Infrared laser based sensor technology for $^{13}CO_2/^{12}CO_2$ isotopic ratio measurements: opportunities and challenges

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OUTLINE

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- Motivation for measuring $^{13}CO_2/^{12}CO_2$ Isotopic Ratios
- Selection of optimum CO_2 Absorption Line Pairs
- Quantum Cascade Laser based Sensor Design in the 2300 cm^{-1} Spectral Region
- Current Status of QCL based CO_2 Isotopic Ratio Spectrometer
- Future Outlook and Conclusions

Motivation for Measuring $^{13}CO_2/^{12}CO_2$ Isotopic Ratios

- Volcano eruption forecasting and gas emission studies (CO_2,HCl,SO_2,HF,H_2S,CO,H_2O)
- Atmospheric Chemistry: Environmental monitoring of C_y gases (CO_2,CO,CH_4)
  - Global warming studies
    - Temporal and spatial variations of the isotopic ratios
    - Identification of carbon sources and sinks
  - Global carbon budget studies
- Study of planetary gases (CO,CO2,H_2O,NH_3)
- Medical applications (Non-invasive breath analysis)
- Combustion diagnostics
- Biology (Photosynthesis)

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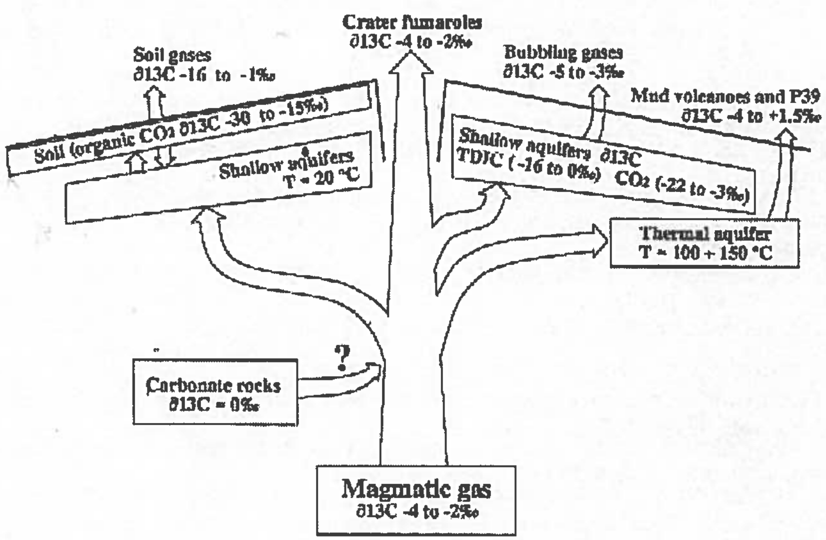
Volcanological application

- CO_2 the most abundant component of volcanic gases after H_2O
- $\delta^{13}C$ is a sensitive tracer of magmatic vs. hydrothermal or groundwater contributions to volcanic gases
- Monitoring $\delta^{13}C$ can be used in eruption forecasting



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Isotopic Ratio Measurement Techniques

- Current standard technique: Isotope Ratio Mass Spectrometry (IRMS) $\Delta\delta \sim 0.01\text{-}0.05\ ^{0}/_{00}$
  - Small mass differences are difficult to measure
  - Not real time
  - Not field deployable
  - Complex sample preparation and sample destruction
- Fourier Transform Spectroscopy $\Delta\delta \sim 0.1\text{-}0.2\ ^{0}/_{00}$
  - Not selective for compact and intermediate sized platform
- Tunable Laser Absorption Spectroscopy $\Delta\delta \sim 0.2\ ^{0}/_{00}$
  - Lead salt lasers
  - Difference Frequency Generation
  - Near-infrared diode
  - mid-infrared quantum cascade lasers

Requirements for a Field Deployable CO_2 Isotopic Ratio Sensor

- General design features for an isotopic ratio sensor include:
  - High precision
    - Temperature stability of cell
    - Pressure stability
    - Humidity effects due to CO_2-H_2O collision broadening
    - Real-time measurements and self calibrating
  - Rugged, compact construction for field use
    - Portable and easy to use by a single operator
    - Low power consumption
    - Low cost
  - Low maintenance
    - Room temperature (TEC) operation with DFB QC lasers
    - Room temperature (TEC) detectors.
- Need to reduce pressure broadening by means of extractive sampling
- Calibration capability (zero and reference standards)
- Availability of lasers may limit choice of operating lines and impact cell design

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Target Specifications for CO_2 Isotopic Ratio Sensor

- The CO_2 isotope spectrometer will have a precision in $\delta^{13}CO_2$ of 1‰ or better

- Adding a third channel would improve precision to $0.1^0/_{00}$ by canceling pulse-to-pulse fluctuations

Parameter	CO_2 Isotope Sensor	
	$^{12}CO_2$	$^{13}CO_2$
Range	0 to 1000 ppmv	0 to 10 ppmv
Precision	$\leq$ 0.3 ppmv	$\leq$ 0.004 ppmv
Size	40x40x50 cm^3	

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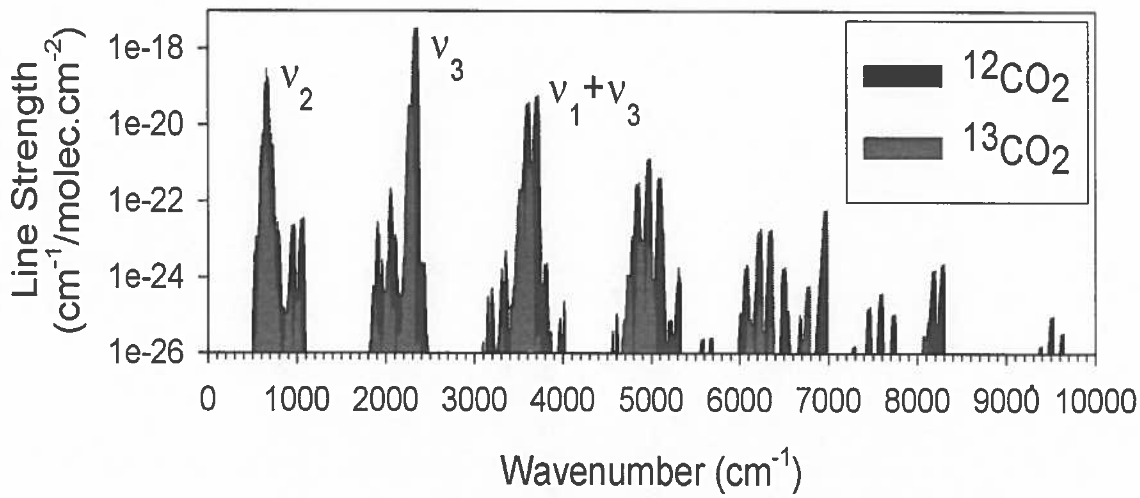
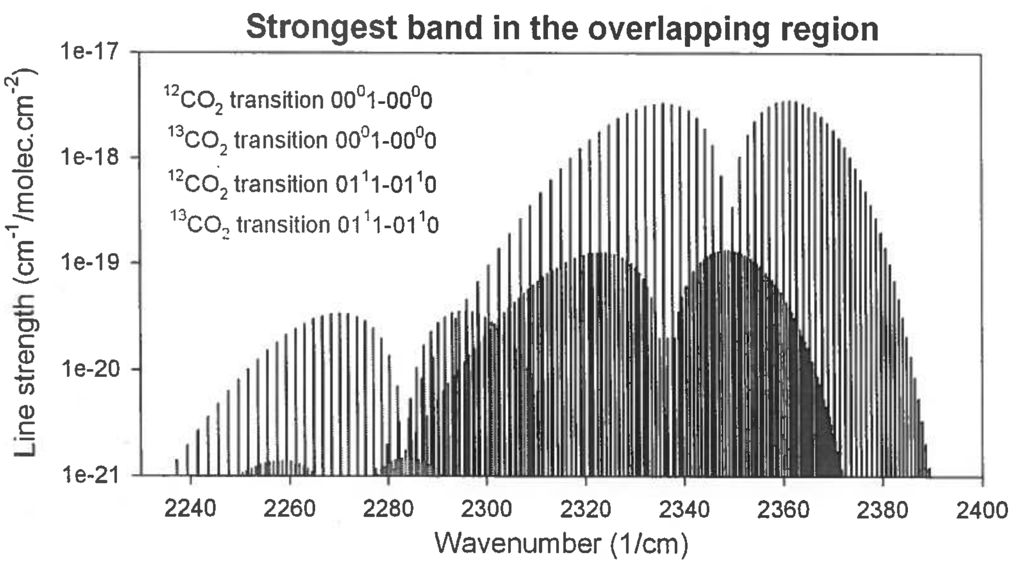
CO_2 Absorption Line Selection Criteria

