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Vibrational polarizability of polyacetylene chains

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Within the double harmonic oscillator approximation, *ab initio* vibrational contributions to the static electric dipole polarizability have been computed for the all-*trans* polyacetylene chains homologous series. Atomic basis set and electron correlation effects have been studied on ethylene and *trans*-butadiene as well as the use of semiempirical Hamiltonians. By using the 6-31G* atomic basis set within the Hartree–Fock and the second order Møller–Plesset procedures as well as by using semiempirical Austin model 1 Hamiltonians, the evolution with chain length of the vibrational polarizability per structural unit has been investigated and compared to the electronic contribution. Although smaller than the electronic contributions ($\alpha_{\text{vibration}} \approx 10\% \alpha_{\text{electronic}}$), the longitudinal component to the polarizability presents a similar exaltation as chain length grows, but a slower saturation to an asymptotic value per unit cell. Inclusion of electron correlation via the second order Møller–Plesset technique turns out to reduce the longitudinal component calculated at the Hartree–Fock level, but to increase the transversal and perpendicular components. Whereas it reproduces correctly the evolution with chain length of the vibrational polarizability tensor components, the Austin model 1 technique underestimates the longitudinal term and overestimates the perpendicular term. The major contribution to the vibrational polarizability results from large charge fluxes associated with asymmetric stretching motions of the carbon backbone and with the torsion motions presenting very low vibrational frequencies. © 1994 American Institute of Physics.

I. INTRODUCTION

The evaluation of the polarizabilities of molecular and polymeric systems is a field of important investigations because it is directly related to the design of new compounds for nonlinear optics application.^{1,2} Most of the efforts have focused on the electronic contribution to the polarizability. Aside this electronic response to the applied electrical external field, there is another contribution originating from the distortion of the vibrational motion which results from the coupling between the electronic and nuclear motions.³ Indeed, the application of an external electrical field leads to a shift of the equilibrium geometry and to modifications of the potential energy surface, i.e., of the vibrational frequencies and motions. Marti *et al.*⁴ called these two contributions to the polarizability the *nuclear relaxation* and *vibrational* terms, respectively, whereas Marti and Bishop⁵ used another terminology $\alpha(\text{disp})$ and $\alpha(\text{curv})$ since the equilibrium geometry is displaced and the curvature of the zero-field potential is altered when a field is switched on. Whereas the zero point vibrational averaging of the electronic contribution is taken into account and included in the $\alpha(\text{curv})$ term, these contributions to what we call the *vibrational polarizability* have, however, to be distinguished from the Boltzmann averaging of the electronic polarizability over the different vibrational states which needs statistical considerations.

Many works have dealt with the vibrational polarizability of diatomic molecules in which refined numerical techniques^{3,6} cope with the anharmonicity of the vibrational motions. More recently, Bishop and Kirtman^{7,8} derived per-

turbation formulas for calculating the vibrational dynamic (hyper)polarizabilities of general polyatomic molecules. Their study is centered on the double harmonic oscillator approximation which can be improved upon inclusion of mechanical and electrical anharmonicity corrections in the vibrational potential and in the dependence of the electrical field-induced polarization potential on nuclear coordinates, respectively. Very recently, general finite field procedures to treat polyatomic systems have been developed by Marti *et al.*⁴ and by Cohen *et al.*,⁹ where, respectively, the electrical anharmonicity and both types of anharmonicity corrections are included in the computation of the static vibrational (hyper)polarizabilities. The relationships between the perturbation theoretic and finite field procedures have been clarified by Marti and Bishop.⁵ At the exception of test calculations performed by Bishop and Kirtman⁷ on CO₂, the investigation of trisilane and pentasilane (Ref. 10); a study of H₂O, CO₂, and NH₃ (Ref. 11); the investigation of methane and ethylene by Marti *et al.*,⁴ and the study of Cohen *et al.*⁹ on H₂O, we are not aware of any other *ab initio* vibrational polarizability calculations on polyatomic systems.

In this paper, one applies the double harmonic oscillator approximation to evaluate the vibrational polarizability tensor of the all-*trans* polyacetylene homologous series. The vibrational spectra of polyenes have already been the subject of many theoretical investigations dealing mainly with the equilibrium geometries, the harmonic force fields, a correct estimation of the carbon–carbon stretching modes with and without scaling procedures, the vibrational frequencies, and the evolution of these properties from the oligomers to the infinite stereoregular polymer (For a review of these works, the reader is referred to Refs. 12–18 and references therein). However, probably as a consequence of the lack of experi-

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mental data, little has been paid on the vibrational polarizability calculations, whereas only two works^{15,16} have dealt with infrared intensities.

Section II briefly summarizes the double harmonic oscillator procedure and describes its inherent approximations. The effects of extending the atomic basis set and of including the electron correlation up to second order in the Møller-Plesset (MP2) perturbation theory on ethylene and *trans*-butadiene are discussed in Sec. III. Bearing in mind the goal of applying the technique to very large systems like the fullerenes, where the important electron-phonon coupling foreshadows substantial vibrational contributions to the polarizability, the validity of semiempirical techniques has been questioned. Then, the method is applied to larger and larger polyacetylene oligomers in order to reach the asymptotic value of the vibrational polarizability per structural unit. A comparison with the electronic contribution is performed in what concerns the saturation of the relative value per unit length as chain length increases, as well as in the description of the frequency-dependent effects.

II. METHODOLOGY

Following the perturbation-theoretic method of Bishop and Kirtman,^{7,8} the static electric dipole polarizability tensor components are given by

$$\alpha_{uv} = 2 \sum_{K,k} \frac{\langle 0,0 | \hat{\mu}_u | K,k \rangle \langle k,K | \hat{\mu}_v | 0,0 \rangle}{E_{K,k} - E_{0,0}}, \quad (1)$$

where the sum runs over all the vibronic wave functions $|K,k\rangle$ of energy $E_{K,k}$ besides the ground state $|0,0\rangle$. The first index of $|K,k\rangle = \Psi_K \Phi_{K,k}$ refers to the electronic state, whereas the second refers to the vibrational one. $\hat{\mu}$ is the

electronic and nuclear dipole moment operator. Straightforwardly, these electric dipole polarizability components can be split into a vibrational

$$\alpha_{uv}^{\text{vib}} = 2 \sum_{k \neq 0} \frac{\langle 0,0 | \hat{\mu}_u | 0,k \rangle \langle k,0 | \hat{\mu}_v | 0,0 \rangle}{E_{0,k} - E_{0,0}} \quad (2)$$

and an electronic term

$$\begin{aligned} \alpha_{uv}^{\text{elec}} &= 2 \sum_{K \neq 0} \sum_k \frac{\langle 0,0 | \hat{\mu}_u | K,k \rangle \langle k,K | \hat{\mu}_v | 0,0 \rangle}{E_{K,k} - E_{0,0}} \\ &\cong 2 \sum_{K \neq 0} \sum_k \frac{\langle 0,0 | \hat{\mu}_u | K,k \rangle \langle k,K | \hat{\mu}_v | 0,0 \rangle}{E_{K,0} - E_{0,0}} \\ &= 2 \sum_{K \neq 0} \left\langle 0_0 \left| \left(\frac{\langle 0 | \hat{\mu}_u | K \rangle \langle K | \hat{\mu}_v | 0 \rangle}{E_K - E_0} \right) \right| 0_0 \right\rangle \end{aligned} \quad (3)$$

