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Recent Advances of Laser based Trace Gas Monitoring Technology: Challenges and Opportunities

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http://ece.rice.edu/lasersci/

OUTLINE

Physics Seminar

Lund, Sweden Nov. 23, 2004

- Motivation and Technology Issues
- Fundamentals of Laser Absorption Spectroscopy
- Selected Applications of Trace Gas Detection
  - Off Axis-ICOS based detection of NO
  - Direct Absorption Spectroscopy of OCS
  - Quartz Enhanced Laser-PAS of N_2O and H_2CO
  - CO_2 Flux and Isotopic Ratio Measurements
- Conclusions and Outlook

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- National Science Foundation
- Texas Advanced Technology Program
- Welch Foundation

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1996 Nobel Laureates in Chemistry, R.F. Curl, H. Kroto & R.E. Smalley

Motivation: Wide Range of Gas Sensing Applications

- **Urban and Industrial Emission Measurements**
  - Industrial Plants
  - Combustion Sources and Processes (eg. early fire sensing)
  - Automobile and Aircraft Emissions
- **Rural Emission Measurements**
  - Agriculture and Animal Facilities
- **Environmental Monitoring**
  - Atmospheric Chemistry
  - Volcanic Emissions
- **Chemical Analysis and Industrial Process Control**
  - Chemical, Pharmaceutical, Food & Semiconductor Industry
- **Spacecraft and Planetary Surface Monitoring**
  - Crew Health Maintenance & Human Life Support Program
- **Medical Diagnostics** (eg. breath analysis)
- **Biohazard and Toxic Chemical Detection**
- **Fundamental Science, Photochemistry and Life Sciences**

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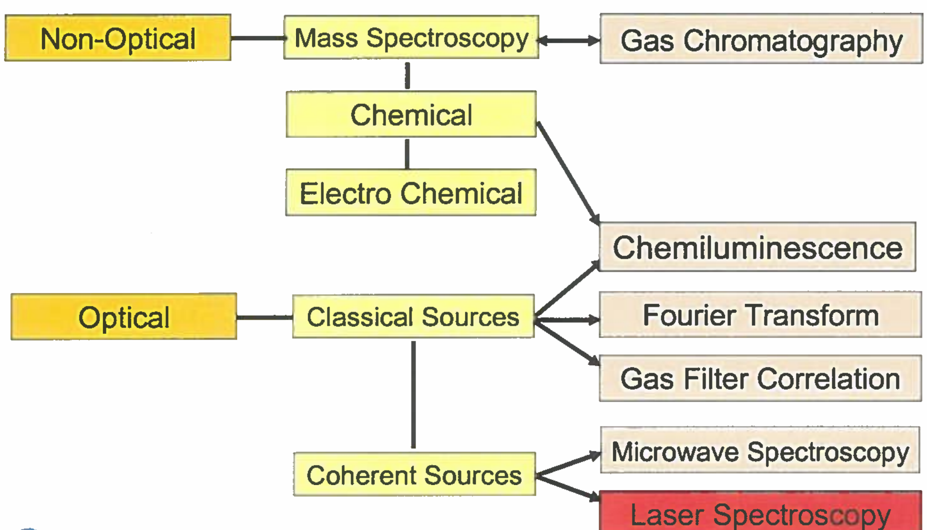
International Space Station

Existing Methods for Trace Gas Detection



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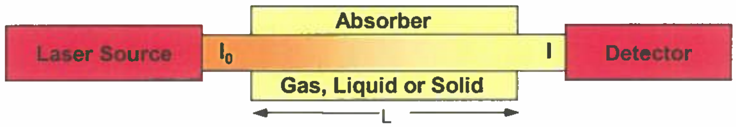
Direct Laser Absorption Spectroscopy

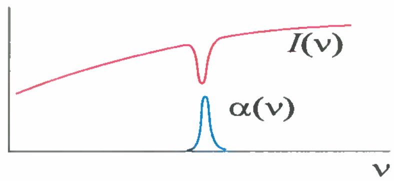


Beer-Lambert's Law of Linear Absorption

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

$\alpha(\nu)$ - absorption coefficient [cm^{-1} atm^{-1}]; L – path length [cm]

ν - frequency [cm^{-1}]; P_a- partial pressure [atm]



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

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)

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Sensitivity Enhancement Techniques

- **Optimum Molecular Absorbing Transition**
  - Overtone or Combination Bands (NIR)
  - Fundamental Absorption Bands (MID-IR)
- **Long Optical Pathlength**
  - Multipass Absorption Cell (White, Herriot)
  - Cavity Enhanced and Cavity Ringdown Spectroscopy
  - Open Path Monitoring (with retro-reflector)
  - Fiberoptic Evanescent Wave Spectroscopy
- **Spectroscopic Detection Schemes**
  - Frequency or Wavelength Modulation
  - Balanced Detection
  - Zero-air Subtraction
  - Photoacoustic Spectroscopy
  - Noise Immune Cavity Enhanced-Optical Heterodyne Molecular Spectroscopy (NICE-OHMS)

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CW IR Source Requirements for Laser Spectroscopy

REQUIREMENTS	**IR SOURCE**
• Sensitivity (% to ppt)	• Power
• Selectivity	• Narrow Linewidth
• Multi-gas Components	• Tunable Wavelengths
• Directionality	• Beam Quality
• Rapid Data Acquisition	• Fast Time Response
• Room Temperature	• No Consumables
• Field deployable	• Compact & Robust

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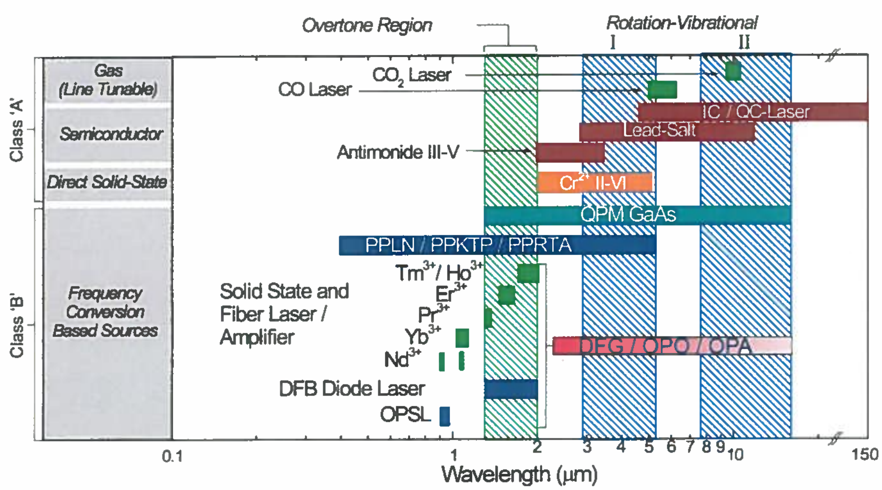
IR Laser Sources and Wavelength Coverage



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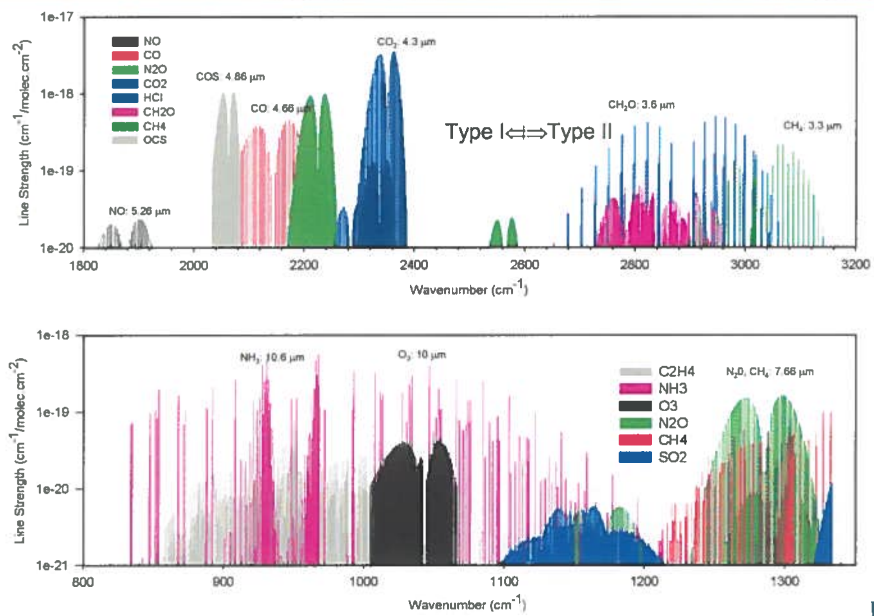
HITRAN Simulation of Absorption Spectra (3.1-5.5 & 7.6-12.5 µm)



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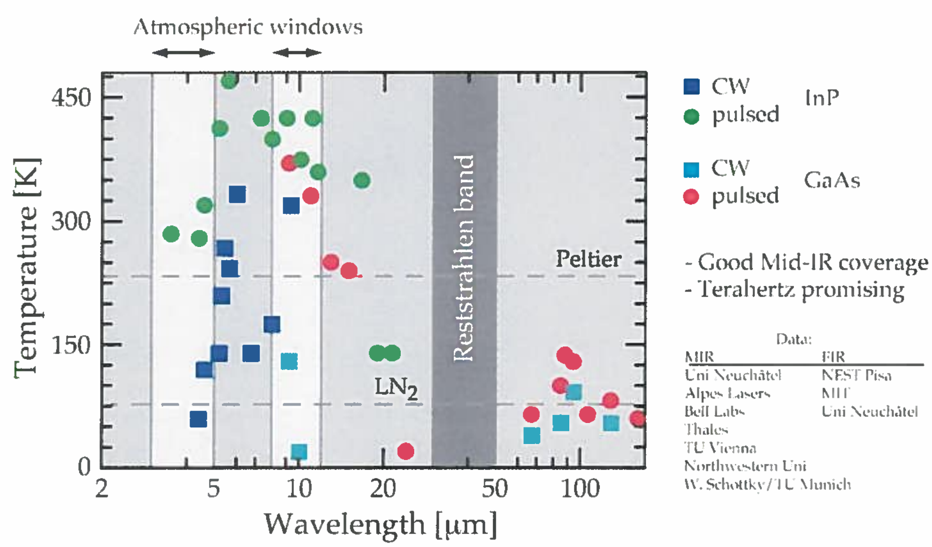
State of the art: QCL performances



