Recent Progress of Semiconductor Laser-Based Infrared Spectroscopic Techniques

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

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OUTLINE

IQCLSW Ascona

Switzerland

Sept. 14-19, 2008

- Motivation: Wide Range of Chemical Sensing
- Fundamentals of Laser Absorption Spectroscopy
- New Laser Sensing Technologies (QEPAS)
- Selected Applications of Trace Gas Detection
  - Quartz Enhanced Photoacoustic Spectroscopy (Ammonia)
  - QEPAS based Chemical Sensing of Broadband Absorbers
- Future Directions and Conclusions

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Wide Range of Trace Gas Sensing Applications

- **Urban and Industrial Emission Measurements**
  - Industrial Plants
  - Combustion Sources and Processes
  - Automobile, Truck, Aircraft and Marine Emissions
- **Rural Emission Measurements**
  - Agriculture, Forestry and 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**

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Needs and Methods in IR Laser Monitoring

Requirements for trace gas sensor platforms: Sensitivity, specificity, multi-gas species, continuous, unattended ,rapid data acquisition, portability, low electrical power consumption and cost

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 and without retro-reflector)
- Evanescent Field Monitoring (fibers & waveguides)

Photoacoustic Spectroscopy

Spectroscopic Detection Schemes

- Frequency or Wavelength Modulation
- Balanced Detection
- Zero-air Subtraction

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Quartz Enhanced Photoacoustic Spectroscopy

From conventional PAS to QEPAS

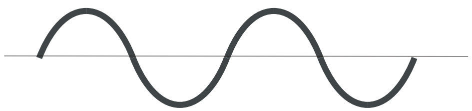
Cavity resonant

***Q*>10,000**

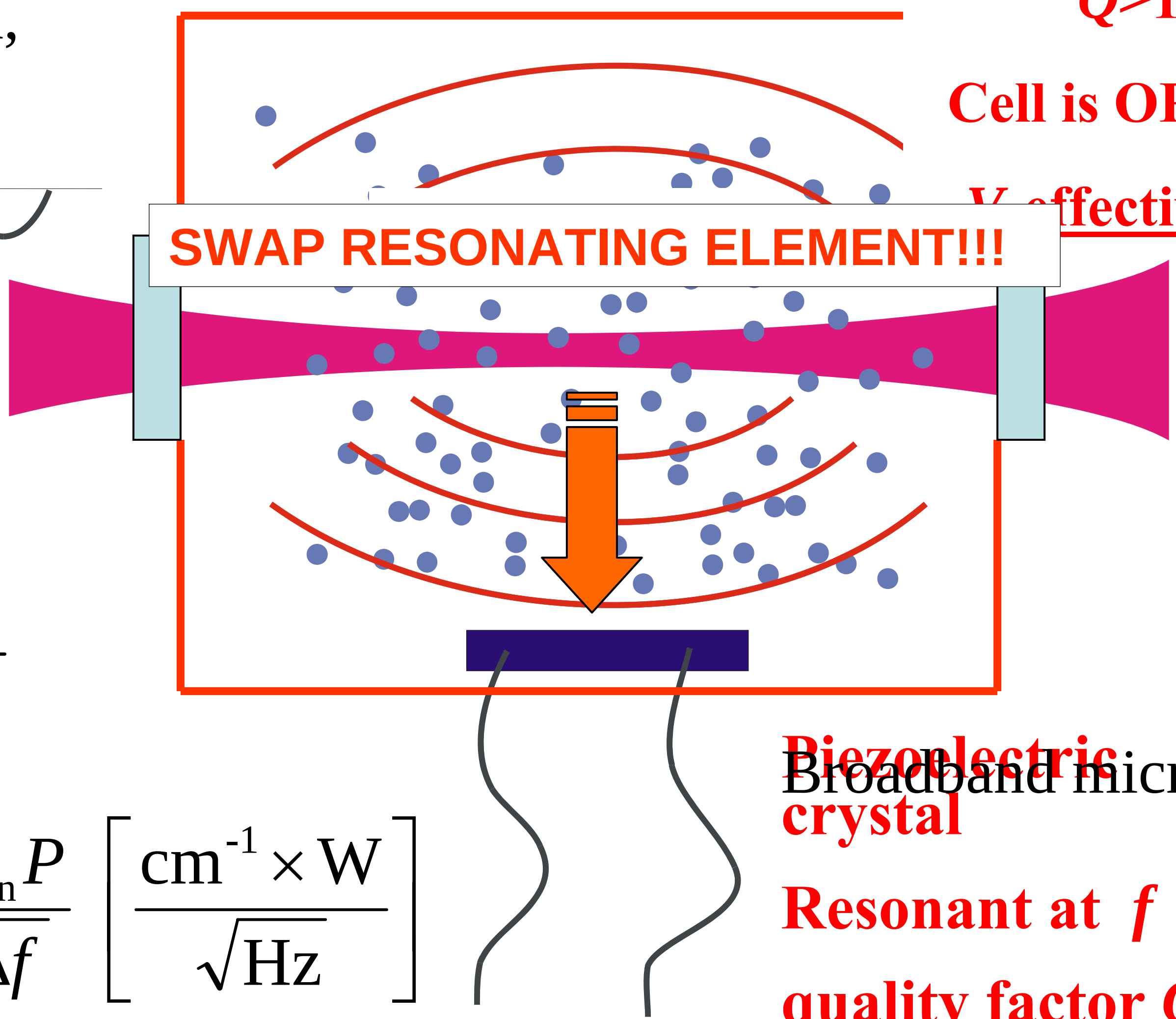
Cell is OPTIONAL!

***V* effective volume**

Laser beam, power *P*



Modulated (*P* or λ) at *f* or *f*/2



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

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

Broadband microphone

Piezoelectric crystal

Resonant at *f*

quality factor *Q*

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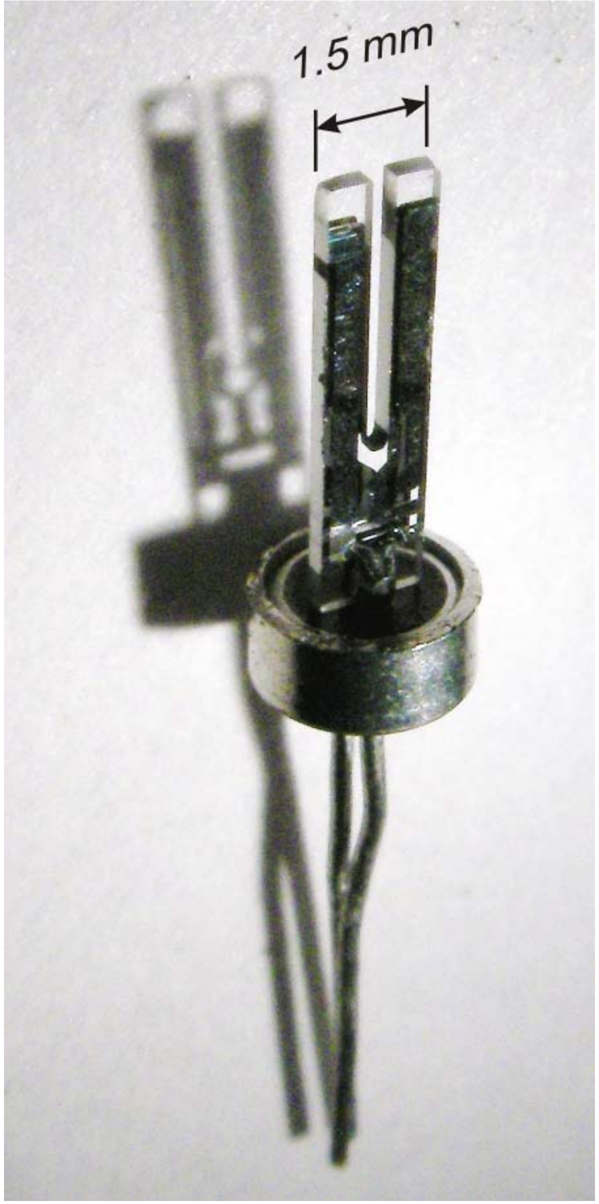
Quartz tuning fork as a resonant microphone



