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I am submitting herewith a thesis written by Maria Gabriela Oliveros entitled “Environmental Analysis and White Cell applications FTIR Spectroscopy.” I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science with a major in Physics.

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Environmental Analysis and White Cell applications using FTIR Spectroscopy

A Thesis
Presented for the
Master of Science Degree
The University of Tennessee, Knoxville

Maria Gabriela Oliveros
Decembert 2008

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DEDICATION

This thesis is dedicated to my parents, Bartolome Oliveros and Mariana Flores, and my sister, Claudia Oliveros. They are awesome role models and my best friends. To the rest of my family and good friends (you know who you are), who have supported all my decisions and believed in me all the time. Thank you for everything.

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I want to thank all those who helped me to complete my Master of Science degree in Chemical Physics. I wanted to start with Dr. Compton for letting me work in his laboratory for two summers. Thanks to Dr. Hager and Dr. Jeff Steel, for guiding and teaching me the concept of Fourier Transform Infrared Spectroscopy.

Lastly, I would like to thank my family and friends, whose encouragement made this work possible.

ABSTRACT

The research is concerned with atmospheric chemistry & physics, and analyzing the environment with respect to the quantity of molecules in the air we breathe. Fourier Transform Infrared Spectroscopy is used to identify the IR active molecules in our atmosphere. FTIR Spectrometer determines the intensity loss for molecules that have absorbed IR light. The FTIR spectroscopy is performed using the light from the sun or a carbon rod light source in the lab. A Sun-tracking device was employed to direct the sunlight into the spectrometer. Open-path measurements were made using multiple mirror reflections of the carbon rod light source over the top of the SERF (Science and Engineering Research Facility) building. From the Open-path measurements it was determined that the CO and N₂O change concentrations during the day and night. Two different open path setups were employed with good success. Time-dependence of the IR spectra for many of the greenhouse gases are presented. In addition, we have performed Gaussian 03 calculations of the IR spectra for many of the greenhouse gases as well as for the nitroethane molecule.

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NOMENCLATURE

°C	Celsius
Wm ²	watts meter squared
cm ⁻¹	inverse centimeter
cm	centimeter
cm/sec	centimeter per second
cm Hz ^{1/2} /W	centimeter times Hertz times half per watts
°F	Fahrenheit
M	meters
in	inches
mol/m ³	molecules per cubic meter
mm	millimeters

Abbreviations

FTIR	Fourier Transform Infrared
CO ₂	carbon dioxide
H ₂ O	water
N ₂ O	nitrous oxide
CO	carbon monoxide
CH ₄	methane
C ₂ H ₅ NO ₂	nitroethane
Sb ₂ S ₃	Diantimony trisulfide
Ge	Germanium
DNA	Deoxyribonucleic acid

CHAPTER I

INTRODUCTION

The atmosphere of the Earth is changing due to natural causes as well as human activities. Of particular concern is the increase of so-called Greenhouse Gases which are believed to contribute to the effects of Global Warming. Carbon dioxide is one of the Greenhouse Gases and a trace gas currently occurring at an average concentration of about 379 parts per million by volume [Reference 2]. The atmospheric emission of CO₂ by human activities has increased to 27 billion tons per year. Emerging nations such as China and India will certainly increase this emission rate. The increase in the Greenhouse Gases throughout the years is believed to be partially responsible for the increase in the Earth's temperature of ~0.5 °C during the 21st century. The CO₂ emissions just in the United States are 5988 million tons per year [Reference 3]. In addition to the global effects of Greenhouse Gases there is also concern about the local effects of atmospheric pollution in industrial and populated areas. The relative strength of the Greenhouse Gases toward global warming is measured in term of the radiative forcing of each individual gas. The radiative forcing due to atmospheric processes can be positive or negative; a positive forcing means that the incoming energy to earth is causing a increase in temperature, and a negative forcing means that the outgoing energy from the earth is causing the temperature to decrease. The relative forcing of some the Greenhouse Gases are: CO₂ (1.46 Wm²), CH₄ (0.48 Wm²), and N₂O (0.15 Wm²). During the summer months, contamination of the troposphere due to air pollution increases as a result of heightened photochemical processes. This pollution primarily results from internal combustion engines as well as factories and other sources expelling harmful gases into the air. Photochemical processes also can convert these pollutants into other molecules (e.g., Polynucleus aromatic hydrocarbon (PAH) and Peroxyacetyl Nitrate (PAN)). This contamination can cause adverse human health effects, especially for those who suffer from respiratory problems such as allergies and asthma. Another type of

effect, tropospheric ozone pollution can reduce the longevity of automobile tires. For this reason it is important to identify and quantify the harmful molecules in the air we breathe. The atmosphere in Knoxville, Tennessee has been identified as one of the most polluted in the country. For example, the high ozone days weight average of 3.7 and the particle pollution weight average of 5.7 in 2007 meaning that the air quality is bad for breathing and exceeds the normal average of particles pollution and ozone [Reference 1].

The objectives of this thesis are to identify and determine the amount of certain molecules, like water (H_2O), carbon dioxide (CO_2), nitrous oxide (N_2O), carbon monoxide (CO), and methane (CH_4), that are present in the atmosphere during selected summer days in Knoxville. The molecular composition was determined from infrared spectroscopy using a Fourier transform infrared spectrometer (FTIR) in which the sun is used as the light source. The FTIR spectrometer has evolved over several decades into an analytical spectroscopy tool which can be applied in many fields of the physics, chemistry and biological sciences. Three of the molecules found in the environment were primary Greenhouse Gases, which are believed to contribute to Global Warming.

CHAPTER II

THEORY

Fourier transform spectroscopy is a method that converts the frequency into the time domain making it possible to attain high resolution and accurate photometry [Reference 4]. Fourier transform spectroscopy is based upon an improved Michelson interferometer. In a classical Michelson interferometer, a light source is collimated and then divided at a beam splitter into two beams of equal amplitude, these two beams are reflected back by two separate mirrors (one fixed and the other movable). After each beam strikes the beam splitter again, they are recombined and this beam is directed to the detector as shown in figure 2.1.

The light hitting the detector will produce an interferogram, which is essentially a signal measured versus displacement of the moving mirror. Interferogram is the result from the interference of two waves. Equation 2.1 is intensity of the interferogram as a function of the displacement of the mirrors,

$$I_o(x) = B(\sigma_o)[1 + \cos(2\pi\sigma_o x)] \quad (2.1)$$

Where $B(\sigma_o)$ is the intensity of the interferogram as a function of x , σ_o is wavenumber, and $I_o(x)$ is the interferogram. Equation 2.1 shows the source light used has just one intensity.

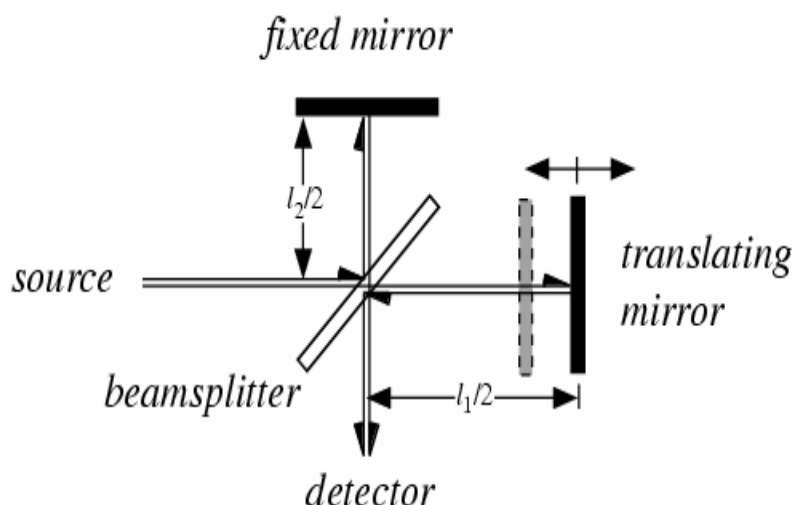


Figure 2.1 – Michelson interferometer set up

The interference occurs when two or more waves are combined in the same region of time and space and their time-dependent amplitudes are added together. There are two types of interference, constructive interference and destructive interference. Constructive interference occurs when the wave amplitudes are either both positive or both negative while destructive interference results when the wave amplitudes are opposite in sign [Reference 11].

Fourier transform spectroscopy results from a mathematical process that takes a time-varying wave and converts it into its constituent frequencies [Reference 5]. The fourier transform method can be used in many types of spectroscopy from mass spectroscopy to NMR. This thesis is involved with FTIR.

CHAPTER III

PROCEDURE

The instrument employed in this thesis was a Bomem AB DA-8 Fourier Transform IR Spectrometer operating in the Mid IR range of 500 to 13,000 cm^{-1} (20 – 76.9 μm). The length of the arm over which the Michelson interferometer travels is half a meter. The nominal resolution of this instrument is 0.013 cm^{-1} . A photograph of the Bomem AB DA-8 spectrometer is shown in figure 3.1. [Reference 8]

The basic layout of the FTIR spectrometer is shown in figure 3.2. The elements of the spectrometer are the Michelson Interferometer, light source, beamsplitter, detector with pre-amplifier, emission ports, multiple output beam configuration, input collimator, output optics, vacuum compatible enclosure and digital data processor. The three light sources employed (Hg lamp, quartz/halogen lamp, and globar), are depicted in the inset A in figure 3.2. In the open path experiments a separate high-intensity, water-cooled, carbon rod, light source was employed. This particular light source will be described later in more detail. [Reference 8]

Wavelength scanning is carried out with an optical retardation of 50 cm, providing a maximum unapodized resolution of 0.013 cm^{-1} . The scanning speed is variable from 0.02 cm/sec to 2 cm/sec in 13 steps. The output beam configuration consists of 5 output beams (two focused and three parallel) and each is computer selectable. The two focused beams are in the sample chamber, and the three parallel beams exit to the right, left or back of the spectrometer. The sample compartment housing can be evacuated and/or purged with two sample beams through isolation valves, see

figure 3.3. There is a vacuum option in the Bomem AB DA-8 FTIR spectrometer program is a purge/vacuum control module and can go from 0.2 torr to atmospheric pressure. [Reference 8]

The auxiliary light sources can be selected as either a globar, quartz halogen lamp or a carbon rod. The globar consists of a silicon carbide rod and operates over a range of 200 to 12,000 cm^{-1} . The globar is employed as a thermal light source for infrared spectroscopy because their spectral behavior corresponds approximately to that of a Planck blackbody radiator. The quartz halogen lamp operates over a range of 2,000 to 25,000 cm^{-1} and is coated with a multi-layered dichroic material which allows visible light to be emitted while reflecting a portion of the infrared radiation back onto the filament. The carbon rod is a blackbody light source with a range of 400 to 40,000 cm^{-1} and is operated using argon gas and water cooling, see figure 3.4. [Reference 6]

The beamsplitters are calcium fluoride (CaF_2) and potassium bromide (KBr). The CaF_2 beamsplitter is 10 cm diameter, coated with Sb_2S_3 , and is complete with a kinematics base-plate having an optical range of 1,400 to 20,000 cm^{-1} . The KBr beamsplitter is 10 cm in diameter coated with Ge connected to a kinematics base-plate with an optical range of 350 to 6,000 cm^{-1} . Also, the majority of the windows used in the FTIR are KBr. [Reference 6]



Figure 3.1 – Bomem AB DA- 8 Fourier Transform IR Spectrometer

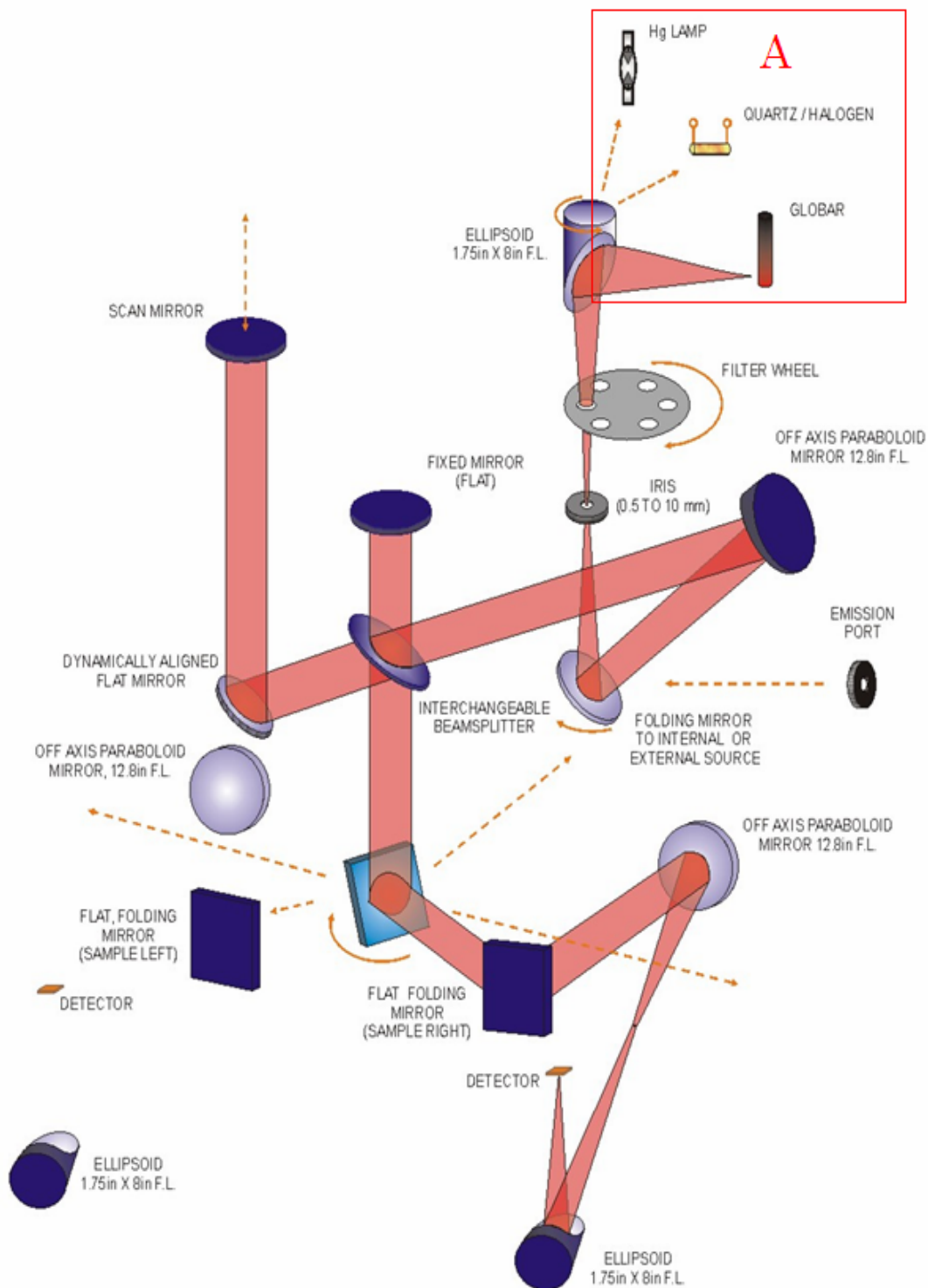


Figure 3.2 – Experimental arrangement of the Bomem AB DA-8 FT-IR Spectrometer

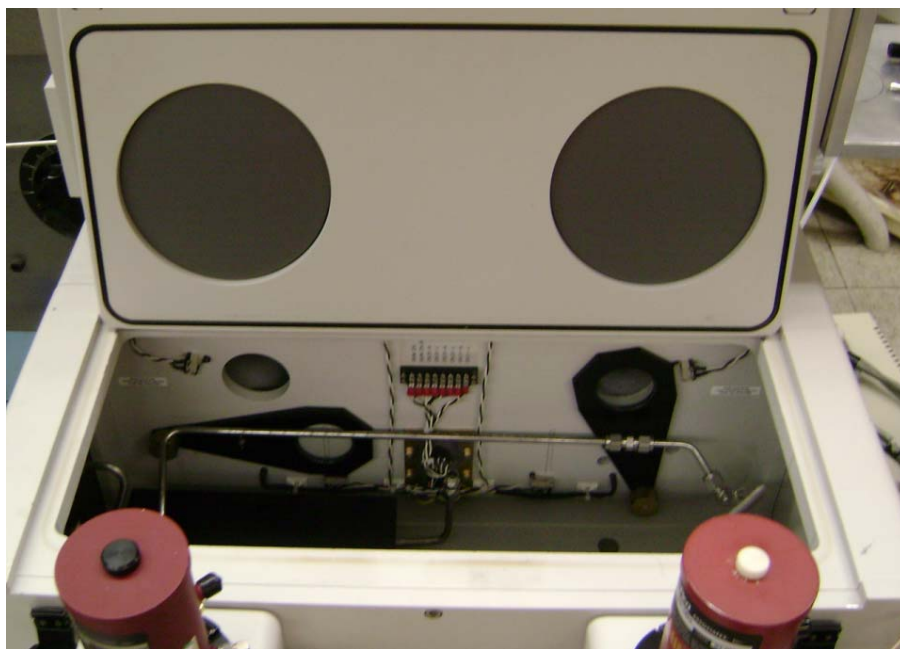


Figure 3.3 – Sample chamber

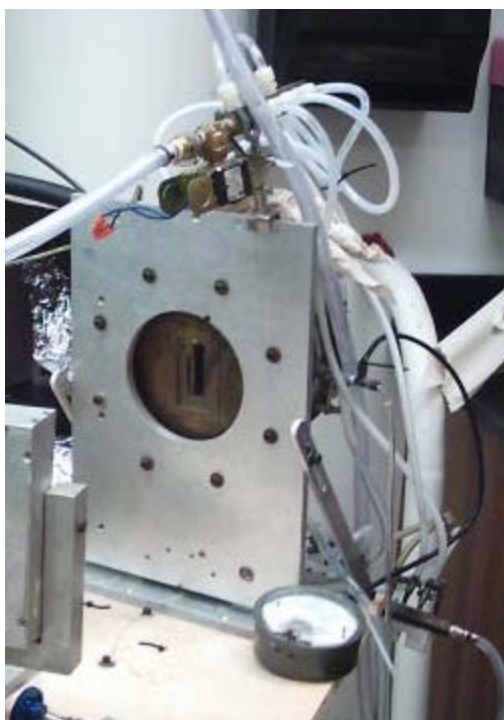


Figure 3.4 – Carbon rod light source

The detectors are all supplied with matched programmable gain pre-amplifiers together with a pre-aligned, collecting optics, and vacuum interface housing. The available detectors are mercury cadmium tellurium (MCT), indium antimony (InSb) and silicon photo-diode. The two MTC detectors are coated with silver with a range from 500 to 5,000 cm^{-1} and from 800 to 5,000 cm^{-1} . The relative efficiency, which is a measurement as a percentage of ionizing radiation hitting a specific detector, of the two are $1 \times 10^{10} \text{ cm Hz}^{1/2}/\text{W}$ and $4 \times 10^8 \text{ cm Hz}^{1/2}/\text{W}$ at an operating temperature of 77 °F (using liquid nitrogen). The InSb detector is coated with silver with a wedged sapphire window and covers the range from 1,800 to 8,500 cm^{-1} . The relative efficiency is $1 \times 10^{11} \text{ cm Hz}^{1/2}/\text{W}$ at an operating temperature of 77 °F (with liquid nitrogen). The silicon photo-diode is coated with aluminum and operates over a range of 8,500 to 50,000 cm^{-1} . The relative efficiency of this detector is $1 \times 10^{12} \text{ cm Hz}^{1/2}/\text{W}$, having a noise equivalent power less than $2 \times 10^{-13} \text{ W/Hz}^{1/2}$, and operation temperature of 300 °F. [Reference 6]

The computer operates using the basic PCDA/GRAMS software and is used to provide complete access to the spectroscopic performance of the DA-8 FTIR Spectrometer. The Resource definition is the CONFIG function and is used to define all resources of the DA-8 FTIR spectrometer installed on the system as well as to define which ones are used to perform the experiment. The specific configuration can be generated and saved in the computer for future use. The Experimental verification and setup represents the CONTROL function which allows one to verify the operation of the instruments (the maximum alignment and the strongest signal), as well as to change the setting of the aperture size in order to improve the signal or ZPD intensity. The Data acquisition

represents the CONTROL function which also allows one to define the sample characteristics, the number of scans needed as well as other experimental parameters. The Acquisition and post processing begins when the PDA starts automatically to the control function for the monitoring of the acquisition process. The GRAMS™ program is used to access and process the data. [Reference 7]

The White Cell, also called a long-path gas cell or multipass gas cell (see figure 3.5), can be used to measure gas concentrations down to the single part per billion level. The cell can have high energy throughput, accommodate multiple gasses, and operate at low pressure. Operation at low-pressure is necessary to reduce collision broadening allowing for high resolution spectra. There are three focusing mirrors (focal length of 2 m) and a flat mirror inside the cell and four KBr windows with two central knobs to adjust the focal mirrors outside the cell. The white cell was pumped by a turbo molecular pump. The pressure gauge used to determine the pressure inside the white cell was a MKS baratron instrument model PQR-C-2.



