Near-Infrared Cavity Ring-Down Spectroscopy System for CO$_2$ Isotope Detection

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Motivation: Carbon Dioxide (CO$_2$)

- Average average atmospheric concentration of ~0.039%
- By product of combustion and several natural processes
- Regulated greenhouse gas

The Keeling curve of atmospheric CO$_2$ concentrations

- Funded in part by NASA ASCENDS Program
  - Develop an understanding of the natural processes driving carbon sources and sinks.

Satellite image of global CO$_2$ concentrations
CO$_2$ Concentration Detection

- Instrument requirements:
  - Bench top proof of concept (ground based system)
  - Accurate and rapid measurements of CO$_2$ concentrations in ppm range
  - Ability to detect secondary and tertiary isotopes

- Absorption Spectroscopy
  - Beer-Lambert Law:
    Transmission = $I_1/I_0 = e^{-\alpha l}$
Absorbance = \( (1 - R) \left( \frac{\tau_0 - \tau}{\tau} \right) \)
Experimental Setup / Components

- Optics
- Sampling Cell
- Laser
- Detector
System Schematic
Laser and Collimation Package

- NTT Electronics Corporation DFB diode Laser with a fiber pigtails output
- Centered around 1604.88 nm
- Wavelength controlled by adjustment of temperature and current

- Fiber output very divergent
- Collimation lens utilized for mode matching purposes
- Approx. 1.3 mm diameter beam inside optical cavity
Acousto-Optic Modulator (AOM)

- Effectively works as an optical switch
- Radio Frequency (RF) driver inputs 40 MHz acoustic wave into AOM
- Laser light diffracts due to traveling acoustic wave
- TTL (Transistor-Transistor Logic) signal from computer turns off AOM at resonant condition
- Allows for decay time measurement out of cavity (Ring-down time)
Optical Cavity

Sampling cell/System
- 90 cm sampling cell
- Capable of sub-atmospheric pressures
- Filter out unwanted particulates
- Rotameter
- Thermocouple
- Pressure Transducer

Cavity Mirrors
- High reflective mirrors ≈ 99.995% reflective
- Mounted on flexible bellows for precise alignment
- Accurate alignment provides cavity with resonances
Primary Detector

- Parabolic focusing mirror
- Indium gallium arsenide diode
- Adjustable gain settings
• Relative wavelength calibration used for spectral fitting
• Mode match confirmation
• Comparison of Free Spectral Ranges of optical cavity and etalon
• A free spectral range is the distance between two resonant conditions

\[ FSR = \frac{c}{2nL} \]

- \( c \): speed of light
- \( n \): index of refraction
- \( L \): length

\[ \frac{FSR_{cavity}}{FSR_{etalon}} = \frac{ncavity/Lcavity}{ncavity/Lcavity} = \frac{n_{cavity}}{n_{etalon}} \]

- \( n_{cavity} \): number of cavity peaks
- \( n_{etalon} \): number of etalon peaks

\( \approx \) 14
Data Acquisition

• National Instruments DAQ card and LabView

• Various inputs and outputs were monitored and/or controlled by the data acquisition system
  
  – Inputs
  
  • Primary detector voltage
  
  • Secondary detector voltage
  
  • Triangle wave generated via function generator

  – Outputs

  • AOM trigger signal
• Laser temperature is set and current is scanned via triangle wave
• Upon experiencing resonance, the AOM is triggered off for approx. 2 milliseconds, at which point laser light is no longer entering the sampling cell
• During this time, the light decaying from the cavity is recorded and a ring-down time is found
Data Processing

- Ring-down times can be correlated to absorptions using: \[ \alpha = \frac{L}{c \cdot \tau} \]
Data Processing

- After recording multiple absorption values while scanning the laser, the Whiting approximation is used to fit a line to the data set

\[ \frac{I_\lambda}{I_{G_L}} = \left[ 1 - \frac{W_I}{W_v} \right] e^{-2.772\left( \frac{\lambda - \lambda_{G_L}}{W_v} \right)^2} + \left[ \frac{W_L}{W_v} \right] \frac{1}{1 + 4\left( \frac{\lambda - \lambda_{G_L}}{W_v} \right)^2} \]
Data Processing

- The area underneath the fit is then found using numerical integration, allowing for the calculation of a corresponding concentration value in molar fraction

\[ Concentration = \frac{A}{PSL} \]
Results

The following graphs and charts show results acquired from a CO₂ line centered at 6233.18 cm⁻¹ and taken at pressures of 0.05 and 0.15 atm.

<table>
<thead>
<tr>
<th>Pressure (atm)</th>
<th>Ave. Conc. (ppm)</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>397</td>
<td>1.8</td>
</tr>
<tr>
<td>0.15</td>
<td>382</td>
<td>1.9</td>
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</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conc. (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>398.3</td>
</tr>
<tr>
<td>2</td>
<td>399.3</td>
</tr>
<tr>
<td>3</td>
<td>396.2</td>
</tr>
<tr>
<td>4</td>
<td>396.2</td>
</tr>
<tr>
<td>5</td>
<td>396.7</td>
</tr>
</tbody>
</table>

St. Deviation: 1.3
Improving Accuracy

Currently, the system is limited in terms of accuracy. A reliable spectroscopic device must have very high accuracy. As such, one of the primary goals in the future is to improve the accuracy of this bench-top CRDS system. In general, several approaches can be considered to improve accuracy:

- Using a calibration gas or reference cell of known concentration
- Compare measured concentration values with other instruments, such as a mass spectrometer
- Compare measured concentrations with other scientists (HITRAN)
Future Plans

Equipment Modification

Additions to the current equipment will also be made. Primarily, an oscillator (piezoelectric) will be added to the back end of the sampling cell cavity mirror in hopes of slightly distorting the free spectral range and getting more data points along a feature peak.

More points increases accuracy of concentration measurements
Another goal of the system is to measure concentrations of weaker CO₂ isotopes (secondary, tertiary). Thus far, only concentrations of primary isotopes have been accurately measured. In the future, the system will be capable of measuring weaker isotopes.
Investigation of Different Wavelengths

A growing interest has been expressed by NASA to equip the CRDS system with a laser at ~1571nm. To date, only a single laser ($\lambda = 1604\text{nm}$) has been used.
Lessons Learned

• Projects ALWAYS take much longer than expected
• Do not plan for a budget that has not yet been received
• Alignment of optics is extremely time intensive
• Begin LabView programming much earlier in the project
• Spectroscopy has a very steep learning curve
• It’s important to have good group dynamics
• Consider all aspects of experimental error
References

- [http://www.tecnozono.com/CO2-dioxido-de-carbono.htm](http://www.tecnozono.com/CO2-dioxido-de-carbono.htm)
QUESTIONS?