Mid-Infrared Semiconductor based Trace Gas Sensor Technologies: Recent Advances and Applications

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OUTLINE

Mirsens2 Intl. Workshop

WUT, Wroclaw, Poland

Oct 18-20, 2012

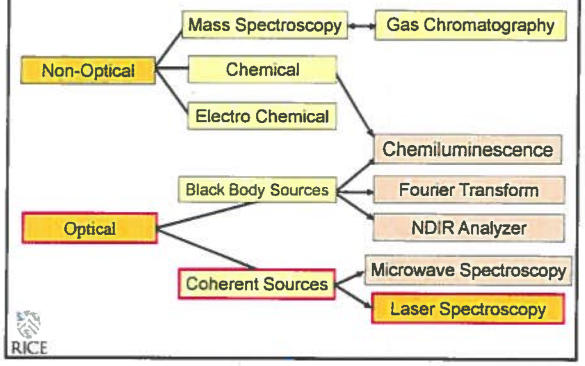
- New Laser Based Sensor Technology
  - Innovative, Compact Multipass Absorption Cell
  - Quartz Enhanced Photoacoustic Spectroscopy
- Examples of Mid-Infrared Sensor Architectures
  - C_2H_6, NH_3, NO, CO, and SO_2
  - Future Directions of Laser Based Gas Sensor Technology and Conclusions

Research supported by NSF ERC MIRTHE, NSF-ANR NexCILAS, the Robert Welch Foundation & Sentinel Photonics via an EPA Phase 1 SBIR Sub-award

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



Non-Optical
Mass Spectroscopy
Gas Chromatography
Chemical
Electro Chemical
Chemiluminescence
Optical
Black Body Sources
Fourier Transform
NDIR Analyzer
Coherent Sources
Microwave Spectroscopy
Laser Spectroscopy

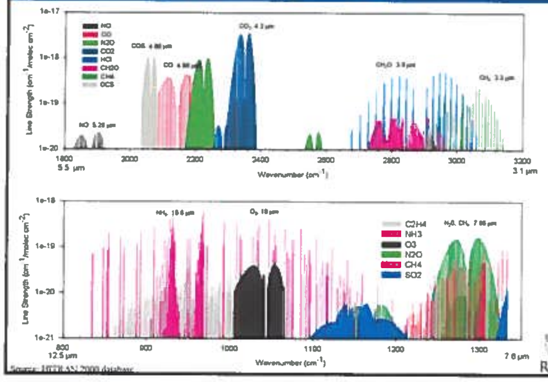
Sensitivity Enhancement Techniques for Laser Spectroscopy

- **Optimum Molecular Absorbing Transition**
  - Overtone or Combination Bands (NIR)
  - Fundamental Absorption Bands (MID-IR)
- **Long Optical Pathlength**
  - Multipass Absorption Cell (White, Herriot)
  - Cavity Enhanced and Cavity Ringdown Spectroscopy
  - Open Path Monitoring (with retro-reflector): Standoff and Remote Detection
  - Fiberoptic Evanescent Wave Spectroscopy
- **Spectroscopic Detection Schemes**
  - Frequency or Wavelength Modulation
  - Balanced Detection
  - Zero-air Subtraction
  - Photoacoustic Spectroscopy

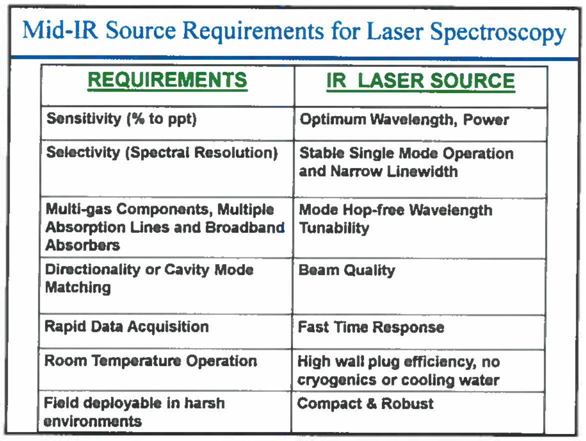
Other spectroscopic methods

- Faraday rotation spectroscopy (limited to some paramagnetic species)
- Noise Immune Cavity Enhanced-Optical HeterodyneMolecular Spectroscopy (NICE-OHMS)
- Frequency Comb Spectroscopy from Mid-IR to VUV
- Laser Induced Breakdown Spectroscopy (LIBS)

HITRAN Simulated Mid-Infrared Molecular Absorption Spectra

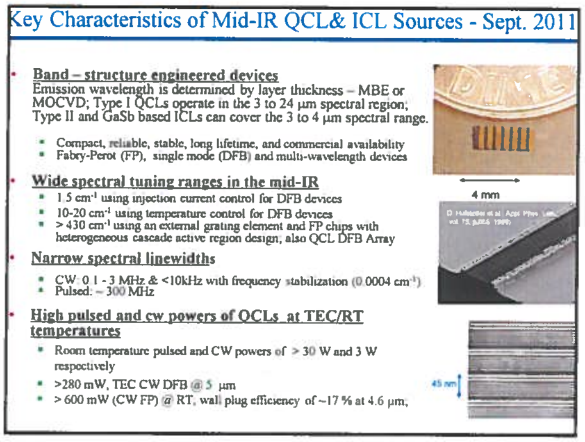


Source: HITRAN 2000 database



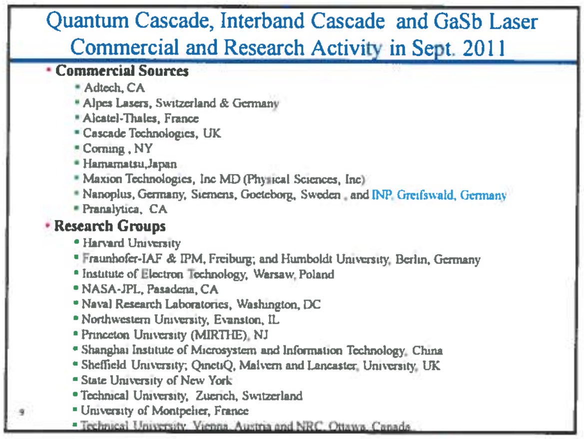
Mid-IR Source Requirements for Laser Spectroscopy

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



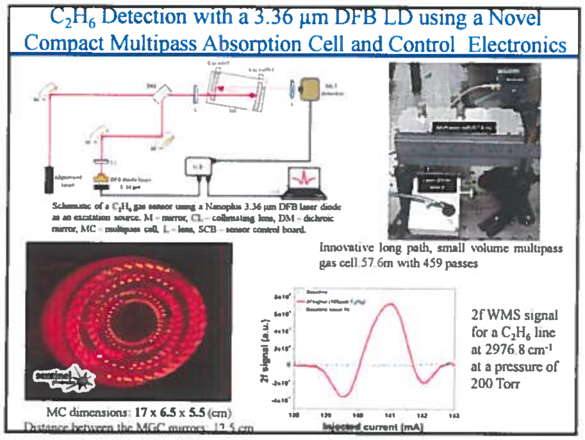
Key Characteristics of Mid-IR QCL& ICL Sources - Sept. 2011

