



# Trends and Innovation of 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/>

OUTLINE

AIOFM

Hefei,  
China

July 7, 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

# 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 University, Houston

---



# Worldwide Megadirty Megacities

	Population, m		Sulphur dioxide	Particulate matter	Lead	Carbon monoxide	Nitrogen dioxide	Ozone
	1990, ext.	2000, proj.						
Bangkok	7.16	10.26	○	●	◊	○	○	○
<b>Beijing</b>	9.74	11.47	●	●	○	-	○	◊
Bombay	11.13	15.43	○	●	○	○	○	-
Buenos Aires	11.58	13.05	-	◊	○	-	-	-
Cairo	9.08	11.77	-	●	●	◊	-	-
Calcutta	11.83	15.94	○	●	○	-	○	-
Delhi	8.62	12.77	○	●	○	○	○	-
Jakarta	9.42	13.23	○	●	◊	◊	○	◊
Karachi	7.67	11.57	○	●	●	-	-	-
London	10.57	10.79	○	○	○	◊	○	○
<b>Los Angeles</b>	10.47	10.91	○	◊	○	◊	◊	●
Manila	8.40	11.48	○	●	◊	-	-	-
Mexico City	19.37	24.44	●	●	◊	●	◊	●
Moscow	9.39	10.11	-	◊	○	◊	◊	-
<b>New York</b>	15.65	16.10	○	○	○	◊	○	◊
Rio de Janeiro	11.12	13.00	◊	◊	○	○	-	-
Sao Paolo	18.42	23.60	○	◊	○	◊	◊	●
Seoul	11.33	12.97	●	●	○	○	○	○
Shanghai	13.30	14.69	◊	●	-	-	-	-
Tokyo	20.52	21.32	○	○	-	○	○	●
Source: United Nations      ● High pollution      ◊ Moderate to heavy pollution      ○ Low pollution      - No data available								

# Monitoring Methane in Rice - Based Agroecosystem

---



# International Space Station

---



# Mars NASA Pathfinder Climate Monitoring

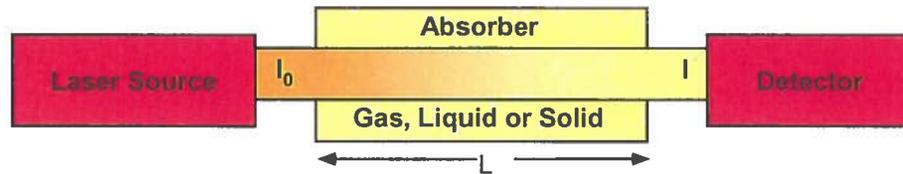
---



# Volcanic Gas Emission Measurements Using Tunable Mid-IR Laser Based Sensors

- Messages from earth's interior
- Study of subsurface magmatic and hydrothermal processes
  - ⇒ Prediction of volcanic eruptions
- Study of environmental impact and medical implications
- Comparison of extractive based semiconductor gas sensors with an open path FTIR gas sensor

# Fundamentals of Laser Absorption Spectroscopy

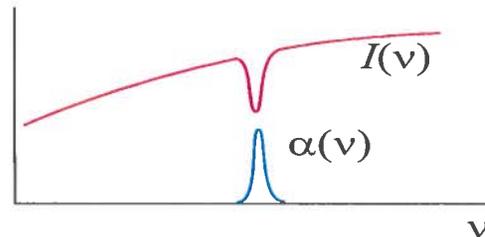


## Beer-Lambert's Law of Linear Absorption

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

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

$\nu$  - frequency [ $\text{cm}^{-1}$ ];  $P_a$  - partial pressure [atm]



$$\alpha(\nu) = C \cdot S(T) \cdot g(\nu - \nu_0)$$

$C$  - total number of molecules of absorbing gas/atm/cm<sup>3</sup> [molecule·cm<sup>-3</sup>·atm<sup>-1</sup>]

$S$  - molecular line intensity [cm·molecule<sup>-1</sup>]

$g(\nu - \nu_0)$  - 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

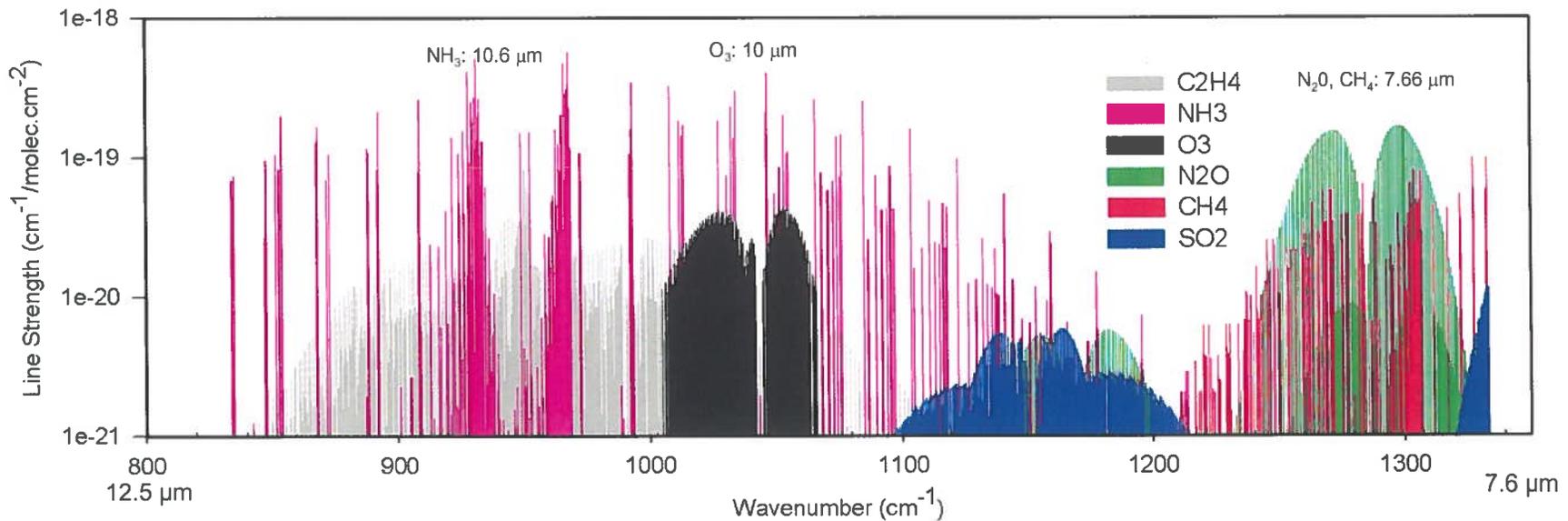
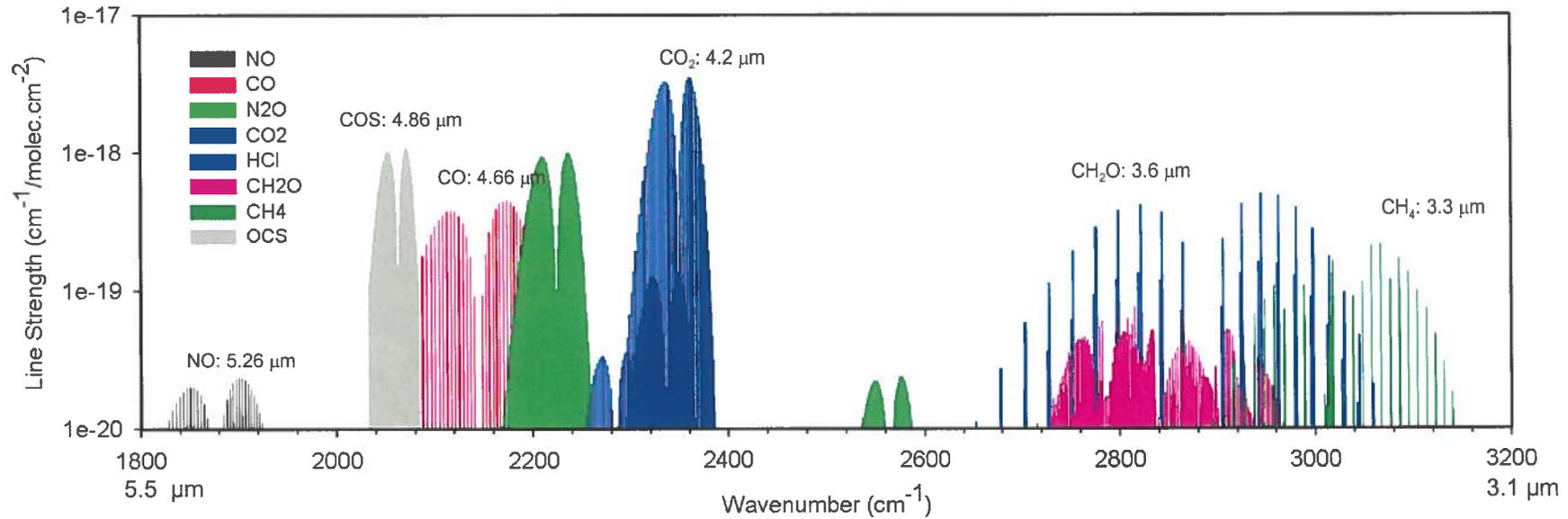
- Wavelength & Frequency Modulation
- Balanced Detection
- Zero-air Subtraction
- Photoacoustic Spectroscopy

# Mid-IR Source Requirements for Laser Spectroscopy

---

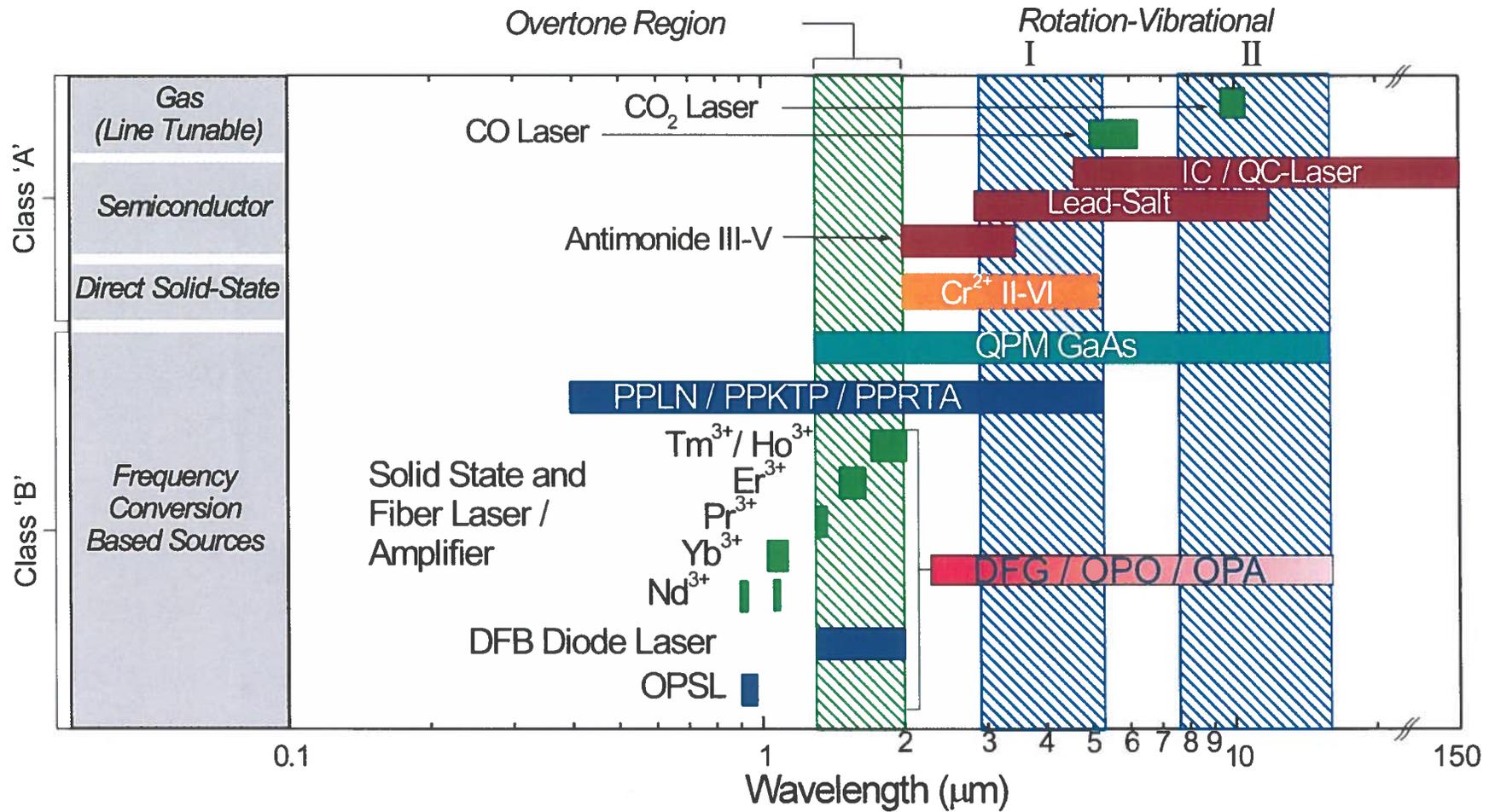
<b><u>REQUIREMENTS</u></b>	<b><u>IR LASER SOURCE</u></b>
<b>Sensitivity (% to ppt)</b>	<b>Wavelength, Power</b>
<b>Selectivity (Spectral Resolution)</b>	<b>Single Mode Operation and Narrow Linewidth</b>
<b>Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers</b>	<b>Tunable Wavelength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

# Molecular Absorption Spectra within the two Mid-IR Atmospheric Windows



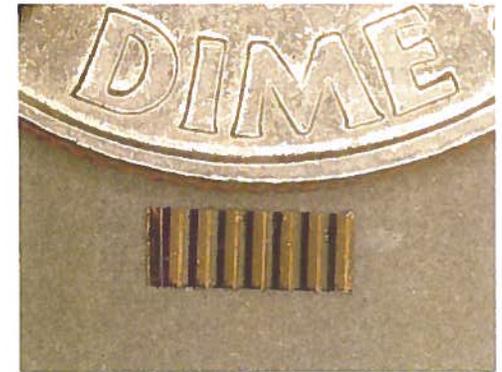
Source: HITRAN 2000 database

# IR Laser Sources and Wavelength Coverage

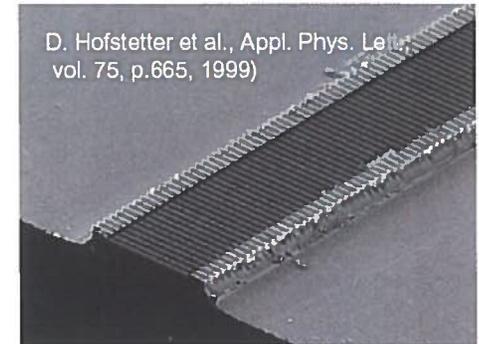


# Key Characteristics of mid-IR QCLs and ICL Sources

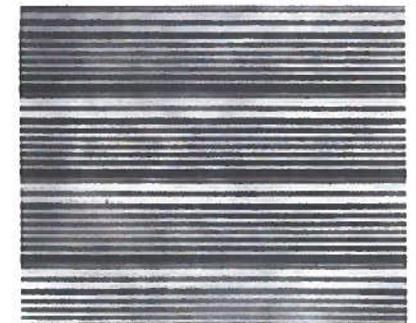
- **Band – structure engineered devices**  
(emission wavelength is determined by layer thickness – MBE or MOCVD);  
mid-infrared QCLs operate from 3 to 24  $\mu\text{m}$
- Compact, reliable, stable, long lifetime, and commercial availability
- Fabry-Perot (FP), single mode (DFB) and multi-wavelength
- **Spectral tuning range in the mid-IR**  
(4-24  $\mu\text{m}$  for QCLs and 3-5  $\mu\text{m}$  for ICLs)
  - 1.5  $\text{cm}^{-1}$  using injection current control
  - 10-20  $\text{cm}^{-1}$  using temperature control
  - > 265  $\text{cm}^{-1}$  using an external grating element and with heterogeneous cascade active region design
- **Narrow spectral linewidth**  
cw: 0.1 - 3 MHz & <10Khz with frequency stabilization ( $0.0004 \text{ cm}^{-1}$ );  
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  $\eta \sim 4\%$ )
  - ~ 50 mW, TEC CW DFB @ 5 and 10  $\mu\text{m}$  Alpes; Princeton,
  - Adtech Optics, Maxion Technologies, Hamamatsu, Daylight  
~ 300 mW @ 8.3  $\mu\text{m}$  (Agilent Technologies & Harvard)
  - > 600 mW (CW FP) @RT & a wall plug efficiency of >9.3%;  
>150 mW (CW DFB) at 298 K (Northwestern)



4 mm

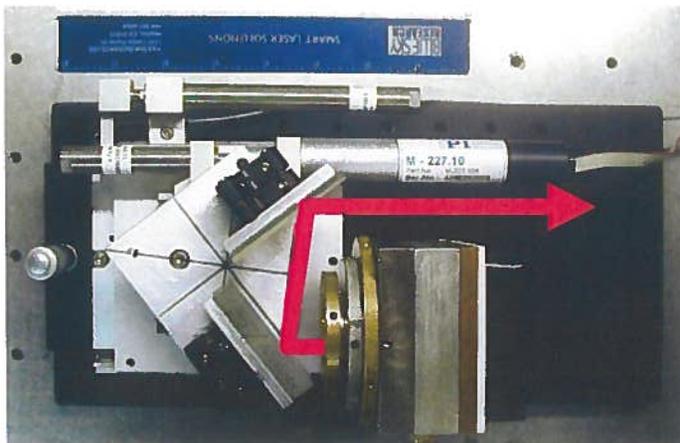
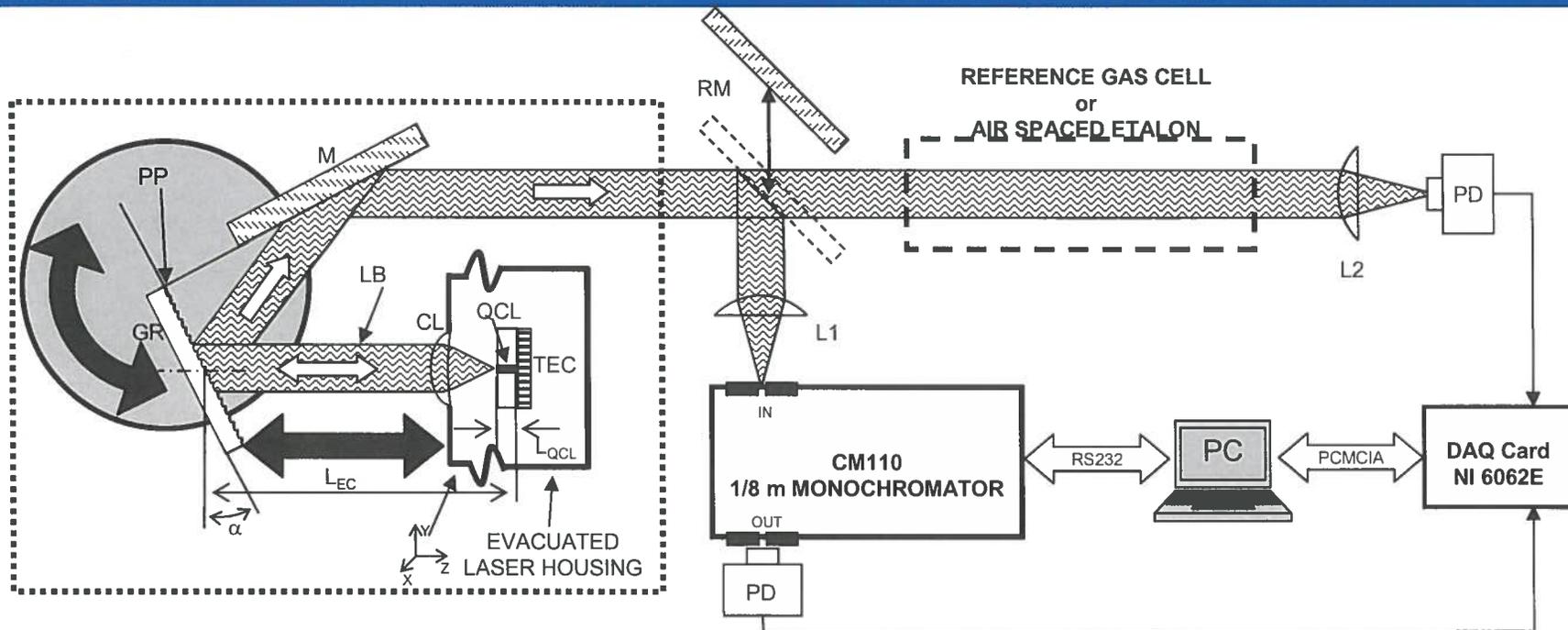


