Compton scattering confirmation of the anomalous ground state of the electrons in nano-confined water

Water is usually viewed as a collection of molecules that remain intact at room temperature and atmospheric pressure, interacting weakly through the hydrogen bonds formed by the attraction of the electrons around the oxygen of one molecule with the protons on another. The water molecules form a tetrahedral network in ice, and a distorted, slowly changing, primarily tetrahedral network in bulk water. Within this picture, the proton in the water molecule exists within a covalent bond in a nearly harmonic well that is softened only slightly by the attraction of the neighboring oxygen.

With the advent of deep inelastic neutron scattering (DINS) it has become possible to observe the momentum distribution of the protons in water. The width and shape of this momentum distribution is due almost entirely, even at room temperature, to the confinement of the proton in the potential provided by its surroundings. The weakly interacting molecule picture above is qualitatively correct for bulk water. The momentum distribution is well approximated by a 3D anisotropic Gaussian, the momentum widths are consistent with the frequencies of oscillation of the proton observed with other techniques, and the width is approximately calculable from perturbation theories that begin with the isolated molecule as an unperturbed system [1]. However, deviations from the weakly interacting molecule model observed with DINS become extreme when water is confined to dimensions on the order of 20 Å. The proton is observed to delocalize coherently over distances of the order of 0.2-0.3 Å in a strongly anharmonic double well potential [2]. Since the potential well the proton sees, is due to the distribution of the electrons of the system, one would expect that the valence electrons in nano-confined water to be distributed spatially very differently than would be the case in individual molecules.

This conjecture was tested at the high energy inelastic scattering beamline **BL08W**, by using X-ray Compton scattering to measure the momentum distribution of the electrons for nano-confined water in conditions for which the proton was known to be delocalized [3]. Two systems were chosen, water in the single walled nano-tube (SWNT) as a function of temperature, and water in two forms of Nafion at room temperature. Nafion is the proton exchange membrane used in many commercial fuel cells because of its high conductivity. The protons are confined in irregular pockets in the polymer (Teflon)

matrix, as shown in Fig. 1. The two materials differed in the length of the side chains (shown in the figure), which donate the proton to the water that makes it a conductor. We discuss only the Nafion results here. The conclusions from the nanotube data are the same.

We show in Fig. 2 the momentum distribution of the protons in the two forms of Nafion. The broad tails on the distribution and the appearance of oscillations demonstrate that the confining potential is far from the nearly harmonic wells of the covalent bond in the molecule. In Fig. 3, we show the results of the X-ray Compton scattering for the change in the momentum distribution for the valence electrons of the water for the two types of Nafion, obtained by subtracting the dry Nafion signal from the signal with water present, and removing the core electron contribution for the water. The amount of water in the Nafion is the same as that in the samples in Fig. 2. The curve in Fig. 3 is a phenomenological fit. Its shape was obtained from X-ray Compton measurements, by others at SPring-8 [4], of the change in the momentum distribution in bulk water when deuterium was substituted for hydrogen. The amplitude in Fig. 3, as measured by the $\Delta J(0)/J(0)$, however, is 46 times greater than observed in those measurements. It is also 17 times greater, by the same criterion, than the change observed as the hydrogen bond in bulk water is disordered by heating from 5° above melting to 5° below boiling at

Nafion™

$(CF_2CF)_m(CF_2CF_2)_n$
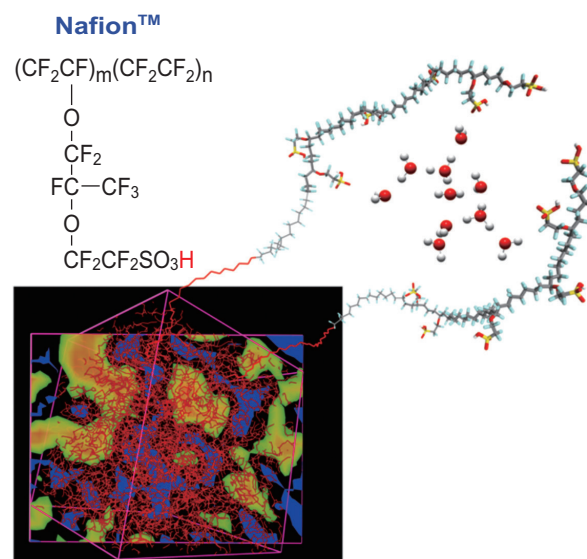|
O
|
CF_2
FC—CF_3
|
O
|
$CF_2CF_2SO_3H$

