Recent Advances in Infrared Semiconductor based Chemical sensing Technologies

F.K. Tittel, L. Dong, A.A. Kosterev, R. Lewicki and D.Thomazy
Rice Quantum Institute, Rice University, Houston, TX, USA
http://ece.rice.edu/lasersci/

OUTLINE

TERA-MIR 2009

Turunc, Turkey

Nov 3-6, 2009

- Motivation: Wide Range of Trace Gas Sensing
- Key Characteristics of QC Lasers: Oct. 2009
- Quartz enhanced Photoacoustic Spectroscopy
- Selected Applications of Trace Gas Detection
  - NH_3 Detection for Environmental and Medical Applications
  - Nitric Oxide detection
- Future Directions and Outlook
  - Development of Semiconductor Laser Arrays
  - Monitoring of broadband absorbers (Detection of UF_6)
  - Optical Power Built-up Cavity (OPBC) for QEPAS Sensor

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Wide Range of Trace Gas Sensing Applications

- **Urban and Industrial Emission Measurements**
  - Industrial Plants
  - Combustion Sources and Processes (e.g. fire detection)
  - Automobile, 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 the Life Sciences**
- **Technologies for Law Enforcement and National Security**
- **Fundamental Science and Photochemistry**

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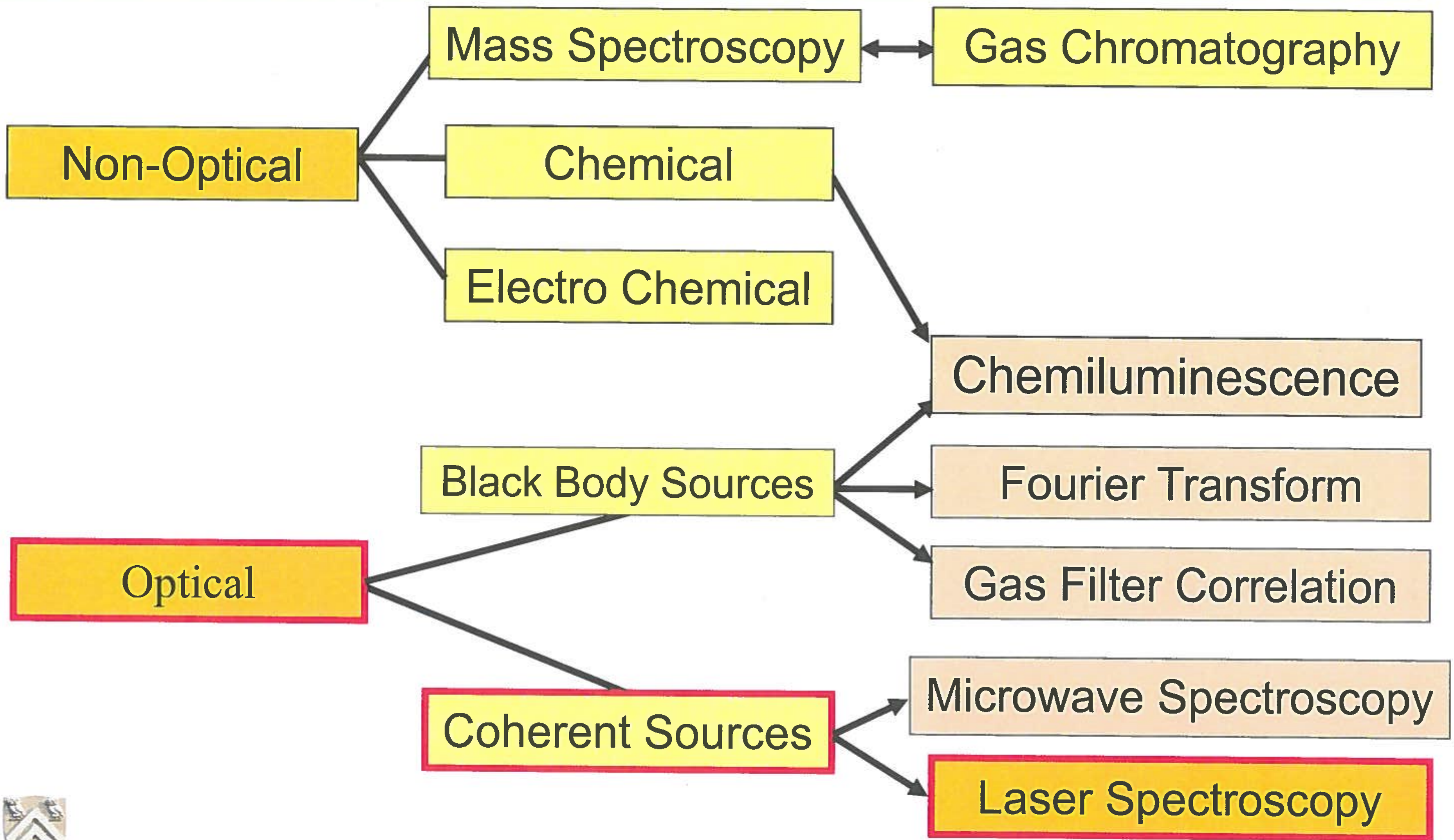
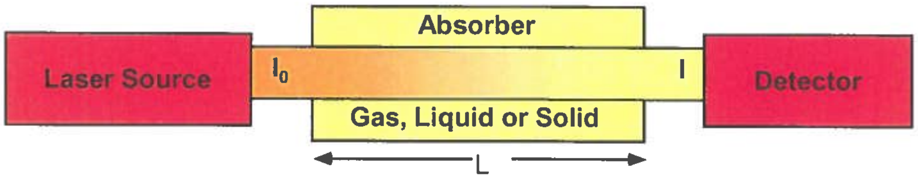
Existing Methods for Trace Gas Detection



Basics of Optical Trace Gas Analyzers

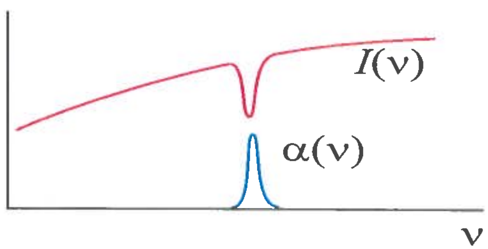


Beer-Lambert's Law of Linear Absorption

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

$\alpha(\nu)$ - 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$\cdot cm^{-3} \cdot atm^{1}$]

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

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

<u>Key Requirements</u>: Sensitivity, specificity, rapid data acquisition and multi-species detection

