Ordering and Clathrate Hydrate Formation in Co-deposits of Xenon and Water at Low Temperatures

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Abstract: Local ordering in co-deposits of water and xenon atoms produced at low temperatures can be followed uniquely by ^{129}Xe NMR spectroscopy. In water-rich samples deposited at 10 K and observed at 77 K, xenon NMR results show that there is a wide distribution of arrangements of water molecules around xenon atoms. This starts to order into the definite coordination for the structure I, large and small cages, when samples are annealed at ~140 K, although the process is not complete until a temperature of 180 K is reached, as shown by powder X-ray diffraction. There is evidence that $Xe \cdot 20\,H_2O$ clusters are prominent in the early stages of crystallization. In xenon-rich deposits at 77 K there is evidence of xenon atoms trapped in $Xe \cdot 20\,H_2O$ clusters, which are similar to the small hydration shells or cages observed in hydrate structures, but not in the larger water clusters consisting of 24 or 28 water molecules. These observations are in agreement with results obtained on the formation of Xe hydrate on the surface of ice surfaces by using hyperpolarized Xe NMR spectroscopy. The results indicate that for the various different modes of hydrate formation, both from Xe reacting with amorphous water and with crystalline ice surfaces, versions of the small cage are important structures in the early stages of crystallization.

Keywords: clathrates • crystal growth • hydrates • ice • NMR spectroscopy • water chemistry • X-ray diffraction

Introduction

The organization of water molecules into ordered arrangements from amorphous precursor states at low temperatures is of considerable interest.[1–7] Our specific interest is the effect of small foreign atoms or molecules on such ordering processes.[5–7] The final product is then a crystalline clathrate hydrate[8–10] with guest atoms or molecules trapped in well-defined cages, rather than the usual bulk ice phase. Previously, we have shown that the crystallization of X-ray amorphous hydrate precursor phases proceeds in a very different manner depending on their mode of preparation; the vapor-deposited THF–water crystallizes directly, whereas the hyperquenched THF–water solutions first phase-separate into cubic ice and solid THF before forming the hydrate.[11] Also, vapor deposition followed by annealing, is one way of forming hydrates of reactive species that hydrolyze in aqueous solution, for example, nitric oxide and formaldehyde.[6b, 7]

An intimate, but amorphous, mixture of the two different molecular species can be produced by slowly co-depositing their respective vapors onto a very cold surface.[12] On progressively warming the co-deposit to higher temperatures, the changes that take place can then be monitored by employing a number of suitable techniques. Previously, Devlin and co-workers have used vibrational spectroscopy to study clathrate formation in vapor-deposited thin films.[12–14] Hallbrucker and Mayer have also observed the formation of crystalline clathrate hydrates on exposing vapor-deposited amorphous ice or cubic ice (Ic) to O_2, N_2, Ar, or CO at pressures of 1 atm and temperatures above 190 K by using X-ray powder diffraction and calorimetry.[6a] It should be noted that X-ray powder diffraction, as used above, probes the long-range order in the vapor deposits. Vibrational spectroscopy primarily relies on identifying band shapes and positions in samples in which the formation of clathrates is certain and relatively complete; fingerprint patterns also exist, which can be used to infer the existence of clathrate hydrates. In this study, we use ^{129}Xe NMR as a probe of local order, and also X-ray powder diffraction to follow the development of long-range order in the vapor deposited bulk solids.

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It is particularly useful that the xenon atom can function as a guest molecule for structure I clathrate hydrate,[8] while at the same time it is an excellent NMR probe sensitive to local order.[15–17] Experiments with hyperpolarized xenon on ice surfaces have shown that the thin hydrate layer which forms on the ice surface also has a predominance of structures akin to small cages ($Xe \cdot 20\,H_2O$) during the nucleation phase and before rapid hydrate growth starts.[17b,c] We have prepared co-deposits of xenon and water at low temperature from the vapor phase, and followed the development of local- and long-range order that results when the samples are annealed at progressively higher temperatures. Recently, there has been an increased interest in the mechanism of hydrate nucleation and growth of hydrates, which exist both naturally[18, 19] and in pipelines utilized for hydrocarbon transport,[20] as well as extra-terrestrial gas hydrates conjectured to exist in comets and the outer planets.[21, 22]

