CO_2 Storage in Novel CO_2-H_2O Phases at High Pressure

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An effective method for capturing and storing carbon dioxide in order to reduce atmospheric concentration is currently a research area of high interest. We investigated the potential of CO_2 storage in H_2O compounds by using optical Raman spectroscopy to analyze the high-pressure behavior of a CO_2-H_2O system *in-situ*. Between 26.9 and 1.0 GPa, we observed a new CO_2-H_2O compound whose vibrational spectra differed dramatically from pure CO_2 and H_2O. When pressure was decreased to <1 GPa, the CO_2 vibrons and OH stretch reverted to those expected for pure CO_2 and H_2O respectively, indicating a CO_2-H_2O mixture rather than a CO_2-H_2O molecular compound. Based on the difference in spectra seen upon pressure cycling, as well as the difference in spectra seen at multiple locations inside the sample, we concluded that multiple forms of the CO_2-H_2O compounds may exist. Our results indicate that the initial structure and composition may play a role in compound formation. These novel materials have potential implications for increasing our understanding of CO_2 interactions with potential host materials for improved CO_2 storage applications.

INTRODUCTION

The increasing amount of carbon dioxide in the atmosphere and its contribution to climate change is a serious global environmental concern. Significant efforts have been launched to develop an effective approach for capturing and storing carbon dioxide as a means of mitigating further damage to the environment.

A number of methods (e.g. oceanic, underground, and geologic storage) have been suggested for reducing the amount of carbon dioxide in the atmosphere, with the main limitations of the proposed storage methods being economic feasibility and temporal permanence. Oceanic storage has been proposed, either directly through the formation of carbonic acid, or indirectly through algae production. Underground storage involves pumping CO_2 into a desolate region, such as an empty oil field, and trapping the CO_2 inside. For geologic storage, the CO_2 is pumped into the ground, where it can react with silicates to form carbonate minerals [1].

We investigated the potential of CO_2 storage in H_2O compounds by studying the CO_2-H_2O system at high pressure. At low temperatures and/or high pressures, water can react with gas molecules to form crystalline inclusion compounds called clathrates. The water molecules form polyhedral cages that can accommodate differently sized guest molecules on the inside (Figure 1).

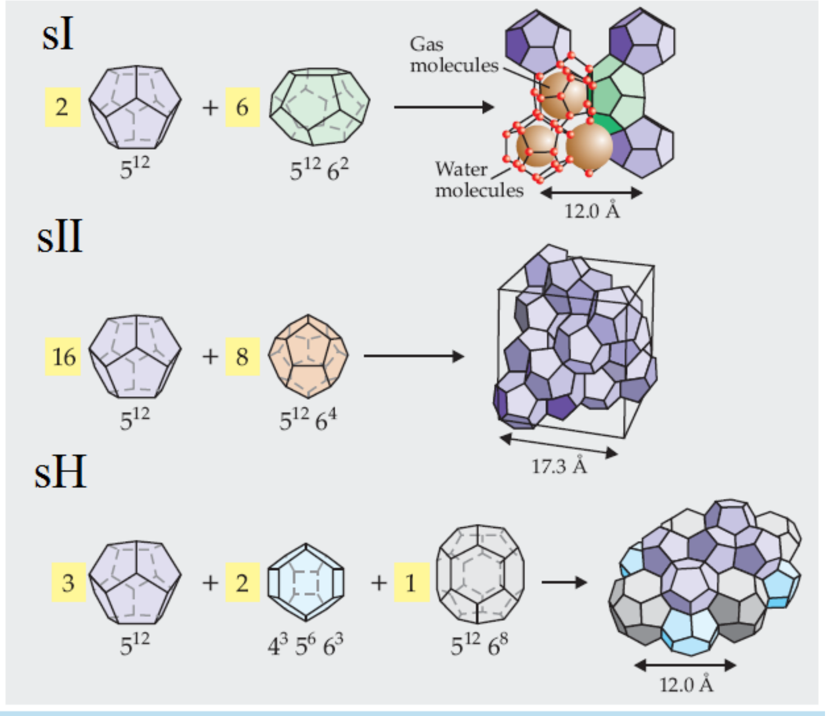

Figure 1: Diagram of the three most common clathrate structures. The notation 5^{12} indicates a water cavity comprising 12 pentagonal faces, $5^{12}6^2$ indicates a water cavity comprising 12 pentagonal and 2 hexagonal faces, etc. The numbers in yellow indicate the number of each type of cage that makes up a unit cell. (Mao et al., Physics Today, 2007)

