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Essential-states mechanism of optical nonlinearity in π-conjugated polymers

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We present a microscopic mechanism of optical nonlinearity in conjugated polymers. 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. We are able to explain the complete frequency dependence of the third-harmonic generation in both *trans*-polyacetylene and polydiacetylene within the same model without invoking weak Coulomb interactions between electrons or interchain interactions.

The nonlinear optical response of π-conjugated polymers is currently a subject of considerable experimental and theoretical interest because of their potential use in all optical devices. Experimentally, polydiacetylenes are known to have very large third-order nonlinear susceptibilities $\chi^{(3)}$. The mechanism of the optical nonlinearity in these systems, however, remains unclear. Controversial, and sometimes contradictory, viewpoints regarding the importance of electron-phonon[1,2] versus electron-electron[3,4] interactions exist. Numerical calculations of $\chi^{(3)}$ for finite systems[3-6] 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 this 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, only two excitation paths involving essential one- and two-photon states at the optical band edge of the infinite chain account for the bulk of the $\chi^{(3)}$. Most importantly, the *nature* of the essential two-photon state depends on the relative contributions of Coulomb interaction between electrons or bond alternation to the optical gap, but its *location* with respect to the optical band edge is completely parameter independent. We are able to give a microscopic explanation of the rapid saturation of $\chi^{(3)}$ with chain length in polyenes. Finally, the full frequency dependence of $\chi^{(3)}$ in both *trans*-polyacetylene[7] and the polydiacetylenes[8] is explained within the same unified model. In contradiction to a earlier claim,[2] it is not necessary to adopt a weak Coulomb interaction model to explain the $\chi^{(3)}$ spectrum of the former, and our results are consistent with the observation of subgap two-photon states in finite polyenes.[9] Similarly, we show that a single-strand model is enough and invoking interchain interactions[4] is unnecessary.

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

$$\chi^{(3)}(-3\omega;\omega,\omega,\omega)=\sum_{l}\sum_{k}\sum_{n}\langle G|\mu|lB\rangle\langle lB|\mu|kA\rangle\langle kA|\mu|nB\rangle\langle nB|\mu|G\rangle[D_1(\omega)+D_1(-\omega)+D_2(\omega)+D_2(-\omega)]\,, \tag{1}$$

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

$$D_1^{-1}(\omega)=(\omega_{lB}+3\omega)(\omega_{mA}+2\omega)(\omega_{nB}+\omega)\,, \tag{2a}$$

$$D_2^{-1}(\omega)=(\omega_{lB}+\omega)(\omega_{mA}+2\omega)(\mu_{nB}-\omega)\,, \tag{2b}$$

with all virtual-state 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 within the Peierls–extended Hubbard model,[10,11]

$$H=U\sum_{i}n_{i\uparrow}n_{i\downarrow}+V\sum_{i}n_{i}n_{i+1}+t\sum_{i,\sigma}(1\pm\delta)(c_{i,\sigma}^{\dagger}c_{i+1,\sigma}+\text{H.c.}) \tag{3}$$

where $c_{i,\sigma}^{\dagger}$ creates an electron of spin σ at site i, $n_{i,\sigma} = c_{i,\sigma}^{\dagger} c_{i,\sigma}$, $n_i = \sum_\sigma n_{i,\sigma}$, U and V are the on-site and nearest-neighbor Coulomb repulsions, t the one-electron hopping integral, and δ the bond alternation parameter. We have chosen $t = 1$ in our calculations. We do not specify the magnitudes of U and V yet. As we demonstrate below, the dominant excitation paths that determine optical nonlinearity are virtually independent of U and V.

In order to arrive at a proper mechanism of optical nonlinearity we have numerically evaluated very individual dipole moment as well as the individual terms that enter into Eq. (1) for linear chains with $N = 4$, 6, and 8 atoms. It is instructive initially to examine the results of these calculations for the simple Peierls (Hückel) model with $U = V = 0$. This allows us to understand precisely the role played by finite-size effects. This is important, since at the chain lengths to which we are limited (or even twice these lengths) interlevel gaps are strongly dominated by finite-size contributions. At large N, the optical gap converges to a finite value, while the low-lying interlevel gaps vanish. A practical way to eliminate most of the finite-size contribution is to do simulations with artificially large δ ($\delta \sim 0.4$–0.5),[12] such that all interlevel separations are close to their asymptotic magnitudes. At the Hückel limit, calculations may be done for very long chains, but the present approach allows comparisons of Hückel and Hubbard chains of the same lengths while minimizing finite-size effects.