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
- Wide temperature range: from 1.56K (superfluid helium) to ~700K
- Temperature, pressure & humidity insensitive
- Compact, small sample volume-< $1mm^3$
- Low cost

Other parameters

- Resonant frequency ~32.8 kHz
- Force constant ~26800 N/m
- Electromechanical coefficient $\sim 7\times 10^{-6}$ C/m

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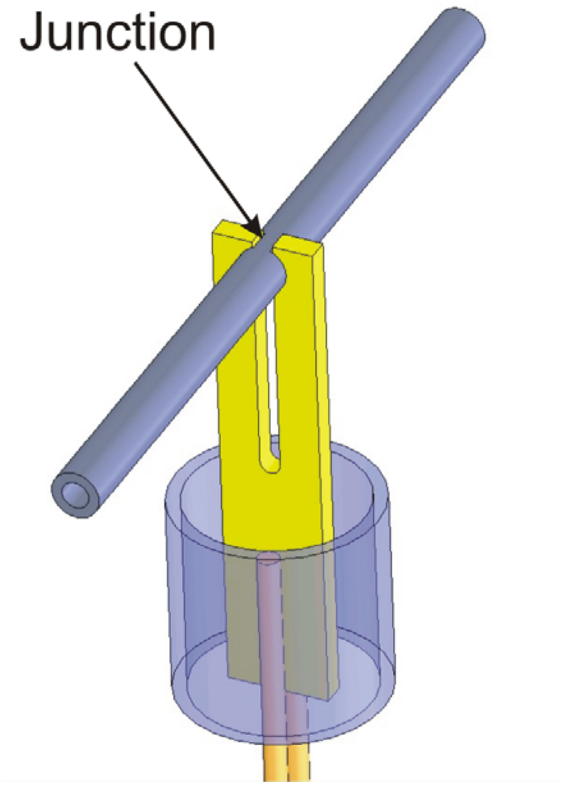
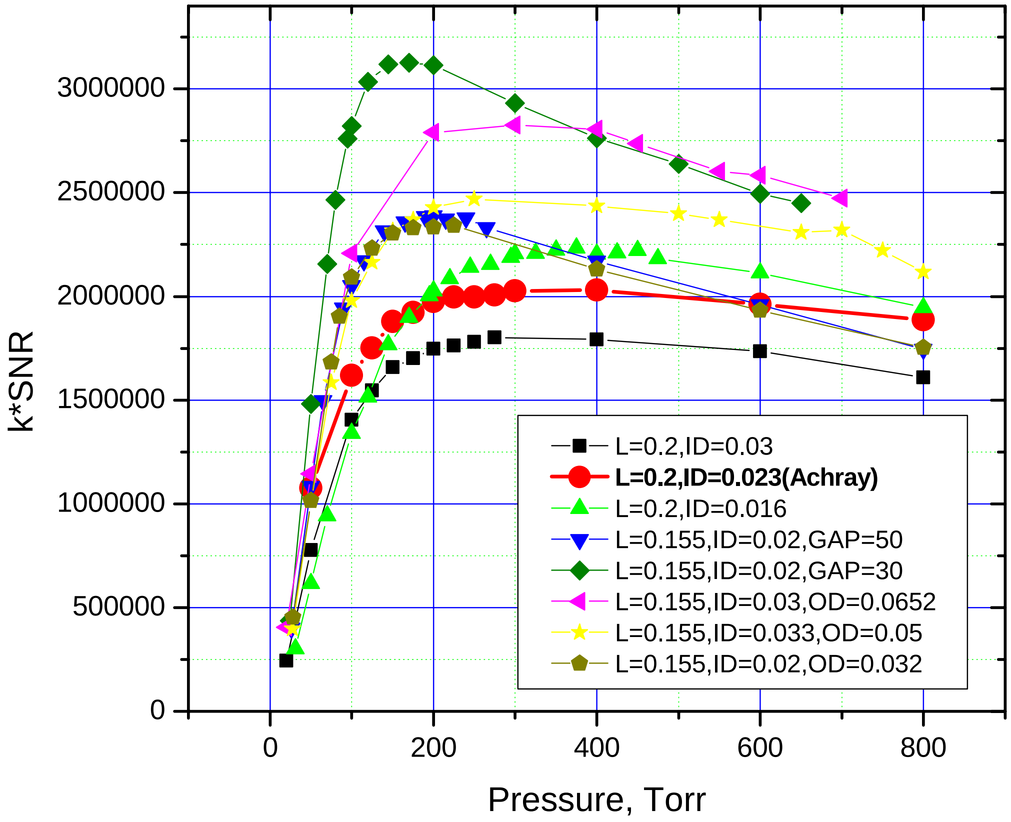
QEPAS SNR Enhancement of Acoustic Microresonator





Microresonator tubes

Must be close to QTF but not touching (i.e. 30-50µm gaps).
Each tube is ~ 5mm long (~l/2 for sound at 32.8 kHz)

