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Random-phase calculations of frequency-dependent polarizabilities and hyperpolarizabilities of long polyene chains

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We apply the double-direct random-phase-approximation (DDRPA) method [Ågren *et al.*, J. Chem. Phys. **98**, 6417 (1993)] to calculate the static and dynamic polarizabilities and hyperpolarizabilities for a sequence of polyene chains. Like the direct self-consistent-field method, DDRPA is driven directly by the atomic-orbital integrals. It further uses iterative techniques based on direct linear transformations for solving the RPA eigenvalue equations and sets of linear equations. This allows applications to long chains, including $C_{28}H_{30}$ in the present study. The calculated optical spectra, viz., excitation energies and transition moments, the polarizabilities, and the hyperpolarizabilities are in excellent agreement with available experimental data. Computations on the longer polyenes are facilitated by the weak basis-set dependency on chain length for the longitudinal components of the (hyper)polarizabilities. The length dependence of the dispersion is significant even at small frequencies, and is quite different for the various tensorial components and for the averaged static, Kerr, and electrical-field-induced second harmonic generation values. Some of the results can be rationalized by the observation that the most intensive ^1B_u transition also determines the band gap, and that the band gap converges very slowly with respect to chain length. The correlation length of the static polarizability is predicted to be about 40 unit cells, while for the static hyperpolarizability the prediction is well over 100.

I. INTRODUCTION

The polyenes form the backbone of a large group of biologically active chromophores, from carotenoids to organic dyes. These molecules contain a polyene chain which strongly influences the photophysical and luminescence properties of chromophores. For example, electronic excitations in polyenes are related to the photochemistry of the vision process. Lately, the polyenes have attracted interest concerning a particular aspect of their optical properties, namely, the strong nonlinearity which makes polyenes promising constituents in materials for optical conductors and switches.

The conjugated and delocalized nature of the π-electronic structure implicates a very strong enhancement of the polarizability and hyperpolarizability along the carbon backbone. Many theoretical studies have concerned the nature of this enhancement. For short members of the polyenes the hyperpolarizability increases exponentially, but it levels off for larger members. One obvious task is to extrapolate the values for these quantities to the asymptotic limit. Connected to this problem is the determination of the correlation length, for which the increase of the polarizability or hyperpolarizability per unit cell has reached a constant value. Other questions concern the organization of the excited states reached by one- or two-photon transitions and the development of the optical band gap, since these quantities can be used to rationalize the source of the strong nonlinearity. Geometric distortion, electron-phonon coupling, and the occurrence of polarons and solitons are yet other issues that have a fundamental impact on the excitation properties and nonlinearity of π-conjugated polymers.[2] Macroscopically prepared polyacetylene is not "infinite" but contains strands of conjugated polymers, which may be some hundred carbon atoms long.[3] From this point of view it is essential to study finite polyene chains without the periodic boundary condition imposed.

Many of the issues discussed above can only be answered theoretically. Most of the theoretical studies have involved semiempirical and model-type calculations, while applications using first-principle methods have mostly been confined to short chains. Extensions to larger members in the series are desirable because they enable a more systematic modeling of these compounds, both for the purpose of interpretation and for prediction by means of extrapolation to the infinite limit. Recent efforts in this direction have been performed by Hurst, Dupuis, and Clementi[4] (static polarizabilities and hyperpolarizabilities), by Karna *et al.*[5] (dynamic hyperpolarizabilities), and by Champagne, Mosley, and André[6] (static polarizabilities, including polyacetylene). In the present work we extend significantly the size of the polyene chains with respect to *ab initio* calculations of polarizabilities and hyperpolarizabilities, including their dispersion. Two recent developments combine to make the present study possible: the validation of the lowest-order response method—the random-phase approximation (RPA)—as an excellent approach for predicting optical properties of short polyenes,[5,7] and the development of direct methods that make the RPA applicable to large molecules, such as the long-chained polyenes.

Agreement between RPA and experiment has been obtained to within 0.2 eV for all optically allowed one-photon states between 0 and 10 eV of ethylene, *trans*-butadiene, *trans*-hexatriene, and *trans*-octatetraene.[7] The RPA polarizabilities are within a few percent of the vapor-phase values for these compounds at the appropriate frequencies. The quadratic RPA method predicts absorption maxima for the two-photon spectra at 1.5–1.7 times the band-gap energy for the even states of *trans*-butadiene, *trans*-hexatriene, and *trans*-octatetraene. The mechanism of optical nonlinearity in the short conjugated polyenes has also been explored by the RPA in relation to the so-called three- and four-state models, and it is found that the validity of these models for calculations of hyperpolarizabilities of the short polyenes is rather limited. These results indicate that for the longer chains explicit calculations of the hyperpolarizabilities are called for.

The second prerequisite for the present work, the implementation of a "direct atomic-orbital" method, is based on using iterative techniques to solve the linear equations for the relevant property and on calculating the quantities entering the RPA equations directly from integrals evaluated in an atomic-orbital (AO) basis. In 1982 Backskay[8] showed how the linear transformations needed for the coupled perturbed Hartree-Fock equations can be implemented based on integrals in the AO basis. This approach has since been extended in several directions and used in calculations of static polarizabilities. In Refs. 9–11 it was demonstrated how the linear transformations needed for the RPA or linear response self-consistent-field (SCF) matrix equations can be made AO driven. It is thus possible to solve the RPA equations for direct SCF wave functions, and this has allowed the calculation of static and dynamic polarizabilities, excitation energies, and transition moments for large molecules. In Ref. 1 a similar algorithm was developed for the quadratic RPA equations, making it practical to calculate dynamic hyperpolarizabilities and two-photon spectra of large organic compounds. This algorithm is employed in the present work.