Our results for the Peierls–Huckel model are as follows. For $\delta = 0.4$, where finite-size effects are minimal,[12] 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,[13] 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 interband and intraband excitations, respectively. The large dipole moment between the $1A$ and the $1B$ states implies that there are only two interband channels, one destroying the particle hole created in the first step, the other creating a second particle-hole pair that also involves the band-edge single-particle 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 $U = V = 0$. These results predict a two-photon resonance at $E_g/2$, where E_g is the band gap, in agreement with previous work.[2]

For nonzero Coulomb interactions, it is not simple to interpret the many-electron wave functions or the excitation paths. It is shown below how dominating excitation paths between total-energy states can still be identified within a valence-bond description.[10] We use exact numerical results for finite chains over a wide range of parameters ($0 < U < 50$, $0 < V < 20$, $0 < \delta < 0.4$) to arrive at general conclusions about dominant pathways in $\chi^{(3)}$ for $N \rightarrow \infty$. Details of our results, which remain valid even for the Pariser-Parr-Pople (PPP) Hamiltonian[3,4] with long-range Coulomb interactions, will be published elsewhere. Here we summarize our most important conclusions.

At the appropriate limits where finite-size contributions have been eliminated, the transition from $1A$ is again very strongly concentrated in the $1B$ state. For different parameters giving the same optical gap (e.g., $\delta = 0.4$, $U = V = 0$ 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 dominate overwhelmingly [Eq. (2)]. For nonzero U, virtual two-photon states are both above and below the $1B$ state. However, calculations indicate that for given U, V, δ, the dipole moment between the $1B$ state and those A states that lie below the $1B$ state decrease rapidly with N, while for a given N these dipole moments decrease with U. 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, δ, and N, we find that a single two-photon state that lies immediately above the $1B$ state dominates $\chi^{(3)}$. We shall refer to this specific A state as the mA state. The dipole moment of this state with $1B$ is 1–2 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 2–3 orders-of-magnitude larger. While large dipole moments between $1B$ and certain higher A states have been found before,[3,4] the result is that there is only *one* such A state, and that its location in *independent* of U, V, δ. Even though the actual magnitude of m is a strong function of U, V, δ, and N, in all cases its energy is bounded by the energies of the $1B$ and $2B$ states. This is shown in Fig. 1 for $N = 6$ and three representative sets of U, V, δ.

Since the mA state is always bounded by $1B$ and $2B$ this state lies very close to the $1B$ state for $N \rightarrow \infty$, and is presumably degenerate. The variation of m as a function of U and N is shown in Fig. 2. It is seen that m saturates

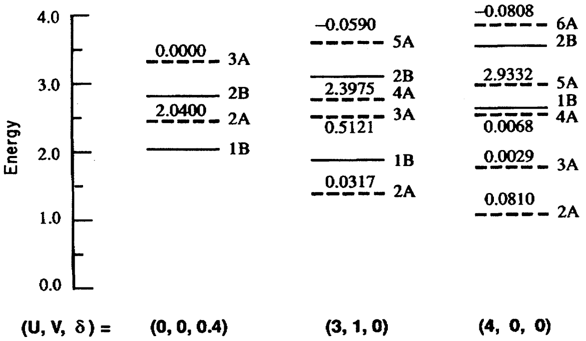

FIG. 1. The $1B$, $2B$ (solid lines) and neighboring A (dashed lines) states for $N = 6$ and several different U, V, and δ. In all cases the ground state is at zero energy. The numbers against the dashed lines are the dipole moments between the corresponding A states and the $1B$ state. In all cases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

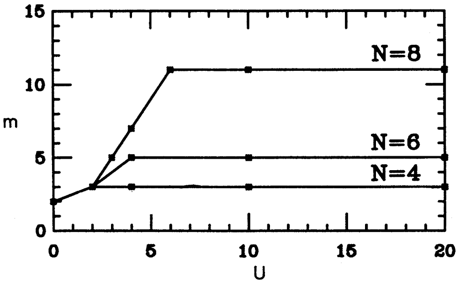

FIG. 2. The quantum number m of the A state which has very large dipole moment with the optical $1B$ state as a function of U for various chain lengths.

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. This identifies the $1B \rightarrow mA$ transition as an "intraband" process in the language of mean-field theory (i.e., the transition is within the upper or lower Hubbard subbands). Taken together with the $U=0$ result discussed above, we conclude that the dominating excitation path is of the intraband-type both at $U=0$ and at large U, for arbitrary δ and N.

