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Recent Advances of Semiconductor Laser based Infrared Spectroscopic Techniques

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

OUTLINE

- 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 (NH₃, Freon 125, acetone & TATP)
 - Nitric Oxide Detection (Faraday Rotation Spectroscopy, Remote Sensing and Cavity Enhanced Spectroscopy)
- Future Directions and Conclusions

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

UT Austin, TX October 17, 2008

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**

Needs and Methods in IR Laser Monitoring

Requirements: Sensitivity, specificity, multi-gas species, rapid data acquisition, cost, portability, low electrical power consumption

Optimum Molecular Absorbing Transition

- Overtone or Combination Bands (NIR)
- Fundamental Absorption Bands (MID-IR)

Long Optical Pathlengths

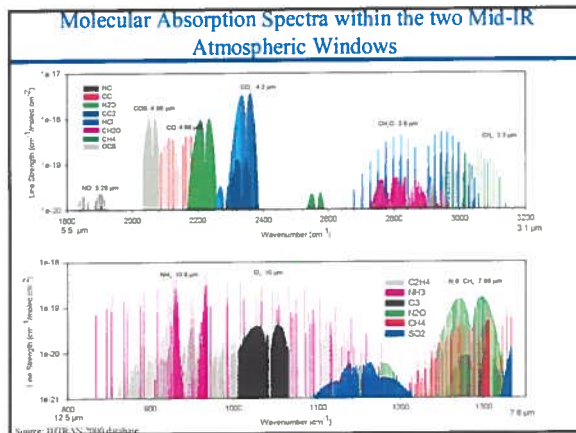
- Multipass Absorption Cell
- Cavity Enhanced, Cavity Ringdown & Intracavity Spectroscopy
- Open Path Monitoring (with and without retro-reflector)
- Evanescence Field Monitoring (fibers & waveguides)

Photoacoustic Spectroscopy

Spectroscopic Detection Schemes

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

IR Laser Sources and Wavelength Coverage



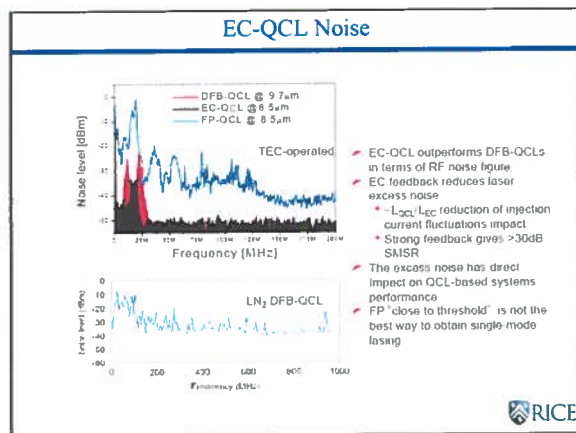
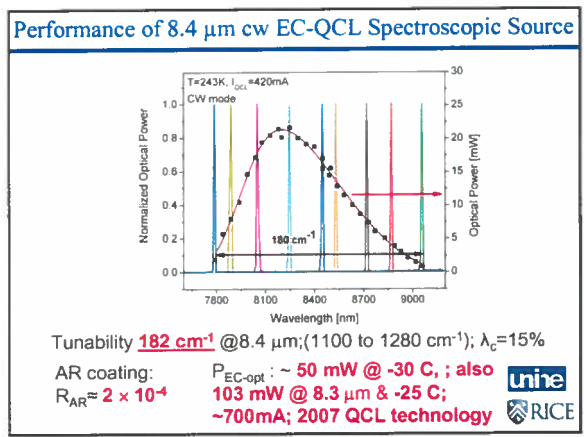
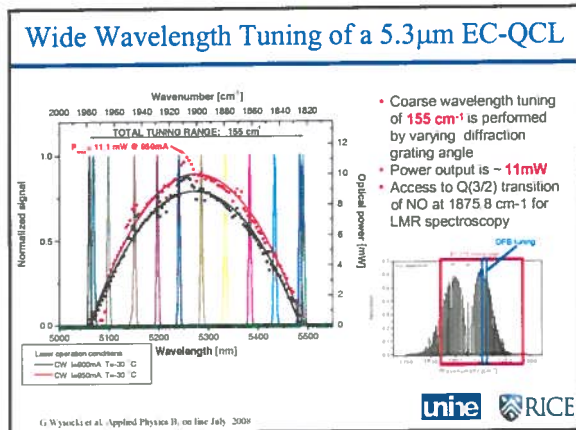
Key Characteristics of mid-IR QCLs and ICL Sources-2008

