Electronic Supplementary Information for:

Crystal engineering the clathrate hydrate lattice with NH_4F

Kyuchul Shin[a,b], Igor L. Moudrakovski,[a,c] Mehdi Davari,[d] Saman Alavi, [a,c] Christopher I. Ratcliffe [a,*], and John A. Ripmeester [a]

[a] *National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6.*
[b] *Division of Ocean Systems Engineering, Korea Advanced Institute of Science and Technology, Daejeon, 305-701, Republic of Korea*
[c] *Department of Chemistry, University of Ottawa, Ottawa, Canada K1N 6N5*
[d] *Theoretical and Computational Biophysics Department, Max Planck Institute for Biophysical Chemistry, Am Fassberg 11, 37077 Göttingen, Germany*

1) PXRD Structural Data and Analysis.

Table S1. Atomic coordinates and isotropic temperature factors for the Str. I pure Xe clathrate hydrate at 183 K.

Atom	*x*	*y*	*z*	*B* (Å^2)	*g*	Site
Wa1	0.1826(4)	0.1826	0.1826	4.1(3)	1	16*i*
Wa2	0	0.3078(5)	0.1206(5)	4.2(2)	1	24*k*
Wa3	0	0.5	0.25	6.5(4)	1	6*c*
Xe1	0.25	0.5	0	6.5(1)	1	6*d*
Xe2	0	0	0	1.9(1)	0.99(1)	2*a*

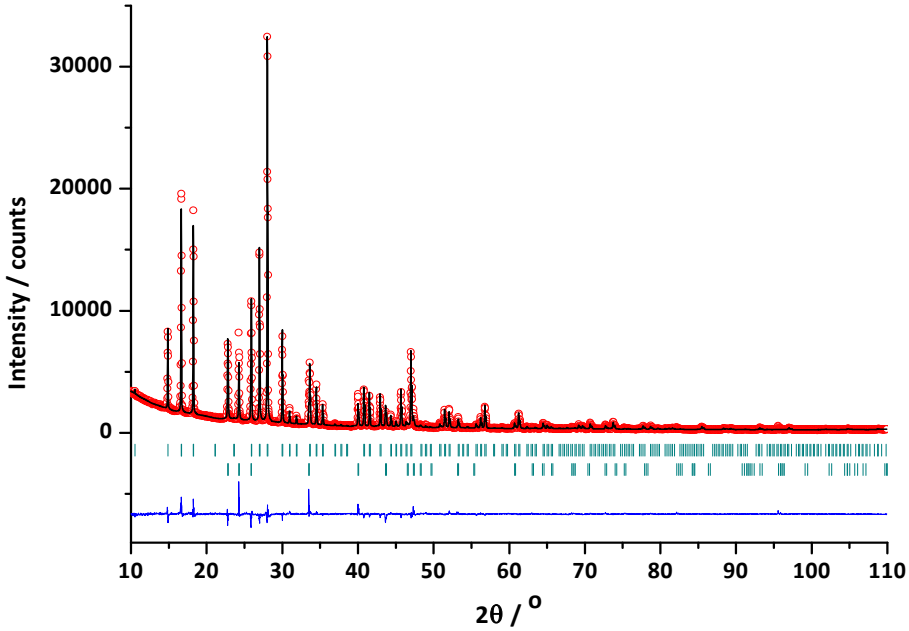

Figure S1. (a) The PXRD pattern of the pure Xe clathrate hydrate at 183 K and the Rietveld refinement results (background subtracted Rwp = 15.4% and χ^2 = 3.75). Tick marks indicate the Bragg positions for Str. I, cubic *Pm-3n* (top), and hexagonal ice, *P6₃/mmc* (bottom). The lattice parameter is 1.19072(2) nm for the Str. I hydrate.

Table S2. Atomic coordinates and isotropic temperature factors for the Str.I Xe clathrate hydrate with 7 mol% NH_4F at 183 K.

Atom	*x*	*y*	*z*	*B* (Å^2)	*g*	Site
Wa1	0.1843(2)	0.1843	0.1843	5.5(2)	1	16*i*
Wa2	0	0.3065(3)	0.1215(3)	5.7(2)	1	24*k*
Wa3	0	0.5	0.25	5.8(2)	1	6*c*
Xe1	0.25	0.5	0	7.5(1)	1	6*d*
Xe2	0	0	0	2.5(1)	0.85(1)	2*a*

