



RICE

## OUTLINE

MirSens  
Workshop

Wroclaw,  
Poland

May 6-8, 2010

# Recent Advances in Mid-infrared Semiconductor Laser based Trace Gas Sensor Technologies

F.K. Tittel, L. Dong, L. Gong, R Griffin, A.A. Kosterev,  
R. Lewicki, D. Thomazy and C. Zaugg

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

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

- Motivation: Chemical Sensing Applications
- Fundamentals of Laser Absorption Spectroscopy
- New Laser Sensing Technologies (QEPAS)
- Selected Applications of Trace Gas Detection
  - NH<sub>3</sub> and NO Detection for Environmental Monitoring & Medical Diagnostics
  - Monitoring of Broadband Absorbers
- Future Directions of Laser based Gas Sensor Technology

Work supported by NSF ERC MIRTHe, NSF Photons, NASA -JSC, DoE STTR and the 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 Biomedical and the Life Sciences**
- **Technologies for Law Enforcement and National Security**
- **Fundamental Science and Photochemistry**

# Mid-IR Source Requirements for Laser Spectroscopy

---

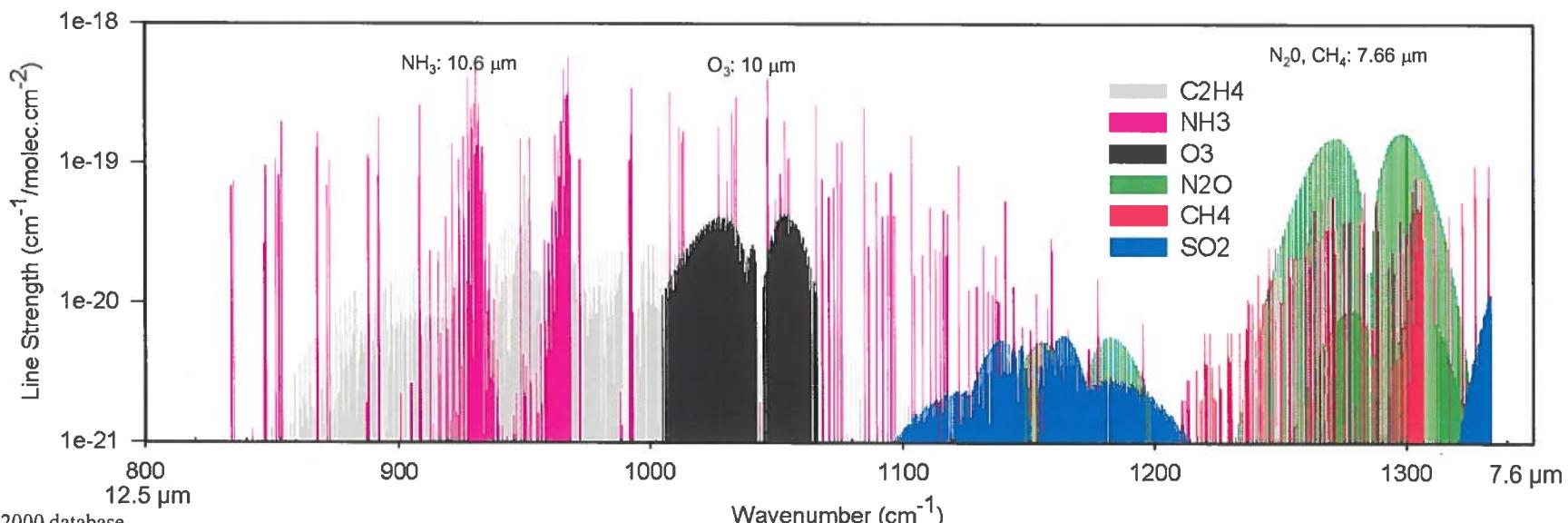
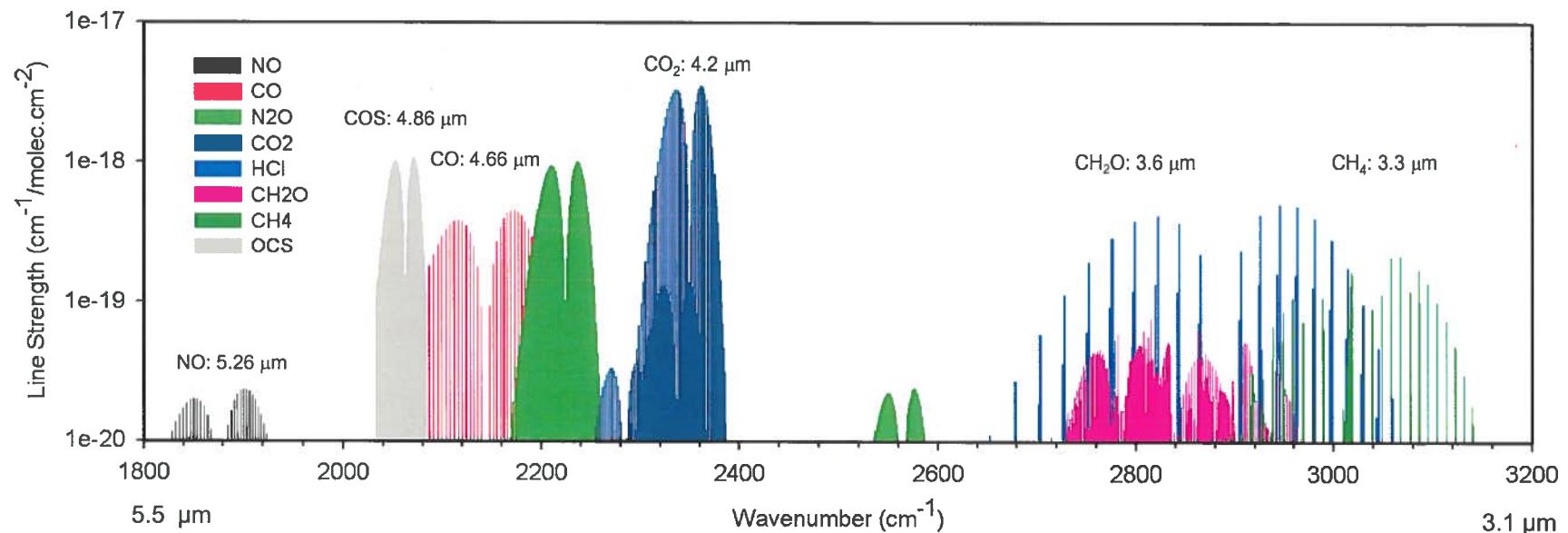
<b><u>REQUIREMENTS</u></b>	<b><u>IR LASER SOURCE</u></b>
<b>Sensitivity (% to ppt)</b>	<b>Optimum Wavelength, Power</b>
<b>Selectivity (Spectral Resolution)</b>	<b>Single Mode Operation and Narrow Linewidth</b>
<b>Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers</b>	<b>Tunable 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>

# Sensitivity Enhancement Techniques for Laser Spectroscopy

---

- **Optimum Molecular Absorbing Transition**
  - Overtone or Combination Bands (NIR)
  - Fundamental Absorption Bands (MID-IR)
- **Long Optical Pathlength**
  - Multipass Absorption Cell (White, Herriot, Chernin)
  - Cavity Ringdown and Cavity Enhanced Spectroscopy
  - Open Path Monitoring (with & without retro-reflector):  
Standoff and Remote Detection
  - Fiberoptic Evanescent Wave Spectroscopy
- **Spectroscopic Detection Schemes**
  - Frequency or Wavelength Modulation
  - Balanced Detection
  - Zero-air Subtraction
  - Photoacoustic Spectroscopy
  - Laser Induced Breakdown Spectroscopy (LIBS)

# Molecular Absorption Spectra within two Mid-IR Atmospheric Windows



Source: HITRAN 2000 database

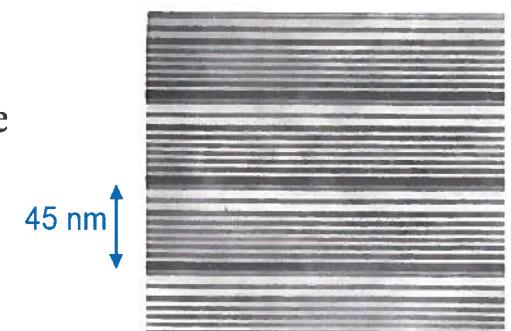
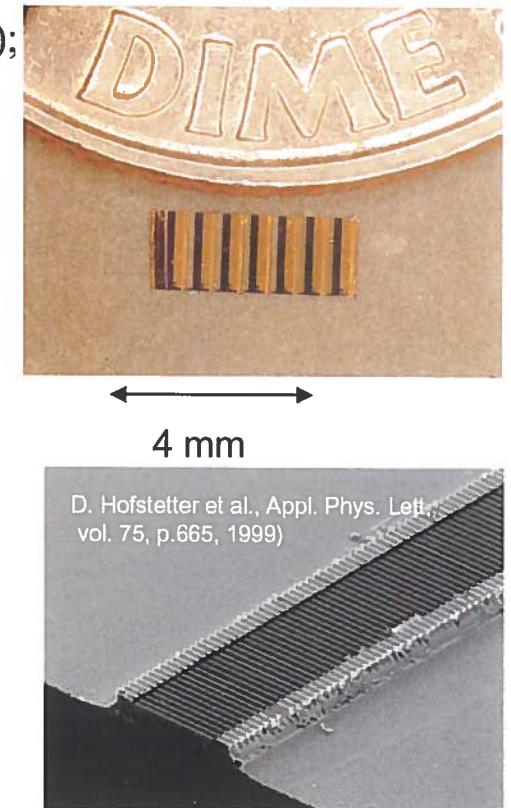
# Key Characteristics of mid-IR QCL and ICL Sources - May 2010

- **Band – structure engineered devices**  
(Emission wavelength is determined by layer thickness – MBE or MOCVD);  
mid-infrared QCLs operate from 3 to 24  $\mu\text{m}$  (AlInAs/GaInAs)
- Compact, reliable, stable, long lifetime, and commercial availability
- Fabry-Perot (FP), single mode (DFB) and multi-wavelength

- **Broad spectral tuning range in the mid-IR**  
(4-24  $\mu\text{m}$  for QCLs and 3-5  $\mu\text{m}$  for ICLs and GaSb diodes)
  - 1.5  $\text{cm}^{-1}$  using injection current control for DFB devices
  - 10-20  $\text{cm}^{-1}$  using temperature control for DFB devices
  - $> 430 \text{ cm}^{-1}$  using an external grating element and FP chips with heterogeneous cascade active region design; also QCL DFB Array

- **Narrow spectral linewidth**
  - CW: 0.1 - 3 MHz & <10KHz with frequency stabilization ( $0.0004 \text{ cm}^{-1}$ )
  - Pulsed:  $\sim 300 \text{ MHz}$

- **High pulsed and cw powers of QCLs at TEC/RT temperatures**
  - Pulsed and CW powers of 34 W and 3 W respectively; high temperature operation  $\sim 300\text{K}$
  - $> 280 \text{ mW}$ , TEC CW DFB @ 5  $\mu\text{m}$
  - $> 600 \text{ mW}$  (CW FP) @ RT; wall plug efficiency of  $\sim 17\%$  at 4.6  $\mu\text{m}$ ;



# Quantum Cascade (QC), Interband (IC) and GaSb Laser Commercial and Research Activity in May 2010

---

- **Commercial Sources**

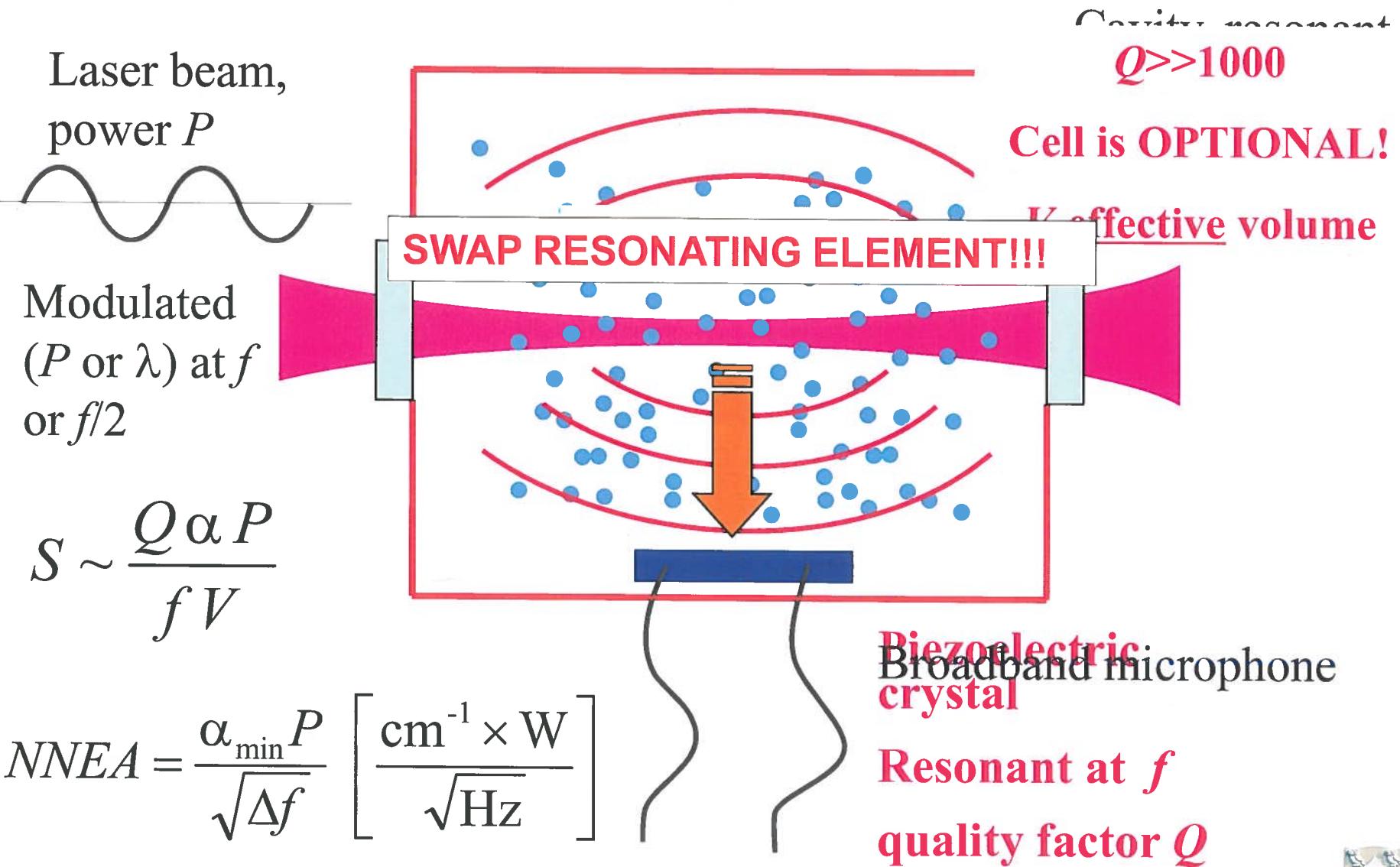
- Adtech, CA
- Alpes Lasers, Switzerland & Germany
- Alcatel-Thales, France
- Cascade Technologies, UK
- Corning , NY
- Hamamatsu, USA & Japan
- Maxion Technologies, Inc MD (Physical Sciences, Inc)
- Nanoplus, Germany
- Pranalytica, CA

- **Research Groups**

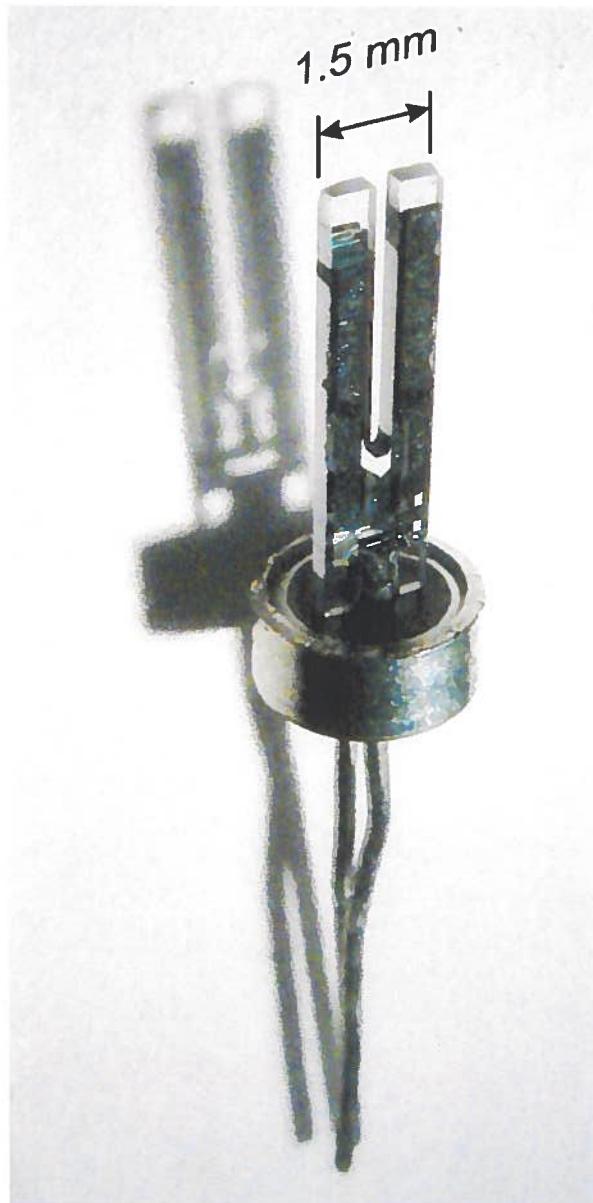
- Harvard University
- Fraunhofer-IAF & IPM, Freiburg, Germany
- **Institute of Electron Technology, Warsaw, Poland**
- NASA-JPL, Pasadena, CA
- Naval Research Laboratories, Washington, DC
- Northwestern University, Evanston, IL
- Princeton University (MIRTHE), NJ
- Shanghai Institute of Microsystem and Information Technology, China
- **Sheffield University, UK**
- State University of New York
- Technical University, Zuerich, CH
- **University of Montpellier, France**
- **University of Vienna, Austria**

