Vol. **109** (2006) *ACTA PHYSICA POLONICA A* No. 6

Third Harmonic Generation Susceptibility of Polyacetylene in Terms of the Chain Temperature

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(Received February 19, 2006; in final form April 20, 2006)

The tight binding Hamiltonian of Su, Schrieffer, and Heeger has been used to describe the physical properties of the polyacetylene chain. The chain temperature is calculated from the potential energy which is directly related to the CH group displacement. Two different forms of the displacements have been considered: random and Gaussian. The third harmonic generation susceptibility spectra have been plotted in terms of the temperature using the four-wave mixing formula. The results show that a second peak at the mid gap energy has occurred for room temperature which is in good agreement with the experimental data.

PACS numbers: 73.61.Ph, 78.66.Qn, 42.65.An

1. Introduction

Organic conducting polymers have great potential for eventual application in nonlinear optical devices. The understanding of the mechanism underlying their nonlinear susceptibilities is necessary for the design and synthesis of new and better materials. Therefore, detailed theoretical and experimental studies of prototype systems like polyacetylene (PA) have been performed. Because of the strong intra-chain bonding and weak interchain coupling characteristic of polyacetylene, the π electrons are delocalized along the chain. Theoretically, such systems can be dealt with as one-dimensional from the electronic point of view.

The behaviour of the third order susceptibility of *trans* polyacetylene has been investigated by third harmonic generation (THG) and four-wave mixing. Kajzar et al. [1] studied the dispersion of $\chi^{(3)}$ in polyacetylene using the third order harmonic generation. They reported for the range of 1.17–1.5 eV a non resonant $\chi^{(3)}$ value of $\sim 10^{-10}$ esu. Sinclair et al. [2] have performed a THG study of *trans* polyacetylene, and they reported a value of $\chi^{(3)} = 4 \times 10^{-10}$ esu. A free electron laser was used by Fann et al. [3] to measure the full spectrum of the third order susceptibility. They found two peaks at 0.6 eV and 0.9 eV in the spectrum that are assigned to three- and two-photon resonance, respectively. The magnitude of $\chi^{(3)}$ reaches $\sim 10^{-8}$ esu — the largest value of $\chi^{(3)}$ in the gap.

In addition to the above experimental work investigating $\chi^{(3)}$, there was some theoretical interest in formulating and calculating $\chi^{(3)}$. Langhoff et al. [4] gave an accurate expression to calculate $\chi^{(3)}$ of linear chains using fourth order perturbation theory. Yu et al. [5] reproduced the Langhoff expression in a form which applies when the ground state has a definite parity. They studied $\chi^{(3)}$ of *trans* and *cis* polyacetylene using the new expression. They found only one peak at 0.6 eV corresponding to the three-photon absorption and the strength of the peak agrees with the experiment within a factor of two. The Genkin–Medins approach has been used by Wu and Sun [6] to formulate the nonlinear optical susceptibility of one-dimensional electron lattice systems. By considering Su, Schrieffer, and Heeger (SSH) model [7], they got an analytical expression of $\chi^{(3)}$. Using a finite lifetime in their formula, they found that the intensity at $\hbar\omega$ being equal to the band gap (two-photon resonance) is greatly depressed although an average conjugated length of $N = 600$ is considered. The Sum Over State approach to express the third order polarizability is used by Shuai and Brédes [8]. Also, they found the peak corresponding to two-photon absorption is washed out as soon as a finite damping factor is introduced. The usual time dependent perturbation theory in the interaction representation has been used by Yu and Su [9] to formulate $\chi^{(3)}$. They reported $\chi^{(3)}(0)$ and $\chi^{(3)}(\omega)$ for different chains lengths. Again, they found the two-photon peak demolished when using a finite lifetime. The effect of the interchain coupling into $\chi^{(3)}$ has been considered by Sabra and Blackman [10]. They found a strong peak corresponding to the three-photon resonance but nothing for two-photon and the coupling tends to weaken the peak. Finally, and very recent, Jiang and Xu [11] gave analytical solutions for the general four-wave mixing hyperpolarizabilities on infinite chains of *trans* polyacetylene under both Su–Schrieffer–Heeeger and Takayama–Lin–Liu–Maki models through the scheme of dipole–dipole correlations. We have plotted their third harmonic solution for different values of the band gap and $\hbar\omega$, but all the spectra had only the three--photon peak.

In this work we study the effect of the internal temperature onto the third harmonic spectra in general and into the two-photon peak in specific, through changing the displacements of the CH groups of the polyacetylene chain.

