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KEYNOTE

Electronic and Vibrational Structure of Liquid Water Probed by Soft X-ray Resonant Inelastic Scattering

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Abstract. X-ray and neutron diffraction techniques have long been used as a direct probe of the hydrogen bond network of liquid water, while in this decade X-ray spectroscopic techniques have been widely used with the development of high brilliance synchrotron radiation sources. X-ray absorption (XAS) and emission (XES) spectra of liquid water are one of the cutting-edge approaches to determine the local hydrogen bond network of liquid water through observation of its local valence electronic structure. From ice to liquid water there exists a substantial decrease of a peak in the post edge of XAS, which has been assigned as tetrahedrally coordinated water. Meanwhile in X-ray emission spectrum of water, two distinct lone pair peaks were observed and they have been assigned as two distinct local structures of water. Here we show ultrahigh resolution O 1s X-ray emission spectra of H_2O and D_2O water across O 1s XAS resonances. In addition to the valence electronic structure, we observed multiple low-energy loss features below the elastic scattering line, which have commonly been interpreted as vibrational excitations due to core hole induced dynamics. The connection between the vibrational energy and the valence electronic structures, how they are related to the debated interpretation of the hydrogen bond network of liquid water are the main topics of this paper.

1. Introduction

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 and post-edge peaks represent hydrogen bond breaking and making, respectively, 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 and post-edge, we applied resonant soft X-ray inelastic scattering (RIXS). Fig. 2 shows schematic of the RIXS process, where the incident soft X-ray excites a core electron to an unoccupied state, and another soft X-ray emits in the subsequent decay of the core hole. When the valence electron decays back to the core hole (Fig. 2(a)), RIXS will represent occupied valence electronic structures of water in various hydrogen bond configurations. On the other hand, when the excited electron decays back to the core hole (Fig. 2(b)), no electronic excitation is left in the final state but other excitations such as vibrational excitations occur in the RIXS process, which we call vibrational RIXS. The resonant excitation of the core electron to a specific unoccupied state should select a water molecule in a particular hydrogen bond configuration. Then using RIXS we will be able to observe the valence electronic structure and vibrational excitation of a water molecule in a particular hydrogen bond configuration. This will help understand the connection between the profile of the RIXS spectra and hydrogen-bond configurations through vibrational spectra.

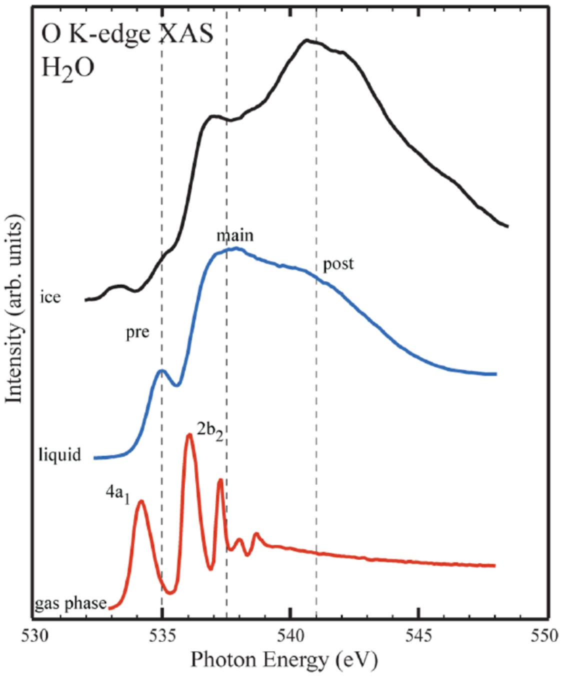

Fig. 1 O 1s X-ray absorption spectra of gaseous, liquid and ice forms of water

2. Experimental

O1s XAS and RIXS experiments of water were performed at the SPring-8 synchrotron radiation facility using high resolution X-ray emission spectrometers at University-of-Tokyo Synchrotron Radiation Outstation beamline BL07LSU[4] and RIKEN Coherent Soft X-ray Spectroscopy beamline BL17SU[5] with a grazing incidence flat field spectrometer in slit-less configuration. 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. The total energy resolution for the XAS and XES measurements was 0.1 and 0.15 eV at BL07LSU and 0.15 and 0.35 eV at BL17SU, respectively. The pure water sample was supplied by a water purifier system by Millipore Co. Ltd., carefully degassed and fed through a tube connected to the inlet port, passing the surface of the Si_3N_4 membrane window and then drained from the

