

# **Carbon Dioxide Absorption in the Near Infrared**

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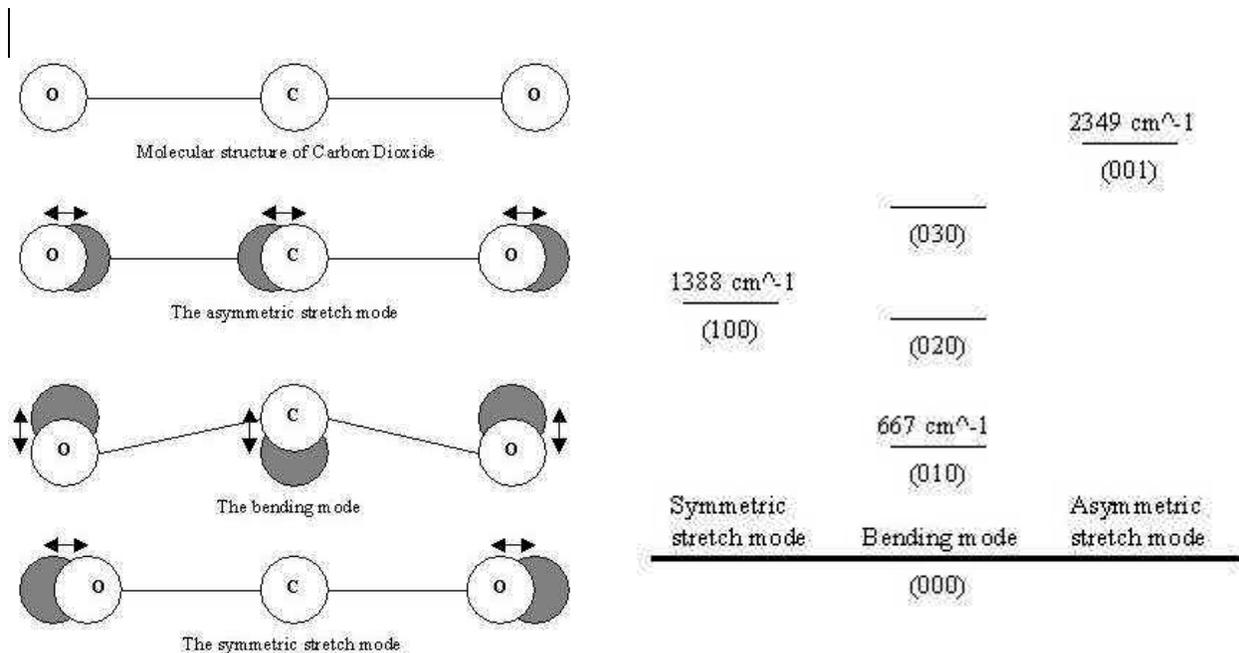
**Abstract**

This experiment explored the absorptivity of four peaks, 1437, 1955, 2013, and 2060 nanometers, in the near-IR (NIR) absorption spectrum of CO<sub>2</sub>. The NIR absorption bands in CO<sub>2</sub> can contribute up to 30% of the total solar heating in the mesosphere. Between the heights of 60-85 km the heating can exceed 1 K/day. (Fomichev & Shved, 1988; Ogibalov & Fomichev, 2003; Fomichev et al., 2004) With CO<sub>2</sub> concentrations increasing (West, 2005) it is ever more important to understand the absorbance properties of this molecule in all of its absorbance bands. Modeling of the Beer Lambert law found the absorption coefficient at 1955 nanometers to be 0.25 m<sup>2</sup> mol<sup>-1</sup> and the absorption coefficient for the peaks at 2013 and 2060 nanometers to be 0.43 m<sup>2</sup> mol<sup>-1</sup>. The absorption peak at 1437 nanometers had an absorption coefficient >>10.

**Introduction**

Due to the increase of anthropogenic carbon dioxide and its highly politicized global effects, there has been much research concerning the absorptivity of CO<sub>2</sub> and its thermal effects. CO<sub>2</sub> contributes to the greenhouse effect by absorbing energy in the infrared (IR) wavelengths, thus trapping heat within the boundaries of the earth's atmosphere. Climate models have been created to accurately portray our current model and make predictions for the future (Berger & Dameris, 1993). Only recently have there been attempts to parameterize the effects of near-IR (NIR) absorption by CO<sub>2</sub>. This research has shown that NIR absorption significantly contributes to heating of the Mesosphere and Lower Thermosphere (MLT). (Fomichev & Shved, 1988; Ogibalov &

Fomichev, 2003; Fomichev et al., 2004) Thus, understanding and quantifying the CO<sub>2</sub> absorption of NIR is an important endeavor at this point in time.



