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Quantum Cascade Laser based Trace Gas Technology: Recent Advances and Applications

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OUTLINE

- Motivation: Wide Range of Chemical Sensing
- Fundamentals of Laser Absorption Spectroscopy
- New laser sources and sensing technologies
- Selected Applications of Trace Gas Detection
  - Detection of nitric oxide and ethanol
  - Quartz Enhanced L-PAS (Freon 125, acetone) and ammonia ...
- Future Directions and Conclusions

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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 National Security**
- **Fundamental Science and Photochemistry**

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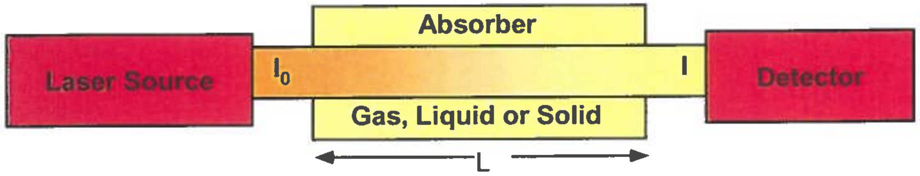
Fundamentals of Laser Absorption Spectroscopy

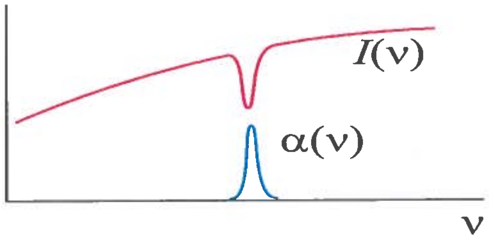


Beer-Lambert's Law of Linear Absorption

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

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

ν - frequency [$\mathrm{cm^{-1}}$]; 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/$\mathrm{cm^3}$ [$\mathrm{molecule \cdot cm^{-3} \cdot atm^{1}}$]

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

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

Requirements: Sensitivity, specificity, multi-gas species, rapid data Acquisition, …..

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

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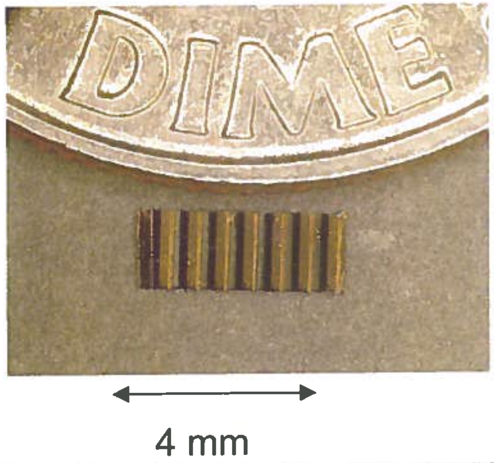
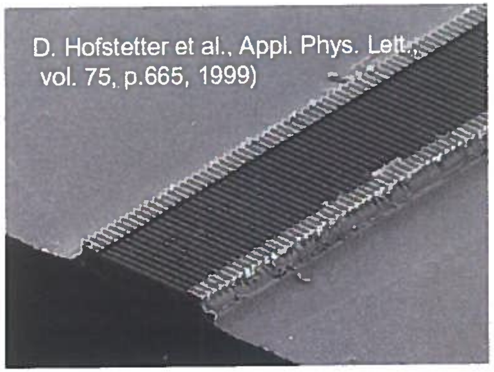
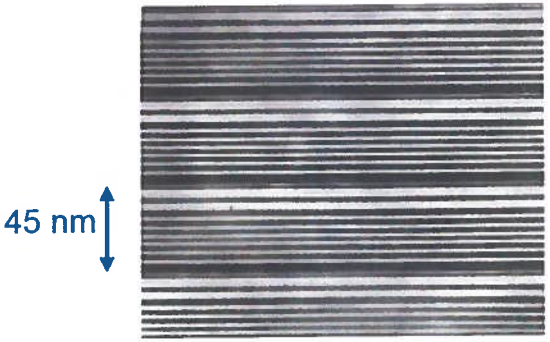
Key Characteristics of mid-IR QCLs and ICL Sources

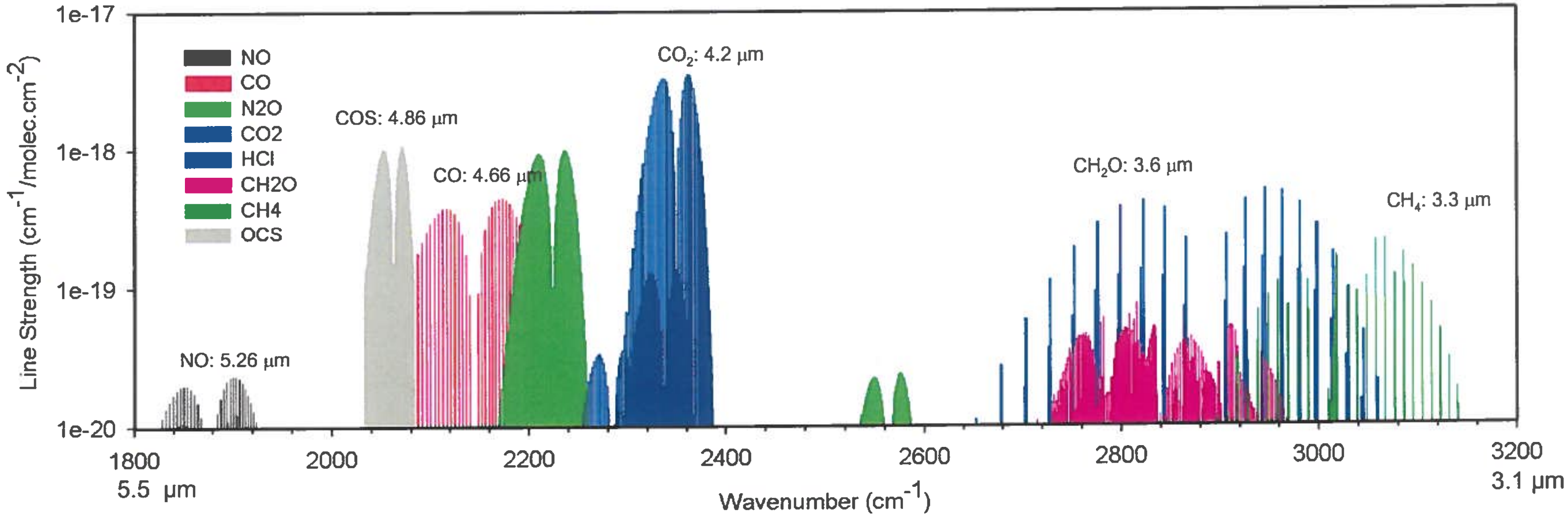
- **Band – structure engineered devices** (emission wavelength is determined by layer thickness – MBE or MOCVD) QCLs operate from 3 to 160 µm
- Compact, reliable, stable, long lifetime, and commercial availability
- Fabry-Perot (FP), single mode (DFB) and multi-wavelength
- **Spectral tuning range in the mid-IR** (4-24 µm for QCLs and 3-5 µm for ICLs)
    - 1.5 cm^{-1} using current
    - 10-20 cm^{-1} using temperature
    - > 200 cm^{-1} using an external grating element
- **Narrow spectral linewidth** cw: 0.1 - 3 MHz & <10Khz with frequency stabilization (0.0004 cm^{-1}); pulsed: ~ 300 MHz (chirp from heating)
- **High pulsed and cw powers at TEC/RT temperatures**
    - Pulsed peak powers of 1.6 W; high temperature operation ~ 425 K
    - Average power levels: 1-600 mW (current wall plug η~4%)
    - ~ 50 mW, TEC CW DFB @ 5 and 10 µm Alpes; Princeton,
    - Adtech Optics, Maxion Technologies, Argos Tech.
      ~ 300 mW @8.3 µm (Agilent Technologies & Harvard)
    - >600 mW (CW FP) and >150 mW (CW DFB) at 298 K (Northwestern)

