NON-LINEAR POLARIZABILITIES OF CONJUGATED CHAINS: REGULAR POLYENES, SOLITONS, AND POLARONS

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The hyperpolarizabilities of linear polyenes are shown to be extremely sensitive to conformational changes and to the presence of charges along the conjugated chain. Geometries corresponding to those of regular polyenes and soliton and polaron defects are examined.

1. Introduction

In the past decade, much attention has been given to the study of the optical properties of conjugated polymers [1–5], since in these highly anisotropic systems the delocalized valence π-electrons give rise to extremely enhanced polarization responses. When an external uniform electric field of strength F acts upon a molecule of polarizability α, the induced dipole moment deviates from a simple linear dependence on the field and can be written as

$$\boldsymbol{\mu}=\boldsymbol{\alpha}\cdot\boldsymbol{F}+\tfrac{1}{2}\boldsymbol{\beta}\cdot\boldsymbol{F}^2+\tfrac{1}{6}\boldsymbol{\gamma}\cdot\boldsymbol{F}^3+\dots .$$

The coefficients β and γ (known respectively as the first and second hyperpolarizability tensors) are associated with the strength of the non-linear response to applied fields in the zero-frequency limit, i.e. the transparent region of the material. Since the first hyperpolarizability β is zero for systems with inversion symmetry, non-linear optical experiments for organic crystals and polymers have usually been devoted to the determination of γ. In addition, the interest in the electronic structure of polyenes, C_NH_{N+2}, has grown tremendously after the suggestion that conformational defects such as solitons [6] and polarons [7,8] should account for the unusual transport properties of polyacetylene, $(CH)_x$. The knowledge about the structure and properties of polyacetylene accumulated since then explains why polyenes are interesting models for the investigation of novel electronic properties of conjugated polymers. At the same time, conformational transitions on the conjugated chain are suspected to play a major role in the dramatic variation of optical properties of polydiacetylene solutions upon dilution or temperature changes [9,10].

2. Calculation

In this Letter we report calculated values of γ for molecules of the polyene family described by a Pariser–Parr–Pople (PPP) Hamiltonian [11]. The method we use is based on a perturbative expansion of the Hartree–Fock (HF) density matrix [12] R; the desired hyperpolarizabilities are directly obtained from the corrections for the electronic energy in sucessive orders. In fact, since the interaction energy can be expanded in terms of the applied field strength, γ is simply related to the coefficient of the fourth power of F. The method does *not* involve a summation over excited states but instead, it implicitly takes into account all excitations from the HF ground state. We consider polyene chains with $N\leqslant 21$ in a variety of geometries: those approximating (i)

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regular polyenes, (ii) solitons, and (iii) polarons. Hyperpolarizabilities for singly charged solitons and polarons, and doubly charged polarons (bipolarons) were also calculated for the same geometry as that of the corresponding neutral species. Different situations occur for open- and closed-shell systems since in the latter case we have a radical and an unrestricted Hartree–Fock (UHF) treatment is required. For both restricted and unrestricted cases, the perturbative density matrix (PDM) approach is competitive to alternative methods of calculation [#1] both in terms of simplicity and accuracy. The precision of the calculation is determined by the degree achieved in imposing that the idempotency of R and its commutation relation to the HF Hamiltonian are preserved to second order, since these two conditions (plus the subsidiary requirement that tr $R=N$) assure both the representability of R in terms of a single-determinant wavefunction and the self-consistent character of the HF equation [12]. In the present case, even for the largest chains both requirements were met to at least 10^{-5}.

Inclusion of electron–electron interaction terms seems to be essential to account for the observed properties of defects in polyacetylene [14]. We have thus adopted the PPP Hamiltonian since it represents an excellent compromise between efficiency and realism in the self-consistent description of the electronic structure of polyenes [15]. The standard parametrization and Ohno's expression for calculating the intersite Coulomb interactions suggested in ref. [15] have been used. Since we were interested in examining the pattern of variation of γ with increasing N for the different chain structures, for computational reasons only the ground-state HF electronic distribution was considered and no basis set optimization or reparametrization was performed. Therefore our results should be considered not in quantitative terms but rather in what they reveal about trends or patterns for the variation of γ with increasing chains and different structures. Even so, it is encouraging that the calculated values for the linear polarizabilities of regular polyenes are in fair agreement with ab initio results [16]. It should be noted that although the non-linear polarizabilities of

[#1] For a review of the quantum theory of electric polarizabilities, see ref. [13].

