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Effect of temperature and large guest molecules on the C–H symmetric stretching vibrational frequencies of methane in structure H and I clathrate hydrates†

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Large molecules such as 2-methylbutane (C₅H₁₂) or 2,2-dimethylbutane (C₆H₁₄) form structure H (sH) hydrates with methane (CH₄) as a help gas. In this study, the Raman spectra of the C–H symmetric stretch region of CH₄ enclathrated within various sH hydrates and structure I CH₄ hydrates were analyzed in the temperature range 137.7–205.4 K. Thermal expansions of these sH hydrate samples were also measured using powder X-ray diffraction. Symmetric stretch vibrational frequencies of CH₄ in host–water cages increased because of varying temperature, and the sizes of the host–water cages also increased; variation of CH₄ in small cages was less than in larger cages. Comparing the variations of the C–H symmetric stretching frequencies of CH₄ in gas hydrates with varying pressure and temperature, we suggest that the observed trend is caused by thermal vibrations of the CH₄ molecule in water cages.

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Introduction

Clathrate hydrates are crystalline inclusion compounds that consist of guest molecules of suitable sizes and shapes trapped in well-defined cages formed by water molecules. Both synthetic and naturally occurring clathrate hydrates with natural gases as guest molecules are commonly known as gas hydrates. Gas hydrates with enclathrated hydrocarbon gases that exist in sea/lake bottom sediments and permafrost layers have attracted considerable interest as a potential source of unconventional natural gas.¹

Three typical crystal structures of clathrate hydrates have been identified on earth: cubic structure I (sI), cubic structure II (sII), and hexagonal structure H (sH).^{2–4} The unit cell of sI hydrates comprises two pentagonal dodecahedral (5¹²) and six tetrakaidecahedral (5¹²6²) water cages.² For sII hydrates, the unit cell is formed by sixteen 5¹² cages and eight hexakaidecahedral (5¹²6⁴) water cages.³ Finally, the unit cell of sH hydrates comprises three 5¹² cages, two irregular dodecahedral (4³5⁶6³) cages, and one icosahedral (5¹²6⁸) cage⁴ as shown in Fig. 1. Small guest molecules such as methane (CH₄) or ethane form sI-type hydrates, whereas larger molecules like propane or 2-methylpropane (C₄H₁₀) form sII hydrates. sH hydrates are obtained from even larger molecules, *e.g.*, 2-methylbutane

(C₅H₁₂) or 2,2-dimethylbutane (C₆H₁₄), in the presence of a help gas as CH₄.¹ Moreover, sH hydrate that is capable of encapsulating these larger molecules in natural gas than either structure I or II hydrates was found at the Barkley Canyon (northern Cascadia margin).⁵ Since sH hydrates exhibit a hexagonal structure (space group *P6/mmm*), there are two unit-cell parameters, *a*-axis and *c*-axis (Fig. 1). Under isothermal conditions, the lattice size of clathrate hydrates has been reported to change depending on the type of guest molecule. For sH hydrates, large guests cause an increase in the *a*-axis direction and a slight decrease in the *c*-axis direction.⁶

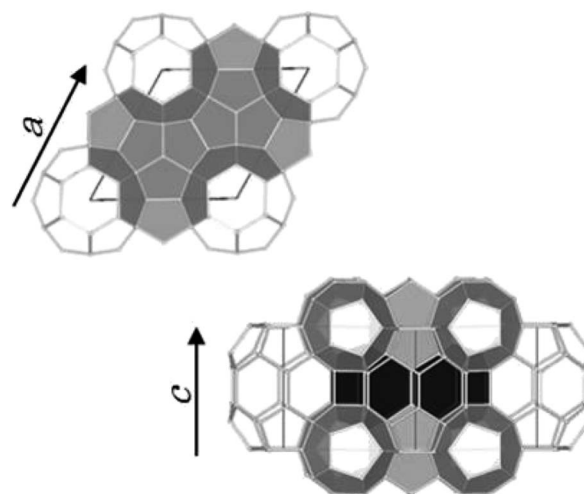


Fig. 1 Unit cell of sH hydrates. The unit-cell comprises three 5¹² cages (light gray), two 4³5⁶6³ cages (black), and one 5¹²6⁸ cage (white).