which includes the zero-point vibrational averaging of the electronic polarizability with respect to the vibrational ground state 0_0 . To get the final form of Eq. (3), one has assumed the generally larger energy separation between the electronic states than between the vibrational levels ($E_{K,k} \cong E_{K,0} = E_K$) and one has used the closure formula ($\sum_k |k_K\rangle \langle k_K| = 1$) which corresponds to the adiabatic approximation and to the developments of Bishop and Kirtman.^{7,8} In this study, the rotational contributions are not considered. One uses the doubly harmonic oscillator approximation. It means that the expansion of the dipole moment operator is limited to the terms linear in the normal coordinate Q_a that the vibrational potential is truncated to the harmonic term which is quadratic in Q_a , and that the zero-point vibrational averaging is zero. Evaluating the vibronic transition matrix elements gives

$$\begin{aligned} \langle 0,0 | \hat{\mu}_u | 0,k \rangle &= \left\langle 0 \left| \mu^0 + \sum_a^{3N-6} \left(\frac{\partial \mu_u}{\partial Q_a} \right)_0 Q_a \right| k \right\rangle = \sum_a^{3N-6} \langle 0 | Q_a | k \rangle \left(\frac{\partial \mu_u}{\partial Q_a} \right)_0 \\ &= \sum_a^{3N-6} \langle 0 | Q_a | \nu_1, \nu_2, \dots, \nu_a, \dots, \nu_{3N-6} \rangle \left(\frac{\partial \mu_u}{\partial Q_a} \right)_0 \\ &= \sum_a^{3N-6} \delta_{0,\nu_1} \delta_{0,\nu_2} \cdots \delta_{0,\nu_{a-1}} \cdots \delta_{0,\nu_{3N-6}} \sqrt{\frac{1}{2\omega_a}} \left(\frac{\partial \mu_u}{\partial Q_a} \right)_0, \end{aligned} \quad (4)$$

where the vibrational states $|k\rangle$ have been defined by their vibrational quantum numbers ν_i associated to each of the $3N-6$ normal modes of the system ($3N-5$ if the molecule is linear) ω_a is the circular frequency. Therefore, in the final expression of the vibrational contribution to the electric dipole polarizability tensor components, the sum runs over all the normal modes of the systems:

$$\alpha_{uv}^{\text{vib}} = \sum_a^{3N-6} \frac{[(\partial \mu_u / \partial Q_a)]_0 [(\partial \mu_v / \partial Q_a)]_0}{\omega_a^2}. \quad (5)$$

In Eqs. (4) and (5), we have used the fact that $\hbar=1$ a.u. Similar expressions can be obtained by following the treatments of Pandey and Santry,¹⁹ of Rinaldi *et al.*²⁰ and of Castiglioni *et al.*²¹ For more details about the techniques, we refer the reader to the reviews of Bishop³ and the papers of Bishop and Kirtman^{7,8} describing the perturbation-theoretic technique to get the vibrational (hyper)polarizabilities. Another approach to deal with the polarizability contribution which arises from the nuclear motion distortion due to external electrical fields is based on the finite field approach. In

that case, the field-dependent energies have to be computed for different field amplitudes. In the first use of this technique completed by Adamowicz and Bartlett,²² the electronic energy surfaces of diatomic molecules have been obtained numerically for different field amplitudes. In a second step, the nuclear equation was solved numerically to get the field-dependent total energies. Very recently, Cohen *et al.*⁹ proposed a general finite field procedure, where the various electronic values for different field amplitudes (dipole moments, polarizabilities, and hyperpolarizabilities as well as their nuclear coordinate dependencies) are obtained analytically from the equilibrium field-free values. Both electrical and mechanical anharmonicities are included up to the different orders. Taking advantage of a procedure providing the field-dependent harmonic vibrational frequencies developed by Duran *et al.*,²³ Marti *et al.*⁴ have drawn a method which includes electrical anharmonicity corrections alone and which distinguishes between the contribution originating from the nuclear relaxations and from the modifications of the potential energy curvature, i.e., of the vibrational frequencies. In an introductory way, Dykstra,²⁴ as well as in a more detailed way, Marti and Bishop,⁵ gave an account of the relationships between the perturbation-theoretic treatment and the finite field techniques. *Within the double harmonic oscillator approach, both types of methods are equivalent and the vibrational contribution to the polarizability is restricted to the nuclear relaxation term.*

In order to evaluate the double harmonic vibrational polarizabilities, the derivatives of the dipole moment with respect to the normal coordinates as well as the vibrational frequencies have been determined by the GAUSSIAN 92 series of programs²⁵ at both the Hartree–Fock and MP2 levels of approximation. Since the dipole derivatives are very sensitive to geometrical structures, the residual forces on the atoms after optimization should be very weak in order to get reliable vibrational polarizability results. A tight convergence threshold has thus been used. Therefore, the threshold on the residual forces on the Cartesian components is set at 1.5×10^{-5} hartree/bohr or hartree/radian. The experimental vibrational polarizability values have been derived from the absolute integrated infrared intensities A_a , which are related to the dipole moment derivatives by the expression

$$A_a = \frac{N_{\text{Avogadro}}}{12 \epsilon_0 c^2} \left[\sum_{i=x,y,z} \left(\frac{\partial \mu_i}{\partial Q_a} \right)^2 \right], \quad (6)$$

where ϵ_0 and c are the vacuum permittivity and the speed of light, respectively.

III. RESULTS AND DISCUSSION

Figure 1 gives the orientation of the molecules under investigation. Assuming full planarity, all-*trans* polyacetylene chains belong to the C_{2h} point group and their normal coordinates transform as the a_g , b_u , a_u , and b_g irreducible representations. Whereas a_g and b_u are in-plane modes, a_u and b_g are out-of-plane motions. Only the a_u and b_u vibrations are infrared active.

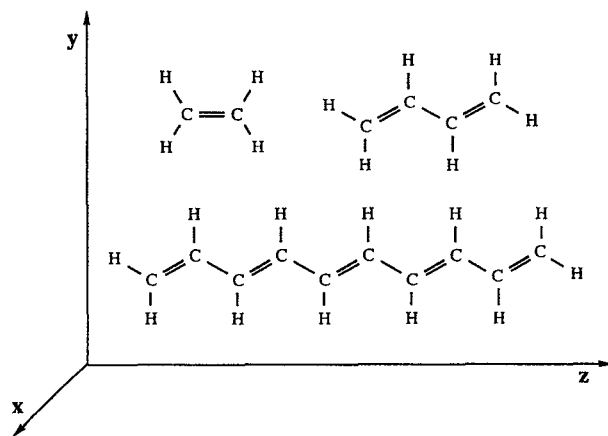


FIG. 1. Ethylene, *trans*-butadiene, and an oligomer of all-*trans* polyacetylene in the Cartesian space.

