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# *In situ* observation of gas hydrate behaviour under high pressure by Raman spectroscopy

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## Abstract

The dynamic process and kinetics of gas hydrate formation and dissociation have been studied by means of Raman spectroscopy. The formation and dissociation of methane and carbon dioxide hydrates as well as the phenomenon of interchange of the components were observed as functions of time, temperature and pressure conditions. From the direct observation, it was found that the reformation of carbon dioxide hydrate occurred at the surface and inside the sample of methane hydrate as well as producing ice crystals.

## 1. Introduction

Gas hydrates are clathrate compounds formed by a lattice of water molecules and gases, and they are stable under conditions of high pressure and low temperature. Many kinds of gas, such as methane and carbon dioxide, can make up the structure of gas hydrate. The dynamic process and kinetics of gas hydrate formation and dissociation have been studied by means of Raman spectroscopy. Raman analysis is very useful as a non-destructive and direct technique for observing the change in components and the structure at the surface of solid hydrate. The formation and dissociation of methane and carbon dioxide hydrates as well as the phenomenon of interchange of the components were observed as functions of time, temperature and pressure conditions. This paper presents a method of direct observation of gas hydrate formation under high pressure, and experimental results on the kinetics of CH<sub>4</sub> and CO<sub>2</sub> gas hydrate formation and replacement.

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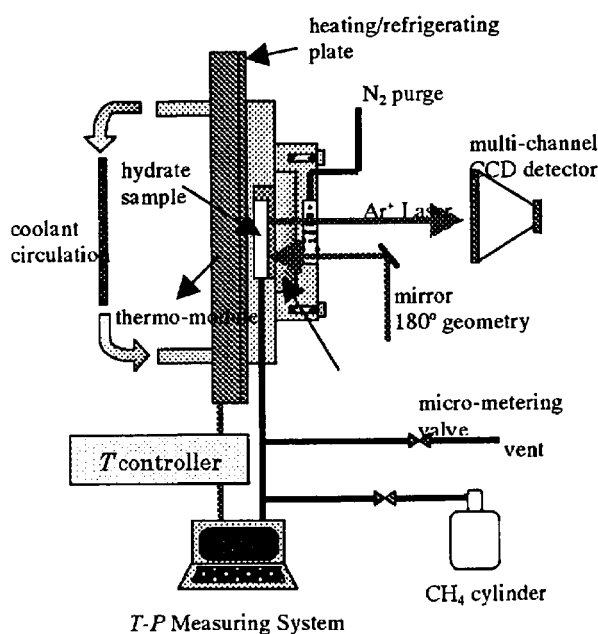


Figure 1. The experimental apparatus and the measuring system.

## 2. Experiment

Gas hydrates are stable as solid under high pressure and low temperature. In this experiment, the kinetic behaviour of gas hydrate, which was formed or dissociated in a pressure cell, was observed by Raman analysis. Figure 1 is a schematic diagram of the apparatus and measuring system used in this work. A constant temperature for the sample chamber was achieved by a thermo-module, which is installed behind the sample chamber. The pressure was controlled around the hydrate stability region to a desired experimental value.

A small-scale optical cell had an internal volume of about 10 ml and was covered by a sapphire window. Ice crystal powder was installed inside the cell for starting nucleation. The Raman spectrometer is a triple monochromator equipped with a CCD detector. The laser beam was from an Ar ion, with 514.53 nm line emission. The laser was focused on the hydrate sample through the window and the scattered radiation was collected in a 180° geometry. Raman measurement was conducted every 10 min after the nucleation of the gas hydrates.

## 3. Results and discussion

### 3.1. CH<sub>4</sub> gas hydrate formation and dissociation

CH<sub>4</sub> gas hydrate samples were synthesized in the solid phase for the replacement experiment using fine grains of ice crystal with an average diameter of 0.1 mm. Figure 2 shows the result of Raman spectroscopic analysis for CH<sub>4</sub> gas hydrate obtained using the procedure. A sharp Raman shift appears around 2905/2915 cm<sup>-1</sup>, indicating the existence of type-I CH<sub>4</sub> gas hydrates. According to a more precise analysis, the hydration number of the samples obtained was in the range of 6.4–6.0; that is, the ratio of occupancy in small cages can be estimated to be approximately 85–95%.

