Infrared semiconductor laser based trace gas sensor technologies: recent advances and applications

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

Rice Quantum Institute, Rice University, Houston, TX, USA
http://ece.rice.edu/lasersci/

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OUTLINE

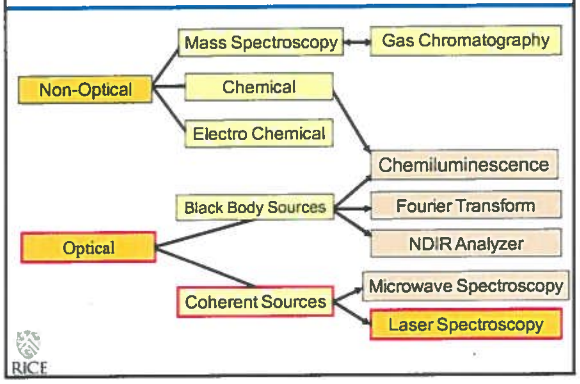
- Motivation: Chemical Sensing Applications
- Fundamentals of Laser Absorption Spectroscopy
- New Laser Sensing Technologies (QEPAS)
- Selected Applications of Trace Gas Detection
  - NH_3 Detection for Environmental Applications
  - Nitric Oxide Detection (LAS & FRS)
  - Monitoring of Broadband Absorbers
- Future Directions of Laser based Gas Sensor Technology

Work supported by NSF ERC MIRTHE, NASA-JSC, DoE STTR and the Welch Foundation

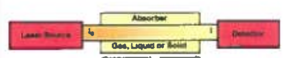
Wide Range of Trace Gas Sensing Applications

- **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**

Existing Methods for Trace Gas Detection



Basics of Optical Trace Gas Analyzers

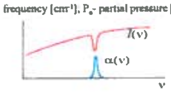


Beer-Lambert's Law of Linear Absorption

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

$\alpha(\nu)$ - 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·cm^{-3}·atm^{-1}]

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

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

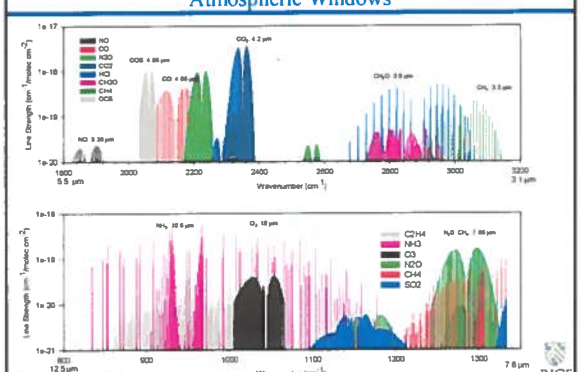
Key Requirements: Sensitivity, specificity, rapid data acquisition and multi-species detection

Optimum Molecular Absorbing Transition
- NIR Overtone or Combination Bands
- **MIR Fundamental Absorption Bands**

Long Optical Pathlengths
- 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

Spectroscopic Detection Schemes
- Wavelength or Frequency Modulation
- Balanced Detection
- Zero-air Subtraction
- Photoacoustic Spectroscopy
- Faraday Rotation Spectroscopy
- NICE-OHMS, LIBS, and LIF

Molecular Absorption Spectra within two Mid-IR Atmospheric Windows



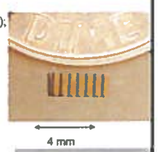
Source: HITRAN 2000 database

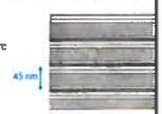
Mid-IR Source Requirements for Laser Spectroscopy

REQUIREMENTS	IR LASER SOURCE
Sensitivity (% to ppt)	Optimum Wavelength, Power
Selectivity (Spectral Resolution)	Stable Single Mode Operation and Narrow Linewidth
Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers	Mode Hop-free Wavelength Tunability
Directionality or Cavity Mode Matching	Beam Quality
Rapid Data Acquisition	Fast Time Response
Room Temperature Operation	High wall plug efficiency, no cryogenics or cooling water
Field deployable in harsh environments	Compact & Robust

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 µm (AlInAs/GaInAs)
- Compact, reliable, stable, long lifetime, and commercial availability
- Fabry-Perot (FP), single mode (DFB) and multi-wavelength devices
- **Spectral tuning range in the mid-IR**
  (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 Array
- **Narrow spectral linewidth**
  - CW: 0.1 - 3 MHz & <10KHz with frequency stabilization (0.0004 cm^{-1})
  - Pulsed: ~ 300 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 ~300K
  - >280 mW, TEC CW DFB @ 5 µm
  - > 600 mW (CW FP) @ RT, wall plug efficiency of ~17 % at 4.6µm,





Quantum Cascade, Interband Cascade 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, Siemens, Goeteborg, Sweden , and INP, Greifswald, Germany
  - Pranalytica, CA
- **Research Groups**
  - Harvard University
  - Fraunhofer-IAF & IPM, Freiburg, and Humboldt University, Berlin, 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; QinetiQ, Malvern and Lancaster, University, UK
  - State University of New York
  - Technical University, Zuerich, Switzerland
  - University of Montpelier, France
  - Technical University, Vienna, Austria and NRC, Ottawa, Canada

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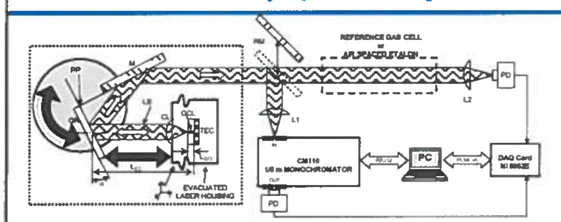
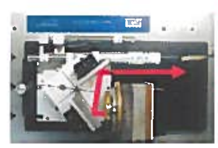
Widely Tunable, CW, TEC Quantum Cascade Lasers

