High-pressure Raman study of methane hydrate “filled ice”

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Abstract. High-pressure Raman scattering measurements for the high-pressure phase III of methane hydrate (MH-III, filled ice structure) have been performed at pressures up to 25 GPa and at 296 K. We have observed the O-H stretching Raman signal in the MH-III phase by growing the MH-III crystals over several days at 1.9 GPa. The O-H stretching vibrational peak in the MH-III phase shows negative pressure dependence indicative of hydrogen bond and disappears above 14 GPa. The symmetrization pressure of hydrogen bond in the MH-III phase is estimated to be about 45 GPa from the pressure dependence of the O-H stretching Raman frequency, which is consistent with the previous theoretical prediction.

1. Introduction

Methane hydrate, called burning ice, is an inclusion compound that contains methane molecules in cages or network of hydrogen-bonded water molecules. Methane hydrate has attracted much attention as a possible substantial future energy resource and also as a powerful greenhouse gas [1,2]. On the other hand, methane hydrate is considered as one of the dominant constituents of the outer planets and their moons, such as Neptune, Uranus and Titan. Therefore, it is important for planetary scientists to investigate the stability and physical properties of the high pressure phase of methane hydrate [3,4].

At room temperature, the cubic structure I of methane hydrate (MH-sI) transforms to a hexagonal structure (MH-II) at 0.9 GPa, and then to an orthorhombic filled ice structure (MH-III) at 1.9 GPa [3,5-7]. MH-sI and MH-II are well known to be a clathrate structure, whereas MH-III has a cage-less hydrogen-bonded water network, in which water molecules form channel structure and guest methane molecules are filled in their channels [5]. In the previous high pressure Raman measurements of methane hydrate, no signal for the O-H stretching and lattice vibrations was observed in the MH-III phase [6-8], in spite of the appearance of those signals in the same filled ice structure of Ar hydrate [9] and Kr hydrate [10]. In this paper, we measured the high-pressure Raman spectra for the O-H stretching vibration in the MH-III phase by growing MH-III crystals near the MH-II to MH-III phase transformation pressure of 1.9 GPa over several days, in order to clarify the origin of the appearance of O-H stretching vibration in the MH-III phase. We also estimated the symmetrization pressure of hydrogen bond in the MH-III phase from the pressure dependence of the O-H stretching Raman frequency up to 14 GPa.

2. Experiment
High-pressure Raman experiments on methane hydrate have been performed using a diamond anvil cell (DAC). For preparing the sample of MH-III, we loaded fluid methane and distilled water into a sample chamber (0.1 mm in diameter, 0.1 mm in depth) of the DAC together with a small ruby ball for pressure calibration. After the loading into the DAC, we grew a single crystal of MH-II in a three-phase equilibrium among MH-II, fluid CH₄ and water phases at about 1.0 GPa and 323 K. Figure 1(a) shows a synthesized single crystal of MH-II at 1.59 GPa at 296 K. Next, we compressed the single crystal of MH-II up to 1.91 GPa [see Figure 1(b)]. At this pressure, it took several days to complete the phase transformation to MH-III, as described below. Since the crystal growth of MH-III always occurred in the region of MH-II crystal, the synthesized MH-III crystals concentrated in the small region of the sample chamber, which was effective in measuring their Raman spectra. Although we compressed the MH-III crystals up to 25 GPa, no visual change about the phase transformation was observed through a microscope.

High-pressure Raman measurements of MH-III have been carried out in a back scattering geometry. The sample was excited by the 532 nm line of a solid-state laser (Coherent Inc., Nd³⁺-YVO₄), and the spectra were obtained by a spectrometer (JASCO Co., NR-1800) equipped with a triple polychromater and a liquid nitrogen cooled charge-coupled device (CCD) detector.

![Figure 1](image.png)

**Figure 1.** Photomicrographs of methane hydrate in the sample chamber of DAC at 296 K. (a) Single crystalline MH-II surrounded by water at 1.59 GPa and 296 K. (b), (c) Polycrystalline MH-III with surrounding ice-VII at 1.91 GPa and 11.3 GPa.

3. Results and discussion

Firstly, we investigated the crystal growth of MH-III by observing the Raman spectra for the C-H symmetric stretching vibration of guest methane molecule and the O-H stretching vibration of host water network as a function of time after the pressurization to 1.91 GPa. Figure 2 shows the Raman spectra for the C-H symmetric stretching vibration of guest methane molecule at 1.91 GPa, which is obviously different from the Raman spectrum of MH-II having two peaks [6,7]. Although the single Raman signal of 2931 cm⁻¹ was clearly observed just after the pressurization (0 h), this signal of 2931 cm⁻¹ gradually disappeared and a new Raman peak of 2943 cm⁻¹ (24 h, 89 h) grew with elapsed time. We also measured the Raman spectra of solid methane by using the same Raman system for MH-III and found that the C-H symmetric stretching Raman frequency is 2932 cm⁻¹ at 1.91 GPa, which is consistent with the previous high-pressure Raman work for solid methane [11]. Therefore, the observed peak of 2931 cm⁻¹ (0 h) undoubtedly comes from the decomposed solid methane. These results mean that the single crystal of MH-II decomposes into solid methane and ice-VII just after the pressurization to 1.91 GPa, and the crystals of MH-III are slowly formed from solid methane and ice-VII over several days at room temperature.

