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Chemical Engineering Science,

Short communication

In situ Raman spectra of hydrogen in large cages of hydrogen+tetrahydrofuran mixed hydrates

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Abstract

Large-cage occupancy of hydrogen (H_2) in the H_2+tetrahydrofuran (THF) hydrates has been ever reported only in the *ex situ* spectroscopic measurements with the quenched hydrate sample. In the present study, to verify the proof-of-concept for the large-cage occupancy of H_2 competitive with THF, *in situ* Raman spectra of H_2 in the H_2+THF mixed hydrates were detected at 74.3 MPa and

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265 K without the quenching procedure. The Raman spectra reveal that H_2 molecules occupy a part of large cages of the H_2+THF mixed hydrates at a thermodynamically unstable region of simple H_2 hydrate.

Keywords: Gas hydrate, Cage occupancy, Raman spectroscopy, Tuning effect

1. Introduction

Clathrate hydrates are solid inclusion compounds. Guest molecules are trapped in cavities of hydrate cages constructed by hydrogen-bonded water molecules. Hydrogen (H_2) and water form structure-II clathrate hydrate (Dyadin et al., 1999; Mao et al., 2002). The unit cell of structure-II clathrate hydrate consists of 16 small and 8 large cages, which are singly and multiply occupied by H_2 molecules, respectively (Lokshin et al., 2004). The small cage (5^{12}, hereafter S-cage) is a dodecahedron composed of 12 pentagonal faces. The large cage ($5^{12}6^{4}$, L-cage) is a hexakaidecahedron of 12 pentagonal and 4 hexagonal faces. Simple H_2 hydrates potentially offer a clean storage medium, however, high pressures and/or low temperatures are required for simple H_2 hydrate formation (Dyadin et al., 1999; Mao et al., 2002; Lokshin et al., 2004). The addition of tetrahydrofuran (THF) makes H_2+THF mixed hydrates at a pressure lower than equilibrium one of simple H_2 hydrates (Florusse et al., 2004; Lee et al., 2005; Hashimoto et al., 2006; Strobel et al., 2006; Anderson et al., 2007; Martin and Peters, 2009). In the H_2+THF mixed hydrates prepared with compressed H_2 and THF aqueous solutions, H_2 molecules occupy only S-cages (Hashimoto et al., 2007). On the other hand, when H_2+THF mixed hydrates are prepared with compressed H_2 and solid mixtures of THF and ice, H_2 molecules occupy not only S-cages but also a part of L-cages (Sugahara et al., 2009, 2010). The phenomenon has been called the tuning effect (Lee et al., 2005). In this case, H_2 storage amount ideally increases to the similar level as that of simple H_2 hydrates. In previous studies, competitive L-cage occupancies of H_2 and THF have been investigated by means of *ex situ* Raman spectroscopy at atmospheric pressure and liquefied nitrogen (LN_2) temperature (Sugahara et al., 2009, 2010). The hydrate samples were taken from high-pressure cells after they were quenched by LN_2. Therefore, some researchers have inferred that the peaks derived from H_2 molecules in L-cages were detected as a result of simple H_2 hydrates generation during quenching process.

In the present study, H_2+THF mixed hydrates were prepared and analyzed at simple H_2 hydrates unstable region (74.3 MPa and 265 K).

2. Experimental section

In the present study, to exclude both effects of the sample quenching and the fluid H_2 in the Raman analysis, we used a different experimental method from the previous reports (Hashimoto et al., 2007; Sugahara et al., 2009). Schematic illustration of the experimental setup and procedure is shown in Figure 1. The small droplet of pure water was directly dropped on a sapphire window of high-pressure optical cell. It was placed in a temperature-controlled room at 263 K, and the droplet was frozen. Then the window with ice was set in main unit of high-pressure cell, and THF was enclosed within a high-pressure pipe line between the valve and the high-pressure optical cell. Once the valve was opened, THF was sprayed on the ice surface by compressed H_2. At this time, H_2 and THF molecules simultaneously supplied to the ice surface results in the hydrate formation. The approximate amount of the enclosed THF corresponds to the stoichiometric concentration of the simple THF hydrate, because the hydrate formation was unable to be detected under a less THF condition. Though it is difficult to comprehend the exact amount of THF reacted with ice, the THF concentration (on an H_2 free basis) in the H_2+THF mixed hydrate is at least less than the stoichiometric concentration of the simple THF hydrate.

