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# Solvent Effect on Hyper-Rayleigh Scattering (HRS) First Hyperpolarizability of Substituted Polyene: Ab Initio Study

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# ABSTRACT

The first hyperpolarizabilities  $\beta_{HRS}$  of substituted hexatriene molecules have been carried out to assess the effects of the bridge length, of the frequency dispersion as well as the solvent polarity. These calculations confirm the particular behaviour of the first hyperpolarizability  $\beta_{HRS}$ , depolarization ratio and the anisotropy factor as a function of the incident light frequency and solvent polarity. The impact of the solvent and expanding the  $\pi$ -conjugated limit to improve the  $\beta_{HRS}$ . Finally, the interplay between  $\beta_{HRS}$  and  $\beta_{//}$ ,  $\beta_{vec}$ ,  $d_{N...N}$ ,  $E_{gap}$  and the Kirkwood–Onsager factor [( $\epsilon$ -1)/(2 $\epsilon$  + 1)] was established.

Keywords: First hyperpolarizability; Hyper-Rayleigh scattering (HRS); push-pull; solvent

## INTRODUCTION

This study deals with the solvent effects on the NLO responses in a series of push-pull polyenes [D- $\pi$ -NO<sub>2</sub>] that have been proposed in view of achieving large second-order NLO responses. Here, we present the results, starting with an investigation of the bridge lengths effects, the frequency dispersion for the selected system as well as the effects of the solvent polarity on the first hyperpolarizability ( $\beta_{HRS}$ ) responses, energy gap and bond length alternation (BLA). Finally, the relationships between the first hyperpolarizability ( $\beta_{HRS}$ ) and  $\beta_{//}$ ,  $\beta_{vec}$ , separation distance ( $d_{N...N}$ ), energy gap ( $E_{gap}$ ) and the Kirkwood–Onsager factor [( $\epsilon$ -1)/(2 $\epsilon$  + 1)]are established<sup>1,2</sup>.

## **COMPUTATIONAL DETAILS**

The dynamic  $\beta_{HRS}(-2\omega;\omega,\omega)$  and static  $\beta_{HRS}(0;0,0)$  first hyperpolarizabilities were evaluated with the time-dependent Hartree–Fock (TDHF) and the coupled perturbed Hartree–Fock (CPHF) schemes<sup>3,4</sup>. To take into account the solvent effects the polarizable continuum model within the integral equation formalism (IEF-PCM) was employed at 6-31+G\* and 6-311+G\* basis sets<sup>3</sup>. Champagne and co-workers<sup>3</sup> developed an ffective method to evaluate the hyper-Rayleigh scattering (HRS) response  $\beta_{HRS}(-2\omega;\omega,\omega)$ , which is described as:

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

 $<\beta^{2}_{ZZZ}>$  and  $<\beta^{2}_{Zxx}>$  are the orientational averages of the molecular  $\beta$  tensor components. All calculations were performed using the Gaussian 09 program<sup>5</sup>.

# **RESULTS AND DISCUSSION**

To model the effect of the solvent polarity, the static and dynamic  $\beta_{vec}$ ,  $\beta_{//}$ ,  $\beta_{HRS}$  and depolarization ratio (DR) of all-trans  $\alpha, \omega$ -nitro, dimethylamino-hexatriene in a variety of solvents ranging dielectric



constants from  $\varepsilon = 2.27$  to  $\varepsilon = 46.83$ , are calculated at the TDHF level of approximation with 6-311+G\* basis set and presented in Fig. 4a and Fig.4b. The solvent enhances the first hyperpolarizabilities ( $\beta_{HRS}$ ) significantly by amplitude depending on the polarity of the solvent and the strength of the substituted groups.



Fig. 1: Solvent polarity effects on calculated static (a) and dynamic (b):  $\beta_{vec}$ ,  $\beta_{//}$ ,  $\beta_{HRS}$  for all-trans  $\alpha, \omega$ nitro, dimethyl amino-hexatriene at the HF/ 6-311+G\* level.

## CONCLUSION

Our calculations allow us to identify the main observations:i) The solvent enhances the first hyperpolarizabilities ( $\beta_{HRS}$ ) significantly by amplitude depending on the polarity of the solvent and the strength of the substituted groups; ii) The specific behavior of the HRS first hyperpolarizability with its anisotropy factor and depolarization ratio as a function of the incident light frequency. iii) A quantitative relationship was established between the first hyperpolarizability  $\beta_{HRS}$  and the separation distance  $d_{N...N}$ , energy gap ( $E_{gap}$ ) and the Kirkwood–Onsager factor [( $\epsilon$  –1)/ (2 $\epsilon$  + 1)].

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