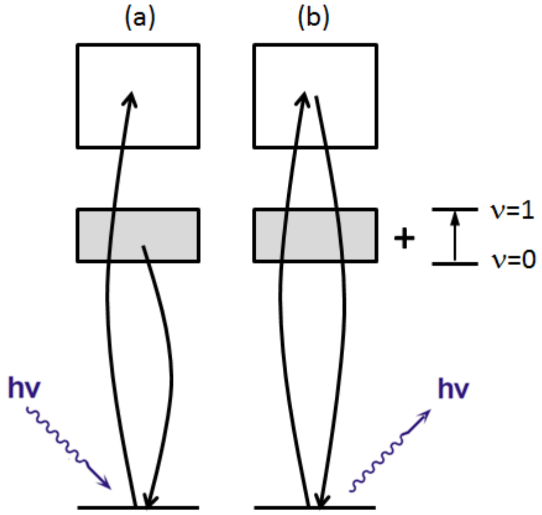

Fig. 2 Schematic of the RIXS process
(a) Valence emission (b) vibrational excitation

outlet port by an aspiration pump. The inner volume of the cell is about 0.06 ml and the sample volume flow rate was typically around 10 ml/min, thus the sample in the cell was exchanged 166 times/min. The linear sample flow rate in the liquid cell was around 20 mm/s which corresponds to a residence time of 0.5 ms taking the X-ray beam size of 10 μm into account. The RIXS energy was calibrated by using the elastic scattering peaks at the corresponding excitation energy.

3. Results and discussion

3.1 Hydrogen-bond configuration selective valence electronic structure of liquid water

Figure 3 shows a series of resonantly excited O 1s RIXS spectra of H_2O (upper) and D_2O (lower) liquid water at selected excitation energies in the XAS spectrum as indicated above the liquid water spectrum in Fig. 1. At nonresonant excitation (550 eV), all the water molecules in various hydrogen bond configurations contribute to the RIXS spectrum. Two sharp peaks in the $1b_1$ region is not expected for the continuum model but rather support the mixture (microheterogeneous) model of liquid water. With decreasing excitation energy, the two RIXS peaks in the $1b_1$ region change relative intensities for main- and pre-edge excitation and also shift closer together for pre-edge excitation. This can be interpreted as follows; the higher $1b_1$ component ($1b_1$" hereafter) represents a broken or highly distorted hydrogen bond configuration. This peak shifts toward lower energy with decreasing excitation energy because the excited electron is trapped in a localized state (XAS pre-edge) [6] and thus the RIXS process behaves fully Raman scattering-like, linearly shifting the emission energy with the excitation energy. On the other hand, the lower $1b_1$ component ($1b_1$' hereafter) represents tetrahedrally coordinated hydrogen bond configuration. In this configuration the excited electron is delocalized through the strong hydrogen bond network and thus the RIXS process behaves fluorescence-like, keeping the emission energy constant irrespective of the excitation energy. Thus we can explain why the two $1b_1$ peaks shift closer together for pre-edge excitation and strongly support the mixture model of liquid water.

