



OUTLINE

**US-UK
Workshop in
Mid-IR to THz
Technology and
Applications**

**Royal Society of
Edinburgh, UK**

Feb. 18-19, 2013

The state-of-the-art and grand Challenges of Mid-infrared Technology and Applications

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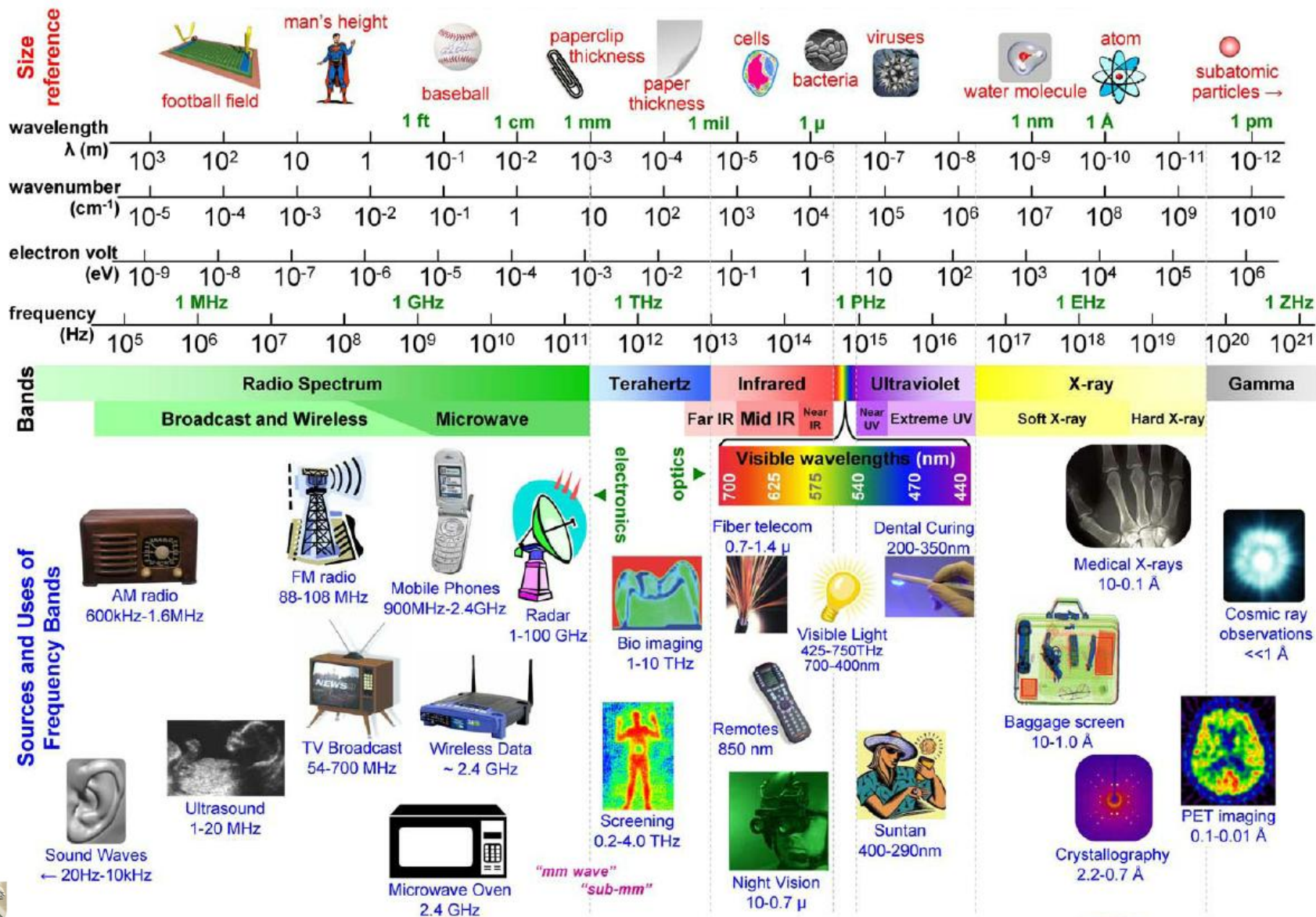
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- New Laser Based Trace Gas Sensor Technology
 - Novel Multipass Absorption Cell & Electronics
 - Quartz Enhanced Photoacoustic Spectroscopy
- Seven Examples of Mid-Infrared Sensor Architectures
 - C₂H₆, NH₃, NO, CO, SO₂, CH₄ & N₂O
 - Future Directions 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 1 SBIR sub-award is acknowledged

Mid-IR and THz Spectroscopic Phenomena



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, Isotopic Signatures
 - 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 Medical Diagnostics and the Life Sciences**
 - Breath Analysis
- **Technologies for Law Enforcement, Defense and Security**
- **Fundamental Science and Photochemistry**

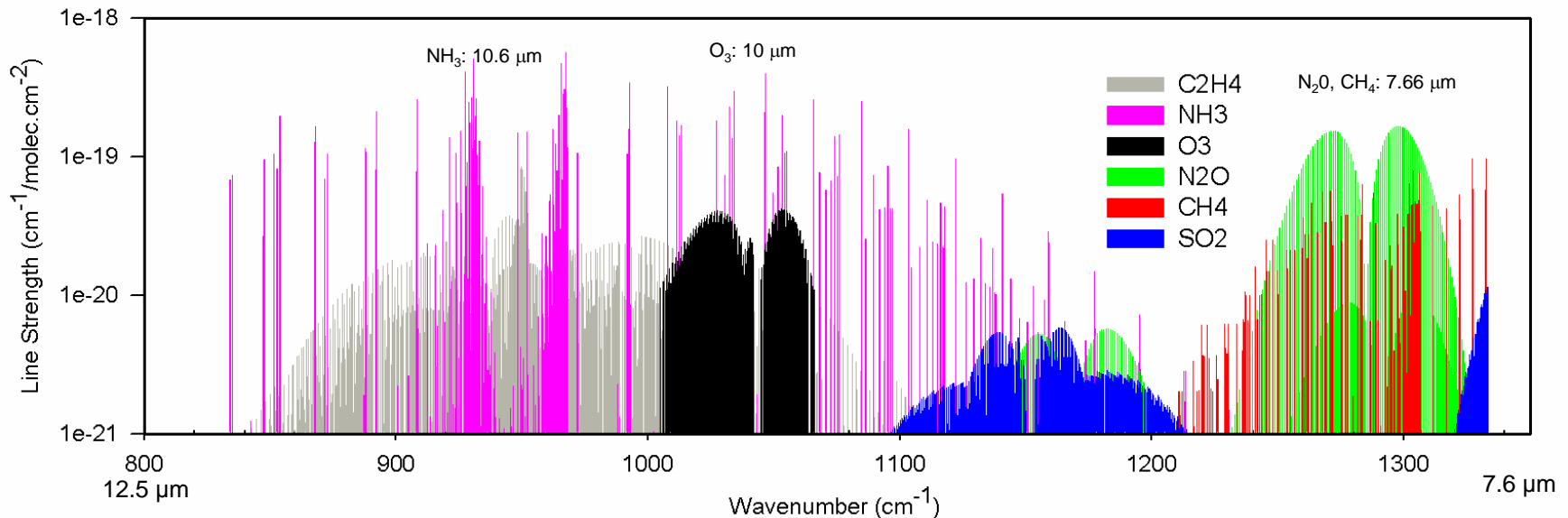
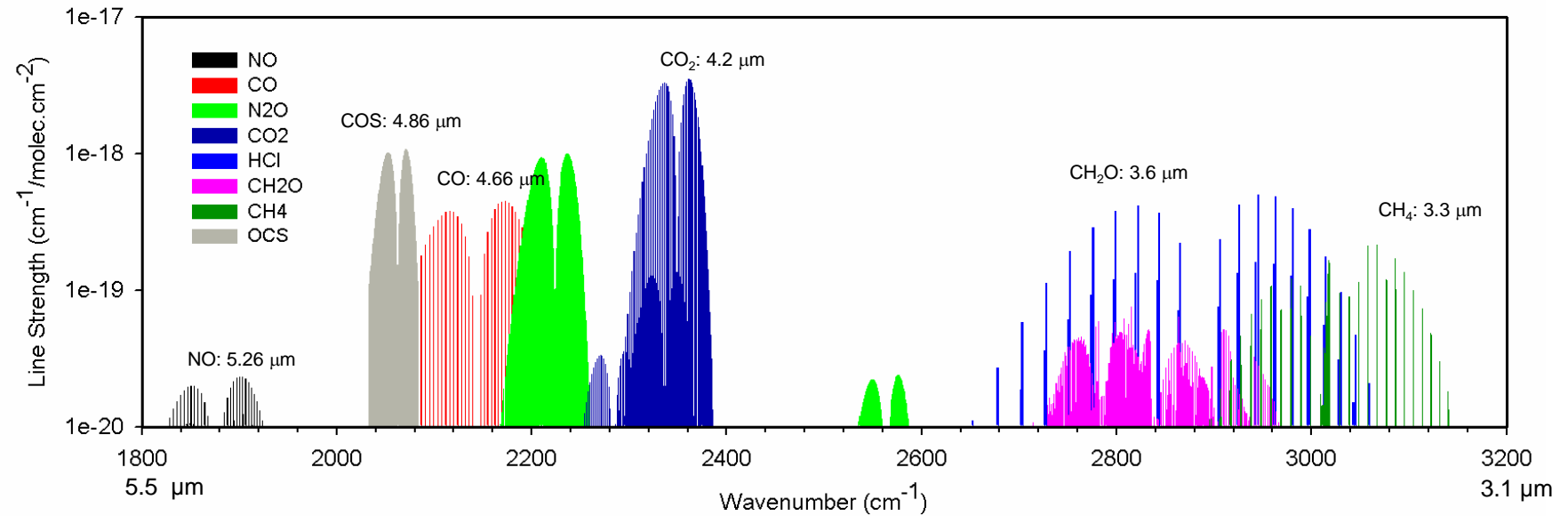
Laser based Trace Gas Sensing Techniques

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

<u>REQUIREMENTS</u>	<u>IR LASER SOURCE</u>
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 – Feb 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**

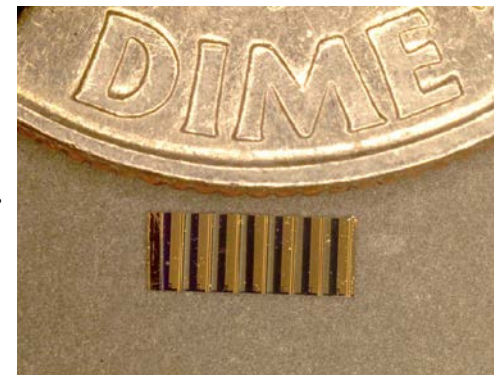
- 1.5 cm^{-1} using injection current control for DFB devices
- 10-20 cm^{-1} using temperature control for DFB devices
- $\sim 100\text{cm}^{-1}$ using current and temperature control for QCL DFB Array
- $\sim 525\text{ cm}^{-1}$ (22% of c.w.) using an external grating element and FP chips with heterogeneous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

- **Narrow spectral linewidths**

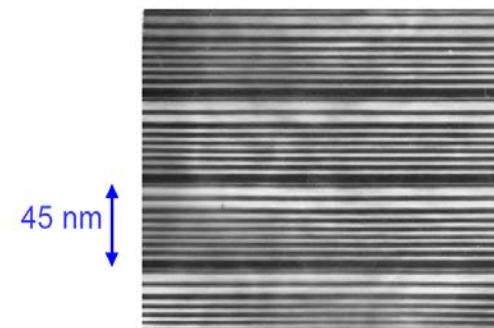
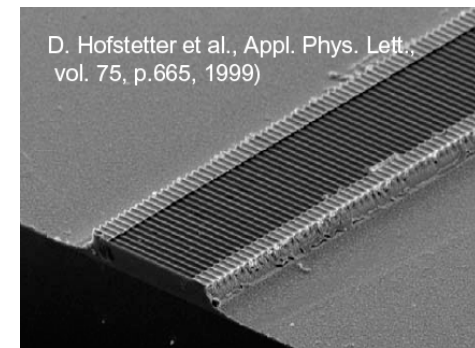
- CW: 0.1 - 3 MHz & $<10\text{kHz}$ with frequency stabilization (0.0004 cm^{-1})
- Pulsed: $\sim 300\text{ MHz}$

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

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



4 mm

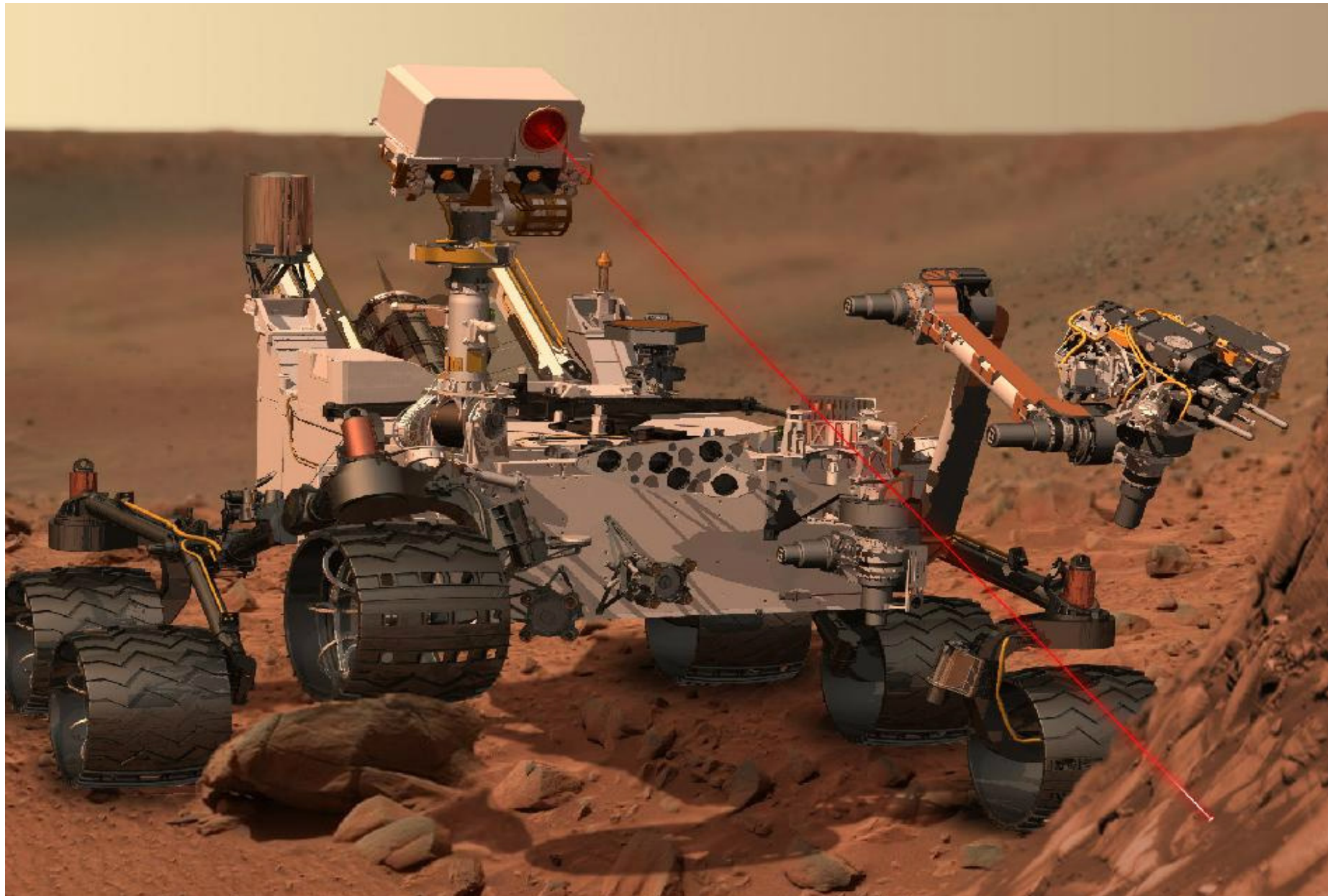


Recent Improvements and New Capabilities of QCLs and ICLs

- Optimum wavelength (> 3 to $< 20 \mu\text{m}$) and power ($> 10 \text{ mw}$ to $< 1 \text{ W}$) 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 TEM₀₀ transverse and axial mode, CW and pulsed operation of mid-infrared laser sources (narrow linewidth of $\sim 300 \text{ MHz}$ to $< 10\text{kHz}$)
- 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...)

