

Atmospheric Carbon Dioxide Measurements Using a Tunable Laser Based System

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Abstract

The burning of coal and other fossil fuels releases large amounts of carbon dioxide (CO₂) into the atmosphere that can adversely affect the Earth's climate. A proposed remedy involves the capture and sequestration of CO₂ in geologic storage sites with several such carbon sequestration pilot projects underway. One requirement for a successful carbon sequestration site is the development of reliable site monitoring and verification techniques. A differential absorption instrument based on a continuous-wave (cw), tunable, distributed feedback (DFB) laser is being developed and tested at Montana State University for such monitoring. The instrument accesses the 2.002-2.004 μm spectral region that contains 4 CO₂ and 2 H₂O absorption lines. The CO₂ concentration, in parts per million, is determined by monitoring the atmospheric transmission as the laser is tuned across the molecular absorption lines. Field experiments were performed in which CO₂ was released underground using a short, vertical injection well. Measurements using the differential absorption instrument showed a background (atmospheric) CO₂ concentration of 321.5 +/- 16.7 ppm while measurements taken over the injection well site showed a concentration increased to 352.0 +/- 29.2 ppm.

I. Introduction

Fossil fuel burning has led to an increase in atmospheric carbon dioxide (CO₂) concentrations. The increased atmospheric concentration of this known greenhouse gas has potential large scale impacts on the Earth's climate through a positive radiative forcing. The concentration of CO₂ in the atmosphere reached an average level of 381 parts per million (ppm) in 2005, an increase of 2.5 ppm over 2004 [1,2]. The use of fossil fuels is predicted to grow over the next several decades with the potential for further increasing the atmospheric concentration of CO₂. A proposed method of mitigating the impacts of an increased atmospheric CO₂ concentration resulting from burning fossil fuels is to capture the CO₂, liquefy it, and store it underground in coal seams, depleted oil wells, or under saline aquifers. One important issue that requires further research and development for successful underground storage of CO₂ is the ability to monitor sequestration sites to verify the site's integrity [3].

Optical remote sensing provides one avenue for monitoring storage sites. Optical remote sensing uses a laser that is able to tune through an absorption feature associated with the molecule of interest. The wavelength associated with the absorption feature can be used to identify the molecule while the amount of the absorption can be used to determine the average concentration over the path length. CO₂ has a strong absorption band near two microns that holds promise of optical remote detection for monitoring sequestration sites. A plot of the

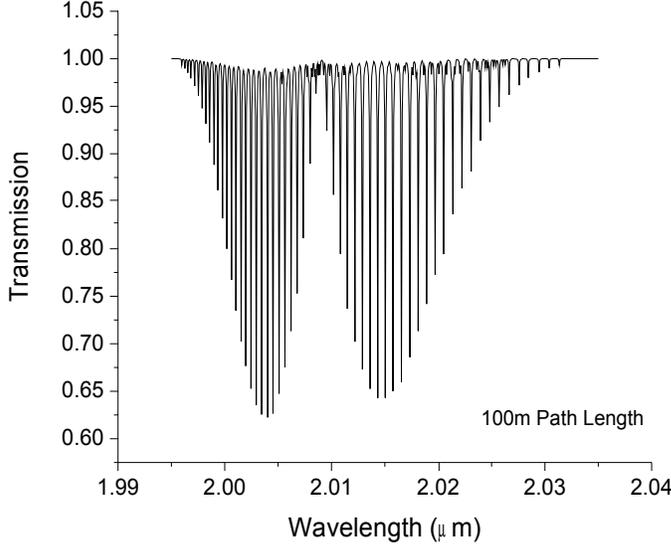


Figure 1 Absorption spectra for carbon dioxide molecule near 2 microns.

