

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

**RICE**

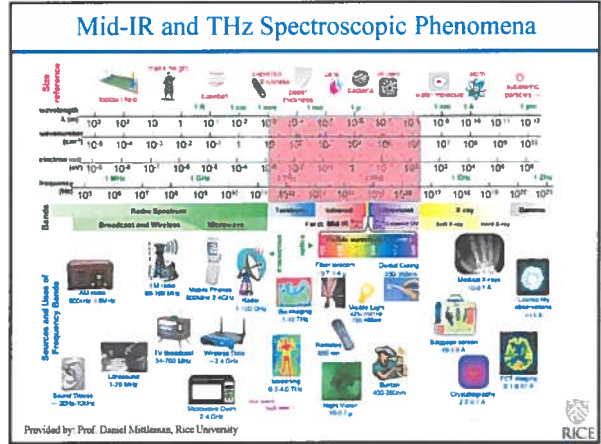
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**OUTLINE**

UAB Innovative Forum  
Center for Optical Sensors and Spectroscopies Birmingham AL  
May 14, 2013

- New Laser Based Trace Gas Sensor Technology
  - Novel Multipass Absorption Cell & Electronics
  - Quartz Enhanced Photoacoustic Spectroscopy
- Examples of Mid-Infrared Sensor Architectures
  - C<sub>2</sub>H<sub>6</sub>, NH<sub>3</sub>, NO, CO, and SO<sub>2</sub>
  - Future Directions of Laser Based Gas Sensor Technology and Conclusions

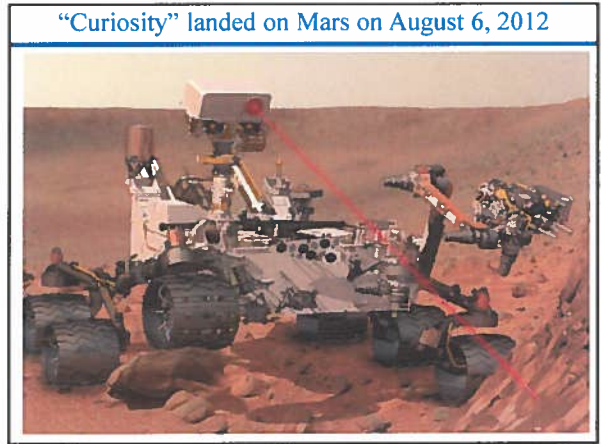
Research support by NSF ERCMBRTHE, NSF-ANR NexCILAS, the Robert Welch Foundation, Scansation, Inc., Teledyne AIT and Sentinel Photonics Inc. via an EPA Phase I SPRR subaward is acknowledged.



**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 (e.g. isotopologues, climate modeling,...)
  - Volcanic Emissions
- **Chemical Analysis and Industrial Process Control**
  - Petrochemical, Semiconductor, Pharmaceutical, Metals Processing, Food & Beverage Industries; Nuclear Technology & Safeguards
- **Spacecraft and Planetary Surface Monitoring**
  - Crew Health Maintenance & Life Support
- **Applications in Medical Diagnostics and the Life Sciences**
- **Technologies for Law Enforcement, Defense and Security**
- **Fundamental Science and Photochemistry**

**RICE**



## Laser based Trace Gas Sensing Techniques

- **Optimum Molecular Absorbing Transition**
  - Overtone or Combination Bands (NIR)
  - Fundamental Absorption Bands (Mid-IR)
- **Long Optical Pathlength**
  - Multipass Absorption Cell (White, Herriot, Chemin, Sentinel Photonics)
  - 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 & Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)

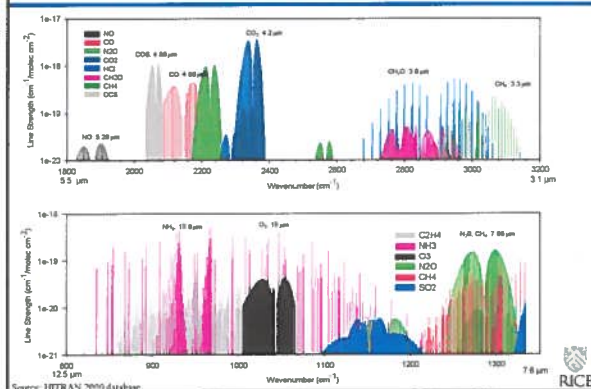


## Other spectroscopic methods

- Faraday Rotation Spectroscopy (limited to paramagnetic chemical species)
- Differential Optical Dispersion Spectroscopy (DODiS)
- Noise Immune Cavity Enhanced-Optical Heterodyne Molecular Spectroscopy (NICE-OHMS)
- Frequency Comb Spectroscopy
- Laser Induced Breakdown Spectroscopy (LIBS)



## HITRAN Simulated Mid-Infrared Molecular Absorption Spectra



## 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 – May 2013

### Band – structure engineered devices

Emission wavelength is determined by layer thickness – MBE or MOCVD. Type I QCLs operate in the 3 to 24  $\mu\text{m}$  spectral region, Type II and GaSb based ICLs can cover the 3 to 6  $\mu\text{m}$  spectral range.