Figure 3.5 – The White Cell

There are three ways in which the experiment can be arranged. In the first set-up the FTIR is coupled with a small multiple reflection cell or White Cell. This type of procedure is comparable with the second set-up which is the Open-path spectroscopy. The Open-path spectroscopy can be considered as simply a larger White Cell. The third set-up is the Sun Tracker atmospheric detection. In all three procedures, the extraction of the molecules in the spectra is done using knowledge of the assigned lines for each molecule.

1. FTIR spectroscopy of nitrous oxide in a multipass White Cell:

As a test of the FTIR experimental operation and performance, spectra of nitrous oxide were recorded. The white cell is located on a laser table as shown in figure 3.5. Figure 3.6 shows a diagram of the various optical elements inside the white cell. The method used during this experiment involves the quartz halogen light source along with a series of mirrors, CaF_2 beamsplitter, and InSb detector. The light is emitted from the DA-8 FT-IR spectrometer from the left port, shown in figure 3.7. This light is reflected from four flat mirrors and one focusing mirror (focus of 2m) and enters the White Cell as shown in figure 6. The path length of the light can be changed by varying the number of passes inside the white cell. Twelve passes is about 23.26 m, sixteen passes is about 27.26 m, and twenty passes is about 31.26 m. The sources of error are alignment, leaks or other types of molecules in the cell, the limited number of passes meaning having less absorption, inaccurate pressure gauges, and pressure fluctuation.

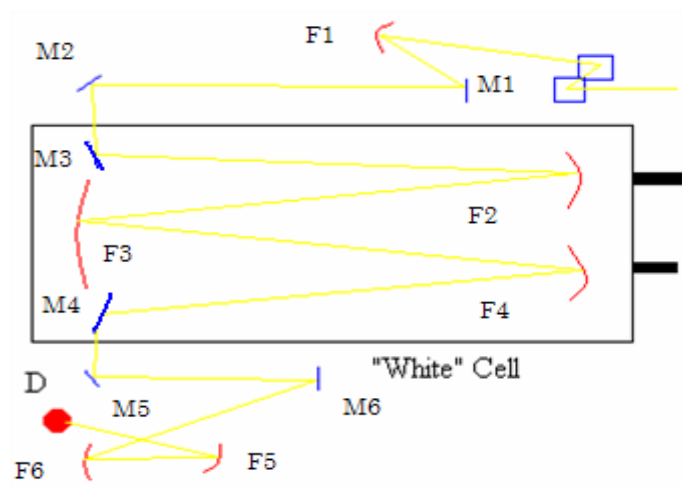


Figure 3.6 – Illustration of the Inside of the White Cell showing the light path from source to the detector

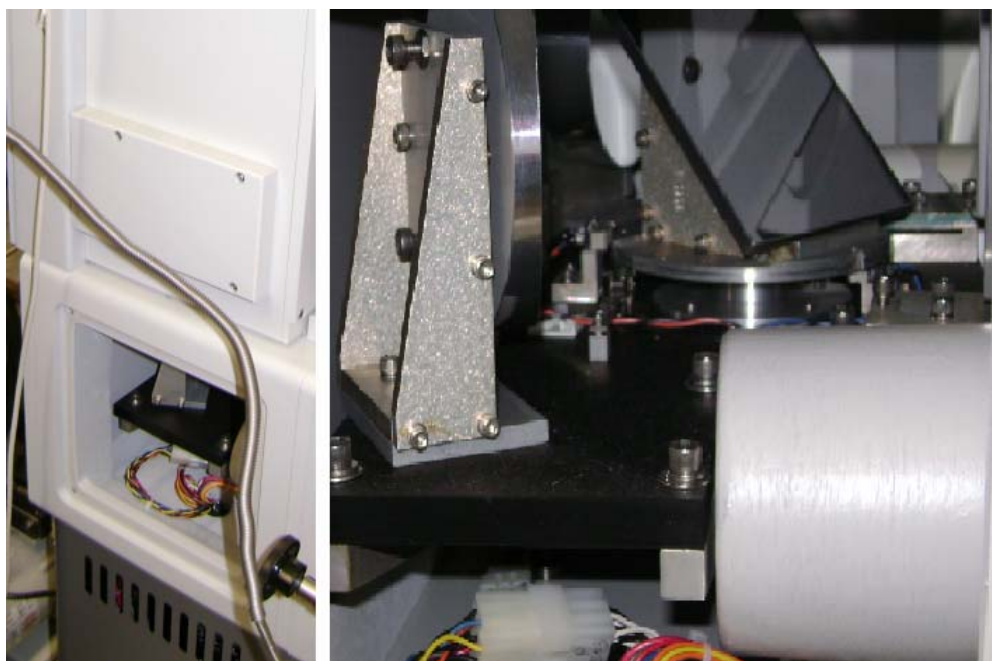


Figure 3.7 – Spectrometer left port

The light exits the cell and reflects from two flat mirrors and two focusing mirrors ($f = 12.8\text{in}$ and $1.75\text{in} \times 8\text{in}$, respectively) and is directed into the detector. A mechanical pump is connected to the White Cell and provides an initial vacuum pressure. The lowest pressure obtained in the empty White Cell (purged) was around 1.5 Torr. The gaseous molecules are introduced into the vacuum chamber through a needle valve. Figure 3.8 shows a sample spectrum of nitrous oxide (N_2O) operating under 12 passes (~ 23.26 meters) at 21.5 torr, and 0.1 cm^{-1} spectral resolution. The two bands shown from 2400 and 2500 cm^{-1} corresponds to the $\nu_1 + 2\nu_2$ combination band.

The path length of the White Cell was ~ 23.26 meter. This was checked by observing the attenuation of light beam for a known pressure of a sample molecule such as N_2O . Knowing the absorption strength and pressure one can estimate the path length using Beer's Law. Estimates of the path length for the different passes inside the white cell and an example calculation will be shown in the results/discussion chapter.

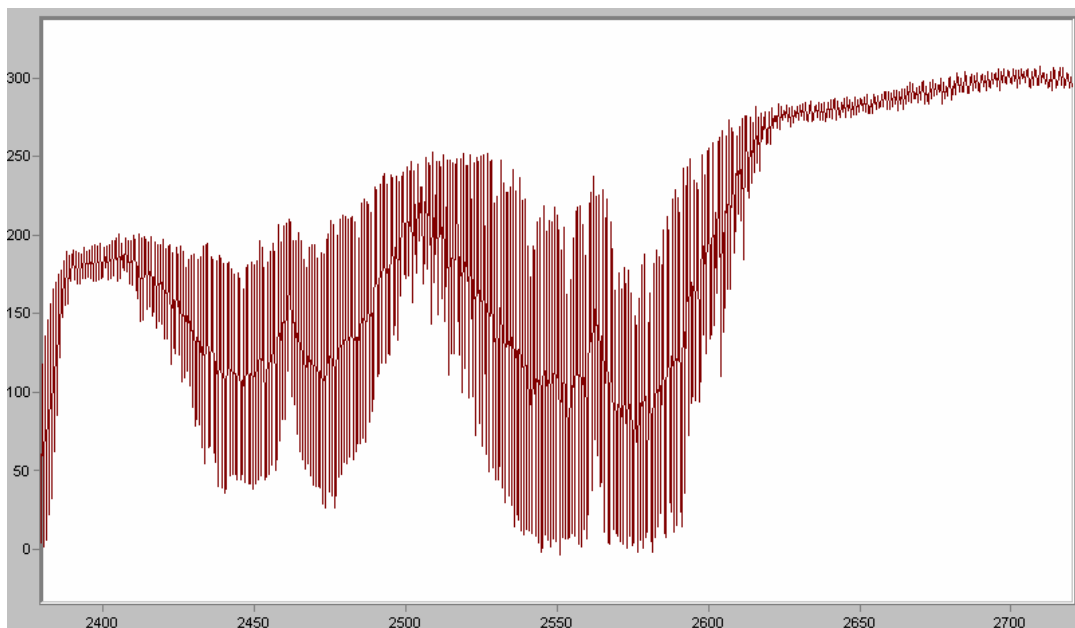


Figure 3.8 – N₂O FTIR Spectrum

2. Solar FTIR Spectroscopy:

The objective of this portion of the thesis is to determine the amount of certain molecules, e.g. water (H₂O), carbon dioxide (CO₂), ozone (O₃), nitrous oxide (N₂O), carbon monoxide (CO), and methane (CH₄), in the atmosphere during selected days in Knoxville, Tennessee. The Sun is used as the light source for the IR spectroscopy and the atmosphere of the Earth as the sample. A Sun-Tracking Mirror is set up and programmed to use the North Star [Reference 10] to continuously direct the sunlight from the top of the SERF Building at the University of Tennessee through a series of mirrors into the FTIR. The sun-tracking device is used to always align with the path of the sun during the daytime in both winter and summer into the FTIR. Figure 3.9 shows the complete IR atmospheric absorption set-up. This sun-tracking device is connected to a computer, which was programmed to follow the path of the sun

during the day. A mirror attached to the tracking device reflects the sun light onto a 16-inch-mirror attached to the base, this mirror reflect the sun light to another 16-inch-mirror at the top of the pipe. The light goes down the pipe form the 8th floor to the FTIR spectrometer on the 6th floor, where it is reflected to another mirror. This mirror, M1, reflects the light to a flat mirror, M2, and is finally reflected to another focal mirror, F1, and passes into the spectrometer.

Inside the spectrometer, the beamsplitter is made of CaF_2 , which is transparent to IR light. The InSb detector is cooled down to liquid nitrogen temperature. A portion of a sample spectrum from June 14th, 2005 with a 0.017 cm^{-1} resolution is shown in figure 3.10.

Infrared light passes through the sample (in this case the atmosphere). The absorbance in light represents the vibration and rotational energy levels of the IR absorbing molecules that make up the air. The transmitted light impinges on the detector and the signal from the detector is fed into the computer that provides a reading of the spectrum. The recorded spectrum provides a unique spectral “finger print” of the molecules in the atmosphere much like DNA fingerprint for the human Genome. A few of the identified species in the spectrum are noted. Most of the features are due to water vapor, the most predominant of the Greenhouse Gases.

The sources of error are alignment and no having an accurate path length and pressure.

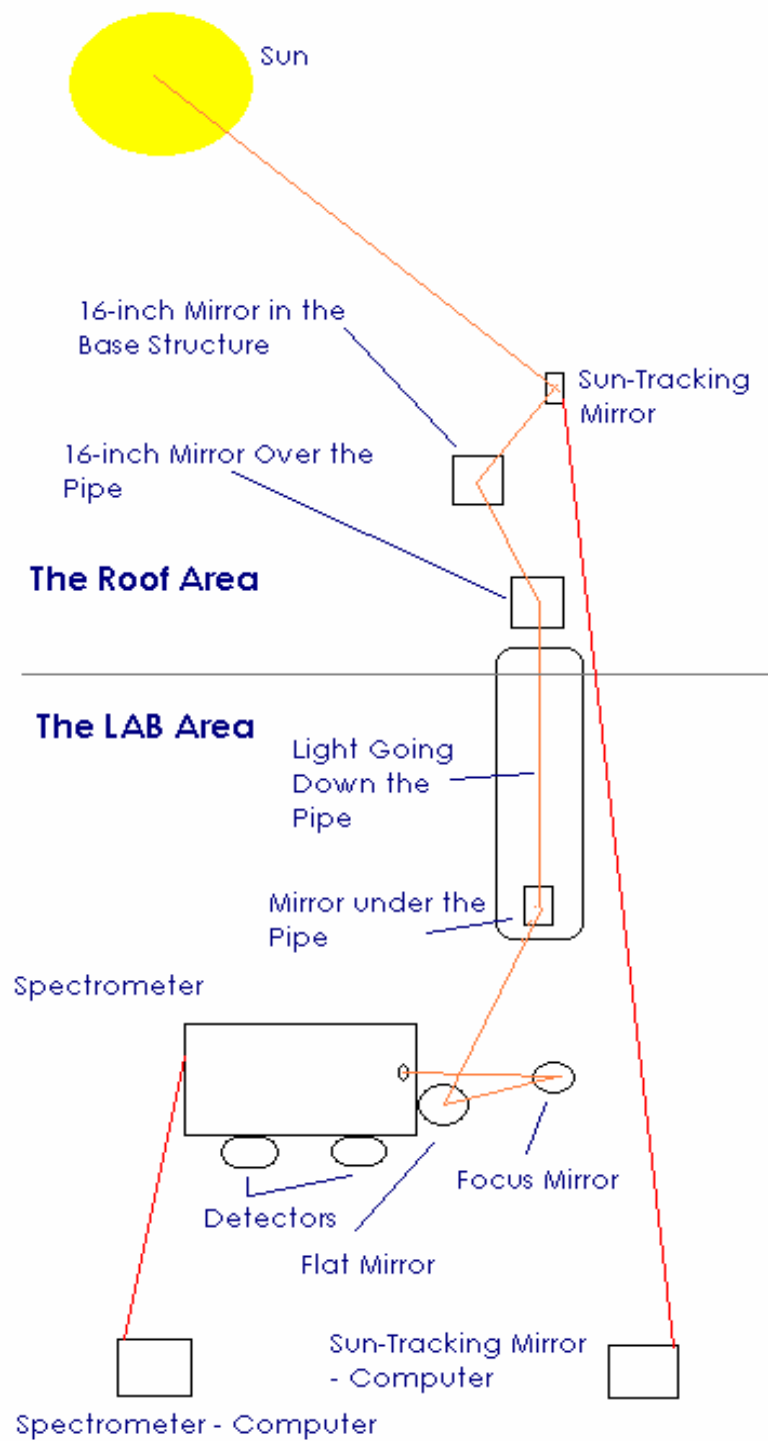


Figure 3.9 – Solar Spectroscopy Setup

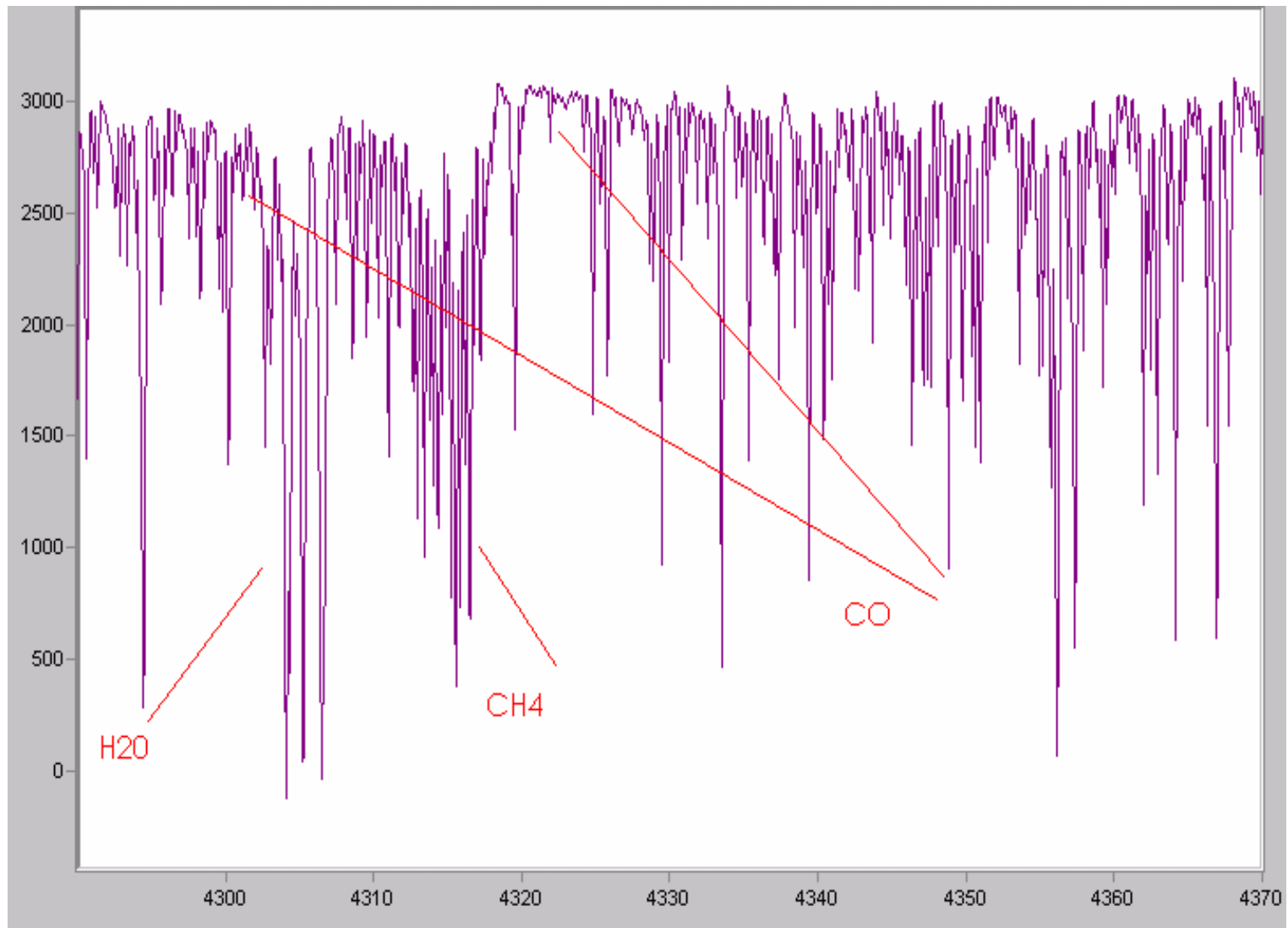


Figure 3.10 – Sample partial Solar Spectrum showing a few of the various gaseous molecules which can be detected in the air

3. Open-Path Spectroscopy:

Figure 3.11 depicts the geometry of the open-path experiment. In the open-path experiment, the light source used is a heated carbon rod. A mirror collimates and reflected the carbon-arc light to a 10-inch flat mirror situated at the bottom of the pipe connecting the roof and 6th floor. Initially the light is directed up the pipe and then reflects onto a 10-inch flat mirror [#1] situated just over the pipe. This mirror then reflects the light into a 16-inch flat mirror [#2]. Mirror #2 reflects the light across the roof to another 16-inch mirror [#3]. The mirror #3 reflects the light to another 16-inch flat mirror [#4] (placed parallel to the mirror #2). The mirror #4 reflects the light to another 16-inch flat mirror [#5] (parallel to mirror #3). The mirror #5 bounces the light to another 16-inch flat mirror [#6] (placed above the mirror #2). The mirror [#6] sends the light to a 10-inch flat mirror [#7] set on the sun-tracking device. From mirror #7 the light goes to a 16-inch flat mirror [#8] on the floor. The mirror #8 reflects the light to another 16-inch flat mirror [#9] over the pipe. The light then proceeds back down the pipe, until it hits a circular gold coated mirror. This mirror then reflects the light to another gold-circular mirror and finally this mirror will reflect it to a focusing mirror and into the spectrometer. Inside the spectrometer, the beam splitters used are CaF_2 and KBr , and the detectors are MCT ($500 - 5,000 \text{ cm}^{-1}$) and InSb . The path length of the open-path experiment is about 200 ± 10 meters in 2005 and 400 ± 40 meters in 2006. The sources of error are alignment of the mirrors and not having an accurate path length. A sample spectrum from July 25th, 2006 with a 0.02 cm^{-1} resolution is shown in Figure 3.12 for the CO_2 molecule. The P, Q, and R branches are clearly visible and provide complete identification of this molecule.

