Mid-infrared semiconductor laser based trace gas technologies: recent advances and applications

F. K. Tittel[1], R. Lewicki[1,4], M. Jahjah[1], P. Stefanski[1,4], J. Tarka[1,4], W. Jiang[1], W. Ren[1], N. Sanchez[2], R. Griffin[2], S. So[4], D Thomazy[4], V. Spagnolo[6], P. Patimisco[1,6], J. Zhang[1,7], S. Herndon[5]
[1] Department of Electrical and Computer Engineering, Rice University, 6100 Main St., Houston, TX 77005, USA
[2] Department of Civil and Environmental Engineering, Rice University, 6100 Main St., Houston, TX 77005, USA
[3] Laser & Fiber Electronics Group, Wroclaw University of Technology, Wroclaw, Poland
[4] Sentinel Photonics, Monmouth Junction, NJ 08852, USA
[5] Aerodyne Inc., Billerica, MA 01821, USA
[6] Physics Dept., University and Politecnico of Bari, 70126 Bari, Italy
[7] Northeast Forestry University, Department of Electromechanical Engineering, Harbin, China
www.ece.rice.edu/lasersci

OUTLINE

Lasers, Optics & Photonics

San Antonio, TX

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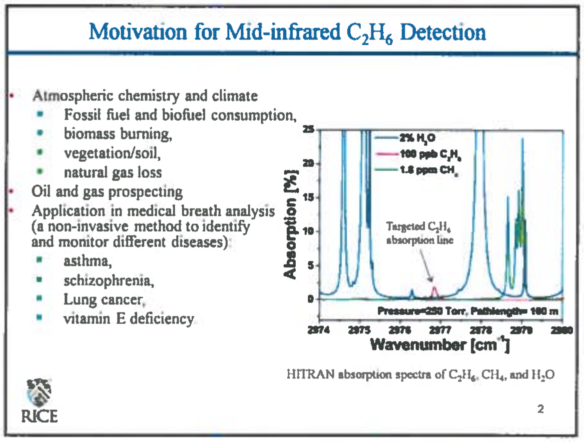
- New Laser Based Trace Gas Sensor Technology
  - Novel Multipass Absorption Cell & Electronics
  - Quartz Enhanced Photoacoustic Spectroscopy
- Four Examples of Mid-Infrared Sensor Architectures
  - C_2H_6, NO, CO and CH_4
  - Future Directions of Laser Based Gas Sensor Technology and Conclusions

Research support by NSF ERC MIRTHE, NSF-ANR NexCILAS, the Robert Welch Foundation, Scinovation, Inc., and Sentinel Photonics Inc. via an EPA Phase I SBIR sub-award is acknowledged



Motivation for Mid-infrared C_2H_6 Detection

- Atmospheric chemistry and climate
  - Fossil fuel and biofuel consumption,
  - biomass burning,
  - vegetation/soil,
  - natural gas loss
- Oil and gas prospecting
- Application in medical breath analysis (a non-invasive method to identify and monitor different diseases):
  - asthma,
  - schizophrenia,
  - Lung cancer,
  - vitamin E deficiency

HITRAN absorption spectra of C_2H_6, CH_4, and H_2O

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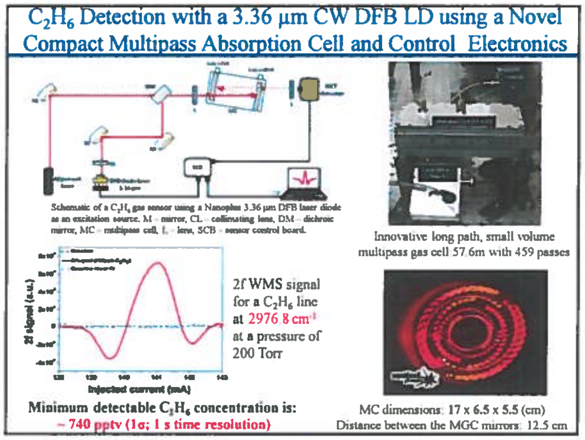


