Soret Effect Study on High-Pressure CO₂-Water Solutions Using UV-Raman Spectroscopy and a Concentric-Tube Optical Cell

CF Windisch Jr.
BP McGrail
GD Maupin

January 2012
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062;
ph: (865) 576-8401
fax: (865) 576-5728
email: reports@anl.gov

Available to the public from the National Technical Information Service
5301 Shawnee Rd., Alexandria, VA 22312
ph: (800) 553-NTIS (6847)
email: orders@ntis.gov <http://www.ntis.gov/about/form.aspx>
Online ordering: http://www.ntis.gov

This document was printed on recycled paper.
(9/2010)
Soret Effect Study on High-Pressure CO$_2$-Water Solutions Using UV-Raman Spectroscopy and a Concentric-Tube Optical Cell

CF Windisch Jr.
BP McGrail
GD Maupin

January 2012

Prepared for
the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99352
Spatially resolved deep-UV Raman spectroscopy was applied to solutions of CO$_2$ and H$_2$O (or D$_2$O), which were subject to a temperature gradient in a thermally regulated high-pressure concentric-tube Raman cell in an attempt to measure a Soret effect in the vicinity of the critical point of CO$_2$. Although Raman spectra of solutions of CO$_2$ dissolved in D$_2$O at 10 MPa and temperatures near the critical point of CO$_2$ had adequate signal-to-noise and spatial resolution to observe a Soret effect with a Soret coefficient with magnitude of $|S_T| > 0.03$, no evidence for an effect of this size was obtained for applied temperature gradients up to 19°C. The presence of 1 M NaCl did not make a difference. In contrast, the concentration of CO$_2$ dissolved in H$_2$O was shown to vary significantly across the temperature gradient when excess CO$_2$ was present, but the results could be explained simply by the variation in CO$_2$ solubility over the temperature range and not to kinetic factors. For mixtures of D$_2$O dissolved in scCO$_2$ at 10 MPa and temperatures close to the critical point of CO$_2$, the Raman peaks for H$_2$O were too weak to measure with confidence even at the limit of D$_2$O solubility.
Acknowledgments

This work was supported by the U.S. Department of Energy (DOE), Office of Fossil Energy. The Pacific Northwest National Laboratory (PNNL) is operated by Battelle for the DOE under Contract DE-AC05-76RL01830.
# Acronyms and Abbreviations

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BBO</td>
<td>beta barium borate</td>
</tr>
<tr>
<td>cm</td>
<td>centimeter</td>
</tr>
<tr>
<td>CO₂</td>
<td>carbon dioxide</td>
</tr>
<tr>
<td>D₂O</td>
<td>heavy water</td>
</tr>
<tr>
<td>H₂O</td>
<td>water</td>
</tr>
<tr>
<td>mm</td>
<td>millimeter</td>
</tr>
<tr>
<td>MPa</td>
<td>megapascals</td>
</tr>
<tr>
<td>NaCl</td>
<td>sodium chloride</td>
</tr>
<tr>
<td>scCO₂</td>
<td>supercritical carbon dioxide</td>
</tr>
<tr>
<td>µm</td>
<td>micron</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>ZERT</td>
<td>Zero Emissions Research and Technology</td>
</tr>
</tbody>
</table>
Contents

Abstract ................................................................................................................................................. iii
Acknowledgments ........................................................................................................................................ iv
Acronyms and Abbreviations ................................................................................................................. v
1.0 Introduction .................................................................................................................................. 1
  1.1 Overall program objective ........................................................................................................ 1
  1.2 Summary of ZERT I results .................................................................................................... 2
  1.3 Justification and description of approach for ZERT II .......................................................... 2
2.0 Experimental Procedure ............................................................................................................... 4
  2.1 Concentric-tube Raman cell design .................................................................................. 4
  2.2 UV-Raman spectrometer .................................................................................................... 7
  2.3 Typical experiment and variables ..................................................................................... 8
3.0 Results .......................................................................................................................................... 11
  3.1 Assessment of Raman cell .................................................................................................... 11
    3.1.1 Position of the microscope objective vs. focal point of the measurement ............. 11
    3.1.2 Estimate of sampling volume ................................................................................... 12
  3.2 Raman spectra ...................................................................................................................... 12
    3.2.1 Experiments on D2O containing CO2 below saturation ........................................ 12
    3.2.2 Experiments on D2O + 1 M NaCl containing CO2 below saturation .................. 17
    3.2.3 Varied pressure study .............................................................................................. 18
    3.2.4 H2O containing CO2 at saturation .......................................................................... 19
    3.2.5 scCO2 containing D2O at saturation ...................................................................... 20
4.0 Discussion ..................................................................................................................................... 22
  4.1 Solutions of CO2 in D2O with CO2 below saturation ............................................................ 22
  4.2 Solutions of H2O saturated with CO2 ................................................................................ 23
  4.2 Concentration calibration plots ........................................................................................... 25
5.0 References .................................................................................................................................... 27
Figures

Figure 1. Simplified schematic of concentric-tube Raman cell. .......................................................... 3
Figure 2. Concentric-tube Raman cell in cross-section showing thicknesses of the tubes and the annuli. .................................................................................................................................................. 4
Figure 3. Comparisons of the UV-Raman spectra of H2O and D2O, at room temperature and atmospheric pressure, with the principal peaks of CO2 (Fermi dyad) also shown........................................ 5
Figure 4. Schematic of the concentric-tube Raman cell within its assembly....................................... 6
Figure 5. Photograph of the concentric-tube Raman cell assembly positioned under the UV-Raman spectrometer microscope objective.......................................................................................................................... 6
Figure 6. Images of the reflected laser light from the stainless steel tube in the center of the Raman cell, (a) with the incident light focus on the bare steel, (b) with the incident light focused on the steel with a high-temperature air-formed film (held at 600°C overnight), and (c) with the incident light focused on a “blued” steel surface................................................................................. 7
Figure 7. Photograph of the concentric-tube Raman cell assembly, UV-Raman spectrometer, and ancillary equipment.............................................................................................................................. 8
Figure 8. Total Raman scattering signal strength (from both CO2 and D2O) as a function of the position of the objective (z value). In relationship to position within the annulus, z = 0 µm corresponds to the inside surface of the sapphire tube, whereas z = 2000 µm is near the outside surface of the stainless steel tube. The photographs are white-light images at these two positions. Circles around each point indicate the approximate sampling volumes. .............................................................................. 11
Figure 9. UV-Raman spectra as a function of position within the annulus (in terms of the microscope position, z), with X(CO2) = 0.0054, T(inside) = 12°C and T(outside) = 30°C. Higher temperature is outside. The spectra were acquired in the direction of increasing z. CO2 is a liquid under these conditions.................................................................................................................................................. 13
Figure 10. UV-Raman spectra as a function of position within the annulus (in terms of the microscope position, z), with X(CO2) = 0.0027, T(inside) = 45°C and T(outside) = 33°C. The higher temperature is inside. The spectra were acquired in the direction of increasing z. CO2 is supercritical under these conditions.................................................................................................................................................. 14
Figure 11. CO2/D2O peak intensity ratio calculated from the Raman spectra as a function of position for X(CO2) = 0.0014 and 0.0027, with different temperature gradients and direction of scan. 15
Figure 12. CO2/D2O peak intensity ratio calculated from the Raman spectra as a function of position for X(CO2) = 0.0054, T(outside) = 30°C and T(inside) = 12°C, in both increasing- and decreasing-z directions.................................................................................................................................................. 15
Figure 13. CO2/D2O peak intensity ratio calculated from the Raman spectra as a function of position for X(CO2) = 0.0027 with T(outside) = T(inside) at 32°C and 40°C. Spectra were collected in the direction of increasing z. ............................................................................................. 16
Figure 14. UV-Raman spectra at two positions within the annulus with X(CO2) = 0.0027 and T(outside) = T(0 µm) = 45°C and with varying T(inside). Spectra are shown for T(inside) = T(2000 µm) = 45°C, 40°C, 35°C, 30°C, 25°C, and 20°C.......................................................................................................................... 17
Figure 15. CO2/D2O peak intensity ratio, for solutions containing 1 M NaCl, as a function of position with X(CO2) = 0.0044, and various temperature gradients. Open symbols are ratios for the same experiments as the corresponding closed symbols, but were calculated using integrated intensities from curve fitting results.................................................................................................................................................. 18
Figure 16. CO$_2$/D$_2$O peak intensity ratio, for solution with X(CO$_2$) = 0.0027 and T(inside) = T(outside) = 40°C, as a function of cell pressure.