II. METHOD AND CALCULATIONS

The frequency-dependent polarizabilities and hyperpolarizabilities are calculated from direct SCF wave functions as described in Refs. 1 and 10. The two basic features of the direct quadratic RPA method are (i) it solves sets of RPA matrix equations using direct linear matrix transformations, and (ii) it determines the solution vectors for the RPA matrix equations entering the quadratic response functions and their residues directly from the two-electron integrals in the AO basis. The RPA matrices are written in terms of contractions of density matrices with two-electron AO integrals, organized in such a way that only one pass through the integrals is required in each iteration. The basic steps in the calculation of a nonlinear molecular property are the solution of three sets of equations (linear response equations and eigenvalue equations), which involve the calculation of linearly transformed trial vectors as the time-consuming step. The response equations are solved simultaneously so that the transformed trial vectors can be obtained for all equations with only one pass through the atomic integrals. It is clear that, just as in the direct SCF method,[12] the operational count of direct quadratic RPA is determined by the $\sum_{\delta\gamma} D_{\delta\gamma} \mathcal{L}_{sr\gamma\delta}$ contraction. The two methods therefore have the same range of application.

The average values of the polarizability α and hyperpolarizability γ which can be compared with the experimental measurements are defined as

$$\alpha = \tfrac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{1}$$

and

$$\gamma = \tfrac{1}{5}(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz}) \; . \tag{2}$$

For the averaged γ we assume Kleinman symmetry, which means that at an optical frequency far away from any resonance the indices $ijkl$ of $\gamma_{ijkl}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)$ can be freely interchanged without interchanging the frequency arguments. This is a good approximation at lower frequencies, but not for frequencies close to the resonance. The validity of Kleinman symmetry has been investigated by several workers, and for short polyenes by Karna *et al.*[5] For a fundamental frequency $\omega = 0.0239$ a.u. as used in this study, the deviation from Kleinman symmetry is fairly small.[5] The dominance of the $xxxx$ long-axis component makes Kleinman symmetry particularly suitable for systems like the polyenes. Several nonlinear optical processes are discussed in the present work, such as the Kerr effect $\gamma(-\omega;\omega,0,0)$, electrical-field-induced second-harmonic generation (ESHG) $\gamma(-2\omega;\omega,\omega,0)$, and third-harmonic generation (THG) $\gamma(-3\omega;\omega,\omega,\omega)$.

The selection of proper basis functions is important in order to obtain reliable polarizabilities and hyperpolarizabilities of polyenes. For the shorter polyenes basis-set investigations have been carried out for static and dynamic polarizabilities and hyperpolarizabilities as well as for the one- and two-photon spectra.[5,7] The basis-set dependence for the static (hyper)polarizabilities of C_4H_6 has been extensively investigated by Hurst, Dupuis, and Clementi,[4] who calculated the α and γ tensors close to the Hartree-Fock limit. A basis set that includes diffuse p and d functions on carbon (with exponents 0.05) in conjunction with a 6-31G basis, was found to yield values for α and γ within 0.1% of those obtained with the largest set (basis J of Ref. 4).

Karna *et al.*[5] carried out RPA calculations for the dynamic polarizabilities and hyperpolarizabilities for the short polyenes (C_2H_4 to C_8H_{10}) using a 4-31G basis augmented with the diffuse p and d diffusions of Hurst, Dupuis, and Clementi[4] on carbon. Good agreement was observed between calculated and experimental numbers. It was also found that the basis-set dependence of the molecular properties is weaker for longer chains.[4] For the static polarizabilities and hyperpolarizabilities the basis-set dependence is weaker for the component along the chain than for the average values. We have therefore chosen to use the same basis set as Karna *et al.*[5] for all the molecules studied here. A similar basis set was used in our previous calculations of the hyperpolarizabilities of *para*-nitroaniline (PNA),[1] which predicted static and dynamic hyperpolarizabilities close to the Hartree-Fock limit.

For the polyene molecules studied here, we used an idealized polyacetylene geometry, which is defined by $R(\mathrm{C{=}C})=1.342$ Å, $R(\mathrm{C{-}C})=1.544$ Å, $R(\mathrm{C{-}H})=1.084$ Å, $\theta(\mathrm{C{=}C{-}C})=121.6°$, and $\theta(\mathrm{C{=}C{-}H})=120°$ in a C_{2h} symmetry. The x axis is in the molecular plane along the chain direction (corresponding to the translational axis in polyactylene), the z axis is the twofold rotation axis. For the short polyenes, including C_4H_6 and C_6H_8, the optimized geometries from MP2 (second order Møller-Plesset) calculations[7] were also used to examine the geometry effect. For C_4H_6 and C_6H_8, the polarizabilities calculated from the idealized and optimized geometries were found to be almost the same. A difference of 3% was observed between the two geometries for the hyperpolarizabilities of C_4H_6 and C_6H_8.

