

Liquid Structure of Water: Observation of Two Structural Motifs

One intriguing question about water, under debate for the last 100 years, is whether liquid water is a continuum of different hydrogen bonding configurations, or could instead consist of a mixture of relatively well-defined species. This debate was initiated in 1892 when Röntgen proposed that water contains a mixture of two components, one ice-like and one unknown [1]. The traditional view of water as a continuum of distorted hydrogen bonds around near-tetrahedral local structure goes back to the work of Bernal and Fowler [2], who in 1933 successfully analyzed the early X-ray diffraction data on water in terms of a disordered quartz-like structure. This picture has been widely used in X-ray and neutron diffraction studies, infrared (IR) and Raman spectroscopy. However, mixture models are also utilized in some cases. For example, in 2004, an X-ray absorption spectroscopy (XAS) study has proposed the existence of two different species with the dominant one related to structures with highly distorted hydrogen bonds and the other more ice-like [3].

Here, we introduce our recent X-ray emission study on the liquid structure of water performed at beamline **BL17SU** [4] (see Fig. 1 for experimental setup). Water can occur in three states: solid (ice), liquid, or gas (water vapor), i.e., three forms of water. The difference between liquid and gas phase water is hydrogen bonding. While gas phase water is an isolated molecule without hydrogen bonding, liquid water has hydrogen bonding that connects molecules. The crystalline ice is where the fraction of hydrogen-bonded molecules reaches the limit; every water molecule is hydrogen bonded with up to four other molecules, i.e., fourfold hydrogen bonded structures. X-ray emission spectroscopy (XES) is used to directly probe the occupied electronic states through radiant decay of a valence electron to fill a vacancy in a core level. Although the valence electrons are delocalized in a condensed phase, the involvement of the core level makes XES a very local spectroscopy with atom-specific sensitivity. The O1s core-hole lifetime is of the order of 3-4 femtoseconds. This time scale is much shorter than any rearrangements of the hydrogen bonding network, and XES thus provides an instantaneous sampling of frozen configurations. Let us take a look the XES spectra of water in three states. Figure 2 shows the XES spectra of liquid water at various temperatures, ice and gas phase water. Spectra of gas phase water and crystalline ice show a simple three peak structure that is attributable to valence molecular orbitals of the water molecule

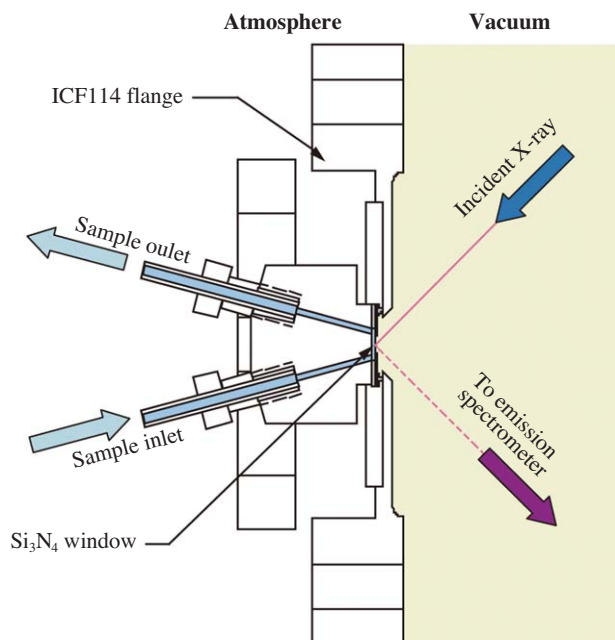


Fig. 1. Schematic of the experimental setup. The liquid flow cell and its internal flow channel are shown in cross-sectional drawings. Samples at ambient condition were fed through a tube connected to the inlet port, passing the surface of the window and then drained from the outlet port using an aspiration pump. A 150-nm-thick Au-coated Si_3N_4 window was used to separate the liquid flow from the high vacuum and to transmit the incoming and outgoing soft X-rays.

(see Fig. 3). The gas phase is at the highest emission energy (527 eV), the crystalline ice at the lowest (525.7 eV), while the liquid peaks are in between. An interesting thing is that in the spectra of liquid water, there are two sharp peaks ($1b_{1'}$ and $1b_{1''}$) in the region of $1b_1$ state. There are also energy shifts in the relative energy positions for different temperatures.

