Laboratory Measurements of the Deep Venusian Atmosphere

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LABORATORY MEASUREMENTS OF THE DEEP VENUSIAN

ATMOSPHERE

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To my parents...
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LABORATORY MEASUREMENTS OF THE DEEP VENUSIAN ATMOSPHERE

TIMOTHY J. PALINSKI

ABSTRACT

NASA Glenn Research Center has designed and built a test chamber that can recreate the hot, dense atmospheric conditions of the deep Venusian atmosphere, where pressures range as high as 92 atmospheres and temperatures as high as 740 K. The majority of this thesis lies in experimentally measuring and quantifying the infrared absorption of CO$_2$ at Venus-like conditions in this laboratory setting. In particular, we describe the challenges and solutions involved in achieving repeatable laboratory test conditions, as well as the iterative process of modifying/optimizing our experimental test setup, including proposed future improvements. We discuss our measured CO$_2$ absorption spectra, qualitatively, in terms of theoretical models, and quantitatively, through comparisons with other available laboratory data. Specifically, we replicated two tests conducted by European Space Agency (ESA) researchers. The first of these tests looked at the effects of high pressure on the infrared absorption of CO$_2$. For this test, a band integration method was used to compare our results to ESA’s, resulting in agreement to 1.08%. The second of these tests involved taking CO$_2$ absorption measurements at conditions found 22 km above Venus’s surface, measuring the effects of
both high pressure and high temperature on the infrared spectra. Band-integrated areas were also calculated for this test, however, since ESA did not publish their band-integrated results, our comparison was based on individual absorbance peaks. For this test, our measurements differed by approximately -12.0% compared with the literature. This difference was attributed to thermal inhomogeneity in our test setup at elevated temperatures, and modifications to improve thermal homogeneity were proposed. Finally, we describe the relevance of this work, especially with regards to the quantification of trace gasses against the strong CO$_2$ background. Specifically, we present data showing how elevated temperatures and pressures modify the spectrum of CO$_2$, and discuss the implications for quantifying the trace gasses with our particular test setup. Based on this research, we expect the quantification of OCS (carbonyl sulfide) at the conditions (and concentrations) found in Venus’s atmosphere to be especially challenging.
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NOMENCLATURE

AU: Absorbance Unit

ESA: European Space Agency

FFT: Fast Fourier Transform

FTIR: Fourier Transform Infrared

GEER: Glenn’s Extreme Environment Rig

HITEMP: High-temperature molecular absorption (database)

HITRAN: High-resolution transmission molecular absorption (database)

IR: Infrared

$P_{cell}$: Gas cell/tubing pressure

NASA: National Aeronautics and Space Administration

NIST: National Institute of Standards and Technology

TC: Thermocouple

$T_{in}$: Gas cell inlet temperature

$T_{out}$: Gas cell outlet temperature

$T_{pr}$: Pressure transducer temperature

$T_{sfc}$: Gas cell surface temperature

VEXAG: Venus Exploration Analysis Group
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CHAPTER I
INTRODUCTION

This thesis is an attempt to illuminate one small portion of the much larger, and more complex problem of making chemical composition measurements of Venus’s atmosphere: in particular, we explore the effects of high pressure and high temperature on the infrared absorption of gasses found in Venus’s atmosphere. The analysis is far from exhaustive, yet we offer our findings to the small body of existing knowledge in this area of laboratory spectroscopy. Furthermore, the focus of this thesis has been narrowed from the broad field of infrared spectroscopy, to a deliverable goal specific to our application, namely that of characterizing our Fourier Transform Infrared (FTIR) spectrometer for measurements of the deep Venusian atmosphere, as simulated in NASA Glenn’s Extreme Environment Rig (GEER) test chamber. The development of this thesis has certainly been a process of continual adjustment and refinement, as we have learned to appreciate the complexity of the problem. Nevertheless, through the course of this research, we were able to find good agreement between our results, and those of other researchers in this area, and it is our hope that this data will be useful for further comparison beyond our specific application.
By continuing to explore Venus scientists hope to learn more about our own planet. In the past sixty years our knowledge of Venus has increased greatly. The third brightest object in the sky, Venus has always been shrouded in mystery – in large part due to the thick, reflective cloud cover, which contributes to the planet’s intense brightness. With the age of spacecraft – beginning in the 1960’s and continuing today – we have been able to peer beneath these thick, mysterious clouds and discover a very unexpected environment.

Early Venus scientists dreamed of lush tropical rainforests, teaming with biological life. They were in for a surprise when the first probes poked beneath the clouds and began returning data to Earth: clouds made of sulfuric acid, a suffocating atmosphere of 97% CO$_2$ with pressures in excess of 1300 psi (90 atm), and temperatures near 900 °F (740 K) [1]. Venus’s atmosphere and surface conditions are unique in the solar system. Scientists have tried to make sense of this data, and yet Venus still continues to defy categories: its orbital period (year) is roughly the same length as its rotational period (day); it rotates in the opposite direction of the rest of the planets; there is no apparent magnetic field; its core and surface dynamics (how the core loses heat) are not well understood; there is an unknown absorber of UV light in the upper atmosphere; a runaway greenhouse effect has scorched the surface of the planet; and high speed winds known as “superrotation” drive the clouds around the planet much faster than the planet’s slow rotation rate would seem to allow – these are just a few of Venus’s yet unsolved mysteries.
These mysteries may be due in part to the nature of planetary science: a unifying, predictive theory of how planets evolve may never be found. While some general principles hold, given the chaotic nature of how planets form, a small change in initial conditions leads to vastly different final planets [1]. In some sense all planets are outliers.

This does not mean there is nothing to learn from our planetary neighbors. As we gain more insight into climate change and the instability and variability of the “Earth system,” scientists are seeking to make comparisons and learn from Venus. Although there are significant differences between our planet and Venus, there is also much in common: Venus and Earth have roughly the same size, composition, and gravity; they are relatively close planetary neighbors and presumably had similar origins. Most significantly, Venus, like Earth, is “alive” as a planet: it has an active core, and a dynamic atmosphere, which is in chemical disequilibrium – implying complex feedback loops between chemical sources and sinks [1]. In physics terms, Venus, like Earth, is a place of very low entropy – it is highly organized, and very far from any sort of equilibrium. Because of this, Venus is a very viable candidate to test some of the theories of Earth’s evolution and dynamic processes. In this way, Venus may act as a second laboratory where we may conduct “controlled” experiments at the planetary level [1]. Given these similarities, the following questions arise [2]:

- How did Venus and Earth evolve so differently?
- What may have caused this divergence? Or, are all planets anomalies?
- Was Venus ever more Earth-like (hospitable to life as we know it)?
- Will Earth one day become more Venus-like?
• What sustains the chemical disequilibrium in the atmosphere?

• What is the mysterious UV-absorber?

• What drives the “superrotation” of the upper clouds?

• How does the core lose heat? (volcanoes? plate tectonics?)

Questions like these continue to motivate our study of Venus, as we try to make sense of our own world in light of this nearby, similarly complex planet.

1.1 Problem Overview and Research Objective

In order to address these questions and others, scientists will need more advanced instruments. Historically, we have learned much about Venus using optical instrumentation: the very first observations were done with the naked eye; later, telescopes were used to view Venus across a wider portion of the electromagnetic spectrum (UV and infrared, in addition to visible); and, similar optical devices (spectrometers) were sent on probes to Venus to measure chemical compositions. It turns out this last application is especially relevant to Venus. Not only do we have a rich history and many years of experience applying optical instrumentation to planetary science, this instrumentation is very robust and especially well suited to Venus’s harsh surface conditions. The sensitive electronics and other fragile components can be isolated from the environment using chemically inert windows, which transmit the spectral information (Figure 1).
Figure 1: Infrared spectrometer used for remotely sensing planetary atmospheres (Mercury Radiometer and Thermal Infra-Red Spectrometer – MERTIS). The optics and electronics are enclosed in a box, and are completely isolated from the environment. This enclosure may be strengthened to withstand more extreme environments, but the principle is the same. Reprinted with permission [3].

While optical sensors can be protected from the corrosive environment and high pressures, without active cooling they will eventually succumb to the high temperatures found on Venus. The parallel development of ultra high temperature electronics and sensors, and active cooling systems are both ongoing research areas at NASA Glenn Research Center. With this improved infrastructure, the next generation sensors (and entire spacecraft) are expected to have much longer lifetimes than previous missions to Venus (where the record time for survival on the surface is 127 minutes [4].
Research Objective

The main goal of this research is to characterize our instrument, a Fourier Transform Infrared (FTIR) spectrometer, for quantitative measurements of Venus’s chemical composition simulated inside of NASA Glenn’s Extreme Environment Rig (GEER) test chamber. This requires an understanding of how the very high temperatures and pressures affect the infrared absorption of molecules in Venus’s atmosphere – in particular CO₂. As theoretical models are known to be incomplete at these conditions, experimental data are required [5]. Therefore, we seek to optimize our test setup for such measurements; to establish our system’s baseline performance; to gather data experimentally, comparing it with known sources; and, finally to understand how the strong CO₂ absorption impacts our ability to detect Venusian trace gasses with our particular system.

1.2 Motivation

Scientists have a very good understanding of how molecules absorb infrared radiation at ambient pressures and temperatures. Much of this understanding comes from studying the properties of Earth’s atmosphere, through many controlled laboratory tests at these conditions [6]. As we diverge greatly from ambient conditions, our understanding of the infrared properties of gasses becomes less clear. This is even true of familiar molecules such as CO₂ and H₂O. For most of the scientific community there is no need to study the properties of gasses at extreme conditions. Planetary scientists, however,
must be comfortable with the infrared response at these conditions in order to develop more effective instruments (for both ground-based and in-situ studies).

One way to gain such familiarity is through ground-based testing. The Venus Exploration Analysis Group (VEXAG) has identified ground-based test facilities as a high priority for future mission development [7]. In order to achieve the greatest science return on missions, surface lander longevity and measurement capability should both be increased significantly over the previous missions [7].

Specifically, the most recent VEXAG report (February ’14) cites ground-based analysis of the optical properties of gasses at Venus-like temperatures and pressures as a high priority [7]. The classes of measurements in this study are divided into two categories: “Category 1 are laboratory data necessary for retrieving Venusian system variables from calibrated instrument data, and Category 2 are laboratory data necessary for characterizing fundamental Venusian processes based on newly revealed Venusian system variables” [7]. Our research in this area at NASA Glenn Research Center is a study of Category 1 measurements. By showing how these gasses behave in a laboratory setting, we may help scientists make sense of their calibrated instrument readings (for both in-situ and remotely sensed data from Venus). More specifically to our project, these data are necessary for making sense of our own measurements; in fact this is where our research began. With this in mind, we turned to the literature.
1.3 Literature Review

While there are very few groups currently researching this particular area (laboratory spectroscopy of high temperature, high pressure gasses), a great resource was found in the European Space Agency’s study of Venus’s atmosphere. The Venus Express mission, launched in 2005, is an orbiter designed to probe the depths of Venus’s atmosphere. Central to this mission is the ability to investigate the newly discovered “nightside windows,” using the Visible and InfraRed Thermal Imaging Spectrometer (VIRTIS) instrument [8]. In order to make sense of the data returned from VIRTIS, scientists in Italy built a test setup very similar to our own, allowing them to study Venus’s infrared absorption in a carefully controlled laboratory environment. Venus’s infrared spectrum is dominated by CO$_2$, so in order to untangle the spectra of the many trace components, this strong CO$_2$ background must first be understood. ESA’s work focuses exclusively on CO$_2$ across a wide range of temperatures and pressures found Venus’s atmosphere, following the descent profile of the Venus International Reference Atmosphere (VIRA) [5, 8 - 11].

The ESA team also references several papers, unrelated to planetary science, which explore the effects of high pressure on CO$_2$ spectra. These studies, which test CO$_2$ at much higher pressures than those found on Venus, reveal previously un-modeled behavior (line-mixing), which was subsequently incorporated into ESA’s first principle model of Venus’s infrared absorption [12]. Figure 2 shows the individual laboratory test points for CO$_2$ absorption at high temperatures and pressures.
Figure 2: Compilation of test points found in literature for laboratory studies of the infrared spectrum of pure CO$_2$ at high temperatures and pressures. References appear in the legend.

Not surprisingly, essentially all of the experimental data at these conditions were taken in support of VIRTIS or closely associated research projects. Notice how the majority of these points are found along a well-defined curve – this is the VIRA descent profile where temperature and pressure both vary inversely with altitude. For each of these points, there exists an associated infrared spectrum. Figure 3 shows how these tests were distributed across the different CO$_2$ absorbance bands.

Figure 3: Laboratory test points for pure CO$_2$ infrared spectra according to absorbance bands.
It is significant that essentially all of the laboratory infrared measurements of CO$_2$ at Venus-like conditions exist within these four bands; the reason why researchers have chosen these particular bands has to do with the signal quality at high absorption levels. The very strong peaks for CO$_2$ (2300 cm$^{-1}$ and 3700 cm$^{-1}$) absorb too much light and “saturate” the absorbance band. It is best practice to stay below 1 absorbance unit (AU) in absorbance intensity [18]; below this threshold the signal contains meaningful information.

Other resources were found which go into the details of how the instrumentation itself (FTIR) may be modeled [13, 14]. A comprehensive system model should include these effects, as well. However, our primary concern was simply understanding how CO$_2$ behaves at very high temperatures and pressures – effects which we believe outweigh the more subtle (and better understood) features introduced by the instrumentation itself (diminished spectral resolution, quantization error, apodization distortions, etc.).
1.4 Contribution and Structure of Thesis

The primary contributions of this thesis are: (1) the development of a system which can deliver repeatable, controllable test conditions of the simulated Venusian atmosphere within our FTIR gas cell; (2) establishing our baseline FTIR performance – which is foundational to future testing – by comparing our results with other experimental data taken at similar conditions; and (3), an analysis of the influence CO$_2$’s infrared absorption is expected to have on the trace components within Venus’s atmosphere, specifically upon our ability to detect these components within our test chamber.

At the beginning of this research, we intended to go into depth in developing a predictive, theoretical model, which we could then compare with our experimental measurements. We quickly realized that such an undertaking would be far beyond the scope of this thesis! Additionally, much work has already been done in seeking to improve theoretical modeling in this area [8]. So, instead of reinventing the wheel, time would be much better spent studying and understanding these existing models – and then if improvements could be made (i.e. if differences between measured and modeled data were noticed), we could revisit the models. Furthermore, the experimental side of this research is more foundational, and proved to be much more challenging – and interesting – than expected. As a result, the majority of our efforts were focused in this area. We feel much more confident in our system because of this work – not just in the experimental workings, but in the theoretical concepts as well, which were illuminated through our experimental testing.
Structure of the Thesis

Chapters 2 and 3 supply the underlying theory, discussing the physics of molecular absorption, and recreating the atmosphere of Venus, respectively. Chapter 2 is especially important, as these theoretical concepts of molecular spectroscopy are referenced throughout the thesis in the descriptions of our data. In Chapter 3, we also discuss our experimental test setup and the iterative process of modifying our system to provide repeatable, controlled conditions of Venus’s atmosphere. Chapter 4 is really the heart of this thesis. Here, we describe the process of achieving our baseline FTIR performance; we make comparisons with other laboratory measurements, and, finally, we describe how CO₂ affects our ability to measure trace gas components in Venus’s atmosphere. Chapter 5 concludes the thesis, tying together the results and discussion from Chapter 4, and offering suggested improvements and future work.
CHAPTER II

MOLECULAR ABSORPTION SPECTROSCOPY

In this chapter, we discuss molecular absorption, as well as available theoretical models and FTIR theory. We begin by exploring the different ways in which matter and light interact in Section 2.1, in Section 2.2 we discuss the modes of vibration specific to CO₂, and, finally, we give an overview of FTIR theory in Section 2.3.

2.1 Interactions Between Matter and Light

The field of spectroscopy is the study of how matter and light (electromagnetic radiation) interact. At the quantum level, things behave somewhat unexpectedly: matter and light can either have particle or wavelike properties, depending on the type of process involved. An interaction between a photon (a “particle” of light) and a particle of matter can be described in terms of a collision. Quantum collisions are a little bit more complicated than collisions between billiard balls, but there are some similarities. Just like collisions between two macroscopic objects, collisions between matter and light can
be either totally elastic, inelastic, or totally inelastic. The main subfields of spectroscopy can be understood in terms of these different types of collisions: Rayleigh scattering refers to totally elastic collisions, Raman scattering refers to inelastic collisions, and absorbance spectroscopy (the type studied in this thesis) refers to totally inelastic collisions. Unlike macroscopic collisions, however, the energies involved in matter-light collisions only take on certain values – they are quantized. For a totally inelastic collision involving two particles, 100% of the energy of one particle is transferred to the other particle. Since one of these particles is a photon, we can describe the energy in the following way,

\[ E = h\nu \]  \hspace{1cm} (1)

and, because quantum particles can only absorb or emit energy at discrete levels, the energy of a photon capable of being absorbed by a particle is described below,

\[ E = \Delta E = (E_u - E_l) = h\nu \]  \hspace{1cm} (2)

where \( E_l \) is the lower (ground) energy state of the particle and \( E_u \) is the particle’s upper (excited) state\(^1\). This equation describes energy absorption across the entire range of the electromagnetic spectrum (shown in Figure 4).

