Infrared Semiconductor Laser based Spectroscopic Sources: Analytical & Medical Applications

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

OUTLINE

Thermo Research Symposium

Houston, TX
Feb. 21, 2008

- Motivation: Wide-range of Chemical Sensing
- Fundamentals of Laser Absorption Spectroscopy
- New Laser Sources and Sensing Technologies
- Selected Applications of Trace Gas Detection
  - Environmental Monitoring (H_2CO)
  - Detection of nitric oxide and ethanol
  - QEPAS based monitoring of broadband absorbers
- Future Directions and Summary

Work supported by NASA, NSF, DoE and 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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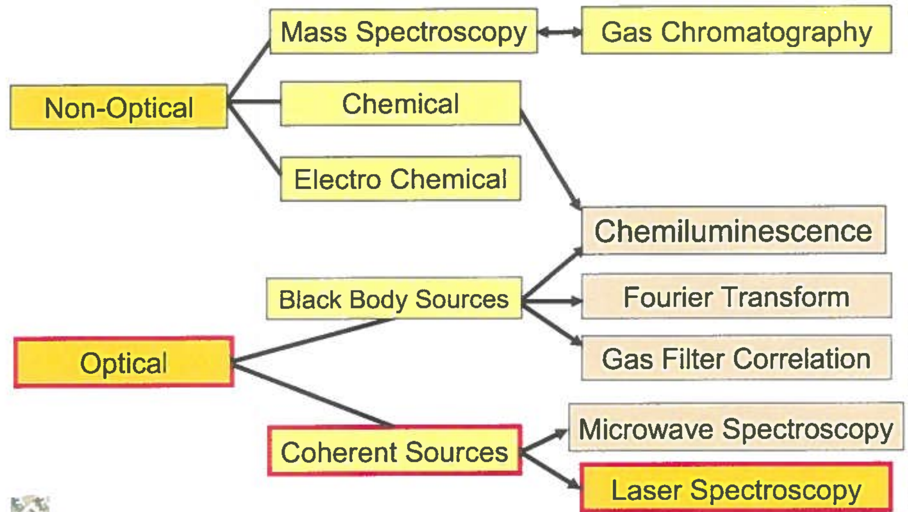
Existing Methods for Trace Gas Detection



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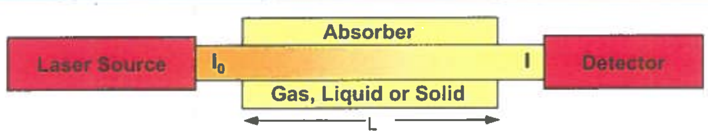
Laser Absorption Spectroscopy

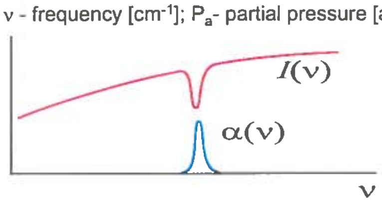


Beer-Lambert's Law of Linear Absorption

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

$\alpha(\nu)$ - absorption coefficient [cm^{-1} atm^{-1}]; L – path length [cm]

ν - frequency [cm^{-1}]; P_a- partial pressure [atm]



$$\alpha(\nu) = C \cdot S(T) \cdot g(\nu - \nu_0)$$

C - total number of molecules of absorbing gas/atm/cm^3 [molecule$\cdot cm^{-3} \cdot atm^{1}$]

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

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

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Sensitivity Enhancement Techniques

- **Optimum Molecular Absorbing Transition**
  - Overtone or Combination Bands (NIR)
  - Fundamental Absorption Bands (MID-IR)
- **Long Optical Pathlengths**
  - Multipass Absorption Cell (White, Herriot)
  - Cavity Enhanced, Cavity Ringdown & Intracavity Spectroscopy
  - Open Path Monitoring (with retro-reflector)
  - Evanescent Wave Spectroscopy (Fibers & Waveguides)
- **Spectroscopic Detection Schemes**
  - Frequency or Wavelength Modulation
  - Balanced Detection
  - Zero-air Subtraction
  - Photoacoustic and Quartz Enhanced Photoacoustic Spectroscopy
  - Noise Immune Cavity Enhanced-Optical Heterodyne Molecular Spectroscopy (NICE-OHMS)

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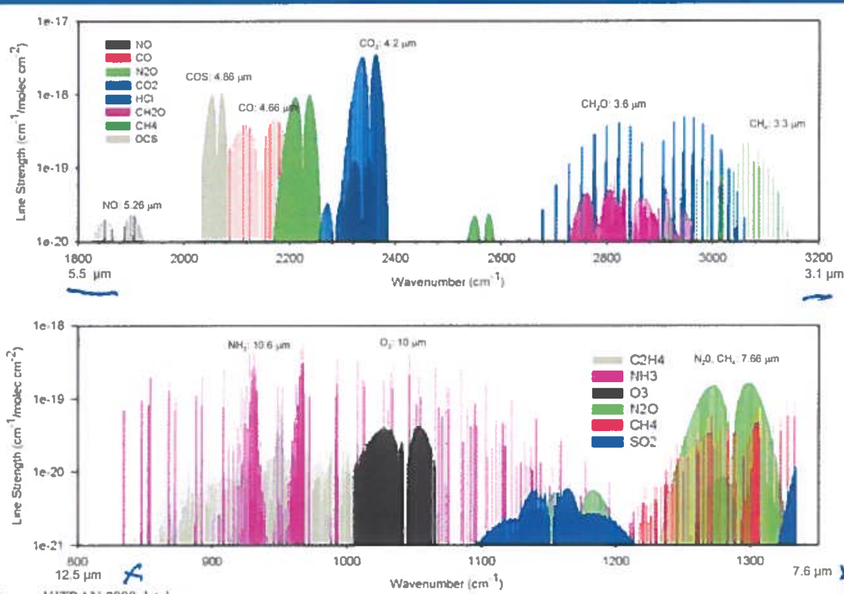
Example Molecular Absorption Spectra within two Mid-IR Atmospheric Windows