45 nm



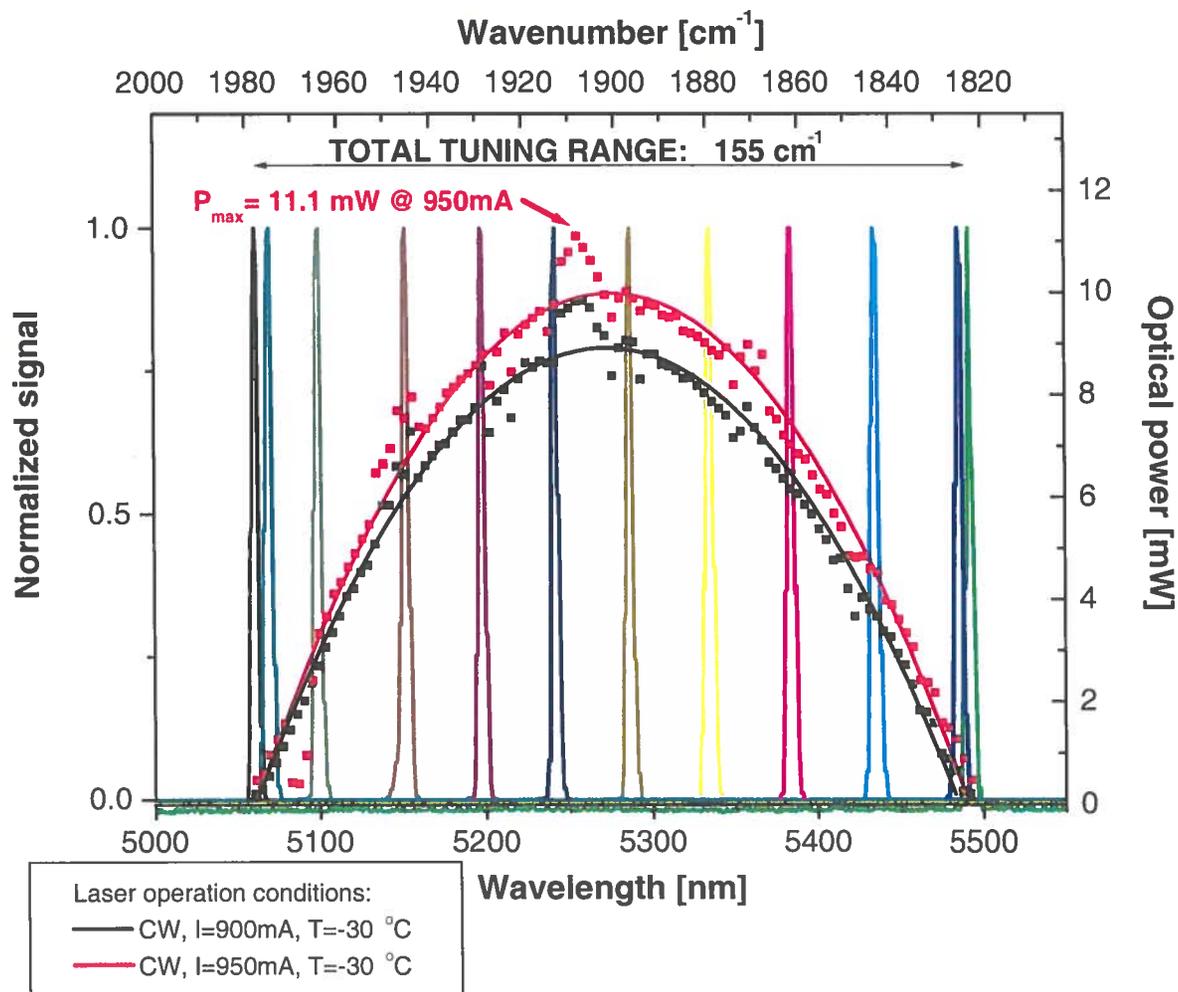
# Widely Tunable, CW, TEC Quantum Cascade Lasers

# Tunable external cavity QCL based spectrometer

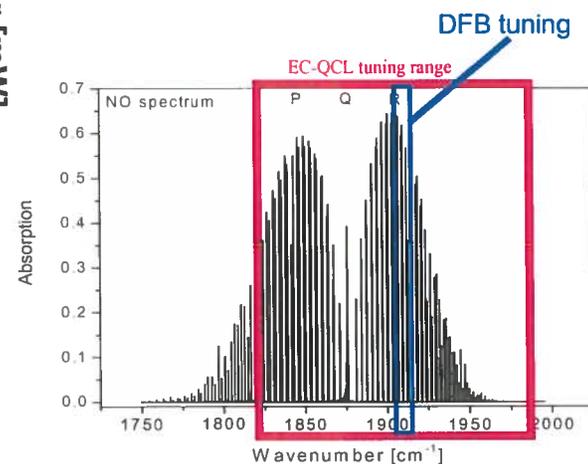


- Fine wavelength tuning
  - PZT controlled EC-length
  - PZT controlled grating angle
  - QCL current control
- Motorized coarse grating angle tuning
- Vacuum tight QCL enclosure with build-in 3D lens positioner (TEC laser cooling + optional chilled water cooling)

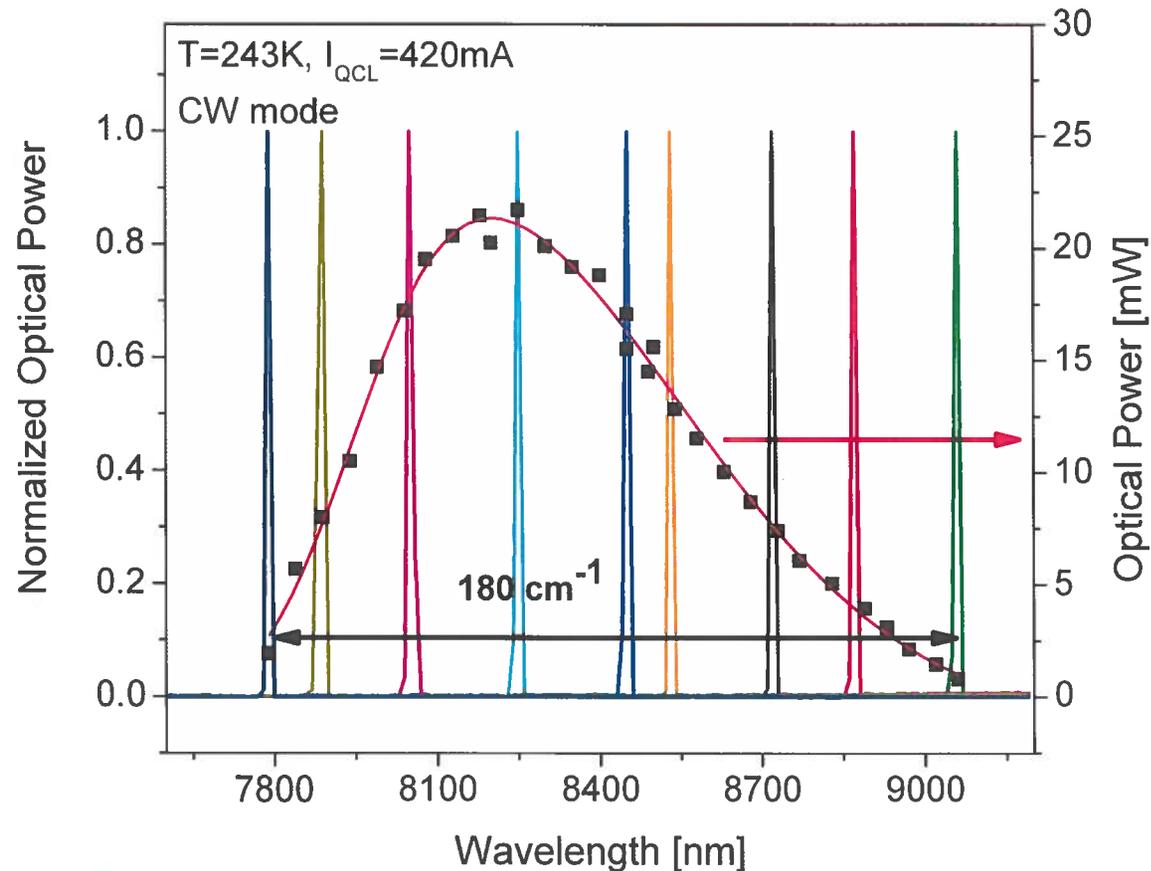
# Wide Wavelength Tuning of a 5.3 $\mu\text{m}$ EC-QCL



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



# Performance of 8.4 $\mu\text{m}$ EC-QCL Spectroscopic Source



Tunability  **$180\text{ cm}^{-1}$**  @  $8.4\ \mu\text{m}$  ( $1100$  to  $1280\text{ cm}^{-1}$ )

AR coating:

$$R_{\text{AR}} \approx 2 \times 10^{-4}$$

$P_{\text{EC-opt}}$  up to **50 mW (cw)**;

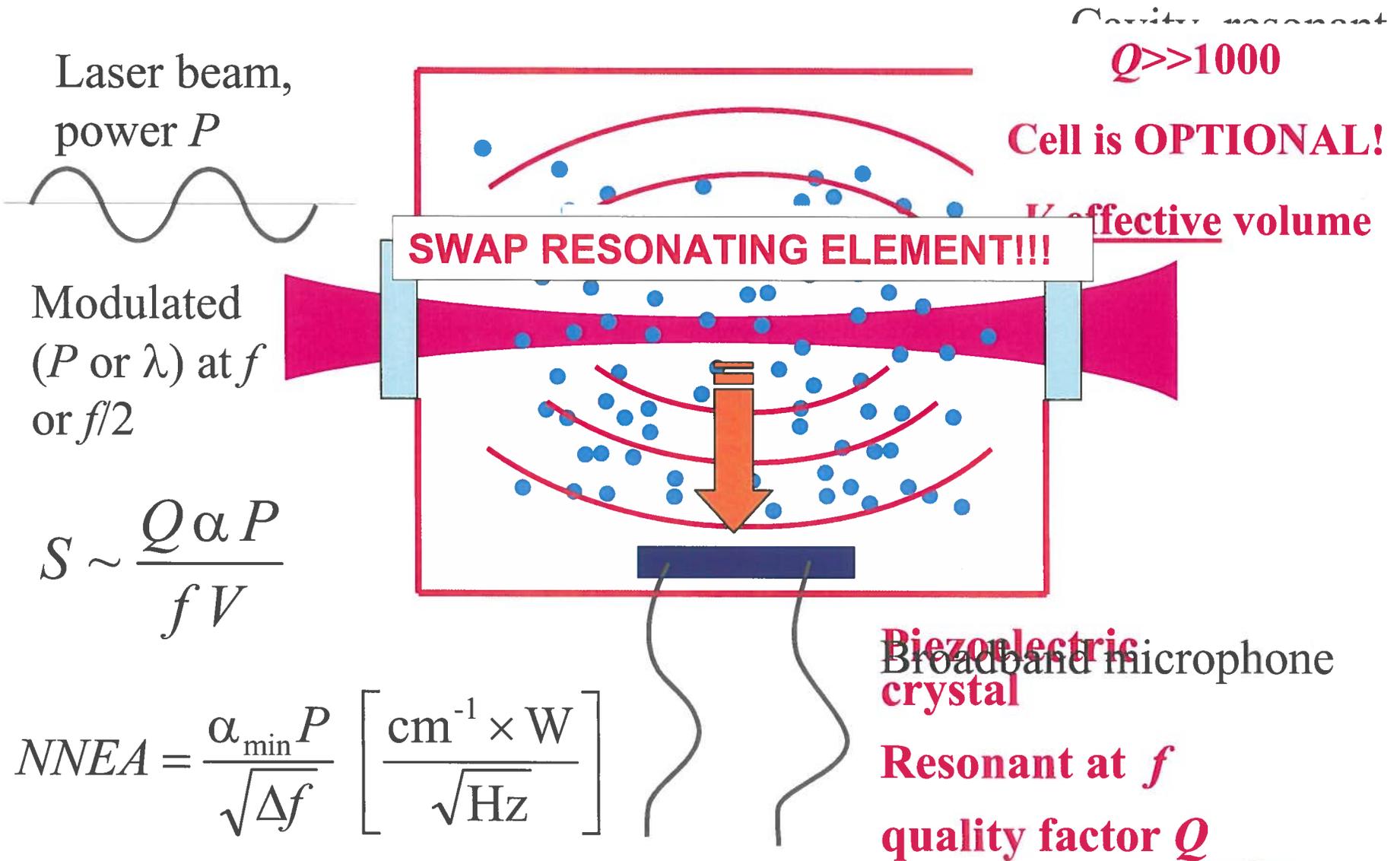
**also ~ 100 mW**

( $I_{\text{QCL}} = 680\text{ mA} \rightarrow P = 44\text{ mW}$ )



# Quartz Enhanced Photoacoustic Spectroscopy

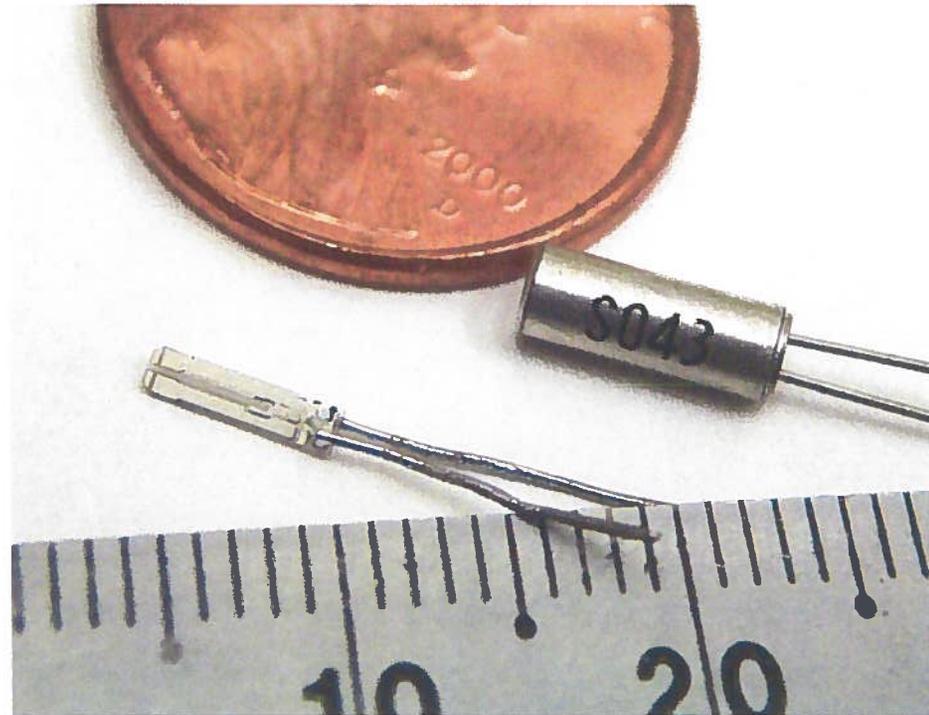
# From conventional PAS to QEPAS



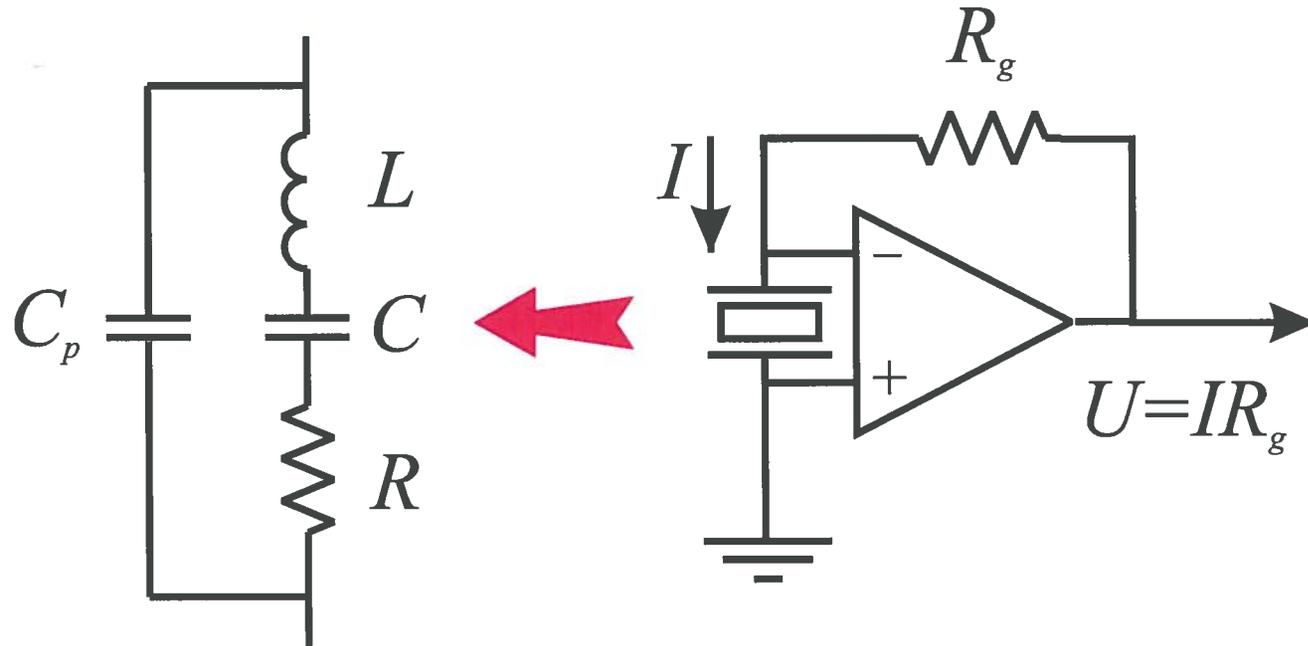
# Quartz Tuning Fork (TF) as a Resonant Microphone



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



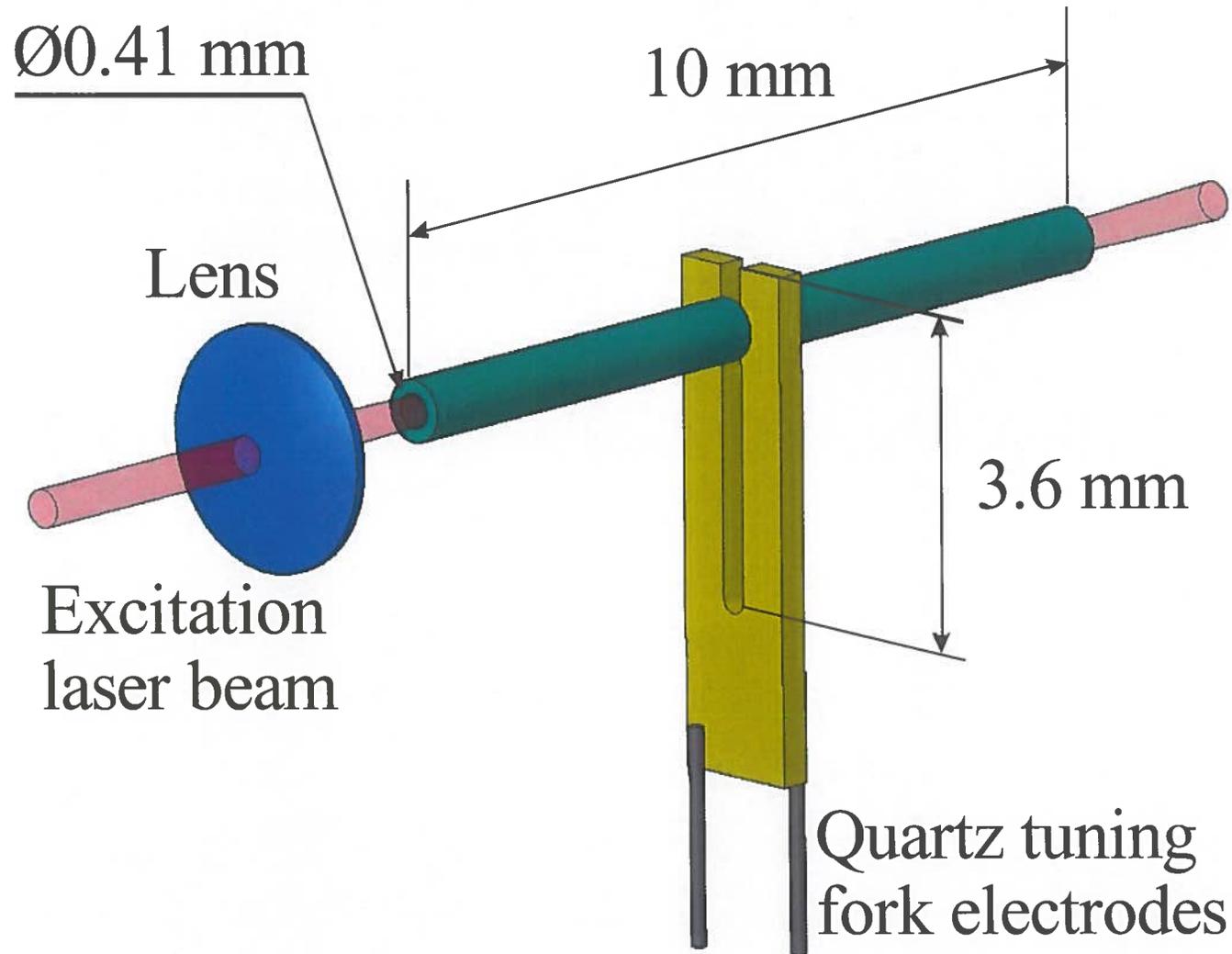
# QEPAS Signal Detection



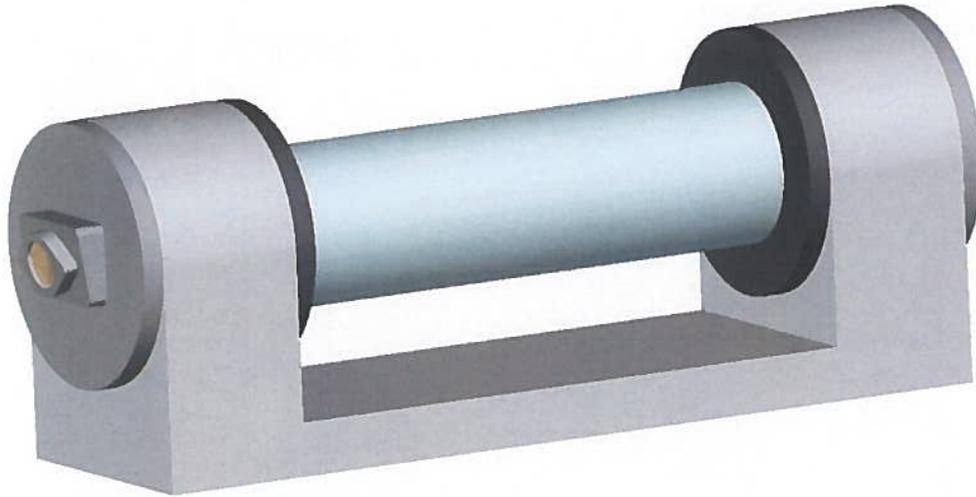
Amplifier:

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

# Absorption Detection Module for QEPAS based Gas Sensor

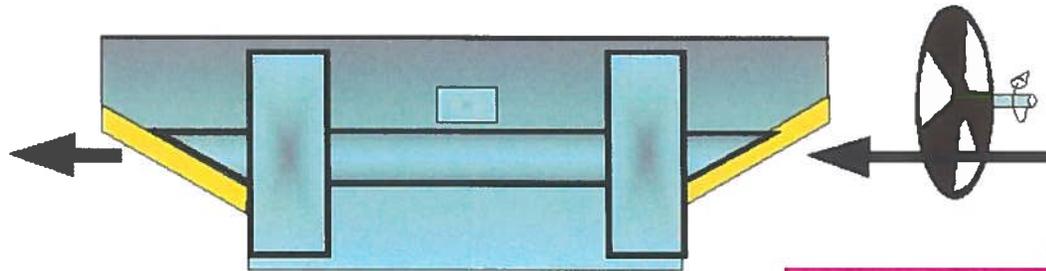


# Comparative Size of Absorption Detection Modules (ADM)



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

Optical multipass cell (100 m):  
 $l \sim 70$  cm,  $V \sim 3000$  cm<sup>3</sup>



Resonant photoacoustic cell (1000 Hz):  
 $l \sim 60$  cm,  $V \sim 50$  cm<sup>3</sup>

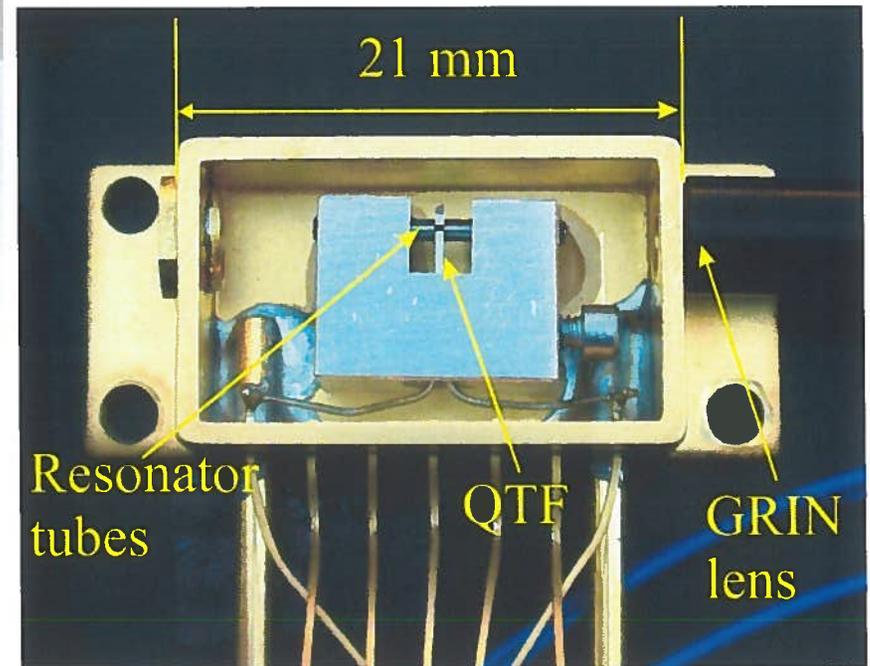
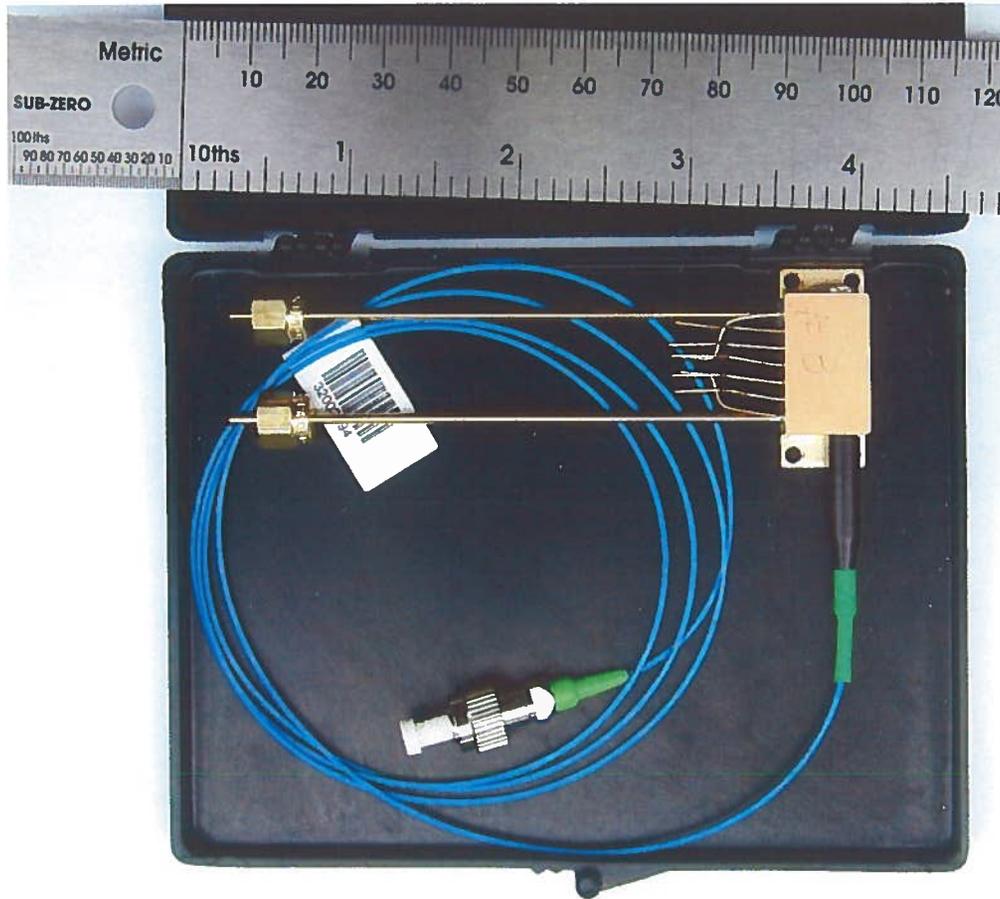


QEPAS spectrophone:  
 $l \sim 1$  cm,  $V \sim 0.05$  cm<sup>3</sup>



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 ( $< 1 \text{ mm}^3$ )
- Applicable over a wide range of pressures
- Temperature, pressure and humidity insensitive
- Rugged and low cost (compared to other optical sensor architectures)

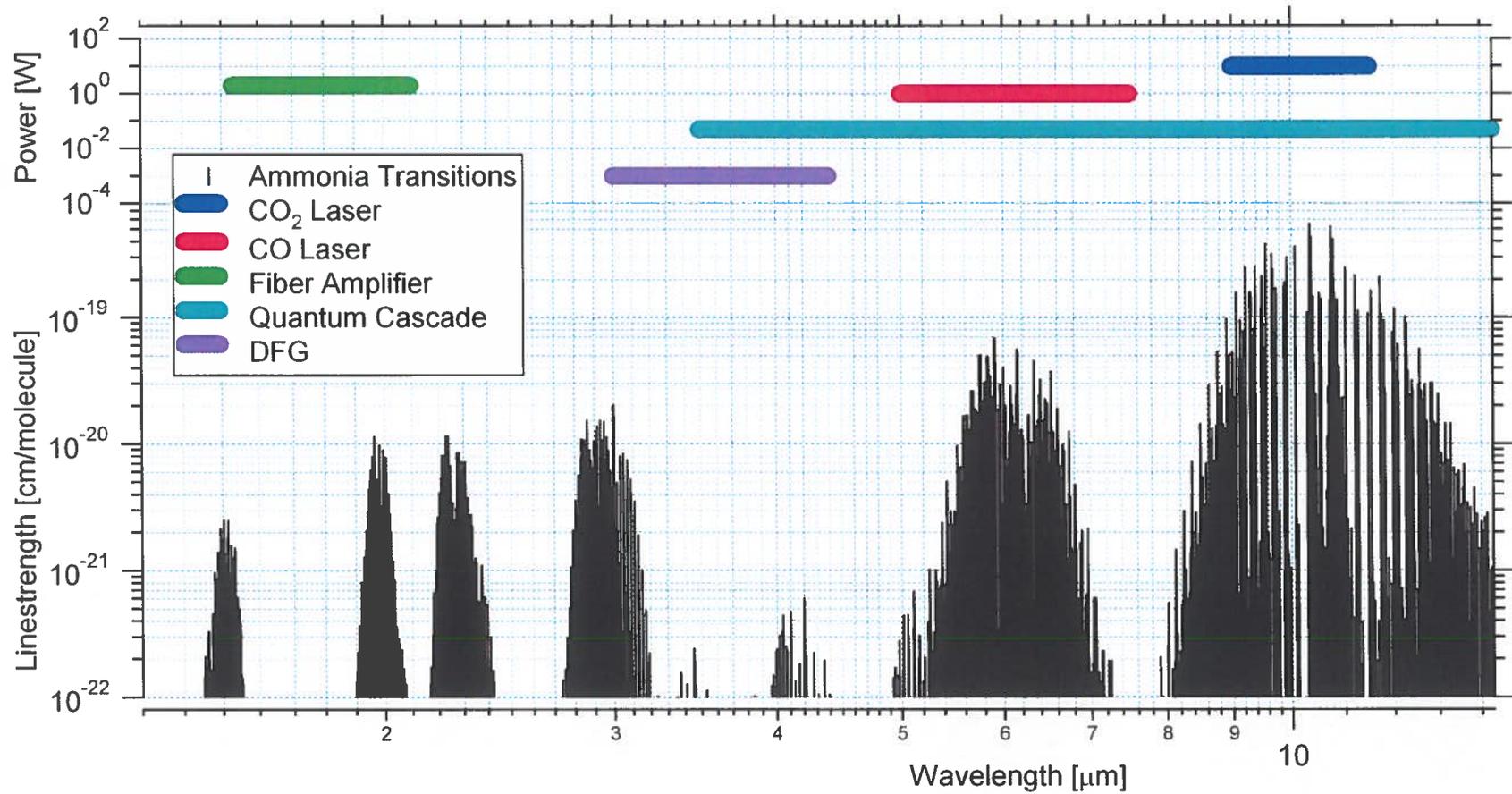
# Trace Gas Sensing Examples

# Motivation for NH<sub>3</sub> Detection

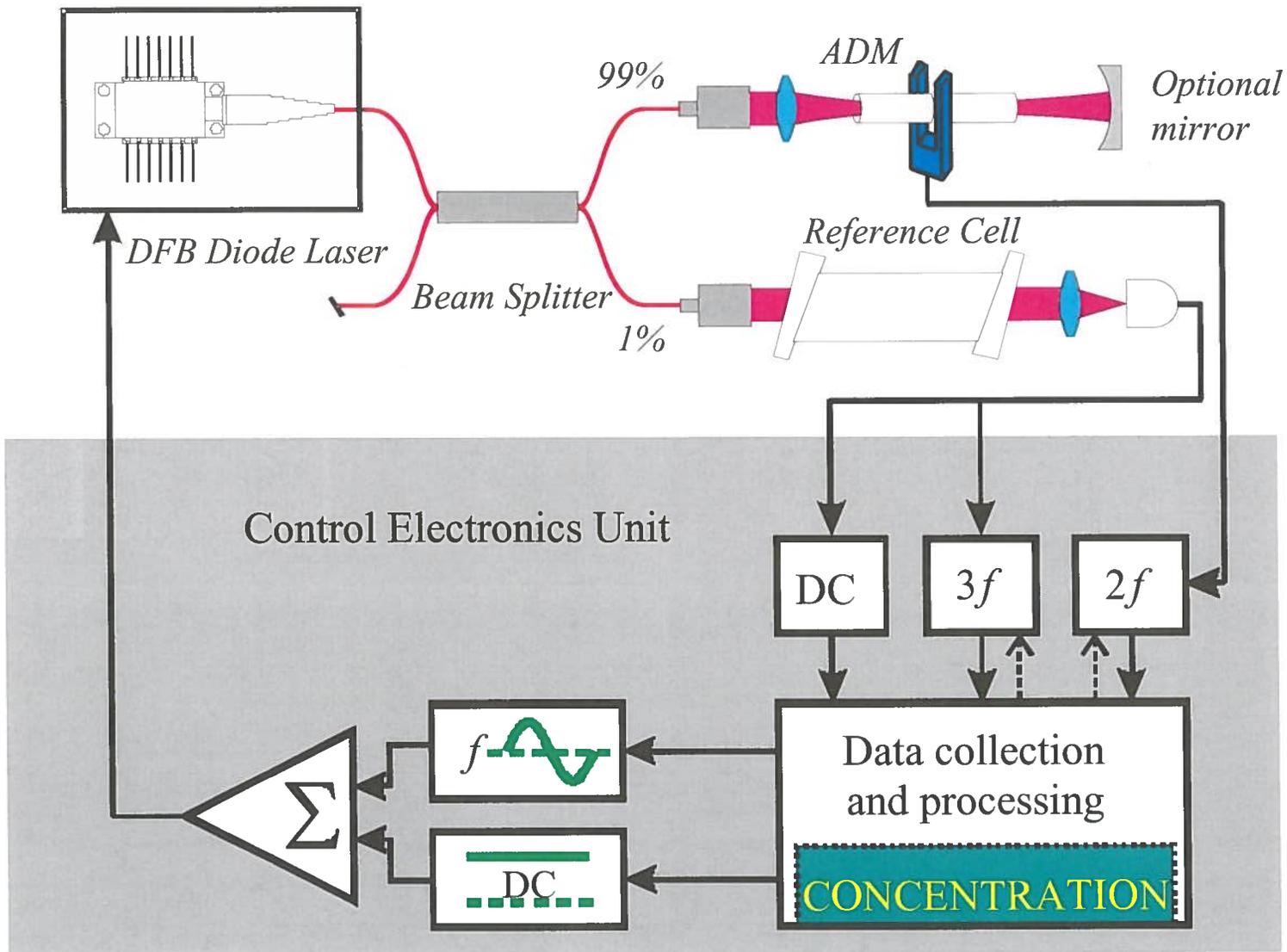
---

- Monitoring of gas separation processes
- Detection of ammonium-nitrate explosives
- Spacecraft related gas monitoring
- Monitoring NH<sub>3</sub> concentrations in the exhaust stream of NO<sub>x</sub> 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)

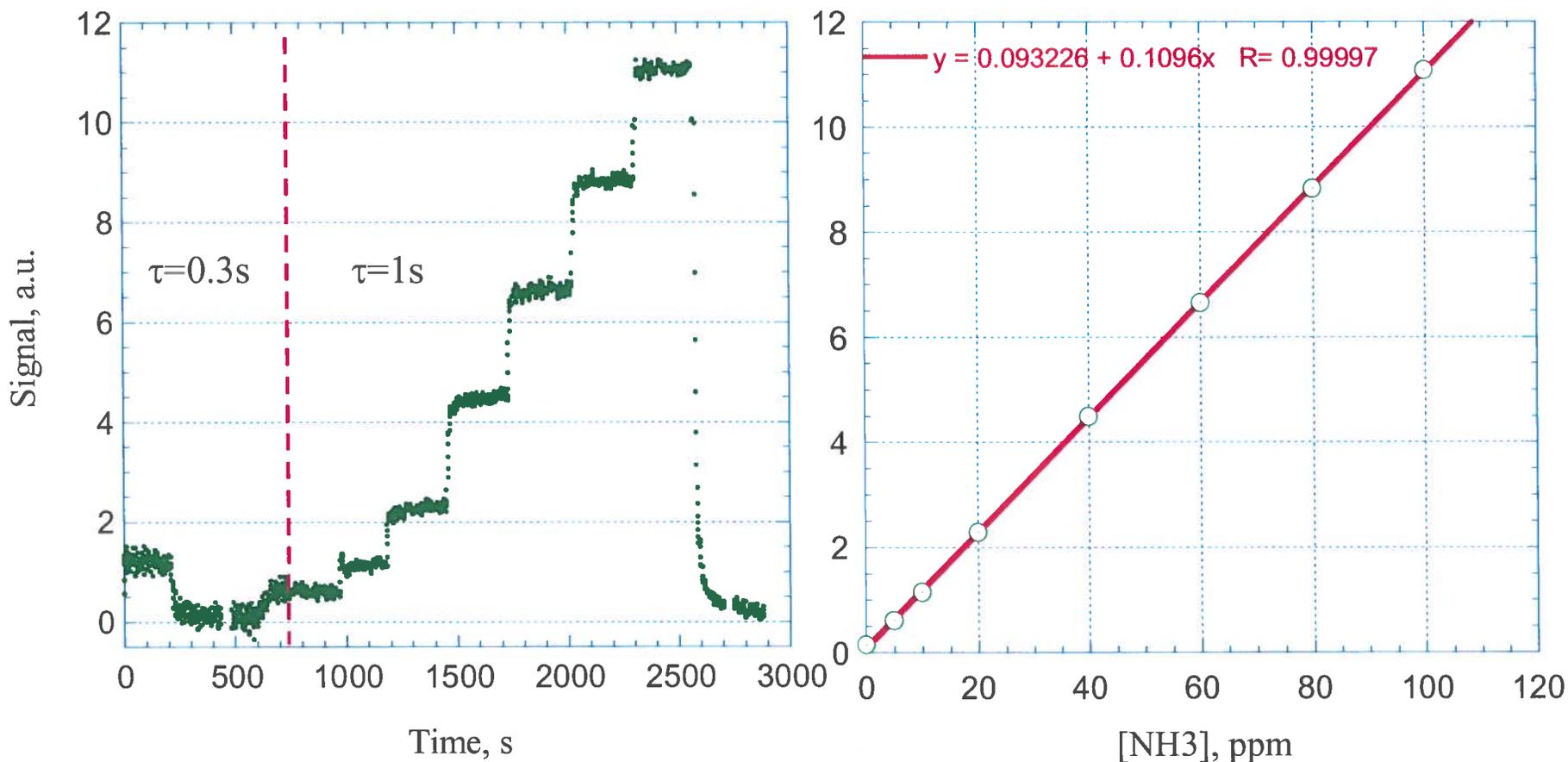
# Infrared NH<sub>3</sub> Absorption Spectra



