Structural Determination of the Hydrophobic Hydration Shell of Kr

Adriano Filipponi
European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble, France

Daniel T. Bowron, Colin Lobban, and John L. Finney
Department of Physics and Astronomy, University College London, Gower Street, London, WC1E 6BT, United Kingdom

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We report the first direct measurement by extended x-ray absorption fine structure spectroscopy of the hydrophobic hydration shell of the noble gas krypton. Measurements were made in aqueous solution at gas pressures in the range 20 to 100 bars and at a temperature of 320 K. Data of excellent quality were collected taking advantage of the high brilliance of a third generation synchrotron radiation source. An advanced data analysis procedure has been applied to determine the Kr-O partial radial distribution function in the short range. [S0031-9007(97)03804-0]

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The structure adopted by liquid water molecules which are in close proximity to nonpolar solutes is a fundamental characteristic of modern theories of hydrophobic hydration and hydrophobic effects—phenomena which are of great relevance to our understanding of many important chemical and biological processes [1]. Because of the intrinsic difficulties faced by structural characterization techniques when unambiguous measurements of interatomic and intermolecular structures are required, direct measurements of this important class of structural correlation have to date, been limited, although isotopic substitution neutron scattering methods have begun to address the questions of molecular correlations in aqueous solutions of nonpolar moieties [2,3]. Current theoretical models of the intermolecular structure and intermolecular orientational correlations in hydrophobic systems have been predominantly based upon indirect thermodynamic information and computer simulation results. Because of this lack of a direct determination of the local molecular order which is present in aqueous solutions of nonpolar moieties, a wide range of competing models has been produced [1].

By virtue of an intrinsic spherical symmetry, aqueous solutions of the noble gases Ne, Ar, Kr, and Xe are ideal candidates for studies of the intermolecular structures involved in the hydrophobic hydration of nonpolar moieties. Unfortunately, one of the principal problems which hampers the detailed structural determination of their hydration shells is the low gas solubilities which are involved [4]. The concentration of a nonpolar gas in water is approximately proportional to the gas partial pressure and is higher for lighter gases. In order to reach a concentration in the 1% range, several tens of bars are usually required, and even if this concentration is achieved the system is often too dilute for direct structural characterization through techniques such as x-ray or neutron diffraction.

To our knowledge, the only previous experimental attempt to measure the hydrophobic hydration structure of a noble gas was made by Broadbent and Neilson [5] for the system Ar in D_2O. Using the technique of isotopic substitution neutron diffraction and taking advantage of the large change in neutron scattering contrast between Ar_{nat} and Ar_{36}, they were able to extract noisy but significant first order difference structure factors to yield combined structural information relating to the Ar-O and Ar-D partial radial distribution functions. Their measurements were made at 230 and 240 bars and their results show a broad peak in the total Ar-X partial distribution function centered around 3.4 Å, in agreement with previous computer simulation results.

The isotopic substitution neutron diffraction technique is not the easiest experimental method by which to probe the short-range structural environment of dilute impurity atoms in low Z matrices and here we demonstrate that valuable structural information can be obtained by x-ray absorption spectroscopy (XAS). XAS performed at the K edge of the noble gas atom should, in theory, reveal clear interference effects usually referred to as extended x-ray absorption fine structure (EXAFS) and associated with the scattering of the photoelectron released by the x-ray absorbing atomic species from its neighboring atoms. XAS has been previously applied to the study of the hydration of Sr [6] ions in supercritical water but attempts on Kr [6] did not reveal any structural signal. The availability of third generation synchrotron radiation sources which are characterized by low vertical emittance, high photon flux, and exceptional beam stability, is particularly well suited to the attempt of XAS experiments on samples subject to extreme environments, like those required for direct experimental investigation of hydrophobic hydration effects.

In this Letter we report the results of a first experiment performed on Kr in water at the following temperature and pressure points: 20 bars 318 K, 41 bars 322 K, 60 bars 322 K, 80 bars 322 K, and 100 bars 321 K.

The experiment has been performed at the European Synchrotron Radiation Facility (ESRF) on the bending magnet x-ray absorption spectroscopy beam line BM29.