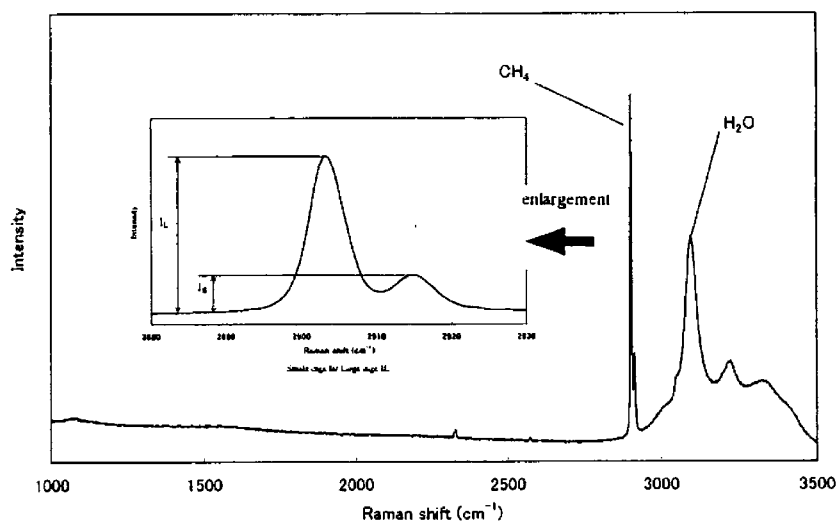


Figure 2. Raman observation of CH<sub>4</sub> gas hydrate.

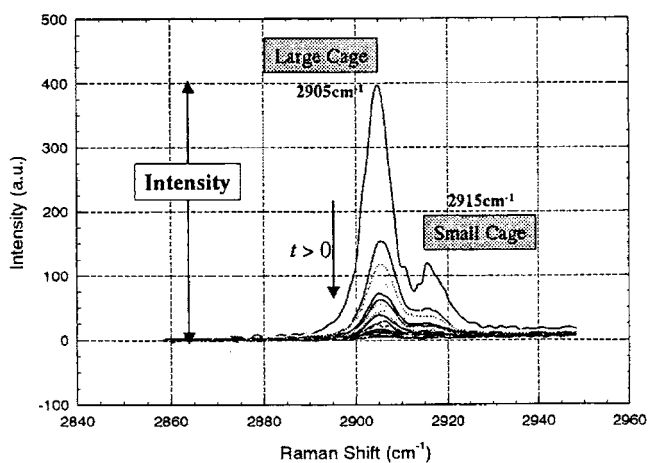


Figure 3. Raman shifts in the disassociation of CH<sub>4</sub> gas hydrate.

The dissociation behaviour of CH<sub>4</sub> gas hydrate was measured by Raman spectroscopy under conditions of changing pressure. Figure 3 shows the trends of Raman shifts during the dissociation of a CH<sub>4</sub> gas hydrate sample. The right-hand small peaks represent the presence of a guest in a small cage and the left-hand peaks represent the presence of a guest in a large cage. The result shows that the both peaks gradually decrease with time, resulting in the dissociation of CH<sub>4</sub> gas hydrate under pressurizing conditions. The dissociation rate can be obtained from the data analysis.

