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Soliton contributions to the third-order susceptibility of polyacetylene

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We report on calculations of the third-order susceptibility of pure dimerized *trans*-polyacetylene, pristine $(CH)_x$ with neutral solitons, and doped $(CH)_x$. Line shapes for pure dimerized $(CH)_x$ are in agreement with recent experiments. Pristine $(CH)_x$ with neutral solitons and doped $(CH)_x$ show additional structure below the lowest frequency for which experimental observations have been reported. Our results indicate that third-harmonic generation may be a useful technique for studying the properties of neutral and charged solitons.

Recent interest in *trans*-polyacetylene $(CH)_x$ has focused on the unusually large third-order susceptibility $\chi^{(3)}(\omega)$ found in the undoped material.[1,2] Theoretical calculations[3] for pristine $(CH)_x$ agree well with experimental line shapes for the undoped samples; however, no calculations have been presented for pristine $(CH)_x$ when neutral solitons exist in the ground state, or for doped $(CH)_x$. Although a number of experiments have contributed to the belief that neutral and charged solitons exist in *trans*-polyacetylene,[4] the case for neutral solitons is weaker than that for charged ones. In this regard we recall that the signatures of solitons seen in the optical and infrared spectra of lightly doped samples are not seen in pristine samples where any solitons, if they exist, are necessarily neutral. The absence of a neutral soliton contribution in the infrared spectrum is explained by noting that neutral solitons are not infrared active. Their absence in optical spectra is attributed to electron-electron interactions which can cause the first order optical absorption from neutral solitons to be pushed into the tail of the interband region. Thus neutral solitons are invisible to both probes. Given that the third-order polarization couples very strongly to local dipole moments, we investigate the possibility that the moments produced by off-center neutral and charged solitons might give rise to observable effects in the third-order susceptibility.

Our model is described by the usual Su-Schrieffer-Heeger Hamiltonian[5] augmented by an on-site Hubbard interaction treated in mean-field approximation. For pristine $(CH)_x$, the electronic part of the Hamiltonian for an electron of spin s is then

$$H_s = -\sum_n [t_0 + \alpha(u_{n+1} - u_n)](C^\dagger_{n+1,s} C_{n,s} + C^\dagger_{n,s} C_{n+1,s}) + U \sum_n C^\dagger_{n,s} C_{n,s} (\langle C^\dagger_{n,-s} C_{n,-s} \rangle - \tfrac{1}{2}) .$$

For lightly doped $(CH)_x$ we include the impurity potential V_n which is screened by a background dielectric constant,[6] and, thus, the Hamiltonian for doped systems has the additional term

$$-\sum_n V_n C^\dagger_{n,s} C_{n,s} .$$

We have chosen the following values for the parameters in the Hamiltonian: $t_0 = 2.5$ eV, $\alpha = 4.37$ eV/Å, $U = 4.0$ eV.

For both a dimerized chain and a chain with an impurity, the energies and wave functions are calculated self-consistently as discussed in Ref. 7. For pristine $(CH)_x$ with a neutral soliton, the energies and wave functions are calculated as a function of soliton position. The third-order susceptibility, $\chi^{(3)}(\omega)$, is then obtained from perturbation theory about the adiabatic ground state and is given by

$$\chi^{(3)}(\omega) = \frac{e^4 \rho_c}{Na} \sum W_{\alpha\beta} W_{\beta\gamma} W_{\gamma\delta} W_{\delta\alpha} n_F(E_\alpha) \times \left\{ \frac{1}{(\omega - \omega_{\beta\alpha} + i\eta)(2\omega - \omega_{\gamma\alpha} + 2i\eta)(3\omega - \omega_{\delta\alpha} + 3i\eta)} - \frac{1}{(\omega - \omega_{\beta\alpha} + i\eta)(2\omega - \omega_{\gamma\alpha} + 2i\eta)(\omega + \omega_{\delta\alpha} + i\eta)} + \frac{1}{(\omega - \omega_{\beta\alpha} + i\eta)(2\omega + \omega_{\gamma\alpha} + 2i\eta)(\omega + \omega_{\delta\alpha} + i\eta)} - \frac{1}{(3\omega + \omega_{\delta\alpha} + 3i\eta)(2\omega + \omega_{\gamma\alpha} + 2i\eta)(\omega + \omega_{\beta\alpha} + i\eta)} \right\} ,$$

where α, β, γ, and δ index single-particle states and the summation is taken over all states for each index. $W_{\alpha\beta}$ is a dipole matrix element, $\omega_{\beta\alpha}$ is the difference in energy between states β and α, and $n_F(E_\alpha)$ is a Fermi factor. The input frequency (in eV) is denoted by ω, and η is a phenomenological damping factor. The (average) bond length is a, while N is the number of sites, and ρ_c is the number of chains per unit area normal to the direction of the chains.