\(^1\) Transitions between other energy states are possible, but the transition from the ground to the first excited stat is the most common [21].
Short, high-energy wavelengths (such as visible light) require large differences in energy levels for absorption (electrons between shells in an atom), while longer wavelengths (such as infrared and microwave) are absorbed at lower energy differences (molecular bond energies). Table 1 shows the energies involved in some different types of matter-light interactions.

Table 1: Types of matter-light interactions and associated energy levels [16].

<table>
<thead>
<tr>
<th>Type</th>
<th>Region</th>
<th>Energy (eV)</th>
<th>Frequency (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionizing</td>
<td>X-ray</td>
<td>&gt;124</td>
<td>&gt; 3.0x10^16</td>
</tr>
<tr>
<td>Ionizing/Electronic</td>
<td>Ultraviolet</td>
<td>3.1 - 124</td>
<td>7.5x10^14 – 3.0x10^16</td>
</tr>
<tr>
<td>Electronic</td>
<td>Visible</td>
<td>1.7 – 3.1</td>
<td>4.0x10^14 – 7.5x10^14</td>
</tr>
<tr>
<td>Vibrational</td>
<td>Infrared</td>
<td>0.001 – 1.7</td>
<td>3.0x10^11 – 4.0x10^14</td>
</tr>
<tr>
<td>Rotational</td>
<td>Microwave</td>
<td>0.00001 – 0.001</td>
<td>1.6x10^9 – 3.0x10^11</td>
</tr>
</tbody>
</table>

Having a photon with the right frequency (energy) is a necessary condition for absorption, but it is not sufficient. The particle itself must be capable of responding to, and interacting with, this photon. When we talk about the frequency of light, we mean the frequency of the oscillating electric (E) and magnetic (B) fields, shown in Figure 5.
In order to interact with the light’s electric field ($E$), the particle must have an electric dipole. For a molecule, this means one side of the molecule must be more positive (or negative) with respect to the other. H$_2$O, for example, has a strong dipole moment, with which an incident photon may interact. In fact, nearly all molecules have some dipole moment (either permanent, or induced)$^2$, and these molecules are said to be IR-active. Only homoatomic molecules, such as N$_2$ and O$_2$, lack a dipole moment altogether. Therefore, these molecules are incapable of interacting with light’s electric field [16]. To summarize, two conditions are required for infrared absorption:

1. The energy of the infrared light (which is proportional to frequency) must match a possible transition energy within the molecule

2. The molecule must be capable of interacting with the electric field of the light (i.e. the molecule must be IR-active)

---

$^2$ An induced dipole moment occurs when vibrations inside of a molecule cause other, previously hidden, dipoles to become active. CO$_2$ is one example of a molecule with induced dipole moments.
**Harmonic Oscillator**

A good place to begin our discussion of how molecular bonds vibrate and absorb energy is by looking at the classical harmonic oscillator. Once we cover the basics, we will move on to the quantum harmonic oscillator, and then briefly discuss a more realistic approximation given by the Morse potential. We begin by considering the simplest harmonic oscillator: an un-damped mass on a spring (Figure 6).

![Figure 6: Classical harmonic oscillator. Minimum and maximum displacement are given by \(-A\) and \(+A\), respectively. Adapted from [19].](image)

The molecular bond (shared electron) is approximated by the spring, while the mass represents one of the atomic nuclei (the other end of the spring is fixed in this simplified example). Hooke’s Law relates force to displacement,

\[ F = -ky \quad (3) \]

where \(y\) is the vertical direction (in Figure 6), and \(k\) is the spring constant. The potential energy function \(U\) is derived below:
\[ F = -\frac{dU}{dy} \]  
(4)

\[ dU = -Fdy \]  
(5)

\[ \int dU = -\int Fdy \]  
(6)

Substituting \( F \) from Equation 3, the total potential energy, \( U \), is given as follows.

\[ U = -\frac{1}{2}ky^2 \]  
(7)

Using this potential energy function, we can find the vibrational frequencies associated with this harmonic oscillator by solving the equation of motion. The resulting frequencies for the single mass system, and for the reduced mass system (\( \mu \)) consisting of two masses (where \( \mu = \frac{m_1m_2}{m_1+m_2} \)) are given below.

\[ n_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \]  
(8)

\[ n_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \]  
(9)

So, we see that the classical frequency of oscillation \( (n_0) \) depends on two things: the mass of the objects in the system (given by \( m \), or \( \mu \)), and the “stiffness” of the spring connecting these objects (\( k \)).
Quantum Harmonic Oscillator

Next, we investigate the quantum harmonic oscillator. Instead of working with masses and springs, we return to atomic nuclei and molecular bonds. For this example, we consider two atoms bound by a single electron. The main difference between the classical and quantum harmonic oscillator is that when “quantum-sized” systems (atoms, molecules, etc.) are bound, only certain energy levels are allowed\(^3\) [21]. This is why spectral lines occur at discrete frequencies. As we will discuss later, there are effects that blur the spectral lines, but in principle, individual transitions are represented by individual spectral lines. The possible energy states (and therefore spectral line positions) for the quantum harmonic oscillator are shown in Figure 7.

\[ E(n) = \left(n + \frac{1}{2}\right) \hbar \omega \quad (n = 0, 1, 2, \ldots) \] (10)

\(^3\) Interestingly, quantum particles that are not bound behave just like macroscopic objects [21].
Equation 10 was found by solving the Schrödinger Equation for the harmonic oscillator potential [22]. In this equation, $n$ is the vibrational quantum number – it represents the discrete vibrational energy states for the quantum harmonic oscillator – and, $n_0$ is the classical vibrational frequency. Even in the ground state ($E(0)$), the bonding electron has some energy – this can be understood in terms of Heisenberg’s Uncertainty Principle: if the electron had zero energy, its position and momentum could both be precisely determined (since it would be resting at the bottom of the potential energy well). This is in violation of what is experimentally observed and described by Heisenberg’s Uncertainty Principle.

Notice that in the quantum harmonic oscillator, the energy levels are evenly spaced: the electron’s energy linearly increases with $n$. The shape of the potential energy function gives the spacing of the energy levels. In real molecular bonds, the potential energy function is more complex than the quantum harmonic oscillator, and as a result, the energy level spacing is different (Figure 8).

![Figure 8: Morse potential compared with quantum harmonic oscillator. Notice how the Morse potential describes bond dissociation, and as a result, the energy level spacing becomes more complicated compared to the quantum harmonic oscillator (public domain image [23]).](image)
In particular, there is a point at which the electron can break free of the two nuclei that hold it – this is called the bond dissociation energy, and is represented by the asymptotic behavior of the potential energy function as the bond length increases beyond equilibrium. Notice also how the Morse potential becomes steeper as the bond length decreases from equilibrium – this more accurately describes the observed behavior of the repulsion of two like charges (see Figure 8: as \( r \) decreases, the positive nuclei repel each other more strongly than the simple quantum harmonic oscillator predicts). In order to account for these effects, the quantum harmonic oscillator energy level equation given above is modified to include a correction factor describing the observed anharmonicity [8].

\[
E(n) = \left( n + \frac{1}{2} \right) n_0 - a n_0 \left( n + \frac{1}{2} \right)^2 \quad (n = 0, 1, 2, \ldots)
\]  

The divergence between the quantum harmonic oscillator and the Morse potential is seen especially at high-energy transitions (as the bond dissociation limit is approached and the spacing becomes increasingly dense).

Rotational-Vibrational Spectra

To really understand molecular spectra, we also must consider how rotations of the molecule modify the positions of the vibrational spectral lines. With rotations, we see the numerous spectral lines clustered around a common vibrational mode (Figure 9).
Figure 9: Rotational-vibrational spectra for HCl.

These rotational lines are best understood by first considering the classical rigid rotor. Consider two masses rotating about their center of mass on a perfectly rigid connector (Figure 10).

![Figure 10: Rigid rotor. Image credit: Kristin Spear, NASA Glenn Research Center. Adapted from [24].](image)

The energy associated with a classical rigid rotor is given by,

$$E = \frac{I^2}{2I}$$  (12)
where, $L$ is the angular momentum, and $I$ is the moment of inertia. Once again, in the quantum-mechanical case, the energies are quantized. The solution to the Schrödinger Equation for rotational energy is shown next [24].

\[
E = \frac{\hbar^2}{2I} J(J + 1) \tag{13}
\]

Here, $J$ is the rotational quantum number, which describes the discrete, observed rotational states. The $\hbar^2/2I$ term is commonly shortened to $B$ (known as the rotational constant), so our expression for the energy due to rotational energy becomes:

\[
E(J) = B(J + 1) \tag{14}
\]

The rotational energy varies like $J^2$, and, unlike vibrational energy, it is possible for the rotational energy to be zero ($J = 0$). This expression describes an ideal (quantum) rigid rotor. For detailed explanations of the quantum physics behind these results, as well as the derivation of the vibrational energy levels, please see the references [22, 24, 33]. In reality, a molecule is not completely rigid, and, as a result there is some bending associated with the rotation [8]. Including a correction factor accounting for this bending effect (where $D$ is the centrifugal constant), we have the following equation.

\[
E(J) = BJ(J + 1) - DJ^2(J + 1)^2 \tag{15}
\]

In Figure 11, we see how rotational energy contributes to the fine structure of the molecule’s energy level spacing: for each vibrational energy level, there are many possible rotational energy levels.
These concepts are summarized in Figure 12, where the relationships between vibrational energy and rotational energy are linked to the infrared spectra of HCl.

Figure 12: Rotational-vibrational spectra for HCl showing how the different rotational energies correspond to different absorption peaks centered around a common vibrational energy mode. Image credit: Kristin Spear, NASA Glenn Research Center. Adapted from [25].

Figure 13 gives a wider view of the absorption for HCl, showing two distinct vibrational modes with the fine rotational structure.
The rotational transitions can be grouped into three categories: $P$-branch (lower wavenumbers), $Q$-branch (central), and $R$-branch (higher wavenumbers). Assuming there is no interaction between the vibrational energy and the rotational energy, the total energy is a function of both $n$ and $J$, and is given by their sum [8, 32].

$$E(n, J) = E(n) + E(J)$$  \hfill (16)

$$E(n, J) = \left(n + \frac{1}{2}\right)n_0 - an_0 \left(n + \frac{1}{2}\right)^2 + BJ(J + 1) - DJ^2(J + 1)^2$$  \hfill (17)
This simplified model predicts the $P$ and $R$ branches to have equal spacing between the rotational lines. However, observations show that the $P$-branch spacing is greater than the $R$-branch [31] (see Figure 14 below, and refer also to the spectra of HCl in Figure 12).

![Figure 14: Increased spacing in $P$-branch and compressed spacing in $R$-branch due to interaction between vibrational and rotational energy [31].](image)

Including coupling terms, which link the vibrational and rotational modes, and account for this observed behavior, we have our final equation for the vibrational and rotational energy levels in a molecule [8].

$$E(n, J) = \left( n + \frac{1}{2} \right) n_0 - an_0 \left( n + \frac{1}{2} \right)^2 + B_0 J(J + 1) - \alpha \left( n + \frac{1}{2} \right) J(J + 1)$$

$$- D_0 J^2 (J + 1)^2 - \beta \left( n + \frac{1}{2} \right) J^2 (J + 1)^2$$

(18)

This equation provides a good description of observed behavior, correctly predicting line spacing and relative intensity. As the thermal energy ($J$) increases, the spacing in the $P$-branch increases further, while the $R$-branch becomes even more compressed [33]. This is consistent with what we observe later in our experimental results, and this underlying theory is helping us understand how high temperatures modify the spectra. Next, we present the selection rules in, Table 2, describing possible (likely) transitions between different energy levels [8].
Table 2: Selection rules for transitioning between different energies within a molecule [8].

<table>
<thead>
<tr>
<th><strong>Vibrational</strong></th>
<th><strong>Rotational</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta n = 0, \pm 1, \pm 2, \pm 3 \ldots ) (anharmonic /Morse potential)</td>
<td>( \Delta J = 0, \pm 1 )</td>
</tr>
<tr>
<td></td>
<td>+1 ( \rightarrow ) R-branch</td>
</tr>
<tr>
<td></td>
<td>-1 ( \rightarrow ) P-branch</td>
</tr>
<tr>
<td></td>
<td>0 ( \rightarrow ) Q-branch</td>
</tr>
</tbody>
</table>

For more detailed discussions of the selection rules and the underlying physics, please see the references [8, 31-33].

*Probability for Absorption*

Recall that in order for infrared absorption to occur, two conditions must be met:
(1) the energy of the photon must match an energy transition inside of the molecule, and
(2) the molecule must be IR-active. The baseline\(^4\) absorbance intensity (peak height) of an individual spectral line is determined by the transition probability. This probability is related to the number of molecules that are able to accept an incident photon at this frequency. In order to absorb a photon, the molecule has to be in a low energy state \((E_l)\), so that it can make the transition to a higher energy state \((E_u)\); the number of the molecules that can participate in absorption is given by the difference of those in the high energy state \((N_u)\) and those in the low energy state \((N_l)\). Therefore, the absorbance intensity \((A)\) has the following relationship:

\[
A \propto (N_u - N_l)
\]  \(\text{(19)}\)

\(^4\) At constant density, and constant environmental conditions – as we will see later, varying any of these impacts the absorbance intensity.
The number of molecules in the low energy state is related to the Boltzmann distribution [21]:

\[ \frac{N_u}{N_i} = e^{-(E_u-E_l)/kT} \]  \hspace{1cm} (20)

where, \( k \) = Boltzmann constant = 1.38x10^{-23} \text{ J/K}, and \( T \) = temperature (K). Substituting Equation 20 into Equation 19, we have:

\[ A \propto (N_i - N_i e^{-(E_u-E_l)/kT}) \]  \hspace{1cm} (21)

So, we can see that as the temperature increases, more molecules enter their excited state and therefore are unable to absorb photons. Practically, this means that when all other variables are held constant, increasing temperature decreases absorbance intensity (peak height). We will see this effect later, in our experimental testing. The overall shape of the spectra is a fundamental property of each molecule; the peak locations and relative intensities allow molecules to be uniquely identified, each one having its own spectral fingerprint – this overall shape is then modified according to the temperature and pressure conditions within the sample.

**Line Broadening Mechanisms**

Understanding the ways in which the extreme environmental conditions modify the spectra is an important part of this thesis. At the individual line level, there are three primary ways in which spectral lines are broadened:

1. Natural line broadening (resulting from Heisenberg’s Uncertainty Principle)
2. Pressure (Lorentz) broadening (due to molecular collisions)

3. Temperature (Doppler) broadening (due to temperature induced velocities)

For our purposes, natural line broadening can be ignored, because of its very small contribution (far below the resolution of a typical infrared spectrometer) [8]. The other two line broadening mechanisms have important, measurable consequences, as described in literature [5, 8, 12]. The effects of Doppler and Lorentz broadening on an individual spectral line are shown in Figure 15.

![Doppler (Gaussian) and pressure (Lorentzian) broadening effects](public domain image [34]).

Detailed, mathematical descriptions of these line-broadening mechanisms are beyond the scope of this thesis, but may be found in literature [8]. For this thesis, we are primarily concerned with qualitatively interpreting our measured spectra in light of these effects. As shown in the simulations in Figure 16, individual line broadening noticeably impacts the overall measured spectra.
In Figure 16a, we see that individual spectral lines are resolved. By increasing pressure (holding temperature constant), these lines broaden and significantly change the overall shape of the spectra (Figure 16b).

A number of theoretical models exist which describe the combined effects of pressure and temperature on individual spectral lines. The High-resolution transmission molecular absorption (HITRAN) database provides this information for a large number of
molecules near ambient temperatures and pressures. The simulations shown in Figure 16 are based on the HITRAN model. As temperatures and pressures increase greatly beyond ambient conditions, HITRAN has been found inadequate in accurately describing these effects [5, 12, 30]. Several improvements to HITRAN may be found in literature. A model implemented by the ESA team does a much better job describing high-pressure spectra [5, 8]. In particular, this model accounts for spectral line-mixing effects and collision-induced absorption at high pressures. Even in this improved, predictive model, the researchers noticed effects that were still best described empirically [5]. Because of this, we can see the value of carefully controlled, experimental measurements.

