

# Application of the ATR-IR Spectroscopic Technique to the Characterization of Hydrates Formed by CO<sub>2</sub>, CO<sub>2</sub>/H<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub>

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The spectroscopic investigation of CO<sub>2</sub>-containing clathrate hydrates is complicated because techniques such as Raman spectroscopy cannot distinguish cage populations. <sup>13</sup>C NMR spectroscopy also has some complications as the isotropic chemical shifts do not change for the different CO<sub>2</sub> cage populations. It is known that CO<sub>2</sub> molecules in the different phases relevant to hydrates give unique infrared vibrational frequencies; however, so far only thin cryogenic films prepared at low pressure have been studied with IR transmission spectroscopy. In this study, hydrates from CO<sub>2</sub>, CO<sub>2</sub>/H<sub>2</sub>, and CO<sub>2</sub>/H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> mixtures were synthesized in a high-pressure attenuated total reflection (ATR) cell and in situ infrared spectroscopy was performed at -50 °C to distinguish the vibrational frequencies from CO<sub>2</sub> in small and large cages in the resultant hydrate and in the other CO<sub>2</sub>-containing phases. Quantitative estimates of cage occupancies and hydration numbers are provided as based on the analysis of the IR spectra and knowledge of hydrate gas composition from gas chromatography.

## Introduction

The fact that CO<sub>2</sub> forms hydrate has been known for many years.<sup>1,2</sup> Recently, CO<sub>2</sub> hydrate has been considered as a means of capturing and sequestering CO<sub>2</sub>.<sup>3</sup> CO<sub>2</sub> hydrate forms a type-I cubic structure (*Pm3n*). Its unit cell contains 46 water molecules in a framework of two dodecahedral (5<sup>12</sup>) and six tetrakaidecahedral cages (5<sup>12</sup>6<sup>2</sup>).<sup>4</sup> If all of the cages are singly occupied, the hydrate composition is CO<sub>2</sub>·5.75H<sub>2</sub>O. A number of spectroscopic and diffraction studies have addressed the composition of the hydrate and it is agreed that CO<sub>2</sub> molecules occupy almost all of the large cages in structure I (sI) as well as a fraction of the small cages, thus giving a hydration number between 5.75 and 7.66.<sup>5–8</sup> Spectroscopic measurements useful for distinguishing cage populations should preferably show resolved signatures for guests in the large (5<sup>12</sup>6<sup>2</sup>) and small cages (5<sup>12</sup>) of the hydrate lattice. Unfortunately, Raman spectroscopic measurements are not able to distinguish the large and small cage populations in CO<sub>2</sub> hydrate,<sup>9,10</sup> although recent single-crystal measurements with polarized radiation have shown some promise.<sup>11</sup> In <sup>13</sup>C NMR spectra the spectral pattern for pure CO<sub>2</sub> hydrate in sI has overlapping signals from the large and small cages, with each site giving a chemical shift anisotropy powder pattern that is partially averaged by the dynamics of the guest molecules, which are in turn influenced by the cage symmetry.<sup>6</sup> Cage populations can be distinguished, but it is not a trivial matter.

Infrared spectroscopy (IR) detects the vibrations characteristic of specific chemical bonds or functional groups in a molecule. When infrared light interacts with matter, molecular vibrations that give changes in the molecular dipole moment tend to absorb infrared radiation in a specific frequency range depending on specific bond lengths and angles and can be more or less

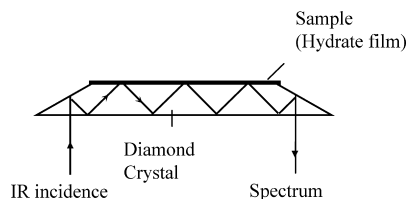
independent of the structure of the rest of the molecule. Bertie and Devlin<sup>12</sup> prepared ethylene oxide hydrate using a cryogenic thin-film vapor-deposition technique and established this approach as a viable option for the study of clathrate hydrates by obtaining transmission FTIR spectra. Later Fleyfel and Devlin<sup>7</sup> used the same method to prepare CO<sub>2</sub> hydrate and identified two separate peaks for CO<sub>2</sub> in large and small cages in sI and structure II (sII) hydrates. They concluded that infrared patterns for guest molecules are usually significantly different from those observed for the same molecule in other phases. Besides this, it was also suggested that lower temperatures often cause a pronounced shifting, narrowing, and peak intensity enhancement by limiting intracage rotational motion. However, they reported that it was difficult to grow thin films of the simple clathrate hydrates of small *nondipolar* polyatomic molecules such as carbon dioxide, and it was only possible to form mixed hydrates having a small amount of a polar help gas such as ethylene oxide.

