RAMAN SPECTROSCOPY OF THE CO$_2$-H$_2$O SYSTEM

A Thesis

Presented in Partial Fulfillment of the Requirements for
the Degree Master of Science
in the Graduate School of The Ohio State University

By

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The Ohio State University
2006

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ABSTRACT

CO₂ is considered to be a major contributor to global climate change. As the climate temperature has already increased by 2 °C since the industrial revolution, the increased concentration of CO₂ predicted to occur within the next few years is of major importance. Sequestration of anthropogenic CO₂ has been suggested as a method of remediation. One method of sequestration of CO₂ is to form CO₂ clathrates in the deep oceans. However, before this method can be utilized, the formation and dissolution of CO₂ clathrates must be better understood than it currently is. In this thesis, the CO₂-H₂O system is analyzed in the aqueous phase and in the clathrate phase (-17 °C and 15 atm) using Raman spectroscopy. The transition from the aqueous phase to the clathrate phase is followed. Frequency shifts are observed, indicating that weak van der Waals interactions occur between the H₂O and CO₂ molecules and is further supported with the spectra of the stretching and bending regions of H₂O. Narrowing of the Fermi diads of CO₂ is also observed after conversion from the solvated phase to the clathrate phase.

In addition, a solubility study is presented and determined the Henry’s law constants to over a temperature range of 27 to 80 °C and a pressure range of 5 to 13 atm. At 27 °C, Henry’s law constant was determined to be 3.42 × 10⁻² M/atm. With increasing temperature, Henry’s law constant decreased but was of the same order of magnitude.
To
My Parents
Tom and Ruth Swartzwelder
ACKNOWLEDGMENTS

Without the support of a large variety of people, I would not have been able to accomplish this goal. Without Dr. Heather Allen allowing me the opportunity to join her lab, I would never have completed this research. In addition, her recognition of my weaknesses and pushing me to overcome them has been the most gratifying part of this experience. I am extremely thankful for her constant support. Thanks to the members of the Allen lab, both past and present, who have all been there to answer my many questions. A special thank you goes to Kandice Harper, Lisa Van Loon, and Laura Voss for the countless brain-storming sessions but most of all for keeping me sane.

I thank my family who listened to all my experiment dilemmas while pretending they understood. Your suffering never went unnoticed. To the most important person in my life, Kyle Tomlin, I would never have survived this journey without your faith. You kept me going on the days I couldn’t see the end. I thank Samantha Farley for proving to be the best friend a person can have. One of these days, though, you’ll have to stop following me.

Finally, without the financial support of the American Chemical Society Petroleum Research Fund, I would not have been able to begin or complete this research.
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LIST OF ABBREVIATIONS

A.U. arbitrary units
atm atmosphere
CCD charge coupled device
CW continuous wave
°C degrees Celsius
FD Fermi diad(s)
$2
\nu_2$ first overtone of the bending mode
FWHM full-width at half-maximum
H Henry’s law constant
Ih hexagonal ice
h hour(s)
IR infrared
K Kelvin
L liter(s)
MΩ Megaohms
m milli
µ micro
min minute(s)
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<tr>
<td>mol</td>
<td>mole(s)</td>
</tr>
<tr>
<td>M</td>
<td>moles per liter</td>
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<tr>
<td>n</td>
<td>nano</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
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<td>ppm</td>
<td>parts per million</td>
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<tr>
<td>Pa</td>
<td>Pascal</td>
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<tr>
<td>PMT</td>
<td>photomultiplier tube</td>
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<tr>
<td>(\alpha)</td>
<td>polarizability</td>
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<tr>
<td>s</td>
<td>second(s)</td>
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<tr>
<td>S/N</td>
<td>signal to noise ratio</td>
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<tr>
<td>sI</td>
<td>structure I</td>
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<tr>
<td>SS</td>
<td>symmetric stretch</td>
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<tr>
<td>v</td>
<td>vibrational energy level</td>
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<td>VI</td>
<td>virtual instrument</td>
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CHAPTER 1

INTRODUCTION

Throughout the scientific community and the public, an increase in atmospheric CO$_2$ is believed to be a major contributor to global climate change. CO$_2$ is the most important greenhouse gas in the atmosphere aside from water. CO$_2$ absorbs radiation that is emitted by Earth that in turn leads to an increase in the temperature of the atmosphere. Current emission rates predict the concentration of CO$_2$ in the atmosphere will increase from 360 ppm to 1500 ppm by the end of the 21st century. This increase is expected to result in a global warming increase of 2 to 5 °C. According to current estimates, about 25% of CO$_2$ from the atmosphere enters the oceans and can form solutions of aqueous CO$_2$ as well as ionic species that can impact the pH of the oceans. In addition, CO$_2$ exists in the form of clathrates in the deep ocean, the permafrost region, and is believed to exist on Mars. It is a commonly accepted view that a way to mitigate anthropogenic CO$_2$ is to sequester CO$_2$ in the deep ocean. Since CO$_2$ exists in a variety of phases on Earth and poses a threat to the environment, understanding the intermolecular interactions between the CO$_2$ and H$_2$O molecules is of great importance in the environmental sciences.
1.1 Solvated CO$_2$

Clusters are of interest because they exhibit properties that are different from the properties of a molecule as well as those of the bulk solution.$^{18}$ CO$_2$ forms a variety of different sized water clusters of the form CO$_2$-(H$_2$O)$_n$ where $n$ is the number of H$_2$O molecules. Depending on the number of H$_2$O molecules in the cluster, the structure, bond lengths, and stability of the cluster will change. It has been found that when $n$ is greater than 3, the water molecules prefer to form a hydrogen bonded network among themselves. In the presence of CO$_2$, a solvation shell typically requires a large number of water molecules such as $n \geq 18$.\textsuperscript{5} The crossover from noncrystalline to crystalline bulklike structure occurs for CO$_2$ clusters for the range of 25-32 molecules.$^{18}$ For smaller complexes, it has been suggested that the cluster is mainly held by electrostatic interactions between the two components with a much smaller van der Waals contribution.$^5$

1.2 Clathrate Background

Clathrates are crystalline inclusion compounds that consist of guest molecules trapped inside polyhedral water cavities formed by a hydrogen bonded water network.$^{19,20}$ Clathrate clathrates form when small (<0.9 nm) nonpolar molecules come in contact with water at ambient temperatures (typically <300K) and moderate pressures (typically >0.6 MPa).$^{15}$ The presence of these guest molecules, in either the cage itself or in a large percentage of the surrounding cages, is required to prevent the clathrates from collapsing under their own attractive forces.$^{16}$ However, no chemical bonding exists between the host water molecules and the guest molecule.$^{21}$
Three common types of clathrates exist: sI clathrate, sII clathrate, and sH clathrate, Figure 1.1.15,19,21,22 Since only one guest molecule may occupy the cavity, the type of clathrate that forms is determined by the size of the guest molecule.19,23 Only molecules with a diameter smaller than the diameter of the cavity will be entrapped.21 The concept of “a ball fitting within a ball” is a good first approximation in understanding the properties of clathrates.23 When fully occupied, the structure of all three clathrates is approximately 85 mol % water and 15 mol % gas.15,23

Structure I (sI) is a body-centered cubic structure that forms with small (0.4-0.55 nm) guest molecules.15 A sI clathrate contains two different types of cavity: a pentagonal dodecahedral cavity (5^{12}) and a tetrakaidecahedral cavity (5^{12}6^2).16,19,23 The water cages are described by the general notation X^n, where X is the number of sides of a cage face and n is the number of cage faces having these X sides.19 The 5^{12} cavity consists of 12 pentagons while the 5^{12}6^2 cavity is comprised of 12 pentagons and 2 hexagons. The unit cell contains 46 water molecules.23 Structure II (sII) consists of a diamond lattice within a cubic framework that is formed with larger molecules (0.6-0.7 nm).15,23 These clathrates form when 5^{12} cavities arrange so that they link together by sharing faces.16,19,23 This arrangement results in the creation of a hexakaidecahedral (5^{12}6^4). The unit cell is comprised of 8 - 5^{12}6^4 cavities and 16 - 5^{12} cavities and contains 136 water molecules.16

Structure H (sH) has a hexagonal framework and occurs in both man-made and natural environments.15 Although sH is able to hold large molecules, it only exists with mixtures of both small and large (0.8-0.9 nm) molecules.15 sH is comprised of three cavities: 5^{12}, 4^35^66^3, and 5^{12}6^8. In addition to the pentagonal and hexagonal faces, sH
also has a square face. Due to its large cavity size, sH is important in the oil industry since it can encage molecules found in crude oil.\textsuperscript{19}

1.3 Solvated CO\textsubscript{2} vs. CO\textsubscript{2} clathrate

The same cages that form the CO\textsubscript{2} clathrate also exist as CO\textsubscript{2} clusters in the aqueous phase. These cages are the dodecahedral cage (20 H\textsubscript{2}O molecules) and the tetrakaidecahedral cage (24 H\textsubscript{2}O molecules). With the addition of the CO\textsubscript{2} molecule, it has been calculated in the literature that the tetrakaidecahedral cluster is stabilized the most relative to the unfilled cage by 8 kcal/mol whereas the dodecahedral cluster is not stabilized at all.\textsuperscript{24} These stabilization energies suggest the preferred cluster cage for CO\textsubscript{2} is the tetrakaidecahedral cluster with a coordination number of 24 water molecules. In addition, Raman and NMR studies have shown that CO\textsubscript{2} only occupies the tetrakaidecahedral cavity of the sI clathrate. Since the preferred CO\textsubscript{2} cage structure for clusters and clathrates are the same, studies of CO\textsubscript{2} cluster cages could provide information about CO\textsubscript{2} clathrate cages.

1.4 The Carbonate System

Accurate analysis of the vibrational modes associated with solvated CO\textsubscript{2} and CO\textsubscript{2} clathrates must account for all species that result from the dissociation of CO\textsubscript{2} in water. Many studies have been done over the years to examine this dissociation and the subsequent equilibrium processes involving carbonate and bicarbonate ions. This equilibrium process is known as the carbonate system and includes the following reactions:
[1] $\text{CO}_2(g) \leftrightarrow \text{CO}_2(aq)$

[2] $\text{CO}_2(aq) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3(aq)$ \hspace{1cm} K_{eq} = 1.3 \times 10^{-3}$

[3] $\text{H}_2\text{CO}_3(aq) \leftrightarrow \text{H}^+(aq) + \text{HCO}_3^-(aq)$ \hspace{1cm} K_{a1} = 2.00 \times 10^{-4}$

[4] $\text{HCO}_3^-(aq) \leftrightarrow \text{H}^+(aq) + \text{CO}_3^{2-}(aq)$ \hspace{1cm} K_{a2} = 4.69 \times 10^{-11}$

Although $\text{H}_2\text{CO}_3$ has not been observed in aqueous solutions using spectroscopy, it exists in both the solid state and in the gas phase$^{17,25,26}$. Carbonic acid is not a stable species and is only present in a very small amount relative to $\text{CO}_2(aq)$ at equilibrium$^{25,26}$.

1.5 Thermodynamics of Clathrates

In 1958, van der Waals and Platteeuw developed the first thermodynamic model to predict clathrate phase equilibria$^{19}$. The well known van der Waals-Platteeuw (VDW-P) model is based on classical statistical thermodynamics. It performs well near the ice point of water but deviates significantly far from the ice point$^{19}$. It is still used today in all later models that have been developed to predict the phase equilibria properties of clathrates. Several assumptions are made and must be considered when this model is used: (i) each cavity can contain at most one guest molecule; (ii) there is no interaction between the gas molecules in different cavities and the gas molecules interact only with the nearest neighbor water molecules; (iii) the gas molecule can freely rotate within the cavity which is treated as being perfectly spherical; and (iv) the clathrate lattice is not distorted by the guest molecule$^{19,22,27}$.

