Carbon Isotope Fractionation during the Formation of CO$_2$ Hydrate and Equilibrium Pressures of $^{12}$CO$_2$ and $^{13}$CO$_2$ Hydrates

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Abstract: Knowledge of carbon isotope fractionation is needed in order to discuss the formation and dissociation of naturally occurring CO$_2$ hydrates. We investigated carbon isotope fractionation during CO$_2$ hydrate formation and measured the three-phase equilibria of $^{12}$CO$_2$–H$_2$O and $^{13}$CO$_2$–H$_2$O systems. From a crystal structure viewpoint, the difference in the Raman spectra of hydrate-bound $^{12}$CO$_2$ and $^{13}$CO$_2$ was revealed, although their unit cell size was similar. The $^{13}$C of hydrate-bound CO$_2$ was lower than that of the residual CO$_2$ (1.0–1.5‰) in a formation temperature ranging between 226 K and 278 K. The results show that the small difference between equilibrium pressures of ~0.01 MPa in $^{12}$CO$_2$ and $^{13}$CO$_2$ hydrates causes carbon isotope fractionation of ~1‰. However, the difference between equilibrium pressures in the $^{12}$CO$_2$–H$_2$O and $^{13}$CO$_2$–H$_2$O systems was smaller than the standard uncertainties of measurement; more accurate pressure measurement is required for quantitative discussion.

Keywords: CO$_2$ hydrate; carbon isotope; isotopic fractionation; phase equilibrium; Raman spectra

1. Introduction

Gas hydrates are crystalline clathrate compounds that have guest gas molecules encapsulated in hydrogen-bonded water cages and can be thermodynamically stable at high pressures and low temperatures. The phase equilibrium pressure-temperature conditions vary depending on the guest molecule type [1]. Gas hydrates with encapsulated natural gases exist in sub-marine/sublacustrine sediments and below the permafrost on Earth. Because they contain copious amounts of greenhouse gases, such as methane, concerns arose that their dissociation could add to global warming [2–4]. Hydrate-bound gas contains both hydrocarbons and CO$_2$ [5–7], and natural gas hydrates encapsulating CO$_2$ have been observed at the venting sites of liquid CO$_2$ [8,9]. On the other hand, the possibility of existing CO$_2$ hydrates on Mars was proposed [10,11] and the conditions for CO$_2$ hydrate formation on Mars have been discussed [12]. As above, CO$_2$ hydrates are critical in both geochemistry and space science and require better understanding.

Since CO$_2$ comprises carbon and oxygen atoms, several isotopic species of CO$_2$ exist, depending on the combination of stable isotopes (isotologues: $^{12}$C, $^{13}$C, $^{16}$O, $^{17}$O, and $^{18}$O). For example, the abundance ratio of $^{13}$CO$_2$ is ~1.1% of the total CO$_2$ and the rest is almost $^{12}$CO$_2$. Stable isotope fractionation of the guest gas during the gas hydrate formation provides information for discussing the formation, maintenance, and decomposition processes of gas hydrates. For example, the trend of hydrogen and carbon isotope fractionation during the formation of synthetic methane and ethane hydrates was
investigated [13]. Moreover, the results were applied to estimate the formation process of natural gas hydrates [14–16]. Carbon isotope fractionation during the formation of CO\textsubscript{2} hydrates was reported [17], revealing that the CO\textsubscript{2} δ\textsuperscript{13}C in the hydrate phase was 0.9‰ lower than that in the gas phase at 268 K [17]. Therefore, \(^{12}\text{CO}_2\) is more easily encapsulated in the hydrate phase than \(^{13}\text{CO}_2\). Because the temperature of existing natural gas hydrates at sea/lake bottom sediments is above 273 K, information about carbon isotope fractionation above the freezing point of water is needed to discuss the formation and dissociation of naturally occurring CO\textsubscript{2} hydrates. Furthermore, CO\textsubscript{2} hydrates have been suggested outside of Earth. Therefore, it is also necessary to confirm isotope fractionation in a wider temperature range.

