Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006.

To cite this article: Dandan Guo (1994): An Essential States Mechanism for Optical Non-Linearity in Conjugated Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 256:1, 105-112

To link to this article: http://dx.doi.org/10.1080/10587259408039237

Mol. Cryst. Liq. Cryst. 1994, Vol. 256, pp. 105–112
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AN ESSENTIAL STATES MECHANISM FOR OPTICAL NONLINEARITY IN CONJUGATED POLYMERS

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Abstract A microscopic many-body theory for the third order optical nonlinearity in conjugated polymers is reviewed. It is found that a correct theory for the optical nonlinearity in conjugated polymers must include electron-electron Coulomb interactions that go beyond the on-site repulsion. Within such a theoretical framework, the bulk of the optical nonlinearity can be quantitatively determined by four essential states. The four essential states give rise to two three-photon resonances and one two-photon resonance in the third harmonic generation (THG) spectrum, and a single narrow two-photon resonance in the two-photon absorption (TPA) spectrum. The theoretical predictions are in excellent agreement with the THG and the TPA experiments in polymers such as polydiacetylenes (PDA), *cis*-polyacetylene (PA), and polysilanes (PS). The THG spectrum of *trans*-PA is also interpreted within the essential states model.

INTRODUCTION

In this paper we review a microscopic many-body theory that we have developed for the third order optical nonlinearity in conjugated polymers[1–6] . Our motivations are to understand the microscopic mechanism of the optical nonlinearity and to find the route to enhanced material properties. The core of our work is the deduction of an essential states four-level model whose results and predictions agree remarkably with experiments in wide variety of materials[4–10]. Our major findings are as follows:

(1) The bulk of the third order optical nonlinearity $\chi^{(3)}$ in one-dimensional systems is determined by four essential states — the ground state, the first odd-parity exciton state, the conduction band threshold, and an even-parity exciton state located between the first odd-parity exciton and the band threshold. The contributions to the third order nonlinearity from all the other states are cancelled out. The four-level model predicts a three-peak spectrum for the THG and an unique narrow resonance peak due to the even-parity exciton in a TPA spectrum.

(2) There are quantitative agreements between the theoretical predictions and experimental results. The excitonic and the band-like natures of the essential states are revealed from the EA experiments. The three-peak spectrum has been observed in materials such as polydiacetylene (PDA)[10,11,12], *cis*-polyacetylene (PA)[10,13], and polysilane (PS)[14], and can be revealed in *trans*-PA. The narrow resonance peaks in the TPA spectra[15,16] illustrate the uniqueness of the even-parity exciton state.

Third Harmonic Generation $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$

To see the roles played by the essential states in the third order optical nonlinearity, we examine the third order susceptibility for THG, $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$.

Since the linear chains are of mirror plane symmetries, the wave functions of the Hamiltonian are either of even-parity, denoted as A_g, or of odd-parity, denoted as B_u. The ground state is the $1A_g$.

With these notations, $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ can be written as

$$\chi^{(3)}(-3\omega;\omega,\omega,\omega)$$

$$= \sum_{j,k,l} \langle 1A_g|\mu|jB_u\rangle\langle jB_u|\mu|kA_g\rangle\langle kA_g|\mu|lB_u\rangle\langle lB_u|\mu|1A_g\rangle$$

$$\times\{D_1(\omega) + D_1(-\omega) + D_2(\omega) + D_2(-\omega)\} + \cdots , \tag{1a}$$

where

$$D_1^{-1}(-\omega) = (\omega_{jB_u} - 3\omega)(\omega_{kA_g} - 2\omega)(\omega_{lB_u} - \omega) \tag{1b}$$

$$D_2^{-1}(-\omega) = (\omega_{jB_u} - \omega)(\omega_{kA_g} - 2\omega)(\omega_{lB_u} + \omega). \tag{1c}$$

In Eq.(1a), the dipole operator μ couples the even- and odd-parity states, and each four-dipole-product term in the numerator of Eq.(1a) corresponds to a pathway, or an optical channel,

$$1A_g \rightarrow jB_u \rightarrow kA_g \rightarrow lB_u \rightarrow 1A_g, \tag{2}$$

that contributs to the $\chi^{(3)}$. A resonance is resulted when any of the denominators in Eq. (1) vanishes.

