Mid-IR Laser Based Trace Gas Sensor Technologies: Recent Advances and Applications in Environmental Monitoring and Medical Diagnostics

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OUTLINE

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- 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

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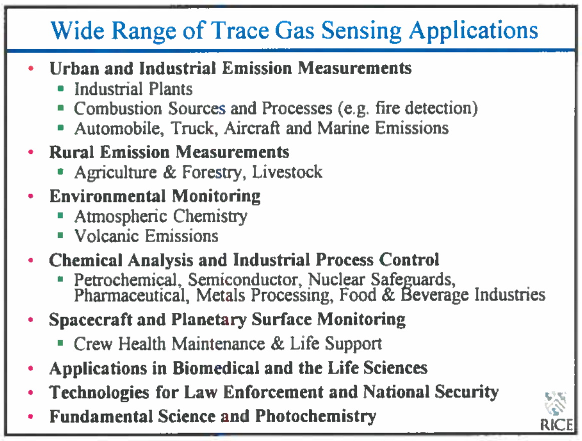

Wide Range of Trace Gas Sensing Applications

- **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**

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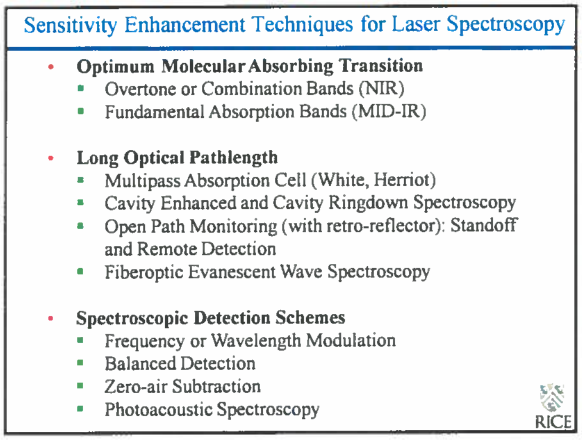

Sensitivity Enhancement Techniques for Laser Spectroscopy

- **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

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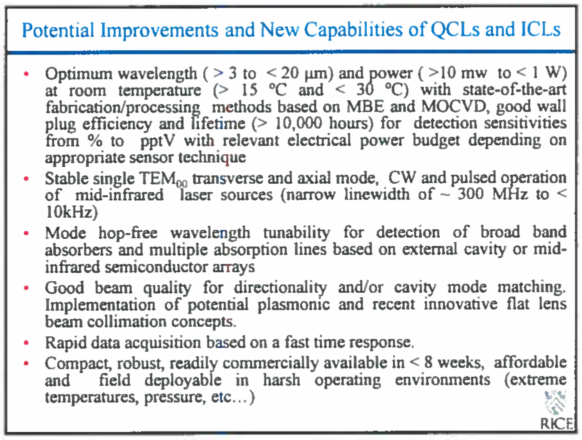

Potential Improvements and New Capabilities of QCLs and ICLs

- 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 recent innovative flat lens beam collimation concepts.
- Rapid data acquisition based on a fast time response.
- Compact, robust, readily commercially available in < 8 weeks, affordable and field deployable in harsh operating environments (extreme temperatures, pressure, etc…)

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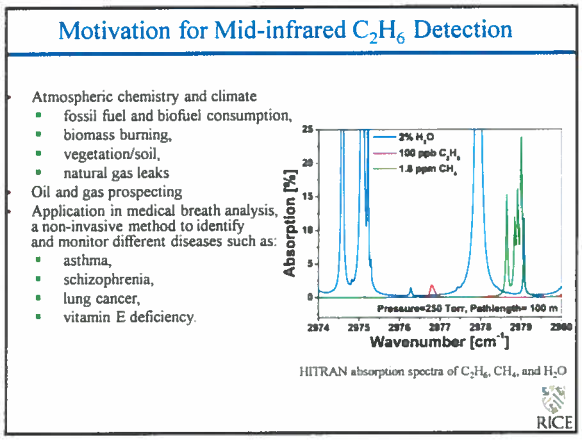

Motivation for Mid-infrared C_2H_6 Detection

- Atmospheric chemistry and climate
  - fossil fuel and biofuel consumption,
  - biomass burning,
  - vegetation/soil,
  - natural gas leaks
- Oil and gas prospecting
- Application in medical breath analysis, a non-invasive method to identify and monitor different diseases such as:
  - asthma,
  - schizophrenia,
  - lung cancer,
  - vitamin E deficiency.

