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IONIC TWO PHOTON STATES AND OPTICAL NONLINEARITY IN π-CONJUGATED POLYMERS

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Abstract A microscopic mechanism of optical nonlinearity in π-conjugated polymers is presented. It is shown that the bulk of the nonlinearity is determined by only two well defined channels, even though an infinite number of channels are possible in principle. The above conclusion is true for both short and long range Coulomb interactions. The complete frequency dependence of the third harmonic generation in both trans-polyacetylene and polydiacetylene are explained within the same theoretical picture.

The nonlinear optical response of π-conjugated polymers is currently a subject of considerable experimental and theoretical interest. Experimentally, polydiacetylenes are known to have very large third order nonlinear susceptibilities $\chi^{(3)}$ as well as fast responses. The figures of merit, however, are still too low for immediate application, and new materials with larger nonlinearity will have to be found for device applications[1]. For a focussed search for new materials it is essential that the microscopic mechanism of the organic optical nonlinearity is understood. The mechanism of the optical nonlinearity in these systems, however, remains unclear and controversial viewpoints regarding the importance of electron-phonon[2,3] versus electron-electron[4,5] interactions exist. Numerical calculations of $\chi^{(3)}$ for finite systems[4-7] are difficult to generalize to infinite systems. Moreover, identification of any possible dominant pathways contributing to $\chi^{(3)}$ is a formidable task from numerical calculations.

In the present paper, we identify the dominant mechanism of optical nonlinearity in π-conjugated polymers. We show that in spite of the large (practically infinite) number of excitation paths that determine the overall magnitude of $\chi^{(3)}$ in an infinite chain, the dominant contributions come from a limited number of well-defined excitation paths. The essential one and two-photon states both lie at the optical band edge in the infinite chain, independent of the magnitude and range of Coulomb interactions or the extent of bond alternation. Most importantly, this is true for both short range (extended Hubbard) and long range (Pariser-Parr-Pople) Coulomb interactions for the infinite chain. Preliminary results for the short range interactions have been presented elsewhere.[8] Here we demonstrate that these results remain unaltered for long range Coulomb interactions. The present "essential states" mechanism of optical nonlinearity explains the rapid saturation of $\chi^{(3)}$ with chainlength. In addition, the full freqency dependence of $\chi^{(3)}$ in both trans-polyacetylene[9] and polydiacetylenes[10] is explained for the first time *without invoking either weak Coulomb interactions*[3] *or interchain interactions.*[5] Our results are also consistent with the observation of subgap two photon states in finite polyenes[11] and a polydiacetylene oligomer.[12]

The third order susceptibility $\chi^{(3)}(-3\omega;\omega\omega\omega)$ which leads to third harmonic generation (THG) is written as,

$$\chi^{(3)}(-3\omega;\omega\omega\omega) = \sum_{l}\sum_{k}\sum_{n} < G|\mu|\ell B >< \ell B|\mu|kA >$$

$$< kA|\mu|nB >< nB|\mu|G > \times \{D_1(\omega) + D_1(-\omega) + D_2(\omega) + D_2(-\omega)\} \qquad (1)$$

where G is the ground state, the B and A states are antisymmetric and symmetric with respect to the mirror plane passing through the center of the chain, and l, k, n are quantum numbers defining the relevant states. The dipole moment couples A states to B states only (the ground state is $1A$). D_1 and D_2 are given by

$$D_1^{-1}(\omega) = (\omega_{\ell B} + 3\omega)(\omega_{kA} + 2\omega)(\omega_{nB} + \omega) \qquad (2a)$$

$$D_2^{-1}(\omega) = (\omega_{\ell B} + \omega)(\omega_{kA} + 2\omega)(\omega_{nB} - \omega) \qquad (2b)$$

with all eigenstates energies being relative to that of the ground state.

Our objective here is to argue that a very small number of states dominate the triple sum, and to identify these states in the infinite chain limit. These states are described by the Hamiltonian,[13,14]

$$H = U\sum_{i} n_{i\uparrow}n_{i\downarrow} + \sum_{i,j} V_j(n_i - 1)(n_{i+j} - 1) + t\sum_{i,\sigma}(1 \pm \delta)(c^{+}_{i,\sigma}c_{i+1,\sigma} + h.c.) \qquad (3)$$

where $c^{+}_{i,\sigma}$ 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_j's are the onsite and intersite Coulomb repulsions, t the one electron hopping integral and δ the bond alternation parameter. We have chosen $t = 1$ in our calculations.