All calculations were carried out on an IBM RS/6000 370 workstation, using the HERMIT/SIRIUS program for multiconfiguration self-consistent field (MCSCF) wave functions and the program RESPONS for the linear and quadratic response functions.[13–16]

III. RESULTS

A. Comparison with experimental data for short polyenes

Most experimental values for polarizabilities and hyperpolarizabilities of polyenes have been measured in solution or solid phases. As shown in previous studies on solvent-induced polarizabilities and hyperpolarizabilities,[17,18] molecular gas-phase values cannot easily be extrapolated from the measurements in solution. Fortunately, experimental gas-phase polarizabilities and hyperpolarizabilities are available for C_4H_6 and C_6H_8, and a direct comparison of calculated and experimental data is therefore possible for these systems. Such a comparison can be used to establish a confidence level for the RPA calculations on longer polyenes.

Table I lists the dynamic RPA polarizabilities and hyperpolarizabilities of C_4H_6 and C_6H_8 at the MP2 geometries. For comparison we include experimental data and other theoretical results. In our previous study on the short polyenes,[7] we employed extended correlation-consistent[19] and polarizability-consistent[20,21] basis sets as well as the standard 4-31G* set. The basis set effect was found to be small. As seen in Table I, these results are in good agreement with those obtained with the 6-31G+PD basis set of Hurst, Dupuis, and Clementi[4] and with the 4-31G basis set of Karna *et al.*[5] Good agreement is also observed with the available experimental dynamic polarizabilities, namely, for C_4H_6.[22]

The experimental values of $\gamma(-2\omega;\omega,\omega,0)$ for C_4H_6

TABLE I. Frequency-dependent polarizabilities $\alpha(\omega)$ and hyperpolarizabilities $\gamma(-2\omega;\omega,\omega,0)$ of *trans*-butadiene and *trans*-hexatriene (all values in atomic units).

		$\omega=0.00$		$\omega=0.0656$		
		Present	Others	Present	Others	Experiment
C_4H_6						
	α_{xx}	87.57	86.92,[a] 84.77,[b] 89.41[c]	92.98	92.37,[a] 95.21[c]	
	α_{yy}	43.04	42.84,[a] 72.79,[b] 43.25[c]	43.88	43.58,[a] 44.13[c]	
	α_{zz}	32.07	33.69,[a] 32.23,[b] 33.33[c]	32.85	34.36,[a] 34.21[c]	
	α	54.23	54.48,[a] 53.27,[b] 55.33[c]	56.57	56.77,[a] 57.83[c]	58.31[d]
	γ_{xxxx}	25 932	23 574,[b] 26 804[c]	49 572	55 632[c]	
	γ	14 348	14 846,[b] 16 797[c]	25 115	29 305[c]	27 400±1550[e]
C_6H_8						
	α_{xx}	160.65	159.64[a] 162.01[c]	176.19	175.24,[a] 176.86[c]	
	α_{yy}	66.92	67.64,[a] 63.63[c]	69.27	69.70,[a] 65.12[c]	
	α_{zz}	42.82	47.02,[a] 46.15[c]	45.99	47.91,[a] 47.23[c]	
	α	90.13	91.43,[a] 87.92,[b] 90.55[c]	97.15	97.62,[a] 96.42[c]	
	γ_{xxxx}	116 991	112 695[c]	305 286	304 491[c]	
	γ	36 393	35 118,[b] 38 002[c]	90 163	88 036[c]	89 700±835[e]

[a] From Ref. 7 with ANO basis set.
[b] From Ref. 4, with 6-31G+PD basis set.
[c] From Ref. 5 with 4-31G basis set.
[d] Reference 22.
[e] Reference 23.

and C_6H_8 in the gas phase have been obtained at the fundamental wavelength of $\lambda=694.3$ nm ($\omega=0.0656$ a.u.).[23] The RPA is in good agreement with experiment also for these values: Differences of about 7% and 1% between theoretical and experimental results are obtained for C_4H_6 and C_6H_8, respectively. Our calculated static values are also in good agreement with those obtained by Hurst, Dupuis, and Clementi[4] using the 6-31H G+PD basis set and with the ones of Karna *et al.*[5]

The hyperpolarizabilities of C_4H_6 and C_6H_8 were also calculated using the idealized geometries. Quite small differences were observed for the hyperpolarizabilities of C_4H_6 at the two geometries, both in the static case and for $\lambda=694.3$ nm. For C_6H_8, the hyperpolarizabilities calculated at the idealized geometry decreased by about 3% and 8% for $\omega=0.0$ and $\omega=0.0656$, respectively. Best agreement with experiment is obtained at the optimized geometries.

The polarizabilities and hyperpolarizabilities of polyenes can thus be described well using the RPA with a relatively compact basis set, here 4-31G*. Calculations indicate that correlation effects are relatively unimportant for these molecules. This is in agreement with our previous studies of the one-photon absorption spectra of short polyenes, C_2H_4, C_4H_6, C_6H_8, and C_8H_{10}.[7] At the RPA level, all transitions between 0 and 10 eV were calculated to within one- or two-tenths of an eV of experiment. In the few cases where experimental oscillator strengths are available, good agreement was also found for these. This allowed a conclusive assignment of the complicated one-photon spectra of *trans*-hexatriene and *trans*-octatetraene,[7] and made it possible to relate the mechanism of strong nonlinearity to the appearance of the one- and two-photon spectra.

