

## Inhomogeneity of Liquid Water - Two Structural Motifs

Liquid water shows many anomalies in its thermodynamic properties, such as compressibility, density variation and heat capacity. In the low-temperature regime, below the freezing point, these properties deviate strongly from normal. Hence, theories related to a liquid-liquid phase transition between high- and low-density water have been proposed to account for these anomalies.

Recently, we have obtained interesting results in X-ray emission spectroscopy (XES) for liquid water using an X-ray emission spectrometer and the liquid flow cell developed at beamline BL17SU [1]. In principle, X-ray emission spectra reflect valence electronic states; thus, the three molecular orbitals  $1b_2$ ,  $3a_1$  and  $1b_1$  are expected to appear in the spectra. The spectra of gas phase water and crystalline ice show a simple three-peak structure that comes from these three valence molecular orbitals. However, X-ray emission spectra of liquid water show two sharp splitting peaks ( $1b_1'$  and  $1b_1''$ ) in the  $1b_1$  region, and these two sharp peaks show clear dependences on phase (gas, liquid, and solid) and temperature. The XES spectra of water in three phases and the temperature dependence of liquid water lead us to interpret the two peaks as representing tetrahedral ice-like and hydrogen-bond distorted structural motifs in liquid water. The existence of two distinct lone-pair peaks provides evidence against an unstructured continuum model of the liquid but is easily explained within a two-component mixture model.

To demonstrate the presence of density fluctuations due to two structural motifs in ambient water, small-angle X-ray scattering (SAXS) was conducted at SSRL [2]. Scattering techniques such as SAXS and small-angle neutron scattering (SANS),

provide us the most direct information about density variations or fluctuations in a liquid. Figure 1 shows the normalized structure factor  $S(Q)$  derived from the SAXS intensity in ambient water ( $H_2O$ ) as a function of  $Q$  for various temperatures. Different from a normal liquid, like  $CCl_4$ , all scattering curves of water show an enhancement approaching  $Q = 0$  after experiencing a minimum at around  $0.4-0.5 \text{ \AA}^{-1}$ . Although a similar enhancement is reported for water in a supercooled region [3] as a proof of density inhomogeneity, the SAXS results indicate the existence of inhomogeneity at around room temperature.

For a further study of thermal properties of two structures, the temperature dependence of XES spectra for liquid heavy water was measured at SPring-8. Figure 2 shows XES spectra of liquid heavy water at various temperatures. The  $1b_1$  peak of the tetrahedral ice-like component ( $1b_1'$ ) is relatively insensitive to temperature, whereas that of the hydrogen-bond distorted component ( $1b_1''$ ) continuously changes its energy as it becomes thermally excited and expands. The SAXS profile at higher temperatures, which shows small enhancement approaching  $Q=0$ , indicates that the density contrast between the high- and low-density components is smaller at higher temperatures. According to thermal properties of the tetrahedral ice-like and hydrogen-bond distorted structures deduced from the XES results, we can conclude that the density of the high-density (hydrogen-bond distorted) component decreases and approaches that of the low-density (tetrahedral) component when the water temperature increases.

