Portable Diode Laser-Based Sensor for $^{13}\text{CO}_2$/$^{12}\text{CO}_2$ Isotopic Ratio Measurements

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

Solfatara Crater near Pozzuoli (Naples)

Motivation for Isotopic Ratio Measurements

- Volcanic gas emission studies. (CO$_2$, H$_2$O, HCl, SO$_2$, HF, H$_2$S, CO), e.g. Colli Albani; Solfatara; Mammoth Mt., Long Valley Caldera, CA (north of L.A.)
- Atmospheric Chemistry [Monitoring of C$_3$ gases: CO$_2$, CO, CH$_4$...]
- Combustion diagnostics
- Non-invasive medical diagnostics (NO, CO, CO$_2$, NH$_3$)
- Biology (Photosynthesis)

Isotope Ratio Strategy

Isotopic ratios are stated in $\delta$ units defined for carbon as:

$\delta^{13}C = \left[ \frac{[^{13}C/^{12}C]_{\text{sample}}}{[^{13}C/^{12}C]_{\text{std}}} - 1 \right] \times 1000 \%$

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

To detect a $\delta$ value with an accuracy of 1 $\%$ 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: < 0.1 per 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 $\mu$m (~0.3 mil)

Absorption Spectroscopy

Beer – Lambert’s Law

$A(v) = -\varepsilon(v) \cdot P \cdot L$

$\varepsilon(v)$: absorption coefficient [cm$^2$ atm$^{-1}$]; $L$: path length [cm];
$P$: partial pressure [atm]

Molecular Absorption Coefficient

$\alpha(v) = C \cdot S \cdot g(v - v_0)$

$C$: total number of molecules of absorbing gas [cm$^{-3}$ atm$^{-1}$] [molecule cm$^{-3}$ atm$^{-1}$]
$g(v - v_0)$: normalized line shape function [cm$^{-1}$] (collision, Lorentzian, Voigt)
Future improvements

- Modular assembly, fiber coupled, ultra compact
- Source and detector (open path)
- Thermal management
- Solid state thermoelectric 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 (<0.1% to 10^-7) and selectivity (10-300 MHz)
  - Fast data acquisition and analysis
  - Detected trace gases: NH3, CH4, H2CO, NO2, N2O, H2O, CO2, CO, NO, HCN, SO2, CH3OH, isotopic species of 13C, 14CH4, 12CH3

- Applications in Trace Gas Detection
  - Environmental monitoring: H2CO, CO, CH4 (NASA, NCAR, NOAA, EPA)
  - Industrial process control and chemical analysis
  - Medical diagnostics (NO, CO, CO2)

- 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

HITRAN Simulation of Suitable CO2 Absorption Lines for Precision Δ13C Measurements

Wide Range of Gas Sensor Applications

- Urban and Industrial Emission Measurements
  - Industrial Plants - Fenceline perimeter monitoring
  - Combustion Diagnostics
  - Automobiles
  - 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

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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For carbon isotopes the most common standard is the Pee Dee Belemnite dolomite carbon standard $^{13}C/^{12}C_{\text{PDB}} = 0.011237$
To detect a $\delta$ value with an accuracy of 1 $\%_{\text{o}}$ requires a measurement of absorbance at the $10^{-6}$ level when detecting two absorption lines of ~ equal intensity.

Isotope-Ratio Measurement Techniques

- Mass spectrometry (Precision: < 0.1per mil)
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- FTIR Spectrometry (~0.1-0.2 per mil)
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  - Infrared heterodyne ratiometry
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$^{12}$CO$_2$ and $^{13}$CO$_2$ HITRAN spectra at 4.3 $\mu$m
Temperature Effect on Isotopic-Ratio Measurements

Absorption spectroscopy requires lines with approximately the same intensity. Natural abundance ratio of $^{12}$CO/$^{13}$CO is typically 1:90.

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

Temperature sensitivity

Special cell design

Absorption Spectroscopy

Beer - Lambert's Law

\[ \varepsilon(v) \text{ - absorption coefficient (cm$^2$ atm$^{-1}$)} \]

\[ \text{I} = I_0 e^{-\varepsilon(v)L} \]

\[ \varepsilon(v) = \frac{\varepsilon \sigma(v)}{N_p} \]

\[ \text{Beer - Lambert's Law} \]

\[ \text{Path length (cm)} \]

Molecular Absorption Coefficient

\[ \alpha(v) = C \cdot S \cdot g(v) \]

C - total number of molecules of absorbing gas atm$^{-1}$ [molecule cm$^2$ atm$^{-1}$]

S - molecular line intensity [cm molecule$^{-1}$]

$g(v)$ - normalized lineshape function [cm$^{-1}$] (Gaussian, Lorentzian, Voigt)

Spectral Coverage by Diode Lasers

Design Features of CW DFG Sensor

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- High Sensitivity (ppb concentrations)
- High Selectivity (<30 MHz)
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Proposed experimental set-up for DFG based carbon isotope-ratio analyzer

Implementation of Isotope-Ratio Strategy
**Summary**

- **Diode Laser-Based Trace Gas Sensors**
  - Compact, tunable, robust (alignment insensitive, fieldable)
  - High sensitivity (<2×10⁻⁶ to 10⁻⁵) and selectivity (10–300 MHz)
  - Fast data acquisition and analysis
  - Detected trace gases: NH₃, CH₄, H₂O, NO₂, NO, H₂O, CO₂, CO, NO, HCl, SO₂, C₂H₅OH, isotopic species of H₂, D₂, CO₂, HCl

- **Applications in Trace Gas Detection**
  - Environmental monitoring: H₂, CO, CO₂, CH₄ (NASA, NCAR, NOAA, EPA)
  - Industrial process control and chemical analysis
  - Medical diagnostics (NO, CO, CO₂)

- **Future Directions**
  - Fiber lasers and amplifiers
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