A. Ethylene

At the *ab initio* Hartree–Fock and MP2 levels of approximation, with the Slater-type orbital STO-3G,²⁶ 3-21G,²⁷ 6-31G,²⁸ 6-31G*,²⁹ 6-31G**,³⁰ 6-311G**,³¹ and the Sadlej medium-size polarized³² atomic basis sets, the vibrational contributions to the polarizability of ethylene have been computed after carrying out the necessary full geometry optimization. Using the semiempirical modified neglect of diatomic overlap (MNDO),³³ modified intermediate neglect of differential overlap (MINDO3),³⁴ Austin model 1 (AM1),³⁵ and parametrized method 3 (PM3)³⁶ Hamiltonians, a similar procedure has been followed. Ethylene belongs to the D_{2h} point group and only vibrational normal coordinates which transform as b_{1u} , b_{2u} , and b_{3u} give rise to vibrational polarizability contributions. Table I lists the calculated infrared-active mode frequencies and their contribution to the vibrational polarizability tensor components as well as experimental values deduced from infrared absolute integrated intensities [Eq. (6)] and other theoretical results. Since the harmonic oscillator approximation has been used in all calculations, the harmonic experimental frequencies and their corresponding vibrational polarizabilities are also given. It is important to note that there is only one type of infrared experimental intensities which obviously include the anharmonicity of the vibrational motions. Contrary to the frequencies, the experimental anharmonic intensities cannot be corrected to give the harmonic intensities. In consequence, these results may be qualified as “semiharmonic” vibrational polarizability values.

It is obvious that techniques reproducing correctly both the vibrational frequencies and infrared intensities are necessary to estimate the vibrational polarizabilities. Whereas the frequencies are only subject to the accuracy of the energy as a function of nuclear displacements, described mainly by the inner valence region, intensities associated with the charge fluxes accompanying the nuclear displacements are more sensitive, via the dipole moment calculations, to the diffuse

TABLE I. Mode contributions to the vibrational polarizability tensor components of ethylene as a function of the method used. The modes are described by their irreducible representation as well as by the type of motion associated to it. The vibrational frequencies ν are given in cm^{-1} and the polarizability α^{vib} in atomic units ($1 \text{ a.u. of polarizability} = 1.6488 \times 10^{-41} \text{ C}^2 \text{m}^2 \text{J}^{-1} = 0.148 \text{ Å}^3$). The orientation of the molecule, given in Fig. 1, is such that every mode contributes only to one component of the polarizability tensor. The exact infrared frequencies are from Ref. 40, while the harmonic frequencies from Ref. 43. Both Refs. 41 and 42 give infrared intensities to which correspond the two sets of vibrational polarizability values.

Symmetry Description	b_{2u} rocking		b_{3u} wagging		b_{1u} scissor	b_{1u} symmetric stretching		b_{2u} asymmetric stretching		
Basis set	ν	α_{yy}^{vib}	ν	α_{xx}^{vib}	ν	α_{zz}^{vib}	ν	α_{zz}^{vib}	ν	α_{yy}^{vib}
Hartree–Fock										
STO-3G	947.5	0.009	1172.2	0.604	1744.2	0.013	3633.7	0.071	3814.9	≤ 0.0005
3-21G	943.4	0.042	1114.7	2.928	1639.8	0.089	3305.7	0.042	3403.0	0.069
6-31G	928.0	0.035	1120.2	3.029	1631.6	0.087	3312.7	0.053	3419.5	0.100
6-31G*	897.0	0.007	1095.1	2.288	1610.2	0.062	3320.8	0.062	3420.6	0.094
6-31G**	894.0	0.006	1092.3	2.246	1597.8	0.076	3297.8	0.056	3401.7	0.090
6-311G**	890.4	0.008	1081.3	2.615	1584.0	0.125	3268.9	0.055	3372.6	0.087
Sadlej	885.5	0.001	1084.7	2.635	1549.2	0.130	3258.2	0.040	3380.1	0.047
MNDO	854.4	0.154	1098.8	0.649	1465.7	0.031	3409.6	0.022	3433.1	0.006
MINDO3	697.5	0.069	979.9	0.494	1305.2	0.112	3524.2	0.164	3556.1	0.462
AM1	834.4	0.024	1067.7	2.316	1412.0	0.025	3185.2	0.031	3217.0	0.095
PM3	821.0	≤ 0.0005	983.7	2.033	1327.4	0.005	3136.9	0.040	3145.5	0.021
Møller–Plesset 2										
STO-3G	880.2	0.015	1039.3	0.636	1632.6	≤ 0.0005	3450.8	0.018	3624.7	0.001
3-21G	893.1	0.061	1005.3	2.794	1572.1	0.050	3171.3	0.033	3279.0	0.067
6-31G	869.8	0.048	1001.1	2.888	1546.8	0.043	3166.1	0.050	3279.1	0.104
6-31G*	849.5	0.034	989.0	2.581	1520.0	0.060	3212.9	0.028	3322.1	0.058
6-31G**	845.8	0.015	992.3	2.261	1522.4	0.045	3238.1	0.030	3356.1	0.059
6-311G**	827.6	0.017	970.6	2.770	1481.0	0.094	3177.6	0.030	3294.0	0.055
Sadlej	823.2	≤ 0.0005	988.7	2.521	1420.4	0.095	3125.0	0.026	3266.4	0.033
STANTON <i>et al.</i> ^a										
Hartree–Fock	890	0.021	1081	2.704	1586	0.135	3303	0.052	3421	0.089
MP2	831	0.043	959	3.096	1506	0.094	3223	0.028	3360	0.055
SDQ-MP4	833	0.020	956	2.893	1513	0.079	3210	0.042	3339	0.079
MP4	825	0.028	939	2.986	1503	0.073	3195	0.040	3326	0.080
EXPERIMENTS										
Exact (Ref. 40)	826.0		949.3		1443.5		3021		3104.9	
Reference 41		0.001		2.541		0.135		0.042		0.073
Reference 42		0.021		2.430		0.128		0.040		0.070
Harmonic (Ref. 43)	843		969		1473		3147		3234	
Reference 41 (semiharmonic)		0.001		2.438		0.130		0.039		0.067
Reference 42 (semiharmonic)		0.020		2.331		0.123		0.037		0.065

^aReference 38.

outer valence region of the electronic density. Basis set and electron correlation effects are thus expected to be more important for the intensity than for the frequency calculations. Results in Table I corroborate this fact. As a result of yielding too steep potential in the vicinity of the equilibrium structure, the Hartree–Fock technique is known to overestimate by roughly 10% the vibrational frequencies. It is then of common practice to scale these values by a $\sqrt{0.8}$ factor¹² to get a better agreement with reality. Our results do not escape from this overestimation. Nevertheless, we did not scale the vibrational frequencies in the present work. Most of the restricted Hartree–Fock error is recovered by including electron correlation at the MP2 level of approximation where the average error in the vibrational frequency drops to 2%–4%. Indeed, the average relative difference between the MP2 results and the harmonic values of Ref. 43 are 3.7%, 2.7%, 2.2%, 2.6%, 1.1%, and 1.9% by using the 3-21G, 6-31G,

6-31G*, 6-31G**, 6-311G**, and Sadlej atomic basis sets, respectively. Many works^{37–39} have shown that using higher correlated methods results, in most of the cases, only in modest improvements. Such highly correlated methods will not be used in this work and the MP2 polarizability results will be chosen as reference values when no experimental data are available. Nevertheless, Table I lists polarizability results deduced from vibrational frequencies and infrared intensities computed by Stanton *et al.*³⁸ with various correlated techniques by using a double zeta basis set augmented with polarization functions.