- Two strategies:
  - Similar strong absorption of $^{12}CO_2$ and $^{13}CO_2$ lines
    - Very sensitive to temperature variations
  - Similar transition lower energies
    - Requires a dual path length approach to compensate for the large difference in concentration between major and minor isotopic species
- Both absorption lines must lie in a laser frequency scan window
- Avoid presence of other interfering atmospheric trace gas species

Ro-vibrational bands suitable for $^{12}CO_2/^{13}CO_2$ ratio measurements





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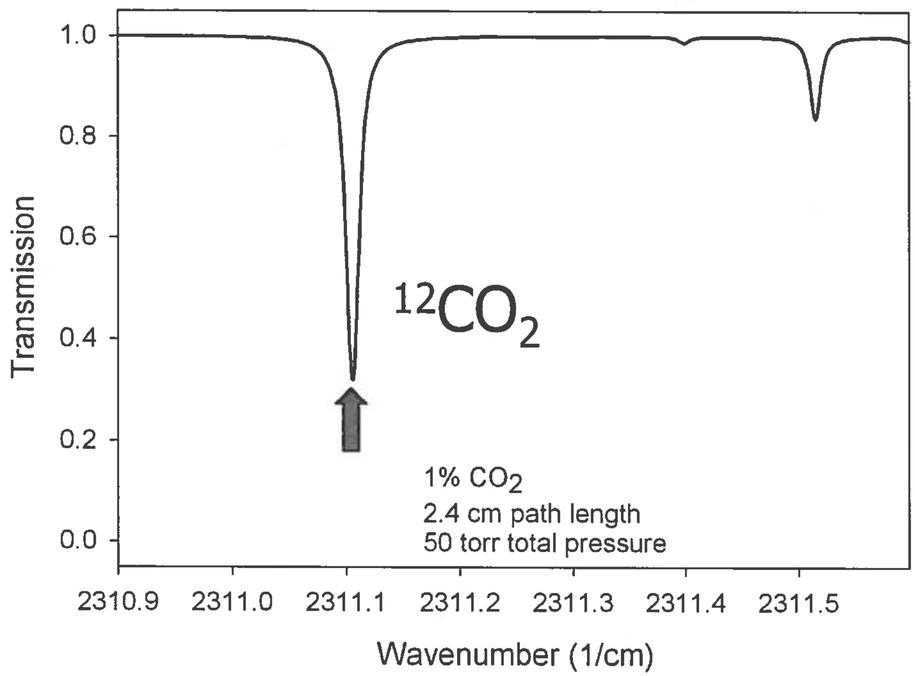
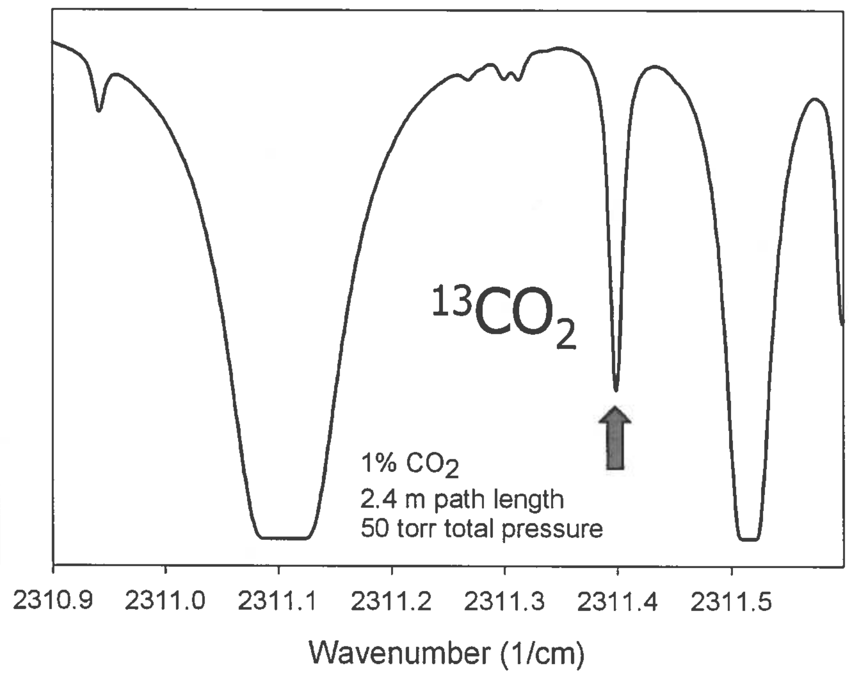
HITRAN Simulation of Selected 2311 cm^{-1} CO_2 Lines

(Dual path length approach)

Calculations for CO_2 present in volcanic fumarolic gases





- 2.4 cm path length

Measurement of [$^{12}CO_2$]

- 2.4 m path length

Measurement of [$^{13}CO_2$]

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Pulsed Quantum Cascade Lasers: Advantages and Drawbacks

