

Spectrum of $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$ in Polyacetylene: An Application of the Free-Electron Laser in Nonlinear Optical Spectroscopy

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(Received 5 January 1989)

We have measured the full spectrum of the third-order optical susceptibility, $\chi^{(3)}(\omega)$, in polyacetylene using an infrared free-electron laser. The magnitude of $\chi^{(3)}(\omega)$ reaches $\sim 10^{-8}$ esu at 0.6 eV, the largest value of an electronic $\chi^{(3)}(\omega)$ inside the gap of a semiconductor. There are two peaks at 0.6 and 0.89 eV in the spectrum of $\chi^{(3)}(\omega)$ that are assigned to three- and two-photon resonance enhancements, respectively, implying that states of opposite symmetry lie near the 1D band gap at $E_g \sim 1.8$ eV.

PACS numbers: 42.60.-v, 42.65.Ky, 78.65.Hc

The extensive recent interest in the nonlinear optical (NLO) properties of conjugated polymers has focused on studies of their third-order susceptibility, $\chi^{(3)}(\omega)$, since almost all of these materials possess a center of symmetry. Although many recent studies have been fueled by the technological implications of the large NLO coefficients in conjugated polymers,¹ an understanding of the large values of $\chi^{(3)}(\omega)$ in polyenes has historically been important because they are the simplest conjugated systems.² Polyacetylene, the infinite polyene, deserves special attention since it is the prototype conjugated polymer and is useful in modeling the NLO properties of conjugated polymers in general.

Most studies of the NLO properties of the polymeric semiconductors have been concerned with third-harmonic-generation (THG) experiments. Besides the demonstration of large $\chi^{(3)}$, THG measurements in polyacetylene have addressed the role of Coulomb correlations,³ and the possibility of new mechanisms for large $\chi^{(3)}$ in conjugated polymers.⁴ Unfortunately most of these studies have been based on single-frequency measurements. In contrast, the spectrum of $\chi^{(3)}(\omega)$ not only provides insight into the origin of such large nonlinearities, but it also determines the operating window for potential applications of conjugated polymers as NLO materials. This is clearly seen in the strong energy dependence of the calculated $\chi^{(3)}(\omega)$ and $n_2(\omega)$, the intensity-dependent part of the index of refraction, for polyacetylene.^{5,6} Our early measurement of the $\chi^{(3)}$ spectrum of polyacetylene had gaps in its energy coverage and did not extend to energies lower than $h\nu \sim 0.8$ eV.³ However, these results hinted at a further rise in the magnitude of $\chi^{(3)}$ for pump photon energies below ~ 0.8 eV, and identified the low-energy region of the $\chi^{(3)}$ spectrum as an important region for further studies.

In this Letter we report the measurement of $\chi^{(3)}(\omega)$ in

trans-polyacetylene down to 0.38 eV (3.3 μm) using an infrared free-electron laser (FEL). In addition to the previously reported resonance enhancement at 0.89 eV,³ we have discovered a much stronger resonance enhancement of $\chi^{(3)}$ at 0.6 eV (2.1 μm). The magnitude of $\chi^{(3)}$ at 0.6 eV is $\sim 10^{-8}$ esu, which is the largest measured electronic $\chi^{(3)}$ in the transparent gap region of any semiconductor. We attribute the peaks in the $\chi^{(3)}$ spectrum at 0.6 and 0.89 eV to three- and two-photon resonances at $\frac{1}{3}$ and $\frac{1}{2}$, respectively, of the semiconducting (optical) gap E_g . The observation that the position of the three-photon resonance is at $\frac{2}{3}$ of the energy of the two-photon resonance implies that the state responsible for the parity-conserving two-photon transition lies at the band edge. This study is the first use of an infrared FEL in nonlinear optical spectroscopy, and emphasizes the importance of a FEL as a tunable, intense source for spectroscopic studies.

The Mark III infrared FEL used to generate the fundamental pump frequency is continuously tunable from 2 to 8 μm .⁷ Its output is in the form of a series of ~ 2 - μs duration *macropulses* every ~ 67 ms. Each macropulse contains 10^4 *micropulses* of ~ 2 -ps duration with Fourier-transform-limited resolution separated by ~ 360 ps from each other [see Fig. 1(a)]. There is some variation in the wavelength of the individual macropulses within the macropulse envelope. However, the monochromaticity of the spectral content of the macropulse [see Fig. 1(b)] is adequate for the high-resolution study of electronic resonances reported in this Letter. Typical micropulse peak powers used in our studies lie in the range 10^4 to 10^5 W.

