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times. Yet, for ethanol, the ratio $D\tau_D/a^2$ is greater than unity, indicating that polarization diffusion effects should be dominant and that solvation should occur much faster than τ_L. The data suggest that the ratio of $D\tau_D/a^2$ may not accurately gauge the importance of polarization diffusion effects.

On the other hand, the molecularly based theories of Calef and Wolynes[31] and Loring and Mukamel,[32] the experimental results of Robinson,[29] and the simulations of Fleming[30] suggest that a range of solvation times need to be considered. Near the solute, relaxation occurs by rotation motion of the individual molecules, an event which occurs on a time scale of τ_D. With increasing distance from the solute, dipolar interaction serves to shorten the time scale of relaxation.[32] The experimentally observed dynamics should reflect the superposition of this range of solvation time and fall between the two limiting dielectric relaxation times. Model calculations reported by both Wolynes[31] and Mukamel[32] for the

solvation of a charge in ethanol support this conclusion. Similar results would be predicted for solvation around a dipole. Our observation for the solvation of the TICT state of DMAPS in ethanol supports this model. It is important to stress that the observation of solvaton times between τ_L and τ_D *cannot* be accounted for by a simple continuum treatment of the solvent.

We are currently examining the solvation dynamics in several other solvent systems. These results will be reported shortly.

Nonlinear Susceptibilities of Finite Conjugated Organic Polymers

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Tight-binding calculations of the length dependence of the third-order molecular hyperpolarizability for polyenes and polyynes are reported. The π-electron wave functions were determined by exploiting the limited translational symmetry of the molecules. Perturbation theory was used to calculate the longitudinal component of the electronic nonresonant hyperpolarizability. To our knowledge, this is the first two-"band" calculation of third-order hyperpolarizabilities on finite π-electron systems of varying length. In contrast to the results of the one-"band" models, the hyperpolarizability densities increase rapidly and then, after about 10–15 repeating units, approach an asymptotic value.

Introduction

Conjugated organic polymers are currently of great interest for use as nonlinear optical materials.[1] This is primarily because of the fast time response possible in the nonresonant (transparent) spectral region and the diversity of their optical, chemical, and physical properties which may allow tailoring of a material for particular applications. One goal of much of the research in this area is concerned with the development of such conjugated polymers with enhanced nonlinear susceptibilities, especially the third-order hyperpolarizability. Of particular importance for the nonlinear optical response of these materials are the delocalized electronic states associated with the conjugated π-electrons.[2] The nonlinear susceptibilities are known to be related to the extent of the electronic delocalization.[2,3] However, we lack sufficient understanding of these effects to have available a reliable set of molecular design principles. At this stage, it is important to develop a full understanding of the relation of the electron delocalization and the susceptibilities to the molecular structure of the polymer. This would include, for example, the effects of the structure of the repeating units, the number of these units, or the chain length.[4] In this Letter we calculate the chain length dependence of the third-order molecular hyperpolarizability of finite polyenes and polyynes.

Conjugated polymers of interest have a minimum of one single and one multiple bond per repeating unit. In the limit of a long polymer, the resulting electronic states cluster into groups (or

bands) with forbidden energy regions between them. Systems of interest produce at least two such bands. In this paper we consider only two-band homoatomic systems, although the method can be extended to more complicated repeating units.

Previous studies of third-order molecular hyperpolarizabilities have been made with the use of several different model Hamiltonians. Constant and sinusoidal pseudopotentials have been utilized to generate eigenstates and from these the hyperpolarizabilities.[3] One difficulty with these models is associated with parametrizing the potentials. Also, for the constant-potential model, the HOMO–LUMO gap decreases with chain length and vanishes for long-chain systems. This is inappropriate for modeling systems with bond alternation. Other models have included molecular details in a tight-binding model but considered only infinite polymer chains.[2] The chain length dependence of the hyperpolarizability has also been calculated in the tight-binding limit for a one-band model of polyene.[4] These calculations also

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give a vanishing gap for long chains but are useful for qualitative predictions.

Theoretical Section

In order to develop a model with chemically meaningful parameters which can be obtained from experiments, we choose a molecular orbital model. The model is developed so that the chain length and the multiband nature of the molecules can be included explicitly in the calculation. Because qualitative predictions of the hyperpolarizability dependence on chain length and unit cell structure do not exist, we have chosen the simplest possible model for the states—a Hückel model. The theoretical elements of the calculation of the third-order molecular hyperpolarizability for the two atom per repeating unit finite-chain systems are now given.