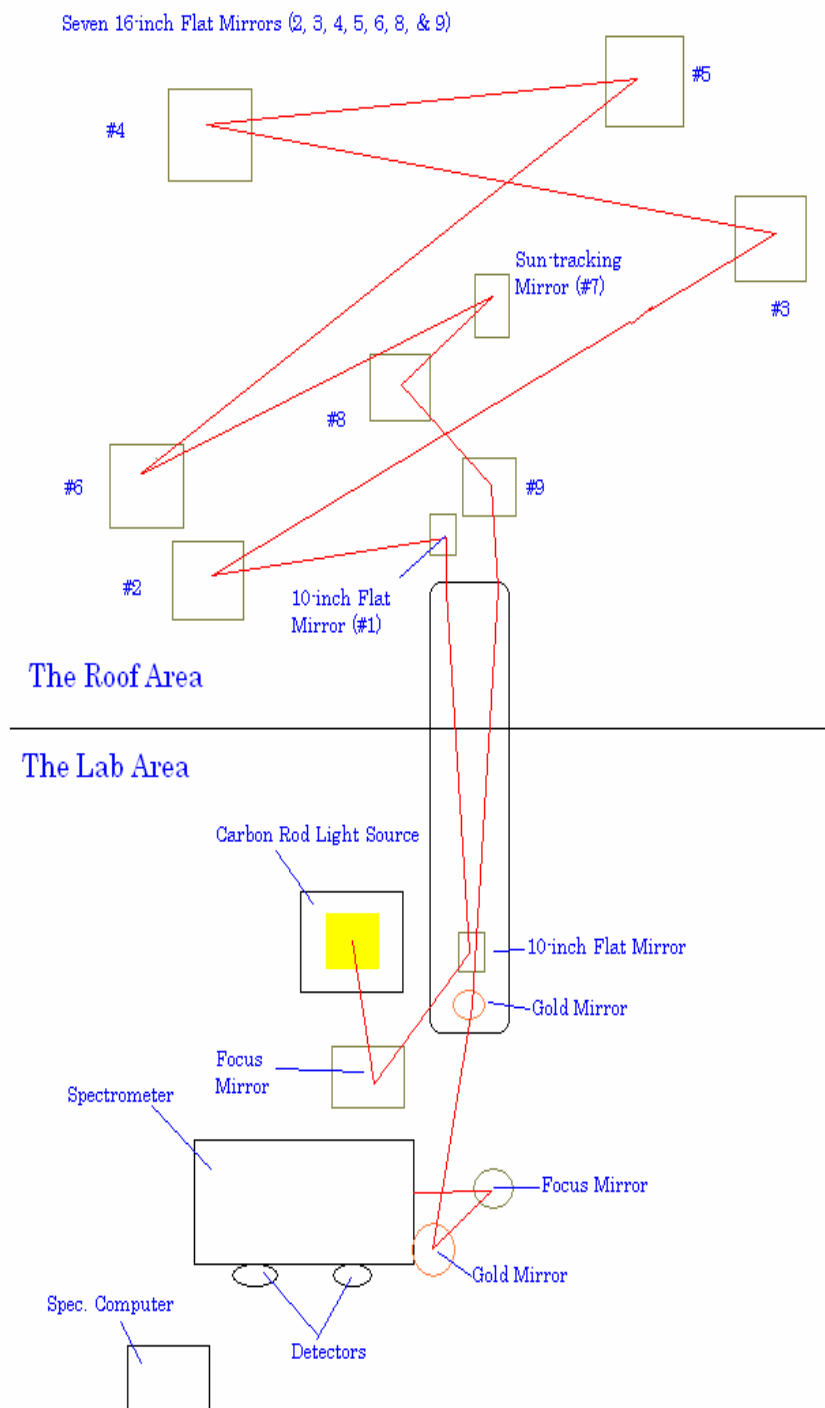


Figure 3.11 – Open Path Spectroscopy Setup

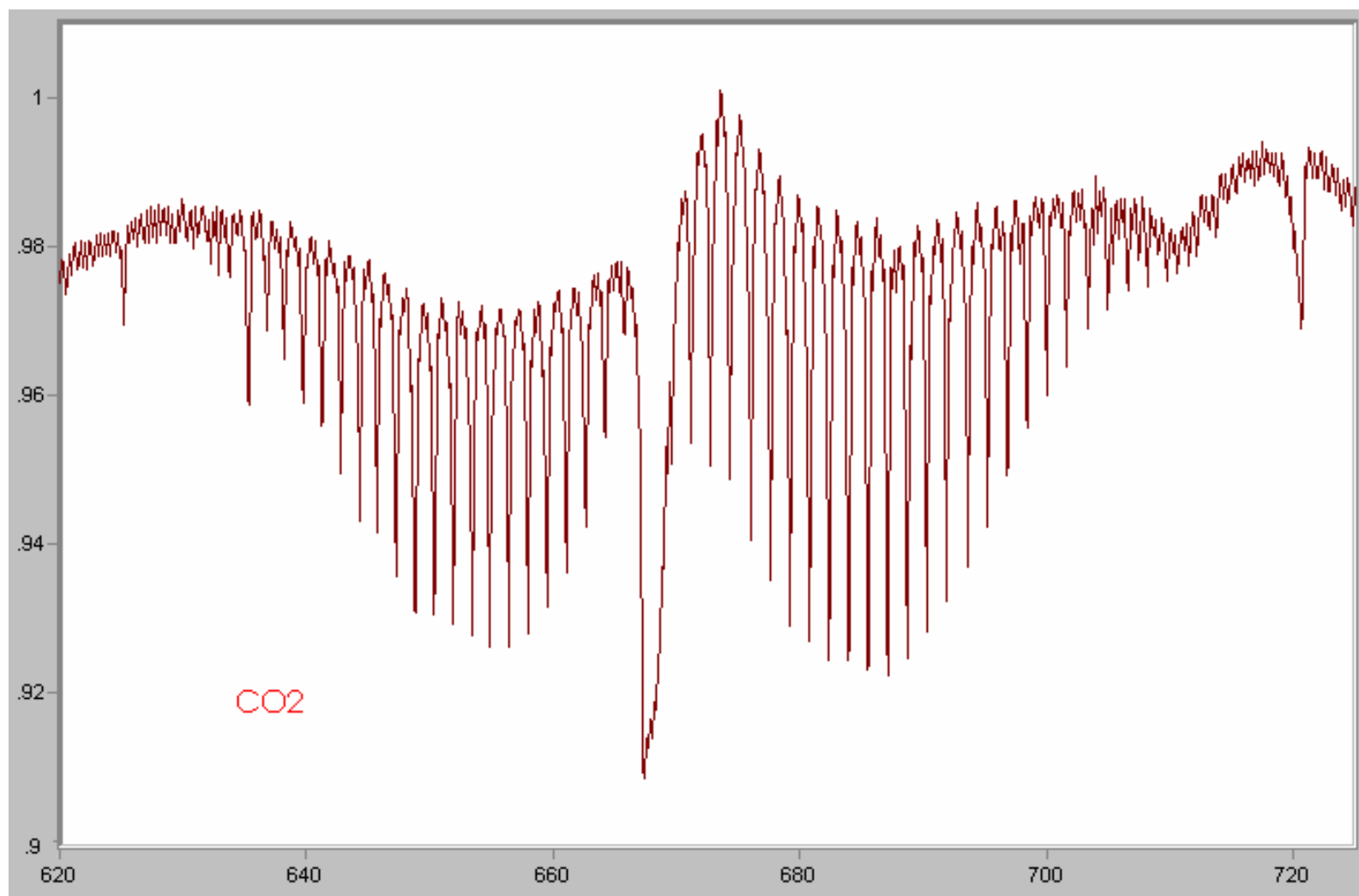


Figure 3.12 – Open Path Spectroscopy Sample of CO₂ PQR Branch Spectrum

CHAPTER IV

DATA ANALYSIS

1. FTIR spectroscopy of nitrous oxide in a multipass White Cell:

The spectrometer is configured using the quartz halogen lamp as the light source, with an aperture of 2.5mm, CaF₂ beamsplitter and a resolution of 0.1cm⁻¹. The gas studied was nitrous oxide (N₂O). The path lengths for the IR light with respect to the number of passes between the mirrors of the White cell are 12, 16 and 20 passes; each path corresponds to 23.26, 27.26, and 31.26 meters, respectively. For a linear molecule, the vibrational degrees of freedom are $3N - 5$, thus the number of vibrational degrees of freedom for N₂O is four of which two of the fundamental vibrations are degenerate. The nitrous oxide molecule is depicted in figure 4.1. The absorbance for N₂O is presented in table 4.1 [Reference 9]. Adding the nitrous gas into the White Cell, there are three different trials for the three different passes refer to table 4.2. Sample Calculation for 12 passes, using ideal gas law equation

$$PV = NRT \quad (4.1)$$

Where N/V is the concentration of the molecule in units of molecule/m³, P is 20.1 torr or 2679.22 Pa, T is 293° K, and R is a constant (8.314 m³ Pa K⁻¹mol⁻¹). Solving for N/V , the result is 1.082 mol/m³. The length of the 3 different passes can be found; refer to table 4.3. The Fourier Transform infrared spectra of nitrous oxide are shown over a wide range of frequencies in figure 4.2 and 4.3. Figure 4.3 is a combination band of N₂O [Reference 10].



Figure 4.1 – Nitrous oxide molecule

Table 4.1 – The Herzberg's IR frequencies

Frequencies (cm ⁻¹)
588.8
588.8
1285
2223.5

Table 4.2 – Absorbance, concentration and pressure of N₂O in the white cell

Passes	Pressure (torr)	Concentration (molecule/m ³)	Absorbance
12	20.1	1.80×10^{-24}	0.74
16	19.9	1.72×10^{-24}	1.22
20	20.3	1.81×10^{-24}	1.54

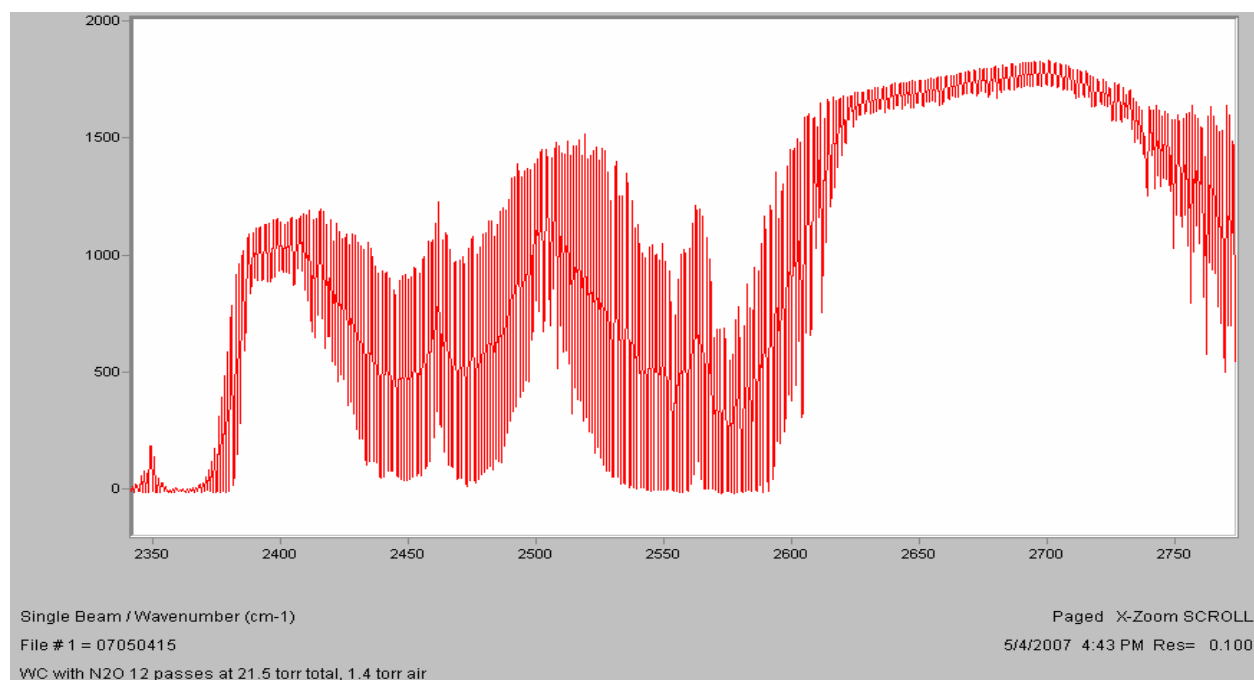


Figure 4.2 – FTIR Spectrum of N₂O in the white cell trial 1. The N₂O pressure at 21.5 torr

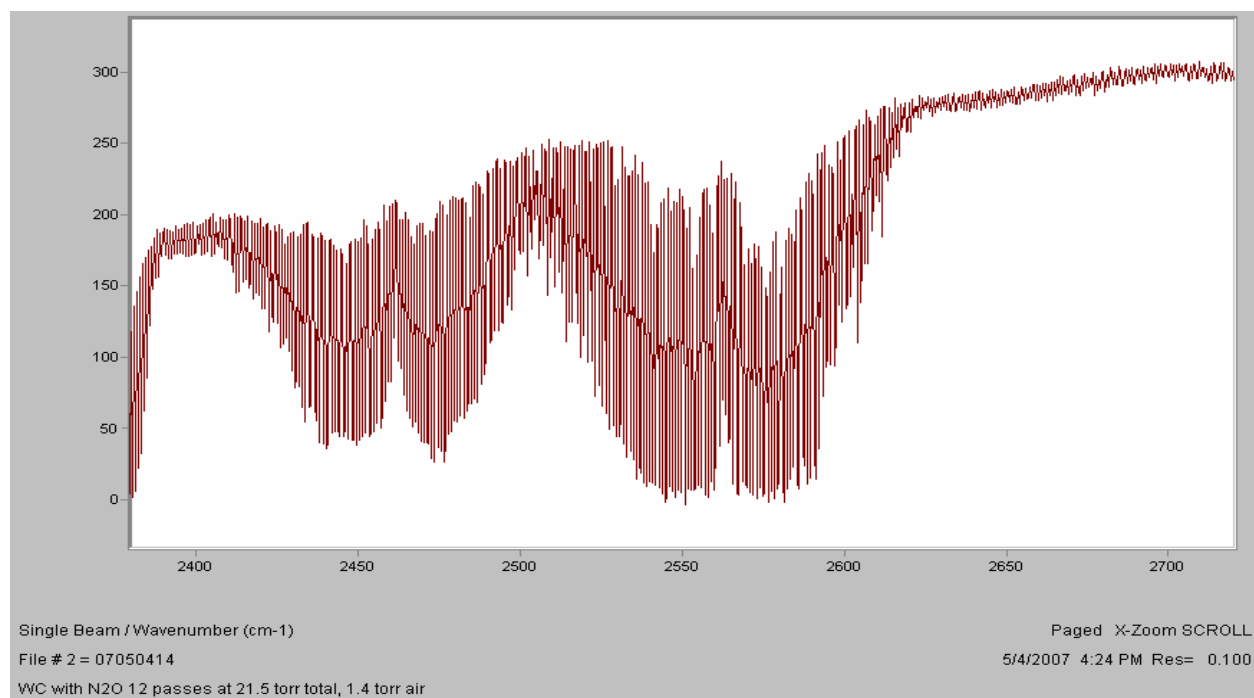


Figure 4.3 – FTIR spectrum of N₂O in the white cell showing the isolation of the $\nu_1 + 2\nu_2$ combination band (2400 – 2500 cm⁻¹)

Table 4.3 – The path length of the different passes in the white cell

Passes	Length (m)	Bar error
12	23.26	± 0.40
16	27.26	± 0.60
20	31.26	± 0.56

2. Solar FTIR Spectroscopy:

The Hitran program used to find the concentration of the molecules for the open-path spectroscopy data was not set up to determinate the concentration to the solar spectroscopy data. This data is used to estimate the concentration of the molecules found in two days during the summer 2005.

- June 14th, 2005: The spectrometer was set up with a resolution of 0.1cm^{-1} as well as a higher resolution of 0.017cm^{-1} . This initial experiment used a base gain at 1, position gain of 4, CaF_2 beam splitter, aperture 1.5mm, InSb 1800 in low, and 10 scans.

Analyzing the spectra, the molecules found in the environment were carbon monoxide (CO), water (H_2O), nitrous oxide (N_2O), carbon dioxide (CO_2), methane (CH_4), and oxygen (O_2); as shown in figures 4.4, 4.5, 4.6, and 4.7. Data from figure 4.4 and 4.5 were taking at 3:24 pm. Data from figure 4.6 and 4.7 were taken at 3:48 pm.

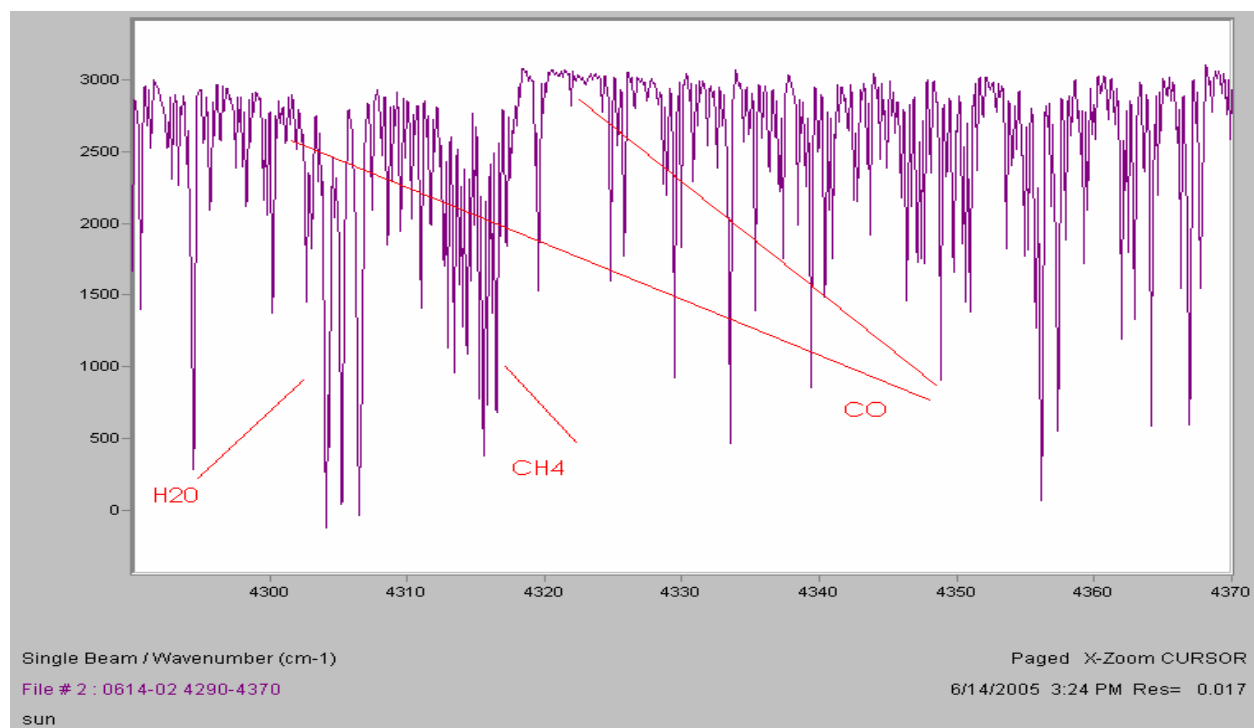


Figure 4.4 – FTIR spectrum for H₂O, CH₄ and CO

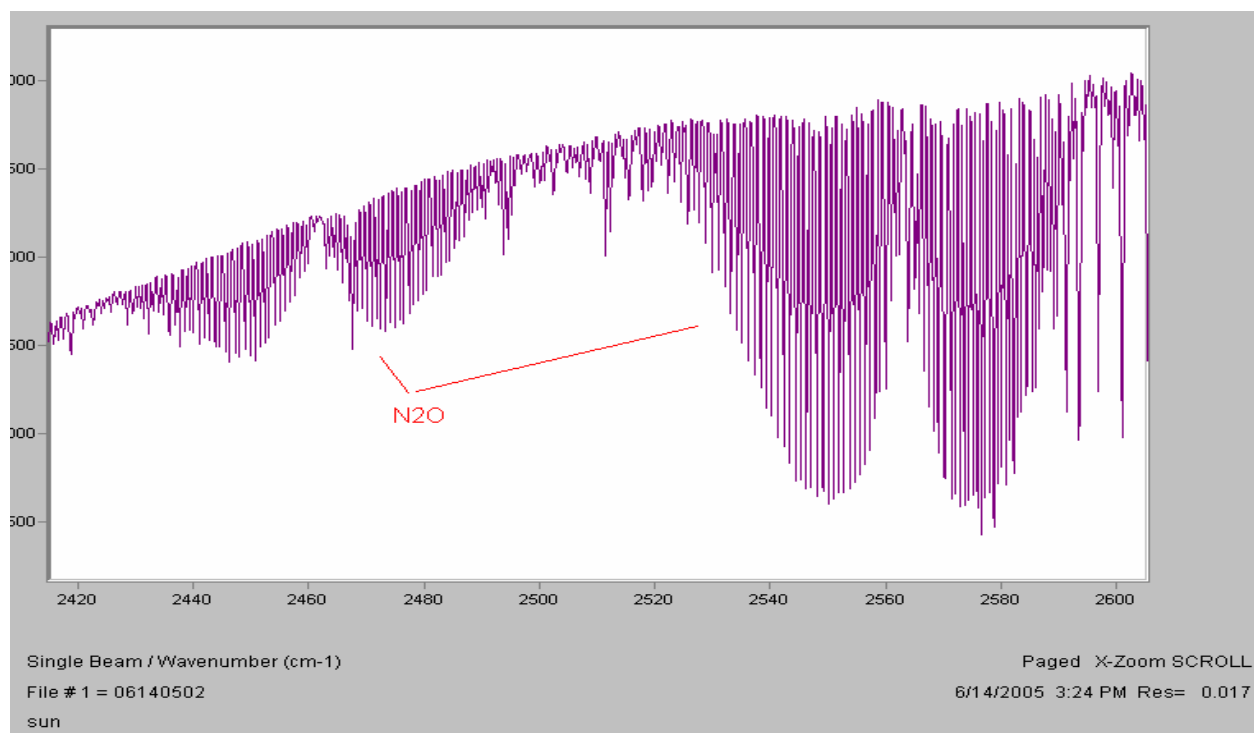


Figure 4.5 – FTIR spectrum for N₂O ($\nu_1 + 2\nu_2$ combination band)

