

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

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OUTLINE

Physics Dept. Seminar
 ETHZ Zuerich
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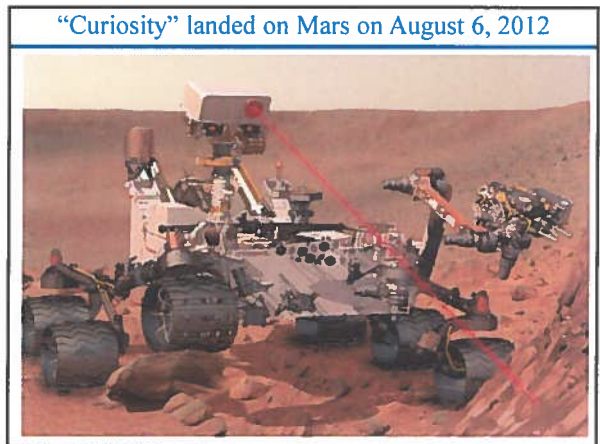
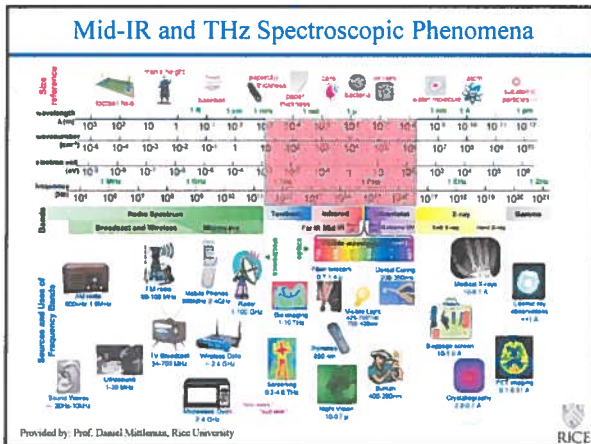
- New Laser Based Trace Gas Sensor Technology
 - Novel Multipass Absorption Cell & Electronics
 - Quartz Enhanced Photoacoustic Spectroscopy
- Examples of Mid-Infrared Sensor Architectures
 - C₂H₆, NH₃, NO, CO, and SO₂
 - Future Directions of Laser Based Gas Sensor Technology and Conclusions

Research support by NSF ERC MRKTHE, NSF-ANR NextCLAS, the Robert Welch Foundation, Scovation, Inc., Teos-Agi and Sentinel Photonics Inc. via an FPA Phase I STTR sub-award 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

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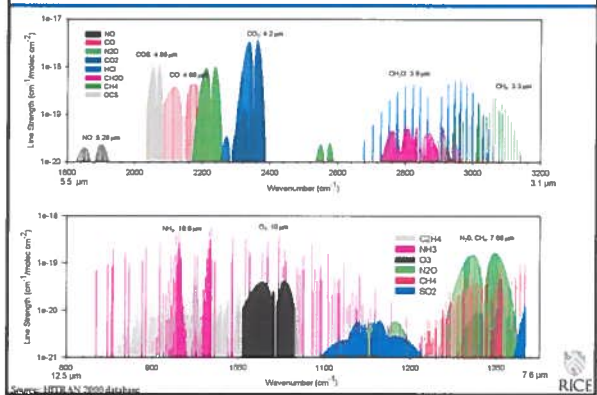


Laser based Trace Gas Sensing Techniques

- **Optimum Molecular Absorbing Transition**
 - Overtone or Combination Bands (NIR)
 - Fundamental Absorption Bands (Mid-IR)
- **Long Optical Pathlength**
 - Multipass Absorption Cell (White, Herriot, Chernin, 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)



HITRAN Simulated Mid-Infrared Molecular Absorption Spectra



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)

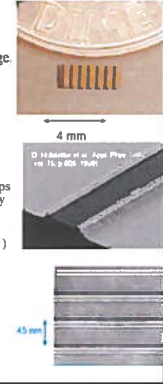


Mid-IR Source Requirements for Laser Spectroscopy

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

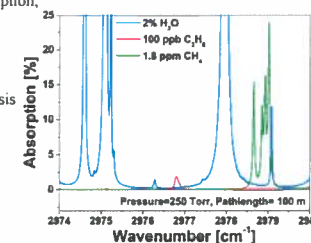
Key Characteristics of Mid-IR QCL & ICL Sources – April 2013

- Band – structure engineered devices**
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 6 μm 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 cm^{-1} using injection current control for DFB devices
 - 10-20 cm^{-1} using temperature control for DFB devices
 - ~100 cm^{-1} using current and temperature control for QCL DFB Array
 - ~525 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 cm^{-1})
 - Pulsed – 300 MHz
- High pulsed and CW powers of OCLs 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 μm
 - > 600 mW (CW FP) @ RT, wall plug efficiency of ~17 % at 4.6 μm .



