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Third-harmonic generation of polyacetylene

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We present an exact calculation of third-harmonic generation (THG) for a one-dimensional electron-lattice system. The result shows that once the conjugated length of a polyene is finite, the transitions between inside-band electronic states will be important. A random distribution of conjugated lengths is used to simulate the polymer chains of polyacetylene. The average spectrum of THG distinctly demonstrates two peaks: one is the three-photon resonance exactly at one third of the energy gap; the other sits near half of the energy gap, which is induced by the transitions between the inside-band states. This spectrum agrees quite well with that of THG experiments for *trans*-polyacetylene.

Experimental studies have demonstrated that conducting polymers, especially *trans*-polyacetylene, possess exceedingly large third-order optical susceptibility, $\chi^{(3)} \sim 10^{-9}$ esu, and extremely short response time, ~ 0.1 ps.[1,2] Such significant properties suggest that the conducting polymers are a promising candidate for high-speed nonlinear optical material. However, many important phenomena in the nonlinear optical susceptibility of polyacetylene have not been understood yet. One of them is that the spectrum of third-harmonic generation $\chi^{(3)}(\omega)$ of *trans*-polyacetylene has two peaks near $\hbar\omega = 0.6$ and 0.9 eV. While the main peak at 0.6 eV is obviously the three-photon resonance enhancement, since the energy gap 2Δ of *trans*-polyacetylene is about 1.8 eV, it seems that the second peak at 0.9 eV is due to two-photon resonance enhancement. But, a careful analysis shows that two-photon absorption in a rigid lattice is forbidden by momentum conservation. Understanding the origin of the second peak is a controversial issue.

Although the two-photon resonance is suppressed, a nonresonance cusp at half of the energy gap sill exists according to Wu's calculation,[3] which is based on the Takayama-Lin-Liu-Maki (TLM) model[4] of polyacetylene, a continuum version of the discrete Su-Schrieffer-Heeger (SSH) model.[5] Wu's theoretical curve is in agreement with the experimental data.[1] However, the present authors[6] recently obtained an analytic expression of third-harmonic generation of conducting polymers based on the SSH model and showed that this nonresonance cusp cannot survive a small damping of excited states. Since the lifetime of the excited states is finite and a small damping always exists in the real case, the second peak is not attributable to this cusp. This result strongly calls for a new mechanism to the nonlinear optical susceptibilities of conducting polymers.

In this Rapid Communication, we propose a mechanism, which is based on the band structure of finite-length chains, to interpret the spectrum of third-harmonic generation $\chi^{(3)}$ of polyacetylene. Our exact calculation shows that once the conjugated length of a polyene is finite, the transitions between inside-band electronic states will be important. A random distribution of conjugated lengths is

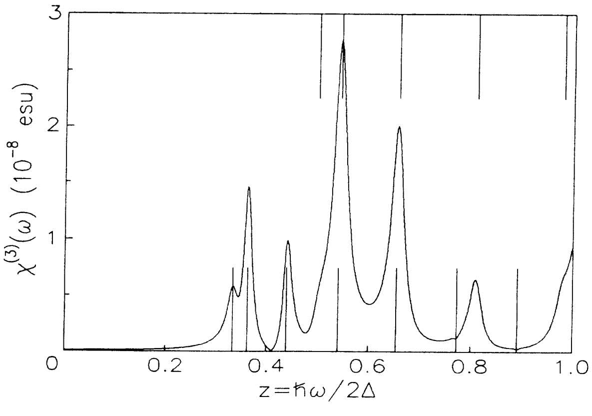

FIG. 1. Third-harmonic generation $\chi^{(3)}(\omega)$ for the system with a short conjugated length $N = 80$. The resonance energies are indicated by upper lines for two-photon resonance and by lower lines for three-photon resonance.

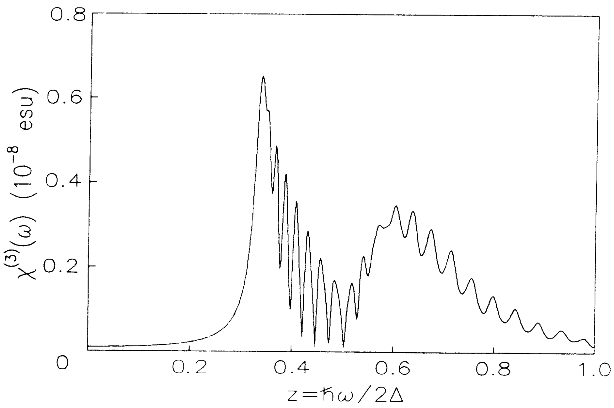

FIG. 2. Third-harmonic generation $\chi^{(3)}(\omega)$ for the system with an intermediate conjugated length $N = 320$.

used to simulate the real material—polyacetylene. The spectrum obtained is in agreement with that of third-harmonic-generation (THG) experiments[1] of *trans*-polyacetylene. The result shows that one of the peaks in the THG spectrum of *trans*-polyacetylene is three-photon resonance enhancement and the other is induced by the transitions between inside-band electronic states due to the finiteness of conjugated lengths.