**Figure 1: Vibrational modes of CO<sub>2</sub> as depicted on Kverno's website. Figure 2: Vibrational energy levels of the CO<sub>2</sub> molecule as depicted on Kverno's website.**

Carbon Dioxide is composed of a single carbon atom covalently bonded to an oxygen atom on either side. This structure allows for CO<sub>2</sub> to have many vibrational and rotational states, making it an effective greenhouse gas. It is able to absorb many wavelengths of light and energy emitted by the earth and transform this into thermal energy. Molecules can only absorb photons energized with the same quantum of energy needed to elevate an electron to a higher energy state, or to elevate the entire molecule to a higher vibrational mode. The frequency of the photon and the vibrational mode must be synonymous. UV and visible light tend to have enough energy to elevate electrons to new energy states, while longer wavelengths such as in the IR spectra match the frequency of vibrational states.

There are three general vibrations for a CO<sub>2</sub> molecule: a symmetric mode, a bending mode, and an asymmetric mode (**Figure 1**). Each mode is able to absorb certain bands of wavelengths, with the bending mode absorbing longer wavelengths (667 cm<sup>-1</sup>) and the asymmetric absorbing shorter wavelengths, 2349 cm<sup>-1</sup> (**Figure 2**). (Kverno) Ultimately, the energy from the photon has two pathways. It can either be converted into thermal energy by the conversion of the internal kinetic energy of the CO<sub>2</sub> molecule to the kinetic energy of a different, inert molecule such as N<sub>2</sub>. Or the molecule can reemit a photon at a lower frequency.

CO<sub>2</sub> and other molecules with a similar structure (e.g. O<sub>3</sub>, H<sub>2</sub>O) insulate the earth. This greenhouse effect keeps the earth's surface temperature at a habitable level of about 14 °C (57°F) instead of the temperature -19 °C (-2.2 °F) which it would have without the atmosphere absorbing the radiated IR. Thus, the greenhouse accounts for approximately a 33°C (59°F) warming (Le Treut et al., 2007). By trapping energy, the greenhouse heats the earth and its atmosphere by raising the radiative equilibrium.

The greenhouse effect was discovered by Joseph Fourier in 1824 and was first investigated quantitatively by Svante Arrhenius in 1896. Svante Arrhenius (1896) stated that the presence of atmospheric water vapor and carbonic acid (referring to carbon dioxide) were the most significant contributors to the re-reflection of solar radiation. He calculated the absorption of CO<sub>2</sub> by comparing the emitted lunar radiation with that observed on earth. The moon was used as a body of relative comparable size to earth, yet one that lacked an atmosphere. He calculated the absorbed radiation in a specified volume of air, and while these calculations were later proven incorrect the general theory was correct. Arrhenius accurately described the relationship between increased

anthropogenic CO<sub>2</sub> emissions from burning fossil fuels and increases in the retention of the sun's radiation through the greenhouse effect.

Much attention has been given to the CO<sub>2</sub> absorption band at 15 microns because this absorption peak has high absorptivity placed in the far-IR region, and the parameterization of its effects have been comparably easy to quantify (Fomichev et al., 1993; Fomichev & Turner, 1998; Kiehl & Briegleb, 1991). Carbon dioxide, though, also absorbs radiation in near-IR (NIR) bands between 1.05-4.3 μm. When a CO<sub>2</sub> molecule absorbs NIR radiation it is excited to the  $\nu_3$  (anti-symmetric) mode. Using the more realistic model of non-local thermodynamic equilibrium (non-LTE), the energy is redistributed by emission in the NIR bands, and converted into thermal energy by colliding with other molecules, or de-excited to the  $\nu_2$  (bending) mode. The  $\nu_2$  energy is either emitted as a photon of lower frequency or it is converted to thermal energy by colliding with other molecules (**Figure 3**). In lower altitudes where pressure is higher, more energy is converted to thermal energy due to more frequent collisions with other molecules such as N<sub>2</sub>. (López-Puertas & López-Valverde, 1990; Fomichev et al., 2004; Ogibalov & Fomichev, 2003)