In the above discussion we have focused on the low-lying covalent A states and the mA state nearly degenerate with the $1B$ state. In analogy with $U=0$, one would have anticipated a higher A state with large dipole moment with the $1B$ state. Transition to such a state would correspond to an "interband" two-particle two-hole channel. For moderate U, we find that the contribution of this channel remains larger than all other processes, but is much smaller than that of the intraband channel discussed above. This is true for all parameters except for relatively small U and large δ, where the system behaves somewhat similar to the Hückel limit, and two different two-photon channels can dominate. Even in these cases, however, the energy of the high-energy two-photon state is considerably lower that what would be expected in a typical interband process. For realistic parameters and large N, this state is expected to contribute little to optical nonlinearity.

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. This is a consequence of one dimensionality alone, and the infinite chain can be considered as a broadened three-level system.

The above explains the observed[3] saturation of $\chi^{(3)}$ as a function of N. 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 important point, however, is that the number of channels for $\chi^{(3)}$ processes remain virtually two, so that once the gaps between the $1B$ and the $1A$ states, and that between the $1B$ and the mA, are close to their asymptotic values, little additional increase in $\chi^{(3)}$ occurs in spite of the increase in the total number of terms in Eq. (1).

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.[3,4,10,11] 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, and δ. This is shown in Fig. 3, where we have plotted $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ for four representative values of U and V with the same lifetime parameters. It is seen that nearly identical spectra are obtained in all cases. The nonzero U, V results are the same as that for $U=0$ for arbitrary N. 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. As seen in Fig. 3, neither the $U=0$ approximation nor interchain interactions need be invoked to explain the THG data.

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[10] it has been argued that the optical gap is dominated by Coulomb correlations, and that such a model can integrate[10] the observations in both polyacetylene and polydiacetylene. Present work would predict that the THG

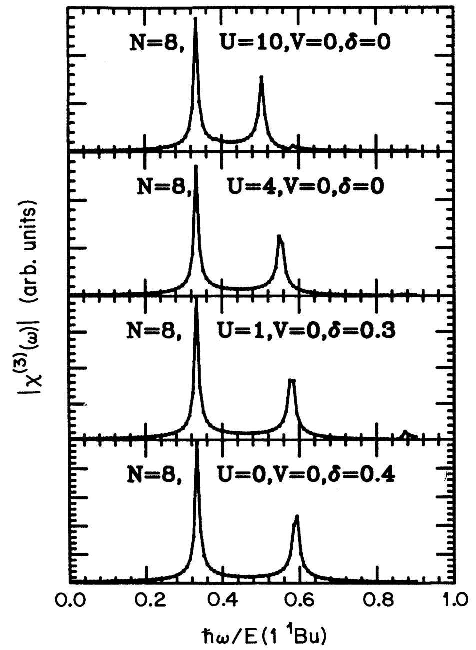

FIG. 3. Frequency-dependent third-order susceptibility for four different sets of parameter values for $N=8$. The strong two-photon resonance moves to $E_g/2$ for $N \rightarrow \infty$. Notice that the subgap two-photon states for finite U are not visible.

of these materials should be similar. Existing THG as well as dc induced second-harmonic generation in a polydiacetylene[8] 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. Shorter effective conjugation lengths in disordered materials and in solutions would push the *mA* state to considerably higher energy. We are aware of the recent two-photon absorption (TPA) experiment of Etemad,[14] who find a broad two-photon state at an energy considerably higher than the $1B$ threshold in poly-4BCMU polydiacetylene (poly-(5,7-dodecadiyne-1,12diol bis(*n*-butoxycarbonylmethylurethane))). We believe that this is in agreement with our theory. The location and the width of the TPA here is strongly influenced by thermochromism induced disorder. As this original version of the paper was being written we received a copy of the unpublished work of Soos, McWilliams, and Hayden,[15] who also stress the role of a high-energy two-photon state in order to explain the above experiment. However, Soos, McWilliams, and Hayden,[15] work with PPP parameters and predict the *mA* state to occur at an energy that is considerably higher than the $1B$ state (at $\sim 1.6E_g$). Interchain interaction is invoked to explain the THG of *trans*-polyacetylene. As shown here, both the TPA experiment and the calculations reflect finite-size behavior. Independent of parameters, the *mA* state remains bounded by the $1B$ and the $2B$, and *m* corresponds to the lowest ionic state.

To summarize, we have shown that the mechanism of optical nonlinearity in rigid-band linear chains is parameter independent. We are able to explain the THG spectra of both polyacetylene and polydiacetylenes without invoking either weak Coulomb interactions or interchain interaction. The similarity in the THG spectra is a clear signature of Coulomb correlations. The generality of our results makes them applicable to a wide variety of systems describable by the Peierls-extended Hubbard Hamiltonian.

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