First-Order Hyperpolarizability Of Triphenylamine Derivatives Containing Cyanopyridine: Molecular Branching Effect

Fonseca Rodriguez, Ruben Dario; Vivas, Marcelo G; Silva, Daniel Luiz; Eucat, Gwennaelle; Bretonnière, Yann; Andraud, Chantal; De Boni, Leonardo; Mendonca, Cleber Renato.

Abstract

In the present work, we report the multibranching effect on the dynamic first-order hyperpolarizability ($\beta(-2\omega; \omega, \omega)$) of triphenylamine derivatives containing cyanopyridine one-branch (dipolar structure), two-branch (V-shaped structure), and three-branch (octupolar structure) structures. For this study, we used the hyper-Rayleigh scattering (HRS) technique involving picosecond pulse trains at 1064 nm. Our results show that β_{HRS} increases from 2.02×10^{-28} to 9.24×10^{-28} cm^5/esu when an extra branch is added to the molecule, configuring a change from a dipolar to a V-shaped (quadrupolar) molecular structure. When a third branch is added, leading to an octupolar structure, a decrease to 3.21×10^{-28} cm^5/esu is observed. Such a significant decrease in β_{HRS} is attributed to a negative contribution presented in the β_{HRS} description by using a three-level energy approach due to their electronic structure and considering a specific combination of the angle between the dipole moments. On the other hand, the enhancement of β_{HRS} found for the quadrupolar structure is associated with the cooperative enhancement due to the electronic coupling between the branches that increases considerably the transition dipole moment and permanent dipole moment change. To explain the β_{HRS} results obtained for different molecules, we employed the HRS figure of merit, $FOM_{HRS} = \beta_{HRS}/N_{eff}^{3/2}$, in which N_{eff} is the effective number of π-conjugated bonds, and the few-energy level approach for β_{HRS} within the Frenkel exciton model. To shed more light on the experimental results interpretation, we performed time-dependent density functional theory calculations combined with a polarizable continuum model to confirm the energy and oscillator strength of the electronic transitions assumed in the Frenkel exciton model employed here.

Keywords