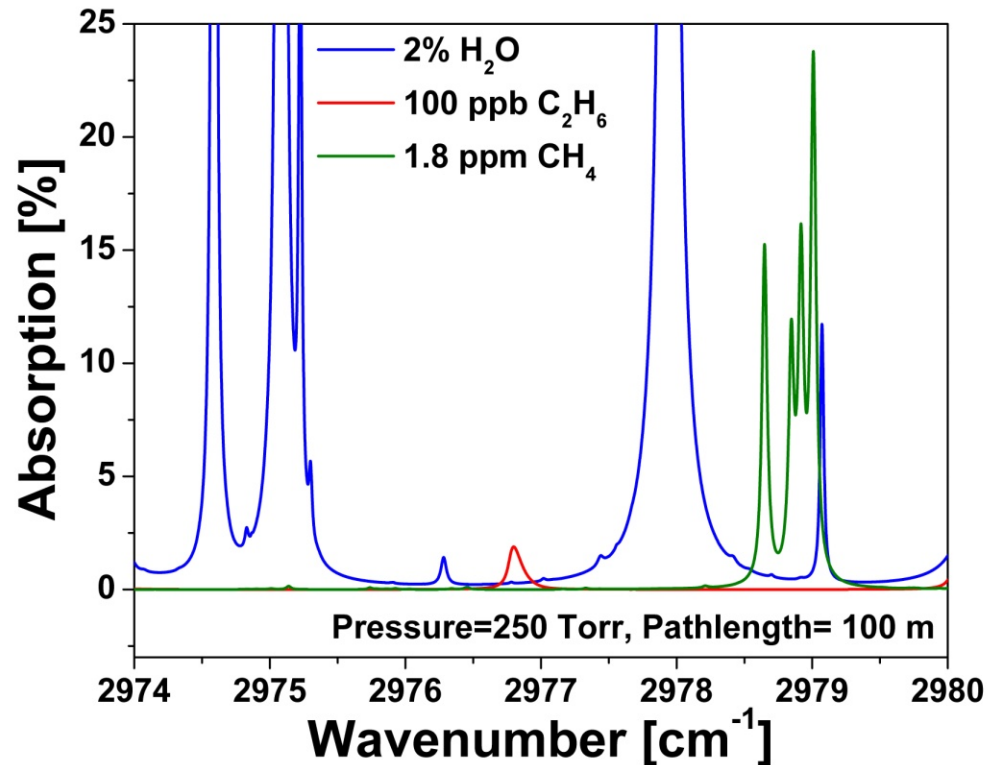


“Curiosity” landed on Mars on August 6, 2012



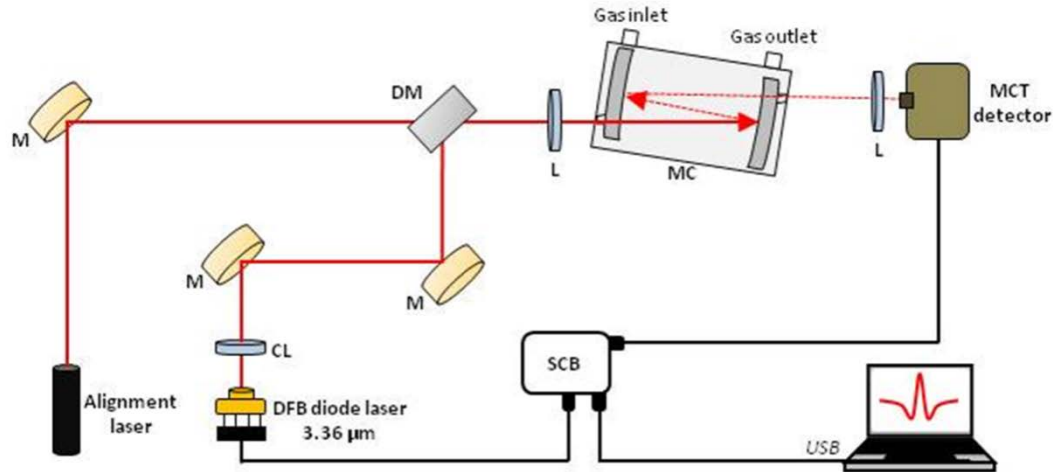
Motivation for Mid-infrared C_2H_6 Detection

- 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,
 - lung cancer,
 - vitamin E deficiency.

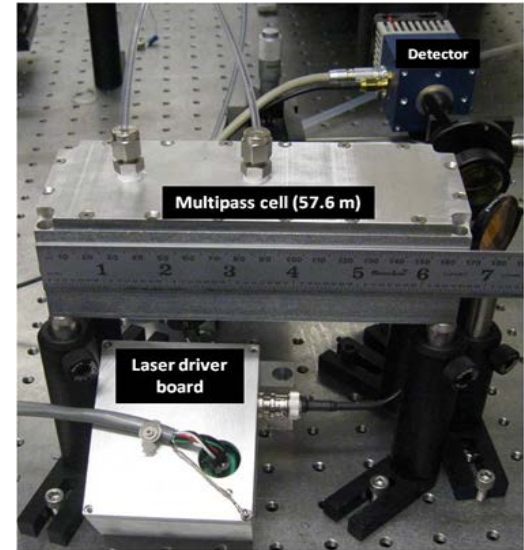


HITRAN absorption spectra of C_2H_6 , CH_4 , and H_2O

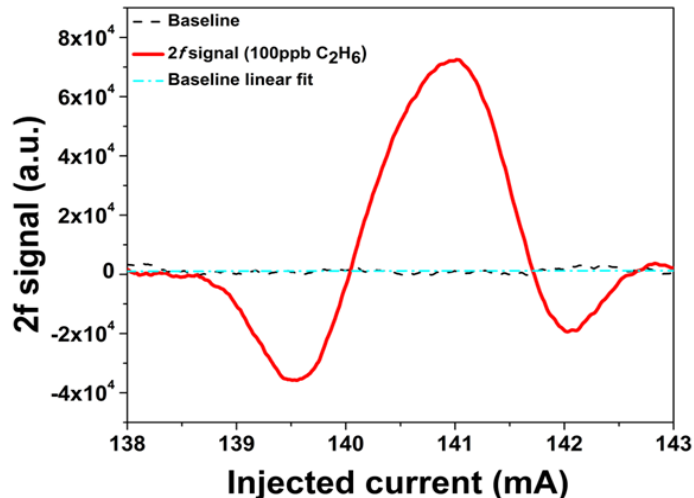
C_2H_6 Detection with a $3.36\ \mu m$ DFB LD using a Novel Compact Multipass Absorption Cell and Control Electronics



Schematic of a C_2H_6 gas sensor using a Nanoplus $3.36\ \mu m$ 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: 57.6 m 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)

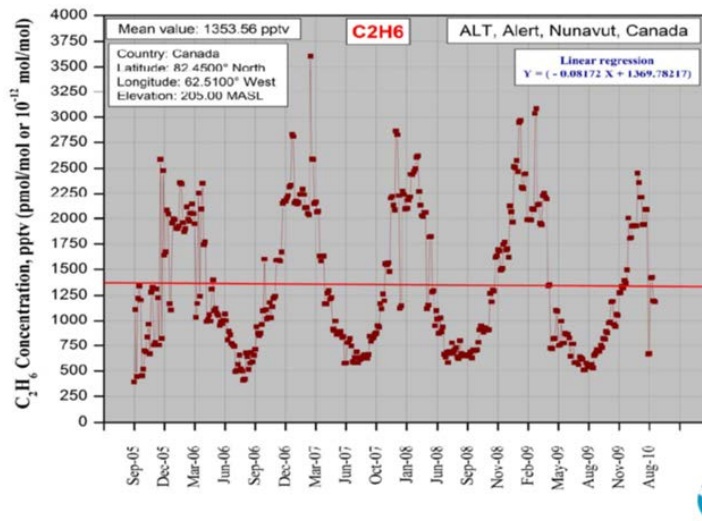


MC dimensions: 17 x 6.5 x 5.5 (cm)
Distance between the MGC mirrors: 12.5 cm

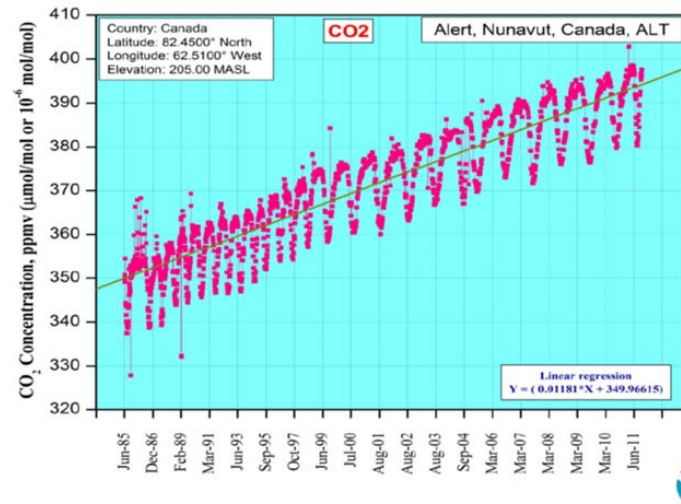
NOAA Monitoring and Sampling Location: Alert (ALT), Nunavut, Canada



General view on Alert NOAA Facility



Ethane Concentration Measurements at ALT



CO₂ Concentration Measurements at ALT

Motivation for NH_3 Detection

- Atmospheric chemistry
- Pollution gas monitoring
- Monitoring NH_3 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

Conventional Photoacoustic Spectroscopy (PAS)

Cell is **OPTIONAL!**

V-effective volume

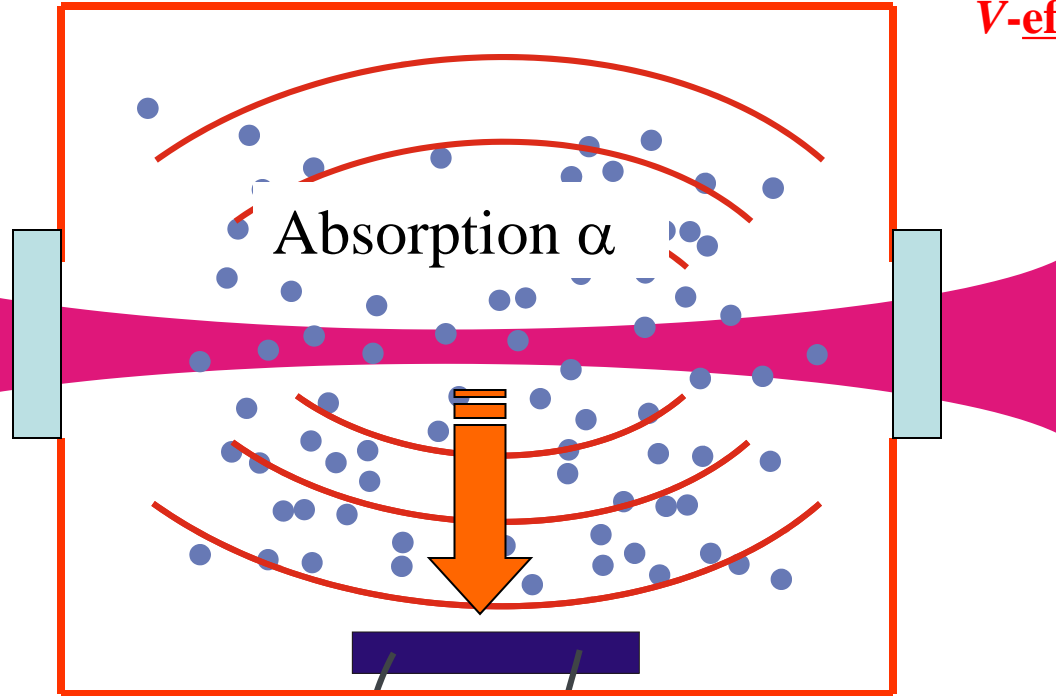
Laser beam,
power P



Modulated
(P or λ) at f
or $f/2$

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

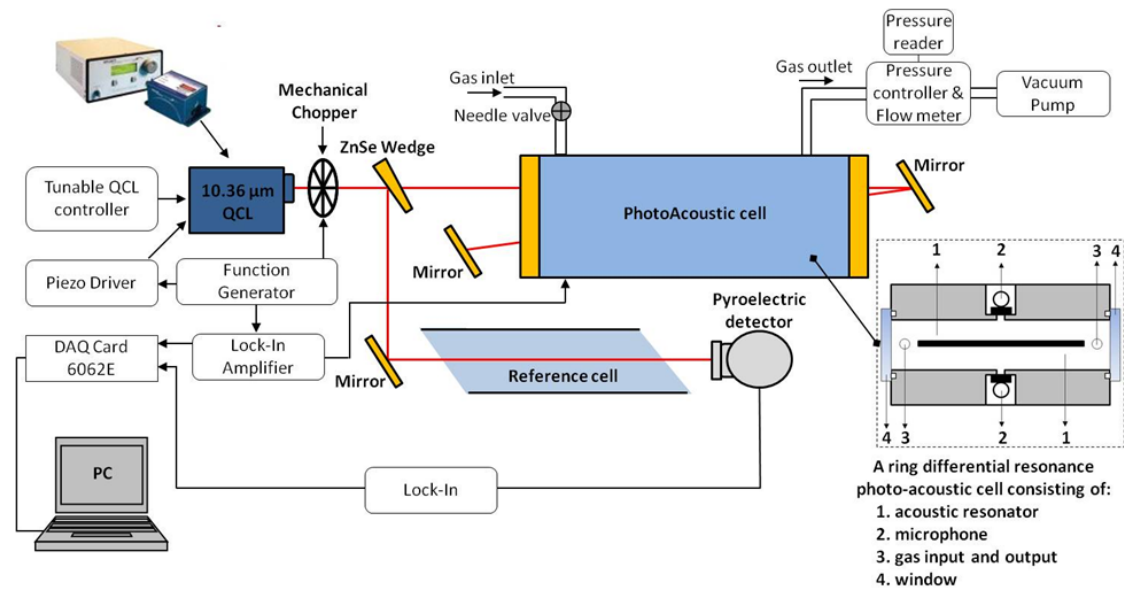
$$NNEA = \frac{\alpha_{\min} P}{\sqrt{\Delta f}} \left[\frac{\text{cm}^{-1} \times \text{W}}{\sqrt{\text{Hz}}} \right]$$