Results and Disussion

Xenon is a highly inert, but quite polarizable atom. These properties make Xe an ideal NMR probe of the atomic environment.[24] The first spectra reported for xenon atoms trapped as a guest in a solid lattice already demonstrated the fact that the smaller the available space occupied by a xenon atom in the lattice, the larger the shift downfield from that of an isolated xenon atom.[15–17] Spectra obtained for xenon trapped in three clathrate hydrate structures show the trend mentioned above, as well as the presence of an anisotropic shift for xenon atoms in nonspherical cages (Figure 1).[17a] The spectra clearly give structure-sensitive and site-specific information.[25, 26] For a structure I hydrate, the low field line at 238 ppm (shifts are given relative to the chemical shift of the infinitely dilute xenon gas) represents a shell of 20 water molecules around Xe in the form of a 5^{12} cage at an average Xe–O distance of 0.391 nm, and the high-field line with an isotropic chemical shift of 142 ppm represents a 24 water molecule shell around xenon in the form of a $5^{12}6^{2}$ cage at an average distance of 0.433 nm.[17a] The spectra provide a direct calibration of the chemical shift in terms of the radius of the trapping site[17a] (-5.147×10^{-4} nm ppm^{-1}).

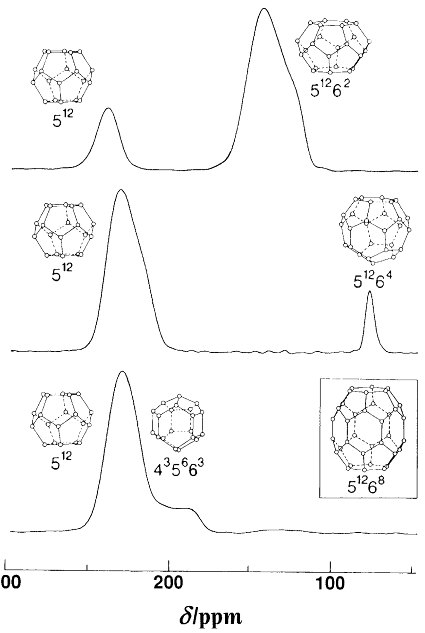

Figure 1. ^{129}Xe NMR spectra of xenon trapped in the cages of strucure I hydrate (top), a butane–xenon structure II hydrate (middle), and a bicyclo[2.2.2]oct-2-ene-xenon structure H hydrate (bottom) recorded at 77 K. The hydrate cages associated with each of the ^{129}Xe signals are indicated.

Typically, the behavior observed was very different for xenon- and water-rich deposits. Firstly, we describe the latter. It should be noted that although the annealing behavior was very similar for these samples, the spectral line width did vary from sample to sample depending on the exact conditions of preparation and composition. Figure 2 shows ^{129}Xe NMR spectra obtained for the 1:6 Xe/H_2O vapor co-deposit. Spectra on the left of Figure 2 were taken with polarization transfer[23] and therefore represent xenon atoms with proton neighbors, those on the right of Figure 2 were recorded from the Bloch decay, in which all of the xenon atoms are observed. Annealing up to 135 K reveals a single, very broad line centered at 203 ± 5 ppm, with a width at a half maximum of 140 ppm. These spectra indicate the presence of a wide distribution of xenon environments, with an average radius of 0.409 nm for the xenon trapping sites. There is no evidence of a signal due to bulk solid xenon, which should give a peak at 317 ppm. This is, as expected, from the amorphous nature of the deposit, which is confirmed by the presence of only diffuse scattering in the corresponding X-ray powder diffraction pattern (Figure 3).

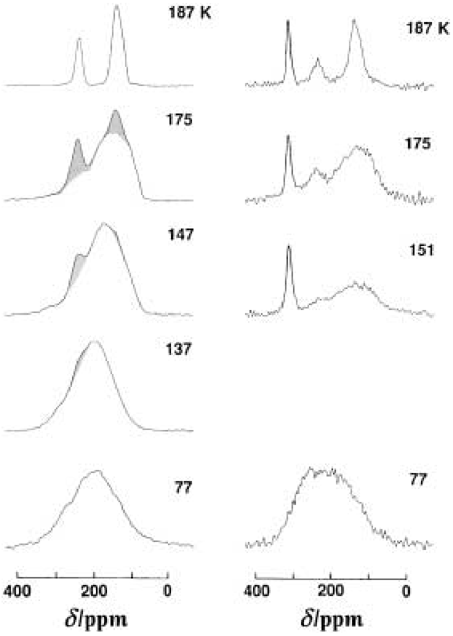

Figure 2. ^{129}Xe NMR spectra at 77 K of a 1:6 Xe/H_2O co-deposit as a function of annealing temperature. Spectra obtained with ^{1}H-^{129}Xe cross-polarization and from Bloch decays are shown on the left and right, respectively. Shaded areas approximate the Xe populations in large (24 water: ~150 ppm) and small (20 water: ~230 ppm) cage envirionments.