In studies on methane hydrates, the equilibrium pressures of CH\textsubscript{3}D and CD\textsubscript{4} hydrates were ~0.04 MPa and ~0.14 MPa higher than those of the CH\textsubscript{4} hydrate, respectively [18]. Because guest molecules, which have lower equilibrium pressure, are preferentially encapsulated in the gas hydrate cages, the difference in equilibrium pressures of CH\textsubscript{3}D and CH\textsubscript{4} hydrates can explain the hydrogen isotope fractionation in methane during methane hydrate formation [18]. Thus, comparing the phase equilibrium \(p-T\) conditions of each gas hydrate encapsulating isotopologues can explain the trend of isotopic fractionation of guest gases during gas hydrate formation. However, the equilibrium pressure of \(^{13}\text{CO}_2\) hydrates has not been reported.

In this study, we synthesized gas hydrate samples, encapsulated CO\textsubscript{2} isotopologues (\(^{12}\text{CO}_2\) and \(^{13}\text{CO}_2\)), and characterized their crystallographic properties using powder X-ray diffraction (PXRD) and Raman spectroscopy. We also measured the equilibrium pressures of \(^{12}\text{CO}_2\) and \(^{13}\text{CO}_2\) hydrates at a temperature range between 269 K and 278 K. We investigated carbon isotope fractionation between hydrate-bound gas and residual gas in a pressure cell in the temperature range of 226 K to 278 K.

2. Results and Discussion

We confirmed the crystallographic structures of \(^{12}\text{CO}_2\) and \(^{13}\text{CO}_2\) hydrates and obtained their lattice constants using the PXRD method. The diffraction patterns of cubic structure I (sI) hydrates were observed from these hydrates (Figure S1). The lattice constants of \(^{12}\text{CO}_2\) and \(^{13}\text{CO}_2\) hydrates were similar at 11.8352(6) Å and 11.8323(5) Å, respectively.

Figure 1 shows the Raman spectra of \(^{12}\text{CO}_2\) and \(^{13}\text{CO}_2\) hydrates and Table 1 summarizes the observed Raman shifts of hydrate-bound isotopologue CO\textsubscript{2} and their assignments to the vibrational modes. Two distinct peaks corresponding to the Fermi dyad of CO\textsubscript{2} in the hydrate cages were observed at 1278.2 cm\(^{-1}\) and 1381.9 cm\(^{-1}\) for \(^{12}\text{CO}_2\) hydrates, corresponding to [19–21]. These peaks shifted to 1256.4 cm\(^{-1}\) and 1365.8 cm\(^{-1}\) for the \(^{13}\text{CO}_2\) hydrate. Qin and Kuhs [21] observed 1366.6 ± 4.0 cm\(^{-1}\) for the upper Fermi dyad of hydrate-bound \(^{13}\text{CO}_2\), and our data were consistent with their results. Definite differences (22 cm\(^{-1}\) and 16 cm\(^{-1}\) for lower and upper peaks, respectively) were found between these Raman peaks caused by the encapsulated \(^{12}\text{CO}_2\) and \(^{13}\text{CO}_2\) molecules.

| Guest Molecule | Raman Shift Gas/cm\(^{-1}\) | Raman Shift Hydrate/cm\(^{-1}\) | Assign | Vibrational Mode |
|----------------|--------------------------|--------------------------|--------|------------------|
| \(^{12}\text{CO}_2\) | 1285.40 [22] | 1278.2 \(^a\), 1277 [19], 1278 [20], 1275.5 ± 0.8 [21] | \(v_1 + 2v_2\) \(^b\) | CO s-stretch + bend \(^b\) |
| \(^{13}\text{CO}_2\) | 1266.03 [22] | 1256.4 \(^a\) | | |
| | 1369.90 [22] | 1365.8 \(^a\), 1366.6 ± 4.0 [21] | | |

\(^a\) This work, uncertainty is <1.1 cm\(^{-1}\). \(^b\) Fermi resonance.
Three-phase equilibrium pressures in the 13CO2–H2O system are higher by 0.007–0.012 MPa compared to the corresponding values in the 12CO2–H2O system between 269 K and 278 K. However, these differences are within the range of uncertainty of the pressure measurements.