**Sensitive
microphone**

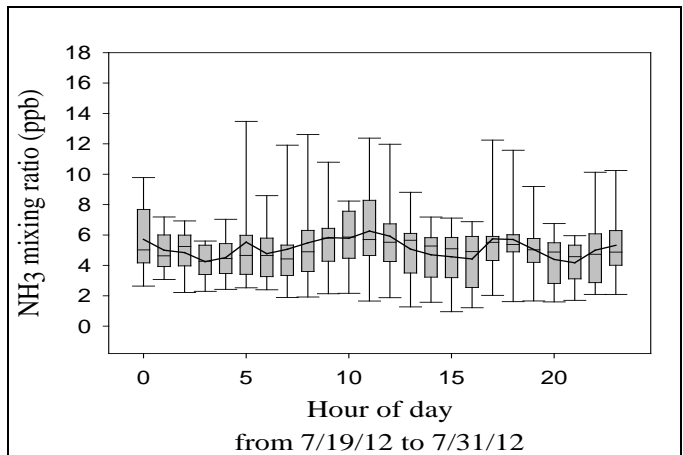


Atmospheric NH₃ Measurements using a CW EC-QCL PAS Sensor

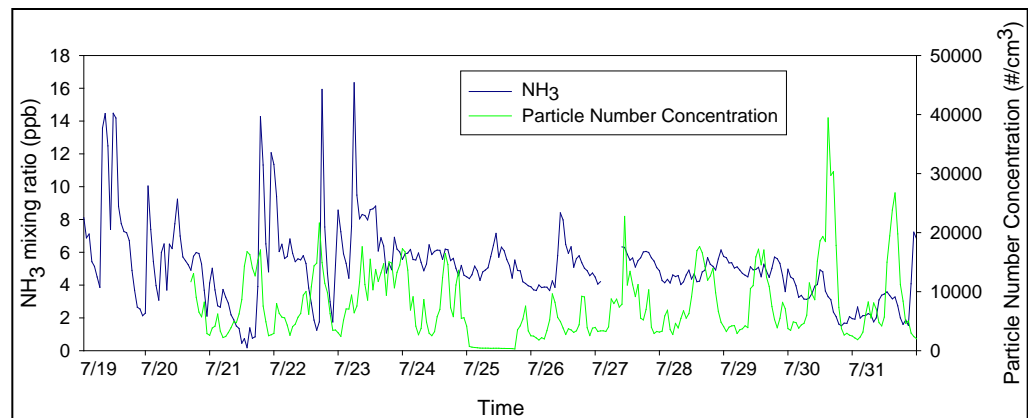


NH₃ sensor deployed at the UH Moody Tower rooftop monitoring site.

Schematic of a Daylight Solutions 10.36 μm CW TEC EC-QCL based PAS NH₃ Sensor.

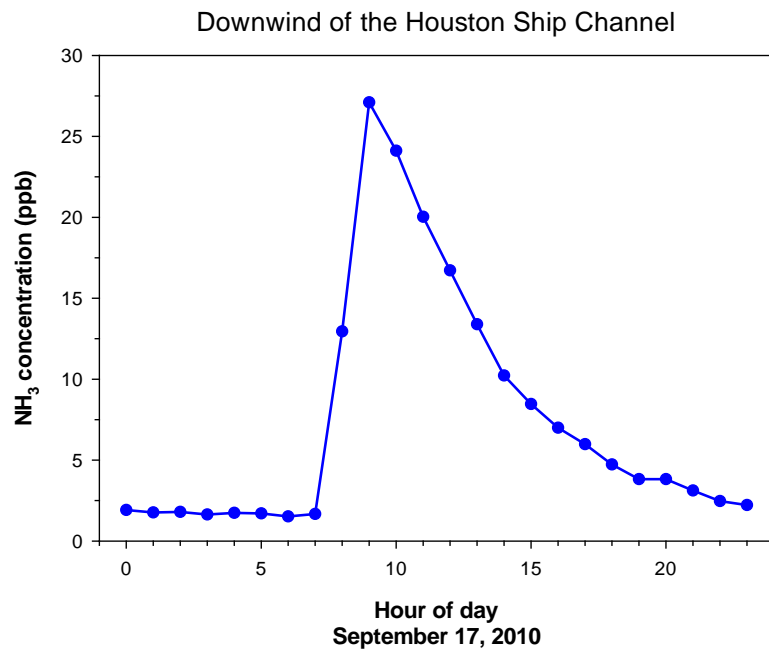
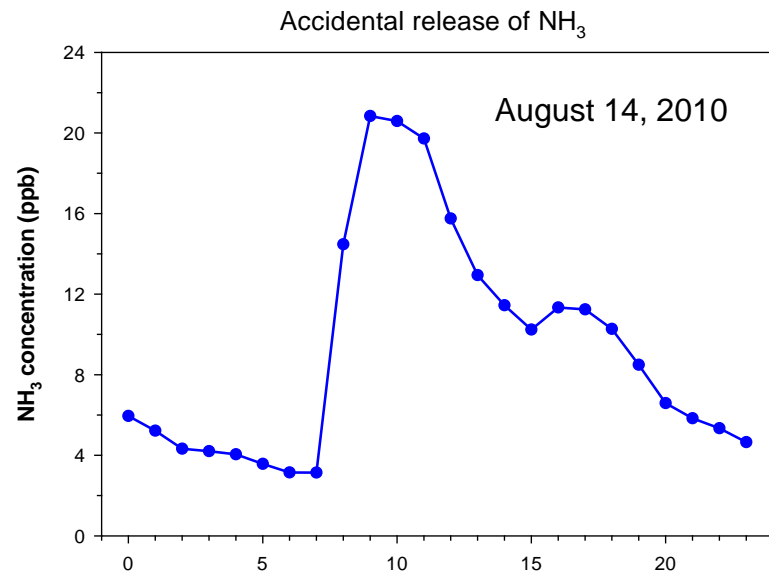


Diurnal profile of atmospheric NH₃ levels in Houston, TX.



Comparison between NH₃ and particle number concentration time series from July 19 to July 31 2012.

NH₃ Detection due to a Fire resulting from a two Truck Collision

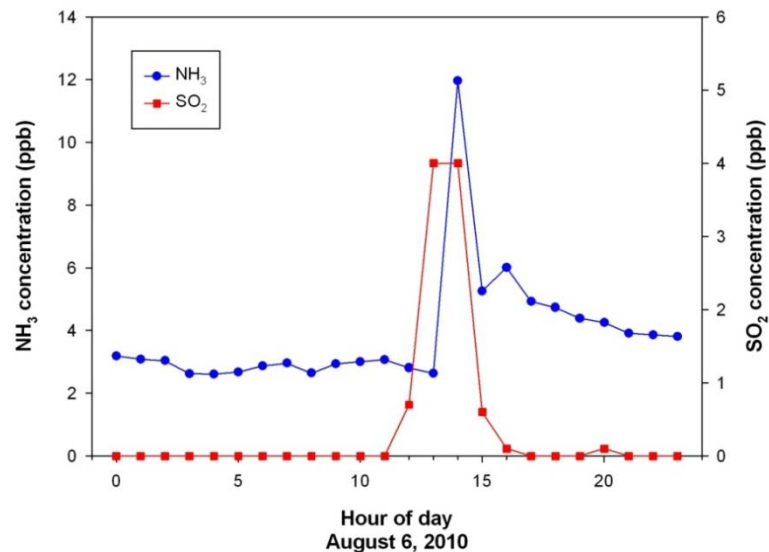
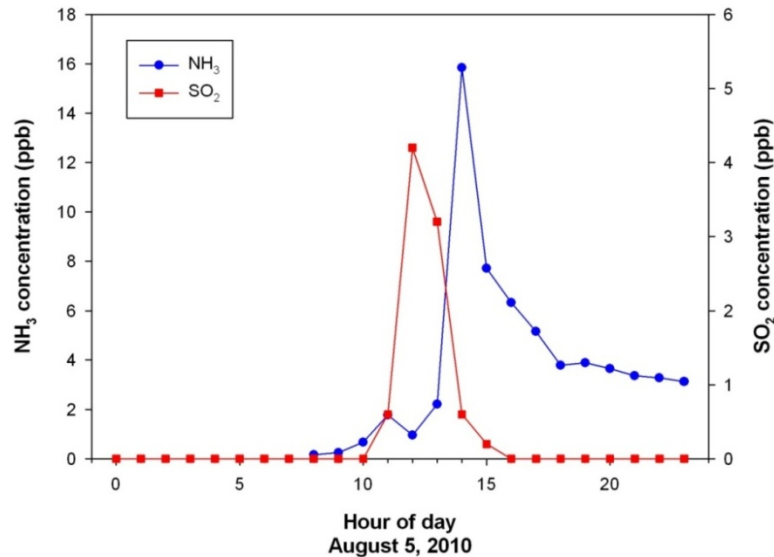


A chemical incident occurred at ~ 6 a.m. after two trucks collided on I-59. Both trucks caught fire. [www.chron.com]



Estimated hourly NH₃ emission from the Houston Ship Channel area is about 0.25 ton. Mellqvist et al., (2007) Final Report, HARC Project H-53.

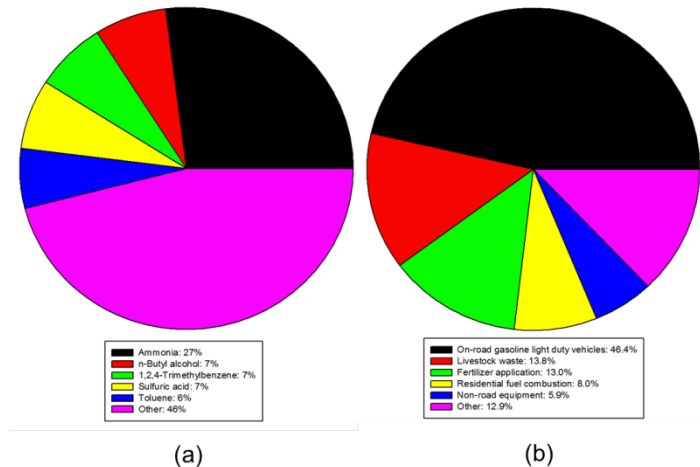
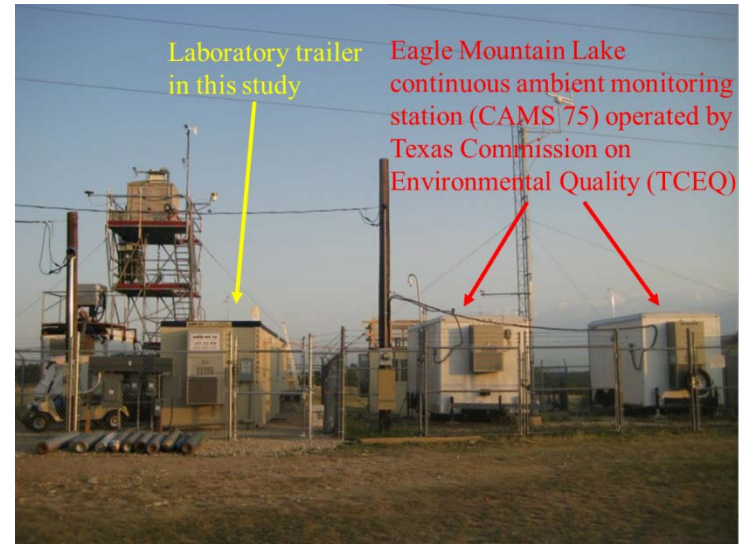
Sporadic increased NH_3 Concentration Levels related to NO_x Emission Reduction by the Parish Electric Power Plant, TX



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

Atmospheric NH_3 measurements and implications for PM formation near Fort Worth

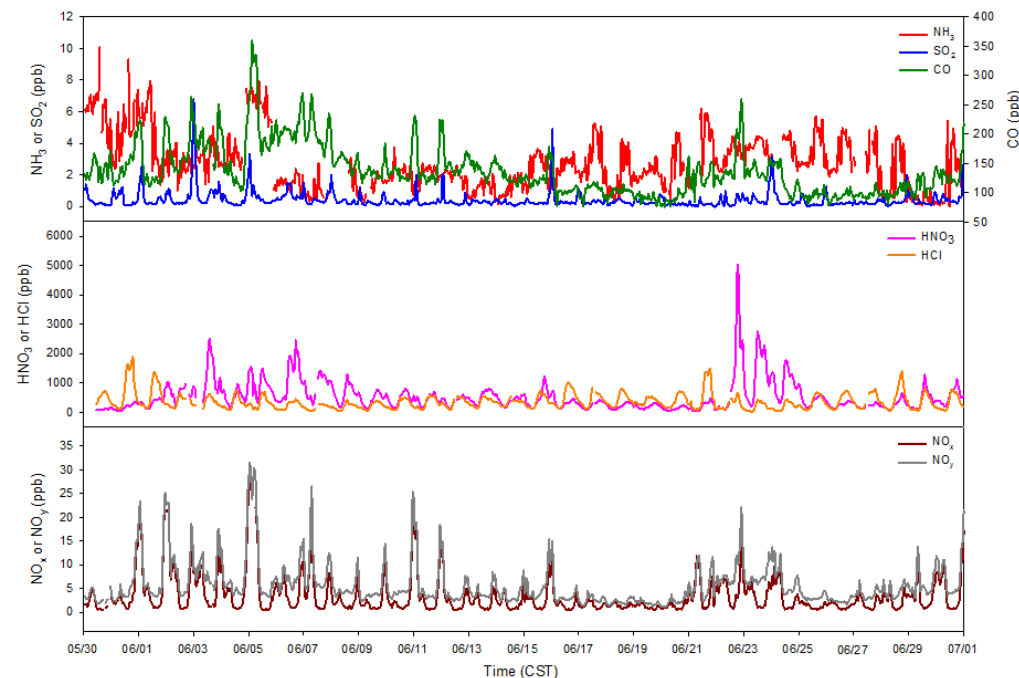
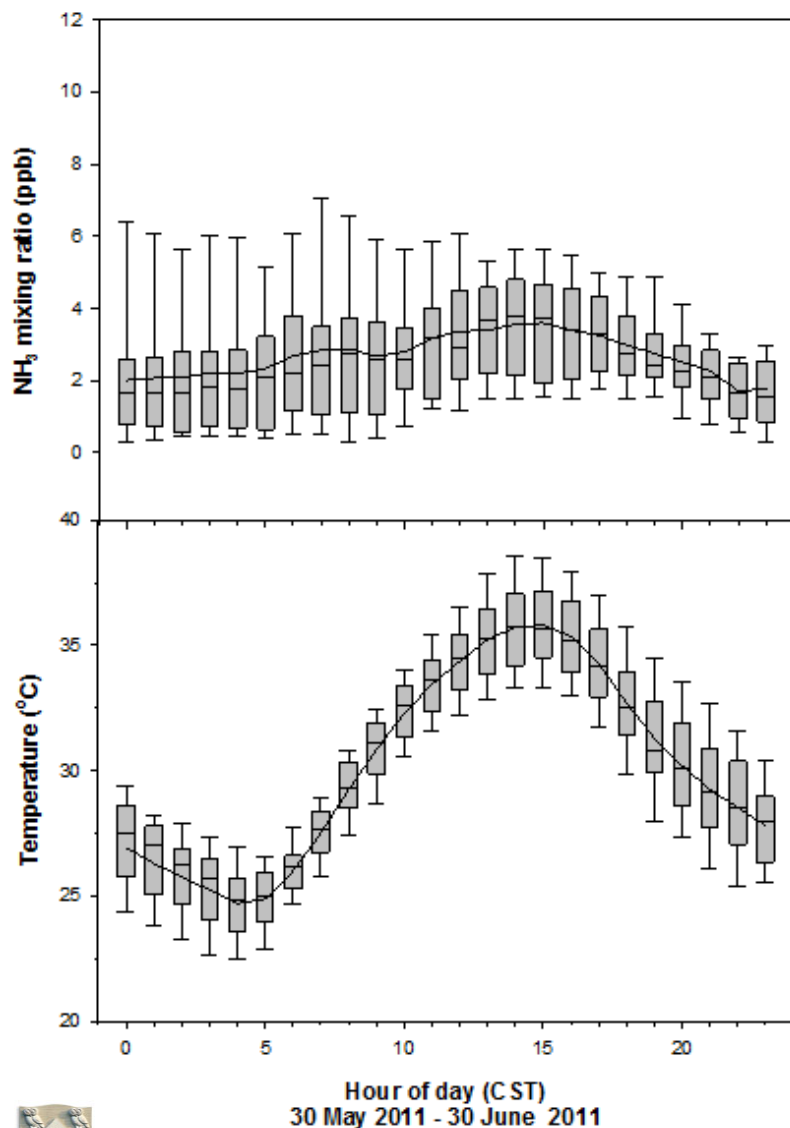
- Four specific aims are being pursued:
 - Investigation of the NH_3 dynamics (e.g., temporal variation);
 - Identification of NH_3 sources using auxiliary data for CO and NO_x ;
 - Performing NH_3 source apportionment using the EPA Positive Matrix Factorization 3.0 model including VOC_s data;
 - Evaluation of NH_3 effects on local and regional air quality with respect to PM formation using aerosol/PM data collected by an Aerodyne High Resolution Time-of-Flight Mass Spectrometer, a Scanning Electrical Mobility Spectrometer, and a Mist Chamber-Ion Chromatography system.



