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Correlated frequency-dependent electronic first hyperpolarizability of small push–pull conjugated chains

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Abstract

The longitudinal component of the dynamic electronic first hyperpolarizability of α,ω-nitro,amino-polyacetylene oligomers containing a small number of unit cells has been computed at the Hartree–Fock, Møller–Plesset and coupled-cluster levels with different atomic basis sets. Using frequency-dependent coupled-cluster results, we have tested the efficiency of the additive and multiplicative corrections to approximate the frequency-dependent correlated values. The multiplicative approach provides frequency-dependent electronic first hyperpolarizability values that are within a few percent of the true correlated ones whereas the additive correction leads to $\beta_L(-\omega_\sigma; \omega_1, \omega_2)$ too small by $\sim 20\%$. It turns out that the MP2/6-31G procedure is a suitable approach to reach a semi-quantitative accuracy. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Investigations focusing on the computation or measure of the first hyperpolarizability, $\beta(-\omega_\sigma; \omega_1, \omega_2)$ $(\omega_\sigma = \omega_1 + \omega_2)$, of push–pull systems have been numerous in the last two decades (see, e.g., Ref. [1] and references therein). These molecules possess large $\beta(-\omega_\sigma; \omega_1, \omega_2)$ values as a consequence of the combination of delocalization along the conjugated space and of electronic asymmetry originating from the donor and acceptor groups. It is surprising that most of the theoretical work devoted to these compounds has been performed at semi-empirical levels, and, when taken into account, the electron correlation (EC) effects are generally treated by means of the CI model.

Most work devoted to substituted polyacetylene (PA) chains, the prototype systems due to the simplicity of their structure and their large non-linear optical (NLO) response, have been limited to small chains which can be synthesized by organic chemistry means. Nevertheless Morley and co-workers have focused on the evolution with chain length of $\beta(-\omega_\sigma; \omega_1, \omega_2)$ with the help of the CNDOVSB

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technique [2–4]. Their evaluations show that a saturation of the 'bulk' NLO response has to be expected for very large chains. This saturation corresponds to a decrease of β per unit cell and thus to the presence of an optimal (maximum β per unit cell) chain length. Aiming at the semi-quantitative determination of the height and the position of this maximum, one needs to use efficient ab initio techniques for both small and large conjugated chains. The purpose of the present Letter is to assess the validity of different computational techniques with respect to different parameters for determining semi-quantitative (i.e. with a $\sim$25% accuracy) $\beta(-\omega_\sigma; \omega_1, \omega_2)$ of large α,ω-nitro,amino-polyacetylene oligomers (see Fig. 1). Three questions have to be answered:

(1) Which atomic basis set is needed? This question has been treated many times for different 'NLO-molecules'. The procedure often developed is the search for a relatively small basis set able to reproduce the results obtained with more extended ones.

(2) Which level of electron correlation (EC) has to be included? Indeed, it has been shown that the inclusion of the first level of EC, i.e. within the second-order Møller–Plesset (MP2) scheme, modifies substantially the Hartree–Fock (HF) hyperpolarizabilities [5–8] whereas the effects of higher-order EC corrections depend on the molecule but are of smaller amplitude [6,8,9]. In particular, for α,ω-nitro,amino-polyacetylene oligomers, we have already shown that higher-order correlation effects are small [8].

(3) How to approximate the frequency dependence in correlated calculations of β for long chains? This last question arises from the computational difficulty to calculate $\beta(-\omega_\sigma; \omega_1, \omega_2)$ for extended systems at an electron correlated level. The standard approach is to combine electron correlated results for the static hyperpolarizability ($\beta^{EC}(0;0,0)$) with static and dynamic Hartree–Fock results ($\beta^{HF}(-\omega_\sigma; \omega_1, \omega_2)$), because both types of calculations can be performed on large molecules. Two procedures have been designed: the additive correction

$$\beta^{EC}(-\omega_\sigma; \omega_1, \omega_2) \approx \beta^{EC}(0;0,0) + \left[\beta^{HF}(-\omega_\sigma; \omega_1, \omega_2) - \beta^{HF}(0;0,0)\right] \quad (1)$$

and the multiplicative correction

$$\beta^{EC}(-\omega_\sigma; \omega_1, \omega_2) \approx \beta^{EC}(0;0,0)\frac{\beta^{HF}(-\omega_\sigma; \omega_1, \omega_2)}{\beta^{HF}(0;0,0)}. \quad (2)$$