**Table 2.** Three-phase equilibrium p–T conditions in 12CO2–H2O and 13CO2–H2O systems.

| T/K  | p12CO2–H2O/MPa | p13CO2–H2O/MPa | Phase in Equilibrium         |
|------|----------------|----------------|-------------------------------|
| 269.47 | 0.953          | 0.963          | ice + hydrate + vapor        |
| 269.67 | 0.960          | 0.969          | ice + hydrate + vapor        |
| 269.88 | 0.967          | 0.977          | ice + hydrate + vapor        |
| 270.08 | 0.973          | 0.984          | ice + hydrate + vapor        |
| 270.28 | 0.980          | 0.990          | ice + hydrate + vapor        |
| 270.47 | 0.987          | 0.999          | ice + hydrate + vapor        |
| 270.67 | 0.994          | 1.004          | ice + hydrate + vapor        |
| 270.88 | 1.002          | 1.011          | ice + hydrate + vapor        |
| 271.08 | 1.009          | 1.018          | ice + hydrate + vapor        |
| 271.28 | 1.016          | 1.025          | ice + hydrate + vapor        |
| 271.48 | 1.023          | 1.031          | ice + hydrate + vapor        |
| 271.67 | 1.034          | 1.043          | water + hydrate + vapor      |
| 271.88 | 1.058          | 1.067          | water + hydrate + vapor      |
| 272.08 | 1.083          | 1.092          | water + hydrate + vapor      |
| 272.28 | 1.109          | 1.118          | water + hydrate + vapor      |
| 272.46 | 1.133          | 1.142          | water + hydrate + vapor      |
| 272.66 | 1.159          | 1.168          | water + hydrate + vapor      |
| 272.86 | 1.185          | 1.195          | water + hydrate + vapor      |
| 273.05 | 1.212          | 1.223          | water + hydrate + vapor      |
| 273.25 | 1.240          | 1.251          | water + hydrate + vapor      |
| 273.45 | 1.270          | 1.280          | water + hydrate + vapor      |
| 273.66 | 1.302          | 1.312          | water + hydrate + vapor      |
| 273.85 | 1.333          | 1.342          | water + hydrate + vapor      |
| 274.05 | 1.365          | 1.376          | water + hydrate + vapor      |
| 274.26 | 1.397          | 1.408          | water + hydrate + vapor      |
| 274.47 | 1.427          | 1.435          | water + hydrate + vapor      |
| 274.67 | 1.461          | 1.469          | water + hydrate + vapor      |
Table 2. Cont.

| T/K  | $P_{12CO_2}$–H$_2$O/MPa | $P_{13CO_2}$–H$_2$O/MPa | Phase in Equilibrium          |
|------|--------------------------|--------------------------|--------------------------------|
| 274.87 | 1.496                           | 1.504                       | water + hydrate + vapor        |
| 275.07 | 1.534                           | 1.542                       | water + hydrate + vapor        |
| 275.27 | 1.569                           | 1.578                       | water + hydrate + vapor        |
| 275.46 | 1.605                           | 1.614                       | water + hydrate + vapor        |
| 275.66 | 1.642                           | 1.651                       | water + hydrate + vapor        |
| 275.86 | 1.682                           | 1.690                       | water + hydrate + vapor        |
| 276.06 | 1.723                           | 1.732                       | water + hydrate + vapor        |
| 276.26 | 1.766                           | 1.774                       | water + hydrate + vapor        |
| 276.44 | 1.806                           | 1.814                       | water + hydrate + vapor        |
| 276.64 | 1.846                           | 1.855                       | water + hydrate + vapor        |
| 276.85 | 1.893                           | 1.901                       | water + hydrate + vapor        |
| 277.04 | 1.939                           | 1.948                       | water + hydrate + vapor        |
| 277.24 | 1.985                           | 1.994                       | water + hydrate + vapor        |
| 277.43 | 2.035                           | 2.044                       | water + hydrate + vapor        |
| 277.64 | 2.088                           | 2.097                       | water + hydrate + vapor        |
| 277.84 | 2.140                           | 2.149                       | water + hydrate + vapor        |
| 278.05 | 2.196                           | 2.205                       | water + hydrate + vapor        |

*Uncertainties of $T$ and $p$ are 0.05 K and 0.05 MPa, respectively.

