Portable Diode Laser-Based Sensor for $^{13}CO_2/^{12}CO_2$ Isotopic Ratio Measurements

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- Motivation and Technology Issues
- Infrared Diode Laser-based Gas Sensors
- Performance Characteristics of mid-IR Sensor
- Summary

Motivation for Isotopic Ratio Measurements

- Volcanic gas emission studies. (**CO_2** H_2O, HCl, SO_2, HF, H_2S, CO), eg Colli Albani ; Solfatara; Mammoth Mt., Long Valley Caldera, CA (north of L.A.)
- Atmospheric Chemistry [Monitoring of C_y gases: **CO_2**, CO, CH_4 ...]
- Combustion diagnostics
- Non-invasive medical diagnostics (NO, CO, **CO_2**, NH_3)
- Biology (Photosynthesis)

Solfatara Crater near Pozzuoli (Naples)

Isotope Ratio Strategy

Isotopic ratios are stated in δ units defined for carbon as:

$$\delta^{13}C=\{[^{13}C/^{12}C]_{sample}/[^{13}C/^{12}C]_{std}-1\}\cdot 1000\ (^0/_{00})$$

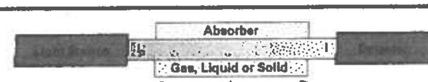
For carbon isotopes the most common standard is the Pee Dee Belemnite dolomite carbon standard $[^{13}C/^{12}C]_{PDB} = 0.011237$

To detect a δ value with an accuracy of 1 $^0/_{00}$ requires a measurement of absorbance at the 10^{-5} level when detecting two absorption lines of ~ equal intensity.

Isotope-Ratio Measurement Techniques

- Mass spectrometry (Precision: < 0.1per mil)
- Gas chromatography (GC-IRMS)
- Nuclear magnetic resonance spectrometry
- FTIR Spectrometry (~0.1-0.2 per mil)
- **Infrared absorption spectroscopy**
  - Infrared heterodyne ratiometry
  - *Laser optogalvanic spectroscopy*
  - **TDLAS spectroscopy: 3.35 μm (~0.3mil)**

Absorption Spectroscopy



Beer – Lambert's Law

$$I(\nu)=I_0\cdot e^{-\alpha(\nu)\cdot P_a\cdot L}$$

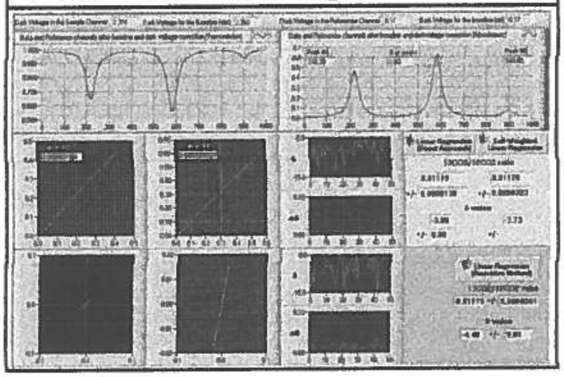
α(ν) - absorption coefficient [cm^{-1} atm^{-1}]; L – path length [cm]
ν - frequency [cm^{-1}]; P_a- partial pressure [atm]

Molecular Absorption Coefficient

$$\alpha(\nu)=C\cdot S\cdot g(\nu-\nu_0)$$

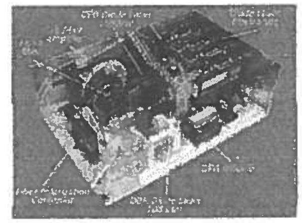
C - total number of molecules of absorbing gas/atm/cm^3 [molecule$\cdot cm^{-3}\cdot atm^{-1}$]
S - molecular line intensity [cm $\cdot$molecule^{-1}]
$g(\nu-\nu_0)$ - normalized lineshape function [cm],(Gaussian, Lorentzian, Voigt)

Labview Processing of CO_2 Spectra at 4.3µm



Future improvements

- *Modular assembly*, fiber coupled, ultra compact
- Source and detector (open path)
- Thermal management
- Solid state thermo-electric cooler
- Replace DFG source by 4.35 µm Sb diode or QC-DFB laser