The Model Hamiltonian

The model Hamiltonian is

$$H = -t\sum_{i,\sigma}[1-(-1)^i\delta][c^+_{i,\sigma}c_{i+1,\sigma} + c^+_{i+1,\sigma}c_{i,\sigma}]$$

$$+U\sum_i n_{i,\uparrow}n_{i,\downarrow} + \sum_i V_i(n_i-1)(n_{i+1}-1), \tag{3}$$

where t is the nearest neighbor hopping integral, δ is the bond alternation parameter and is chosen fixed for rigid band calculations, $c^+_{i,\sigma}$ creates an electron of spin σ at site i, $n_{i,\sigma} = c^+_{i,\sigma}c_{i,\sigma}$, $n_i = \sum_\sigma n_{i,\sigma}$, U and V_i are the on-site and the inter-site Coulomb repulsion parameters. For the sake of simplicity, we discuss in detail the case of the extended Hubbard mode, in which $V_1 \equiv V \neq 0$, $V_{i>1} = 0$.

In the following, we first summarize the results and the predictions of the theory, and then compare the experiments with the theoretical conclusions.

ESSENTIAL STATES MECHANISM OF THIRD ORDER NONLINEARITY

The Essential States

An essential state satisfies two conditions: (1) It has large dipole moments with other essential states of opposite symmetry to give a sizable four-dipole-product in the optical channel shown in Eq. (1). (2) The $\chi^{(3)}$ contribution from one channel is not cancelled out by those from other channels. A complete cancellation occurs when the $\chi^{(3)}$ from the channels, say,

$$1A_g \to jB_u \to kA_g \to lB_u \to 1A_g$$

and

$$1A_g \to jB_u \to kA_g \to l'B_u \to 1A_g\ ,$$

where $l \neq l'$, are equal in magnitude and opposite in sign.

The four essential states we found are the ground state $1A_g$, the first odd-parity exciton state $1B_u$, an even-parity exciton state mA_g located above the $1B_u$ and below the conduction band, and the band threshold nB_u. The exciton nature of the mA_g and the band nature of the nB_u are parameter independent, although the values of the quantum numbers m and n are parameter dependent. In the strong interaction limit, i.e. $U >> V >> t$, the $1B_u$ is about $U - V$ above the ground state $1A_g$ and the gap between the excitons $1B_u$, mA_g and the band threshold nB_u is of the order of V. Such a gap resulted from nonzero V is crucial

to the presence of the exciton binding and is responsible for nonvanishing intensity of the mA_g two-photon resonance in the $\chi^{(3)}$ spectrum, which is discussed in the next section on the intensities of two-photon resonances.

The mA_g: The mA_g is an unique even-parity exciton state that is strongly coupled to the $1B_u$ exciton[1-3]. For systems with weak bond alternation, the mA_g is nearly degenerate with the $1B_u$ in long chain limit. In short chains and in the system with strong bond alternations the mA_g is in higher energy and closer to the band threshold nB_u. In the weak coupling limit, the mA_g is the $2A_g$ because of its large dipole moment with the $1B_u$. However, a strong cancellation between the optical channels diminishes the role of the $2A_g$ in the third order nonlinearity (see the next section).

The nB_u: Besides the $1B_u$, there is only one B_u state, the nB_u, that is strongly coupled to the mA_g[4,6]. The nB_u is recognized to be the conduction band threshold from examining the properties of the wave functions[5]. First, the study on the dipole couplings between the B_u states and their neighboring A_g states finds an onset of strong dipole couplings at nB_u, indicating that a band with dense states and large intra-band couplings is reached. Second, the particle-hole correlations for a give B_u state, say jB_u, defined as

$$\langle jB_u|\sum_{i=1}(n_i-1)(n_{i+l}-1)|jB_u\rangle, \qquad l>0,$$

decrease sharply once the quantum number j is raised to n, implying that conduction occurs at nB_u. Note that the first band A_g state is always above the nB_u for the Hamiltonian in Eq.(3). The above band threshold characters of the nB_u exist in both strong and intermediate Coulomb parameter regimes, are expected to persist even in weaker Coulomb interaction limit. The EA experiment in a polydiacetylene[5,7] has shown that the nB_u is indeed the conduction band threshold.

