High resolution spectroscopy and trace-gas detection with thermoelectrically cooled cw quantum cascade lasers

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2nd Int. Workshop on QC Lasers

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Outline

- Motivation and Background Issues
- Mid-IR Quantum Cascade Laser based Gas Sensors
  - CW, TEC cooled, high power DFB QCLs
  - CW, TEC cooled, widely tunable QCLs
  - CW, LN_2 & TEC cooled, DFB interband cascade lasers
- Selected Applications of Trace Gas Detection
  - Off Axis-ICOS Detection of Nitric Oxide
  - LAS based monitoring of formaldehyde and ethylene
  - Quartz Enhanced PAS detection of HC_2O, CO, N_2O & broadband absorbers (C_2HF_5)
- Conclusions, Challenges and Future Directions

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Wide Range of Trace Gas Sensing Applications

- **Urban and Industrial Emission Measurements**
  - Industrial Plants
  - Combustion Sources and Processes (e.g. fire detection)
  - Automobile, Aircraft and Marine Emissions
- **Rural Emission Measurements**
  - Agriculture & Forestry, Livestock
- **Environmental Monitoring**
  - Atmospheric Chemistry
  - Volcanic Emissions
- **Chemical Analysis and Industrial Process Control**
  - Petrochemical, Semiconductor, Nuclear Safeguards, Pharmaceutical, Metals Processing & Food Industries
- **Spacecraft and Planetary Surface Monitoring**
  - Crew Health Maintenance & Life Support
- **Applications in Medicine and Life Sciences**
- **Technologies for Law Enforcement and Homeland Security**
- **Fundamental Science and Photochemistry**

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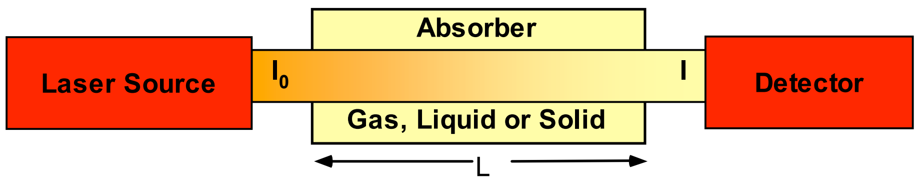
Fundamentals of Laser Absorption Spectroscopy

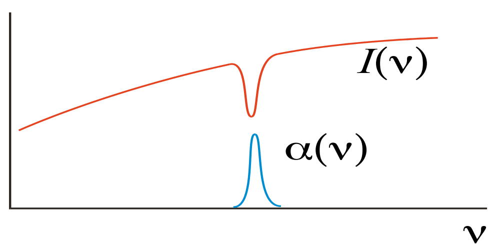


Beer-Lambert's Law of Linear Absorption

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

$\alpha(\nu)$ - 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·cm^{-3} ·atm^1]

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

$g(\nu - \nu_0)$ – 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)
- Evanescent Field Monitoring (fibers & waveguides)

Spectroscopic Detection Schemes

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

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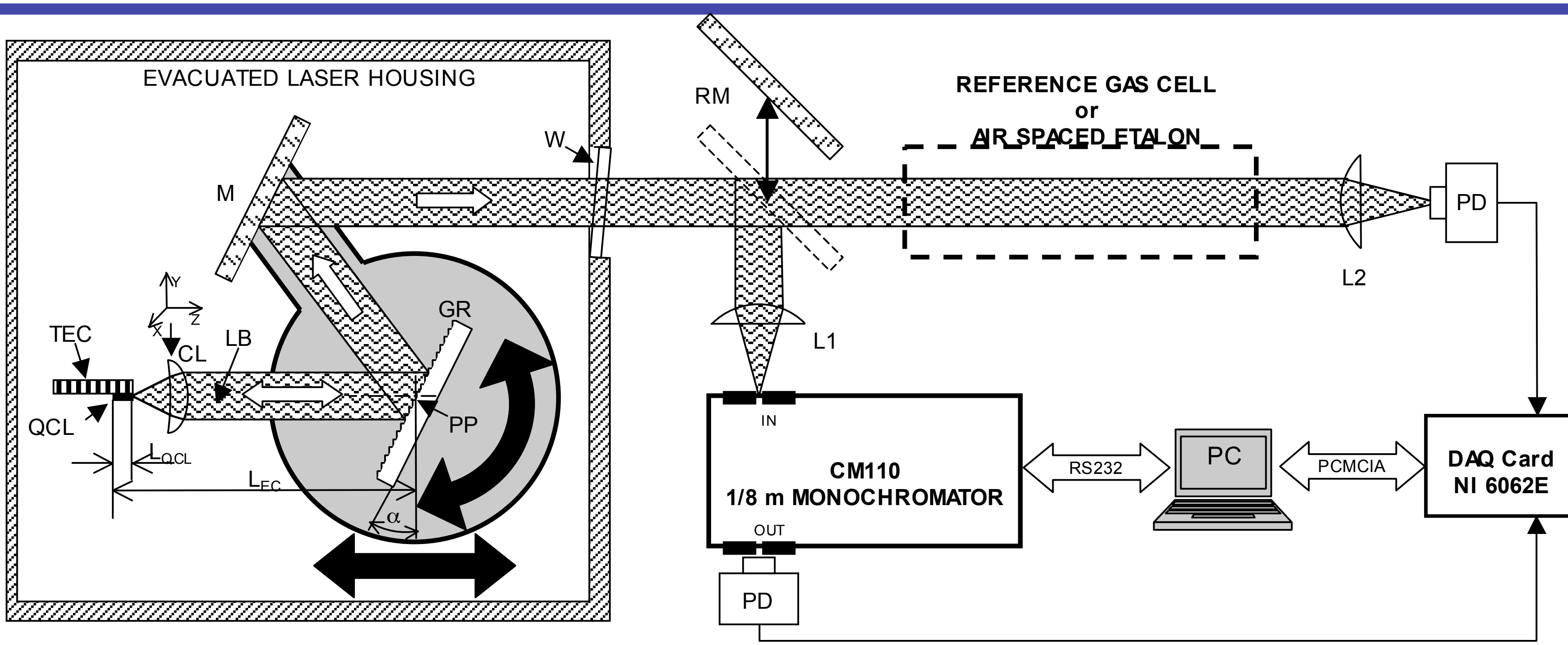
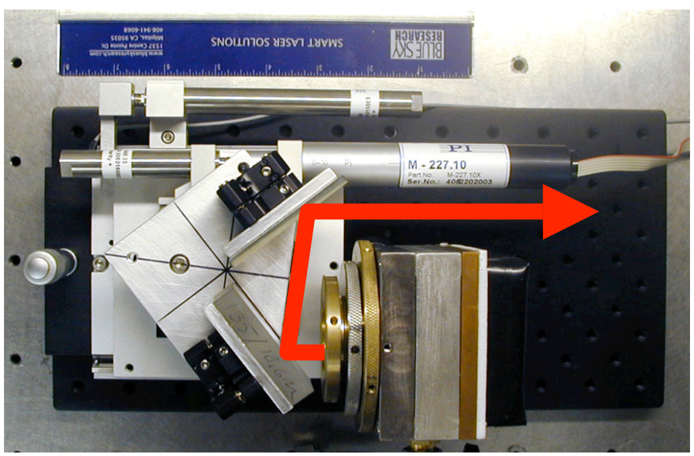
Tunable external cavity QCL based spectrometer



EC QCL, June 2006



- PZT controlled EC-length
- PZT controlled grating angle
- QCL current control
- Optimization of cavity alignment performed by means of lens positioning using electrically controlled 3D translation stage
- 35 cm^{-1} wavelength tunability with present gain chip

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

Motivation for Nitric Oxide Detection

- Atmospheric Chemistry
- Environmental pollutant gas monitoring
  - NO_x monitoring from automobile exhaust and power plant emissions
  - Precursor of smog and acid rain
- Industrial process control
  - Formation of oxynitride gates in CMOS Devices
- NO in medicine and biology
  - Important signaling molecule in physiological processes in humans and mammals (1988 Nobel Prize in Physiology/Medicine)
  - Treatment of asthma, COPD, acute lung rejection