Fig. 1. Multiscale simulation of the structure of Nafion. Blue areas are primarily polymer, red orange primarily water. Samples differ in the length of the side chains.
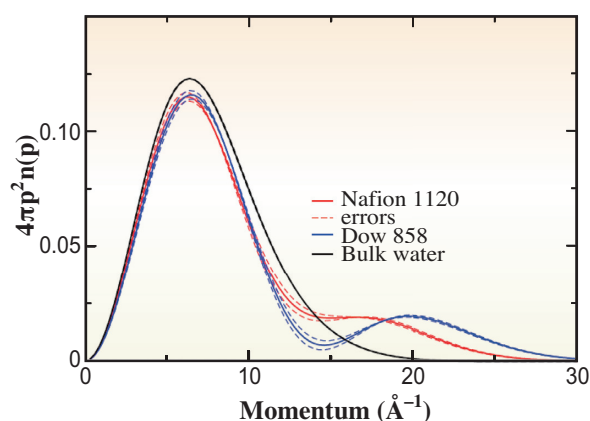
Fig. 2. Proton radial momentum distribution in water confined in two types of Nafion, compared with that of bulk water.

atmospheric pressure [5]. The changes observed here are far outside the range of what can be achieved by the weakly interacting molecule model. The changes in the electron distribution indicate the ability of the electron backbone for the hydrogen bond network to shift electrons around in order to create the Born-Oppenheimer potential that leads to the momentum distribution for the protons shown in Fig. 2.

These measurements demonstrate that the ground state of the electrons and protons in nano-confined water is qualitatively different from the usual weakly interacting molecule model. Presumably the frustration due to confinement of the geometric configuration preferred by the tetrahedral ordering raises the energy of that state, allowing an energetically nearby configuration of the electrons and protons, better adapted to the confinement, to become the ground state. In any case, the existence of this state has profound implications for biology. 20 Å is the characteristic distance between the elements of a biological cell. It is likely that evolution was making use of the properties of this state of water when life evolved, and that the functioning of cells depends on its properties.
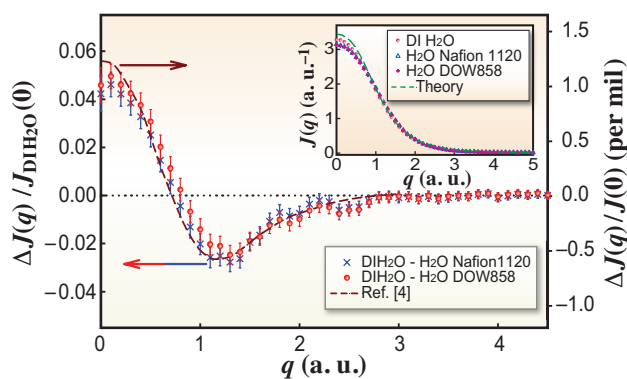

Fig. 3. The difference Compton profile (CP) of water in Nafion 1120 and Dow 858 subtracted from the CP of bulk water. The red dashed line is a fit to the difference (H_2O-D_2O) between H_2O and D_2O, rescaled to fit our data; a rescaling by a factor of 46 is needed. The inset shows the experimental CP for deionized (DI) water, confined water in two types of Nafion (Nafion 1120 and DOW 858) and theoretical CP (green dashed line) of isolated water molecule.

George F. Reiter[a,*], Aniruddha Deb[b] and Stephen J. Paddison[c]

[a] Physics Dept., University of Houston, USA
[b] Dept. of Chemistry, University of Michigan, USA
[c] Dept. of Chemical and Biomolecular Engineering, University of Tennessee, USA

*E-mail: greiter@uh.edu

References
[1] C. J. Burnham et al.: Chem. Phys. **135** (2011) 144502.
[2] G. Reiter et al.: Physical Review B **85** (2012) 045403.
[3] G.F. Reiter, A. Deb, Y. Sakurai, M. Itou, V.G. Krishnan and S.J. Paddison: Phys. Rev. Lett. **111**(2013) 036803.
[4] K. Nygård et al.: J. Chem. Phys. **126** (2007) 154508.
[5] M. Hakala et al.: J. Chem. Phys. **125** (2006) 084504.