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ABSTRACT

Recently, a new gas hydrate structure has been discovered. This structure, sX, is unique in a sense that it is so far the only gas hydrate with chiral channels. It is formed by hydrogen-water or carbon dioxide-water mixtures at pressures above 0.300 GPa, and it has been shown that it is the only clathrate hydrate that is refillable with hydrogen. This property makes it a possible storage material for gases. By analyzing neutron diffraction data and calculations based on density-functional theory, we show that sX is also refillable with nitrogen; the guest:host ratio will be shown to be 2.6(3). Furthermore, we report sX's decomposition behavior and give evidence that it undergoes several transitions into the exotic hydrates sH and sIII that have not been observed at these pressure and temperature conditions—before forming the stable nitrogen hydrate sII.

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I. INTRODUCTION

Water has a very complex phase diagram with at least 18 recorded crystal structures,^{1–6} several amorphous^{7–10} and one, possibly two, liquid phases¹¹—depending on temperature and pressure. When incorporated into binary mixtures, additional rich complexity is observed. At present, there are at least ten guest host structures reported in which a small “guest” molecule is confined in a “host” lattice consisting of water.^{12–15} Some of these are based on cages, the so-called clathrate hydrates where the water network forms cagelike structures (from *kleithron*, Greek: door bar). Others are based on ice structures with the guest molecules filling holes in a water network based on a known ice structure,¹⁴ and another, sX, is based on a network of spiral channels.^{15–17}

The structures are stabilized by the interplay between hydrogen bonds and hydrophobic interactions.¹⁸ The host network is held together by hydrogen-bonded water molecules, while the guest-host interaction is mainly of a hydrophobic nature (exceptions exist¹⁹). Hence, gas hydrates provide the means to probe van der Waals, hydrophobic, and hydrogen-bond forming interactions and their interplay.¹⁸ These forces are crucial in many biochemical processes such as protein and DNA folding, protein-ligand interaction, formation of the cell wall, and the overall structure of the

cell.^{20,21} Gas hydrates provide relatively simple systems against which to test models of intermolecular potentials.²² Furthermore, they also occur commonly in nature, e.g., methane clathrate hydrate present on the ocean floor makes up most of Earth's methane reserve.^{18,23,24} Methane hydrate is also believed to have been the dominant methane-containing phase in the nebula from which the outer planets and their satellites formed (for example, Enceladus and Titan²⁵). Finally, gas hydrates have potential technological applications, for example, in the transport and storage of gases, e.g., hydrogen.²⁶

Among the hydrate water networks, sX, first discovered as part of the C₀ structure of hydrogen hydrate,²⁷ stands out: it is chiral, has channels rather than cages, and is not based on a stable ice structure (such as the filled ice II structure²⁸), and its network does not have an analog in either silica or zeolite structures.^{15,29} It does, however, exist in some ternary Zintl compounds and has been suggested as a metastable group-14 structure.^{30–32} The structure proposed initially was based on channels that contained sites partially occupied by nonhydrogen bonded water molecules.²⁷ Based on the observed high mobility of hydrogen in this structure²⁷ and molecular-dynamics modeling, Smirnov and Stegailov proposed what emerged to be the correct structure: they suggested that the water molecules in the channels were

in fact nitrogen molecules that had been absorbed from the liquid storage medium between recovery and the diffraction measurement.³³ Subsequently, del Rosso *et al.* were able to empty C_0 of hydrogen and to identify the structure as a new form of ice, ice XVII.^{3,16} Finally, Amos *et al.* found that sX also exists in the carbon dioxide:water system and determined the full structure of both hydrogen and carbon dioxide hydrates *in situ* using neutron diffraction.¹⁵

Due to the high guest-host ratio, the reversibility of the filling and emptying, and the high mobility of hydrogen in the cavities, the sX/ice XVII system has been proposed as a possible hydrogen storage material.^{34,35} Other possible applications, however, have not been discussed. With its channel structure, and high surface area, ice XVII resembles activated charcoal and could therefore be used as a low-temperature molecular sieve. Here, we show using high-pressure neutron diffraction data that ice XVII can, indeed, absorb nitrogen molecules. Furthermore, we show that nitrogen sX undergoes a series of transformations into other, exotic, hydrate types before forming the stable sII structure.

