A LOW SYMMETRY FORM OF STRUCTURE H CLATHRATE HYDRATE

Konstantin A Udachin, Christopher I. Ratcliffe, John A. Ripmeester*

Steacie Institute for Molecular Sciences

National Research Council Canada

Ottawa, ON K1A 0R6

Canada

ABSTRACT

In this paper we report a low symmetry version of structure H hydrate that results from the hexagonal form on cooling below 167 K. Phase changes with temperature in the common clathrate hydrates structural families I, II and H have not been observed before, except in doped systems where ordering transitions take place or in the structure I hydrate of trimethylene oxide where the guest molecule dipoles are known to order. Since there is an inverse relationship between the effect of temperature and pressure on ices, it may well be that the low symmetry form reported at low temperature can also be reached by applying high pressure, and that in fact some of the observed high pressure phases are lower symmetry versions of hexagonal sH.

Clathrate hydrates are crystalline guest-host materials where small guest molecules are trapped in cages formed by hydrogen bonded molecules[1,2]. The three common families of hydrate structures, known as cubic structures I (sI) and II (sII) and hexagonal structure H (sH), form when the different cage types are packed into ordered three dimensional structures. All three hydrate structures have been identified as occurring in nature, with hydrocarbon guests, H_2S, CO_2, O_2, N_2 and traces of the noble gases, either offshore on the continental margins [3,4,5], under the permafrost[6], or deep inside glaciers[7].

Normally methane forms sI hydrate, but sII has been observed as well as a transient phase[8] and at higher pressures a variety of new phases have been observed. A methane hydrate phase that is either sH or close to sH in structure is known to form at high pressure, which transforms to a "filled ice" above ~ 2 GPa[9-14]. The high pressure phases are not known to occur naturally on earth, but have been implicated as perhaps playing a role on the icy outer planets[8]. Similarly, noble gas atoms or small molecules that normally form sI or sII hydrates are known to transform to other hydrate structures, including sH hydrate[15-20] under application of high pressure. Hexagonal sH was first identified from NMR spectroscopy and powder neutron data[21,22] with the structure confirmed from single crystal X-ray diffraction[23,24]. We note that the high pressure methane hydrate phase (MH-II) has been described as not exactly having the hexagonal clathrate structure but one that may be closely related to it, although other work has concluded that this high pressure phase indeed is hexagonal sH[19]. Clearly there is a great interest in the diversity of hydrate structures and the conditions under which these form.

In this paper we report a low symmetry version of sH hydrate that results from the hexagonal form[21,24] on cooling below 167 K. Phase changes with temperature in the common clathrate hydrates structural families I, II and H have not been observed before, except in doped systems where ordering transitions take place[25] or in the sI hydrate of trimethylene oxide where the guest molecule dipoles are known to order[26]. Since there is an inverse relationship between the effect of temperature and pressure on ices, it may well be

that the low symmetry form reported at low temperature can also be reached by applying high pressure, and that in fact some of the observed high pressure phases are lower symmetry versions of hexagonal sH.

EXPERIMENTAL

sH hydrate, with cyclooctane as the large cage guest and Xenon and hydrogen sulphide in the small cages was confirmed to form sH some years ago[22]. The single crystal resulted upon storing a sealed sample for several years in a freezer at -40 C°. The crystal was recovered and mounted on the diffractometer at low temperatures. Data was collected on a Bruker Smart diffractometer at a temperature of 125K. Integration was carried out using the program SAINT, and an absorption correction was performed using SADABS[27]. The

Table 1. Summary of X-ray structural data

	Structure H	Structure H'
Space group	P6/mmm	P-3
Unit-cell parameters, Å	a=12.313(1) c=10.054(1)	a=24.433(2) c=10.010(2)
Unit-cell volume, Å^3	1320.1(1)	5175.1(10)
Temperature, K	215.0(1)	125.0(1)
Reflections collected	14992	58779
Reflections unique	700	8551
Reflections >2σ(I)	618	5884
Number of parameters	143	845
Number of restrains	80	569
Goodness of fit	1.079	1.092
R_1	0.018	0.035
wR_2	0.047	0.094
residual electron density, eÅ^{-3}	max. 0.29, min. -0.25	max. 0.40, min. -0.84

structure was solved by direct methods and refined by full-matrix least-squares routines using the SHELXTL program suite[28]. All atoms were refined anisotropically. Hydrogen atoms on cyclooctane molecules were placed in calculated positions and allowed to ride on the parent atoms.