2. Mathematical models

2.1. Su, Schrieffer, and Heeger Hamiltonian

Su, Schrieffer, and Heeger in 1980 constructed a model Hamiltonian to describe the polyacetylene chain based on the tight binding approximation. Mathematically, the Hamiltonian can be formulated in terms of u_n the deviation of the nth site from the equilibrium position, and the annihilation operator $\langle n|$ of the

π electron at the nth lattice site. The model can be written using the staggered displacements as

$$H = -\sum_n [t_0 + (-1)^n \alpha(u_n + u_{n+1})] (|n+1\rangle\langle n| + \text{c.c.}) \\ +(K/2)\sum_n (u_n + u_{n+1})^2, \tag{1}$$

where t_0 is the intrachain electron hopping, α is the electron–phonon coupling constant, and K is the spring constant. The total energies are calculated directly after the diagonalization of the Hamiltonian. The sum is performed over the N occupied states for the pristine chain. The total energies, usually, scale as t_0 and the gap energy depends upon the electron–phonon constant. The intrachain electron hopping $t_0 = 2.5$ eV, the electron–phonon constant $\alpha = 4.1$ eV/Å, and the spring constant $K = 21.0$ eVÅ^{-2} are quoted from *trans*-polyacetylene [12] data. The total energy is minimized in terms of u by using the technique which is developed from the perturbation theory [13]. A gap of 1.3 eV will open at Fermi level due to the distortion. The periodic boundary conditions are imposed to eliminate the end effects.

2.2. Internal temperature

The SSH Hamiltonian could explain most of the physical properties of the PA chain, except those related to temperature. The effect of the temperature would appear through the displacements u_i of the (CH)$_i$ groups. We know the displacements from the above Hamiltonian, but not the temperature, which should be calculated.

Each CH group of the chain has got only one degree of freedom along the chain axis and the amplitude of the displacement is very small comparing with the lattice spacing, 5% of the carbon–carbon bond. Thermodynamically the contribution of each group to the internal potential energy will be $k_B T/2$ according to the principle of equipartition of energy [14]. For a chain consisting of N groups it will be $Nk_B T/2$. This energy is equivalent to the sum of the potential energy $Ku_i^2/2$ over the whole chain, since classically each carbon atom is assumed to vibrate individually as a first approximation. So, the temperature will be

$$T = K\sum_i^N u_i^2/k_B N. \tag{2}$$

Statistically, there are many ways to change the displacements of the CH groups. But, here we will restrict ourselves to:

1. The Fortran random number generator function $rand(x)$ as

$$u(i) = A_1 rand(x) \qquad A_1 \in R, \tag{3}$$

where R is the real number set.

2. The Gaussian shape, i.e

$$u(i) = u_0 + \frac{A_2}{\sqrt{2\pi}\sigma}\exp\left(-\frac{(i-i_0)^2}{2\sigma^2}\right) \qquad A_2 \in R, \tag{4}$$

where σ is the standard deviation and u_0 is the ground state displacement. Changing A_1, A_2, and σ we get many different temperatures.

2.3. Four-wave mixing susceptibility formulation of polymers

The general formula of $\chi^{(3)}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)$ for atomic or molecular system is given by [15]:

$$\chi^{(3)}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)=\frac{Ne^4}{\epsilon_0 3!\hbar^3}S_T\sum_{abcd}\rho_0(a)$$

$$\times\left[\frac{r^{\mu}_{ab}r^{\alpha}_{bc}r^{\beta}_{cd}r^{\gamma}_{da}}{(\Omega_{ba}-\omega_\sigma)(\Omega_{ca}-\omega_2-\omega_3)(\Omega_{da}-\omega_3)}\right.$$

$$+\frac{r^{\mu}_{ab}r^{\alpha}_{bc}r^{\beta}_{cd}r^{\gamma}_{da}}{(\Omega_{ba}+\omega_1)(\Omega_{ca}-\omega_2-\omega_3)(\Omega_{da}-\omega_3)}$$

$$+\frac{r^{\mu}_{ab}r^{\alpha}_{bc}r^{\beta}_{cd}r^{\gamma}_{da}}{(\Omega_{ba}+\omega_1)(\Omega_{ca}+\omega_1+\omega_2)(\Omega_{da}-\omega_3)}$$

$$\left.+\frac{r^{\mu}_{ab}r^{\alpha}_{bc}r^{\beta}_{cd}r^{\gamma}_{da}}{(\Omega_{ba}+\omega_1)(\Omega_{ca}+\omega_1+\omega_2)(\Omega_{da}+\omega_\sigma)}\right], \tag{5}$$

where b, c, d denote excited states of the system. a denotes the ground state. r_{ij} is the matrix element between the states i and j in general. μ,α,β,γ are the coordinates associated with absorption or emission $(-\omega_\sigma;\omega_1,\omega_2,\omega_3)$ processes, respectively. $\rho_0(a)$ is the statistical weight of molecules which have energy E_a in balance condition. S_T expresses all the probable permutations of $(\mu,-\omega_\sigma)$ and (α,ω_1), (β,ω_2), (γ,ω_3) pairs which are 24. Equation (5) comes from permuting $(\mu,-\omega_\sigma)$. Permuting the others we get another 20 terms.

