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

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OUTLINE

TDLS 2013

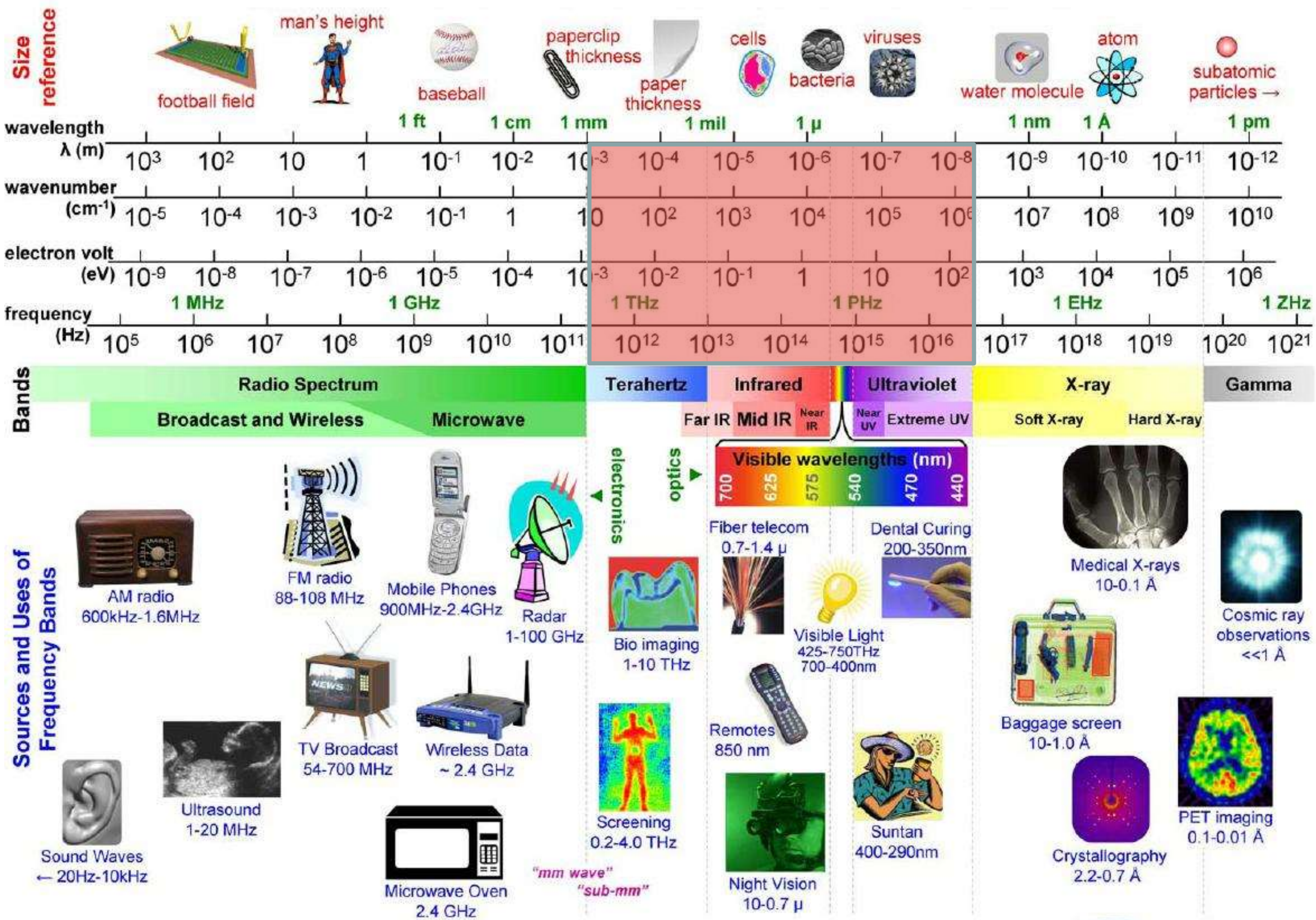
Moscow, Russia

June 19, 2013

- New Laser Based Trace Gas Sensor Technology
  - Novel Multipass Absorption Cell & Electronics
  - Quartz Enhanced Photoacoustic Spectroscopy
- Examples of Mid-Infrared Sensor Architectures
  - C_2H_6, NH_3, NO, CO, SO_2, CH_4 and N_2O
  - 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., Testo AG and Sentinel Photonics Inc. via an EPA Phase 1 SBIR sub-award is acknowledged

Mid-IR and THz Spectroscopic Phenomena



Provided by: Prof. Daniel Mittleman, Rice University

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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 (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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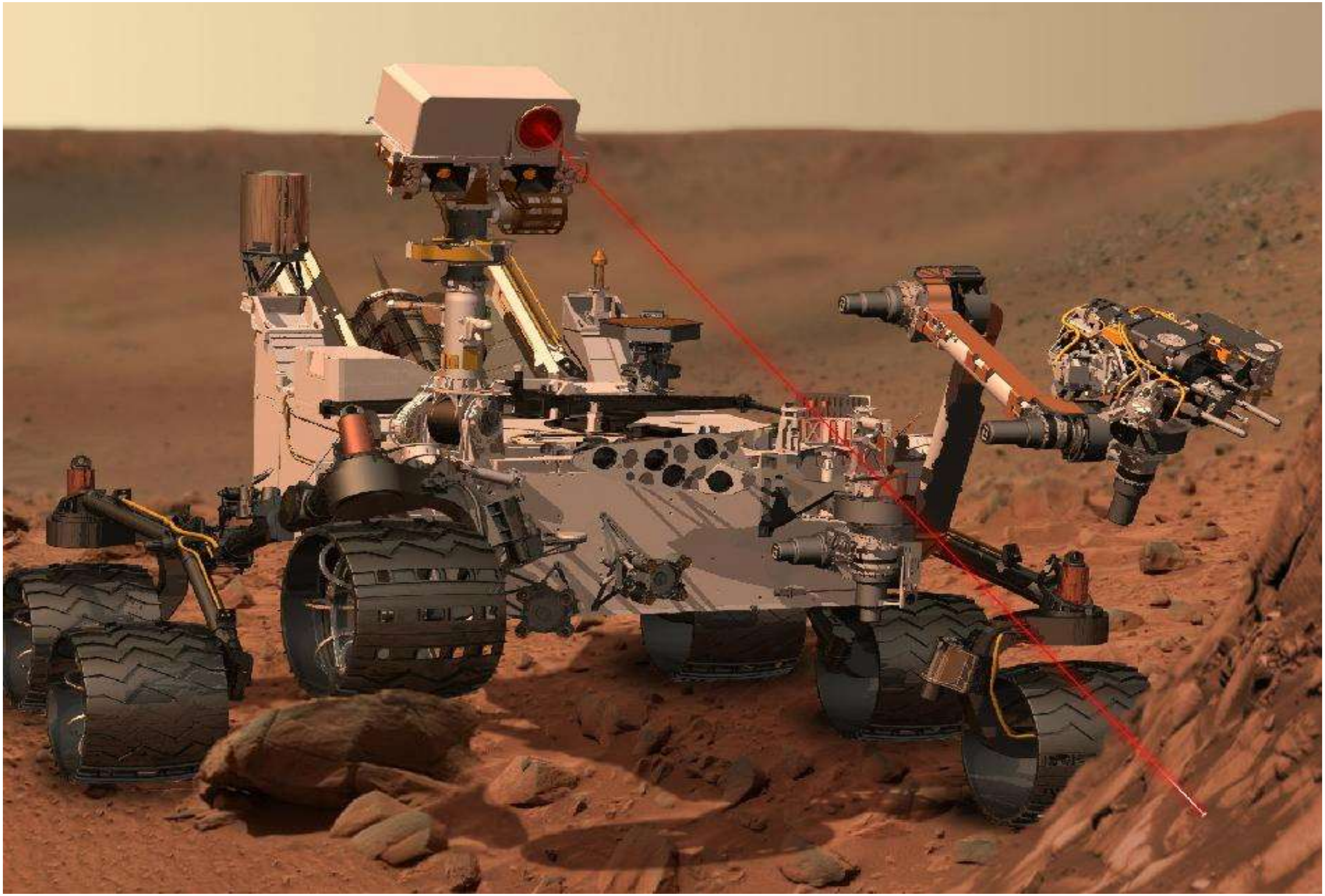
“Curiosity” landed on Mars on August 6, 2012



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)

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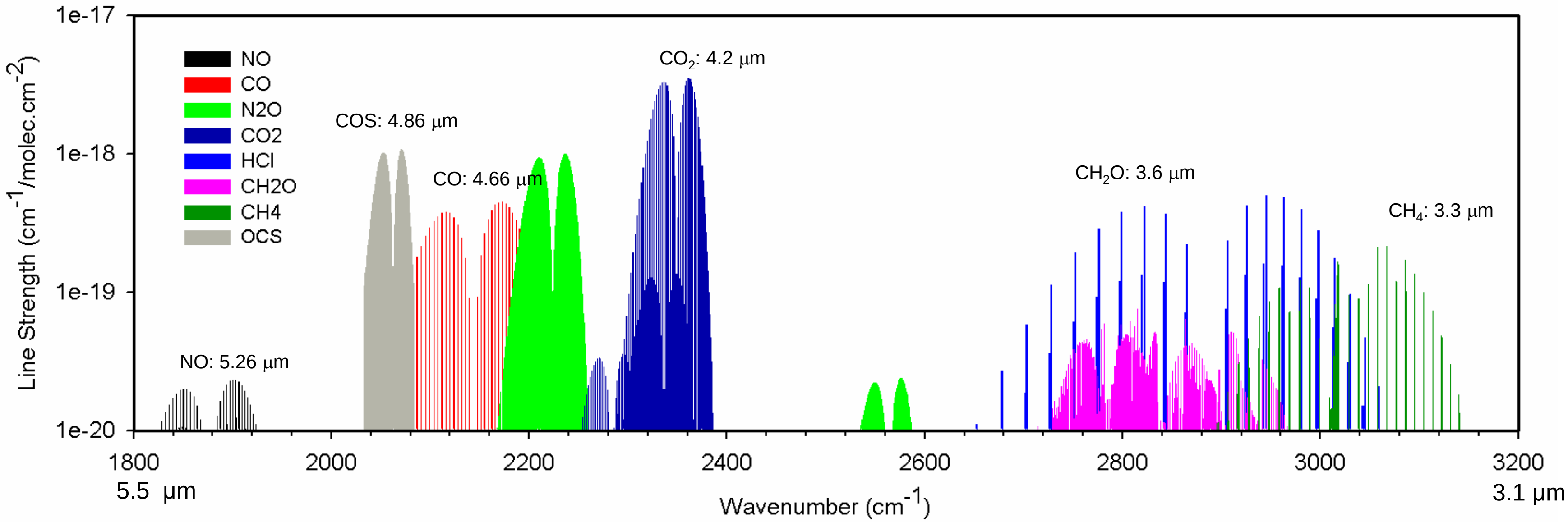
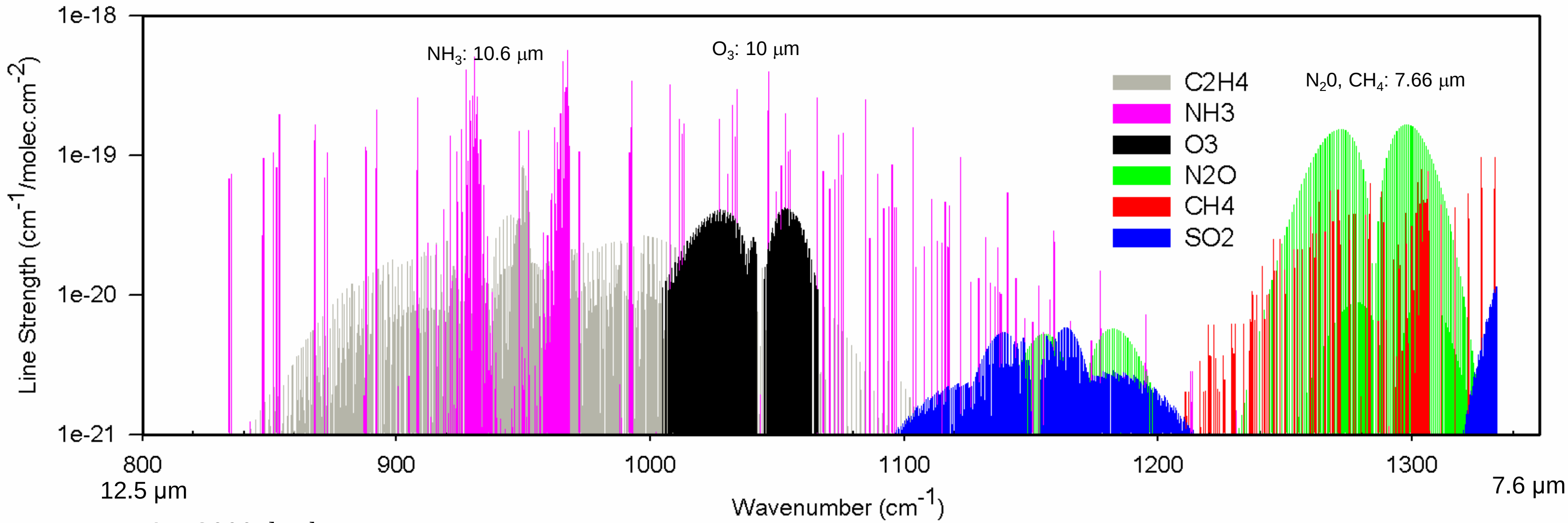
Other spectroscopic methods

