RAMAN STUDY OF THE METHANE + TBME MIXED HYDRATE IN A DIAMOND ANVIL CELL

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ABSTRACT

It is well known that methane hydrate undergoes several phase transformations at high pressures. At room temperature and low to moderate pressure, methane and water form a stable cubic structure I (sI) hydrate that is also known as MH-I. The structure is transformed to a hexagonal phase (sH/MH-II) above 1.0GPa. Another phase transformation occurs above 1.9GPa where the filled ice structure (MH-III) is stable up to 40 GPa before a new high pressure phase transition occurs. Experiments at such high pressures have to be performed in a diamond anvil cell (DAC). Our main interest, though, is to form sH methane hydrate at a lower pressure than reported in previous studies but with some methane in the large cages consequently increasing the methane content. This can be accomplished by introducing the molecules of the large hydrate forming substance (tert-butyl methyl ether/TBME) at a concentration slightly below the stoichiometric amount as suggested by molecular dynamics simulations. In this study we have synthesized mixed methane hydrate of sI and sH and loaded the clathrate with methane into several DACs. Raman spectra were collected at room temperature and pressures in the range of 0.1 to 11.3 GPa. The existence of sH methane hydrate was observed down to 0.2 GPa. However, the existence of methane in the large cages was visible only at pressure higher than 1.0 GPa. The excess methane in the system apparently destabilizes the sH clathrate at pressure below 1.0 GPa as it transforms to sI clathrate.

Keywords: Structure H, hydrate, high pressure, methane, TBME

INTRODUCTION

Interest in methane clathrate studies exists mainly due to its importance and challenges related to energy and environmental applications [1]. This inclusion compound is found naturally under the permafrost regions, in marine environments and it has been postulated to exist in the outer solar system where methane and water are in contact under suitable pressure and temperature conditions. Synthetic clathrate also can be prepared in the laboratory although the studies have been carried

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out mostly at low to moderate pressure conditions due to its practicality. High pressure clathrate studies are thus far mainly relevant to planetary science only. Hence, it is challenging to see if the high pressure clathrate phases can be stabilized at lower pressure so that these can be utilized for practical applications.

It is well-known that methane and water form a cubic structure I (sI / MH-I) clathrate under low to moderate pressure conditions. The existence of cubic structure II (sII) hydrate been reported only as a kinetic product that eventually transformed back to sI hydrate [2,3]. The existence of methane in sI hydrate has been reported up to ~1.0 GPa before it transforms into the hexagonal structure H (sH / MH-II) [4-6]. The hexagonal structure is transformed to a filled ice structure (MH-III) above ~1.9 GPa. Methane in the filled ice structure is stable up to ~40 GPa before it transforms into a denser filled ice structure [7].

It is well known that the low pressure sH clathrate generally requires two different sizes of guest molecule for stability. It is uncommon for such a small molecule like methane to fill a large cage. Methane occupies the large cage only at high pressures (above ~1.0 GPa). Consequently, multiple methane molecules are required to provide the much needed repulsive forces and without these the host large cage collapses. It was believed that an occupancy of between two to three molecules is more likely and there is also a dependency on the pressure and temperature [8,9]. Since multiple numbers of methane molecules can be incorporated in the large cage of sH hydrate, the methane storage density is obviously higher. The gas content thus can be increased by 40% to 100% depending on how many methane molecules that are captured inside the large cages. The drawback however is that the pressure required is in the giga-Pascal range, which is impractical.

Recent molecular dynamics simulations have indicated that the inclusion of small amount of a well known sH hydrate former such as *tert*-butyl methyl ether (TBME) in some large cages may enable the clathrate to be more stable [9] and thus the pressure required for synthesis is expected to be less. This is exactly the same principle that has been reported for hydrogen hydrates where a significant pressure drop can be achieved by adding a small amount of THF [10,11]. Obviously however, there is a trade off between the hydrate stability and a higher gas content.

The objective of this study is to verify experimentally the MD simulation results that both methane and the TBME molecule may co-exist in the large cages and the clathrate is more stable at lower pressure than the pure sH methane clathrate. This is achieved by adding less TBME than the stoichiometric requirement.