Figure 17. UV-Raman spectra as a function of position within the annulus (in terms of the microscope position, z), for H$_2$O saturated with CO$_2$, i.e., X(CO$_2$) ~ 0.028. T(inside) = 11°C and T(outside) = 15°C. Spectra were acquired in the direction of increasing z. Spectral intensities are normalized with respect to the H$_2$O peak at 1640 cm$^{-1}$.

Figure 18. CO$_2$/( CO$_2$ + D$_2$O) peak intensity fraction calculated from the Raman spectra as a function of position, for H$_2$O saturated with CO$_2$, i.e., X(CO$_2$) ~ 0.028. Results are shown for measurements made with both increasing and decreasing z. Linear regression in the absence of the two low-z points is shown.

Figure 19. UV-Raman spectra as a function of position within the annulus for solutions of scCO$_2$ containing D$_2$O at saturation (i.e., X(D$_2$O) ~ 0.003). T(inside) = 32°C and T(outside) = 40°C.

Figure 20. Re-plot of Figure 11 showing straight lines fitted by eye to limits of error bars of the data for X(CO$_2$) = 0.0014.

Figure 21. Re-plot of Figure 17 noting intensity values at z = 0 µm and z = 2000 µm that were used to compare the observed variation with temperature to predictions based on solubility.

Figure 22. Plot of the fraction of total Raman scattering intensity attributed to CO$_2$ versus the mole fraction of CO$_2$ in the mixture as calculated from the quantities used in preparation.

Figure 23. Plot of the fraction of total Raman scattering intensity attributed to CO$_2$ versus the mole fraction of CO$_2$ in the mixture as calculated from the quantities used in preparation.
1.0 Introduction

1.1 Overall program objective

Considerable work on flow processes in CO2-water\textsuperscript{1} systems has been done in geothermal reservoir engineering. However, significant uncertainties remain with respect to mixing processes that occur in supercritical CO2-water systems, especially in porous media. For the case where supercritical CO2 is injected into a deep saline formation, the important processes to be considered include the following: (1) forced convective flow around the injection well, (2) dissolution rate of CO2 into the brine, and (3) heat of solution as CO2 dissolves into the formation brine.

As CO2 dissolves into water, the negative heat of solution consumes approximately 17 kJ/mol at typical reservoir conditions (Bastelli 1997; White 2002). Also, pipeline supply of CO2 will result in cold CO2 reaching the wellhead. Reservoir calculations suggest that temperature gradients on the order of 5 to 10°C cm\textsuperscript{-1} can easily be generated as a result. A temperature gradient induces coupled feedback effects on the rate of convective mixing in two ways: (1) through changes in physical properties (density, viscosity, surface tension) and (2) nonlinear thermal diffusion or Soret effects (Kempers 2001; Nejad 2001). The Soret effect is the tendency of a mixture of two or more components to separate under the influence of a temperature gradient. The effect is quantified by the Soret coefficient, $S_T$, which is derived by considering Fick’s law under conditions where the flux results from a combination of thermal and concentration gradients.

Empirical descriptions treat the mass flux associated with a thermal gradient, $\mathbf{j}_T$, as

$$\mathbf{j}_T = -D_T c \nabla T \quad (1)$$

where $D_T$ is the thermal diffusion coefficient of the diffusing species in the solution, $c$ is the concentration and $T$ is the temperature. It is considered a separate process from the mass flux associated with a concentration gradient, $\mathbf{j}_c$, which is given by

$$\mathbf{j}_c = -D \nabla c \quad (2)$$

where $D$ is the ordinary (mass) diffusion coefficient. Under steady-state conditions, $\mathbf{j}_T = -\mathbf{j}_c$, yielding (Duhr 2006):

$$\nabla c = -c S_T \nabla T \quad (3)$$

where $S_T = D_T/D$ and is called the Soret coefficient. In concentrated mixtures, $S_T$ is also a function of the solute concentration and can even change sign (Kolodner et al. 1988; Slavtchev et al. 1999).

\textsuperscript{1}CO2-water is the general term for the solutions studied here. Both isotopic forms of water, H\textsubscript{2}O and D\textsubscript{2}O, were used for reasons discussed in the text. For specific experiments, the form of water is called out in the notation, e.g., CO2-D\textsubscript{2}O.
Because of rapid changes in thermochemical properties near critical points (Zhang 2002) and based on independent measurements of supercritical CO₂ fluids (Swinney 1968), Soret effects have been predicted to be strong in near-critical liquids (Kempers 2001). The primary objective of the Fundamental Studies Task of Zero Emissions Research and Technology (ZERT) was to use laser Raman spectroscopy to study the Soret effect in CO₂-water mixtures across a temperature gradient near the critical point of CO₂. The proposed approach is based on other optical studies of the phenomenon (Xu 2003; Duhr 2006; Ning 2006; Koniger 2010) and the recognition that Raman spectroscopy is very sensitive to both H₂O and CO₂ under both subcritical and supercritical conditions (Cabaco 2007, 2010a, 2010b). Two specific goals of the Task were (1) to determine whether the technique can be used to substantiate thermal diffusion in CO₂-water mixtures and, if so, (2) to quantify the Soret effect as a function of conditions.

1.2 Summary of ZERT I results

In ZERT I, a specially designed high-pressure Raman cell suitable for supercritical studies with an imposed temperature gradient, specifically a 10-20°C temperature gradient across an optical window through which Raman measurements could be acquired as a function of position, was built and applied to CO₂-water mixtures over a range of experimental conditions. Results were inconclusive over the range of conditions studied. In particular, even though variations in composition (CO₂ in H₂O) were measured between the two temperatures across the cell, the magnitude of the variations was very small. Soret coefficients calculated from this data were on the order of 10⁻³, several orders of magnitude less than expected from published values of the ordinary and thermal diffusion coefficients of the components (Xu 2003; Amirkhanov 1987; Swinney 1968).

The surprisingly small values of S_T were attributed to two experimental difficulties. The first involved the design of the Raman cell, which appeared to offer insufficient thermal management under the imposed temperature gradient. The large size of the cell and its windows were speculated to induce convection currents that interfered with the measurements by evening out the concentrations across the cell. The second problem related to the range of compositions of the mixtures that were “accessible” in the study. The solubility of H₂O in scCO₂ is too low (mole fraction ~ 10⁻³) to obtain Raman spectra with sufficient S/N for quantitative measurements. On the other hand, CO₂ dissolves in liquid H₂O to a degree that is an order of magnitude higher under similar pressure and temperature conditions. Research under ZERT II addressed these difficulties as follows: (1) a new Raman cell was designed and built with a smaller volume, better spatial resolution, and improved thermal management through the use of temperature-controlled windows, and (2) measurements were largely confined to the system “CO₂ dissolved in water” under conditions where CO₂ is either liquid or a supercritical fluid.