The storage ring was operating in 2/3 fill mode and with typical currents between 150 and 200 mA at an electron energy of 6 GeV. The monochromator was equipped with a pair of flat Si(111) crystals which were detuned by 50% for harmonic rejection. Primary slits of 200 μm of vertical aperture were used to avoid masking from the small x-ray aperture of the pressure cell. Under these conditions the energy resolution is approximately 1.3 eV full width at half maximum (FWHM) to be compared with the Kr K-edge core hole broadening of 2.7 eV FWHM. The absorption coefficient in transmission mode was measured using photodiode detectors and metal foil fluorescence converters. The energy scale was calibrated putting the inflection point of the Kr gas K edge at 14.3236 keV following previous determinations [7].

The sample was contained in a cell suitable for x-ray absorption measurements above 12 keV in the liquid water temperature range and capable of withstanding pressures up to 100 bars. The cell has an internal gap of 4 mm and the volume occupied by the liquid is delimited by two 3 mm thick epoxy resin windows. The cell was loaded with outgassed water and sealed with a copper gasket and connected to a gas line. This gas line was purged and filled with Kr gas (99.998% purity) at the desired pressure. The gradual dissolution of Kr into water was monitored by the increment of absorption above the Kr K edge. The phenomenon had a time constant of the order of 20 min. Measurements were taken after equilibration of both temperature, pressure, and concentration.

In Fig. 1 we report the raw x-ray absorption measurements corresponding to the empty cell, the cell filled with H_2O and the pressurized system at increasing Kr pressures. It is evident that, on top of the flat H_2O + cell x-ray absorption background, a Kr K edge develops with a step roughly proportional to the Kr pressure. In spite of the considerable absorption of the cell windows and of the water, a very good signal to noise ratio is obtained (a noise level of 2×10^{-4}) and the good contrast of the Kr edge step allows for the clear identification of the structural signal.

As usual, the signals are better evidenced by plotting $\chi(k) = (\alpha - \alpha_{\mathrm{bkg}})/\alpha_{\mathrm{nor}}$ as a function of the photoelectron wave vector modulus $k = \sqrt{2m(E - E_e)}/\hbar$, where α_{bkg} accounts for the nonstructural atomic background and the normalization function α_{nor} is taken as a smooth atomic cross section model for Kr scaled by the edge discontinuity; E_e is the energy of the inflection point at the Kr K edge. In order to show the importance of a correct background analysis, we compare, in Fig. 2, the spectrum of the 100 bars sample (top curve) with that of gaseous Kr at low pressure, ≈0.1 bar (middle curve), confined in a sealed cell 15 cm in length. Both spectra are recorded with the same x-ray beam conditions and the $\chi(k)$ is extracted using the same three-region polynomial spline to account for α_{bkg}. The middle spectrum clearly shows the well known background features due to the opening of several double electron excitation channels involving $4p$, $4s$, $3d$, and $3p$ electrons (see [8], and references therein). These effects are characteristic of the Kr atom and therefore are present in any Kr K-edge spectrum. On top of them, however, the upper spectrum clearly shows an additional oscillating contribution that can only have a structural origin. General criteria to account for atomic background effects in EXAFS analysis have been proposed [9]. For the purposes of the present investigation we find that the gas spectrum, after a proper normalization for the different absorption discontinuity, can be directly used as a background model for the solution data. This atomic background "transferability" is favored by the absence of any chemical bonding in Kr and is particularly true for the $3d \rightarrow 4d$ shakeup features at $k \geq 5.4$ Å^{-1} which are completely removed. This is because the overlap integral $\langle 3d|4d' \rangle$ is mainly confined in an inner region of the Kr atom. The resulting spectrum for the 100 bars data after such a subtraction is reported in Fig. 2. It is clear that all the main anomalies are eliminated and clean oscillations can be detected up to $k \approx 7$ Å^{-1}.

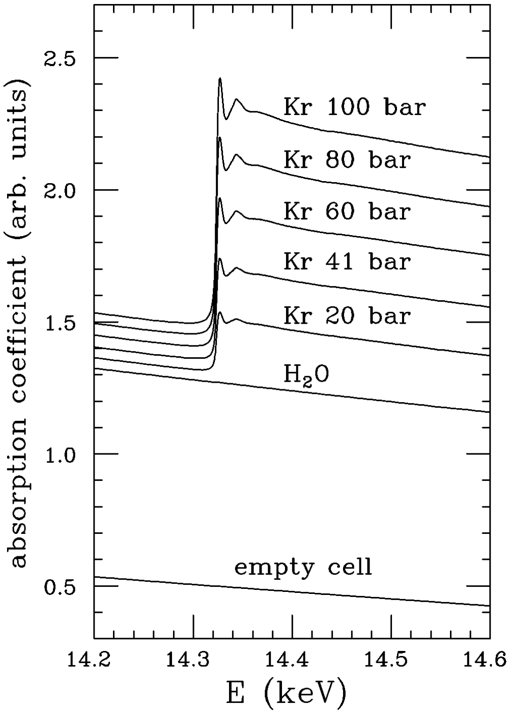

FIG. 1. X-ray absorption spectra at the Kr K edge of Kr pressurized in water at 20, 41, 60, 80, and 100 bars. The absorption background corresponding to the empty cell and cell filled with H_2O are reported for comparison. Notice that the scale is not absolute and includes the effect of the detector efficiencies. The absolute absorption of the empty cell is about 1.5 in this energy range.

