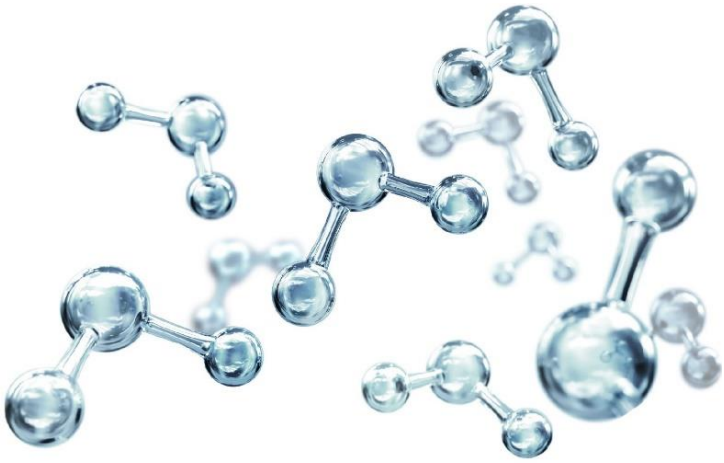
Seminar

CMWS Centre for Molecular Water Science

27th November 2025
12:00 h (CET)

Zoom Virtual Meeting:
https://tuhh.zoom.us/j/82631283465
Meeting-ID: 826 3128 3465
Password: 978444



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Correlated vibrational spectroscopy: quantifying charge transfer and nuclear quantum effects in water

Correlated vibrational spectroscopy (CVS) is a hyper-Raman-based nonlinear optical method, designed to separately measure vibrational spectra of interacting and single molecules in a liquid [1]. In a typical linear or nonlinear spectroscopic measurement, the recorded intensity contains mixed signatures from single molecules in an averaged environment as well as those of interacting molecules. This mixing is inherent to the measurement of intensity, and spectral interpretation/decomposition is typically achieved by additional analysis, e.g. by means of molecular dynamics simulations. CVS resolves this issue by using a procedure based on symmetry, providing separate spectra for only interacting molecule and only single molecule contribution. CVS spectra can be recorded in the entire vibrational frequency range, which opens up possibilities to directly asses low frequency vibrational modes, which are particularly sensitive to intermolecular interactions.

For hydrogen (H)-bonding, H-bond stretch and bending modes, as well as librational modes are particularly informative. Frequency shifts and intensities are readily converted into bond strength changes and changes in the number of H-bonds. As an example of the capabilities of CVS, charge transfer and nuclear quantum effects were probed in water and acidic and basic solutions, using the H-bond stretch mode of water. Hydroxide ions donate ~8 % more negative charge to the H-bond network of water and protons accept ~<4 % less negative charge from the H-bond network of water compared to water itself. In heavy water there are ~9 % more H-bonds compared to light water, and acidic solutions display clear nuclear quantum effects, in contrast to basic solutions which do not display them. A second example will feature the molecular origins of specific ion effects [2].

References [1] M. Flór, D. M. Wilkins, M. de la Puente, D. Laage, G. Cassone, A. Hassanali, S. Roke, Science 386, 1110 (2024), DOI: 10.1126/science.ads4369. [2] Unraveling the molecular pathways for structure ‘making’ and ‘breaking’ by ions in water, M. Flór, V. Vorobev, V. Mandalaparthy, N. F. A. van der Vegt, Paul S. Cremer, S. Roke, J. Am. Chem. Soc. (2025), DOI: https://doi.org/10.1021/jacs.5c10984