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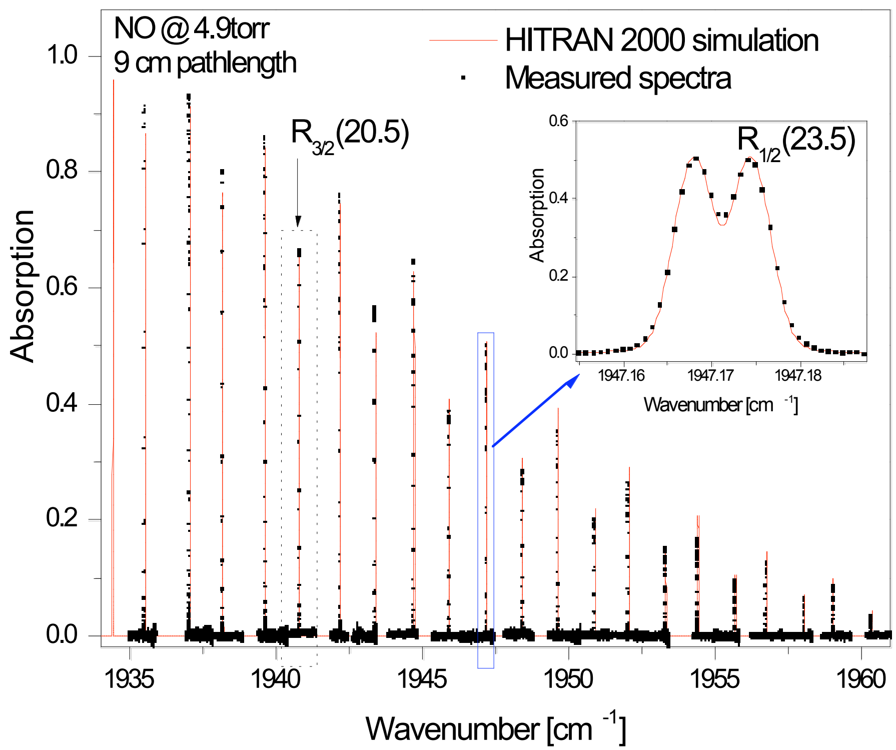
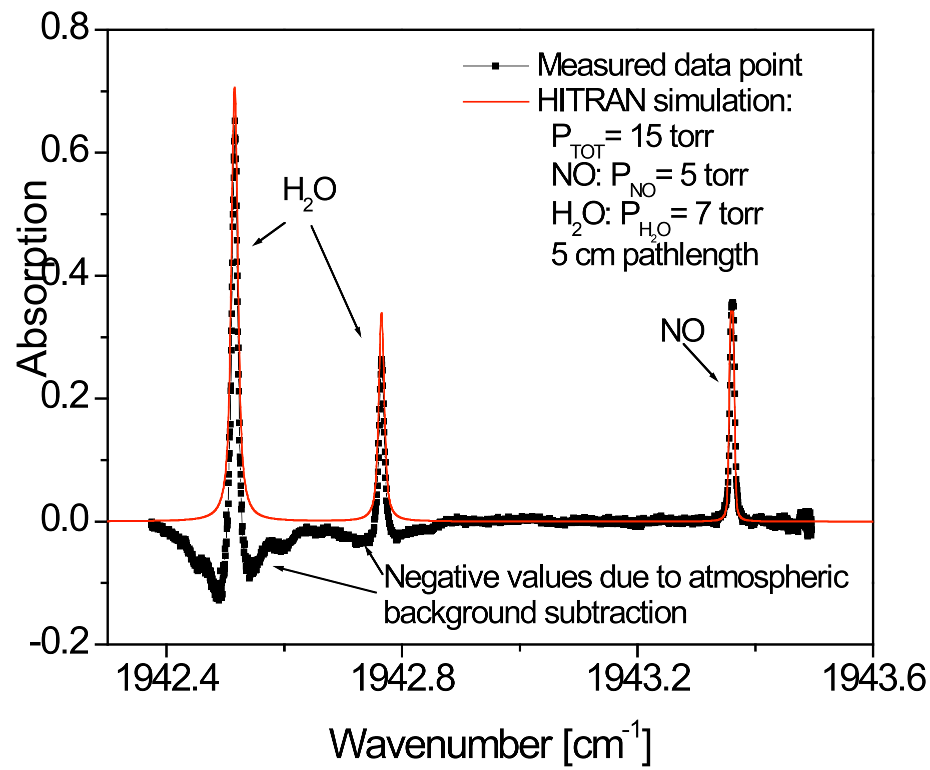
Mid-IR NO Absorption Spectra Acquired with a Tunable EGC-QCL



Nitric oxide absorption spectra measured at different diffraction grating angles of the external cavity quantum cascade laser. The narrow EGC- QC laser linewidth allows resolution of two spectral peaks separated by ~ 0.006 cm^{-1}



Single spectral scan of NO and strong neighboring H_2O lines. Background measurement was performed with the reference gas cell removed from the beam path.

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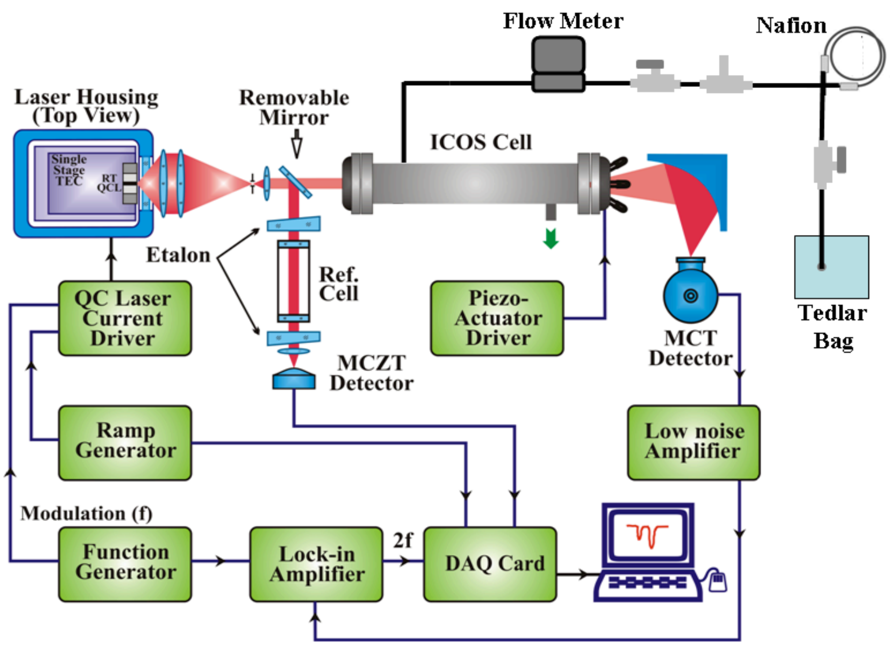
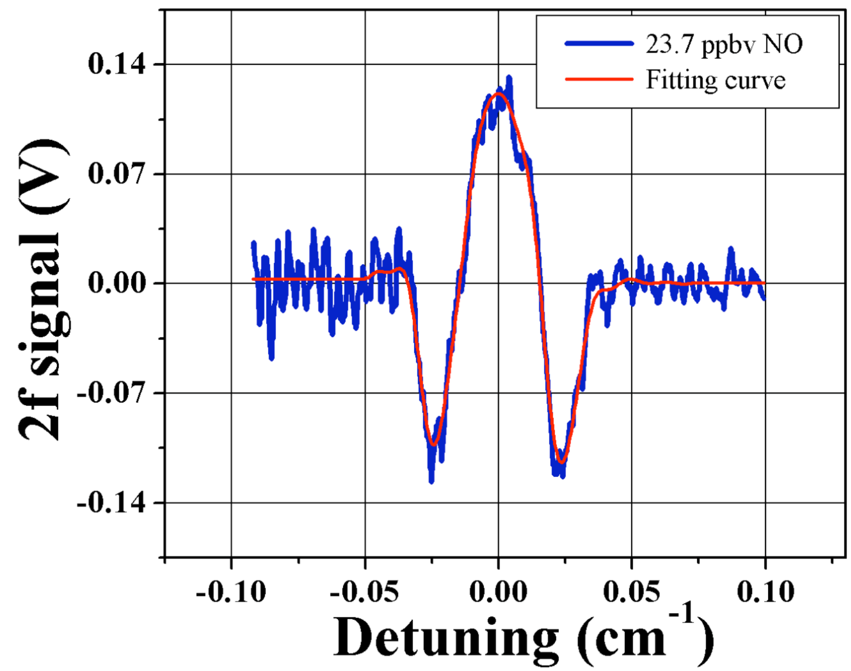
Laser-based ICOS Nitric Oxide Sensor





A 1σ deviation of the amplitude corresponds to a 700 ppt detection limit (1sec.)

Yu. A. Bakhirkin et. al. "Sub-ppbv Nitric Oxide Concentration Measurements using CW Room-Temperature Quantum Cascade Laser based Integrated Cavity Spectroscopy", Applied Physics B 82,149-154 (2006)

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Motivation for Monitoring of H_2CO

- Toxic pollutant due to incomplete fuel combustion processes
- Potential trace contaminant in industrial manufactured products (eg. resins, foam)
- Atmospheric H_2CO is a key hydrocarbon oxidation product which leads to the photochemical generation of ozone and release of hydrogen radicals
- Medically important gas