The FEL results cover the range from 1.15 to 3.3 μm . Between 2.1 and 3.3 μm the pump is generated directly by the FEL. In order to fill the gaps in the data reported in our earlier study,³ we have extended the short-wave-

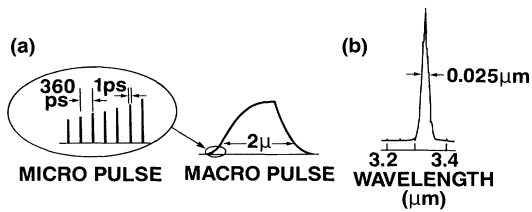


FIG. 1. (a) The structure of a 2- μ s duration *macropulse* and \sim 2-ps duration *micropulses* in the Mark III infrared free-electron laser. (b) The spectral content of a typical *macropulse* that contains 10^4 Fourier-transform-limited *micropulses*.

length range of the laser by a combination of frequency-doubling schemes using an AgGaSe₂ crystal for the 1.8 to 2.1- μ m range and a LiNbO₃ crystal for the 1.15 to 1.25- μ m range. The wavelength range from 1.6 to 1.8 μ m is reached by operating the FEL at its third harmonic.⁸ Two Ge plates set around Brewster's angle are placed in front of the sample to block the intrinsic harmonic light generated within the FEL. The polyacetylene sample used in THG experiments is a thin (\sim 1000 Å) film directly polymerized on a sapphire substrate and sealed in rectangular glass tubing under vacuum after isomerization. The third-harmonic light generated by the sample or the reference is filtered with a set of 10-nm notch filters placed before an infrared-sensitive photomultiplier tube (PMT). The TH intensities are measured by synchronously gating the output of the PMT. As detailed elsewhere, at each wavelength the absolute calibration of $\chi^{(3)}(\omega)$ is carried out by comparing the signal from the polymer with that from a silica plate used as a reference.³ These results are corrected for the absorption and scattering of light at the fundamental and TH frequencies using the equation for THG efficiency in thin films.⁹ The index of refraction at ω and 3ω used in the calculation of $\chi^{(3)}(\omega)$ from THG results was measured directly by an ellipsometric technique.¹⁰

Figure 2 shows the spectrum of $\chi^{(3)}(\omega)$ from 0.4 to 1.5 eV. The closed squares are the results obtained using the infrared FEL, and the open squares are from our earlier work.³ Points with error bars show the variation in the measured value of $\chi^{(3)}$ from different runs on different days. This variation is caused by the slow drift in the spectral content of the macropulse, since the TH signals from the sample and the reference are not measured simultaneously. The length of the error bars is twice the standard deviation of a normal distribution used to obtain the average value of $\chi^{(3)}$ for different runs at a given wavelength. The solid and dashed lines are fits to the experimental points using two recent calculations of $\chi^{(3)}$ that are based on weakly and strongly correlated models for polyacetylene, respectively.^{5,11}

We identify two distinct regions in the spectrum of $\chi^{(3)}(\omega)$: the off-resonance regime that extends from

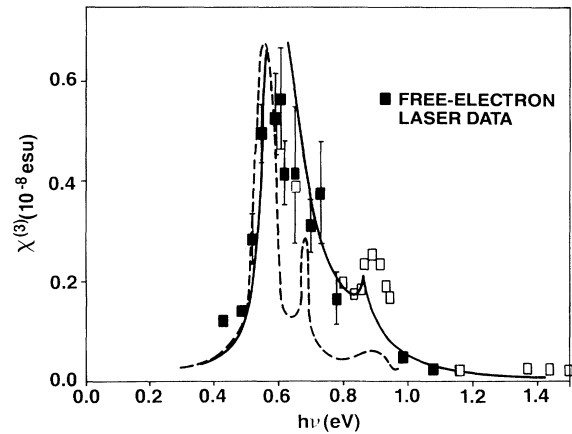


FIG. 2. The $\chi^{(3)}(\omega)$ spectrum in *trans*-(CH)_x. The results obtained using the free-electron laser (filled squares) and those obtained from previous work (Ref. 3) (open squares) are shown. The solid and dashed lines are calculations of $\chi^{(3)}$ within the free-electron (Ref. 5) and highly-correlated-electron (Ref. 11) models, respectively.

