RICE

Development of QCL Based Sensor Technology for Trace Gas Monitoring Applications

F.K. Tittel, Yu. Bakhirkin, R.F.Curl, A.A. Kosterev, S. So, D.Weidmann & G.Wysocki

Rice Quantum Institute, Rice University, Houston, TX

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

OUTLINE

- 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

5th QCL Workshop

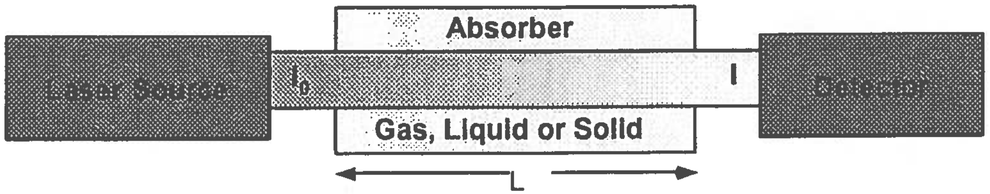
Freiburg Sept. 23-24, 2004

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 (eg ecosystems and airborne)
  - 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 and Photochemistry**

RIC

Fundamentals of Laser Absorption Spectroscop)

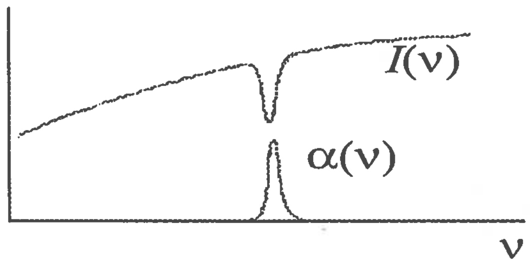


Beer-Lambert's Law of Linear Absorption

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

$\alpha(\nu)$ - 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$\cdot cm^{-3} \cdot atm^{1}$]

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

$g(\nu - \nu_0)$ – normalized spectral lineshape function [cm], (Gaussian, Lorentzian, Voigt)

Optimum Molecular Absorbing Transition

- Overtone or Combination Bands (NIR)
- Fundamental Absorption Bands (MID-IR)

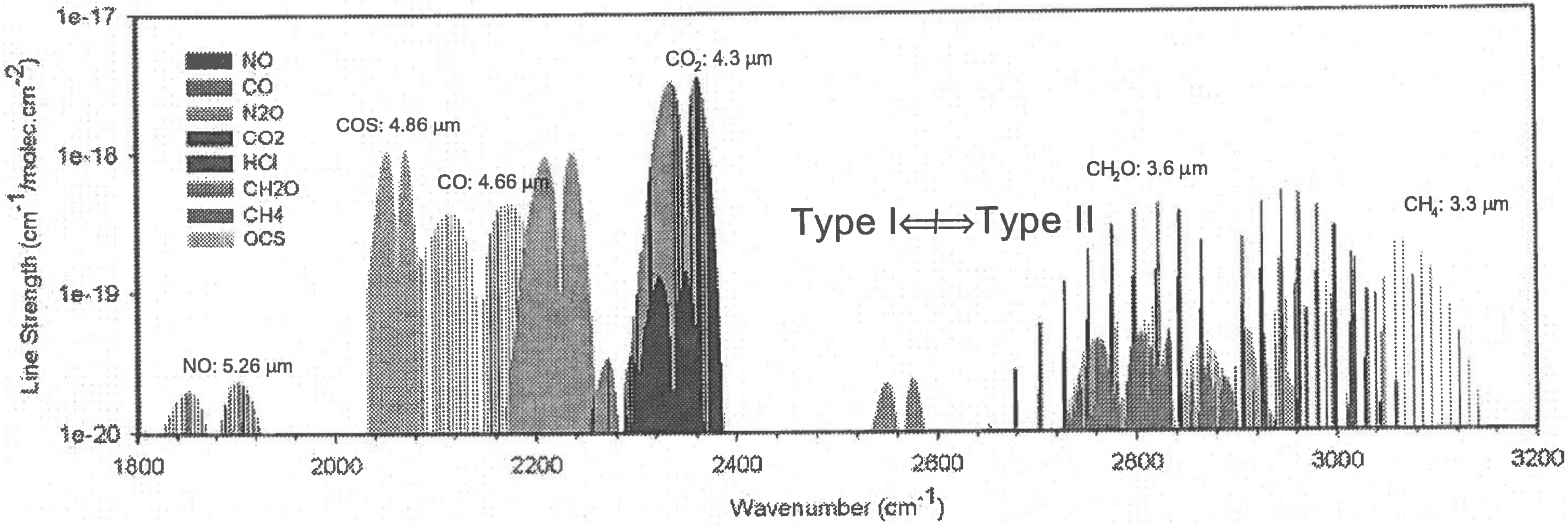
Long Optical Pathlengths

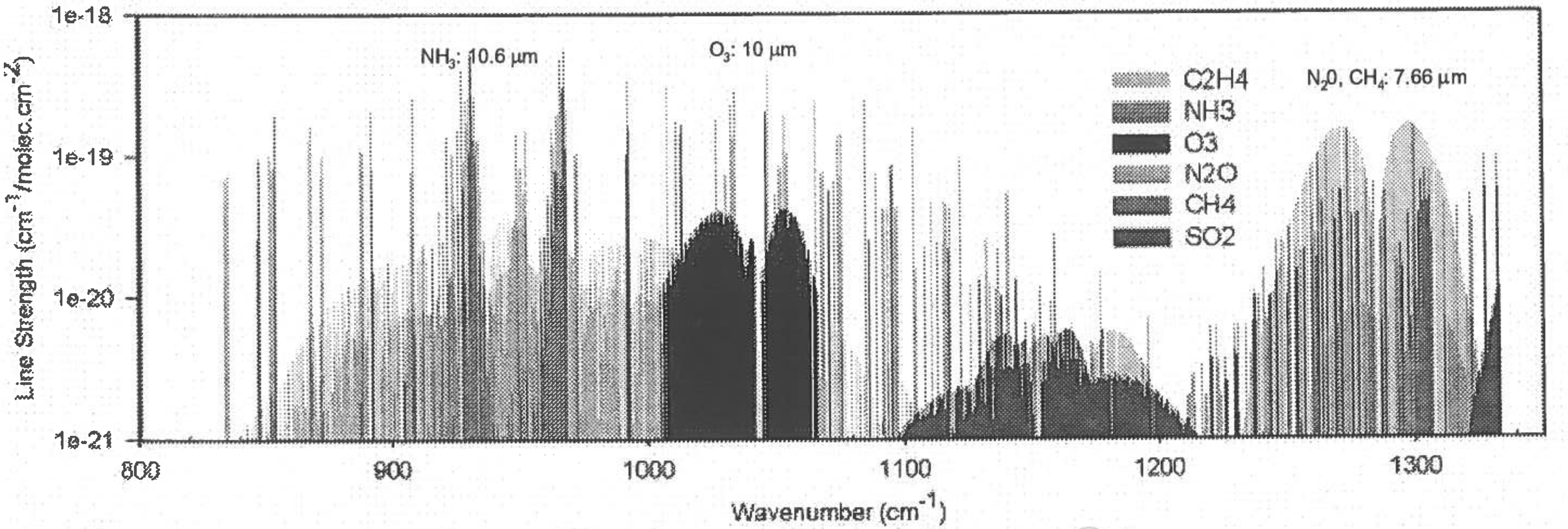
- Multipass Absorption Cell
- Cavity Enhanced and Cavity Ringdown Spectroscopy
- Open Path Monitoring (with retro-reflector)

Spectroscopic Detection Schemes

- Frequency or Wavelength Modulation
- Balanced Detection
- Zero-air Subtraction
- Photoacoustic Spectroscopy

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





RIC

CW IR Source Requirements for Laser Spectroscopy

REQUIREMENTS

- Sensitivity (% to ppt)
- Selectivity
- Multi-gas Components
- Directionality
- Rapid Data Acquisition
- Room Temperature

IR SOURCE

- Power
- Narrow Linewidth
- Tunable Wavelength
- Beam Quality
- Fast Response
- No Consumables

RIC

Key Characteristics of Mid-IR Quantum Cascade Lasers for Spectroscopy

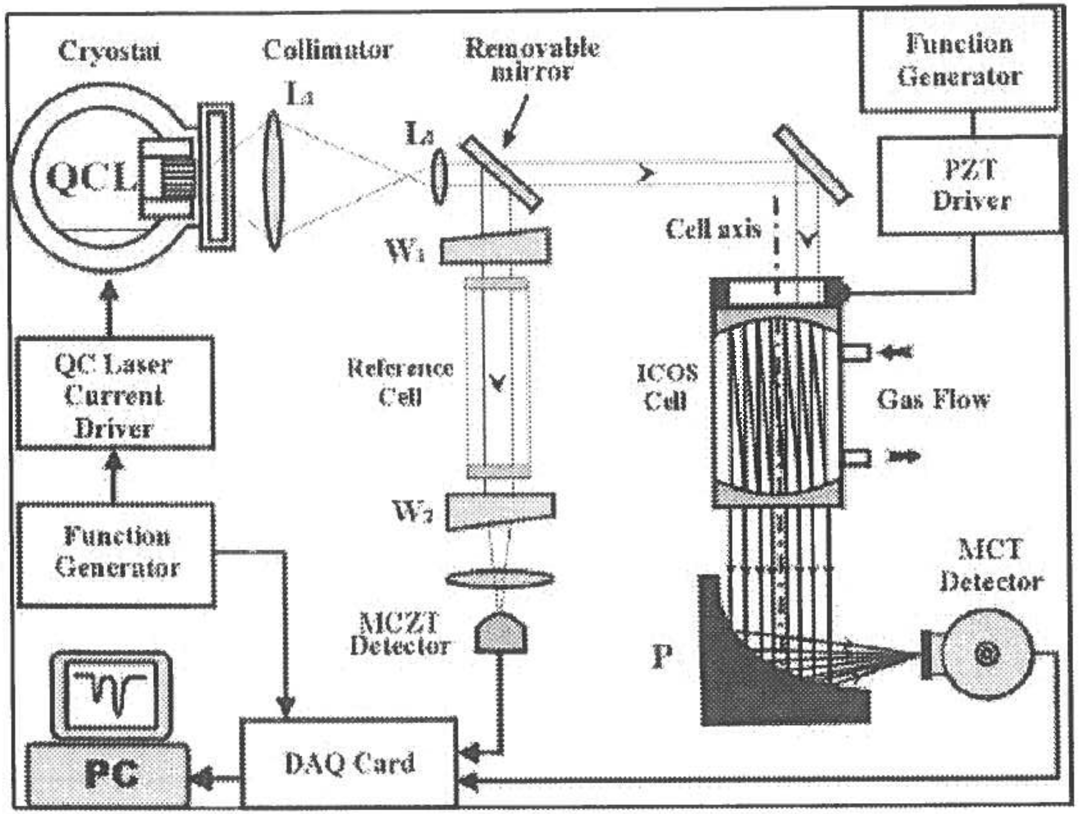
- QC laser wavelengths cover entire mid-IR range from 3.3 t 24 μm determined by thickness of the quantum well and barrier layers of the active region
- Intrinsically high power lasers (determined by number of stages of injector-active quantum well gain regions)
  - CW:~100 mW @ 80°K and 1- 640 mWs @ 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 (single frequency:<kHz - 330MHz)
- Wavelength tunable by current (~1cm^{-1}) or temperature scanning (~10 cm^{-1}); ~150 cm^{-1} with external cavity grating
- High reliability: long lifetime, robust operation and reproducible emission wavelengths

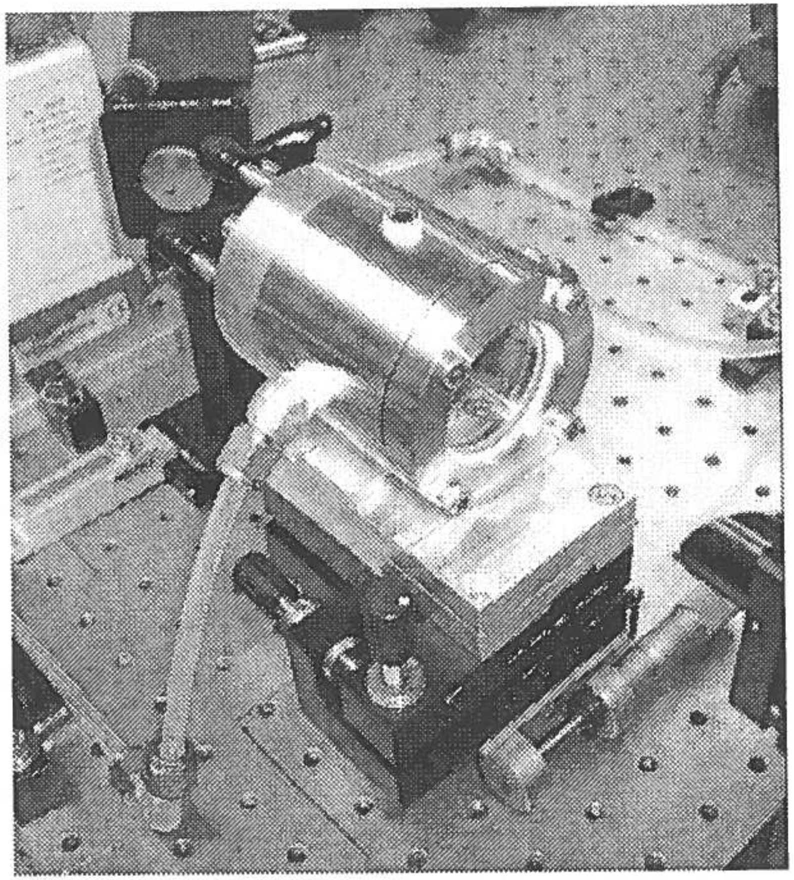
RIC

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**
[illegible]	[illegible]	[illegible]