The basic equations for the VDW-P model are shown in Equations 1.1-1.2$^{16,19,27}$:

$$\mu_Q = \mu_Q^\beta + kT \sum_i v_i \ln \left( 1 - \sum_k y_k \right)$$

(1.1)
\[ y_{K_i} = \frac{C_{K_i} f_K}{1 + \sum_j C_{J_j} f_J} \]  

(1.2)

Here \( \mu_Q \) is the chemical potential of the solvent (water molecules) in the clathrate and \( \mu_Q^\beta \) is the chemical potential of the metastable empty clathrate lattice, \( f_K \) is the fugacity of solute \( K \), \( y_{K_i} \) is the probability of finding a solute molecule \( K \) in a host cavity of type \( I \), \( C_{K_i} \) is an equilibrium constant for the \( K^{\text{th}} \) type of guest in the \( i^{\text{th}} \) type of cavity, and \( v_i \) is the number of cavities of type \( i \) per water molecule in the clathrate lattice.
Figure 1.1: The three common clathrate structures with their corresponding unit cells.
CHAPTER 2

THEORY AND EXPERIMENTAL

2.1 Raman Theory

Photons involved with the interaction of electromagnetic radiation are refracted, reflected, or scattered.\textsuperscript{28} In Raman spectroscopy, detected scattered light from molecules is used to study the energy changes that result from this interaction. Information on the vibrational modes characteristic of the molecule is provided by the energy changes that are associated with the polarizability of the molecule.

Electromagnetic radiation is comprised of oscillating magnetic and electric fields which interact with the molecules.\textsuperscript{28} Classically, light can cause electron clouds in a chemical bond to oscillate or polarize. This oscillation results in emission of light. The emitted light is called scatter.\textsuperscript{28-31} Quantum mechanically, scatter is described by transitions between energy levels.\textsuperscript{28} A molecule in the ground state absorbs a photon from the incident light and is excited to a virtual or intermediate level. A virtual level is not a real energy level of the molecule but exists due to the distortion of the electron distribution of the molecule.\textsuperscript{30} This virtual state is not stable, and the light is immediately released as scattered radiation. In addition, the shape of the distorted electron cloud
depends on the magnitude of energy transferred to the molecule. Therefore, different frequencies of light affect the polarizability of the molecule differently.

There are two types of scatter: Rayleigh scatter and Raman scatter. The most intense form of scatter is Rayleigh scatter. The excited molecules relax back to the ground state by emitting a photon of the same frequency as that of the incident light. No significant energy change occurs. This is also known as an elastic process due to the absence of an energy change. A less common event, known as Raman scatter, also occurs where only one of every $10^7$ scattered photons is attributed to Raman scatter. This is an elastic process. Raman scatter occurs when the incident light interacts with the electron cloud and the nuclei move at the same time. The molecule can either increase or decrease in energy depending on the original state of the molecule. This increase or decrease in energy is known as Stokes or anti-Stokes Raman scattering, respectively. When the molecule rests at a higher vibrational level after emitting a photon, the emitted photon has less energy indicating energy was transferred to the molecule. This process is known as Stokes scatter. On the other hand, anti-Stokes scatter occurs when the emitted photon has more energy than the incident photon. In this case, the molecule has returned to a lower vibrational level. The molecule has decreased in energy. The types of scatter are shown in Figure 2.1. The two states marked $m$ and $n$ are different vibrational states of the ground electronic state.

The energy of the virtual state depends on the energy of the incident light. Therefore, the frequency of the absorption must account for the incident light. Raman frequencies are reported as the shift from the incident frequency. Equation 2.1 shows the
Raman shift equation where $\Delta \nu$ is the frequency of the vibrational mode, $\nu_R$ is the Rayleigh or incident laser energy, and $\nu_S$ is the Stokes energy.

$$\Delta \nu = \nu_R - \nu_S$$  (2.1)

Prior to exposure to radiation, most molecules are likely to reside in the ground vibrational state at room temperature. At thermal equilibrium, the ratio of Stokes and anti-Stokes intensities is determined by the Boltzmann distribution, Equation 2.2, where $N_n$ is the number of molecules in the excited vibrational energy level ($n$), $N_m$ is the number of molecules in the ground vibrational energy level ($m$), $g_i$ is the degeneracy of the level $i$ and $m$, $\Delta E$ is the energy difference between the vibrational energy levels, and $k$ is Boltzmann’s constant. At thermal equilibrium, a lower vibrational level is more heavily populated than a higher vibrational level. Since Stokes scatter intensity is dependent on the number of molecules in the lowest vibrational level, it will always be larger than the anti-Stokes scatter intensity.30-32 Therefore, the majority of Raman scattering is Stokes Raman scatter.

$$\frac{N_n}{N_m} = \frac{g_n}{g_m} \exp \left[ -\frac{\Delta E}{kT} \right]$$  (2.2)

2.2 Vibrational Modes

The following is a brief description of vibrational modes. Further information can be found in the literature.28,30,33,34 For a molecule with $k$ normal modes, let each vibrational mode be described by the wave function $\psi_i(\nu_i)$ where $i$ represents the $i$th normal mode of the molecule and $\nu_i$ represents the $k$th quantum state of that mode. To describe the total vibrational wave function, $\psi$, of the molecule, the product of the individual vibrational wave functions may be used, Equation 2.3.
\[ \psi_v = \psi_1(\nu_1) \psi_2(\nu_2) \psi_3(\nu_3) \ldots \psi_k(\nu_k) \] (2.3)

The molecule is in its vibrational ground state when each \( \nu_i \) is zero. If one vibrational mode is excited to the \( \nu_i = 1 \) state by absorption of radiation while the remaining normal modes remain in the lowest states, then the molecule has undergone a fundamental transition for that particular vibration. A fundamental transition occurs when a molecule obeys \( \Delta \nu = +1 \) and starts in the ground state.

The number of normal vibrational modes a molecule is given by \( 3N-5 \) if linear and \( 3N-6 \) if non-linear. \( N \) is the number of atoms. However, not all of these vibrational modes are observed in a Raman spectrum. Those that are observed can be predicted by selection rules and are called Raman active. Selection rules state if the transition of a fundamental vibration will be observed in the spectrum but it does not predict the intensity of a particular band.

The selection rules for Raman spectroscopy are dependent on the polarizability, \( \alpha \), as indicated in Equation 2.4:

\[ \int \psi^*(\nu')\alpha\psi(\nu)d\tau \] (2.4)

where \( \psi(\nu') \) represents the excited state and \( \psi(\nu) \) represents the ground state of the molecule. For this integral to be nonzero, its integrand must be totally symmetric, meaning that the product of the ground state, the operator, and the excited state symmetry must be totally symmetric. This selection rule states that the vibration will only be observed when the polarizability changes during the transition. This change in polarizability is the basis of Raman spectroscopy.

Since \( \text{CO}_2 \) is a linear molecule with three atoms, it has four fundamental vibrational modes: a symmetric stretch, an asymmetric stretch, and two degenerate
bending modes, Figure 2.2. However, only the symmetric stretch of CO₂ is Raman active, and it appears at 1334 cm⁻¹. The other three vibrational modes are IR active and will not be discussed further. Although only one normal mode is Raman active, other vibrational modes are observed. This is because transitions exist in addition to the fundamental transitions.

Overtone transitions are observed in the CO₂(g) Raman spectra. An overtone occurs when a mode is excited beyond the ν=1 state. The mode can be excited to the ν=2, 3,… from the ground state. Since multiple overtones can occur for the same vibrational mode, a naming system is used to identify different overtones. If the mode is excited to the ν=2 or ν=3 state, it is called the first or second overtone of the vibrational mode, respectively. The first overtone of the CO₂(g) bending mode ν₂ is observed at 1340 cm⁻¹. Hot bands are also observed in the CO₂(g) spectrum. Hot bands occur when an already excited vibrational mode is further excited. For example, if a vibrational mode in the ν=1 state is excited to the ν=2 state.

2.3 Raman Experimental Setup

A 532 nm continuous wave (CW) laser (Spectra-Physics, Millennia II, ~95 mW) was used to obtain the Raman spectra. A fiber optic probe (InPhotonics, RP 532-05-15-FC) both delivers the laser excitation source to the sample and collects the scattered light. A 200 µm collection fiber optic (InPhotonics, Inc.) delivers the scattered light to the entrance slit of a 500 mm monochromator (Acton Research, SpectraPro 500i). A 1200 g/mm grating blazed at 1 µm was used. The slit width was set to 50.0 µm with a resolution of 2.23 cm⁻¹. A liquid nitrogen cooled CCD camera (Roper Scientific,
N400EB, 1340 x 400 pixel array, back-illuminated and deep depletion CCD) collected
the data. The CCD was calibrated using the 435.83 nm line of a fluorescent lamp. The
1382 cm\(^{-1}\) peak of a crystalline naphthalene spectrum was used to calibrate the
wavenumber position by comparing the observed position to literature values.\(^{29}\) Data
collection and display were performed using the SpectraSense software (Acton Research,
version 4.2.9). A basic diagram of the Raman setup is shown in Figure 2.2.

2.4 CO\(_{2}\)\((g)\)

CO\(_{2}\)\((g)\) (99.9 % purity) was bubbled into a stainless steel cell (200 mL volume). A
spectrum of CO\(_{2}\)\((g)\) was acquired at 10 atm using a 300 s integration time. The
experiment was performed at 23 ± 2 °C.

2.5 The Carbonate System

An experiment was done to investigate the vibrational modes of the carbonate
system. A reference solution of 3.0 M KHCO\(_{3}\) was made. The experiment was done at
23 ± 2 °C. Raman spectra were acquired to determine the vibrational frequencies of the
HCO\(_{3}\)\(^{-}\) and CO\(_{3}\)\(^{2-}\) species. In addition, the spectrum was examined for the existence of
the H\(_{2}\)CO\(_{3}\) and CO\(_{2}\) species. Spectra were acquired with a 30 s acquisition time. Two
spectra were averaged to obtain the final spectrum.

2.6 Solvated CO\(_{2}\)

Solvated CO\(_{2}\) experiments were done using a pressure range from 8 to 15 atm at
23 ± 2 °C. The experimental parameters used were outside the CO\(_{2}\) clathrate forming
region, Figure 2.4. A stainless steel cell (200 mL volume) was filled with 100.0 mL of
nano-pure water (18.2 MΩ • cm). CO\(_{2}\)\((g)\) was bubbled into the stainless steel cell at a
known pressure. Solvated CO$_2$ spectra were acquired every ten minutes for eight hours. A 4 min integration time was used. At the completion of the experiment, the pressure was then adjusted to obtain solvated CO$_2$ data at other pressures.

Solvated spectra were also acquired at -15 ± 2 °C. Since this temperature was within the temperature range to form clathrates, only pressures outside of the clathrate region were used. A pressure range of 5 to 10 atm was used. The cell was moved to the freezer after equilibrium was achieved at 23 ± 2 °C. Spectra were acquired every ten minutes for ten hours using a 4 min integration time.

2.7 CO$_2$ Clathrate

Once equilibrium was achieved at solvated conditions, the inlet valve on the stainless steel cell was closed so the cell could be removed from the gas flow. The cell was placed in a freezer and was maintained at a temperature of -15 ± 2 °C. The gas flow was restarted. The pressure was maintained at 15 atm to allow the formation of clathrates. These experimental parameters are within the CO$_2$ clathrate forming region, Figure 2.4. Spectra were acquired every ten minutes for ten hours using a 4 min integration time.

The above experimental parameters and conditions were adjusted to perform additional experiments to investigate the CO$_2$ clathrate system. For one experiment, a magnetic stirrer was added to the system. For another experiment, the volume of H$_2$O was decreased from 100 mL to 75 mL.

A series of experiments were done by warming and cooling the stainless steel cell over a period of three days. The cell was originally at 23 ± 2 °C and maintained at 7 atm for ten hours. The cell was then cooled to -15 ± 2 °C and remained in the freezer for an
additional ten hours. The pressure was then increased to 15 atm and the cell was slowly warmed to 0 ± 2 °C and was maintained at these pressure and temperature conditions during spectral acquisition. The pressure was maintained for the duration of the experiment. The cell was cooled back down to -15 ± 2 °C. This series of warming and cooling was repeated six times.

