Benchmarking quantum methods with experimental data: exploring rotational spectroscopy of water and alcohol complexes

Melandri, S.,[1]* Maris, A.,[2] Evangelisti, L.,[2] Lv, D.,[2] Song, W.[2]
*presenter
[1]sonia.melandri@unibo.it, University of Bologna, Italy
[2] University of Bologna, Italy

As is widely recognized, the environment within living organisms is intricate and dynamic, wherein water serves as the foundation for numerous interactions among biomolecules. The way molecules dissolve can significantly affect these important processes. Conformational alterations during the dissolution process have the potential to influence the activity and bioavailability of molecules. [1]

The study of small clusters in the gas phase offers a unique opportunity to characterize both experimentally and theoretically models of the molecular interactions which occur in bulk water solutions. [2,3] The conformational space of such systems is generally shaped by non-covalent interactions (NCIs) occurring within the molecule or with the surroundings. Moreover, they usually possess a high number of low-energy conformations undergoing large amplitude motions through shallow potential energy surfaces. For these reasons, the properties of such systems are difficult to predict and are challenging for theoretical calculations.

High-resolution spectroscopy, in particular rotational spectroscopy, allows the deduction of several molecular properties such as structural parameters (e.g. the moment of inertia, electric dipole moments, centrifugal distortion and hyperfine coupling constants (i.e., nuclear quadrupole, spin-rotation, and spin-spin quadrupole) which can be very well determined, both numerically and also in terms of their physical description. The results of high-resolution spectroscopy studies can be directly compared to the outcomes of theoretical calculations as regards the energy order of the stable configurations and their geometries. Consequently, they offer valuable insights into the underlying driving forces governing interactions between water and solute.

The rotational spectra of a few water and alcohol complexes of small organic molecules (e.g. cysteamine and acrolein) will be presented. Very detailed structural information is obtained from the observation of the normal and isotopic species which, integrated with the results of quantum chemical calculations yielded valuable data for the determination of r_s and r_0. In addition, our studies also consider the impact of the weak interactions and large amplitude structural averaging correction. The comprehensive analysis of intermolecular interactions, employing diverse methodologies, has provided a thorough and in-depth insight into the behavior of the molecules in the complexes.

---

[1] Ball P. Water as an active constituent in cell biology *Chem. Rev.* **2008**, *108*, 1, 74–108 Ruzi, M.; Anderson, D. T. Photodissociation of N-methylformamide isolated in solid parahydrogen. *J. Chem. Phys.* **2012**, *137*, 194313.
[2] Richardson, J. O. et al. Concerted hydrogen-bond breaking by quantum tunneling in the water hexamer prism *Science* **2016** 351,1310-1313.
(2016).
[3] Evangelisti, L.; Brendel, K.; Maeder, H.; Caminati, W. and Melandri, S. Rotational Spectroscopy Probes Water Flipping by Full Fluorination of Benzene, *Angew. Chem. Int. Ed*. **2017**, 56, 13699 –13703