1.3 Justification and description of approach for ZERT II

The Raman cell in ZERT II consisted of a set of three concentric tubes. The CO₂-water mixture was contained in the annulus (white region in Figure 1) between a tube of transparent sapphire on the outside, which also served part of the optical window, and an inner tube of stainless steel on the other. Temperature-controlled water circulated through the outer annulus between the sapphire tube and an outer tube of transparent quartz (blue region in Figure 1) and also through the inner stainless steel tube (red region in Figure 1). With the two water streams held at two different temperatures by external temperature controllers, a temperature gradient was established across the inner annulus containing the
A high-resolution UV-Raman microscope system was used to make the measurements in this study. The beam was focused within the bulk of a static CO₂-water solution contained in the inner annulus of the concentric-tube cell, positioned directly under the Raman microscope. As described above, the central stainless steel tube and the outer annulus contained water at near-ambient pressure circulated between two thermostatically controlled temperature baths, separated in temperature by the desired gradient for the Soret study. The result was a temperature gradient imposed across the solution in the inner annulus without the presence of thermally unregulated windows. Thermal regulation of the windows is one of the features that distinguished this design from that of the cell employed in ZERT I. The optical window consisted of the outer quartz tube, the circulating water circulating through the outer annulus, and the sapphire tube containing the CO₂-water solution.

Using the microscope, Raman spectra were collected as a function of depth, or distance between the thermally controlled walls of the inner annulus containing the CO₂-water solution. From these measurements, composition profiles (based on spectral features from CO₂ and water) within the solution and across the inner annulus were determined and, from the imposed temperature gradient, the occurrence and magnitude of the Soret effect was determined.

The depth resolution of Raman microscopes have improved significantly over the past few years, particularly with the advent of UV-Raman spectroscopy. PNNL recently acquired a Horiba Jobin Yvon LabRAM HR high-resolution UV-Raman system that was considered suitable for these measurements. This instrument, which has all reflective optics providing excellent quality Raman spectra with minimal signal distortion and resolution of +/- 2 cm⁻¹, also has distinct advantages in depth profiling. Studies on polished Si have demonstrated (Horiba Jobin Yvon Raman Application Note 2011) depth resolution of a fraction of a micrometer is achievable, depending on the excitation wavelength (shorter is better and our system uses deep-UV excitation at 244 nm), the characteristics of the material under study and the configuration of the optics, especially the size of the pinhole used for confocal measurements. In these measurements where a larger pinhole was required to achieve acceptable signal strength, we estimated a sampling volume (taken as spherical) with a diameter of about 500 µm. Although significantly poorer than anticipated, this depth-resolution was more than adequate to obtain several Raman spectra as a function of reasonable distinct distances between the two temperature reservoirs.
2.0 Experimental Procedure

2.1 Concentric-tube Raman cell design

The Raman cell used in these experiments was designed to withstand pressures of 10 MPa at temperatures up to about 45°C. This allowed measurements to be obtained on mixtures of CO₂ and water at 10 MPa (above the critical pressure of CO₂, 7.38 MPa) and temperatures in the regions below and above the critical temperature of CO₂ (31.04°C). The cell consisted of three concentric tubes: an outer tube made of quartz, a middle tube of sapphire and an inner tube of 316 stainless steel. A diagram of the configuration with dimensions of the components is given in Figure 2.

![Concentric-tube Raman cell in cross-section showing thicknesses of the tubes and the annuli.](image)

The steel tube in the center (gray in Figure 2) was used to carry constant temperature water (red in Figure 2), at T(inside), controlled by a Julabo (Vista, California) F12ED Refrigerated/Heating Circulator. The outer annulus with an outer wall of quartz (green in Figure 2) and an inner wall of sapphire (tan in Figure 2) contained water (blue in Figure 2) controlled at the second temperature T(outside) set with a separate Julabo circulator. The inner annulus contained the static mixture of CO₂ and water. It had an inner wall of steel (controlled at T(inside)) and an outer wall of sapphire (controlled at T(outside)). The dimensions of the sapphire tube were those required to withstand pressures up to 10 MPa and temperatures to 45°C. Pressure testing of the system was performed with water and nitrogen gas prior to the experiments to establish compatibility of this design with the test conditions.

In each measurement, the laser beam was imaged at different positions within the inner annulus containing the CO₂-water mixture. In this configuration, there were three components of the optical windows: (1) the outer quartz tube, (2) the thermally regulated H₂O circulating in the outer annulus, and (3) the sapphire tube. Since one of these components was H₂O, it was necessary to modify the procedure so that water in the inner annulus could be distinguished spectroscopically from water in the window. Consequently, D₂O was used in place of H₂O in most of the mixtures under study (i.e., in the inner...
Figure 3 shows the spectra of $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ in the spectral region under study. Positions of the principal peaks of $\text{CO}_2$ (the Fermi dyad) are also shown to illustrate that all of the key peaks of these three Raman-active components ($\text{CO}_2$, $\text{D}_2\text{O}$, and $\text{H}_2\text{O}$) can be distinguished when all are present together. Sapphire also gave rise to distinct Raman bands that, with the one exception discussed below, are also sufficiently spaced from the peaks of the solution components to be unambiguous.

**Figure 3.** Comparisons of the UV-Raman spectra of $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$, at room temperature and atmospheric pressure, with the principal peaks of $\text{CO}_2$ (Fermi dyad) also shown.

The sapphire tube was purchased from Saint-Gobain (Hiram, Ohio) in a 6-inch length, machined slightly at the ends, and capped with specialized Swagelok (Solon, Ohio) 316 stainless steel fittings at the ends using Viton seals. The specialized fittings allowed a length of $\frac{1}{4}$ inch outside diameter. stainless steel tubing to be inserted through the center of the sapphire tube (used for carrying one of the circulated water streams) and also accommodated a section of stainless steel tubing at $90^\circ$ to the sapphire tube (used for filling/emptying the cell with the CO$_2$-water solution). Approximately 1 inch at each end of the sapphire tube was retained within the fittings, leaving approximately 10 cm exposed for imaging and spectral study. A wider-diameter quartz tube was used as the container for the outer circulated water stream. It was equipped with quartz-tube side ports (for connecting to the circulator) and was sealed to the sapphire tube at the ends with epoxy. Remaining cell parts included 316 stainless steel fittings, valves and tubing purchased from Swagelok Inc. as well as a Cecomp Electronics (Libertyville, Illinois) digital pressure gauge, assembled as shown in Figure 4. An ISCO Inc. (Lincoln, Nebraska) 1000D pump was used to pressurize the cell with the CO$_2$-water mixtures. The cell assembly was mounted on a floating optical table using position-adjustable Newport Inc. (Irvine, California) stages to provide stability and facilitate alignment of the laser beam on the sample. Lexan blast shields were incorporated for safety. A photograph of the assembled cell (positioned under the UV-Raman microscope) is shown in Figure 5. The volume of the cell and all tubing leading from (but not including) the pump and to a Tescom (Elk River, Minnesota) back pressure regulator, used to control back pressure and empty the cell, was approximately 70 mL. The $\text{D}_2\text{O}$ used in the study was 99.9% pure and obtained from Sigma-Chemical Company (St. Louis, Missouri), while the $\text{CO}_2$ gas was 99.99% pure and purchased from Polar Cryogenics (Portland, Oregon).
To minimize specular reflection and elastic scattering from the stainless steel tube (both are potential interferences in Raman spectroscopy), the stainless steel tube was coated with black oxide using a proprietary method similar to “bluing.” The resulting coating, consisting of transition metal oxides, was black and gave no significant Raman spectrum in the region of interest. Figure 6 illustrates the degree to which specular reflection was attenuated by the coating.
2.2 UV-Raman spectrometer

