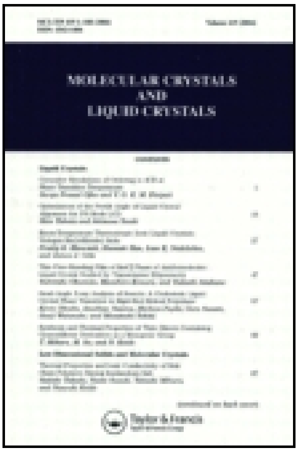

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Optical Nonlinearity Associated with Biexcitonic States in Conjugated Polymers

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OPTICAL NONLINEARITY ASSOCIATED WITH BIEXCITONIC STATES IN CONJUGATED POLYMERS

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Abstract The nonlinear optical absorption spectrum of conjugated polymers is theoretically studied in the Pariser-Parr-Pople model. The method of configuration interaction among single and double excitations is employed for relatively long chains up to 40 sites with the cyclic boundary condition. Calculated spectra in the case of moderate electron-electron interactions are characterized by two groups of peaks: low energy peaks mainly due to excitonic states and high energy peaks with main contributions from biexcitonic states. The latter peaks are much stronger than the former. We examine also how the spectrum depends on the bond alternation and the interaction strength.

INTRODUCTION

Excitons play important roles in the optical properties of many insulators and semiconductors. Conjugated polymers are by no means an exception. One of the authors together with coworkers studied exciton states[1] and their roles in various nonlinear optical spectra[2] of conjugated polymers. The Pariser-Parr-Pople (PPP) model was treated by the method of single-excitation configuration interaction (S-CI), assuming moderate electron-electron (e-e) interactions in the solid state. On the other hand, calculations for small chains with strong electron correlation indicated that the S-CI is not enough to describe the electronic structures of polyene oligomers.[3] Nonlinear optical spectra have also been calculated for the strong correlation models.[4,5] So far the relationship between the results of these different approaches is not well understood. To clarify this point, we

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have carried out CI calculations including all single and double excitations (SD-CI). SD-CI calculations were reported in the past for polyene oligomers with the conventional PPP parametrization.[3] We are interested in the properties of bulk polymer solids, so that we treat relatively long chains by using the cyclic boundary condition and vary interaction strength within an intermediate range. We focus on the nonlinear (or two-photon) absorption spectrum calculated as the imaginary part of $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$.

MODEL AND APPROACH

We consider N electrons on a ring of N sites, N being an even number. An electron with spin s ($=\uparrow$ or $\downarrow$) is created at site n ($=1,\ldots, N$) by the operator $a^\dagger_{ns}$. We use the PPP Hamiltonian with bond alternation[1]:

$$H = H_0 + H_{\text{e-e}} \,, \tag{1}$$

$$H_0 = -\sum_n \left[t + (-1)^n \delta t\right]\left(a^\dagger_n a_{n-1} + a^\dagger_{n-1} a_n\right) , \tag{2}$$

$$\begin{aligned} H_{\text{e-e}} &= \sum_n U\left(a^\dagger_{n\uparrow}a_{n\uparrow} - \tfrac{1}{2}\right)\left(a^\dagger_{n\downarrow}a_{n\downarrow} - \tfrac{1}{2}\right) \\ &+ \tfrac{1}{2} \sum_{\substack{n,m \\ (n\neq m)}} \sum_{s,s'} V_{nm}\left(a^\dagger_{ns}a_{ns} - \tfrac{1}{2}\right)\left(a^\dagger_{ms'}a_{ms'} - \tfrac{1}{2}\right) . \end{aligned} \tag{3}$$

The interaction potential V_{nm} is assumed in Pople's form $V_{nm} = Va/R_{nm}$, where R_{nm} is the distance between sites n and m, and a is the average distance between adjacent sites. A simple form $R_{nm} = |n-m|a$ used in Ref.1 is again employed in the present paper.

In order to treat as large systems as possible, we take all the symmetry properties into account: (i) the translational symmetry; (ii) the spatial mirror symmetry; (iii) the charge conjugation symmetry. According to these symmetries, each state is characterized by (i) the modulus of wave number $|K|$, (ii) A (symmetric) or B (antisymmetric), and (iii) – or + (Pariser's notation).