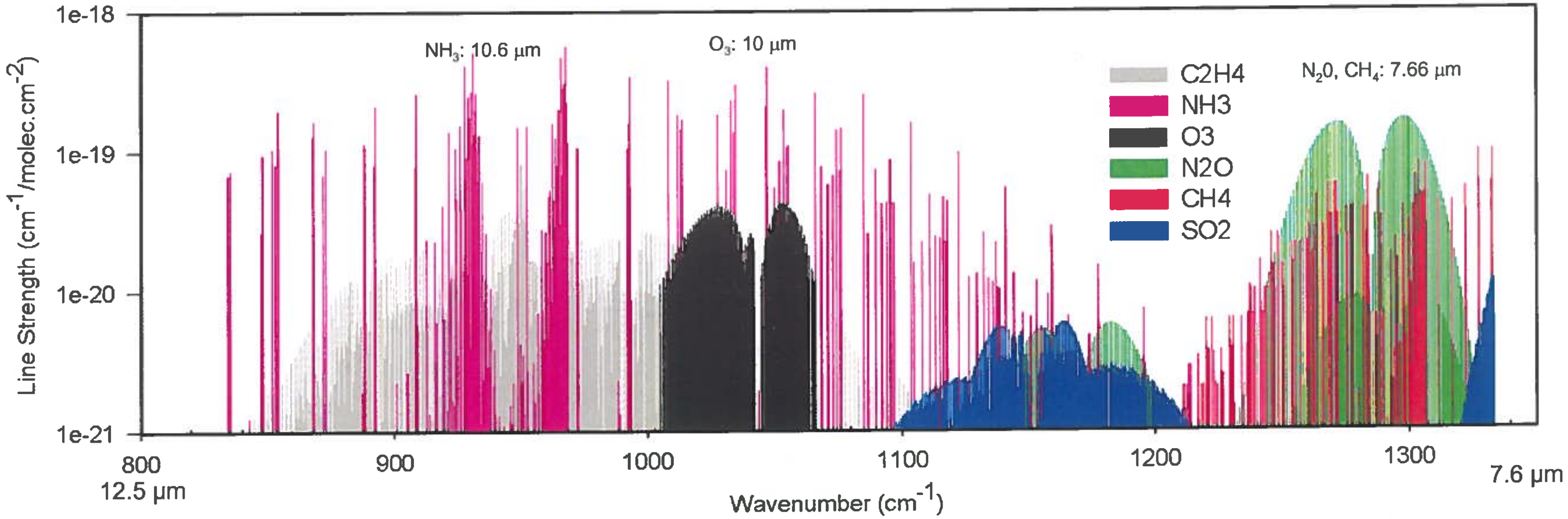



D. Hofstetter et al., Appl. Phys. Lett., vol. 75, p.665, 1999)



Example Molecular Absorption Spectra within two Mid-IR Atmospheric Windows



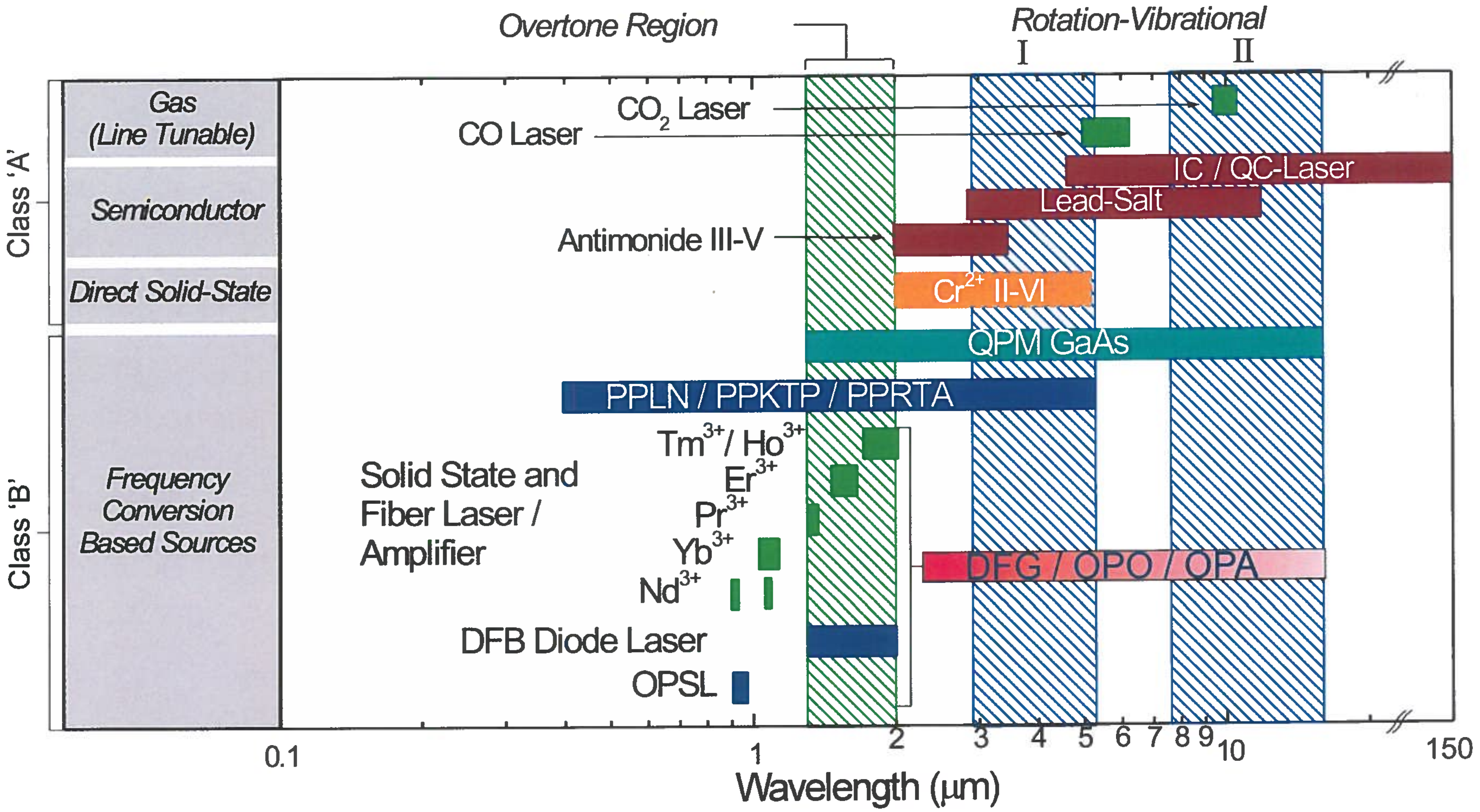


Source: HITRAN 2000 database

Mid-IR Source Requirements for Laser Spectroscopy

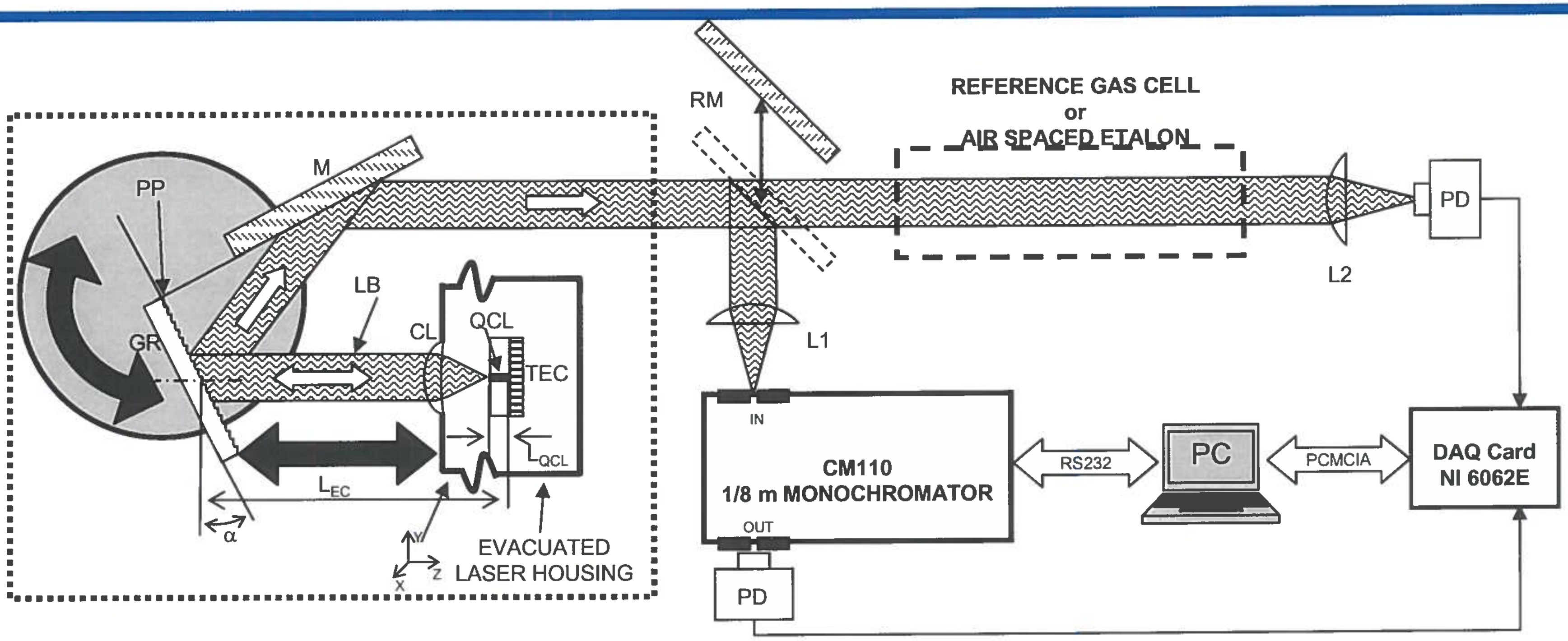
REQUIREMENTS	IR LASER SOURCE
Sensitivity (% to ppt)	Wavelength, Power
Selectivity (Spectral Resolution)	Single Mode Operation and Narrow Linewidth
Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers	Tunable Wavelength
Directionality or Cavity Mode Matching	Beam Quality
Rapid Data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

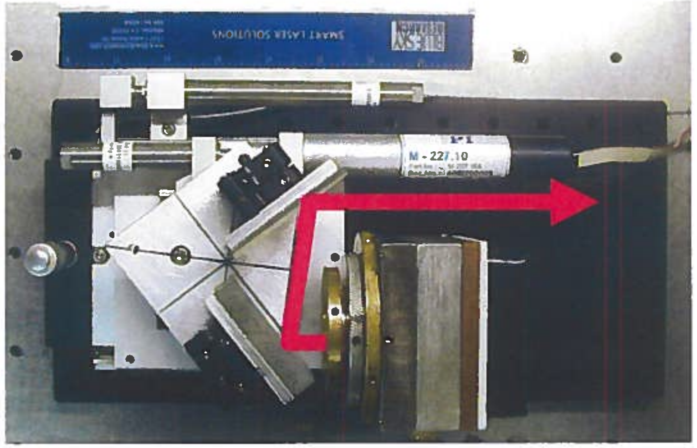
IR Laser Sources and Wavelength Coverage



Widely Tunable, CW, TEC
Quantum Cascade Lasers

Tunable external cavity QCL based spectrometer





- Fine wavelength tuning
  - PZT controlled EC-length
  - PZT controlled grating angle
  - QCL current control
- Motorized coarse grating angle tuning
- Vacuum tight QCL enclosure with build-in 3D lens positioner (TEC laser cooling + chilled water cooling)

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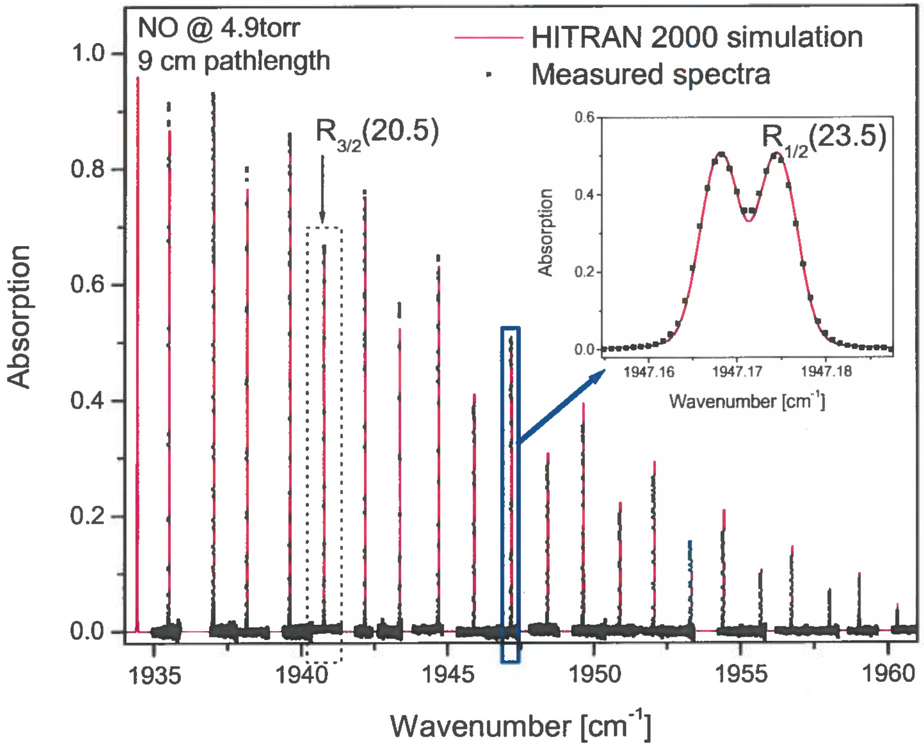
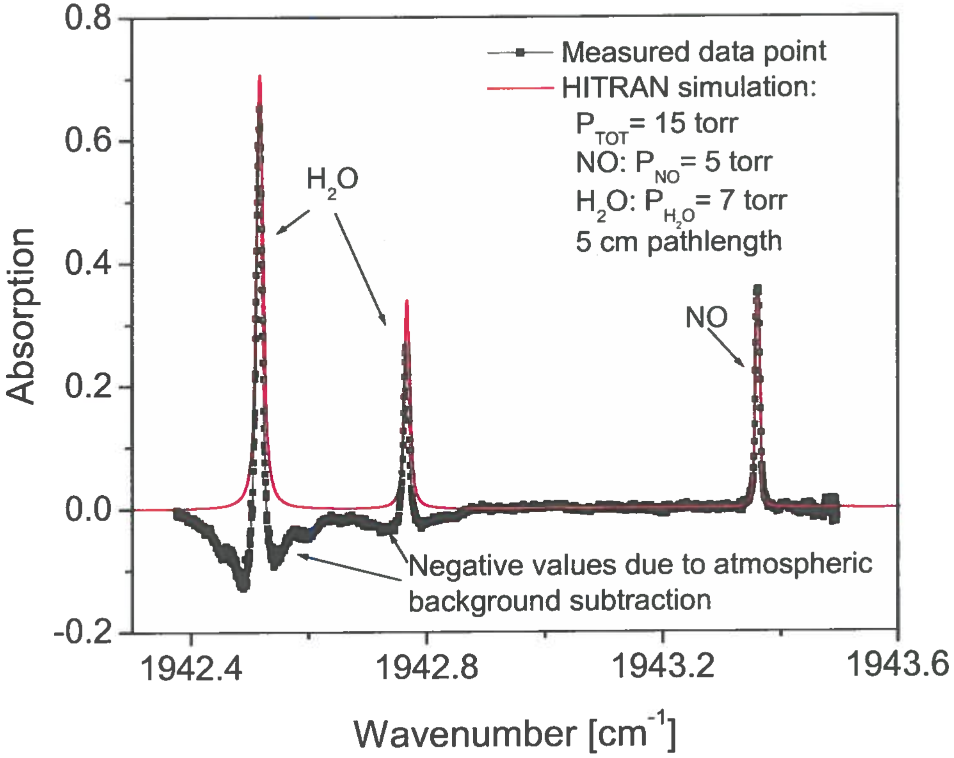
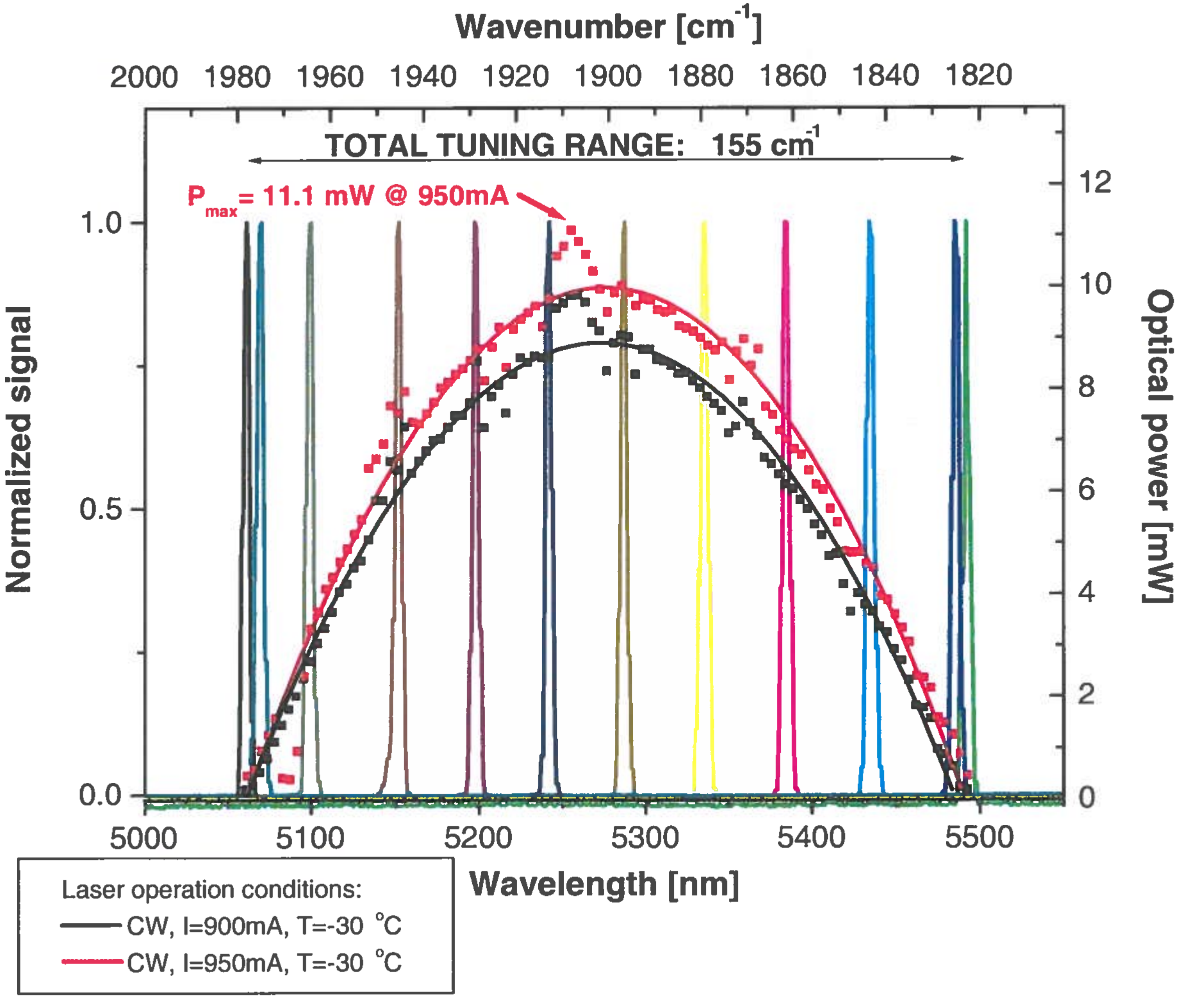
Mid-IR NO Absorption Spectra acquired with a Tunable TEC QCL