Source: HITRAN 2000 database

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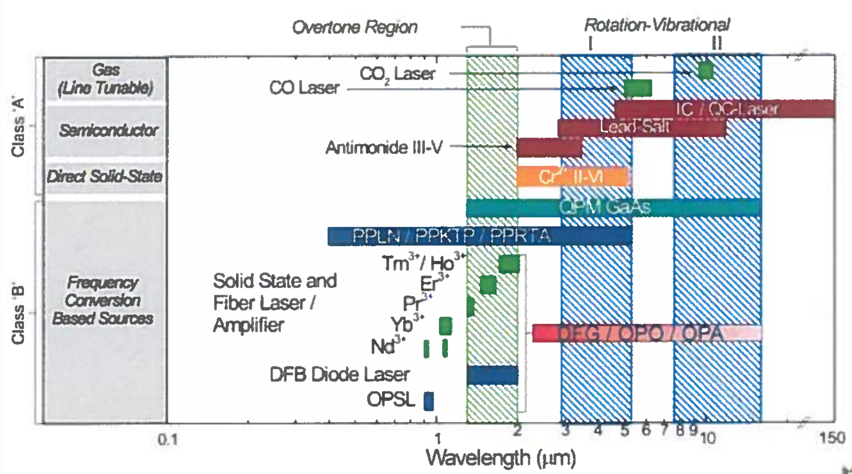
Mid-IR Source Requirements for Laser Spectroscopy

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

IR Laser Sources and Wavelength Coverage



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Key Characteristics of Mid-IR Quantum Cascade Lasers for Spectroscopy

- Laser wavelengths cover the entire Mid-IR range from 3 to 24 μm
- High power (>500 mW cw, >5W peak for pulsed)
- High spectral purity - single frequency with DFB structure or external cavity: < kHz to 33 MHz
- Continuous tuning by temperature (~10 cm^{-1}), current (~1 cm^{-1}) or external cavity (>200 cm^{-1} → pulsed mode)
- High reliability: low failure rate, long lifetime and robust
- <u>Capable of room temperature operation</u>
  - Pulsed: up to +150°C
  - CW: up to RT

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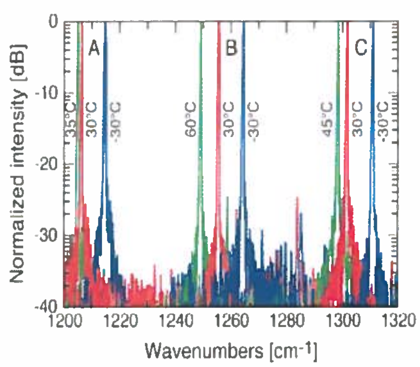
Spectra of CW DFB QC at 7.8μm



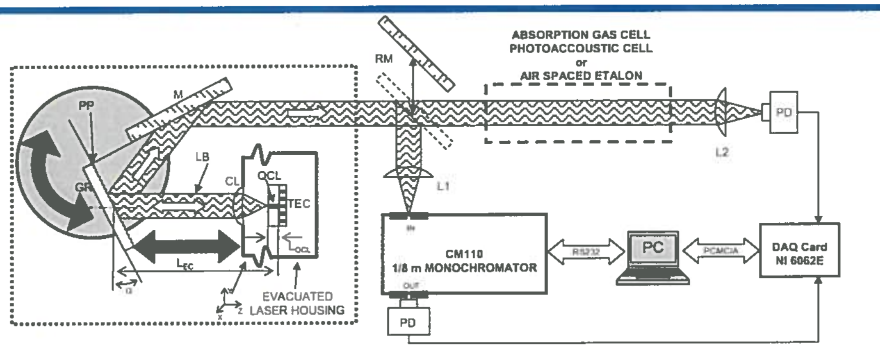
- Single mode emission with SMSR>25 dB (resolution limited by FTIR)
- Wavelength coverage:
  One laser: ~ 10-15 cm^{-1}
  In total: > 100cm^{-1} (7.7-8.3μm)
- Average R_{th}~12.4 K/W Average tuning coefficient β~8.88*10^{-5} K^{-1}

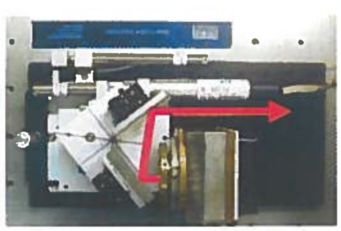
S. Blaser, A. Wittmann, L. Hvozdara, The 2nd International Workshop on Quantum Cascade Lasers

Alpes Lasers

Widely Tunable, CW, TEC Quantum Cascade Lasers

Tunable external cavity QCL based spectrometer, 2006





- High resolution mode-hop free wavelength tuning
  - PZT controlled EC-length
  - PZT controlled grating angle
  - QCL current control
- Motorized coarse grating angle tuning
- Vacuum tight QCL enclosure with built-in 3D lens positioner (TEC laser cooling & chilled water cooling)

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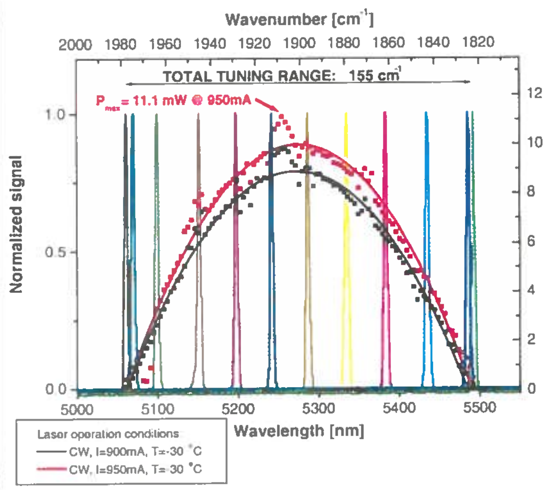
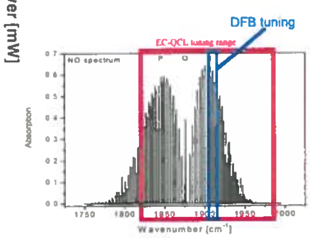
Wide Wavelength Tuning of a 5.3μm EC-QCL