(a) Annual total air releases by species in the DFW area (U.S. EPA TRI, 2010); (b) Annual NH_3 emissions by source categories in Tarrant County, Texas (U.S. EPA NEI, 2008)



NH₃ vs. Temperature data & Time series of NH₃, SO₂, CO



- 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%)



From Conventional PAS to QEPAS

$Q \gg 1000$

Cell is **OPTIONAL!**

V-effective volume

Laser beam,
power P

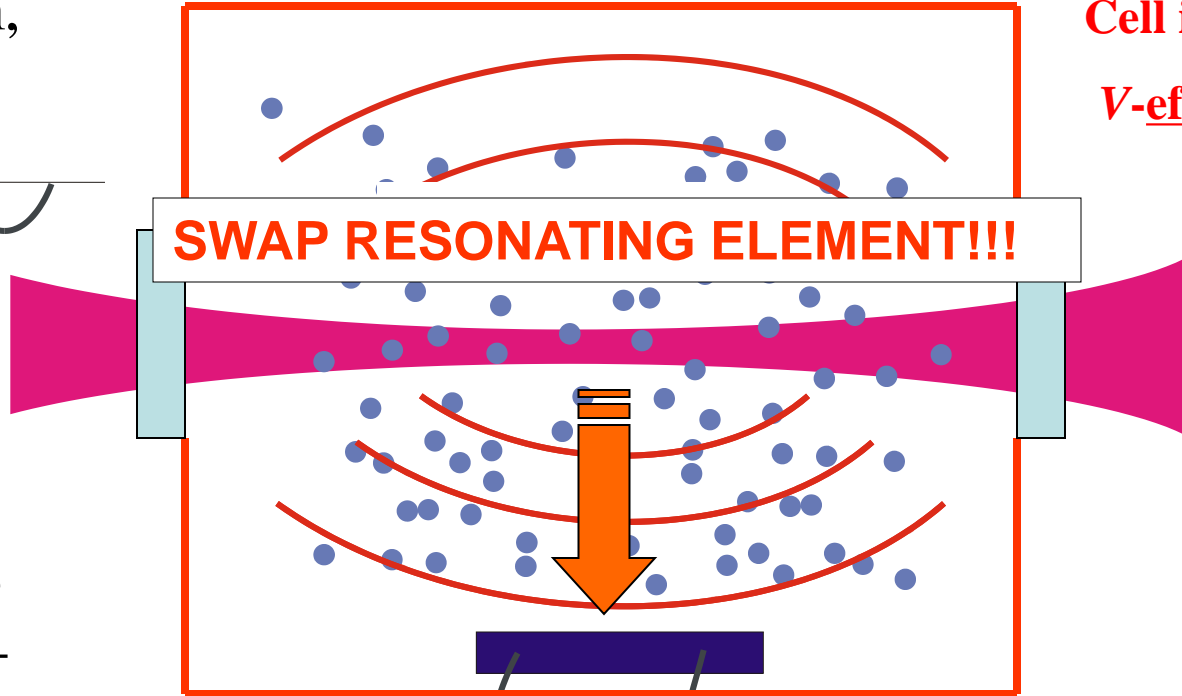


Modulated
(P or λ) at f
or $f/2$

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

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

SWAP RESONATING ELEMENT!!!



**Piezoelectric
crystal**

**Resonant at f
quality factor Q**



Quartz Tuning Fork as a Resonant Microphone for QEPAS

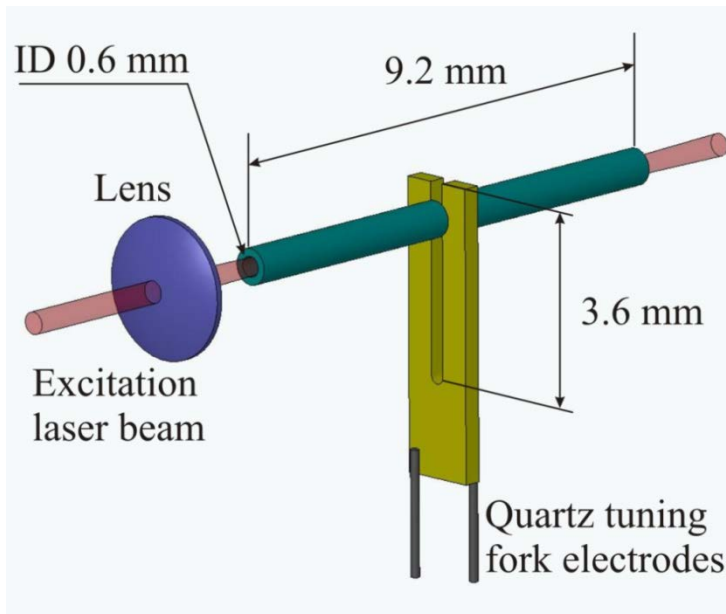


Unique properties

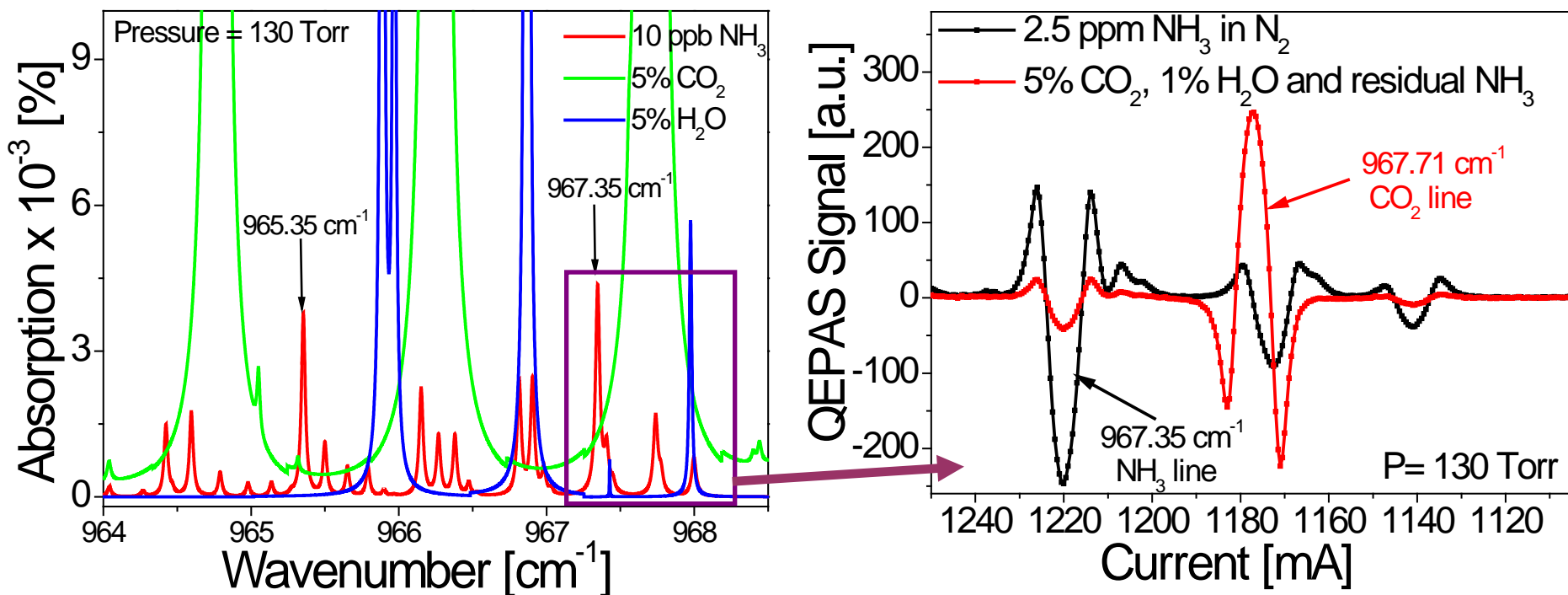
- Extremely low internal losses:
 - $Q \sim 10\,000$ at 1 atm
 - $Q \sim 100\,000$ in vacuum
- Acoustic quadrupole geometry
 - Low sensitivity to external sound
- Large dynamic range ($\sim 10^6$) – linear from thermal noise to breakdown deformation
 - 300 K noise: $x \sim 10^{-11}$ cm & breakdown: $x \sim 10^{-2}$ cm
- Wide temperature range: from 1.6K to ~ 700 K
- Low cost (< \$ 0.30)
- Resonant frequency;: ~ 32.8 KHz

Acoustic Micro-resonator (mR) tubes

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



Optimum NH_3 Line Selection for a $10.34\text{ }\mu\text{m}$ CW TEC DFB QCL

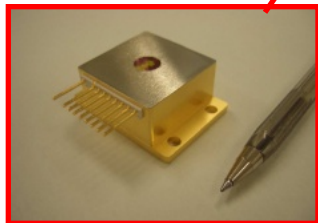
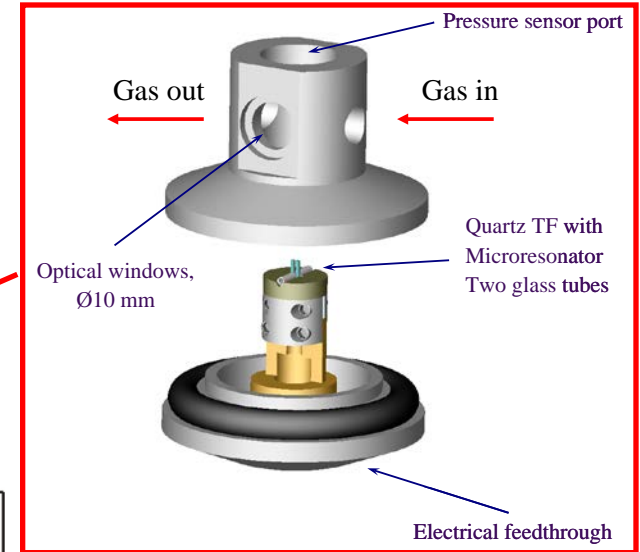
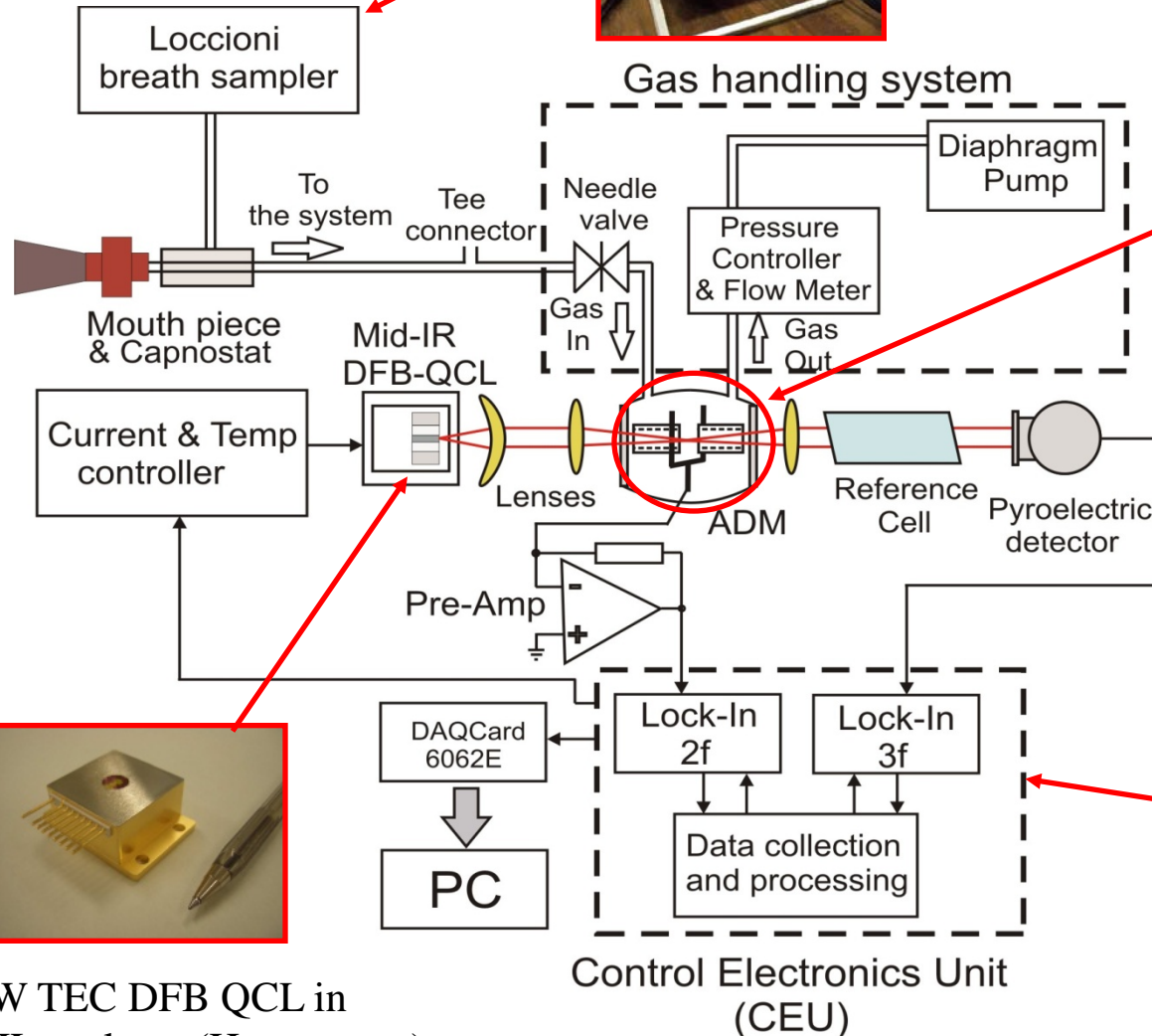


Simulated HITRAN high resolution spectra @ 130 Torr indicating two NH_3 absorption lines of interest

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 R branch of the ν_2 band.