Full SD-CI calculations are carried out as follows.[6] We first determine the Hartree-Fock ground state and one-electron states. Then the total excitation Hamiltonian is diagonalized within the basis consisting of the ground state, single electron-hole (e-h) excitations, and double e-h excitations for each symmetry class. Details of calculations will be published elsewhere.[7] To test our numerical program we calculated the energy levels of the benzene ring in the S-CI and SD-CI approximations with the same input parameters as in Ref.6. Our program gives a complete coincidence with the results of Ref.6.

We note that the SD-CI is not size-consistent[3] and hence does not give a convergent result in the limit of $N \to \infty$. We have chosen the case N=40, which seems large enough to grasp main features of large systems and at the same time not so large that the deficiency of the SD-CI description would strongly influence the relative energy distances of two-photon excited states.

We calculated the nonlinear susceptibility $\chi^{(3)}_{xxxx}(-\omega;\omega,-\omega,\omega)$ for the case of electric fields and polarizations parallel to the x axis, by using the formula of Orr and Ward.[8] This formula takes small damping into account in a phenomenological way, being applicable for a wide range of frequencies ω except the resonant excitation case.

RESULTS AND DISCUSSION

In the following discussion we define a quantity which we will call the contribution of double excitations to a calculated state. After the diagonalization, the wave function of every calculated state is represented as an expansion over the wave functions of the Hartree-Fock ground, single-excited and double-excited states, which satisfy the chosen symmetry of the calculated state (A or B, – or +, and particular value of $|K|$). The sum of the squares of modulus of the expansion coefficients related with the wave functions of double excited states is called here the contribution of double excitations.

In Fig.1 we present the spectrum of the imaginary part of $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$ per site for $\delta t=0.2t$, $U=2t$, and $V=t$. These values were used in the previous S-CI calculations.[2] For simplicity the damping was chosen the same for all excitations, and its value ($\Gamma=0.02t$) is rather small in order to resolve all energy states. All the calculated excitation energies are much larger than those obtained in the S-CI description. This is a defect associated with the size-inconsistency of the SD-CI description. The energies will be shifted to lower values if we take into account multiple excitations higher than double excitations. In the lower part of Fig.1, we display the contribution of double excitations to the two-photon excitations, which has A$^-$ symmetry.

From the curves in Fig.1 we see that there are two groups of absorption peaks: low-energy peaks mainly due to single excitations and high-energy peaks to which double excitations contribute dominantly. The low energy part corresponds to the two-photon absorption obtained within the S-CI calculation. The magnitude of the lowest energy peak in Fig.1 is more than one order of magnitude smaller than that obtained by the S-CI calculation.[2] This is presumably because the system size N=40 used here is still smaller than the size of the A$^-$ exciton responsible for the two-photon absorption.[1] The high energy peaks may be interpreted as due to biexcitonic states, because they originate mainly from double excitations.

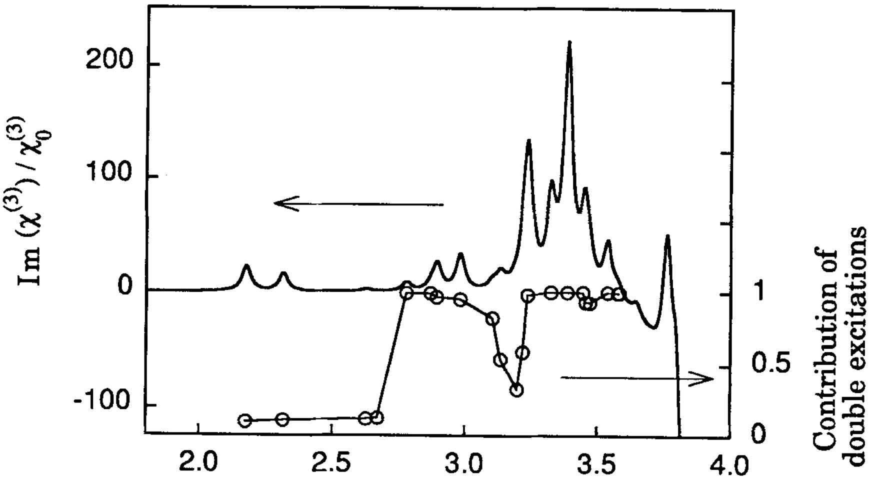

FIGURE 1 Nonlinear absorption per site (thick curve) and the contribution of double excitations to the two-photon excitations (circles) for a ring of N=40 sites with δt=0.2t, U=2t, V=t, and Γ=0.02t. $\chi_0^{(3)} = e^4a^4/t^3$.