The system temperature was controlled at 265 K. Hydrate samples were analyzed through a sapphire (Ti free) window by means of *in situ* Raman spectroscopy using a laser Raman confocal microprobe spectrophotometer with multichannel CCD detector at 74.3 MPa and 265 K. To maximally inhibit the overlap of fluid H_2 on the Raman spectrum, that is, to improve the spatial resolution in the confocal Raman arrangement, the minimal sizes of a slit and an aperture were used. As a compensation of the improved spatial resolution, detected peak intensities are generally sacrificed. The argon ion laser (wavelength: 514.5 nm, laser spot diameter: 2 μm) was irradiated to the hydrate crystal and the backscatter was taken in through the same lens. The spectral resolution was ~0.7 cm^{-1}. The system temperature was measured within an uncertainty of 0.2 K using a RTD thermistor (Eutech, Temp 6). The system pressure was measured by a pressure gauge (Valcom, VPRH series) with an estimated maximum uncertainly of 0.2 MPa.

Research grade H_2 (mole fraction purity is 0.999999) was obtained from the Neriki Gas Co., Ltd. The maximum impurity was 0.2 ppm of nitrogen. Research grade THF (mole fraction purity is 0.999 and the main impurity was water) was obtained from the Merck, Ltd. The distilled water was obtained from the Wako Pure Chemical Industries, Ltd. All of them were used without further purifications.

3. Results and discussion

Raman peaks corresponding to the intramolecular H–H stretching vibration mode of H_2 in L-cage are strongly affected by surrounding temperature (Mao et al., 2002). It has been reported that the peak derived from single H_2 molecule in S-cages (hereafter, peak (S)) is detected at 4132 cm^{-1} and the peaks derived from multiple H_2 molecules in L-cages (peaks (L)) are detected at 4144 cm^{-1} and 4152 cm^{-1} (Amano et al., 2010). Note that the peak widths and positions are different from those recorded at an extremely low temperature and the peak (S) is broad and seems to be single at ambient temperature. Figure 2 shows the Raman spectra of the H–H vibration of H_2 molecules in the H_2+THF mixed hydrate and fluid H_2 phases. Figure 2(a) indicates the Raman spectrum of H_2 in the H_2+THF mixed hydrates prepared with the present experimental method. Figure 2(a) also involves the slight contribution of the fluid H_2. It was very difficult, even with the confocal Raman arrangement, to completely exclude the effect of H_2 in fluid phase. Figure 2(b) is the spectrum prepared from compressed H_2 and THF aqueous solutions. In this case, no H_2 molecule occupies L-cage even at low THF concentrations (Hashimoto et al., 2007). The peak (S) in Figure 2(a) has a shoulder at the high wavenumber side, while it does not appear in Figure 2(b). In order to elucidate that the peaks (L) exist in Figure 2(a), a difference spectrum between Figure 2(a) and Figure 2{(b)+(c)} is shown in Figure 3(a). When the difference spectrum was obtained, Figure 2(b) and (c) were normalized by the intensities of the peaks detected at 4132 and 4159 cm^{-1}, respectively. Figure 3(a) indicates two peaks assuredly at 4140 to 4160 cm^{-1}. They were fitted by use of Voigt function with the baseline correction. The deconvoluted peaks are shown in the green and blue lines. They are in good agreement with the peaks (L) of simple H_2 hydrates (Amano et al., 2010) as shown in Figure 3(b). This result reveals that H_2 molecules occupy a part of L-cages in the H_2+THF mixed hydrates prepared with the present experimental method. In other words, the competitive L-cage occupancy of H_2 with THF in H_2+THF mixed hydrates surely occurs ~~without quenching procedure~~, not always derived from the simple H_2 hydrate formation. The lower L-cage occupancy of H_2 than previous reports (Sugahara et al., 2009, 2010) results from the present experimental procedure to verify the proof-of-concept, that is, to exclude the effect of fluid H_2 in Raman analysis. Optimizing a preparation procedure and condition would make improvements.

