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Polymorphism in Br_2 Clathrate Hydrates

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The structure and composition of bromine clathrate hydrate has been controversial for more than 170 years due to the large variation of its observed stoichiometries. Several different crystal structures were proposed before 1997 when Udachin et al. (Udachin, K. A.; Enright, G. D.; Ratcliffe, C. I.; Ripmeester, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 11481) concluded that Br_2 forms only the tetragonal structure (TS-I). We show polymorphism in Br_2 clathrate hydrates by identifying two distinct crystal structures through optical microscopy and resonant Raman spectroscopy on single crystals. After growing TS-I crystals from a liquid bromine−water solution, upon dropping the temperature slightly below −7 °C, new crystals of cubic morphology form. The new crystals, which have a limited thermal stability range, are assigned to the CS-II structure. The two structures are clearly distinguished by the resonant Raman spectra of the enclathrated Br_2, which show long overtone progressions and allow the extraction of accurate vibrational parameters: $\omega_e = 321.2 \pm 0.1$ cm^{-1} and $\omega_e x_e = 0.82 \pm 0.05$ cm^{-1} in TS-I and $\omega_e = 317.5 \pm 0.1$ cm^{-1} and $\omega_e x_e = 0.70 \pm 0.1$ cm^{-1} in CS-II. On the basis of structural analysis, the discovery of the CS-II crystals implies stability of a large class of bromine hydrate structures and, therefore, polymorphism.

Clathrate hydrates are a ubiquitous class of crystalline inclusion compounds with nonstoichiometric composition, consisting of guest molecules trapped in a lattice of polyhedral water cages.[1] The resurgence of interest in this fascinating class of solids is, in part, motivated by the recognition of the vastness of natural deposits of methane hydrates[2] and their potential global implications with respect to energy and the environment.[3,4] Understanding the stability and structures of clathrate hydrates remains a challenge since they are controlled by a delicate balance of hydrogen bonding within the lattice and weak interactions between the water lattice and the guest molecule. Bromine hydrate was one of the first clathrate hydrates discovered and played an important role in the development of models describing thermodynamic stability and physical properties of clathrate hydrates.[5] Nevertheless, since its discovery in 1828 by Lowig,[6] the structure and composition of Br_2 hydrates has been controversial. The reported hydration numbers, which varied between 7 and 12,[7−9] were previously assumed to arise from polymorphism, that is, more than one crystal structure.[10] In 1997, the mystery of the bromine clathrate structure was believed to be resolved through single-crystal X-ray diffraction studies by Udachin et al.[11] They concluded that "... different crystals of distinct compositions ($Br_2/8.62H_2O$ to $Br_2/10.68H_2O$) and morphologies showed that there is just a single structure (tetragonal, the structure originally proposed by Allen and Jeffrey) with considerable variation in the degree of occupancy of the large cages."[11] The identified tetragonal crystal structure, TS-I, consists of 5^{12} (D), $5^{12}6^2$ (T), and $5^{12}6^3$ (P) cages, in a 10:16:4 ratio, in a unit cell comprised of 172 water molecules (Figure 1a).

Here, we report that this conclusion is not quite correct. When tetragonal bromine hydrate, in equilibrium with its mother liqueur, is slowly cooled through −7 °C, a phase transition occurs. New crystals are formed on the surface of the tetragonal crystals, which grow at a much faster rate than the original. On the basis of morphology and resonance Raman spectra, the new crystalline phase can be identified to have a cubic type-II structure (CS-II), which consists of 5^{12} (D) and $5^{12}6^4$ (H) cages in a 16:8 ratio, in a unit cell comprised of 136 water molecules (Figure 1b).