The simplest one-electron tight-binding[5] Hamiltonian for one π-cloud of a two atom per repeating unit unsaturated hydrocarbon polymer is

$$H = \sum_{i=1}^{N} \beta_1 (a_{2i}^{\dagger} a_{2i-1} + \text{c.c.}) + \sum_{i=1}^{N-1} \beta_2 (a_{2i}^{\dagger} a_{2i+1} + \text{c.c.}), \quad \beta_2/\beta_1 < 1 \tag{2.1}$$

a_i ($a_i^{\dagger}$) destroys (creates) an electron in the p atomic orbital orthogonal to the σ-backbone on the ith atom. β_1 (β_2) is the Hückel exchange parameter between orbitals in a multiple (single) bond. N is the number of repeating units (half of the number of carbon atoms) in the chain. Rather than diagonalizing the entire $2N \times 2N$ Hamiltonian matrix numerically, we exploit the translational symmetry of the molecule to write the wave function as

$$\Psi = \sum_{n=1}^{N} \exp(in\theta) [a_+ \phi_n^{(l)}(\vec{x} - \vec{a}_n^{(l)}) + b_+ \phi_n^{(r)}(\vec{x} - \vec{a}_n^{(r)})] + \\ \exp(-in\theta) [a_- \phi_n^{(l)}(\vec{x} - \vec{a}_n^{(l)}) + b_- \phi_n^{(r)}(\vec{x} - \vec{a}_n^{(r)})] \tag{2.2}$$

where $\vec{a}_n^{(l,r)}$ is the position of the atom on the left (l) or right (r) side of the nth unit cell. ϕ_n is the p orbital at position n on the left (l) or right (r) side of the unit cell. θ for each state is a root of eq 2.4. Standard methods[6] of solving the Schrödinger equation give the expression for the energy

$$E^2 = \beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos \theta \tag{2.3}$$

The allowed values of θ are given by the boundary condition[4a,6]

$$\beta_1 \sin (N+1)\theta + \beta_2 \sin N\theta = 0 \tag{2.4}$$

From the symmetry of the Hamiltonian, the wave function can now be written explicitly as

$$\Psi_{\pm} = (1/\mathcal{N})^{1/2} \sum_{n=1}^{N} [\phi_n^{(r)} \sin n\theta \pm \phi_n^{(l)} \sin (N+1-n)\theta] \tag{2.5}$$

where

$$\mathcal{N} = N + (1/2) - (1/2) \sin (2N+1)\theta/\sin \theta \tag{2.6}$$

Hence, the only computational work required to determine the eigenvalues and eigenvectors is to determine the N roots of θ from the transcendental equation, eq 2.4.

The wave functions and eigenvalues determined above are now used to compute the hyperpolarizability by using time-independent perturbation theory.[2] The third-order molecular hyperpolarizability is proportional to the fourth-order energy correction due

to the field to all occupied states, if the process is sufficiently nonresonant.[2] For a given occupied state m, the energy correction is, in the dipole approximation

$$\epsilon_m^{(4)} = \langle \Psi_m | e E_x x | \psi_m^{(3)} \rangle$$

$$= \sum_{l \neq m} \sum_{k \neq m} \sum_{n \neq m} \frac{H_{ml} H_{kn} H_{nm} H_{lk}}{\omega_{ml} \omega_{mk} \omega_{mn}} - \sum_{l \neq m} \sum_{n \neq m} \frac{|H_{lm}|^2 |H_{mn}|^2}{\omega_{ml}^2 \omega_{mn}} \tag{2.7}$$

where the H's are matrix elements between the unperturbed wave functions and the ω's are their energy differences. $\psi^{(3)}$ is the third-order wave function correction due to the field, and E_x is the field in the direction of the chain. The matrix elements are calculated in the usual way,[4] assuming that

$$\langle \phi_i^{l,r}(\vec{r} - \vec{a}_i^{l,r}) | x | \phi_j^{l,r}(\vec{r} - \vec{a}_j^{l,r}) \rangle = \delta_{l,r} \delta_{i,j} x_j^{l,r} \tag{2.8}$$

where $x_j^{l,r}$ is the x coordinate of the left or right atom in the jth repeating unit. The third-order hyperpolarizability is[4]

$$\gamma_{xxxx} = \frac{-4}{E_x^4} \sum_m 2\epsilon_m^{(4)} \tag{2.9}$$

and the units of γ_{xxxx} are $e^4 a^4/\beta_1^3$ where a is half of the unit cell length measured along the C–C bonds and β_1 is the larger interaction parameter. The factor of 2 in eq 2.9 arises from the double occupancy of the bonding states. The susceptibility of an isolated multiple bond is $\gamma^0_{xxxx} = 1/16$ in the above units. When comparing the hyperpolarizabilities of homologous series of molecules of varying lengths, it is appropriate to compare the hyperpolarizability per repeating unit normalized to the hyperpolarizability for an isolated repeating unit. This gives a normalized hyperpolarizability density.

