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Static and dynamic third-harmonic generation in long polyacetylene and polyparaphenylene vinylene chains

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We have calculated the full spectrum of the third-order optical susceptibility, $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ in long oligomers of polyacetylene and polyparaphenylene vinylene, in the framework of a simple one-electron tight-binding approach. All doubly excited states are explicitly included in a sum-over-states formulation. The damping factors associated with resonances with excited states are modulated as a function of excited-state energy. Both the length dependence and the dynamic behavior of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ are found to be in excellent agreement with experiment. Our results thus show that, contrary to the situation in very short polyenes, a one-electron theory can provide an accurate description of the nonlinear optical response in conjugated polymers.

Great experimental and theoretical interests have recently been paid to the nonlinear optical (NLO) properties of conjugated polymers.[1-3] Due to their structural simplicity, linear polyenes and polyacetylene have been the focus of most of the theoretical work.[4-11] Very elegant quantum-chemical calculations have been performed, which take explicit account of the details of the molecular structure and electron-electron interaction effects.[4-8] Because of computer limitation problems, such calculations are, however, restricted to short polyenes, containing typically less than twenty carbons.

This is the reason why polyacetylene, the infinite polymer chain system, has been treated within a one-electron approach by Wu,[9] Wu and Sun,[10] and Yu *et al.*[11] Wu[9] and Wu and Sun[10] have obtained results in qualitative agreement with experiment. For instance, these authors found the presence of two peaks in the $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ spectrum at about 0.6 and 0.9 eV. However, as pointed out by Wu and Sun,[10] the 0.9-eV two-photon peak is washed away as soon as a finite damping factor is included to treat the resonance behavior. Moreover, Yu *et al.*[11] have not been able to reproduce the two-photon resonance peak at all, within their one-electron approach. On the other hand, in the context of a strongly correlated electron theory applied to short chains, Soos and Ramesesha obtain the two-photon peak to be shifted too low in frequency and to have too small an intensity relative to the experimental peak.[12]

In this work we deal with another approach. Within single-electron theory including double excited states, we apply a sum-over-states (SOS) formalism to oligomer chains of increasing length in order to be able to produce simultaneously the chain-length dependence and the dispersion of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$.

In linear polyenes, Garito *et al.*[4] have shown that the NLO response is primarily a function of the molecular length rather than conformation (*trans* or *cis*) of the compound. Therefore, we have simply modeled the polyacetylene chains as one-dimensional (1D) dimerized systems in the framework of a Su-Schrieffer-Heeger (SSH) Hamiltonian.[13] The lattice constant is taken to be $2a=2.44$ Å; the electron-phonon coupling constant is set at $\alpha=7.5$ eV/Å and the dimerization factor at $u=0.03$ Å for all chain lengths. These parameters lead to a one-electron band gap of 1.8 eV for very long chains, in agreement with the experimental data.

Within an SOS approach, the third-order polarizability can be expressed as[14]

$$\gamma_{\alpha\beta\gamma\delta}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)=h^{-3}K(-\omega_\sigma;\omega_1,\omega_2,\omega_3)\times\left[\sum_p\left\{\sum_{m,n,p(\neq g)}\frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\delta|g\rangle}{(\omega_{mg}-\omega_\sigma-i\Gamma_{mg})(\omega_{ng}-\omega_1-\omega_2-i\Gamma_{ng})(\omega_{pg}-\omega_1-i\Gamma_{pg})}\right\}-\sum_p\left\{\sum_{m,n(\neq g)}\frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\sigma|g\rangle}{(\omega_{mg}-\omega_\sigma-i\Gamma_{mg})(\omega_{ng}-\omega_1-i\Gamma_{ng})(\omega_{ng}+\omega_2-i\Gamma_{ng})}\right\}\right]. \quad (1)$$

