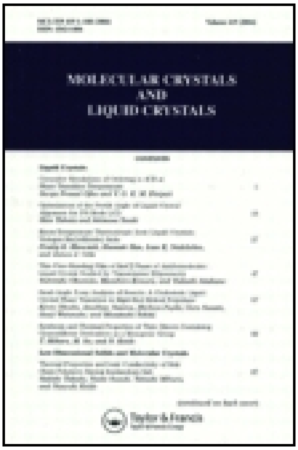

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Third Harmonic Generation in Conjugated Polymers: Exciton Effect and Influence of Disorder

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THIRD HARMONIC GENERATION IN CONJUGATED POLYMERS: EXCITON EFFECT AND INFLUENCE OF DISORDER

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Abstract Nonlinear optical susceptibilities of conjugated polymers are studied in the Su-Schrieffer-Heeger model supplemented by long-range Coulomb interactions, taking account of the formation of excitons and the influence of disorder. In the calculated third-harmonic generation spectrum, on the high energy side of the main peak (due to the lowest singlet exciton) a second peak (due to the three-photon resonance to the electron-hole continuum) is found that is strong enough to remain significant even in the presence of disorder. The results are in good agreement with experiments in polydiacetylene and polythiophene.

INTRODUCTION

Recently there has been an increasing interest in the nonlinear optical properties of conjugated polymers, among which one of the most extensively studied families of materials is polydiacetylene (PDA).[1,2] The optical properties of PDA crystals have indicated the formation of excitons.[3] On the other hand, nonlinear optical experiments[4,5] have often been carried out for non-crystalline PDA films, where disorder may also play an important role. In this paper we report calculations of third-order nonlinear optical susceptibilities $\chi^{(3)}$ for long chains in the Su-Schrieffer-Heeger model[6] supplemented by long-range Coulomb interactions, considering the formation of excitons and the influence of disorder, too.

We have recently calculated[7] the linear susceptibility $\chi^{(1)}$ and a variety of third-order nonlinear susceptibilities $\chi^{(3)}$, including two-photon absorption, electroabsorption and third harmonic generation (THG). The results obtained without any disorder indicate that various experiments in PDA can be consistently interpreted in the present model by using only moderate interaction strength. The present paper concentrates on the THG spectrum, appropriately taking the disorder into account.

MODEL AND APPROACH

Our model is described by the Hamiltonian

$$H = H_0 + H_{\text{e-e}}$$

$$H_0 = -\sum_{n,s} t_{n,n+1} \left(C^\dagger_{n+1,s} C_{n,s} + C^\dagger_{n,s} C_{n+1,s}\right)$$

$$H_{\text{e-e}} = \sum_{n} U \rho_{n\uparrow} \rho_{n\downarrow} + \frac{1}{2} \sum_{n,m(\neq n)} \sum_{s,s'} \frac{V}{|n-m|} \rho_{n,s} \rho_{m,s'} \; .$$

Here $C^\dagger_{n,s}$ creates an electron at site n with spin s, and $\rho_{n,s} \equiv C^\dagger_{n,s} C_{n,s} - \frac{1}{2}$. The nearest-neighbor transfer energies $t_{n,n+1}$ depend on the bond lengths. We assume $t_{n,n+1} = t + (-1)^n \delta t + \Delta t_n$, where δt is due to bond alternation (neglecting an additional modulation with the period of four atoms in PDA for simplicity) and Δt_n are random deviations due to bond-length disorder. The interaction $H_{\text{e-e}}$ is characterized by the on-site Coulomb energy U and the nearest-neighbor Coulomb energy V which represents the long range interaction.

The calculation procedure is a standard one.[8] We first obtain the ground state of the one-electron Hamiltonian H_0, and construct the excited states of a single electron-hole (e-h) pair from the ground state. Then the matrix of the total Hamiltonian within the single-excitation subspace is diagonalized. Actual calculations have been carried out numerically for a finite chain of N sites, where the number of the single excitations is $(N/2)^2$. For a perfect chain (Δt_n=0), we adopt the cyclic boundary condition, so that the excited states can be classified by the total wave number K. In this case a matrix of dimension $\sim N/2$ is numerically diagonalized for each K. For a disordered chain, in which the translational symmetry is broken, we do not use the cyclic boundary condition, so that the full matrix of dimension $\sim (N/2)^2$ must be diagonalized.

