Advanced Infrared Semiconductor Laser based Chemical Sensing Technologies

F.K. Tittel, Y. Bakhirkin, R.F. Curl, A.A. Kosterev, R. Lewicki, S. So and G. Wysocki

Rice Quantum Institute, Rice University, Houston, TX, USA

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

RICE

OUTLINE

Prokhorov Seminar on TDLS

Moscow, Russia

March 12, 2008

- Motivation: Wide Range of Chemical Sensing
- Fundamentals of Laser Absorption Spectroscopy
- New laser sources and sensing technologies
- Selected Applications of Trace Gas Detection
  - Quartz Enhanced L-PAS (ammonia, Freon 125 and acetone)
  - Nitric Oxide Detection (Faraday Rotation & Remote Sensing)
- Future Directions and Conclusions

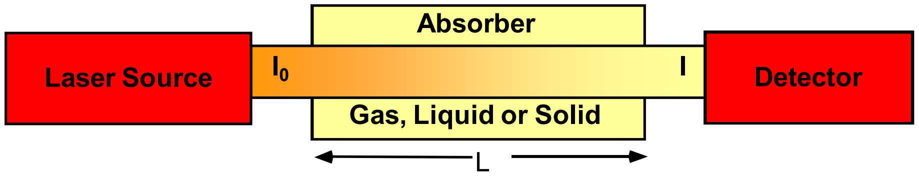
Work supported by NSF, NASA, DOE, and Robert Welch Foundation

Wide Range of Trace Gas Sensing Applications

- **Urban and Industrial Emission Measurements**
  - Industrial Plants
  - Combustion Sources and Processes (e.g. fire detection)
  - Automobile, Truck, 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 & Beverage Industries
- **Spacecraft and Planetary Surface Monitoring**
  - Crew Health Maintenance & Life Support
- **Applications in Health and Life Sciences**
- **Technologies for Law Enforcement and National Security**
- **Fundamental Science and Photochemistry**

RICE

Fundamentals of Laser Absorption Spectroscopy

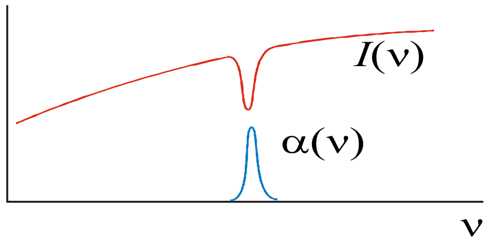


Beer-Lambert's Law of Linear Absorption

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

$\alpha(\nu)$ - 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)

Key Requirements: Sensitivity, specificity, rapid data acquisition and multi-species detection

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)

Spectroscopic Detection Schemes

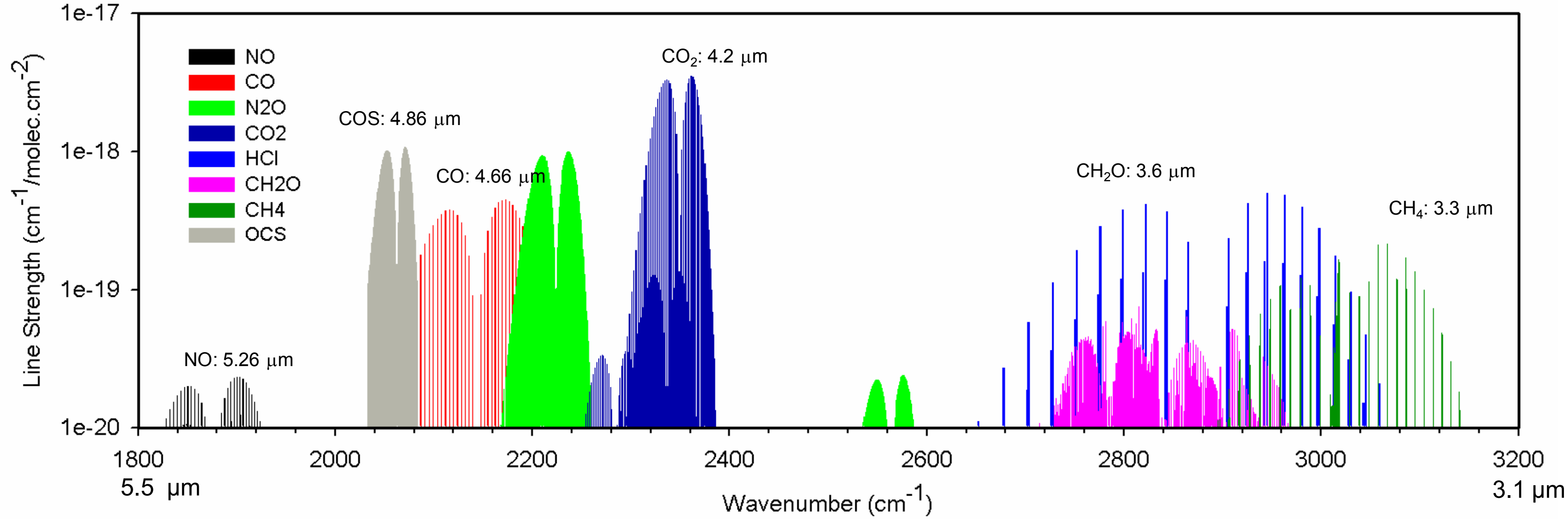
- Wavelength & Frequency Modulation
- Balanced Detection
- Zero-air Subtraction
- Photoacoustic Spectroscopy

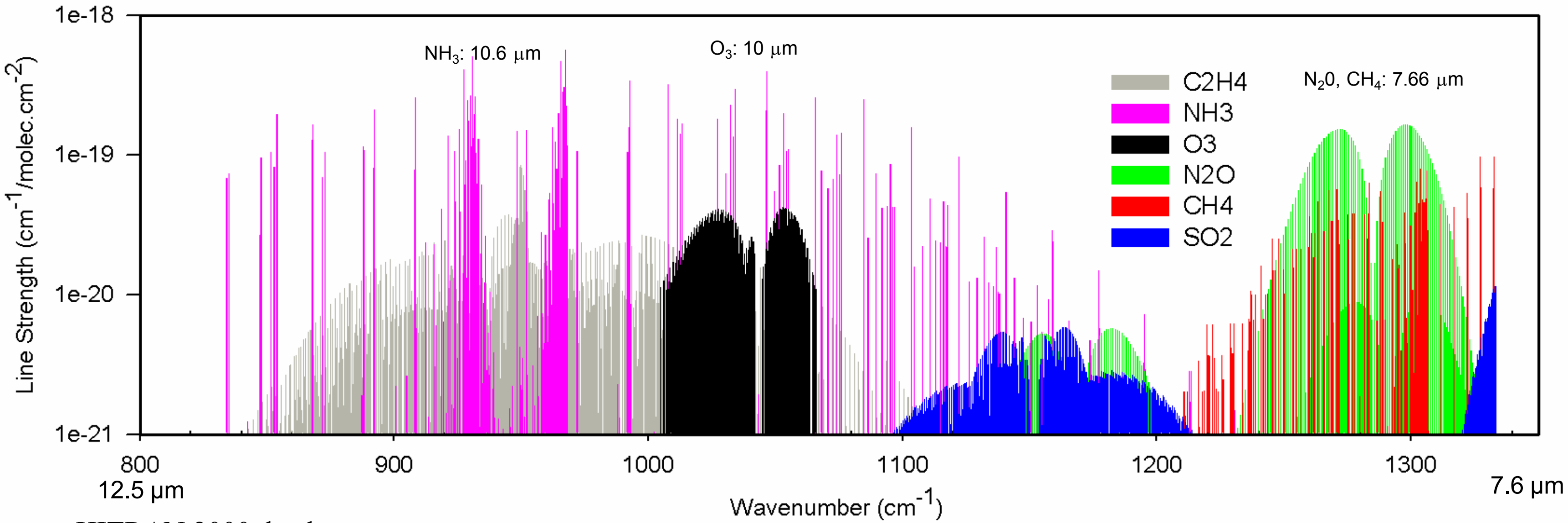
RICE

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

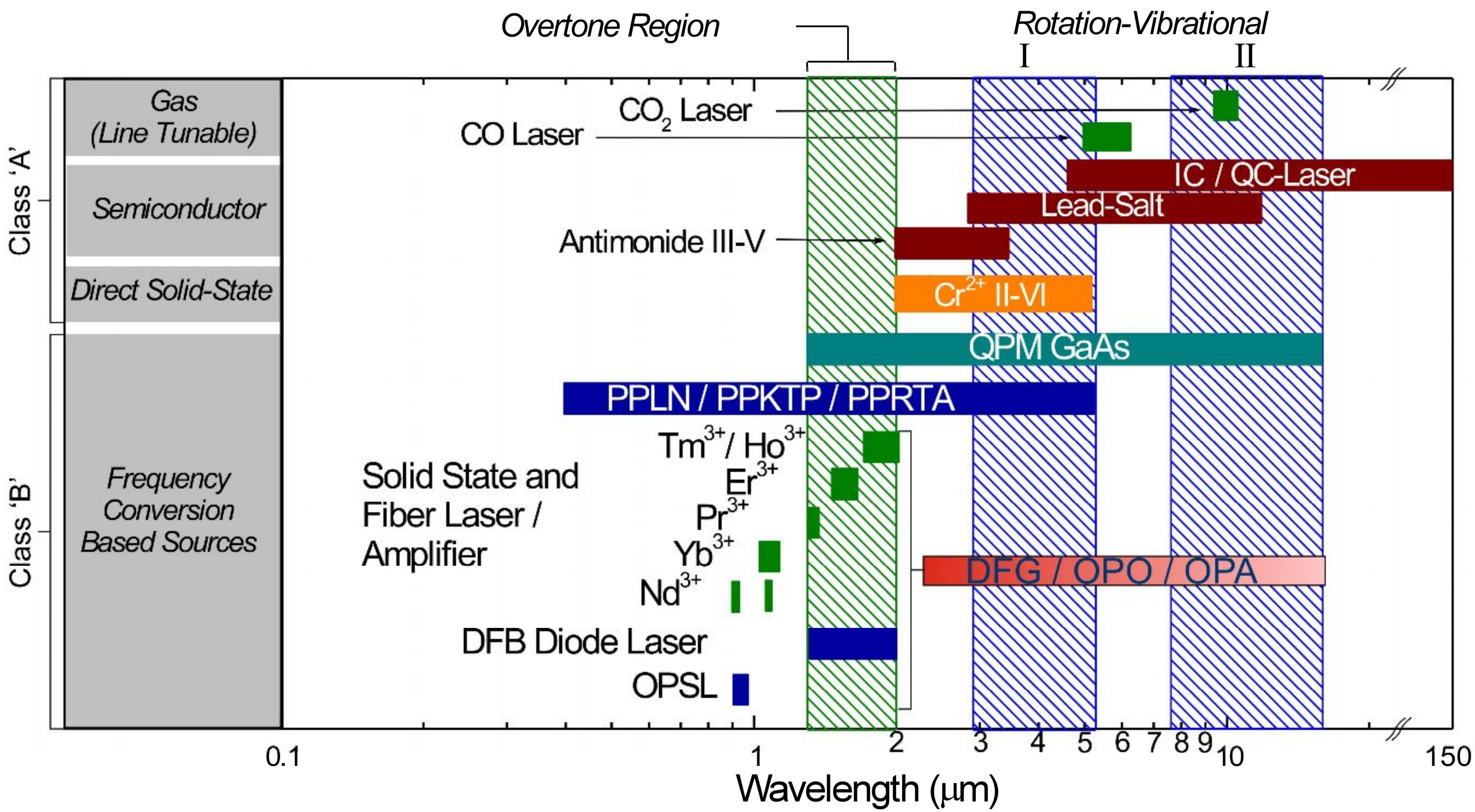
Molecular Absorption Spectra within two Mid-IR Atmospheric Windows





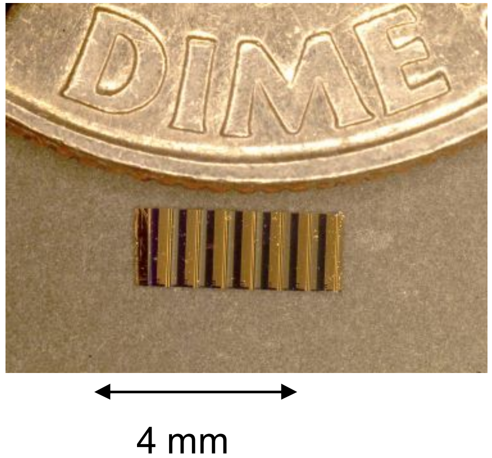
Source: HITRAN 2000 database

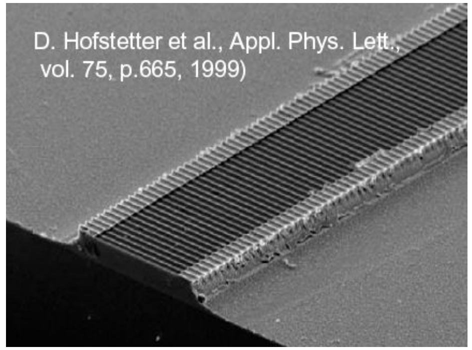
IR Laser Sources and Wavelength Coverage

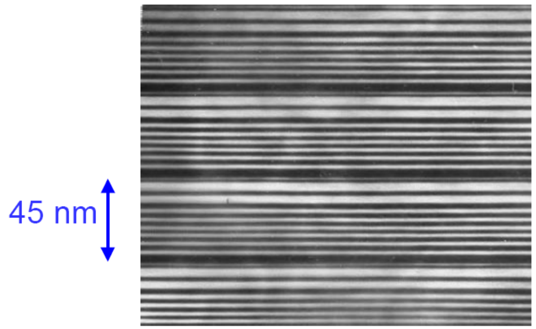


Key Characteristics of mid-IR QCLs and ICL Sources

- **Band – structure engineered devices**
  (emission wavelength is determined by layer thickness – MBE or MOCVD); mid-infrared QCLs operate from 3 to 24 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 injection current control
  - 10-20 cm^{-1} using temperature control
  - > 265 cm^{-1} using an external grating element and with heterogeneous cascade active region design
- **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 ~425K
  - 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, Hamamatsu, Daylight
    ~ 300 mW @ 8.3 μm (Agilent Technologies & Harvard)
  - > 600 mW (CW FP) @RT & a wall plug efficiency of >9.3%;
    >150 mW (CW DFB) at 298 K (Northwestern)