2.8 H₂O

A sample vial of nano-pure H₂O(l) (18.2 MΩ•cm) was made. It was maintained at 1 atm and 23 ± 2 °C. A Raman spectrum of the stretching region (2900-3700 cm⁻¹) and the bending region (1500-1800 cm⁻¹) was acquired using an integration time of 60 s. A pure H₂O(l) spectrum of both the stretching and bending region was acquired of the stainless steel system prior to being exposed to CO₂. It was maintained at 15 atm and 23 ± 2 °C. During the solvated CO₂ experiment, the bending mode was observed in the spectral window. Since the stretching region was not included in the spectral windows, the stretching region of H₂O was acquired at the end of the solvated CO₂ experiment.

When the stainless steel cell was placed in the freezer to acquire CO₂ clathrate spectra, the sample vial was also placed in the freezer. Both systems were maintained at -15 ± 2 °C but the sample vial was at 1 atm while the cell was at 15 atm. The bending region was acquired with CO₂ clathrate spectra. The stretching region was taken at the end of the CO₂ clathrate experiment.

2.9 Data Analysis

All spectra were evaluated using Igor Pro (Wavemetrics, Version 4.0.5.1). A graphing macro (Appendix C), written by Dr. Laura Voss and Lisa Van Loon of the Allen lab, loaded individual spectra into one graph and table. The spectra were fit with a
Voigt function. The peak positions, areas, and FWHM of the Fermi diads were determined using built-in functions.

2.10 Experimental Controls

The laser energy stability and peak shifts of naphthalene and solvated CO$_2$ peak used to test the stability of the laser system during the experiments. The laser energy was read with a laser power meter (Molectron Detector Inc., Power Max 500D) before and after acquiring spectra to verify energy stability. The energy varied by ±5 mW during the course of the experiment. It was determined during another experiment (Appendix A) that the laser energy was not destructive to the sample. A naphthalene spectrum was acquired prior to and after obtaining solvated CO$_2$ spectra as well as at the end of the experiment. The 1382 cm$^{-1}$ peak of naphthalene was evaluated for shifts in peak position. Throughout the experiment, the peak shifted less than 1 cm$^{-1}$. Solvated CO$_2$ spectra were evaluated over a period of ten hours to determine if the peak would shift as a function of time. The peak shifts observed for both Fermi diads were less than 1 cm$^{-1}$. Therefore, any peak shift greater than 1 cm$^{-1}$ observed during the clathrate experiment is real and is not attributed to instrument fluctuations.
Figure 2.1: Diagram of the Rayleigh and Raman scattering processes. The lowest energy vibrational state $m$ is shown at the bottom. States of increasing energy are above state $m$. 
Figure 2.2: The fundamental vibrational modes of CO$_2$ are shown with their vibrational energies, where $v_s$ is the symmetric stretch, $v_{as}$ is the asymmetric stretch, and $\delta_d$ is the doubly degenerate bending mode.
Figure 2.3: Schematic of Raman setup for obtaining CO₂ clathrate spectra: a) Spectra-Physics Millenia II laser; (b) fiber optic Raman probe; (c) monochromator; (d) freezer; (e) CO₂ tank; (f) gas inlet valve; (g) computer
Figure 2.4: Schematic pressure-Temperature diagram of the carbon dioxide-water system at 250-310 K.\textsuperscript{68}
CHAPTER 3

RESULTS AND DISCUSSION

3.1 Gaseous CO₂

The Raman spectrum of CO₂(g) is shown in Figure 3.1. This spectrum is composed of two major peaks assigned to the Fermi diads and two minor peaks attributed to hot peaks. The Fermi diads are at 1285 cm⁻¹ and 1387 cm⁻¹ and will be called the SS-FD and 2ν₂-FD, respectively. The assignments of the Fermi diads use the vibrational mode that is the major contributor to the observed peak. This assignment will be discussed in more detail later. The two hot bands are at 1264 cm⁻¹ and 1409 cm⁻¹.

As discussed in Chapter 2, there are four fundamental modes of CO₂. Only the symmetric stretch (ν₁) is Raman active and it has an observed Raman shift of 1334 cm⁻¹. However, the first overtone of the bending mode (2ν₂) is also allowed in the Raman spectrum. Since the bending mode occurs at 670 cm⁻¹, the first overtone occurs at 1340 cm⁻¹. The intensity of the overtone is generally less than one tenth the intensity of its fundamental transition because it is dependent on the anharmonicity of the molecule’s polarizability as well as the vibrational potential.

In the case of CO₂, the vibrational wave functions of both the symmetric stretch and the first overtone have nearly the same vibrational frequencies. In addition, both
vibrational wave functions have the same symmetry ($\sigma_g^+$).\textsuperscript{33,34} The combination of the similar frequency and symmetry leads to a perturbation of the energy levels.\textsuperscript{33-37} The levels split forming new energy levels that are a combination of the symmetric stretch level and the overtone level. A “mixing” of the two energy levels occurs, and the weak overtone “borrows” intensity from the nearby fundamental. As a result, two strong peaks, the Fermi resonances, are observed at 1388 cm\textsuperscript{-1} and 1286 cm\textsuperscript{-1}.\textsuperscript{36,34,33,17} Although the energy levels are perturbed, both levels contain some of the properties of the original two levels.\textsuperscript{36} Fermi resonance is not special to CO\textsubscript{2}. It is observed in many molecules and especially in large molecules of low symmetry.\textsuperscript{36}

In the Raman spectrum of CO\textsubscript{2}, the hot bands are weak in intensity compared to the Fermi diads. The Boltzmann distribution predicts this weak intensity. Unlike a fundamental transition, the lower level of a hot band is an excited state. According to Equation 2.2, the likelihood of an excited state being occupied is low at thermal equilibrium. Therefore, the hot bands observed in the spectrum are of weak intensity.

\textbf{3.2 The Carbonate System}

When H\textsubscript{2}O is exposed to CO\textsubscript{2}, reactions occur in addition to the solvation of CO\textsubscript{2}. To investigate the possibility of the formation of other species, a reference spectrum of a 3.0 M KHCO\textsubscript{3} solution is compared to the solvated CO\textsubscript{2} spectrum. Both systems are maintained at 23 °C. The solvated CO\textsubscript{2} system is held at 12 atm and the reference solution is held at 1 atm. The most prominent peak of the reference spectrum is a large peak at 1014 cm\textsuperscript{-1}(Figure 3.2). This peak is assigned to the C-OH stretch of HCO\textsubscript{3}-. The small peak at 1061 cm\textsuperscript{-1} corresponds to the C=O symmetric stretch of CO\textsubscript{3}\textsuperscript{2-}. The broad region between 1200 and 1450 cm\textsuperscript{-1} reveals two peaks. The weaker peak at 1300 cm\textsuperscript{-1} is
attributed to the C-OH bending mode of HCO₃⁻ while the stronger peak at 1359 cm⁻¹ corresponds to the C=O symmetric stretch of HCO₃⁻.²⁵,³⁸,³⁹ Table 3.1 includes the vibrational assignments observed. There is no spectroscopic evidence of H₂CO₃. Also, no CO₂ Fermi diads are observed in the reference solution. This is expected due to the low pressure used.

The large intensity of the three peaks attributed to HCO₃⁻ compared to the peak attributed to CO₃²⁻ indicates a large concentration of HCO₃⁻ exists in the reference solution. These results are supported by the acid equilibrium constants of the system. Refer to Chapter 2 for the reactions of the carbonate system. The reaction forming H₂CO₃ from HCO₃⁻ has an equilibrium constant of 2.25 x 10⁻⁸ (calculated).¹⁷ The reaction of HCO₃⁻ to form CO₃²⁻ has an equilibrium constant of 4.84 x 10⁻¹¹.¹⁷ The smaller equilibrium constant for the formation of CO₃²⁻ indicates the formation of CO₃²⁻ is favored over H₂CO₃. Therefore, obtaining spectroscopic evidence of CO₃²⁻ and HCO₃⁻ and not H₂CO₃ is reasonable.

The peaks attributed to CO₃²⁻ are of weaker intensity than that of HCO₃⁻. This intensity difference is attributed to the lower concentration of CO₃²⁻ (3.76 x 10⁻² M) compared to the HCO₃⁻ concentration (3.0 M). In addition, the equilibrium constants indicate CO₃²⁻ is favored over H₂CO₃. However, H₂CO₃ does exist in the solution with a concentration of 2.63 x 10⁻⁴ M. Since the H₂CO₃ concentration is below the Raman detection limit of 10⁻² M, it will not be observed in the spectrum.

3.3 Aqueous CO₂

In the solvated CO₂ Raman spectrum, two peaks are observed at 1275 cm⁻¹ and 1382 cm⁻¹ (Figure 3.2). Table 3.1 includes the solvated CO₂ vibrational assignments.
These peaks are attributed to the Fermi diad peaks of solvated CO₂. The peak at 1165 cm⁻¹ is an artifact of the silica window. No other peaks are observed. This observation indicates the system favors CO₂(aq) over carbonic acid. These results are supported by a large rate constant of k = 2.63 x 10² s⁻¹ for the formation of H₂CO₃ from CO₂(aq). At room temperature, ~99.8% of the dissolved CO₂ remains as CO₂(aq) while only ~0.2% reacts with water to form H₂CO₃. The high pressure used in our clathrate experiments is not enough to shift the reaction toward a detectable concentration of H₂CO₃. At 15 atm, the concentration of H₂CO₃ is 6.05 x 10⁻⁴ M, which is below the Raman detection limit of 10⁻² M. Experimental data (not shown) obtained at pressures close to atmospheric pressure do not show any peak attributed to the carbonate system, including CO₂(aq), since the concentrations are below the Raman detection limit. This observation is supported by the need for high pressures to obtain observable CO₂ concentrations in water.

Solvated CO₂ Raman spectra are taken after CO₂ is bubbled into the cell containing H₂O (Figure 3.3). Spectra are acquired every ten minutes for ten hours. The two peaks observed at 1275 cm⁻¹ and 1382 cm⁻¹ are the Fermi diads of CO₂ as seen in the CO₂(g) spectrum. A dotted line is used to highlight the peak position of the Fermi diads and verifies there is no significant shift during the integration period. For further discussion, see Section 2.J.

The Fermi diads of CO₂ are much broader in water than in the gas phase. The observation of this broadening is an indication that interactions are occurring between the CO₂ and H₂O molecules. If hydrogen bonding was involved in the solvated phase, the restrictions placed upon the CO₂ molecule by the strong hydrogen bonds could break the
symmetry of CO₂ found in the gas phase. If the symmetry was broken, the Fermi diads would no longer be observable. Instead, a weak peak and a strong peak attributed to the first overtone and the symmetric stretch, respectively, would be observed. If upon hydration one of the vibrational modes has a significant change in frequency, the vibrational energy levels would be shifted farther apart. This shift would reduce the perturbation of the energy levels resulting in an increase in the level separation and reducing the intensity effect. An *ab initio* study computed the C-O bond lengths to be 1.176 Å and 1.177 Å in the gas phase and aqueous phase, respectively.⁴⁰ The small difference in the bond length of the different phases is in agreement with the small change observed in the Fermi diads as a result of hydration. *Ab initio* studies also show the clathrate CO₂ molecule prefers the same symmetry as that of its gaseous state, D₅h.⁴⁰ Therefore, the symmetry is not broken during the transition from the gaseous state to the aqueous state.

The hot bands observed in the CO₂(\text{g}) spectrum are not observed in the solvated CO₂ spectrum. The intensity ratio of the SS-FD in the gas phase to the aqueous phase is 22.5. In the gaseous phase, the intensity ratio of the SS-FD to the lower frequency hot band is 18.7. Assuming the ratio between the SS-FD and the lower frequency hot band is the same for the aqueous phase as that of the gaseous phase, the hot band should have an intensity of 52.7 A.U. This low intensity is below the detection limit of 570 A.U.

