Nonlinear Optical Response of Excitons Confined to One Dimension

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We present femtosecond time-resolved transient reflectivity measurements on polydiacetylene performed at the peak of the exciton resonance. The magnitude of the nonlinear refractive index at 1.97 eV was found to be 3.0×10^{-8} cm^2/W. We discuss a model which accounts quantitatively for the large resonant and nonresonant optical nonlinearity observed in polydiacetylene in terms of phase-space filling by one-dimensional excitons.

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Considerable effort has been directed toward understanding the optical and electrical properties of polyconjugated molecular solids.[1-3] Recently, the possibility of optical-device applications has inspired a new initiative towards characterization of the sizable nonlinear optical responses manifest in these materials.[4-8] In this paper we report new time-resolved measurements performed on an already extensively studied polymer, poly-[2,4-hexadiyn-1,6-diol-*bis*(*p*-toluene sulfonate)], hereafter referred to as PTS. We specifically examine the magnitude and temporal decay of the resonant nonlinear refractive index n_2. We interpret the magnitude of n_2 with a model for phase-space filling by excitons confined to one dimension (1D), suggested by recent work on excitons confined to 2D in multiple quantum wells (MQW's). Additionally, we describe a simple extension of this model which provides a quantitative explanation for the large nonlinearity observed below the exciton energy.

Recently there has been a report of a large enhancement of optical nonlinearity in PTS as the phonon energy becomes close to that of the exciton. Carter *et al.*[9] found that n_2 was a factor of ~20 greater in the tail of the exciton absorption as compared with the value in the transparent region in the optical gap. Their measurement could not be continued above the energy where the sample absorption, α, exceeded $\sim10^4$ cm^{-1} since their technique relied upon transmission through a ~1-μm-thick sample. In our measurements we have used a technique based on reflectivity to characterize the nonlinear response at the peak of the exciton resonance.

All measurements were performed at room temperature on thermally polymerized single-crystal samples of PTS. A PTS single crystal is an assembly of parallel, semiconducting, polymer chains. Bulky side groups keep the electronically active backbone of the polymer well isolated from its neighbors. The optical absorption of PTS is dominated by a narrow (~100 meV at 300 K) peak at ~2.0 eV polarized along the chain axis, which is excitonic in origin.[10] The enhanced oscillator strength and binding energy of the 1D confined exciton in PTS follows the trend observed in passing from 3D to 2D in the GaAs-GaAlAs MQW system.[11] Experiments were performed with 70-fs FWHM laser pulses at 1.97 eV which were generated with a 10-Hz amplified colliding-pulse mode-locked (CPM) dye laser.[12] All light was propagated perpendicular to a natural crystal facet, with $\mathbf{E}\parallel b$, i.e., along the molecular chain axis. The size of the reflectivity change due to resonant excitation was measured by a straightforward pump and probe technique. In order to measure the dynamics of ground-state recovery after the excitation pulse, the transient grating method was found to be more sensitive. In this technique two spatially and temporally coincident 1.97-eV pulses overlap on the sample to form an intensity grating. The sample responds via its nonlinear refractive index, resulting in a spatially periodic modulation in reflectivity. A third, time-delayed probe pulse (derived by passage of a white-light continuum pulse through a 32-meV-FWHM spectral notch filter centered at 1.97 eV) diffracts from the reflectivity grating and is detected. Since this is a zero-background technique, the signal-to-noise ratio is considerably better than in a standard time-resolved reflectivity measurement.

The pump and probe experiment showed that excitation with a pulse of intensity 1.0×10^8 W/cm^2 resulted in a reduction in reflectivity of 0.05. We used the transient grating to measure the kinetics of the recovery of the ground-state reflectivity. Figure 1 displays the intensity of the diffracted beam as a function of time delay after excitation with pulses of 6.0×10^8 W/cm^2. The decay is exponential with a time constant of 1.0×0.2 ps. This corresponds to a recovery time of 2.0 ps because diffraction efficiency varies quadratically with grating amplitude.[13,14] The reflectivity change varied linearly with pump intensity below 10^9 W/cm^2.

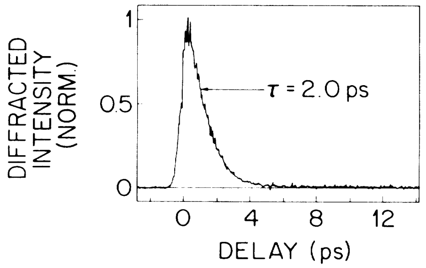

FIG. 1. Normalized diffraction efficiency vs delay time for an incident intensity of 6×10^8 W/cm^2. The decay corresponds to a ground-state recovery time of 2.0 ps since the diffraction efficiency varies quadratically with grating amplitude.