HITRAN absorption spectra of C_2H_6, CH_4, and H_2O

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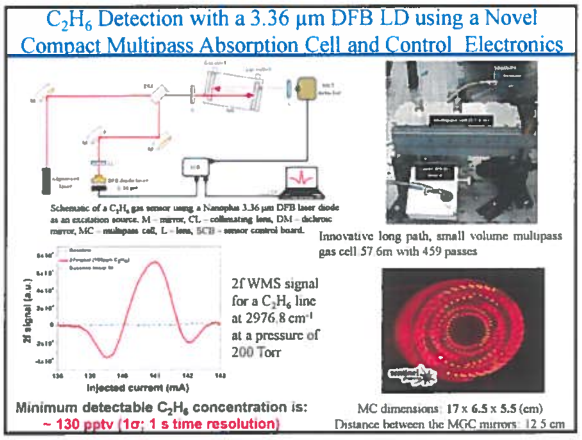


C_2H_6 Detection with a 3.36 µm DFB LD using a Novel Compact Multipass Absorption Cell and Control Electronics

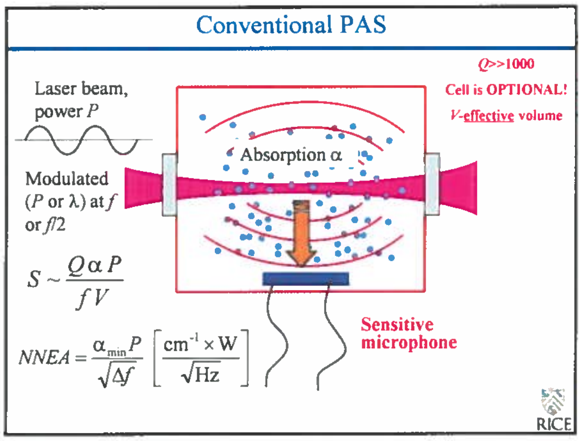
Schematic of a C_2H_6 gas sensor using a Nanoplus 3.36 µm DFB laser diode as an excitation source. M – mirror, CL – collimating lens, DM – dichroic mirror, MC – multipass cell, L – lens, SCB – sensor control board.

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

Minimum detectable C_2H_6 concentration is:
~ 130 pptv (1σ; 1 s time resolution)

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



Conventional PAS

Laser beam, power *P*

Modulated (P or λ) at f or $f/2$

Absorption α

Q>>1000

Cell is OPTIONAL!

***V*-effective volume**

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

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

Sensitive microphone

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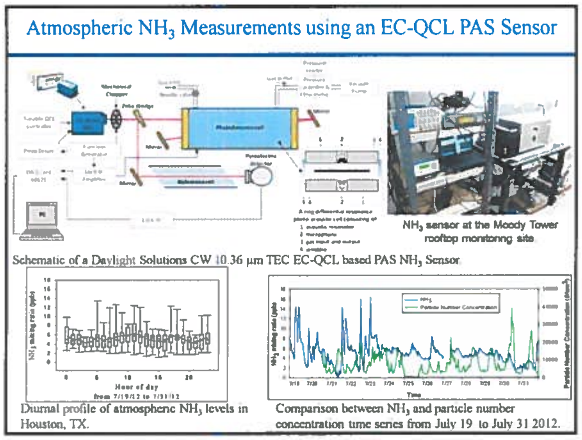


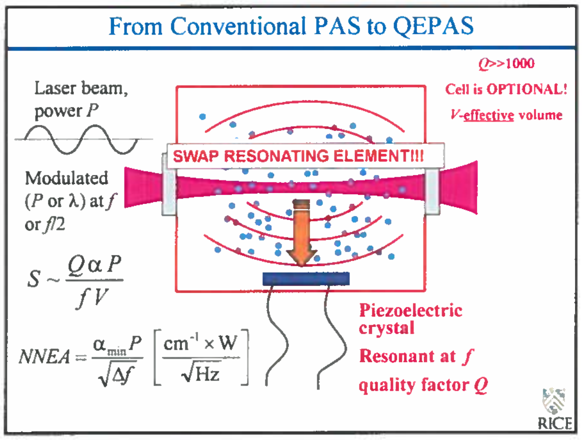
Atmospheric NH_3 Measurements using an EC-QCL PAS Sensor

NH_3 sensor at the Moody Tower rooftop monitoring site

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 to July 31 2012.



From Conventional PAS to QEPAS

Laser beam, power *P*

Modulated (P or λ) at f or $f/2$

SWAP RESONATING ELEMENT!!!

Q>>1000

Cell is OPTIONAL!