- Compact, reliable, stable, long lifetime, and commercial availability
- Fabry-Perot (FP), single mode (DFB) and multi-wavelength devices

### Wide spectral tuning ranges in the mid-IR

- 1.5  $\text{cm}^{-1}$  using injection current control for DFB devices
- 10-20  $\text{cm}^{-1}$  using temperature control for DFB devices
- ~100 $\text{cm}^{-1}$  using current and temperature control for QCL DFB Array
- ~525  $\text{cm}^{-1}$  (22% of c.w.) using an external grating element and FP chips with heterogeneous cascade active region design, also QCL DFB Array

### Narrow spectral linewidths

- CW: 0.1 - 3 MHz & <10kHz with frequency stabilization (0.0004  $\text{cm}^{-1}$ )
- Pulsed: ~300 MHz

### High pulsed and CW powers of QCLs at TEC/RT temperatures

- Room temperature pulsed power of > 30 W with 27% wall plug efficiency and CW powers of ~ 5 W with 21% wall plug efficiency
- > 1W, TEC CW DFB @ 4.6  $\mu\text{m}$
- > 600 mW (CW FP) @ RT, wall plug efficiency of ~17 % at 4.6  $\mu\text{m}$ ,



## Improvements and New Capabilities of QCLs and ICLs

- Optimum wavelength (> 3 to < 20  $\mu\text{m}$ ) and power (> 10 mW to < 1 W) at room temperature (> 15  $^{\circ}\text{C}$  and < 30  $^{\circ}\text{C}$ ) with state-of-the-art fabrication/processing methods based on MBE and MOCVD, good wall plug efficiency and lifetime (> 20,000 hours) for detection sensitivities from % to pptv with low electrical power budget
- Stable single TEM<sub>00</sub> transverse and axial mode, CW and pulsed operation of mid-infrared laser sources (narrow linewidth of ~ 300 MHz to < 10kHz)
- Mode hop-free ultra-broad 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 innovative 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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## Motivation for Mid-infrared C<sub>2</sub>H<sub>6</sub> Detection

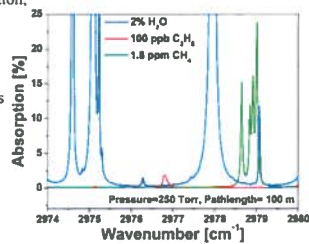
### Atmospheric chemistry and climate

- 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)

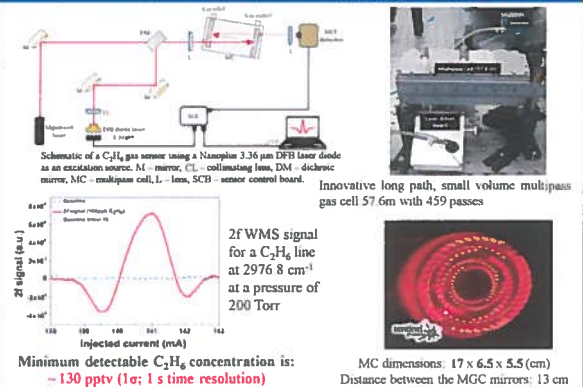
- asthma,
- schizophrenia,
- Lung cancer,
- lung cancer,
- vitamin E deficiency.



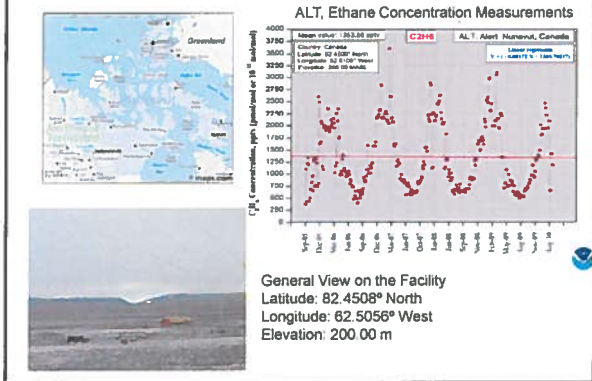
HITRAN absorption spectra of C<sub>2</sub>H<sub>6</sub>, CH<sub>4</sub>, and H<sub>2</sub>O



## C<sub>2</sub>H<sub>6</sub> Detection with a 3.36 $\mu\text{m}$ CW DFB LD using a Novel Compact Multipass Absorption Cell and Control Electronics