Previous work has established that carbon dioxide can be contained in a clathrate structure [2, 3]. The phase of the carbon dioxide trapped inside each clathrate may affect the stability of the clathrate itself, due to the high levels of polymorphism exhibited by CO_2 at high pressures and temperatures [4, 5]. In addition, theoretical free energy calculations at 270K and 5 MPa indicate that sI CO_2 clathrate is more stable than sI CH_4 clathrate, suggesting that CO_2 sH may be stable since sH CH_4 has been previously synthesized [6]. According to Chazallon et al., CO_2 hydrate peaks are located at 1377 and 1274 cm^{-1}[7], while free CO_2 is expected at 1389 and 1286 cm^{-1} [8]. Another method for trapping carbon dioxide is the replacement of methane with carbon dioxide at 281K and 4 MPa [9]. All of these publications indicate that the carbon dioxide clathrate does exist at some pressure and condition.

Brewer et al. showed that at higher oceanic pressures (MPa), clathrates form in the ocean [10], while Holder et al. experimented with the oceanic clathrate up to 25 GPa [11]. These experiments were carried out in a water-excess environment. Since the phases formed in the H_2O-CO_2 system may be heavily dependent on the initial ratio of the compounds, we based our study on higher CO_2:H_2O ratios over a broader pressure range.

In this study, we examined the effects of pressure and CO_2:H_2O ratios on the behavior of CO_2-H_2O compounds using optical Raman spectroscopy to over 50 GPa. We also explored the compositional dependency of the formation of CO_2-H_2O compounds by looking at samples with excess CO_2. Although the efficiency of carbon dioxide storage in crystalline H_2O compounds is unknown, further research in this field could improve our understanding of the interactions between carbon dioxide and water under high pressures. This may provide guidance for future carbon dioxide storage methods.

METHODOLOGY

Experiment

The objective of this study was to explore the CO_2-H_2O system at high pressure using optical Raman spectroscopy. Raman spectroscopy is used as an *in-situ* probe to study the vibrational and rotational modes in our samples through a process that relies on the inelastic scattering of an incident laser beam. The frequency of the Raman shift, in wave numbers (cm^{-1}), was used to characterize bonding changes in the sample.

We examined the high-pressure optical Raman spectra of CO_2-H_2O compounds compressed in a symmetric diamond anvil cell (DAC) (Figure 2). In our first run, droplets of H_2O water were first loaded into a tungsten gasket, along with small ruby chips for pressure calibration [12]. The DAC was then inserted into a gas pressure vessel in which CO_2 was introduced and compressed to 200 MPa. After sealing the sample in the gasket, the DAC was removed from the gas vessel and further compressed to 54 GPa. In our second run, we used an identical procedure but with a different ratio of CO_2:H_2O.

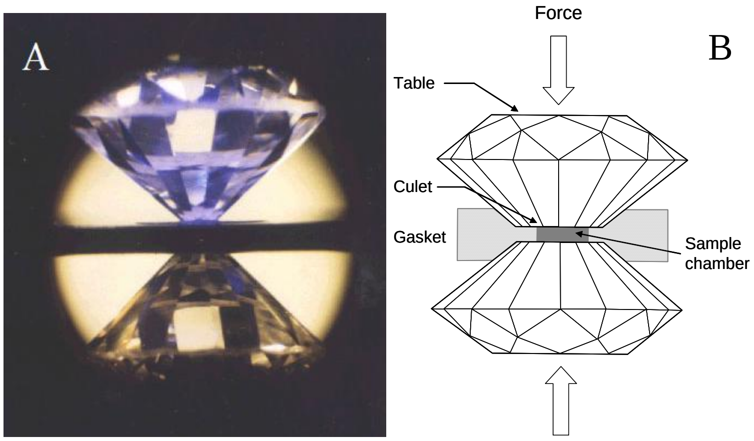

Figure 2: A. Photo of diamond anvil cell. B. Diamond anvil cell schematic. The sample was loaded into a small 150 μm diameter chamber drilled into a metallic tungsten gasket, which was then compressed between the culets of two opposing gem-quality diamond anvils. (Mao et al., Physics Today, 2007)