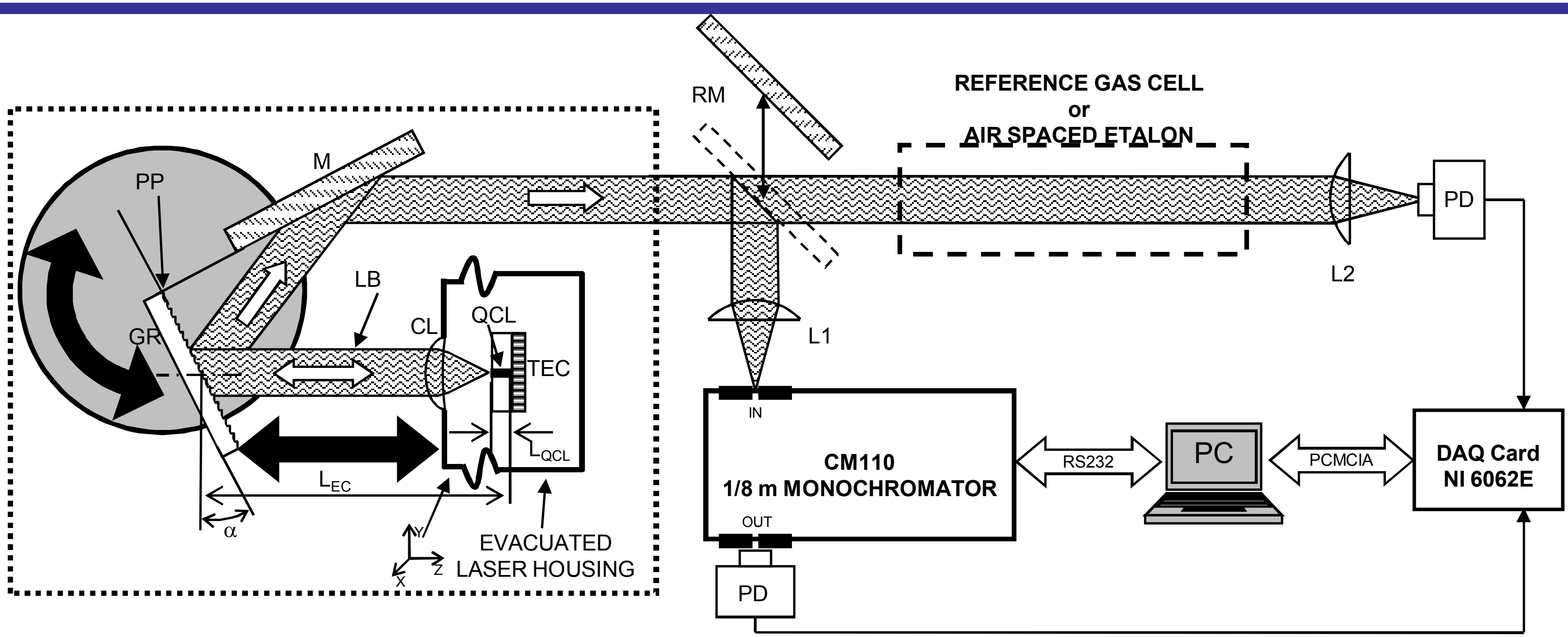


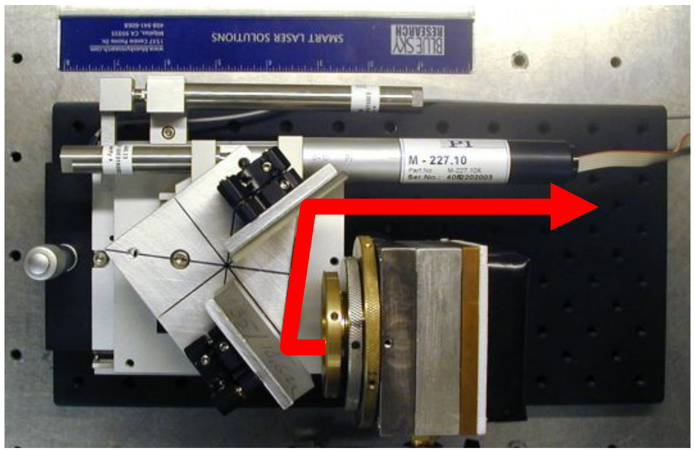




Widely Tunable, CW, TEC
Quantum Cascade Lasers

Tunable external cavity QCL based spectrometer

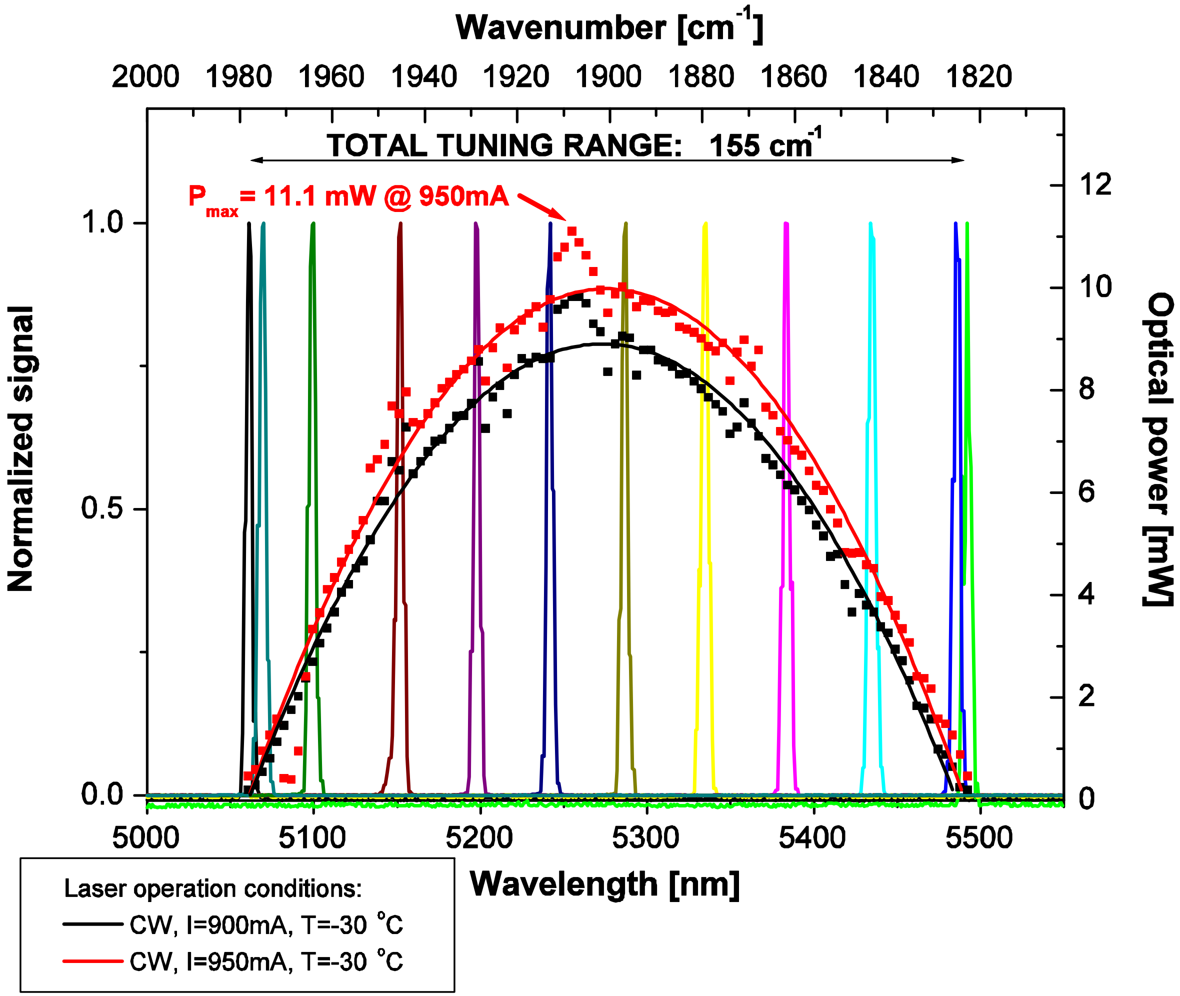




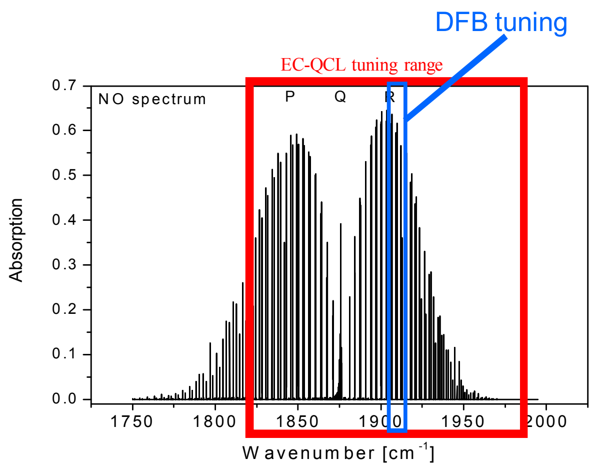
- Fine wavelength tuning
  - PZT controlled EC-length
  - PZT controlled grating angle
  - QCL current control
- Motorized coarse grating angle tuning
- Vacuum tight QCL enclosure with build-in 3D lens positioner (TEC laser cooling + optional chilled water cooling)

RICE

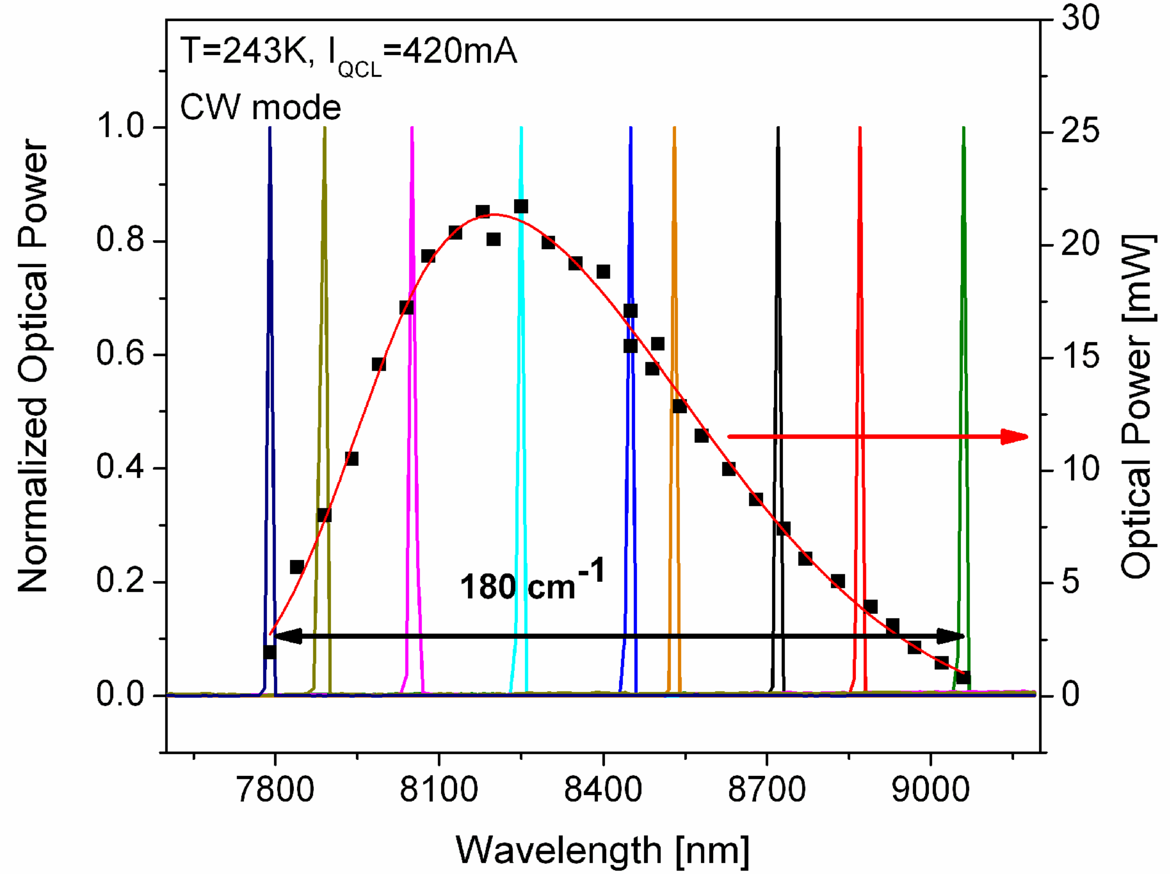
Wide Wavelength Tuning of a 5.3μm EC-QCL



- 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



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}≈ **2 × 10^{-4}**

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

Quartz Enhanced
Photoacoustic Spectroscopy

From conventional PAS to QEPAS

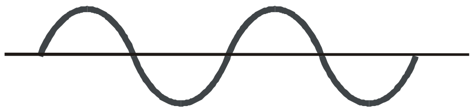
Cavity resonant

Q>>1000

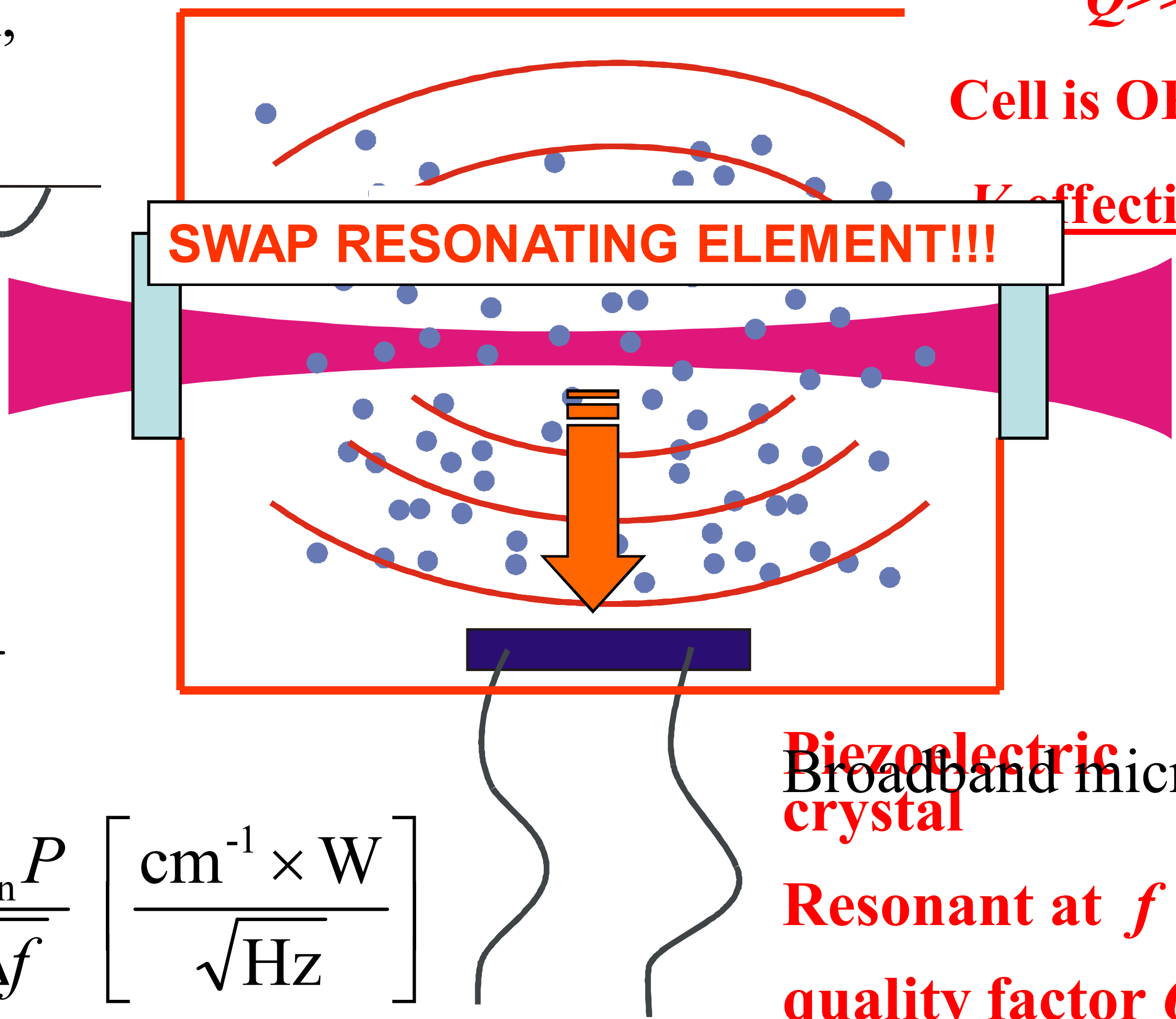
Cell is OPTIONAL!

