



**Experiment title:** Hydrophobic Hydration of Noble Gases: An EXAFS Study

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**Report:**

Hydrophobic hydration is the term used to describe the structural correlations that arise on the aqueous solvation of a non-polar or predominantly non-polar moiety. The structure that is induced in the first hydration shell of water molecules is of particular interest, i.e. the structural correlations involving those water molecules which are in direct contact with the solute. This interest is due to the conventional interpretation of hydrophobic phenomena, where much significance is placed on the theory that first shell hydration water adopts structural configurations which are more closely related to the network structure of ice than those configurations found in normal liquid water.

To date, direct experimental investigation of the hydration of largely non-polar moieties has only been possible through the technique of isotopic substitution neutron diffraction. This technique, although powerful is restricted to systems for which suitable isotopes for substitution are available and to solute concentrations which are sufficiently high so as to give reasonable signal strengths, generally  $>0.05$  mole fraction. This latter constraint is particularly problematic for the study of hydrophobic solutes, for as their name implies they have low solubility in the aqueous environment. Hence, to study hydrophobic effects by neutron techniques, suitable solutes have to be selected either from

1. amphiphilic systems such as the monohydric alcohols, where the partly polar nature of the solute provides sufficient solubility to achieve the required solute concentrations, or
2. more ideal non-polar solutes such as the noble gases, where sufficient solute concentrations can be achieved through the application of high pressure (several hundred bar).

Both solutions to this low solubility problem are arguably not ideal, the effect of the presence of local polar groups or significant applied pressure can complicate the interpretation of the results in terms of pure hydrophobic effects.

Here we report the first studies of hydrophobic hydration performed using the Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy technique, and our chosen solute moieties for this study were the noble gases krypton and xenon. As these gases are extremely non-polar and insoluble, a certain degree of pressure is required, but because the EXAFS technique is far more sensitive to low concentrations of the selected atomic species than the aforementioned technique of isotopic substitution neutron diffraction, gas pressures of a few tens of bar are sufficient, c.f. >250bar for characterisation by neutron techniques.

For this experiment we made use of a pressure cell designed to allow operation in the pressure range 1bar to 250bar, and in the temperature range 0°C to 200°C. This cell had small X-ray windows of approximately 8mm x 1mm and a sample containment area which was adjusted to a suitable path length for the absorption edge under study - allowance was made for the expected gas solubilities in water in the pressure and temperature ranges under investigation. The cell was first loaded with outgassed water and then sealed. Gas pressure was applied directly using the noble gas chosen for investigation and the pressure maintained during dissolution by direct connection to the gas reservoir. The dissolution of the gas into the aqueous environment was simply monitored through the height of the measured absorption edge, and equilibration times of the order of 20 minutes were found to be sufficient for stabilisation of the observed absorption edge step and associated EXAFS.

Data of excellent quality were collected at a number of pressure points. Our initial results show that no variation in hydration structure as a function of pressure in the range 6bar to 100bar is visible. In this our first experiment using this sample environment, the ultimate applied pressure was limited to the fill pressure of the lecture bottles containing the respective noble gases. Our preliminary temperature data suggest that the influence of thermal effects is more striking, but time restrictions limited our attempts to correlate the two variable experimental parameters. The figure below illustrates some of our early findings.

Figure 1: X-ray absorption spectra at the Kr K-edge of Kr pressurised into water at 6bar and 19bar. For illustration, the background absorption contributions of the empty cell and water are shown. (When corrected to an absolute scale, the absorption of the empty cell is approximately 1.5).