Off-Axis Integrated Cavity Output Spectroscopy Based Gas Sensor

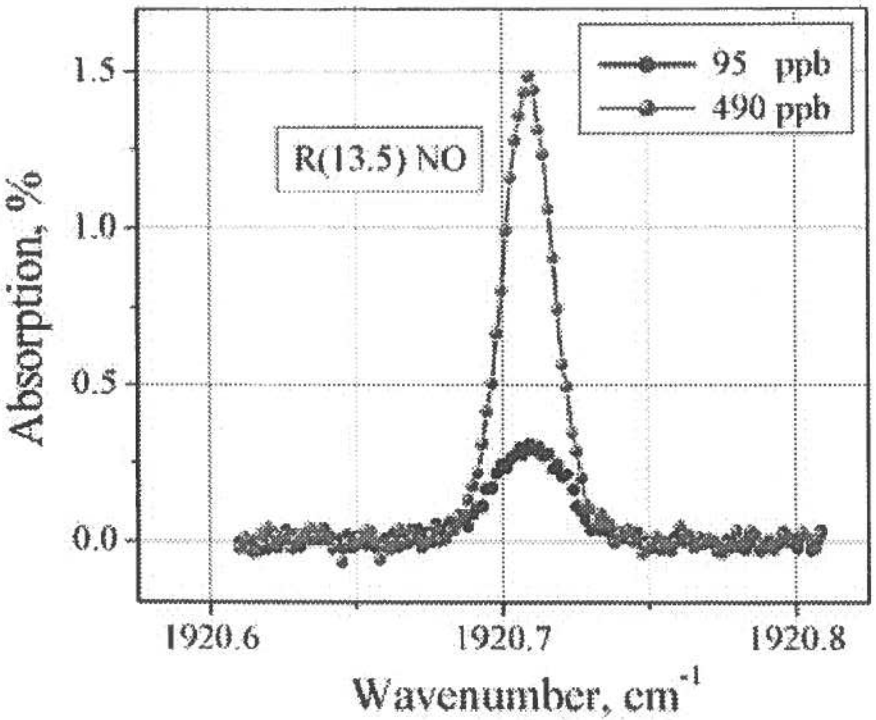


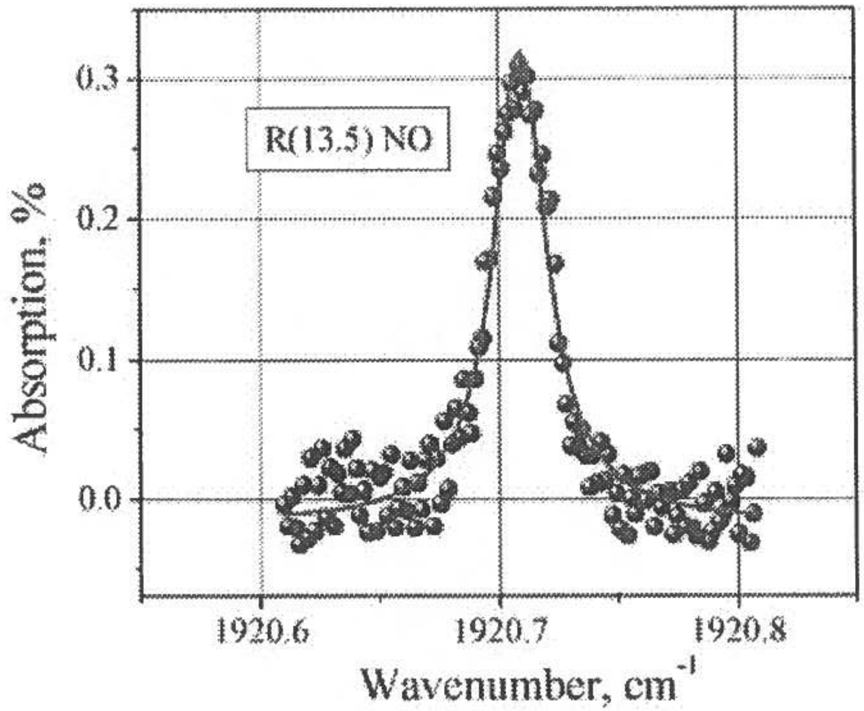


- Novel compact gas cell design of length: 3.8 – 5.3 cm and cell volumes < 80 cm³;
- Low loss mirrors (ROC 1m):~60-250 ppm, R~99.975, L_{eff}=170-800 m
- Rapid eNO concentration measurements during a single breath cycle feasible

PSI LGR

Off-axis ICOS Detection of NO





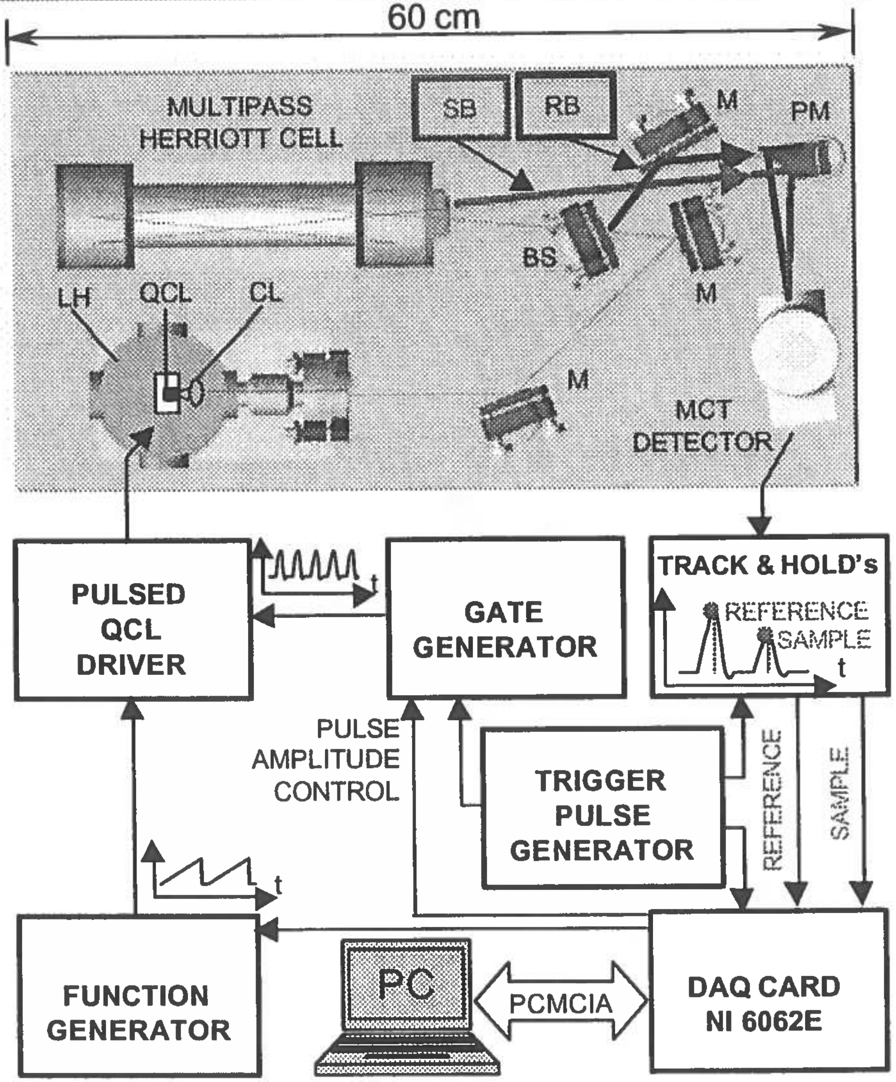
- 95 and 490 ppb NO/N_2 calibration mixture at 100 Torr total pressure
- Effective optical path ~ 70 m (1,350 passes)

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

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

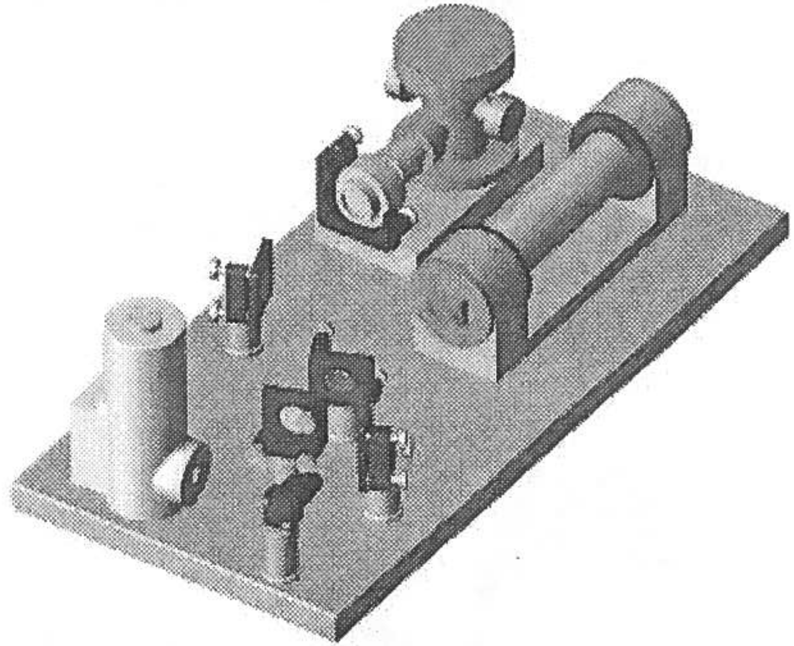
RICE

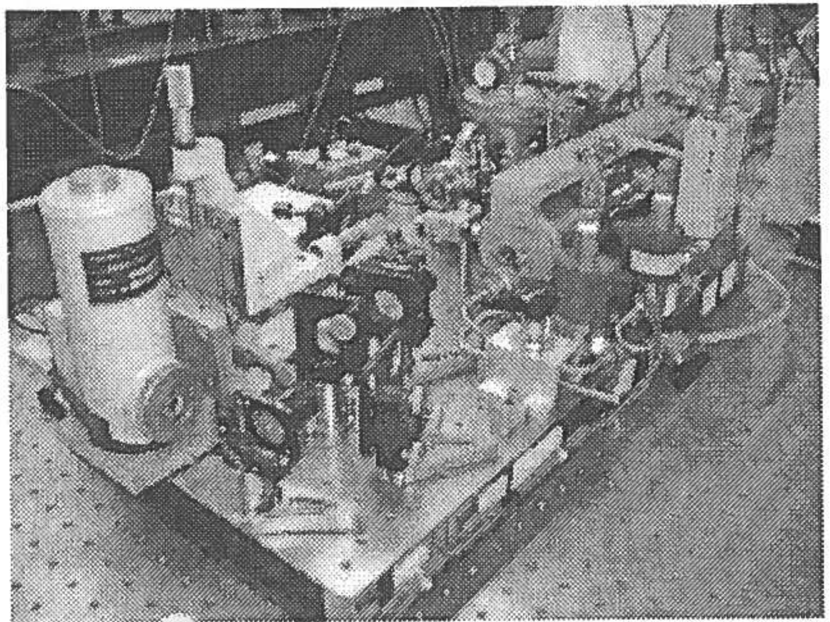
OCS Sensor Architecture



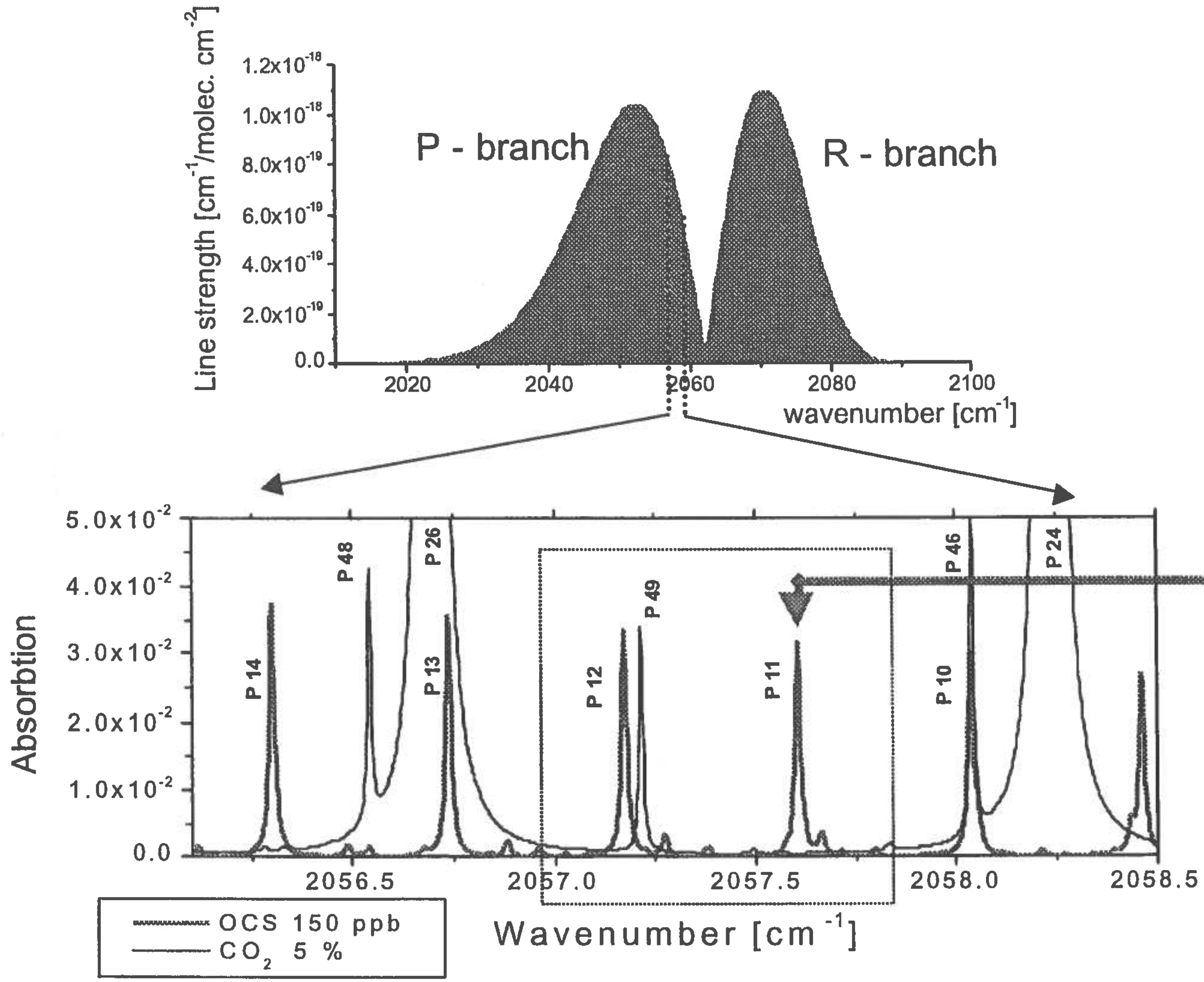
QCL – quantum cascade laser chip
LH - laser housing
CL – collimating lens
SB – sample beam