- <u>Band – structure engineered devices</u>
  Emission wavelength is determined by layer thickness – MBE or MOCVD; Type I QCLs operate in the 3 to 24 μm spectral region; Type II and GaSb based ICLs can cover the 3 to 4 μm spectral range.
  - Compact, reliable, stable, long lifetime, and commercial availability
  - Fabry-Perot (FP), single mode (DFB) and multi-wavelength devices
- <u>Wide spectral tuning ranges in the mid-IR</u>
  - 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
- <u>Narrow spectral linewidths</u>
  - CW: 0.1 - 3 MHz & <10kHz with frequency stabilization (0.0004 cm^{-1})
  - Pulsed: ~ 300 MHz
- <u>High pulsed and cw powers of QCLs at TEC/RT temperatures</u>
  - Room temperature pulsed and CW powers of > 30 W and 3 W respectively
  - >280 mW, TEC CW DFB @ 5 μm
  - > 600 mW (CW FP) @ RT, wall plug efficiency of ~17 % at 4.6 μm;



Quantum Cascade, Interband Cascade and GaSb Laser Commercial and Research Activity in Sept. 2011

- **Commercial Sources**
  - Adtech, CA
  - Alpes Lasers, Switzerland & Germany
  - Alcatel-Thales, France
  - Cascade Technologies, UK
  - Corning , NY
  - Hamamatsu,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



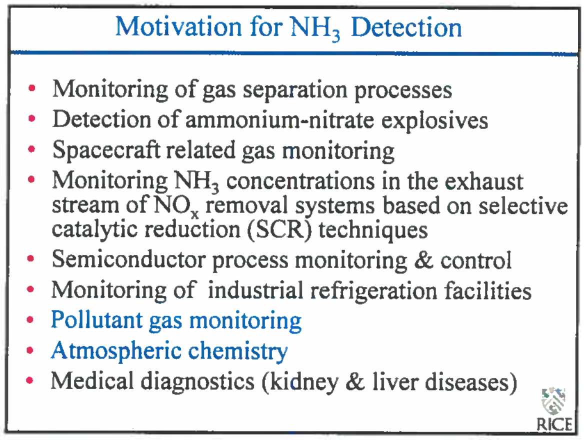
C_2H_6 Detection with a 3.36 μm DFB LD using a Novel Compact Multipass Absorption Cell and Control Electronics

Schematic of a C_2H_6 gas sensor using a Nanoplus 3.36 μm DFB laser diode as an excitation source. M – mirror, CL – collimating lens, DM – dichroic mirror, MC – multipass cell, L – lens, SCB – sensor control board.

Innovative long path, small volume multipass gas cell 57.6m with 459 passes

MC dimensions: 17 x 6.5 x 5.5 (cm)
Distance between the MGC mirrors: 12.5 cm

2f WMS signal for a C_2H_6 line at 2976.8 cm^{-1} at a pressure of 200 Torr



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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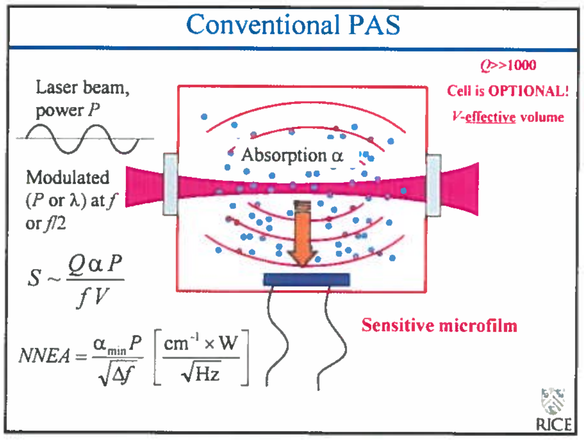


Conventional PAS

Laser beam, power *P*

Modulated (*P* or λ) at *f* or *f*/2

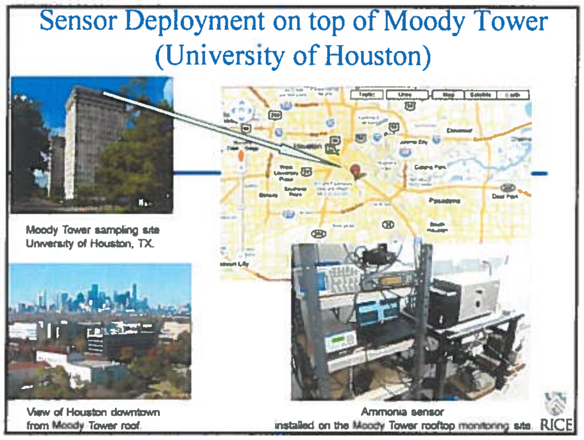
$$S \sim \frac{Q \alpha P}{f V}$$

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

Q>>1000
Cell is OPTIONAL!
V-effective volume

Sensitive microfilm

RICE

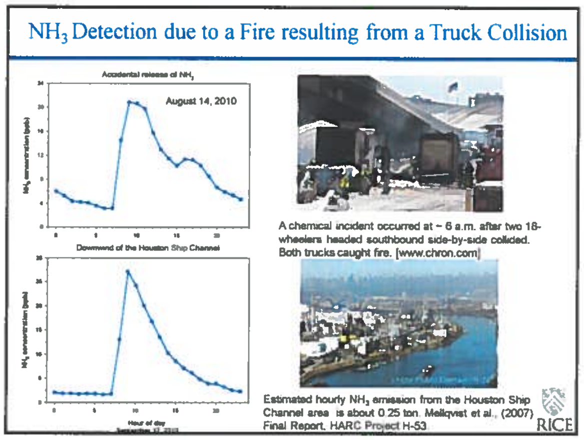


Sensor Deployment on top of Moody Tower (University of Houston)

Moody Tower sampling site
University of Houston, TX.

View of Houston downtown
from Moody Tower roof.

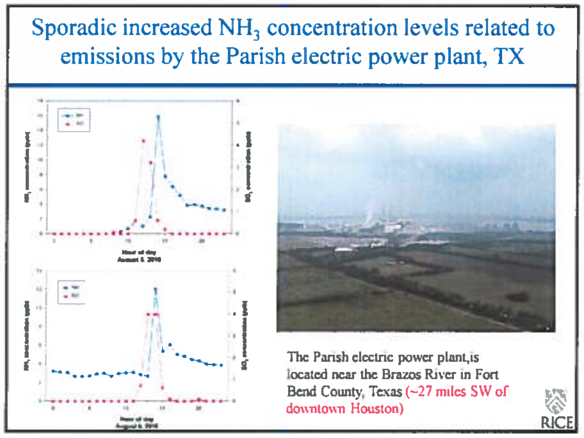
Ammonia sensor
installed on the Moody Tower rooftop monitoring site