In this expression, $\omega_\sigma=\omega_1+\omega_2+\omega_3$ is the polarization response frequency; $\omega_1,\omega_2,\omega_3$ indicate the frequencies of perturbing radiation fields [for third-harmonic-generation (THG) processes, $\omega_1=\omega_2=\omega_3=\omega$]; K is a numeric coefficient determined by the nature of the nonlinear optical process, for THG, $K=\frac{1}{4}$;[14] $\sum_p$ indicates a summation over the 24 terms obtained by permuting the frequencies; m, n, and q denote excited states and g, the ground state (all states correspond to single Slater determinants); μ_α is the $\alpha(=x,y,z)$ component of the dipole operator; ω_{ng} is the transition frequency between the n and g states and Γ_{ng} is the damping of the excited state n. The calculation of transition elements in molecules is carried out in the context of Slater determinants D's.[15] Ground state $|g\rangle=D_0$, where all doubly occupied one-electron levels are taken; excited state $|m\rangle=D_{i\rightarrow r}$, $i(\in$ occ.) is substituted by $r(\in \text{unocc.})$. In this way, orthogonality is fully guaranteed by the orthogonal character of the one-electron levels. There are three possibilities to construct $|n\rangle$ in the first term of Eq. (1), in order to have nonzero $\langle m|\mu|n\rangle$ transition moments: (i) $|n\rangle = D_{i\to s}$; (ii) $|n\rangle = D_{j\to r}$; (iii) $|n\rangle = D_{(i\to r, j\to s)}$, i.e., the doubly excited states ($i,j \in$ occ., $r,s \in$ unocc.). Excited state $|p\rangle$ should correspond to a one-electron excitation with respect to $|g\rangle$ and depends on actual $|n\rangle$ state. Considering the charge conjugation symmetry in the Hückel approach, and noticing that the second term of Eq. (1) is canceled when including double excitations in the first term,[5] (which ensures that below resonance, the γ value is positive), we can illustrate the three relevant summation channels mentioned above by the three schemes given in Fig. 1. We should point out that the contribution from Fig. 1(a) is positive, while that from Fig. 1(b) is negative. Figure 1(c) is the double excitation channel after extracting the unlinked processes, so quantitatively it is not important. Only in this way that the contributions from Fig. 1(b) always counteract those from Fig. 1(a), can the saturation reach. It explains that within the correlated electron theory there is no indication for saturation even for a system with 20 double bonds.[7] The reason is that one kept only the contributions of the Fig. 1(a) kind, for instance, $|m\rangle = |p\rangle = 1B_u$.[4-6] For small N, Fig. 1(b) is really not important, but with increasing N, it becomes comparable to Fig. 1(a).

For the THG coefficient in 3D average,[2] $\chi^{(3)}$ is expressed as

$$\chi^{(3)} = \frac{\sigma}{Na} f_L \gamma_{xxxx}/5 ,$$

where σ is the number of chains per unit section; for polyacetylene $\sigma_{\mathrm{PA}} = 3.2\times10^{14}\ \mathrm{cm}^{-2}$.[11] The f_L term corresponds to the local field correction and following Yu *et al.*[11] is taken to be equal to 10.

In Fig. 2, we display the chain-length dependence of the static $\chi^{(3)}_{\mathrm{THG}}(0)$ for polyacetylene oligomers, together with an effective $\tilde{\chi}^{(3)}_{\mathrm{THG}}(0)$ in order to remove the length dependence of the band gap. For a chain containing N carbons, the effective $\tilde{\chi}^{(3)}_{\mathrm{THG}}$ is written as

$$\tilde{\chi}^{(3)}_{\mathrm{THG}}(0) = \chi^{(3)}_{\mathrm{THG}}(0)\frac{E_g^3(N)}{E_g^3(\infty)} .$$

We find that $\chi^{(3)}_{\mathrm{THG}}(0)$ saturates around $N = 50$ carbon sites, i.e., a chain length on the order of 60 Å. This is in excellent agreement with the estimate of Garito *et al.*,[4] based on an extrapolation of their short-chain calculations and a comparison with the infinite polymer data.