***V*-effective volume**

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

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

Piezoelectric crystal

Resonant at *f*

quality factor *Q*

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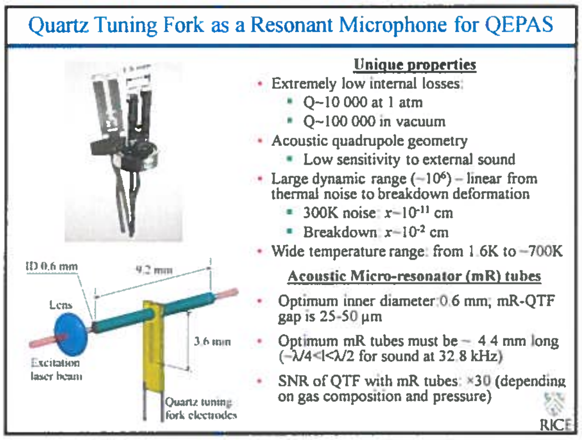

Quartz Tuning Fork as a Resonant Microphone for QEPAS

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)

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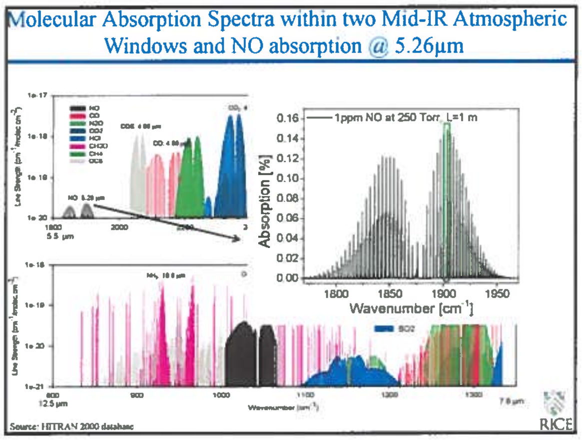

Molecular Absorption Spectra within two Mid-IR Atmospheric Windows and NO absorption @ 5.26µm

Source: HITRAN 2000 database

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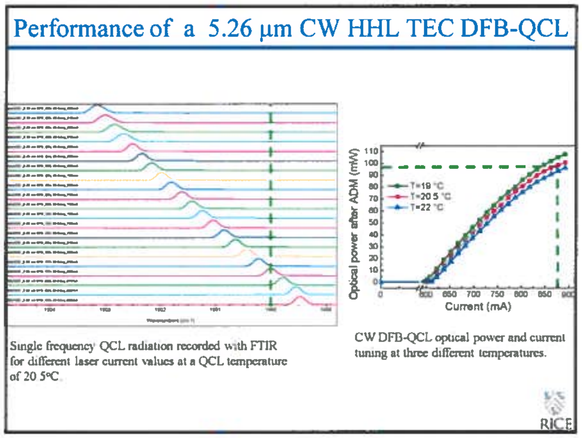

Performance of a 5.26 µm CW HHL TEC DFB-QCL

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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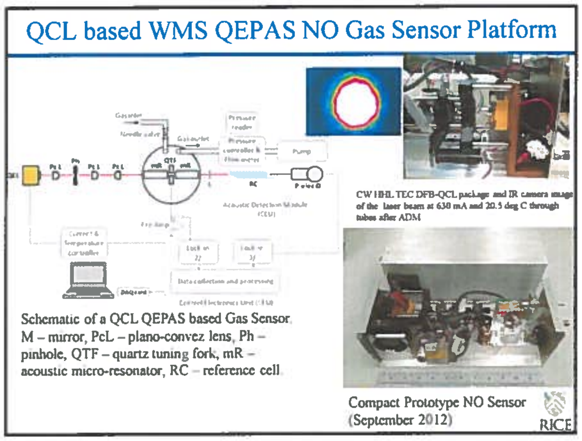
QCL based WMS QEPAS NO Gas Sensor Platform



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.

CW HHL TEC DFB-QCL package and IR camera image of the laser beam at 630 mA and 20.5 deg C through tubes after ADM

Compact Prototype NO Sensor (September 2012)

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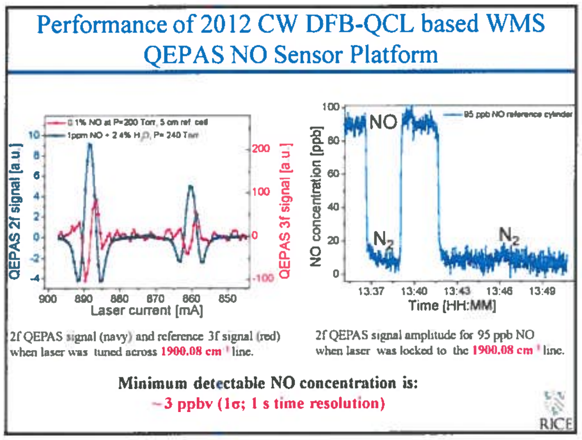
Performance of 2012 CW DFB-QCL based WMS QEPAS NO Sensor Platform