NH_3 Detection due to a Fire resulting from a Truck Collision

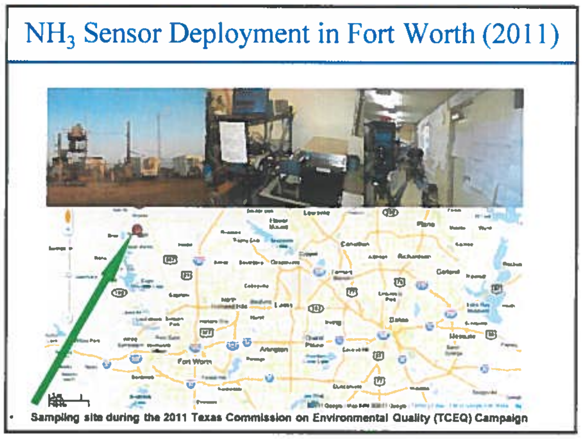
A chemical incident occurred at ~ 6 a.m. after two 18-wheelers headed southbound side-by-side collided. Both trucks caught fire. [www.chron.com]

Estimated hourly NH_3 emission from the Houston Ship Channel area is about 0.25 ton. Mellqvist et al., (2007) Final Report, HARC Project H-53



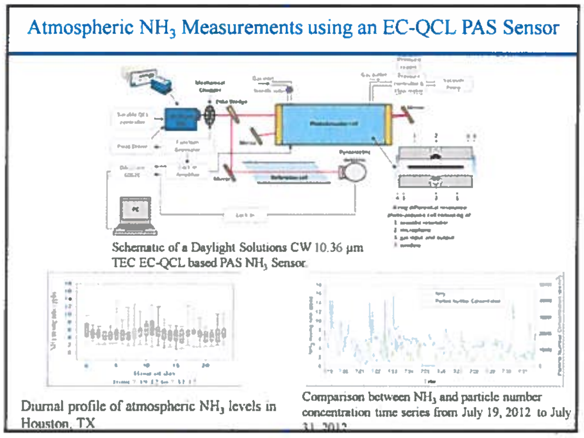
Sporadic increased NH_3 concentration levels related to emissions by the Parish electric power plant, TX

The Parish electric power plant,is located near the Brazos River in Fort Bend County, Texas (~27 miles SW of downtown Houston)



NH_3 Sensor Deployment in Fort Worth (2011)

- Sampling site during the 2011 Texas Commission on Environmental Quality (TCEQ) Campaign

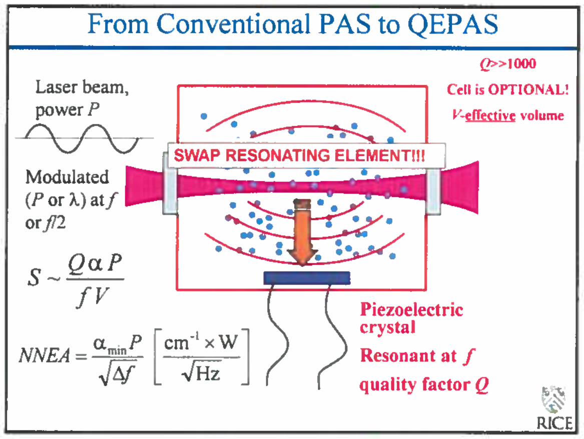


Atmospheric NH_3 Measurements using an EC-QCL PAS Sensor

Schematic of a Daylight Solutions CW 10.36 μm TEC EC-QCL based PAS NH_3 Sensor

Diurnal profile of atmospheric NH_3 levels in Houston, TX

Comparison between NH_3 and particle number concentration time series from July 19, 2012 to July 31, 2012



From Conventional PAS to QEPAS

Laser beam, power P

Modulated (P or λ) at f or $f/2$

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

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

Q>>1000

Cell is OPTIONAL!

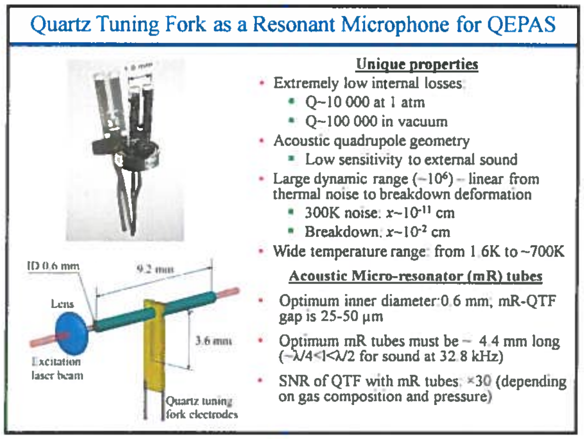
V-effective volume

SWAP RESONATING ELEMENT!!!

Piezoelectric crystal

Resonant at f

quality factor Q



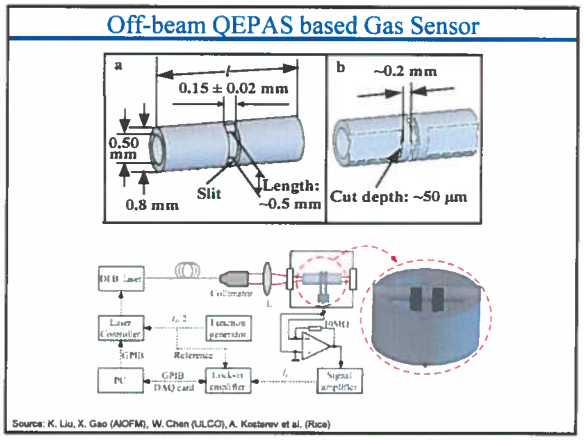
Quartz Tuning Fork as a Resonant Microphone for QEPAS

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: $x \sim 10^{-11}$ cm
  - Breakdown: $x \sim 10^{-2}$ cm
- Wide temperature range: from 1.6K to ~700K

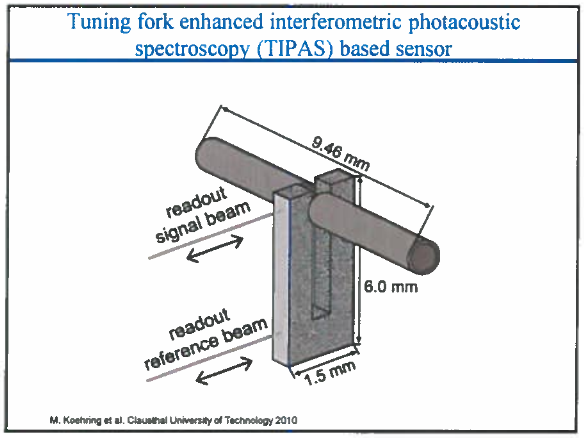
Acoustic Micro-resonator (mR) tubes

- Optimum inner diameter:0.6 mm; mR-QTF gap is 25-50 µm
- Optimum mR tubes must be ~ 4.4 mm long (~λ/4<l<λ/2 for sound at 32.8 kHz)
- SNR of QTF with mR tubes: ×30 (depending on gas composition and pressure)