(The argument here to distinguish excitonic and biexcitonic states is by no means rigorous, because the ground state itself has some contribution of double excitations in the SD-CI description.) We found that, in increasing N, the energy separations of the peaks become small, while the number of peaks increases. As a result, the envelope of the biexcitonic absorption does not change. Therefore, the biexcionic absorption will have a broad spectrum in the limit of $N \to \infty$.

We have examined[7] how the spectrum depends on the parameters δt, U and V. It turned out that the distinction of the excitonic and biexcitonic structures becomes less clear with either increasing interaction strength or decreasing bond alternation δt. Increase in interaction strength results in a substantial decline of the two-photon absorption, while decrease in δt has an opposite effect. In Fig.2 we show plots similar to Fig.1 but for δt=0.1t, U=4t, and V=2t. Clearly, single and double excitations are fairly mixed even in the low energy region. In spite of decreased δt, the two-photon absorption is about one order of magnitude less due to increased U and V. We may conclude that conjugated polymers with strongly

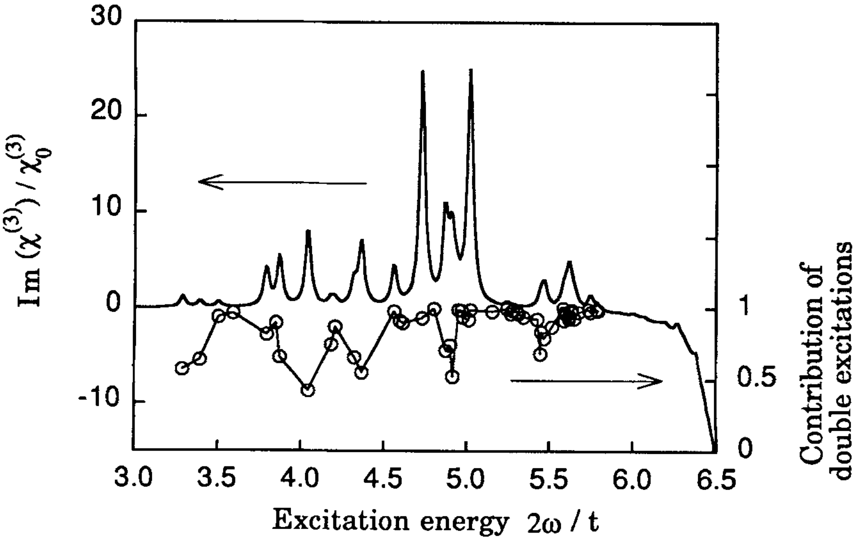

FIGURE 2 Nonlinear absorption per site (thick curve) and the contribution of double excitations to the two-photon excitations (circles) for a ring of N=40 sites with δt=0.1t, U=4t, V=2t, and Γ=0.02t. $\chi_0^{(3)} = e^4 a^4 / t^3$.

correlated electrons are poor candidates for highly nonlinear optical systems.

As for the states corresponding to the maximum of two-photon absorption, the situation in the two cases is identical — such states are practically pure two-electron excited states. The same feature was demonstrated in Ref.4 for relatively short polyenes. The overall structure of the two-photon absorption spectrum in Fig.2 coincides with that obtained in Ref.4.

In summary, we have studied the two-photon absorption spectrum of the Pariser-Parr-Pople model of conjugated polymers. Taking into account broadening in real materials, we can say, for long polymers with weak electron-electron interaction, that in the low energy part of the two-photon absorption spectrum there is a small peak, which we associate with mainly one-electron excitations (excitonic states), while the higher energy part, which results mainly from two-electron excited states (biexcitonic states), shows a wide peak with the intensity about one order of magnitude higher than the intensity of the low energy peak.

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