# QEPAS based Gas Sensor Architecture



# Calibration and Linearity of a 1.53 $\mu\text{m}$ QEPAS based $\text{NH}_3$ Sensor



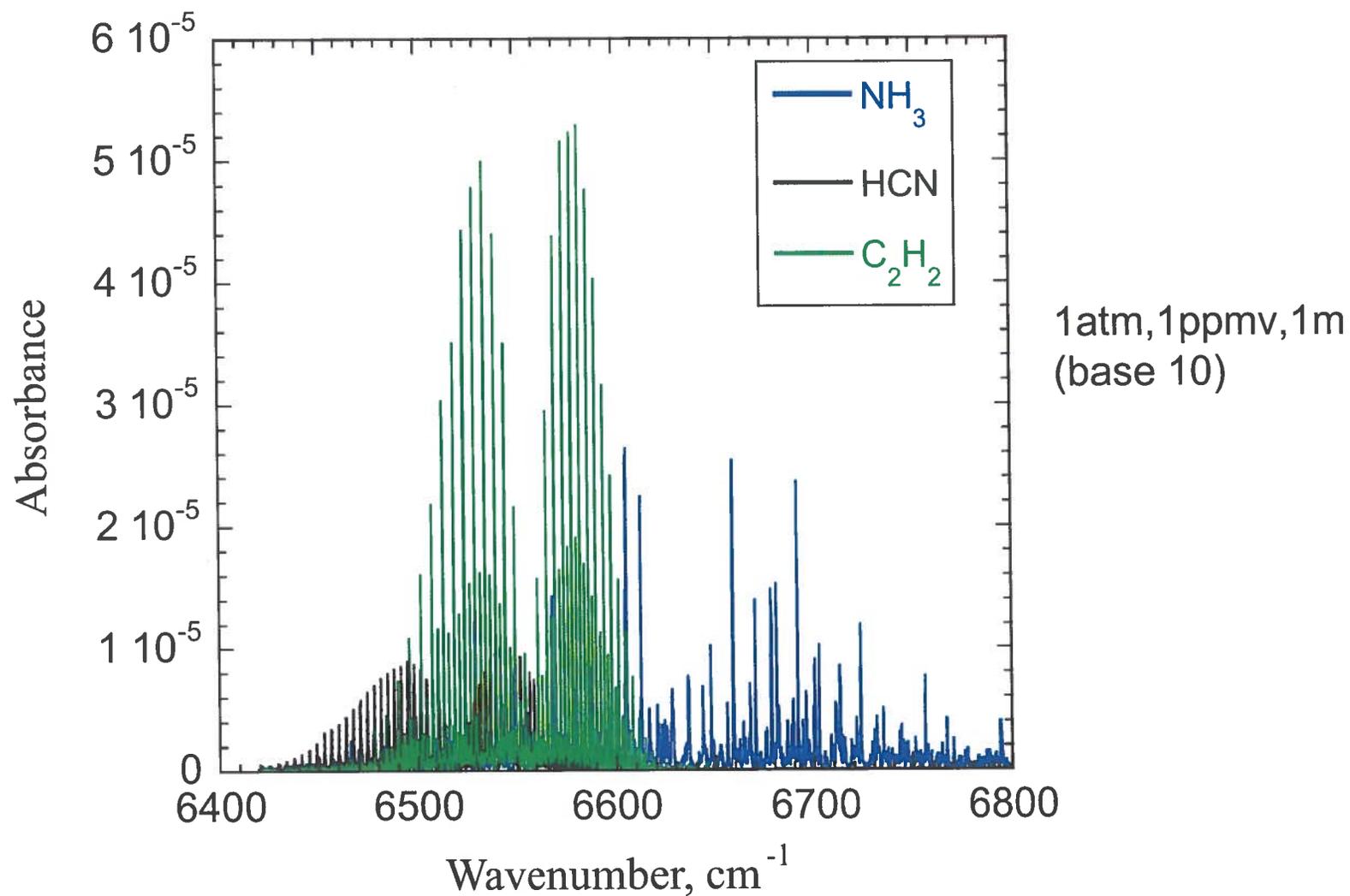
Noise-equivalent concentration (NEC).  
for  $t=1\text{s}$  time constant is 0.06 ppm for  
60mW excitation power at  $6528.76\text{ cm}^{-1}$

90 last points of each step averaged

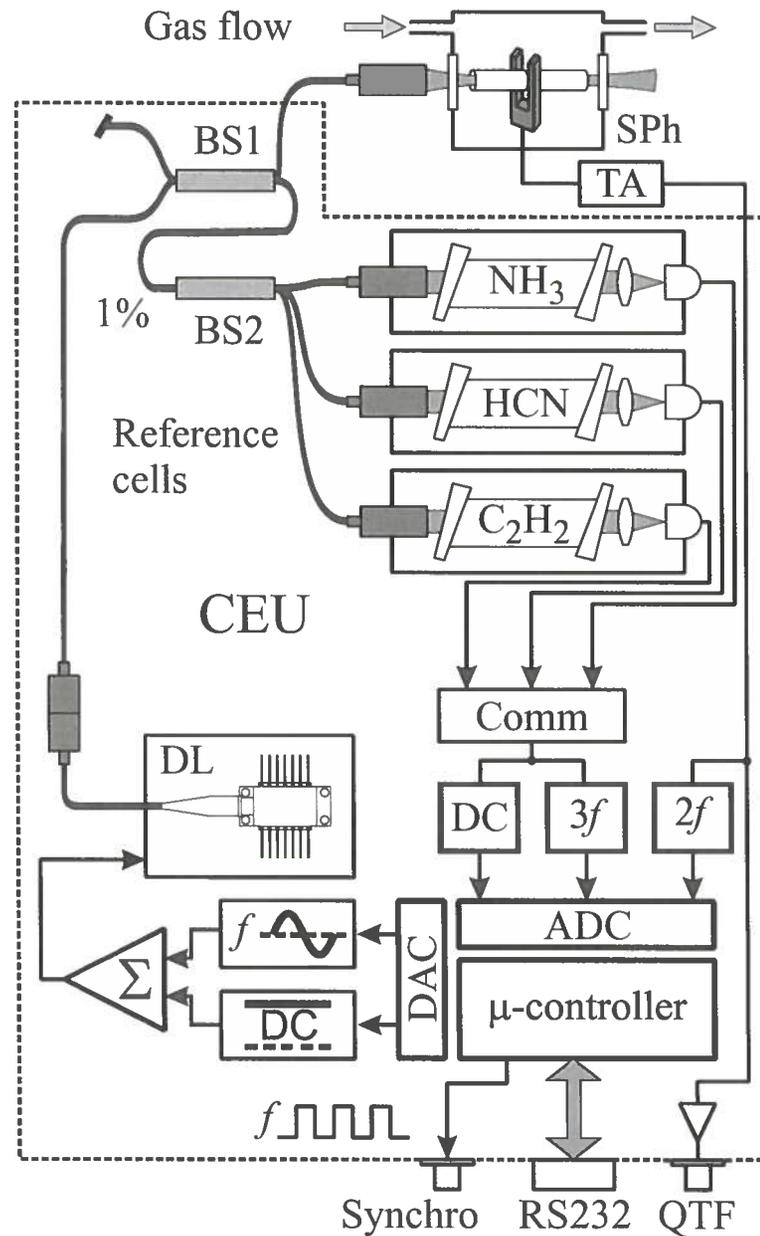
**Noise-equivalent absorption (NEA) coefficient  $k=3.1 \times 10^{-9}\text{ cm}^{-1}\text{W}/\text{Hz}^{1/2}$**



# Infrared $\text{NH}_3$ , $\text{HCN}$ and $\text{C}_2\text{H}_2$ Absorption Spectra



# QEPAS based Multi-Gas Sensor Architecture



# Biomarkers Present in Exhaled Human Breath

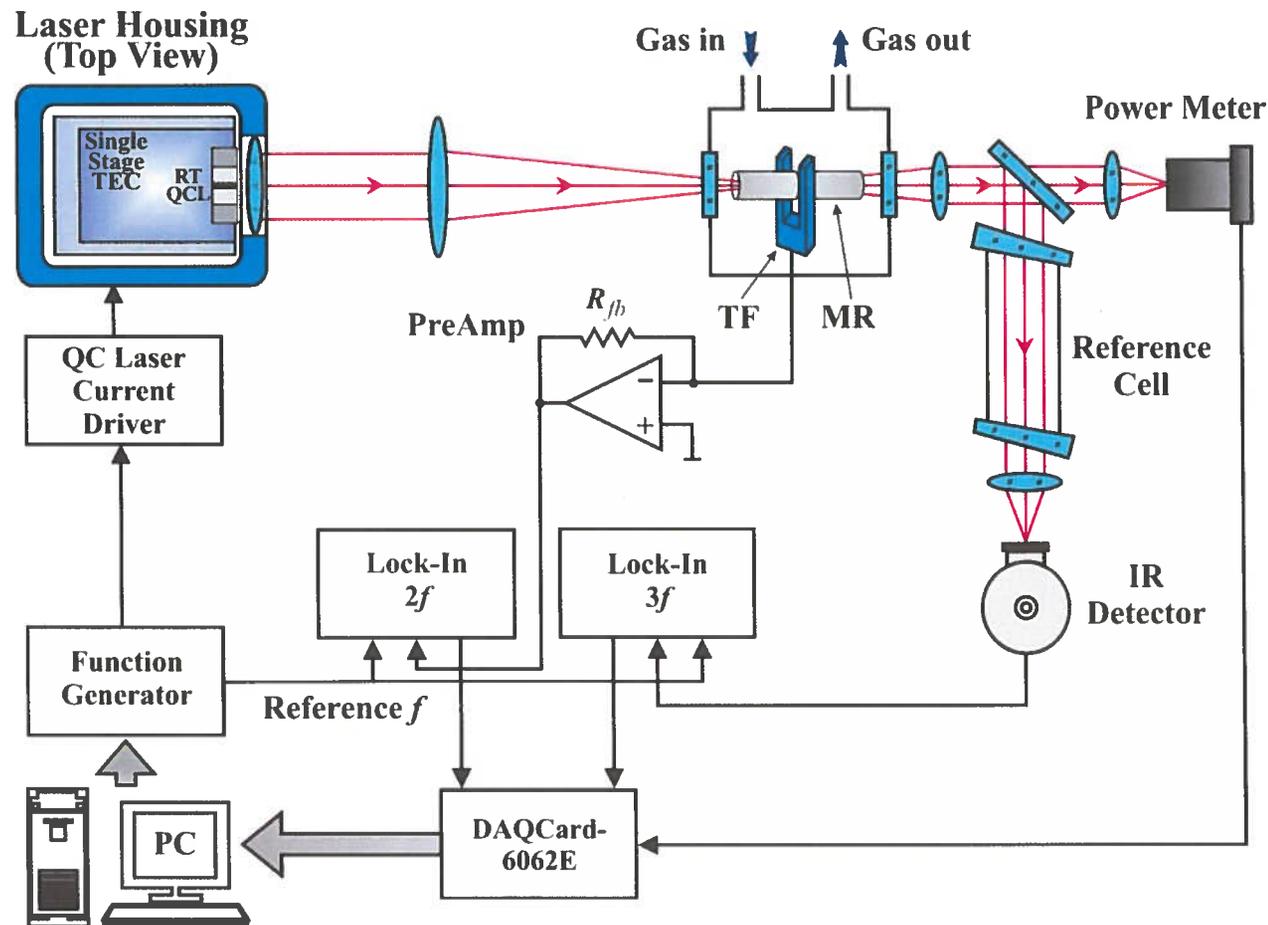
More than 400 different molecules in breath;  
many with well defined biochemical pathways

**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, Helicobacter pylori
Carbon disulfide	ppb	Gut bacteria, schizophrenia
Carbon monoxide	ppm	Production catalyzed by <i>heme oxygenase</i>
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 <i>nitric oxide synthase</i>
Oxygen	%	Required for normal respiration
Pentane	ppb	Lipid peroxidation, oxidative stress
Water	%	Product of respiration

# 9.56 $\mu\text{m}$ CW DFB QCL based QEPAS Ammonia Sensor



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

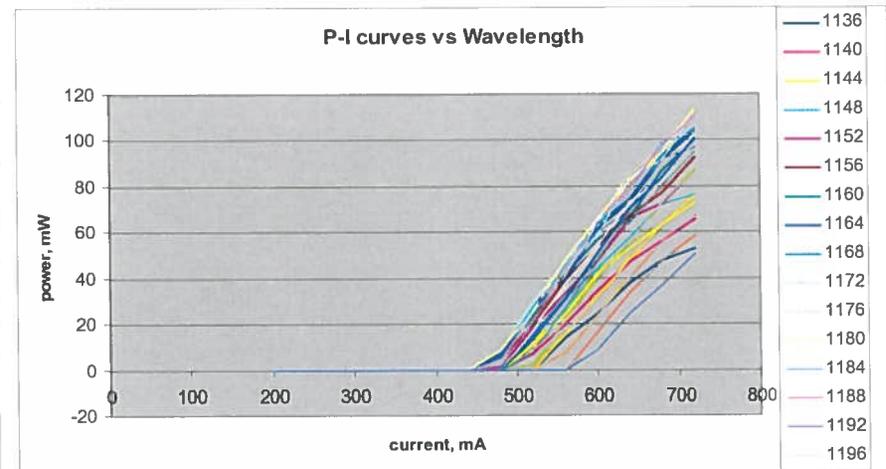
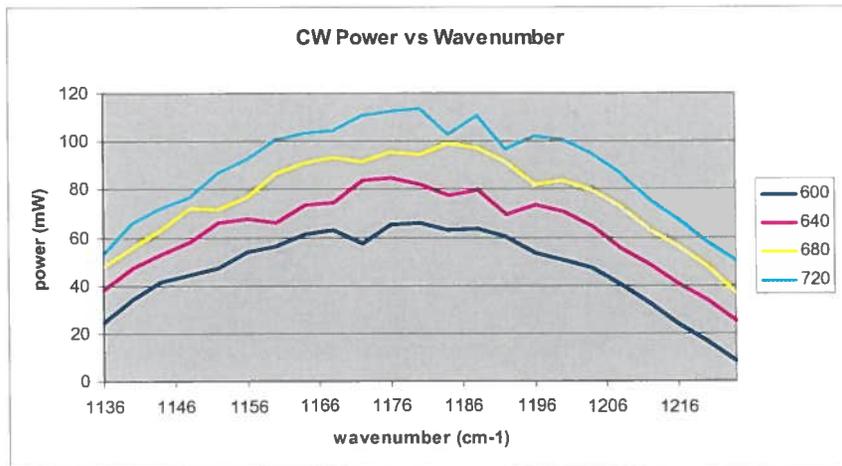
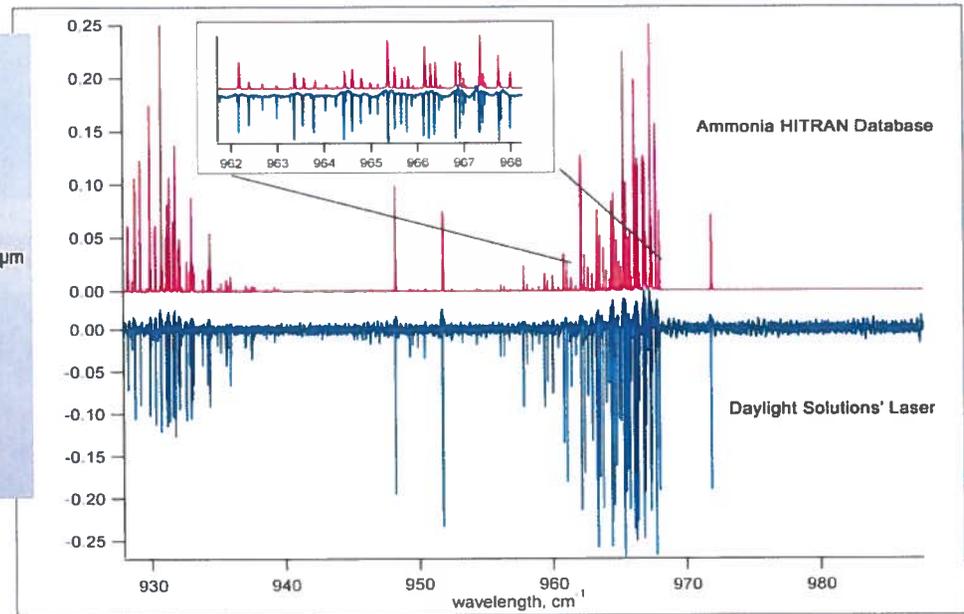


# Commercial widely tunable cw EC-QCL

## Mid-IR Lasers From Daylight Solutions



- CW, Mode-Hop Free
- Linewidth <math> < 0.001 \text{ cm}^{-1}</math>
- Center wavelengths from 4 to 12  $\mu\text{m}$
- Broad tuning range up to 10%
- No cryogenic cooling
- Average power up to 50 mW
- Tuning speed: full range <math> < 2\text{s}</math>
- Superb wavelength accuracy
- Shipping in September 2007



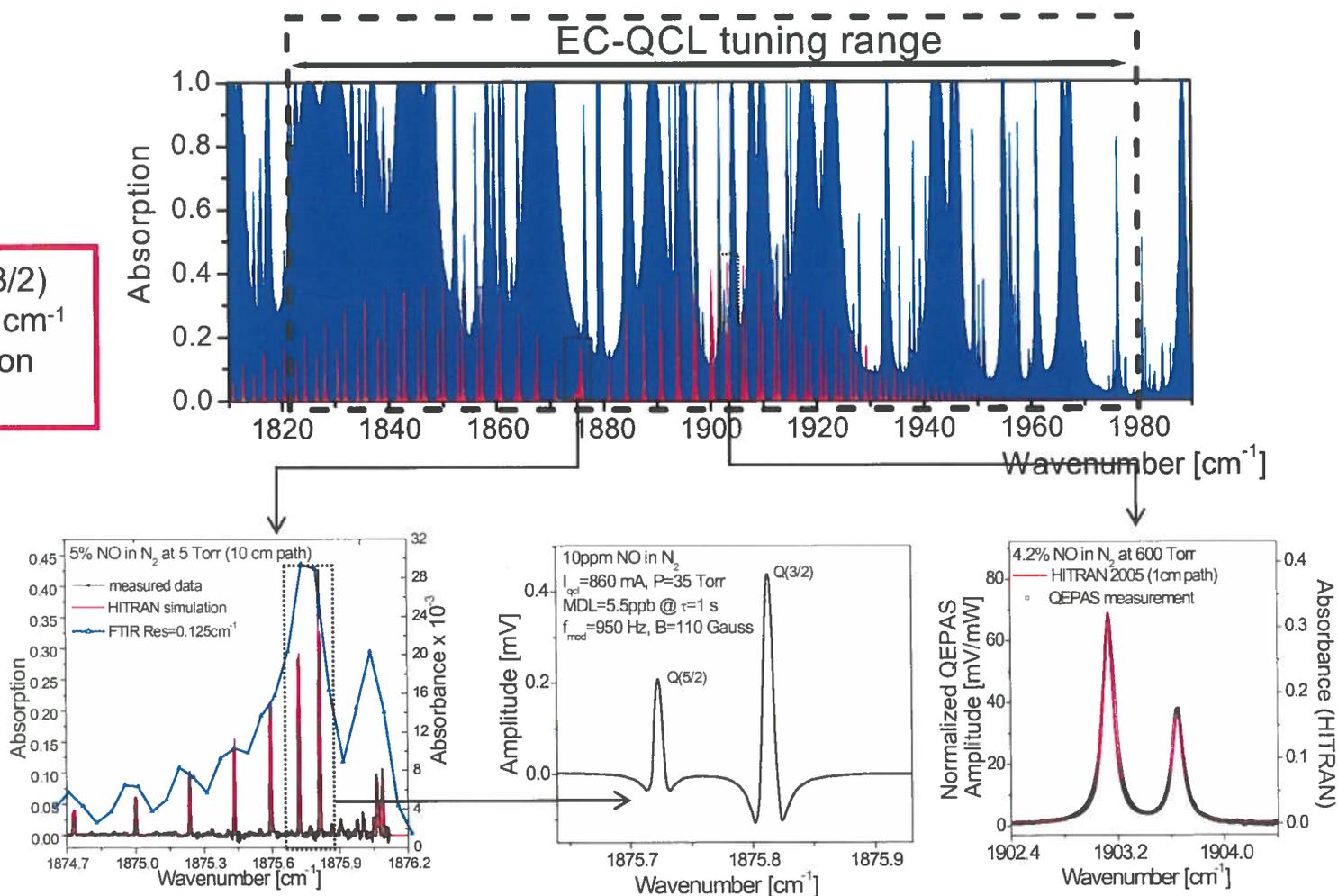
# Motivation for Nitric Oxide Detection

---

- Atmospheric Chemistry
- Environmental pollutant gas monitoring
  - $\text{NO}_x$  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