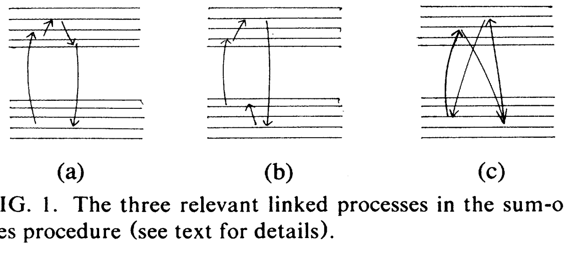

FIG. 1. The three relevant linked processes in the sum-over-states procedure (see text for details).

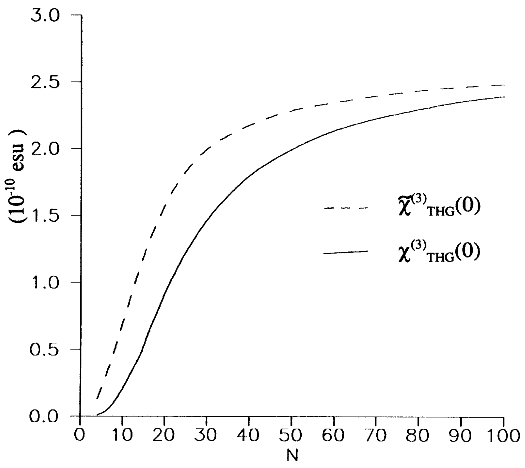

FIG. 2. The length dependence of $\chi^{(3)}_{\mathrm{THG}}(0)$ and the effective $\tilde{\chi}^{(3)}_{\mathrm{THG}}$ for linear polyenes.

For the short-chain oligomers ($N \sim 10$), we calculate a chain-length dependence of $\gamma(0)$ as

$$\gamma(0) \sim N^{4.32} .$$

This 4.32 exponent also agrees remarkably well with the exponents derived from quantum-chemical calculations on short polyenes, which explicitly include electron-electron interaction and electron correlation effects.[4-8] These calculations provide a power dependence in the range 4.0–4.6. As already pointed out by Soos, Hayden, and McWilliams,[5] one-electron approaches are currently the only ones allowing to calculate directly the saturation dependence, as this requires to deal with very long chains.

When considering the $\chi^{(3)}_{\mathrm{THG}}$ dispersion behavior, the originality of our methodology lies in the treatment of the damping factor. We simply consider that the higher the excited state, the shorter the lifetime of the state,[16] we therefore assume the damping as

$$\Gamma_{mg} = \alpha\Delta\epsilon_m ,$$

where $\Delta\epsilon_m$ is the one-electron level separation of excited state and α is an adjustable constant. (Note that the precise choice of the α value does not affect at all the off-resonance value and the relative intensities between the resonance peaks calculated in the $\chi^{(3)}_{\mathrm{THG}}$ dispersion spectrum.) By doing so, we eliminate all the fluctuations caused by the divergence of the denominator in Eq. (1).

In Fig. 3, we display the $\chi^{(3)}_{\mathrm{THG}}$ spectrum of a long polyacteylene chain containing 200 carbons and compare it to the free-electron laser data of Fann *et al.*[12] and the single-frequency ($\hbar\omega = 1.17$ eV) result of Sinclair *et al.*[17] To match the absolute values of the resonance peaks at 0.6 eV (three-photon resonance) and 0.9 eV (two-photon resonance), the α value is set at 6.