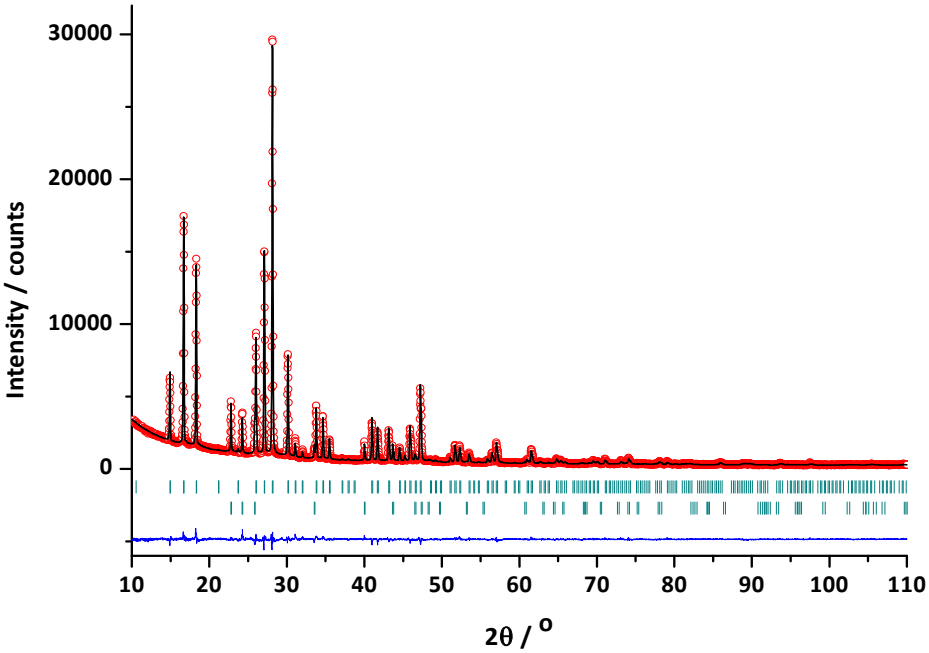

Figure S2. (a) The PXRD pattern of the Xe clathrate hydrate with 7 mol% NH_4F at 183 K and the Rietveld refinement results (background subtracted Rwp = 11.4% and χ^2 = 2.22). Tick marks indicate the Bragg positions for Str. I, cubic *Pm-3n* (top), and hexagonal ice, $P6_3/mmc$ (bottom). The lattice parameter is 1.18550(2) nm for the Str. I hydrate.

Table S3. Atomic coordinates and isotropic temperature factors for the Str. I Xe clathrate hydrate with 15 mol% NH_4F at 183 K.

Atom	*x*	*y*	*z*	*B* (Å^2)	*g*	Site
Wa1	0.1841(3)	0.1841	0.1841	3.3(2)	1	16*i*
Wa2	0	0.3064(4)	0.1194(3)	3.3(2)	1	24*k*
Wa3	0	0.5	0.25	2.1(3)	1	6*c*
Xe1	0.25	0.5	0	6.5(1)	0.99(1)	6*d*
Xe2	0	0	0	4.3(2)	0.65(1)	2*a*

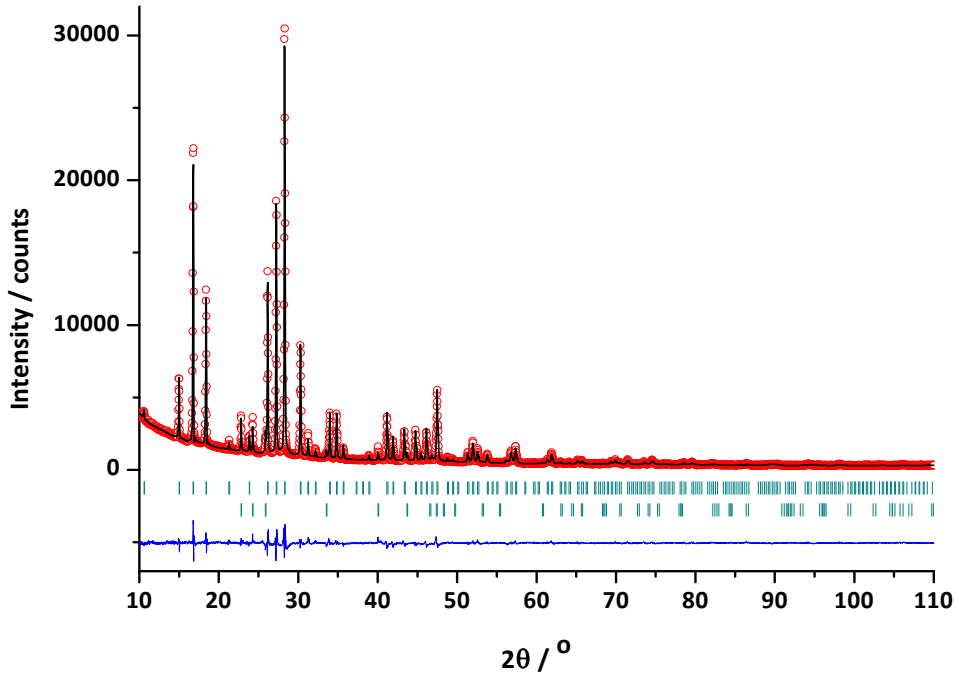

Figure S3. (a) The PXRD pattern of the Xe clathrate hydrate with 15 mol% NH_4F at 183 K and the Rietveld refinement results (background subtracted Rwp = 15.3% and χ^2 = 3.75). Tick marks indicate the Bragg positions for Str. I, cubic *Pm-3n* (top), and hexagonal ice, *P6₃/mmc* (bottom). The lattice parameter is 1.17958(3) nm for the Str. I hydrate.

Table S4. Atomic coordinates and isotropic temperature factors for the Str. I Xe clathrate hydrate with 27 mol% NH_4F at 183 K.