Application to Polyenes and Polyynes

To implement the theory for calculations on polyenes and polyynes, the values of β_1 and β_2 must be chosen. The usual assumption when applying one-electron calculations such as these is that β_2/β_1 equals the ratio of the overlap between the p_z orbitals involved in the single and multiple bond, respectively. In these calculations we assume an ideal planar geometry for the polyenes and a rigid linear geometry for the polyyne. By use of the available bond lengths,[7] the ratios β_2/β_1 are calculated to be approximately 0.77 for polyyne and 0.79 for polyene. The absolute values of β_1 can be estimated by using the optical gaps and the ratios calculated above.[6b] We prefer to make relative rather than absolute predictions at this point because it is the general chain length dependence which we wish to present in this Letter. Both parameters, β_1 and β_2, could be determined by fitting the optical gap and the integrated absorption cross section (via the optical theorem of scattering theory).[8] In order to make direct comparison of our theoretical calculations to experimental data, such a normalization of the parameters will be performed in future work. At this point we calculate the wave functions using the estimates of β_2/β_1 and the eigenvalues in units of β_1.

The matrix elements required for the calculation of $\epsilon_m^{(4)}$ must now be evaluated. To calculate the dipole matrix elements, we fix the origin at the center of the molecule and assume all bond lengths are a. This approximation simplifies the calculation and, in the case of polyyne, introduces errors of $<5\%$ for chains of more than four repeating units. No such assumption was used in the calculation of the β's. Using the values of $\epsilon_m^{(4)}$, one can directly calculate $\gamma_{xxxx}(N)$ with eq 2.9. The numerical accuracy of the calculation was verified, for the case $\beta_1 = \beta_2$, by comparison with the one-band calculation of McIntyre and Hameka.[4b]

In Figure 1 is shown the normalized hyperpolarizability density, $\gamma'_{xxxx} \equiv \gamma_{xxxx}/N\gamma^0_{xxxx}$, as a function of chain length for polyenes and polyynes. Here γ^0_{xxxx} is the value for an isolated multiple bond aligned with the applied fields. We also plot the one-band

(5) Because π-electrons in the conjugated systems of interest are much more delocalized than the σ-electrons, only the π-electrons are included in our Hamiltonian. All of the remaining electrons are essentially localized, and the only way they appear in this model is through the effective potential. The electron–electron interactions for the delocalized states, as in many solid-state physics examples, can be neglected in first order because these electrons are delocalized and most of the interaction is screened by the medium. Contributions to the hyperpolarizability from the σ-electrons are negligible compared to those from the π-electrons.[2]

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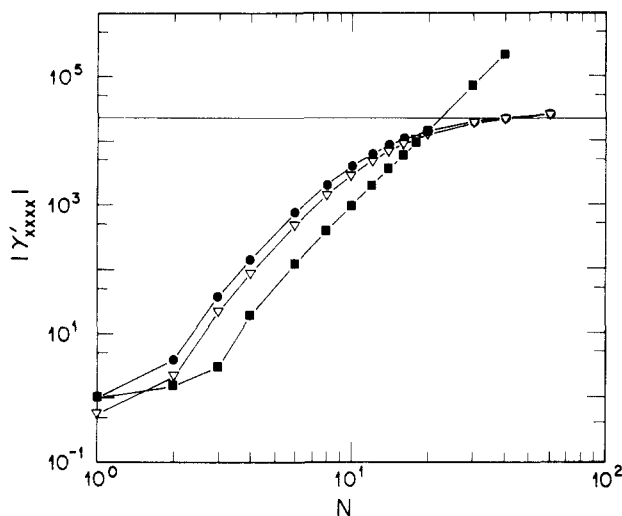(8) Merzbacher, E. *Quantum Mechanics*, 2nd ed.; Wiley: New York, 1970.