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

2f QEPAS signal amplitude for 95 ppb 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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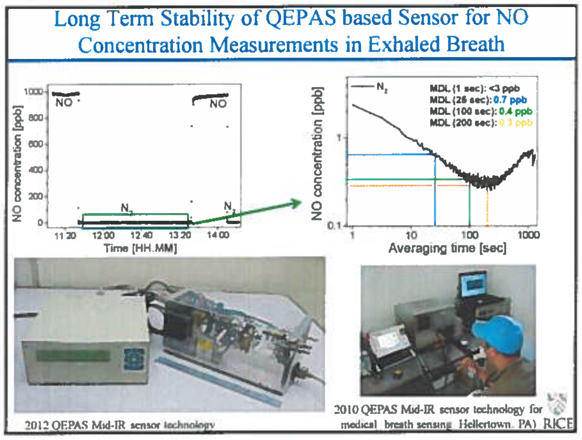
Long Term Stability of QEPAS based Sensor for NO Concentration Measurements in Exhaled Breath



2012 QEPAS Mid-IR sensor technology

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

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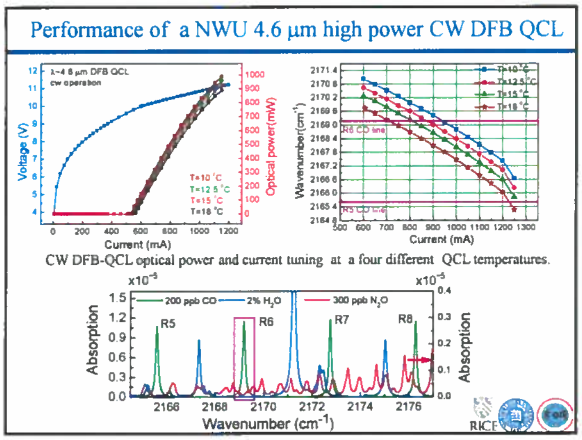
Performance of a NWU 4.6 μm high power CW DFB QCL



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

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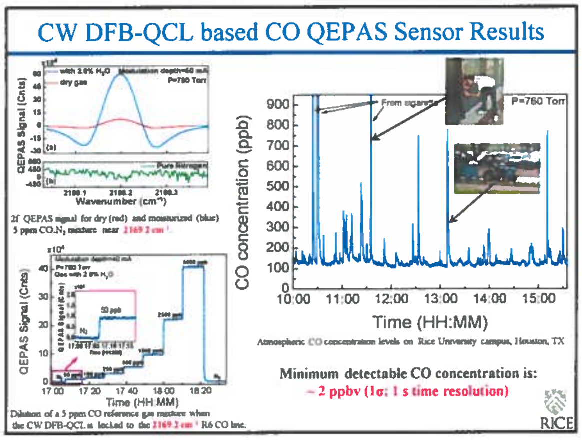
CW DFB-QCL based CO QEPAS Sensor Results



2f QEPAS signal for dry (red) and moisturized (blue) 5 ppm CO:N₂ 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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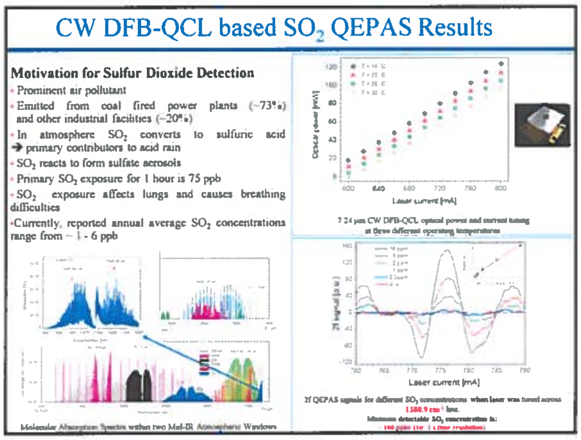
CW DFB-QCL based SO$_2$ QEPAS Results



Motivation for Sulfur Dioxide Detection

- Prominent air pollutant
- Emitted from coal fired power plants (~73%) and other industrial facilities (~20%)
- In atmosphere SO$_2$ converts to sulfuric acid ➔ primary contributors to acid rain
- SO$_2$ reacts to form sulfate aerosols
- Primary SO$_2$ exposure for 1 hour is 75 ppb
- SO$_2$ exposure affects lungs and causes breathing difficulties
- Currently, reported annual average SO$_2$ concentrations range from ~ 1 - 6 ppb