NOAA Monitoring & Sampling Location: Alert, Nunavut, Canada

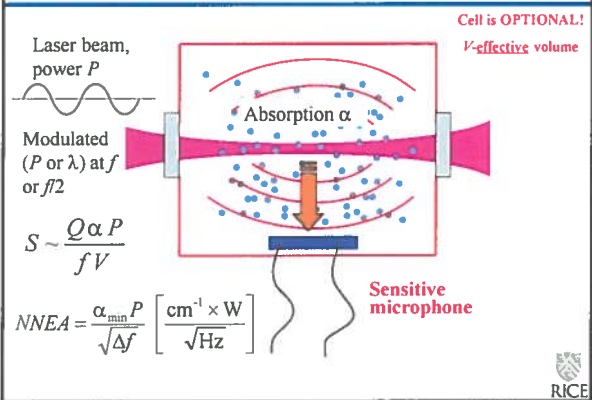


Motivation for NH<sub>3</sub> Detection

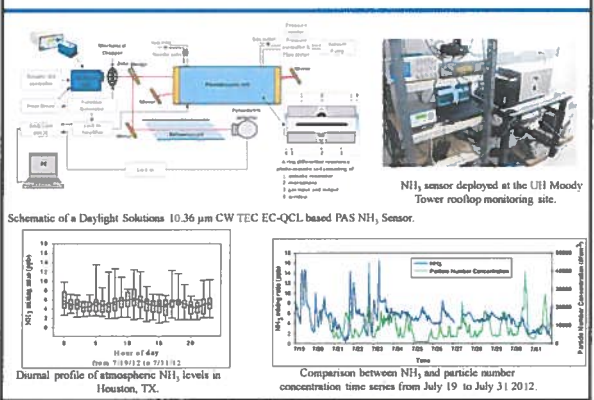
- Atmospheric chemistry
- Pollution gas monitoring
- Monitoring NH<sub>3</sub> concentrations in the exhaust stream of NO<sub>x</sub> removal systems based on selective catalytic reduction (SCR) techniques
- Spacecraft related trace gas monitoring
- Semiconductor process monitoring & control
- Monitoring of industrial refrigeration facilities
- Monitoring of gas separation processes
- Medical diagnostics (kidney & liver diseases)
- Detection of ammonium-nitrate explosives



Conventional PAS

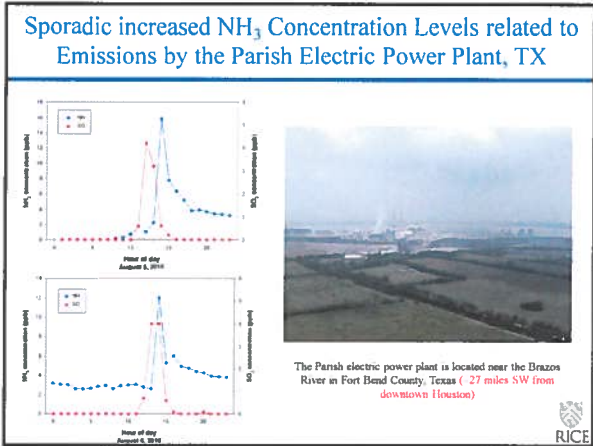
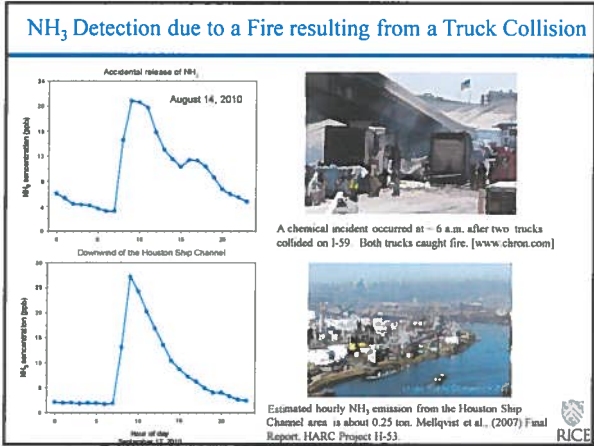