\sim 1.0 to $>$ 1.5 eV, and the multiphoton-resonance regime that extends from \sim 0.4 to \sim 1.0 eV. In addition to the previously found peak in $\chi^{(3)}(\omega)$ at 0.89 eV, the FEL measurements have uncovered a broader and much stronger peak at $\frac{2}{3}$ of that value, 0.6 eV. Both peaks correspond to multiphoton-resonance enhancements of $\chi^{(3)}$ since there is not a similar structure in the spectrum of $\chi^{(1)}$, the absorption coefficient.¹² We note that no other structure of comparable intensity and width appears in the energy range extending down to $\frac{1}{4}$ of E_g , the optical gap.

The $\chi^{(3)}(\omega)$ measured by THG experiments is the $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$ component of the third-order optical nonlinearity tensor. Since the $\chi^{(3)}$ of a semiconductor is determined by contributions from one-, two-, and three-photon energies, its measurement provides information on all excited states irrespective of their symmetry.¹³ In particular, resonance enhancements in $\chi^{(3)}$ occur whenever the energy of one, two, or three photons couples two states with a large transition probability. Clearly, a full understanding of the nonlinear optical response of a semiconductor requires measurements at all frequencies inside the gap.

Since our measurements (see Fig. 2) extend below $E_g/4$, the intense three-photon resonance enhancement of $\chi^{(3)}(\omega)$ that couples the even-symmetry ground state to the odd-symmetry band edge must lie in this energy range. This statement is true for a free-electron model,⁵ as well as for a highly-correlated-electron model for polyacetylene.¹¹ Since both $\chi^{(3)}$ and $\chi^{(1)}$ correspond to transitions between states of opposite symmetry and $\chi^{(1)}(\omega)$ peaks at \sim 2 eV¹² [see Fig. 3(a)], we assign the newly found peak at 0.6 eV to the three-photon resonance enhancement of $\chi^{(3)}(\omega)$. The dashed line shows

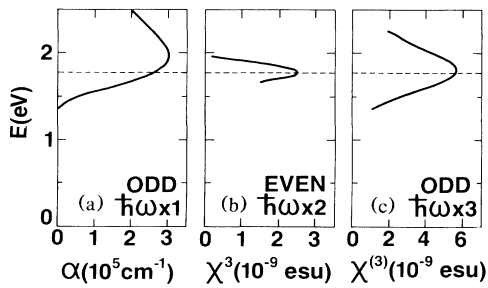


FIG. 3. (a) The spectrum of absorption coefficient $\chi^{(1)}(\omega)$ in *trans*-(CH)_x as a function of ω (Ref. 12). (b) The spectrum $\chi^{(3)}(\omega)$ in the vicinity of the two-photon resonance as a function of 2ω . (c) The spectrum $\chi^{(3)}(\omega)$ in the vicinity of the three-photon resonance as a function of 3ω . The dashed line is the position of the 1D energy gap (Ref. 14).

the position of the 1D energy gap in *trans*-(CH)_x at 1.8 eV.¹⁴ In Fig. 3(c) we replot the spectrum of this peak in $\chi^{(3)}(\omega)$ as a function of 3ω . This is to be compared with the spectrum of $\chi^{(1)}$ in Fig. 3(a). We note that, consistent with the assignment of the 0.6-eV feature as a three-photon resonance, the two spectra shown in Figs. 3(a) and 3(c) are quite similar. The faster drop in the intensity of $\chi^{(3)}(3\omega)$ compared to $\chi^{(1)}(\omega)$ at higher energies results from extra energy-dependent terms in the expression for $\chi^{(3)}$ that decrease with increasing energy above the band edge.¹³

The peak in $\chi^{(3)}(\omega)$ at 0.89 eV is assigned to a two-photon resonance enhancement since the spectrum of $\chi^{(1)}$ does not show a similar structure at the same or 3 times that energy.¹² The significance of the $\frac{2}{3}$ ratio in the positions of the two peaks in $\chi^{(3)}(\omega)$ becomes clear by plotting the spectrum of the two-photon resonance peak as a function of 2ω in Fig. 3(b) and comparing the result with the other two spectra in Figs. 3(a) and 3(c). It is clear that the excited-state energy levels responsible for the parity-conserving and parity-nonconserving transitions are at the same position near the band edge. As discussed in the following, the positions of resonance enhancements associated with these two types of transitions are important fitting parameters in evaluating the role of Coulomb correlations in polyacetylene.

