Laser-Based Sensor Technology for High Precision $^{13}CO_2/^{12}CO_2$ Isotopic Ratio Measurements

RICE

Frank K. Tittel, Chad Roller, K.Uehara and Robert F.Curl

Rice University
Houston, TX

fkt@rice.edu
http://www.ruf.rice.edu/~lasersci/

OUTLINE

Biocomplexity Kick-off Meeting
October 10-11, 2002
NCAR
Boulder, CO

- Motivation and Technology Issues
- Background of Previous Related Experience
- Concept of mid-IR Sensor Architecture
- Rice Biocomplexity Research Objectives

Milestones of Collaboration between APOL- NCAR and LSG-Rice

- David Lancaster, Alan Fried, Bryan Wert, and Frank Tittel,"DFG based tunable absorption spectrometer for detection of atmospheric HCHO Applied Optics 39, 4436-4443, 2000
- NOAA Grant 2000-2002 , PIs: A.Fried, F.Tittel, B.Henry, and J.R.Drummond " Development of Advanced Instrumentation for Airborne Measurements of HCHO using DFG
- Dirk Richter, Alan Fried, Bryan Wert, James Walega and Frank Tittel, Applied Physics B, October 2002
- M.Erdelyi, D.Richter and F.K.Tittel, Applied Physics B, October 2002
- **NSF Grant 2002-2005**, PIs: D.J. Carlson, A.Fried, D.Richter, F.K.Tittel and J.W.White," **High-Precision $^{13}CO_2/^{12}CO_2$ Ratio Measurements using an Optical Fiber Based DFG Laser Source"**

Motivation for Isotopic Ratio Measurements

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

Rice NSF Biocomplexity Research Objectives (2002-2004)

- Support APOL-NCAR Effort (**Roller**, Curl and Tittel)
  - Development of optimal signal processing algorithms of CO_2 spectra based on NCAR and Rice DFG based sensors (Year 1)
  - Investigation of materials compatibility in design of sample and reference CO_2 flow system and absorption cells (Year 1)
  - Participation in sensor design and performance tests of NCAR DFG based 4.3 μm sensor (Years 1 and 2)
- Develop QC Laser Based Isotopic Ratio Measurements (**to be named postdoc, Roller, Uehara, Kosterev**, Curl and **Tittel)**
  - Determine optimal CO_2 absorption lines (Year1)
  - Design and test prototype CO_2 sensor (Year 1)
  - Demonstrate measurement precision and long term stability for volcanic isotopic CO_2 emission monitoring (Year 2)
  - Educational Activities (Tittel, Curl, Uehara, Fraser)

Measurement Strategy of Isotopic Abundance Ratios

Isotopic ratios are stated in δ units and in the case of carbon is defined as:

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

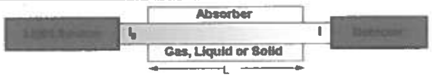
For carbon isotopes the most common standard is the Pee Dee Belemnite dolomite carbon standard $[^{13}C/^{12}C]_{PDB} = 0.011237$

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

- Isotope Ratio Mass Spectrometry (IRMS) Precision: ~ 0.01per mil
- Gas chromatography (GC) -IRMS
- Nuclear magnetic resonance spectrometry
- FTIR Spectrometry (~0.1-0.2 per mil)
- **Infrared absorption spectroscopy**
  - Infrared heterodyne ratiometry
  - Non-dispersive infrared spectroscopy
  - Laser optogalvanic spectroscopy
  - **TDLAS spectroscopy:** δ ($^{13}CO_2$) ~ 0.2mil

Measurement Principle of Absorption Spectroscopy



Beer – Lambert's Law

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

$\alpha(\nu)$ - 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·cm^{-3}·atm^{-1}]
S - molecular line intensity [cm·$molecule^{-1}$]
$g(\nu - \nu_0)$ - normalized lineshape function [cm], (Gaussian, Lorentzian, Voigt)