<u>Optimum Molecular Absorbing Transition</u>

- NIR Overtone or Combination Bands
- **MIR Fundamental Absorption Bands**

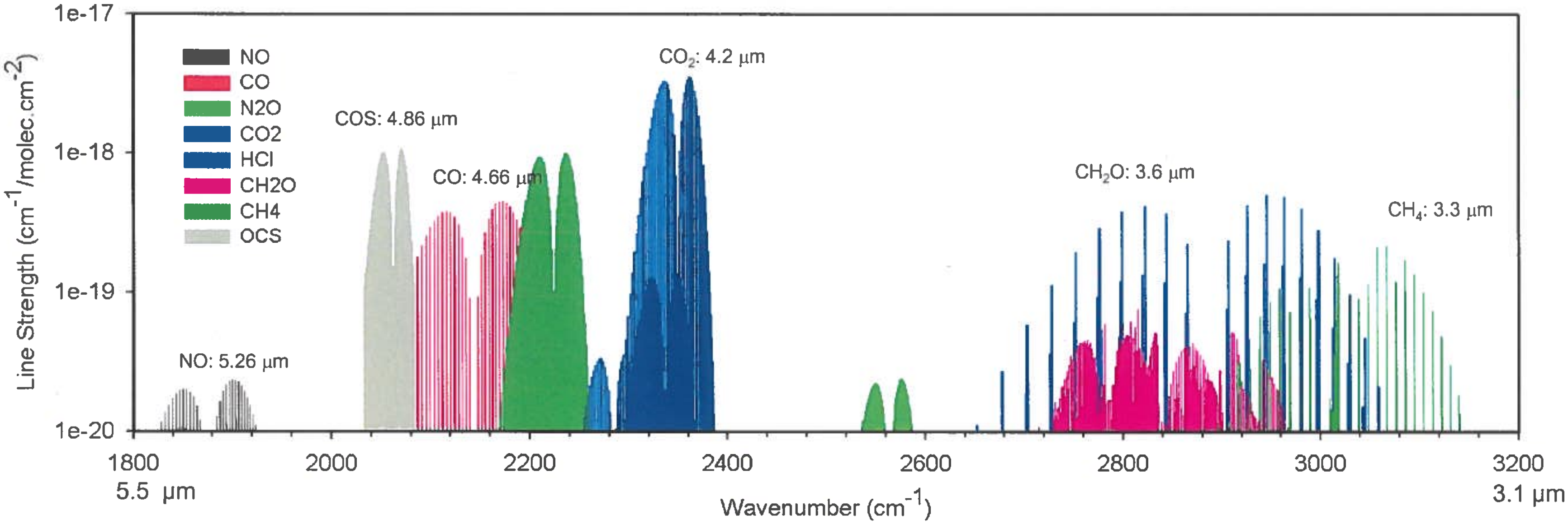
<u>Long Optical Pathlengths</u>

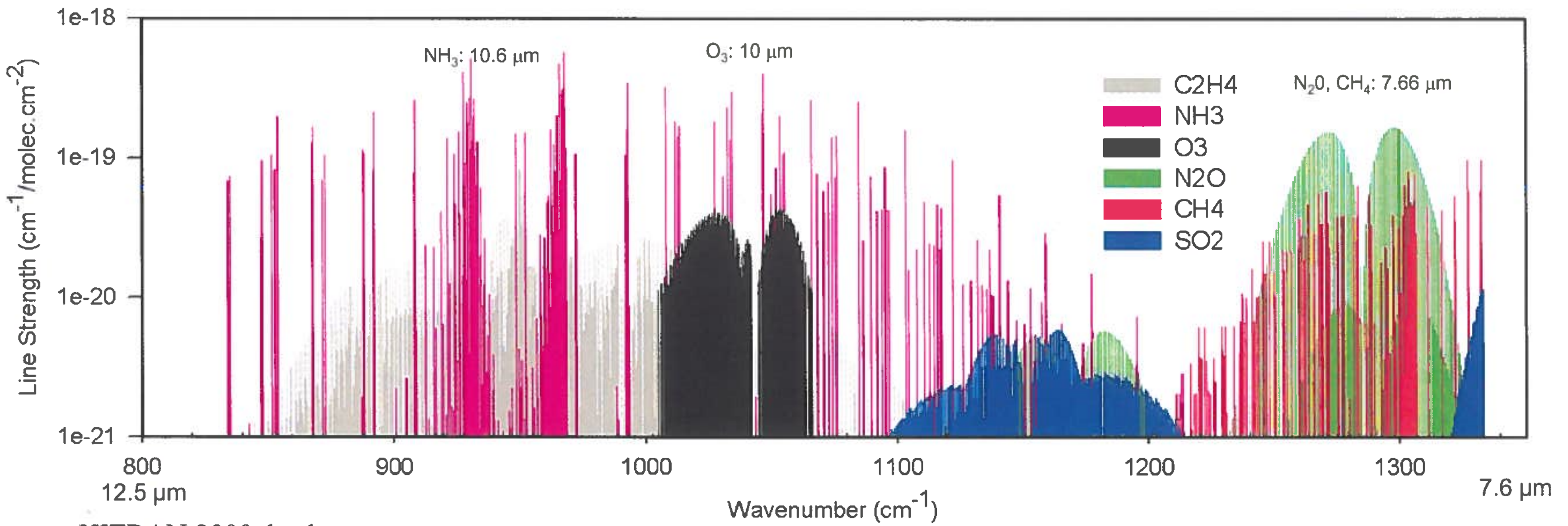
- Multipass Absorption Cell White, Herriott)
- Cavity Enhanced, Cavity Ringdown & Intracavity Spectroscopy
- Open Path Monitoring (with retro-reflector); Standoff and Remote Detection
- Fiberoptic evanescent wave Spectroscopy

<u>Spectroscopic Detection Schemes</u>

- Wavelength or Frequency Modulation
- Balanced Detection
- Zero-air Subtraction
- Photoacoustic Spectroscopy (PAS or QEPAS
- Laser Induced Breakdown Spectroscopy

Molecular Absorption Spectra within the two Mid-IR Atmospheric Windows





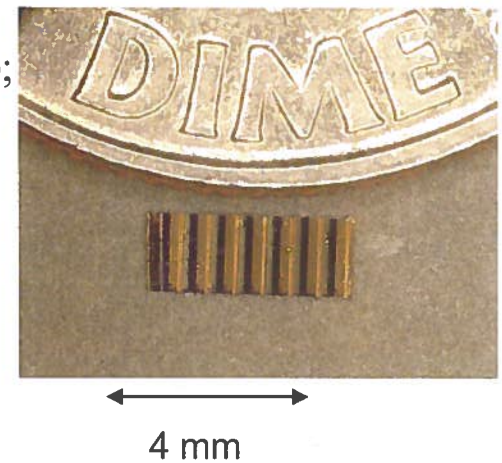
Source: HITRAN 2000 database

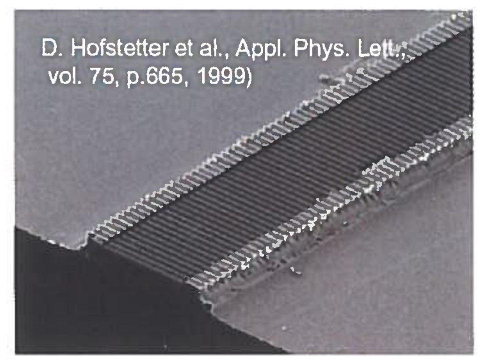
Mid-IR Source Requirements for Laser Spectroscopy

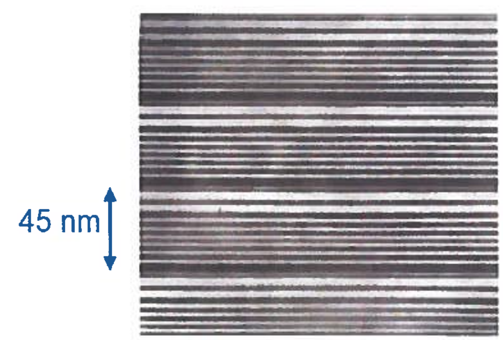
REQUIREMENTS	IR LASER SOURCE
Sensitivity (% to ppt)	Optimum Wavelength, Power
Selectivity (Spectral Resolution)	Single Mode Operation and Narrow Linewidth
Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers	Tunable Wavelength
Directionality or Cavity Mode Matching	Beam Quality
Rapid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

Key Characteristics of mid-IR QCLs and ICL Sources-2009

- **Band – structure engineered devices**
  (Emission wavelength is determined by layer thickness – MBE or MOCVD); mid-infrared <u>QCLs operate from 3 to 24 μm (AlInAs/GaInAs)</u>
- Compact, reliable, stable, long lifetime, and commercial availability
- Fabry-Perot (FP), single mode (DFB) and multi-wavelength
- <u>**Broad spectral tuning range in the mid-IR**</u>
  (4-24 μm for QCLs and 3-5 μm for ICLs and GaSb diodes)
  - 1.5 cm^{-1} using injection current control for DFB devices
  - 10-20 cm^{-1} using temperature control for DFB devices
  - > 430 cm^{-1} using an external grating element and FP chips with heterogeneous cascade active region design; also QCL DFB r array
- <u>**Narrow spectral linewidth**</u>
  - CW: 0.1 - 3 MHz & <10Khz with frequency stabilization (0.0004 cm^{-1})
  - Pulsed: ~ 300 MHz
- <u>**High pulsed and cw powers of QCLs and ICLs at TEC/RT temperatures**</u>
  - Pulsed and CW powers of ~ 1.5 W; high temperature operation ~300K
  - >50 mW, TEC CW DFB @ 5 and 10 μm
  - > 600 mW (CW FP) @ RT; wall plug efficiency of ~15 % at 4.6μm;







Quantum Cascade (QC), Interband (IC) and GaSb Laser Availability in Oct. 2009

- Commercial Sources
  - Adtech, CA
  - Alpes Lasers, Switzerland & Germany
  - Alcatel-Thales, France
  - Corning, NY
  - Hamamatsu, Japan
  - Physical Sciences, Inc (Maxion Technologies, Inc),
  - Nanoplus, Wuerzburg, Germany
- Research Groups
  - Harvard University
  - Fraunhofer-IAF, Freiburg, Germany
  - NASA-JPL, Pasadena, CA
  - Naval Research Laboratories, Washington, DC
  - Northwestern University, Evanston, IL
  - Princeton University (MIRTHE), NJ
  - Sheffield, UK
  - State University of New York
  - Technical University, Zuerich, CH
  - University of Montpelier, France

Quartz Enhanced Photoacoustic Spectroscopy

Quartz Tuning Fork as a Resonant Microphone

Unique properties

- Extremely low internal losses:
  - Q~10 000 at 1 atm
  - Q~100 000 in vacuum
- Acoustic quadrupole geometry
  - Low sensitivity to external sound
- Large dynamic range – 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 ~700K
- Low cost (<$1)

Other parameters

- Resonant frequency ~32.8 kHz
- Force constant ~26800 N/m
- Electromechanical coefficient $\sim 7\times10^{-6}$ C/m

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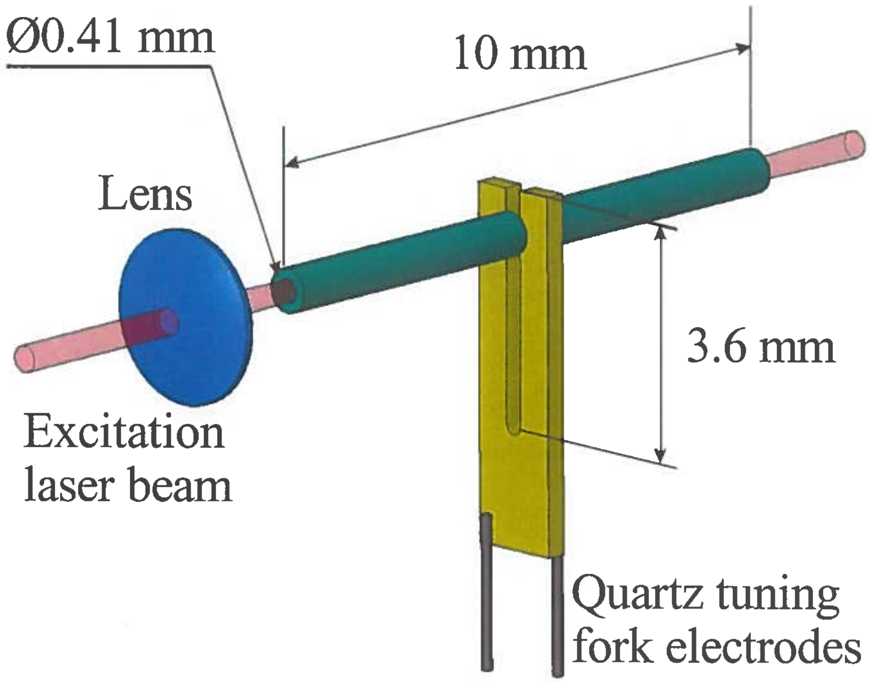
QEPAS spectraphone



Microresonator tubes

- Must be close to the QTF but not touching it (30-50 mm gaps).
- Inner diameter 0.41 mm; 10% lower signal with 0.6 mm diameter tubes.
- Each piece ~5mm long (~l/2 for sound at 32.8 kHz)

Gain: ×10 to ×20

Windows

- Must be tilted to prevent the reflected light from going back into the microresonator.
- Exact positioning is not important, to the best of our current knowledge.