The excellent agreement between SCF linear response calculations and the experimental data for the excitation energies and polarizabilities has many ramifications for the study of nonlinear properties of the longer polyenes described in the next sections. Apparently, the valence- and nonvalence-electron correlations tend to cancel for polyenes and related hydrocarbons. The RPA, being the lowest-order response method, evidently provides a more balanced description of excited states than do many methods based on explicit π correlation (PPP, extended Hubbard, or CASSCF). The CASSCF method even reversed the order for the ^1B_u states of butadiene and hexatriene with the valence state above the Rydberg states.[24] In fact, only the CASPT2 method gives results compatible with the RPA for the excitation energies of the shorter polyenes.[7]

B. Length dependence of optical gap

The most intensive transitions in the one-photon electronic absorption spectra of polyenes are determined by the first optically allowed $1\,^1B_u$ state. The excitation energies of this state, which determine the optical gap, are therefore important for understanding the dispersion of the polarizabilities and hyperpolarizabilities. It has been argued that for longer polyenes, the one-photon forbidden $2\,^1A_g$ state is located below the $1\,^1B_u$ state. However, this state has a very small two-photon amplitude[7,25] and is therefore not likely to contribute significantly to the nonlinear properties of the polyenes, although it might intrude in the one-photon band gap.[26] As noted above, the RPA method gives unambiguous assignments for the one-photon electronic absorption spectra[7] and determines the optical gap. The calculation of the longer polyenes must necessarily be carried out with the small basis set, and it is therefore essential to calibrate the results for the optical gap for calculations using the small and large basis sets, here 431-G* and ANO.

Table II shows the excitation energies and oscillator strengths for the $1\,^1B_u$ states of polyenes together with the experimental values of excitation energies. The RPA results are in good agreement with experiment already at the 4-31G * level. For C_4H_6 and C_6H_8, the ANO basis set improves the calculated values by less than a tenth of an eV. These results are quite remarkable in the sense that for a long time the accurate description of the $1\,^1B_u$ state has been considered a difficult computational challenge, especially for butadiene.[27,24] A large number of theoretical studies have been reported for this state (the so-called *V* state in Mulliken's terminology, with a mixed valence-Rydberg character), but with disparate and rather unsatisfactory results.[27] With the RPA method, an accurate description is obtained quite independently of the basis set; see Table II. Of course, a large basis set, such as the one used in our previous studies,[7] must be employed in order to have a good overview of the full one-photon absorption spectrum for C_4H_6.

For the "intermediate" polyenes decapentaene ($C_{10}H_{12}$) and dodecahexane ($C_{12}H_{14}$), the decrease of the band gap seems to be slower for the RPA than given by experiment. Unfortunately, the experimental data for these two molecules have been extrapolated using simple solvent-shift theory to analyze data from a number of different solvents.[28] Solvent effects of π-π^* type transitions in general lead to redshifts of the optical excitations[29] (solvatochromatic shifts), although for polyacetylene blueshifts can occur due to temperature-induced conformational changes.[30] For the longer polyenes one can anticipate strong enhancement of the dipolar polarization and reaction field contributions to such redshifts.

TABLE II. Excitation energies (eV) and oscillator strengths of $1\,^1B_u$ states of polyenes.

	E_g				
N	RPA		Expt.	Osc. str.	
C_4H_6	6.06	5.93[a]	5.91[b]	0.889	0.803[a]
C_6H_8	5.17	5.08[a]	4.93[b]	1.404	1.333[a]
C_8H_{10}	4.41	4.45[a]	4.40[b]	1.907	1.841[a]
$C_{10}H_{12}$	4.36		4.02[b,c]	2.460	
$C_{12}H_{14}$	4.10		3.65[b,c]	2.987	
$C_{16}H_{18}$	3.76			4.081	
$C_{20}H_{22}$	3.55			5.116	
$C_{28}H_{30}$	3.30			7.173	

[a] Reference 7 with ANO basis set.
[b] Quoted in Ref. 28.
[c] Corrected to the gas phase using simple solvent-shift theory.

This may be one reason for the relatively large difference between the calculated results and the experimental data in Table II for decapentaene and dodecahexane.

Both series of data display slow convergence of the optical band gap and indicate that the solid polyacetylene value of 2.0 eV can only be reached for very long chains, and probably only if medium effects are accounted for in the computations. The slow convergence of the optical band gap is important for the asymptotic extrapolation for the static and, in particular, the dynamic hyperpolarizabilities discussed below.

The oscillator strength of the $1\,^1B_u$ state increases with the chain length. There is an almost perfect linear relation between the oscillator strength $f(N)$ and the number of unit cells N. We find that

$$f(N)=0.815+0.541(N-2)\ . \tag{3}$$

The oscillator strength per unit cell $f(N)/N$ converges quickly,

$$f(N)/N=0.541-0.267/N\ , \tag{4}$$

when N tends to infinity, the converged value for $f(N)/N$ being 0.541.

C. Length dependence of frequency-dependent polarizabilities

The static dipole polarizabilities of longer polyenes have been studied in more detail than either the static hyperpolarizabilities or the dynamic counterparts of these two quantities. Still, only a few of these calculations have been carried out at the *ab initio* level. One of the most important is the study reported by Hurst, Dupuis, and Clementi,[4] who used coupled perturbed Hartree-Fock theory to determine the static polarizabilities of polyene chains ranging from C_4H_6 to $C_{22}H_{24}$. Dynamic polarizability calculations have been carried out for polyenes as long as $C_{10}H_{12}$.[5] A comprehensive review of the previous polarizability calculations of polyene systems can be found in Ref. 6.