The decrease in intensity of the Fermi diads observed in the aqueous phase is of great importance. Since Raman intensity is proportional to concentration, the number of molecules of CO₂ will be determined for both phases at a pressure of 10 atm and a temperature of 25 °C. In the gaseous phase, the ideal gas law is used to determine the
number of molecules of CO$_2$ in the cell. In the aqueous phase, Henry’s law is used to calculate the number of molecules in solution. It is determined that there are $4.96 \times 10^{22}$ molecules in the gas phase compared to $1.87 \times 10^{22}$ molecules in the aqueous phase. To compare the intensities of the Fermi diads in the gas phase to the aqueous phase, the gas phase intensities are corrected by using the concentration ratio of CO$_2$ in the aqueous and gas phases. As shown in Figure 3.4, correcting the gas phase intensities for the concentration difference did not result in the Fermi diads being of the same intensity. Since a large intensity difference still remains, the concentration difference between the two phases is not the only factor for the diminished intensity of the Fermi diads. This observation is an indication that the CO$_2$ molecules are interacting with the surrounding water molecules.

When CO$_2(g)$ is exposed to liquid water at 23 °C, the peak intensity of the CO$_2$ Fermi diads increases for up to six hours, indicating that the concentration of CO$_2$ molecules in water is increasing. In Figure 3.5, the peak area and peak intensity of the 2$\nu_2$-FD are shown over a period of six hours. The SS-FD is not observed initially due to a low S/N ratio. For the first three hours, CO$_2$ dissolves rapidly in water before slowly leveling off. Equilibrium is reached in the system in approximately six hours.

### 3.4 CO$_2$ Clathrate

In Figure 3.6, a CO$_2$ clathrate spectrum and a solvated CO$_2$ spectrum are compared. Dashed lines are used to highlight the peak positions of the solvated CO$_2$ Fermi diads. Figure 3.7 shows the spectral fits and raw data used to determine the peak shifts and FWHM of the Fermi diads. Table 3.3 shows the calculated values for the peak position, area, and FWHM for the Fermi diads. The Fermi diads of solvated CO$_2$ are at
1278.2 cm\(^{-1}\) and 1386.2 cm\(^{-1}\). The Fermi diads of CO\(_2\) clathrates are at 1280.5 cm\(^{-1}\) and 1384.7 cm\(^{-1}\). Vibrational assignments for CO\(_2\) clathrate are included in Table 3.1. A small blue-shift of 1.8 cm\(^{-1}\) occurs for the SS-FD from solvated to clathrate phase, and a small red-shift of 1.7 cm\(^{-1}\) occurs for the 2\(\nu_2\)-FD. With respect to the solvated Fermi diads, the observed blue-shift and red-shift for the SS-FD and 2\(\nu_2\)-FD, respectively, are reported in the literature as a sign of CO\(_2\) clathrate formation.\(^4\)\(^1\)

As the spectrum shows in Figure 3.5, the Fermi diads are not further split. This is an important observation since splitting of the peaks would indicate that CO\(_2\) is partitioned between the small (5\(^1\)\(2\)) and large (5\(^1\)\(2\)6\(^2\)) cavities of sI.\(^4\)\(^1\),\(^1\)\(^5\),\(^1\)\(^9\),\(^4\)\(^2\) For example, the stretching mode of CH\(_4\) is split in the clathrate phase because it occupies both cavities of sI. Raman and NMR studies confirm CO\(_2\) occupies only the large cavity of sI.\(^4\)\(^2\)

The shift in the Fermi diads shows that the clathrate cage affects the vibrational modes of CO\(_2\). Interestingly, one Fermi diad is blue-shifted while the other is red-shifted. Therefore, the clathrate cage has a different effect on the individual vibrational modes that make up the Fermi diad. The 2\(\nu_2\)-FD is dependent upon the first overtone of the bending mode (2\(\nu_2\)).\(^3\)\(^2\),\(^4\)\(^3\) Any changes observed in the frequency of the overtones of the bending mode are a direct result of how the bending mode is affected by its environment. Therefore, to completely understand the red-shift of the Fermi diad at 1383 cm\(^{-1}\) the bending mode frequency is briefly discussed. The bending mode is IR active only and occurs in the gas phase at 667 cm\(^{-1}\).\(^4\)\(^4\) The gas spectrum shows the bending mode frequency decreases with clathrate formation. The decrease in frequency would then cause the overtones to also decrease in frequency. On the other hand, the SS-FD increases in frequency. The SS-FD is heavily dependent upon the symmetric stretch
Although the Fermi diads shift when transitioning from the aqueous to the clathrate phase, the effect is small. If stronger interactions, such as hydrogen bonding, occurred between the CO$_2$ molecules and the H$_2$O molecules composing the clathrate cage, the shift would be appreciably greater. As a result of hydrogen bonding, both Fermi diads would red-shift as the strong intermolecular interactions would weaken the CO$_2$ vibrational modes. In addition, the existence of the Fermi diads indicates there is no break in symmetry, which could also occur with the restrictions placed upon the vibrations of CO$_2$ if there was hydrogen bonding. In addition, CO$_2$ in the solid phase is held together primarily by weak van der Waals forces. The Fermi diads of the solid phase are 1276 cm$^{-1}$ for the SS-FD and 1384 cm$^{-1}$ for the 2$\nu_2$-FD. In the solid phase, the SS-FD is red-shifted by 8 cm$^{-1}$ and the 2$\nu_2$-FD is red-shifted by 3 cm$^{-1}$. Both shifts are larger than that in the aqueous phase and the clathrate phase. Therefore, any intermolecular interactions between the CO$_2$ molecule and the clathrate cage must be weak. This data is evidence that the forces required to prevent the clathrate cage from collapsing are van der Waals forces, which is assumed in the VDW-P model.

The peak shift of both Fermi diads can be observed in Figure 3.8. Both Fermi diads shift when transitioning from the solvated phase to the clathrate phase. At low pressure (5 atm), the positions of both peaks do not shift significantly indicating that clathrates do not form under these conditions. The CO$_2$ phase diagram (Figure 2.4) illustrates that these conditions are not within the clathrate phase. With a pressure increase (15 atm) and temperature decrease (-17 $^\circ$C), a significant increase and decrease
in the peak positions are observed for the SS-FD and 2ν2-FD, respectively. At -17 °C and 15 atm, the phase diagram conforms that the experimental conditions are favorable for clathrate formation. As the system is warmed up to 22 °C, the peaks shift back to the position attributed to solvated CO2. This trend is observed each time the system is cooled and warmed.

The FWHM has been evaluated for both Fermi diads in the aqueous and clathrate phases and are shown in Figure 3.9. In the aqueous phase, the FWHM of the Fermi diads are much wider than that in the clathrate phase with the FWHM of the SS-FD and 2ν2-FD being on average 13 and 19 cm⁻¹, respectively. However, in the clathrate phase, the FWHM of the Fermi diads narrow significantly until both peaks have similar FWHM of 8 cm⁻¹. The FWHM increases and decreases as the system transitions from the solvated phase to the clathrate phase and back. A comparison of the FWHM of the Fermi diads in the gas, aqueous, and clathrate phases are shown in Table 3.2. The broadening of the Fermi diads in the aqueous phase is the result of interactions between CO2 and H2O molecules. The FWHM in the clathrate phase decreases and is similar to the FWHM of the Fermi diads in the gas phase. Since the FWHM in the clathrate phase decreases, the intermolecular interactions between CO2 and H2O molecules are weaker in the clathrate phase than in the aqueous phase and CO2 is more “gas-like.”

Using a cavity model for gas clathrates, consider a CO2 molecule trapped in a spherical cavity. The carbon atom of the CO2 molecule resides at the center of the cavity. The vibration frequency ν' in the cavity can be related to that in a vacuum, ν₀, by Equations 3.3-3.4

\[ \nu' / \nu_0 = (1 / \epsilon^*)^2 \]  (3.3)
\[
\varepsilon^* = \frac{1}{c} \int \frac{db}{1 - \left( \frac{\varepsilon' - 1}{\varepsilon' - 0.5} \right) \left( \frac{b}{a} \right)^3}
\]  \hspace{1cm} (3.4)

where \( b \) is an arbitrary radius from the center of the cavity and \( c \) is the interatomic distance between carbon and oxygen in CO\(_2\). The radius between CO\(_2\) and H\(_2\)O was calculated to be 2.50 Å and 3.07 Å in the aqueous phase and the clathrate phase, respectively.\(^{41}\) These calculations suggest that CO\(_2\) molecules in the aqueous phase are closely surrounded by H\(_2\)O molecules but formation of clathrates increases this spacing. Therefore, it is reasonable to suggest the decrease in the FWHM upon clathrate formation is due to decreased intermolecular interactions.

In all the phases, the combinations of the peak shifts, FWHM, and intensity changes of the Fermi diads of CO\(_2\) indicate the vibrational modes are sensitive to their surroundings. The decrease in wavenumber separation between the two Fermi diads in the clathrate spectrum suggests that the vibrational energy levels are perturbed more than they are in the aqueous phase. Using a perturbation model, the unperturbed theoretical bending mode and symmetric stretch mode frequencies in the gas, aqueous, and clathrate phases can be calculated for Equations 3.5-3.7.\(^{41,46}\) The unperturbed frequencies can be thought of as the normal mode frequency if there was no interaction between them. The perturbed frequencies are the frequencies of the Fermi diads in the spectra. Table 3.3 includes the theoretical frequencies of normal modes.

\[
\nu_1 = 0.5(\nu_1 + \nu_u) - 0.5\Delta 
\]  \hspace{1cm} (3.5)

\[
\nu_2 = 0.5(0.5(\nu_1 + \nu_u) + 0.5\Delta) 
\]  \hspace{1cm} (3.6)

\[
\Delta^2 = X^2 - 4W_{10^0-02^0}^2 
\]  \hspace{1cm} (3.7)
In Equation 3.7, $\Delta$ is the theoretical separation between the unperturbed vibrational levels, $X$ is the experimentally observed frequency separation of the two components and $W$, the Fermi coupling constant for CO$_2$, is $-50.98$ cm$^{-1}$ in the literature. Using the perturbed frequencies observed in the Raman spectrum, the unperturbed frequencies, $\nu_1$ and $\nu_2$, of the aqueous phase are calculated to be $1314.4$ cm$^{-1}$ and $675.0$ cm$^{-1}$. For the clathrate phase, they are calculated to be $1321.9$ cm$^{-1}$ and $671.6$ cm$^{-1}$, respectively. In the gas phase, the values are $1334.6$ cm$^{-1}$ and $669.4$ cm$^{-1}$. In addition, the solid phase perturbed frequency separation was determined to be $108$ cm$^{-1}$. This distance is slightly larger than the perturbed frequency separation of the aqueous phase ($107.1$ cm$^{-1}$).

Since CO$_2$ molecules in the solid phase undergo weak van der Waals interactions with the neighboring CO$_2$ molecules, this suggests the interactions in both the clathrate and aqueous phases are weakly interacting with the surrounding H$_2$O molecules via van der Waals forces. In the clathrate phase, the separation between the unperturbed frequencies decreases from that of the aqueous phase and approaches the smaller separation found for the gas phase. These results show the CO$_2$ molecules in the aqueous phase are experiencing more interactions with the surrounding water molecules than when in the clathrate phase. Therefore, CO$_2$ is more “gas-like” in the clathrate phase than in the aqueous phase.