Sample 1 contained a mixture of CO_2 and H_2O and was studied from approximately 54 GPa to 1 GPa, while sample 2 contained much more CO_2 than H_2O and was studied between approximately 5 GPa and 35 GPa. The pressure in sample 1 was gradually lowered until 1 GPa (referred to as cycle 1), and then re-compressed to 10 GPa (referred to as cycle 2). Sample 2 consisted of only a decrease in pressure.

Measurement

In this experiment, we examined the vibrational peaks caused by the intramolecular vibrations of the C-O and O-H stretching bonds in CO_2-H_2O compounds. The presence of particular Raman peaks indicates the presence of a particular molecular species, while the position and intensity provide information about the behavior and the relative concentration, respectively.

The measurements were obtained using an open optical micro-Raman system with a 1500 grating and a 30 second exposure time. The shift of the ruby fluorescence lines was used to determine the pressure inside the cell [12].

Raman spectra were taken at various locations in order to test if any phase separations existed inside the sample. Vibrational, librational, and rotational modes in the sample were excited, using a blue 457.935 nm line from a solid state laser. Spectra without the sample were also taken for comparison in order to identify any background noise or interference.

Analysis

Computational software (Igor Pro) was used to fit the spectra with Gaussian peaks to determine the position, area, and width of the Raman peaks. The data were then graphed as a function of pressure, and spectra from the different locations were compared. The data were also compared to previous experiments in order to identify similarities and differences.

RESULTS

I. *Sample heterogeneity*

For a given pressure, we compared the spectra at the different locations. Two peaks observed in the 1200-1400 cm^{-1} range were identified as the $\nu+$ and $\nu-$ peaks of carbon dioxide. Between 54 and 4.6 GPa, the sample appeared homogenous. At 4.6 GPa, we observed a distinct second phase in the middle of the sample (Figure 3). The spectra collected from each phase were slightly different. When the pressure dropped below 1 GPa, the two-phase characteristic of the sample disappeared.

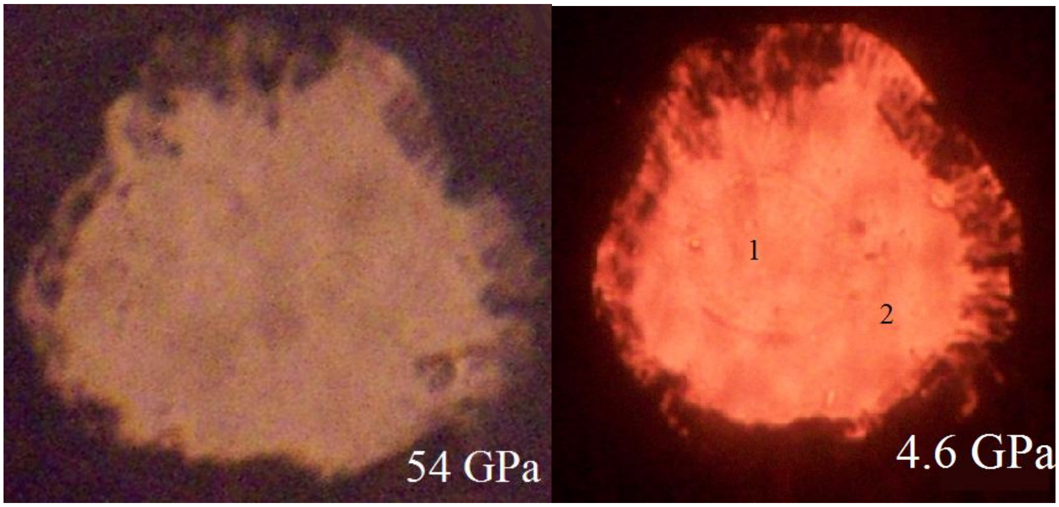

Figure 3: Photomicrograph of the CO_2-H_2O sample, under different lighting conditions. The sample at 54 GPa appeared homogeneous. Two phases in the sample were observed at 4.6 GPa (labeled 1 and 2). The sample chamber is 100 micrometers wide and 250 micrometers thick.