# High resolution spectroscopy with a 5.3 $\mu\text{m}$ EC-QCL

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

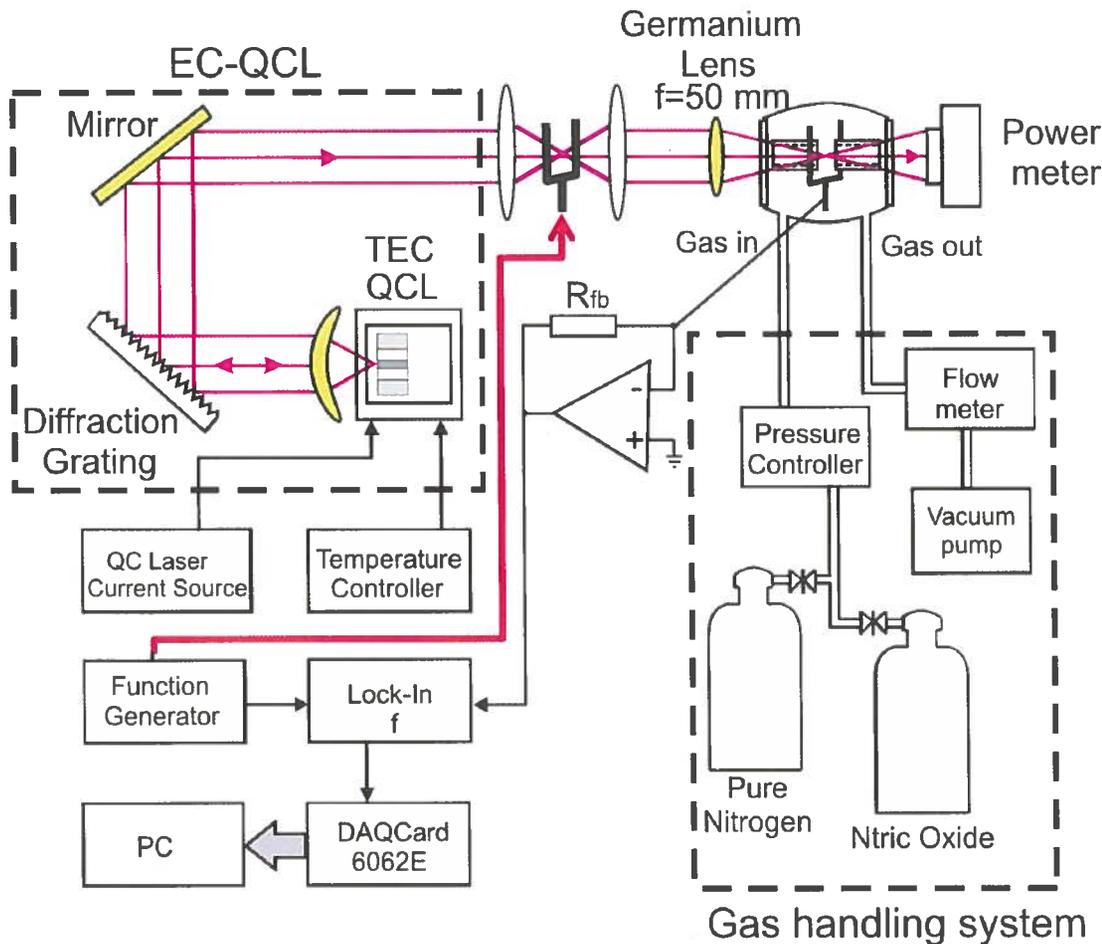


- Mode hop free scan of up to  $\sim 2.5 \text{ cm}^{-1}$  with a resolution  $< 0.001 \text{ cm}^{-1}$  (30MHz) can be performed anywhere within the tuning range

In collaboration with:



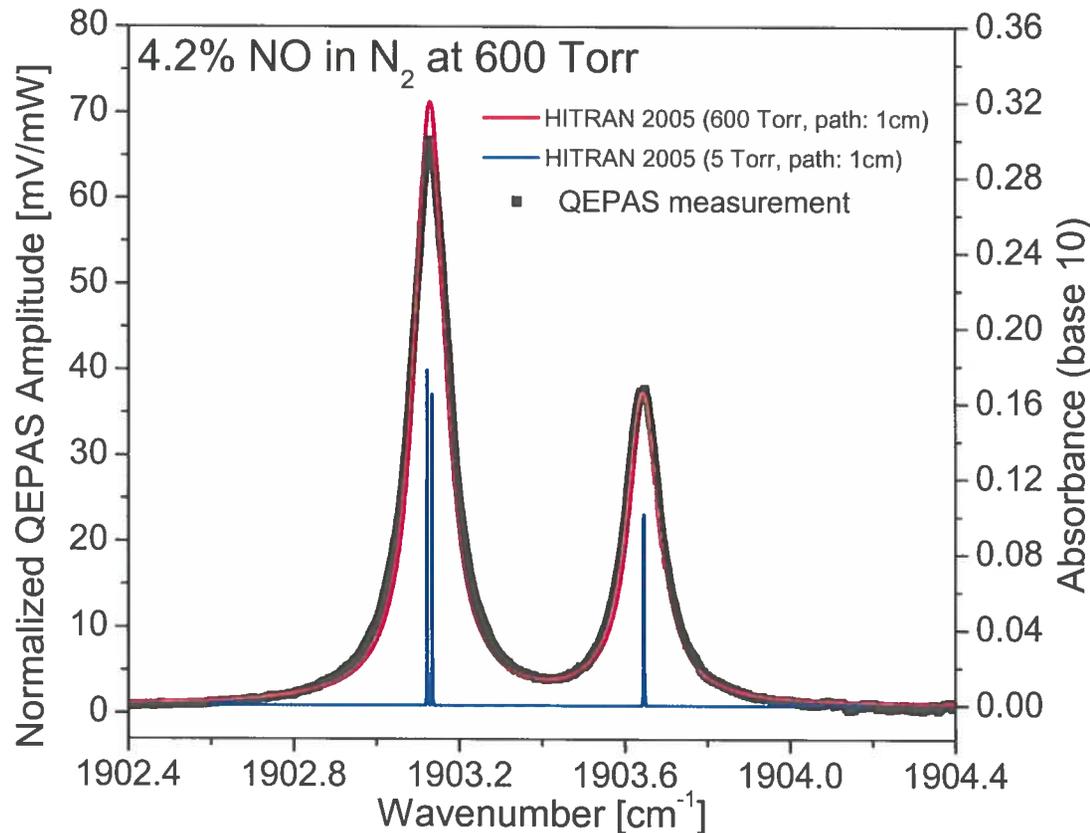
# QCL based Quartz-Enhanced Photoacoustic Gas Sensor



## QEPAS characteristics:

- High sensitivity (ppm to ppb)
- Excellent dynamic range
- Immune to environmental noise
- Ultra-small sample volume ( $< 1\text{ mm}^3$ )
- 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

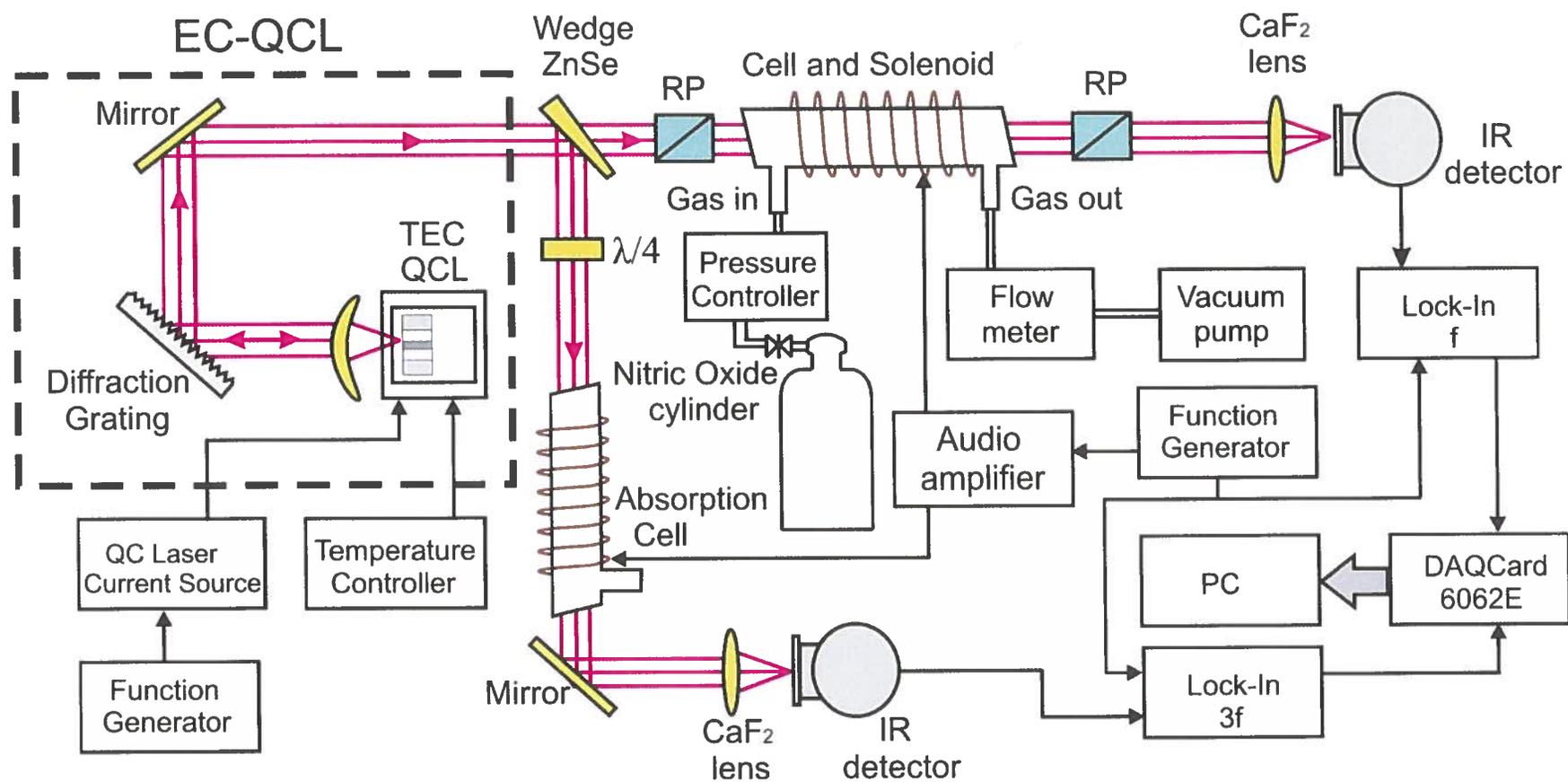


## External Amplitude Modulation:

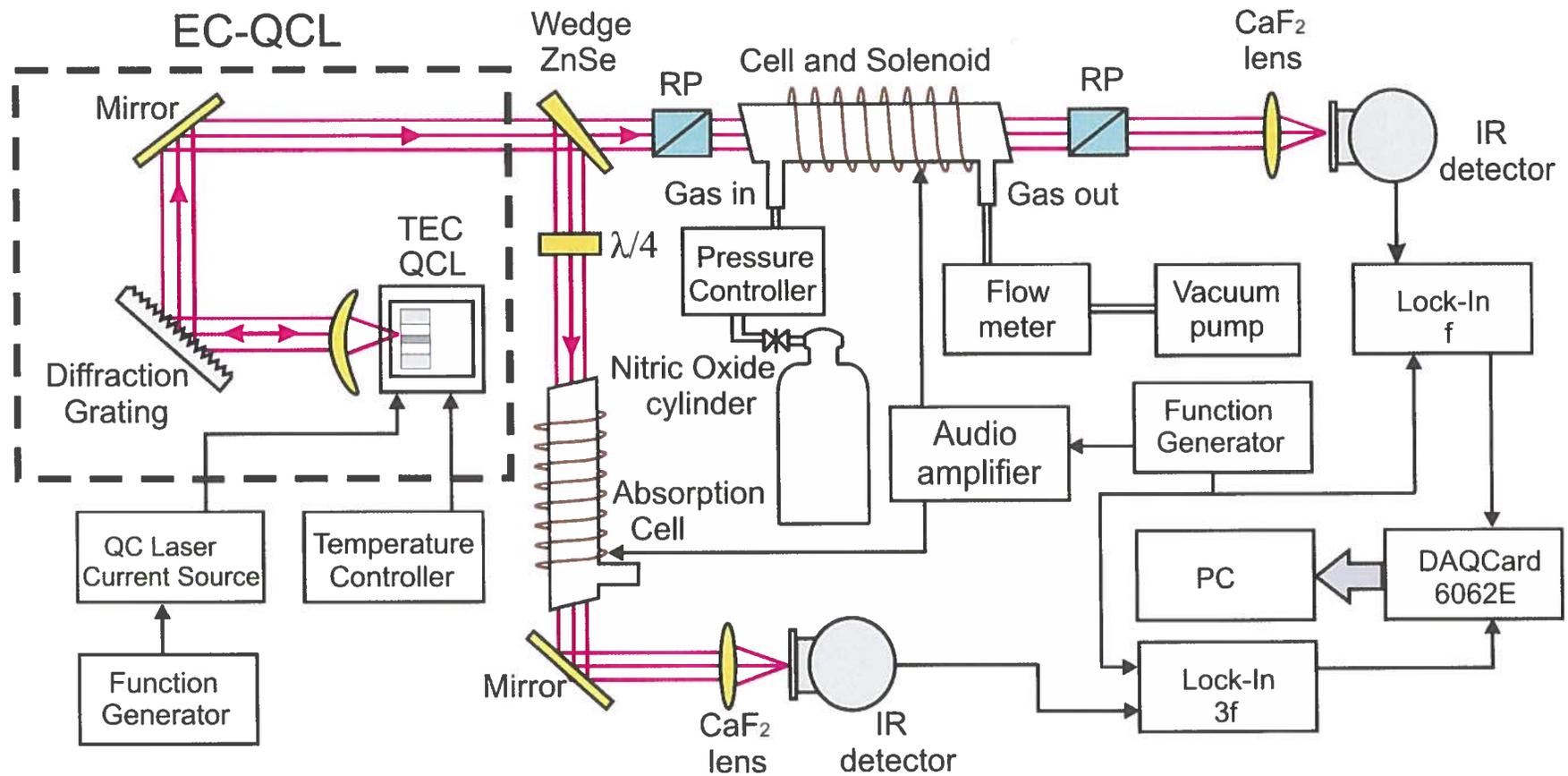
- QTF is used as a mechanical chopper at  $f \sim 32\text{kHz}$
- No chirp associated with the laser current modulation
- High resolution mode-hop-free tuning is possible