Sensitivity Enhancement Techniques

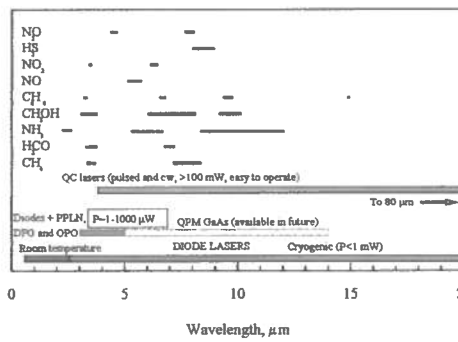
- Optimum Absorbing Transition
  - Overtone or Combination Band
  - **Fundamental Band**
- Long Pathlength
  - Multipass Cell
  - Cavity Enhanced, Cavity Ringdown
  - Open Path [with retro-reflector]
  - Fiberoptic Evanescent Wave Spectroscopy
- Detection Schemes
  - Frequency Modulation, Wavelength Modulation, Two-tone frequency modulation
  - **Balanced Detection**
  - **Zero-air Subtraction**

RICE

CW IR Source Requirements for Spectroscopy

REQUIREMENTS	SOURCE
• Sensitivity	• Power
• Specificity	• Line Width
• Multi-gas Components	• Tunable
• Directionality	• Beam Quality
• Rapid Data Acquisition	• Fast Response
• Room Temperature	•No Consumables

Spectral Coverage by Diode & QC Lasers



RICE

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

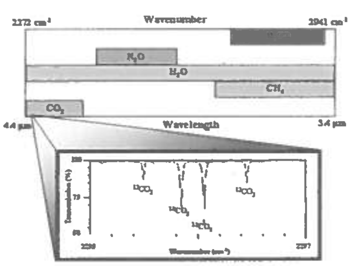
↓

Temperature sensitivity

↓

Special cell design

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



$$C[ppm] = \frac{\ln\left(\frac{100}{Tr}\right) \cdot \pi \cdot \gamma(T) \cdot \left(\frac{T}{296}\right) \cdot 10^6}{S(T) \cdot N_L \cdot P \cdot L}$$

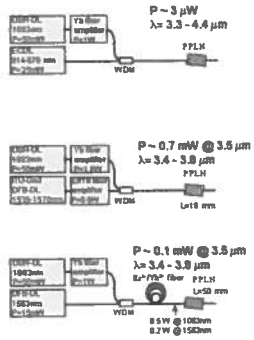
Molecule	$^{13}CO_2$	$^{12}CO_2$
Wavenumber (cm^{-1})	2295.845	2296.057
Lower State Quanta	R16	P56
Line Strength (S) (cm mol^{-1})	$3.579 \cdot 10^{[illegible]}$	$4.559 \cdot 10^{[illegible]}$
Lower Energy Level (cm^{-1})	$1.061 \cdot 10^{3}$	$1.244 \cdot 10^{3}$
Transmission (Tr) (%)	68.2	57.4

