

# ELECTRON CORRELATION EFFECTS AND DIPOLAR/OCTUPOLAR CONTRIBUTION ON THE FIRST HYPERPOLARIZABILITY OF PUSH-PULL OLIGOMER SYSTEMS

## EFFECTOS DE CORRELACIÓN ELECTRÓNICA Y CONTRIBUCIÓN DIPOLAR / OCTUPOLAR EN LA PRIMERA HIPERPOLARIZABILIDAD DE SISTEMAS PUSH-PULL OLIGÓMEROS

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The hyper-Rayleigh scattering first hyperpolarizabilities  $\beta_{HRS}$  of a series of push-pull oligomer are studied using theoretical chemistry methods. Several DFT XC functionals have been used while reliable atomic basis sets have been selected for their evaluations. The behavior of hyper-Rayleigh scattering first hyperpolarizability is studied as a function the basis sets, of electron correlation, of solvent as well as the strength of the electron donor groups to address structure-property relationships. It has been observed that the electron correlation effects are huge, the Moller–Plesset results reproduces the values of the first hyperpolarizability obtained with the reference CCSD(T) level. Among density functional theory exchange-correlation functionals, B3LYP, M062X and CAM-B3LYP are reliable to the MP2 for characterizing the static and dynamic first hyperpolarizability. Finally, the EFISHG first hyperpolarizabilities values put on view different ordering and present more delicate variations as a function of the substituted oligomers. The depolarization ratios follow an opposite ordering as the anisotropy factors while they display an extensive separation dipolar-octupolar character.

Las primeras hiperpolarizabilidades de dispersión hiper-Rayleigh  $\beta_{HRS}$  de una serie de oligómeros push-pull se estudian utilizando métodos de química teórica. Se han utilizado varias funciones DFT XC, mientras que se han seleccionado conjuntos de bases atómicas fiables para sus evaluaciones. La primera hiperpolarizabilidad  $\beta_{HRS}$  se estudia en función de los conjuntos de bases, de correlación de electrones, del disolvente, así como de la fuerza de los grupos donantes de electrones para abordar las relaciones estructura-propiedad. Se ha observado que los efectos de correlación electrónica son enormes, los resultados de Moller-Plesset reproducen los valores de la primera hiperpolarizabilidad obtenidos con el nivel de referencia CCSD (T). Entre las funciones de intercambio-correlación de la teoría funcional de densidad, B3LYP, M062X y CAM-B3LYP son fiables para la primera hiperpolarizabilidad estática y dinámica. Finalmente, los primeros valores de hiperpolarizabilidades de EFISHG ponen a la vista diferentes ordenamientos y presentan variaciones más delicadas en función de los oligómeros sustituidos. Las relaciones de despolarización siguen un orden opuesto al de los factores de anisotropía, mientras que muestran un carácter de separación dipolar-octupolar extenso.

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### I. INTRODUCTION

Second-order nonlinear optical organic materials are interesting due to their high potential in photonic applications such as active wavelength filters, optical switches, modulators and for THz wave generation [1–3]. For high-speed second-order nonlinear optical (NLO) applications, such as electro optics (EO), second-harmonic generation (SHG), optical parametric oscillation (OPO), and optical rectification (OR), including terahertz (THz) wave generation, a highly asymmetric electronic response of the material to the external electric field is required [4].

The level of SHG response of a given material is intrinsically dependent upon its structural attributes. On a molecular scale, the extent of charge transfer (CT) across the NLO chromophore determines the level of SHG output; the greater the CT, the larger the SHG output [1–5]. The search for larger first hyperpolarizabilities combines the selection of a bridge and the better donor/acceptor substituted groups,

which maximises the nonlinear optical response of materials. Consequently, a number of quantum mechanical studies have been devoted to predict these properties. First and second Hyperpolarizabilities have been evaluated with several methods, i.e., HF, DFT, MP2, MP4, CCSD, and CCSD(T), using the 6-31G(d), 6-31G+(d), and 6-311+G(d), aug-cc-pVDZ and aug-cc-pVTZ basis sets [6]–[12]. The SOS method was used for calculation of static and dynamic hyper polarizabilities at Time-dependent Hartree-Fock (TDHF) and Time-dependent density functional (TDDFT) levels [13].

After many years of investigations, there is a need to reconsider some basic concepts using density functional DFT methods. So, further refinement and better basis sets are still needed to obtain more qualitative and quantitative results.

In this study, density functional method was applied to predict and analyze the first hyperpolarizability  $\beta_{HRS}$  of push–pull oligomer [D- $\pi$ -NO<sub>2</sub>]. This is achieved by performing quantum chemical calculations at different levels

of approximation and discussing the relative performance of different methods for assessment of MP2 and DFT schemes with respect to CCSD(T) method. In addition, we address for a series of all-trans oligomer  $\text{NO}_2\text{-(CH=CH)}_3\text{-D}$ , the substitution effects on the first hyperpolarizabilities ( $\beta_{\text{HRS}}$ ) that can be measured using the electric field induced second harmonic generation (EFISHG) technique. Also, we discuss the theoretical separation of the octupolar and dipolar contributions to the HRS first hyperpolarizability.

## II. COMPUTATIONAL DETAILS

The geometries were fully optimized in vacuum and in acetonitrile solvent at the density functional theory (DFT) level using the B3LYP exchange–correlation functional and the 6-311G\* basis set.

The dynamic  $\beta_{\text{HRS}}(-2\omega, \omega, \omega)$  and static  $\beta_{\text{HRS}}(0; 0, 0)$  first hyperpolarizabilities were evaluated with different schemes. Firstly, at the time-dependent Hartree-Fock (TDHF) [14], coupled perturbed Hartree-Fock (CPHF) and secondly at the time-dependent density functional theory (TDDFT) [15]. To take into account the solvent effects, the polarizable continuum model within the integral equation formalism (IEF-PCM) [16] was used.

The TDDFT calculations were carried out using the common wavelength ( $\lambda$ ) of 1064 nm. Only some DFT XC functionals were selected to calculate  $\beta$ : the B3LYP [17], M05-2X and M05 [18], LC-BLYP [19], CAM-B3LYP [20], M062X [21], BHHLYP [22] and B3P86 [23]. The LC XC functionals have been shown to correct conventional DFT schemes for their short-sighted drawbacks [24].

Champagne and co-workers [25] developed an effective method to evaluate the hyper-Rayleigh scattering (HRS) response  $\beta(-2\omega; \omega, \omega)$ , which is described as:

$$\beta_{\text{HRS}}(-2\omega, \omega, \omega) = \sqrt{(\langle \beta_{\text{ZZZ}}^2 \rangle) + (\langle \beta_{\text{ZXX}}^2 \rangle)} \quad (1)$$

$\langle \beta_{\text{ZZZ}}^2 \rangle$  and  $\langle \beta_{\text{ZXX}}^2 \rangle$  are the orientational averages of the molecular  $\beta$  tensor components.

The molecular geometric information is given by the depolarization ratio (DR), which is expressed by:

$$\text{DR} = \frac{\langle \beta_{\text{ZZZ}}^2 \rangle}{\langle \beta_{\text{ZXX}}^2 \rangle} \quad (2)$$

The amplitude of DR depends on the angle between the chromophores as well as the strengths of the Donnor/Acceptor groups. For an ideal system within substituted Donnor/Acceptor groups the  $\text{DR} = 5$  [24, 25].