As shown in Table I, the vibrational polarizabilities are strongly influenced by the basis set. The largest contribution, the out-of-plane contribution (α_{xx}^{vib}), presents the smallest variations if one excludes the STO-3G minimal basis set results. Indeed, at the Hartree–Fock level, the minimal STO-3G basis set underestimates significantly the α_{xx}^{vib} value

by reproducing only 26% of the reference value chosen to be the semiharmonic results obtained from Ref. 42. For that component associated with the wagging motion, increasing the basis set by using valence double zeta sets provides polarizability values which are 20%–25% too large. Adding polarization functions (either d on the carbon atoms, or d on the carbon atoms and p on the hydrogen atoms) gives values 6%–8% too small. A further increase of the calculated values is obtained by using the valence triple zeta and the Sadlej basis sets, the latter having been constructed to give correct estimates of the electric dipole moments and polarizabilities.³² At the exception of the y components originating from asymmetric stretching of the C–H bonds and the rocking of the CH₂ groups, the polarizability variation is small by going from the 6-311G** basis set to the Sadlej basis set. As depicted in Table I, the infrared intensities of the CH₂ rocking mode is difficult to assess. In addition, its comparison with experiment is hindered by the existence of two different sets of values. Our Hartree–Fock *ab initio* values agree very well with the nuclear relaxation polarizability contributions evaluated by Marti *et al.*⁴ by using a triple zeta plus double polarization basis set. The inclusion of electron correlation, by going from the Hartree–Fock to the MP2 results, leads to small variations of the largest contribution (x component $\pm 10\%$), but large variations of the smallest contributions (y component $\pm 30\%$ and z component -50%). By including more electron correlation, additional variations of the vibrational polarizability contributions of $\pm 30\%$ occur, although an exact estimation of these effects would require the use of a more extended basis set than in Ref. 38. Among the semiempirical treatments, the MNDO and MINDO3 schemes fail in reproducing the HF and/or MP2 *ab initio* results. This corroborates the results of Rinaldi *et al.*,²⁰ who found the MNDO technique inadequate to reproduce the infrared-deduced experimental vibrational

TABLE II. Diagonal vibrational polarizability tensor components of *trans*-butadiene as a function of the methods used. The orientation of the molecule is given in Fig. 1. The polarizability values are given in atomic units. ^aThe 1.316 value represents the in plane contribution to the polarizability, i.e., $\alpha_{yy}^{(\text{vib})} + \alpha_{zz}^{(\text{vib})}$.

Method	Basis	α_{xx}^{vib}	α_{yy}^{vib}	α_{zz}^{vib}
<i>H</i>	STO-3G	1.116	0.048	0.677
<i>A</i>	3-21G	5.485	0.181	0.845
<i>R</i>	6-31G	5.308	0.222	0.969
<i>T</i>	6-31G*	4.064	0.214	1.160
<i>R</i>	6-31G**	3.931	0.211	1.167
<i>E</i>	6-311G**	4.678	0.223	1.231
<i>E</i>	Sadlej	4.649	0.183	1.404
<i>F</i>	MNDO	2.264	0.179	0.204
<i>O</i>	MINDO3	1.315	1.055	0.708
<i>C</i>	AM1	4.876	0.186	0.357
<i>K</i>	PM3	4.433	0.096	0.169
<i>M</i>	STO-3G	1.260	0.014	0.342
	3-21G	5.477	0.171	0.540
	6-31G	5.293	0.235	0.605
	6-31G*	4.720	0.175	0.772
<i>2</i>	6-31G**	4.084	0.176	0.754
	6-311G**	5.199	0.193	0.809
Pulay <i>et al.</i> (Ref. 12)		4-21G	6.070	1.316 ^a
Hartree–Fock				

polarizabilities. Using the MINDO3 parametrization even permutes the relative importance of the x and y components to the vibrational polarizability tensor. The PM3 and mainly the AM1 Hamiltonians give better satisfaction in reproducing the *ab initio* trends for both the vibrational frequencies and infrared intensities.

B. *Trans*-butadiene

Similar calculations have been performed for the *trans*-butadiene molecule. To our knowledge, only qualitative in-

TABLE III. Mode frequencies and contributions to the vibrational polarizability of *trans*-butadiene as a function of the technique used. The frequencies are given in cm⁻¹ while the polarizability is given in atomic units. The observed experimental frequencies are from Refs. 44 and 46. The total contribution for each type of motion is given in bold at the end of the individual contributions.

Hartree–Fock 6-31G*		MP2 6-31G*		AM1		Hartree–Fock 4-21G ^a		Experiment	
ν	α_{vib}	ν	α_{vib}	ν	α_{vib}	ν	α_{vib}	ν^b	ν^c
3415.2	0.104	3307.4	0.057	3214.9	0.214	3112	0.108	3102	3101
3342.9	0.038	3214.8	0.012	3183.8	0.079	3045	0.039	3056	3029
3331.8	0.074	3205.8	0.059	3158.0	0.024	3032	0.044	2985	2997
1818.8	0.134	1675.2	0.070	1831.9	<0.0005	1596	0.098	1599	1601
1546.6	0.027	1451.8	0.042	1402.8	0.046	1398	0.014	1385	1387
1438.1	0.037	1349.6	0.030	1302.3	0.001	1302	0.051	1296	1293
1088.5	0.052	1025.0	0.065	1003.3	0.042	999	0.073	991	995
318.9	0.908	297.9	0.612	324.2	0.135	287	0.889	301	300
	b_u 1.374		b_u 0.947		b_u 0.542		b_u 1.316		
1161.1	0.602	1054.5	0.962	1052.6	2.511	1017	0.844	1013	1019
1069.0	2.450	915.8	2.555	951.4	1.017	913	3.514	908	908
581.5	0.908	533.9	0.966	490.0	0.886	516	1.304	524	527
167.0	0.103	158.6	0.238	87.7	0.462	163	0.408	163	162
	a_u 4.063		a_u 4.721		a_u 4.876		a_u 6.070		

^aReference 9.

^bReference 46.

^cReference 44.

TABLE IV. Mode frequencies and contributions to the vibrational polarizability of all-*trans* hexatriene as a function of the technique used. The frequencies are given in cm^{-1} , while the polarizability is given in atomic units. The observed experimental frequencies are from Ref. 13. The total contribution for each type of motion is given in bold at the end of the individual contributions.