Required Temperature Stabilization: $30 \frac{mK}{‰}$

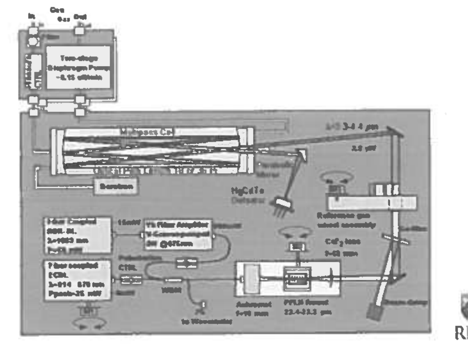
Two DFG Based Gas Sensing Approaches

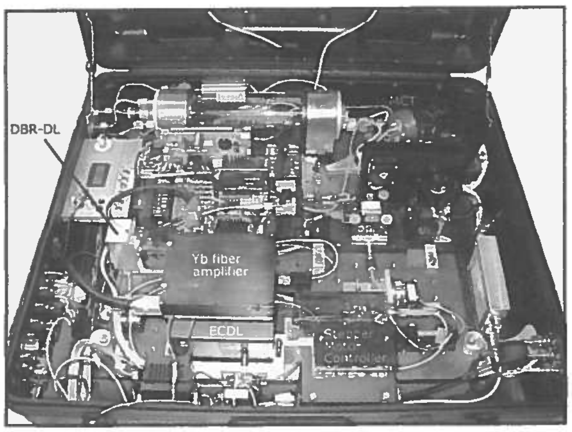
Multi-species detection:
- widely tunable: 3.3-4.4μm
- moderate DFG power
- good sensitivity

Single-species detection:
- ITU-diode laser selection
- high DFG power
- high sensitivity

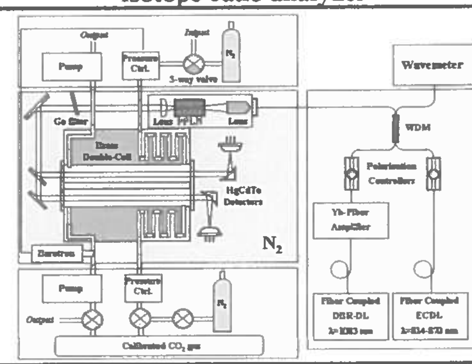


Automated Multi-Component Gas Sensor

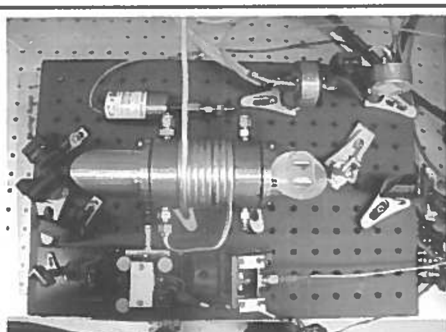




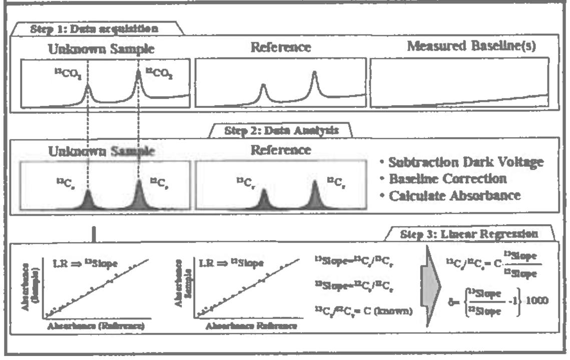
Experimental set-up for DFG based carbon isotope-ratio analyzer



CO_2 Dual Absorption Cell



Implementation of Isotopic Abundance Ratio Measurement Strategy

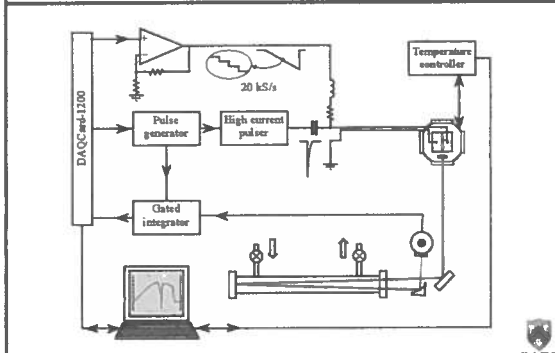


Key Characteristics of Quantum Cascade Lasers

- Laser wavelengths cover entire range from 3.5 to 66 μm determined by layer thickness of same material
- Intrinsically high power lasers (determined by number of stages)
  - CW:~100 mW @ 80°K, mWs @300 °K
  - Pulsed: 1 W peak at room temperature, ~50 mW avg. @ 0 °C (up to 80 % duty cycle)
- High Spectral purity (single mode: <kHz - 330MHz)
- Wavelength tunable by current or temperature scanning
- High reliability: low failure rate, long lifetime, robust operation and reproducible emission wavelengths