The main reason for studying the length dependence of the molecular properties of polyenes is to be able to extrapolate the values for finite chains to an infinite-chain system, polyacetylene. The longitudinal (hyper)polarizability increases exponentially with increasing size of the oligomers until a linear evolution, or a "correlation length," is reached. The polarizability per unit cell thus increases until a saturation point is reached. At this point the polarizability per unit cell becomes identical to that of the infinite periodic system.[6]

Different approaches and different fitting functions have been used for extrapolating to the asymptotic value per unit cell; see Ref. 6 and references therein. We use the fitting function suggested by Hurst, Dupuis, and Clementi,[4] i.e.,

$$\log_{10}Q(N)=a+\frac{b}{N}+\frac{c}{N^2}\ . \tag{5}$$

Following the discussion of Champagne, Mosley, and André,[6] the fitting function $Q(N)$,

$$\log_{10}Q(N)=a+\frac{b}{N}+\frac{c}{N^2}+\frac{d}{N^3}\ , \tag{6}$$

has also been applied. Here a, b, c, and d are the fitting parameters and N the number of unit cells (or the number of double bonds). The asymptotically extrapolated values for infinite polyacetylene are thus given as 10^a.

Table III presents the static and dynamic polarizabilities of polyenes, for various members of the series up to $C_{28}H_{30}$. The dispersion of the polarizability at $\omega=0.024$ a.u. is very small since this frequency is far from resonance. The dispersion increases with the chain length. For instance, at $\omega=0.048$ a.u. the value of the dispersion is raised from 1.4% for C_2H_4 to 11% for $C_{20}H_{22}$. This simply reflects the fact that the optical gap of the polyenes becomes smaller as the chain length increases, in agreement with the observation in the previous section.

The length dependence of polarizabilities per unit cell, α_i/N, i representing the different components, is plotted in Fig. 1. The relation between $\log_{10}[\alpha_i(N)/N]$ and N is illustrated in Fig. 1(b). The hump at $N=4$ in Figs. 1(a) and 1(b) reflects the switch from optimized to idealized geometries. A similar behavior is also found for the optical gap and the hyperpolarizabilities. The expression $\log_{10}[\alpha_i(N)/N]$ gives a better indication of the convergence behavior for the different components of the polarizabilities per unit cell than does α_i/N. The fitting parameters and the asymptotically extrapolated values for two different fitting functions are listed in Table IV. The asymptotically extrapolated values of α_{xx}/N, α_{yy}/N, and α/N increase by about 10% when the d/N^3 term is introduced in the fitting function, while the values for α_{zz}/N decrease slightly. Our results for the extrapolated values of α_{xx}/N and α/N are in close agreement with those reported by Hurst, Dupuis, and Clementi at the 6-31G* level.[4] The extrapolated values of α_{xx}/N, α_{yy}/N, α_{zz}/N, and α/N are 146.2, 35.5, 11.0, and 63.1 a.u., respectively.

D. Length dependence of frequency-dependent hyperpolarizabilities

The length dependence of the static hyperpolarizabilities has been discussed by Hurst, Dupuis, and Clementi based on coupled Hartree-Fock results.[4] No calculations have been presented for the dynamic hyperpolarizabilities

TABLE III. Frequency-dependent polarizabilities in a.u. of polyenes.

	$\omega=0.0$		$\omega=0.024$		$\omega=0.048$	
N	α_{xx}	α	α_{xx}	α	α_{xx}	α
C_2H_4	35.88	24.68	36.04	24.77	36.53	25.03
C_4H_6	87.38	53.38	88.05	53.67	90.13	54.56
C_6H_8	160.65	90.13	162.47	90.86	168.29	93.18
C_8H_{10}	267.77	139.75	272.27	141.50	287.00	147.21
$C_{10}H_{12}$	347.51	179.08	353.51	181.43	273.24	189.12
$C_{12}H_{14}$	461.09	231.33	470.35	234.94	501.16	246.91
$C_{16}H_{18}$	704.37	339.74	722.05	346.60	782.14	369.87
$C_{20}H_{22}$	974.70	461.02	1002.79	471.93	1099.88	509.43
$C_{28}H_{30}$	1550.08	716.97				

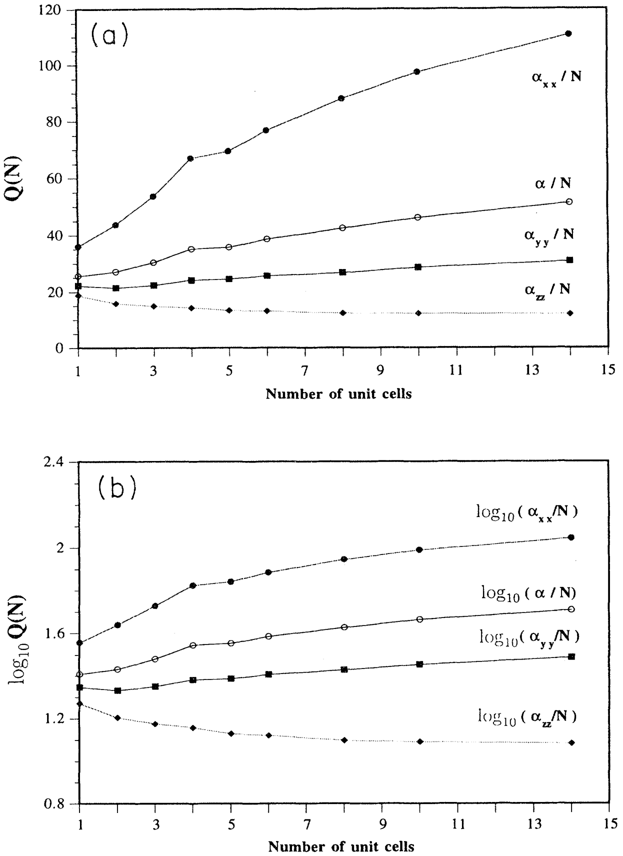

FIG. 1. Length dependence of static polarizabilities of polyenes.

