The Structure of the First Coordination Shell in Water

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Water is the key compound for our existence on this planet and it is involved in nearly all biological, geological and chemical processes. Knowledge about the hydrogen-bonded network structure in water is essential for understanding its unusual chemical and physical properties. In its condensed phase, ice (Ih) e.g., each water molecule is coordinated by four others in a semi tetrahedral arrangement forming an ordered crystal structure. In contrast, in liquid water a statistical distribution of different coordinations can be assumed due to the dynamical motion of the atoms causing the H-bonds to break and reform on a picosecond (ps)-time scale. The present experimental information relies largely on neutron and x-ray diffraction data, providing radial distribution functions, and has the inherent characteristic of averaging interatomic distances over all directions. Due to this lack of information about angular correlations a unique experimental determination of local arrangements is not possible. A different approach to determine molecular arrangements is to probe how chemical bonding perturbs the local valence electronic structure.

Wernet et al. [Science Express Reports, 10.1126/science.1096205 (2004)] studied the first hydration shell of a water molecule in bulk liquid water by probing its electronic structure using X-ray Absorption Spectroscopy (XAS) and X-ray Raman Scattering (XRS). From carefully designed experimental models as well as theoretical spectra simulations, with results contrary to molecular dynamics simulations, Wernet and coworkers conclude that...
the local surrounding of an H$_2$O molecule in liquid water resembles that in the topmost layer of ice, i.e., it is characterized by a substantial number of broken H-bonds. The results of the study shows that water, on the probed sub-femtosecond time-scale, consists mainly of structures with two strong hydrogen-bonds, one donating and one accepting, compared to the four-hydrogen-bonded tetrahedral structure in ice. This implies that most molecules are arranged in strongly H-bonded chains or rings embedded in a disordered cluster network connected mainly by weak H-bonds.

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