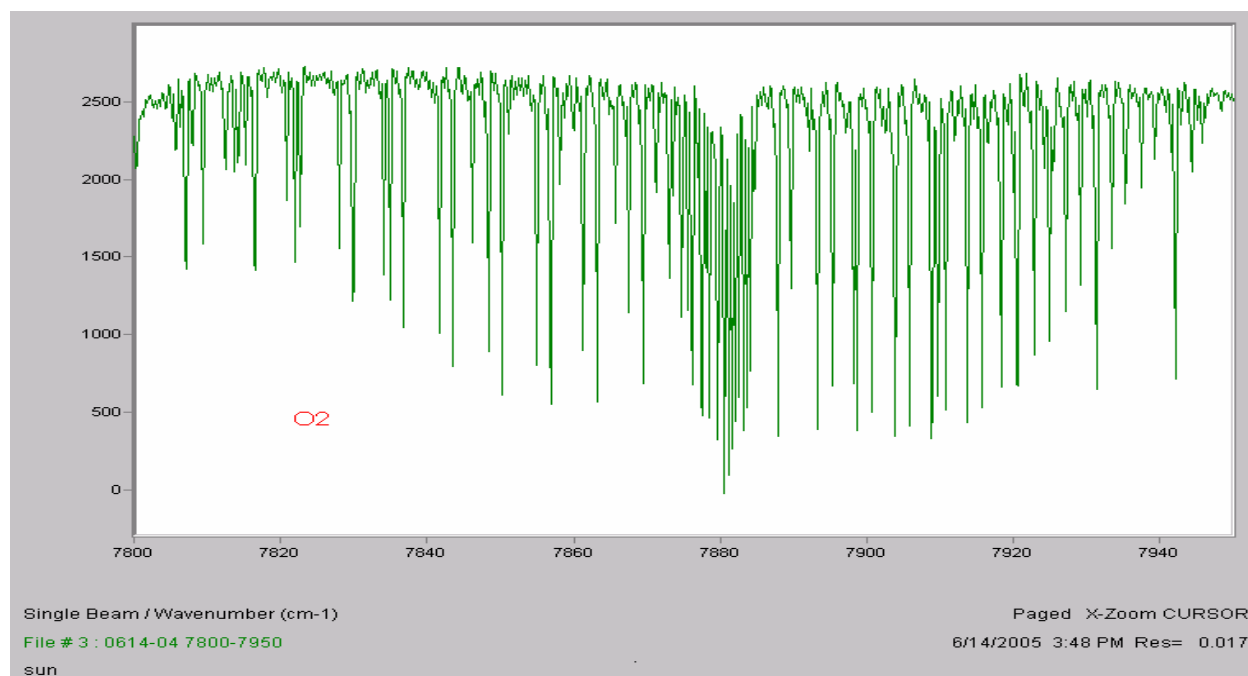


Figure 4.6 – New IR infrared spectrum of O₂ showing the $^3\Sigma_g^+ \rightarrow ^1\Delta_g^+$ highly forbidden transition

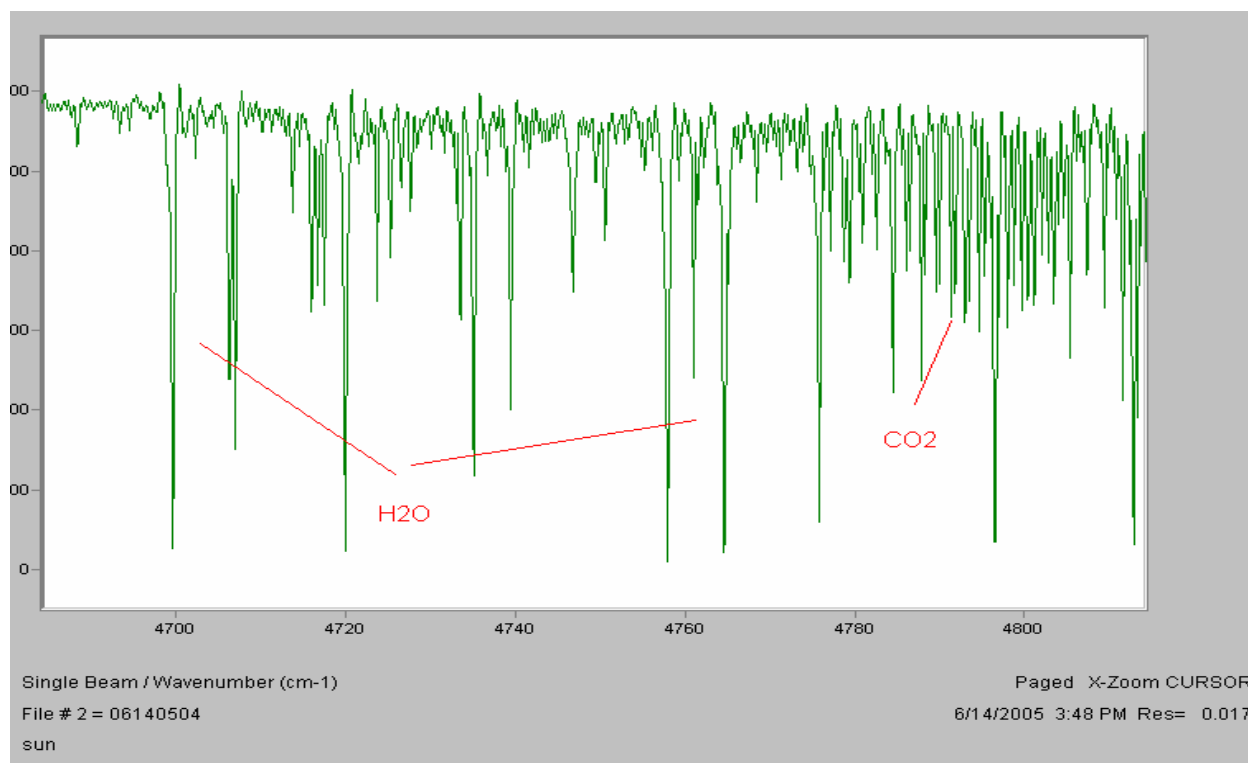


Figure 4.7 – FTIR spectrum for H₂O, and CO₂

- June 15th, 2005: the spectrometer was set up with a resolution of 0.017cm^{-1} , base gain at 1, position gain at 4, CaF_2 beam splitter, aperture 1.0mm, InSb 1800 in low, and 10 scans.

Analyzing the spectra, the molecules found in the atmosphere were again carbon monoxide (CO), water (H_2O), nitrous oxide (N_2O), carbon dioxide (CO_2), methane (CH_4), and oxygen (O_2); as shown in figures 4.8, 4.9, and 4.10.

Data in figure 4.8, 4.9, and 4.10 were taken at 11:57 am.

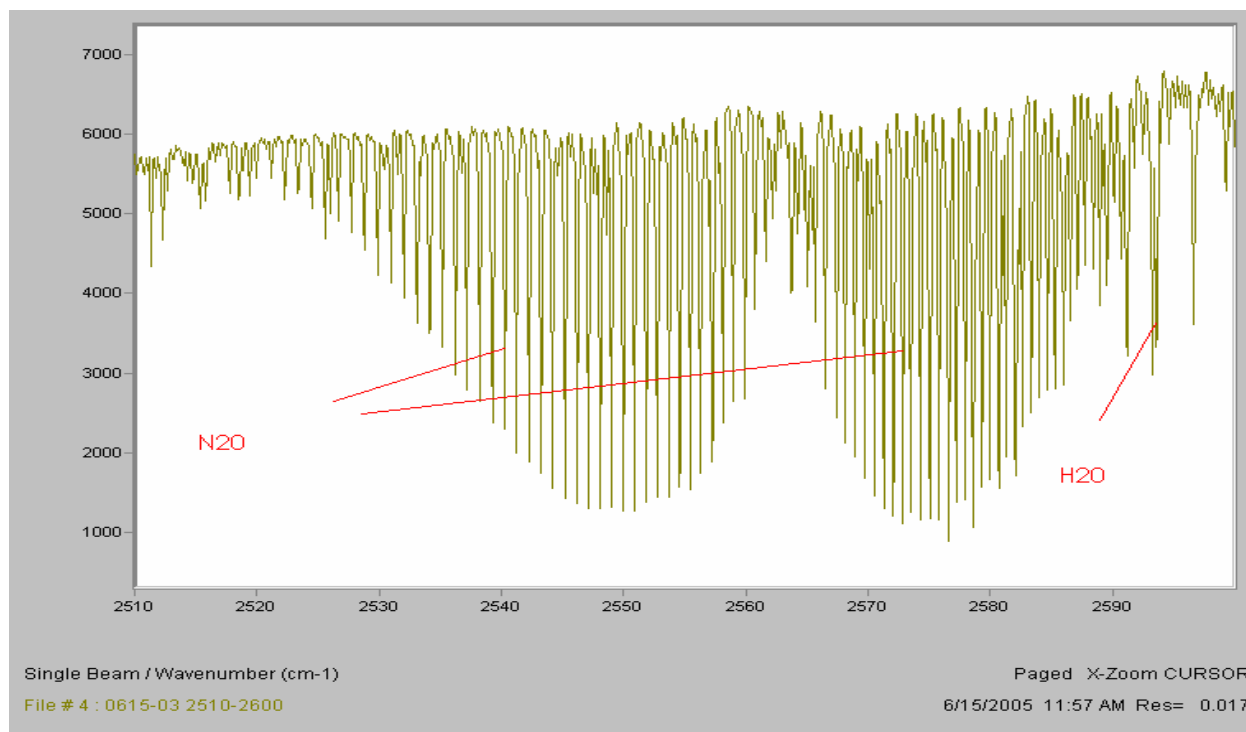


Figure 4.8 – FTIR spectrum for N_2O and H_2O

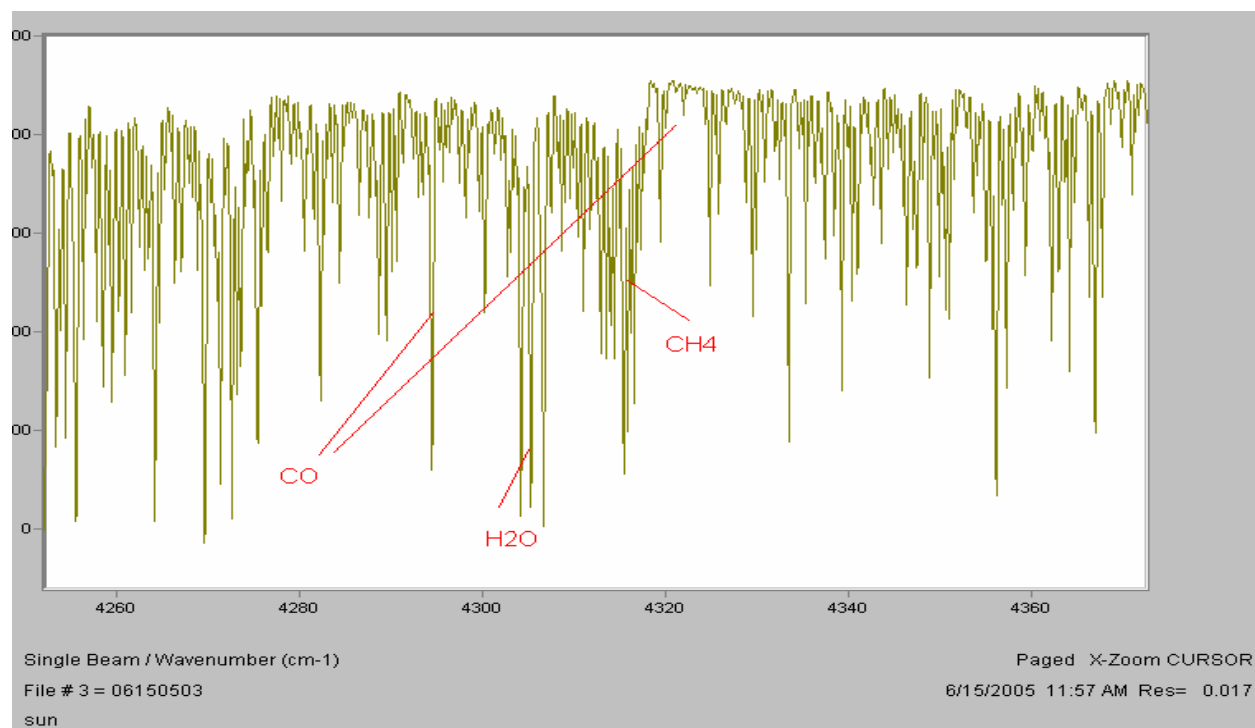


Figure 4.9 – FTIR spectrum for CH₄, H₂O, and CO

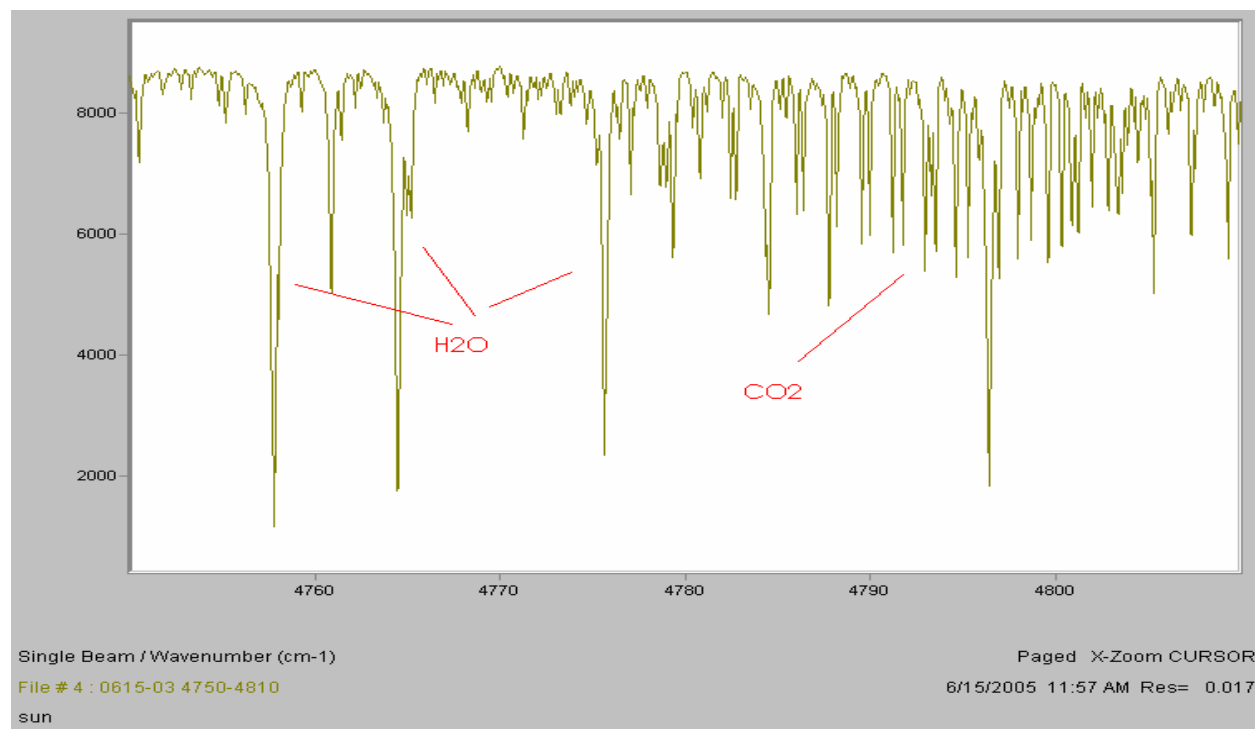


Figure 4.10 – FTIR spectrum for H₂O and CO₂

3. Open-Path Spectroscopy:

The determination of the concentration of many of the infrared active molecular constituents in the atmosphere can be carried out using infrared absorption spectroscopy. Early applications of FTIR spectroscopy employed Beer's Law, i.e.

$$\%T = \frac{I}{I_o} = e^{-\ell\sigma\rho} \quad (4.2)$$

In order to obtain the molecular density, the amount of light absorbed depends on the path length (ℓ), cross section (σ) and concentration (ρ) as shown in equation 4.2. In more recent studies a more sophisticated application of Beer's law is used. In our work we employed a program developed by Dr. Stewart Hager that simulates a spectrum using Beer's Law, using known cross sections for the molecule and the absorption path length [Reference 10]. Selecting a range of wavenumbers, the spectrum is cut off with a specific number of lines. This section is normalized and saved as a PRN file. Using this procedure one can rapidly determine the molecular concentration. Figure 4.11 is used to illustrate the method in which an open path spectra in air shows absorption peaks for carbon dioxide, methane and nitrous oxide in the top figure. The bottom figure shows the computer fit to all of the peaks observed. The fact the various IR peaks of the component gases are overlapping are accounted for using the fitting procedure. The source of error using this program is visual fitting, which has ~ 5% error.

This procedure is used to determine the concentrations of gaseous components in the solar FTIR spectra.

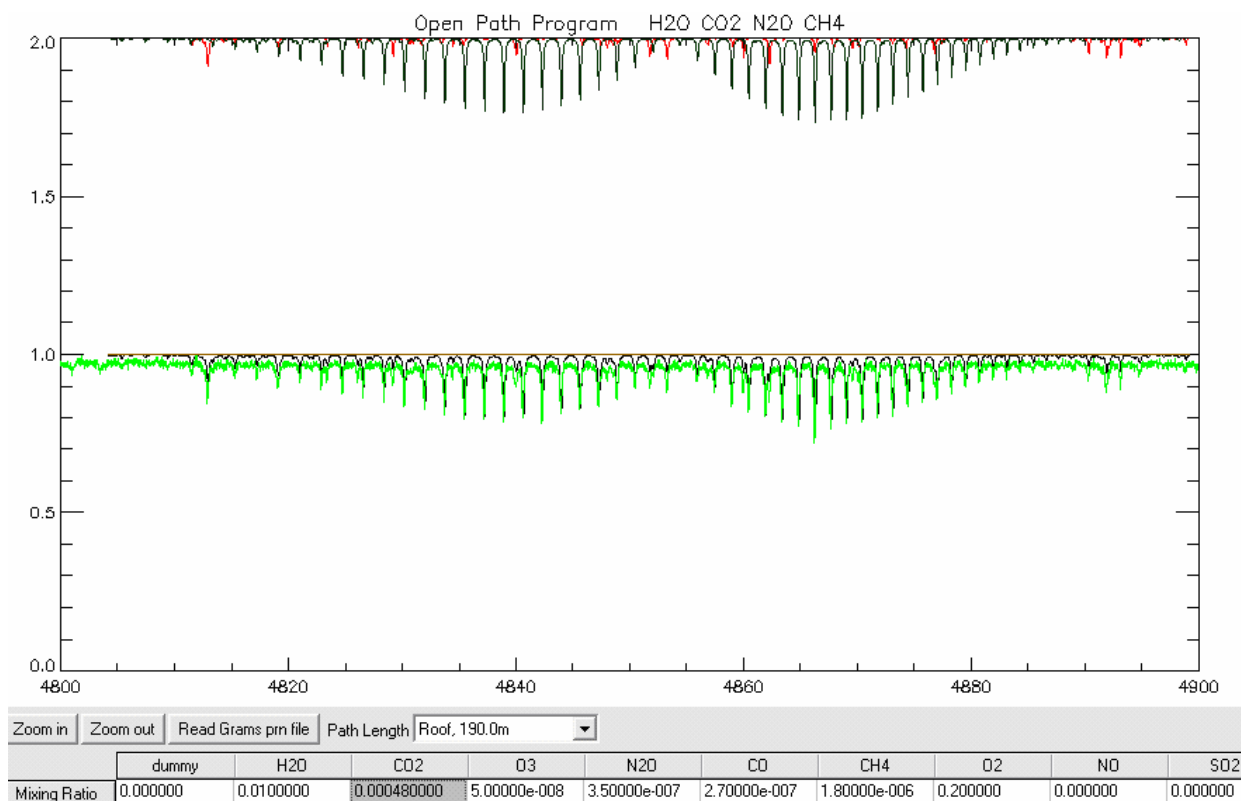


Figure 4.11 – Spectra simulation

For this section, the data were recorded in the summer of 2005 and 2006 in order to compare the yearly change in concentration.

- June 15th, 2005: the spectrometer was set up with CF₂ beam splitter, InSb 1800 and a resolution of 0.1cm⁻¹, aperture 2.5mm, base gain at 16, position gain at 64 and 20 scans. The light source was the carbon rod as described in the procedure.

The molecules found in the environment were carbon monoxide (CO), water (H₂O), nitrous oxide (N₂O), and carbon dioxide (CO₂); as seen in figures 4.12 and 4.13.

The concentrations for each molecule are recorded in table 4.4.