RICE

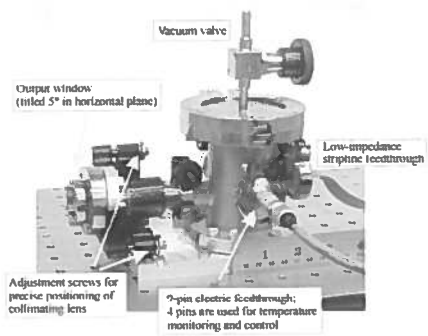
Pulsed QC Laser Based Gas Sensor



A. Kosterev et al, Applied Optics 41, 573 2002

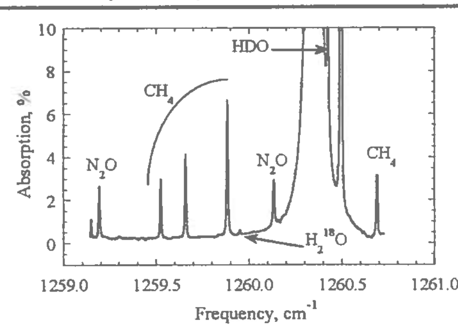
RICE

QC Laser Housing



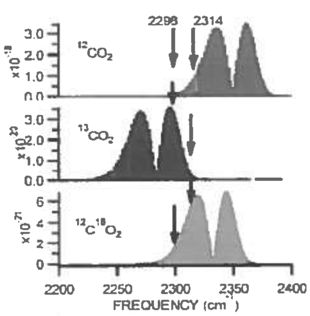
RICE

Absorption Spectrum of Room Air



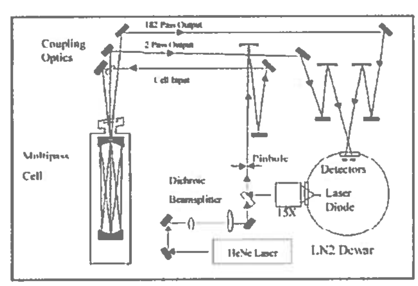
RICE

Spectral lines of CO_2 isotopes at 4.3 μm (2300 cm^{-1})



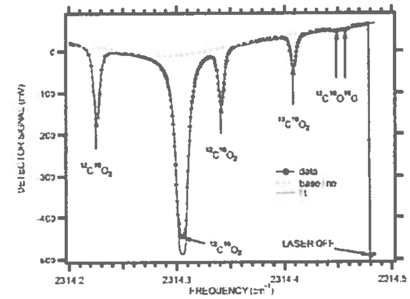
J B McManus et al Spectrochemica (2002)

TDLAS Based for Isotopic Ratio Measurements



J B McManus et al Spectrochemica (2002)

TDL spectrometer scan near 2314 cm^{-1}, showing CO_2 isotopomer lines for ($^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{13}C^{16}O^{18}O$)



J. B. McManus et al. Spectrochemica (2002)

Summary

- **Mid-IR DFG Based Isotopic Ratio CO_2 Sensor at 4.35 µm**
  - Compact, tunable, modular, robust (alignment insensitive), fieldable
  - High sensitivity ($<2 \cdot 10^{-4}$) and selectivity (<30 MHz)
  - Fast data acquisition and analysis
- **Applications of $^{13}CO_2/^{12}CO_2$ Isotopic Ratio Measurements**
  - Atmospheric chemistry (monitoring of C_y gases with a δ of 0.1 mil)
  - Volcanic gas emission studies in US and Italy
    - Strategy considerations and implementation of CO_2 isotopic ratio measurements
  - Medical diagnostics
- **Future Directions**
  - Optical fiber pumped DFG based spectroscopic laser source using most recent advances in photonic device technology
  - Comparison of a DFG source by 4.35 µm DFB-QC laser

RICE