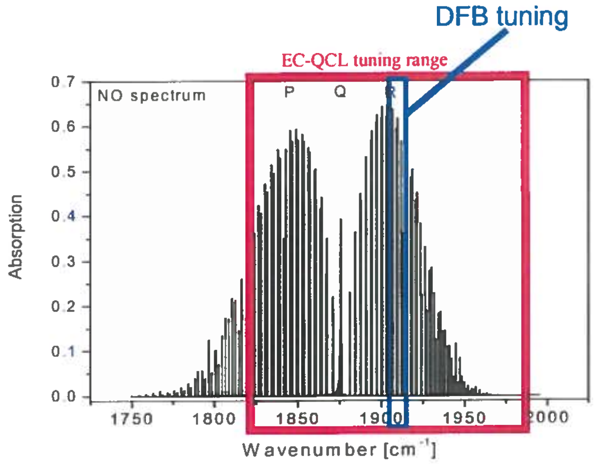


G. Wysocki, R.F. Curl, F.K. Tittel, R. Maulini, J. Faist, *Appl. Phys. B* 81, 769-777 (2005)

Wide Wavelength Tuning of a 5.3µm EC-QCL

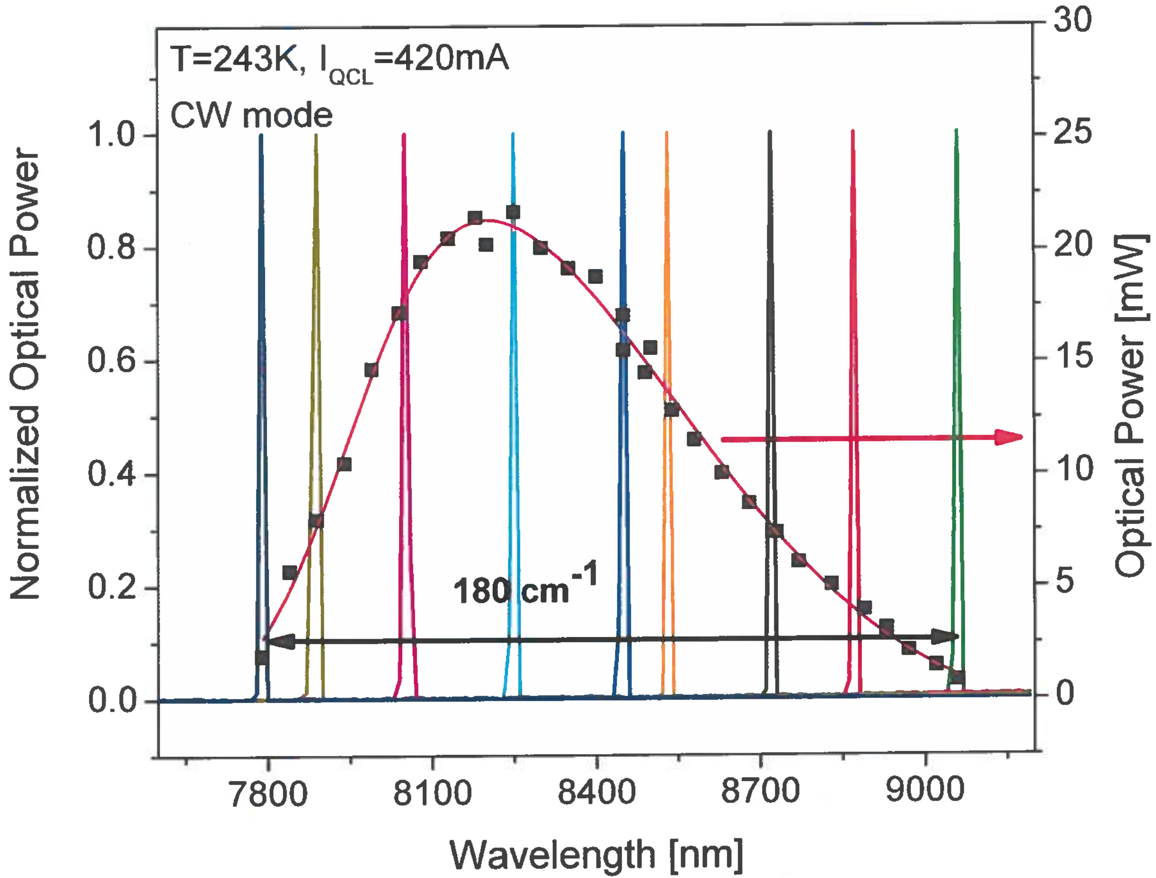


- Coarse wavelength tuning of **155 cm^{-1}** is performed by varying diffraction grating angle
- Power output is ~ **11mW**
- Access to Q(3/2) transition of NO at 1875.8 cm-1 for LMR spectroscopy



G. Wysocki, R. F. Curl ,F. K. Tittel, R. Maulini, J. Faist, manuscript in preparation 2007

Performance of 8.4 µm EC-QCL Spectroscopic Source



Tunability **180 cm^{-1}** @8.4 µm (1100 to 1280 cm^{-1})

AR coating:
$R_{AR} \approx$ **2 × 10^{-4}**

$P_{EC\text{-}opt}$ up to **50 mW (cw)**
(I_{QCL}= 680 mA -> P = 44 mW)

G. Wysocki, R. F. Curl ,F. K. Tittel, F. Capasso, L. Diehl, M. Troccoli, R. Maulini, J. Faist, Optics Express (June 11, 2007)

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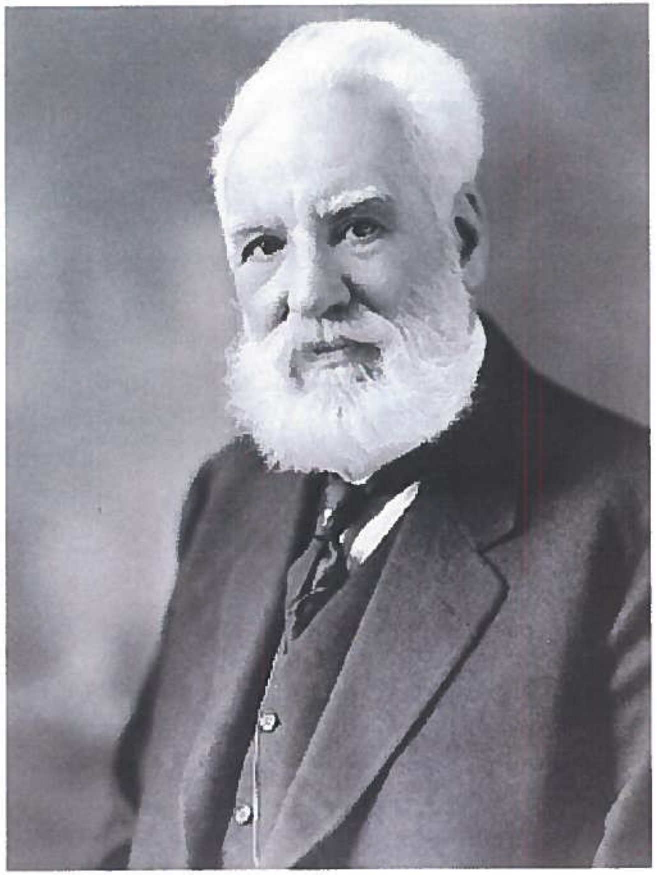
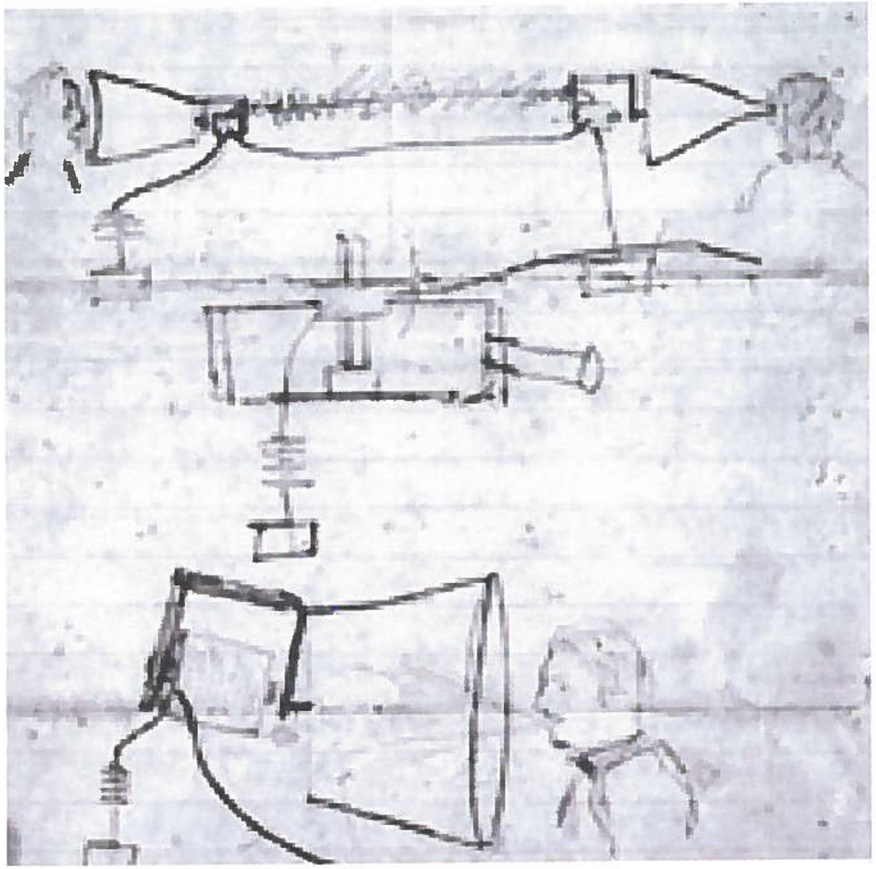
Quartz Enhanced Photoacoustic Spectroscopy