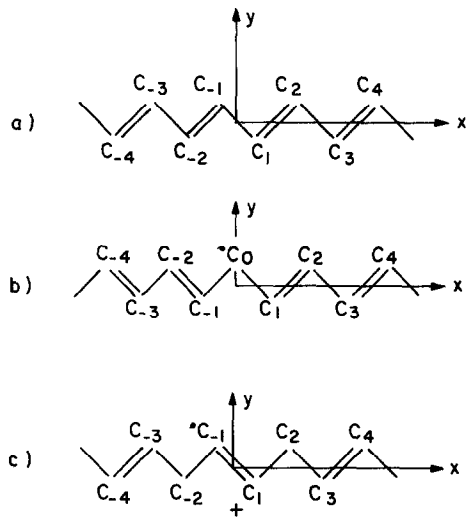

Fig. 1. Schematic geometry adopted for (a) regular polyene, (b) soliton-, and (c) polaron-like chains.

some short-chain polyenes have been studied before by different methods (such as a finite field treatment [17] and a perturbative expansion including singly and doubly excited configurations [18] for the PPP Hamiltonian, and a PDM expansion within a CNDO approximation [19]), the only previous systematic studies of second hyperpolarizabilities of members of the polyene family were performed for regular chains at the free-electron [20] and simple Hückel levels [21,22]. The geometry adopted for the different structures analyzed is schematized in fig. 1. All molecules were assumed to be planar, and the bond angles were taken equal to 120°. For regular polyenes we have assumed double and single bonds of lengths equal to 1.35 and 1.46 Å, respectively. For the defects it is well known that geometric relaxation effects are responsible for the pinning of the extra charge or spin density near the center of the molecule [11]. Therefore, for these structures the positions of the carbon atoms were chosen as

$$\boldsymbol{r}_n=(x_0+nr_0+u_n)\cos 30^\circ\,\hat{\imath} + (-1)^n\tfrac{1}{2}r_0\sin 30^\circ\,\hat{\jmath}\,,$$

where $r_0=1.405$ Å and $u_0=0.0275$ Å, and for solitons

$$x_0=0,\quad u_n=(-1)^{n+1}u_0\tanh(n/\nu)\,,\quad 0\leqslant n\leqslant \tfrac{1}{2}(N-1)\,,$$

while

$$x_0 = -\tfrac{1}{2} r_0,$$

$$u_n = (-1)^n u_0[-1 + 2\,\mathrm{sech}(0.65848n)],$$

$$1 \leqslant n \leqslant \tfrac{1}{2}N$$

for polarons. For the soliton geometry, the parameter ν was determined by requiring that the lengths for the terminal bonds be as close as possible to that of a "true" double bond (1.35 Å); for $N=5$, 9, 13, 17, and 21 the optimum values of ν were 1.7080, 1.9756, 2.3096, 2.6425, and 2.9667, respectively. For polarons, the above functional form assures that C_2 is connected through "single" bonds to each one of its neighbors.

After obtaining the PPP density matrix for the isolated molecule, the effect of the external uniform electric field $\boldsymbol{F}=F\hat{\imath}$ upon the electronic distribution of the system is considered. The extra one-electron term in the Hamiltonian can be written as $f_{ij}=eFx\delta_{ij}$ (where δ_{ij} is the Kronecker delta) and is treated as a perturbation. The corresponding changes in the electronic distribution introduce a correction in the density matrix of the system, and this in turn leads to higher-order corrections in the self-consistent part of the Hamiltonian. Thus, in a restricted HF treatment, both h and R can be expanded as [12]