On the other hand, the central quantity  $\beta_{\parallel}(-2\omega; \omega, \omega)$  corresponds to the projection of the vector part of  $\beta$  on the dipole moment vector:

$$\beta_{\parallel} = \frac{3}{5} \sum \frac{\mu_i \beta_i}{\|\mu\|} \quad (3)$$

where  $\|\mu\|$  is the norm of the dipole moment and  $\mu_i$  and  $\beta_i$  are the components of the  $\mu$  and  $\beta$  vectors.

The relative contribution of the octupolar and dipolar components is given by the nonlinear anisotropy ratio:

$$\rho = \frac{|\beta_{J=3}|}{\beta_{J=1}} \quad (4)$$

where  $\beta_{J=1}$  and  $\beta_{J=3}$  are the dipolar and octupolar contributions of the  $\beta$  response.

Then, the nonlinear anisotropy parameter  $\rho$  is employed to evaluate the ratio of the octupolar [ $\Phi_{\beta J=3} = \rho/(1 + \rho)$ ] and dipolar [ $\Phi_{\beta J=1} = 1/(1 + \rho)$ ] contribution to the hyperpolarizability tensor.

To account for frequency dispersion at the Møller-Plesset (MP2) level, we employed the multiplicative approximation, which consists of multiplying the static MP2 value by the ratio between the TDHF and CPHF values. In the case of  $\beta$  this expression reads:

$$\beta_{\text{MP2}}(-2\omega; \omega, \omega) = \beta_{\text{MP2}}(0; 0, 0) \times \frac{\beta_{\text{TDHF}}}{\beta_{\text{CPHF}}} \quad (5)$$

This approximation, which assumes that frequency dispersion is the same at both the HF and correlated MP2 levels, has been shown to be a satisfactory approximation for different systems [27]. All reported  $\beta$  values are given in a.u. [1 a.u. of  $\beta = 3,6213 \times 10^{-42} \text{ m}^4 \text{V}^{-1} = 3,2064 \times 10^{-53} \text{ C}^3 \text{m}^3 \text{J}^{-2} = 8,639 \times 10^{-33} \text{ esu}$ ] within the T convention [5]. All calculations were performed using the Gaussian 09 program [28].

## III. RESULTS AND DISCUSSION

### III.1. Optimized geometry

The principal geometrical parameters of the all trans  $\alpha, \omega$ -nitro, dimethylamino-hexatriene are displayed in figure 1 and presented in Table S1 (Supporting information). The B3LYP/6-311G\* optimized geometry shows a planar structure, the calculated dihedral angles are  $\theta_{\text{N8C7C6C5}} = 180^\circ$ ,  $\theta_{\text{C2C3C4C5}} = 180^\circ$  and  $\theta_{\text{C7C6C5C4}} = 180^\circ$ . In addition, the bond lengths of the C=C bonds are not the same. The middle  $\text{C}_4=\text{C}_5$  bond has a length of 1,363 Å while the  $\text{C}_2=\text{C}_3$  and  $\text{C}_6=\text{C}_7$  bonds at the ends of the molecule have lengths of 1,366 Å and 1,349 Å, the  $\text{C}_2=\text{C}_3$  bond in close proximity to the substituted alkylamine group  $-\text{N}(\text{Me})_2$  is more longer. The C–N bonds elongate, the  $\text{C}_2-\text{N}(\text{Me})_2$  bond is shorter 1,358 Å than the  $\text{C}_7-\text{NO}_2$  bond close to 1,493 Å. The carbon-carbon single bonds  $\text{C}_3-\text{C}_4$  and  $\text{C}_5-\text{C}_6$  are reduced to 1,43 Å long, also off from the standard 1,54 Å length of carbon-carbon single bonds. However, the difference between the bond lengths of the  $\text{C}_4=\text{C}_5/\text{C}_3-\text{C}_4$  and  $\text{C}_4=\text{C}_5/\text{C}_5-\text{C}_6$  bonds in the middle leads to an average bond length alternation (BLA) for the  $\pi$ -conjugate bridge about 0,063 Å. Moreover, an increase of 0,014 Å in bond-length alternation takes place from the middle to the end of the acceptor-side- $\text{NO}_2$ , the BLA between the  $\text{C}_6=\text{C}_7$  and  $\text{C}_5-\text{C}_6 = 0,077$  Å. However, on the donor-side  $-\text{N}(\text{Me})_2$  the BLA between the  $\text{C}_2=\text{C}_3$  and  $\text{C}_3-\text{C}_4$  is close to 0,059 Å and a

decrease of  $-0,004 \text{ \AA}$  in bond-length alternation is observed.

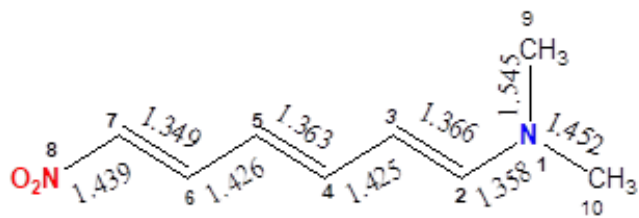


Figura 1. B3LYP/6-311G\* optimized structure for the all trans  $\alpha,\omega$ -nitro, dimethylamino-hexatriene with the principal interatomic distances ( $\text{\AA}$ ).

### III.2. Basis sets effects

The choice of atomic orbital basis set for determining the static and dynamic HRS first hyperpolarizabilities was addressed by considering the trans  $\alpha,\omega$ -nitro, dimethylamino-hexatriene as test compound (1) and the B3LYP level of theory using different base sets (6-31G\*, 6-311G\*, 6-311G\*\*, 6-31G\*\*, 6-31+G\*, 6-311+G\*, 6-311+G\*\*, cc-pVDZ, cc-pVTZ, and aug-cc-pVTZ) with taking into account the effects of acetonitrile solvent using the IEFPCM scheme.

The results for basis sets effects on the static and dynamic  $\beta_{||}$ ,  $\beta_{vec}$  and  $\beta_{HRS}$  of the trans  $\alpha,\omega$ -nitro, dimethylamino-hexatriene determined at the B3LYP level are presented in figure 2a and 2b and Table S2 (Supporting information). These results show that the largest basis set aug-cc-pVTZ, the smallest 6-31G\* and the rather extended cc-pVTZ provides the largest and the smallest values respectively. The variations in  $\beta_{HRS}$  upon adding diffuse polarization, or valence functions in the basis set are similar, but the agreement with the reference values is partially different. So, though the 6-31+G\* and 6-311+G\* basis set reproduces the aug-cc-pVTZ result within 5.52% and 4.25% respectively. This difference increases to about 27.28% for the 6-31G\* values and by 31.70% to 18.22% for the moderately extended cc-pVDZ and cc-pVTZ basis sets respectively. Adding diffuse functions in the basis set has a small impact on the agreement with more complete basis sets. Indeed, although the difference in  $\beta$  between the 6-31G\* and 6-311G\* basis sets and the 6-31+G\* basis sets attains 27%–31%, the amplitude of the deviations with respect to the aug-cc-pVTZ basis set is similar and fluctuates between 5% and 27%. These results also demonstrates that the effect of polarization functions is seen very clearly, *d*-polarization functions tend to decrease in the hyperpolarizabilities magnitude of both  $\beta_{HRS}$  and  $\beta_{||}$ . Whereas the *p*-polarization functions leads to smaller changes. Going from a double- $\zeta$  to a triple- $\zeta$  basis set leads an increase but not dramatic on hyperpolarizabilities. When adding diffuse functions this always leads to an increase in  $\beta_{HRS}$  values. It can be concluded that diffuse and polarization functions lead to opposite trends for  $\beta_{HRS}$ . Several studies have demonstrated that the use of a split-valence or split-valence plus polarization basis set augmented with a set of *p* and *d* diffuse functions on the second row atoms enables the reproduction of hyper-polarizability of large- and medium-size  $\Pi$ -conjugated systems calculated