There is a significant decrease in intensity in the Fermi diads when clathrates form, Figure 3.10. This decrease is not supported by all the literature, but clathrate formation has been found to be highly dependent on the apparatus setup and experimental conditions, and is possibly due to the clathrate nucleation site. Nucleation is the initial stage of a phase transition and the kinetics of nucleation often control the selection of the
dominant kinetic path. Therefore, it is critical to understand where nucleation occurs. In condensed phases, nucleation leads to the spontaneous formation of small, unstable clusters of a new crystalline phase.22,47

A cluster nucleation hypothesis was developed by Sloan et al. to explain the clathrate nucleation.22,48 Water molecules form clusters around dissolved guest molecules. Cluster size is dependent on the guest molecule size, and for CO₂, 24 water molecules are required. The clusters then form unit cells. Coordination numbers of 20 (5₁²) and 24 (5₁²6²) are required to form sI. If the liquid phase has clusters of only one coordination number, nucleation is not allowed until the clusters rearrange to make the needed size. Breaking and making hydrogen bonds are required for this process. For the sI clathrate, CO₂ only occupies the large cavity. Since the large cavity coordination number is the same as that preferred for CO₂ clusters, clathrate formation will result in the transformation of the 5₁²6² cavity into the 5₁² cavity. Therefore, the rate limiting step in CO₂ clathrate formation is the transformation of the large cavity into the small cavity.49,15

The time of clathrate nucleation has not been predictable in bulk experiments, but the clathrate formation has always initiated at a surface, most commonly the vapor-water interface.21,22 The vapor-water interface is favored for clathrate formation because of the large concentration of both the host and guest molecules. These large concentrations are required for clusters to grow to the supercritical size required for nucleation to occur.22

Since the bulk liquid phase contains a small concentration of guest molecules compared to that at the interface, there is little nucleation in the bulk phase. As Raman spectroscopy probes the bulk phase of the system, the experimental setup will greatly
determine the observed vibrational modes. Variations of the clathrate experiment were
done to evaluate if the Fermi diads would change in intensity as a result of the setup used.
Figure 3.11 shows the Raman spectrum acquired during these altered experiments. A
smaller volume of water was used to lower the vapor-water interface. By lowering the
interface closer to the area probed, it was believed an increase would occur in the
intensity of the Fermi diads due to a larger concentration of clathrates. When a volume
of 75 mL was used, the interface was 0.2 cm above the probed area compared to the 1.0
cm distance when using the 100 mL. However, this was not the case as there was no
difference between this spectrum and the spectra using a larger water volume. In
addition, a magnetic stirrer was used to stir the solution while cooling. This would allow
for better mixing of the interfacial gas, liquid, and crystal structures within the liquid. Therefore, the intensity of the Fermi diads would increase due contribution from “bulk nucleation.” The intensity of the peaks did not change indicating there is another reason
complete conversion to clathrates is not observed.

Figure 3.12a shows the peaks decrease steadily for two hours before intense
peaks attributed to the clathrate phase form. Once the clathrates form (Figure 3.12b), the
intensity does not change, which indicates complete conversion to the clathrate structure.
However, it also takes two hours for the solution to freeze. It is suggested that the frozen
solution greatly reduces the rate of clathrate formation. To maximize clathrate formation,
the solution was allowed to reach equilibrium before being cooled to equilibrium to
saturate the solution with CO₂. When starting with a saturated solution, clathrate growth
is diffusion controlled. When ice forms, the process is still controlled by the diffusion
rate of CO₂ molecules through the accumulating clathrate layer. The rate of formation
has been shown to increase significantly at higher temperatures when a quasi-liquid layer forms.\textsuperscript{50,51} Almost complete conversion (~98\%) to the clathrate phase is observed when the temperature is raised near the melting point of ice (-10 to 0 °C).\textsuperscript{50,51} For solutions where the availability of CO\textsubscript{2} is sufficiently high, the temperature in these experiments is the main limiting factor.\textsuperscript{52} Since the system is allowed to reach equilibrium before cooling, the significant decrease in intensity of the Fermi diads is attributed to the temperature being the limiting factor. Therefore, the decreased intensity of the Fermi diads indicates the temperature is hindering complete conversion from the aqueous system to clathrates.

In addition, increased light scattering occurs with a crystalline substance. Since the solution is now frozen, the decrease in intensity can be attributed to increased scatter from hexagonal ice and the clathrate cavities. Therefore, the decreased intensity of the Fermi diads could be attributed to several factors, such as the experimental setup or increased scatter.

3.5 Pure Water vs. Solvated

A comparison between pure water and water in a CO\textsubscript{2} solvated environment has been done to evaluate the affect of the addition of CO\textsubscript{2} on the water structure. Both systems are at 23 °C. The pure water system is at 1 atm and the CO\textsubscript{2} solvated system is at 15 atm. The different pressures used for acquiring the pure and solvated spectra will not be of major consequence as the mole fraction ratio of water is 1.01. The stretching region, Figure 3.13a, is fit with three peaks at 3291 cm\textsuperscript{-1}, 3459 cm\textsuperscript{-1}, and 3640 cm\textsuperscript{-1}. The peak at 3291 cm\textsuperscript{-1} is attributed to the symmetric vibrational modes from the four oscillating dipoles associated with four-coordinate, hydrogen-bonded water molecules.
The peak at 3459 cm\(^{-1}\) is attributed to the more asymmetrically oscillating dipoles from four-coordinate hydrogen-bonded water molecules, and one hydrogen is a poor hydrogen bond donor. The peak at 3640 cm\(^{-1}\) is assigned to the modes associated with three-coordinate asymmetrically hydrogen-bonded water molecules where one OH bond is involved in strong hydrogen bonding and the other is weakly hydrogen-bonded.\(^{53}\) The peak at 1600 cm\(^{-1}\) (Figure 3.13b) is attributed to the bending mode of H-O-H. In the case of solvated CO\(_2\), the stretching and bending region are both identical in peak position and intensity to that of pure water. The stretching region remains unchanged during the addition of CO\(_2\), suggesting that CO\(_2\) does not form hydrogen bonds with H\(_2\)O molecules.\(^{54}\)

### 3.6 Ice vs. Clathrate

A study was done to investigate the CO\(_2\) clathrate structure. Hexagonal ice, which forms at the same conditions that were used to form clathrates, will be used to compare structures. Both systems were at -17 \(^\circ\)C. The CO\(_2\) clathrate spectrum was acquired at 15 atm while hexagonal ice was at 1 atm. The different pressures used for acquiring the Ih and clathrate spectra will not be of major significance as the mole fraction ratio of water is 1.01. Figure 3.14a show peaks at 3148 cm\(^{-1}\), 3265 cm\(^{-1}\), and 3379 cm\(^{-1}\). The 3148 cm\(^{-1}\) peak dominates the O-H stretching region of Ih. This peak is assigned to H\(_2\)O molecules with symmetric stretch vibrations that are all in-phase with each other.\(^{46,55}\) This peak is attributed to the companion OH to the “free OH.”\(^{54}\) In addition, the 3265 cm\(^{-1}\) is attributed to the in-phase O-H stretching motions of a hydrogen bonded aggregate consisting of a central H\(_2\)O molecule and its nearest neighbors while the 3379 cm\(^{-1}\) is attributed to the O-H stretching motions of the H\(_2\)O molecules that lost
the phase relationship. The bending region (Figure 3.14b) shows no significant peak attributed to the bending mode. The stretching and bending region of the CO\textsubscript{2} clathrate are both identical in peak position and intensity to that of I\textsubscript{h}. There is no significant difference between the two spectra.

The absence of the bending mode at 1600 cm\textsuperscript{-1} in Figure 18b is due to a mixing of the bending mode of H\textsubscript{2}O and the overtone of the librational mode. The librational mode increases significantly with increasing hydrogen bond strength unlike that observed for the symmetric stretch. This indicates the hydrogen bonds of the water structure in the solvated phase strengthen when transitioning to CO\textsubscript{2} clathrates.
Figure 3.1: The Raman spectrum of CO$_2$(g). The SS-FD is at 1308 cm$^{-1}$ and the 2$\nu_2$-FD is at 1410 cm$^{-1}$. The hot bands are at 1286 cm$^{-1}$ and 1433 cm$^{-1}$. 
Figure 3.2: The Raman spectra of a 3.0 M KHCO₃ solution compared to CO₂(aq) at 7 atm. The peak at 1165 cm⁻¹ is an artifact of the silica cell window. There are two bands associated with the Fermi diad of CO₂(aq) at 1275 cm⁻¹ and 1382 cm⁻¹. The broad band at 1630 cm⁻¹ is due to the bending mode of H₂O. The band at 1014 cm⁻¹ is the C-OH stretch of HCO₃⁻, at 1061 cm⁻¹ is the C=O SS of CO₃²⁻, at 1300 cm⁻¹ is the C-OH bending mode of HCO₃⁻, and at 1359 cm⁻¹ is the C=O SS of HCO₃⁻.
Figure 3.3: Raman spectra showing the growth of the aqueous CO₂ Fermi diads when exposed to H₂O. The peaks increase rapidly with initial exposure. Equilibrium is reached after 7 hours. The spectra are acquired at 23 ± 2 °C and a pressure of 15 atm.
Figure 3.4: The CO$_2$(g) spectrum after adjusting the intensity by the concentration ratio of 1.32. The original CO$_2$(aq) spectrum is shown.
Figure 3.5: Analysis of the $2\nu_2$-FD of CO$_2$ upon exposure to H$_2$O as a function of time: (a) is the peak area and (b) is the peak intensity as a function of time.
Figure 3.6: A comparison of solvated CO$_2$ and CO$_2$ clathrate spectra. The solvated CO$_2$ Fermi diad peak positions are highlighted with a dotted line to guide the eye to the peak shift that occurs when clathrates form. The solvated CO$_2$ spectrum is acquired at 15 atm and 23 ± 2 °C. The CO$_2$ clathrate spectrum is acquired at 15 atm and -17 ± 2 °C.
Figure 3.7: Spectral fits of the Raman spectra at various conditions during the 3600 min (3 day) experiment. The fits were used to determine the FWHM and peak shift data. The time range shown. Component peaks are shown in green as are the calculated fits. Raw data are shown as black circles.

Continued
Figure 3.7 Continued
Figure 3.7 Continued
Figure 3.7 Continued

![Graphs showing Raman spectroscopy data at different times: 2900 min, 3030 min, 3210 min, and 3490 min.](image-url)
Figure 3.8: (a) SS-FD shift and (b) $2\nu_2$-FD shift analysis while adjusting the temperature and pressure conditions. The shifts shown were taken over a period of 3600 min (3 days).
Figure 3.9: FWHM analysis of the Fermi diads in the clathrate and solvated phase while adjusting the temperature and pressure conditions. The FWHM shown are taken over a period of 3600 min (3 days).
Figure 3.10: Raman spectra of solvated CO$_2$ and CO$_2$ clathrates. The black dotted lines are located at the solvated CO$_2$ peak positions to show the peak shift associated with clathrate formation.
Figure 3.11: Raman spectra of solvated CO$_2$ and CO$_2$ clathrates. The spectra are acquired at 15 atm and $23 \pm 2$ $^\circ$C and $-17 \pm 2$ $^\circ$C, respectively. The black dotted lines show the peak shift with respect to the solvated CO$_2$ spectrum. (a) A volume of 75 mL of nano-pure water is used. In (b), the solution was stirred continuously.
Figure 3.12: (a) The formation of CO$_2$ clathrates from solvated CO$_2$ as a function of time. The arrows show the decrease in intensity while the system is cooling to a clathrate temperature. (b) The formation of CO$_2$ clathrates once formation begins.
Figure 3.13: Water spectra in the pure and solvated environments. (a) The stretching region of water; (b) The bending region of water, including the CO$_{2aq}$ Fermi diads. Both spectra for (b) are offset.
Figure 3.14: Spectra of hexagonal ice and clathrates. (a) The stretching region of water; (b) The bending region of water including the CO$_2$(aq) Fermi diads. Both spectra are offset in (b).
Table 3.1: Vibrational assignments of KHCO₃ in aqueous solution and CO₂ in the gas, aqueous, and clathrate phases

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<th>Frequency (cm⁻¹)</th>
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<td>2ν₂-FD; fermi diad of CO₂(g)</td>
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<tr>
<td>1382</td>
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<td>2ν₂-FD; fermi diad of CO₂(c)</td>
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<tr>
<td>1014</td>
<td>C-OH stretch of HCO₃⁻</td>
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Table 3.3: The calculated values of the gas, clathrate, and solvated phases of the observed frequency separation of the two Fermi diads (X), the separation of the unperturbed vibrational levels (Δ), the unperturbed symmetric stretch (ν₁), and the unperturbed bending mode (ν₂).

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<th>SS-FD cm⁻¹</th>
<th>2ν₂-FD cm⁻¹</th>
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Table 3.2: The FWHM of the SS-FD and 2ν₂-FD in the gas, clathrate, and solvated phases.