Atom	*x*	*y*	*z*	*B* (Å^2)	*g*	Site
Wa1	0.1844(2)	0.1844	0.1844	4.4(2)	1	16*i*
Wa2	0	0.3077(3)	0.1205(3)	5.6(1)	1	24*k*
Wa3	0	0.5	0.25	5.5(2)	1	6*c*
Xe1	0.25	0.5	0	6.6(1)	1	6*d*
Xe2	0	0	0	2.1(2)	0.83(1)	2*a*

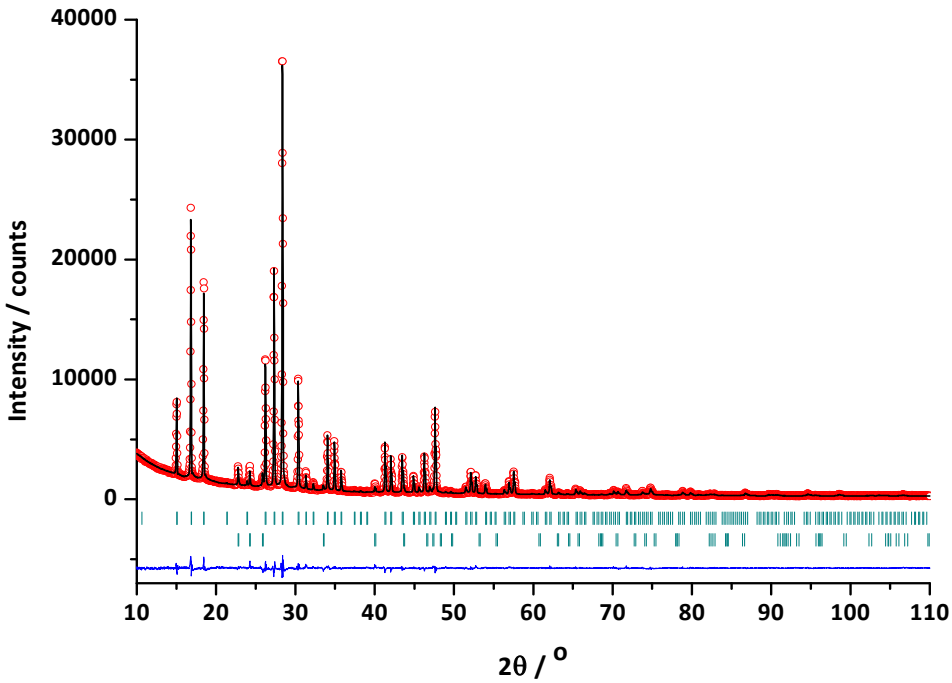

Figure S4. (a) The PXRD pattern of the Xe clathrate hydrate with 27 mol% NH_4F at 183 K and the Rietveld refinement results (background subtracted Rwp = 11.9% and χ^2 = 2.41). Tick marks indicate the Bragg positions for Str. I, cubic *Pm-3n* (top), and hexagonal ice, *P6₃/mmc* (bottom). The lattice parameter is 1.17634(2) nm for the Str. I hydrate.

Table S5. Atomic coordinates and isotropic temperature factors for the Str. II THF + Xe clathrate hydrate at 183 K.

Atom	*x*	*y*	*z*	*B* (Å^2)	*g*	Site
Wa1	0.125	0.125	0.125	6.4(0)	1	8*a*
Wa2	0.2247(1)	0.2247	0.2247	18.5(7)	1	32*e*
Wa3	0.1842(2)	0.1842	0.3735(2)	6.6(2)	1	96*g*
OL1	0.0679	0.1081	0.6096	0.2(8)	0.0417	192*i*
ML2	0.1009	0.1575	0.5524	0.2	0.0417	192*i*
ML3	0.1007	0.1319	0.6815	0.2	0.0417	192*i*
ML4	0.1052	0.2208	0.6777	0.2	0.0417	192*i*
ML5	0.1044	0.2383	0.5896	0.2	0.0417	192*i*
Xe1	0	0	0	2.9(1)	0.74(1)	16*c*

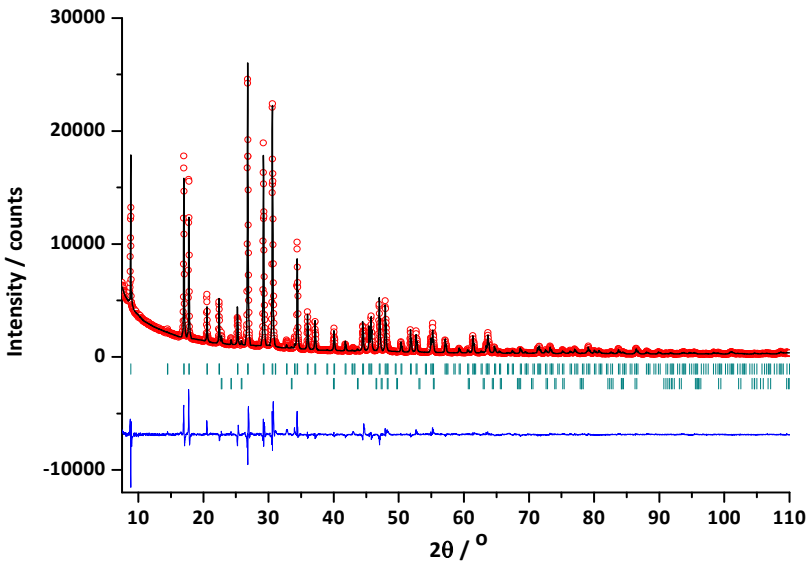

Figure S5. (a) The PXRD pattern of the THF + Xe clathrate hydrate at 183 K and the Rietveld refinement results (background subtracted Rwp = 23.1% and χ^2 = 9.79). Tick marks indicate the Bragg positions for Str. II, cubic *Fd-3m* (top), and hexagonal ice, *P6₃/mmc* (bottom). The lattice parameter is 1.72778(4) nm for the Str. II hydrate.

Table S6. Atomic coordinates and isotropic temperature factors for the Str. II THF + Xe clathrate hydrate with 7 mol% NH_4F at 183 K.