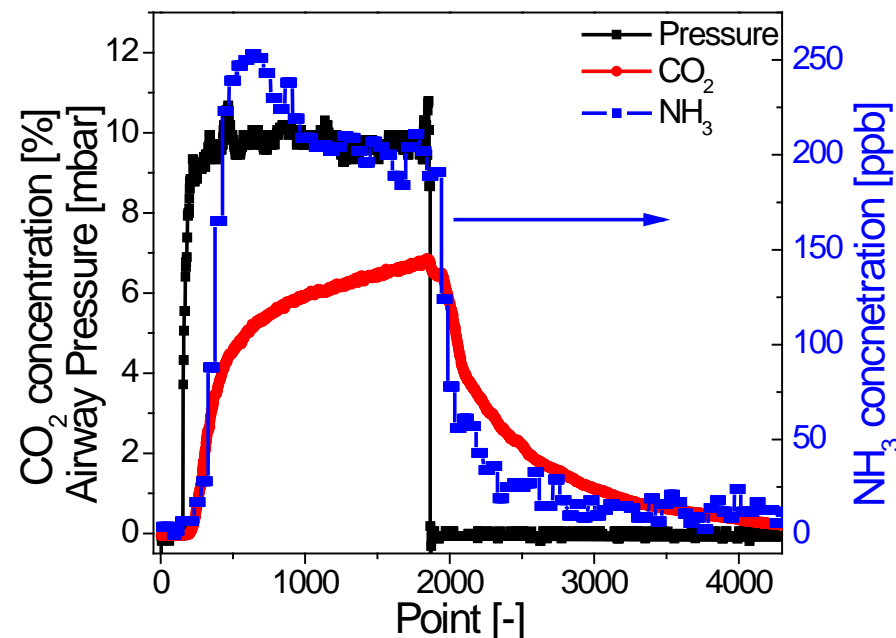
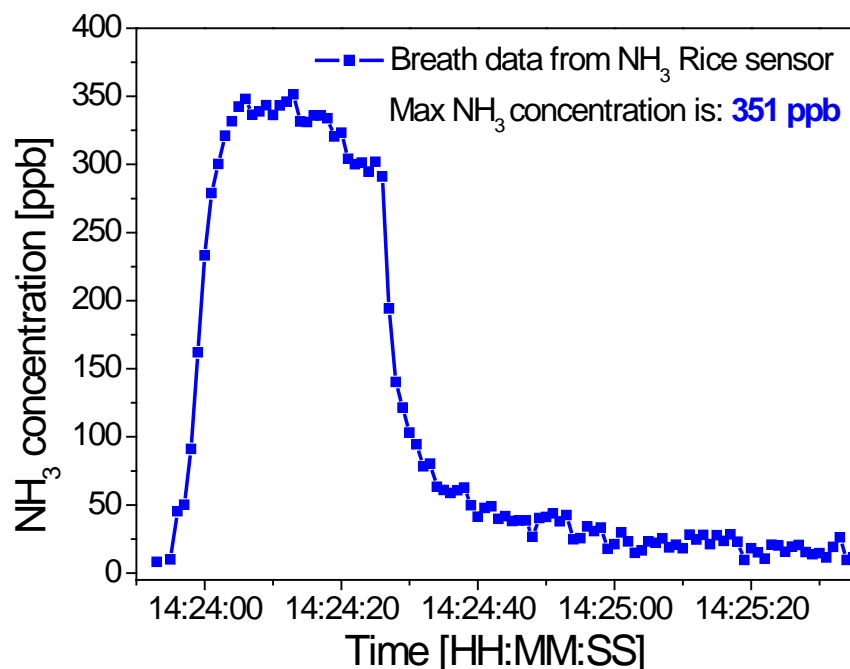


QEPAS based NH_3 Gas Sensor Architecture



CW TEC DFB QCL in
HHL package (Hamamatsu)

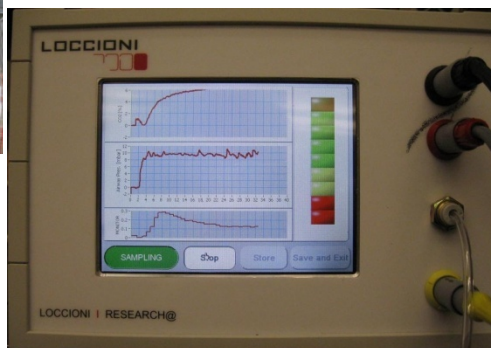
Real-time exhaled human NH_3 Breath Measurements



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)

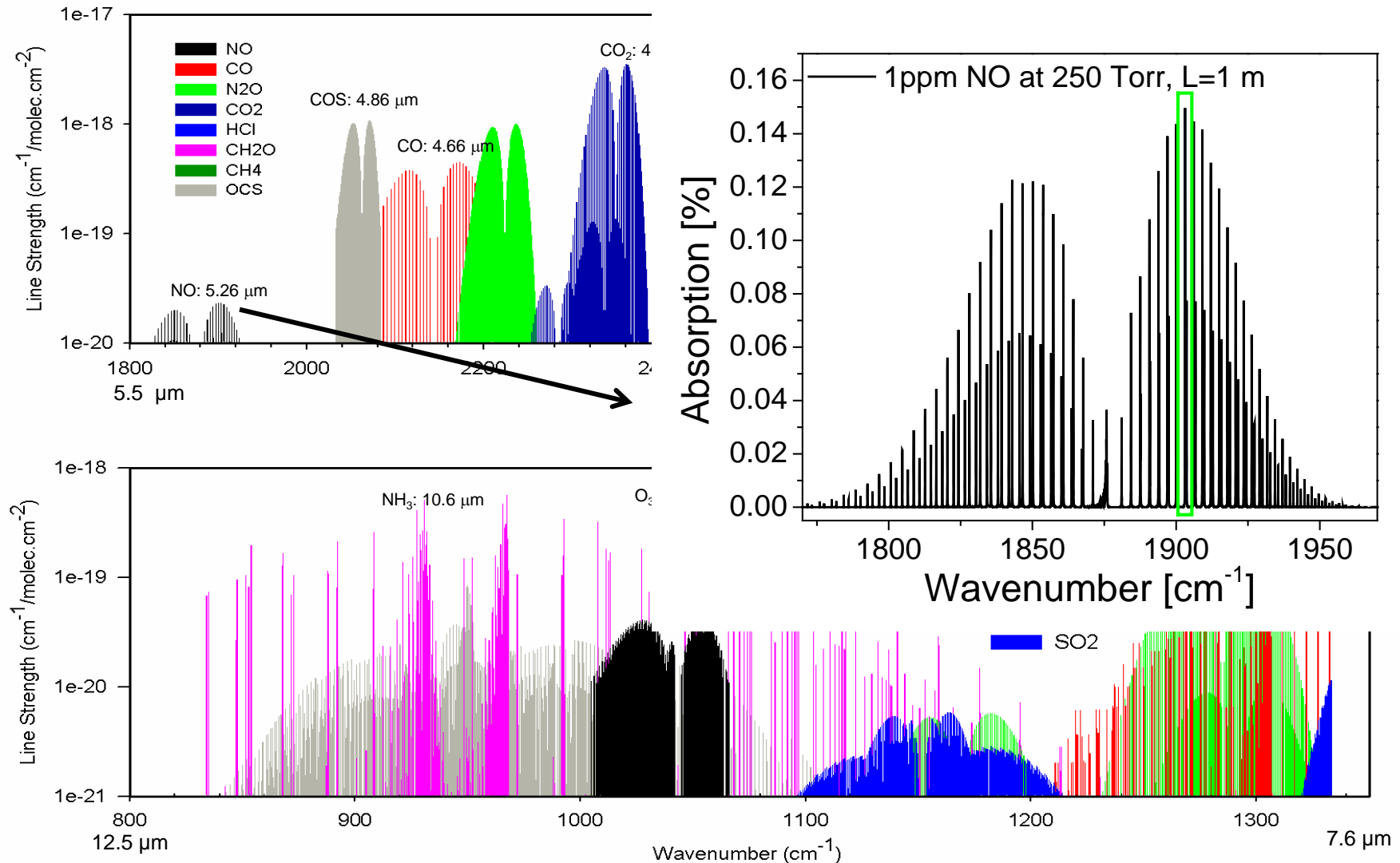
Minimum detectable concentration of NH_3 is:
~ 6 ppbv at 967.35 cm⁻¹ (1 σ ; 1 s time resolution)



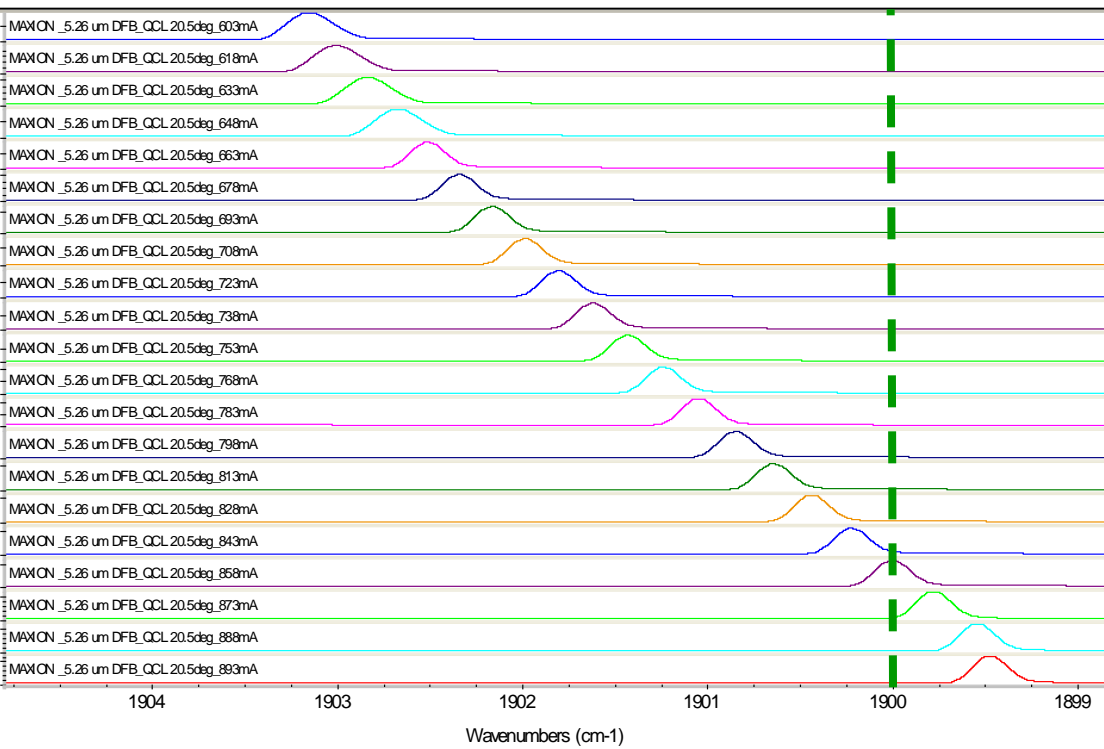
Motivation for Nitric Oxide Detection

- 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

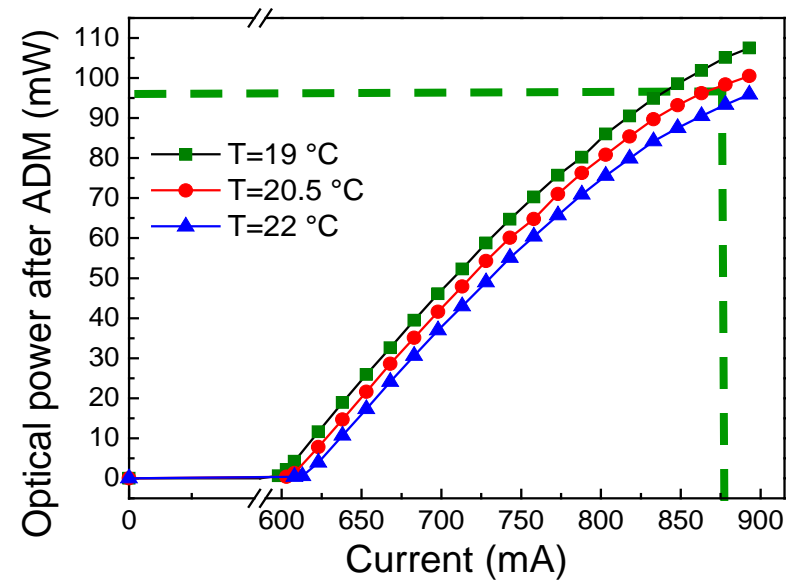
Molecular Absorption Spectra within two Mid-IR Atmospheric Windows and NO absorption @ 5.26 μm



Performance of a 5.26 μm CW HHL TEC DFB-QCL



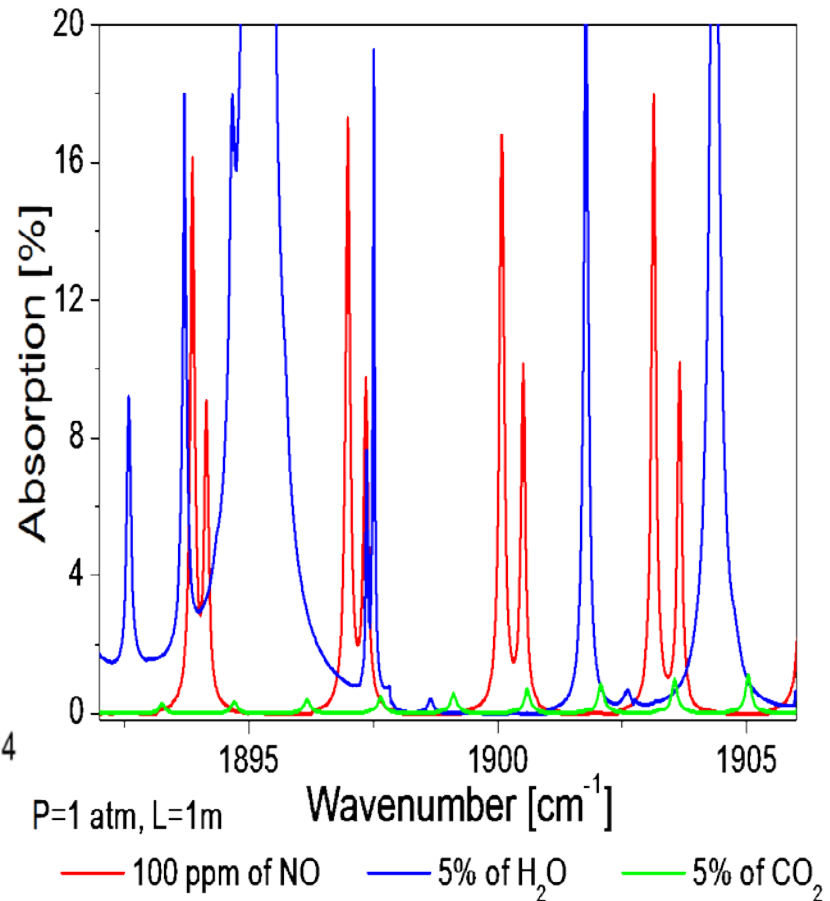
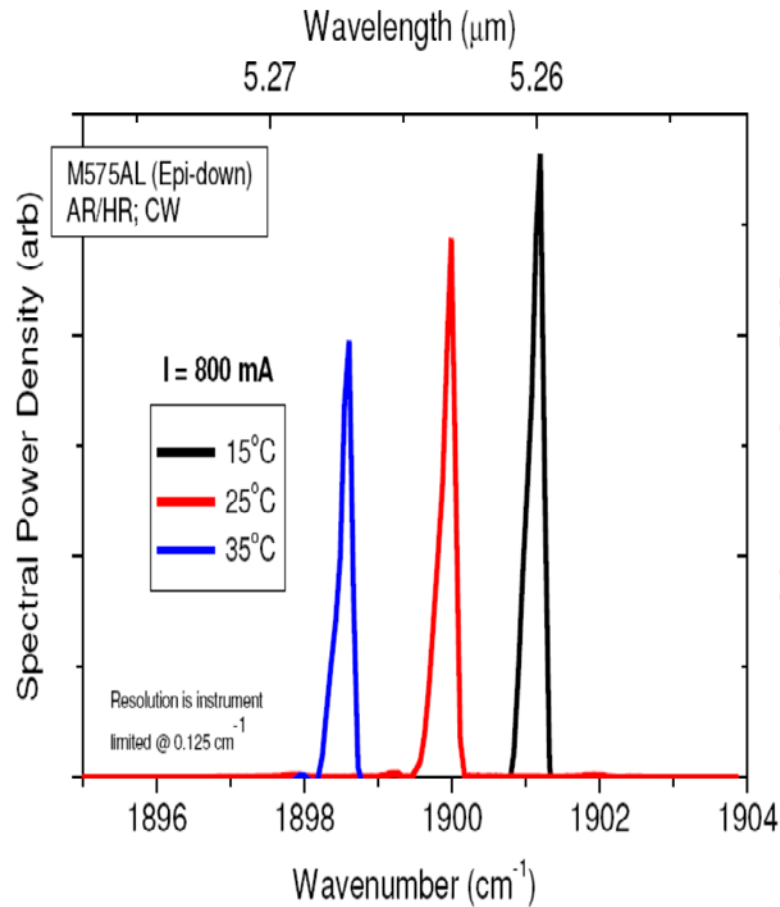
Single frequency QCL radiation recorded with FTIR for different laser current values at a QCL temperature of 20.5°C.