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<th>Δ cm⁻¹</th>
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Table 3.3: The calculated values of the gas, clathrate, and solvated phases of the observed frequency separation of the two Fermi diads (X), the separation of the unperturbed vibrational levels (Δ), the unperturbed symmetric stretch (ν₁), and the unperturbed bending mode (ν₂).
Table 3.4: Calculated values for the Fermi diads of CO$_2$ for the peak position, peak area, and peak FWHM for the SS-FD and $2v_2$-FD. The Voigt fit function is used.

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The Fermi diads of CO$_2$ were investigated in the aqueous and clathrate phases using Raman spectroscopy. As CO$_2$ clathrates form from the aqueous phase, the Fermi diads are observed to shift by ~1 cm$^{-1}$. This shift is evidence that the CO$_2$ vibrational modes, such as symmetric stretch and bending modes, are affected by the formation of the clathrate cage. In addition, the Fermi diads shift closer together because the SS-FD blue-shifts and the 2$\nu_2$-FD red-shifts. These shifts indicate the bonds involved in the symmetric stretch become stronger with clathrate formation while the bending mode shows the CO$_2$ molecule is less hindered by the surrounding H$_2$O molecules.

The small shift illustrates the intermolecular interactions between the CO$_2$ molecule and H$_2$O molecules are weak. Hydrogen bonding would result in a larger shift than was observed. Therefore, the small shift supports van der Waals forces as the sole force for preventing the clathrate cage from collapsing.

The bending mode and stretching region of H$_2$O were evaluated using Raman spectroscopy to examine the effect of the addition of CO$_2$ under solvated and clathrate conditions. The bending mode and stretching region in pure H$_2$O and the aqueous phase were both similar in intensity and peak position. The “free OH” band remains unchanged
in the solvated system suggesting no hydrogen bonding occurs between H₂O and CO₂ molecules.

The bending mode and stretching region in hexagonal ice and the clathrate phase were both similar in intensity and peak position. A stronger hydrogen bonding network is found in hexagonal ice compared to pure H₂O. Therefore, the similar structures of the two regions show that the CO₂ clathrate cages consist of a stronger hydrogen bonded network than the CO₂ aqueous phase.

Although the majority of these results have been reported in the literature previously, these experiments are unique because they have been conducted under different experimental conditions. Most of the literature investigates the region at temperatures of 0 °C and higher using very high pressures of up to GPa. The coexistence region of the CO₂ phase diagram is another region of great interest in the literature. The conditions in this study are unique because they are well within a three-phase region while still using ambient temperatures and pressures. Another important difference between the current literature and these results is the cell setup. Several cell setups use a cooling rod in the center of the cell that is kept cooler than the surrounding solution. The formation of clathrates initiates on the cooling rod instead of growing throughout the solution. This method significantly decreases the scatter associated with a crystallized substance resulting in a more accurate quantitative analysis of the sample.

Continued analysis of CO₂ clathrates is needed, as many details of the kinetics of formation and dissociation are still unknown. In addition, the sequestration of CO₂ in the ocean via storage of CO₂ clathrates requires accurate information regarding the effect of CO₂ clathrates when mixed with salt solutions. Natural oceanic occurrences such as
earthquakes and currents will affect the CO$_2$ clathrate stability and could cause uncontrollable clathrate dissociation. Therefore, it is of vital importance to continue studying CO$_2$ clathrates to make an informed assessment of the effects sequestration of CO$_2$ will have on the environment.
CHAPTER 5

HENRY’S LAW

5.1 Introduction

Being the second largest contributor to the greenhouse effect, CO₂ significantly impacts the environment. With a rise of anthropogenic CO₂ predicted throughout the coming years, it is necessary to find a solution to decrease CO₂ in the atmosphere. It has been suggested that sequestering CO₂ in the oceans could be a solution for the high concentration of anthropogenic CO₂. For this to occur, the CO₂-water system must be thoroughly understood for these methods to be successfully applied. The solubility of CO₂ in water is an important parameter when considering the disposal of CO₂ in the oceans. Therefore, reliable solubility information, such as Henry’s law constants, must be obtained over a wide range of pressures and temperature conditions before CO₂ can be stored in the oceans.

The Henry’s law constant describes the partitioning of a species between the gas and the aqueous phases (Figure 5.1). Henry’s law is described in terms of pressure and concentration in Equation 5.1.

\[ [X]_{aq} = H \cdot P_x \]  

(5.1)
When X is a gas, \([X]_{\text{aq}}\) is concentration of the gas in solution. \(H\) is the Henry’s law constant in units of \(\text{M/atm}\), and \(P_x\) is the partial pressure of the gas phase at equilibrium. In general, the most soluble gases have a Henry’s law constant of \(10^5\ \text{M/atm}\) while insoluble gases have a Henry’s law constant of \(~10^{-3}\ \text{M/atm}\).\(^{60}\) However, \(\text{CO}_2\) can react further to produce the ionic species as shown in the following reactions. These reactions allow larger concentrations of \(\text{CO}_2\) to be taken up into solution. Most importantly, Henry’s law is only valid for systems at equilibrium.\(^{60,61}\)

\[
\begin{align*}
\text{[1]} \quad & \text{CO}_2(\text{g}) \leftrightarrow \text{CO}_2(\text{aq}) \\
\text{[2]} \quad & \text{CO}_2(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3(\text{aq}) \quad \text{\(K_{\text{eq}} \approx 1.3 \times 10^{-3}\)}} \\
\text{[3]} \quad & \text{H}_2\text{CO}_3(\text{aq}) \leftrightarrow \text{H}^+_{(\text{aq})} + \text{HCO}_3^{-_{(\text{aq})}} \quad \text{\(K_{a1} = 2.00 \times 10^{-4}\)}} \\
\text{[4]} \quad & \text{HCO}_3^{-_{(\text{aq})}} \leftrightarrow \text{H}^+_{(\text{aq})} + \text{CO}_3^{2-_{(\text{aq})}} \quad \text{\(K_{a2} = 4.69 \times 10^{-11}\)}} 
\end{align*}
\]

5.2 Experimental Setup

A 532 nm continuous wave (CW) laser (Spectra-Physics, Millennia II, \(~95\ \text{mW}\)) was used to obtain the Raman spectra. A fiber optic probe (InPhotonics, RP 532-05-15-FC) both delivers the laser excitation source to the sample and collects the scattered light. A 200 \(\mu\text{m}\) collection fiber optic (InPhotonics, Inc.) delivers the scattered light to the entrance slit of a 500 mm monochromator (Acton Research, SpectraPro 500i). A 1200 g/mm grating blazed at 1 \(\mu\text{m}\) was used. The slit width was set to 50.0 \(\mu\text{m}\). A liquid nitrogen cooled CCD camera (Roper Scientific, LN400EB, 1340 x 400 pixel array, back-illuminated and deep depletion CCD) collected the data. The CCD was calibrated using the 435.83 nm line of a fluorescent lamp. The 1382 \(\text{cm}^{-1}\) peak of a crystalline naphthalene spectrum was used to calibrate the wavenumber position by comparing the
observed position to literature values. Data collection and display were performed using the SpectraSense software (Acton Research, version 4.2.9).

A stainless steel cell (volume of 200 mL) was filled with 100.0 mL nano-pure H$_2$O (18.2 MΩ•cm). A pressure transducer (MKS Baratron pressure transducer, 10,000 torr) was attached to the cell lid and the pressure was read from a digital recorder (MKS PDR2000 Dual Capacitance Manometer). The solution was stirred during the course of the experiment. A thermister was attached to the outside of the cell, and heat tape was placed around the cell. A digital controller (Wattow 96) was used to control the temperature of the cell. When the desired temperature was achieved, the pressure was recorded. This pressure was used as the partial pressure of H$_2$O in the cell.

A calibration curve was used to relate the peak area of the CO$\textsubscript{2}$ Fermi diad to the concentration of CO$\textsubscript{2}$ in solution at 30 ± 2 °C. The following experimental setup was used. When 100 mL of water reached the desired temperature, the partial pressure was recorded. CO$_{2(g)}$ (99.9% purity) was then bubbled into the cell. The cell was allowed to reach equilibrium before the pressure was increased. Equilibrium was observed in the system when the intensity of the Fermi diads leveled off. At each new pressure, the system reached equilibrium after 60 min. The pressure was increased during the experiment from 6 to 12 atm. Spectra were acquired every 10 min with a 6 min acquisition time.

5.3 Henry’s Law

The temperature of the system was varied from 27 to 80 °C to determine the Henry’s law constant. Prior to introducing CO$_2$ into the cell, the water reached a desired temperature and the pressure was recorded. At this time, 5 atm of CO$_{2(g)}$ was added to
the cell. When the system reached equilibrium (the intensity of the Fermi diads remained constant for 60 min), the pressure was recorded. Upon achieving equilibrium, the pressure was again increased. Raman spectra were taken as previously described. The pressure was adjusted from 5 to 13 atm during the experiment. A 6 min integration time was used to acquire all spectra and a spectrum was obtained every 10 minutes. Each data point in the graphs shown in Figure 5.3 is an average of 3 to 6 spectra. The Raman areas and the standard deviations of the averages are shown in Table 5.1.

5.4 Data Analysis

All spectra were evaluated using Igor Pro (Wavemetrics, Version 4.0.5.1). A graphing macro (Appendix C), written by Dr. Laura Voss and Lisa Van Loon of the Allen lab, loaded individual spectra into one graph and table. The spectra were fit with a Voigt function, and the peak area of the $2\nu_2$-FD was determined. The $2\nu_2$-FD was chosen for analysis because it has a large S/N at all pressures used in the experiment. The peak areas of spectra acquired for a given pressure and temperature were averaged to determine the peak area for that pressure.

5.5 Results

Quantitative analysis of Raman spectra relates the concentration of a species to the Raman intensities and areas of a corresponding peak. The relation between Raman intensity and concentration of molecules in a sample are shown in Equation 5.2-5.3.28

$$I = N_i \sigma(v_{ex}) v_{ex}^4 E_0 e^{-E_i/kT}$$  \hspace{1cm} (5.2)
The intensity of Raman scattering $I$ is described by $\sigma(\nu_{\text{ex}})$, the Raman cross section in cm$^2$, $\nu_{\text{ex}}$ is the frequency of the excitation source, $N_i$ which is the number density in state $i$, and the exponential term, $e^{-E_i/kT}$, is the Boltzmann factor for state $i$. The Raman intensity is also directly proportional to the source of irradiance, $E_0$. The intensity is directly proportional to the number density $N_i$ of the species of interest.$^{28,31,36}$ This means the concentration of the species being probed, i.e. aqueous CO$_2$, can be determined by the peak intensity. For this study, a calibration curve is used to relate the concentration of a species to the Raman area.

The calibration curve (Figure 5.2) was determined using the peak area of the $2\nu_2$-FD at $30 \pm 2 \degree$C. Table 5.2 shows the determined values for the Raman area and the standard deviation for the $2\nu_2$-FD. The partial pressure of CO$_2$ was determined by assuming the partial pressure of H$_2$O was the pressure recorded prior to addition of CO$_2$ in the cell. All recorded pressures were corrected for the partial pressure of H$_2$O. An average of known Henry’s law constants at $30 \degree$C$^{62,63}$ was substituted into Equation 5.1 to calculate the concentrations of CO$_2$ in solution. Henry’s law constants from the literature are shown in Table 5.6. The determined concentrations were then plotted against the corresponding peak area. The data was fit with a linear regression line as shown in Figure 5.2.

To determine the Henry’s law constant at a particular temperature, the average of the peak areas after achieving equilibrium for each pressure was calculated. Tables 5.1-5.4 show all the calculated values for the pressures as well as their corresponding deviation. The calculated spectral fits are shown in Figures 5.3-5.5. The peak area average and the CO$_2$ partial pressure were substituted into the calibration equation. The
resulting concentration of CO₂ was graphed as a function of CO₂ partial pressure (Figure 5.6). The data was fit with a linear regression. In Equation 5.1, the slope is the Henry’s law constant for a given temperature. All calculated Henry’s law constants are included in Table 5.5. The values are in good agreement with literature values, which are shown in Table 5.6.⁶²-⁶⁴

The Henry’s law constants decrease as the temperature increases. A small Henry’s law constant of 10⁻³ indicates low solubility of a gas. At all temperatures, the Henry’s law constants for CO₂ are 10⁻² M/atm indicating that CO₂ is a relatively insoluble gas. Independent of temperature, Figure 5.6 shows that the concentration of CO₂ is proportional to pressure. With an increase in pressure, the number of molecules in the gas phase increases⁶¹ resulting in more molecules striking the surface of liquid water. Therefore, the solution must take up more CO₂ molecules, resulting in an increased solubility.