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To date, Raman spectroscopy has been commonly used for gas hydrates to identify the type of crystal phase^{7–9} and phase transformations^{10,11} or to analyze cage occupancy,⁷ type of guest molecule,⁹ and hydration number.^{7,12} The Raman spectra of the C–H symmetric stretch region of enclathrated CH₄ are commonly used to identify the types of crystal phase and guest molecules.¹³ Trends in the C–H stretching vibrational frequency of CH₄ enclosed in different clathrate hydrate cages have therefore been studied. Experimentally, the Raman spectra of hydrocarbon hydrates have demonstrated that the C–H stretching frequency of CH₄ in large cages is generally lower than that for CH₄ in small cages.^{7–9} This observation was rationalized by Subramanian and Sloan⁹ in terms of the guest–cage intermolecular interactions using the loose cage–tight cage (LCTC) model as an explanation for matrix-isolation IR experiments.¹⁴ Also, a qualitative agreement between experimental results and theoretical calculations for CH₄ enclathrated in sI and sH hydrates was obtained using *ab initio* MD simulations.^{15–17} Additionally, using quantum-chemical computations, the C–H stretching frequencies of hydrocarbons in different clathrates were demonstrated to be lower in larger cages.¹⁸ This vibrational frequency for CH₄ enclosed in a water cage may change depending on temperature, and these information are useful for better understanding of the stability of gas hydrates under natural setting. However, thermal effects such as thermal expansion of water cages have not been considered for these calculations yet.

In this study, various sH CH₄ and large-molecule mixed hydrates and an sI CH₄ hydrate were prepared, and the Raman spectra in the C–H symmetric stretch region of enclathrated CH₄ were studied in a temperature range of 137.7–205.4 K. Thermal expansions of all samples were also measured using powder X-ray diffraction (PXRD). From these results, the variations in Raman spectra of the C–H symmetric stretch and the guest–host interaction energy with varying temperature are discussed; moreover, the differences in crystal structures are analyzed. The results of this study help to consider computational elements of follow theoretical calculation study of thermal effect on sH hydrate and sI CH₄ hydrates, also may help to better understand the effect of temperature on clathrate hydrate stability and guest–host interactions.

Experimental section

Sample preparation

In this study, six large-molecule guest substances as shown in Fig. 2 were used. Six gas hydrate samples were prepared: CH₄ + 2,2-dimethylbutane (22DMB); CH₄ + 2,3-dimethylbutane (23DMB); CH₄ + 3-methylpentane (3MP); CH₄ + 2-methylbutane (2MB); CH₄ + methylcyclopentane (MCP); and CH₄ + methylcyclohexane (MCH). To synthesize these gas hydrate samples, fine ice powder (3.0 g) was prepared and loaded onto a high-pressure cell (internal volume: ~20 mL), which was precooled in a freezer at 253 K. Afterwards, 0.3 mL of the large-molecule guest was added into the cell (Wako Pure Chemical Industries Ltd.; 22DMB 99.3%; 23DMB 99.9%; 3MP 99.6%; 2MB 99.6%; MCP 97.9%; MCH 99.8%). To prevent melting of ice or

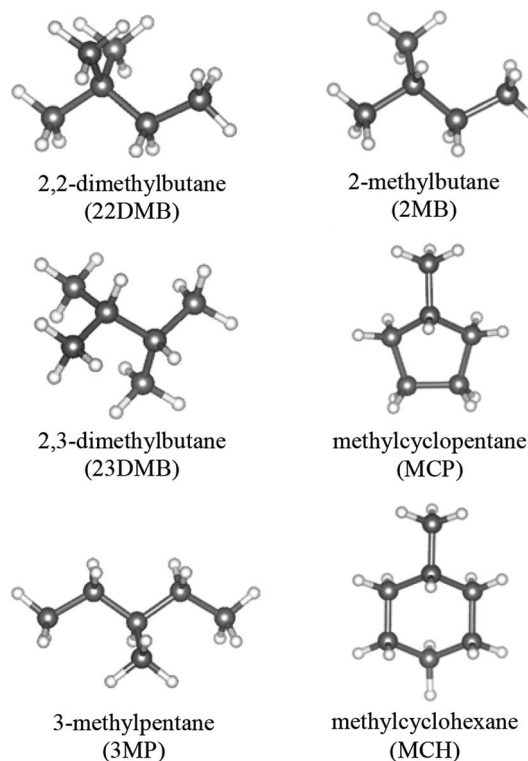


Fig. 2 Structures of the large-molecule guest.

evaporation of the guest molecules, the high-pressure cell and hydrate components were precooled in a cold room at 253 K. After loading at 253 K, the high-pressure cell was cooled to below 90 K and pure CH₄ gas (99.99% certified purity; Takachiho Chemical Industrial Co. Ltd.) was slowly introduced into the cell. Then, the high-pressure cell was transferred into a water bath at 273.2 K for hydrate formation. The CH₄ applied pressure was maintained at 2.2–2.3 MPa to not form pure sI CH₄ hydrate. As the hydrates formed, the pressure decreased. When the pressure stabilized, the cell was cooled below 90 K and the sample was removed from the cell. For the sI CH₄ hydrate (MH), powder ice (3.0 g) was loaded into the cell, and the cell was pressurized using CH₄ to over 2.6 MPa.