QEPAS Signal Gain: ×10 to ×20

Optimum Geometry:
ID=0.02".Gap=25-30µm
OD=0.023";L=4.4mm

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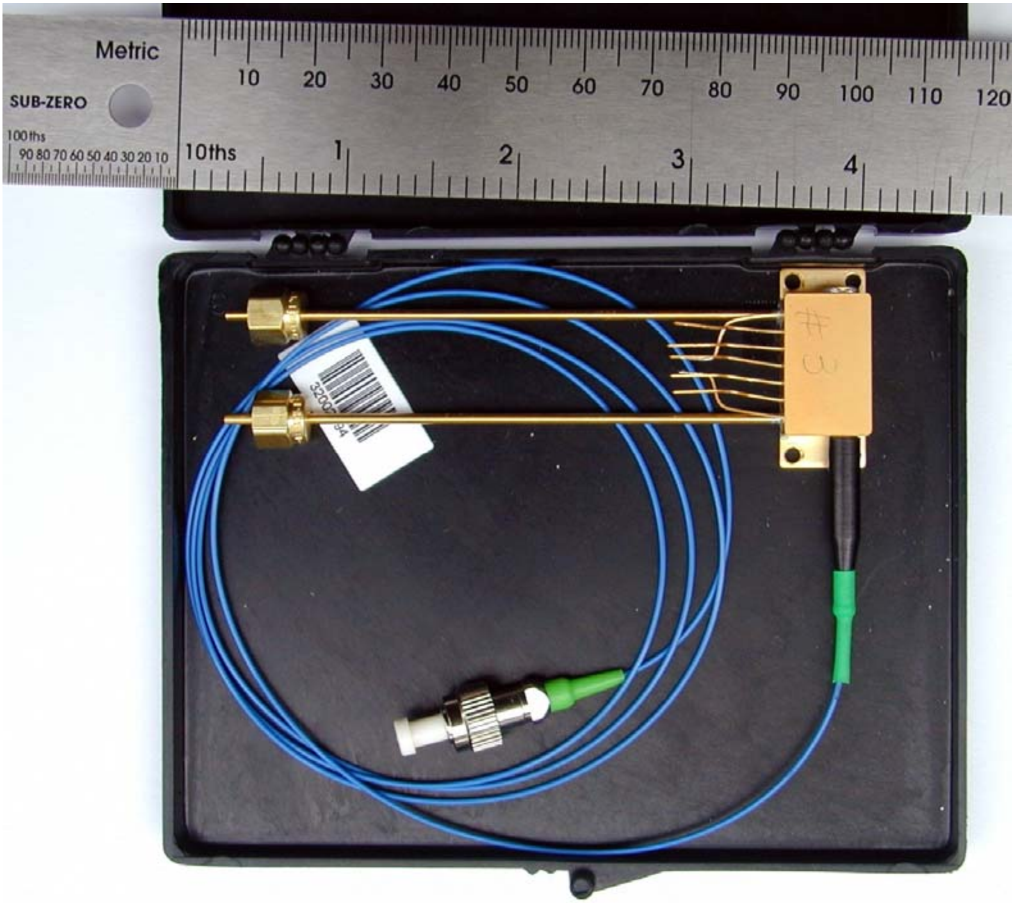
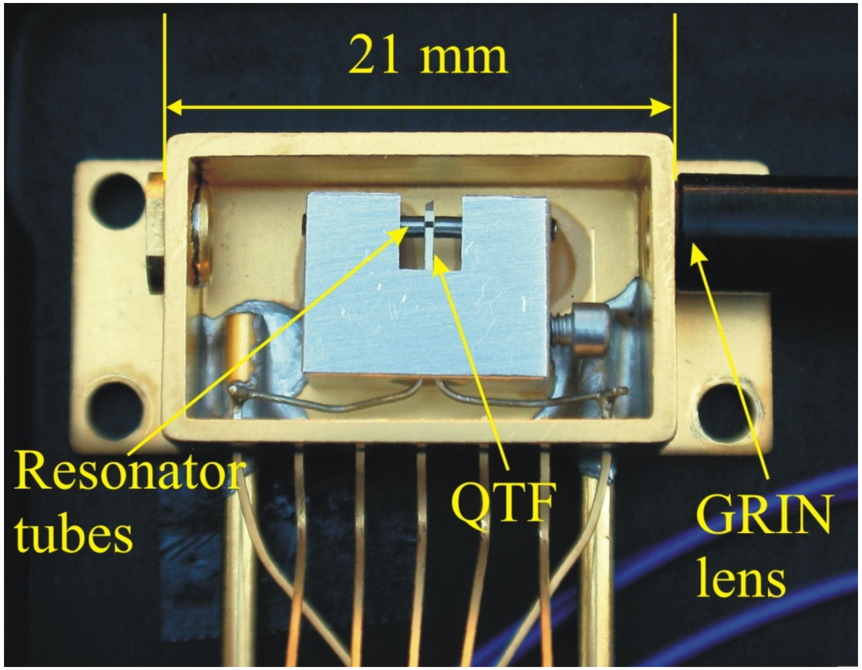
Alignment-free QEPAS Absorption Detection Module





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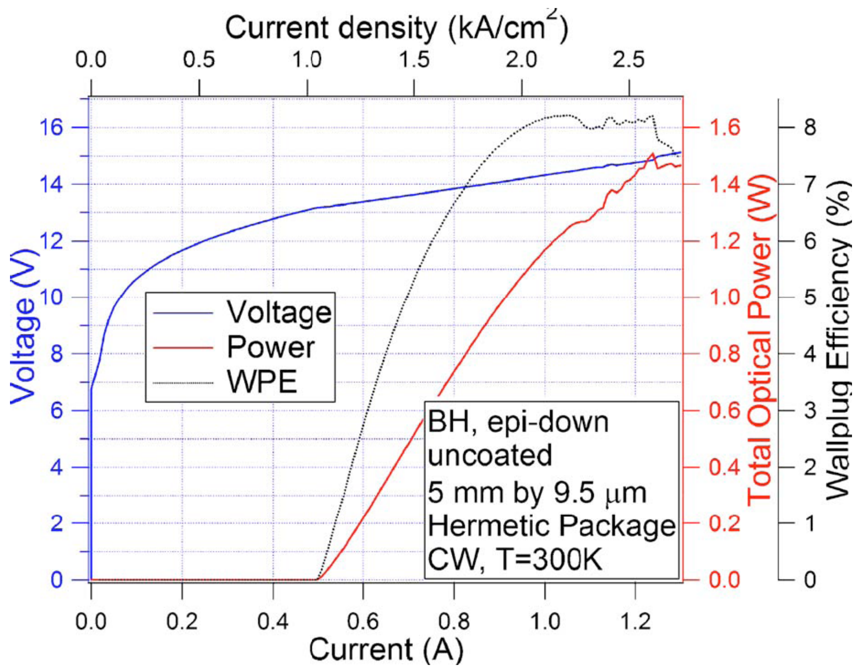
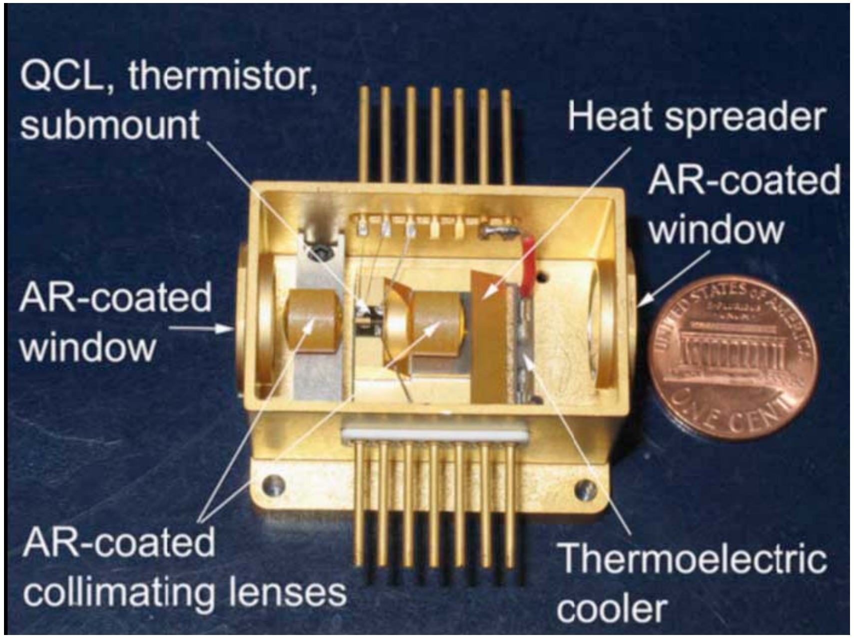
High Performance 4.6 μm CW, RT QC Laser - 2008





