Recent Advances and Applications of Semiconductor Laser based Gas Sensor Technology

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OUTLINE

LACSEA
2006

Incline Village, NV

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- Motivation: Wide Range of Chemical Sensing
- Fundamentals of Laser Absorption Spectroscopy
- Selected Applications of Trace Gas Detection
  - LAS with a widely tunable QCL sensor at 5.2 um (NO)
  - Quartz Enhanced Laser-PAS (H_2CO, CO_2)
  - QCL based CO2 isotopic ratio measurements
- Summary and Conclusions

Work supported by NASA, PNNL, NSF, NIH and Welch Foundation

Motivation: Wide Range of Gas Sensing Applications

- **Urban and Industrial Emission Measurements**
  - Industrial Plants
  - Combustion Sources and Processes (eg. early fire detection)
  - Automobile and Aircraft Emissions
- **Rural Emission Measurements**
  - Agriculture and Animal Facilities
- **Environmental Gas Monitoring**
  - Atmospheric Chemistry (eg ecosystems and airborne)
  - Volcanic Emissions
- **Chemical Analysis and Industrial Process Control**
  - Chemical, Pharmaceutical, Food & Semiconductor Industry
  - Toxic Industrial Chemical Detection
- **Spacecraft and Planetary Surface Monitoring**
  - Crew Health Maintenance & Advanced Human Life Support Technology
- **Biomedical and Clinical Diagnostics** (eg. breath analysis)
- **Forensic Science and Security**
- **Fundamental Science and Photochemistry**

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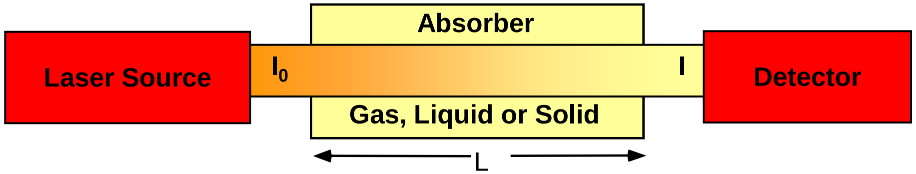
Fundamentals of Laser Absorption Spectroscopy

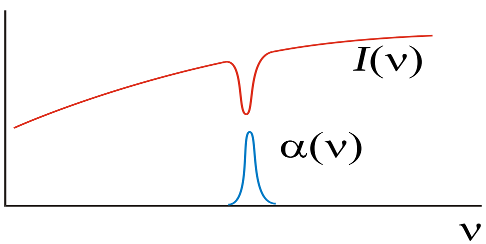


Beer-Lambert's Law of Linear Absorption

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

$\alpha(\nu)$ - 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, Cavity Ringdown & Intracavity Spectroscopy
- Open Path Monitoring (with retro-reflector)
- Evanescent Field Monitoring (fibers & waveguides)

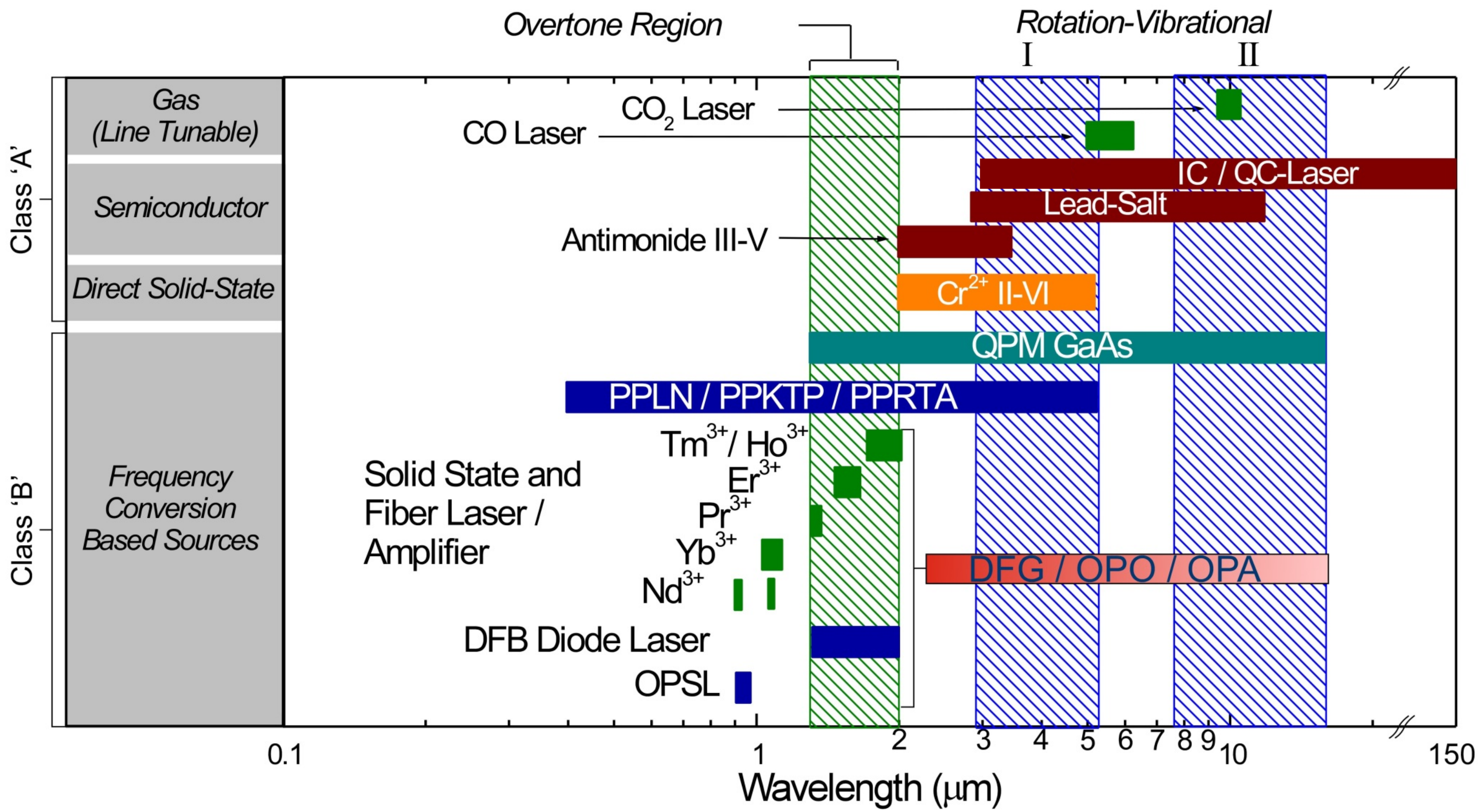
Spectroscopic Detection Schemes

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

Mid-IR Source Requirements for Laser Spectroscopy

REQUIREMENTS	IR LASER SOURCE
Sensitivity (% to ppt)	Power
Selectivity	Single Mode Operation and Narrow Linewidth
Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers	Tunable Wavelengths
Directionality or Cavity Mode Matching	Beam Quality
Rapid Data Acquisition	Fast Time Response
Room Temperature Operation	No Consumables
Field deployable	Compact & Robust

IR Laser Sources and Wavelength Coverage



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Quantum and Interband Cascade Laser: Basic Facts

- Band – structure engineered devices (emission wavelength is determined by layer thickness – MBE or MOCVD) QCLs operate from 4 to 160 μm (limited by the CB offset on the short wavelength side)
  - Unipolar devices
  - Cascading (each electron creates N laser photons and the number of periods N determines laser power)

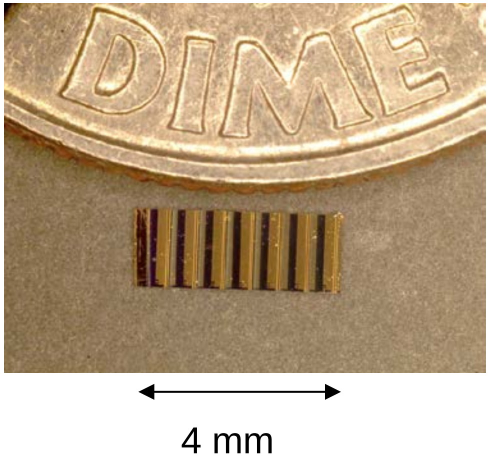
- Compact, reliable, stable, long lifetime, commercial availability

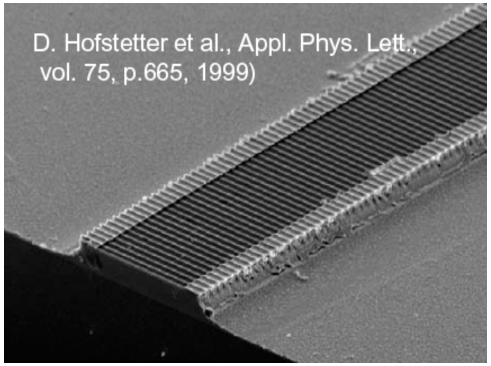
- Fabry-Perot (FP) or single mode (DFB)

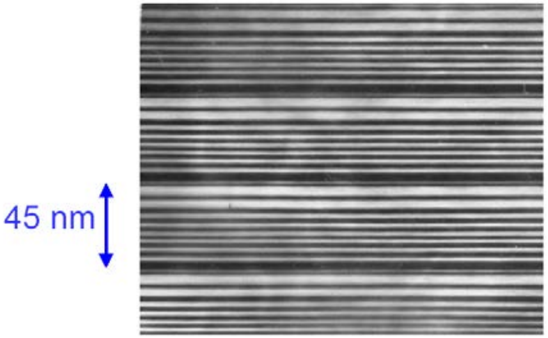
- <u>Broad spectral tuning range in the mid-IR</u> (4-24 μm for QCLs and 3-5 μm for ICLs)
  - 1.5 cm^{-1} using current
  - 10-20 cm^{-1} using temperature
  - > 150 cm^{-1} using an external grating element