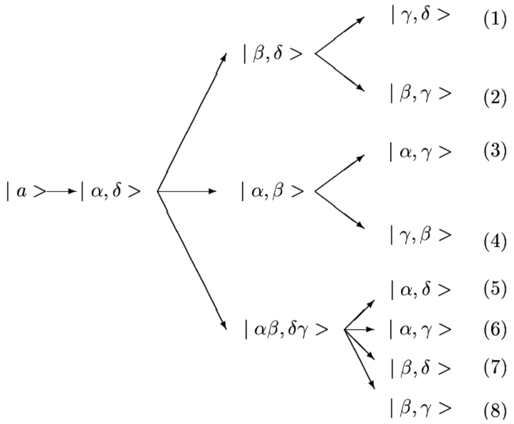

Fig. 1. Schematic representation of all possible transitions between valence and conduction bands.

The matrix elements in the previous relation are independent of the time order of the electron transition from one state to another. So, omitting the superscripts will not affect the calculation of susceptibility. Formula (5) is not appropriate for calculating the susceptibilities of polymeric systems because there are valence and conduction bands, therefore it must be modified. In this case the transition will occur between the states of these two bands according to the schematic representation shown in Fig. 1, where $|a\rangle$ is the ground state and $|\alpha, \delta\rangle$ (in general) represents a state created by annihilating an electron from $|\alpha\rangle$ in valence band and creating that electron in state $|\delta\rangle$ in the conduction band. $\alpha, \beta, \gamma, \delta$ represent states belonging to valence and conduction bands. We notice from the schematic representation that the contribution from the transitions (1) and (3) are equal, and from (2) and (4) are also equal because of the symmetry between valence and conduction bands. Transitions (6) and (7) may be reduced as we will see later. Transitions (5) and (8) are equal with opposite signs [16]. So, we will write the formulae of the susceptibility in the case of the transitions (1), (2), (6), and (7) only.

2.3.1. Transition (1)

The relations between the single particle energy and the many-body energy are

$$\Omega_{da} = \varepsilon_{\delta\gamma}, \quad \Omega_{ca} = \varepsilon_{\delta\beta}, \quad \Omega_{ba} = \varepsilon_{\delta\alpha}, \tag{6}$$

substituting into Eq. (5) we get:

$$\begin{aligned} \chi_1^{(3)}(-\omega_\sigma) = \frac{Ne^4}{\epsilon_0 3!\hbar^3} \sum_{\alpha,\beta,\gamma<0,\ \delta>0} (r_{ab} r_{bc} r_{cd} r_{da}) \\ \times \left[\frac{1}{(\varepsilon_{\delta\alpha} - \omega_\sigma)(\varepsilon_{\delta\beta} - \omega_2 - \omega_3)(\varepsilon_{\delta\gamma} - \omega_3)} \right. \\ + \frac{1}{(\varepsilon_{\delta\alpha} + \omega_1)(\varepsilon_{\delta\beta} - \omega_2 - \omega_3)(\varepsilon_{\delta\gamma} - \omega_3)} \\ + \frac{1}{(\varepsilon_{\delta\alpha} + \omega_1)(\varepsilon_{\delta\beta} + \omega_1 + \omega_2)(\varepsilon_{\delta\gamma} - \omega_3)} \\ \left. + \frac{1}{(\varepsilon_{\delta\alpha} + \omega_1)(\varepsilon_{\delta\beta} + \omega_1 + \omega_2)(\varepsilon_{\delta\gamma} + \omega_\sigma)} \right]. \end{aligned} \tag{7}$$

2.3.2. Transition (2)

The relations between the single particle energy and many-body energy can be given as

$$\Omega_{ba} = \varepsilon_{\delta\alpha}, \quad \Omega_{ca} = \varepsilon_{\beta\alpha}, \quad \Omega_{da} = \varepsilon_{\beta\gamma}, \tag{8}$$

substituting into Eq. (5) we find:

$$\chi_2^{(3)}(-\omega_\sigma) = \frac{Ne^4}{\epsilon_0 3!\hbar^3} \sum_{\alpha,\gamma<0,\ \delta,\beta>0} (r_{ab}r_{bc}r_{cd}r_{da})$$
$$\times\left[\frac{1}{(\varepsilon_{\delta\alpha}-\omega_\sigma)(\varepsilon_{\beta\alpha}-\omega_2-\omega_3)(\varepsilon_{\beta\gamma}-\omega_3)}\right.$$
$$+\frac{1}{(\varepsilon_{\delta\alpha}+\omega_1)(\varepsilon_{\beta\alpha}-\omega_2-\omega_3)(\varepsilon_{\beta\gamma}-\omega_3)}$$
$$+\frac{1}{(\varepsilon_{\delta\alpha}+\omega_1)(\varepsilon_{\beta\alpha}+\omega_1+\omega_2)(\varepsilon_{\beta\gamma}-\omega_3)}$$
$$\left.+\ \frac{1}{(\varepsilon_{\delta\alpha}+\omega_1)(\varepsilon_{\beta\alpha}+\omega_1+\omega_2)(\varepsilon_{\beta\gamma}+\omega_\sigma)}\right]. \tag{9}$$