First Report of PAS in 1880

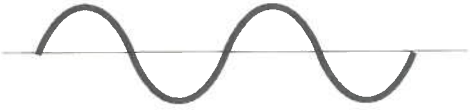




Alexander Graham Bell's "photophone" used a voice coil to modulate a mirror which transmitted sunlight to a receiver containing a selenium resistor.
Nature, Sept. 23, **1880**, pp. 500-503

From conventional PAS to QEPAS

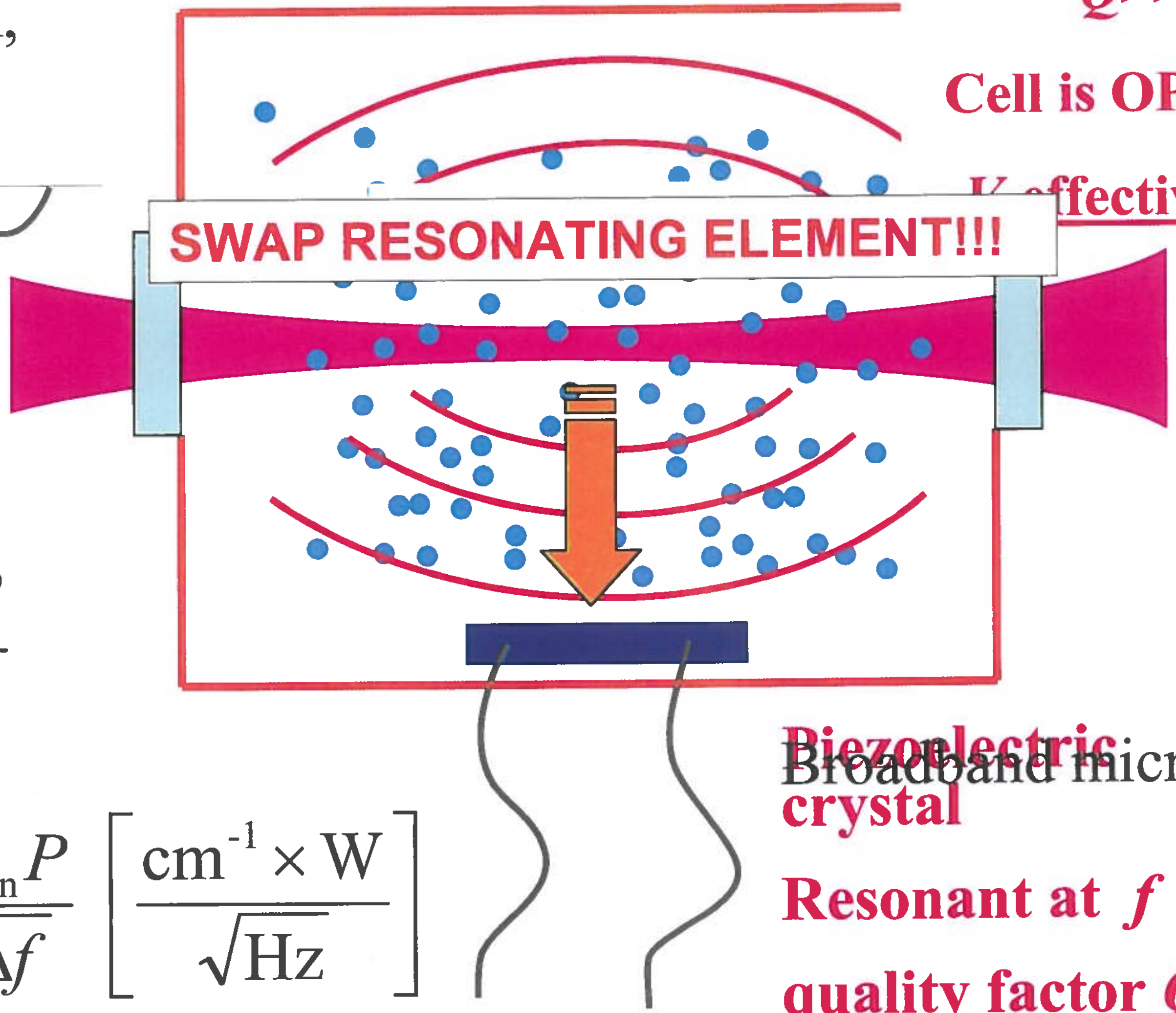
Laser beam,
power *P*



Modulated
(*P* or λ) at *f*
or *f*/2

$$S \sim \frac{Q \alpha P}{f V}$$

$$NNEA = \frac{\alpha_{\min} P}{\sqrt{\Delta f}} \left[\frac{\mathrm{cm}^{-1} \times \mathrm{W}}{\sqrt{\mathrm{Hz}}} \right]$$



Cavity resonant

Q>>1000

Cell is OPTIONAL!