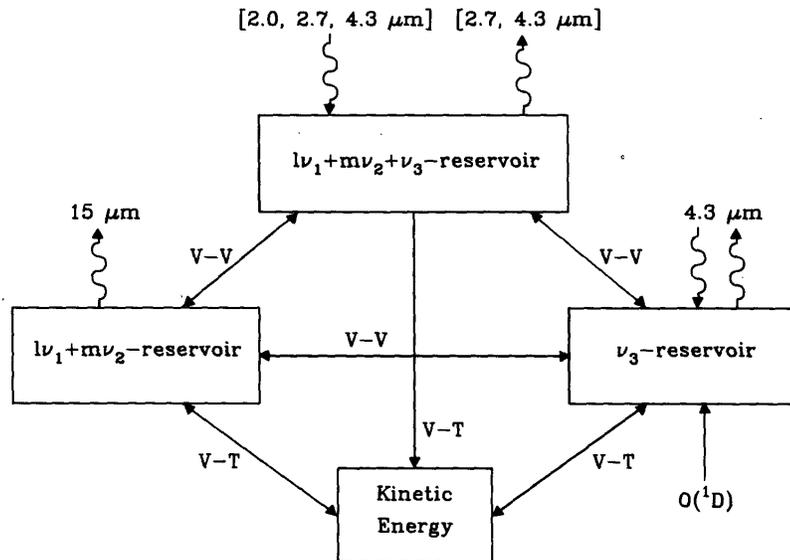
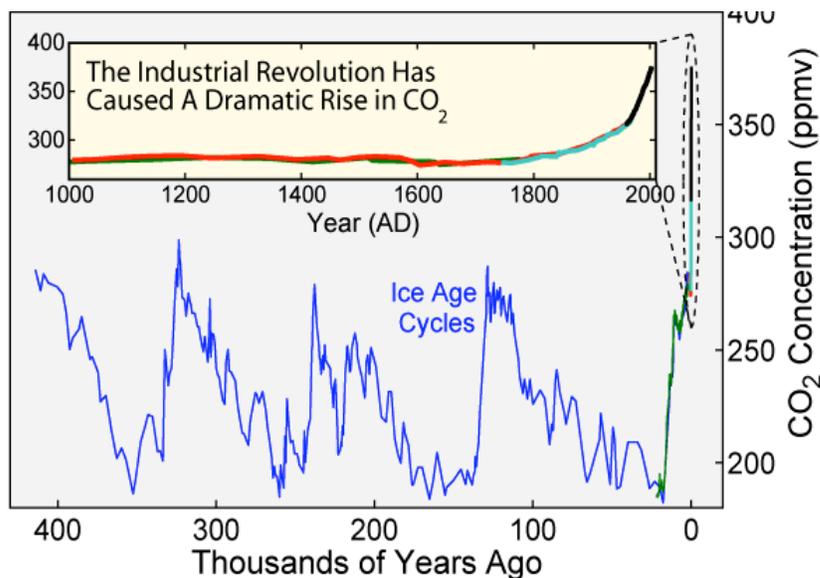


Fig. (3) From López-Puertas et al. (1990). Diagram of the pathways followed by radiation absorbed by CO<sub>2</sub> infrared bands. V-V represents exchange of vibrational energy and V-T represents the conversion of vibrational energy into kinetic energy in collisions.

The NIR bands of absorption in CO<sub>2</sub> significantly affect the thermal budget of the mesosphere. NIR absorption by CO<sub>2</sub> can contribute up to 30% of the total solar heating in the mesosphere. Between the heights of 60-85 km the heating can exceed 1 K/day. This is due to the local minimum of O<sub>3</sub> concentrations in this region. (Fomichev & Shved, 1988; Ogibalov & Fomichev, 2003; Fomichev et al., 2004) Due to the energy effect, narrow region of importance, and the necessity to consider non-LTE effects, though, there has only recently been an adequate parameterization developed for the NIR CO<sub>2</sub> bands. Ogibalov and Fomichev (2003) developed a parameterization for NIR CO<sub>2</sub> bands which includes non-LTE treatment. The inclusion of the NIR CO<sub>2</sub> heating parameters in the Canadian Middle Atmosphere Model (CMAM) results in a warming of up to 8 K in the mesosphere. However, the inclusion of NIR parameters does not significantly change the

model's thermal response to a doubling of CO<sub>2</sub>; therefore, the radiative forcing not strong enough to have an overall effect. (Fomichev et al., 2004)

