

## Inhomogeneity of liquid water revealed by resonant soft X-ray vibrational spectroscopy

The unique properties of water, e.g., high boiling and melting points compared to molecules like non-metal hydrides and its reduced density of the solid form are explained by the attractive force between water molecules called hydrogen bonds. There are many proposed local structural models that describe a water network. Among them two are well known: the continuum model and the mixture (micro-heterogeneity) model. In the former, hydrogen bonds in water are distorted, broken, and reformed continuously, but water itself is composed of a single component, whereas in the latter, the network is considered as a mixture of various hydrogen bond configurations. However, which model better describes the hydrogen bonding property of liquid water is controversial.

X-ray or neutron diffraction is one of the best methods to reveal local structural information of liquid water. When combined with recent highly brilliant synchrotron sources, not only the distance between the nearest neighbors but also those distances several water molecules apart can be discussed by diffraction techniques [1]. However, these methods collect signals mostly from scattering of an X-ray by a core electron or of a neutron by atomic nucleus, and thus indirectly reflect information about hydrogen bonds. Consequently, X-ray spectroscopies have attracted much attention in this decade as alternatives to diffractions since they provide direct information about hydrogen bonds through observations of the valence electronic structure.

One of the most famous works was performed by Wernet *et al.* in 2004 [2]. They focused on the O 1s X-ray absorption (XAS) profile of water in the gaseous, liquid, and solid phases (Fig. 1 [3]). They concluded that the XAS pre-edge peak represents a hydrogen bond breaking and the number of hydrogen bonds in liquid water is much less than generally considered. Their interpretation has been challenged by many experimental and theoretical works. In particular, the presence of the XAS pre-edge peak has been interpreted not as the hydrogen bond breaking but distortions that leave the hydrogen bond intact. The interpretation of the XAS pre-edge peak is quite important since the hydrogen-bond-broken and hydrogen-bond-intact pictures lead to the mixture (micro-heterogeneity) and the continuum models of liquid water, respectively.

To clarify the origin of the XAS pre-edge, we applied resonant soft X-ray vibrational spectroscopy, which leaves only vibrational excitations in the soft X-ray Raman process (Fig. 2). The resonant excitation of the core electron to a specific unoccupied state

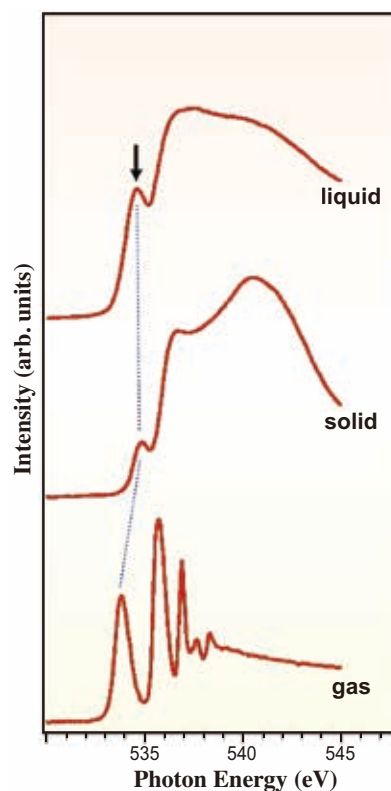


Fig. 1. O 1s X-ray absorption profile of water in the liquid, solid, and gas phases. Arrow in the XAS spectrum of liquid water indicates the pre-edge structure.

should relate the observed energies without electronic excitation to the vibrational excitations of a water molecule in a particular hydrogen bond configuration. The experiments were carried out using high resolution X-ray emission spectrometers at University-of-Tokyo Synchrotron Radiation Outstation beamline **BL07LSU** and RIKEN Coherent Soft X-ray Spectroscopy beamline **BL17SU**.

