A Quantum Chemical Investigation of the Second Hyperpolarizability of *P*-nitroaniline

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The third-order nonlinear optical responses which are associated to interesting phenomena such as the optical Kerr effect (OKE), the static electric field induced second harmonic generation (EFISHG), or the third harmonic generation (THG) are characterized at the molecular level by the second hyperpolarizability (γ). Calculating γ remains a challenge for quantum chemical (QC) methods because many effects/aspects must be considered. In the present contribution, performances of QC methods in the calculation of γ of the *p*-nitroaniline molecule are evaluated and compared to the CCSD(T) reference calculations. The γ quantities were evaluated using different schemes, combining numerical derivatives (the finite field (FF) method[1] and the Romberg's[2] quadrature procedure) and coupled-perturbed methods. After finding the optimal "numerical" conditions, it has been shown that:

(i) flexible basis sets with diffuse and polarization functions are necessary for predicting accurate second hyperpolarizabilities. Diffuse functions are important for describing the hyperpolarization perpendicular to the molecular plane.

(ii) electron correlation brings a substantial contributions to γ[3]. Though the CCSD(T) method can provide reference values, its application to systems of interest in nonlinear optics is generally computationally too demanding. Thus, we gauged the reliability of more approximate and computationally more affordable methods such as MP2, MP3, MP4 [D, DQ, SDQ and SDTQ], and CCSD methods and we found that MP2 offers the best accuracy/cost ratio for computing the static γ, although its good performance results from compensation of errors.

(iii) DFT is an alternative to the wavefunction methods, but an appropriate XCF must be chosen. We show that γ depends strongly on Hartree-Fock exchange as well as on dynamic electron correlation. Among the selected XCFs, the double-hybrid B2-PLYP functional provides accurate estimates of static γ values.

(iv) finally, from frequency-dependent OKE and EFISHG responses calculated for different incident photon wavelengths, THG values were evaluated for small frequencies by using polynomial expressions linking the static and frequency-dependent hyperpolarizabilities.

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