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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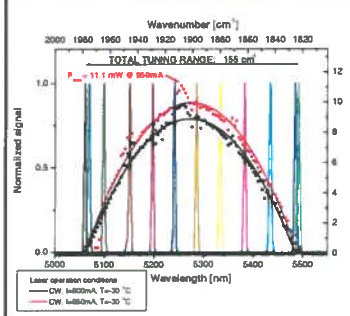
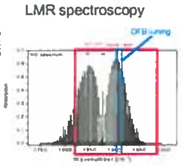
Wide Wavelength Tuning of a 5.3µm EC-QCL





- 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

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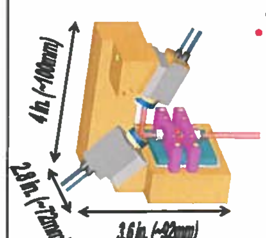
New design of fast broadly tunable EC-QCLs



- New optical configuration
  Folded cavity
- 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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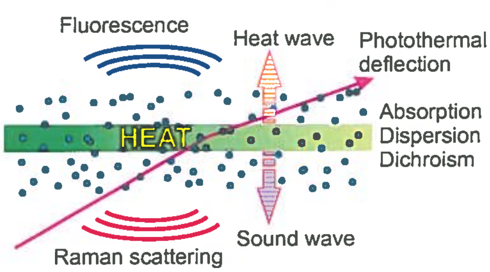
Daylight ???

Quartz Enhanced Photoacoustic Spectroscopy

Radiation-matter interaction



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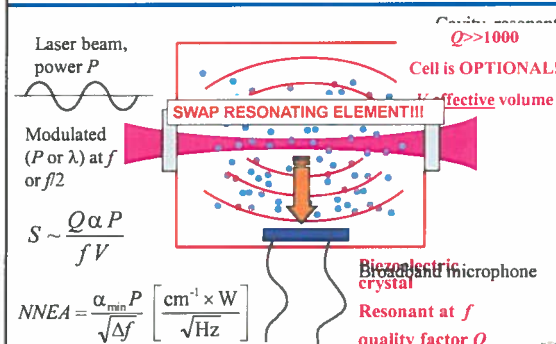
From conventional PAS to QEPAS



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

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

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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 (~10^6) – linear from thermal noise to breakdown deformation
  - 300K noise: x~10^{-11} cm
  - Breakdown: x~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 ~7×10^{-6} C/m

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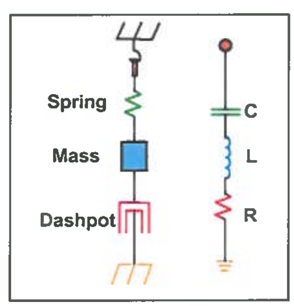
Equivalent electrical circuit of a quartz tuning fork (QTF)



$$q = \alpha x$$

$$L = \frac{m}{2\alpha^2} \quad C = \frac{2\alpha^2}{k} \quad R = \frac{m\gamma}{2\alpha^2}$$

$$U = \frac{F}{2\alpha}$$

$$\omega_0 = \sqrt{\frac{1}{LC}} \qquad Q = \frac{1}{R}\sqrt{\frac{L}{C}}$$

$$\sqrt{\langle I_N^2 \rangle} = \sqrt{\frac{4k_B T}{R}}$$

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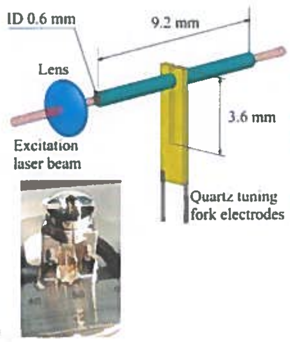
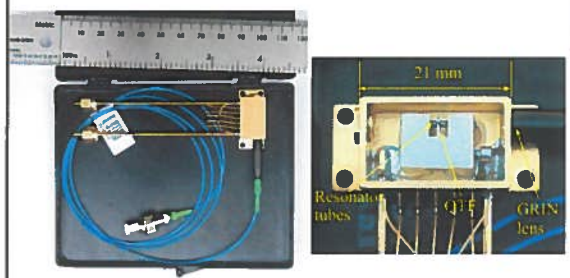
QEPAS spectrophone



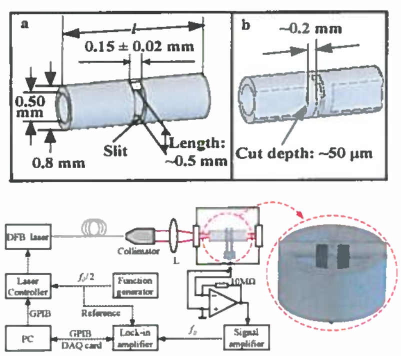
Micro-resonator (mR) tubes

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

Alignment-free QEPAS Absorption Detection Module

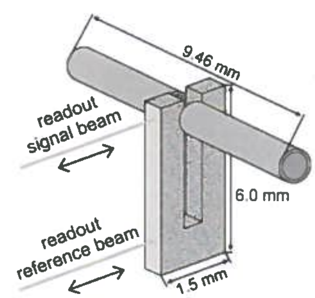


Off-beam QEPAS based Gas Sensor



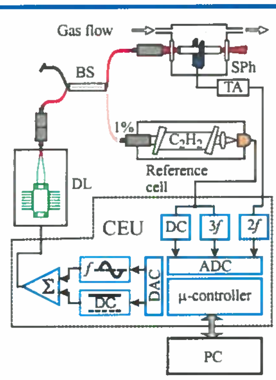
Source: K. Liu, X. Gao (AIOFM), W. Chen (ULCO), A. Kosterev et al. (Rice)

Tuning fork enhanced interferometric photoacoustic spectroscopy (TIPAS) based sensor