In order to arrive at a proper mechanism of optical nonlinearity we have numerically evaluated every individual dipole moment as well as the individual terms that enter into Eq. (1) for linear chains with $N = 4, 6$, and 8 atoms. We start with the simple Peierls (Hückel) model with $U = V_j = 0$ because this model allows us to understand precisely the role played by finite size. To eliminate most of the finite size contributions, we make δ artificially large ($\delta \sim 0.4 - 0.5$) such that all interlevel separations are close to their asymptotic magnitudes.[15] For nonzero Coulomb interactions, we present the results for short range (extended Hubbard) and long range (PPP) Coulomb interactions seperately. In all cases, our motivation is to understand the behavior of the ideal infinite polyene rather than to fit the data for finite molecules.

Our results for the Peierls-Hückel model are as follows. For $\delta = 0.4$, where finite size effects are minimal,[15] the oscillator strength of the allowed linear absorption from the ground state is concentrated in the $1B$ state. This concentration is strong enough that retaining a single term ($l = n = 1$) in each of the two sums over B states in Eq. (1) is enough to yield the bulk of the $\chi^{(3)}$ at all nonresonant frequencies. This is a consequence of one dimensionality,[16] and is true for arbitrary N as long as the single B state is interpreted as a small collection of states at the conduction band edge. The relevant excitations out of the $1B$ state are of two kinds, involving inter and intraband excitations respectively. The large dipole moment between the $1A$ and the $1B$ states implies that there are only two interband channels. In one of these the particle-hole created in the first step is destroyed, in the other a second particle-hole pair is created. The single particle states involved in the latter process are also band edge states. The oscillator strength of the intraband process is found to be overwhelmingly concentrated in the $2A$ state, which lies immediately above the $1B$ state and is degenerate with the latter for $N \rightarrow \infty$. Thus there are only three dominant channels contributing to $\chi^{(3)}$ for $U = V_j = 0$. These results predict a two-photon resonance at $E_g/2$, where E_g is the band gap, in agreement with previous work.[3]

For short range Coulomb interactions (U, $V_1 \neq 0$; $V_j = 0$ for $j \geq 2$), the transition from $1A$ is again very strongly concentrated in the $1B$ state. For different parameters giving the same optical gap (e.g., $\delta = 0.4$, $U = V_1 = 0$ vs. $\delta = 0.3$, $U = 1.0$ and $\delta = 0$, $U = 2.0$) the dipole moment between the $1A$ and $1B$ states are nearly the same. Once again the $l = n = 1$ terms in Eq.(1) dominate overwhelmingly. Appearance of subgap A states below the $1B$ state characterizes correlated systems. Calculations, however, indicate that the dipole moments between subgap A states and the $1B$ state, normalized to

$< G|\mu|\ell B >$, decrease with N for fixed U, V_1, δ and with U for fixed N. Both these features imply that the contribution of subgap A states to nonlinear optical properties of the *infinite* chain is negligible.

Independent of U, V_1, δ and N we find that a single A state that lies immediately above the 1B state dominates $\chi^{(3)}$. We refer to this specific A state as the mA state. The dipole moment of this state with $1B$ is one to two orders of magnitude larger than the average dipole moment between an arbitrary A state and the $1B$ state, so that the corresponding term that goes in the triple sum in Eq. (1) is two to three orders of magnitude larger. Calculations were done for a very wide range of parameters $(0 \leq U \leq 50, 0 \leq V_1 \leq 20, 0 \leq \delta \leq 0.4)$, and while in a few cases there is another A state between the mA and $1B$, in all cases the mA state is bounded by the $1B$ and the $2B$ states. Large dipole moments between $1B$ and higher A states have been noted before. The new result is that there is only one such state, and that its location is independent of U, V_1, δ and N, even though the quantum number m depends on each of these parameters. This is shown in Fig.1 for $N = 6$ and representative U, V_1 and δ.

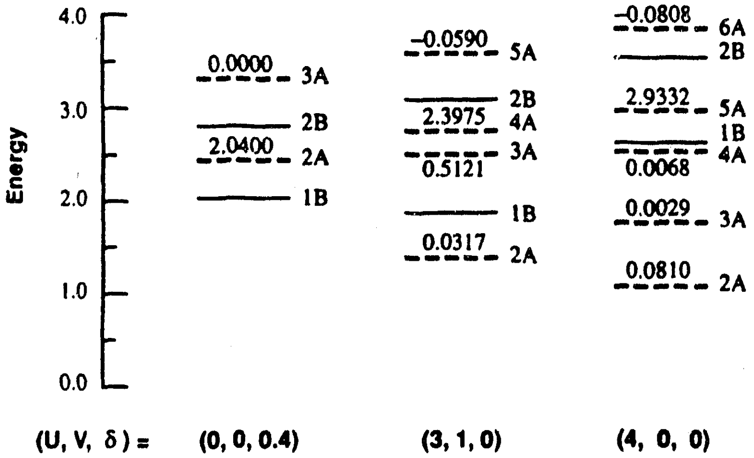

FIGURE 1 The $1B$, $2B$ (solid lines) and neighboring A (dashed lines) states for $N = 6$ and several different U, V_1 and δ. In all cases the ground state is at zero energy. The numbers against the dashed lines are the dipole moments between the corresponding A states and the $1B$ state. In all cases this dipole moment is very large for an A state located between $1B$ and $2B$ states.