V effective volume

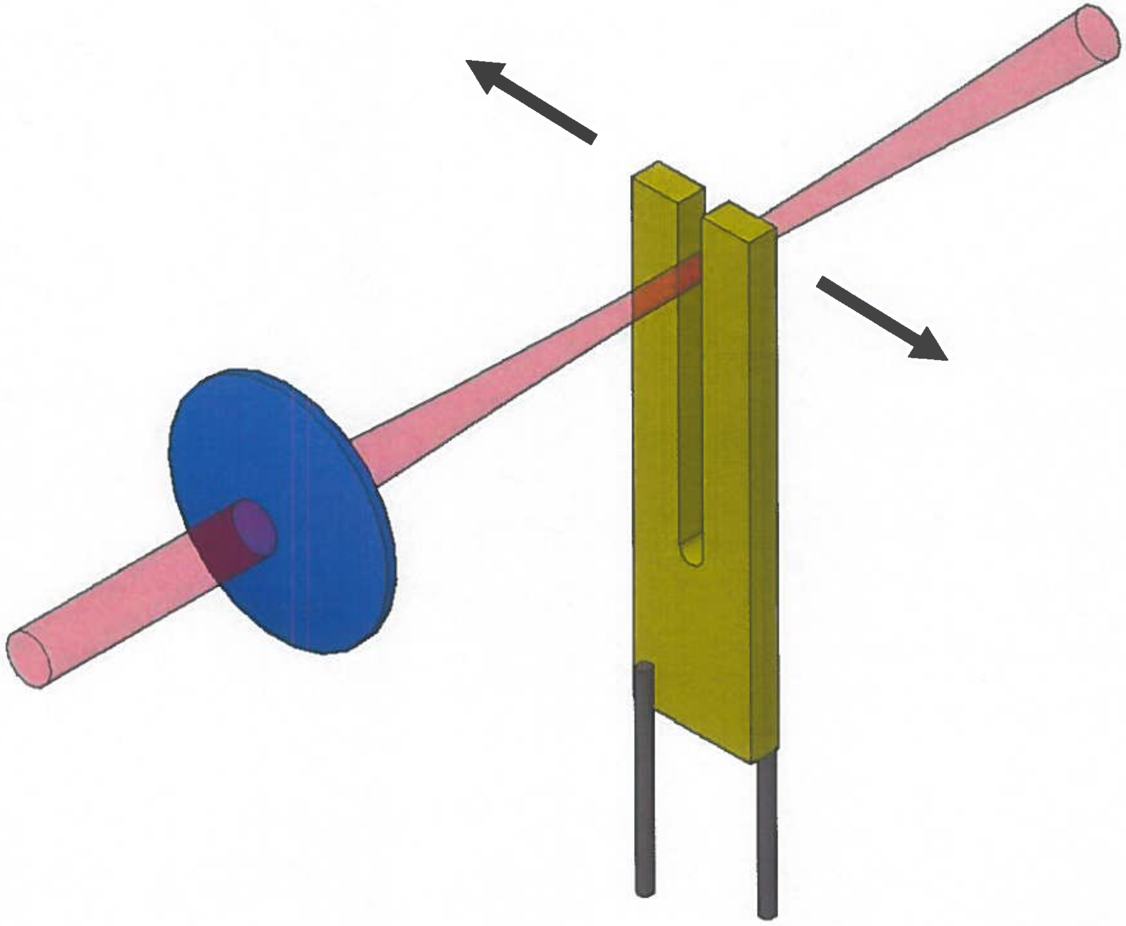
Broadband microphone

Piezoelectric crystal

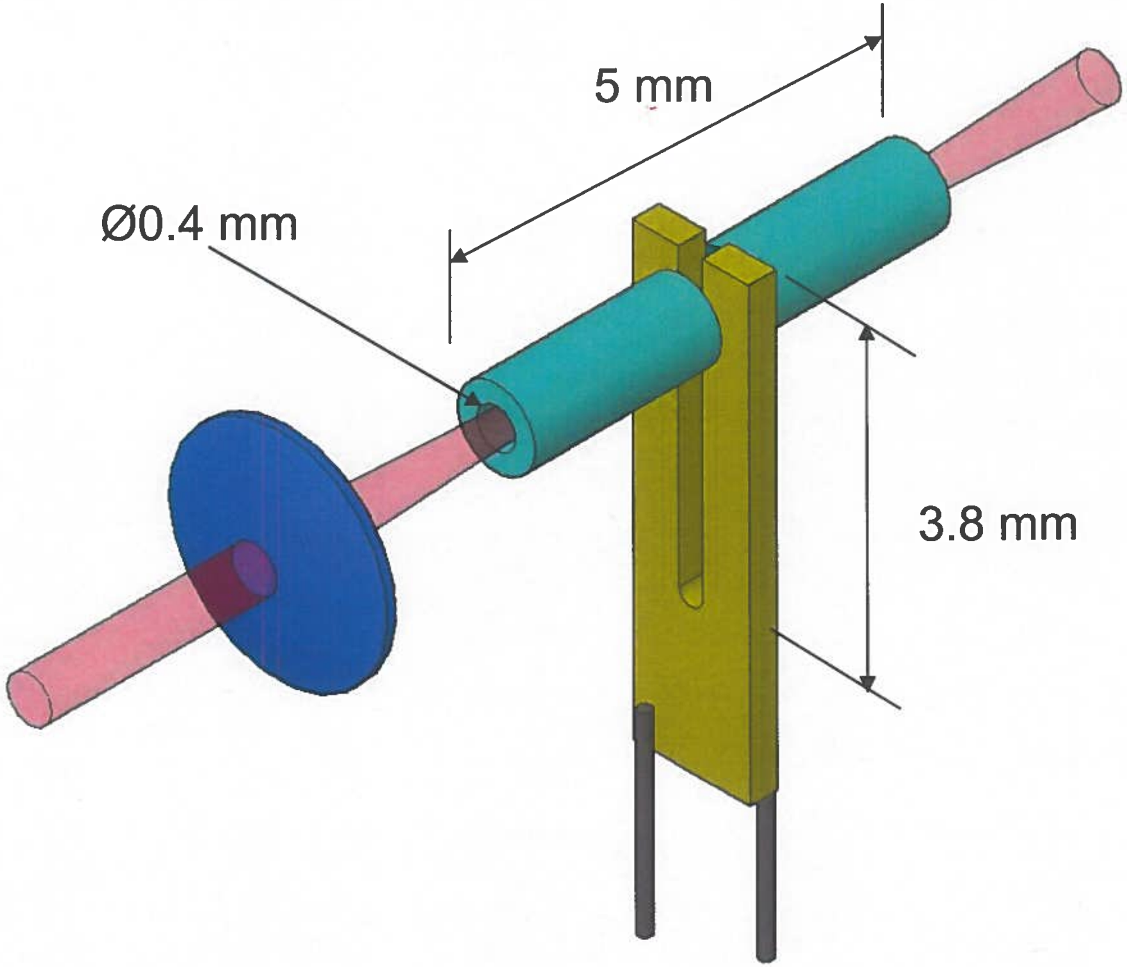
Resonant at f

quality factor Q

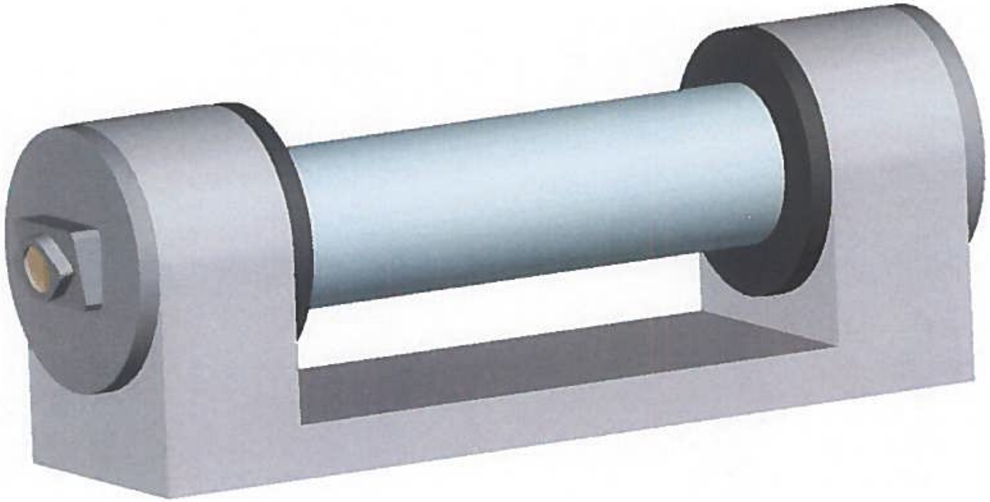
TF based spectrophone



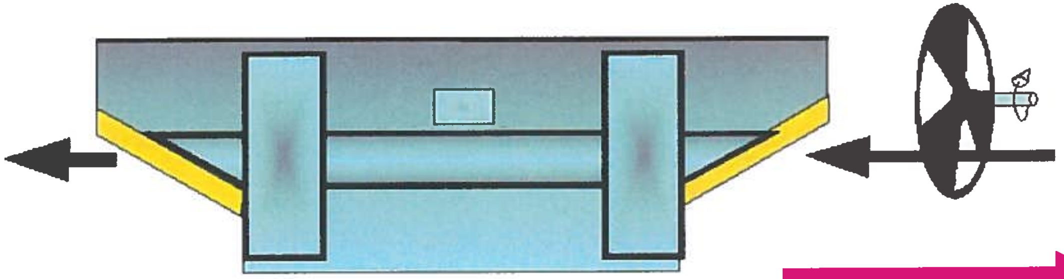
TF based spectrophone



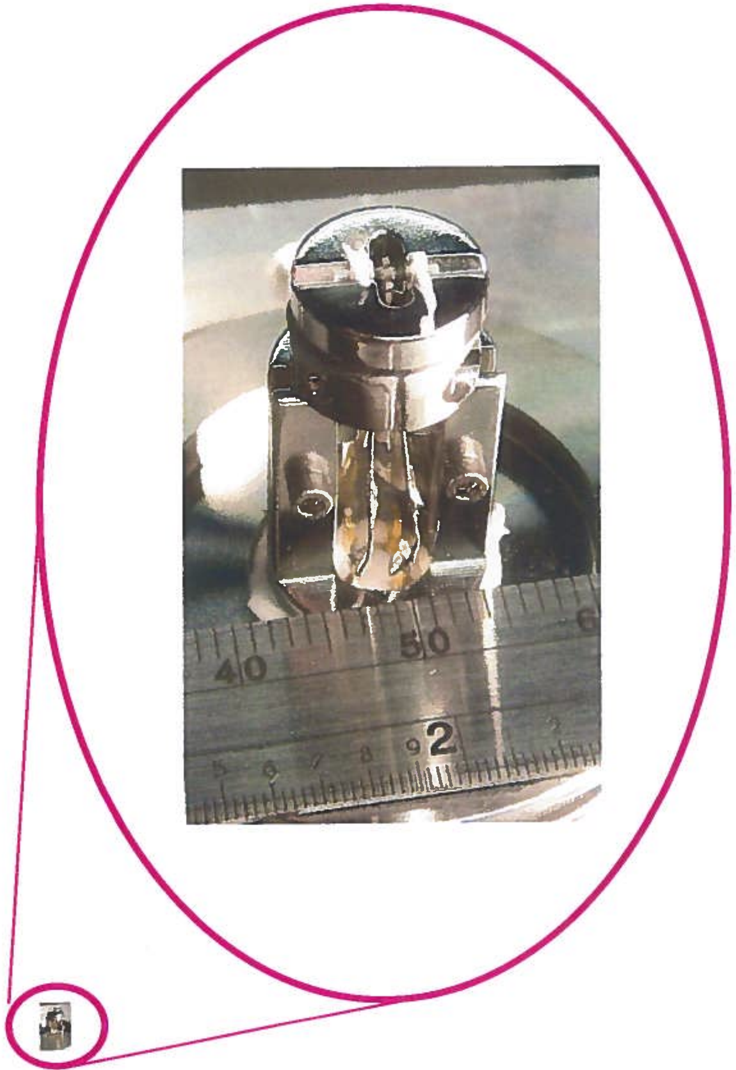
Comparative Size of Absorbance Detection Modules (ADM)



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 spectrophone:
l~1 cm, V~0.05 cm^3

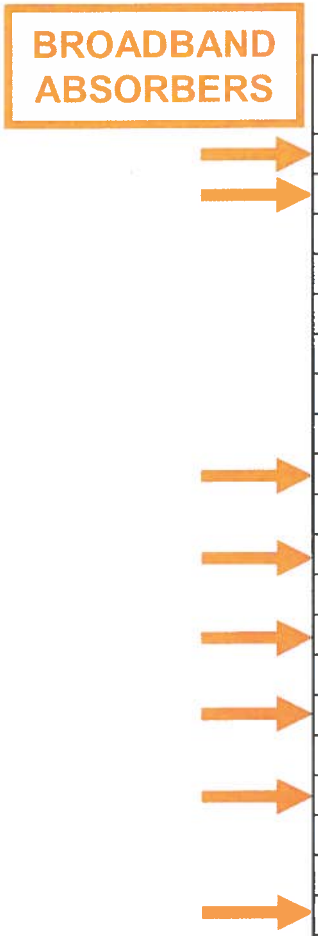
Trace Gas Sensing Examples

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 (1998 Nobel Prize in Physiology/Medicine)
  - Treatment of asthma, COPD, acute lung rejection

Biomarkers Present in Exhaled Human Breath

As many as 400 different molecules in breath; many with well defined biochemical pathways

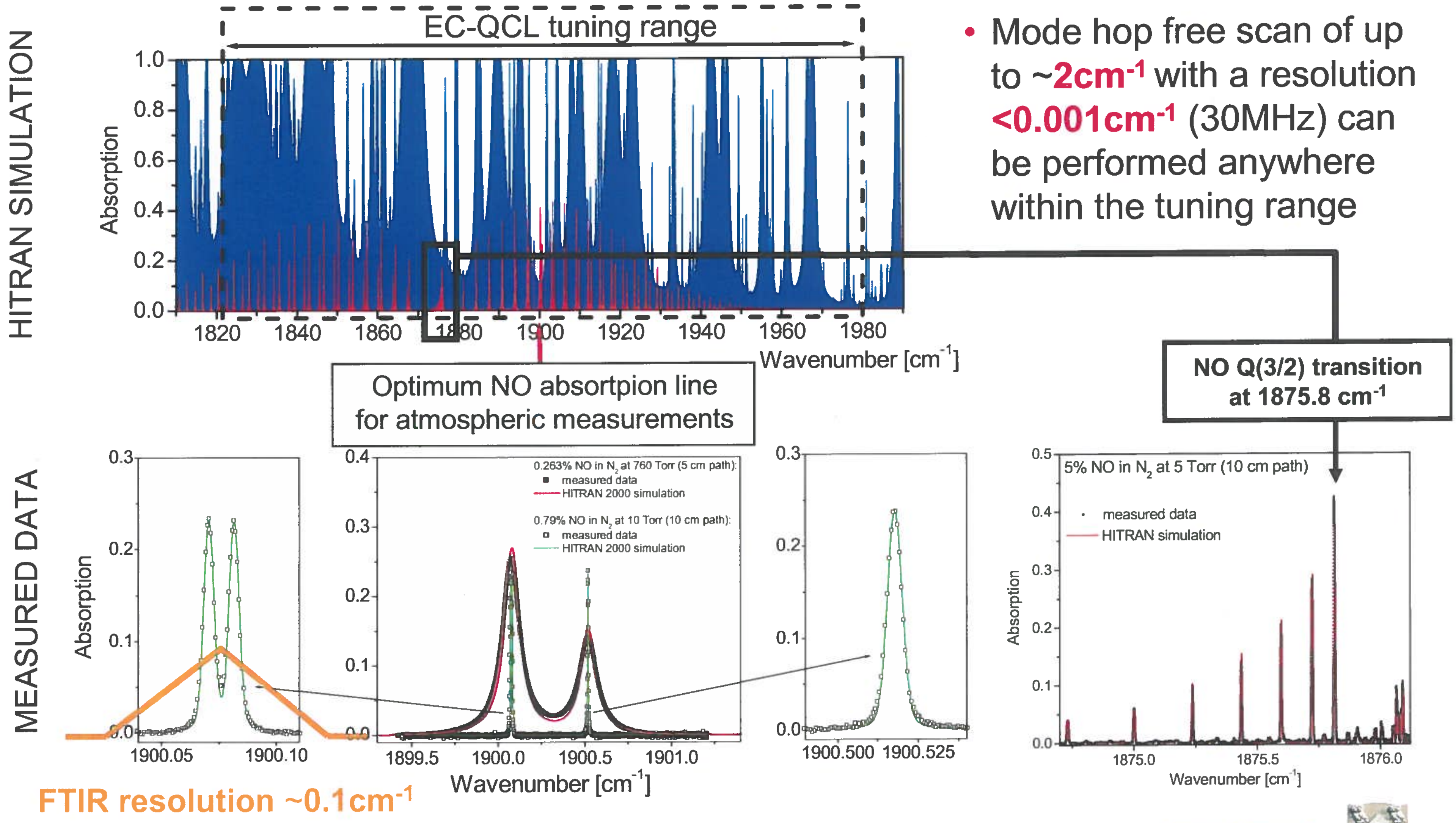


Compound	Concentration	Physiological basis/Pathology Indication
Acetaldehyde	ppb	Ethanol metabolism
Acetone	ppm	Decarboxylation of acetoacetate, diabetes
Ammonia	ppb	protein metabolism, liver and renal disease
Carbon dioxide	%	Product of respiration, Heliobacter pylori
Carbon disulfide	ppb	Gut bacteria, schizophrenia
Carbon monoxide	ppm	Production catalyzed by *heme oxygenase*
Carbonyl sulfide	ppb	Gut bacteria, liver disease
Ethane	ppb	Lipid peroxidation and oxidative stress
Ethanol	ppb	Gut bacteria
Ethylene	ppb	Lipid peroxidation, oxidative stress, cancer
Hydrocarbons	ppb	Lipid peroxidation/metabolism
Hydrogen	ppm	Gut bacteria
Isoprene	ppb	Cholesterol biosynthesis
Methane	ppm	Gut bacteria
Methanethiol	ppb	Methionine metabolism
Methanol	ppb	Metabolism of fruit
Methylamine	ppb	Protein metabolism
Nitric oxide	ppb	Production catalyzed by *nitric oxide synthase*
Oxygen	%	Required for normal respiration
Pentane	ppb	Lipid peroxidation, oxidative stress
Water	%	Product of respiration

Terence Risby, Johns Hopkins University

High resolution spectroscopy with a 5.3μm EC-QCL

- Mode hop free scan of up to ~**2cm^{-1}** with a resolution **<0.001cm^{-1}** (30MHz) can be performed anywhere within the tuning range