To understand the magnitude and sign of the resonant optical nonlinearity in polydiacetylene we have made use of ideas developed recently to explain similar effects in MQW's.[15] The essential element of this model is simply that excitons are not true Bose particles; rather, they are composite bosons which consist of a bound pair of fermions. In the presence of a nonzero exciton population, some of the single-particle band states needed to form the exciton wave function are already occupied. This results in a reduction in the strength of the exciton transition given by

$$\delta f/f = -\mathcal{N}/\mathcal{N}_s, \tag{1}$$

where f is the oscillator strength, $\mathcal{N}$ is the exciton density per unit length, and $\mathcal{N}_s$ is a saturation density. $\mathcal{N}_s$ can be estimated in a straightforward way. In 1D, if the exciton length is denoted by ξ_0, then the optically active, $K=0$, exciton is constructed from band states which are within a wave vector $2\pi/\xi_0$ from the band minimum. There are L/ξ_0 such states, where L is the chain length, so that $\mathcal{N}_s \simeq \xi_0^{-1}$. The saturation density corresponds simply to the density at which the exciton wave functions begin to overlap in space.

Recently Schmitt-Rink, Chemla, and Miller[15] have used a multiexciton Wannier formalism to calculate $\mathcal{N}_s$ exactly. They find that

$$\mathcal{N}_s^{-1} = L^{-1}\textstyle\sum_k \phi_k\,|\phi_k|^2/\phi(x=0), \tag{2}$$

where $\phi(x)$ is the exciton wave function and ϕ_k are the corresponding Fourier coefficients. To apply this to 1D we have assumed the simple form $\phi(x)=\xi_0^{-1/2}\times\exp(-|x|/\xi_0)$, with ϕ_k given by $\phi_k=2\xi_0^{1/2}(1+k^2\xi_0^2)^{-1}$. Substituting this wave function into Eq. (2) we obtain $\mathcal{N}_s^{-1}=3\xi_0/2$. Since the chains are assembled into a 3D crystal it is useful to convert to a volume density N_s by writing $N_s=\mathcal{N}_s/\sigma=2/3\sigma\xi_0$, where σ is the cross-sectional area per chain.

Within this picture, the only unknown parameter governing the strength of the optical nonlinearity is the exciton length, ξ_0. Our measurement of the optically induced reduction in reflectivity, δR, can be used to determine ξ_0. At. 1.97 eV, $\mathrm{Re}\,\epsilon \gg 1$,[10] where ϵ is the complex dielectric constant, so that ϵ is linearly proportional to f. We may use Eq. (1) and the definition $\hat{n}\equiv\sqrt{\epsilon}$ to write

$$\delta n/n = \delta k/k = -\tfrac{1}{2}N/N_s, \tag{3}$$

where n and k are the real and imaginary parts of $\hat{n}$, and N is the density of excitons in the semiconductor. Then, differentiating R with respect to n and k, we obtain

$$\delta R = -2\frac{N}{N_s}\left[\frac{n(n^2-k^2-1)+2nk^2}{(n+1)^2+k^2}\right]. \tag{4}$$

At 1.97 eV, $n=6.0$ and $k=1.9$,[10] so that $\delta R=-0.17N/N_s$. Assuming that each photon creates an exciton, we calculate that an incident intensity of 1.0×10^8 W/cm^2 produces a mean exciton density of 6.0×10^{19} cm^{-3}. Recalling that $\delta R=-0.05$, Eq. (4) yields $N_s=2.0\times10^{20}$ cm^{-3}. Using the value for σ of 100 Å^2 in PTS,[16] we finally deduce an exciton length of 33 Å.

To prove the applicability of the phase-space–filling model to PTS it is necessary to show that the change in the exciton resonance with photoexcitation is characterized simply by a reduction in oscillator strength. In principle this involves measuring either δR or $\delta\alpha$ as function of probe photon energy. From measurements of δR vs $\hbar\omega$ we have found that it is very difficult to distinguish a reduction in oscillator strength from a shift or broadening of the exciton resonance. Although transmission data would be more straightforward to interpret, it is not possible to obtain transmission spectra for PTS because sufficiently thin ($\lesssim 200$ Å) samples of high quality are not yet available. As a result we can only argue the plausibility of the phase-space–filling model based on the agreement of our measurement of the exciton length with other determinations of ξ_0. There exist two independent determinations of ξ_0, one theoretical and the other experimental. Suhai[17] has performed a first-principles calculation of the exciton wave function in polydiacetylenes and finds that it extends over $\simeq 25$ Å. Sixl[18] and co-workers, and Wudl and Bitler,[19] have measured the peak of the exciton absorption as a function of chain length for short polydiacetylene segments. They find that for chains shorter than five repeat units (or again $\simeq 25$ Å) the peak begins to shift dramatically towards higher energy. This effect is analogous to the shift of the exciton energy which takes place in MQW's when the well width becomes comparable to the exciton Bohr radius.[20] The fact that these determinations of ξ_0 agree with that found from the phase-space–filling analysis of the nonlinear polarizability argues for the plausibility of the model.