Raman spectroscopy

A Raman spectrometer (JASCO Corporation, RMP-210) equipped with a 532 nm excitation source (100 mW), a single holographic diffraction grating (1800 grooves per mm), and a CCD detector was used. The spectrum pixel resolution, which is the sampling interval of the spectrum, was 0.9 cm⁻¹ per pixel in the range of 2500–3000 cm⁻¹. A polypropylene peak at 1460 cm⁻¹ was used for routine calibration of the monochromator. The wave number was also calibrated using atomic emission lines from a neon lamp. The Raman spectra for the C–H symmetric stretch region of enclathrated CH₄ in small cages of six sH mixed-gas hydrates and the sI CH₄ hydrate were obtained for a temperature range of 137.7–205.4 K. The sample temperature was confirmed using a thermocouple (Type T; Ninomiya Electric Wire Co. Ltd., 01-T). The calibrated thermocouple was accurate



within 0.1 °C. Here, the peak position can be rigorously analysed by Voigt fitting functions to obtain a high positional accuracy. Based on the reproducibility of the CH₄ peak position of the sH 5¹² and 4³5⁶6³ cages of CH₄ + 2MB hydrate at 163.6 K, the standard deviation of peak positions, which is 18 times measurement at same sample position, was approximately 0.1 cm⁻¹.

Powder X-ray diffraction

PXRD measurements were performed using a laboratory X-ray diffractometer (40 kV, 40 mA; RIGAKU model Ultima-III) with parallel beam optics and a low-temperature chamber. Fine powder hydrate samples were mounted on a PXRD sample holder made of 2.5 mm thick Cu at a temperature comparable to liquid N₂ (~100 K). Each measurement was obtained in a $\theta/2\theta$ step scan mode with a step width of 0.02° using Cu K α radiation ($\lambda = 1.541 \text{ \AA}$).

Results and discussion

As expected, PXRD measurements showed that the crystal structure of the six different gas hydrates was sH (Fig. S1†). The effect of temperature on the unit-cell parameters in the range of 93–168 K is shown in Fig. 3 for all samples. Each unit-cell size and effect of temperature varied with varying unit-cell parameters differ with guest molecules. However, unit-cell parameters of all the samples increased with increasing temperature and volume expansion of unit cells.

Fig. 4 also depicts the C–H symmetric stretch of CH₄ in the 5¹² and 5¹²6² cages of the sI CH₄ hydrate for comparison. Information from each Raman spectrum of CH₄ in the 5¹² and 5¹²6² cages is summarized in Table 1. In the case of sI CH₄ hydrate, Raman spectra on CH₄ vibrations in the 5¹² and 5¹²6² cages agree well with those of natural methane hydrate²¹ and results from molecular dynamics simulation.²² Sum *et al.* reported that the Raman peaks of CH₄ in the 5¹² cages of sI and sH are 2915 and 2913 cm⁻¹, respectively.⁷ Experimental results in this study are in agreement with the earlier study. It is suggested that CH₄ is enclathrated into the sH 5¹²6⁸ cages under high-pressure condition at above 1.36 GPa and the Raman peak appears around 2930 cm⁻¹.²³ However, such peaks were not detected at around 2930 cm⁻¹ (Fig. 4) because large molecules fully occupied the 5¹²6⁸ cages as is reported in earlier studies.^{24–26}

Fig. 5 depicts the effect of temperature on the C–H symmetric stretch of CH₄. These Raman shifts increased with increasing temperature. For CH₄ + 22DMB, CH₄ + 23DMB, CH₄ + 3MP, CH₄ + 2MB, and CH₄ + MCH hydrates, the slope of Raman shifts was about 1.2–1.9 cm⁻¹/100 K, whereas for CH₄ + MCP, it was 0.7 cm⁻¹/100 K (Table 1). This is consistent with the C–H stretching frequency of gaseous CH₄, which shifts to higher wavenumbers as the temperature increases.²⁷ Except for CH₄ + MCP, the temperature effect on the Raman shift of CH₄ in the sH hydrate seemed to be the same as that for CH₄ in the 5¹² cages of sI CH₄ hydrates. These results suggest that there is a general trend of the Raman shift with the size of the host cage.