Motivation for Mid-infrared C₂H₆ 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.



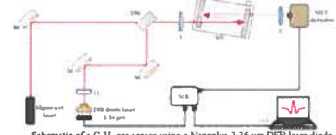
HITRAN absorption spectra of C₂H₆, CH₄, and H₂O

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 (> 20,000 hours) for detection sensitivities from % to pptv with low electrical power budget
- Stable single TEM₀₀ 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...)



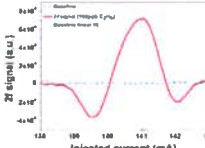
C₂H₆ Detection with a 3.36 μm CW DFB LD using a Novel Compact Multipass Absorption Cell and Control Electronics



Schematic of a C₂H₆ 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 C₂H₆ line at 2976.8 cm^{-1} at a pressure of 200 Torr

Minimum detectable C₂H₆ concentration is:
 = 130 pptv (1 σ ; 1 s time resolution)



MC dimensions: 17 x 6.5 x 5.5 (cm)
 Distance between the MGC mirrors: 13 cm

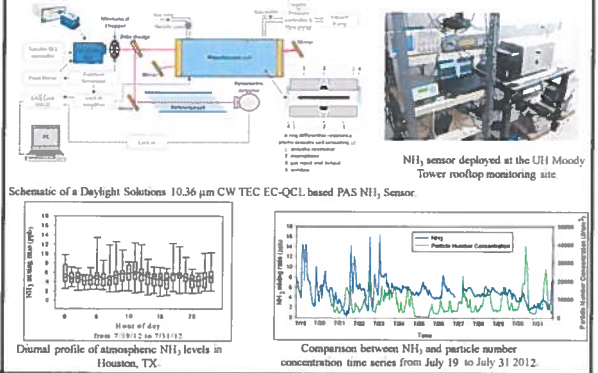


Motivation for NH₃ Detection

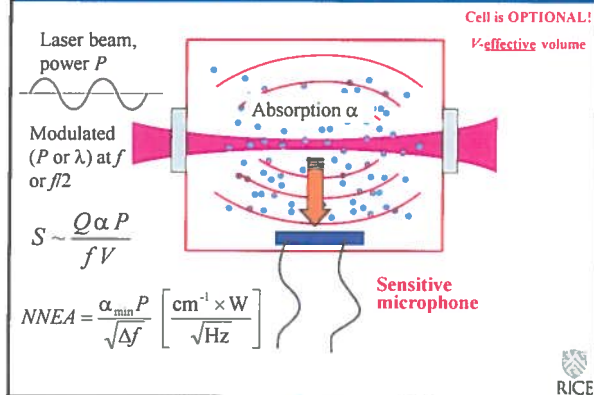
- Atmospheric chemistry
- Pollution gas monitoring
- Monitoring NH₃ concentrations in the exhaust stream of NO_x removal systems based on selective catalytic reduction (SCR) techniques
- Spacecraft related trace gas monitoring
- Semiconductor process monitoring & control
- Monitoring of industrial refrigeration facilities
- Monitoring of gas separation processes
- Medical diagnostics (kidney & liver diseases)
- Detection of ammonium-nitrate explosives



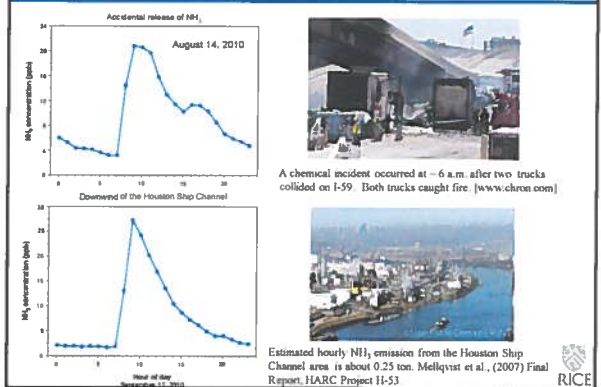
Atmospheric NH₃ Measurements using an EC-QCL PAS Sensor