- Band – structure engineered devices** (emission wavelength is determined by layer thickness - MBE or MOCVD); mid-infrared QCLs operate from 2 to 24 µm
- Compact, reliable, stable, long lifetime, and commercial availability
- Fabry-Perot (FP), single mode (DFB) and multi-wavelength
- Spectral tuning range in the mid-IR** (4-24 µm for QCLs and 3-5 µm for ICLs)
 - 1.5 cm⁻¹ using injection current control
 - 10-20 cm⁻¹ using temperature control
 - ~300 cm⁻¹ using an external grating element and heterogeneous cascade active region design; also QC laser array (Harvard)
- Narrow spectral linewidth**
 - CW: 0.1 - 3 MHz & ~10KHz with frequency stabilization (0.0004 cm⁻¹)
 - Pulsed: ~300 MHz (chirp from heating)
- High pulsed and cw powers of QCLs at TEC/RT temperatures**
 - Pulsed and CW powers of ~1.5 W, high temperature operation ~3001
 - >50 mW, TEC CW DFB at 5 and 10 µm (EILS, Alpes)
 - >600 mW (CW FP) at RT & wall plug efficiency of ~12% at 4.6 to 45 µm; Princeton, Adtech, Opics, Harvard, Pranalytica, Northwestern Hamamatsu

**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)



Commercial widely tunable CW EC-QCL

Mid-IR Lasers From Daylight Solutions

- CW wavelength 8-10 μm
- Output power 100-200 mW
- Broad tuning range 10-15% (no spectroscopy)
- Average beam spot 15 mm
- Long-term stability > 1000 hours
- Output wavelength accuracy < 0.1 nm (100000 ppm)

CW Power vs Wavelength

Bit current vs Wavelength

Quartz Enhanced Photoacoustic Spectroscopy

From conventional PAS to QEPAS

Laser beam, power P

Modulated (P or λ) at f or $f/2$

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

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

$Q \gg 1000$

Cell is OPTIONAL!

Effective volume

SWAP RESONATING ELEMENT!!!

Piezoelectric crystal

Resonant at f quality factor Q

Broadband microphone

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Quartz tuning fork as a resonant microphone

1.5 mm

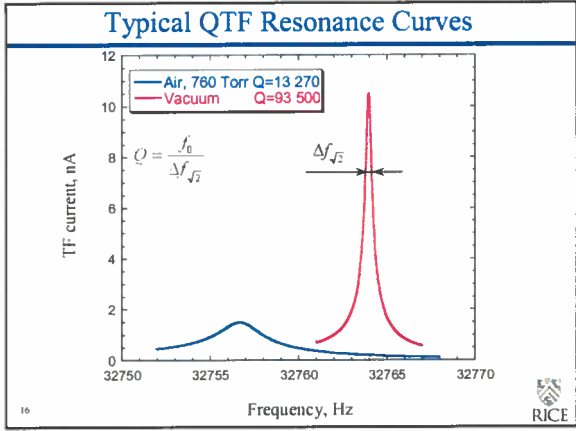
Unique properties

- 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 – linear from thermal noise to breakdown deformation
- Wide temperature range: from 1.56K (superfluid helium) to $\sim 700\text{K}$
- Temperature, pressure & humidity insensitive
- Compact, small sample volume: $< 1\text{mm}^3$
- Low cost

Other parameters

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

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QEPAS SNR Enhancement of Acoustic Microresonator

Junction

Microresonator tubes
Must be close to QTF but not touching ($\approx 30\text{-}50\mu\text{m}$ gaps).
Each tube is $\sim 5\text{mm}$ long ($\sim 1/2$ for sound at 32.8 kHz)

QEPAS Signal Gain: $\times 10$ to $\times 20$

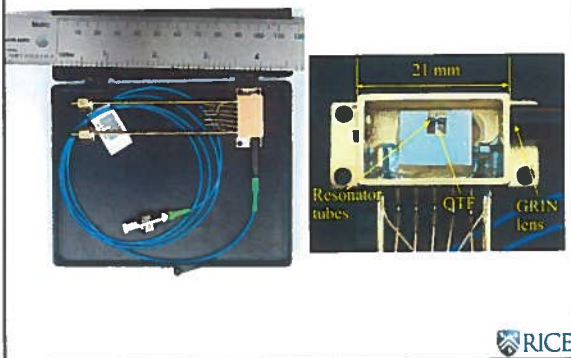
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Merits of QEPAS based Trace Gas Detection