4. Conclusions

The competitive L-cage occupancy of H_2 molecules in H_2+THF mixed hydrates has been *in situ* observed in a thermodynamically unstable region of the simple H_2 hydrate. The additional Raman peaks, other than the peak derived from single H_2 molecule in S-cage, reveal ~~that~~ the competitive L-cage occupancy of H_2 with THF (so-called tuning effect) ~~is independent of the quenching procedure~~.

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Figure captions

Figure 1 Schematic illustration of the experimental setup and procedure.

Figure 2 Raman spectra corresponding to the H–H vibrations of H_2 molecules in the H_2+THF mixed hydrates and fluid phase; (a) H_2+THF mixed hydrate partially with fluid H_2 (prepared from ice and THF in present study), (b) H_2+THF mixed hydrate (prepared from THF aqueous solution, Hashimoto et al 2007), (c) fluid H_2 phase, (d) sapphire window (Ti free) used in the present study.

Figure 3 (a) Difference spectrum between Figure 2(a) and Figure 2{(b)+(c)}, (b) the Raman spectrum of H_2 in the simple H_2 hydrate (Amano et al., 2010).

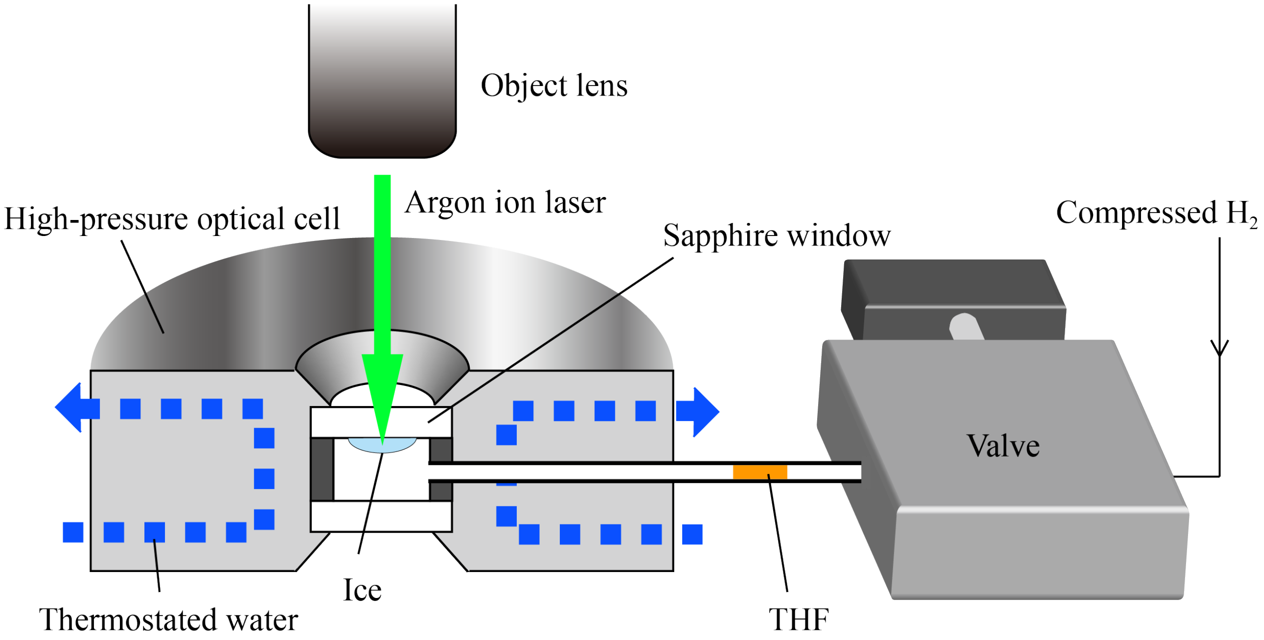
Object lens
Argon ion laser
High-pressure optical cell
Sapphire window
Compressed H_2
Valve
Ice
Thermostated water
THF