The spectra were graphed together for comparison, to determine if pressure affected intensity. Although intensity generally appeared to decrease as pressure decreased, there was a larger difference in the inner and outer phases seen in Figure 3 at 4.6 GPa. The intensity of the outer phase in the sample was consistently lower than that of the inner phase (Figure 4).

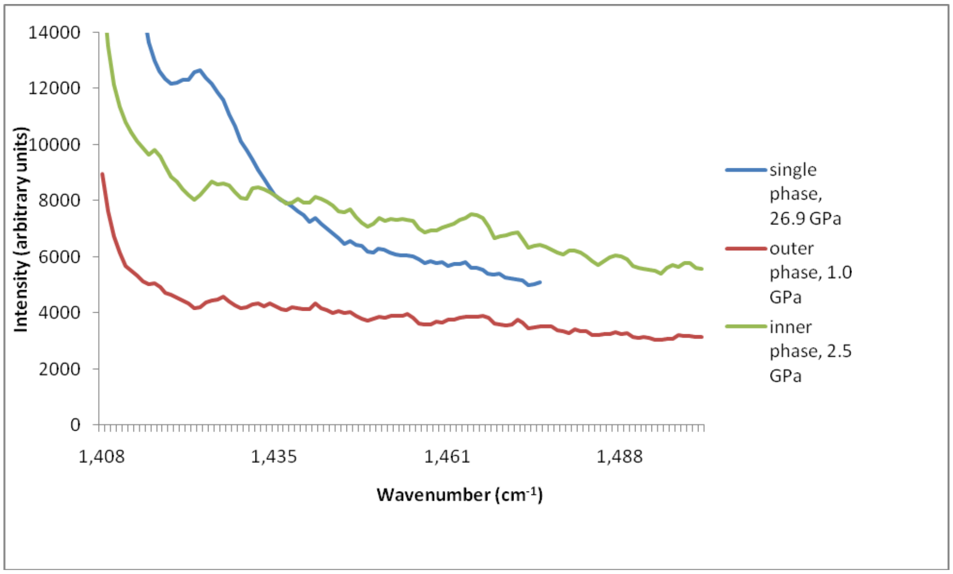

Figure 4: Raman spectra of the ν+ CO_2 peak seen in sample 1, cycle 1. The ν+ peak is very weak, but gradually shifts to higher frequencies with lower pressure. Arbitrary peaks were chosen to show the differences caused by pressure.

In the second sample, we observed crystallization of the structure. As the pressure changed, we noticed changes in the physical appearance of the sample, and we collected the Raman spectra in different areas in the sample (Figure 5). We compared the spectra obtained at each location and found that there were differences in the vibron peaks.

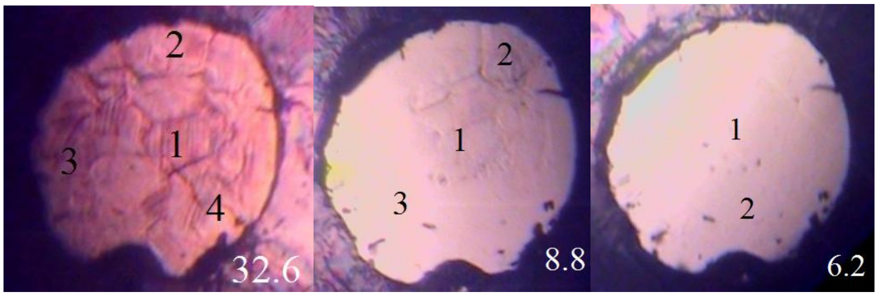

Figure 5: Location assignments for the sample from 35.6 to 11.6 GPa, from 11.6 to 8.8 GPa, and below 6.2 GPa, from left to right respectively. Raman spectra were measured at each of the numbered locations.