2.3.3. Transition (6)

In this case the relations between the single particle energy and many-body energy can be written as

$$\Omega_{ba}=\varepsilon_{\delta\alpha},\quad \Omega_{ca}=\varepsilon_{\delta\alpha}+\varepsilon_{\gamma\beta},\quad \Omega_{da}=\varepsilon_{\gamma\alpha}, \tag{10}$$

substituting back into Eq. (5) we get:

$$\chi_6^{(3)}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \frac{Ne^4}{\epsilon_0 3!\hbar^3} \sum_{\alpha,\beta<0,\ \delta,\gamma>0} (r_{ab}r_{bc}r_{cd}r_{da})$$
$$\times\left[\frac{1}{(\varepsilon_{\delta\alpha}-\omega_\sigma)(\varepsilon_{\delta\alpha}+\varepsilon_{\gamma\beta}-\omega_2-\omega_3)(\varepsilon_{\gamma\alpha}-\omega_3)}\right.$$
$$+\frac{1}{(\varepsilon_{\delta\alpha}+\omega_1)(\varepsilon_{\delta\alpha}+\varepsilon_{\gamma\beta}-\omega_2-\omega_3)(\varepsilon_{\gamma\alpha}-\omega_3)}$$
$$+\frac{1}{(\varepsilon_{\delta\alpha}+\omega_1)(\varepsilon_{\delta\alpha}+\varepsilon_{\gamma\beta}+\omega_1+\omega_2)(\varepsilon_{\gamma\alpha}-\omega_3)}$$
$$\left.+\ \frac{1}{(\varepsilon_{\delta\alpha}+\omega_1)(\varepsilon_{\delta\alpha}+\varepsilon_{\gamma\beta}+\omega_1+\omega_2)(\varepsilon_{\gamma\alpha}+\omega_\sigma)}\right]. \tag{11}$$

2.3.4. Transition (7)

Again the relations between the single particle energy and many-body energy in this case are similar to that of transition (6) except for Ω_{da} will be $\varepsilon_{\delta\beta}$

$$\Omega_{ba}=\varepsilon_{\delta\alpha},\quad \Omega_{ca}=\varepsilon_{\delta\alpha}+\varepsilon_{\gamma\beta},\quad \Omega_{da}=\varepsilon_{\delta\beta}, \tag{12}$$

substituting back into Eq. (5) we find:

$$\chi_7^{(3)}(-\omega_\sigma) = \frac{Ne^4}{\epsilon_0 3!\hbar^3} \sum_{\alpha,\beta<0,\ \delta,\gamma>0} (r_{ab}r_{bc}r_{cd}r_{da})$$

$$\times\left[\frac{1}{(\varepsilon_{\delta\alpha}-\omega_\sigma)(\varepsilon_{\delta\alpha}+\varepsilon_{\gamma\beta}-\omega_2-\omega_3)(\varepsilon_{\delta\beta}-\omega_3)}\right.$$

$$+\frac{1}{(\varepsilon_{\delta\alpha}+\omega_1)(\varepsilon_{\delta\alpha}+\varepsilon_{\gamma\beta}-\omega_2-\omega_3)(\varepsilon_{\delta\beta}-\omega_3)}$$

$$+\frac{1}{(\varepsilon_{\delta\alpha}+\omega_1)(\varepsilon_{\delta\alpha}+\varepsilon_{\gamma\beta}+\omega_1+\omega_2)(\varepsilon_{\delta\beta}-\omega_3)}$$

$$\left.+\frac{1}{(\varepsilon_{\delta\alpha}+\omega_1)(\varepsilon_{\delta\alpha}+\varepsilon_{\gamma\beta}+\omega_1+\omega_2)(\varepsilon_{\delta\beta}+\omega_\sigma)}\right]. \tag{13}$$

The terms of the transitions (6) and (7) can be summed together (see Appendix A) to give:

$$\chi_{67}^{(3)}(-\omega_\sigma) = \frac{Ne^4}{\epsilon_0 3!\hbar^3} \sum_{\alpha,\beta<0,\ \delta,\gamma>0} (r_{ab}r_{bc}r_{cd}r_{da})$$

$$\times\left[\frac{1}{(\varepsilon_{\delta\alpha}-\omega_\sigma)(\varepsilon_{\gamma\alpha}-\omega_3)(\varepsilon_{\delta\beta}-\omega_2)}\right.$$

$$+\frac{1}{(\varepsilon_{\delta\alpha}+\omega_1)(\varepsilon_{\gamma\alpha}-\omega_3)(\varepsilon_{\delta\beta}-\omega_2)}$$

$$+\frac{1}{(\varepsilon_{\delta\alpha}+\omega_1)(\varepsilon_{\gamma\beta}+\omega_2)(\varepsilon_{\delta\beta}-\omega_3)}$$

$$\left.+\frac{1}{(\varepsilon_{\delta\alpha}+\omega_1)(\varepsilon_{\gamma\beta}+\omega_2)(\varepsilon_{\delta\beta}+\omega_\sigma)}\right]. \tag{14}$$