Single crystals of Br_2 hydrate of the known TS-I structure (**1**) were grown from a saturated solution of Br_2 and distilled water in a two-window cell at 4 °C. The crystals, which primarily belonged to the tetragonal bipyramidal class, had a melting point of 5.8 °C, consistent with the melting point of TS-I bromine hydrate. Cooling the sample below −7 °C initiated a rapid growth of new crystals (**2**) with very different morphologies (Figure 2b). Single crystals grew either as thin plates, needles, or regular octahedra bound by {111} faces. This crystal habit is characteristic of CS-II clathrate hydrates,[12] such as those of THF[13,14] and Kr.[15] In analogy with these known structures, it is suggested that **2** belongs to the same symmetry group, namely, $Fd\bar{3}m$. After the crystals reached dimensions of 50−150 μm, the surrounding liqueur was frozen (∼−17 °C), and the temperature was dropped to −45 °C to record resonance Raman (RR) spectra. Once frozen in ice, **1** survives cooling down to −45 °C. In contrast, **2**, which has a RR spectrum distinct from **1**, slowly converts to a polycrystalline mass with the same RR spectrum as that of **1**. While we do not know the

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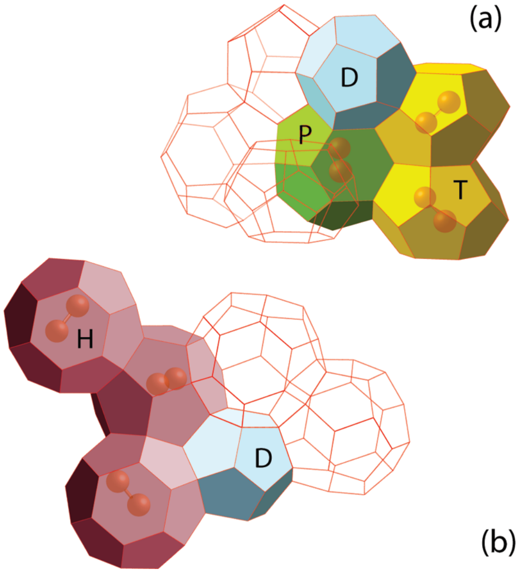

Figure 1. Parts of the polyhedral network in the TS-I (1a) and CS-II (2b) bromine hydrate structures. D, T, P, and H are standard notations for the convex polyhedra formed by hydrogen-bonded water molecules. Since the unstrained tetrahedral angle of ~109° is closest to the interior angle of a regular pentagon, 108°, maximally hydrogen-bonded water networks are obtained in polyhedra having the maximum number of pentagonal faces. The dodecahedron with 12 pentagonal faces, D (5^{12}) is optimum; however, dodecahedra alone cannot pack into a 3-D lattice, They must be supplanted with polyhedra of larger cavities, such as the 14-polyhedron, T ($5^{12}6^2$), 15-polyhedron, P ($5^{12}6^3$), and 16-polyhedron, H ($5^{12}6^4$) having 12 pentagonal and 2, 3, and 4 hexagonal faces, respectively. Effective diameters of the cages are 8.0 Å (D), 8.6 Å (T), 9.2 Å (P), and 9.4 Å (H).

exact temperature at which these new crystals become unstable, we do know that they remain stable (and grow) down to the freezing point of the liqueur of −17 °C. It is notable that the formation temperature of the new crystals closely corresponds to the freezing point of neat Br_2. Given the stoichiometries of the TS-I and CS-II structures, $Br_2/8.62H_2O$ versus $Br_2/17H_2O$, the freezing out of Br_2 can, in principle, provide a thermodynamic force to favor the formation of CS-II. However, under the experimental conditions, we see no evidence of solid Br_2.