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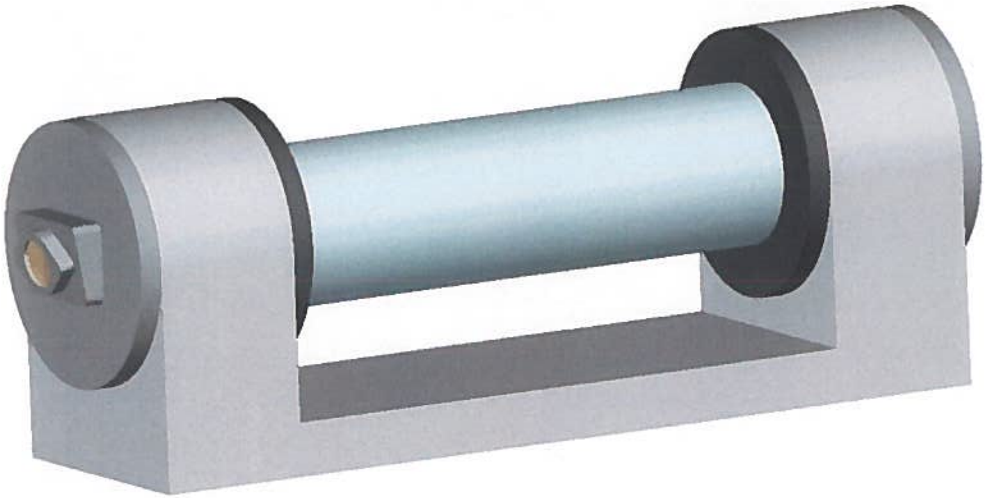
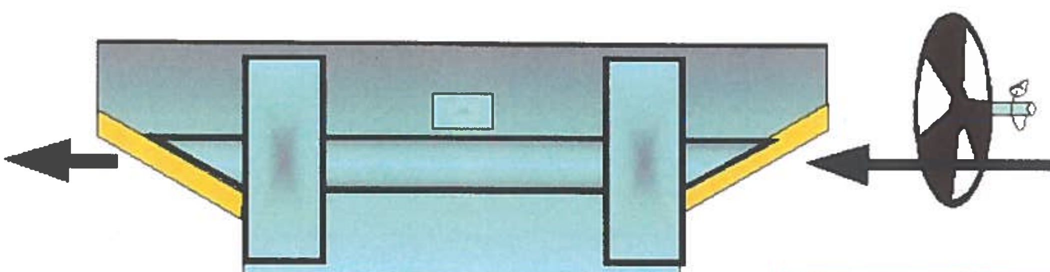
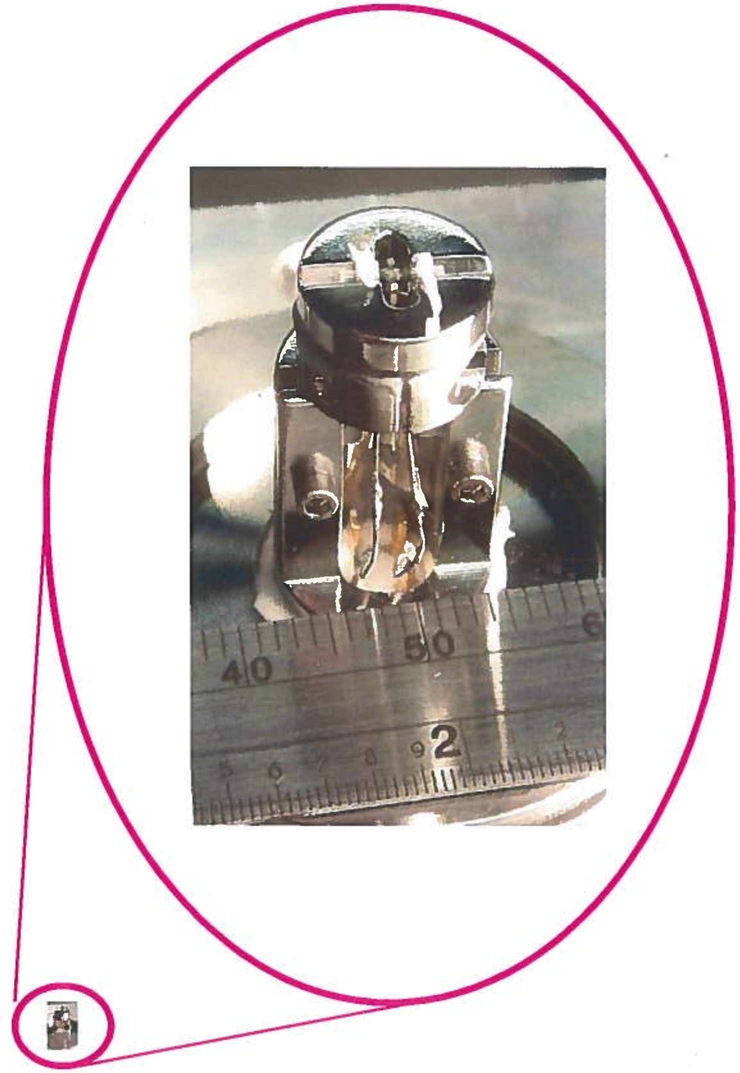
Comparative Sizes of QEPAS & PAS ADMs



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

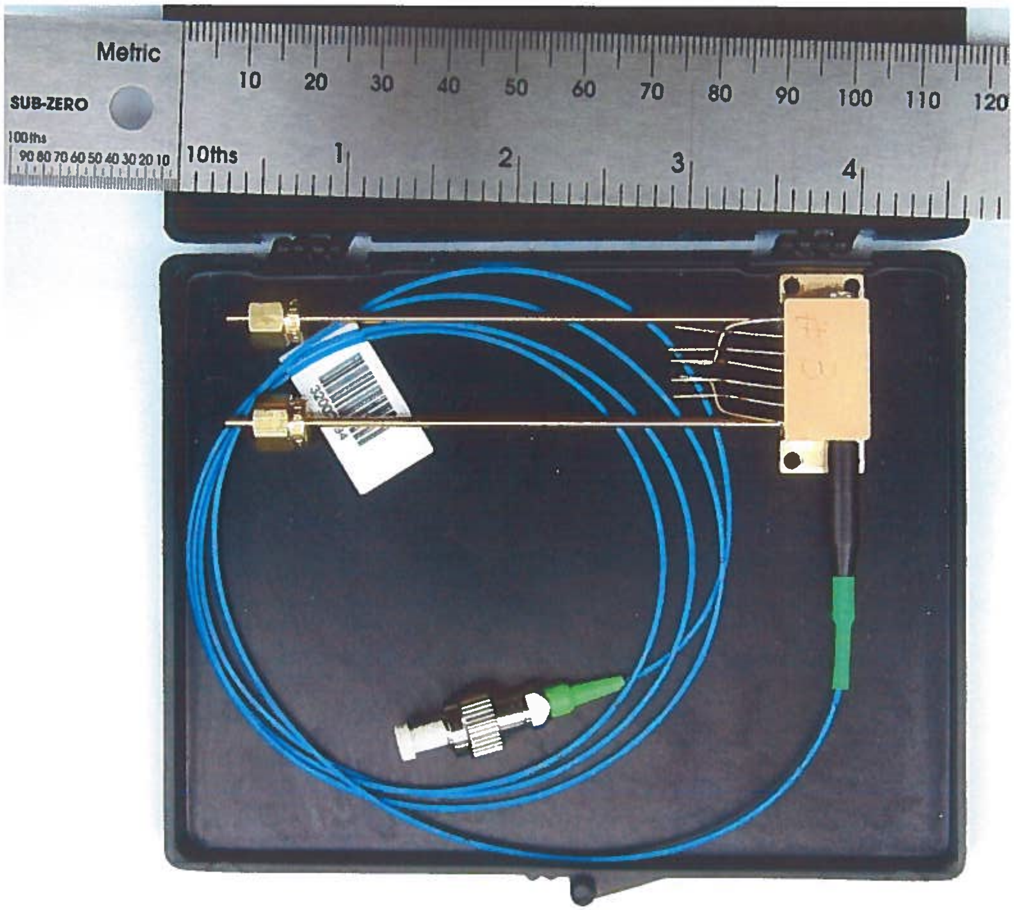


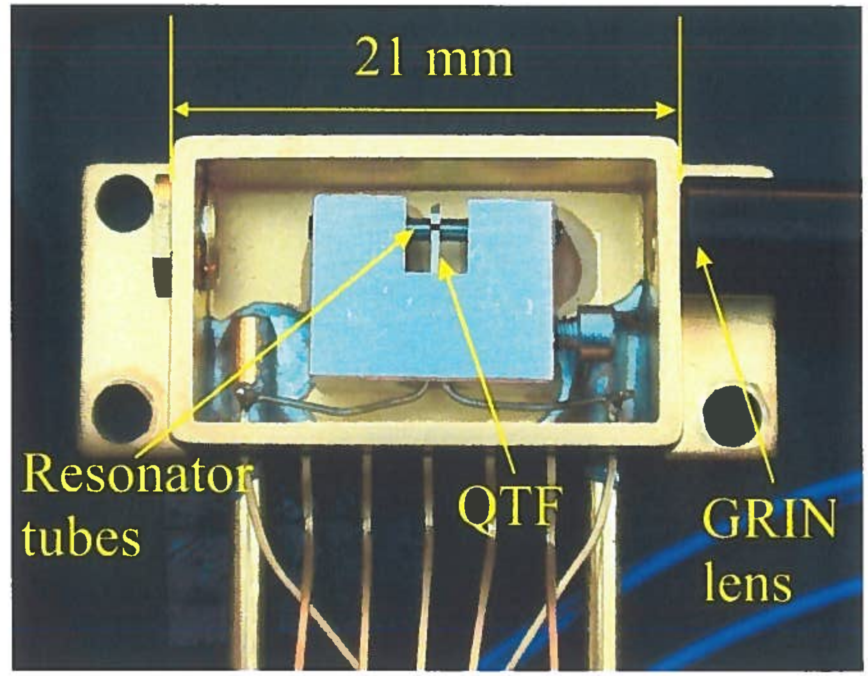
Resonant photoacoustic cell (1000 Hz):
l~60 cm, V~50 cm^3



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

Alignment-free QEPAS Absorption Detection Module





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Recent Applications of QCL based Trace Gas Sensors

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 diseases)