RB – reference beam
M – mirror
BS – beam splitter
PM – off-axis parabolic mirror





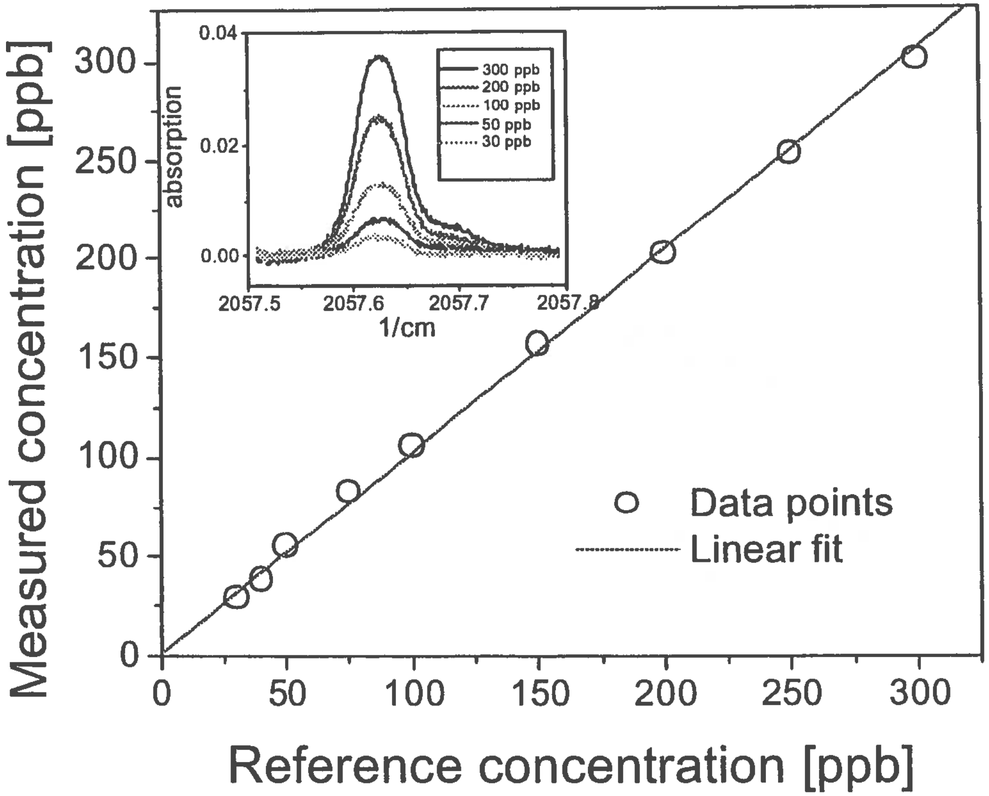
OCS ro-vibrational Spectrum



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

OCS Concentration Calibration of QCL Sensor

Calibration curve

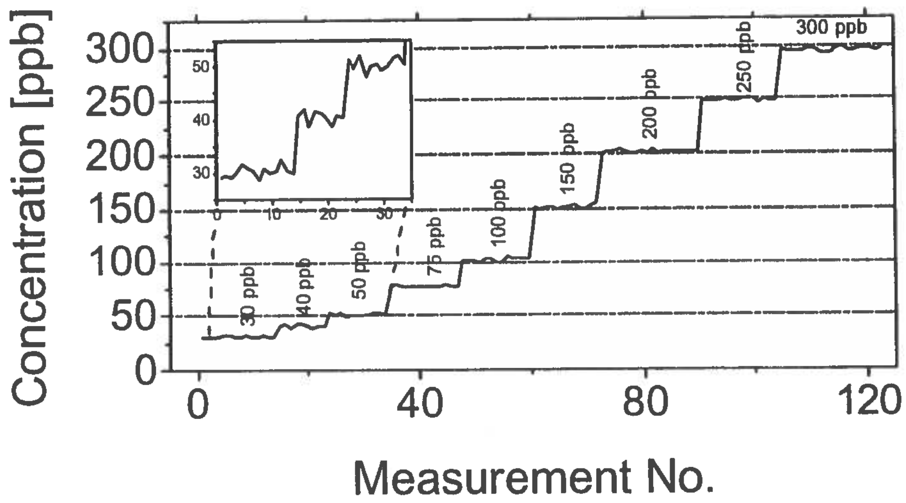


1000 spectra averaged acquired within t = 4 s
and fitted to 300 ppb OCS reference spectrum

Theoretical sensitivity:

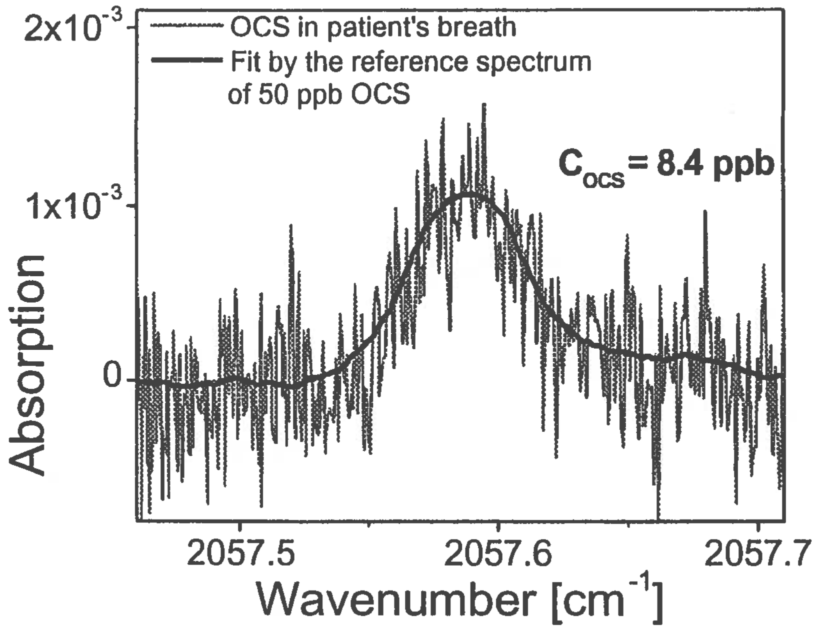
$$0.27\ ppb \cdot \sqrt{1000/100} = 0.85\ ppb$$

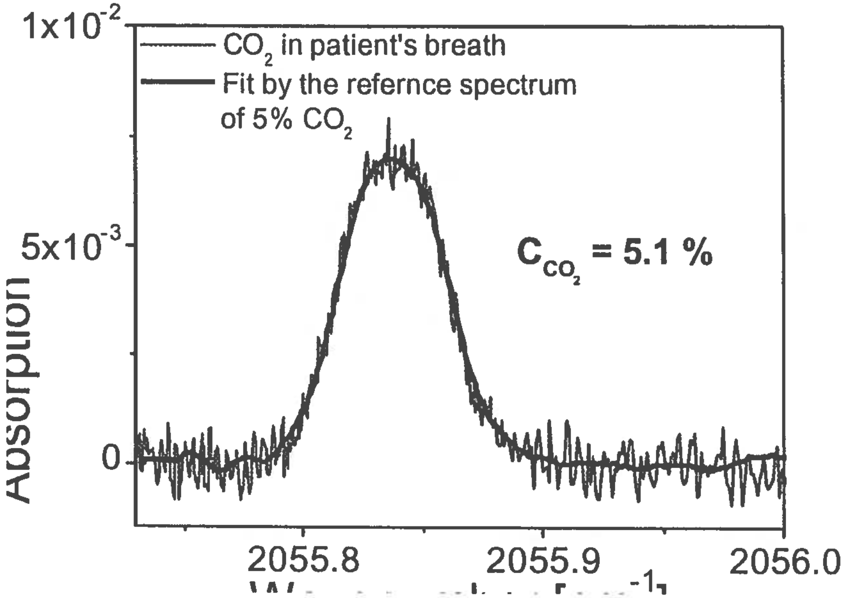
Scattering of the concentration measurement: **σ = 1.2 ppb**



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

OCS and CO_2 Concentration Measurements in Exhaled Breath

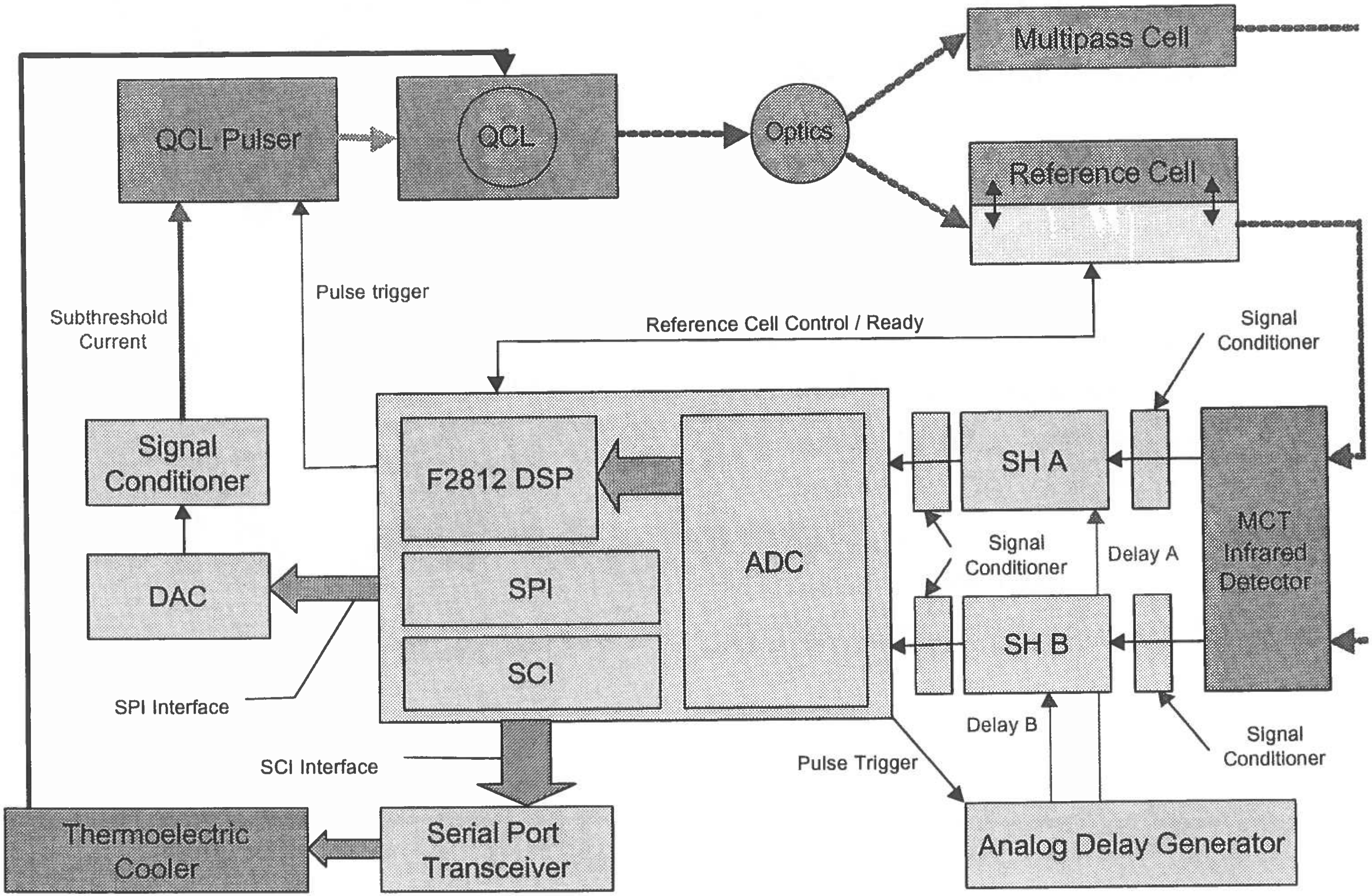




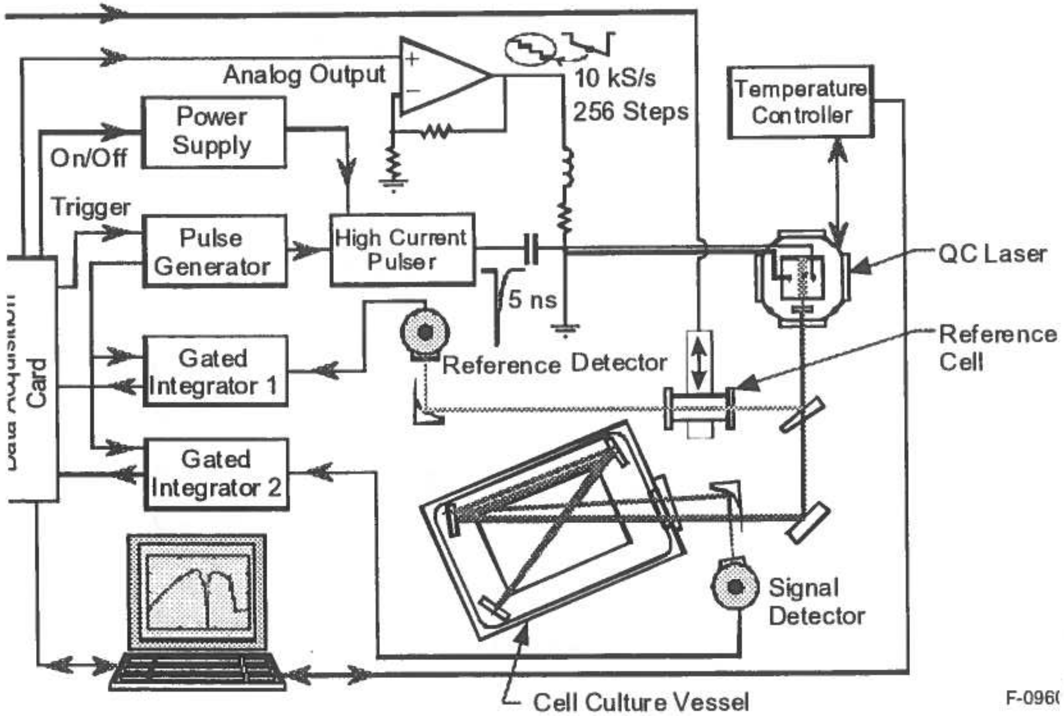
- Sample was taken from lung transplant patient with suspected bronchiolitis*
- Sampling was performed using chemically inert 1 liter tedlar sampling bags and analyzed within 2 hours after collection
- Spectrum was measured at a total pressure of 60 torr

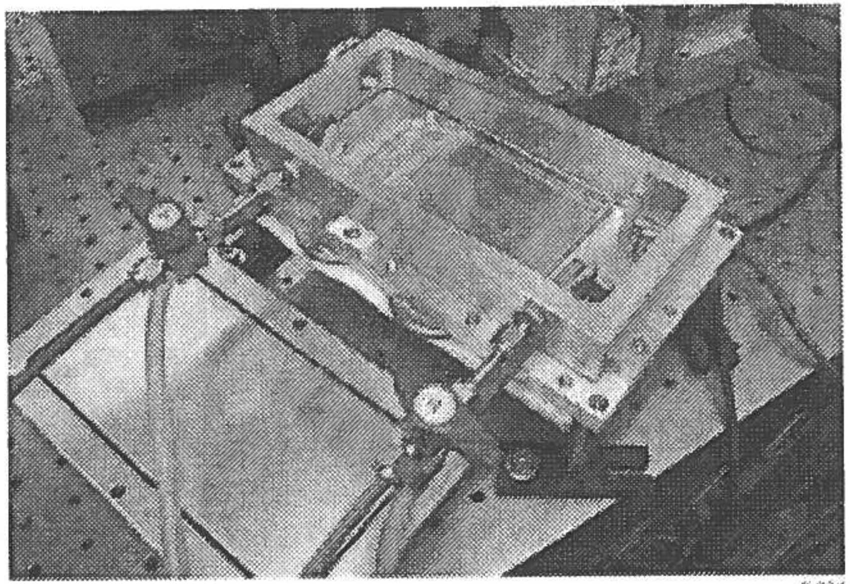
*The authors wish to thank Dr. Remzi Bag and Carolyn M. Paraguaya from Baylor College of Medicine, Houston, TX for supplying breath samples