The RR spectra of **1** and **2** are shown in Figure 2. A progression of Br_2 vibrational overtones up to $\upsilon = 9$ is observed, allowing an accurate determination of the harmonic frequency, ω_e, and first anharmonicity, $\omega_e x_e$, of the molecule trapped in the two different crystal structures. Birge−Sponer plots constructed from the observed peak maxima are shown in Figure 3. The spectra are fitted, taking into account the isotopic abundance of Br_2 and thermal population of the vibrational levels. The latter consideration allows for correction of the parameters obtained from the Birge−Sponer plots of the observed maxima. The refined values for $^{79,81}Br_2$ are $\omega_e = 321.2 \pm 0.1$ cm^{-1} and $\omega_e x_e = 0.82 \pm 0.05$ cm^{-1} in **1** and $\omega_e = 317.5 \pm 0.1$ cm^{-1} and $\omega_e x_e = 0.70 \pm 0.1$ cm^{-1} in **2**. These should be compared to the parameters of the free molecule,[16] $\omega_e = 323.3$ cm^{-1} and $\omega_e x_e = 1.06$ cm^{-1}, and of the molecule in aqueous solution, where the fundamental appears at 306 cm^{-1} and no progression is observed. The RR spectra place the octahedral, platelet, and needle crystals (see Figure 2b) in one class, distinct from the tetragonal structure. The spectral changes are clearly the result of differences in the cage structure and the cage−guest relative orientation, dictated by induction and dispersive interactions. We note that the 317.5 cm^{-1} frequency of the bromine in **2** is, in fact, a significant shift toward a lower frequency from that in **1**. This strongly suggests that the cage containing the bromine molecule in the new structure is larger than either of the occupied cages in **1**.[17] The only common

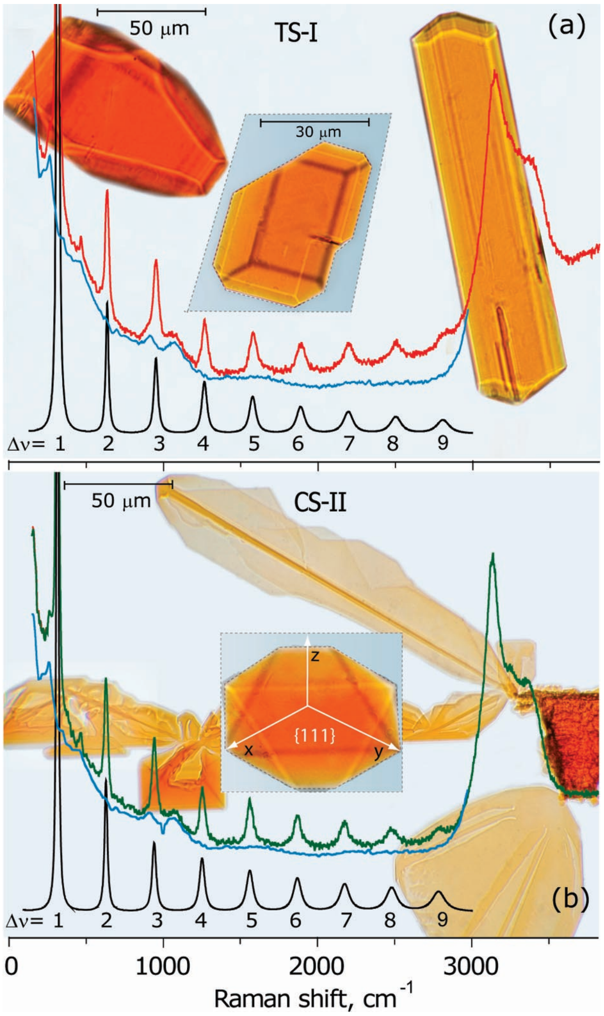

Figure 2. Single crystals and resonance Raman spectra of two different structures of Br_2 hydrate, (a) TS-I, with space group $P4_2/mnm$ (**1**) and (b) CS-II, with space group $Fd\bar{3}m$ (**2**). The spectra were recorded using a confocal Raman spectrometer with laser excitation at 532 nm, resonant with valence electronic transitions of Br_2. Shown are the experimental spectra of the single crystals, (**1**) in red and (**2**) in green, the background spectra recorded in the vicinity of the crystals (in blue), and the synthetic spectra using the extracted parameters (in black; see text). The effective temperature of the sample in the focal spot was approximately −10 °C due to heating of the sample with the excitation laser. The broad feature at ~3200 cm^{-1} is the OH stretching band of the water lattice.

