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Hyperpolarizabilities of conjugated polymers

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The hyperpolarizabilities of conjugated polymers are studied within a tight-binding model. Exact evaluation of $\chi^{(3)}(3\omega)$ is carried out numerically for polymer chains of varying lengths, *cis*-polyacetylene and polythiophene. Effects of solitons on $\chi^{(3)}$ are considered.

Among many interesting properties of conjugated polymers, the unusually large optical nonlinearity has received much attention recently. Aside from possible optoelectronic applications, the third-order susceptibility $\chi^{(3)}$ also provides unique information about the excited states. It is therefore useful to calculate $\chi^{(3)}$ from theoretical models and to compare it with experiment.

Due to mathematical complications not many realistic calculations are available. Model calculations[1,2] involving electron-electron interactions have been carried out only for very short chains, whereas the remarkable chain-length dependence of $\chi^{(3)}$ persists for moderately long chains. Recently, Wu[3] performed a Green's-function calculation of the $\chi^{(3)}$ of an infinite chain using the Takayama, Lin-Liu, and Maki (TLM) model[4] of polyacetylene. In this paper we use the discrete Su-Schrieffer-and Heeger (SSH) model[5] and compute $\chi^{(3)}$ by direct summation of the intermediate states. Besides providing an independent check of Wu's results, the flexibility of the method allows us to study other interesting aspects of the problem.

$$\chi^{(3)}(3\omega;\omega,\omega,\omega)=e^4\sum_{n,m,l} f_{gn}f_{nm}f_{ml}f_{lg} \times\left[\frac{1}{(E_{ng}-3\omega)(E_{mg}-2\omega)(E_{lg}-\omega)}+\frac{1}{(E_{ng}+\omega)(E_{mg}-2\omega)(E_{lg}-\omega)} + \frac{1}{(E_{ng}+\omega)(E_{mg}+2\omega)(E_{lg}-\omega)}+\frac{1}{(E_{ng}+\omega)(E_{mg}+2\omega)(E_{lg}+3\omega)}\right], \tag{1}$$

where $E_{ng}=E_n-E_g$, $\hbar=1$, and $f_{\alpha\beta}$ are dipole matrix elements. As it stands formula (1) is not quite correct. Because the summation over m includes the ground state, $E_{mg}-2\omega$ becomes zero in the static limit and, therefore, (1) diverges formally. The correct expression for $\chi^{(3)}$ can be found in Refs. 6 and 7. The last reference also considers finite lifetime of the excited states.

Since the correct general expression for $\chi^{(3)}$ is fairly complicated, we reproduce here only the formula which applies when the ground state has a definite parity,

$$\begin{aligned}\chi^{(3)}(3\omega;\omega,\omega,\omega)=e^4 &\sum_{n\neq g}\sum_{m\neq g}\sum_{l\neq g} f_{gn}f_{nm}f_{ml}f_{lg}\\ &\times[(E_{ng}\pm3\omega)^{-1}(E_{mg}\pm2\omega)^{-1}(E_{lg}\pm\omega)^{-1}+(E_{ng}\pm\omega)^{-1}(E_{mg}\mp2\omega)^{-1}(E_{lg}\mp\omega)^{-1}]\\ &-e^4\sum_{n\neq g}\sum_{m\neq g} f_{gn}f_{ng}f_{gm}f_{mg}[(E_{ng}\pm3\omega)^{-1}(E_{ng}\pm\omega)^{-1}(E_{mg}\pm\omega)^{-1}\\ &+(E_{ng}\pm\omega)^{-1}(E_{mg}+\omega)^{-1}(E_{mg}-\omega)^{-1}]\ .\end{aligned} \tag{2}$$

The SSH model Hamiltonian is the following:

$$H=-\sum_{n,s}[t_0+\alpha(u_n-u_{n+1})](C^\dagger_{n+1,s}C_{n,s}+\text{H.c.})+K/2\sum_n(u_n-u_{n+1})^2+M/2\sum_n \dot{u}_n^2\ , \tag{3}$$

where $c^\dagger_{n,s}$ creates a π electron with spin s on the n-th carbon site. The π electrons hop with a transfer integral which is modulated by the change in bond length; u_n denotes the displacement of the carbon along the chain. According to our most recent estimate[8] for *trans*-polyacetylene, the elastic constant K is about 53 eV/Å^2 and the electron-phonon coupling constant α is 7.0 eV/Å.

