ESRF	**Experiment title:** Temperature dependence of the oxygen near-K-edge structure in water measured with X-ray Raman Scattering	**Experiment number:** HE-3039
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Report:

Despite decades of study, the local structure of liquid water is still the subject of intense discussion (Refs. 1–3 and references therein). The anomalous temperature behavior of many of water's macroscopic response functions remains without a satisfactory explanation at the molecular level. Controversial interpretations based on a mixture model of co-existing components of low-density and high-density water are continuously brought forward and debated [4].

The oxygen K-edge x-ray absorption near-edge structure (XANES) has been shown to be sensitive to distortion and breaking of hydrogen bonds [2]. However, the interpretation of the spectral changes (i) between hexagonal ice and liquid water, and (ii) induced by temperature in liquid water, remain controversial [2,5]. Measurements made with soft x-rays have up to now provided better resolution than those based on x-ray Raman scattering (XRS) [6]. Soft x-ray measurements, however, are subject to many experimental artifacts such as surface sensitivity and signal saturation (depending on the detection scheme).

To address these issues, we have performed a systematic high-resolution XRS study on the effect of temperature on the O near-K-edge spectrum in liquid water. The sample was ultrapure water contained in a peristaltic-pump-based flow setup, which produced a 2-mm diameter vertical liquid jet from a stainless steel nozzle. The temperature of the flow was controlled with an inhouse-developed thermal exchanger consisting of a large Cu block with an integrated heating element and a cooling circuit connected to an ethanol-circulating chiller. Spectra were gathered at 12 temperatures ranging from 1.6 °C to 85.0 °C.

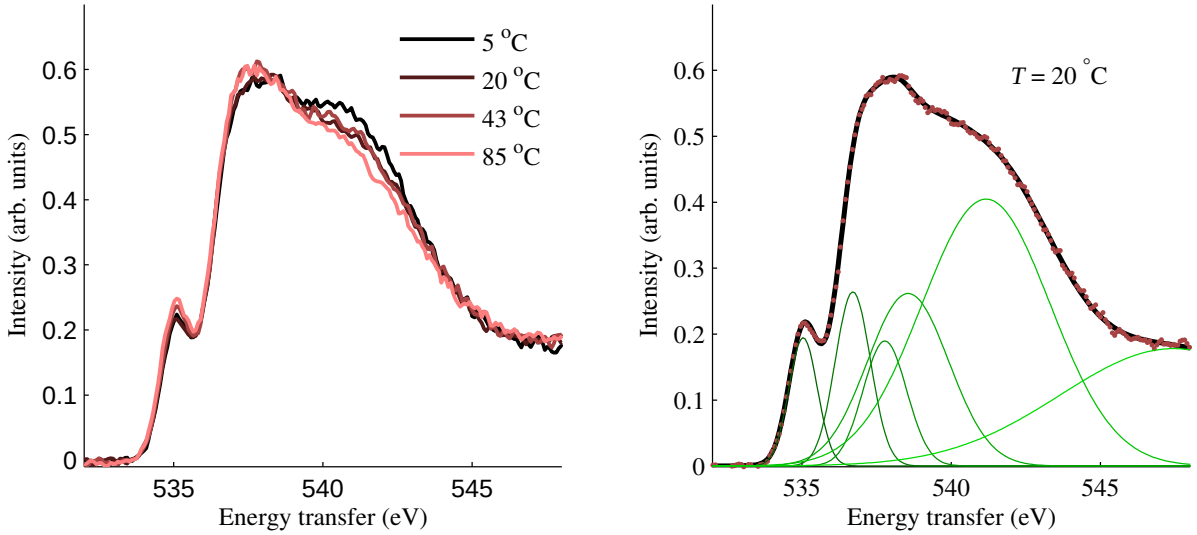

Figure 1. (*Left*). The O K-edge XANES of liquid water at selected temperatures. (*Right*). Example fit based on a deconvolution to six Gaussians components. Dots: measurement, thin lines: fitted Gaussian components, thick line: summed fit.

The temperature of the flow was measured at (1) the surface of the steel nozzle producing the liquid jet, and at (2) the jet collection point (∼1 cm after beam spot). Position (1) was used to regulate the heating power of the thermal exchanger, and position (2) to determine the actual sample temperature. The setup achieved an overall temperature stability of better than ±0.1°C.

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 an average scattering angle of $2\theta = 36°$, corresponding to a momentum transfer $q = 1.7$ a.u.

Preliminary results are shown in Figure 1. The quality of the spectra are significantly improved compared to previous XRS measurements of liquid water. The high systematic accuracy allows observing temperature-induced changes in specific spectral regions via e.g. a deconvolution to Gaussian components. A detailed study of these components and the reliability of such an analysis is underway.

[1] F. H. Stillinger. Water revisited. *Science* 209, 451 (1980).

[2] Ph. Wernet *et al.* The structure of the first coordination shell in liquid water. *Science* 304, 995 (2004).

[3] T. Head-Gordon and M. E. Johnson. Tetrahedral structure or chains for liquid water. *Proc. Natl. Acad. Sci. USA* 103, 7973 (2006).

[4] For a recent example, see: C. Huang *et al.* The inhomogeneous structure of water at ambient conditions. *Proc. Natl. Acad. Sci. USA*, DOI: 10.1073/pnas.0904743106 (2009).

[5] J. D. Smith *et al.*, Energetics of hydrogen bond network rearrangements in liquid water. *Science* 306, 851 (2004); J. D. Smith *et al.*, *J. Phys. Chem. B* 110, 20038 (2006).

[6] U. Bergmann *et al.*, Isotope effects in liquid water probed by x-ray Raman spectroscopy. *Phys. Rev. B* 76, 024202 (2007).