V effective volume

Laser beam, power P



Modulated (P or λ) at f or $f/2$



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

Broadband microphone

Piezoelectric crystal

Resonant at f

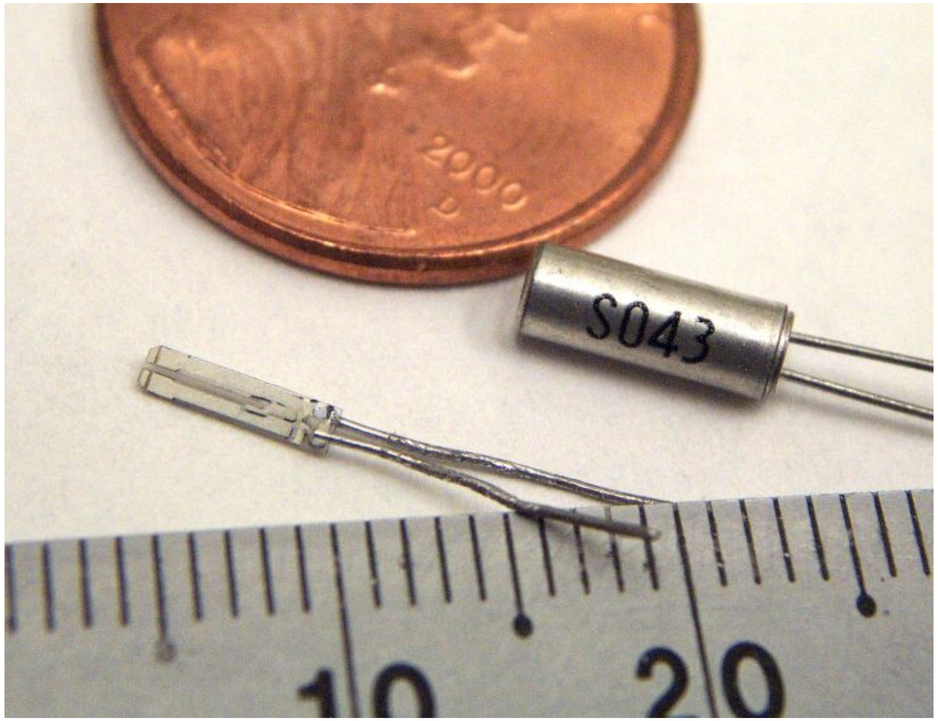
quality factor Q

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

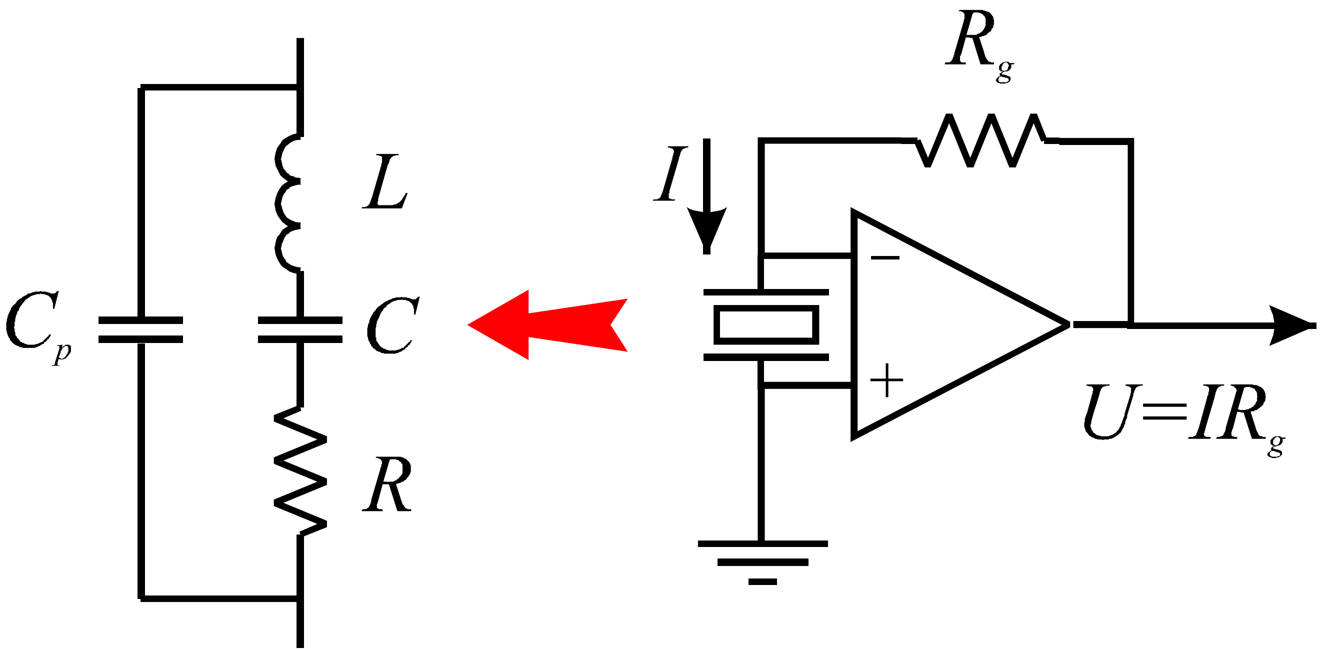
RICE

Quartz Tuning Fork (TF) as a Resonant Microphone

- Resonant frequency f=32.8 kHz
- Intrinsically high Q factor: $Q_{vacuum} \sim 125\ 000$, $Q_{air} \sim 10\ 000$ at ambient conditions;
- Piezoelectric: requires no transducer
- Miniature size
- Mass produced for clocks – low cost



QEPAS Signal Detection

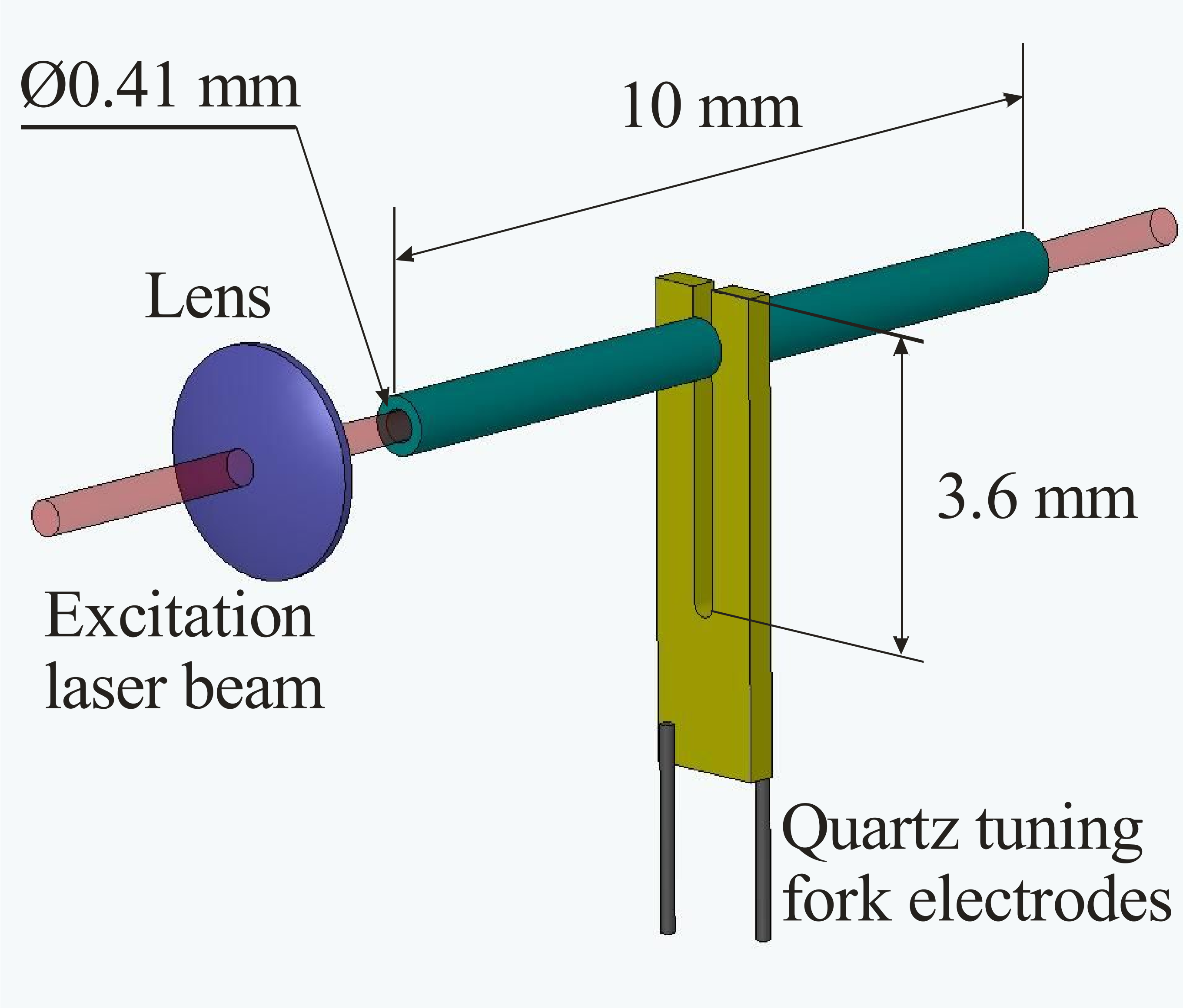


Amplifier:

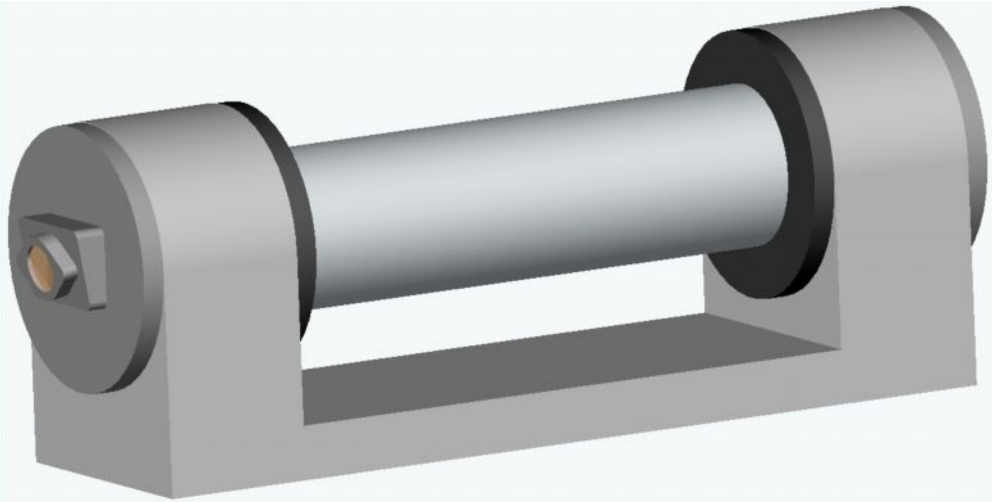
- •Fast
- •Low noise
- •High impedance
- •Low 1/f noise

RICE

Absorption Detection Module for QEPAS based Gas Sensor

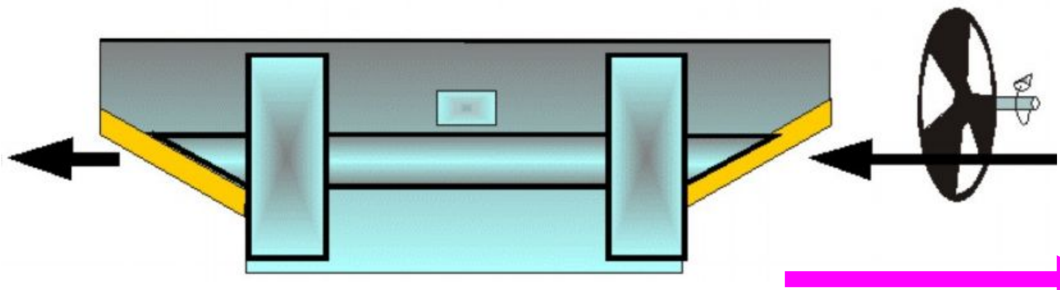


Comparative Size of Absorption Detection Modules (ADM)

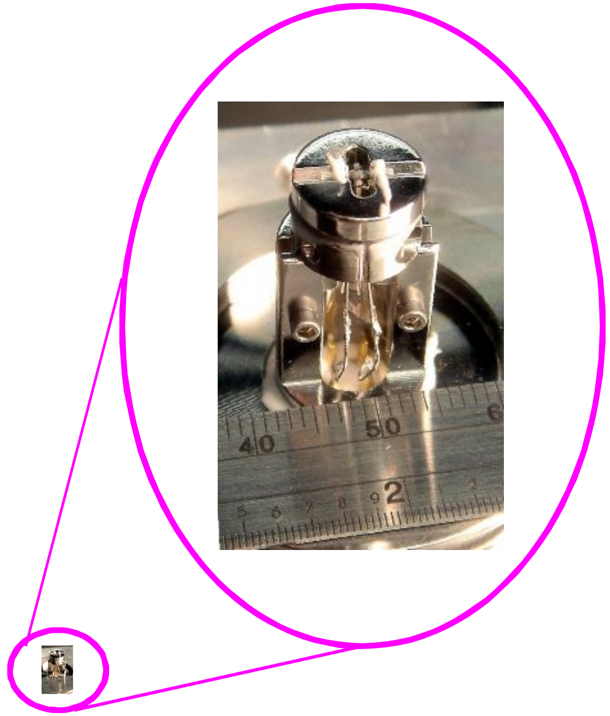


- Resonant frequency f = 32.8 kHz
- Intrinsically high Q factor: Q_{vacuum} ~ 125 000
  Q_{air}~10 000 for ambient conditions
- Piezoelectric: requires no transducer
- Miniature size
- Mass produced for watches & clocks – low cost