5.6 Conclusion

The sequestration of CO₂ in the ocean has been proposed as a means for reducing atmospheric CO₂. However, the CO₂-H₂O system must be understood before CO₂ can be administered into the oceans for storage. One major contributor to obtaining valuable information for this system is to understand the solubility of CO₂ under deep ocean conditions by using Henry’s law. Henry’s law constants for CO₂ have been determined using Raman spectroscopy for a range of pressures from 5 to 13 atm and temperatures from 27 – 80 °C.
Figure 5.1: Diagram illustrating the transfer of a gaseous species $[X]_g$ to an aqueous species $[X]_{aq}$. The equilibrium constant ($K_{eq}$) equation is shown as well as the Henry’s law equation. $X$ is CO$_2$ and $P_x$ is the partial pressure. The solid blue line represents the gas-liquid interface.
Figure 5.2: The calibration curve used to relate the Raman area to the concentration of CO₂ molecules in solution at 30 °C. The linear fit is shown in blue. Pressures from 5 to 13 atm were used.
Figure 5.3: Spectral fits used to determine the peak area of the Fermi diad. The pressure and temperature conditions are shown. The calculated fits are in green and the raw data are shown as black circles.
Figure 5.3 Continued

- 5.39 atm, 50°C
- 10.61 atm, 50°C
- 5.32 atm, 60°C
- 11.54 atm, 60°C
- 5.96 atm, 70°C
- 10.56 atm, 70°C

Continued
Figure 5.3 Continued

5.88 atm
80 ^\circ\text{C}

10.61 atm
80 ^\circ\text{C}
Figure 5.4: The linear regression fits used to calculate Henry’s law constants. The temperature varies from 27 to 80°C.
### 27 °C

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**Table 5.1**: Fitted values for the Raman area of the 2ν₂-FD used to determine the Henry’s law constant at 27 °C. The deviations are included. The 30 °C data was used for the calibration curve as shown in Figure 5.2.
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Table 5.2: Henry’s law constants determined over a temperature range of 27 to 80 °C.

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Table 5.3: Henry’s law constants from the literature compared against calculated Henry’s law constants.
LIST OF REFERENCES


(38) Frantz, J. D. Raman spectra of potassium carbonate and bicarbonate aqueous fluids at elevated temperatures and pressures: comparison with theoretical simulations, *Chem. Geol.* **1998**, 152, 211.


(58) Portier, S.; Rochelle, C. Modelling CO₂ solubility in pure water and NaCl-type waters from 0 to 300 ºC and from 1 to 300 bar Application to the Utsira Formation at Sleipner, *Chem. Geol.* **2005**, *217*, 187.


A shift of less than two wavenumbers is what distinguishes solvated CO$_2$ vibrational modes from CO$_2$ clathrate vibrational modes. Therefore, the detection system must be very accurate. The Andor CCD camera that was originally used for the clathrate experiments has a resolution of 7 cm$^{-1}$ and does not have the accuracy needed. A more accurate system is required to verify the experimental parameters used are sufficient to form CO$_2$ clathrates. One possible way to solve this problem is to use a photomultiplier tube (PMT). A PMT has extremely high sensitivity and low noise compared to other photosensitive devices. The high sensitivity and low noise could provide a better resolution through a decrease of the slit widths. A brief discussion of the PMT follows.

A.2 PMT Background

A PMT (Figure A.1) is composed of a photoemissive cathode (photocathode), an electron multiplier (dynodes), and an electron collector (anode) in a vacuum tube. The PMT uses the photoelectric effect to convert optical photons into photoelectrons when radiation enters the photocathode. These photoelectrons are emitted and accelerated toward an increasingly more positive series of dynodes. The secondary electron emission
process that occurs at each dynode results in a “cascading effect” or amplification of electrons\textsuperscript{28,65,66}.

This amplification process results in a large charge packet at the anode for each photoelectron collected by the first dynode. By the time the electrons have left the last dynode and are collected at the anode, they have been amplified by a factor of $10^6$. This current amplification is also known as the gain\textsuperscript{28}. The gain, $\mu$, is the average number of electrons per anode pulse and depends highly on the power supply voltage, as shown in Equation 1:

$$\mu = \frac{A^n}{(n+1)^{\alpha}} \cdot V^{\alpha}$$

(1)

where $A$ is a constant, $n$ is the number of dynodes, $\alpha$ is a constant determined by the structure and material of the electrodes, and $V$ is the supply voltage. Due to the high internal gain, a PMT can detect low-level signals.

The PMT conversion efficiency or radiant sensitivity is dependent upon the photocathode material. The dynodes are made of a secondary emission material that establishes the energy threshold. If the photons entering the photocathode have energy greater than the threshold energy, the photoelectrons escape the dynodes. The production probability of photoelectrons emitted when one photon strikes the photocathode is called the quantum efficiency\textsuperscript{28} and is shown in Equation 2

$$QE = \frac{S \times 1240}{\lambda} \times 100$$

(2)

where $S$ is the cathode radiant sensitivity in A/W at a given wavelength $\lambda$ in nm. Due to its dependence on wavelength, the photocathode chosen for this experiment must have
maximum quantum efficiency at 574 nm. The cathode radiant sensitivity and quantum
efficiency of the PMT used for experiments are shown in Figure A.2.

A.3. Experimental Setup

The experimental setup is shown in Figure A.3. A 532 nm continuous wave
(CW) laser (Spectra-Physics, Millennia II) was used to obtain spectra. A fiber optic
probe (InPhotonics, RP 532-05-15-FC) was used to both deliver the laser excitation
source to the sample and to collect the scattered light. The scattered light was delivered
to the entrance slit of a 500 mm monochromator (Acton Research, SpectraPro 500i) via a
200 µm collection fiber optic (InPhotonics, Inc.). The scatter was dispersed using a 1200
g/mm grating blazed at 500 nm, and data was collected to a photomultiplier tube
(Hamamatsu Photonics, R3896, multi-alkali, side-on, UV glass window). The voltage
was supplied to the PMT via a power supply (Spectral Products, AD110B Photobyte-P).
A virtual instrument program (LabVIEW 7.1) was used to collect and display the data.
Data was evaluated using Igor Pro (Wavemetrics, Version 4.0.5.1). Section A.4
describes the procedure used to optimize the PMT detection setup.

A.4. Determining the Experimental Parameters

The PMT was calibrated using the 475.8 nm line from a fluorescent light and the
wavenumber position was confirmed by taking a spectrum of naphthalene. The peak
positions of fluorescent light and naphthalene were compared to the literature values.29
The fluorescent light spectrum was obtained using 200.0 µm entrance and exit slit widths
and a spectral range of 575 to 579 nm (Figure A.4). The 1382 cm⁻¹ peak of naphthalene
(Figure A.5) was obtained with 100.0 µm entrance and exit slit widths over a spectral range of 574 to 578 nm. A 0.01 nm step size, and a PMT integration period consisting of 1,000 scans was used for both spectra.

The gain to be used for the experiments was determined by obtaining spectra of naphthalene with 150.0 µm entrance and exit slit widths. The spectral range covered 574 to 577 nm. A 0.5 nm step size and a PMT integration period consisting of 500 scans were used. Gains of 2, 4, 8, and 16 were tested, Figure A.6. As the gain increased, the S/N ratio improved. It was concluded that a gain of 16 resulted in the best S/N and would be used for future PMT experiments.

Initial solvated CO2 spectra were obtained using a spectral region of 572 to 576 nm with a 0.20 nm step size. A PMT integration period of 1000 scans was used. A stainless steel cell was filled with 100.0 mL of nano-pure water (18.2 MΩ•cm). A pressure transducer (MKS PDR2000 Dual Capacitance Manometer) was used to verify the cell pressure was maintained at 12.73 atm. The entrance and exit slits were adjusted simultaneously to determine the appropriate slit width to be used for experiments. A solvated CO2 peak was not observed until slit widths of 500 µm were reached. (Figure A.7) A reproducible peak was not observed until 650 µm due to low S/N.

A resolution experiment was performed to determine if 650 µm slit widths provided a better resolution than the CCD camera. The resolution of the PMT was determined by using the 1382 cm⁻¹ peak of naphthalene. The step size was 0.01 nm and the spectral range covered 572 to 576 nm. A PMT integration period consisting of 1,000 scans was used. The entrance and exit slits were adjusted from 30.0 µm to 450.0 µm, simultaneously. The data was fit with a Voigt function. The FWHM of the 1382 cm⁻1
peak was determined for each slit width, Figure A.8. The FWHM was plotted as a function of the slit width. For slit widths below 50 µm, a poor fit due to low S/N resulted in inaccurate FWHM determinations. The near level slope at 5 cm⁻¹ shows the FWHM is nearly constant for several slit widths indicating this FWHM is the minimum resolution. In addition, the slope indicates a slit width below 100 µm will not improve the resolution. The 100 µm slit width was used for experiments.

Further reduction of the slit width was attempted by increasing the integration period of the PMT and by taking the average of several spectra. It was hoped that increasing the integration period and taking an average of ten to seventeen spectra would enhance the S/N. The integration period of the PMT was adjusted from 1,000 scans to 100,000 scans. For each integration period, a spectrum was acquired using a 450 µm slit width and a 0.5 nm step size. The data was fit with a Voigt function. Although increasing the integration period of the PMT improved the S/N slightly, the integration time increased from minutes to hours, Figure A.9.

Experiments were done varying the PMT integration period from 100 scans to 1,000 scans while averaging ten spectra. The experimental parameters remained the same. Standard deviations of the averages were calculated and are shown in the plots. Obtaining an average of several spectra (Figure A.10) with shorter integration periods actually improved the S/N more than just varying the integration time but still not enough to reduce the slit width.

Neither increasing the PMT integration time nor averaging the spectra decreased the slit width to the needed 100 µm indicated by the resolution study. The last experiment to decrease the slit width involved increasing the laser energy from 148 mW to 201 mW.
The slit width was set at 100 µm and a step size of 0.1 nm was used. The PMT integration was 10,000 scans and seventeen spectra were averaged. The resulting spectra indicated solvated CO₂ peaks could be observed with an input laser energy of 201 mW. Standard deviations of the averages were calculated and are shown in Figure A.11. Energies below 201 mW were insufficient at 100 µm to observe a solvated CO₂ peak.

Since such a high energy was required to obtain data, it was necessary to determine if the energy required to obtain data would destroy the sample. The CCD camera was used with a shorter integration time of 90 s due to its improved S/N. A slit width of 50 µm and a 1200 g/mm grating were used to acquire the spectrum. SpectraSense software (Acton Research, version 4.2.9) acquired spectra. An input of energies from 77 mW to 180 mW was used. The stainless steel cell was filled with 100.0 mL of nanopure water (18.2 MΩ•cm). The cell was kept at -15 ± 2 °C and allowed to freeze. During the experiment, the cell temperature was maintained while the cell was exposed to the laser for the entire experiment. The stretching region of H₂O(s) (2900–3800 cm⁻¹) was evaluated for up to three hours. A decrease in intensity of the ~3051 cm⁻¹ peak and an increase in the ~3300 cm⁻¹ peak would indicate the ice was melting. Refer to Chapter 3 for vibrational assignments. However, even at the highest energy the shape of the peaks did not change for three hours indicating the laser energy was not sample destructive, Figure A.12.