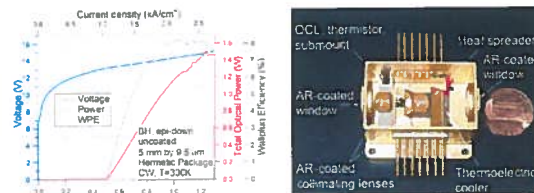
- Ultra-compact, small sample volume $< 1\text{mm}^3$
- Rugged and low cost transducer – quartz monocrystal
- High immunity to environmental acoustic noise
- Sensitivity is limited by the fundamental thermal TF noise – $k_B T$ energy in the TF symmetric mode, directly observed
- White noise spectrum – SNR scaling as \sqrt{t} up to $t=3$ hours was observed
- High Sensitivity (ppm to sub ppb) and excellent dynamic range
- Applicable over a wide range of pressures
- Temperature, pressure and humidity insensitive

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Alignment-free QEPAS Absorption Detection Module



High Performance 4.6 μm CW, RT QC Laser - 2008



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

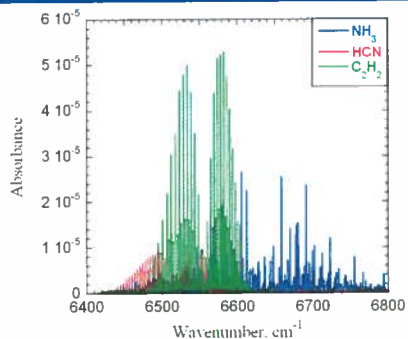
Trace Gas Sensors Areas Explored at Rice

- Methods employed
 - Extended pathlengths (Multipass Gas Cells & Retroreflector)
 - Cavity Ringdown
 - 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 , $\text{C}_2\text{H}_5\text{OH}$, C_2HF_3 , 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



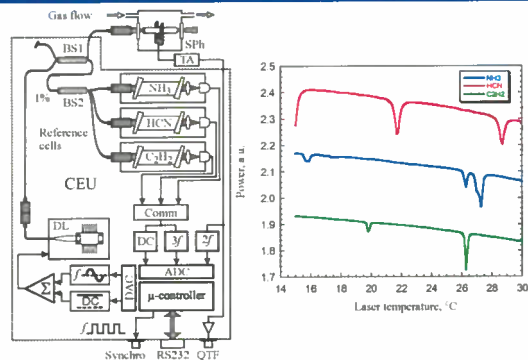
Examples of QEPAS and TDLAS Spectroscopic Techniques

Overlapping NIR absorption bands



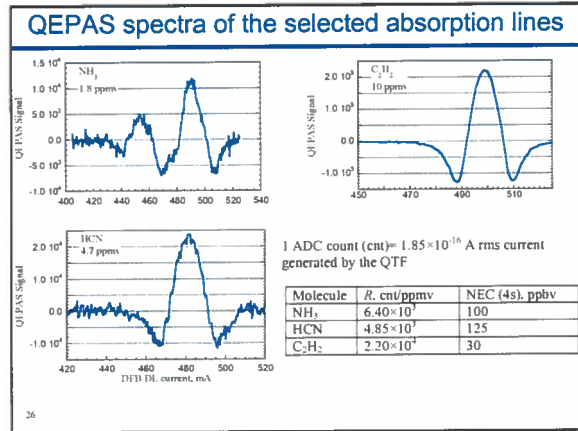
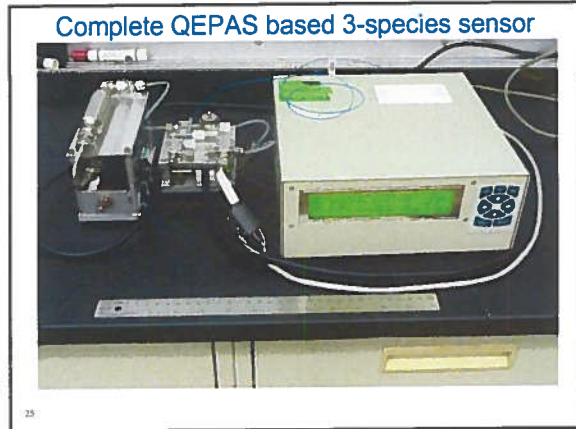
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The multispecies QEPAS trace gas sensor