Figure 3(a) shows the vibrational excitations through O 1s resonant excitation to the XAS pre-edge of liquid H<sub>2</sub>O and D<sub>2</sub>O water [4]. The high resolution ( $E/\Delta E > 2000$ ) reveals isolated multiple peak structures. The energy separation of the corresponding peaks in H<sub>2</sub>O from the elastic line is  $\sqrt{2}$  times larger than those in D<sub>2</sub>O, reflecting an isotope effect on the OH stretching energy. Owing to the strong dissociation potential in the presence of an excited electron in the antibonding state, which is localized on one OH (OD) lobe, multiple peak structures extend over the energy window between the valence band maximum around 527 eV and the

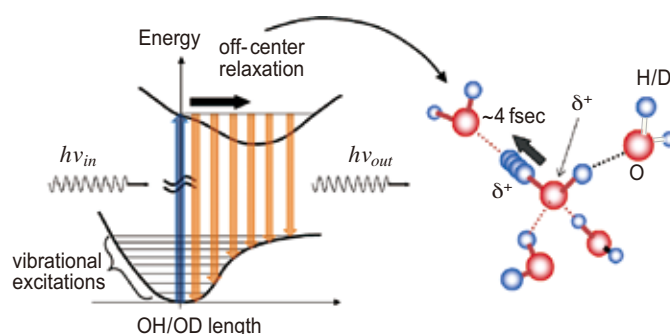


Fig. 2. Schematic of the soft X-ray Raman process that leaves vibrational excitations. In the core excited state, ultrafast dissociation occurs within the lifetime of the core hole ( $\sim 4$  fs) due to the presence of core excited electron in the antibonding orbital on one of the OH (OD) lobes, which facilitates elongation of the OH (OD) bond as illustrated in the right panel.

elastic line at 535 eV. The energy separation of the neighboring peaks, which decreases at higher order vibrational excitations (Fig. 3(b)), can be explained by a Morse function.

What should be noted here is the absolute value of the first vibrational energy. In both  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ , the value is very close to the OH (OD) stretching vibrational energy of an isolated water molecule estimated from

the optical Raman experiment ( $\text{H}_2\text{O}$ : 0.45–0.46 eV,  $\text{D}_2\text{O}$ : 0.33–0.34 eV), but it is slightly ( $\sim 30$  meV) higher than the centroid of the OH(OD) stretch band of liquid water ( $\text{H}_2\text{O}$ : 0.42 eV,  $\text{D}_2\text{O}$ : 0.31 eV), as shown in Fig. 3(b). This is clear evidence that the XAS pre-edge peak mainly originates from a water molecule in a broken hydrogen bond configuration, and thus supports the mixture (micro-heterogeneity) model of liquid water. This is also in accordance with the interpretation of our previous X-ray emission results on liquid water reported since 2008 [5].

As demonstrated in this study, core spectroscopy of liquid water is now connected to vibrational Raman spectroscopy, and can clarify the hydration structure, the role of water in various chemical and catalytic reactions, and hydrogen bonds in biological organisms.

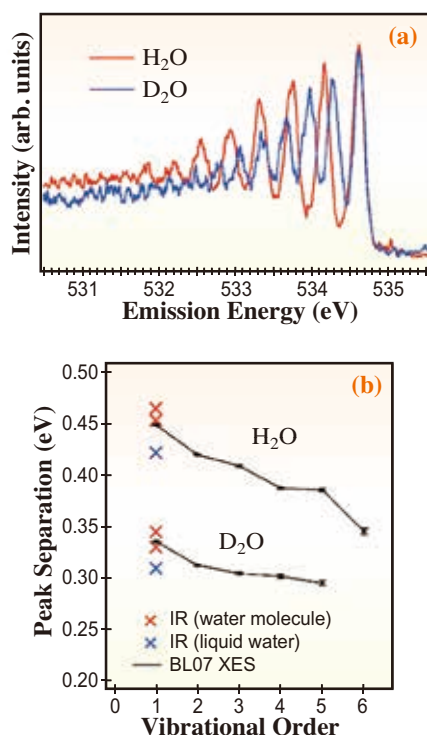


Fig. 3. (a) Comparison of multiple vibrational excitation spectra between  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . (b) Energy separation of each neighboring peak in the resonant soft X-ray vibrational spectrum of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . Red and blue crosses denote the OH stretching energy estimated from Raman spectra of gaseous and liquid water, respectively.

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