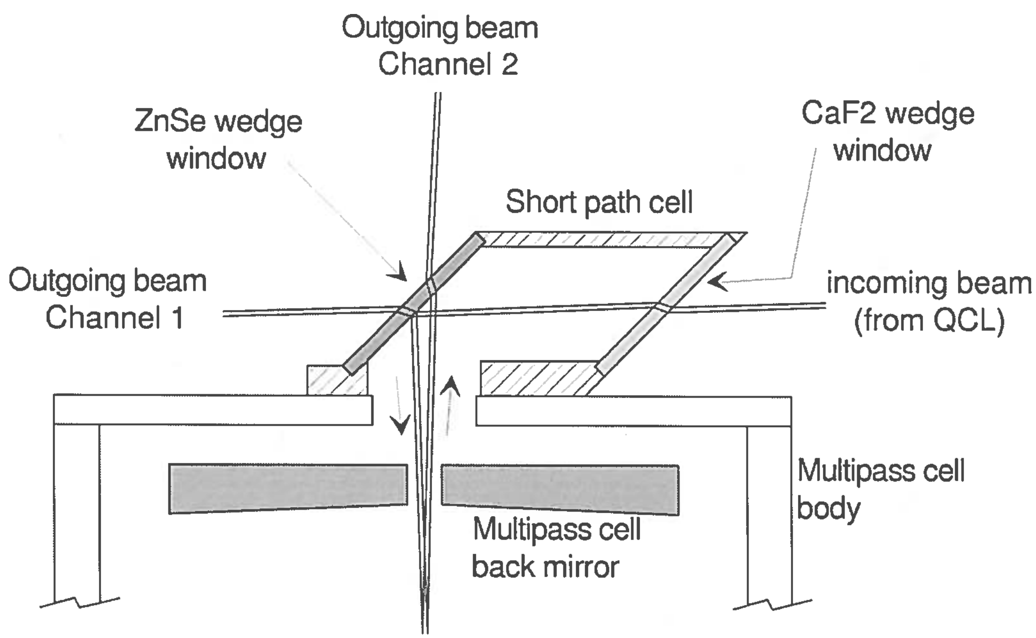
- Advantages
  - Fundamental band (ν_3) in mid-IR spectral region can be targeted
  - DFB-QCLs provide sufficient selectivity ~ 3 to 300 MHz
  - Compact, robust and tunable laser
  - No need for cryogenic cooling
  - Less complex than other laser based systems
- Drawbacks due to pulse mode operation
  - Dominant noise is pulse-to-pulse intensity fluctuations
  - Larger laser linewidths due to thermal chirp

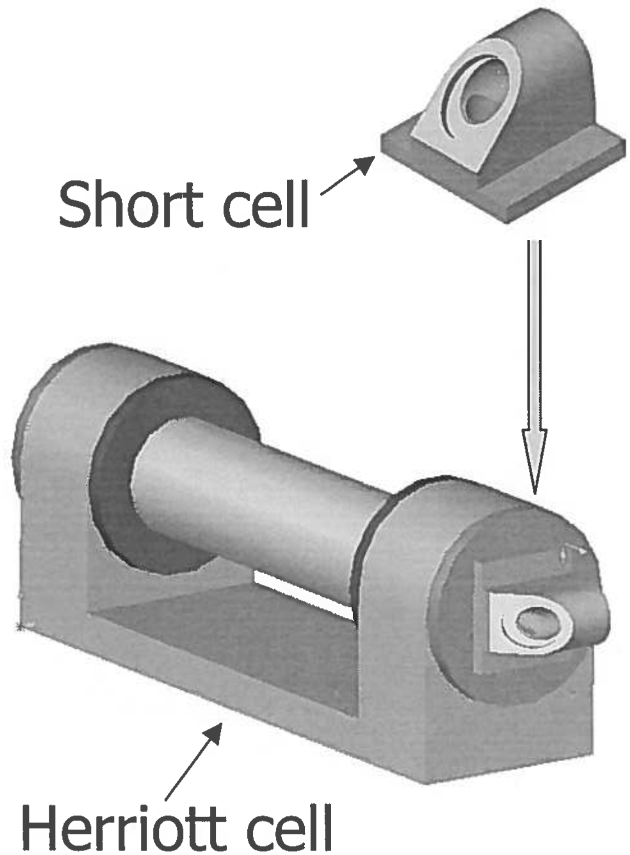
Comparison of CO_2 line selection and strategy for different current US mid-IR laser-based isotopic ratiometers

Group	Technology	Frequency 12/13 [cm^{-1}]	δT [K]	Precision
NCAR, UC and Rice U. A. Fried et al; Erdelyi	**DFG with NIR TDLs and fiber amplifiers**	**2299.642** **2299.795**	**0.005**	0.8 ‰*
Aerodyne, Harvard U. M. Zahniser et al.	Direct Scan PbSalt TDL, QCL, DFG; Dual optical paths	2314.304 2314.408	0.213	0.2 ‰
Physical Sciences D. Sonnenfroh et al	QCL	2318.1		0.5 to 1‰
Rice University Tittel et al	**QCL** **Dual optical paths**	**2311.105** **2311.399**	**181** **Very large**	<1 ‰
U. of Utah Bowling, Picarro	PbSalt TDLs Campbell Scientific Instrum.	2308.225 2308.171	0.006	0.2 ‰
JPL C. Webster	TDLs and QCL, LAS	2303.7 2303.5	0.007	TBD ‰
NASA-Ames Becker et al; Jost, LGR	Direct Scan PbSalt TDLs & QCLs with ICOS	2291.542 2291.680	0.004	4 ‰

* Erdelyi, Richter, and Tittel, *Appl. Phys.* **B75**, 289 (2002)

Dual optical pathlength configuration for a Herriott gas absorption cell





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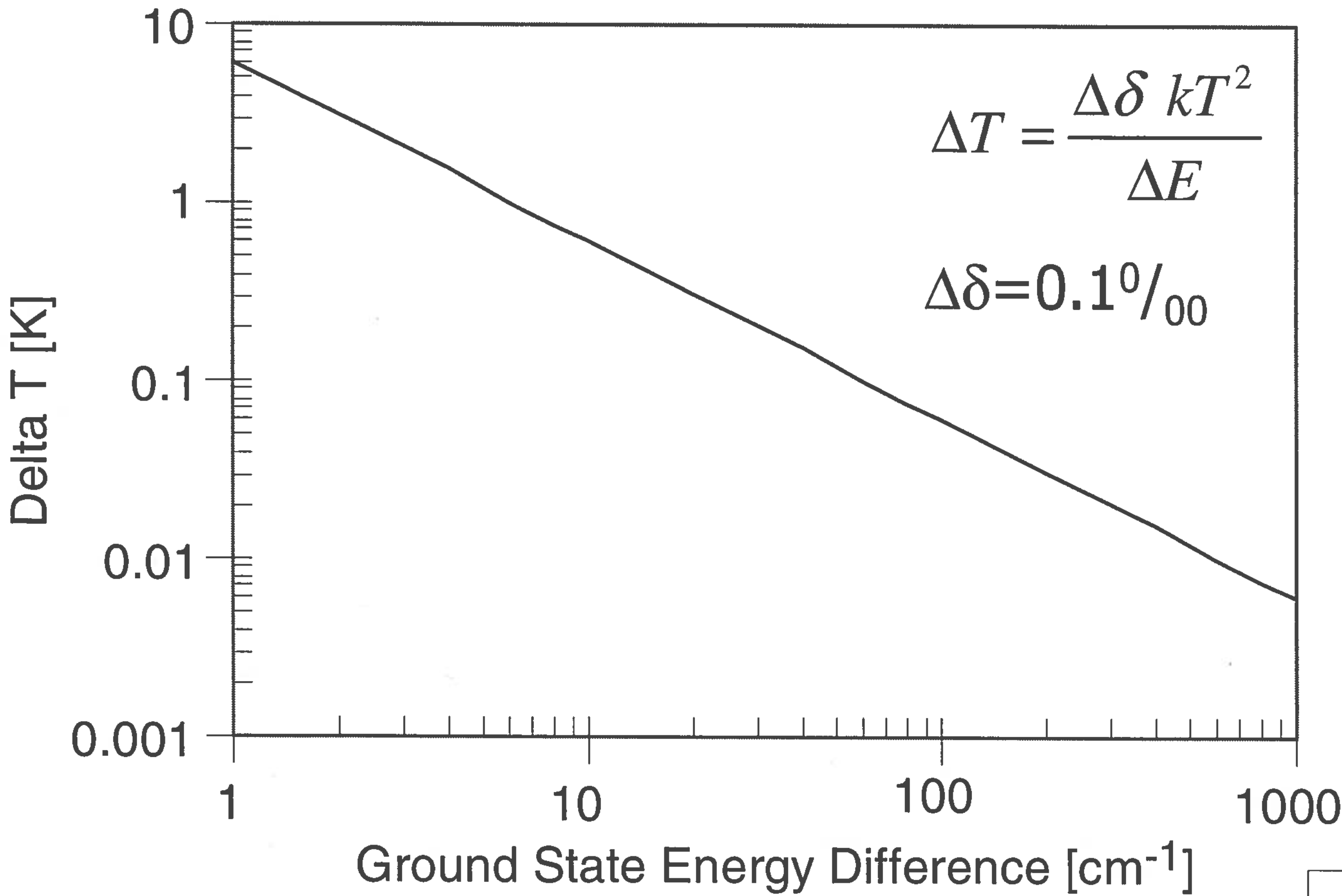
Required Temperature Stability



