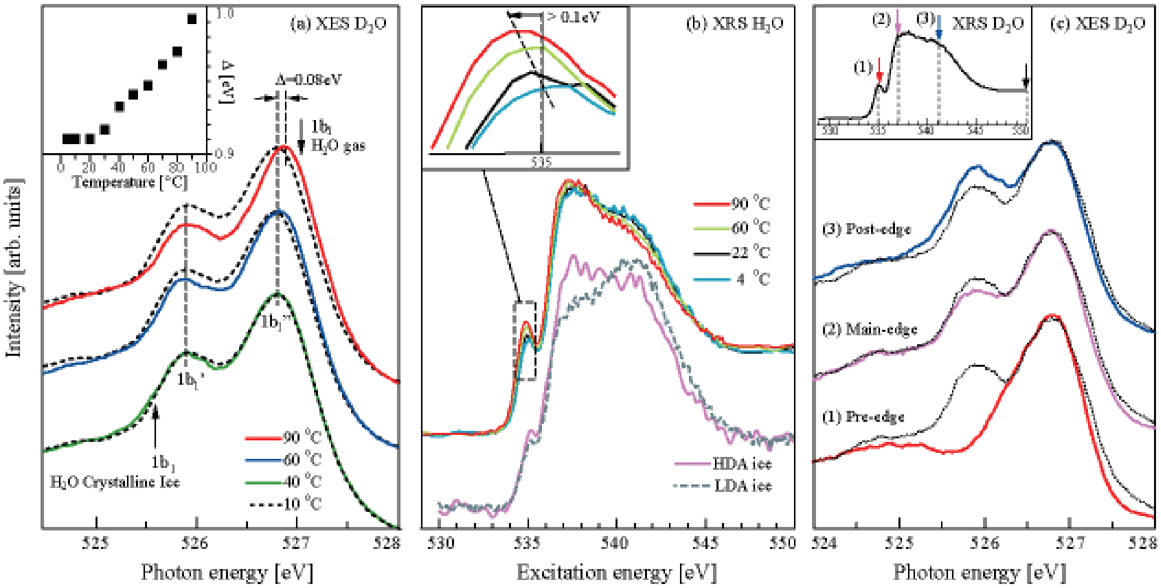
The Inhomogeneous Structure of Water at Ambient Conditions

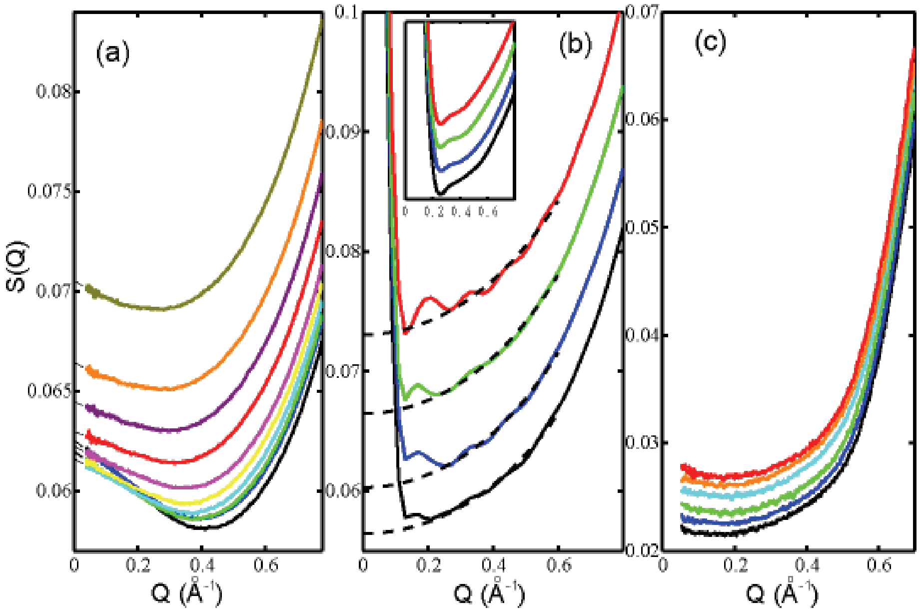
The water molecule, H_2O, has deceptively simple structure, but contains all the prerequisites for building complexity. The oxygen atom has a greater affinity for electrons and pulls them away from the hydrogens making them slightly positive. On the back side of molecule oxygen has a lone pair – electrons that do not assist in binding the hydrogens in the molecule, but to which the hydrogens of another water molecule can be attracted to form a so-called hydrogen bond (H-bond). Hydrogen bond is much weaker than the bonding inside water molecule, but it is still strong enough with the possibility to make from one up to four H-bonds per water molecule. The network connected by H-bonds between water molecules makes liquid water so special compared to other normal liquids with about 66 anomalies, e.g. density maximum at 4 °C and large heat capacity. The anomalies of water become extreme in the supercooled region (below freezing point), whilst they are also present at ambient conditions where most of waters' physical, chemical and biological processes of importance occur. Water at ambient conditions has traditionally been considered as a homogeneous distribution of near- tetrahedral H-bonded structures with thermal fluctuations increasing with temperature. This picture has been challenged by recent studies based on x-ray Raman (XRS), x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy (XES), suggesting two distinct local structures with tetrahedral as a minority and highly H-bond distorted asymmetrical as the majority. In particular, the proposed predominant asymmetrical structure has caused intense debate in the last years.