Hartree-Fock 6-31G*		MP2 6-31G*		AM1		Hartree-Fock ^a 4-21G		Experiment ^b
ν	α_{vib}	ν	α_{vib}	ν	α_{vib}	ν	α_{vib}	ν
3415.7	0.105	3306.9	0.055	3215.0	0.295	3009	0.110	3091
3343.5	0.106	3213.6	0.015	3182.7	0.123	3042	0.141	3040
3336.3	0.085	3201.1	0.107	3170.0	0.096	3035	0.045	3012
1865.6	0.184	1713.2	0.061	1862.5	<0.0005	1634	0.161	1623
1602.7	0.018	1507.4	0.033	1451.7	0.004	1445	0.021	1429
1447.6	0.060	1354.0	0.054	1353.2	0.099	1301	0.065	1294
1397.5	0.084	1313.2	0.017	1314.1	0.003	1270	0.088	1255
1230.1	0.099	1187.7	0.104	1262.3	0.006	1126	0.130	1130
1045.6	0.041	1000.0	0.065	1007.0	0.059	957	0.097	963
580.6	0.420	548.8	0.293	556.2	0.050	530	0.457	540
159.0	2.891	147.6	1.935	165.8	0.349	143	2.918	/
	a_u 4.104		b_u 2.758		b_u 1.086		b_u 4.239	
1160.9	1.284	1050.8	1.748	1052.4	2.535	1026	1.816	1011
1090.1	0.669	967.3	0.042	980.6	0.020	953	1.109	941
1061.6	1.895	906.6	2.650	961.9	2.312	922	2.491	899
776.6	0.497	704.6	0.428	646.4	0.353	679	0.721	658
267.2	0.812	248.7	0.825	211.4	0.980	242	0.968	
98.3	0.412	93.2	0.913	57.0	1.339	94	1.258	
	a_u 5.569		a_u 6.606		a_u 7.540		a_u 8.363	

^aReference 11.

^bReference 13.

formations about the integrated infrared intensities are available in the literature.⁴⁴ The same situation characterizes longer polyenes.^{45,46} Then, the MP2 results are used as reference. As shown in Fig. 1, the *trans*-butadiene molecule has been oriented in a way to mimic the growing polyacetylene chain of which the z axis corresponds to the periodicity axis. From the results given in Table II, one remarks that the out-of-plane motions still give the largest contribution. Among the Hartree-Fock and MP2 results, it is important to note the weak polarizability tensor component variations from the split-valence 3-21G to the extended 6-311G** atomic basis sets for all three diagonal tensor components. Definitely, the MNDO and MINDO3 parametrizations seem to be avoided in the investigations of the vibrational polarizability of these compounds. Whereas it reproduces in a suitable way the transversal and perpendicular components, the AM1 parametrization underestimates, with respect to the Hartree-Fock results, the longitudinal term. This underestimation is due mainly to the small calculated dipole moment derivatives. Indeed, the frequencies are closer to experiment than the *ab initio* Hartree-Fock values. The PM3 parametrization provides similar out-of-plane polarizability results to the AM1, but further underestimates the in-plane contributions by a factor of ~ 2 . Including electron correlation results mainly in an important decrease (up to 50%) of the longitudinal component, the difference with the AM1 results becoming thus smaller. The larger vibrational polarizability values obtained by using the vibrational frequencies and infrared intensities calculated by Pulay *et al.*¹² with the 4-21G atomic basis set result from their scaling of the force fields to reproduce the fundamental frequencies. Indeed, as presented in Table III,

their Hartree-Fock vibrational frequencies are very close to the experimental values⁴⁷ and, therefore, are $\approx 10\%$ smaller than our Hartree-Fock results.

It is striking to note the overall smaller effect of the basis set on *trans*-butadiene than on ethylene results, although these effects are enhanced when electron correlation is included. Such phenomena have already been pointed out in the calculation of the electronic polarizabilities of conjugated polymeric chains for which the quality of the basis set is improved in the longitudinal direction as chain length grows. Our further investigations performed with the 6-31G* atomic basis set rely on this fact. One selects this basis set because of the good agreement among the 6-31G*, 6-311G**, and Sadlej atomic basis set results.

C. Longer polyenes and extrapolation to the infinite stereoregular polyacetylene chain

As shown in the previous paragraph, by going from ethylene to *trans*-butadiene, the out-of-plane component nearly doubles (the average C_2H_6/C_2H_4 ratios by excluding the too small STO-3G atomic basis set results are 1.77 and 1.86 at the RHF and MP2 levels, respectively), the transversal in-plane y component doubles (the average C_4H_6/C_2H_4 ratios evaluated as for the out-of-plane contribution are 1.93 and 2.21 at the RHF and MP2 levels, respectively), whereas the longitudinal in plane z component drastically increases (the average C_4H_6/C_2H_4 ratios are 8.42 and 7.47 at the RHF and MP2 levels, respectively) (we are aware of the fact that the ethylene molecule should be inclined by roughly 29° to fit the increasing polyacetylene chain). Similar enhancement ef-

TABLE V. Mode frequencies and contributions to the vibrational polarizability of all-*trans* octatetraene as a function of the technique used. The frequencies are given in cm^{-1} , while the polarizability is given in atomic units. The observed experimental frequencies are from Ref. 46. The total contribution for each type of motion is given in bold at the end of the individual contributions. *MIDI-4 is a valence double-zeta atomic basis set designed by Tatewaki and Huzinaga (Ref. 51).

Hartree-Fock 6-31G*		AM1		Hartree-Fock MIDI-4 ^a *		Hartree-Fock ^b 4-21G		Experiments ^c
ν	α_{vib}	ν	α_{vib}	ν	α_{vib}	ν	α_{vib}	ν
3415.8	0.108	3215.2	0.357	3093	0.100	3102	0.116	3091
3343.4	0.198	3182.5	0.149	3018	0.266	3037	0.267	3030
3338.8	0.083	3173.7	0.206	3012	0.036	3030	0.053	
3330.6	0.014	3157.3	0.013	3006	0.022	3024	0.018	3009
3326.6	0.013	3141.4	0.006	3001	0.004	3019	0.004	2967
1887.4	0.173	1876.1	<0.005	1631	0.232	1634	0.221	1632
1794.7	0.068	1831.6	0.001	1583	0.169	1584	0.081	1558,1569
1579.3	0.012	1425.9	0.008	1412	0.041	1423	0.092	1405
1459.5	0.002	1342.5	0.049	1304	0.005	1317	0.169	1303
1438.2	0.141	1324.6	0.103	1284	0.186	1293	0.642	1280
1367.1	0.166	1296.3	0.004	1232	0.141	1245	0.184	1229
1245.8	0.192	1233.8	0.041	1135	0.238	1138	0.591	1139
1018.7	0.012	985.4	0.054	932	0.075	929	0.176	
608.8	0.294	611.3	0.028	571	0.358	559	0.356	565
419.3	0.876	415.2	0.102	390	0.802	377	0.954	390
93.6	6.208	98.8	0.681	87	5.732	84	6.534	96
	a_u 8.560		b_u 1.802		b_u 8.407		b_u 10.458	
1160.5	2.210	1052.4	2.531	1018	3.583	1027	2.936	1011
1109.9	0.404	986.0	0.020	965	0.745	976	0.564	960
1062.8	2.206	966.0	3.621	905	3.685	926	3.055	900
959.9	0.080	869.4	<0.0005	832	0.302	843	0.145	840
698.8	0.544	589.9	0.476	618	1.172	617	0.776	629
239.6	0.256	150.5	1.019	251	0.473	239	0.332	245
179.7	0.709	120.1	0.157	172	0.825	167	0.778	181
61.4	0.783	38.7	2.579	61	2.915	58	2.418	
	a_u 7.192		a_u 10.403		a_u 13.700		a_u 11.004	

^aReference 18.