Kindly provided by Prof. J. Faist, University of Neuchatel, Nov. 2004

Key Characteristics of Mid-IR Quantum Cascade Lasers for Spectroscopy

- QC laser wavelengths cover entire mid-IR range from 3.3 to 24 μm determined by thickness of the quantum well and barrier layers of the active region
- Intrinsically high power lasers (determined by number of stages of injector-active quantum well gain regions)
  - CW:~100 mW @ 80°K and 1- 640 mWs @ 295 °K
  - Pulsed: >1 W peak at room temperature, ~50 mW avg. @ 0 °C (up to 80 % duty cycle) to 100 mWs (56% d.c)
- High spectral purity:<kHz - 330MHz (.01 to .001 cm^{-1})
- Wavelength tunable by current (~1cm^{-1}) or temperature scanning (~10 cm^{-1}); ~160 cm^{-1} with external cavity grating
- High reliability: long lifetime, robust operation and reproducible emission wavelengths

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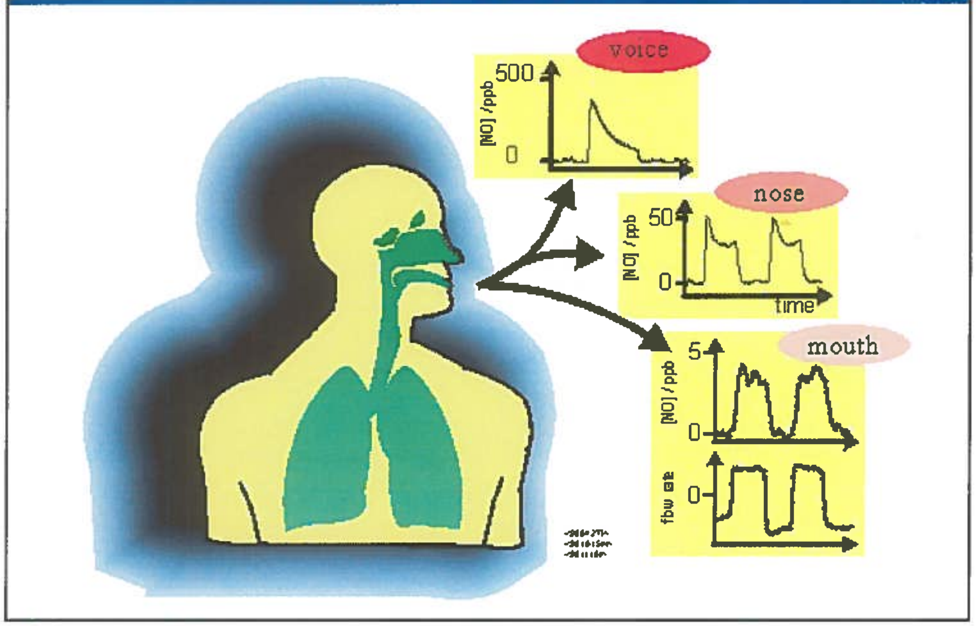
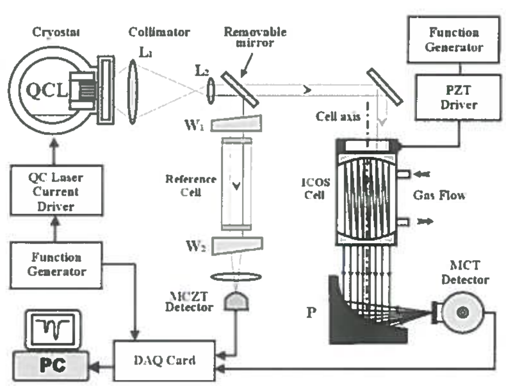
Important Biomedical Target Gases

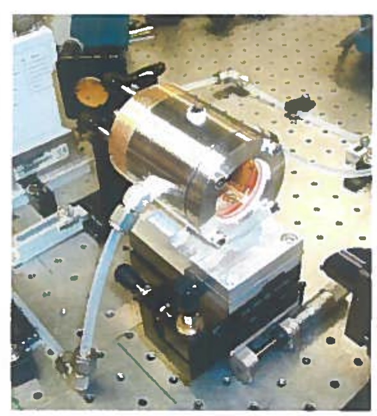
Molecule	Formula	Biological/Pathology Indication
Pentane	$CH_3(CH_2)_3CH_3$	Lipid peroxidation, oxidative stress associated with inflammatory diseases, transplant rejection, breast and lung cancer
Ethane	C_2H_6	Lipid peroxidation and oxidative stress
CO_2 isotope ratio	$^{13}CO_2$ / $^{12}CO_2$	Marker for Heliobacter pylori infection, Gastrointestinal and hepatic function
Carbonyl Sulfide	**COS**	**Liver disease and acute rejection in lung transplant recipients (10-500 ppb?)**
Carbon disulfide	CS_2	Schizophrenia
Ammonia	**NH_3**	**Hepatic encephalopathy, liver and renal diseases, fasting response**
Formaldehyde	**HCHO**	**Cancerous tumors, breast cancer (400-1500 ppb)**
Nitric Oxide	**NO**	**Inflammatory and immune responses (e.g., asthma) and vascular smooth muscle response (6-100 ppb)**
Hydrogen Peroxide	H_2O_2	Airway Inflammation, Oxidative stress (1-5 ppb)
Carbon Monoxide	**CO**	**Smoking response, CO poisoning, vascular smooth muscle response, platelet aggregation (400-3000 ppb)**
Ethylene	**$H_2C=CH_2$**	**Oxidative stress, cancer**
Acetone	CH_3COCH_3	Fasting response, diabetes mellitus response, ketosis

Nitric Oxide Concentrations in Exhaled Breath by Healthy Humans



Off-Axis Integrated Cavity Output Spectroscopy Based Gas Sensor





- Novel compact gas cell design of length: 3.8 – 5.3 cm and cell volumes < 80 cm^3;
- Low loss mirrors (ROC 1m):~60-250 ppm, R~99.975, L_{eff}=170-800 m
- Rapid eNO concentration measurements during a single breath cycle.are feasible

PSI Physical Sciences Inc. LGR RICE

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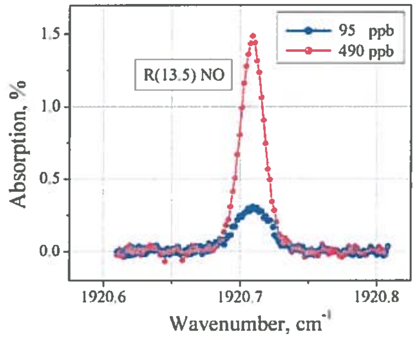
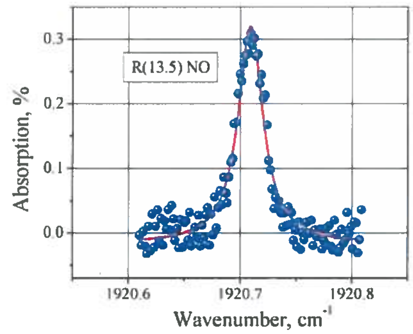
Off-axis ICOS Detection of NO





- 95 and 490 ppb NO/N_2 calibration mixture at 100 Torr total pressure
- Effective optical path ~ 70 m (1,350 passes)

Voigt fit of measured NO absorption line at 1920.7 cm^{-1} for a concentration of 95 ppb

Noise-equivalent sensitivity is 10 ppb for 1σ deviation of the best fit coefficient.
Detection sensitivity: 1.0×10^{-7} cm^{-1} $Hz^{-1/2}$

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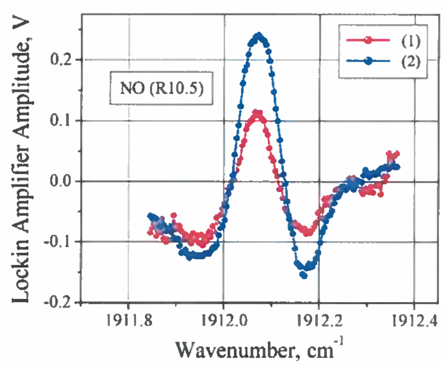
NO from Nasal Exhaled Air (OA-ICOS and wavelength modulation spectroscopy)

Medically approved collection bag for human breath samples



Averaged 2f signal of the OA-ICOS cavity output

(1) Nasal NO concentration: 53 ppb
(2) 95 ppb NO/N_2 calibration mixture

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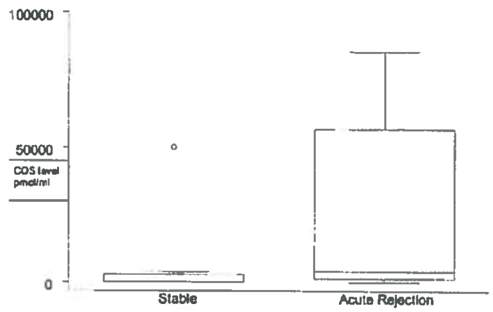
Exhaled Carbonyl Sulfide

- A 2001 study by the T. H. Risby group at John Hopkins University demonstrated that elevated levels of COS could have a diagnostic role in the detection of <u>acute</u> allograft <u>rejection</u> in lung transplant recipients
  - S. M. Studer, et. al., J. of Heart and Lung Transplantation, **20**(11), 1158-66 (2001).

