High-Pressure Phase Behavior and Cage Occupancy for the CF_4 Hydrate System

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The three-phase coexisting curve of CF_4 hydrate + water + fluid CF_4 and laser Raman spectroscopic analysis for the CF_4 hydrate system have been investigated in a temperature range of 276 to 317 K and at pressures up to 454 MPa. The present experimental results show that the CF_4 molecule is able to occupy both the S- and M-cages in the high-pressure region (above 70 MPa) similar to the cyclopropane hydrate system. The pressure independence of the intermolecular O−O vibration reveals that the CF_4 hydrate cage is hardly shrunk by pressurization.

Introduction

Gas hydrates, having attracted much attention as a key substance for global environment problems, consist of guest molecules and hydrogen bonded water cages.[1] Gas hydrates have three typical lattice structures, that is, structure I,[2] structure II,[2] and structure H,[3] which belong to the cubic (*Pm*3*n*), cubic (*Fd*3*m*), and hexagonal (*P*6/*mmm*) space groups, respectively. Structure I is composed of two kinds of hydrate cages; one is the S-cage of pentagonal dodecahedron (5^{12}), the other is the M-cage of tetrakaidecahedron ($5^{12}6^2$). A combination of the S-cage and L-cage (hexakaidecahedron, $5^{12}6^4$) constitutes structure II.

The cage occupancy by the guest molecule provides important information about the gas hydrates. The molecular size of the guest species has an effect upon the hydrate structure and cage occupancy. For example, the methane molecule generates the structure I hydrate and occupies both the S- and M-cages. On the other hand, it has been argued that some molecules such as ethane, ethylene, and cyclopropane cannot occupy the S-cage since they have larger molecular sizes than the S-cage. However, we have reported elsewhere direct evidence of S-cage occupancy by ethane,[4] ethylene,[5] and cyclopropane[6] from Raman spectroscopic analysis of the intramolecular vibrations within the limit pressures of 500 MPa. Tanaka[7] has predicted that the CF_4 molecule, whose size is similar to that of ethane, can occupy the S-cage at relatively moderate pressures from the van der Waals Platteuw theory. In Jeffrey's book,[8] the CF_4 hydrate belongs to structure I. However, information on CF_4 cage occupancy is not mentioned there.

The thermodynamic stability boundary for the CF_4 hydrate system has been reported by several investigators.[9−11] However, all of these studies are limited to the low-pressure region. The thermodynamic stabilities of gas hydrates at high pressure (above 100 MPa) are informative and important for the understanding of gas hydrate properties, for example, the structural phase transition.[12,13] In the present study, the three-phase coexisting state (CF_4 hydrate (H) + water (L_1) + fluid CF_4 (F)) for the CF_4 hydrate system in a temperature range of 276 to 317 K and at pressure up to 454 MPa has been measured. The intramolecular symmetric C−F stretching vibration of CF_4 in each phase and the intermolecular O−O vibration between the water molecules are measured using laser Raman spectroscopy at the three-phase coexisting ($H + L_1 + F$) conditions. In addition, the pressure dependencies are also analyzed in a pressure range up to approximately 400 MPa.

Materials

Research grade CF_4 of purity 99.999 mol % was obtained from Neriki Gas Co., Ltd. The distilled water was purchased from Yashima Pure Chemicals Co., Ltd. Both were used without further purification.

Experimental Apparatus and Procedures

The experimental apparatus used in the present study is essentially the same as our previous one,[14] which consists of a high-pressure optical cell with a couple of sapphire windows (inner volume, 0.2 cm^3; maximum working pressure, 500 MPa; made of stainless steel, SUS630), a mixing ruby ball, a high-pressure pump, an intensifier, pressure gages, a temperature control system, a charge-coupled device (CCD) camera, and a laser Raman microprobe spectrometer (Jobin Yvon Ramanor T64000).