Additionally, the effects of increased temperature are captured in the HITEMP database. While individual line shapes are well described with HITRAN’s temperature modeling, transitions at high thermal energies are missing [30]. These high-temperature transitions (whose theory is described above, in the section on rotational-vibrational spectra) significantly contribute to the overall spectra. The HITEMP database includes these new transitions, offering a much better picture of high-temperature absorption. To our knowledge, a unified model that accurately incorporates both pressure (line-mixing) and temperature (HITEMP transitions) is still lacking, further highlighting the importance of experimental measurements at temperature and pressure extremes.
2.2 Modes of Vibration for CO$_2$

Since most of our time will be spent studying CO$_2$, we take a closer look at how this molecule absorbs infrared light. CO$_2$ is a strong absorber of infrared light because it can vibrate/bend/stretch and absorb energy in many ways. Other important greenhouse gasses, like H$_2$O, share this characteristic. In general, the more degrees of freedom a molecule has, the more ways it can accept energy. For linear molecules, the number of fundamental modes is of vibration given by $3N - 5$ (where $N$ is the number of atoms), and $3N - 6$ for nonlinear molecules. Since CO$_2$ is a linear molecule consisting of three atoms, there are four fundamental modes of vibration (Figure 17).

![Figure 17: Vibrational modes of CO$_2$. Image credit: Kristin Spear, NASA Glenn Research Center. Adapted from [28].](image)

The first mode, $v_1$, is not IR active, since the dipole moment of the molecule does not change. As a result, this mode of vibration does not appear in the spectra. The others, $v_2$ and $v_3$, are shown in Figure 18.
Other modes of vibration can also occur: overtones, which are integer multiples of the fundamental vibrational modes, and linear combinations of the fundamental vibrational modes. For example, the absorption feature appearing near 3700 cm\(^{-1}\) is a linear combination of the \(v_1\) and \(v_3\) modes. Note that the quantum harmonic oscillator does not predict overtones or combination bands, since it only allows transitions between adjacent states [27]. The Morse potential does a better job of describing what is empirically observed, as it handles these other transitions.
2.3 FTIR Spectroscopy

A Fourier Transform Infrared (FTIR) spectrometer was used for all of the spectral measurements in this thesis. In this section, we describe how the FTIR works, as well as the theory behind quantitative measurements. First, we describe the most fundamental law in quantitative spectroscopy. The Beer-Lambert Law (commonly shortened to Beer’s Law) relates the measured absorbance intensity $A$ to the molar concentration of the sample $c$ (mol/m$^3$).

$$A = \varepsilon lc$$  \hspace{1cm} (22)

In order to avoid ambiguity with the term concentration, throughout the rest of this thesis we will refer to molar concentration as density (notice that the units are the same). Referring to Equation 22, we can see there is a linear relationship between $A$ and $c$, that is scaled by two parameters: $\varepsilon$, the absorptivity (describing the likelihood of absorption), and $l$, the pathlength of the light through the sample. This makes sense: for a constant density (molar concentration), increasing the pathlength increases the amount of possible photon-molecule interactions, and results in a stronger absorbance peak. Similarly, a higher absorptivity means that the molecule is more likely to make the given transition, also resulting in stronger absorbance. As we will discuss later, there are limitations to Beer’s Law, but as long as it is used properly, it is a powerful tool for quantitative analysis [27]. Figure 19 shows the transmittance of incident light with $I_0$ through a sample of pathlength $l$, resulting in the transmitted light with intensity $I_t$. 

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Beer’s Law may be rewritten in a form that describes absorbance in terms of the incident and transmitted light shown above:

$$\log_{10}\left(\frac{I_0}{I_t}\right) = A = \epsilon lc$$  \hspace{1cm} (23)

A very good first principles derivation of Beer’s Law may be found in the references [21].

The main feature of a spectrometer, which makes spectral analysis possible, is the ability to split the continuous spectra into its component frequencies. A prism is a well-known device that separates light into its spectrum. However, the prism creates a continuous spectrum, whereas in spectrometer, we need to look at each frequency independently. One way to do this is with a diffraction grating. This device is similar to a prism, but it has the ability isolate individual frequencies – these frequencies of light may then be sent, one-at-a-time to a detector where their intensities are measured. In order to measure all of the frequencies, the dispersive spectrometer must increment the grating through each frequency. For high-resolution spectra, many lines (and therefore many increments) are required for a measurement; this takes a long time – up to 20 minutes per measurement.
As an improvement over this technique, the FTIR spectrometer was developed in the 1960’s. The FTIR was really made possible by the advent of the modern computer, which allowed previously impractical calculations to be made efficiently, reducing measurement times from minutes to seconds. Figure 20 shows the main components of an FTIR spectrometer, and how the signal is modified as it passes through the system.

Figure 20: Fourier Transform Infrared Spectrometer details [29].

At the heart of an FTIR spectrometer is a device called an interferometer. This ingenious device converts frequency content into a time domain signal, capturing spectral information from the continuous spectra of the source and encoding this information into the time domain signal (the interferogram)\(^5\). For our purposes, it is important to understand some of the ways in which the instrument itself modifies our measurements. In particular, any time there is a conversion between one type of information to another, some information is lost. Referring to Figure 20 above, when we convert from the frequency domain of the source (1) to the time domain of the interferogram signal (2),

\(^5\) The interferometer was originally developed in hopes of proving the existence of the “ether,” in the famous Morely-Michaelson experiment in 1887. It has since been applied to many different areas including spectroscopy and radar.
some resolution (ability to separate individual spectral lines) is lost. This is because of the mechanics of the interferometer, and is described in detail in the references [13]. This time domain signal then passes through the sample (3), where the molecules within this sample absorb some of its energy. In order to untangle the spectral information, and determine which individual frequencies were absorbed, the signal is converted back to the frequency domain by performing a Fast Fourier Transform (FFT) on the data acquisition computer (5). Once again, with this second conversion, some information is lost. Prior to taking the FFT, a windowing function known as an “apodization” function is applied to the interferogram to smooth the edges of this time domain signal, removing some of the distortions that would otherwise show up in the transformed signal. This is seen in another small decrease in resolution. The effective resolution in most FTIR spectrometers is still very good, and the measurements taken in this thesis were taken with a resolution of 1 cm⁻¹. So, the combination of the interferometer, and the FFT serves the same function as the diffraction grating mentioned above, but with greater efficiency. There are two other significant advantages to the FTIR technique, and these are listed below [29]:

1. **Multiplex advantage (Fellgett’s advantage):** Simultaneous measurement of input frequencies – this allows many scans to quickly be taken and averaged, greatly increasing the sign-to-noise ratio (SNR)

2. **Throughput advantage (Jaquinot’s advantage):** More light (energy) reaches the detector because of the FTIR’s less complicated optical path – this results in a further increase in SNR, allowing previously undetectable features to become apparent
CHAPTER III
RECREATING VENUS

The larger goal of this study, in addition to exploring the optical properties of gasses at Venus-like conditions, is to help enable high fidelity, on-line measurements of the chemical composition inside of NASA Glenn’s Extreme Environment Rig (GEER) test chamber. This facility has been designed to test materials and components for future missions to Venus, in addition to performing studies of minerals/geochemistry at Venus surface conditions. In both cases, it is important to measure and control the chemical environment. At the time of writing, this facility is currently being characterized and prepared for these tests.

This chapter begins with a discussion of Venus’s atmosphere in Section 3.1, followed by a description of the overall GEER test facility in Section 3.2. Next, in Section 3.3 the FTIR setup is described, and, finally in Section 3.4 we discuss some of the challenges in achieving repeatable test conditions inside of our FTIR gas cell.
3.1 Atmospheric Structure and Chemical Composition

Venus’s atmosphere is a very active place, and, in fact, this is one of the main reasons scientists would like to learn more about it. In particular, the atmosphere maintains itself in a chemical state of disequilibrium, implying hidden chemical sources and sinks [1]. Chemicals, such as H2SO4, SO2, OCS, CO and H2O, all vary with altitude [15], suggesting reactions and complex feedback loops, while CO2, the primary component of Venus’s atmosphere, is constant with altitude (below ~100 km). Understanding the actual conditions of CO2 on Venus is especially relevant to our experimental testing, which, in this thesis, focuses entirely on the infrared absorption CO2. Since its concentration is constant, our primary concern is the ability to meet the correct pressure and temperature combinations found in Venus’s atmosphere. The most reliable source of this information is found in the Venus International Reference Atmosphere (VIRA)\(^6\). From this curve, other researchers have plotted their test plans, and we have done the same. The vertical profile given by VIRA is shown in Figure 21, and is followed by the overall chemical composition in Table 3.

\(^6\) VIRA is a compilation of data from many different missions to Venus, combining information from orbiters, entry probes, and surface landers. As new data arrives from missions such as Venus Express, VIRA is likely to be updated in the near future.
Figure 21: Venus International Reference Atmosphere (VIRA) profiles [8].

Table 3: Composition of Venus’s atmosphere [1].

<table>
<thead>
<tr>
<th>Gas species</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>96.5 %</td>
</tr>
<tr>
<td>N₂</td>
<td>3.5 %</td>
</tr>
<tr>
<td>SO₂</td>
<td>180 ppm</td>
</tr>
<tr>
<td>HCl</td>
<td>0.4 ppm</td>
</tr>
<tr>
<td>HF</td>
<td>0.01 ppm</td>
</tr>
<tr>
<td>OCS</td>
<td>4.4 ppm</td>
</tr>
<tr>
<td>CO</td>
<td>23 ppm</td>
</tr>
<tr>
<td>H₂O</td>
<td>30 ppm</td>
</tr>
</tbody>
</table>

Next, we show some images, which depict the structure of Venus’s atmosphere: Figure 22 illustrates Venus’s greenhouse effect, showing how short-wavelength radiation from the sun is converted to thermal infrared radiation, and then re-radiated back toward space, where it is absorbed and trapped by the thick atmosphere of CO₂ (Chapter 2 describes why gases like CO₂ absorb so strongly in the infrared). This image is followed by Figure 23, which shows the expected chemistry in Venus’s atmosphere.
Figure 22: Venus’s greenhouse effect. Image credit: Carter Emmart. Reprinted with permission [1].
Our test facility, described in the next section, has been designed to recreate these challenging conditions, and, with the help of our FTIR, we will eventually include the full chemistry described in Table 3. Before making spectral measurements, it was important to first prove that we were actually achieving Venus-like conditions inside of our FTIR test cell. Therefore, a large portion of this thesis covers our work of achieving repeatable, accurate conditions along the VIRA curve, and this process is described in the following sections.
3.2 Facility Description

Designing a facility to simulate, and withstand the extreme conditions found on Venus’s surface is no small feat; in some ways the facility itself is a research project of its own. Early on in the course of this project, candidate materials for the main test chamber were tested in a similar facility at NASA Goddard Space Flight Center. Because of the corrosive nature of chemicals found in Venus’s atmosphere (SO$_2$, HCl, HF), these tests investigated a number of corrosion resistant nickel-based alloys, including Hastelloy, Inconel, and different varieties of stainless steel. Even CO$_2$, the major component of Venus’s atmosphere, was found to be corrosive at Venus surface conditions. Ultimately, a type of stainless steel (Type 304) was chosen as the material for the test chamber. In order to withstand the immense pressure inside, its walls are 2 1/8 in. thick, and its front and back end caps are 11 in. and 9 in. thick, respectively. This massive chunk of stainless steel tips the scales at over 10 tons (see Figure 24).
Figure 24: NASA Glenn’s Extreme Environment Rig (GEER).

Having dimensions of 3 ft. in diameter by 4 ft. in length, the GEER test chamber is the largest of its kind in the world. Its large internal volume allows larger scale components and possibly even small probes/landers to be tested. In addition to its large internal dimensions, we have the ability to introduce different gas species into the test chamber. This chemistry capability is really what sets GEER apart from other Venus test facilities, as it will enable the most accurate laboratory studies of the Venusian atmosphere to date. However, as we will see throughout this thesis, the complexities of measuring and controlling the chemical environment are some of the biggest challenges we are faced with in this facility. Table 4 summarizes the capabilities of other known Venus test chambers.
In order to achieve Venus conditions inside of our test chamber, we need three things: (1) chemistry, (2) pressure, and (3) temperature. Our operating procedure begins by filling the chamber with the desired masses of each component gas (beginning with the smallest concentration, and finishing with the largest). Since this is an isochoric process (constant volume), the mass sent into the chamber at the beginning of the test should equal the mass at the end of the test (assuming there are no leaks). A specially designed gas delivery system, using thermal mass flow controllers, is used to carefully meter in the desired mass of each component. Once the initial fill is complete, the chamber is heated, which in turn causes the pressure to rise. If the initial fill calculations are correct, we should arrive at our desired operating point. Incase there are leaks during
the course of testing, or if the initial fill was incorrect, gasses may be injected into the chamber using a gas booster system. Of course, the ability to correct a mix depends heavily on the current mixture inside of the chamber: if the deviations are too large, or if too much of a certain component is present, the chamber will have to be vented and refilled.

Figure 25: GEER facility and FTIR (white box) in foreground.

Figure 25 shows where the FTIR fits into the system (shown in the foreground). This instrument will eventually help us make reliable, real-time measurements of the chemical composition inside of our test chamber, verifying our initial mixture, and letting us know if we need to make corrections later on. But first we have to understand how the instrument itself responds to this extreme environment.
3.3 FTIR Hardware Overview

Our system consists of an ABB MB3000 Bomem style spectrophotometer, connected to a custom made high-pressure, high-temperature gas cell manufactured by CIC Photonics. The gas cell is made of Inconel, and is outfitted with sapphire windows sealed against special high-temperature Kalrez o-rings. The optical path length through the cell is 10 cm. Two band heaters wrapped around the gas cell are controlled by a PID controller and help ensure stable, repeatable temperature conditions inside. Since temperature and pressure play a big role in determining density (and therefore absorbance intensity), both of these variables are measured and controlled in the gas cell/associated tubing. The FTIR spectrophotometer housing and gas cell are shown in Figure 26.

![FTIR system](image1.png)

![Close-up of gas cell](image2.png)

Figure 26: (a) FTIR system, (b) close-up of gas cell.

The entire FTIR system (spectrophotometer, gas cell, valves, instrumentation, etc.) is located some distance away from the main chamber. In its present configuration,
the FTIR is set up to be used in a batch-sampling mode: samples travel through about 6 ft. of tubing, and may be selected from one of two ports on the main chamber: one near the top and one near the bottom – this should illuminate any differences in mixture consistency (stratification), if present. After a sample is taken, the gas cell is vented and prepared for the next sample. Although this volume of gas is very small (compared to the overall volume of the chamber), a recycling system is being planned in order to avoid decreasing the overall mass in the system each time a sample is taken. Figure 27 shows how the FTIR is integrated into the overall system.

![Diagram](image)

**Figure 27: FTIR connection to main chamber.**

The FTIR may also be operated completely independent of the main chamber, by pressurizing the gas cell directly from a K-bottle. This feature is especially useful for calibrating the FTIR, and this is how the majority of the data were taken for this thesis. Detailed descriptions of the specific test setup details, and the methods used in each test are given later in Chapter 4.
3.4 Experimental Test Setup

This section covers our experimental test setup in more detail, and discusses some of the challenges we encountered with our test setup. In any scientific measurement, and especially when venturing into unknown territory (away from comparisons to known results), it is important to establish the validity of the instrument and measurement process. In some sense, all scientific experiments are excursions into the unknown: if we knew what we were going to find, why look in the first place? We must therefore distinguish between the truly unknown quantity of interest, and uncontrolled variables in the system/process. Since our instrument had not been used before (i.e. there was no available calibration/measurement history), and is intended to operate at conditions that are not well understood, a good deal of time was spent building confidence in our equipment and measurement process. In fact, this testing might end up being the biggest contribution for this thesis, as it helps lay the groundwork for future testing.

3.4.1 Achieving Repeatable Test Conditions

Especially key to successful FTIR measurements and calibrations is the ability to create repeatable, controllable test conditions. This means carefully controlling the environment both inside of the spectrophotometer housing and inside of the gas cell – essentially every part of the optical path must be controlled (recall from Figure 20 that light travels from the source, through the interferometer, through the gas cell, and finally to the detector). In the spectrophotometer housing (where the source, interferometer, and detector may be found), a continuous N₂ (infrared transparent) purge is used to maintain a
clean background spectrum – if the background changes over time, this will be reflected in the absorbance intensities, contributing to a source of error; therefore, this variable must be controlled. By purging with N₂, we eliminate many sources of absorbance error (including impurities from water and CO₂). Despite this purging, other effects may still cause the background to change over time. For reasons described in more detail in Section 4.2, Measurement Uncertainty Analysis, it is important to keep a continuous N₂ purge running and take frequent background spectra. The conditions inside of the gas cell (pressure and temperature) must also be controlled. And this latter case, in particular, has proven to be especially challenging. To understand the importance of keeping these variables controlled, recall that according to Beer’s Law, absorbance intensity, our measured quantity of interest, is directly proportional to density\(^7\). Therefore, repeatable absorbance measurements require repeatable densities inside of the gas cell. CIC Photonics has provided a heater and insulation on the gas cell, for temperature control. Repeatable pressure control is also important, and for this purpose we use a manually controlled metering valve. While this is adequate for now, planned enhancements to the pressure control capability are described later. Next, we describe in detail how these variables (temperature and pressure) were controlled.