Measured with gas chromatography and flame ionization detection



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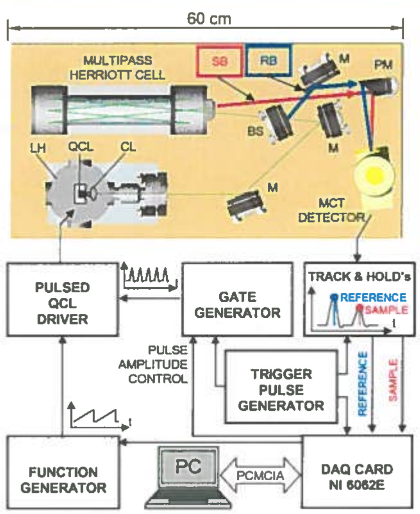
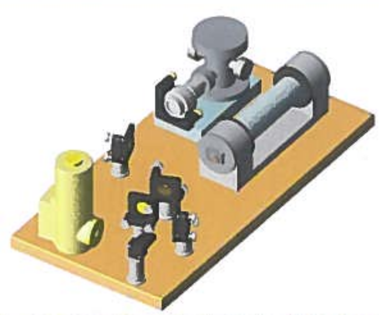
OCS Sensor Architecture

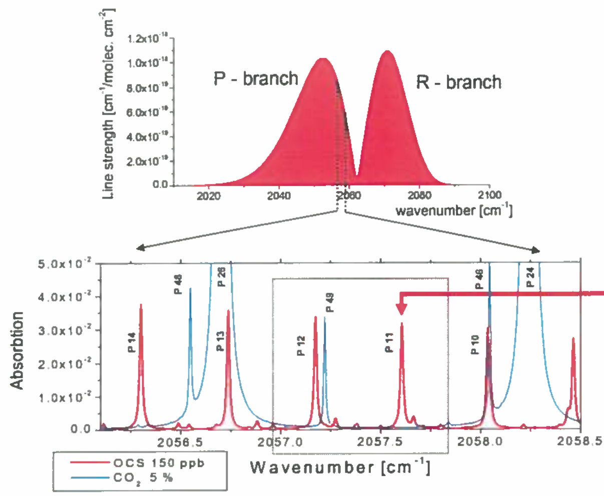


QCL – quantum cascade laser chip
LH - laser housing
CL – collimating lens
SB – sample beam
RB – reference beam
M – mirror
BS – beam splitter
PM – off-axis parabolic mirror



G. Wysocki et al. Applied Optics 43, 6040-6046, 2004

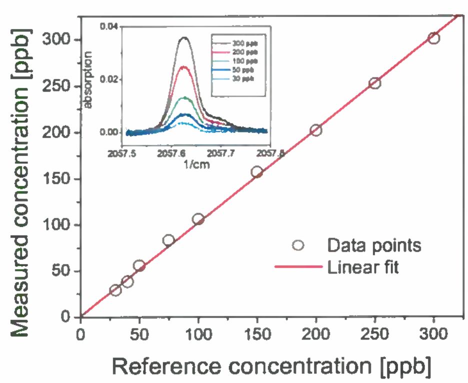
OCS ro-vibrational ν_3 spectrum at ~ 4.85μm



- OCS line intensity:
- 7.49·10^{-19} cm^{-1}/molecule·cm^{-2}
- Minimal spectral interference by nearby CO_2 and H_2O absorption lines
- Availability of a CO_2 line within the fast tuning range of the QCL for ventilation monitoring simultaneously with an OCS measurement

OCS Concentration Calibration of QCL Sensor

Calibration curve

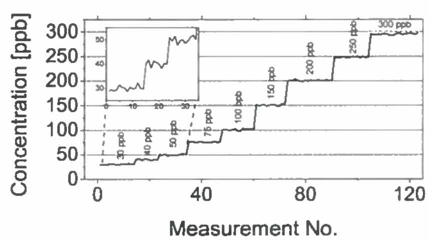


1000 spectra averaged acquired within t = 4 s and fitted to 300 ppb OCS reference spectrum

Theoretical sensitivity:

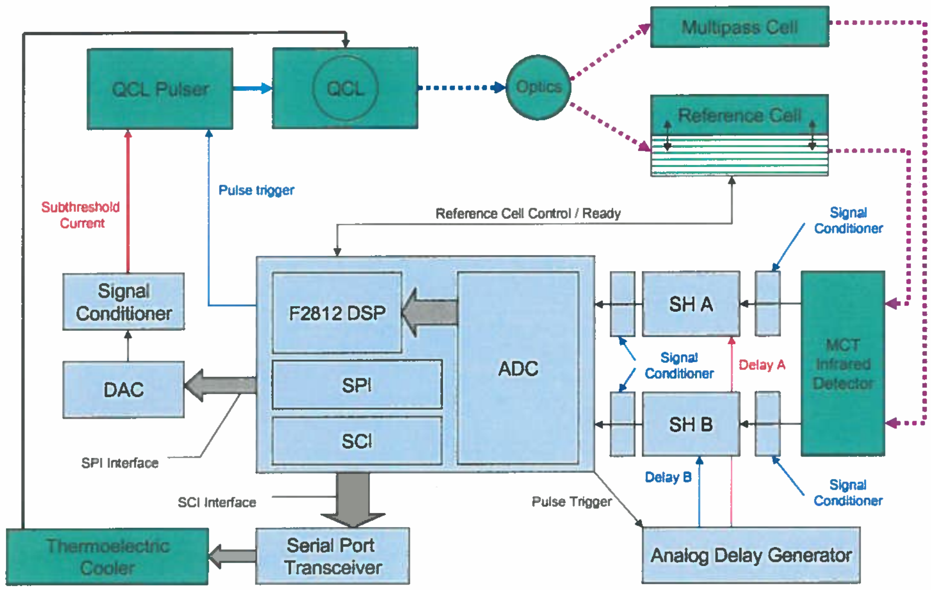
$$0.27\ ppb \cdot \sqrt{1000/100} = 0.85\ ppb$$

Scattering of the concentration measurement: **σ = 1.2 ppb**



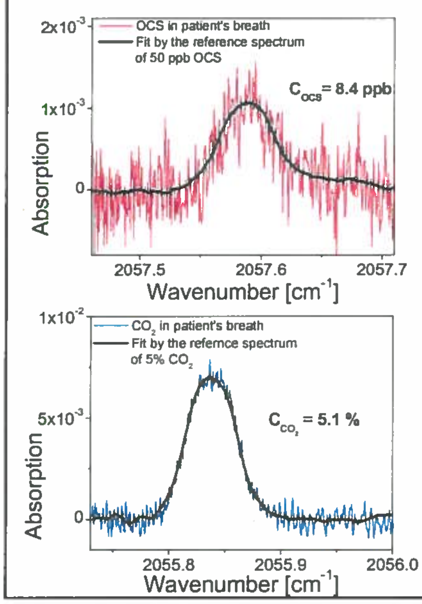
100 spectra averaged acquired within t = 0.4 s and fitted to 300 ppb OCS reference spectrum

DSP Fast Data Acquisition Architecture*



* Joint development by Physical Sciences Inc. & Rice University

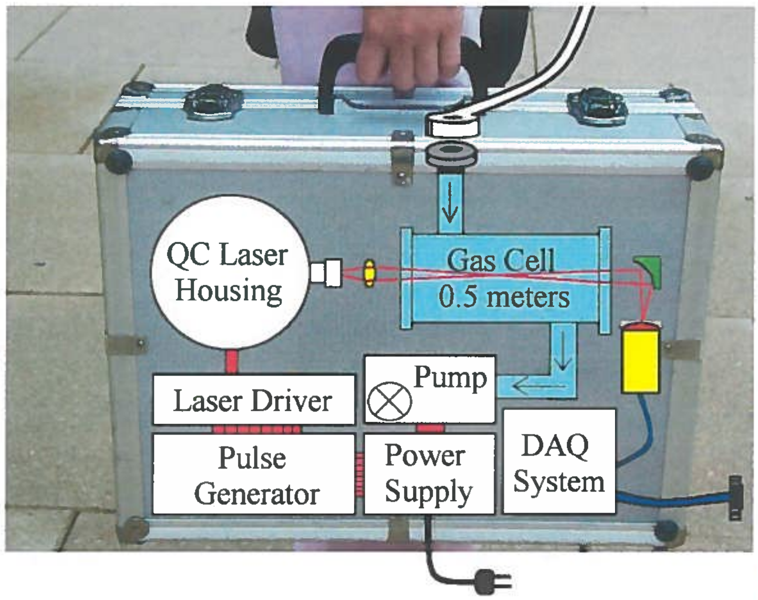
OCS and CO_2 Concentration Measurements in Exhaled Breath



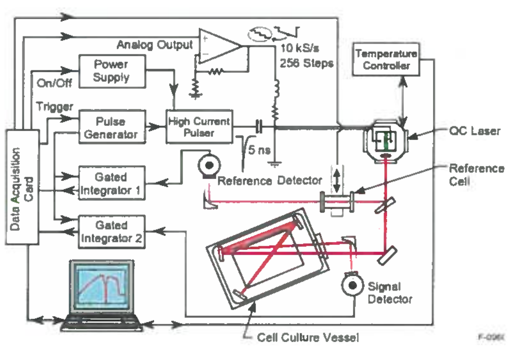
- Sample was taken from lung transplant patient with suspected bronchiolitis*
- Sampling was performed using chemically inert 1 liter tedlar sampling bags and analyzed within 2 hours after collection
- Spectrum was measured at a total pressure of 60 torr

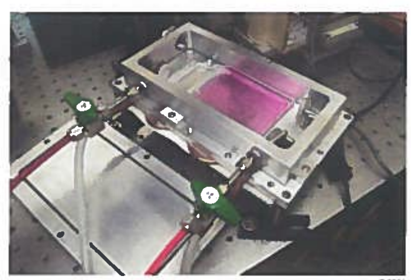
*The authors wish to thank Dr. Remzi Bag and Carolyn M. Paraguaya from Baylor College of Medicine, Houston, TX for supplying breath samples

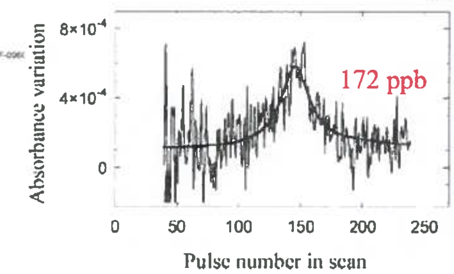
Schematic of a Portable LAS System



QC laser based measurements of CO trace gas above cell cultures







- Measured CO production rates of viable cultures of vascular smooth muscle cells
- Achieved a detection limit of for CO of ~20 ppb