C_2H_6 Detection with a 3.36 µm CW DFB LD using a Novel Compact Multipass Absorption Cell and Control Electronics

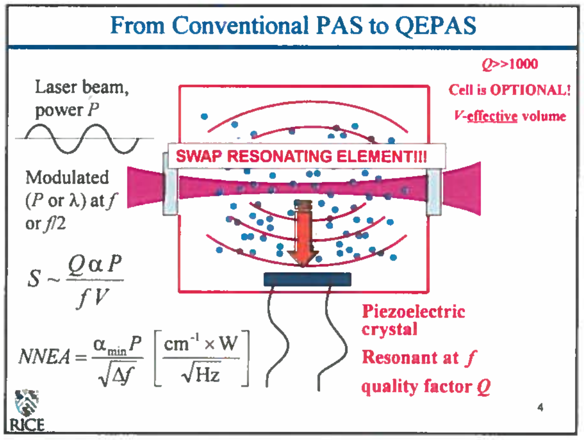
Schematic of a C_2H_6 gas sensor using a Nanoplus 3.36 µm DFB laser diode as an excitation source. M – mirror, CL – collimating lens, DM – dichroic mirror, MC – multipass cell, L – lens, SCB – sensor control board.

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

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

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

Minimum detectable C_2H_6 concentration is:
~ 740 pptv (1σ; 1 s time resolution)



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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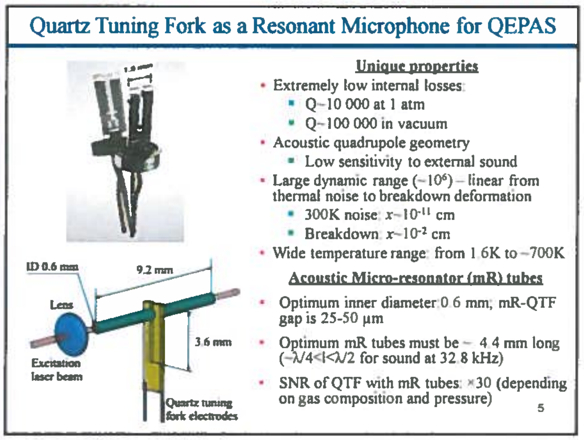


Quartz Tuning Fork as a Resonant Microphone for QEPAS

Unique properties

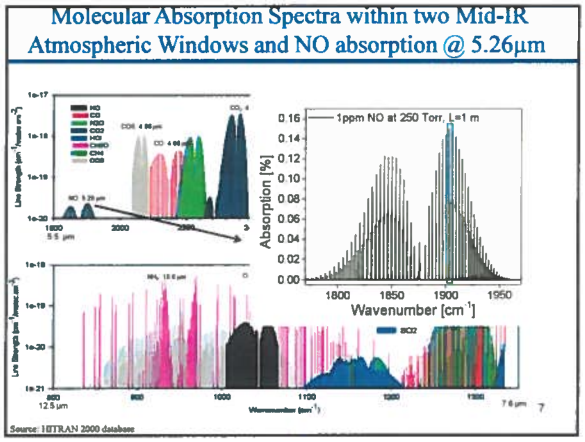
- Extremely low internal losses:
  - Q~10 000 at 1 atm
  - Q~100 000 in vacuum
- Acoustic quadrupole geometry
  - Low sensitivity to external sound
- Large dynamic range (~10^6) – linear from thermal noise to breakdown deformation
  - 300K noise: x~10^{-11} cm
  - Breakdown: x~10^{-2} cm
- Wide temperature 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)