This paper is organized as follows. An overview of measuring molecular absorption is presented in section II. The design of the CO₂ differential absorption instrument for free-space measurements is presented in section III along with experimental absorption measurements of CO₂ at a controlled release experiment at the Montana State University field site. In section IV, progress towards the development of the fiber-based instrument is presented. Finally, some brief

Molecule	Wavelength	Line Intensity	Normalized Lineshape
	(μ m)	$\times 10^{-21}$ (cm/molecule)	(cm)
CO2	2.00110	0.8112	1.16
H2O	2.00122	0.00137	1.0916
H2O	2.00128	0.00066	4.5473
H2O	2.00133	0.0002	4.681
CO2	2.00156	0.9316	1.1516
CO2	2.00203	1.048	1.1401
H2O	2.00230	0.00976	0.8972
CO2	2.00251	1.153	1.1304
H2O	2.00283	0.0449	1.0596
CO2	2.00300	1.241	1.1161
H2O	2.00347	0.00071	1.296
CO2	2.00350	1.302	1.1022
CO2	2.00402	1.332	1.0842
CO2	2.00449	0.01618	1.1754
H2O	2.00449	0.01909	1.3792
H2O	2.00453	0.00608	1.4135
H2O	2.00454	0.02319	0.9622
CO2	2.00454	0.01463	1.1772
CO2	2.00455	1.322	1.0653
CO2	2.00494	0.01969	1.1703
CO2	2.00496	0.01796	1.172

Table 1 Absorption intensity and line width given per molecule and wavelength.

absorption as a function of wavelength for CO₂ is shown in figure 1. This plot was generated using the HITRAN software [4].

In this paper, we present the design of two optical instruments for differential absorption measurements of CO₂. The first instrument is based on free-space above ground measurements of the absorption due to CO₂ using a tunable diode laser. The second instrument is based on absorption measurements in an underground absorption cell also using a tunable diode laser. We envision replacing the underground absorption cell with a photonic band gap fiber to produce an all fiber underground differential absorption sensor.

concluding remarks are presented in section V.

II. Absorption Theory

Optical monitoring of CO₂ is based on the fact that CO₂ molecules absorb light at specific wavelengths. The information presented in Table 1 shows the wavelength, the line intensity, and the normalized line shape function for the molecular species that have any appreciable absorption at wavelengths accessible with the tunable diode laser used in the differential absorption instrument. The concentration of the molecule of interest can then be found using the line intensity and normalized line shape function also given in Table 1.

The normalized transmission (T) measured by the differential absorption instrument allows the determination of the concentration (C) of the particular molecular species to be calculated using the following equation [5]

$$C = \frac{P_a}{P_T} = \frac{-\ln(T)}{Sg(v-v_0)N_L\left(\frac{296}{T_a}\right)P_T L} \quad (1)$$

where T is the measured normalized transmission, L is the laser path length, S is line intensity given for a particular wavelength and molecular species, $g(v-v_0)$ is the normalized line shape function, N_L is Loschmidt's number, T_a is the path temperature in Kelvin, and P_T is the barometric total pressure.

III. Free Space Instrument

A. Instrument Description

The schematic of the free space differential absorption instrument for measuring path integrated CO_2 concentrations is shown in figure 2 and a picture of the instrument is shown in figure 3. The instrument fits on a 61 cm by 122 cm (2' x 4') optical breadboard. A distributed feedback (DFB) diode laser is used as the source for this instrument. The laser has a nominal wavelength of $2.003 \mu\text{m}$ and can be tuned via temperature. The DFB laser is packaged in a sealed TO 8 can with an integrated peltier cooler for temperature control and thermistor for temperature monitoring. Current is supplied to the diode laser with a commercial current driver while the temperature of the diode is monitored and controlled also with a commercial temperature controller with GPIB capabilities. The output of the DFB laser is collimated using an anti-reflection (AR) coated lens. Next, the beam is incident on a wedged pickoff that reflects 4% of the outgoing light through a focusing lens and onto a reference detector. An extended InGaAs detector with a responsivity cutoff of $2.2 \mu\text{m}$ is used to monitor the outgoing optical power. The detector, placed in a TO can for protection, has a thermoelectric cooler (TEC) used to stabilize the detector temperature. The TO can window is made of sapphire and has an AR coating for $2 \mu\text{m}$. The sapphire window surfaces are wedged at four degrees to prevent etalon effects. The light that passes through the wedged pickoff exits the instrument and is incident on a corner cube that can be placed to provide the desired optical path length. Light reflected from the corner cube is directed back through a focusing lens and is incident on a transmission detector that is identical to the reference detector described above. The voltage signal from both the reference and transmission detectors is