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



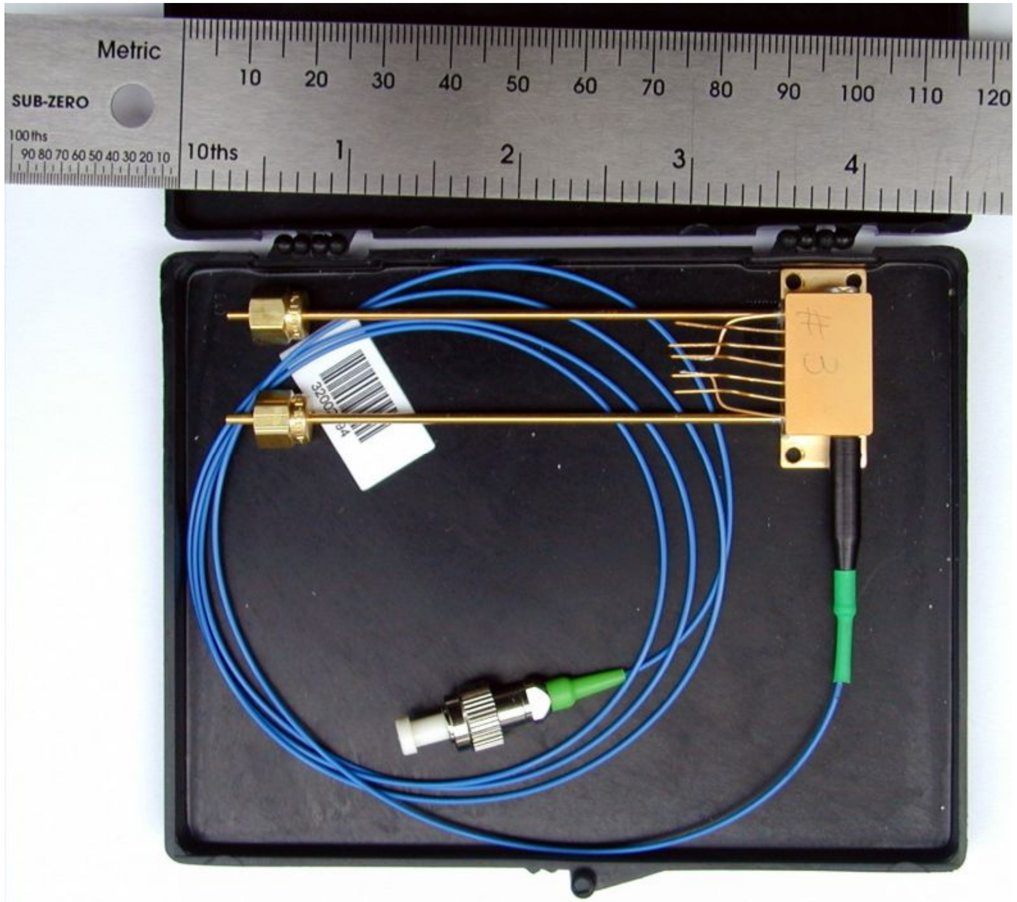
Resonant photoacoustic cell (1000 Hz):
l~60 cm, V~50 cm^3

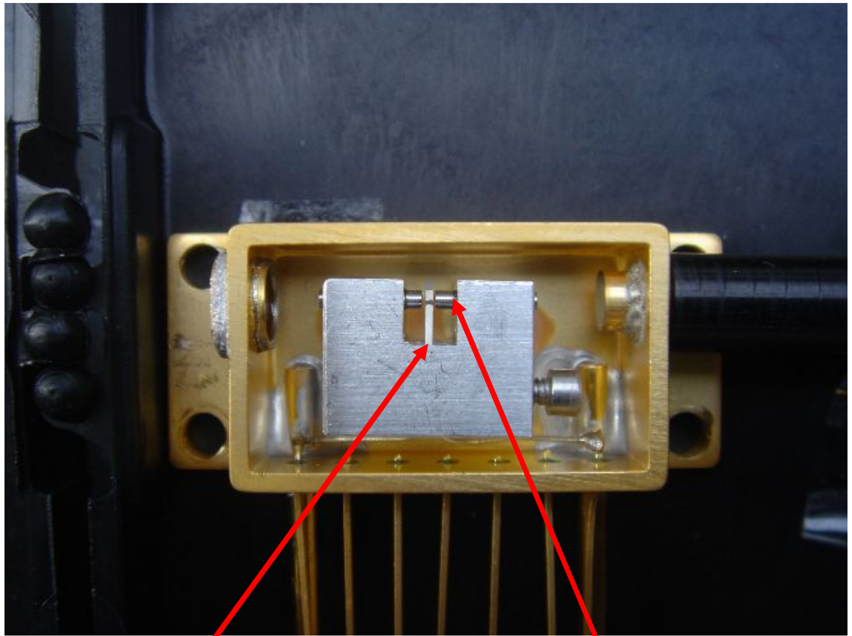


QEPAS spectrophone:
l~1 cm, V~0.05 cm^3

RICE

Alignment-free QEPAS Absorption Detection Module





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)

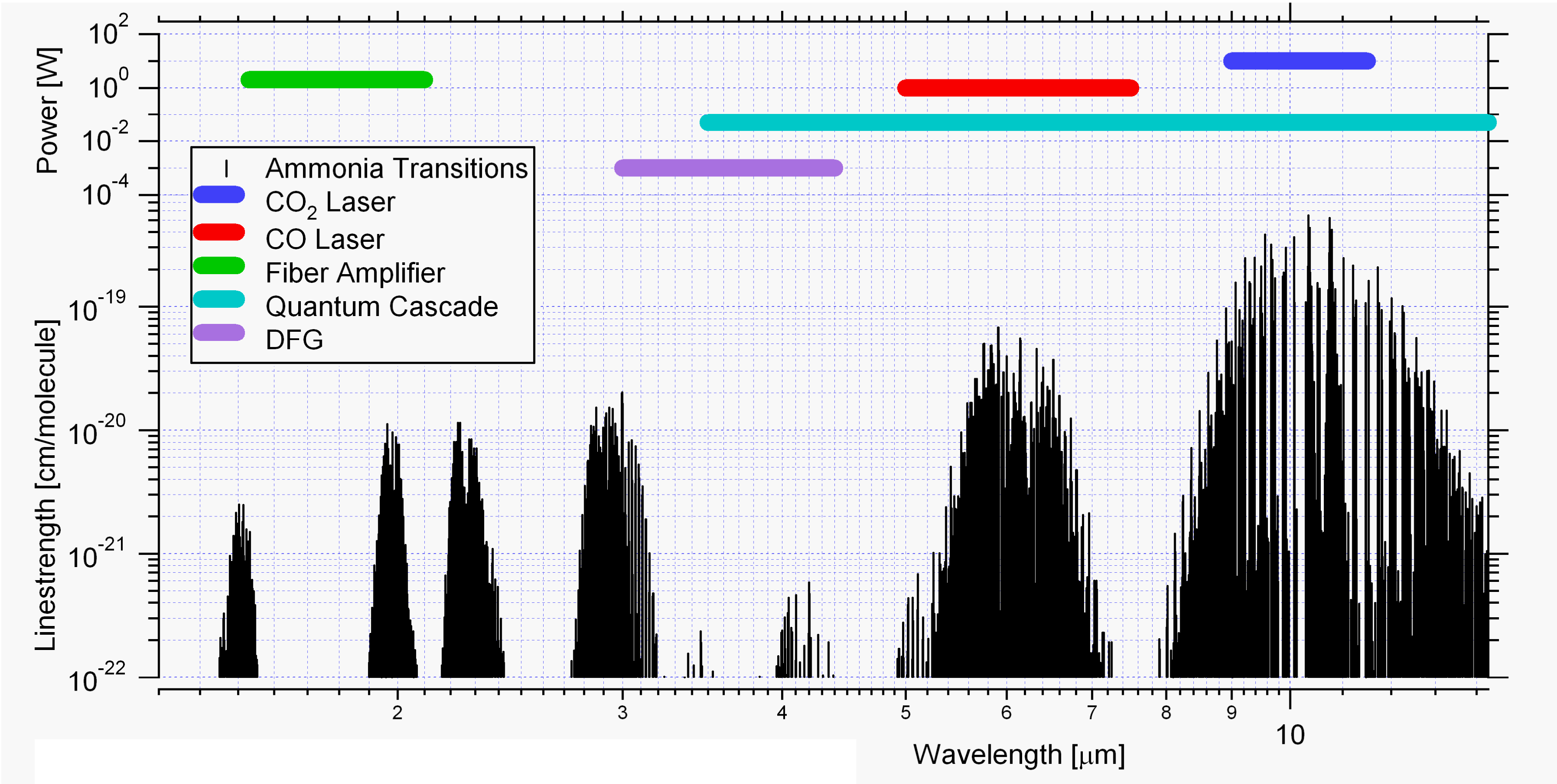
RICE

Trace Gas Sensing Examples

Motivation for NH_3 Detection

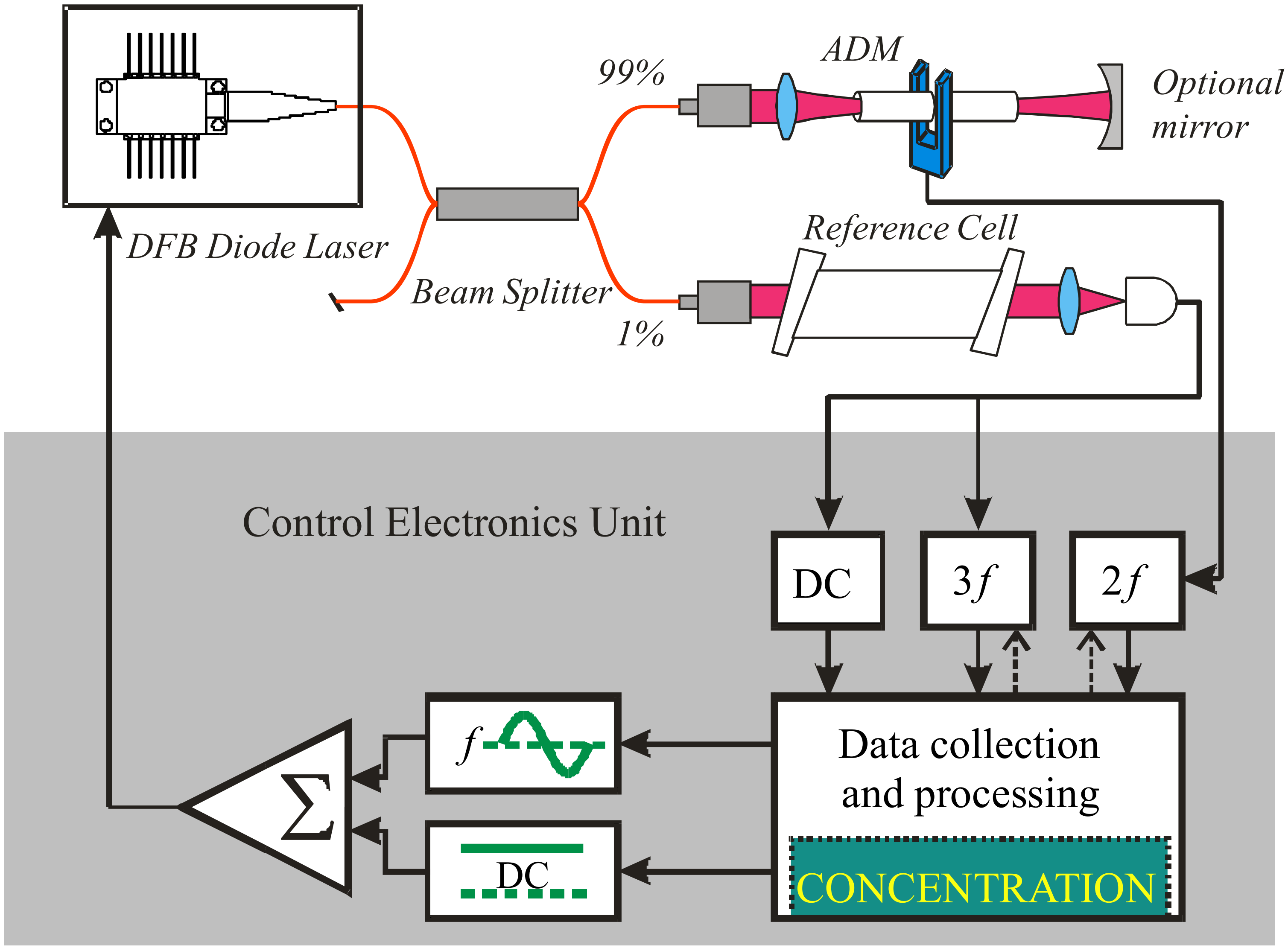
- Monitoring of gas separation processes
- Detection of ammonium-nitrate explosives
- Spacecraft related gas monitoring
- Monitoring NH_3 concentrations in the exhaust stream of NO_x removal systems based on selective catalytic reduction (SCR) techniques
- Semiconductor process monitoring & control
- Monitoring of industrial refrigeration facilities
- Pollutant gas monitoring
- Atmospheric chemistry
- Medical diagnostics (kidney & liver dysfunctions)

Infrared NH_3 Absorption Spectra



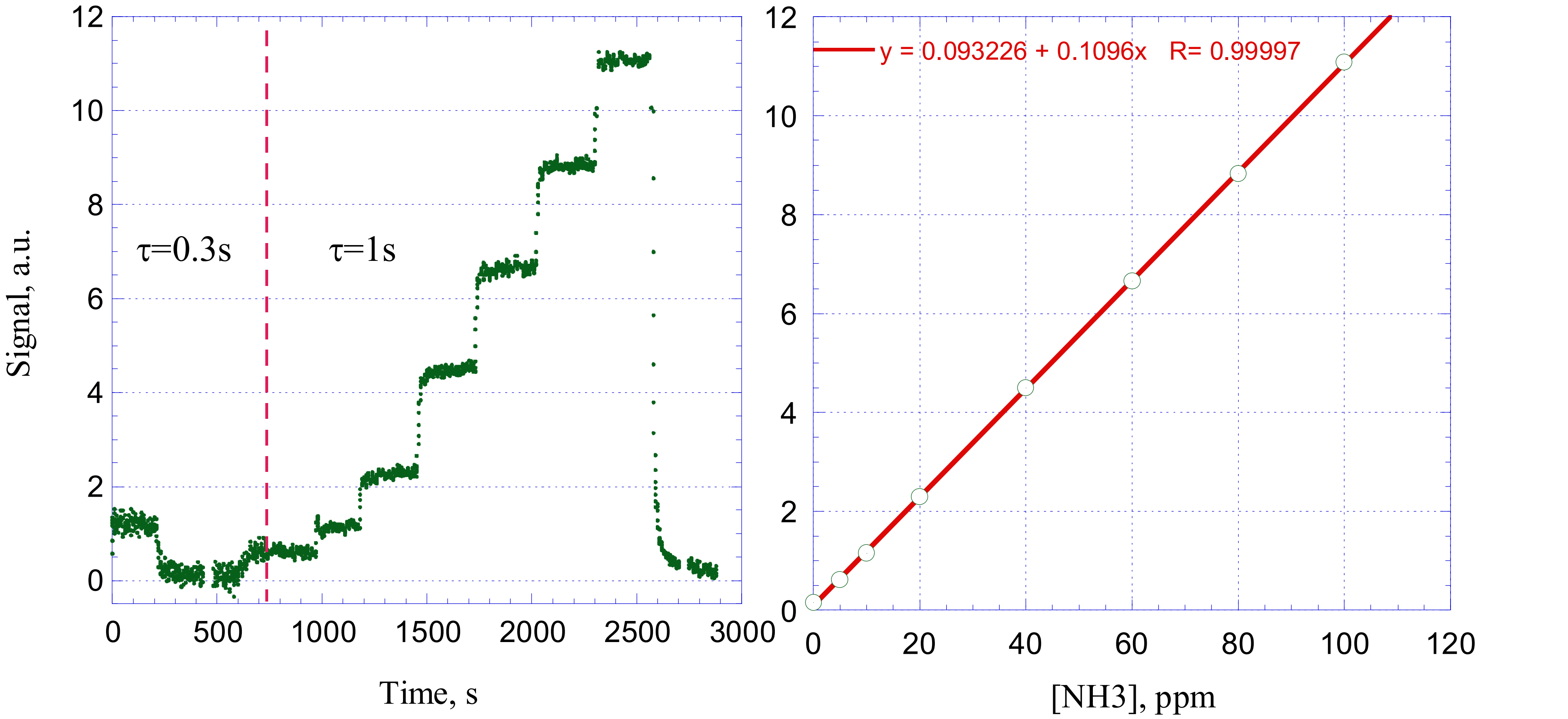
M. Webber et al. 2003, Pranalytica

QEPAS based Gas Sensor Architecture



RICE

Calibration and Linearity of a 1.53 μm QEPAS based NH_3 Sensor



Noise–equivalent concentration (NEC).
for t=1s time constant is 0.06 ppm for
60mW excitation power at 6528.76 cm^{-1}