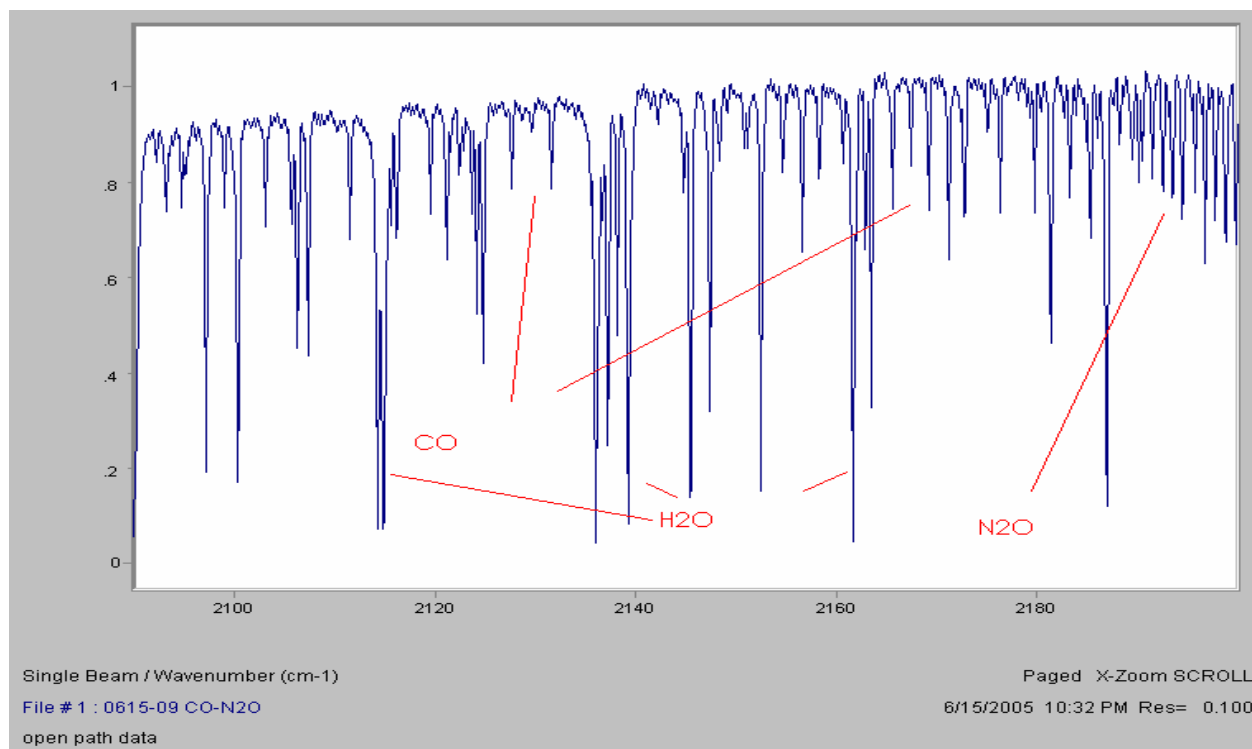


Figure 4.12 – FTIR spectrum for CO, H₂O, and N₂O (10:32pm)

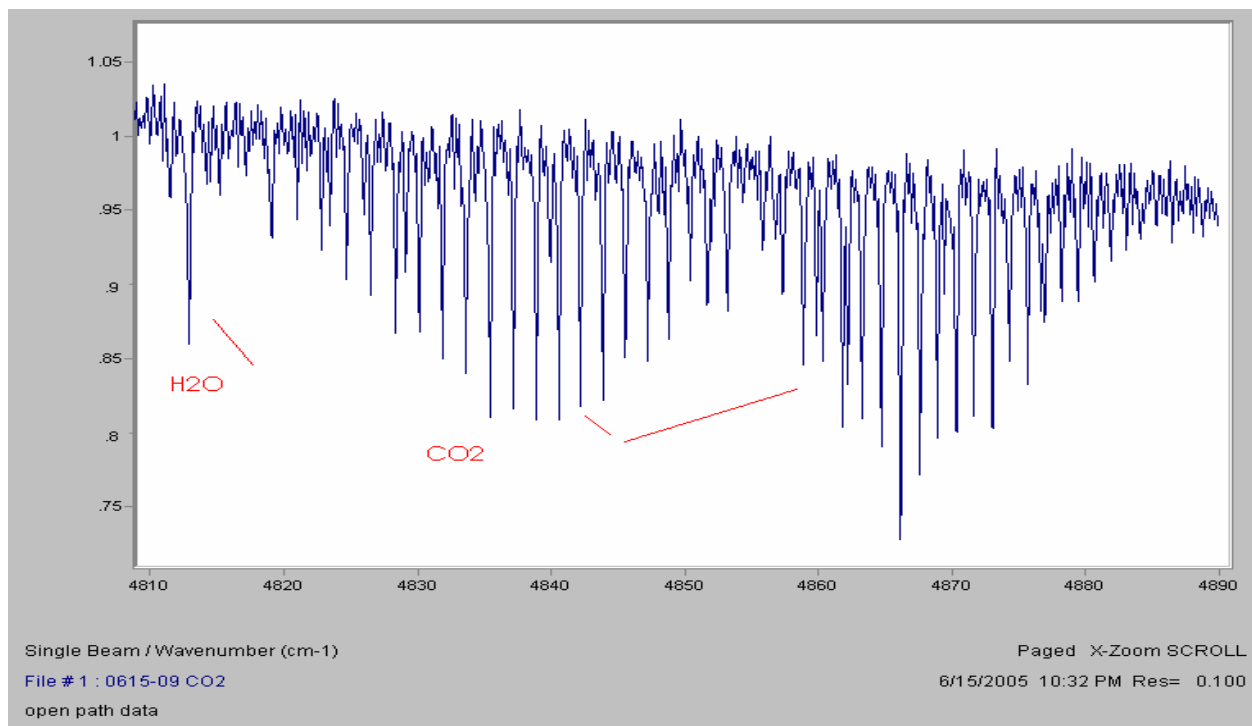


Figure 4.13 – FTIR spectrum for H₂O and CO₂ (10:32pm)

Table 4.4 – Concentration of the molecules (June 15th, 2005)

Molecules	Time	Concentration (parts per total)	Error	% Difference
CO	10:27pm	3.0×10^{-7}	$\pm 0.1 \times 10^{-7}$	> 20%
	10:32pm	3.0×10^{-7}	$\pm 0.3 \times 10^{-7}$	> 20%
	10:40pm	3.5×10^{-7}	$\pm 0.5 \times 10^{-7}$	> 40%
H ₂ O	10:27pm	0.017	± 0.1	--
	10:32pm	0.017	± 0.3	--
	10:40pm	0.019	± 0.5	--
N ₂ O	10:27pm	3.5×10^{-7}	$\pm 0.1 \times 10^{-7}$	> 9%
	10:32pm	3.5×10^{-7}	$\pm 0.3 \times 10^{-7}$	> 9%
	10:40pm	3.6×10^{-7}	$\pm 0.5 \times 10^{-7}$	> 12 %
CO ₂	10:27pm	5.45×10^{-4}	$\pm 0.1 \times 10^{-4}$	> 44%
	10:32pm	5.45×10^{-4}	$\pm 0.3 \times 10^{-4}$	> 44%
	10:40pm	5.46×10^{-4}	$\pm 0.5 \times 10^{-4}$	> 44 %

Comparing to the relative humidity, the water vapor found in table 4.4 corresponds to a temperature above 90°F. The level for carbon monoxide in the atmosphere has increase by 20% and 40% relative to 250 parts per billion. The level for nitrous oxide in the atmosphere has increased by 9% and 12% relative to 319 parts per billion and carbon dioxide has increased by 44% relative to 379 part per million. The value for nitrous oxide at this time is high as a result of the emission from factories and other machinery during the morning hours.

- June 16th, 2005: the spectrometer was set up with CF₂ beam splitter, InSb 1800 and a resolution of 0.1cm⁻¹, aperture 2.5mm, base gain at 16, position gain at 64 and 20 scans. The light source was the carbon rod as described in the procedure.

The molecules found in the environment were carbon monoxide (CO), water (H₂O), nitrous oxide (N₂O), and carbon dioxide (CO₂); as seen in figures 4.14 and 4.15.

The concentrations for each molecule are recorded in table 4.5.

Comparing to the relative humidity, the water vapor found in table 4.5 corresponds to a temperature above 90°F. The level for carbon monoxide in the atmosphere has increase by 8% and 16% relative to 250 parts per billion. The level for nitrous oxide in the atmosphere has increased by 9% and 16% relative to 319 parts per billion and carbon dioxide has increased by 32% and 40% relative to 379 part per million.

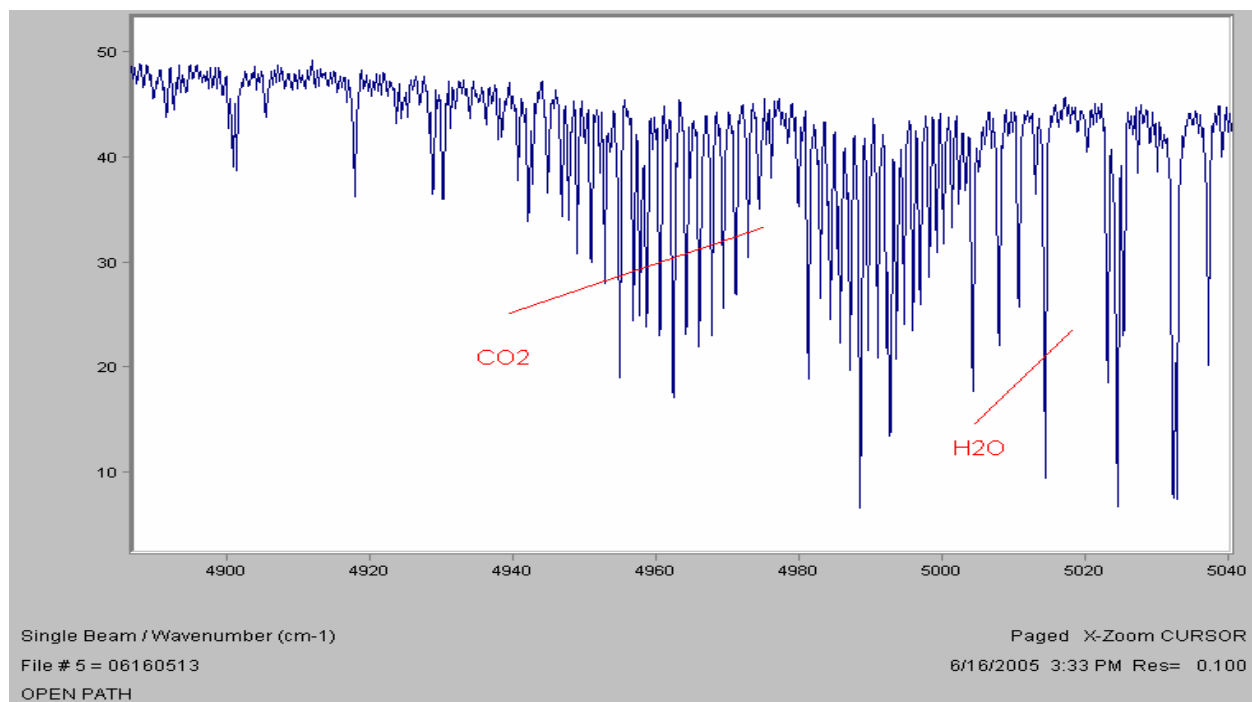


Figure 4.14 – FTIR spectrum for H₂O and CO₂ (3:33pm)

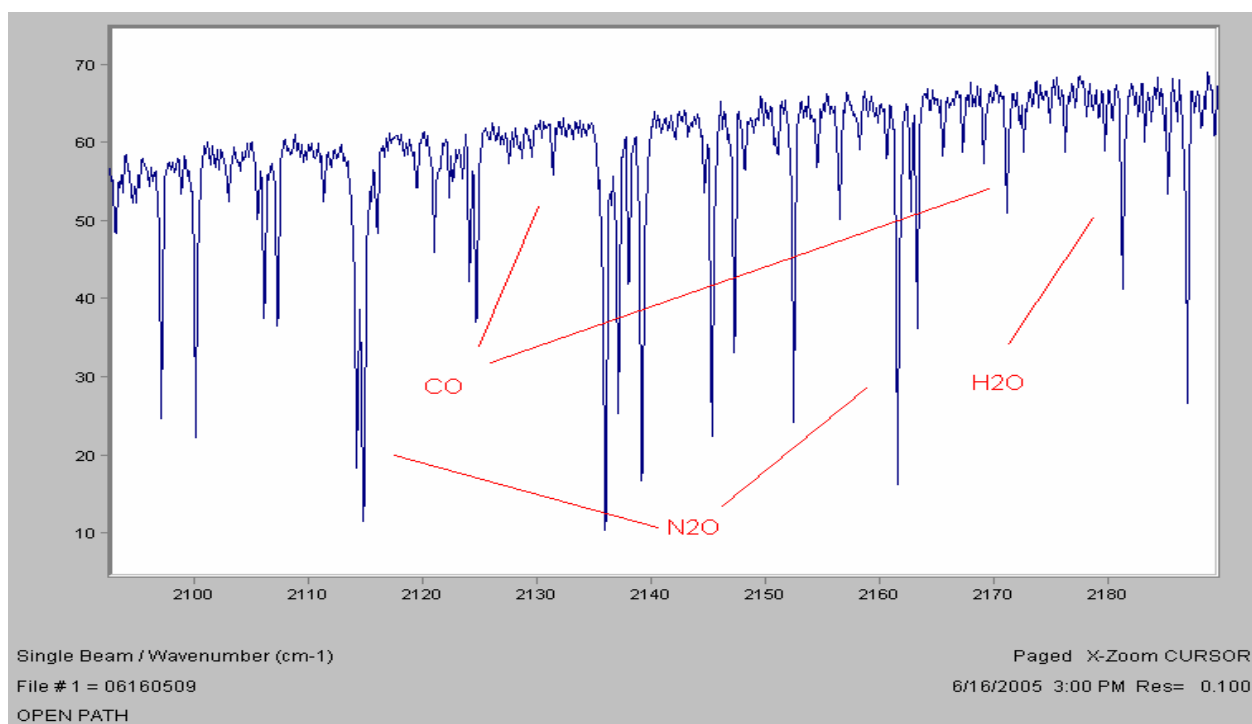


Figure 4.15 – FTIR spectrum for CO, N₂O, and H₂O (3:00pm)

Table 4.5 – Concentration of the molecules (June 16th, 2005)

Molecules	Time	Concentration (parts per total)	Error	% Difference
CO	3:00pm	2.7×10^{-7}	$\pm 0.2 \times 10^{-7}$	> 8 %
	3:33pm	2.9×10^{-7}	$\pm 0.1 \times 10^{-7}$	> 16 %
H ₂ O	3:00pm	0.020	± 0.2	--
	3:33pm	0.021	± 0.1	--
N ₂ O	3:00pm	3.5×10^{-7}	$\pm 0.2 \times 10^{-7}$	> 9 %
	3:33pm	3.7×10^{-7}	$\pm 0.1 \times 10^{-7}$	> 16 %
CO ₂	3:00pm	5.0×10^{-4}	$\pm 0.2 \times 10^{-4}$	> 32 %
	3:33pm	5.3×10^{-4}	$\pm 0.1 \times 10^{-4}$	> 40 %

- June 19th, 2005: the spectrometer was set up with a KBr beam splitter, MCT 1800, resolution 0.1cm^{-1} , aperture 2.5mm, and 30 scans. The light source was the carbon rod. Molecules found in the atmosphere were carbon monoxide (CO), water (H₂O), nitrous oxide (N₂O), and carbon dioxide (CO₂); as reported in figures 4.16 and 4.17.

The concentrations for each molecule are recorded in table 4.6. Comparing to the relative humidity, the water vapor found in table 4.6 corresponds to a temperature above 88°F. The level for carbon monoxide in the atmosphere has increase by 2.4% relative to 250 parts per billion. The level for nitrous oxide in the atmosphere has increased by 10% relative to 319 parts per billion and carbon dioxide has increased by 27% relative to 379 part per million.

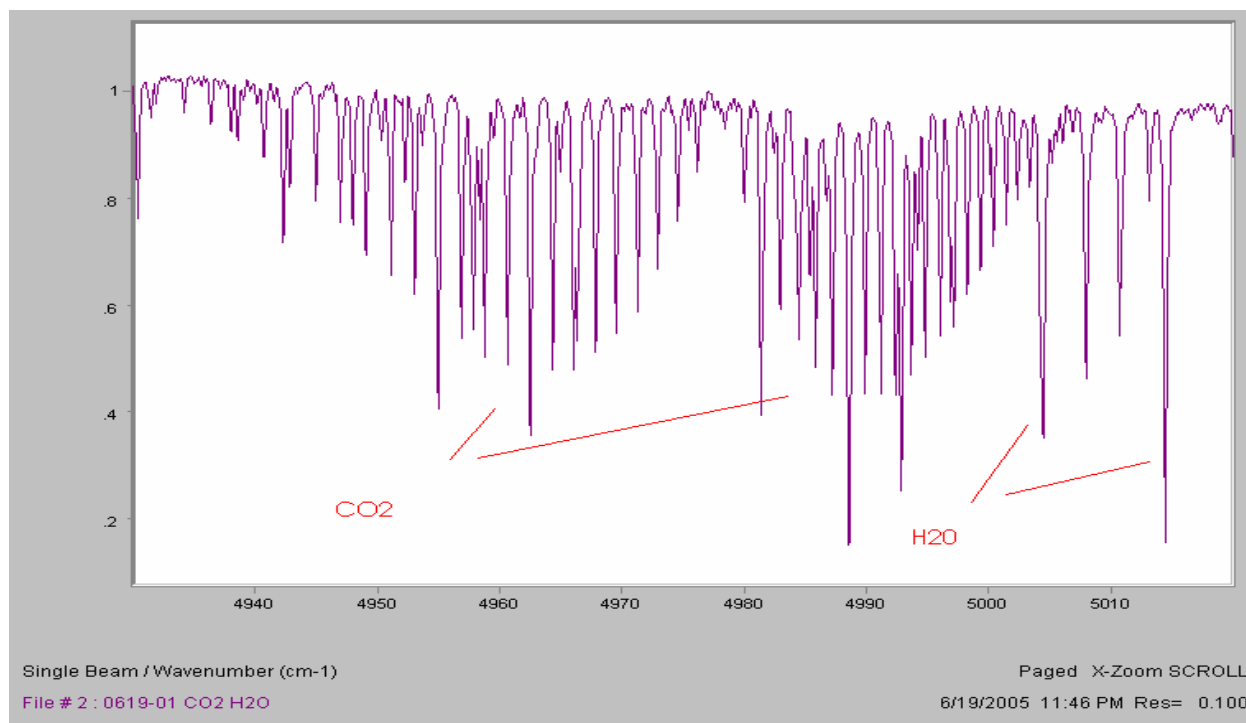


Figure 4.16 – FTIR spectrum for CO₂ and H₂O (11:39pm)

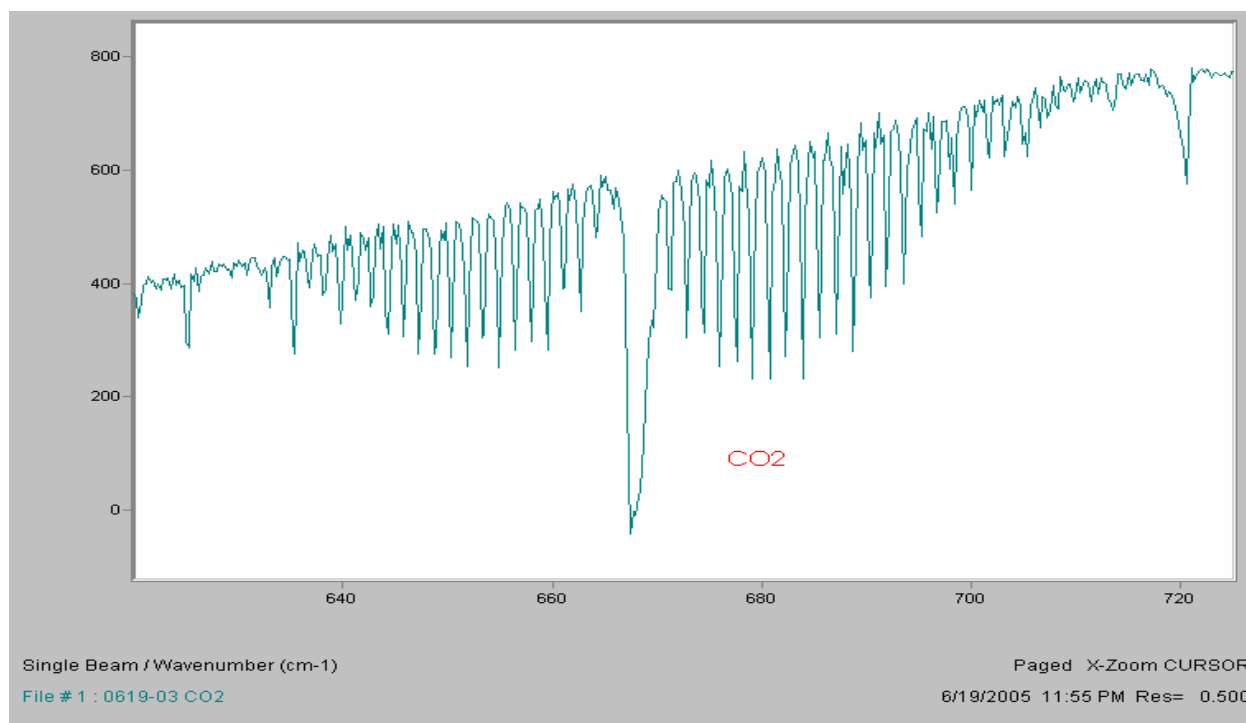


Figure 4.17 – FTIR spectrum for open pass spectra showing the PQR branch of CO₂ (11:39pm)

Table 4.6 – Concentration of the molecules (June 19th, 2005)

Molecules	Time	Concentration (parts per total)	Error	% Difference
CO	11:39pm	2.56×10^{-7}	$\pm 0.4 \times 10^{-7}$	> 2.4 %
H ₂ O	11:39PM	0.023	± 0.4	--
N ₂ O	11:39pm	3.5×10^{-7}	$\pm 0.4 \times 10^{-7}$	> 10 %
CO ₂	11:39pm	4.8×10^{-4}	$\pm 0.4 \times 10^{-4}$	> 27 %

- 2 July 26th, 2005: the carbon rod was used as the light source. The spectrometer was set up with a CaF₂ beam splitter, InSb 1800 in low, resolution 0.1cm⁻¹, aperture 3.5mm, 20 scans, base and position gain at 64.