II. METHODS

We have conducted this experiment in an aluminum gas pressure cell at the PEARL beamline, the dedicated high-pressure powder instrument at the ISIS neutron source at the Rutherford Appleton Laboratory (RAL, Oxfordshire, UK).³⁶ This instrument has access to a d -spacing range out to beyond 4 Å, which is necessary to record sX's 101 Bragg reflection at 4.1 Å. This peak is very sensitive to the guest site occupation. The analysis of the diffraction patterns was carried out by either the Rietveld or LeBail profile refinement using the GSAS-II crystallographic software package.³⁷

Enthalpy calculations based on density functional theory (DFT) were performed using the CASTEP code³⁸ on sets of approximate

sX structures with a range of tractable guest-host ratios as well as fully filled nitrogen hydrate III (NH-III). Exchange-correlation effects were described within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional³⁹ and ultrasoft pseudopotentials as generated “on-the-fly” by CASTEP with radii cutoffs of 1.1 Bohr for oxygen and nitrogen and 0.6 Bohr for hydrogen. Geometry optimizations were performed with plane wave cutoffs of 1000 eV and a Monkhorst-Pack⁴⁰ k-point spacings of no more than $2\pi \times 0.04 \text{ \AA}^{-1}$. The calculations were performed on water networks with hydrogen arrangements to give a zero net dipole moment per unit cell. To calculate stable compounds, we compare enthalpy values, $H = U + PV$, where U is the internal energy per molecule and P and V are the pressure and molecular volume, respectively. To compare with a decomposition into the pure molecular phases, we also perform calculations on ices XI, IX, XV, and VIII and the relevant phases of α -, γ -, and ϵ - N_2 .⁴¹ The nitrogen hydrate compounds which form the convex hull of the relative formation enthalpies,

$$\Delta H(x) = H((H_2O)_x(N_2)_{(1-x)}) - xH(H_2O) - (1-x)H(N_2), \quad (1)$$

are thermodynamically stable against decomposition.

Deuterated water (D_2O)⁴² was frozen to produce ice I_h and ground under liquid nitrogen to a fine powder. The powder then was filled into a cooled hydrogen-compatible gas cell at 77 K and pressurized with hydrogen gas to 0.300 GPa. To control the temperature in the cell during the experiment, an ILL pattern “Orange” helium cryostat was used. Upon heating to 195 K at 0.300 GPa, the $H_2 - I_h$ mixture undergoes transitions first to the C_{-1} hydrate at 160 K and than to C_0 (H_2 -sX) above 180 K.^{43,44} After the full transformation to C_0 , the sample was cooled to 80 K and the pressure was released. It is well known that ice XVII can easily be formed by pumping off the hydrogen in sX; however, the same can be achieved by heating the hydrogen hydrate at ambient pressure to 130 K.⁴³

