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Spectrum of the Third-Order Nonlinear Susceptibility of Trans-Polyacetylene

by

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Abstract

Spectrum of the Third-Order Nonlinear Susceptibility

of Trans-Polyacetylene

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By considering the finite lifetime of excitation and the band structure of a finite polymer chain, the two-peak structure in the spectrum  $\chi^{(3)}(\omega)$  of the third order nonlinear susceptibility of trans-polyacetylene is interpreted in this letter. The numerical result of our theoretical calculation agrees with the spectrum  $\chi^{(3)}(\omega)$  observed in experiments.

In recent years significant progress has been achieved in the study of conducting polymers, where it is found that some conducting polymers possess not only unusually large third-order nonlinear optical susceptibility ( $\chi^{(3)} > 10^{-9}$  esu) but also extremely fast response (sub-picosecond) [1-3]. Even in the infrared region far from the three-photon resonance, such organic material can still keep strong nonlinearity [4]. Noticing that the polymer has much smaller refractive index than the inorganic semiconductor, the effective nonlinear susceptibility  $\chi^{(3)}/n^2$  of the polymer becomes more efficient. The advantages of both strong nonlinearity and quick response suggest that the conducting polymer is promising material to produce ~~the~~ all-optical switching devices.

The spectrum  $\chi^{(3)}(\omega)$  of the third-order nonlinear susceptibility of trans-polyacetylene has resonance structure

ctive. By exploiting the resonance property, it is possible to enhance its nonlinearity further. The study of the spectrum structure is important for understanding and improving the optical nonlinear functions of the conducting polymer. The experiments demonstrate <sup>that</sup> there are two peaks in the spectrum  $\chi''(\omega)$  of trans-polyacetylene, the main peak ~~is~~ near 0.6 eV and the second one near 0.9 eV [1,3]. Since the optical gap  $2\Delta$  of trans-polyacetylene is about 1.8 eV, it is obvious that the position of the main peak is at one third of the gap and this peak is due to the three-photon resonance. Meanwhile the position of the second peak is at ~~the~~ half of the gap. As a naive speculation, it was thought that the second peak came from the two-photon resonance enhancement. But, in a careful consideration, it can be seen that the two-photon absorption in a rigid-band model is forbidden by momentum conservation [5]. So the second peak has some deep origin.

Recently many theoretical works have been devoted to explaining the structure of the third-order nonlinear susceptibility spectrum [5-10], but ~~this~~ <sup>the</sup> problem has not been solved yet. Actually this issue has become a hot topic in the area of conducting polymers. W. Wu and S. Kivelson established a systematic theory for the nonlinear susceptibility of the conducting polymer [10]. By using the Keldysh Green's Function method they derived an analytic expression for  $\chi''(\omega)$  over the full frequency range. Their theoretical results rigorously present a divergence at  $\hbar\omega = 2\Delta/3$  and a cusp at  $\hbar\omega = \Delta$ . The significance is  $\chi''$

there is no any adjustable parameter in their theory and the positions of the divergence and the cusp are in excellent agreement with those two peaks <sup>observed in</sup> experiments. As is emphasized in their paper [10], the cusp is not the two-photon resonance enhancement. Due to the momentum conservation the transition matrix element for the two-photon process, vanishes at  $\hbar\omega = \Delta$ . They concluded that the second peak was induced by a large polarizability near that frequency.

However, this agreement between their theory and the experiments is challenged. C. Wu and one of the present authors (X.S.) <sup>have pointed out</sup> ~~pointed out~~ that their theory ~~was~~ dealt with an ideal case, in which the damping of the excitation is neglected [11]. By using the Genkin-Mednis approach [12], C. Wu and X. Sun derive a general analytic formula of the nonlinear susceptibility from the SSH (Su-Schrieffer-Heeger) model [13]. In the limit of  $\Delta/W \rightarrow 0$ , where  $W$  is the bandwidth, C. Wu and Sun's formula of  $\chi''(\omega)$  exactly reduces to that of W. Wu and S. Kivelson. It is to be expected, since W. Wu and Kivelson started from the TIM (Takahama-Lin-Liu-Maki) model [14], which is a continuum version of the SSH model. The point is, when a small damping of the excitation is taken into account, the cusp is greatly suppressed, and there is only a small bump left at that place [11]. The bump is too small to interpret the second peak near 0.9 eV. Due to the residual electron-lattice interaction and the imperfection of the lattice, the excitation always has some damping and its lifetime

should be finite. The cusp is so sensitive to the damping that a reasonable <sup>ly</sup> small damping can almost eliminate it. So the origin of the second peak has to be studied further.