We now present the results for long range interactions. Straightforward

PPP calculations will place the mA state above the $2B$ state.[4,5] This result, although correct for finite polyenes, is not representative for the infinite chain. Mazumdar and Campbell had earlier derived several exact results[14] for arbitrary long range convex interactions for the infinite chain. Many of these become invalid for finite open chains whose lengths are shorter than the range of the interaction. This implies extremely strong finite size effect which can be eliminated only by assuming Coulomb interactions that are periodic (for e.g., $V_7 = V_1, V_6 = V_2$ and $V_5 = V_3$ for $N = 8$) while, however, not allowing electron transfer between sites 1 and N. This immediately brings the mA state between the $1B$ and $2B$ states, as shown in Fig.2. Details will be published elsewhere.

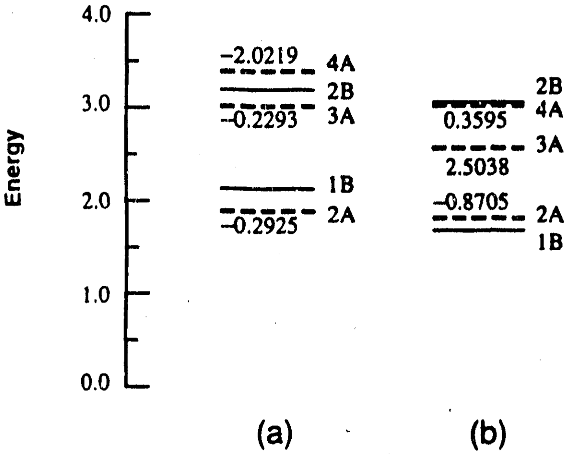

FIGURE 2 The $1B$ and $2B$ (solid lines) and neighboring A (dashed lines) for $N = 6$ PPP parameters. (a)Regular PPP parameters. (b)PPP parameters with periodic V_j's. The numbers against the dashed lines have the same meaning as in Fig.1.

Since the mA state is always bounded by $1B$ and $2B$ this state lies very close to the $1B$ state for $N \to \infty$, and is presumably degenerate. The variation of m as a function of U and N is shown in Fig. (3). It is seen that m saturates to final values of $m = 3$, 5, and 11 for $N = 4$, 6, and 8 respectively. These numbers are significant. The number of covalent valence bond diagrams for $N = 4$, 6, and 8 are 2, 5 and 14, and these combine to give 2, 4 and 10 A states that are coupled to the B states in Eq. (1). Thus in all cases the saturation values necessarily correspond to the *lowest ionic A state.*

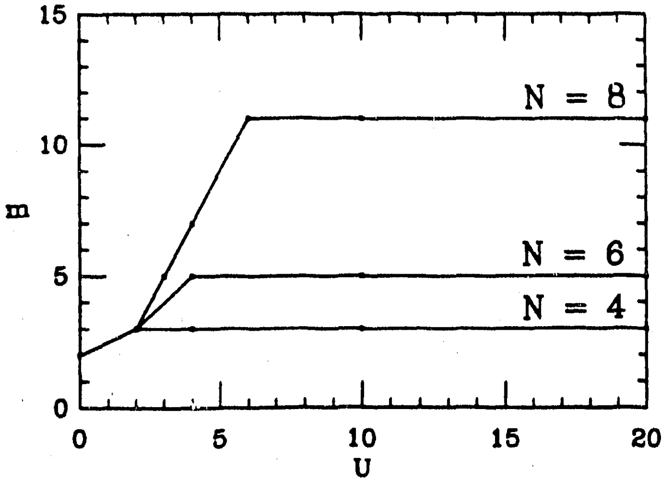

FIGURE 3 The quantum number m of the A state which has very large dipole moment with the optical $1B$ state as a function of U for various chain lengths.

Summarizing the above results, we conclude that only the very lowest *ionic* A and B states contribute strongly to the $\chi^{(3)}$ of the infinite chain. A states that are far from the optical "band edge" on either side make only small quantitative contributions. As a consequence of one dimensionality, all dipole moments are concentrated at the lower edges of the relevant subspaces, and hence the infinite chain can be considered as a broadened three level system.