# EC-QCL based Magnetic Rotation Spectroscopy

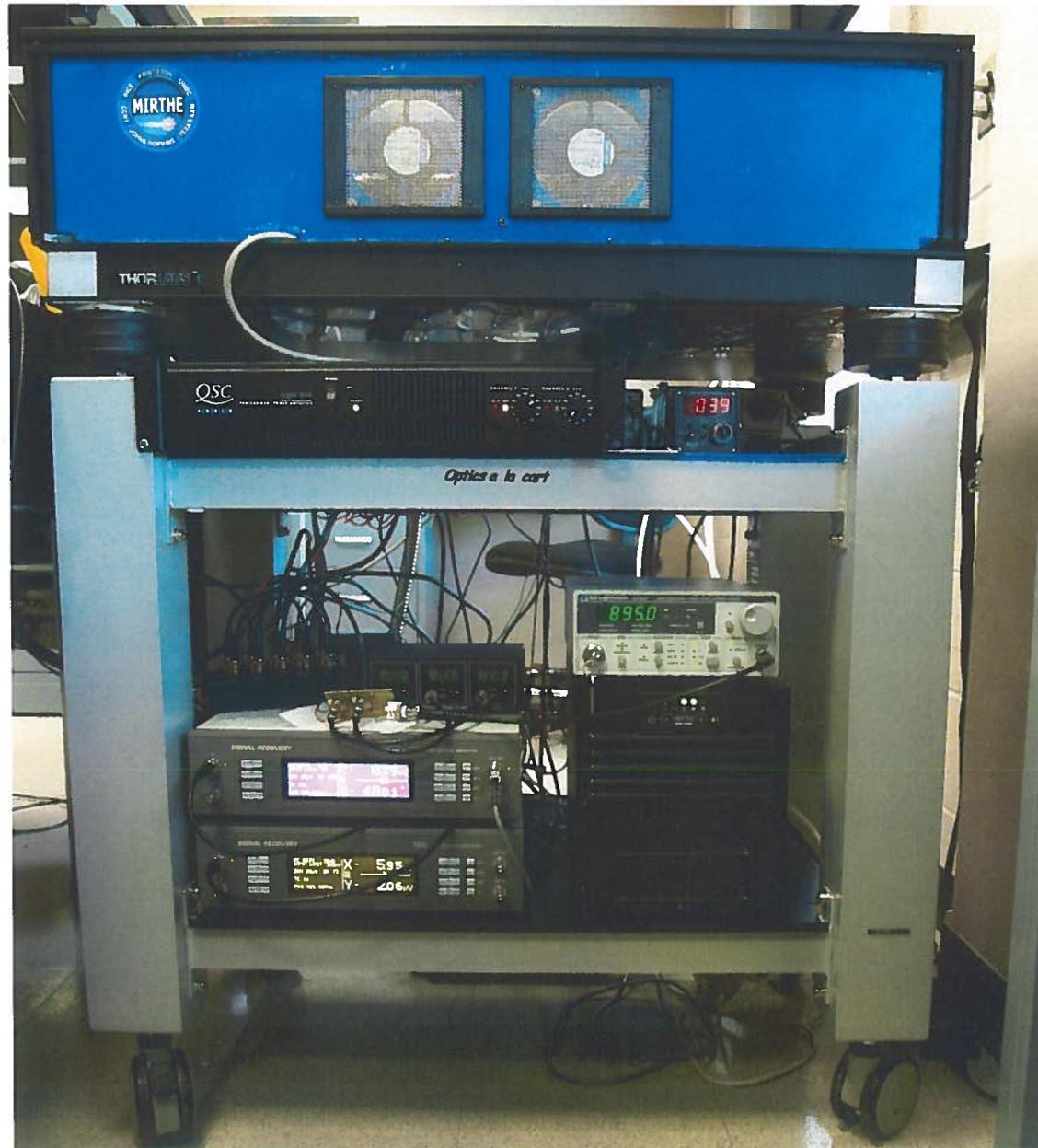


# EC-QCL based Magnetic Rotation Spectroscopy

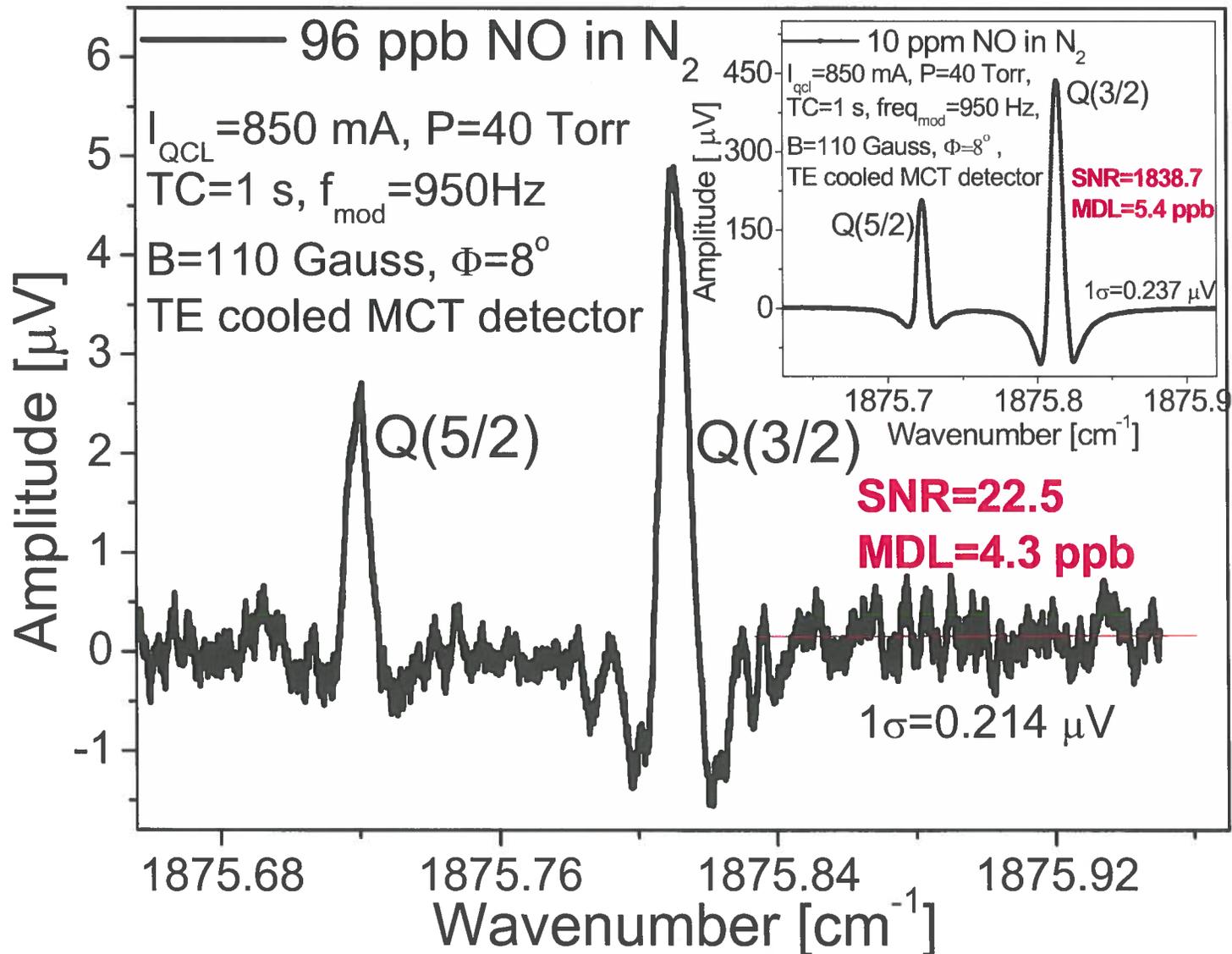


# EC-QCLbased MRS NO Sensor for IAP, Beijing

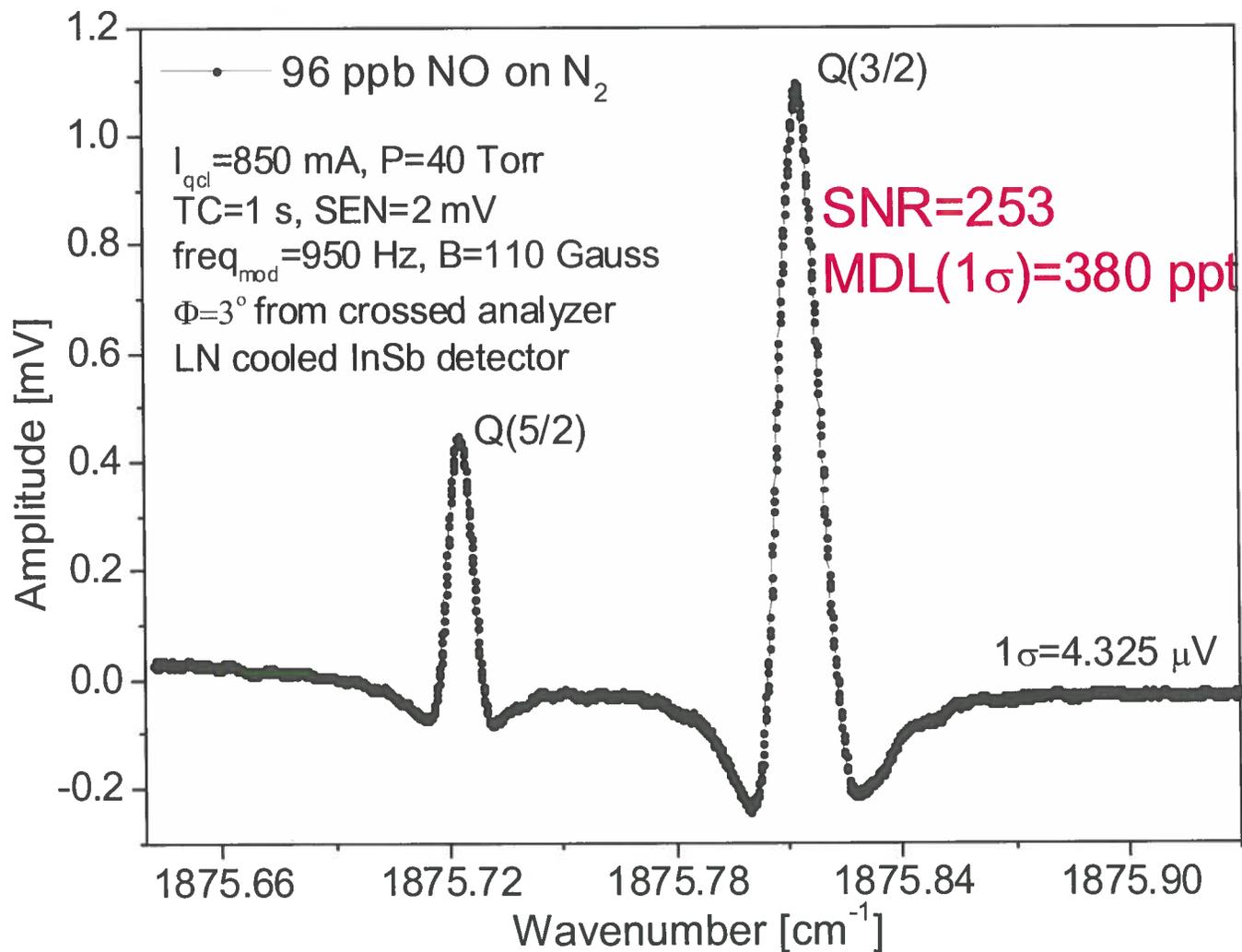
---



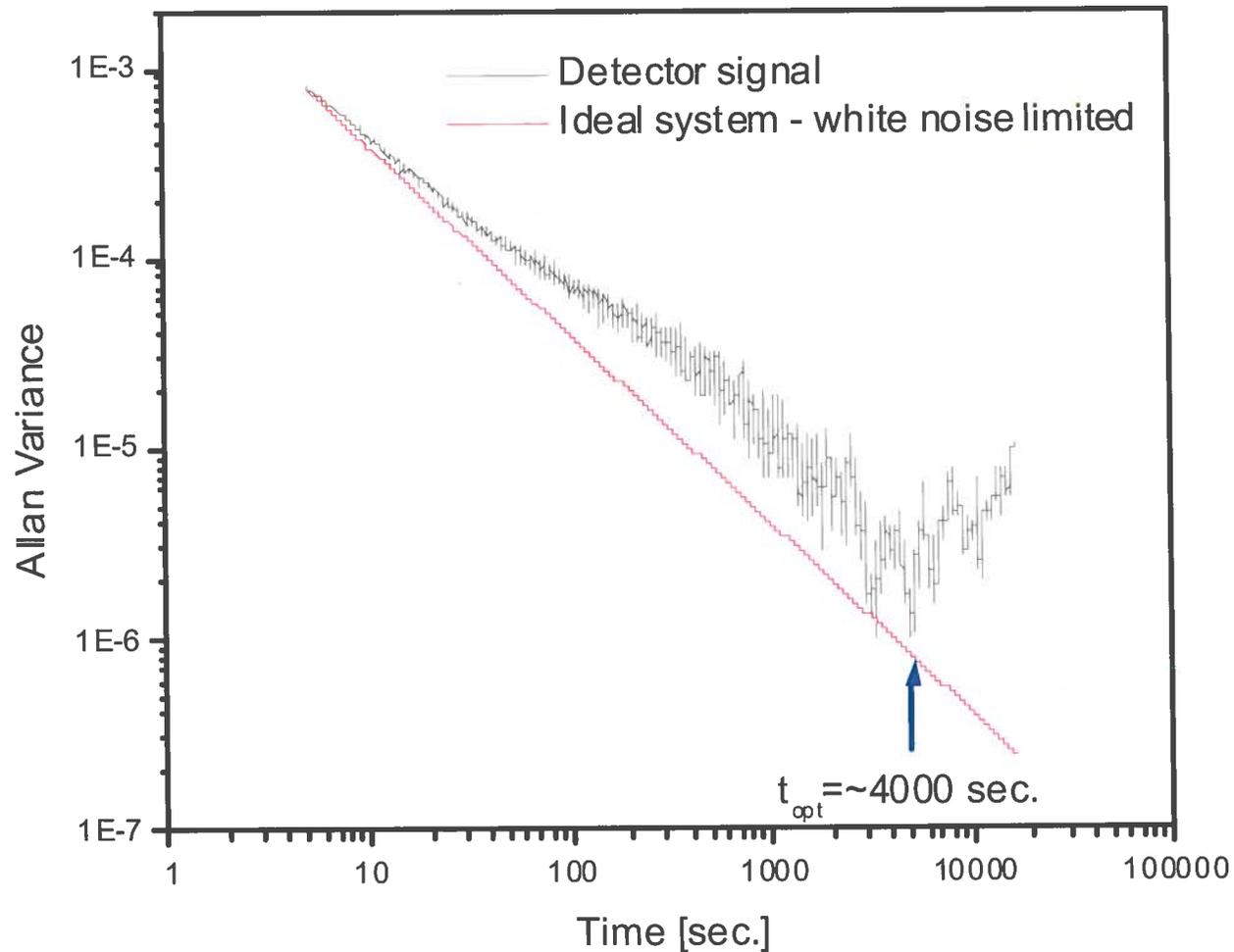
# Magnetic rotation spectrum of Q(3/2) and Q(5/2) transitions of nitric oxide



# Magnetic Rotation Spectroscopy of Nitric Oxide



# Magnetic rotation spectrum of Q(3/2) and Q(5/2)

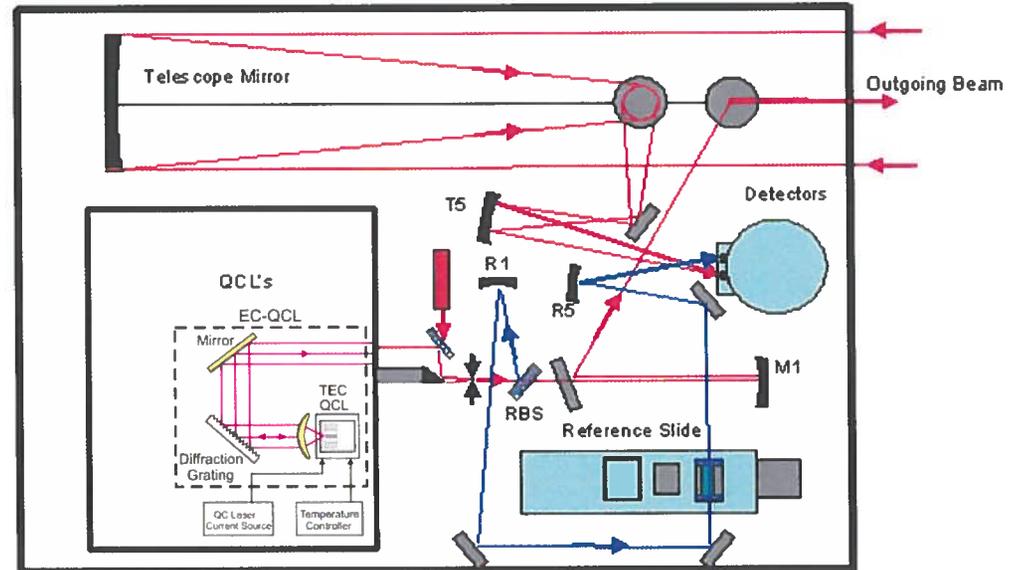
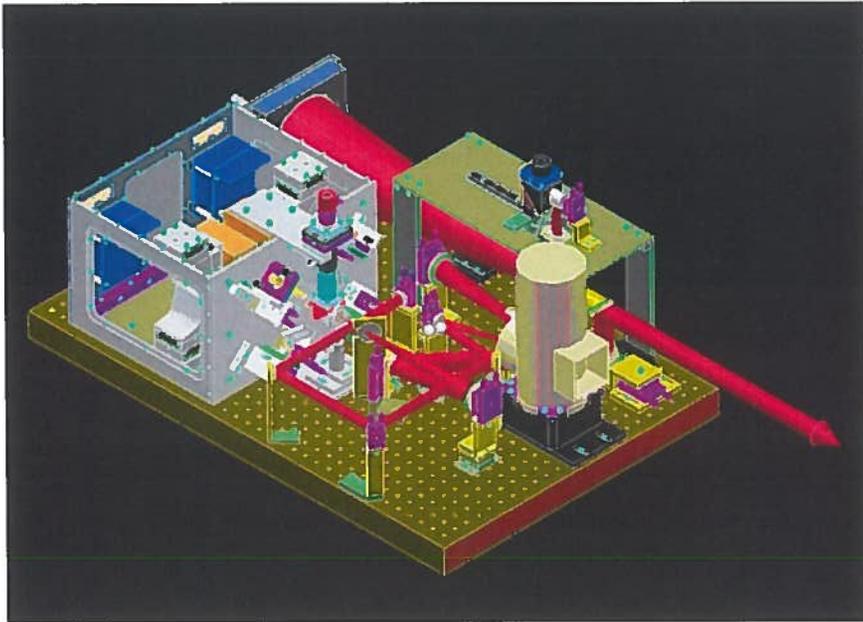


# National Stadium, Beijing, July-Sept. 2008

---

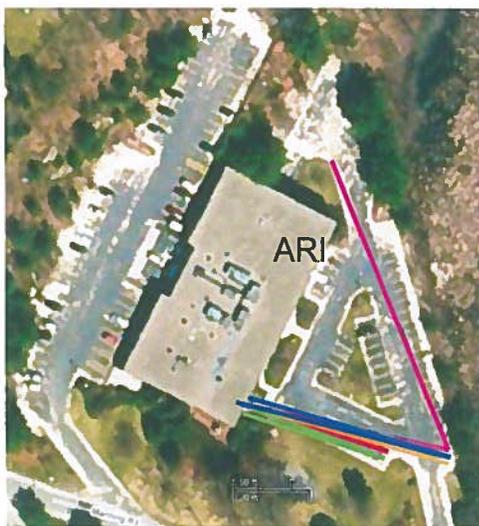
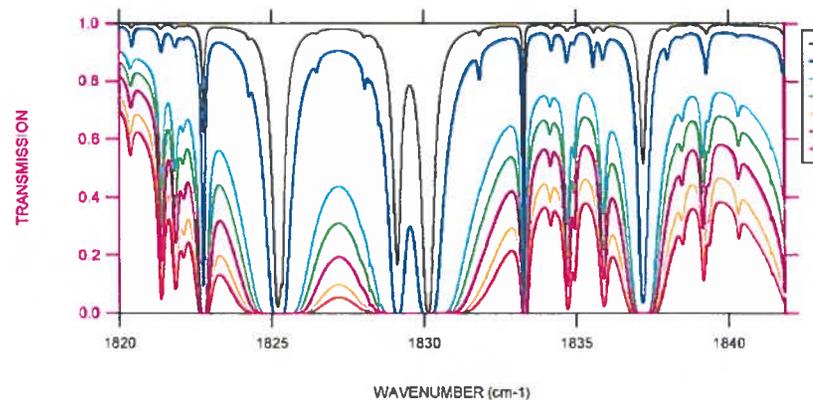
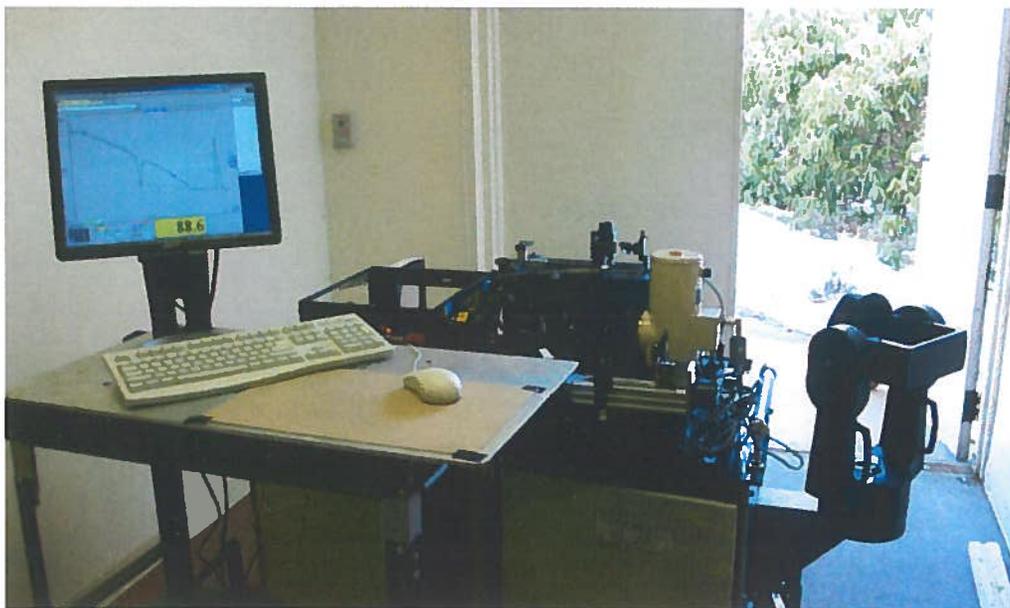


# Design of an EC-QCL Based Remote Sensing System



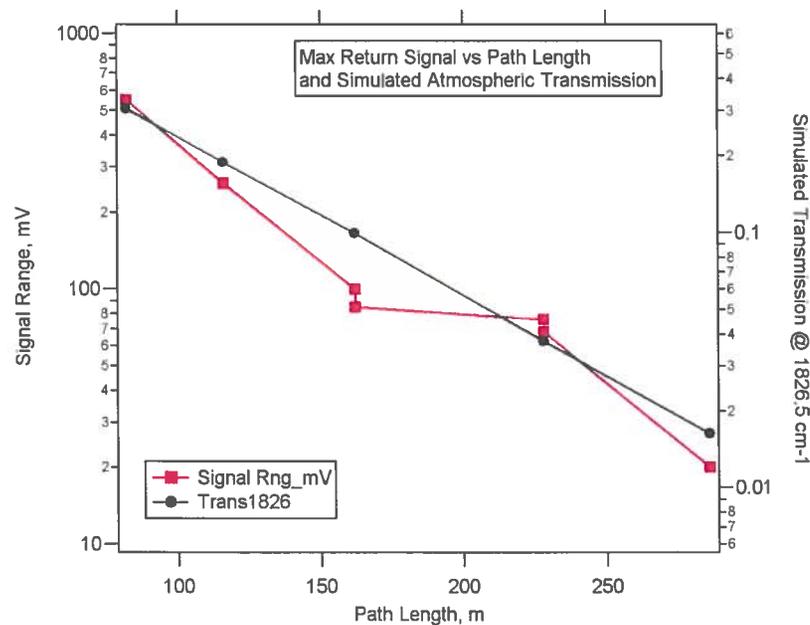
- An upgraded version of a four-laser pulsed QCL system
- The optical set-up, electronics and control software modified for CW-QCL operation
- First tests performed with a DFB CW-QCL operating at  $\sim 5.5\mu\text{m}$

# Outdoor Open Path Measurements (Influence of Atmospheric Transmission)



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

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



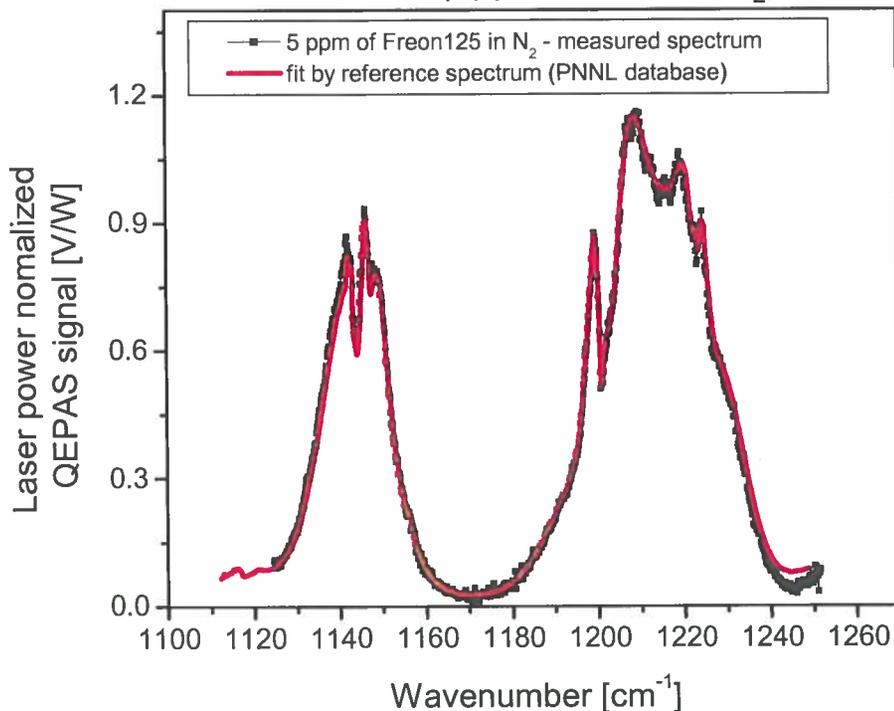
# Monitoring of broadband absorbers

---

- 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

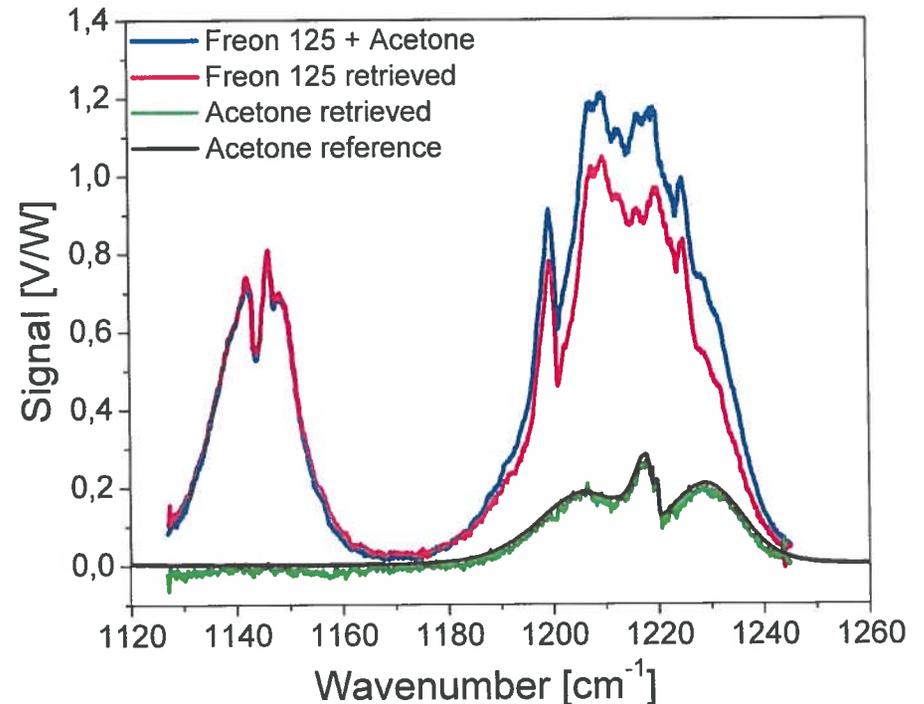
# QEPAS based Freon 125 and Acetone concentration measurements with a tunable 8.4 $\mu\text{m}$ CW EC-QCL