- Coarse wavelength tuning of **155 cm^{-1}** is performed by varying diffraction grating angle
- Max. CW power ~**11mW**
- Access to Q(3/2) transition of NO at 1875.8 cm^{-1} for LMR spectroscopy



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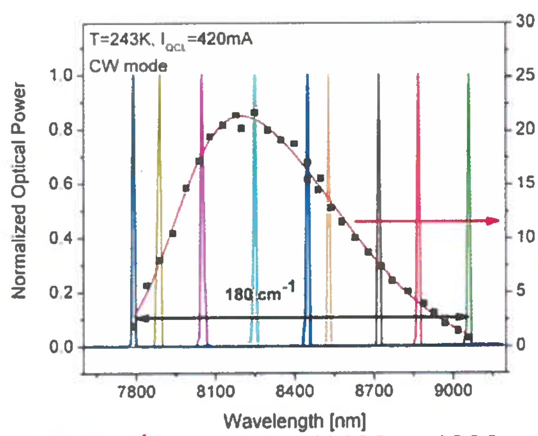
G. Wysocki, R. F. Curl ,F. K. Tittel, R. Maulini, J. Faist, manuscript in preparation 2007

ITIR

Performance of 8.4 μm EC-QCL Spectroscopic Source



Tunability **180 cm^{-1}** @8.4 μm (1100 to 1280 cm^{-1})

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

$P_{EC\text{-}opt}$ up to **50 mW (cw)**
(I_{QCL} = 680 mA -> P = 44 mW)

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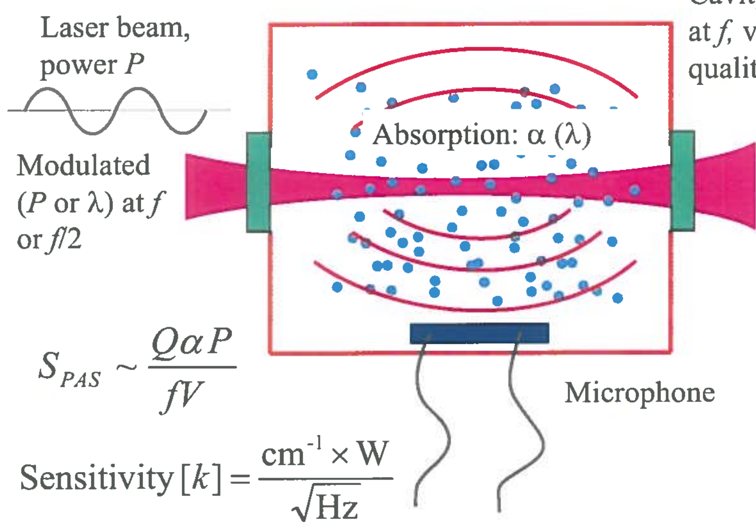
G. Wysocki, R. F. Curl ,F. K. Tittel, F. Capasso, L. Diehl, M. Troccoli, R. Maulini, J. Faist, Optics Express (June 11, 2007)

Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)

Resonant photoacoustic spectroscopy



$$S_{PAS} \sim \frac{Q\alpha P}{fV}$$

$$\text{Sensitivity}\,[k] = \frac{\text{cm}^{-1} \times \text{W}}{\sqrt{\text{Hz}}}$$

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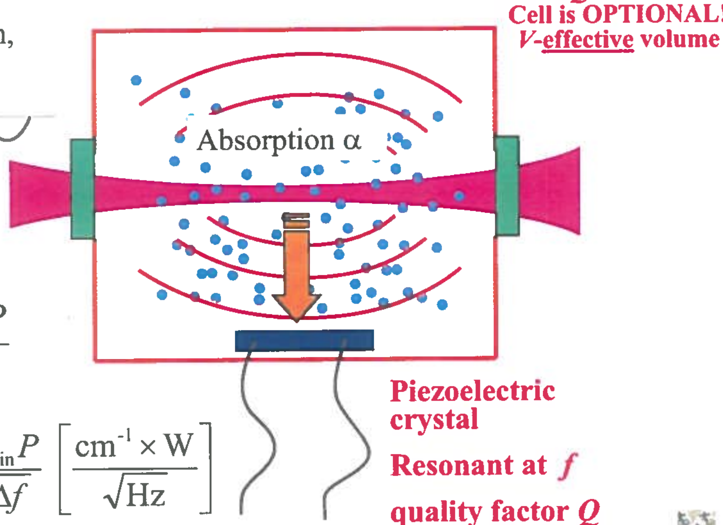
Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)