A.5. Conclusion

Data obtained with the PMT and LabVIEW VI is reproducible and indicates the PMT setup works correctly. However, the resolution was not improved over the use of
the Roper Scientific CCD camera. The Roper Scientific monochromator with CCD camera will be used in future experiments.
Figure A.1: Diagram of the R3896 PMT with a closeup of the dynodes. (www.sales.hamamatsu.com)
Figure A.2: The cathode radiant sensitivity (blue) and the quantum efficiency (red) of the R3896 PMT at 574 nm. (www.sales.hamamatsu.com)
Figure A.3: Schematic of PMT Raman setup: (a) computer; (b) Spectra-Physics Millenia II laser; (c) stainless steel cell; (d) gas inlet valve; (e) gas outlet valve; (f) fiber optic Raman probe; (g) monochromator; (h) photomultiplier tube; (i) AD110B power supply; (j) A/D connector; (k) MKS PDR2000 Dual Capacitance Manometer; (l) pressure transducer. The inset shows a picture of the R3896 PMT. (www.sales.hamamatsu.com)
Figure A.4: Spectrum of fluorescent light showing the 577 and 579 nm lines obtained with a 200 µm slit width, a 0.01 nm step size, and a PMT integration period consisting of 1000 scans. The spectral fit is shown in blue.
Figure A.5: Spectrum of naphthalene showing the 1382 cm\(^{-1}\) peak. The spectrum was obtained using a 100 µm slit width, a 0.01 nm step size, and a PMT integration period consisting of 1000 scans. The spectral fit is shown in blue.
Figure A.6: Naphthalene spectra were evaluated with varying gains, a 0.5 nm step size, and a PMT integration period consisting of 500 scans. The red lines indicate the 1390 and 1465 cm\(^{-1}\) peaks. As the gain increased, the S/N increased. The data are offset for easier observation.
Figure A.7: Solvated CO$_2$ spectra acquired using the PMT while varying the entrance and exit slits, simultaneously. A PMT integration period consisting of 1000 scans and a 0.2 nm step size was used to acquire spectra. The red line highlights the solvated CO$_2$ peak position at 1390 cm$^{-1}$. The data are offset for easier observation.
Figure A.8: The FWHM of the 574 nm line of napthalene as a function of the slit width. Resolution was determined from the plot. Spectra were obtained using a 0.01 nm step size and a PMT integration period consisting of 1000 scans. The near level slope (red) indicates the minimum resolution of the PMT while the positive slope (black) indicates the resolution at other slit widths.
Figure A.9: Spectra of the solvated CO$_2$ peak obtained with a 450 um slit width and a 0.5 nm step size with PMT integration periods consisting of (a) 1,000, (b) 50,000, and (c) 100,000 scans. The spectral fit is shown in blue.
Figure A.10: Spectra of solvated CO$_2$ determined by averaging 10 spectra using different PMT integration periods consisting of (a) 100 Scans, (b) 500 Scans, and (c) 1,000 Scans. The spectra were obtained with a 450 um slit width and a 0.5 nm step size. The fits are shown in blue. Standard deviation error bars of the average are shown.
Figure A.11: Spectra of solvated CO₂ obtained with a PMT integration period consisting of 10,000 scans and an average of 17 spectra was used at laser energies of (a) 148 mW and (b) 201 mW. The spectra were obtained with a slit width of 100 um and a step size of 0.1 nm. The standard deviation error bars of the average are shown. A solvated CO₂ peak is observed in (b) only, and its spectral fit is shown in blue.
Figure A.12: The stretching region of H$_2$O$_{la}$ exposed to (a) 77 mW and (b) 180 mW laser energy for up to 3 hours. The spectra were obtained with the CCD camera with an integration time of 90 s, a 1200 g/mm grating, and a 50 um slit width.
APPENDIX B

PHOTOMULTIPLIER TUBE LABVIEW 7.1

B.1. Introduction

This appendix describes the LabVIEW 7.1 VI program used to obtain Raman spectra using a photomultiplier tube with a monochromator. The 500i PMT VI program allows communication between two instruments, the Spectral Products AD110B Photobyte-P PMT Detection System and the SpectraPro 500i Monochromator. This program is designed to easily obtain a spectrum by utilizing a scan setup with continuous data acquisition. A time delay is used to control the number of scans obtained at a set collection frequency. All spectra are individually saved as a dat file.

This LabVIEW VI program is a modified version of the one originally written by Gibum Kim and Paul Cremer from Texas A&M University. Dr. Dingfang Liu of the Allen Lab modified the LabVIEW VI program for using the AD110B Photobyte-P PMT detection system with other instruments in the laboratory. Modifications for use with the 500i monochromator were done with the assistance of Chris Beekman of the Allen Lab. An AD110B VI program developed by Spectral Products was modified and inserted into the 500i PMT VI program. Acton Research supplied the monochromator drivers.
B.2. Using the 500i PMT VI

This section explains the steps that must be followed to accurately collect data with the 500i PMT VI program. The monochromator must be turned on before opening the program, or it will not be recognized by the program.

1. Open SpectraSense. Go to Hardware Setup. The mirror position must be changed so the light is directed into the PMT instead of the CCD camera. On the monochromator image, two exit slits will be observed. Click on the exit slit that corresponds to the PMT. A click will be heard in the monochromator. The arrow direction will appear as shown in Figure B.1. To return to the CCD camera, click on the corresponding exit slit, and the arrow direction will appear as shown in Figure B.2.

2. Select appropriate grating.

3. Manually open the entrance slit by placing a checkmark in the box beside open.


5. Open 500i PMT VI. The Front Panel is shown in Figure B.3. The Block Diagram is shown in Figure B.4.

6. Press the stop button on the navigation bar on the Front Panel because the program automatically runs when opened.

Front Panel Setup for the 500i PMT VI

All white boxes on the Front Panel require user input.
1) SCAN SETUP

7. Verify the Scan Mode is set at Scan. The 500i PMT VI program is designed to halt data collection if set at Fixed.

8. Enter the starting wavelength in Begin nm. Enter the final wavelength in End nm. The scan is designed to stop one wavelength past the End nm.

9. Indicate the number of scans to be obtained per nm in Scans per nm.

10. Enter the step increment to be used in nm steps, i.e. if 10 points per nm is needed, enter 0.10.

11. Enter the number of scans to be obtained in Scans to run.

12. The Scan Delay is used to prevent continuous running of the program. Insert the time (in milliseconds) between scans.

2) FILE SETUP

13. Under Directory, enter where the data is to be stored. The C drive is best for the programs used to display the data. Also, include the common name of the spectra, i.e. C:\Ashley\napth where “C:\Ashley” is the location and “napth” is the common name of the spectra.

3) PMT SETUP

14. The Gain may be adjusted to whatever gain the user desires. The default is set at x2, but x16 is recommended.

15. Set the Voltage Setting to ~900 V. The maximum voltage is dependent upon the PMT used. With the R3896 PMT, the maximum is 1000 V.

16. Under Scans, indicate the number of scans.

17. Open the laser shutter and turn on the PMT power supply.
18. Press the single arrow on the navigation bar at the top of the *Front Panel* to begin the scan.

**Running 500i PMT VI Program**

An update box is located between the *PMT SETUP* and the *SCAN CONTROL* boxes. A number of gray boxes, or indicators, verify the program is correctly controlling the monochromator. These indicators are vital to the program so a description follows:

19. *Points* indicates how many data points will be taken and plotted for each scan.

20. *Set Mono Wavelength* indicates at what wavelength the monochromator grating has been set. At the beginning of each scan, it will default to the begin nm and will auto-increment by the number entered in *nm steps*.

21. *Current NM* is the wavelength to which the monochromator is set. This is to verify the monochromator is working correctly and is vital to the program. If a –1.000 is observed instead of the number inserted into *Set Mono Wavelength*, the monochromator is not communicating effectively. The computer may need to be rebooted and/or the monochromator turned off.

22. *Elapsed Time* indicates the duration of the scan.

23. *Scans Completed* keeps the user informed of the progress of the scans.

24. The *Actual PMT Voltage* shows the voltage of the PMT after the scan is completed.

25. *Data* shows the signal voltage values.

26. *AVG* is the data point to be plotted for that wavelength. It is the average of all the PMT scans (i.e. 1000) and should correspond to the voltage from *Data*. 
Figure B.1: SpectraSense monochromator diagram showing the laser path is towards the PMT.
Figure B.2: SpectraSense monochromator diagram showing the laser path is towards the CCD camera.
Figure B.3: Front Panel of the 500i PMT VI
Figure B.4: Block diagram of the 500i PMT VI
C.1. Introduction

This appendix describes the Igor Pro (Wavemetrics, Version 4.0.5.1) macro used to analyze the Raman spectra acquired using SpectraSense (Acton Research, Version 4.2.9). The Raman macro was written by Lisa Van Loon of the Allen Lab to use with SpectraSense. The macro is designed to load individually saved spectra into one graph and table. Background subtracted spectra is provided as an option.

C.2. Using the Raman Macro

This section explains the steps that must be followed to accurately graph spectra.

1) Selecting Procedure

1. Open IgorPro. Go to File.

2. Go to Open File.


5. Select Raman.ipf.

6. Set limM equal to number of spectra minus one.

2) Napthalene Spectrum
7. Specify the file location where spectra are stored in *NewPath/O path* “_”, i.e. “C:Ashley:08.10.06:”. Colons are used to separate files.

8. For *filename*, insert the default name SpectraSense is using. Use the naphthalene spectrum, i.e. "napth.arc_data"

3) Raw Data

9. Specify the file location where spectra are stored in *NewPath/O path* “_”, i.e. “C:Ashley:08.10.06:”. This should be the same location as naphthalene.

10. For *basefile*, indicate the common file name. This name is set in SpectraSense before acquisition, i.e. “clathrate1”

11. For *filename*, insert the default name used by SpectraSense. Use only the initial spectra, i.e. "clathrate1_001_Area01.arc_data"

4) Running the Raman Macro

12. To run macro, type `Raman()` into the command line of the command window.

13. Press *Enter*.

5) Background Subtraction Option

14. Repeat Step B. Use the background file instead of the naphthalene file.

15. Repeat Step C.

16. Delete the “//” inserted in the macro command: `wave1=wave1// - bkgd`

17. Repeat Step D.

The Raman macro written to analyze spectra acquired with SpectraSense is shown below:

```c
#pragma rtGlobals=1            // Use modern global access method.
#include <Waves Average>

Macro raman()
```
Silent 1

KillWaves/A/Z

string filename, wave0name, wavenumbers, basefile, xaxisname, bkgdcorrected
string numstring

variable /g m, limM

m = 0
limM = 100 // number of sample spectra minus one

NewPath/O path "c:ashley:08.10.06:" // specify file location
filename = "naphth.arc_data" // specify background file name
LoadWave/G/A/P = path filename

Rename wave0, wavenumbers
Rename wavel, bkgd

Edit wavenumbers, bkgd // starts table
Display bkgd vs wavenumbers as "bkgd"

NewPath/O path "c:ashley:08.10.06:" // specify file location
basefile="clathrate1" // specify the common file name
filename = "clathrate1_001_Area01.arc_data" // change this to match the data file name Raman: loading the initial spectrum
LoadWave/G/A/P = path filename

do
sprintf numstring, "%03d", (m+1)
filename = basefile + "_" + numstring + "_Area01.arc_data"
LoadWave/G/A/P = path filename

wave1=wave1// - bkgd // to load waves with no bkgd correction remove - bkgd

wave0name = basefile + num2str(m+1) + "cm-1"
wavelname = basefile + num2str(m+1) + "au"

Rename wave0, $wave0name
Rename wavel, $wavelname

AppendtoTable $wavelname

if (m == 0) then
Display $wavelname vs wavenumbers as "data"
else

Append $wavelname$ vs wavenumbers

endif

ModifyGraph rgb($wavelname$)=(10000,5000,m*100)

ModifyGraph tick(left)=2,mirror(left)=1,minor(left)=0,notation(left)=1
ModifyGraph font(left)="Arial"
Label left "Intensity (A.U.)"
ModifyGraph tick=2,mirror=1,minor=0,font="Arial"
Label bottom "Raman Shift (cm\S-1\M)"
ModifyGraph minor=1
SetAxis bottom 1200, 1500

m = m + 1

while (m<limM)

end