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LETTER TO THE EDITOR

**The spectrum of third-order non-linear susceptibility of *trans*-polyacetylene**

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**Abstract.** By considering the finite lifetime of excitation and the band structure of the finite chain in the polymer, we interpret the two-peak structure in the spectrum of the third-order non-linear susceptibility of *trans*-polyacetylene. The numerical result of our theoretical calculation agrees with the spectrum observed in experiments.

In recent years another significant advance has been made in the study of conducting polymers: it has been found that some possess not only unusually large third-order non-linear optical susceptibilities ( $\chi^{(3)} > 10^{-9}$  esu) but also extremely fast responses (sub-picosecond) [1–3]. Even in the infrared region far from the three-photon resonance, such organic material can still retain strong non-linearity [4]. Noticing that the polymer has a much smaller refractive index than the inorganic semiconductor, we see that the effective non-linear susceptibility  $\chi^{(3)}/n^2$  of the polymer becomes more efficient. The advantages of both strong non-linearity and quick response suggest that the conducting polymer could be a potential material for all-optical switching devices.

The spectrum  $\chi^{(3)}(\omega)$  of *trans*-polyacetylene has a resonance structure. By exploiting the resonance property, it is possible to enhance its non linearity further. The study of the spectrum structure is important to the understanding and improvement of the optical non-linear functions of the conducting polymer. The experiments demonstrate that there are two peaks in the spectrum  $\chi^{(3)}(\omega)$  of *trans*-polyacetylene: the main peak sits near 0.6 eV and the second 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 this interval and that this peak is due to the three-photon resonance. Meanwhile the position of the second peak is at the midpoint of the gap. It was originally thought

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that the second peak came from the two-photon resonance enhancement, but, after 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 much theoretical work has been devoted to explaining the structure of the third-order non-linear susceptibility spectrum [5–10], but this problem has not yet been solved. In fact this issue has become a hot topic in the area of conducting polymers. W Wu and S Kivelson established a systematical theory for the non-linear susceptibility of the conducting polymer [10]. By using the Keldysh Green's function method they derived an analytic expression for  $\chi^{(3)}(\omega)$  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 that there is no adjustable parameter in their theory and that the positions of the divergence and the cusp are in excellent agreement with the two experimental peaks. As is emphasized in their paper [10], the cusp is not the two-photon resonance enhancement. Due to momentum conservation, the transition matrix element for the two-photon process vanishes at  $\hbar\omega = \Delta$ . They conclude that the second peak is induced by a large polarizability near that frequency.

However, this agreement between their theory and experiment is challenged. C Wu and one of the present authors (XS) point out that their theory deals 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 for the non-linear susceptibility from the SSH (Su–Schrieffer–Heeger) model [13]. In the limit  $\Delta/W \rightarrow 0$ , where  $W$  is the bandwidth, C Wu and X Sun's formula for  $\chi^{(3)}(\omega)$  exactly reduces to that of W Wu and S Kivelson. This is to be expected, since W Wu and S Kivelson started from the TLM (Takayama–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 only a small bump is left at that place [11]. The bump is too small to be interpreted as 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 reasonably weak damping can almost eliminate it. So the origin of the second peak has to be studied further.

It should be noticed that in realistic polymers not only the lifetime of the excitation but also the length of the chain is finite. The experiments have shown that the polyenes possess strong chain-length dependence of the third-order non-linear susceptibility [15]. The finiteness of the chain is also of importance to the band structure of a one-dimensional system. It is well known that the density of states in a one-dimensional system has singularities at the band edges. But the divergence of the density of states 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  $10^2$  CH monomers, the singularity will no longer exist, and the density of states inside the band will be comparable with that at the band edges. Then the transition between the states inside the valence band and the conduction band, for which the energy difference is larger than the gap  $2\Delta$ , will notably contribute to the third-order non-linear susceptibility in the region of frequency higher than  $\hbar\omega = 2\Delta/3$ . As a result, the bump will be enhanced. The following calculation will show that another distinct peak near 0.9 eV does indeed exist when the length of the chain is shorter than 150 CH monomers. It will also be seen that when the length of the chain increases, 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 also increase and

the transition between the top edge of the valence band and the bottom edge of the conduction band dominates, then only the main peak is left. This confirms the conclusion reached, taking into consideration the damping of the excitation, in [11], that the infinite chain has only one peak at  $\hbar\omega = 2\Delta/3$ .