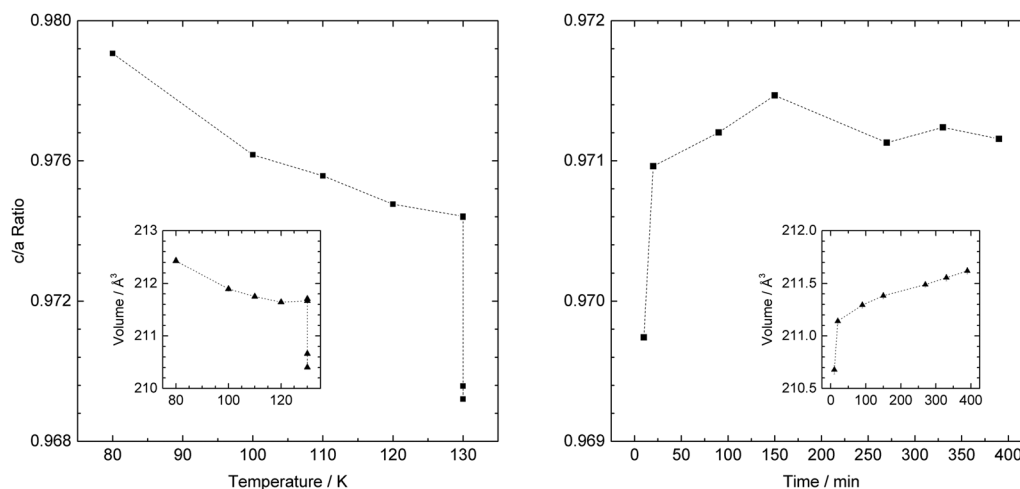


FIG. 1. Left: The c/a ratio and overall unit cell volume of hydrogen sX as a function of temperature (the three values at 130 K were recorded over a period of about 7 h). The shrinking of the overall volume indicates the removal of hydrogen from the channels. Right: The c/a ratio and overall unit cell volume of hydrogen sX as a function of time. The increase in volume (primarily along the c -axis) indicates the uptake and incorporation of nitrogen into the chiral channels. In both plots, the uncertainties are smaller than the symbols and hence, error bars have been omitted.

As the hydrogen left the structure, the volume of the unit cell started to decrease, indicating the emptying of the channels in *sX*. To ensure that the starting material for the experiment is pure ice XVII, diffraction patterns were collected every hour. The transformation was considered complete after about 12 h, at which point the volume of the unit cell did not shrink any further with time (see the left panel in Fig. 1). In addition, Rietveld refinements were carried out on the diffraction pattern; the hydrogen ratio in the channels was refined to a non-traceable amount.

III. RESULTS AND DISCUSSION

The emptied C_0 hydrate (ice XVII) was then pressurized with nitrogen to 0.018 GPa (the pressure of a full gas bottle) at 130 K. Uptake of gas was observed. Additional gas had to be added to the system regularly to maintain the pressure, and an expansion of the *c*-axis of *sX* (the axis that contracts most on removal of hydrogen) was observed—see the right panel in Fig. 1.

After ~ 7 h, the changes in pressure and lattice parameters appeared to have saturated and data were accumulated for about 5 h for full structural analysis. The results of a Rietveld profile refinement are shown in Fig. 2, together with the refined crystal structure. We were able to fit the known pattern of the *sX* structure to our data. As in the CO_2 and H_2 hydrates based on *sX*, the space group is $P6_122$ or $P6_522$. From the refinement, we were able to obtain the lattice parameters $a = 6.240(3)$ Å and $c = 6.065(2)$ Å. According to the established numbering methodology, we propose the name nitrogen hydrate V (NH-V) for this new *sX*-type hydrate. The resulting structural parameters for NH-V are summarized in Table I. We find a nitrogen-water guest-host ratio of 1:2.6(3).

To model the disorder in the H-bonded water lattice, a 2-site model was used; two deuterium atoms with an occupancy of 0.5 were placed along the O–O axis, one representing the covalent O–D bond and the other the $\text{D}\cdots\text{O}$ hydrogen bond.

As shown by del Rosso *et al.*, guest molecules in the *sX* structure are highly mobile and are not locked into one position.^{34,35} This results in a rather continuous nitrogen density along the helical channels. In order to model this continuous nitrogen occupancy in the channels, two nitrogen atoms were placed on two 12-fold sites.