Laser beam,
power P

Modulated (P or λ) at f or $f/2$



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

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

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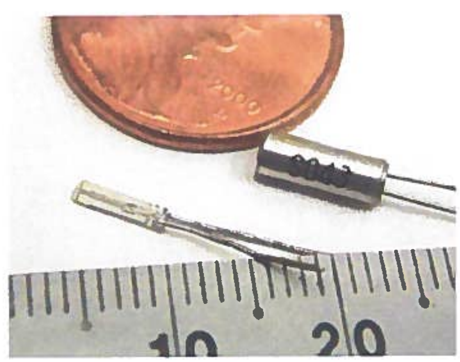
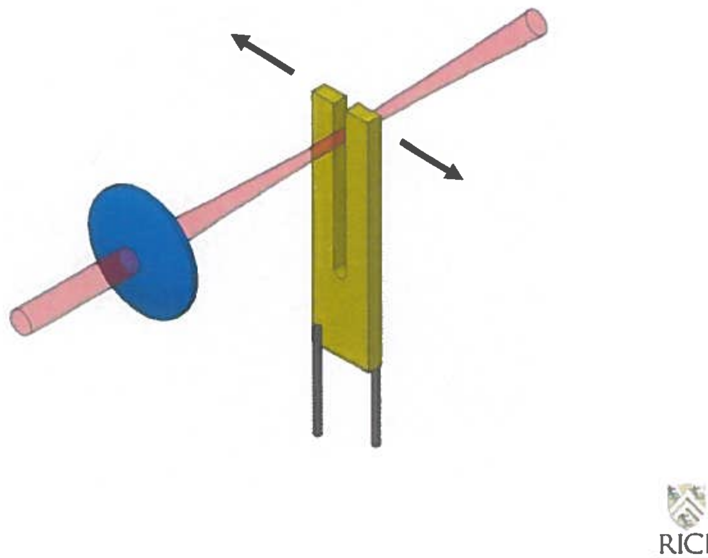
Quartz Tuning Fork (TF) as a Resonant Microphone

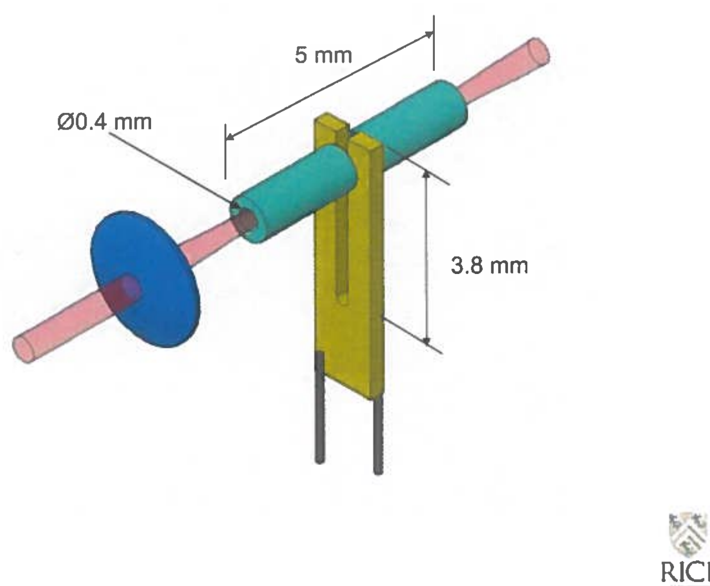
- Resonant frequency f=32.8 kHz
- Intrinsically high Q factor: $Q_{vacuum} \sim 125\,000$, $Q_{air} \sim 10\,000$ at ambient conditions;
- Piezoelectric: requires no transducer
- Miniature size
- Mass produced for clocks – low cost



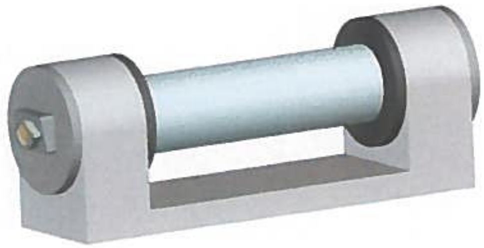
QEPAS gas sensor



QEPAS gas sensor

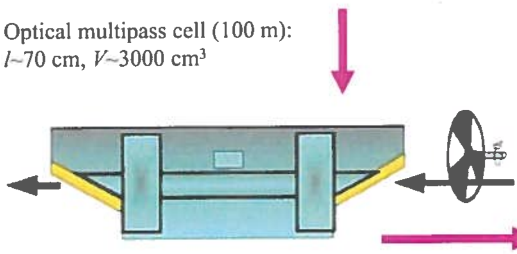


Comparative Size of Absorption Detection Modules (ADM)

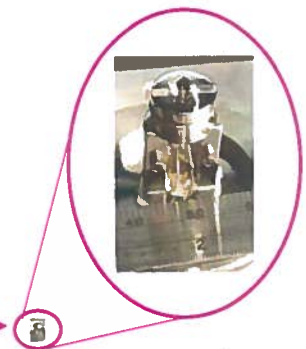


- Resonant frequency f = 32.8 kHz
- Intrinsically high Q factor: Q_{vacuum} ~ 125 000
  Q_{air} ~10 000 for ambient conditions
- Piezoelectric: requires no transducer
- Miniature size
- Mass produced for watches & clocks – low cost

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



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



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

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Current Trace Gas Sensor Areas being Explored at Rice

- Methods employed
  - Extended pathlengths
  - Cavity ringdown spectroscopy (CRDS)
  - Integrated cavity output spectroscopy (ICOS)
  - Wavelength and amplitude modulation
  - Pulse-to-pulse fluctuation removal by comparing the same pulse on the same or another detector
  - Quartz tuning fork based photoacoustic spectroscopy
- 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
- Practical applications
  - NASA Crew Health Maintenance & Life Support - H_2CO, NH_3
  - DoE radioactive site remediation
  - Medical breath analysis - OCS, NO, CO_2, acetone
  - Industry catalyst poisoning - CO
  - Urban air smog - H_2CO

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Motivation for Precision Monitoring of H_2CO

- Precursor to atmospheric O_3 production
- Pollutant due to incomplete fuel combustion processes
- Potential trace contaminant in industrial manufactured products
- Medically important gas

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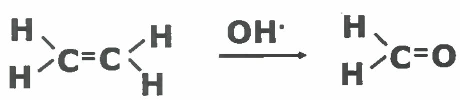
Megacity Air Pollution: Houston, TX