We observe an extremely good agreement between our theoretical results and the experimental spectra, in terms of (i) absolute $\chi^{(3)}_{\mathrm{THG}}$ values outside of resonance, and (ii) relative intensities of resonance peaks. For instance, off resonance at $\hbar\omega = 1.17$ eV, we calculate a value for $\chi^{(3)}_{\mathrm{THG}}(1.17\ \mathrm{eV}) = 2.88\times10^{-10}$ esu, while the experimental

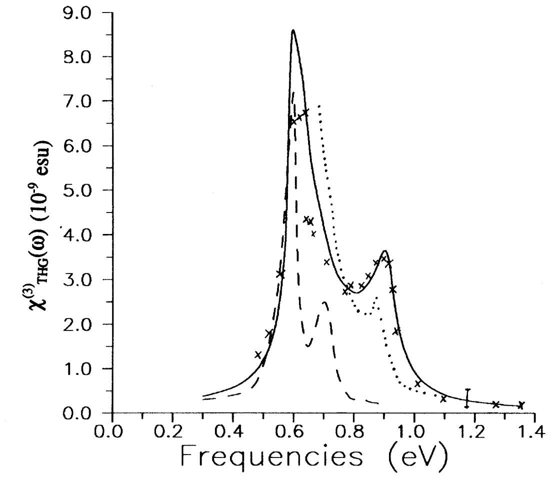

FIG. 3. Third harmonic generation in polyacetylene: crosses represents the experimental data of Fann *et al.* (Ref. 12); the dashed line indicates the correlated electron theory results of Soos and Ramesesha for short polyene ($N=8$) (Ref. 5); the dotted line is the one-electron theory results of Wu (Ref. 9); the solid line shows the results of the present work on a 200-carbon chain.

number reported by Sinclair *et al.* is $(4\pm2)\times10^{-10}$ esu.[17] The peak intensities present a calculated ratio around 3:1 for the 0.6:0.9 eV resonances; experimentally, the peak intensities correspond to $\sim6\times10^{-9}$ esu at 0.6 eV and $\sim2\times10^{-9}$ esu at 0.9 eV.

The implications of our results are important. They suggest that (i) polyacetylene can be described as a weakly interacting system, as proposed by Wu and Kivelson,[18] even when referring to its NLO properties. (ii) The first A_g excited state (two-photon state) of importance for the $\chi^{(3)}_{\rm THG}$ response of polyacetylene is located near the $1B_u$ band gap. This does not imply that lower-lying A_g excited state(s) are not present in the gap (our one-electron methodology cannot describe such states), but if so, they appear not to affect the resonance at 0.6 eV appreciably. (iii) Since our approach based on a rigid-lattice approximation works well, it also seems that the role of lattice quantum fluctuations[11] in the THG nonlinear response is relatively minor. We note that Yaron and Silbey[19] have recently shown that the vibrational contributions to the polyacetylene γ amount to about 10% of the value obtained ignoring vibrations. (iv) We note that, for the first time to the best of our knowledge, the 0.9-eV peak is calculated, at the one-electron theory level, to correspond to a real resonant feature. As mentioned previously, in earlier contributions, this peak was found to disappear as soon as a finite damping was introduced.

We have also applied the same formalism to polyparaphenylene vinylene (PPV), a conjugated polymer which

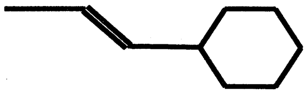

FIG. 4. Molecular geometry of PPV.

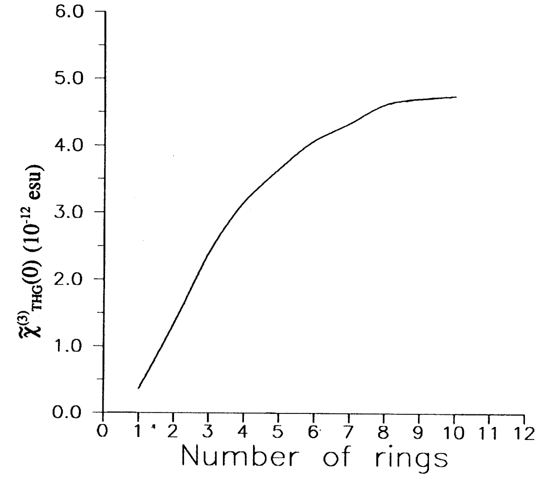

FIG. 5. The length dependence of the third-harmonic generation in PPV.