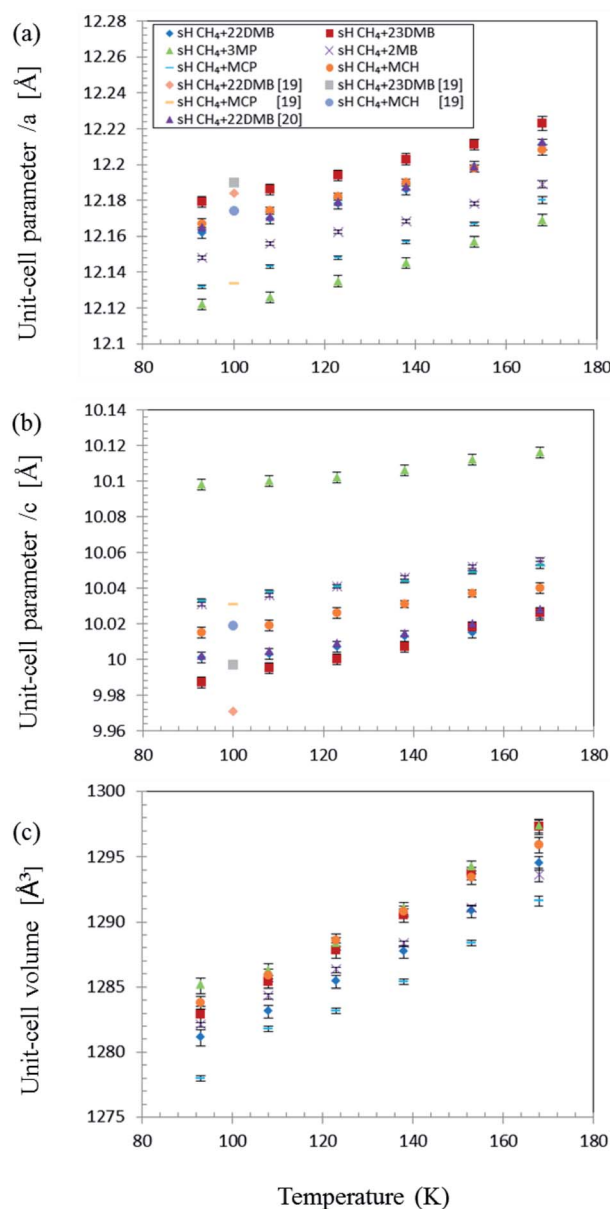


Fig. 3 Effect of temperature on sH hydrate unit-cell parameters with various guest molecules and CH₄. (a) *a*-axis; (b) *c*-axis; (c) unit-cell volume.^{19,20}

If Raman measurements with higher resolution can be obtained, it is possible to discuss effect of temperature depending on the size and/or shape of large guest molecules.

To evaluate the increase with temperature in the Raman shift of CH₄ in the sH hydrate, the overlap of Raman peaks for the 5¹² and 4³5⁶6³ cages needs to be considered. The temperature effect on peak full widths at half maxima (FWHMs) of all peaks from Fig. 5 are shown in Fig. 6. FWHMs of all samples increased when temperature increased from 137.7 to 190.6 K. Here, we focus on the values of increase in FWHMs from 137.7 to 190.6 K. In the case of CH₄ + 22DMB, CH₄ + 23DMB, CH₄ + 3MP, CH₄ + 2MB, and the sI 5¹² cage, the FWHMs increased by 0.86–0.97 cm⁻¹. In the case of CH₄ + MCP, CH₄ + MCH, and the sI