A. Lyakh et al., Pranalytica, Harvard, Adtech, Applied Physics Letters 92, 111110, 2008

Trace Gas Sensors Areas Explored at Rice

- Methods employed
  - Extended pathlengths (Multpass Gas Cells & Retroreflector)
  - Cavity R
  - ingdown
  - Off-Axis Integrated Cavity Output Spectroscopy
  - Faraday Rotation Spectroscopy
  - Wavelength Modulation
  - Pulse-to-pulse fluctuation removal by comparing the same pulse on the same or another detector
  - Quartz Tuning fork based photoacoustic spectroscopy (QEPAS)
- 16 gases detected: NH_3, CH_4, H_2S, N_2O, CO_2, CO, NO, C_2H_2 H_2O, OCS, C_2H_4, SO_2, C_2H_5OH, C_2HF_5, H_2CO, C_2H_6, HCN and isotopic species of C, O and N
- Practical applications
  - Crew Health Maintenance & Life Support - H_2CO, NH_3
  - Fire and Post Fire Detection
  - Radioactive site remediation
  - Medical breath analysis - NO, NH_3, CO_2, CH_3COCH_3, OCS
  - Industry catalyst poison - CO
  - Urban air smog - H_2CO

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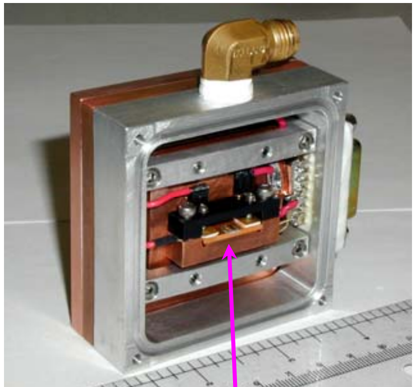
Biomarkers Present in Exhaled Human Breath

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

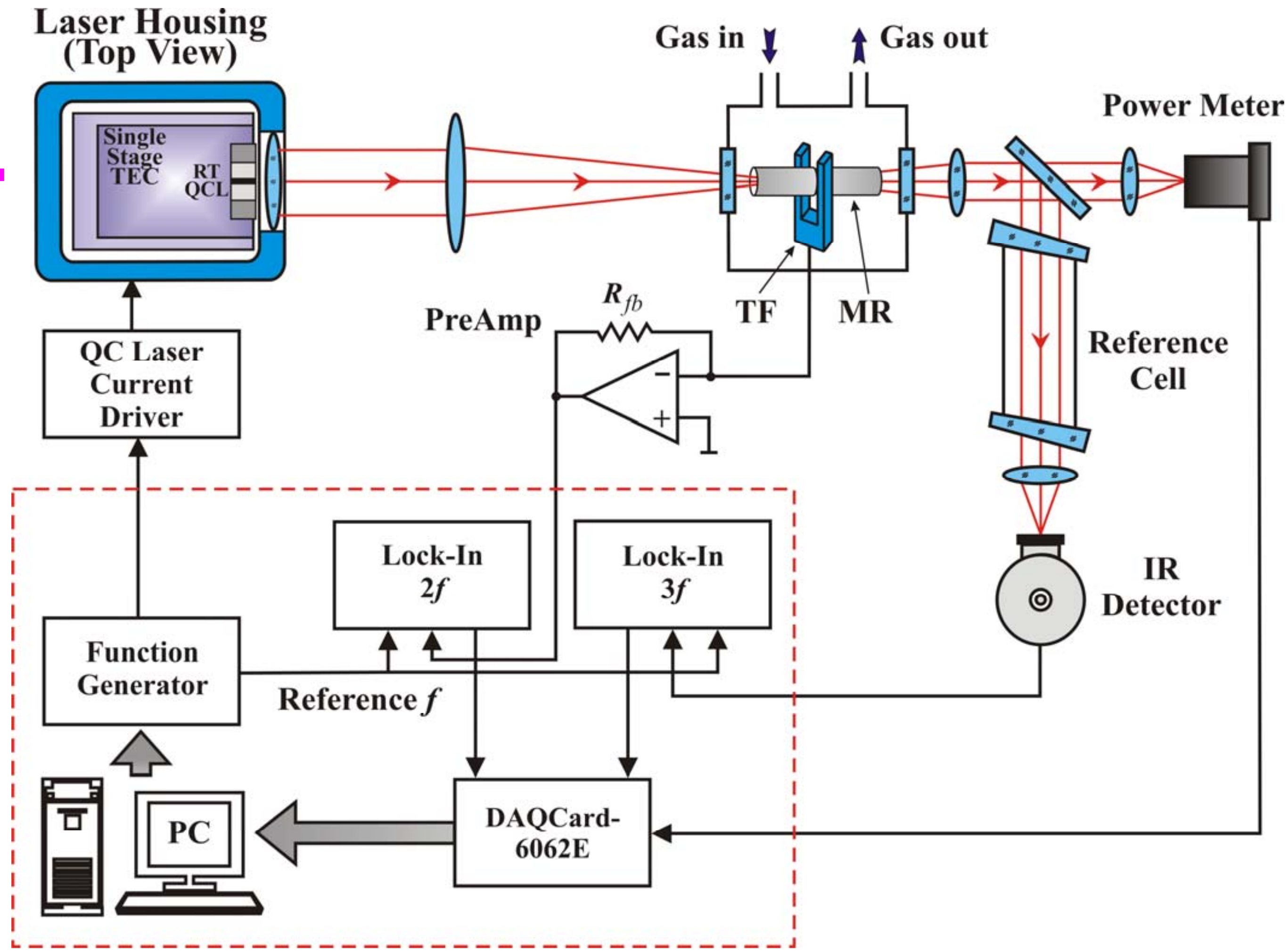
compound	concentration	physiological basis
Acetaldehyde	ppb	ethanol metabolism
Acetone	ppm	decarboxylation of acetoacetate
Ammonia	ppb	protein metabolism
Carbon dioxide	%	product of respiration
Carbon disulfide	ppb	gut bacteria
Carbon monoxide	ppm	production catalyzed by *heme oxygenase*
Carbonyl sulfide	ppb	gut bacteria
Ethane	ppb	lipid peroxidation
Ethanol	ppb	gut bacteria
Ethylene	ppb	lipid peroxidation
Hydrocarbons	ppb	lipid peroxidation/metabolism
Hydrogen	ppm	gut bacteria
Isoprene	ppb	cholesterol biosynthesis
Methane	ppm	gut bacteria
Methanethiol	ppb	methionine metabolism
Methanol	ppb	metabolism of fruit
Methylamine	ppb	protein metabolism
Nitric oxide	ppb	production catalyzed by *nitric oxide synthase*
Oxygen	%	required for normal respiration
Pentane	ppb	lipid peroxidation
Water	%	product of respiration