90 last points of each step averaged

Noise-equivalent absorption (NEA) coefficient *k*=3.1×10^{-9} $cm^{-1}W/Hz^{1/2}$

RICE

Biomarkers Present in Exhaled Human Breath

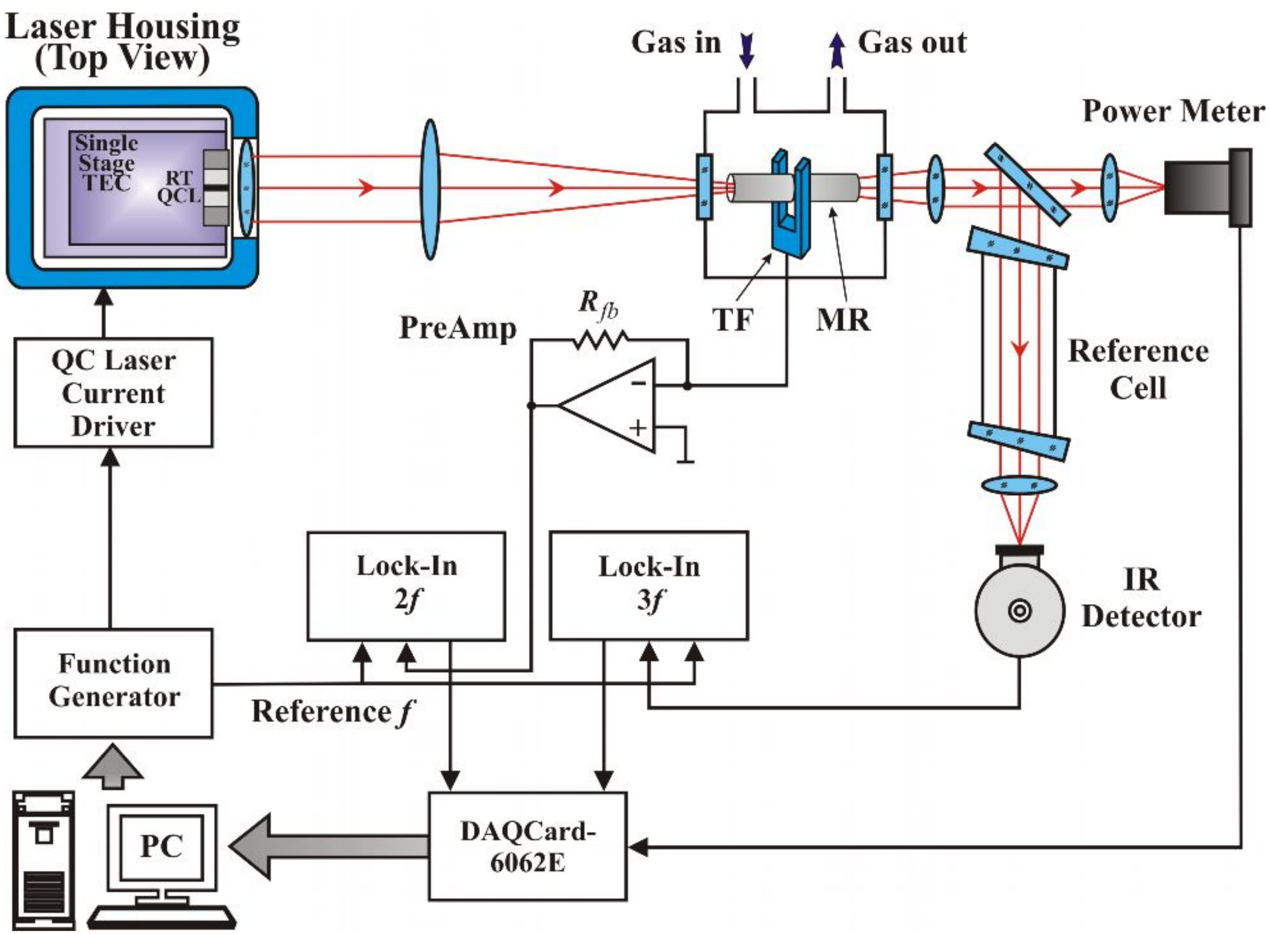
More than 400 different molecules in breath;
many with well defined biochemical pathways

BROADBAND ABSORBERS

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

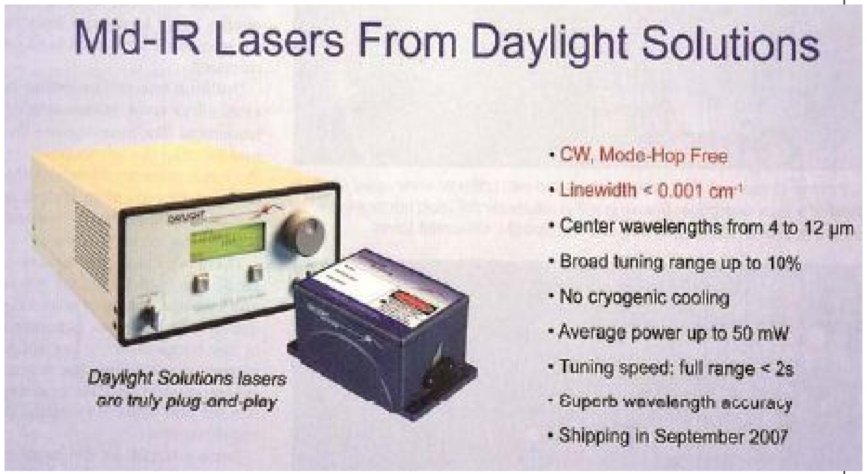
Terence Risby, Johns Hopkins University

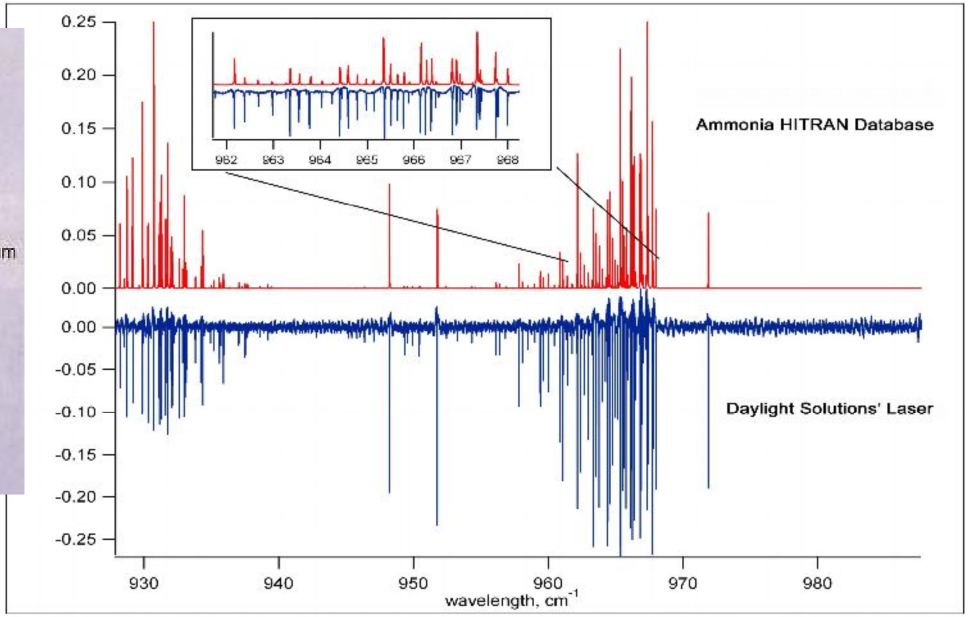
9.56 μm CW DFB QCL based QEPAS Ammonia Sensor

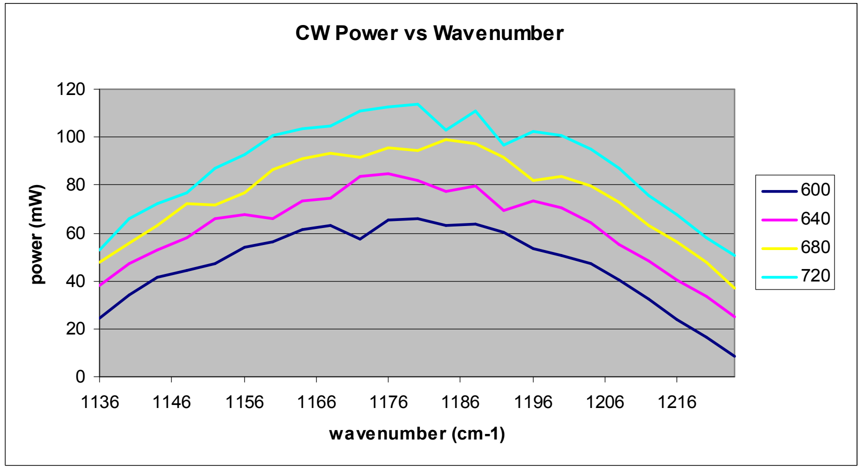


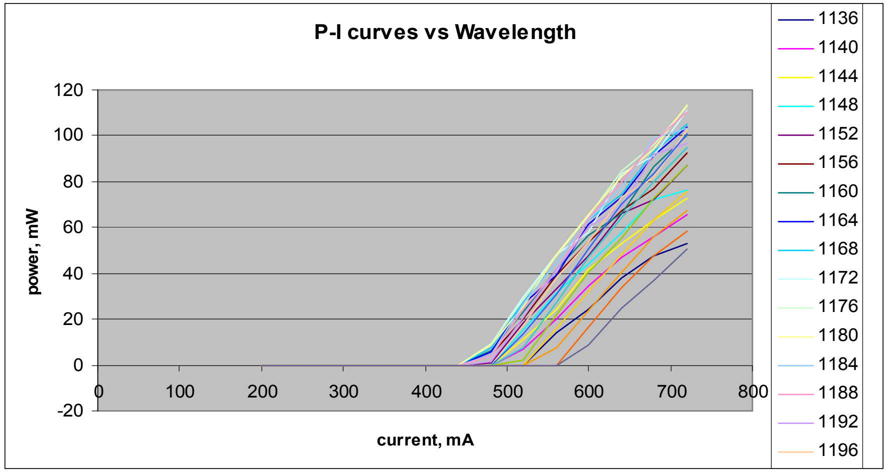
Noise–equivalent concentration (NEC)
for t=1s time constant is 0.006 ppm for 20mW
excitation power at 1046.4 cm^{-1} (110 Torr)