TABLE I. Unit cell lattice parameters (*a* and *c*), oxygen and nitrogen fractional coordinates (*x*, *y*, *z*), occupancies, and multiplicities and Wyckoff positions of the sites for NH-V from neutron diffraction (values obtained at 0.018 GPa and 130 K). The space group of NH-V is either $P6_122$ or $P6_522$ with lattice parameters of $a = 6.240(3)$ Å and $b = 6.065(2)$ Å.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}	Occ.
O (6b)	0.764(5)	0.5270(18)	0.250(9)	0.022(15)	1.00(0)
D (6b)	0.377(10)	0.071(6)	0.532(4)	0.024(8)	0.50(0)
D (6b)	0.563(8)	0.335(6)	0.458(3)	0.022(9)	0.50(0)
N (12c)	0.957(10)	0.142(14)	0.652(13)	0.05(7)	0.22(4)
N (12c)	0.213(8)	0.065(12)	0.883(12)	0.04(6)	0.16(2)

The difference in the nitrogen occupancy of these two atoms is most likely a result of statistically preferred positions inside the channel.

In addition to this experimental work, DFT simulations were carried out to determine the optimal filling ratio of the channels. The relative enthalpies of formation, $\Delta H(x)$, for a series of NH-V approximants with guest-host ratio 1:*n* ($n = 2, 3, 4, 6$; $x \approx 0.67, 0.75, 0.80, 0.86$) are shown in Fig. 3(a) as a function of pressure.

To estimate the stability of intermediate guest-host ratios, a quadratic is fitted to the formation enthalpies of the four NH-V approximants. The curve segment of the quadratic which forms the convex hull of Eq. (1) corresponds to the most favorable guest-host ratios. For NH-V, guest-host ratios of between 1:2.8 and 1:3 are most stable across the entire pressure range. This can be seen in Fig. 3(b) which shows the composition-pressure phase diagram of nitrogen hydrates. There is a spread of metastable NH-V structures with similar filling ratios indicated by the dotted region. In comparison, similar calculations on H_2 -*sX* (C_0) and CO_2 -*sX* suggest a guest: host ratios of 1:2 and 1:4, respectively, roughly in agreement with experimental findings.¹⁵

Along a fixed stoichiometry of 1:3 $\text{N}_2\text{:H}_2\text{O}$, the calculations predict a transition from NH-III to NH-V at around 2.5 GPa. (NH-III is a tetragonal hydrate, *sT*, in the space group $P4_2/mnm$ and the lattice parameters $a = 6.342$ Å and $c = 10.610$ Å.¹⁴) The latter

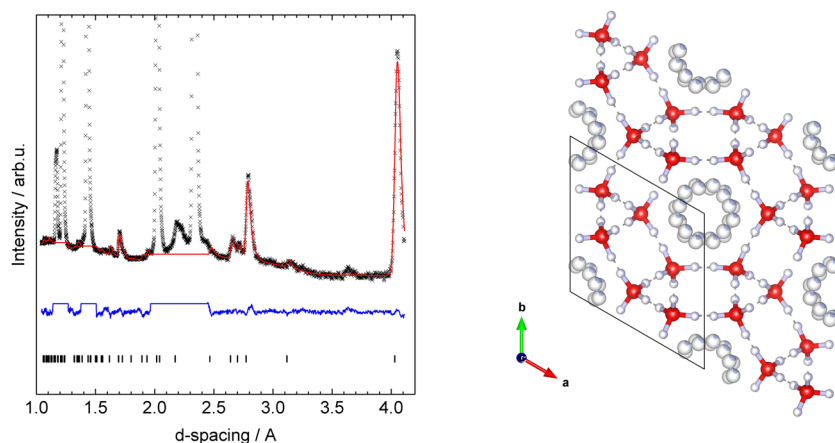


FIG. 2. Left: The results of a Rietveld profile refinement of data collected at 0.018 GPa and 130 K using the nitrogen *sX* structure. Black crosses are measured data points, the red curve gives the calculated pattern, and the blue line represents the difference between observed and calculated profiles. The excluded sections correspond to regions affected by the Bragg reflections of the aluminum pressure cell. Right: Refined structure from the neutron diffraction data with oxygen atoms (red), deuterium atoms (white), and nitrogen atoms (blue). Disorder is displayed by partially colored atoms.