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A. Kosterov et al., SAE Proc of 2008 ICES, San Francisco, CA



Future developments: multilaser chips

Data Sheet
FRL137CW-086-11111 Full Band Tunable DFB Laser Module
Date January 17, 2008 ODC-7AH001B

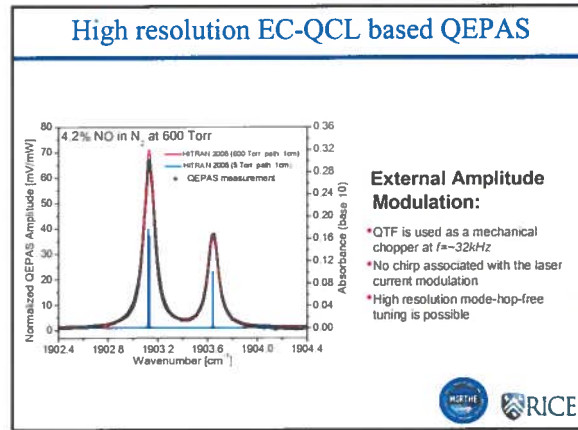
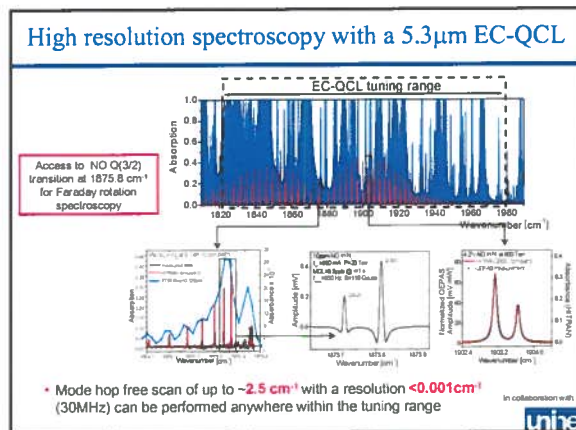
Full Band Tunable DFB Laser Module

Applications

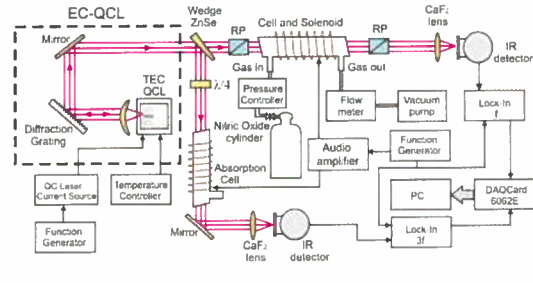
- Long Haul or Metropolitan DWDM Transmission Systems
- Dynamic Wavelength Provisioning and Add/Drop Multiplexer

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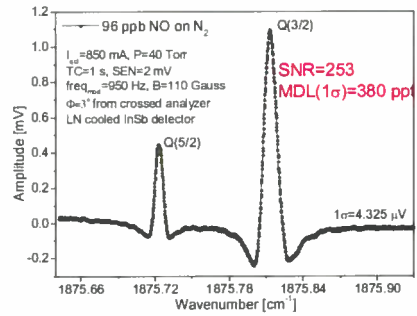
- ### Motivation for Nitric Oxide Detection
- Atmospheric Chemistry
 - Environmental pollutant gas monitoring
 - NO_x monitoring from automobile exhaust and power plant emissions
 - Precursor of smog and acid rain
 - Industrial process control
 - Formation of oxynitride gases in CMOS Devices
 - NO in 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)



EC-QCL based Magnetic Rotation Spectroscopy



Magnetic Rotation Spectroscopy of Nitric Oxide



National Stadium, Beijing, July-Sept. 2008

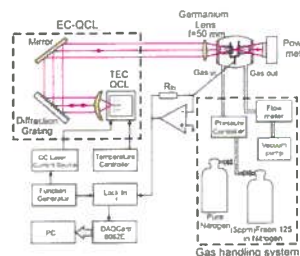


Monitoring of broadband absorbers

- 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



8.4 μm RT CW EC-QCL based QEPAS trace gas sensor



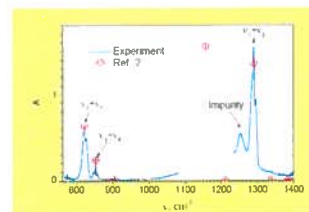
QEPAS Characteristics:

- High sensitivity (ppm to ppb)
- Excellent dynamic range
- Immune to environmental noise
- Ultra-small sample volume (< 1 mm³)
- Sensitivity is limited by the fundamental thermal TP noise
- Compact, rugged and low cost
- Potential for trace gas sensor networks

R. Lewicki, G. Wysocki, A.A. Kosters, F.K. Tittel "QEPAS based detection of broadband absorbing molecules using a widely tunable, cw quantum cascade laser at 8.5 μm ". *Optics Express*, 17(5): 7266 (2007).