- 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





Source: HITRAN 2000 database

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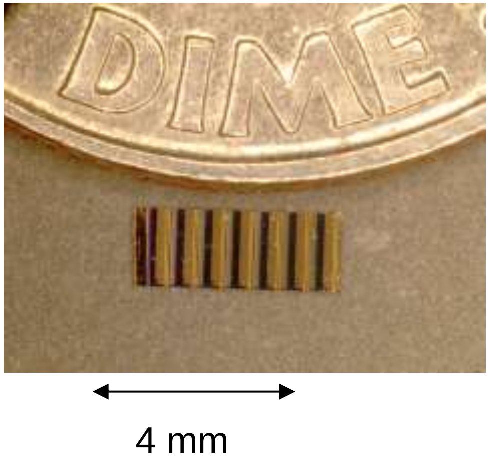
Mid-IR Source Requirements for Laser Spectroscopy

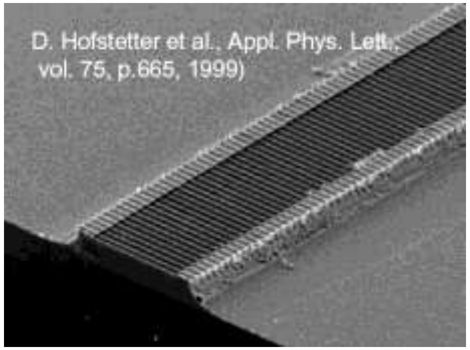
REQUIREMENTS	IR LASER SOURCE
Sensitivity (% to ppt)	Optimum Wavelength, Power
Selectivity (Spectral Resolution)	Stable Single Mode Operation and Narrow Linewidth
Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers	Mode Hop-free Wavelength Tunability
Directionality or Cavity Mode Matching	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 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

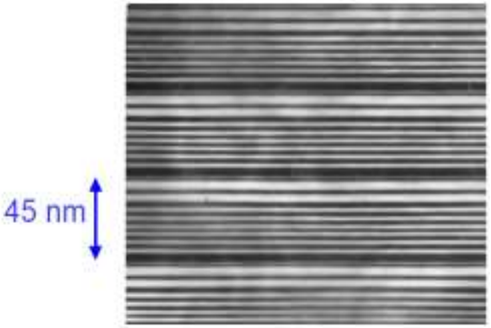


- **Wide spectral tuning ranges in the mid-IR**
  - 1.5 cm^{-1} using injection current control for DFB devices
  - 10-20 cm^{-1} using temperature control for DFB devices
  - ~100cm-1 using current and temperature control for QCL DFB Array
  - ~ 525 cm^{-1} (22% of c.w.) using an external grating element 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 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 µm
  - > 600 mW (CW FP) @ RT; wall plug efficiency of ~17 % at 4.6 µm;



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 ºC and < 30 ºC) 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_{00} 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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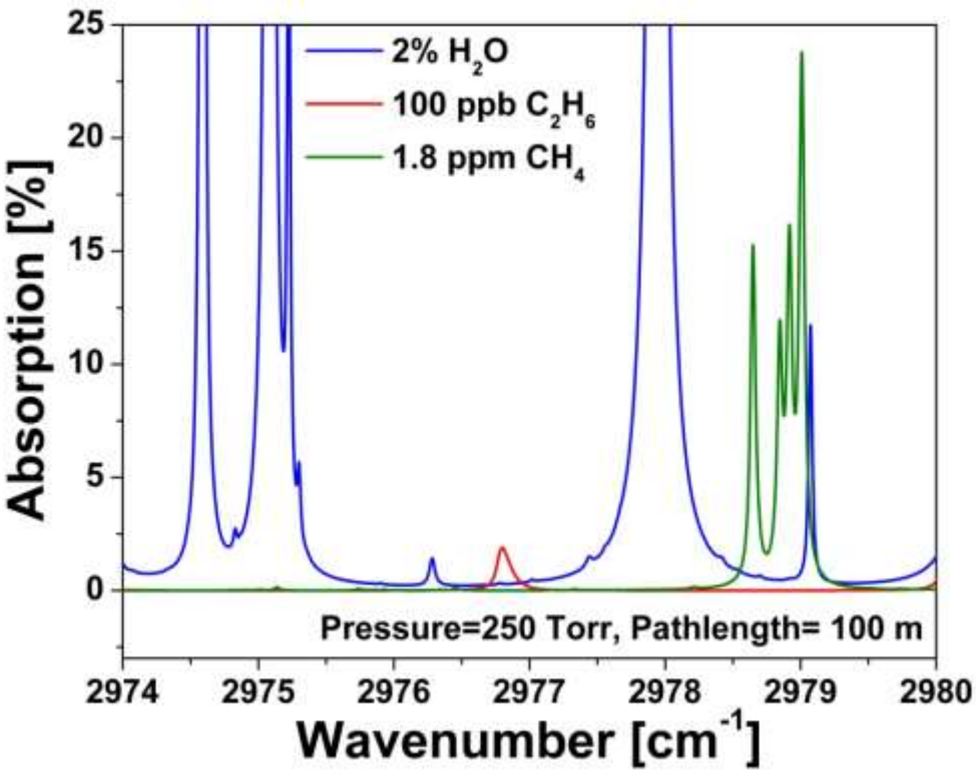
Motivation for Mid-infrared C_2H_6 Detection

- 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,
  - schizophremia,
  - Lung cancer,
  - lung cancer,
  - vitamin E deficiency.



HITRAN absorption spectra of C_2H_6, CH_4, and H_2O

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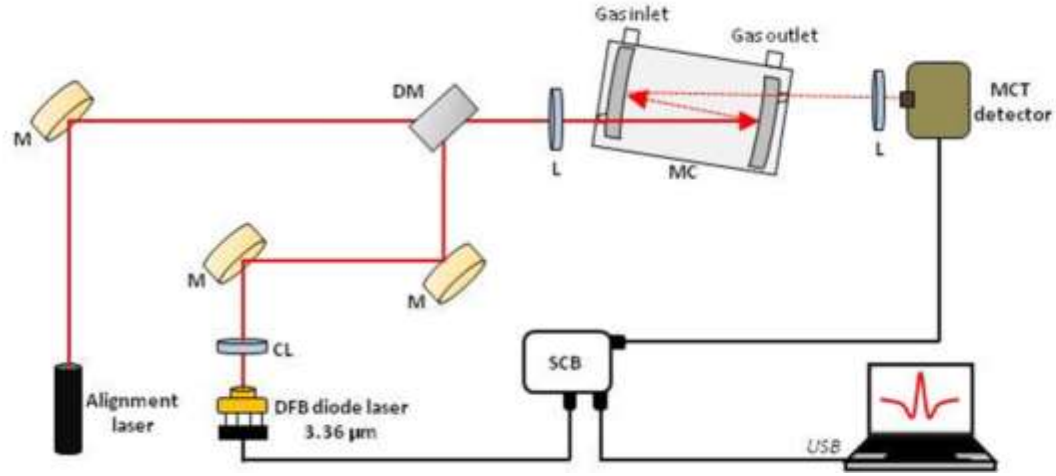
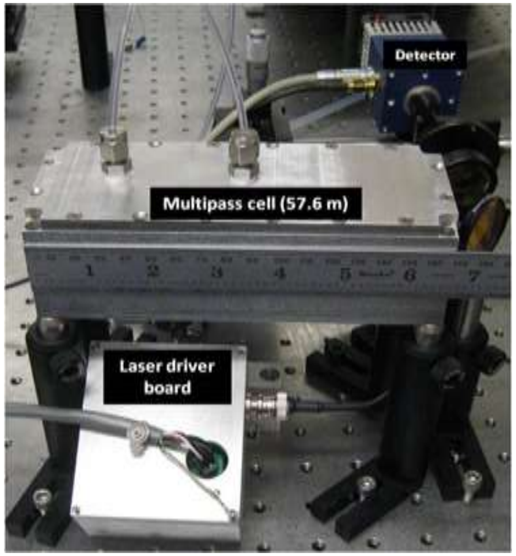
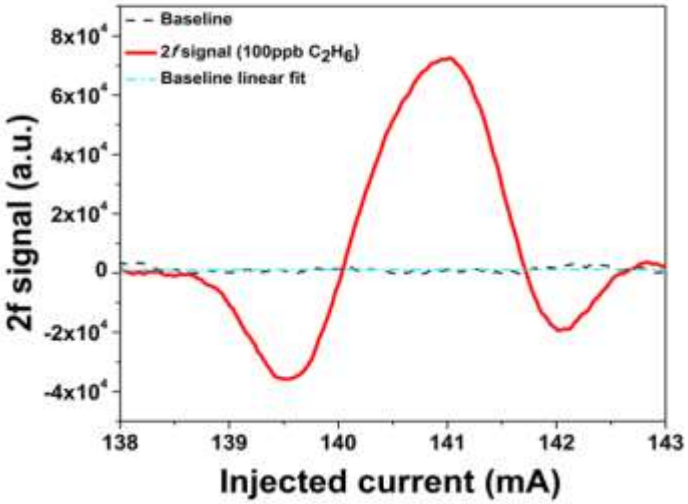
C_2H_6 Detection with a 3.36 µm CW DFB LD using a Novel Compact Multipass Absorption Cell and Control Electronics



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



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



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

Minimum detectable C_2H_6 concentration is:

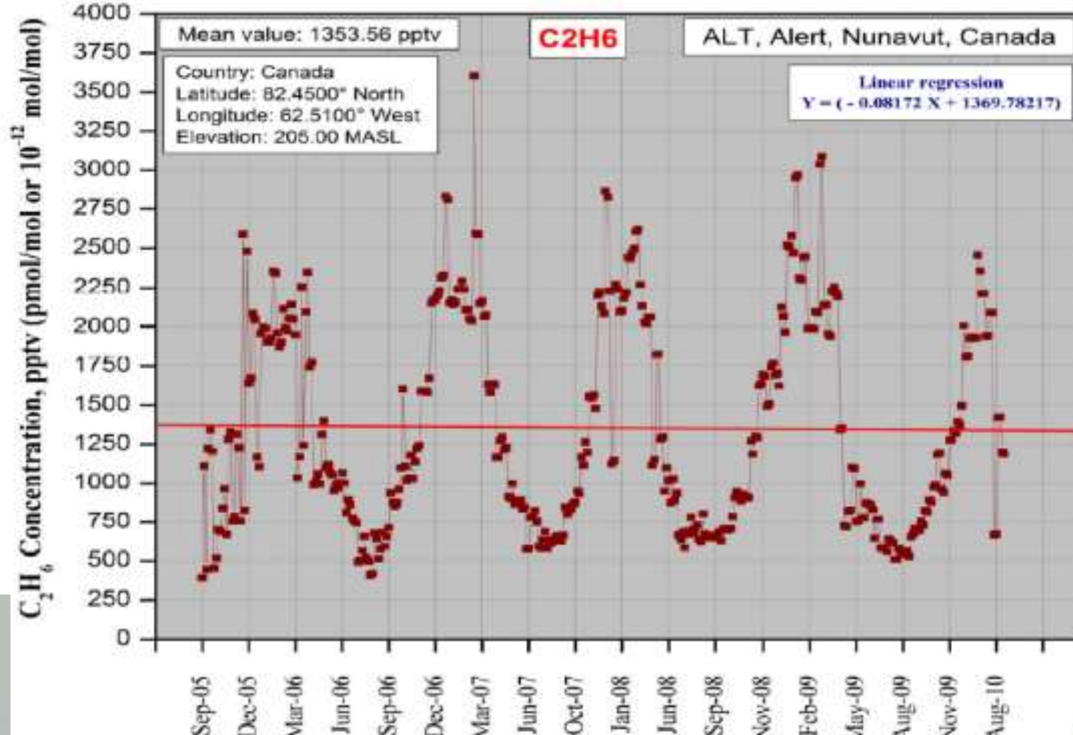
~ 130 pptv (1σ; 1 s time resolution)