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Sensitivity Criteria of Spectrometer to Experimental Parameters

- Concentration retrieval by line integration

$$C = \frac{\int \alpha d\nu \cdot R \cdot T}{L \cdot S \cdot N_A \cdot P}$$

  - Path length tolerance $\Delta L = 2.4\ \mu m$
  - Pressure tolerance $\Delta P > 5$ mT
  - Water vapor-CO_2 collision broadening
    ⇒ Need for a water trap

Spectrometer noise will ultimately limit $\Delta\delta$

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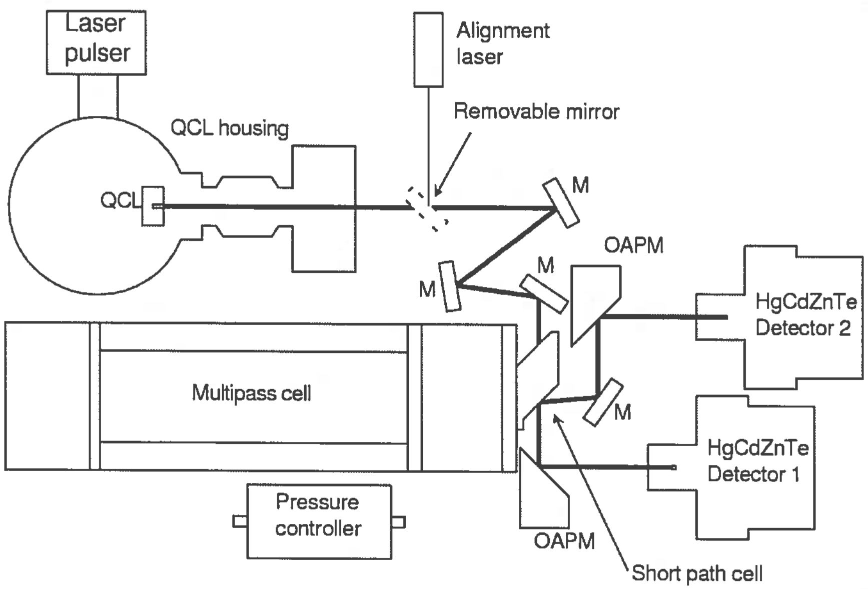
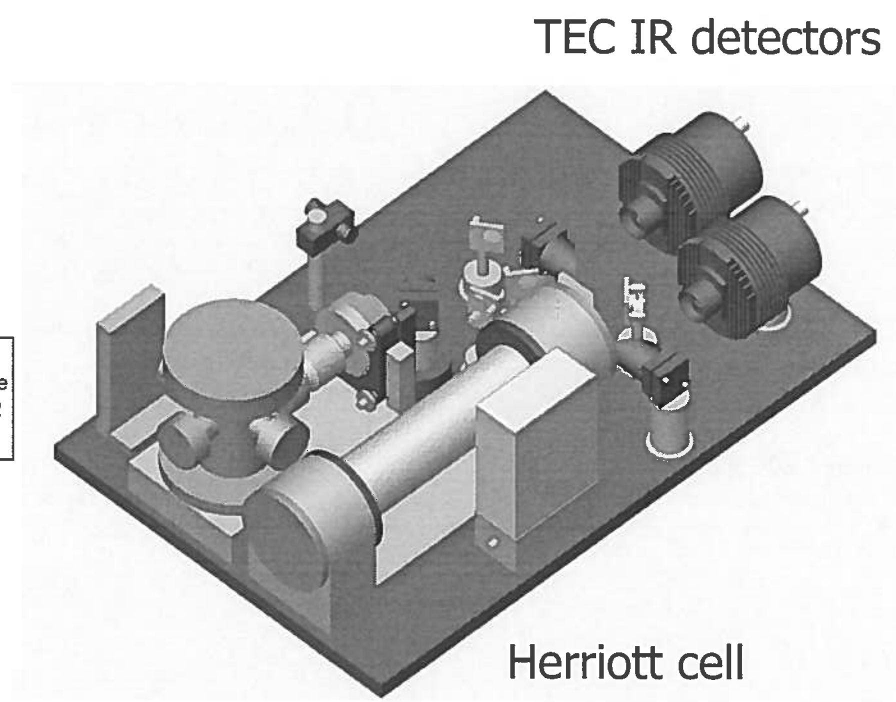
QC laser based Isotopic Ratio Sensor Layout





Bread board: 12x18" (30x45 cm)

The sensor must be operated in a dry nitrogen atmosphere to eliminate atmospheric CO_2 background