with larger, and computationally less affordable, basis sets [29,30]. The basis set effects on the depolarization ratios (DR) are negligible (see Table S2 Supporting information).

In summary, the influence of the basis set on the  $\beta$  quantities is generally important. Considering the interplay between accuracy and computational requirements, the 6-311+G\* and 6-31+G\* basis set was selected for the rest of the study.

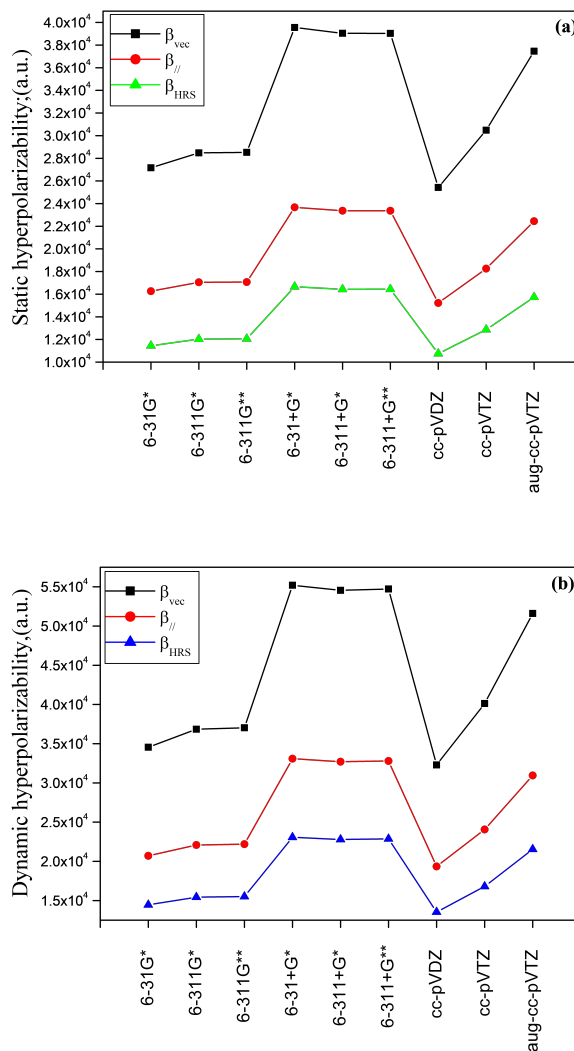


Figura 2. Basis sets effects on the static (a) and dynamic (b) hyperpolarizability:  $\beta_{||}$ ,  $\beta_{vec}$  and  $\beta_{HRS}$  for the trans  $\alpha,\omega$ -nitro, dimethylamino-hexatriene determined at the B3LYP level within the IEFPCM scheme and acetonitrile as solvent.

### III.3. Assessment of the DFT functionals to evaluate the first hyperpolarizability

Reliable predictions of  $\beta$  quantities at the density functional (DFT) level of theory using the 6-31+G\* basis set requires the study of the impact of the exchange correlation (XC) functionals (LC-BLYP, B3LYP, B3P86, CAM-B3LYP, M052X, M05, M062X and BHandHLYP). The results collected in Table S3 (Supporting information) and displayed in figure 3, highlights the impact of the electron correlation on the

assessment of the static and dynamic first hyperpolarizability  $\beta_{vec}$ ,  $\beta_{||}$  and  $\beta_{HRS}$ , depolarization ratio (DR) and anisotropy factor ( $\rho$ ) of the trans  $\alpha,\omega$ -nitro,dimethylamino-hexatriene.

The results in Table S3 (Supporting information) highlight the impact of the electron correlation on the assessment of hyperpolarizabilities  $\beta_{||}$  and  $\beta_{HRS}$  and depolarization ratio (DR) for isolated all trans  $\alpha,\omega$ -nitro,dimethylamino-hexatriene using 6-31+G\* basis set: (i) As shown in figure 3a, the effects of electron correlation are much larger for the static first hyperpolarizabilities. The  $\beta_{HRS}(MP2)/\beta_{HRS}(HF)$  and  $\beta_{||}(MP2)/\beta_{||}(B3LYP)$  ratios are close to 2.43 and 1.37, respectively.

(ii) the  $\beta_{HRS}(SCS - MP2)/\beta_{HRS}(HF) = 2.48$  and  $\beta_{HRS}(SCS - MP2)/\beta_{HRS}(B3LYP) = 1.73$ . The  $\beta_{HRS}$  difference between MP2 and SCS-MP2 is 2.02 % only.

(iii) At the DFT approach, the M05 functional behaves badly, leading to an overestimations of  $\beta_{HRS}$  by 44.53 % when compared to the MP2 level. The calculated ratio  $\beta_{HRS}(MP2)/\beta_{HRS}(M05)$  is close to 1.80. Whereas it is often ranging between  $\beta_{HRS}(MP2)/\beta_{HRS}(X) = 1.37$  and 1.73 for the others DFT approaches.

The effects of electron correlation might be much different from one exchange correlation (XC) functional to another. This statement is verified for analogous DFT approaches:  $\beta_{HRS}(MP2)/\beta_{HRS} = 1.80 > \beta_{HRS}(MP2)/\beta_{HRS}(B3P86) = 1.73 > \beta_{HRS}(MP2)/\beta_{HRS}(B3LYP) = 1.70 > \beta_{HRS}(MP2)/\beta_{HRS}(BHandHLYP) = 1.61 > \beta_{HRS}(MP2)/\beta_{HRS}(M052X) = 1.51 > \beta_{HRS}(MP2)/\beta_{HRS}(CAM - B3LYP) = 1.44 > \beta_{HRS}(MP2)/\beta_{HRS}(M062X) = 1.42 > \beta_{HRS}(MP2)/\beta_{HRS}(LC - BLYP) = 1.37$ .

The values obtained at the MP2 level of theory appear to be in better agreement with the calculated LC-BLYP, M062X, CAM-B3LYP and M052X functionals, the ratios are rather small. However, slightly worse agreement is obtained for the B3LYP, B3P86 and M05 functionals, even though M05 method show more significant overestimation of the first hyper- polarizability  $\beta_{HRS}$ .

The  $\beta_{HRS}$  predicted by LC-BLYP, CAM- M062X and CAM-B3LYP are almost the same and are comparable with those obtained by MP2 method.