Intensities of the Two-Photon Resonances:

(1) **The $2A_g$:** In the noninteracting limit ($U = V_i = 0$), the $2A_g$ is strongly coupled to the $1B_u$. On the other hand, the $2A_g$ is equally strongly coupled to the $2B_u$, and the dipole products $\langle 1A_g|\mu|1B_u\rangle\langle 1B_u|\mu|2A_g\rangle$ and $\langle 1A_g|\mu|2B_u\rangle\langle 2B_u|\mu|2A_g\rangle$ have opposite signs because of charge conjugation symmetry. Because of the sign difference, the $\chi^{(3)}$ contributions from the optical channels

$$1A_g \rightarrow 1B_u \rightarrow 2A_g \rightarrow 1B_u \rightarrow 1A_g$$

and

$$1A_g \rightarrow 1B_u \rightarrow 2A_g \rightarrow 2B_u \rightarrow 1A_g$$

cancel. In the infinite chain limit, $\langle 1A_g|\mu|1B_u\rangle\ \langle 1B_u|\mu|2A_g\rangle = -\ \langle 1A_g|\mu|2B_u\rangle\ \langle 2B_u|\mu|2A_g\rangle$, $E(1B_u) = E(2B_u)$, and the cancellation is exact (see Eq.(1)). Consequently, the intensity of the $2A_g$ two-photon resonance vanishes in the $\chi^{(3)}$ spectrum[5,19].

In the interacting-electron models ($U \neq 0$, $V \neq 0$) where the mA_g is not the $2A_g$ (i.e. $m \neq 2$), irrespective that the $2A_g$ is below or above the $1B_u$, the cancellation in the intensity of the $2A_g$ two-photon resonance remains strong. A recent study in the systems with large bond alternation also shows that the $2A_g$, although above the $1B_u$, gives rise to vanishingly weak two-photon resonance in TPA[18]. On the other hand, the dipole coupling between the $2A_g$ and the $1B_u$ is weak in correlated systems. Therefore, the $2A_g$ plays little role in the third order optical nonlinearity in the interacting-electron models as well as in the independent-electron models.

(2) **The mA_g:** Because $\langle 1A_g|\mu|1B_u\rangle\ \langle 1B_u|\mu|mA_g\rangle$ and $\langle 1A_g|\mu|nB_u\rangle\ \langle nB_u|\mu|mA_g\rangle$ have opposite signs, the cancellation exists between the optical cannels involving the mA_g,

$$1A_g \rightarrow 1B_u \rightarrow mA_g \rightarrow 1B_u \rightarrow 1A_g$$

and

$$1A_g \rightarrow 1B_u \rightarrow mA_g \rightarrow nB_u \rightarrow 1A_g.$$

However, the presence of a gap between the excitons and the conduction band ($E(1B_u) \neq E(nB_u)$) greatly suppresses the cancellation. Therefore, the intensity of the mA_g two-photon resonance is not completely cancelled out in the correlated systems with exciton binding (i.e. $V \neq 0$).

Theoretical Predictions

Based on the essential states model, one expect the following:

(1) There are three resonances in the $\chi^{(3)}_{THG}$ spectrum: the $1B_u$ three-photon resonance, the nB_u three-photon resonance, and the mA_g two-photon resonance.

(2) The intensity of the nB_u three-photon resonance is larger than that of the mA_g two-photon resonance because of the cancellation among the mA_g optical channels.

