

X-ray Raman Scattering of Water near the Supercritical Point

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Water above the supercritical point ($T=647\text{K}$, $P=22.1\text{MPa}$, and density= 0.32g/cm^3 , see Fig.1) is in a unique state and plays an important role in a variety of processes ranging from the origin of life, treatment of hazardous wastes, to noncatalytic chemical reactions (Akiya and Savage, Chem. Rev. 2002). To explain its properties, it is of great importance to elucidate its electronic and bonding structure near the supercritical state. As we demonstrated recently (Cai et al, PRL 2005), high-resolution inelastic hard x-ray Raman scattering offers a particularly powerful probe for systems under extreme environment such as high pressure and temperature. We have therefore proposed to use XRS to investigate the electronic and bonding structure of water as it approaches the supercritical point (Fig.1). The spectral variation is expected to reveal rich information on the change of covalent, hydrogen, and ionic bonding of the H_2O framework that is important to the understanding of the unique properties of supercritical water.

In this report, we present the oxygen K -edge spectra of water near to the liquid-gas critical point ($T_c = 647.096\text{ K}$, $P_c = 22.064\text{ MPa}$, $\rho_c = 0.322\text{ gcm}^{-3}$), using XRS. Spectra with good S/N ratio obtained under various P-T conditions near the supercritical point are shown in Fig. 2 with background subtracted. We measured from liquid to gas at densities of $\rho = 1.02 - 0.16\text{ gcm}^{-3}$ ($= 3.2 - 0.5\rho_c$), measuring along both an isotherm (Fig1. b, c, d, e, f) and an isochore (Fig1. g, h, d) that pass near to the critical point. Measuring along both an isotherm (Fig.2.(A)) and an isochore (Fig.2.(B)) that pass near to the critical point. As can be seen in Fig.2(A), the strong density dependence of the spectral line-shape, especially the pre-edge intensity, was observed. In particular, the intensity in the pre-edge ($\sim 535\text{eV}$) and main-edge region ($\sim 537\text{eV}$) is assigned to water molecules with a broken or distorted HB on the donor side, whereas the post edge feature ($\sim 541\text{eV}$) has been identified with molecules having four strong and highly symmetric HB or large degree of HB. This results agrees with the tendency from ambient liquid [2] to rarefied gas [3]. Detailed analysis of the data concerning about near the critical point is in progress.

References

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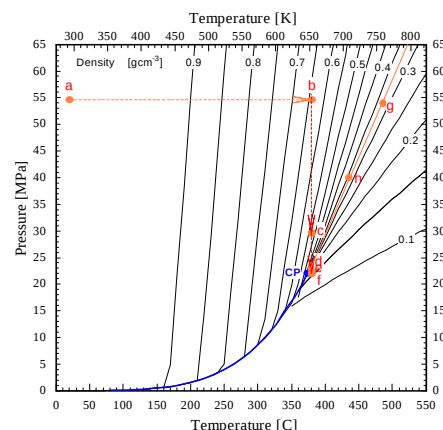


Figure 1. Isochores of H_2O . The P-T path of the XRS experiment is indicated.

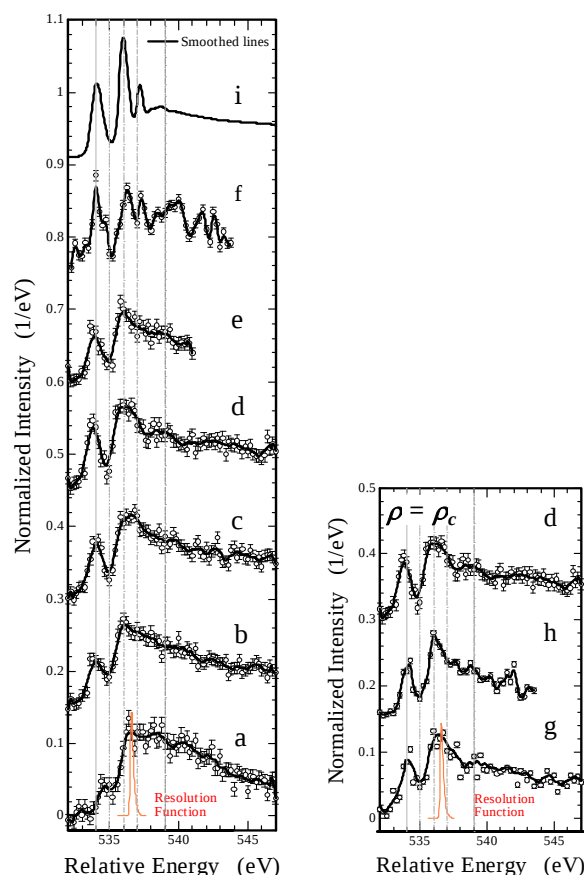


Figure 2. Oxygen XRS spectra of water under various P-T conditions near the supercritical point.