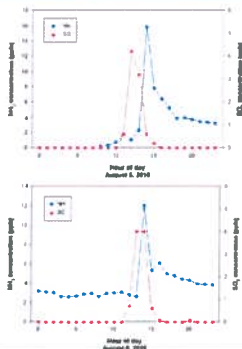
Conventional PAS



NH₃ Detection due to a Fire resulting from a Truck Collision



Sporadic increased NH₃ Concentration Levels related to Emissions by the Parish Electric Power Plant, TX

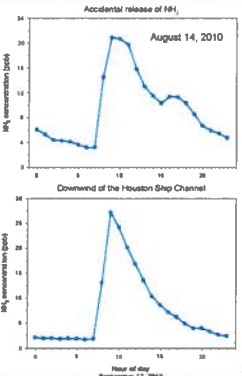


The Parish electric power plant is located near the Brazos River in Fort Bend County, Texas (~ 27 miles SW from downtown Houston)



Species/parameter	Measurement technique
NH ₃	Daylight Solutions External Cavity Quantum Cascade Laser (Photo-acoustic Spectroscopy)
CO	Thermo Electron Corp. 48C Trace Level CO Analyzer (Gas Filter Correlation)
SO ₂	Thermo Electron Corp. 43C Trace Level SO ₂ Analyzer (Pulsed Fluorescence)
NO _x	Thermo Electron Corp. 42C Trace Level NO-NO ₂ -NO _x Analyzer (Chemiluminescence)
NO ₂	Thermo Electron Corp. 42C-Y NO ₂ Analyzer (Molybdenum Converter)
HNO ₃	Mist Chamber coupled to Ion Chromatography (Dionex, Model CD20-1)
HCl	Mist Chamber coupled to Ion Chromatography (Dionex, Model CD20-1)
VOC _s	IONCON Analytik Proton Transfer Reaction Mass Spectrometer and TCEQ Automated Gas Chromatograph
PBL height	Vaisala ceilometer CL31 with updated firmware to work with Vaisala Boundary Layer View software
Temperature	Campbell Scientific 16P45C Platinum Resistance Thermometer
Wind speed	Campbell Scientific 05103 R.M. Young Wind Monitor
Wind direction	Campbell Scientific 05103 R.M. Young Wind Monitor

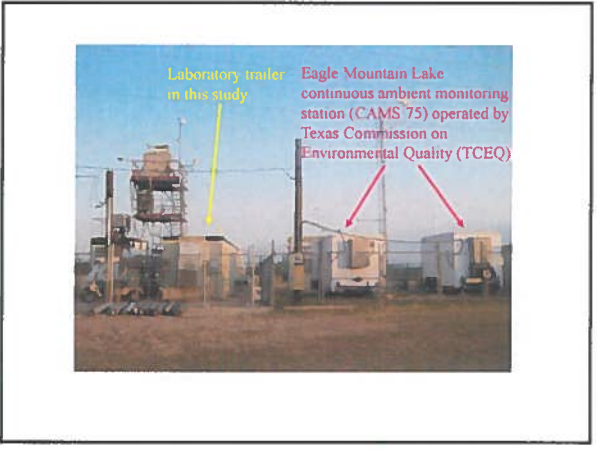
NH₃ Detection due to a Fire resulting from a Truck Collision

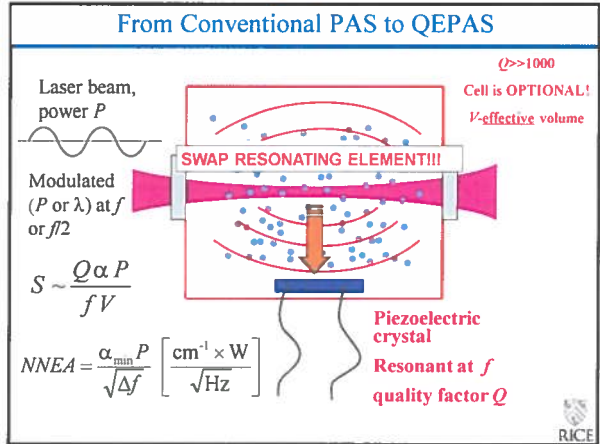
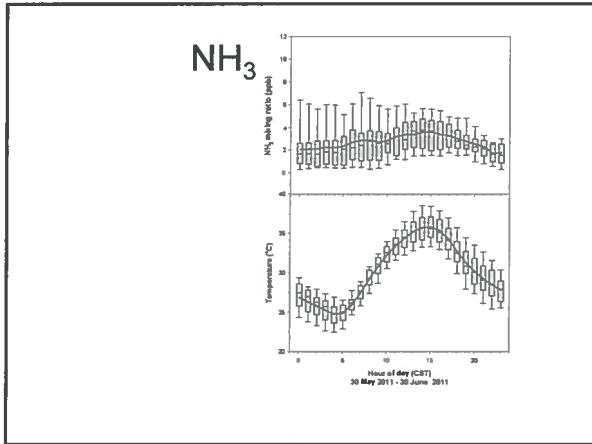


