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Names and affiliations of applicants (* indicates experimentalists):

Felix Lehmkühler[1,*] , Christian Sternemann[2,*] , Thomas Büning[2,*] , Hasan Yavas[1,*] , Mikko O. Hakala[3]

[1]Deutsches Elektronen Synchrotron DESY, Notkestr. 85, 22607 Hamburg, Germany

[2]TU Dortmund, Fakultät Physik/DELTA, 44221 Dortmund, Germany

[3]University of Helsinki, Department of Physics, 00014 University of Helsinki, Finland

Report:

The structure of liquid water is one of the unsolved problems in condensed matter physics [1]. Supercooled water in particular has been proposed to show a variety of local structures ranging from clathrate-like clusters to mixtures of high and low density structures in the framework of the two liquids hypothesis [2], however, experimental studies were not able to prove such models so far. A deep-inelastic neutron scattering study reported on an excess of the proton kinetic energy in slightly supercooled water [3]. This was suggested to be originated in a delocalizing of the proton between two oxygen atoms of neighbouring water molecules. Such a delocalizing results in significant changes in the bond network, most notably in an increase of the covalent intramolecular OH bond length. While the statistical accuracy of deep-inelastic neutron scattering experiments makes the estimation of bond lengths impossible, this can be done in state-of-the-art x-ray Compton scattering calculations and experiments [5-9], which is the analog technique to deep inelastic neutron scattering, using x-rays instead of neutrons.

In experiment HD 614 we measured Compton profiles of water in the temperature range between room temperature and supercooled conditions of 256.5 K. We used the standard Compton scattering set-up of ID15B. The custom made sample cell including a temperature control via a chiller and heating foils was holding a glass capillary (sample thickness around 2 mm) and placed onto the sample stage. The 13-element Ge solid state detector was mounted at a scattering angle of about 150°. To keep a constant flux, we used a wedge shaped absorber in front of the sample. The formation of ice was controlled by x-ray diffraction patterns measured at least every 60 min during a Compton measurement run. The Compton scattering data was stored every 10 minutes and checked afterwards for consistency. During the analysis, the data was corrected for background scattering, relativistic cross section and absorption, before summing up, see [4] for details.

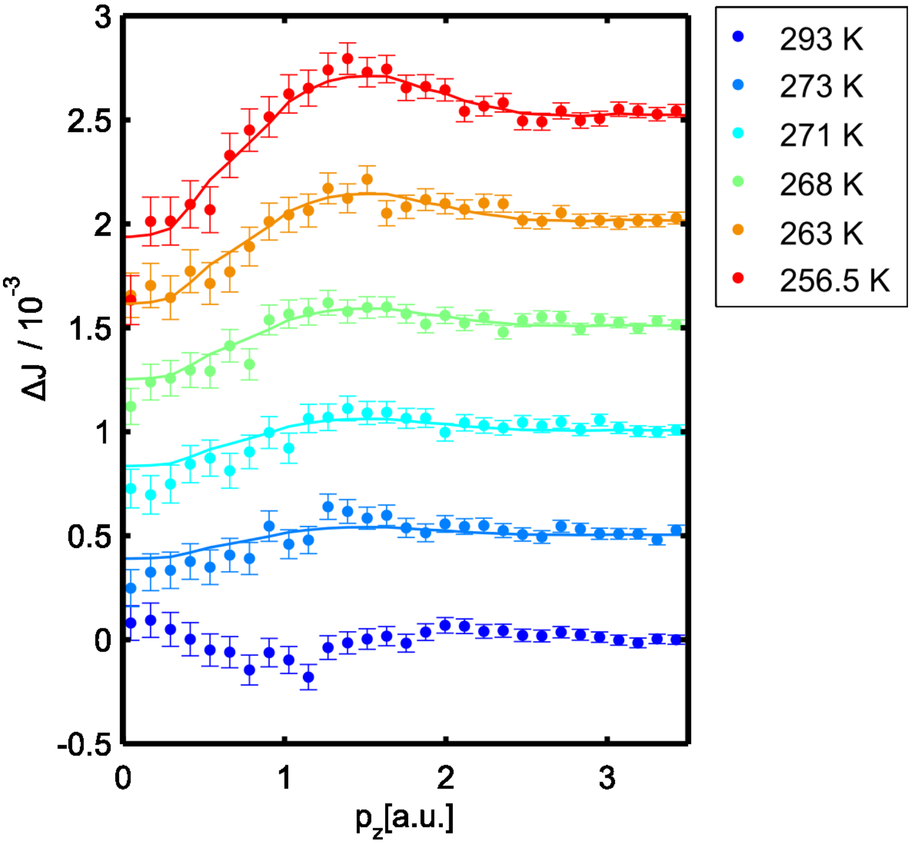

Figure 1: Compton profle difference with respect to the measurement at 277 K. The solid lines represent scalings of the difference to 256.5 K.

First Compton profile differences are shown in Fig. 1. Here, the profile measured at 277 K was chosen as reference and subtracted from the other ones as indicated in the legend. The differences for 293 K resemble the typical shape and amplitude corresponding to the temperature effect on the water hydrogen bond network [4]. Surprisingly, this changes dramatically upon supercooling, where the observed differences are much more pronounced than expected from the common temperature effect. This suggests a remarkable change of the water's bond network, already in the slightly supercooled state. The amplitude of the differences increases linearly. In a next step we will compare the experimental data to DFT calculation to obtain qualitative results such as bond length changes for the supercooled state and extract configurational energies to obtain information on thermodynamic changes upon supercooling [4].

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