AB INITIO STRUCTURE DETERMINATION OF GAS HYDRATES AND REFINEMENT OF GUEST MOLECULE POSITIONS BY POWDER X-RAY DIFFRACTION

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ABSTRACT

Structure determination of powdered crystals is still not a trivial task. For gas hydrates, the difficulty lies in how to determine the rotational disorder and cage occupancies of the guest molecules without other supporting information or constraints because the complexity of the problem for the powder diffraction technique generally depends on the number of atoms to be located in the asymmetric unit. Here, the crystal structures of gas hydrates of CO_2, C_2H_6, C_3H_8, and Methylcyclohexane/CH_4, as determined by the direct-space and Rietveld techniques are reported. The resultant structures and cage occupancies were consistent with results found from conventional experimental methods using single crystal x-ray diffraction or solid-state ^{13}C-NMR. It was shown that the procedures reported in this study make it possible to determine guest disorder and absolute cage occupancy of gas hydrates even from powder crystal.

Keywords: *ab initio*, clathrate, direct-space method, hydrate, powder x-ray diffraction

INTRODUCTION

Single crystal x-ray diffraction is the most powerful technique for determining crystal structures. However, this method does not work for solids that cannot be prepared in the form of single crystals of sufficient size and quality. To determine the structure of such solids, we must instead use powder diffraction. For structural solutions by traditional powder diffraction techniques, the complexity of the problem generally depends on the number of atoms to be located in the asymmetric unit. Recently, significant advances have been made in the application of powder diffraction methods. Direct-space techniques using powder diffraction overcome intrinsic problems encountered in the structure-solution stage of the structure determination process.[1] For structural solutions by direct-space techniques, the complexity of a direct-space search procedure depends more directly on the number of degrees of freedom in the optimization rather than on the number of atoms in the asymmetric unit. For gas hydrates, the main advantage of the direct-space techniques is the possibility of refining the guest molecule positions in the cage structures. Here, crystal structures of gas hydrates structure I (space group *Pm*-3*n*), structure II (space group *Fd*-3*m*), and structure H (space group *P6*/*mmm*) as determined by the direct-space technique using powder x-ray diffraction (PXRD) are reported. The procedure reported here is useful for the estimation of gas storage capacity of gas hydrate crystals from their

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cage occupancies, which encage large guest molecules such as THF with H_2 or CH_4.[2]

EXPERIMENTAL

Gas hydrate samples were synthesized from fine ice powder using a method reported previously.[3] Crystallite size of each synthesized powder sample was examined by measuring their Debye-Scherrer ring because it is important to eliminate preferred orientation effects of the crystallites when recording PXRD data. The Debye-Scherrer rings were collected with MoKα radiation (λ = 0.7107 Å) on a BRUKER axs model SMART CCD diffractometer.

PXRD measurements were done using in lab x-ray diffractmeter (40 kV, 40 mA; BRUKER axs model D8 Advance equipped with a solid state detector model LynxEye) in θ/θ step scan mode using CuKα radiation (λ = 1.5406 Å) with a step width of 0.01966° in the 2θ range of 5.0–90.0°. Powdered hydrate samples were mounted on a PXRD sample holder made from Cu 2.5 mm in thickness under a N_2 gas atmosphere kept below 100 K. The temperature was kept at 163 K using a low-temperature chamber (Anton Paar model TTK 450) during each PXRD measurement.

STRUCTURE ANALYSIS

Structure solution calculations of gas hydrates encaging guest molecules were initiated by a global optimization of experimental diffraction profiles using a parallel tempering approach implemented in the direct-space method program FOX.[4] A large number of trial structures were calculated by rotation and translation of guest molecules and cage occupancy changes. Using the best fit model by the direct-space technique, refinements of the crystal structure of the hydrates were performed by a Rietveld method using the RIETAN-2000 program.[5] To model the disorder of guest molecules, rigid-body constraints were used. Virtual chemical species, *Wa* and *M*, whose atomic scattering factors are equal to the sum of those for H_2O and CH_4, -CH_3 or -CH_2 were used instead of refining hydrogen positions.