Finally, we can write the total susceptibility as a sum of the contributions from (1), (2), (6), and (7) transitions, i.e.

$$\chi^{(3)}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = 2\chi_1^{(3)}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) - 2\chi_2^{(3)}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)$$

$$-\chi_{67}^{(3)}(-\omega_\sigma;\omega_1,\omega_2,\omega_3). \tag{15}$$

The minus sign comes from the matrix elements permutations (see Appendix B). In the case of the THG susceptibility ($\omega_1 = \omega_2 = \omega_3 = \omega$), Eq. (15) becomes identical with the formulae (7–11) of [9].

3. Results and discussion

A Fortran program has been written to diagonalize the SSH Hamiltonian. The diagonalization yields the energy eigenvalues and the wave functions. The immediate physical properties of the system that can be calculated after the diagonalization is the ground state energy. The ground state energy is the sum over all occupied energy levels, and is given in terms of the distortion parameter $u_i = u_0$ [12]. For the above given parameters and for $N = 256$ CH groups, the minimum energy is found for a distortion parameter of $u_0 = 0.0397$ Å. According to Eq. (2) the temperature of the isolated chain is 390 K. This is much higher than the room temperature, or the ground state temperature of the sample in the laboratory. But, in fact the polyacetylene chains are found in three dimensions and the reported distortion parameter experimentally is 0.035 Å (see [12] and references therein). Such distortion corresponds to a temperature of 298.52 K, which is the 3D ground state temperature or the laboratory one.

The change of temperature due to any reason, like the heat comes from the laser during the experiment, should be measured from the ground state energy temperature. The linear optical absorption and the third harmonic generation susceptibility results in terms of temperature are shown in the next subsections.

3.1. Linear optical absorption

The optical study of the PA chain is important to understand the electronic structure of the material in general and the changes in the band gap in our case due to the temperature in special.

Within the tight binding formalism, such as the SSH model, and the golden rule [17], the optical absorption $\alpha(\omega)$ has been derived for a system consisting of

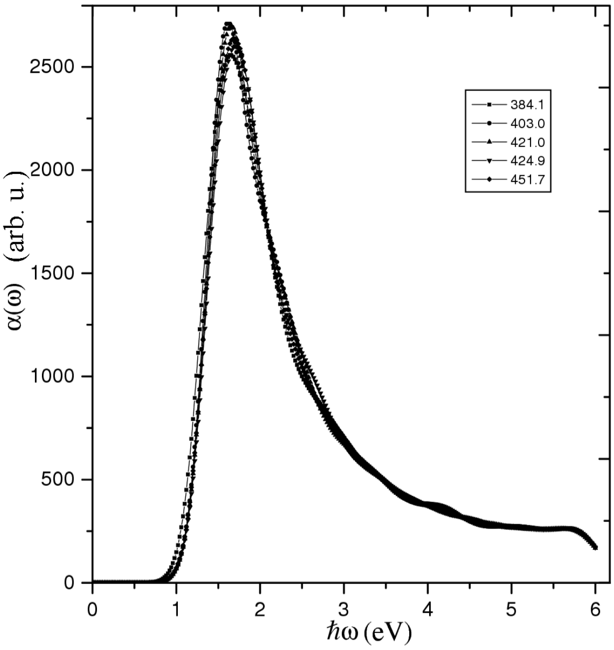

Fig. 2. Linear absorption in the case of random displacements vs. energy for different values of temperature (in K).

two chains of PA [18]. For a single chain, the optical absorption can be written as:

$$\alpha(\omega) = (4\pi^2 Me^2/\tilde{C}\hbar^3\omega)\sum_{\lambda}\delta(\omega-\omega_\lambda)$$
$$\times\left|\sum_{n} V_n[V'_{n+1}t^{+}_{nn+1}X^{+}_{nn+1} - V'_{n-1}t^{-}_{nn-1}X^{-}_{nn-1}]\right|^2 , \qquad (16)$$

where M is the number of polymer molecules per unit volume, λ denotes an excited state of the system. V_n and V'_n are the projections of the wave functions of these states, respectively, into the nth site of the chain. ω_λ is defined as $(E_\lambda - E_{\lambda'})/\hbar$, E_λ and $E_{\lambda'}$ are the eigenvalues associated with the states λ and λ'. $\tilde{C}$ is the speed of light. $t^{\pm}_{nn\pm1} = t_0 \pm \alpha(u_n + u_{n\pm1})$ and $X^{\pm}_{nn\pm1} = (X_n - X_{n\pm1})$. It is assumed that the light is polarized along the chain direction and the momentum $\boldsymbol{p}$ is in that direction also.

