

The Structure of the First Coordination Shell in Water

Ph. Wernet¹, D. Nordland², U. Bergmann³, M. Cavalleri², M. Odelius², H. Ogasawara⁴, L. Å. Naslund⁴, T. K. Hirsch⁵, L. Ojamae⁶, P. Glatzel⁷, L. G. M. Pettersson², A. Nilsson^{4*}

¹ *Stanford Synchrotron Radiation Laboratory, Post Office Box 20450, Stanford, CA 94309, USA; Present address: BESSY, Albert-Einstein-Strasse 15, D-12489 Berlin, Germany.*

² *FYSIKUM, Stockholm University, AlbaNova, S-106 91 Stockholm, Sweden.*

³ *Stanford Synchrotron Radiation Laboratory, Post Office Box 20450, Stanford, CA 94309, USA.*

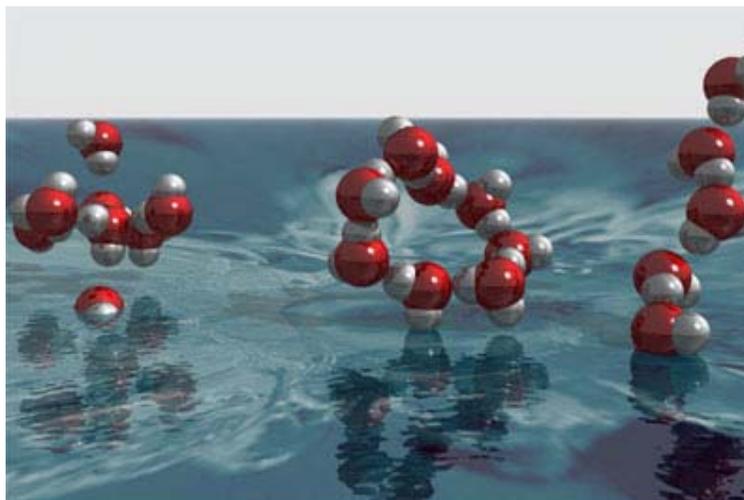
⁴ *Stanford Synchrotron Radiation Laboratory, Post Office Box 20450, Stanford, CA 94309, USA; FYSIKUM, Stockholm University, AlbaNova, S-106 91 Stockholm, Sweden.*

⁵ *Department of Physical Chemistry, Stockholm University, S-106 91 Stockholm, Sweden.*

⁶ *Department of Chemistry, Linköping University, S-58183 Linköping, Sweden.*

⁷ *Department of Inorganic Chemistry and Catalysis, Debye Institute, Utrecht University, 3584 CA Utrecht, Netherlands.*

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



The Structure of the First Coordination Shell in Liquid Water Illustration by H. Ogasawara

In ice, each water molecule is surrounded by 4 other molecules in a tetrahedral arrangement (left). The new result on liquid water shows that the molecules are connected only with 2 others. This implies that most molecules are arranged in strongly hydrogen bonded rings (middle) or chains (right) embedded in a disordered cluster network connected mainly by weak hydrogen bonds. The oxygen atoms are red and the hydrogen atoms grey in the water (H₂O) molecules.

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 H₂O 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.

* To whom correspondence should be addressed.

A. Nilsson , E-mail: nilsson@slac.stanford.edu

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