Atom	*x*	*y*	*z*	*B* (Å^2)	*g*	Site
Wa1	0.125	0.125	0.125	5.2(4)	1	8*a*
Wa2	0.2194(3)	0.2194	0.2194	8.8(5)	1	32*e*
Wa3	0.1851(2)	0.1851	0.3731(2)	7.2(2)	1	96*g*
OL1	0.1073	0.1174	0.5647	0.4(8)	0.0417	192*i*
ML2	0.0534	0.1784	0.5496	0.4	0.0417	192*i*
ML3	0.1658	0.1505	0.6131	0.4	0.0417	192*i*
ML4	0.1227	0.2049	0.6695	0.4	0.0417	192*i*
ML5	0.0455	0.2232	0.6266	0.4	0.0417	192*i*
Xe1	0	0	0	4.0(1)	0.76(1)	16*c*

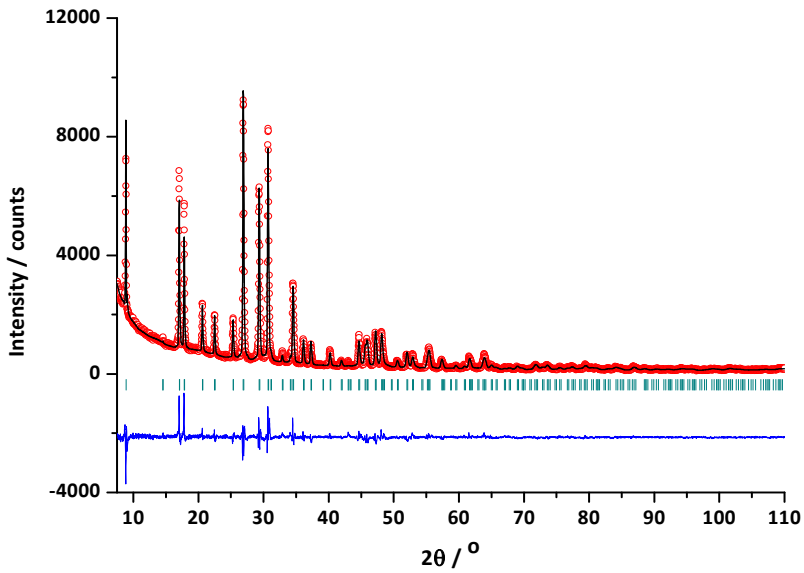

Figure S6. (a) The PXRD pattern of the THF + Xe clathrate hydrate with 7 mol% NH_4F at 183 K and the Rietveld refinement results (background subtracted Rwp = 21.2% and χ^2 = 3.93). Tick marks indicate the Bragg positions for Str. II, cubic *Fd-3m* phase. The lattice parameter is 1.72110(8) nm for the Str. II hydrate.

Table S7. Atomic coordinates and isotropic temperature factors for the Str. II THF + Xe clathrate hydrate with 15 mol% NH_4F at 183 K.

Atom	*x*	*y*	*z*	*B* (Å^2)	*g*	Site
Wa1	0.125	0.125	0.125	2.6(4)	1	8*a*
Wa2	0.2172(2)	0.2172	0.2172	4.6(4)	1	32*e*
Wa3	0.1859(2)	0.1859	0.3724(2)	6.5(2)	1	96*g*
OL1	0.1616	0.1563	0.5689	6.7(9)	0.0417	192*i*
ML2	0.1343	0.0899	0.6102	6.7	0.0417	192*i*
ML3	0.1553	0.2201	0.6214	6.7	0.0417	192*i*
ML4	0.1791	0.1879	0.7015	6.7	0.0417	192*i*
ML5	0.1657	0.0989	0.6935	6.7	0.0417	192*i*
Xe1	0	0	0	3.9(1)	0.77(1)	16*c*

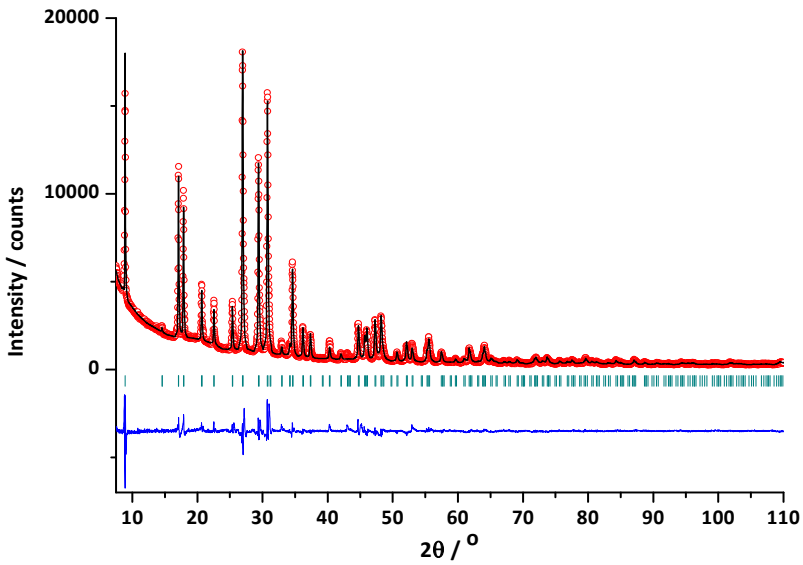

Figure S7. (a) The PXRD pattern of the THF + Xe clathrate hydrate with 15 mol% NH_4F at 183 K and the Rietveld refinement results (background subtracted Rwp = 20.3% and χ^2 = 6.50). Tick marks indicate the Bragg positions for Str. II, cubic *Fd-3m* phase. The lattice parameter is 1.71854(7) nm for the Str. II hydrate.