To obtain nonlinear susceptibilities, matrix elements between ground and excited states and among excited states have been calculated for the dipole $-e\,\Sigma_n x_n C^\dagger_n C_n$, where x_n is the coordinate of the site n. In the case of the periodic boundary condition, we assume that the chain is a perfect ring, i.e., $x_n = (Na/2\pi)\cos(2\pi n/N)$, otherwise we simply use $x_n = na$, where a is the lattice constant. These different choices yield some discrepancy in the intensities of the computed spectra. A constant life-time broadening is assumed for all the excited states and the respective imaginary energy Γ is taken into account properly[9] in the calculation of $\chi^{(3)}$.

PERFECT CHAINS

First we show results for a perfect ring of 800 sites with $\delta t=0.2t$, $V=t$ and $U=2t$. These values turn out to give approximately correct exciton energies in PDA.[7] A chain size of at least $N=100$ is necessary to obtain the bulk properties.

Figure 1 displays the magnitude and the phase of the THG spectrum $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$. Here $\chi_0^{(3)}$ is the characteristic cubic susceptibility defined by $\chi_0^{(3)} \equiv e^4a^4/t^3$ per site. Typical parameter values like $a \sim 1.4$Å and $t \sim 2$eV for PDA give $\chi_0^{(3)} \sim 6\times10^{-35}$ esu per site. The three energies E_1, E_2, and E_c ($E_1 < E_2 < E_c$) denote the energies of the lowest $^1\mathrm{B_u}$ exciton, the lowest $^1\mathrm{A_g}$ exciton, and the edge of the e-h continuum. (There are a few more exciton states between E_2 and E_c.) The two low-energy peaks in $|\chi^{(3)}|$ are due to the three-photon resonances with the lowest $^1\mathrm{B_u}$ exciton at E_1 and with the $^1\mathrm{B_u}$ states around E_c (weakly bound as well as unbound electron-hole states). This second peak is interesting because the linear absorption spectrum[7] does not show a strong peak near the corresponding energy E_c. The high-

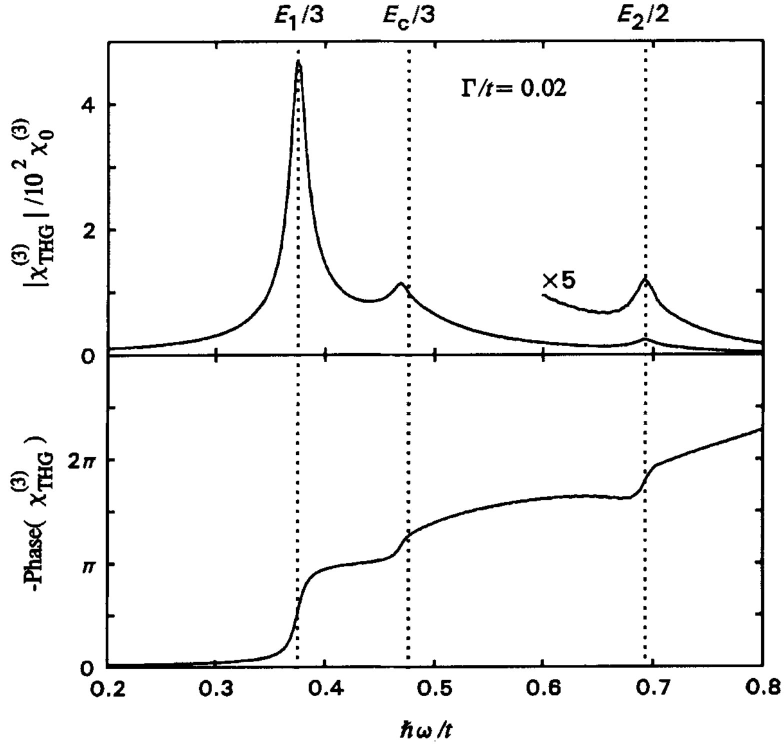

FIGURE 1 Absolute value and phase of the complex susceptibility $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ for third-harmonic generation in a perfect ring of $N=800$ sites, for $\delta t=0.2t$, $V=t$, $U=2t$, and $\Gamma=0.02t$.

energy peak at $E_c/2$ in Fig.1 is due to the two-photon resonance to the ^1A_g exciton.

The negative phase of $\chi^{(3)}$ (corresponding to the phase delay of the induced polarization compared with cube of the applied electric field) increases almost monotonically as a function of ω, exhibiting interesting step-like behavior around the three peaks, providing additional information to characterize the THG resonances.

INFLUENCE OF DISORDER

Numerical calculations for disordered systems have been carried out for a chain of $N=100$ by assuming a Gaussian distribution with the same standard deviation σ for all Δt_n. This disorder can be considered as due to static structural disorder or due to lattice vibrations in the Franck-Condon (semi-classical) approximation.