Atmospheric NH<sub>3</sub> Measurements using an EC-QCL PAS Sensor

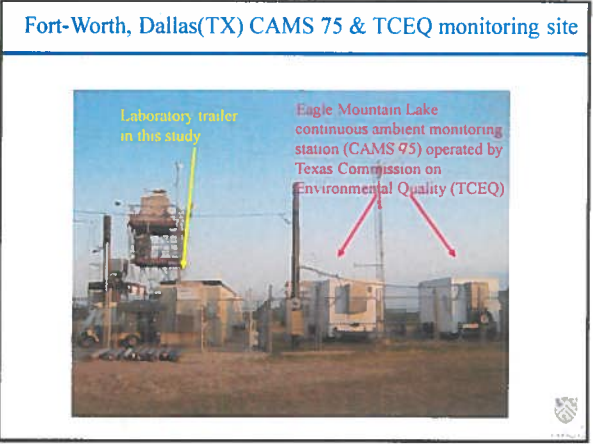
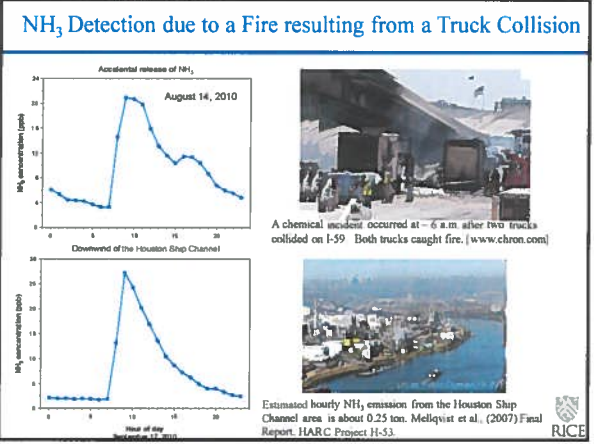


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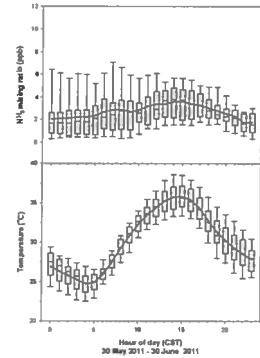


### Instrumentation available at CAMS 75 & TCEQ monitoring site

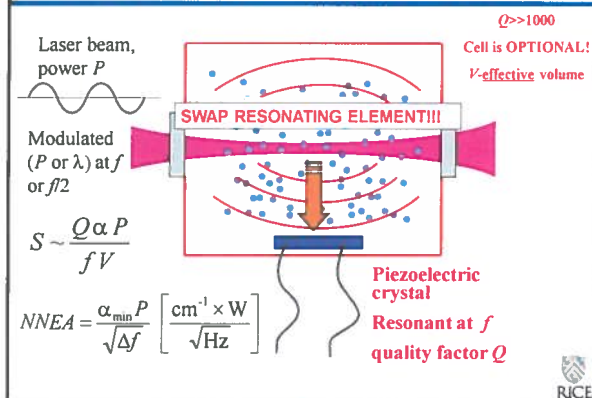
Species/parameter	Measurement technique
NH <sub>3</sub>	Daylight Solutions External Cavity Quantum Cascade Laser (Photo-acoustic Spectroscopy)
CO	Thermo Electron Corp. 48C Trace Level CO Analyzer (Gas Filter Correlation)
SO <sub>2</sub>	Thermo Electron Corp. 43C Trace Level SO <sub>2</sub> Analyzer (Pulsed Fluorescence)
NO <sub>x</sub>	Thermo Electron Corp. 42C Trace Level NO-NO <sub>2</sub> -NO <sub>x</sub> Analyzer (Chemiluminescence)
NO <sub>2</sub>	Thermo Electron Corp. 42C-Y NO <sub>2</sub> Analyzer (Molybdanum Converter)
HNO <sub>3</sub>	Mist Chamber coupled to Ion Chromatography (Dionex, Model CD20-1)
HCl	Mist Chamber coupled to Ion Chromatography (Dionex, Model CD20-1)
VOC <sub>s</sub>	IONICON Analytik Proton Transfer Reaction Mass Spectrometer and TCEQ Automated Gas Chromatograph
PBL height	Vaisala Celiometer CL31 with updated firmware to work with Vaisala Boundary Layer View software
Temperature	Campbell Scientific 16M15C Platinum Resistance Thermometer
Wind speed	Campbell Scientific 05103 R. M. Young Wind Monitor
Wind direction	Campbell Scientific 05103 R. M. Young Wind Monitor

### NH<sub>3</sub> source attribution & temperature variations

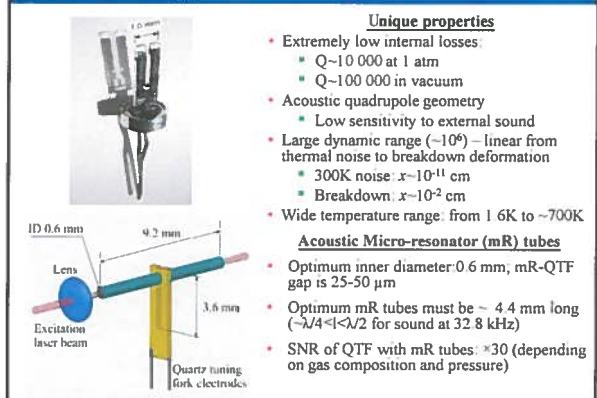
- Emission events from specified point sources (i.e., industrial facilities)
- Estimated NH<sub>3</sub> emissions from cows (1.3 tons/day)
- Estimated NH<sub>3</sub> emissions from soil and vegetation (0.15 tons/day)
- EPA PMF (biogenic: 74.1%; light duty vehicles: 12.1%; natural gas/industry: 9.4%; and heavy duty vehicles: 4.4%)
- Livestock might account for approximately 66.4% of total NH<sub>3</sub> emissions
- Increased contribution from industry (→ 18.9%)