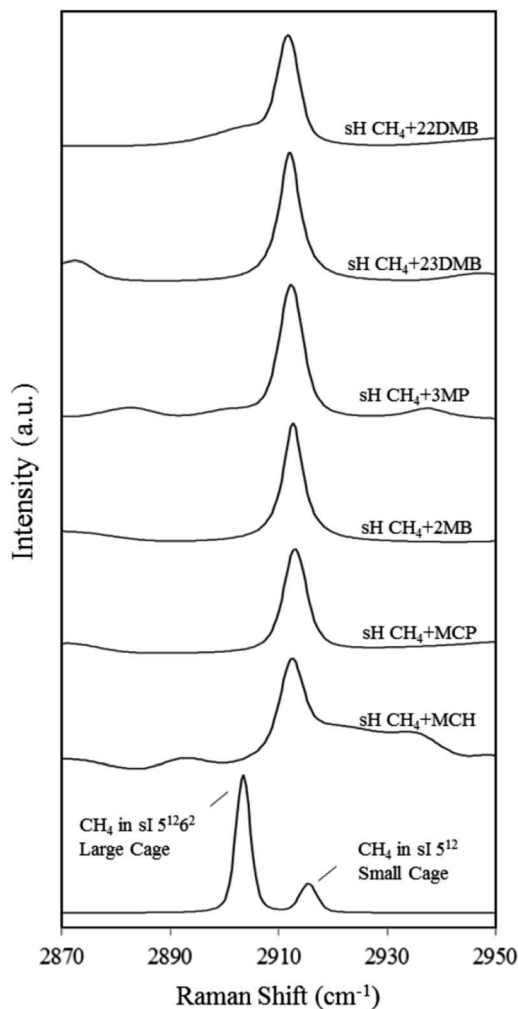


Fig. 4 Raman spectra of CH₄ in the 5¹² (small) and 5¹²6² (large) cages of the sI hydrate (MH) and the 5¹² and 4³5⁶6³ cages of six types of sH hydrates at 137.7 K. Raman peaks for CH₄ in the 5¹² and 4³5⁶6³ sH cages overlap; only one peak was observed.

5¹²6² cage, the FWHMs increased by 0.53 cm⁻¹, 0.30 cm⁻¹ and 1.42 cm⁻¹, respectively. The variations of the effect of temperature on FWHMs were almost the same or lower for the overlapped sH CH₄ peaks than those for the sI CH₄ Raman peaks in the 5¹² and 5¹²6² cages. Hence, it was indicated that the effects of temperature on the sH CH₄ Raman peaks in both 5¹² and 4³5⁶6³ cages are comparable to each other, although each of the Raman peak for CH₄ in the sH 5¹² and 4³5⁶6³ cages were not measured separately.

The C–H stretching frequency of the guest CH₄ is usually lower in larger cages than in smaller ones under isothermal conditions, as predicted by the LCTC model.^{9,15,18} The experimental results in this study indicate that Raman shifts of the C–H symmetric stretch of the guest CH₄ increased with temperature because of thermal vibration of the CH₄ molecule in water cages; however, cage size also increased, and this might induce a decrease in Raman shifts due to unit-cell expansions with temperature (Fig. 3).

Table 1 Raman shifts of C–H symmetric stretch CH₄ in 5¹² and 5¹²6² cages of sI hydrate, 5¹² and 4³5⁶6³ cages of six types sH hydrates and these variations with temperature. Those errors are the standard deviation of 9 times measurement at different sample positions

Cage type and guest molecules	Raman shift of CH ₄ at 137.7 K [cm ⁻¹]	Slope of Raman shift between 137.7–205.4 K [cm ⁻¹ /100 K]
sH CH ₄ + 22DMB	2912.0 ± 0.2	1.2
sH CH ₄ + 23DMB	2911.9 ± 0.2	1.7
sH CH ₄ + 3MP	2912.2 ± 0.2	1.7
sH CH ₄ + 2MB	2912.6 ± 0.4	1.9
sH CH ₄ + MCP	2912.9 ± 0.3	0.7
sH CH ₄ + MCH	2912.2 ± 0.2	1.4
sI 5 ¹² CH ₄	2915.4 ± 0.1	1.5
sI 5 ¹² 6 ² CH ₄	2903.2 ± 0.2	2.8

Fig. 5 illustrates that the effect of temperature on Raman shifts of the sI 5¹², sH 5¹², and sH 4³5⁶6³ cages were smaller than that of the sI 5¹²6² cage. This may suggest different interactions between the host, water, and guest (CH₄) in these cages. In previous studies, the distribution of CD₄ molecules in a sI deuterated hydrate cage was analyzed using neutron diffraction experiments.^{28,29} It was shown that CD₄ in the sI 5¹²6² cage distributes longitudinally within the cage at temperatures higher than 80 K, whereas in the 5¹² cage, CD₄ distributes spherically around the center of the cage even at higher temperatures. It was suggested that the distance change between the guest and host molecules in the sI 5¹²6² cage is smaller than that in the sI 5¹² cage due to changes in temperature. Accordingly, the experimental results in Fig. 5 show that the Raman shifts of the C–H symmetric stretch of enclathrated CH₄ in the sI 5¹²6² cage increased with temperature more than in the sI 5¹², sH 5¹², and sH 4³5⁶6³ cages. The size of these small cages might be too small for translational motion of CH₄ within the cages.