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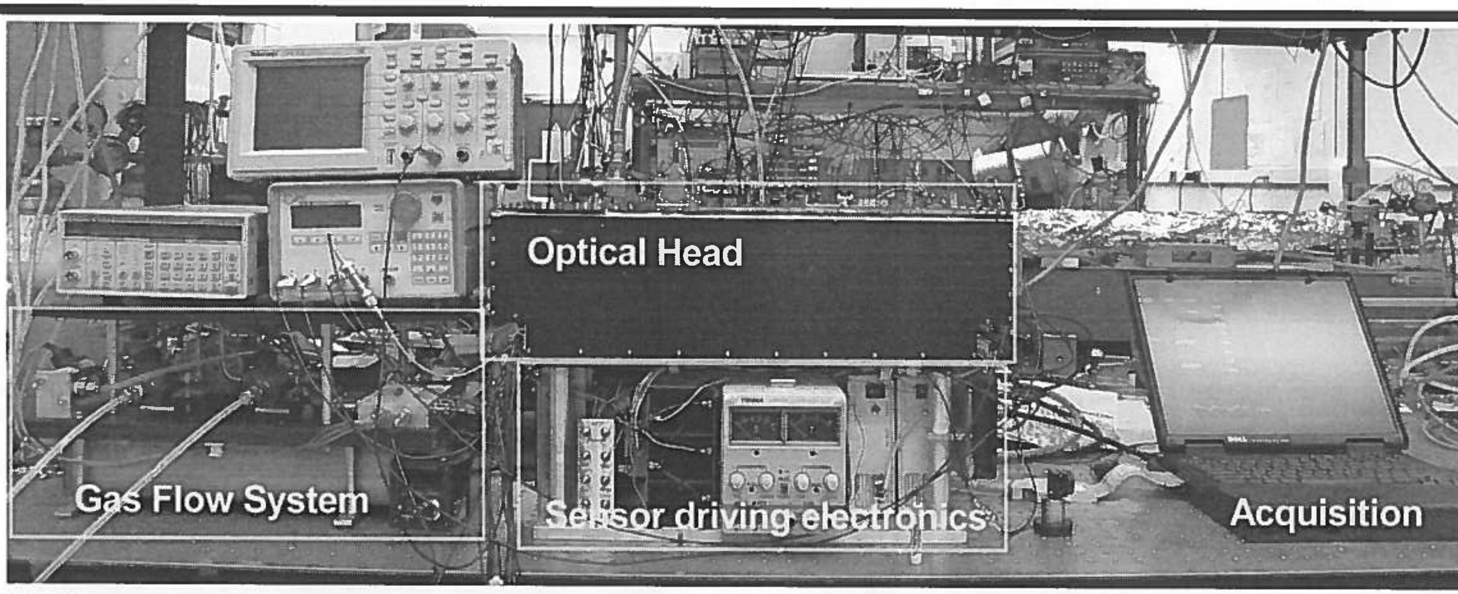
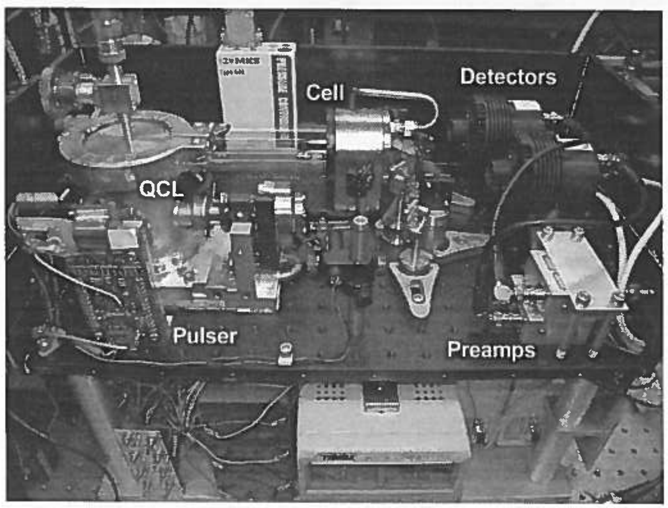
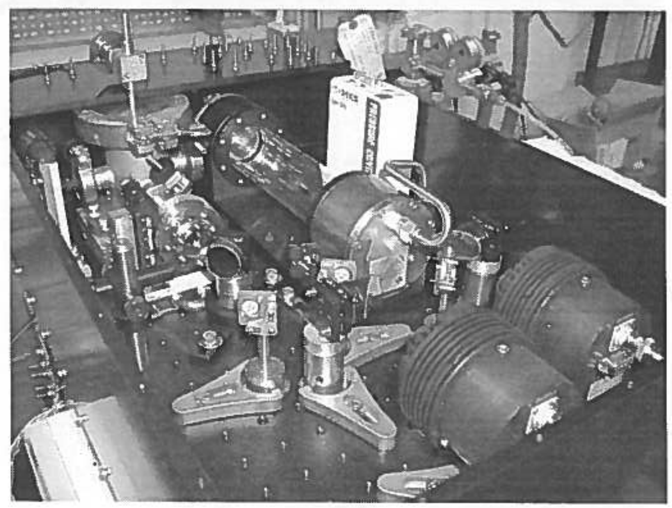
QC laser based CO_2 isotopic ratio gas sensor







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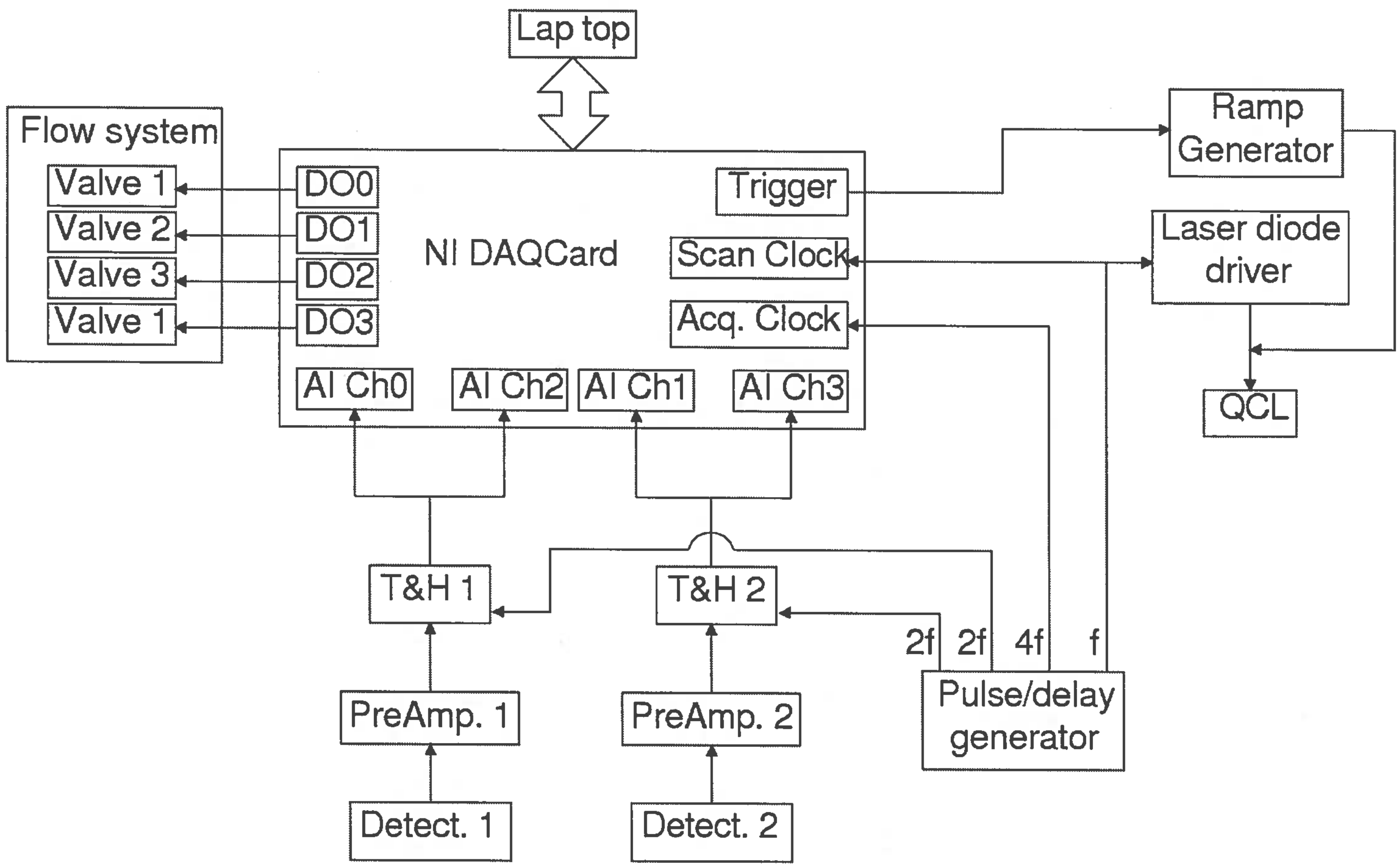
Data acquisition and control system flow chart