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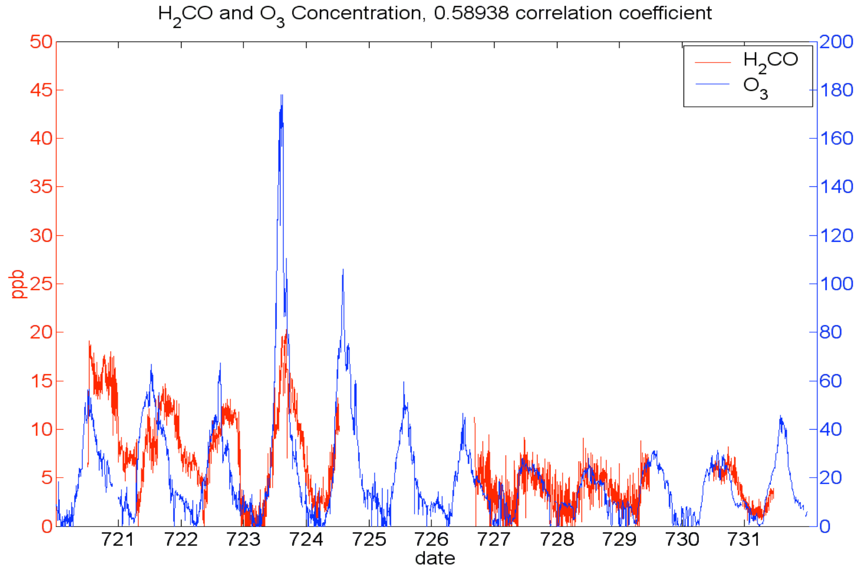
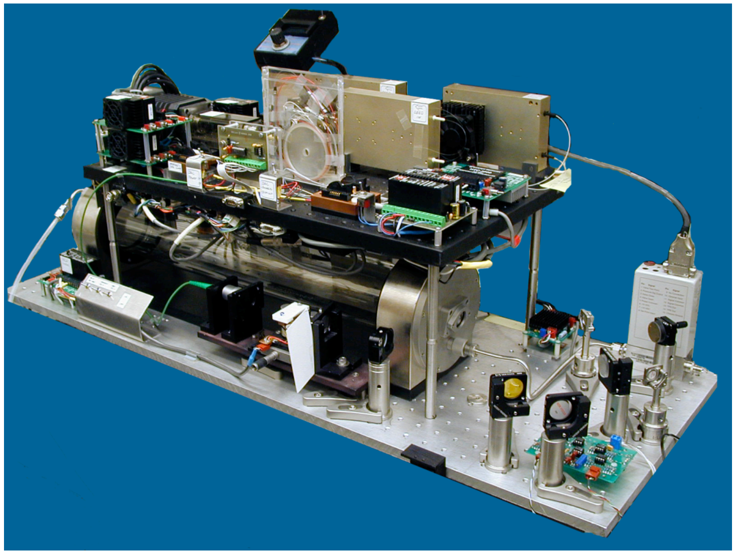
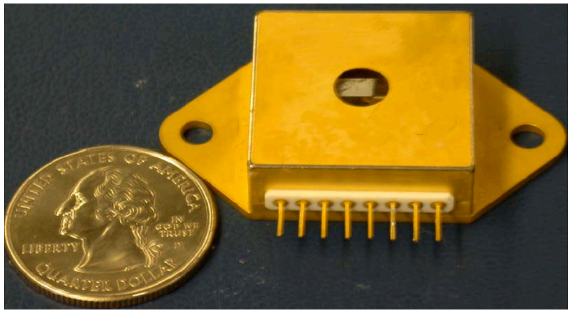
DFG and ICL based H_2CO Sensor for studying Urban Air Pollution



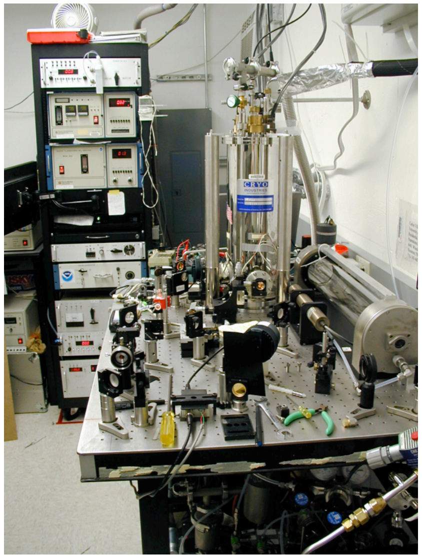
H_2CO & O_3 concentrations at Deer Park (2003)



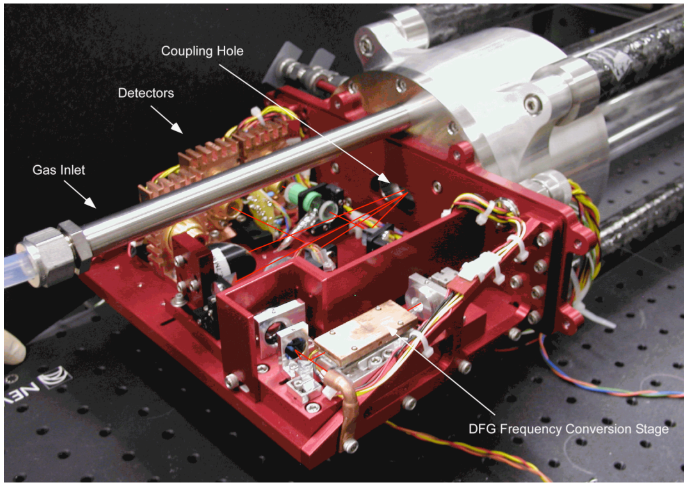
Rice DFG system (2003)



JPL 3.3 μm cw,TEC cooled ICL (2006)

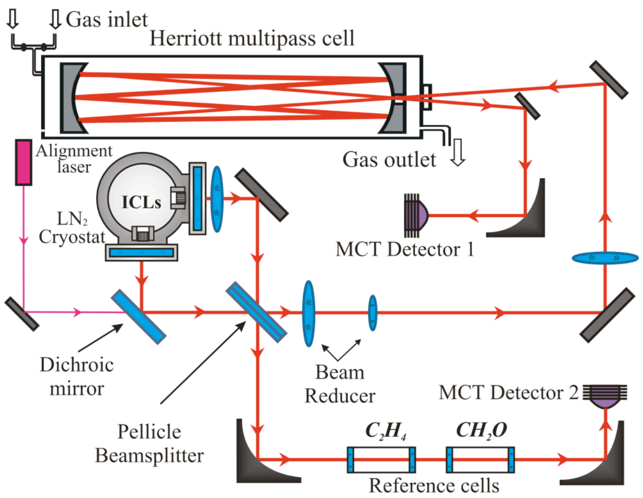


Rice dual ICL system (2006)

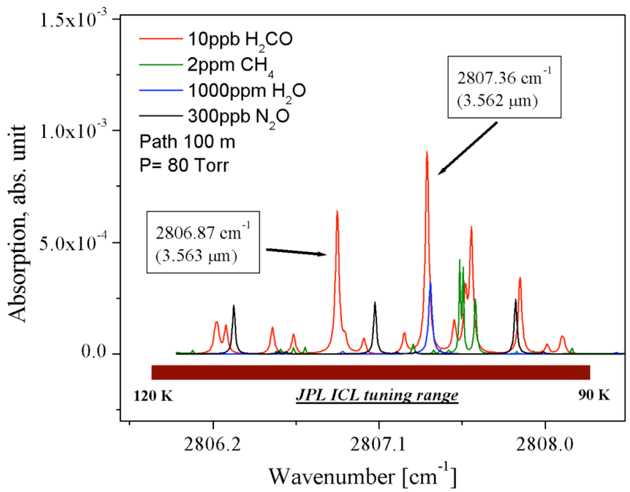


NCAR DFG system (2006)

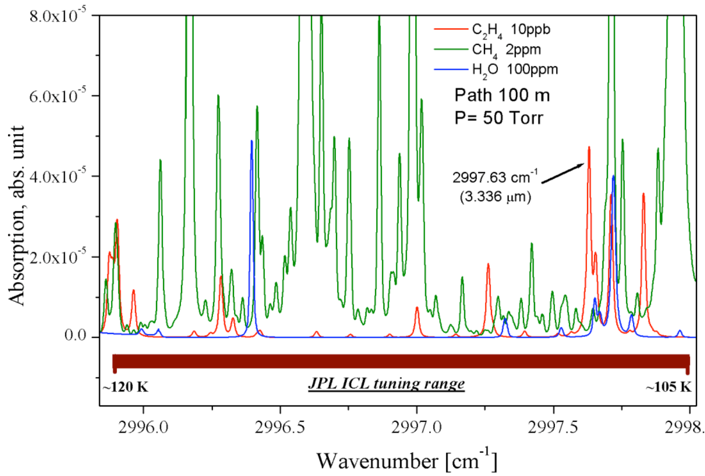
CW ICL Based H_2CO and C_2H_4 Sensor for TexAQS '06



Moody Tower UH campus, earth Google satellite photo.



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



HITRAN Based Simulation of C_2H_4-H_2O-CH_4 Spectrum in Tuning Range of a 3.33-3.35 μm IC Laser

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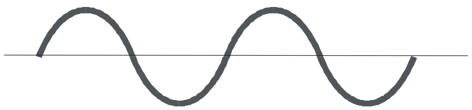
From conventional PAS to QEPAS