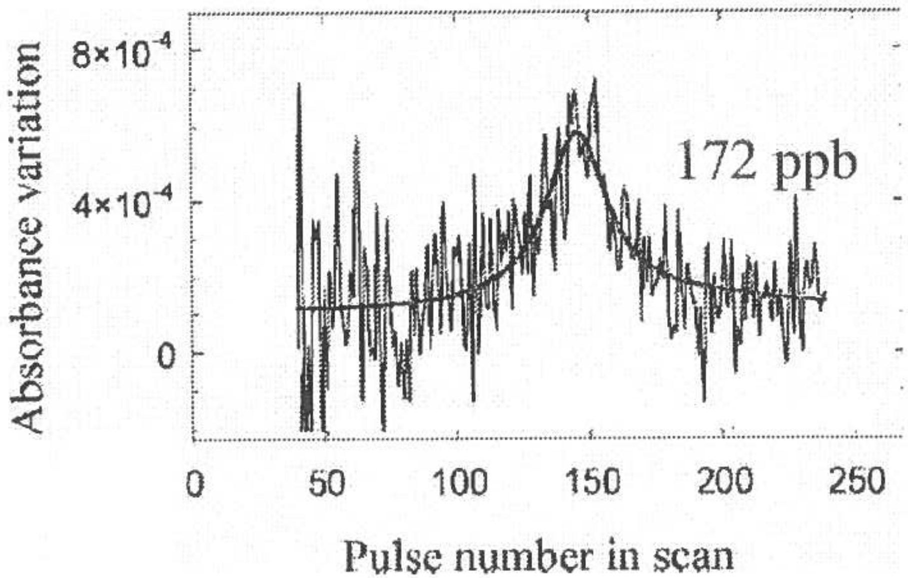
DSP Fast Data Acquisition Architecture*



QC laser based measurements of CO trace gas above cell cultures







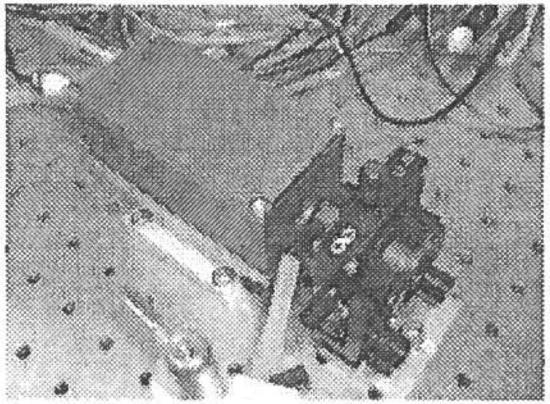
- Measured CO production rates of viable cultures of vascular smooth muscle cells
- Achieved a detection limit of for CO of ~20 ppb

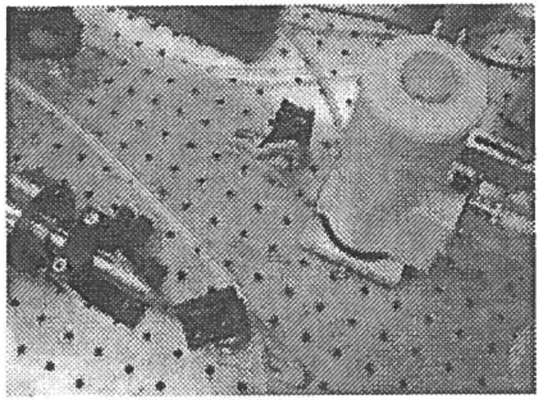
A. Kosterev et al. Appl. Phys. B 74, 95–99 (200

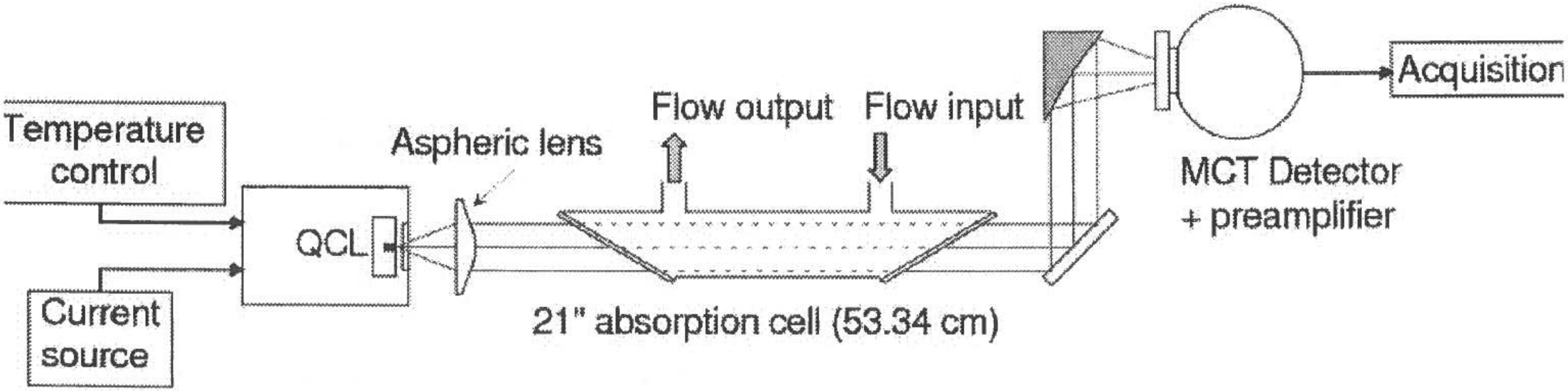
Towards CW Mode Operation of DFB QCLs

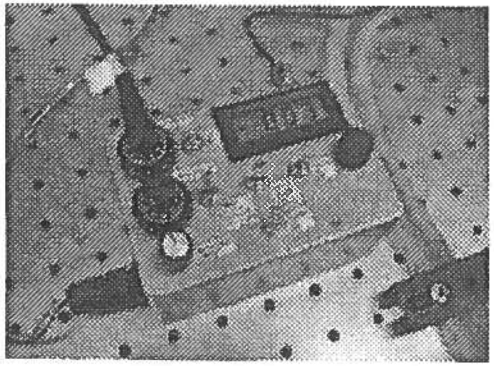
- Main drawbacks of QCL pulsed operation
  - Pulse to pulse intensity variation
  - Linewidth broadening by thermal chirp
  - Requirement of nanosecond electronics
- Efforts towards achieving quasi-RT CW DFB QCLs
  - M. Beck *et al.*, Science, **295**, 301-305, 2002
  - T. Aellen *et al.*, Applied Physics Letters, **83**, 1929, 2003
  - A. Evans, *et al.*, Applied Physics Letters, **84**, 314, 2004 [NON DFB QCL]

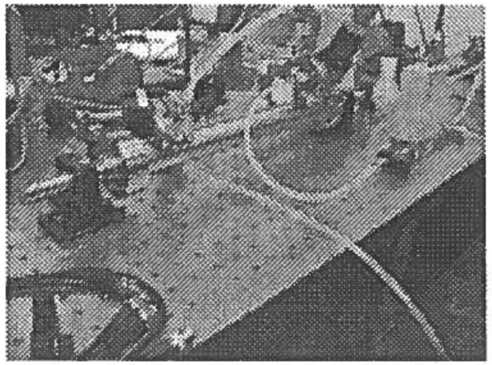
Direct Absorption Based Gas Sensor Architecture

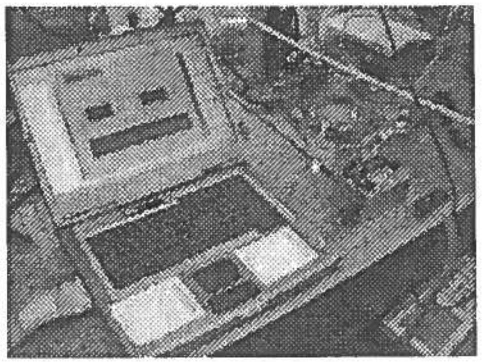






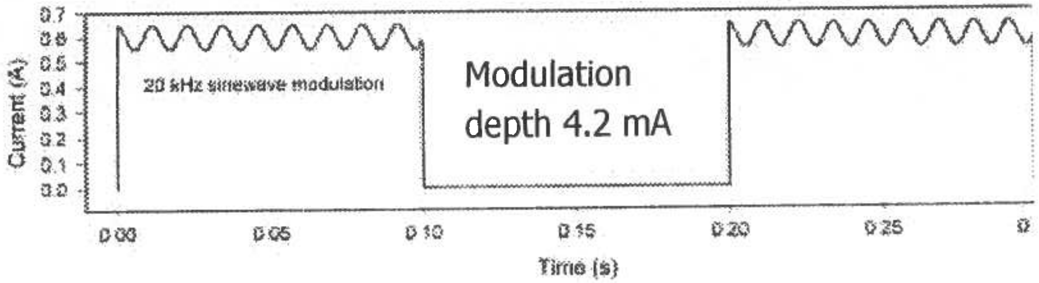


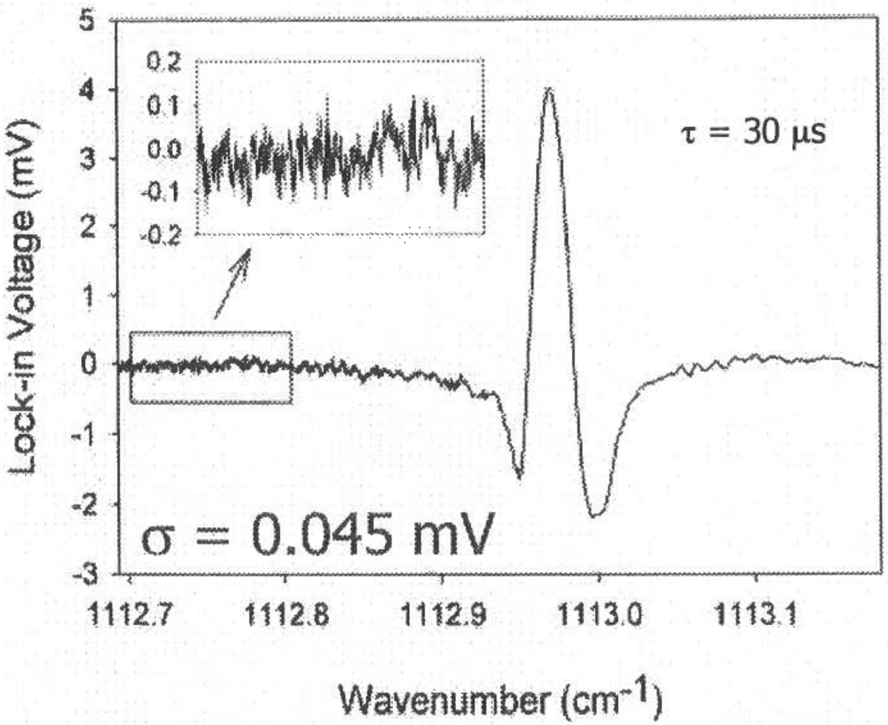




Wavelength Modulation Spectroscopy

- QCL Drive Current :
  Quasi CW +
  Wavelength modulation





- Calibration with a 1038 ppm $\mathbf{NH_3:N_2}$ mixture

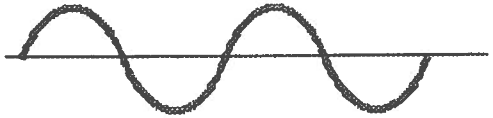
  1σ extrapolated sensitivity
  82 ppb.m/√Hz