### 3.4.2 Thermodynamics and Temperature Control

Some of our first tests using the FTIR system consisted of filling the gas cell with a volume of a CO₂-N₂ mixture (95%-5%), and applying heat to this fixed volume of gas. We then observed the pressure vs. temperature response, as well as the effects on the

\(^7\) This assumes constant temperature.
infrared spectra. Since our goal is ultimately to map the infrared spectra of Venus’s atmosphere (first CO$_2$, then trace components) over a wide range of temperatures and pressures in the laboratory, we wanted to gain familiarity with this type of testing as soon as possible.

To see if we were on track, we compared our pressure vs. temperature data with the NIST Chemistry Webbook [36]. It should be noted that the NIST data are based on pure substances (100% CO$_2$), while we were actually using a 95% CO$_2$, 5% N$_2$ mixture. Given the high percentage of CO$_2$ in our mixture, the differences here are expected to be small. Additionally, the data provided by NIST are generated using a sophisticated model that is widely accepted by research/industry, so this represents a good approximation to reality. Therefore, we would expect our measured isochoric curve to closely follow the predicted isochoric data: an increase in temperature should produce a predictable increase in pressure. What we found, however, was a large discrepancy between the measured and predicted curves (Figure 28).

![Figure 28: Discrepancy between measured and predicted pressure.](image-url)
The data seemed to indicate a lower actual gas temperature compared to the measured temperature (since our system was shown to be leak-tight, this was the most likely description of the discrepancy). At this point, our only temperature measurement was a single thermocouple on the exterior of the gas cell, and this single measurement point was soon called into question. Given the insulation and heaters, we assumed good thermal conductivity between the gas cell and the interior gas; both locations should reach thermal equilibrium, but the data seemed to disagree.

While the gas cell itself was heated and insulated, our initial test setup contained comparably large volumes of unheated, un-insulated piping. Therefore, the average temperature of the isolated (fixed volume of gas) was definitely much lower than the surface, and even internal cell temperatures. Since pressure is dependent on the average temperature, and large volumes of cool gas were pulling the average down, our pressure vs. temperature curve failed to meet the NIST curve. To clarify, though, our system itself did not fail; in hindsight, it provided just the kind of results one would expect: the low average gas temperature was reflected in the low pressure measurement. So, it became clear that we were not actually measuring the quantities of interest (especially the actual gas temperature). Even more importantly, this testing showed that not only were parts of our system unmeasured, they were uncontrolled as well. Figure 29 shows a thermal infrared image of the gas cell and tubing.
Since our goal is repeatability and homogeneity within the *entire* isolated volume of gas, it became apparent that we needed to modify our test setup in order to achieve more repeatable test conditions. In particular, we made the following changes:

- Excess (uncontrolled) line volume was minimized (pressure boundary was moved closer to the gas cell – see Figure 30)

- Heat tape was added to any remaining line volume up to the isolation valves

- Two probe-type thermocouples were added in-line in the gas stream to measure the actual gas temperature and observe the effectiveness of our modifications
Figure 30: FTIR piping before (a), and after (b) modifications (pressure boundary is denoted by the green lines). Also notice the heat tape around the tubing in (b).

The modifications described above were successful in bringing us closer to the NIST predicted curve (Figure 31).

Figure 31: Thermodynamic performance before (red) and after modifying experimental setup (blue).
However, our modifications introduced a new problem: in limiting the unheated/un-insulated volume of tubing, we began to approach the upper limit of our pressure transducer’s temperature range. Notice the close proximity of the heat tape to the pressure transducer (Figure 30b, left side). To solve this problem, we needed to add some unheated/un-insulated tubing back into the system, to prevent the pressure transducer from overheating (Figure 32b).

![Figure 32: Pressure transducer location before (a), and after (b) extension tubing.](image)

The placement and shape of this extension tubing were strategically chosen to help offset the effects of reintroducing unheated/un-insulated tubing into the system. Time did not allow for a quantitative thermodynamic analysis of this system; instead we briefly describe our rationale for the placement and shape of this extension tubing in qualitative terms. Recall from our original test setup, Hardware Configuration 1 (shown in Figure 30a) – before the inlet and outlet lines were heated – these lines were continuously wicking heat away from the gas cell (evident in the thermal gradient from...
orange/yellow to blue/green in Figure 29). So, warm gas rising from the gas cell would be cooled in these “cooling fins,” sink back down into the heated cell, and continue this cycle, maintaining an equilibrium gas temperature much lower than the heater setpoint. In an attempt to break this cycle, we heated the far end of this extension tubing (away from the pressure transducer) and gave the extension piece a downward turn, to let gravity help us set up a thermal gradient where cool gas would sink down into the pressure transducer and stratify, rather than convectively cycling as before (see Figure 33).

![Figure 33: Pressure transducer extension tubing thermal gradient.](image)

Ideally, we would like to eliminate this extension tubing altogether and heat right up to the pressure transducer. This would require a high-temperature pressure transducer that could safely be located directly on the heated and insulated gas cell/tubing (anywhere within the controlled volume of gas). To further understand the effects of pressure and temperature on absorbance intensity, we give a more detailed, quantitative description of the underlying principles in Section 4.1, Sensitivity to Temperature and Pressure.
3.4.3 Contamination Inside of the Gas Cell

Besides temperature and pressure, this initial testing revealed another source of variability: the windows of the gas cell. Recall that any component within the optical path can contribute unwanted/unintended absorptions, and the windows are no exception. In particular, after putting the gas cell through several heat cycles, we noticed some unidentified absorbance features appearing in the spectrum (see Figure 34).

![Figure 34: Single beam spectra of unknown absorbance peaks (red) compared with background (blue).](image)

Purging with N\textsubscript{2} alone failed to remove the contaminant. However, after approximately 6 hours of simultaneous bake-out (with heaters set to 473 K) and a continuous N\textsubscript{2} purge, most of the contaminant was released, although some small features stubbornly held on. After putting the gas cell through some more heat cycles, the peaks began to reappear. This time, instead of baking and purging the cell, the system was disassembled and visually inspected (Figure 35).
Figure 35: Gas cell contamination; inlet side (a) and outlet side (b).

Inside of the gas cell, we found an opaque residue completely coating the inlet window, while the outlet window was nearly spotless. There was also some particulate debris on the bottom of the gas cell (with a few pieces stuck to the windows as well). What could have caused such a mess? Two possible candidates include the isolation valves and the Kalrez o-rings.

We were operating near the upper temperature limit of the o-rings (600 K), and it may be possible that they were beginning to outgas inside of the gas cell. However, the o-rings are rated for **continuous** use at 600 K, and we only spent short periods of time (< 2 hours per test) at high temperature (~575 K) – nevertheless, could they be outgassing anyway? Also, why was only one window coated? If the o-rings were losing material wouldn’t they both be losing it at the same rate? Maybe the inlet side was getting hotter than the outlet side – this would definitely accelerate any outgassing that may have been occurring. In fact, data taken during these tests indicate slightly higher temperatures on the inlet side. This may be another indication that we still have not fully controlled the temperature profile inside of our gas cell.
The other possibility – the isolation valves – may be the more likely culprit. Once the gas cell and valves were disassembled, large amounts of debris (including dark particulates like those in the bottom of the gas cell) were found inside the valves, and in the fittings immediately connected to the valves. These valves use a type of grafoil packing, which may be deteriorating and contaminating the gas cell. The only way to find out for sure was to head to the lab for chemical analysis. In particular, samples of our o-rings, gas cell windows, and particulate debris were analyzed using the chemistry lab’s FITR spectrophotometer.

The results indicated the presence of aliphatic compounds (C-H stretches around 2900 cm\(^{-1}\)), which may originate from either the hydrocarbon-based valve packing material, or the o-rings. In addition to these C-H stretches, some C-F stretches were also found (around 1400 cm\(^{-1}\)), and these almost certainly came from the perfluorinated Kalrez o-rings. Figure 36 shows the spectra taken with the chemistry lab’s FTIR.

![Absorption spectra of contaminant taken with chemistry lab’s FTIR](image)
Notice that the range of the spectral data taken with this FTIR includes lower wavenumbers (down to 700 cm\(^{-1}\)), compared with our system, which has a lower limit of about 1800 cm\(^{-1}\). This is because the chemistry lab’s windows (germanium crystal) are IR-transparent over a wider range, while our sapphire windows absorb strongly at low IR wavenumbers. Sapphire was chosen in our case because of its resistance to corrosion, and, fortunately, most of the data we are interested may be found above 1800 cm\(^{-1}\).

After a thorough cleaning of all components, further testing will hopefully determine the identity of these contaminants, so they can be eliminated. The contaminant peaks were small enough, and in locations far enough away from the main CO\(_2\) absorbance features, that they did not interfere with the testing in this thesis. In the future, though, the source of these contaminants needs to be understood and removed.

### 3.4.4 Hardware Configuration Summary

In this section, we outline the different iterations of our FTIR system configuration, summarizing the different modifications described above.

**Hardware Configuration 1:**

- Original test setup with large volumes of unheated/uncontrolled tubing
- Pressure control via. regulator on K-bottle (not directly at gas cell)
- *Tests using this configuration: 95% CO\(_2\), 5% N\(_2\) Pressure Test*
Hardware Configuration 2:

- Lengths of tubing limited, heat tape added
- Probe-type thermocouples installed in inlet and outlet lines
- Metering valve added to gas cell outlet for better pressure control
- *Tests using this configuration: Pure CO$_2$ Tests 1-3*

Hardware Configuration 3:

- Same as Hardware Configuration 2, except extension tubing added to protect pressure transducer
- *Tests using this configuration: Pure CO$_2$ Test 4, Pure CO$_2$ Test 5*

The parts list for our current configuration (Hardware Configuration 3) is shown in Table 5.

Table 5: FTIR parts list.

<table>
<thead>
<tr>
<th>Item</th>
<th>Manufacturer</th>
<th>Model / Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTIR Spectrometer</td>
<td>ABB</td>
<td>MB3000</td>
</tr>
<tr>
<td>Gas cell</td>
<td>CIC Photonics</td>
<td>Scout EN (Inconel body, sapphire windows, 10 cm path length)</td>
</tr>
<tr>
<td>Gas cell heater</td>
<td>Tempco</td>
<td>200 W (x2)</td>
</tr>
<tr>
<td>Gas cell temperature controller</td>
<td>Tempco</td>
<td>TPC-1000</td>
</tr>
<tr>
<td>Inlet / outlet heat tape</td>
<td>Omega</td>
<td>Omegalux 313 W</td>
</tr>
<tr>
<td>Heat tape temperature controller</td>
<td>Staco Energy Co.</td>
<td>Variable autotransformer</td>
</tr>
<tr>
<td>Surface thermocouple</td>
<td>Omega</td>
<td>Type K (surface mount)</td>
</tr>
<tr>
<td>Inlet thermocouple</td>
<td>Omega</td>
<td>Type K (1/16” probe)</td>
</tr>
<tr>
<td>Outlet thermocouple</td>
<td>Omega</td>
<td>Type K (1/16” probe)</td>
</tr>
<tr>
<td>Pressure transducer</td>
<td>GE</td>
<td>Unik5000, 0-1500 psia</td>
</tr>
</tbody>
</table>
CHAPTER IV
EXPERIMENTAL TESTING

In this chapter, we present our experimental test results. Section 4.1 describes the sensitivity of our absorbance measurements to pressure and temperature, in Section 4.2 we show our measurement uncertainty analysis, Section 4.3 describes our baseline FTIR performance and our measured infrared absorption of CO$_2$ at Venus atmospheric conditions, in Section 4.4 we examine the overall spectra of Venus, finally, in Section 4.5 we draw some conclusions, discussing the meaning/implications of these experimental results.

4.1 Sensitivity to Pressure and Temperature

We have mentioned that pressure and temperature affect density, and therefore the absorbance intensity (there are other things, too, that affect absorbance, as we saw earlier). Since we are attempting to actively control these variables, we would like to know how sensitive the system is to their variation; given a small change in either
pressure or temperature, how does the absorbance intensity change? In this section we present a simplified derivation of this relationship, based on the ideal gas law. A higher fidelity model is beyond the scope of this thesis; we just want to understand roughly how changes in the measurement conditions will affect our results. For now, we will continue with all derivations based on the ideal gas law. We begin by returning once again to Beer’s Law, this time expanding it to show dependencies on pressure ($P$), temperature ($T$), and wavelength ($\nu$):

$$A(P, T, \nu) = \varepsilon(T, \nu)lc(P, T)$$  \hspace{1cm} (24)

In this discussion, we will focus on the contribution of the $c(P, T)$ term. Notice, though, that in this model, the absorptivity ($\varepsilon$) is also dependent on temperature. Because of this, our results will only be meaningful if we restrict ourselves to isothermal predictions. Note that the optical path length ($l$) is a constant. Beginning with the ideal gas law,

$$PV = nRT$$  \hspace{1cm} (25)

we rearrange this equation, to show how the density ($n/V$) changes with pressure and temperature:

$$\frac{n}{V} = c(P, T) = \frac{P}{RT}$$  \hspace{1cm} (26)

---

8 Absorptivity is also affected by pressure but these effects (pressure broadening, line-mixing, etc.) are not included in this simple model – see the following references for a detailed treatment of this topic [5,8,12].
The units make sense here, because in Beer’s Law, $c$ has units mol/m$^3$, and in the ideal gas law $n$ is the number of mols and $V$ is the volume in m$^3$. Next, to see how this multivariable function changes, we take the partial derivatives with respect to both pressure and temperature:

\[
\frac{\partial c}{\partial P} = \frac{1}{RT}
\]  

(27)

\[
\frac{\partial c}{\partial T} = \frac{-P}{RT^2}
\]

(28)

The gradient vector generalizes the derivative concept, and describes how density changes across the entire range of possible pressures and temperatures:

\[
\nabla c = \frac{\partial c}{\partial P} \vec{P} + \frac{\partial c}{\partial T} \vec{T}
\]

(29)

Lines of constant volume (density) and constant temperature are particularly important, since the majority of our tests in this thesis are either isochoric or isothermal (Figure 37).

Figure 37: Pressure-temperature-volume surface for an ideal gas. Image credit: Kristin Spear, NASA Glenn Research Center. Adapted from [37].
4.2 Measurement Uncertainty Analysis

In this section, we describe the main sources of error in our absorbance measurements, and derive a model combining these uncertainties. The NASA Measurement Uncertainty Analysis Principles and Methods reference outlines several key steps for conducting an uncertainty analysis [38]:

1. Define the measurement process
2. Develop the error model
3. Identify error sources and distributions
4. Estimate uncertainties
5. Combine uncertainties
6. Report results

Measurement Process

Our measurement process can be summarized as follows: purge/evacuate gas cell, take background spectrum, vent gas cell, purge with CO₂, begin test (either isochoric or isothermal – described in more detail in Section 4.3) and record spectra throughout test. The measured quantity of interest is absorbance intensity:

\[ A(P, T, \nu) = \varepsilon(T, \nu)lc(P, T) \]  \hspace{1cm} (30)
**Error Model**

The error model consists of the measured value $A$, the true value $A_{true}$, and the uncertainty associated with the measurement $\delta_A$:

$$A = A_{true} + \delta_A$$  \hspace{1cm} (31)

where, $\delta_A$ contains all of the uncertainties in measuring $A$. These error sources are described next.

**Error Sources and Distributions**

In her doctoral dissertation [8], the author cites two major sources of error associated with FTIR measurements. First, detector nonlinearity is mentioned as a potential error source. A linear relationship should exist between measured voltage signal and the intensity of the light impinging on the detector. This source of error can be eliminated, by selecting the appropriate detector gain setting in the FTIR software, keeping the detector within its optimal range [8].

The single-beam error is mentioned as the other significant source of error. This refers to differences between the background spectrum and the measured spectrum. By keeping a continuous $N_2$ purge flowing through our system, we eliminate (most of) this error source (due to contaminants such as $H_2O$, etc.). However, baseline shifting was also noticed during some of our testing, and this is another way the background spectrum may vary with respect to the measured spectra. This was especially noticed at elevated temperatures: as the detector heated up, it lost some of its sensitivity, therefore changing its response to the measured light intensity. Since this happened throughout the course of
a test, it was not possible to take a new background sample (during the test). This relationship is not fully understood at this time, and more work would be needed to quantify its effects. In the future, we recommend conducting each test a number of times, to gain a better sense of repeatability (including things like this variable background spectrum).