Houston Ozone Chemistry

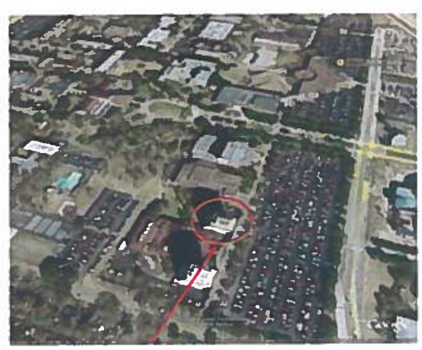
- Rapid oxidation of highly reactive VOCs leads to ozone formation in urban areas
- As a major petrochemical center, the Houston region produces ~30 billion pounds of ethylene annually



TexAQS II Field Campaign Summer 2006

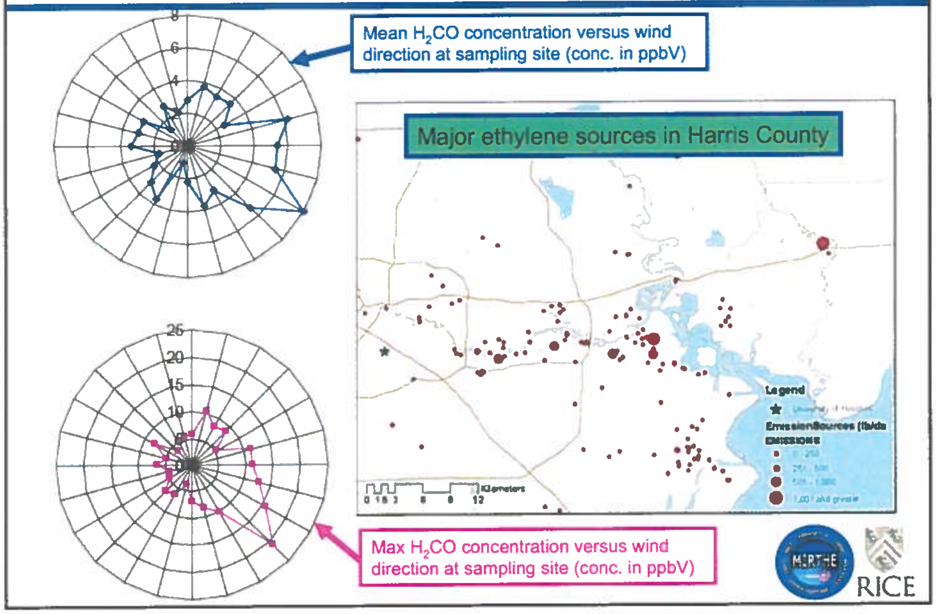
- To study ozone formation and transport, a coordinated field study was conducted during August to September 2006 in the Greater Houston area
- 5 aircraft, one ship, two ground chemistry sites, ~20 periphery and meteorological sites were employed during TexAQS II
- Participation by ~300 scientists from academia, national laboratories, industry and government agencies

FTIRS



Moody Tower, UH Campus

H_2CO Concentration (ppb) Versus Wind Direction



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

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NO as a Biomarker

- NO is biochemically involved in most tissues and physiological processes in the human body
- NO excretion increases in exhaled breath in lung diseases such as :
  - ✓ Asthma[1]
  - ✓ Chronic Obstructive Pulmonary Disease[2]
  - ✓ Acute lung rejection[3]
  - ✓ Acute respiratory distress syndrome[4]
  - ✓ Pneumonia (useful for intubated patients)[5]

[1]Alving K, E Weitzberg, JM Lundberg. Increased amount of NO in exhaled air of asthmatics. Eur Repir J 1993; 6: 1368-1370.
[2]Wasim M, S Loukides, S Culpritt, P Sullivan, S Kharitonov, P Barnes. Exhaled NO in COPD. Am J Repir Crit Care Med 1998; 157. pp 998-1002.
[3]Silkoff PE et al. Exhaled NO in human lung transplantation. A noninvasive marker of acute rejection. Am J Repir Crit Care Med 1998; 157(6): 1822-1828.
[4]Brett SJ, Evans TW. Measurement of endogenous NO in the lungs of patients with the ARDS. Am J Repir Crit Care Med 1998; 157 (3 Pt 1): 993-7.
[5]Adrie C et al. Exhaled and nasal NO as a maker of pneumonia in ventialed pateints. Am J Repir Crit Care Med 2001; 163(5):1143-9.

Biomarkers Present in Exhaled Human Breath

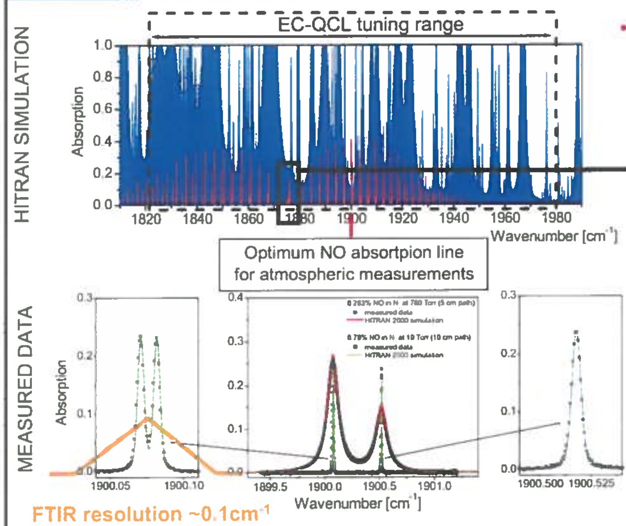
As many as 400 different molecules in breath; many with well defined biochemical pathways