Surprisingly, the crystal proved not to be sH hydrate but a lower symmetry version. A differential scanning calorimetry scan revealed a weak endotherm at -106 C° suggesting the presence of a phase transition. A second data set taken at -85C°, above the phase transition, was consistent with the previously determined sH structures as determined from previous single crystal studies[23,24]. A summary of the X-ray structural data is given in Table 1.

RESULTS AND DISCUSSION

After the low temperature structure was discovered to be different from the usual hexagonal sH clathrate, attempts were made to see if this phase was the stable one for this particular large guest molecule. However, it was found that at -85C° the phase had transformed to the hexagonal form, and that the single crystal survives the phase change. The transition temperature was identified to be -106C° from differential scanning calorimetry (fig.1). This is the first example of a
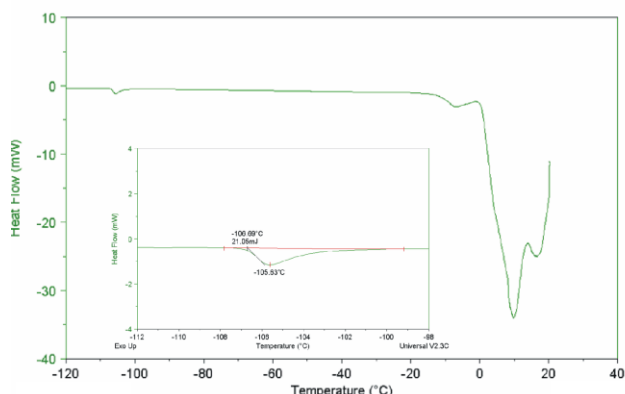

Figure 1. Differential Scanning Calorimetry traces of the thermal transitions in sH hydrate. Inset shows a detail of the phase change region.

temperature-induced symmetry lowering transition in the lattice of the common clathrate families. However, such transitions are well-documented in the silica clathrates that are isostructural with the water clathrates and known as clathrasils [30, 31].

The low temperature structure has a space group of reduced symmetry as compared to that determined at high temperature: P6/mmm (a= 12.313(1) Å, c= 10.054(1) Å, V = 1320.1(1) Å^3, T=215K) to P3bar (a= 24.433(2) Å c=10.010(1) Å V = 5175.1(1) Å^3, T=125K). So, there is a doubling of the a lattice parameter (fig.2), and the unit cell volume at low temperature (200K) is exactly the same
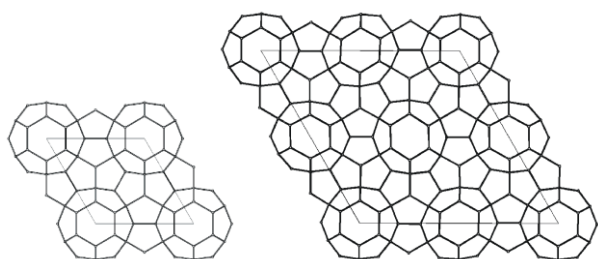
Figure 2. General views of the structures of sH hydrate, low and high temperature forms.

(within the calculated errors) as the quadrupled volume of the high temperature (206K) cell. Table 2 shows structure H' and structure H unit-cell parameters and cell volumes at different temperatures. This is a good illustration of the flexibility of water framework as the distortion of the large cages is compensated by an equivalent distortion in the small cages.

Table 2. Structure H' and structure H unit-cell parameters and cell volumes at different temperatures.

Temperature, K	a	c	V
80K	24.445(2)	10.005(1)	5177(1)
100K	24.458(2)	10.007(1)	5184(1)
125K	24.496(2)	10.015(1)	5204(1)
150K	24.525(2)	10.026(1)	5222(1)
175K	24.577(2)	10.034(1)	5248(1)
200K	24.629(2)	10.052(1)	5280(1)
206K	12.315(1)	10.056(1)	1320.8(3)
215K	12.327(1)	10.062(1)	1324.0(3)
225K	12.331(1)	10.067(1)	1325.7(3)

There are considerable implications for the sizes and shapes of the various cages that make up sH. The high temperature unit cell can be described as $3D \cdot 2D' \cdot E \cdot 34H_2O$, where $D = 5^{12}$, $D'=4^35^66^3$ and $E = 5^{12}6^8$, with the cage symmetries given in table 3. The low temperature unit cell becomes $6D^a \cdot 6D^b \cdot 4D'^a \cdot 4D'^b \cdot 2E^a \cdot 2E^b \cdot 136H_2O$, with a considerable loss of symmetry for all of the cages.