We have seen that for quantitative FTIR analysis, pressure and temperature both have a significant role in determining the density, and therefore absorbance. Similarly, errors in our temperature and pressure measurements will also propagate through to our absorbance measurement. So, for this analysis, we will concentrate on the errors due to variability in the density (molar concentration). The expression for errors associated with $A$ is simply:

$$\delta_A = \varepsilon l \delta_{density} \quad (32)$$

where $\varepsilon$ and $l$ are assumed to be constant, containing zero uncertainty. Of course there is also uncertainty associated with these values, and a more complete error model would include these uncertainties as well.

**Estimate Uncertainties**

Next, we estimate the uncertainty associated with our density error. The expression for density error is expanded to show its pressure and temperature components:

$$\delta_{density} = c_p \delta_p + c_T \delta_T \quad (mol/m^3) \quad (33)$$
$c_p$ and $c_T$ are sensitivity coefficients, and may be found by taking the partial derivatives of $c$ with respect to $P$ and $T$, respectively:

$$c_p = \frac{\partial c}{\partial P} = \frac{1}{RT} \left( \frac{\text{mol}}{Pa \text{ m}^3} \right)$$  \hspace{1cm} (34)$$

$$c_T = \frac{\partial c}{\partial T} = -\frac{P}{RT^2} \left( \frac{\text{mol}}{K \text{ m}^3} \right)$$  \hspace{1cm} (35)$$

The units work out here, as our final result for $\delta_{\text{density}}$ needs to be in $(\text{mol/m}^3)$. Next, we apply to variance operator, since the uncertainty in our measurement is the square root of the variance in the measurement error [38]:

$$\text{var}(\delta_{\text{density}}) = \text{var}(c_p \delta_p + c_T \delta_T)$$  \hspace{1cm} (36)$$

$$\text{var}(\delta_{\text{density}}) = \text{var}(c_p \delta_p) + \text{var}(c_T \delta_T) + 2c_p c_T \text{cov}(\delta_p, \delta_T)$$  \hspace{1cm} (37)$$

There is no reason to believe an error in pressure measurement is correlated with an error in temperature measurement (they are measured by different devices, powered by different sources, etc.), so the covariance term may be eliminated:

$$\text{var}(\delta_{\text{density}}) = \text{var}(c_p \delta_p) + \text{var}(c_T \delta_T)$$  \hspace{1cm} (38)$$

Finally, our uncertainty due to density variability can be expressed as follows:

$$u_{\delta_{\text{density}}} = \sqrt{c_p^2 u_{\delta_p}^2 + c_T^2 u_{\delta_T}^2}$$  \hspace{1cm} (39)$$
In order to calculate our total uncertainty due to density, we assume the individual uncertainties due to pressure and temperature to be normally distributed – this is generally a good approximation [38]:

\[ u = \frac{L}{\Phi^{-1} \left( \frac{1 + p}{2} \right)} \]  

(40)

Here, \( \pm L \) are the containment limits (given by manufacturer’s specifications), \( p \) is the containment probability (either given by the manufacturer, or estimated based on experience/calibration history), and \( \Phi^{-1} \) is the inverse normal function. We apply this equation to \( u_{\delta_p} \) and \( u_{\delta_T} \) below:

\[ u_{\delta_p} = \frac{0.10207 \text{ atm}}{\Phi^{-1} \left( \frac{1 + 0.99}{2} \right)} \]  

(41)

\[ u_{\delta_T} = \frac{2 K}{\Phi^{-1} \left( \frac{1 + 0.90}{2} \right)} \]  

(42)

With this information (and the sensitivity coefficients previously calculated), we are now able to calculate our uncertainty due to density error (\( u_{\delta_{\text{density}}} \)). Since we are not including other errors (such as those associated with repeatability) at this time, this represents our total uncertainty for the absorbance at a single wavenumber (\( v \)). This model is applied to our absorbance measurements in the following sections, and the results are reported along side of our measurements.
4.3 Experimental Test Descriptions

In this section, we describe a number of tests that were used to gain familiarity with our system and to begin determining its baseline performance. We culminate our testing with recreating the conditions of CO$_2$ at the 22 km altitude in Venus’s atmosphere. These tests can be broken into two categories: isothermal and isochoric. Each category is described in more detail below.

*Isothermal Testing*

The isothermal tests were conducted to observe the effects on the infrared spectra of CO$_2$ of changing just one variable: pressure. We began our experimental testing with a low temperature isothermal test, in an effort to reproduce results found in the literature [5]. After an interlude of isochoric testing (described later), we finally concluded our experiments with one more isothermal test (this time at high temperature). The isothermal test process is outlined below:

1. Purge gas cell with N$_2$ and record clean background spectrum
2. Vent gas cell
3. Purge the gas cell with CO$_2$ to sweep out any residual N$_2$
4. Pressurize gas cell with CO$_2$ to each desired pressure setpoint (holding temperature constant$^9$) and record data

$^9$ Since filling a volume naturally raises the temperature slightly (due to compression), it is necessary to wait for the temperatures to stabilize after filling.
**Isochoric Testing**

The primary goal of the isochoric testing was to observe the effects on the infrared spectra of CO\textsubscript{2} caused by simultaneously changing both temperature and pressure. Here the FTIR was operated in a similar manner to the main chamber: the gas cell was pressurized to an initial setpoint and then heat was applied to reach the final operating point. Below we give an overview of our isochoric test procedure:

1. Purge gas cell with N\textsubscript{2} and record clean background spectrum

2. Vent gas cell

3. Purge the gas cell with CO\textsubscript{2} to sweep out any residual N\textsubscript{2}

4. Pressurize gas cell with CO\textsubscript{2} to the desired initial pressure

5. Apply heat to the system\textsuperscript{10}, holding volume (mass) constant
   - First, increase gas cell heater setpoint; allow temperature ($T_{sfc}$) to stabilize and record data
   - Then, increase tubing heat tape temperature until all three temperatures ($T_{in}$, $T_{out}$, and $T_{sfc}$) indicate thermal equilibrium\textsuperscript{11} and record data

6. Repeat 5 for the desired number of test points

\textsuperscript{10} The two-step process for heating the system described here was used for Tests 1-4. In Test 5 we heated both volumes simultaneously. This is reflected in the temperature vs. time plots for each test, but the net result (i.e. final temperature) is the same in both cases.

\textsuperscript{11} Approximate thermal equilibrium; because of the small heat leaks it would take a long time truly reach equilibrium.
A matrix with the test descriptions and data associated with each test in this chapter is shown in Table 6:

Table 6: Test Matrix.

<table>
<thead>
<tr>
<th>Test name</th>
<th>Test type</th>
<th>Gas mix</th>
<th>Press. Range (atn)</th>
<th>Temp. Range (K)</th>
<th>P, T vs. time</th>
<th>P vs. T</th>
<th>Spectra</th>
<th>Config.</th>
</tr>
</thead>
<tbody>
<tr>
<td>95% CO$_2$, 5%N$_2$ Pressure Test</td>
<td>Iso-thermal</td>
<td>95% CO$_2$, 5% N$_2$</td>
<td>9.68-34.57</td>
<td>293</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>1</td>
</tr>
<tr>
<td>Pure CO$_2$ Test 1</td>
<td>Iso-choric</td>
<td>100% CO$_2$</td>
<td>20-30</td>
<td>295-475</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>2</td>
</tr>
<tr>
<td>Pure CO$_2$ Test 2</td>
<td>Iso-choric</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure CO$_2$ Test 3</td>
<td>Iso-choric</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure CO$_2$ Test 4</td>
<td>Iso-choric</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure CO$_2$ Test 5a</td>
<td>Iso-thermal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure CO$_2$ Test 5b</td>
<td>Iso-thermal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notice that columns 6-8 contain information about what type of data were taken for each test. For the majority of these tests (Pure CO$_2$ Test 2 onward) we can correlate data between the time, pressure and wavenumber domains. This allows us to look at our data from a number of different angles, and has proven to be useful in making sense of some of the unexpected behavior we observed. Also, note that the last column “Config.” refers to the different hardware configurations described previously in Chapter 3. Shown below in Table 7 are the common parameters used in the FTIR system and software for the testing in this thesis.

Table 7: FTIR Parameters.

<table>
<thead>
<tr>
<th>Path length</th>
<th>Apodization function</th>
<th># Scans avg’d</th>
<th>IR Source</th>
<th>Detector type</th>
<th>Beam-splitter</th>
<th>Range</th>
<th>Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 cm</td>
<td>Cosine</td>
<td>16</td>
<td>Ceramic Globar</td>
<td>DTGS</td>
<td>ZnSe</td>
<td>1800-7500 cm$^{-1}$</td>
<td>1 cm$^{-1}$</td>
</tr>
</tbody>
</table>
For the infrared spectra analysis of CO$_2$ in this chapter, we focus mostly on the 6850-7050 cm$^{-1}$ range. Given our high CO$_2$ densities, and our test conditions, this is a good band to observe some of the subtle features of the spectral response to both pressure and temperature, and this is consistent with the literature (see Chapter 1). All spectra are plotted in terms of Absorbance Units (AU) on the y-axis vs. wavenumbers (cm$^{-1}$) on the x-axis.

Throughout all of our experiments, the initial density (molar concentration) $c_{\text{initial}}$ was calculated using the NIST Chemistry Webbook (using our initial pressure and average temperature). Given the highly homogeneous thermal conditions at the beginning of each test (all components being in thermal equilibrium at ambient temperature), we are confident in the validity of these initial density calculations. We then assume this value will remain constant during each of these tests. However, as we will see later, leaks in the system will lower the density significantly throughout the course a test.

In order to quantify our recorded measurements, we needed to choose a measurable performance metric, which could be used later to gauge repeatability. While we discuss our results qualitatively in terms of the theory described in Chapter 2, we needed a simple, yet precise way to quantify our measurements. We decided upon integrating under the area of the spectra over the region of interest, and using this integrated area as our performance indicator. Recall, our measurement quantity of interest is absorbance intensity (peak height) at a given wavenumber – in quantum mechanical terms, this quantity is the “observable” of our system. However, random errors associated with measuring a single, discrete peak height would increase our measurement uncertainty. By integrating over a large area, random errors will have less influence on
the final result, making for a more robust comparison metric. Additionally, this integration method is used elsewhere in literature as a means to quantify FTIR performance [5]. In this reference, the authors use integrated area to show how their system follows Beer’s Law (for isothermal testing). Below we give the derivation of this integration method, beginning with the original Beer’s Law equation, in which we once again consider dependencies on \( \nu \), \( P \) and \( T \).

\[
A(P, T, \nu) = \varepsilon(T, \nu)lc(P, T) \tag{43}
\]

Since we are holding temperature constant, Beer’s Law becomes:

\[
A(P, \nu) = \varepsilon(\nu)lc(P) \tag{44}
\]

Next, we integrate the right side of this equation and set the result equal to a function of \( P \) (since ultimately we want to show how integrated absorbance intensity changes with \( P \)).

\[
I(c(P)) = lc(P) \int_{\nu_1}^{\nu_2} \varepsilon(\nu) d\nu \tag{45}
\]

So, our result is the integrated intensity \( I \), which depends upon the overall shape of the spectra (described by \( \varepsilon(\nu) \)) and is scaled by both the pathlength \( l \), and the density (molar concentration) \( c(P) \). See Figure 38.
For isothermal tests, we assume the shape of the spectra to be constant, so we should have linear behavior between \( I \) and \( c \) (as shown in Figure 38). It should be noted that this analysis assumes the linearity of Beer’s Law. In reality, there are physical phenomena, which cause Beer’s Law to deviate from this linear relationship. For example, at very high pressures, pressure broadening of individual lines has a significant effect on the overall spectral shape. Some researchers have also noticed that absorptions in certain spectral regions are overestimated by current pressure broadening models (especially in the “wing” regions, away from the central peaks), resulting in further deviations from Beer’s Law [5, 12]. In other words, the shape of the spectra does not remain perfectly constant with respect to pressure (even when temperature is constant). Despite these limitations, the Beer’s Law approximation offers a good starting point for interpreting our isothermal results [5, 8]. However, this model cannot be applied in the same way for isochoric tests, because of the more significant temperature dependencies described by the absorptivity term. Peak height depends strongly on the transition probability between two quantum mechanical states (see discussion in Chapter 2), and this translates into significant deviations from Beer’s Law and a nonlinear relationship between \( I \) and \( c \).
4.3.1 95% CO$_2$, 5% N$_2$ Pressure Test (ESA high-pressure test)

This test series involved looking at the spectral effects of increasing pressure on a 95% CO$_2$, 5% N$_2$ mixture, while holding temperature constant, and closely follows a series of tests performed by a research group in support of the Venus Express mission [5]. This marks our first attempt to repeat other researcher’s results – an important step toward understanding our system’s performance. Figure 39 shows the spectra recorded at each point during this test series.

![Spectra throughout 95% CO$_2$, 5% N$_2$ Pressure Test.](image)

Notice that each curve represents the molecular absorption at a given density. Since we are dealing with high pressure gasses, it is more appropriate to speak in terms of density (molar concentration) rather than pressure (because of the non-ideal behavior of real gasses) [5]. In Figure 40, we plot the integrated peak intensity vs. number density$^{12}$ (in units of amagat).

$^{12}$ One amagat equals 44.615036 mol/m$^3$.  

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We chose amagat here, so a direct comparison could be made with the results found in literature [5]. For convenience, however, we typically use mol/m$^3$ for density. From the linear best fit we obtain a slope of 0.176 AU-cm$^{-1}$/amagat. To see if we were on track, we compared this with the data in literature taken at similar conditions. The results of their test showed a slope of 0.0465 AU-cm$^{-1}$/amagat. The majority of this difference can be attributed to the difference in gas cell pathlengths: our gas cell has a pathlength of 10 cm compared to their pathlength of 2 cm. Assuming all other variables are constant between these tests, according to Beer’s Law our results should differ by a factor of five (absorbance intensity scales linearly with pathlength). Proceeding with the assumption that all of the other variables were in fact held constant, our results were found to differ by a scaling factor of 3.78. However, given our coarse pressure control during this test (using Hardware Configuration 1), we were not able to precisely hit the same density setpoints that we were trying to target. In order to determine how this may contribute to the measured differences, we list our actual density values side-by-side with those we
were attempting to match in Table 8, followed by a plot of the actual density vs. the target density in Figure 41.

Table 8: Target and actual densities.

<table>
<thead>
<tr>
<th>Target density (amagat)</th>
<th>Actual density (amagat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.81</td>
<td>9.48</td>
</tr>
<tr>
<td>22.66</td>
<td>16.63</td>
</tr>
<tr>
<td>35.51</td>
<td>27.68</td>
</tr>
<tr>
<td>51.28</td>
<td>40.00</td>
</tr>
</tbody>
</table>

Figure 41: Actual density vs. target density.

The slope of the best-fit line (in Figure 41) shows that our actual densities were approximately 75% of the target value. This is consistent with our measured scaling factor of 3.78. Multiplying our predicted scaling factor of 5.0 by 75% gives 3.75 and shows good agreement between our results and the reference’s. A comparison between our corrected slope and the target (reference) slope is given below:
\[ S_{corrected} = \frac{(0.176 \pm 0.0470)}{(5)(0.7491)} = 0.0470 \left( \frac{AU \cdot cm^{-1}}{amagat} \right) \]  \hspace{1cm} (46)

\[ S_{target} = 0.0465 \left( \frac{AU \cdot cm^{-1}}{amagat} \right) \]  \hspace{1cm} (47)

\[ \% Difference = \frac{0.0470 - 0.0465}{0.0465} \times 100\% = +1.075\% \]  \hspace{1cm} (48)

Considering the reference result to be the standard, we found a +1.075\% difference between our slope and theirs. Table 9 summarizes all of the results for this test.

**Table 9: 95% CO\textsubscript{2}, 5% N\textsubscript{2} pressure test.**

<table>
<thead>
<tr>
<th>( T_{avg} ) (K)</th>
<th>( P ) (atm)</th>
<th>Density (mol/m(^3))</th>
<th>Density (amg)</th>
<th>Integrated area 6850-7050 cm(^{-1}) (AU-cm(^{-1}))</th>
<th>Error (AU-cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.25</td>
<td>9.68</td>
<td>423.06</td>
<td>9.48</td>
<td>1.83466</td>
<td>± 0.01185</td>
</tr>
<tr>
<td></td>
<td>16.34</td>
<td>742.09</td>
<td>16.63</td>
<td>3.01853</td>
<td>± 0.01444</td>
</tr>
<tr>
<td></td>
<td>25.61</td>
<td>1235.12</td>
<td>26.68</td>
<td>4.68763</td>
<td>± 0.01865</td>
</tr>
<tr>
<td></td>
<td>34.57</td>
<td>1784.58</td>
<td>40.00</td>
<td>7.09394</td>
<td>± 0.02519</td>
</tr>
</tbody>
</table>

The measurement uncertainty is reported in the rightmost column above. Note that our simplified error model only includes errors due to density. See Appendix A for a description on how our error model is applied to these band integration calculations. A more realistic error model is recommended for future work.
4.3.2 Pure CO$_2$ Test 1

This was the first test to put our newly modified experimental setup through its operational range (Hardware Configuration 2). Our plan for this test was to push the gas cell/system through a wide range of operating conditions, and observe the thermal characteristics and controllability. The initial conditions of the test were the following: $P_{cell} = 20.15$ atm, $T_{sfc} = 294.1$ K, $T_{in} = 293.6$ K, $T_{out} = 293.3$ K, $c_{initial} = 945.92$ mol/m$^3$. Table 10 outlines our test points for Pure CO$_2$ Test 1.