- <u>Narrow spectral linewidth</u> cw, 0.1 - 3 MHz & <10Khz with frequency stabilization
  Linewidth is ~ 300 MHz of pulsed QCLs (chirp from heating)

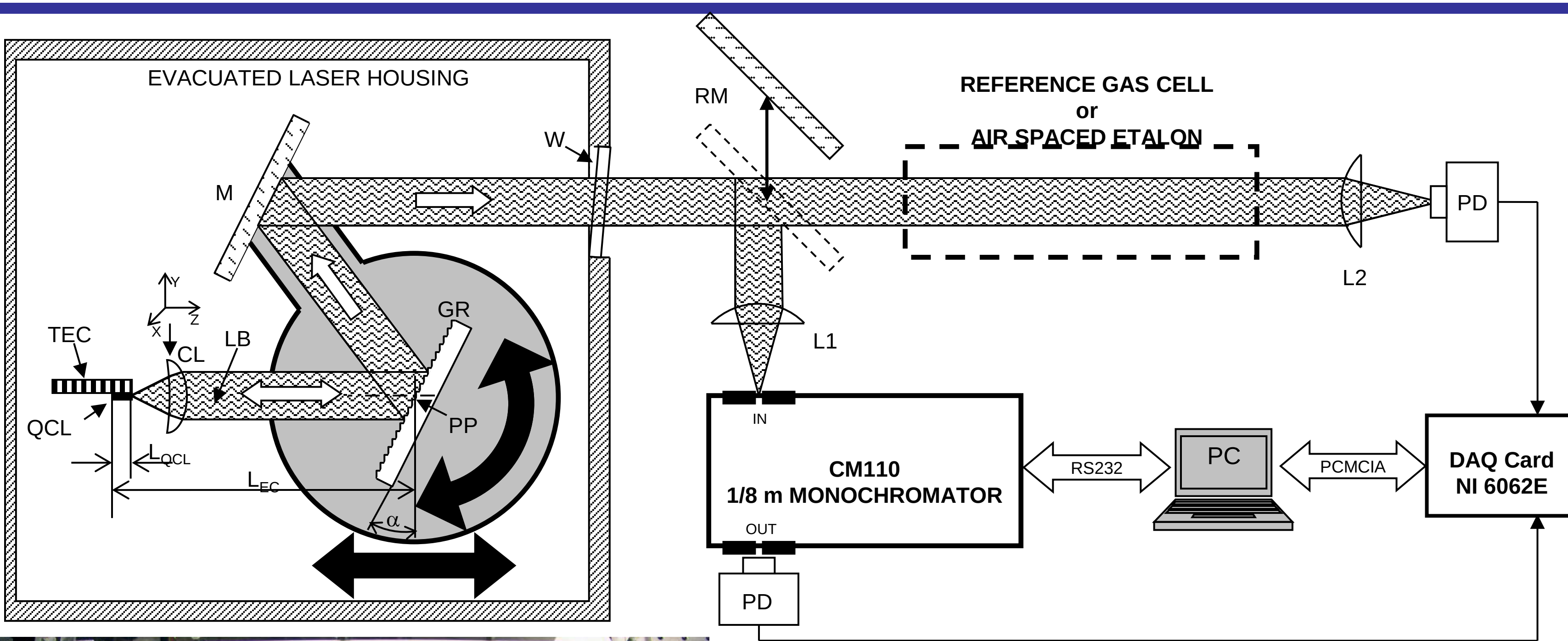
- <u>High output powers at TEC/RT temperatures</u>
  - Pulsed peak powers of 1.6 W; high temperature operation ~ 425 K
  - Average power levels: 1-600 mW
  - ~ 50 mW, TEC CW DFB @ 5 and 10 μm (Alpes & Unine); Princeton ~ 200 mW @8.3 μm (Agilent Technologies & Harvard)
  - >600 mW (CW FP) and >150 mW (CW DFB) at 298 K (Northwestern)

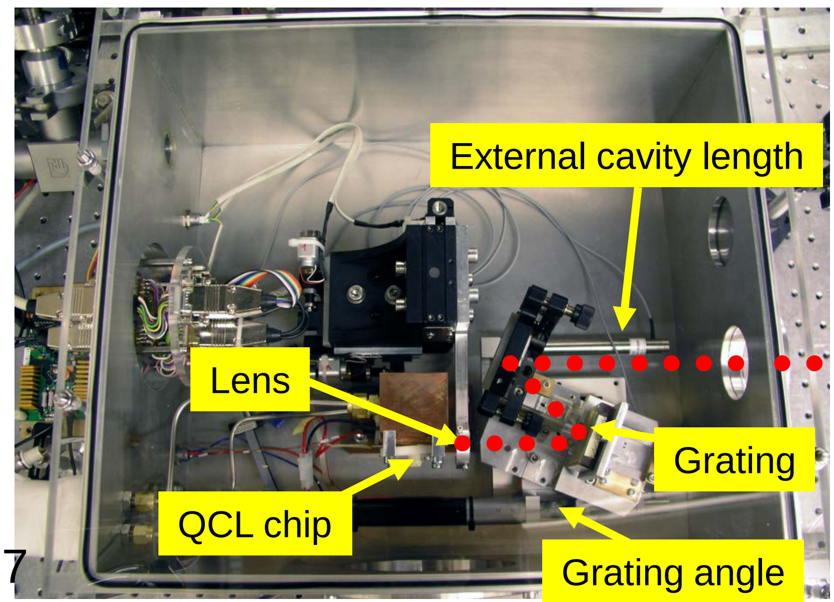






External Cavity QCL Based Spectrometer





- PZT controlled EC-length
- PZT controlled grating angle
- Optimization of cavity alignment performed by means of lens positioning using electrically controlled 3D translation stage
- 35 cm-1 tunability with the present gain chip

G. Wysocki et al. Applied Physics B, 81, 769-777 (2005)

Motivation for NO Detection

- Atmospheric Chemistry
- Environmental pollutant gas monitoring
  - NO_x monitoring from automobile exhaust and power plant emissions
  - Photochemical smog
- Industrial process control
  - Oswald process which converts NH_3 into HNO_3
- NO in medicine and biology
  - Treatment of asthma
  - Important signaling molecules in humans and mammals (1988 Nobel Prize in Physiology/Medicine)

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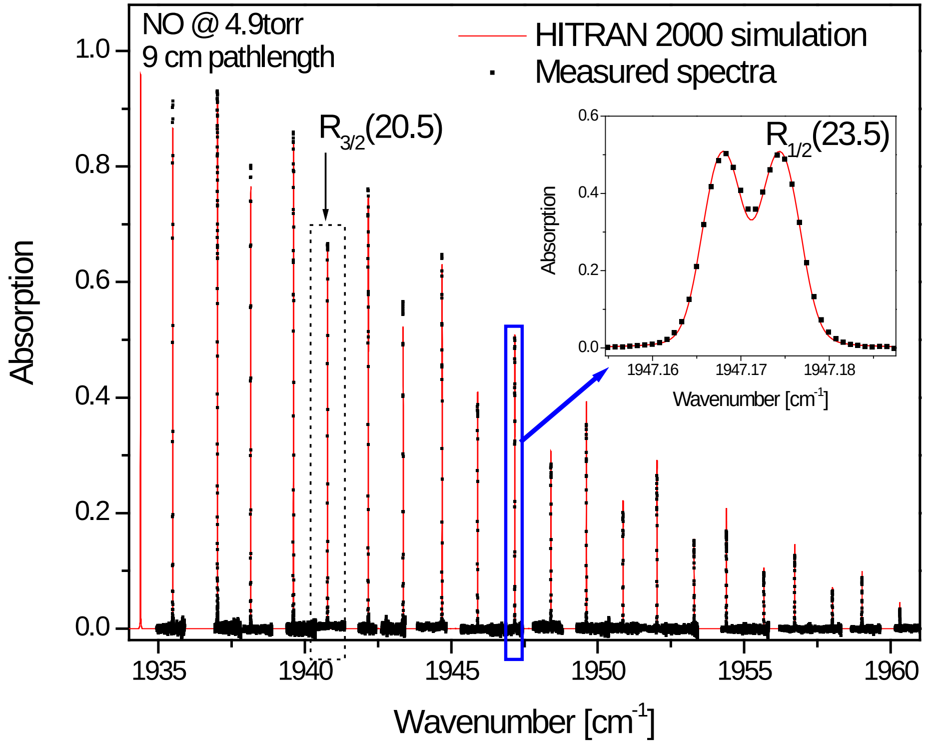
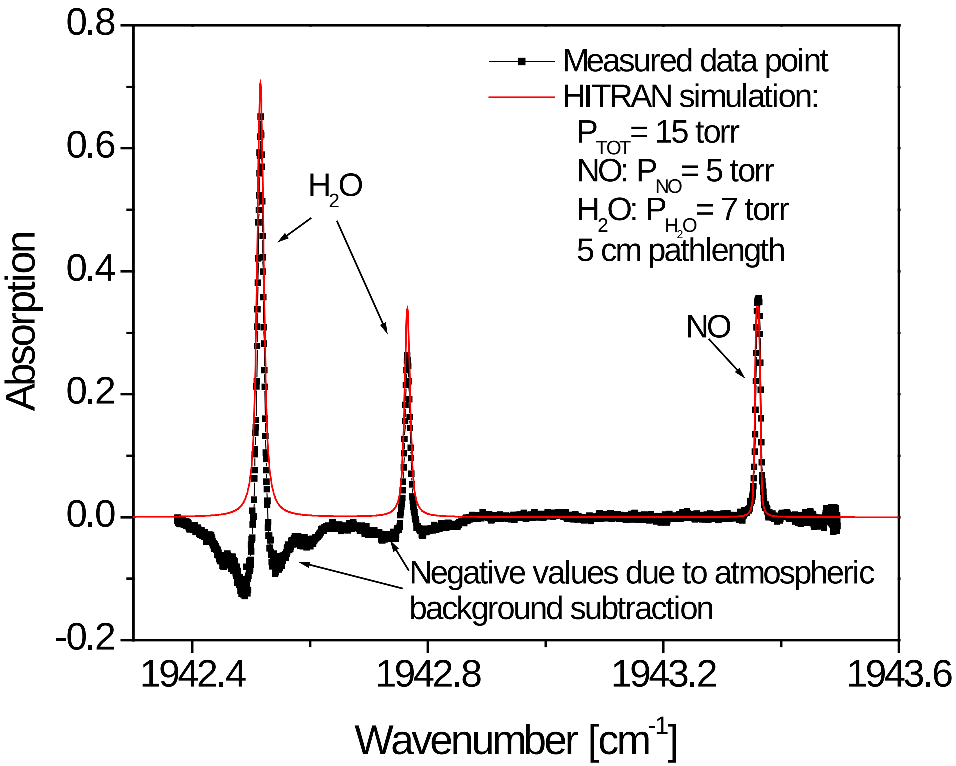
Mid-IR NO Absorption Spectra Acquired with a Tunable TEC QCL