Figure 1. $|\gamma'_{xxxx}|$ is shown as a function of N. Plotted are the dependences for (■) $\nu = 1$ (180° bond angle), (▽) $\nu = 0.79$ (120° bond angle), and (●) $\nu = 0.77$ (180° bond angle). These values correspond to models of cumulene, planar polyene, and polyyne. The cumulene and polyyne values are the contribution per orthogonal π-system; the full values are higher by a factor of 2. For $\nu = 0.77$, the approximate value of γ'_{xxxx} predicted in ref 2 for the infinite-chain limit is shown with a solid line.

TABLE I: γ_{xxxx} for Selected Chain Length Polymers and Polyynes[a]

repeating units	γ_{xxxx}[b]	
	polyyne[c]	polyene
2	4.836×10^{-1}	2.592×10^{-1}
10	2.651×10^3	1.841×10^3
40	5.993×10^4	5.773×10^4

[a] $\nu = 0.77$ and 0.79 for polyyne and polyene, respectively. [b] The units of γ_{xxxx} (the unnormalized hyperpolarizability) are $e^4 a^4/\beta_1{}^3$. [c] The values given for polyynes represent the contribution per orthogonal π-system; the full values are higher by a factor of 2.

result ($\beta_1 = \beta_2$), which would be appropriate for a cumulene structure. In contrast to the one-band system, the two-band systems display a saturation of γ'_{xxxx} with chain length. If β_2/β_1 were identical for polyenes and polyynes, the linear geometry of the polyynes would enhance γ'_{xxxx} by a factor of $(2/\sqrt{3})^4 \approx 1.78$, at all chain lengths. The larger β_2/β_1 ratio for polyene compensates this effect increasingly with chain length, as demonstrated in Figure 1 and Table I. For chains of about 40 or more repeating units, the calculated γ'_{xxxx} for polyenes and polyynes are within a few percent. The calculated values of γ'_{xxxx} shown in the figure for the polyynes and cumulenes represent the contribution from only one of the two degenerate π-clouds. The full calculated values of γ'_{xxxx} for polyynes are higher by a factor of 2.

At this stage we have calculated only γ'_{xxxx}. This tensor component can be measured when the polymer chains all have the same spatial orientation and the incident electric field polarization is parallel to the chains. In systems with a variety of chain orientations other tensor elements will contribute to the

observed susceptibility and therefore must be calculated explicitly.[4b]

Flytzanis and co-workers calculated the third-order susceptibility of an infinite polymer (with $\nu \equiv \beta_2/\beta_1 \simeq 1$). To compare our result with theirs, we calculate the normalized hyperpolarizability per repeating unit predicted with their model to be

$$\gamma'_{xxxx} \simeq \frac{16}{45\pi}\left(\frac{1+\nu}{1-\nu}\right)^6 \qquad (3.1)$$

Our finite-chain calculations show that γ'_{xxxx} for long chains (≥ 40 repeating units) is the same order of magnitude as their approximate infinite-chain result.

Discussion

We have developed a method for analytically calculating the π-electron Hückel wave functions for some finite-length polymers with two atoms per repeating unit. The method has been applied to determine the chain length dependence of the third-order molecular hyperpolarizability of some simple unsaturated hydrocarbons. To model conjugated hydrocarbons with bond alternation, a minimum of two parameters is needed to properly represent the two-band nature of the electronic structure. In contrast to the one-"band" result, the values of γ'_{xxxx} per π-cloud for the two-"band" cases are higher for short chains and approach an asymptotic value whereas the one-"band" γ'_{xxxx} values continue to increase without bound.[3,4]

We have found that γ'_{xxxx} for conjugated hydrocarbons with bond alternation increases rapidly with chain length for short chains (<10 repeating units) and changes very slowly with chain length beyond about 15 repeating units. For this reason, we might expect that inclusion of relatively short chain length "active" oligomers (nonlinear chromophores) in materials with desirable physical properties would be advantageous.

Future work on this topic will proceed in two directions. One will exploit the method developed here to study the chain length dependence of the third-order hyperpolarizability tensor for more complicated repeating units. The influence of conjugation defects and chain terminal substituents will also be studied. The second emphasis of future work will be to introduce refinements to the theory as necessitated by experimental measurements. Such refinements will include improvements of the parameter set and, if necessary, inclusion of electron correlation effects in the Hamiltonian.

The models developed here have been aimed at idealized rigid structures. The introduction of conformational disorder, substitutional impurities, and vibrational motion will perturb the idealized symmetry used in the model. These effects could be treated with a similar model by introducing a distribution of diagonal and/or off diagonal matrix elements.