In the SSH model, given any lattice configuration $\{u_n\}$, the Hamiltonian can be diagonalized numerically to give electronic eigenstates. The dipole transition matrix elements $f_{\alpha\beta}$ are then calculated and a straightforward summation over all possible many-body intermediate states is carried out using formula (2). To get a smooth frequency dependence we add an imaginary part $i\Gamma$ to the excited-state energies.

The strong chain-length dependence of the $\chi^{(3)}$ for polyenes has been well documented.[9] Figure 1 shows $\chi^{(3)}$ at frequency $\hbar\omega = 0.65$ eV versus number of carbon sites, N. The upper curve corresponds to a given set of values for the electron-phonon coupling constant and the elastic constant mentioned above. These parameters are determined from the absorption spectrum of *trans*-polyacetylene.[8] For small N the corresponding energy gap is smaller than the experimental value. By adjusting the parameters so the two agree, one obtains the lower curve. The data with error bars are taken from the paper by Hermann and Ducuing.[9] Fairly good agreement is achieved. In particular, the power-law dependence of $\chi^{(3)}$ on N with an exponent of about 4 is obtained in a model without electron-electron interactions, in contrast to the claim of Heflin *et al.*[1]

For the readers who are unfamiliar with the structure of the material used for the data in Fig. 1(a), we show a typical structure—β-carotene—in Fig. 1(b). The β-carotene molecule, which belongs to the polyene family, offers with its 11 double bonds an interesting example of a long conjugated chain. The similarity of the backbone structure of polyenes to *trans*-polyacetylene is obvious. Therefore the SSH model should provide a reasonable description.

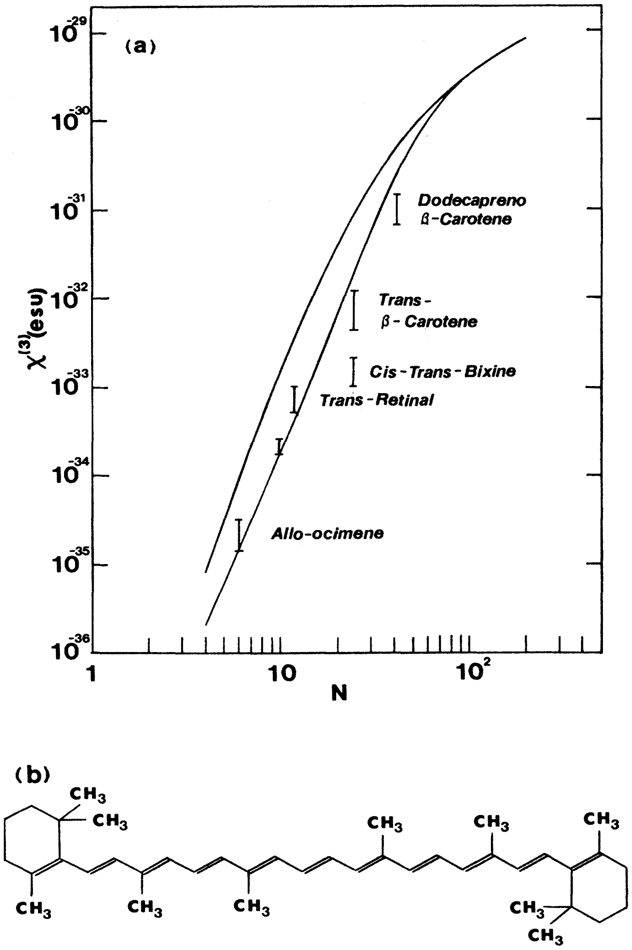

FIG. 1 (a) $\chi^{(3)}$ of polyenes vs chain length N. The photon energy $\hbar\omega$ is 0.65 eV for all N. (b) Structure of the β-carotene molecule.