For a given pressure, we compared the spectra at the different locations. Two carbon dioxide peaks observed in the 1250-1400 cm^{-1} wavenumber range were identified as the same ν+ and ν- found in Olijnyk et al. [13]. The spectra obtained at each location were graphed together in order to compare the spectra (Figure 6).

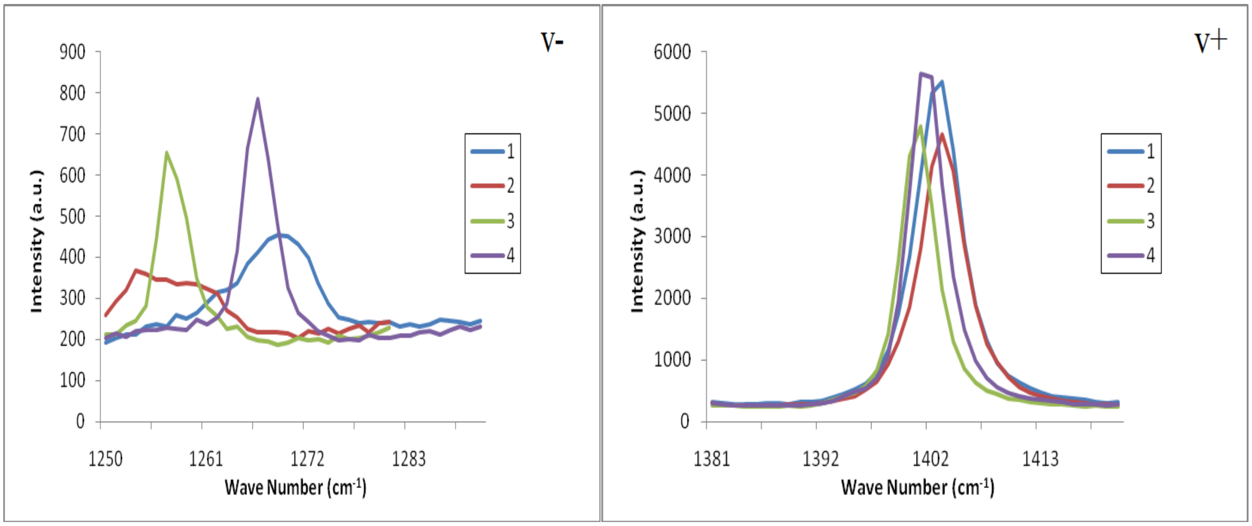

Figure 6: A comparison of the carbon dioxide ν- and ν+ spectra at 11.6 GPa. The four spectra correspond to the four areas observed at 11.6 GPa and above (Figure 5).

For the carbon dioxide vibron peaks, the maximum positional difference for the weaker ν- peak was 10 cm^{-1} while that of the more intense ν+ peak was 5 wavenumbers. The ν- peak varied drastically in both its shape and intensity. At locations 1 and 2, a broader and less intense peak was observed. Consequently, locations 3 and 4 yielded a stronger and more intense peak.

II. *Comparison with published data*

We first compared the ν+ vibron peaks for pure CO_2 with the data collected in our study (Figure 7). The cycle 2 Raman shifts from both samples increased linearly with pressure. A comparison to the results of Olijnyk et al. [13] shows that these shifts are similar to that of pure CO_2. On the other hand, the sample 1, cycle 1 data decreased with higher pressure.