Laser beam, power P



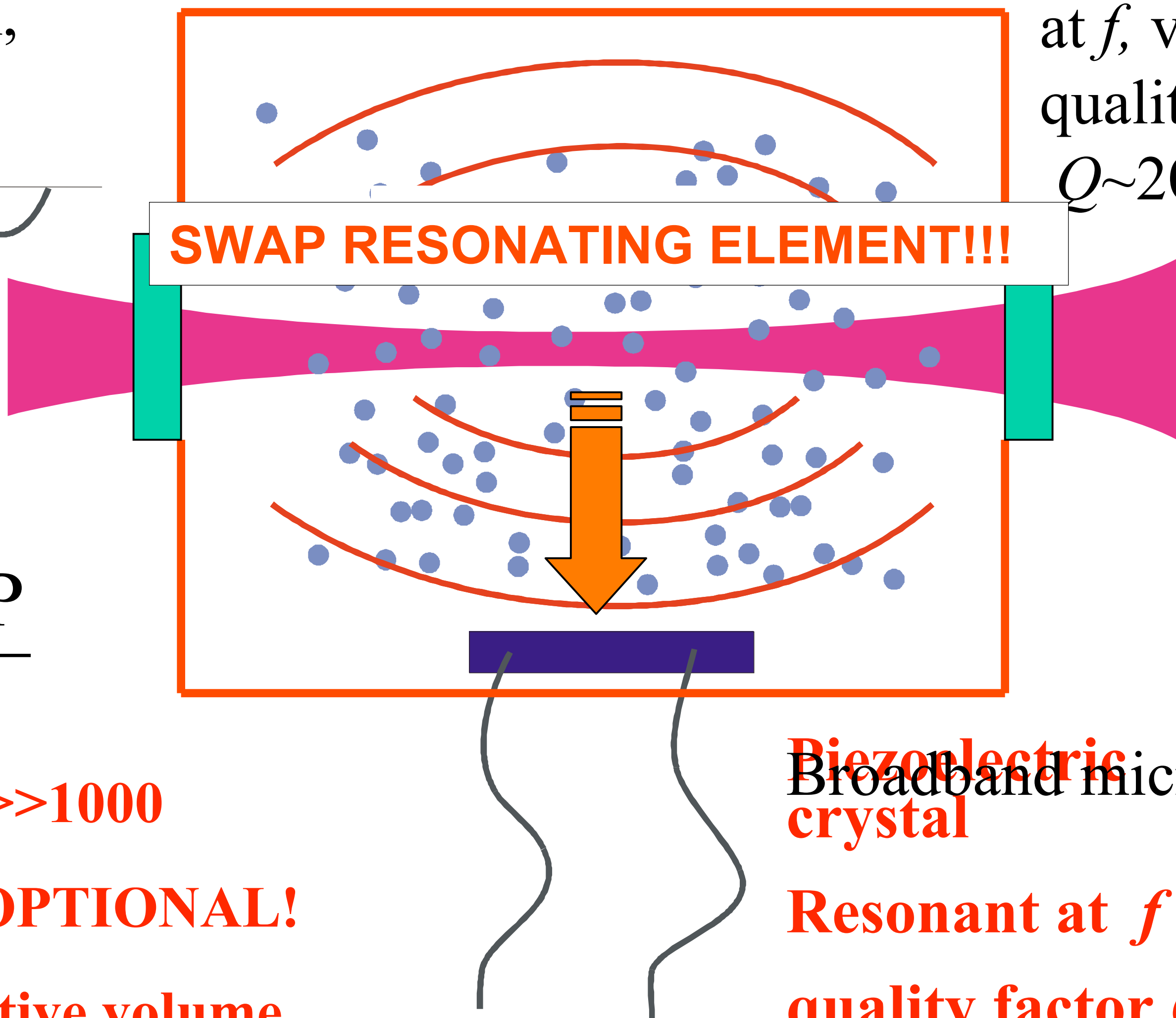
Modulated (P or λ) at f or $f/2$

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

Q>>1000

Cell is OPTIONAL!

V-effective volume



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

Broadband microphone

Piezoelectric crystal

Resonant at f

quality factor Q

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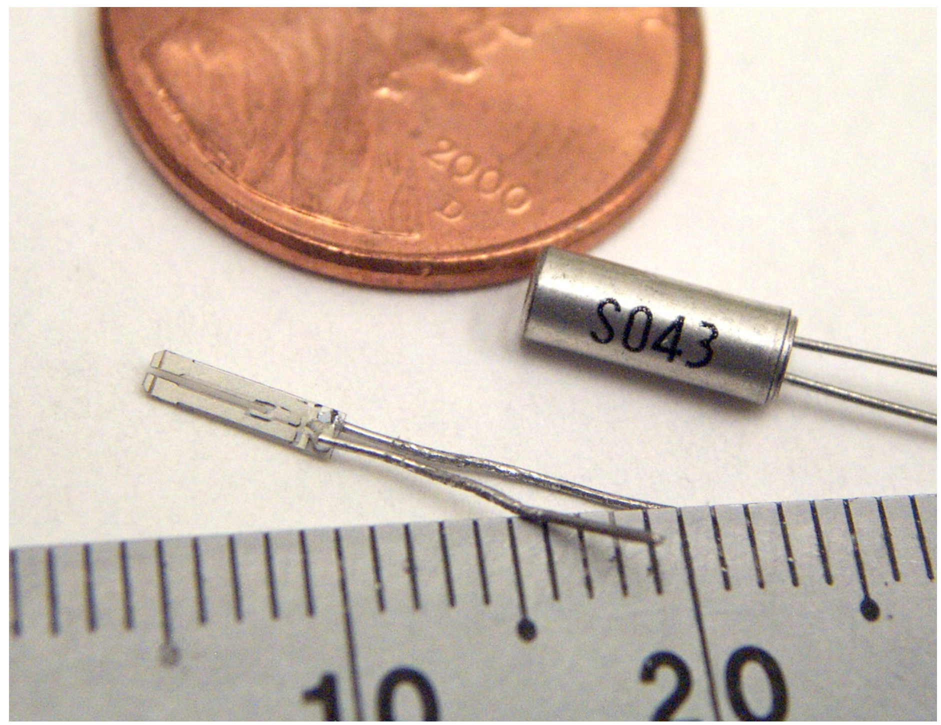
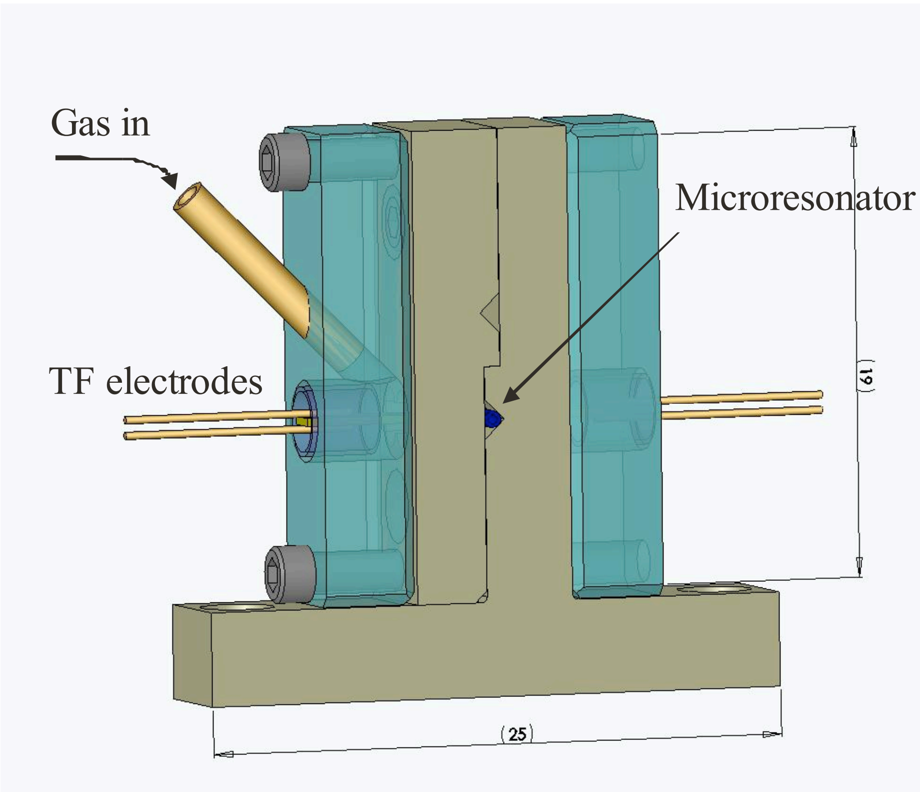
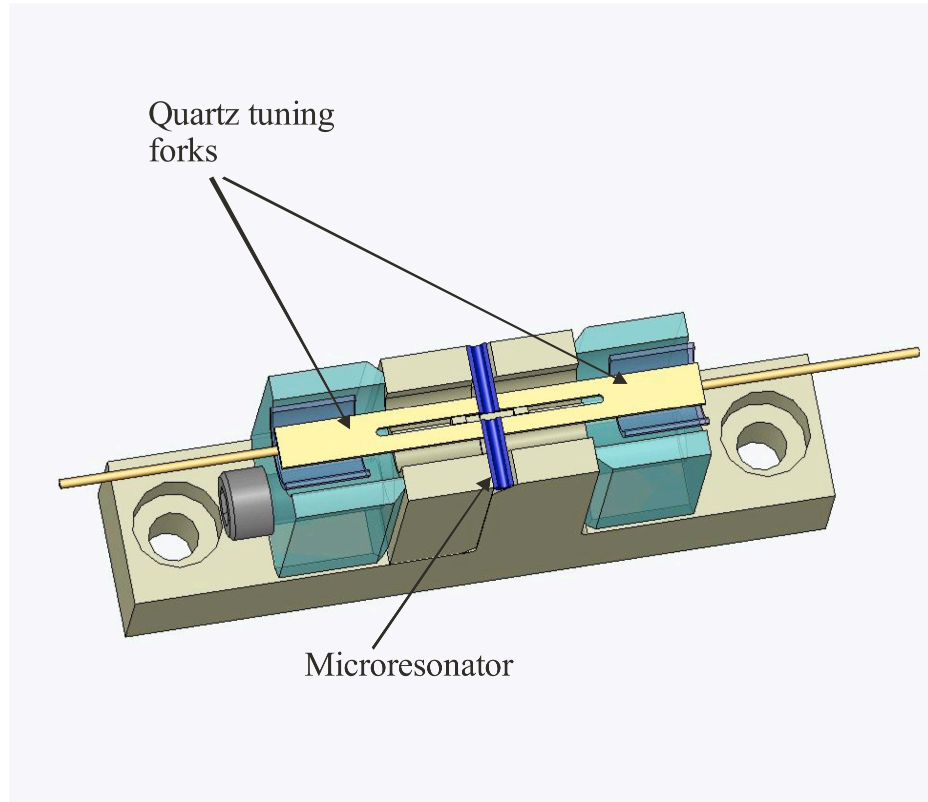
Quartz Tuning Fork as a Resonant Microphone for PAS