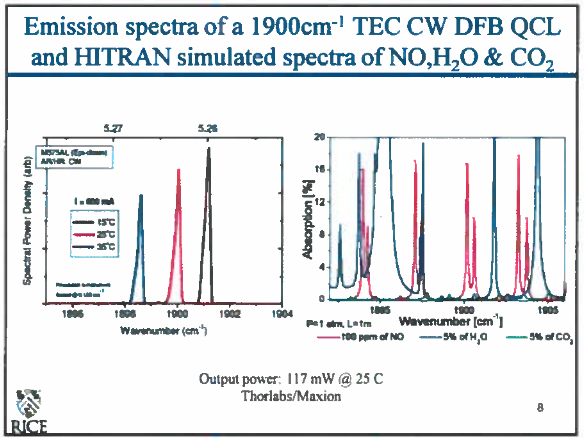
Motivation for Nitric Oxide Detection

- 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



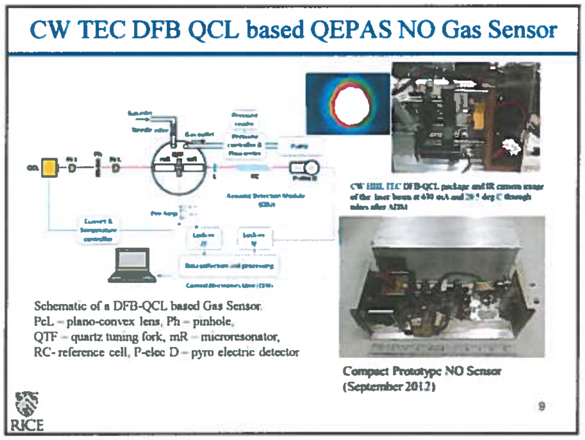
Molecular Absorption Spectra within two Mid-IR Atmospheric Windows and NO absorption @ 5.26μm

Source: HITRAN 2000 database



Emission spectra of a 1900cm^{-1} TEC CW DFB QCL and HITRAN simulated spectra of NO,H_2O & CO_2

Output power: 117 mW @ 25 C
Thorlabs/Maxion

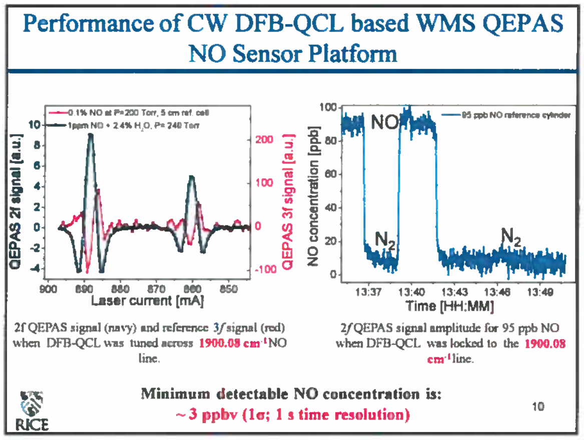


CW TEC DFB QCL based QEPAS NO Gas Sensor

CW HHL TEC DFB-QCL package and IR camera image of the laser beam at 430 mA and 20 deg C through

Schematic of a DFB-QCL based Gas Sensor.
PcL – plano-convex lens, Ph – pinhole,
QTF – quartz tuning fork, mR – microresonator,
RC- reference cell, P-elec D – pyro electric detector

Compact Prototype NO Sensor
(September 2012)



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

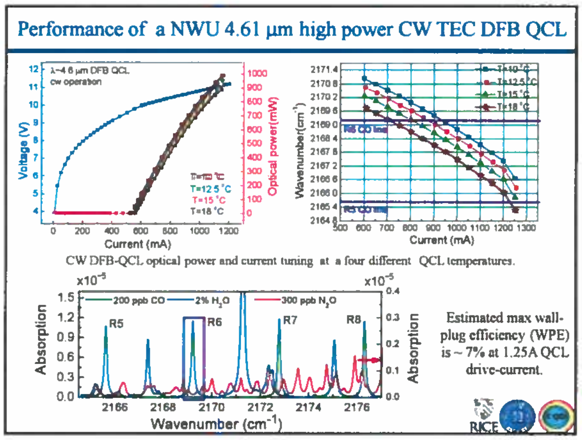
2f QEPAS signal (navy) and reference 3f signal (red) when DFB-QCL was tuned across **1900.08 cm^{-1}** NO line.