Table S8. Atomic coordinates and isotropic temperature factors for the Str. II THF + Xe clathrate hydrate with 25 mol% NH_4F at 183 K.

Atom	*x*	*y*	*z*	*B* (Å^2)	*g*	Site
Wa1	0.125	0.125	0.125	5.0(4)	1	8*a*
Wa2	0.2245(4)	0.2245	0.2245	17.1(6)	1	32*e*
Wa3	0.1854(2)	0.1854	0.3716(2)	7.1(2)	1	96*g*
OL1	0.6616	0.6127	0.6684	13.1(10)	0.0417	192*i*
ML2	0.6065	0.5781	0.6164	13.1	0.0417	192*i*
ML3	0.6473	0.6947	0.6653	13.1	0.0417	192*i*
ML4	0.5579	0.7038	0.6607	13.1	0.0417	192*i*
ML5	0.5300	0.6238	0.6283	13.1	0.0417	192*i*
Xe1	0	0	0	3.6(1)	0.77(1)	16*c*

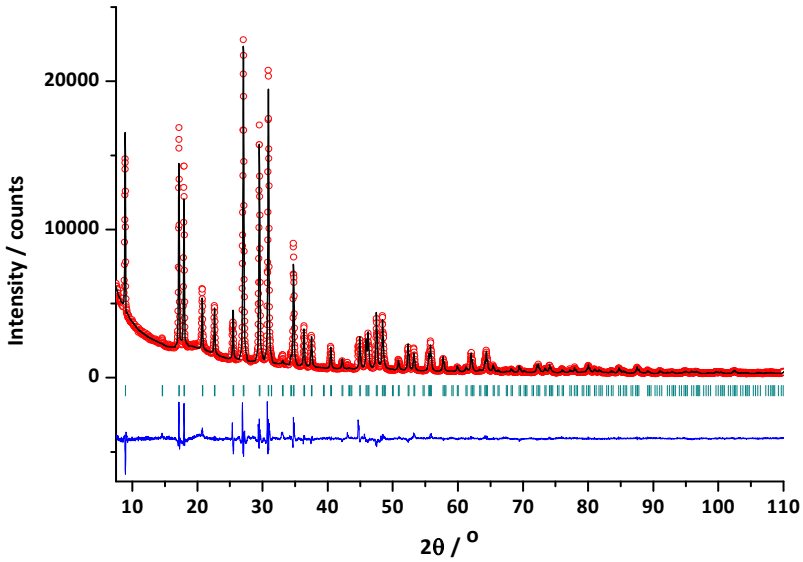

Figure S8. (a) The PXRD pattern of the THF + Xe clathrate hydrate with 25 mol% NH_4F at 183 K and the Rietveld refinement results (background subtracted Rwp = 19.4% and χ^2 = 7.58). Tick marks indicate the Bragg positions for Str. II, cubic *Fd-3m* phase. The lattice parameter is 1.71110(4) nm for the Str. II hydrate.

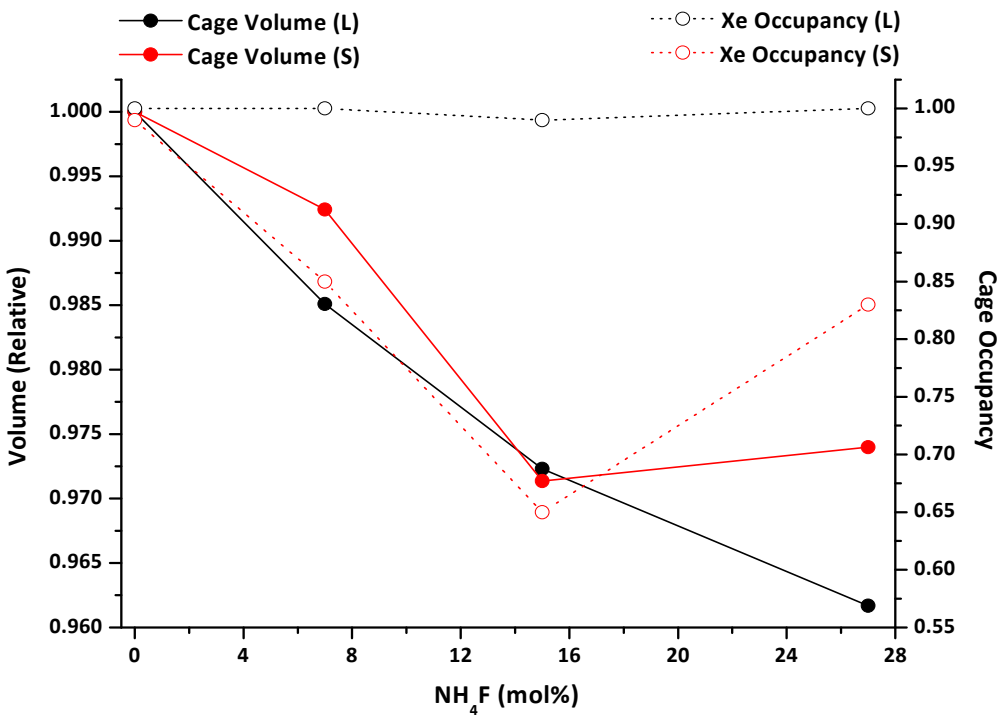

Figure S9. The relative cage volumes and Xe occupancies of the Str. I Xe hydrates doped with NH_4F obtained from the Rietveld refinement results.