Another interesting feature of Fig. 1 is that the curve becomes linear for N larger than 100. This provides a nontrivial consistency check of our calculation. The full $\chi^{(3)}$ spectrum is shown in Fig. 2 for *trans*-polyacetylene with $N = 160$. The imaginary part of excited-state energy Γ is taken to be 0.05 eV. The right-hand-side scale is the bulk $\chi^{(3)}$, assuming a polymer chain density[10] of 3.2×10^{14} cm^{-2}. To facilitate comparison with experimental data, one needs to multiply the theoretical result by a local-field correction factor[11]

$$f_{\omega}^{3} f_{3\omega} , \qquad (4)$$

where

$$f_{\omega} = (2 + n_{\omega}^{2})/3 . \qquad (5)$$

n_{ω} is the refractive index. Equation (4) is ~ 10 for $n_{\omega} \sim 1.8$. The random orientation of the chains is already taken into account in the experimental data.[12-14] In our calculation the energy gap E_g is about 1.8 eV. The value of $\chi^{(3)}$ at $\hbar\omega = 0.9$ eV is about 2.5×10^{-9} esu, which is about twice of the experimental value. At this energy this is no clear indication of a two-photon resonance peak. The zigzag is a finite-size effect. The height of three-photon resonance peak at $\hbar\omega = 0.6$ eV also agrees with experiment[14] within a factor of 2. In Wu's calculation the dielectric effect is treated very differently.

The experimentally[12] observed two-photon resonance peak is not completely understood; a possible explanation[15] involves the quantum lattice fluctuation. Another point worth noting about Fig. 2 is the off-resonance value of $\chi^{(3)}$ at the low-frequency limit is indeed very large, i.e., 2×10^{-10} esu.

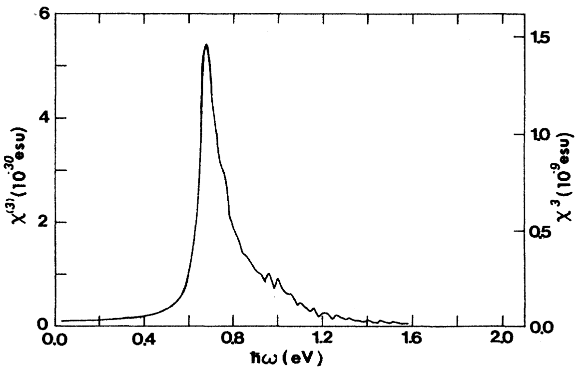

FIG. 2. $\chi^{(3)}$ spectrum for *trans*-polyacetylene with $N = 160$ and $\Gamma = 0.05$ eV.

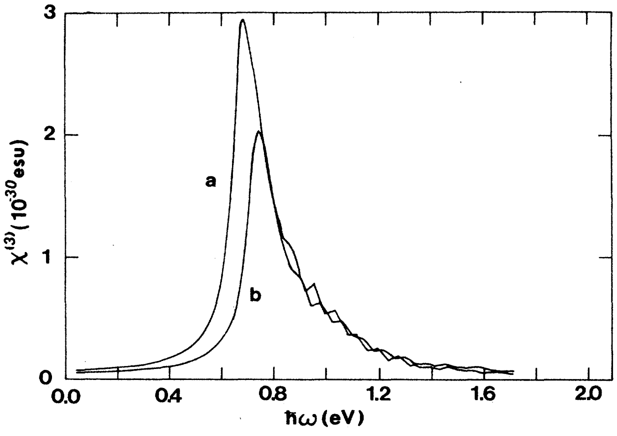

FIG. 3. $\chi^{(3)}$ spectra for *trans*-polyacetylene (curve *a*) and *cis*-polyacetylene (curve *b*). For both curves $\Gamma=0.1$ eV and $N=160$.

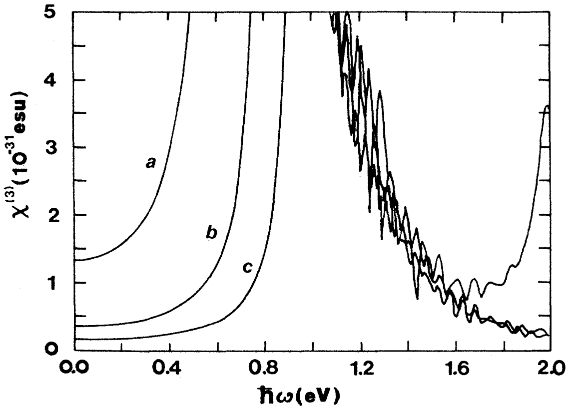

FIG. 4. $\chi^{(3)}$ spectra for *trans*-polyacetylene (curve *a*), polythiophene (curve *b*), and P3HT (curve *c*). $N=160$ and $\Gamma=0.05$ eV for all three curves.