Table 3. Symmetry of the cages in the high and low temperature forms of sH hydrate

Structure H $E.3D.2D'.34H_2O$	$5^{12}(D)$	mmm
	$4^35^66^3(D')$	m2
	$5^{12}6^8(E)$	6/mmm
Structure H' $4[E.3D.2D'.34H_2O]$	$5^{12}(D)$	1
	$5^{12}(D)$	1
	$4^35^66^3(D')$	1
	$4^35^66^3(D')$	3
	$5^{12}6^8(E)$	-1
	$5^{12}6^8(E)$	-1

The most profound effect of the structural change is on the large E cages and their guest distributions. Fig.3 shows that the two cages alternate along the x direction. Both cages are deformed and the cage located on the 3-fold axes is disordered over three symmetry related positions with equal site occupancy (fig.4). They both have symmetry -1. The longest and the shortest diameters within the 001 plane are 9.12 and 9.77 Å for the ordered E-cage and 9.22 and 9.64 Å for the disordered E-cage as compared to those in the high temperature symmetric cage (9.45 Å). This is also noticeable from the distribution of the cyclooctane molecule sites in the cage: in the low symmetry cage the
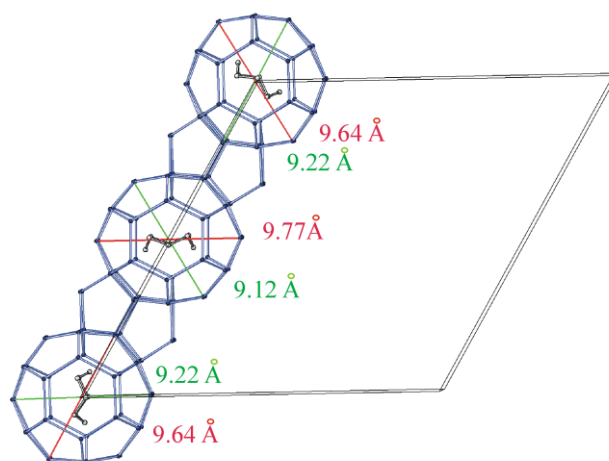

Figure 3. Detail of structure showing the alternating E cages along the *x* direction; the two E cages showing the cage distortions and the cyclooctane guest positions
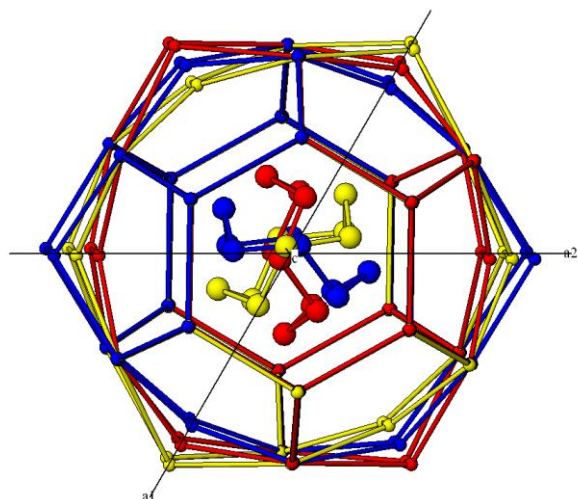
Figure 4. Disordered E cage and cyclooctane orientations in structure H' (cage deformation is slightly exaggerated for clarity).

favored positions of the guest lie along the stretched dimension of the cage (fig.4). We may speculate that the ability to distort the cage comes from the fact that the cyclooctane guest is quite large and asymmetric (in its most stable conformation).

Cyclooctane conformations are approximately the same in structure H and in both large cages of structure H'. Cage volumes calculated at 206 K for structure H and at 200 K for structure H' are approximately the same ($268\pm2\text{Å}^3$). The volumes were calculated using the PLATON program[29]. The low symmetry large cages in structure H' are deformed, but have the same volume. The same is true for the small cages. Both small and large cages are deformed, but the volumes of the cages and the unit-cell volumes (exactly 4 times larger for structure H') remain the same.