# Quartz Enhanced Photoacoustic Spectroscopy

# From conventional PAS to QEPAS



# Quartz Tuning Fork as a Resonant Microphone



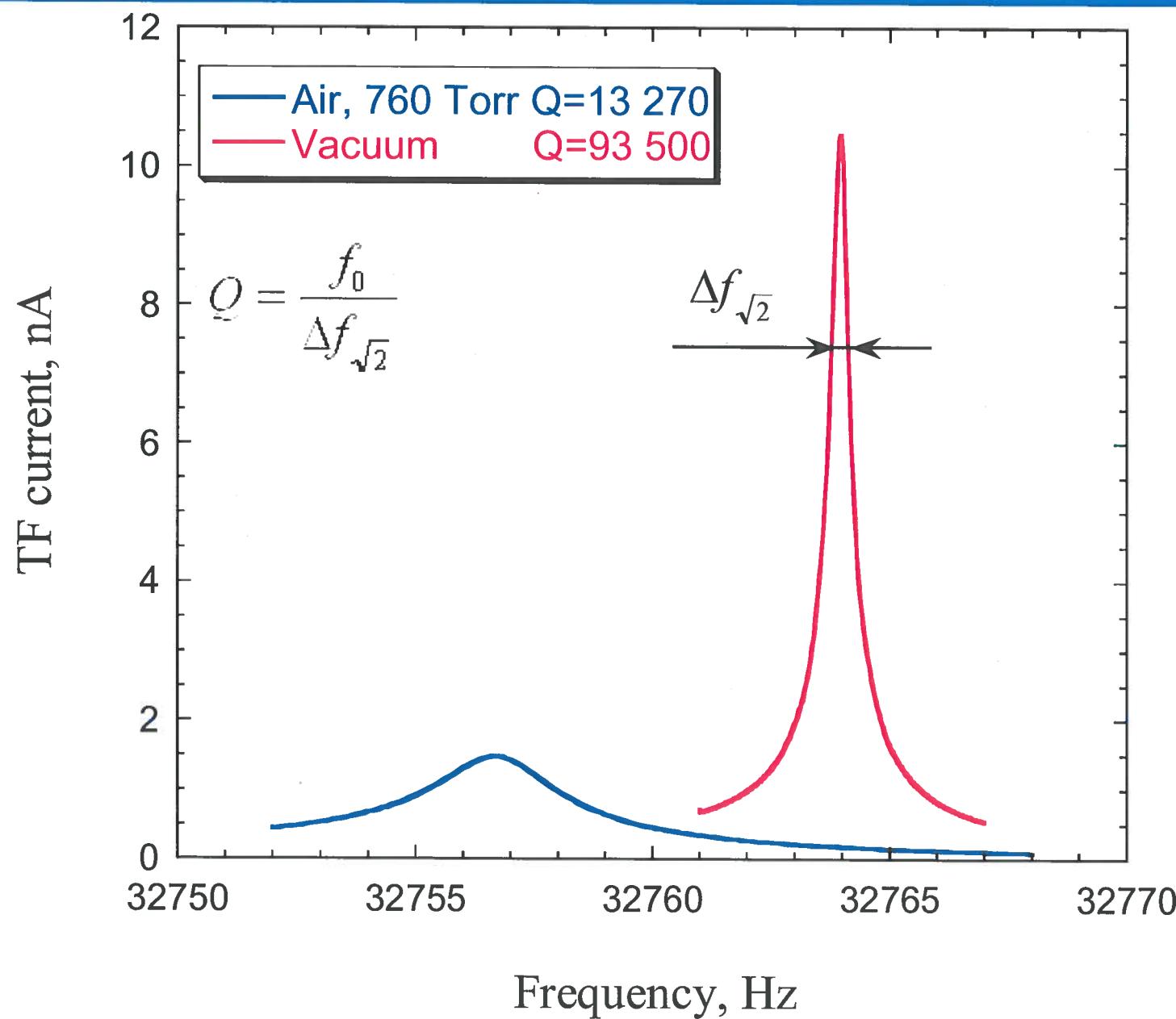
## Unique properties

- Extremely low internal losses:
  - $Q \sim 10\,000$  at 1 atm
  - $Q \sim 100\,000$  in vacuum
- Acoustic quadrupole geometry
  - Low sensitivity to external sound
- Large dynamic range ( $\sim 10^6$ ) – linear from thermal noise to breakdown deformation
  - 300K noise:  $x \sim 10^{-11}$  cm
  - Breakdown:  $x \sim 10^{-2}$  cm
- Wide temperature range: from 1.56K (superfluid helium) to  $\sim 700$ K
- Low cost (<\$1)

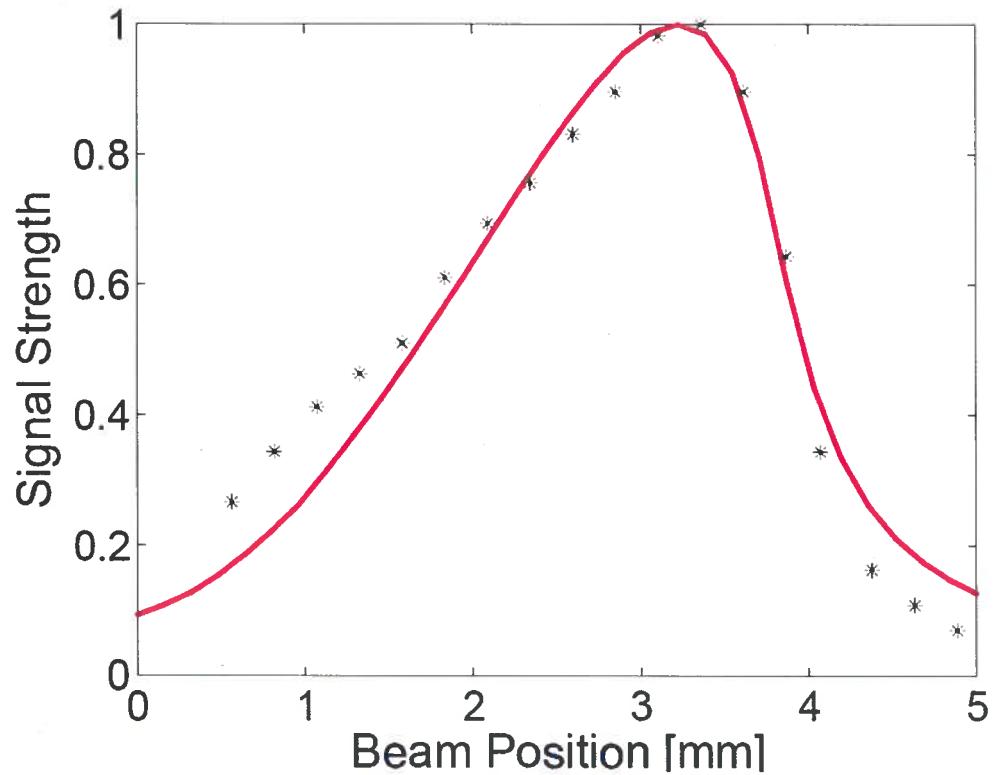
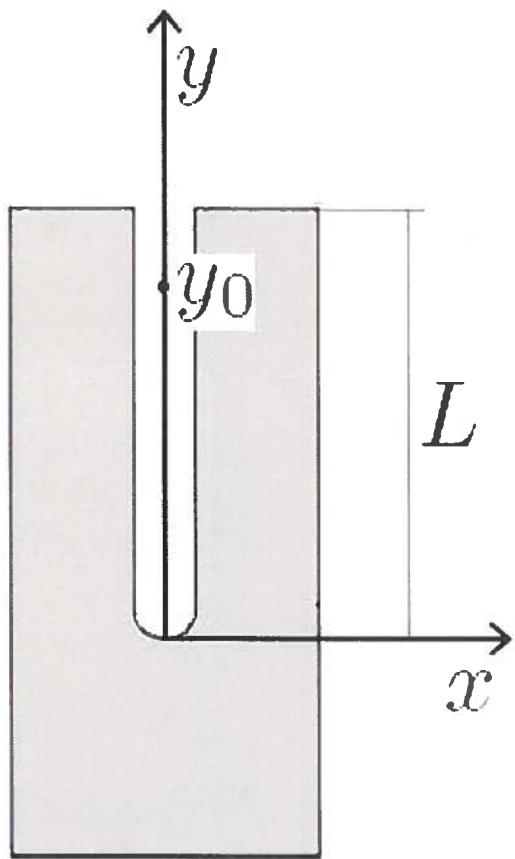
## Other parameters

- Resonant frequency  $\sim 32.8$  kHz
- Force constant  $\sim 26800$  N/m
- Electromechanical coefficient  $\sim 7 \times 10^{-11}$  C/m

# Typical QTF Resonance Curves



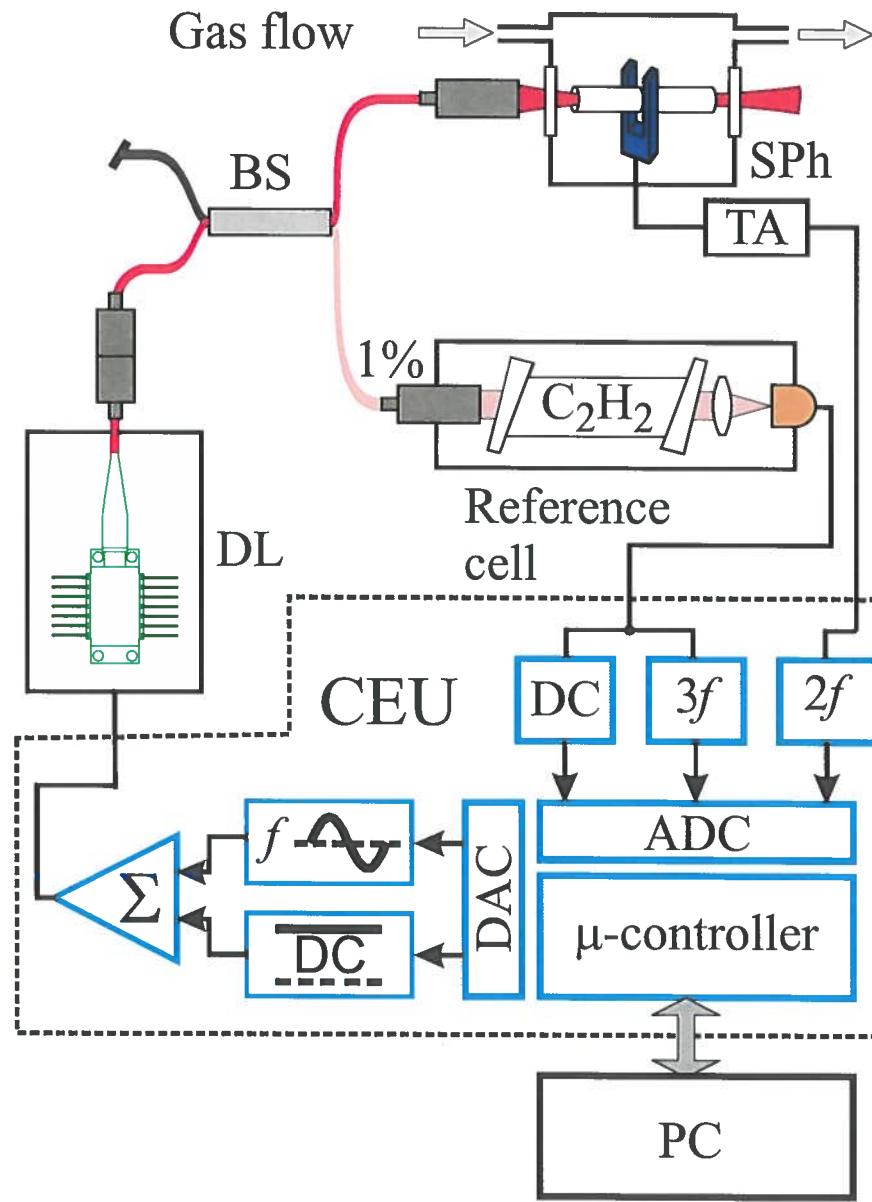
# What about QEPAS Modeling ?



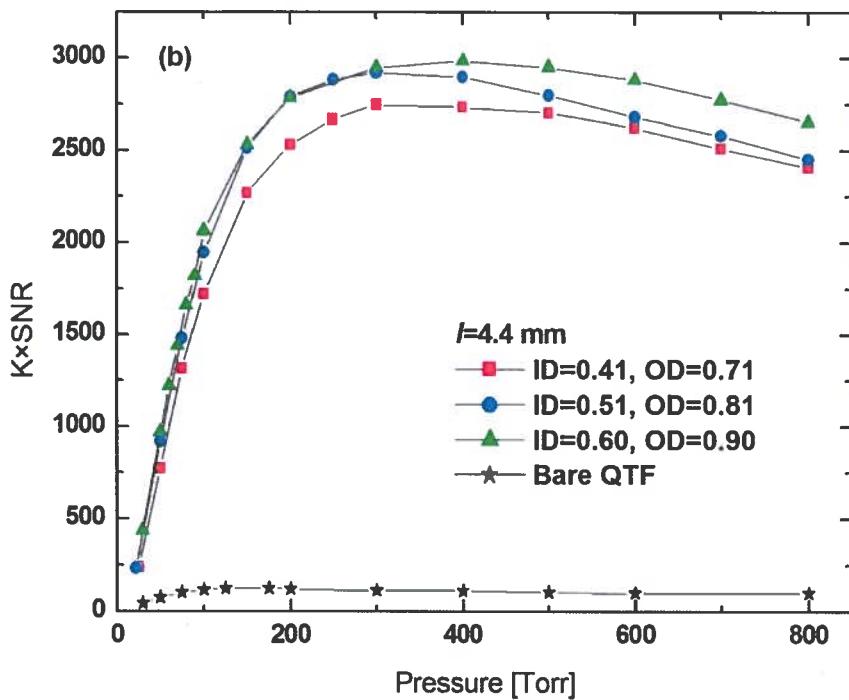
MIRTHE UMBC team :N. Petra, J. Zweck, A. A. Kosterev, S. E. Minkoff and D. Thomazy, "Theoretical Analysis of a Quartz-Enhanced Photoacoustic Spectroscopy Sensor", Appl. Phys B 94, 673-680 (2009)

Also: S. L. Firebaugh, F. Roignant & E.A. Terray, "Modelling the Response of Photoacoustic Gas Sensors"; Comsol Conf, Boston, MA ; Oct 8-10,2009

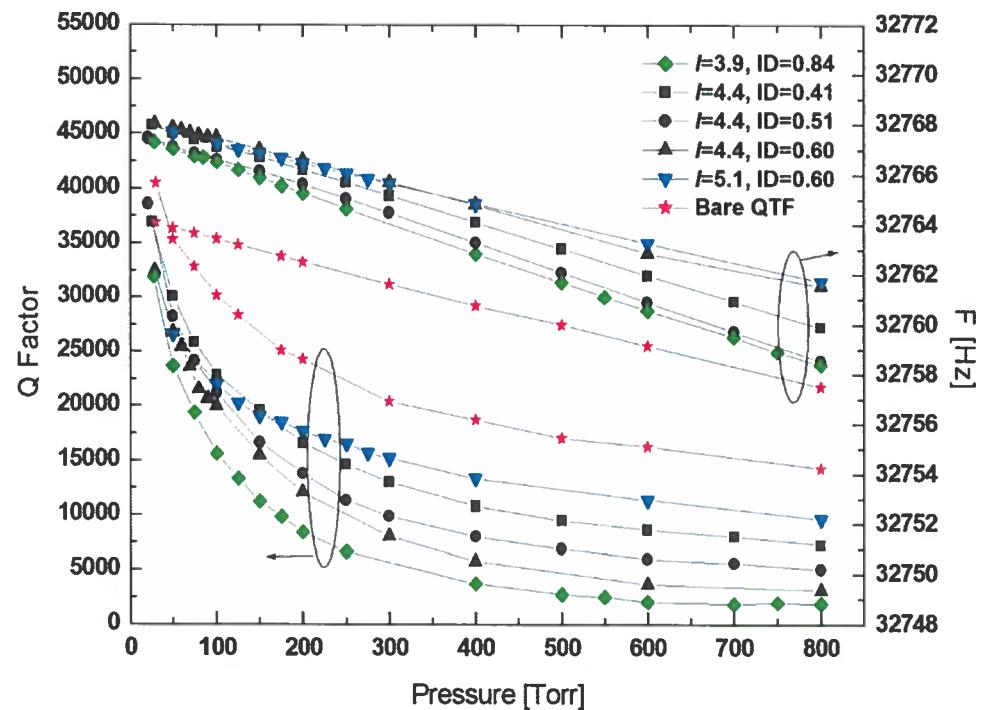
# Principal Architecture of a QEPAS Gas Sensor



# Signal-to-noise ratio as a function of pressures

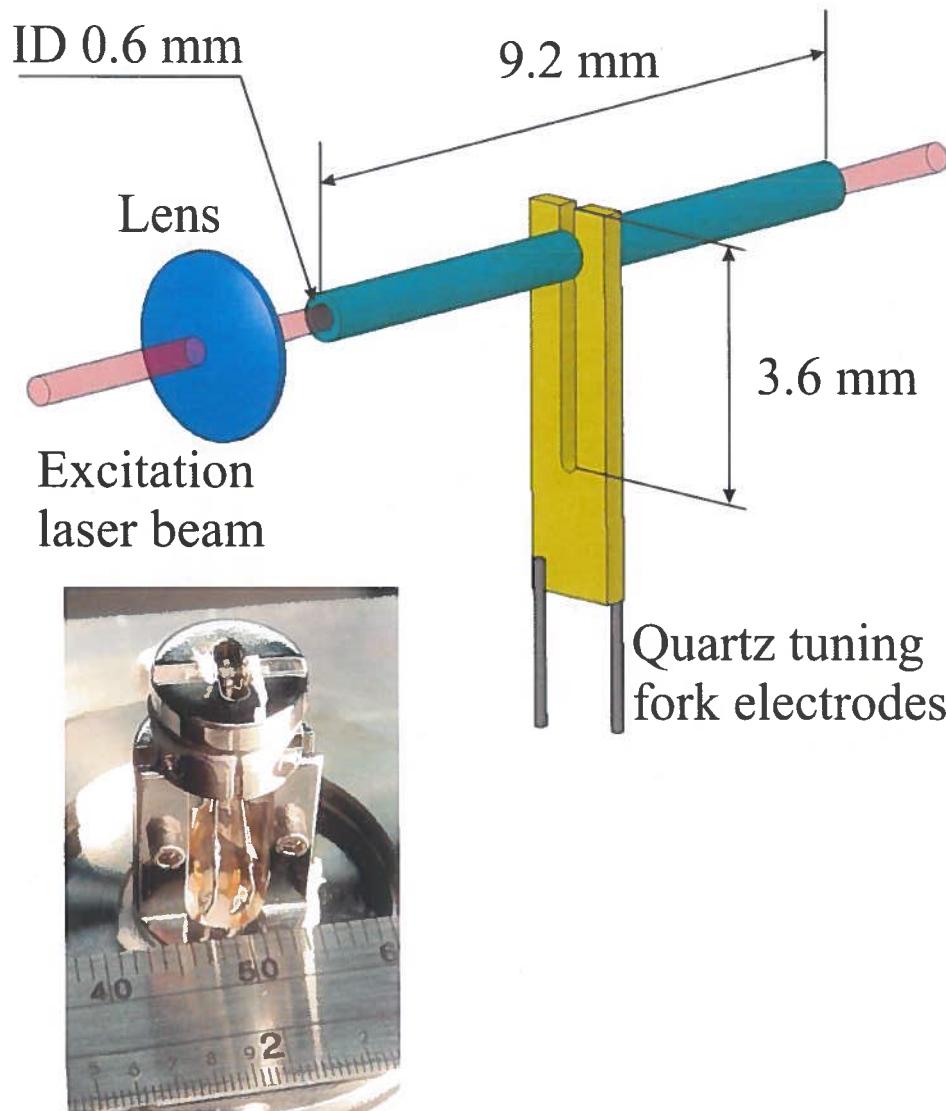


Signal-to-noise ratio as a function of pressures for different tube sizes and bare QTF.