QEPAS concentration measurement of Freon 125 (5ppm mixture in  $\text{N}_2$ )



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

QEPAS concentration measurement of a Freon 125 and acetone mixture



- Wide tunability enables excellent molecular selectivity for broad band absorbers



# QEPAS Performance for 12 Trace Gas Species (July '08)

Molecule (Host)	Frequency, $\text{cm}^{-1}$	Pressure, Torr	NNEA, $\text{cm}^{-1}\text{W}/\text{Hz}^{1/2}$	Power, mW	NEC ( $\tau=1\text{s}$ ), ppmv
$\text{H}_2\text{O}$ ( $\text{N}_2$ )**	7306.75	60	$1.9 \times 10^{-9}$	9.5	0.09
$\text{HCN}$ (air: 50% RH)*	6539.11	60	$< 4.3 \times 10^{-9}$	50	0.16
$\text{C}_2\text{H}_2$ ( $\text{N}_2$ )*	6523.88	720	$4.1 \times 10^{-9}$	57	0.03
$\text{NH}_3$ ( $\text{N}_2$ )*	6528.76	575	$3.1 \times 10^{-9}$	60	0.06
$\text{C}_2\text{H}_4$ ( $\text{N}_2$ )*	6177.07	715	$5.4 \times 10^{-9}$	15	1.7
$\text{CH}_4$ ( $\text{N}_2$ )*	6057.09	950	$2.9 \times 10^{-8}$	13.7	2.1
$\text{CO}_2$ (breath ~100% RH)	6361.25	150	$8.2 \times 10^{-9}$	45	40
$\text{H}_2\text{S}$ ( $\text{N}_2$ )*	6357.63	780	$5.6 \times 10^{-9}$	45	0.20
$\text{CO}_2$ ( $\text{N}_2+1.5\% \text{H}_2\text{O}$ ) *	4991.26	50	$1.4 \times 10^{-8}$	4.4	18
$\text{CH}_2\text{O}$ ( $\text{N}_2:75\% \text{RH}$ )*	2804.90	75	$8.7 \times 10^{-9}$	7.2	0.12
$\text{CO}$ ( $\text{N}_2$ )	2196.66	50	$5.3 \times 10^{-7}$	13	0.5
$\text{CO}$ (propylene)	2196.66	50	$7.4 \times 10^{-8}$	6.5	0.14
$\text{N}_2\text{O}$ (air+5% $\text{SF}_6$ )	2195.63	50	$1.5 \times 10^{-8}$	19	0.007
$\text{C}_2\text{H}_5\text{OH}$ ( $\text{N}_2$ )**	1934.2	770	$2.2 \times 10^{-7}$	10	90
$\text{C}_2\text{HF}_5$ ( $\text{N}_2$ )***	1208.62	770	$7.8 \times 10^{-9}$	6.6	0.009
$\text{NH}_3$ ( $\text{N}_2$ )*	1046.39	110	$1.6 \times 10^{-8}$	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  $\tau=1\text{s}$  time constant, 18 dB/oct filter slope.

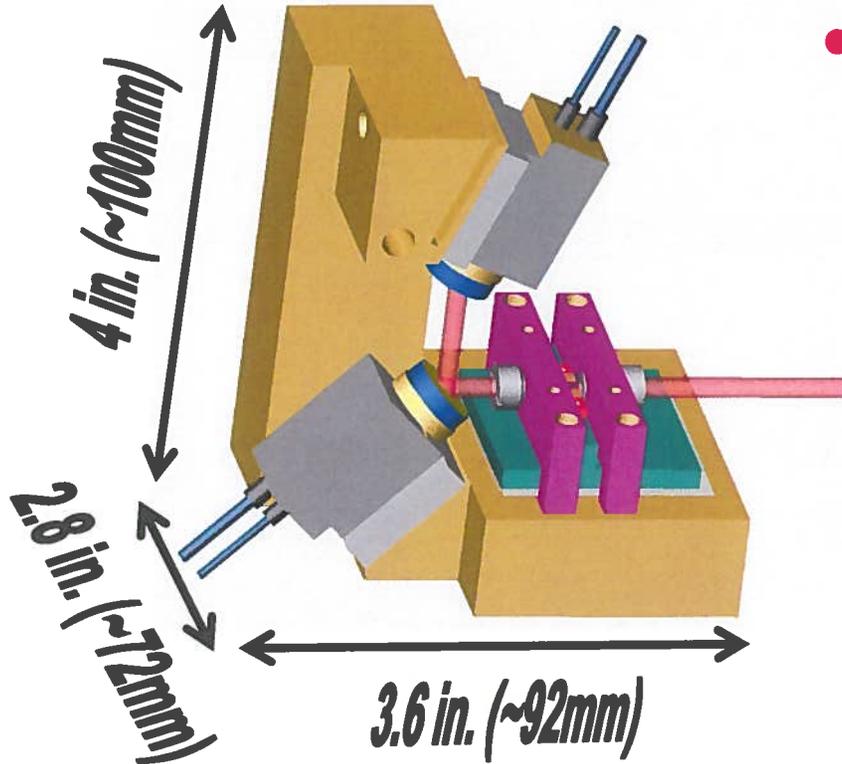
**For comparison: conventional PAS 2.2  $(2.6) \times 10^{-9} \text{ cm}^{-1}\text{W}/\sqrt{\text{Hz}}$  (1,800; 10,300 Hz) for  $\text{NH}_3$ \*. (\*\*)**

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



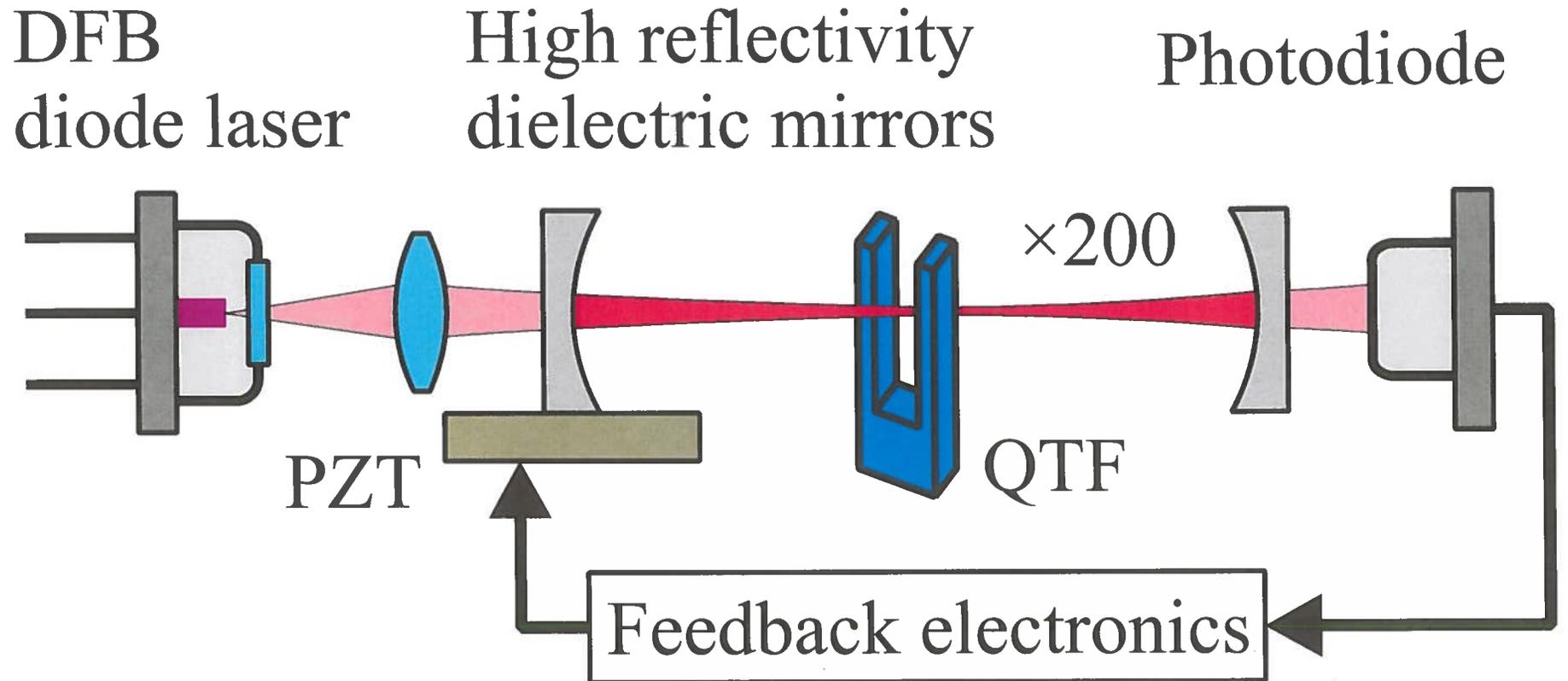
# Future of Chemical Trace Gas Sensing

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

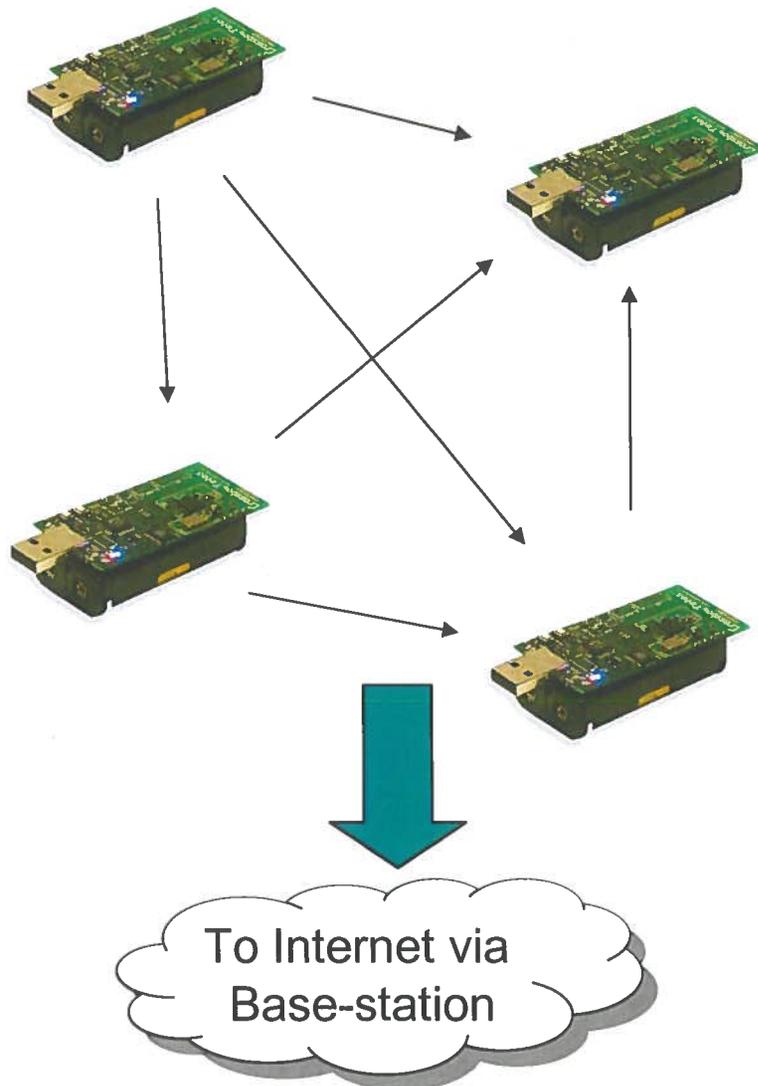


- New optical configuration  
*Folded cavity (configuration #1)*
- Fast tuning capabilities:
  - Coarse Broadband Scanning  
( $\sim 55 \text{ cm}^{-1}$  @  $5 \mu\text{m}$ ) **up to 5 KHz**  
(compared to available technologies  $< 10 \text{ Hz}$ )
  - High resolution mode-hop free tuning ( $\sim 3.2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

# Proposed QEPAS-OPBC Sensor Configuration

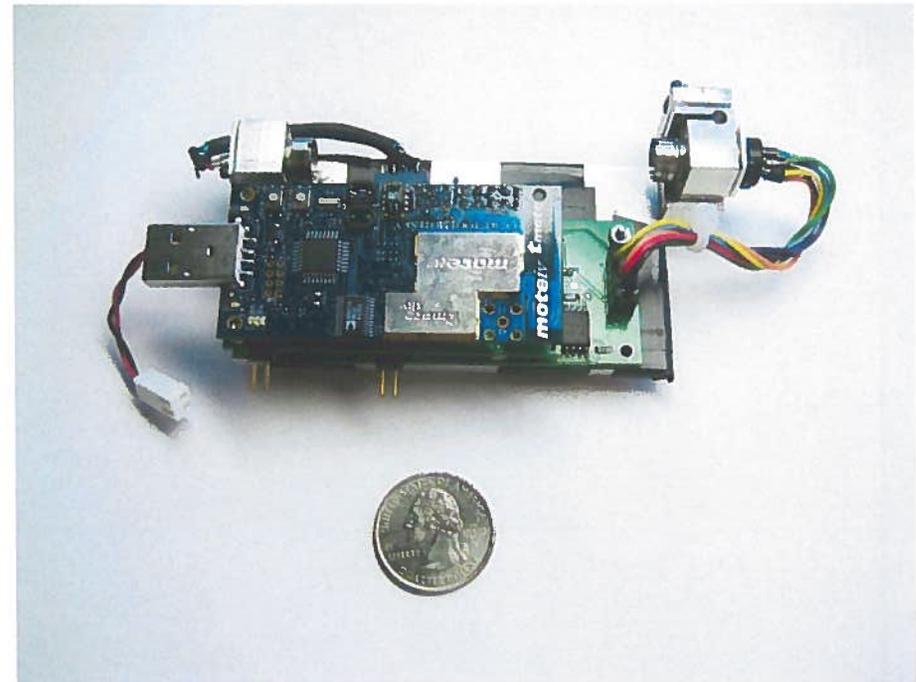
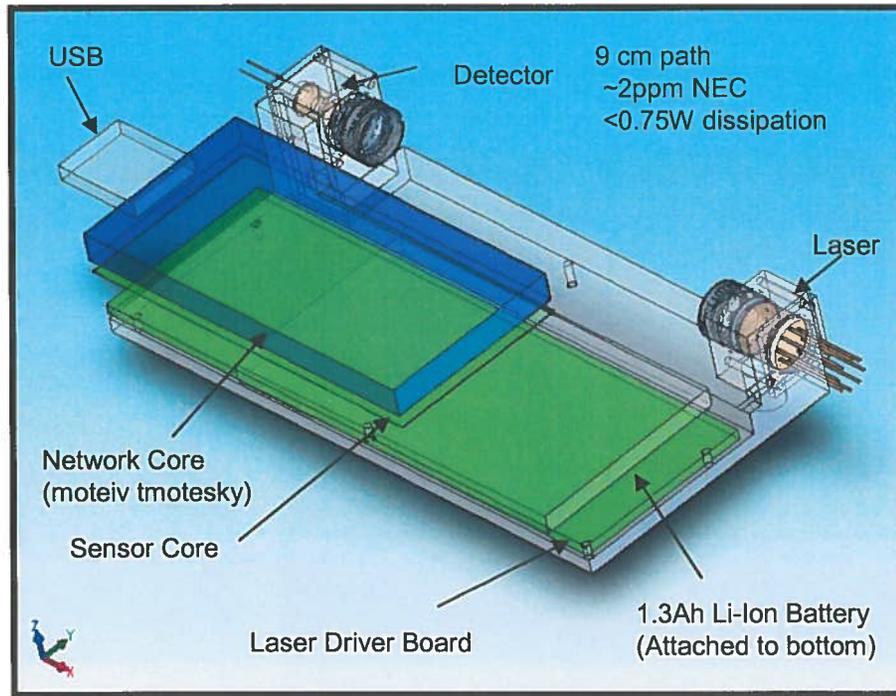


# Wireless Sensor Networks for Gas Sensing



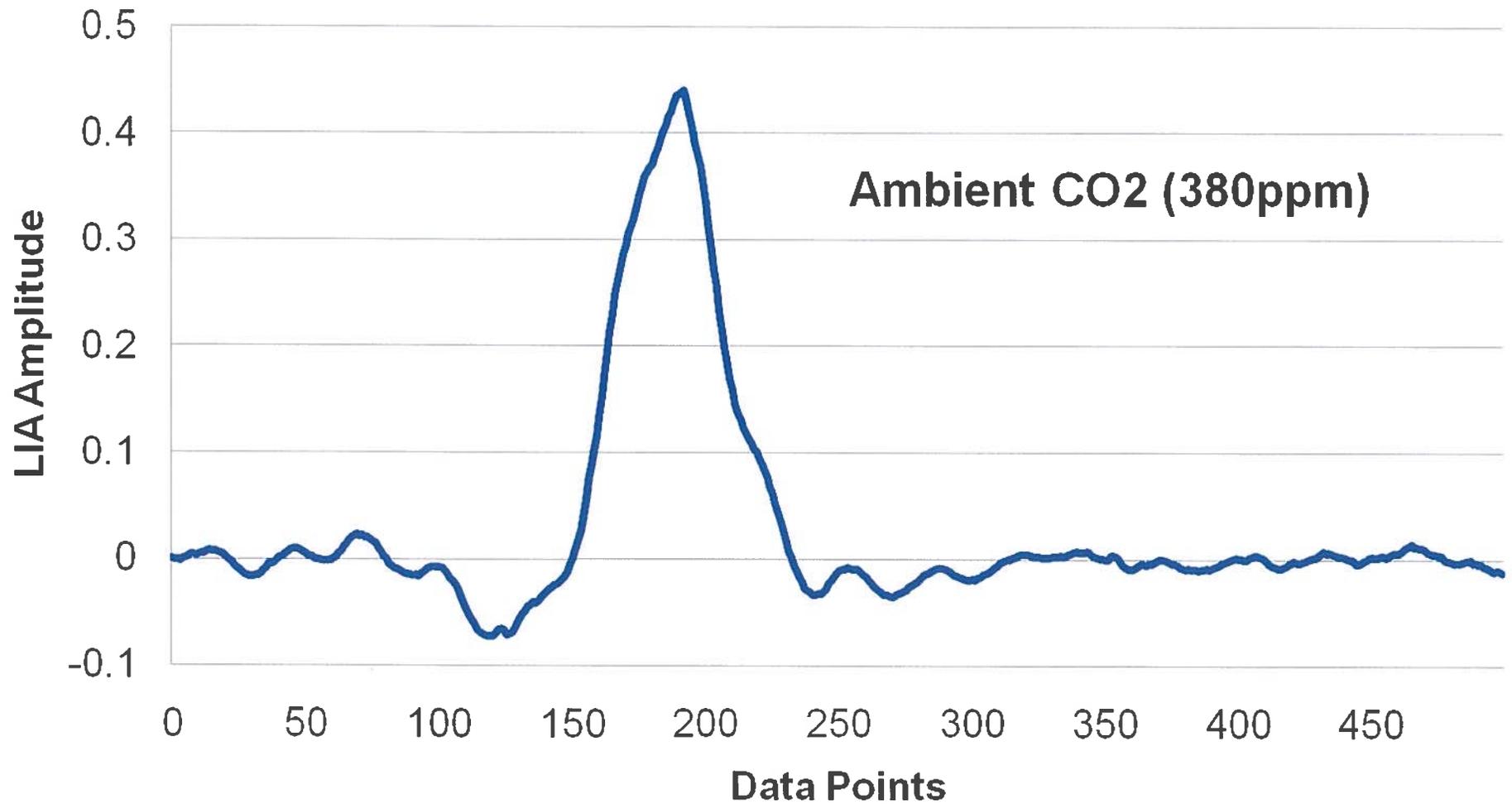
- Each point called “mote”
- Advantages?
  - Spatial resolution
  - Measure fluxes
- What is needed?
  - Low power
  - Low cost
  - Ultra miniature
  - Replicable
  - Autonomy