- Miniature size, 0.3 mm^3 detection volume
- Dimensions in <u>mm</u>: length = 3.8, gap size = 0.3, thickness = 0.3, width = 0.58
- Piezo-active material
- Signal currents ≈ pA
- Intrinsically high Q factor, ~10,000 at ambient pressure; Q_{vacuum} ~ 125,000



Design of a new QTF based Absorption Detection Module





- **Compact & integrated design**
- **Laser-induced background reduction**
- **Machining precision of : +/- 10µm**

- **Two QTFs connected in parallel results in enhanced √2 SNR**
- **Minimum exposure of QTFs to QCL radiation**
- **Efficient for gas flow to micro-resonator**

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Merits of QE PAS based Trace Gas Detection

- High sensitivity (ppm to ppb gas concentration levels) and excellent dynamic range
- Immune to ambient and flow acoustic noise, as well as laser noise and etalon effects
- Dramatic reduction of sample volume (< 1 mm^3)
- Applicable over a wide range of pressures, including atmospheric pressure
- Rugged and low cost compared to other spectroscopic techniques that require infrared detector(s)
- Sensitive to phase shift introduced by V-T relaxation processes – additional selectivity
- Potential for trace gas sensor networks

Motivation for H_2CO Monitoring

- Pollutant due to incomplete combustion processes
- Potential trace contaminant in industrial manufactured products
- Atmospheric H_2CO is a key hydrocarbon oxidation product which leads to the photochemical generation of ozone and release of hydrogen radicals
- Medically important gas

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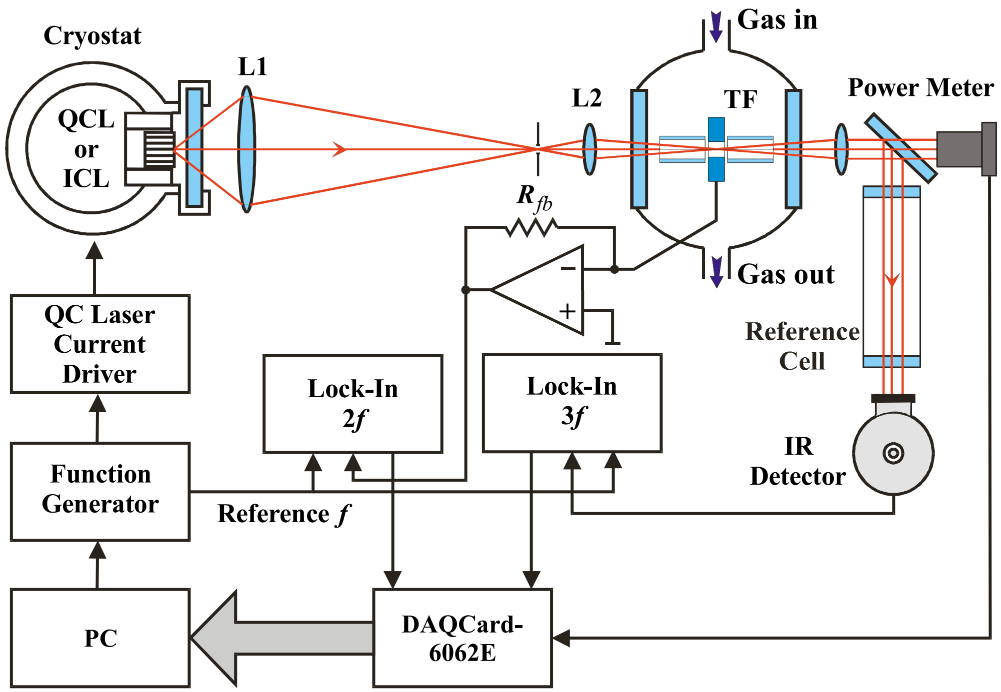
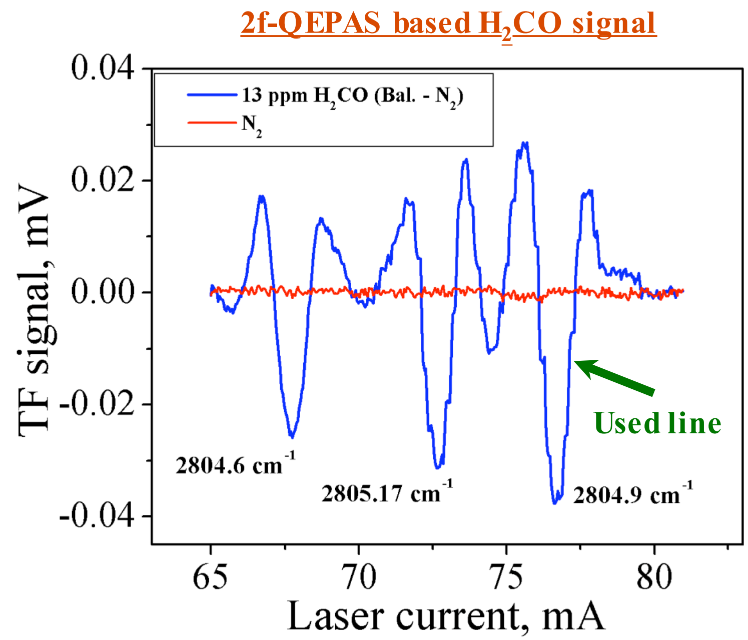
QCL or ICL based Quartz-Enhanced Photoacoustic Gas Sensor





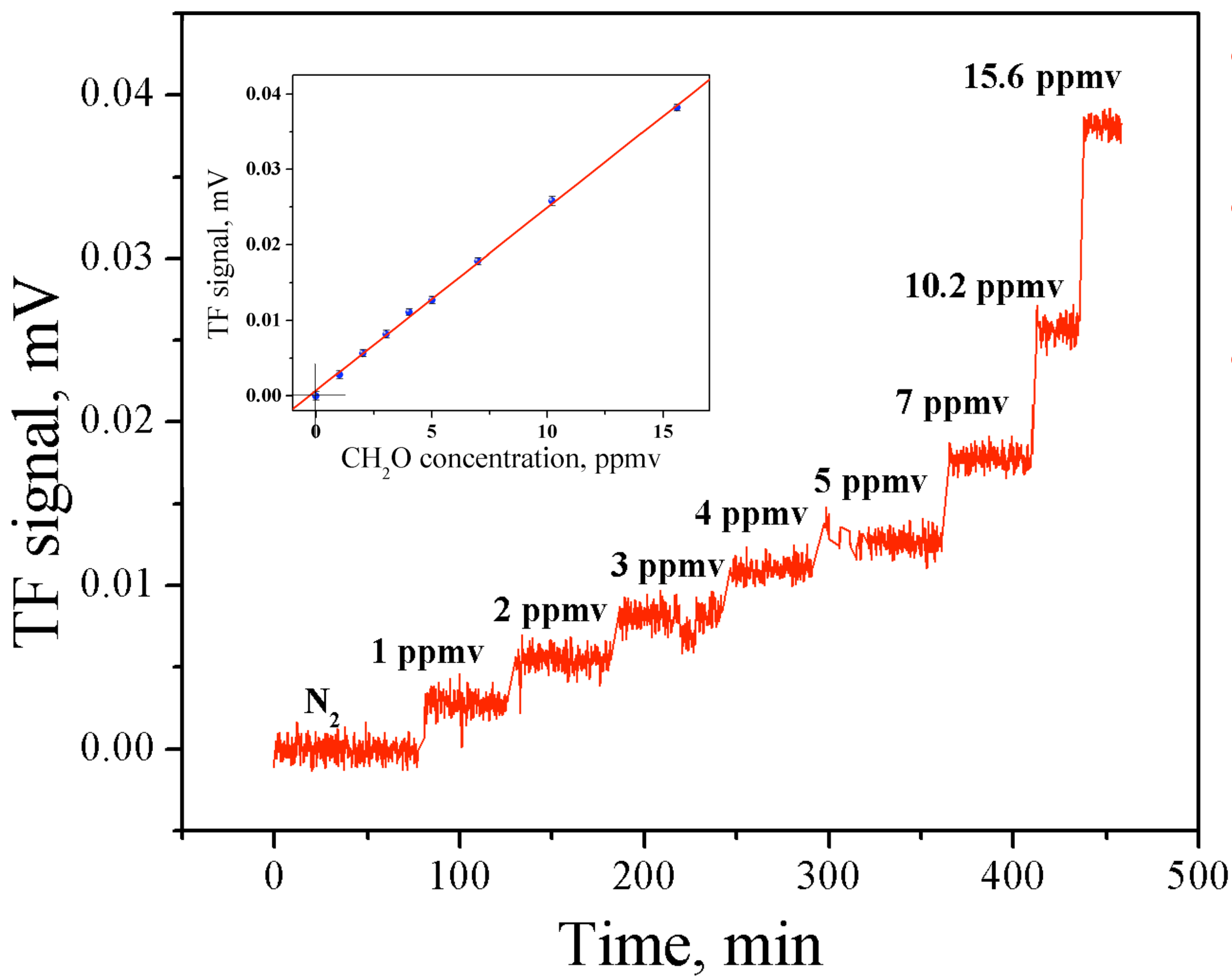
- $[H_2CO]$: 13 ppm
- QEPAS NNEA Sensitivity (for 2804.9 cm^{-1}): $0.92\times10^{-8}cm^{-1}$ W/√Hz;
- NEC (τ=1s): 0.18 ppmv (~ 6.5 mW)