The CH₄ hydrate phase is known to transition from the sI to sH structure at 0.9 GPa, and the structure is maintained until about 1.9 GPa.²⁵ In this work, the Raman shift of CH₄ in the sH 5¹² and 4³5⁶6³ cages was larger than that for the sI 5¹² cage at 0.9 GPa.³⁰ This suggests that the sH 5¹² cage is smaller than the sI 5¹² cage as predicted by the LCTC model.^{9,15,18} Conversely, variations in the C–H symmetric stretching frequency of CH₄ with changing pressure under isothermal conditions are not the same as the temperature-induced changes obtained in this study. With pressures of up to 0.8 GPa, the variation of the C–H symmetric stretching frequency of CH₄ in the sI 5¹² cage is higher than that in the sI 5¹²6² cage.³⁰ Contrastingly, the variations of the frequencies of CH₄ enclathrated in larger cages (sI 5¹²6² and sH 5¹²6⁸ cage) are smaller than that in the 5¹² and 4³5⁶6³ cages with changing pressure.³⁰ Therefore, it can be implied that the increase in temperature enhances the C–H symmetric stretching frequency of guest CH₄ because of thermal vibration, whereas the increase in pressure enhances this stretching frequency because of shrinking of cages, as predicted by the LCTC model. The increase in pressure from



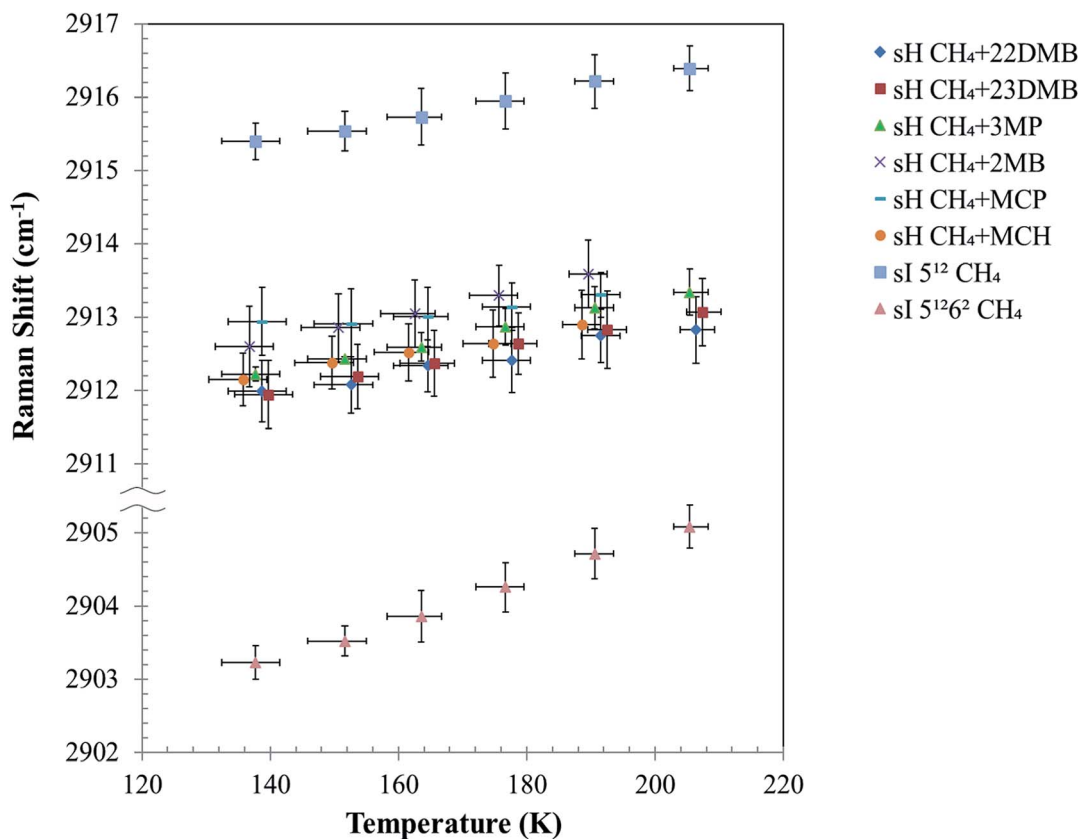


Fig. 5 Temperature effect on Raman shift of C–H symmetric stretch of enclathrated CH₄ in 5¹² and 4³5⁶6³ cages of six types sH hydrates and in 5¹² (small) and 5¹²6² (large) cages of sI CH₄ hydrate (MH). In the case of CH₄ + 2MB, CH₄ + MCP and CH₄ + MCH, samples dissociated at 205.4 K. The errors in the temperature are the max and minimum values of 10 times measurements.