2f QEPAS signal amplitude for 95 ppb NO when DFB-QCL was locked to the **1900.08 cm^{-1}** line.

Minimum detectable NO concentration is:
~ 3 ppbv (1σ; 1 s time resolution)

Motivation for Carbon Monoxide Detection

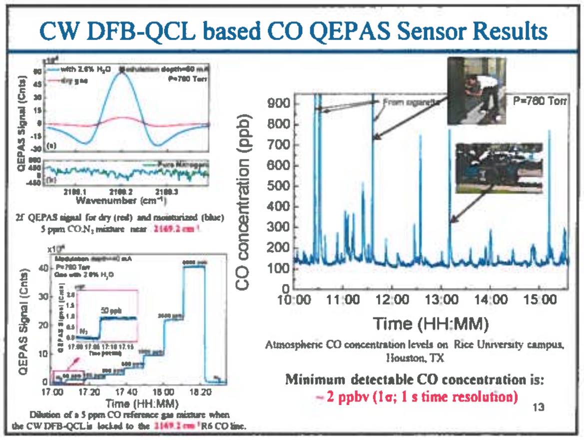
- Atmospheric Chemistry
  - Incomplete combustion of natural gas, fossil fuel and other carbon containing fuels.
  - Impact on atmospheric chemistry through its reaction with hydroxyl (OH) for troposphere ozone formation and changing the level of greenhouse gases (e.g. CH_4).
- Public Health
  - Extremely dangerous to human life even at a low concentrations. Therefore CO must be carefully monitored at low concentration levels.
- CO in medicine and biology
  - Hypertension, neurodegenerations, heart failure and inflammation have been linked to abnormality in CO metabolism and function.



Performance of a NWU 4.61 μm high power CW TEC DFB QCL

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

Estimated max wall-plug efficiency (WPE) is ~ 7% at 1.25A QCL drive-current.



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)

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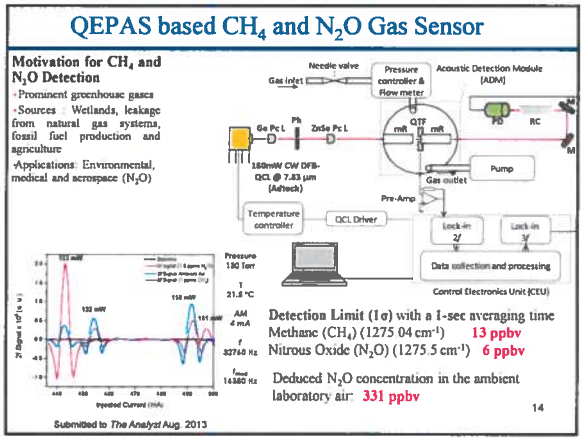

QEPAS based CH_4 and N_2O Gas Sensor

Motivation for CH_4 and N_2O Detection

- Prominent greenhouse gases
- Sources : Wetlands, leakage from natural gas systems, fossil fuel production and agriculture
- Applications: Environmental, medical and aerospace (N_2O)

Detection Limit (1σ) with a 1-sec averaging time
Methane (CH_4) (1275.04 cm^{-1}) **13 ppbv**
Nitrous Oxide (N_2O) (1275.5 cm^{-1}) **6 ppbv**