RESULTS AND DISCUSSION

Figure 1-1 shows a comparison of the measured PXRD pattern of CO_2 hydrate with the calculated pattern using the Rietveld method. There are some extra diffraction peaks indicating the coexistence of hexagonal ice (10.6 wt %). Figure 1-2 shows
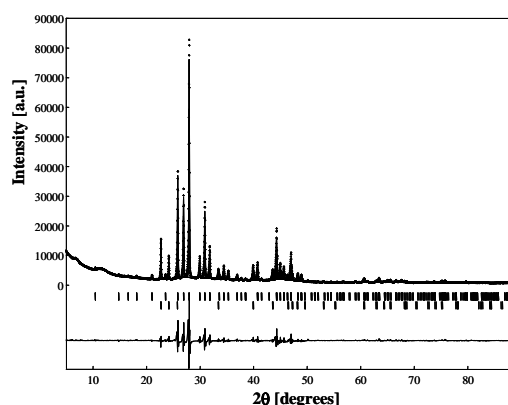

Figure 1-1 PXRD pattern of the CO_2 hydrate at 163 K. The plus marks (+) denote the observed intensities; the solid line is that calculated from the best-fit model of the Rietveld refinement. The bottom curve represents the deviation of observed and calculated intensities. Rwp = 10.1 %, χ^2 = 28.5. The upper tick marks represent the calculated peak positions for the structure I hydrate and the lower tick marks represent those for the hexagonal ice.
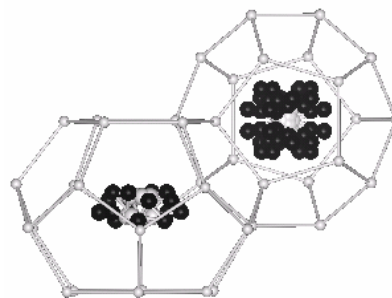

Figure 1-2 CO_2 molecules (Carbon atom: white, Oxygen atom: black) in structure I large ($5^{12}6^2$) and small (5^{12}) cage with full symmetry shown.
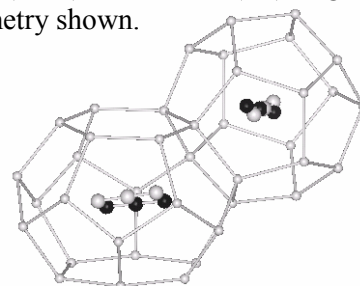

Figure 1-3 CO_2 molecules in CO_2 hydrate found in this study (black) and by the single crystal x-ray diffraction (grey) reported by Udachin et al.[6] for comparison. The Structure I large cage is on the left, the small cage on the right.

the CO_2 molecules with full symmetry in small and large cages in cubic structure I (a = 11.882(6) Å). Figure 1-3 shows the comparison of CO_2 positions refined by PXRD with single crystal analysis. The refined model showed that CO_2 occupied 99 % of the large cages and 67 % of the small cages in this study, whereas it was found that 100 % of the large cage and 71 % of the small cage by the single crystal analysis in the earlier study.[6] Refined atomic coordinates and isotropic displacement parameters for the structure are given in Table 1.

Figure 2-1 shows the comparison of the measured PXRD pattern of C_2H_6 hydrate with the calculated pattern using the Rietveld method. There are some extra diffraction peaks indicating the coexistence of hexagonal ice (14.4 wt %). Figure 2-2 shows the C_2H_6 molecules with full symmetry in small and large cages in cubic structure I (a = 12.009(3) Å). Figure 2-3 shows the comparison of C_2H_6 position refined by the PXRD with single crystal analysis. The refined model showed that C_2H_6 occupied 98 % of the large cages and 12 % of the small cages in this study, whereas it was found to be 100 % of the large cages and 5.8 % of the small cages by single crystal analysis in the earlier study.[7] Refined atomic coordinates and isotropic displacement parameters for the structure are given in Table 2.