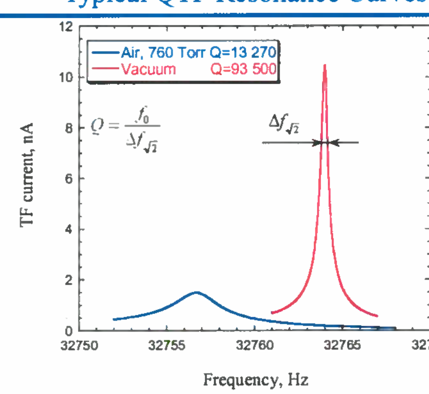


M. Koehring et al. Clausthal University of Technology 2010

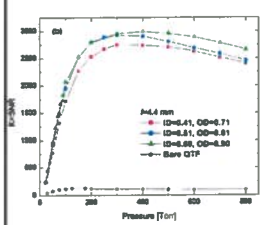
Principal Architecture of a QEPAS Gas Sensor



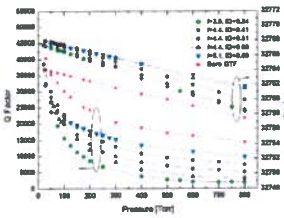
Typical QTF Resonance Curves



Signal-to-noise ratio as a function of pressures

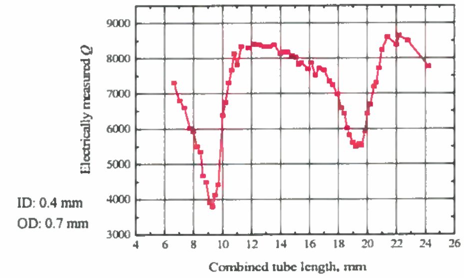


Signal-to-noise ratio as a function of pressures for different tube sizes and bare QTF



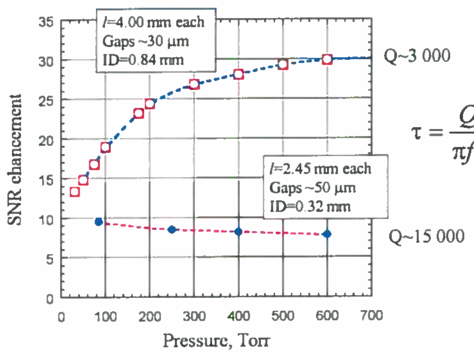
Q factor and frequency of the QTF as a function of pressure for different tube lengths and diameters

Acoustic and quartz resonators - interaction



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

Non-resonant and resonant tubes



$$\tau = \frac{Q}{\pi f_0}$$

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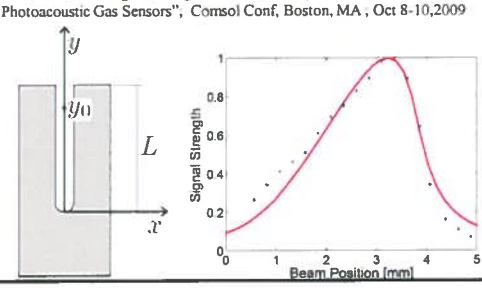
What about QEPAS Modeling ?

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



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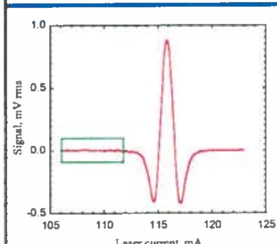
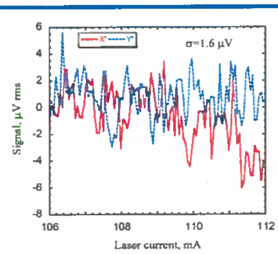
WM QEPAS signal for H_2O line @ 7306.75 cm^{-1}, 48 ppmv





Laser power in cell: 9.5 mW; Time constant: 1s; SNR=550

Peak absorbance: 4.8×10^{-5} cm^{-1} (HITRAN); RHS: thermal background

⇒ NNEA=1.9×10^{-9} $cm^{-1}W/(Hz)^{1/2}$; NEC=90 ppbv

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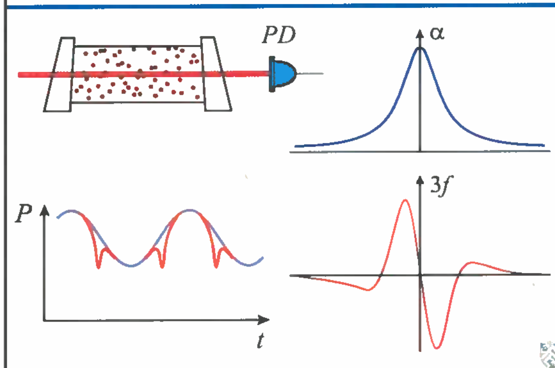
Line locking based on 3f detection



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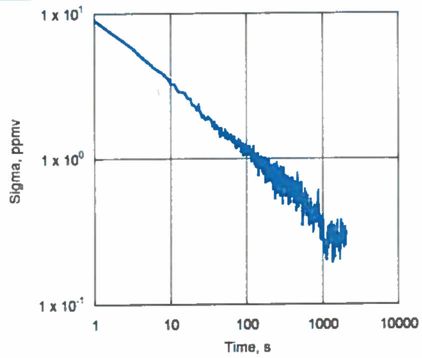
Long-term Averaging: H_2S, Allan Variance Analysis



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Merits of QEPAS based Trace Gas Detection

- Very small sensing module and sample volume (a few mm^3)
- 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_BT 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_2O
- Cross sensitivity issues