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Protocol of CO_2 Isotopic Ratio Measurements

- 1st step

Reference CO_2 flowing in the cell → QC Laser Scan Recording of spectra → $^{12}CO_2$ & $^{13}CO_2$ concentration measurement ↓

Delta value

- 2nd step

Sample CO_2 flowing in the cell → QC Laser Scan Recording of spectra → $^{12}CO_2$ & $^{13}CO_2$ concentration measurement ↑

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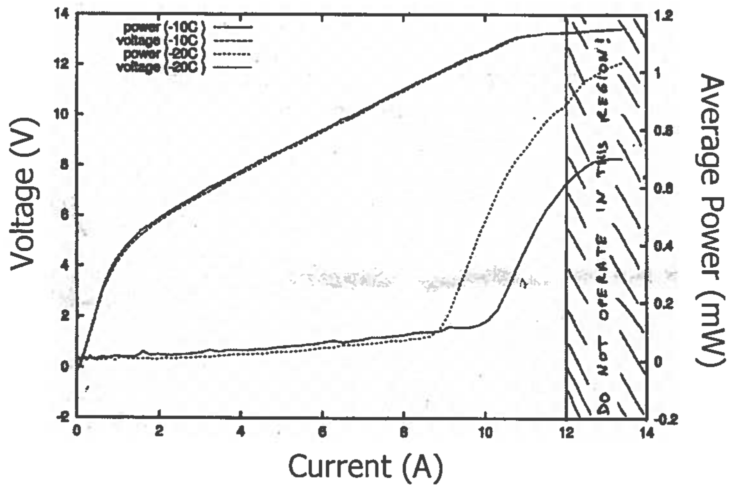
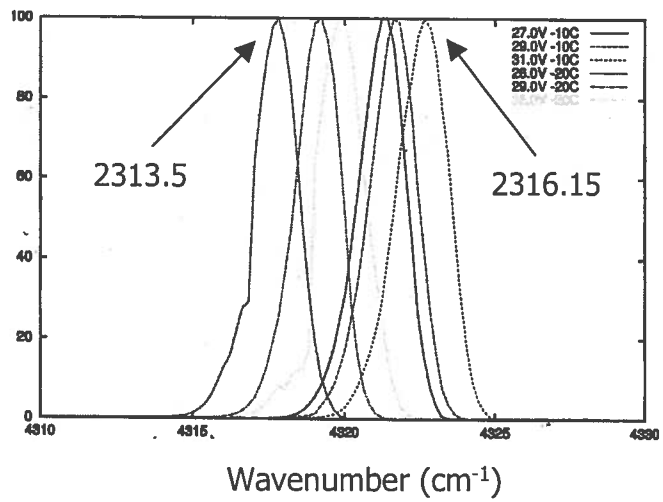
Characterization of Pulsed DFB-Quantum Cascade Laser at ~2320 cm^{-1} (4.3 um)