exhibits attractive NLO properties.[20] Due to the availability of a soluble precursor route, thin films of PPV can be synthesized which present good environmental stability, mechanical properties, and optical quality. X-ray scattering data[21] (lattice constants: $a=8.15$ Å, $b=6.07$ Å, $c=6.6$ Å), and Hartree-Fock semiempirical AM1 (Austin Model 1) geometry optimization calculations[22] result in a PPV molecular structure as shown in Fig. 4. We have previously worked out the parameterization of a SSH-type Hamiltonian to describe the geometry and electronic structure of PPV.[23] The same parameterization is now applied to investigate the third-order NLO response. From the x-ray data, the number of chains per section is $\sigma_{\rm PPV}=2\times10^{14}$ cm^{-2}.[21]

Looking at the chain-length dependence of $\chi^{(3)}_{\rm THG}(0)$, saturation is found for a number of unit cells of ca. 8, which amounts to ≈64 carbon atoms (see Fig. 5). The saturation thus occurs in the same range as for polyenes. The dynamical $\chi^{(3)}_{\rm THG}$ susceptibility is shown in Fig. 6. The

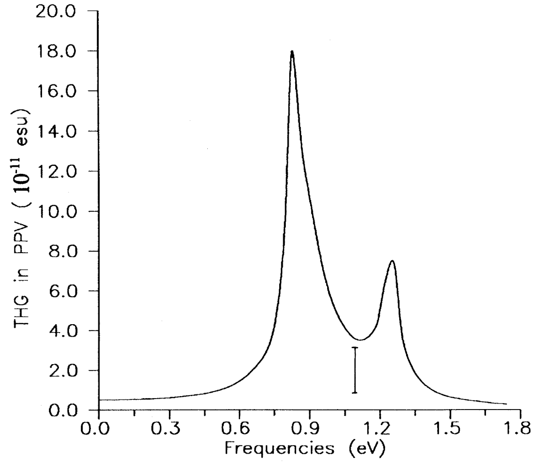

FIG. 6. Calculated third-harmonic-generation spectrum in PPV, the single frequency measurement of McBranch *et al.* (Ref. 20) is indicated with the corresponding error bar.

behavior is similar to that in polyacetylene. Because of the lack of $\chi^{(3)}_{\mathrm{THG}}$ dispersion measurements for the whole spectrum in PPV, we are able to compare our results to measurements for a single frequency at 1.17 eV. The theoretical value is $\chi^{(3)}_{\mathrm{THG}}(\omega=1.17\ \mathrm{eV})=3.8\times10^{-11}$ esu, to be compared to an experimental estimate ranging from 10^{-11} to 10^{-10} esu.[20] We thus also obtain a very reasonable agreement between theory and experiment in the case of PPV.

In summary, we have applied a one-electron theory approach including double excited states in a SOS formalism, to study the third-order NLO response in linear polyenes, i.e., polyacetylene oligomers, and PPV. Investigating the chain-length dependence of the static $\chi^{(3)}_{\mathrm{THG}}$, we calculate saturation to occur in both polymers around 50–60 carbon sites; the exponent describing this length dependence in short polyenes is in very good accord with the results of higher-level quantum-chemical calculations. For very large polyacetylene chains containing over 200 carbon sites, the dynamical $\chi^{(3)}_{\mathrm{THG}}$ susceptibility is found to be in excellent *quantitative* agreement with the free electron laser experimental data. The quality of description appears to be as good in PPV, though experimental data are scarcer for this polymer.

To conclude, we should stress we are not claiming a one-electron theory approach suffices to describe all the details of the NLO response in conjugated polymer chains. However, it is striking to realize the excellent description that such a theory is able to provide for the static and dynamic third-order optical susceptibility in representative systems such as polyacetylene and polyparaphenylene vinylene. This feature should be borne in mind when results of more refined calculations are discussed.

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