Raman spectra were collected using a Horiba JY (Edison, New Jersey) LabRAM HR (high-resolution) Raman (confocal) microscope system. With a focal length of 0.8 m and dual gratings with groove density of 2400 grooves/mm the instrument can achieve a nominal spectral resolution of 1-2 cm\(^{-1}\). Excitation was provided by the deep-UV 244-nm line of a Lexel (Fremont, California) Model 85-SHG frequency-doubled Ar\(^+\) ion laser equipped with a non-linear beta barium borate (BBO) crystal. Laser power was 25 mW at the source and approximately 1 mW at the objective. Significant further attenuation of power is expected through the Raman cell. A 10x UV-compatible microscope objective (numerical aperture = 0.25) with a working distance of 15 mm was used. The spectrometer pinhole was kept fairly large, at 400 \(\mu\)m, resulting in less-than-optimal depth and lateral resolution. However, laser throughput was improved with the larger pinhole, giving acceptable band intensities when collected with an exposure time of 500 s. The spectral range was restricted to Raman shift above 450 cm\(^{-1}\). Measurements at lower frequencies were not possible because of the presence of a factory-installed edge filter for eliminating the exciting line. Spectral analysis, including curve fitting, was performed using Thermo Scientific (Waltham, Massachusetts) Grams/32 AI software. Any curve fitting used the Levenburg-Marquardt non-linear peak fitting method (Levenberg 1944) with baseline correction to remove background from Rayleigh scattering or fluorescence. A photograph of the spectrometer with a cell positioned for data collection is given in Figure 7.
2.3 Typical experiment and variables

The following procedures were used in the collection of spectra in most of the experiments:

- The pump, then cell, were filled with pure D$_2$O under ambient conditions and pressurized to the pressure of the experiment, 10 MPa. The cell was then valved off from the ISCO pump.

- The pump pressure was reduced to the pressure of the CO$_2$ cylinder and the volume of D$_2$O remaining in the pump was noted. A volume of CO$_2$ gas at this pressure (approximately 5.8 MPa) was then added to the pump to give the required concentration of CO$_2$ in the final test mixture. Following this, the pump was sealed off from the CO$_2$ cylinder and the pump pressure increased to 10 MPa. To help mix the CO$_2$ and D$_2$O, the pressure in the pump was dropped back to 5.8 MPa and then returned to 10 MPa, and this procedure was repeated approximately five times.

- The mixture in the pump was allowed to sit overnight so the CO$_2$ could dissolve in the D$_2$O at 10 MPa. During this time, the cell itself still contained pure D$_2$O at 10 MPa.

- On the following day, the valve between the pump and cell was opened, and the mixture in the pump was slowly metered into the cell to replace the pure D$_2$O in the cell. The metering was done by slowly opening and closing the pressure reducing valve at the exit of the cell. The procedure was performed carefully to minimize any flashing of CO$_2$ in the cell. Done properly, the solution in the cell remained homogeneous with no gas bubbles or liquid CO$_2$ separating from solution. (Phase separation was evident by the appearance of a second phase in the sapphire tube.) After flowing about 150 mL through the cell, the cell was considered completely charged with the fluid mixture. The pump remained on and connected to the cell to maintain pressure at 10 MPa throughout the experiment.

- The temperature controllers were turned on and thermostated water was circulated through the two thermal reservoirs at the desired temperatures.
• Raman spectra were collected after waiting at least two hours for thermal equilibration.

• The Raman spectrometer was first calibrated by focusing on the sapphire tube and using the Raman bands of sapphire (e.g., the strong sapphire peak at 746 cm⁻¹).

• The microscope objective was then moved so that the bottom of the sapphire tube was put in visible focus using an objective suited to visible light. This position was defined as z = 0 µm.

• The UV objective was then substituted, with its position configured to retain z = 0 µm, at the focal position without further adjustment of the microscope.

• Raman spectra were acquired as a function of position across the annulus containing the CO₂-D₂O solution. The first measurement was usually obtained at the inside surface of the sapphire tube (z = 0), taken as T = T(outside), or very near to it (z = 200 µm). Subsequent measurements were usually made at increments of 200 µm from this position (here reported as positive values of z) and toward the stainless steel tube (shown to be at z = 2000 µm, as discussed below), where T = T(inside). Because of optical and cell geometry constrains, no independent temperature measurements could be made at the exact positions from where the spectra were acquired. However, calculations predicted that minimal temperature drop occurred across the sapphire and the stainless steel tubes, so the assumption of thermal equilibration between the temperature reservoirs and fluid at z = 0 and z = 2000 µm was considered valid.

• Immediately after collecting Raman spectra in the increasing-z direction, a series of spectra were collected in the decreasing-z direction ending up at the position z = 0, or close to it.

Some experiments employed special procedures as follows:

• To lower the possibility of condensation of water vapor on the outside of the cell, T(outside) was usually kept higher than T(inside). Some experiments used T(inside) greater than T(outside) to make sure that there was no unexpected effect of the direction of the thermal gradient.

• A series of experiments were performed with T(outside) = T(inside) to account for the possibility of any spectral variations across the annulus in the absence of an applied temperature gradient.

• A series of experiments were performed with the outer quartz jacket removed. This permitted the use of CO₂-H₂O instead of CO₂-D₂O mixtures since there was no spectral interference from the H₂O in the outer thermal reservoir. The configuration had the added advantage of much higher signal-to-noise since there was no loss of signal by scattering from the quartz, reservoir water, and the accompanying interfaces. In these experiments, T(outside) was taken at the value measured on the outside of the sapphire tube with a thermocouple.

• A series of experiments (2-position measurements) were performed on a given CO₂-D₂O mixture in which spectra were acquired at two positions (e.g., z = 500 µm and 2000 µm) with varying temperature gradients imposed across the cell. T(inside) was held constant while T(outside) was changed). These experiments provided data on a single mixture over a wider variety of thermal conditions than those in which more extensive data as a function of z were acquired.

• Mixtures of D₂O dissolved in scCO₂, instead of CO₂ dissolved in D₂O or H₂O, were also performed. These were considered more challenging for two reasons: (1) the solubility of D₂O in scCO₂ was about an order of magnitude less than CO₂ in D₂O (mole fraction 10⁻³ vs. 10⁻²) under the same conditions of temperature and pressure (i.e., 10 MPa, and 12°C to 45°C), (2) with mostly scCO₂, the
amount of stored energy in the cell increased significantly and, with it, the level of safety concerns. Nevertheless, experiments of this sort were still conducted to determine if D₂O could be detected at these concentrations (the stronger C-D stretching bands were used in an attempt to compensate for the lower concentration) and, if so, whether a Soret effect was observed at “the other end” of the phase diagram of the mixture.

- Some experiments used deuterated brine (D₂O + 1 M NaCl) instead of pure D₂O.

The key variables in this study were:

- **Position** (z) relative to the top of the sapphire tube. Values of z with increments of 200 µm were usually used.

- **Direction of scan**, i.e., either increasing z or decreasing z. In most cases, data were collected in both directions during the same experiment.

- **Values of temperature** and **size of temperature gradient**. In most cases, a given experiment spanned a temperature range below the critical point of CO₂ (31.04°C) or above it, to avoid the effects of density fluctuations (on the relative intensities of the Fermi dyad components in CO₂) known to occur at this temperature. A series of two-position experiments were also conducted where the temperature gradient was changed in increasing increments, while making measurements at only two positions in the cell.

- **Direction of temperature gradient**, i.e., T(outside) > T(inside) or T(inside) > T(outside).