To our knowledge, the only tests of the validity of these corrections have been carried out by Rice and Handy at the MP2 level on ammonia and formaldehyde [10], by Sekino and Bartlett with the coupled-cluster (CC) procedure on ammonia [11], by Aiga and Itoh at MP2 level on ammonia and water [12] and by Oddershede and co-workers with the MCSCF technique on a set of di- and triatomic molecules [13]. Rice and Handy have shown that the additive correction works well for formaldehyde whereas for ammonia, for which MP2 affects strongly $\beta(0;0,0)$, the use of Eq. (1) leads to a strong underestimation of $\beta^{EC}(-\omega_\sigma; \omega_1, \omega_2)$. The results of Sekino and Bartlett [11] and Aiga and Itoh [12] seem to indicate that Eq. (2) is a valid approximation. Dalskov et al. showed that, relatively, $\beta^{HF}(-\omega_\sigma; \omega_1, \omega_2)$ changes less with frequency than $\beta^{EC}(-\omega_\sigma; \omega_1, \omega_2)$ and, when the discrepancies are small, both the addition and the multiplication are valid approximations [13]. The range of validity of Eq. (1) and Eq. (2) is further specified by considering the link between the static and dynamic β's, given by the power series expansion [14–17]:

$$\beta(-\omega_\sigma; \omega_1, \omega_2) = \beta(0;0,0)\left[1 + A\omega_L^2 + B\omega_L^4 + C\omega_L^6 + \ldots\right], \quad (3)$$

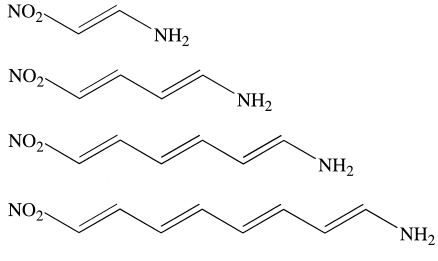


Fig. 1. Schematic representation of the four first oligomers (N = 1, 2, 3 and 4) of α,ω-nitro,amino-polyacetylene oligomers.

where

$$\omega_L^2 = \omega_\sigma^2 + \omega_1^2 + \omega_2^2 . \quad (4)$$

It is interesting to note that the expansion coefficients A and B depend only on the molecule but not on the optical process considered [17]. Within CC response theory, analytical forms have been derived for these expansion coefficients [18]. Provided the expansion can be truncated after the first (A) term, i.e. at low frequencies), the validity of the multiplicative and additive correction schemes is determined by comparing the coefficients A^{EC} and A^{HF}: if $A^{EC} = A^{HF}$ the multiplicative approximation is more efficient, while if $\beta^{EC}(0;0,0)A^{EC} = A^{HF}\beta^{HF}(0;0,0)$ the additive correction has to be preferred [13].

2. Methodology

The ground state geometry of each molecule has been fully optimized at the MP2/6-31G level. The geometry optimizations have been carried out with convergence thresholds corresponding to the tight keyword in GAUSSIAN94 [19]. Afterwards the longitudinal electronic first hyperpolarizability ($\beta_L(-\omega_\sigma;\omega_1,\omega_2)$, from now referred to as β instead of β_L.) has been computed, as explained below. Although the geometry could substantially influence the β values, we have decided, in the present study, to fix the geometry and concentrate upon the other parameters.