Figure 2. Three-phase (ice/water + hydrate + vapor) equilibrium $p$–$T$ conditions for $^{12}$CO$_2$ and $^{13}$CO$_2$ hydrates. Green circles, $^{12}$CO$_2$–H$_2$O (this work); brown circles, $^{13}$CO$_2$–H$_2$O (this work); open squares, $^{12}$CO$_2$–H$_2$O [24]; open triangles, $^{12}$CO$_2$–H$_2$O [25]; open diamonds, $^{12}$CO$_2$–H$_2$O [26]; open circles, $^{12}$CO$_2$–H$_2$O [23].

Figure 3 shows the differences in $\delta^{13}$C between the residual and hydrate-bound CO$_2$ ($\Delta\delta^{13}$C) in the temperature range of 226 K to 278 K. The $\delta^{13}$C of hydrate-bound CO$_2$ was lower (1.0–1.5‰) than that of residual CO$_2$ in the temperature range used in this study. This result correlates with a previous study that reported ~0.9‰ of $\Delta\delta^{13}$C at 268 K [17]. These results indicate that $^{12}$CO$_2$ molecules are preferentially encapsulated in hydrate cages as guest molecules rather than $^{13}$CO$_2$ molecules during the formation of CO$_2$ hydrates in the temperature range of 226 K to 278 K.
An earlier study reported hydrogen isotope fractionation in methane during the formation of methane hydrates [13]. The δD of hydrate-bound methane was 4.8 ± 0.4‰ lower than that of residual molecules [13]. On the other hand, the equilibrium pressures of CH₃D and CH₄ hydrates were ~0.04 MPa and ~0.14 MPa higher than those of the CH₄ hydrate, respectively [18]. For example, the equilibrium pressure of the C₂H₆ hydrate is lower than that of the CH₄ hydrate [24], resulting in a preferential C₂H₆ concentration in the hydrate phase during the formation process of CH₄ and C₂H₆ mixed-gas hydrate [24,27]. Ozeki et al. explained that the difference in equilibrium pressures between CH₃D and CH₄ hydrates causes the isotopic fractionation of hydrogen in methane during the formation of methane hydrates [18]. In this study, carbon isotope fractionation in CO₂ (the difference in δ¹³C between the residual and hydrate gases) during the formation of CO₂ hydrates was 1.0–1.5‰ (Figure 3). As above, this trend of carbon isotope fractionation of CO₂ is reasonable because the equilibrium pressures of the ¹²CO₂–H₂O system seem slightly lower than those of the ¹³CO₂–H₂O system. However, it cannot be discussed here because these differences in equilibrium pressures (Table 2) are smaller than the experimental uncertainty (0.05 MPa).

3. Materials and Methods

3.1. Crystallographic Analysis

We formed fine powder samples of ¹²CO₂ and ¹³CO₂ hydrates in small pressure cells (internal volume: 8 mL). Research-grade CO₂ (purity 99.999% for CO₂, including ~1.1% of ¹³CO₂, Takachiho Chemical Industrial) and ¹³CO₂ (purity 99%, Taiyo Nippon Sanso) were used as the guest ¹²CO₂ and ¹³CO₂, respectively. 1 g of fine ice powder was placed in the high-pressure cell, and the air was vacuumed at 77 K. CO₂ isotopologues were introduced to each cell and the temperature was increased from 77 K to 273.2 K to form their gas hydrates. CO₂ sublimated and increased the internal pressure. We confirmed hydrate formation by the decrease in pressure at 273.2 K. The samples were recovered and stored at 77 K for the crystallographic analysis.

PXRD measurements were performed using an X-ray diffractometer (model Ultima-III, Rigaku Co., Tokyo, Japan) with parallel beam optics and a low-temperature chamber. Finely-powdered hydrate samples were mounted on a PXRD sample holder made of 2.5 mm thick Cu at 93 K. Each measurement was performed in a θ/2θ step scan mode with a step width of 0.02° using Cu Kα radiation (λ = 1.541 Å).