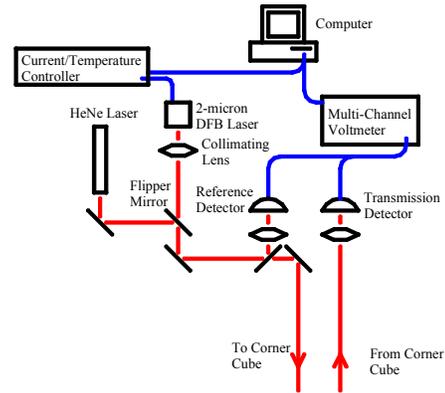


Figure 2 Schematic of the carbon dioxide differential absorption measurement instrument



Figure 3 Photograph of the optics and equipment that form the instrument.

desired optical path length. Light reflected from the corner cube is directed back through a focusing lens and is incident on a transmission detector that is identical to the reference detector described above. The voltage signal from both the reference and transmission detectors is

monitored using a multi-channel voltmeter with GPIB capabilities. Data is collected in the following manner. First, the computer sets the operating temperature of the DFB. Next, the reference and transmission detector voltages are read by the computer. The computer steps the temperature to a new value and the process is repeated. A dwell time between the temperature step and the voltage reading allows the laser operating temperature to stabilize and can be set in the data acquisition program. We have found that a one second dwell time is enough to allow the laser temperature and hence the laser wavelength to stabilize for small temperature steps. Large changes in the laser operating temperature require longer dwell times.

The flipper mirror shown in figure 2 is used to choose as the output of the instrument either the DFB laser or a HeNe laser. Two apertures (not shown in figure 2) are centered on the DFB laser beam with the flipper mirror in the down position. The flipper mirror is then placed in the up position and the path of the HeNe beam is adjusted using so the HeNe beam is also centered on the two apertures. In this way, the HeNe beam and DFB laser beam are spatially overlapped and colinear. When the instrument is taken into the field, initial alignment is completed using the HeNe beam because of the difficulty monitoring the position of a two micron laser beam. The flipper mirror is then put in the down position so that the output of the instrument is now the 2 micron beam from the DFB laser. Fine adjustments are made to first maximize the power on the reference detector and then maximize the power on the transmission detector. At this point, absorption measurements can now be made.

Measurements with the instrument have been made in the lab, outside over a green lawn and

at a test carbon dioxide injection site. The data shown in figure 4 is a plot of the transmission as a function of wavelength for an open-air path length of 77.5 m. The red line represents the measured transmission spectrum measured in a lab-type environment using the differential absorption instrument while the black line indicates the predicted transmission spectrum using the HITRAN database. The data clearly demonstrates that long laser path lengths are achievable.

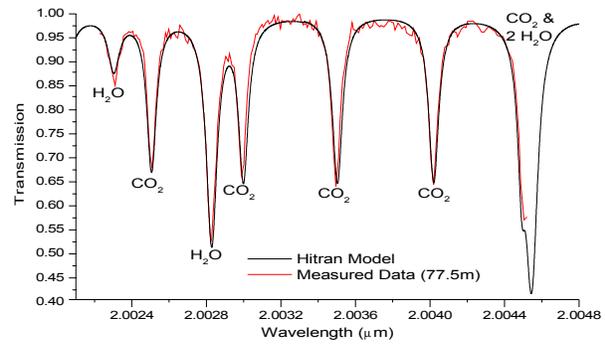


Figure 4 Data measured plotted together with data taken from the Hitran model for the same path length