MC dimensions: **17** x **6.5** x **5.5** (cm)

Distance between the MGC mirrors: 13 cm

NOAA Monitoring & Sampling Location: Alert, Nunavut, Canada

ALT, Ethane Concentration Measurements



General View on the Facility
Latitude: 82.4508º North
Longitude: 62.5056º West
Elevation: 200.00 m

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

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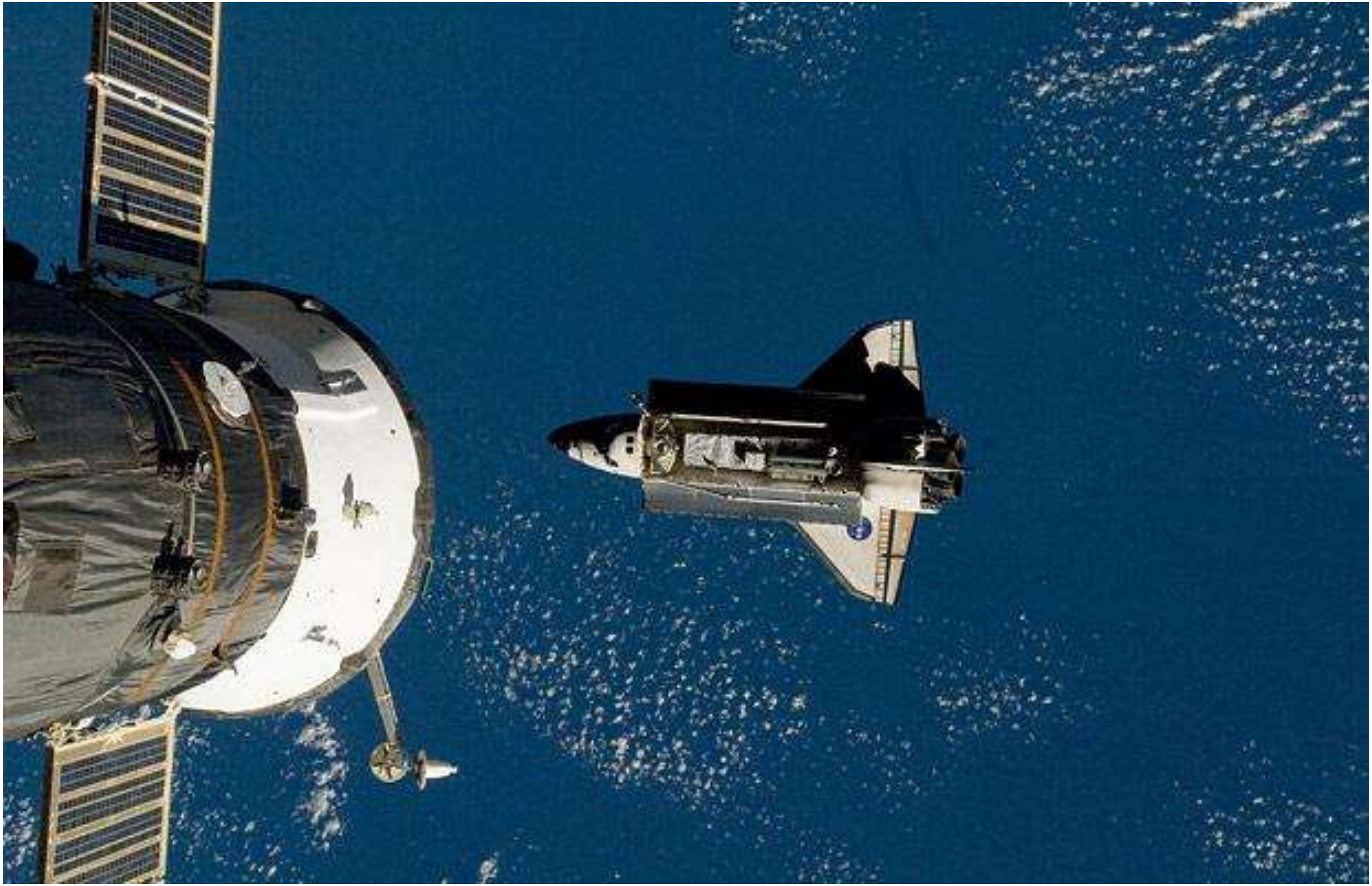
Ammonia Leaks from ISS May 2013

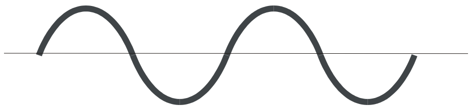


Conventional PAS

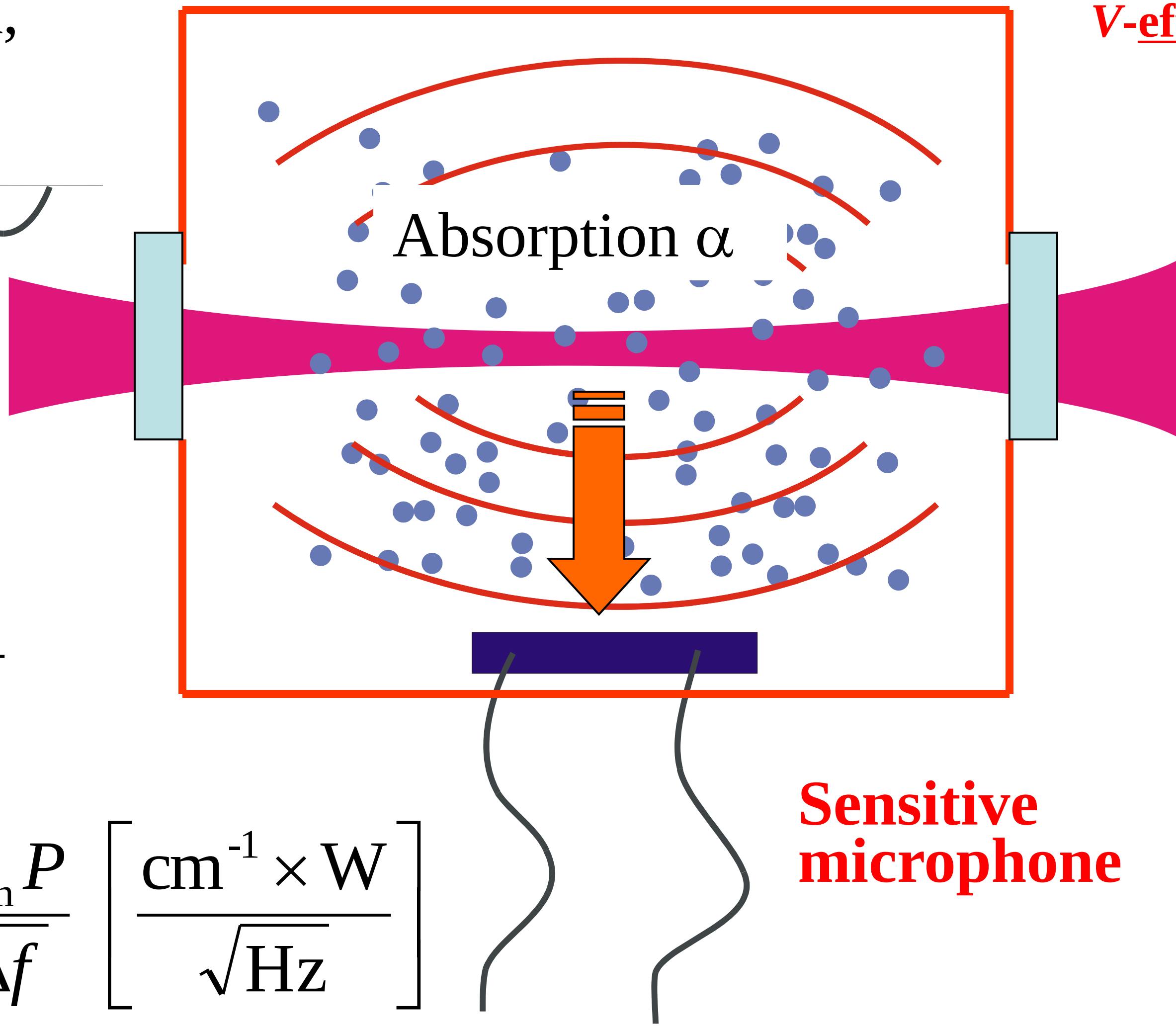
Cell is OPTIONAL!

***V*-<u>effective</u> volume**

Laser beam,
power *P*



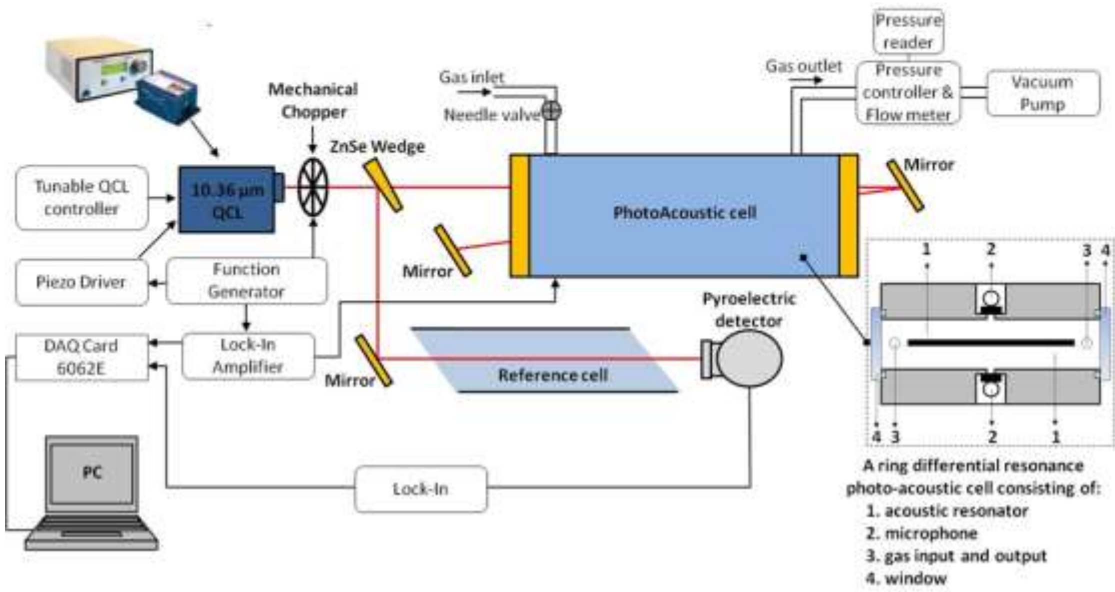
Modulated
(*P* or λ) at *f*
or *f*/2

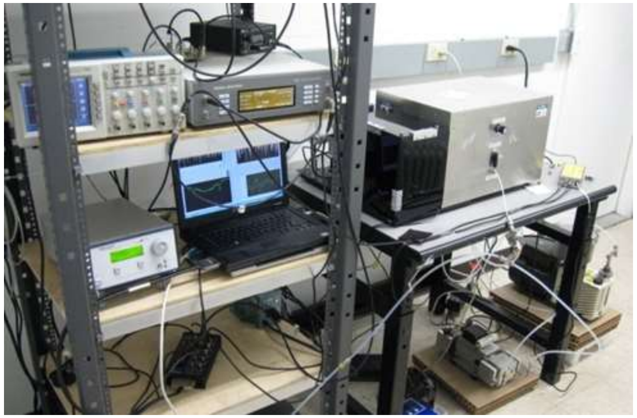


$$S \sim \frac{Q\,\alpha\,P}{f\,V}$$

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

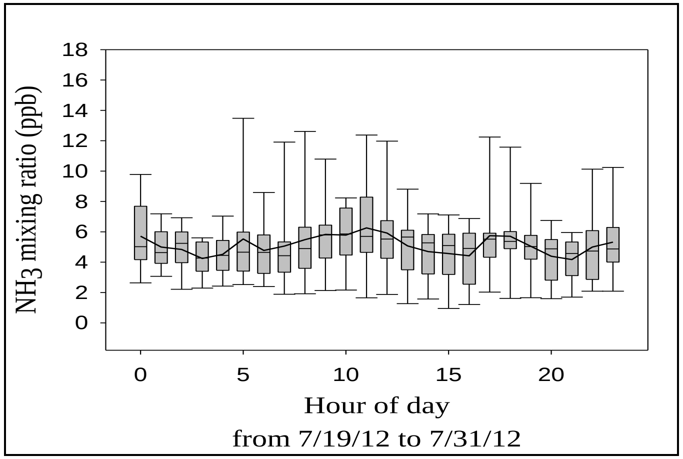
Atmospheric NH_3 Measurements using an EC-QCL PAS Sensor



