High-pressure Raman study on single crystalline methane hydrate surrounded by methane in a diamond anvil cell

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Abstract. High-pressure Raman measurements have been performed for single crystalline methane hydrate (MH) surrounded by fluid or solid methane in a diamond anvil cell. We successfully obtained the pure O-H stretching and lattice vibration spectra in MH-sI and MH-II phases. In these Raman spectra, there is no Raman band from water or ice-VI. The observed pressure of phase transformation from MH-sI to MH-II is 0.9 GPa, which is the same result as methane hydrate surrounded by water.

1. Introduction

Methane hydrate (MH), having attracted great interest recently as a new energy resource, is a special class of ice that contains methane as guest in host cages or networks of hydrogen-bonded water molecules [1]. In other respects, methane is a powerful greenhouse gas, and its outgassing from MH may contribute substantially the prospect of global warming. Therefore, the study of MH properties under high pressure is of fundamental importance in understanding the physical chemistry of clathrate hydrates of natural gases. At room temperature, the initial structure I of methane hydrate (MH-sI) successively transforms to MH-II (sH) and MH-III (sO, filled ice) at 0.9 GPa and 1.9 GPa, respectively [2-11]. These phase behaviors were observed in two phase coexistent state between methane hydrate and water. In our high pressure Raman measurements of methane hydrate, no signal for the O-H stretching and lattice vibrations was observed in MH-III phase, in spite of the appearance of those signals in the same sO phase of Ar hydrate [12] and Kr hydrate [13]. This disappearance in MH-III phase is probably caused by the weak Raman signals of MH-III and the strong Raman spectra of the surrounding ice-VII. Therefore, it is worth observing the O-H stretching and lattice vibration spectra of methane hydrate surrounded by fluid or solid methane. In addition to that, such a condition may induce the different phase behavior of methane hydrate.

The purposes of this paper are to make a coexistent state between methane hydrate and fluid methane in a diamond anvil cell (DAC) and to obtain the pure Raman spectra for the O-H stretching and lattice vibrations of host water networks. This is the preliminary work for observing the Raman signals of water networks in MH-III phase. In order to perform these experiments, we firstly loaded rich fluid methane and a small amount of pure water into a sample chamber of a DAC, and grew single crystals of MH-sI in fluid methane. By performing high-pressure Raman measurements, we obtained the pure O-H stretching and lattice vibration spectra in MH-sI and MH-II phases without the hindrance of the Raman band from water or ice-VI. Moreover, the phase transformation pressure of 1.9 GPa

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from MH-sI to MH-II is almost the same as that of methane hydrate surrounded by water, in spite of the different phase equilibrium condition of methane hydrate.

2. Experiment
In the present experiment, it is very important to make a coexistent state between methane hydrate and fluid methane (or solid methane), for observing the O-H stretching and lattice vibrations of host water networks. To do this, we firstly loaded rich fluid methane and a small amount of distilled water into a sample chamber (diameter 0.5 mm, depth 0.3mm) of a DAC, and grew single crystals of MH-sI in fluid methane. Figure 1 shows a photomicrograph of single crystals of MH-sI in fluid methane at 0.22 GPa. Unlike the case of methane hydrate in water, it is difficult to make a fine single crystal of MH-sI. In a three phase equilibrium state among MH-sI, fluid methane and water, crystalline MH-sI hardly grew, because MH-sI quickly enveloped a droplet of water and probably prevented methane dissolving in water. The pressure was measured by the ruby-scale method. The pressure accuracy in this experiment was $\pm 0.02$ GPa. All high-pressure Raman scattering measurements for MH have been carried out in a back-scattering geometry at 296 K. The sample was excited by a 532.0 nm line of solid-state laser (COHERENT, Nd$^+$-YVO$_4$) and the spectra were obtained by a spectrometer (JASCO, NR1800) equipped with a triple polychromater and a liquid-nitrogen-cooled charge-coupled device (CCD) detector.

![Figure 1. Photomicrograph of single crystals of methane hydrate structure I (MH-sI) in fluid methane at 0.22 GPa.](image)

3. Results and discussion
By applying the high-pressure Raman scattering spectroscopy to single crystals of MH surrounded by fluid or solid methane, we obtained the pressure dependences of Raman spectra for the lattice and O-H modes as shown in figures 2(a) and 3(a). For comparison, the Raman spectra for MH coexisting with water or ice-VI are also illustrated in figures 2(b) and 3(b). Raman peaks from methane hydrate and ice-VI are indicated by open and solid triangles in these figures, respectively. So far the measured Raman spectra of MH-II above 1.3 GPa were accompanied with those of ice-VI as shown in figures 2(b) and 3(b). [The Raman spectra of MH in water at 0.08 GPa, 0.79 GPa and 1.15 GPa have no obvious band about water, since the water has no contribution to the lattice region and broad bands (3100-3600 cm$^{-1}$) for O-H stretching vibrations. (See the spectra for water at 0.08 GPa in figure 2(b) and 3(b)) These signals from high-pressure ices have prevented us observing pure Raman signals for high-pressure MH phases.]