Terence Risby, Johns Hopkins University

Mid-IR QEPAS based NH_3 Gas Sensor Architecture



MAXION CW DFB QCL DQ9-M532P



QEPAS Driver

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

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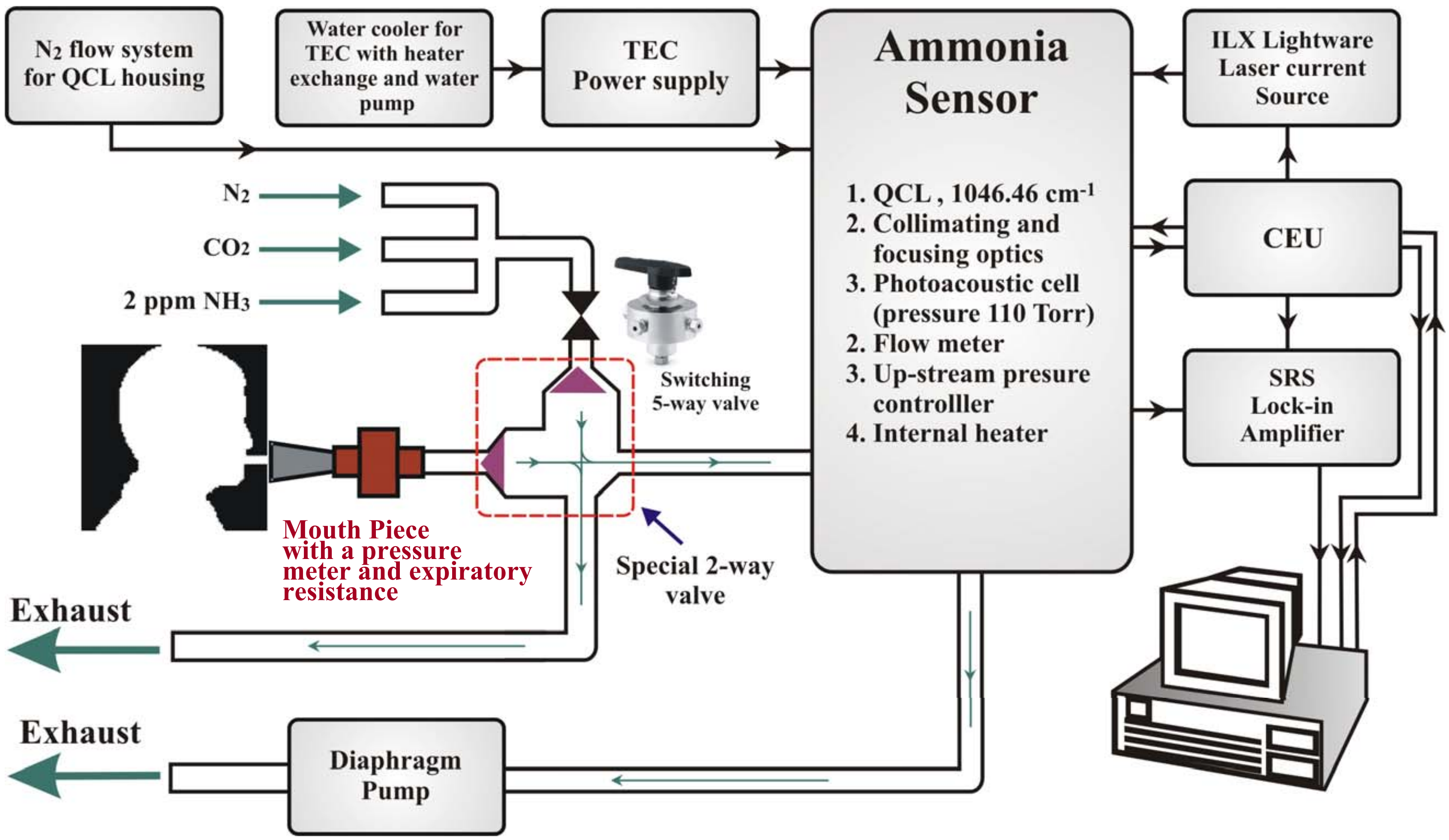
Interface for Real-time Breath NH_3 Analyzer



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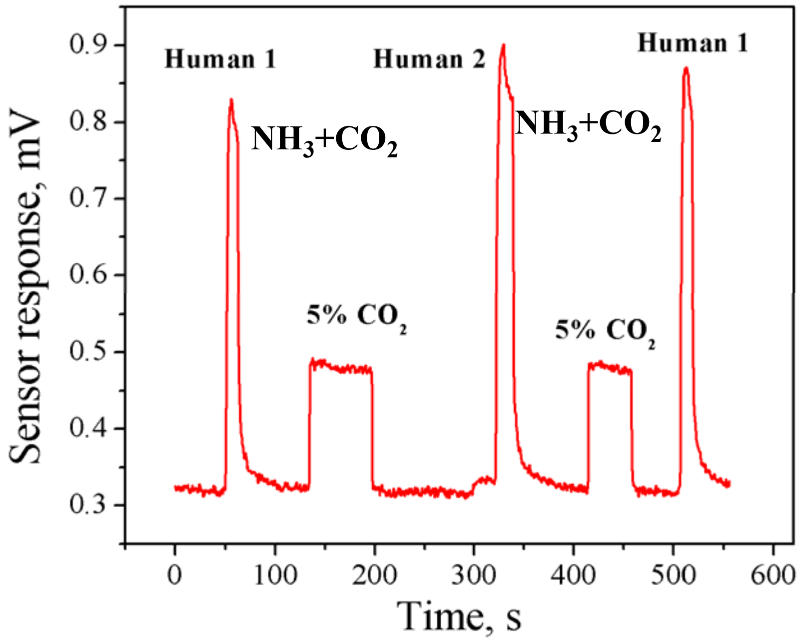
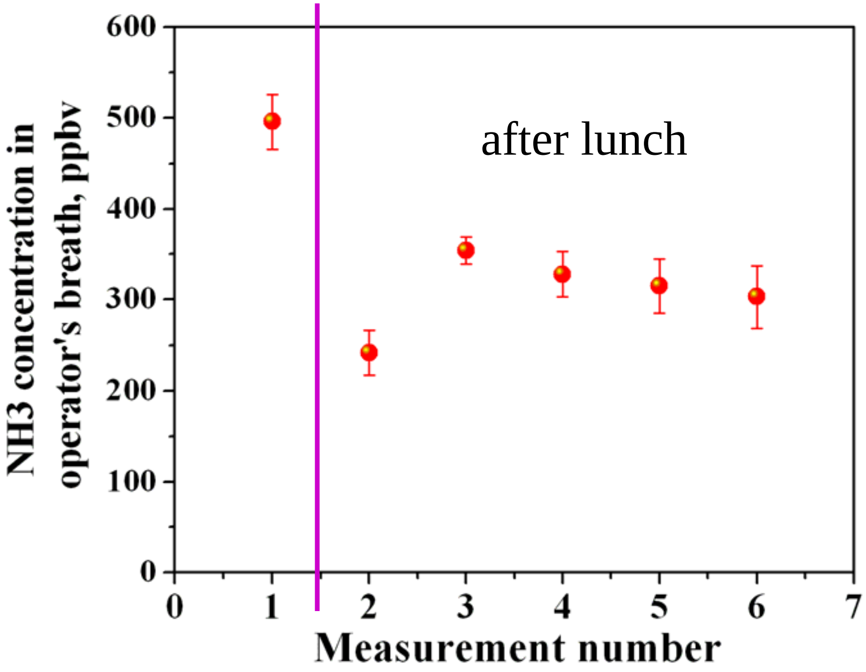
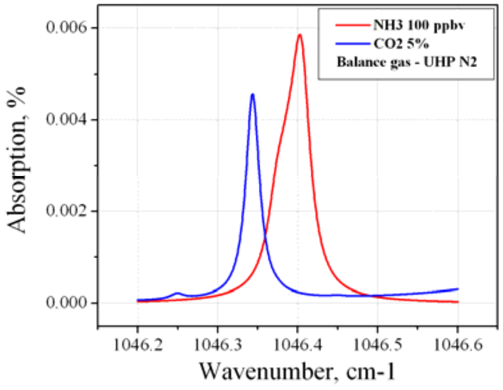
Real-time Breath NH_3 Samples