A known amount of CF_4 fluid was introduced into the evacuated and cooled cell. A mixing ruby ball in the cell was vibrated for agitation from the outside. The contents were pressurized up to a desired pressure by a successive supply of water. After the formation of the CF_4 hydrate, to establish the three-phase (CF_4 hydrate + water + fluid CF_4) equilibrium, the system temperature was gradually increased and the contents were agitated intermittently. The phase behavior of the system was observed by the CCD camera through the sapphire window. The equilibrium temperature was measured within an accuracy of ±0.02 K by a thermistor probe (Takara D-641) placed into a hole in the cell wall. The pressure was measured by a strain gage (Valcom VPRT) or a pressure transducer (NMB STD-5000 K) within an accuracy of ±0.01 MPa (up to 50 MPa) or ±1 MPa (above 50 MPa), respectively.

The single crystal of the CF_4 hydrate prepared in the high-pressure optical cell was analyzed using a laser

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Table 1. Three-Phase Coexisting Curve for the CF_4 Hydrate System

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
276.62	7.48	282.84	30.75	291.51	95	306.28	270
277.47	9.49	283.56	34.41	292.05	101	308.15	299
298.34	11.48	285.68	47.41	293.46	114	310.00	324
279.11	13.60	286.60	53	295.31	135	311.39	349
279.68	15.84	287.30	58	296.76	151	312.76	372
280.34	17.79	288.37	67	297.71	164	315.27	420
280.95	20.67	289.15	73	298.92	178	317.05	454
281.60	23.78	289.89	80	300.55	199		
281.99	26.14	290.35	85	302.06	220		
282.46	28.62	291.00	90	304.43	248		

Raman microprobe spectrometer with a multichannel CCD detector. The light source for excitation was an argon ion laser whose wavelength, power level, and spot diameter were 514.5 nm, 100 mW, and 2 μm, respectively. The laser beam from the object lens irradiated the CF_4 hydrate through a sapphire window, and the backscatter in the opposite direction was taken in with the same lens. The CCD detector was kept at 140 ± 5 K by liquid nitrogen for heat-noise reduction. The integration time was varied from 60 to 300 s, depending on the intensity of light scattering. The spectral resolution was about 1 cm^{-1}.

Results and Discussion

The stability boundary curve ($H + L_1 + F$) for the CF_4 hydrate system is listed in Table 1 and plotted on the plane of logarithmic pressure versus temperature in Figure 1 accompanied with the methane hydrate system. As the present experimental equipment is not suitable for measuring phase equilibrium at a temperature below the ice point (273 K), we could not compare with some literature values.[9,10] The data of Mooijer-Van den Heuvel[11] in the lower pressure region up to 13 MPa are located in a slightly higher temperature region than that of the present study. Compared with the methane hydrate system,[15,16] the stability zone of the CF_4 hydrate system exists in a higher pressure (lower temperature) region than that of the methane hydrate system, and the equilibrium pressures increase monotonically and moderately with temperature. The smoothness of the three-phase coexisting curve suggests that there is no structural phase transition point in the experimental region of the present study, that is, the CF_4 hydrate is still structure I in the high-pressure region of about 500 MPa.

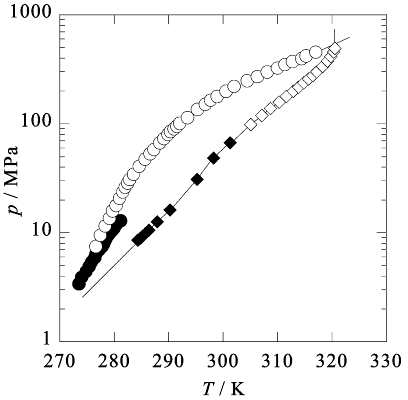

Figure 1. Three-phase coexisting curve for the CF_4 hydrate system (circular keys) accompanied with the methane hydrate system (lozenge keys): ○, this study; ●, Mooijer-Van den Heuvel et al. (ref 11); ◇, Nakano et al. (ref 15); ◆, Ohgaki and Hamanaka (ref 16).