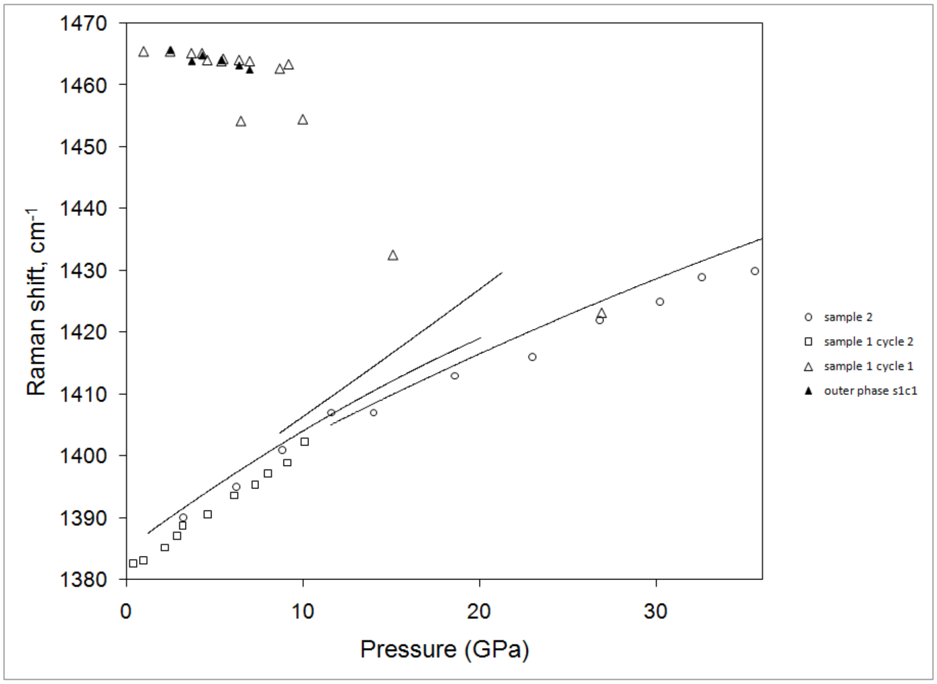

Figure 7: Raman shift of the CO_2 ν+ vibron as a function of pressure. The open triangles denote the pressure decrease in sample 1, the squares represent the pressure increase in sample 1, and the circles correspond to the data gathered in sample 2. The lines represent the shift of solid CO_2.

In sample 1, cycle 1, we noticed a visible difference in the sample at 4.6 GPa (Figure 3), but the maximum positional variation in spectra between the inner and outer areas was only about 5 wavenumbers. These data points are represented in Figure 7 as filled triangles. Although the deviation between these two areas differ by a small margin, it is important to note that they are not perfectly identical due to variation in intensity.

We also examined the OH peak in our study. The initial decrease of sample 1, cycle 1 does not match any previous data (Figure 8). However, during cycle 2 of sample 1, the OH peaks matched the data from Walrafen et al. for pure H_2O [14]. The OH stretch for sample 2 was not shown because the water peak was extremely weak and inconsistent, as the sample was initially loaded with very little water.