The Fortran program has been extended to include Eq. (16) to calculate $\alpha(\omega)$ for both cases random and gaussian displacements and for different values of temperature. Figure 2 shows the spectra of $\alpha(\omega)$ in terms of T in the range from 390 K, the ground state temperature, up to 452 K for the random displacements with a Gaussian broadening of $z = 0.15$ eV. We note that the band edge absorption occurs at an energy of 1.6 eV, a little bit higher than the ground state band gap of 1.3 eV. Figure 3 presents $\alpha(\omega)$ in the case of Gaussian displacements in the range of 379.4–431.1 K with a Gaussian smearing of $z = 0.15$ eV. The band edge absorption

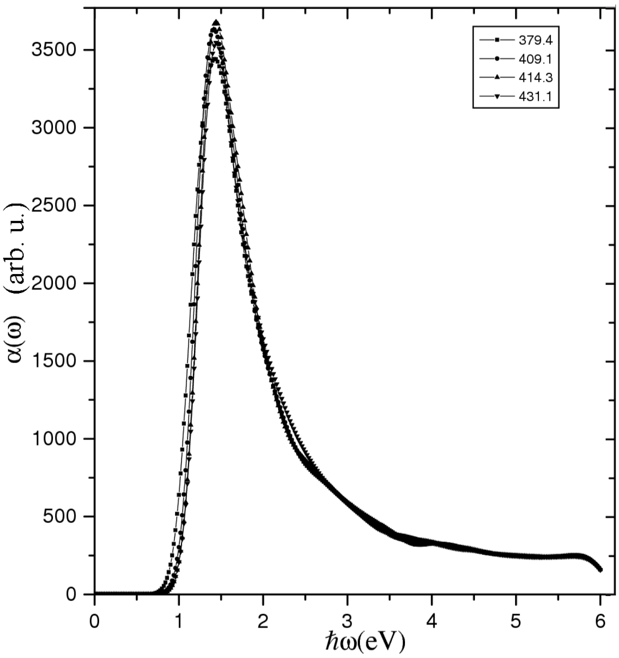

Fig. 3. Linear absorption in the case of Gaussian displacements vs. energy for different values of temperature (in K).

occurs at 1.4 eV which is considerably closer to the ground state band gap energy than the random case. This nominates the Gaussian type of displacement to be more reliable for explaining the experimental results.

3.2. Third harmonic generation susceptibility

Another way to probe the electronic structure of the material is the nonlinear optical properties. These properties can be understood in conjugated electronic systems by invoking the conceptual separation of σ and π electrons and the differences in their behaviour. The π bonds are weaker than the σ bonds, therefore, it is easy to delocalize them. This behaviour of the π electrons makes their distribution highly deformable along the chain, which also gives rise to large optical nonlinearities. To calculate the third harmonic generation susceptibility, we programmed Eq. (12) to consider all possible transitions in Fig. 1 for both cases, random and Gaussian displacements and for different values of temperature. The THG susceptibility spectra in the case of random displacements in the temperature range of 390.1–451.6 K are shown in Fig. 4, where two peaks appear at about 1/3 of the band gap corresponding to three-photon resonance and another one at about 1/2 of the band gap corresponding to two-photon resonance. The positions of the peaks do agree with the experimental results, but the ratio of these two peaks does not. According to [3] the ratio is 2/3, while for the random case it does not exceed 0.5.

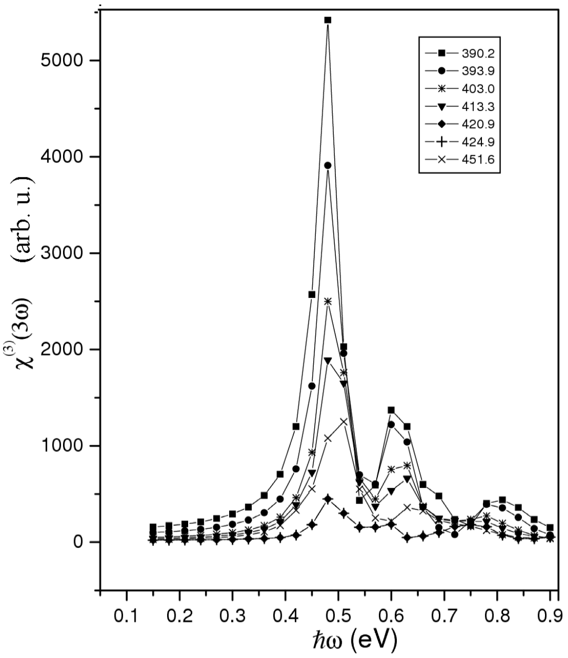

Fig. 4. Third harmonic generation susceptibility in the case of random displacements vs. energy for different values of temperature (in K).