(iv) the DR ranges from 4.60 to 4.74 as a function of the approximation level. However, MP2 and SCS-MP2 methods produce typical values of dipolar compound DR=4.90 and 4.93, respectively. The ratio between the references methods DR (SCS-MP2)/DR (MP2) is close to 1.01 (Table S4 Supporting information).

(v) The electron correlation effects on  $\beta_{||}$  leads to an important increase with a factor  $\beta_{||}(MP2)/\beta_{||}(X)$  ranging from 0.34 for LC-BLYP to 2.55 for HF method. The ratio between the reference method  $\beta_{||}(MP2)/\beta_{||}(SCS - MP2)$  is close to 0.97. At 6-31+G\* basis set the  $\beta_{||}$  (parallel) presents the highest value of 23673 (a.u.) at the LC-BLYP functional.

(vi) For the dynamic hyperpolarizability in figure 3b, the reference MP2 method give the highest  $\beta_{HRS}$  value of 26465.58(a.u.). When considering XC functionals, the

BHandHLYP, M05, M052X, LC-BLYP and B3P86 functionals behaves poorly, leading to an underestimations of the  $\beta_{HRS}$  by 23 %, 14.71 %, 13.82 %, 12.84 % and 12.70 %, respectively. For the M062X, CAM-B3LYP and B3LYP functionals a much better agreement is observed, they appear to behave in a similar manner with the MP2 results the differences are 5.96 %, 6.30 % and 7.30 %, respectively.

The  $\beta_{HRS}$  predicted by B3LYP, B3P86 and M062X are almost the same and are comparable with those obtained by MP2 method. In addition, results obtained for the static and dynamic depolarization ratio  $DR(1046 \text{ nm})/DR(\infty)$  appear to be close to 1.00 (Table S4 supporting information).

(vii) The calculated contrasts between the dynamic and static HRS first hyper-polarizability using the  $\beta_{HRS}(1046 \text{ nm})/\beta_{HRS}(\infty)$  ratios are ordered as follows: 0.44 for LC-BLYP, 1.74 for MP2 and SCS-MP2, 2.24 for M062X, 2.22 for M052X, 2.57 for M05 and 2.63 for B3LYP. The same trend was observed for  $\beta_{||}$  with  $\beta_{||}(1046 \text{ nm})/\beta_{||}(\infty)$  ranges from 0.44 to 2.68.

From the calculated dynamic first hyperpolarizability for all trans  $\alpha,\omega$ -nitro,dimethylamino-hexatriene, we observed a small difference between the DFT and MP2 results. However, an exception is observed for M05 and BHandHLYP functionals which are not recommended for the determination of the static and dynamic HRS first hyperpolarizability. Also, we propose scaling  $\beta_{HRS}$  values at B3LYP/ 6-31+G\* by factors of 1.14 and 1.73 to obtain the MP2 dynamic and static  $\beta_{HRS}$  at a low computational cost.

#### III.4. Electron correlation effects on the first hyperpolarizability

The electron correlation effects were carried out using the second-order Møller-Plesset (MP2) approximation as a reference method. Then, the validity of MP2 calculations has been verified by the MP4 (fourth-order electron correlation) and the reference techniques CCSD(T). The results of electron correlation impact on the static and first hyperpolarizabilities ( $\beta_{HRS}$ ) of the typical trans  $\alpha,\omega$ -nitro,dimethylamino-hexatriene are given in figure 4 and Table S5 (Supporting information).

The effects of electron correlation are much larger for the first hyperpolarizability  $\beta_{HRS}$ , the HF and DFT methods leads to the first hyperpolarizability ( $\beta_{HRS}$ ) values smaller with the corresponding reference CCSD(T) results. The HF method with basis sets lacking diffuse functions underestimates  $\beta$  values by about 54.56 %.

However, including diffuse functions in the basis set leads to an underestimation of 3.43 %. The  $\beta(HF)/\beta(CCSD(T))$  ratios are growing from 0.43 to 0.47 for the used 6-31+G\*, 6-311G\* and 6-31G\* basis sets. A difference between 3 % to 6 % was observed for basis sets with and without diffuse functions (6-31+G\*/aug-cc-pVDZ and 6-31+G\*/ aug-cc-pVTZ).

For the DFT method within the B3LYP functional, the electron correlation effects on  $\beta_{HRS}$  are much smaller and increase by 27-35 %. The  $\beta(B3LYP)/\beta(CCSD(T))$  ratios are 0.74, 0.75 and 0.76 for 6-31G\*, 6-311G\* and 6-31+G\* basis sets, respectively.



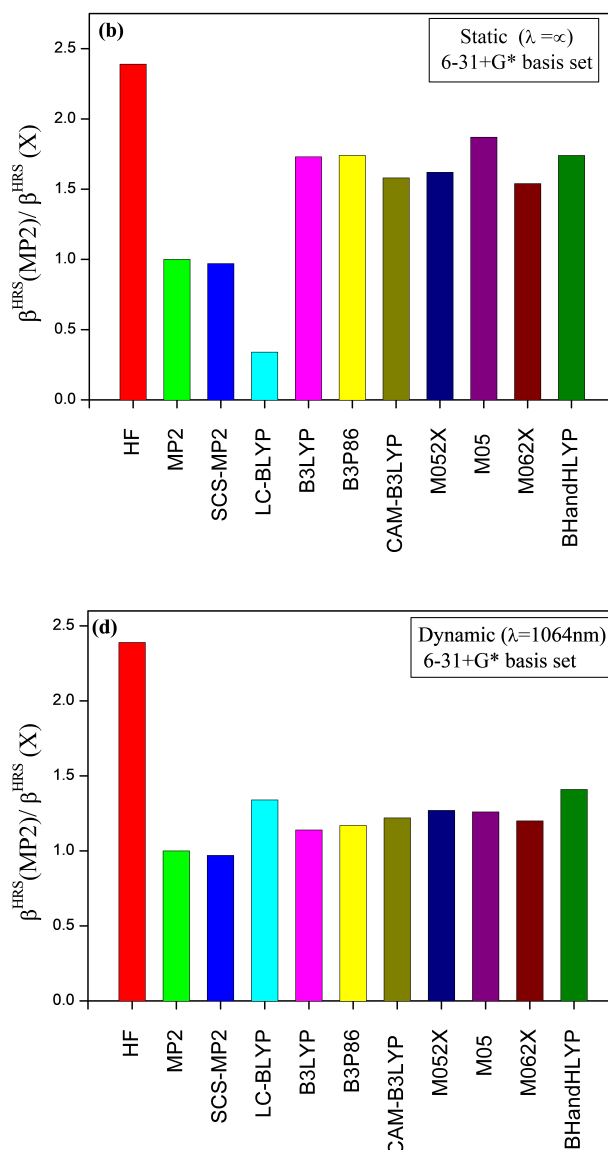
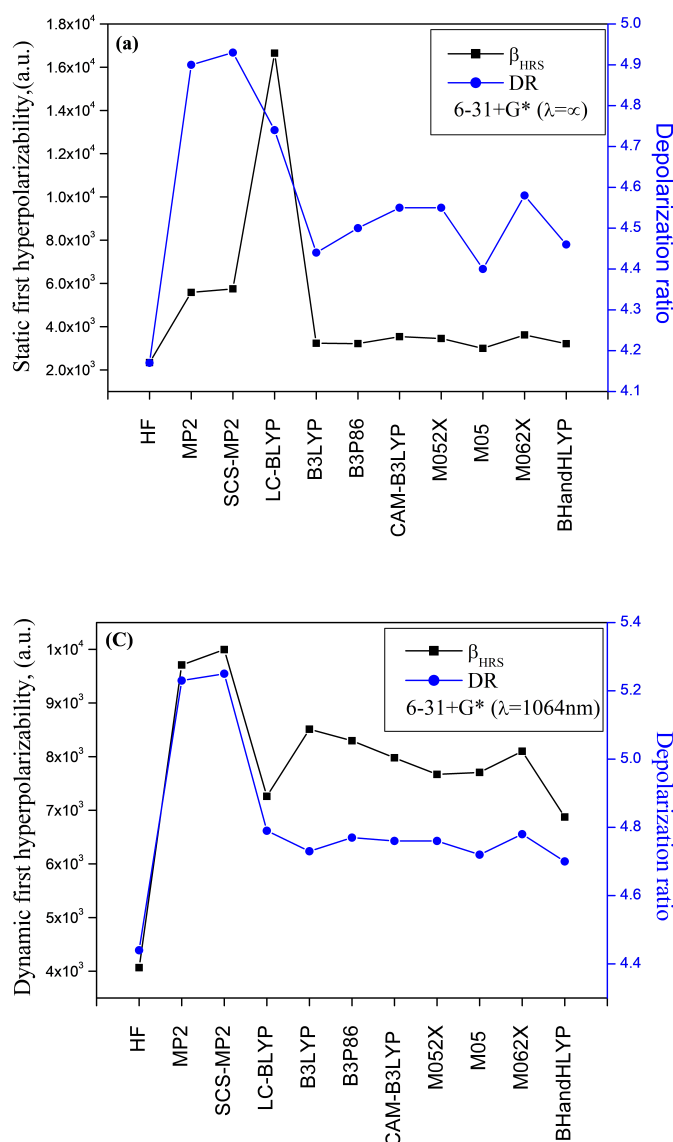


