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The short-term memory of water

Researchers of the Max-Born-Institute and the University of Toronto find extremely fast fluctuations in liquid water – Publication in Nature.

A research team of the Max-Born-Institute in Berlin-Adlershof and the University of Toronto has succeeded – for the first time – to observe ultrafast fluctuations in the structure of liquid water with new methods of femtosecond vibrational spectroscopy. As reported in Nature (Vol. 434, p. 199), the memory of the fluctuating hydrogen bond network gets lost within 50 femtoseconds, faster than in any other liquid. A time interval of 1 femtosecond (fs) equals 10^{-15} or 0.000000000000001 seconds, i.e. one millionth of a billionth of a second).

Water (H_2O) is the liquid essential for life on earth. It functions as the medium for the most important biological processes, be it as “solvent” for biomolecules, or as supplier of protons for charge transport. Liquid water consists of a disordered network of H_2O molecules, held together by hydrogen bonds, that are relatively weak chemical bonds. This network continuously undergoes fluctuations, where the water molecules are reorienting and their interactions change. Hydrogen bonds are continuously broken and reformed due to these fluctuations. Despite much research effort, the understanding of the structural dynamics of water, that typically evolves in the femtosecond time regime, has until now been rather limited.

In the experiments a light pulse with a duration of 70 fs tuned in the mid-infrared (3 micrometer wavelength) excites an extremely thin water film (0.5 micrometer thickness, 1 micrometer = 10^{-6} m) and induces a local molecular vibration, the so called hydrogen stretching mode (see animation 1). The vibrating molecule functions as probe for the fluctuations of the molecular network that cause changes in the molecular vibrational frequency and phase. Using the method of two-dimensional spectroscopy these changes are observed in real-time, from which the time scale and mechanism of these fluctuations can be derived. It turns out that upon excitation of the molecular vibration the existing structure of the hydrogen bond network disappears in approximately 50 fs, a time interval that is much shorter than the lifetime of the hydrogen bonds (which is on average 1000 fs). The reason for the extreme fast decay of the initial structure lies in so-called librational motions of the hydrogen bonds (see animation 2), i.e., hindered tilting and rotational motions of the coupled molecules. Librational motions change the relative orientation of water molecules and - thus - contribute to the loss of structural memory in the liquid. In addition, on a somewhat longer time scale of 100 fs, the initially localized vibrational excitation is transmitted to neighbouring molecules. The ultrafast structural dynamics and the extremely fast decay of local excitations are important for stabilizing biological systems in aqueous solutions.

The results of the German-Canadian collaboration, financially supported by the German Science Foundation (Sonderforschungsbereich 450) and the Alexander von Humboldt Foundation (Humboldt prize for R. J. Dwayne Miller), show for the first time the extreme short structural memory of neat water. Future investigations of this collaboration will focus on this behaviour in similar systems, e.g. aqueous solutions, and its role for biological function.

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Animation 1: http://www.mbi-berlin.de/en/research/projects/2-04/highlights/water_asymmetric_o-h_stretch.gif

Stretching vibration of the water molecule. An ultrashort infrared pulse excites the asymmetric stretching vibration of the angled water molecule (red: oxygen atom, gray: hydrogen atom). The water molecule is part of a network of hydrogen bonds between the hydrogen and oxygen atoms on neighboring molecules (small gray symbols). Shown are the elongations of the atoms during the stretching vibration with a vibrational period of 10 fs. (Animation by Jens Dreyer, MBI)

Animation 2: http://www.mbi-berlin.de/en/research/projects/2-04/highlights/water_librational_mode.gif

Librational motion of water. Librational motions change the relative orientation of water molecules and - thus - contribute to the loss of structural memory in the liquid. A period of the librational mode shown lasts approximately 40 fs. (Animation by Jens Dreyer, MBI)