- **Concentration of CO₂** in the mixture (i.e., mole fraction CO₂ or X(CO₂)). In most cases the concentration was kept below the solubility of CO₂ in H₂O (approximately 0.028 mole fraction under these conditions). Some experiments were run with H₂O saturated with CO₂. A few experiments were also performed with scCO₂ saturated with D₂O (i.e., X(H₂O) ~ 0.003). A solution of CO₂ dissolved **in brine**, D₂O + 1 M NaCl, was also tested.

- A few experiments were conducted where **pressure was varied** while holding the temperature values constant.
3.0 Results

3.1 Assessment of Raman cell

3.1.1 Position of the microscope objective vs. focal point of the measurement

During preliminary testing, it became clear that increments in the vertical position of the microscope objective (denoted by the z value) did not correspond to increments in the position of the focus spot within the annulus of the cell. This is attributed to refraction of the laser beam through the three components of the window (quartz tube, water layer, and sapphire tube) between the objective and the fluid. It was estimated by Snell’s law that the major deviation was caused by refraction through the relatively thick sapphire tube. Calculations indicated that a z value of 3000 µm actually corresponded to a distance of 2000 µm within the fluid, and this was born out by experiment. First, when using white light illumination, visual images of a “surface” were obtained at approximately these two locations (i.e., z = 0 and 2000 µm). Second, as shown in Figure 8 (for an experiment with \(X(CO_2) = 0.0027\), \(P = 10\) MPa, and \(T(\text{outside}) = T(\text{inside}) = 40^\circ\text{C}\)), the total integrated intensity of peaks (from both CO\(_2\) and D\(_2\)O) at \(z = 0\) µm is roughly half its maximum value and the sapphire peaks show a markedly sudden decrease in intensity. For \(z > 2000\) µm, the total signal drops significantly due to focusing beyond the stainless steel tube, but does not completely disappear because there is still some out-of-focus Raman scattering.

![Figure 8](image)

**Figure 8.** Total Raman scattering signal strength (from both CO\(_2\) and D\(_2\)O) as a function of the position of the objective (z value). In relationship to position within the annulus, \(z = 0\) µm corresponds to the inside surface of the sapphire tube, whereas \(z = 2000\) µm is near the outside surface of the stainless steel tube. The photographs are white-light images at these two positions. Circles around each point indicate the approximate sampling volumes.

In each experiment, Raman spectra were acquired between \(z = 0\) and \(z = 2000\) µm (pink region in Figure 8), usually at increments of \(z = 200\) µm. Given that width of the annulus was 3.4 mm, that the
range of \( z \)-values relevant to the annulus was 2000 \( \mu m \), and also that the relationship between the two scales is probably non-linear, it was difficult to correlate exactly the position of the focused beam with the \( z \) value. However, the important variable in this study was temperature and not position. For this reason, we took the following approach in our analysis: (1) the spectrum corresponding to \( T(\text{outside}) \) was taken as the spectrum at \( z = 0 \) \( \mu m \); (2) the spectrum corresponding to \( T(\text{inside}) \) was taken as the spectrum at \( z = 2000 \) \( \mu m \); and (3) the spectra for positions with \( z \) between 0 and 2000 \( \mu m \) (pink region in Figure 8) were deemed to vary continuously between these two limits. To estimate the Soret coefficient, we used the spectra at the end points. If spectra at these positions could not be obtained directly, they were determined by extrapolation from the observed variations in the spectra within the annulus.

3.1.2 Estimate of sampling volume

Figure 8 also illustrates the effects of the two principal causes of signal attenuation in the Raman cell. The first was important for \( z \) values between 0 and 500 \( \mu m \), where the Raman scattered signal was “diluted” by the contribution of the sapphire tube. Peaks from the sapphire (including the very strong one at 746 cm\(^{-1}\)) were still strong in this region due to contribution from significant out-of-focus scattering. At positions greater than 500 \( \mu m \), almost all of the signal came from the fluid. The results not only explain the loss of signal near the sapphire tube, but help establish an approximate volume from which most of the scattering occurred. In the present case, the volume (approximated by a sphere) had a likely diameter of about 500 \( \mu m \) (or about 25% of the annulus distance). This suggests that increments less than \( z = 500 \) \( \mu m \) exhibit marked overlap of scattered signals. Since the total thickness of the annulus is 2000 \( \mu m \), about 4 unique measurements were therefore possible across it, sufficient for a reasonably good estimate of a significant gradient in any of the spectral parameters. To illustrate this, a circle with a diameter of 500 \( \mu m \) is drawn around each data point in Figure 8. Even though the circles overlap, there is “enough \( z \)” represented to capture the variation across the annulus. The same could be argued for individual spectra collected at these positions.

For \( z \) values greater than about 500 \( \mu m \) but less than 2000 \( \mu m \), the total signal strength again decreases. This is attributed to additional scattering of the Raman light as it returns to the objective from positions deep within the sample. The deeper the focal point, the more significant the losses will be from this phenomenon.

Finally, it is important to note that any changes in the ratios of individual band intensities (e.g., CO\(_2\) band relative to D\(_2\)O band) arising from variation in composition of the mixture across the annulus should be unaffected by variations in the total Raman scattering signal. Consequently, the only effect that variations in the total spectral intensity will have on determining Soret coefficient is with regard to signal-to-noise. A smaller total scattering intensity, in most cases, resulted in a smaller signal-to-noise and a greater uncertainty in measured or calculated spectral parameters.

3.2 Raman spectra

3.2.1 Experiments on D\(_2\)O containing CO\(_2\) below saturation

Raman spectra were obtained as a function of distance (related to the \( z \) value) across annulus containing the CO\(_2\) + D\(_2\)O mixture with concentrations of CO\(_2\) in D\(_2\)O below its solubility value.
conditions of this study, this value corresponds to X(CO$_2$), approximately 0.028. The specific compositions studied in this work were X(CO$_2$) equal to 0.0014, 0.0027, and 0.0054, corresponding to approximately 5%, 11%, and 22% of saturation. Spectra are shown in Figures 9 and 10 as a function of the z value X(CO$_2$) = 0.0054, and 0.0027, respectively, and with two different temperature gradients. The results for 0.0014 showed similar trends but the CO$_2$ peaks were extremely weak. Spectra were also collected with different temperatures and temperature gradients applied. Generally, for a given experiment, the temperature gradient was maintained on one or the other side of the critical temperature, 31.1°C. For measurements below the critical point, the reservoir temperatures were 30°C and 12°C (clathrates form below 12°C); for measurements above the critical point, the temperature reservoirs were at 33°C and 45°C (the approximate upper limit for the cell). Spectra shown in Figures 9 and 10 are for one of the temperature gradients for each composition. Results for other temperature gradients showed the same results. Spectra collected upon increasing the z value are shown, although spectra for decreasing z, with all other conditions the same, were essentially identical.

![Figure 9](image.png)

**Figure 9.** UV-Raman spectra as a function of position within the annulus (in terms of the microscope position, z), with X(CO$_2$) = 0.0054, T(inside) = 12°C and T(outside) = 30°C. Higher temperature is outside. The spectra were acquired in the direction of increasing z. CO$_2$ is a liquid under these conditions.
Figure 10. UV-Raman spectra as a function of position within the annulus (in terms of the microscope position, z), with \( X(\text{CO}_2) = 0.0027, \ T(\text{inside}) = 45^\circ \text{C} \) and \( T(\text{outside}) = 33^\circ \text{C} \). The higher temperature is inside. The spectra were acquired in the direction of increasing z. \text{CO}_2 \) is supercritical under these conditions.