<table>
<thead>
<tr>
<th>Time</th>
<th>Cell Heater setpoint (K)</th>
<th>Tubing Variac output (%)</th>
<th>$P_{cell}$ (atm)</th>
<th>$T_{sfc}$ (K)</th>
<th>$T_{in}$ (K)</th>
<th>$T_{out}$ (K)</th>
<th>$T_{avg}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:00</td>
<td>--</td>
<td>0</td>
<td>20.15</td>
<td>294.1</td>
<td>293.6</td>
<td>293.3</td>
<td>293.7</td>
</tr>
<tr>
<td>14:45</td>
<td>373.15</td>
<td>0</td>
<td>23.75</td>
<td>373.0</td>
<td>294.8</td>
<td>294.1</td>
<td>320.6</td>
</tr>
<tr>
<td>15:40</td>
<td>373.15</td>
<td>29</td>
<td>25.53</td>
<td>371.3</td>
<td>372.1</td>
<td>370.0</td>
<td>371.1</td>
</tr>
<tr>
<td>15:50</td>
<td>473.15</td>
<td>29</td>
<td>29.57</td>
<td>473.1</td>
<td>372.3</td>
<td>371.1</td>
<td>405.5</td>
</tr>
<tr>
<td>16:23</td>
<td>473.15</td>
<td>50</td>
<td>31.71</td>
<td>470.3</td>
<td>471.3</td>
<td>470.0</td>
<td>470.5</td>
</tr>
</tbody>
</table>

The columns highlighted in blue were used to create the pressure vs. temperature plot below, in Figure 42.
Figure 42: Pressure vs. temperature for Pure CO\textsubscript{2} Test 1.

We can see a large improvement in the pressure vs. temperature curve over our original experimental test setup, discussed in Section 3.4 (see Figure 31). This gave us confidence going forward, however we still did not quite match the NIST curve. The last data point (470.5 K, 31.71 atm), in particular, falls short of the predicted data. We believe this difference may be attributed to either thermodynamics or a small leak. Recall from Chapter 3 that there was a very small (but nonzero) volume of un-insulated/unheated tubing at the pressure transducer in Hardware Configuration 2; this may lower the average gas temperature enough to account for the deviation. Also, recall the numerous Swagelok fittings/connectors in the tubing; these present an opportunity for small leaks. Of course, the difference may be caused by a combination of the two effects, further emphasizing the importance of creating repeatable test conditions.
4.3.3 Pure CO\textsubscript{2} Test 2

Pure CO\textsubscript{2} Test 2 was essentially the same as Pure CO\textsubscript{2} Test 1, except this time the infrared spectra were recorded as well, since this is ultimately what we are concerned with measuring. The test points achieved during Pure CO\textsubscript{2} Test 2 are shown below in Table 11 (with initial conditions given in the first row, and with density (molar concentration) \(c_{\text{initial}} = 959.08 \text{ mol/m}^3\)).

Table 11: Test points for Pure CO\textsubscript{2} Test 2 (4/1/14).

<table>
<thead>
<tr>
<th>Time</th>
<th>Cell Heater setpoint (K)</th>
<th>Tubing Variac output (%)</th>
<th>(P_{\text{cell}}) (atm)</th>
<th>(T_{\text{sfc}}) (K)</th>
<th>(T_{\text{in}}) (K)</th>
<th>(T_{\text{out}}) (K)</th>
<th>(T_{\text{avg}}) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13:01</td>
<td>--</td>
<td>0</td>
<td>20.69</td>
<td>297.1</td>
<td>296.9</td>
<td>296.9</td>
<td>297.0</td>
</tr>
<tr>
<td>13:12</td>
<td>373.15</td>
<td>0</td>
<td>24.07</td>
<td>374.1</td>
<td>297.3</td>
<td>297.0</td>
<td>322.8</td>
</tr>
<tr>
<td>14:14</td>
<td>373.15</td>
<td>28</td>
<td>25.46</td>
<td>373.0</td>
<td>373.3</td>
<td>372.5</td>
<td>372.9</td>
</tr>
<tr>
<td>14:25</td>
<td>473.15</td>
<td>28</td>
<td>29.37</td>
<td>473.1</td>
<td>374.5</td>
<td>372.6</td>
<td>406.7</td>
</tr>
<tr>
<td>14:58</td>
<td>473.15</td>
<td>49</td>
<td>31.03</td>
<td>471.0</td>
<td>473.0</td>
<td>473.2</td>
<td>472.1</td>
</tr>
</tbody>
</table>

Once again the columns in blue were used to create the pressure vs. temperature plot shown in Figure 43.
Figure 43: Pressure vs. temperature for Pure CO$_2$ Test 2.

Notice how the last data point once again falls short of this NIST curve, this time even more so than in Pure CO$_2$ Test 1. Because nothing else changed between Tests 1 and 2, this seemed indicate the presence of a leak. A data point taken six hours after the test was completed confirmed this suspicion: the pressure dropped from 31.03 atm to 16.25 atm over that six hour window. The system was pressure leak-checked prior to testing, however it is possible that thermal cycling may have introduced leaks during the test.

How did the spectra change throughout the course of this test? This is what really matters, after all. A recording of the spectrum was taken at each test point indicated in Table 11, and can be correlated with the spectral plots via the timestamp in the leftmost column. These spectra are shown below in Figure 44 and the timestamp is given in parentheses in the legend.
Figure 44: Spectra throughout Pure CO\textsubscript{2} Test 2.

Qualitatively, the spectra change in a way that is consistent with other existing data in this spectral region (following ESA experimental data and roughly following HITRAN simulations): as temperature increases, the rightmost (R-branch) peak sharpens (6985 cm\textsuperscript{-1}) and the overall envelope shape changes (due to changing absorptivity coefficients, resulting from the physics of high-temperature energy transitions). Since these are isochoric tests, the mass of CO\textsubscript{2} (and therefore density) should be constant during the entire test. At constant temperature and pressure, the absorbance intensity depends only on density. However, since we are not holding temperature and pressure constant (by the definition of these tests), we cannot expect the peak heights to remain the same (even though the density should be constant) – this is largely because of the temperature dependence of absorptivity.

Notice also how the overall baseline begins to shift up as the temperature increases. The detector losing some sensitivity at increased temperatures causes this effect. In order to bring all the spectra (for a given test) to the same baseline, a bias was
applied (this does not affect the relative peak intensities, and helps make a more for meaningful comparisons). In the longer-term, a means to eliminate or reduce this baseline shift should be investigated. One possible option could be the addition of some form of active cooling (a fan, for example) on the FTIR detector. In the near-term, we simply adjust the baseline for the comparisons. The baseline-shifted spectra for Pure CO$_2$ Test 2 are shown below, in Figure 45.
Once we established a common baseline, we could make some more meaningful comparisons with the spectra. In particular, notice how new absorbance features begin to show up at higher temperatures trailing off towards the left (lower wavenumbers) of the main peaks (starting at 6200 cm\(^{-1}\) in Figure 45a, and 6880 cm\(^{-1}\) in Figure 45b). This is
because as the gas heats up, new rotational modes are activated and these tend to be spread out toward lower wavenumbers in the left peak (the $P$-branch), and become compressed in the right peak (the $R$-branch) due to vibrational-rotational coupling as the temperature (rotational energy) increases – see the discussion in Chapter 2. Given this observation, we have a great place to start looking for where CO$_2$ may influence other spectral peaks at elevated temperatures and pressures. Since one of our main goals with this research lies in understanding how the extreme temperatures and pressures affect our ability to detect the trace components in Venus’s atmosphere, we examine all of the major absorbance features of CO$_2$ (in Section 4.4), paying close attention to this observed behavior of new absorbance features spreading out to the left of the primary peaks.

Notice also, how overall peak heights diminish with increased temperature. This is consistent with the physics of infrared absorption: at higher temperatures there are fewer molecules in the low energy ($E_l$) state to make the transition to the first excited state ($E_u$), the most likely transition. This illustrates our discussion in Chapter 2: absorption intensity does not just depend on the number of molecules present, but the number of these molecules that are capable of making the transition from $E_l$ to $E_u$. As the temperature increases, more molecules are already in $E_u$ and therefore are not available to make the transition from $E_l$ to $E_u$ (see the discussion in Chapter 2 for more details). Next, we integrated the area between 6850-7050 cm$^{-1}$ for each spectrum shown in Figure 45b. The results of this test are summarized in Table 12.
Table 12: Pure CO₂ Test 2 summary \( (c_{\text{initial}} = 959.08 \text{ mol/m}^3) \).

<table>
<thead>
<tr>
<th>( T_{\text{avg}} ) (K)</th>
<th>( P ) (atm)</th>
<th>Integrated area 6850-7050 cm(^{-1}) (AU·cm(^{-1}))</th>
<th>Error (AU·cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>296.97</td>
<td>20.69</td>
<td>4.23606</td>
<td>±0.01802</td>
</tr>
<tr>
<td>322.80</td>
<td>24.07</td>
<td>3.59463</td>
<td>±0.01529</td>
</tr>
<tr>
<td>372.93</td>
<td>25.46</td>
<td>3.64270</td>
<td>±0.01550</td>
</tr>
<tr>
<td>406.67</td>
<td>29.73</td>
<td>3.14168</td>
<td>±0.01336</td>
</tr>
<tr>
<td>472.10</td>
<td>31.03</td>
<td>3.58352</td>
<td>±0.01524</td>
</tr>
</tbody>
</table>

4.3.4 Pure CO₂ Test 3

Again, this test was very similar to the first two. This time we also continuously recorded the temperature and pressure throughout the duration of the test, adding another dimension to our data. The initial density (molar concentration) \( c_{\text{initial}} = 958.15 \text{ mol/m}^3 \); the rest of the test information can be found in Table 13.

Table 13: Test points for Pure CO₂ Test 3 (4/2/14).

<table>
<thead>
<tr>
<th>Time</th>
<th>Cell Heater setpoint (K)</th>
<th>Tubing Variac output (%)</th>
<th>( P_{\text{cell}} ) (atm)</th>
<th>( T_{\text{sfC}} ) (K)</th>
<th>( T_{\text{in}} ) (K)</th>
<th>( T_{\text{out}} ) (K)</th>
<th>( T_{\text{avg}} ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15:55</td>
<td>--</td>
<td>0</td>
<td>\textbf{20.60}</td>
<td>296.5</td>
<td>295.9</td>
<td>296.1</td>
<td>\textbf{296.2}</td>
</tr>
<tr>
<td>16:04</td>
<td>373.15</td>
<td>0</td>
<td>\textbf{23.84}</td>
<td>373.8</td>
<td>296.9</td>
<td>296.6</td>
<td>\textbf{322.5}</td>
</tr>
<tr>
<td>16:23</td>
<td>373.15</td>
<td>28</td>
<td>\textbf{24.99}</td>
<td>372.0</td>
<td>372.0</td>
<td>370.3</td>
<td>\textbf{371.4}</td>
</tr>
<tr>
<td>16:32</td>
<td>473.15</td>
<td>28</td>
<td>\textbf{28.41}</td>
<td>473.8</td>
<td>371.3</td>
<td>369.3</td>
<td>\textbf{404.8}</td>
</tr>
<tr>
<td>17:06</td>
<td>473.15</td>
<td>49</td>
<td>\textbf{28.45}</td>
<td>470.8</td>
<td>475.3</td>
<td>471.0</td>
<td>\textbf{472.4}</td>
</tr>
</tbody>
</table>
Figure 46: Pressure vs. temperature for Pure CO$_2$ Test 3.

This time, the last point falls well short of the predicted value – much more than the previous tests. Between the last two test points the average temperature increased from 404.8 K to 472.4 K, while the pressure only rose 0.04 atm (less than 1 psi). We clearly had some leaks, but we continued the test anyway, as even this situation could provide valuable information: the presence of leaks would be detected in the recorded temperature and pressure data, which could then be correlated with changes in the measured spectra. Figure 47 shows the temperature and pressure vs. time plot for this test.
As the cell was first pressurized – shown by the sharp jump in the red curve (gas cell pressure) – the pressure was manually controlled using a small metering valve (resulting in some overshoot). Next, the gas cell heaters were turned on, shown by the quick jump in the green curve (gas cell surface temperature), just before 15:57. Pressure naturally increased with temperature. After the green curve (mostly) stabilized, the heat tape was turned on, in order to help attain thermal homogeneity within the isolated volume of gas. Just after 16:12, all three measured temperatures (gas cell surface, inlet probe and outlet probe) were within reasonable agreement, near 373 K. A similar process was used to reach the final setpoint of 473 K. Notice, however, that the pressure (red curve) never stabilizes. Once again, the pressure begins to increase with temperature (between 16:26 and 16:30), but then reaches a maximum (around 16:40), and finally begins to decrease (between 16:40 and 16:55), even though the average temperature is increasing. This clearly indicates the presence of a leak. By the end of the test (just
before 17:09) the pressure had dropped nearly to the starting point of this phase of the test (the 473 K setpoint). A wider view (Figure 48), shows how the pressure continued to decrease after the temperatures had completely stabilized (beyond ~21:00).

Figure 48: Pressure and temperature vs. time for Pure CO\textsubscript{2} Test 3 (overall).

So, what impact did this leak have on the infrared absorption spectra? Remember, absorbance it is not simply a function of density (which is relatively easy to track, using the simplified model described in Section 4.1), but it is complicated by the fact that absorptivity is also strongly affected by temperature. In order to try to understand these effects, we turn to Figure 49.
Figure 49: Spectra throughout Pure CO₂ Test 3.

The most obvious difference between this series of spectra and those recorded in Pure CO₂ Test 2 (Figure 44) is the height of the 472.4 K peak. The height is noticeably lower than the same peak here, in Figure 49. This is consistent with a system that is losing mass\footnote{This assumes that everything else was held constant between Tests 2 and 3.}. Once again, all of the spectra in this test series were brought to a common baseline, as shown in Figure 50.
Figure 50: Spectra for Pure CO$_2$ Test 3 with baseline adjustment.

Once again we calculated the band-integrated areas for the 6850-7050 cm$^{-1}$ region of the spectrum (corresponding to Figure 50b). These results are shown in Table 14.
Table 14: Pure CO₂ Test 3 summary ($c_{\text{initial}} = 958.15 \text{ mol/m}^3$).

<table>
<thead>
<tr>
<th>$T_{\text{avg}}$ (K)</th>
<th>$P$ (atm)</th>
<th>Integrated area 6850-7050 cm$^{-1}$ (AU·cm$^{-1}$)</th>
<th>Error (AU·cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>296.17</td>
<td>20.60</td>
<td>4.29613</td>
<td>±0.01832</td>
</tr>
<tr>
<td>322.53</td>
<td>23.84</td>
<td>3.63674</td>
<td>±0.01550</td>
</tr>
<tr>
<td>371.43</td>
<td>24.99</td>
<td>3.80435</td>
<td>±0.01622</td>
</tr>
<tr>
<td>404.80</td>
<td>28.41</td>
<td>3.21717</td>
<td>±0.01372</td>
</tr>
<tr>
<td>472.37</td>
<td>28.45</td>
<td>3.53367</td>
<td>±0.01507</td>
</tr>
</tbody>
</table>

4.3.5 Pure CO₂ Test 4

For Pure CO₂ Test 4 we were much more confident in our system’s leak-tightness. As we have mentioned, leaks must be eliminated, since they introduce variability into a system that we are attempting to control. They also make it difficult to decode observed pressure vs. temperature data (shown by the failure to meet predicted pressure vs. temperature curve for a constant density).

Upon completion of Pure CO₂ Test 3, we unwrapped the heat tape from the inlet and outlet tubing, and noticed several fittings in need of re-tightening. We also consulted with a representative from Swagelok on the applicability of these fitting to our system, as well as the proper tightening procedure. Our hardware was fine, but our procedures were modified. Having addressed these issues, we were confident that our present configuration was as leak-tight as possible. Pressure leak-checks were once again conducted before and after testing. For both Pure CO₂ Tests 4 and 5 our system was found to be leak-tight.
Any further differences between predicted and measured pressure vs. temperature would most likely be caused by differences in the measured and actual average gas temperature. The test points are shown in Table 4 ($c_{initial} = 961.87 \text{ mol/m}^3$).