Q factor and frequency of the QTF as a function of pressure for different tube lengths and diameters.

# QEPAS spectrophone



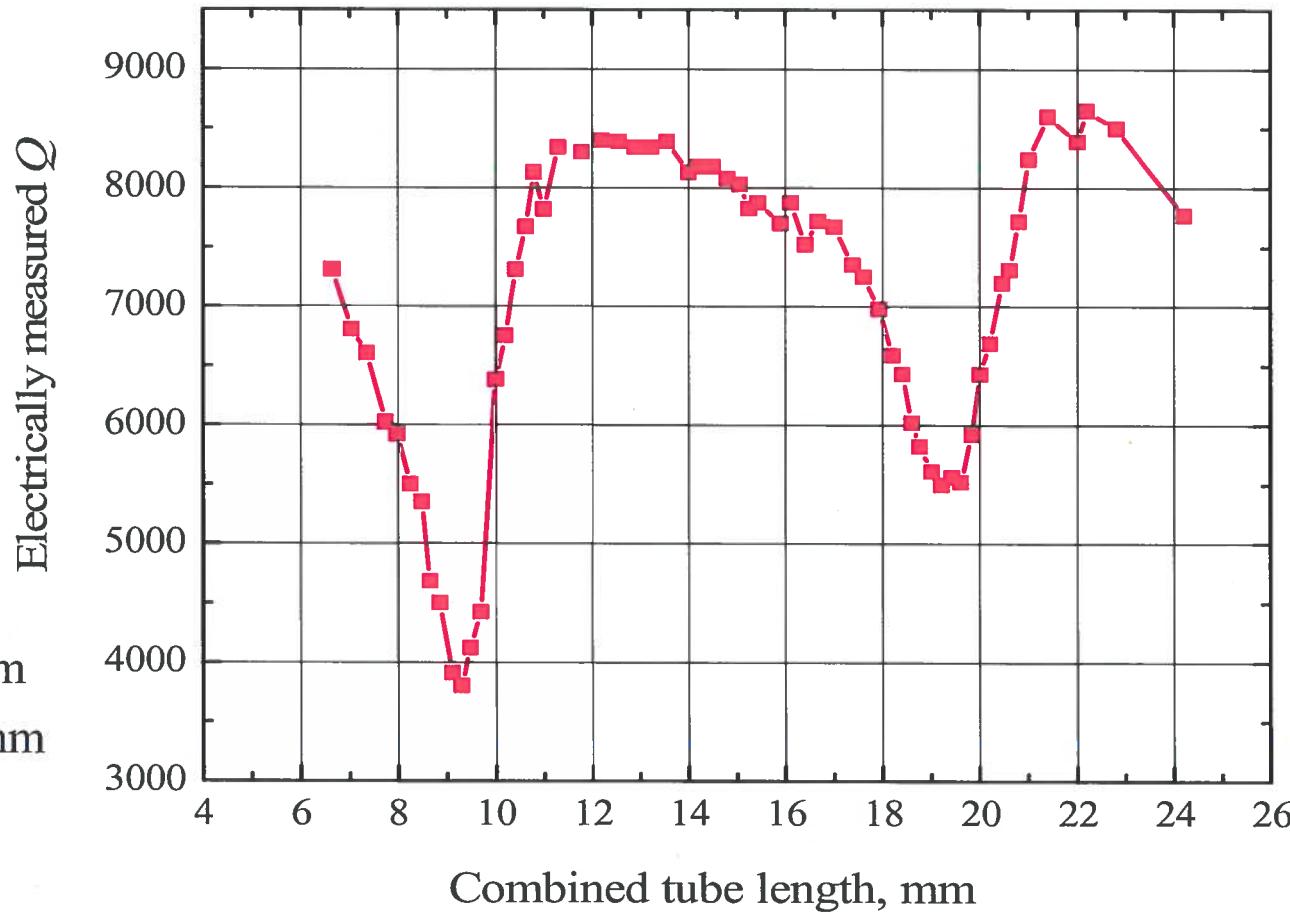
## Micro-resonator (mR) tubes

- Must be close to QTF but not touch QTF (25-50  $\mu\text{m}$  gaps).
- Optimum inner diameter 0.6 mm
- Optimum micro-resonator tubes are 4.4 mm long ( $\sim\lambda/4 < l < \lambda/2$  for sound at 32.8 kHz)
- **Maximum SNR of QTF with mR tubes:  $\times 30$**  (depending gas composition and pressure)

# Acoustic and quartz resonators - interaction

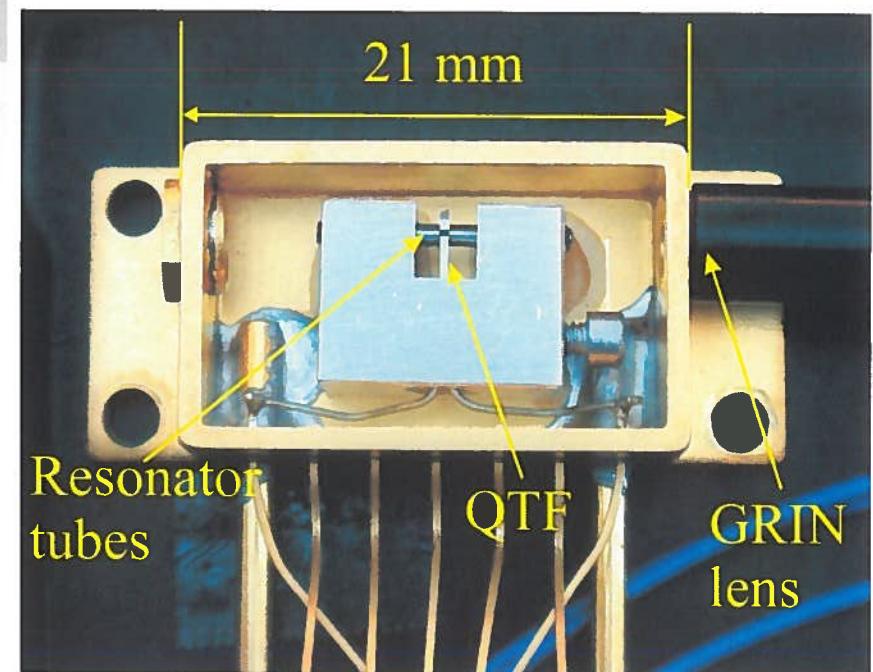
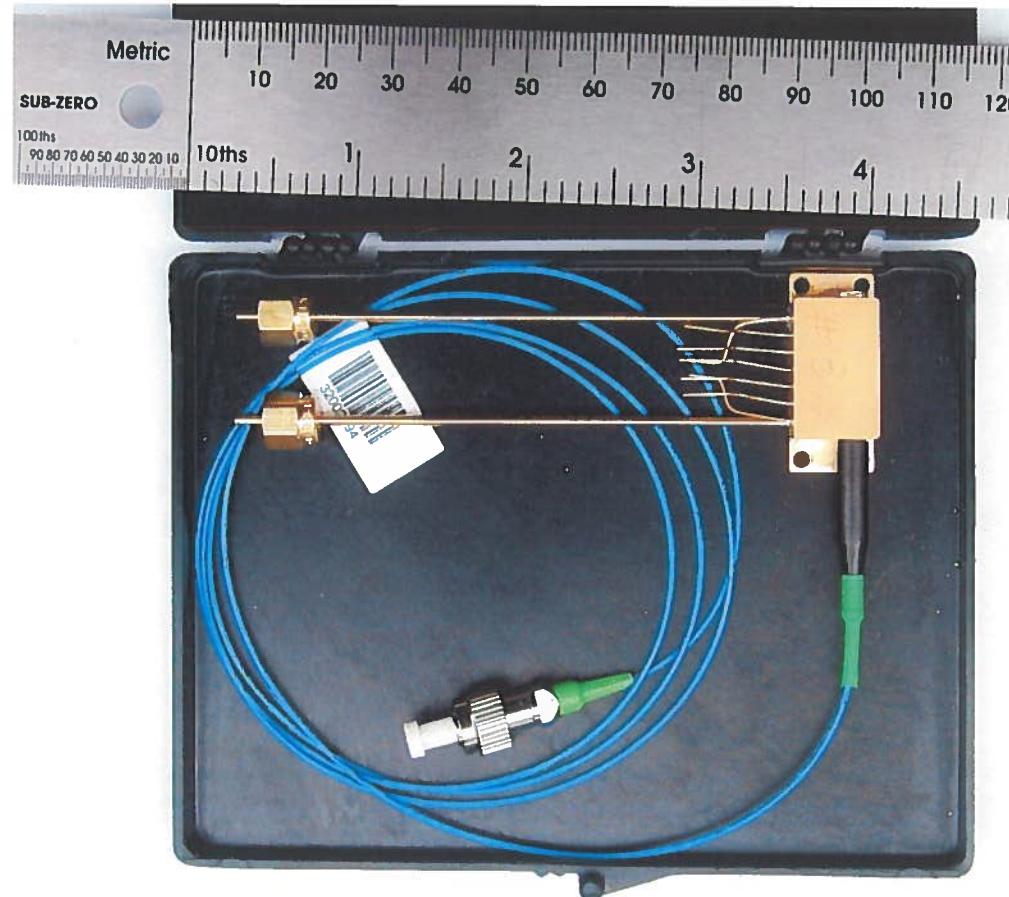
---

ID: 0.4 mm  
OD: 0.7 mm



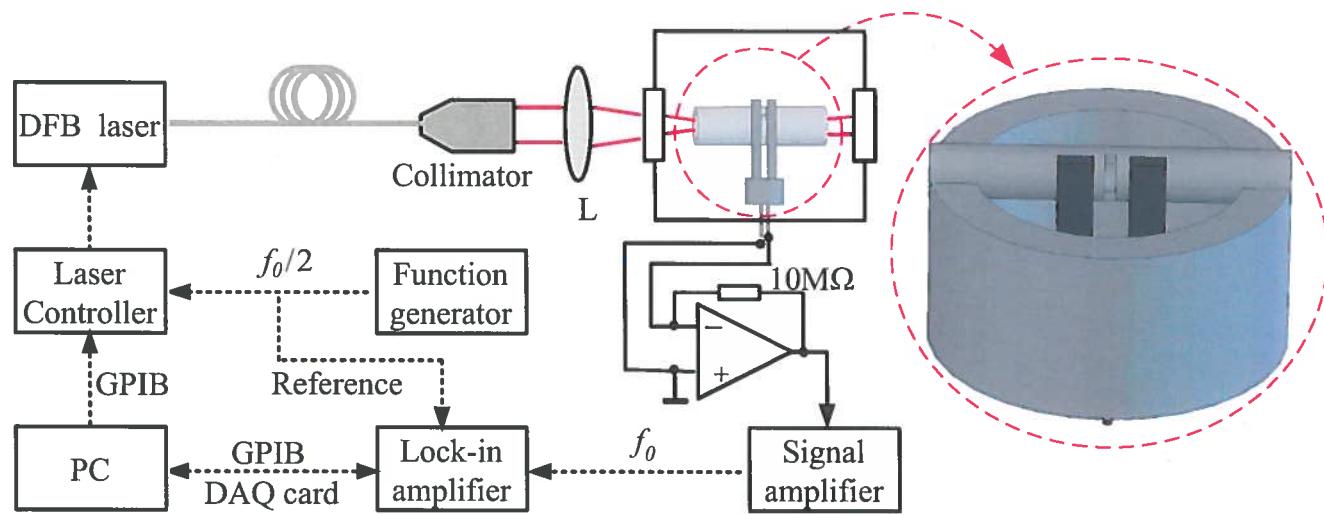
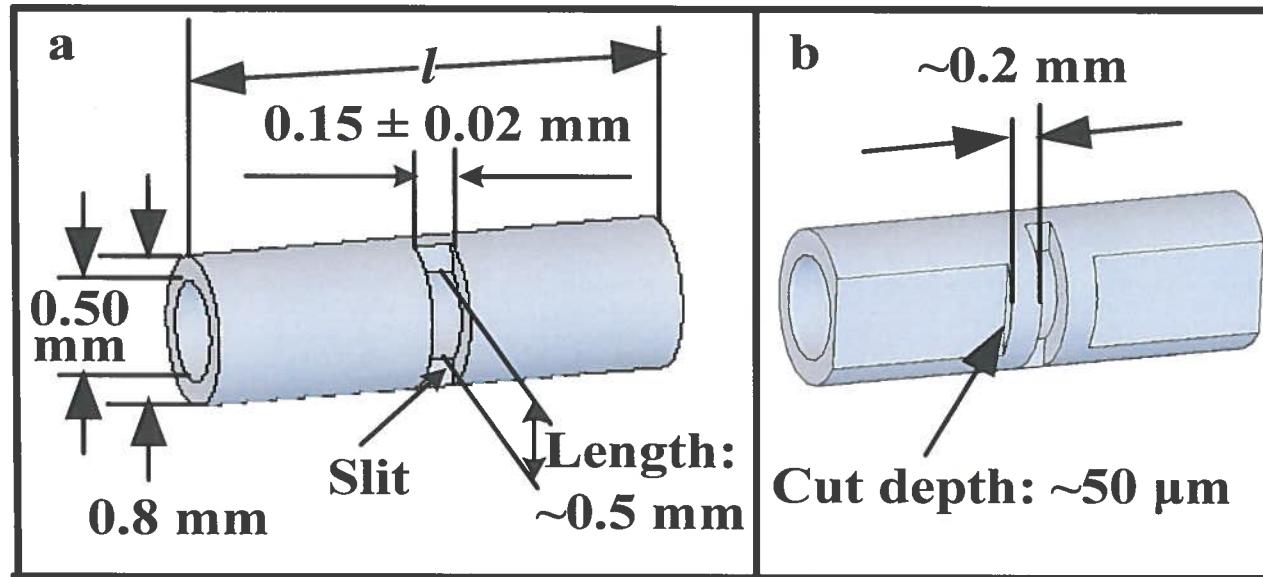
When acoustic and QTF resonances coincide,  
the measured  $Q$  is significantly reduced.

# Alignment-free QEPAS Absorption Detection Module



RICE

# Off-beam QEPAS based Gas Sensor



Source: K. Liu, X. Gao (AIOFM), W. Chen (ULCO), A. Kosterev et al. (Rice)

# Merits of QEPAS based Trace Gas Detection

---

- Very small sensing module and sample volume (a few mm<sup>3</sup>)
- Extremely low dissipative losses
- Optical detector is not required
- Wide dynamic range
- Frequency and spatial selectivity of acoustic signals
- Rugged transducer – quartz monocrystal; can operate in a wide range of pressures and temperatures
- Immune to environmental acoustic noise, sensitivity is limited by the fundamental thermal TF noise:  $k_B T$  energy in the TF symmetric mode
- Absence of low-frequency noise: SNR scales as  $\sqrt{t}$ , up to  $t=3$  hours as experimentally verified

## QEPAS: some challenges

- Responsivity depends on the speed of sound and molecular energy transfer processes
- Sensitivity scales with laser power
- Effect of H<sub>2</sub>O
- Cross sensitivity issues

# QEPAS Performance for 15 Trace Gas Species (May '10)

Molecule (Host)	Frequency, cm <sup>-1</sup>	Pressure, Torr	NNEA, cm <sup>-1</sup> W/Hz <sup>½</sup>	Power, mW	NEC ( $\tau=1$ s), ppmv
H <sub>2</sub> O (N <sub>2</sub> )**	7306.75	60	1.9×10 <sup>-9</sup>	9.5	0.09
HCN (air: 50% RH)*	6539.11	60	4.6×10 <sup>-9</sup>	50	0.16
C <sub>2</sub> H <sub>2</sub> (N <sub>2</sub> )*	6523.88	720	4.1×10 <sup>-9</sup>	57	0.03
NH <sub>3</sub> (N <sub>2</sub> )*	6528.76	575	3.1×10 <sup>-9</sup>	60	0.06
C <sub>2</sub> H <sub>4</sub> (N <sub>2</sub> )*	6177.07	715	5.4×10 <sup>-9</sup>	15	1.7
CH <sub>4</sub> (N <sub>2</sub> +1.2% H <sub>2</sub> O)*	6057.09	760	3.7×10 <sup>-9</sup>	16	0.24
CO <sub>2</sub> (breath ~50% RH)	6361.25	150	8.2×10 <sup>-9</sup>	45	40
H <sub>2</sub> S (N <sub>2</sub> )*	6357.63	780	5.6×10 <sup>-9</sup>	45	5
HCl (N <sub>2</sub> dry)	5739.26	760	5.2×10 <sup>-8</sup>	15	0.7
CO <sub>2</sub> (N <sub>2</sub> +1.5% H <sub>2</sub> O) *	4991.26	50	1.4×10 <sup>-8</sup>	4.4	18
CH <sub>2</sub> O (N <sub>2</sub> :75% RH)*	2804.90	75	8.7×10 <sup>-9</sup>	7.2	0.12
CO (N <sub>2</sub> )	2196.66	50	5.3×10 <sup>-7</sup>	13	0.5
CO (propylene)	2196.66	50	7.4×10 <sup>-8</sup>	6.5	0.14
N <sub>2</sub> O (air+5%SF <sub>6</sub> )	2195.63	50	1.5×10 <sup>-8</sup>	19	0.007
NO (N <sub>2</sub> +H <sub>2</sub> O)	1900.07	250	7.5×10 <sup>-9</sup>	100	0.003
C <sub>2</sub> H <sub>5</sub> OH (N <sub>2</sub> )**	1934.2	770	2.2×10 <sup>-7</sup>	10	90
C <sub>2</sub> HF <sub>5</sub> (N <sub>2</sub> )***	1208.62	770	7.8×10 <sup>-9</sup>	6.6	0.009
NH <sub>3</sub> (N <sub>2</sub> )*	1046.39	110	1.6×10 <sup>-8</sup>	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  $\tau=1$ s time constant, 18 dB/oct filter slope.