Each spectrum in Figures 9 and 10 contains three bands of interest: the two peaks corresponding to the Fermi dyad of \text{CO}_2, positioned at approximately 1273 and 1377 cm\(^{-1}\), respectively, and the band at 1203 cm\(^{-1}\) from the bending mode of \text{D}_2\text{O}. The band positions are a little lower than those indicated in Figure 3 for neat compounds, especially the Fermi dyad of \text{CO}_2. The variance, which was reproducible for all mixtures with concentrations of \text{CO}_2 below saturation, was surprising and its cause unknown at this time. However, as discussed later in this report, the peak frequencies from mixtures with high sc\text{CO}_2 concentrations are closer to the values in Figure 3, suggesting the likely explanation involves molecular interactions, arguably different for \text{CO}_2 surrounded by other \text{CO}_2 \) molecules (at high \text{CO}_2 concentration) and \text{CO}_2 \) surrounded by water molecules (at low \text{CO}_2 concentration).

A band at approximately 1350 cm\(^{-1}\) also appears in the spectra for measurements taken close to the sapphire tube (small z). The Raman spectrum of sapphire does not normally have a peak at this frequency, however no published spectra of sapphire with UV excitation have been previously reported, to our knowledge. It is possible that the peak is due to sapphire, observed here because of resonant enhancement in the UV. Another possibility is that it arises from a carbon impurity associated with the surface of the sapphire. Amorphous carbon has a strong peak due to sp\(^3\) carbon (C-C stretch) at approximately 1360 cm\(^{-1}\). Regardless of the cause, this peak appears to be associated with the surface of the sapphire and is disregarded in this study. Another observation that may be of fundamental significance, but is not addressed further in this study, is the apparent asymmetry of some of the peaks, particularly the stronger Fermi dyad component at 1377 cm\(^{-1}\), in spectra of mixtures where the \text{CO}_2 peaks are weak relative to \text{D}_2\text{O} (see Figure 10). This characteristic of the Fermi dyad probably relates to molecular interactions and how they change with concentration, particularly when \text{CO}_2 \) concentrations are low. Similar to the effect on peak frequencies, reported above, a definitive explanation of the band shape is not forthcoming from this study, nor is it within its scope.
The primary objective of this study was to determine whether changes in the Raman spectra occur as a function of position across the annulus when a temperature gradient is applied. *As indicated by Figures 9 and 10, the spectra exhibit no obvious changes as a function of position (other than overall intensity changes and changes related to the contribution from extraneous bands) for a given solution composition. This is the first qualitative evidence that a Soret effect is not inordinately pronounced for solutions studied in this work.*

Several characteristics of the spectra, including relative peak areas, intensities and band shapes, were scrutinized quantitatively and none showed significant change across the annulus. Figure 11, for example, shows the variation of the ratio of the intensity of the strongest peak in the Fermi dyad of CO₂ (1377 cm⁻¹) to the intensity of the peak due to D₂O (1203 cm⁻¹) for solutions with X(CO₂) = 0.0014 and 0.0027. Figure 12 shows the variation in the same ratio for solutions with X(CO₂) = 0.0054. Data for several temperature gradients are shown, as are data from experiments with increasing-z and decreasing-z, and with the gradient imposed in two directions (higher temperature inside and outside). The results all point to the same conclusion: regardless of the way the experiment was performed, there was no significant variation of the intensity ratio across the annulus for a given value of X(CO₂). (Variation of the ratio with the X(CO₂) value of each experiment is discussed later in this report.) Uncertainties were taken as twice the standard deviation of the intensity of peaks calculated from the curve fits. Note that the uncertainties are much greater for small z. This is due to the relative weakness of the bands in spectra acquired at these locations, as well as the need to subtract a correspondingly larger background with stronger extraneous bands (i.e., from the sapphire tube) in determining the CO₂ and D₂O peak intensities.

![Figure 11](image.png)

*Figure 11. CO₂/D₂O peak intensity ratio calculated from the Raman spectra as a function of position for X(CO₂) = 0.0014 and 0.0027, with different temperature gradients and direction of scan.*
Figure 12. CO\textsubscript{2}/D\textsubscript{2}O peak intensity ratio calculated from the Raman spectra as a function of position for $X$(CO\textsubscript{2}) = 0.0054, T(outside) = 30°C and T(inside) = 12°C, in both increasing- and decreasing-$z$ directions.

Spectra as a function of $z$ were also acquired in a series of experiments where the same temperature was imposed on both sides of the annulus, i.e., T(outside) = T(inside). Results from two of these studies, at 23°C and 40°C, are shown in Figure 13. The intended purpose of these “isothermal” measurements was to address questions that might arise in the event the relative Raman intensities showed a significant and reproducible trend as a function of position within the annulus. In particular, could this variation be due to something other than the temperature gradient? Given the lack of variation shown in Figures 11 and 12, the results in Figure 13 are expected, and therefore, somewhat academic. They also show no significant difference in the Raman intensity ratio as a function of position across the annulus.

Figure 13. CO\textsubscript{2}/D\textsubscript{2}O peak intensity ratio calculated from the Raman spectra as a function of position for $X$(CO\textsubscript{2}) = 0.0027 with T(outside) = T(inside) at 32°C and 40°C. Spectra were collected in the direction of increasing $z$. 
As a further confirmation of the lack of significant variation in the relative Raman intensities across the annulus, a series of “2-point temperature ramps” were performed. In this study, Raman spectra of a CO₂-D₂O mixture were obtained at only two positions (z values) within the annulus containing a given solution but using different temperature gradients. For the data in Figure 14, T(outside) was held at 45°C and T(inside) was varied as indicated. A Raman spectrum was acquired at the two positions for each gradient, after allowing sufficient time (about 2 hours) for thermal equilibration. The spectra shown in the figure were background-adjusted and intensity-normalized so the D₂O peak overlapped for measurements at the two positions (different color correspond to the different temperature gradients and positions). Inspection of the CO₂ peaks under these conditions indicates no significant change in the spectra results from changing the temperature gradient over a significant range of values, other than the single case (red spectrum in Figure 14) that appears to have a slightly smaller background toward higher frequencies. The results are consistent with the spectra in Figures 9-13 that showed no significant variation in the relative intensities of the CO₂ and D₂O peaks across the annulus.

**Figure 14.** UV-Raman spectra at two positions within the annulus with X(CO₂) = 0.0027 and T(outside) = T(0 µm) = 45°C and with varying T(inside). Spectra are shown for T(inside) = T(2000 µm) = 45°C, 40°C, 35°C, 30°C, 25°C, and 20°C.

### 3.2.2 Experiments on D₂O + 1 M NaCl containing CO₂ below saturation

Results similar to the aforementioned experiments, but using 1 M NaCl in D₂O instead of pure D₂O, are shown in Figure 15. The presence of the NaCl does not appear to make a difference in the response of the Raman intensity ratios to a temperature gradient imposed across the annulus. Similar to results without the NaCl, there is no significant change in the intensity ratios.
Figure 15. CO$_2$/D$_2$O peak intensity ratio, for solutions containing 1 M NaCl, as a function of position with X(CO$_2$) = 0.0044, and various temperature gradients. Open symbols are ratios for the same experiments as the corresponding closed symbols, but were calculated using integrated intensities from curve fitting results.

3.2.3 Varied pressure study

Raman spectra were also acquired in an experiment with X(CO$_2$) = 0.0027 and temperature held constant at 40°C (above the critical temperature with no temperature gradient), but where the cell pressure was changed. The purpose of this experiment was to see if pressure had an effect, independent of concentration, on the relative intensities of the CO$_2$ and D$_2$O bands. The lowest pressure studied was 1 MPa, where the solubility of CO$_2$ in water at 40°C is approximately 0.004. Since X(CO$_2$) = 0.0027, a single phase was maintained throughout this study and this was confirmed by the absence of phase separation in the cell at any time. Spectra were measured in the center of the cell (z = 1000 µm) for each pressure. The results, shown in Figure 16, indicate that there was no significant variation in the CO$_2$/D$_2$O intensity ratio with cell pressure, for a single-phase solution, over the range of pressures studied in this work.
Figure 16. CO\textsubscript{2}/D\textsubscript{2}O peak intensity ratio, for solution with X(CO\textsubscript{2}) = 0.0027 and T(inside) = T(outside) = 40°C, as a function of cell pressure.