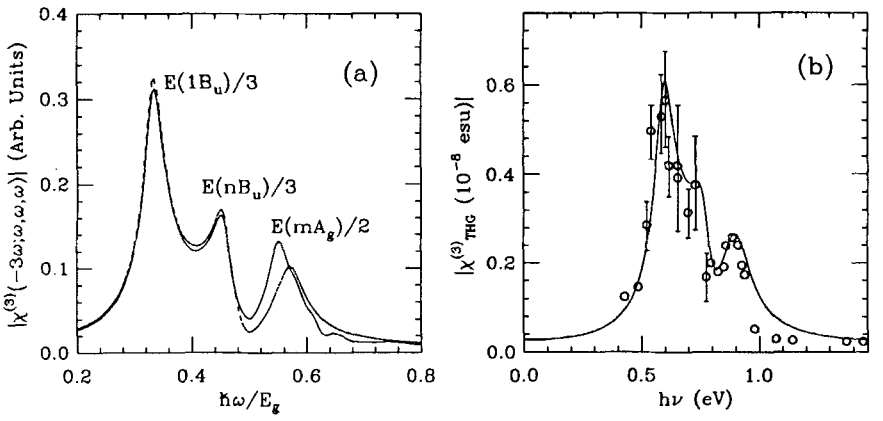

FIGURE 1. (a) The THG spectrum for $N = 8$, $U = 10$, $V = 3.5$, $\delta = 0.1$, and $t = 1$. Solid curve — the THG spectrum obtained from all the states ($\sim 10^3$ states). Dashed curve — the THG spectrum obtained from the four essential states. In the infinite chain limit, such a three-peak spectrum is expected even for weaker Coulomb interactions, as long as the interaction is strong enough to give exciton binding. (b) The experimental data for the THG spectrum of *trans*-PA from Ref. 21 (circles) and the fit from the essential states model (see the text).

(3) There exists only one strong two-photon resonance, the mA_g two-photon resonance, in the TPA spectrum. The intensity of the two-photon resonance to the $2A_g$ is vanishingly small.

The theoretical three-peak $\chi^{(3)}_{THG}$ spectrum is shown in Fig. 1a.

COMPARISON WITH EXPERIMENTS

The experimental THG spectra of PDAs[11,12], *cis*-PA[13], and a PS[14], have been identified to have three resonance peaks[6,10]. In addition, the intensity of the mA_g two-photon resonance in each of the spectrum is weaker than that of the nB_u three-photon resonance. The TPA in a polysilane[15] shows a narrow resonance that is attributed to the mA_g, indicating that the the mA_g is unique. The intensity of the two-photon resonance to the $2A_g$ in the THG spectrum of poly-4BCMU is an

order of magnitude smaller than that of the mA_g[16], which supports our conclusion about the $2A_g$ and agrees with the observation that no appreciable effect due to the $2A_g$ is detected in an EA experiment[5].

On the THG of *trans*-PA

The THG spectrum of *trans*-PA has long been viewed as a two-peak spectrum[21,22,23]. In the experimental data by Fann *et al.*, if the resonances at 0.6 eV and 0.9 eV are attributed to the three-photon resonance to the $1B_u$ and the two-photon resonance to the mA_g respectively, the $1B_u$ is placed at 1.8 eV and the mA_g is nearly degenerate with the $1B_u$, which is consistent with our expectation and an experimental result in β-carotene[20]. The three-photon resonance to the nB_u may be recognized from the peak-like structure near 0.7 eV. This predicts the energy of the nB_u to be about 2.1 eV. Moreover, there are other clues for the energy of the nB_u (2.1 eV) in *trans*-PA. First, the EA signal in *trans*-PA vanishes at and above 2.1 eV[24], similar to the case of PDA where the EA vanishes above the band threshold because of a cancellation effect inside the conduction band[5]. Second, the linear absorption in the *cis*-PA sample with small fraction of *trans*-PA is not small above the gap ($\sim$ 2.0 eV)[24]. A possible origin of the above gap absorption is the absorption to the conduction band of *trans*-PA. Because of smaller gap between the ground state and the band in *trans*-PA, the linear absorption to the band is expected not to be negligible, which is different from the case of PDA in which larger ground state-band gap leads to very weak absorption to the band[7]. Assuming nB_u at 2.1 eV, the $\chi^{(3)}_{THG}$ of *trans*-PA can be fitted by a three-peak spectrum, which is shown in Fig. 1(b).

Because the ground state of *trans*-PA is two-fold degenerate, it is possible to optically generate soliton-antisoliton pairs[25] and a soliton mechanism for the optical nonlinearity in *trans*-PA is proposed[26]. However, according to the EA in *trans*-PA[24], the onset of the soliton absorption is at $1.4 - 1.5$ eV. This rules out the possibility of soliton contribution to the THG in which the pump energy is less than 1 eV.

ACKNOWLEDGEMENTS

Most of the work is conducted by collaborating with Professor Sumit Mazumdar. The writing of the paper is supported by a grant from National Science Fundation

(NSF-DMR 89-20538). The Author thanks Dr. S. Etemad for his kind permission to use the experimental data of *trans*-PA.

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