Commercial widely tunable cw EC-QCL









DAYLIGHT
SOLUTIONS

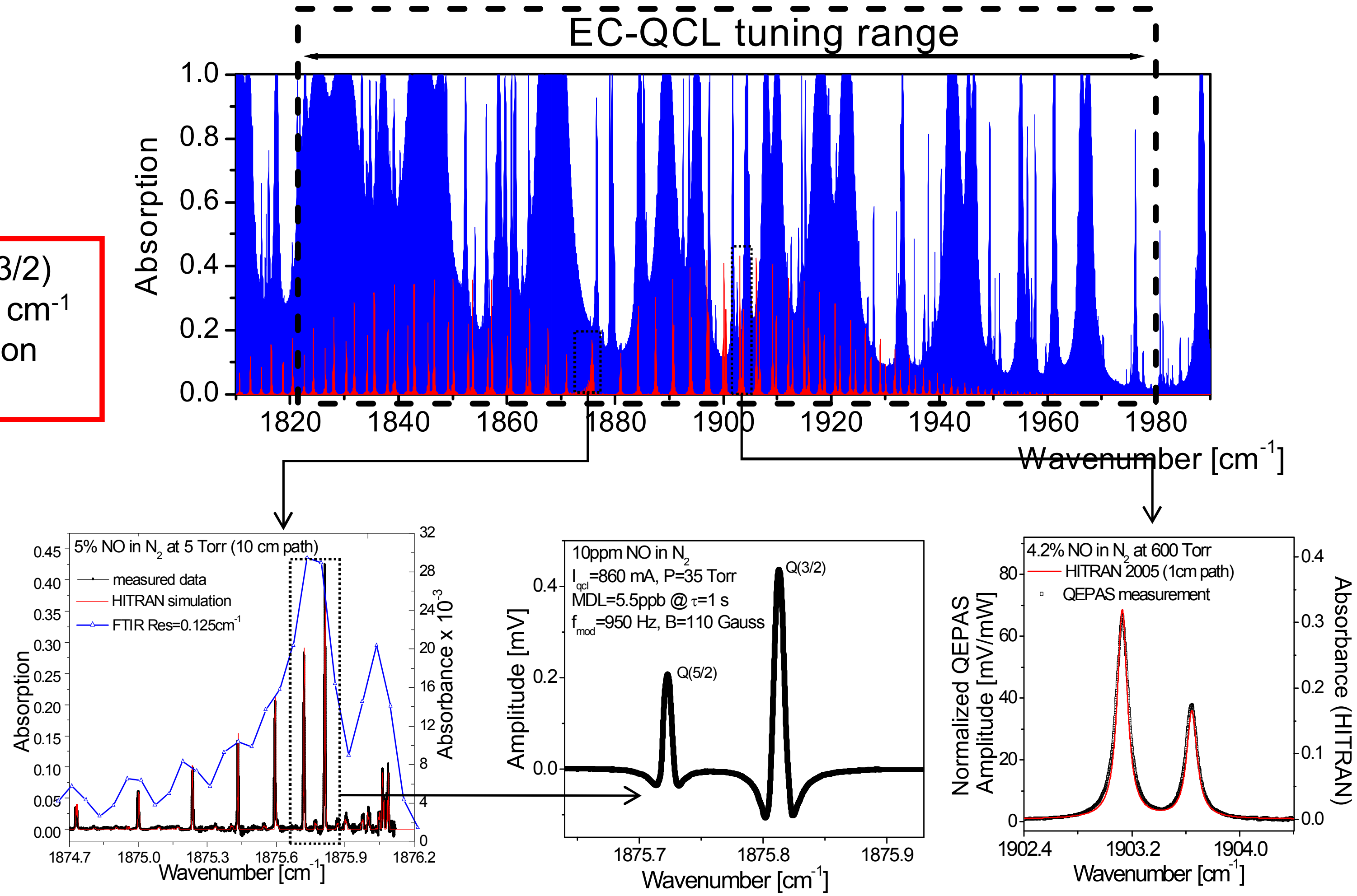
Motivation for Nitric Oxide Detection

- 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

RICE

High resolution spectroscopy with a 5.3μm EC-QCL

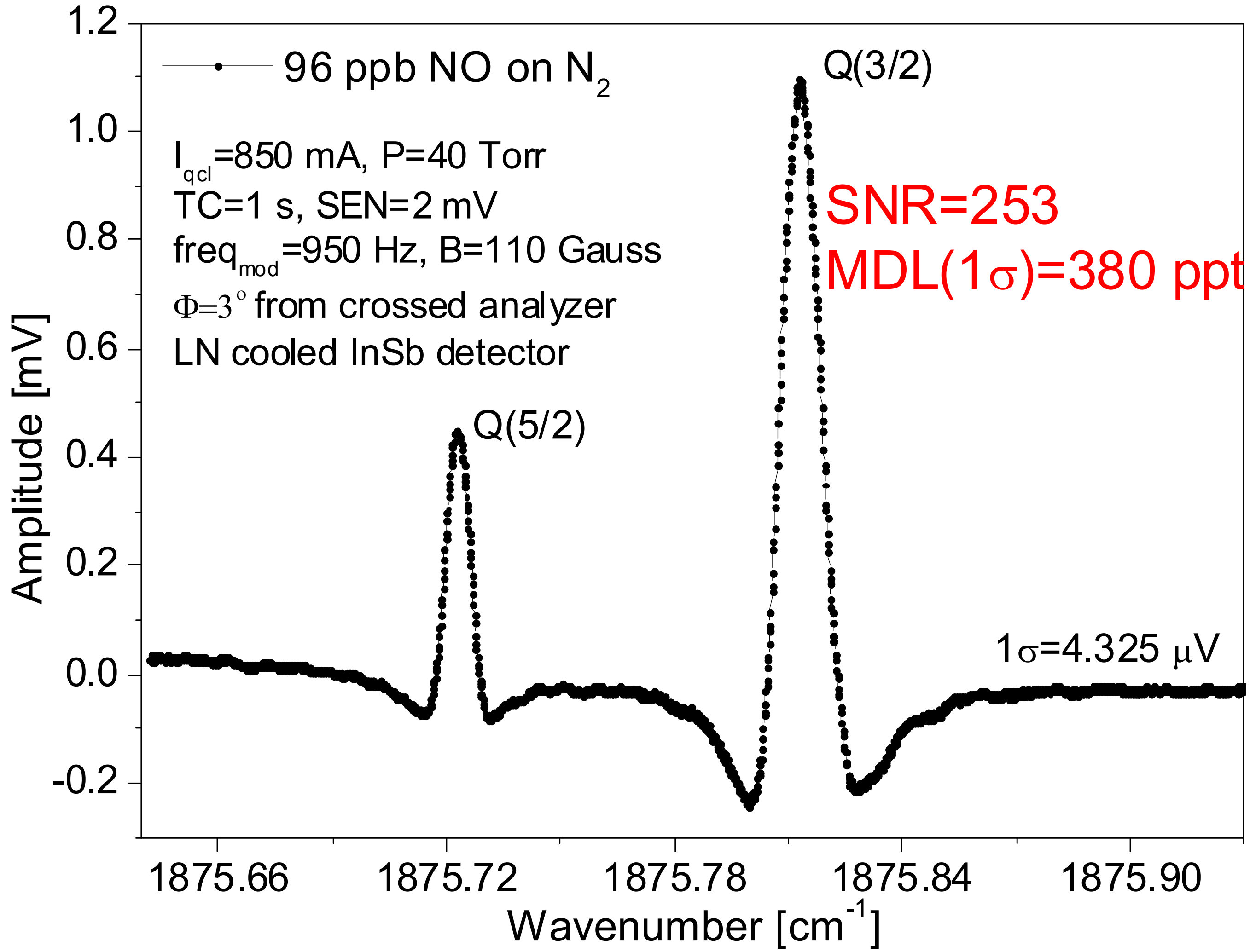
Access to NO Q(3/2) transition at 1875.8 cm^{-1} for Faraday rotation spectroscopy



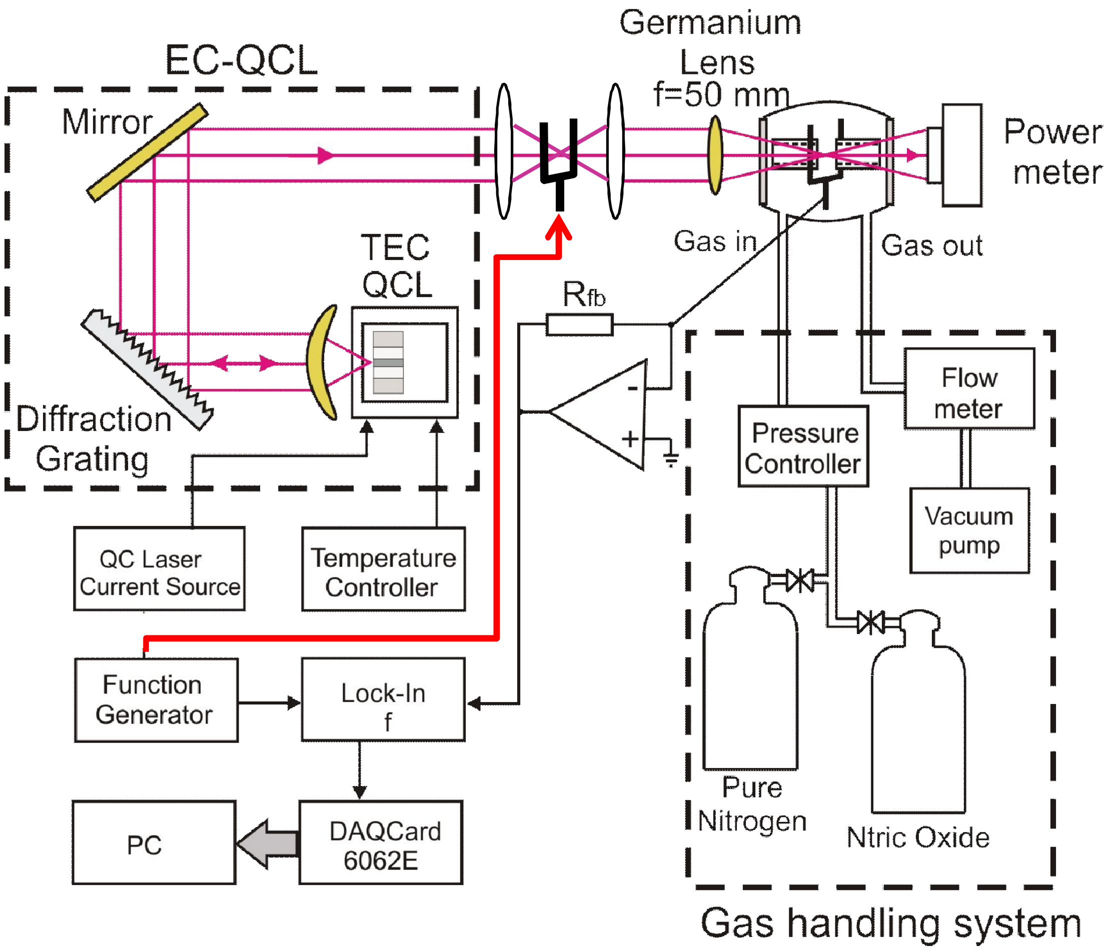
- Mode hop free scan of up to ~**2.5 cm^{-1}** with a resolution **<0.001cm^{-1}** (30MHz) can be performed anywhere within the tuning range

In collaboration with:

Magnetic Rotation Spectroscopy of Nitric Oxide



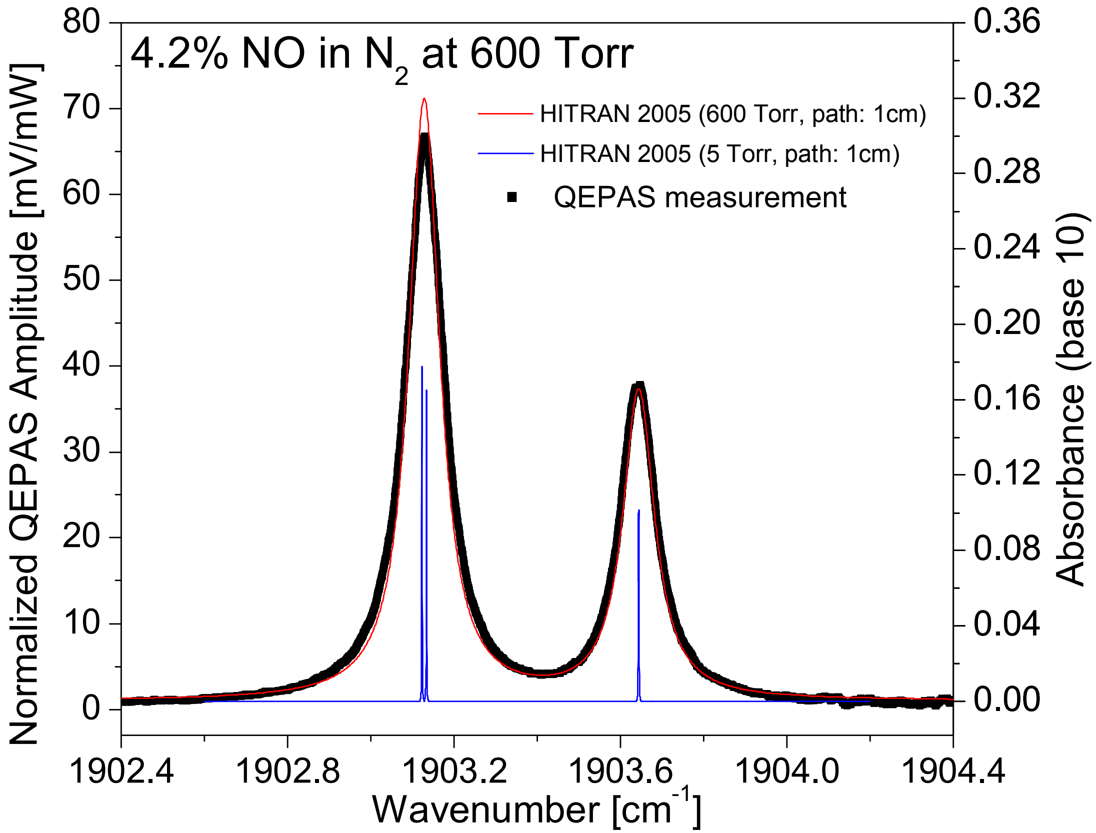
QCL based Quartz-Enhanced Photoacoustic Gas Sensor



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

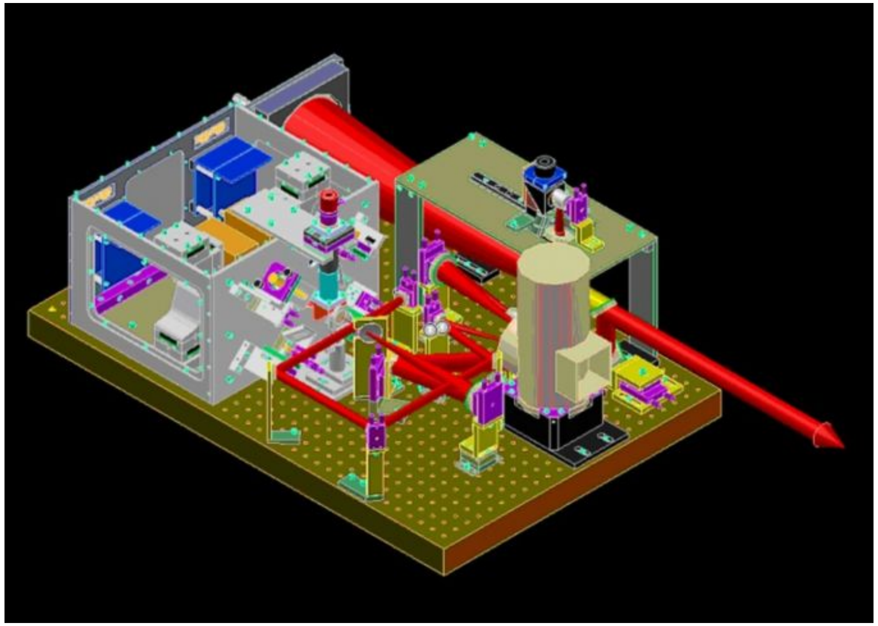
High resolution EC-QCL based QEPAS

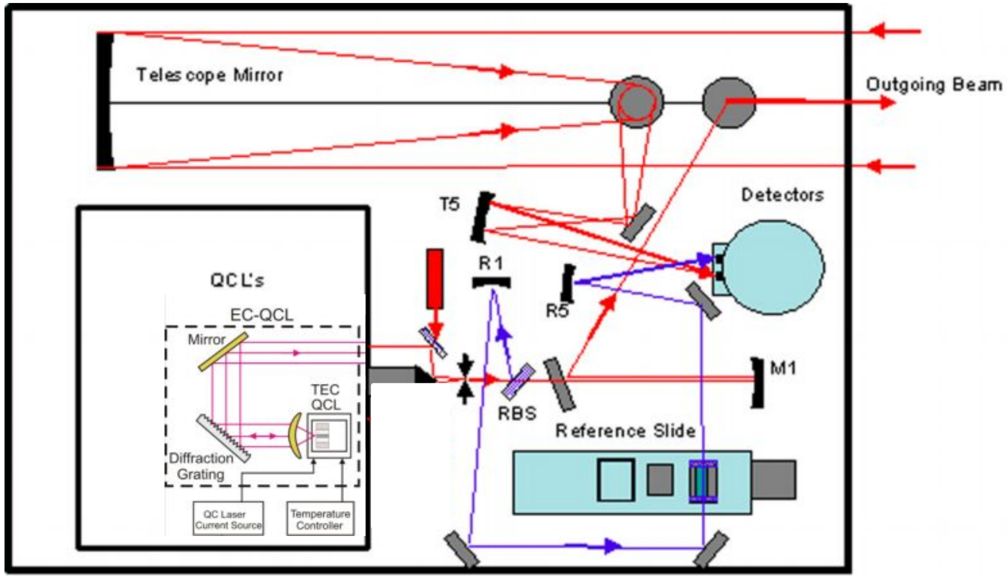


External Amplitude Modulation:

- 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

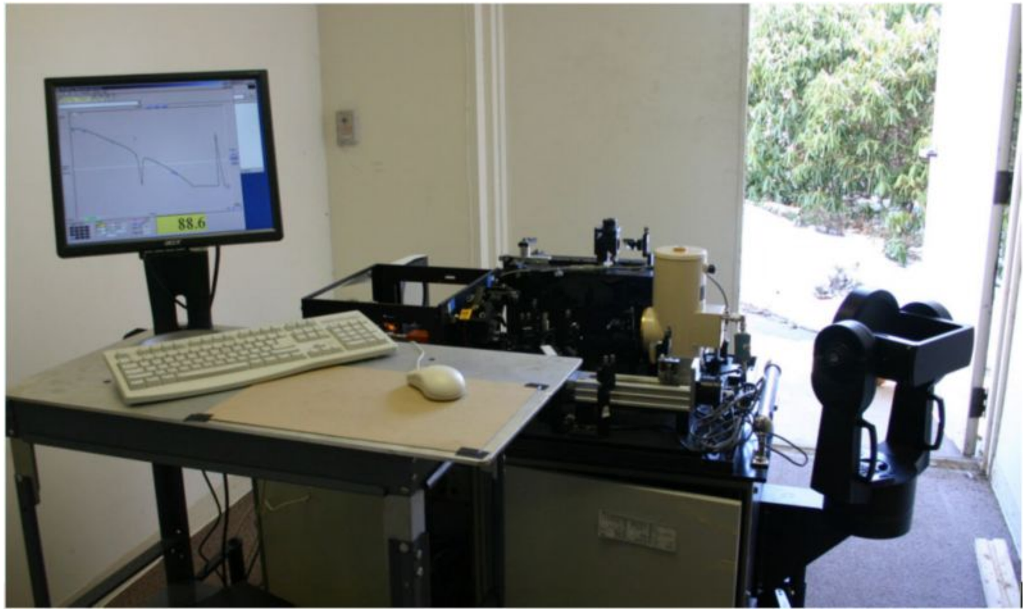
Design of an EC-QCL Based Remote Sensing System