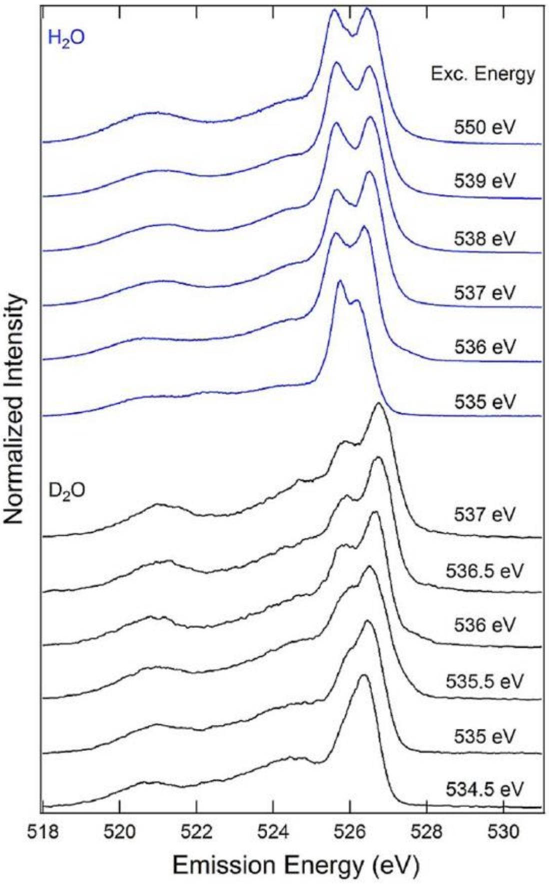

Fig. 3 Selectively excited XES (RIXS) spectra of liquid H_2O and D_2O at various incoming photon energies. [8]

3.2 Hydrogen-bond configuration selective vibrational structure of liquid water

Figure 4 shows vibrational excitations through O 1s resonant excitation to the XAS pre-edge of liquid H_2O and D_2O water [7]. The high resolution ($E/\Delta E > 2000$) reveals isolated multiple peak structures. The energy separation of the corresponding peaks in H_2O from the elastic line is $\sqrt{2}$ times larger than those in D_2O, 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 elastic line at 535 eV. The energy separation of the neighboring peaks, which decreases at higher order vibrational excitations, can be explained by a Morse function.

What should be noted here is the absolute value of the first vibrational energy. In both H_2O and D_2O, the value is very close to the OH (OD) stretching vibrational energy of an isolated water molecule estimated from the optical Raman experiment (H_2O:0.45-0.46 eV, D_2O: 0.33-0.34 eV), but it is slightly (~30 meV) higher than the centroid of the OH(OD) stretch band of liquid water (H_2O:0.42 eV, D_2O:0.31 eV). 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 (microheterogeneous) model of liquid water. This is also in accordance with the interpretation of our valence RIXS results on liquid water [8].

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.

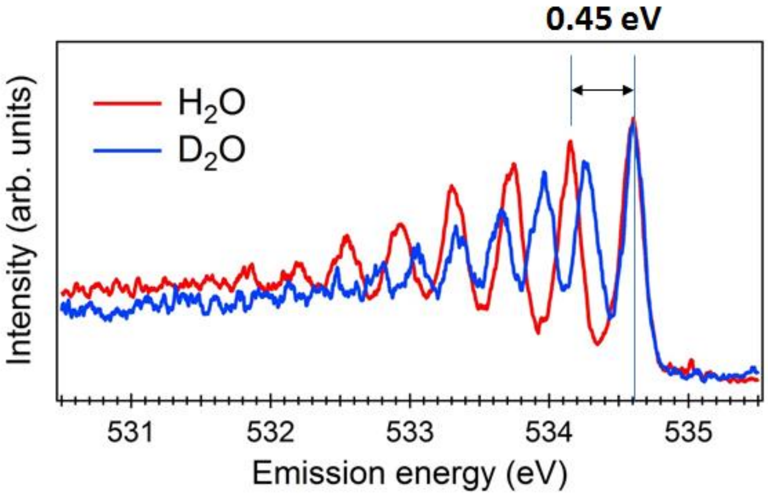

Fig. 4 Vibrational RIXS spectra of liquid H_2O and D_2O water[7].

4. Conclusion

X-ray spectroscopic tools combined with brilliant synchrotron radiation are quite useful to directly probe the local hydrogen bond network of liquid water. Both O 1s valence emission and vibrational excitations of liquid water support the mixture (inhomogeneous) model, i.e. tetrahedrally coordinated water in a sea of highly distorted or broken hydrogen bond configuration.

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