EXPERIMENTAL METHODOLOGY

The low pressure experiments were conducted in a 50 ml pressure vessel. The clathrate was synthesized from ~5 g of finely ground ice with ~0.75 g of TBME. The TBME amount was chosen in such a way that it corresponds to ~80% of the stoichiometry required if all water is converted into hydrate. TBME is also one of sH hydrate formers that has considerable solubility in water [12]. Synthesis experiments were conducted at 253 K with the initial starting pressures of 10 MPa and 20 MPa. Approximately a 1 MPa pressure drop was observed in both experiments. The solid phase was analyzed by X-Ray diffraction and NMR spectroscopy to obtain structural information and clathrate composition [13].

It was reported that the kinetics are slow for tuning sII clathrate [14]. Hence, it is expected that the encapsulation of methane into the large cages is also expected to be slow. The hydrate was therefore grown for two to six months in this study to ensure that the clathrate composition was homogeneous and high conversion was achieved. In addition, the vessel was placed on a ball mill, thus rotating the cell inside a freezer for mixing. Three sets of stainless steel bars were placed inside the vessel to create fresh surfaces for promoting the clathrate formation. The vessel was shaken manually several times to ensure the steel bars did not stick to the wall. The temperature of the freezer was increased to ~ 274 K after two days for several hours to speed up the clathrate conversion [15] before lowering it back down to 253K. At the end of the experiment, where no gas pressure change was observed, the clathrate was collected and kept in liquid nitrogen temperature. The solid phase properties were also characterized by X-Ray diffraction and solid-state NMR spectroscopy to determine the crystal structure and composition.

The experimental procedure for the solid state analysis is given elsewhere [13].

Gasketed diamond anvil cells (DACs) were employed for high pressure experiments. The clathrate synthesized at low pressure was ground into very fine powder and then loaded into the DAC kept cold at liquid nitrogen temperature. The loading was performed with extra care to minimize sample contamination with ice. A ruby sphere was inserted into the DAC as a pressure indicator. The pressure was obtained by measuring the ruby luminescence shift with respect to room temperature and atmospheric pressure conditions [16]. Raman spectra were collected at various spots on the sample. Special attention was taken around the C-H (~2900 to 3000 cm⁻¹), O-H (~3000 to 3600 cm⁻¹), and C-C spectral range (~500 to 1000 cm⁻¹).

In some experiments, extra methane was added into the DAC sample chamber. This is because the amount of methane gas available in the original system is only from the loaded clathrate where all cages are singly occupied. Hence, adding more methane may be needed when multiple methane molecules go into the large cages or else some hydrate lattice may decompose into water or a high pressure ice phase, depending on the pressure condition and temperature conditions. The methane gas was liquefied by condensing the gas inside copper coil tubing that was immersed in liquid nitrogen. Before adding the methane, the clathrate and the ruby were loaded first and the cell was closed up to ensure that the clathrate stayed in the DAC. Then the DAC was opened and some clathrate sample was removed from the DAC to allow enough space for the liquid methane. Subsequently, the DAC was immersed in the pool of liquid methane for about 10-20 seconds before it was finally closed to trap extra methane.

RESULTS AND DISCUSSION

Methane-TBME Clathrate at low pressure up to 20 MPa

The solid phase analyses of the low pressure clathrate are summarized in Table 1. The samples contained $\sim 60\%$ sH and 40% sI clathrate and the clathrate content was higher than >90%. The lattice constants were slightly bigger than our previous measurements [13] because of higher temperature from the current XRD measurements.

Struc- ture	Lattice constant	Pressure	Cage occupancy		
			$\theta_{\rm S}$	$\theta_{\rm M}$	θ_{L}
sI	a = 12.00 (2)	~10 MPa	0.68	-	1.00
		~ 20 MPa	0.69	-	1.00
sH	a = 12.38 (2) c = 10.10 (4)	~10 MPa	0.83	0.88	1.00
		~ 20 MPa	0.79	0.96	1.00

Table 1. Solid state analysis of synthesized mixed methane and TBME clathrate.

Methane occupied both cages in sI but only the small and medium cages were filled by methane in sH clathrate as shown in Fig. 1. The occupancies of methane in the small cages of sI clathrate were smaller than for pure methane sI clathrate. The methane occupancies in the medium cages of sH are also larger and increase with pressure. However, none of those samples contained methane in the large cages of sH clathrate. The TBME molecule is likely to occupy the large cage under low pressure conditions although the amount of TBME was less than the stoichiometric required. Hence, the subsequent experiment was conducted in a DAC at higher pressure.



Figure 1. ¹³C solid-state NMR spectra of clathrate synthesized at low pressure. The methane signals are magnified. Other strong signals correspond to TBME in clathrate phase.

