Measuring Supercritical CO2 Density Using Raman Spectroscopy

Dr. Jinbo Chen (East Carolina University), chenji21@ecu.edu

INTRODUCTION

The lack of an accurate and fast thermodynamic model for measuring and computing the properties of supercritical carbon dioxide is a key challenge for sCO_2 system development. Given the importance of accurate CO_2 density data for processes involving energy, combustion, turbomachinery, etc., this research aims to develop a method for measuring CO_2 density by calibrating CO_2 density as a function of the Fermi diad of CO_2 in the Raman spectrum.

Raman spectroscopy is a non-destructive technique that utilizes laser light to measure the molecular vibrations of a sample. When the laser light interacts with molecules, a small fraction of the light is scattered, resulting in a shift in energy that corresponds to the vibrational modes of the molecules. These energy shifts, known as Raman shifts, are displayed as peaks in a spectrum, with each peak representing a specific molecular vibration.

The Fermi diad in the Raman spectrum of CO_2 arises from a phenomenon known as Fermi resonance. This occurs when two vibrational energy levels are close in frequency and interact, causing a splitting of the spectral line into two distinct peaks. The separation between these peaks is directly related to the density of CO_2, making it a valuable parameter for developing a CO_2 densimeter.

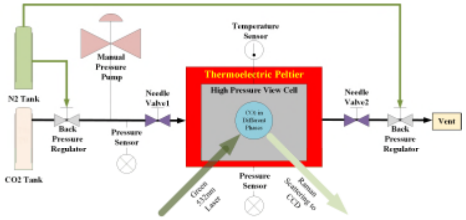
MATERIALS & METHODS

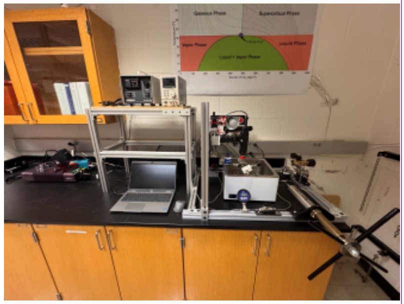
Raman spectra of CO_2 at varying densities were collected by adjusting temperature and pressure for each measurement. Temperature was controlled using a thermoelectric Peltier device with a variable voltage power supply and a water bath, while pressure was regulated with a manual pump and pressure regulators.

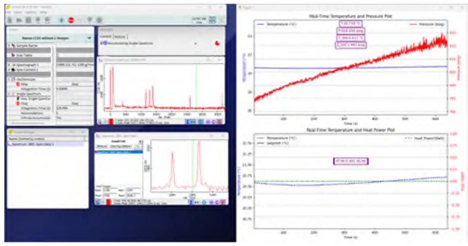
A Python script maintains temperature stability and continuously records temperature and pressure while acquiring spectra using a portable Raman spectrometer. Each spectrum was acquired using 5 accumulations, with each lasting for 120 seconds.

The Fermi diad peaks were identified by plotting Raman shift (cm^{-1}) vs. Intensity (au) and using Lorentzian peak-fitting in MATLAB. To correct and calibrate variations in Fermi diad separation for data collected on different days but under the same P-T conditions, known Raman peaks near the Fermi diad region are used, such as neon emission lines or a Raman-active chemical like cyclohexane. Experimental error was quantified by combining measurement error due to the precision of the sensors and environmental error due to the slight temperature and pressure fluctuations during the spectrum accumulation period.

SYSTEM DESIGN & EXPERIMENTAL RESULTS





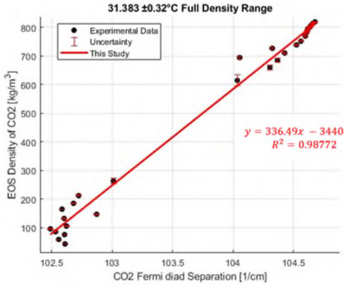


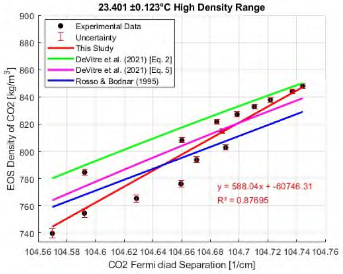
System Design:

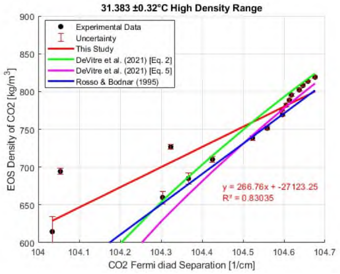
CO_2 is supplied to the chamber through a back-pressure regulator that is regulated by a nitrogen supply tank. The chamber is isolated by needle valves and features a view cell window that allows the laser beam to pass through. The pressure is adjusted by a manual pump, and the temperature is controlled by a thermoelectric Peltier plate inside a water bath. The exit flow is controlled by a second back-pressure regulator. Temperature and pressure sensors are connected to the inside of the view cell. The laser passes through the view cell, and the scattered light reflection is captured by a camera for measurement.

Results and Discussion:

The results of this study demonstrate strong agreement with previous studies, particularly in the high-density range above 600 kg/m³. The plots compare the experimental data from this study with calibration equations from earlier research. Our study has a broad temperature range, providing a more comprehensive analysis. A clear correlation exists between Fermi diad separation and CO_2 density, with high R^2 values indicating a strong alignment with the data trend.







Future Research & Potential Application

1. Extend the calibration of CO_2 density across a wider range of pressures and temperatures to improve the accuracy of the method for various industrial applications.
2. Investigate improvements in the experimental setup, such as optimizing the Raman laser/camera settings and temperature and pressure stability to further reduce measurement uncertainties. Specifically for the lower-density region (<120 $\frac{kg}{m^3}$) where Raman peaks are less visible.
3. Enhance the efficiency of supercritical CO_2 in power generation systems, including waste heat recovery, nuclear, and renewable energy applications.
4. Improve modeling and optimization of combustion processes, contributing to cleaner and more efficient fuel burning.
5. Real-time CO_2 density monitoring can optimize the design and operation of turbomachinery, which can improve efficiency and stability in applications involving CO_2.
6. Advanced Raman Spectroscopy Systems, such as WITEC360, are available for a more accurate and faster response measurement, which can capture more details near the critical point region.

REFERENCES

1. Lamadrid, H. M., et al. "Reassessment of the Raman CO2 densimeter." Chemical Geology 450 (2017): 210-222.
2. DeVitre, Charlotte L., Chelsea M. Allison, and Esteban Gazel. "A high-precision CO2 densimeter for Raman spectroscopy using a fluid density calibration apparatus." Chemical Geology 584 (2021): 120522.
3. Rosso, K. M., and R. J. Bodnar. "Microthermometric and Raman spectroscopic detection limits of C02 in fluidinclusions and the Raman spectroscopic characterization of C02." Geochimica et CosmochimicaActa 59.19 (1995): 3961-3975.
4. Anton Paar. "Raman spectroscopy applications: Anton Paar Wiki," https://wiki.anton-paar.com/en/basics-of-raman-spectroscopy/raman-spectroscopy-applications/

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