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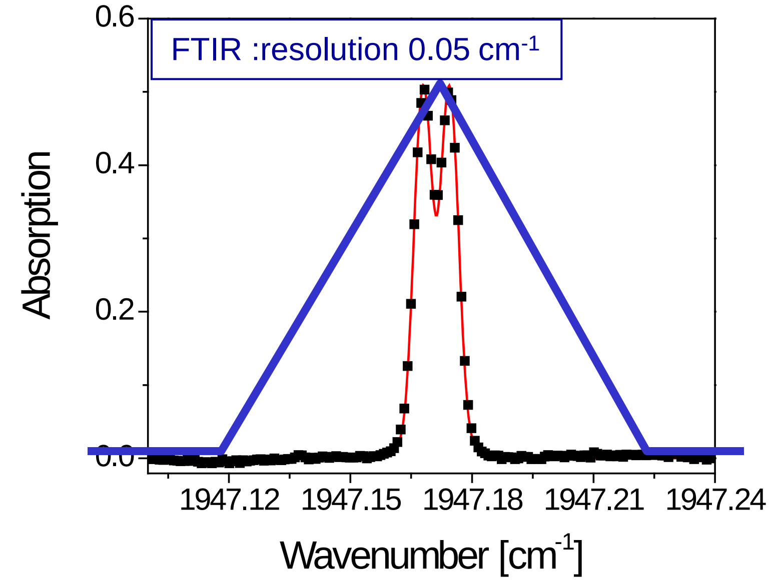
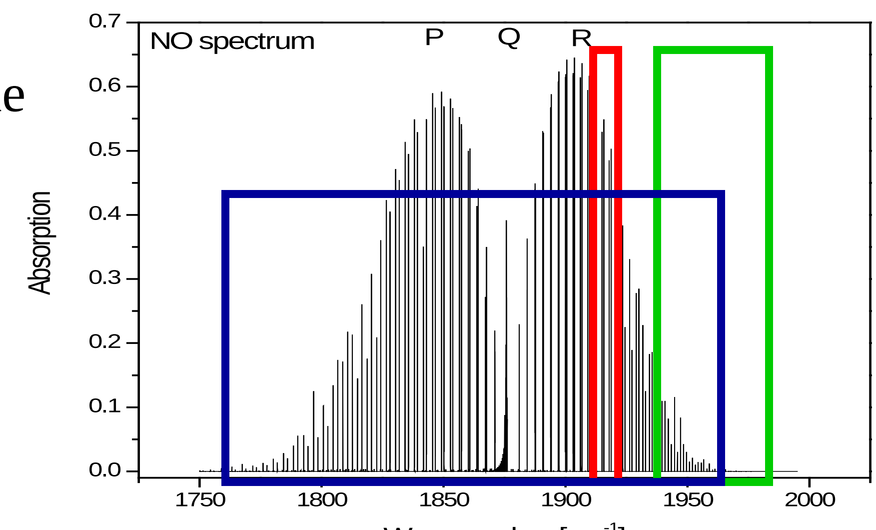
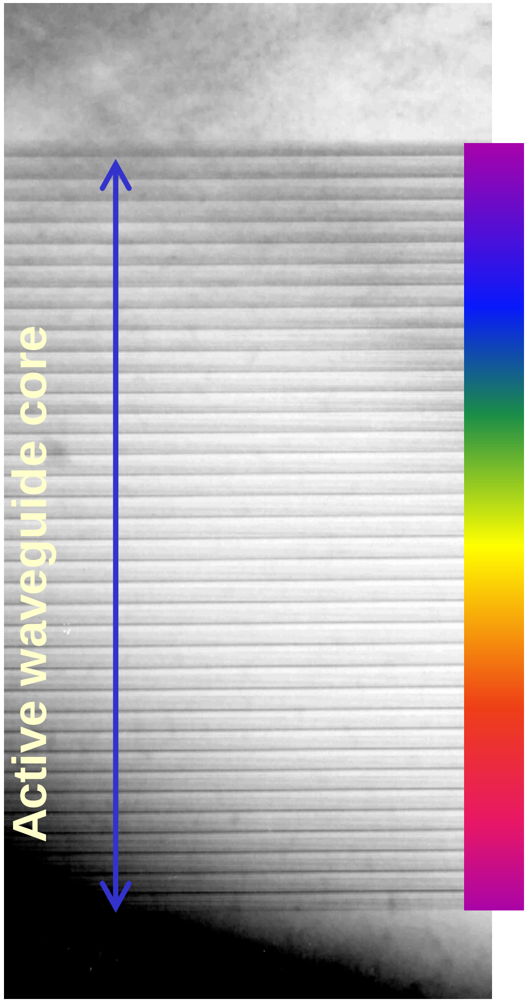
Important facts of novel EC-QCL technology

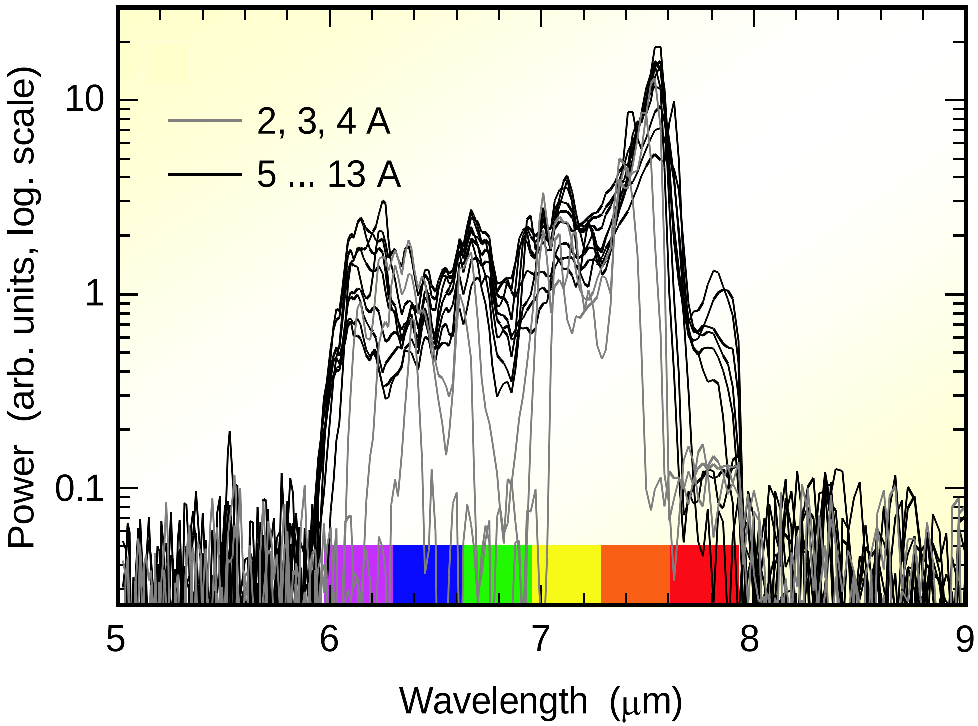
- Laser spectroscopy provides superior resolution compared to other techniques e.g. FTIR
- Single mode operation of the laser is required
- Wavelength tunability of single mode (DFB) mid-IR semiconductor lasers is ~10cm-1
- Demonstrated wavelength tunability of the Rice EC QCL is ~ 35 cm-1 (limited by the gain chip properties and not by the designed EC configuration)
- Gain chips, which can provide tunability of >200 cm^{-1} are already reported in the literature





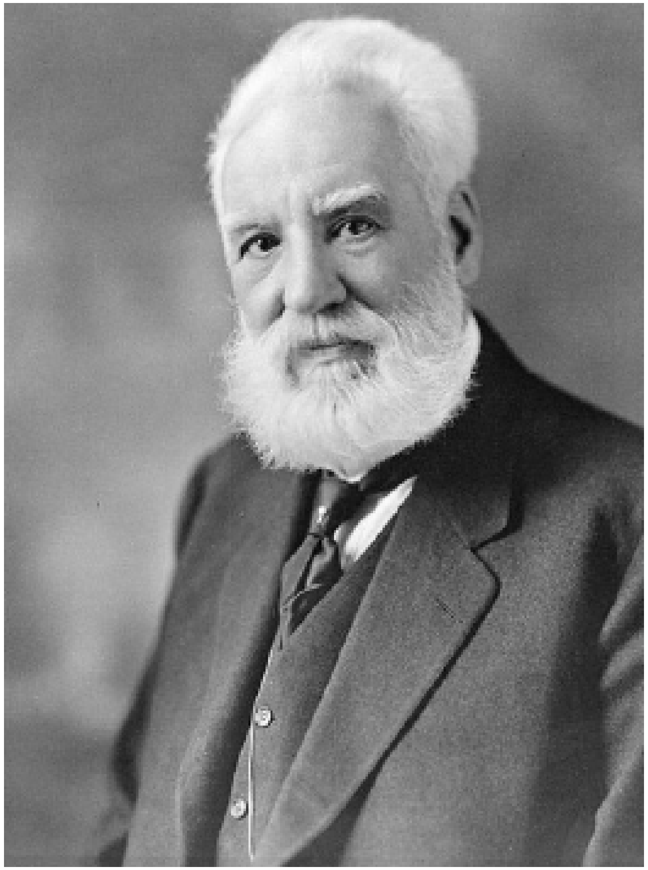
QC lasers with inhomogeneously broadened gain