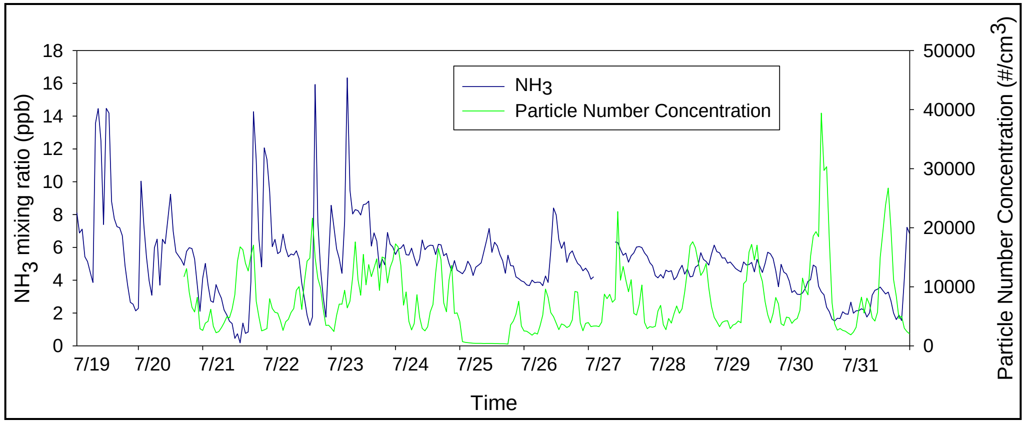


NH_3 sensor deployed at the UH Moody Tower rooftop monitoring site.

Schematic of a Daylight Solutions 10.36 µm CW TEC EC-QCL based PAS NH_3 Sensor.

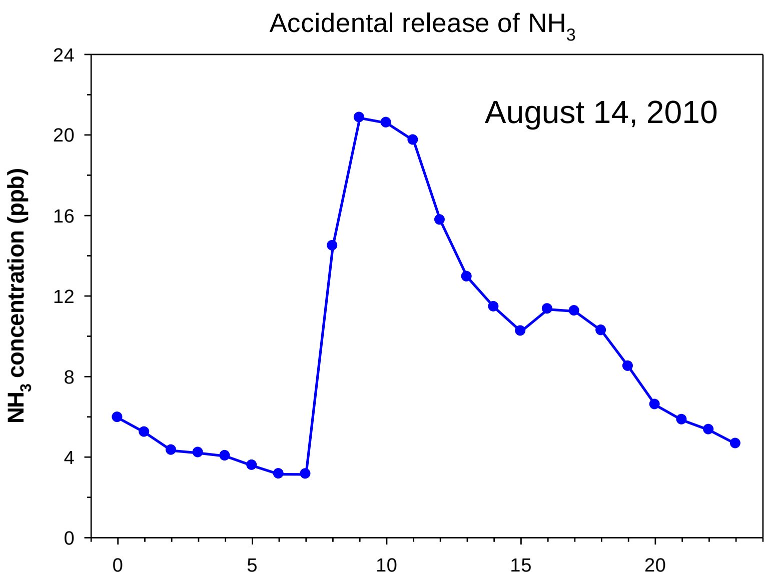


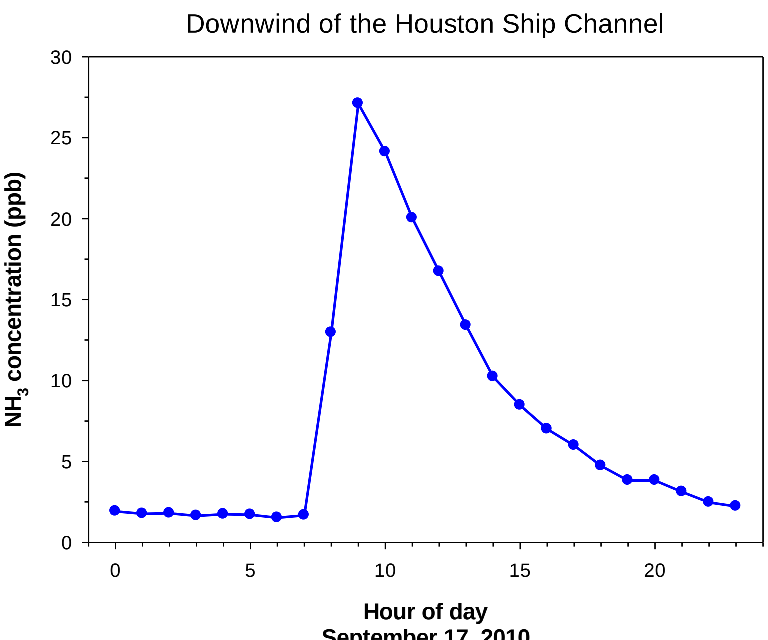
Diurnal profile of atmospheric NH_3 levels in Houston, TX.



Comparison between NH_3 and particle number concentration time series from July 19 to July 31 2012.

NH_3 Detection due to a Fire resulting from a Truck Collision

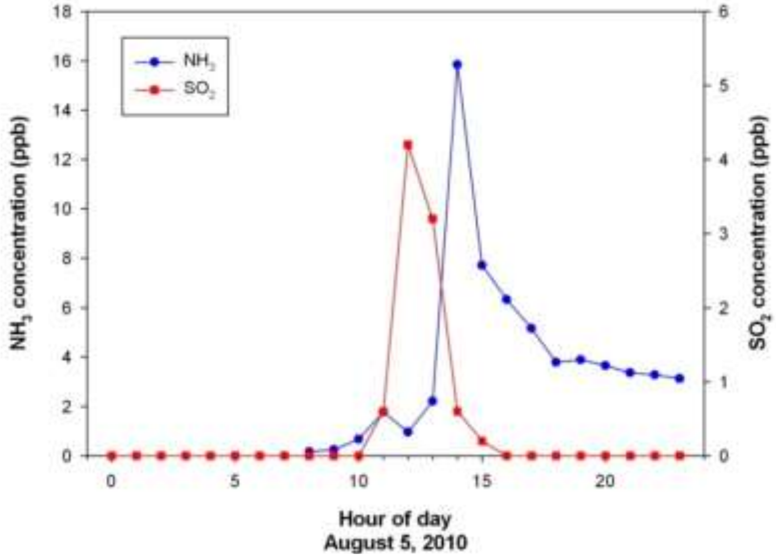


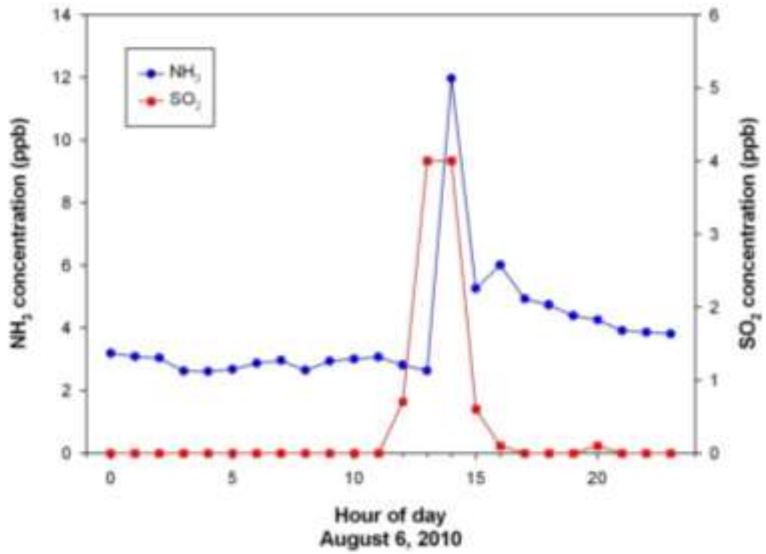


A chemical incident occurred at ~ 6 a.m. after two trucks collided on I-59. Both trucks caught fire. [www.chron.com]

Estimated hourly NH_3 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 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)

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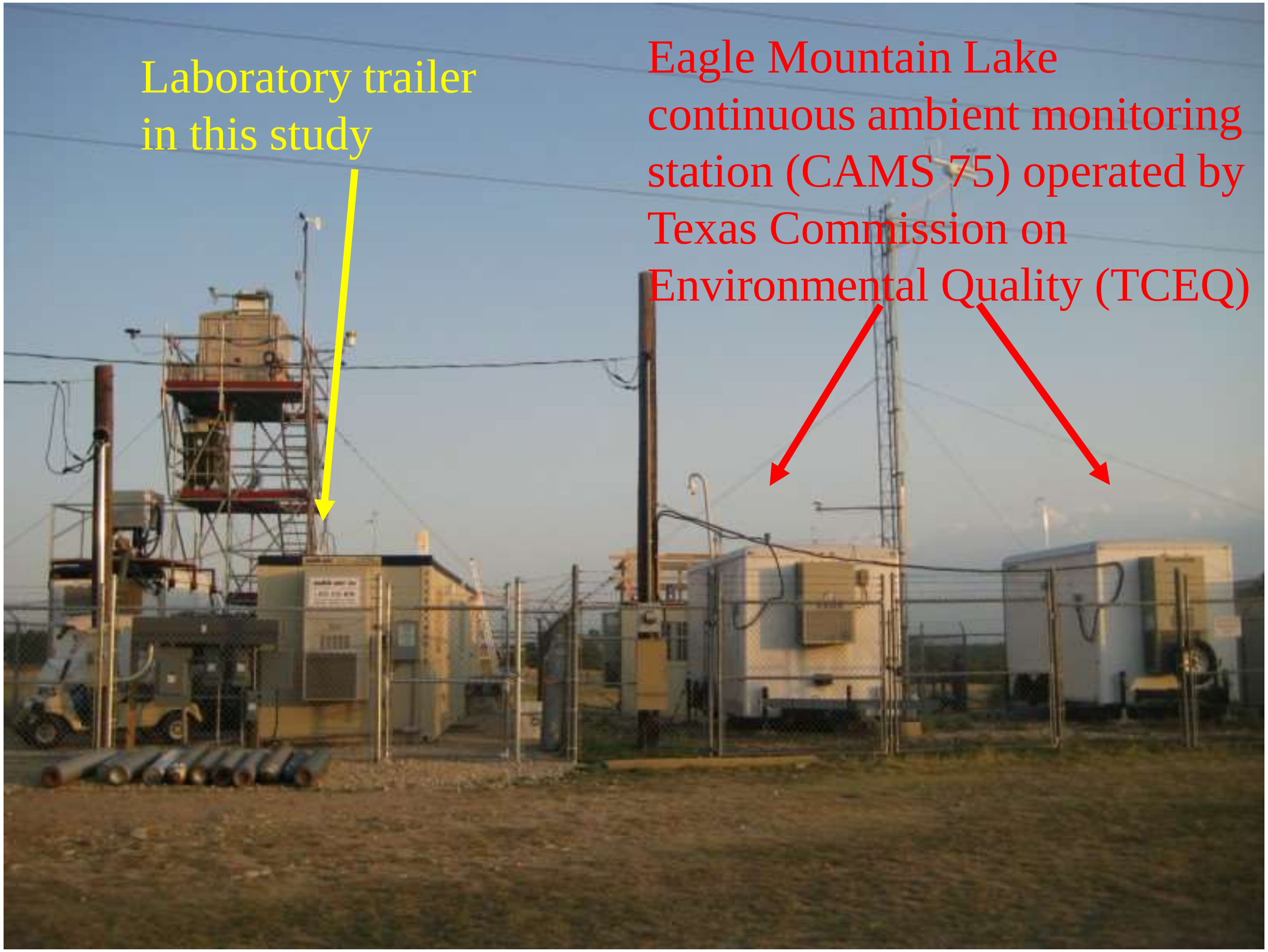
Fort-Worth, Dallas(TX) CAMS 75 & TCEQ monitoring site