For comparison: conventional PAS 2.2 (2.6) $\times$ 10<sup>-9</sup> cm<sup>-1</sup>W/ $\sqrt{\text{Hz}}$  (1,800; 10,300 Hz) for NH<sub>3</sub>\*, (\*\*)

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



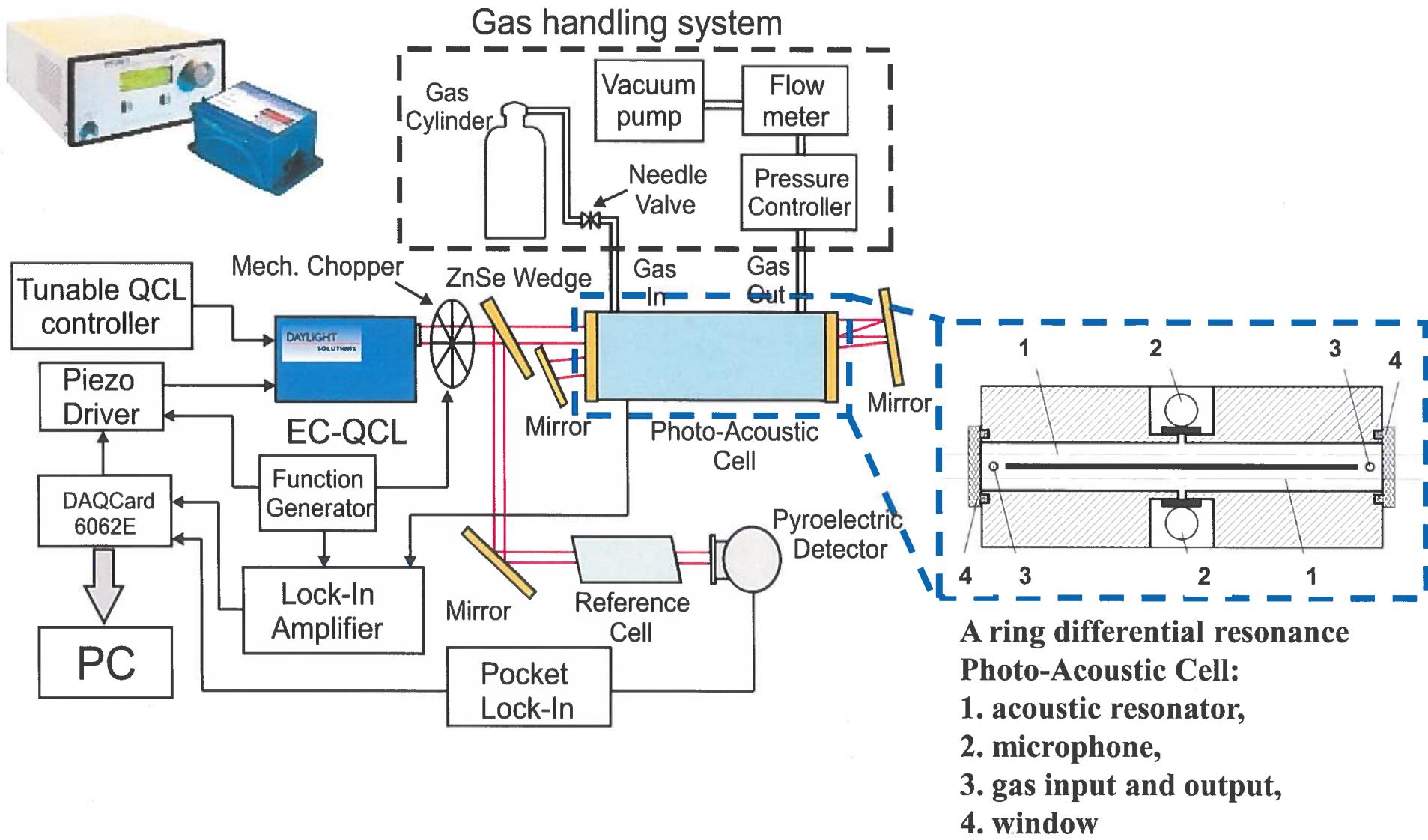
# Recent Applications of mid-infrared Laser based Trace Gas Sensors

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

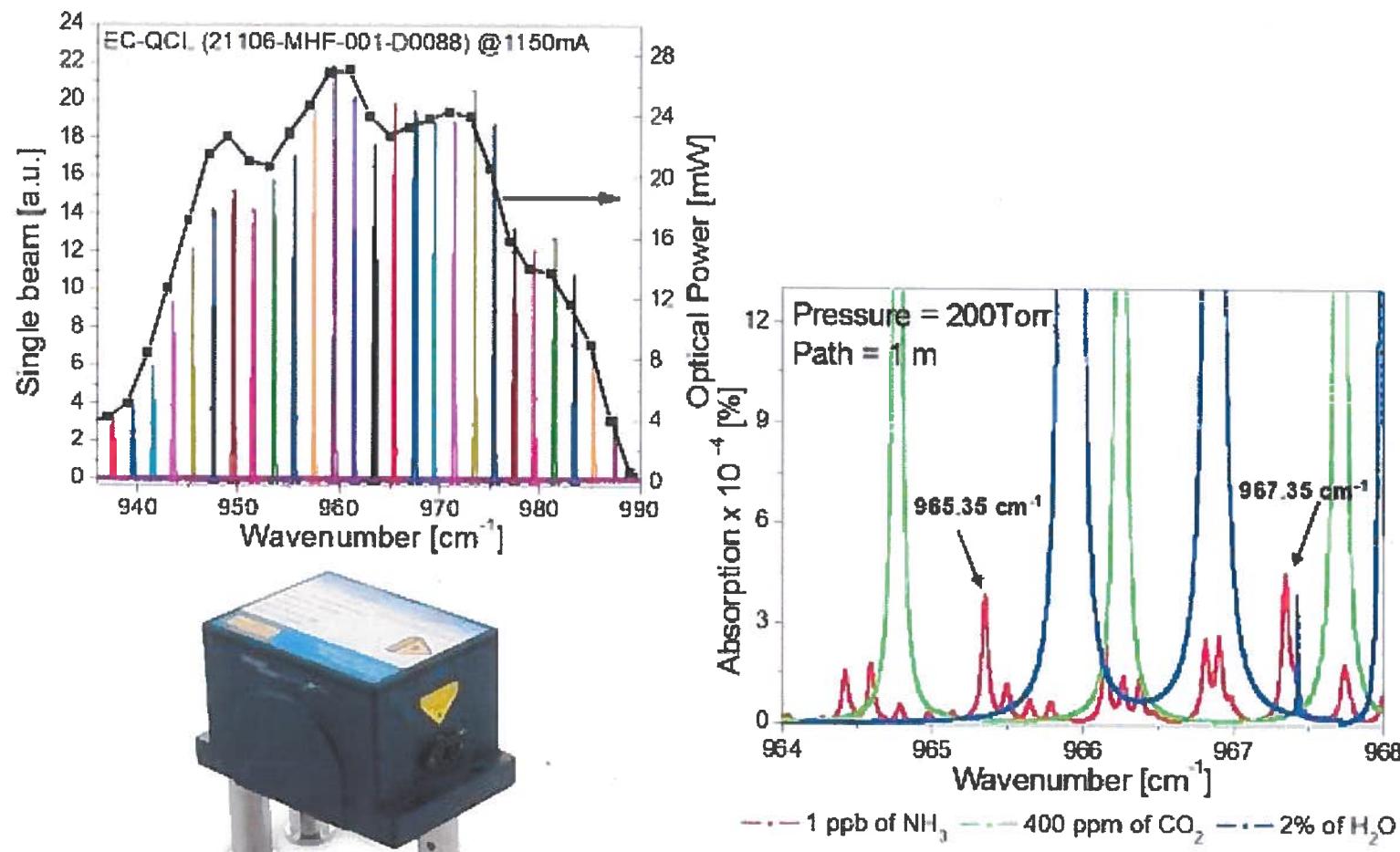
---

- 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 diseases)

# Mid-IR EC-QCL based AM-PAS Sensor for atmospheric NH<sub>3</sub> Detection



# Tuning range of a Daylight Solutions CW TEC 10.34 $\mu\text{m}$ EC-QCL and HITRAN simulated spectra at 200Torr



RICE

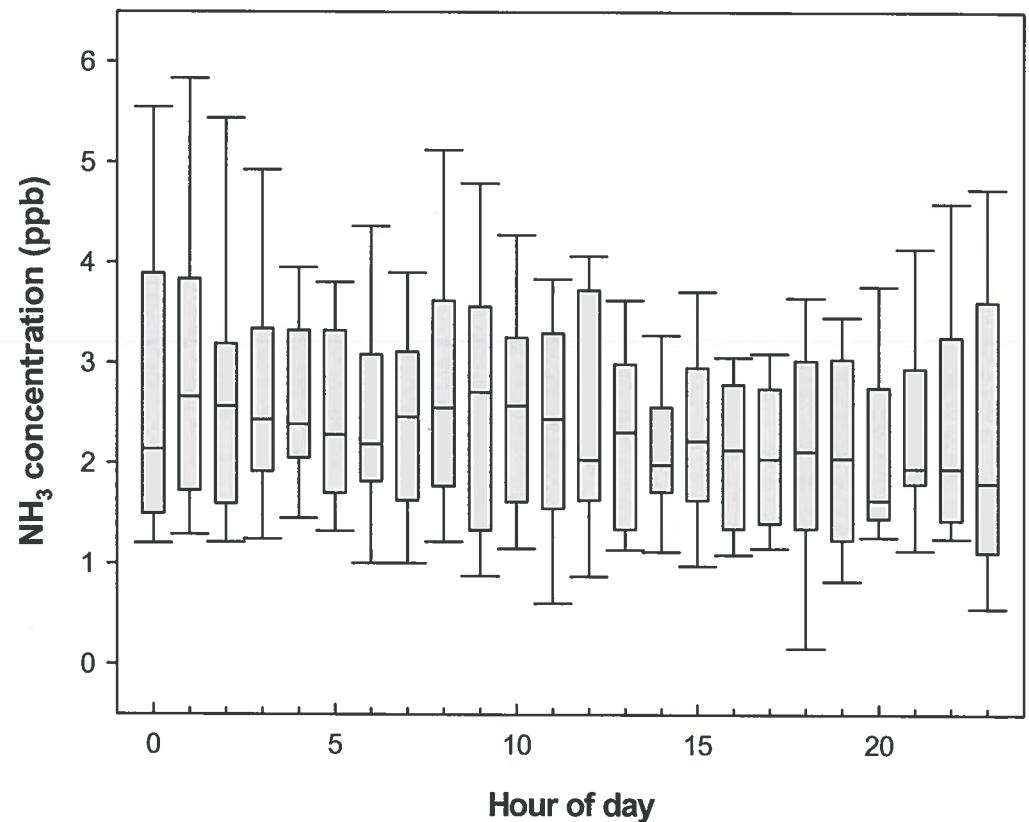
# Preliminary $\text{NH}_3$ Data after Sensor Installation on the 100 m high Moody Tower Roof (UH campus)



Moody Tower at the UH campus, Houston, TX



Ammonia sensor and electronics  
installed on Moody Tower roof.

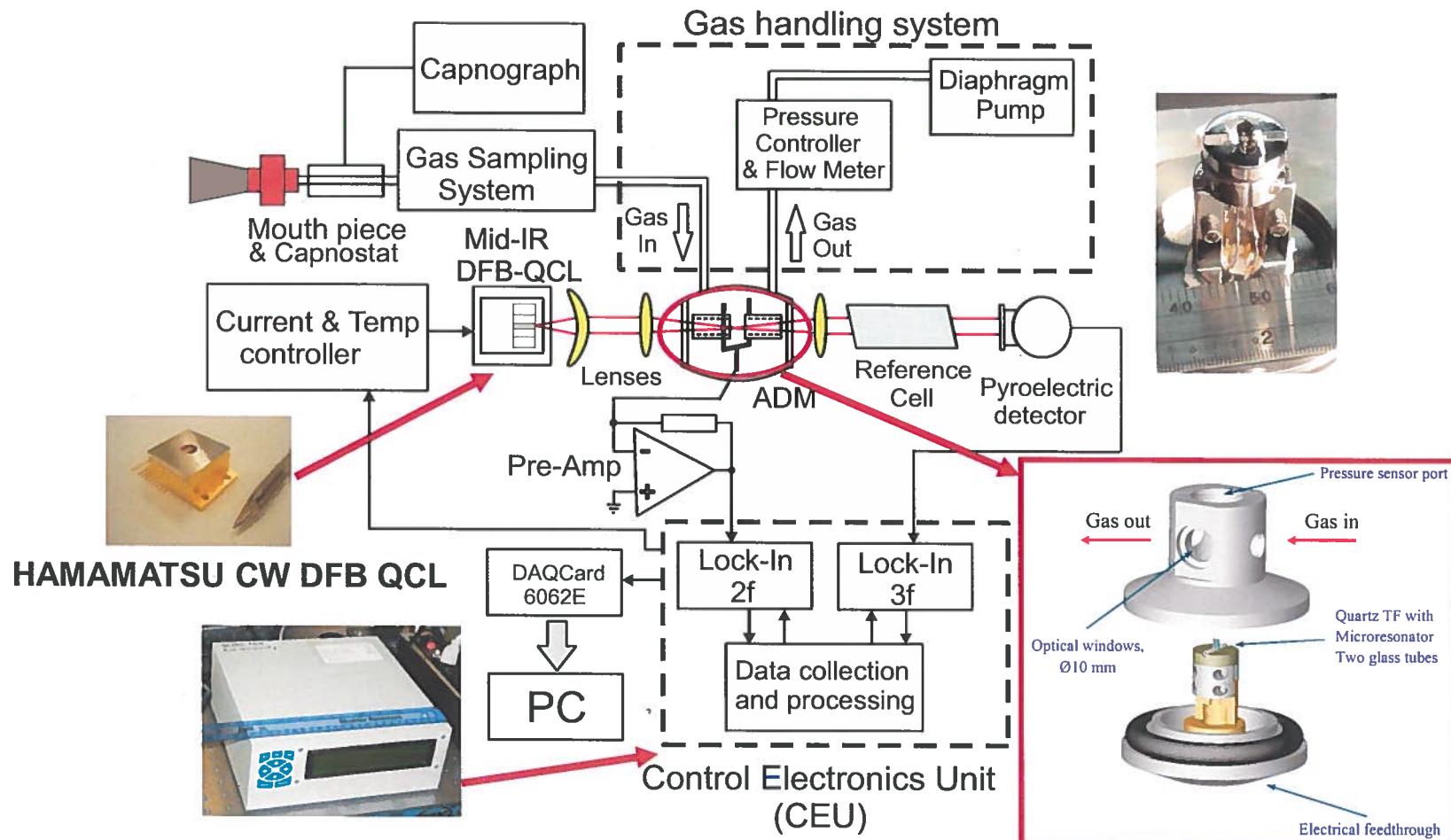


Diurnal trend of  $\text{NH}_3$  concentration by using acquired data for a period of 16 days (Feb. 12 – Mar. 1, 2010)

# Important Biomedical Species

Molecule	Formula	Biological/Pathology Indication	Center wavelength [μm]
Pentane	C <sub>5</sub> H <sub>12</sub>	Inflammatory diseases, transplant rejection	6.8
Ethane	 C <sub>2</sub> H <sub>6</sub>	Lipid peroxidation and oxidation stress, lung cancer (low ppbv range)	6.8
Carbon Dioxide isotope ratio	<sup>13</sup> CO <sub>2</sub> / <sup>12</sup> CO <sub>2</sub>	Helicobacter pylori infection (peptic ulcers, gastric cancer)	4.4
Carbonyl Sulfide	 COS	Liver disease, acute rejection in lung transplant recipients (10-500 ppbv)	4.8
Carbon Disulfide	CS <sub>2</sub>	Disulfiram treatment for alcoholism	6.5
Ammonia	 NH <sub>3</sub>	Liver and renal diseases, exercise physiology	10.3
Formaldehyde	 CH <sub>2</sub> O	Cancerous tumors (400-1500 ppbv)	5.7
Nitric Oxide	 NO	Nitric oxide synthase activity, inflammatory and immune responses (e.g. asthma) and vascular smooth muscle response (6-100 ppb)	5.3
Hydrogen Peroxide	H <sub>2</sub> O <sub>2</sub>	Airway inflammation, oxidative stress (1-5 ppbv)	7.9
Carbon Monoxide	 CO	Smoking response, lipid peroxidation, CO poisoning, vascular smooth muscle response	4.7
Ethylene	 C <sub>2</sub> H <sub>4</sub>	Oxidative stress, cancer	10.6
Acetone	 C <sub>3</sub> H <sub>6</sub> O	Ketosis, diabetes mellitus	7.3

# QEPAS based NH<sub>3</sub> Gas Sensor Architecture



Advantages of using CW DFB-QCL in the sensor architecture:

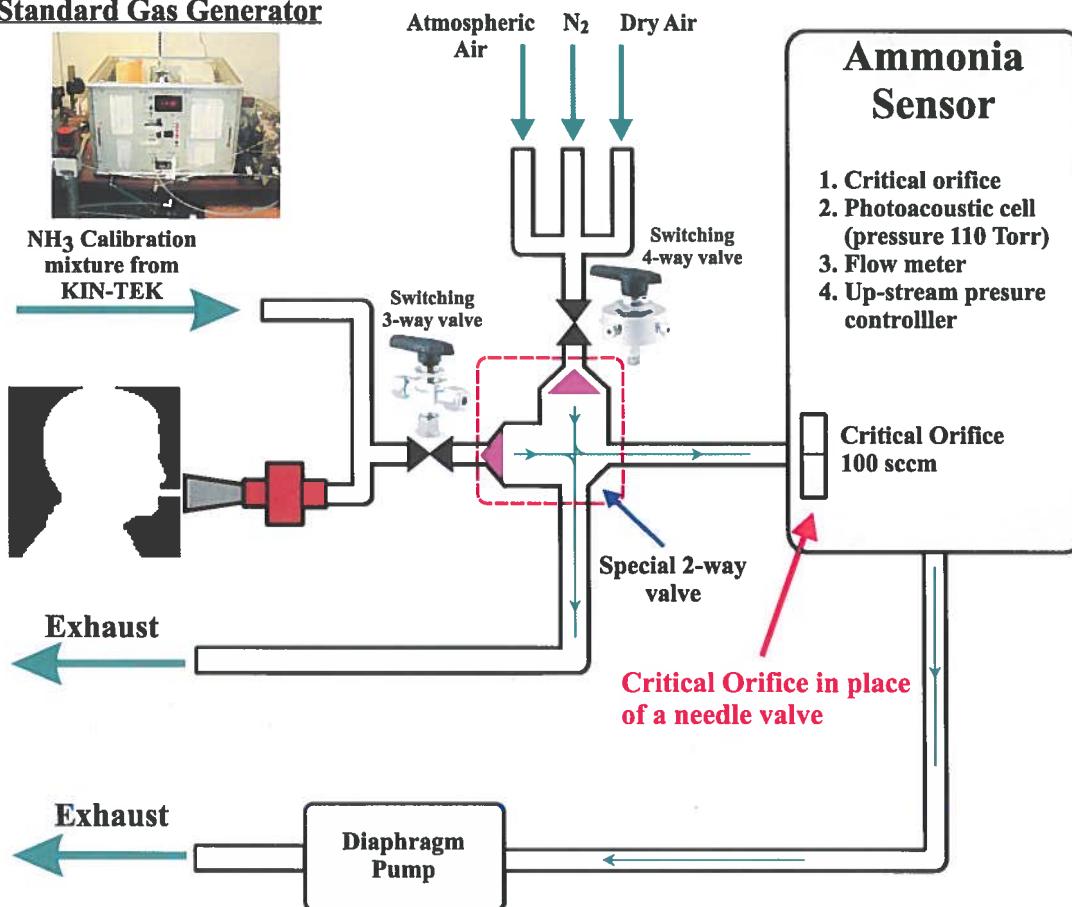
- Small laser package -> system compactness,
- DFB-QCL room temperature operation,
- Performing WM spectroscopy at optimum modulation depth,
- Baseline reduction with 2f WM.