Because of its ability to probe chemical bonds, infrared spectroscopy is a technique of choice for analyzing surface complexes. However, water strongly absorbs IR, and methods based on internal reflection spectroscopy have been developed to analyze wet samples. Attenuated total reflection infrared (ATR-IR) spectroscopy is used for analysis of the surface of materials.<sup>13</sup> For either the bulk material or a film, special sample preparation is not required for ATR analysis. FTIR analysis on SO<sub>2</sub> clathrate made from aqueous supercooled solutions in an ATR cell has been reported previously.<sup>14</sup> In ATR-IR spectroscopy, the infrared radiation is passed through an infrared-transparent crystal with a high refractive index, allowing the radiation to reflect within the ATR element several times (Figure 1). Either the surface to be sampled is pressed into intimate optical contact with the top surface of the crystal or, if possible, a thin film of sample is formed on the crystal for in situ analysis.<sup>15</sup> The IR radiation from the spectrometer enters the crystal at an angle chosen such that it will be totally reflected

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**Figure 1.** Schematic of ATR-IR experiment.

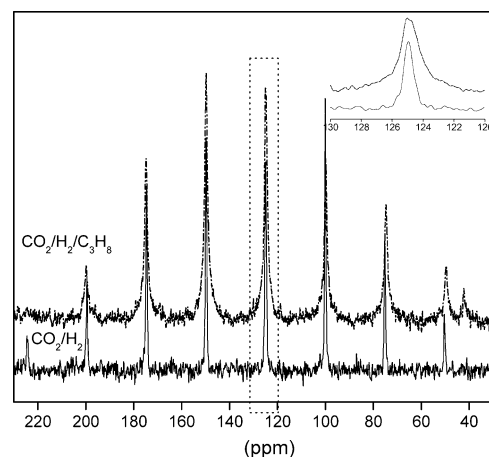
at the sample-crystal interface. There exists an evanescent wave, which means that even though the light is completely reflected, an oscillating electric field penetrates approximately one wavelength into the sample. Species with resonant transitions can absorb energy from this field. After a sufficient number of passes, the beam is directed out of the crystal and back into the normal beam path of the spectrometer.

In this paper, we use ATR FTIR spectroscopy to analyze a thin film of hydrate and show that this method, which is simple to use and obviates the need for helper molecules, corroborates results from the transmission approach used earlier by Fleyfel and Devlin.<sup>7</sup> In addition, the cage occupancies of CO<sub>2</sub>, CO<sub>2</sub>/H<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> hydrates are determined on the basis of peak area ratios of the CO<sub>2</sub> asymmetric stretch vibrations in the small and large cages obtained from the FTIR spectra and the hydrate phase composition obtained from gas chromatography.

### Materials and Experimental Setup

All of the gases used for the experiments were supplied by Praxair Canada Inc., pure CO<sub>2</sub>, pure H<sub>2</sub> and C<sub>3</sub>H<sub>8</sub> (99.5% purity) were used to prepare the gas mixture. Apart from pure CO<sub>2</sub> hydrate, an 80/20 (mol %) CO<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> mixture, a 40/60 (mol %) CO<sub>2</sub>/H<sub>2</sub> mixture, and a 38.2/59.2/2.6 (mol %) CO<sub>2</sub>/H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> mixture were used for the hydrate formation. The supercritical fluid analyzer version of a Specac Golden Gate Diamond ATR was slightly modified to synthesize and analyze the hydrates sample in situ. The stainless steel sample chamber of this ATR cell is capable of withstanding pressures up to 40 MPa, and when coupled with a temperature controller, it can be operated over a range of temperatures. The system as purchased was designed to work from ambient to temperatures as high as 300 °C. This setup was modified to run at subzero temperatures by making a provision to cool the cell by circulating nitrogen gas chilled by passing it through liquid nitrogen. The temperature controller maintained the desired operating temperature by heating the diamond top plate.