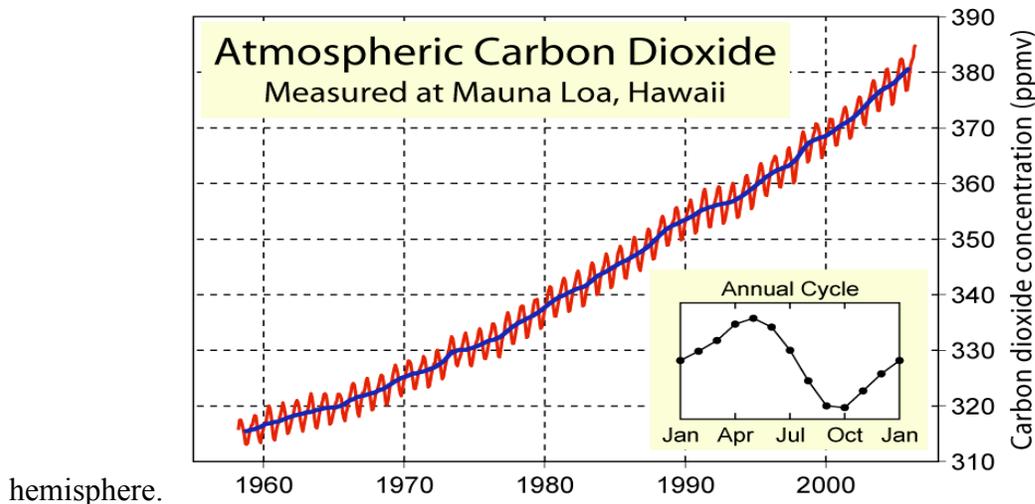
Atmospheric CO<sub>2</sub> levels are currently at about 380 parts per million, or .04% of the volume of the atmosphere. Historically, the CO<sub>2</sub> levels fluctuate due to geological processes. Volcanic eruptions produce large amounts of CO<sub>2</sub>, “releasing on average between 130-230 million tons of CO<sub>2</sub> into the atmosphere every year” (USGS). Other natural sources of CO<sub>2</sub> include the release of gas from natural hot springs, combustion of organic material, and the aerobic activity of organisms. Ice ages also cause variations of atmospheric CO<sub>2</sub> levels on a 100,000 year scale (**Figure 4**). Glaciers trap large amounts of gas as they form, decreasing the amount of CO<sub>2</sub> in the atmosphere. As they melt, this



**Figure 4: Atmospheric carbon dioxide levels pre-industrial revolution.**

gas is released and the level of atmospheric CO<sub>2</sub> increases. Aerobic activity trends in CO<sub>2</sub> have been well documented (**Figure 5**). Photosynthesis, simplified as  $6 \text{ CO}_2 + 12 \text{ H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{ O}_2 + 6 \text{ H}_2\text{O}$ , takes CO<sub>2</sub> out of the air for the production of organic matter.

This elevated sink for CO<sub>2</sub> during periods of high photosynthesis causes seasonal oscillations due to the higher concentration of terrestrial biomass in the northern



hemisphere.

**Figure 5: Keeling curve.**

Since the industrial revolution, CO<sub>2</sub> levels have been increasing due to anthropogenic production of atmospheric CO<sub>2</sub>. The burning of fossil fuels, like coal and petroleum, as well as deforestation all lead to increased atmospheric CO<sub>2</sub>. Deforestation is now reported as the second leading cause of anthropogenic CO<sub>2</sub> (Forster et al., 2007). Pre-industrial measurements of atmospheric CO<sub>2</sub>, performed using ice cores, show that the “level was at around 278ppm between 1000 and 1800 and did not vary by more than 7ppm during this time” (West, 2005). Since the industrial revolution, there has been an approximate increase of about 36 percent. Between 1958 and 2004, “CO<sub>2</sub> concentrations went from 315ppm to 378ppm” (West, 2005). There is a clear anthropogenic rise in the CO<sub>2</sub> level post industrial revolution, thus it is increasingly more important to research and understand the effects of atmospheric carbon dioxide.

Understanding the effects of increased atmospheric CO<sub>2</sub> is a key to understanding future climate change. Only recently have all of the absorption peaks of CO<sub>2</sub> been

analyzed and incorporated into heating models, and these models are still being fine tuned. This experiment will examine the absorption of NIR at the 1.4, 1.9, 2.0, and 2.1  $\mu\text{m}$  absorption peaks and create absorption models for these four peaks.

## **Methods**

The first attempt to create an infrared radiation absorption spectrometer was unsuccessful. We began by aligning the three mirrors of the cell so that the beam of light can travel into the chamber of the device, bounce through the cell 16 times and then exit out the other side. The path length was set to 16 passes and the total path length was calculated using the dimensions of the chamber. Next, a light source, chopper, and infrared spectrophotometer were aligned so that the light would pass through the cell and into the light receptor and multiplier. This was done with the help of the Wesleyan Earth and Environmental Science and Physics departments. The light source was an old slide projector; the spectrophotometer was a Pyroelectric radiometer system; and the chopper was borrowed from the physics department. The parts were mounted on wooden blocks to align them to the appropriate height. Unfortunately, the chopper's speed was not be synchronized to the spectrophotometer's pulsed intake of light, which made the displayed measurement variable and sporadic. The frequency of the chopper could not be matched to that of the spectrophotometer without a cord communicating between the two pieces of equipment,.

The second experimental design yielded massive amounts of data. The  $\text{CO}_2$  chamber from the first experimental design was set up in the Wesleyan planetary lab though all other components were changed. The light source was a dissecting microscope lamp with three power settings and a well directed beam of light. A Field Spec Pro

(Analytical Spectral Devices) was used to analyze absorption of the near infrared light. This unit transferred light to the detector via a fiber optic wiring from a series 6320 pistol grip that takes absorption readings in the visible and near infrared spectra (350-2500 nm). These two devices were connected to a computer which stored and displayed the data with remote sensing software programs called R2S and ViewSpecPro. The experiments were performed between Thursday April 24 and Friday May 2, 2008.