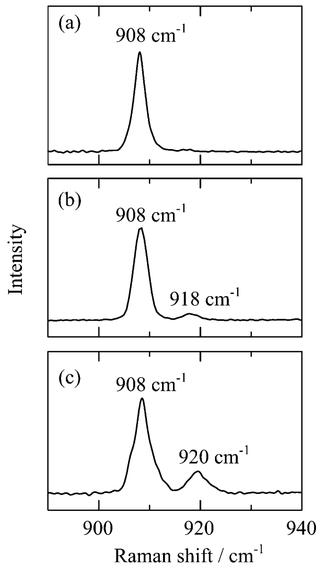

Figure 2. Raman spectra of the symmetric C−F vibration mode of CF_4 in the CF_4 hydrate crystal: (a) 50 MPa, (b) 150 MPa, and (c) 400 MPa.

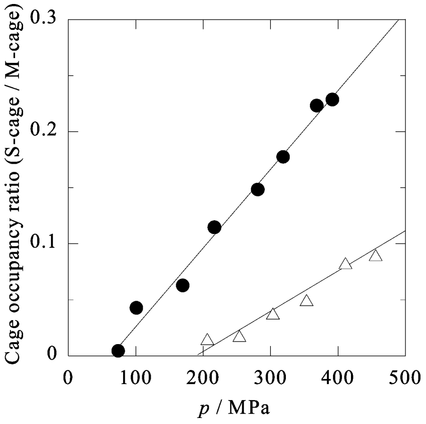

Figure 3. Pressure effect on the cage occupancy of guest species: ●, CF_4; △, cyclopropane (ref 6).

The CF_4 molecule has four Raman active vibration modes. In the present study, we noticed the symmetric C−F vibration mode (ν_1, detected at 908.5 cm^{-1} at atmospheric pressure[17]) because it exhibits sharp and high intensity. The Raman spectrum of the symmetric C−F vibration for the CF_4 hydrate crystal was a single peak (around 908 cm^{-1}) below 70 MPa. A typical Raman spectrum observed in the CF_4 hydrate crystal at 50 MPa is shown in Figure 2a. The Raman spectrum of the symmetric C−F vibration mode for the fluid CF_4 phase was a single peak (around 909 cm^{-1}) at a slightly higher frequency than that of the hydrate phase. Unfortunately, we could not analyze the Raman spectrum of the symmetric C−F vibration of CF_4 molecules dissolved in the liquid water phase because it was very weak. As the system pressure increases, an additional Raman peak is detected around 918 cm^{-1} in the CF_4 hydrate phase as shown in Figure 2b (at 150 MPa). The split of the Raman peak reveals that the CF_4 molecules are entrapped in two different cages, that is, the CF_4 molecule is able to occupy both the S- and M-cages. The Raman peak area ratio of the CF_4 molecule in the S-cage becomes larger at 400 MPa as shown in Figure 2c. The relative Raman peak area of S-cage ($S_{\text{S-cage}}$) to M-cage ($S_{\text{M-cage}}$) versus pressure is shown in Figure 3. The peak area ratio ($S_{\text{S-cage}}/S_{\text{M-cage}}$) increases in acceleration with pressure. This means that the CF_4 molecule shows peculiar

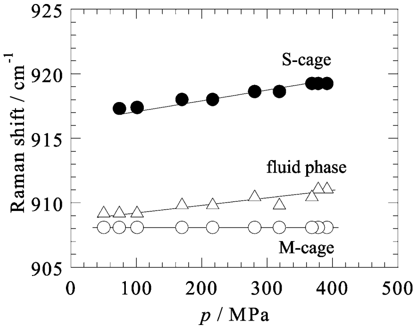

Figure 4. Pressure effect on the symmetric C−F stretching vibration in the CF_4 hydrate system: ●, S-cage; ○, M-cage; △, fluid phase.