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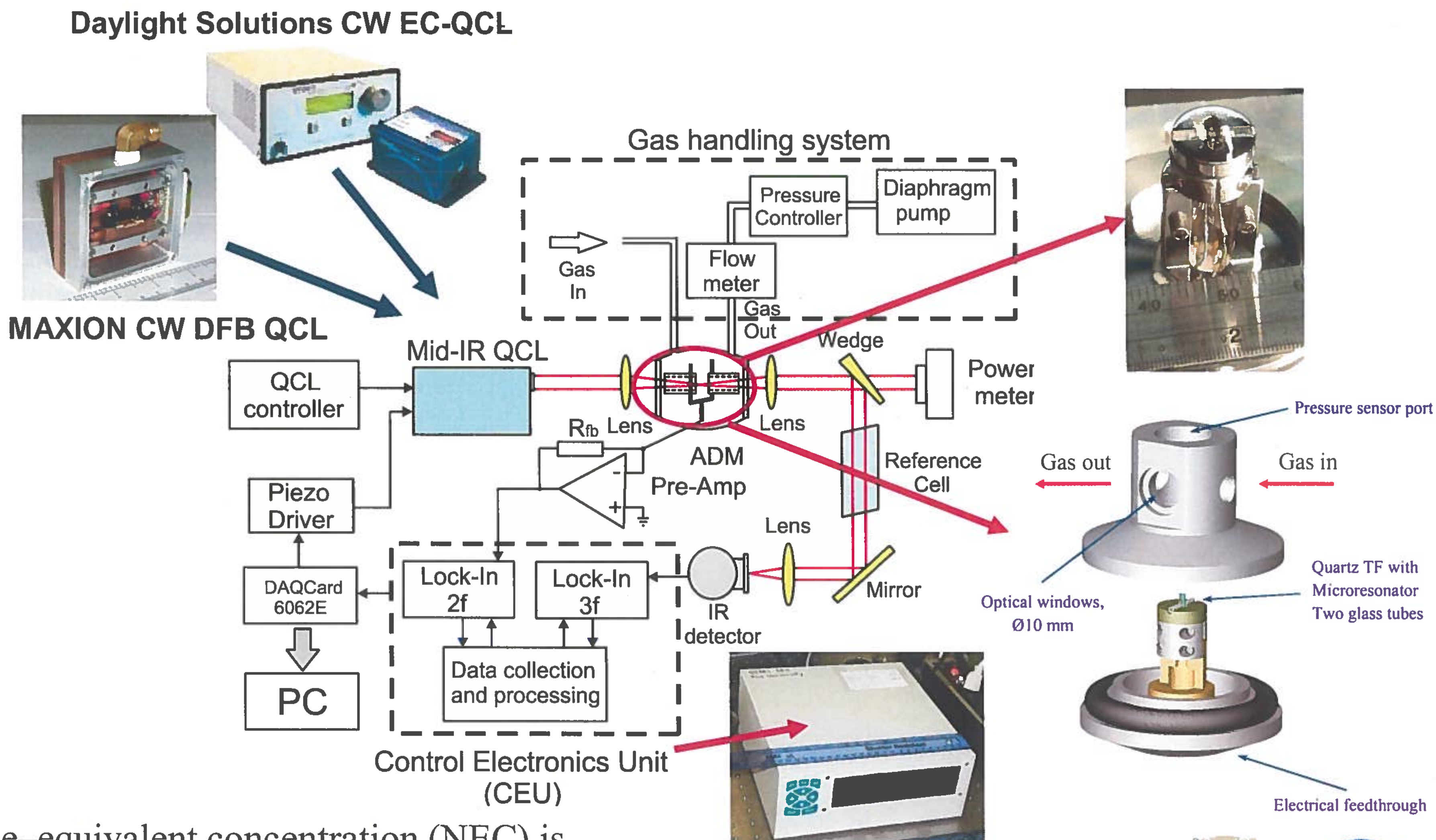
Important Biomedical Target Gases in Exhaled Human Breath

Molecule	Formula	Biological/Pathology Indication
Pentane	$CH_3(CH_2)_3CH_3$	Lipid peroxidation, oxidative stress associated with inflammatory diseases, immune responses, transplant rejection, breast and lung cancer
Ethane	C_2H_6	Lipid peroxidation and oxidative stress
Carbon Dioxide isotope ratio	$^{13}CO_2$ / $^{12}CO_2$	Marker for Helicobacter pylori infection, Gastrointestinal and hepatic function
Carbonyl Sulfide	COS	Liver disease & acute rejection in lung transplant recipients (10-500 ppb)
Carbon disulfide	CS_2	Schizophrenia
Ammonia	NH_3	Hepatic encephalopathy, liver and renal diseases, fasting response
Formaldehyde	HCHO	Cancerous tumors, breast cancer (400-1500 ppb)
Nitric Oxide	NO	Inflammatory and immune responses (e.g., asthma) and vascular smooth muscle response (6-100 ppb)
Hydrogen Peroxide	H_2O_2	Airway Inflammation, Oxidative stress (1-5 ppb)
Carbon Monoxide	CO	Smoking response, CO poisoning, vascular smooth muscle response, platelet aggregation (400-3000 ppb)
Ethylene	$H_2C=CH_2$	Oxidative stress, cancer
Acetone	CH_3COCH_3	Fasting response, diabetes mellitus response, ketosis

Mid-IR QEPAS based NH_3 Gas Sensor Architecture



Noise–equivalent concentration (NEC) is 6 ppb for a1s time constant and 20mW excitation power at 1046.4 cm^{-1} (110 Torr)

T.Risby: 12:00 Sept.7 & Poster

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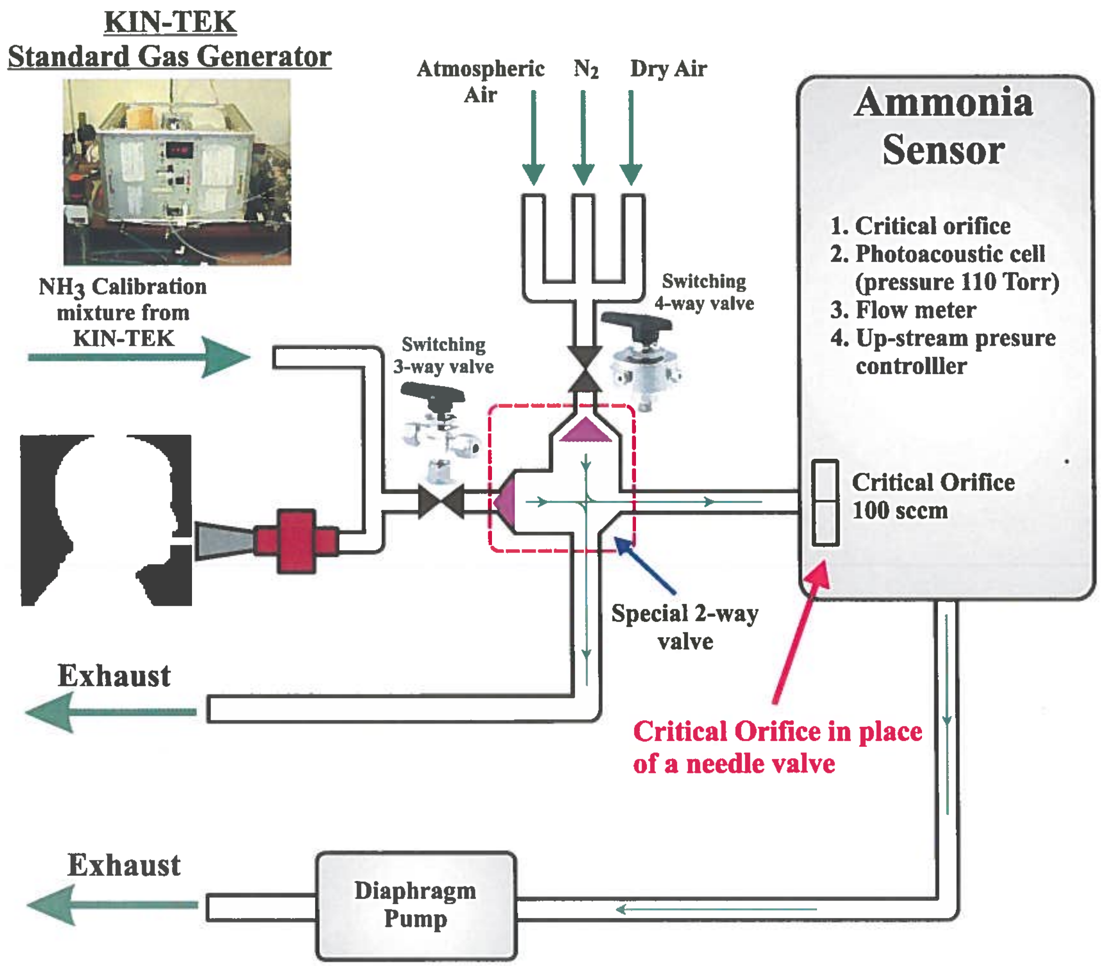
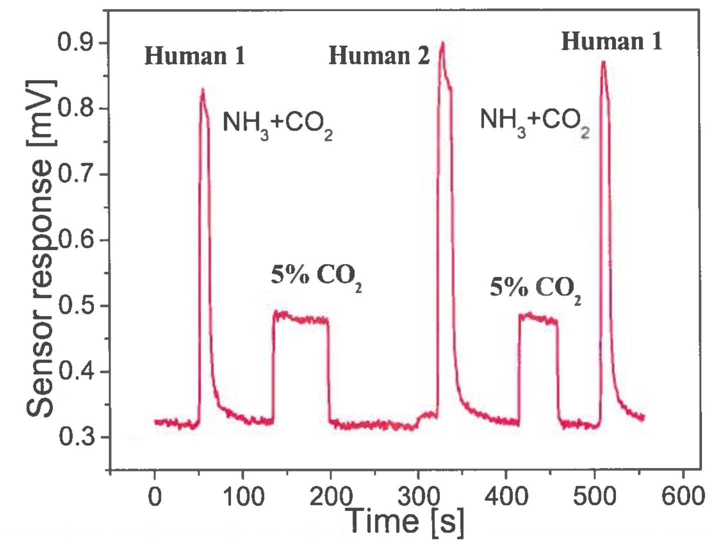
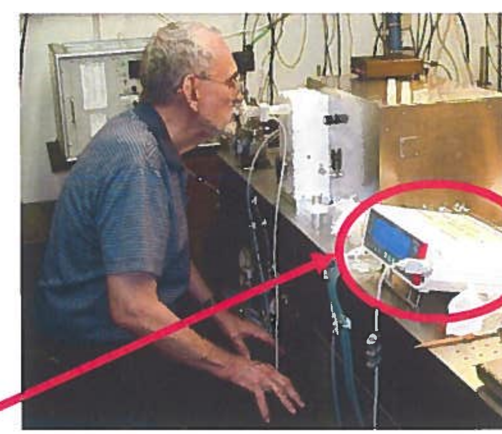
Real-time Breath Monitor Interface