UF₆ Mid-Infrared Absorption Bands



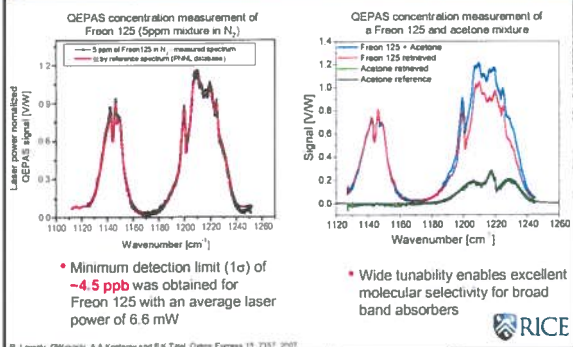
Assignment	ν , cm ⁻¹	ν , cm ⁻¹ (lit)
$\nu_1(\nu_2)$	1386(12)	0.0018
$\nu_1(\nu_2)$	1311	0.0088
$\nu_1(\nu_2)$	1290 (10.5)	0.12
$\nu_1(\nu_2)$	1211(2)	0.0047
$\nu_1(\nu_2)$	1156 (10.5)	0.82
$\nu_1(\nu_2)$	805(2)	0.0035
$\nu_1(\nu_2)$	852 (10.5)	0.12
$\nu_1(\nu_2)$	821	0.33
ν_1	425	150

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.

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

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



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

Molecule (Host)	Frequency, cm ⁻¹	Pressure, Torr	N.E.A., cm ² W/Hz ²	Power, mW	NEC (ppb), ppm
H ₂ O (N ₂) ^{***}	7308.75	60	1.3 × 10 ⁴	9.3	0.09
HCN (air; 50% RH) ^{**}	6339.11	60	4.3 × 10 ³	50	0.16
C ₂ H ₆ (N ₂) [*]	6523.88	730	4.1 × 10 ³	57	0.03
NH ₃ (N ₂) [*]	6528.36	575	3.1 × 10 ³	60	0.05
C ₂ H ₄ (N ₂) [*]	6177.07	715	5.4 × 10 ³	15	1.7
CH ₄ (N ₂) [*]	6057.09	950	2.9 × 10 ³	13.7	2.1
CO ₂ (breath ~100% RH)	6361.23	150	8.2 × 10 ³	45	40
H ₂ S (N ₂) [*]	6357.63	780	3.6 × 10 ³	45	5
CO ₂ (N ₂ ; 1.5% RH) [*]	4991.36	50	1.4 × 10 ⁴	4.4	18
CH ₃ (N ₂ ; 75% RH) ^{**}	2804.90	75	8.7 × 10 ³	7.2	0.12
CO (N ₂)	2196.66	50	5.3 × 10 ³	13	0.5
CO (propylene)	2196.66	50	7.4 × 10 ³	6.5	0.14
N ₂ O (air; 5% SF ₆)	2193.63	50	1.9 × 10 ⁴	19	0.007
C ₂ H ₂ OH (N ₂) ^{***}	1914.2	770	2.2 × 10 ³	10	90
C ₂ H ₂ (N ₂) ^{***}	1208.82	770	7.8 × 10 ³	6.6	0.059
NH ₄ (N ₂) [*]	1046.79	110	1.6 × 10 ⁴	20	0.006

For comparison: conventional PAS 2.2 (2.6 × 10⁴ cm²W/Hz) @ 1,000; 10,000 Hz for NH₃^{*,***}

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Future of Chemical Trace Gas Sensing