The application of an external uniform electric field $\boldsymbol{E}$ on a molecule leads to a reorganization of its electrons and, subsequently, a modification of its energy (ϵ). In the dipolar approximation, this energy stabilization is characterized by the alignment of the dipole moment with the electric field. The first hyperpolarizability corresponds to the second-order response of the dipole moment to the external electric fields:

$$\mu_i(\omega_\sigma) = \mu_i^0 + \frac{1}{1!}\sum_j \alpha_{ij}(-\omega_\sigma;\omega_1)E_j(\omega_1) + \frac{1}{2!}K^2\sum_{j,k}\beta_{ijk}(-\omega_\sigma;\omega_1,\omega_2)E_j(\omega_1)\times E_k(\omega_2) + \cdots , \quad (5)$$

where i, j and k are the Cartesian coordinates and K^2 is necessary in order that the $\beta(-\omega_\sigma;\omega_1,\omega_2)$ corresponding to the different NLO processes converge towards the same static limit ($\beta(0;0,0)$). μ^0 is the dipole moment of the molecule in the absence of a field and α_{ij} stands for the different components of the electric dipole polarizability tensor. Due to the large π-electron delocalization along the carbon backbone, the longitudinal part of the β tensor of α,ω-nitro,amino-PA chains dominates all the other components, especially in the longer chains. So, we have restricted our study to this longitudinal part of the β tensor, the most interesting to be maximized.

At the HF level analytic $\beta(-\omega_\sigma;\omega_1,\omega_2)$ have been computed within the time-dependent Hartree–Fock method (TDHF) [20] implemented in the HONDO95.3 program [21]. The static limit of the TDHF value corresponds to the coupled Hartree–Fock (CHF) value which can be obtained by the coupled perturbed Hartree–Fock (CPHF) method [22] or the finite field (FF) approach applied to the RHF wavefunction and energy.

When EC is included via the Møller–Plesset partioning scheme, the $\beta(0;0,0)$ values of the various oligomers have been computed by adopting the numerical (FF) procedure:

$$\beta^{0,k}(0;0,0) = \lim_{E\to 0}\frac{\epsilon(-2^{k+1}E) - 2\epsilon(-2^kE) + 2\epsilon(2^kE) - \epsilon(2^{k+1}E)}{2(2^kE)^3}, \quad (6)$$

where ϵ is the total energy of the molecule and $E = 2\times 10^{-4}$ a.u. (1 a.u. of electric field = 5.1422×10^{11} V m^{-1}) is the basic static external electric field amplitude. k ($k = 0,1,2,\ldots,6$) defines the successive field amplitudes used. The field amplitudes are following a power-of-two pattern to permit the application of the Romberg procedure [23]. Indeed, starting with the values obtained by using different k in Eq. (6), one could systematically improve the accuracy on the β values by applying the iterative formula:

$$\beta^{p,k}(0;0,0) = \frac{4^p\beta^{p-1,k}(0;0,0) - \beta^{p-1,k+1}(0;0,0)}{4^p - 1}, \quad (7)$$

where p is the number of the Romberg iteration. The FF calculations have been realized with the GAUSSIAN94 program [19]; during the calculations the SCF convergence criterion has been tightened to 10^{-13} a.u. Comparison between the FF–HF and CPHF results provides an insight into the numerical accuracy of the FF procedure. In our case the largest discrepancies were of the order of 0.1%. During the MP calculations the core electrons were kept frozen. This has been shown to have no significant influence [6].

The CC2 and CCSD calculations for the static and frequency-dependent hyperpolarizabilities β and for the hyperpolarizability dispersion coefficient A have been carried out using the implementation of the coupled-cluster quadratic response approach in a local version of the DALTON program [24], as described in Refs. [18,25,26].