Summary

- Diode Laser Based Trace Gas Sensors
  - Compact, tunable, robust (alignment insensitive),fieldable
  - High sensitivity ($<2\cdot10^{-4}$ to 10^{-5}) and selectivity (10–300 MHz)
  - Fast data acquisition and analysis
  - Detected trace gases: NH_3, CH_4, H_2CO, NO_2, N_2O, H_2O, **CO_2**, CO, NO, HCl, SO_2, C_2H_5OH, **isotopic species of $^{12,13}C$, $^{16,17,18}O$, $^{35,37}Cl$**
- Applications in Trace Gas Detection
  - Environmental monitoring: H_2CO, CO, CH_4 (NASA, NCAR, NOAA, EPA)
  - Industrial process control and chemical analysis
  - Medical diagnostics (NO, CO, **CO_2**)
- Future Directions
  - **Fiber lasers and amplifiers**
  - Longer mid-IR wavelengths with orientation patterned GaAs and **QC lasers**, detection of complex molecules
  - Cavity enhanced and cavity ringdown spectroscopy

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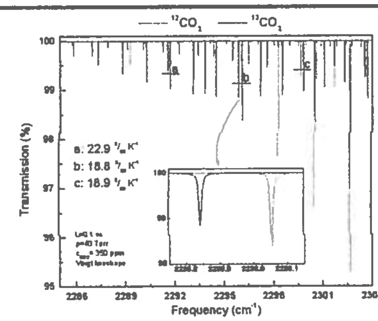
HITRAN Simulation of Suitable CO_2 Absorption Lines for Precision $\delta^{13}C$ Measurements



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Wide Range of Gas Sensor Applications

- Urban and Industrial Emission Measurements
  - Industrial Plants - Fenceline perimeter monitoring
  - Combustion Diagnostics
  - Automobile
- Rural Emission Measurements
  - Agriculture
- Environmental Monitoring
  - Atmospheric Chemistry
  - **Volcanic Emissions**
- Spacecraft and Planetary Surface Monitoring
  - Crew Health Maintenance & Life Support
- *Diagnostic and Industrial Process Monitoring*
  - Petrochemical and Semiconductor Industry
- Medical Diagnostics

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Design Features of CW DFG Sensor

- Adequate Mid-infrared DFG Power
- High Sensitivity (ppb concentrations)
- High Selectivity (<30 MHz)
- Wavelength Tunable (Single or Multiple Trace Gases)
- Fast Data Acquisition and Analysis
- Room Temperature
- Non-invasive, Point or Remote Monitoring
- Compact, Lightweight and Robust
- Power Efficient
- No Consumables , Low Maintenance and Cost Effective

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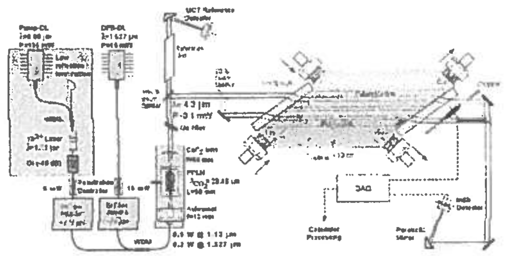
Optical Fiber Pumped Difference-Frequency Laser Source



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OSA

Long Beach, CA

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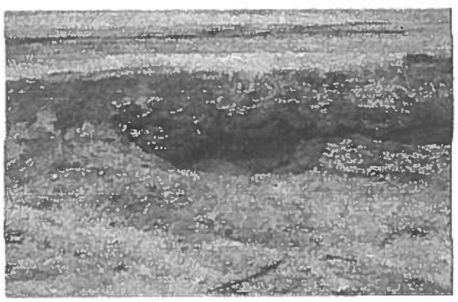

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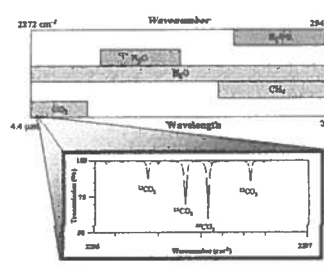
$^{12}CO_2$ and $^{13}CO_2$ HITRAN spectra at 4.3 μm



Molecule	$^{13}CO_2$	$^{12}CO_2$
Wavenumber (cm⁻¹)	2295.845	2296.057
Lower State Quanta	R16	P56
Line Strength (S) (cm mol⁻¹)	$3.579 \cdot 10^{-20}$	$4.559 \cdot 10^{-20}$
Lower Energy Level (cm⁻¹)	$1.061 \cdot 10^{2}$	$1.244 \cdot 10^{3}$
Transmission (Tr) (%)	68.2	57.4