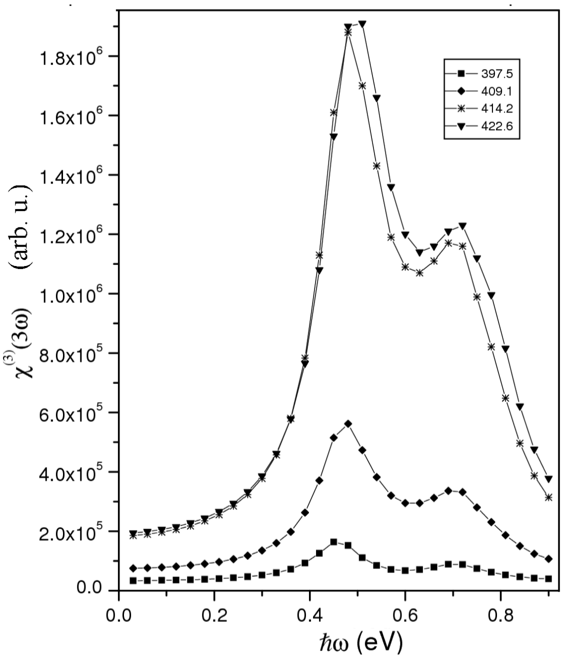

Fig. 5. Third harmonic generation susceptibility in the case of Gaussian displacements vs. energy for different values of temperature (in K).

Figure 5 represents the THG susceptibility spectra in the case of Gaussian displacements. Here again there are two peaks corresponding to three- and two-photon resonance, respectively. The ratio of the peaks increases with temperature up to a certain amount and then starts to decrease. In fact the ratio about 2/3 which is in good agreement with the experimental data is reached for a temperature of about 422 K.

4. Conclusion

The tight binding approximation type Hamiltonian has been used to describe the physical properties of polyacetylene chain. Within the framework of this two-band model the general formula of the four-wave mixing susceptibility has been derived.

The linear and nonlinear optical properties of PA are studied in terms of temperature for two different types of displacements, random and Gaussian. The linear absorption spectra show one peak occurring at the band edge for both cases, but the band gap in the case of random displacements is a little bit wider than the ground state one, while in the case of Gaussian it appears nearly at the ground state band gap. The intensity of the peak changes slowly with temperature in both cases.

The third harmonic generation susceptibility, a special case of the general formula, has been calculated in terms of temperature. Two peaks have been found in both cases at 1/3 and 1/2 of the band gap designated as three- and two-photon resonance, respectively. The ratio of the two-photon to the three-photon is below the experimental one in the random case, but it matches the experimental data in the Gaussian case for a temperature of 422 K. This temperature is higher than our theoretical ground state one by 32 K. In practice this difference will be smaller due to the three-dimensional environment around the chain.

Acknowledgments

The author would like to thank Prof. I. Othman for his permanent support and Prof. V. Heine for his useful discussions.

Appendix A: Summing terms

We will give an example of summing two terms of transitions (6) and (7) (cf. Fig. 1). The rest of the terms can be found in the same way.

$$\frac{1}{(\varepsilon_{\delta\alpha}-\omega_\sigma)(\varepsilon_{\delta\alpha}+\varepsilon_{\gamma\beta}-\omega_2-\omega_3)(\varepsilon_{\gamma\alpha}-\omega_3)}$$

$$+\frac{1}{(\varepsilon_{\delta\alpha}-\omega_\sigma)(\varepsilon_{\delta\alpha}+\varepsilon_{\gamma\beta}-\omega_2-\omega_3)(\varepsilon_{\delta\beta}-\omega_2)} =$$

$$\frac{1}{(\varepsilon_{\delta\alpha}-\omega_\sigma)(\varepsilon_{\delta\alpha}+\varepsilon_{\gamma\beta}-\omega_2-\omega_3)}\left[\frac{1}{\varepsilon_{\gamma\alpha}-\omega_3}+\frac{1}{\varepsilon_{\delta\beta}-\omega_2}\right] =$$

$$\frac{1}{(\varepsilon_{\delta\alpha}-\omega_\sigma)(\varepsilon_{\delta\alpha}+\varepsilon_{\gamma\beta}-\omega_2-\omega_3)}\left[\frac{\varepsilon_{\delta\beta}+\varepsilon_{\gamma\alpha}-\omega_2-\omega_3}{(\varepsilon_{\delta\beta}-\omega_2)(\varepsilon_{\gamma\alpha}-\omega_3)}\right] =$$

$$\frac{1}{(\varepsilon_{\delta\alpha}-\omega_\sigma)(\varepsilon_{\gamma\alpha}-\omega_3)(\varepsilon_{\delta\beta}-\omega_2)}, \tag{17}$$

because

$$\varepsilon_{\delta\beta}+\varepsilon_{\gamma\alpha}-\omega_2-\omega_3=\varepsilon_\delta-\varepsilon_\beta+\varepsilon_\gamma-\varepsilon_\alpha-\omega_2-\omega_3=$$

$$\varepsilon_{\delta\alpha}+\varepsilon_{\gamma\beta}-\omega_2-\omega_3.$$

This is the first term in Eq. (14).