# Real-time Breath Monitor Interface

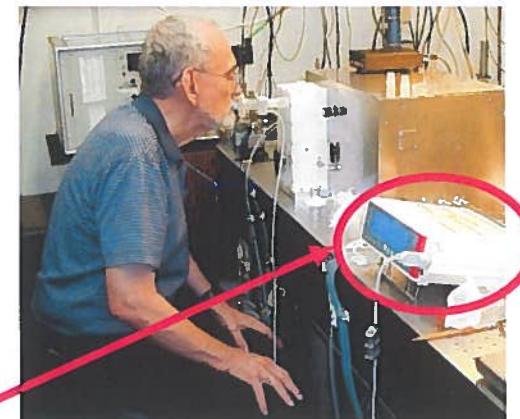
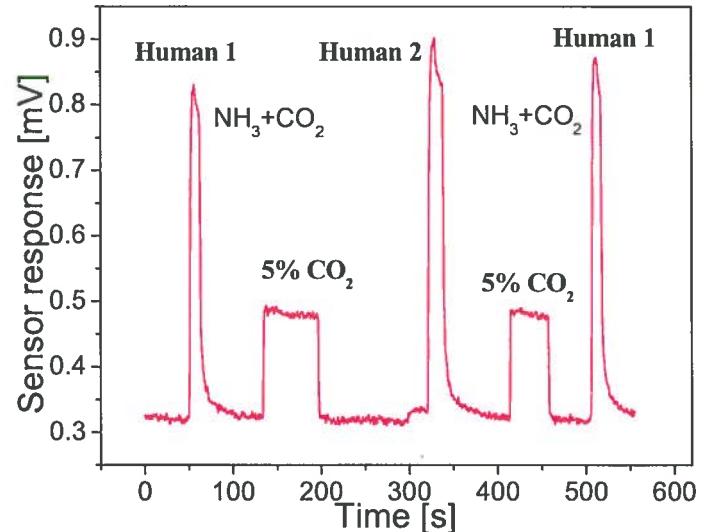
## KIN-TEK Standard Gas Generator



NH<sub>3</sub> Calibration mixture from KIN-TEK

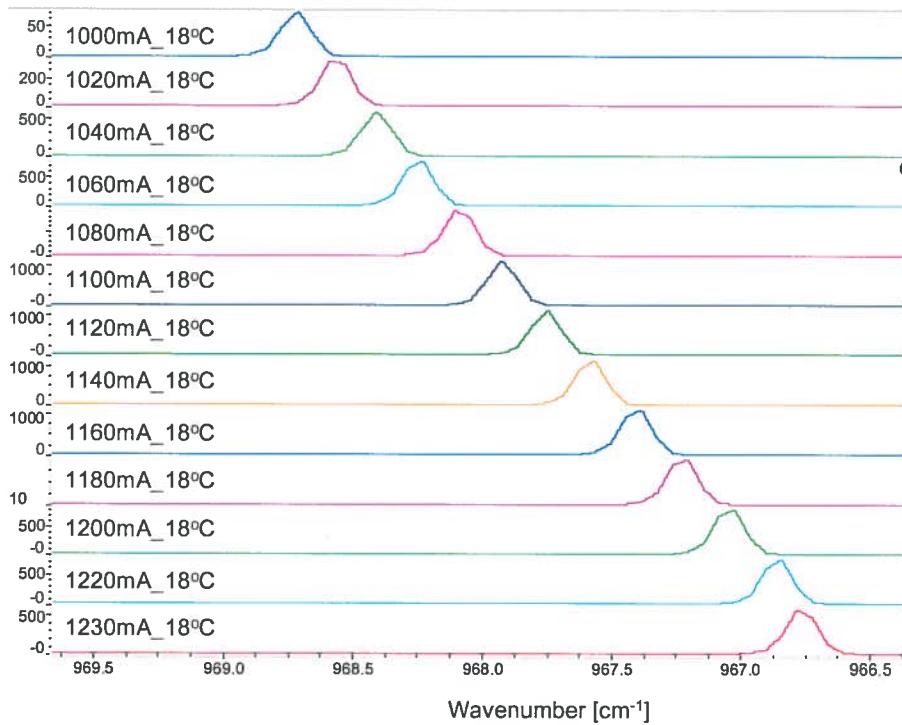


- Controlled flow
- Continuous control of mouth pressure
- Continuous monitoring of CO<sub>2</sub> concentration (capnograph) and its use in QEPAS data processing

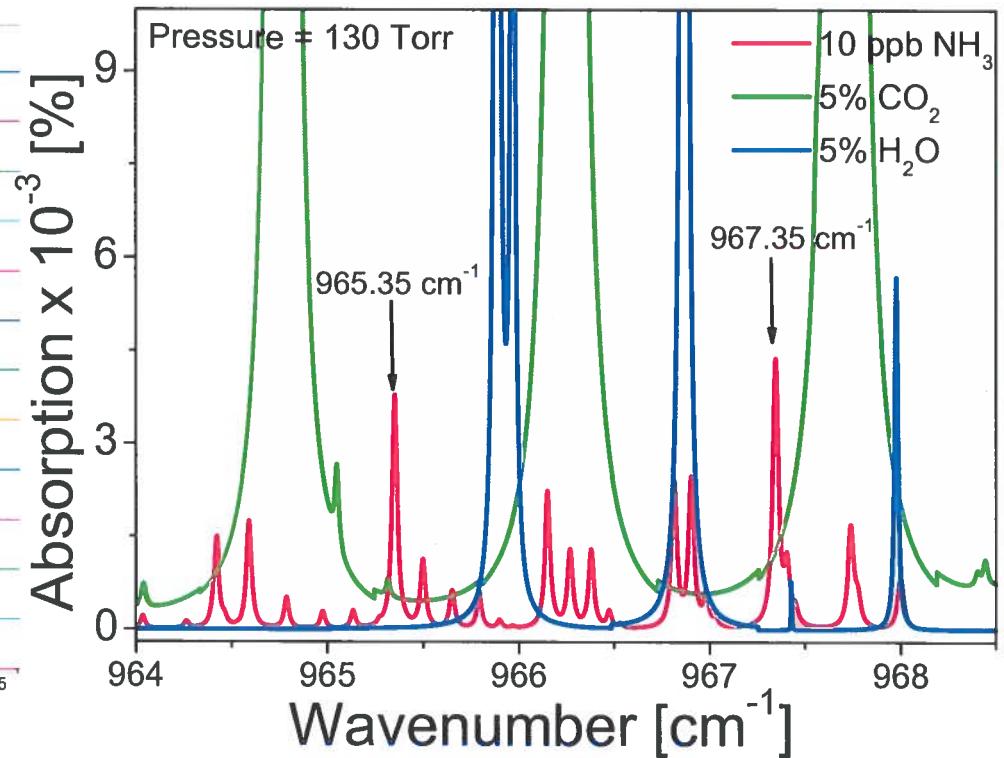


RICE

# Line selection for HAMAMATSU CW DFB QCL



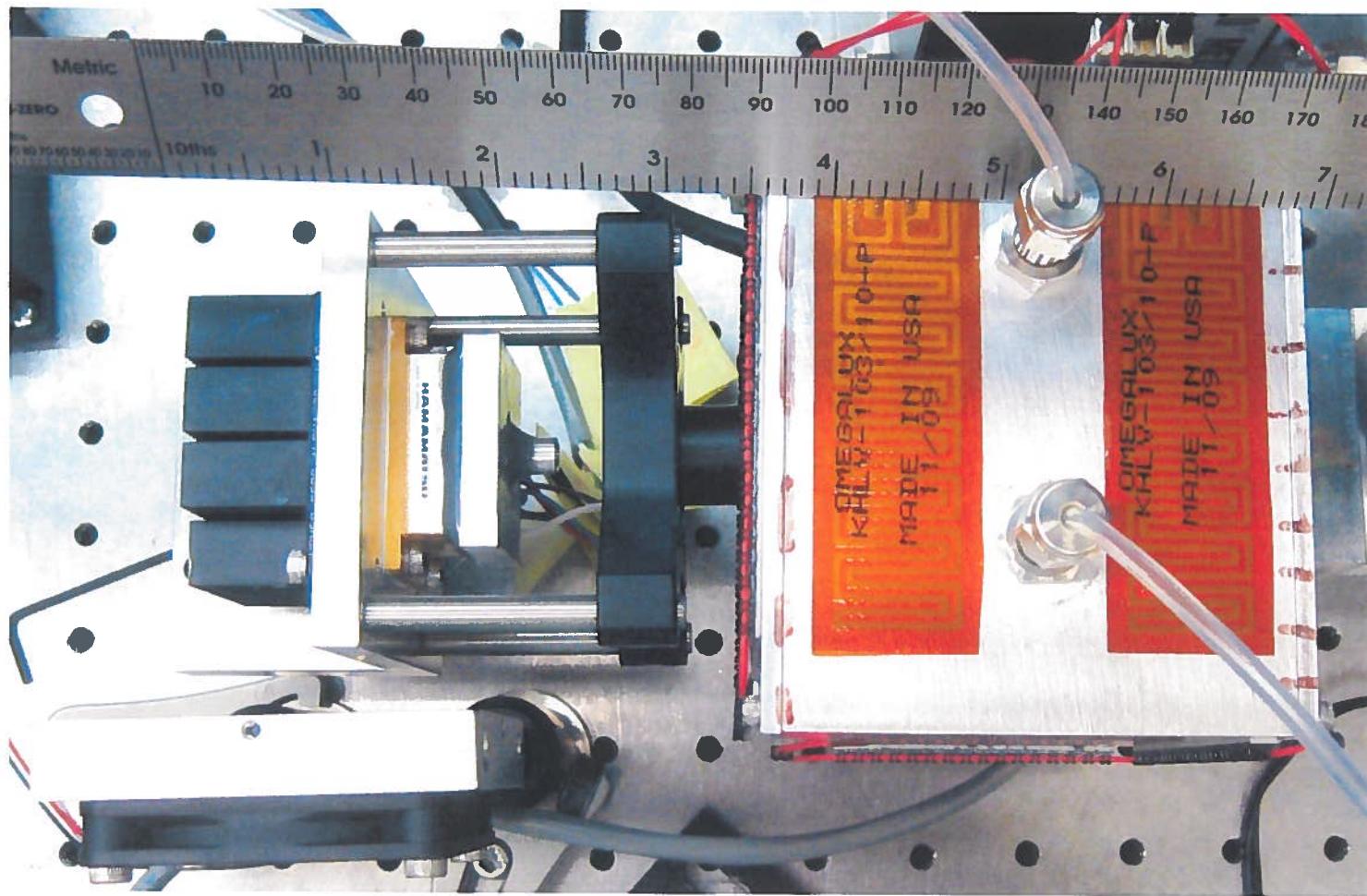
Single mode QCL radiation recorded with FTIR for different laser current values at laser temperature of 18°C.



HITRAN simulated spectra @ 130 Torr indicating two NH<sub>3</sub> absorption lines of interest

# QEPAS based breath analyzer using a DFB-QCL

---



# Motivation for Nitric Oxide Detection

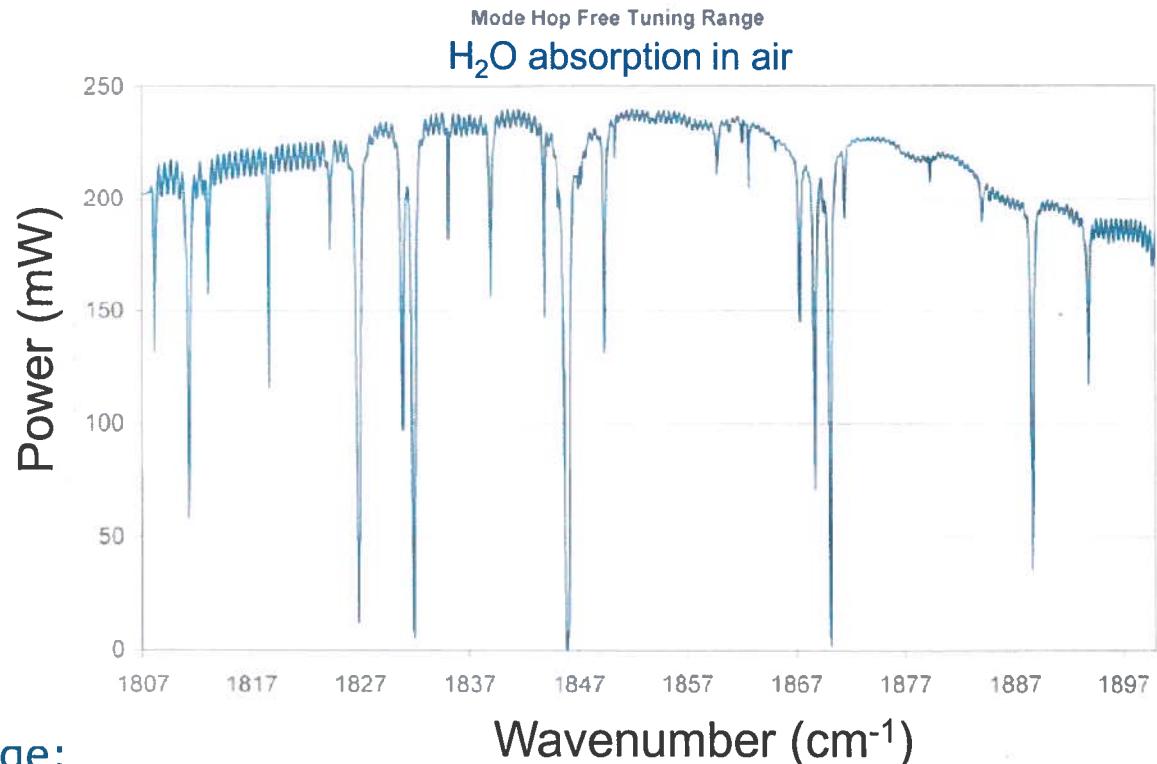
---

- Atmospheric Chemistry
- Environmental pollutant gas monitoring
  - NO<sub>x</sub> 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
- Photofragmentation of nitro-based explosives (TNT)

# High power fiber-coupled QCL for NO detection



CW Operation at 16.5C, 450mA



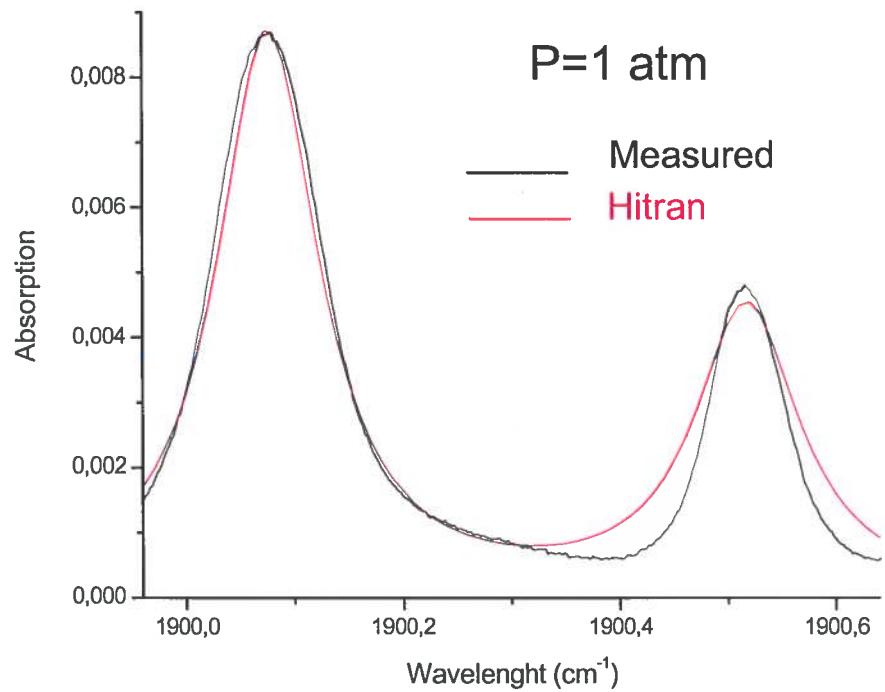
- **Mid-IR EC-QCL (DLS)**

- Wavelength tuning range:  
5.26-5.53  $\mu\text{m}$  (1807-1900  $\text{cm}^{-1}$ )
- MHF spectral range 5% of center wavelength:  
5.4  $\mu\text{m}$ ; (1846 $\text{cm}^{-1}$ )
- Maximum tuning Rate 38 nm/sec
- Highest optical power: ~250 mW
- TE cooling, RT operation

Collaboration with:  
V. Spagnolo  
Politecnico Bari and CNR-LIT<sup>3</sup>

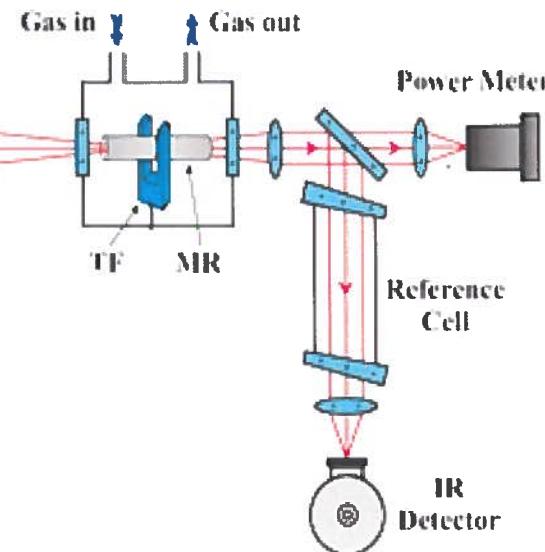
# NO absorption line selection

0.05% NO in  $\text{N}_2$  at 1 atm



P=1 atm

Measured  
Hitran



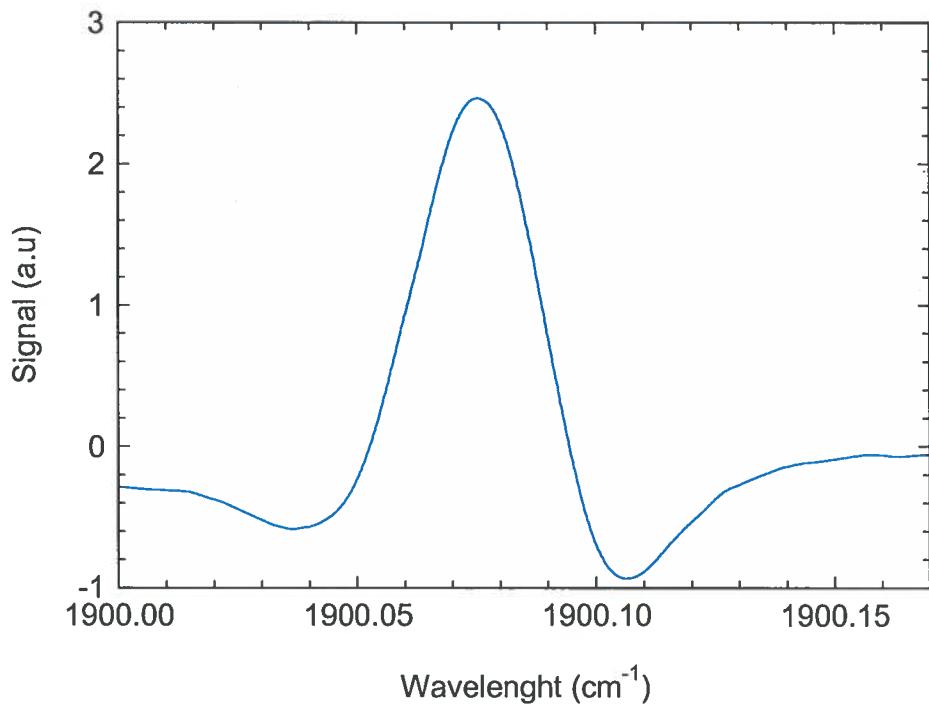
- Selected NO line  $1900.08 \text{ cm}^{-1}$
- High resolution mode-hop-free tuning is possible
- Laser Power:  $\sim 170 \text{ mW}$