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

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[illegible]	9.5	0.09
HCN (air: 50% RH)*	6539.11	60	4.6×10[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+1.2% H_2O)*	6057.09	760	3.7×10[illegible]	16	0.24
CO_2 (breath ~50% RH)	6361.25	150	8.2×10[illegible]	45	40
H_2S (N_2)*	6357.63	780	5.6×10[illegible]	45	5
HCl (N_2 dry)	5739.26	760	5.2×10[illegible]	15	0.7
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
NO (N_2+H_2O)	1900.07	250	7.5×10[illegible]	100	0.003
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^{-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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Recent Applications of mid-infrared Laser 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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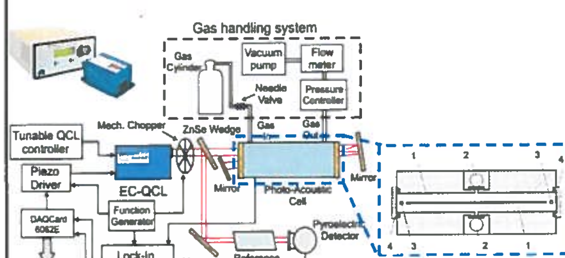
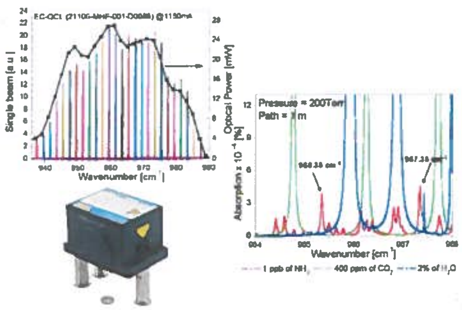
Mid-IR EC-QCL based AM-PAS Sensor for atmospheric NH_3 Detection



A ring differential resonance Photo-Acoustic Cell:
1. acoustic resonator,
2. microphone,
3. gas input and output,
4. window

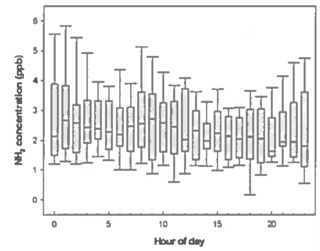
Tuning range of a Daylight Solutions CW TEC 10.34 μm EC-QCL and HITRAN simulated spectra at 200Torr



Preliminary 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 NH_3 concentration by using acquired data for a period of 16 days (Feb. 12th – Mar. ...)

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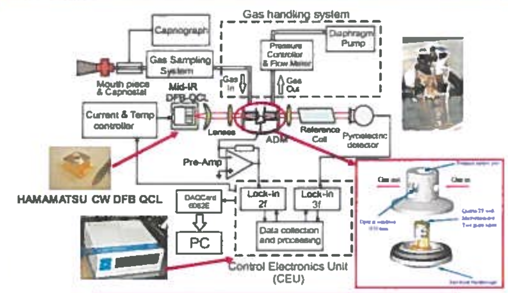
Important Biomedical Species

Molecule	Formula	Biological/Pathology Indication	Center wavelength [μm]
Pentane	C_5H_{12}	Inflammatory diseases, transplant rejection	6.8
Ethane	C_2H_6	Lipid peroxidation and oxidation stress, lung cancer (low ppbv range)	6.8
Carbon Dioxide isotope ratio	$^{13}CO_2/^{12}CO_2$	Helicobacter pylori infection (peptic ulcers, gastric cancer)	4.4
Carbonyl Sulfide	COS	Liver disease, acute rejection in lung transplant recipients (10-600 ppbv)	4.9
Carbon Disulfide	CS_2	Disulfiram treatment for alcoholism	6.5
Ammonia	NH_3	Liver and renal diseases, exercise physiology	10.3
Formaldehyde	CH_2O	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_2O_2	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_2H_4	Oxidative stress, cancer	10.6
Acetone	C_3H_6O	Ketosis, diabetes mellitus	7.3

QEPAS based NH_3 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.

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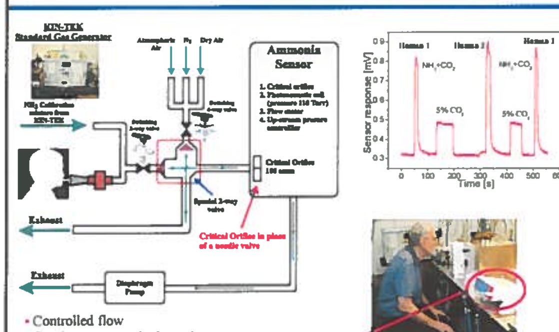
Real-time Breath Monitor Interface



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

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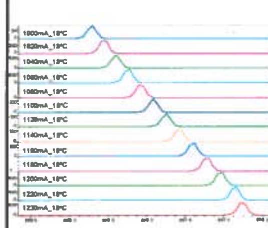
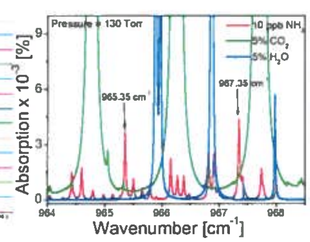
Line selection for HAMAMATSU CW DFB QCL

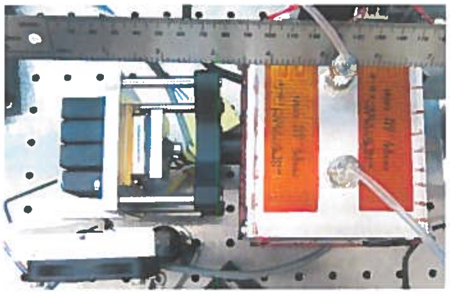


Single mode QCL radiation recorded with FTIR for different laser current values at laser temperature of 18°C.



HITRAN simulated spectra @ 130 Torr indicating two NH_3 absorption lines of interest

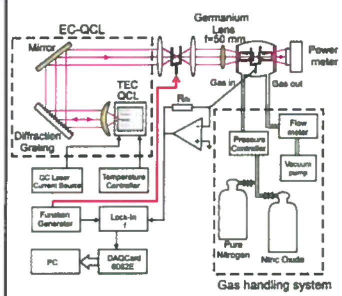
QEPAS based breath analyzer using a 10.4 μm DFB-QCL



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)

5.3 μm 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

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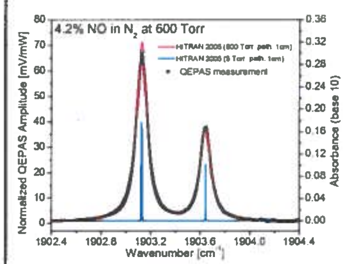
High resolution EC-QCL based NO Spectrum