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

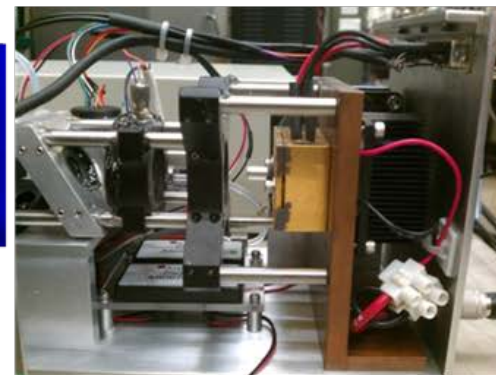
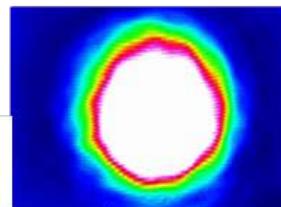
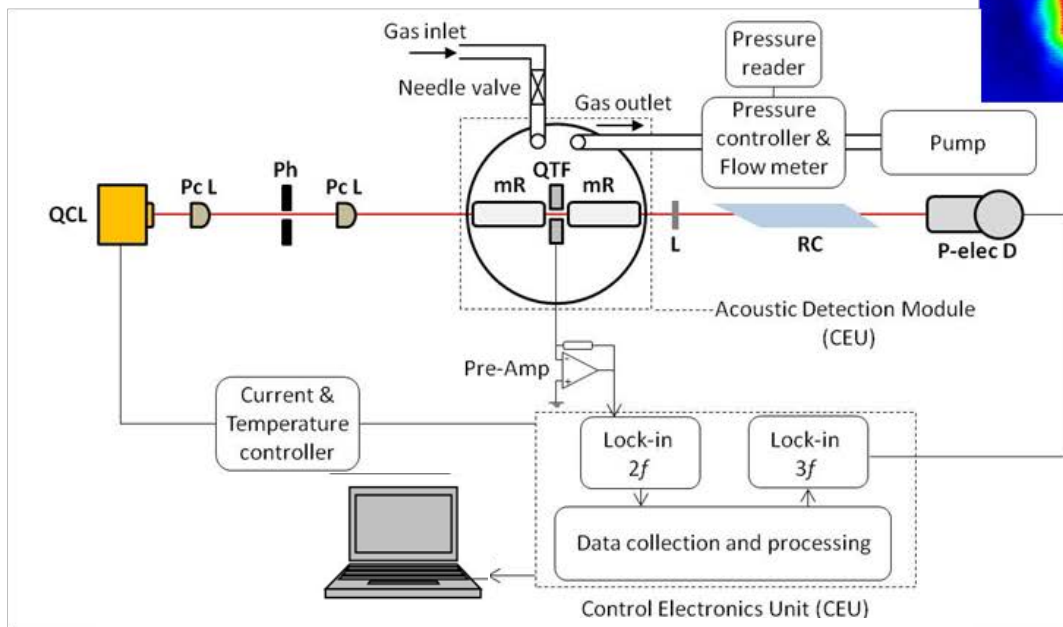


Emission spectra of a 1900cm^{-1} TEC CW DFB QCL and HITRAN Simulated spectra



Output power: 117 mW @ 25 C

CW TEC DFB QCL based QEPAS NO Gas Sensor



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)

Schematic of a DFB-QCL based Gas Sensor.

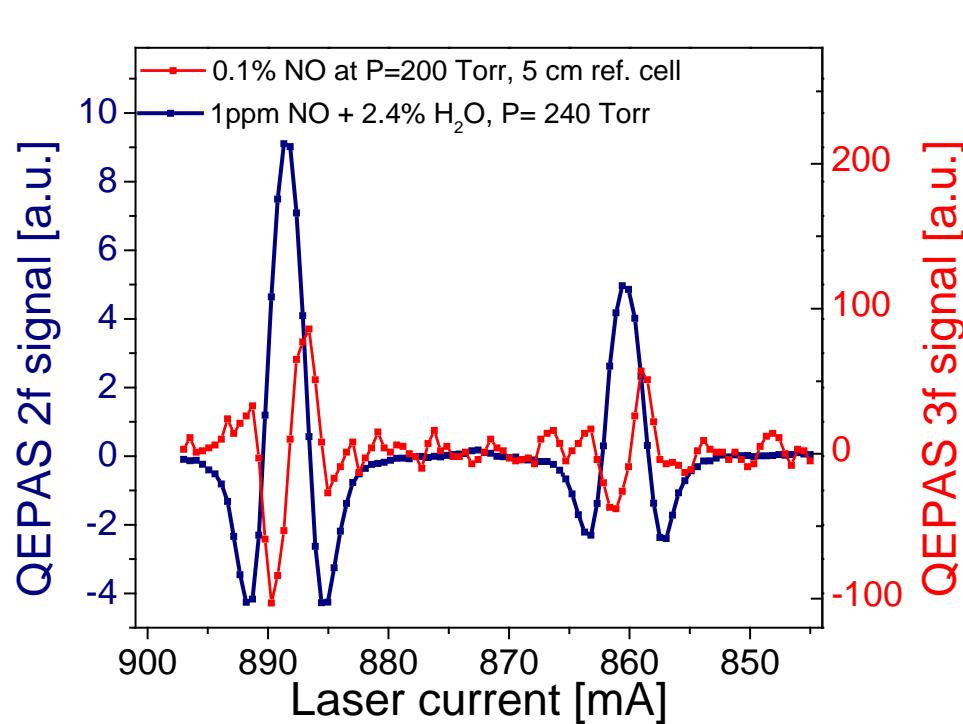
PcL – plano-convex lens, Ph – pinhole,

QTF – quartz tuning fork, mR – microresonator,

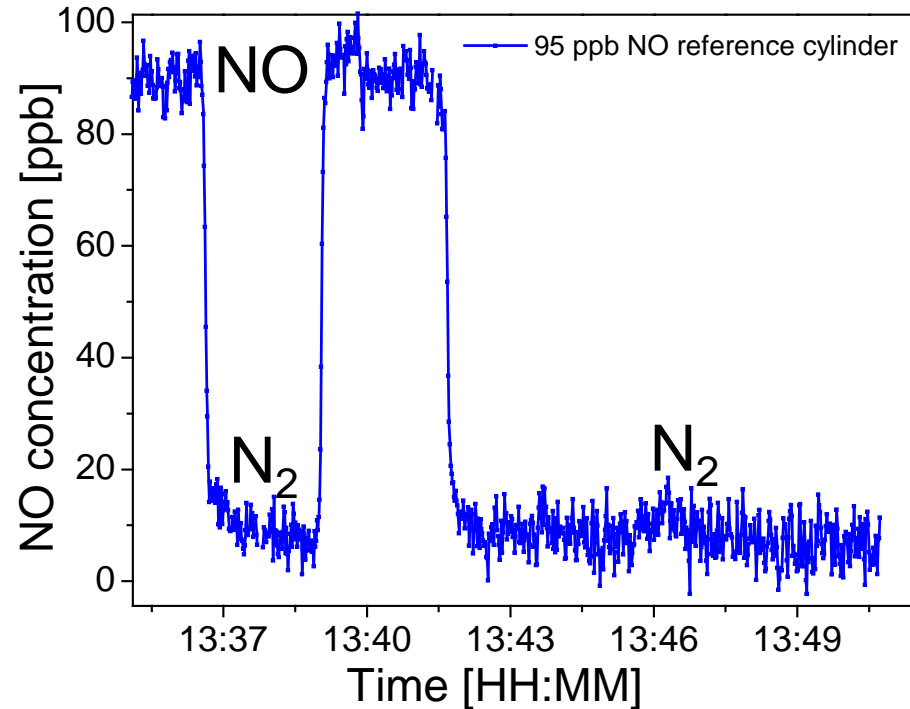
RC- reference cell, P-elec D – pyro electric detector



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.



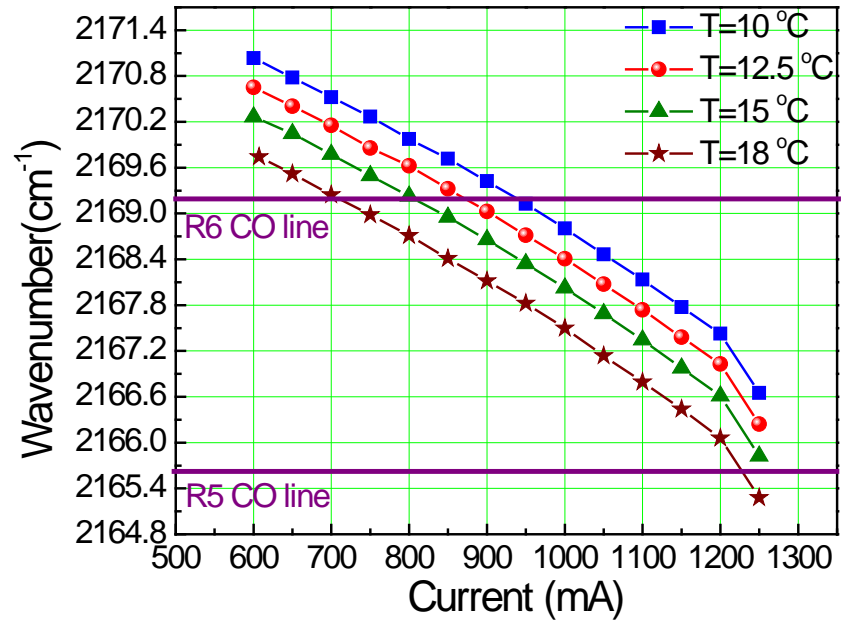
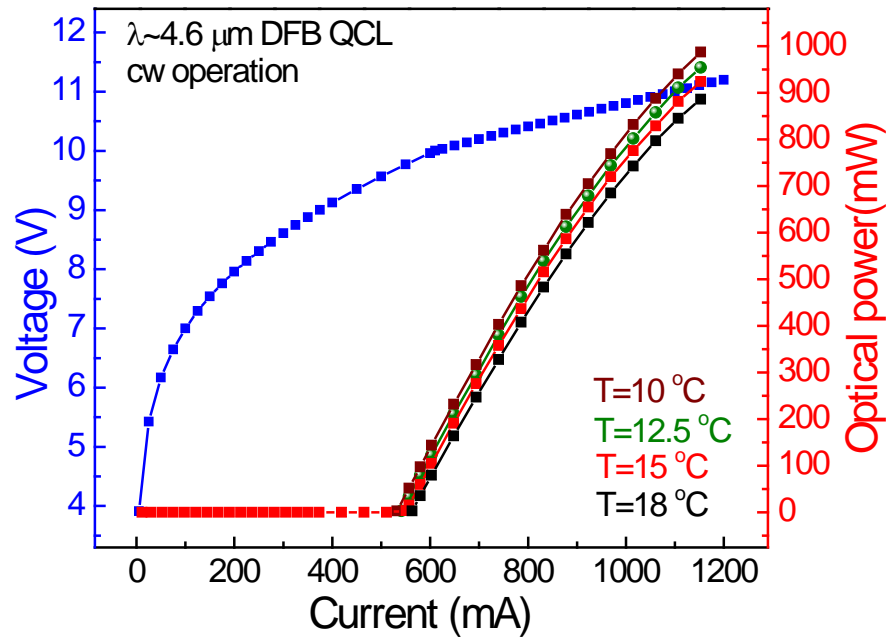
2f QEPAS signal amplitude for 95 ppb NO when DFB-QCL was locked to the **1900.08 cm⁻¹** line.

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

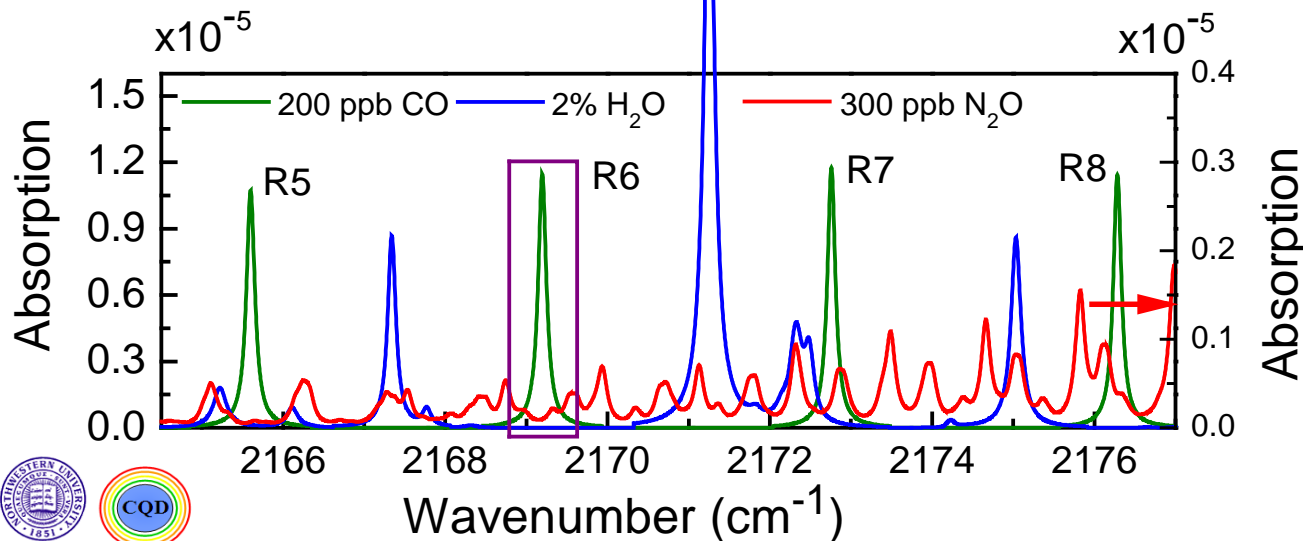
Motivation for Carbon Monoxide Detection

- 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. 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.

