

Supporting Information for:

**Selective occupancy of methane by cage symmetry in TBAB ionic
clathrate hydrate**

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1. Experimental details of single crystal X-ray diffraction

The materials used in this study were CH₄ gas provided by Prax Air with 99.97 % certified purity, tetra-*n*-butylammonium bromide (TBAB) provided by Aldrich Chemical Company with 99 % certified purity, and water provided by EMD Chemicals Inc. (WX0004).

The single crystals were formed in the high pressure cell having a glass cylinder. The cell was equipped with a pressure sensor. We injected 0.0061 mole fraction (0.099 in mass fraction) of aqueous TBAB solution to the cell. The residual air in the cell was once evacuated by a vacuum pump up to approximately 3 kPa, and the cell was charged and discharged with 1 MPa pressure of methane five times. We supplied methane gas to 2 MPa. After the gas supply, the cell was immersed in the temperature-controlled bath, and kept steady. The bath temperature was maintained at 284.5 K during the single crystal growth. After substantial amount of crystals grew, they were removed from the cell under below 240 K. The single crystal sample was selected and mounted on the X-ray diffractometer (Bruker Kappa APEX II CCD). The sample was kept below 250 K during the process. The crystal structure was solved by direct methods and refined by least-square refinement with the SHELX program.[9 in the context] All atoms except for hydrogen were refined to be anisotropic. The detail of the X-ray diffraction measurement was summarized in Table S1.

Table S1. Crystal data and structure refinement results for the TBAB + CH₄ hydrate formed in the conditions ($x_{\text{TBAB}} = 0.0061$, $P = 2$ MPa, $T = 284.5$ K).

| | |
|---|---|
| empirical formula | C _{17.9} H _{116.4} BrNO ₃₈ |
| formula weight, g·mol ⁻¹ | 1024.56 |
| temperature, K | 100.0 (1) |
| wavelength, Å | 0.71070 |
| crystal system, space group | Orthorhombic, Pmma |
| unit cell dimensions, Å | $a = 21.0329(15)$ $b = 12.5972(9)$ $c = 12.0333(8)$ |
| volume, Å ³ | 3188.3(4) |
| Z, calculated density, g·cm ⁻³ | 2, 1.067 |
| absorption coefficient μ | 0.723 |
| $F(000)$ | 1130.0 |
| crystal size, mm | 0.2 × 0.2 × 0.6 |
| θ range for data collection | 1.69, 29.00 |
| index ranges | -28 < h < 28 -16 < k < 17 -16 < l < 16 |
| reflections collected/unique | 4515/ 4169 |
| completeness to 2θ | 0.993 |
| refinement method | F^2 against all reflections |
| data/restraints/parameters | 4515/ 250/ 528 |
| goodness-of-fit on F^2 | 1.175 |
| final R indices [$I > 2\Sigma(I)$] R_1 , wR_2 | 0.0549, 0.1649 |
| R indices (all data) R_1 , wR_2 | 0.0592, 0.1670 |

2. Supplementary Information

2.1 Structure of the TBAB crystal phase and summary of D cage symmetry and occupancy for TBAB ionic hydrates

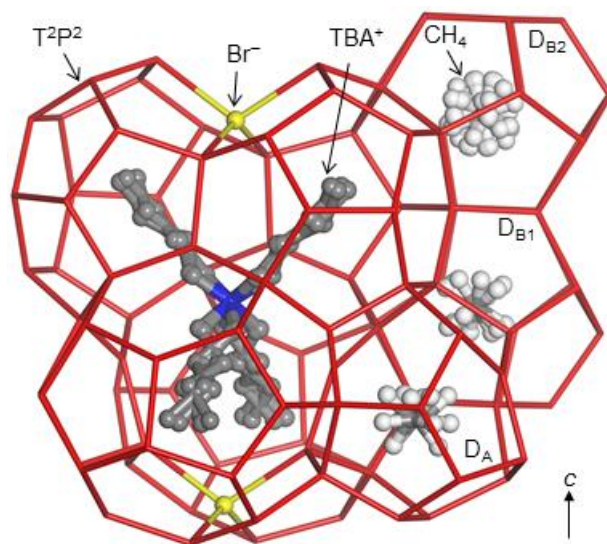


Figure S2. Structure of the T²P² cage with the encapsulated TBA cation and the D_A and D_B cages in the TBAB + CH₄ hydrate.

Table S2. Summary of D cage symmetry and occupancy for TBAB ionic hydrates and canonical clathrate hydrates.

| Hydrate | Lattice | Distorted D _A cage | | Regular D _B cages | | Averaged occupancy ^b |
|-------------------------------------|--------------|---------------------------------------|-----------|---------------------------------------|--------------------|---------------------------------|
| | | Symmetry | Occupancy | Symmetry | Occupancy | |
| TBAB + CH ₄ | Orthorhombic | <i>mm2</i> (<i>C</i> _{2v}) | 0.174 | <i>2/m</i> (<i>C</i> _{2h}) | 0.991 ^a | 0.719 |
| TBAB + CO ₂ ^c | Orthorhombic | <i>2/m</i> (<i>C</i> _{2h}) | 0.867 | <i>2</i> (<i>C</i> ₂) | 0.490 | 0.616 |
| TBAB ^d | Orthorhombic | <i>mm2</i> (<i>C</i> _{2v}) | - | <i>2/m</i> (<i>C</i> _{2h}) | - | - |
| sI | Cubic | - | - | <i>m-3</i> (<i>T</i> _h) | - | - |
| sII | Cubic | - | - | <i>3m</i> (<i>C</i> _{3v}) | - | - |
| sH | Hexagonal | - | - | <i>mmm</i> (<i>D</i> _{2h}) | - | - |

^a Averaged value for D_{B1} and D_{B2} cages.