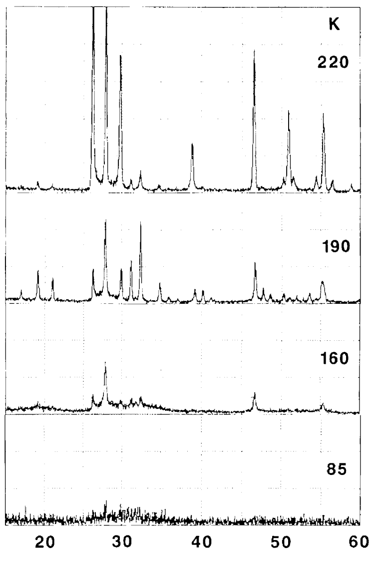

Figure 3. X-ray powder diffraction patterns of the 1:6 Xe/H_2O co-deposit as a function of annealing temperature.

When the co-deposit is annealed above 140 K, redistribution of intensity occurs (Figure 2). The total xenon spectrum now shows a line for solid bulk xenon, this indicates that phase separation has occurred. This reaction evidently accompanies the transitions of some of the amorphous ice, which is reported to undergo a glass transition in the 124–135 K region and a transformation to ice Ic in the 135–160 K region.[5, 6] The X-ray powder diffraction pattern at 160 K confirms the presence of ice Ic. Our main interest, however, is in the remainder of the deposit, that is, the intimately mixed water/xenon portion of the deposit in which the water molecules do not transform to cubic ice. In the 140–175 K range, the broad xenon NMR line first develops an asymmetry, then splits into a broad main peak and shoulder; this shows a gradually increasing separation, primarily due to line narrowing. This is perhaps because of a gradual organization of the water molecules around the xenon atoms into the coordination pattern observed for the crystalline structure I hydrate. In the cross-polarization spectra on the left of Figure 2, it can be seen that signals from Xe atoms in 20-water hydration shells become prominent much more quickly than Xe atoms in the larger 24-water molecule shells, indicating the important role of the small-cage environment in the nucleation-crystallization environment as seen before from surface films.[17b,c] The width of the lines reflect the fact that even though the coordination numbers may be the same as in a fully crystalline sample, there are considerable variations in the Xe–O distances. Unfortunately, there will be an unknown small contribution to the line width from chemical shift anisotropy. If we ignore contributions from anisotropy, for the more spherical of the two cages, an estimate of the distribution in Xe–O distances can be made from the line width. The line width decreases from 42 to 19 ppm as the temperature increases from 175 to 187 K. This corresponds to a decrease in the width of the Xe–O distance distribution of 0.012 nm, or ±0.006 nm about the expected single site value. The slightly different pictures one gets from the cross-polarization and the Bloch decay spectra, reflect the individual characteristics of the two experimental methods: the importance of nearness to protons for the cross-polarization experiment, and a sufficiently short relaxation time for the Bloch decay experiment.

The X-ray powder diffraction patterns also indicate a developing, but incomplete long-range order. For instance, the reflections near $2\theta = 20^\circ$ that are absent at 77 K exhibit only weak, broad lines at 140 K, but are quite distinct at 170 K. Perhaps the best description of the mixed deposit in this temperature region is a pseudo-crystalline clathrate, since both the long-range and local order, as present in this material, are imperfect. A final sharpening of the spectral lines occurs only above 175 K, an event which may well correspond to the phase transition assigned by Hallbrucker and Mayer to clathrate formation in the ice–O_2, and ice–N_2 systems.[6a] The kind of behaviour illustrated here is quite distinct from that observed by Devlin and co-workers for co-deposited thin films, in which the crystallization process was observed to occur at around 130 K.[11–13] This difference can be attributed to the nature of the guest molecules in the co-deposits. Only those guests that are able to promote water molecule reorientation, presumably through the injection of Bjerrum L defects into the lattice, appear to be able to induce crystallization at 130 K.[8, 27] The crystallization process apparently requires reorientational freedom of the water molecules and/or proton transfer. In the absence of defect-inducing guest molecules, the recrystallization process cannot occur until the thermal population of defects is sufficiently high, apparently only at temperatures above about 175 K. We have confirmed with ^1H NMR spectroscopy that isolated water molecules in co-deposits of H_2O and D_2O remain intact on annealing up to about 170 K.[28] Above this temperature there is a significant conversion to HDO on a timescale of minutes. For the xenon–water system, or other systems of water and nonpolar guests, there would appear to be a phase, intermediate in order between amorphous and crystalline, designated as a pseudo-crystalline clathrate hydrate.