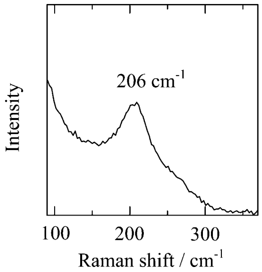

Figure 5. Raman spectrum of the intermolecular O−O vibration mode in the CF_4 hydrate crystal at 400 MPa.

cage occupancy, so-called “pressure oppressive S-cage occupancy”, as does cyclopropane.[6] The S-cage occupancy of CF_4 is higher than that of cyclopropane and has strong pressure dependence. Tanaka[7] has predicted that the CF_4 molecule could occupy both the S- and M-cages in a relatively low-pressure region. However, we have obtained a single peak in the low-pressure region (Figure 2a). In addition, when the peak area ratio is extrapolated (Figure 3), the S-cage occupancy of the CF_4 molecule becomes zero around 70 MPa. These findings indicate that the CF_4 molecule can occupy both the S- and M-cages of the structure I hydrate at least above 70 MPa.

The pressure dependence of the Raman shift for the symmetric C−F stretching vibration is shown in Figure 4. The higher frequency peak for the S-cage shows weak pressure dependence (0.5 cm^{-1}/100 MPa). On the other hand, the lower one for the M-cage is independent of pressure. Similar behavior was also observed in the previous study for some hydrate systems.[4−6,13−15] These results also support the idea of no structural phase transition and suggest that the inner volume of the M-cage is still large enough for the CF_4 molecule even if the pressure is raised to 500 MPa.

The intermolecular O−O vibration mode of the hydrate crystal is usually detected around 205 cm^{-1}. The Raman spectrum of the intermolecular O−O vibration mode in the CF_4 hydrate crystal at 400 MPa is detected at 206 cm^{-1} as shown in Figure 5. The pressure effect on the O−O vibration in the CF_4 hydrate is shown in Figure 6 accompanied with our previous results for nitrogen,[13] CO_2,[14] methane,[15] ethane,[4] ethylene,[5] and cyclopropane[6] hydrate systems. The O−O vibration in the CF_4 hydrate crystal is almost independent of pressure, and this behavior is similar to those of ethane, ethylene, and cyclopropane hydrate systems, while nitrogen, CO_2, and methane hydrate systems show weak pressure dependence. The pressure independence for the CF_4 hydrate system means that the hydrate cages are hardly shrunk by pressurization.

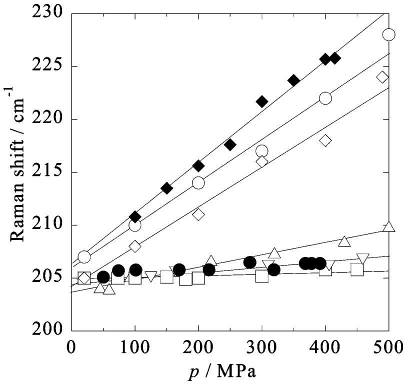

Figure 6. Pressure effect on the O−O vibration in the hydrate systems: ●, CF_4; ◆, nitrogen (ref 13); ◇, CO_2 (ref 14); ○, methane (ref 15); □, ethane (ref 4); △, ethylene (ref 5); ▽, cyclopropane (ref 6).

Conclusions

The three-phase coexisting curve of CF_4 hydrate + water + fluid CF_4 was investigated up to 454 MPa by use of a high-pressure optical cell. The equilibrium pressure increases monotonically with temperature in the present experimental region. The behavior of the three-phase coexisting curve supports that the structure I CF_4 hydrate never changes any other lattice structure in the present experimental conditions.

The Raman spectra of the intramolecular symmetric C−F stretching vibration of the CF_4 molecule and the intermolecular O−O vibration modes were observed in the pressure range up to approximately 400 MPa. The split of Raman spectra for the symmetric C−F vibration in the CF_4 hydrate phase is detected in the pressure range higher than 70 MPa. This fact indicates that the CF_4 molecule can occupy both the S- and M-cages of the structure I hydrate in the high-pressure region above 70 MPa. In addition, the S-cage occupancy of the CF_4 molecule becomes larger with increasing pressure. The O−O vibration of the CF_4 hydrate crystal is almost independent of pressure.