### 3.2. CO<sub>2</sub> gas hydrate formation

During the crystal growth of CO<sub>2</sub> gas hydrate, the variations of Raman shifts were measured as functions of temperature and pressure. Figure 4 shows the trend of the Raman shifts obtained

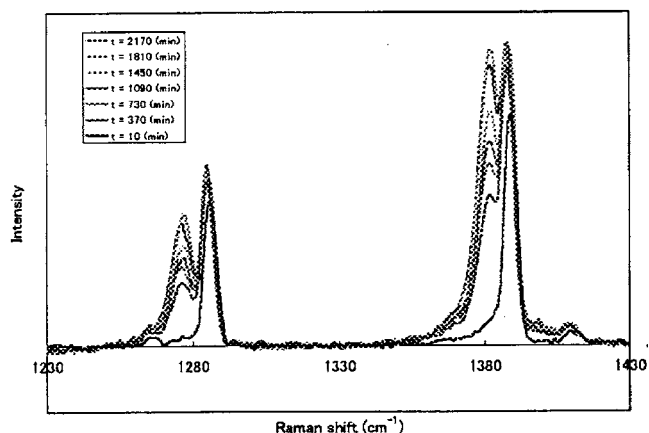


Figure 4. CO<sub>2</sub> hydrate formation at pressure 2.0 MPa.

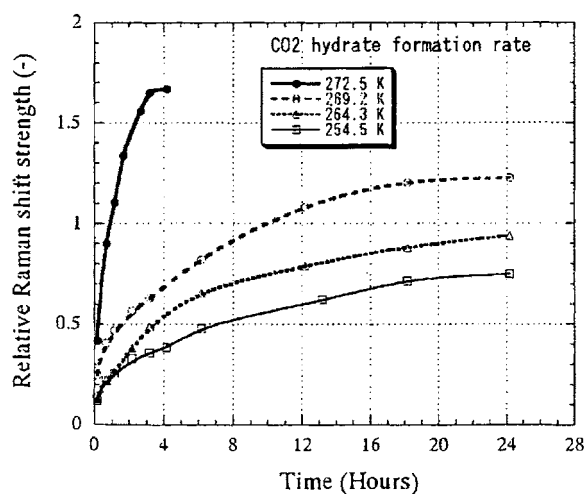


Figure 5. The formation rates of CO<sub>2</sub> gas hydrate.

from 10 to 2170 min after nucleation. Four Raman shift peaks were detected, in which peaks of around 1276 and 1381  $\text{cm}^{-1}$  are due to the existence of a guest in the CO<sub>2</sub> gas hydrate structure. It is found in this figure that the values of peak strength increase with time after the nucleation of the gas hydrate. As the peak strength closely corresponds to the numbers of molecules in the structure, the formation rate can be estimated from the peak strength.

Figure 5 shows the formation rates of CO<sub>2</sub> gas hydrate obtained at temperatures from 254.5 to 274.5 K. The formation rates of gas hydrate changed greatly with temperature, especially in the range between 269 and 275 K. This suggests that the existence of quasi-liquid phase water, a type of slightly melting ice, plays an important role in promoting formation of gas hydrate at the gas–solid interface. On the basis of the behaviour of CO<sub>2</sub> formation, the temperature for the replacement process was set around 273–275 K.

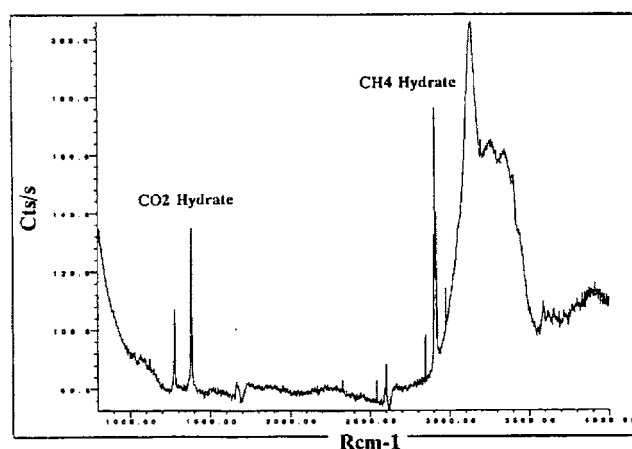


Figure 6. The coexistence of CO<sub>2</sub> and CH<sub>4</sub> gas hydrates.