Combined with the experimental results of SAXS

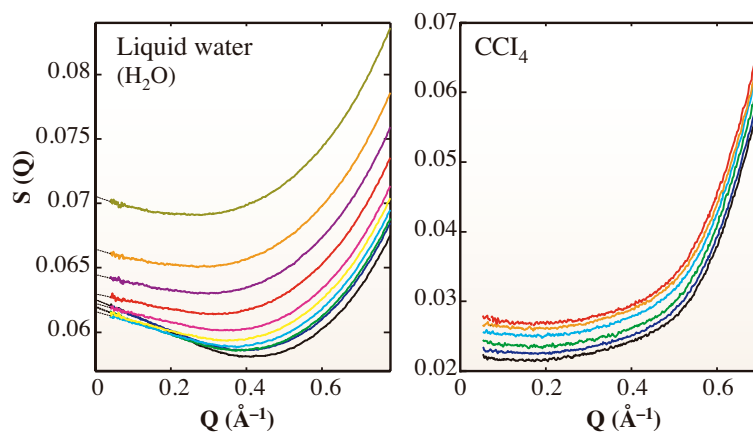


Fig. 1. Experimental structure factor  $S(Q)$  derived from scattering intensity for ambient water and  $CCl_4$  liquid as a function of scattering momentum transfer  $Q$ . For liquid water, the curves, from bottom to top, correspond to the temperatures 7, 11, 16, 20, 25, 29, 38, 47, 56, and 74°C. For liquid  $CCl_4$ , the curves, from bottom to top, correspond to the temperatures 6, 11, 16, 21, 25, and 30°C.

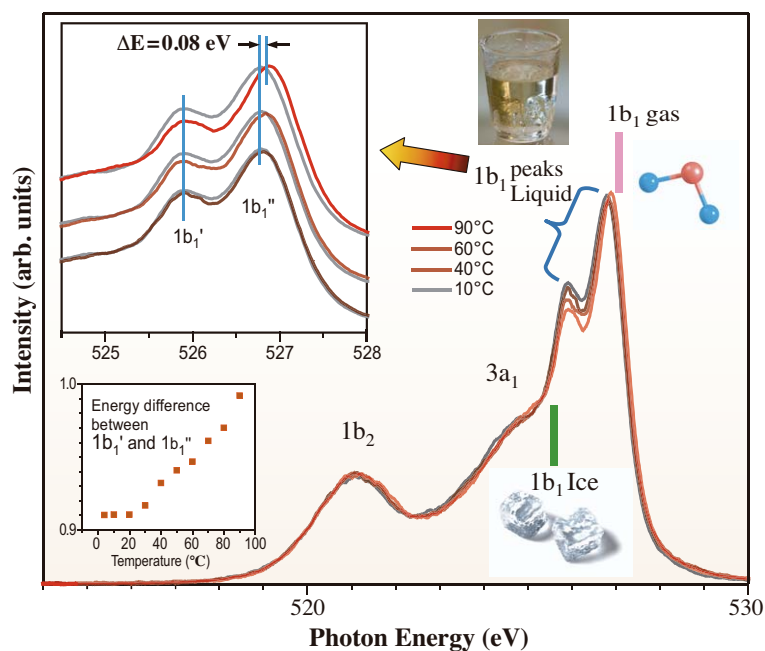


Fig. 2. O  $1s$  X-ray emission spectra of liquid heavy water ( $D_2O$ ) at different temperatures. The excitation energy is 550 eV, which is well above the ionization threshold. Peak components are labeled on the basis of the molecular orbitals of water molecule. The  $1b_1$  peaks of the gas phase and the crystalline ice are indicated by red and green vertical lines, respectively.

and XES, we propose that the contrast of density difference in SAXS is due to fluctuations between tetrahedral ice-like and hydrogen-bond distorted structures related to, low- and high-density water,

respectively. Figure 3 shows an illustration based on the results of our present studies, which indicates the presence of density fluctuations in ambient water on a physical length scale of around 1 nm.

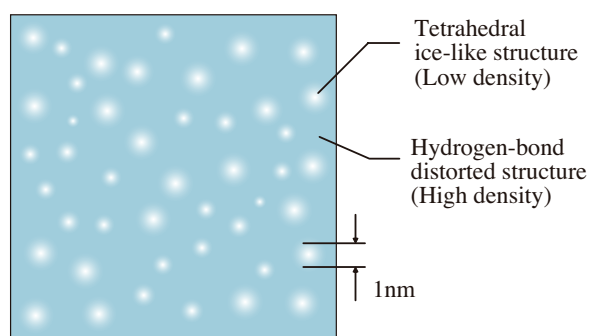


Fig. 3. Illustration of inhomogeneity of water based on results obtained using X-ray emission spectra, X-ray Raman scattering, and small-angle X-ray scattering. The different microstructures in water are shown in color. The structure is actually three-dimensional, but it is two-dimensionally drawn for simplicity.

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