Deduced N_2O concentration in the ambient laboratory air: **331 ppbv**

Submitted to *The Analyst* Aug. 2013

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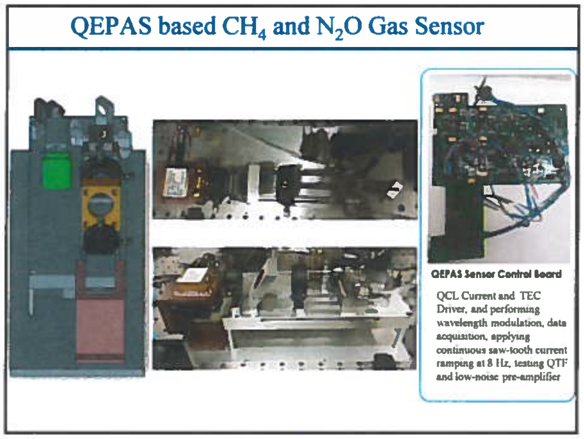
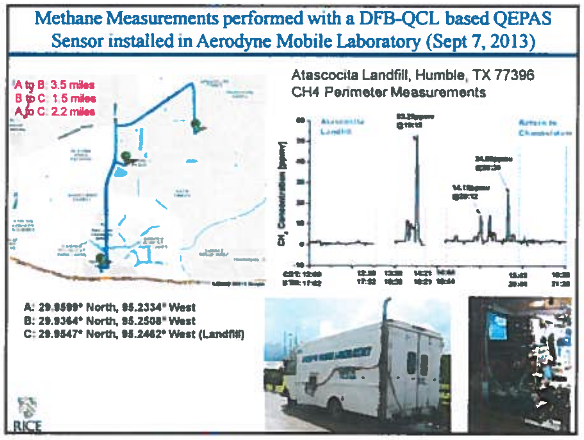


QEPAS based CH_4 and N_2O Gas Sensor

QEPAS Sensor Control Board

QCL Current and TEC Driver, and performing wavelength modulation, data acquisition, applying continuous saw-tooth current ramping at 8 Hz, testing QTF and low-noise pre-amplifier



Methane Measurements performed with a DFB-QCL based QEPAS Sensor installed in Aerodyne Mobile Laboratory (Sept 7, 2013)

A to B: 3.5 miles
B to C: 1.5 miles
A to C: 2.2 miles

Atascocita Landfill, Humble, TX 77396
CH4 Perimeter Measurements

A: 29.9599° North, 95.2334° West
B: 29.9364° North, 95.2508° West
C: 29.9547° North, 95.2462° West (Landfill)

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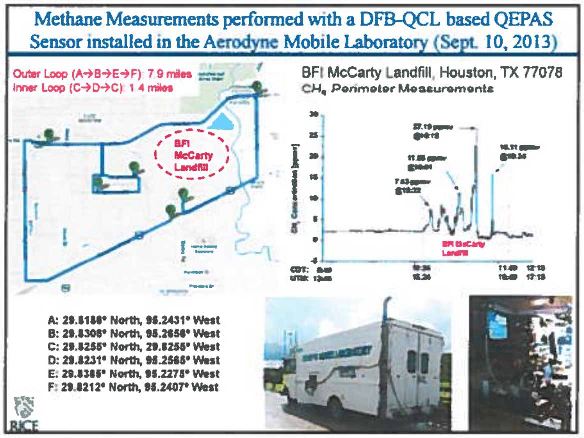

Methane Measurements performed with a DFB-QCL based QEPAS Sensor installed in the Aerodyne Mobile Laboratory (Sept. 10, 2013)

Outer Loop (A→B→E→F): 7.9 miles
Inner Loop (C→D→C): 1.4 miles

BFI McCarty Landfill, Houston, TX 77078
CH_4 *Perimeter Measurements*

A: 29.8186° North, 95.2431° West
B: 29.8306° North, 95.2656° West
C: 29.8255° North, 29.8255° West
D: 29.8231° North, 95.2565° West
E: 29.8385° North, 95.2275° West
F: 29.8212° North, 95.2407° West