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

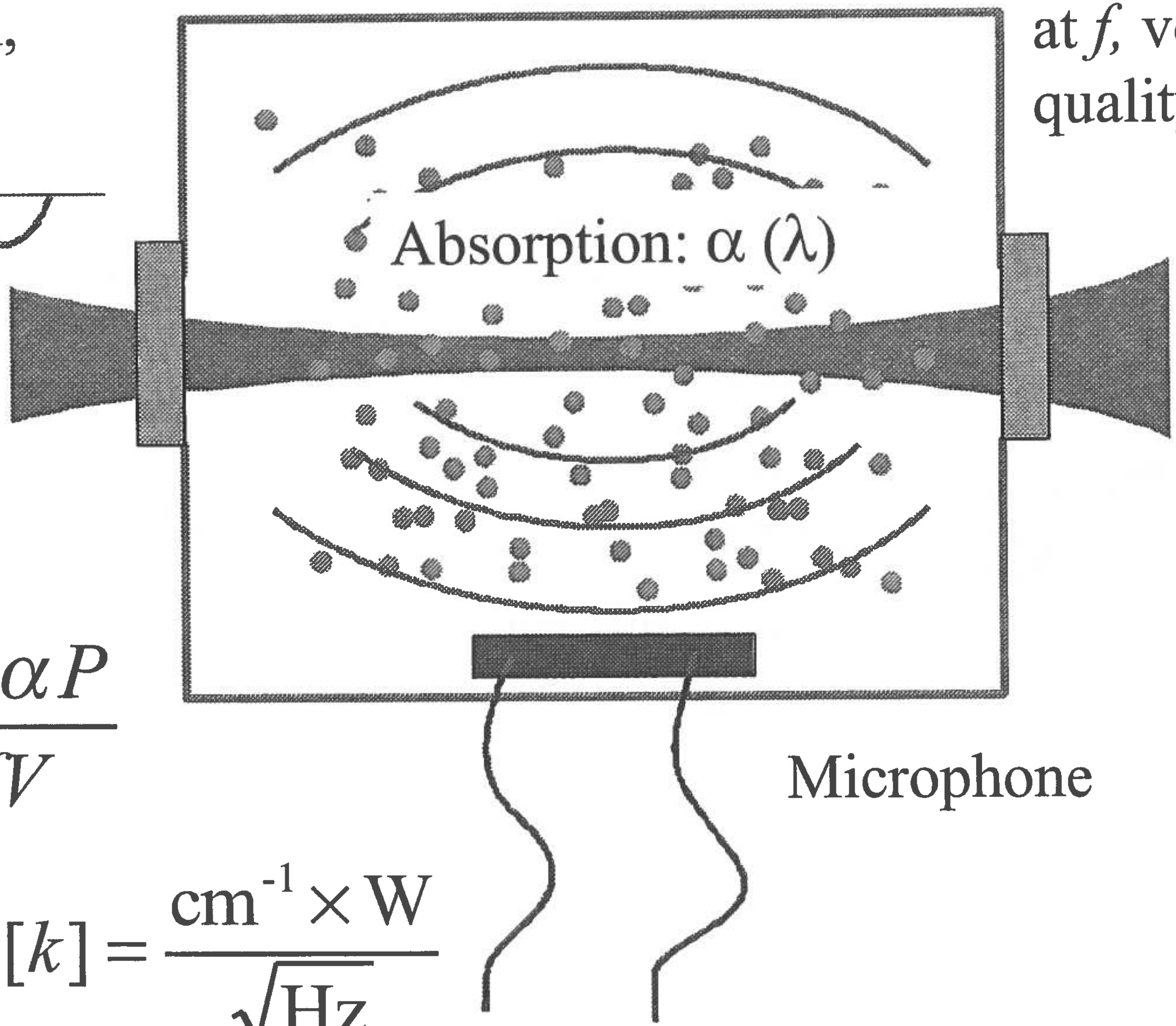
Resonant photoacoustic spectroscopy

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

Laser beam, power *P*



Modulated (*P* or λ) at *f* or *f*/2



Microphone

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

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

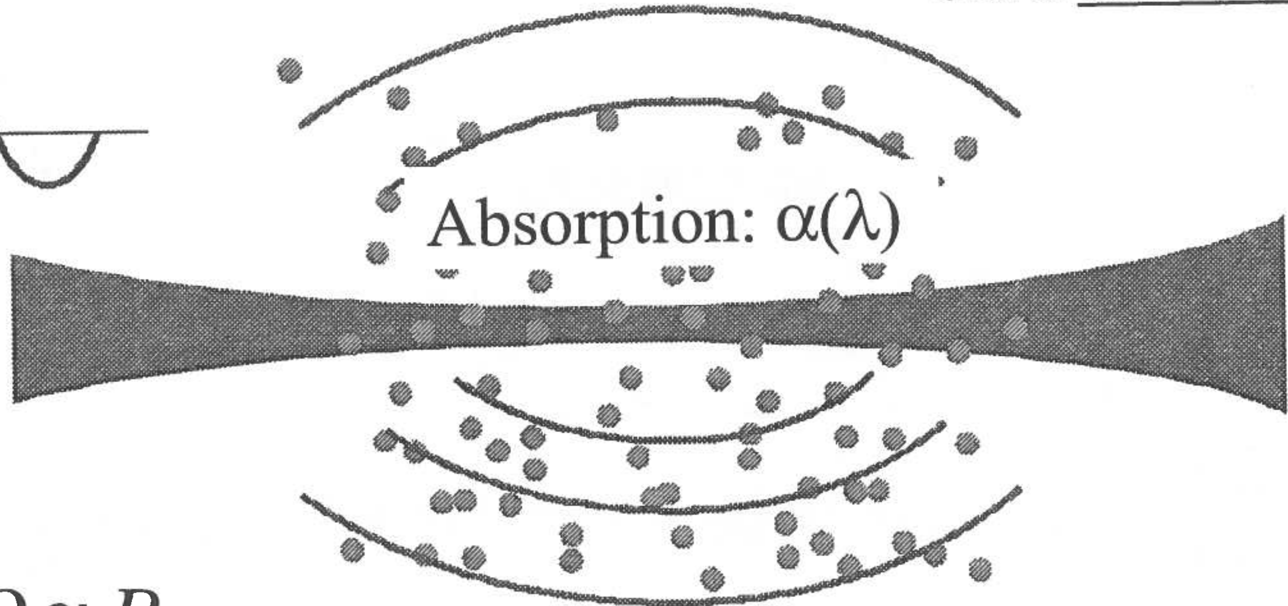
RICE

Quartz-Enhanced Photoacoustic Spectroscopy (QEPAS)

- Resonant Cavity in L-PAS
- Cell is <u>OPTIONAL</u> in QEPAS.

Laser beam,
power *P*

Modulated
(*P* or λ) at *f*
or *f*/2



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

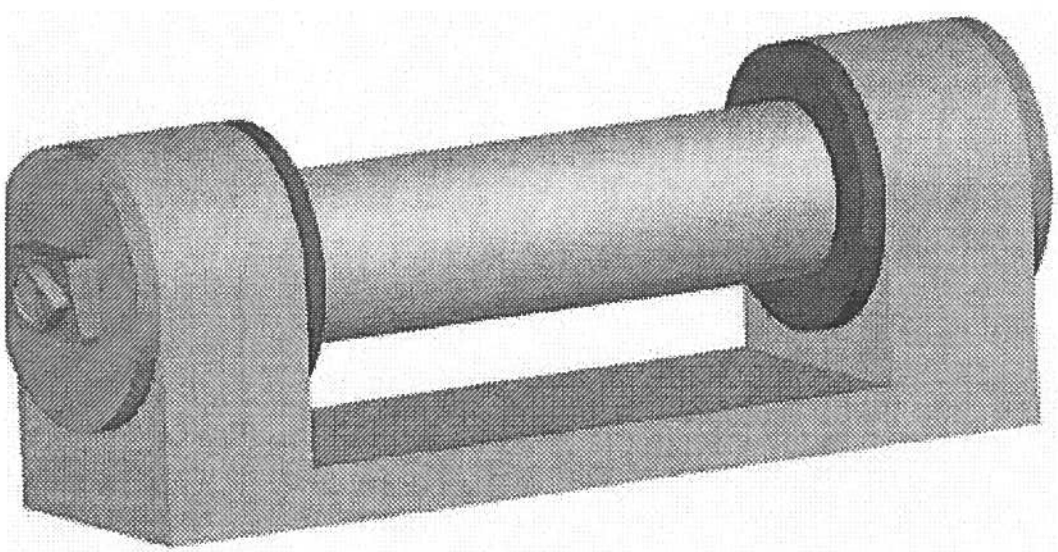
$$\text{Sensitivity}\,[k] = \frac{\text{cm}^{-1} \times \text{W}}{\sqrt{\text{Hz}}}$$

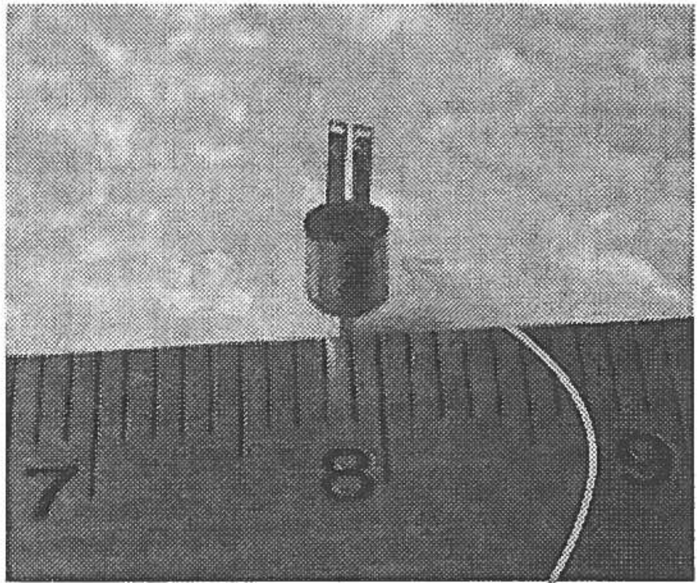
Piezoelectric quartz crystal
(instead of microphone)

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

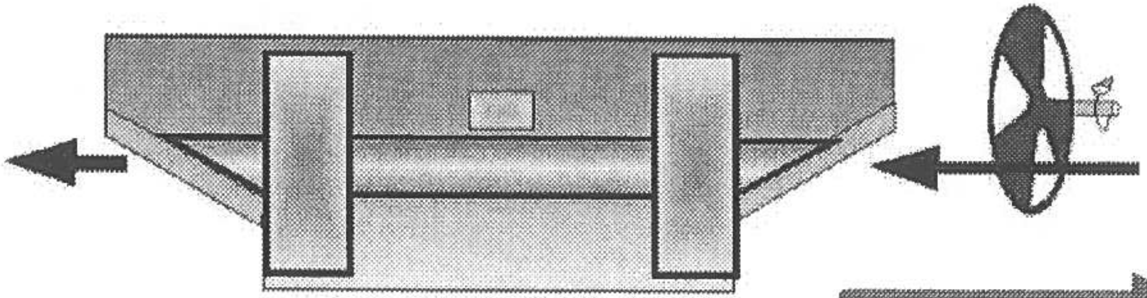
A. Kosterev et al. Optics Letters 27, 1902, 2002

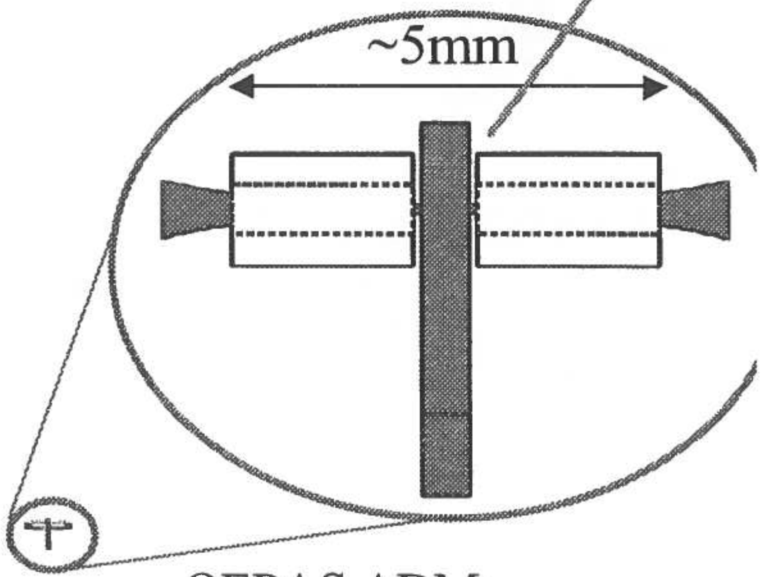
Comparative Size of Absorbance Detection Modules (ADM)





Optical multipass cell (100 m):
l~70 cm, V~3000 cm^3

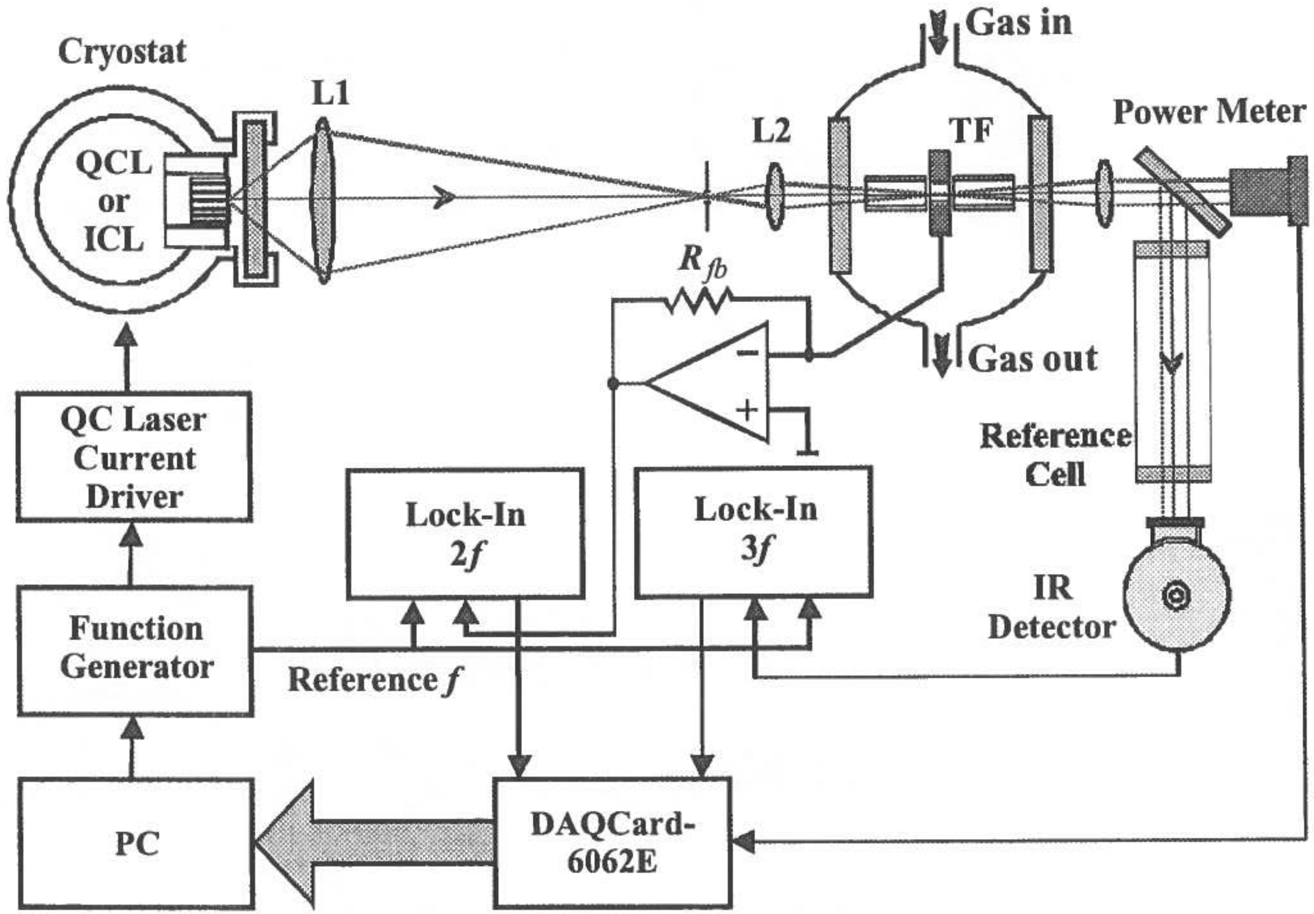


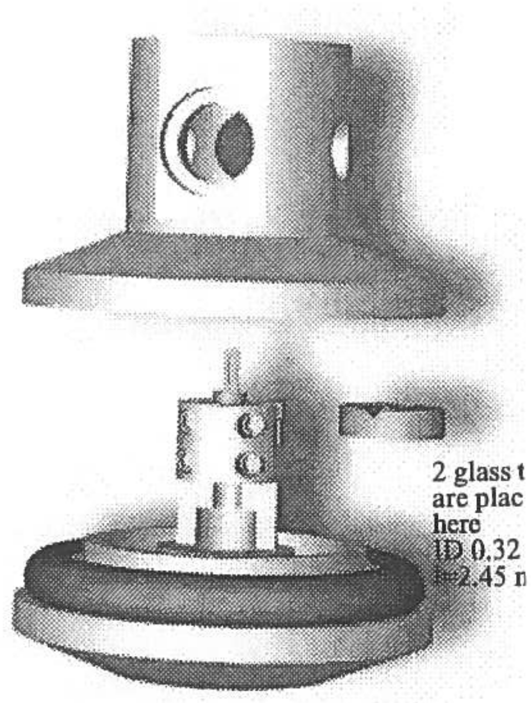


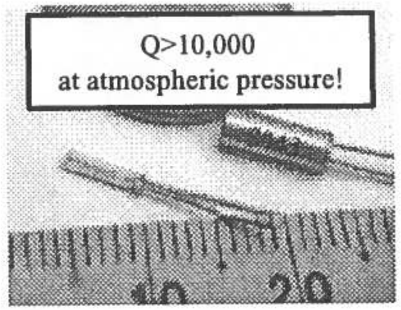
Resonant photoacoustic cell (1000 Hz):
l~60 cm, V~50 cm^3