EC-QCL tuning range

Optimum NO absorpion line for atmospheric measurements

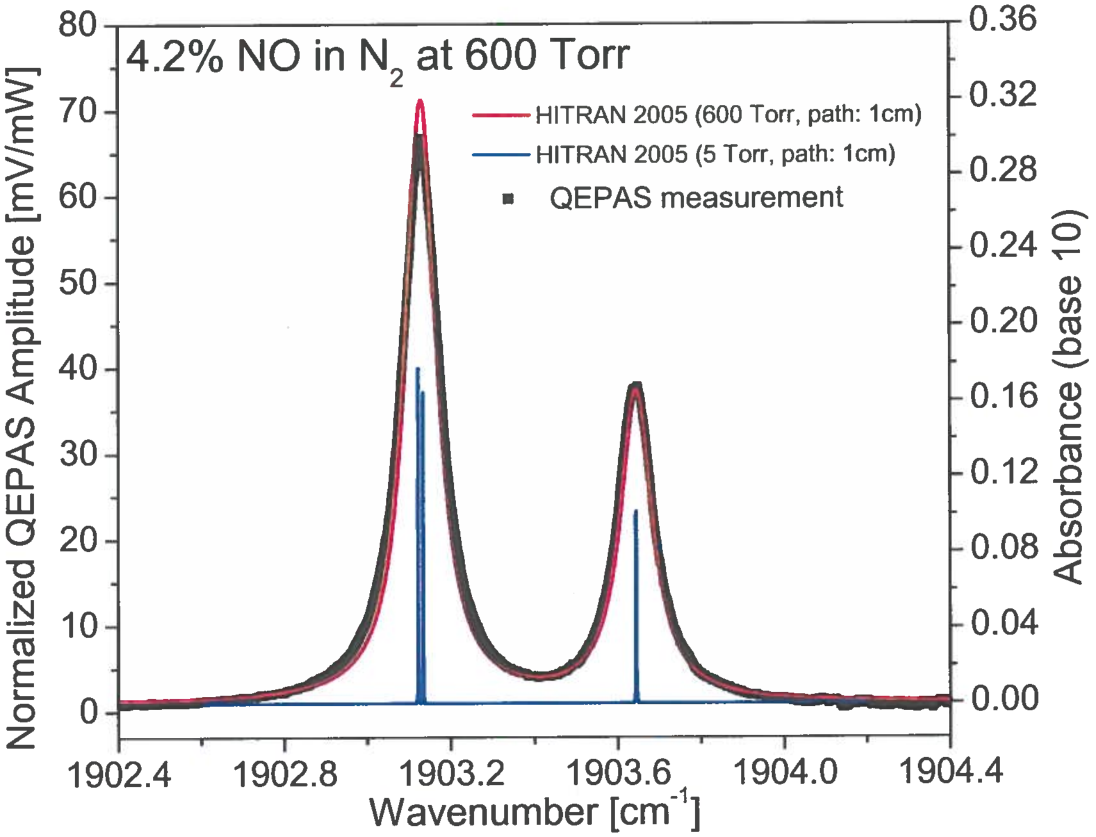
NO Q(3/2) transition at 1875.8 cm^{-1}

FTIR resolution ~0.1cm^{-1}

G. Wysocki, R. F.Curl ,F. K. Tittel, R. Maulini, J. Faist, manuscript in preparation 2007

earlier work: G. Wysocki R. F.Curl ,F. K. Tittel, R. Maulini, J. M. Bulliard, J. Faist, Applied Physics B, 81, 769-777 (2005)

High resolution EC-QCL based QEPAS



External Amplitude Modulation:

- QTF is used as a mechanical chopper at *f=~32kHz*
- No chirp associated with the laser current modulation
- High resolution mode-hop-free tuning is possible

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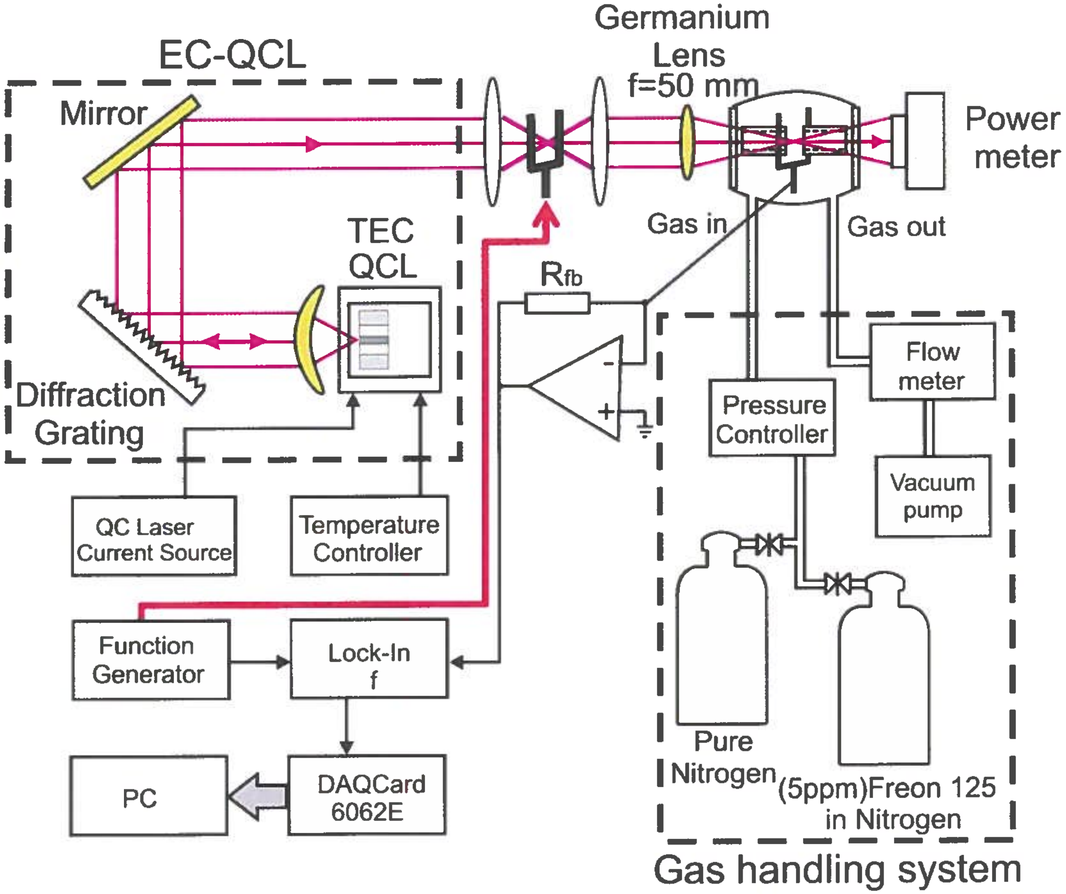
Monitoring of broadband absorbers

- Freon 125 (C_2HF_5)
  - Refrigerant (leak detection)
  - Safe simulant for toxic chemicals e.g. chemical warfare agents
- Acetone (CH_3COCH_3)
  - Recognized biomarker for diabetes

QCL based Quartz-Enhanced Photoacoustic Gas Sensor



QEPAS characteristics:

- High sensitivity (ppm to ppb)
- Excellent dynamic range
- Immune to environmental noise
- Ultra-small sample volume (< 1 mm^3)
- Sensitivity is limited by the fundamental thermal TF noise
- Compact, rugged and low cost
- Potential for trace gas sensor networks

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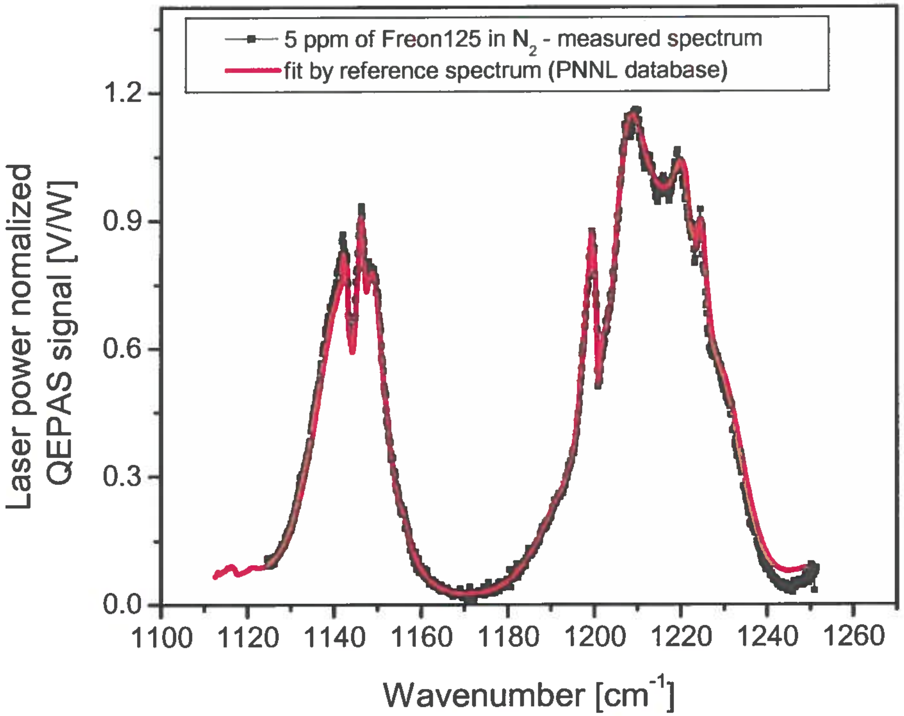
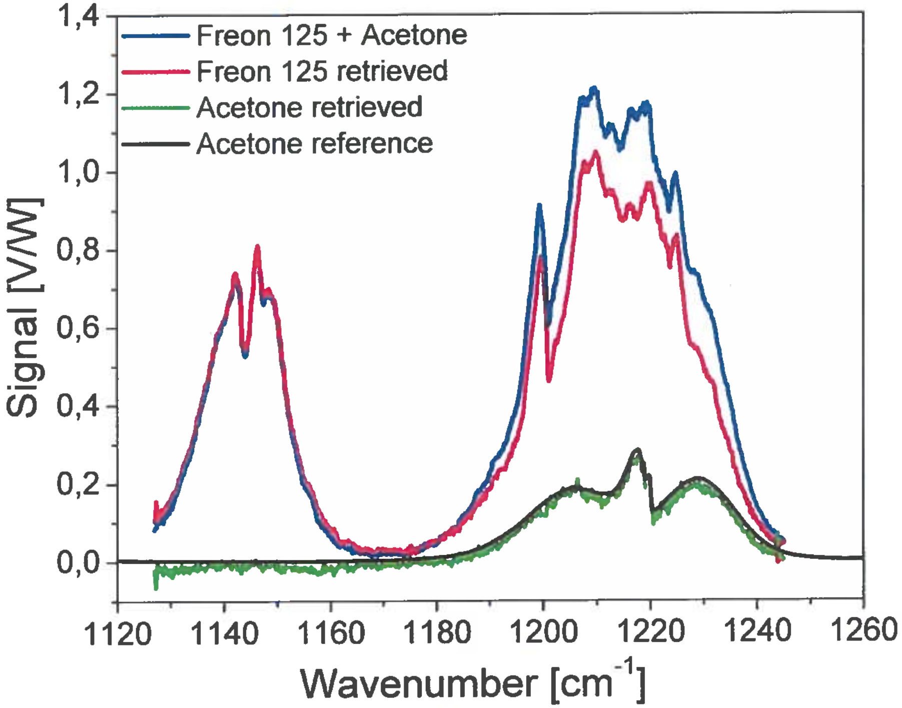
Spectroscopy of Freon 125 and Acetone with a Widely Tunable 8.4 μm CW EC-QCL

QEPAS concentration measurement of Freon 125 (5ppm mixture in N_2)