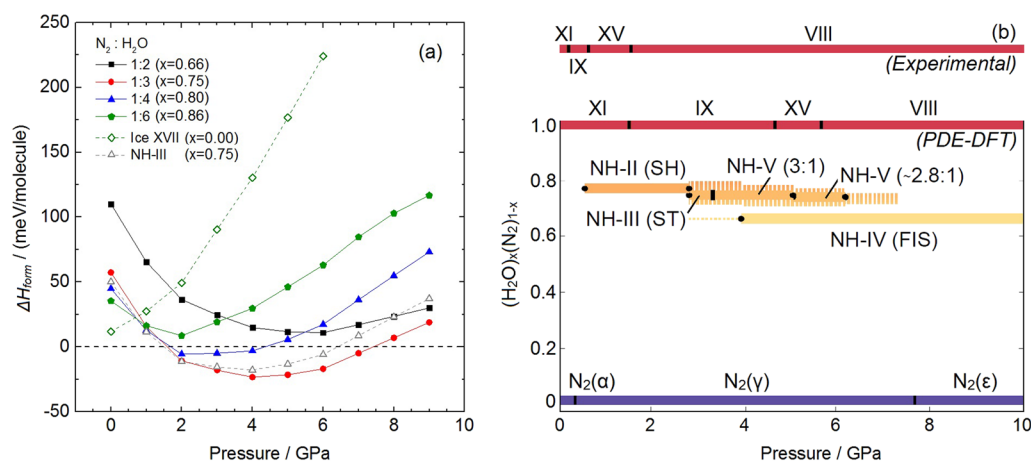


FIG. 3. (a) Relative enthalpies of NH-V with a range of filling ratios against decomposition into pure ice and N_2 calculated from Eq. (1). For comparison, the metastability of pure ice XVII is indicated, as well as the formation enthalpy of NH-III hydrate. (b) Composition-pressure phase diagram of nitrogen hydrates. Solid lines correspond to stable points on the convex hull, and dotted lines correspond to metastable points within 5 meV of the hull. For comparison, the experimental phase evolution of ice is shown along the top.

structure is stabilized by having a smaller molecular volume due to efficient packing of the nitrogen molecules.

The semilocal exchange-correlation functional used for these calculations does not fully account for longer range dispersion interactions which may be present. As a result, the pressure estimations appear higher than seen in experiment, an effect well known for ice.⁴⁵ To illustrate this, we show the experimental low temperature phase evolution of ice in the same pressure range in Fig. 3. However, PBE usually provides at least qualitative agreement with experiment (sometimes much better than that⁴⁶) and taken together with the experimental results provides good evidence for the existence of NH-V.

In the experiment, the nitrogen pressure was then increased to 0.300 GPa at 130 K. This led to changes in the diffraction pattern—the intensity of the peak at 4.12 Å decreased, while a new peak at about 3.64 Å slowly emerged, indicating a structural change in the sample. To speed this process up, the temperature was increased—first in 10 K steps to 160 K under a static pressure of 0.300 GPa, then in larger temperature steps. At every temperature, diffraction patterns were collected for about 1 h each. A pressure drop in the sample chamber upon every increase in temperature was observed, indicating additional gas uptake. In Fig. 4, the respective diffraction patterns upon heating are depicted, with the first, blue curve being the pattern recorded at 0.018 GPa and 130 K. The newly emerging peak at 3.64 Å is close to a d -spacing that would suggest a doubling of the sX unit cell (it would be the 211 peak). Upon closer investigation, however, this theory was proven wrong, and we could identify this peak to belong to the hexagonal clathrate structure sH, a high-pressure phase hitherto only observed above 0.85 GPa.^{18,47} This structure comprises two different small cages and one large cage, which runs the length of the unit cell along the c -axis. The sH structure is found in many simple gas hydrates (for example, Ar, Kr, Xe, methane, and N_2) but generally in the pressure range ~1–2 GPa.^{47–49} Here, the sH structure has the lattice constants $a = 11.82(4)$ Å and $c = 9.82(4)$ Å.