The above explains the observed saturation of $\chi^{(3)}$ as a function of N.[3] At small N both "interband" and "intraband" gaps are dominated by finite size effects. Allowed dipole moments are known to increase with the decrease in the gaps. These gaps decrease very rapidly with increasing N in the small N region, leading to a rapid increase in the numerator and a decrease in the denominator in Eq. (1). The number of channels for $\chi^{(3)}$ processes, however, remain virtually two, so that once the gaps between the $1B$ and the $1A$, and that between the $1B$ and the mA are close to their asymptotic values, little additional increase in $\chi^{(3)}$ occurs.

Most importantly, we show that the essential states mechanism explains the complete frequency dependence of $\chi^{(3)}$ within an isolated strand model for realistic Coulomb correlations[3,4,13,14] without invoking any interchain interactions.[5] Since the dominating two photon state is shown to lie immediately above the $1B$ state in the infinite chain, a two photon resonance in THG is expected at $E_g/2$ for arbitrary U, V_j and δ. This is shown in Fig.4, where we have plotted $\chi^{(3)}(-3\omega;\ \omega,\ \omega,\ \omega)$ for four representative values of U and V_1 with the same lifetime parameters. It is seen that that *nearly identical spectra are obtained* in all cases. The nonzero U, V_1 results are the same as that for $U = 0$ for arbitrary N. From Fig.2, the same result is expected for the infinite PPP chain. For the smallest nonzero lifetimes, all other two photon resonances, be they above or below the optical gap, disappear, indicating that the nonresonant contributions from the essential states to $\chi^{(3)}$ outweigh the resonant contributions. This therefore explains not only the location of the two photon resonance but also why only *one* such resonance is observable. Neither the $U = 0$ approximation nor interchain interactions need be invoked to explain the THG data.

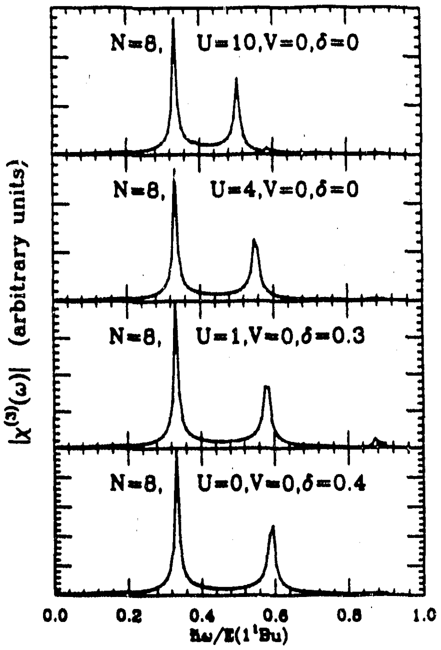

FIGURE 4 Frequency dependent third order susceptibility for four different sets of parameter values for $N = 8$. The strong two photon resonance moves to $\frac{E_g}{2}$ for $N \rightarrow \infty$. Notice that the subgap two photon states for finite U are not visible.

The applicability of a "finite U" model then would depend on whether or not the model is able to explain seemingly incompatible data and materials. Elsewhere[13] it has been argued that the optical gap is dominated by Coulomb correlations, and that such a model can integrate[13] the observations in both polyacetylene and polydiacetylene. Present work would predict that the THG of these materials should be similar. Existing THG as well as D.C. induced second harmonic generation in polydiacetylenes[10(a),10(b)] strongly support our model, – in both experiments a two photon resonance was observed at an energy that was nearly half the optical frequency. While it is not possible for us to predict whether the mA state is exactly degenerate with the $1B$, we would predict that it is bounded by the excitonic state at 2.0 eV and the conduction "band" at 2.5 eV in the ordered polydiacetylenes. As shown in Fig.2, shorter effective conjugation lengths in disordered materials or solutions would push the mA to considerably higher energy. Experimentally also shorter conjugation lengths lead to larger gaps between mA and $1B$ states.[17] We are aware of the recent two photon absorption (TPA) experiment of Fann et.al.,[18] who find a broad two photon state at an energy considerably higher than the $1B$ threshold in poly-4BCMU polydiacetylene. Soos et al.[19] attempt to explain this within the PPP model, and predict the mA state at ~ 1.6 Eg. As shown here, this result is an artifact of finite size calculation. We therfore believe that the location and the width of the observed TPA in poly-4BCMU is strongly influenced by disorder indeuced thermochromism.

To summarize, we have determined the mechanism of optical nonlinearity in organic conjugated polymers for the first time. We are able to explain the THG spectra of both polyacetylene and the polydiacetylenes within the same model. It is not necessary to invoke either weak interactions or interchain interaction. The similarity in the THG spectra is a clear signature of the role of Coulomb correlations. Our work is consistent also with experiments on finite polyenes[11] and a polydiacetylene oligomer.[12]

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