### 3.3. Replacement of CO<sub>2</sub> and CH<sub>4</sub> gas hydrates in solid

The replacement experiment on CO<sub>2</sub> and CH<sub>4</sub> gas hydrates was carried out using a bulk scale testing apparatus. Samples of pure CH<sub>4</sub> gas hydrate were installed in a pressure cell, and then gaseous CO<sub>2</sub> was introduced into the sample under controlled pressure and temperature conditions. During the process of replacement, the pressure of CO<sub>2</sub> was 2.0 MPa and the temperature was  $274 \pm 0.5$  K. Figure 6 illustrates the Raman shifts obtained from the replaced hydrate sample observed 1 h following CO<sub>2</sub> introduction. Two typical peaks appeared in the Raman spectra, at 2905/2915 cm<sup>-1</sup> for CH<sub>4</sub> hydrate and around 1275/1380 cm<sup>-1</sup> for CO<sub>2</sub> hydrate. This means that both CH<sub>4</sub> and CO<sub>2</sub> gas hydrates coexist in the structure of the replaced hydrate sample. Based on quantitative analysis, the ratios of occupancy for CO<sub>2</sub>/CH<sub>4</sub> gas hydrates in the replaced hydrate samples were 40 and 45%, respectively. The proportion of CO<sub>2</sub> gas hydrate in the sample increased with time.

Figure 7 shows the trend of CO<sub>2</sub>/CH<sub>4</sub> components in the solid hydrate after CO<sub>2</sub> introduction as a function of time. The data were obtained from *in situ* observation and the analysis of peak strength for the Raman shifts. This result indicates that the replacement of guest elements in solid gas hydrates could be achieved within a short period of 12 h, if the pressure and temperature are precisely controlled in the pressure cell. It is also considered that a period of 2 h is sufficient for nucleation of CO<sub>2</sub> hydrate at the surface of the sample, and then crystal growth proceeds as a result of CO<sub>2</sub> transport into the solid hydrate. Because the transport of CO<sub>2</sub> gas should be fast in porous media, the *in situ* replacement of CO<sub>2</sub> gas hydrate may be used for the extraction of gas hydrates from their reservoirs. To obtain engineering data for practical use, more systematic research is necessary to elucidate the phenomenon underlying gas hydrate replacement.

## 4. Conclusions

Experimental study on the dynamic behaviour of gas hydrates was carried out using a specially designed apparatus. The *in situ* observation method using Raman spectroscopy is very powerful for measuring the kinetics of formation and dissociation of gas hydrate under high pressure. The rate of dissociation of CH<sub>4</sub> gas hydrate and the reformation of CO<sub>2</sub> gas hydrate were quantitatively observed and analysed on the basis of Raman shift data. The results of the bulk

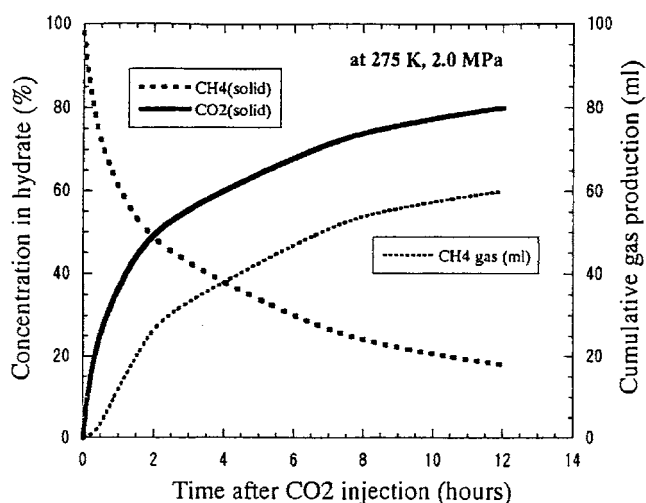


Figure 7. The change in the components of gas hydrates during the replacement experiment.

scale experiment showed that replacement of CO<sub>2</sub> gas hydrate could be achieved within a period of 12 h in pure samples of CH<sub>4</sub> gas hydrate that had been synthesized as solid crystal, if the pressure and temperature were precisely controlled in the pressure cell.

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