The stainless steel sample cell has a volume of 28 μL; even less than 28 μL of water is sufficient to form a thin layer of a hydrate film on the diamond surface. Hydrate was allowed to form by pressurizing the cell with the appropriate gas for several hours at -20 °C (in situ). This hydrate was then decomposed by raising the temperature of the cell to room temperature and allowing the hydrate to form again by lowering the temperature slowly (0.4 °C/min) and waiting for 2 h at -20 °C. After 2 h, the temperature is further reduced to -50 °C, and the FTIR spectrum is obtained in the region of the CO<sub>2</sub> asymmetric stretch vibrations in the hydrate phase. Similarly, spectra for CO<sub>2</sub> in the gas phase and CO<sub>2</sub> dissolved in water were obtained at suitable temperatures and pressures. A Digilab Excalibur Series FTIR working at a nominal resolution of 1 cm<sup>-1</sup> was used for this study, 50 scans were required to obtain good signal-to-noise ratios. A volume of 2 mL of water with CO<sub>2</sub>/H<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> gas mixtures was used to synthesize gas hydrate separately under similar conditions to the ATR experiment, in



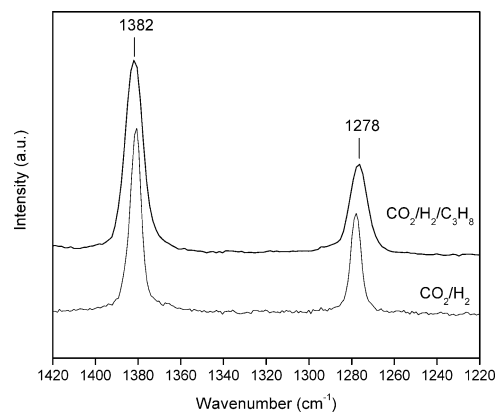
**Figure 2.** <sup>13</sup>C NMR spectra for CO<sub>2</sub>/H<sub>2</sub> (sI) and CO<sub>2</sub>/H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> (sII) hydrate obtained at atmospheric pressure and 173 K, spinning speed of 2500 Hz. The inset shows the close-up view of the peak at 125 ppm.

a 10 mL reactor and the hydrate phase composition was analyzed by gas chromatography, using an SRI 8610 C gas chromatograph (GC).

### Results and Discussion

The determination of the cage occupancies for the mixed hydrates of CO<sub>2</sub>/H<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> represents a considerable challenge.<sup>16</sup> For determining CO<sub>2</sub> cage occupancies in the hydrate cage, <sup>13</sup>C NMR is not completely straightforward as one must use the anisotropic chemical shift patterns that give overlapping contributions for CO<sub>2</sub> in small and large cages.<sup>5</sup> Figure 2 shows <sup>13</sup>C MAS NMR spectra of CO<sub>2</sub> in the hydrate phase for CO<sub>2</sub>/H<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> hydrate. Only one signal (isotropic shift ~125 ppm) can be resolved in the spectrum for both CO<sub>2</sub>/H<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> hydrates. The observed spinning sideband pattern is characteristic of chemical shift anisotropy (CSA), as one may expect for pure CO<sub>2</sub> hydrate in sI,<sup>5</sup> where the spectrum reflects partial averaging of the CSA tensor for CO<sub>2</sub> due to dynamic processes in the anisotropic environment of the sI large cage in CO<sub>2</sub>/H<sub>2</sub> hydrate, and from large as well as small cages in CO<sub>2</sub>/H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> (sII) hydrate. It is important to note that the CO<sub>2</sub> resonances in sI and sII hydrates are at the same isotropic chemical shift (within experimental resolution). However, the peak width for CO<sub>2</sub> in sII hydrate is greater than that of CO<sub>2</sub> in sI hydrate (insert in Figure 2). Depending upon the CO<sub>2</sub> and C<sub>3</sub>H<sub>8</sub> concentration in the hydrate phase the peak width (full width at half height) varies. As reported earlier<sup>16</sup> for CO<sub>2</sub>/H<sub>2</sub> hydrate, CO<sub>2</sub> only occupies the large cages of the resultant structure I hydrate and the small cages either are occupied by H<sub>2</sub> or remain nearly empty with a very small amount of CO<sub>2</sub> (<2%) in the small cages. However, for CO<sub>2</sub>/H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> hydrate, CO<sub>2</sub> occupies the large cages as well as a significant portion of the small cages and it is possible that the presence of CO<sub>2</sub> in small as well as large cages in sII hydrate results in two resonances which, however, could not be resolved. A similar situation was observed for structure H hydrate of methane.<sup>17</sup>

Raman spectra for CO<sub>2</sub>/H<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> hydrate were obtained to determine the change in the vibrational frequency of the molecules when incorporated into the hydrate lattice.<sup>16</sup> Figure 3 shows the two peaks that correspond to the Fermi diad of CO<sub>2</sub> in the hydrate cages, one at 1278 cm<sup>-1</sup> and the other 1382 cm<sup>-1</sup>. We do not observe a splitting of the CO<sub>2</sub> bands for