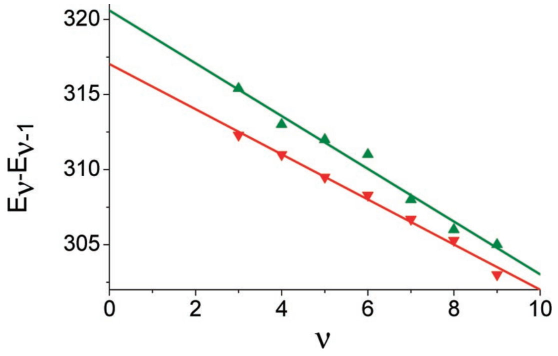

Figure 3. Birge−Sponer plot of the RR progressions observed in the TS-I (▲) and CS-II (▼) obtained from the peak maxima and their linear fits. The extracted values of the harmonic frequencies and first anharmonicities, which are reported in the text, are corrected for the thermal occupation of vibrational states (which skews lines).

clathrate hydrate structure consistent with this observation is CS-II, with the bromine molecule occupying the H cage. This further supports the structural assignment made above based on growth characteristics of the thin plates and regular octahedra. The red shift of the vibrational frequency in the H cage relative to the smaller cages of the TS-I lattice is due to dispersion and induction, the latter principally governed by the polarization of the molecule when eccentrically trapped in a loose-fit multipolar cage.[18] In **1**, according to X-ray analysis,[11] Br_2 occupies P and T cages in a 1:4 ratio. Yet, we observe a single progression in the RR spectrum, which evidently does not distinguish between these cages. We note that the spectra make it clear that the molecular rotation is completely quenched in all structures.[19] We defer the quantitative analysis of the spectra to the future; here, we suffice by noting that the RR spectra clearly identify at least two distinct crystal structures. The observed spectral signature (red shift) along with the crystal morphology strongly suggests that Br_2 forms CS-II at $T < -7$ °C.

Given the identification of two structures, which must have very similar free energies even though the Br_2/H_2O ratios are quite different, we surmise that others could also exist. The argument is direct. Most known clathrate frameworks contain only D, T, P, and H cages and can be constructed using three fundamental building blocks, 3D•2T•2P, 2D•6T, and 4D•2H[20,21]

$$(3D\cdot 2T\cdot 2P)_i(2D\cdot 6T)_j(4D\cdot 2H)_k$$

where i, j, and k are integer numbers with some restrictions on the possible combinations. A variety of frameworks having different combinations of these units exist. For example, $(i,j,k) = (2,2,0)$ corresponds to structure **1**, and two combinations, $(i,j,k) = (0,1,0)$ and $(i,j,k) = (0,0,4)$, generate cubic structures CS-I (primitive) and CS-II (face-centered). It is then possible to classify the relative stability of the building blocks under the assumption that Br_2 molecules occupy all larger cages. At temperatures above −7 °C, the stable form of Br_2 hydrate is **1**, TS-I. The 3D•2T•2P block must be responsible for the stabilization of TS-I; otherwise, Br_2 would form CS-I.[22] Accordingly, the stability of CS-II in the range of $-17 < T < -7$ °C signifies that Br_2 stabilizes the larger H cavities and that the 4D•2H block is the most favorable in this temperature range. Therefore, the combination of the 3D•2T•2P and 4D•2H blocks could also give stable or metastable structures since barriers for the transformation between phases are expected to be high. Dyadin et al.[9] proposed that Br_2 forms hexagonal and orthorhombic structures with hydration numbers of 10 and 12. Indeed, the unit cell formula for these structures can be presented as a combination of the stable fundamental blocks $(3D\cdot 2T\cdot 2P)\cdot 40H_2O$ and $(3D\cdot 2T\cdot 2P)_2(4D\cdot 2H)_2\cdot 148H_2O$. Topologically, clathrate hydrates belong to the class of tetrahedrally close-packed (TCP) structures, with which they share many physical properties. Our analysis could be useful in a search of possible polymorphs of TCP compounds of not only clathrate hydrates but also of such species such as clathrates of semiconductors.[23]

In conclusion, we have identified two stable structures of Br_2 hydrate and, on the basis of our structural analysis, believe that other structures are likely, making Br_2 hydrate a fascinating example of polymorphism.