At this time, we can only speculate on the reason for the transformation of the sH framework as the temperature is lowered. The unit cell and cage volumes appear to be identical in both phases but the loss of symmetry may offer a clue, however. In the high temperature phase, the cyclooctane guest is disordered over 6 positions, whereas in the low temperature phase there is just one guest orientation although the cage orientations are disordered. Guest dynamics have not been studied in detail for sH hydrate, but in at least one sH system (methylcyclohexane) the guest rotates between the 6 equivalent positions that lie about the symmetry axis of the E cage. This suggests that freezing in of guest motion in one of the equivalent
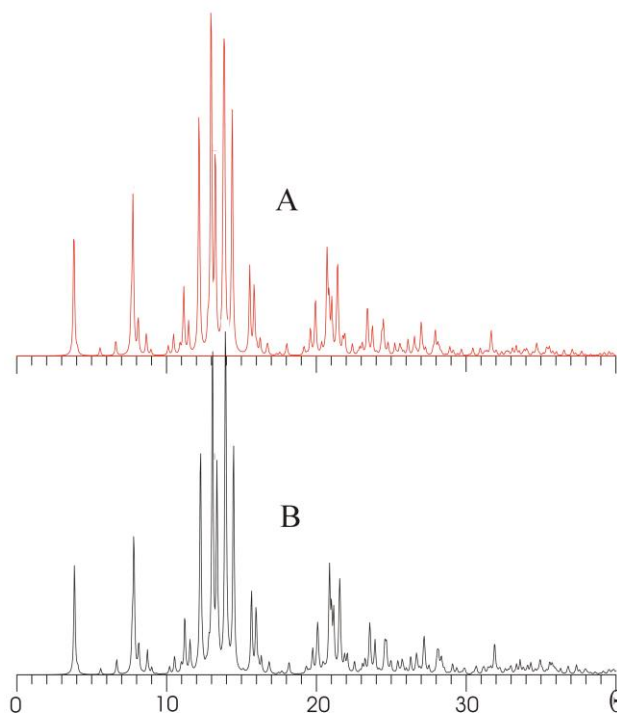

Figure 5. Calculated powder X-ray diffraction patterns for low (A) and high (B) symmetry forms of cyclooctane hydrate.

positions in the large cage may occur, and once this happens the cage distorts to maximize host-guest interaction. Cyclooctane, as a stationary molecule, departs quite markedly from cylindrical symmetry, as do the close fitting E cages in the low temperature phase. The transition then can be considered to be driven by the freezing in of the motion of a tightly fitting low symmetry guest, thus distorting the host cavity. This situation should not be expected to be unique for this particular guest. Other large guests, or asymmetric configurations of small molecules such as in the high pressure phases, may well drive sH hydrate to its lower symmetry version. We note that some clathrasils, clathrate compounds of silica and isostructural with the clathrate hydrates[29], show progressive symmetry lowering as the temperature is lowered, implicating restricted guest dynamics and symmetry lowering of the host lattice[30].

We also note that it is not possible to distinguish the low and high symmetry forms by powder X-ray diffraction, as the patterns are exactly the same (fig.5).

[1] G. A. Jeffrey, in *Comprehensive Supramolecular Chemistry*, Eds. J. L. Atwood, J.E.D. Davies, D.D. MacNicol, F. Vogtle, J. –M. Lehn, Pergamon, Elsevier Science, New York, 1996,Vol. 6, Ch.23.

[2]. J. A. Ripmeester, C. I Ratcliffe, K. A. Udachin, *Clathrate Hydrates* in *Encyclopedia of Supramolecular Chemistry,* Ed. J. L. Atwood, J. W. Steed, Dekker Encyclopedias, Taylor and Francis, 274 – 280 (2004)

[3].D.W. Davidson, S.K. Garg, S.R. Gough, Y.P. Handa, C.I. Ratcliffe, J.A. Ripmeester, J.S. Tse and W.F. Lawson., *Geochim. Cosmochim. Acta* 50, 619 (1986).