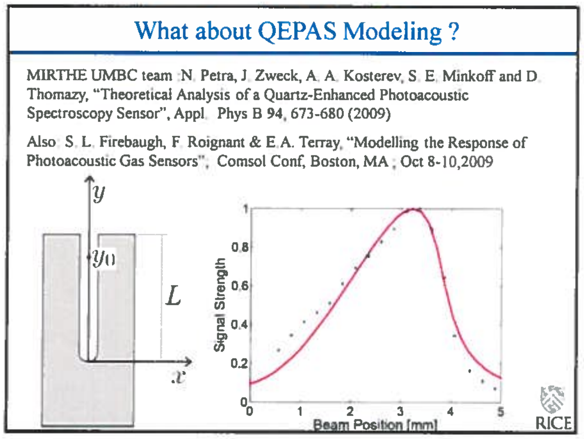
Off-beam QEPAS based Gas Sensor

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



Tuning fork enhanced interferometric photoacoustic spectroscopy (TIPAS) based sensor

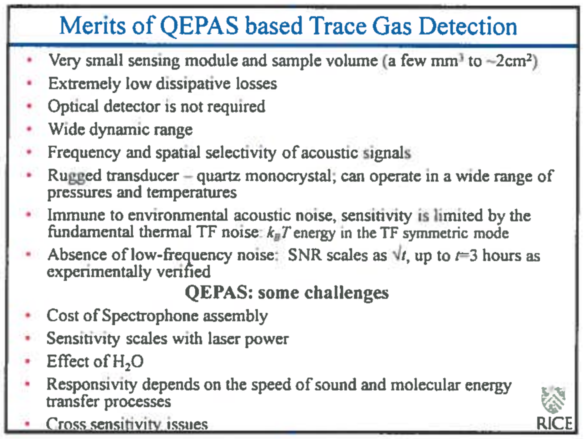
M. Koehring et al. Clausthal University of Technology 2010



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

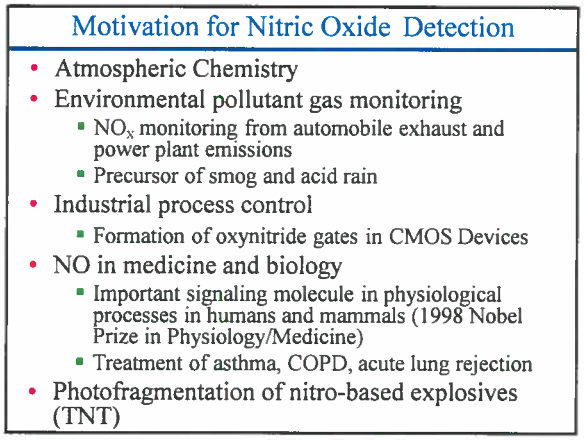


Merits of QEPAS based Trace Gas Detection

- Very small sensing module and sample volume (a few mm^3 to ~$2cm^2$)
- 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

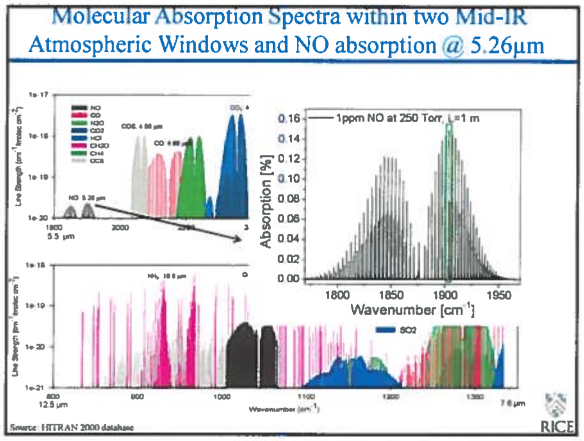
QEPAS: some challenges

- Cost of Spectrophone assembly
- Sensitivity scales with laser power
- Effect of H_2O
- Responsivity depends on the speed of sound and molecular energy transfer processes
- Cross sensitivity issues



Motivation for Nitric Oxide Detection

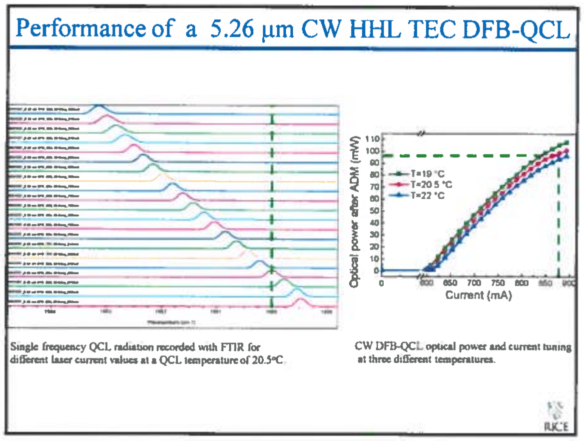
- Atmospheric Chemistry
- Environmental pollutant gas monitoring
  - NO_X monitoring from automobile exhaust and power plant emissions
  - Precursor of smog and acid rain
- Industrial process control
  - Formation of oxynitride gates in CMOS Devices
- NO in medicine and biology
  - Important signaling 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)



Molecular Absorption Spectra within two Mid-IR Atmospheric Windows and NO absorption @ 5.26µm

Source: HITRAN 2000 database

RICE



Performance of a 5.26 µm CW HHL TEC DFB-QCL

Single frequency QCL radiation recorded with FTIR for different laser current values at a QCL temperature of 20.5°C.

CW DFB-QCL optical power and current tuning at three different temperatures.

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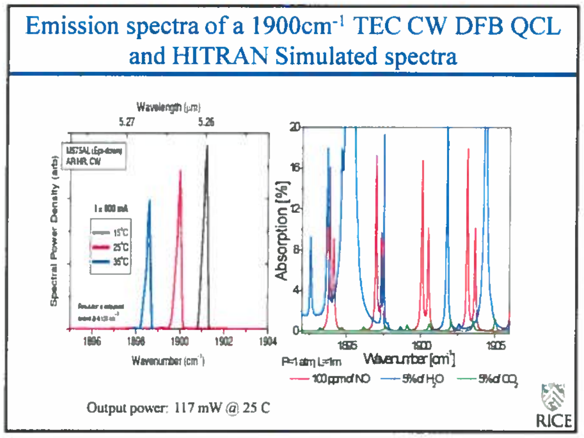

Emission spectra of a 1900cm^{-1} TEC CW DFB QCL and HITRAN Simulated spectra

Output power: 117 mW @ 25 C

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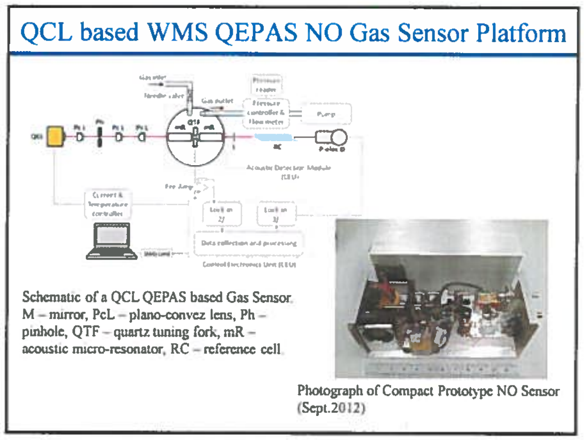
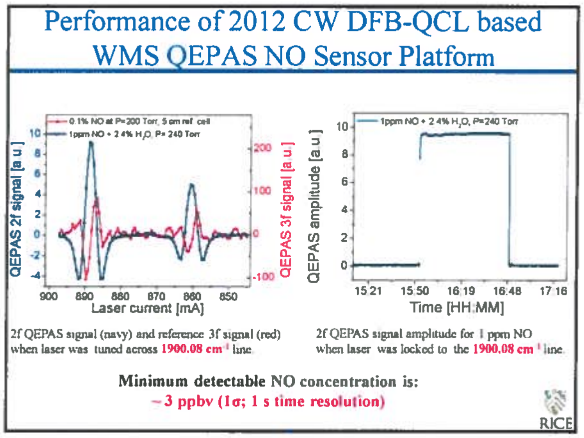