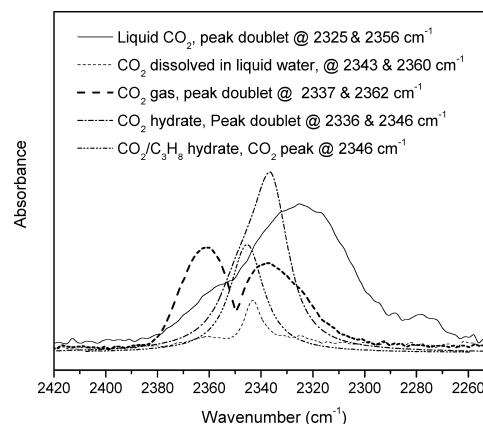


**Figure 3.** Raman Spectra showing Fermi diad of CO<sub>2</sub> in the hydrate phase for CO<sub>2</sub>/H<sub>2</sub> (sI) and CO<sub>2</sub>/H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> (sII) hydrate.

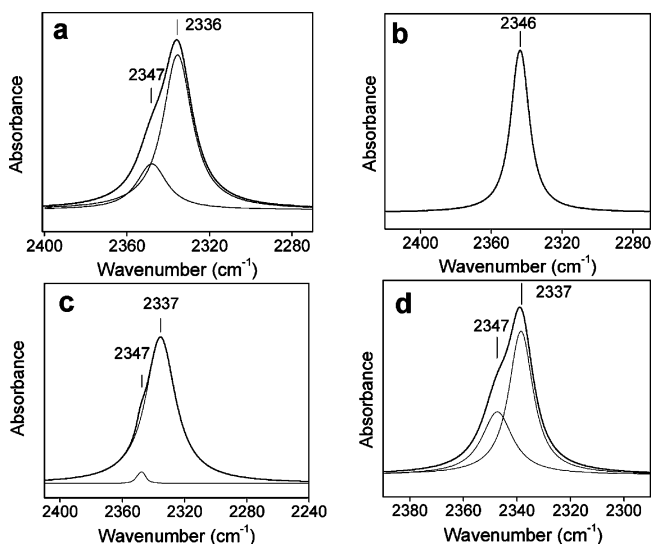
CO<sub>2</sub> in small and large cages. Also the peak positions for CO<sub>2</sub> in sI and in sII hydrate are almost the same, within the resolution of our Raman setup ( $\pm 1$  cm<sup>-1</sup>). However, again we see that the half-width of the CO<sub>2</sub> peak ( $\sim 9.0$  cm<sup>-1</sup>) in the hydrate phase for sII hydrate is larger than that of CO<sub>2</sub> ( $\sim 5.5$  cm<sup>-1</sup>) in the sI hydrate. As reported earlier<sup>16</sup> for the sI hydrate of CO<sub>2</sub>/H<sub>2</sub>, CO<sub>2</sub> occupies all of the large cages and a very small number of CO<sub>2</sub> molecules ( $< 2\%$ ) actually reside in the small cavities. However, in the sII hydrate formed by the CO<sub>2</sub>/H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> mixture, CO<sub>2</sub> occupies the large as well as a significant portion of the small cages. It is possible that CO<sub>2</sub> generates two peaks, one for small cages and one for large cages; however, the peak positions are too close to each other and hence result in a broader single peak.<sup>17,18</sup> This result is similar to what we observed for <sup>13</sup>C NMR; i.e., the CO<sub>2</sub> peak in sII is broader compared to that in the sI hydrate. It is also possible that the influence of local environments (e.g., the presence of C<sub>3</sub>H<sub>8</sub>) for CO<sub>2</sub> in sII results in a broader peak. It is clear from Figures 2 and 3 that, if CO<sub>2</sub> occupies a significant portion of the small and large cages in the hydrate phase, it results in a broad signal in the Raman spectrum, as well as in the <sup>13</sup>C NMR spectra, as compared to a hydrate where CO<sub>2</sub> occupies only the large cages. Moreover, the difference in peak position is not enough for a reliable deconvolution of the CO<sub>2</sub> peak in such a hydrate and hence quantitative determination of CO<sub>2</sub> hydrate is not straightforward.

To evaluate the feasibility of the ATR-FTIR technique, and the sensitivity of the CO<sub>2</sub> spectrum to the environment, the infrared spectrum of CO<sub>2</sub> in the antisymmetric stretching region was recorded for CO<sub>2</sub> in different phases. The results shown in Figure 4 demonstrate that the vibrational frequency for CO<sub>2</sub> in different phases varies considerably, as does the bandwidth. Solid CO<sub>2</sub> was not observed, as the temperature of analysis did not go below  $-50$  °C. Since the spectra for CO<sub>2</sub> in the different phases give unique peak positions, infrared spectra recorded by the ATR technique can be used to good advantage for CO<sub>2</sub> hydrate characterization work.