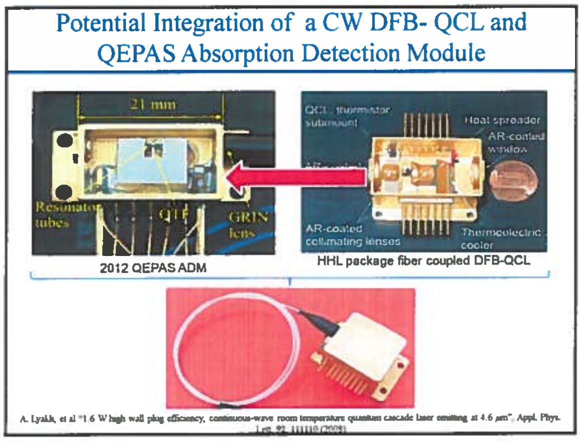
7.24 μm CW DFB-QCL optical power and current tuning at three different operating temperatures

Molecular Absorption Spectra within two Mid-IR Atmospheric Windows

2f QEPAS signals for different SO$_2$ concentrations when laser was tuned across 1380.9 cm⁻¹ line.

Minimum detectable SO$_2$ concentration is:

100 pptv (1σ; 1 s time resolution)

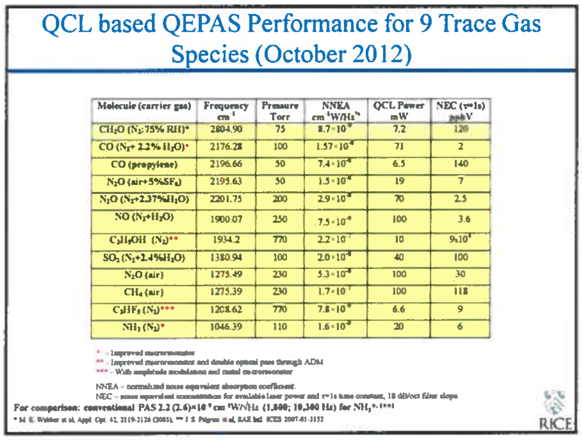


Potential Integration of a CW DFB- QCL and QEPAS Absorption Detection Module

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)



QCL based QEPAS Performance for 9 Trace Gas Species (October 2012)

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}
SO_2 (N_2+2.4%H_2O)	1380.94	100	2.0×10^{-8}	40	100
N_2O (air)	1275.49	230	5.3×10^{-8}	100	30
CH_4 (air)	1275.39	230	1.7×10^{-7}	100	118
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/√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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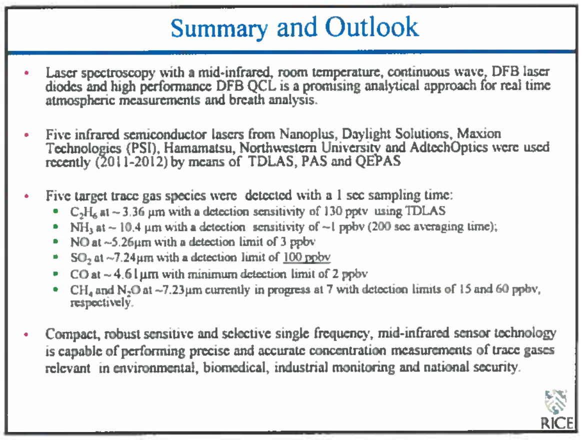

Summary and Outlook

- Laser spectroscopy with a mid-infrared, room temperature, continuous wave, DFB laser diodes and high performance DFB QCL is a promising analytical approach for real time atmospheric measurements and breath analysis.
- Five infrared semiconductor lasers from Nanoplus, Daylight Solutions, Maxion Technologies (PSI), Hamamatsu, Northwestern University and AdtechOptics were used recently (2011-2012) by means of TDLAS, PAS and QEPAS
- 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 130 pptv using TDLAS
  - NH_3 at ~ 10.4 μm with a detection sensitivity of ~1 ppbv (200 sec averaging time);
  - NO at ~5.26μm with a detection limit of 3 ppbv
  - SO_2 at ~7.24μm with a detection limit of 100 ppbv
  - CO at ~ 4.61μm with minimum detection limit of 2 ppbv
  - CH_4 and N_2O at ~7.23μm currently in progress at 7 with detection limits of 15 and 60 ppbv, respectively.
- Compact, robust sensitive and selective single frequency, mid-infrared sensor technology is capable of performing precise and accurate concentration measurements of trace gases relevant in environmental, biomedical, industrial monitoring and national security.

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