QCL based WMS QEPAS NO Gas Sensor Platform

Schematic of a QCL QEPAS based Gas Sensor. M – mirror, PcL – plano-convez lens, Ph – pinhole, QTF – quartz tuning fork, mR – acoustic micro-resonator, RC – reference cell.

Photograph of Compact Prototype NO Sensor (Sept.2012)



Performance of 2012 CW DFB-QCL based WMS QEPAS NO Sensor Platform

2f QEPAS signal (navy) and reference 3f signal (red) when laser was tuned across 1900.08 cm^{-1} line.

2f QEPAS signal amplitude for 1 ppm NO when laser was locked to the 1900.08 cm^{-1} line.

Minimum detectable NO concentration is:

~3 ppbv (1σ; 1 s time resolution)

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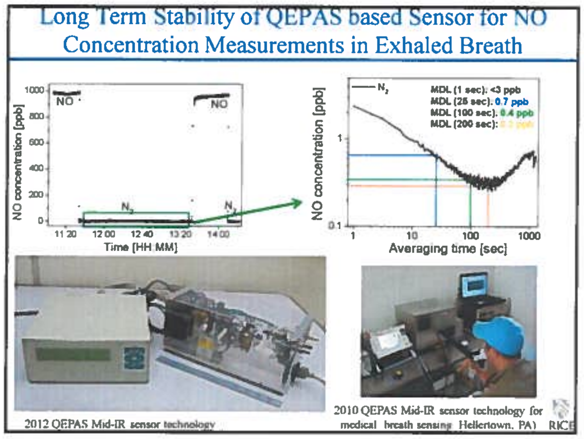

Long Term Stability of QEPAS based Sensor for NO Concentration Measurements in Exhaled Breath

MDL (1 sec): <3 ppb
MDL (25 sec): 0.7 ppb
MDL (100 sec): 0.4 ppb
MDL (200 sec): [illegible]

2012 QEPAS Mid-IR sensor technology

2010 QEPAS Mid-IR sensor technology for medical breath sensing Hellertown, PA)

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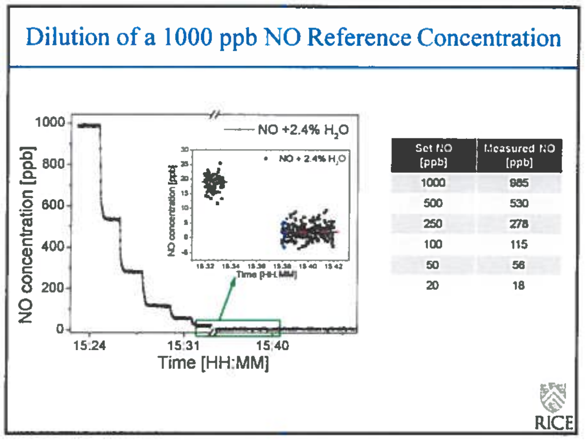
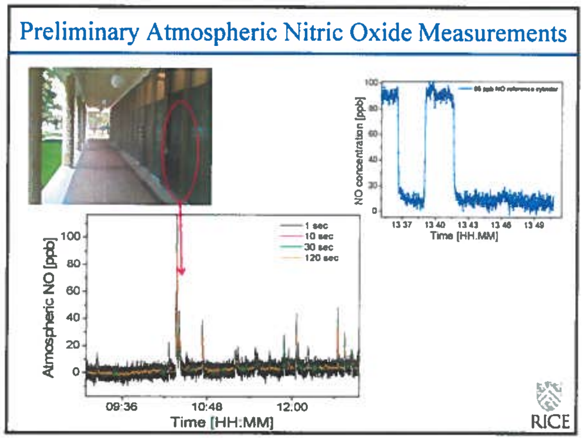
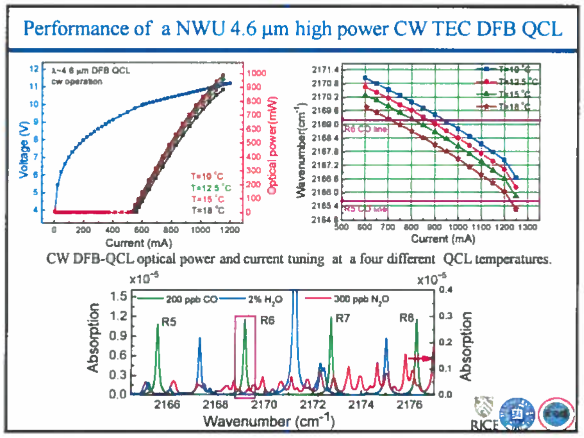


Dilution of a 1000 ppb NO Reference Concentration

Set NO [ppb]	Measured NO [ppb]
1000	985
500	530
250	278
100	115
50	56
20	18

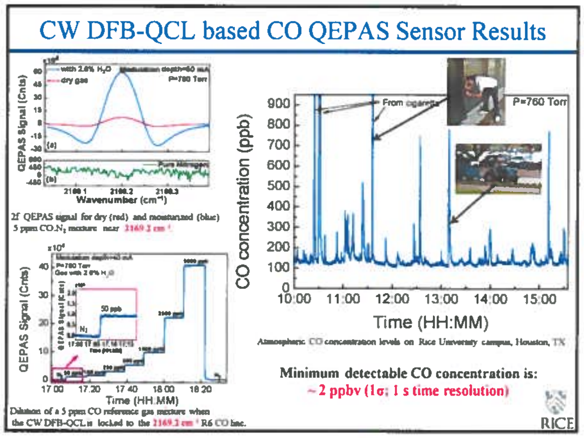


Preliminary Atmospheric Nitric Oxide Measurements



Performance of a NWU 4.6 μm high power CW TEC DFB QCL

CW DFB-QCL optical power and current tuning at a four different QCL temperatures.