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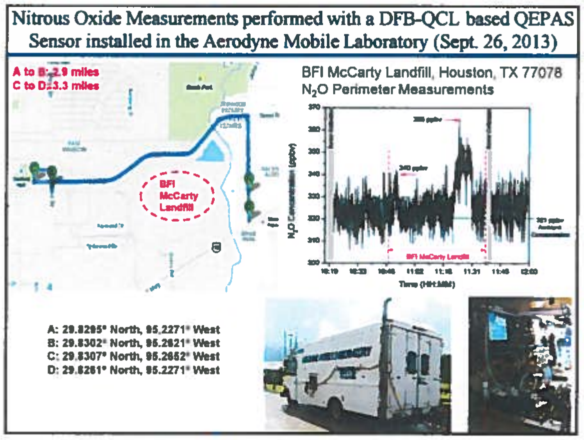
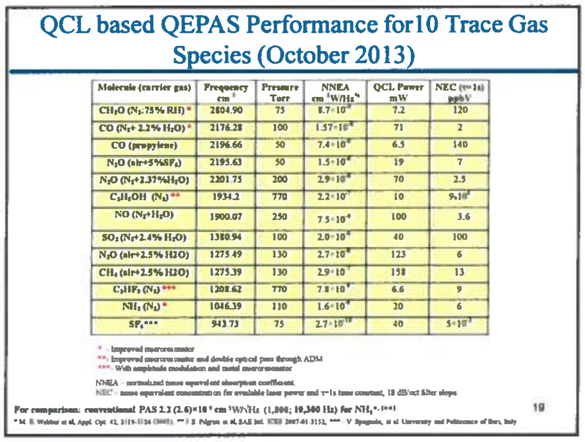


Nitrous Oxide Measurements performed with a DFB-QCL based QEPAS Sensor installed in the Aerodyne Mobile Laboratory (Sept. 26, 2013)

A to B: 2.9 miles
C to D: 3.3 miles

BFI McCarty Landfill, Houston, TX 77078
N_2O Perimeter Measurements

A: 29.8295° North, 95.2271° West
B: 29.8302° North, 95.2621° West
C: 29.8307° North, 95.2652° West
D: 29.8261° North, 95.2271° West



QCL based QEPAS Performance for10 Trace Gas Species (October 2013)

Molecule (carrier gas)	Frequency cm^{-1}	Pressure Torr	NNEA $cm^{-1}W/Hz^{1/2}$	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
C_2H_5OH (N_2) **	1934.2	770	2.2×10^{-7}	10	9×10^{4}
NO (N_2+H_2O)	1900.07	250	7.5×10^{-9}	100	3.6
SO_2 (N_2+2.4% H_2O)	1380.94	100	2.0×10^{-8}	40	100
N_2O (air+2.5% H2O)	1275.49	130	2.7×10^{-8}	123	6
CH_4 (air+2.5% H2O)	1275.39	130	2.9×10^{-7}	158	13
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
SF_6***	943.73	75	2.7×10^{-10}	40	5×10^{-2}

* - Improved microresonator

**- Improved microresonator and double optical pass through ADM

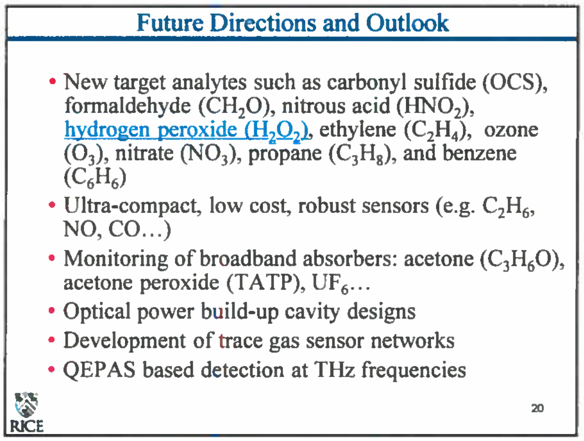
***- With amplitude modulation and metal microresonator

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⁻¹W/√Hz (1,000; 10,300 Hz) for NH_3*,(**)

