

HyDRA: Bringing vibrational theory and experiment together in a double-blind manner for organic monohydrate complexes at low temperature

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Experimental vibrational spectroscopy often relies heavily on quantum-chemical input. The assignment of transient species, the understanding of vibrational resonances and the quantification of isomers profits from theoretical predictions based on density functional or wave function theory for the electrons and on some kind of nuclear dynamics treatment. This is certainly true for the field of non-covalent interactions, such as the embedding of molecules in a solvent or in a matrix. Every group in the field has its favorite methods, basis sets, scaling factors and other twists to match theory and experiment in a useful way, often exploiting more or less systematic error compensation.

Among the zoo of computational methods, one can always find one which reproduces a given vibrational wavenumber for a single species. But are there affordable methods which reliably predict this observable for a multitude of species? One way to find out is to measure it for a set of new systems and to keep the results secret until modeling groups have submitted their predictions.

We have initiated a first step in this direction¹ by picking monohydrate complexes of organic molecules. Their study at low temperature in supersonic jets makes sure that calculations without environment and without thermal excitation can be right for the right reason. By using a new gas recycling concept in combination with infrared spectroscopy² we can also address expensive compounds and isotopologues in direct absorption.

The initial observable is the red- or downshift of the OH stretching fundamental of a single water molecule engaged in moderately strong hydrogen bonds to organic compounds, relative to the symmetric stretch of an isolated water molecule. A training set consisting of 10 previously published complexes, some of them showing a newly assigned anharmonic resonance³, was provided to the theory groups. They were given 6 months to also predict the shifts of 10 vibrationally uncharacterised complexes (test set), while these were experimentally investigated. The procedure and outcome of this blind challenge will be discussed in the talk. Are anharmonic treatments already sufficiently mature to compete with (scaled) harmonic predictions? Is machine learning already having an impact? Is correct assignment a practical issue on the theory side, as it is in experiment? Are the models performing better for the disclosed training set than for the undisclosed test set? What are the next steps to be made to ensure that right answers are obtained for good reasons?

¹ Fischer, T. L.; Bödecker, M.; Zehnacker-Rentien, A.; Mata, R. A.; Suhm, M. A. Setting up the HyDRA blind challenge for the microhydration of organic molecules. *ChemRxiv* **2021**, <https://doi.org/10.26434/chemrxiv-2021-w8v42>.

² Gottschalk, H. C.; Fischer, T. L.; Meyer, V.; Hildebrandt, R.; Schmitt, U.; Suhm, M. A. A sustainable slit jet FTIR spectrometer for hydrate complexes and beyond. *Instruments* **2021**, *5*, 12.

³ Fischer, T. L.; Wagner, T.; Gottschalk, H. C.; Nejad, A.; Suhm, M. A. A rather universal vibrational resonance in 1:1 hydrates of carbonyl compounds. *J. Phys. Chem. Lett.* **2021**, *12*, 138.