Recent Advances of Semiconductor Laser based Infrared Spectroscopic Techniques

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

OUTLINE

UT Austin, TX

October 13, 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 (NH_3, 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

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**

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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)
- Evanescent Field Monitoring (fibers & waveguides)

Photoacoustic Spectroscopy

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

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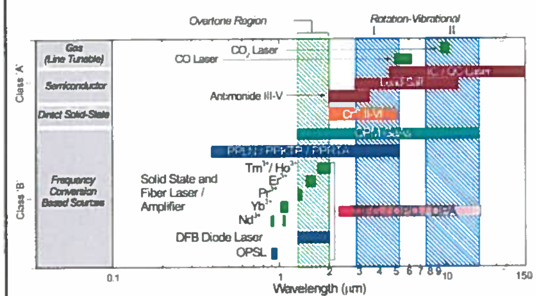
IR Laser Sources and Wavelength Coverage



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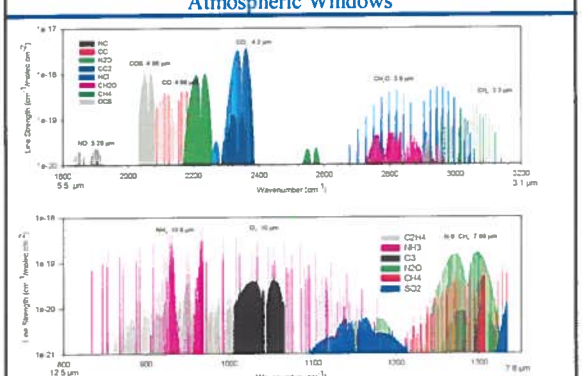
Molecular Absorption Spectra within the two Mid-IR Atmospheric Windows



Source: HITRAN 2000 database

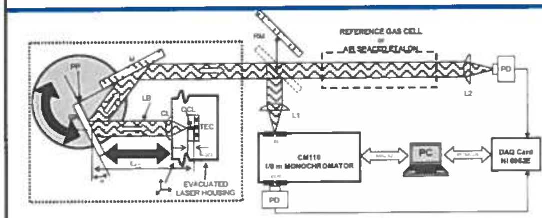
Key Characteristics of mid-IR QCLs and ICL Sources-2008

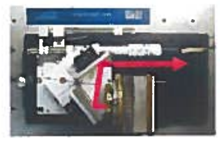
- **Band – structure engineered devices** (emission wavelength is determined by layer thickness – MBE or MOCVD); mid-infrared QCLs operate from 3 to 24 µm
- Compact, reliable, stable, long lifetime, and commercial availability
- Fabry-Perot (FP), single mode (DFB) and multi-wavelength
- **Spectral tuning 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 ~300 K
  - >50 mW, TEC CW DFB @ 5 and 10 µm (DLS, Alpes)
  - > 600 mW (CW FP) @ RT & wall plug efficiency of ~12 % at 4.6 to µm, Princeton, Adtech Optics, Harvard, Pranalytica, Northwestern Hamamatsu

4 mm

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)

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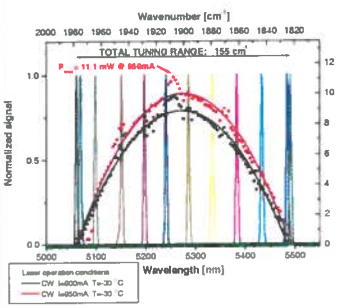
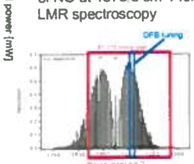
Wide Wavelength Tuning of a 5.3μm EC-QCL



- Coarse wavelength tuning of **155 cm⁻¹** is performed by varying diffraction grating angle
- Power output is ~ **11mW**
- Access to Q(3/2) transition of NO at 1875.8 cm-1 for LMR spectroscopy



G. Wysocki et al, Applied Physics B, on line July 2008

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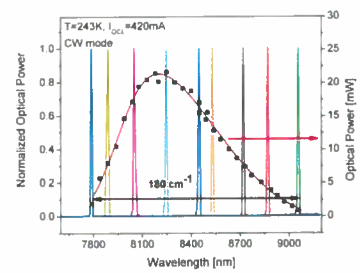
Performance of 8.4 μm cw EC-QCL Spectroscopic Source