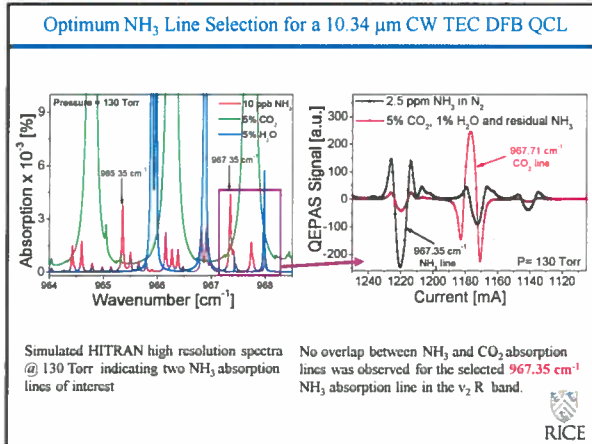


### From Conventional PAS to QEPAS

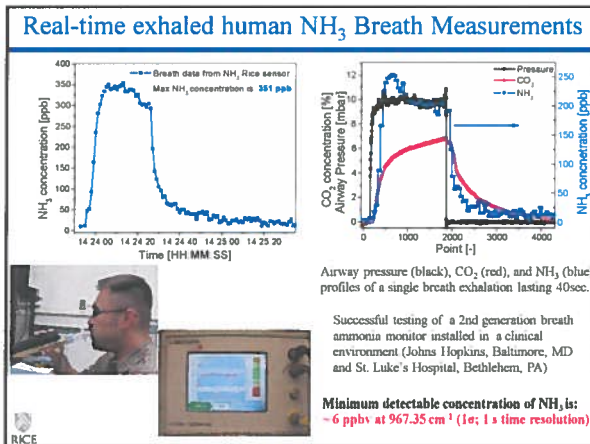
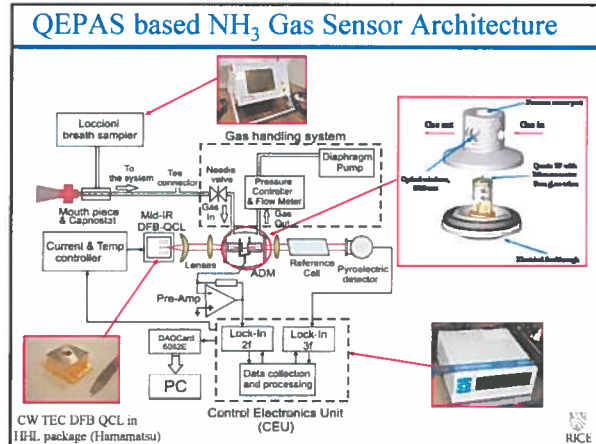