Figure 5a shows the FTIR spectra of CO<sub>2</sub> hydrate synthesized in the ATR cell at 3.2 MPa. The spectra shown were obtained at  $-50$  °C. Vibrational frequencies for CO<sub>2</sub> in small and large cages are better resolved at lower temperatures and, in this case, a temperature significantly lower than the hydrate formation temperature was required to obtain well-resolved peaks. A higher operating temperature (compared to analysis temperature of  $-50$  °C) for hydrate formation was chosen for a better growth rate of the CO<sub>2</sub> hydrate.<sup>19</sup> As shown in Figure 5a, the infrared-active asymmetric stretch mode of CO<sub>2</sub> in pure CO<sub>2</sub> hydrate shows structure and can be deconvoluted into two peaks, one smaller



**Figure 4.** ATR-IR spectra of CO<sub>2</sub> showing unique peaks under different conditions.



**Figure 5.** ATR-IR spectra showing CO<sub>2</sub> in the small and large cages of hydrate phase for (a) simple CO<sub>2</sub> hydrate, (b) CO<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> (sII) hydrate, (c) CO<sub>2</sub>/H<sub>2</sub> (sI) hydrate, and (d) CO<sub>2</sub>/H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> (sII) hydrate. (a) and (b) also appears in Figure 4.

peak at 2347 cm<sup>-1</sup> and a more intense peak at 2336 cm<sup>-1</sup>. On the basis of the work of Fleyfel and Devlin, we can assign the smaller peak at 2347 cm<sup>-1</sup> to CO<sub>2</sub> in the small cages (5<sup>12</sup> cages) and the larger peak at 2336 cm<sup>-1</sup> can be assigned to CO<sub>2</sub> in the large (5<sup>12</sup>6<sup>2</sup>) cages of the resultant structure I hydrate.

Propane (C<sub>3</sub>H<sub>8</sub>) forms a stable simple structure II hydrate with all of the large cages occupied by C<sub>3</sub>H<sub>8</sub>, and all of the small cages empty.<sup>20</sup> If a suitable CO<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> gas mixture (where C<sub>3</sub>H<sub>8</sub> concentration is substantially above stoichiometric requirements for completely filled large cages) is allowed to form hydrate such that all of the large cages are occupied by C<sub>3</sub>H<sub>8</sub>, CO<sub>2</sub> can only occupy the small cages of the resultant structure II hydrate. This would allow us to check the peak position for CO<sub>2</sub> in small cages of structure II hydrate in the absence of any contribution from CO<sub>2</sub> in the large cages and would help to provide a cross reference to verify the peak positions for pure CO<sub>2</sub> hydrate. A gas mixture of 20% C<sub>3</sub>H<sub>8</sub> with the remainder being CO<sub>2</sub> was used to form hydrate at 2 MPa (by following the same procedure as mentioned in the experimental section) such that all of the large 5<sup>12</sup>6<sup>4</sup> cages were occupied by C<sub>3</sub>H<sub>8</sub> molecules (this was verified by figure 5b, where signals from CO<sub>2</sub> in the large cages are absent) and the smaller 5<sup>12</sup> cages of the resultant structure II hydrate by CO<sub>2</sub>. As seen in Figure 5b, the FT-IR spectra of the hydrate product results in a single peak at 2346 cm<sup>-1</sup>, which

**TABLE 1: Estimate of Cage Occupancy Values Obtained by Combination of Results from Infrared Spectroscopy and Gas Chromatography<sup>a</sup>**

description	hydrate structure	H <sub>2</sub> $\theta_s$	CO <sub>2</sub>		C <sub>3</sub> H <sub>8</sub> $\theta_L$	hydration no. $N$
			$\theta_s$	$\theta_L$		
CO <sub>2</sub>	sI		0.81	1.0		6.04
CO <sub>2</sub> /H <sub>2</sub>	sI	0.23 (0.25)	0.06 (0.0)	1.0 (1.0)		6.92 (7.1)
CO <sub>2</sub> /H <sub>2</sub> /C <sub>3</sub> H <sub>8</sub>	sII	0.029 (0.006)	0.20 (0.34)	0.79 (0.57)	0.21 (0.43)	11.7 (10.1)

<sup>a</sup> Cage occupancies obtained from NMR<sup>16</sup> are shown in parentheses.

is the contribution of CO<sub>2</sub> present in the small cages of structure II CO<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> hydrate. This also supports the assignment of the infrared peak at about 2347 cm<sup>-1</sup> ( $\pm 1$ ) at -50 °C in Figure 5a to CO<sub>2</sub> occupying the small cages of sI.