of systems containing more than ten carbon atoms. As discussed in Sec. I, in order to compare with experiment, the calculation must be carried out at the same frequency as in the experiment. For instance, the calculated dynamic hyperpolarizability γ for hexatriene is in good agreement with its experimental counterpart. In contrast, the calculated static value is about 2.5 times smaller than experiment at a fundamental frequency $\omega=0.0656$ a.u. The mismatch between theory and experiment in this respect has recently been resolved by new formulations for dynamic hyperpolarizabilities[31,16,29] allowing for direct experimental comparisons.

TABLE IV. Fitting parameters and asymptotic extrapolated static polarizabilities per unit cell of polyacetylene in a.u. using Eqs. (5) and (6).

		a	b	c	d	$\lim_{N\to\infty} Q(N)$
α_{xx}	Eq. (5)	2.12	−1.42	0.87		130.62
	Eq. (6)	2.17	−2.00	2.43	−1.04	146.22
α_{yy}	Eq. (5)	1.51	−0.61	0.45		32.36
	Eq. (6)	1.55	−1.11	1.82	−0.91	35.48
α_{zz}	Eq. (5)	1.05	0.47	−0.21		11.22
	Eq. (6)	1.04	0.61	−0.70	0.33	10.96
α	Eq. (5)	1.75	−1.02	0.68		56.23
	Eq. (6)	1.80	−1.61	2.29	−1.07	60.12

The dynamic hyperpolarizabilities can be approximated well by the formula[32–34]

$$\gamma_{xxxx}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)=\gamma_{xxxx}(0;0,0,0)(1+A\omega_L^2+\cdots)\,,$$
$$\gamma(-\omega_\sigma;\omega_1,\omega_2,\omega_3)=\gamma(0;0,0,0,0)(1+A'\omega_L^2+\cdots)\,, \tag{7}$$

where $\omega_L^2=\omega_\sigma^2+\omega_1^2+\omega_2^2+\omega_3^2$ and the expansion coefficients A and A' are frequency independent.[34] The dispersion in the low-frequency region is well described by the ω_L^2 term. This has been shown by experimental measurements.[35] However, in order to obtain an accurate description for the dispersion, the ω_L^4 term is needed.[36] The frequency-dependent hyperpolarizability satisfies

$$\gamma(\text{static})<\gamma(\text{Kerr})<\gamma(\text{ESHG})<\gamma(\text{THG})\,,$$

because the first resonance is approached by addition of 0, 1, 2, and 3 frequencies, respectively. Table V lists the static hyperpolarizabilities for polyenes up to $C_{28}H_{30}$. The dynamic hyperpolarizabilities are also listed in terms of the expansion coefficient A. Only the largest component γ_{xxxx} and the averaged value γ are given; the other components are much smaller than γ_{xxxx}. The fundamental frequency of $\omega=0.0239$ a.u., corresponding to the wavelength $\lambda=1907$ nm, has been chosen for the calculations of the Kerr $[\gamma(-\omega;\omega,0,0)]$ and ESHG $[\gamma(-2\omega;\omega,\omega,0)]$ quantities, and used to obtain the expansion coefficient A. The expansion in Eq. (7) yields similar values of A for ESHG and Kerr quantities, the difference between 5% for a short chain and 10% for a long chain. This frequency was chosen to reduce resonance effects, which become more important for the longer chains. Even at this small frequency, a significant length dependence of the dispersion can be discerned. As for the polarizability, the dispersion increases with chain size, reflecting a narrowing of the optical gap. The relation between the hyperpolarizability per unit γ_{xxxx}/N and the number of unit cells N is plotted in Fig. 2(a) for different processes. Different length dependences can be observed for the static, Kerr, ESHG, and THG values. The THG values are obtained from Eq. (7), assuming the same A as for ESHG. It can be expected that the differences become larger at higher frequencies. Similar relations have been found for γ/N; see Fig. 2(b).

As for the polarizability, the convergence of function γ/N with chain length is very slow. Even the logarith-

TABLE V. Frequency-dependent hyperpolarizabilities (in 10^4 a.u.) of polyenes.

N	$\gamma_{xxxx}(0;0,0,0)$	A	$\gamma(0;0,0,0)$	A
C_4H_6	2.59	24.78	1.43	20.40
C_6H_8	11.70	28.68	3.63	27.33
C_8H_{10}	41.64	39.59	10.00	39.68
$C_{10}H_{12}$	85.75	47.57	18.90	40.45
$C_{12}H_{14}$	176.44	56.94	37.09	55.30
$C_{16}H_{18}$	518.50	69.22	104.19	68.35
$C_{20}H_{22}$	1085.12	79.52	217.69	79.36
$C_{28}H_{30}$	2811.99		563.22	

mic function $\log_{10}Q(N)$ has not flattened out at 10 unit cells; see Fig. 3. The fitting parameters and the asymptotically extrapolated values for the static hyperpolarizabilities per unit cell of polyacetylene are obtained using the fitting equations (5) and (6) and are listed in Table VI.