# PHOTONS v4.0 - 2.7 $\mu$ m CO<sub>2</sub> Direct Absorption Based Sensor



- Small size
- Relatively low cost
- High efficiency switching power supplies
- PWM Peltier cooler driver
- 0.2W control system power consumption
- Detection sensitivity of CO<sub>2</sub> 1 ppm with 1sec. lock-in time constant
- Over 100x improvement in sensitivity is possible @ 4.2 $\mu$ m

## LAS based CO<sub>2</sub> Spectrum at 2.7 μm



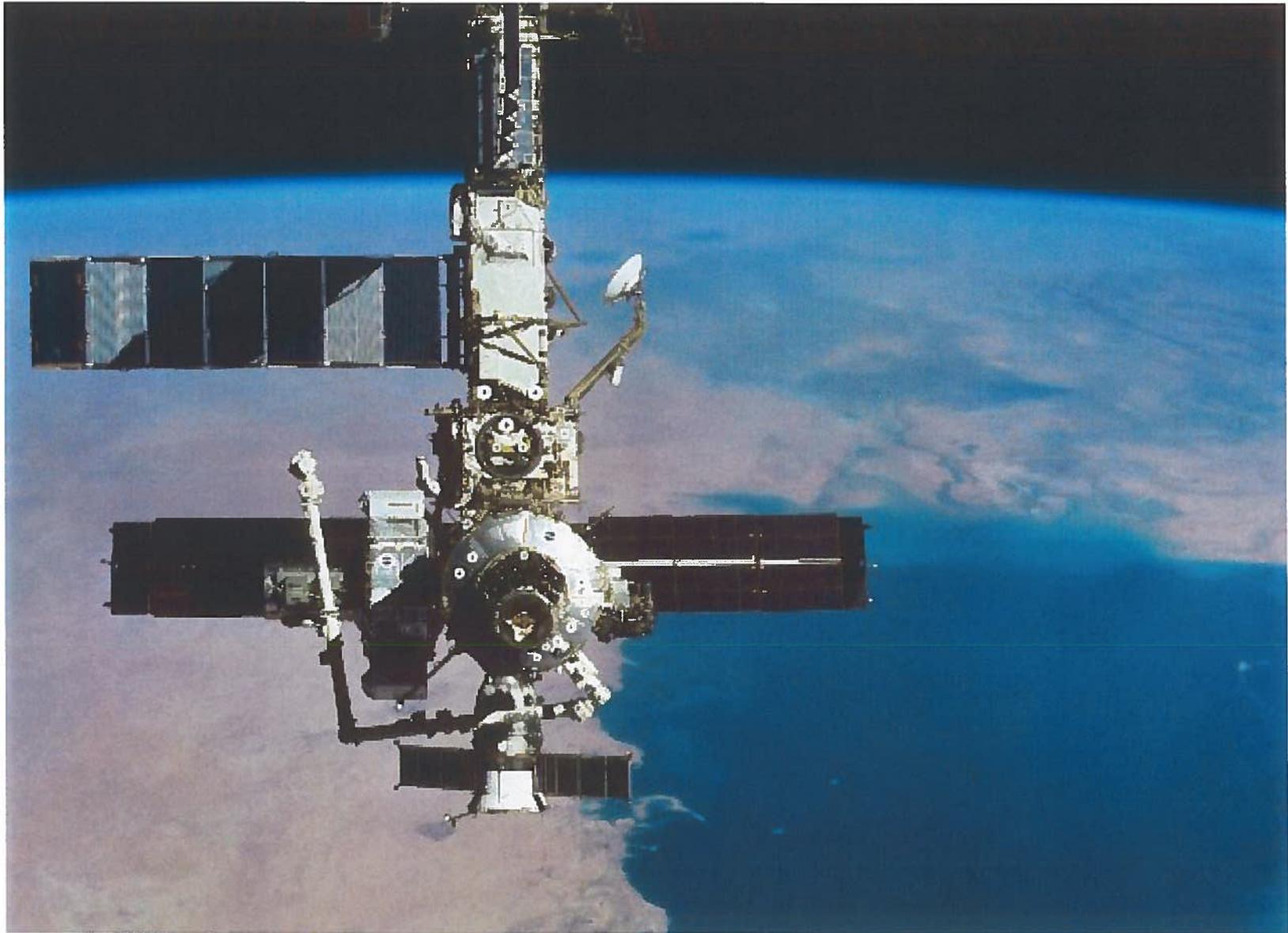
# Summary & Future Directions of QCL based Gas Sensor Technology

---

- **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:  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{NO}$ ,  $\text{H}_2\text{O}$ ,  $\text{COS}$ ,  $\text{C}_2\text{H}_4$ ,  $\text{H}_2\text{CO}$ ,  $\text{SO}_2$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_2\text{HF}_5$  and several isotopic species of C, O, N and H.
- **New Applications of Trace Gas Detection**
  - Environmental Monitoring (urban quality -  $\text{H}_2\text{CO}$  and, isotopic ratio measurements of  $\text{CO}_2$  and  $\text{CH}_4$ , fire detection and quantification of engine exhausts)
  - Industrial process control and chemical analysis (  $\text{NO}$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{H}_2\text{S}$ )
  - Medical & biomedical diagnostics ( $\text{NO}$ ,  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{H}_2\text{CO}$  and  $\text{CH}_3\text{COCH}_3$ )
  - Hand-held sensors and sensor network technologies ( $\text{CO}_2$ )
- **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

# ISS Passing over Persian Gulf July 27, 2001

---



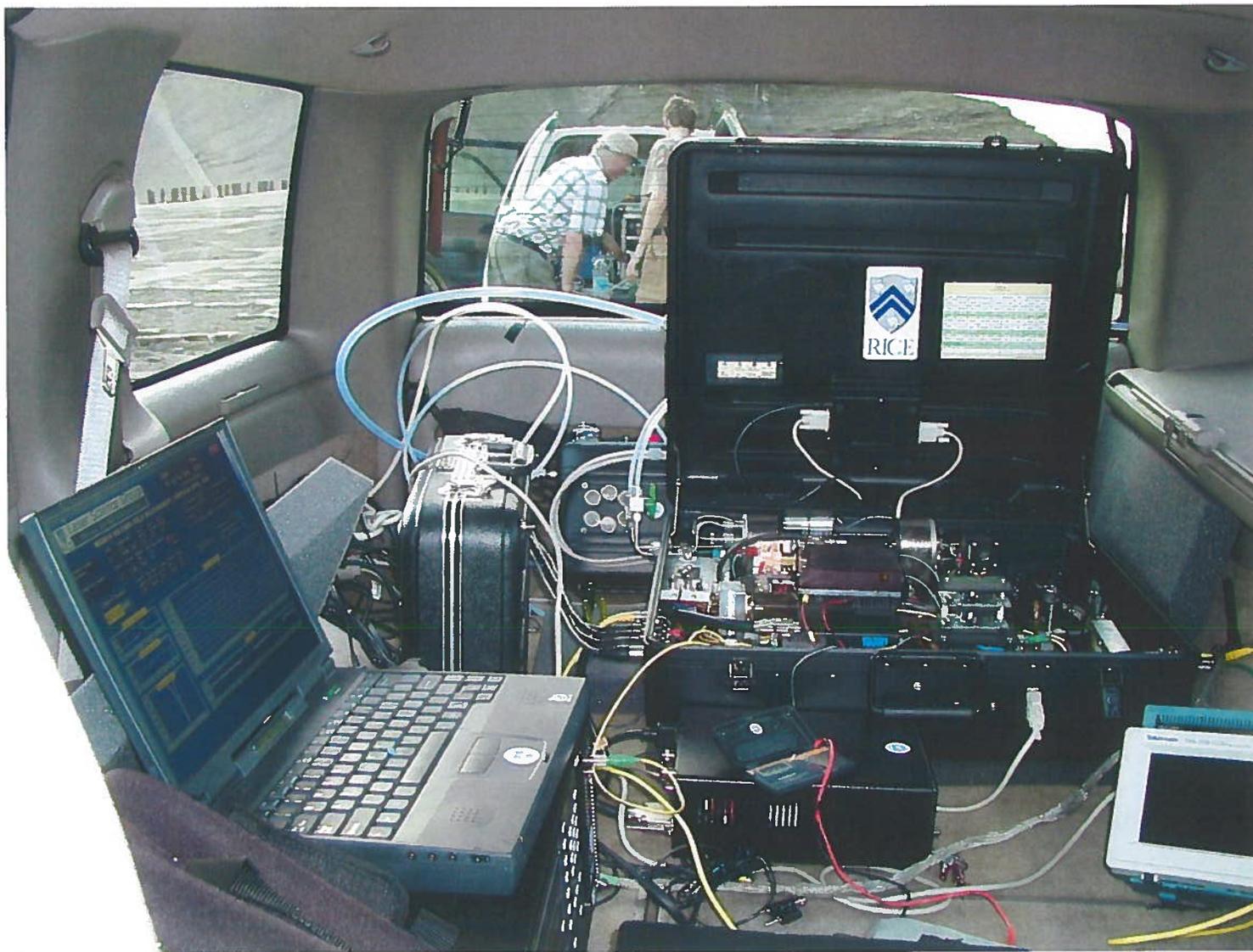
# ISS Seen From STS-108 Dec. 2001 Over Miami

---

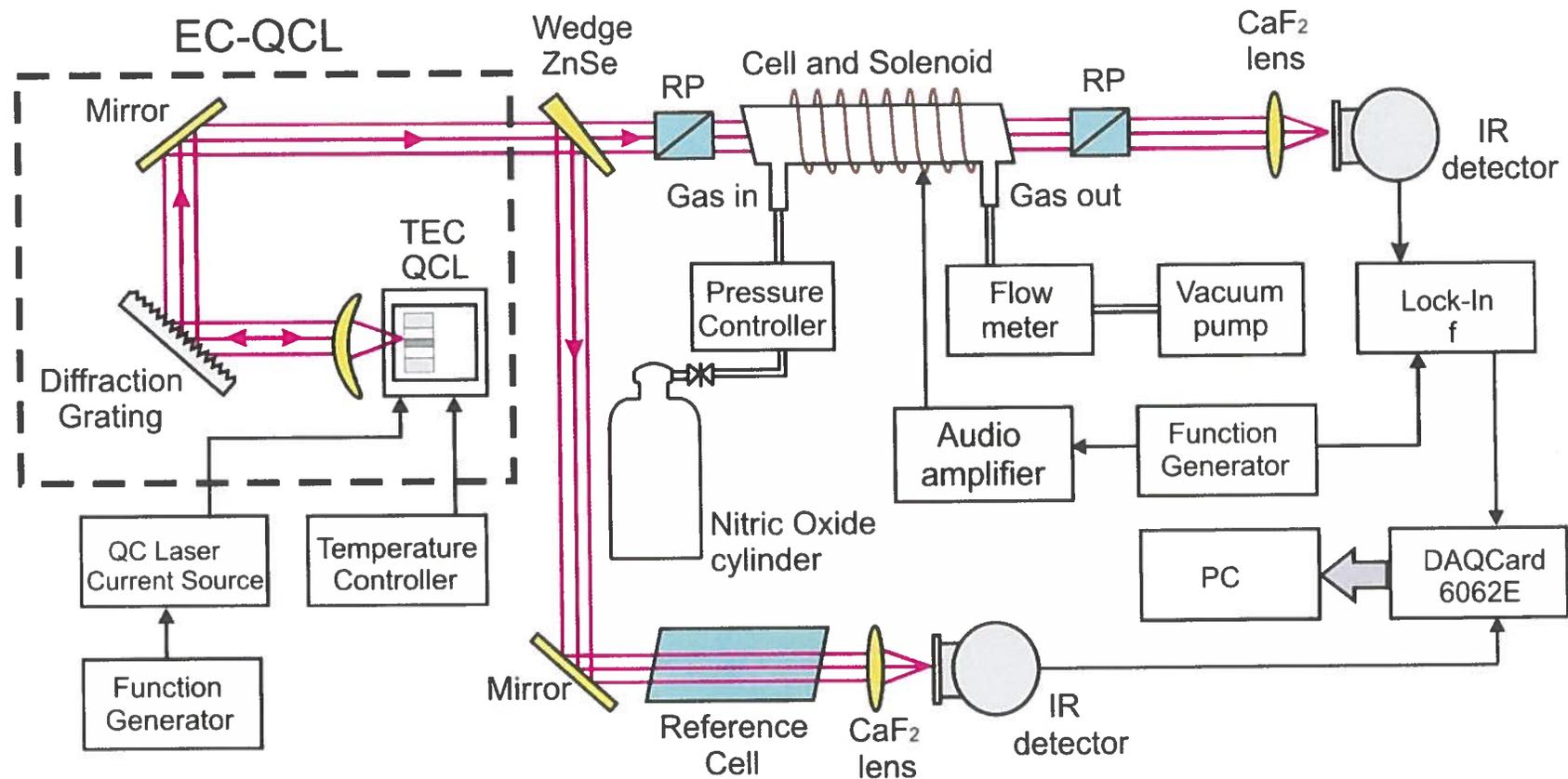


# Masaya Volcano Emissions Campaign April 2000

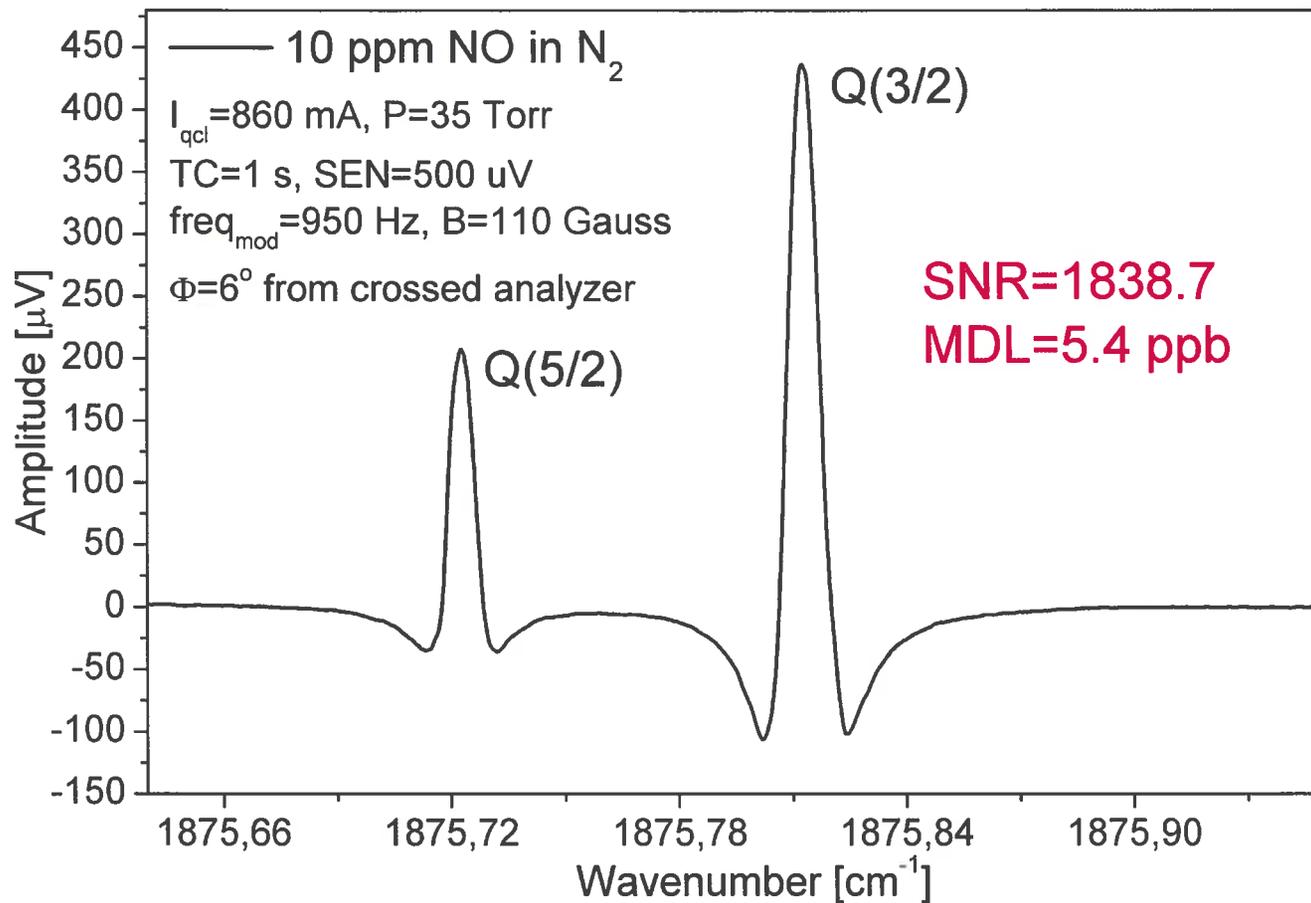
---



# QCL based MRS Nitric Oxide Sensor

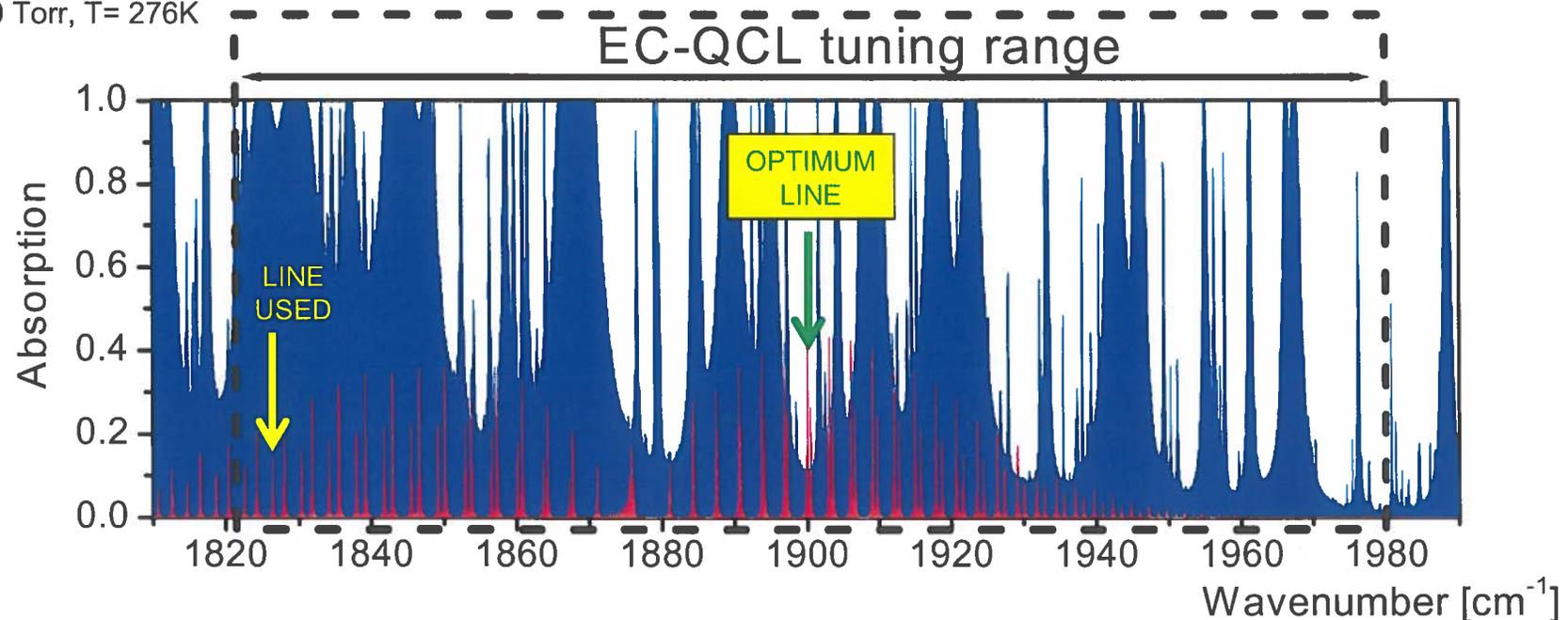


# Magnetic Rotation Spectroscopy of Nitric Oxide



# High resolution spectroscopy with a 5.3 $\mu\text{m}$ EC-QCL

286m open path  
H<sub>2</sub>O mixing ratio: 0.006  
CO<sub>2</sub> 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