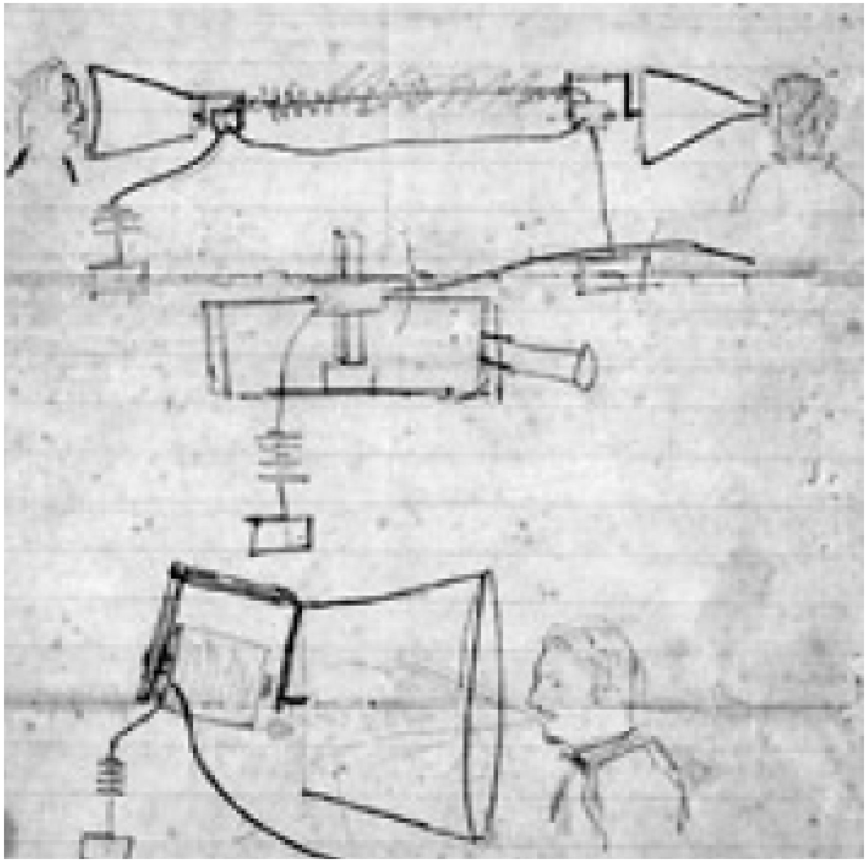




C. Gmachl et al., Nature 415, 883-887 (2002)

Motivation: Wide Range of Gas Sensing Applications

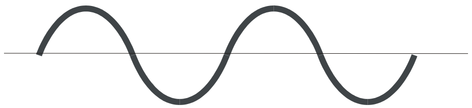




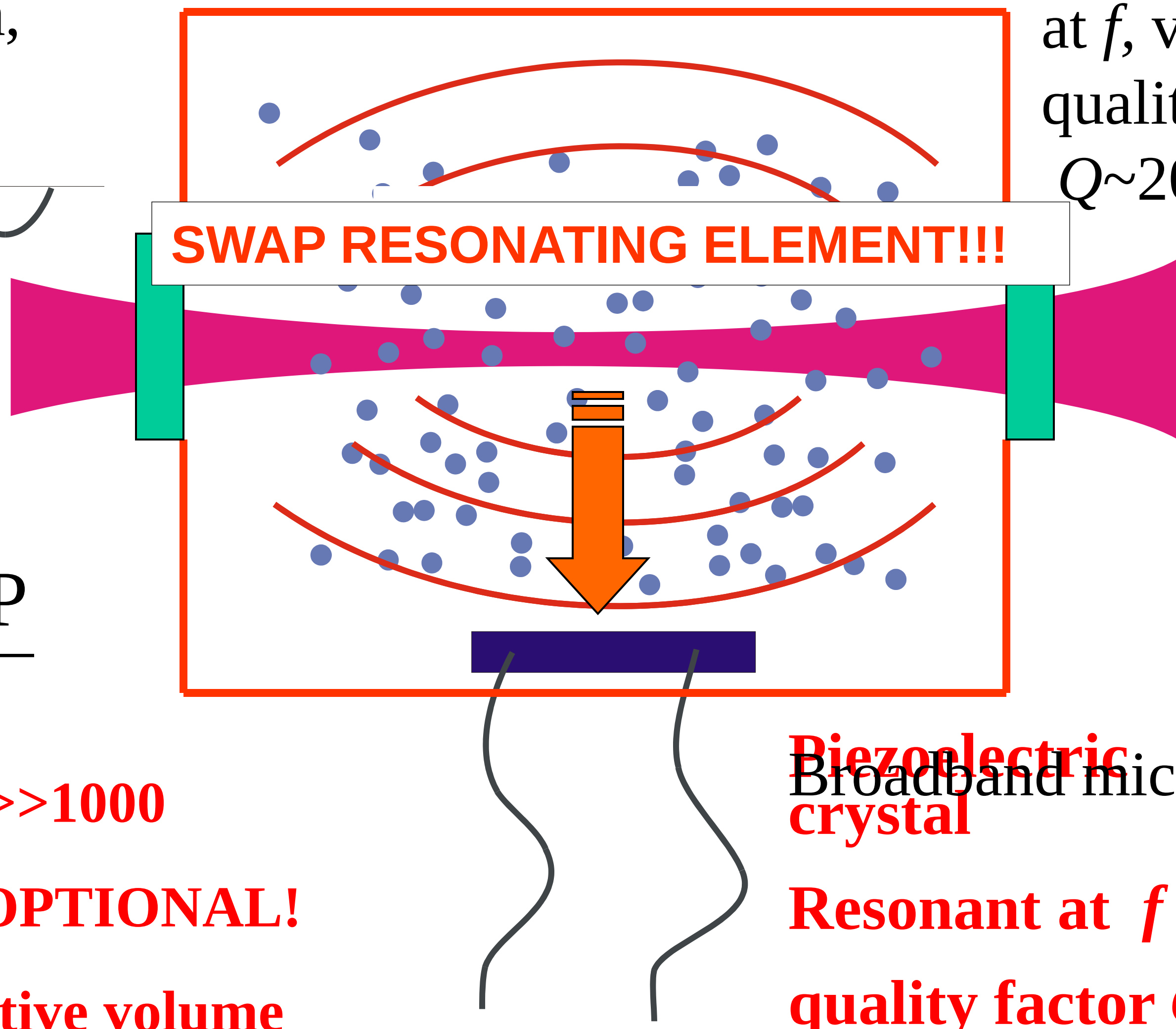
Alexander Graham Bell's "photophone" used a voice coil to modulate a mirror which transmitted sunlight to a receiver containing a selenium resistor.
Nature, Sept. 23, **1880**, pp. 500-503

From conventional PAS to QEPAS

Laser beam,
power *P*



Modulated (P or λ) at f or $f/2$



Cavity, resonant at f, volume V, quality factor Q~20-200

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

Q>>1000

Cell is OPTIONAL!

***V*-<u>effective</u> volume**

Broadband microphone

Piezoelectric crystal

Resonant at *f*

quality factor *Q*

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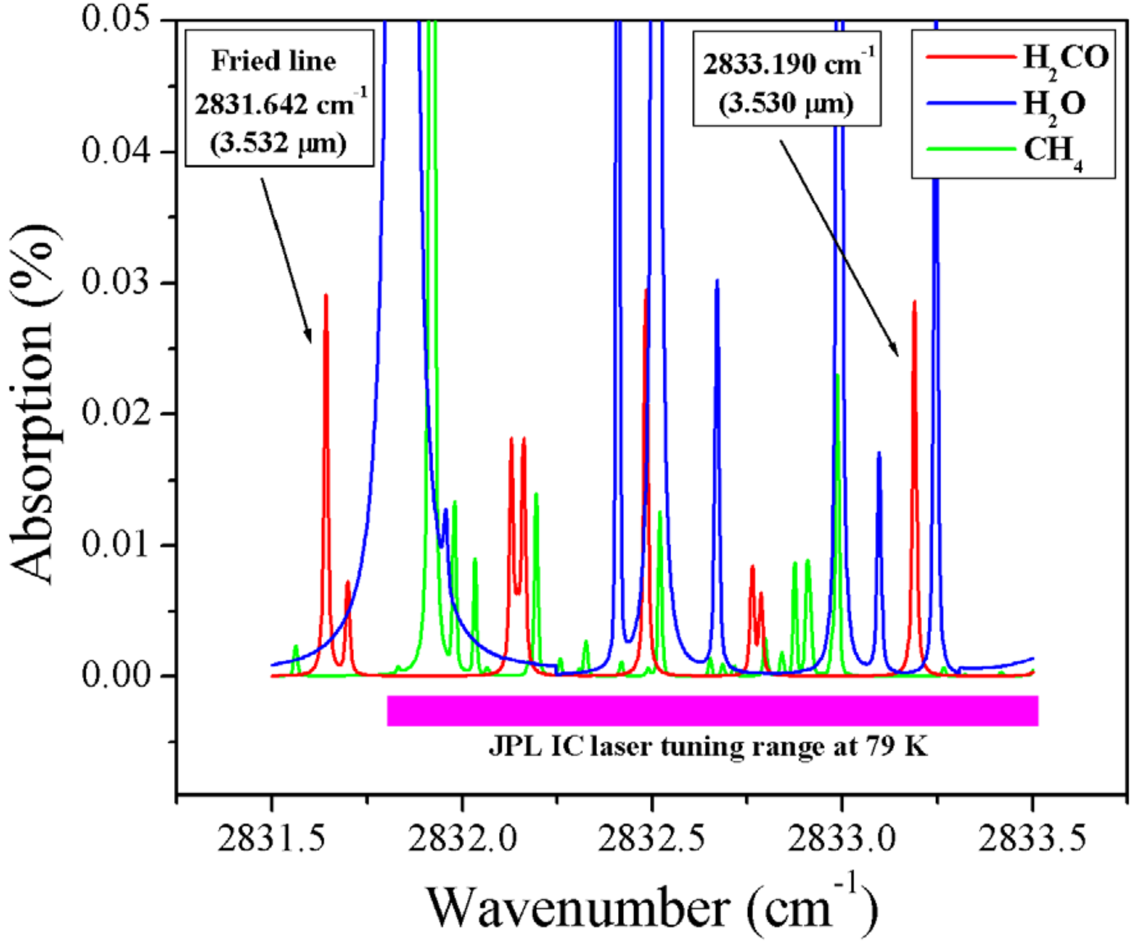
Motivation for Precision Monitoring of H_2CO