Figure 1a shows the temperature dependence in the lone pair $1b_1$ region of the XES spectra for D_2O. All spectra show a split of the lone pair into two peaks, denoted $1b_1$' and $1b_1$", where the former is close in energy position to the $1b_1$ in crystalline ice and the latter to $1b_1$ in water vapor. The two peaks can thereby be related to tetrahedral ($1b_1$') and H-bond distorted ($1b_1$") local structures with further support for this assignment given below. Figure 1b top part shows the temperature-dependent XRS spectra with energy resolution of 0.5 eV, which are denoted as pre-edge (535 eV), main-edge (537-538 eV) and post-edge (540-541



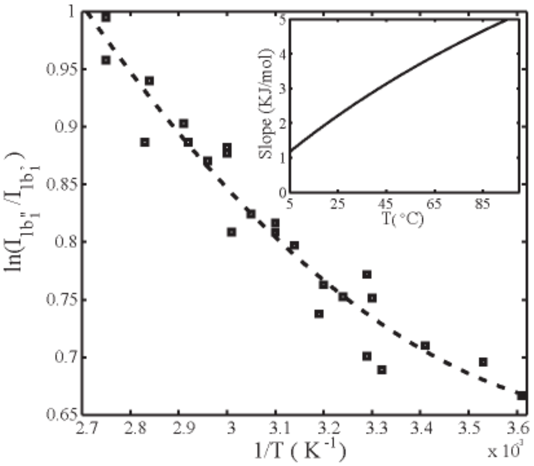
eV). Tuning the energy to the specific resonant features (pre-, main- and post-edge) in the absorption spectrum makes a connection between XRS and XES by selecting the corresponding structural species for XES. This is shown in Fig. 1c where resonant XES spectra are compared with non-resonant (550 eV) XES. We find that pre-edge excitation essentially eliminates the $1b_1'$ (tetrahedral) peak (red), excitation on the main edge gives a slight enhancement of the $1b_1''$ (distorted) (green), while excitation on the post-edge instead enhances the $1b_1'$ (tetrahedral) peak compared to the $1b_1''$ (blue). Since the absorption post-edge feature in ice is much stronger than in the liquid, the resonant XES (blue) is consistent with that the $1b_1'$ peak is related to tetrahedral-like species. The pre-edge peak in XRS has, on the other hand, been assigned to distorted H-bonding configuration. This assignment is consistent with the observed absence of the $1b_1'$ (tetrahedral) and the strong enhancement of the $1b_1''$ (distorted) peak when resonantly exciting on the pre-edge feature (red).

