

# How to interpret the Second Harmonic Scattering of liquid water?

Guillaume Le Breton,<sup>a</sup> Oriane Bonhomme,<sup>a</sup> Emmanuel Benichou<sup>a</sup> and Claire Loison<sup>a</sup>

<sup>a</sup> Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, Villeurbanne, France

Non-Linear Optical (NLO) technics are increasingly used to probe structural properties of matter. In Second Harmonic Generation (SHG) two photons with the same fundamental frequency interact with matter to generate a new photon with twice the energy of the initial photons. In the bulk phase, one can measure of the second harmonic generated by a liquid in function of the incoming and outcoming polarization, see Figure 1 a). At the molecular point of view and in the laboratory frame, the intensity collected,  $I$ , can be written in terms of the contribution of the different dyes molecules  $n$  and  $m$ :

$$I \propto \underbrace{\sum_n |\mathbf{p}^n|^2}_{\text{incoherent}} + \underbrace{\sum_{n \neq m} (\mathbf{p}^n) \times (\mathbf{p}^m)^* \exp[i\Delta\mathbf{q} \cdot (\mathbf{r}^n - \mathbf{r}^m)]}_{\text{coherent}}. \quad (1)$$

Where  $\mathbf{p}^n$  is the induced dipole moment of the molecule  $n$  at the second harmonic frequency,  $\mathbf{r}^n - \mathbf{r}^m$  the vector between molecule  $n$  and  $m$  and  $\Delta\mathbf{q}$  the fundamental to second harmonic wave-vector difference. The first term of Equation 1 is called *incoherent* and is due to the emission of single molecule. The second term is called *coherent*: if the liquid structure is strictly centro-symmetric this term averaged to zero. A typical example would be a highly-diluted SHG-dyes molecule in the bulk phase, such an experiment is called Hyper-Rayleigh Scattering (HRS) [1]. Hence, the obtained signal can be related solely to the response of a single molecule and is often linked to the molecular symmetry.

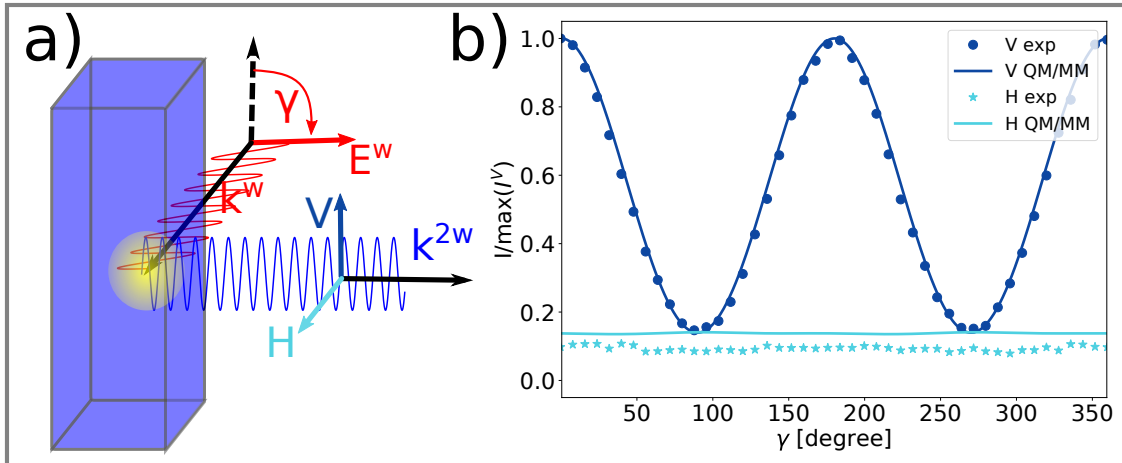


Figure 1: a) Scheme of the HRS or SHS experiments: the fundamental and the collecting direction are orthogonal. The fundamental is shown along several  $\gamma$  polarization angle, the outcoming intensity at twice the frequency is collected for 2 polarization: V and H. The yellow sphere represents the SHG generation in the liquid phase. b) Obtained SHS intensity depending on the incoming polarization angle  $\gamma$  and outcoming polarization for neat water. The dark-blue dot is the V experimental results and the sky-blue stars the H. Full lines are the predicted signal using single-molecule based QM/MM results.

Recently, such SHG experiment in pure liquid has been done, and especially on neat water [2]. In this case, we rather called it Second Harmonic Scattering (SHS), since all the molecules in the sample participate equally to the collected second harmonic intensity. The total intensity is still impacted by the single-molecule term, incoherent, but also by the correlations between the molecule. For instance, we know that water is structured within the first solvation layers and we may expect to see its impact on the SHS intensity: for close molecule  $n$  and  $m$  we can expect the coherent term of Equation 1 not to average to zero. Moreover, studies [3, 4] have interpreted the SHS of liquid signal using a long-range correlation in the liquid phase. Indeed, because of the phase exponential factor, even a small correlation but at great distance can be enhanced and thus may be observed. Therefore, SHS is an interesting tool to observe the deviation of the liquid structure to the expected centro-symmetry.

SHS raises many questions as its interpretation is made difficult by the entanglement of the different contributions. In this work, we used QM/MM based first hyperpolarizability [5, 6] to compute *ab-initio* the SHS intensity of neat water. We questioned many approximations commonly used in the literature and also study the role of the solvation layers to the SHS signal. First, we demonstrate that the understanding of the incoherent part using the molecular symmetry is not possible for water because of the strong fluctuation of the first hyperpolarizability in the liquid phase. Second, we found that this technique is indeed sensitive to the local structure throughout the coherent part. By including the coherent response up to the third solvation layer, we have a quantitative agreement with the experimental result without any fitting parameter, see Figure 1 b). We will also discuss how to include the possible long-range correlation of liquid in this numerical approach.

## References

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