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Literature Cited

(1) Sloan, E. D., Jr. *Clathrate Hydrate of Natural Gases*, 2nd ed.; Marcel Dekker: New York, 1998.

(2) Stackelberg, M. v.; Müller, H. R. Feste Gashydrate II. *Z. Elektrochem.* **1954**, *58*, 25−39.

(3) Ripmeester, J. A.; Tse, J. S.; Ratcliffe, C. I.; Powell, B. M. A new clathrate hydrate structure. *Nature* **1987**, *325*, 135−136.

(4) Morita, K.; Nakano, S.; Ohgaki, K. Structure and stability of ethane hydrate crystal. *Fluid Phase Equilib.* **2000**, *169*, 167−175.

(5) Sugahara, T.; Morita, K.; Ohgaki, K. Stability boundaries and small hydrate-cage occupancy of ethylene hydrate system. *Chem. Eng. Sci.* **2000**, *55*, 6015−6020.

(6) Suzuki, M.; Tanaka, Y.; Sugahara, T.; Ohgaki, K. Pressure dependence of small-cage occupancy in the cyclopropane hydrate system. *Chem. Eng. Sci.* **2001**, *56*, 2063−2067.

(7) Tanaka, H. The stability of Xe and CF_4 clathrate hydrates. Vibrational frequency modulation and cage distortion. *Chem. Phys. Lett.* **1993**, *202*, 345−349.

(8) Jeffrey, G. A. Hydrate Inclusion Compounds. In *Inclusion Compounds*; Academic Press: London, 1984; Vol. 1, Chapter 5.

(9) Miller, S. L.; Eger, E. I.; Lundgreen, C. Anasthetic Potency of CF_4 and SF_6 in Dogs. *Nature* **1969**, *221*, 468−469.

(10) Garg, S. K.; Gough, S. R.; Davidson, D. W. A wide-line NMR study of reorientation of some spherical-top molecules enclathrated in water. *J. Chem. Phys.* **1975**, *63*, 1646−1654.

(11) Mooijer-van den Heuvel, M. M.; Peters, C. J.; de Swaan Arons, J. Influence of water-insoluble organic components on the gas hydrate equilibrium conditions of methane. *Fluid Phase Equilib.* **2000**, *172*, 73−91.
(12) Manakov, A. Y.; Goryainov, S. V.; Kurnosov, A. V.; Likhacheva, A. Y.; Dyadin, Y. A.; Larionov, E. G. Clathrate Nature of the High-Pressure Tetrahydrofuran Hydrate Phase and Some New Data on the Phase Diagram of the Tetrahydrofuran−Water System at Pressures up to 3 GPa. *J. Phys. Chem. B* **2003**, *107*, 7861−7866.
(13) Sugahara, K.; Tanaka, Y.; Sugahara, T.; Ohgaki, K. Thermodynamic Stability and Structure of Nitrogen Hydrate Crystal. *J. Supramol. Chem.* **2002**, *2*, 365−368.
(14) Nakano, S.; Moritoki, M.; Ohgaki, K. High-Pressure Phase Equilibrium and Raman Microprobe Spectroscopic Studies on the CO_2 Hydrate System. *J. Chem. Eng. Data* **1998**, *43*, 807−810.
(15) Nakano, S.; Moritoki, M.; Ohgaki, K. High-Pressure Phase Equilibrium and Raman Microprobe Spectroscopic Studies on the Methane Hydrate System. *J. Chem. Eng. Data* **1999**, *44*, 254−257.
(16) Ohgaki, K.; Hamanaka, T. Phase-Behavior of CO_2 Hydrate−Liquid CO_2−H_2O System at High Pressure. *Kagaku Kougaku Ronbunshu* **1995**, *21*, 800−803.
(17) Monostori, B.; Weber, A. The Raman Spectrum of Gaseous CF_4. *J. Chem. Phys.* **1960**, *33*, 1867−1868.

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