- Controlled flow
- Continuous control of mouth pressure
- Continuous monitoring of CO_2 concentration (capnograph) and its use in QEPAS data processing

T.Risby: 12:00 Sept.7 & Poster

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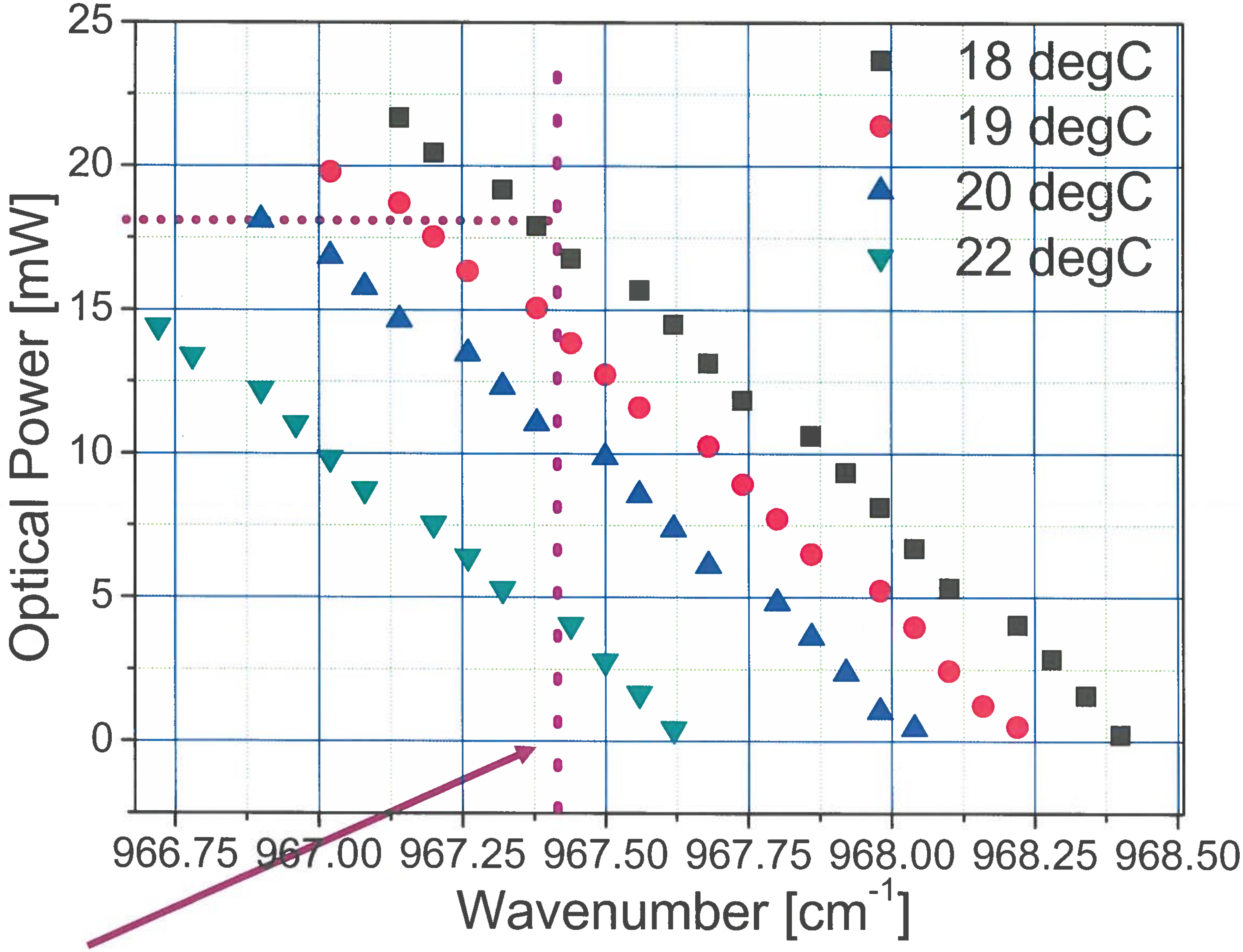
Wavenumber dependance of CW RT DFB QCL output power



NH_3 absorption line of interest (967.35 cm^{-1}) 2009 Hamamatsu QCL

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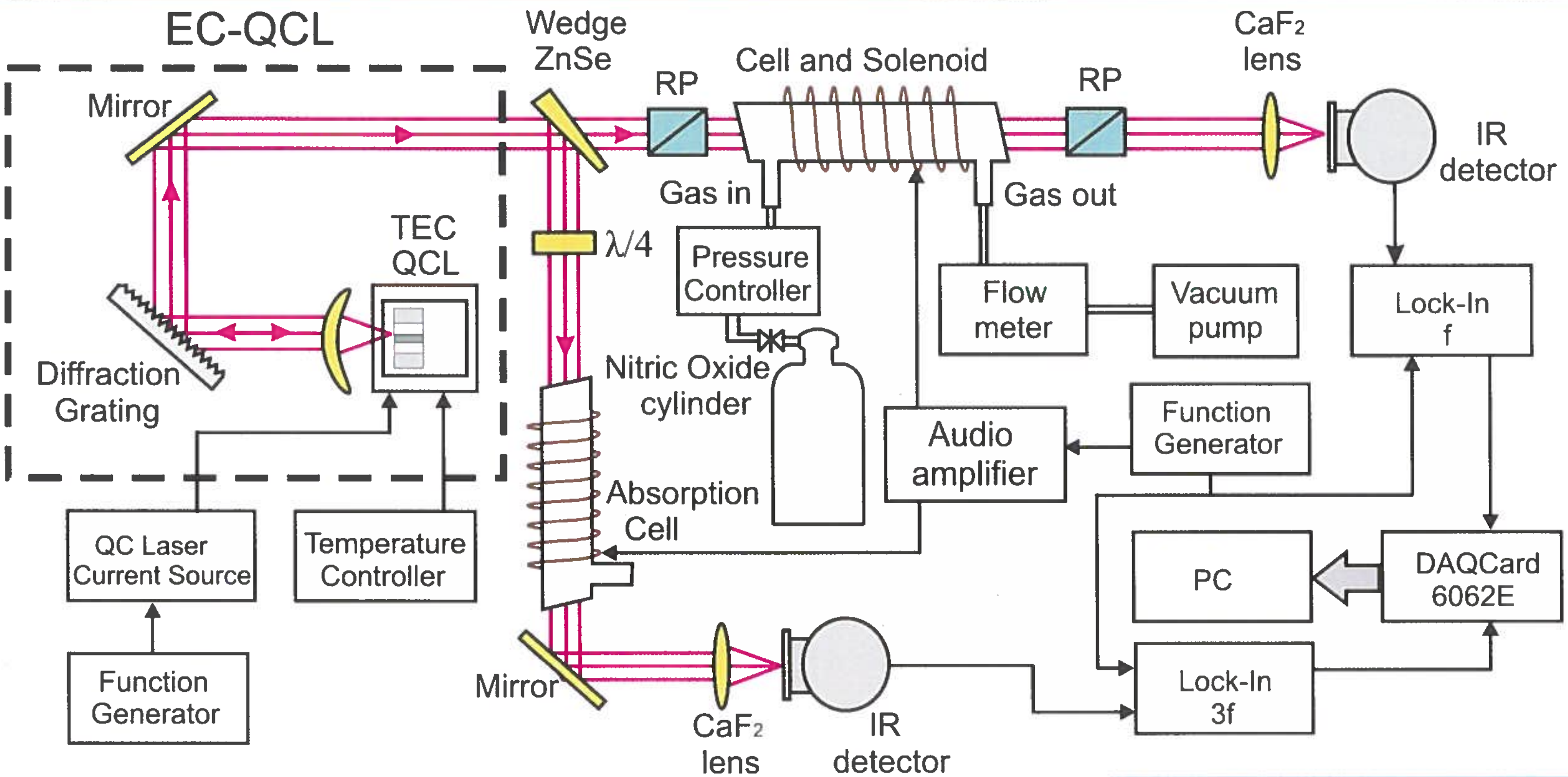
Motivation for Nitric Oxide Detection

- 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
- Photofragmentation of nitro-based explosives (TNT)

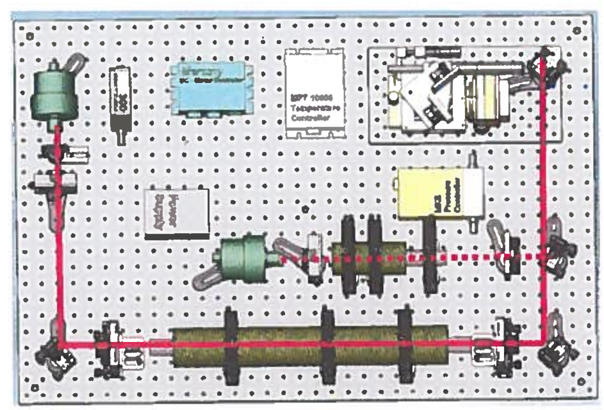
Motivation for Nitric Oxide Detection

- Environmental pollutant
  - Product of fossil fuel combustion process (automobile and power plant emissions)
  - Precursor of smog and acid rain