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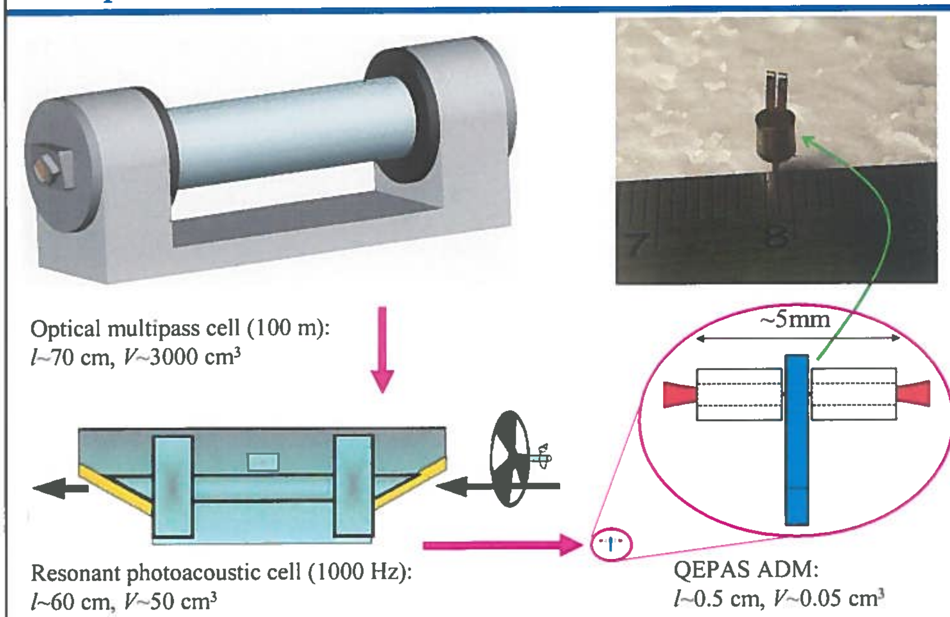
A. Kosterev et al. Appl. Phys. B 74, 95–99 (2002)

Comparative Size of Absorbance Detection Modules (ADM)



Merits of QE Laser-PAS based Trace Gas Detection

- Immune to ambient and flow acoustic noise, laser noise and etalon effects
- Dramatic reduction of sample volume (< 1 mm^3)
- High sensitivity (ppm to ppb gas concentration levels) and excellent dynamic range
- Applicable over a wide range of pressures
- Temperature, pressure and humidity insensitive
- Rugged and low cost compared to LAS that requires a multipass absorption cell and infrared detector(s)
- Potential for optically multiplexed concentration measurements

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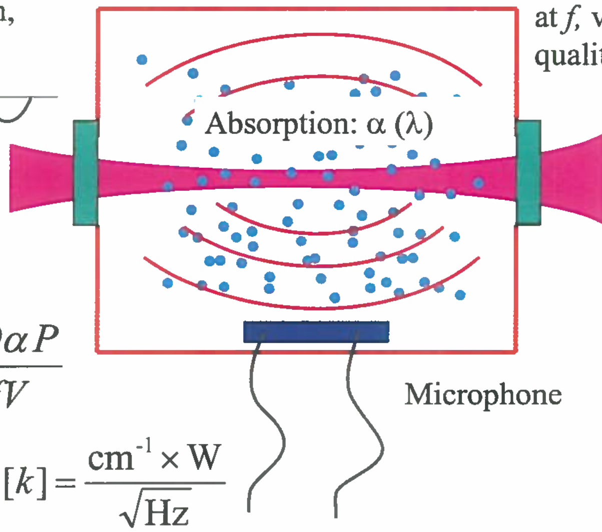
Resonant photoacoustic spectroscopy

Laser beam, power P

Modulated (P or λ) at f or $f/2$

Cavity, resonant at f, volume V, quality factor Q



$$S_{PAS} \sim \frac{Q\alpha P}{fV}$$

$$\text{Sensitivity}\,[k] = \frac{\text{cm}^{-1} \times \text{W}}{\sqrt{\text{Hz}}}$$

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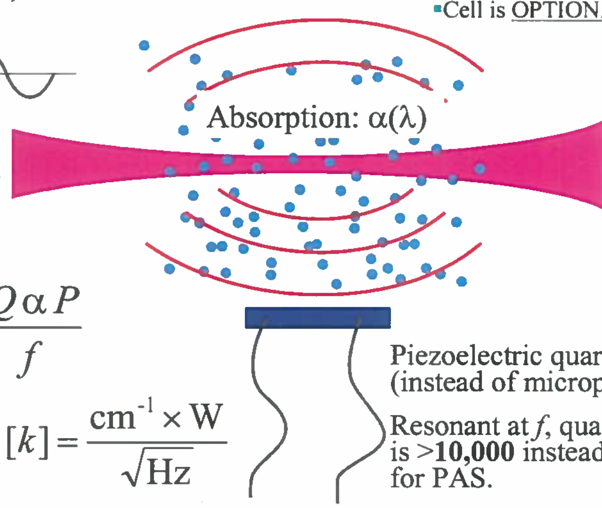
Quartz-Enhanced Photoacoustic Spectroscopy (QEPAS)

Laser beam, power P

Modulated (P or λ) at f or $f/2$

- Resonant Cavity in L-PAS
- Cell is OPTIONAL in QEPAS.



$$S_{QEPAS} \sim \frac{Q\alpha P}{f}$$

$$\text{Sensitivity}\,[k] = \frac{\text{cm}^{-1} \times \text{W}}{\sqrt{\text{Hz}}}$$

Piezoelectric quartz crystal (instead of microphone)

Resonant at f, quality factor Q is >**10,000** instead of 20-200 for PAS.

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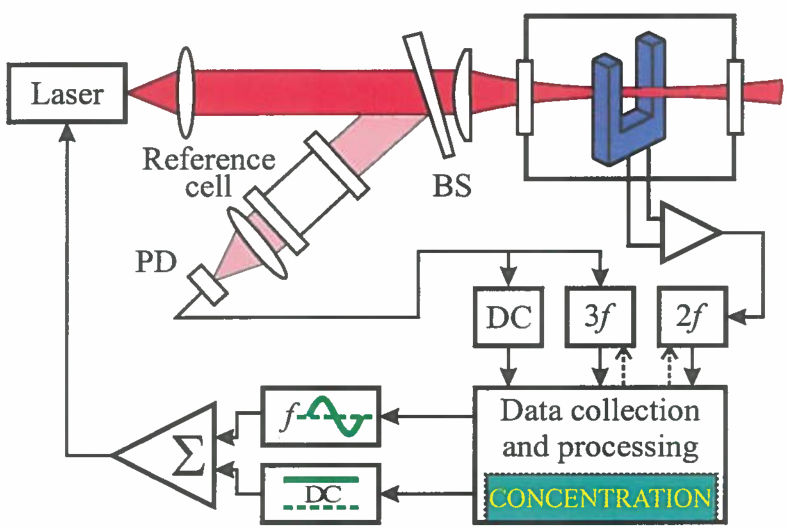
A. Kosterev et al. Optics Letters 27, 1902, 2002

QEPAS versus Traditional PAS

Parameter	Traditional PAS	QEPAS
f, Hz	100 to 4000	Presently ~32 760
Q	20 to 200	10 000 to 30 000
Q vs. pressure	INCREASES (high spectral resolution is problematic)	DECREASES (high spectral resolution is achievable)
Sample volume	>10 cm^3	<1 mm^3
Sensitivity to ambient acoustic and flow noise	Usually high	None observed
Pathlength involved	~10 cm	(a) 0.3mm, (b) 5mm

Diode Laser based QEPAS Gas Sensor Architecture



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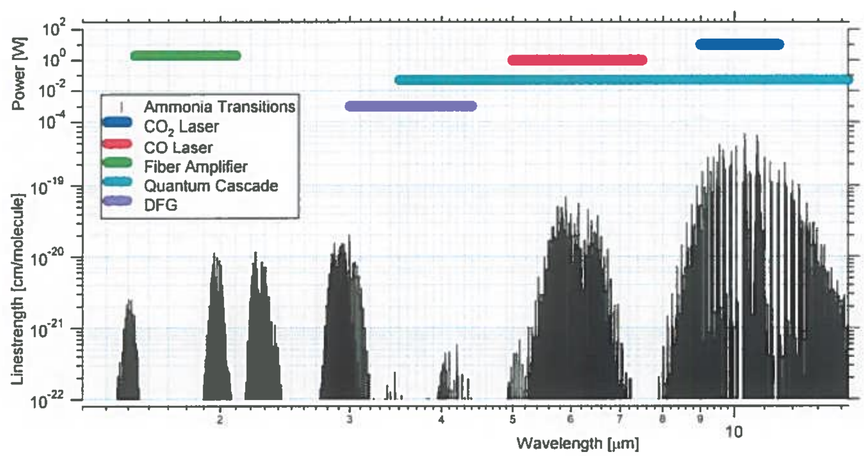
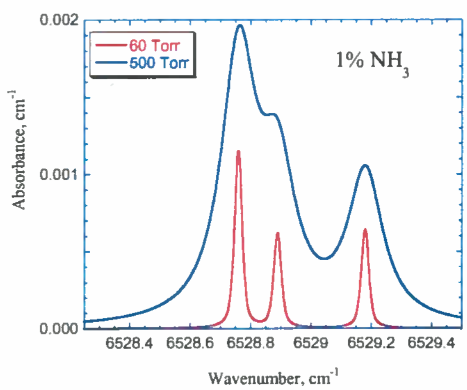
Infrared NH_3 Absorption Spectra