On the other hand, the present results for MH crystals surrounded by methane show no Raman signals from ice-VI and provide the pure Raman spectra for lattice and O-H vibration of MH-II at 1.71 GPa in figures 2(a) and 3(a). Although fluid methane transforms to plastic phase I at 1.6 GPa [14], the fcc plastic phase of methane generally shows no lattice band [15]. Therefore, both liquid and solid I phases of methane contribute no signal to lattice region.
Figure 2. Pressure dependences of Raman spectra for lattice mode of (a) methane hydrate (MH) in fluid or solid methane and (b) MH in water or ice-VI. For comparison, Raman spectra for water and ice-VI are presented by broken lines at 0.8 GPa and 1.71 GPa, respectively. Open and solid triangles stand for the Raman peaks of lattice mode from MH and ice-VI, respectively. FM and SM indicate fluid and solid methane, respectively.

At the phase transformation from MH-sI to MH-II, the excess water is excluded from MH-sI because of the reduction of the hydration number of MH. If this excess water remains inside the MH-II crystal, the Raman spectra of ice-VI appear even in the coexisting state between MH and methane. Therefore, in this experiment, the excess water from MH-sI was totally formed into MH-II at 0.9 GPa. In MH-III phase, we couldn’t observe the Raman signals from the MH-III, because of the strong signals from ice-VII and the weak signals from host cage of MH-III. If only the MH-III is grown in solid phase of methane above 1.9 GPa, we should observe the Raman spectra in MH-III phase similar to those in the MH-II phase in this experiment.

Next, we investigate the phase transformation from MH-sI to MH-II in fluid methane. From the high-pressure Raman study on Kr hydrate [13], it is known that the Raman signal at 120 cm\(^{-1}\) disappears only in the MH-sI phase. From the present Raman spectra for methane hydrate, we observed that the signal at 120 cm\(^{-1}\) appeared above 0.9 GPa. This result clearly indicates that the MH-sI phase transforms into the MH-II phase. In addition, we also confirmed this phase transformation through the microscopic observation. From these results of the Raman spectra and the microscopic observation for MH surrounded by methane, we found that the phase transformation pressure from MH-sI to MH-II is the same pressure of 0.9 GPa as in the case of MH surrounded by water. Therefore, the surrounding fluid methane doesn’t contribute to the phase transformation of MH and its pressure.

4. Summary
We successfully made single crystalline MH surrounded by methane in a diamond anvil cell. By applying the high-pressure Raman spectroscopy to this MH coexisting with fluid or solid methane, we obtained the pure O-H stretching and lattice vibration spectra in MH-sI and MH-II phases. In these
Raman spectra, there is no Raman band from water or ice-VI differing from the results of MH with water or ice-VI. From the results of the Raman spectra and the microscopic observation for MH in methane, we found that the phase transformation pressure from MH-sI to MH-II is the same pressure of 0.9 GPa as in the case of MH surrounded by water. Therefore, surrounding methane has no contribution to phase change and its pressure with respect to the MH-sI to MH-II transformation.

Figure 3. Pressure dependences of Raman spectra for O-H stretching mode of (a) methane hydrate (MH) in fluid or solid methane and (b) MH in water or ice-VI. For comparison, Raman spectra for water and ice-VI are presented by broken lines at 0.8 GPa and 1.71 GPa, respectively. Open and solid triangles stand for the Raman peaks of O-H stretching mode from MH and ice-VI, respectively. FM and SM indicate fluid and solid methane, respectively, and vertical dotted lines stand for the positions of the asymmetrical stretching vibration of methane molecules. The strong asymmetrical stretching signals in figure 3(a) come from the surrounding methane around MH.

References
[1] Sloan Jr. E D 1998 Clathrate Hydrates of Natural Gases, second ed. (New York, Marcel Dekker)
[2] Loveday J S, Nelmes R J, Guthrie M, Belmonte S A, Allan D R, Klug D D, Tse J S and Handa Y P 2001 Nature 410 661
[3] Hirai H, Hasegawa M, Yagi T, Yamamoto Y, Nagashima K, Sakashita M, Aoki K and Kikegawa T 2000 Chem. Phys. Lett. 325 490
[4] Loveday J S, Nelmes R J, Guthrie M 2001 Chem. Phys. Lett. 350 459
[5] Shimizu H, Kumazaki T, Kume T and Sasaki S 2000 J. Phys. Chem. B 106 30
[6] Hirai H, Uchihara Y, Kawamura T, Yamamoto Y and Yagi T 2002 Proc. Jpn. Acad. 78B 39
[7] Loveday J S, Nelmes R J, Klug D D, Tse J S and Desgreniers S 2003 Can. J. Phys. 81 539
[9] Hirai H, Tanaka T, Kawamura T, Yamamoto Y and Yagi T 2003 Phys. Rev. B 68 172102
[10] Kumazaki T, Kito Y, Sasaki S, Kume T and Shimizu H 2004 Chem. Phys. Lett. 388 18
[11] Hirai H, Tanaka T, Kawamura T, Yamamoto Y and Yagi T 2004 J. Phys. Chem. Solids 65 1555
[12] Shimizu H, Hori S, Kume T and Sasaki S 2003 Chem. Phys. Lett. 368 132
[13] Sasaki S, Hori S, Kume T and Shimizu H 2006 J. Phys. Chem. B 110 9838
[14] Hebert P, Polian A, Loubeyre P and Le Toullec R 1987 Phys. Rev. B 36 9196
[15] Wu Y H, Sasaki S and Shimizu H 1995 J. Raman Spectrosc. 26 963