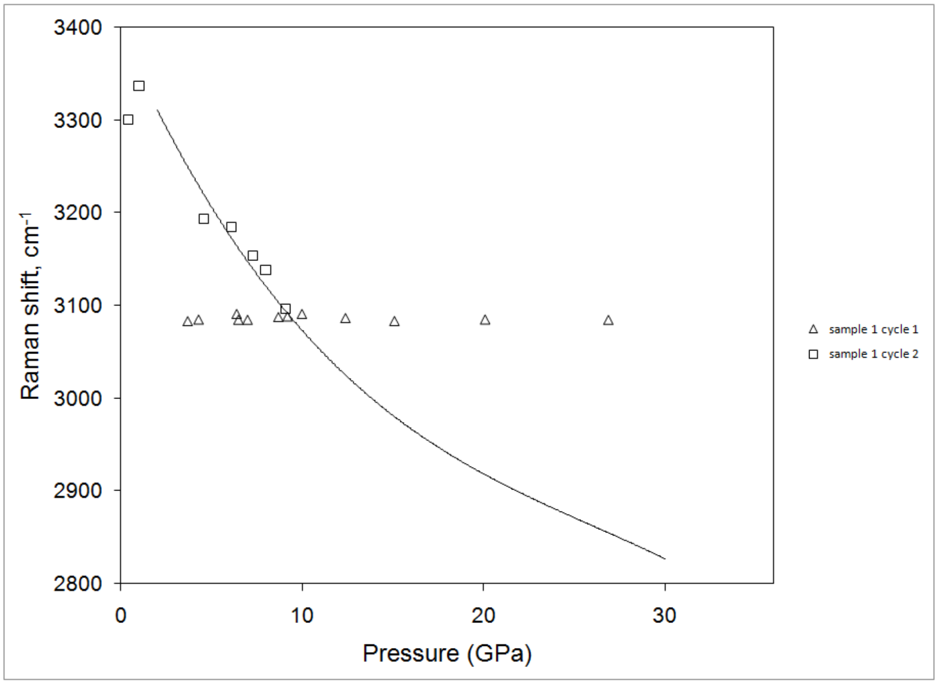

Figure 8: Raman shift of the OH stretch as a function of pressure. The points represent our study, while the line represents the experiments for pure water.

III. *Raman shift of carbon dioxide*

In sample 2, the spectra of the ν+ and ν- were monitored as a function of pressure, and these peaks were also grouped by location. Although the measurements were taken at different locations inside the sample, all of the points are plotted on the same graph to show similar trends with pressure (Figure 9).

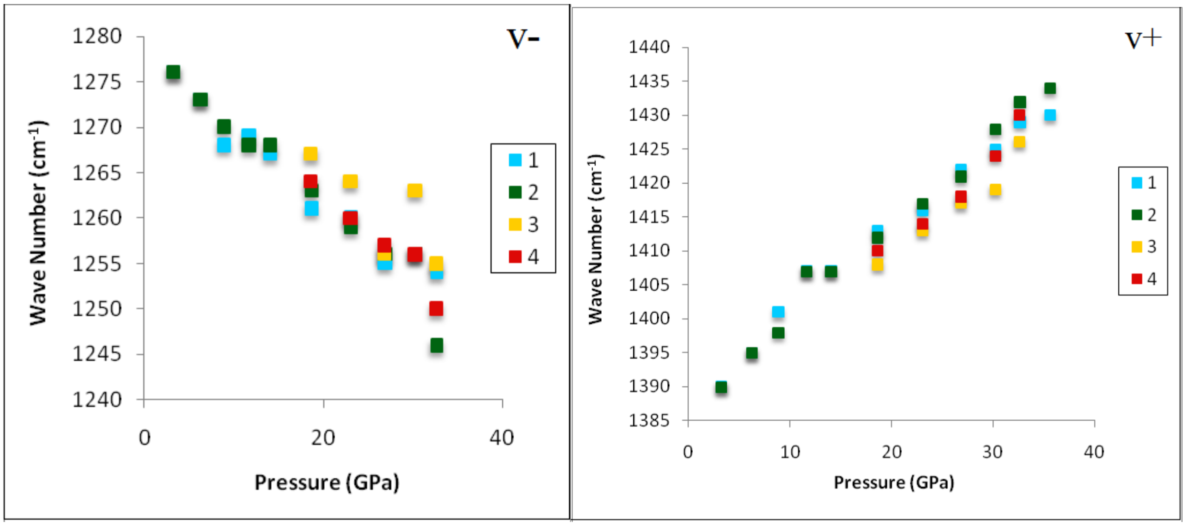

Figure 9: Carbon dioxide ν- and ν+ peaks, respectively, as functions of pressure. The number represents the location at which the measurements were taken (Figure 5).

While the ν+ peaks exhibited a linear shift to higher frequencies with increasing pressure, the ν- peak exhibited a softening behavior, shifting linearly to lower frequencies with higher pressures.

Once the water was loaded into the system, we expected the OH stretch to be found around the 2800-3300 cm^{-1} region. However, in this study, we did not observe this OH stretch until the pressure was decreased to 8.8 GPa, due to overlap with the second order diamond Raman. Even then, the peak was extremely weak and very broad. The softening behavior observed in the compound was different from that of pure H_2O, where the OH peak has been observed up to 30.0 GPa [14]. This indicates that little to no ice VII was formed, which was what we expected to observe. However, since we saw distinct carbon dioxide peaks, we can conclude that there was CO_2 in our sample.

