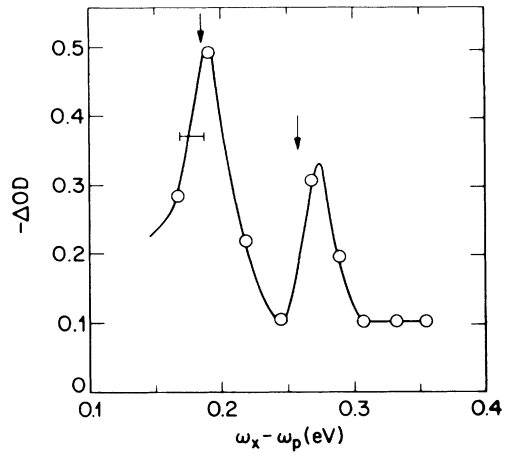

FIG. 2. Bleaching of exciton absorption, measured at ≃1.98 eV, vs pump detuning. Horizontal bar indicates pump spectral bandwidth. Solid line through data (circles) serves only as a guide to the eye. Arrows indicate phonon energies obtained from Raman spectra.

tively. These differential spectra are dramatically different from each other. Following excitation at $\omega_p \simeq 2$ eV, the exciton resonance is bleached uniformly, in a manner which is consistent with the PSF model. Nonresonant excitation at $\omega_p \simeq 1.8$ eV, however, appears "to burn a hole" near, but slightly below, the peak of the exciton absorption. The depth of this hole increases linearly with pump intensity, reaching a value of the ΔOD/OD ratio of ~ -0.2 at the highest intensity, $I_p \simeq 3$ GW/cm^2. Note that our results obtained with nonresonant excitation differ completely from results of analogous experiments in MQWS, where a uniform bleaching and rigid blue shift of the exciton line were observed.[4]

The pump-frequency dependence of ΔOD, for $\omega_p < \omega_x$, is shown in Fig. 2. The values of ΔOD plotted are those at the peak of the decrease in absorption which shifts as ω_p is varied. The incident photon flux for all pump frequencies was $I_p \simeq 3$ GW/cm^2. Again, the results are completely unlike those in the MQWS system. Instead of a monotonic decrease in ΔOD with increasing detuning,[3,5,7] there are two maxima in the response, each of which occurs when $\omega_p - \omega_x$ is near the frequency (indicated by an arrow) of an optic phonon of the polydiacetylene chain. These two phonons are known from resonance Raman spectroscopy to be those which couple most strongly to the exciton.[9]

The experimental results summarized above indicate that the origin of optical nonlinearity near the exciton resonance is entirely different in PTS as compared with MQWS. Whereas in MQWS nonlinearity results from an interaction between virtual excitons due to the exclusion principle, in PTS it apparently results from interactions in which the optic phonons have a crucial role. A possible reason for the difference is that in 1D systems, such as PTS, it is expected that there is no barrier for self-trapping of the exciton and that the time scale for structural change following photoexcitation is the inverse of the phonon frequency, ω_o^{-1}. Molecular-dynamics calculations for polyacetylene have shown this structural change very dramatically.[12] If $\omega_x - \omega_p \lesssim \omega_o$, then in 1D systems the virtual exciton lifetime is sufficiently long to develop a lattice distortion similar to that of a real exciton. It is then likely that the interaction between virtual excitons will be mediated by phonons.

At present we are aware of no numerical calculations which predict the effects we have observed in PTS (although there are recent calculations of the changes in optical absorption which accompany generation of *real* excitons[13]). In the absence of such calculations, we have found it especially useful to explore analytical solutions to a simpler model which illustrate the phenomena described in Figs. 1 and 2. We consider the steady-state response of a system in which excitons a ($a^\dagger$) are driven by pump and test fields

$$E_{p,t}\exp(-\omega_{p,t}t) + E_{p,t}^*\exp(i\omega_{p,t}t),$$

and coupled to a single Einstein mode b ($b^\dagger$).[14] In the rotating frame, we write the Hamiltonian

$$H = (\omega_x - \omega_p)a^\dagger a + \omega_o b^\dagger b - \lambda a^\dagger a Q - \mu_x a^\dagger (E_p + E_t e^{-i\Delta t}) - \mu_x^* a (E_p^* + E_t^* e^{i\Delta t}), \quad (1)$$

where λ is the exciton-phonon coupling constant, $Q = b + b^\dagger$ the lattice displacement, μ_x the dipole matrix element, and

$\Delta=\omega_t-\omega_p$. Here, the momentum dependence of the various terms has been neglected.

From Eq. (1) we obtain the equations of motion for the exciton and phonon amplitudes (including dephasings γ_x and γ_o)

$$\langle\dot{a}\rangle+i(\omega_x-\omega_p-i\gamma_x)\langle a\rangle = i\lambda\langle Qa\rangle+i\mu_x(E_p+E_te^{-i\Delta t}), \quad (2a)$$

$$\langle\ddot{Q}\rangle+\gamma_o\langle\dot{Q}\rangle+\omega_o^2\langle Q\rangle=2\omega_o\lambda\langle a^\dagger a\rangle. \quad (2b)$$

For $\omega_x-\omega_p\gg\gamma_x$, the amount of real excitations is small, and the decompositions $\langle a^\dagger a\rangle=|\langle a\rangle|^2$ and $\langle Qa\rangle-\langle Q\rangle\langle a\rangle$ can be made in Eq. (2). In the absence of the test field, $E_t=0$, this yields the coherent amplitudes of virtual excitons and stimulated phonons $\langle a\rangle_0=\mu_xE_p/(\omega_{xH}-\omega_p-i\gamma_x)$ and $\langle Q\rangle_0=2\lambda|\langle a\rangle_0|^2/\omega_o$, respectively, where $\omega_{xH}=\omega_x+\Sigma_H$, and $\Sigma_H=-2\lambda^2|\langle a\rangle_0|^2/\omega_o$ describes the lattice relaxation energy. The nonlinear optical susceptibility, χ_p, experienced by the pump beam is $\chi_p=N\mu_x^*\langle a\rangle_0/VE_p$, where N/V is the dipole density. It is interesting to compare this χ_p with the contribution due to the PSF mechanism.[7] The ratio is $\Sigma_H/(\omega_x-\omega_p)$, with Σ_H evaluated at the saturation density, which shows that the optical nonlinearity experienced by a single (pump) beam is dominated by PSF when the detuning is large compared with the lattice relaxation energy.

