ESRF	**Experiment title:** X-ray Raman scattering measurement of the high-pressure ice phases V-VIII	**Experiment number:** HE-2883
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Report:

Ice exhibits a stunning number of phases (at least 13 crystalline phases have been identified so far), which is of fundamental interest to condensed matter physics. The high-pressure polymorphism of ice is also relevant to applied sciences such as geophysics and planetary physics. [1] An earlier XRS study on low-temperature ice phases [2] demonstrated that the near-edge spectra show marked differences between the different ice phases (especially in the pre-edge region), and linked these to changes in proton ordering and the Madelung potential. Low statistics, however, prevented a systematic comparison with electronic structure calculations. Given that the structure of the hydrogen bond network in liquid water is still not completely characterized [3], ice phases provide very interesting model systems. Difficulties in modeling the pre-edge signal in liquid water and its implications of a substantial hydrogen-bonding asymmetry in the liquid phase has lead to an ongoing debate. Providing new experimental information on structurally known H_2O systems will be highly relevant to this issue, and also in the modeling of other hydrogen bonded liquids.

X-ray Raman scattering (XRS) allows the measurement of low-energy x-ray absorption edges (535 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 applied an earlier developed setup for measuring high-resolution XRS spectra using a panoramic diamond anvil cell with a beryllium gasket (HE-2740) to three previously unmeasured ice phases: VI (tetragonal, $\rho = 1.37$ g/cm^3), VII (cubic, $\rho = 1.60$ g/cm^3) and VIII (the proton-ordered form of ice VII).

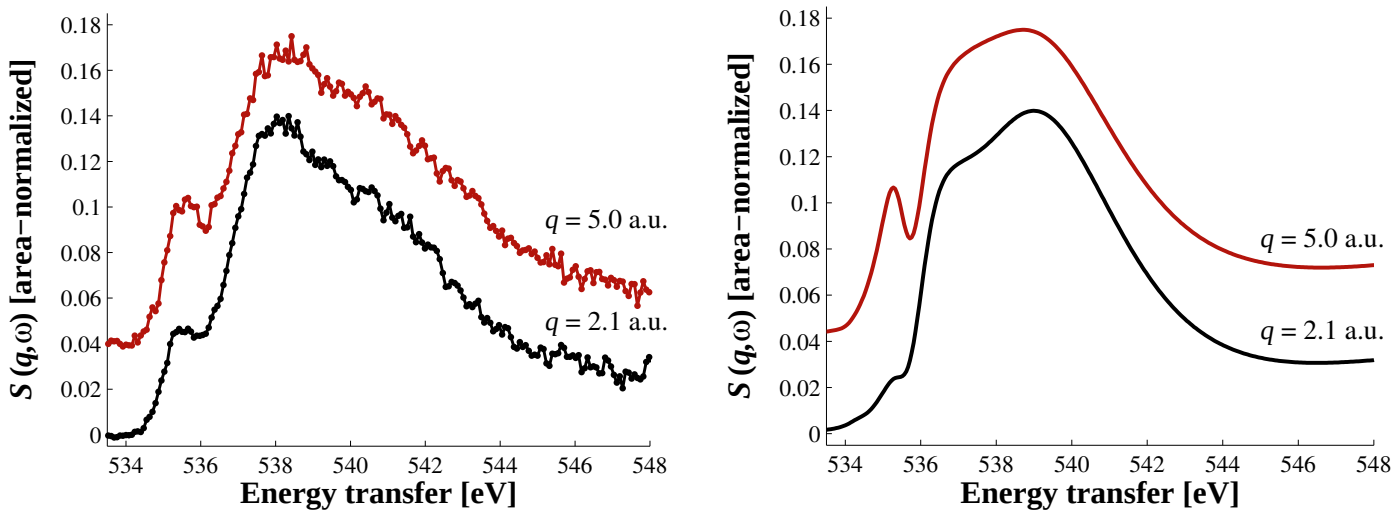

Figure 1. The O K-edge XANES of ice VI as measured by x-ray Raman scattering. (a) Background-removed spectra. (b) Spectra calculated with a density-functional theory based method [4].

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 ∼300 μm. XRS spectra were recorded at 1.7 GPa and room temperature (RT) (ice VI), 2.2 GPa and RT (ice VII), and 2.2 GPa and −10 °C (ice VIII). For ice VIII, the cell was cooled with a cryo-cooled flow of dry air. The phases were identified with *in situ* x-ray diffraction using a Mar CCD area detector.

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)×50(V) μm^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). Spectra were measured at two spectrometer positions, $2\theta = \{46°, 134°\}$, corresponding to momentum transfers $q = \{2.1, 5.0\}$ a.u.

Preliminary results for ice VI are shown in Figure 1a. The quality of the background-removed spectra are substantially improved compared to the previous high-pressure ice XRS measurement [2]. We will analyze the results with the help of density-functional theory based spectral calculations [4] using model clusters, taking into account the effect of momentum transfer; an example is shown in Figure 1b.

[1] R. J. Hemley *el al.* Static compression of H_2O-ice to 128 GPa. *Nature* 330 (1987) 737. V. F. Petrenko and R. W. Whitworth. *Physics of Ice.* Oxford University Press, 1999. D. D. Klug. Dense ice in detail. *Nature* 420 (2002) 749. [2] Y. Q. Cai *el al.* Ordering of Hydrogen Bonds in High-Pressure Low-Temperature H_2O. *Phys. Rev. Lett.* 94 (2005) 025502. [3] F. H. Stillinger. Water revisited. *Science* 209 (1980) 451. Ph. Wernet *et al.* The structure of the first coordination shell in liquid water. *Science* 304 (2004) 995. T. Head-Gordon and M. E. Johnson. Tetrahedral structure or chains for liquid water. *Proc. Natl. Acad. Sci. USA* 103 (2006) 7973. D. Prendergast and G. Galli. X-ray absorption spectra of water from first principles calculations. *Phys. Rev. Lett.* 96 (2006) 215502. [4] A. Sakko, M. Hakala, J. A. Soininen, and K. Hämäläinen. Density functional study of x-ray Raman scattering from aromatic hydrocarbons and polyfluorene. *Phys. Rev. B* 76 (2007) 205115.