RICE

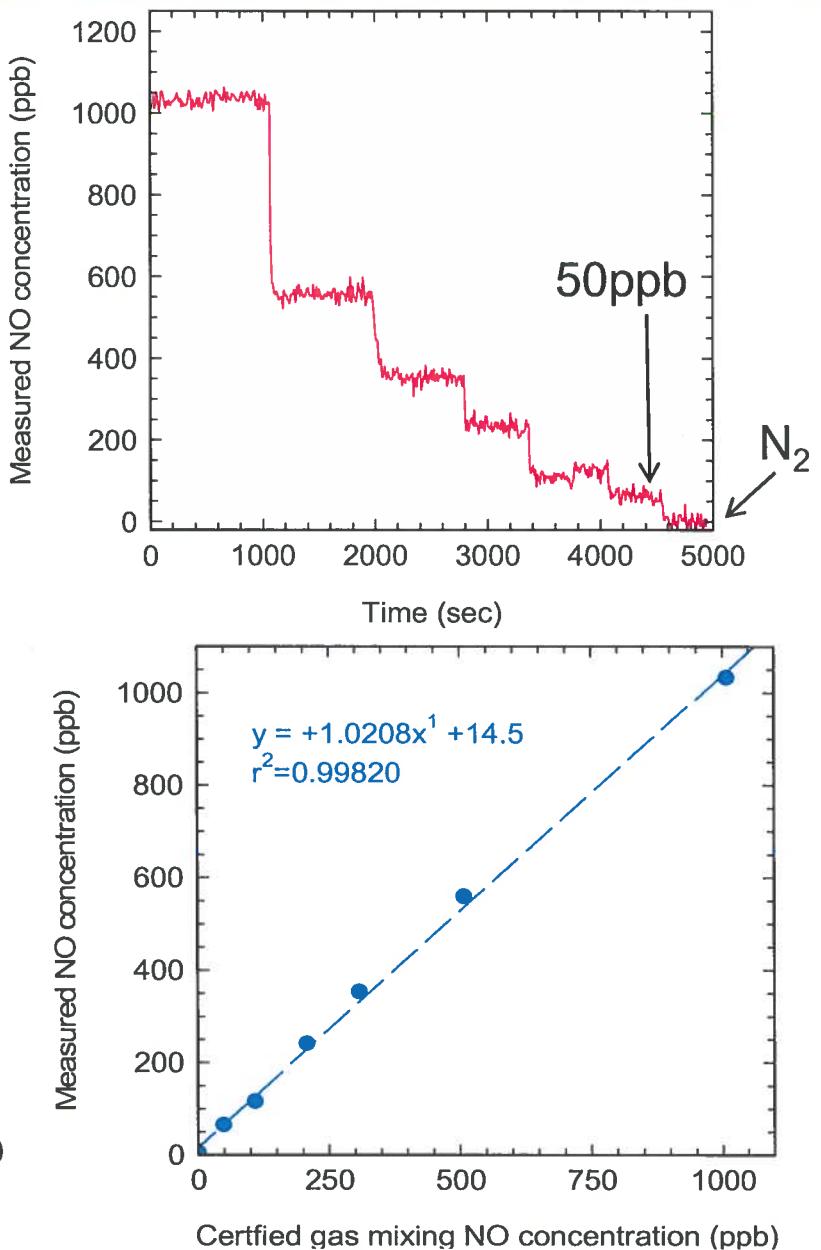
# CW MHF QCL based QEPAS NO sensor

3 ppm NO in N<sub>2</sub> and H<sub>2</sub>O at 250 Torr  
after background subtraction

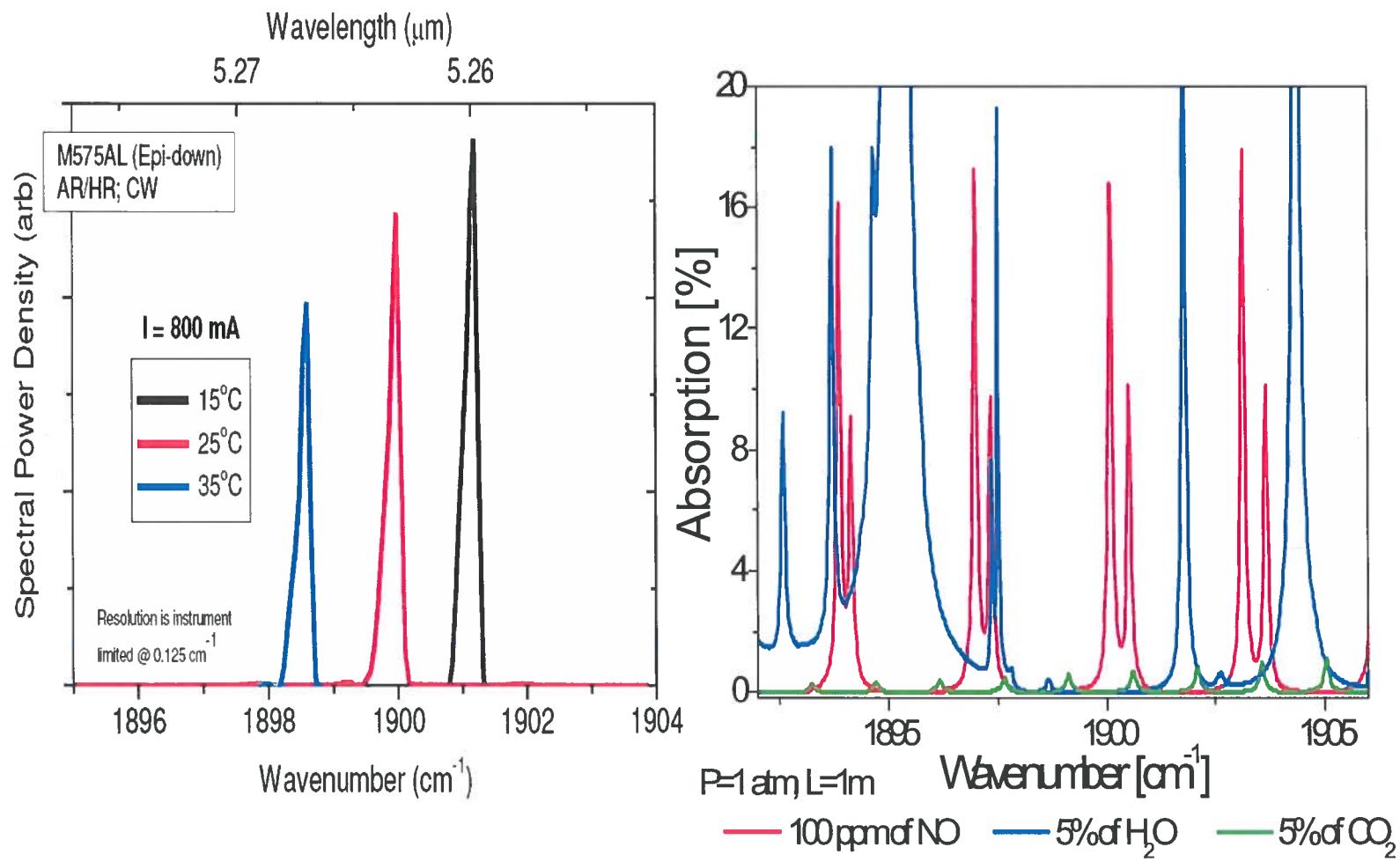


**Signal to noise >200**

- **Lowest detectable concentration < 15ppb**

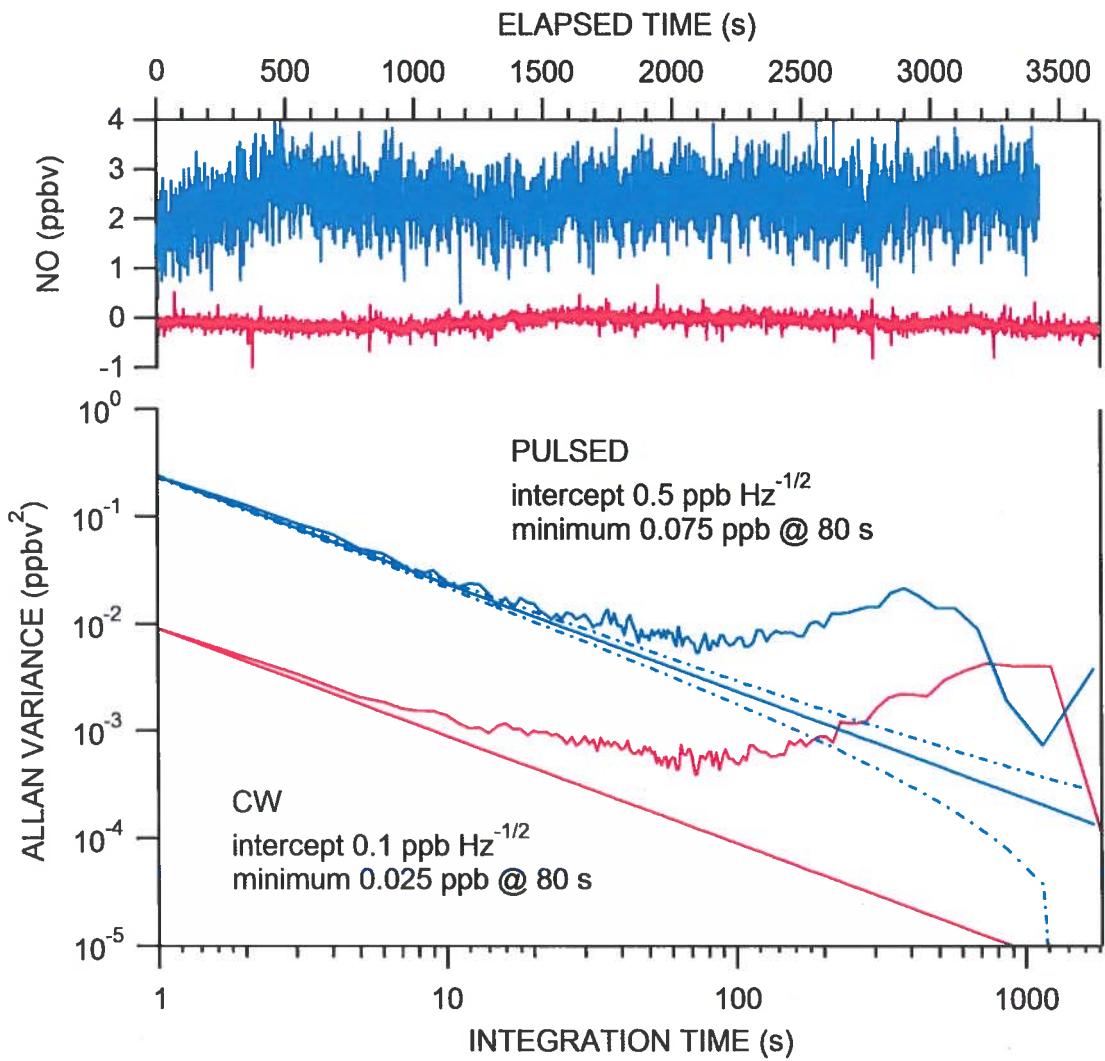


# Emission spectra of the Maxion 1900cm<sup>-1</sup> CW DFB TEC QCL and HITRAN simulated spectra



# CW vs. Pulsed: Allan Variance for Measured NO

- Narrow Line width
  - Improved specificity
  - Greater absorption
  - Improved accuracy
- Higher Power
  - TE-cooled detectors
  - Longer path lengths
- But, can be more susceptible to optical fringes
- TE-Cooled Detector (VIGO)
- Variance vs. integration time shows
  - the limits of averaging
- NO line at  $1900\text{ cm}^{-1}$  measured
- CW and pulsed, same laser
- Concentration noise, sdev @ 1 Hz
  - CW: 0.1 ppb
  - Pulsed: 0.5 ppb



Source: M. Zahniser, et. al. Aerodyne, FACSS 2009

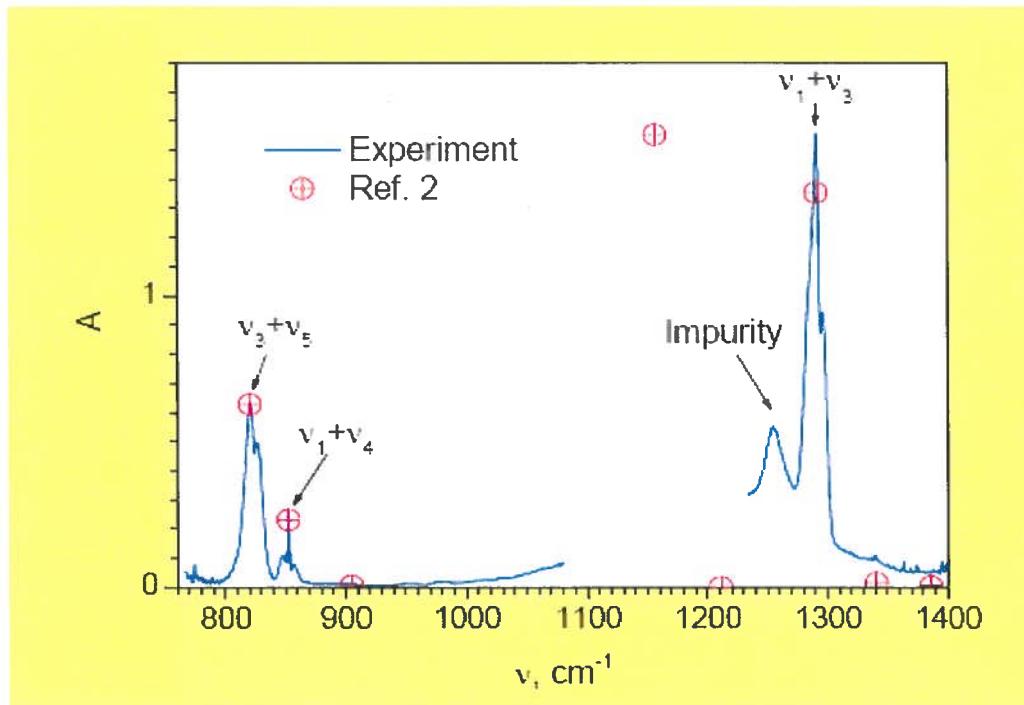
# Future Directions and Outlook of Chemical Trace Gas Sensing Technology

# Monitoring of Broadband Absorbers

---

- Freon 125 ( $\text{C}_2\text{HF}_5$ )
  - Refrigerant (leak detection)
  - Safe simulant for toxic chemicals, e.g. chemical warfare agents
- Acetone ( $\text{CH}_3\text{COCH}_3$ )
  - Recognized biomarker for diabetes
- TATP (Acetone Peroxide,  $\text{C}_6\text{H}_{12}\text{O}_4$ )
  - Highly Explosive
- Uranium Hexafluoride ( $\text{UF}_6$ )
- Hydrazine ( $\text{N}_2\text{H}_4$ )

# $\text{UF}_6$ Mid-Infrared Absorption Bands

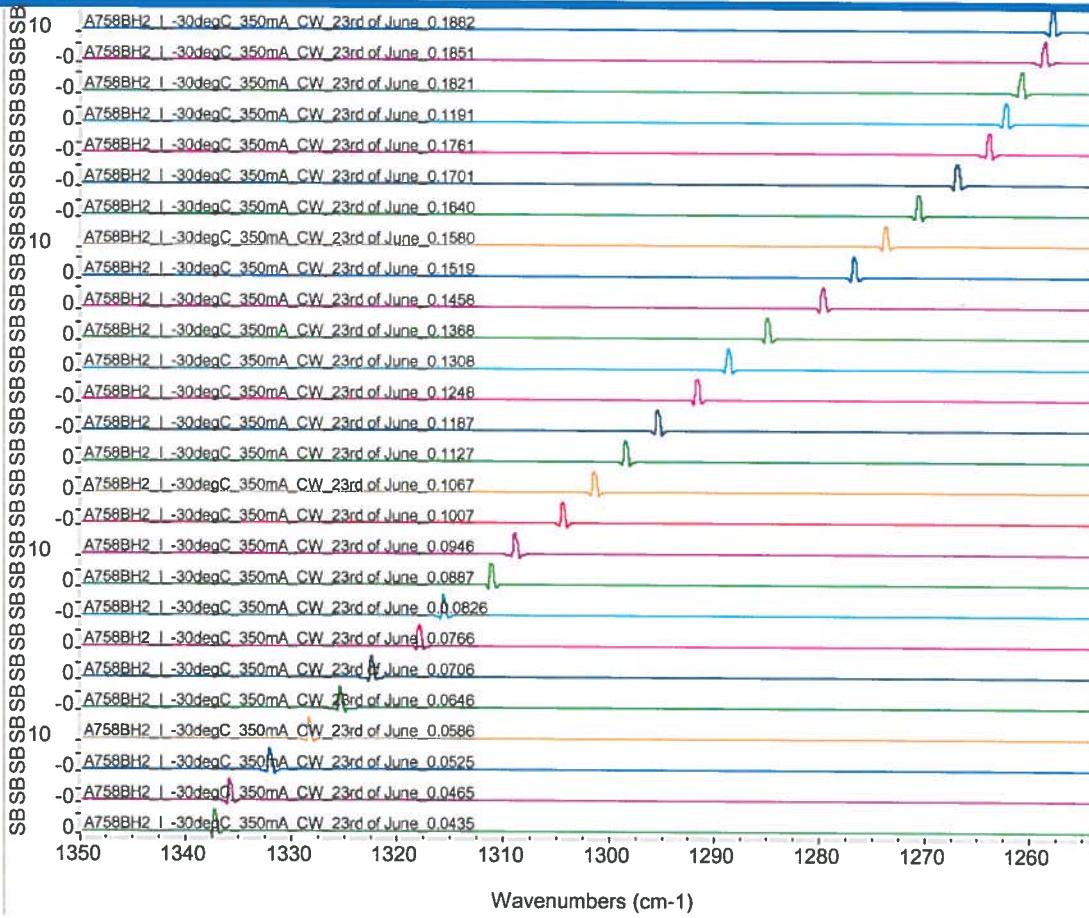


Absorption spectrum of gas mixture under investigation and observed spectral features identification.