Upon further heating above 160 K (turquoise curve in Fig. 4), the intensity of sH's peaks stayed constant, while the peaks from NH-V (and from the residual ice XVII) decreased. Simultaneously, new peaks belonging to the sII clathrate hydrate structure appeared in the diffraction pattern. Note that only the NH-V peaks disappeared, and the peaks assigned to sH remained. This suggests that sII does not form directly from sH, but rather that it is formed from NH-V. Analogous observations in the H_2 – H_2O system support this hypothesis. Donnelly *et al.* found that hydrogen sX (C_0) transforms into sII upon heating at 0.300 GPa.^{43,44} Furthermore, it would not be surprising that residual ice XVII, a metastable structure, transformed in the presence of a suitable guest into sII as well. The transformation $NH-V \rightarrow sII$ therefore gives a second possible route for the decomposition.^{52,53}

Upon further heating, the N_2 – H_2O mixture undergoes another remarkable transition—the sH peaks start to disappear and another (metastable) phase is formed. This phase could be fitted with the known pattern of a clathrate of the structure III type (sIII). For this purpose, a Rietveld refinement was carried out to match not only the peak positions but also the respective intensities. Hitherto this clathrate type has only been known in bromine-water mixtures.¹³ Type III clathrate hydrate has a tetragonal structure with space group $P4_2/mnm$ and a cell volume of 6300 Å³, the largest known unit cell for a clathrate. The cell consists of 172 water molecules which form 16 14-hedral cavities ($5^{12}6^2$), four 15-hedral cavities ($5^{12}6^3$), and ten dodecahedral cavities (5^{12}). The lattice parameters we obtained from our measurements are $a = 22.914(9)$ Å and $c = 12.003(7)$ Å. Almost 200 years after the first description of bromine hydrate, we show that the sIII structure can serve as a host to a second molecular guest species.^{50,51} For this nitrogen hydrate, we propose the name nitrogen hydrate VI (NH-VI). Finally, as it warms close to room temperature, NH-VI forms the stable clathrate hydrate of type sII. This transition sequence is an excellent example of Ostwald's rule of stages, an empirical law