As an interesting comparison, we have studied the $\chi^{(3)}$ of nondegenerate polymers. The Hamiltonian[16] for the systems is obtained by adding the following term to the SSH Hamiltonian

$$\sum_{n,s} \Delta_e(-1)^n(C^\dagger_{n+1,s}C_{n,s}+\text{H.c}) . \qquad (6)$$

Δ_e is determined by fitting the optical-absorption data. In Fig. 3 (curve *b*) we have plotted the $\chi^{(3)}$ spectrum of *cis*-polyacetylene ($N=160$); Γ is taken to be 0.1 eV. The energy gap of *cis*-polyacetylene has been set to 2.25 eV. Curve *a* is the result of *trans*-polyacetylene with this new value of Γ. We have presented the $\chi^{(3)}$ for *trans*-polyacetylene for two different values of Γ so the reader can see the effect of Γ on the theoretical results.

From Fig. 3 we see little change in $\chi^{(3)}$ in going from *trans*-polyacetylene to *cis*-polyacetylene. This disagrees markedly with the experiment[13,15] and calls for an alternative model for *cis*-polyacetylene or a different mechanism for $\chi^{(3)}$ such as the quantum lattice fluctuation.[15]

For two other nondegenerate polymers—polythiophene and poly(3-hexylthienylene) (P3HT)—we have a better understanding[17] in terms of a SSH-type model. The corresponding $\chi^{(3)}$'s are plotted in Fig. 4. Curve *a* is for *trans*-polyacetylene, curve *b* for polythiophene, and curve *c* for P3HT, and for all three curves $N=160$ and $\Gamma=0.05$ eV. The energy gap of the latter two compounds are 2.5 and 2.8 eV, respectively. The static value of $\chi^{(3)}$ scales like E_g^{-6} as expected.[18]

The direct-summation method that we have used in this paper can be readily applied to calculate the $\chi^{(3)}$ of any lattice configuration. As an example, in Fig. 5 we present the $\chi^{(3)}$ of a doped *trans*-polyacetylene chain with four soliton-antisoliton ($S\bar{S}$) pairs. Such a uniform soliton lattice can be experimentally realized in the Na-doped polyacetylene.[19] The three-photon resonance park is strongly enhanced due to the presence of midgap states associated with the solitons. There is almost no feature at $\hbar\omega=0.5$ eV corresponding to the two-photon resonance.

In summary, we have carried out a very careful study of the hyperpolarizabilities of conjugated polymers within a tight-binding model. The results provide a basis for further refinements, such as inclusion of the electron-electron interactions and the quantum lattice effect.

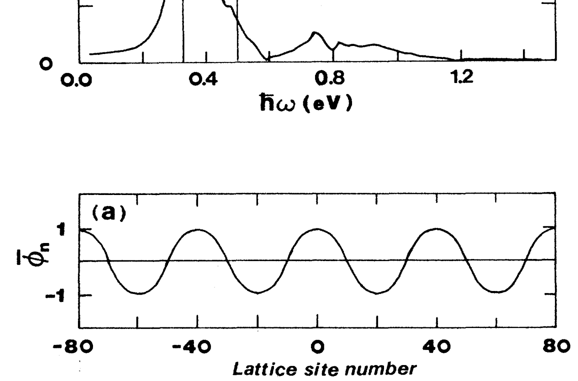

FIG. 5 (a) A doped *trans*-polyacetylene chain with four charged $S\bar{S}$ pairs. The normalized staggered carbon displacement $\bar{\Phi}_n$ is plotted against the site number. (b) $\chi^{(3)}$ spectrum corresponding to the lattice configuration in (a). $\Gamma=0.05$ eV.

Comparison with existing data seems to indicate that the quantum lattice effect is needed. More theoretical study and experimental data along these lines can throw some light on the importance of the electron-electron interactions on $\chi^{(3)}$.

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