The molecules found in the environment were carbon monoxide (CO), water (H₂O), nitrous oxide (N₂O), and carbon dioxide (CO₂); as seen in figures 4.18 and 4.19.

Using the Hitran program, the molecular concentrations are reported in table 4.7. The results differ because both spectra were taken 30 minutes apart, illustrating the temporal variation of these gases, except for CO₂.

Comparing to the relative humidity, the water vapor found in table 4.7 corresponds to a temperature above 87°F. The level for carbon monoxide in the atmosphere has increased by 44% and 72% relative to 250 parts per billion. The level for nitrous oxide in the atmosphere has increased by 0.3% and decreased by 12% relative to 319 parts per billion and carbon dioxide has increased by 47% and 49% relative to 379 part per million.

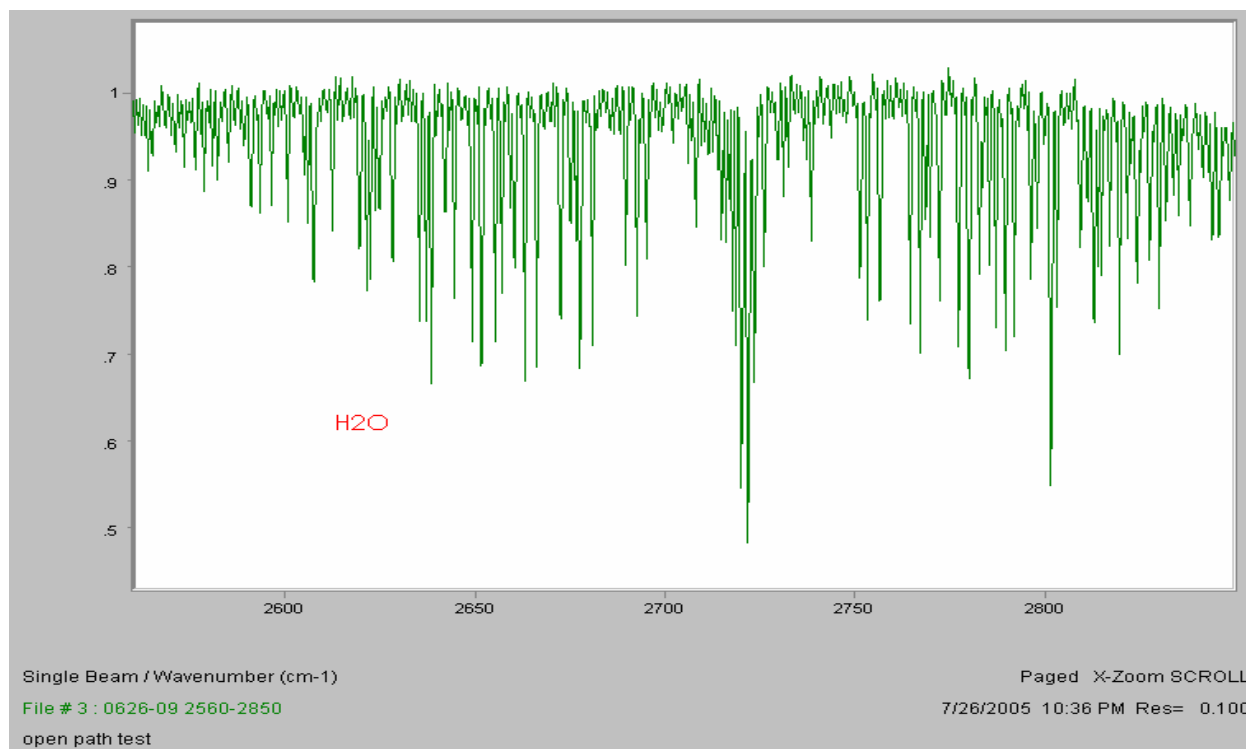


Figure 4.18 – FTIR spectrum for H₂O (10:22pm)

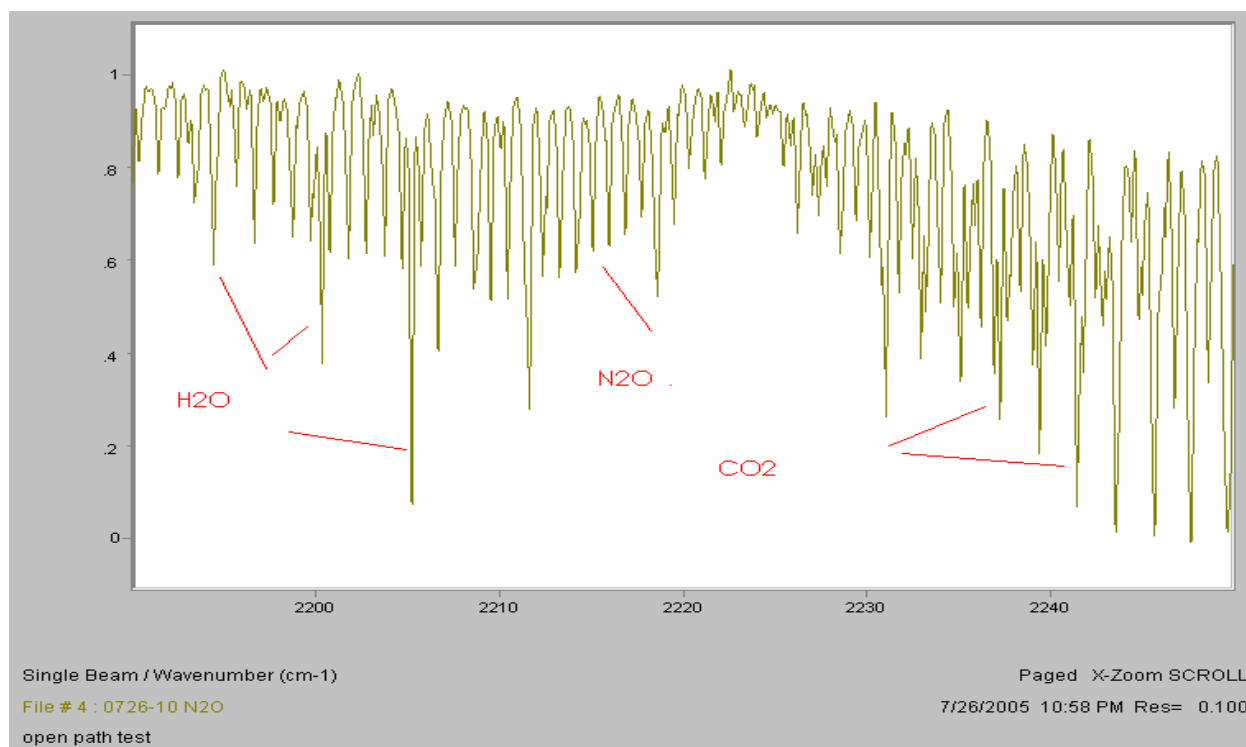


Figure 4.19 – FTIR spectrum for H₂O, N₂O, and CO₂ (10:58pm)

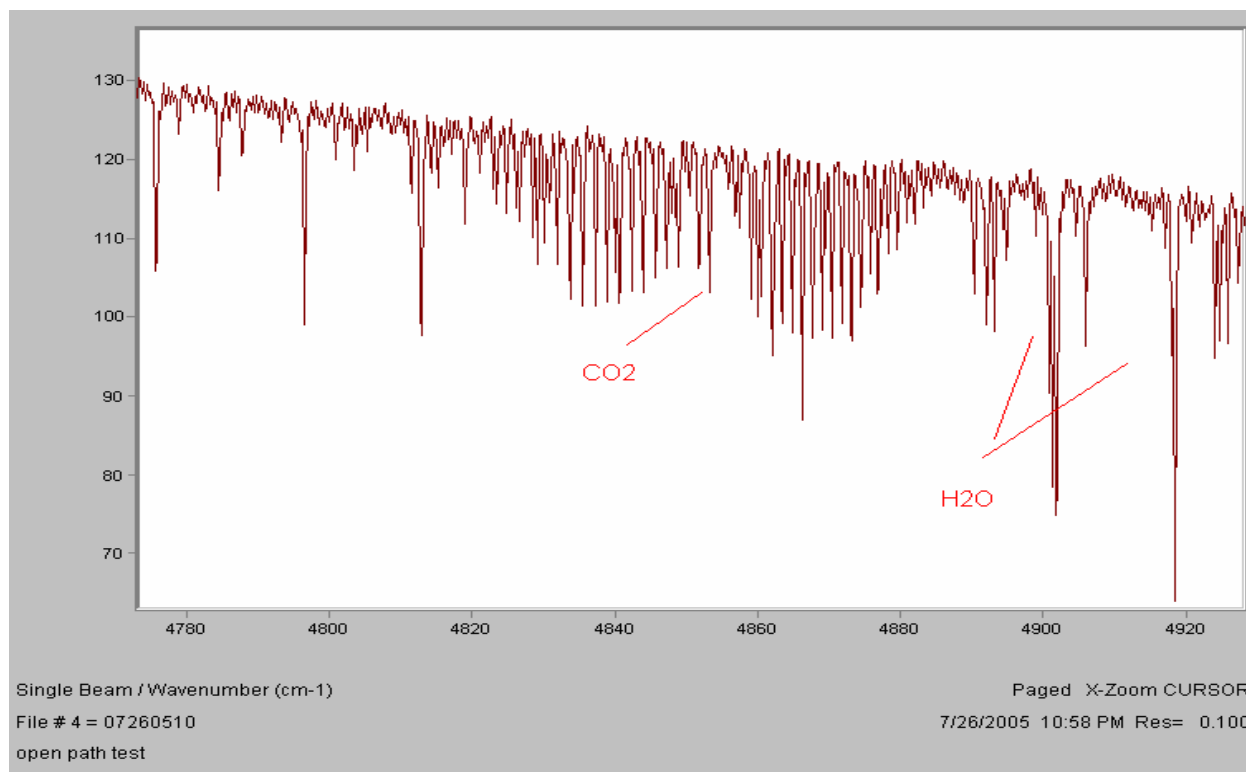


Figure 4.20 – FTIR spectrum for H₂O and CO₂ (10:58pm)

Table 4.7 – Concentration of the molecules (July 26th, 2005)

Molecules	Time	Concentration (parts per total)	Error	% Difference
CO	10:22pm	3.6×10^{-7}	$\pm 0.5 \times 10^{-7}$	> 44 %
	10:58pm	4.3×10^{-7}	$\pm 0.8 \times 10^{-7}$	> 72 %
H ₂ O	10:22pm	0.033	± 0.5	--
	10:58pm	0.035	± 0.8	--
N ₂ O	10:22pm	3.2×10^{-7}	$\pm 0.5 \times 10^{-7}$	> 0.3 %
	10:58pm	2.8×10^{-7}	$\pm 0.8 \times 10^{-7}$	< 12 %
CO ₂	10:22pm	5.57×10^{-4}	$\pm 0.5 \times 10^{-4}$	> 47 %
	10:58pm	5.65×10^{-4}	$\pm 0.8 \times 10^{-4}$	> 49 %

- July 7th, 2006: two passes on the roof and the spectrometer was set up with CF₂ beam splitter, InSb 1800 in low, resolution 4.0, 0.2, or 0.05cm⁻¹, aperture 2.5mm, base gain at 4, position gain at 16 and 64 scans. The light source was the carbon rod.

The molecules found in the environment were carbon monoxide (CO), water (H₂O), nitrous oxide (N₂O), and carbon dioxide (CO₂); as shown in figures 4.21 through 4.26.

Using the Hitran program, the concentrations for the molecules were again determined and recorded in Table 4.8. Comparing to the relative humidity, the water vapor found in table 4.8 corresponds to a temperature above 90°F. The level for carbon monoxide in the atmosphere has increase by 8%, 20%, and 28%; and decrease by 44%, and 52% relative to 250 parts per billion. The level for nitrous oxide in the atmosphere has increased by 25%, 10%, and 11%; and decrease by 37% relative to 319 parts per billion and carbon dioxide has decrease by a 6%, 7%, 11%, 12%, and 13% relative to 379 part per million.

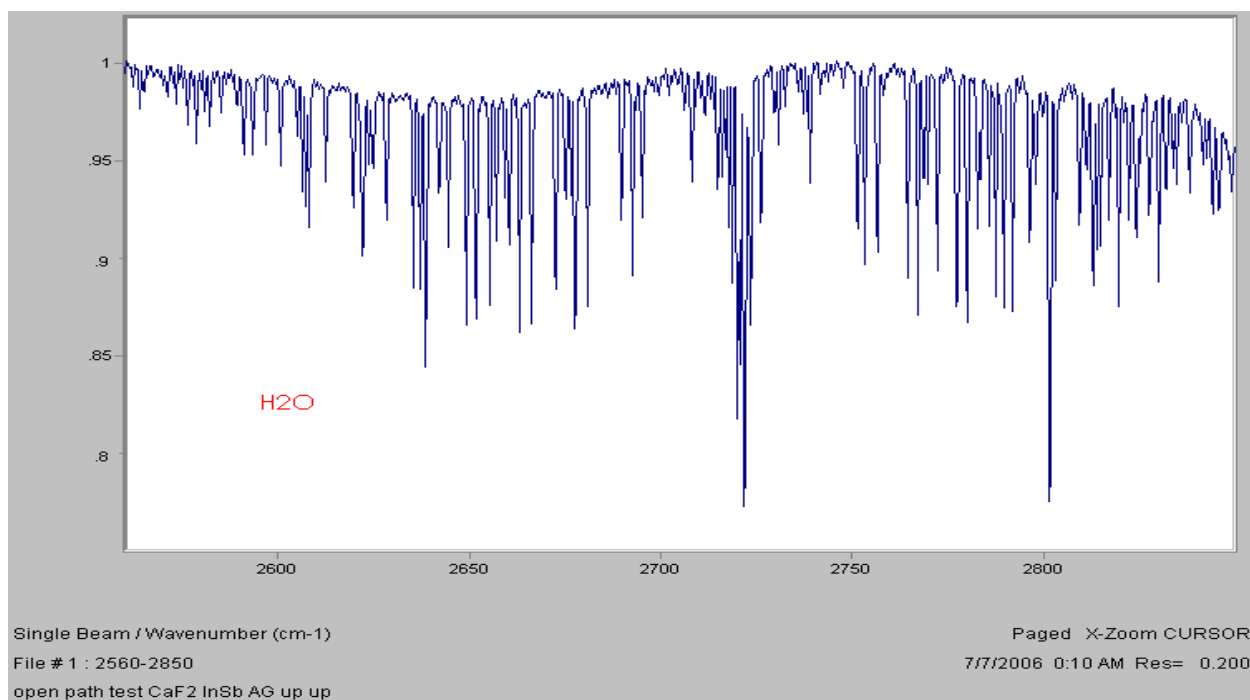


Figure 4.21 – FTIR spectrum for H₂O (12:10am)

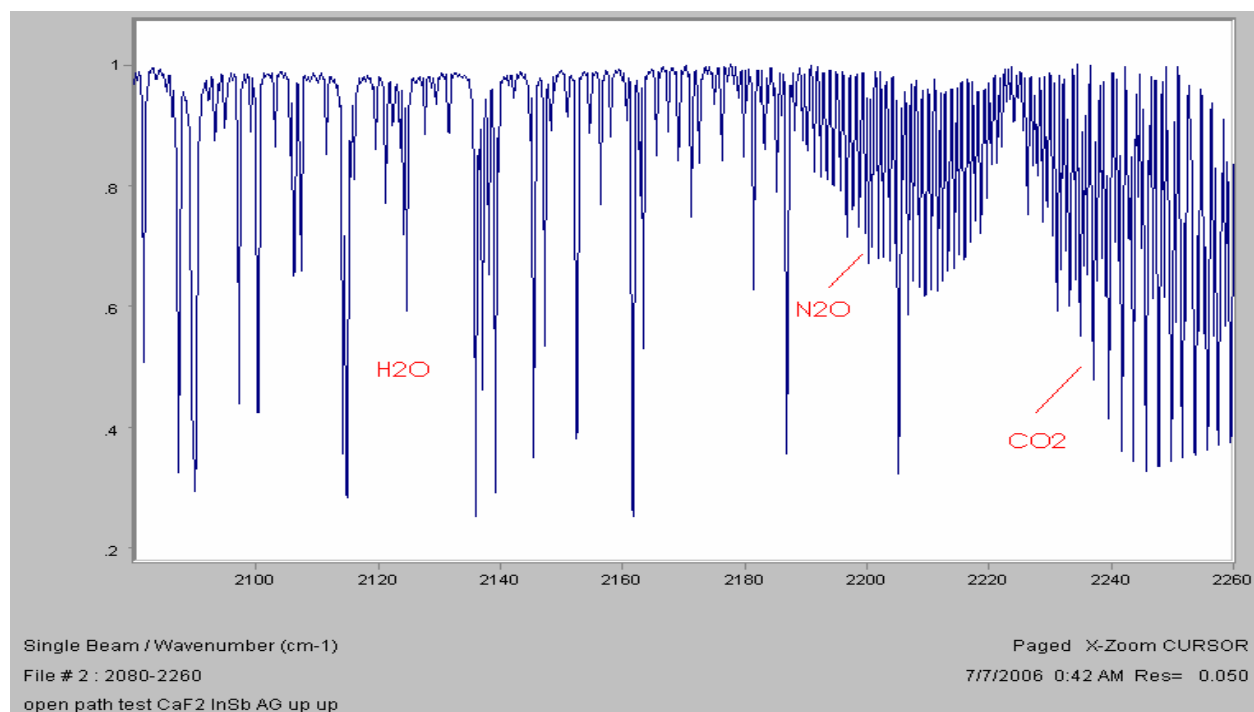


Figure 4.22 – FTIR spectrum for H₂O, N₂O and CO₂ (12:42am)

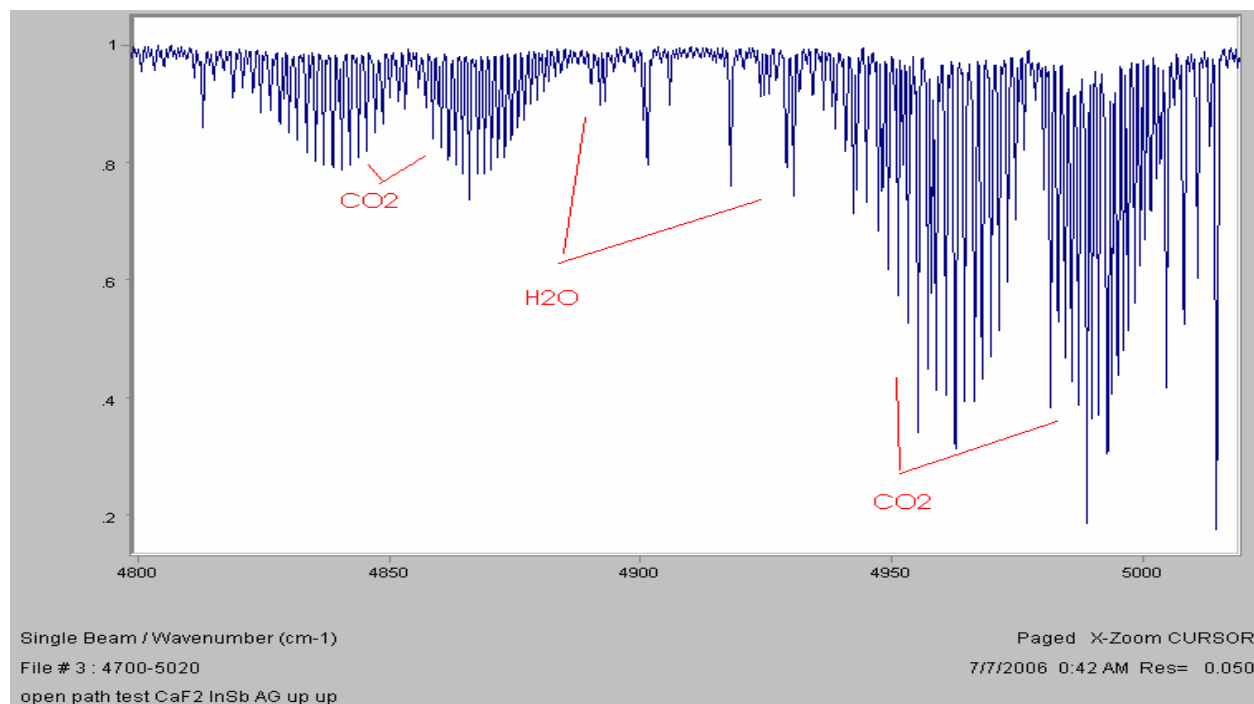


Figure 4.23 – FTIR spectrum for CO₂ and H₂O (12:42am)