3. Results and discussion

3.1. Choice of the atomic basis set

In Table 1 we display the ratios between the MP2 $\beta(0;0,0)$ obtained with the 6-31G and with four other atomic basis sets: 6-31G + pd [27], cc-pVDZ [28], 6-311G* [29] and aug-cc-pVDZ [28,30]. The 6-31G + pd basis has been optimized by Hurst and co-workers in order to obtain second hyperpolarizability (γ) values of PA oligomers close to those evaluated with more extended basis sets. A similar procedure has been followed by Dupuis and co-workers for push–pull molecules [7,31]. Hurst et al. have worked on unsubstituted chains and gave no exponent for the additional p and d diffuse gaussians centered on nitrogen and oxygen atoms. For N and O atoms, we have used exponents of 0.07 and 0.10, respectively, to be consistent with the ratios between the exponents of the diffuse functions of the Sadlej [32–34] and Dunning basis sets [28,30].

With the exception of the aug-cc-pVDZ basis, the ratios in Table 1 tend to be closer to one when chain lengthens, i.e. for medium (and large) oligomers, the 6-31G basis set seems adequate to reproduce $\beta(0;0,0)$ values obtained with more extended basis. The ratios of Table 1 do not vary very strongly between consecutive oligomers. It is well known that polarization and diffuse gaussians are needed in order to achieve a balanced description of $\beta(0;0,0)$. With that respect, the 6-31G basis is even more satisfying because it compares well with aug-cc-pVDZ. Our limited computational resources have, nevertheless, hampered to test this observation on chains longer than the trimer. An additional CPHF calculation with the very large d-aug-cc-pVTZ basis set gives a ratio of 0.948 with respect to the 6-31G basis set for the monomer, confirming the ability of the 6-31G basis to mimmic the $\beta(0;0,0)$ obtained with extremely accurate calculations. Hurst et al. [27] have explained the good behaviour of the 6-31G basis set for extended compounds, by the fact that the functions centered on each carbon atom helps the description of the adjacent carbons.

Table 1
$\beta(0;0,0)$ (CPHF/X) / $\beta(0;0,0)$ (CPHF/6-31G) and $\beta(0;0,0)$ (FF-MP2/X) / $\beta(0;0,0)$ (FF-MP2/6-31G) ratio as a function of the number, N of CH = CH unit cells of the all-trans α,ω-nitro,amino-polyacetylene chains. All results have been obtained at the MP2/6-31G geometry.

X	6-311G*		6-31G + pd		cc-pVDZ		aug-cc-pVDZ	
N	HF	MP2	HF	MP2	HF	MP2	HF	MP2
1	0.818	0.798	1.229	1.204	0.733	0.721	1.003	0.939
2	0.838	0.813	1.149	1.177	0.776	0.746	0.931	0.919
3	0.841	0.824	1.116	1.156	0.789	0.764	0.899	1.067
4	0.842	0.839	1.094	1.142	0.796	0.783		
5	0.843	0.858			0.803	0.806		
6	0.844	0.880						
7	0.847	0.903						

3.2. Choice of the correlation technique

The results of the MP2, MP3, MP4, CC2 and CCSD calculations on oligomers containing up to 4 unit cells displayed in Table 2, prove that the MP2 level is rather satisfactory for the substituted PA oligomers. Indeed, in all cases the CPHF values are too small by a factor ~ 2.5, the MP2 technique includes the largest part of the EC correction to $\beta(0;0,0)$ and the higher-order contributions only modulate $\beta(0;0,0)$. In this way, the discrepancies observed between the MP2 and MP4 $\beta(0;0,0)$ are negligible whereas the differences between the MP2 and CCSD values are small ($<30\%$) but seems to increase with N. CCSD and CCSD(T) finite field calculations performed with GAUSSIAN94 on the two smallest systems have result in very small differences between the DALTON and GAUSSIAN94 CCSD values and a negligible triple contribution (CCSD(T)-HF ratio: 2.963 and 2.421 for $N=1$ and $N=2$, respectively). We note that all the ratios of Table 2 decrease slowly with chain length showing that the impact of EC goes down with N. The CCSD/HF ratio is slowly converging with respect to N.