Figure 3. Effect of electron correlation on the static and dynamic HRS first hyperpolarizability and depolarization ratio (a and c);  $\beta_{HRS}$  contrasts for all trans  $\alpha,\omega$ -nitro,dimethylamino-hexatriene calculated at various levels of approximation with the 6-31+G\* basis set (b and d).

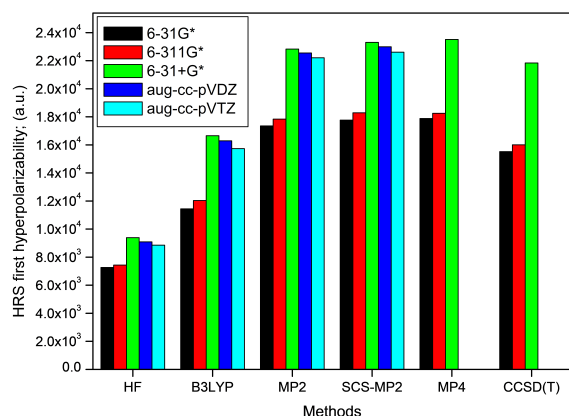


Figure 4. Static first hyperpolarizabilities ( $\beta_{HRS}$ ) of all-trans  $\alpha,\omega$ -nitro,dimethylamino-hexatriene at different levels of calculation for the isolated molecule.

The first hyperpolarizability exhibit stronger dependence on the basis set and these effects are enhanced from the smallest 6-3G\* to the largest aug-cc-pVTZ by 34 % to 29 %. However, the 6-31+G\*  $\beta_{HRS}$  values are similar to those evaluated at aug-cc-pVDZ and aug-cc-pVTZ basis sets.

When going from the 6-31G\* to the aug-cc-pVTZ basis set, the MP2 (6-31G\*)/ B3LYP (6-31+ G\*) and MP2(aug-cc-pVTZ)/ B3LYP(aug-cc-pVTZ) ratio ranges between 1.37 to 1.41, leading to a difference of 0.04. The results leads to state that, basis sets like 6-31+G\*, aug-cc-pVDZ and aug-cc-pVTZ are enough to provide accurate estimation and ensuring the best computational costs.

Moving from MP2 to MP4 leads to a small increase of  $\beta_{HRS}$ , the difference between MP2 and MP4 is less than 3 %. While, the computational cost with MP4 is largely increased compared to MP2. Moreover, when using a basis set with diffuse functions

the difference between the MP2, MP4 and CCSD(T) is smaller and decrease by 11 % and 13 % respectively.

The MP2 scheme provides first hyperpolarizability values in good agreement with the CCSD (T) and MP4 results, the estimated MP2/CCSD(T) ratios using the 6-31G\*, 6-311G\* and 6-31+G\* basis sets range from 1.12 to 1.05.

### III.5. Substitution effects on first hyperpolarizability ( $\beta_{HRS}$ )

The calculated static and dynamic hyper-Rayleigh scattering (HRS) first hyperpolarizability ( $\beta_{HRS}$ ), electric field-induced second harmonic generation (EFISHG) first hyperpolarizability ( $\beta_{||}$ ), depolarization ratio (DR) and the nonlinear anisotropy parameter ( $\rho$ ) for the solvated and isolated all trans hexatriene  $\text{NO}_2-(\text{CH}=\text{CH})_3-\text{D}$  (figure 5) are given in figure 6.

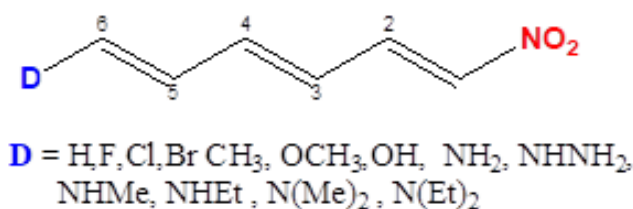


Figure 5. Molecular structures of substituted all-trans hexatriene  $\text{NO}_2-(\text{CH}=\text{CH})_3-\text{D}$ .

The results in figure 6a and 6b and Table S6 (Supporting information) established the influence of different donor substituent on the  $\beta_{HRS}$  of substituted oligomer ( $\text{D}-\pi-\text{NO}_2$ ). The  $\beta_{HRS}$  value of the mono-substituted  $\text{H}-\pi-\text{NO}_2$  all-trans hexatriene 1 is rather small, supporting the absence of strong donor groups. The  $\beta_{HRS}$  values for isolated molecules are the largest for the disubstituted hexatriene than for the mono substituted ones, a remarkable increase of the  $\beta_{HRS}$  is observed for diethylamino  $-\text{NEt}_2$  and dimethylamino  $-\text{NMe}_2$  electron-donating groups, the  $\beta_{HRS}^\infty(\text{NO}_2, \text{NMe}_2)/\beta^\infty(\text{NO}_2, \text{H}) = 3.78$  and  $\beta_H^{1064} \text{RS}(\text{NO}_2, \text{NMe}_2)/\beta^{1064}(\text{NO}_2, \text{H}) = 4.37$ .