### Quartz Tuning Fork as a Resonant Microphone for QEPAS



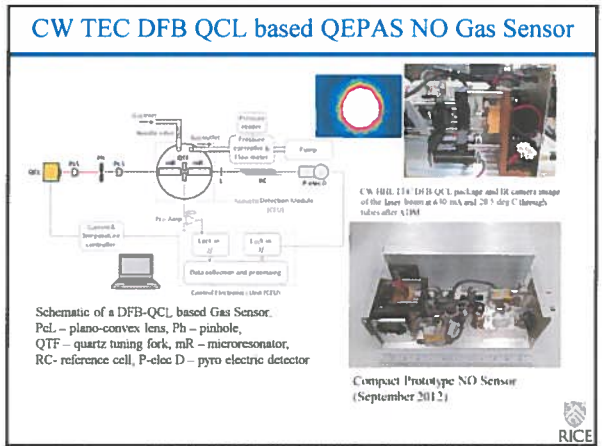
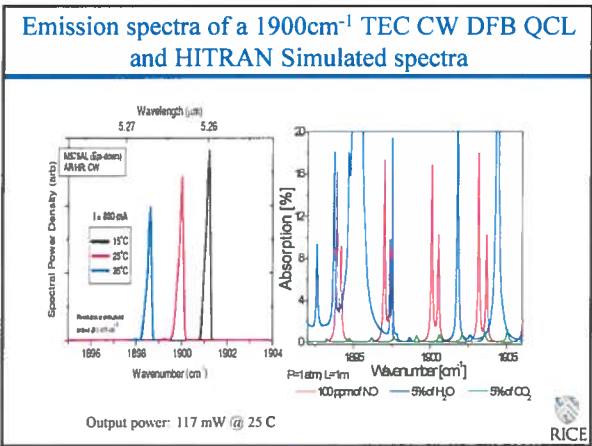
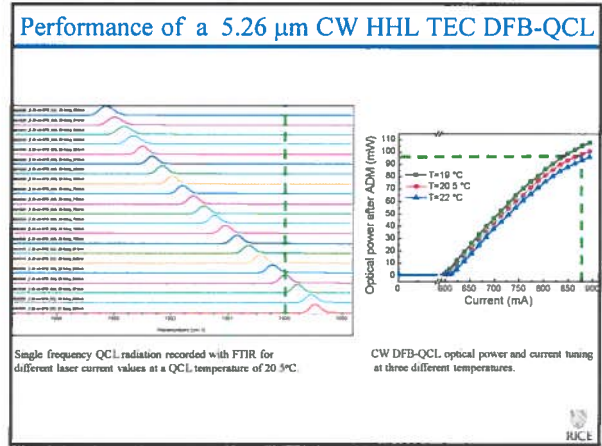
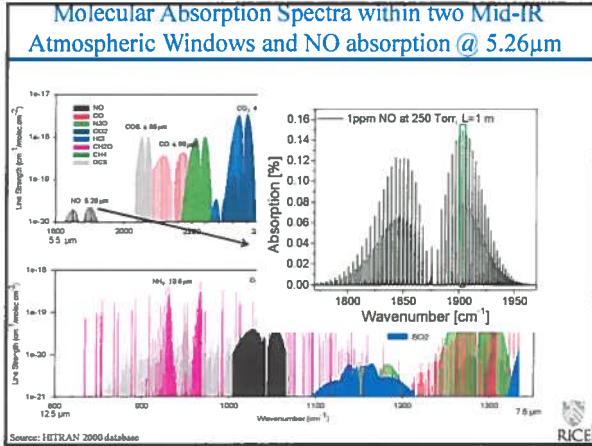


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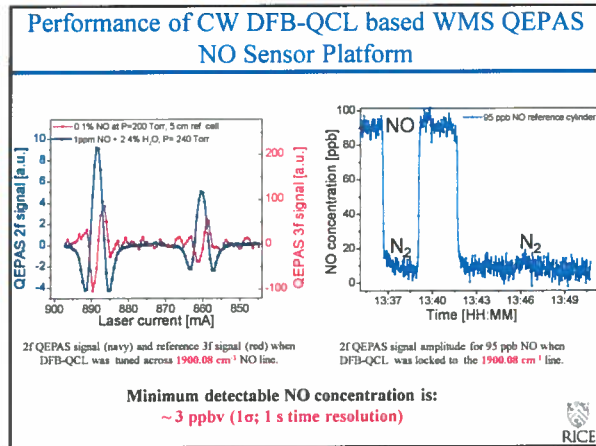


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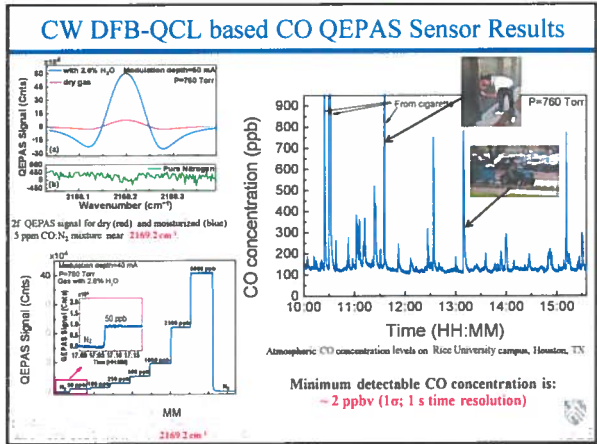
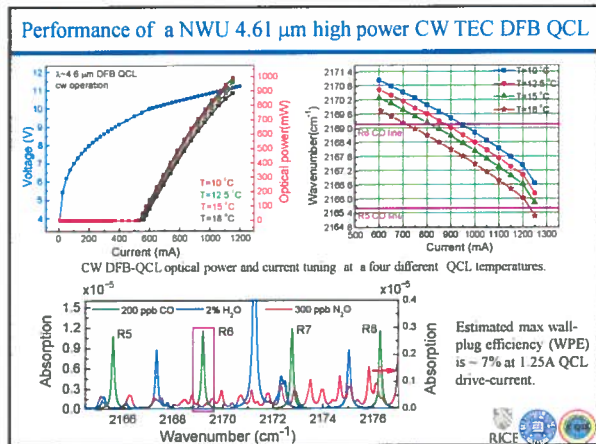
- ### Motivation for Nitric Oxide Detection
- Atmospheric Chemistry
  - Environmental pollutant gas monitoring
    - NO<sub>x</sub> monitoring from automobile exhaust and power plant emissions
    - Precursor of smog and acid rain
  - Industrial process control
    - Formation of oxynitride gates in 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