QEPAS ADM:
l~0.5 cm, V~0.05 cm^3

QCL based Quartz-Enhanced Photoacoustic Spectromete



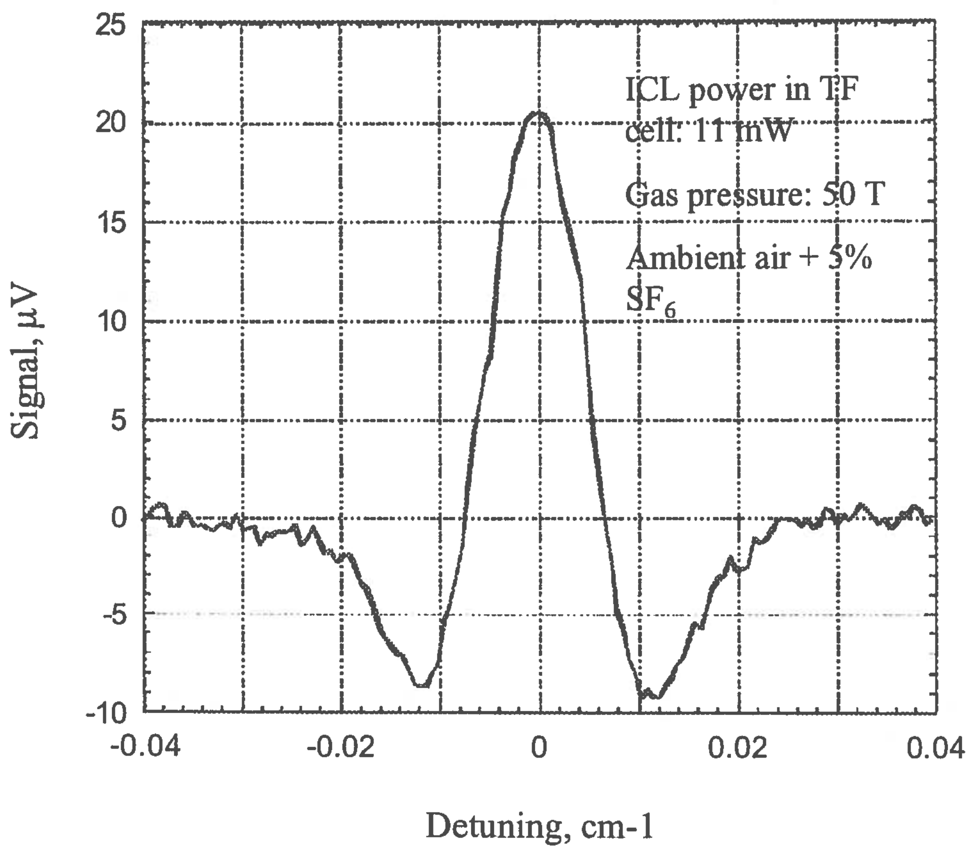


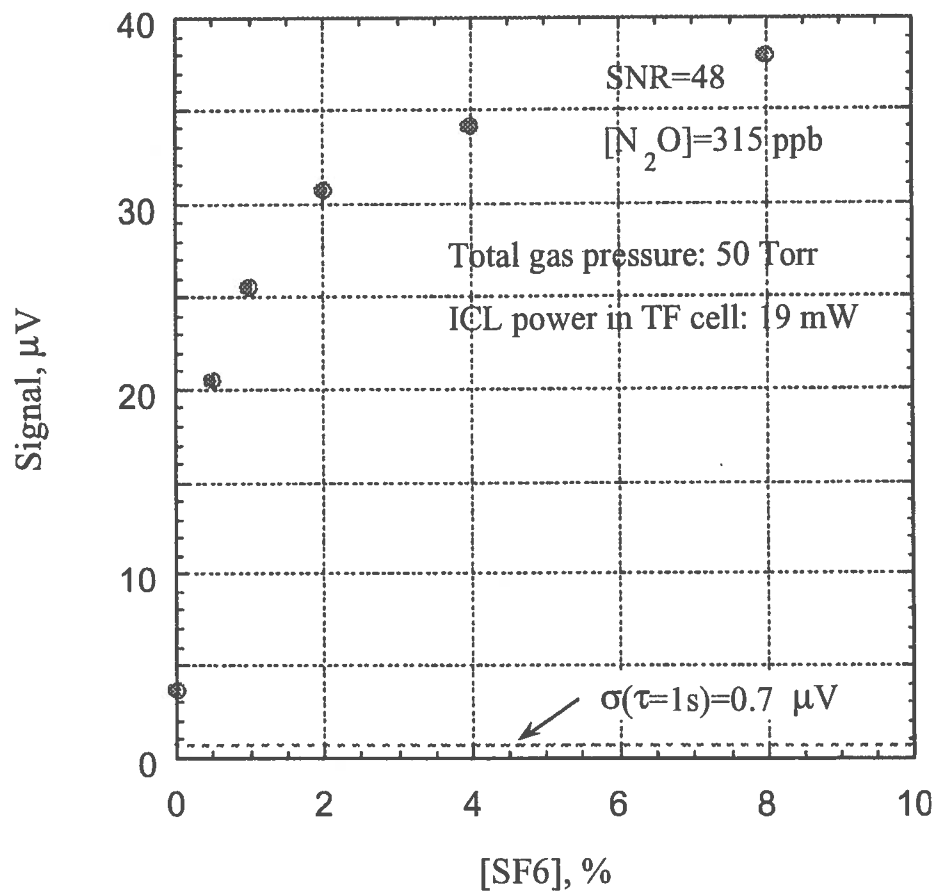


Noise-equivalent sensitivity (α_{min}): 8.1×10^{-9} cm^{-1}W/√Hz (Rice Dec. 2003)

cf. traditional PAS 1.1 $\times 10^{-8}$ cm^{-1}W/√Hz (Webber et al. Appl. Phys.B **77**, 381, 2003)

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





RICI

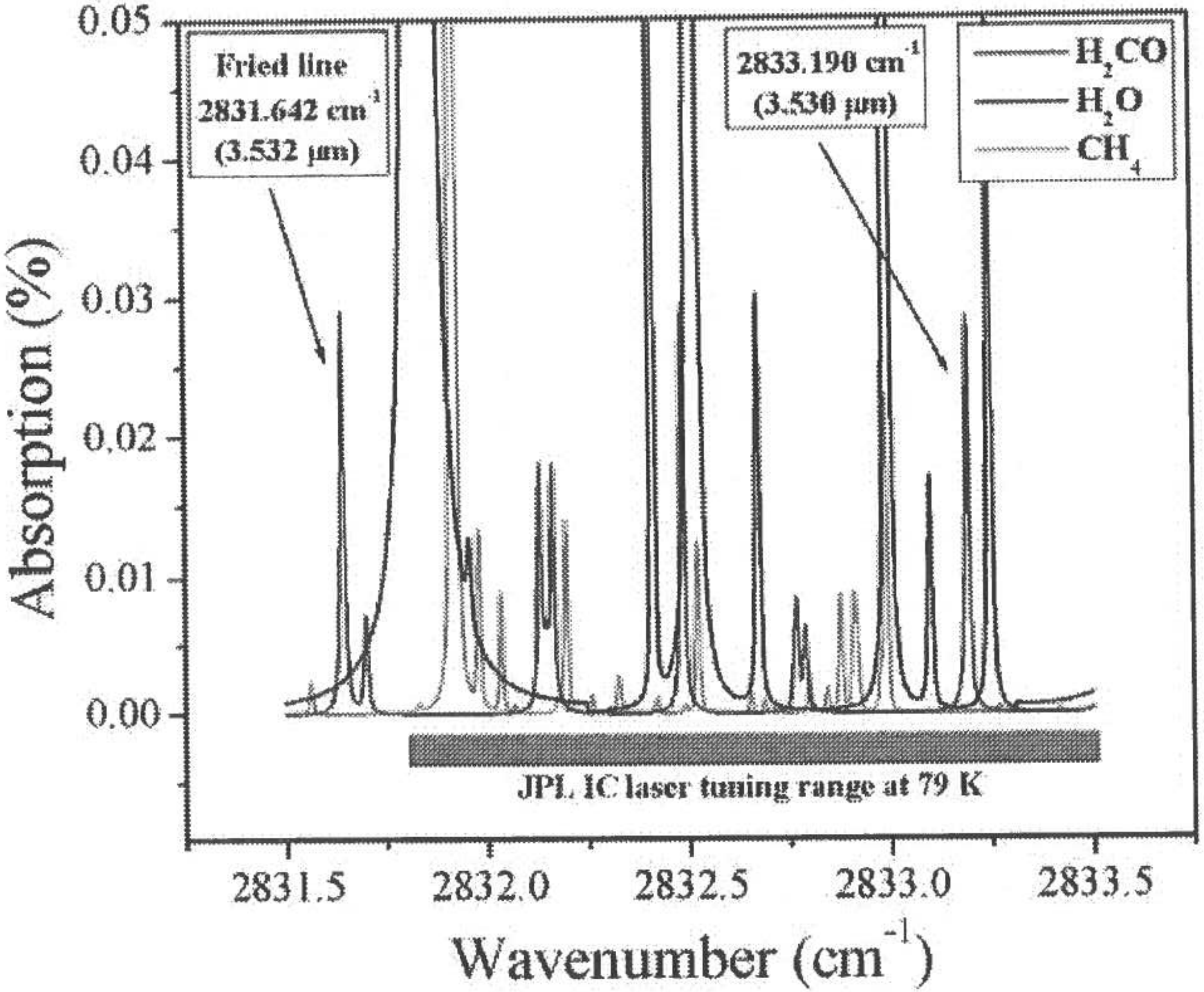
Merits of QE Laser-PAS based Trace Gas Detection

- High sensitivity (ppm to ppb gas concentration levels) and excellent dynamic range
- **Immune to ambient and flow acoustic noise, laser noise and etalon effects**
- **Significant reduction of sample volume (< 1 mm^3)**
- 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

QEPAS vs. 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

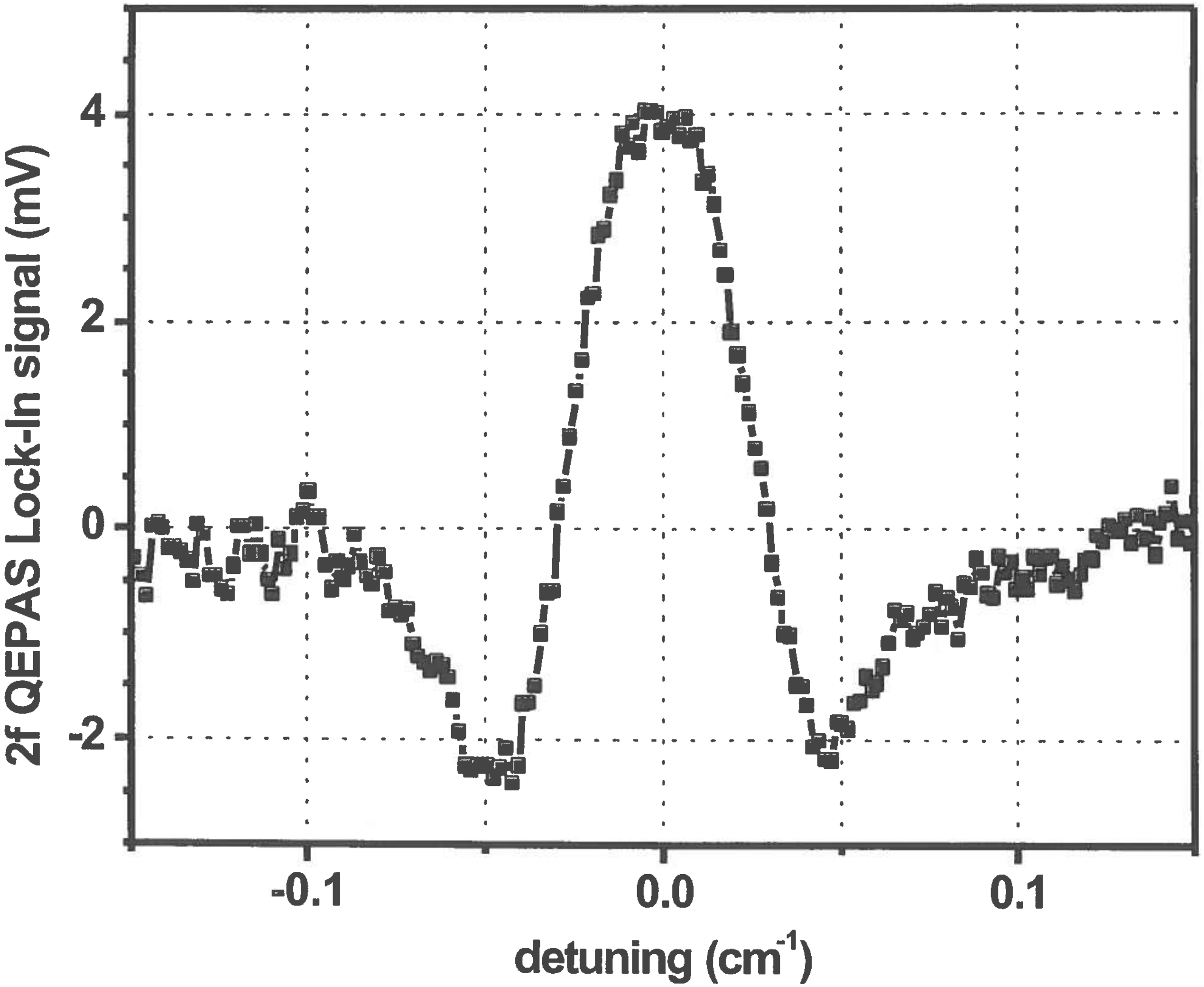
HITRAN Based Simulation of a H_2CO-H_2O-CH_4 Spectrum in Tuning Range of a 3.53µm IC Laser