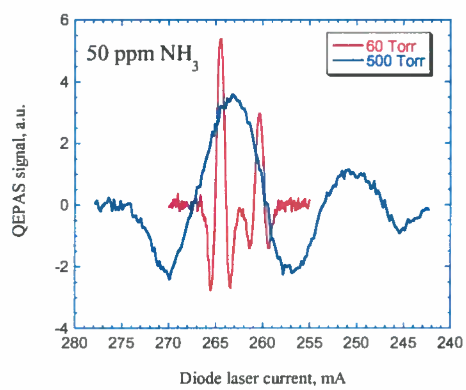


M. Webber et al. 2003, Pranalytica

Ammonia Detection using a 1.53 µm Telecom Diode Laser



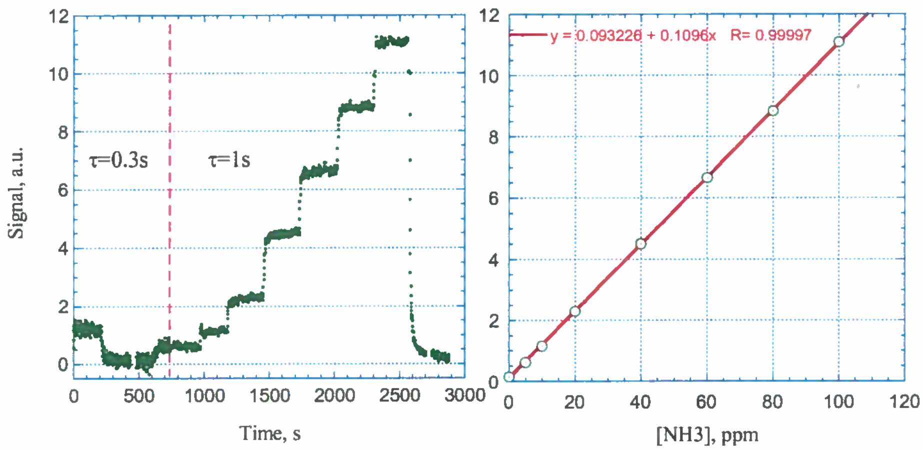
Spectral simulations based on data from Webber et al., APPLIED OPTICS **40**, 2031-2042 (2001)]



QEPAS spectra at different pressures of NH_3:N_2 gas mixture; t=0.3s, 38 mW diode laser excitation power at 6529 cm^{-1}

To appear in Applied Optics (Nov 2004)

Calibration and Linearity of QEPAS based NH_3 Sensor

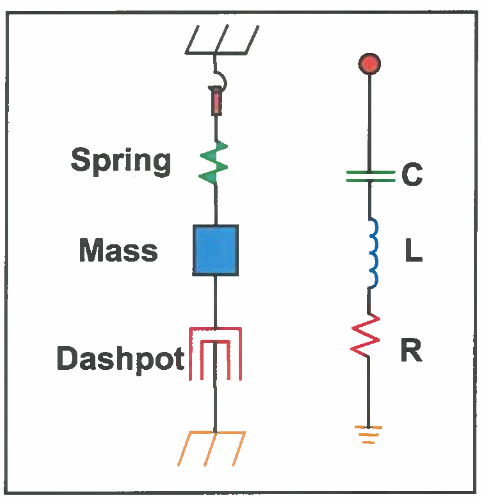


Noise –equivalent (1s) concentration (NEC). for τ=1s time constant is 0.65 ppm for 38 mW excitation power

90 last points of each step averaged

Noise-equivalent absorption (NEA) coefficient $k=7.2\times10^{-9}$ $cm^{-1}W/Hz^{1/2}$

Equivalent circuit of a quartz TF



$$\omega_0 = \sqrt{\frac{1}{LC}}$$

$$Q = \frac{1}{R}\sqrt{\frac{L}{C}}$$

$$\sqrt{\langle I_N^2 \rangle} = \sqrt{\frac{4k_BT}{R}}$$

"QUARTZ CRYSTAL RESONATORS AND OSCILLATORS For Frequency Control and Timing Applications", tutorial by John R. Vig, U.S. Army Communications-Electronics Command (July 2001)

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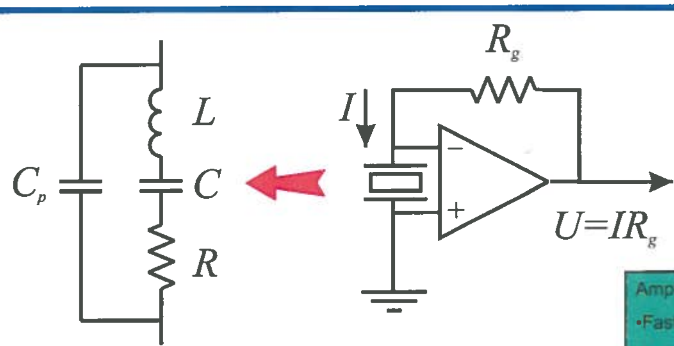
Noise analysis



Amplifier:
- Fast
- Low noise
- High impedance
- Low 1/f noise

$$S_1 = \sqrt{4k_B T R_g}; \quad R_g = 10\ \text{M}\Omega \Rightarrow S_1 = 4.1\cdot 10^{-7}\ \frac{\text{V}}{\sqrt{\text{Hz}}}$$

$$S_2 = \sqrt{\frac{4k_B T}{R}} R_g; \quad R = 100\text{k}\Omega \Rightarrow S_2 = 4.1\cdot 10^{-6}\ \frac{\text{V}}{\sqrt{\text{Hz}}}\ \text{(at 760 Torr)}$$

$$S = \sqrt{S_1^2 + S_2^2} \approx S_2 \quad \text{(at resonance)}$$

Noise goes up as $\sqrt{\text{Q}}$.

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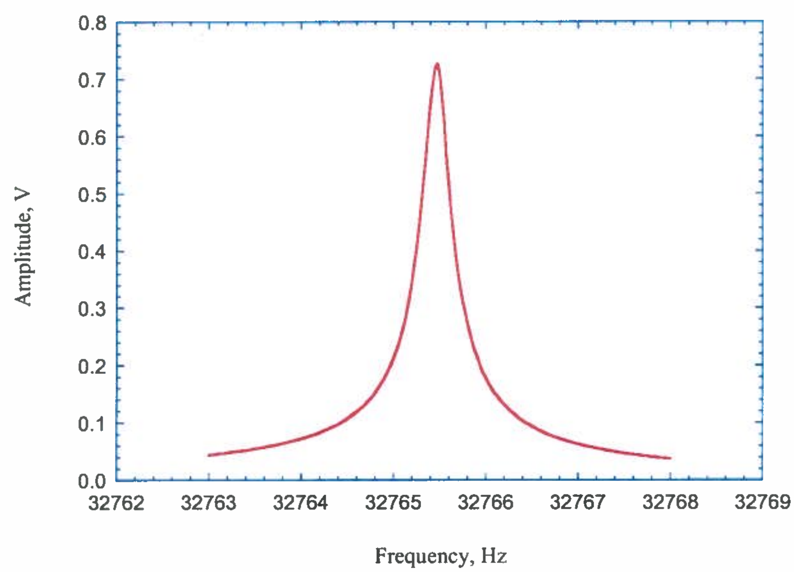
Resonant Response, Q=116 600



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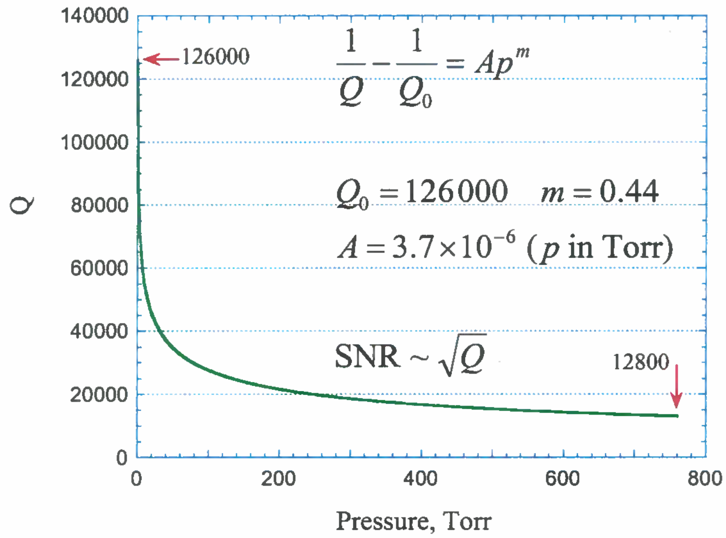
Pressure Dependence of Q Factor of a Typical TF



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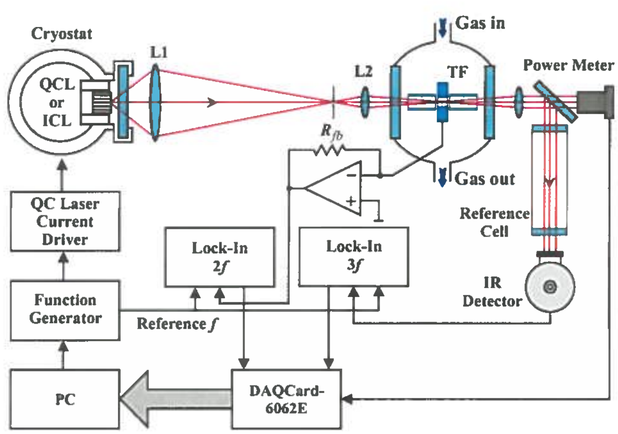
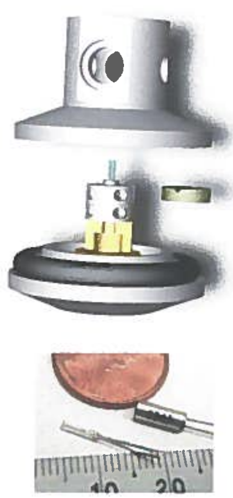
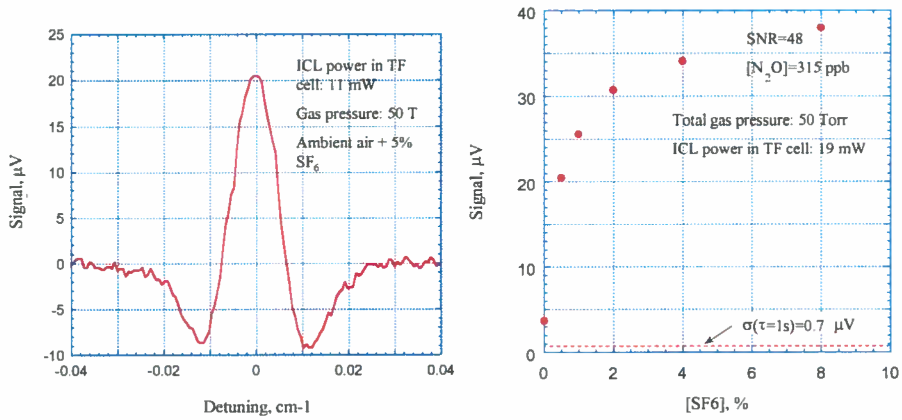
QCL based Quartz-Enhanced Photoacoustic Spectrometer





N_2O Detection in Ambient Air at 4.6µm (2195.6 cm^{-1})