BROADBAND ABSORBERS

Compound	Concentration	Physiological basis/Pathology Indication
Acetaldehyde	ppb	Ethanol metabolism
Acetone	ppm <200ppb)	Diabetes mellitus response, fasting response
Ammonia	ppb(< 15ppm)	Protein metabolism, liver and renal disease
Carbon dioxide	%	Product of respiration, Heliobacter pylori
Carbon disulfide	ppb	Gut bacteria, schizophrenia
Carbon monoxide	ppm (<3ppm)	Production catalyzed by *heme oxygenase*
Carbonyl sulfide	ppb	Gut bacteria, liver disease
Ethane	ppb (<10 ppb)	Lipid peroxidation and oxidative stress
Ethanol	ppb	Gut bacteria
Ethylene	ppb (<10ppb)	Lipid peroxidation, oxidative stress, cancer
Hydrocarbons	ppb	Lipid peroxidation/metabolism
Hydrogen	ppm	Gut bacteria
Isoprene	ppb	Cholesterol biosynthesis
Methane	ppm (<40ppm	Intestinal methanogic bacteria
Methanethiol	ppb	Methionine metabolism
Methanol	ppb	Metabolism of fruit
Methylamine	ppb	Protein metabolism
Nitric oxide	ppb (<100 ppb)	Production catalyzed by *nitric oxide synthase*
Oxygen	%	Required for normal respiration
Pentane	ppb	Lipid peroxidation, oxidative stress
Water	%	Product of respiration

Terence Risby, Johns Hopkins University

High resolution spectroscopy with a 5.3µm EC-QCL



- Mode hop free scan of up to **~2cm^{-1}** with a resolution **<0.001cm^{-1}** (30MHz) can be performed anywhere within the tuning range

G. Wysocki, R. F.Curl ,F. K. Tittel, R. Maulini, J. Faist, manuscript in preparation 2007

earlier work: G. Wysocki R. F.Curl ,F. K. Tittel, R. Maulini, J. M. Bulliard, J. Faist, Applied Physics B. 81, 769-777 (2005)

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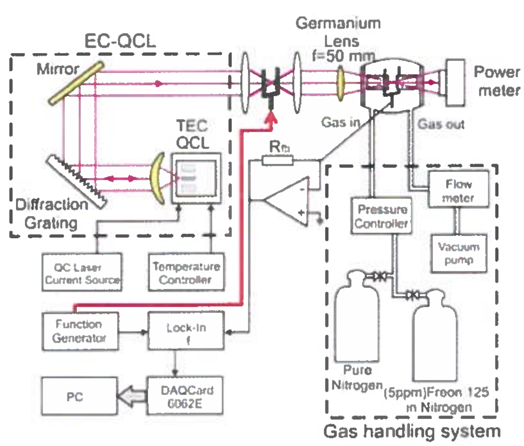
QCL based Quartz-Enhanced Photoacoustic Gas Sensor



QEPAS characteristics:

- High sensitivity (ppm to ppb)
- Excellent dynamic range
- Immune to environmental noise
- Ultra-small sample volume (< 1 mm^3)
- Sensitivity is limited by the fundamental thermal TF noise
- Compact, rugged and low cost
- Potential for trace gas sensor networks

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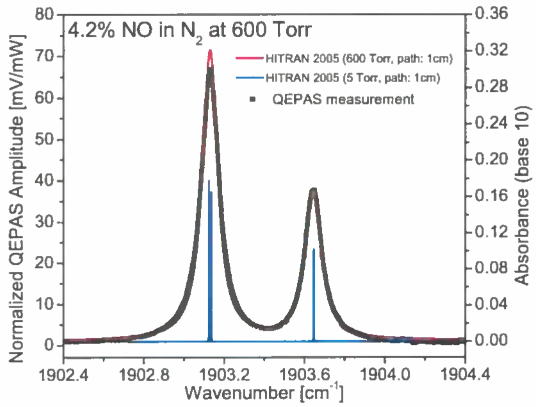
High resolution EC-QCL based QEPAS of NO



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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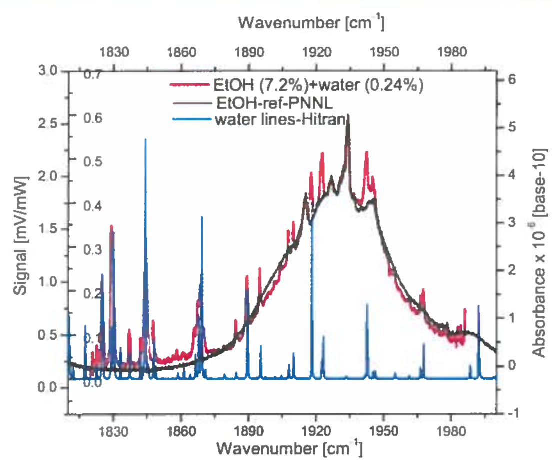
QEPAS Ethanol Spectrum between 1825 & 1980 cm^{-1}



Reference spectrum from the PNNL spectral database (red line). Sharp features on the ethanol spectrum correspond to the water absorption lines (blue line depicts water absorption spectrum simulated using HITRAN database)

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Monitoring of two broadband absorbers: C_2HF_5 & C_3H_6O

- Freon 125 (C_2HF_5)
  - Refrigerant (leak detection)
  - Safe simulant for toxic chemicals e.g. chemical warfare agents
- Acetone (C_3H_6O)
  - Recognized biomarker for diabetes and fasting response

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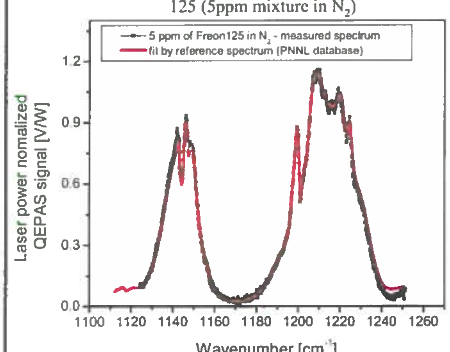
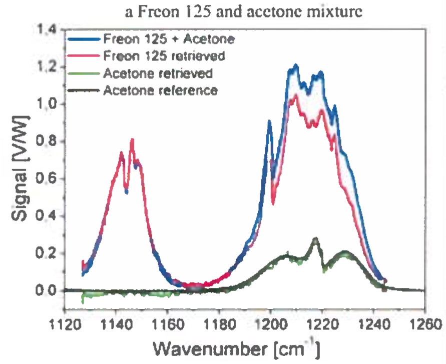
Spectroscopy of Freon 125 and Acetone with a Widely Tunable 8.4 μm CW EC-QCL

