

Local structure of guest molecules in gas hydrates - a model study of Kr and Xe clathrates

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Gas hydrates constitute a class of solids in which small molecules occupy cavities inside an ice-like structure. There is enormous scientific and technological interest in understanding the structure, stability and formation mechanism of clathrates. We developed and constructed a variable temperature high-pressure cell for x-rays measurements, which allows in situ studies of clathrate formation or decomposition. We used XAFS and Diffraction techniques to study the evolution of the structure during formation and decomposition. We studied two clathrate structures, structure **I** (Xe) and structure **II** (Kr). We were able to identify the local structure around the guest atom. We identified the rare gas-water complexes that act as precursor to the formation of the crystalline phases. We observed the transformation of the clathrate from structure **II** to structure **I** when Xe is added to Kr clathrates.

Keywords: clathrates, krypton, xenon, diffraction, pressure, hydrates.

Introduction

Gas hydrates (clathrates) are the solids formed from the combination of gases and/or volatile liquids with water. The first observation of this phenomenon dates back to Davy who reported to the Royal Society in 1910 that an aqueous solution of chlorine froze more readily than pure water. Since then clathrates have attracted considerable interest in the scientific community. Hydrate formation takes place when water molecules come into contact with gas molecules (such as methane, propane, Ar, Kr, Xe, etc...) at high pressures and low temperatures. The fundamental system of classification is according to the structure of the host lattice (Jeffrey and McMullan, 1967). The known clathrate hydrates with rare exceptions (structure H, hexagonal) appear in two structures **II** and **I**. Structure **I** is characterized by a lattice parameter of 12 Å with space group Pm3n, there are two types of cages where guest molecules can be accommodated: tetradecahedra and dodecahedra. Structure **II** has a lattice parameter of 17 Å and space group Fd3m, there are two types of cages: dodecahedral and hexadecahedra. In structure **I** there are 46 water molecules per unit cell, by contrast in structure **II** there are 136. The number of large cages in structure **I** is 6 (diameter 8.6 Å) in structure **II** is 8 (diameter 9.46 Å). The number of small cages is 2 (diameter 7.88 Å) for structure **I** and 16 (diameter 7.82 Å) for structure **II**. It seems that the size of the molecules is the most important parameter determining what type of structure the clathrate will have. However, one can not disregard the molecular structure of the guest as well as the polarity in determining the details of the guest host interactions and the mobility of the molecule.

Krypton clathrates has been reported to crystallize in structure **II** and Xe in structure **I**. The van der Waals diameter for Xe is 4.4 Å and for Kr 4.0 Å (Davidson et al, 1998). The average cage radii for the structure **I** are 3.91 Å for the small cage and 4.2 Å for the large cage. We must point out that there is very limited information on local structures in clathrates, to a great extent due to the lack of appropriated analytical tools. Recently (Filipponi et al 1997, Bowron et al, 1998) XAFS were reported of Kr clathrates, they provided the first information on the local structure around the guest atom.

It is clear that our microscopic understanding of the clathrate hydrates is deficient and direct measurements of the local structure must be performed. We performed such measurements using Kr and Xe as our guest molecules. XAFS and Diffraction measurements were performed at the respective K-edges under various conditions of clathrate formation. Our objective was to measure the local structure at the early stages of clathrate formation as function of temperature and pressure. We measured both Kr and Xe, but due space constrain we put our main emphasis in the Kr results.

Experimental

We developed and constructed a variable temperature high-pressure cell (-5 to 50 C and up to 300 bars) for x-rays measurements, which allows in situ studies of clathrate formation or decomposition (details will be published elsewhere). We used this cell at the Basic Energy Sciences Synchrotron Radiation Center (BESSRC) beam lines (12-BM and 11-ID-D) at the Advanced Photon Source for the determination of the structure of gas-water complexes at all stages of clathrate formation. This beam line delivers at 14 keV in a focus beam a flux of 5×10^{11} photons/sec. We used XAFS and Diffraction techniques to study the evolution of the clathrate structure. This information is crucial to understand the microstructure responsible for the formation and stabilization of clathrates. Diffraction techniques provide information on the lattice structure and overall arrangement of the atoms in the lattice, whereas XAFS gives information on the local structure around the guest molecule. We studied pure Kr (Xe) clathrates as well as mixtures of both gases.