Because we are interested in the region of the spectrum which exhibits resonant behavior, we must keep η finite but still small enough so that it does not completely wash

out the resonant features. Physically, η can be thought of as a self-energy correction due to neglected higher-order effects and as a smoothing parameter to account for the fact that a typical sample will contain chains of varying length. For first-order calculations η can safely be chosen to be somewhat larger than the maximum energy-level separation deep within the valence or conduction band of a long chain ($\gtrsim 100$ sites). We have chosen η on empirical grounds by varying η for a dimerized chain so as to reproduce the shape of the spectrum found for pure samples. For the calculations reported below, $\eta = 0.1$ eV.

Our results for the magnitude of $\chi^{(3)}(\omega)$ for a 150-site dimerized chain are shown as the dashed line in Fig. 1. The susceptibility is expressed in arbitrary units since the result depends on the density of chains in the sample and typical chain length. For typical chain densities and assuming that 150-site chains are typical, the susceptibility is of the order of 10^{-9} esu in the frequency range shown. The higher energy peak which we find at ~ 0.9 eV is in excellent agreement with the experimental result of 0.91 eV. The lower energy peak at ~ 0.6 eV is in agreement with previous calculations[3] but was not seen in the original experiment of Kajzar, Etemad, Baker, and Messier[1] because $\chi^{(3)}(\omega)$ was not measured for $\omega < 0.65$ eV. The authors of Ref. 1 noted, however, that an upward trend on the low end of the spectrum strongly suggested a peak below 0.65 eV. Recent experiments[8] probing $\chi^{(3)}(\omega)$ below 0.65 eV indicate a peak at ~ 0.6 eV. The physics that gives rise to the two peaks is simply revealed by examining the calculated spectrum of $\chi^{(1)}(\omega)$. The two peaks in third order are then found to be $\frac{1}{3}$ (the "three-photon peak") and $\frac{1}{2}$ (the "two-photon peak") of the frequency at which the first-order spectrum peaks (~ 1.8 eV). Due to the symmetry of the dipole matrix elements, the three-photon peak is due to a resonance between two states of opposite parity while the two-photon peak is a resonance between two states of the same parity which are coupled through a virtual transition to an intermediate state of opposite parity.

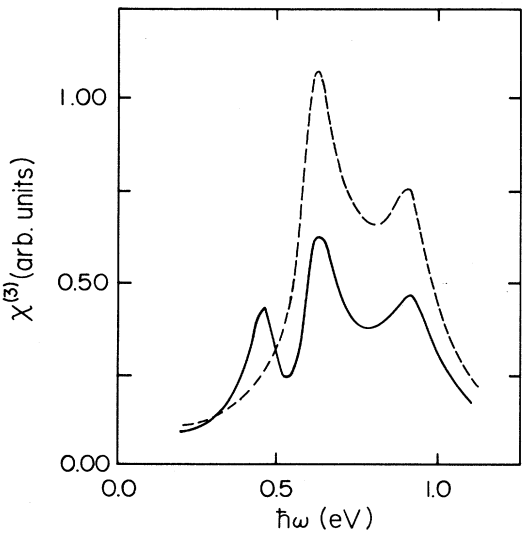

FIG. 1. Third-order susceptibility, $\chi^{(3)}(\omega)$, for pure dimerized $(CH)_x$ and $(CH)_x$ with a neutral soliton. The solid line is for a chain with 149 CH groups and a neutral soliton. The spectrum is an average of $\chi^{(3)}(\omega)$ over all possible neutral soliton locations, each being equally likely. The dashed line is for a dimerized chain with 150 CH groups.

For the range of frequencies probed by experiment, the shape of the spectrum is well accounted for by assuming a dimerized lattice. Pristine $(CH)_x$, however, is believed to contain neutral solitons. Theoretically, neutral solitons exist in the adiabatic ground state of chains with an odd number of CH groups due to topological constraints whereas the adiabatic ground state of even chains is dimerized. Although even chains are energetically favored over odd ones because of the neutral soliton creation energy, in actual polyacetylene films it is expected that both types of chains will arise during material preparation. Thus, we investigate the third-order susceptibility arising from chains with neutral solitons. Specifically, we consider a 149-site chain which is long compared to the neutral soliton width of ~ 12 lattice constants. The system energy is then nearly independent of soliton position except near the ends where it rises steeply due to end repulsion.[6] Thus, the neutral soliton moves in a potential which is closely approximated by a square well. At room temperature, where the experiment is performed, the thermal energy is sufficient to populate many levels in the well and, thus, the probability of finding the soliton at any location on the chain is nearly uniform. The solid line in Fig. 1 shows $\chi^{(3)}(\omega)$ for a neutral soliton equally likely to be found at any point on the chain.