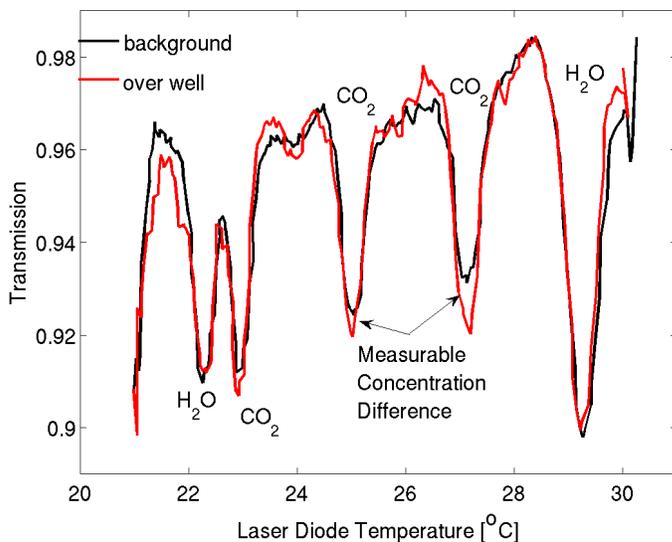


Figure 5 Data measured at the ZERT release experiment on Sep. 28th , 2006. Taken over an injection site and over the adjacent field. The change in measured transmission is evident for carbon dioxide while no change is seen in transmission for water vapor.

B. Carbon Dioxide Release Experiment

At the end of the summer in 2006, the Zero Emission Research Technology (ZERT) center sponsored two tests in which CO₂ was injected into the ground at the ZERT field site located on the Campus of Montana State University. These tests were conducted using short vertical wells (several meters deep). The wells were located in an alfalfa field near the Montana State University campus. The free-space instrument was setup up so that the laser would follow a path parallel to the prevailing winds and pass very near the injection well site. Data was taken with the instrument in this configuration. Then the instrument was moved so that the laser would follow a path perpendicular to the prevailing winds and several meters away from the injection well. The two separate laser paths were kept close to the same path length for easy comparison later. Data was taken in this configuration with the instrument. Data was taken from one site on the 28th of September, 2006 and at the other site on the 6th of October, 2006.

A plot of one set of data measured on the September 28th release date from each configuration is shown in figure 5. The red line represents measurements taken over the well while the black line represents measurements taken away from the well. The difference in transmission due to different CO₂ concentration between the two laser paths is evident in figure 5. Note that there is no change in the transmission due to water vapor as expected for the two different laser paths. Several measurements were made from which an average and standard deviations for the data were calculated. The CO₂ concentrations were found to be 321.5 +/- 16.7 ppm for over the alfalfa background versus 352.0 +/- 29.2 ppm for over the injection well.

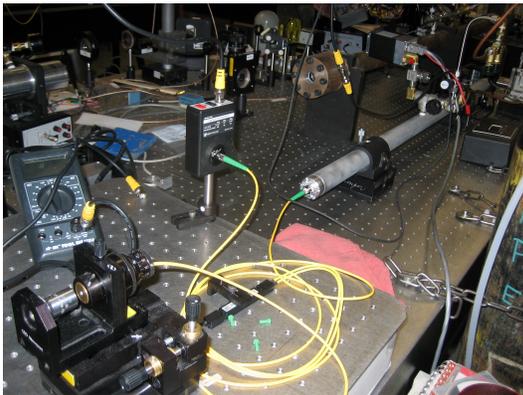


Figure 7 A picture of the underground sensor undergoing testing in the laboratory.

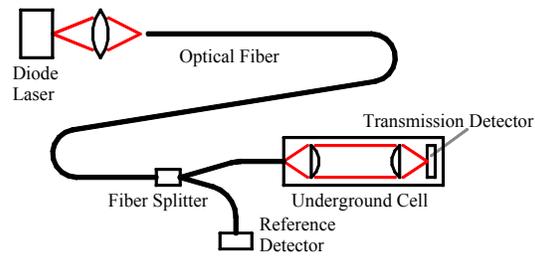


Figure 6 Schematic of the initial underground differential absorption instrument.