QEPAS concentration measurement of Freon 125 (5ppm mixture in N_2)



- Minimum detection limit (1σ) of **~4.5 ppb** was obtained for Freon 125 with an average laser power of 6.6 mW

QEPAS concentration measurement of a Freon 125 and acetone mixture



- Wide tunability enables excellent molecular selectivity for broad band absorbers

R. Lewicki et al Optics Express 15, 7357, 2007

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QEPAS Performance for 14 Trace Gas Species (Feb.'08)

Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, $cm^{-1}W/Hz^{1/2}$	Power, mW	NEC (τ=1s), ppmv
H_2O (N_2)**	7306.75	60	1.9×10^{-9}	9.5	0.09
HCN (air: 50% RH)*	6539.11	60	$< 4.3\times10^{-9}$	50	0.16
C_2H_2 (N_2)**	6529.17	75	$\sim2.5\times10^{-9}$	~ 40	0.06
NH_3 (N_2)*	6528.76	575	3.1×10^{-9}	60	0.06
C_2H_4 (N_2)*	6177.07	715	5.4×10^{-9}	15	1.7
CH_4 (N_2 + 0.3% H_2O)*	6057.09	950	1.0×10^{-8}	13.7	0.8
CO_2 (breath ~100% RH)	6361.25	90	1.6×10^{-8}	26	410
H_2S (N_2)*	6357.63	780	5.6×10^{-9}	45	0.20
CO_2 (N_2+1.5% H2O) *	4991.26	50	1.4×10^{-8}	4.4	18
CH_2O (N_2:75% RH)*	2804.90	75	8.7×10^{-9}	7.2	0.12
CO (N_2)	2196.66	50	5.3×10^{-7}	13	0.5
CO (propylene)	2196.66	50	7.4×10^{-8}	6.5	0.14
N_2O (air+5%SF_6)	2195.63	50	1.5×10^{-8}	19	0.007
C_2H_5OH (N_2)**	1934.2	770	2.2×10^{-7}	10	90
C_2HF_5 (N_2)***	1208.62	770	7.8×10^{-9}	6.6	0.009
NH_3 (N_2)*	1046.39	110	1.6×10^{-8}	20	0.006

* - Improved microresonator
** - Improved microresonator and double optical pass through ADM
*** - With amplitude modulation and metal microresonator

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

For comparison: conventional PAS 2.2 (2.6)×10^{-9} $cm^{-1}W/\sqrt{Hz}$ (1,800; 10,300 Hz) for NH_3*, (**)

* M. E. Webber et al, Appl. Opt. 42, 2119-2126 (2003); ** J. S. Pilgrim et al, SAE Intl. ICES 2007-01-3152

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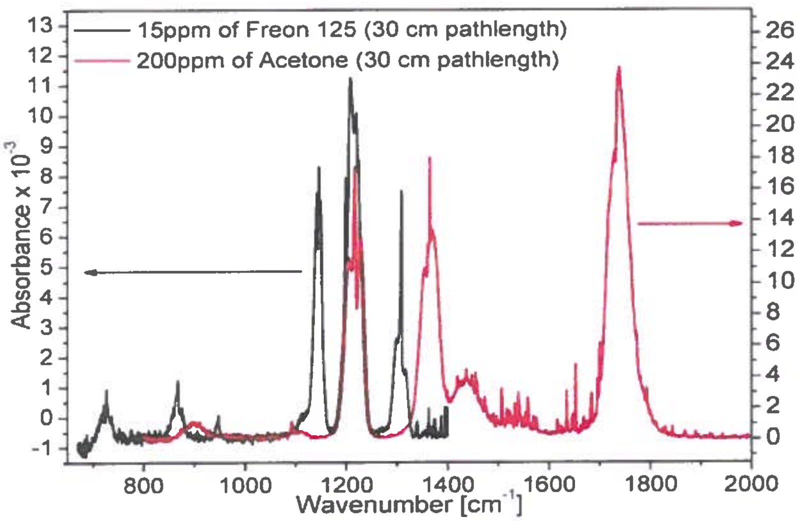
Impact of FTIR on Laser based Chemical Trace Gas Sensing

Unresolved spectra of Broadband Absorbing Molecules



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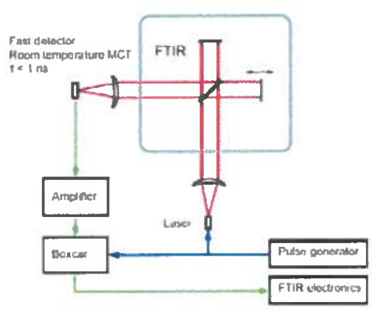
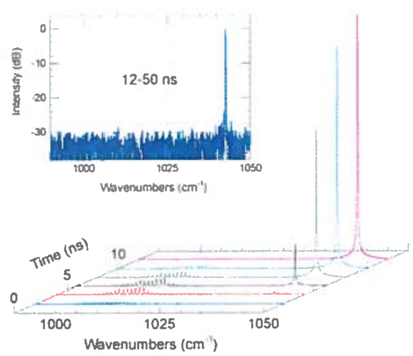
EC-QCL: FTIR Time-resolved Spectra





Time-resolved spectra of the pulsed EC-QCL.
Single-mode behavior was observed after the first 12 ns