Initially, the instruments were set up on a flat surface in this order: computer, Field Spec Pro, light source, CO<sub>2</sub> chamber, and lastly the pistol grip held by a freestanding clamp. Next, the Field Spec Pro was turned on, followed by the laptop. The power setting of the lamp and position of the lamp and pistol grip were adjusted while monitoring the live stream of data on the computer. This was done until the measured light spectrum was as intense as could be visibly observed on the computer.

Many preliminary runs were done to get a full understanding of the experiment, to achieve more accurate results, and to amass a plethora of data. The first runs were done by flushing the CO<sub>2</sub> chamber with a diatomic molecule, Nitrogen, which does not absorb light. Once the chamber was flushed, pure CO<sub>2</sub> was injected into the chamber and data was gathered in 10 ml intervals. This was done until the volume of the injected gas was greater than the volume of the chamber (~653.91 cm<sup>3</sup>). The chamber was not sealed, though. Thus, some injected gas was lost to the surrounding atmosphere. The chamber was then flushed with CO<sub>2</sub> to ensure that the chamber was fully saturated with CO<sub>2</sub>. This method yielded some results but there was a large gap in the data between full saturation and the measured injected intervals of CO<sub>2</sub>.

In order to solve these problems a new system of injection was devised according to the law of diminishing proportions. Full saturation requires that the volume of gas

injected be three times the volume of the container according to the law of diminishing proportions. Therefore, after flushing the chamber with Nitrogen, 10 ml of CO<sub>2</sub> were injected three times, then 20 ml three times, then 30 ml three times and so forth. As saturation was neared, more and more CO<sub>2</sub> needed to be added at a time. The concentration of CO<sub>2</sub> was determined using the following mass balance: [CO<sub>2</sub>] by volume = ([CO<sub>2</sub>]previous\*volume + volume pure CO<sub>2</sub> added - [CO<sub>2</sub>]previous\*amount added) / Total volume.

A final run using this experimental design was done in a reverse order using the above mass balance for concentration calculation, except solving for concentration of nitrogen and then taking one minus the concentration by volume of nitrogen to find concentration by volume carbon dioxide. This run is the source of the bulk of data within this report. First, the chamber was saturated with CO<sub>2</sub> and the spectrum was gathered. Next, Nitrogen was added to the chamber in intervals (see above). The absorption spectrum was thus created by starting with saturation of a greenhouse gas, CO<sub>2</sub>, and ending with saturation of a non greenhouse gas, Nitrogen.

The data recorded the transmitted light from the original spectra of the light source. Thus, in comparing the spectra of an experimental run (I<sub>1</sub>) with the original spectra created with air (I<sub>0</sub>), transmittance data was gathered.

Equation 1

$$T = I_1/I_0$$

The amount of absorption at this given wavelength can then be calculated from the transmittance.

Equation 2

$$a = -\log T = \log(I_0/I_1)$$

Ultimately, the light transmitted, depends upon the molar extinction coefficient and the concentration of the absorbing material. The molar extinction coefficient is a measure of how well a material absorbs a wavelength a light, which depends upon its vibrational modes. All of these parameters are related with the Beer-Lambert Absorption law:

Equation 3

$$I = I_0 e^{-\alpha l n}$$

A Beer-Lambert Absorption law model was formulated from the said law. Molar density was calculated using the ideal gas law and varied as a function of the molar volume.