Presence of CO_2 in breath (≥ 5%) contributes to resulting sensor response signal. This fact must be taken into account in the quantification of exhaled ammonia concentrations

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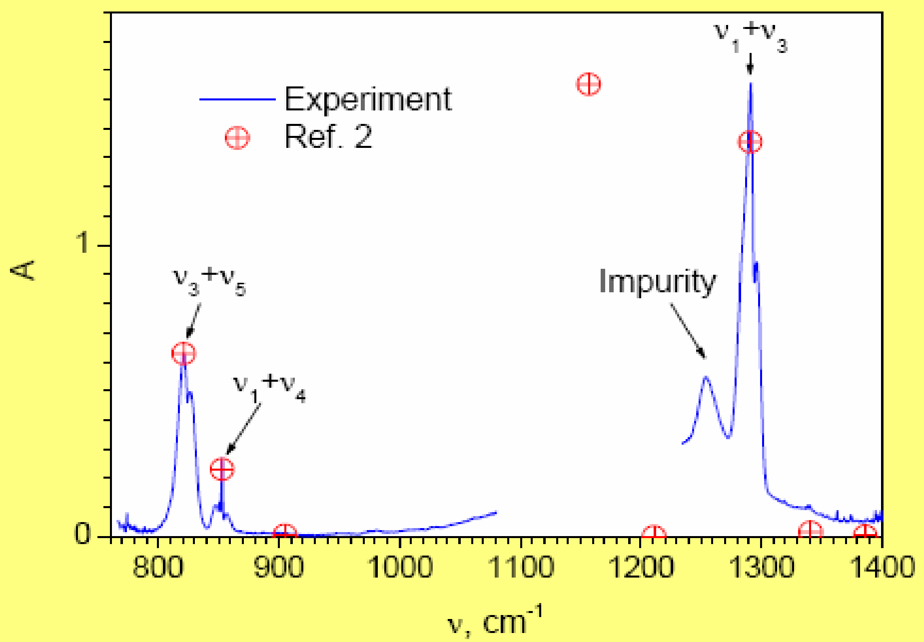
Monitoring of broadband absorbers

- Freon 125 (C_2HF_5)
  - Refrigerant (leak detection)
  - Safe simulant for toxic chemicals, e.g. chemical warfare agents
- Acetone (CH_3COCH_3)
  - Recognized biomarker for diabetes
- TATP, Acetone Peroxide ($C_6H_{12}O_4$)
  - Highly Explosive
- UF_6 Analytical Enrichment Measurements by IAEA, Vienna.

UF_6 Mid-Infrared Absorption Bands



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

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

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.

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

Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, $cm^{-1}W/Hz^{½}$	Power, mW	NEC (τ=1s), ppmv
H_2O (N_2)**	7306.75	60	$1.9{\times}10^{-9}$	9.5	0.09
HCN (air: 50% RH)*	6539.11	60	< $4.3{\times}10^{-9}$	50	0.16
C_2H_2 (N_2)*	6523.88	720	$4.1{\times}10^{-9}$	57	0.03
NH_3 (N_2)*	6528.76	575	$3.1{\times}10^{-9}$	60	0.06
C_2H_4 (N_2)*	6177.07	715	$5.4{\times}10^{-9}$	15	1.7
CH_4 (N_2)*	6057.09	950	$2.9{\times}10^{-8}$	13.7	2.1
CO_2 (breath ~100% RH)	6361.25	150	$8.2{\times}10^{-9}$	45	40
H_2S (N_2)*	6357.63	780	$5.6{\times}10^{-9}$	45	5
CO_2 (N_2+1.5% H2O) *	4991.26	50	$1.4{\times}10^{-8}$	4.4	18
CH_2O (N_2:75% RH)*	2804.90	75	$8.7{\times}10^{-9}$	7.2	0.12
CO (N_2)	2196.66	50	$5.3{\times}10^{-7}$	13	0.5
CO (propylene)	2196.66	50	$7.4{\times}10^{-8}$	6.5	0.14
N_2O (air+5%SF_6)	2195.63	50	$1.5{\times}10^{-8}$	19	0.007
C_2H_5OH (N_2)**	1934.2	770	$2.2{\times}10^{-7}$	10	90
C_2HF_5 (N_2)***	1208.62	770	$7.8{\times}10^{-9}$	6.6	0.009
NH_3 (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 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