The striking feature for the chain with a neutral soliton is the presence of a peak below the region probed by experiment. Inspection of the single-particle spectrum shows that the peak is due to a three-photon resonance involving the occupied neutral soliton level and levels close to the conduction-band edge. In a previous paper[9] we showed that in first order the neutral soliton peak is pushed into the tail of the interband peak by just the same on-site Hubbard interaction as used here. Thus, the mechanism which hides the neutral soliton from first-order probes is unable to do so in third order. In third order, as in first order, the Hubbard term pushes the neutral soliton peak into the tail of the interband peak, but the nonlinear effects enhance the strength of the neutral soliton contribution to such an extent that a bimodal distribution is produced. By examining $\chi^{(3)}(\omega)$ as a function of neutral soliton position, one finds that the large oscillator strength of the neutral soliton peak is due to off-center solitons whose dipole moments couple strongly to the third-order polarization.

The above results indicate that off-center neutral solitons give rise to observable effects in the third-order susceptibility. In our model, off-center neutral solitons arise as a consequence of neutral soliton mobility. The mobility, as discussed, is due to the fact that the potential for translational motion of the soliton is nearly flat over a large portion of the chain. The question of neutral soliton mobility has been the subject of numerous investigations[4] over the years and seems as yet unsettled. In this regard we point out that mobility is not crucial to our results. Assume a model in which neutral solitons are pinned by

confinement potentials.[10] Integration of $\chi^{(3)}(\omega)$ over a macroscopic region will then produce a bimodal distribution (indicative of off-center neutral solitons) as long as pinning near the chain center is not favored over off-center pinning locations. Thus, barring the possibility that the majority of the neutral solitons are immobile and pinned near the chain center, effects due to neutral solitons should be observable in the third-order susceptibility.

Having studied the third-order susceptibility due to neutral solitons we now investigate $\chi^{(3)}(\omega)$ for charged solitons whose presence in lightly doped $(CH)_x$ is firmly established.[4] Based on our results for off-center neutral solitons we expect that off-center charged solitons will also give rise to large oscillator strengths. Results for a chain with a single charged soliton are shown in Fig. 2. Because a charged soliton in lightly doped $(CH)_x$ is pinned to the impurity which creates it, we have shown the dependence of $\chi^{(3)}(\omega)$ on impurity location. As expected, the oscillator strength is greatly enhanced for off-center impurity locations. For lightly doped $(CH)_x$ ($y < 0.005$) the impurities are randomly distributed for both donors and acceptors[11] and, thus, as previously discussed for confined neutral solitons, we expect a bimodal distribution. Above about 0.5% impurity concentration, x-ray diffraction data[12] suggest the formation of ordered structures for both donors and acceptors. Due to limitations of computer time, however, we have not yet had the opportunity to investigate the third-order susceptibility for these more complicated structures. As far as we know, however, no experimental results for $\chi^{(3)}(\omega)$ have been reported for doped $(CH)_x$. The above numerical results suggest that, in lightly doped $(CH)_x$, interesting structure may be found at energies below the interband contributions.

In conclusion, we have shown that off-center neutral and charged solitons give rise to large oscillator strengths in the third-order susceptibility below the lowest frequency for which experimental observations have been reported. Off-center neutral solitons exist in pristine $(CH)_x$ as a consequence of either neutral soliton mobility or off-center confinement centers. In lightly doped $(CH)_x$ the impurities are randomly distributed and known to pin the charged solitons they create. The existence of off-center charged solitons in the lightly doped material then follows naturally from the randomness of the impurity distribution. Thus, the third-order susceptibility offers the possibility of observing dramatic effects due to neutral and charged solitons. We hope that future experiments will explore these possibilities.

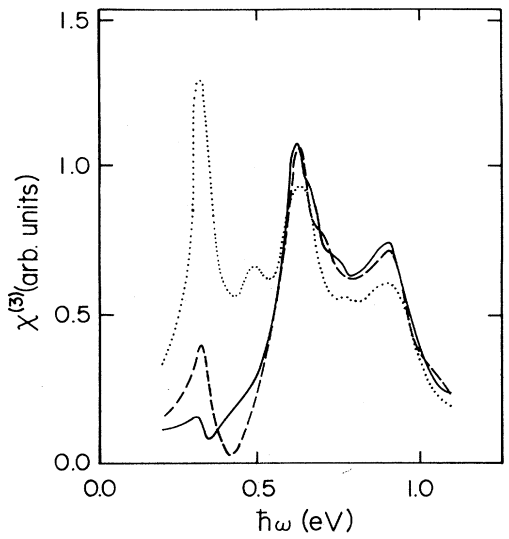

FIG. 2. Third-order susceptibility for a negatively charged $(CH)_x$ chain with 149 CH groups and a donor impurity located 2 Å from the chain. The solid line is for the impurity in the center of the chain, the dashed line is for the impurity 15 sites off center, and the dotted line is for the impurity 30 sites off center.

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[10]Early calculations by D. Baeriswyl and K. Maki [Phys. Rev. B **28**, 2068 (1983)] indicated that neutral solitons in crystalline regions of $(CH)_x$ are confined for $T < 35$ K due to interchain coupling. Neutral solitons in amorphous regions, however, would not be confined by such a mechanism. It is notable, however, that the third-order susceptibility measurements are carried out at room temperature where the interchain confinement is inoperative. Confinement due to conjugational defects, however, is still a possibility.

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