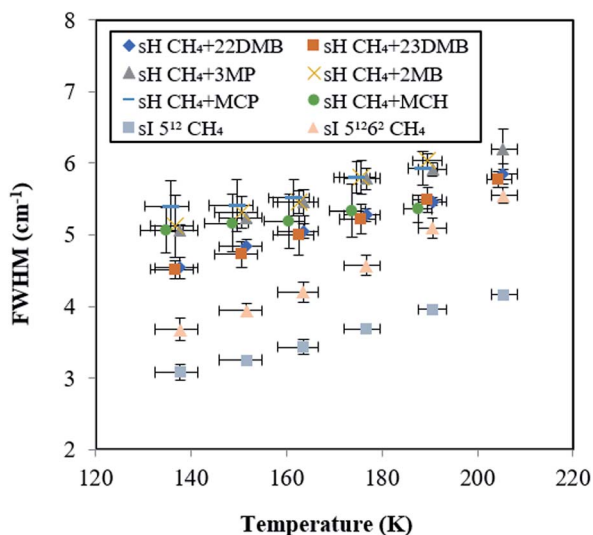


Fig. 6 Temperature effect on peak full widths at half maximums (FWHMs) for CH₄ in sI and in six types sH hydrates. These errors in the FWHM of 0.4 cm⁻¹ are standard deviation of 9 times measurement.

0.9 GPa to 1.9 GPa under isothermal conditions causes a volume reduction of 3% for sH,³¹ and the increase in temperature from 93 K to 168 K causes a volume expansion of 1% for sI and sH

(Fig. S2†). Therefore, the difference in these volume expansion ratios affects the trend of C–H stretching frequency of CH₄ in the cages.

These experimental trends of temperature effect of C–H stretching frequency of CH₄ in the water cages may help to consider computational elements of follow theoretical calculation study of thermal effect on sH hydrate and sI CH₄ hydrates, although it is not yet complete. For example, the difference in unit-cell sizes is different depending on the type of guest molecule and may change the guest–host interactions. In fact, for CH₄ + 22DMB, CH₄ + 23DMB, CH₄ + 3MP, CH₄ + 2MB, CH₄ + MCH; the Raman shifts increased by 0.7–1.0 cm⁻¹, but that of CH₄ + MCP was smaller. Raman measurements with higher resolution coupled with precise crystal structure data are necessary for further understanding of other correlating factors.

Conclusions

In this work, six different sH clathrate hydrates with CH₄ as a help gas were investigated: CH₄ + 22DMB; CH₄ + 23DMB; CH₄ + 3MP; CH₄ + 2MB; CH₄ + MCP; and CH₄ + MCH. PXRD measurements and Raman spectra of the C–H symmetric stretch region of the enclathrated CH₄ within these sH hydrates were analyzed in the temperature range of 137.7–205.4 K.



The C–H symmetric stretch vibrational frequencies of enclathrated CH₄ in the sH and sI hydrates increase with increasing temperature. Raman shifts of the C–H symmetric stretch vibrational frequencies of CH₄ enclathrated in larger cages decreased than in smaller cages. However, in this work, these Raman shifts increased even though unit-cell sizes of all samples increased with increasing temperature.

The distribution of CH₄ in the water cage increases with increasing temperature, implying that the distance between the CH₄ and water molecules of the lattice is small. The variation of the C–H symmetric stretching frequency of CH₄ in the large cages was greater than that in small cages, because the thermal vibration of CH₄ in the former were bigger than that in the latter.