A chemical incident occurred at ~ 5 a.m. after two trucks collided on I-59. Both trucks caught fire. [www.chron.com]



Estimated hourly NH₃ emission from the Houston Ship Channel area is about 0.25 ton. Mellqvist et al., (2007) Final Report. IARC Project II-33





- ### Source attribution
- Emission events from specified point sources (i.e., industrial facilities)
 - Estimated NH₃ emissions from cows (1.3 tons/day)
 - Estimated NH₃ 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 NH₃ emissions
 - Increased contribution from industry (→ 18.9%)

Quartz Tuning Fork as a Resonant Microphone for QEPAS

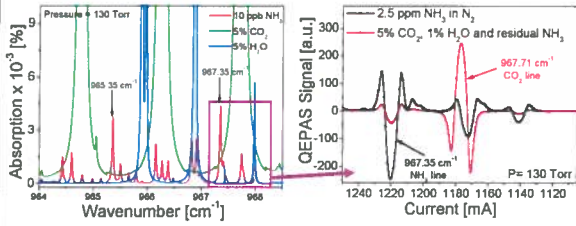
Unique properties

- Extremely low internal losses:
 - $Q \sim 10\,000$ at 1 atm
 - $Q \sim 100\,000$ in vacuum
- Acoustic quadrupole geometry
 - Low sensitivity to external sound
- Large dynamic range ($\sim 10^6$) – 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 -700 K

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 ($-\lambda/4 < l < \lambda/2$ for sound at 32.8 kHz)
- SNR of QTF with mR tubes: $\times 30$ (depending on gas composition and pressure)

Optimum NH₃ Line Selection for a 10.34 μm CW TEC DFB QCL

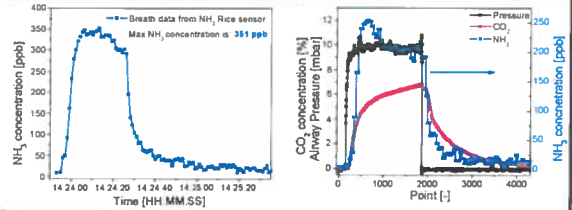


Simulated HITRAN high resolution spectra @ 130 Torr indicating two NH₃ absorption lines of interest

No overlap between NH₃ and CO₂ absorption lines was observed for the selected 967.35 cm⁻¹ NH₃ absorption line in the ν₂ R band.



Real-time exhaled human NH₃ Breath Measurements



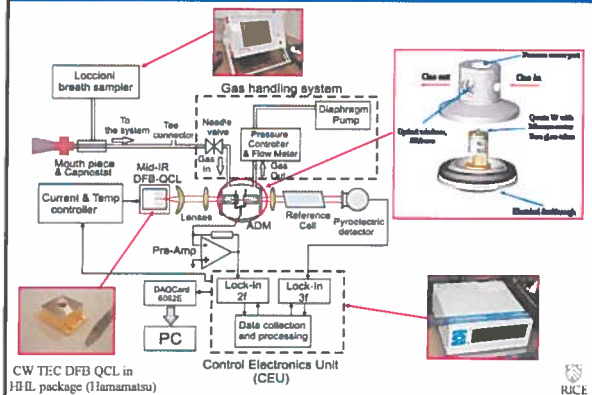
Airway pressure (black), CO₂ (red), and NH₃ (blue) profiles of a single breath exhalation lasting 40sec.