For comparison:

NIR QEPAS NNEA Sensitivity for NH_3 : $5.4\times10^{-9}cm^{-1}W/\sqrt{}$ Hz

NEC (τ=1s): 0.5 ppmv (38 mW)

Calibration Measurements of a QEPAS based H_2CO Sensor with a Trace Gas Standard Generator



- H_2CO absorption frequency: 2804.9 cm^{-1}
- Lock-In time constant: 1 sec.
- QEPAS parameters
  - Resonance frequency: 32.760 KHz
  - Q-factor: ~ 8800
  - Pressure: 200 Torr
  - Gas Flow: ~50 sccm
  - IC laser power: ~ 6.5 mW

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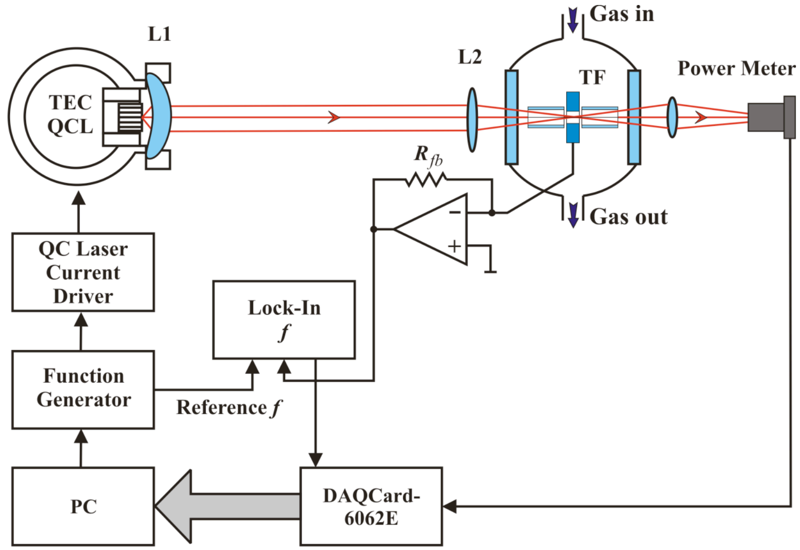
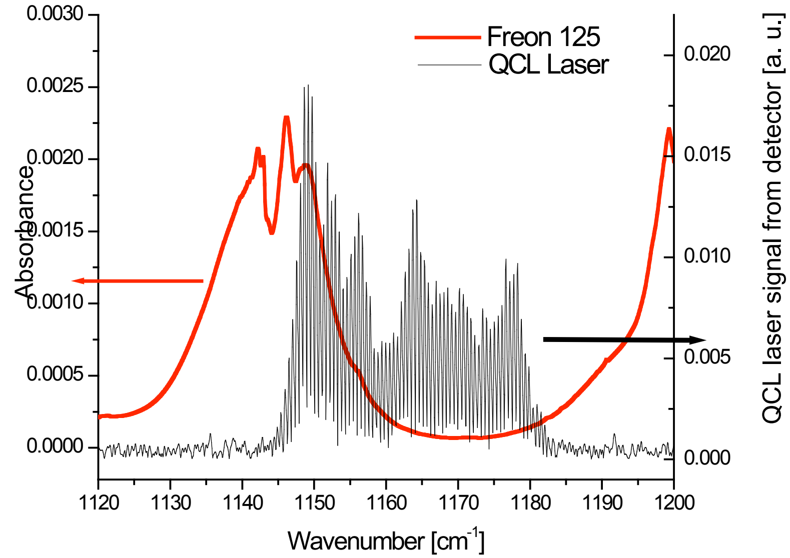
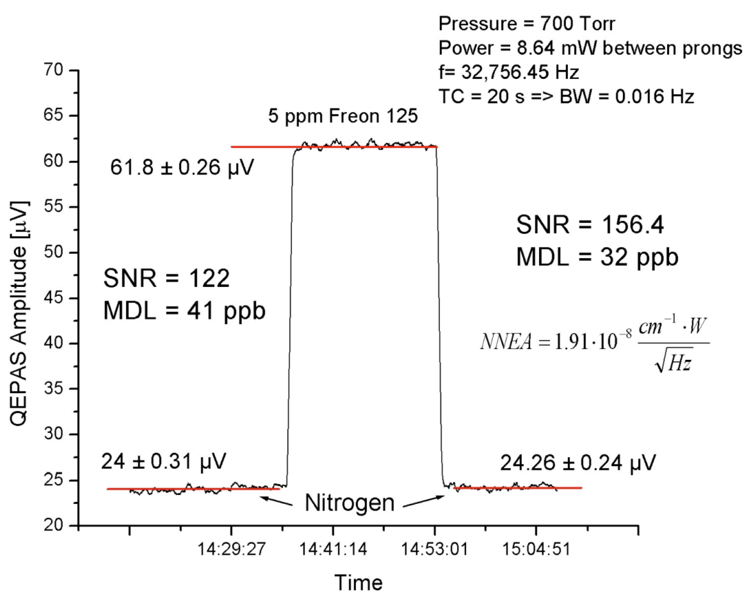
Amplitude Modulated 8.6 µm QCL based QEPAS Freon 125 Sensor





Spectral comparison of Freon 125 with emission coverage from a 8.6 µm FP QCL based on the PNNL database



Freon 125 QEPAS signal and optical baseline noise

QEPAS Performance for 9 Trace Gas Species (Sept.'06)

Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, $cm^{-1}W/Hz^{-}$	Power, mW	NEC (τ=1s), ppmv
H_2O (N_2)**	7306.75	60	1.9_10^{-9}	9.5	0.09
HCN (air: 50% RH)*	6539.11	60	$< 4.3\_10^{-9}$	50	0.16
C_2H_2 (N_2)**	6529.17	75	$\sim 2.5\_10^{-9}$	~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+1.5% H2O)	4991.26	50	1.4_10^{-8}	4.4	18
CH_2O (N_2:75% RH) *	2804.90	75	9.2_10^{-9}	6.5	0.18
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
C_2HF_5 (Freon 125)***	1162.79	700	1.9_10^{-8}	4.0	0.04

* - Improved microresonator
** - Improved micror esonator and double optical pass through ADM
*** - With amplitude modulation and 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 et al, Appl. Opt. 42, 2119-2126 (2003)

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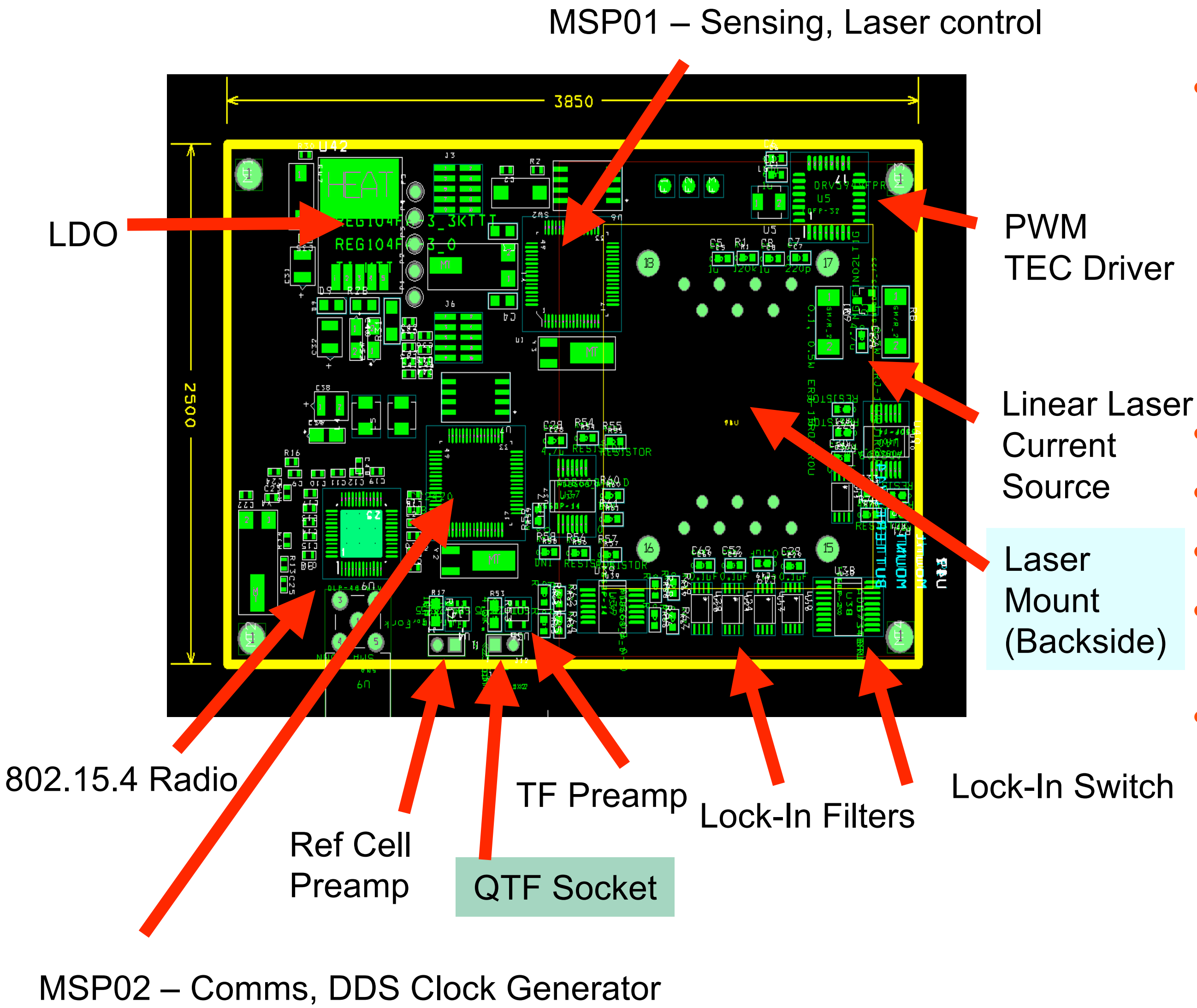
Future Work – Mini-QEPAS Sensor System