[4] H. Lu, I. Moudrakovski, M. Riedel, G. Spence, R. Dutrisac, J. Ripmeester, F. Wright, S. Dallimore, *J. Geopys. Res*. 110, B10204 (2005)

[5] H. Lu, Y. Seo, J. Lee, I. L Moudrakovski, J. A. Ripmeester, N. R.Chapman, R.B. Coffin, G. Gardner, J. Pohlman, *Nature*, 445, 303 (2007)

[6]. C. A. Tulk, C. I. Ratcliffe and J. A. Ripmeester, Bull. *Geol. Survey Canada* 544 251-263 (1999)

[7] T. Uchida, T. Hondoh, S. Mae, V. Y. Lipenkov, P. Duval, *J. Glac*. 40, 79-86 (1994)

[8] J. Schicks and J. A. Ripmeester, *Angew. Chem. Int'l Ed'n*, 43, 3310-13 (2004)

[9] J.S. Loveday, R.J. Nelmes, M. Guthrie, S.A. Belmonte, D.R. Allan, D.D. Klug, J. S. Tse, Y.P. Handa, *Nature* 410, 661–663 (2001)

[10] I. M. Chou, A. Sharma, R. C. Burruss, F. F. Shu, H. K. Mao, R. J. Hemley, A. F. Goncharov, L. A. Stern and S. H. Kirby, *Proc. Nat. Acad. Sci*. 97, 13484 (2000)

[11] H. Hirai, T. Kondo, M. Hasegawa, T. Yagi, Y. Yamamoto, T. Komai, N. Nagashima, M. Sakashita, H. Fujihisa and K. Aoki, *J. Phys. Chem. B*, 104 1429 (2000)

[12] J. S Loveday, R. J. Nelmes, M. Guthrie, D. D. Klug, J. S. Tse, *Phys. Rev. Lett.* 87, 215501-1–215501-4. (2001)

[13] H. Shimizu, T. Kumazaki, T. Kume, S. Sasaki, *J. Phys. Chem. B* 106, 30–33 (2002).

[14] J.S. Loveday, R.J. Nelmes, M. Guthrie, *Chem. Phys. Lett*. 350, 459 (2001)

[15] A. Y. Manakov, V. I. Voronin, A. V. Kursonov, A. E. Teplykh, E. G. Larionov, and Y. A. Dyadin, *Dokl. Phys. Chem*. 378, 148 (2001)

[16] H. T. Lotz and J. A. Schouten, *J. Chem. Phys*. 111 10242 (1999)

[17]. M. G. E. van Hinsburg, M. I. M. Scheerboom and J. A. Schouten, *J. Chem. Phys*. 99, 752 (1993)

[18] C. Sanloup, H. K. Mao and R. J. Hemley, *Proc. Nat. Acad. Sci* 99, 25 (2002)

[19] J. S. Loveday, R. J. Nelmes, D. D. Klug, J. S. Tse and S. Desgreniers, *Can. J. Phys*. 81, 539 (2003)

[20] S. Alavi, J.A. Ripmeester, and D.D. Klug, *J. Chem. Phys*.125, 104501 (2006)

[21] J. A. Ripmeester, J. S. Tse, C. I. Ratcliffe and B. M. Powell, *Nature* 325, 135 (1987).

[22] J.A. Ripmeester and C.I. Ratcliffe. *J. Phys. Chem*. 94, 8773 (1990).

[23] K. A. Udachin, C. I. Ratcliffe, G. D. Enright and J. A. Ripmeester, *Supramol. Chem*. 8, 173, (1997)

[24] K. A. Udachin, C. I. Ratcliffe and J. A. Ripmeester, *J. Supramol. Chem*. 2 405-408 (2002)

[25] H. Suga, T. Matsuo and O. Yamamuro, *Pure Appl. Chem*. 64 17-26 (1992)

[26] J. A. Ripmeester, C. I. Ratcliffe and K. A. Udachin, *J. Phys. Chem. B* 111, 11366-72 (2007)

[27] G. M. Sheldrick, *SADABS Version 2.03*, University of Gottingen, Germany 2002

[28] G. M. Sheldrick, *SHELXTL*, *Version 6.10;* Bruker AXS Inc., Madison, Wisconsin, USA, 2000.

[29] A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, A. L. Spek, 1998.

[30] H. Gies, *Clathrasils and zeosils:inclusion compounds with silica host frameworks, in Inclusion Compounds*, Ed. J.L Atwood, D. D. MacNicol and J. E. D. Davies, Oxford University Press, 5, 1 – 31 (1991)

[31] J. S. Tse, M. Desando, J. A. Ripmeester and Y. P. Handa, *J. Am. Chem. Soc*. 115, 279 (1993)

of cyclooctane hydrate.