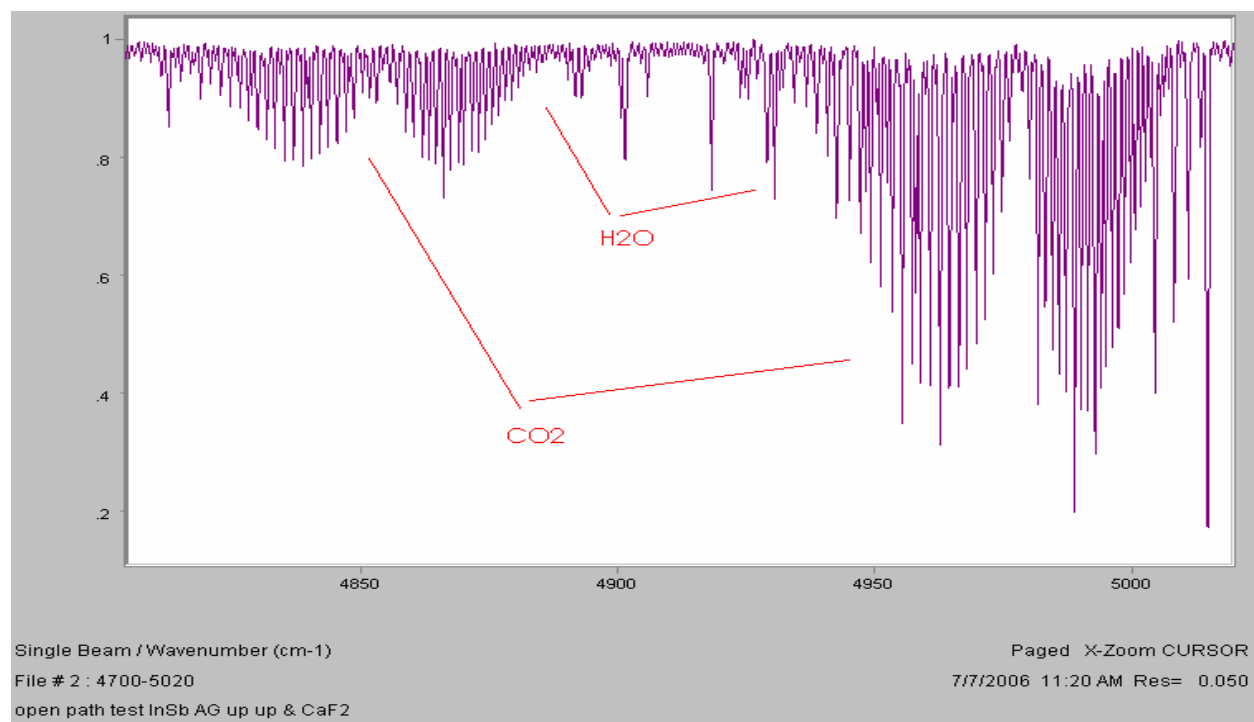


Figure 4.24 – FTIR spectrum for H₂O and CO₂ (11:20am)

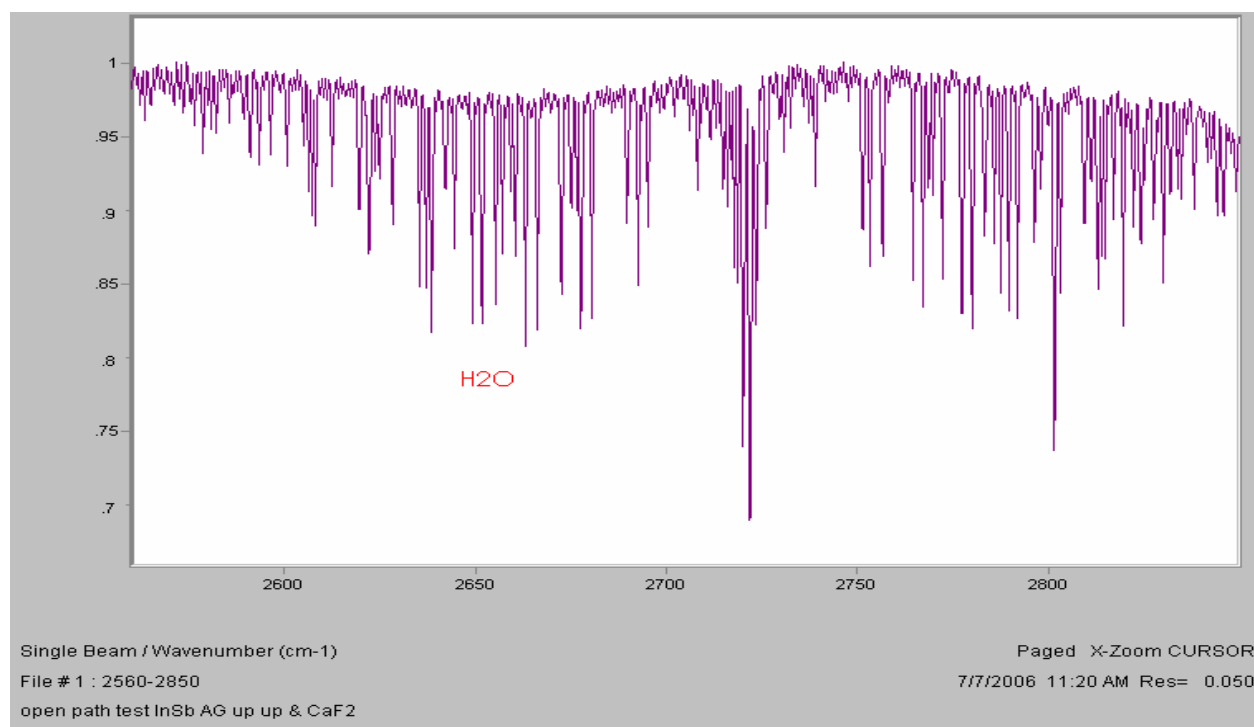


Figure 4.25 – FTIR spectrum of H₂O (11:20am)

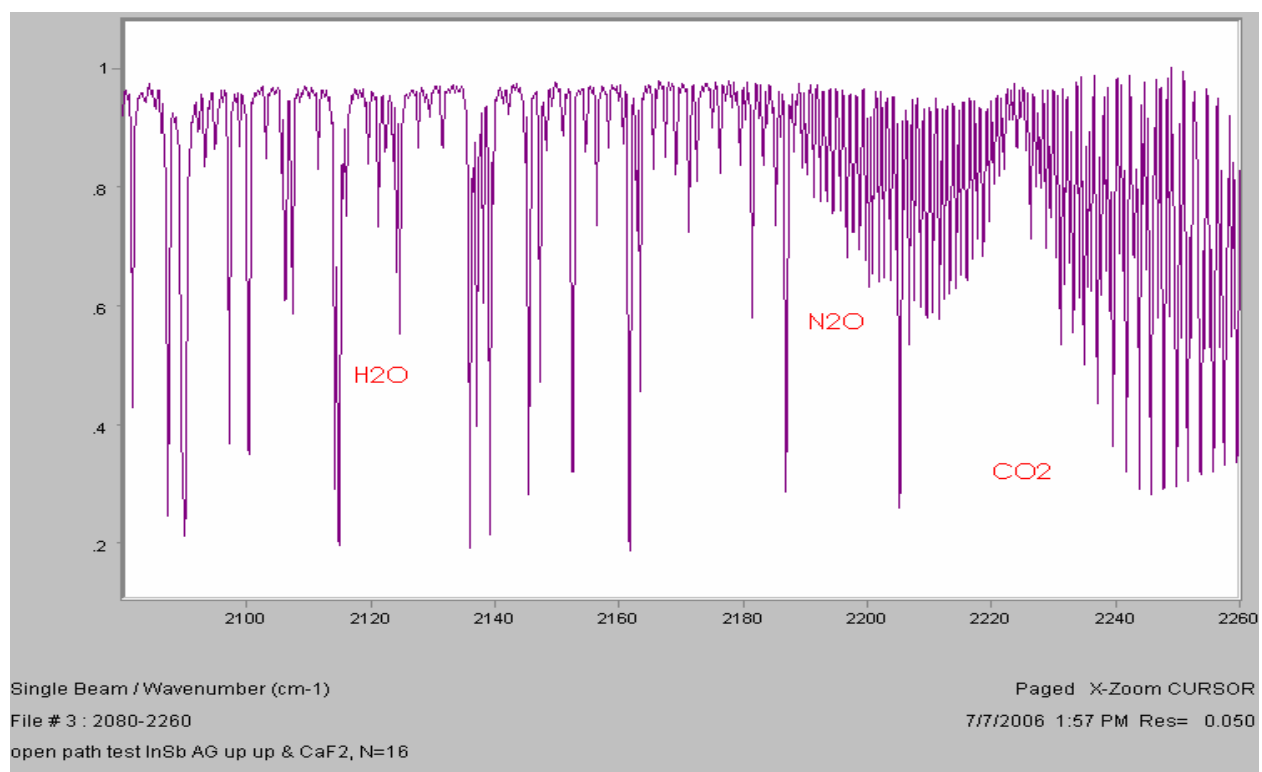


Figure 4.26 – FTIR spectrum of H₂O, N₂O and CO₂ (1:57pm)

Table 4.8 – Concentration of the molecules (July 7th, 2006)

Molecules	Time	Concentration (parts per total)	Error	% Difference
CO	12:10am	1.20×10^{-7}	$\pm 0.5 \times 10^{-7}$	< 52 %
	12:42am	1.40×10^{-7}	$\pm 0.3 \times 10^{-7}$	< 44 %
	11:20am	2.70×10^{-7}	$\pm 0.6 \times 10^{-7}$	> 8 %
	1:57pm	3.00×10^{-7}	$\pm 0.2 \times 10^{-7}$	> 20 %
	3:45pm	3.20×10^{-7}	$\pm 0.1 \times 10^{-7}$	> 28 %
H ₂ O	12:10am	0.0300	± 0.5	--
	12:42am	0.0280	± 0.3	--
	11:20am	0.0200	± 0.6	--
	1:57pm	0.0280	± 0.2	--
	3:45pm	0.0290	± 0.1	--
N ₂ O	12:10am	2.00×10^{-7}	$\pm 0.5 \times 10^{-7}$	< 37 %
	12:42am	2.40×10^{-7}	$\pm 0.3 \times 10^{-7}$	> 25 %
	11:20am	3.50×10^{-7}	$\pm 0.6 \times 10^{-7}$	> 10 %
	1:57pm	3.55×10^{-7}	$\pm 0.2 \times 10^{-7}$	> 11 %
	3:45pm	3.53×10^{-7}	$\pm 0.1 \times 10^{-7}$	> 11 %
CO ₂	12:10am	3.58×10^{-4}	$\pm 0.5 \times 10^{-4}$	< 6 %
	12:42am	3.52×10^{-4}	$\pm 0.3 \times 10^{-4}$	< 7 %
	11:20am	3.30×10^{-4}	$\pm 0.6 \times 10^{-4}$	< 13 %
	1:57pm	3.35×10^{-4}	$\pm 0.2 \times 10^{-4}$	< 12 %
	3:45pm	3.37×10^{-4}	$\pm 0.1 \times 10^{-4}$	< 11 %

- July 24th, 2006: four passes on the roof and the spectrometer was set up with CaF_2 beam splitter, InSb 1800 in low, resolution 0.05 or 0.08cm^{-1} , aperture 3.5mm , 32 scans, base and position gain at 16. The light source was the carbon rod.

Analyzing the spectra, the molecules found in the environment were carbon monoxide (CO), water (H_2O), nitrous oxide (N_2O), and carbon dioxide (CO_2); as seen in figures 4.27, 4.28, and 4.29.

Using the program, the concentrations for each molecule were determined and shown in table 4.9. Comparing to the relative humidity, the water vapor found in table 4.9 corresponds to a temperature above 85°F . The level for carbon monoxide in the atmosphere has increase by 24% and 20% relative to 250 parts per billion. The level for nitrous oxide in the atmosphere has decreased by 40% and 37% relative to 319 parts per billion and carbon dioxide has increased by 8% and 7% relative to 379 part per million.

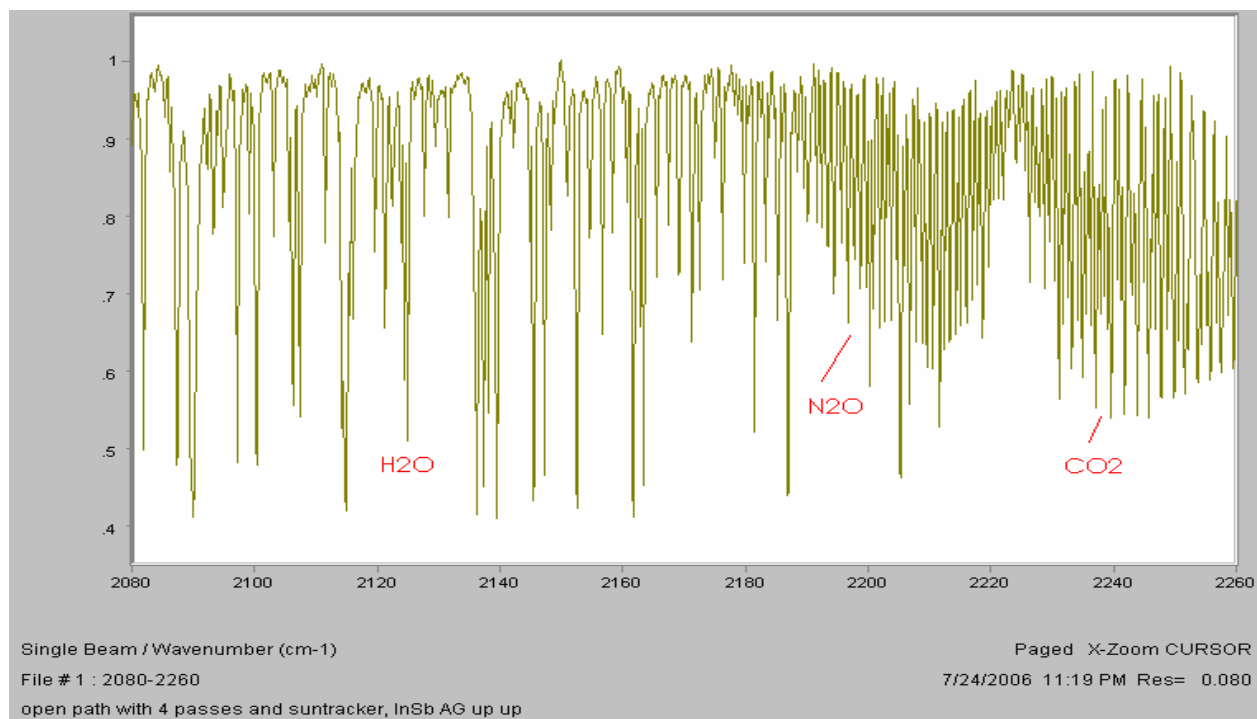


Figure 4.27 – FTIR spectrum for H₂O, N₂O and CO₂ (11:19pm)

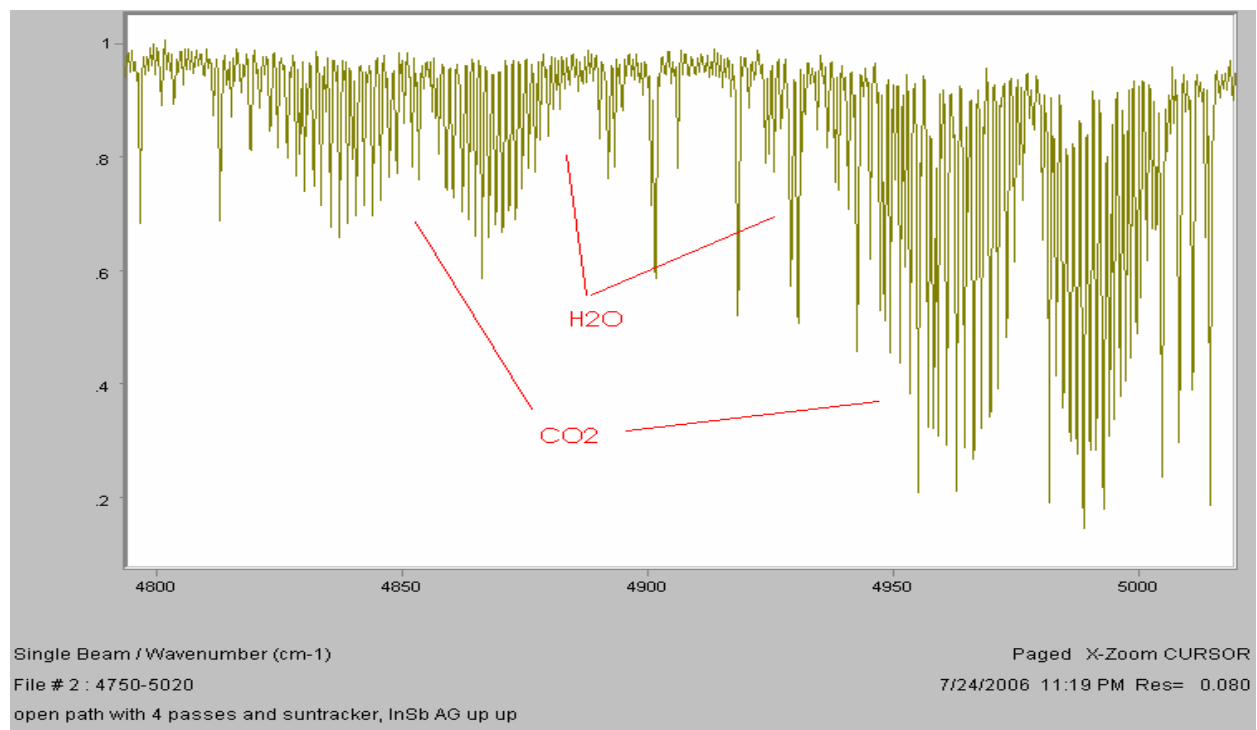


Figure 4.28 – FTIR spectrum for H₂O and CO₂ (11:19pm)

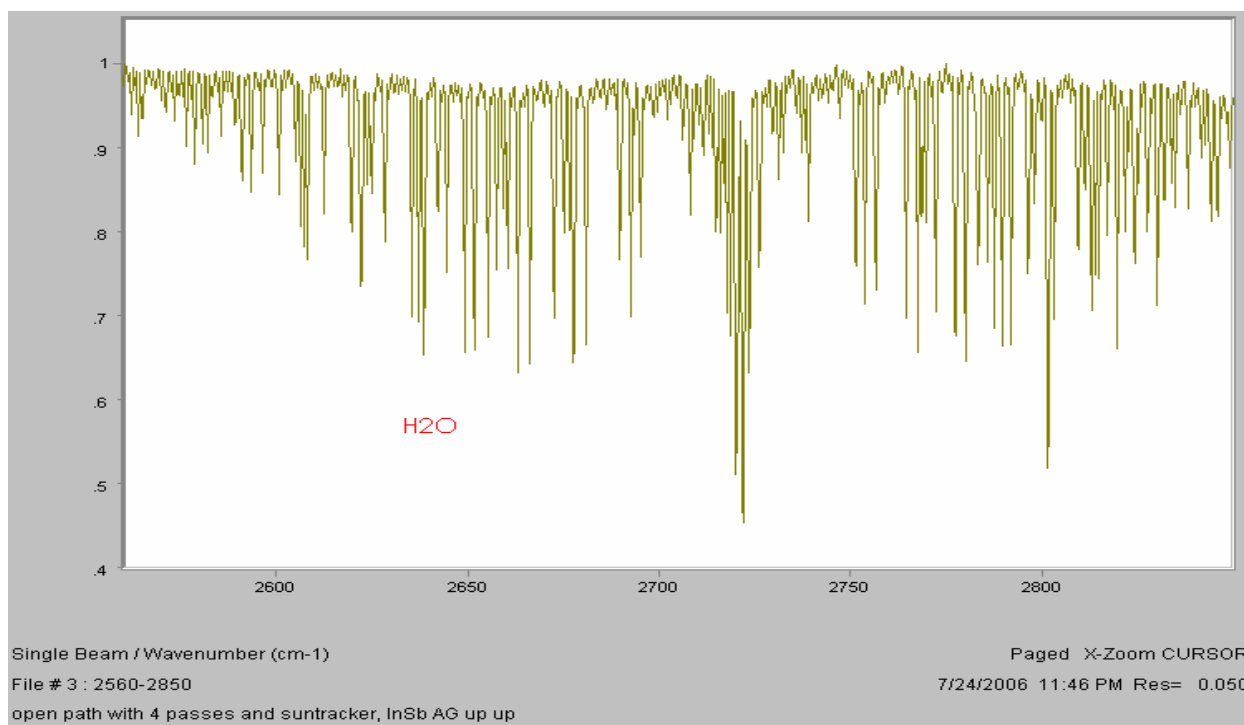


Figure 4.29 – FTIR spectrum for H₂O (11:49pm)

Table 4.9 – Concentration for the molecules (July 24th, 2006)

Molecules	Time	Concentration (parts per total)	Error	% Difference
CO	11:19pm	3.10×10^{-7}	$\pm 0.1 \times 10^{-7}$	< 24 %
	11:49pm	3.00×10^{-7}	$\pm 0.3 \times 10^{-7}$	< 20 %
H ₂ O	11:19pm	0.060	± 0.1	--
	11:49pm	0.055	± 0.3	--
N ₂ O	11:19pm	1.90×10^{-7}	$\pm 0.1 \times 10^{-7}$	> 40 %
	11:49pm	2.00×10^{-7}	$\pm 0.3 \times 10^{-7}$	> 37 %
CO ₂	11:19pm	3.50×10^{-4}	$\pm 0.1 \times 10^{-4}$	> 8 %
	11:49pm	3.52×10^{-4}	$\pm 0.3 \times 10^{-4}$	> 7 %

- July 25th, 2006: four passes on the roof and the spectrometer was set up with KBr beam splitter, MCT 500 in low, resolution 0.02cm^{-1} , aperture 3.5mm, 32 scans, base and position gain at 16. The light source used was the carbon rod. Analyzing the spectra, the molecule found in the environment was carbon dioxide, refer to figure 4.30.