In xenon-rich deposits the behavior is remarkably different. The ^{129}Xe spectrum of the highest ratio sample, 5:1 xenon–water, shows that the deposit was probably not amorphous (Figure 4). The main Xe peak is essentially at the crystalline xenon position although its line width, 14.5 ppm, is greater by ~6 ppm than that for crystalline xenon. This broadening is most likely due to the presence of water clusters inside the solid xenon. The main peak shows two side peaks at 288 and 238 ppm. Cross-polarization experiments have confirmed that the side peaks indeed are due to xenon atoms with near-neighbor water molecules. The line that shifted the least from the crystalline xenon position can be taken as arising from bulk xenon atoms next to water molecules. On the other hand, the line at 238 ppm has the correct chemical shift for xenon atoms inside a 20 water molecule cage, that is, small cages similar to those observed in structure I (5^{12}), II (5^{12}) or H (5^{12}, $4^3 5^6 6^3$).[17a] We note that there is no evidence for resonances near 142 or 76 ppm, the characteristic shifts for xenon trapped inside the 24 ($5^{12}6^2$) and 28 ($5^{12}6^4$) water molecule cage clusters. At first view this may be somewhat surprising, because, under equilibrium conditions the structure I hydrate

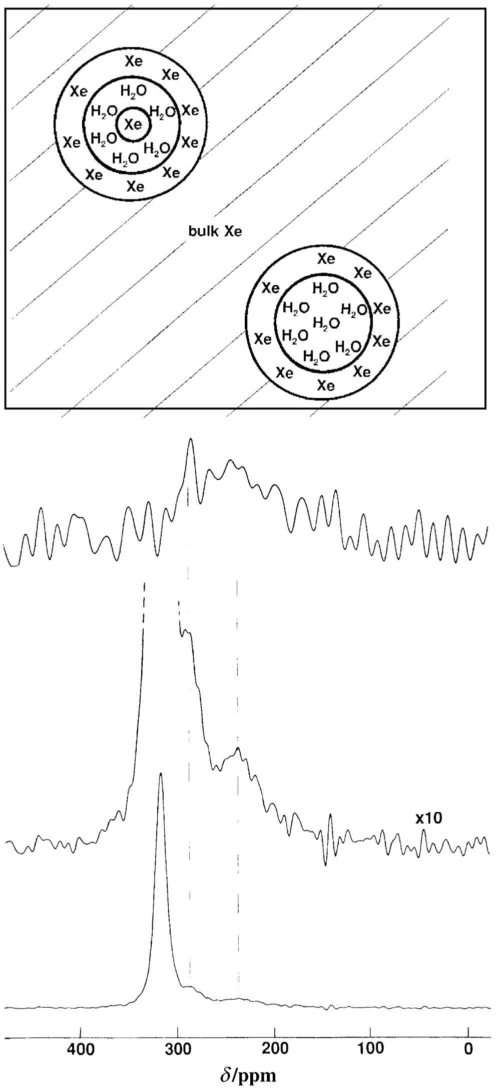

Figure 4. ^{129}Xe NMR spectra at 77 K of a 5:1 Xe/H_2O co-deposit. The top spectrum was recorded with ^{1}H cross-polarization, and shows only xenon atoms with nearest neighbour water molecules. The inset shows the only Xe atoms that should be visible in the top spectrum: Xe atoms inside water clusters, and Xe atoms surrounding water clusters.