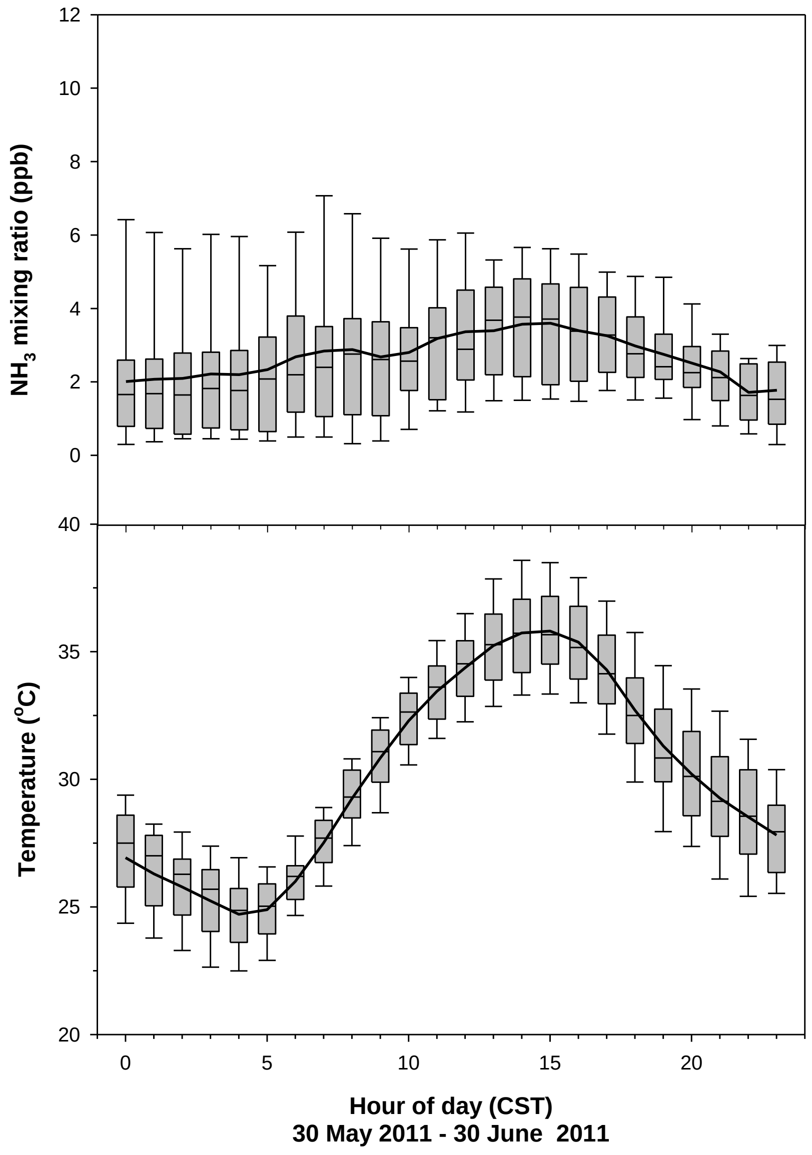


Instrumentation available at CAMS 75 & TCEQ monitoring site

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_y	Thermo Electron Corp. 42C-Y NO_Y 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	IONICON 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 HMP45C Platinum Resistance Thermometer
Wind speed	Campbell Scientific 05103 R. M. Young Wind Monitor
Wind direction	Campbell Scientific 05103 R. M. Young Wind Monitor

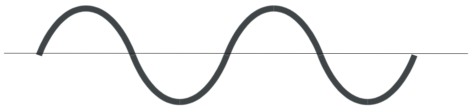
NH_3 source attribution & temperature variations

- Emission events from specified point sources (i.e., industrial facilities)
- Estimated NH_3 emissions from cows (1.3 tons/day)
- Estimated NH_3 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_3 emissions
- Increased contribution from industry (→ 18.9%)



From Conventional PAS to QEPAS

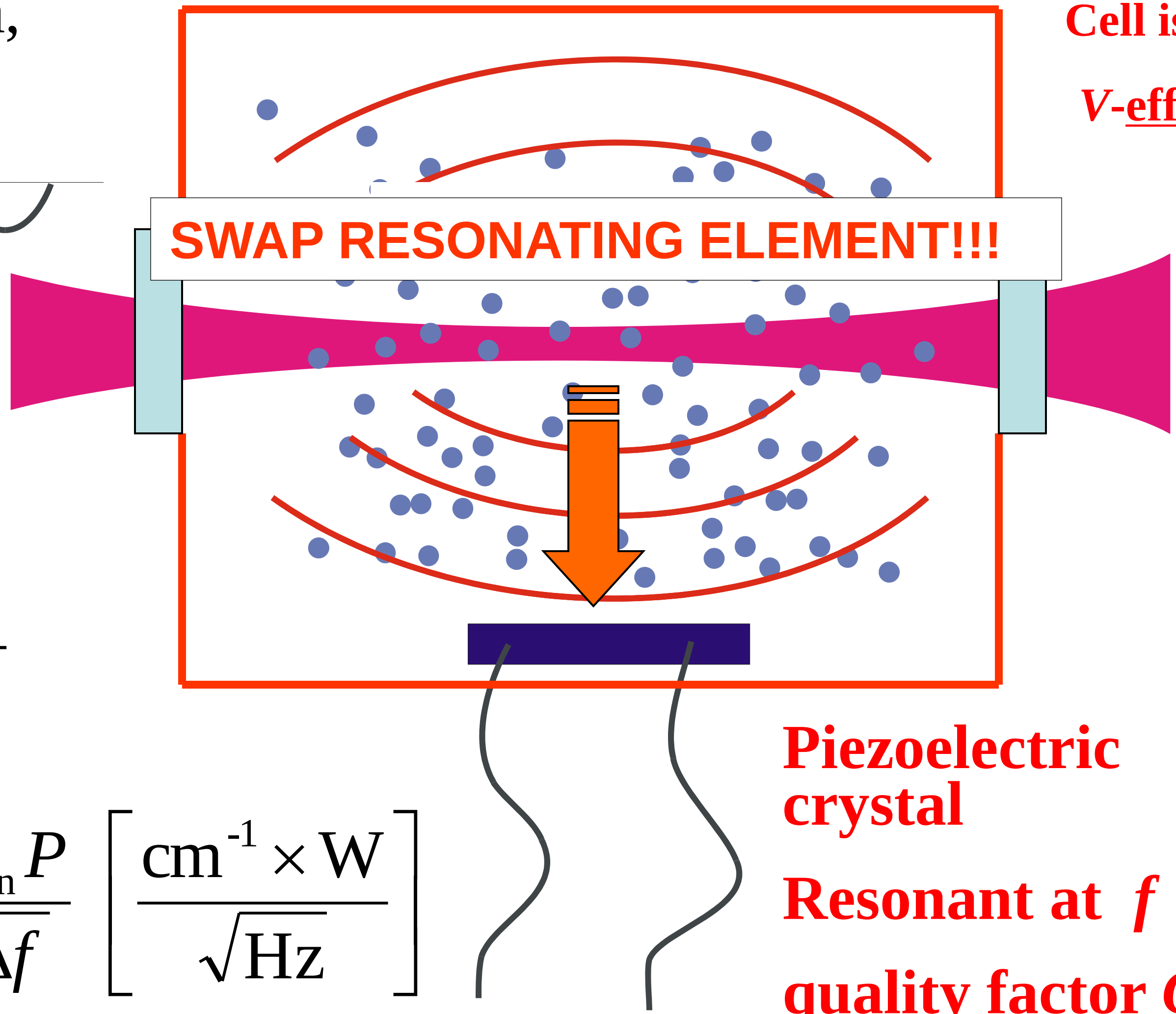
Laser beam,
power *P*



Modulated
(*P* or λ) at *f*
or *f*/2

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

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



***Q*>>1000**

Cell is OPTIONAL!

***V*-effective volume**

Piezoelectric crystal

Resonant at *f*

quality factor *Q*

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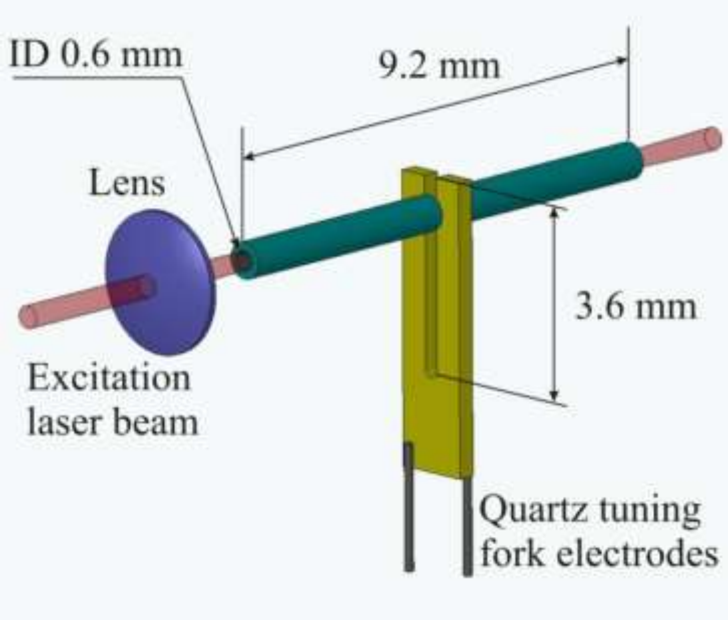
Quartz Tuning Fork as a Resonant Microphone for QEPAS



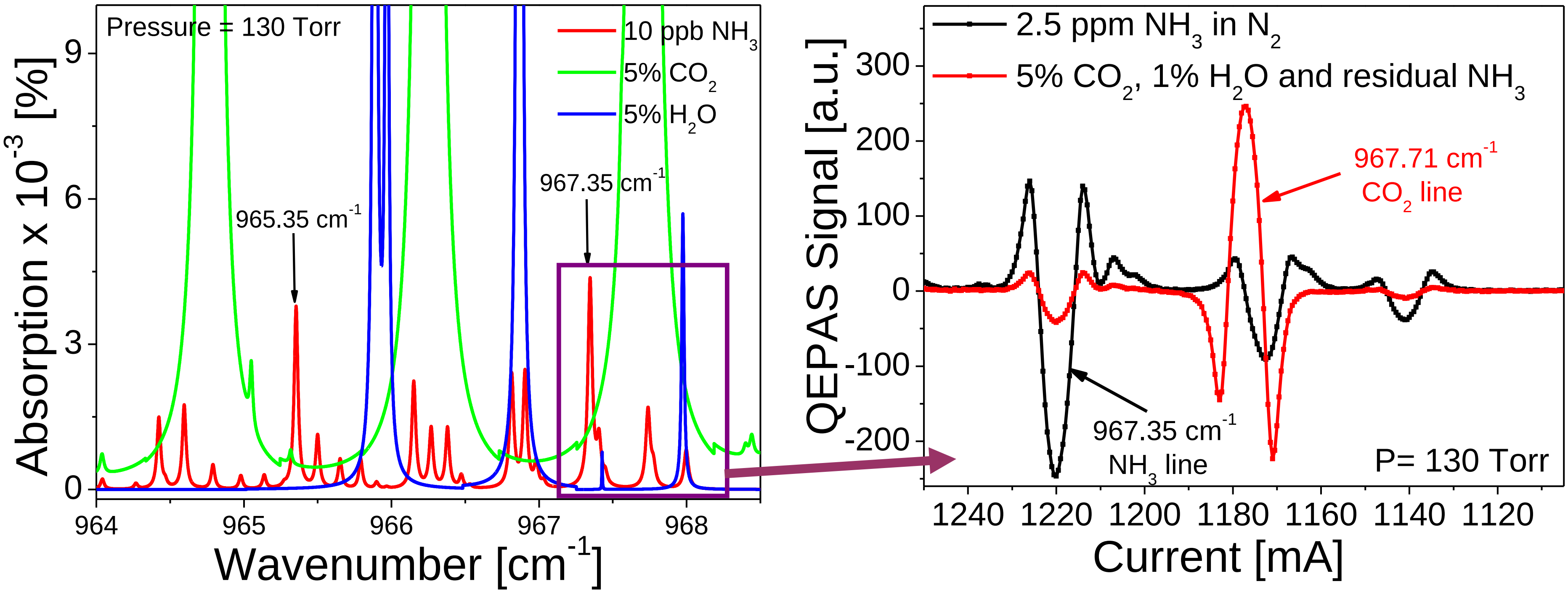
Unique properties

- 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)

Optimum NH_3 Line Selection for a 10.34 μm 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 ν_2 R band.