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 NH₃ is: ~6 ppb at 967.35 cm⁻¹ (1σ; 1 s time resolution)

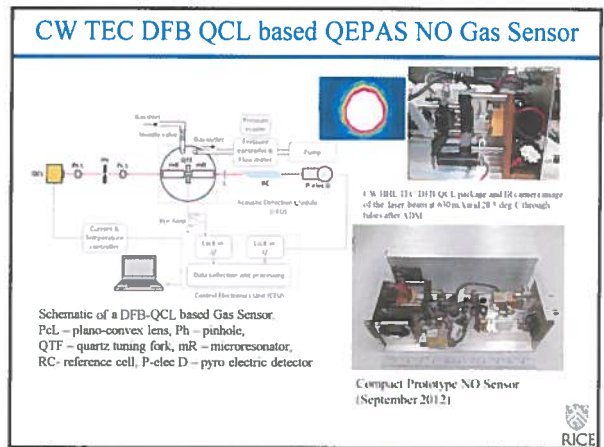
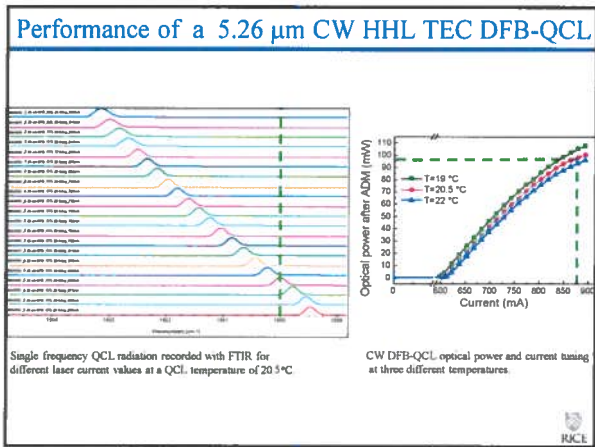
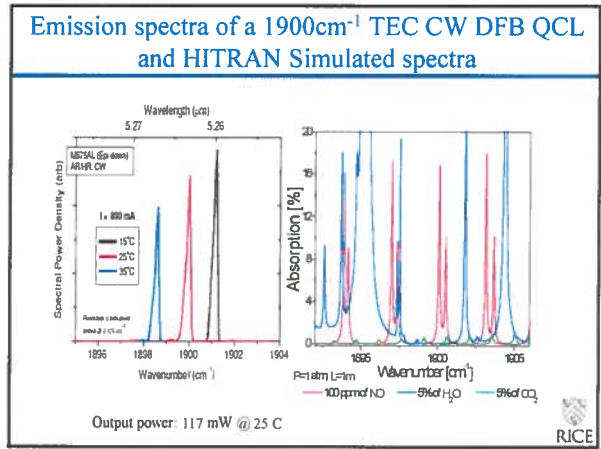
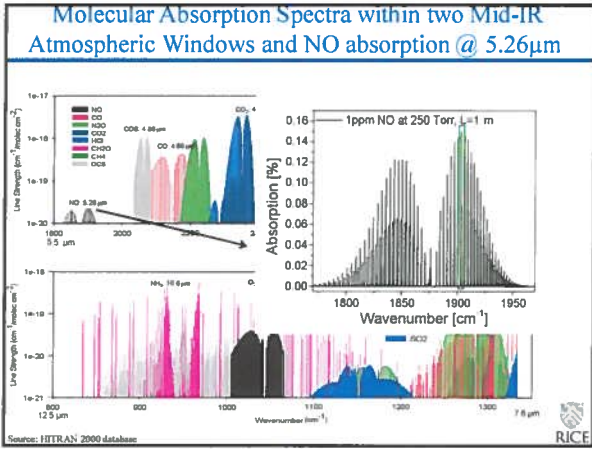