Tunability **182 cm⁻¹** @8.4 μm;(1100 to 1280 cm⁻¹); λ_c=15%

AR coating: $R_{AR}\approx$ **2 × 10⁻⁴**

$P_{EC\text{-}opt}$: **~ 50 mW @ -30 C, ; also 103 mW @ 8.3 μm & -25 C; ~700mA; 2007 QCL technology**

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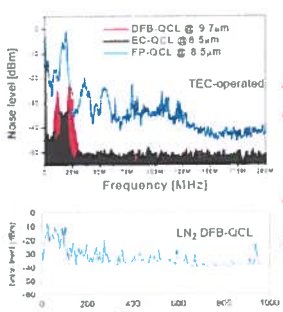
EC-QCL Noise



- EC-QCL outperforms DFB-QCLs in terms of RF noise figure
- EC feedback reduces laser excess noise
  - ~L_{QCL}/L_{EC} reduction of injection current fluctuations impact
  - Strong feedback gives >30dB SMSR
- The excess noise has direct impact on QCL-based systems performance
- FP "close to threshold" is not the best way to obtain single-mode lasing

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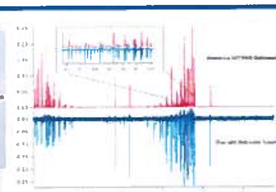
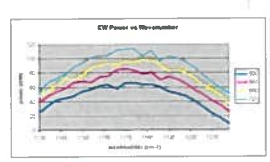
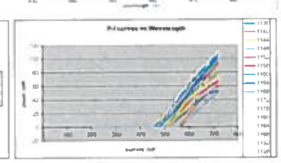
Commercial widely tunable CW EC-QCL







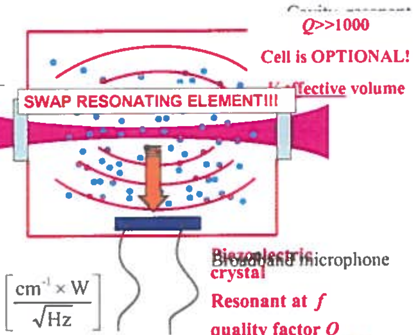
DAYLIGHT

Quartz Enhanced Photoacoustic Spectroscopy

From conventional PAS to QEPAS

Laser beam, power P

Modulated (P or λ) at f or $f/2$



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

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

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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-< 1mm³
- Low cost

Other parameters

- Resonant frequency ~32.8 kHz
- Force constant ~26800 N/m
- Electromechanical coefficient ~7×10⁻⁶ C/m

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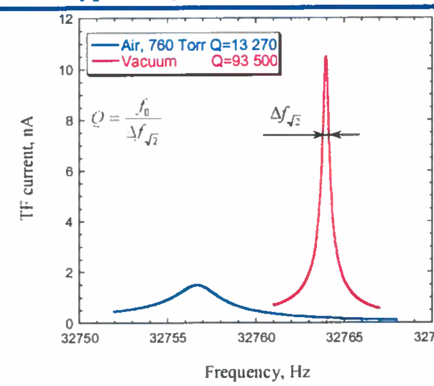
Typical QTF Resonance Curves



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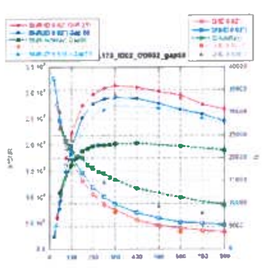
QEPAS SNR Enhancement of Acoustic Microresonator



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

QEPAS Signal Gain: ×10 to ×20

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Merits of QEPAS based Trace Gas Detection

- Ultra-compact, small sample volume - <1mm³
- 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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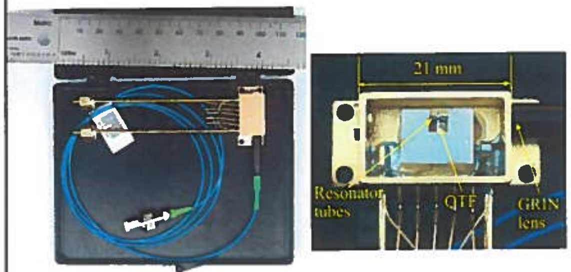
Alignment-free QEPAS Absorption Detection Module