After correction, the experimental $k\chi(k)$ spectra are compared in Fig. 3 revealing very little differences besides a slight increase in the noise for the lower contrast (low pressure) measurements. The bottom spectrum in Fig. 3 is composed of all the available data overlapped and demonstrates that there is no detectable variation of the structure versus pressure in the investigated range.

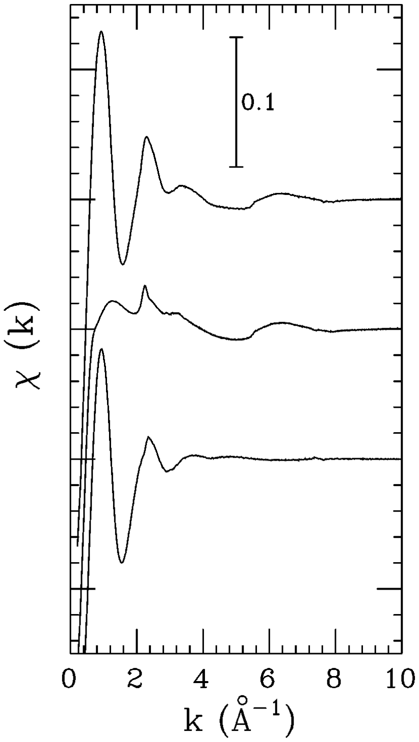

FIG. 2. EXAFS spectra of Kr samples. Top curve: Kr in H_2O at 100 bars; middle curve: Kr gas at low pressure, both extracted with a conventional three-region polynomial spline; bottom curve: Kr in H_2O at 100 bars extracted using the Kr gas spectrum as background function. In this way all the double-electron excitation effects are eliminated.

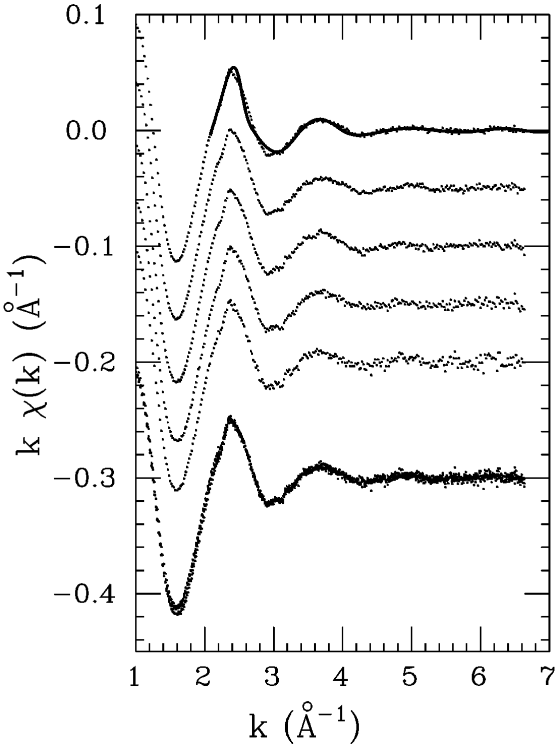

FIG. 3. Experimental EXAFS spectra of Kr in H_2O at various pressures from 100 (top curve) to 20 bars (bottom curve). The best fit of the 100 bars data is reported as a solid line. Lower curves: overlapped spectra showing no detectable structural changes in the 20–100 bars range.

To extract the structural information from the data we used an advanced data analysis scheme [10] based on a multiple scattering formalism and which uses a complex energy dependent self-energy [11]. This method is well suited to treat the case of disordered systems where a continuous distribution of atomic distances, described by a radial distribution function $g(r)$, occurs. As previously shown [12,13], in these cases it is incorrect to model the signal as the contribution from a single shell of atoms; rather, it is preferable to perform a constrained short-range refinement of a model $g(r)$ maintaining long-range integral properties to which EXAFS is not sensitive but that can be measured by diffraction experiments or simulated.