DISCUSSION

The data from sample 1, cycle 1 was especially interesting due to its drastic differences in the Raman shift of CO_2 and H_2O. At high pressures, we found that the ν+ peaks of the CO_2 and OH stretch did not match that of pure CO_2 and H_2O. It is very peculiar that both shifts reverted to that of CO_2 after the pressure dropped below 1 GPa, and remained that way even after continued cycling. These data suggest that the CO_2-H_2O compound that forms through high initial pressure reverts to pure CO_2 and H_2O after the pressure falls below 1 GPa. The OH bond in our new compound did not change much with pressure, as its graph for Raman shift stayed relatively flat. On the other hand, the CO_2 ν+ frequency was much higher for our compound than for pure CO_2, which indicates stiffening of the bond.

At 4.6 GPa in cycle 1 of sample 1, we saw a visible difference in the sample. A possible explanation for this discrepancy in physical sample homogeneity was the existence of multiple phases. Examining the spectra of these separate phases revealed that although the peak locations were similar, the intensity of the spectra was not. Some factors were uncontrollable in our experiment, such as fluctuations in temperature or in the power and stability of laser lines. In addition, with our system it was impossible to take spectra in exactly the same position every time. However, the data were collected using the same exposure time each time, and under the same general conditions. After considering these factors, we can conclude that the two phases are different.

In sample 2, we also noticed physical variations in the sample. Differences seen in the spatial variation of the spectra may be caused by pressure gradients in the sample, which are created by uneven tightening of the DAC. However, these differences might also be due to multiple forms of the compound.

Another interesting feature is the Raman shift of sample 2 almost precisely matching the ν+ and ν- modes of pure carbon dioxide [13]. We have to consider that carbon dioxide also exists in multiple phases [15, 16, 17], and therefore, could probably also exhibit phase changes. Since the ν+ and ν- data match the solid CO_2 data so well, and because the OH peak was extremely weak in the few spectra where it showed up, we have reason to believe that sample 2 actually consists mainly of solid carbon dioxide due to its lack of water. The gas loading system was designed to minimize the amount of liquid in the system, while maximizing the amount of gas. However, it seems that the minimal amount of water we loaded in sample 2 resulted in the formation of a structure for pure carbon dioxide.

The data suggest that there are other phases of carbon dioxide clathrate that have yet to be discovered, depending on the sample composition. The variation in the different positions and intensities is sufficient to conclude that there are possibly multiple forms of the CO_2 clathrate. In addition, if different amounts of water in the sample can affect the resulting compound, as exhibited by the different structures formed in samples 1 and 2, then it is very likely that even more configurations of the CO_2 clathrate exist. It is possible that one of these structures may be well-suited for efficient carbon dioxide storage.

CONCLUSION

Using Raman spectroscopy, we observed that carbon dioxide and water formed different compounds depending on the CO_2:H_2O ratio inside the sample. Analysis of the differences in the spectra and Raman shift suggests that many different CO_2-H_2O compounds form under varying composition and pressure. When the pressure inside the DAC was decreased to <1 GPa and cycled, the carbon dioxide and water peaks behaved similarly to pure CO_2 and H_2O. This indicates that the two molecules formed a unique structure, but only at high pressures.

However, many aspects of the project remain to be examined. We have not yet tested the effects of temperature on our new compound or on the CO_2-H_2O system in general. At high and low temperatures, there may be additional phases waiting to be discovered. In addition, since the composition of the sample using the gas-loading method is inconsistent, the effects of composition, or initial CO_2:H_2O ratio, on clathrate formation would be another interesting basis for future work. We also need to determine the amount of carbon dioxide that the compound can store. X-ray diffraction may be able to help determine the structure of the new CO_2-H_2O compound that we observed, since Raman spectroscopy alone can not identify configuration, and although we know that the compound must consist of carbon dioxide and water, we do not know the molecular arrangement or interaction.

While we do not have exact details about the compound, it remains a promising step in the study of CO_2 storage. Carbon dioxide has always played a role in environmental chemistry, by trapping heat within the atmosphere and causing fluctuations in global temperatures. This novel CO_2-H_2O structure may prove useful for developing improvements in carbon dioxide storage material.

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