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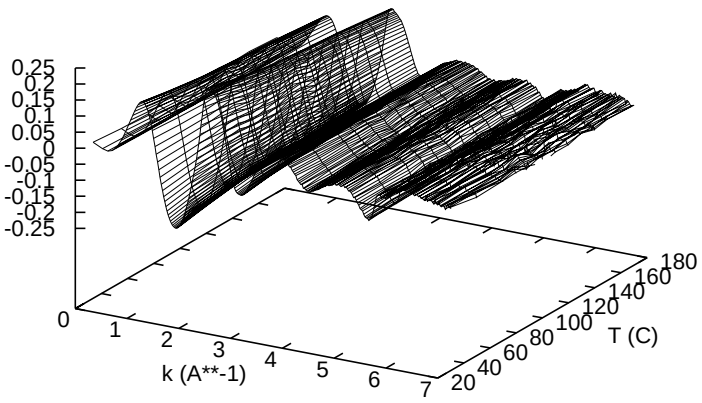
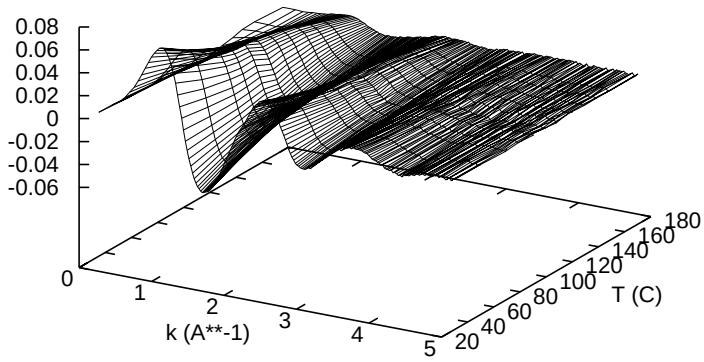
Report:

This experiment was designed to perform a detailed investigation of the structural aspects of noble gas hydrophobic hydration at high temperatures (>100°C) and pressure (400 *bar*). The aim of this study was to cast light on the the well known but as yet not fully explained noble gas solubility minimum that occurs at approximately 110°C. For this experiment we have used the high pressure liquid mixing system developed at the ESRF [1], that allows the mixing of gases (Kr) and liquids (H_2O) and their subsequent circulation at a fixed concentration through a high pressure measurement cell equipped with x-ray transparent polymer windows. This setup, previously used during experiment CH781, was further improved with the installation of a heating system based on remotely controlled hot air flow stabilised by a PID controller.

The scientific objective of the experiment was to observe subtle effects in the temperature variation of the EXAFS signal. This requires an extremely stable and reproducible operation of the beamline components. Regrettably, data collected in the first few days of this experiment proved unusable. A detailed diagnosis of showed that there was a mechanical instability in the beamline monochromator at that time. Fortunately, it was possible to find a short term solution to this problem in the course of the experiment, and useful data were obtained in the last two days of allocated beamtime. However, insufficient time remained for collection of data on the comparison Kr/D_2O system.





Previous experiments on the Kr/H_2O system [2] up to 80 °C already revealed a dramatic change in the intensity of the Kr K-edge EXAFS signal as a function of temperature. The present data confirm our previous findings and extend the available range to 190 °C. Spectra have been collected at regular temperature intervals every 10 or 20 °C both raising and lowering the cell temperature. An example of the EXAFS data is reported in the upper left figure as $k\chi(k)$ as a function of k and T. The $\chi(k)$ was extracted using a three-region spline and the resulting oscillation contains both structural signal and atomic background features such as double-electron excitations involving [1s4p], [1s3d] visible at $k \approx 6$ Å^{-1}, and [1s3p] double hole final states [3].

We have successfully attempted a preliminary data analysis based on the direct subtraction of the experimental data, as shown in the upper right figure. The difference spectra were obtained by subtracting from all $k\chi(k)$ data, a reference spectrum collected at 190 °C. The temperature dependence of the structural signal is quite evident in this plot. Further analysis will be attempted by calculating the temperature derivative of the signal and finally performing a fitting of the short range shape of the Kr-O distribution as in previous studies [2,3]. The advantage of this differential approach is the exact cancellation of the background features, which are theoretically temperature independent, and in the possibility to subsequently highlight reliably, very small changes in the EXAFS spectra. Such studies are only possible thanks to the low noise and reproducibility in the data that were finally achieved in the present experiment (noise/signal$\simeq 10^{-4}$).

Preliminary results indicate the occurrence of a gradual disordering of the Kr hydration shell as the temperature is raised through the gas solubility minimum. The quantitative analysis of this effect and the thermodynamic implications will be the subject of extended publications presently in preparation.

[1] D. T. Bowron, R. Weigel, A. Filipponi, M. A. Roberts, and J. L. Finney, Mol. Phys. **xxx**, xxx (2001).

[2] D. T. Bowron, A. Filipponi, C. Lobban, and J. L. Finney, Chem. Phys. Lett. **293**, 33 (1998).

[3] A. Filipponi, D. T. Bowron, C. Lobban, and J. L. Finney, Phys. Rev. Lett. **79**, 1293 (1997).