The concentration of CO_2 on the atmosphere was 3.54×10^{-4} parts at 12:20pm, 3.55×10^{-4} parts at 1:12pm, and 3.56×10^{-4} parts at 1:49pm. The level for carbon dioxide has decrease by 7% and 6% relative to 379 part per million.

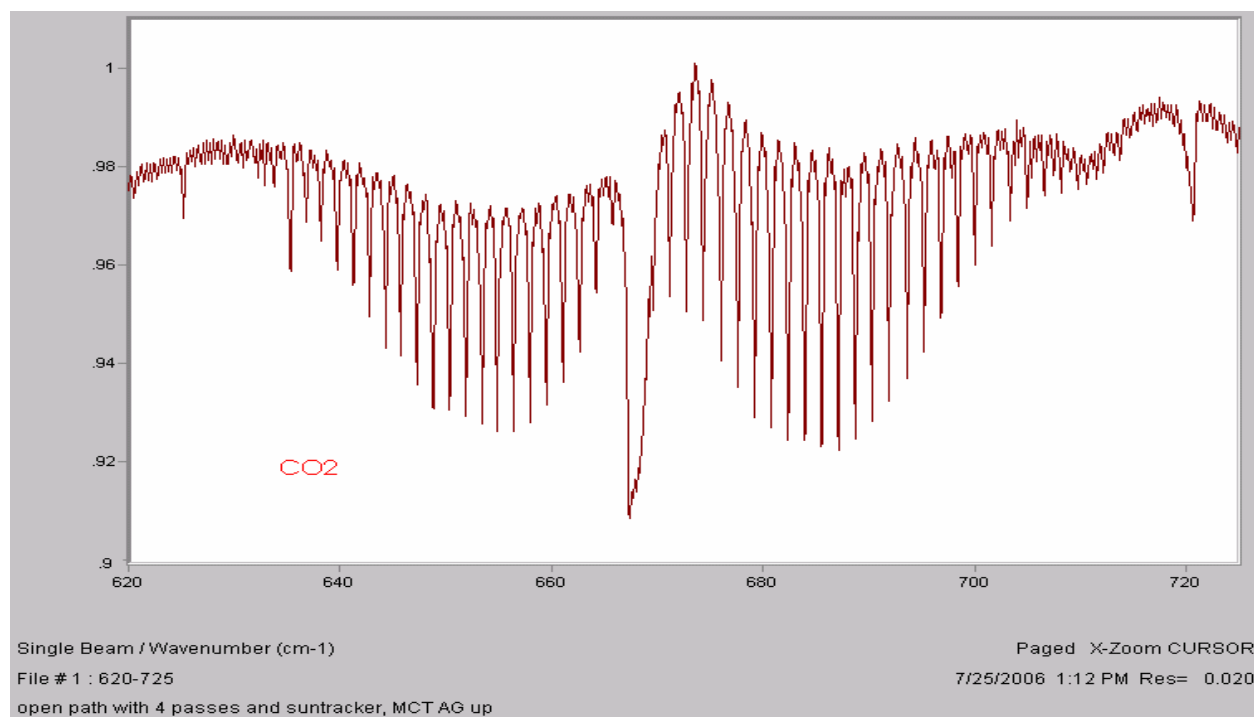


Figure 4.30 – FTIR spectrum of CO_2 (1:12pm)

Comparing both years, there is a big difference between the molecular concentrations. A graph was made with excel to express the change in concentration during two summer seasons, as seen in figures 4.31, 4.32 and 4.33.

In figure 4.31, the carbon monoxide and nitrous oxide molecules are compared between both summers (2005 and 2006). The data taken were taken between the day and the night and the concentrations changes. For CO, the higher the concentrations were taken during the morning or afternoon, where the use of automobiles was greater than during the night. For N₂O, the data was taken during the morning or afternoon and the highest points are due to the sewage treatment around the city.

In figure 4.32, the water vapor that was seen those days were high meaning that those specific days were hotter or humid than other days. In particular July 24, 2006, the concentration of the water vapor was the highest one and probably this data was taken after a raining and hot day.

In figure 4.33, the carbon dioxide data were taken during the morning and afternoon. As seen in the graph, the concentration of the CO₂ decreases during the years. It is difficult to explain the apparent decrease in CO₂ concentration except through different wind directions altering the emissions from the Bull Run Steam Plant.

All of these concentration values varied for multiple reasons, such as the humidity of the day, the wind blowing at a different speed and in a different direction each day, the time when the data was taken if it was during the morning, afternoon, and night, as well as the noise from the spectra and the fluctuation of the detectors.

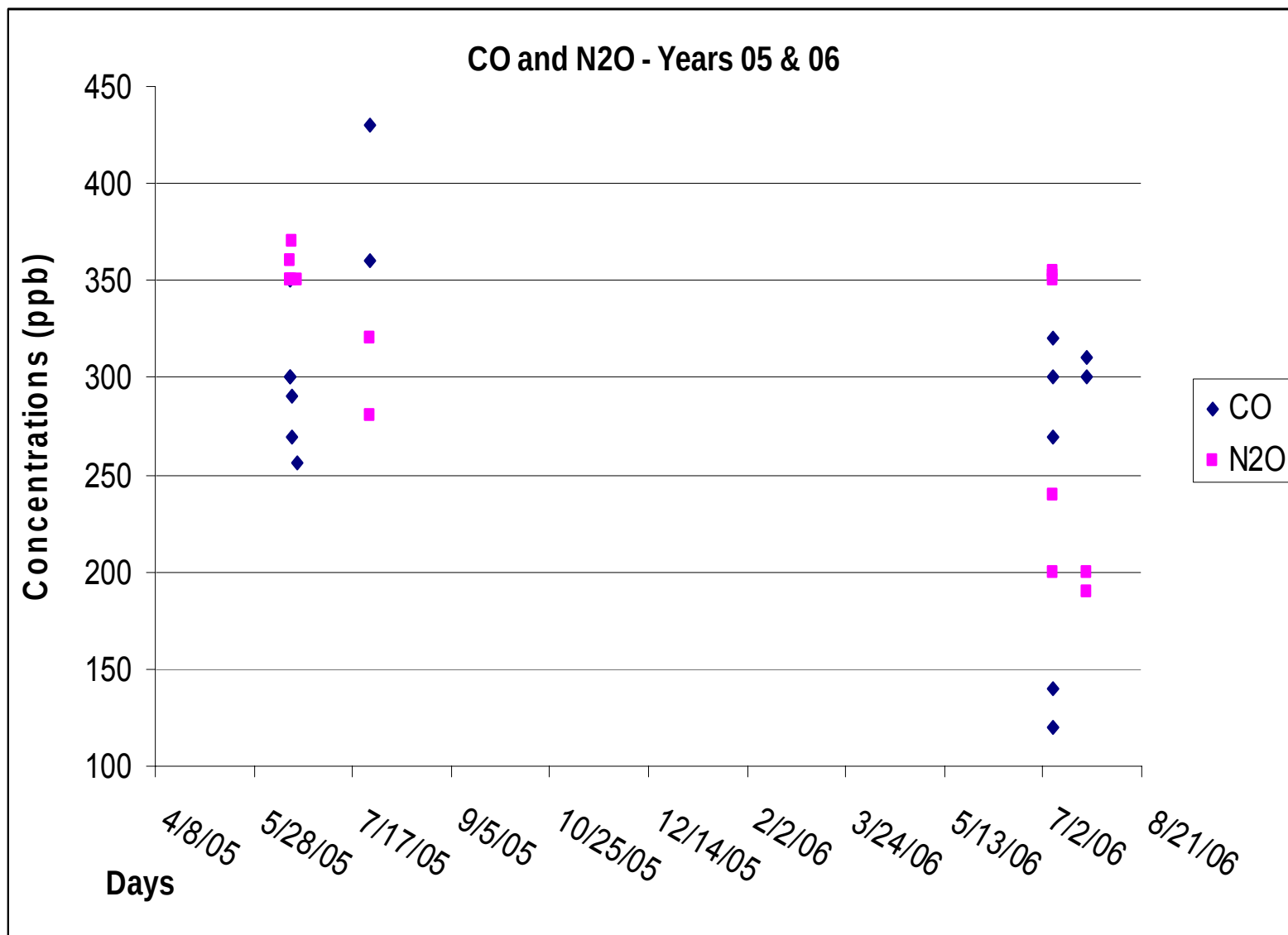


Figure 4.31 – Comparing CO, N₂O and CH₄ molecules during the summer 2005 and 2006.

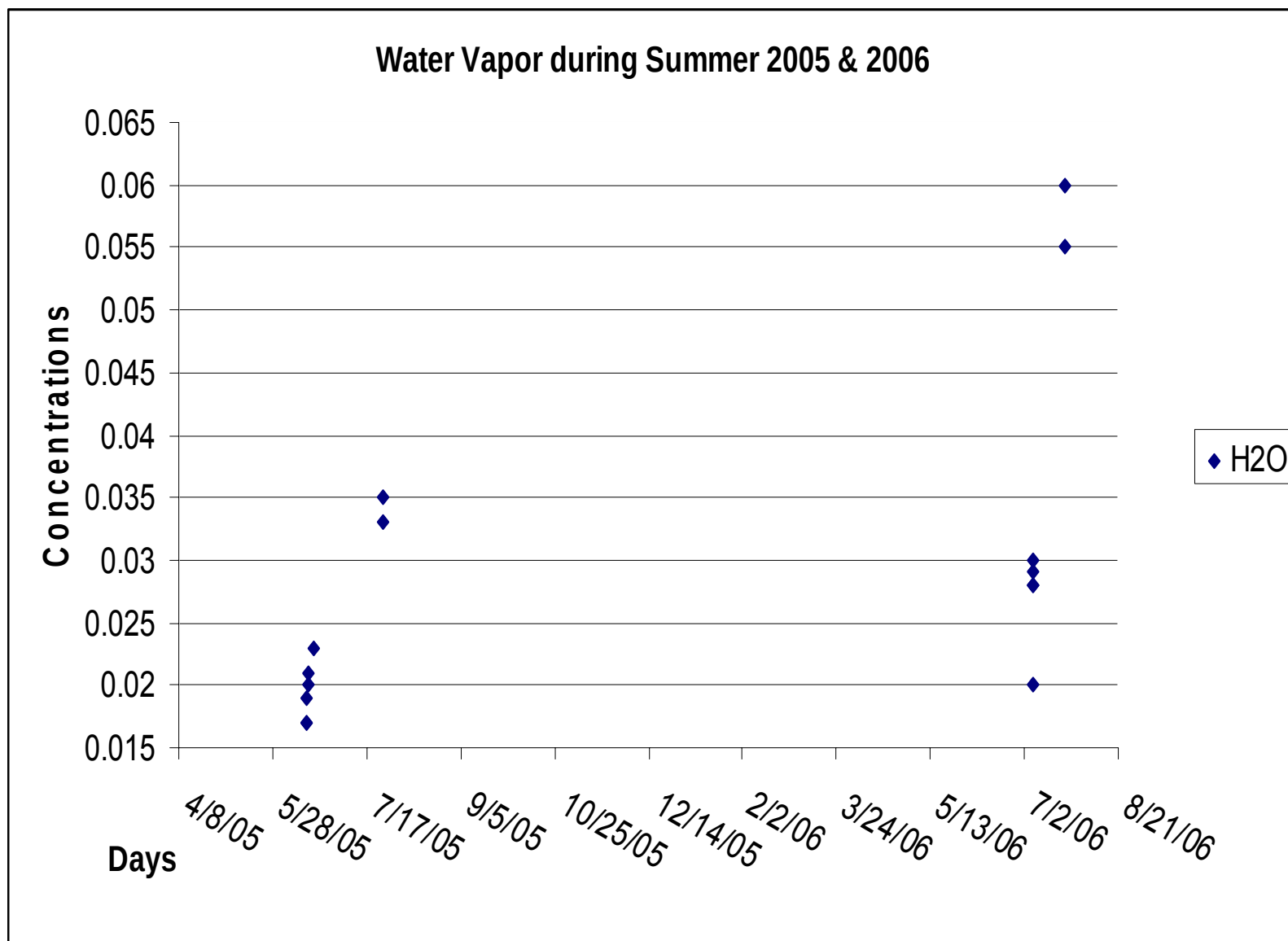


Figure 4.32 – Comparing water vapor in the air during the summer 2005 and 2006.

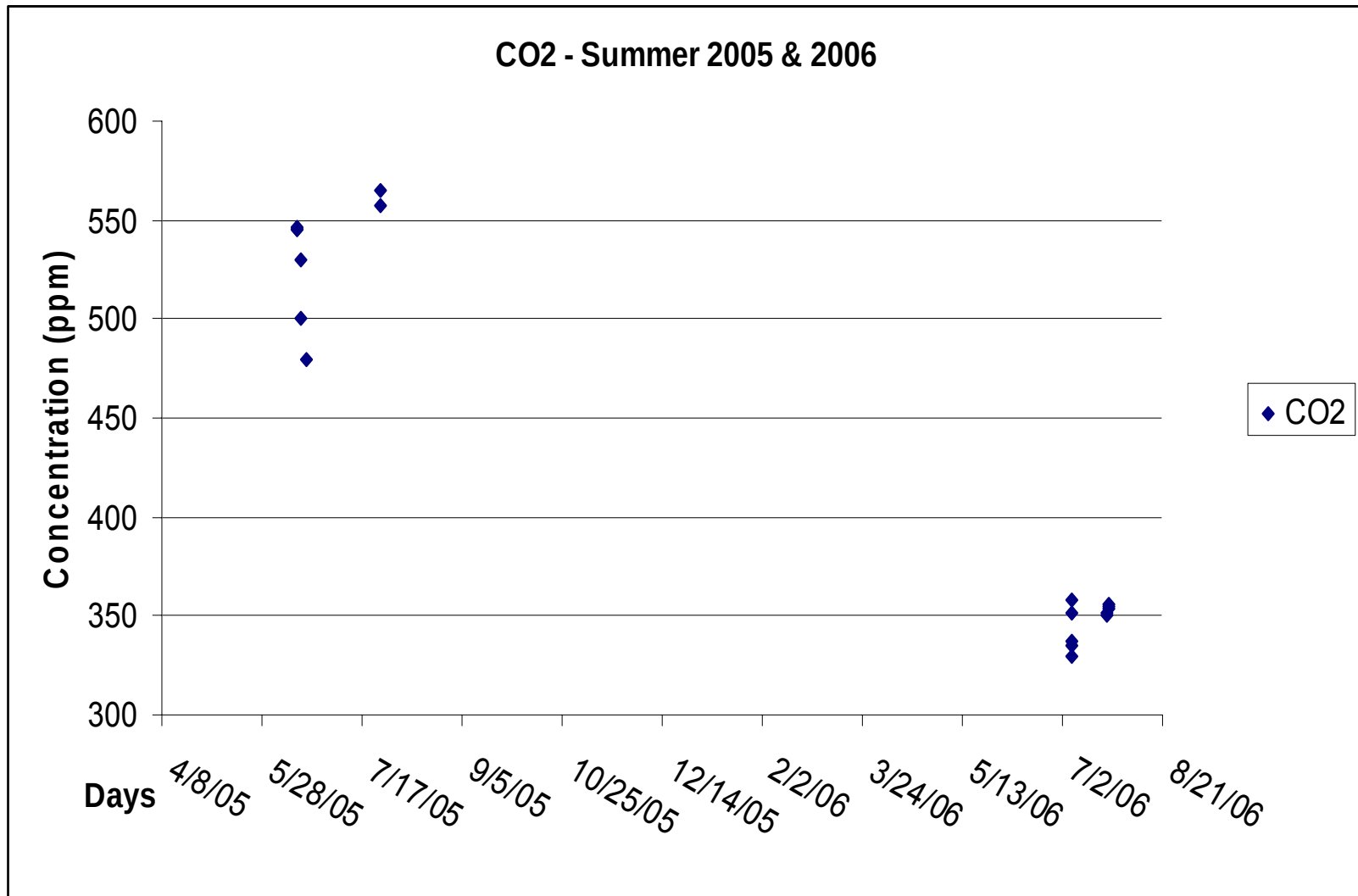


Figure 4.33 – Comparing CO₂ during the summer 2005 and 2006.

CHAPTER V

CONCLUSIONS

This thesis had two main goals: (1) to evaluate the operation of a long-pass White Cell coupled to an FTIR spectrometer for spectroscopy purposes and (2) to use FTIR as a method to record the time-dependence of various gases present in the atmosphere in Knoxville, Tennessee.

Nitrous oxide was employed in the White Cell in order to assess properties of the long pass operation of the FTIR set-up. Using nitrous oxide and changing the number of passes inside the White Cell, we calculate the approximate total path length for 12, 16 and 20 passes only knowing that the three focus mirrors inside the White Cell (refer to figure 3.6) are 1 meter apart from each other. The length between the two mirrors changes for the three different passes (12, 16, and 20 passes), the length inside the White Cell is 12, 16 and 20 meters with respect of the passes. This means that the ration between the passes 12:16:20 is equal to one. The total length of the experiment is adding 11.26 meters for each length inside the White Cell. The total path length for 12, 16 and 20 passes being 23.26 m, 27.26 m, and 31.26 m, respectively. As expected to see, an increase in the path length of the white cell increases the absorption of the molecule; comparing 23.26 meters with absorption of 0.74, 27.26 meters with absorption of 1.22, and 31.26 meters with absorption of 1.54. Under conditions in which the absorption is not saturated, this method can be used to determine unknown concentrations for a given molecular constituent.

Atmospheric infrared spectroscopy using a sun-tracker in order to identify and quantify atmospheric gases showed excellent result. Molecules which are Greenhouse gases

were found during the morning or afternoon were attributed to automobiles or factories, plus the daily activities of people.

The open path spectroscopy results were also very informative. In 2005, the concentration of a number of molecules were found to change: CO ($2.46 \times 10^{-7} - 4.5 \times 10^{-7}$), H₂O (0.017 – 0.035), N₂O ($2.8 \times 10^{-7} - 3.5 \times 10^{-7}$), and CO₂ ($4.8 \times 10^{-4} - 5.65 \times 10^{-4}$). In 2006, using the two passes set-up, the concentrations of each molecule varied: CO ($1.20 \times 10^{-7} - 4.3 \times 10^{-7}$), H₂O (0.02 – 0.03), N₂O ($1.9 \times 10^{-7} - 3.50 \times 10^{-7}$), and CO₂ ($3.3 \times 10^{-4} - 3.30 \times 10^{-4}$). Comparing data recorded over two different days during the night and one time in the morning it was found that the amount of each molecule increased the period recorded and during the different days. In 2006, using a four pass set-up, the concentrations were found to be: CO (31.0×10^{-7}), H₂O (0.06), N₂O (1.90×10^{-7}), and CO₂ ($3.50 \times 10^{-4} - 3.55 \times 10^{-4}$).

Comparing the two open path set-ups, which are the two passes and the four passes, we can conclude that there is a measurable difference between the two. It is clear that the four passes set-up is capable of obtaining a more accurate concentration reading of the molecular constituents of the air. The White cell experiment and the open-path spectroscopy have the same result as greater the path length one gets a better and higher absorption for the molecules in the environment. In the case of the White the molecules are contained in a metal cylinder in the lab (refer to figure 3.5) and for the open-path spectroscopy molecules in the troposphere are studied.

In both set-ups, the open-path spectroscopy CO₂ was present in great amounts. In 2005, carbon dioxide was between 27% and 49% greater than its expected global average concentration of 379 parts per million. In 2006, CO₂ was just in the open-path

spectroscopy 6% and 13% greater than its average concentration. The amount of H₂O detected varied depending on the weather conditions ,i.e., the humidity and temperature of the day.

These results could represent a start to focus more attention and invest more time in knowing the molecules and their concentration in the air we breathe. Future improvements could be expanding the path length of the open-path spectroscopy to include Neyland stadium or perhaps across the river, in order to include a much broader space over which the molecules can be measured.

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VITA

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Maria got her masters in physics (concentration: chemical physics) at the University of Tennessee, Knoxville in 2008.