* M. E. Webber et al, Appl. Opt. 42, 2119-2126 (2003); ** J. S. Pilgrim et al, SAE Intl. ICES 2007-01-3152; *** - V. Spagnolo, et al University and Politecnico of Bari, Italy



Future Directions and Outlook

- New target analytes such as carbonyl sulfide (OCS), formaldehyde (CH_2O), nitrous acid (HNO_2), hydrogen peroxide (H_2O_2), ethylene (C_2H_4), ozone (O_3), nitrate (NO_3), propane (C_3H_8), and benzene (C_6H_6)
- Ultra-compact, low cost, robust sensors (e.g. C_2H_6, NO, CO…)
- Monitoring of broadband absorbers: acetone (C_3H_6O), acetone peroxide (TATP), UF_6…
- Optical power build-up cavity designs
- Development of trace gas sensor networks
- QEPAS based detection at THz frequencies

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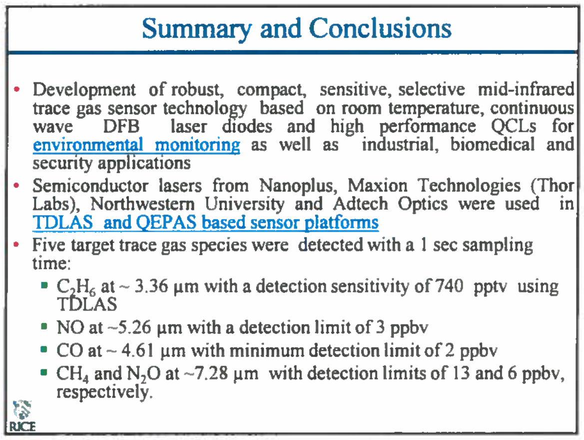

Summary and Conclusions

- Development of robust, compact, sensitive, selective mid-infrared trace gas sensor technology based on room temperature, continuous wave DFB laser diodes and high performance QCLs for environmental monitoring as well as industrial, biomedical and security applications
- Semiconductor lasers from Nanoplus, Maxion Technologies (Thor Labs), Northwestern University and Adtech Optics were used in TDLAS and QEPAS based sensor platforms
- Five target trace gas species were detected with a 1 sec sampling time:
  - C_2H_6 at ~ 3.36 µm with a detection sensitivity of 740 pptv using TDLAS
  - NO at ~5.26 µm with a detection limit of 3 ppbv
  - CO at ~ 4.61 µm with minimum detection limit of 2 ppbv
  - CH_4 and N_2O at ~7.28 µm with detection limits of 13 and 6 ppbv, respectively.

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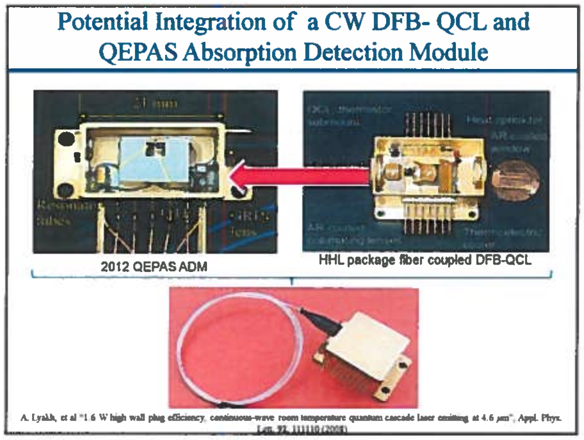
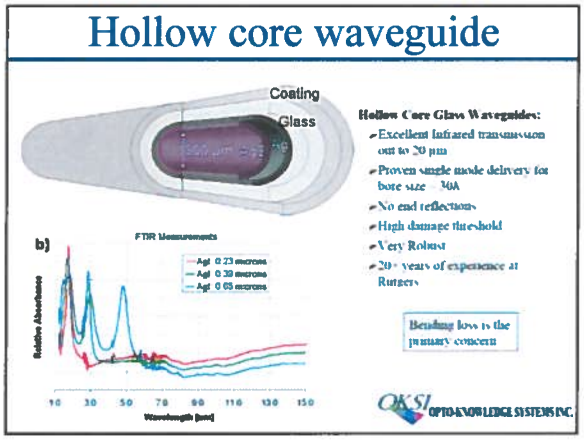


