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

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## Introduction and objectives

The interaction between an electric field ( $\vec{F}$ ) and a molecular system induces a dipole moment:

$$\Delta\vec{\mu}(\vec{F}) = \alpha \cdot \vec{F} + \frac{1}{2!} \beta : \vec{F}^2 + \frac{1}{3!} \gamma : \vec{F}^3 + \dots$$

where  $\alpha$  is the polarizability (rank 2 tensor) and  $\beta, \gamma$  are the first and second hyperpolarizabilities (rank 3 and 4 tensors). The experiments rely on relative rather than absolute measurements, which requires precise knowledge of the response of these reference compounds.  $\beta_{SHS}$  was already investigated for different systems,<sup>1</sup> but there are only TWO recent experimental studies for  $\gamma_{THS}$  by Van Steertegem *et al.* and Rodriguez.<sup>2</sup>

The goals of this work<sup>3</sup> are:

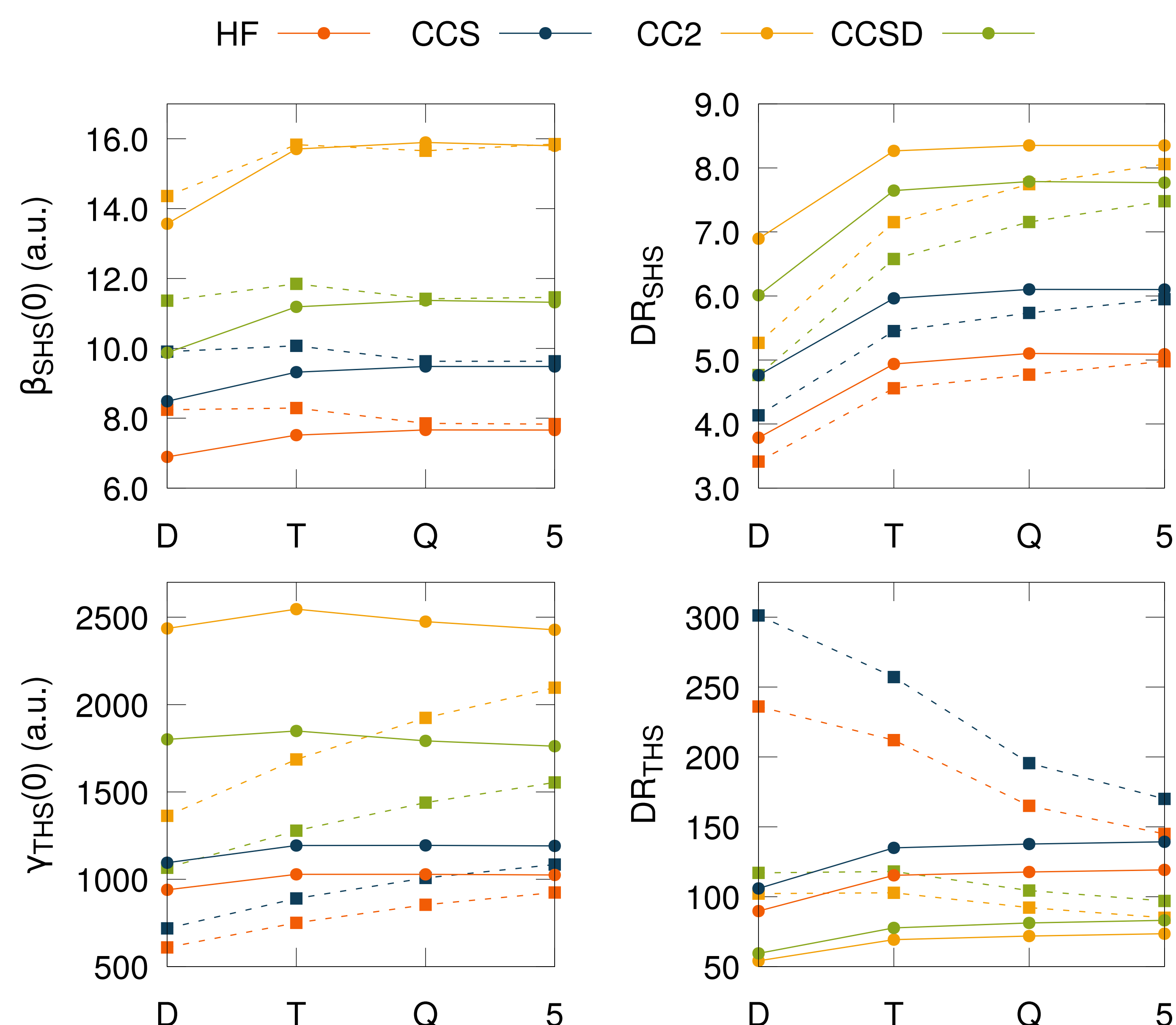
- The definition of reference values. 6 molecules were selected: H<sub>2</sub>O, CH<sub>3</sub>Cl, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, CCl<sub>4</sub> and CH<sub>3</sub>CN;
- The definition of an appropriate level of approximation since it is the first quantum chemistry investigation on  $\gamma_{THS}$ ;
- To establish structure-activity relationships, the calculation and interpretation of the irreducible spherical components.