EC-QCL Based Faraday Rotation Spectrometer



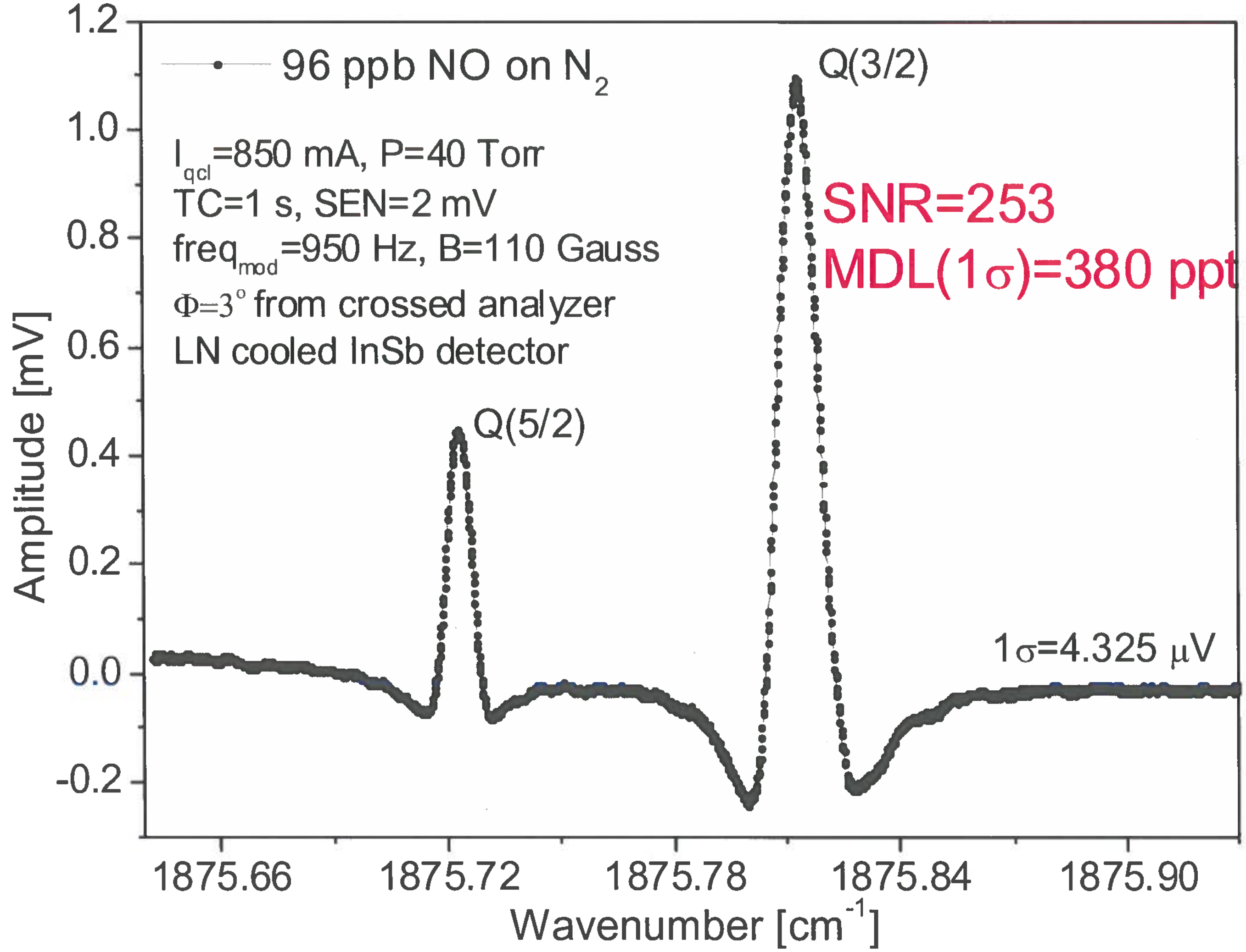
- EC-QCL Operating at 5.3μm – NO Fundamental Band
- 44cm effective optical pathlength
- Rochon Polarizer Extinction Ratio $<10^{-5}$
- Not sensitive to water interference
- Sensitivity Not Limited by Interference Fringes
- Gas Cell Volume (~ 250ml)
- Easy and Robust Optical Alignment
- Continuous NO Monitoring (Absorption Line Locking enabled with mode-hop free tuning using Zeeman Modulation at 3rd harmonic)



(3 x 2 ft.)

PRINCETON UNIVERSITY

Faraday Rotation Spectroscopy of Nitric Oxide



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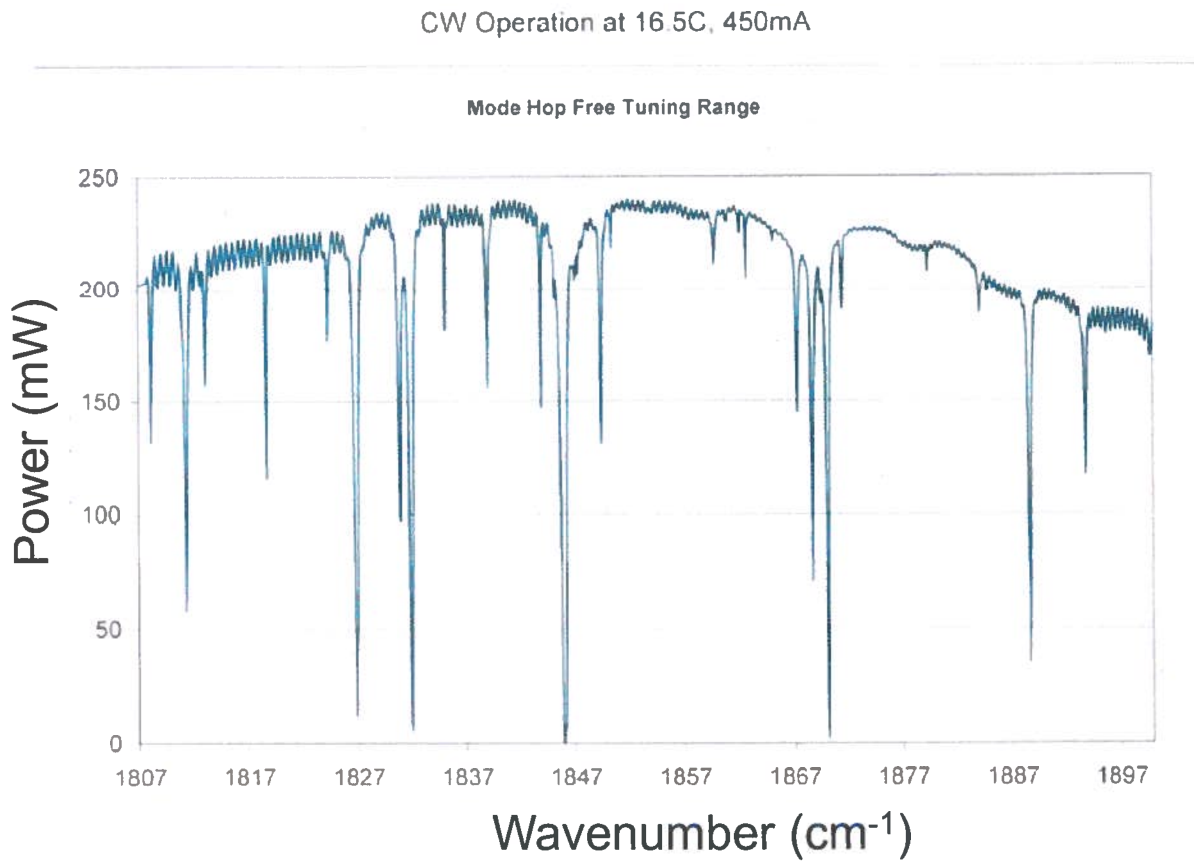
Future Directions and Outlook of Chemical Trace Gas Sensing Technology

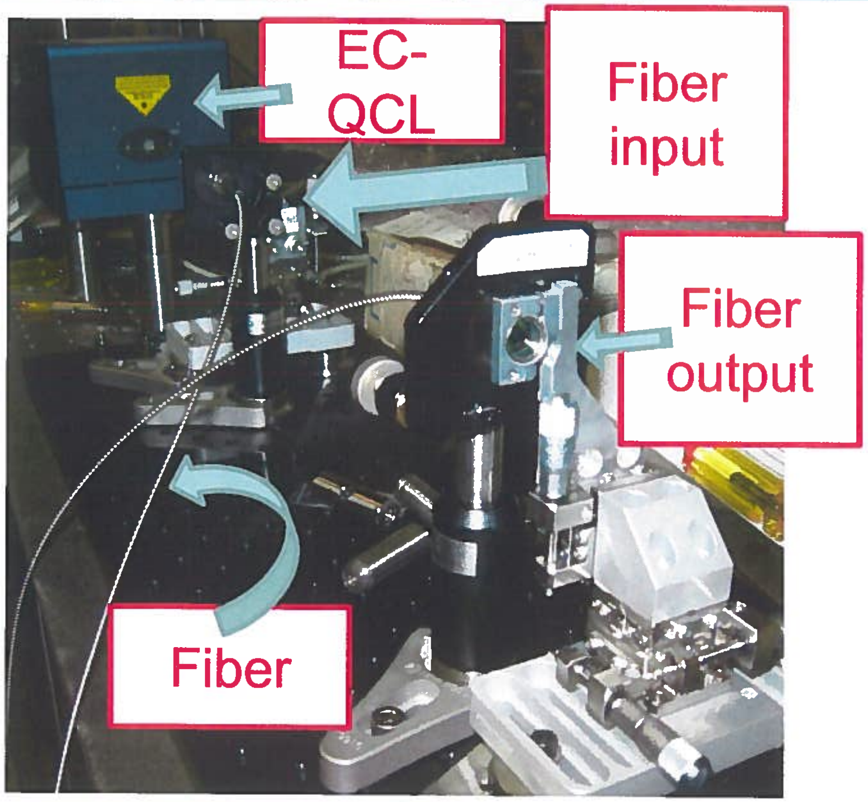
High power fiber-coupled QCL for NO detection



- LASER SOURCE EC-QCL (Daylight Solutions, Inc)
  - Tuning range 5.13-5.67 μm
  - Maximum tuning Rate 38 nm/sec
  - Highest optical power: ~250 mW
  - TE cooling, RT operation

Collaboration with: V. Spagnolo
Politecnico Bari and CNR-LIT[3]

Fiber coupled QCL and QEPAS detection system



- High coupling efficiency of laser output to fiber
- Beam size matching to QEPAS after collimation
- Aspheric lenses for both coupling and re-collimating.
- 86% coupling efficiency

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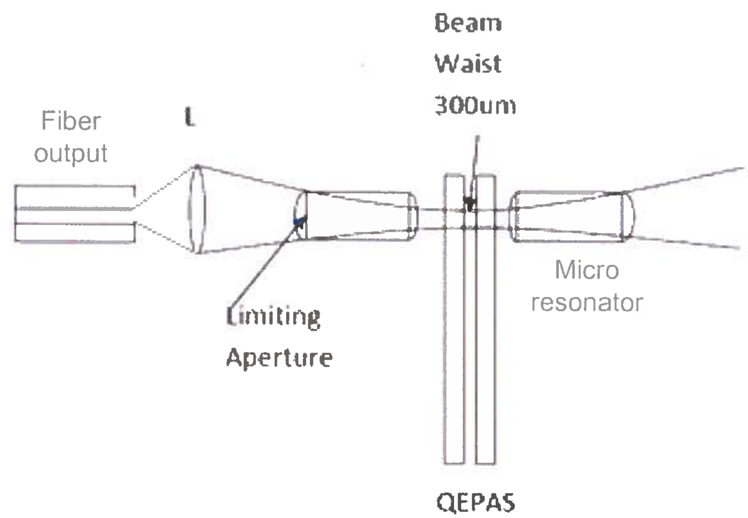
Material: $AsSe_3$,
- 22 μm core diameter
- Single mode operation
- FC-PC termination
- AR Coated.