Fig. 1

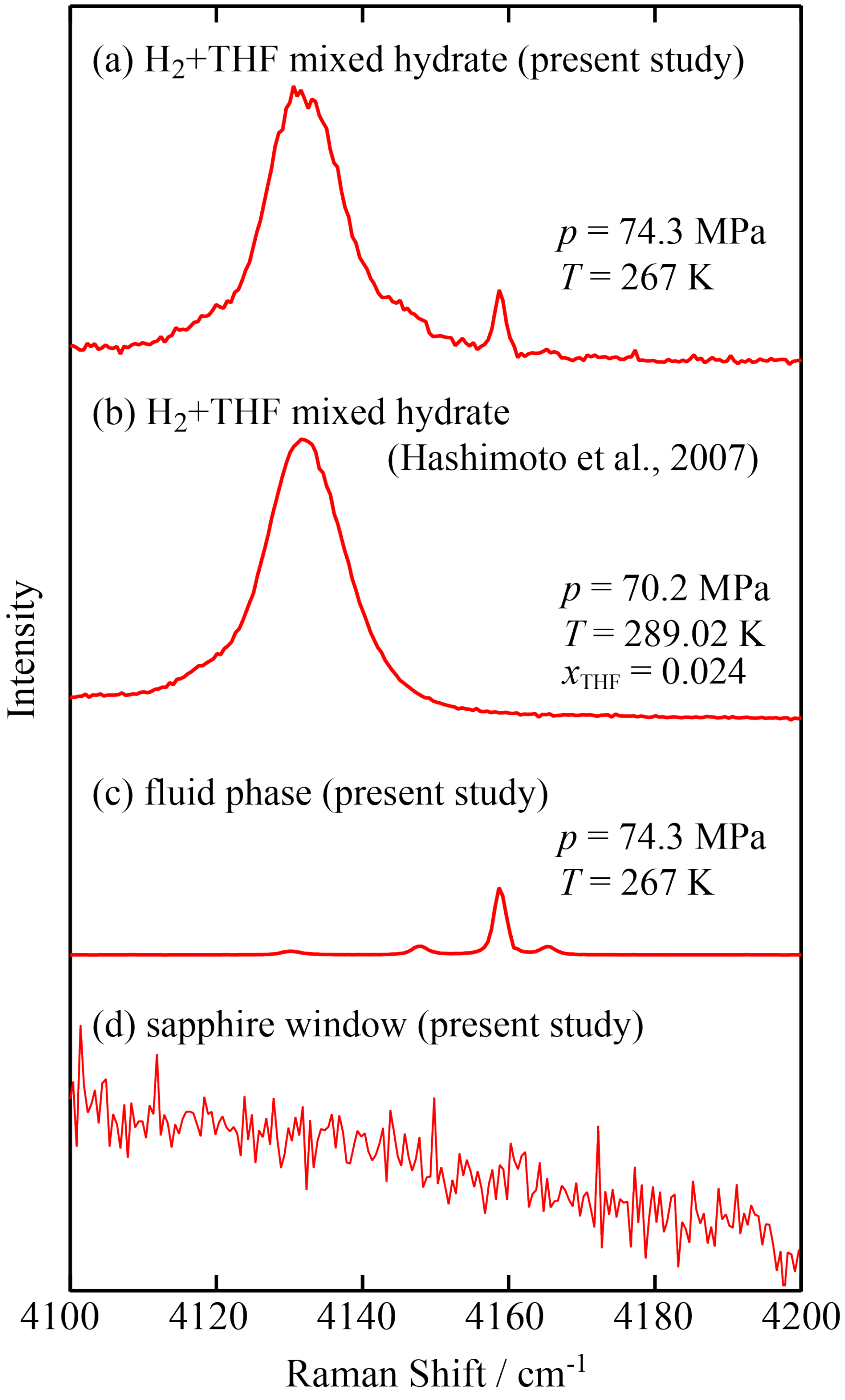
(a) H_2+THF mixed hydrate (present study)
p = 74.3 MPa
T = 267 K
(b) H_2+THF mixed hydrate
(Hashimoto et al., 2007)
p = 70.2 MPa
T = 289.02 K
x_{THF} = 0.024
(c) fluid phase (present study)
p = 74.3 MPa
T = 267 K
(d) sapphire window (present study)
Intensity
4100
4120
4140
4160
4180
4200
Raman Shift / cm^{-1}