Noise-equivalent absorption coefficient k**=1.5×10^{-8} cm^{-1}W/Hz$^{1/2}$**

To appear in Applied Physics B 2004

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Motivation for Precision Monitoring of H_2CO

- Precursor to atmospheric O_3 production
- Pollutant due to incomplete fuel combustion processes
- Potential trace contaminant in industrial manufactured products
- Medically important gas

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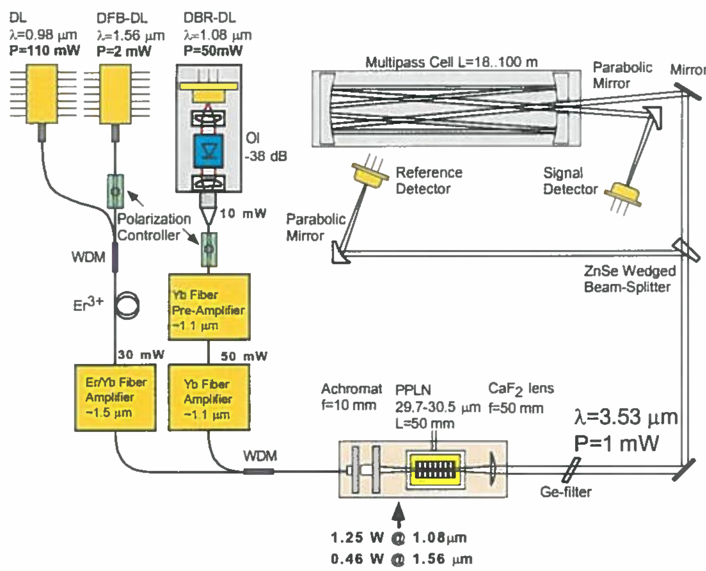
Mid-IR DFG Based H_2CO Sensor



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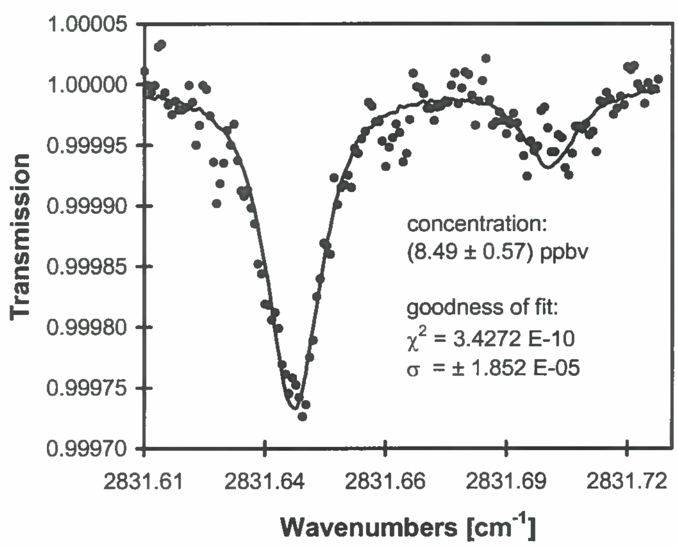
H_2CO Detection in Ambient Air at 3.53 μm



D. Rehle et al. Applied Physics **B72**, 947-952 (2001)

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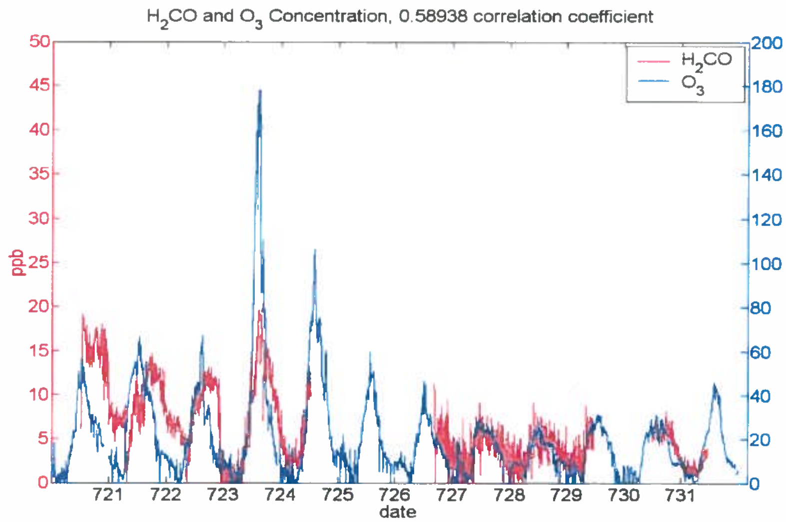
H_2CO and O_3 Concentrations at Deer Park, TX for July 20-31, 2003



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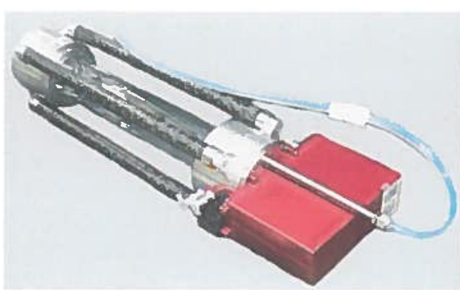
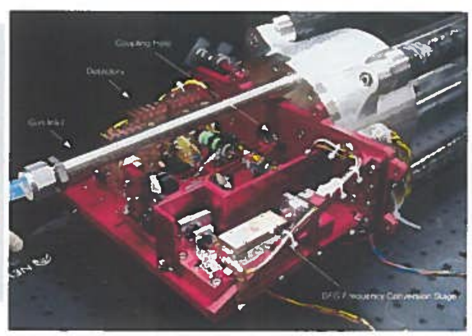
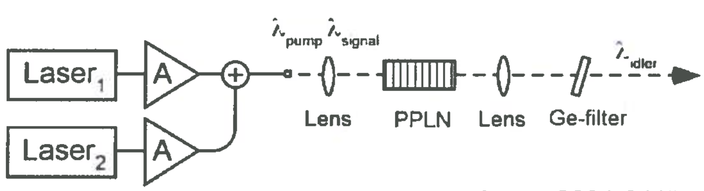
Advanced DFG System for H_2CO Detection







λ_{idler} = 2831.6417 cm^{-1}

$Laser_1$ = 1560 nm
$Laser_2$ = 1083 nm

A. Fried et al, Development iof DFG source inn progress

Motivation for a NCAR Biocomplexity Project (2003-2005)

- Study of the Carbon Cycle: Land, Ocean, Atmosphere
- Combustion of fossil fuels increase atmospheric CO_2 levels and in turn global temperatures
- Currently, oceanic and terrestrial biospheres absorb 50% of anthropogenic atmospheric carbon. Will the sinks cease to take up CO_2 ?

- Major sources and sinks have been identified, but their specific mechanisms are still unclear
- Flexible and real time sensor is needed.
- Bring the instrument to the sample: Land, sea, troposphere, stratosphere, planets !

NCAR C-130

Accurate measurements of $^{12/13}CO_2$ ratios and other trace gases are key to attain detailed knowledge of the carbon cycle processes

Intercontinental Chemical Transport Experiment 2004

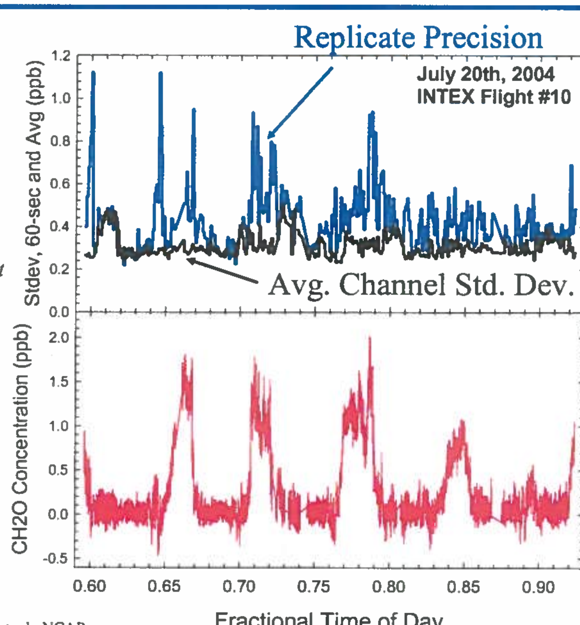
Each CH_2O Point
Replicate Precision
Over 1 min, N = 60

Avg. Channel Std. Dev

$$\sigma_{1min} = \sigma_{1sec}/\sqrt{n} \cong 200ppt/\sqrt{60} \cong 26ppt$$

Each Point
1-second data points

Concentration determined by least squares fit of Calibration spectrum to Sample spectra



INTEX July 2004, data provided by Alan Fried et. al., NCAR Boulder, CO

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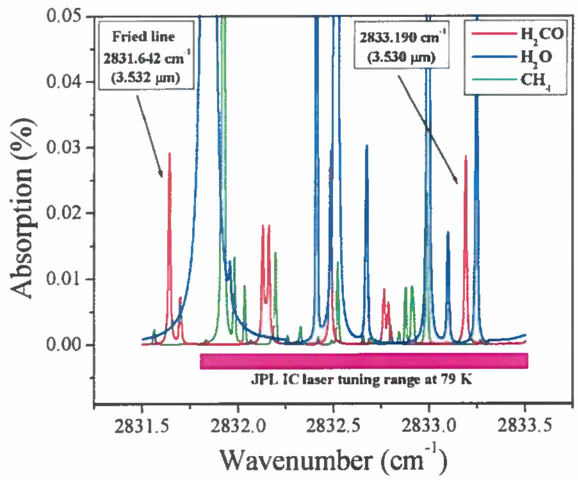
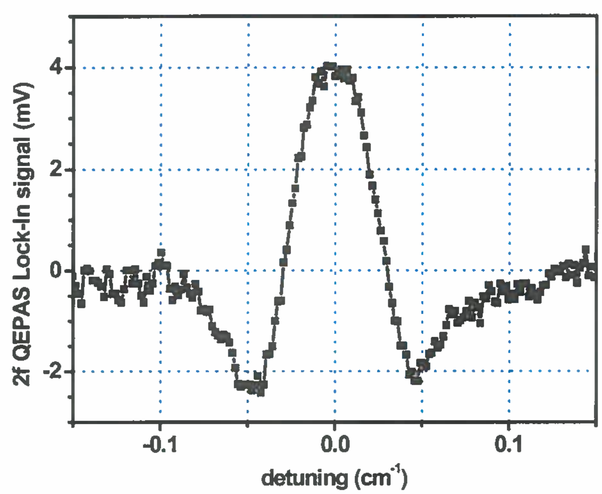
HITRAN Based Simulation of a H_2CO-H_2O-CH_4 Spectrum in Tuning Range of a 3.53μm IC Laser



