

Hydrogen-bonding networks in nanoconfined water

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Hydrogen-bonding (H-bonding) networks in liquid water define its physico-chemical properties, phase boundaries, and structure-reactivity trends for solvated species. In the liquid phase, H₂O dipoles arrange into H-bonding networks, where one H₂O can interact with up to four other H₂O molecules. For water-filled rigid nanopores with diameters of <10 nm, the electrical double-layers extending from the opposing surfaces can overlap, leading to re-structuring of H-bonding networks inside the nanopores.

Here we use vibrational spectroscopy and molecular dynamics (MD) simulations to assess how nanoconfinement changes H-bonding networks in liquid water confined in silica (SiO₂) nanopores as a function of surface charge and temperature. In the Raman spectroscopy experiments, we use SBA-15 series mesoporous SiO₂ with pore diameters of 7 nm and 4 nm. The mesoporous SiO₂ is saturated with isotopically-dilute H₂O/D₂O aqueous solutions at controlled pH (from 2 to 8). We collect Raman spectra in 1000-4000 cm⁻¹ range to assess OH and OD stretching modes, and the H-O-H and H-O-D bending modes in nanoconfined solutions. The temperature is gradually increased from room temperature to 90 °C (363 K). Our preliminary results indicate that (1) the mesoporous structures and pore sizes of SiO₂ are unchanged during heating in the aqueous solutions; and (2) with increasing temperature the fraction of 4-coordinated H₂O molecules decays faster for nanoconfined water, compared to the bulk phase. This could reflect the change in the liquid-vapor phase boundary in SiO₂ nanopores, with the H₂O boiling point shifting to lower temperature. The earlier studies of H₂O confined in carbon nanotubes and graphene slit pores predicted both decrease and increase in H₂O boiling temperature with nanoconfinement. Preliminary MD simulation results for pure water near neutral surfaces show a significant shift in the water O-H stretching mode only for the first layer of water molecules directly H-bonded to the surface. Results will also be presented using our newly parameterized model for negatively charged silica surfaces.

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