FTIR spectra of CO<sub>2</sub>/H<sub>2</sub> (40/60 mol %) hydrate synthesized at 8 MPa were obtained at -50 °C. The spectrum between 2250 and 2400 cm<sup>-1</sup> is shown in Figure 5c. The peak with a shoulder shows the presence of CO<sub>2</sub> in the hydrate cages. The spectral traces are deconvolved, which results in two peaks, one larger peak at 2337 cm<sup>-1</sup> indicating the presence of CO<sub>2</sub> in the large cages and a minor peak at 2347 cm<sup>-1</sup> showing the presence of CO<sub>2</sub> in the small cages. Figure 5d shows the spectra recorded for CO<sub>2</sub>/H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> (38.2/59.2/2.6 mol %) hydrate synthesized at 3.8 MPa. The spectra show two overlapping peaks, with an appearance similar to that for pure CO<sub>2</sub> hydrate. The spectrum in Figure 5d can be deconvolved into two peaks: one at 2347 cm<sup>-1</sup> due to CO<sub>2</sub> in the small 5<sup>12</sup> cages and a more intense peak at 2337 cm<sup>-1</sup> resulting from the presence of CO<sub>2</sub> in the large 5<sup>12</sup>6<sup>4</sup> cages.

Looking at the integrated peak intensities for CO<sub>2</sub> in the binary and ternary hydrates, parts c and d of Figure 5, respectively, the peak at 2347 cm<sup>-1</sup> is much more prominent in Figure 5d than the peak at 2347 cm<sup>-1</sup> in Figure 5c. It has been shown that the ternary hydrate is a structure II hydrate and has a 2:1 ratio of small to large cages.<sup>16</sup> Thus, there are more CO<sub>2</sub> molecules present in small cages as compared to the binary structure I hydrate, which has a 1:3 ratio of small to large cages. With just 2.6% C<sub>3</sub>H<sub>8</sub> in the ternary gas mixture, which is not sufficient for 100% occupancy of all the large cages, the large cages in the resulting structure II hydrate are shared by C<sub>3</sub>H<sub>8</sub> and CO<sub>2</sub>, and a significant amount of CO<sub>2</sub> occupies the smaller 5<sup>12</sup> cages, along with H<sub>2</sub>. In the binary hydrate, CO<sub>2</sub> occupies all of the large cages and a very small amount of CO<sub>2</sub> actually goes into the small cages, leaving almost all of the small cages for H<sub>2</sub>.

### Quantitative Determination of the Cage Occupancy

It is generally accepted that Raman spectroscopy cannot be used to determine the relative concentration of different guests in the hydrates quantitatively without proper cross-calibration with another quantitative technique.<sup>21</sup> However, we have shown previously that with weakly polar guest molecules in hydrate cages a quantitative estimate of cage occupancies can be made with reasonable accuracy.<sup>22</sup> In the previous work Raman spectra were used along with the knowledge of the resultant structure from independent PXRD patterns and the hydrate phase composition from gas chromatography measurements. With the knowledge of the CO<sub>2</sub> ratio in the small and large cages (from FTIR spectra) along with the knowledge of hydrate structure (from PXRD pattern) and hydrate composition (from gas chromatography), we will calculate the cage occupancies and compare these with cage occupancies obtained from NMR spectroscopy.<sup>16</sup>

The powder XRD pattern obtained from the synthetic hydrate reveals that pure CO<sub>2</sub> hydrate synthesized at 3 MPa and binary CO<sub>2</sub>/H<sub>2</sub> hydrate synthesized at 8 MPa<sup>16</sup> are structure I hydrates, whereas ternary CO<sub>2</sub>/H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> hydrate synthesized at 3.8 MPa<sup>16</sup> forms structure II. Hydrates were synthesized in a 10 mL stainless steel reactor with 2 mL of water under similar conditions as for the in situ ATR-IR setup for calculating the hydrate phase composition. All of the hydrates synthesized were decomposed and the evolved gas was analyzed by gas chromatography. The binary CO<sub>2</sub>/H<sub>2</sub> hydrate gave 93.0  $\pm$  0.2% CO<sub>2</sub> and 7.0  $\pm$  0.2% H<sub>2</sub>, whereas the ternary CO<sub>2</sub>/H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> hydrate gave 76.2  $\pm$  0.2% CO<sub>2</sub>, 4.0  $\pm$  0.2% H<sub>2</sub>, 19.8  $\pm$  0.2% C<sub>3</sub>H<sub>8</sub>. Several measurements of CO<sub>2</sub> hydrate were performed by FTIR to obtain good spectra with good signal-to-noise ratio for obtaining occupancies and hydration numbers. All of the spectra collected were identical to that shown in Figure 5a. As CO<sub>2</sub> partitions between the small and large cavities of structure I, we were able to deconvolve the band shown in Figure 5a into two separate peaks. We take the area of the bands to represent the number of CO<sub>2</sub> molecules in each cavity. The ratio of the integrated intensities of the bands is 3.7, which we take to be the ratio of CO<sub>2</sub> molecules in large to small cages. After accounting for the fact that there are 3 times as many large as small cavities in sI, we obtained the cage occupancies.

