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Vibrational properties of liquid and supercritical water: Insights from ab initio molecular dynamics and Raman spectroscopy

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Aqueous fluids are key agents in most geological processes of the Earth's crust and upper mantle. They have a profound influence on physical properties of rocks and drive geochemical reactions. Knowledge of the molecular structure and the corresponding chemical bonding in such fluids is required to develop a fundamental understanding of fluid-rock interactions. Pure water has been subject to a large number of experimental and theoretical studies. While diffraction experiments provide important fingerprint information on the short and intermediate range order in the fluid, spectroscopic methods such as Raman, IR or x-ray absorption spectroscopy are more site-specific sensitive to the local molecular environment. Typically, the different analytical techniques are complementary and may be linked, e.g., via appropriate molecular modeling. Still, water remains a challenging system to study as our current understanding of its structure, physical and chemical properties is at least partly controversial.

Here, we use a combination of ab initio molecular dynamics simulations and in-situ Raman spectroscopy to shed new light on the vibrational properties of liquid and supercritical water in a wide range of pressures and temperatures. Spectral densities of quasi-normal modes derived from the simulations using a mode-projection technique [1] are broadly consistent with the experimental data. Changes in the water structure with variations in pressure and temperature are reflected in the positions and the widths of the vibrational bands. The most significant changes are observed in the region of symmetric and antisymmetric stretching vibrations, i.e. between 2900 and 3700 cm^{-1}. The respective Raman band at ambient conditions has a complex shape with at least three contributions. The intensity at lower wavenumbers is commonly attributed to 'network' water. Increasing temperature leads to a shift of the band to higher frequencies and narrowing of the peak. This can be interpreted as a breakdown of the network structure, which eventually leads to the spectrum of an isolated molecule at low density and high temperature. Increasing pressure results in a broadening and red-shift of the Raman band, even at the highest temperatures considered here (about 700 °C), with increasing intensity at lower wavenumbers implying speciation changes towards higher coordination. As the simulation provides partial spectra from individual water molecules, the contribution of different structural units to the total vibrational bands will be evaluated and discussed.

[1] Spiekermann et al. (2012) J. Chem. Phys. 136, 154501.