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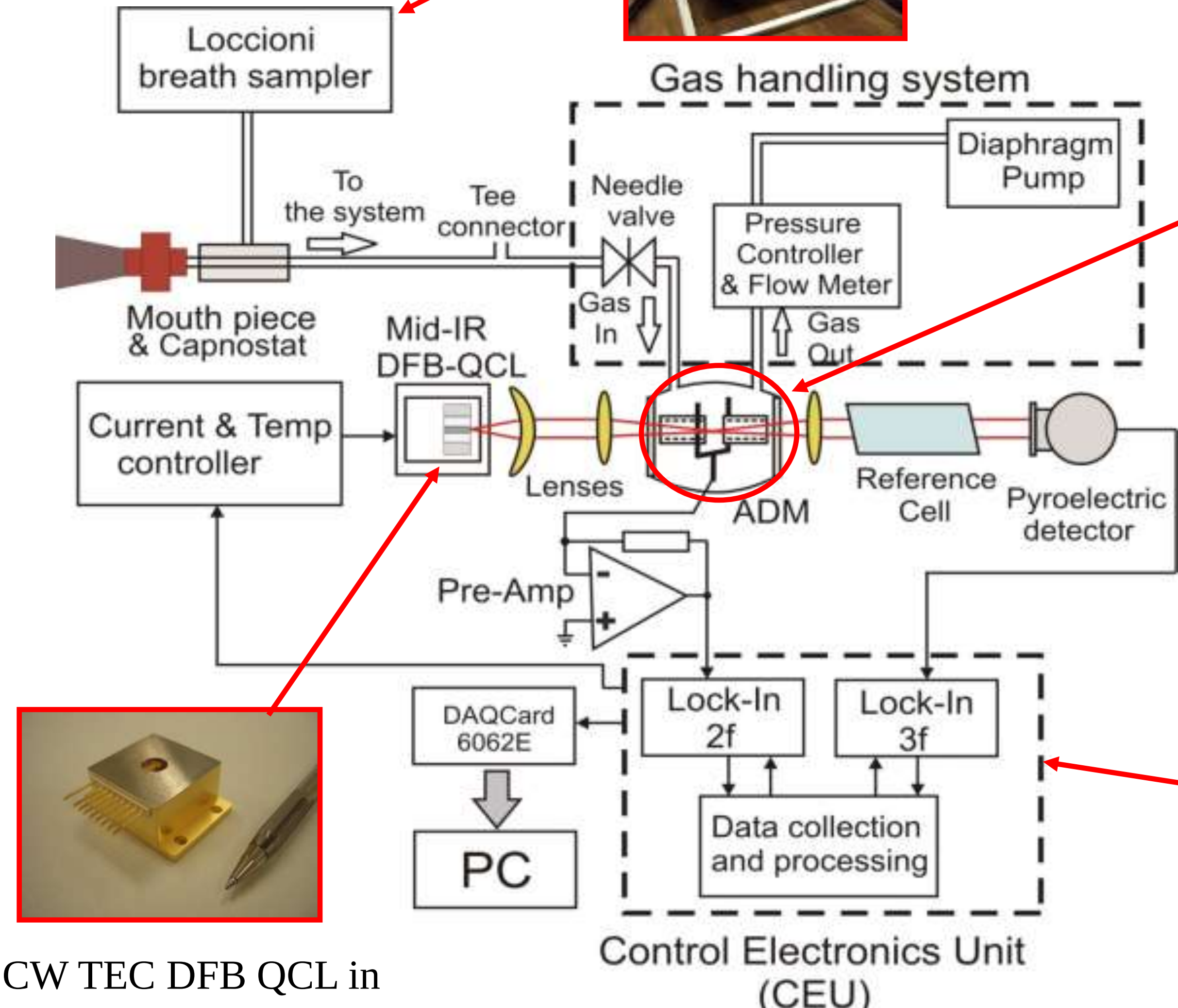
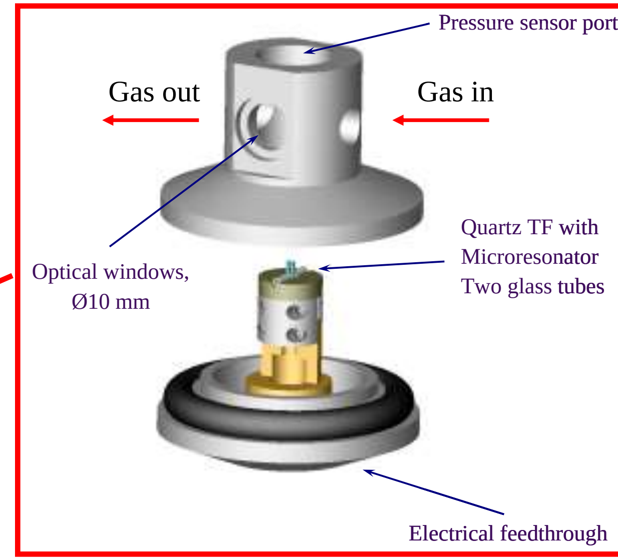
QEPAS based NH_3 Gas Sensor Architecture





CW TEC DFB QCL in
HHL package (Hamamatsu)

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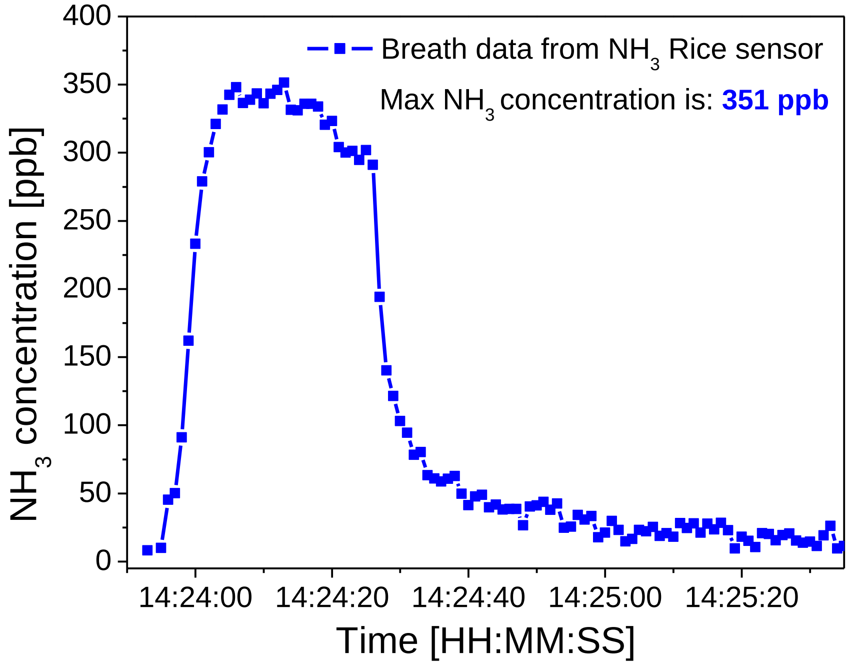
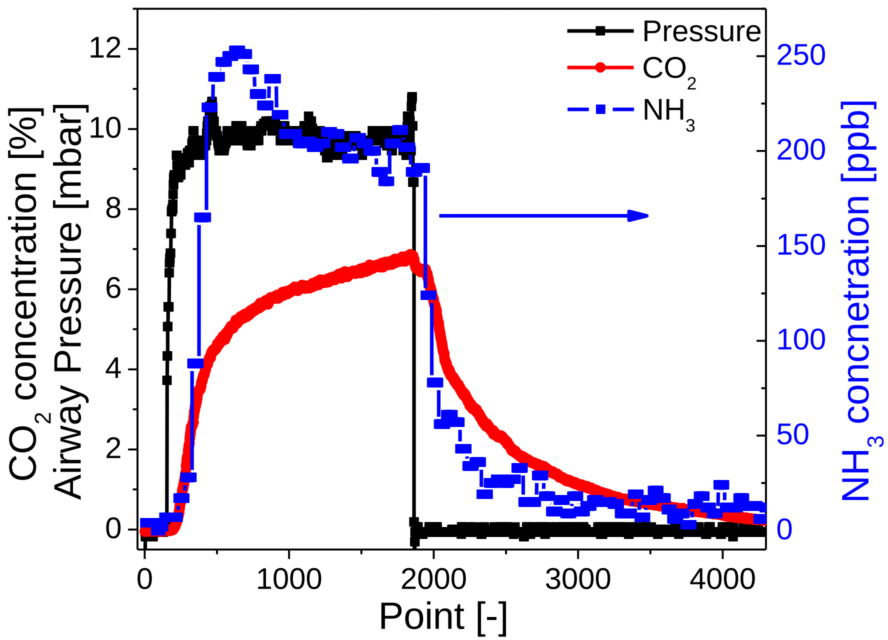
Real-time exhaled human NH_3 Breath Measurements





Airway pressure (black), CO_2 (red), and NH_3 (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} (1σ; 1 s time resolution)