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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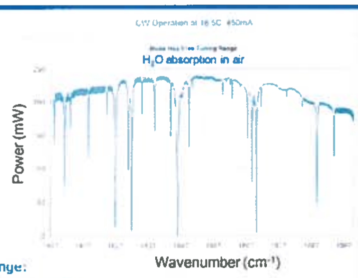
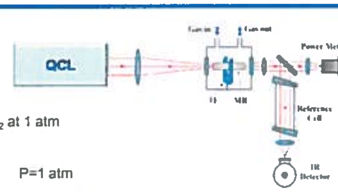
High power fiber-coupled QCL for NO detection



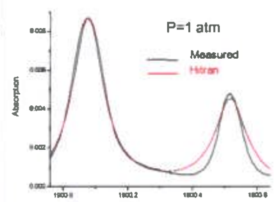
- **Mid-IR EC-QCL (DLS)**
  - Wavelength tuning range: 5.26-5.53 μm (1807-1900 cm^{-1})
  - MHF spectral range 5% of center wavelength: 5.4 μm; (1846cm^{-1})
  - Maximum tuning Rate 38 nm/sec
  - Highest optical power: ~250 mW
  - TE cooling, RT operation

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

NO absorption line selection



0.05% NO in N_2 at 1 atm



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

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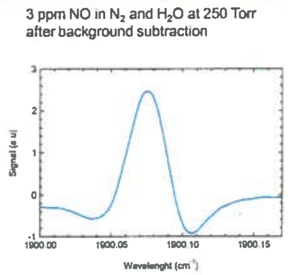
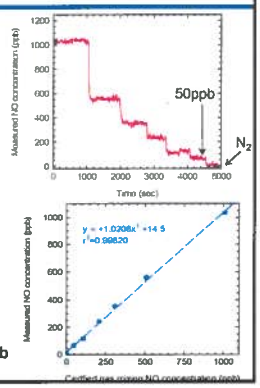
CW MHF QCL based QEPAS NO sensor

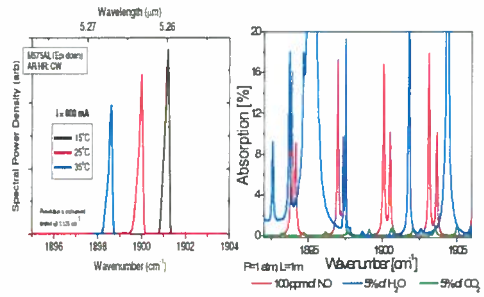




Signal to noise >200

- **Lowest detectable concentration < 15ppb**

Emission spectra of a 1900cm^{-1} TEC CW DFB QCL and HITRAN simulated spectra



Output power: 117 mW @ 25 C

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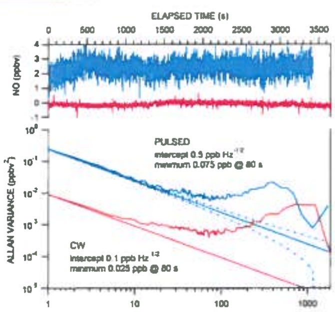
CW vs. Pulsed: Allan Variance for Measured NO

- 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 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

Motivation for Nitric Oxide Detection in Beijing 2008

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

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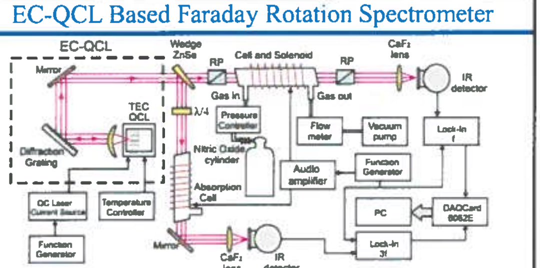
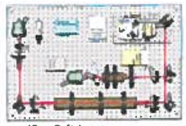
EC-QCL Based Faraday Rotation Spectrometer



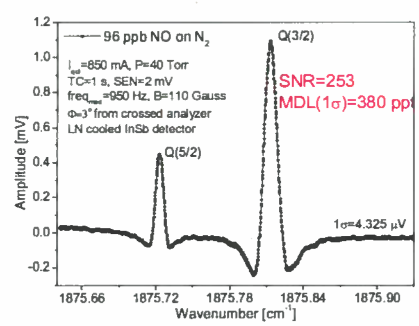
- EC-QCL Operating at 5.3μm – NO Fundamental Band
- 44cm effective optical pathlength
- Rochon Polarizer Extinction Ratio <10^{-6}
- Not sensitive to water interference
- Sensitivity Not Limited by Interference Fringes
- Gas Cell Volume (~ 250ml)
- Easy and Robust Optical Alignment
- Continuous NO Monitoring (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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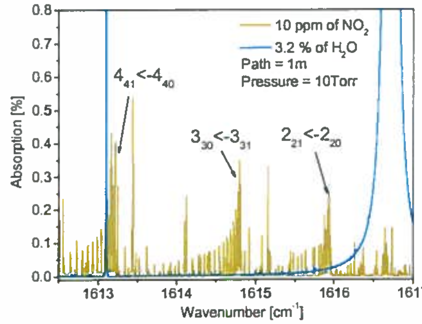
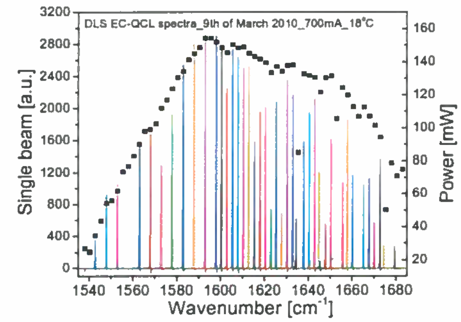
Optimum NO_2 transition for FRS experiment



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

Tuning range of a Daylight Solutions CW 6.19 μm NO_2 EC-QCL (21062-MHF-012)