Collaboration with :V. Spagnolo, Politecnico Bari and CNR-LIT[3]

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
- TATP (Acetone Peroxide, $C_6H_{12}O_4$)
  - Highly Explosive
- Uranium Hexafluoride (UF_6)

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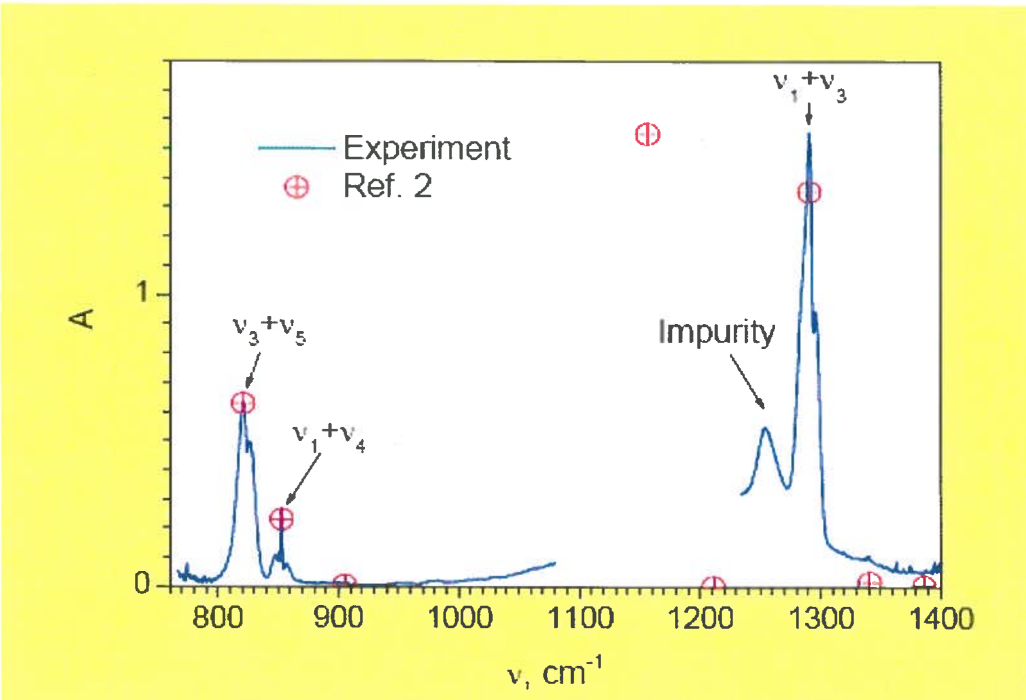
UF_6 Mid-Infrared Absorption Bands



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

Assignment	ν, cm^{-1}	σ, cm^{-1}/atm
$2\nu_3+\nu_6$	1386±2	0.0018
$\nu_1+\nu_2+\nu_6$	1341	0.0088
$\nu_1+\nu_3$	1290.9±0.5	0.72
$2\nu_2+\nu_6$	1211±2	0.0007
$\nu_2+\nu_3$	1156.9±0.5	0.82
$\nu_3+2\nu_6$	905±2	0.0035
$\nu_1+\nu_4$	852.8±0.5	0.12
$\nu_3+\nu_5$	821	0.33
ν_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.

A. Nadezhdinskii et al, GPI, Moscow, March 2008

Also: G. Baldaccini et al., Nuovo Cimento 8, 203, 1986

QEPAS MDAL comparison with CRDS, ICOS & TDLAS

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

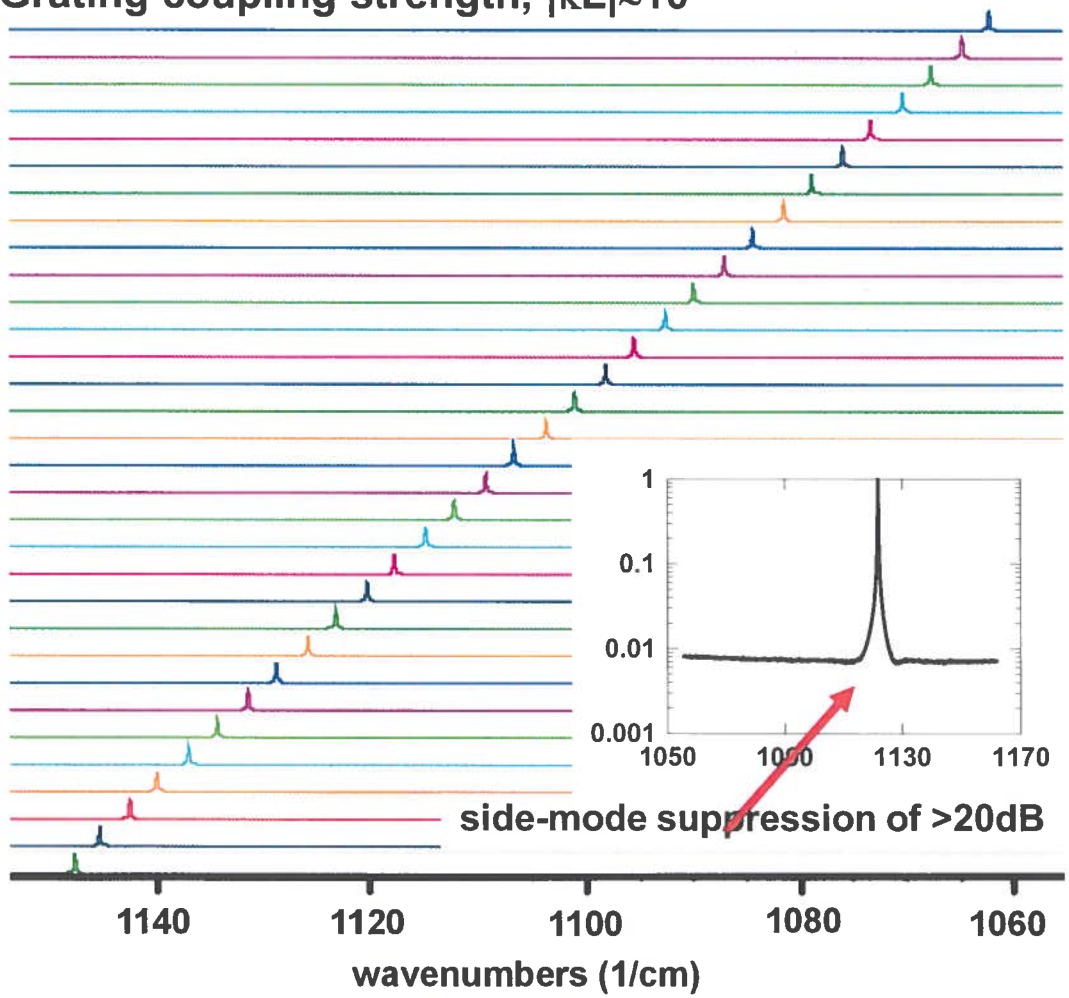
- Cavity Ring Down Spectroscopy (CRDS) : $\sim 3\times10^{-11}$
- Integrated Output Spectroscopy (ICOS): $\sim 3\times10^{-11}$
- Multipass Gas Cell based TDLAS: $\sim 2.\times10^{-11}$

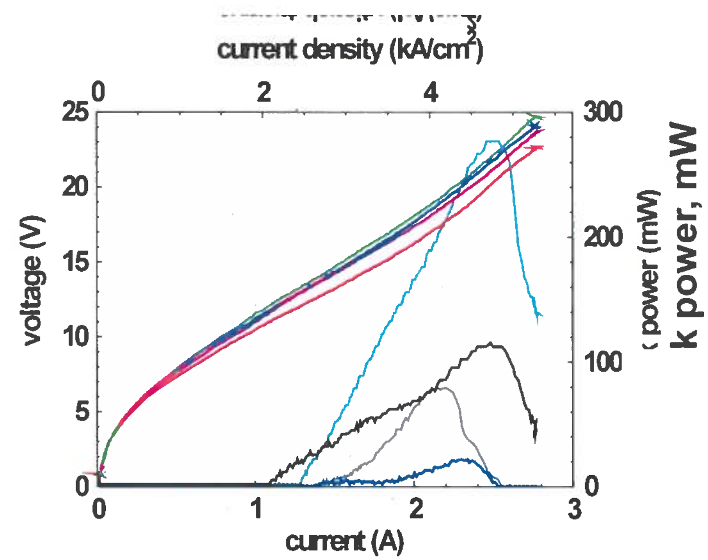
- QEPAS (Sept 2009) MDAL (DFB 100mW): 1.9×10^{-8}
- QEPAS-OPBC MDAL (DFB 20 mW): 3.2×10^{-10}
- QEPAS-OPBC + μresonator (estimated): $\sim 7\times10^{-12}$