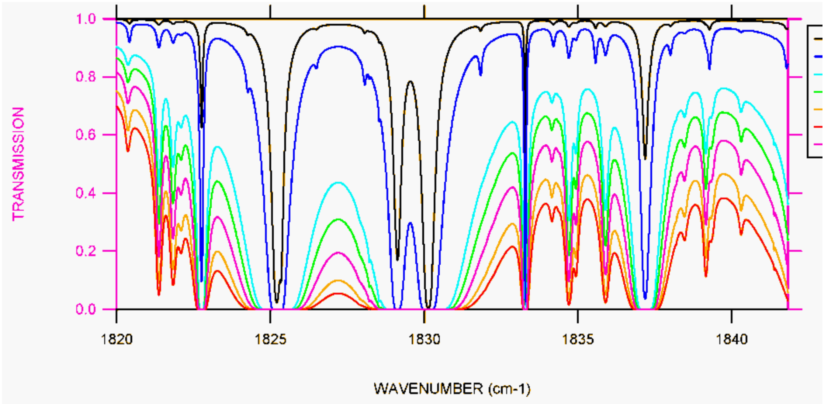




- An upgraded version of a four-laser pulsed QCL system
- The optical set-up, electronics and control software modified for CW-QCL operation
- First tests performed with a DFB CW-QCL operating at ~5.5μm

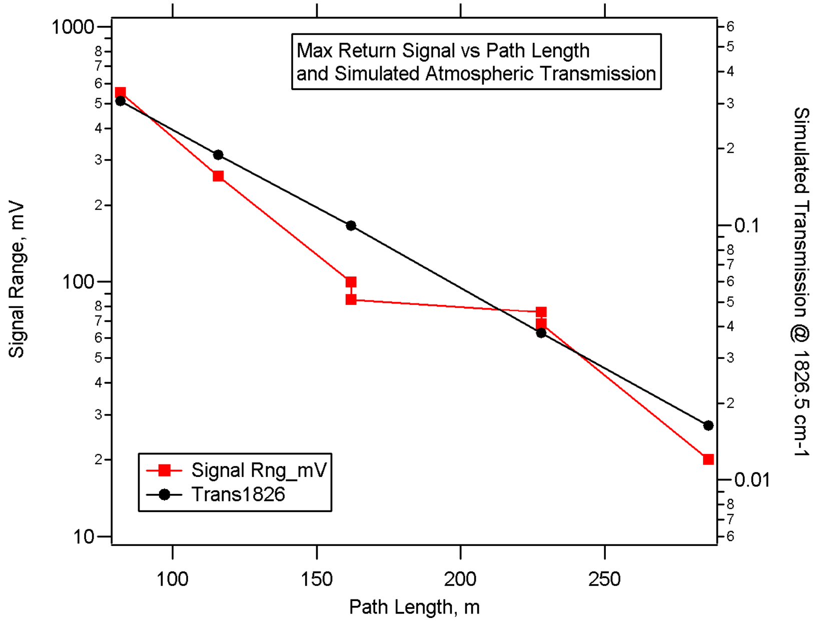
Outdoor Open Path Measurements
(Influence of Atmospheric Transmission)

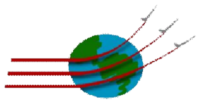




Open Path Measurements CW QCL $1826\ cm^{-1}$

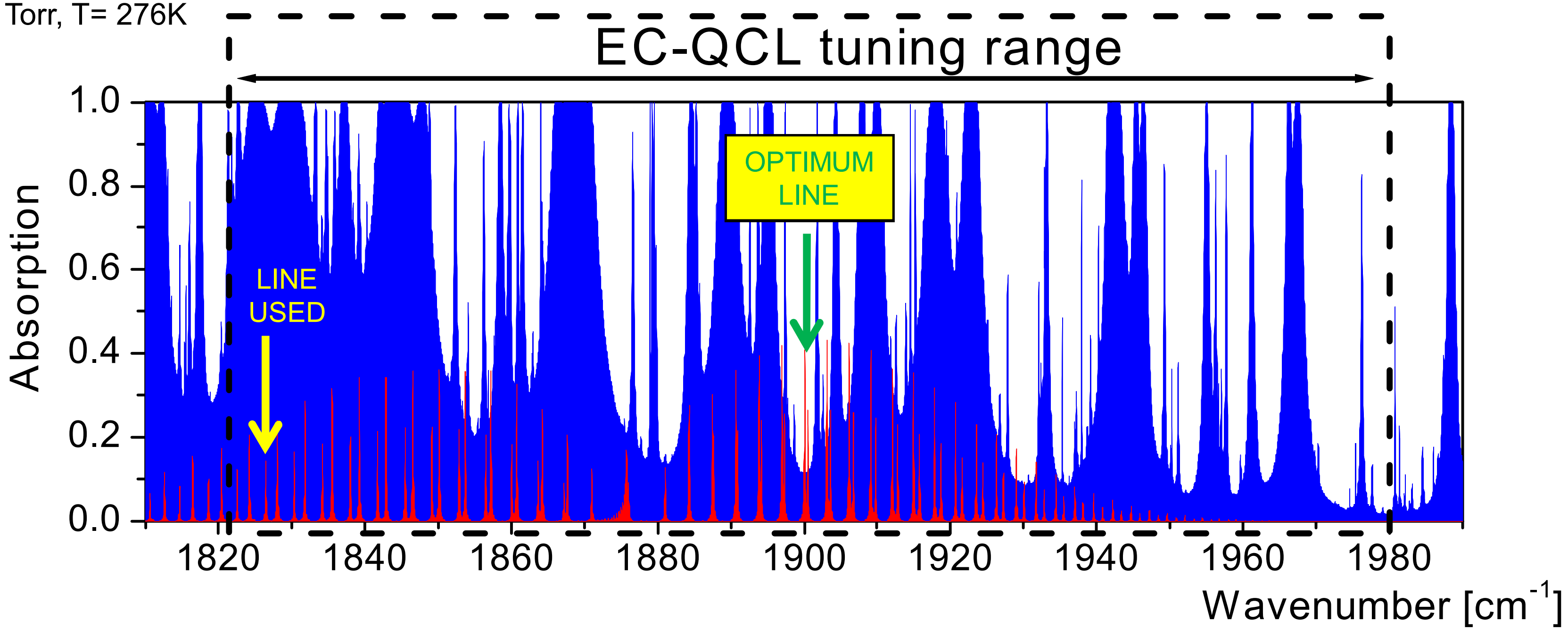
Ranges (1/2 total)
#1, 41m
#2, 58m
#3, 81m
#4, 114m
#5, 143m





High resolution spectroscopy with a 5.3μm EC-QCL

286m open path
H_2O mixing ratio: 0.006
CO_2 mixing ratio: 380 ppm
P=760 Torr, T= 276K



EC-QCL allows selection of an absorption line with:

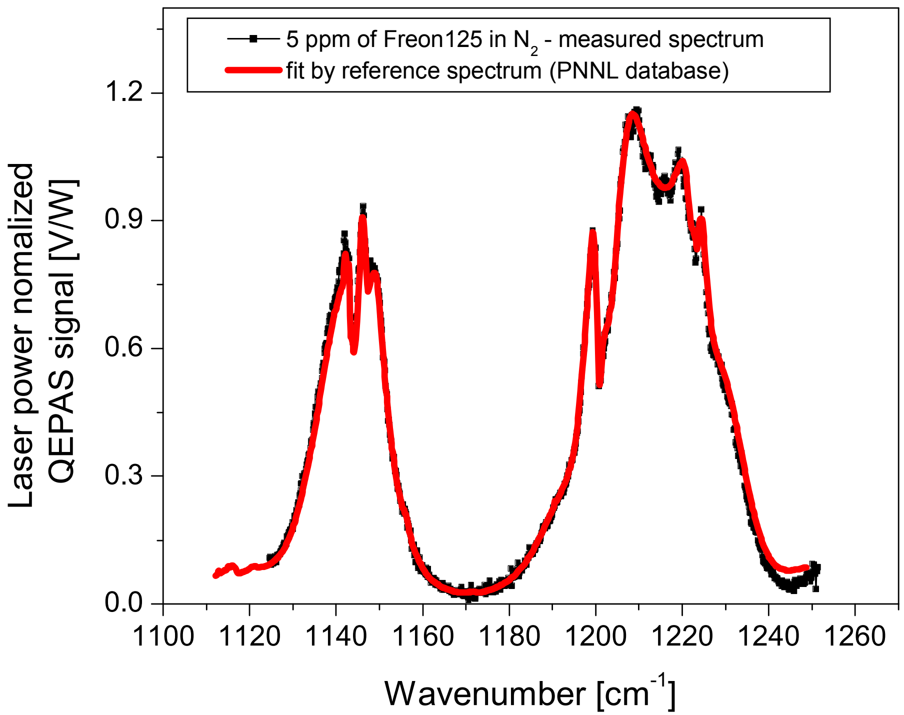
- Higher Line Intensity
- Lower Spectral Interference
- Higher Atmospheric Transmission

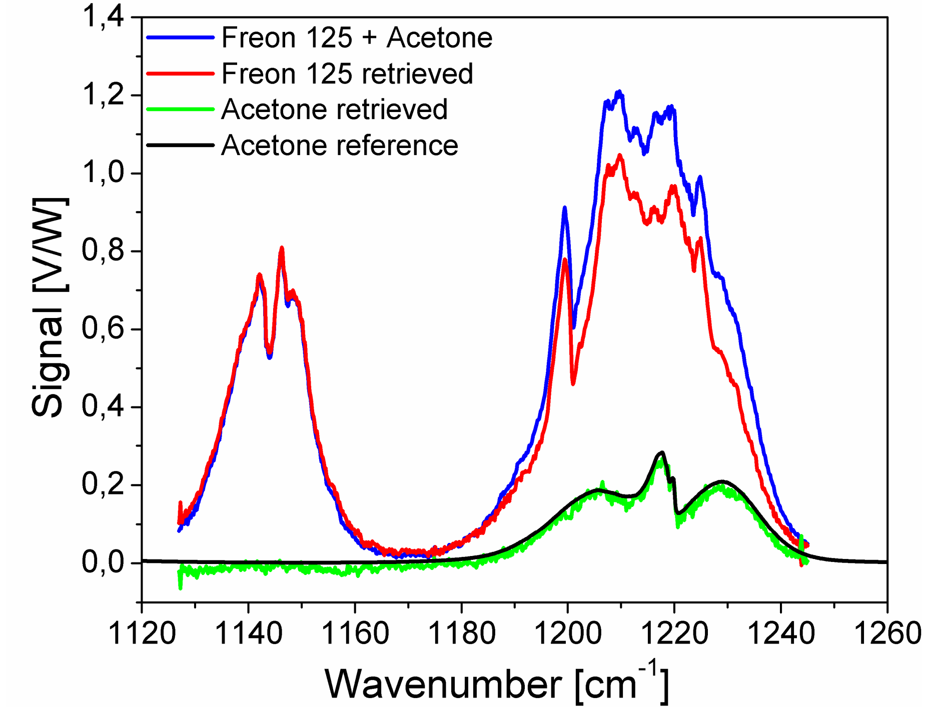
Monitoring of broadband absorbers

- 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

RICE

QEPAS based Freon 125 and Acetone concentration measurements with a tunable 8.4 μm CW EC-QCL





- 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

RICE

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

QEPAS Performance for 12 Trace Gas Species (March '08)

Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, $cm^{-1}W/Hz^{1/2}$	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	$< 4.3\times10^{-9}$	50	0.16
C_2H_2 (N_2)*	6523.88	720	4.1×10^{-9}	57	0.03
NH_3 (N_2)*	6528.76	575	3.1×10^{-9}	60	0.06
C_2H_4 (N_2)*	6177.07	715	5.4×10^{-9}	15	1.7
CH_4 (N_2)*	6057.09	950	2.9×10^{-8}	13.7	2.1
CO_2 (breath ~100% RH)	6361.25	150	8.2×10^{-9}	45	40
H_2S (N_2)*	6357.63	780	5.6×10^{-9}	45	0.20
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	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 (N_2)**	1934.2	770	2.2×10^{-7}	10	90
C_2HF_5 (N_2)***	1208.62	770	7.8×10^{-9}	6.6	0.009
NH_3 (N_2)*	1046.39	110	1.6×10^{-8}	20	0.006

* - Improved microresonator
** - Improved microresonator and double optical pass through ADM
*** - 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, 18 dB/oct filter slope.

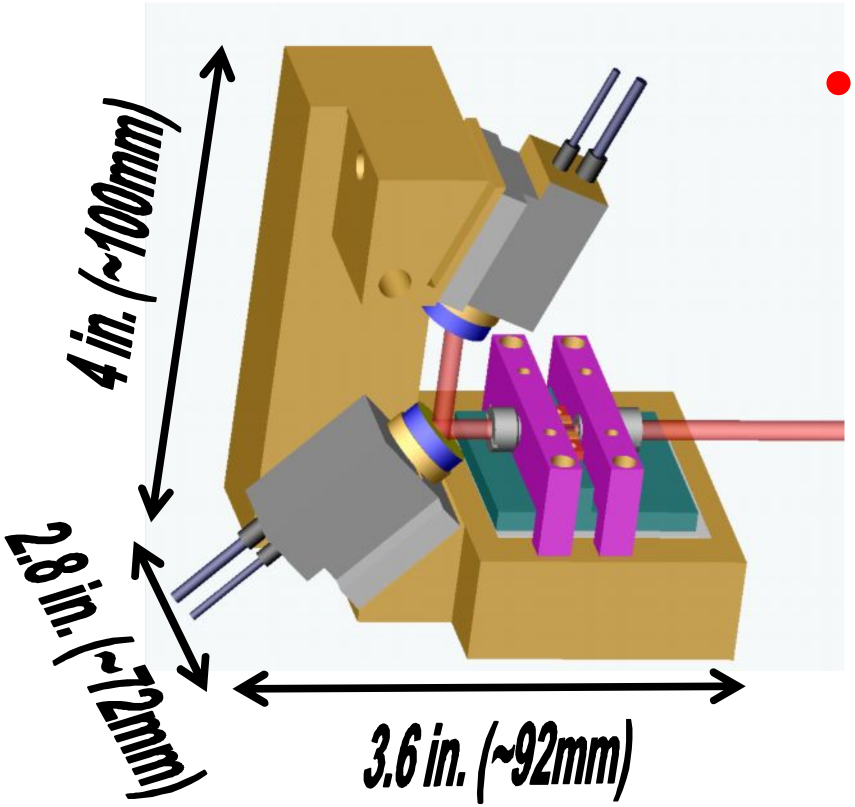
For comparison: conventional PAS 2.2 (2.6)×10^{-9} $cm^{-1}W/\sqrt{Hz}$ (1,800; 10,300 Hz) for NH_3*, (**)

* M. E. Webber et al, Appl. Opt. 42, 2119-2126 (2003); ** J. S. Pilgrim et al, SAE Intl. ICES 2007-01-3152