Correlation effects on the optical response of 1D electronic systems are of fundamental importance and have been the subject of several theoretical treatments.^{5,15-17} Because of the simplicity of its molecular structure, polyacetylene is a model system to evaluate the effects of Coulomb correlations in conjugated polymers as 1D electronic systems. There are two types of elementary excitations which are related to the optical responses of such a system: (i) charged excitations associated with one- and three-photon transitions and (ii) neutral excitations which involve a parity-conserving two-photon transition. The relative positions of the gap to charged excitations Δ_c (the *ionic* or optical gap) and the gap to neutral exci-

tations Δ_n (the *covalent* gap) depend upon the strength of the electron-electron interactions in the system.¹⁵⁻¹⁷ In the weakly correlated system $\Delta_c \sim \Delta_n$, while for the strongly correlated system $\Delta_c \gg \Delta_n$. Thus, the multiphoton resonances of strongly and weakly correlated systems should appear in different positions in the spectrum of $\chi^{(3)}$. For the weakly correlated system, the lowest two-photon resonance in $\chi^{(3)}(\omega)$ occurs at $\frac{1}{2}$ of the optical gap or $\frac{3}{2}$ of the energy of the three-photon resonance.⁵ In contrast, for the strongly correlated system, the energy of the lowest two-photon resonance is lowered considerably compared to $E_g/2$.¹¹

We now compare our experimental results with the spectrum of $\chi^{(3)}$ calculated for the two opposite limits of Coulomb interactions.^{5,11} The critical test of these calculations of $\chi^{(3)}(\omega)$ is in their ability to predict the relative positions and intensities of the two- and three-photon resonances. The full spectrum of $\chi^{(3)}$ in *trans*-(CH)_x contains *only* two resolvable resonance enhancement peaks; one at 0.89 eV and the other at 0.6 eV (see Fig. 2). Their assignment to the lowest-energy two- and three-photon resonance peaks, respectively, is consistent with the picture that in polyacetylene the gap to charged excitations has the same magnitude as the gap to neutral excitations, as expected for a noninteracting-electron model. The solid line in Fig. 2 represents the result of the calculation of electronic $\chi^{(3)}$ within the noninteracting-electron model.⁵ For this fit we have used the experimentally determined value of $E_g \sim 1.8$ eV for the 1D band gap.¹⁴ The agreement between the experimental points and this theoretical curve is reasonable. However, as seen in Fig. 2, there is a clear enhancement in the experimental two-photon resonance peak compared to the prediction of a noninteracting-electron model of polyacetylene. This enhancement can be accounted for by the quantum lattice fluctuation contribution to $\chi^{(3)}$ in *trans*-(CH)_x that is not in the electronic part.⁴

The dashed line in Fig. 2 represents the result of the valence-bond approach to exact calculation of $\chi^{(3)}$ using $E_g \sim 1.65$ eV for the optical gap.¹¹ This is an exact calculation of $\chi^{(3)}$ within an extended Hubbard model that incorporates a realistic expression for Coulomb interaction between the electrons on different sites. These calculations can be carried out only on finite-size systems such as the small polyene models of polyacetylene. As a result, the resonances are sharper, and the absolute magnitude of $\chi^{(3)}$ is considerably smaller than the infinite polyene limit, consistent with the experiments and approximate calculations on the length dependence of $\chi^{(3)}$.^{2,18} Therefore, in our fit the magnitude of $\chi^{(3)}$ is arbitrarily scaled to compare the results with experimental points. With the choice of $E_g \sim 1.65$ eV, the lowest-energy two-photon resonance enhancement in $\chi^{(3)}$ is the sharp peak at 0.68 eV. The next-order two-photon resonance is, however, very weak and lies in the small peak near ~ 0.9 eV together with two other higher-order resonances.¹¹

As seen in Fig. 2, a strong three-photon resonance and weak two-photon resonance(s) also exist in the highly-correlated-electronic models of polyacetylene where the lattice distortion plays only a minor role. The exact magnitude of theoretical $\chi^{(3)}$ at the three-photon resonance peak is not known since neither of these two works has applied a realistic rounding of the divergence due to the 1D density of states at the band edge.^{5,11} Such a divergence does not appear in the case of a two-photon resonance enhancement peak.^{5,6} An important observation is that, in both fits to the data (see Fig. 2), the intensity of the calculated two-photon resonance enhancement in $\chi^{(3)}$ is much smaller than the experimental peak at 0.9 eV. Using a value of $E_g \sim 1.8$ eV makes a better fit to the three-photon resonance peak and identifies the strong first two-photon peak that would be at ~ 0.75 eV as the candidate for the experimental peak at 0.9 eV. But, there is a need to further increase the energy of this two-photon resonance peak. The recent theoretical study of $\chi^{(3)}$, where the intrachain Coulomb interactions are reduced by the interchain screening effects, appears to have the needed ingredients to account for the experimental results.¹⁹