In general, one can observe that if  $\beta_{HRS}$  and  $\beta_{||}$  of a structure are strongly enhanced by the presence of  $\text{NO}_2$  group,  $\beta_{HRS}$  and  $\beta_{||}$  are also substantially enhanced by the pair of  $-\text{NO}_2/-\text{N}(\text{Et})_2$ . This behavior tends to attribute to the hexatriene backbone's ability to exhibit smaller or larger first hyperpolarizabilities. Indeed, including solvent effects increases static and dynamic  $\beta_{HRS}$  of most substituted hexatriene by 52~70 % and 68-76.50 %, respectively.

The static ( $\lambda = \infty$ ) enhancement factor for  $\beta_{HRS}$  goes from 1.10 to 4.62 against 1.10 to 5.54 for the dynamic ( $\lambda = 1064 \text{ nm}$ ) case. The  $\beta_{HRS}$  amplitudes ordering changes with respect to the strength of substituted groups. In addition, large  $\beta_{HRS}$  are illustrated by the solvated (acetonitrile) compounds 12 and 13, while their DR are also the largest. The relative amplitudes are quantified by the static ratio  $\beta_{HRS}^\infty(\text{NO}_2, \text{NMe}_2)/\beta^\infty(\text{NO}_2, \text{H}) = 4.26$  and  $\beta_{HRS}^\infty(\text{NO}_2, \text{NMe}_2) > \beta^\infty(\text{NO}_2, \text{H}) = 4.62$ , the dynamic ratio  $\beta_H^{1064} \text{RS}(\text{NO}_2, \text{NMe}_2)/\beta^{1064}(\text{NO}_2, \text{H})$  close to 4.87 and

$\beta_H^{1064} \text{RS}(\text{NO}_2, \text{NMe}_2)/\beta^{1064}(\text{NO}_2, \text{H}) = 5.54$ . The smallest  $\beta_{HRS}$  values are observed for substituted halogen groups 1, 2, 3, 4, and 5. Compounds with hydroxyl  $-\text{OH}$  and alkoxy  $-\text{OCH}_3$  substituted groups (6 and 7) display an HRS response of intermediate amplitude. Turning to the  $\beta_{||}$  response the same behavior is observed, compounds 13 and 12 possess the largest values whereas the smallest  $\beta_{||}$  responses are characteristics of compounds 1-5, those with halogens ( $-\text{Cl}$ ,  $-\text{Br}$  and  $-\text{F}$ ) and methyl  $-\text{CH}_3$  substituted donor groups. Considering the DR quantities, compounds 13 and 12 also possess the largest values whereas the smallest DR values are associated with compounds 1 and 2. Finally, the largest  $\beta_{HRS}$ ,  $\beta_{||}$  and DR are achieved by compounds 13 and 12 having the most voluminous substituted electron-donating groups, considering the effect of the solvent (acetonitrile) and the strength of each substituted electron-donating groups (1-13) we propose similar decreasing ordering of  $\beta_{HRS}$  for the solvated and isolated disubstituted all-trans hexatriene at ( $\lambda = \infty$ ) and ( $\lambda = 1064 \text{ nm}$ ):  $13 > 12 > 11 > 10 > 9 > 8 > 7 > 6 > 5 > 4 > 3 > 2 > 1$ .

Looking further at the solvent effects, the calculated static ( $\lambda = 0$ ) and dynamic ( $\lambda = 1064 \text{ nm}$ ) first hyperpolarizability ( $\beta_{HRS}$ ) obtained in vacuum and in acetonitrile. As shown in figure 6a and 6b, the solvent effect significantly enhances the dynamic first hyperpolarizability ( $\beta_{HRS}$ ) of the substituted hexatriene by a factors ( $\beta_{HRS}^{\text{sol}}(1064 \text{ nm})/\beta_{HRS}^{\text{vac}}(1064 \text{ nm})$ ) ranging from 2.10 for ( $\text{NO}_2, \text{Br}$ ) to 2.71 for ( $\text{NO}_2, \text{NMe}_2$ ). However, the static ones are somewhat smaller the corresponding ratios ( $\beta_{HRS}^{\text{sol}}(\infty)/\beta_{HRS}^{\text{vac}}(\infty)$ ) range from 3.14 for ( $-\text{NO}_2, -\text{Cl}$ ) to 4.081 for ( $-\text{NO}_2, -\text{NMe}_2$ ).

The HRS first hyperpolarizabilities  $\beta_{HRS}$  in acetonitrile increases even more rapidly than in vacuum, with increasing the strengthening of each electron-donating group (D), the curves display an accelerating trend rather than a linear relationship revealing a pronounced strengthening electron-donating effect encountered for alkylamine groups  $-\text{NMe}_2$  and  $-\text{NEt}_2$  leading to significant enhancement of the  $\beta_{HRS}$  response.

The depolarization ratios (DR) for all substituted molecules are near the typical value of 5. In addition, for the dynamic and the static case the ratios  $\text{DR}^{\text{sol}}(1064 \text{ nm})/\text{DR}^{\text{vac}}(1064 \text{ nm})$  range from 1.03 to 1.05 and  $\text{DR}^{\text{sol}}(\infty)/\text{DR}^{\text{vac}}(\infty)$  range from 1.01 to 1.03, respectively. Acetonitrile solvent has little effect on the depolarization ratio (DR).

In order to clarify the solvent effects on the  $\beta_{HRS}$  for each substituted molecules, we plot in figure 6c and 6d the variation of the static and dynamic  $\beta_{HRS}$  for isolated and solvated (acetonitrile) molecules versus their values in vacuum.

The results for the solvated static ( $\lambda = \infty$ ) first hyperpolarizability of each substituted hexatriene molecule versus its static value in vacuum shows a good linear relationship ( $R = 0.99$ ) with the slope of 4.47, revealing that the solvent has a consistent influence to this class of substituted hexatriene. However, the link between the dynamic ( $\lambda = 1064$ ) first hyperpolarizability  $\beta_{HRS}$  in acetonitrile versus its value in vacuum lead to an excellent linear relationship characterized by a positive slope  $\beta_{HRS}^{\text{sol}}(1064 \text{ nm})/\beta_{HRS}^{\text{vac}}(1064 \text{ nm}) = 2.94$  and

a correlation coefficient close to 1.00. This result indicates that the solvent enhances the first hyperpolarizabilities significantly by an amplitude depending on the strength of the substituted groups. Also, an excellent relationship was

established between the static and dynamic  $\beta_{HRS}$  for isolated and solvated molecules, allowing an easy determination of  $\beta$  values.