To determine the absolute occupancy of CO<sub>2</sub> in the small and large cavities, we used the statistical thermodynamic expression eq 1, for the chemical potential of water molecules in sI hydrate. The value for  $\Delta\mu_w^0$  used in the calculation is 1297 J/mol.<sup>23</sup>  $R$  is the universal gas constant, and  $T$  is the temperature in Kelvin.  $\theta_s$  and  $\theta_l$  are the fractional occupancy of small and large cages, respectively.

$$-\Delta\mu_w^0 = \frac{R \cdot T}{46} [6 \ln(1 - \theta_{l(\text{CO}_2)}) + 2 \ln(1 - \theta_{s(\text{CO}_2)})] \quad (1)$$

Equation 1 implies that unoccupied large cages represent a large energy penalty and effectively constrain  $\theta_l$  to be almost unity ( $\theta_l = 1$ ). On the basis of this and the information in the FTIR spectra ( $\theta_l/\theta_s = 3.7$ ), the occupancy of the small cavities by CO<sub>2</sub> ( $\theta_s$ ) was determined. The results are shown in Table 1. The column labeled  $n$  in Table 1 is the hydration number, calculated from eq 2, where the sum is carried over all cages and all guests. Equation 2 also demonstrates the hydration number calculation for CO<sub>2</sub> hydrate.  $\theta_{L-C}$  and  $\theta_{S-C}$  are the occupancies of CO<sub>2</sub> in the large and small cages of resultant sI hydrate, which are multiplied by numbers of each type of cages in a unit cell;  $n_{\text{H}_2\text{O}}$  is the number of water molecule per unit cell. The value 6.04 for the hydration number obtained in the current study is in acceptable agreement with those obtained for CO<sub>2</sub> hydrate from single crystal X-ray structures, which range from 6.2 to 6.7 depending on hydrate synthesis pressure and temperature.<sup>8</sup>

$$n = \frac{n_{\text{H}_2\text{O}}}{\sum \theta_{\text{cage, guest}}} = \frac{n_{\text{H}_2\text{O}}}{2\theta_{\text{S-C}} + 6\theta_{\text{L-C}}} = \frac{46}{2 \times 0.81 + 6 \times 1} = 6.04 \quad (2)$$

Figure 5c shows the FTIR spectra of binary CO<sub>2</sub>/H<sub>2</sub> hydrate. To obtain the hydrate guest composition, integration of the areas of the CO<sub>2</sub> bands was done and the occupancies were calculated. From the fitted curves of Figure 5c, the ratio of the integrated intensities of CO<sub>2</sub> in large cages to CO<sub>2</sub> in the small cages is 49.8 (eq 3). Equation 4 expresses the H<sub>2</sub>/CO<sub>2</sub> ratio obtained from gas chromatography, along with the assumptions that the large cages must be 100% occupied by CO<sub>2</sub> for stability of the hydrate, and that at these modest pressures multiple cage occupancy of H<sub>2</sub> can be neglected.

$$\frac{3\theta_{\text{L-C}}}{\theta_{\text{S-C}}} = 49.8 \quad (3)$$

$$\frac{\theta_{\text{S-H}}}{3\theta_{\text{L-C}} + \theta_{\text{S-C}} + \theta_{\text{S-H}}} = 0.07 \quad (4)$$

$\theta_{\text{L-C}}$  and  $\theta_{\text{S-C}}$  are the occupancies of CO<sub>2</sub> in the large and small cages of resultant sI hydrate, and  $\theta_{\text{S-H}}$  is the occupancy of the small cages by hydrogen. H<sub>2</sub> is not expected to occupy the large cages of this binary hydrate especially considering the fact that this hydrate was synthesized at 8 MPa. Also, our previous work based on proton NMR suggests that this assumption holds.<sup>16</sup> Equation 3 gives 0.06 for  $\theta_{\text{S-C}}$ . Equation 4 then implies 23% of the small cages are occupied by hydrogen. The cage occupancy values along with hydration number are also reported in Table 1.

