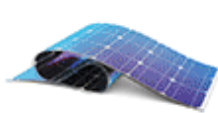



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Experimental and theoretical investigation of the first-order hyperpolarizability of a class of triarylamine derivatives

J. Chem. Phys. **142**, 064312 (2015); <https://doi.org/10.1063/1.4906893>Daniel L. Silva^{1,2, a)}, Ruben D. Fonseca³, Marcelo G. Vivas⁴, E. Ishow⁵, Sylvio Canuto², Cleber R. Mendonca³, and Leonardo De Boni^{3, a)}[View Affiliations](#)[View Contributors](#) PDF

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ABSTRACT

This paper reports on the static and dynamic first-order hyperpolarizabilities of a class of push-pull octupolar triarylamine derivatives dissolved in toluene. We have combined hyper-Rayleigh scattering experiment and the coupled perturbed Hartree-Fock method implemented at the Density Functional Theory (DFT) level of theory to determine the static and dynamic (at 1064 nm) first-order hyperpolarizability (β_{HRS}) of nine triarylamine derivatives with distinct electron-withdrawing groups. In four of these derivatives, an azoaromatic unit is inserted and a pronounceable increase of the first-order hyperpolarizability is reported. Based on the theoretical results, the dipolar/octupolar character of the derivatives is determined. By using a polarizable continuum model in combination with the DFT calculations, it was found that although solvated in an aprotic and low dielectric constant solvent, due to solvent-induced polarization and the frequency dispersion effect, the environment substantially affects the first-order hyperpolarizability of all derivatives investigated. This statement is supported due to the solvent effects to be essential for the better agreement between theoretical results and experimental data concerning the dynamic first-order hyperpolarizability of the derivatives. The first-order hyperpolarizability of the derivatives was also modeled using the two- and three-level models, where the relationship between static and dynamic first hyperpolarizabilities is given by a frequency dispersion model. Using this approach, it was verified that the dynamic first hyperpolarizability of the derivatives is satisfactorily reproduced by the



azobenzene unit, the use of a damped two-level model is essential for, considering also the molecular size of such derivatives, a good quantitative agreement between theoretical results and experimental data to be observed.

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