QEPAS concentration measurement of a Freon 125 and acetone mixture

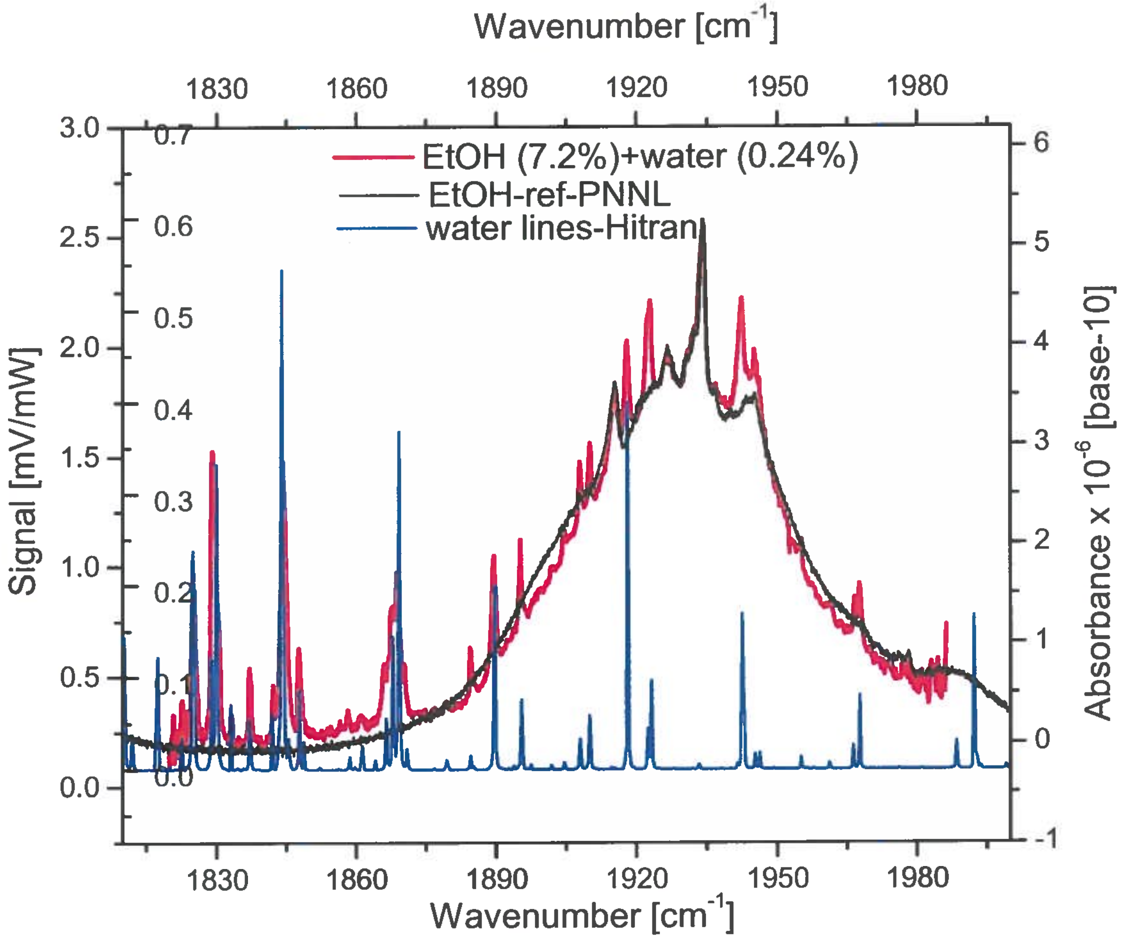


- Minimum detection limit (1σ) of **~4.5 ppb** was obtained for Freon 125 with an average laser power of 6.6 mW

- Wide tunability enables excellent molecular selectivity for broad band absorbers

R. Lewicki et al Optics Express 15, 7357, 2007

QEPAS Ethanol Spectrum between 1820 & 1980 cm^{-1}



Reference spectrum from the PNNL spectral database (red line). Sharp features on the ethanol spectrum correspond to the atmospheric water absorption lines (blue line depicts water absorption spectrum simulated using HITRAN database)

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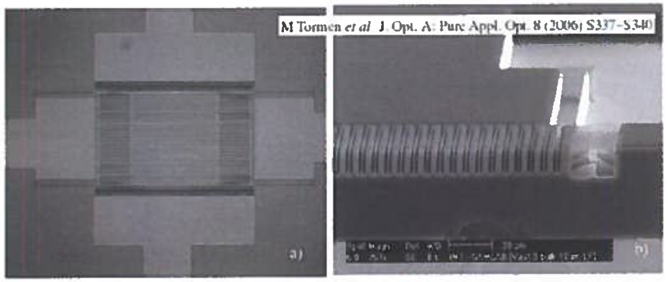
Future of Chemical Trace Gas Sensing

Future development of EC-QCL technology

- Complete mid infrared wavelength coverage
- Faster tuning speed
- Solid state designs
  - MEMS

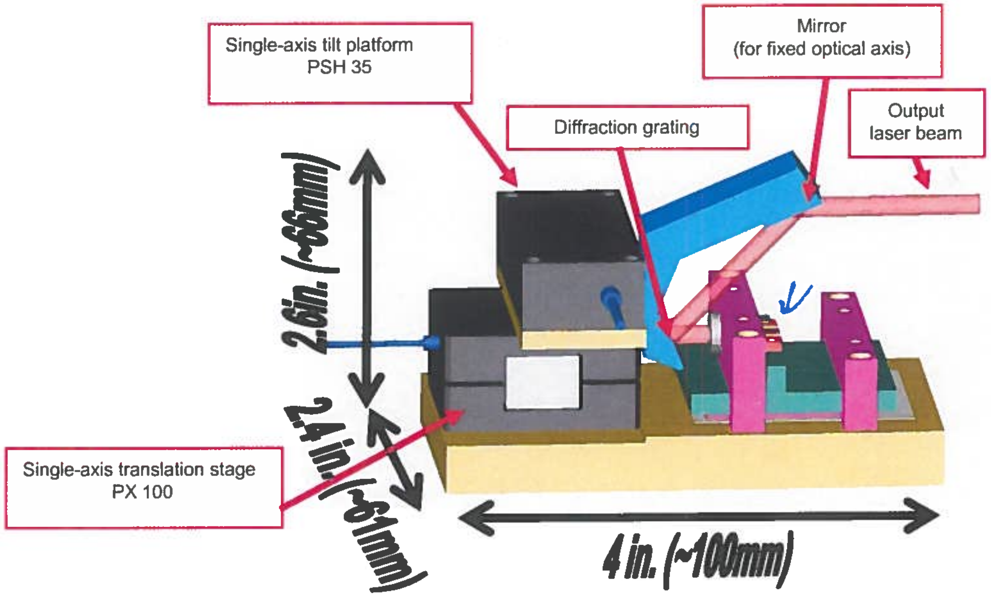


M Tormen *et al* J. Opt. A: Pure Appl. Opt. 8 (2006) S337–S340

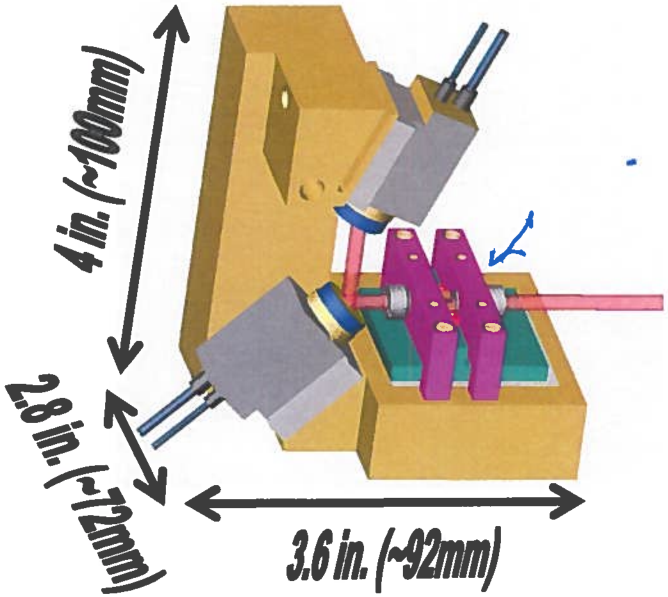
  - Electrical tuning (in collaboration with QCL-research groups)
    - Tunable Distributed Bragg Reflectors (DBR)

      (carrier-induced refractive index tuning)
    - Electronically tunable extraordinary transmission gratings (tunable mirrors and filters) (work presently carried out at Princeton)

New designs of fast broadly tunable EC-QCLs (2007)



- Optical configuration based on the previous EC-QCLs
- Fast tuning capabilities:
  - Broadband tuning up to 1KHz
  - High resolution mode-hop free tuning up to 400Hz



- New optical configuration
- Fast tuning capabilities:
  - Broadband tuning up to 6 KHz
  - High resolution mode-hop free tuning up to 6 KHz

Commercial Tunable Mid-IR EC QCL

Introduced in 2006

Room Temperature—No Cryogenic Cooling

Center Wavelengths:	4.5 µm 5.5 µm 8.5 µm 9.5 µm 10.5 µm
Tuning Range:	>10%
Average Power (CW):	1 mW–10 mW

DAYLIGHT
SOLUTIONS

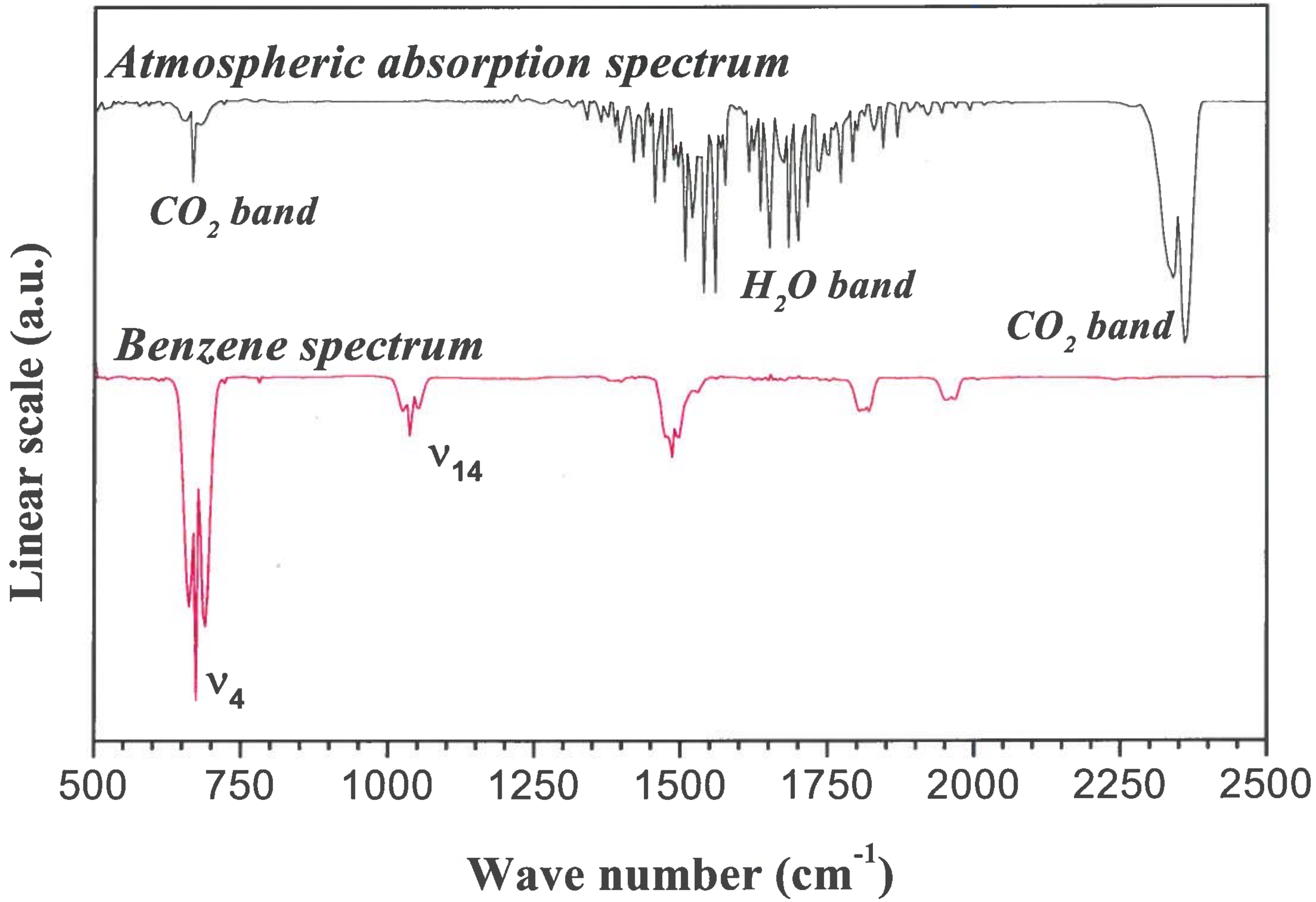
Summary & Future Directions of mid-IR Sensor Technology

- **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.
- **New Applications of Trace Gas Detection are the main driving force to the field**
    - Distributed sensor networks for Environmental monitoring (NH_3, CO, CH_4, C_2H_4, N_2O, CO_2 and H_2CO)
    - Inexpensive and sensitive sensors for Industrial process control and chemical analysis (HCN, NO, NH_3, H_2O)
    - Wearable sensors for Medical & Biomedical Diagnostics (NO, CO, COS, CO_2, NH_3, C_2H_4)
    - Hand-held sensors and sensor network technologies for Law Enforcement and Homeland Security
- **Future Directions and Collaborations**
    - Improvements of the existing sensing technologies using novel, thermoelectrically cooled, cw, high power, and broadly wavelength tunable mid-IR interband and intersubband quantum cascade lasers
    - New applications enabled by novel broadly wavelength tunable quantum cascade lasers (especially sensitive concentration measurements of broadband absorbers, in particular VOCs and HCs)
    - Development of optically multiplexed gas sensor networks based on QEPAS