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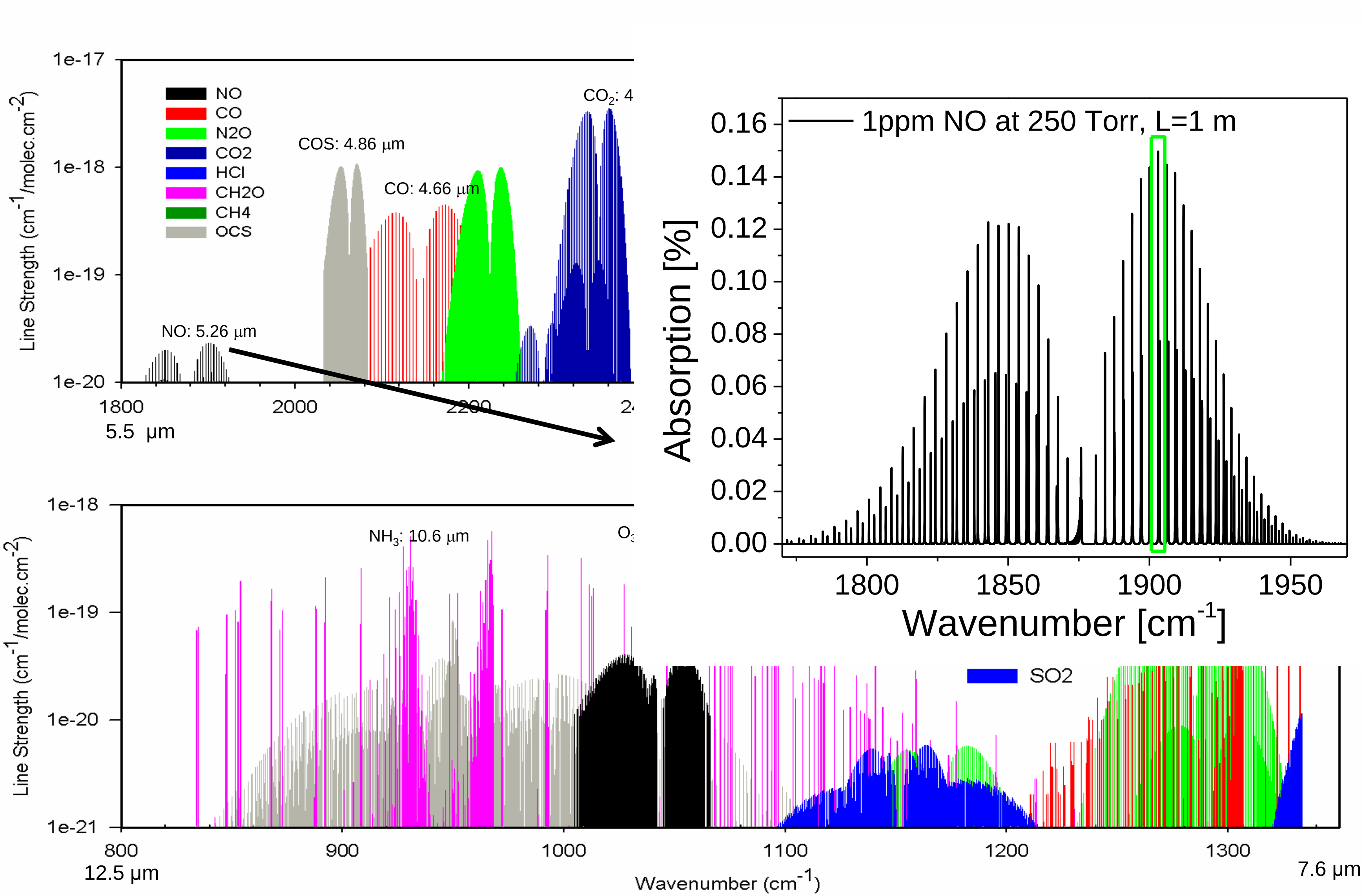
Motivation for Nitric Oxide Detection

- Atmospheric Chemistry
- Environmental pollutant gas monitoring
  - NO_x monitoring from automobile exhaust and power plant emissions
  - Precursor of smog and acid rain
- Industrial process control
  - Formation of oxynitride gates in CMOS Devices
- NO in medicine and biology
  - Important signaling molecule in physiological processes in humans and mammals (1998 Nobel Prize in Physiology/Medicine)
  - Treatment of asthma, COPD, acute lung rejection
- Photofragmentation of nitro-based explosives

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



Source: HITRAN 2000 database

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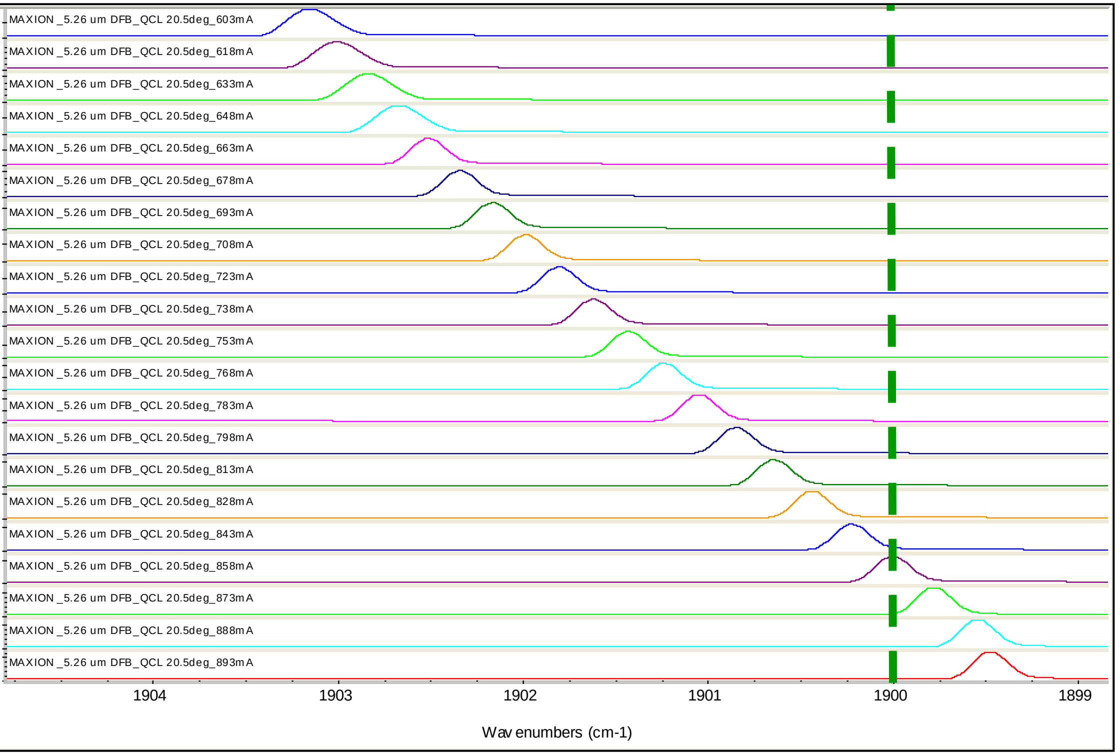
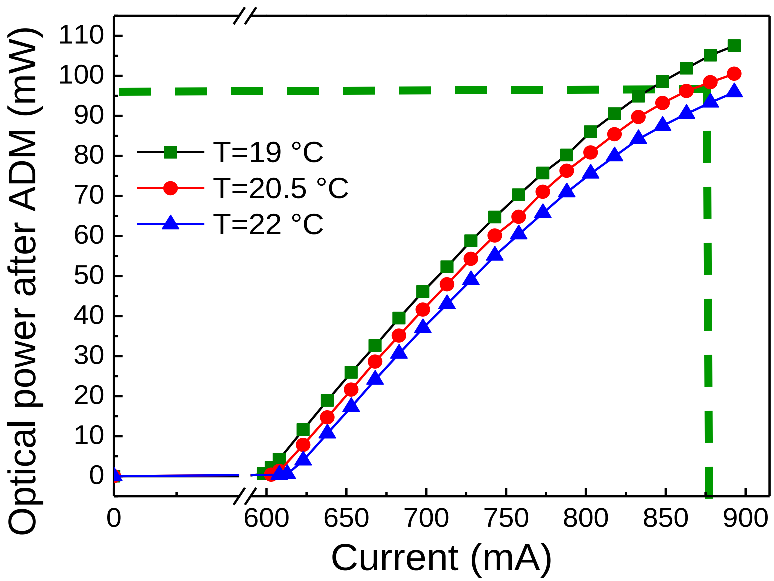
Performance of a 5.26 μm CW HHL TEC DFB-QCL



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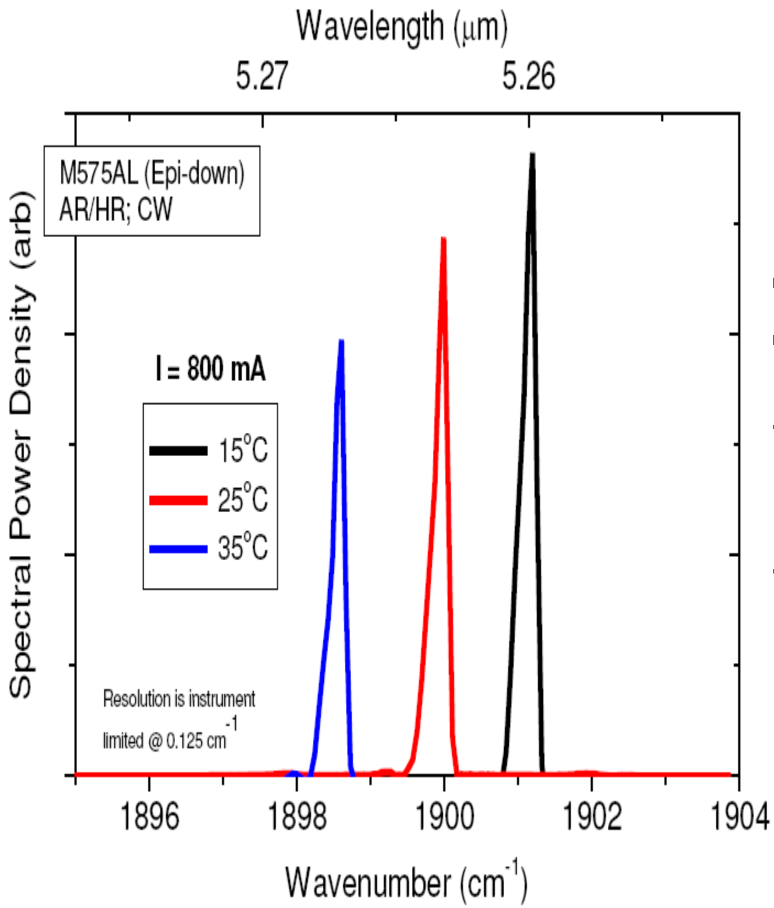
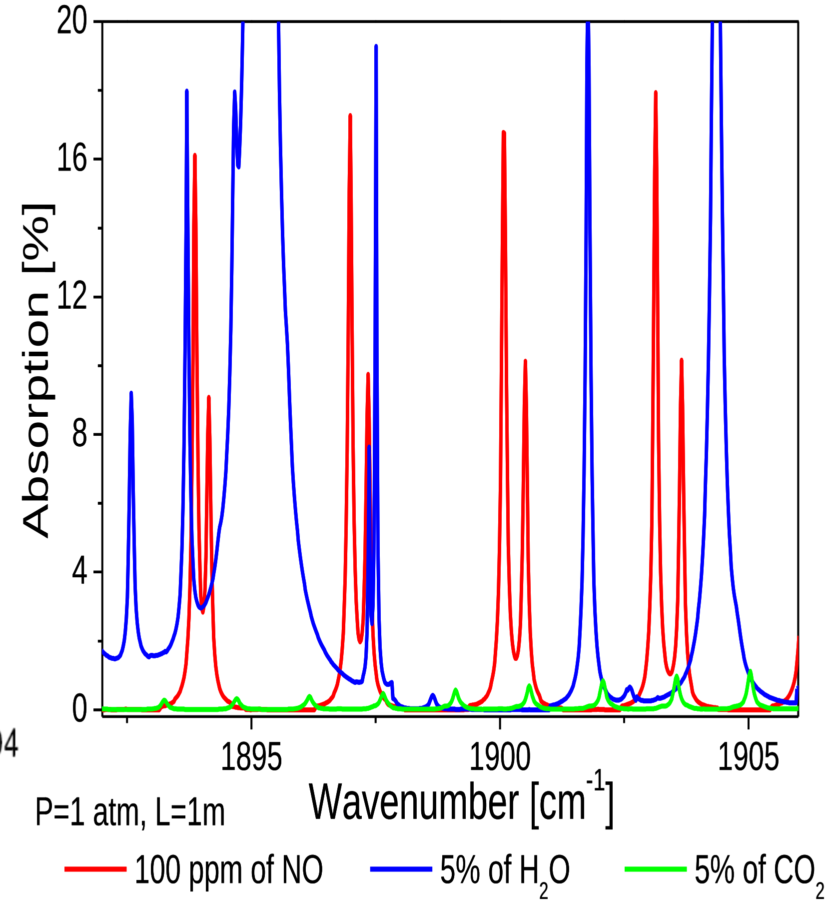
Emission spectra of a 1900cm^{-1} TEC CW DFB QCL and HITRAN Simulated spectra