3.2.4 H\textsubscript{2}O containing CO\textsubscript{2} at saturation

Raman spectra as a function of position across the annulus, between T(inside) = 11°C and T(outside) = 15°C, were also obtained for a solution of H\textsubscript{2}O saturated with CO\textsubscript{2} at 10 MPa and the two temperatures, roughly corresponding to X(CO\textsubscript{2}) = 0.029 and 0.028, respectively. The results are shown in Figures 17 and 18.

Figure 17. UV-Raman spectra as a function of position within the annulus (in terms of the microscope position, z), for H\textsubscript{2}O saturated with CO\textsubscript{2}, i.e., X(CO\textsubscript{2}) ∼ 0.028. T(inside) = 11°C and T(outside) = 15°C. Spectra were acquired in the direction of increasing z. Spectral intensities are normalized with respect to the H\textsubscript{2}O peak at 1640 cm\textsuperscript{-1}. 
Figure 18. CO\textsubscript{2}/(CO\textsubscript{2} + D\textsubscript{2}O) peak intensity fraction calculated from the Raman spectra as a function of position, for H\textsubscript{2}O saturated with CO\textsubscript{2}, i.e., X(CO\textsubscript{2}) \sim 0.028. Results are shown for measurements made with both increasing and decreasing z. Linear regression in the absence of the two low-z points is shown.

H\textsubscript{2}O was used instead of D\textsubscript{2}O in these studies because they were performed in the absence of the outer temperature reservoir. T(outside) was controlled by the air temperature and measured with a thermocouple as equal to 15° C. Unlike the experiments on solutions with lower concentrations of CO\textsubscript{2}, these results show a clear trend with changing z. The ratio of intensities of the CO\textsubscript{2} to H\textsubscript{2}O peaks increases in going from the higher temperature side, T(outside) or z = 0 \mu m, to the lower temperature side, T(inside) = 11° C or z = 2000 \mu m. Because the CO\textsubscript{2} peaks are so large in this study, it was more prudent to plot the CO\textsubscript{2} peak intensity (1389 cm\textsuperscript{-1}) in terms of the fraction of total intensity of the H\textsubscript{2}O (1640 cm\textsuperscript{-1}) + CO\textsubscript{2} (1389 cm\textsuperscript{-1}) peaks, rather than using the CO\textsubscript{2}/H\textsubscript{2}O intensity ratio. The results, shown in Figure 18, clearly illustrate the significant and consistent trend in the relative size of the CO\textsubscript{2} peak as function of position, and therefore temperature, within the annulus. Assuming the relative intensity scales with concentration, Figure 18 indicates a preferential segregation of CO\textsubscript{2} to the colder side of the annulus in this experiment.

3.2.5 scCO\textsubscript{2} containing D\textsubscript{2}O at saturation

Experiments were also performed on the other side of the phase diagram of the CO\textsubscript{2}-water solution, i.e., with D\textsubscript{2}O dissolved in scCO\textsubscript{2}. The CO\textsubscript{2} was the majority species in these studies and was in the supercritical state. Since the solubility of D\textsubscript{2}O in scCO\textsubscript{2} is much lower than CO\textsubscript{2} in D\textsubscript{2}O, i.e., X(D\textsubscript{2}O) = 0.003 compared to X(CO\textsubscript{2}) = 0.028 to 0.029, under similar conditions, using the C-D stretching mode, instead of the much weaker bending mode, for quantitative analysis seemed prudent. The results of a series of measurement across the annulus of one of these studies, with T(outside) = 40° C and T(inside) = 32° C, are shown in Figure 19.
Figure 19. UV-Raman spectra as a function of position within the annulus for solutions of scCO$_2$ containing D$_2$O at saturation (i.e., $X$(D$_2$O) $\sim$ 0.003). T(inside) = 32°C and T(outside) = 40°C.

As expected from the concentration, the CO$_2$ Fermi dyad is very strong in these spectra. Unfortunately, the D$_2$O peaks are also extremely weak. The expected position of the C-D stretching bands, around 2500 cm$^{-1}$, is illustrated by the spectrum of neat D$_2$O that is also plotted in the figure. It is difficult to discern even the slightest contribution from these modes to the spectra obtained from the solution, precluding the determination of the relative intensities of bands from the two components and, consequently, concentration trends across the annulus.
4.0 Discussion

4.1 Solutions of CO$_2$ in D$_2$O with CO$_2$ below saturation

Raman spectra showed no significant variation with respect to the relative intensities and areas of peaks associated with CO$_2$ and D$_2$O as a function of position within the cell annulus between the two imposed temperatures, regardless of the concentration of CO$_2$, as long as it was below saturation. The behavior was obtained independent of the direction of the scan (increasing or decreasing $z$), the size of the temperature gradient (between 11°C and 45°C), whether the data was collected below or above the critical temperature of CO$_2$, the direction of the temperature gradient (higher temperature or colder temperature on the outside), pressure (up to 10 MPa), or in the presence of 1 M NaCl. These results argue to the presence of no detectable Soret effect, corresponding to $S_T \sim 0$ within the uncertainty of the measurements.

An estimate of uncertainty in $S_T$ can be obtained by inspection of the uncertainties in the intensity ratio vs. $z$-position plots. As illustrated in the case of the study with X(CO$_2$ = 0.0014), T(outside, $z = 0$ µm) = 30°C and T(inside, $z = 2000$ µm) = 12°C, shown in Figure 20, straight lines are easily drawn to bracket the error bars in an experiment. We now make use of Equation (3), after rearranging and integrating between the two temperatures $T_o = T$(outside, $z = 0$ µm) = 30°C and $T = T$(inside, $z = 2000$ µm) = 12°C where concentrations are $c_o$ and $c$, respectively:

\[
\ln \left( \frac{c}{c_o} \right) = -S_T \left( T - T_o \right) \tag{4}
\]

or, in terms of the absolute magnitude of $S_T$:

\[
|S_T| = \left[ \frac{1}{(T - T_o)} \right] \ln \left( \frac{c}{c_o} \right) \tag{5}
\]

Applying Equation (5) to the endpoints of the error-bracketing lines in Figure 20 gives an estimate of the maximum slope of the relationship (assuming linearity) as well as an estimate of the ratio of the intensities of the CO$_2$ and D$_2$O peaks at $T_o = T$(outside, $z = 0$ µm) and $T = T$(inside, $z = 2000$ µm). Since the concentration of CO$_2$ is always small, the intensity ratios approximate the mole fraction of CO$_2$ in D$_2$O and can be substituted for the concentrations in Equation (5). Substituting these ratios, 0.124 and 0.210, and the respective temperatures, 30°C and 12°C, gives:

\[
|S_T|_{\text{max}} = \left[ \frac{1}{(12 - 30)} \right] \ln \left( \frac{0.210}{0.125} \right) = 0.03 \tag{6}
\]

Similar results are obtained from the uncertainty values in the other plots, providing a reasonable estimate of the minimum absolute value for $S_T$ than can be measured in these experiments. In conclusion, the results of this study indicate that
If the absolute magnitude of $S_T$ is smaller than 0.03, it is unlikely that it could be measured using the experimental approach employed here.

![Figure 20](image)

**Figure 20.** Re-plot of Figure 11 showing straight lines fitted by eye to limits of error bars of the data for $X(\text{CO}_2) = 0.0014$.