Fig. 2

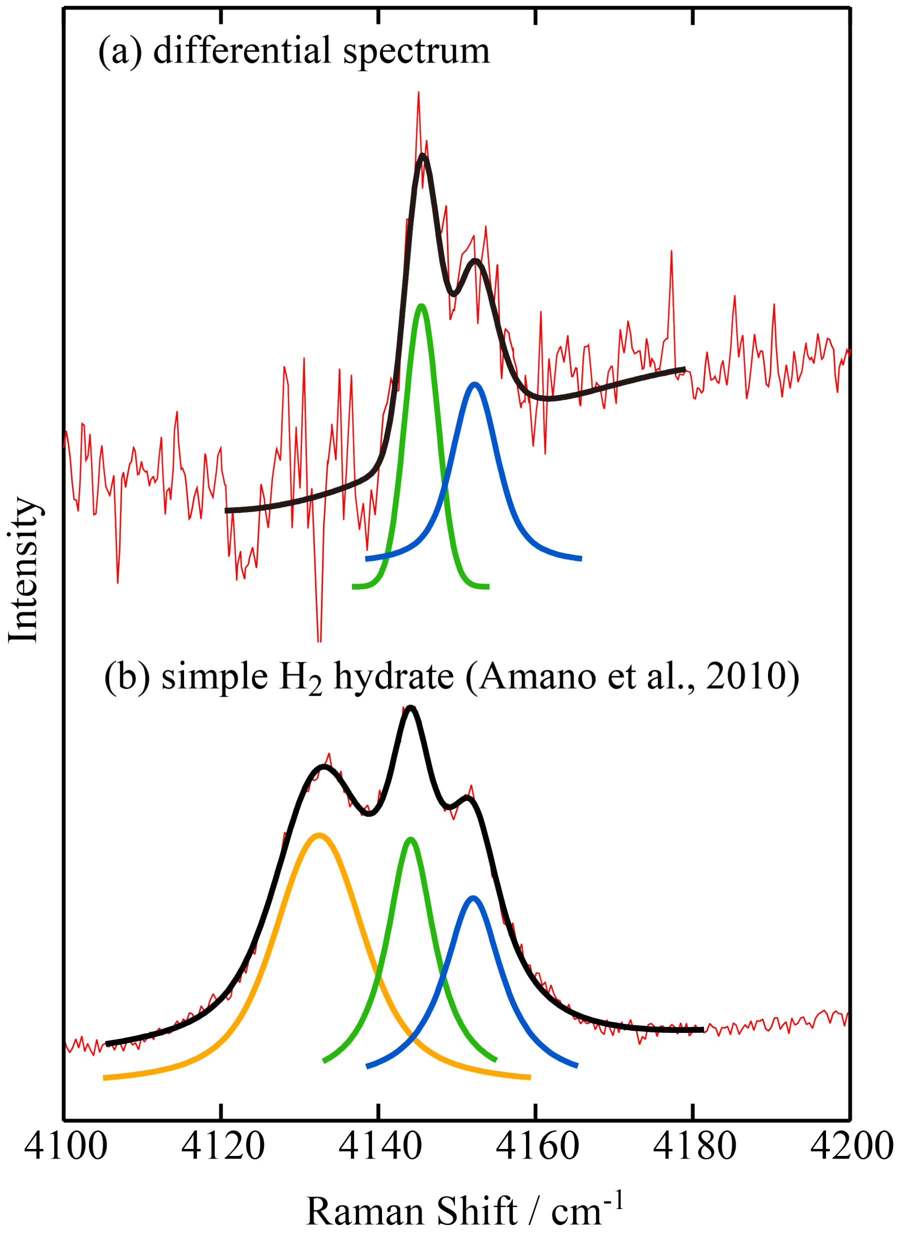
(a) differential spectrum
(b) simple H2 hydrate (Amano et al., 2010)
Intensity
4100
4120
4140
4160
4180
4200
Raman Shift / cm-1

Fig. 3