In the presence of a test beam, resonant enhancement of the nonlinearity occurs when $\Delta\simeq\omega_o$, as a result of exchange of phonons between pump and test beam via intermediate exciton states. Application of the test field, E_t, drives small deviations $\delta\langle a\rangle$ and $\delta\langle Q\rangle$ from $\langle a\rangle_0$ and $\langle Q\rangle_0$. Using the *Ansatz*

$$\langle a\rangle=\langle a\rangle_0+\delta\langle a\rangle_+e^{-i\Delta t}+\delta\langle a\rangle_-^*e^{i\Delta t}, \quad (3a)$$

$$\langle Q\rangle=\langle Q\rangle_0+\delta\langle Q\rangle_+e^{-i\Delta t}+\delta\langle Q\rangle_-^*e^{i\Delta t}, \quad (3b)$$

we find, after linearizing Eq. (2) in E_t,

$$\delta\langle a\rangle_+=\mu_xE_t(\omega_{xHF}-\omega_p+\Delta+i\gamma_x)/[(\omega_{xHF}-\omega_p)^2-\Sigma_B(\Delta)\Sigma_B^*(-\Delta)-(\Delta+i\gamma_x)^2], \quad (4)$$

where

$$\omega_{xHF}=\omega_x+\Sigma_H+\Sigma_F(\Delta),$$

$$\Sigma_F(\Delta)=2\omega_o\lambda^2|\langle a\rangle_0|^2/(\Delta^2+i\gamma_o\Delta-\omega_o^2),$$

and

$$\Sigma_B(\Delta)=(\langle a\rangle_0/\langle a^*\rangle_0)\Sigma_F(\Delta).$$

The optical susceptibility, χ_t, experienced by the test beam is finally given by $\chi_t=N\mu_x^*\delta\langle a\rangle_+/VE_t$.

Figure 3 shows $\chi_t=\chi_1+i\chi_2$ for parameters appropriate to PTS[9] and our experimental conditions: $V/N=500$ Å^3, $4\pi N|\mu_x|^2/V=1$ eV, $\omega_o=0.2$ eV, $\lambda=0.1$ eV, and $\gamma_o=2\times10^{-3}$ eV. In Figs. 3(a) and 3(b) the pump is ω_o below the center of the exciton resonance and narrow holes are seen in the absorptive part of χ_t. Increasing the pump power, from $|\mu_xE_p|=10^{-1}$ eV to 2×10^{-2} eV in going from (a) to (b), results in deepening and broadening of the hole. Figs. 3(c) and 3(d) illustrate the effect of increasing the detuning. When $\omega_p+\omega_o$ is in the wing of the exciton resonance, Fig. 3(c), the feature χ_2 becomes smaller and acquires a dispersive line shape. Finally in (d), for $\omega_p+\omega_o$ below the resonance, a peak develops in χ_2. Similar effects have been reported in calculations which use three-level systems to model optical nonlinearity in molecules.[15]

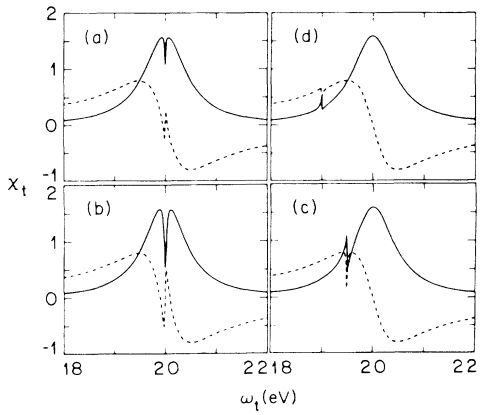

FIG. 3. Real (dashed lines) and imaginary (full lines) parts of the susceptibility seen by a test beam in the presence of a pump beam, for various pump frequencies, ω_p, and Rabi frequencies, $R\equiv|\mu_xE_p|$: (a) $\omega_p=1.8$ eV, $R=10^{-2}$ eV; (b) $\omega_p=1.8$ eV, $R=2\times10^{-2}$ eV; (c) $\omega_p=1.75$ eV, $R=2\times10^{-2}$ eV; (d) $\omega_p=1.7$ eV, $R=2\times10^{-2}$ eV.

The spectra shown in Fig. 3 reproduce the general features observed in PTS. There are, however, several important differences between calculation and experiment. Experimentally, the hole never moves to the center of the exciton line but instead remains slightly below. In addition, it is wider than predicted by Eq. (4). These discrepancies are not surprising in view of the simplicity of the model; we have considered only one phonon mode, have neglected spontaneous and thermal phonon effects, and have not calculated the transient response of the system.

In conclusion, we have demonstrated that—unlike in recent MQWS experiments—"nearly resonant" excitonic optical nonlinearities in the quasi-1D semiconductor polydiacetylene-toluene sulfonate are governed by phonon-mediated exciton-exciton interactions. We have developed a simple model to describe these effects and have shown that they are dominated by the PSF effect when the pump beam is detuned from the exciton resonance by an amount which is large compared to the lattice relaxation energy.

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