Table 15: Test points for Pure CO$_2$ Test 4 (4/4/14).

<table>
<thead>
<tr>
<th>Time</th>
<th>Cell Heater setpoint (K)</th>
<th>Tubing Variac output (%)</th>
<th>$P_{cell}$ (atm)</th>
<th>$T_{sfc}$ (K)</th>
<th>$T_{in}$ (K)</th>
<th>$T_{out}$ (K)</th>
<th>$T_{avg}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10:16</td>
<td>--</td>
<td>0</td>
<td>20.72</td>
<td>296.9</td>
<td>296.3</td>
<td>296.8</td>
<td>296.7</td>
</tr>
<tr>
<td>10:40</td>
<td>373.15</td>
<td>0</td>
<td>23.95</td>
<td>374.1</td>
<td>297.4</td>
<td>296.9</td>
<td>322.8</td>
</tr>
<tr>
<td>11:05</td>
<td>373.15</td>
<td>28</td>
<td>25.89</td>
<td>372.0</td>
<td>377.0</td>
<td>374.5</td>
<td>374.5</td>
</tr>
<tr>
<td>11:14</td>
<td>473.15</td>
<td>28</td>
<td>29.57</td>
<td>473.6</td>
<td>377.1</td>
<td>374.6</td>
<td>408.4</td>
</tr>
<tr>
<td>11:46</td>
<td>473.15</td>
<td>49</td>
<td>31.67</td>
<td>470.8</td>
<td>479.0</td>
<td>472.6</td>
<td>474.1</td>
</tr>
</tbody>
</table>

Figure 51 and Figure 52 show the improved pressure vs. temperature response and the time evolution of the system for this test, respectively.

Figure 51: Pressure vs. temperature for Pure CO$_2$ Test 4.
Figure 52: Pressure and temperature vs. time for Pure CO\textsubscript{2} Test 4.

Next, the spectra for Pure CO\textsubscript{2} Test 4 are displayed in Figure 53 and Figure 54, followed by Table 16, summarizing the results from this test.

Figure 53: Spectra throughout Pure CO\textsubscript{2} Test 4.
Figure 54: Spectra for Pure CO$_2$ Test 4 with baseline adjustment.
Table 16: Summary of Pure CO2 Test 4 ($c_{initial} = 961.87 \text{ mol/m}^3$).

<table>
<thead>
<tr>
<th>$T_{avg}$ (K)</th>
<th>$P$ (atm)</th>
<th>Integrated area 6850-7050 cm$^{-1}$ (AU·cm$^{-1}$)</th>
<th>Error (AU·cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>296.67</td>
<td>20.72</td>
<td>5.03560</td>
<td>±0.02142</td>
</tr>
<tr>
<td>322.80</td>
<td>23.95</td>
<td>4.34234</td>
<td>±0.01847</td>
</tr>
<tr>
<td>374.50</td>
<td>25.89</td>
<td>4.70347</td>
<td>±0.02000</td>
</tr>
<tr>
<td>404.40</td>
<td>29.57</td>
<td>4.24305</td>
<td>±0.01805</td>
</tr>
<tr>
<td>472.60</td>
<td>31.67</td>
<td>4.69338</td>
<td>±0.01996</td>
</tr>
</tbody>
</table>

4.3.6 Pure CO$_2$ Test 5a

Pure CO$_2$ Test 5 is broken into two sections: 5a, which is described first, is an isochoric test similar to tests 1-4, while 5b is an isothermal test. The purpose of this testing was to twofold: first, to achieve supercritical CO$_2$ conditions inside of the gas cell (during part a), and then to meet the same high-temperature, high-pressure conditions as tested by the European Space Agency (ESA) at the 22 km altitude mark in Venus’s atmosphere (in part b).

In order to reach supercritical conditions (within our system’s temperature range ~575 K), we needed to begin with an initial density of at least 1800 mol/m$^3$. This meant filling with full CO$_2$ bottle pressure (36.7 atm). Given this starting pressure, and our homogeneous initial temperatures, we used the NIST Chemistry Webbook to calculate $c_{initial} = 1911.5 \text{ mol/m}^3$. Following the predicted NIST curve, we would reach the critical point at approximately 500 K (with a pressure of 72 atm). Unfortunately, as we can see in Figure 55, we were unable to meet this point.
Figure 55: Pressure vs. temperature for Pure CO\textsubscript{2} Test 5a.

Our system (which was proven leak-tight at this point), was still not delivering homogeneous temperatures. (If it had, we followed the predicted curve, and we would have reached the critical point.) This thermal inhomogeneity can be seen most clearly in Figure 56, during part (a) of this test (between 15:10 and 16:10) where the outlet temperature lags the other two temperatures by nearly 15 K.
This lower temperature on the outlet can be attributed to the piece of extension tubing used to protect the pressure transducer from the high gas temperature inside the cell. Refer back to Figure 33, which shows the sharp thermal gradient produced across this tubing. Because of the cool temperature and high pressure inside of this tubing, it is also possible that CO₂ was condensing near the pressure transducer. This would certainly affect the pressure reading: with fewer molecules in the gas phase, the pressure would be much lower. Figure 57 shows the spectra taken during both phases of Pure CO₂ Test 5 (correlated with the time in Figure 56), and is followed by close-ups of the baseline-adjusted spectra for 5a (Figure 58).
Figure 57: Spectra throughout Pure CO₂ Test 5.
Figure 58: Spectra for Pure CO\textsubscript{2} Test 5a with baseline adjustment.

Pure CO\textsubscript{2} Test 5a differs from Pure CO\textsubscript{2} Tests 1-4 in that we started with a much higher initial pressure (and therefore CO\textsubscript{2} density) in our attempt to reach the critical point (36 atm, as opposed to 20 atm), and, we increased the upper temperature as well (565 K, as opposed to 475 K). We expect that this would affect the spectra, and indeed it
does. Most obviously, the overall peak heights are higher. This is what we would expect by following Beer’s Law. More interestingly, though, notice the more intense “expansion” to the left of 6930 cm\(^{-1}\). We noticed this expansion before, in Tests 1-4, and explained it in terms of new rotational modes appearing at elevated temperatures, and the coupling between rotational and vibrational modes. Now, with even higher temperatures, this effect is more pronounced. An in depth analysis of the underlying physics describing this observation would be a great area for future work. The existing models outlined in Chapter 2 may already account for this behavior, and any analysis should begin there. For now, it is important to understand this expansion experimentally, as it will impact our quantitative analysis (discussed in more detail in Section 4.4).

### 4.3.7 Pure CO\(_2\) Test 5b (ESA 22 km test)

The second part of Pure CO\(_2\) Test 5 consisted of venting some pressure from the gas cell, while holding the temperature constant\(^{14}\). The goal of this test was to recreate another test found in the literature [8], this time at both high pressure and high temperature (recall, the first test described in this section replicated some existing high pressure results [5]). The targeted test point of 18.97 atm, and 565.1 K lies on the VIRA profile and corresponds to an altitude of 22 km above Venus’s surface.

While we used the NIST Chemistry Webbook to calculate our initial density, because of the inhomogeneous temperatures (inherent to our test setup) this method could

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\(^{14}\) Any time the gas cell is pressurized or vented, the temperature increases or decreases correspondingly. Even though we are controlling the temperature using a PID controller, the system naturally needs some time to recover from this load (speed is not an issue in our case; we just need to wait until things are stable before the measurements can be analyzed).
not be used to determine our density for 5b. Instead, we use the absorbance information from our spectra, combined with Beer’s Law, to derive our estimated density for part 5b.

Next, we compare this result with our predicted density for 5b, using the simplified model described in Section 4.1. These processes, and, the assumptions involved, are described next. We begin by writing Beer’s Law equations for the absorbance intensity at \( \nu = 6986 \text{ cm}^{-1} \) (the highest peak in the 6850-7050 cm\(^{-1} \) region).

\[
A_1(\nu) = \varepsilon l c_1 = \varepsilon (0.1m) \left( 1911.5 \frac{mol}{m^3} \right) = 0.1936 \text{ AU} \tag{49}
\]

Note that \( c_1 \) was obtained using NIST. Next, assuming \( \varepsilon \) is constant with pressure, we can solve for this value and substitute it into the next equation, allowing us to find our final density \( (c_2) \), based on measured changes in absorption.

\[
A_2(\nu) = \varepsilon l c_2 = (0.001013)(0.1m)c_2 = 0.0832 \text{ AU} \tag{50}
\]

\[
c_2 = 821.32 \left( \frac{mol}{m^3} \right) \tag{51}
\]

Once again, this assumes the linearity of Beer’s Law, and that \( \varepsilon \) is unaffected by pressure. In reality, things are more complicated – this is simply an approximation. Next, we compare this result with our predicted final density, based on our simplified (ideal gas) model, \( P_1 = 67.07 \text{ atm}, \ P_2 = 19.05 \text{ atm}, \) and an average temperature \( T_{\text{avg}} = \frac{T_1 + T_2}{2} = \frac{(555.6 \text{ K} + 564.23 \text{ K})}{2} = 559.9 \text{ K} \) (recall, this model is only valid for isothermal tests):

\[
\frac{\partial c}{\partial P} = \frac{1}{RT_{\text{avg}}} \tag{52}
\]

104
\[ \partial c = \frac{1}{RT_{avg}} \partial P \]  \hspace{1cm} (53)

\[ \int \partial c = \frac{1}{RT_{avg}} \int_{P_1}^{P_2} \partial P \]  \hspace{1cm} (54)

\[ \int \partial c = \frac{1}{RT_{avg}} (P_2 - P_1) = -1045.19 \ (mol/m^3) \]  \hspace{1cm} (55)

So, the predicted total change in density is -1045.19 mol/m³. Adding this value to our original density of 1911.5 mol/m³ gives our predicted value for \( c_2 = 866.31 \) mol/m³. In order to quantify these results, we consider the estimated value for \( c_2 \) (derived from the measured absorptions) to be the standard, because of the known limitations of our simple ideal gas model.

\[ c_{2_{estimated}} = 821.32 \ (mol/m^3) \]  \hspace{1cm} (56)

\[ c_{2_{predicted}} = 866.31 \ (mol/m^3) \]  \hspace{1cm} (57)

\[ \% \ Difference = \frac{866.31 - 821.32}{821.32} \times 100\% = 5.48\% \]  \hspace{1cm} (58)

The ideal gas model overestimates the final density by 5.48%. Based on the assumptions involved, this was an acceptable ballpark figure.
In Figure 59, we show the transition between 5a and 5b, by plotting the spectra on either side of this transition (with the stronger absorption belonging to 5a, and the lower absorption to 5b).

![Figure 59: Isothermal transition between Pure CO₂ Test 5a and 5b.](image)

Notice how the overall peak shape is roughly the same, and the peaks are scaled by a factor proportional to the change in pressure, consistent with what we would expect for an isothermal test (approximately following Beer’s Law). The curve for 5b shown in Figure 59 (blue) represents the infrared absorption for CO₂ at an altitude of 22 km in Venus’s atmosphere. We measured the peak heights at two different points, and made comparisons with existing data taken by ESA researchers. The peak heights for the literature data were estimated based on the scale of the graph [8]. The results are shown below in Table 17.
Table 17: ESA vs. NASA measured absorption at 22 km.

<table>
<thead>
<tr>
<th></th>
<th>ESA P (atm), T (K)</th>
<th>NASA P (atm), T (K)</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>ESA absorption (AU)</th>
<th>NASA absorption (AU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P = 18.97</td>
<td>6950</td>
<td>0.011</td>
<td>0.050</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T = 565.1</td>
<td>6988</td>
<td>0.020</td>
<td>0.085</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As we have noted before, our gas cell differs from ESA’s by a factor of five (10 cm compared with their 2 cm cell), so all other factors being constant, we would expect our absorption intensities to be five times greater than theirs. However, we were not able to hit exactly the same pressure and temperature setpoint, so some additional uncertainty is introduced. The measured differences for each absorbance measurement are given below.

\[
\text{% Difference at 6950 cm}^{-1} = \frac{0.050 - 5(0.011)}{5(0.011)} \times 100\% = -9.09\% \tag{59}
\]

\[
\text{% Difference at 6988 cm}^{-1} = \frac{0.085 - 5(0.020)}{5(0.020)} \times 100\% = -15.00\% \tag{60}
\]

Comparing our measured temperature and pressure (see Table 17), one would expect our density (molar concentration) to be higher than ESA’s, and therefore our absorptions should be greater than five times theirs. However, as shown above, we observe the opposite: our absorbance differences are negative, instead of positive. The discrepancy may result from the inhomogeneous conditions inside of our gas cell (described in Chapter 3). Because of the cool piece of tubing protecting the pressure transducer (Section 3.4.2), our system contains areas of relatively low density (where it is warmer) along with areas of relatively high density (where it is cooler). The volume
inside of the gas cell itself (where the infrared beam passes through) is expected to be an area of relatively lower density (because of the higher temperature and better thermal control). Since lower density means lower absorption intensity, this is one possible explanation for our lower-than-expected absorption measurements. In order to achieve more meaningful pressure and temperature information, a high-temperature pressure transducer is being installed directly on the heated/insulated gas cell volume (eliminating the unheated/un-insulated tubing). For future work, repeating this test with the new pressure transducer and improved thermal homogeneity is highly recommended.

Next, we integrate the area under these two curves over the 6850-7050 cm\(^{-1}\) window, to determine how well this test follows Beer’s Law. The plot of integrated intensity vs. density for this part of the test is given in Figure 60.

![Figure 60: Integrated intensity vs. density for Pure CO\(_2\) Test 5b.](image)

For this isothermal portion of the test, our band-integrated areas were found to be: 6.86241 ± 0.01209 AU-cm\(^{-1}\) (5a), and 3.00620 ± 0.00530 AU-cm\(^{-1}\) (5b). Between these points, we measured a slope of approximately 0.16 AU-cm\(^{-1}\)/amagat. Since we do not
have existing data with which to compare this integration (as before, in our first test), we will have to accept this data until further analysis can be done. Adding more test points (different densities) along this curve would help verify our results, and would also illuminate any nonlinear behavior (recall, Beer’s Law does not always hold). As another check, we could also integrate in different regions of the spectra, and compare the results. Finally, as mentioned above, this test should be repeated with the new pressure transducer and better thermal control. The improved test setup, combined with more complete integration checks, would give us a much better picture of our system’s performance. Both of these are important areas for future work.

Next, in Figure 61, Figure 62 and Figure 63, we show all of the spectra taken during 5b, corresponding to Venus’s 22 km altitude. We focus only on the meaningful spectra whose peak absorbance intensities are below 1 AU.

![Figure 61: Measured spectra for Venus’s 22 km altitude (2000-2150 cm⁻¹).](image)
Figure 62: Measured spectra for Venus’s 22 km altitude (4700-5200 cm\(^{-1}\)).

These images show how different regions of the CO\(_2\) spectrum look at Venus-like conditions (22 km altitude). The 2000-2150 cm\(^{-1}\) region is modified in a similar way to the 6850-7050 region: the \(R\)-branch peaks sharpen (become more compressed), while \(P\)-branch peaks spread out. In the 4700-5200 cm\(^{-1}\) region (Figure 62), the \(R\)-branch peaks retain basically the same shape throughout Test 5, while the \(P\)-branch peaks spread out significantly at elevated temperatures.

Figure 63: Measured spectra for Venus’s 22 km altitude (6850-7050 cm\(^{-1}\)).
4.4 Influence of CO$_2$ Absorption on Trace Component Spectra

A major goal of this research was to find out how the extreme pressures and temperatures found in Venus’s deep atmosphere might impact our ability to quantify chemical compositions. The FTIR spectroscopic technique is very good for qualitative analysis – identifying the presence of different chemicals. But, it is a bit trickier for quantitative analysis – measuring how much of each component is present [27]. This is because of the variables that must be understood and controlled. As we have seen, this includes the temperature dependence of overall spectral shape, and the pressure and temperature dependence of density (and therefore absorbance intensity). Also, as we have discussed, the precise way in which these extreme conditions modify the spectra is not well documented, and is best studied experimentally in a laboratory setting such as ours. So, in this section we look at a HITRAN simulation the overall absorption of CO$_2$, showing where we expect to find the trace components (Figure 64). Then, we examine some areas of interest within the experimental spectra taken in our simulation of CO$_2$ at Venus’s 22 km altitude.
As we can see in Figure 64, most of the trace components are found in areas well outside of the main CO\textsubscript{2} absorbance features (shown in green) – except for the 2000-2200 cm\textsuperscript{-1} region. We expected this area to cause the most difficulty, especially with the quantification of OCS, whose absorbance is overlapped by a strong CO\textsubscript{2} peak near 2100 cm\textsuperscript{-1}. As a result, most of our discussion is focused on this region. In Figure 65, we zoom in on this area of interest and increase OCS concentrations, until the OCS peak becomes apparent.
Figure 65: HITRAN simulation ($P = 20$ atm, $T = 296$ K and $l = 0.1$ m): 100 ppm OCS, balance CO$_2$ (top), 1000 ppm OCS, balance CO$_2$ (middle), and 0.01% OCS, balance CO$_2$ (bottom).
Figure 65 shows that we are unable to distinguish OCS from the CO$_2$ peak until we reach 1000 ppm OCS. This is much higher than our target concentration for OCS (4.4 ppm as shown in Table 3). Distinguishing OCS from CO$_2$ in this region will be an important area for future work. Since we already knew that this would be a difficult task, we show our measured CO$_2$ spectra in this region (Figure 66), to help understand how the high pressure and temperature changes things, especially our ability to detect OCS here.