In summary, we have extended the spectrum of $\chi^{(3)}$ in polyacetylene to an energy less than $E_g/4$ using an infrared free-electron laser, the first use of such a laser for nonlinear optical spectroscopy. The spectrum of $\chi^{(3)}$ shows an off-resonance regime from 1.0 to > 1.5 eV, and two resolvable multiphoton resonances at 0.6 and 0.89 eV. The magnitude of $\chi^{(3)}$ reaches $\sim 10^{-8}$ esu at the peak of a strong three-photon resonance at 0.6 eV. The position of the three-photon resonance is $\frac{2}{3}$ of the position of the two-photon resonance, implying that states of opposite parity lie at the band edge. We find that neither of the two recent calculations of $\chi^{(3)}$ that consider weak and strong limits of the Coulomb correlations in polyacetylene provide a complete explanation of the experimental results.

This work was supported by ONR Contract No. N0014-8615 and by NSF Contract No. CMR83-16982. We are grateful to Professor R. S. Feigelsen and Dr. R. Route for providing the AgGaSe₂ crystal which was prepared under ONR Contract No. N00014-86-K-0343, and to B. Hooper for assistance in its use.

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¹For recent developments, see *Optical Properties of Polymers*, edited by A. J. Heeger, J. Orenstein, and D. R. Ulrich, MRS Symposia Proceedings No. 109 (Materials Research Society, Pittsburgh, 1988).

²J.-P. Hermann, D. Richard, and J. Ducuing, *Appl. Phys. Lett.* **23**, 178 (1973).

³F. Kajzar, S. Etemad, G. L. Baker, and J. Messier, *Synth. Met.* **17**, 563 (1987); *Solid State Commun.* **63**, 1113 (1987).

⁴M. Sinclair, D. Moses, C. McBranch, A. J. Heeger, J. Yu, and W. P. Su (to be published).

⁵Weikang Wu, *Phys. Rev. Lett.* **61**, 1119 (1988).

⁶G. P. Agrawal, C. Cojan, and C. Flytzanis, *Phys. Rev. B* **17**, 776 (1985).

⁷S. Benson, J. Schultz, B. A. Hooper, R. Crane, and J. M. J. Madey, *Nucl. Instrum. Methods Phys. Res., Sect. A* **272**, 22 (1988).

⁸S. Benson and J. M. J. Madey, *Phys. Rev. A* **39**, 1579 (1989).

⁹F. Kajzar and J. Messier, *Thin Solid Films* **132**, 11 (1985).

¹⁰M. K. Kelley, D. E. Aspnes, S. Etemad, and G. L. Baker (to be published).

¹¹Z. G. Soos and S. Ramasesha, *J. Chem. Phys.* **90**, 1067 (1989).

¹²B. R. Weinberger, C. B. Roxlo, S. Etemad, G. L. Baker, and J. Orenstein, *Phys. Rev. Lett.* **53**, 86 (1984); N. Suzuki, M. Ozaki, S. Etemad, A. J. Heeger, and A. G. MacDiarmid, *Phys. Rev. Lett.* **45**, 1209 (1980).

¹³D. C. Hanna, M. A. Yuratich, and D. Cotter, *Nonlinear Optics of Free Atoms and Molecules*, Springer Series in Optical Sciences Vol. 17 (Springer-Verlag, Berlin, 1979).

¹⁴D. Moses, A. Feldblum, E. Ehrenfreund, A. J. Heeger, T.-C. Chung, and A. G. MacDiarmid, *Phys. Rev. B* **26**, 3361 (1982).

¹⁵For a review of the physical consequences of the correlation effects in 1D systems, see V. J. Emery, in *Highly Conducting One-Dimensional Solids*, edited by J. T. Devreese (Plenum, New York, 1979).

¹⁶Z. G. Soos and S. Ramasesha, *Phys. Rev. B* **29**, 5410 (1984).

¹⁷P. Tavan and K. Schulten, *Phys. Rev. B* **36**, 4337 (1987).

¹⁸J. R. Heflin, K. Y. Wong, O. Zamani-Khamiri, and A. F. Garito, *Phys. Rev. B* **38**, 1573 (1988).

¹⁹Z. Soos, G. W. Hyden, and S. Etemad, *Bull. Am. Phys. Soc.* **34**, 770 (1989).