Assignment	$\nu$ , $\text{cm}^{-1}$	$\sigma$ , $\text{cm}^{-1}/\text{atm}$
$2v_3+v_6$	$1386 \pm 2$	0.0018
$v_1+v_2+v_6$	1341	0.0088
$v_1+v_3$	$1290.9 \pm 0.5$	0.72
$2v_2+v_6$	$1211 \pm 2$	0.0007
$v_2+v_3$	$1156.9 \pm 0.5$	0.82
$v_3+2v_6$	905 $\pm 2$	0.0035
$v_1+v_4$	$852.8 \pm 0.5$	0.12
$v_3+v_5$	821	0.33
$v_3$	625	350

R.S. McDowell, L.B. Asprey, R.T. Paine, Vibrational spectrum and force field of uranium hexafluoride. -J. of Chemical Physics, Vol. 61, No. 9, 1974.

# HR coated CW 7.74 $\mu\text{m}$ FP-QCL in EC-configuration @ -30°C

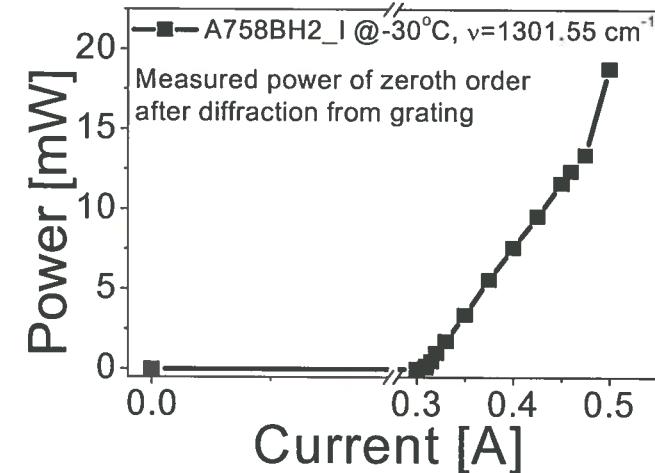
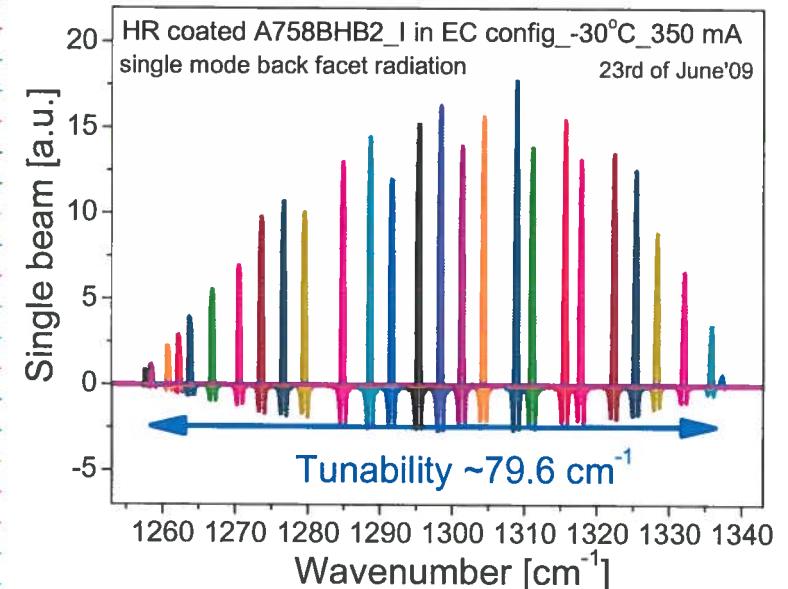


FTIR spectra for 2mm cavity length 7.74  $\mu\text{m}$  FP-QCL (A758BHB2\_I) in external cavity

Resistance @ RT is  $R = 650\Omega$

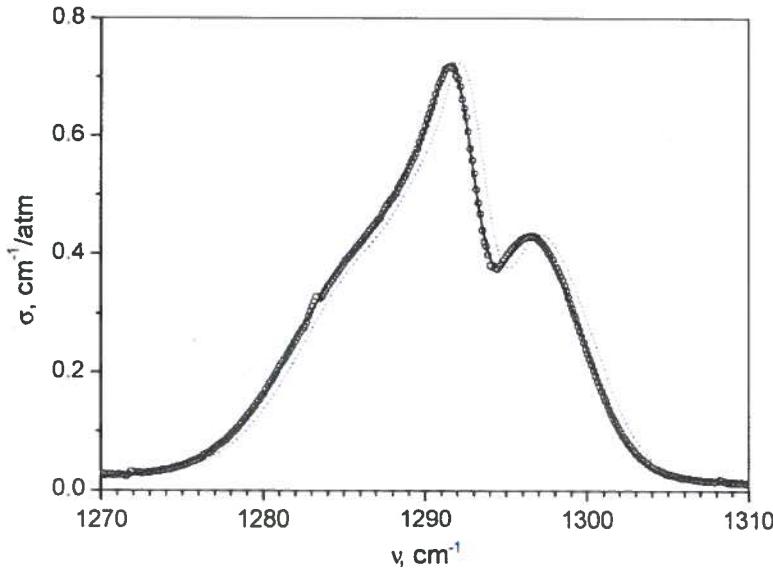
Threshold with grating  $I_{\text{th}} = 301.5\text{mA}$

Threshold without grating  $I_{\text{th}} = 350\text{mA}$

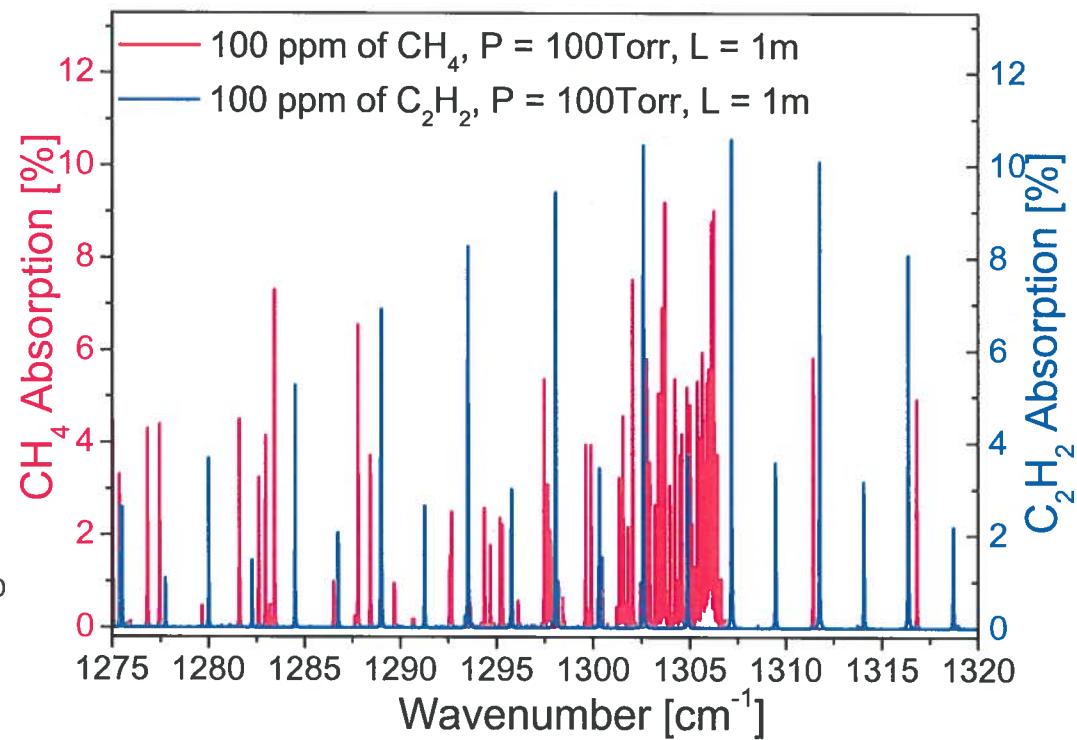


# Simulant molecules for $\text{UF}_6$

Single mode spectral frequency tuning range of the tested FP-QCLs cover the  $v_1 + v_3$   $\text{UF}_6$  combination band centered at  $\sim 1291\text{cm}^{-1}$  and several methane ( $\text{CH}_4$ ) and acetylene ( $\text{C}_2\text{H}_2$ ) absorption lines.

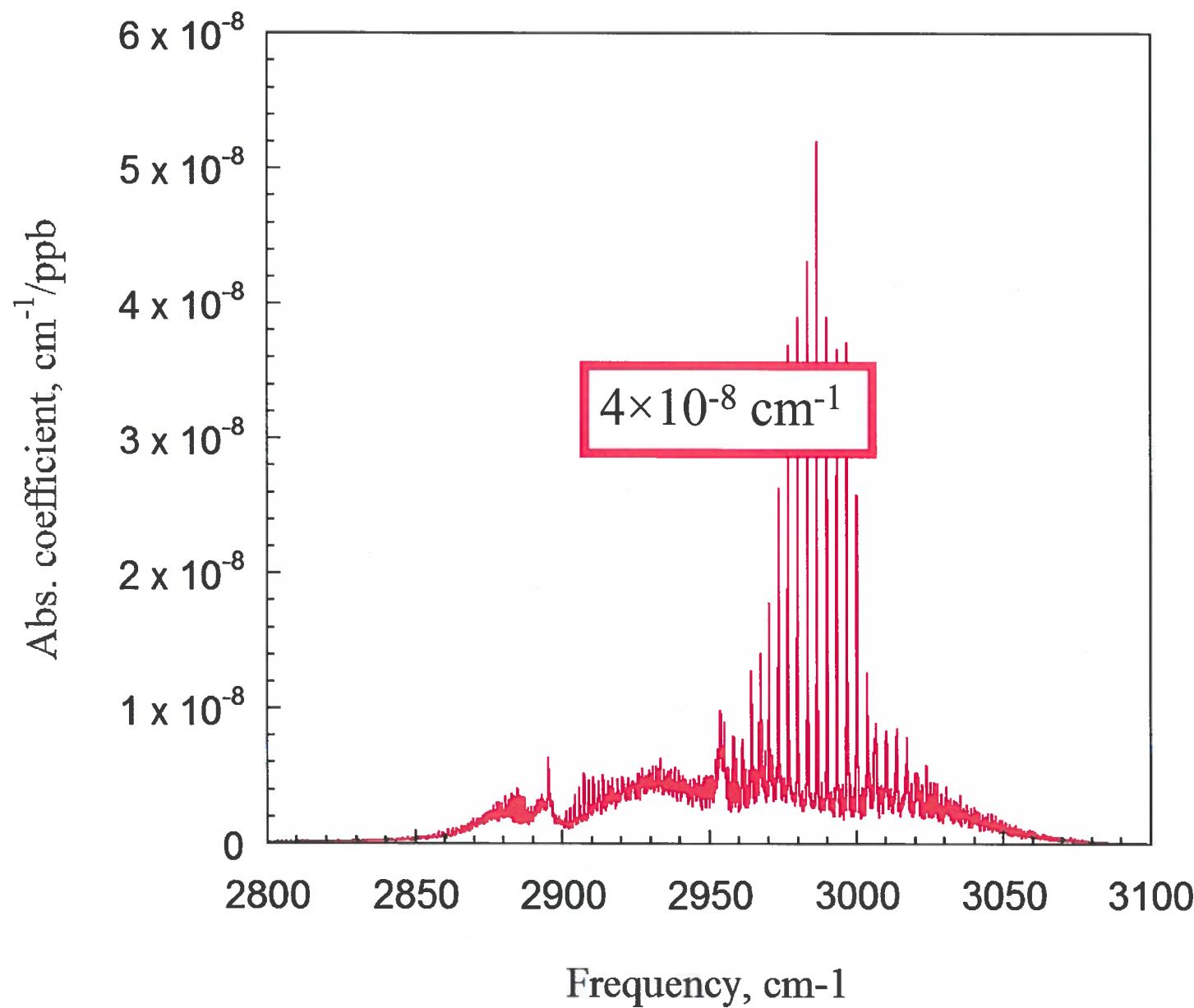


Experimental spectrum of absorption cross-section  $\sigma$  of the analyzed uranium hexafluoride sample (circles) as well as the obtained model spectra of  $^{238}\text{UF}_6$  (solid line) and  $^{235}\text{UF}_6$  (dotted line) [1].



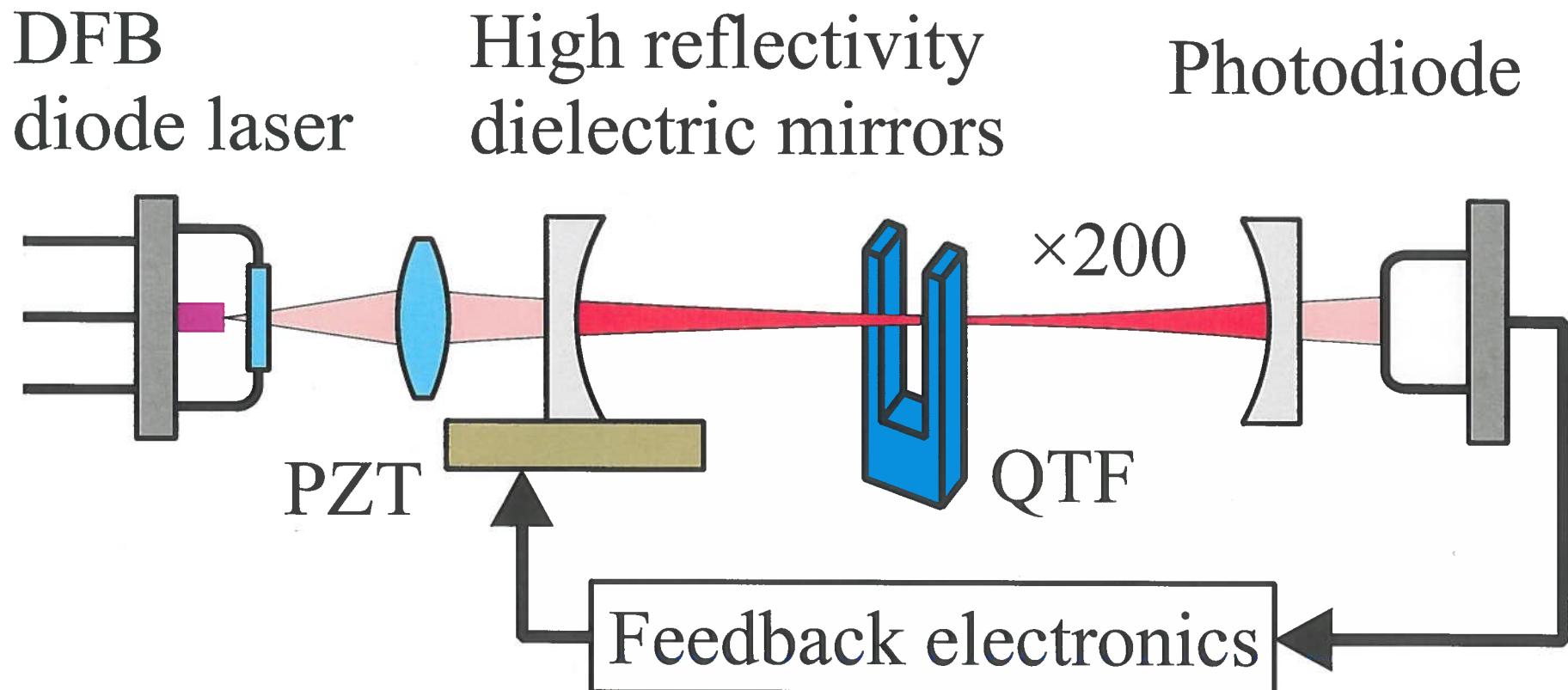
HITRAN simulation for 100 ppm of  $\text{CH}_4$  and  $\text{C}_2\text{H}_2$  concentrations. Spectra were simulated at a 100 Torr pressure and 1 meter pathlength.

# Ethane absorption spectrum



RICE

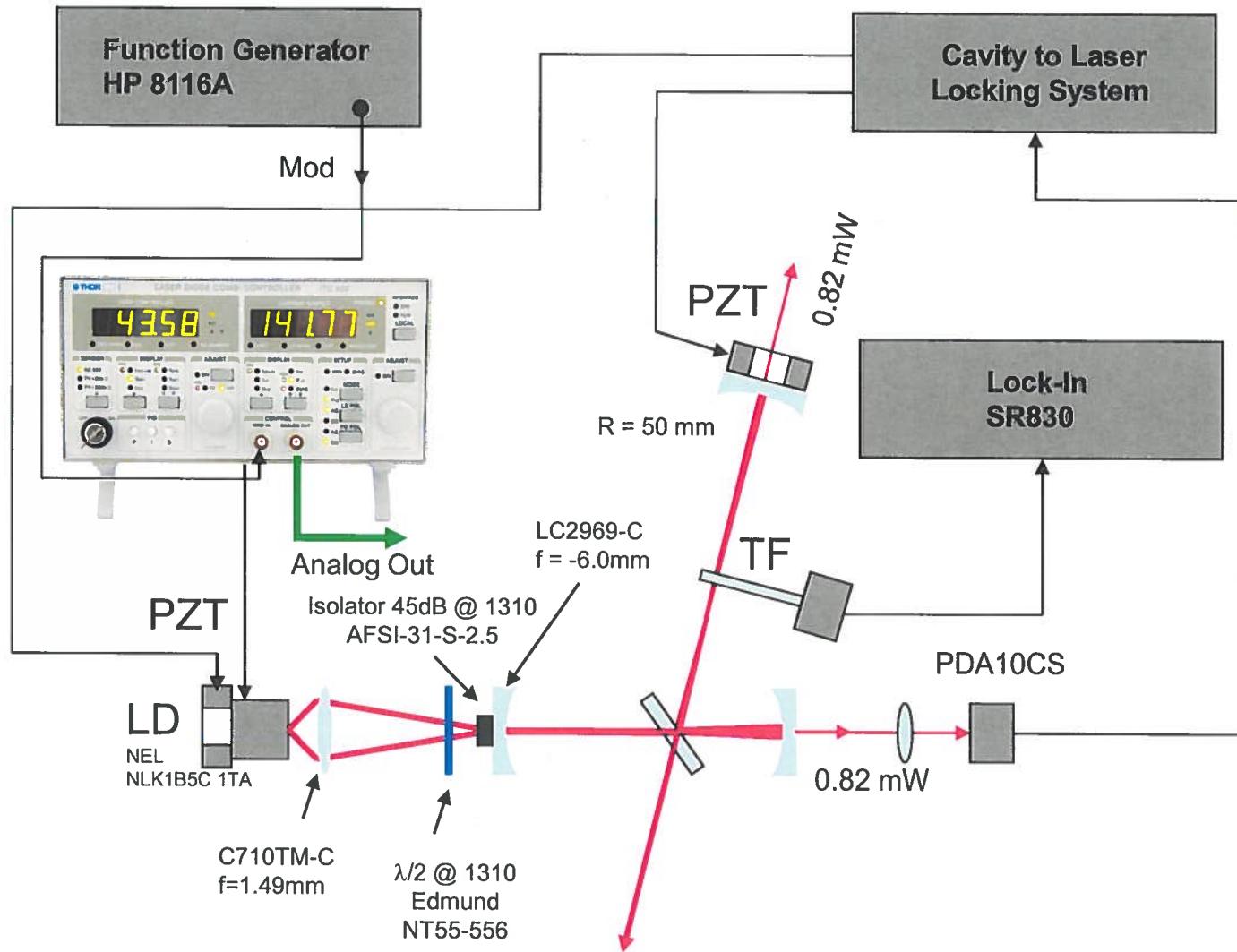
# Proposed QEPAS-OPBC Sensor Configuration