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

NASA JPL RICE

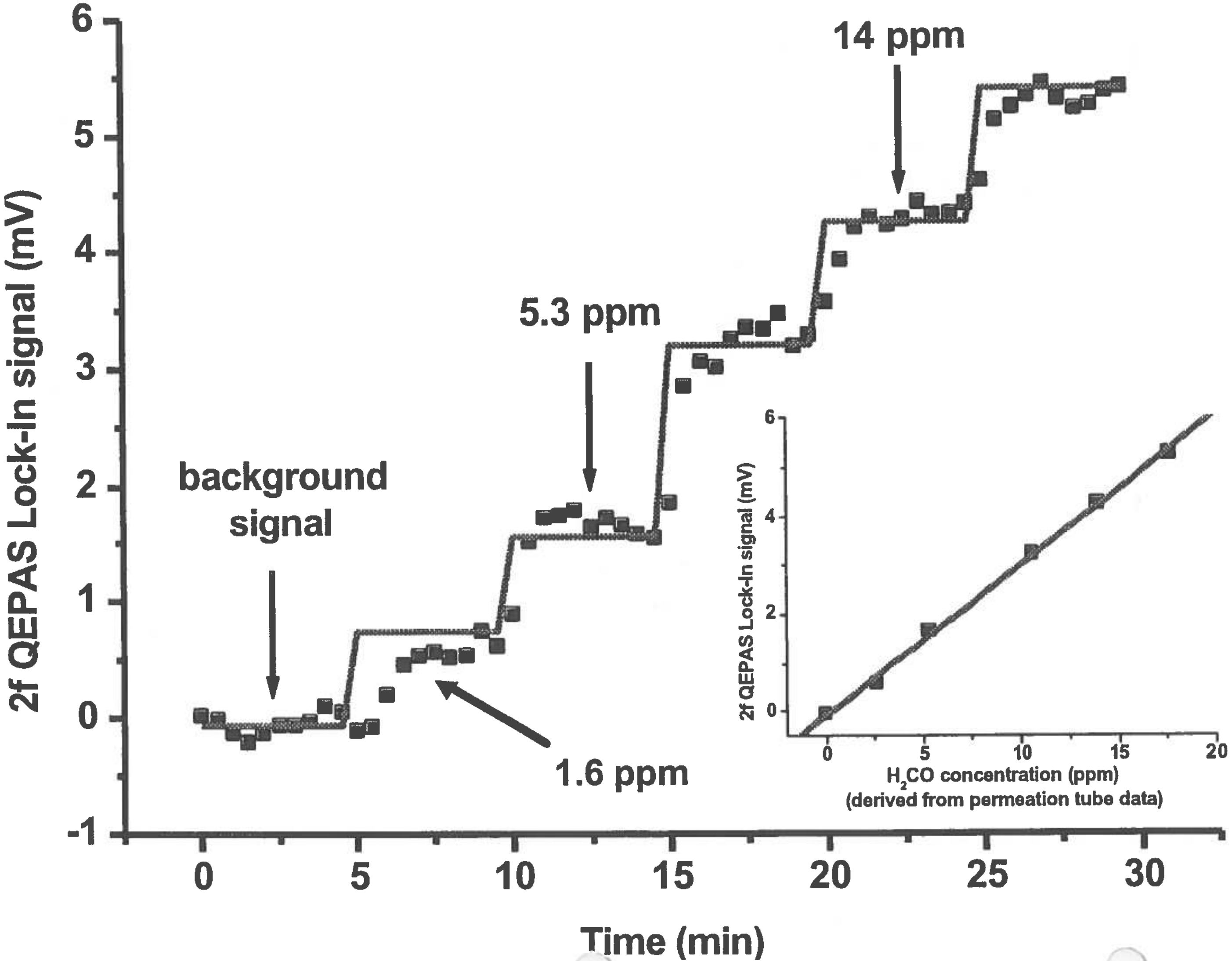
2f QEPAS based H_2CO signal at 3.53 μm (2832.48 cm^{-1})



- $[H_2CO]$: 13.27 ppm
- Sensitivity: $7.10^{-8} cm^{-1} W/\sqrt{Hz}$
- QEPAS NE sensitivity for NH : $8.10^{-9} cm^{-1} W/\sqrt{Hz}$ (For comparison)

NASA JPL RICE

C laser based formaldehyde calibration measurement with a gas standard generator



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

NASA JPL RIC

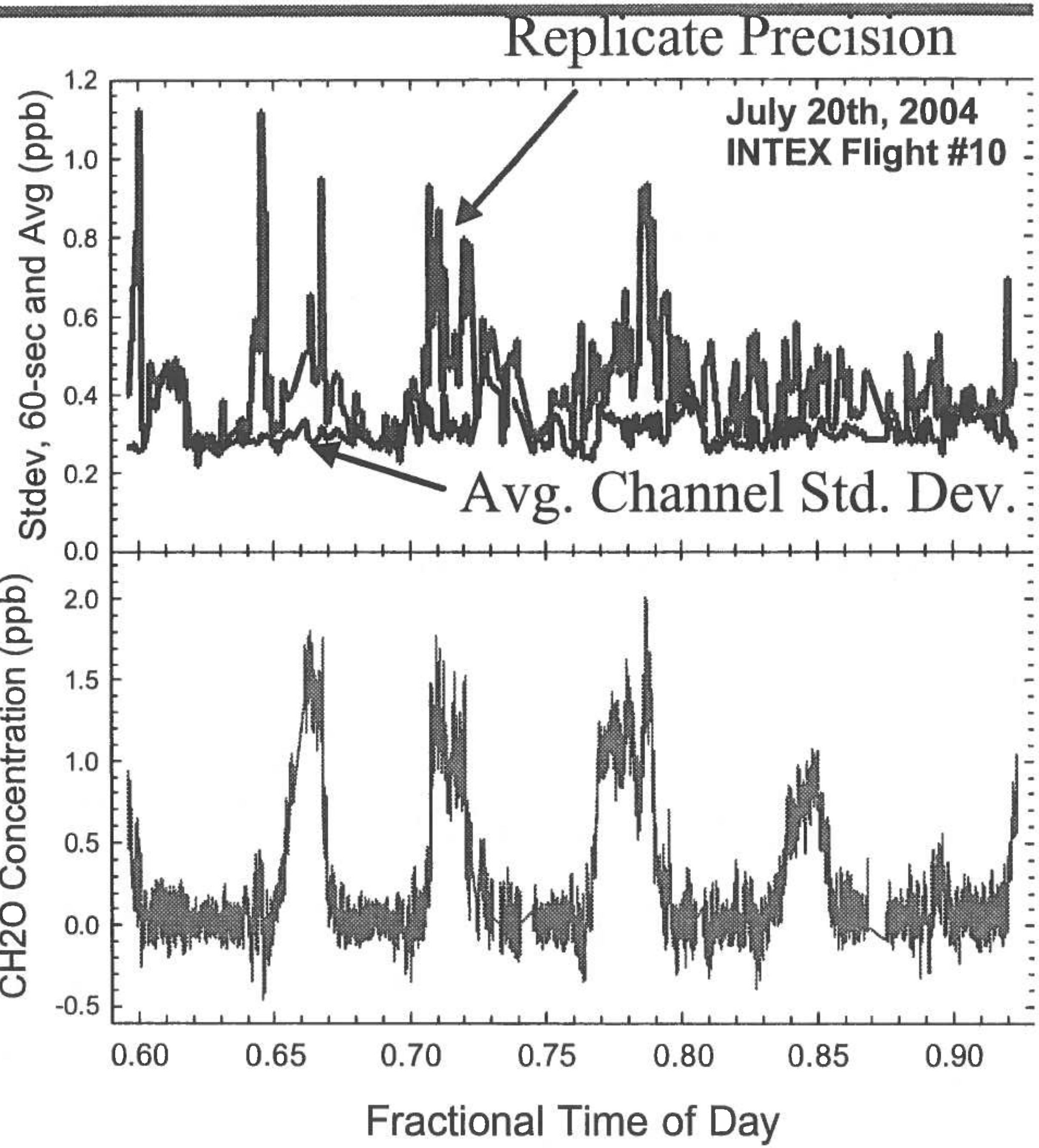
Intercontinental Chemical Transport Experiment 2004

Each Point
Replicate Precision
Over 1 min, N = 60
And
Avg. Channel Std. Dev

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

Each Point
1-second data points

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



Data provided by Alan Fried et. al., NCAR
Boulder, CO

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,H_2O, CO,N_2O 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 (e.g. for Mars: CO, CO_2, H_2O, CH_4, O_3, OCS)
- Medical applications (non-invasive human health monitoring)

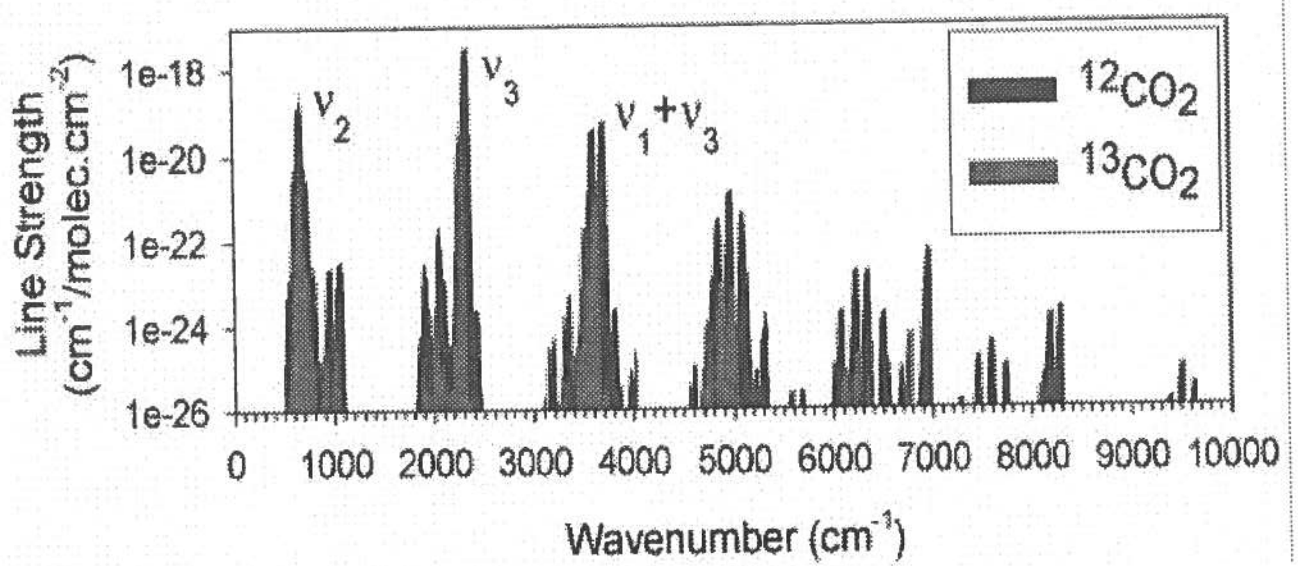
RICE

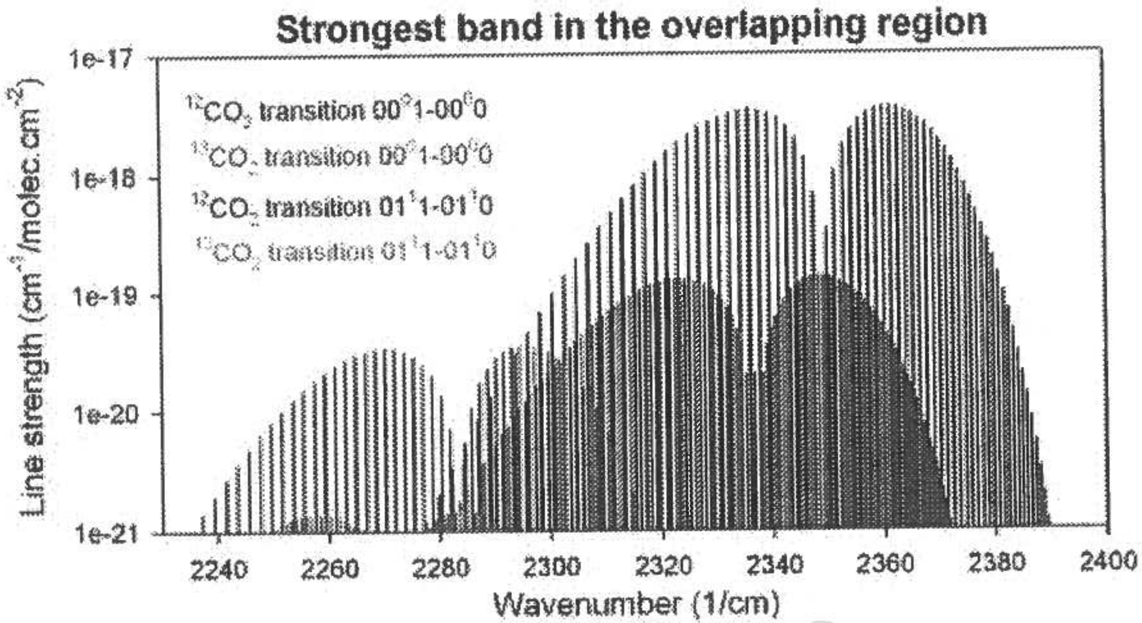
CO_2 Absorption Line Selection Criteria

- 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

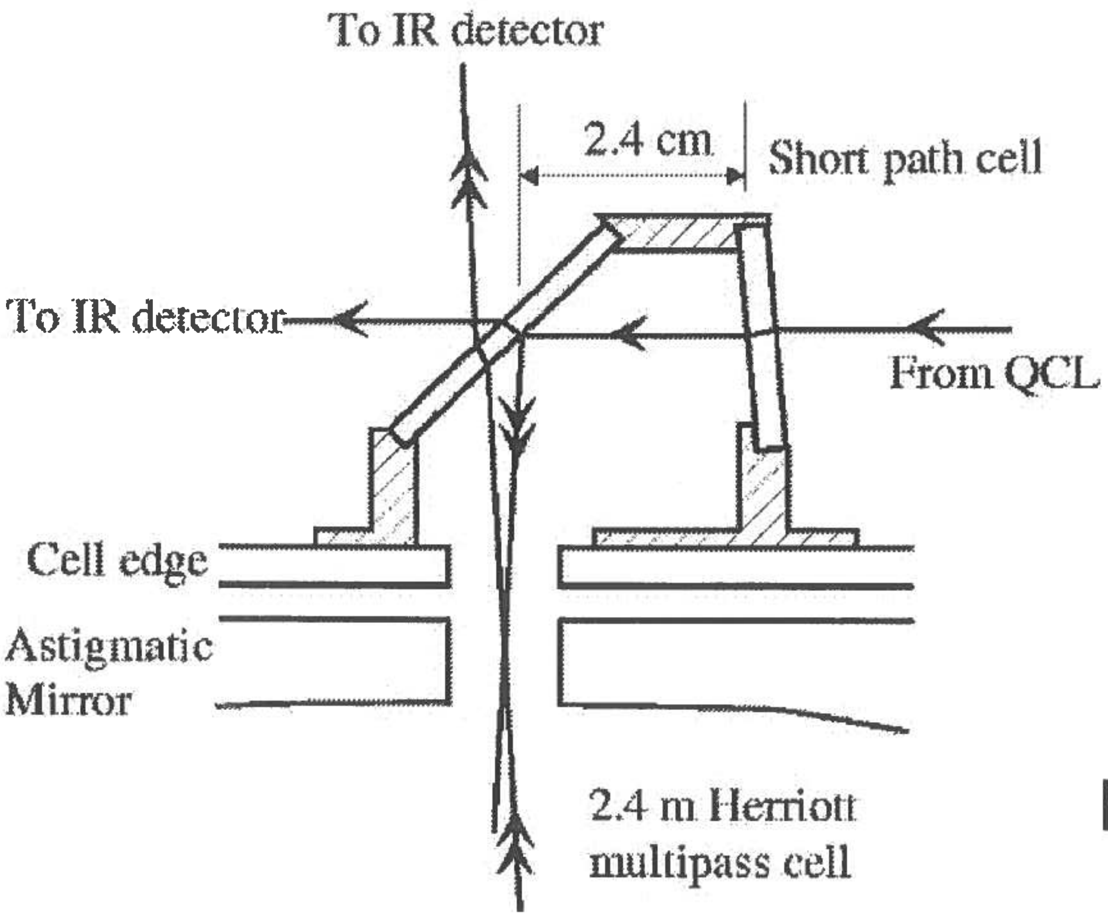
* Proposed scheme by Curl, Uehara, Kosterev, et al, Oct. 2002