^bReference 50.

^cReference 46.

fects are common when considering the evolution of the electronic contribution to the polarizability tensor of conjugated systems as a result of electron delocalization along the polymer backbone.⁴⁸ For the smallest oligomers, the longitudinal component increases exponentially with chain length, then the evolution becomes linear as chain length is larger (around 15–20 double bonds for polyacetylene⁴⁹). Indeed, increasing the degree of polymerization leads to a number of very regular and systematic trends, provided no drastic conformational changes occur. How fast the convergence of the oligomeric to the bulk properties is reached depends very much on the system under consideration and the property under investigation. In the case of polyacetylene chains, π -electron delocalization along the polymer backbone plays a key role and, indeed, the saturation of the properties due to π electrons is attained when the polymer chain is, at least, as long as the delocalization length. The example of the evolution of the bond length alternation parameter and of the first optically allowed excitation energy with chain length accounts for this fact. When the evolution with chain length is supralinear, it is usual to consider the polarizability per structural unit and to investigate the asymptotic limit of this quantity. First, Tables III–VI list the contributions of each individual infrared-active mode to the polarizability of *trans*-butadiene, all-*trans* hexatriene, all-*trans* octatetraene, and

all-*trans* decapentaene obtained at the Hartree-Fock and MP2 (only *trans*-butadiene and all-*trans* hexatriene) levels by using the 6-31G* atomic basis set or by using the AM1 technique. These vibrational polarizability contributions are compared to those obtained by the groups of Pulay^{12,13} and Karpfen¹⁸ that we have calculated by using their computed vibrational frequencies and infrared intensities. A comparison with observed experimental frequencies is carried out.

The Hartree-Fock, as well as to a lesser extent the MP2, 6-31G* frequencies overestimate the observed values. As already pointed out, the scaling procedures correct that overestimation. The AM1 technique provides good frequency estimates at the exception of those corresponding to motions involving the CC single and double bonds. Moreover, the difference between Hartree-Fock and MP2 results is also the largest for these carbon backbone motions. This should be related to the too large bond length alternation evaluated at the Hartree-Fock level and to the difficulty of obtaining the correct force fields.^{17,18} Indeed, adequate bond length alternation values require taking into account electron correlation effects. No systematic differences characterize the effects of the method on the computed infrared intensities. Our calculated infrared intensities are always in good qualitative agreement with the experimental observed quantities.^{44–46} The general trends are the same as for ethylene and *trans*-

TABLE VI. Mode frequencies and contributions to the vibrational polarizability of all-*trans* decapentaene as a function of the technique used. The frequencies are given in cm^{-1} while the polarizability is given in atomic units. The total contribution for each type of motion is given in bold at the end of the individual contributions.

Hartree-Fock 6-31G*		AM1		Hartree-Fock MIDI-4 ^a	
ν	α_{vib}	ν	α_{vib}	ν	α_{vib}
3415.9	0.111	3215.0	0.404	3093	0.103
3343.3	0.308	3182.2	0.162	3018	0.431
3340.2	0.071	3175.0	0.351	3015	0.024
3333.5	0.031	3164.4	0.029	3008	0.034
3328.2	0.011	3149.6	0.003	3002	0.006
3324.5	0.005	3139.4	0.014	3001	0.005
1893.6	0.157	1874.6	<0.0005	1627	0.137
1829.7	0.123	1847.3	<0.0005	1604	0.332
1595.2	0.010	1476.9	0.006	1422	0.036
1480.4	0.009	1401.9	0.015	1313	0.014
1450.7	0.013	1336.7	0.127	1297	0.058
1434.2	0.244	1328.0	0.001	1281	0.281
1350.4	0.263	1308.1	0.071	1220	0.231
1259.5	0.234	1285.1	0.004	1157	0.024
1225.5	0.008	1224.7	0.064	1140	0.259
1032.4	0.012	985.5	0.056	943	0.076
586.9	0.036	582.4	0.002	548	0.009
520.1	0.826	518.7	0.088	488	0.957
294.8	1.289	296.5	0.136	274	1.192
61.2	10.944	65.1	1.144	57	10.016
	b_u 14.705		b_u 2.677		b_u 14.225
1160.2	2.746	1052.6	2.529	1019	4.850
1123.7	0.316	988.8	0.014	980	0.568
1071.1	0.904	971.9	0.072	920	1.208
1059.7	1.425	968.0	4.843	902	2.630
993.5	0.061	906.7	0.013	859	0.323
732.9	0.505	614.4	0.406	642	1.145
421.7	0.146	344.5	0.193	384	0.184
190.6	0.477	119.3	1.208	194	1.009
139.4	0.683	91.5	0.156	133	0.767
41.1	1.115	27.3	4.001	40	3.390
	a_u 8.378		a_u 13.435		a_u 16.074

^aReference 18.

butadiene, i.e., (i) including electron correlation decreases the in-plane contribution and increases the out-of-plane one. Using the 6-31G* atomic basis set, the $\alpha_{zz}(\text{MP2})/\alpha_{zz}(\text{HF})$ ratio seems converging as chain length increases. Indeed, since the α_{zz}^{vib} values are 0.089, 0.772, and 2.498 a.u. at the MP2 level and 0.119, 1.160, and 3.806 a.u. at the RHF level for ethylene, *trans*-butadiene, and all-*trans*-hexatriene, respectively, the corresponding $\alpha_{zz}(\text{MP2})/\alpha_{zz}(\text{RHF})$ ratios are 0.75, 0.67, and 0.66. Improving the accuracy of the MP2/RHF ratio by dealing with larger chains is, however, impossible because these systems are actually out of range when employing that MP2 technique on our computer resources; (ii) the AM1 in-plane contributions are strongly underestimated, whereas the out-of-plane component is similar to the ones computed with the *ab initio* techniques; (iii) the use of scaled force fields^{12,13,18} modifies mainly the out-of-plane contribution which increases roughly by 50%.

The largest contributions to the vibrational polarizability are due to asymmetric stretching motions of the carbon backbone as well as out-of-plane torsion motions having very low vibrational frequencies. In the infinite polymer limit, these out-of-plane torsion contributions become negligible with re-

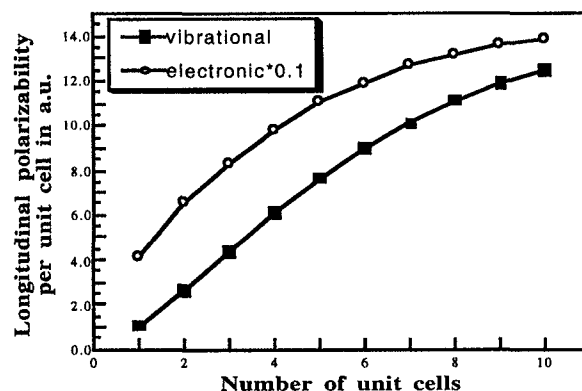


FIG. 2. Evolution with chain length of the 6-31G* Hartree-Fock longitudinal tensor component of the vibrational and electronic polarizabilities per unit cell of polyacetylene chains. To fit all curves in the same diagram, the electronic contributions have been reduced by a factor of 10.