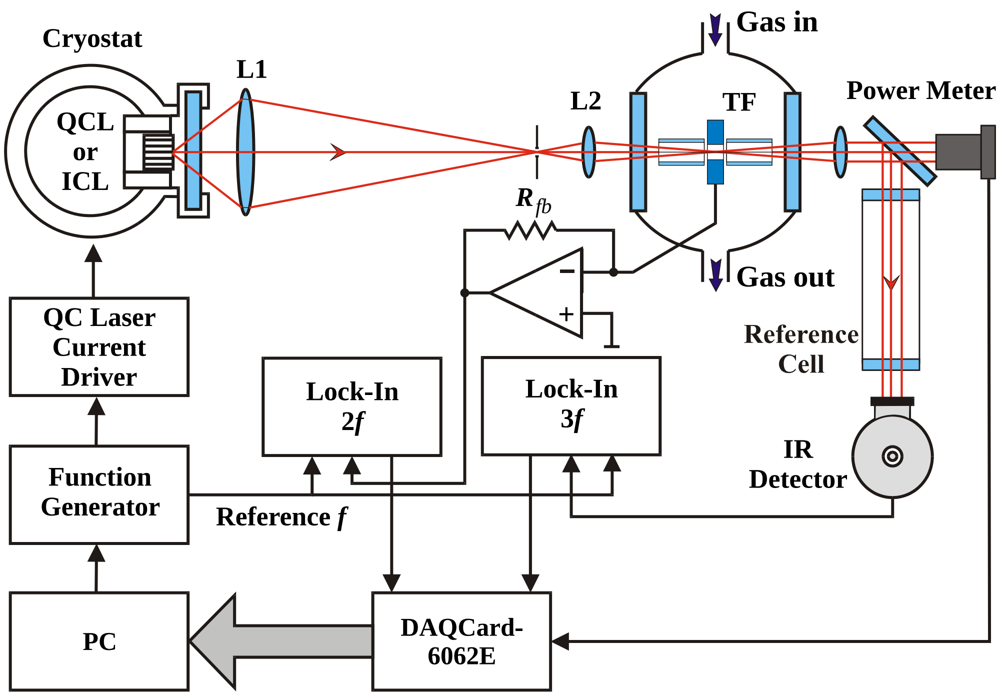
- Precursor to atmospheric O_3 production
- Potential trace contaminant in industrial manufactured products
- Pollutant due to incomplete fuel combustion processes
- Medically important gas

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

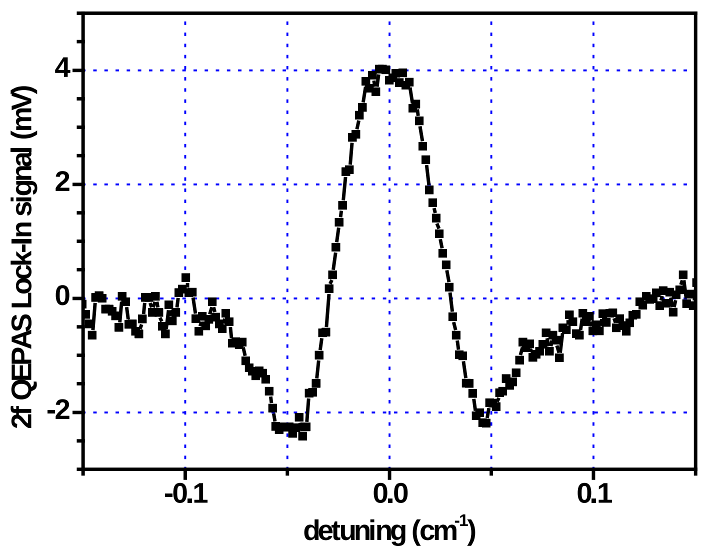


- H_2CO: 10 ppb
- H_2O: 3%
- CH_4: 2 ppm
- Optical path: 100 m
- Total pressure: 30 Torr

QCL based Quartz-Enhanced Photoacoustic Sensor



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



- [H_2CO]: 13.27 ppm
- QEPAS NNEA Sensitivity:

  $1.1\times10^{-8} cm^{-1} W/\sqrt{Hz}$;

  NEC (τ=1s): 0.28 ppmv (5 mW)

  For comparison:

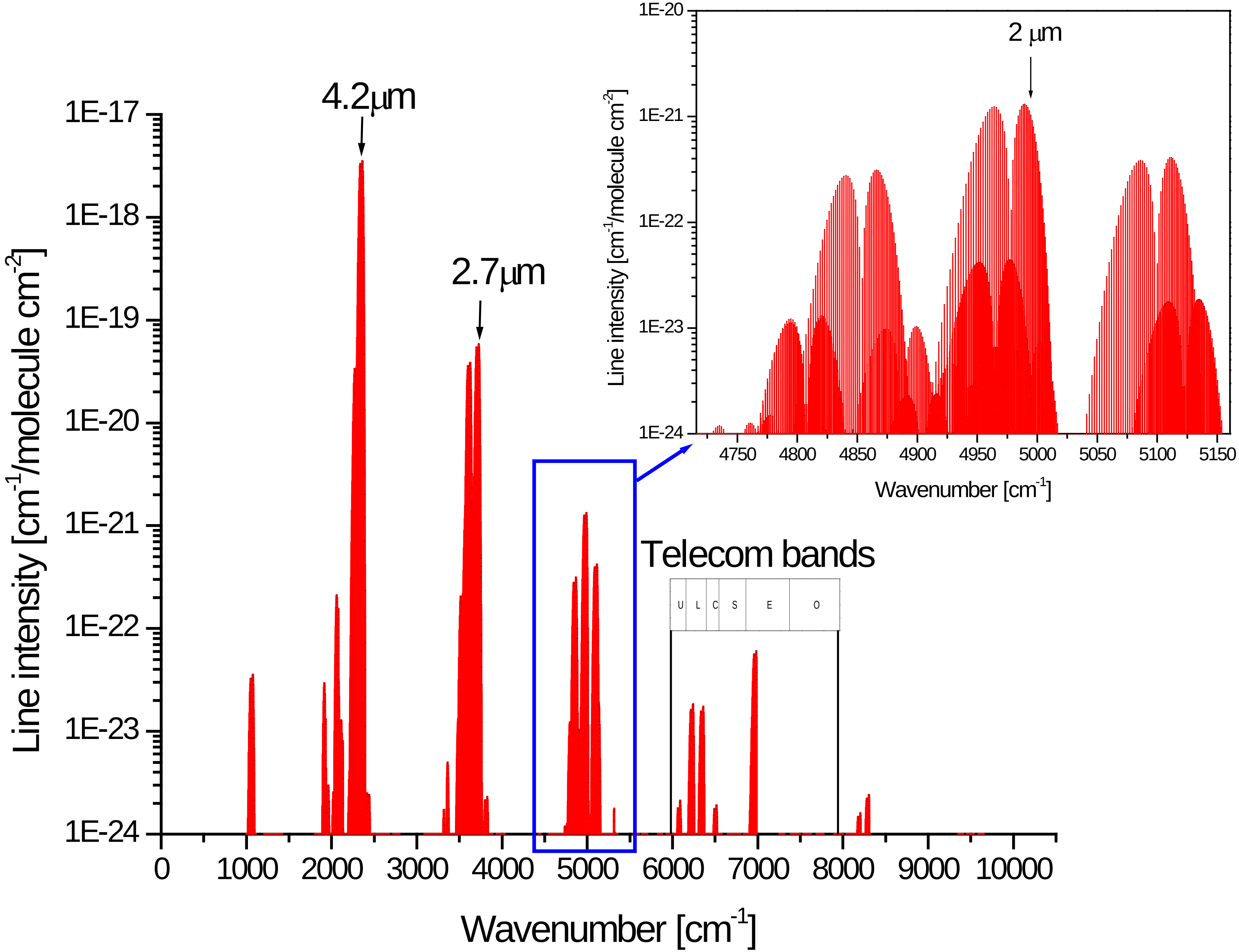
  QEPAS Sensitivity for NH_3 :

