Modeling the Vibrational Circular Dichroism spectroscopy of Phenylcyclohexanediol and Ionic Liquids to probe solvation properties

Emeline Boyer[1], Lou d'Haese[2], Jessica Bowles[3], Anne Zehnacker[4], Florent Calvo[5], Van-Oahn Nguyen-Thi[1], Carine Clavaguéra[1]

[1] *Université Paris-Saclay, CNRS, Institut de Chimie Physique UMR8000, 91405, Orsay, France*
[2] *Unité de recherche en chimie physique, théorique et structurale, Université de Namur, 5000 Namur, Belgique*
[3] *Vrije Universiteit Brussel [Bruxelles] – Belgique*
[4] *Université Paris-Saclay, CNRS, Institut des Sciences Moléculaires d'Orsay UMR8214, 91405, Orsay, France*
[5] *Université Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, France*

Vibrational circular dichroism (VCD) unveils molecular conformational nuances by discerning absorption differences in right- and left-circularly polarized light within the infrared range [1]. This subtle technique elucidates molecular interactions, especially those that are sensitive to hydrogen bonding, thereby offering particular insight into the structure of unconventional solvents. Interpreting VCD signals necessitates meticulous comparison with theoretical models. However, incorporating environmental effects posed challenges, now mitigated by advancements in computational modeling. Recently, we proposed a new methodology [2] based on classical molecular dynamics simulations associated with the AMOEBA polarizable force field [3] to calculate VCD spectra of flexible molecules. The crucial element in these VCD simulations is determining the magnetic dipole moment, an intrinsic dynamical quantity. Highly flexible molecules, ionic liquids (ILs) and deep eutectic solvent (DES) turn out to be particularly interesting to study with this methodology. The 1-phenyl-1,2-cyclohexanediol (PC), a highly flexible molecule, was successfully studied in dimethyl sulfoxide (DMSO) solvent, by calculating both infrared and VCD spectra and the comparison with experimental data. Furthermore, these spectra were calculated for ILs and DES, to probe their long-range organization which appears challenging, especially for VCD spectra. In particular a studied was made on spirocyclic pyrrolidinium tetrafluoroborate and menthol acetic acid respectively. Modeling both the infrared and VCD spectra for these systems reveals useful microscopic-scale information on solvation at the molecular level.

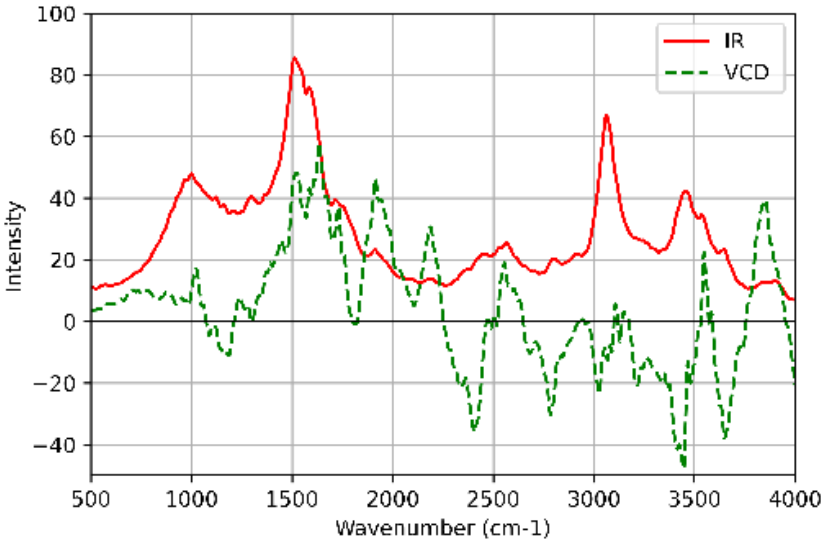

Figure : *Infrared and VCD spectra of PC in a box of solvent (DMSO)*

References:

[1] Nafie, L. A. Infrared and Raman vibrational optical activity: theoretical and experimental aspects. Annu. Rev. Phys. Chem 1997, 48, 357–386.
[2] Bowles, J.; Jähnigen, S.; Agostini, F.; Vuilleumier, R.; Zehnacker, A.; Calvo, F.; Clavaguéra, C. . ChemPhysChem 2024, 25 (8).
[3] Ponder, J. W.; Wu, C.; Ren, P.; Pande, V. S.; Chodera, J. D.; Schnieders, M. J.; Haque, I.; Mobley, D. L.; Lambrecht, D. S.; DiStasio, R. A. et al. Current Status of the AMOEBA Polarizable Force Field. J. Phys. Chem. B 2010, 114, 2549–25.