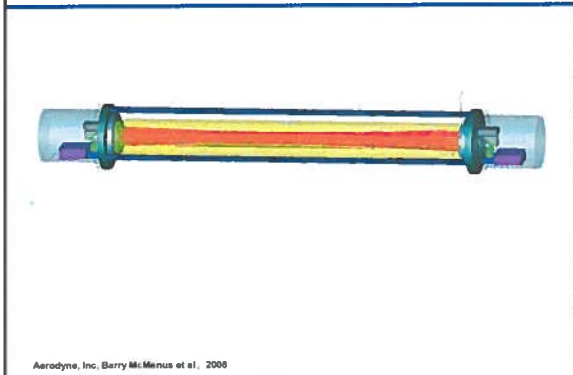
New design of fast broadly tunable EC-QCLs (2008)

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

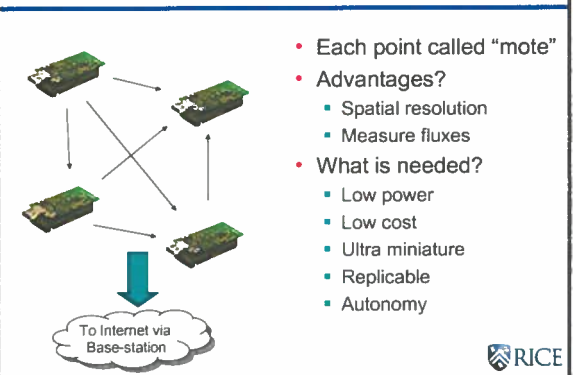
Patent pending, G. Wysocki, F. K. Tittel, 2007

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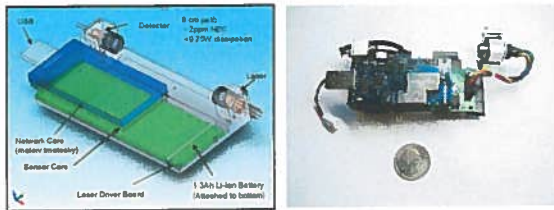
Conceptual Design of Ultra-compact QCL Trace Gas Sensor



Wireless Sensor Networks for Trace Gas Sensing



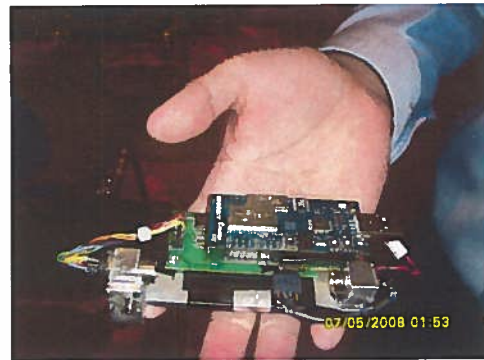
PHOTONS v4.0 - 2.7 μ m CO₂ Direct Absorption Based Sensor



- Small size
- Relatively low cost
- High efficiency switching power supplies
- PWM Peltier cooler driver
- 0.2W control system power consumption
- Detection sensitivity of CO₂ 1 ppm with 1 sec. lock-in time constant
- Over 100x improvement in sensitivity is possible @ 4.2 μ m



Ultra-compact Diode Laser based Trace Gas Sensor



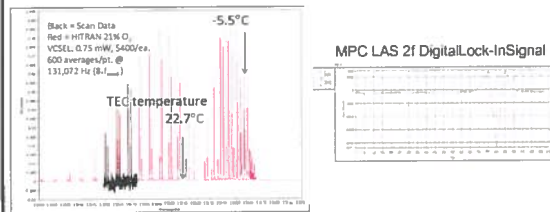
Rapid Prototyped Multipass Cell based TDLAS Platform

- Designed for T05 Packaged CW Lasers with Integrated TEC (VCSELS, Sb, QCLs)
- Wavelength modulation capability (scan. 1 f. or 2f)
- Quadrature digital lock-in amplifier
- Low noise current driver
- TEC driver. 0.001 °C stability
- Battery Powered
- Cost: ~ \$1,000

Wireless Networking Module



763 nm VCSEL based Oxygen TDLAS sensor



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: NH₃, CH₄, N₂O, CO₂, CO, NO, H₂O, COS, C₂H₂, H₂CO, SO₂, C₂H₅OH, C₂HF₃ and several isotopic species of C, O, N and H.
- **New Applications of Trace Gas Detection**
 - Environmental Monitoring (urban quality - H₂CO and isotopic ratio measurements of CO₂ and CH₄, fire detection and quantification of engine exhausts)
 - Industrial process control and chemical analysis (NO, NH₃, H₂O, and H₂S)
 - Medical & biomedical diagnostics (NO, NH₃, N₂O, H₂CO and CH₃COCH₃)
 - Hand-held sensors and sensor network technologies (CO₂)
- **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