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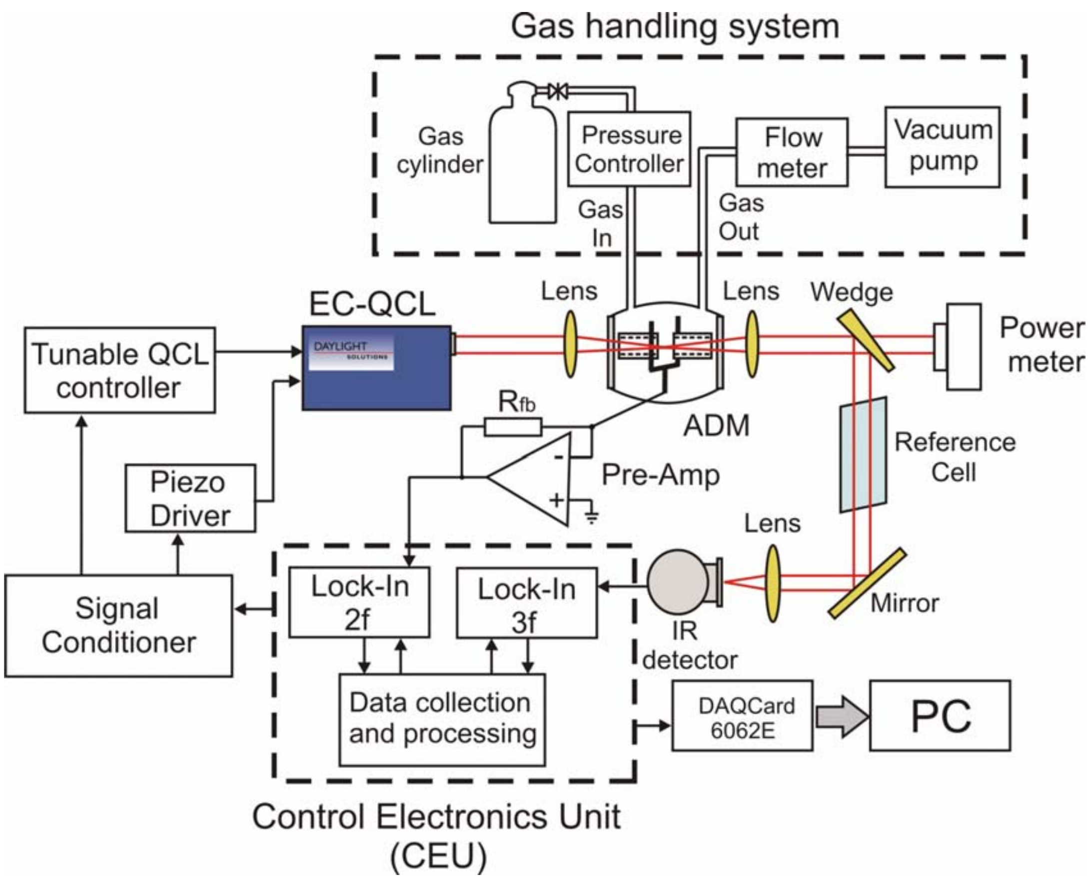
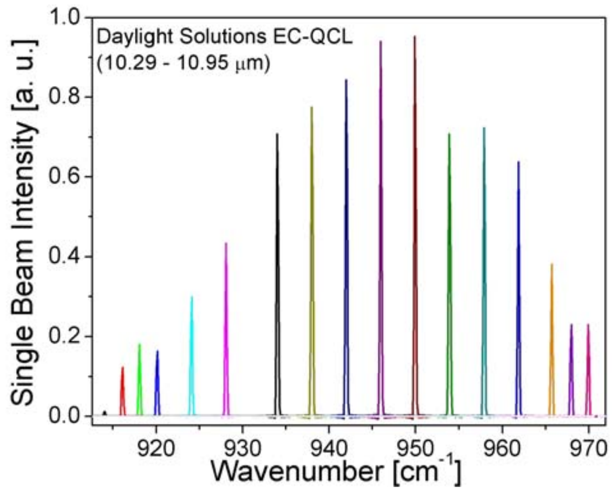
Future of Chemical Trace Gas Sensing

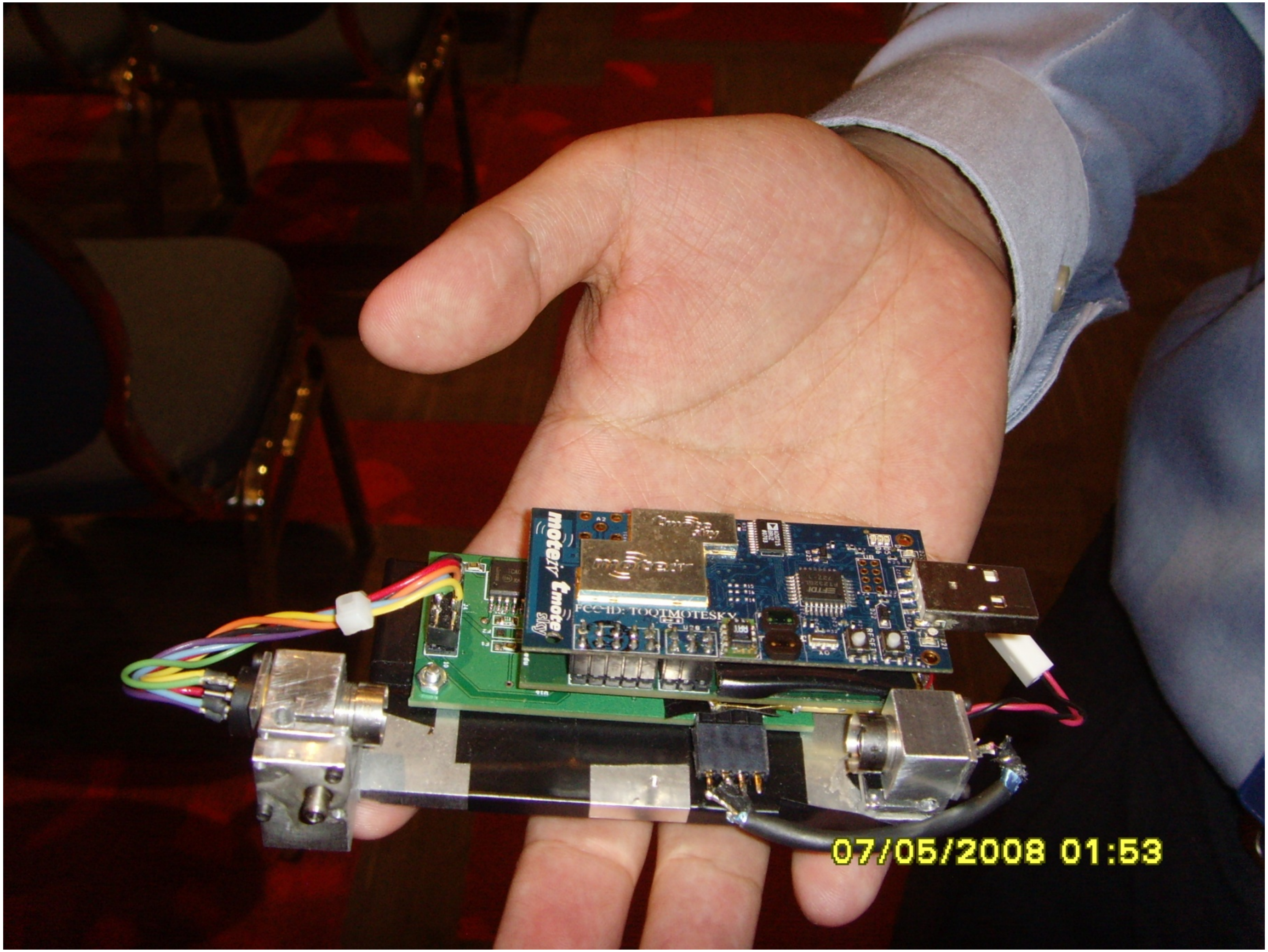
DLS tunable 10.6µm CW EC-QCL based QEPAS Sensor