The dynamic hyperpolarizabilites per unit cell of polyacetylene have also been rationalized in terms of the coefficient A. Our static values for the asymptotically extrapolated hyperpolarizabilities are 8.51×10^6 and 1.55×10^6 for γ_{xxxx}/N and γ/N, respectively, in close agreement with the ones obtained by Hurst, Dupuis, and Clementi at the 6-31G level.[4] The influence of the d/N^3 term on the asymptotically extrapolated values is quite significant. These values as fitted by Eq. (6) are about 1.5 and 2 times larger than those fitted by Eq. (5) for γ_{xxxx}/N and γ/N, respectively. Since all components contributing to the averaged hyperpolarizability γ are found to be positive, the asymptotically extrapolated value of γ_{xxxx}/N should be smaller than that of $5\gamma/N$. Such a relation can be found for the asymptotically extrapolated values of γ_{xxxx}/N and γ/N fitted by Eq. (6), but not for those fitted by Eq. (5). The values obtained by Hurst, Dupuis, and Clementi who used the fitting function Eq. (5), do not follow this relation either. This indicates that the fitting function Eq. (6) is more reliable than Eq. (5). The asymptotically extrapolated values of the static γ_{xxxx}/N and γ/N values are 1.26×10^7, 3.24×10^6, respectively. The dispersions at frequency $\omega=0.0239$ a.u. for asymptotically extrapolated hyperpolarizability per cell γ_{xxxx}/N are 25% and 59% for Kerr and ESHG values, respectively. Some effects would be seen by adding the e/N^4 term in the fitting function, however, it would require more theoretical points as optimized parameters to perform the fitting in order to get a reliable value (see also arguments made in Ref. 6). It is difficult to know in advance what kind of fitting function should be used, and we follow here some recommendations of previous studies, for instance, Refs. 4 and 6. Evidently, in order to obtain an accurate value for the "correlation length," direct calculations for very long chains would be required.

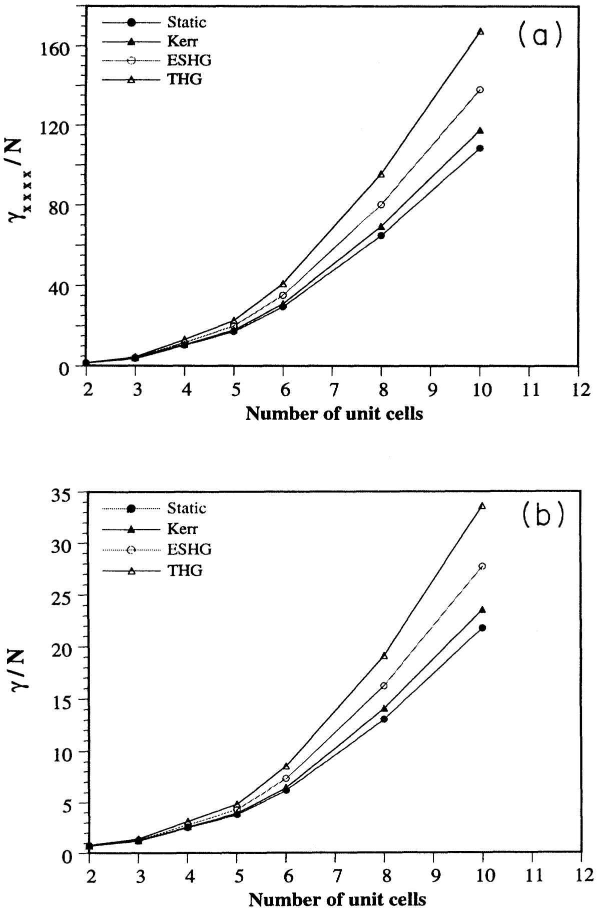

FIG. 2. Length dependence of different nonlinear optical processes for polyenes (a fundamental frequency $\omega=0.0239$ a.u. has been used for the frequency dependent hyperpolarizabilities). The THG values are obtained by using Eq. (7).

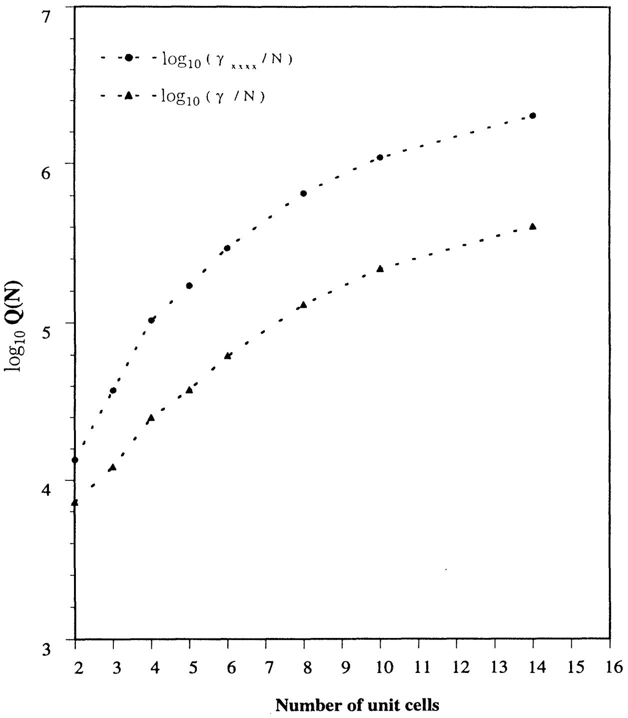

FIG. 3. Length dependence of static hyperpolarizabilities of polyenes.

