ESRF	**Experiment title:** EXAFS Studies of Hydrophobic Hydration: The Pressure Dependence of the First Hydration Shell in the range 0.1kbar to 1.0kbar.	**Experiment number**: CH-781
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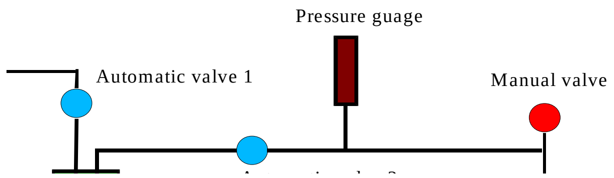
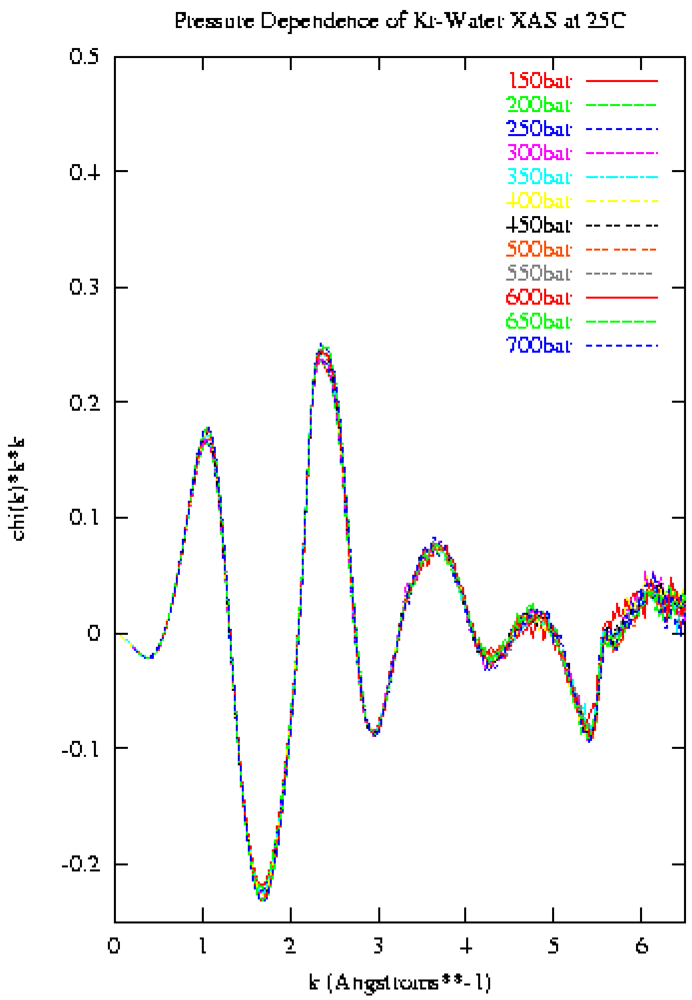
Report:

In this experiment, we have investigated the effect of pressure in the 100bar to 1kbar range, on the structure of the hydrophobic hydration shell of krypton. The scientific aim of this project is to resolve the controversial question relating to the effect of pressure on the direct hydrophobic hydration shell. This structural interaction is often quoted as one of the key (and unknown) aspects in theories of the molecular mechanisms responsible for the pressure denaturation of proteins.



The experimental methods utilized to perform this experiment involved the development of a liquid pressure cell capable of operating in the required pressure range as well as a gas-liquid mixing system capable of fixing the dissolved gas concentration. This task is achieved by equilibrating the gas concentration at a fixed pressure, for example 100bar, after which the mixture is isolated from the gas reservoir and direct pressure is applied to the liquid in the cell. A schematic diagram of this system is shown in Figure 1, and it is controlled by means of a dedicated PLC, interfaced with the beamline computer system (R.Weigel, ESRF).

Figure1: Schematic of the liquid pressure system.



In Figure 2 are shown the measured X-ray absorption spectra at the Kr K-edge (14.326keV) for the gas dissolved in water at room temperature. The noise level in the measured signal is consistently in the low 10^{-4} range for all measured pressures. Within the experimental uncertainties, there is no evidence for any significant perturbation of the local atomic environment of Kr gas in water as a function of pressure in the investigated range.

This resilience displayed by the krypton hydration shell to the application of pressure in the measured range, has considerable implications for our understanding of conventional models of the pressure interaction in systems governed by hydrophobic effects.

As has been shown in our earlier investigations of the Kr-water system[1-3], the measured signal is dominated by the Kr-O_{water} atomic pair correlations. The experimental result obtained here suggests that the noble gas atom provides, to a very good approximation, a spherical hard core potential against which the oxygen atoms are pressed. This result contrasts with computer simulation findings for the pressure dependence of methane hydration in the same range [4], even though these solutes are of similar size (largest van der Waals diameters[5] of 4Å (Kr) and 4.1Å (CH_4)). The result of these simulations[4], suggested a considerable modification of both the CH_4-H_{water} and CH_4-O_{water} correlations as the system pressure was increased. The contrasting experimental finding for krypton thus raises serious questions about the reliability of current simulation results to test the pressure response. These differences now demand clarification which can be obtained for example, by parameterising the simulation study with conventionally accepted parameters for krypton rather than methane.

[1] A.Filipponi, D.T.Bowron, C.Lobban and J.L.Finney. *Phys. Rev. Lett.* **79** 1293 (1997)
[2] D.T.Bowron, A.Filipponi, C.Lobban and J.L.Finney. *Chem. Phys. Lett.* **293** 33 (1998)
[3] D.T.Bowron, A.Filipponi, M.A.Roberts and J.L.Finney. *Phys. Rev. Lett.* **81** 4164 (1998)
[4] P.-L.Chau and R.L.Mancera. *Mol. Phys.* **96** 109 (1999)
[5] D.W.Davidson in *Water - A Comprehensive Treatise* edited by F.Franks, Plenum Press (1973) vol. 2, chap. 3, p.131