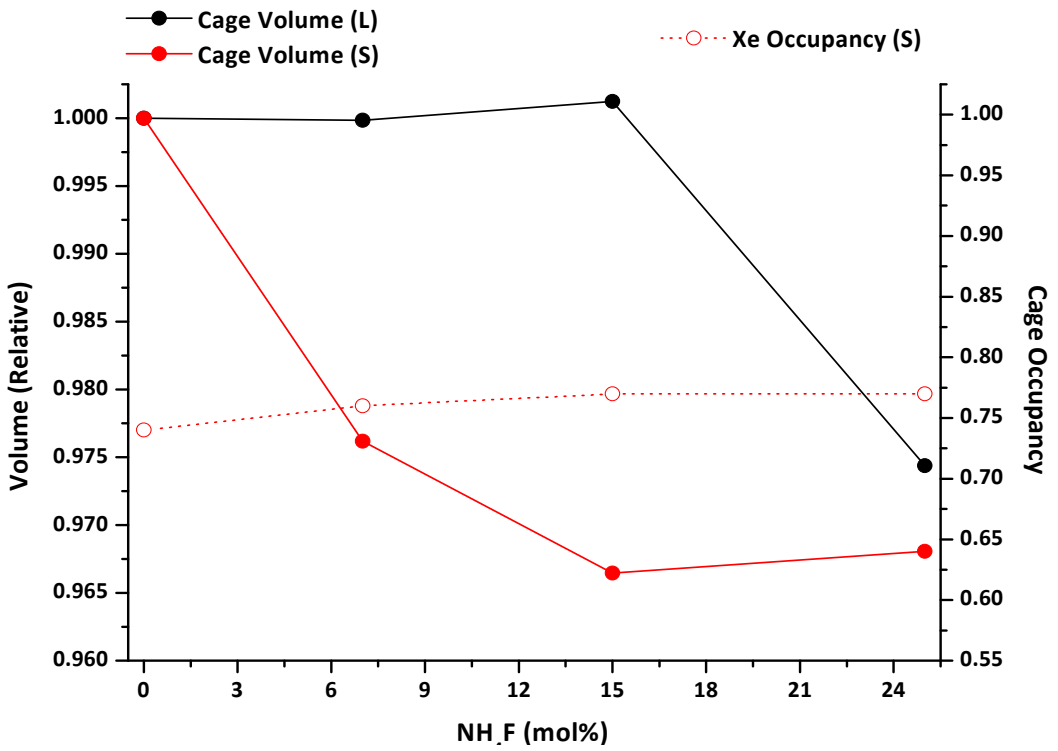

Figure S10. The relative cage volumes and Xe occupancies of the Str. II THF + Xe hydrates obtained from the Rietveld refinement results.

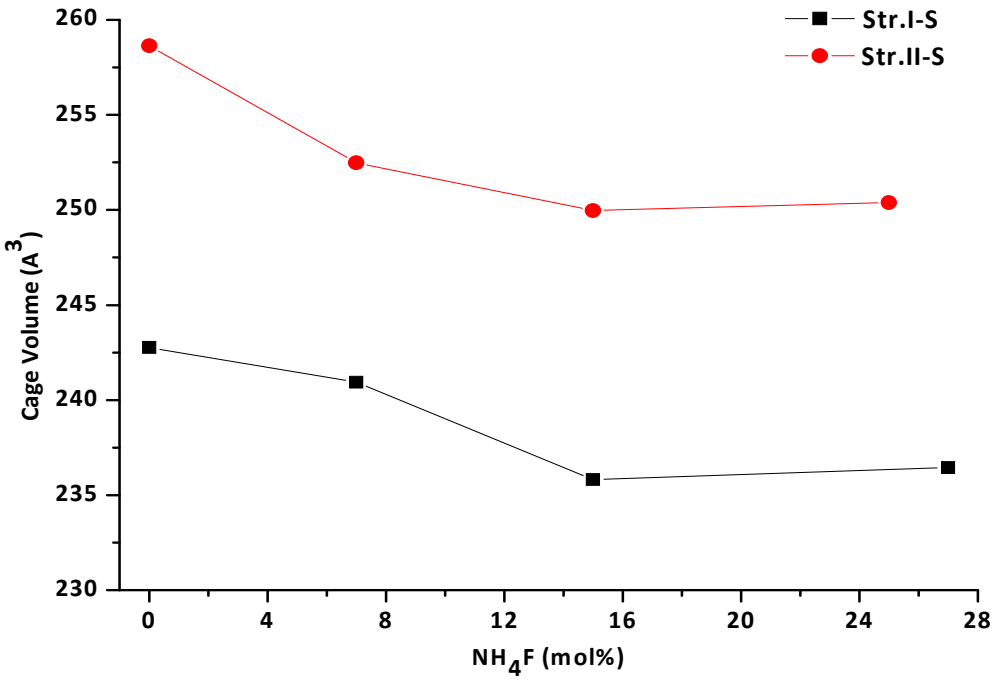

Figure S11. Estimated volumes of small cages in the Str. I Xe and Str. II THF + Xe clathrate hydrates doped with NH_4F calculated from the Rietveld refinement results.