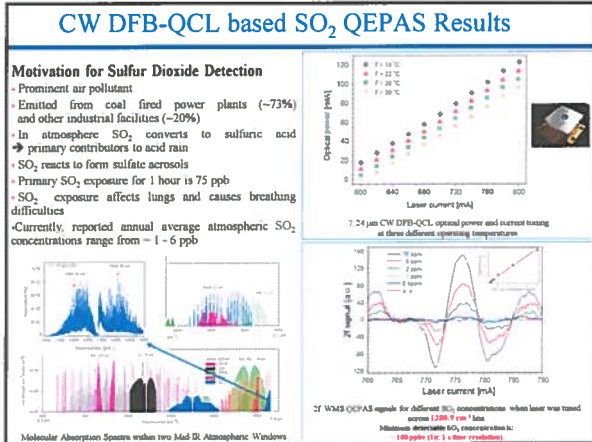






- ### Motivation for Carbon Monoxide Detection
- Atmospheric Chemistry
    - Incomplete combustion of natural gas, fossil fuel and other carbon containing fuels.
    - Impact on atmospheric chemistry through its reaction with hydroxyl (OH) for troposphere ozone formation and changing the level of greenhouse gases (e.g.  $\text{CH}_4$ ).
  - 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.





### QCL based QEPAS Performance for 10 Trace Gas Species (May 2013)

Molecule (carrier gas)	Frequency cm <sup>-1</sup>	Pressure Torr	SNEA cm <sup>3</sup> WHz <sup>-1</sup>	QCL Power mW	NEC (ppbV)
CH <sub>2</sub> O (N <sub>2</sub> ; 75% RH) <sup>a</sup>	2804.90	75	8.7 · 10 <sup>3</sup>	7.2	120
CO (N <sub>2</sub> ; 2.2% H <sub>2</sub> O) <sup>a</sup>	2176.28	100	1.57 · 10 <sup>4</sup>	71	2
CO (propylene)	2196.66	50	7.4 · 10 <sup>3</sup>	6.3	140
N <sub>2</sub> O (air; 5% SF <sub>6</sub> )	2193.63	50	1.5 · 10 <sup>4</sup>	19	7
N <sub>2</sub> O (N <sub>2</sub> ; 2.37% H <sub>2</sub> O)	2201.75	200	2.9 · 10 <sup>4</sup>	70	2.3
C <sub>2</sub> H <sub>2</sub> OH (N <sub>2</sub> ) <sup>a, b</sup>	1934.2	770	2.2 · 10 <sup>3</sup>	10	9 · 10 <sup>4</sup>
NO (N <sub>2</sub> ; H <sub>2</sub> O)	1900.07	250	7.5 · 10 <sup>3</sup>	100	3.6
SO <sub>2</sub> (N <sub>2</sub> ; 2.4% H <sub>2</sub> O)	1380.94	100	2.0 · 10 <sup>3</sup>	40	100
N <sub>2</sub> O (air)	1275.49	230	5.3 · 10 <sup>3</sup>	100	30
CH <sub>4</sub> (air)	1275.39	230	1.7 · 10 <sup>3</sup>	100	118
C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> (N <sub>2</sub> ) <sup>a, b, c</sup>	1208.62	770	7.8 · 10 <sup>3</sup>	6.6	9
NH <sub>3</sub> (N <sub>2</sub> ) <sup>a</sup>	1046.39	110	1.6 · 10 <sup>3</sup>	20	6
SF <sub>6</sub> <sup>a, b, c</sup>	943.73	75	2.7 · 10 <sup>3</sup>	40	5 · 10 <sup>2</sup>

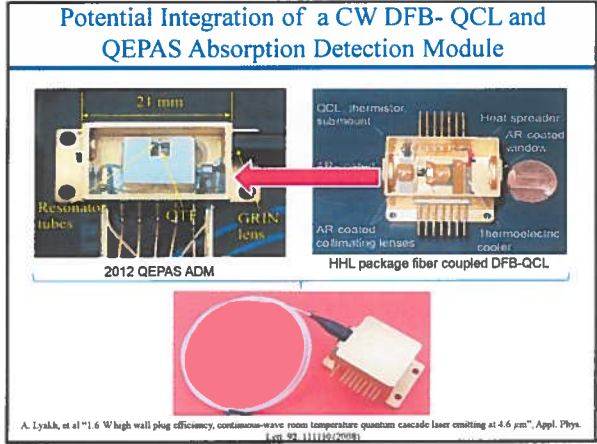
<sup>a</sup> Improved microresonator  
<sup>b</sup> Improved microresonator and double optical pass through ADM  
<sup>c</sup> With amplitude modulation and metal microresonator  
<sup>d</sup> With amplitude modulation and metal microresonator  
 SNEA = normalized noise equivalent absorption coefficient  
 NEC = noise equivalent concentration for available laser power and  $\tau = 1$  s time constant, 18 dB/oct filter slope