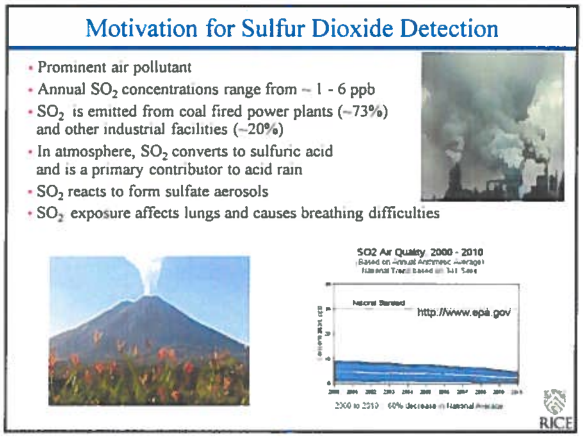
CW DFB-QCL based CO QEPAS Sensor Results

2f QEPAS signal for dry (red) and moisturized (blue) 5 ppm CO:N_2 mixture near 2169.2 cm⁻¹

Dilution of a 5 ppm CO reference gas mixture when the CW DFB-QCL is locked to the 2169.2 cm⁻¹ R6 CO line.

Atmospheric CO concentration levels on Rice University campus, Houston, TX

Minimum detectable CO concentration is:
~2 ppbv (1σ; 1 s time resolution)

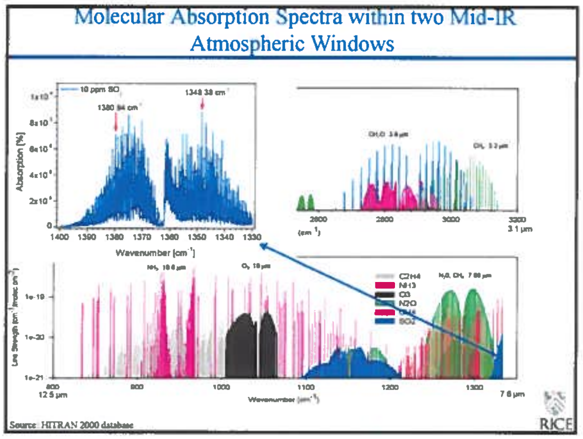


Motivation for Sulfur Dioxide Detection

- Prominent air pollutant
- Annual SO_2 concentrations range from ~ 1 - 6 ppb
- SO_2 is emitted from coal fired power plants (~73%) and other industrial facilities (~20%)
- In atmosphere, SO_2 converts to sulfuric acid and is a primary contributor to acid rain
- SO_2 reacts to form sulfate aerosols
- SO_2 exposure affects lungs and causes breathing difficulties

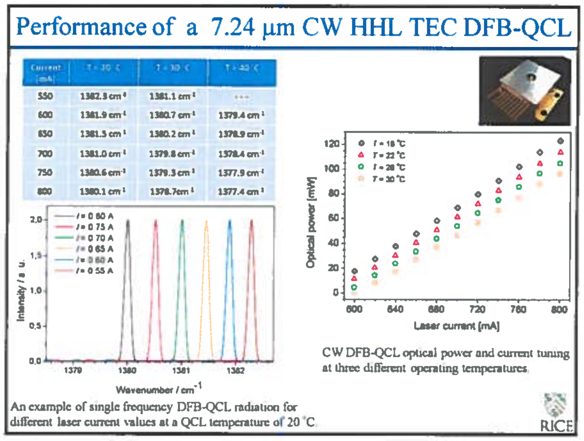
SO2 Air Quality, 2000 - 2010
(Based on Annual Arithmetic Average)
National Trend based on 341 Sites

2000 to 2010: 60% decrease in National Average



Molecular Absorption Spectra within two Mid-IR Atmospheric Windows

Source: HITRAN 2000 database

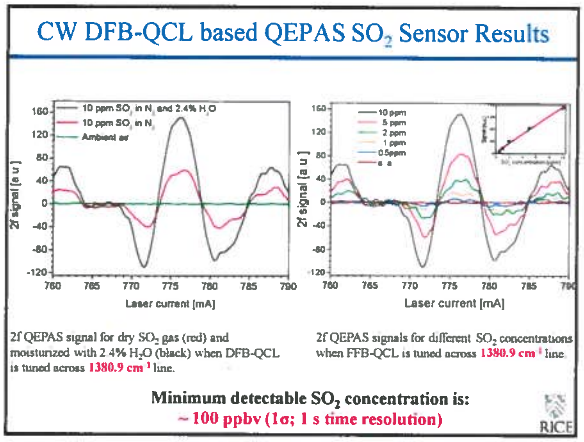


Performance of a 7.24 µm CW HHL TEC DFB-QCL

Current [mA]	T = 20 °C	T = 30 °C	T = 40 °C
550	1382.3 cm⁻¹	1381.1 cm⁻¹	---
600	1381.9 cm⁻¹	1380.7 cm⁻¹	1379.4 cm⁻¹
650	1381.5 cm⁻¹	1380.2 cm⁻¹	1378.9 cm⁻¹
700	1381.0 cm⁻¹	1379.8 cm⁻¹	1378.4 cm⁻¹
750	1380.6 cm⁻¹	1379.3 cm⁻¹	1377.9 cm⁻¹
800	1380.1 cm⁻¹	1378.7cm⁻¹	1377.4 cm⁻¹

An example of single frequency DFB-QCL radiation for different laser current values at a QCL temperature of 20 °C

CW DFB-QCL optical power and current tuning at three different operating temperatures

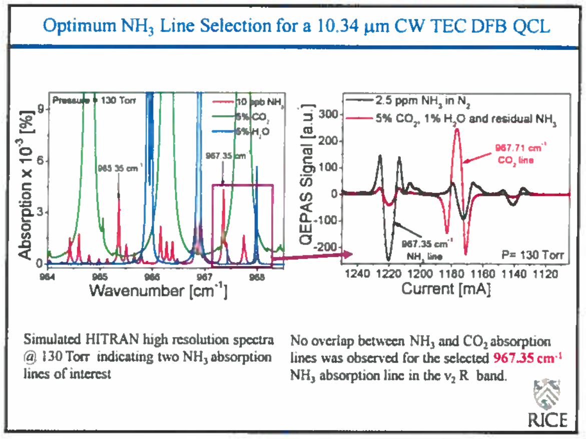


CW DFB-QCL based QEPAS SO_2 Sensor Results

2f QEPAS signal for dry SO_2 gas (red) and moisturized with 2.4% H_2O (black) when DFB-QCL is tuned across **1380.9 cm^{-1}** line.