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

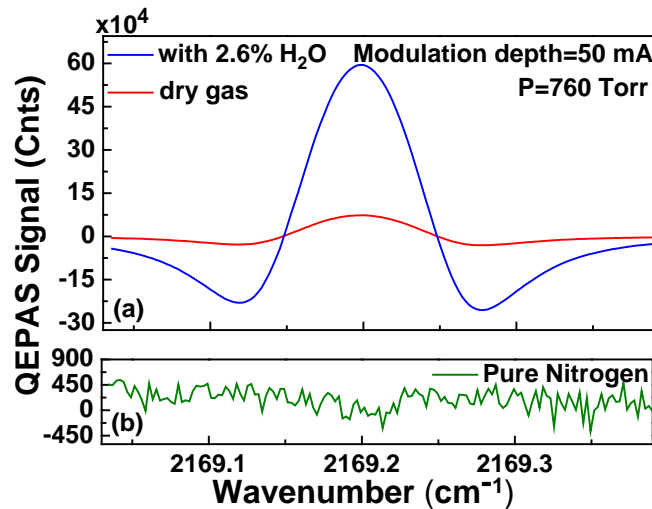


CW DFB-QCL optical power and current tuning at a four different QCL temperatures.

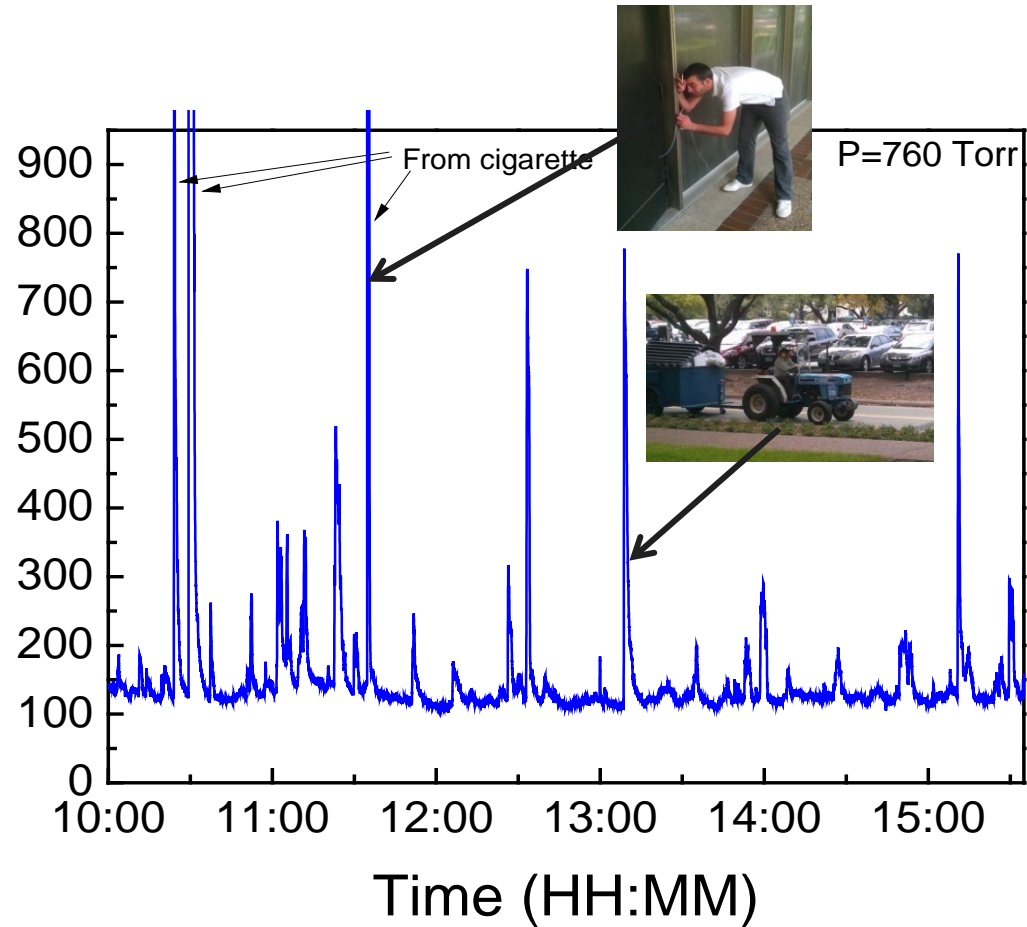


Estimated max wall-plug efficiency (WPE) is $\sim 7\%$ at 1.25A QCL drive-current.

CW DFB-QCL based CO QEPAS Sensor Results

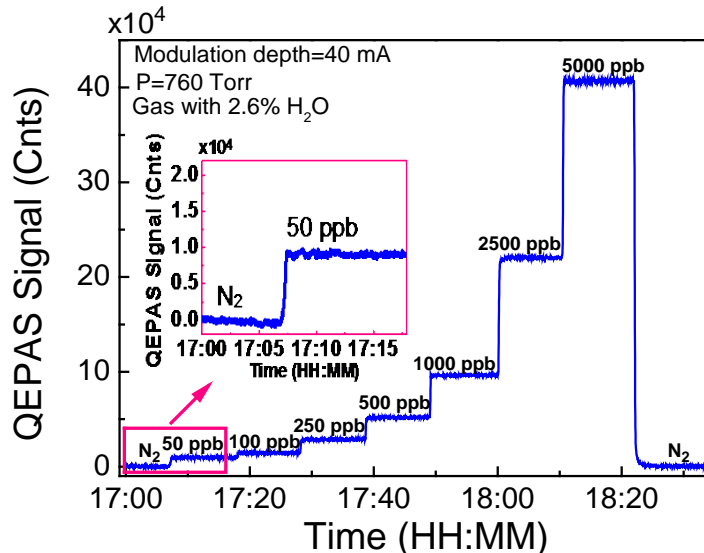


CO concentration (ppb)



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

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

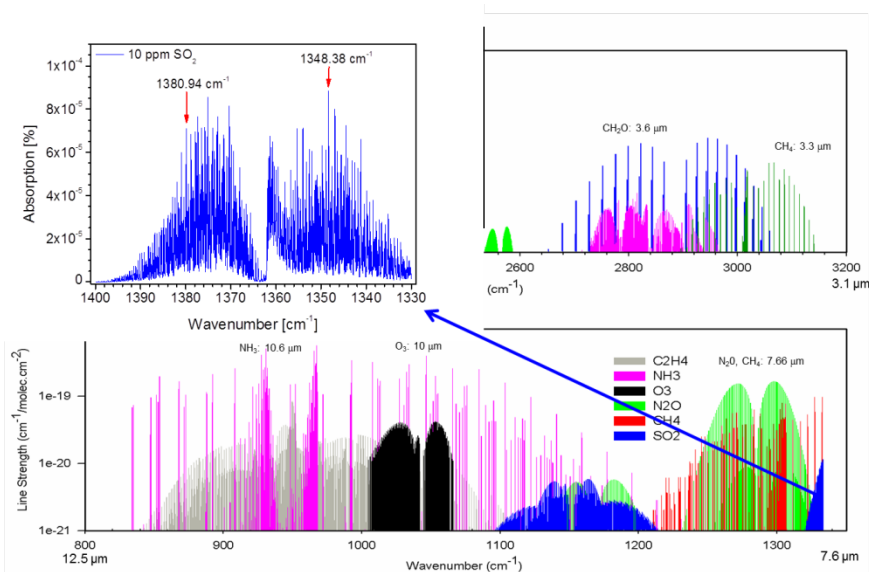


Dilution of a 5 ppm CO reference gas mixture when the CW DFB-QCL is locked to the 2169.2 cm^{-1} R6 CO line.

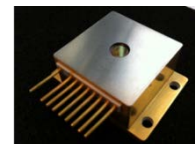
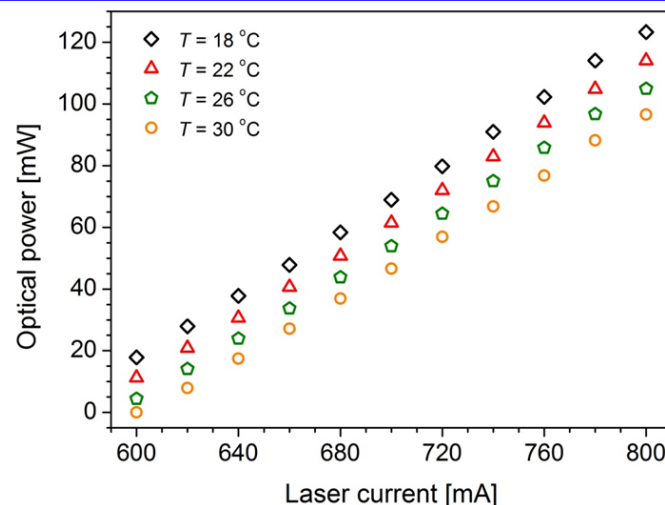
CW DFB-QCL based SO₂ QEPAS Sensor Results

Motivation for Sulfur Dioxide Detection

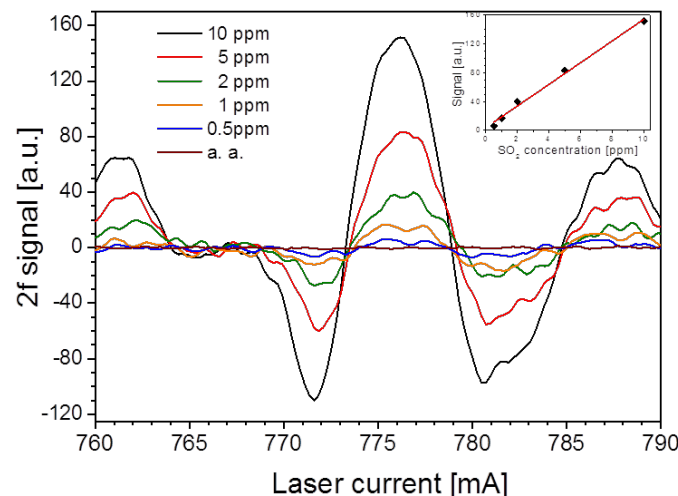
- Prominent air pollutant
- Emitted from coal fired power plants (~73%) and other industrial facilities (~20%)
- In atmosphere SO₂ converts to sulfuric acid
➔ primary contributors to acid rain
- SO₂ reacts to form sulfate aerosols
- Primary SO₂ exposure for 1 hour is 75 ppb
- SO₂ exposure affects lungs and causes breathing difficulties
- Currently, reported annual average atmospheric SO₂ concentrations range from ~ 1 - 6 ppb



Molecular Absorption Spectra within two Mid-IR Atmospheric Windows



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

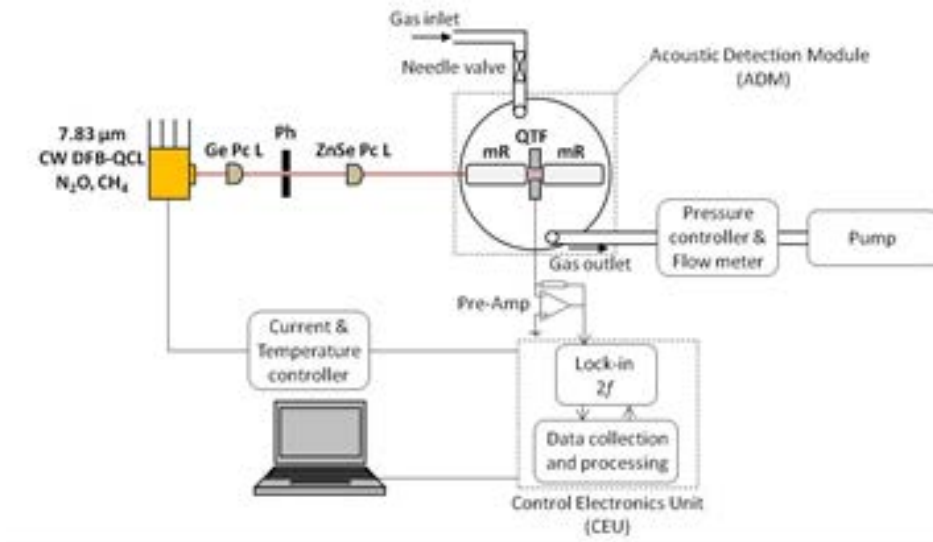


2f WMS QEPAS signals for different SO₂ concentrations when laser was tuned across **1380.9 cm⁻¹** line.

Minimum detectable SO₂ concentration is:

~ 100 ppbv (1σ; 1 s time resolution)

CW TEC DFB QCL based QEPAS CH_4 & N_2O Gas Sensor



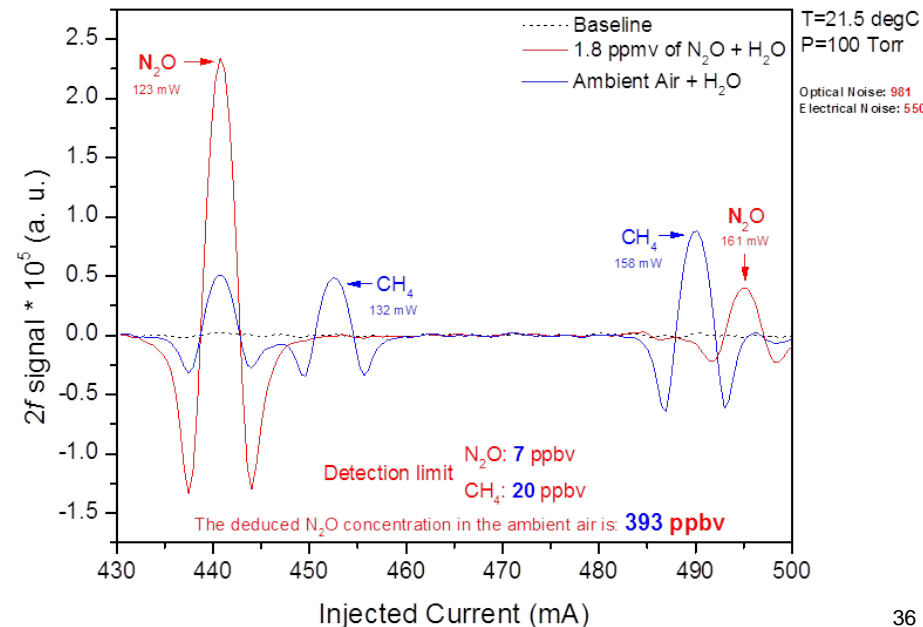
Ge Pc L and ZnSe Pc L – plano-convex lenses, Ph – pinhole, QTF – quartz tuning fork, mR – acoustic micro-resonator

Motivation for CH_4 Detection

- Prominent greenhouse gas
- Leakage from Natural Gas Systems
- Animal Husbandry
- Fossil Fuel Production

Motivation for N_2O Detection

- Major greenhouse gas and air pollutant
- Agriculture
- Fossil Fuel Combustion
- Wastewater Management
- Industrial processes
- Medical Applications



