How many water molecules are needed to solvate one?

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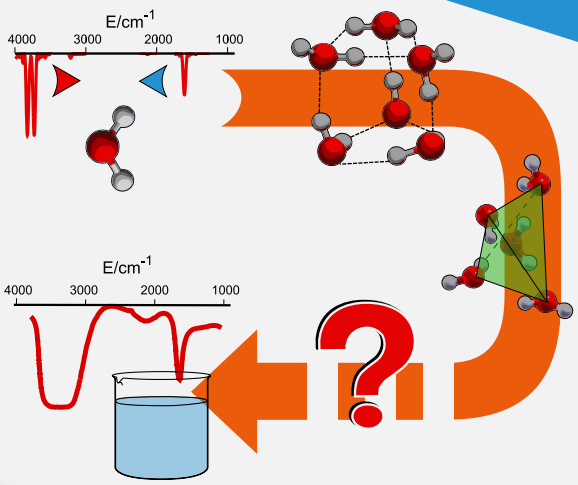
Abstract

Several questions are still open in the field of water solvation:

- Is tetrahedral coordination necessary to achieve solvation?
- Is it a sufficient requirement?
- What is the minimum solvation shell of water?

By applying semiclassical spectroscopy methods to increasingly large water clusters, we were able to track the solvation of a single water molecule and to obtain vibrational signals compatible to the ones of bulk water.



The Divide-and-Conquer strategy

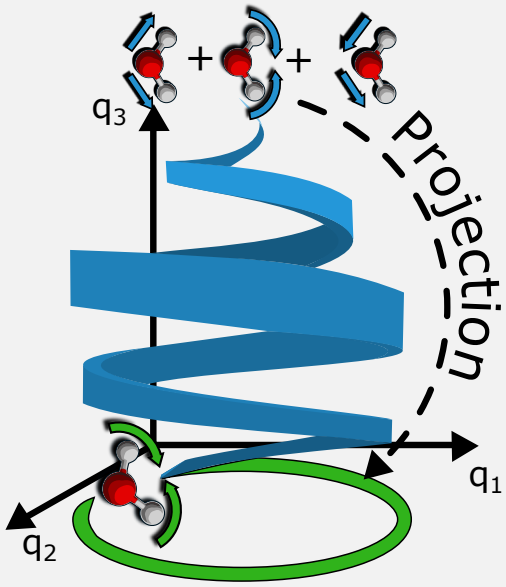
Divide-and-Conquer Semiclassical Initial Value Representation (DC SCIVR) relies on the semiclassical approximation to the quantum propagator. Key additions include:

- Time-averaging filter
- Tailored reference states
- Projection onto subspaces

The DC-SCIVR expression for the spectral density is:

$$\tilde{I}(E) = \frac{1}{(2\pi)^N} \iint d\tilde{\mathbf{p}}_0 d\tilde{\mathbf{q}}_0 \frac{1}{2\pi T} \left| \int_0^T dt \, \langle \tilde{\chi} | \tilde{\mathbf{p}}_t, \tilde{\mathbf{q}}_t \rangle \, e^{i\left(\tilde{S}_t(\mathbf{p}_0,\mathbf{q}_0) + \tilde{\phi}_t(\mathbf{p}_0,\mathbf{q}_0) + Et\right)} \right|^2$$

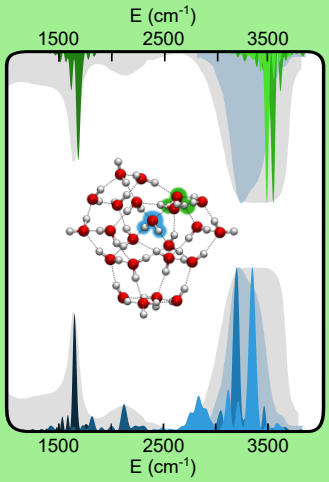
A. Kaledin and W. H. Miller, J. Chem. Phys. **118**, 7174 (2003)
M. Ceotto, S. Atahan, G. F. Tantardini, and A. Aspuru-Guzik, J. Chem. Phys. **119**, 234113 (2009)
M. Ceotto, G. Di Liberto, and R. Conte, Phys. Rev. Lett. **130**, 010401 (2017)



Results

We found that:

- Tetrahedral coordination is not sufficient for solvation
- At least 20 surrounding water molecules are needed to completely solvate one
- The second solvation shell must be complete for solvation
- Particular care must be reserved to the description of the combination band between bending and librations



A. Rognoni, R. Conte, and M. Ceotto, Chem. Sci. **12**, 2060-2064 (2021)

What's next?

Deconstructing the complex IR spectrum of the formic acid dimer