As has been done in our previous work,[6] we use the Genkin-Mednis approach[7] to derive the expression of third-order nonlinear optical susceptibility $\chi^{(3)}$. After a very complicated by straightforward calculation, we have

$$
\begin{aligned}
\chi^{(3)}(\Omega;\omega_1,\omega_2,\omega_3) = -\frac{e^4}{6\hbar^3 V}\sum_{k,s(\mathrm{occ})}\sum_{P}\Bigg\{ & \frac{1}{(\omega_{cv}+\omega_1+\omega_2)}\frac{\partial}{\partial k}\left(\frac{\Omega_{vc}}{\omega_{cv}+\omega_1}\right)\frac{\partial}{\partial k}\left(\frac{\Omega_{cv}}{\omega_{cv}-\Omega}\right) \\
& +\frac{1}{2}\left(\frac{\Omega_{vc}\Omega_{cv}\Omega_{vc}\Omega_{cv}}{(\omega_{cv}-\Omega)(\omega_{cv}+\omega_1)(\omega_{cv}-\omega_2)}+\frac{\Omega_{vc}\Omega_{cv}\Omega_{vc}\Omega_{cv}}{(\omega_{cv}+\Omega)(\omega_{cv}+\omega_1)(\omega_{cv}-\omega_2)}\right) \\
& -\frac{\partial}{\partial k}\Bigg[\frac{1}{2}\frac{\Omega_{vc}}{(\omega_{cv}+\omega_3)(\omega_{cv}-\omega_1-\omega_2)}\frac{\partial}{\partial k}\left(\frac{\Omega_{cv}}{\omega_{cv}-\omega_1}\right) \\
& \qquad +\frac{1}{2}\frac{\Omega_{cv}}{(\omega_{cv}-\omega_3)(\omega_{cv}+\omega_1+\omega_2)}\frac{\partial}{\partial k}\left(\frac{\Omega_{vc}}{\omega_{cv}+\omega_1}\right) \\
& \qquad +\frac{\Omega_{vc}}{(\omega_{cv}-\omega_1-\omega_2-\omega_3)(\omega_{cv}-\omega_1-\omega_2)}\frac{\partial}{\partial k}\left(\frac{\Omega_{cv}}{\omega_{cv}-\omega_1}\right) \\
& \qquad +\frac{\Omega_{cv}}{(\omega_{cv}+\omega_1+\omega_2+\omega_3)(\omega_{cv}+\omega_1+\omega_2)}\frac{\partial}{\partial k}\left(\frac{\Omega_{vc}}{\omega_{cv}+\omega_1}\right)\Bigg]\Bigg\}, \qquad (1)
\end{aligned}
$$

where $\hbar\omega_{cv}\equiv\varepsilon_c(k)-\varepsilon_v(k)$ is the energy difference between the conduction and valence electrons, $\Omega\equiv-(\omega_1+\omega_2+\omega_3)$, $\sum_P$ stands for summation over terms obtained by all permutations of $\omega_1,\omega_2,\omega_3$, and Ω, the dipole transition strength, is

$$\Omega_{nn'}(k)=\int dr\, u_{nk}^{*}(r)\frac{\partial}{\partial k}u_{n'k}(r)\,, \qquad (2)$$

where $u_{nk}(r)$ is the amplitude modulation part of Bloch wave functions and n,n' are the band indices. In this expression, we have dropped the terms containing the factor $(\Omega_{vv}-\Omega_{cc})$, since it is zero in our case.