What is the assignment of the two $1b_1$ peaks of liquid water? The answer is found in the measured spectra. As is commonly accepted, the fraction of hydrogen bonded molecules decreases with increasing temperature, while the number of distorted or broken hydrogen bonds increases. The higher energy $1b_{1''}$ peak increases with temperature relative to the $1b_{1'}$ peak, and we can assign the $1b_{1'}$ and $1b_{1''}$ peaks as due to fourfold and less than fourfold hydrogen-bonded structures in the liquid, respectively. The assignment of the $1b_{1'}$ peak as due to a structures in the liquid with ice-like coordination is consistent with the coinciding peak location of the $1b_{1'}$ peak of the liquid (525.9 eV) and the sharp low-energy $1b_1$ peak of crystalline ice at 525.7 eV. The position of the liquid $1b_{1''}$ peak is much closer in energy to the

gas phase value, which is also consistent with the interpretation of liquid water as a distribution of structures where the hydrogen bonds are significantly weakened or distorted.

The XES spectra of water in three states and the temperature dependence of liquid water leads us to interpret the two peaks as representing tetrahedral-like and highly distorted structural motifs. The existence in the experiment 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.

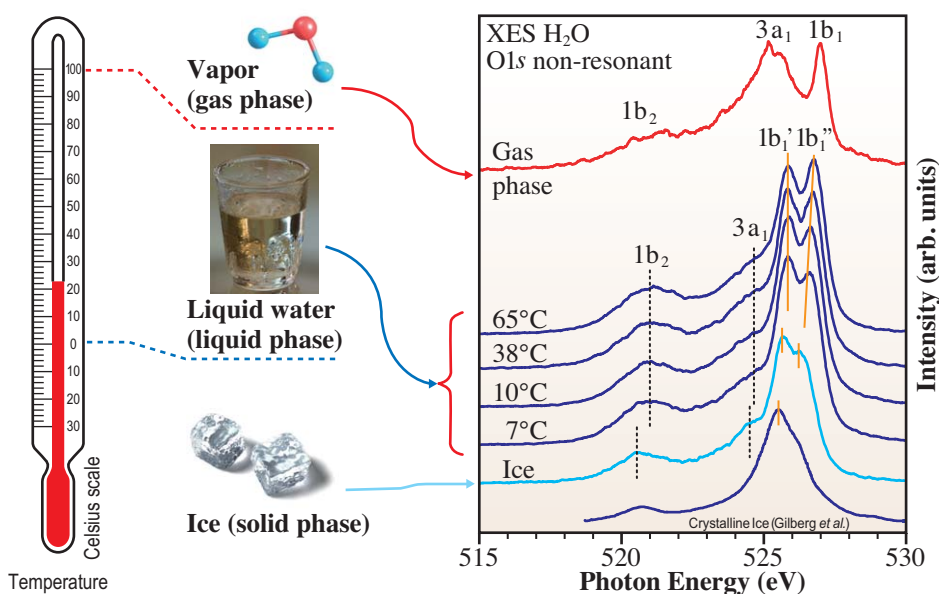


Fig.2. O 1s soft X-ray emission spectra of gas phase water, liquid water at different temperatures and amorphous and crystalline ice. The excitation energy is 550 eV, well above the ionization threshold. Peak components are labeled on the basis of the molecular orbitals for a water molecule. The XES spectra of ice (amorphous) and crystalline ice from Gilberg *et al.* [5] are included for comparison. In a previous study by Gilberg *et al.*, both crystalline and amorphous or polycrystalline ice were studied using high resolution XES, where the spectrum of the amorphous ice is rather similar to that in the current study. The energy scale of the spectrum of crystalline ice is adjusted on the basis of the very similar amorphous ice spectra.

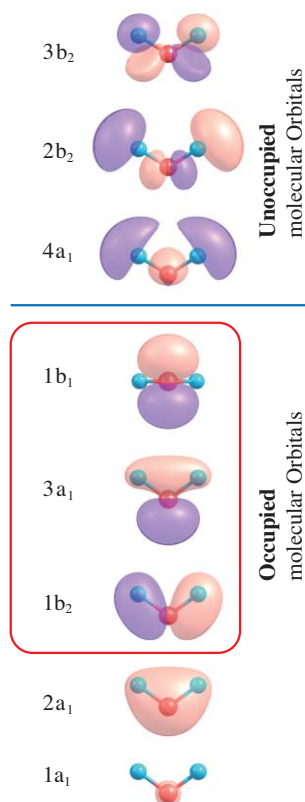


Fig. 3. Schematic of the five occupied and the lowest three unoccupied molecular orbitals of the isolated molecule. In principle, three occupied states indicated by a red box were observed by XES.

T. Tokushima^{a,*}, Y. Harada^{a,†} and S. Shin^{a,b}

^a SPring-8/RIKEN

^b Institute for Solid State Physics (ISSP),
The University of Tokyo

*E-mail: toku@spring8.or.jp

† Present address: Department of Applied Chemistry,
The University of Tokyo

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