

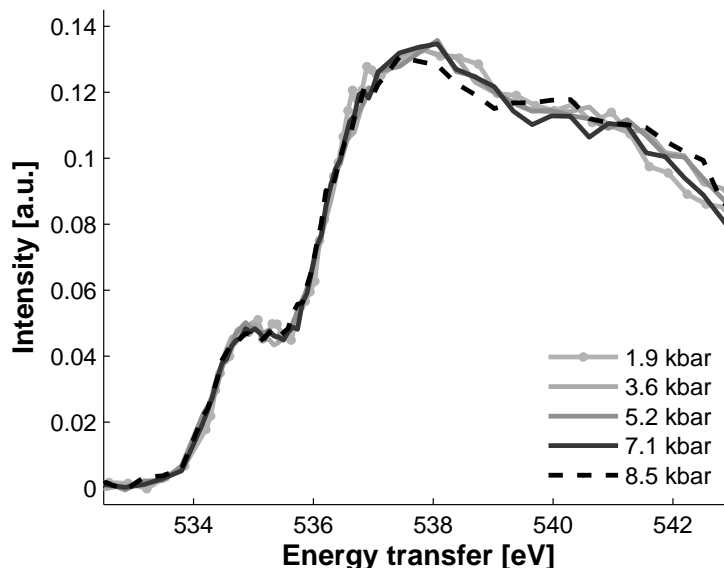


<b>ESRF</b>	<b>Experiment title:</b> X-ray Raman scattering measurement of oxygen <i>K</i> -edge XANES in water under high pressure	<b>Experiment number:</b> HE-2740	
	<b>Beamline:</b> ID16	<b>Date of experiment:</b> from: 11 June 2008                      to: 17 June 2008	<b>Date of report:</b> 31 August 2008
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#### Report:

Owing to the great general interest in the structure of water at different conditions, the effect of pressure has been studied with various methods. X-ray and neutron diffraction, infrared Raman spectroscopy and molecular dynamics simulation studies imply that as pressure is increased, water undergoes a continuous structural transition into 'high-density water' (HDW) which bears similarities to high-density amorphous ice (HDA) [1]. While density increases upon transition to HDW, hydrogen bonds have been assumed to remain intact, as almost no changes can be observed in their distance and directional characteristics with the above-mentioned techniques. However, significant changes have been seen in the second coordination shell, which grows denser by incorporating 'interstitial' molecules (i.e. molecules not bonded to the first shell). Intriguingly, a XANES measurement can detect very small changes in coordination, offering unique information on pressure-induced changes in the first shell, including changes in hydrogen bond strengths and distortions.

X-ray Raman scattering (XRS) allows the measurement of low-energy x-ray absorption edges (530 eV for the O *K*-edge) using high-energy x-rays ( $\sim 10$  keV at ID16). This lifts the constraints of soft x-ray measurements and allows access to difficult sample environments such as high pressure cells. We have optimized a setup for measuring high-resolution XRS spectra using a diamond anvil cell. We performed a systematic study of the O *K*-edge of water under pressure with unprecedented accuracy. Earlier studies were performed with either high resolution but low statistics [2] or high statistics but low resolution [3]. These studies reported conflicting changes upon increasing pressure [2,3], which we can now address with higher accuracy.



**Figure 1.** The pressure dependence of the O *K*-edge XANES as measured by X-ray Raman scattering. The spectra are area-normalized and shifted to align at the edge.

We used a panoramic diamond anvil cell with a beryllium gasket, which allows measuring inelastic scattering spectra in the gasket plane at arbitrary angles. The cell was loaded with ultrapure water and a small ruby chip for pressure calibration using the pressure dependence of the ruby fluorescence line. The diamond culet size was 1 mm, the gasket diameter 5 mm, and the sample size under pressure 350  $\mu\text{m}$ . XRS spectra were recorded at pressures of 1.9, 3.6, 5.2, 7.1 and 8.5 kbar (with accuracy of  $\pm 0.5$  kbar in all cases), as well as at ambient pressure using a liquid flow setup.

The incoming radiation was monochromatized with a double-crystal Si(111) monochromator followed by a Si(440) channelcut. The beam was focused into a 130(H) $\times$ 50(V)  $\mu\text{m}^2$  spot by a Rh-coated toroidal mirror. The measurements were performed utilizing a multianalyzer spectrometer, in which the scattered radiation is focused on the 2D photon-counting Maxipix2 detector by 9 spherically bent Si(110) crystal analyzers. Spectra were gathered scanning the incident energy while analyzing the scattered radiation using the Si(660) reflection near backscattering, giving an elastic energy  $E_0 = 9.68$  keV and energy resolution of  $\Delta E = 0.5$  eV (FWHM). The mean scattering angle was  $2\theta = 46^\circ$ , corresponding to a momentum transfer range of  $q = 2.1 \pm 0.4$  a.u.

Preliminary results are shown in Figure 1. The spectra are found to be remarkably stable under pressure, at odds with previously reported results [2,3]. In particular, the pre-edge feature is constant within the statistical accuracy. Further analysis is underway into the subtle pressure dependence of the post-edge features.

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- [2] Y. Q. Cai *et al.* Ordering of Hydrogen Bonds in High-Pressure Low-Temperature  $\text{H}_2\text{O}$ . *Phys. Rev. Lett.* 94 (2005) 025502.
- [3] H. Fukui *et al.* Oxygen *K*-edge fine structures of water by x-ray Raman scattering spectroscopy under pressure conditions. *J. Chem. Phys.* 127 (2007) 134502.