Potential Integration of a CW DFB- QCL and QEPAS Absorption Detection Module

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)



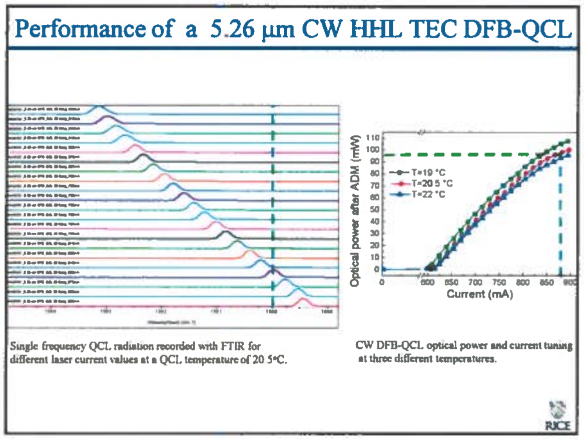
Hollow core waveguide

Hollow Core Glass Waveguides:

- Excellent Infrared transmission out to 20 µm
- Proven single mode delivery for bore size ~ 30λ
- No end reflections
- High damage threshold
- Very Robust
- 20+ years of experience at Rutgers

Bending loss is the primary concern

OKSI OPTO-KNOWLEDGE SYSTEMS INC.



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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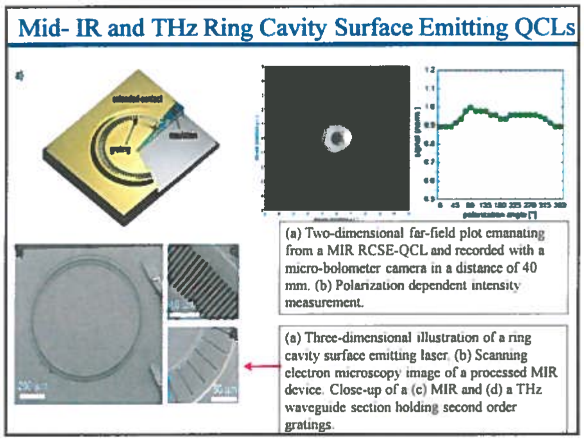
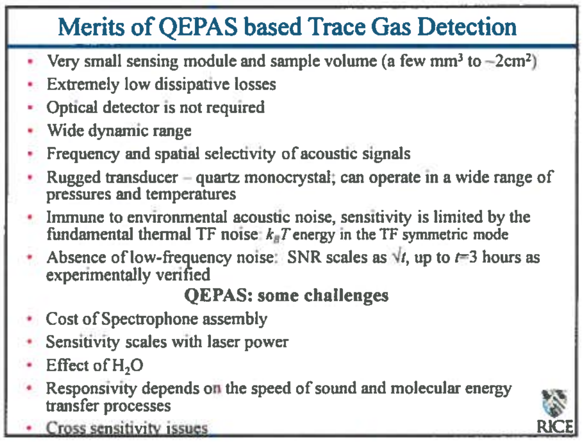


Mid- IR and THz Ring Cavity Surface Emitting QCLs

(a) Two-dimensional far-field plot emanating from a MIR RCSE-QCL and recorded with a micro-bolometer camera in a distance of 40 mm. (b) Polarization dependent intensity measurement.

(a) Three-dimensional illustration of a ring cavity surface emitting laser. (b) Scanning electron microscopy image of a processed MIR device. Close-up of a (c) MIR and (d) a THz waveguide section holding second order gratings.



Merits of QEPAS based Trace Gas Detection

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

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