![Figure 66: Measured CO$_2$ behavior near OCS absorbance feature.](image)

Notice that in Figure 65 (middle), the OCS feature begins to appear in the “crook” between the two regions of the CO$_2$ absorbance feature at about 2065 cm$^{-1}$. Experimentally, as we heat our isolated volume, this “crook” region gradually deepens (Figure 66). This effect may work in our favor, as it might help the OCS feature stand out more in this area. However, we do not know, experimentally, how OCS behaves in this region. This is an area for future work. Although the other trace gasses are not strongly influenced by CO$_2$ in the way OCS is, more research is also needed in this area, to determine our system’s capabilities.
4.5 Data Analysis and Conclusions

In this section, we summarize the significant results from the testing described above. The main questions we had in interpreting our data are listed below:

- Does thermal inhomogeneity affect the spectra significantly?
- How does our simplified model (described in 4.1) predict the effects of changing pressure (for isothermal tests)?
- How do our results compare with those in literature?
- What is the impact of CO$_2$’s absorption on nearby trace component spectra?

**Thermal Homogeneity and the Spectra**

We spent a good deal of time optimizing our system for repeatable, controllable test conditions. This included minimization of unheated/un-insulated tubing and fittings, and the addition of heat tape. These modifications made it possible to more closely meet our desired pressure and temperature setpoints. While these modifications helped us achieve Venus-like conditions inside of the entire isolated volume of gas (as indicated by the more meaningful pressure measurements), the effect on the spectra was more subtle.

In Pure CO$_2$ Tests 1-4, when a step-wise heating approach was used, little difference was observed in the spectra as the temperature increased. By separating the heaters, we could individually observe their effects on the system. Referring to the baseline-corrected spectra in Figure 45, for Pure CO$_2$ Test 2, we notice the similarity
between the spectra recorded at 13:12 (with just the gas cell heaters on, and an average temperature of 322.8 K), and the spectra recorded at 14:14 (when both the gas cell heaters and the heat tape were on, raising the average temperature to 372.9 K). Similar behavior is seen in the step-wise heating leading to our next setpoint, when we first increased the gas cell temperature to ~473 K, while leaving the heat tape at ~373 K (14:25), and then bringing the heat tape up to the final setpoint (14:58).

This same effect is noticed in any test where the step-wise heating approach is used: once the gas cell heater reaches its setpoint, the spectra essentially assumes its final form, regardless of the heat tape. The conclusion here is that thermal inhomogeneity does not significantly affect the spectra. However, as we saw in Pure CO$_2$ Test 5 (when we compared our absorbance intensities with ESA’s), our measured spectra seemed to indicate locally lower density in the gas cell than the pressure and temperature measurements registered. So, in order to maintain repeatable test conditions and meaningful pressure and temperature measurements, it is recommended to control the line conditions using heat tape.

Performance of Simplified Model

We developed a simplified model, which shows how absorbance intensity changes based on density, using the ideal gas law. This model only applies to isothermal testing because it omits the temperature dependence upon absorption, described by the absorptivity term $\varepsilon$. As we saw in Section 4.3.7, we used this model to reasonably predict the change in density (based on the change in pressure) seen in the transition between Pure CO$_2$ Test 5a and 5b. Comparing our estimated final density (based on changes in absorption peak height), with our predicted final density, we found the prediction to be
off by +5.48%. This calculation assumes our estimated density to be the standard (i.e. no error). Realistically, there is also some error associated with our estimated densities, but these are expected to be much lower. Given the known limitations of the ideal gas law at these conditions, this was an acceptable amount of error for our rough estimate of changes in density.

**Comparison with Literature**

There were two specific tests in which we attempted to replicate results found in literature. The first one, 95% CO$_2$, 5% N$_2$ Pressure Test, was found to be in good agreement through both visually inspecting the spectra, and quantitative analysis using a band integration comparison. Specifically, we used the band-integrated areas to create a Beer’s Law plot, showing how absorbance intensity follows density (Section 4.3.1). Since our test conditions differed slightly from those in the literature (different gas cell pathlengths, slightly different densities), our data was scaled to bring it into the same range as the literature data. After scaling, the slope of our Beer’s Law plot was found to be 0.0470 AU-cm$^{-1}$/amagat compared with their slope of 0.0465 AU-cm$^{-1}$/amagat. Considering their slope to be the standard, we found our measured difference to be +1.08%. This gave us confidence that we were on track, as we began to push beyond the typical (ambient) range of operating conditions inside of our gas cell.

Next, we applied both high pressure and high temperature, and compared the results with ESA’s 22 km measurements (Pure CO$_2$ Test 5b). Here, we had good visual agreement (the peak heights and spectral shapes looked right), and we once again calculated the band-integrated areas. However, this time we did not have band-integrated areas with which to compare our results, and we identified a more in-depth analysis as an
area for future work. In lieu of the (preferred) band-integration comparison, we chose two individual peaks within the 6850-7050 cm\(^{-1}\) window for our comparison (6950 cm\(^{-1}\), and 6988 cm\(^{-1}\)). Estimating their peak heights from the scale on the graph [8], these points were then scaled and brought into the same range as ours for comparison. This time we simply multiplied the literature results by a factor of five, to account for our different pathlengths – differences in density were ignored, for reasons described below. In both cases, our measured absorption peak heights were lower than those at the same wavenumbers in the literature. On average, our measurement differences were approximately –12.0%. This was attributed to thermal inhomogeneity (resulting in hard-to-quantify, yet significant changes in density), and further testing with an improved (more homogeneous) test setup was recommended future work. Overall, though, we were pleased with the results of the comparisons; these tests helped us gain confidence with our system by beginning to establish our baseline performance.

**CO\(_2\)’s Impact on Nearby Trace Component Spectra**

We saw in Section 4.4 that OCS is the trace component most seriously affected by CO\(_2\)’s absorption. In particular, the region around 2065 cm\(^{-1}\) offers our only glimpse of OCS within our spectral range, and this area is strongly overlapped by CO\(_2\). Through a HITRAN simulation, we showed that OCS only becomes distinguishable from the CO\(_2\) peak above 1000 ppm (well above our target 4.4 ppm OCS). As we heat the fixed volume of gas (in our isochoric test, Pure CO2 Test 5a), the overall shape of the CO\(_2\) spectra begins to change in our favor; the area where OCS may be found decreases in intensity, possibly allowing OCS to be detected at a lower concentration. We do not know exactly how OCS will behave in this region, but we can make an educated guess. The main peak
will likely decrease with increased temperature (just like CO$_2$’s), and the peak shape should sharpen (as we have seen in CO$_2$), which would help it stand out more from the CO$_2$ background. However, our very small OCS target concentration of 4.4 ppm may prevent its detection in this region altogether. There are other areas of OCS absorption within our spectrometer’s range (near 2900 cm$^{-1}$ and 4100 cm$^{-1}$), but they are much weaker, and given our gas cell’s relatively short pathlength (10 cm), these are not viable regions to measure. There is definitely more work required in this area.
CHAPTER V
CONCLUSION AND FUTURE WORK

5.1 Conclusion

In this thesis we have described experimental work exploring the infrared absorption of CO$_2$ at high temperatures and pressures, specifically with the goal of characterizing an FTIR spectrometer for measurements in NASA Glenn’s Extreme Environment Rig (GEER) test chamber. We have developed a more repeatable, controllable test environment for our FTIR samples, and showed good agreement with available laboratory experimental data in this area. In particular, we were able to replicate a high-pressure test using CO$_2$ and found a pathlength and density corrected Beer’s Law slope of 0.0470 AU-cm$^{-1}$/amagat, compared with the literature’s 0.0465 AU-cm$^{-1}$/amagat. We also replicated a test conducted by the European Space Agency (ESA), measuring the CO$_2$ spectrum at atmospheric conditions found 22 km above Venus’s surface. Our measured absorbance peak of 0.085 AU at 6988 cm$^{-1}$ was compared with ESA’s value of
0.100 AU. The difference between these values was attributed to thermal inhomogeneity (locally higher temperature, and therefore lower density and lower absorption in our gas cell), and testing at more homogeneous conditions was recommended future work. The data in this thesis were also interpreted in terms of the underlying physics and were found to be consistent with the theoretical predictions. However, when examined carefully (as several researchers have noted), divergences between measured and theoretical data exist, and, as a result, experimental data are weighted more heavily than theoretical models.

5.2 Suggested Future Work

The areas for future work can be broadly grouped into three categories: (1) experimental test setup modifications, (2) experimental testing, and (3), theoretical modeling.

Experiment Test Setup

We have emphasized the importance of creating repeatable, controllable test conditions. With this in mind, there are several areas that could be improved upon in our experimental setup, and some suggested modifications are listed below:

- Replace Swagelok connectors/tubing with orbital-welded manifold, improving leak-tightness of the system
- Implement brazed sapphire windows and metal seals, eliminating potential outgassing from Kalrez o-rings
• Install high-temperature pressure transducer mounted directly on gas cell, eliminating extension tubing and improving thermal homogeneity

• Automate pressure control using backpressure regulator or proportional valve at gas cell outlet, improving repeatability over current manual valve

• Install pneumatically actuated ball valves at gas cell inlet and outlet, to fully automate cell fill/vent procedures

• Add active cooling, to improve detector performance/reduce baseline shift

A CAD model showing these proposed modifications can be seen in Figure 67.

Figure 67: Proposed modifications to FTIR system: (1) orbital-welded manifold, (2), high-temperature pressure transducer, (3) brazed sapphire gas cell windows, (4) automatic pressure control, (5) automated inlet/outlet valves. Image credit: Mike McVetta, NASA Glenn Research Center.
Experimental Testing

Since so little experimental laboratory data exists for gasses at extreme (high-temperature and high-pressure) conditions, there is much room for future work in this area. In particular, we would like to continue to verify our baseline performance using CO$_2$, by testing at other altitudes of Venus’s atmosphere found in literature (24 km, 28 km, 32 km, etc.). It would also be interesting to see how the spectrum of CO$_2$ is modified by the conditions found below 22 km (the lowest altitude simulated in literature). Pressure and temperature both increase inversely with altitude, so yet to be discovered features may be found as the conditions extend beyond the available data and models. Further testing of system repeatability is also recommended: each test should be repeated numerous times, in order to firmly establish the baseline performance.

Similarly, the infrared properties of the trace gasses in Venus’s atmosphere could be studied in our FTIR gas cell at Venus-like conditions. With components made of Inconel, sapphire, and Kalrez, the entire gas cell is capable of withstanding the corrosive trace components found in Venus’s atmosphere. This would represent a significant contribution to the scientific community in this area, as previous laboratory spectroscopy for Venus has focused exclusively on CO$_2$.

Finally, with respect to our own specific research goals, we need to understand the detectability of trace components within our gas cell. Several limiting factors exist: a short pathlength gas cell (10 cm), very small concentrations of some components (ppm and ppb), and significant spectral overlap (OCS/CO$_2$ in particular). With these challenges more work is needed, both experimentally and theoretically.
**Theoretical Modeling**

A theoretical model, which could be used to predict our system’s response to various combinations of pressures, temperatures, and chemical compositions, would be very useful. This way we could take requirements for a desired atmosphere (altitude setpoint) and estimate our system’s ability to make the requested measurement. This type of model would need to include the effects of pressure and temperature described in this thesis, as well as the effects introduced by the FTIR itself (apodized resolution, source/detector combination, etc.). There are many other areas of interesting research, including measurements of different planetary atmospheres and even exoplanets, and it is our hope that this thesis may help enable further study in this field of high-pressure/high-temperature laboratory spectroscopy.
REFERENCES


APPENDIX A: Measurement Uncertainty Analysis for Band-Integrated Areas

In this appendix, we apply the error model developed in Section 4.2 to the band-integrated area calculations found throughout Chapter 4. Recall that our error model describes the error associated with the absorbance at a single wavenumber. Beer’s Law gives absorbance intensity,

\[ A(P, T, \nu) = \varepsilon(T, \nu)lc(P, T) \]  

where \( A \) is our measured quantity of interest, and is actually the sum of the true (unknown) absorbance, \( A_{true} \), combined with the uncertainty associated with the measurement:

\[ A = A_{true} + \delta_A \]  

We simplified our model to only include error contributions from errors in density:

\[ \delta_{density} = \frac{\delta_A}{\varepsilon l} \]  

Because of this simplification, our inputs to the model are simply temperature and pressure. From these inputs, we can determine where on the P-V-T surface we fall (for an ideal gas), and from this we can calculate the sensitivity to temperature and pressure (using the sensitivity coefficients in Section 4.2), to determine how a small change (or
error) in either of these values impacts density and therefore absorbance intensity (our measured quantity of interest).

We begin our derivation with writing Beer’s Law as a function of wavenumber (since we are holding pressure and temperature constant, and any small variation – errors – in these terms are handled by our error model):

\[ A(\nu) = \varepsilon(\nu)lc \]  
\[ \text{(A.4)} \]

Next, we integrate both sides of this equation between our lower and upper limits (for our analysis in Chapter 4, this meant integrating between 6850 cm\(^{-1}\) and 7050 cm\(^{-1}\)):

\[ \int_{\nu_1}^{\nu_2} A(\nu) d\nu = lc \int_{\nu_1}^{\nu_2} \varepsilon(\nu) d\nu \]
\[ \text{(A.5)} \]

The left hand side of this equation is our integrated area, based on measured absorbance values. On the right hand side, \( l \) and \( c \) are assumed to be constant with respect to \( \nu \), so they are pulled out in front of the integral. We are not yet considering the error terms, but we need to solve for the integral on the right hand side first, as it is used in later calculations. Ignoring errors (due to changes in \( c \)) is a valid assumption at this point, as they are not correlated with errors in \( \varepsilon \) (in fact we are assuming these to be zero in this simplified model). Solving for this integral, we obtain:

\[ \int_{\nu_1}^{\nu_2} \varepsilon(\nu) d\nu = \frac{\int_{\nu_1}^{\nu_2} A(\nu) d\nu}{lc} \]
\[ \text{(A.6)} \]

where, the left hand side is simply our measured band-integrated area, scaled by \( l \) and \( c \).

Now, we introduce the error terms:
\[
\int_{\nu_1}^{\nu_2} (A(\nu) + u_{\delta_A}) \, d\nu = l(c + u_{\delta_{density}}) \int_{\nu_1}^{\nu_2} \epsilon(\nu) \, d\nu \quad \text{(A.7)}
\]

The error due to density is known from our error model calculations; with this information, we can find its impact on the absorbance error.

\[
\int_{\nu_1}^{\nu_2} A(\nu) \, d\nu + \nu u_{\delta_A} \bigg|_{\nu_1}^{\nu_2} = l(c + u_{\delta_{density}}) \int_{\nu_1}^{\nu_2} \epsilon(\nu) \, d\nu \quad \text{(A.8)}
\]

Solving for our unknown quantity of interest, we obtain our total error over a band-integrated range:

\[
\nu u_{\delta_A} \bigg|_{\nu_1}^{\nu_2} = l \left( c + u_{\delta_{density}} \right) \int_{\nu_1}^{\nu_2} \epsilon(\nu) \, d\nu - \int_{\nu_1}^{\nu_2} A(\nu) \, d\nu \quad \text{(A.9)}
\]

\[
\nu u_{\delta_A} \bigg|_{\nu_1}^{\nu_2} = l u_{\delta_{density}} \int_{\nu_1}^{\nu_2} \epsilon(\nu) \, d\nu + l c \int_{\nu_1}^{\nu_2} \epsilon(\nu) \, d\nu - \int_{\nu_1}^{\nu_2} A(\nu) \, d\nu \quad \text{(A.10)}
\]

The rightmost two terms are equal (via Equation A.5), so they cancel, giving our final result:

\[
\nu u_{\delta_A} \bigg|_{\nu_1}^{\nu_2} = l u_{\delta_{density}} \int_{\nu_1}^{\nu_2} \epsilon(\nu) \, d\nu \quad \text{(A.11)}
\]

This model assumes constant temperature and pressure, and determines how small changes (errors) in the measurements of either of these values affect our band-integrated absorbance calculations across the range \( \nu_1 \) to \( \nu_2 \).
APPENDIX B: Reference Spectra [26]