RICE

Future of Chemical Trace Gas Sensing

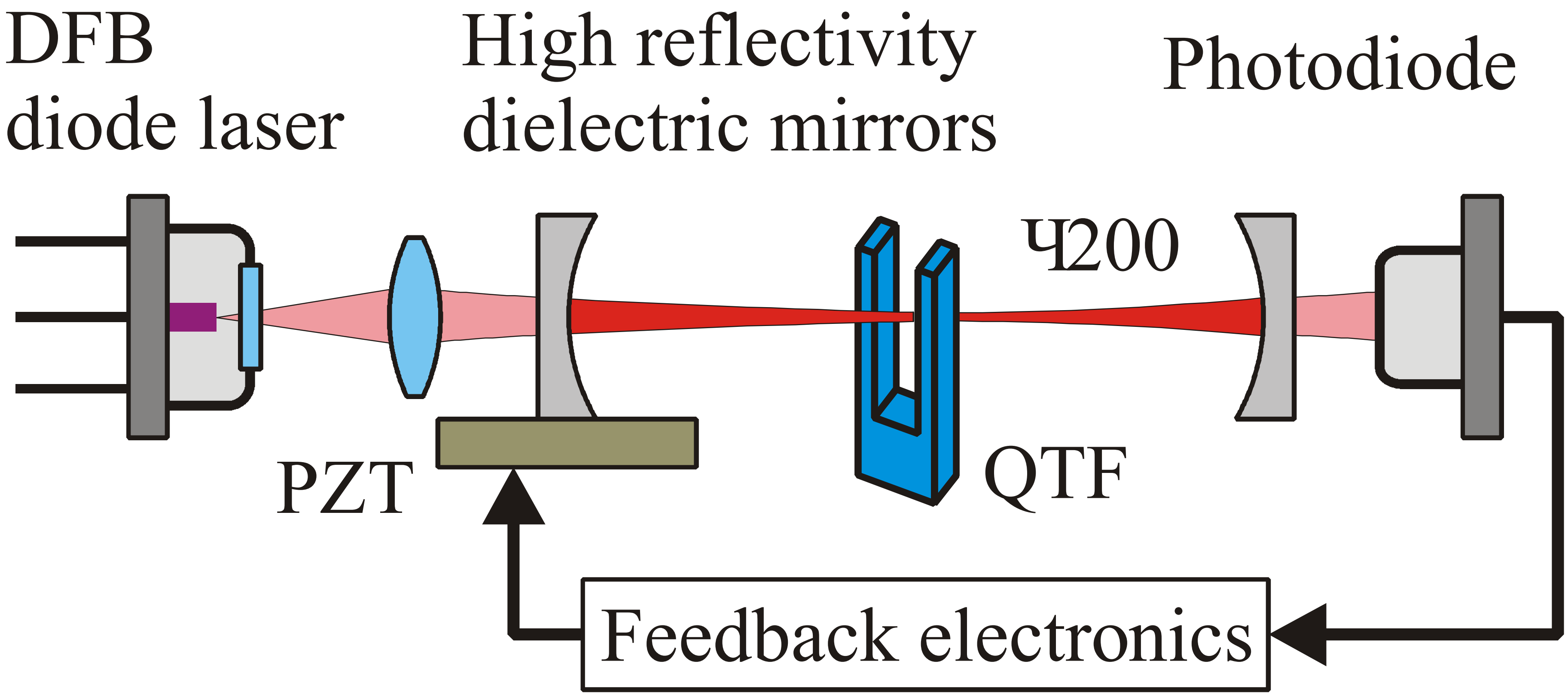
New design of fast broadly tunable EC-QCLs (2008)



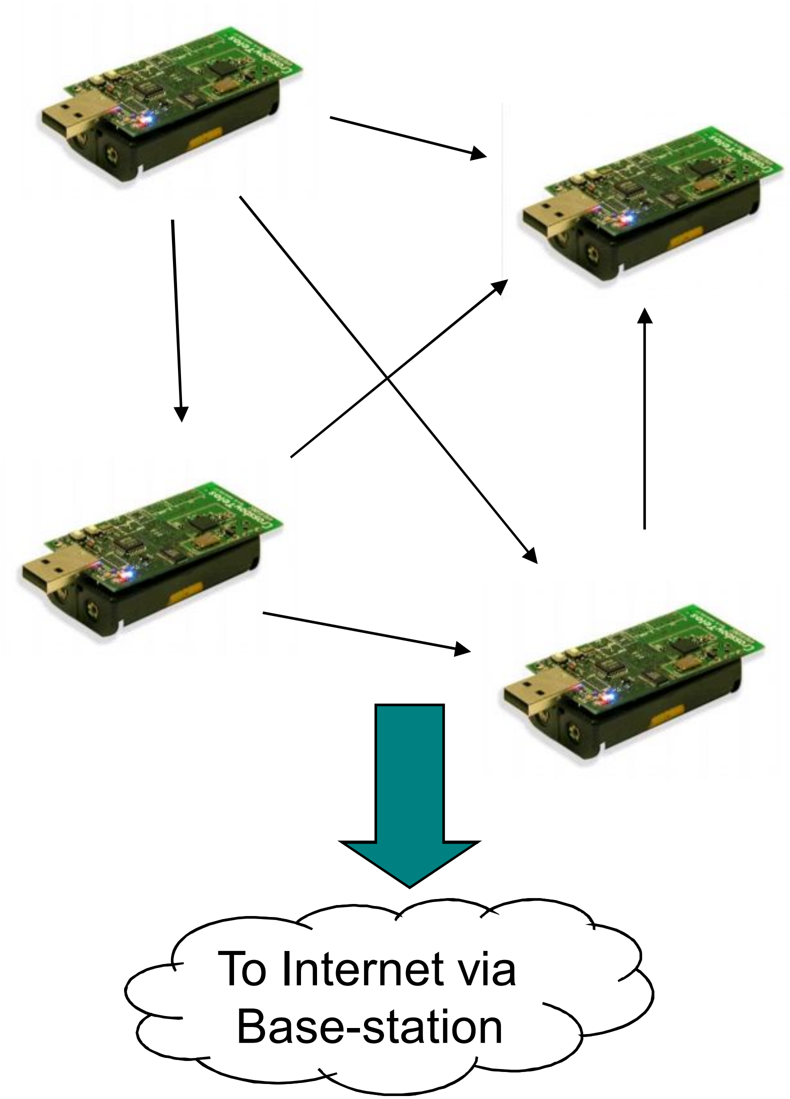
- New optical configuration
  Folded cavity (configuration #1)
- Fast tuning capabilities:
  - Coarse Broadband Scanning (~*55 cm^{-1}* @5μm) ***up to 5 KHz***
    (compared to available technologies ***<10Hz****)*
  - High resolution mode-hop free tuning (~*3.2 cm^{-1}* @5μm)
    up to 5 KHz
    (compared to available technology ***100-200 Hz****)*

Patent pending, G. Wysocki, F. K. Tittel, 2007

Proposed QEPAS-OPBC Sensor Configuration



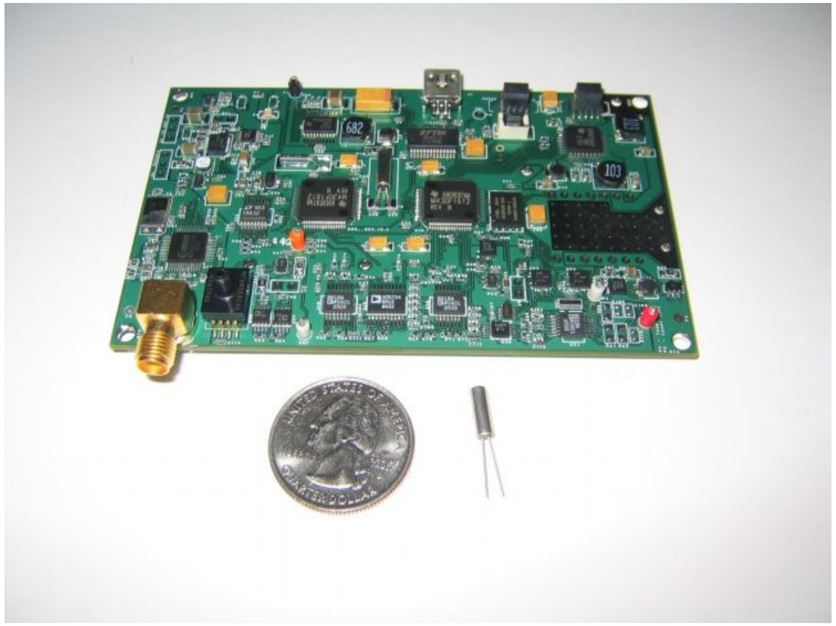
Wireless Sensor Networks for Gas Sensing

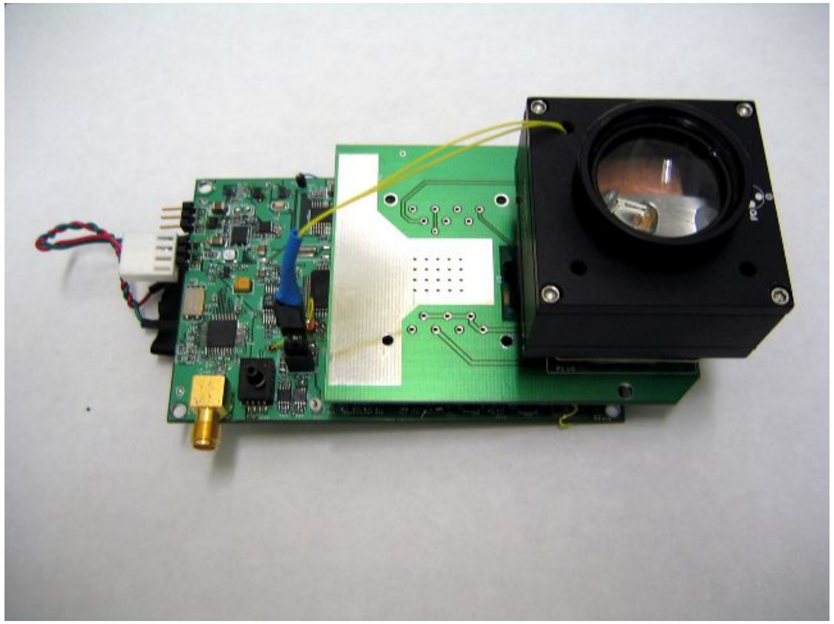


- Each point called "mote"
- Advantages?
  - Spatial resolution
  - Measure fluxes
- What is needed?
  - Low power
  - Low cost
  - Ultra miniature
  - Replicable
  - Autonomy

RICE

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



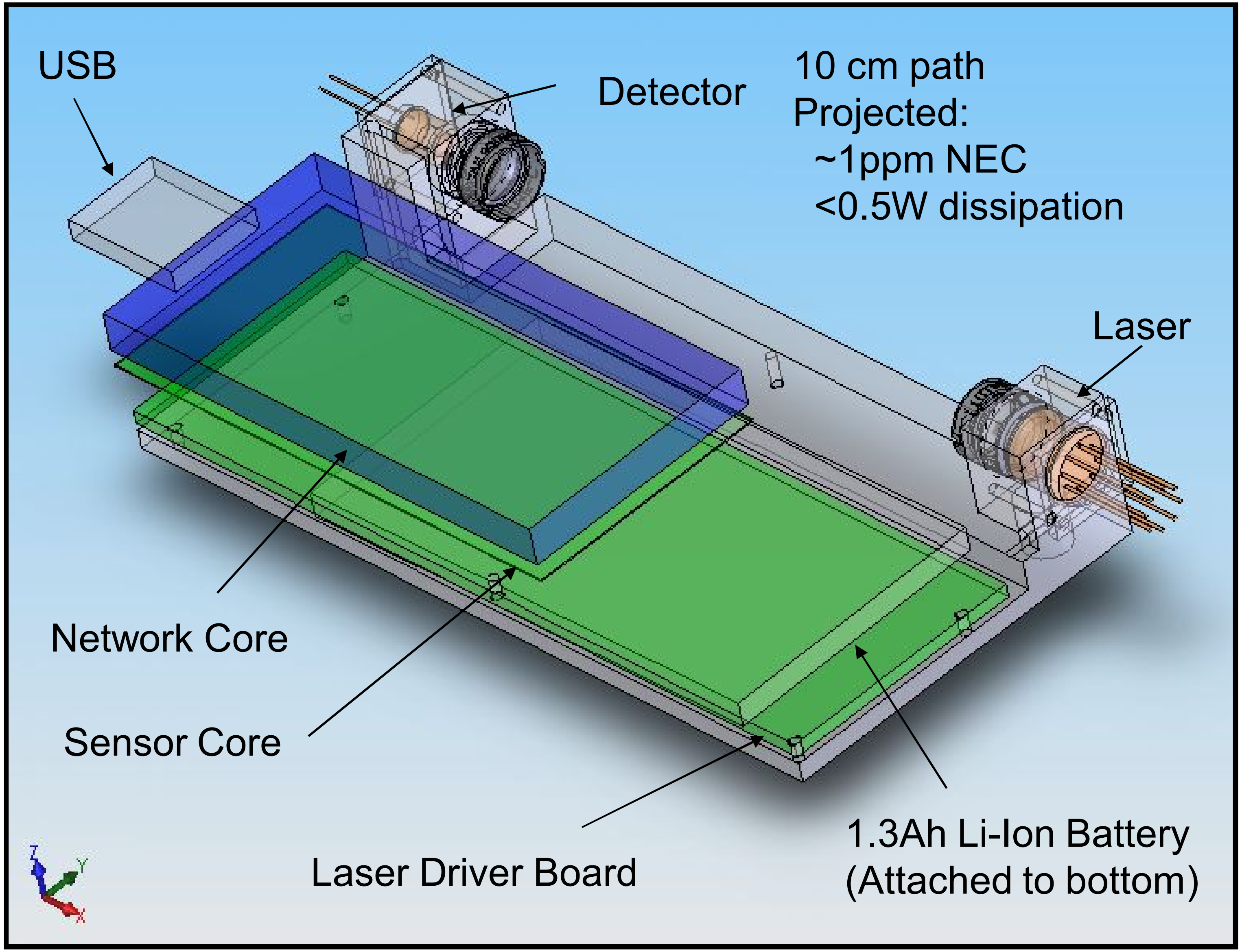


- Small size
- Relatively low cost
- High efficiency switching power supplies
- PWM Peltier cooler driver
- 0.2W control system power consumption
- Detection sensitivity* of CO_2 110 ppm with 1sec. lock-in TC
- Over 10^3 improvement in sensitivity is possible @4.2μm

*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

Miniature LAS CO_2 sensor (λ=2.7μm) boards



Summary & Future Directions of QCL based Gas 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)
  - Capable of fast data acquisition and analysis
  - Detected 13 trace gases to date: NH_3, CH_4, N_2O, CO_2, CO, NO, H_2O, COS, C_2H_4, H_2CO, SO_2, C_2H_5OH, C_2HF_5 and several isotopic species of C, O, N and H.
- **New Applications of Trace Gas Detection**
  - Environmental Monitoring (urban quality - H_2CO and, isotopic ratio measurements of CO_2 and CH_4, fire detection and quantification of engine exhausts)
  - Industrial process control and chemical analysis (NO, NH_3, H_2O, and H_2S)
  - Medical & biomedical diagnostics (NO, NH_3, N_2O, H_2CO and CH_3COCH_3)
  - Hand-held sensors and sensor network technologies (CO_2)
- **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 based on heterogeneous EC-QCL (i.e sensitive concentration measurements of broadband absorbers, in particular VOCs, HCs and multi-species detection)
  - Development of optically gas sensor networks based on QEPAS and LAS

RICE