$$h = h_0 + f + G(R^{(1)}) + G(R^{(2)}) + \ldots,$$

$$R = R_0 + R^{(1)} + R^{(2)} + \ldots,$$

where $G(R^{(i)})$ is the ith order correction in the two-electron part of the Hamiltonian. In any order these variations of R must be subject to the constraints of idempotency and commutation with h discussed above. We have found that the corresponding equations are most efficiently solved in the basis in which h_0 (and therefore R_0) is diagonal. The electronic energy is given by [12] $E=2\,\mathrm{tr}[h'R]$, where $h'=f+\frac{1}{2}G(R)$; the different order corrections can be found after appropriate combinations of the changes in h and R. For the UHF problem a similar treatment can be separately developed to both "up" and "down" spins. In any case the second hyperpolarizability is directly related to the fourth-order correction of E

$$E^{(4)} = -\frac{1}{24}\sum_{i,j,k,l} \gamma_{ijkl} F_i F_j F_k F_l$$

and depends explicitly both on $R^{(1)}$ and $R^{(2)}$. In order to solve for the components of the polarizabilities, the calculation must be repeated for different field directions. There are only five non-zero independent components of γ_{ijkl} for the chains corresponding to the geometries of regular polyenes and polarons (C_{2h} group). The symmetry of the soliton chains (C_{2v} group) reduces this number to three. For molecules in solution or in the gas phase the measured hyperpolarizability γ is an average of the $xxxx$, $xxyy$, and $yyyy$ components. For oriented films and crystals, on the other hand, the individual components can in principle be determined experimentally.

3. Results and discussion

As expected, we have found that in all cases the component of γ along the chain has the largest absolute value. For the neutral molecules γ_{xxxx} is positive; its variation with increasing chain lengths is represented in fig. 2. An interesting behavior is found for the $xxxy$ component of regular polyenes and neutral chains with polaron geometry which, while negative for the smaller chains, have a sharp change of sign with the increase of N. All other remaining components of γ are negative; in spite of this, the orientationally averaged hyperpolarizability turns out to be positive for all neutral chains.

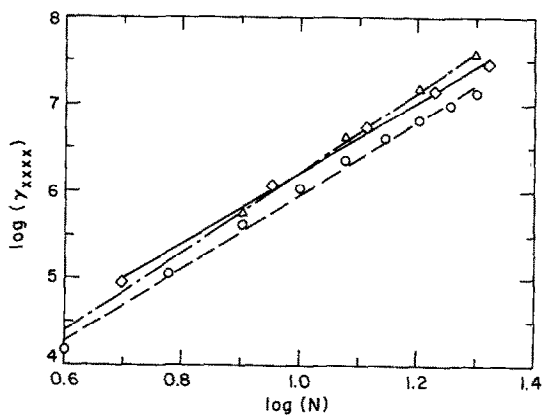

Fig. 2. Second hyperpolarizabilities γ_{xxxx} (in au) for increasing chain sizes of (i) regular polyenes (○), (ii) neutral soliton- (◇), and (iii) neutral polaron-like molecules (△) The straight lines are corresponding linear least-squares fittings to the calculated points.

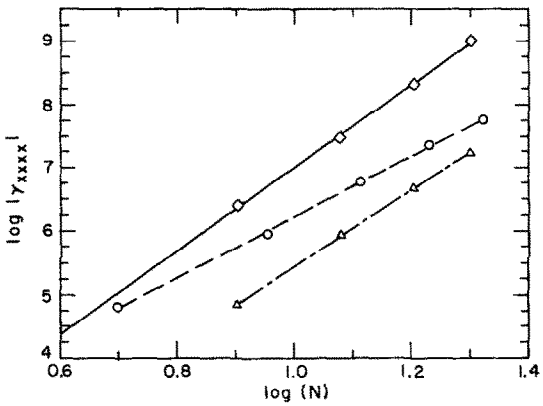

Fig. 3. Absolute values of the second hyperpolarizabilities γ_{xxxx} (in au) for increasing chain sizes of (i) singly charged solitons (○), (ii) singly charged polarons (◇), and (iii) bipolarons (△). The straight lines are corresponding linear least-squares fittings to the calculated points.