Figure 5d shows the FTIR spectra of the ternary CO<sub>2</sub>/H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> hydrate, and again the deconvolved areas of the peaks are used to determine that the occupancy ratio of CO<sub>2</sub> in large to small cages is 1.8. In structure II hydrate there are twice as many small cages as large ones; hence the intensity ratio takes the form given in eq 5. It can safely be assumed that C<sub>3</sub>H<sub>8</sub> only occupies the large cages and H<sub>2</sub> only the small cages. Also, for a stable hydrate, the combined occupancy of C<sub>3</sub>H<sub>8</sub> and CO<sub>2</sub> in the large cages should be close to unity. These assumptions and the gas chromatography results are expressed in eqs 6 and 7a–c. Solving eqs 5, 6, and 7a–c gives the cage occupancy values and hydration number shown in Table 1. Note that eq 2 for hydration number calculation must be modified (to eq 8), as there are 16 small cages, 8 large cages, and 136 water molecules in the unit cell of sII hydrate.

$$\frac{\theta_{\text{L-C}}}{2\theta_{\text{S-C}}} = 1.8 \quad (5)$$

$$\theta_{\text{L-C}} + \theta_{\text{L-P}} = 1 \quad (6)$$

$$\frac{\theta_{\text{L-P}}}{\theta_{\text{L-P}} + \theta_{\text{L-C}} + 2\theta_{\text{S-C}} + 2\theta_{\text{S-H}}} = 0.198 \quad (7a)$$

$$\frac{\theta_{\text{L-C}} + 2\theta_{\text{S-C}}}{\theta_{\text{L-P}} + \theta_{\text{L-C}} + 2\theta_{\text{S-C}} + 2\theta_{\text{S-H}}} = 0.762 \quad (7b)$$

$$\frac{2\theta_{\text{S-H}}}{\theta_{\text{L-P}} + \theta_{\text{L-C}} + 2\theta_{\text{S-C}} + 2\theta_{\text{S-H}}} = 0.04 \quad (7c)$$

$$n = \frac{n_{\text{H}_2\text{O}}}{\sum \theta_{\text{cage, guest}}} = \frac{136}{16\theta_{\text{S-C}} + 8\theta_{\text{L-C}} + 16\theta_{\text{S-H}} + 8\theta_{\text{L-P}}} \quad (8)$$

The cage occupancy values obtained here are in good agreement with the quantitative results, which we obtained by <sup>13</sup>C NMR studies performed on binary CO<sub>2</sub>/H<sub>2</sub> hydrate. However, the cage occupancy values obtained for ternary CO<sub>2</sub>/H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> hydrate analyzed by FTIR shows significant variation from the <sup>13</sup>C NMR results.<sup>16</sup> It must be noted that in this study hydrates were synthesized in 2 h, instead of over a 2 day experiment, as in the case of Kumar et al.<sup>16</sup> This change in cage occupancy values can be attributed to dependency of cage dynamics on kinetics of hydrate formation. Also, leaking away of H<sub>2</sub> molecules during the NMR measurement was observed. Finally, the technique presented in this work can be used to evaluate occupancies in CO<sub>2</sub> containing systems that demonstrate structure changes as a function of pressure.<sup>24–26</sup>

## Conclusions

This work demonstrates that ATR-Infrared spectroscopy is a straightforward and valuable analytical tool for investigating the properties of the CO<sub>2</sub> clathrate hydrate phases under in situ temperature and pressure conditions. Unlike the Raman-active vibrational modes, the infrared active stretching mode of CO<sub>2</sub> in the hydrate cages provides a signature for CO<sub>2</sub> in small and large cages. Although the data must be supplemented with information from other techniques, ATR-IR is useful for the qualitative and quantitative determination of occupancy ratios and hydration numbers for simple and mixed hydrates of CO<sub>2</sub>. For pure CO<sub>2</sub> hydrate, the large cages are almost fully occupied and the small cages were about 81% occupied. Similarly, it was observed that in the presence of excess C<sub>3</sub>H<sub>8</sub>, CO<sub>2</sub> only occupies the small cages of the resultant sII hydrate. The experimental values obtained for the hydrate cage occupancies are in good agreement with the values reported in the literature. Hydration numbers were indirectly determined from the occupancy of CO<sub>2</sub> in the small and large cavities of sI (CO<sub>2</sub>/H<sub>2</sub>) and sII (CO<sub>2</sub>/H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub>) hydrate. In addition, we have shown that ATR-IR spectroscopy combined with hydrate phase composition results obtained by gas chromatography can give information similar to that obtained from the more difficult NMR spectroscopic analysis, often considered the technique of choice in the quantitative analysis of hydrates.

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