Methane-TBME Clathrate at high pressure up to 11 GPa

The methane-TBME clathrate that was synthesized at 20 MPa was used for the high pressure experiments. Raman spectra from the sH and filled ice regions at various pressures are summarized in Figure 2 and 3.



Figure 2. Raman spectra of mixed methane+TBME sH clathrate in the DAC at room temperature.



Figure 4. Raman spectra of filled ice methane and ice VII in the DAC at room temperature.

Some spectra were obtained while increasing or decreasing the pressure, however they generally do not differ. The spectra obtained while increasing the pressure are indicated by the green star. The methane peak is always the most intense one among other peaks. In fact, the peaks from the water and TBME are almost invisible at pressures below 2 GPa compared to the methane peak. Hence, the O-H stretching from the ice VI and clathrate in Fig. 2 are hard to see. Those peaks become more intense and visible only at pressures above 2 GPa. The arrows in Figs. 2 and 3 are provided to help identify the peaks from TBME and water with pressure. The pink arrow corresponds to the C-H bond of TBME. The dark and light blue arrows are from the ice VII phase. The Raman shift usually increases with pressure for the C-H bond but goes in the opposite direction for the O-H bond. A strong signal is also seen in all spectra at ~3569 cm⁻¹ that comes out of the reflection from the aluminum stage and is most likely due to stray laser light. It does not change with pressure and hence it is used as a reference for the Raman shift.

The existence of mixed sH methane+TBME clathrate was observed down to 0.2 GPa in our high pressure experiments. This is a substantial reduction from the pure sH methane clathrate (MH-II). However, it is difficult to determine if the clathrate is still stable below 0.2 GPa because it is close to the lower pressure limit for this DAC experiment. Moreover, the methane peak from the large cage of sH clathrate is not clearly seen below 1.0 GPa. Only one methane peak is visible that presumably is from both small (5^{12}) and medium $(4^{3}5^{6}6^{3})$ cages of the sH hydrate, which are indistinguishable [13]. Consequently, the large cages are presumably occupied by TBME molecules only. The methane peak from the large cages is evident only at higher pressures above 1.0 GPa. Fig. 2 indicates the appearance of broad shoulders at the higher frequencies that are from the methane in the large cages, as also reported by Kumazaki et al. [6]. The intensity ratio between the methane Raman peak from the large to (small+medium) cages are found anywhere between ~ 0.4 to 0.7 as it is dependent on pressure. Hence, this suggests that there are two to four methane molecules occupying a large cage.

In most cases, the initial pressure after loading was above 2.0 GPa, which is in the stability region of filled ice methane structure (MH-III). Hence, the subsequent experimental step would be to reduce the pressure and record the spectra in order to see the low pressure sH clathrate. In one experiment, we successfully arrived at 0.57 GPa after loading and for this experiment the presence of both mixed sI and sH clathrate was observed. This is because initially the sample contained both clathrate structures. However, the sI methane clathrate (MH- I) was transformed into sH clathrate (MH-II) upon increasing the pressure above 1.0 GPa. Once the sI clathrate was gone, reducing the pressure below 1.0 GPa did not reform the sI clathrate but the sH clathrate remained although it was in the stability region of pure sI clathrate. This suggests that the sH clathrate with TBME is more stable or perhaps driven by faster kinetics than the pure sI methane clathrate to form. That is likely the reason that mixed sH clathrate was observed below 1.0 GPa without any sI clathrate.



Figure 4. Raman shift change with pressure.

Fig. 4 summarizes the Raman shifts of all methane Raman signals with respect to pressure. The highest wavenumber is from the solid methane. The methane in all clathrate phases is shifted to a lower frequency than that of pure methane (gas/liquid/solid). The slopes differ among different phases. Hence, the change of slope from the Raman shift with pressure can be used to identify the phase stability and change. Initially, the methane peak in the two smaller cages of sH clathrate were observed at low pressure before the methane in the large cages became visible at ~1.0 GPa. At around ~2.0 to ~2.2 GPa, the phase transformation occurs from sH to filled ice structure that is stable up to 11 GPa.

The Raman shift corresponding to TBME and O-H bonds are shown in Figure 5. Unfortunately, the TBME peaks below ~2.0 GPa (bottom) are so weak and hence, the identification of TBME in the clathrate phase is only visible by looking at the C-C stretching vibration peaks. There are many C-C peaks from the TBME but they are mostly weak peaks except one at around ~700 cm⁻¹ that is plotted in Figure 5 (top). As seen, there is a change of slope from this strong C-C signal of TBME observed at around ~2.0 GPa that is consistent with the observable phase transformation from the sH to filled ice structures. Hence, the TBME participated in the sH clathrate as well as the methane. This confirms the co-existence of both methane and TBME in the large cage of sH hydrate and explains why the sH clathrate is stable at lower pressure than the pure sH methane clathrate. The Raman shift change from the O-H bond of ice VII (blue) has similar negative slope with pressure.