It should be noticed that in ~~the~~ realistic polymers not only the lifetime of the excitation but also the length of the chain are finite. The experiments have already shown that ~~the~~ polyenes possess strong chain-length dependence of the third-order nonlinear susceptibility [15]. The finiteness of the chain is also a substantial matter for the band structure of one-dimensional system. It is well known that the density of state in one-dimensional system has singularity at the band edges. But the divergence of the density of state appears only if the length of the chain is infinite. If the chain is not very long, e.g. in the case of trans-polyacetylene, the length is about  $10^3$  CII-monomers, the singularity will no longer persist, and the density of state inside the band is comparable with that at the band edges. Then the transition between the states inside the valence band and the conduction band, ~~with~~ <sup>which</sup> energy difference is larger than the gap  $2\Delta$ , will give considerable contribution to the third-order nonlinear susceptibility in the region with higher frequency than  $\hbar\omega = 2\Delta/3$ . As a result, the bump will be enhanced. The following calculation will show there indeed exists another distinct peak near 0.9eV when the length of the chain is shorter than 150 CII-monomers. It will also be seen ~~that~~ <sup>that</sup> when the length of the chain is getting longer, the second peak will decrease. The reason is simple, when the length of the chain increases, the density

of states at the band edges will become larger and larger and the transition between the top edge of the valence band and the bottom edge of the conduction band dominant then only the main peak is left. It confirms the conclusion made in Ref. [11] that the infinite chain has only one peak at  $\hbar\omega = 2\Delta/3$  after considering the damping of the excitation.

Now we are going to conduct the theoretical calculation in the light of the above analysis. Since the size of the chain is much smaller than the wavelength of the incident light, the chain can be considered as a big molecule, and the Orr and Ward's perturbation theory [16] can be used to calculate the third-order nonlinear susceptibility,

$$\chi_{\alpha\beta\gamma\delta}^{(3)}(-\omega; \omega, \omega, \omega) = \frac{K}{\hbar^3} \sum_{\alpha} \left\{ \sum_{\substack{m, n, q \\ \neq \alpha}} \frac{\langle g | \mu_\alpha | m \rangle \langle m | \mu_\beta | n \rangle \langle n | \mu_\gamma | \beta \rangle \langle \beta | \mu_\delta | \alpha \rangle}{(\omega_{m\alpha} - \omega)(\omega_{n\alpha} - \omega)(\omega_{q\alpha} - \omega)} \right\} + \left\{ \sum_{m, n, q} \frac{\langle g | \mu_\alpha | m \rangle \langle m | \mu_\beta | \beta \rangle \langle \beta | \mu_\gamma | n \rangle \langle n | \mu_\delta | \beta \rangle}{(\omega_{m\alpha} - \omega)(\omega_{n\alpha} - \omega)(\omega_{q\alpha} + \omega)} \right\}, \quad (1)$$

where  $\omega = \omega_i + \omega_j + \omega_k$ ,  $\alpha, \beta, \gamma, \delta$  are the component indices,  $g$  is ground state and  $m, n, q$  are excited states.  $K$  is a numerical factor, for the third harmonic generation, it is  $1/4$ .  $\sum_{\alpha}$  is the summation for the permutation of the frequencies.  $\mu_\alpha$  is the  $\alpha$ -component of the di-

pole.  $\frac{1}{2}(\omega_m)$  is the energy difference between the excited state  $m$  and the ground state  $g$ .

For a finite dimerized chain consisting of  $2N$  atoms and  $2N$  electrons, the wave functions of both the ground state and the excited states can be obtained by solving the eigen-equation of the SSH Hamiltonian

$$H/t_0 = - \sum_{n,s} (1 + (-1)^n (\mu_{n+1} + \mu_n)) (a_{n,s}^\dagger a_{n+1,s} + h.c.) + \frac{1}{\pi\lambda} \sum_n (\mu_{n+1} + \mu_n)^2, \quad (2)$$

where  $t_0$  is the hopping constant,  $\lambda$  the coupling constant,  $u_n$  the dimensionless displacement of lattice in site  $n$ ,  $a_{n,s}^\dagger$  and  $a_{n,s}$  the creation and annihilation operators of electron in the site  $n$  with spin  $s$ . For the trans-polyacetylene

$$t_0 = 2.5\text{eV}, \quad \lambda = 0.2.$$

Since the photon momentum is very small, only the transitions with momentum conservation are important, and the dipole transition matrix between different excited states vanishes, then the Eq.(1) requires that the two-photon resonance is constrained, it is the same conclusion as W.Wu's [5].