QEPAS based NH₃ Gas Sensor Architecture

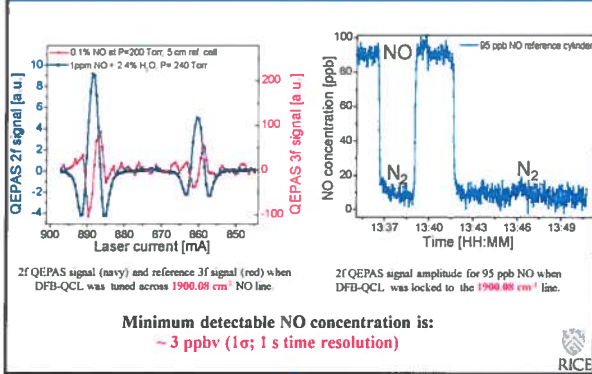


Motivation for Nitric Oxide Detection

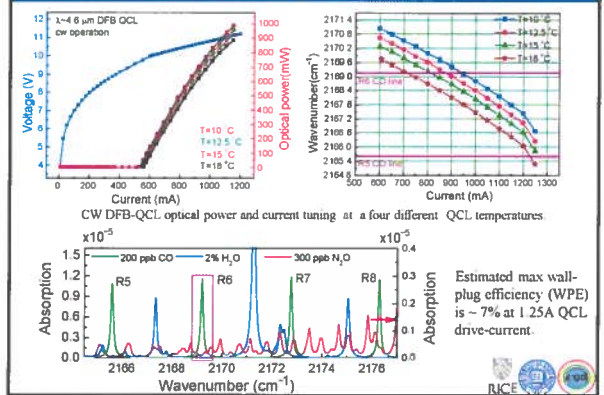
- Atmospheric Chemistry
- Environmental pollutant gas monitoring
 - NO_x monitoring from automobile exhaust and power plant emissions
 - Precursor of smog and acid rain
- Industrial process control
 - Formation of oxynitride gates in CMOS Devices
- NO in medicine and biology
 - Important signaling molecule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



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



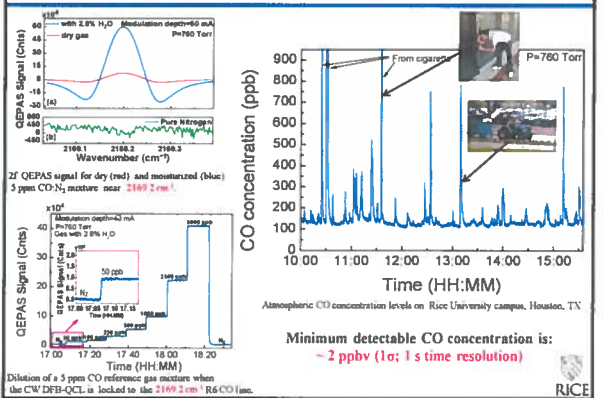
Performance of a NWU 4.61 μm high power CW TEC DFB QCL

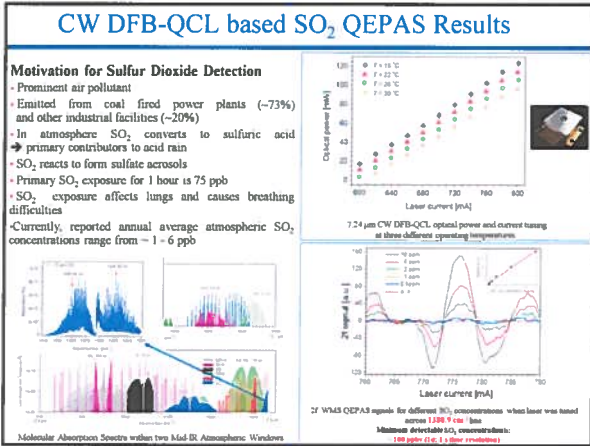


Motivation for Carbon Monoxide Detection

- 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. CH₄).
- 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.

CW DFB-QCL based CO QEPAS Sensor Results



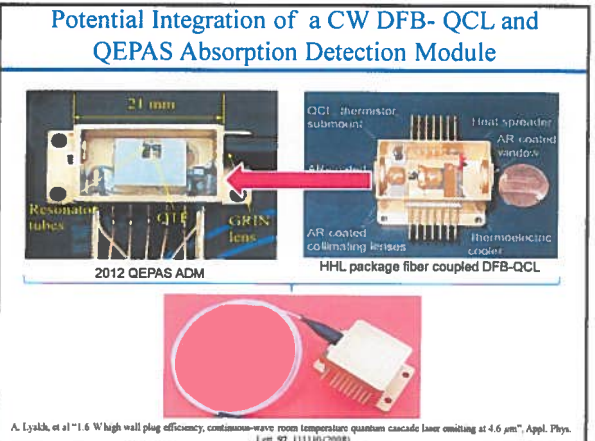


- ### Merits of QEPAS based Trace Gas Detection
- Very small sensing module and sample volume (a few mm³ to ~2cm³)
 - Extremely low dissipative losses
 - Optical detector is not required
 - Wide dynamic range
 - Frequency and spatial selectivity of acoustic signals
 - Rugged transducer – quartz monocrystal, can operate in a wide range of pressures and temperatures
 - Immune to environmental acoustic noise, sensitivity is limited by the fundamental thermal TF noise: $k_B T$ 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 H₂O
 - Responsivity depends on the speed of sound and molecular energy transfer processes
 - Cross sensitivity issues