TABLE VII. Vibrational and electronic polarizability tensor components of increasingly large polyacetylene chains obtained at the Hartree-Fock level by using the 6-31G* atomic basis set. The polarizability differences between consecutive oligomers [$\alpha(N) - \alpha(N-1)$], which represents the polarizability per unit cell, are given in italics and are intercalated between the polarizability values. The orientation of the molecule is given in Fig. 1. The polarizability values are given in atomic units. The last line provides the extrapolated values of the polarizability per unit cell.

6-31G* <i>N</i>	Vibrational			Electronic		
	α_{xx}	α_{yy}	α_{zz}	α_{xx}	α_{yy}	α_{zz}
1	2.288	0.107	0.118	8.297	22.481	28.816
	<i>1.776</i>	<i>0.107</i>	<i>1.042</i>	<i>6.938</i>	<i>17.846</i>	<i>44.638</i>
2	4.064	0.214	1.160	15.235	40.327	73.454
	<i>1.505</i>	<i>0.084</i>	<i>2.646</i>	<i>6.792</i>	<i>17.470</i>	<i>65.228</i>
3	5.569	0.298	3.806	22.027	57.797	138.682
	<i>1.423</i>	<i>0.073</i>	<i>4.383</i>	<i>6.762</i>	<i>17.521</i>	<i>83.242</i>
4	6.992	0.371	8.189	28.789	75.318	221.924
	<i>1.381</i>	<i>0.067</i>	<i>6.078</i>	<i>6.748</i>	<i>17.614</i>	<i>98.184</i>
5	8.373	0.438	14.267	35.537	92.932	320.108
	<i>1.371</i>	<i>0.061</i>	<i>7.625</i>	<i>6.742</i>	<i>17.704</i>	<i>110.074</i>
6	9.744	0.499	21.892	42.279	110.636	430.182
	<i>1.358</i>	<i>0.057</i>	<i>8.998</i>	<i>6.738</i>	<i>17.780</i>	<i>119.292</i>
7	11.102	0.556	30.890	49.017	128.416	549.474
	<i>1.341</i>	<i>0.055</i>	<i>10.104</i>	<i>6.736</i>	<i>17.839</i>	<i>126.331</i>
8	12.443	0.611	40.994	55.753	146.255	675.805
	<i>1.345</i>	<i>0.053</i>	<i>11.119</i>	<i>6.734</i>	<i>17.885</i>	<i>131.676</i>
9	13.788	0.664	52.113	62.487	164.140	807.481
	<i>1.340</i>	<i>0.053</i>	<i>11.886</i>	<i>6.733</i>	<i>17.920</i>	<i>135.699</i>
10	15.128	0.717	63.999	69.220	182.060	943.180
	<i>1.331</i>	<i>0.052</i>	<i>12.476</i>	<i>6.732</i>	<i>17.948</i>	<i>138.904</i>
11	16.459	0.769	76.475	75.952	200.008	1081.984
Extrapolated value per unit cell	1.33±0.01	0.052±0.001	14.35±0.90	6.731±0.002	18.04±0.01	148.6±0.2

spect to the in-plane contribution. While Table VII gives the vibrational and electronic polarizability tensors of increasingly large polyacetylene chains, the evolution of the tensor components of both the vibrational and electronic polarizabilities per unit cell is depicted in Fig. 2 as a function of chain length.

For comparison, AM1 values are given in the case of the vibrational contributions (Table VIII and Fig. 3). As chain length increases, the longitudinal vibrational and electronic polarizabilities per unit cell increase then saturate for longer chains, whereas the transversal and perpendicular components are nearly constant. As depicted in Fig. 2, the vibrational longitudinal values per unit cell saturate more slowly than the electronic ones. This suggests that the underlying phenomena of vibrational polarization are related to more delocalized features than the electronic polarization. Since the oligomeric values obtained for $C_{22}H_{24}$ do not attain the plateau, one has to extrapolate in order to predict the polymeric result. This value is obtained by extrapolating to infinite length the expression

$$\alpha_{zz}(N) - \alpha_{zz}(N-1) = a - be^{-cN}, \quad (7)$$

of which the parameters have been obtained by fitting the molecular results. The asymptotic polymeric values, equal to a , are given at the bottom of Table VII. Four points associated with the largest oligomers have been used in that fitting. The imprecision on the extrapolated values corresponds to their fluctuations by adding a fifth point in the fitting procedure.

TABLE VIII. Vibrational and electronic polarizability tensor components of increasingly large polyacetylene chains obtained at the AM1 semiempirical level. The orientation of the molecule is given in Fig. 1. The polarizability differences between consecutive oligomers [$\alpha(N) - \alpha(N-1)$], which represent the polarizability per unit cell, are given in italics and are intercalated between the polarizability values. The polarizability values are given in atomic units.

AM1 <i>N</i>	Vibrational		
	α_{xx}	α_{yy}	α_{zz}
1	2.316	0.097	0.078
	<i>2.550</i>	<i>0.089</i>	<i>0.279</i>
2	4.866	0.186	0.357
	<i>2.674</i>	<i>0.138</i>	<i>0.404</i>
3	7.540	0.324	0.761
	<i>2.863</i>	<i>0.166</i>	<i>0.547</i>
4	10.403	0.490	1.308
	<i>3.030</i>	<i>0.194</i>	<i>0.684</i>
5	13.433	0.684	1.991
	<i>3.169</i>	<i>0.222</i>	<i>0.781</i>
6	16.602	0.906	2.752
	<i>3.277</i>	<i>0.245</i>	<i>0.867</i>
7	19.879	1.151	3.619
	<i>3.318</i>	<i>0.232</i>	<i>0.573</i>
8	23.197	1.383	4.192
	<i>3.377</i>	<i>0.263</i>	<i>1.698</i>
9	26.574	1.646	5.890
	<i>3.383</i>	<i>0.373</i>	<i>0.686</i>
10	29.957	2.019	6.576
	<i>3.446</i>	<i>0.322</i>	<i>0.903</i>
11	33.403	2.341	7.479

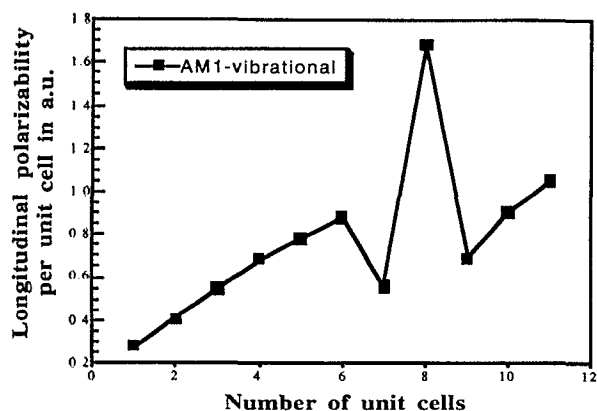


FIG. 3. Evolution with chain length of the AM1 longitudinal tensor component of the vibrational polarizability per unit cell of polyacetylene chains.