We obtained the Raman spectra of ¹²CO₂ and ¹³CO₂ hydrates. A Raman spectrometer (RMP-210, Jasco Co., Tokyo, Japan) was used equipped with a 532 nm excitation source.
(100 mW), a single holographic diffraction grating (1800 grooves per mm), and a charged coupled device detector. The spectrum pixel resolution, which is the spectrum’s sampling interval, was 1.1 cm\(^{-1}\) per pixel in the range of 1200–1400 cm\(^{-1}\). The wavenumber was calibrated using atomic emission lines from a neon lamp. The Raman spectra for the C–O symmetric stretch region (1200–1400 cm\(^{-1}\)) of the encapsulated CO\(_2\) molecules in the gas hydrate water cages were obtained at ambient pressure and 140 K using a cooling stage (THMS600, Linkam Scientific Instruments Ltd., Tadworth, UK). The peak positions could be rigorously analyzed by fitting the data to a Voigt function, allowing us to obtain high positional accuracy.

3.2. Measurement for Equilibrium Pressure

To obtain the data of equilibrium pressures of \(^{12}\)CO\(_2\) and \(^{13}\)CO\(_2\) hydrates, we formed them in the same small pressure cells as those used for crystallographic analysis. The experimental setup to achieve their equilibrium condition was described in [18]. 1 g of fine ice powder was placed in the cell, evacuated at 77 K, and CO\(_2\) isotopologues were introduced in the amount needed to achieve equilibrium conditions of the ice/liquid water, hydrates, and vapor at ~273.2 K. The hydrate-enclathrated CO\(_2\) isotopologues were formed by melting the ice powder at 273.2 K under high pressure of CO\(_2\). The decrease in pressure due to hydrate formation was observed at 273.2 K.

The equilibrium hydrate dissociation and formation conditions were determined using a phased isochoric method of heating and cooling [18]. Three-phase (ice/water + hydrate + vapor) equilibrium conditions were achieved by increasing the temperature by 0.4 K and then decreasing it by 0.2 K. Since two values of equilibrium pressure at each temperature by heating and cooling were obtained, we determined the phase equilibrium points as their average temperatures and pressures. The phase equilibrium data of \(^{12}\)CO\(_2\) and \(^{13}\)CO\(_2\) hydrates were obtained between 269 K and 278 K. The uncertainties of the temperature and pressure measurements were 0.05 K and 0.05 MPa, respectively.

3.3. Gas Analysis for Detecting Carbon Isotope Fractionation

The preparation method of gas hydrate samples for measuring isotopic fractionation was the same as that of [13]. Research-grade CO\(_2\) gas was used as the guest gas (purity 99.999% for CO\(_2\), including ~1.1% of \(^{13}\)CO\(_2\), Takachiho Chemical Industrial). Distilled and deionized water was used as host molecules. The temperature effect on isotope fractionation was confirmed by forming CO\(_2\) hydrate samples at 226 K, 246 K, 254 K, 258 K, 263 K, 268 K, 273 K, 274 K, and 278 K. For the samples formed below the freezing point of water, fine ice powder (0.7 g) was filled in a high-pressure cell (internal volume: 42 mL) in a cold room at 253 K. For the samples formed above the freezing point of water, 5 g water was filled into a high-pressure cell equipped with a stirring device (internal volume: 150 mL). These high-pressure cells were cooled to below 90 K, vacuumed inside the air, and CO\(_2\) was introduced into the cell. The amount of CO\(_2\) was controlled to reach above the equilibrium pressure of CO\(_2\) hydrates and below the CO\(_2\) liquefaction pressure at each temperature. These cells were set into a circulating constant-temperature bath (>255 K) or cold rooms (226 K and 246 K) to maintain each temperature for hydrate formation. The trapped CO\(_2\) in the cells sublimated and reached the desired pressure at each temperature. The internal pressure decreased as the CO\(_2\) hydrates formed. When the pressure stabilized and the pressure decrease rate was lower than 0.01 MPa h\(^{-1}\), the residual gas that was not encapsulated in the gas hydrate was collected. The cell was cooled below 90 K and the hydrate sample was recovered from the cell. The residual and hydrate-bound gases were retrieved in a vacuum line system and their pressures were adjusted to atmospheric pressure.