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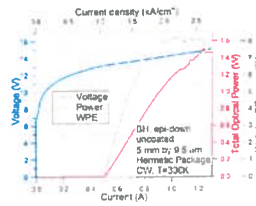
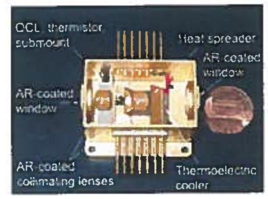
High Performance 4.6 μm CW, RT QC Laser - 2008





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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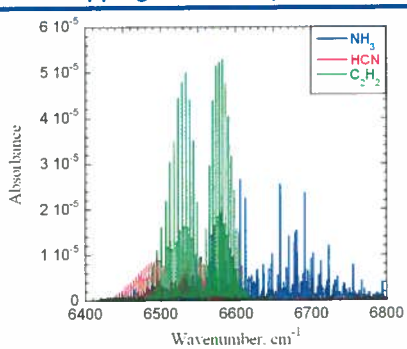
Examples of QEPAS and TDLAS Spectroscopic Techniques

Overlapping NIR absorption bands



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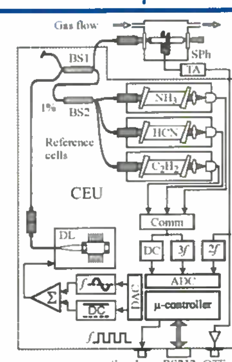
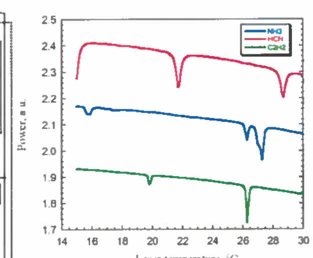
The multispecies QEPAS trace gas sensor





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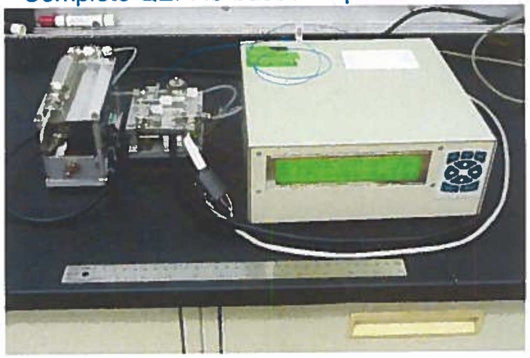
A Kosterev et al., SAE Proc of 2008 ICES, San Francisco, CA

Complete QEPAS based 3-species sensor



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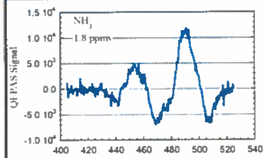
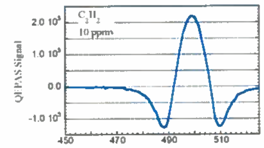
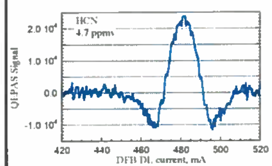
QEPAS spectra of the selected absorption lines







1 ADC count (cnt)= 1.85×10^{-16} A rms current generated by the QTF

Molecule	*R*, cnt/ppmv	NEC (4s), ppbv
NH_3	6.40×10^3	100
HCN	4.85×10^3	125
C_2H_2	2.20×10^4	30

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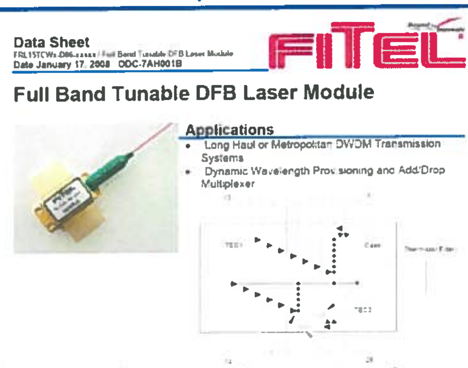
Future developments: multilaser chips



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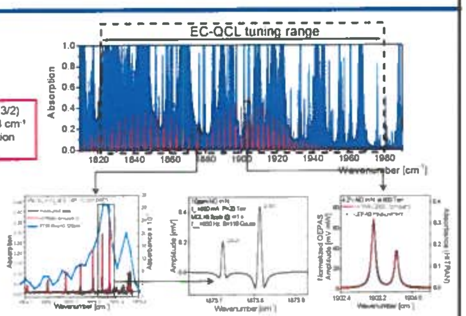
Motivation for Nitric Oxide Detection