  $5.4\times10^{-9} cm^{-1} W/ \sqrt{Hz}$

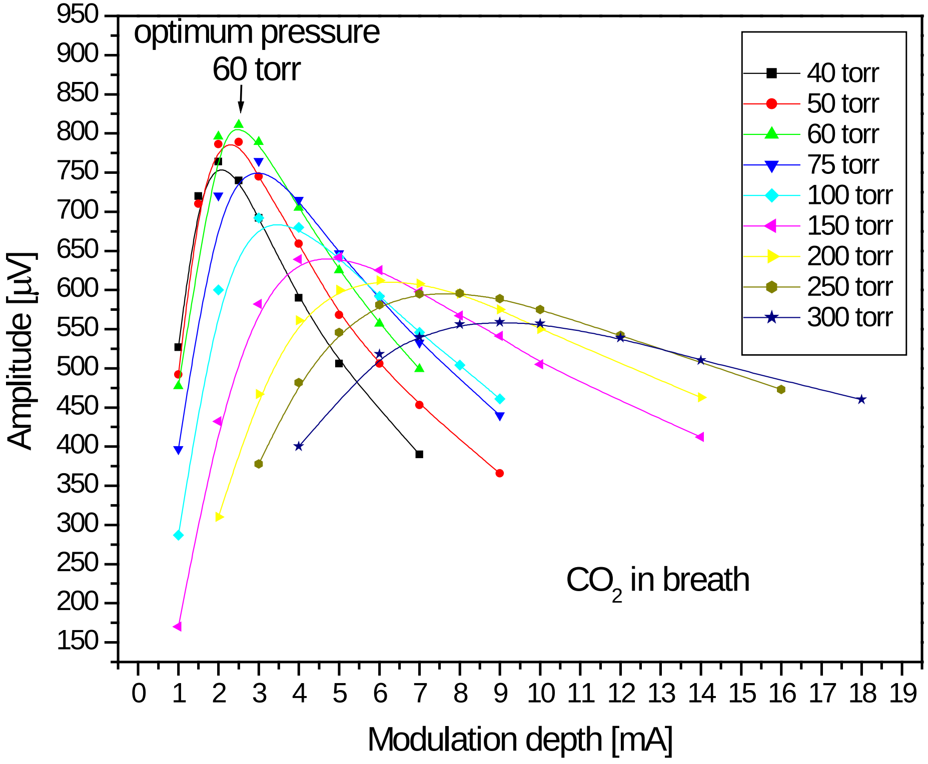
  NEC (τ=1s): 0.50 ppmv (38 mW)

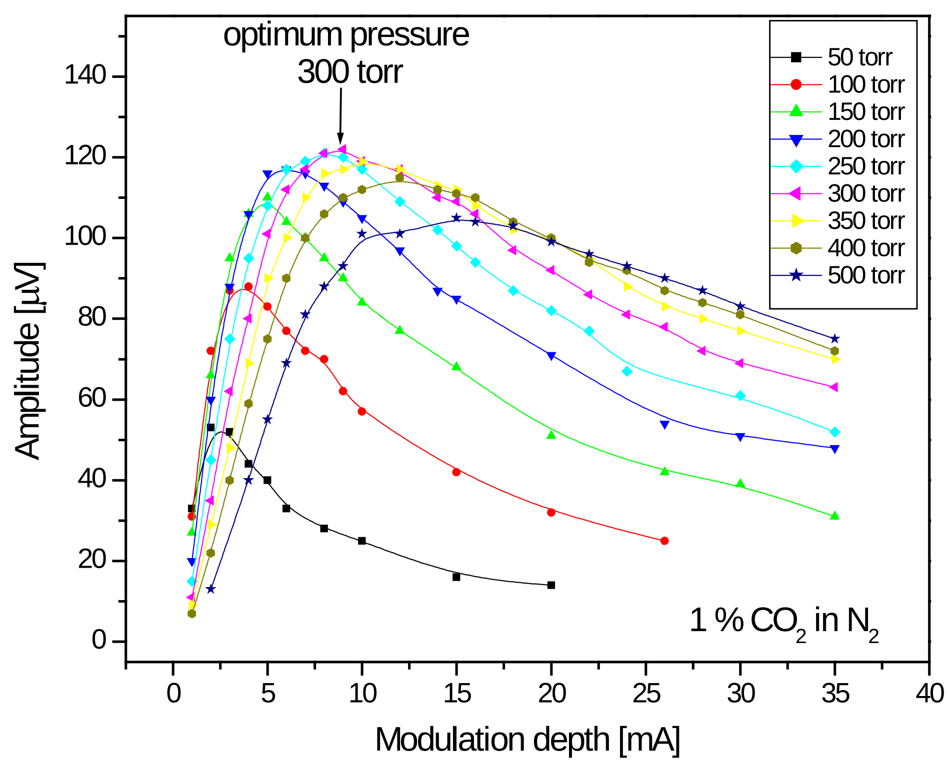
M. Horstjann et. al., Applied Physics **B 79**, 799, 2004

CO_2 Detection at 2 μm



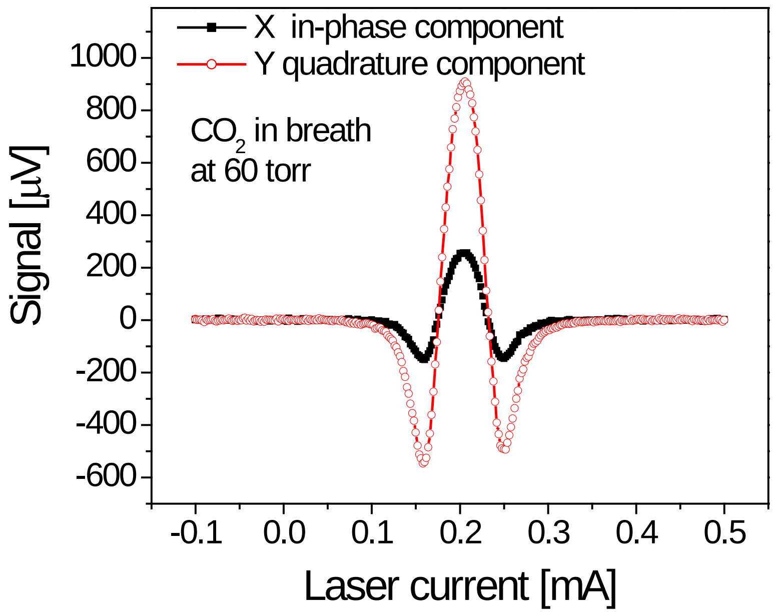
Effect of H_2O on V-T relaxation

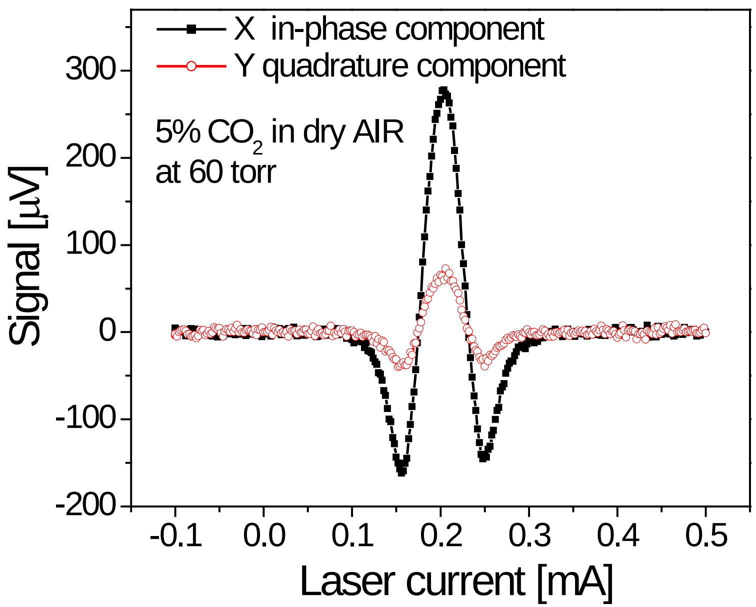




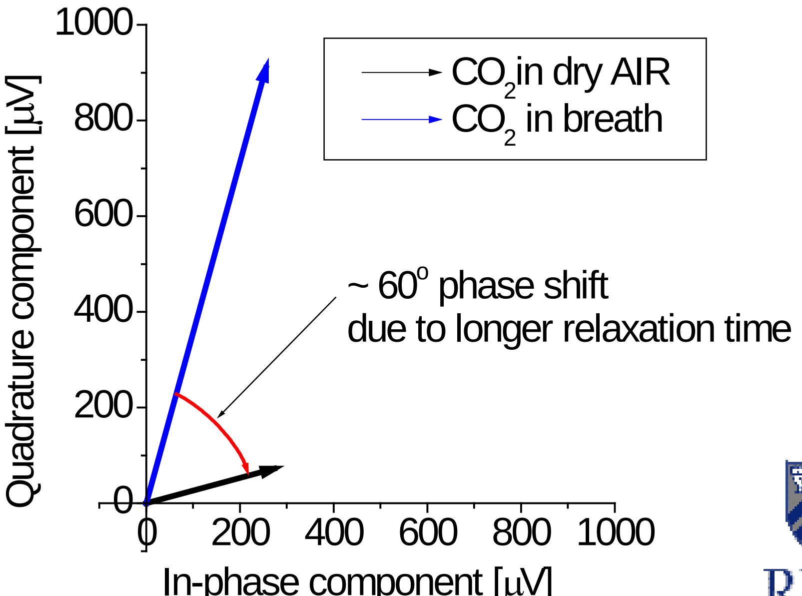
High concentration of H_2O in breath causes instantaneous thermalization of the absorbed laser power. In such a situation the optimal conditions depend mainly on the Q factor and absorption within the gas sample

QEPAS signal for CO_2 in dry and humid air





- Significant difference in signal strength due to longer relaxation time for dry CO_2 mixture at lower pressures
- Further increase in signal phase difference between dry and moist gas mixture (60 deg. comparing 50 deg. at 300torr)