^b Ratio of distorted D cage to regular one is 1 : 2.

^c Reported in reference 2 in the main article.

^d Reported in reference 7(a) in the main article.

2.2 Computational Methods

Molecular dynamics simulations are performed starting from the single crystal X-ray structure of the TBAB semiclathrate phase with incorporated CH₄ guests. The water proton positions in the semiclathrate phase are disordered and in these simulations proton positions are randomly chosen such that the ice rules are satisfied to the extent possible and the unit cell dipole moment is minimized. Some tolerance for Bjerrum defects is built into the MD procedure as water molecule can rotate to more stable configurations during the MD run. The presence of the Br⁻ ions in water-like lattice positions, where they form “hydrogen bonds” with water molecules, can lead to the formation of Bjerrum defects in the lattice. A more detailed analysis of proton disorder in the semiclathrate phases will remain for future work. The positions of the butyl chains of the *tetra*-butylammonium ion are disordered among sets of sites and one set was consistently chosen for each of the cations. The positions of the N atoms of the cation and Br⁻ positions are not disordered in the lattice. The initial CH₄ positions were chosen from one of the disordered sites in the crystal structure. There are two sets of 5¹² cages, D_A and D_B in the unit cell and their CH₄ occupancies are different. In the analysis of the geometric distribution and dynamics, these two groups of CH₄ molecules are considered separately. Simulations using experimental occupancies of 17% for the D_A 5¹² small cages and 100% for the D_B small cages are considered.

A 2×2×4 replica of the unit cell was used in the simulations. There were a total of 2432 water molecules, 64 TBAB molecules, and 133 CH₄ molecules in the simulation.

The intermolecular van der Waals potentials between atoms *i* and *j* on different molecules are considered to be the sum of Lennard-Jones (LJ) and electrostatic point charges,

$$V(r_{ij}) = \sum_{i,j} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}, \quad (\text{S1})$$

where σ_{ij} and ϵ_{ij} are the distance and energy parameters of the ij pair separated by a distance of r_{ij} and q_i and q_j are the electrostatic point charges on the atoms. Water molecules of the clathrate were modeled using the TIP4P four-charge model,[S1] while the tetra-butylammonium and bromine ions were modeled with the general AMBER force field,[S2] and the force field for bromide by Canongia Lopes and Pádua.[S3] The Tse-Klein-McDonald potential was chosen for methane [S4] helper guest molecules. The values for the parameters σ_{ii} and ϵ_{ii} for selected atom types are given in Table S1. Potentials between unlike atoms are calculated using the standard combination rules, $\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2}$ and $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$. Partial electrostatic charges on the atoms of the guest molecules were determined from charges from electrostatic potential grid (CHELPG) calculations [S5] with the Gaussian 98 suite of programs [S6] at the B3LYP/6-311++G(*d,p*) level of theory. The complete set of guest point charges and Lennard-Jones parameters are given in Table S3.

Given the ionic nature of the environment, the use of polarizable force fields for water could be appropriate for the ionic clathrate hydrates. However, since we are modeling an intact ionic hydrate phase and not the ionic hydrate formation, and since our focus is on methane guest dynamics in the simulations, we believe our present force field is sufficient. In a more detailed study of these materials in the future would use polarizable force fields.

Classical molecular dynamics simulations have been used to study clathrate hydrate phases for 30 years and have recently been extended to ionic clathrate hydrate phases. These simulations give a good representation of the guest and hydrate phase behavior as evidenced by the agreement of many predictions of classical MD simulations with structural and spectroscopic measurements.

Constant volume – constant temperature NVT molecular dynamics simulations on periodic simulation cells were performed using the DL_POLY software program version 2.20.[S7] The Nosé-Hoover thermostat [S8] is used thermostat relaxation time of 0.2 ps. The Verlet leapfrog algorithm was used with a time step of 1 fs. Long-range electrostatic

interactions were calculated using the Ewald summation method [S8] and all intermolecular interactions in the simulation box were calculated within a cut-off distance of $R_{\text{cutoff}} = 13.0$ Å. All simulations were performed for a total time of 500 ps, with 10 ps of temperature scaled equilibration. Structural and dynamics parameters were extracted from the run times. Temperatures of 100 (X-ray structure determination temperature), 200, and 250 K with ambient pressure were used in the simulations.

TABLE S3. Atomic point charges and Lennard-Jones parameters for TIP4P water, atoms on tetra-*n*-butylammonium ion, bromine ions, and CH₄ guest molecules.

| Atom | q (e) | $\epsilon_{ii} / \text{kcal mol}^{-1}$ | $\sigma_{ii} / \text{Å}$ |
|----------------------------|-------------|--|--------------------------|
| OW | 0.0 | 0.155 | 3.153 |
| HW | +0.52 | 0.0 | 0.0 |
| M (H ₂ O) | -1.0400 | 0.0 | 0.0 |
| N (TBA) | +0.560 | 0.170 | 3.25 |
| C ₁ (methylene) | -0.262 | 0.109 | 3.340 |
| C ₂ (methylene) | +0.031 | 0.109 | 3.340 |
| C ₃ (methylene) | -0.167 | 0.109 | 3.340 |
| C ₄ (methyl) | -0.270 | 0.109 | 3.340 |
| H ₁ (methylene) | +0.096 | 0.016 | 1.960 |
| H ₂ (methylene) | +0.021 | 0.016 | 2.649 |
| H ₃ (methylene) | -0.009 | 0.016 | 2.649 |
| H ₄ (methyl) | +0.076 | 0.016 | 2.649 |
| Br | -1.0 | 0.20554 | 3.970 |
| CH ₄ | 0.0 | 0.326 | 3.64 |

References in Supporting information

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