Current CH_4 & N_2O Sensor Platform

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

Molecule (carrier gas)	Frequency cm ⁻¹	Pressure Torr	NNEA cm ⁻¹ W/Hz ^{1/2}	QCL Power mW	NEC (τ=1s) ppbV
CH₂O (N₂:75% RH)*	2804.90	75	8.7×10 ⁻⁹	7.2	120
CO (N₂+ 2.2% H₂O)*	2176.28	100	1.57×10 ⁻⁸	71	2
CO (propylene)	2196.66	50	7.4×10 ⁻⁸	6.5	140
N₂O (air+5%SF₆)	2195.63	50	1.5×10 ⁻⁸	19	7
N₂O (N₂+2.37%H₂O)	2201.75	200	2.9×10 ⁻⁸	70	2.5
C₂H₅OH (N₂)**	1934.2	770	2.2×10 ⁻⁷	10	9×10 ⁴
NO (N₂+H₂O)	1900.07	250	7.5×10 ⁻⁹	100	3.6
SO₂ (N₂+2.4%H₂O)	1380.94	100	2.0×10 ⁻⁸	40	100
N₂O (air)	1275.49	230	5.3×10 ⁻⁸	100	30
CH₄ (air)	1275.39	230	1.7×10 ⁻⁷	100	118
C₂HF₅ (N₂)***	1208.62	770	7.8×10 ⁻⁹	6.6	9
NH₃ (N₂)*	1046.39	110	1.6×10 ⁻⁸	20	6
SF₆***	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 (1,800; 10,300 Hz) for NH₃*, ()**

* 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

Merits of QEPAS based Trace Gas Detection

- Very small sensing module and sample volume (a few mm³ to ~2cm²)
- 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

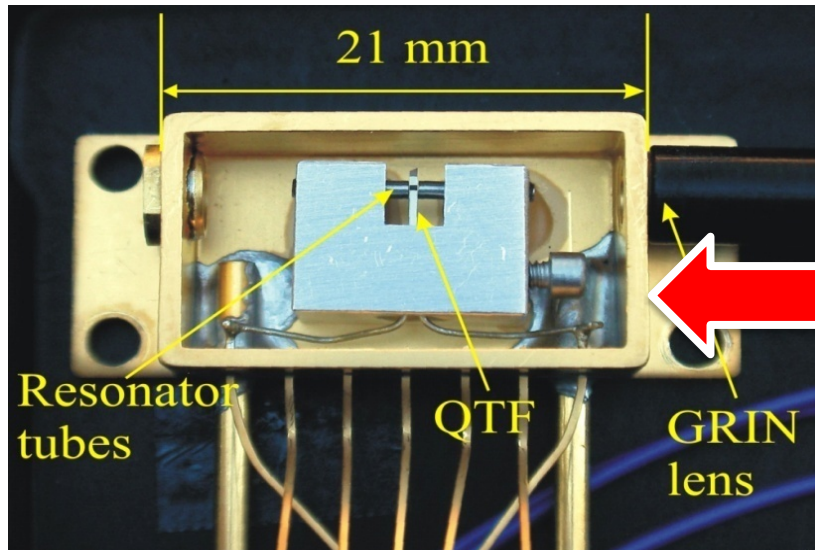
QEPAS: some challenges

- 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

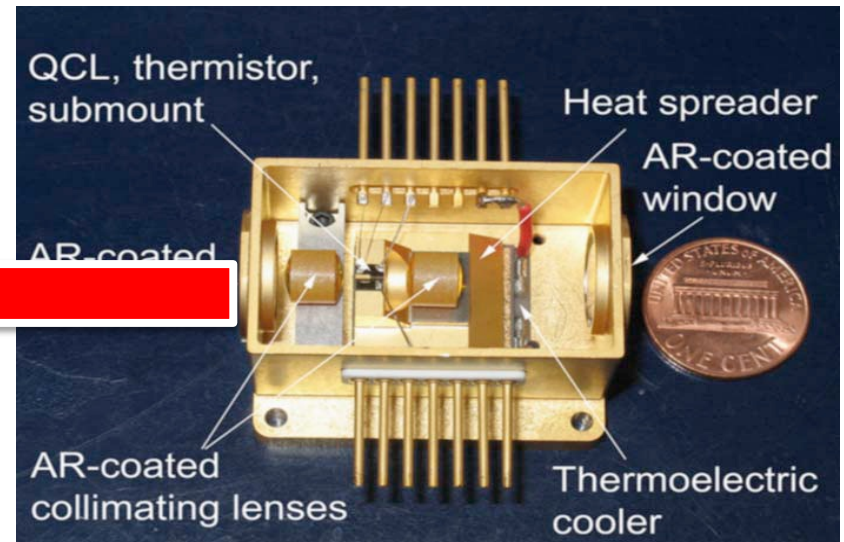
Future Directions and Outlook

- New target analytes such as OCS, CH_2O , nitrous acid (HNO_2), H_2O_2 , ethylene (C_2H_4), 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 ($\text{C}_3\text{H}_6\text{O}$), acetone peroxide (TATP), UF_6 ,...
- Low divergence surface emitting quantum cascade lasers
- Finite Element Modeling for on-axis and off-axis micro resonators for QEPAS
- Optical power build-up cavity designs
- Development of trace gas sensor networks

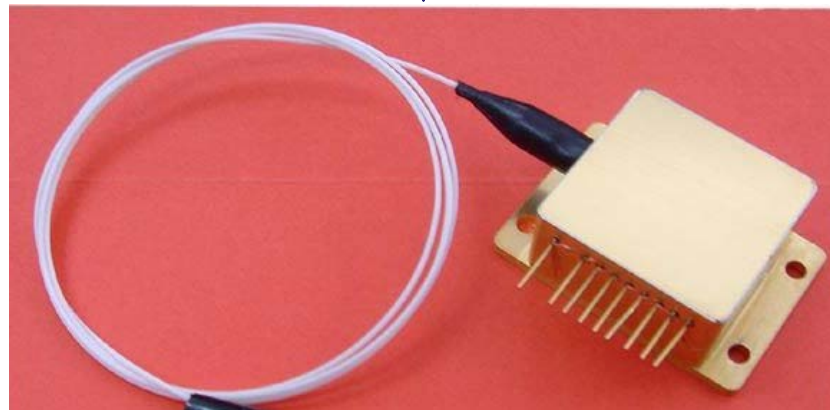
Potential Integration of a CW DFB- QCL and QEPAS Absorption Detection Module



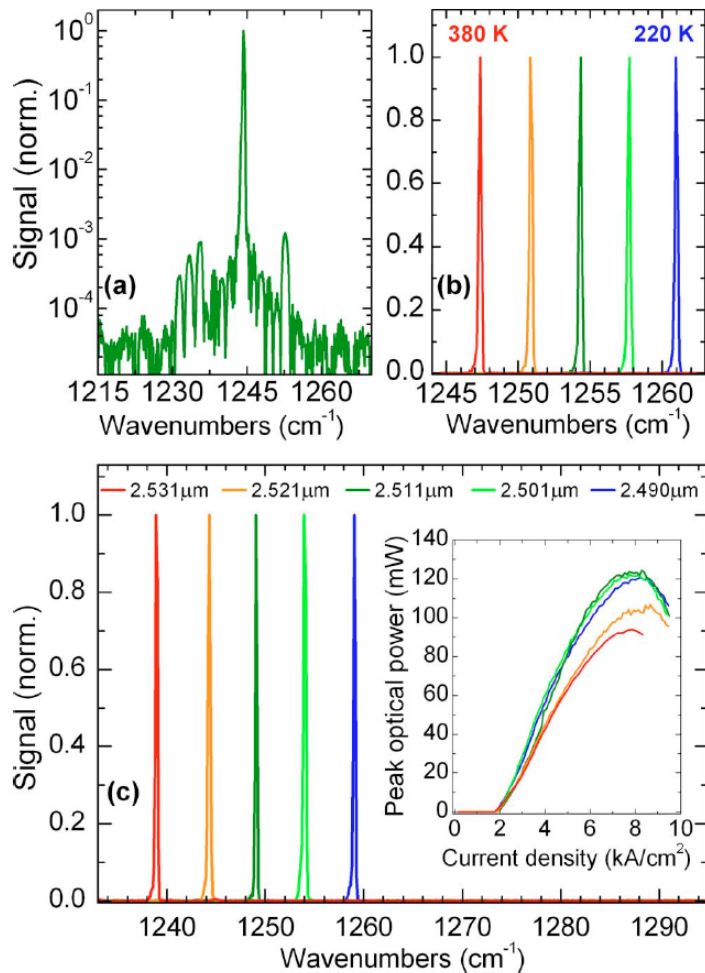
2012 QEPAS ADM



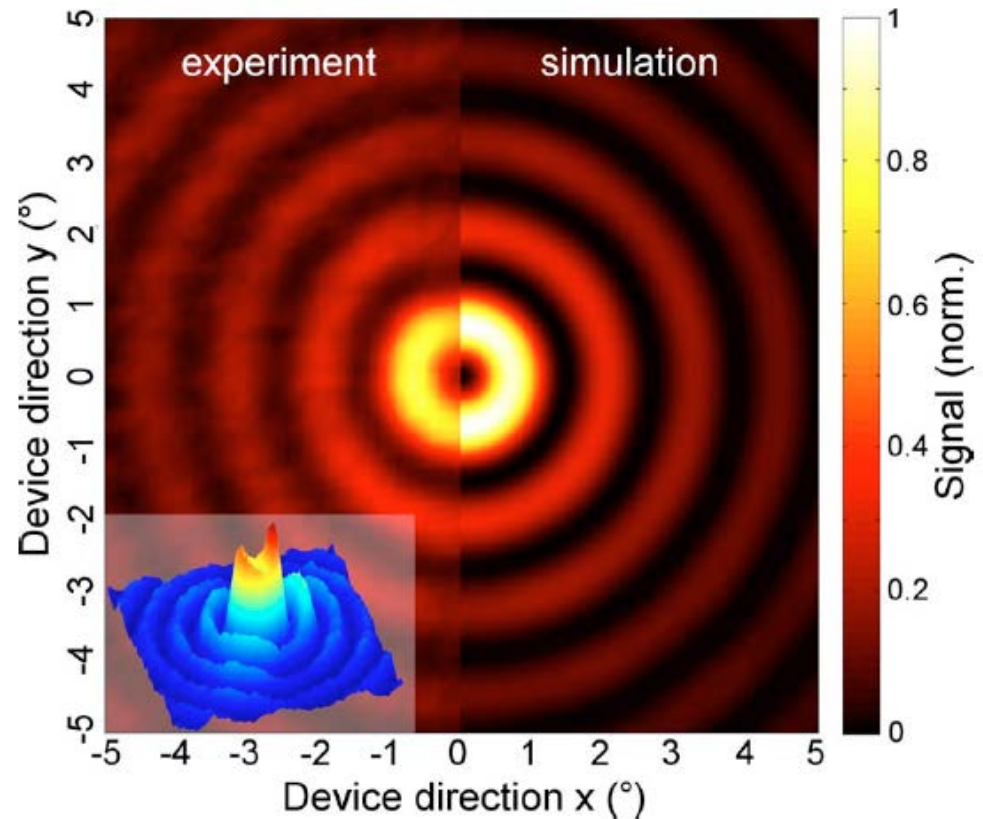
HHL package fiber coupled DFB-QCL



Ring resonator-based surface emitting QCL



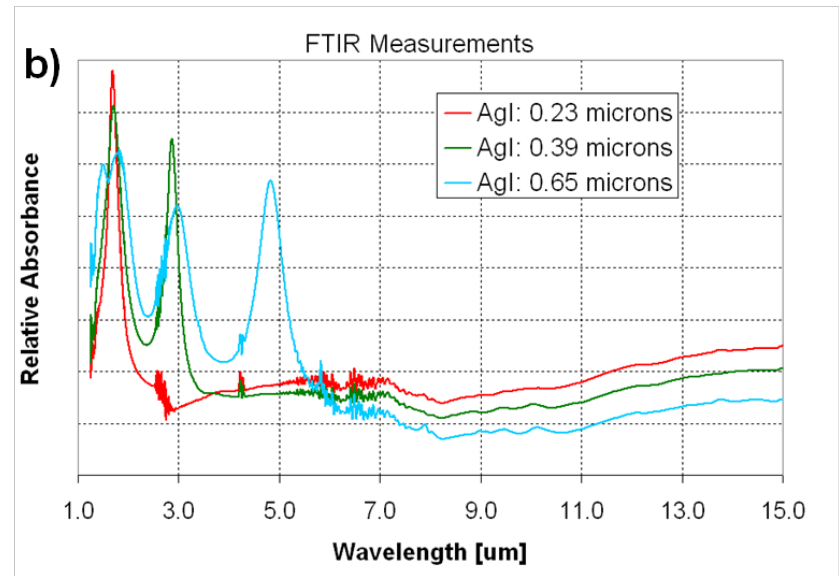
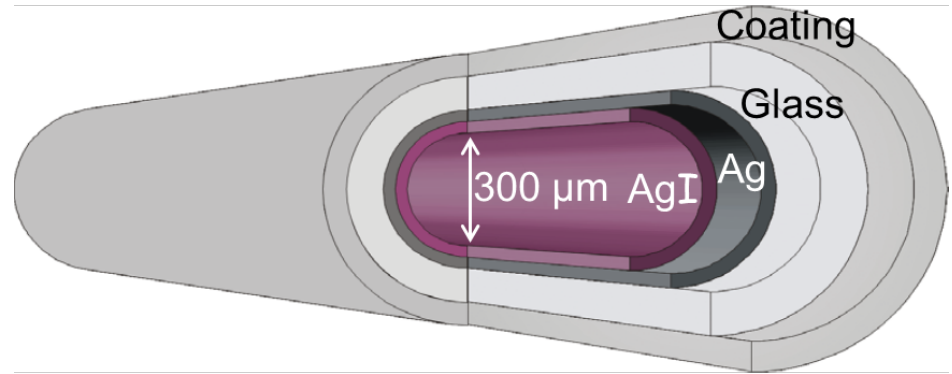
(a) Single-mode spectrum (b) Surface emission spectra recorded at different temperatures. (c) Linear tuning of the resonance. The inset illustrates the corresponding optical power curves.



Measured (left half) and simulated (right half) surface emission far-field pattern.

Hollow core waveguide

- Hollow Core Glass Waveguides
 - Excellent Infrared transmission out to $20\text{ }\mu\text{m}$
 - Proven single mode delivery for bore size $\sim 30\lambda$
 - No end reflections
 - High damage threshold
 - Very Robust
 - Bending loss is a primary concern



Summary

- Laser spectroscopy with mid-infrared, TEC, CW, DFB laser diodes, high performance DFB QCLs and tunable EC-QCLs is a promising analytical approach for real time environmental, biomedical and industrial monitoring as well as technology for national security.
- Six mid-infrared from Nanoplus, Daylight Solutions, Maxion Technologies (Thor Labs), Hamamatsu, Northwestern University and Adtech Optics were used recently (2011-2013) in three sensor platforms: TDLAS, PAS and QEPAS
- Seven target trace gas species were detected with a 1 sec sampling time:
 - C_2H_6 at $\sim 3.36 \mu\text{m}$ with a detection sensitivity of 130 pptv using TDLAS
 - NH_3 at $\sim 10.4 \mu\text{m}$ with a detection sensitivity of ~ 1 ppbv (200 sec averaging time);
 - NO at $\sim 5.26 \mu\text{m}$ with a detection limit of 3 ppbv
 - CO at $\sim 4.61 \mu\text{m}$ with minimum detection limit of 2 ppbv
 - SO_2 at $\sim 7.24 \mu\text{m}$ with a detection limit of 100 ppbv
 - CH_4 and N_2O at $\sim 7.28 \mu\text{m}$ currently in progress with detection limits of 20 and 7 ppbv, respectively.