Due to the strong anisotropy in the polymer chain, the direction along the chain is most important, and only the parallel component of the susceptibility is

needed to be calculated. For the third harmonic generation,  $\omega_1 = \omega_2 = \omega$ , then the spectrum  $\chi^{(3)}(\omega)$  is

$$\chi^{(3)}(\omega) = \chi_{x,x,x,x}^{(3)}(-3\omega; \omega, \omega, \omega). \quad (3)$$

As it has been pointed that the excitation possesses damping, the excitation energy should include a small imaginary part  $i\eta$ , for the trans-polyacetylene,  $\eta$  is about 0.03 in the unit of  $2\Delta$  [8,9]. It is straightforward to make the numerical calculation for the spectrum  $\chi^{(3)}(\omega)$  based on the above formulism.

Our theoretical results are shown in the Fig.1. The solid line is the spectrum of the chain with length  $2N = 90$ , it contains two distinct peaks near 0.6 eV and 0.9 eV respectively. This solid line is quite close to the experimental data, which are demonstrated in the Fig.1 by the crosses. In the Fig.1, a longer chain with  $2N = 180$  is also presented by the dashed line.

As we have analysed previously, when the length of the chain increases, the transition from the top edge of the valence band to the bottom edge of the conduction band gradually becomes dominant, then the second peak is getting weaker. So there appears a shoulder rather than a

peak near 0.9ev in the dashed line. It should be mentioned that the real material consists of chains with different lengths, it can be considered that the observed spectrum is some average over the different lengths. Evidently the results shown in the Fig.1 indicate that our theory is a reasonable interpretation for the spectrum  $\chi^{(1)}(\omega)$  of the trans-polyacetylene. On the other hand, our theory has neglected many other effects, such as the electron correlation, the lattice fluctuation, various defects etc. These effects should be included further when we are going to improve our theory and to get better quantitative agreement with the experimental data.

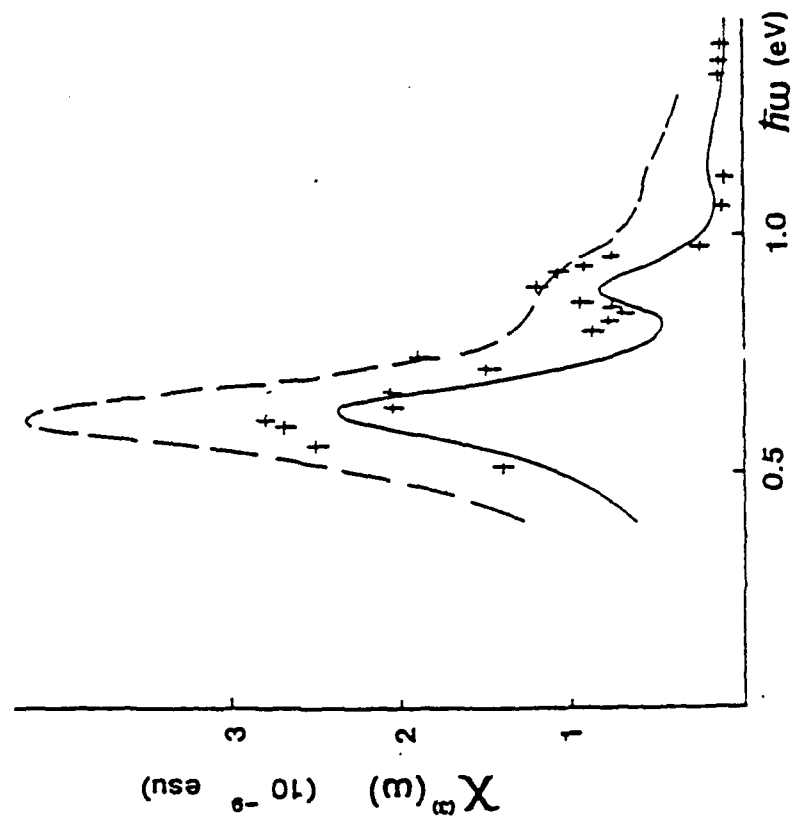
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Caption

Fig.1 The theoretical spectra  $\chi^{(1)}(\omega)$  of finite chains with  $2N = 90$  (solid line) and  $2N = 180$  (dashed line). The crosses are the experimental data.



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