Figure 3-1 shows the comparison of the measured PXRD pattern of C_3H_8 hydrate with the calculated pattern using the Rietveld method. There are some extra diffraction peaks indicating the coexistence of hexagonal ice (4.1 wt %). Figure 3-2 shows the C_3H_8 molecules with full symmetry in large cage of cubic structure II (a = 17.172(5) Å). Figure 3-3 shows a comparison of C_3H_8 position refined by PXRD with single crystal analysis. The refined model showed that C_3H_8 occupied 93 % of the large cages and 0 % of the small cages in this study, whereas it was found 100 % of the large cages and 0 % of the small cages were occupied in the single crystal analysis in the earlier study.[8] Refined atomic coordinates and isotropic displacement parameters for the structure are given in Table 3.
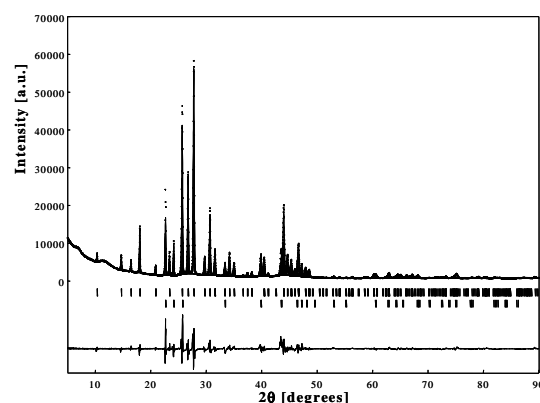

Figure 2-1 PXRD pattern of the C_2H_6 hydrate at 163 K. The plus marks (+) denote the observed intensities; the solid line is that calculated from the best-fit model of the Rietveld refinement. The bottom curve represents the deviation between the observed and calculated intensities. Rwp = 10.5 %, χ^2 = 28.6. The upper tick marks represent the calculated peak positions for the structure I hydrate and the lower tick marks represent those for the hexagonal ice.
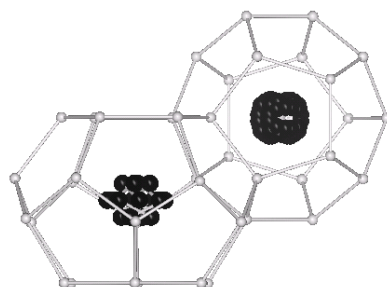

Figure 2-2 C_2H_6 molecules in structure I large ($5^{12}6^2$) and small (5^{12}) cage are shown with full symmetry. Solid spheres express the virtual chemical species -CH_3.
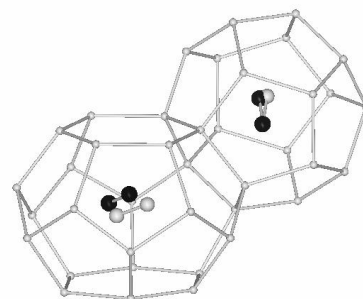

Figure 2-3 C_2H_6 molecules in C_2H_6 hydrate found in this study (black) and by single crystal x-ray diffraction (grey) reported by Udachin et al.[7] for comparison.
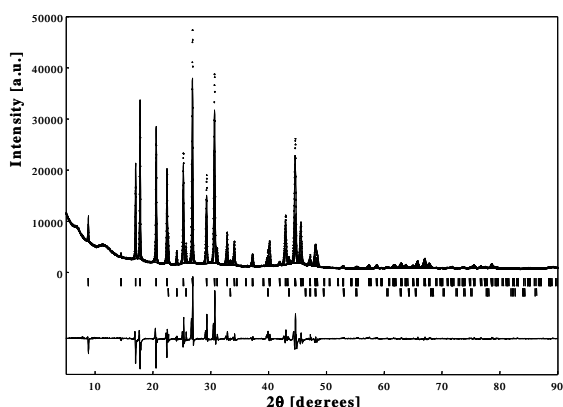
Figure 3-1   PXRD pattern of the C_3H_8 hydrate at 163 K. The plus marks (+) denote the observed intensities; the solid line is that calculated from the best-fit model of the Rietveld refinement.   The bottom curve represents the deviation between the observed and calculated intensities. Rwp = 11.2 %, χ^2 = 33.1. The upper tick marks represent the calculated peak positions for the structure II hydrate and the lower tick marks represent those for the hexagonal ice.
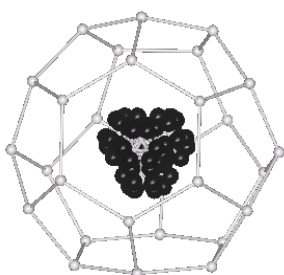
Figure 3-2 C_3H_8 molecules in structure II large ($5^{12}6^4$) shown with full symmetry. Solid spheres express the virtual chemical species -CH_2 and -CH_3.
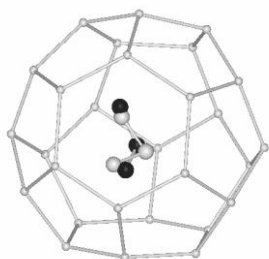
Figure 3-3 C_3H_8 molecules in C_3H_8 hydrate found in this study (black) and by the single crystal x-ray diffraction (grey) reported by Udachin et al.[8] for comparison. Only the large cage of structure II is shown.