The dispersion for the THG is about three times that for the ESHG, according to Eq. (7). However, it should be noticed that this value is much smaller than the real one. Since at this point the optical gap is close to the solid polyacetylene value of 2.0 eV, even with the small frequency used here, $\omega=0.0239$ a.u., the frequency of third-harmonic generation, $3\omega=0.0717$ a.u. $=1.95$ eV, is very close to the resonance. The same dispersion should be found for asymptotically extrapolated hyperpolarizability per unit cell, γ/N, since at that point the value of γ is almost completely determined by the $xxxx$ component.

TABLE VI. Fitting parameters and asymptotic extrapolated hyperpolarizabilities per unit cell of polyacetylene in a.u. using Eqs. (5) and (6).

		Fitting parameters					
		a	b	c	d	$\lim_{N\to\infty} Q(N)$	A[a]
γ_{xxxx}	Eq. (5)	6.93	−10.05	8.93		8.51×10^6	109.37
	Eq. (6)	7.10	−12.50	18.57	−10.93	1.26×10^7	171.36
γ	Eq. (5)	6.19	−9.94	10.60		1.55×10^6	
	Eq. (6)	6.51	−14.32	27.82	−19.53	3.24×10^6	

[a] The coefficient A is determined by the ESHG values.

IV. DISCUSSION

We have found the evolution of the static and dynamic polarizabilities and hyperpolarizabilities with respect to the polyene chain length to be very slow. By comparing the values obtained per unit cell from extrapolation and from calculations of the largest considered oligomer, one can obtain an idea about the correlation lengths for these different quantities. The extrapolated values depend critically on the fitting functions as discussed in the preceding paragraph. For the static polarizabilities, the longest system for which calculations are carried out—$C_{28}H_{30}$—does not seem to be too far from the correlation length: At about $N=40$ a value is reached that is 10% from the asymptotic value. Very recently, a semiempirical calculation suggested the "correlation length" to be around 28 carbon atoms.[37]

For the hyperpolarizability and in particular its dispersion the situation is different. For the static hyperpolarizability the calculations indicate correlation lengths well over 100. A more precise prediction cannot be made based on the present fitting functions and set of oligomers. For the dynamic values the question arises as to how to define the correlation length. The dispersions of the different tensor components have different chain-length dependencies, and simple relationships with respect to the number of unit cells are therefore difficult to extrapolate. The very slow convergence of the band gap implies slow convergence for the dynamic values. There are also substantial differences between the different hyperpolarizabilities. The dependence increases in the sequence static, Kerr, ESHG, and THG, depending on the number of frequencies involved. These observations are of course also of consequence for using experimental finite-frequency data to derive the nonlinear character of polyene-related compounds.

It is relevant to relate the findings for the hyperpolarizability of the polyenes with corresponding studies of small species because these offer the possibilities to monitor various contributions to the hyperpolarizability in great detail; viz., the role of correlation, basis sets, frequency dependence, vibrational contributions, and solvent effects; see, for example, recent publications in Refs. 38–45, 17 and 46.

(1) Concerning the role of correlation, we have established the random-phase approximation as an excellent approach for calculations of (hyper)polarizabilities and optical spectra of the polyenes; see also Refs. 5 and 7.

(2) Basis-set investigations show that, although quite extended basis sets are needed for an accurate prediction of the full optical spectra of the shorter polyenes,[7] rather moderate basis sets are sufficient for the length dependence of the optical gap and for the hyperpolarizabilities (cf. the work of Hurst, Dupuis, and Clementi[4]). This observation can partly be explained by the fact that the lowest ^1B_u transition, which determines the band gap, also collects most of the one-photon intensity.

(3) The frequency dependence of the polarizability and the hyperpolarizability is found quite significant, which, together with the fact that the band gap converges slowly, makes extrapolation of these quantities much harder than for their static counterparts.

(4) The solvent effects on hyperpolarizabilities have mostly been analyzed through empirical so-called local-field factors, although recently more refined quantum models have been proposed.[18,17,47] These models have indeed established the strong influence of a solvent on hyperpolarizabilities, both for smaller molecules[18] and for some charge-transfer complexes.[17,47] Unfortunately, these models are not yet applicable to long oligomer chains. One can, nevertheless, anticipate very strong enhancements from the media on the (hyper)polarizabilities of polyacetylene purely on grounds of the large vacuum values for these quantities, since these govern the strengths of both the induced solute fields and the solvent reaction fields. Temperature-dependent conformational changes may also be induced by the solvent, which widens the band gap for polyacetylene[30] and thus reduces the susceptibility.

(5) For small molecules one generally finds vibrational contributions for the frequency-dependent (hyper)polarizabilities to be small, and so also vibrational averaging and geometric effects[38,43,46,48] (at most up to 10% of the electronic value). This is, however, probably not the case for polyene-related compounds. For these one can anticipate important effects also due to vibronic or electron-phonon coupling. These dynamic effects may break the single- to double-bond alternation, and introduce soliton states in the band gap.[2] Such states would alter the hyperpolarizability and the nonlinear properties quite drastically. For prediction of the macroscopic susceptibility of solid polyacetylene it is thus probably just as important to monitor effects due to solitons and the interacting medium as it is to further increase the number of units cell for a single oligomer chain.

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