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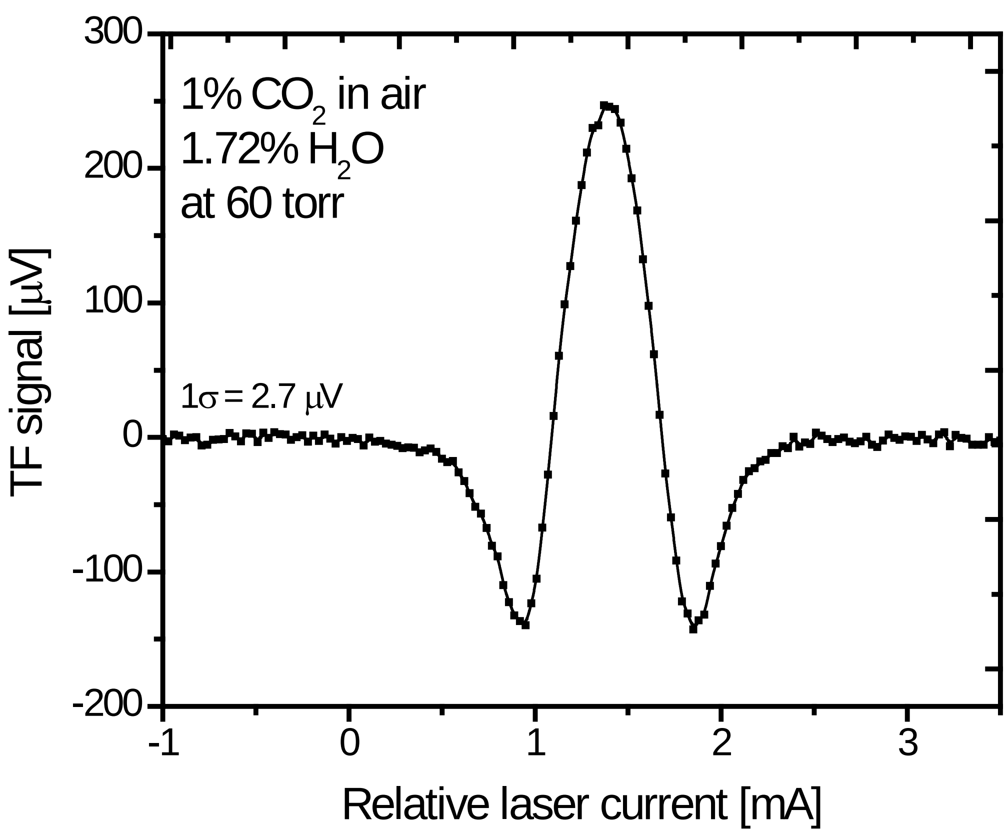
CO_2 detection limit



- SNR : ~ 91.4 (minimum detectable concentration ~110 ppm of CO_2)
- Laser power: ~ 4.6 mW
- Lock-in time constant: 1 s
- Peak absorption coefficient: ~ 1.4×10^{-3} cm^{-1}

- Normalized noise equivalent sensitivity for CO_2 in humid air:

$$NES = 1.25\times10^{-7}\ cm^{-1}W/\sqrt{Hz}$$

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QEPAS Performance for 10 Trace Gas Species (Feb'05)

Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, $cm^{-1}W/Hz^{½}$	Power, mW	NEC (τ=1s), ppmv
H_2O (N_2)**	7181.17	60	2.1×10^{-9}	5.8	0.18
HCN (air: 50% hum) **	6539.11	60	$< 2.6\times10^{-9}$	50	0.1
C_2H_2 ((N_2)**	6529.17	75	$\sim2.5\times10^{-9}$	~40	0.06
NH_3 (N_2)*	6528.76	60	5.4×10^{-9}	38	0.50
CO_2 (exhaled air)	6514.25	90	1.0×10^{-8}	5.2	890
CO_2 (N_2) ***	4990.00	300	1.25×10^{-7}	4.6	110
CH_2O (N_2) *	2832.48	100	1.1×10^{-8}	4.6	0.28
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
N_2O (air+5%SF_6)	2195.63	50	1.5×10^{-8}	19	0.007

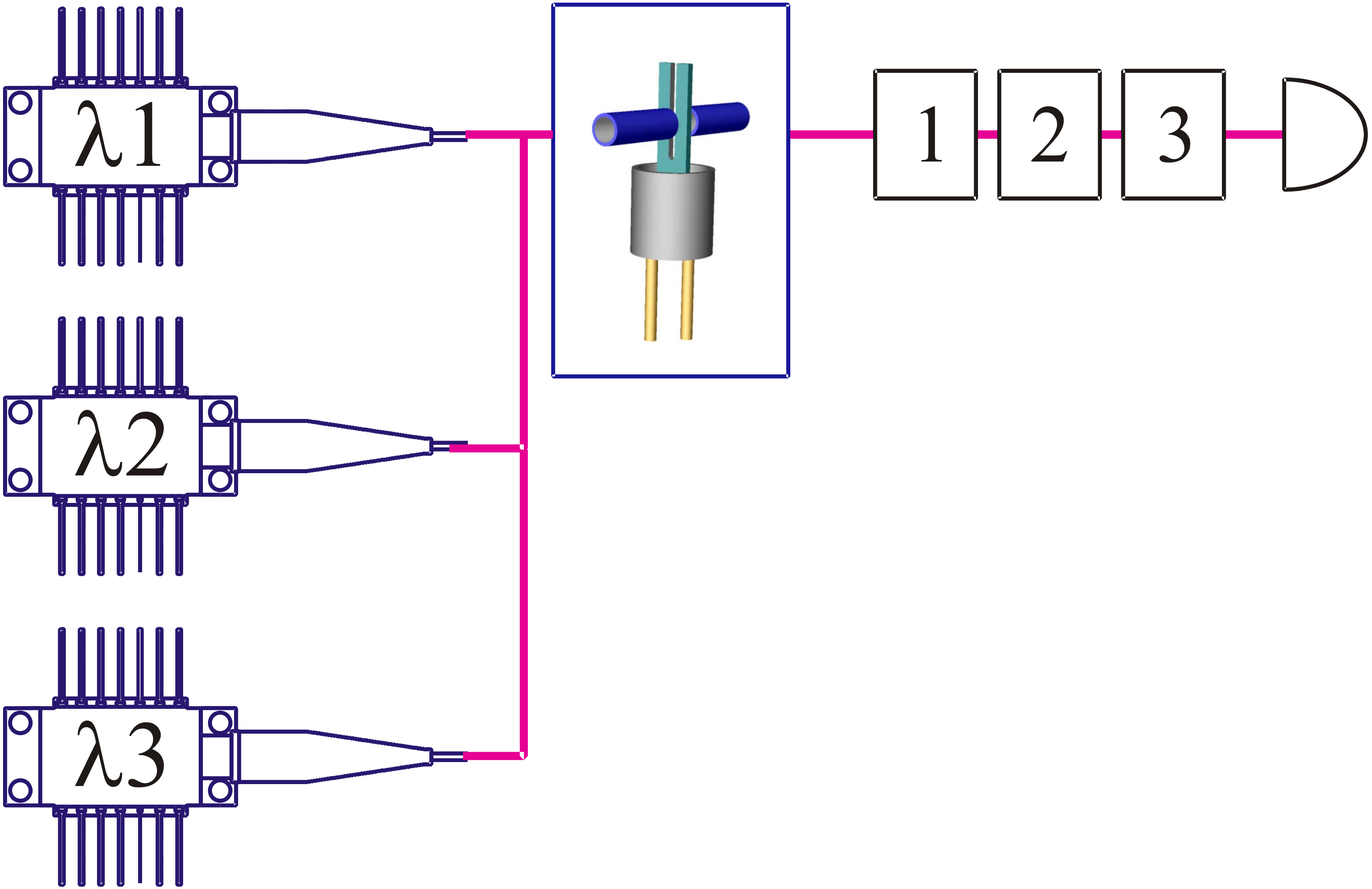
* - Improved microresonator
** - Improved microresonator and double optical pass through QTF
*** - Without microresonator

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

For comparison: conventional PAS 2.2×10^{-9} $cm^{-1}W/\sqrt{Hz}$ (1,800 Hz) for NH_3*

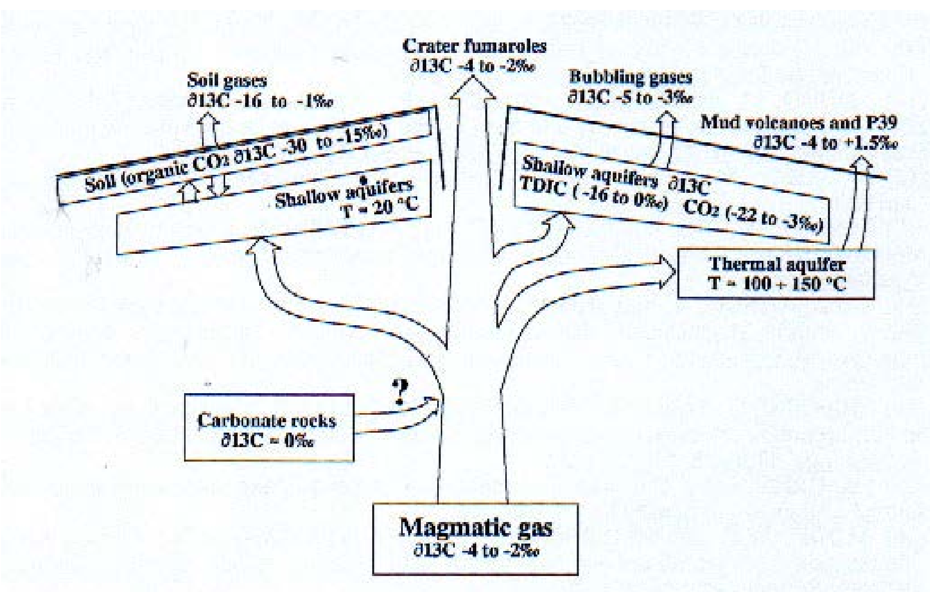
* M. E. Webber, M. Pushkarsky and C. K. N Patel, Appl. Opt. 42, 2119-2126 (2003)