- 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)

High resolution spectroscopy with a 5.3μm EC-QCL

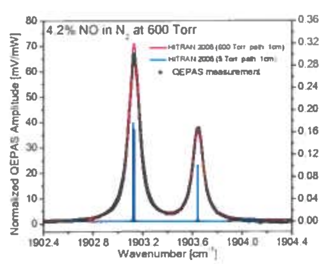
Access to NO Q(3/2) transition at 1875.8 cm^{-1} for Faraday rotation spectroscopy



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

In collaboration with unine

High resolution EC-QCL based QEPAS



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

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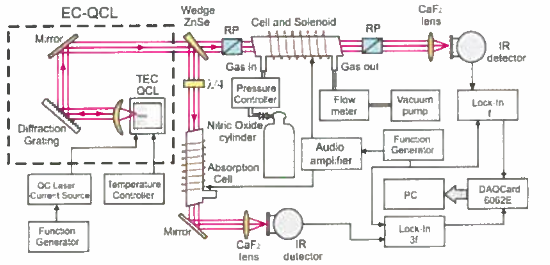
EC-QCL based Magnetic Rotation Spectroscopy



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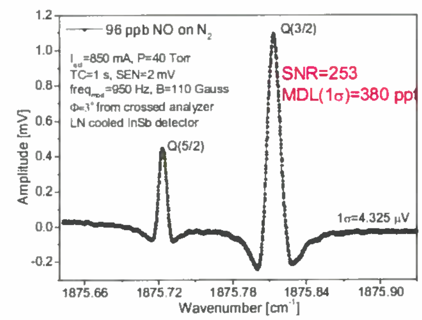
Magnetic Rotation Spectroscopy of Nitric Oxide



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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

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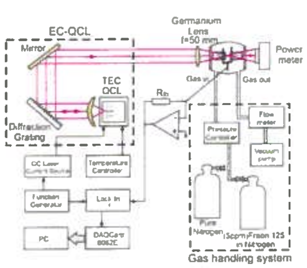
8.4 μm RT CW EC-QCL based QEPAS trace gas sensor



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 TF noise
- Compact, rugged and low cost
- Potential for trace gas sensor networks

R. Lewicki, G. Wysocki, A.A. Kosterev, F.K. Tittel "QEPAS based detection of broadband absorbing molecules using a widely tunable, cw quantum cascade laser at 8.5 μm", Optics Express, 7357-7366 (2007)

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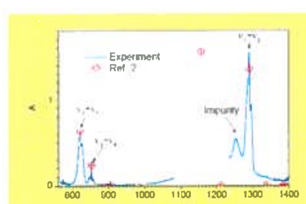
UF_6 Mid-Infrared Absorption Bands



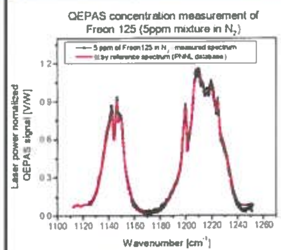
Absorption spectrum of gas mixture under investigation and observed spectral features identification.

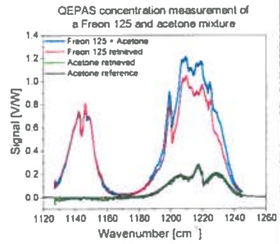
Assignment	ν, cm⁻¹	σ, cm⁻²/atm
[illegible]	1386±2	0.0018
[illegible]	1311	0.0068
$\nu_1+\nu_3$	1290.9±0.5	9.72
[illegible]	1211±2	0.0007
$\nu_2+\nu_3$	1156.9±0.5	0.82
[illegible]	905±2	0.0035
[illegible]	852.8±0.5	0.12
[illegible]	821	0.33
ν_3	626	350

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

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





- Minimum detection limit (1σ) of ~4.5 ppb was obtained for Freon 125 with an average laser power of 6.6 mW
- Wide tunability enables excellent molecular selectivity for broad band absorbers

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R. Lewicki, G. Wysocki, A.A. Kosterev and F.K. Tittel, Optics Express 15, 7357, 2007