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Future Directions and Outlook of Chemical Trace Gas Sensing Technology

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)
- Hydrazine

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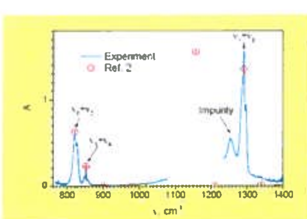
UF_6 Mid-Infrared Absorption Bands



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

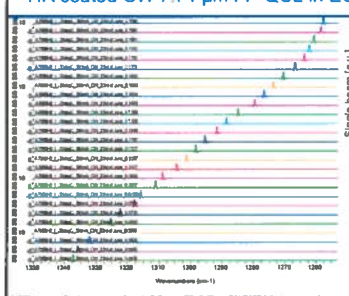
Assignment	ν, cm^{-1}	σ, cm^{-1}atm^{-1}
$2\nu_3+\nu_6$	1380±2	0.0018
$\nu_1+\nu_2+\nu_6$	1341	0.0088
$\nu_1+\nu_3$	1290.9±0.5	0.72
$2\nu_2+\nu_6$	1211±2	0.0007
$\nu_2+\nu_3$	1156.9±0.5	0.82
$\nu_3+2\nu_6$	905±2	0.0035
$\nu_1+\nu_4$	852.8±0.5	0.12
$\nu_3+\nu_4$	821	0.33
ν_3	625	350

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

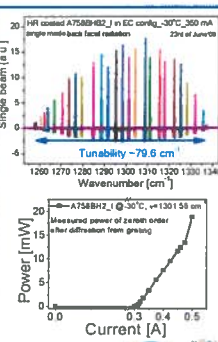
A. Nadezhdinskii et al, GPI, Moscow, March 2008

Also: G. Baldacci et al., Nuovo Cimento B, 203, 1986

HR coated CW 7.74 μm FP-QCL in EC-configuration @ -30ºC



FTIR spectra for 2mm cavity length 7.74 μm FP-QCL (A758BHB2 I) in external cavity



Resistance @ RT is R= 650Ω

Threshold with grating I_{th}= 301.5mA

Threshold without grating I_{th}= 350mA

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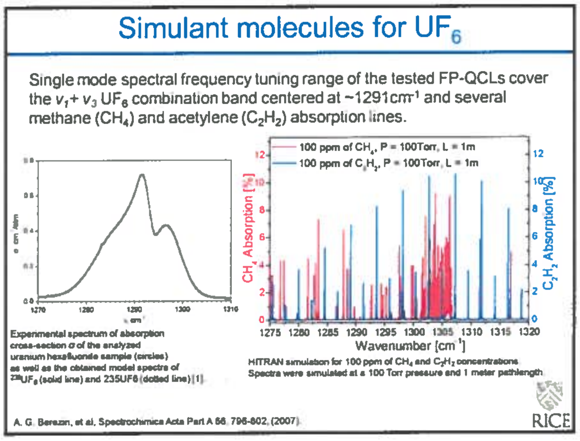
Simulant molecules for UF6
Single mode spectral frequency tuning range of the tested FP-QCLs cover the ν1+ ν3 UF6 combination band centered at ~1291cm-1 and several methane (CH4) and acetylene (C2H2) absorption lines.
100 ppm of CH4, P = 100Torr, L = 1m
100 ppm of C2H2, P = 100Torr, L = 1m
CH4 Absorption [%]
C2H2 Absorption [%]
1275 1280 1285 1290 1295 1300 1305 1310 1315 1320
Wavenumber [cm-1]
HITRAN simulation for 100 ppm of CH4 and C2H2 concentrations
Spectra were simulated at a 100 Torr pressure and 1 meter pathlength
Experimental spectrum of absorption cross-section σ of the analyzed uranium hexafluoride sample (circles) as well as the obtained model spectra of 238UF6 (solid line) and 235UF6 (dotted line) [1]
A. G. Berezin, et al, Spectrochimica Acta Part A 66, 796-802, (2007)
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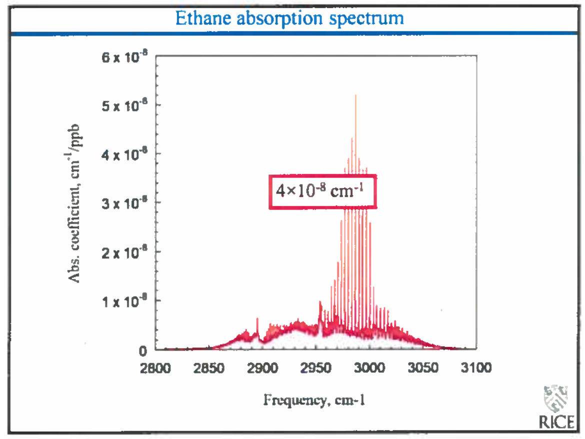
Ethane absorption spectrum
Abs. coefficient, cm-1/ppb
6 x 10-8
5 x 10-8
4 x 10-8
3 x 10-8
2 x 10-8
1 x 10-8
0
4×10-8 cm-1
2800 2850 2900 2950 3000 3050 3100
Frequency, cm-1
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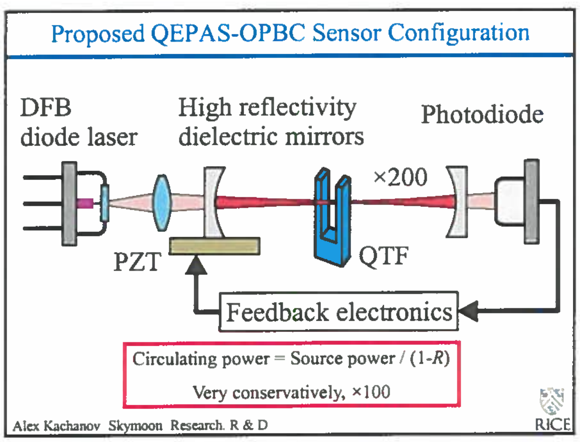
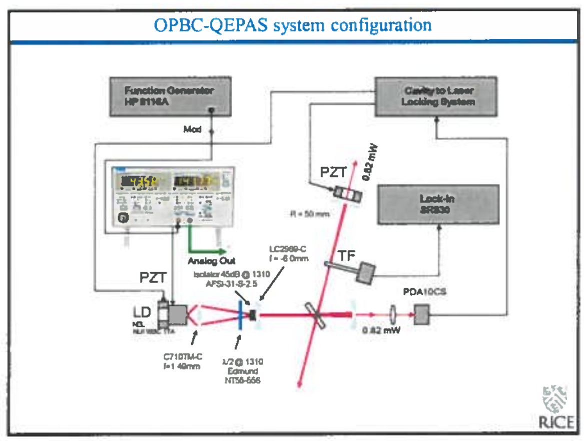