The O-H stretching Raman spectra at 1.91 GPa also show the similar spectral change in Figure 3. Initially, there was no obvious Raman peak in the O-H vibrational region except for ice-VII. However, a new O-H stretching Raman signal of 3219 cm⁻¹ corresponding to MH-III gradually increased in its intensity with elapsed time. The appearance of the O-H stretching vibration suggests that the synthesis...
of MH-III at 1.9 GPa was not enough to measure the Raman spectra in the previous Raman studies of MH-III [6-8]. On the other hand, we could easily detect the O-H stretching Raman bands in the filled ice phases of Ar hydrate and Kr hydrate, just after the pressurization to the phase transformation point. This implies that the filled ice structure of Ar hydrate and Kr hydrate is quickly formed after the compression to the phase transformation point, different from the MH-III filled ice.

![C-H symmetric stretching mode](image1)

![O-H stretching mode](image2)

**Figure 2.** Raman spectra for the C-H symmetric stretching vibration of methane molecule at 1.91 GPa and 296 K as a function of time after the pressurization to 1.91 GPa.

**Figure 3.** Raman spectra for the O-H stretching vibration at 1.91 GPa and 296 K as a function of time after the pressurization to 1.91 GPa. Open and solid triangles stand for the peaks of the O-H stretching vibrations of MH-III and surrounding ice-VII, respectively.

Secondly, we measured the pressure dependence of Raman spectra for the O-H stretching vibration of host water network of MH-III. The O-H stretching vibrational band of MH-III were clearly observed up to 13.7 GPa, as shown in Figure 4. With increasing pressure, the O-H stretching Raman band shows red shift, and its peak becomes weak and vanishes above 14 GPa. We plotted the peak frequency of the observed O-H stretching band of MH-III as a function of pressure, as shown in Figure 5. For comparison, the same data for the surrounding ice-VII and the filled ices of Ar hydrate [9] and Kr hydrate [10] are also plotted. The negative slope of the peak frequency of the O-H stretching vibration is due to the feature of hydrogen bond. Moreover, there is no transformation up to 14 GPa judging from the pressure dependence of Raman spectra and their peak frequency of the O-H stretching band.

The pressure dependence of the O-H stretching vibrational frequency of MH-III is apparently different from that of Ar hydrate and Kr hydrate in spite of the same filled ice structure. Since the peak frequency of the O-H stretching band may depend on the length of hydrogen-bond, the above difference means that each filled ice structure has individual compressibility. In other words, larger guest methane molecule (0.43 nm in diameter) than Ar (0.38 nm in diameter) and Kr (0.40 nm in diameter) [1] effectively sustains the host water network, and induces small compressibility (small pressure gradient in Figure 5).
From the pressure dependence of the O-H stretching vibrational frequency of MH-III, the symmetrization pressure of hydrogen bond in MH-III phase could be estimated to be about 45 GPa, assuming that the symmetrization occurs when the O-H stretching vibration as a soft mode becomes zero frequency, where the squares of Raman frequency are linearly extrapolated to high pressure region \([12,13]\) (see the inset of Figure 5). The expected symmetrization pressure of 45 GPa is consistent with the first-principles calculation \([4]\).

**Figure 4.** Pressure dependence of Raman spectra for the O-H stretching vibration of MH-III at 296 K. Open and solid triangles stand for the peaks of the O-H stretching vibrations of MH-III and surrounding ice-VII, respectively. Open and solid circles indicate the peaks of the C-H symmetric and asymmetric stretching vibrations in the MH-III phase, respectively. The asymmetric band of 2720 cm\(^{-1}\) comes from the second-order Raman signal of diamond anvils.

**Figure 5.** Pressure dependence of Raman peak frequencies \(\nu_{\text{OH}}\) for the O-H stretching vibration of MH-III, surrounding ice-VII, and the filled ices of Ar hydrate (ArH) \([9]\) and Kr hydrate (KrH) \([10]\) at 296 K. Open and solid squares stand for the peak frequencies of MH-III and surrounding ice-VII, respectively. Red and green lines indicate the peak frequencies for ArH and KrH, respectively. The inset shows the \(\nu_{\text{OH}}^{2}\) of MH-III as a function of pressure, with the linear extrapolation of \(\nu_{\text{OH}}^{2}\) indicated by solid line.

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