

# On the third-order nonlinear optical responses of *cis* and *trans* stilbene – a quantum chemistry investigation

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Based on the recent measurements of the second hyperpolarizability ( $\gamma$ ) using third harmonic scattering experiment, there is renewed interest in calculating and interpreting  $\gamma$ .<sup>1,2</sup> In the present study,  $\gamma$  of the stilbene molecular switch in its *trans* and *cis* forms have been calculated using quantum chemistry methods to address their third-order nonlinear optical contrasts, to assess the reliability of lower-cost DFT methods, and to make comparisons with experiments. First, a high sophisticated wave function method in an extended basis set, i.e. the CCSD(T)/6-311+G(d) calculation shows that *trans*-stilbene presents a  $\gamma$  value by about twice larger than its *cis* isomer. Among more cost-effective methods, reliable results are obtained at the MP2 as well as with DFT, provided the CAM-B3LYP or  $\omega$ B97X-D XCFs are employed. Supplementary DFT calculations have investigated the relationships between the accuracy of the exchange-correlation functionals, the fulfillment of Koopmans' theorem, and the delocalization error, and they demonstrated that satisfying Koopmans' theorem is not the condition for the best accuracy but that functionals with small delocalization errors are generally efficient. Using the selected CAM-B3LYP, large  $\gamma$  enhancements by about 70% (*trans*-stilbene) and 50% (*cis*-stilbene) have been evidenced when accounting for solvent effect using an implicit solvation model (IEFPCM), even for apolar solvents. Then, the frequency dispersion of the  $\gamma$  responses has been described using Bishop polynomial expansions, allowing comparisons with a broad set of experimental data. To a certain extent, no systematic agreement between the calculations and the measured values was found. On the one hand, the agreement is satisfactory for the  $\gamma(-\omega; \omega, -\omega, \omega)$  quantities, provided the dominant vibrational contribution is taken into account. On the other hand, the agreement is poor for the  $\gamma(-2\omega; \omega, \omega, 0)$  and  $\gamma(-3\omega; \omega, \omega, \omega)$  quantities, while some inconsistencies between experimental values are also highlighted.<sup>3</sup>

<sup>1</sup> N. Van Steerteghem, K. Clays, T. Verbiest, and S. Van Cleuvenbergen, *Anal. Chem.* **89**, 2964 (2017).

<sup>2</sup> V. Rodriguez, *J. Phys. Chem. C* **121**, 8510 (2017).

<sup>3</sup> K. S. kaka, F. Castet, and B. Champagne, *Phys. Chem. Chem. Phys.* (2024), [doi.org/10.1039/D4CP00522H](https://doi.org/10.1039/D4CP00522H).