Each gas sample was introduced into a continuous-flow isotope ratio mass spectrometer (CF-IRMS, Delta V, Thermo Fisher Scientific Inc., Waltham, MA, USA) coupled with a gas chromatograph (TRACE GC Ultra, Thermo Fisher Scientific Inc., Waltham, MA, USA) using a syringe injection. The gas chromatograph was equipped with a CP-PoraPLOT Q
Carbon isotope compositions were reported as δ values (‰),

\[
\delta [\text{‰}] = \left( \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right) \times 1000 \tag{1}
\]

where \( R \) denotes the \(^{13}\text{C}/^{12}\text{C} \) ratio. \( \delta^{13}\text{C} \) is given referring to the V-PDB standards, determined using NIST RM8544 (NBS19). The analytical precision was 0.1 ‰. The difference between the \( \delta^{13}\text{C} \) of the hydrate-bound gas and that of the residual gas was determined (\( \delta^{13}\text{C} \) of the residual gas – \( \delta^{13}\text{C} \) of the hydrate-bound gas, defined as \( \Delta \delta^{13}\text{C} \)).

4. Conclusions

We synthesized isotopologue \( \text{CO}_2 \) hydrates to obtain their crystallographic properties. From the Raman spectra of \(^{12}\text{CO}_2\) and \(^{13}\text{CO}_2\) hydrates, definite differences were found in the Raman shift of Fermi dyad of \(^{12}\text{CO}_2\) and \(^{13}\text{CO}_2\) encapsulated in hydrate cages, although their unit cell size was similar. We investigated carbon isotope fractionation during the formation of \( \text{CO}_2 \) hydrates and measured the three-phase equilibria of \(^{12}\text{CO}_2–\text{H}_2\text{O}\) and \(^{13}\text{CO}_2–\text{H}_2\text{O}\) systems. The \( \delta^{13}\text{C} \) of hydrate-bound \( \text{CO}_2 \) was lower than that of the residual \( \text{CO}_2 \) (1.0–1.5 ‰) in the formation temperature range between 226 K to 278 K. From the results of isotopic fractionation, differences in equilibrium pressures were expected. The equilibrium pressures in the \(^{12}\text{CO}_2–\text{H}_2\text{O}\) system were slightly lower by 0.007–0.012 MPa compared with the corresponding values in the \(^{13}\text{CO}_2–\text{H}_2\text{O}\) system between 269 K to 278 K. We concluded that the small difference in equilibrium pressures of ~0.01 MPa between \(^{12}\text{CO}_2\) and \(^{13}\text{CO}_2\) hydrates causes carbon isotope fractionation of 1.0–1.5 ‰. However, the pressure differences obtained were within the range of the uncertainty of the pressure measurements. More accurate measurements of equilibrium pressure are needed for further discussion. These results caused by carbon isotope fractionation will be useful for a better understanding of the formation and dissociation of naturally occurring \( \text{CO}_2 \) hydrates.

**Supplementary Materials:** The following is available online: Figure S1, Powder X-ray diffraction patterns of the hydrate enclathrated \( \text{CO}_2 \) isotopologues.

**Author Contributions:** H.K. prepared the samples, analyzed the gas data, and conducted Raman spectroscopy; G.F. wrote the draft of paper; S.T. conducted the PXRD analysis; and A.H. designed the experiments and supervised this project. All authors commented on and approved the paper. All authors have read and agreed to the published version of the manuscript.

**Funding:** Gas measuring system in this research was funded by the Japan Society for the Promotion of Science KAKENHI 26303021.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Available from the authors.

**Acknowledgments:** The authors gratefully acknowledge Jumpei Matsuda and Yuki Kikuchi for their technical support during the experiments.

**Conflicts of Interest:** The authors declare no conflict of interest.

**Sample Availability:** Samples of the compounds are not available from the authors.

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