In Fig.2, we show the THG spectra calculated for various degrees of disorder with the same δt, V and U as in Fig.1. The oscillations above $E_c/3$ are a finite size effect, masking the two-photon resonance at $E_2/2$ found in the larger system (Fig.1). With increasing disorder the exciton peak at $E_1/3$ weakens and broadens. The second peak near $E_c/3$ also broadens, but the intensity does not change very much. This can be attributed partly to the observation that these states are spatially more extended than the lowest exciton and hence may be less affected by the disorder. Moreover, the second peak is due to many states near E_c, so that many broadened tails can add up to the original intensity. We also note that both the first and the second peak shift to lower energies by disorder. This is due to the disorder-induced broadening of the conduction and the valence band, i.e., the narrowing of the band gap. In contrast, the life-time broadening only yields a decrease of intensity, but no shift.

COMPARISON WITH EXPERIMENTS

The recently observed THG spectrum of an oriented PDA film[5] shows a strong peak at about 1/3 of the peak energy ($\sim$2eV) of the linear absorption and a second structure $\sim$0.2eV above. These observations are in good agreement with the calculated peaks at $E_1/3$ and $E_c/3$ in Fig.1 or Fig.2 by assuming $t\sim 2$eV.

Previously, a peak in the THG spectrum of a PDA Langmuir-Blodgett multilayer was found[4] below $E_1/2$ and interpreted as a two-photon resonance to an A_g state assumed below E_1.[4] This cannot be supported by the present model. No data confirming the interpretation by other nonlinear optical measurements exist, to the best of our knowledge. Our alternative interpretation is that the peak corresponds to the three-photon resonance to E_c shown in Fig.1.

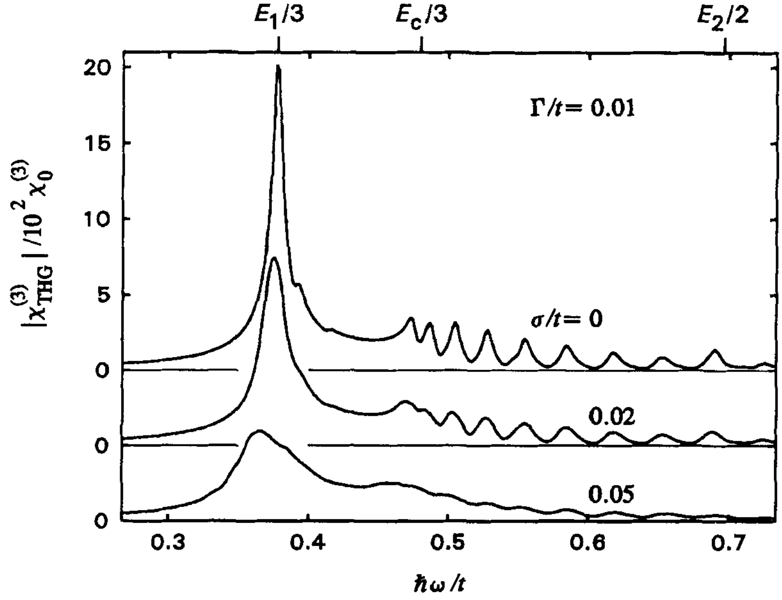

FIGURE 2 Effect of disorder on the third-harmonic generation spectrum in a linear chain of $N=100$ sites, for $\delta t=0.2t$, $V=t$, $U=2t$, and $\Gamma=0.01t$. For disorder $\sigma = 0.02t$ ($0.05t$) the spectrum was averaged over 120 (400) samples.

We note that agreement between theory and experiment has been achieved by assuming $V \approx t \approx 2$ eV and $U \approx 4$ eV. These values of U and V are much smaller than those commonly used in strong-correlation models[10], namely $U \approx 11$ eV and $V \approx 8$ eV of the Ohno potential. This fact indicates the importance of screening in condensed phases and partly justifies our approach (i.e., the restriction to single excitations).

Finally, we briefly discuss a possible application of the present model to another family of conjugated polymers, polythiophene. The recently reported THG spectra[11] of this family show a hump on the high energy side of the main peak, in a similar manner as polydiacetylene and our calculated results. The phase of $\chi^{(3)}$ has also been measured and is in agreement with the calculated phase in Fig.1. This suggests that the same model may apply to polythiophene as well, although at present there is not enough experimental evidence of exciton formation in this system compared with PDA. Further measurements of various nonlinear spectra and comparison with calculations will be necessary to substantiate this possibility.

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