Figure 4-1 PXRD pattern of the MCH/CH_4 hydrate at 163 K. The plus marks (+) denote the observed intensities; the solid line is that calculated from the best-fit model of the Rietveld refinement.   The bottom curve represents the deviation between the observed and calculated intensities. Rwp = 11.3 %, χ^2 = 30.0. The upper tick marks represent the calculated peak positions for the structure H hydrate and the lower tick marks represent those for the hexagonal ice.
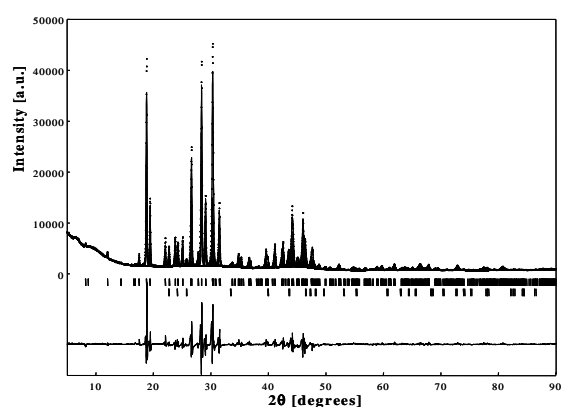

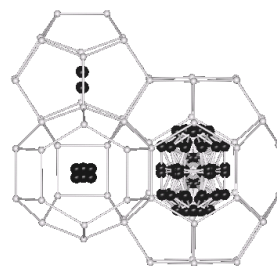Figure 4-2 MCH molecule in structure H large ($5^{12}6^4$) cage and CH_4 molecules in medium ($4^35^66^3$) and small (5^{12}) cage with full symmetry shown. Solid spheres express the virtual chemical species -CH_2, -CH_3, and CH_4.
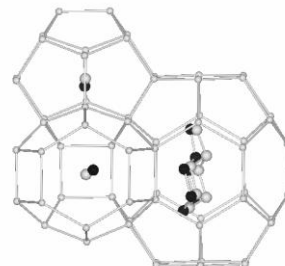

Figure 4-3 MCH and CH_4 molecules in MCH/CH_4 hydrate found in this study (black) and by the single crystal x-ray diffraction (grey) reported by Udachin et al.[7] for comparison.

Figure 4-1 shows a comparison of the measured PXRD pattern of Methylcyclohexane(MCH)/CH$_4$ hydrate with the calculated pattern using the Rietveld method. There are some extra diffraction peaks indicating the coexistence of hexagonal ice (1.7 wt %). Figure 4-2 shows the MCH molecule in the large cage and the CH$_4$ molecules in small and medium cages in hexagonal structure H (a = 12.2362(6) Å, c = 10.0525(5) Å). It is a comparison of MCH and CH$_4$ positions refined by PXRD with single crystal analysis. The refined model showed that MCH occupied 100 % of the large cages, and CH$_4$ occupied 95 % of the small cages and 91 % of the medium cages in this study, whereas it was found MCH occupied 100 % of the large cages, and CH$_4$ occupied 82 % of the small cages and 81 % of the medium cages by single crystal analysis in the earlier study.[7] The cage occupancies of MCH/CH$_4$ hydrate synthesized in the same batch as the sample for the PXRD suggest good consistency between PXRD result with C^{13}-NMR result: MCH occupied 100 % of the large cage, CH$_4$ occupied 90 % of the small cage, and 99 % of the medium cage by C^{13}-NMR. Refined atomic coordinates and isotropic displacement parameters for the structure are given in Table 4.