Phase shifts have been calculated in the muffin-tin approximation using radii of 1.32 Å for Kr, 0.72 Å for O, and 0.44 Å for H. Our starting $g(r)$ model was based on published molecular dynamics simulations on the hydration shell of Ar [14]. Both O and H atoms from the surrounding H_2O molecules can, in principle, contribute to the EXAFS spectra, and solute-H contributions have been considered in previous EXAFS investigations [15]. In the present case, O atoms provide the dominant contribution due to their larger scattering power and the comparable disorder and closest approach distance to Kr with respect to H. The H/O amplitude intensity ratio is found to be 1/10 at $k = 2.5$ Å^{-1} for the starting model.

Along the line of previous investigations [12,13] we have performed a constrained fitting of the EXAFS signals, here using three contributions to the $g(r)$ model–two asymmetric peaks plus a fixed tail. The applied constraints are the total coordination number and the second moment of the atomic density [13]. This gives a total of six free model parameters. Additional empirical parameters were E_0, the energy corresponding to the zero of the theoretical energy scale, and S_0^2 [10] fixed to 0.9. The best fit of the data at 100 bars for $k \geq 2$ Å^{-1} is reported in Fig. 3 overlapped to the experimental data.

The reconstructed Kr-O partial radial distribution function and the corresponding running coordination number $N(r) = \int_0^r 4\pi\rho t^2 g(t)\, dt$ (calculated using $\rho = 0.033\,34$ atoms/Å^3) are shown in Fig. 4. Error bars are reported in the r region affected by the EXAFS refinement and refer to the 95% statistical error as determined from the correlated statistical uncertainty in the parameters. The present experimental uncertainties on the peak height and distance scale are about ±0.15 and ±0.06 Å, respectively, the latter mainly arising from the uncertainty in E_0, and in principle they can be reduced by a factor of 5 in the presence of a suitable model compound. Further advances in the understanding of the atomic background, and the account for H EXAFS, will also improve the present data analysis possibly accounting for the signals below 2 Å^{-1}.

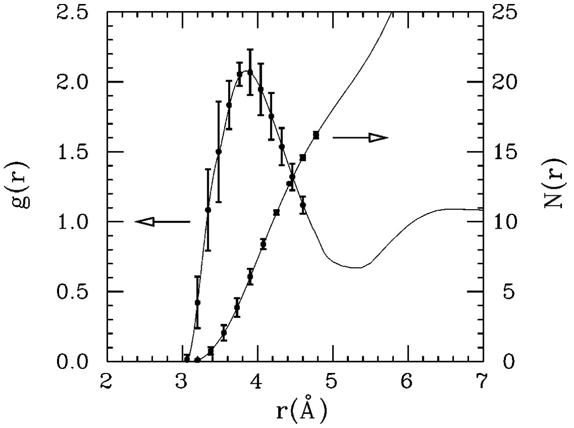

FIG. 4. Refined Kr-O partial radial distribution functions $g(r)$ and integrated coordination number $N(r)$ corresponding to 100 bars fit reported in Fig. 3. The existence of an ordered hydrophobic hydration shell is quite evident.

In conclusion, an x-ray absorption experiment has for the first time been performed on the hydrophobic hydration of Kr by taking advantage of the increasing availability of advanced synchrotron radiation sources. Using a quantitative data analysis technique, realistic Kr-O partial distribution functions have been obtained that show an ordering of water oxygen correlations around the Kr atom through the existence of a well defined hydration structure. Figure 4 clearly shows a Kr-O correlation centered around 3.8 Å and characterized by a slightly asymmetric shape. This shell is consistent with a hydration number of approximately 20 water molecules, up to $r \sim 5$ Å.

With this experiment, we have demonstrated the feasibility of using the EXAFS technique to study directly the structural nature of hydrophobic effects in aqueous solutions, an area of research that previously has largely been the preserve of indirect studies by techniques such as thermodynamic measurements or computer simulation. Although neutron diffraction studies have proven to be a most powerful technique by which to address many of the questions posed by these challenging and important systems, the complexities of such experiments render them impractical for characterization of the many parameter space which governs this important class of intermolecular interaction, e.g., pressure, temperature, solution pH, ionic cosolute concentration, and species. In contrast, the EXAFS technique, now demonstrated as feasible, will allow us to perform comprehensive studies of these systems as a function of all these parameters and can in principle establish the long awaited structural base line from which further more detailed studies can be performed.

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