Required Temperature Stabilization: 50 mK

Temperature Effect on Isotopic- Ratio Measurements

Absorption spectroscopy requires lines with approximately the same intensity

Natural abundance ratio of $^{13}CO_2/^{12}CO_2$ is typically 1:90

↓

To reduce the $^{12}CO_2$ line an intensity comparable with $^{13}CO_2$, a low Boltzmann factor is required. The lower energy level of the $^{12}CO_2$ transmission is significantly higher than the lower energy level of the $^{13}CO_2$ line

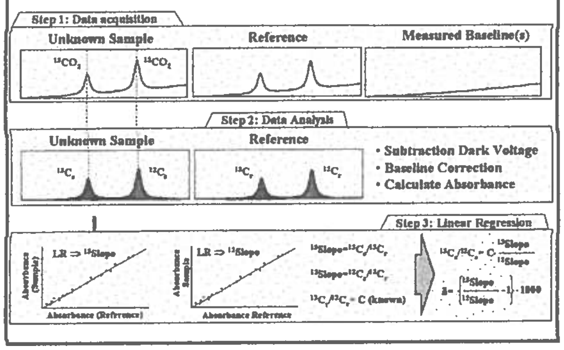
↓

Temperature sensitivity

↓

Special cell design

Implementation of Isotope-Ratio Strategy



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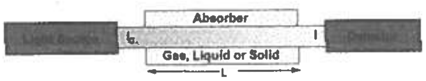

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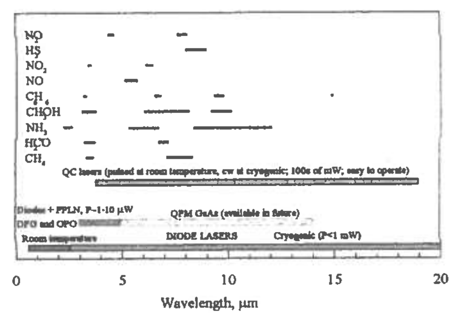
Spectral Coverage by Diode Lasers



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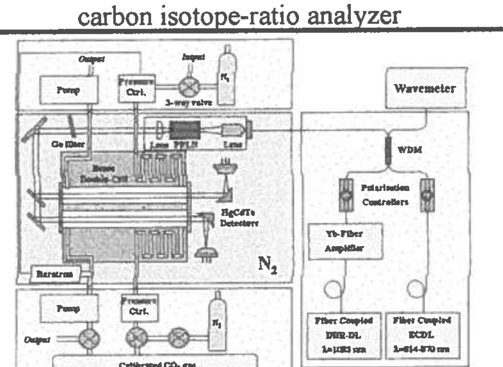
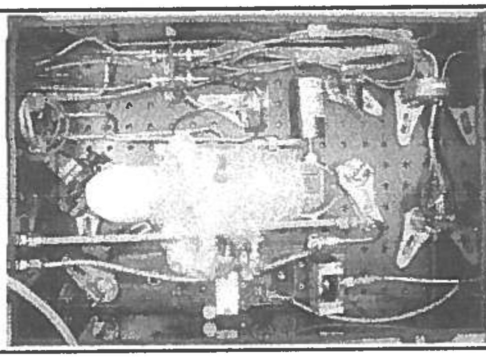
Proposed experimental set-up for DFG based carbon isotope-ratio analyzer



CO_2 Dual Absorption Cell



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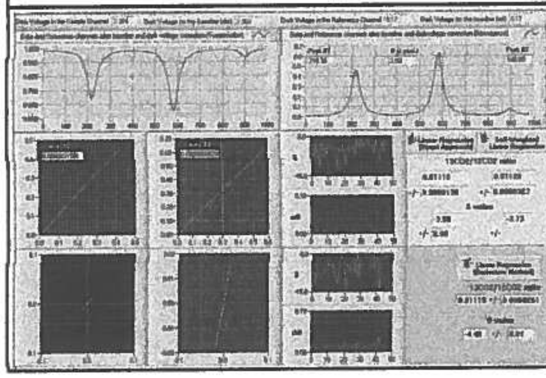

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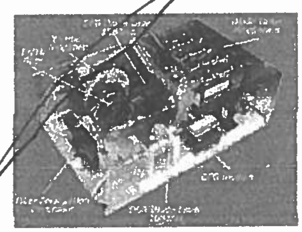

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