Results

Pure Kr (Xe) clathrates: The clathrates were prepared in the high-pressure cell by loading it with distilled water and the appropriate gas pressure. Typical pressures for Kr were from 100 to 200 bars, the cell was shaken and cooled until the clathrate diffraction peaks were observed. Figure 1 shows the Kr-clathrate characteristic structure **II** pattern at 0.2 C and 110 bars. The structure is stable until about 20 C (same pressure), where decomposition starts. The EXAFS data gave Kr-O distances characteristic of the small (3.93 Å) and large cage (4.8 Å) (Sloan 1997). The fit to the data improves if inter-cagdistances are also included, although the interpretation with so many parameters becomes questionable. The Xe clathrates were formed using a similar technique, except that the pressure needed was significantly less. Figure 1 shows the characteristic x-ray diffraction pattern for structure **I** observed in Xe (at 2.2 C and 68 bars).

The Xe-clathrates are very stable and observable well above room temperature. We ran EXAFS spectra of the Xe K-edge, details of which will be published elsewhere.

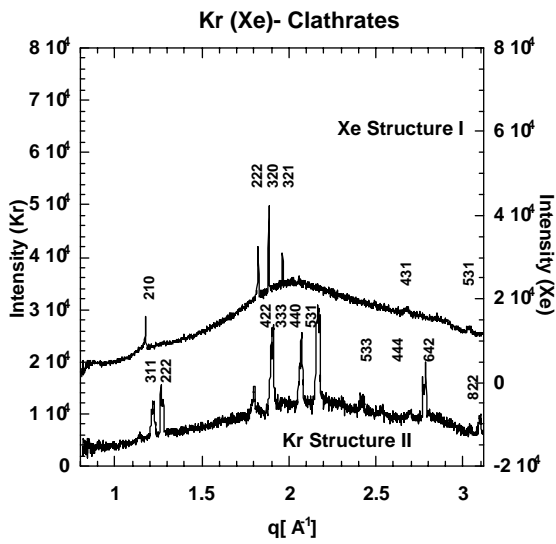


Figure 1. Xe clathrate structure I and KrClathrate structure II.

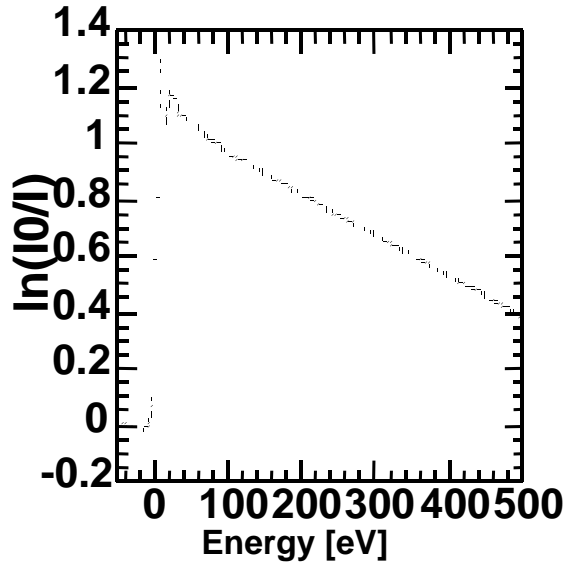


Figure 3. EXAFS spectrum of Kr in H₂O at 140 bars. $\ln(I_0/I)$ versus energy (eV).

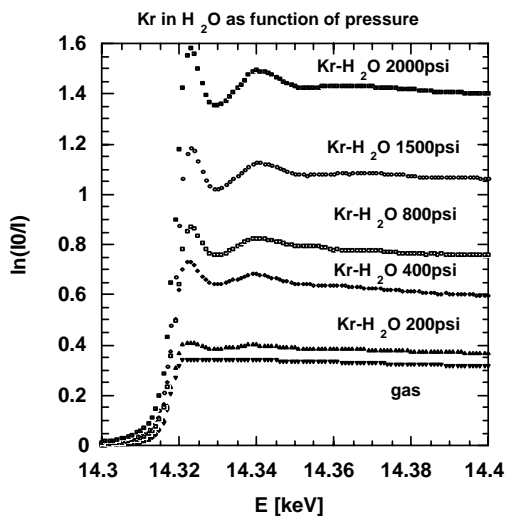


Figure 2. Kr in water vs. pressure.

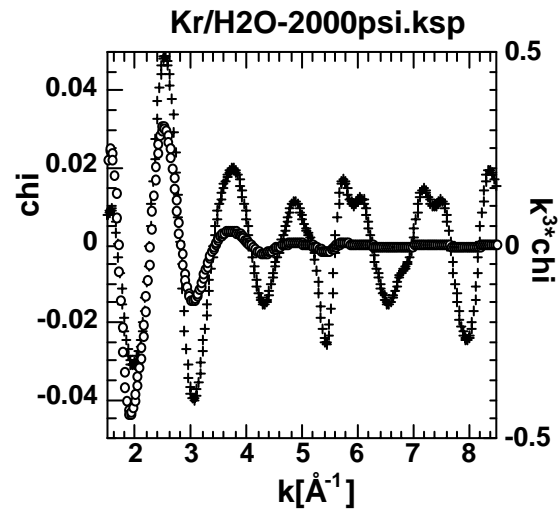


Figure 4. Kr in water at 140 bars, raw data X and $X^3 \cdot k^3$.