Equation 4

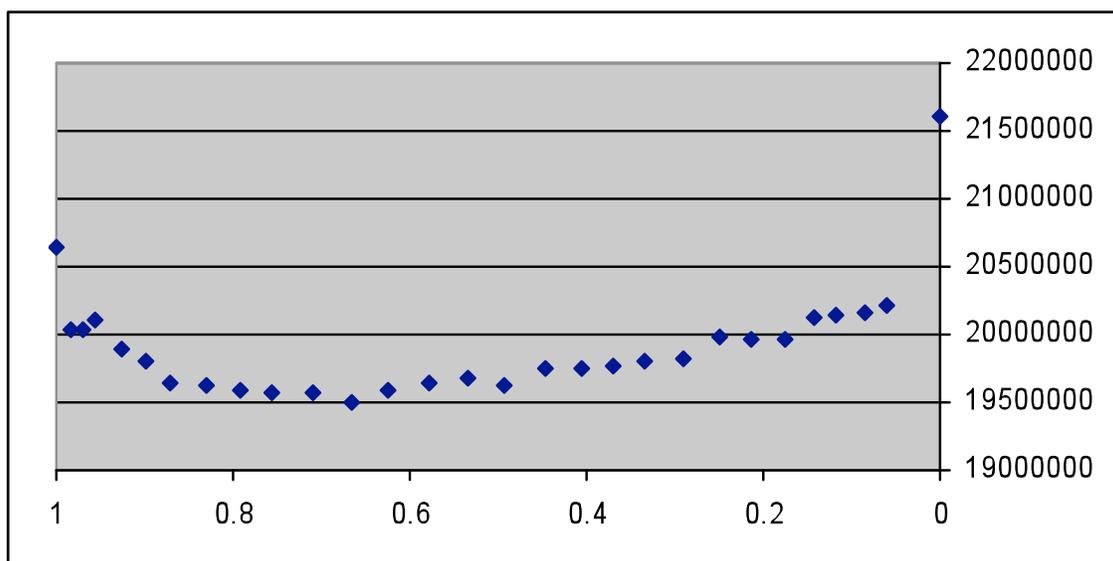
$$n = (f_{CO_2} * P * V) / (R * T)$$

Length of the multi pass cell was determined by counting dots and multiplying by 4 passes per dot and then 17 centimeters, the height of the cell. This distance was found to be 27.2 decimeters. The absorption coefficient was found by fitting the model curve to the data with different values until the highest coefficient of determination ( $R^2$ ) was found.

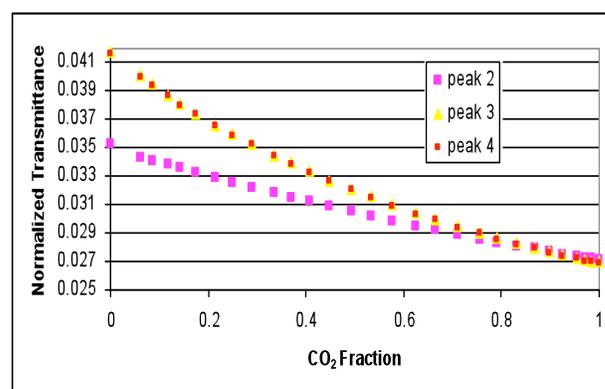
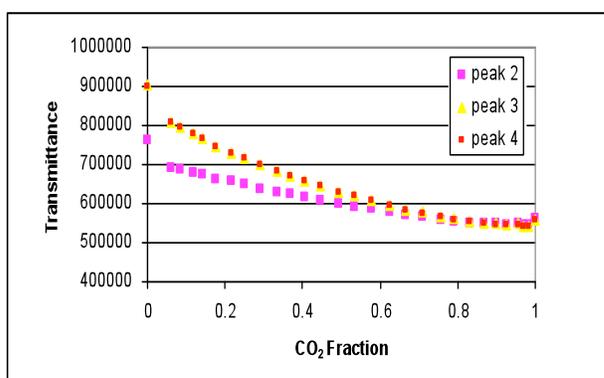
## Results

The light source was initially unstable and its output decreased over the first 7 runs (**Figure 6**). Runs 13 through 30 were characterized by an increase in the amount of light transferred through the cell. The instability of the lamp at the beginning was mirrored by changes in absorption in peak areas unrelated to the gas mixture (**Figure 7**). This led us to normalize the data to the total output of the lamp using excel by dividing the sum of all wavelength counts in absorption regions by the sum of all wavelength

counts in the spectrum.

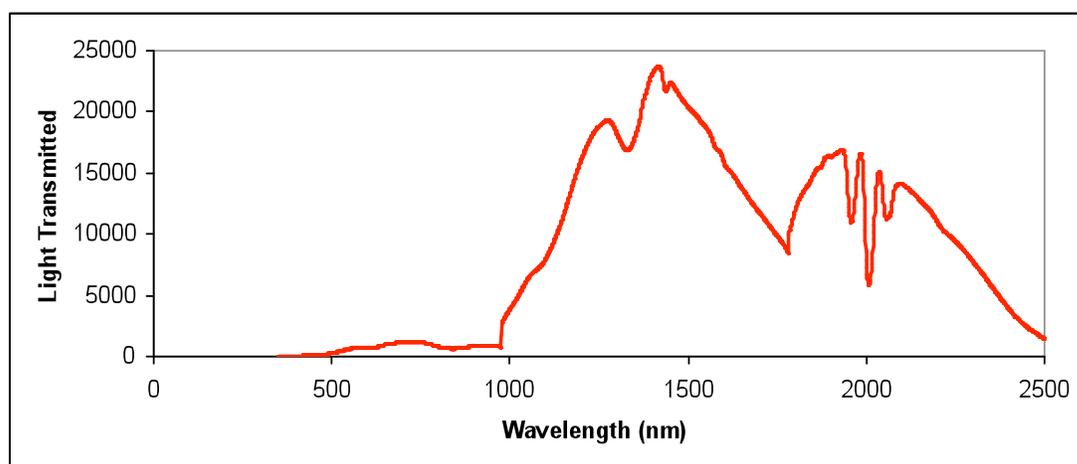


**Figure 6. Changes in light intensity over the course of the experiment. The Y axis is total counts for all wavelengths of the spectrum and the X axis is the fraction of CO<sub>2</sub> in the gas mixture. The experiment started at the CO<sub>2</sub> fraction of 1 and ran to 0.**