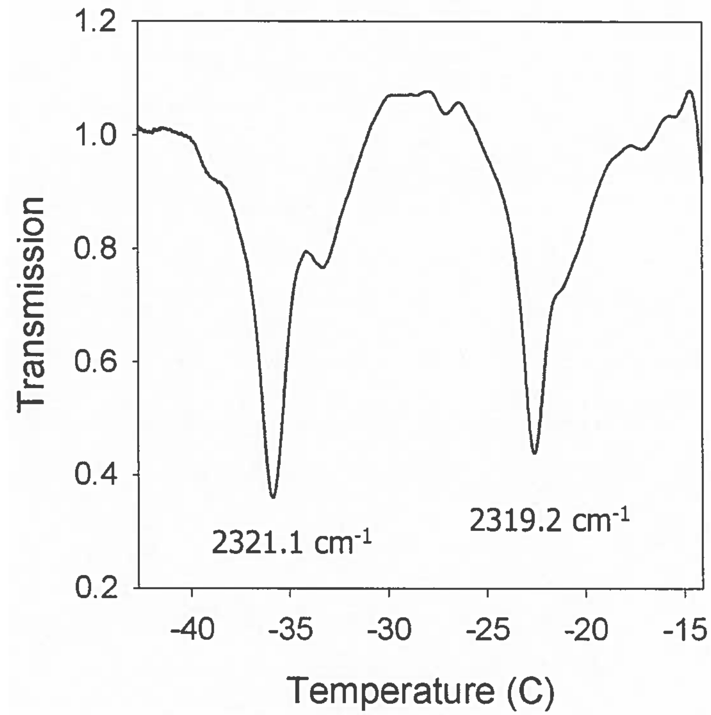
- QCL I-V-L data from Alpes





- CO_2 Spectrum taken at Rice

Atmospheric CO_2
I = 10 A; pulse width 15 ns



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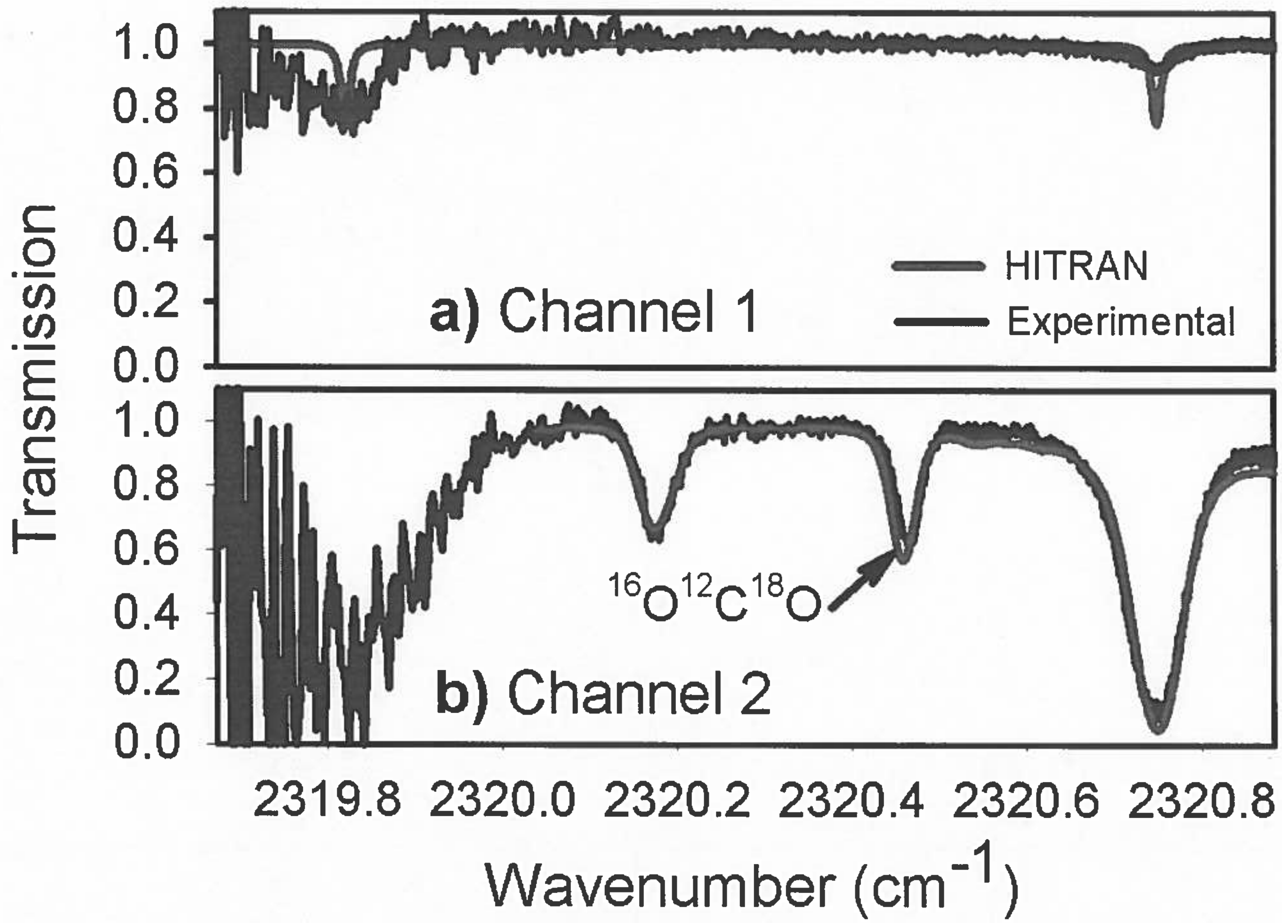
$^{16}O^{12}C^{18}O$ Spectra at 2320.2 cm^{-1}



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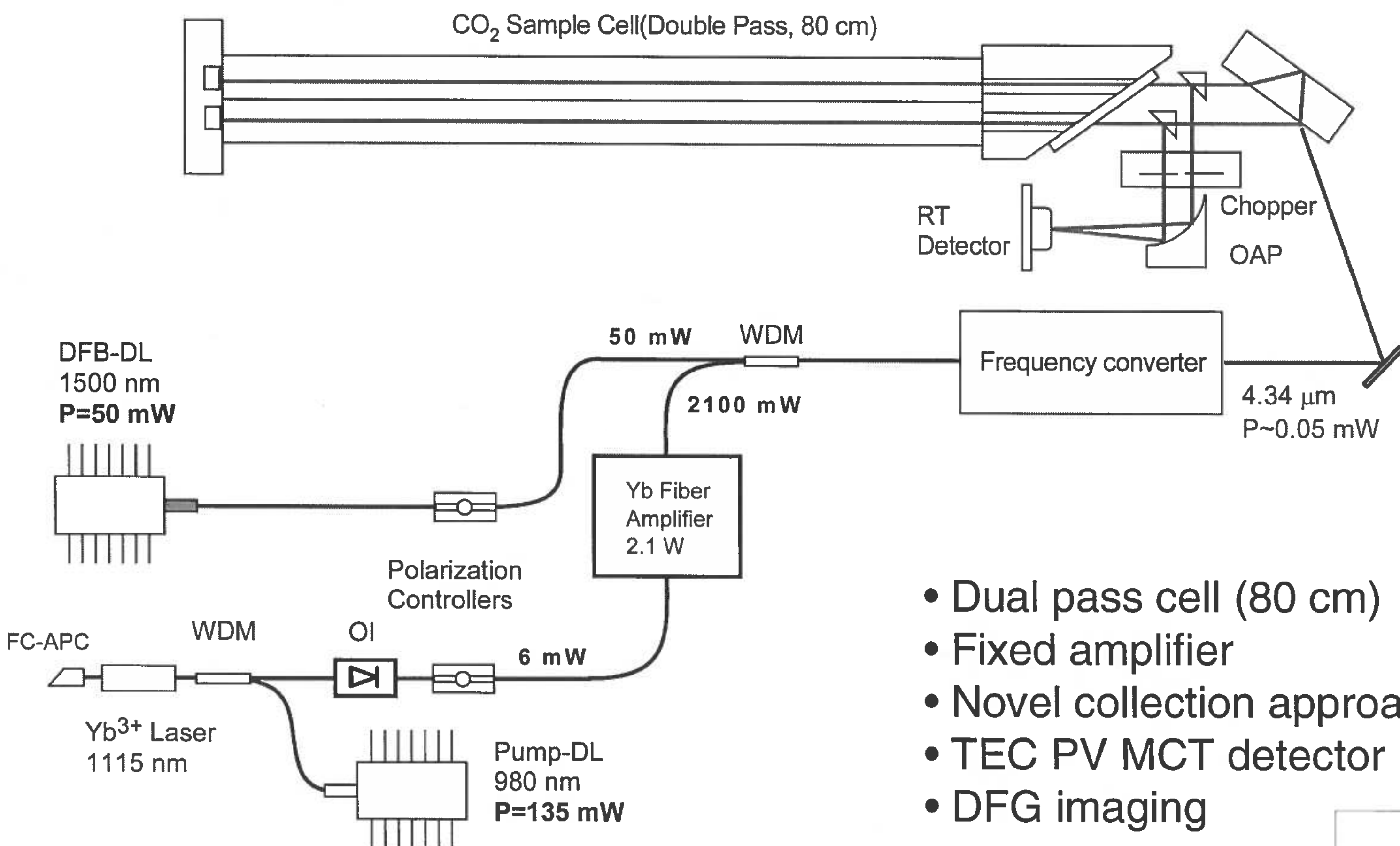
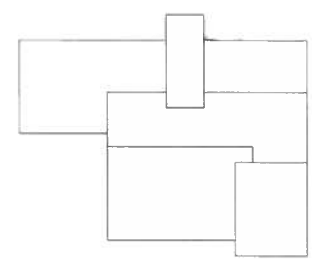
NCAR Biocomplexity System: Architecture of DFG based $^{12}CO_2/^{13}CO_2$ gas sensor



- Dual pass cell (80 cm)
- Fixed amplifier
- Novel collection approach
- TEC PV MCT detector
- DFG imaging



Conclusions and Future Outlook

- QC laser based isotopic CO_2 ratiometer has been built
- Line pair selected for this work is insensitive to temperature variations (balanced detection)
- Dual path length approach
- Compact and LN_2 free-instrument
- $1^0/_{00}$ is initially targeted, $0.1^0/_{00}$ may require a three channel configuration
- Volcanic gas emission studies in Italy and US are planned
- Design, construction and evaluation DFG based system ratiometer is in progress (NSF funded 2003-2005 collaboration: NCAR-UC-Rice)
- Several DoE & NASA funded instrumentation projects are being pursued (Harvard-Aerodyne, Ames-LGR, JPL, Picarro-UU, PSI)