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

Molecule (carrier gas)	Frequency cm ⁻¹	Pressure Torr	NNEA cm ² /W/Hz ²	QCL Power mW	NEC (τ=1s) ppbV
CH ₂ O (N ₂ /75% RH)	2804.50	75	8.7 · 10 ⁸	7.2	120
CO (N ₂ / 2.1% H ₂ O)	2176.28	100	1.57 · 10 ⁸	71	2
CO (propylene)	2196.66	50	7.4 · 10 ⁸	6.5	140
N ₂ O (air/ 5% SF ₆)	2193.63	50	1.5 · 10 ⁸	19	7
N ₂ O (N ₂ / 2.37% H ₂ O)	2201.75	200	2.9 · 10 ⁸	70	2.5
C ₂ H ₅ OH (N ₂) ^{***}	1934.2	770	2.2 · 10 ⁷	10	9.10 ²
NO (N ₂ / H ₂ O)	1900.07	250	7.5 · 10 ⁹	100	3.6
SO ₂ (N ₂ / 2.4% H ₂ O)	1380.94	100	2.0 · 10 ⁸	40	100
N ₂ O (air)	1273.49	230	5.3 · 10 ⁸	100	30
CH ₄ (air)	1273.39	230	1.7 · 10 ⁷	100	114
C ₂ H ₂ F ₂ (N ₂) ^{***}	1268.62	770	7.8 · 10 ⁸	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) · 10⁹ cm²/W/Hz (1,800; 10,300 Hz) for NH₃^{*}, (1^{***})



Future Directions and Outlook

- New target analytes such as carbonyl sulfide (OCS), formaldehyde (CH₂O), nitrous acid (HNO₂), hydrogen peroxide (H₂O₂), ethylene (C₂H₄), ozone (O₃), nitrate (NO₃), propane (C₃H₈), and benzene (C₆H₆)
- Ultra-compact, low cost, robust sensors (e.g. C₂H₆, NO, CO.....)
- Monitoring of broadband absorbers: acetone (C₃H₆O), acetone peroxide (TATP), UF₆.....
- Optical power build-up cavity designs
- Development of trace gas sensor networks



Summary and Outlook

- An AM-PAS technique was employed to monitor NH₃ with a 65 mW, 10.34 μm CW TEC EC-QCL. The minimum detection limit (MDL) obtained for an absorption line at 965.35 cm⁻¹ was ~0.7 ppbv for a 300 sec averaging time.
- A 5.26 μm CW TEC HHL packaged DFB-QCL based QEPAS sensor for NO detection was demonstrated. For an interference free NO absorption line located at 1900.08 cm⁻¹ a 1σ MDL of 3 ppbv was achieved at a gas pressure of 240 Torr and a sampling time of 1 sec.
- A 4.61 μm CW DFB-QCL based QEPAS sensor for CO detection was demonstrated. A 1σ MDL of 2 ppbv was obtained at atmospheric pressure and sampling time of 1 sec for a CO absorption line at 2169.2 cm⁻¹.
- Addition of 2.6% H₂O vapor to a NO and CO trace gas mixture results in an improved QEPAS signal of 60 and 8 times, respectively.
- Next objective will be CH₄, H₂O₂ and N₂O detection with a high power mid-infrared CW TEC HHL packaged DFB-QCL based QEPAS sensor platform.
- Availability of compact, robust sensitive and selective mid-IR based QEPAS sensor technology will permit sensitive, selective, real-time environmental, industrial and biomedical emission measurements.



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:
 - C₂H₆ at ~3.36 μm with a detection sensitivity of 130 pptv using TDLAS
 - NH₃ at ~10.4 μm with a detection sensitivity of ~1 ppbv (200 sec averaging time);
 - NO at ~5.26 μm with a detection limit of 3 ppbv
 - CO at ~4.61 μm with minimum detection limit of 2 ppbv
 - SO₂ at ~7.24 μm with a detection limit of 100 ppbv
 - CH₄ and N₂O at ~7.28 μm currently in progress with detection limits of 20 and 7 ppbv, respectively.
- New target analytes such as OCS, CH₂O, HONO, H₂O₂, C₂H₄,
- Monitoring of broadband absorbers such as acetone, C₃H₈, C₆H₆ and UF₆
- 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.