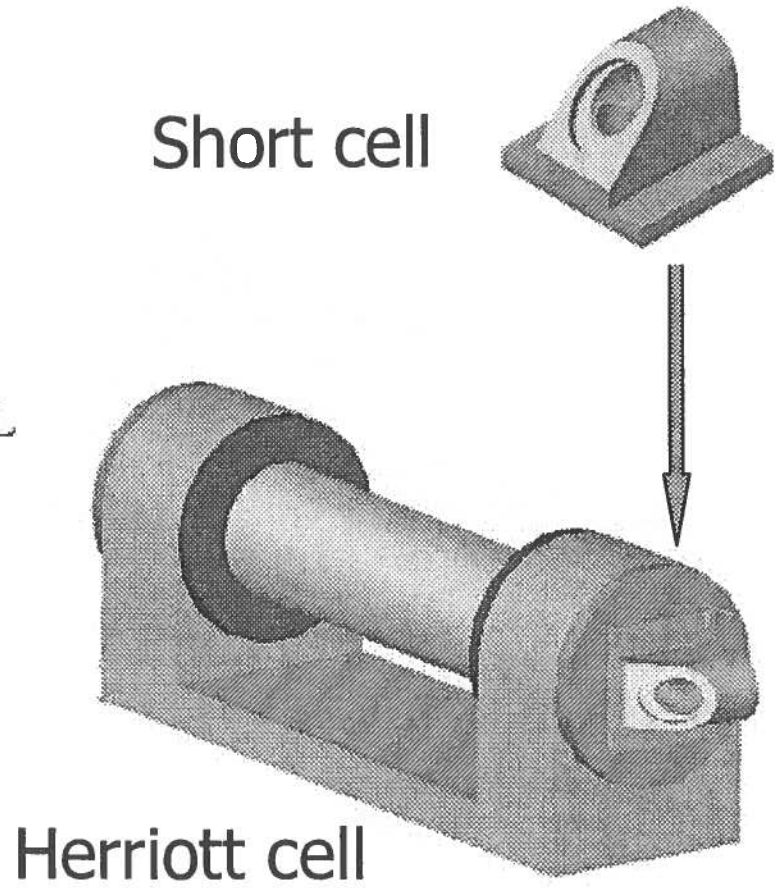
Ro-vibrational bands suitable for $^{12}CO_2/^{13}CO_2$ ratio measurements



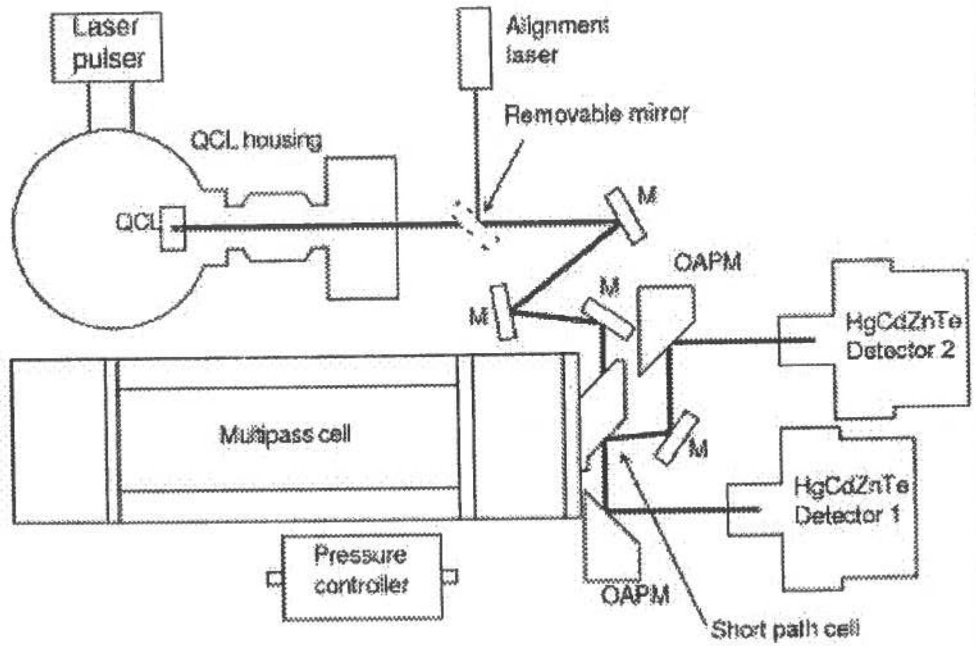


Dual path length gas cell design

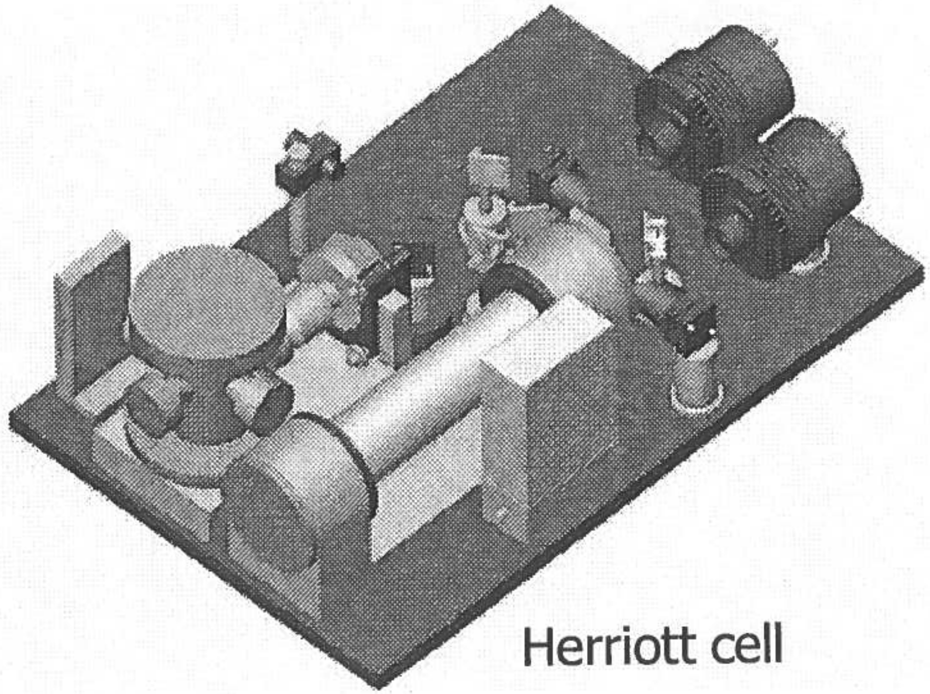




QC laser based Isotopic Ratio Sensor Layout



TEC IR detectors

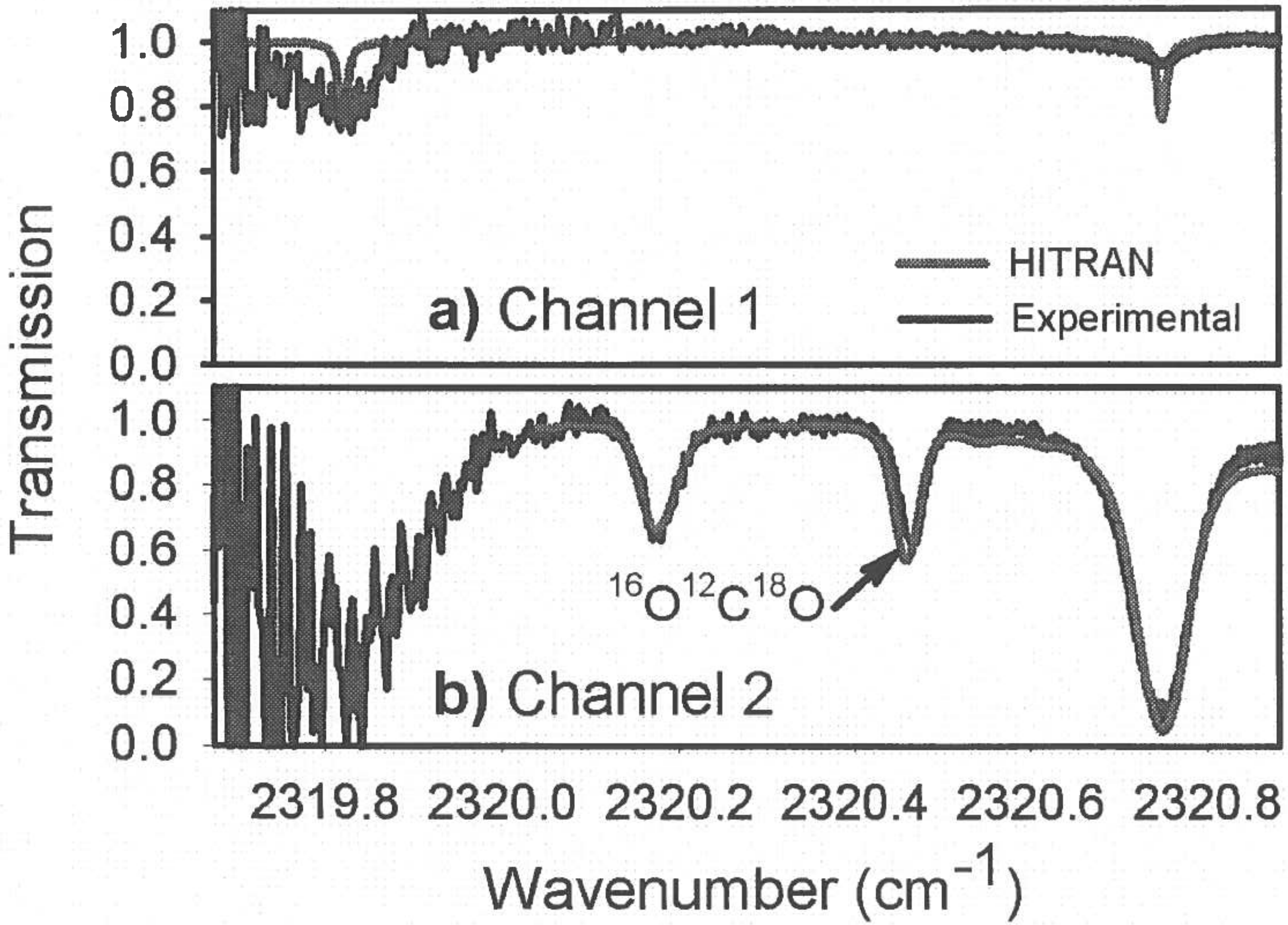


Herriott cell

Bread board: 12x18" (30x45 cm)

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

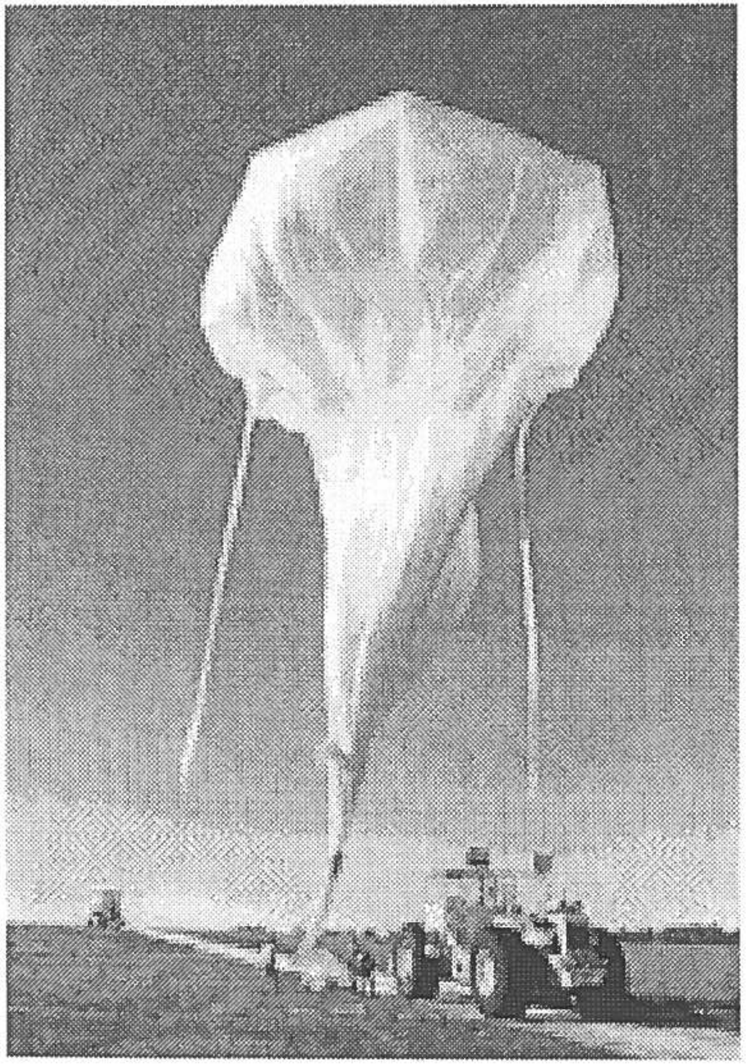
$^{16}O^{12}C^{18}O$ Spectra at 2320.2 cm^{-1}



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

NASA Atmospheric & Mars Gas Sensor Platforms



Tunable laser based sensor
for stratospheric measurements

Aircraft based laser absorption spectromet

Tunable laser planetary spectrometer