- **3.85 inch x 2.5 inch (9.8 cm x 6.4 cm)**
- Low power
  - 3W max for TEC
  - 3W max for Laser Bias
  - 0.5W max for electronics (μW sleep mode)
- Embedded Laser
- Embedded TF module
- Embedded Radio
- 2 cell Li-Pol Battery + Charging
- Low cost

Summary, Technological Challenges and Future Directions of QCL based Applications

- **Quantum and Interband Cascade Laser based Trace Gas Sensors**
  - Compact, tunable, and robust
  - High sensitivity ($<10^{-4}$) and selectivity (3 to 500 MHz)
  - Fast data acquisition and analysis
  - Detected 12 trace gases to date: NH_3, CH_4, N_2O, CO_2, CO, NO, H_2O, COS, C_2H_4, SO_2, C_2H_5OH, C_2HF_5 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 and H_2CO)
  - Industrial process control and chemical analysis (HCN, NO, NH_3, H_2O)
  - Medical & Biomedical Diagnostics (NO, CO, COS, CO_2, NH_3, C_2H_4)
  - Sensor Technologies for Law Enforcement and Homeland Security
- **Future Directions and Collaborations**
  - New applications using novel, thermoelectrically cooled, cw, high power, and broadly wavelength tunable near-IR interband and mid-IR intersubband quantum cascade lasers
  - Improvements of Cavity Enhanced and QEPAS based spectroscopic techniques using broadly wavelength tunable quantum cascade lasers
  - Development of optically multiplexed gas sensor networks based on QEPAS
  - Potential and limitations of amplitude modulated QEPAS for monitoring of broadband absorbers, in particular VOCs and HCs

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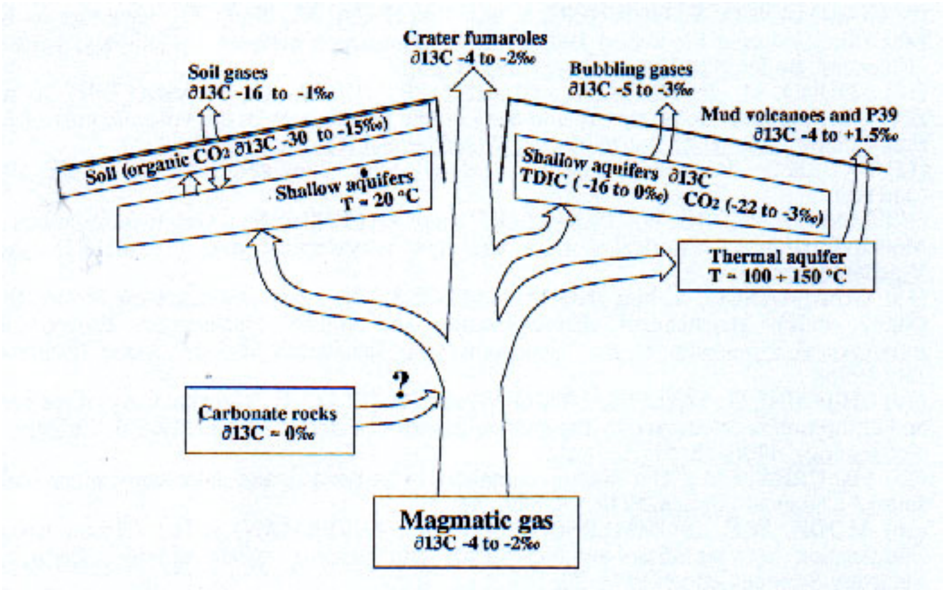
Mt. Etna, Italy, Europe's largest volcano

Photos provided by C. Oppenheimer, Cambridge University, UK

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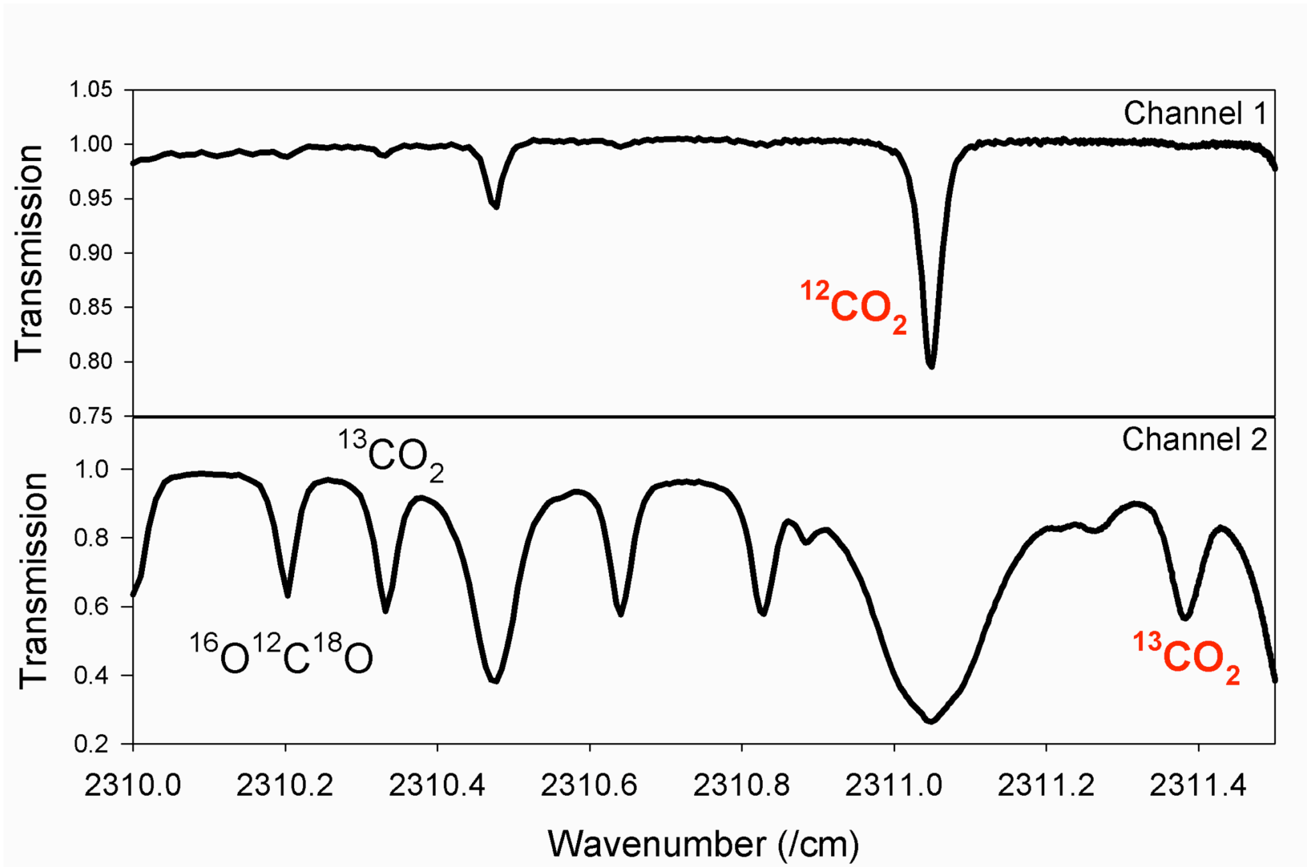
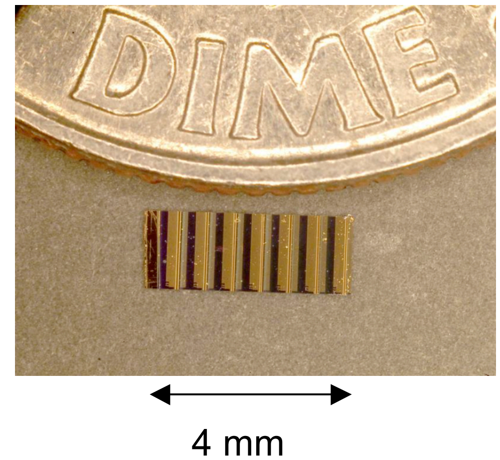
High resolution CO_2 absorption spectrum at 2311 cm^{-1}