Proposed QEPAS-OPBC Sensor Configuration
DFB diode laser
High reflectivity dielectric mirrors
Photodiode
×200
PZT
QTF
Feedback electronics
Circulating power = Source power / (1-R)
Very conservatively, ×100
Alex Kachanov Skymoon Research R & D
RICE


OPBC-QEPAS system configuration
Function Generator HP 8116A
Cavity to Laser Locking System
Mod
PZT
0.82 mW
Lock-in SR830
R = 50 mm
Analog Out
LC2969-C f = -6.0mm
TF
PZT
Isolator 45dB @ 1310 AFSI-31-8-2.5
PDA10CS
LD
0.82 mW
C710TM-C f=1.40mm
λ/2 @ 1310 Edmund NT55-556
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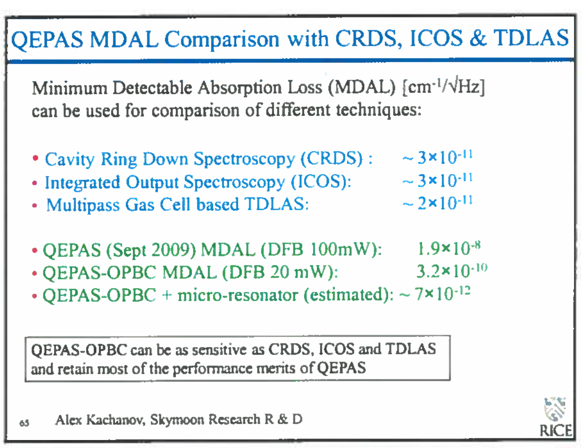
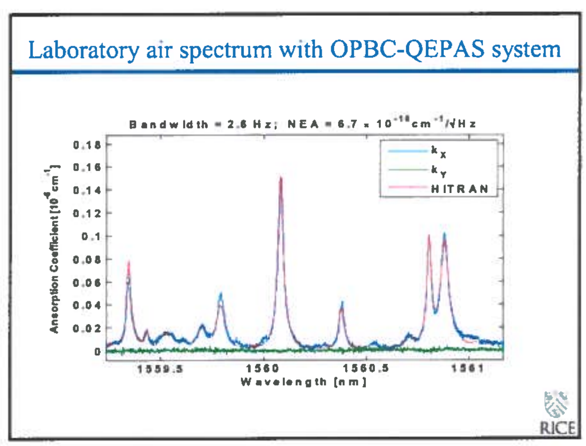

QEPAS MDAL Comparison with CRDS, ICOS & TDLAS
Minimum Detectable Absorption Loss (MDAL) [cm-1/√Hz] can be used for comparison of different techniques:
• Cavity Ring Down Spectroscopy (CRDS) : ~ 3×10-11
• Integrated Output Spectroscopy (ICOS): ~ 3×10-11
• Multipass Gas Cell based TDLAS: ~ 2×10-11
• QEPAS (Sept 2009) MDAL (DFB 100mW): 1.9×10-8
• QEPAS-OPBC MDAL (DFB 20 mW): 3.2×10-10
• QEPAS-OPBC + micro-resonator (estimated): ~ 7×10-12
QEPAS-OPBC can be as sensitive as CRDS, ICOS and TDLAS and retain most of the performance merits of QEPAS
65 Alex Kachanov, Skymoon Research R & D
RICE


Laboratory air spectrum with OPBC-QEPAS system
Bandwidth = 2.6 Hz; NEA = 6.7 x 10-11cm-1/√Hz
kx
ky
HITRAN
Absorption Coefficient [10-6 cm-1]
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
1559.5 1560 1560.5 1561
Wavelength [nm]
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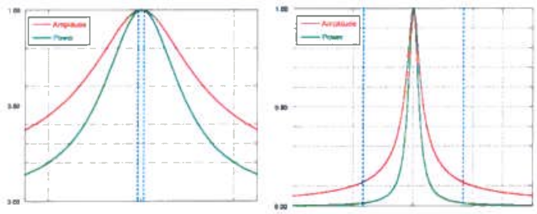
Narrowband vs. Wideband QEPAS



$$\sqrt{\langle V_N^2 \rangle} = R_g \sqrt{\frac{4k_BT}{R}\Delta f}$$

$$\sqrt{\langle V_N^2 \rangle} = R_g \sqrt{\frac{k_BT}{L}}$$

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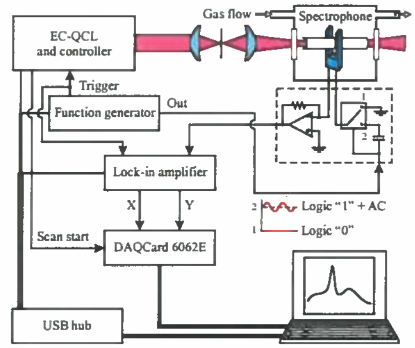
Sensor Schematic