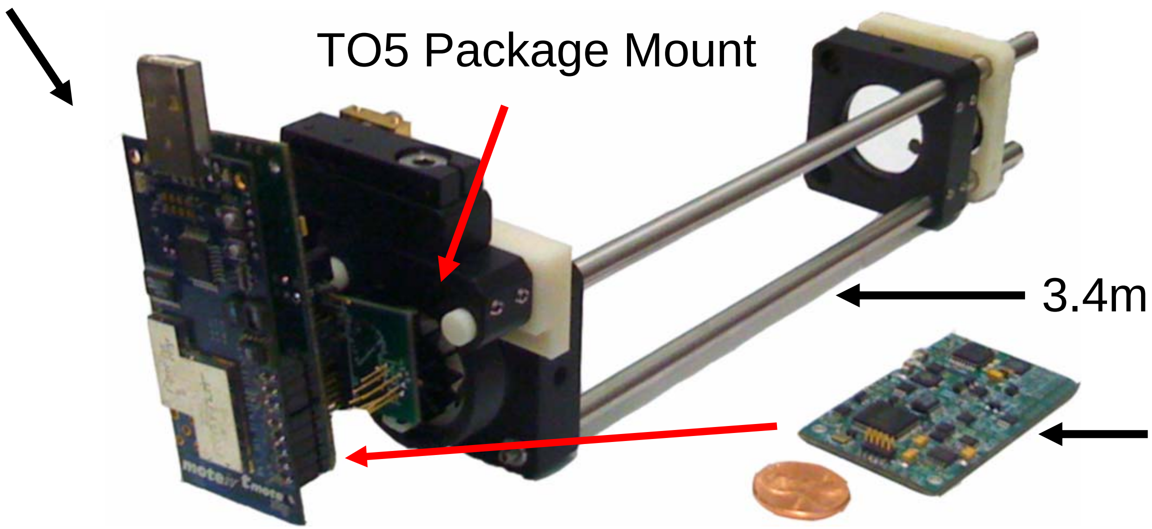
DLS CW EC QCL
NH_3 @944 cm^{-1}; 34mW,
Tuning Range:54cm^{-1}

Ultra-compact Semiconductor Laser based Trace Gas Sensor



Rapid Prototyped Multipass Cell based TDLAS Platform

- Designed for TO5 Packaged CW Lasers with Integrated TEC (VCSELs, Sb, QCLs)
- Wavelength modulation capability (scan, 1f, or 2f)
- Quadrature digital lock-in amplifier
- Low noise current driver
- TEC driver, 0.001 °C stability
- Battery Powered
- Cost: ~ $1,000



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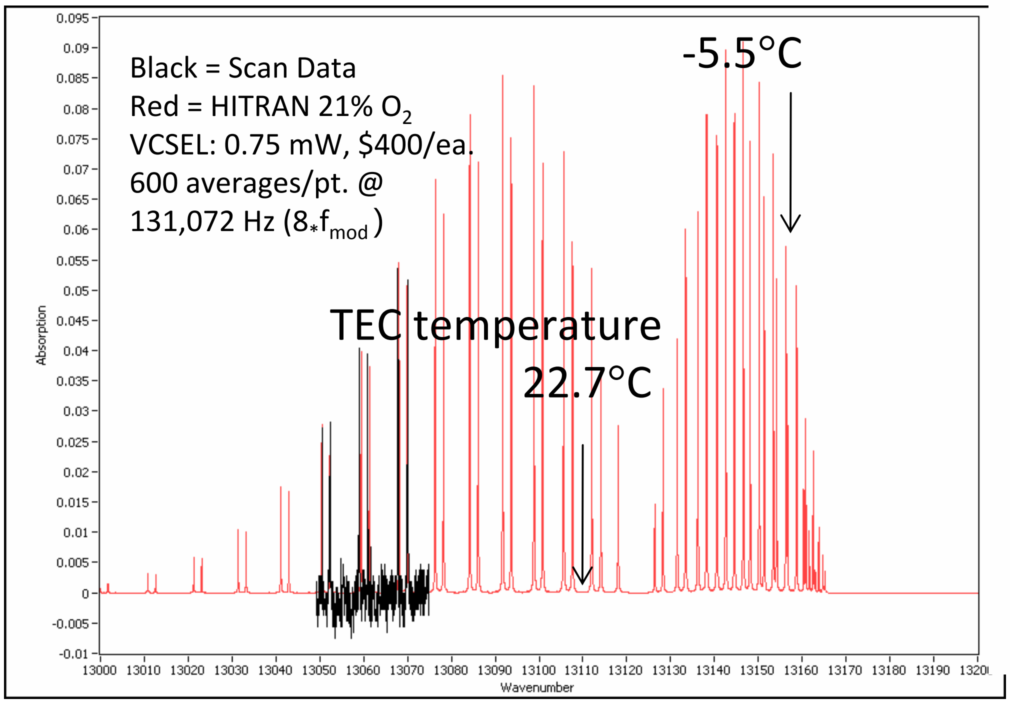
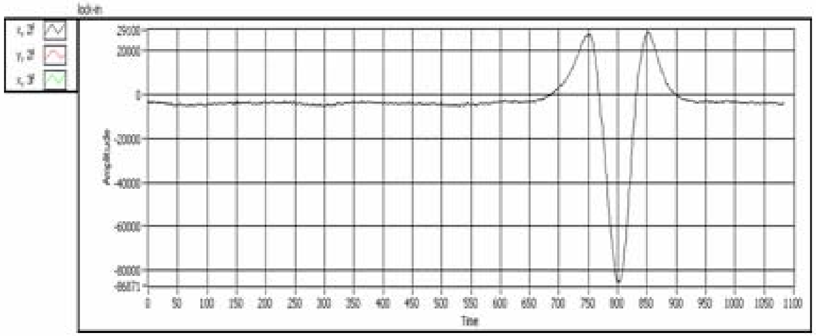
763 nm VCSEL based Oxygen TDLAS sensor



MPC LAS 2f DigitalLock-InSignal



Also CO_2 LAS detection:
1 ppm (1 sec.) @2.7µm
Power consumption:: 0.2W
> 100x improvement @4.3µm

Summary & Future Directions of Infrared based Gas Sensor Technology

- **Quantum Cascade, Interband Cascade, GaSb Laser and VCSEL based Trace Gas Sensors**
  - Compact, tunable, and robust sensor platforms
  - High sensitivity ($<10^{-4}$) and selectivity (3 to 500 MHz)
  - Capable of fast data acquisition and analysis
  - Detected 13 trace gases to date: NH_3, CH_4, N_2O, CO_2, CO, NO, H_2O, COS, C_2H_4, H_2CO, SO_2, C_2H_5OH, C_2HF_5 and several isotopic species of C, O, N and H.
- **New Applications of Trace Gas Detection**
  - Environmental Monitoring (urban quality - H_2CO and, isotopic ratio measurements of CO_2 and CH_4, fire detection and quantification of engine exhausts)
  - Industrial process control and chemical analysis (NO, NH_3, H_2O, and H_2S)
  - Medical & biomedical diagnostics (NO, NH_3, N_2O, H_2CO and CH_3COCH_3)
  - Hand-held sensors and sensor network technologies (CO_2, NH_3, CO)
- **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 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

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