These results contribute to understand the stability and guest–host interactions of sH hydrate and sI CH₄ hydrates. These results of C–H stretching frequency of CH₄ in the water cages may help to consider computational elements of follow theoretical calculation study of thermal effect on sH hydrate and sI CH₄ hydrates. However, the trend of the Raman spectra peaks of CH₄ in the sH hydrate has not yet been interpreted. For example, variations of the C–H symmetric stretching frequency of CH₄ in sH hydrates vary depending on the guest molecule. To further comprehend other correlating factors, Raman spectroscopy with higher resolution coupled with precise crystal structure data is needed.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 E. D. Sloan and C. A. Koh, *Clathrate Hydrates of Natural Gases*, CRC Press/Taylor&Francis Group, Boca Raton, FL, 3rd edn, 2008.
- 2 H. R. Müller and M. V. Stackelberg, *Naturwissenschaften*, 1952, **39**, 20.
- 3 M. V. Stackelberg and H. R. Müller, *Naturwissenschaften*, 1951, **38**, 456.
- 4 J. A. Ripmeester, J. S. Tse, C. I. Ratcliffe and B. M. Powell, *Nature*, 1987, **325**, 135.
- 5 H. Lu, Y. T. Seo, J. W. Lee, I. Moudrakovski, J. A. Ripmeester, N. R. Chapman, R. B. Coffin, G. Gardner and J. Pohlman, *Nature*, 2007, **445**, 303–306.
- 6 S. Takeya, A. Hori, T. Uchida and R. Ohmura, *J. Phys. Chem. B*, 2006, **110**, 12946.
- 7 A. K. Sum, R. C. Burruss and E. D. Sloan, *J. Phys. Chem. B*, 1997, **101**, 7371–7377.
- 8 S. Subramanian, R. A. Kini, S. F. Dec and E. D. Sloan, *Chem. Eng. Sci.*, 2000, **55**, 1981–1999.
- 9 S. Subramanian and E. D. Sloan, *J. Phys. Chem. B*, 2002, **106**, 4348–4355.
- 10 M. M. Murshed and W. F. Kuhs, *J. Phys. Chem. B*, 2009, **113**, 5172–5180.
- 11 T. Uchida, S. Takeya, Y. Kamata, I. Y. Ikeda, J. Nagao, T. Ebinuma, H. Narita, O. Zatsepina and B. A. Buffett, *J. Phys. Chem. B*, 2002, **106**, 12426–12431.
- 12 T. Uchida, T. Hirano, T. Ebinuma, H. Narita, K. Gohara, S. Mae and R. Matsumoto, *AIChE J.*, 1999, **45**, 2641–2645.
- 13 S. Subramanian and E. D. Sloan, *Ann. N. Y. Acad. Sci.*, 2000, **912**, 583–592.
- 14 G. C. Pimentel and S. W. Charles, *Pure Appl. Chem.*, 1963, **7**, 111.
- 15 J. S. Tse, *J. Supramol. Chem.*, 2002, **2**, 429.
- 16 M. Hiratsuka, R. Ohmura, A. K. Sum and K. Yasuoka, *J. Chem. Phys.*, 2012, **136**, 044508.
- 17 M. Hiratsuka, R. Ohmura, A. K. Sum and K. Yasuoka, *J. Chem. Phys.*, 2012, **137**, 144306.
- 18 Y. Liu and L. Ojamäe, *J. Phys. Chem. C*, 2015, **119**, 17087–17089.
- 19 K. Tezuka, K. Murayama, S. Takeya, S. Alavi and R. Ohmura, *J. Phys. Chem. C*, 2013, **117**, 10476.
- 20 K. Murayama, S. Takeya, S. Alavi and R. Ohmura, *J. Phys. Chem. C*, 2014, **118**, 21323–21330.
- 21 K. C. Hester, Z. Huo, A. L. Ballard, C. A. Koh, K. T. Miller and E. D. Sloan, *J. Phys. Chem. B*, 2007, **111**, 8830–8835.
- 22 J. A. Greathouse, R. T. Cygan and B. A. Simmons, *J. Phys. Chem. B*, 2006, **110**, 6428–6431.
- 23 T. Kumazaki, Y. Kito, S. Sasaki, T. Kume and H. Shimizu, *Chem. Phys. Lett.*, 2004, **388**, 18–22.
- 24 K. A. Udachin, C. I. Ratcliffe and J. A. Ripmeester, *J. Supramol. Chem.*, 2002, **2**, 405–408.
- 25 M. T. Kirchner, R. Boese, W. E. Billups and L. R. Norman, *J. Am. Chem. Soc.*, 2004, **126**(30), 9407–9412.
- 26 S. Takeya, K. A. Udachin, I. L. Moudrakovski, R. Susilo and J. A. Ripmeester, *J. Am. Chem. Soc.*, 2010, **132**(2), 524–531.
- 27 L. Shang, I. M. Chou, R. C. Burruss, R. Hu and X. Bia, *J. Raman Spectrosc.*, 2014, **45**, 696–702.
- 28 C. Gutt, B. Asmussen, W. Press, M. R. Johnson, Y. P. Handa and J. S. Tse, *J. Chem. Phys.*, 2000, **113**, 4713–4721.
- 29 A. Hoshikawa, N. Igawa, H. Yamauchi and Y. Ishii, *J. Chem. Phys.*, 2006, **125**(3–6), 034505.
- 30 H. Shimizu, T. Kume and S. Sasaki, *J. Phys. Chem. B*, 2002, **106**, 30–33.
- 31 H. Hirai, Y. Uchihara, H. Fujihisa, M. Sakashita, E. Katoh, K. Aoki, K. Nagashima, Y. Yamamoto and T. Yagi, *J. Phys. Chem.*, 2001, **115**, 7066–7070.