2f QEPAS signals for different SO_2 concentrations when FFB-QCL is tuned across **1380.9 cm^{-1}** line

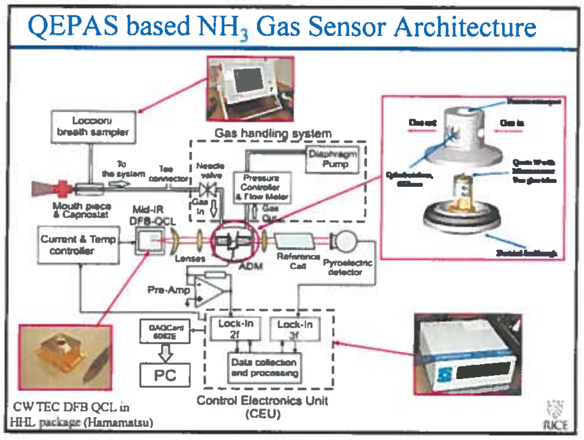
Minimum detectable SO_2 concentration is:
~ 100 ppbv (1σ; 1 s time resolution)



Optimum NH_3 Line Selection for a 10.34 µm CW TEC DFB QCL

Simulated HITRAN high resolution spectra @ 130 Torr indicating two NH_3 absorption lines of interest

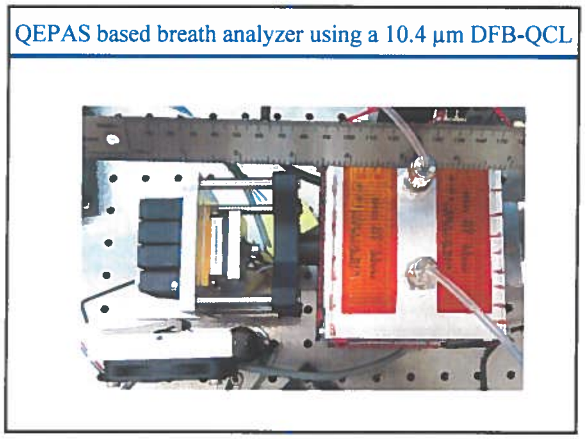
No overlap between NH_3 and CO_2 absorption lines was observed for the selected **967.35 cm^{-1}** NH_3 absorption line in the v_2 R band.



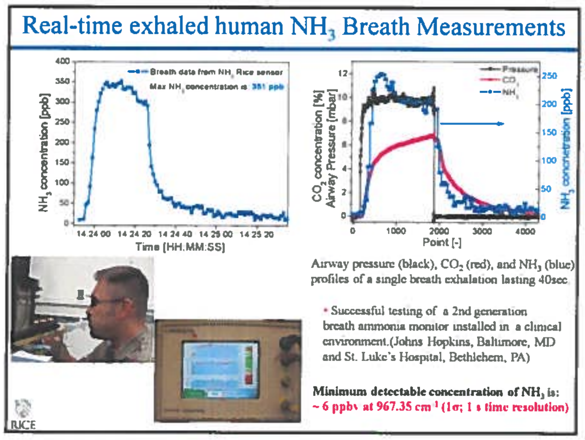
QEPAS based NH_3 Gas Sensor Architecture

CW TEC DFB QCL in HHL package (Hamamatsu)

Control Electronics Unit (CEU)



QEPAS based breath analyzer using a 10.4 µm DFB-QCL

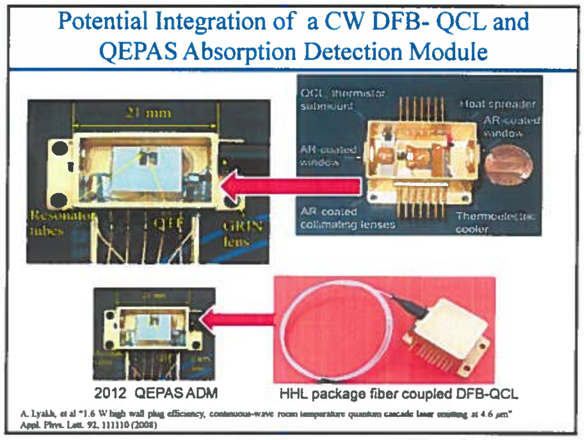


Real-time exhaled human NH_3 Breath Measurements

Airway pressure (black), CO_2 (red), and NH_3 (blue) profiles of a single breath exhalation lasting 40sec

- Successful testing of a 2nd generation breath ammonia monitor installed in a clinical environment.(Johns Hopkins, Baltimore, MD and St. Luke's Hospital, Bethlehem, PA)

Minimum detectable concentration of NH_3 is:
~ 6 ppbv at 967.35 cm^{-1} (1σ; 1 s time resolution)

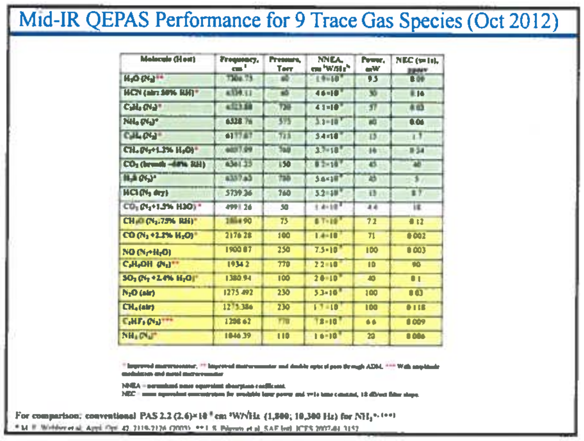


Potential Integration of a CW DFB- QCL and QEPAS Absorption Detection Module

2012 QEPAS ADM

HHL package fiber coupled DFB-QCL

A. Lyakh, et al "1.6 W high wall plug efficiency, continuous-wave room temperature quantum cascade laser emitting at 4.6 μm" Appl. Phys. Lett. 92, 111110 (2008)



Mid-IR QEPAS Performance for 9 Trace Gas Species (Oct 2012)

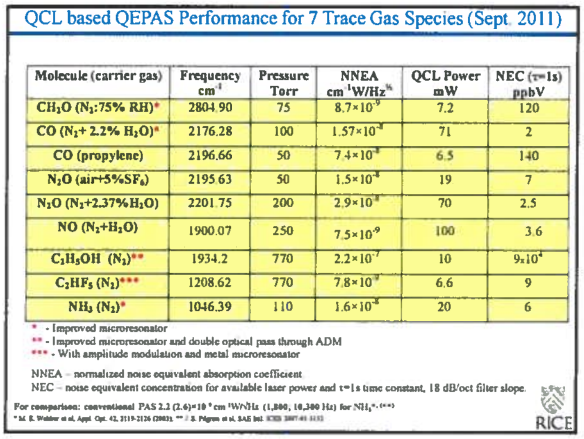
Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, $cm^{-1}W/Hz^{½}$	Power, mW	NEC (τ=1s), ppmv
H_2O (N_2)**	7306.75	60	1.9×10[illegible]	9.5	0.09
HCN (air: 50% RH)*	6539.11	60	4.6×10[illegible]	50	0.16
C_2H_2 (N_2)*	6523.88	720	4.1×10[illegible]	57	0.03
NH_3 (N_2)*	6528.76	575	3.1×10[illegible]	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+2.2% H_2O)*	2176.28	100	1.4×10[illegible]	71	0.002
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
SO_2 (N_2+2.4% H_2O)*	1380.94	100	2.0×10[illegible]	40	0.1
N_2O (air)	1275.492	230	5.3×10[illegible]	100	0.03
CH_4 (air)	1275.386	230	1.7×10[illegible]	100	0.118
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



QCL based QEPAS Performance for 7 Trace Gas Species (Sept. 2011)