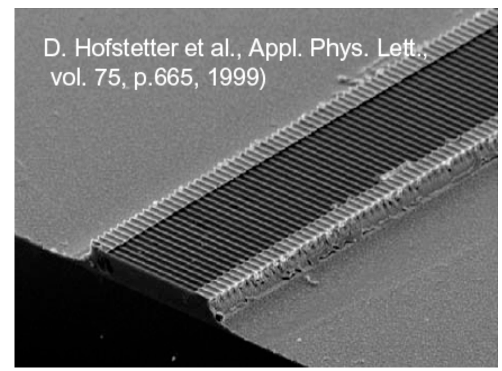


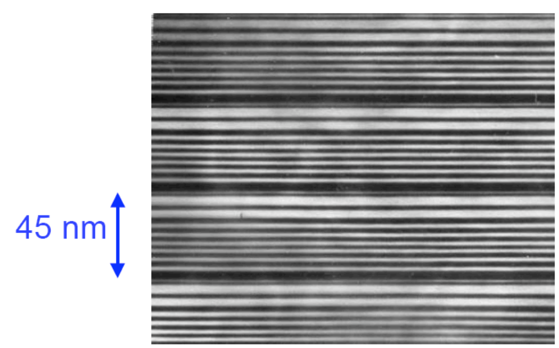
OSA Optics and Photonics News, May 2006

Quantum and Interband Cascade Laser: Basic Facts

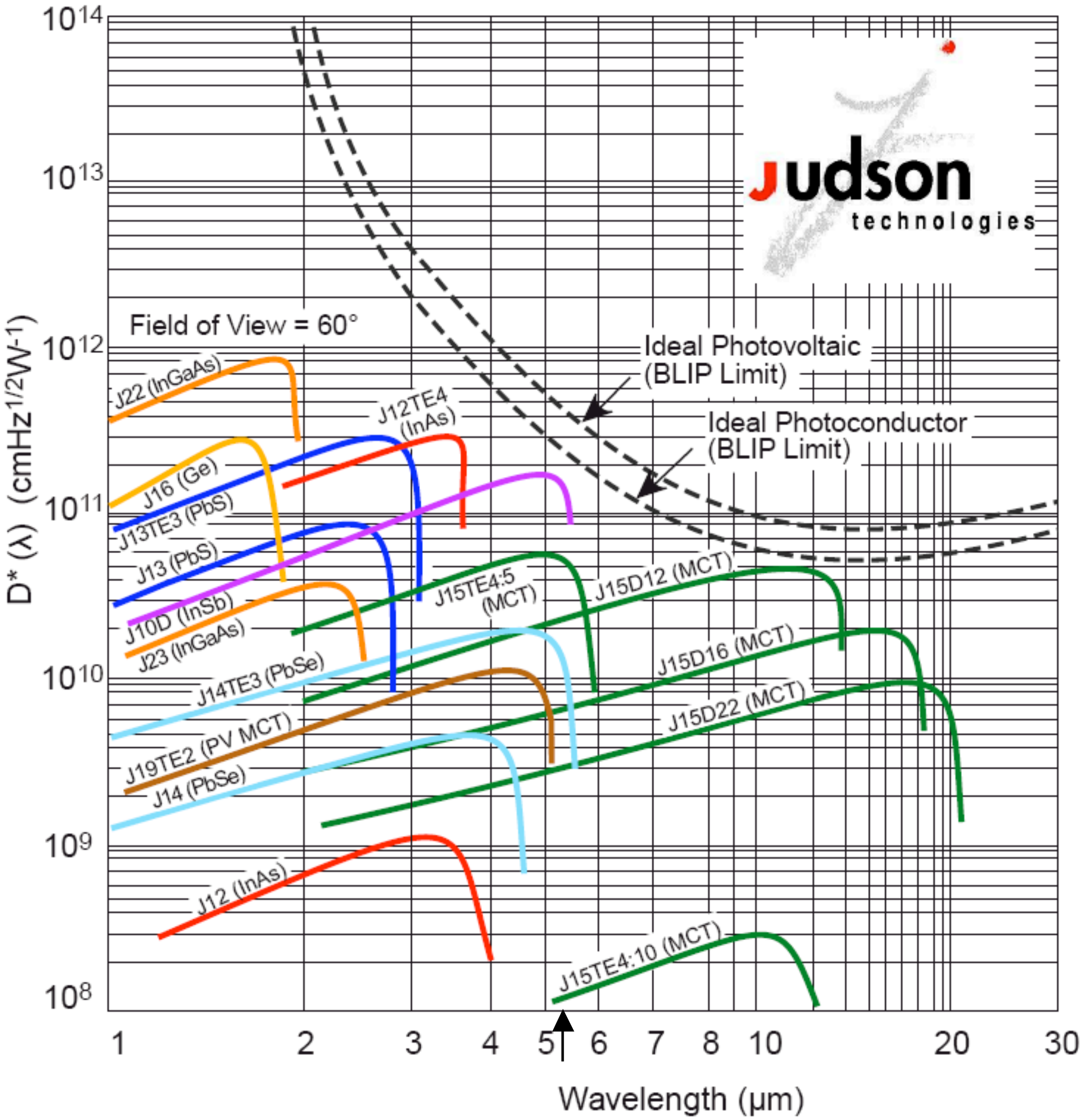
- Band – structure engineered devices (emission wavelength is determined by layer thickness – MBE or MOCVD) QCLs operate from 4 to 160 μm
  - Unipolar devices
  - Cascading (each electron creates N laser photons and the number of periods N determines laser power)
- Compact, reliable, stable, long lifetime, and commercial availability
- Fabry-Perot (FP), single mode (DFB) and multi-wavelength
- <u>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 (0.0004 cm^{-1}); pulsed: ~ 300 MHz (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 (wall plug η~4%)
  - ~ 50 mW, TEC CW DFB @ 5 and 10 μm (Alpes & Unine); Princeton, AdTech Optics, Maxion, Argos Technology.
    ~ 300 mW @8.3 μm (Agilent Technologies & Harvard)
  - >600 mW (CW FP) and >150 mW (CW DFB) at 298 K (Northwestern)



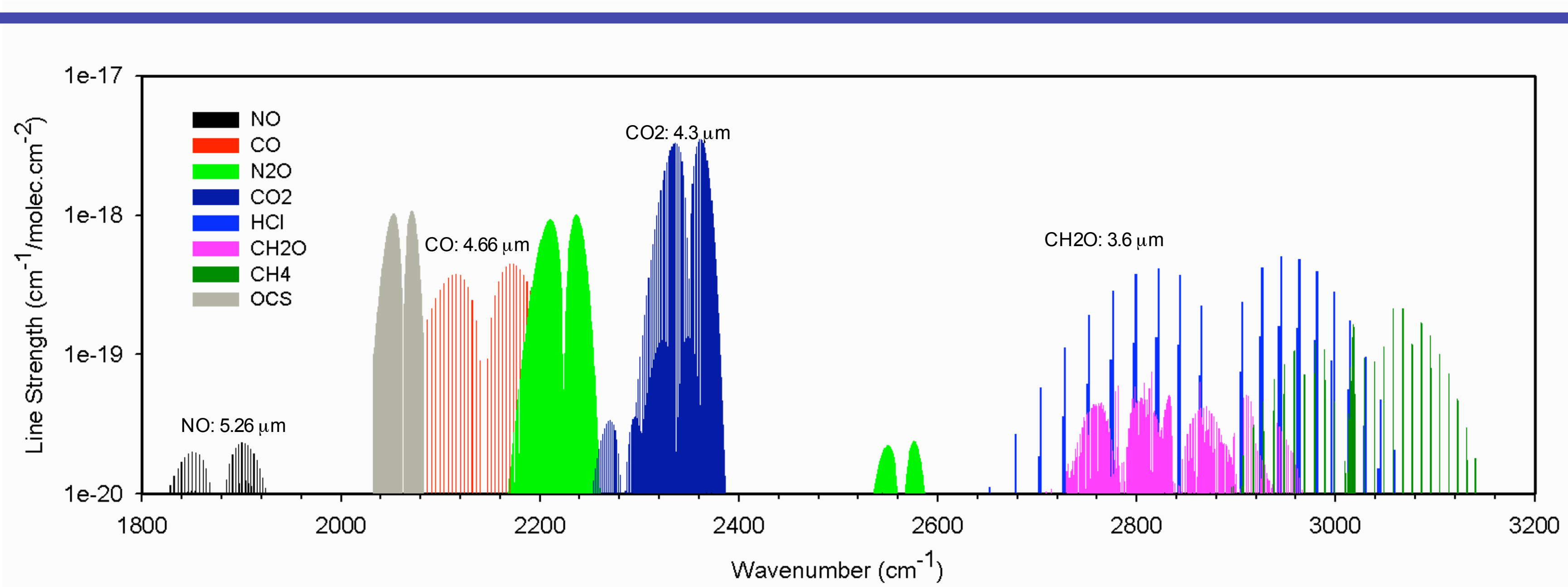




Wavelength Coverage of IR Detectors



Major Technological Challenges for QCL based Applications



- **What are quantum cascade laser design requirements for improved trace gas sensor platform technology**
  - Availability of QCLs operating at key molecular target wavelengths
  - Wavelength tunability and narrow spectral linewidth operation
  - High power, cw operation at quasi room temperatures
  - Packaging and reliability

- **Can we find both high value and high volume QCL based applications in Trace Gas Detection**
  - Environmental monitoring (HCHO, CO_2)
  - Medical Diagnostics (NO, CO, COS, CO_2)
  - Industrial process control and chemical analysis (eg. NO, CO, NH_3 and broad band absorbers)