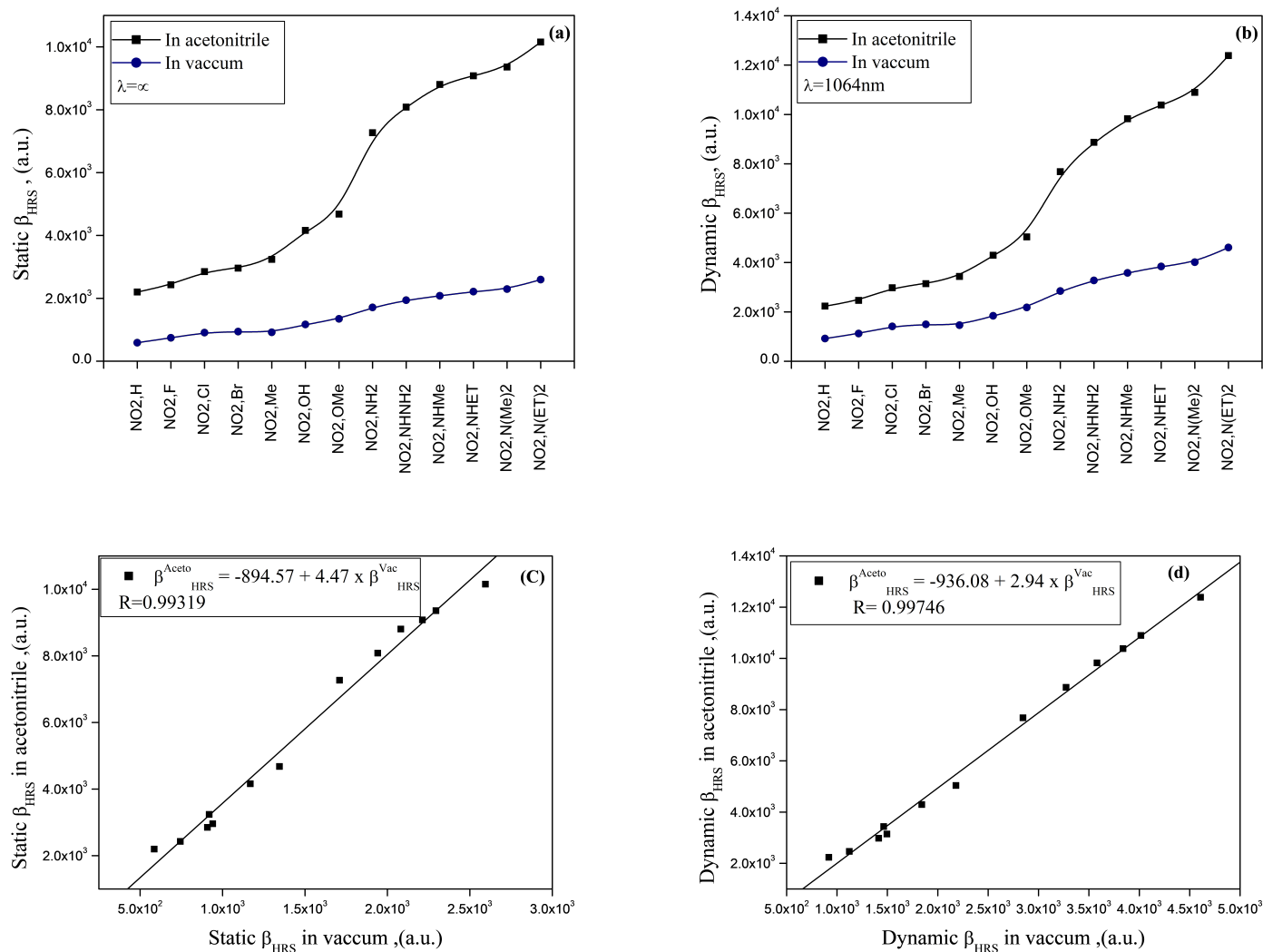


Figura 6. Static (a) and dynamic (b)  $\beta_{HRS}$  for isolated and solvated (acetonitrile) substituted molecules;  $\beta_{HRS}$  in acetonitrile versus its value in vacuum of each substituted molecule (c and d).

### III.6. Dependence of $\beta_{HRS}$ on the dipolar/octupolar components of the first hyperpolarizability

of the substituted hexatriene systems in term of their dipolar/octupolar character.

In order to compare the contribution of the dipolar and octupolar components to the static and dynamic first hyperpolarizability  $\beta_{HRS}$  response considering the solvated (acetonitrile) substituted hexatriene molecules. The  $\beta$  tensor is decomposed into the  $|B_j = 1|$  (dipolar) and  $|B_j = 3|$  (octupolar) components.

The DR, as well as the dipolar  $[\Phi|B_j = 1| = 1/(1 + \rho)]$  and octupolar  $[\Phi|B_j = 3| = \rho/(1 + \rho)]$  contributions to first hyperpolarizability  $\beta_{HRS}$  response with respect to the nonlinear anisotropy parameter  $\rho$  is displayed in figure 7a and 7b to provide a quantitative classification

From Fig.6a, for the static case ( $\lambda = \infty$ ) a large amount of the disubstituted hexatriene molecules with the largest and strongest substituents characterized by nitrogen (N) atom at the donor groups like ( $-\text{NH}_2$ ,  $-\text{NHNH}_2$ ,  $-\text{NHMe}$ ,  $-\text{NHET}$ ,  $-\text{NMe}_2$  and  $-\text{NEt}_2$ ) fall in the area of the  $\rho \leq 1$  axis, indicating that most of them correspond to a more pronounced dipolar character. Moreover, for the weak substituted electron-donor groups: alkyl, alkoxy, hydroxyl and halogens ( $-\text{CH}_3$ ,  $-\text{OCH}_3$ ,  $-\text{OH}$ , and  $-\text{F}$ ) the anisotropy factor is slightly higher than unity ( $\rho \approx 1$ ) and ranging from 1.03 for ( $-\text{OH}$  and  $-\text{OCH}_3$ ) to 1.08 for ( $-\text{F}$ ). In addition, all-trans substituted hexatriene molecules fit into the dipolar molecules with the dipolar

contribution [ $\Phi|B_j = 1|$ ] of 48-50 %. Nevertheless, these dipolar molecules should be further divided into two categories, including substituted electro-donating groups (1)  $-H$ ,  $-Br$ ,  $-CH_3$  and  $-OH$  belonging to category A with the dipolar contribution [ $\Phi|B_j = 1|$ ] of 48-49 % and (2)  $-F$ ,  $-Cl$ ,  $-OCH_3$ ,  $-NH_2$ ,  $-NHNH_2$ ,  $-NHMe$ ,  $-NHet$ ,  $-NMe_2$  and  $-NEt_2$  to category B with the dipolar contribution [ $\Phi|B_j = 1|$ ] of 50 %. An exception is noted for the monosubstituted ( $-NO_2$ ,  $-H$ ) and the disubstituted ( $-NO_2$ ,  $-F$ ) which can be considered as weak octupolar molecules with the [ $\Phi|B_j = 3|$ ] of 54 and 52 % and an anisotropy factor close to  $\rho = 1,17$  and  $1.08$   $\hat{z}$ 1.