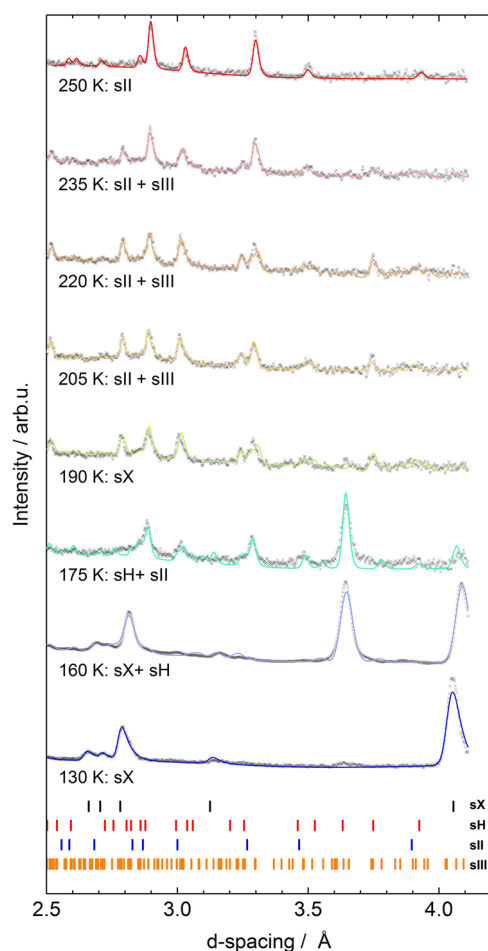


FIG. 4. Neutron diffraction patterns recorded while heating the sample at 0.300 GPa. The first curve (blue) gives the pattern of the pure nitrogen sX. The main components of the respective patterns are from bottom to top: sX, sX + sH, sH + sII, sII + sIII, sII + sIII, sII + sIII, sII + sIII, sII + sIII, and sII. Black crosses are measured data points, and the solid curves give the calculated patterns.

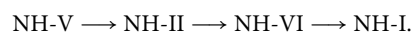
stating that a metastable phase will transform to the stable phase, by passing through metastable phases in order of their Gibbs free energy. All nitrogen hydrates observed in this study are summarized in Table II.

TABLE II. Space group and unit cell lattice parameters (a and c) for the N_2 variants of sX, sH, sIII, and sII at 0.300 GPa.

Hydrate	Space group	a (Å)	c (Å)
NH-V	sX $P6_122$	6.240(3)	6.065(2)
NH-II	sH $P6/mmm$	11.82(4)	9.82(4)
NH-I	sII $Fd\bar{3}m$	17.152(4)	17.152(4)
NH-VI	sIII $P4_2/mnm$	22.914(9)	12.003(7)

IV. CONCLUSIONS

We have shown that nitrogen-water mixtures can form the chiral clathrate hydrate structure, sX. This new nitrogen hydrate (NH-V) is obtained by refilling ice XVII at 130 K. Neutron diffraction data suggest that nitrogen NH-V is hexagonal with space group $P6_122$ or $P6_522$ and lattice parameters $a = 6.240(3)$ Å and $b = 6.065(2)$ Å. Experimentally, a guest:host ratio of 1:2.6(3) per molecule was found, close to DFT calculations that find NH-V stable with a filling ratio of 1:3 for a fixed stoichiometry and 1:2.8 for the minimum of the convex hull fit. The values for the filling ratios obtained from the DFT simulation are well within the error bars of the experimental ones—theory and experiment are therefore in good accordance,



At 0.300 GPa, we found that nitrogen NH-V transforms into the hexagonal NH-II; however, the transition only occurs very slowly. NH-II (sH) then, upon heating, undergoes transitions into NH-VI (sIII) and finally into NH-I (sII) clathrate hydrates. This is somewhat surprising. The sIII structure is an oddity in that it has so far only been observed in the bromine-water system. To find it in a simple gas system such as nitrogen-water is unexpected. Similarly, sH is generally found at pressures above ~ 1 GPa and the ability to form it as part of a cascade of metastable structures at the much lower pressure of 0.300 GPa may be useful technologically.

In addition, we report another possible route for the decomposition of NH-V—heating it at an elevated pressure leads to a direct formation of the stable nitrogen hydrate I (sII),



We have hereby demonstrated that ice XVII is a microporous material that can be loaded with different gases. The unique channel layout of the sX network gives it a large amount of flexibility: the guest gases it can absorb span an unusually large size range (from H_2 via N_2 to CO_2), with the gas uptake ratio adjusting accordingly (from 1:2 to 1:4) to avoid steric repulsion of the guest molecules. At the same time, guest species exhibit high mobility along the channels, which makes determinations of the guest content from diffraction difficult. So far, DFT calculations have proved very useful in constraining the guest-host ratio. If necessary, more nuanced descriptions of the electronic structure, e.g., through local-MP2 calculations, could be applied.⁴⁶

The universality of the sX host network raises the interesting possibility that if ice XVII can be loaded with oxygen (a molecule of similar size to nitrogen but with a triplet ground state), a magnetic sX-based hydrate might be produced. With sufficient cooling, this hydrate might be induced to order magnetically.

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