2) Ab initio calculations:
i) Additional conformations

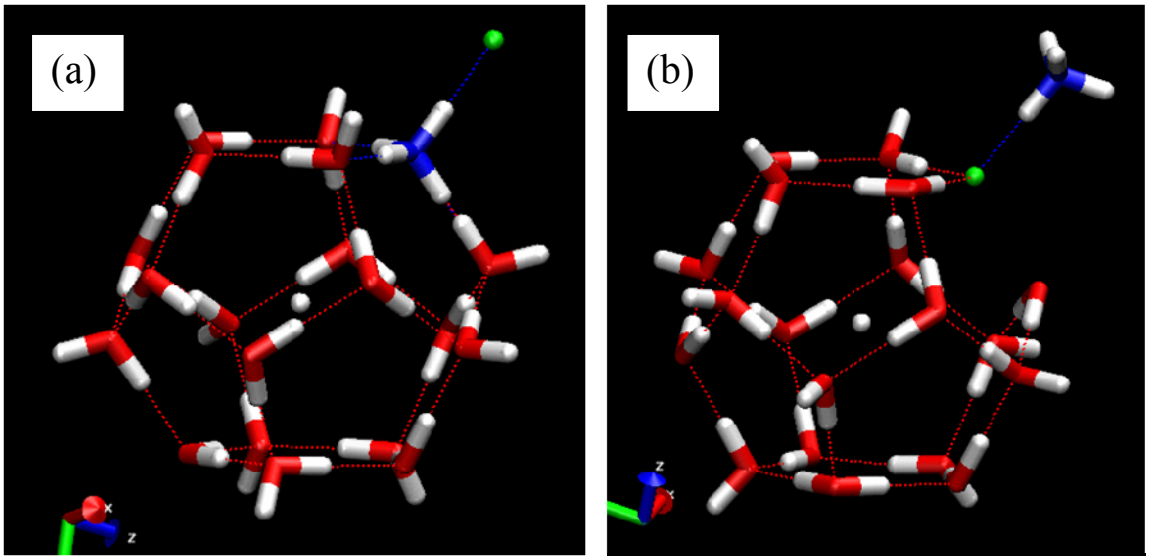

Figure S12. (a) Small Str. I cage with NH_4^+ in a cage site and F^- in an adjacent cage. (b) Small Str.I cage with F^- in a cage site and NH_4^+ in an adjacent cage.

ii) Relative energies of NH_4F in different configurations of the isolated cages

Quantum chemical calculations show the configuration with the NH_4F ions in the pentagonal faces shown in Fig. 4(d) of the paper, is 9.4 kcal·mol^{-1} lower in energy than the configuration with the NH_4F ions in the hexagonal faces, Fig. 4(c). The energy of the other configurations with one of the NH_4^+ and F^- in a hexagonal face and the other in a pentagonal face shown in Figure S12 are considerably higher than the configurations with the ions in the purely hexagonal or pentagonal faces.

iii) Table S9.

Calculated NMR chemical shifts (with respect to gas phase) for xenon in the Str. I small and large cages in the absence and presence of NH_4OH dopant in different configurations.

Str. I cage and NH_4OH configuration	Chemical shift / ppm
Small cage	257.0
Small cage with NH_4^+ and OH^- in adjacent sites	251.6
Small cage with NH_4^+ in cage and OH^- in neighbouring cage	259.9
Small cage with OH^- in cage and NH_4^+ in neighbouring cage	259.3
Large cage	121.0
Large cage with NH_4^+ and OH^- adjacent in a hexagonal face	121.2
Large cage with NH_4^+ and OH^- adjacent in a pentagonal face	121.7
Large cage with NH_4^+ in hexagonal and OH^- in adjacent pentagonal face	140.4
Large cage with NH_4^+ in pentagonal and OH^- in adjacent hexagonal face	139.9
Large cage with NH_4^+ in the cage and OH^- in neighbouring cage	124.9
Large cage with OH^- in the cage and NH_4^+ in neighbouring cage	119.3

In the water environment in the presence of NH_4F, a variety of small and large Str. I and Str. II cages with NH_4^+, NH_3, F^-, H_2O, OH^-, and H_3O^+ species may be potentially observed. These species are important since NH_3 is a weak base and in water environments, NH_4^+ can undergo a proton transfer reaction,

$$NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+, \quad \text{(S1)}$$

to produce ammonia and the hydronium ion. Therefore, we might have combinations of NH_3, H_3O^+, and F^- in cages at different sites. Hydrofluoric acid (HF) is a strong acid and we do not expect large concentrations of HF and OH^- in the environment. Xenon chemical shift calculations with different possible ions and locations will remain for future work.

3) Table S10. Crystallographic O atom sites in Str. I and II clathrate hydrates.

	Wyckoff site	Unit cell content	Small cage	Large cage	Number of small cages	Number of large cages
Str. I	*k*	24	12	12	2	6
	i	16	8	8		
	c	6	-	4		
Str. II	*g*	96	12	24	16	8
	e	32	6	4		
	a	8	2	-		