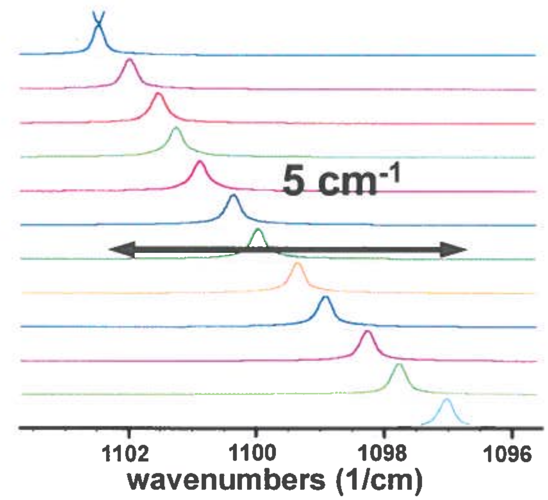
QEPAS-OPBC can be as sensitive as CRDS, ICOS and TDLAS as well as retain most of the merits of QEPAS

DFB QCL array performance

Emission spectrum of a DFB-QCL array
Pulsed operation (80kHz, 50ns) at room temperature
Grating coupling strength, |κL|≈10



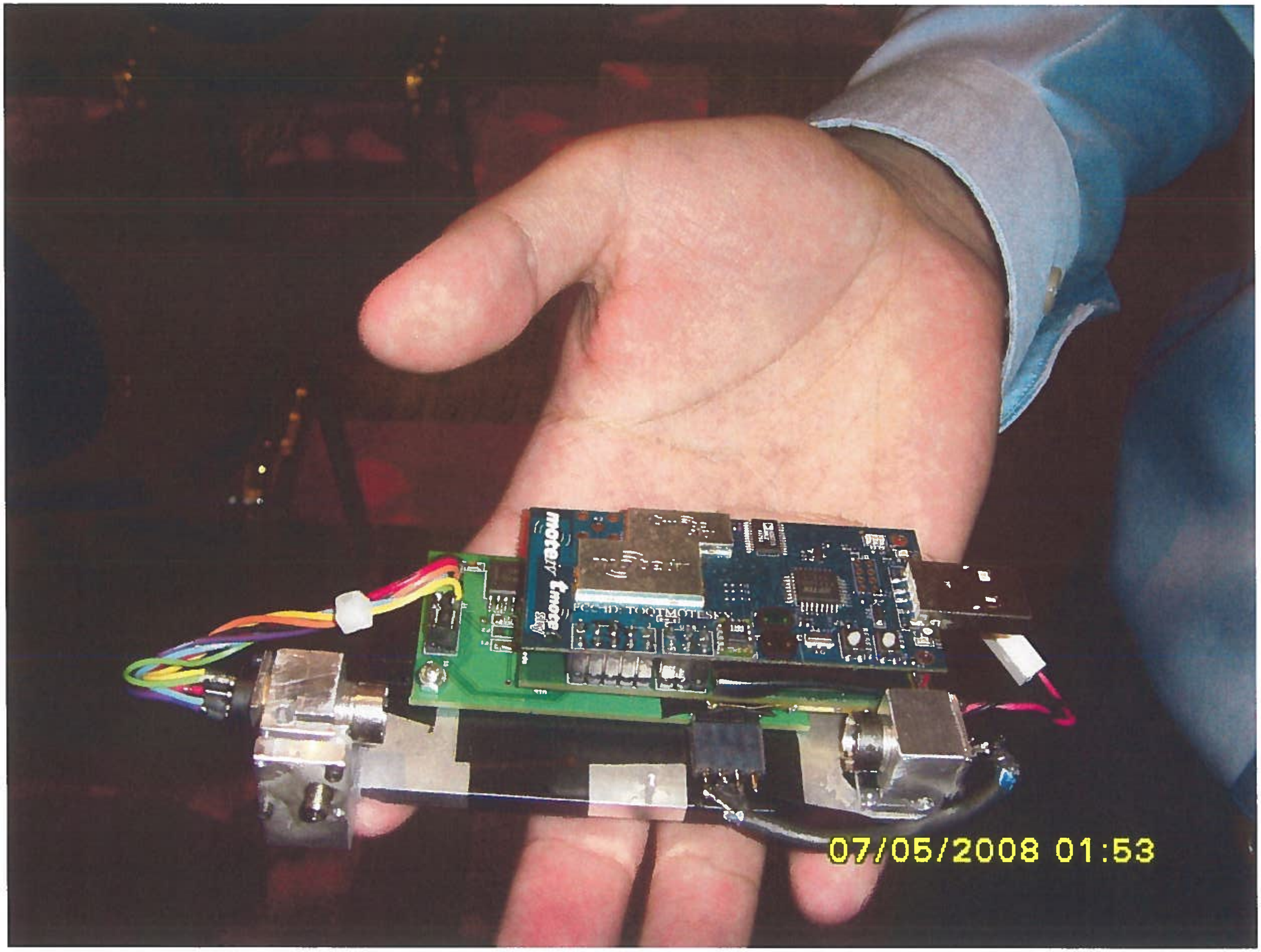




Temperature tuning by DC current

Lee, Belkin, et al., APL 2007

Ultra-compact Diode Laser based Trace Gas Sensor



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_3, CH_4, N_2O, CO_2, CO, NO, H_2O, COS, C_2H_4, H_2S, H_2CO, SO_2, C_2H_5OH, C_2HF_5 TATP and several isotopic species of C, O, N and H.
- **New Applications of Trace Gas Detection**
  - Environmental Monitoring (urban quality – NH3, H_2CO, NO, isotopic ratio measurements of CO_2 and CH_4, fire and post fire detection; quantification of engine exhausts)
  - Industrial process control and chemical analysis (NO, NH_3, H_2O, and H_2S)
  - Medical & biomedical non-invasive diagnostics (NH_3, NO, N_2O and CH_3COCH_3)
  - Ultra-compact, low cost, robust sensors (CO and CO_2)
- **Future Directions and Collaborations**
  - Improvements of the existing sensing technologies using novel, thermoelectrically cooled, cw, high power, and broadly wavelength tunable near and 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_6 and multi-species detection)
  - Development of optically gas sensor networks based on QEPAS and LAS

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Merits of QEPAS based Trace Gas Detection

- High sensitivity (ppm to ppb gas concentration levels) and excellent dynamic range
- Low sensitivity to environmental acoustic noise
- Significant reduction of sample volume (< 1 mm^3)
- Applicable over a wide range of pressures
- Rugged transducer-quartz monocrystal, which can operate in a wide range of pressures and temperatures and is humidity insensitive
- Ultra-compact, rugged and low cost detection module (compared to other laser based sensor architectures)

QEPAS Performance for 13 Trace Gas Species (Sept. '09)

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+1.2% H_2O)*	6057.09	760	3.7×10^{-9}	16	0.24
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	5
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.

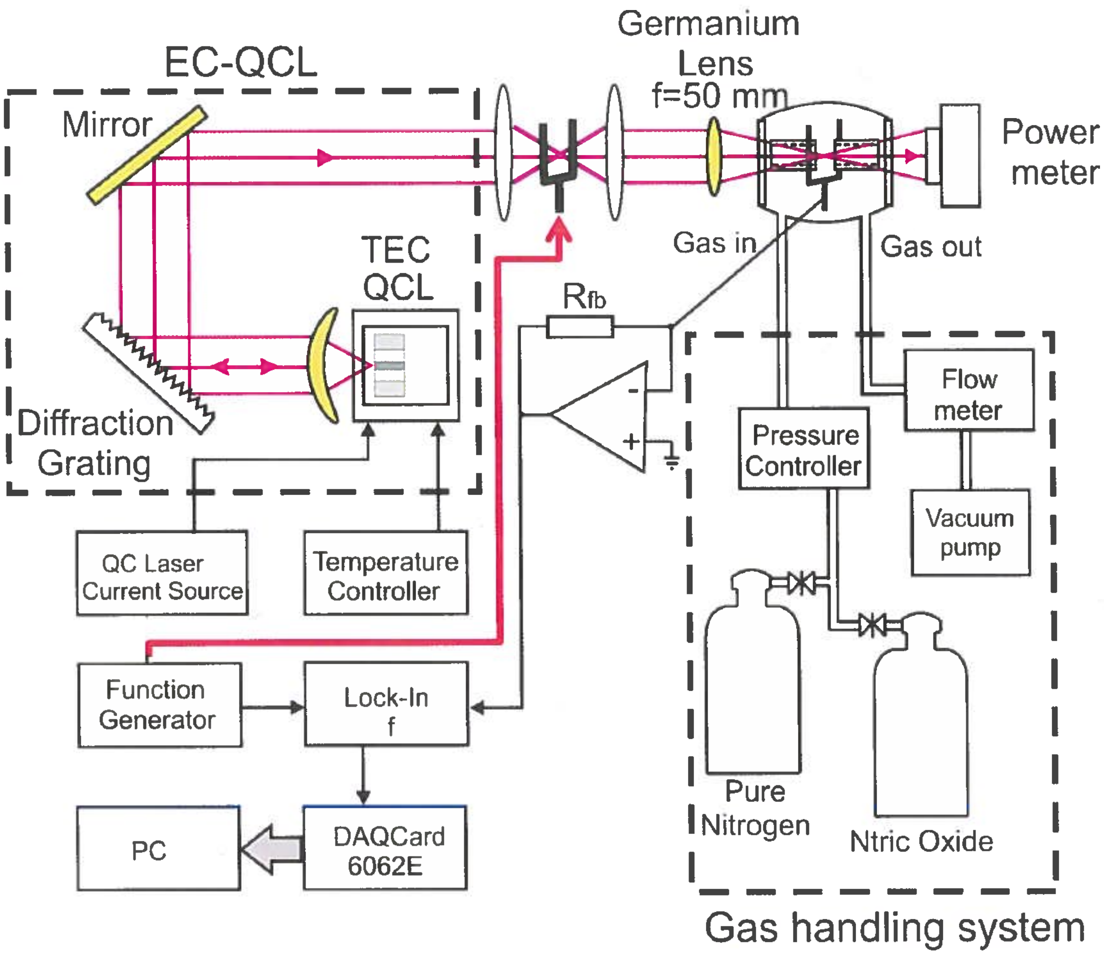
NEC – noise equivalent concentration for available laser power and τ=1s time constant, 18 dB/oct filter slope.

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

5.3μm QCL based QEPAS Gas Sensor for NO detection



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

High resolution EC-QCL based NO Spectrum