Circulating power = Source power / (1-R)

Very conservatively,  $\times 100$

# OPBC-QEPAS system configuration



RICE

# QEPAS MDAL Comparison with CRDS, ICOS & TDLAS

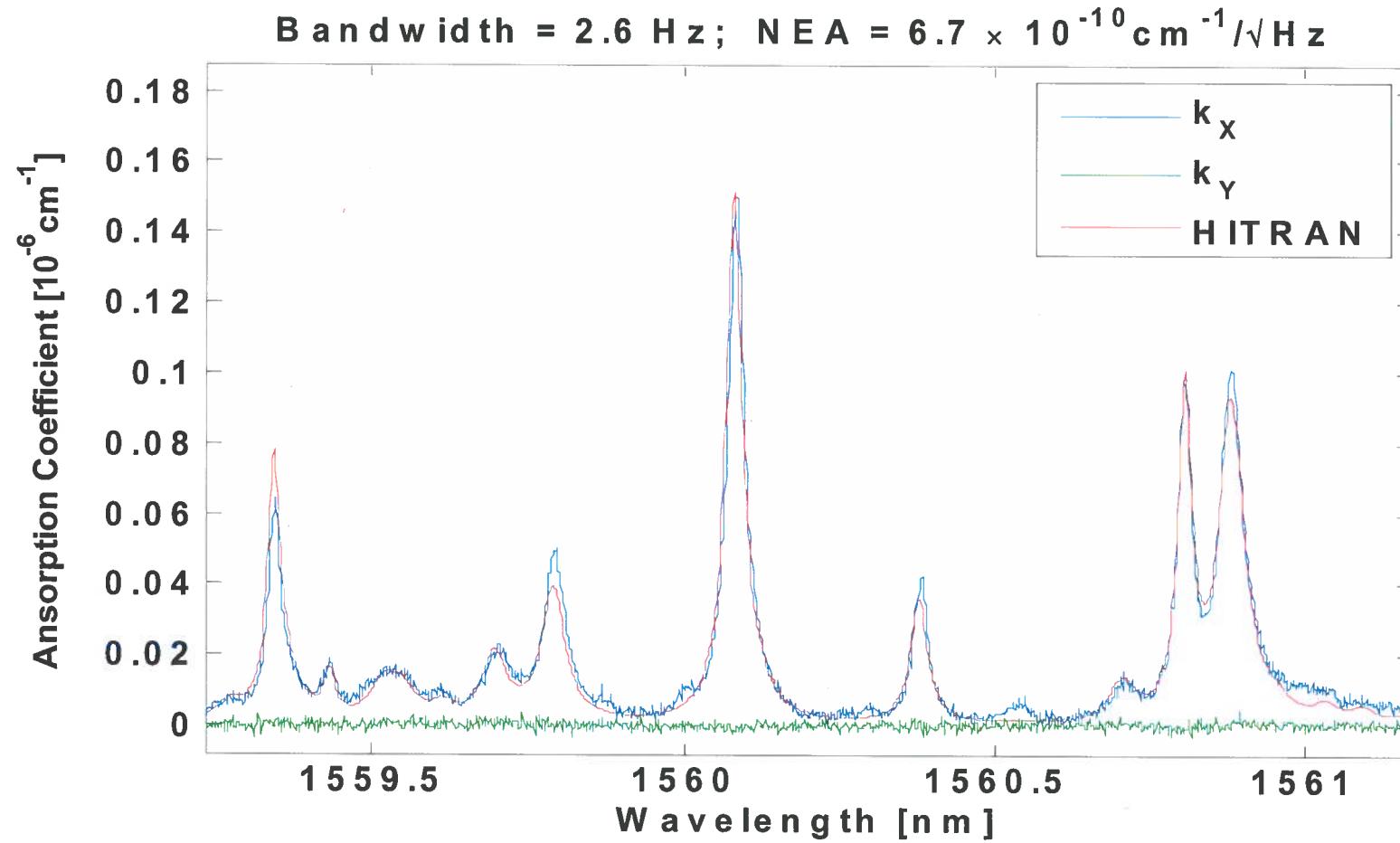
---

Minimum Detectable Absorption Loss (MDAL) [ $\text{cm}^{-1}/\sqrt{\text{Hz}}$ ]  
can be used for comparison of different techniques:

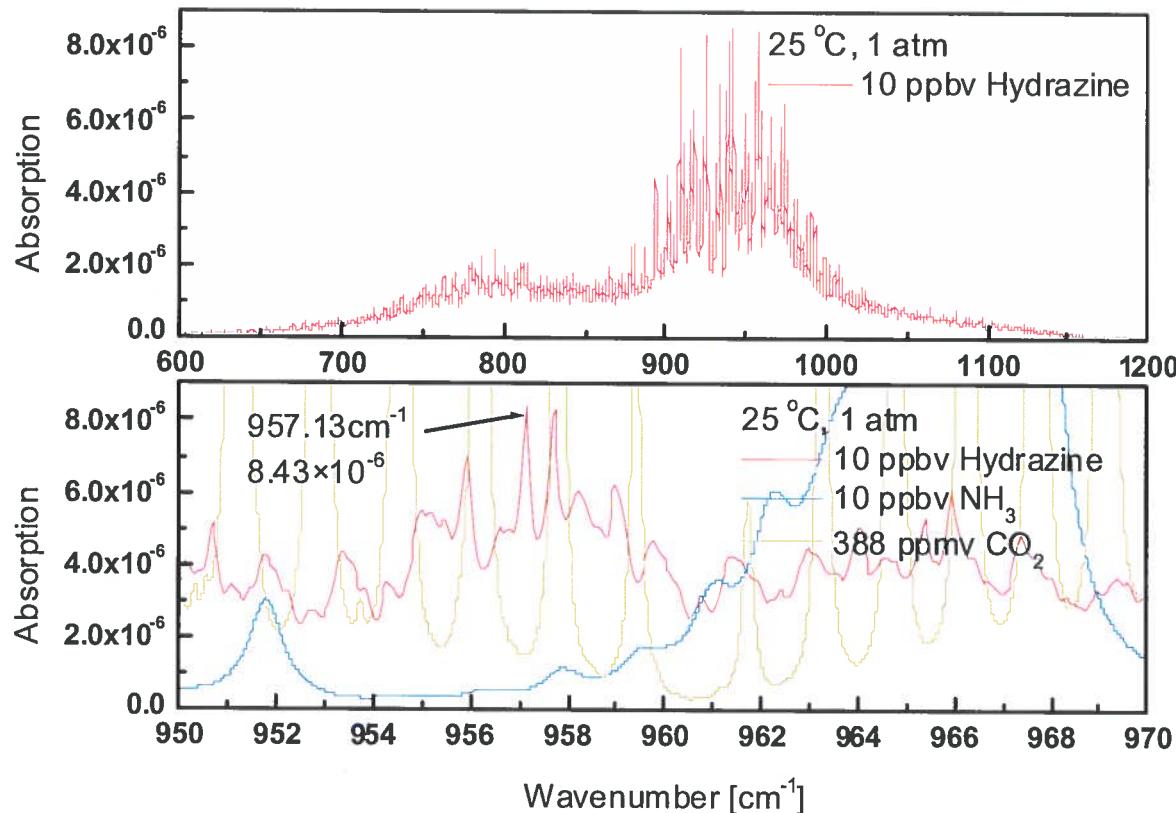
- Cavity Ring Down Spectroscopy (CRDS) :  $\sim 3 \times 10^{-11}$
- Integrated Output Spectroscopy (ICOS):  $\sim 3 \times 10^{-11}$
- Multipass Gas Cell based TDLAS:  $\sim 2 \times 10^{-11}$
  
- QEPAS (Sept 2009) MDAL (DFB 100mW):  $1.9 \times 10^{-8}$
- QEPAS-OPBC MDAL (DFB 20 mW):  $3.2 \times 10^{-10}$
- QEPAS-OPBC + micro-resonator (estimated):  $\sim 7 \times 10^{-12}$

QEPAS-OPBC can be as sensitive as CRDS, ICOS and TDLAS  
and retain most of the performance merits of QEPAS

# Laboratory air spectrum with OPBC-QEPAS system



# $\text{N}_2\text{H}_4$ detection with a QCL based QEPAS sensor



The proposed QEPAS based  $\text{N}_2\text{H}_4$  sensor would use a thermoelectrically cooled CW, DFB, QCL operating at  $\sim 957 \text{ cm}^{-1}$  ( $10.5 \mu\text{m}$ ) with an output power of 100 mW. At this wavelength and assuming a noise equivalent absorption coefficient of  $\sim 5.10^{-9} \text{ cm}^{-1} \text{ W}/\sqrt{\text{Hz}}$ , and a  $\text{N}_2\text{H}_4$  absorption of  $\sim 7.10^{-6} \text{ cm}^{-1}/\text{ppm}$  at 1 atm, the estimated detection sensitivity will be  $\sim 7 \text{ ppbV}$  for a 1 Hz bandwidth



# Summary & Future Directions of Laser based Gas Sensor Technology

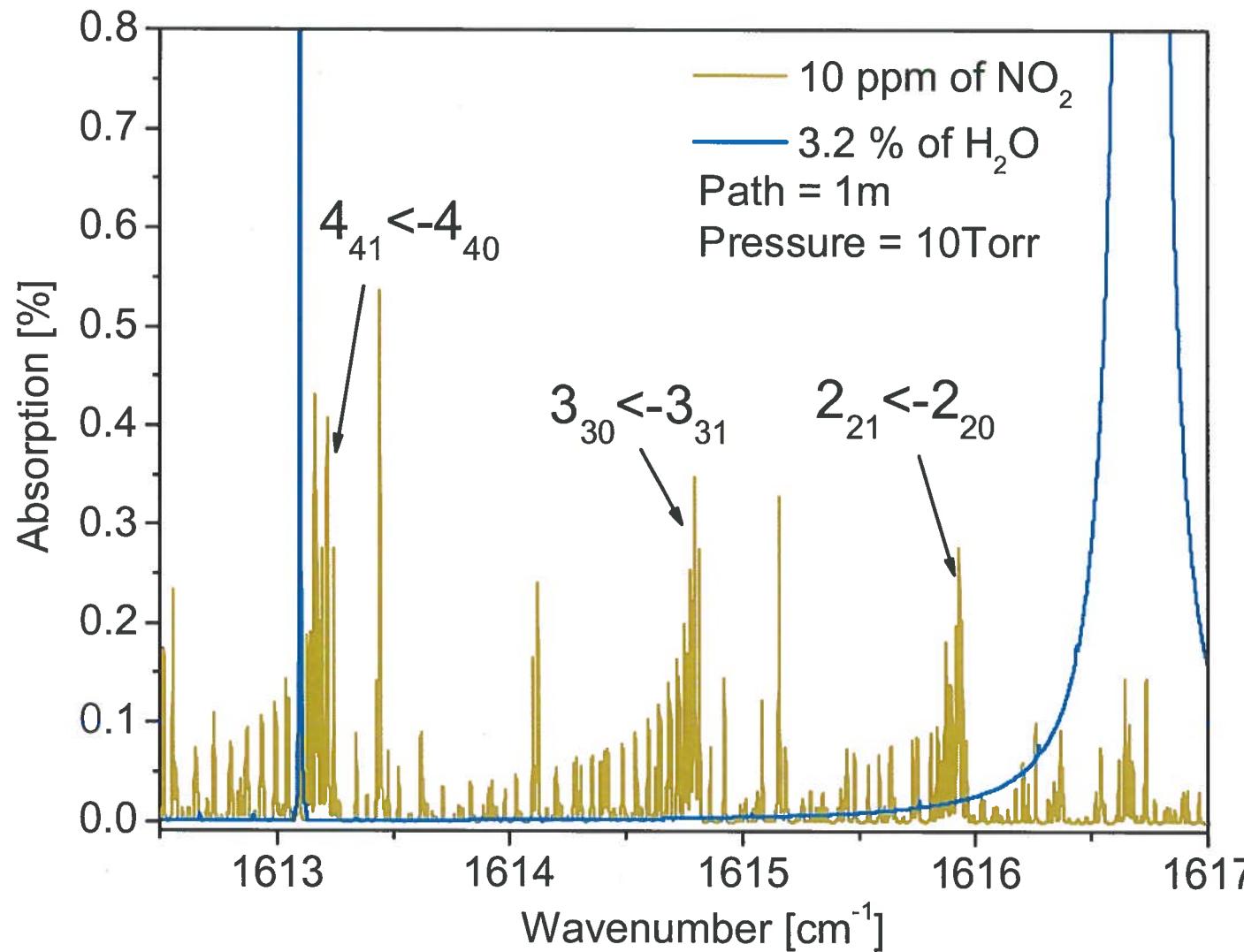
---

- **Semiconductor 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 14 trace gases to date: NH<sub>3</sub>, CH<sub>4</sub>, N<sub>2</sub>O, CO<sub>2</sub>, CO, NO, H<sub>2</sub>O, COS, C<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>S, H<sub>2</sub>CO, SO<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>OH, C<sub>2</sub>HF<sub>5</sub>, TATP and several isotopic species of C, O, N and H.
- **New Applications of Trace Gas Detection**
  - Environmental Monitoring (urban quality – NH<sub>3</sub>, H<sub>2</sub>CO, NO, isotopic ratio measurements of CO<sub>2</sub> and CH<sub>4</sub>, fire and post fire detection; quantification of engine exhausts)
  - Industrial process control and chemical analysis ( NO, NH<sub>3</sub>, H<sub>2</sub>O, and H<sub>2</sub>S)
  - Medical & biomedical non-invasive diagnostics (NH<sub>3</sub>, NO, N<sub>2</sub>O and CH<sub>3</sub>COCH<sub>3</sub>)
  - Ultra-compact, low cost, robust sensors (CO and CO<sub>2</sub>)
- **Future Directions and Collaborations**
  - Improvements of the existing sensing technologies using novel, thermoelectrically cooled, cw, high power, and broadly wavelength tunable mid-IR intersubband and interband quantum cascade lasers
  - Further development of spectraphone technology
  - 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 HCs, UF<sub>6</sub> and multi-species detection)
  - Development of optically gas sensor networks based on QEPAS and LAS



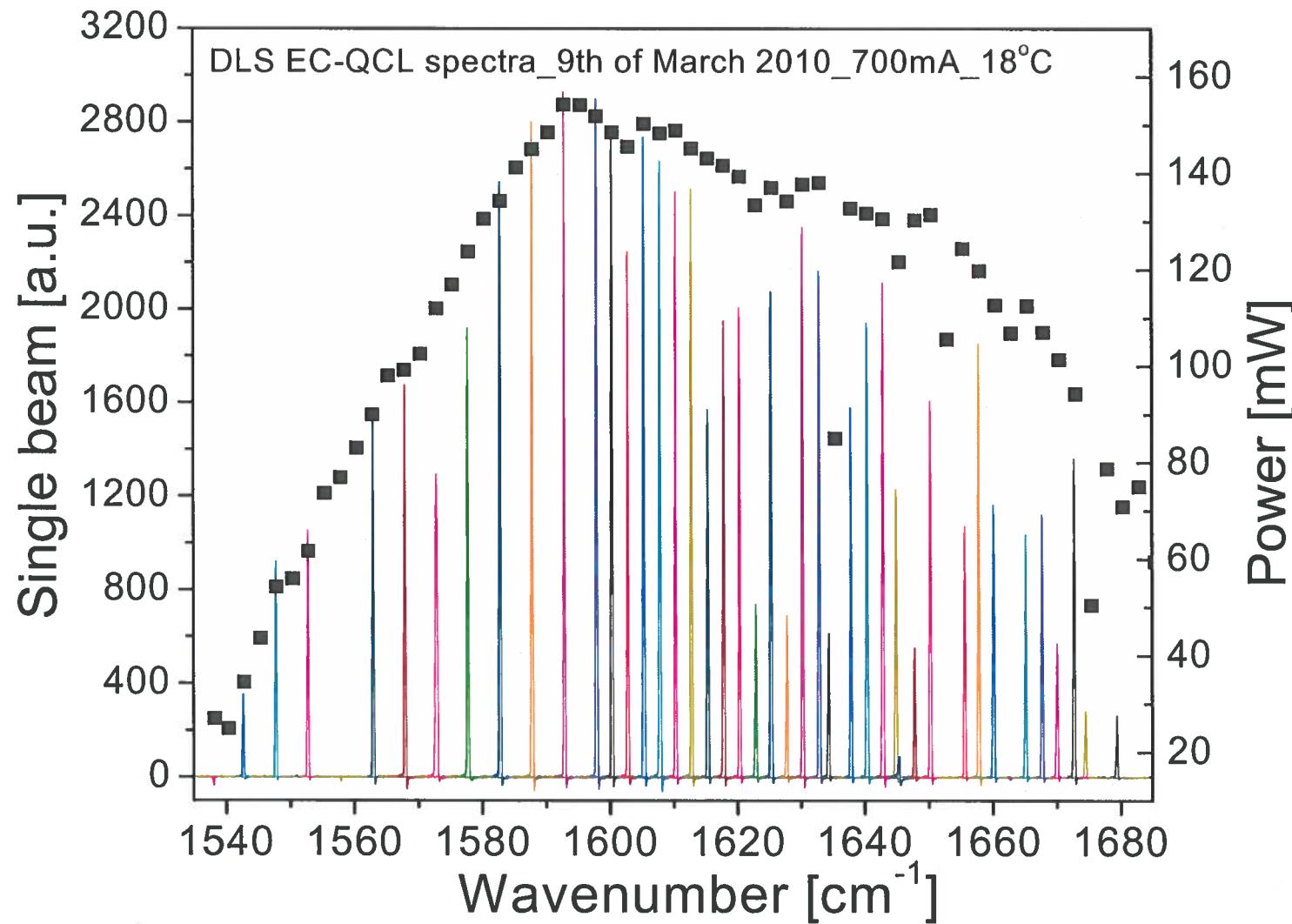
RICE

# Optimum NO<sub>2</sub> transition for FRS experiment



$4_{41} <- 4_{40}$  at 1613.245 cm<sup>-1</sup>,  $3_{30} <- 3_{31}$  at 1614.813 cm<sup>-1</sup> or  $2_{21} <- 2_{20}$  at 1615.929 cm<sup>-1</sup>

# Tuning range of a Daylight Solutions CW 6.19 $\mu\text{m}$ NO<sub>2</sub> EC-QCL (21062-MHF-012)



RICE