Small angle x-ray scattering (SAXS) give further sight into the length-scale on which the two distinct local structures are fluctuated. Figure 2a shows the normalized structure factor, $S(Q)$, derived from the SAXS intensity in ambient water at temperatures from 7 to 74 °C. All scattering curves show an enhancement approaching $Q = 0$ after experiencing a minimum around 0.4-0.5 Å^{-1}, which to first approximation directly indicates the presence of density heterogeneities. In particular, the enhancement becomes *smaller* with increasing temperature in strong contrast to expectation from simple thermal density fluctuations. In order to address if the enhancement at low *Q* can be related to and reproduced by thermal fluctuations in common water models, we have performed molecular dynamics (MD) simulations as shown in Figure 2b. The most important scattering enhancement observed at small *Q* in the experiment is completely missing from the SPC/E MD data even down to $Q = 0.13$ Å^{-1}. For comparison, Fig. 2c shows $S(Q)$ of CCl_4 measured at temperatures from 6 to 30 °C and regarded as representing a "normal" liquid. It is clear that SAXS of CCl_4 shows no temperature-dependent variation at low *Q*, which is observed, in contrast, in the ambient water.



We analyze the SAXS data within the framework of Ornstein-Zernicke (OZ) theory assuming the density fluctuations to result from the presence of either a spinodal or critical point. The resulting OZ correlation length is around 3.1 Å, slowly decreasing with increasing temperature. The zero-angle anomalous structure factor, on the other hand, is found to decrease more dramatically with temperature. We further analyze the density fluctuations in the SAXS data in terms of the picture indicated by XES and XRS, namely that, on the time-scale of x-ray scattering, the liquid can be viewed as tetrahedral patches surrounded by thermally excited H-bond distorted structures. Although we lack information on the time-scale of the fluctuations, the attosecond interaction time of the x-ray scattering process, compared to picoseconds for H-bond dynamics, allows considering the SAXS data as an instantaneous snapshot of the structure. Consequently, we infer a physical picture of the derived OZ correlation length ξ in terms of the radius of gyration, R_G. The relationship $R_G = \sqrt{3}\xi$ gives R_G decreasing from 5.6 at 7 °C to 5.1 Å at 74 °C. In order to get a sense of the physical dimensions of the tetrahedral patches we assume a spherical shape giving a diameter, *D*, of 14.5-13.2 Å.

In Fig. 3, we fitted the XES spectra at each temperature into two spectral components to obtain the intensity ratio $I_{1b1''}/I_{1b1'}$ between distorted and tetrahedral structures. We note that the data deviate from a straight line, i.e. an Arrhenius behavior, indicating that energy and entropy differences vary with temperature between the two local structures. Since the tetrahedral structure in both XES and XRS shows little spectral change with temperature we can assume that energy and entropy variation are mainly attributable to changes of the distorted structure. The shifting of $1b_1''$ position in XES (Fig. 1a) and the pre-edge in XRS (Fig. 1b) with temperature indicate an increase in entropy of the distorted component as it becomes thermally excited. All of these observations are consistent with that the tetrahedral structure is of lower energy - lower entropy and the distorted structure of higher energy - higher entropy.



In summary, we use SAXS to demonstrate the presence of density fluctuations in ambient water on a physical length-scale of around 1 nm. The length-scale is retained while the magnitude of fluctuations is enhanced in ambient water with decreasing temperature. In contrast, the magnitude of fluctuations in a normal liquid of CCl_4 exhibits little temperature-dependence. Based on XES and XRS data we propose that the density difference contrast in SAXS is due to fluctuations between tetrahedral-like and H-bond distorted structures related respectively to low and high density water. We combine our experimental observations to propose a model of water as a temperature-dependent, fluctuating equilibrium between the two types of local structures driven by incommensurate requirements for minimizing enthalpy (strong near-tetrahedral hydrogen-bonds) and maximizing entropy (non-directional H-bonds and disorder). The present results provide experimental evidence that the extreme differences anticipated in the H-bonding environments in the deeply supercooled regime surprisingly remain in bulk water even at conditions ranging from ambient up to close to the boiling point.

Primary Citation

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