QEPAS Architecture Flexibility: Optical Multiplexing



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



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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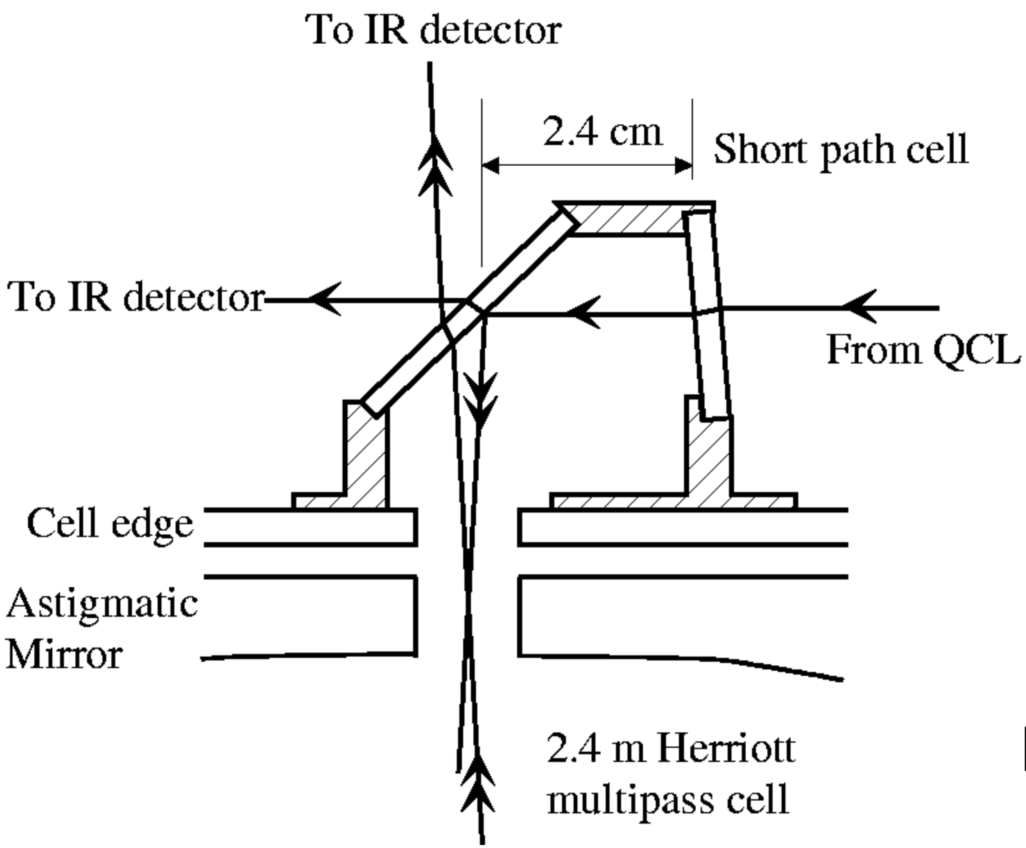
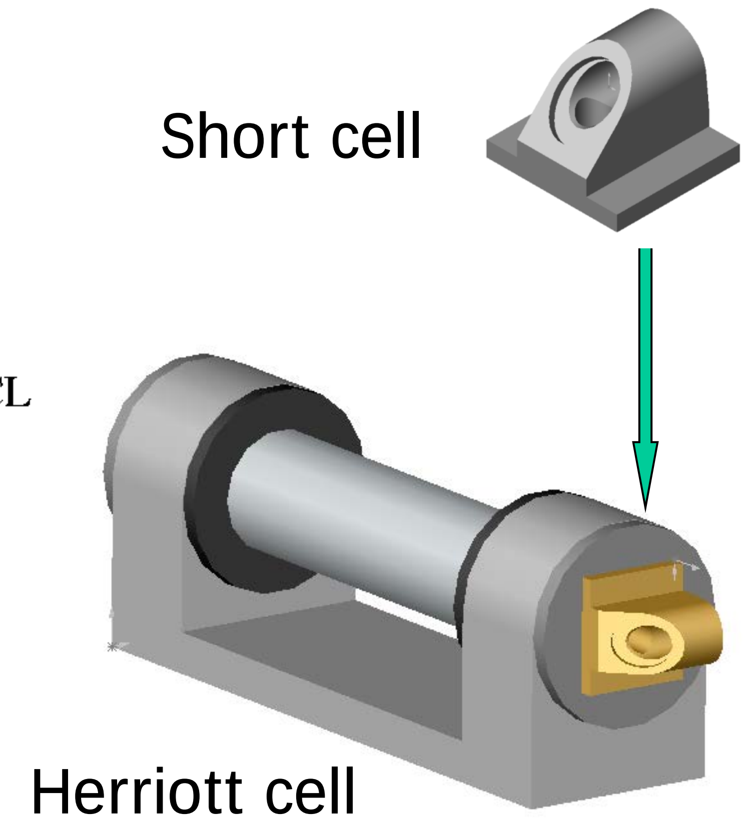
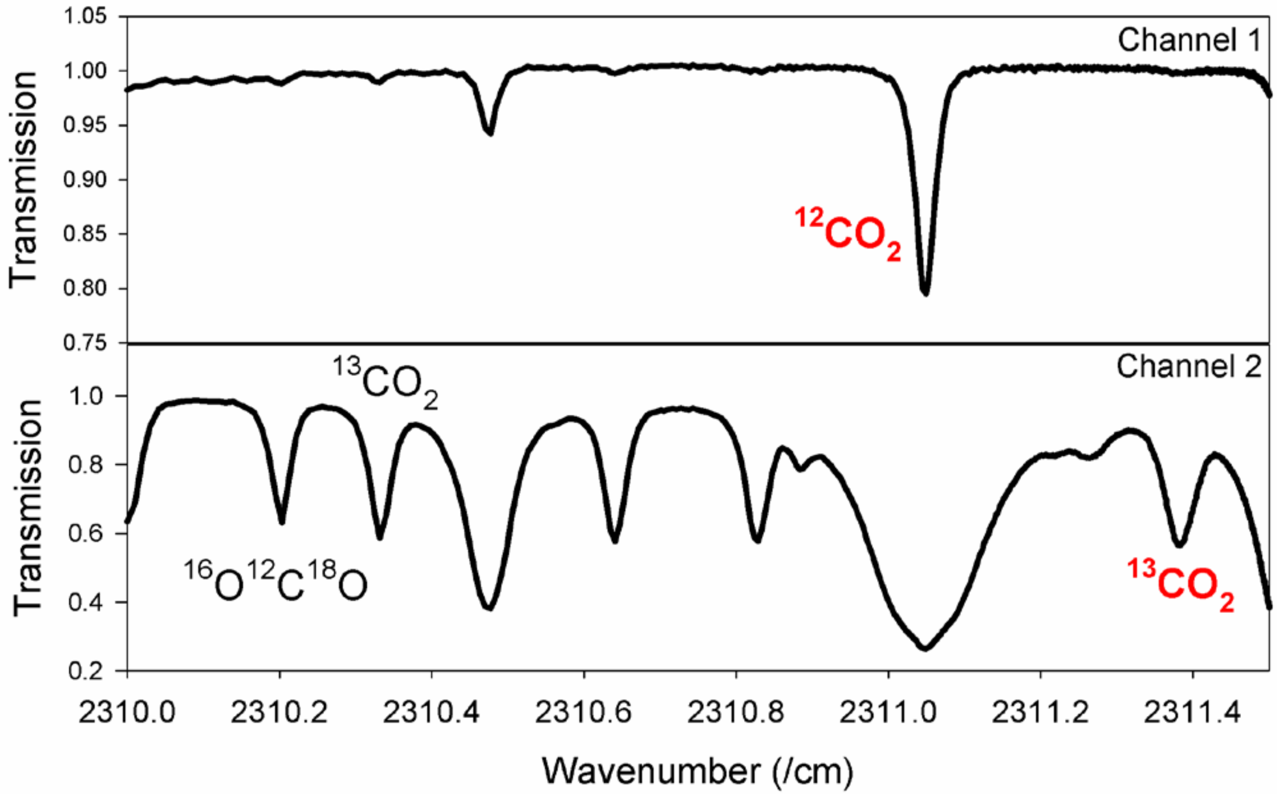
Dual path length gas cell design for infrared ratio spectrometry





High resolution CO_2 absorption spectrum at 2311 cm^{-1}



To appear in Optics and Photonics News, 2006

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Summary and Future Directions

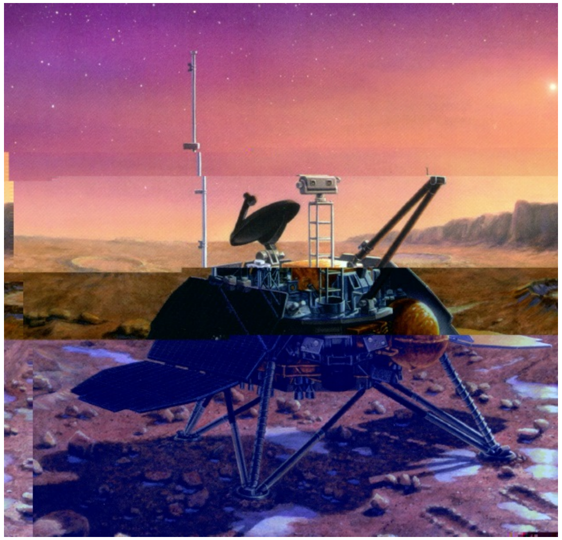
- **Quantum Cascade Laser based Trace Gas Sensors**
  - Compact and robust sensors based on QC-LAS and QE L-PAS
  - High sensitivity (10^{-4}-10^{-5}) and selectivity (3 to 500 MHz)
  - Dramatic reduction of sample volume (~0.2 mm^3)
  - Detected 14 trace gases to date: NH_3, CH_4, N_2O, CO_2, CO, NO, 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
  - QE L-PAS based applications using novel thermoelectrically cooled cw and broadly wavelength tunable quantum and interband cascade lasers
  - Investigate QTFs with lower resonant frequencies
  - New target gases, in particular VOCs and HCs
  - Development of optically multiplexed gas sensor networks based on QE L-PAS

NASA Atmospheric & Mars Gas Sensor Platforms

Tunable laser sensors for earth's stratosphere

Aircraft laser absorption spectrometers

Tunable laser planetary spectrometer



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 ‰

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)