Many crystal structures of gas hydrates have been solved using the Rietveld method by localizing the disordered guest molecule in the center of cages.[9-16] However, all of the guest molecules found in this study lie off the geometrical center of the cages, and the positions are quite similar to those found by the single crystal x-ray diffraction technique in the earlier studies. The absolute cage occupancies determined in this study are also similar to those refined by the single crystal diffraction technique even though there are small differences because of different hydrate formation conditions.[17] We suggest that the guest disorder model for gas hydrates as solved by the direct-space technique is sufficient for structural refinement of nonstoichiometric guest molecules. For the estimation of absolute cage occupancies, the appropriate disorder model for guest molecules should be used due to a strong correlation between displacement parameters and cage occupancies. Here, we conclude that the procedure reported in this study is suitable to refine guest disorder and absolute cage occupancies using PXRD data.

atom	x	y	z	B (Å^2)
Wa1	0.1839(2)	0.1839	0.1839	4.8(1)
Wa2	0	0.3095(3)	0.1173(2)	4.8
Wa3	0	1/2	1/4	4.8
C1L	0.0362	0.2209	0.4862	0.5(4)
O1L	0.1177	0.2330	0.5383	0.5
O2L	-0.0453	0.2089	0.4340	0.5
C1S	0.4835	0.5026	0.5108	0.5
O1S	0.5590	0.4730	0.4564	0.5
O2S	0.4080	0.5322	0.5651	0.5

Table 1. Atomic coordinates and isotropic displacement parameters for CO$_2$ hydrate

atom	x	y	z	B (Å^2)
Wa1	0.1843(2)	0.1843	0.1843	3.6(1)
Wa2	0	0.3066(3)	0.1157(2)	3.6
Wa3	0	1/2	1/4	3.6
M1L	0.0804	0.2499	0.5355	1.7(4)
M2L	-0.0362	0.1991	0.5270	1.7
M1S	0.9518	0.0272	0.0385	1.7
M2S	1.0540	-0.0318	-0.0098	1.7

Table 2. Atomic coordinates and isotropic displacement parameters for C$_2$H$_6$ hydrate

atom	x	y	z	B (Å^2)
Wa1	3/8	3/8	3/8	2.4(1)
Wa2	0.2822(1)	0.2822	0.2822	2.4
Wa3	0.3176(1)	0.3176	0.1299(1)	2.4
M1L	0.9428	0.8933	0.9233	0.6(5)
M2L	0.8927	0.9123	0.8523	0.6
M3L	0.8071	0.9051	0.8753	0.6

Table 3. Atomic coordinates and isotropic displacement parameters for C$_3$H$_8$ hydrate

atom	x	y	z	B (Å^2)
Wa1	0.1310(3)	0.2620	0	3.1(1)
Wa2	1/3	2/3	0.1392(8)	3.1
Wa3	0.2091(2)	0.4182	0.2236(4)	3.1
Wa4	0.3873(3)	0.3873	0.3630(4)	3.1
M1L	1.0033	0.9722	0.4290	6.1(7)
M2L	1.0992	1.0896	0.5053	6.1
M3L	1.0670	1.0779	0.6560	6.1
M4L	1.0498	0.9525	0.7153	6.1
M5L	0.9561	0.8368	0.6324	6.1
M6L	0.9941	0.8530	0.4863	6.1
M7L	1.0298	0.9843	0.2786	6.1
M1S	0.5269	0.0470	0.0429	2.4(4)
M1M	0.2892	0.6427	0.4766	2.4

Table 4. Atomic coordinates and isotropic displacement parameters for MCH/CH$_4$ hydrate

CONCLUSIONS

We have shown that powder x-ray diffraction analysis by means of the direct-space technique and the Rietveld method is a powerful tool for determining gas hydrate structures and compositions. If high quality powder samples can be obtained, it is possible to obtain absolute cage occupancies without the need of a single crystal.

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