Appendix B: Matrix elements permutations

The diagonalization of the Hamiltonian leads to the wave function of the following form:

$$|\lambda\rangle=\sum_n V_n^\lambda|n\rangle, \tag{18}$$

where V_n^λ is the projection of the wave function $|\lambda\rangle$ onto the site $\langle n\rangle$. Then the matrix element $r_{\alpha\beta}$ between states $|\beta\rangle$ and $|\alpha\rangle$ can be written as:

$$r_{\alpha\beta} = \langle\alpha|d|\beta\rangle, \tag{19}$$

$\langle R\rangle$ the dipole moment operator between these two states. This operator can be written in terms of annihilation A and creation $A^\dagger$ operators as:

$$R = \sum_{\alpha\beta} d_{\alpha\beta} A^\dagger_\alpha A_\beta. \tag{20}$$

There are three transitions having different matrix elements out of the eight transitions sketched in the schematic representation given in Fig. 1. In the case of transition (1), the order of transitions is:

$$|a\rangle \to |\alpha,\delta\rangle \to |\beta,\delta\rangle \to |\gamma,\delta\rangle \to |a\rangle, \tag{21}$$

where $|a\rangle$ is the ground state, $|\alpha,\delta\rangle$ in general a state formed by annihilating an electron in level $|\alpha\rangle$ from valence band and creating that electron in the level $|\delta\rangle$ in conduction band. The $|\alpha,\delta\rangle$ and $\langle\alpha,\delta|$ can be written in terms of annihilation and creation operators as:

$$|\alpha,\delta\rangle = A_\alpha A^\dagger_\delta|a\rangle, \quad \langle\alpha,\delta| = \langle a|A_\delta A^\dagger_\alpha. \tag{22}$$

So, Eq. (21) will be:

$$\langle a|RA_\alpha A^\dagger_\delta|a\rangle\langle a|A_\delta A^\dagger_\alpha RA_\beta A^\dagger_\delta|a\rangle\langle a|A_\delta A^\dagger_\beta RA_\gamma A^\dagger_\delta|a\rangle\langle a|A_\delta A^\dagger_\gamma R|a\rangle. \tag{23}$$

To make life simple we will deal with each term alone, i.e.:
The first term:

$$\langle a|RA_\alpha A^\dagger_\delta|a\rangle = r_{\alpha\delta}\langle a|A^\dagger_\alpha A_\delta A_\alpha A^\dagger_\delta|a\rangle = -r_{\alpha\delta}. \tag{24}$$

The second term:

$$\langle a|A_\delta A^\dagger_\alpha RA_\beta A^\dagger_\delta|a\rangle = r_{\beta\alpha}\langle a|A_\delta A^\dagger_\alpha A^\dagger_\beta A_\alpha A_\beta A^\dagger_\delta|a\rangle = r_{\beta\alpha}. \tag{25}$$

The third term:

$$\langle a|A_\delta A^\dagger_\beta RA_\gamma A^\dagger_\delta|a\rangle = r_{\gamma\beta}\langle a|A_\delta A^\dagger_\beta A^\dagger_\gamma A_\beta A_\gamma A^\dagger_\delta|a\rangle = r_{\gamma\beta}. \tag{26}$$

The fourth term:

$$\langle a|A_\delta A^\dagger_\gamma R|a\rangle = d_{\delta\gamma}\langle a|A_\delta A^\dagger_\gamma A^\dagger_\delta A_\gamma|a\rangle = -r_{\delta\gamma}. \tag{27}$$

Substituting Eqs. (24–27) in (23) we find the matrix elements of transition (1) (cf. Fig. 1) to be

$$r_{\delta\gamma}r_{\gamma\beta}r_{\beta\alpha}r_{\alpha\delta}. \tag{28}$$

In a similar way we find the matrix elements of transition (2)

$$|a\rangle \to |\alpha,\delta\rangle \to |\beta,\delta\rangle \to |\beta,\gamma\rangle \to |a\rangle \tag{29}$$

to be:

$$-r_{\delta\gamma}r_{\gamma\beta}r_{\beta\alpha}r_{\alpha\delta}. \tag{30}$$

and for transitions (6) and (7)

$$-r_{\delta\gamma}r_{\gamma\beta}r_{\beta\alpha}r_{\alpha\delta}. \tag{31}$$

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