Figure 5. Raman shift change from C-C bonds of TBME (top/pink), O-H bonds of ice VII (blue) and C-H bonds of TBME (bottom/pink) with respect to pressure.

Two more experiments were conducted by adding extra methane along with the methane-TBME clathrate into the DAC after loading the clathrate. The Raman spectra from the sample at pressures above ~ 2.0 GPa do not change with the presence of excess methane. The excessive amount of methane may in fact dominate and bury the methane peak from the clathrate phase underneath because of its high concentration in different regions of the sample. Four representative Raman spectra are shown in Fig. 6.



Figure 6. Raman spectra around methane spectral region with excess methane.

The top spectrum, recorded at 2.08 GPa corresponds to that of the filled ice structure (MH-III) with ice VII before it transformed to the expected sH clathrate (MH-II) at 1.67 GPa. Upon releasing the pressure, the ice VII was transformed to ice VI however the methane peak from the smaller cages of sH clathrate were not seen. Only one strong peak was observed at 2928 cm⁻¹ which supposedly belong to methane present in the large cages of sH clathrate (see the inset).

Luminescence arising from the diamond anvils is detected in the same spectral range as the Raman signal from the C-C vibrations that have impeded the confirmation of the presence of the TBME molecules in the mixed clathrate phase. Because of the extra methane, the solid methane peak may also be observed in some spots as shown in Fig. 6. Interestingly, the sH clathrate was not stable at pressures below ~1.0 GPa where it was transformed into sI methane clathrate (MH-I). This is seen by the presence of methane peak at 2905 cm⁻¹ that corresponds to methane in the large cage of sI clathrate and 2917 cm⁻¹ that corresponds to fluid methane at 0.68 GPa. The methane peak from the small cage is buried under the fluid methane peak.



Figure 7. Raman spectra in sH clathrate region with and without excess methane at 1.68 GPa.

Fig. 7 shows the comparison between Raman spectra of this clathrate with and without the addition of extra methane at the same pressure (1.68 GPa). As seen, the spectra with clathrate loading only has a stronger methane signal at \sim 2920 cm⁻¹ from the small and medium cages where the signal from the large cages appear only

as a shoulder at ~2928 cm⁻¹. On the other hand the spectrum of the clathrate loaded with excess methane shows a strong signal exactly at the position where methane from the large cage of sH clathrate is located. No shoulder is seen at around ~2920 cm⁻¹. This is rather surprising because the molecular dynamics simulation performed at the same conditions indicates that the sH clathrate is not stable when all the small and medium cages are empty. Hence, there is a good possibility that another type of clathrate structure may exist. To identify this structure will remain as future work.

CONCLUSIONS

Experiments were conducted to explore the possibility of increasing the methane content in structure H clathrate. In order to minimize the high pressure required to stabilize the structure H, tertbutyl methyl ether (TBME) as the large guest molecule was employed. The amount of TBME used was ~80% from the stoichiometric required to allow methane occupying the remaining large cages. It was found that the clathrate consisted of mixed sI and sH with the ratio of 2:3 when synthesized at low pressure up to 20 MPa. The occupancies of the cages were measured by solidstate NMR spectroscopy and no methane in the large cages was found. The clathrate was then loaded into several diamond anvil cells (DACs) with and without the addition of extra methane.

The high pressure experiments carried out in DACs were conducted between 0.1 to 11 GPa and room temperature. The experiments performed without adding more methane indicate that the phase transition of methane clathrate from structure I (MH-I) to filled ice structure (MH-III) is practically the same as for the pure methane hydrate. However, the mixed structure H clathrate of methane and TBME is more stable than pure sH methane clathrate (MH-II) with decreasing the pressure. The existence of the mixed sH clathrate was observed down to 0.2 GPa. Unfortunately, the presence of methane in the large cages of sH clathrate was only visible at pressures greater than 1.0 GPa. Nevertheless, the occurrence of both methane and TBME in the large cages of sH clathrate has been demonstrated. The addition of methane did not seem to increase the methane occupancy in the large cages and stabilize the sH clathrate at pressure below 1.0 GPa.

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