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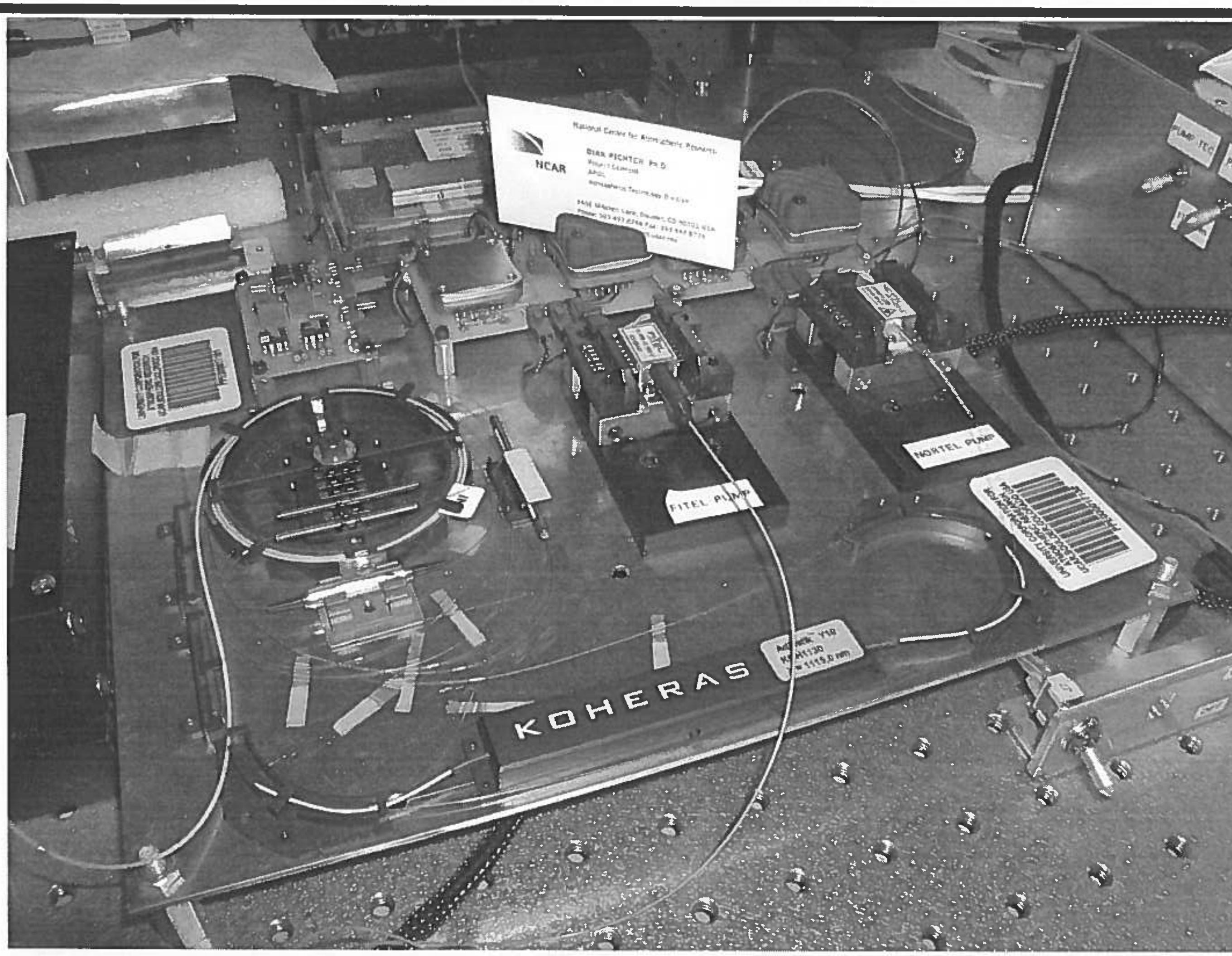
Seed Diode Laser and Driver platform



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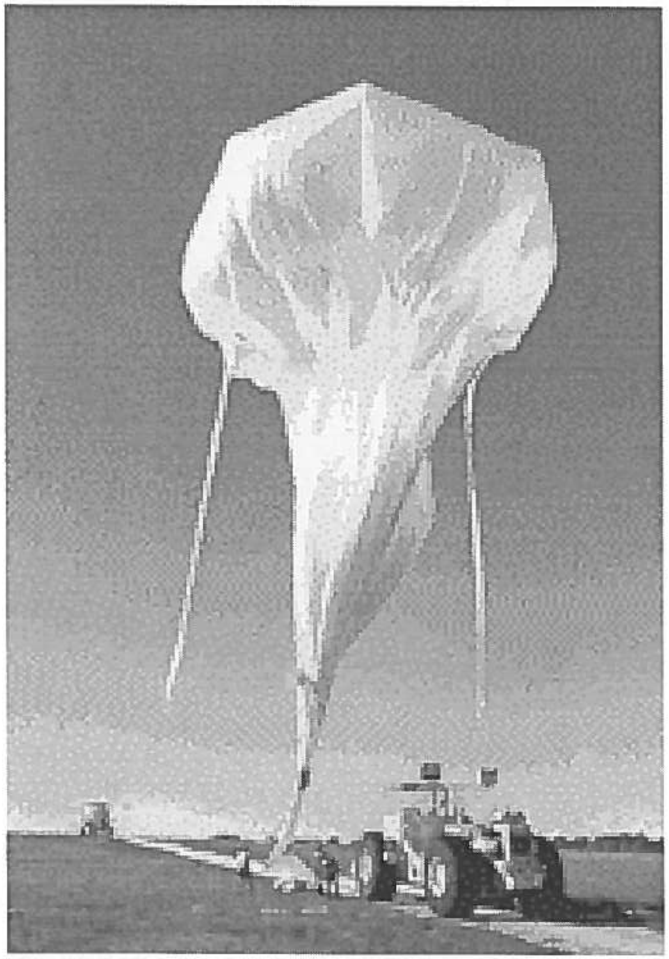
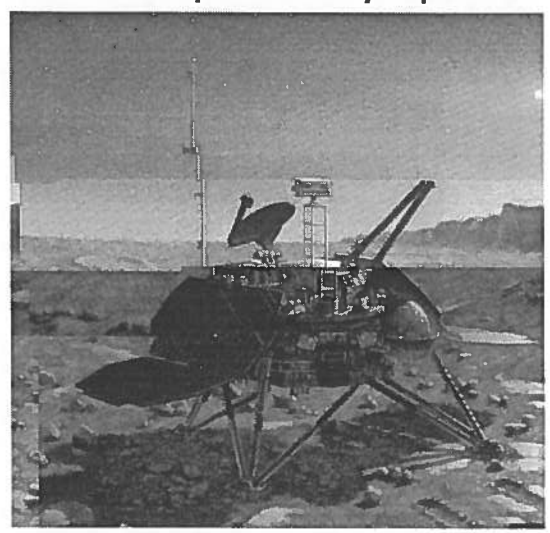
NASA Atmospheric & Mars Gas Sensor Platforms



Tunable laser sensor for earth's stratosphere

Aircraft laser absorption spectrometer

Tunable laser planetary spectrometer



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