## Computational details

Geometry optimized at the M06/6-311G(d) (water) and MP2/cc-pVTZ levels. Gas phase hyperpolarizabilities computed with Dalton 2016, with a hierarchy of coupled cluster methods (CCS, CC2, CCSD), in combination with quadratic/cubic response functions<sup>6</sup> and (d-)aug-cc-pVXZ basis sets to check basis set convergence.

## Results

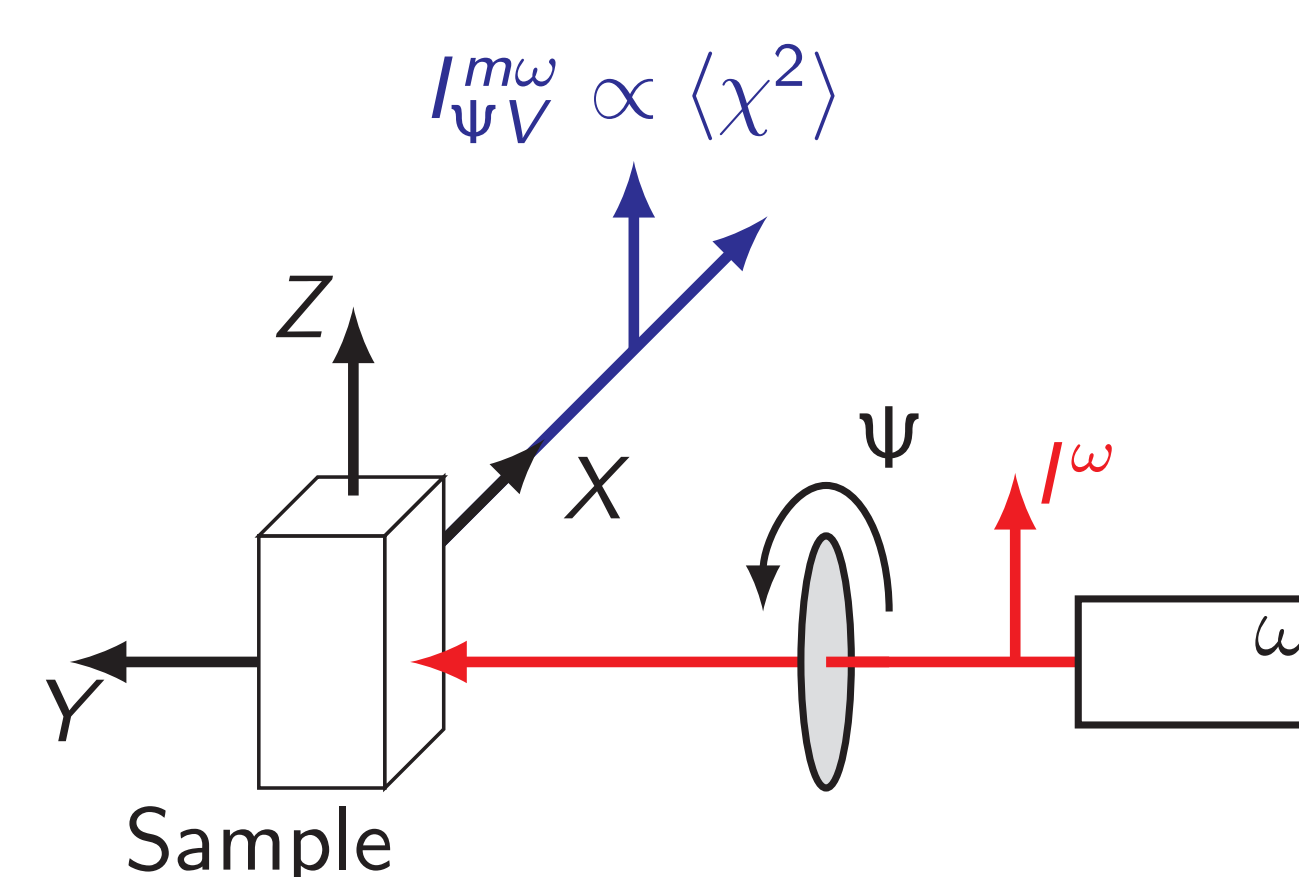
- Impact of the basis set (d-aug-cc-pVXZ in plain, aug-cc-pVXZ in dashed) and of the method on the static first and second hyperpolarizabilities of water:



Substantial electron correlation and basis sets effects are evidenced (especially for DR<sub>THS</sub>), but the effect seems less important for the other molecules: the CCSD/d-aug-cc-pVDZ level was selected. Note that the impact of CC3 is negligible with respect to CCSD.

- Static CCSD/d-aug-cc-pVDZ results for the six reference molecules: dipolar character of  $\beta_{SHS}$  increase from CCl<sub>4</sub> to H<sub>2</sub>O, and  $\gamma_{THS}$  dominated by its isotropic ( $J=0$ ) contribution, followed by its quadrupolar ( $J=2$ ) contribution.

## SHS and THS measurements



Geometry	$\langle \chi^2 \rangle$	
	$m=2$	$m=3$
$I_{VV} (\Psi = \pi/2)$	$\langle \beta_{ZZZ}^2 \rangle$	$\langle \gamma_{ZZZZ}^2 \rangle$
$I_{HV} (\Psi = 0)$	$\langle \beta_{ZXX}^2 \rangle$	$\langle \gamma_{ZXXX}^2 \rangle$

For a non-polarized incident signal,<sup>4</sup>

$$\beta_{SHS} = \sqrt{\langle \beta_{ZZZ}^2 \rangle + \langle \beta_{ZXX}^2 \rangle}$$

$$DR_{SHS} = \frac{\langle \beta_{ZZZ}^2 \rangle}{\langle \beta_{ZXX}^2 \rangle}$$