4) Methanol NH_4F-H_2O clathrates

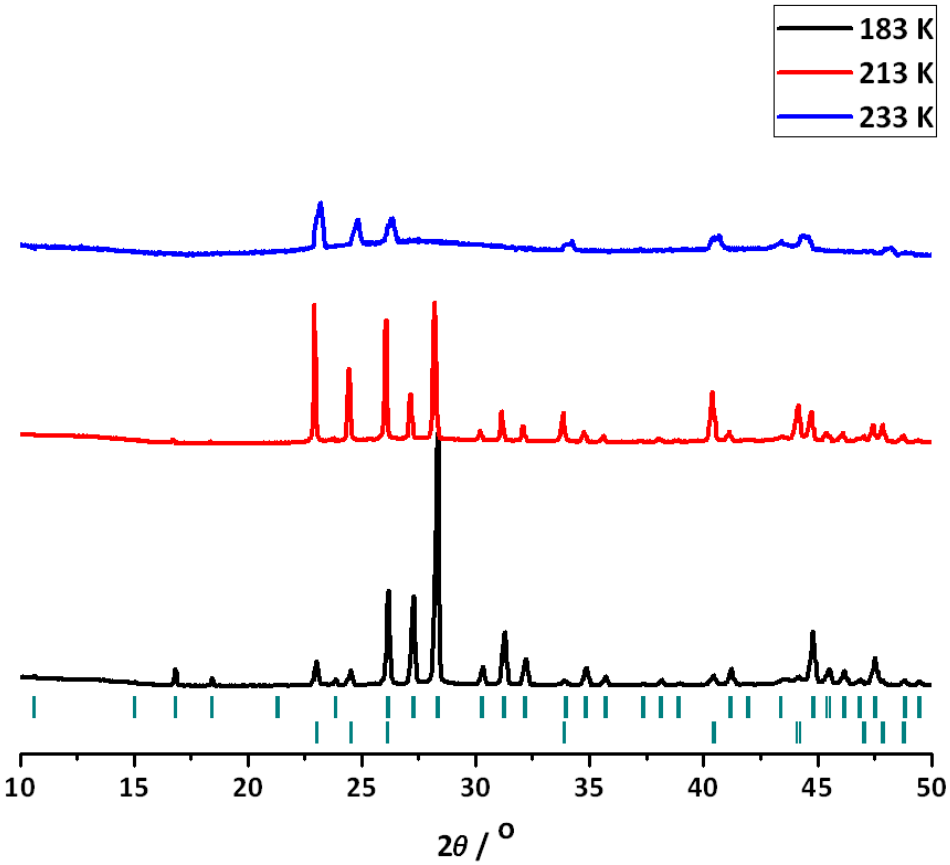

Figure S13. The PXRD patterns of the methanol clathrate hydrate with 27 mol% ammonium fluoride at 183, 213, 233 K. Tick marks indicate the Bragg positions for the Str. I hydrate (top) and the ammonium fluoride-ice solid solution (bottom).

Table S11. Atomic coordinates and isotropic temperature factors for methanol Str. I clathrate hydrate with 27 mol% ammonium fluoride at 183 K.

Atom	x	y	Z	B (Å^2)	g	site
Wa1	0.1838(1)	0.1838	0.1838	6.8(1)	1	16*i*
Wa2	0	0.3107(2)	0.1195(1)	8.4(1)	1	24*k*
Wa3	0	0.5	0.25	8.6(2)	1	6*c*
ML1	1.0198	0.3180	0.4610	3.5(3)	0.125	48*l*
OL2	0.9106	0.2666	0.4601	3.5	0.125	48*l*
MS1	0.0183	0.0204	-0.0144	3.8(6)	0.0303(3)	48*l*
OS2	-0.0148	-0.0599	0.0695	3.8	0.0303	48*l*

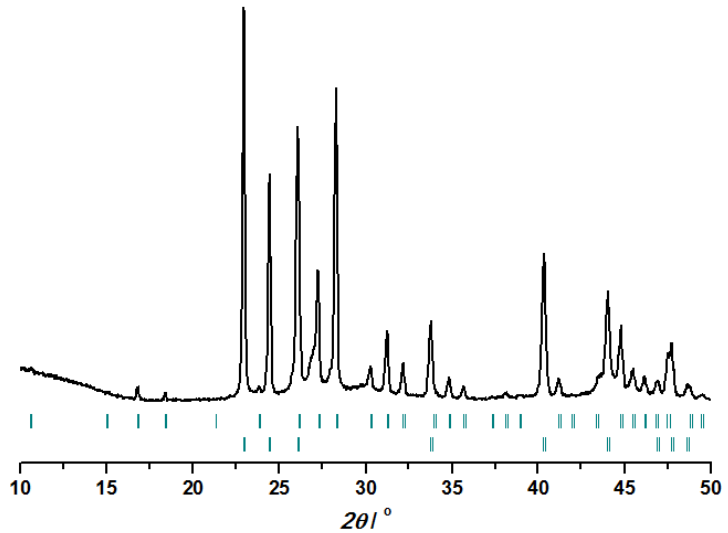

Figure S14. The PXRD pattern of the mixture of CD_3OH, 15 mol% NH_4F, and H_2O at 150 K. Tick marks indicate the Bragg positions for the Str. I hydrate (top) and the hexagonal ammonium fluoride-ice solid solution (bottom).

Table S12. Atomic point charges and Lennard-Jones parameters for H_2O, NH_4F, CH_3OH, and Xe used in the MD simulations of NH_4F-doped Str. I methanol clathrate hydrate.

Atom	q / e	σ_{ii} / nm	ε_{ii} / kJ·mol^{-1}
O_W (H_2O)	0.0	0.3153	0.6485
H_W (H_2O)	+0.5200	0.000	0.000
EE (H_2O)	-1.0400	0.000	0.000
F_H (F^-)	-1.0000	0.2997	0.2092
N_H (NH_4^+)	-0.4000	0.3250	0.7113
H_N (NH_4^+)	+0.3500	0.000	0.000
M_L (CH_3OH)	+0.2650	0.3740	0.8746
O_L (CH_3OH)	-0.7000	0.3030	0.7191
H_L (CH_3OH)	+0.4350	0.000	0.000
Xe (Xe)	0.0	0.39235	1.3891