IV. Underground Sensor

The underground differential absorption instrument is based on the same DFB laser as the free space differential absorption instrument described in section III above. The output from the DFB laser is coupled into a standard single mode telecommunications optical fiber. At 2 μ m, the measured fiber attenuation was -21.3 dB/km indicating light can propagate about 1 km with a 1% transmission. A schematic of the below ground differential optical detector based on a 2.54 cm diameter by 100 cm long absorption cell is shown schematically in figure 6. The

shorter absorption cells are feasible to use in underground measurements because the CO₂ concentration is a factor of ten to one hundred times higher underground as in the atmosphere. A 90%/10% inline fiber splitter is used to send 10% of the fiber coupled light to a reference detector while the remaining 90% is launched into the absorption cell. Light launched into the absorption cell is monitored using a second transmission detector placed at the end of the absorption cell. A picture of the laboratory set up is shown in figure 7.

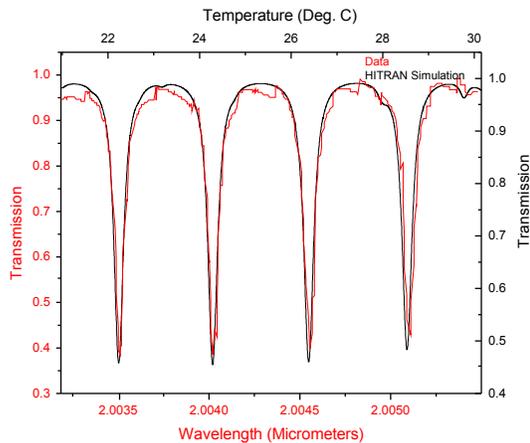


Figure 8 A plot of the transmission as a function of wavelength. The red line represents the measured transmission spectrum while the black line indicates the predicted transmission spectrum using the HITRAN database.

Initial testing of the absorption cell was completed in the laboratory in the following manner. First, a known amount of CO₂ and N₂ were placed in the absorption cell. Next, the DFB laser was tuned across several absorption lines and the normalized transmission was used to calculate the CO₂ concentration using eq. (1). A plot of the transmission as a function of wavelength is shown in figure 8 for the initial absorption cell measurements. The red line represents the measured transmission spectrum while the black line indicates the predicted transmission spectrum using the HITRAN database [4].

The next step in developing an underground sensor for differential measurements of CO₂ concentrations involves preparing the absorption cell to be placed underground. First, a series of slits will be machined into the absorption cell. The slits will then be covered with a gas permeable membrane that allows soil gases to diffuse into the absorption cell but keeps out water and dirt. Initial diffusion measurements indicate Gore-Tex will work for this purpose. Once this machining is done, the cell will be placed underground. Light will be delivered to the absorption cell via the single mode optical fiber and the reference and transmitted detectors will be monitored via BNC cables.

The final step in developing the underground differential absorption CO₂ involves replacing the absorption cell with a photonic band gap optical fiber. The core of the photonic band gap optical fiber is hollow and allows the guided laser beam to interact with the soil gases. This allows measurements of CO₂ concentrations to be made using an all optical underground fiber optic based detector.

V. Conclusion

The successful sequestration of CO₂ requires monitoring and verification capabilities for storage site integrity. An above ground differential absorption instrument for monitoring CO₂ concentrations has been developed at Montana State University. Initial testing at the ZERT field site indicates this instrument has the potential for detecting CO₂ seepage from storage sites. Work has also begun on the development of an optical fiber based differential absorption instrument for CO₂. This instrument has many potential advantages over above ground monitoring including no sunlight or changing background lighting, no wind dispersing the CO₂, no variation of CO₂ due to photosynthesis, and higher CO₂ concentrations.

Acknowledgments

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