- H_2CO : 10 ppb
- H_2O : 3%
- CH_4 : 2 ppm
- Optical path: 100 m
- Total pressure: 30 Torr

NASA JPL RICE

2f - QEPAS based H_2CO signal at 3.53 μm (2832.48 cm^{-1})

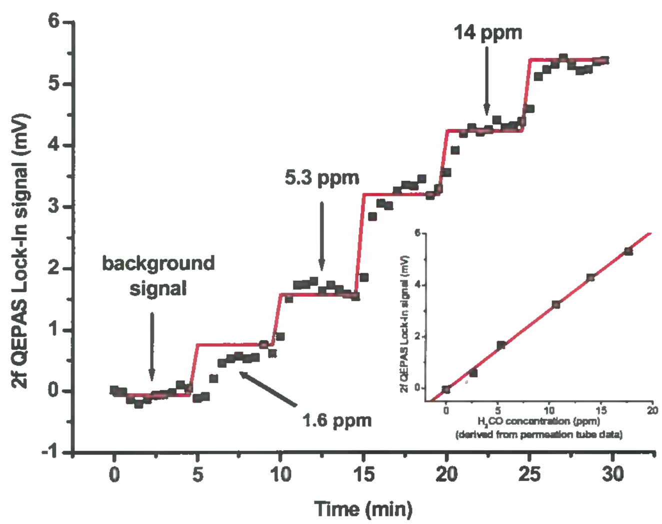


- [H_2CO]: 13.27 ppm
- Sensitivity: $2.2\times10^{-8}cm^{-1}W/\sqrt{Hz}$
- QEPAS NE sensitivity for NH_3: $7.2\times10^{-9}cm^{-1}W/\sqrt{Hz}$ (For comparison)

Applied Physics B 79, 799-803, 2004

NASA JPL RICE

IC Laser based Formaldehyde Calibration Measurements with a Gas Standard Generator



- H_2CO absorption frequency: 2832.5 cm^{-1}
- Lock-In time constant: 10 s
- QEPAS parameters
  - Resonance frequency: 32.760 KHz
  - Q-factor: 17336
  - Pressure: 200 Torr
  - Gas Flow: 75 sccm
  - IC laser power: 6 mW

NASA JPL RICE

QEPAS Performance for 7 Trace Gas Species (2004)

Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, cm^{-1}W/Hz$^{1/2}$	Power, mW	NEC (τ=1s), ppmv
NH_3 (N_2)	6528.76	60	7.2×10^{-9}	38	0.65
H_2O (exhaled air)	6541.29	90	8×10^{-9}	5.2	580
CO_2 (exhaled air)	6514.25	90	1.0×10^{-8}	5.2	890
N_2O (air+5%SF_6)	2195.63	50	1.5×10^{-8}	19	0.007
CO (N_2)	2196.66	50	5.3×10^{-7}	13	0.5
CO (propylene)	2196.66	50	7.4×10^{-8}	6.5	0.14
CH_2O (air)	2832.48	200	2.2×10^{-8}	3.4	0.55

NNEA – normalized noise equivalent absorption coefficient.

NEC – noise equivalent concentration for available laser power and τ=1s time constant.

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

- Atmospheric Chemistry: Environmental monitoring of C_y gases (CO_2, H_2O, CO, N_2O, CH_4)
  - Global warming studies
    - Temporal and spatial variations of isotopic ratios
    - Identification of carbon sources and sinks
  - Global carbon budget studies
- Study of planetary gases (e.g. for Mars: CO, CO_2, H_2O, CH_4, O_3, OCS)
- Volcano eruption forecasting and gas emission studies (CO_2, HCl, SO_2, HF, H_2S, CO, H_2O)
- Geochemistry
- Medical applications (non-invasive human health monitoring)

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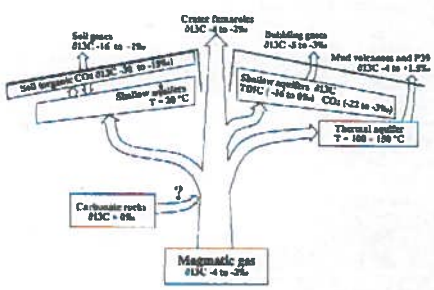
Volcanological applications

- 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 and volcanic hazard assessment



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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

CO_2 Absorption Line Selection Criteria

- Three 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-or-
    - Can be realized if different vibrational transitions are selected for the two isotopes (4.35 μm for $^{13}CO_2$ and 2.76 μm for $^{12}CO_2$)*
- For the first 2 strategies both absorption lines must lie in a laser frequency scan window
- Avoid presence of other interfering atmospheric trace gas species

* Proposed scheme by Curl, Uehara, Kosterev and Tittel, Oct. 2002

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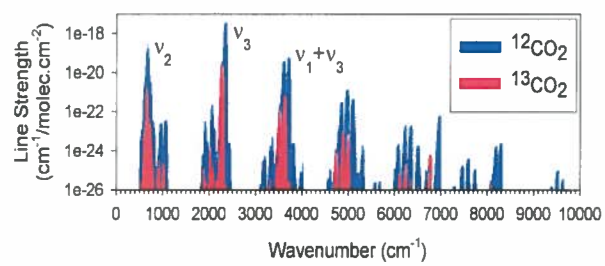
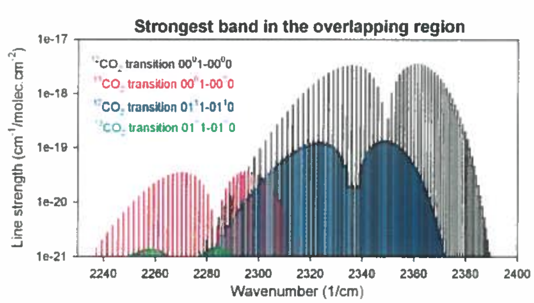
Comparison of CO_2 line selection and strategy for different current US mid-IR laser-based isotopic ratiometers

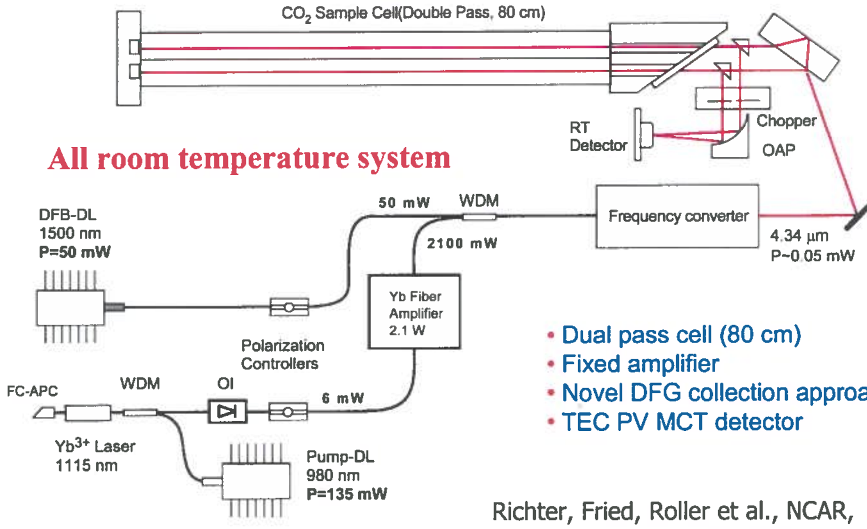
Group	Technology	Frequency 12/13 [cm^{-1}]	δT [K]	Precision
NCAR, UC and Rice U. A. Fried et al; Erdelyi	**DFG with NIR TDLs and fiber amplifiers**	**2299.642 2299.795**	**0.005**	0.8 ‰*
Aerodyne, Harvard U. M. Zahniser et al.	Direct Scan PbSalt TDL, QCL, DFG; Dual optical paths	2314.304 2314.408	0.213	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 ‰

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





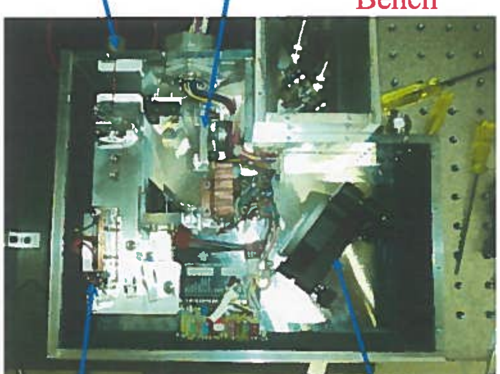
Mid-IR DFG Isotopic Ratio Spectrometer

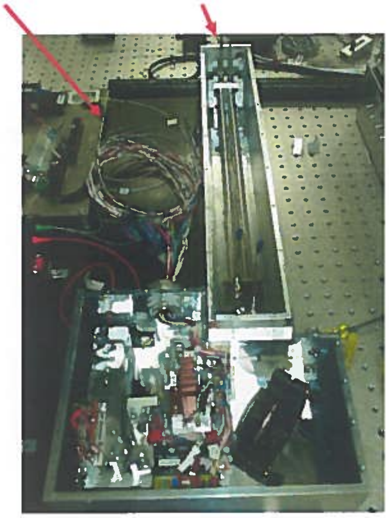


- Dual pass cell (80 cm)
- Fixed amplifier
- Novel DFG collection approach
- TEC PV MCT detector