large cage is completely occupied (within experimental error), whereas, one quarter of the small cages are empty.[15, 25] However, this illustrates the fact that the stability conditions for the solid-crystal lattice on the one hand, and isolated individual cages on the other, are quite different. Calculations have shown that the individual empty 5^{12} cages are no more stable than clusters of 19 or 21 water molecules,[27] but both calculations[29] and experiments[30] suggest that H_3O^+ can stabilize a cluster of 20 water molecules. The individual larger cages, $5^{12}6^{2}$, $5^{12}6^{4}$, and $5^{12}6^{8}$ are expected to be even less stable than the 5^{12} cage, as the ratio of hexagonal to pentagonal faces, and hence the strain energy, increases. However, it should be emphasized that in the present instance the "cage" is not isolated, in the sense that it is surrounded by a solid matrix of Xe atoms and possibly a few water molecules. On the other hand, within the framework of the van der Waals and Platteeuw model[31] for clathrate hydrates, at equilibrium the minimum occupancy of the cages is linked to the free-energy difference between the empty clathrate and ice. The instability of the empty lattice has also been confirmed by molecular dynamics simulations.[32] Furthermore, recent molecular dynamics simulations have shown that $Xe \cdot 20\,H_2O$ clusters arise quite naturally in Xe – water mixtures.[33]

These results suggest that a hydration cage of 20 water molecules has a certain natural stability when it contains a guest, and that it may exist as a hydrate precursor or nucleator. In the case of xenon, and other structure I hydrate formers, it is clear that the guest populations must re-adjust themselves on going from more or less isolated hydration cages to an ordered crystal lattice, as the stability considerations for each entity (isolated cages vs a crystal lattice) are entirely different. It is also relevant to note that the other two major families of hydrate structures, II and H, can be constructed from face-shared 5^{12} cages, so that the notion of lattice assembly might be extended to hydrate frameworks that involve guests which are too large to fit into a 5^{12} cage when there are small help gas molecules in the small cages. Whether this is a tenable model for the formation of hydrates in which there are no small cage guests, is a moot question. However, this can be checked by comparing nucleation and growth rates of Xe with those of larger guests that cannot occupy small cages. If one considers that there is some evidence that the oxonium ion can act as a stabilizing guest for a 5^{12} cage, perhaps the detailed water chemistry also becomes important in considering molecular models for hydrate nucleation and growth. Of course, Xe is a very specific case, since the van der Waals' radius of Xe is a near-perfect fit for the 20 water-molecule shell. Larger guests may well have somewhat different mechanisms; however, if a small cage is critical in the hydrate crystallization process, this should be reflected in the nucleation statistics or induction times.

The role of clathrate hydrates in the solar system has been considered before,[21, 22] and this was discussed recently by Hallbrucker and Mayer.[5] With regards to the existence and formation of clathrates in the solar system, our results suggest that clathrate hydrate formation at temperatures as low as 35 – 45 K, as suggested by Bar-Nun et al.,[34] is unlikely. On the other hand, our results do indicate that clathrate formation starts at temperatures as low as 140 K for Xe, significantly lower than the 200 K reported by Hallbrucker and Mayer,[5] although the product may be a poorly ordered material. One might expect both the reactions between vapor-deposited solid water and guest vapor, as well as the annealing processes documented here, to be important processes under conditions typical of the outer solar system.

Experimental Section

Co-deposits of H_2O and Xe were formed by mixing metered quantities of the vapors, and then condensing the mixture onto a cold block at 10 K in an evacuated chamber over a period of several hours. ^{129}Xe NMR spectra were obtained at 77 K by using Bruker CXP-180 and MSL-200 NMR spectrometers. Samples were sealed in 10 mm OD Pyrex tubes and placed in the coil of a double resonance probe tuned to ^{1}H and ^{129}Xe frequencies, which were immersed directly into liquid nitrogen. Some spectra were obtained through polarization transfer from protons,[23] which then discriminates against xenon atoms without near-neighbor protons.

Other spectra were derived directly from the proton-decoupled Bloch decay, which samples all of the xenon atoms present, providing that the relaxation delays are sufficiently long. Samples were annealed at constant temperature in slush baths for a period of 10 minutes, after which they were quenched in liquid nitrogen and re-inserted into the NMR probe.

X-ray powder diffraction patterns were recorded at several temperatures on a Rigaku $\theta-\theta$ diffractometer equipped with a graphite monochromator and a Paar temperature control unit. The radiation used was $Cu_{K\alpha}$ (0.15405 nm).

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