Summary & Future Directions

- **Widely tunable, continuous wave and thermoelectrically cooled EC-QCLs operating at 5.3µm and 8.5µm** were demonstrated
- **Mode-hop free wavelength tuning** enables high resolution (**<0.001cm^{-1}**) spectroscopic applications
- **PZT actuated mode tracking system** allows employing gain chips operating at both shorter and longer wavelengths without modification of its mechanical construction (chips with lower efficiency AR coatings can be used)
- Wavelength tunability up to **15%** of the center wavelength was demonstrated
- Output optical power up to **50 mW**
- The main limitations in the scanning speed (limited by the mechanical resonances of the EC-QCL construction), which will be addressed in future EC-QCL designs.
- The novel broadly wavelength tunable quantum cascade lasers enable **new applications in laser based trace gas sensing**
    - Sensitive concentration measurements of broadband absorbers, in particular VOCs and HCs
    - Multi-species detection

FT-IR survey absorption spectrum of benzene vapor (C_6H_6)

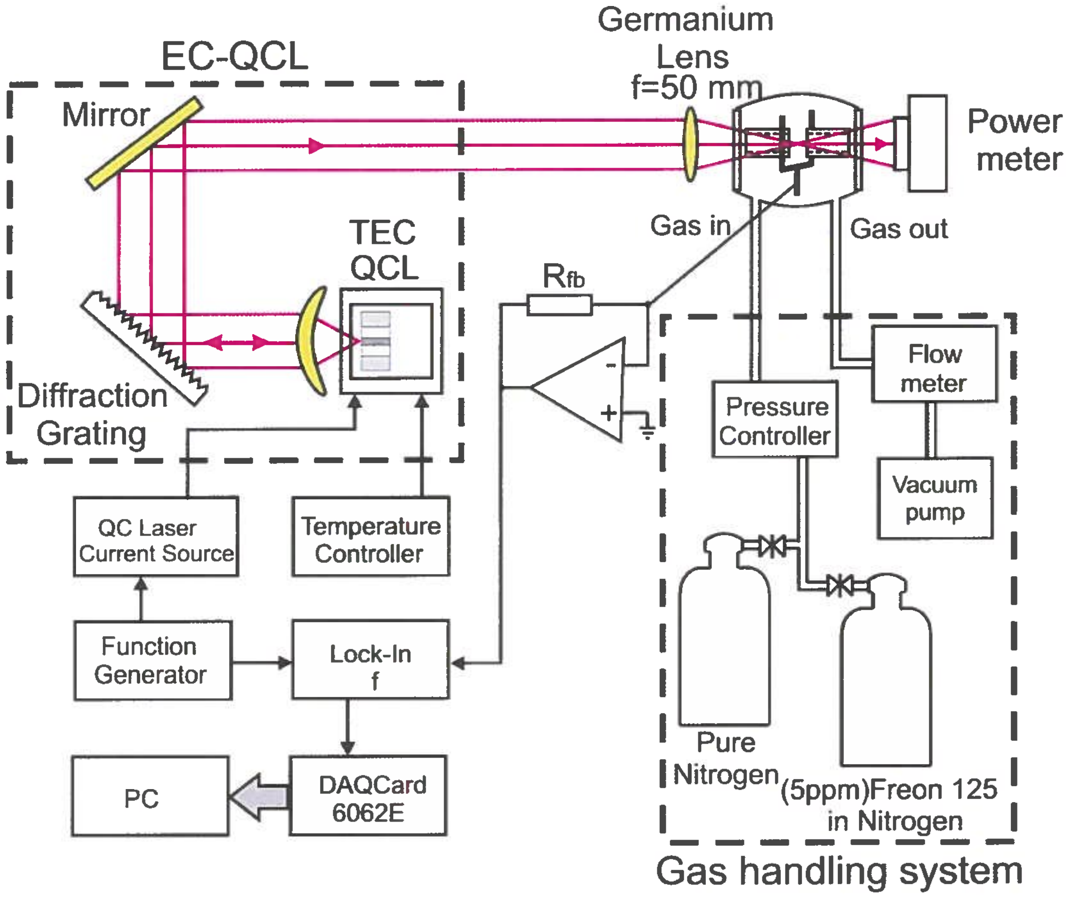


W.Chen, F.Cazier, F.K. Tittel and D.Boucher, Appl. Optics 39, 6238, 2000

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 other optical sensor architectures)

QCL based Quartz-Enhanced Photoacoustic Gas Sensor

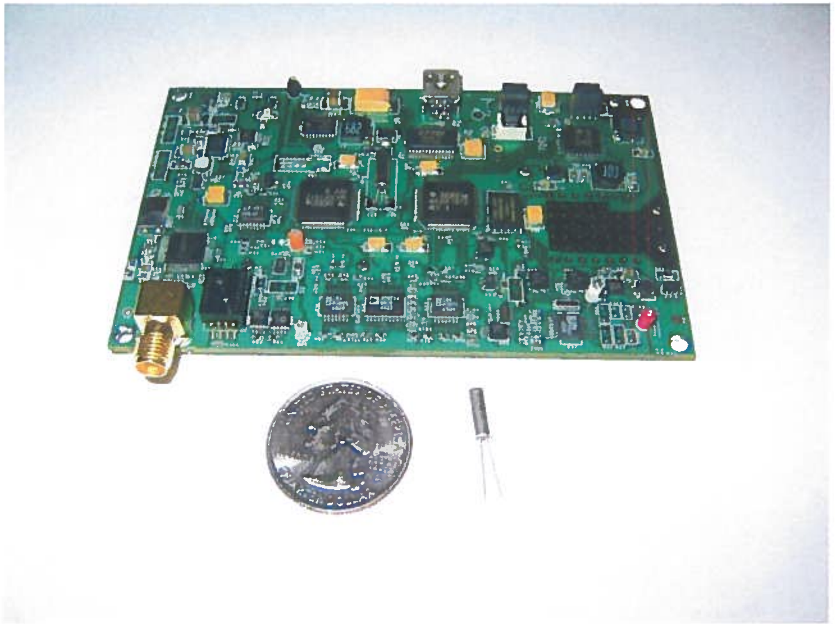


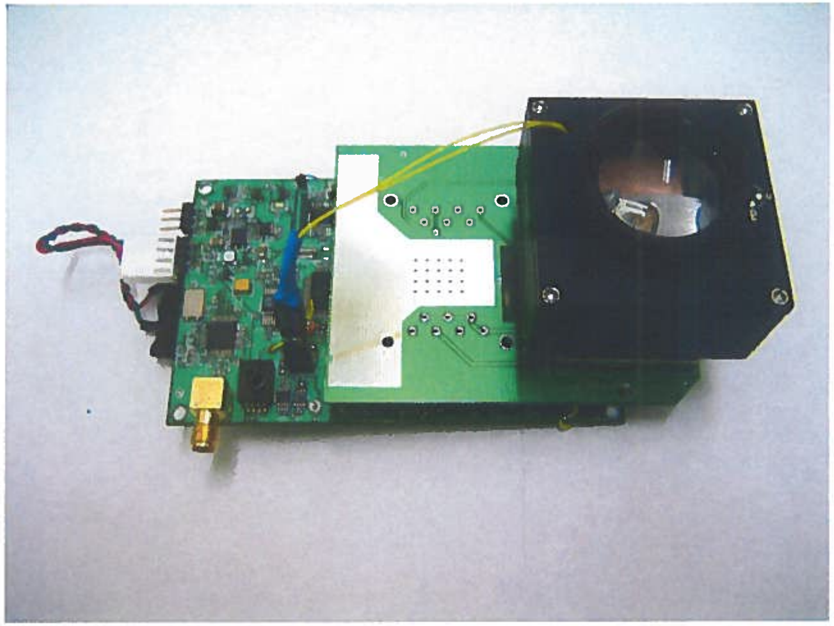
QEPAS characteristics:

- High sensitivity (ppm to ppb)
- Excellent dynamic range
- Immune to environmental noise
- Ultra-small sample volume (< 1 mm^3)
- Sensitivity is limited by the fundamental thermal quartz tuning fork (QTF) noise
- Compact, rugged and low cost
- Potential for trace gas sensor networks

R. Lewicki, G. Wysocki, A.A. Kosterev, F. K. Tittel „QEPAS based detection of broadband absorbing molecules using a widely tunable, cw quantum cascade laser at 8.5 μm", submitted to Optics Express, April 2007

Miniature QEPAS CO_2 sensor (λ=2μm) v2.0 boards



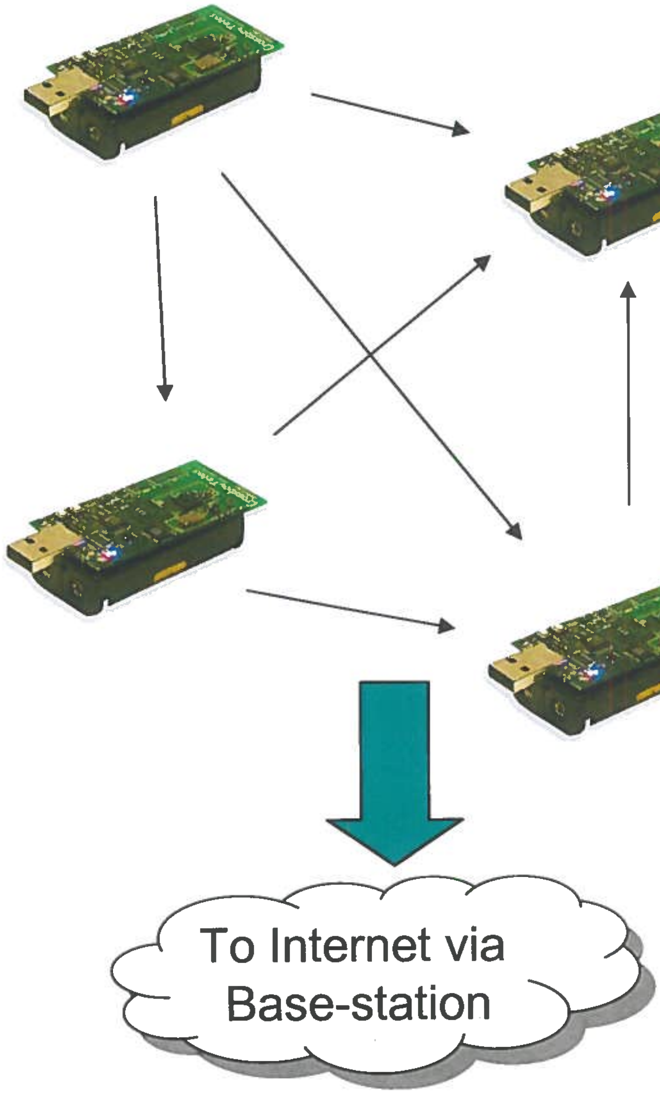


- Small size
- Relatively low cost
- High efficiency switching power supplies
- PWM Peltier cooler driver
- 0.2W control system power consumption
- Projected sensitivity* to CO_2 110 ppm with 1sec. lock-in TC
- Over 10^3 improvement in sensitivity @4.2μm

*G. Wysocki, A. A. Kosterev, and F. K. Tittel "Influence of Molecular Relaxation Dynamics on Quartz-Enhanced Photoacoustic Detection of CO_2 at λ = 2 μm", Applied Physics B 85, 301-306 (2006)

RICE

Wireless Sensor Networks for Gas Sensing



To Internet via Base-station

- Each point called “mote”
- Advantages?
  - Spatial resolution
  - Measure fluxes
- What is needed?
  - Low power
  - Low cost
  - Ultra miniature
  - Replicable
  - Autonomy

QCL based QEPAS Performance for 5 Trace Gas Species (May 2007)

Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, cm^{-1}W/Hz^{½}	Power, mW	NEC (τ=1s), ppmv
CH_2O (N_2:75% RH)*	2804.90	75	8.7×10^{-9}	7.2	0.12
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_2H_5OH **	1934.2	770	2.2×10^{-7}	10	90
C_2HF_5 (Freon 125)***	1208.62	770	2.6×10^{-9}	6.6	0.003

* - Improved microresonator
** - Preliminary (estimated) with amplitude modulation and metal microresonator
*** - With amplitude modulation and metal microresonator

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

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

* M. E. Webber et al, Appl. Opt. 42, 2119-2126 (2003)

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