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	1.9×10[illegible]	9.5	0.09
HCN (air: 50% RH)*	6539.11	60	< 4.3×10[illegible]	50	0.16
C_2H_2 (N_2)*	6523.88	720	4.1×10[illegible]	57	0.03
NH_3 (N_2)*	6528.76	575	3.1×10[illegible]	60	0.06
C_2H_4 (N_2)*	6177.07	715	5.4×10[illegible]	15	1.7
CH_4 (N_2)*	6057.09	950	2.9×10[illegible]	13.7	2.1
CO_2 (breath ~100% RH)	6361.25	150	8.2×10[illegible]	45	40
H_2S (N_2)*	6357.63	780	5.6×10[illegible]	45	5
CO_2 (N_2+1.5% H_2O)*	4991.26	50	1.4×10[illegible]	4.4	18
CH_2O (N_2:75% RH)*	2804.90	75	8.7×10[illegible]	7.2	0.12
CO (N_2)	2196.66	50	5.3×10[illegible]	13	0.5
CO (propylene)	2196.66	50	7.4×10[illegible]	6.5	0.14
N_2O (air+5%SF_6)	2195.63	50	1.5×10[illegible]	19	0.007
C_2H_5OH (N_2)**	1934.2	770	2.2×10[illegible]	10	90
C_2HF_5 (N_2)***	1208.62	770	7.8×10[illegible]	6.6	0.009
NH_3 (N_2)*	1046.39	110	1.6×10[illegible]	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[illegible] cm^{-1}W/√Hz (1,000; 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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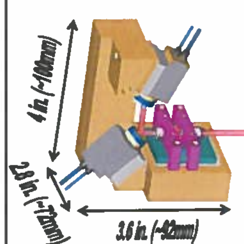
Future of Chemical Trace Gas Sensing

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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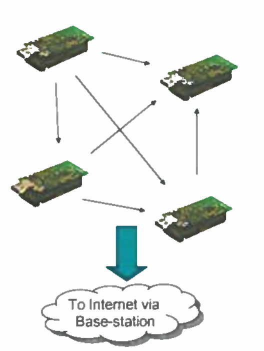
Conceptual Design of Ultra-compact QCL Trace Gas Sensor

Aerodyne, Inc, Barry McManus et al, 2008

Wireless Sensor Networks for Trace Gas Sensing



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

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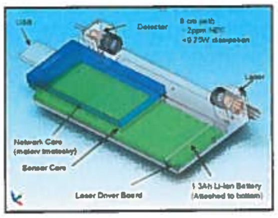
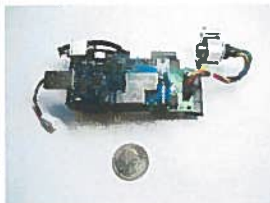
PHOTONS v4.0 - 2.7µm CO2 Direct Absorption Based Sensor





- Small size
- Relatively low cost
- High efficiency switching power supplies
- PWM Peltier cooler driver
- 0 2W control system power consumption
- Detection sensitivity of CO_2 1 ppm with 1sec. lock-in time constant
- Over 100x improvement in sensitivity is possible @ 4.2µm

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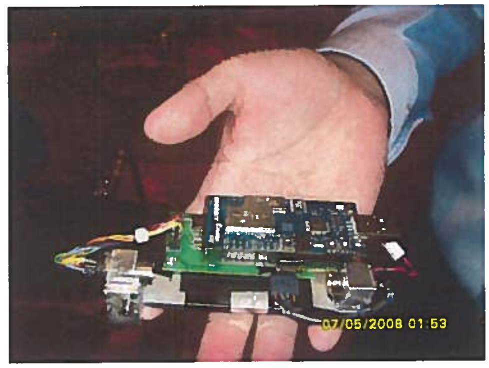
Ultra-compact Diode Laser based Trace Gas Sensor



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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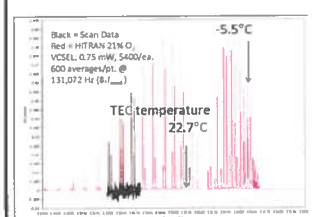
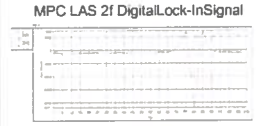
763 nm VCSEL based Oxygen TDLAS sensor



MPC LAS 2f DigitalLock-InSignal



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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: 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)
- **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

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