



ESRF

	Experiment title: The pressure and temperature dependence of the hydrophobic hydration of the noble gases krypton and xenon. An EXAFS study.	Experiment number: CH371
Beamline: BM29	Date of Experiment: from: 25-11-97 to: 5-12-97	Date of Report: 21-1-98
Shifts: 18	Local contact (s) : A.Filipponi	<i>Received at ESRF:</i> - 3 MAR. 1998

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Report:

In our previous experiment (CH202), we demonstrated the capability of the EXAFS technique to provide us with detailed insight into the structure of the hydrophobic hydration shells of the noble gases Kr and Xe, when they are in aqueous solution [1]. The ability of this structural probe to make a **direct** measurement of such structure has opened up a further means by which the poorly understood, but extremely important, hydrophobic effect can be studied. Prior to our measurements with the EXAFS technique, **direct** measurements of non-polar moiety hydration structure were largely confined to the neutron scattering techniques such as H/D isotopic substitution methods [2].

Hydrophobic effects are generally divided into two categories, **hydrophobic hydration** and the **hydrophobic interaction**, both of which are extremely important to our understanding of many processes such as the stability of colloids, the mechanisms of protein folding and numerous others [3]. Hydrophobic hydration is the term used to describe the structure adopted by solvent water when in contact with a non-polar or largely non-polar solute. In the conventional model of hydrophobic effects, this interaction is believed to result in an increase in the local ordering of the solvent [4]. This hydrophobic hydration is consequently theorised to drive the hydrophobic interaction, by which non-polar solutes are found to associate when in the aqueous environment. Essentially this is thought to be an **entropy driven** effect, the association of non-polar solutes reduces the total non-polar surface exposed to the aqueous solvent and the resulting release of hydration water, consequently produces a favourable increase in system entropy.

As hydrophobic phenomena are closely related to the entropic balance within an aqueous system, they are particularly sensitive to thermal conditions (T). This is easily seen from the well known relationship between the free energy (G), enthalpy (H) and entropy (S):

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

In this experiment (CH371) we have continued our investigation of the Kr and Xe hydrophobic hydration to include the effect of temperature upon the structure in the first hydration shell. We have obtained spectra for both the Kr and Xe system in the temperature range from 10°C to 95°C and clear trends in the hydration shell structure are visible. In Figures 1 and 2, we show the effect of increasing temperature on the measured EXAFS signals for the Kr and Xe systems respectively. Analysis of these data has been performed within a radial distribution function analysis scheme [5], though our detailed results will be presented elsewhere [6].

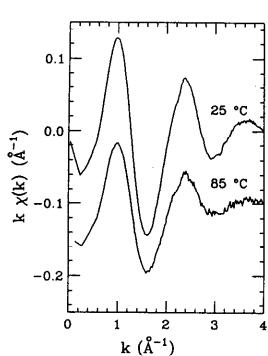


Figure 1

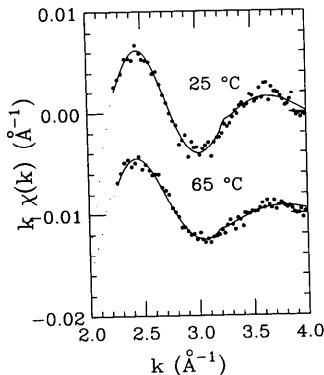


Figure 2

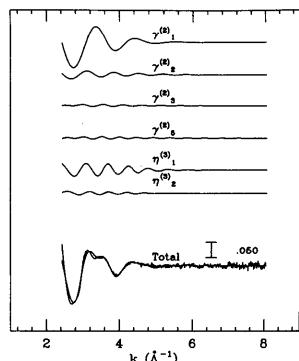


Figure 3

Furthermore, as stated in our proposal for this experiment, we have also measured the EXAFS for a solid Kr-water system, by going to low temperatures ($\approx -10^{\circ}\text{C}$) - the type II clathrate hydrate structure. This novel crystal structure is known to be stabilized by the repulsive forces between the guest molecules and the hydrogen bonded water network. This invaluable information will further allow us to refine our results of the liquid state structural correlations and to study the subtleties of the structural changes as the transition from the liquid state hydrate of the gas to the solid state system progresses. The structural comparison for hydrophobic systems in the liquid and solid states is particularly suitable for clarifying the conventional models of hydrophobic hydration that currently abound in the literature.

We believe that this is the first measurement of this system that has ever been performed by the EXAFS technique and figure 3 shows our preliminary analysis of this complex crystalline form. The result demonstrates the importance of higher shell correlations that are needed to satisfactorily model the observed EXAFS signal.

Our preliminary analysis fits well with the known crystallographic structure of a type II clathrate hydrate, though there are some indications that there may be a slight preference for the filling of the small water cages in the structure over the filling of the larger cavities. A more detailed analysis of our data on this interesting system is currently in progress and the results will be presented elsewhere [7].

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- [7] D.T.Bowron, A.Filipponi, M.A.Roberts and J.L.Finney *in preparation*