

## A Quantum-Mechanical approach to Raman Optical Activity to model solvent and resonance effects

Tommaso Giovannini<sup>1</sup>, Luciano Vidal<sup>2</sup>, Marta Olszowka<sup>3</sup>, Chiara Cappelli<sup>1</sup>

<sup>1</sup> Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126, Pisa, Italy

<sup>2</sup> Chemistry and Biology Department, Federal University of Technology - Parana', Rua Dep. Heitor de Alencar Furtado, 4900, 81280-340, Curitiba, Brazil

<sup>3</sup> Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Moruzzi 13, 56124, Pisa, Italy

In the last decades Raman Optical Activity (ROA) has attracted numerous new researchers because of its power in assisting the assignment of the absolute configuration of chiral molecules [1].

It has been amply demonstrated that a unambiguous chiral assignment can only be achieved by comparing experimental data with Quantum-Mechanical (QM) calculations. The use of accurate Hamiltonians and a large basis sets may not be sufficient to predict not only the absolute value, but especially the sign of ROA signals. In fact, experimental spectra are usually measured in solution [2] and solvent effects can be large and can affect not only the absolute value but also the sign of this property. Therefore an appropriate model to reproduce them is needed.

In the first part of the talk, a fully polarizable mixed explicit-implicit QM/MM/PCM model, where the MM portion is described in terms of Fluctuating Charges [3] is presented. The model has been recently developed and successfully extended to the calculation of various molecular properties, including Raman Optical Activity [4-9].

Moreover, a recognized shortcoming of ROA is the weakness of the signal, which in some cases makes the experimental study of complex molecular systems or the investigation of some specific spectral regions difficult or almost impossible. For this reason, several ways to enhance the ROA signal have been proposed [10-11]. The second part of the talk, will focus on a novel theoretical approach to calculate ROA spectra in the resonance regime, i.e. when an external frequency that is at resonance with one or more excited states of the molecule is exploited [12]. This model, which considers both Frank-Condon (FC) and Herzberg-Teller (HT) effects in the electronic transition moments, is to date the most accurate approach to calculate such spectra for solvated systems.

### References

- [1] Polavarapu, P. L. *Chem. Rec.*, **7**, 125 (2007).
- [2] Nafie, L.A. *Vibrational Optical Activity*, John Wiley & Sons, Chichester (2011).
- [3] Lipparini, F., Barone, V. *J. Chem. Theory Comput.*, **7**, 3711 (2011).
- [4] Lipparini, F., Cappelli, C., Barone, V. *J. Chem. Theory Comput.*, **8**, 4153 (2012).
- [5] Lipparini, F., Cappelli, C., Scalmani, G., De Mitri, N., Barone, V. *J. Chem. Theory Comput.*, **8**, 4270 (2012).
- [6] Lipparini, F., Cappelli, C., Barone, V. *J. Chem. Phys.*, **138**, 234108 (2013).
- [7] Lipparini, F., Egidi, F., Cappelli, C., Barone, V. *J. Chem. Theory Comput.*, **9**(4), 1880 (2013).
- [8] Giovannini, T., Olszowka, M., Cappelli, C. *submitted* (2016).
- [9] Giovannini, T., Olszowka, M., Cappelli, C., *in preparation* (2016).
- [10] Johannessen, C., White, P. C., Abdali, S. *J. Phys. Chem A*, **111**, 7771 (2007).
- [11] Nafie, L. A. *Chem. Phys.*, **205**, 309 (1996).
- [12] Vidal, L. N., Egidi, F., Barone, V., Cappelli, C. *J. Chem. Phys.*, **142**, 174101 (2015).