The observation that the ground-state reflectivity recovers in 2 ps indicates a remarkably short exciton lifetime in PTS. The mechanism which facilitates this rapid recombination has recently been investigated.[21] Knowledge of the recovery time allows us to express the magnitude of the resonant nonlinearity in PTS in terms of the useful phenomenological parameters n_2 and k_2, defined by the relations $\delta n \equiv n_2 I$ and $\delta k \equiv k_2 I$. Since the exciton density N is given by $\alpha I \tau_p (1-R)$, where τ_p is the duration of the laser pulse, we can use Eq. (3) to obtain

$$n_2 = (1-R)(\alpha\tau_p/h\nu)(n/2N_s)$$

and

$$k_2 = (1-R)(\alpha\tau_p/h\nu)(k/2N_s).$$

The maximum effective n_2 and k_2 are obtained if τ_p is made equal to the recovery time of 2 ps. If this condition is fulfilled, we obtain values for n_2 and k_2 of 3×10^{-8} cm^2/W and 1×10^{-8} cm^2/W, respectively. Note that this is a factor of 10^4 larger than the nonresonant value of n_2 and almost 3 orders of magnitude larger than that found in the region of the absorption tail. From the previous discussion we see that this results simply from linear dependence of exciton density on the absorption coefficient.

Stimulated by the success of the phase-space–filling model in accounting for the nonlinearity due to strongly absorbed light, we have extended these ideas to excitation below the exciton energy. Several groups have measured the change in index of refraction of PTS due to laser illumination in the transparent region below the exciton peak.[4,6,9] Measurements by various techniques agree on a value for the nonresonant n_2 of roughly -10^{-12} cm^2/W. The nonresonant nonlinearity in PTS is the largest known for any semiconductor. Previous efforts to explain the large n_2 have been based on one-electron band theory[22] or three-level systems.[23] Neither model has been completely successful in predicting the magnitude or sign of n_2. A fundamentally different origin of the nonresonant optical nonlinearity in PTS is suggested by the concept of phase-space filling. As we have seen, resonant excitation generates excitons which interact due to the exclusion principle. For nonresonant excitation, where the photon frequency ω is well below the exciton frequency Ω, virtual excitons are created. By a natural extension of the previous discussion, we expect that virtual excitons will interact as well. To apply the phase-space–filling model we need only calculate the density of virtual excitons, N_{vx}, which results from a given photon flux.

We use the polariton picture to calculate N_{vx}. In this picture the correct description of the excitations of a semiconductor is a linear combination of excitons and photons. For $\omega \ll \Omega$ the exciton component of the polariton, $S(\omega)$, is given approximately by $[(\epsilon_0-\epsilon_x)/\epsilon_0] \times(\omega/\Omega)$,[24] where ϵ_0, and ϵ_∞, are the values of Reϵ below, and above, the exciton resonance, respectively. The product of $S(\omega)$ and the polariton density yields $N_{vx} \simeq [(\epsilon_0-\epsilon_\infty)/\epsilon_0](nI/c\hbar\Omega)$. Substituting this density into Eq. (3) yields the following expression for n_2 due to phase-space filling by virtual excitons:

$$n_2 = -(\epsilon_0-\epsilon_\infty)/2cN_s\hbar\Omega. \tag{5}$$

Notice that this is a remarkably simple result in which the only material parameter not obtainable from linear spectroscopy is N_s, which we have determined previously from resonant excitation. The evaluation of Eq. (6) by use of $\epsilon_0-\epsilon_\infty = 4$ [15] yields $n_2 = -1.1\times10^{-12}$ cm^2 in excellent agreement with the recent measurement by Carter *et al.*[9] The quantitative success of this formulation suggests that it contains the correct physics underlying the optical nonlinearity in PTS.

In conclusion, we have demonstrated that the concept of exciton phase-space filling accounts for the observed optical nonlinearity in polydiacetylene. For the case of strongly absorbed excitation we have applied the model of Schmitt-Rink, Chemla, and Miller developed for excitons in MQW's to excitons confined to 1D. Our experimental finding that n_2 at the peak of the exciton absorption is 3×10^{-8} cm^2/W, 3 orders of magnitude larger than previous measurements in the absorption tail, follows from the linear dependence of n_2 on α. This is a direct consequence of the phase-space–filling model. Finally, we have accounted for the large nonresonant nonlinearity in PTS in a model which does not invoke the anharmonicity of the electron restoring force. Instead the nonlinearity results from the interaction between polaritons mediated by their fermion component. The model yields a simple and accurate value for n_2 in the optical gap. In the future this model could be developed further by treating from first principles the many-polariton wave function.

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