

Electronic and vibrational structure in liquid water probed by soft X-ray resonant inelastic scattering and modeling

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Summary: Recent high-resolution soft X-ray resonant inelastic X-ray scattering technique enables us to distinguish valence electronic structure of water molecules having different hydrogen-bond configurations in the liquid phase. Moreover, in the elastic region, well-separated multiple vibrational structures appear, which corresponds to the internal OH stretch vibration in the ground state. Both the valence band profile and the vibrational energy of OH stretch in the $\nu = 1$ state varies with the excitation energy. Connecting the vibrational energy to the conventional Raman spectroscopy, this indicates that water molecules with a particular hydrogen bond configuration can selectively be excited by tuning the excitation energy. Recent state-of-the-art simulation has successfully reproduced the valence band spectra and strongly supported a heterogeneous picture of liquid water with fluctuating patches of high and low density hydrogen bond configurations.

Introduction: 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 [1]. 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 [2].

Here we show ultrahigh resolution O 1s X-ray emission spectra of H₂O water across O 1s XAS resonances. In addition to the well debated 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 [3]. 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, and what is the origin of the previously-unexpected local structure with fluctuating patches of high and low density hydrogen bond configurations, are the main topics of this presentation.

Methods: H₂O water obtained from a water purifier (Millipore Simpli-Lab UV) were used for the experiment. O 1s XAS and XES experiments of water were performed using high resolution soft x-ray emission spectrometers at BL07LSU [4] of SPring-8. XAS measurements were performed in a partial fluorescence yield mode using a silicon drift detector (SDD). The total energy resolution for O 1s XAS was around 0.15 eV while for O 1s XES the resolution was 0.16 eV.

Results and Discussion: Figure 1 shows energy comparison of the $\nu = 1$ vibrational state in the RIXS spectrum at pre-edge resonance with the OH stretching mode of liquid H₂O water in the Raman spectrum. The RIXS spectrum is blue shifted because water molecules with a highly weakened or broken donating hydrogen bond are selected by the pre-edge excitation [5].

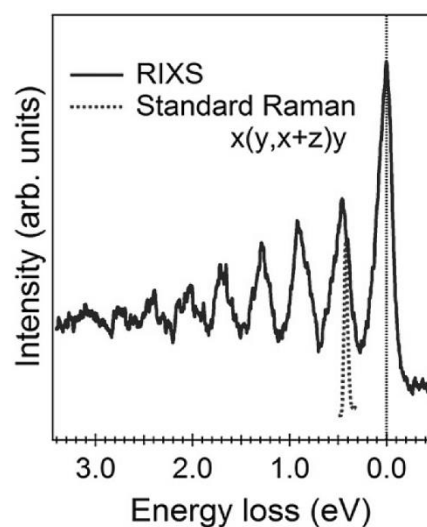


Figure 1. Multiple vibrational structure in the O 1s RIXS at pre-edge excitation of liquid H₂O water compared with a standard Raman spectrum (dotted curve) in the same experimental configuration [5].

The peak position of the $\nu = 1$ vibrational state is extracted in terms of OH stretch energy loss and plotted in Fig. 2 as a function of excitation energy. Here also the XAS spectrum of liquid water [6] is shown as well in order to correlate the excitation energies with the various XAS resonances. The various OH stretch frequencies can be directly compared to the various parts of the visible Raman spectrum shown vertically on the right hand side of Fig. 2. The Raman spectrum has three clearly visible spectral features with the main broad structure at around 3400 cm^{-1} , a

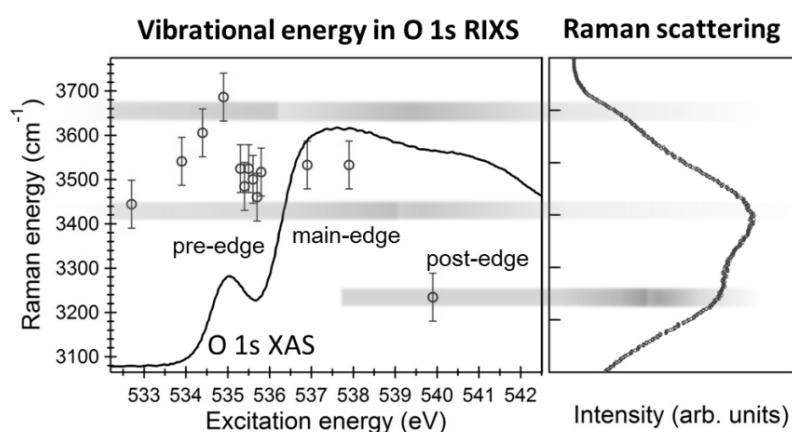


Figure 2. Comparison between (a) vibrational energy in O 1s RIXS and (b) Raman scattering in the OH stretching region for liquid H_2O water.

2nd almost as intense broad structure at 3220 cm^{-1} and a weak shoulder at 3630 cm^{-1} [7]. These features have been fitted by many different sub-peaks [7-9] but here we only consider the observable spectral structures. In Fig. 2 we observe that when the X-ray excitation energy is below the XAS spectrum the obtained vibrational frequency is reflected to be close to the main Raman peak at 3400 cm^{-1} . This can be understood since far below the XAS threshold there is no selective excitation and thereby all configurations are probed and the resolution in the XES measurements is not sufficient to resolve the fine structure leading to that we mainly detect the strongest peak in the green region. However, when the excitation energy is increased into the pre-edge region the vibrational frequency becomes high related to the blue region [5, 10]. Whereas increasing further into the main-edge energy of the XAS spectrum the frequency becomes close to the Raman main peak. Interestingly when the excitation energy is much higher in the middle of the broad post-edge XAS resonance the frequency are shifted to lower energy and coincides with the 2nd strongest feature. Here we observe that indeed the electronic selectivity in the resonant XES process selects the various sub-ensembles of local structures through the XAS process. This directly infers that we can view that there are essentially a heterogeneous distribution of local frequencies in the OH stretch region.

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