The situation is different when considering the frequency dependence ( $\lambda = 1064$  nm), as can be seen in figure 7b all

molecules manifest pure dipolar character with the dipolar contribution [ $\Phi|B_j = 1|$ ] of 51-53 % and fall in the area where the anisotropy factor is clearly  $\rho < 1$ . However, the octupolar contribution [ $\Phi|B_j = 3|$ ] ranges from 51 for ( $-NO_2$ ,  $-H$ ) to 47 % for ( $-NO_2$ ,  $-NEt_2$ ). In addition, As shown in figure 7a, the depolarization ratio value decreases with increasing the anisotropy factor  $\rho$  from 4.28 for ( $-NO_2$ ,  $-NEt_2$ ) to 3.74 for ( $-NO_2$ ,  $-H$ ), covering the anisotropy factor range from 1.00 to 1.17 at ( $\lambda = \infty$ ) and from 4.64 for ( $-NO_2$ ,  $-NEt_2$ ) to 4.18 for ( $-NO_2$ ,  $-H$ ), covering the anisotropy factor range from 0.90 to 1.02. In all the cases, the dipolar contribution decreasing order is as follows:  $13 > 12 > 11 > 10 > 9 > 8 > 7 > 6 > 5 > 4 > 3 > 2 > 1$ , and the octupolar sequence is just the reverse.

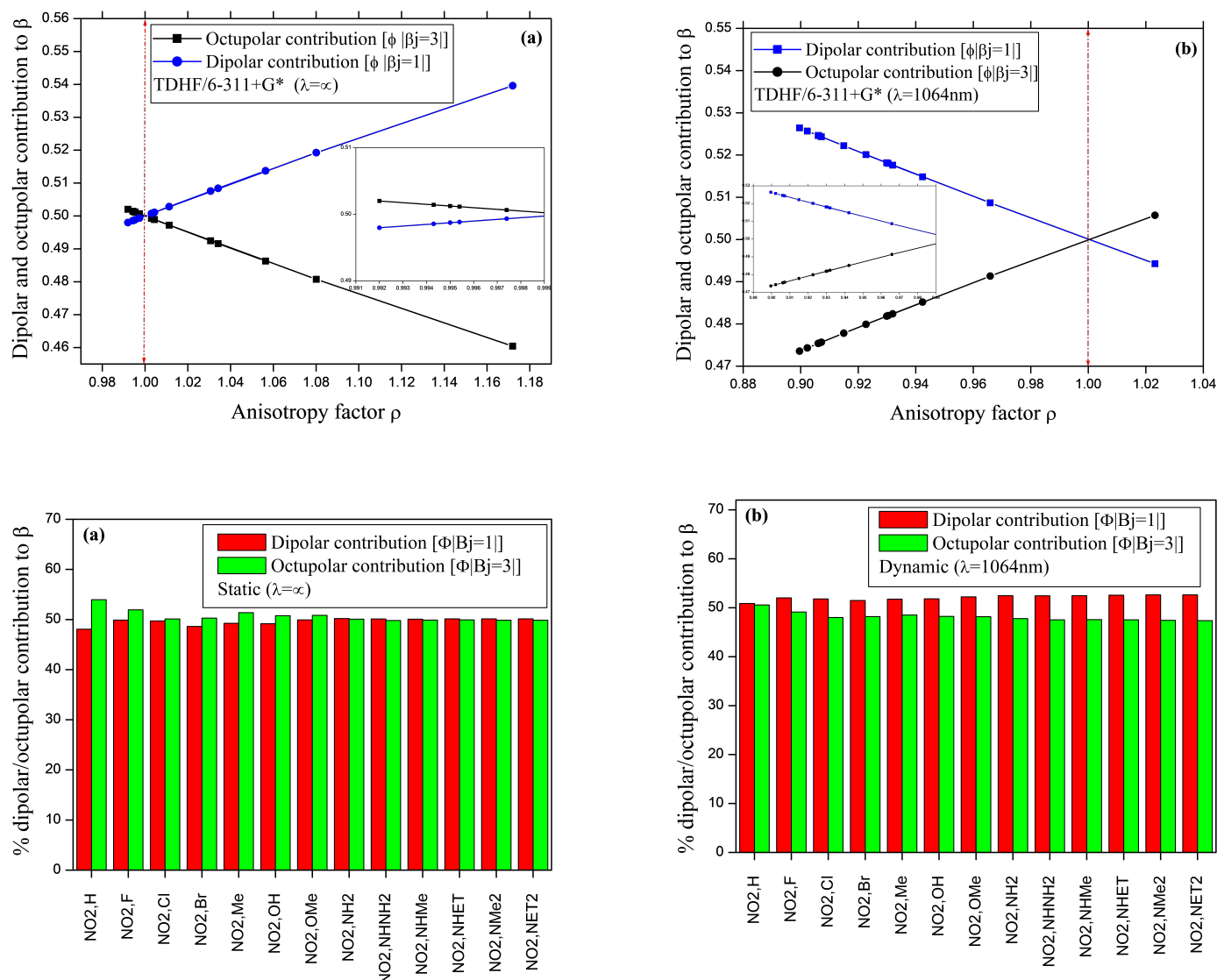


Figure 7. Evolution of static (a) and dynamic (b) depolarization ratio DR as well as the dipolar [ $\Phi|B_j = 1|$ ] and octupolar [ $\Phi|B_j = 3|$ ] contributions to the  $\beta_{HRS}$  response as a function of anisotropy factor  $\rho$  within the IEFPCM (acetonitrile) scheme.



## IV. CONCLUSIONS

In this work, we have investigated the geometrical structure and first hyperpolarizabilities of substituted push-pull oligomer using theoretical chemistry methods. First, the geometries of the ground state have been optimized at the B3LYP/6-311G\* level. Then, reliable atomic basis sets for computing the first hyperpolarizability ( $\beta_{HRS}$ ) have been selected. Several DFT XC functionals, have then been used to calculate the variations of the first hyperpolarizabilities ( $\beta_{HRS}$ ). The electron correlation effects were carried out using the MP2 level and the validity of the chosen method is further demonstrated by considering the CCSD(T) results.

The main results in this work include: Reliable predictions of static and dynamic  $\beta$  values requires (i) To assess the importance of the electron correlation effects; (ii) To choose an extended basis set including in most cases one or more sets of diffuse functions (like 6-31+G\*, 6-311+G\*, aug-cc-pVTZ and aug-cc-pVDZ); (iii) to account for the effects of frequency; (iv) The correlation between the  $\beta$  values obtained with MP2, MP4, B3LYP, CAM-B3LYP, B3LYP and M062X methods is generally very good. In particular, with considering the solvent effects the B3LYP, CAM-B3LYP and M062X values are very similar; (iv) The solvent effects within the IEFPCM scheme leads to a preferential enhancement of the first hyperpolarizability of the Nitro-alkyl amine (NO<sub>2</sub>/NHMe, NH<sub>2</sub>Et, NMe<sub>2</sub> and NEt<sub>2</sub>) substituted hexatriene oligomers; (v) When placing NO<sub>2</sub>, NEt<sub>2</sub> groups at terminal position, the all-trans hexatriene presents the largest  $\beta$  response with a depolarization ratio close to 5. However,  $\beta_{HRS}$  decreases when adding halogenes (F, Cl and Br) or alkyl (CH<sub>3</sub>) groups; (vi) All substituted molecules manifest dipolar character with a dipolar contribution [ $|\Phi|B_j = 1|$ ] > 50 %. The theoretical separation of the octupolar/dipolar contributions to the first hyperpolarizability lets us control the second-order NLO response by varying the strength of the substituted donor/acceptor groups.

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