For the SSH Hamiltonian[5] of the system with a dimerized lattice,

$$H=-\sum_{l,s}[t_0+(-1)^{l+1}\tfrac{1}{2}\Delta](C_{l+1,s}^{+}C_{l,s}+C_{l,s}^{+}c_{l+1,s})\,, \qquad (3)$$

we have the eigenenergies

$$
\begin{aligned}
\varepsilon_v(k) &= -\varepsilon_c(k) \\
&= -\{[2t_0\cos(ka)]^2+[\Delta\sin(ka)]^2\}^{1/2}\,, \qquad (4)
\end{aligned}
$$

and the dipole transition strength

$$
\begin{aligned}
&\Omega_{vv}(k)=\Omega_{cc}(k)=0\,, \\
&\Omega_{cv}(k)=-\Omega_{vc}(k)=[t_0 a\Delta/\varepsilon_c^2(k)]\mathrm{sgn}(k)\,;
\end{aligned} \qquad (5)
$$

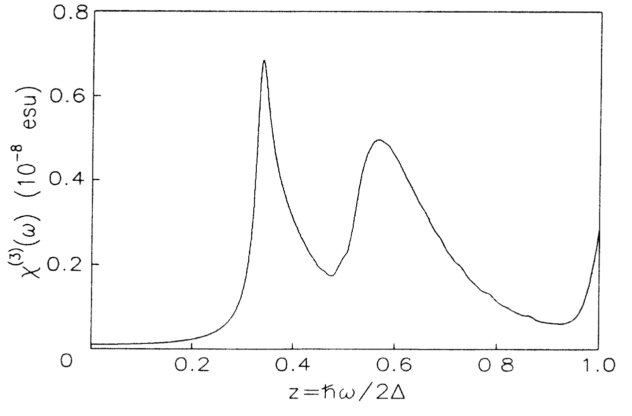

FIG. 3. Third-harmonic generation $\chi^{(3)}(\omega)$ for the system with a random distribution of conjugated lengths. The weight-average conjugated length is $\bar{N}=320$.

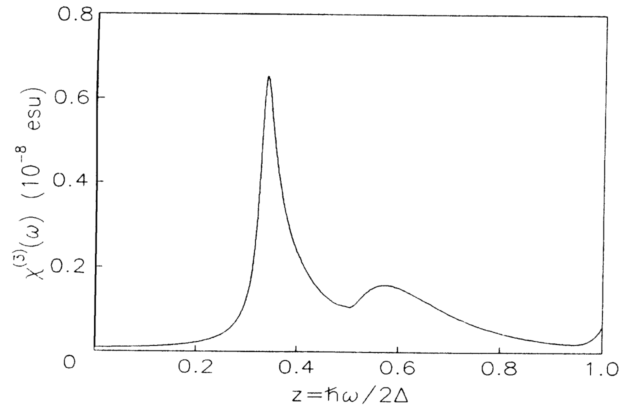

FIG. 4. Third-harmonic generation $\chi^{(3)}(\omega)$ for the system with a random distribution of conjugated lengths. The weight-average conjugated length is $\bar{N}=600$.

then, the third-harmonic generation susceptibility can be obtained by taking $\omega_1=\omega_2=\omega_3=\omega$,

$$\chi^{(3)}(\omega)\equiv\chi^{(3)}(-3\omega;\omega,\omega,\omega)=\chi_0^{(3)}\frac{5\pi}{1024\delta}\frac{1}{N}\sum_{k,s(\mathrm{occ})}[A(x,z)+B(x,z)]\,, \tag{6}$$

where

$$\chi_0^{(3)}=\frac{4}{45}\frac{e^4\sigma}{\pi}\frac{(2t_0a)^3}{\Delta^6}\,, \tag{7}$$

$\delta(\equiv 2\Delta/4t_0)$ is the energy gap in the unit of bandwidth $4t_0$, and

$$A(x,z)=\frac{1}{x^9}\left[\frac{5-8x^2(1+\delta^2)+20\delta^2x^4}{x^2-z^2}+\frac{2048(x^2-1)(1-\delta^2x^2)}{x^2-(2z)^2}+\frac{19683-17496x^2(1+\delta^2)+15228\delta^2x^4}{x^2-(3z)^2}\right], \tag{8}$$

$$\begin{aligned}B(x,z)=\frac{24}{x^9}\Bigg[&7\left[\frac{7-6x^2(1+\delta^2)+5\delta^2x^4}{x^2-z^2}-\frac{2(x^2-1)(1-\delta^2x^2)}{(x^2-z^2)^2}\right]\\&+5x^2\left[\frac{5-4x^2(1+\delta^2)+3\delta^2x^4}{(x^2-z^2)^2}-\frac{4(x^2-1)(1-\delta^2x^2)}{(x^2-z^2)^3}\right]\\&-61\left[\frac{7-6x^2(1+\delta^2)+5\delta^2x^4}{x^2-(2z)^2}-\frac{2(x^2-1)(1-\delta^2x^2)}{[x^2-(2z)^2]^2}\right]\\&-27\left[\frac{7-6x^2(1+\delta^2)+5\delta^2x^4}{x^2-(3z)^2}-\frac{2(x^2-1)(1-\delta^2x^2)}{[x^2-(3z)^2]^2}\right]\Bigg].\end{aligned} \tag{9}$$

$x(\equiv\hbar\omega_{cv}/2\Delta)$ is a function of the wave vector k, $z\equiv\hbar\omega/2\Delta$, σ is the number of chains in units cross-sectional area, and the polymer chains are assumed to be oriented.

