**Coupled cluster evaluation of the second and third harmonic scattering responses of small molecules**

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The static and dynamic second harmonic (βSHS) and third harmonic (γTHS) scattering hyperpolarizabilities and depolarization ratios of water, carbon tetrachloride, chloroform, dichloromethane, chloromethane, and acetonitrile have been evaluated at the coupled cluster response theory level of approximation [1,2]. Following two recent publications on their measurements [3,4], this is the first quantum chemical investigation on γTHS and on its decomposition into its spherical tensor components. Substantial electron correlation and basis set effects are evidenced for βSHS and γTHS and for their depolarization ratios and they depend on the nature of the molecule. Then, using the selected CCSD/d-aug-cc-pVDZ level, the chlorinated methane derivatives have been studied, showing that:

1. The γTHS response is dominated by its isotropic contribution ;
2. For βSHS the dipolar contribution increases from carbon tetrachloride to dichloromethane, chloroform, chloromethane, and acetonitrile.

Comparisons with the experimental data obtained from measurements in liquid phase show that the increase of γTHS with the number for chlorine atoms is well reproduced by the calculations and suggest that the solvation effects are smaller for γTHS than for βSHS. [5]

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