The different components of the total MP4 contribution can be evaluated separately. For the trimer the relative importance to the MP4 correction (-137 a.u.) to β are: -945 a.u. for the singles, 1488 a.u. for the doubles, 255 a.u. for the triples and -935 a.u. for the disconnected quadruples excitations and the associated renormalization. The (cpu-consuming) triple component is the smallest but is essential to obtain a correctly balanced MP4 correction. However, the absolute importance of the MP4 contribution is always very small.

For calculations on longer compounds ($N>4$), the MP2 level which provides a good estimate of the total EC effect seems a good compromise between accuracy and computational difficulty.

3.3. Approximation of the dispersion

In Table 3 we display the static and dynamic first hyperpolarizabilities obtained for three different experimental frequencies by the TDHF and CCSD schemes, as well as the results of performing the approximations given in Eq. (1) and Eq. (2).

As expected, the dispersion effects are quite large for these conjugated molecules. For the tetramer, at CCSD level, the use of an electric field of wavelength equal to 632.8 nm gives rise to a $\beta(-\omega;\omega,0)$ 83% larger than the static value. The absolute differences between the TDHF and CCSD results is important (a factor of ~ 2). Relatively, they are, however, both affected in a similar way by the frequency of the incident electric field. For this reason, the multiplicative approximation reveals very powerful for these compounds. Indeed, the relative difference between the exact CCSD values and the one obtained by employing Eq. (2) is smaller than 4% for the monomer, 3% for the dimer, 1% for the trimer and 4% for the tetramer. We can, however, not be sure that the almost perfect efficiency of Eq. (2) will go on for longer chains. Indeed, when the chain further grows, the value of the lowest-energy dipole-allowed excitation (LEDAE) decreases and the TDHF excitation energies become less accurate: the multiplicative approach should become less reliable. To evaluate the LEDAE we have used the A coefficients obtained when replacing β by α in Eq. (3). Indeed, $1/\sqrt{A}$ for the polarizability provides an estimate of the value of LEDAE. For the four oligomers investigated, it was found that the difference between TDHF and CCSD LEDAE is decreasing with chain length. The additive correction pro-

Table 2
$\beta(0;0,0)$ of all-*trans* α,ω-nitro,amino-polyacetylene oligomers: comparison between the different EC techniques. All results have been obtained using the 6-31G basis set (1 a.u. of first hyperpolarizability $= 3.2063\times10^{-53}$ C^3 m^3 J^{-2} $= 8.641\times10^{-33}$ esu)

N	HF	MP2/HF	MP3/HF	MP4/HF	CC2/HF	CCSD/HF
1	379.2	2.890	2.682	2.791	2.912	3.003
2	1 798.1	2.580	2.575	2.573	2.480	2.523
3	5 008.9	2.464	2.524	2.460	2.307	2.104
4	10 500.4	2.374	2.357	2.349	2.201	1.741

Table 3
β of all-*trans* α,ω-nitro,amino-polyacetylene oligomers: comparison between the TDHF, exact and approximated CCSD dynamic responses for three different frequencies. All results are in a.u. and have been obtained with the 6-31G basis. λ is the wavelength corresponding to the frequency ω

		$\lambda = 632.8$ nm	$\lambda = 1064$ nm	$\lambda = 1907$ nm	
N	$\beta(0;0,0)$	$\beta(-\omega;\omega,0)$	$\beta(-\omega;\omega,0)$	$\beta(-\omega;\omega,0)$	$\beta(-2\omega;\omega,\omega)$
TDHF:					
1	379.2	514.5	420.6	391.5	417.7
2	1798.1	2705.4	2059.4	1838.0	2040.5
3	5008.9	8469.1	5943.1	5274.9	5874.1
4	10500.4	20025.6	12906.5	11172.9	12725.1
CCSD:					
1	1138.6	1602.0	1275.7	1178.8	1266.0
2	4536.3	7024.0	5234.0	4737.3	5183.2
3	10537.8	17854.7	12493.4	11093.2	12348.6
4	18283.7	33492.0	22184.4	19378.7	21891.8
Approx. CCSD dispersion by addition (Eq. (1)):					
1		1273.9	1180.0	1150.9	1177.1
2		5443.6	4797.6	4576.2	4778.7
3		13998.0	11472.0	10803.8	11403.0
4		27808.9	20689.8	18956.2	20508.4
Approx. CCSD dispersion by multiplication (Eq. (2)):					
1		1544.9	1262.9	1175.5	1254.2
2		6825.3	5195.5	4637.0	5147.8
3		17817.4	12503.2	11097.4	12358.0
4		34869.3	22473.3	19454.7	22157.4