From the general expression of THG susceptibility (6), we can easily see that the two-photon resonance at Δ, which is due to the transition between the band-edge states ($x=1$), is suppressed since the functions A and B always yield a finite number at $x=2z=1$. But for other transitions between inside-band states, the two- and three-photon resonances are all possible. A typical feature is shown in Fig. 1 for the system with a short conjugated length $N=80$ atoms. The parameters for polyacetylene are taken as[5] $t_0=2.5$ eV, $\Delta=0.9$ eV, and $\sigma=3.2\times10^{14}$ cm^{-2}; next we have $\delta=0.18$ and $\chi_0^{(3)}\approx1.0\times10^{-10}$ esu. A small imaginary part of the energy of excited states is included, i.e., $x\equiv\hbar\omega_{cv}/2\Delta\rightarrow x+i\eta$ in Eq. (6); η is the damping of excited states in units of 2Δ. For polyacetylene, $\eta\sim0.03$.[8] The resonance energies are also indicated in Fig. 1 by upper lines for two-photon resonance and by lower lines for three-photon resonance. Since a small damping η has been included in the calculations, a few resonance peaks are suppressed. In fact, each transition between inside-band states will induce one two-photon and one three-photon resonance and all resonance peaks can be observed when the damping η is small enough. Figure 2 shows the THG spectrum for the system with an intermediate conjugated length $N=320$. For this system, there are many resonance peaks and its envelope curve gives two peaks which agree with that of THG experiments.[1] Furthermore, we also calculate the THG spectrum for the system with a long conjugated length, which gives only one three-photon resonance at $2\Delta/3$, which is expected, based on the result for an infinite system.[6] The reason is that the transition probability is proportional to the density of states. For inside-band states, the transition probability is of the order of $1/N$. So the resonances due to transitions between inside-band states will be suppressed in a large system, especially in an infinite system. However, a three-photon resonance at $2\Delta/3$ can be observed in an infinite system since the density of states at band edges is divergent for one-dimensional systems.

Since all resonance energies except the three-photon resonance at $2\Delta/3$ are sensitive to the electronic energy levels, then to the conjugated length of polymers, we should consider the distribution of conjugated lengths of polyacetylene. To simulate the real case of polyacetylene, we take the random distribution of conjugated lengths, which provides a broad distribution in lengths and is widely used to represent polymer chain-length distribution.[9] This distribution best represents the distribution of conjugated lengths for polyacetylene. For this distribution,

$$W(m)=(1-p)^2mp^{m-1}\quad(m=1,2,\dots)\,, \tag{10}$$

which yields

$$\bar{m}=(1+p)/(1-p)\,, \tag{11}$$

where p is a probability that defines the distribution. We restrict the number of atoms $N\equiv4m$ in this paper, then the weight-average conjugated length $\bar{N}\equiv4\bar{m}$. Figure 3 shows the THG spectrum for the system with an intermediate weight-average conjugated length $\bar{N}=320$, which is in good agreement with that of polyacetylene observed in experiments.[1] Two peaks distinctly exist in Fig. 3: One is the three-photon resonance exactly at $2\Delta/3$; the other sits near Δ, which is induced by the transitions between the inside-band states. That is the origin of two peaks in the THG spectrum of polyacetylene.

We have calculated the average THG spectra for different weight-average conjugated lengths. The THG spectrum for $\bar{N}=600$ is shown in Fig. 4, from which we find that the height of the three-photon resonance at $2\Delta/3$ is not dependent on the distributions, while that of the second peak decreases with the increase of the weight-average conjugated lengths and its position and width are almost unchanged. From this result we infer that the average conjugated length of polyacetylene is of an intermediate value.

In summary, we should point out that our theory only gives a qualitative picture. The second peak is induced by the transitions between inside-band states due to the finiteness of conjugated lengths of polyacetylene, which is very helpful to understand the experimental results. Quantitative agreement with the experiments is difficult since the model we adopted is too simple to describe such a complex material. To reach a quantitative agreement, more effects need to be carefully considered.

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