**Figure 7.** Transmittance of light in the absorption regions (Y-axis) as a function of CO<sub>2</sub> fraction (X-axis).

Absorption was found in the visible region, as well as at wavelengths of 1437, 1955, 2013, and 2060 nanometers (**Figure 8**). These peaks did not shift though they were noticeably broader at higher CO<sub>2</sub> fractions. (**Figure 9**) The peaks at 2013 and 2060 nanometers changed identically with increased CO<sub>2</sub> fraction. The only difference found in the size of peak at 1437 nanometers was between the N<sub>2</sub> blank and the rest of the samples.



**Figure 8.** Spectrum of transmitted light through 2.72 meter path in gas cell filled with pure CO<sub>2</sub>.

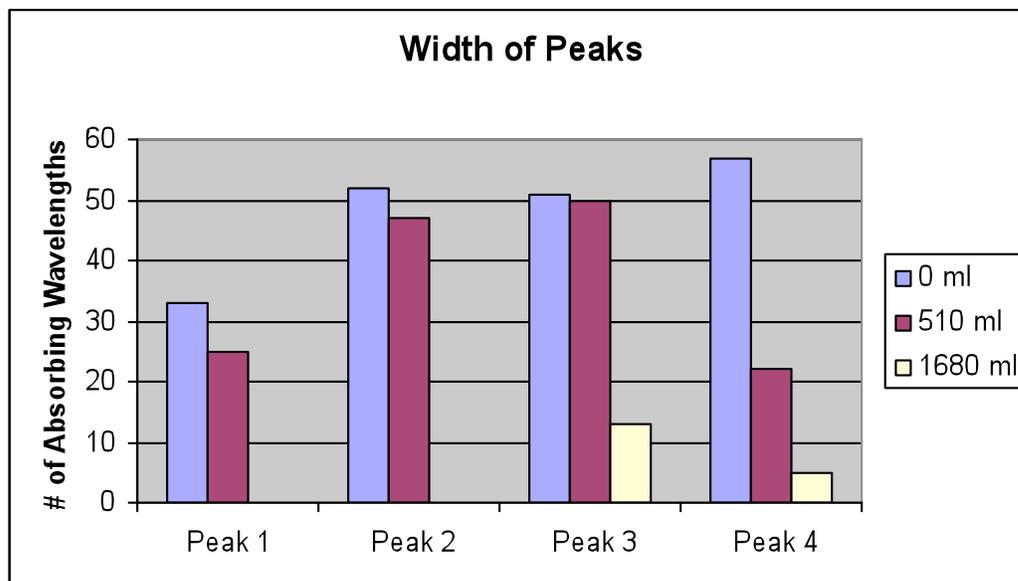
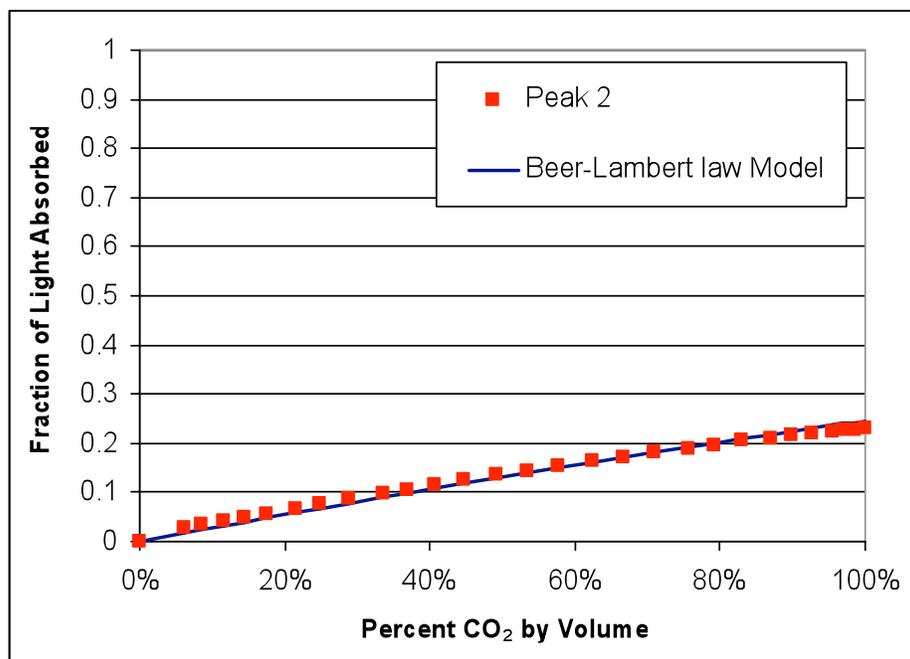
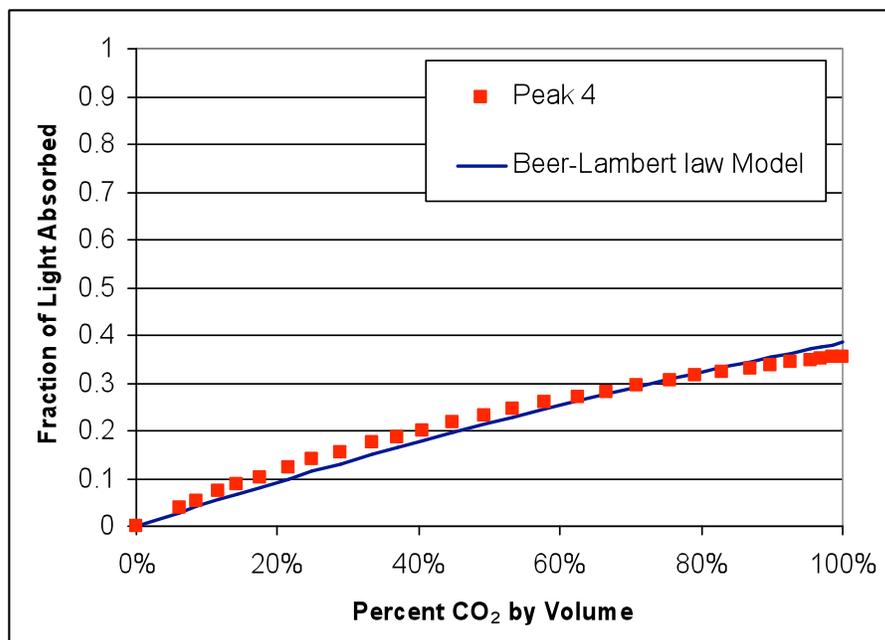