vides less interesting results (maximum difference of 20%, 22%, 22% and 17% for the monomer, dimer, trimer and tetramer, respectively) than the multiplicative correction. Moreover, as expected, the two approximate schemes work better at longer wavelength because the dispersion effects are smaller (Eq. (3)). Indeed, for the $\beta(-\omega;\omega,0)$ computed at a wavelength of 1907 nm, the multiplicative (additive) procedure is off by 2%, 0% and 0% (3%, 6% and 2%), for the dimer, trimer and tetramer, respectively.

According to Dalskov et al. [13], the explanation for the good behavior of the multiplicative correction scheme can be found by comparing the A's obtained at the HF and CC levels of approximation (Table 4). For the three molecules the CC and HF A's are similar: the impact of the wavelength of the electric field on $\beta(-\omega_\sigma;\omega_1,\omega_2)$ is well reproduced with the TDHF technique. Obviously, the push–pull molecules considered here can be classified in the category of the 'well-behaving' ones of Dalskov. It is also interesting to note that for the trimer and tertramer $A^{CCSD}/A^{HF} < 1$, i.e. the TDHF dispersion is more pronounced; this has not been found in any of the six molecules tested in Ref. [13]. It can be important to define the frequency range in which the $A\omega_L^2$ term accounts for most of the frequency disper-

Table 4
Comparison between the first coefficient of the dispersion expansion (A of Eq. (3)) obtained by the TDHF, CC2 and CCSD methods. The TDHF A's have been obtained by a least-squares fitting with the function $[1 + A\omega_L^2 + B\omega_L^4 + C\omega_L^6]$ realized on a set of nine $\beta(-\omega;\omega,0)$ points corresponding to frequencies = 0.00; 0.05; …; 0.4 u.a. The CC A's are determined directly by the analytic procedure used

N	TDHF	CC2	CCSD
1	27.6	31.5	30.1
2	35.8	40.5	37.5
3	45.0	50.6	44.4
4	53.6	60.5	50.2

sion, i.e. the terms associated to B, C, ... of Eq. (3) are negligible. To do so we have define the value of the energy such that $B(\hbar\omega_L)^4 = A(\hbar\omega_L)^2/10$ as in Ref. [35]. At the TDHF level for $\beta(-\omega;\omega,0)$, we have found border values of 1.37, 1.19, 1.04 and 0.97 eV for the monomer, dimer, trimer and tetramer, respectively. The CCSD limits are slightly smaller.

4. Conclusions and outlook

We have computed and analyzed the behavior of the longitudinal dynamic electronic first hyperpolarizability of α,ω-nitro,amino-polyacetylene oligomers containing a small number of unit cells by including electron correlation effects. Although the absolute β values are very different at HF and correlated levels, the multiplicative correction approximation for estimating the correlated dynamic β values is very powerful for the molecules considered because the shape of the dispersion is very similar at both TDHF and CCSD levels. For long chains, the basis set extension required to attain a semi-quantitative precision decreases and the split-valence 6-31G turns out to be satisfactory. For reaching this precision, inclusion of electron correlation is also required. For the oligomers investigated the difference between second-order Møller–Plesset and coupled-cluster with single and double excitations is limited to $\sim$ 30%.

Calculations using the multiplicative combination of TDHF/6-31G $\beta(-\omega_\sigma;\omega_1,\omega_2)$ and MP2/6-31G $\beta(0;0,0)$ of longer chains are currently being made in order to assess the saturation behavior of β.

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