R. Maulini, M. Beck, and J. Faist, E. Gini, App. Phys. Lett. Vol 84, No 10, 2004

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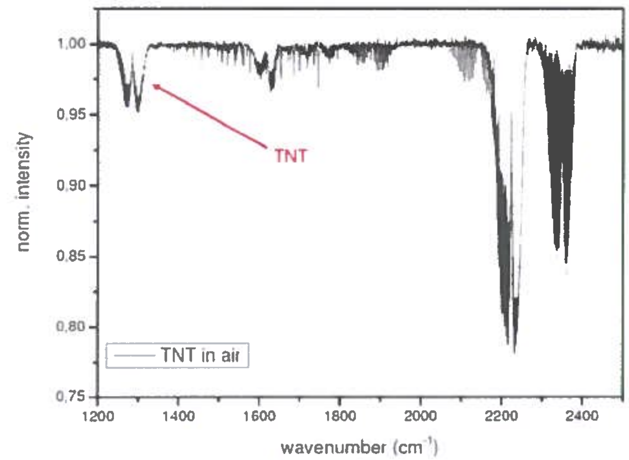
FTIR Spectrum of TNT Photo-fragmented in Air



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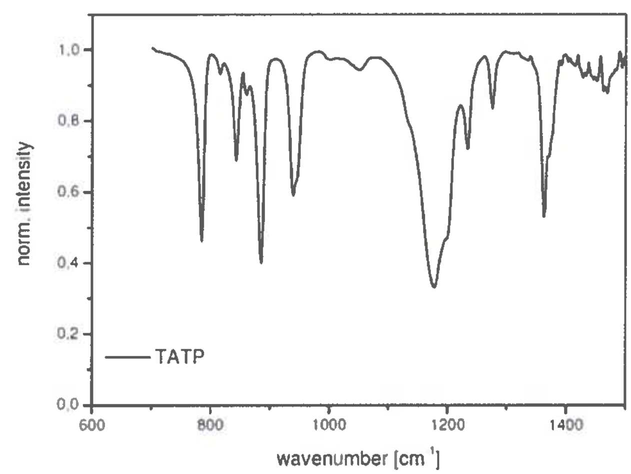
Peroxide based Explosives: TATP – FTIR measurement



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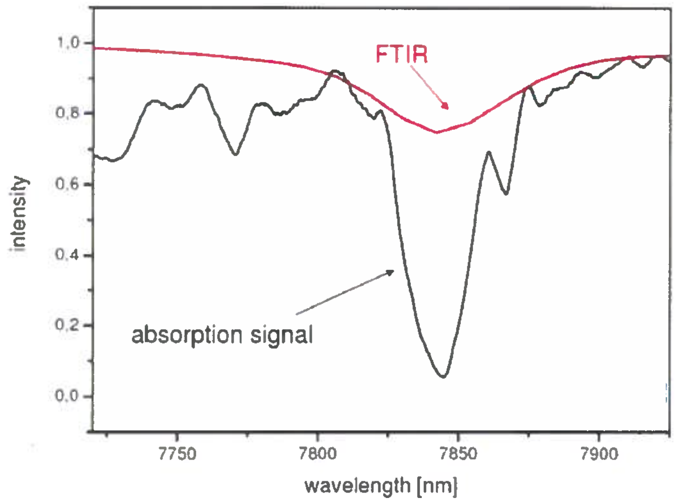
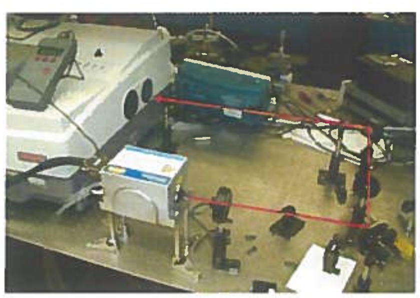
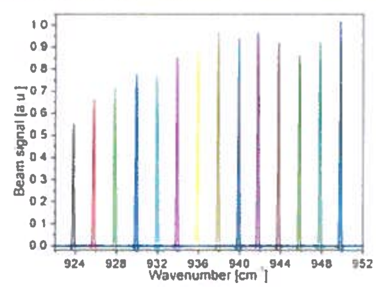
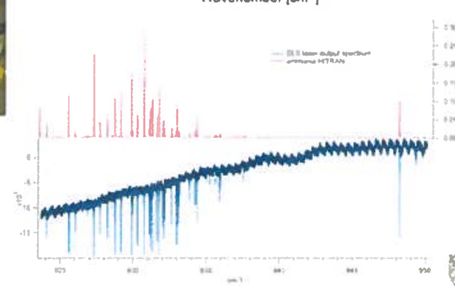
TATP spectrum with a commercial EC – QCL and FTIR



Tuning range of 10.6 μm CW RT EC-QCL







Summary and Future Directions

- **Near and Mid-Infrared Semiconductor Laser based Trace Gas Sensors**
  - Compact, robust sensor technology based on multipass cell absorption, cavity enhanced and quartz enhanced photoacoustic spectroscopy (QEPAS)
  - High sensitivity ($<10^{-4}$) and selectivity (3 to 500 MHz)
  - Fast data acquisition and analysis
  - Detected 13 trace gases to date: NH_3, CH_4, H_2S, N_2O, CO_2, CO, NO, H_2O, COS, C_2H_4, SO_2, C_2H_5OH, C_2HF_5 and isotopic species of C, O, N and H.

- **New Applications of Trace Gas Detection**
  - Distributed sensor networks for environmental monitoring (NH_3, CO, CH_4, C_2H_4, N_2O, CO_2 and H_2CO)
  - Inexpensive and sensitive sensors for industrial process control and chemical analysis (HCN, NO, NH_3, H_2O)
  - Sensors for medical and biomedical diagnostics (NO, CO, COS, CO_2, NH_3, C_2H_4)
  - Hand-held sensors and sensor network technologies for law enforcement

- **Future Directions and Collaborations**
  - Further improvements of the existing sensor technologies using novel, thermoelectrically cooled, cw, high power mid-IR interband and intersubband quantum cascade lasers and QEPAS
  - New applications enabled by novel widely tunable quantum cascade lasers (especially sensitive concentration measurements of broadband absorbers, in particular VOCs and HCs)
  - Development of gas sensor networks based on QEPAS and LAS

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