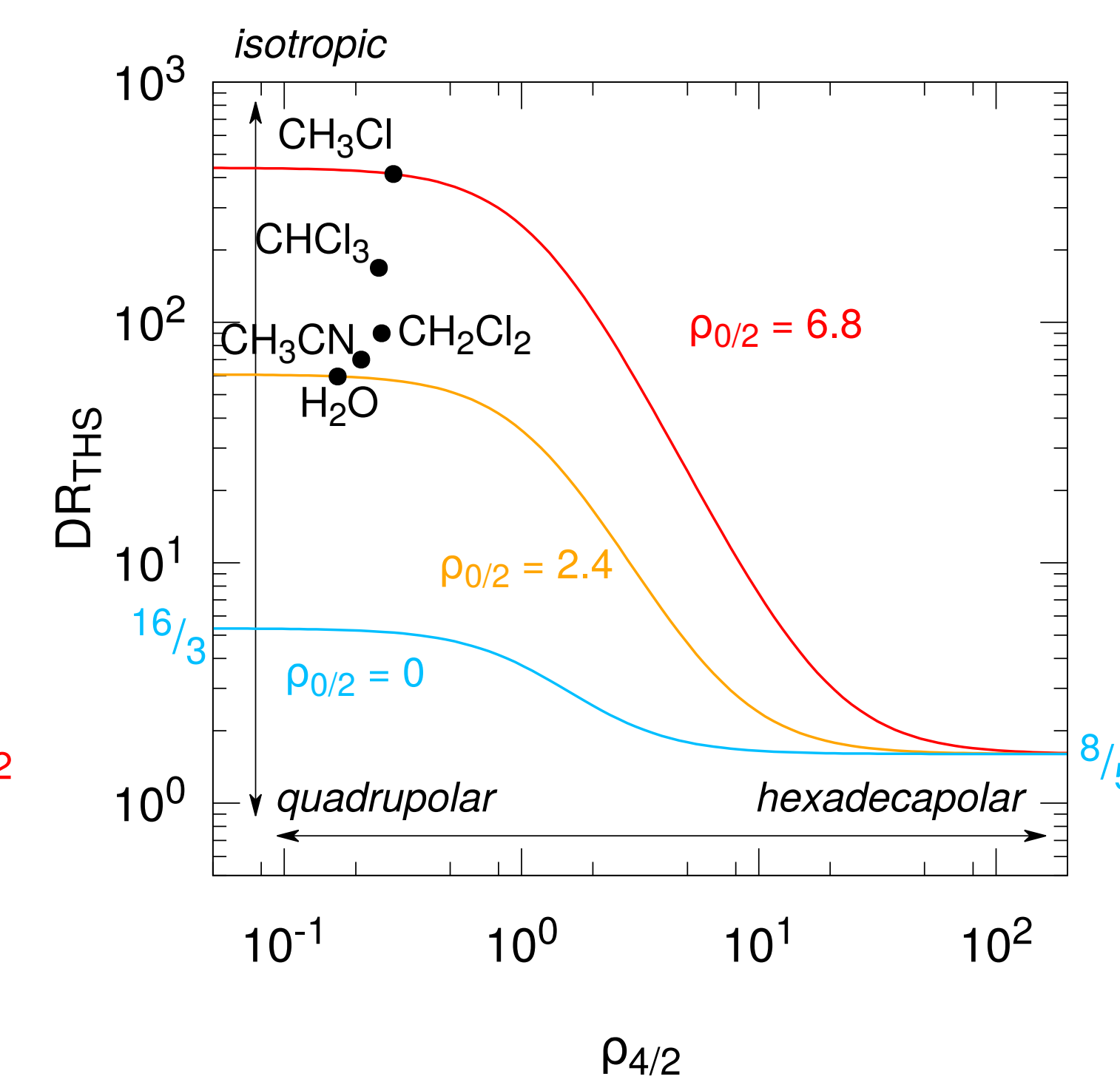
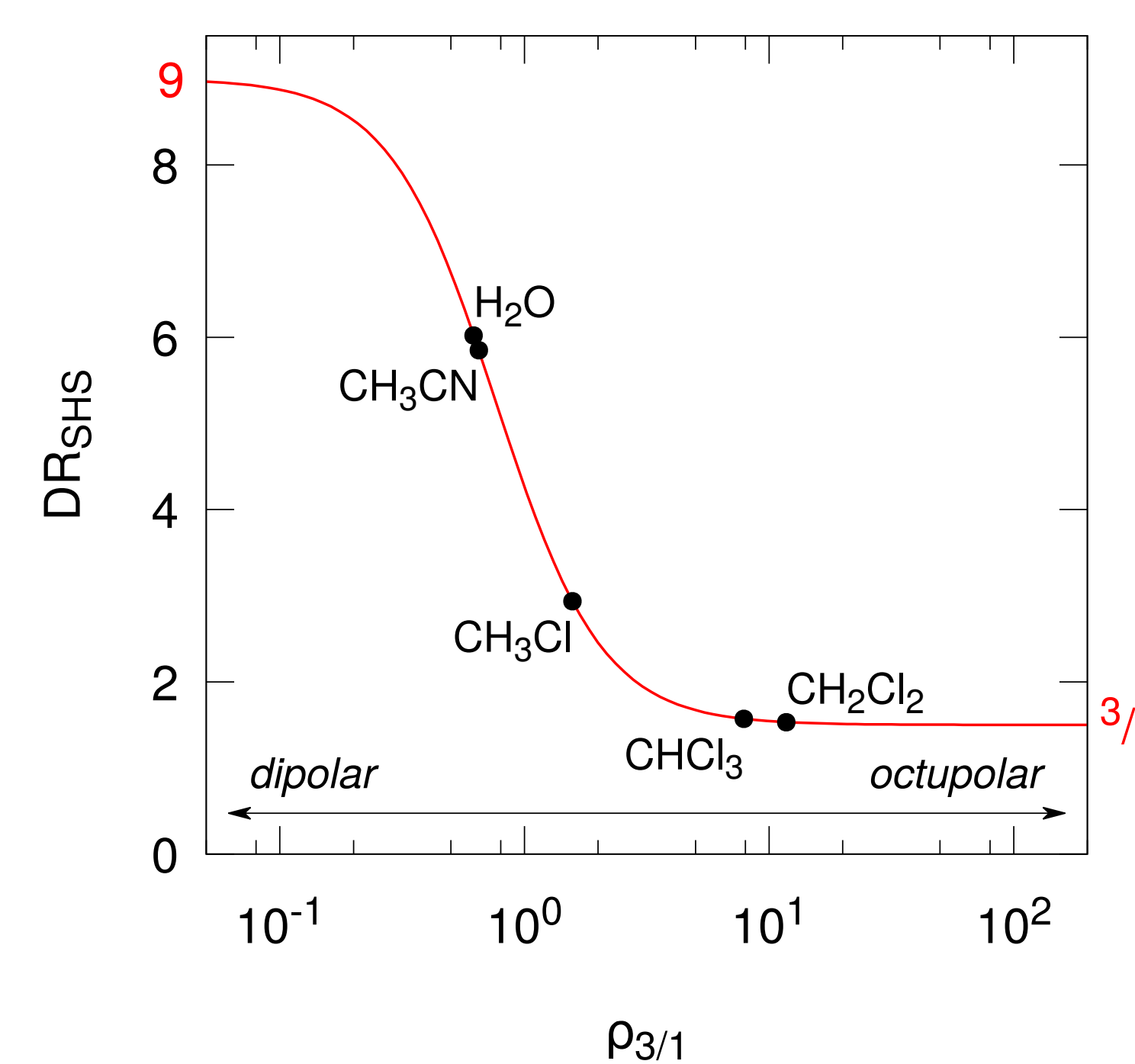
$$\gamma_{THS} = \sqrt{\langle \gamma_{ZZZZ}^2 \rangle + \langle \gamma_{ZXXX}^2 \rangle}$$