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 treated as a big molecule, and the Orr and Ward perturbation theory [16] can be used to calculate the third-order non-linear susceptibility,

$$\chi_{\alpha\beta\gamma\delta}^{(3)}(-\omega; \omega_1, \omega_2, \omega_3) = \frac{K}{\hbar^3} \sum_p \left( \sum_{m,n,q \neq g} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\gamma|q\rangle\langle q|\mu_\beta|g\rangle}{(\omega_{mg} - \omega)(\omega_{ng} - \omega_1 - \omega_2)(\omega_{qg} - \omega_1)} \right. \\ \left. - \sum_{m,n \neq g} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\beta|g\rangle}{(\omega_{mg} - \omega)(\omega_{ng} - \omega_1)(\omega_{ng} + \omega_2)} \right) \quad (1)$$

where  $\omega = \omega_1 + \omega_2 + \omega_3$ ,  $\alpha, \beta, \gamma, \delta$  are the component indices,  $g$  is the ground state and  $m, n$  and  $q$  are excited states.  $K$  is a numerical factor: for the third-harmonic generation, it is  $\frac{1}{3}$ .  $\sum_p$  is the summation for the permutation of the frequencies.  $\mu_\alpha$  is the  $\alpha$ -component of the dipole.  $\hbar\omega_{mg}$  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 wavefunctions of both the ground state and the excited states can be obtained by solving the eigen-equation of the SSH Hamiltonian

$$H/t_0 = -\sum_{n,s} [1 + (-1)^n(u_{n+1} + u_n)](a_{n,s}^+ a_{n+1,s} + \text{HC}) + \frac{1}{\pi\lambda} \sum_n (u_{n+1} + u_n)^2 \quad (2)$$

where  $t_0$  is the hopping constant,  $\lambda$  the coupling constant,  $u_n$  the dimensionless displacement of the lattice at site  $n$  and  $a_{n,s}^+$  and  $a_{n,s}$  the creation and annihilation operators for an electron at site  $n$  with spin  $s$ . For the *trans*-polyacetylene  $t_0 = 2.5$  eV and  $\lambda = 0.2$ .

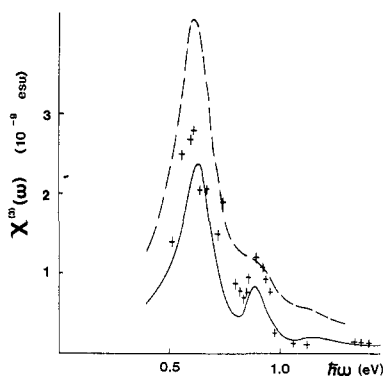
Since the photon momentum is very small, only the transitions that conserve momentum are important, and the dipole transition matrix between different excited states vanishes. Then equation (1) requires that the two-photon resonance be constrained, this conclusion being the same as that reached by W Wu [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 needs to be calculated. For the third-harmonic generation,  $\omega_1 = \omega_2 = \omega_3$ , the spectrum  $\chi^{(3)}(\omega)$  is

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

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

Our theoretical results are shown in figure 1. The full curve is the spectrum of the chain with length  $2N = 90$  and contains two distinct peaks near 0.6 eV and 0.9 eV. This full curve is quite close to the experimental data, which are denoted by crosses. In the figure, a longer chain with  $2N = 180$  is shown as a broken curve. As we have already explained, 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, and the second peak weakens. There then appears a shoulder rather than a peak



**Figure 1.** The theoretical spectra  $\chi^{(3)}(\omega)$  of finite chains with  $2N = 90$  (full curve) and  $2N = 180$  (broken curve). The crosses represent the experimental data.

near 0.9 eV in the broken curve. It should be mentioned that the real material consists of chains with different lengths. The observed spectrum can be considered to be some average over the different lengths. Evidently the results shown in figure 1 indicate that our theory is a reasonable interpretation for the spectrum  $\chi^{(3)}(\omega)$  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 if we are to improve our theory and obtain better quantitative agreement with the experimental data.

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