Using the AM1 technique, the longitudinal component of the vibrational polarizability per unit cell increases with increasing chain length, but oscillates too. Smaller oscillations characterize the evolution with chain length of the other tensor components. This is due to the numerical procedure used in that case which is less accurate than the analytical method followed in the HF and MP2 calculations. In what concerns the vibrational polarizability per unit cell of the longest chains, both AM1 and *ab initio* 6-31G* methods give out-of-plane contributions having the same order of magnitude, the AM1 results being nearly three times as large as the 6-31G* ones. This is not true for the in-plane contributions. Indeed, whereas the AM1 procedure leads to transversal polarizability per unit cell values nearly one order of magnitude larger than that obtained with the 6-31G* atomic basis set, it estimates the longitudinal component to be one order of magnitude smaller.

D. Frequency-dependent vibrational polarizability

The frequency-dependence effects on the vibrational polarizability are substantial at the optical wavelength usually employed in the measurements. Indeed, these photon sources possess wavelengths in the range 589–1907 nm which correspond to photon energies ranging from 2.11 to 0.65 eV, or from 0.0774 to 0.0239 a.u., or in terms of frequency units, from 16 990 to 5250 cm^{-1} . Then, since these energies are larger than the separation between the vibrational levels, in most of the cases, the resonance phenomena related to the vibrational levels are not seen and the frequency dependence results in an important decrease of the vibrational polarizability (one or two order of magnitude) as well as a change of sign. In these cases, at frequency ω , the dispersion effect associated to the contribution of each vibrational mode can be characterized by the ratio

$$\frac{\alpha_k(\omega)}{\alpha_k(0)} = \frac{\omega_k^2}{\omega_k^2 - \omega^2} \approx -\frac{\omega_k^2}{\omega^2}. \quad (8)$$

Figure 4 represents that frequency dispersion at small (infrared domain) and large (UV/visible domain) frequency values

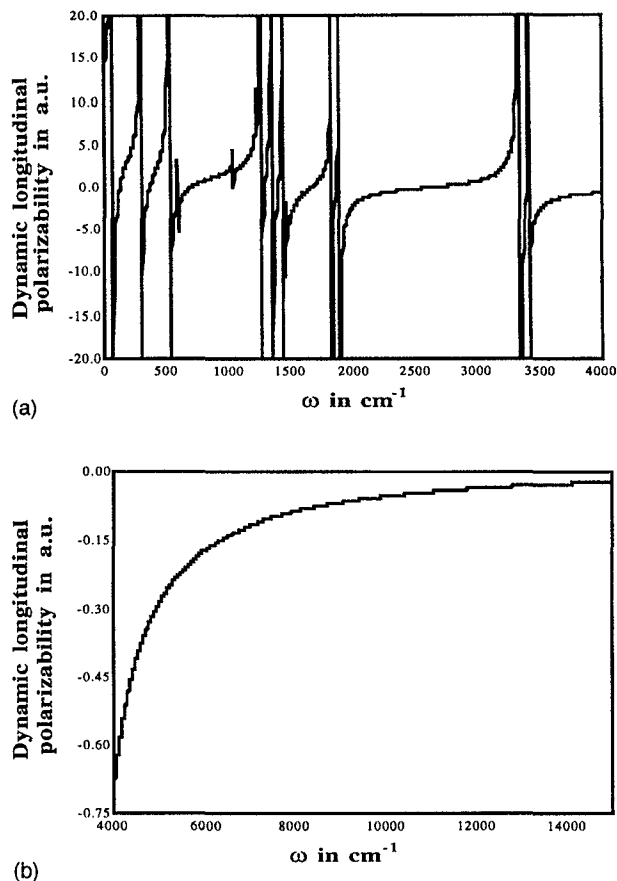


FIG. 4. Frequency dispersion of the longitudinal vibrational polarizability of all-*trans* decapentaene obtained at the Hartree–Fock level by using the 6-31G* atomic basis set. (a) Frequency in the infrared domain; (b) frequency in the UV/visible domain.

for the longitudinal polarizability tensor component of all-*trans* decapentaene, computed with the 6-31G* atomic basis set at the Hartree–Fock level. In these calculations, the method would not be valid at and near resonance if the damping is zero (the relaxation time is infinite). By taking care of the finite relaxation time, the real part of the dynamic vibrational polarizability associated with each of the $3N-6$ ($3N-5$ for linear molecules) modes is therefore expressed with respect to the static value

$$\alpha_k(\omega) = \alpha_k(0) \frac{\omega_k^2 [\omega_k^2 - \omega^2 + (\Gamma_k^2/4)]}{[\omega_k^2 - \omega^2 + (\Gamma_k^2/4)]^2 + \omega^2 \Gamma_k^2}, \quad (9)$$

where Γ_k the damping is the inverse of the radiative lifetime. To draw Fig. 4, a damping factor of 0.01 cm^{-1} corresponding to a relaxation time of $\approx 2 \times 10^{-8} \text{ s}$ has been employed. This dispersion of the vibrational polarizability with the frequency of the source has to be related with that of the electronic one, which consists of increases by going from the static situation to the usually employed UV/visible frequencies.⁵² This polarizability increases range from 5%–10% for the smallest oligomers to 10%–20% and even more for the largest chains as a consequence of the decrease of the first singlet excitation energy as chain length grows. At the optical wavelength used in experiments, the asymptotic C–H

motions contribute most to the vibrational polarizability as a consequence of their very large infrared intensities. On the other hand, the important static contribution arising from the torsion motions of low vibrational frequency is damped by the frequency effect.

IV. CONCLUSION AND OUTLOOKS

This first study of the effects of the extent of the atomic basis set and the inclusion of electron correlation on the vibrational contribution to the electric dipole polarizability of small and large oligomeric systems indicate the reliability of using a split-valence basis set augmented by polarization functions on the carbon atoms to investigate the polyacetylene chains. Inclusion of electron correlation influences mainly the longitudinal component. This result is connected with the bond length alternation decrease which is obtained at the MP2 level and which better fits reality. It has been shown that the vibrational longitudinal polarizability per unit cell increases with chain length as the electronic contribution until a saturation is attained. The extrapolated value of the vibrational contribution is approximately one order of magnitude smaller than the electronic ones in the case of polyacetylene chains. In addition, at the UV/visible optical wavelength generally employed in the polarizability measurements, the vibrational contribution is lowered by one or two orders of magnitude and changes of sign.

Further investigations would require the assessment of the anharmonicity effects. Indeed, by including electrical anharmonicity, Marti *et al.*⁴ have shown in the case of the ethylene molecule that the modification of the vibrational levels upon electrical field switch provides a contribution to the polarizability nearly as large as that originating from the nuclear displacements.

Moreover, the slow convergence to the polymeric limit of the longitudinal polarizability per unit cell with chain length suggests the interest of developing polymeric techniques, taking into account the translational periodicity of the polymers and providing directly the asymptotic value per unit cell.

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