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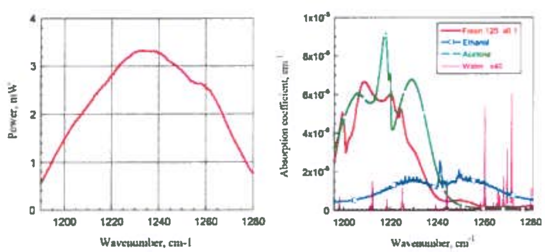
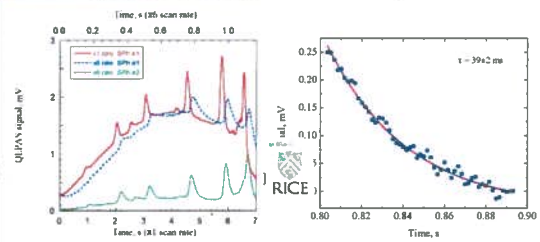
Fast frequency scans using an EC-QCL



Scanning rate:
from ×1 (12.9 cm^{-1}/s, 85 cm-1 in 6.5s)
to ×6 (77.3 cm^{-1}/s, 85 cm-1 in 1.1s)

DAYLIGHT SOLUTIONS

Fast frequency scans: QEPAS and EC-QCL

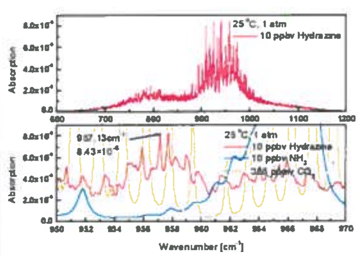


Calculated $\tau = Q/\pi f$
Red, blue 42 ms
Green 19 ms

Calculated $\tau = Q/\pi f$ 42 ms

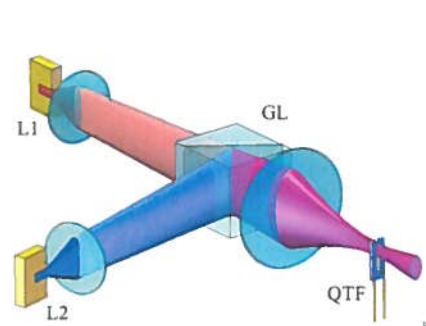
DAYLIGHT SOLUTIONS

N_2H_4 detection with a QCL based QEPAS sensor



The proposed QEPAS based N_2H_4 sensor would use a thermoelectrically cooled CW, DFB, QCL operating at ~ 957 cm^{-1} (10.5 μm) with an output power of 100 mW. At this wavelength and assuming a noise equivalent absorption coefficient of ~5.10^{-9} cm^{-1} W/√Hz, and a N_2H_4 absorption of ~7.10^{-6} cm-^{1}/ppm at 1 atm, the estimated detection sensitivity will be ~ 7 ppbV for a 1 Hz bandwidth

Optical setup of the MOCAM-QEPAS based hydrazine sensor



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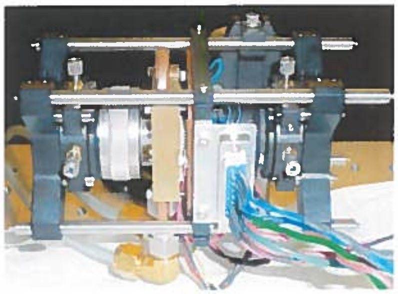
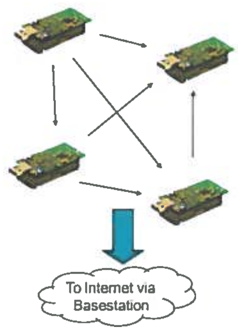
Laser source module based on a ~1W wide stripe NIR diode laser



Wireless Sensor Networks for Trace Gas Sensing



- Advantages?
  - Spatial resolution
  - Measure fluxes
  - Detect spike before diffusion
- What is needed?
  - Ultra low power
  - Fast duty cycling capability
  - Low cost, Replicable
  - Ultra miniature
  - Autonomy (no consumables; auto-processing; auto start)

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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 – NH_3, 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 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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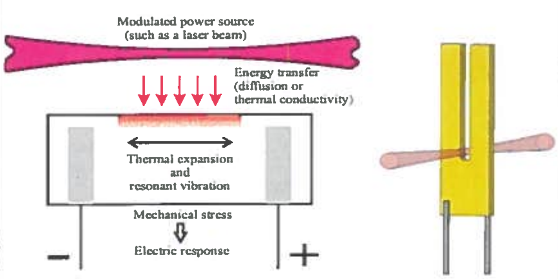
Principle of ROTADE Sensor Operation



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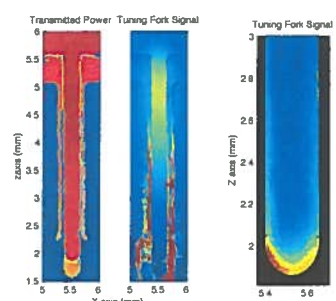
ROTADE



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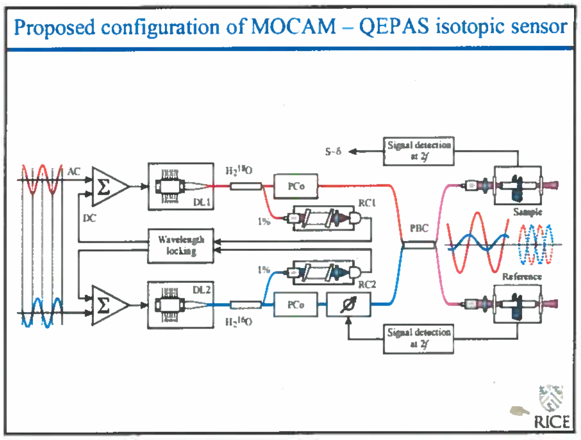
Proposed configuration of MOCAM – QEPAS isotopic sensor
AC
DC
DL1
DL2
$H_2^{18}O$
$H_2^{16}O$
PCo
PCo
RC1
RC2
1%
1%
Wavelength locking
S-δ
Signal detection at 2f
Signal detection at 2f
PBC
Sample
Reference
RICE