



	Experiment title: Pressure dependence of local structure of water with X-ray Raman spectroscopy on oxygen <i>K</i> -edge	Experiment number: HE-1909
Beamline: ID-16	Date of experiment: From 6 to 11 July 2005	Date of report: 16 February 2006
Shifts: 17	Local contact(s): Dr Simo Huotari	<i>Received at ESRF:</i>

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Report: Water presents unique physical and chemical properties. We have performed X-ray Raman spectroscopy (XRS) [1, 2] at the oxygen *K*-edge of water under high-pressure conditions using diamond anvil cells. XRS provides information similar to that of X-ray absorption spectroscopy [3 - 6] and has certain advantages when measuring unoccupied electron density of state (DoS) and the local structure of light elements.

A series of high-pressure XRS experiments was carried out at ID16 of ESRF. The incident X rays were monochromatized with a double crystal monochromator (DCM) utilizing the Si(111) reflection. When measuring fine near-edge spectra, a Si(220) high-resolution monochromator (HRM) was also installed. Scattered X ray was monochromatized to 7.9 keV with Si(444) reflection or 9.8 keV with Si(555) reflection of a bent silicon crystal analyzer and a 1-m arm goniometer. Total energy resolution was 520 meV, 1.0, and 1.5 eV with Si(444) and DCM+HRM, with Si(444) and DCM, and with Si(555) and DCM, respectively. The scattering angle was fixed at 40 degrees. Momentum transfer Q was 4.54 and 5.62 nm⁻¹ for measurements with Si(444) and Si(555) reflection, respectively. Both conditions satisfy dipole condition (Qr , where r is 6.9 pm for oxygen 1s orbital radius, is 0.19 and 0.24, respectively). Pure water was used as a sample. For ambient-pressure measurement, a cell with 25-micron Kapton windows and a 2-mm thick water sample were used. Diamond anvil cells with beryllium gaskets were used for high-pressure measurements. Generated pressure at 0.16, 0.21, 0.27, 0.47 and 0.60 GPa was estimated with ruby fluorescence method under hydrostatic conditions.

Figure 1 shows the Fourier transforms (FT) of k^3 -weighed X-ray Raman spectra normalized to their peak values. The pressure dependence of the peak positions should be reliable even though their absolute values can be affected by phase shifts. Inter-atomic distances from oxygen to the first neighbor hydrogen (OH1), to the second neighbor hydrogen (OH2), and to the first neighbor oxygen (OO) become longer with increasing pressure up to at least 0.27 GPa as a general trend. At 0.47 GPa, the peaks due to OH1 and OH2 are not separated from each other. This is probably due to the relatively narrow energy range of X-ray Raman spectra and thus low real space resolution, and also because of OH1 distance finally overlapping with that of OH2. The OH1 distance was the longest at 0.47 GPa whereas OH2 distance at 0.47 GPa became shorter than that at 0.27 GPa. The OH1, OH2, and OO distances at 0.60 GPa are clearly shorter than at 0.27 GPa.

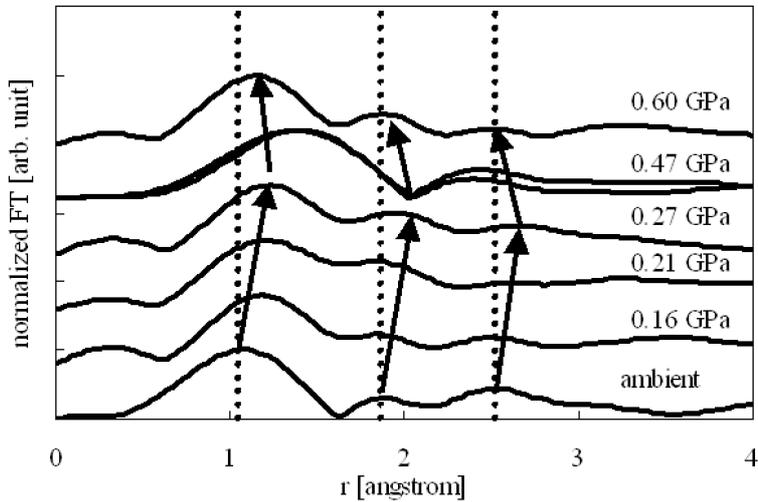


Figure 1. Fourier transforms of k^3 -weighted X-ray Raman spectra normalized by each maximum value.

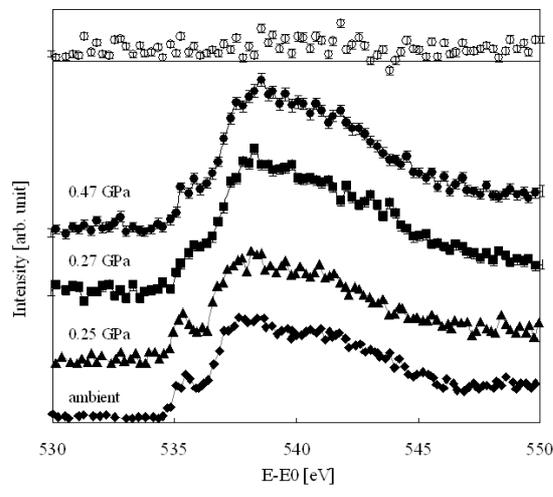


Figure 2. Near-edge spectra obtained at 0.27 and 0.47 GPa indicated by solid squares and circles, respectively, and their differential (open circles) with those reported at ambient and 0.25 GPa [7]

Figure 2 shows the near-edge spectra of X-ray Raman band of oxygen K -edge for water obtained at 0.27 GPa and 0.47 GPa, and their differential. XRS spectra from literature [7] were also shown. All spectra look similar except for the small difference in the pre-edge peak shape. The differential does not show any distinct features. We observed interesting behavior of inter-atomic distance at 0.27 GPa and 0.47 GPa. The inter-atomic distances at 0.47 GPa are less reliable because of the short energy range. However, the OO distance increases up to 0.27 GPa and then becomes slightly shorter at 0.60 GPa than that at ambient pressure. In contrast, the present near-edge spectra of O K -edge X-ray Raman band at ambient pressure, 0.25 GPa, 0.27 GPa, and 0.47 GPa show little difference between each others. This result directly means that the unoccupied electron DoS of oxygen p -orbitals changes only little between these conditions. In order to study this variation in detail, more precise measurements and accurate simulations are required.

The authors appreciate to K. Ohwada for beryllium gaskets and G. Vankó for help and advice on this experiment. HF also wishes to thank M. Krisch for his valuable suggestions.

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