For comparison: conventional PAS 2.2 (2.6) · 10<sup>4</sup> cm<sup>3</sup>WHz<sup>-1</sup> (1,000; 10,000 Hz) for NH<sub>3</sub><sup>a, b, c</sup>

<sup>a</sup> M. E. Wobser et al, Appl. Opt. 43, 2119-2126 (2004); <sup>b</sup> S. Pilger et al, SAE Int. JCTD 2007-01-3152; <sup>c</sup> V. Spagnolo, et al University and Politecnico di Bari, Italy


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- ### Merits of QEPAS based Trace Gas Detection
- Very small sensing module and sample volume (a few mm<sup>3</sup> to ~2cm<sup>2</sup>)
  - Extremely low dissipative losses
  - Optical detector is not required
  - Wide dynamic range
  - Frequency and spatial selectivity of acoustic signals
  - Rugged transducer – quartz monocystal, can operate in a wide range of pressures and temperatures
  - Immune to environmental acoustic noise, sensitivity is limited by the fundamental thermal TF noise:  $k_B T$  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<sub>2</sub>O
  - Responsivity depends on the speed of sound and molecular energy transfer processes
  - Cross sensitivity issues



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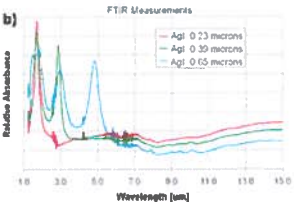
## Hollow core waveguide



**Hollow Core Glass Waveguides:**


- Excellent Infrared transmission out to 20 μm
- Proven single mode delivery for bore size ~ 300 μm
- No end reflections
- High damage threshold
- Very Robust
- 20+ years of experience at Rutgers

Bending loss is the primary concern

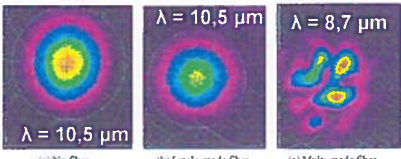


**OKSI OPTIK-KNOWLEDGE SYSTEMS INC**

## QCL-fiber beam profile and losses



**HWG Fiber with 300 μm bore size allows single mode beam delivery @ 10,5 μm**



Bore Size	300 μm
Straight Losses	1 dB/m
Bending Losses	0,1 dB/m

Beam Profiling measurement setup and sample beam profiles

FART

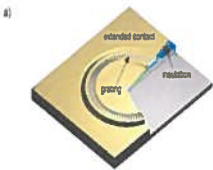
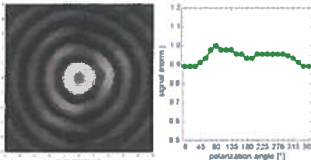


THz

## Future Directions and Outlook

- New target analytes such as carbonyl sulfide (OCS), formaldehyde (CH<sub>2</sub>O), nitrous acid (HNO<sub>2</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>), ozone (O<sub>3</sub>), nitrate (NO<sub>3</sub>), propane (C<sub>3</sub>H<sub>8</sub>), and benzene (C<sub>6</sub>H<sub>6</sub>)
- Ultra-compact, low cost, robust sensors (e.g. C<sub>2</sub>H<sub>6</sub>, NO, CO.....)
- Monitoring of broadband absorbers: acetone (C<sub>3</sub>H<sub>6</sub>O), acetone peroxide (TATP), UF<sub>6</sub>.....
- Optical power build-up cavity designs
- Development of trace gas sensor networks

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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.

## Summary

- 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.
- Six 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
- Seven target trace gas species were detected with a 1 sec sampling time:
  - $C_2H_6$  at  $\sim 3.36 \mu m$  with a detection sensitivity of 130 pptv using TDLAS
  - $NH_3$  at  $\sim 10.4 \mu m$  with a detection sensitivity of  $\sim 1$  ppbv (200 sec averaging time),
  - NO at  $\sim 5.26 \mu m$  with a detection limit of 3 ppbv
  - CO at  $\sim 4.61 \mu m$  with minimum detection limit of 2 ppbv
  - $SO_2$  at  $\sim 7.24 \mu m$  with a detection limit of 100 ppbv
  - $CH_4$  and  $N_2O$  at  $\sim 7.28 \mu m$  currently in progress with detection limits of 20 and 7 ppbv, respectively
- New target analytes such as OCS,  $CH_3O$ , HONO,  $H_2O_2$ ,  $C_2H_4$ ,
- Monitoring of broadband absorbers such as acetone,  $C_2H_2$ ,  $C_6H_6$  and  $UF_6$
- Compact, robust sensitive and selective single frequency, mid-infrared sensor technology that is capable of performing precise, accurate and autonomous concentration measurements of trace gases relevant in environmental, biomedical, industrial monitoring and national security