On the other hand, the results indicate that solutions of CO$_2$ dissolved in water do not exhibit $S_T$ values as large as those determined for some other mixtures near their critical point of one of the components. Kempers (Kempers 2001) reported values of the thermal diffusion factor, $\alpha_T$, significantly above 10 for mixtures of methane and propane above the critical point of methane. Given that $\alpha_T$ is related $S_T$ in Equation (3) by $S_T \sim \alpha_T/T$ for dilute solutions, similar values of $\alpha_T$ in our experiments would have led to $|S_T| > 0.03$ (using an average temperature of 35°C). The sensitivity analysis performed above indicates that values of $S_T$ of this magnitude should have been observable with the experimental approach used here. Consequently, it appears that solutions of CO$_2$ dissolved in water solutions do not exhibit the inordinately large Soret effect of other mixtures under conditions near the critical point of one of the components. This could be partly attributed to the low concentration of the “supercritical” component CO$_2$ compared to mixtures studied by Kempers where components were present at mole fractions exceeding 0.1.

### 4.2 Solutions of H$_2$O saturated with CO$_2$

Figures 17 and 18 seem to suggest the presence of a Soret effect in solutions of H$_2$O containing CO$_2$ above its solubility. The peak intensity parameter related to CO$_2$ is clearly smaller close to $z = 0$ $\mu$m (where $T = 15^\circ$C) than it is near $z = 2000$ $\mu$m (where $T = 11^\circ$C). The slope of the line connecting the two limiting positions is positive. However, it is important to remember that these experiments were conducted with excess CO$_2$ present. The H$_2$O phase was saturated with CO$_2$ at all temperatures and, since all temperatures were below the critical temperature of CO$_2$, the excess CO$_2$ was in the form of a
secondary liquid phase. For this reason, it seems more likely that the variation in Figures 16 and 17 is due to the relationship between solubility and temperature (i.e., position), rather than kinetic parameters. To check this possibility, we compared the fractional variation in concentration with temperature observed in this experiment with that expected from the variation in solubility.

Using the endpoints of the data in Figure 18, shown again in Figure 21, and substituting intensities for concentrations as discussed previously,

\[
\frac{\Delta c}{c_o} \approx \frac{1}{T - T_o} \left( c - c_o \right) \approx \frac{1}{T - T_o} \left( I - I_o \right) = \frac{1}{11 - 15} \left( 1 - 0.876 \right)
\]

(8)

\[
\frac{\Delta c}{c_o} \approx -0.03 \pm 0.01 \, ^\circ C^{-1}
\]

Performing the same calculation using solubility data for CO₂ in H₂O at 10 MPa between 12°C and 15°C (Spycher 2002) gives

\[
\frac{\Delta c}{c_o} = \frac{1}{T - T_o} \left( c - c_o \right) \approx \frac{1}{12 - 15} \left( 0.001 \right)
\]

(9)

\[
\frac{\Delta c}{c_o} \approx -0.01 \pm 0.01 \, ^\circ C^{-1}
\]

A good case is made from the above comparative calculations that the trend in CO₂ concentrations within the annulus, in the case of H₂O saturated with CO₂ and excess liquid CO₂ present, is a simple consequence of the variation in solubility of CO₂ as a function of temperature.

**Figure 21.** Re-plot of Figure 17 noting intensity values at z = 0 µm and z = 2000 µm that were used to compare the observed variation with temperature to predictions based on solubility.
4.2 Concentration calibration plots

The final calculations performed in this work concern the values of the relative Raman intensities measured over the course of several experiments with different mole fraction CO$_2$. Values of the intensity ratios (for the strongest peak of CO$_2$ to the D$_2$O or H$_2$O peak) were amassed and plotted versus the mole fraction of CO$_2$ in each mixture. Since minimal variation in concentration occurred within the annulus for experiments where a temperature gradient was applied, the ratios from both isothermal experiments and experiments with a temperature gradient were all used. The ratios were converted to the fraction of total intensity associated with CO$_2$ (to be slightly more quantitative relative to concentration) and results are shown in Figure 22.

![Figure 22](image_url)

*Data for $x_{CO_2} = 0.0044$ applies to solutions containing 1M NaCl.*

**Figure 22.** Plot of the fraction of total Raman scattering intensity attributed to CO$_2$ versus the mole fraction of CO$_2$ in the mixture as calculated from the quantities used in preparation.

As shown in Figure 22, the CO$_2$ intensity fraction scales linearly with the mole fraction of CO$_2$ for concentrations less than about 0.005. When the values for the CO$_2$-saturated solutions are included (at two temperatures), significant non-linearity is observed. The non-linearity is due to two factors. First, the CO$_2$-saturated solutions contained H$_2$O instead of D$_2$O and, consequently, the H-O-H bending mode instead of the D-O-D bending mode was used. Slight differences between the scattering cross sections for H$_2$O and D$_2$O may exist. Second, and most important, the CO$_2$ Fermi dyad has a significantly greater scattering cross section than the H-O-H bending mode. The impact of this difference is illustrated by calculations for the two extreme of CO$_2$ concentration as given below:

For low concentration of CO$_2$:

$$\frac{c_{CO_2}}{c_{CO_2} + c_{H_2O}} \approx \frac{c_{CO_2}}{c_{H_2O} (\sim 1)} = \frac{s_{CO_2} I_{CO_2}}{s_{H_2O} I_{H_2O}} = \text{const.} \left( \frac{I_{CO_2}}{I_{H_2O}} \right)$$
At low \( \text{CO}_2 \) concentrations, the intensity ratio (or fraction) should scale directly with the concentration. At high \( \text{CO}_2 \) concentrations, the ratio will approach unity. Given the relative size of the scattering coefficients, \( s_{\text{CO}_2} \gg s_{\text{H}_2\text{O}} \), the transition to asymptotic behavior (curve approaching unity) should occur at relatively small \( \text{CO}_2 \) concentrations. In this case, the \( \text{CO}_2 \) bands come to dominate the spectra at mole fractions significantly below the saturation concentration.

The alternative calibration plot shown in Figure 23 corroborates the statements made above. In this figure, the measured intensity ratios were converted to ratios of the mole fractions (\( \text{CO}_2 / \text{D}_2\text{O} \)) using the solubility of \( \text{CO}_2 \) in \( \text{H}_2\text{O} \) as a single calibration point (i.e., \( X(\text{CO}_2) = 0.028 \)). The formula used for the conversion is shown in the figure, where \( f \) is the conversion factor determined from the \( \text{CO}_2 \) solubility. The converted intensities ratios were then plotted against the ratios of concentrations calculated from the amounts of \( \text{CO}_2 \) and \( \text{D}_2\text{O} \) (or \( \text{H}_2\text{O} \)) mixed during sample preparation. The resulting plot is near-linear as expected, with some small deviations near the origin attributed to difficulties in quantitative transfer of the gas to the pump, assurance of complete dissolution of the \( \text{CO}_2 \) in the water during mixing, and the presence of a systematic uncertainty in the pump volume.

\[
\frac{s_{\text{CO}_2} I_{\text{CO}_2}}{s_{\text{CO}_2} I_{\text{CO}_2} + s_{\text{H}_2\text{O}} I_{\text{H}_2\text{O}}} \approx \frac{s_{\text{CO}_2} I_{\text{CO}_2}}{s_{\text{CO}_2} I_{\text{CO}_2}} = 1
\]

**Figure 23.** Plot of the fraction of total Raman scattering intensity attributed to \( \text{CO}_2 \) versus the mole fraction of \( \text{CO}_2 \) in the mixture as calculated from the quantities used in preparation.
5.0 References