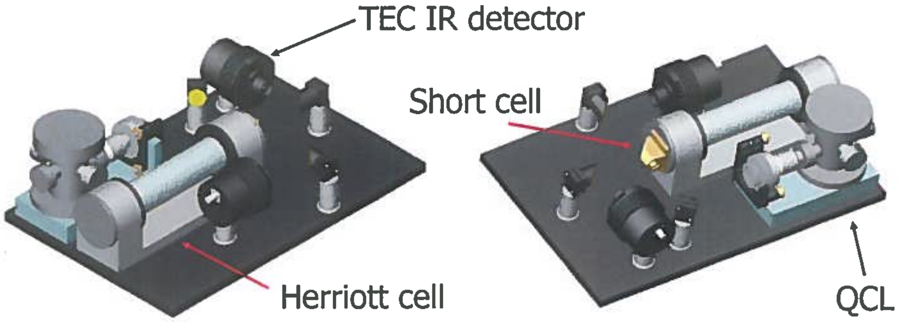
Richter, Fried, Roller et al., NCAR, Boulder, CO, Aug. 2004

Current Status of DFG based IRS System at NCAR





QC laser based Isotopic Ratio Sensor at Rice



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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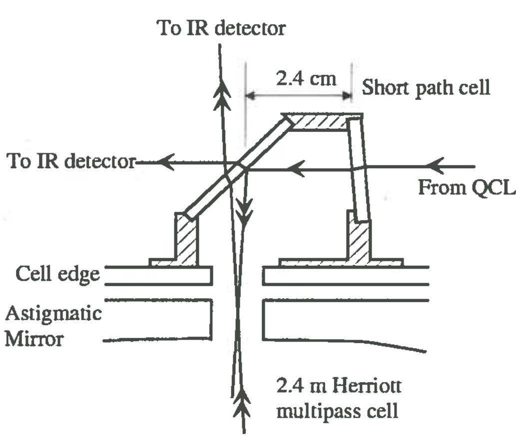
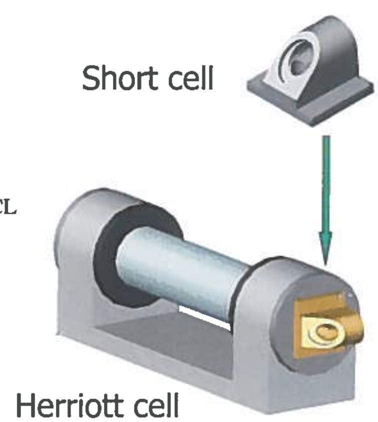
Dual path length gas cell design for infrared ratio spectrometry





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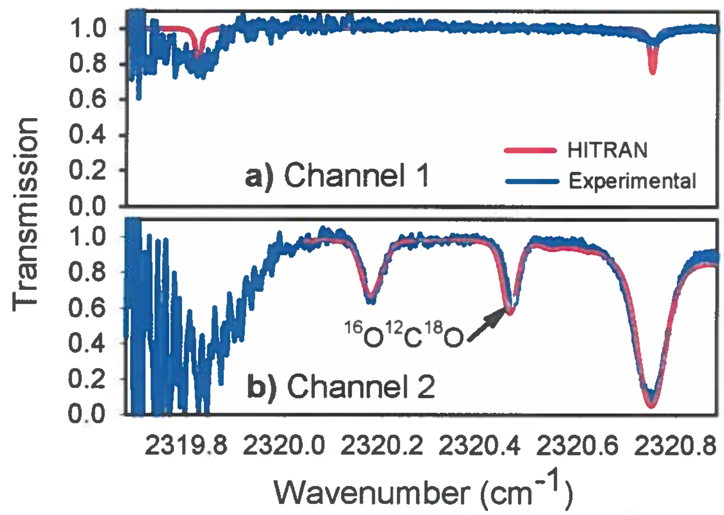
$^{16}O^{12}C^{18}O$ Spectra at 2320.2 cm^{-1}



D. Weidmann et al. Applied Physics B 2004

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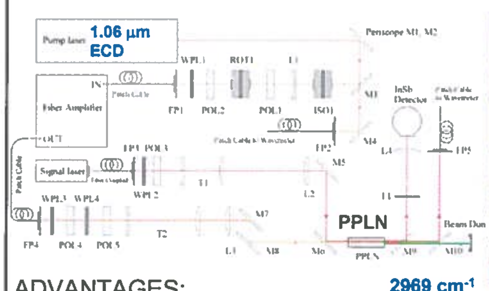
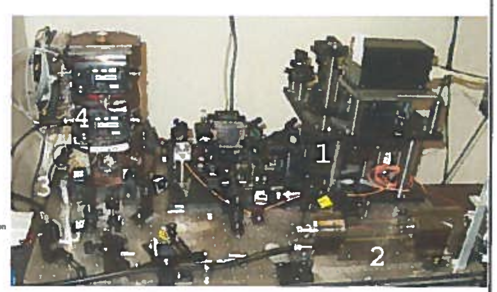
DFG of $^{13}CH_4$/$^{12}CH_4$ at 3.3 μm



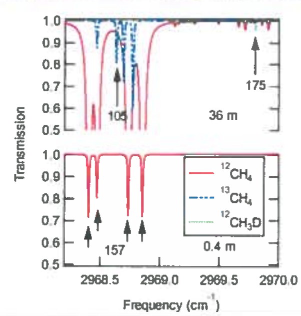


ADVANTAGES:

- WIDELY TUNABLE
- NARROW LINEWIDTH <0.001 cm^{-1}
- EXCELLENT BEAM QUALITY

DISADVANTAGE:

- COMPLEXITY



AERODYNE, Inc. M. Zahniser et. al.
SANDIA NATIONAL LABORATORY

Towards CW Operation of DFB QCLs

- Main drawbacks of QCL pulsed operation
  - Pulse to pulse intensity variation
  - Linewidth broadening by thermal chirping
  - Requirement of nanosecond electronics
- Efforts towards achieving quasi-RT CW DFB QCLs
  - M. Beck *et al.*, Science, **295**, 301-305, 2002
  - T. Aellen *et al.*, Applied Physics Letters, **83**, 1929, 2003
  - A. Evans, *et al.*, Applied Physics Letters, **84**, 314, 2004 [FP QCL]
  - M. Troccoli *et. al.*, 5th Workshop on Quantum Cascade Lasers, Freiburg, Sept. 23-24 2004

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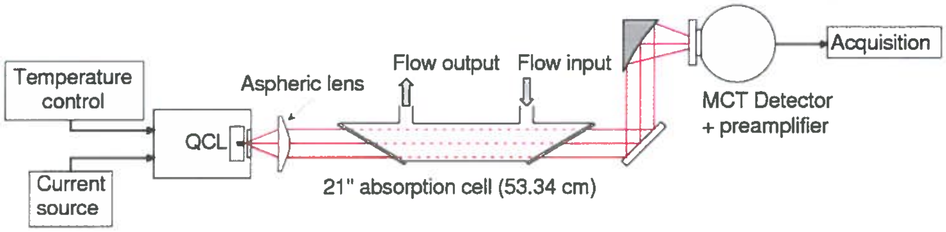
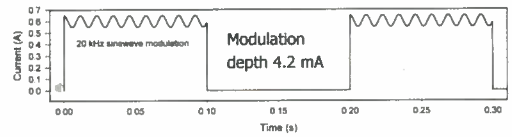
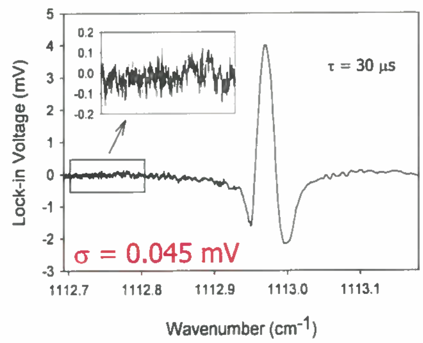
CW RT DFB QC laser based NH_3 Sensor @ 9 μm (1113 cm^{-1})



Wavelength Modulation Spectroscopy of NH_3

- QCL Drive Current : Quasi CW + Wavelength modulation





- Calibration with a 1038 ppm $NH_3:N_2$ mixture

1σ extrapolated sensitivity
82 ppb.m/√Hz

⇒ Improvement by a factor of 3 compared to direct absorption spectroscopy

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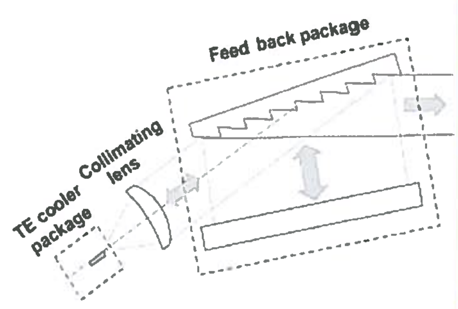
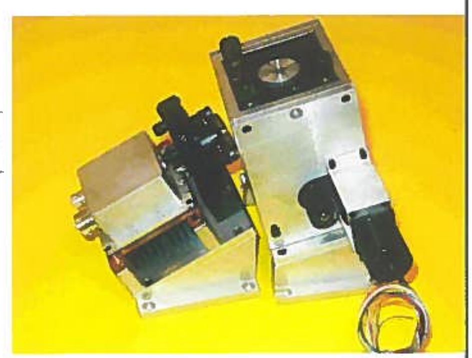
λ-Tunable Pulsed QC Laser GCEC Architecture





H. Le et al., Univ. of Houston

NASA Atmospheric & Mars Gas Sensor Platforms

Tunable laser sensor for earth's stratosphere

Aircraft laser absorption spectrometer

Tunable laser planetary spectrometer

Conclusions and Future Directions

- **Quantum Cascade Laser based Trace Gas Sensors**
  - Compact and robust sensors based on QC-LAS and QE L-PAS
  - High sensitivity (10^{-4}-10^{-5}) and selectivity (3 to 500 MHz)
  - Dramatic reduction of sample volume (~0.2 mm^3)
  - Detected trace gases: NH_3, CH_4, N_2O, CO_2, CO, NO, H_2O, COS, C_2H_4, C_2H_5OH, SO_2. H_2CO and several isotopic species of C, O, N and H.
- **Applications in Trace Gas Detection**
  - Environmental monitoring (NH_3, CO, CH_4, C_2H_4, N_2O, CO_2)
  - Industrial process control and chemical analysis (NO, NH_3)
  - Medical Diagnostics (NO, CO, COS, CO_2, C_2H_4)
- **Future Directions and Collaborations**
  - Cavity enhanced (ICOS) and QE L-PAS spectroscopy based applications using novel thermoelectrically cooled cw and broadly wavelength tunable quantum cascade lasers
  - Applications using new near IR interband and far-IR intersub-band quantum cascade lasers

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