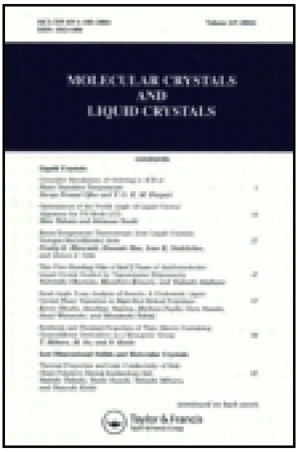

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Anisotropy of the Third Order Nonlinear Optical Susceptibility in a Degenerate Ground State Conjugated Polymer; *Trans*-$(CH)_x$

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The promise of conducting polymers as fast response nonlinear optical materials has been recently emphasized.[1–3] Polymers such as polyacetylene, polythiophene and the soluble (and processible) poly(3-alkylthienylenes) contain a high density of π-electrons, and they are known to exhibit photoinduced absorption and photoinduced bleaching, indicating major shifts of oscillator strength upon photoexcitation.[2,4] For polyacetylene, these nonlinear effects have been studied in detail in the picosecond[5a,b] and subpicosecond[5c] time regime and correlated with the photoproduction of charge carriers through fast photoconductivity measurements.[6] The data have demonstrated ultra-fast response with nonlinear shifts in oscillator strength occurring at times of the order of 10^{-13} seconds. These *resonant* nonlinear optical properties are intrinsic; they originate from the nonlinearity of the self-localized photoexcitations[7] which characterize this class of polymers: solitons, polarons and bipolarons.[4]

In any material where photoexcitation results in shifts of oscillator strength (as is the case in conducting polymers), the optical properties will be highly nonlinear. The magnitude of the *resonant* $\chi^{(3)}$ can be estimated from the magnitude and frequency dependence of the photoinduced absorption and bleaching. For example, as a result of the shift in oscillator strength subsequent to photoexcitation, the complex index of refraction is intensity dependent

$$n(\omega) = n_0(\omega) + n_2(\omega, \omega_p)\, I(\omega_p) \tag{1}$$

where the second term describes the nonlinear response at frequency ω due to an intense pump at pump frequency ω_p. Under pumping conditions which are resonant with the $\pi-\pi^*$ transition of polyacetylene ($\hbar\omega_p = 2.0$ eV), the existing data yield an estimate[2,7] for $n_2(1.4\text{eV}, 2.0\text{eV}) \approx 10^4\ (\text{MW/cm}^2)^{-1}$. This large value for n_2 implies a correspondingly large value for $\text{Im}\chi^{(3)}$ through the relation

$$n_2 = 4\pi^2/c\epsilon\ \chi^{(3)} \tag{2}$$

where ϵ is the dielectric constant at the probe frequency (ω). Using the above value for n_2, we obtain $\text{Im}\chi^{(3)}(-\omega_2 = \omega_1 - \omega_1 - \omega_2) = 5 \times 10^{-8}$ esu, an impressive value even under resonant conditions. From a Kramers-Kronig analysis of the photoinduced absorption data, one concludes that the real parts of n_2 and $\chi^{(3)}$ are correspondingly large. Based upon these observations, an experimental studies of third harmonic generation in polyacetylene and related conducting polymers were initiated in order to explore directly the third order susceptibility under nominally *nonresonant* conditions where the pump is well below the principal interband ($\pi-\pi^*$) transition.

We have determined the magnitude of the third order susceptibility associated with tripling the fundamental of the Nd:YAG laser (1.06 μm, 1.17 eV) to be $\chi^{(3)}(3\omega;\omega,\omega,\omega) = (4 \pm 2) \times 10^{-10}$ esu, where $\chi^{(3)}$ refers to that component of the third order susceptibility tensor with all indices parallel to the chain direction. By measuring anisotropic third harmonic generation in oriented films, we have shown that this component dominates. The magnitude and anisotropy were directly compared with results obtained from single crystals of polydiacetylene-(toluene-sulfonate) measured in the same apparatus. The third harmonic power generated by PDA-TS was found to be about a factor of two greater than that of *trans*-$(\text{CH})_x$ (for pumping at 1.06 μm). The anisotropy of the THG for both *trans*-$(\text{CH})_x$ and PDA-TS demonstrates that the nonlinear optical properties are entirely associated with the nonlinear polarizability of the π-electrons in the conjugated polymer backbone.

The close agreement between the THG in *trans*-$(\text{CH})_x$ and PDA-TS was inferred to be simply accidental; the nonlinear mechanisms in the two cases are different, and in neither case is the conceptually simple nonlinearity arising from the rigid band structure in third-order perturbation theory the appropriate mechanism.

Third harmonic generation was measured in both *cis*-rich and *trans* isomers of the same sample (before and after thermal isomerization). The measured response of the *cis*-rich samples was found to scale with the residual *trans* content, indicating that $\chi^{(3)}$ of the *trans* isomer is at least an order of magnitude larger than that of the *cis* isomer.

Since $\chi^{(3)}(\omega = \omega_1 + \omega_2 + \omega_3)$ is a function of three independent variables, the measured $\chi^{(3)}(3\omega = \omega + \omega + \omega)$ represents a single point on a complex three-dimensional surface. The larger $\chi^{(3)}$ values implied by the resonant photoinduced absorption measurements are located in another region of this parameter space. These two regions are not unrelated, however, since one knows that the nonresonant values of the third order susceptibility will be determined by the nature of the excited states which dominate the resonant properties.

The symmetry specific aspect of $\chi^{(3)}$ is an important result and implies a mechanism which is sensitive to the existence of a degenerate ground state, as in *trans*-$(CH)_x$. This experimental fact is consistent with a mechanism for the third order nonlinear optical susceptibility of polyacetylene which involves the generation of virtual nonlinear solitons. This mechanism has been explored in considerable detail,[8] and the connection was made to the nonlinear quantum zero point fluctuations of the polyene chain. In the absence of quantum fluctuations of the lattice, nonlinear excitations such as solitons do not affect nonresonant processes. These configurations involve lattice distortions around the photogenerated carriers; since there are no direct matrix elements between the ground state and the soliton excited states, they could only be produced by photoexcitation and subsequent decay. Inclusion of quantum fluctuations allows matrix elements directly connecting the ground state and the nonlinear excited states and thereby enables virtual solitons to affect nonresonant processes. Expressions have been derived[8] for $\chi^{(3)}(\omega,\omega_p,-\omega_p)$ (which leads to an intensity dependent complex index of refraction), and for $\chi^{(3)}(\omega,\omega,\omega)$ (which leads to third harmonic generation). In both cases, the magnitude of the virtual soliton terms are large enough to make important contributions to $\chi^{(3)}$. We conclude, therefore, that the nonlinear zero point fluctuations of the ground state lead to an important mechanism for nonlinear optical properties, particularly in polymers with a degenerate ground state. Lifting the ground state degeneracy suppresses the nonlinear response, in agreement with our experimental results. In addition, the usual interband transitions (i.e. electron-hole pairs) can be expected to influence $\chi^{(3)}$. An important goal of future work will be to sort out the relative importance of the two processes in order to understand the large nonlinear susceptibility of *trans*-polyacetylene and in order to guide the development of new and better materials.

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