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References and Notes

(1) Sloan E. D.; Koh C. A. *Clathrate Hydrates of Natural Gases*, 3rd ed.; Taylor & Francis CRC Press: Boca Raton, FL 2007.

(2) Miller, S. L. *Proc. Natl. Acad. Sci. U.S.A.* **1961**, *47*, 1798.

(3) Koh, C. A.; Sloan, E. D. *AIChE J.* **2007**, *53*, 1636.

(4) Reeburgh, W. S. *Chem. Rev.* **2007**, *107*, 486.

(5) van der Waals, J. H.; Platteeuw, J. C. *Adv. Chem. Phys.* **1959**, *2*, 1.

(6) Lowig, C. *Ann. Chim. Phys., Ser.* 2 **1829**, *42*, 113.

(7) Mulders, E. M. J. Dissertation, Tech. Hogeschool, Delft, 1936.

(8) Allen, K. W.; Jeffrey, G. A. *J. Chem. Phys.* **1963**, *38*, 2304.

(9) Dyadin, Y. A.; Aladko, L. S. *Zh. Strukt. Khim.* **1977**, *18*, 51.

(10) Dyadin, Y. A.; Belosludov, V. R. *Compr. Supramol. Chem.* **1996**, *6*, 789.

(11) Udachin, K. A.; Enright, G. D.; Ratcliffe, C. I.; Ripmeester, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 11481.

(12) Smelik, E. A.; King, H. E., Jr.; *Am. Mineral.* **1997**, *82*, 88

(13) Makogon, T. Y.; Larsen, R.; Knight, C. A.; Sloan, E. D. *J. Cryst. Growth* **1997**, *179*, 258.

(14) Knight, C. A.; Rider, K. *Philos. Mag. A* **2002**, *82*, 1609.

(15) Sasaki, S.; Hori, S.; Kume, T.; Shimizu, H. *J. Phys. Chem. B* **2006**, *110*, 9838.

(16) Linstrom, P. J., Mallard, W. G., Eds. *NIST Chemistry WebBook*, NIST Standard Reference database Number 69; National Institute of Standards and Technology: Gaithersburg MD, 20899, June 2005 (http://webbook.nist.gov).

(17) Pimentel, G. C.; Charles, S. W. *Pure Appl. Chem.* **1963**, *7*, 111.

(18) Senekerimyan, V.; Goldschleger, I. U.; Apkarian, V. A. *J. Chem. Phys.* **2007**, *127*, 214511.

(19) Were the molecule to rotate freely, then a rotational envelope of 42 cm^{-1} would be expected at 263 K, which is much greater than the deduced line width of the fundamental transition, 12 cm^{-1}.

(20) Frank, F. C.; Kasper, J. S. *Acta Crystallogr.* **1959**, *12*, 483.

(21) Sullivan J. M. Proceedings of the 3rd EuroConference on Foams, Emulsions and Applications (EuroFoam 2000), Delft, The Netherlands, 2000; Zitha, P. L. J., Banhart, J., Verbist, G., Eds.; Verlag MIT Publishing: Bremen, Germany, 2000; pp 111−119.

(22) The chemical potential of the CS-I is lower, while the Br_2 hydration number is larger. Therefore, in the case of similar stability of the 3D•2T•2P and 2D•6T blocks, bromine would form CS-I.

(23) Kovnir, K. A.; Shevelkov, A. V. *Russ. Chem. Rev.* **2004**, *73*, 923.