**Prediction and analysis of the electronic and vibrational contributions to the second and third harmonic scattering responses using *ab initio* methods**

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Since many years, harmonic generation phenomena have been exploited to probe and understand interaction between matter and electro-magnetic fields. Here, the static and dynamic second harmonic (SHS) and third harmonic (THS) scattering hyperpolarizabilities and depolarization ratios of 6 reference molecules (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.

This talk will outline that 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 (for its good performance/cost compromise) CCSD/d-aug-cc-pVDZ level, it was shown that for the electronic part:[5]

1. The γTHS response is dominated by its isotropic contribution,
2. Comparisons with the experimental data obtained from measurements in liquid phase[3] show that the increase of THS as a function of the number for chlorine atoms is well reproduced by the calculations and suggest that the solvation effects are smaller for THS than for SHS.
3. For SHS the dipolar contribution increases from carbon tetrachloride to dichloromethane, chloroform, chloromethane, and acetonitrile.

In addition, preliminary results on the amplitudes of the vibrational contributions[6] (pure vibrational and zero-point vibrational averaging) to these quantities computed at the same level of approximation will also be presented and discussed.

[1] Hättig, C.; and Jørgensen, P. *Theo. Chem. Acc.* **100**, 230 (1998).

[2] Hättig, C.; and Jørgensen, P. *Adv. Quant. Chem.* **35**, 111 (1999).

[3] Van Steerteghem, N.; Clays, K.; Verbiest, T.; Van Cleuvenbergen, *S. Anal. Chem.* **89**, 2964 (2017).

[4] Rodriguez, V. *J. Chem. Phys. C* **121**, 8510 (2017).

[5] Beaujean, P.; and Champagne, B. *Theor. Chem. Acc.* **137**, 50(2018).

[6] Bishop, D. M.; Luis, J. M.; and Kirtman, B. J. Chem. Phys. **109**, 10013 (1998).