Molecule (carrier gas)	Frequency cm^{-1}	Pressure Torr	NNEA $cm^{-1}W/Hz^{½}$	QCL Power mW	NEC (τ=1s) ppbV
CH_2O (N_2:75% RH)*	2804.90	75	8.7×10^{-9}	7.2	120
CO (N_2+ 2.2% H_2O)*	2176.28	100	1.57×10^{-8}	71	2
CO (propylene)	2196.66	50	7.4×10^{-8}	6.5	140
N_2O (air+5%SF_6)	2195.63	50	1.5×10^{-8}	19	7
N_2O (N_2+2.37%H_2O)	2201.75	200	2.9×10^{-8}	70	2.5
NO (N_2+H_2O)	1900.07	250	7.5×10^{-9}	100	3.6
C_2H_5OH (N_2)**	1934.2	770	2.2×10^{-7}	10	9×10^{4}
C_2HF_5 (N_2)***	1208.62	770	7.8×10^{-9}	6.6	9
NH_3 (N_2)*	1046.39	110	1.6×10^{-8}	20	6

* - 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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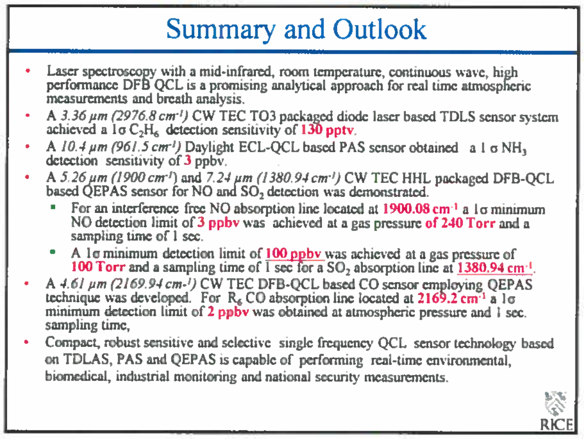

Summary and Outlook

- Laser spectroscopy with a mid-infrared, room temperature, continuous wave, high performance DFB QCL is a promising analytical approach for real time atmospheric measurements and breath analysis.
- A *3.36 μm (2976.8 cm^{-1})* CW TEC TO3 packaged diode laser based TDLS sensor system achieved a 1σ C_2H_6 detection sensitivity of **130 pptv**.
- A *10.4 μm (961.5 cm^{-1})* Daylight ECL-QCL based PAS sensor obtained a 1 σ NH_3 detection sensitivity of **3** ppbv.
- A *5.26 μm (1900 cm^{-1})* and *7.24 μm (1380.94 cm^{-1})* CW TEC HHL packaged DFB-QCL based QEPAS sensor for NO and SO_2 detection was demonstrated.
  - For an interference free NO absorption line located at **1900.08 cm^{-1}** a 1σ minimum NO detection limit of **3 ppbv** was achieved at a gas pressure **of 240 Torr** and a sampling time of 1 sec.
  - A 1σ minimum detection limit of **100 ppbv** was achieved at a gas pressure of **100 Torr** and a sampling time of 1 sec for a SO_2 absorption line at **1380.94 cm^{-1}**.
- A *4.61 μm (2169.94 cm-^{1})* CW TEC DFB-QCL based CO sensor employing QEPAS technique was developed. For R_6 CO absorption line located at **2169.2 cm^{-1}** a 1σ minimum detection limit of **2 ppbv** was obtained at atmospheric pressure and 1 sec. sampling time,
- Compact, robust sensitive and selective single frequency QCL sensor technology based on TDLAS, PAS and QEPAS is capable of performing real-time environmental, biomedical, industrial monitoring and national security measurements.

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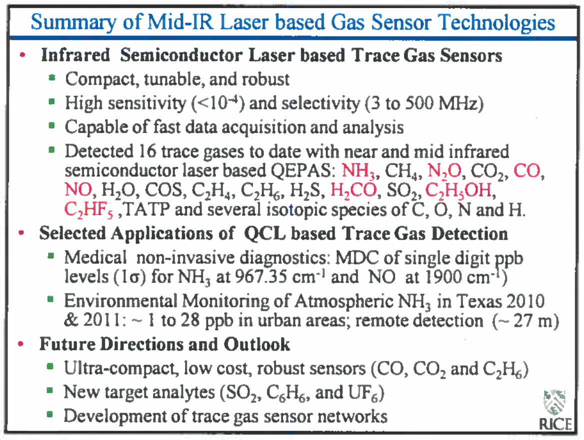

Summary of Mid-IR Laser based Gas Sensor Technologies

- **Infrared 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 16 trace gases to date with near and mid infrared semiconductor laser based QEPAS: NH_3, CH_4, N_2O, CO_2, CO, NO, H_2O, COS, C_2H_4, C_2H_6, H_2S, H_2CO, SO_2, C_2H_5OH, C_2HF_5 ,TATP and several isotopic species of C, O, N and H.
- **Selected Applications of QCL based Trace Gas Detection**
  - Medical non-invasive diagnostics: MDC of single digit ppb levels (1σ) for NH_3 at 967.35 cm^{-1} and NO at 1900 cm^{-1})
  - Environmental Monitoring of Atmospheric NH_3 in Texas 2010 & 2011: ~ 1 to 28 ppb in urban areas; remote detection (~ 27 m)
- **Future Directions and Outlook**
  - Ultra-compact, low cost, robust sensors (CO, CO_2 and C_2H_6)
  - New target analytes (SO_2, C_6H_6, and UF_6)
  - Development of trace gas sensor networks

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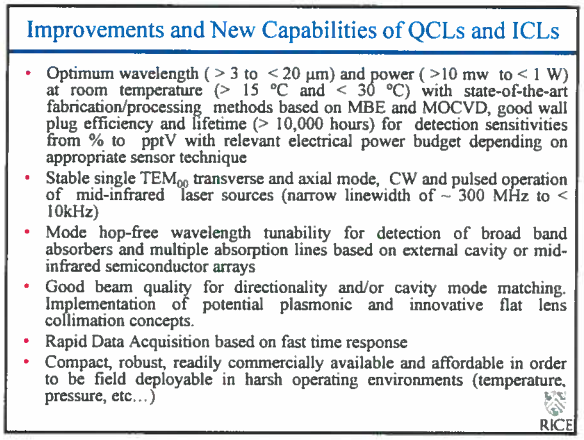

Improvements and New Capabilities of QCLs and ICLs

- Optimum wavelength (> 3 to < 20 μm) and power (>10 mw to < 1 W) at room temperature (> 15 °C and < 30 °C) with state-of-the-art fabrication/processing methods based on MBE and MOCVD, good wall plug efficiency and lifetime (> 10,000 hours) for detection sensitivities from % to pptV with relevant electrical power budget depending on appropriate sensor technique
- Stable single TEM_{00} transverse and axial mode, CW and pulsed operation of mid-infrared laser sources (narrow linewidth of ~ 300 MHz to < 10kHz)
- Mode hop-free wavelength tunability for detection of broad band absorbers and multiple absorption lines based on external cavity or mid-infrared semiconductor arrays
- Good beam quality for directionality and/or cavity mode matching. Implementation of potential plasmonic and innovative flat lens collimation concepts.
- Rapid Data Acquisition based on fast time response
- Compact, robust, readily commercially available and affordable in order to be field deployable in harsh operating environments (temperature, pressure, etc…)

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