Figure 9. Qualitative comparison between widths of peaks when saturated with CO<sub>2</sub> (0 ml N<sub>2</sub>), partial saturation (510 ml N<sub>2</sub>), and pure N<sub>2</sub> (1680 ml N<sub>2</sub>). Peak 1-1437, Peak 2-1955, Peak 3-2013, Peak 4-2060.

The normalized data was plotted and a Beer-Lambert Absorption model was created for each curve (Figure 10).





**Figure 11. Beer – Lambert law fit to data. Both models varied with CO<sub>2</sub> fraction as a function molar density scaled by the ideal gas law. Path length (l) was 2.72 meters. R<sup>2</sup> for Peak 2 fit was 0.997 and for peak 3&4 fit was 0.970.**

## Discussion

At the beginning of the experiment, light intensity decreased due to the warming up of the bulb to stable operating temperature. This decrease in intensity warranted the normalization of all data by division by total output. The total output of the bulb was found to be correlated to the spread of the unnormalized data with the R<sup>2</sup> of the curves ranging from 0.33 to 0.36. This is not entirely accurate though, as the absorption regions made up ~10% of the total spectrum, so the shrinking of the absorption regions with decreasing CO<sub>2</sub> fraction would cause the total light to increase. Normalization by this technique removed the “bumpiness” from the first 5 data points (**Figure 8**).

Modeling of the Beer – Lambert law found the absorption coefficient at 1955 nanometers to be 0.25 m<sup>2</sup> mol<sup>-1</sup> and the absorption coefficient for the peaks at 2013 and 2060 nanometers to be 0.43 m<sup>2</sup> mol<sup>-1</sup> (**Figure 11**). Unfortunately, no literature values

could be found to compare these values to. The absorption peak at 1437 nanometers had an absorption coefficient  $\gg 10$ , but no more information could be elucidated from the data taken, as none of the gas mixtures tested fell on the curve of this peak.

This experimental setup is a prototype that should be developed further to remove errors inherent to its design. First and foremost, the light, gas cell, and detector should be fastened to a solid surface, because every injection of gas resulted in a slight movement of the gas cell relative to the light and detector. Second, a check valve should be installed on the outflow of the gas cell to prevent leaking of the high concentration gas between measurements. Finally, a pressure gauge should be installed inside the cell so that the molecular density can be more accurately measured, as this value is critical to determination of the absorption coefficient.

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