Kr in H₂O at room temperature: We loaded the high-pressure cell with distilled water and Kr gas. We measured the XAFS patterns as a function of Kr gas pressure, Figure 2 shows the spectra from pure Kr gas at atmospheric pressure to about 2000 psi (~140 bars). One can clearly observe the appearance of a well defined near edge structure (Filipponi et al 1967). This structure reflects the arrangement of atoms in space about the absorbing krypton. There are no bound state transitions possible for the Kr inside the water cages, the observed resonances are attributable to continuum state effects. This is reflected both in the fact that the edge position does not shift and that discrete electronic transitions are absent. They are very similar in magnitude position and shape to the resonances observed in solid krypton (Kutzler et al, 1983). So the observed shape is solely due to cage formed around the krypton atom due to the van der Waals forces. The quantity of such local cages in the water solution is strongly a function of gas pressure. When the temperature is lowered the cages start to interact and the clathrate structure forms. In our experiments there was no evidence of long range order at room temperature. The EXAFS analysis gave a distribution of sizes that deviate from the pure clathrate, Kr-O distances varies between 3.2 to 7.2 Å. This is an indication that the cages around the guest atom are not symmetric.

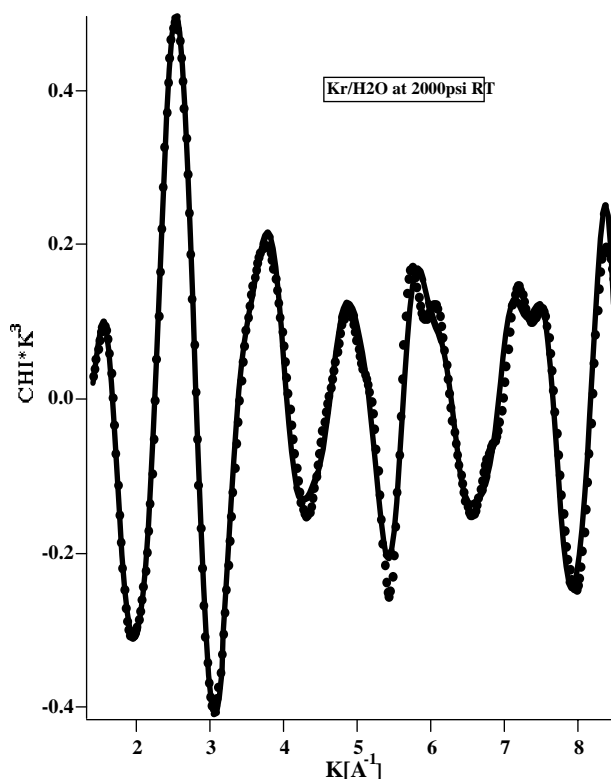


Figure 5. Fit to the EXAFS data for Kr in H₂O at 24 C and 140 bars.

We show in figure 3 the the EXAFS spectrum for Kr in water at 140 bars. The raw data for X and $X \cdot k^3$ for the Kr sample in water at a pressure of 140 bars (2000psi) at room temperature. The data is shown after background subtraction. The data was collected in transmission over a long period of time in order to obtain a good signal to noise ratio. The beam line where the data was collected delivers 5×10^{11} photons/sec at 14.4 keV. Figure 5 shows the fit to the data assuming that only Kr-O are involved, the radial distribution function varies from 3 to 8 Å, with other distances becoming effectively zero. We assume a coordination number characteristic of the small cages, however heavily weighted by the Debye-Waller factor. In the analysis we used a Poisson distribution of interatomic distances inside the cage in order to take into consideration the disorder induced by the water in solution.

Mixtures of Kr and Xe: We prepared samples of Kr/Xe clathrates for different gas loading. We observed that already for 2% Xe loading the crystal structure was **I**. The pressured required were in the same range as for the pure clathrates. EXAFS analysis of the data reveals that the cage Kr-O distances are those of structure **I**, this is more obvious for the large cage (4.35 Å vs 4.75 Å). Consequently a small amount of Xe is enough to stabilize structure **I** and force the Kr lattice to change symmetry.

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