To examine the hyperpolarizabilities of charged species, we have considered the same geometry as that of the corresponding neutral molecule. Recently [23], directly photogenerated charged solitons have been unequivocally identified in polyacetylene. Immediately after excitation, the corresponding electron states will find themselves in a "foreign lattice", and a time lag of the order of picoseconds is involved before the chain will relax to minimize the introduced strain [24]. While this relaxation will certainly alter the absolute values of the calculated polarizabilities, we do not expect a drastic change in the pattern of variation of γ. Our results indicate that for singly charged solitons and polarons, γ_{xxxx} is negative. As could be expected from symmetry arguments, exactly the same values for the second hyperpolarizabilities are found for positively and negatively charged species. Of all structures considered, charged polarons have the largest absolute values of γ_{xxxx}, for a given N. Bipolarons on the other hand have positive and smaller absolute values for this component. The variation of the magnitude of γ_{xxxx} with increasing chain length for charged defects is represented in fig. 3. The orientationally averaged hyperpolarizability turns out to be negative for the singly charged soliton and polaron chains.

The data of figs. 2 and 3 are reasonably well reproduced by a fit of general form $\gamma_{xxxx}=aN^b$. The appropriate values of a and b are presented in table 1. The estimated increase of the magnitude of γ_{xxxx} with the size of regular polyene chains should be compared to that predicted by a free-electron model ($b=5.0$) [20] and simple Hückel theory ($b=5.257$) [21]. Of course these expressions describe the initial behavior of the polarization response of the analyzed systems as a function of N, since one should expect saturation to occur for larger chains. In fact, an ab initio study [16] has indicated that the onset of saturation of the unit-cell longitudinal component of the linear polarizability of polyenes should occur for $N\approx 18$. The present results suggest a much slower convergence rate for the second hyperpolarizabilities. There are no available experimental values for the non-linear polarizabilities of large polyene chains. Comparison of our results to the measured total γ of gas phase mixtures of cis and trans isomers of butadiene and hexatriene [25] seem to indicate a weaker N dependence than predicted here. This is not surprising, since configuration interaction with low-lying excited states (which could have a significant contribution to the hyperpolarizability of small molecules [26]) and sigma electron contributions (which should be more important for the small N molecules) are not included in the present model. We feel confident, however, that the predicted qualitative behavior of γ_{xxxx} for the different chain structures is not an artifact of our method and will be confirmed by more elaborate treatments of the electronic structures. More striking in our view, is the prediction of negative γ_{xxxx} for charged solitons and polarons.

Table 1
a and b parameters derived from linear least-squares fitting ($\gamma_{xxxx}=aN^b$) for calculated values (in au) of the second hyperpolarizabilities of finite chains of regular polyenes (rp), neutral solitons (ns), neutral polarons (np), charged solitons (cs), charged polarons (cp), and bipolarons (bp)

	rp	ns	np	cs	cp	bp
a	52.0	146	42.0	−27.0	−2.66	0.247
b	4.25	4.05	4.60	4.80	6.57	6.04

As the values of table 1 reveal, the presence of these conformational defects in conjugated polymers and crystals could dominate their non-linear optical response in the limit where the concentration of defects is large enough to render them experimentally observed and yet sufficiently small for their mutual interaction to remain negligible and consis-

tent with the present model. In addition, we believe that even at the low-concentration limit, conformational defects can make a non-negligible additive contribution to the total polarization response of the system; this contribution could then be identified by observing the changes on the polarizability components when defects are introduced in an originally pristine conjugated material. The present results also suggest that the substitution by polar side groups can be a convient way of preparing conjugated systems with high hyperpolarizabilities. At present, the sign of γ for polydiacetylene (PDA) samples is object of recent interest: while intensity-dependent coupling measurements have determined γ to be negative for PDA crystals [27], the opposite result is found for PDA solutions through third-harmonic generation techniques [28]. Since the size of the conjugation length seems to be a determinant factor in the optical properties of PDA solutions [9,10], it will be interesting to examine the conformational dependence of the hyperpolarizability in this material. Work along these lines is currently underway using the present model.

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