$$DR_{THS} = \frac{\langle \gamma_{ZZZZ}^2 \rangle}{\langle \gamma_{ZXXX}^2 \rangle}$$

$\beta$  and  $\gamma$  tensors can also be decomposed into irreducible spherical components.<sup>5</sup> Assuming Kleinman conditions, the  $\beta$  tensor is decomposed into dipolar ( $J=1$ ) and octupolar ( $J=3$ ) components and the  $\gamma$  tensor is decomposed into isotropic ( $J=0$ ), quadrupolar ( $J=2$ ) and hexadecapolar ( $J=4$ ) components. Assuming  $\rho_{3/1} = |\beta_{J=3}|/|\beta_{J=1}|$ ,  $\rho_{0/2} = |\gamma_{J=0}|/|\gamma_{J=2}|$  and  $\rho_{4/2} = |\gamma_{J=4}|/|\gamma_{J=2}|$ ,

$$DR_{SHS} = \frac{18 \rho_{3/1}^2 + 63}{12 \rho_{3/1}^2 + 7}$$

$$DR_{THS} = \frac{32 \rho_{4/2}^2 + 252 \rho_{0/2}^2 + 144}{20 \rho_{4/2}^2 + 27}$$



	CCl <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>	CH <sub>3</sub> Cl	CH <sub>3</sub> CN	H <sub>2</sub> O
$\beta_{SHS}$	15.63	13.41	16.32	12.32	16.74	9.87
DR <sub>SHS</sub>	1.50	1.53	1.57	2.94	5.87	6.01
$\rho_{3/1}$	$\sim \infty$	11.75	7.88	1.57	0.65	0.62
$\gamma_{THS}$	12719	8474	10993	5065	4037	1801
DR <sub>THS</sub>	5744	90	169	414	70	60
$\rho_{0/2}$	$\sim \infty$	3.089	4.280	6.823	2.677	2.437
$\rho_{4/2}$	$\sim \infty$	0.257	0.250	0.288	0.211	0.168

These analyses are confirmed for dynamic quantities (about 30 and 10% of increase at 1064 nm for  $\beta_{SHS}$  and  $\gamma_{THS}$ , respectively, and the DR are mostly unaffected).

- Comparison with dynamic  $\gamma_{THS}$  calculations (at 1300 nm) and experimental liquid phase results: CH<sub>3</sub>CN (Experimental/gas phase calculated ratio of 1.49), CH<sub>2</sub>Cl<sub>2</sub> (1.11), CHCl<sub>3</sub> (0.97) and CCl<sub>4</sub> (1.02). The experimental increase of  $\gamma_{THS}$  with the number of chlorine is reproduced by the calculation. This also suggests that the solvation effect are smaller for  $\gamma_{THS}$  than for  $\beta_{SHS}$ .

## Outlook

Impact of solvation, Kleinman conditions (on the tensor decomposition), and amplitude of the vibrational contributions still need to be investigated.

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