Output power: 117 mW @ 25 C

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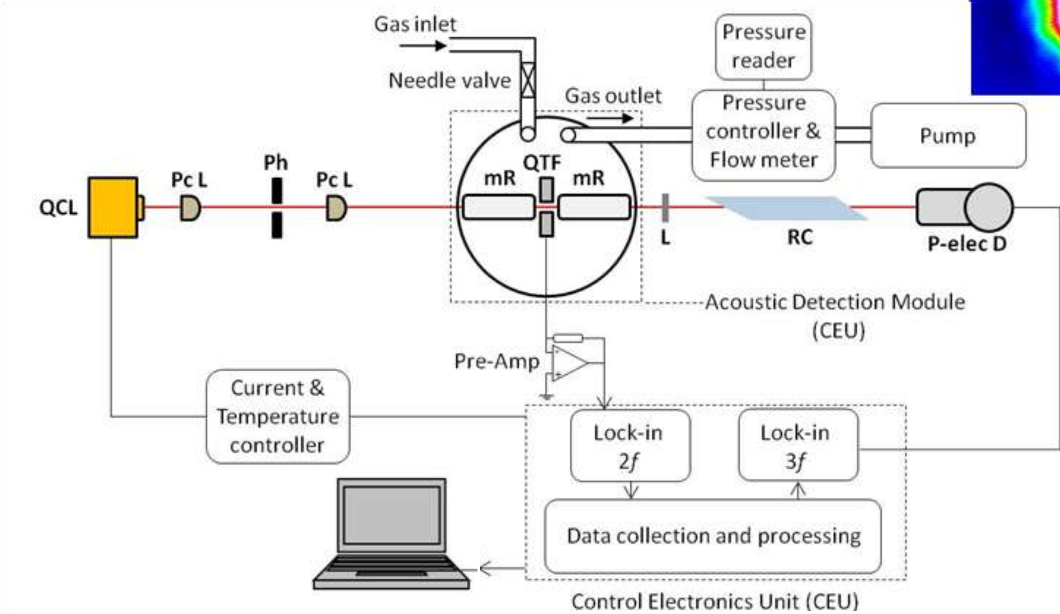
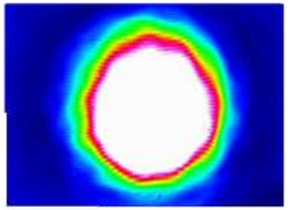
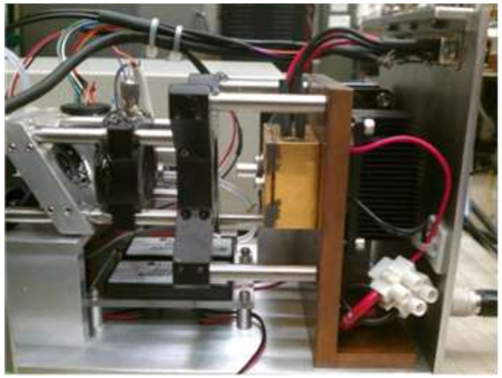
CW TEC DFB QCL based QEPAS NO Gas Sensor

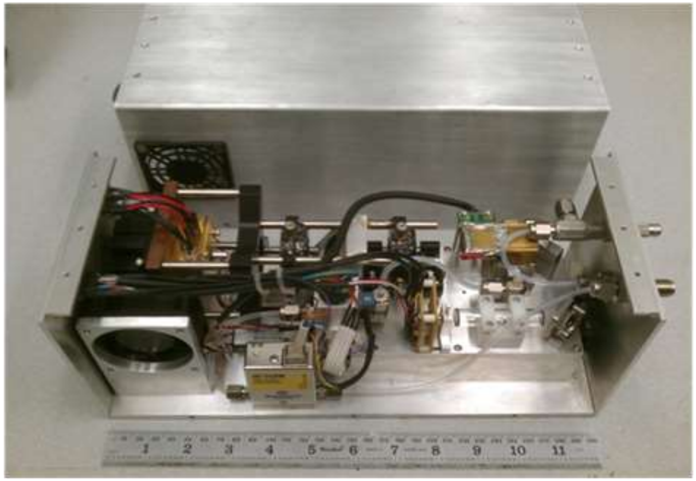


Schematic of a DFB-QCL based Gas Sensor.
PcL – plano-convex lens, Ph – pinhole,
QTF – quartz tuning fork, mR – microresonator,
RC- reference cell, P-elec D – pyro electric detector





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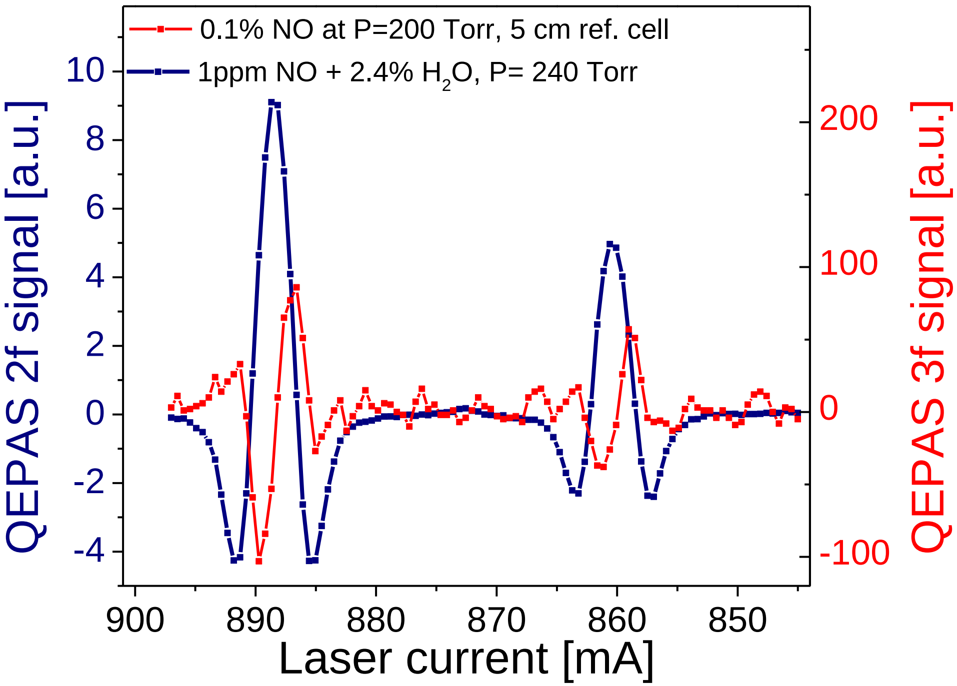
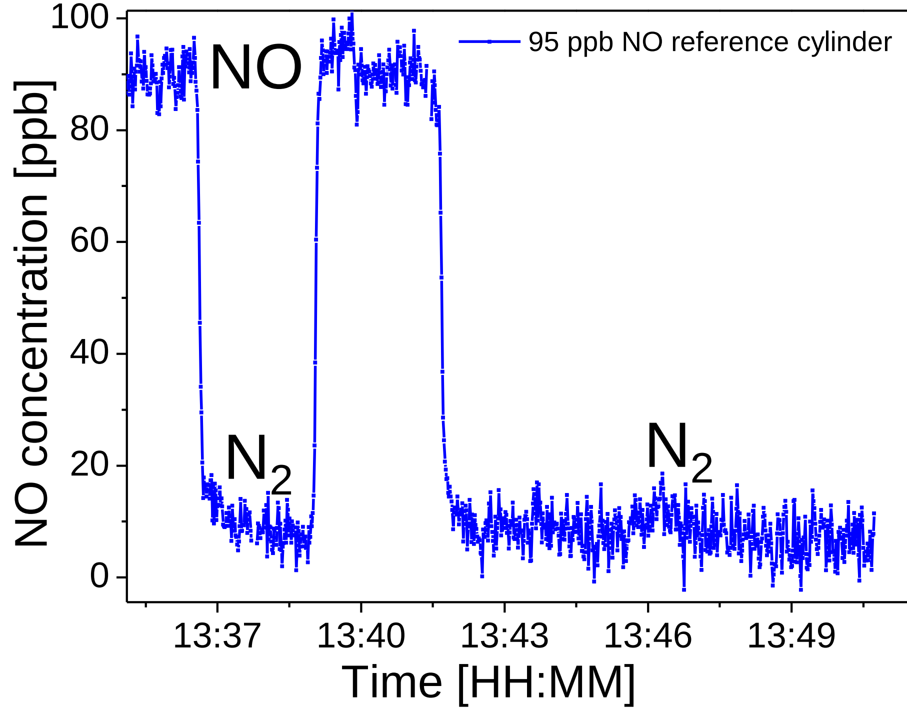
Performance of CW DFB-QCL based WMS QEPAS NO Sensor Platform



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



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

Minimum detectable NO concentration is:

~ 3 ppbv (1σ; 1 s time resolution)

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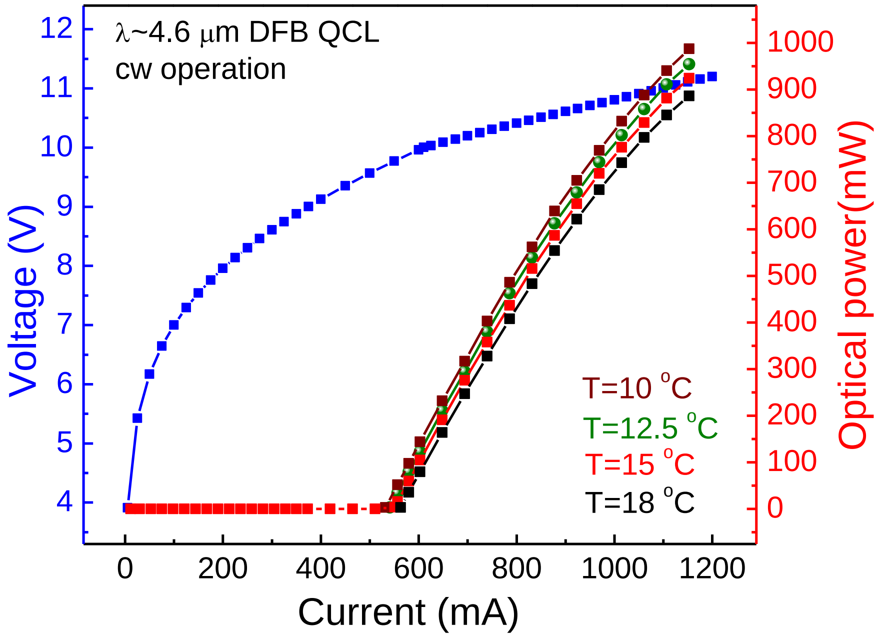
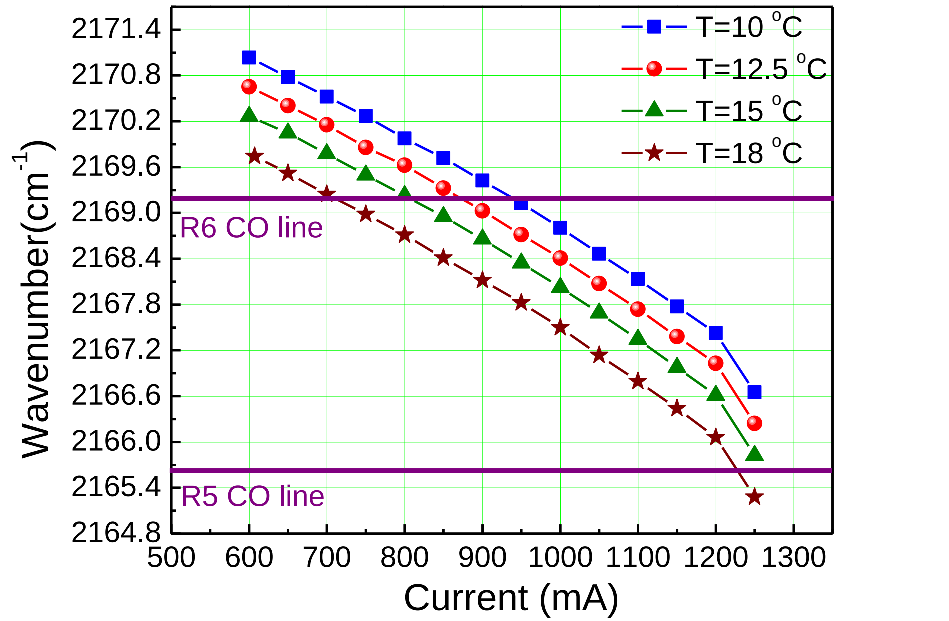
Motivation for Carbon Monoxide Detection

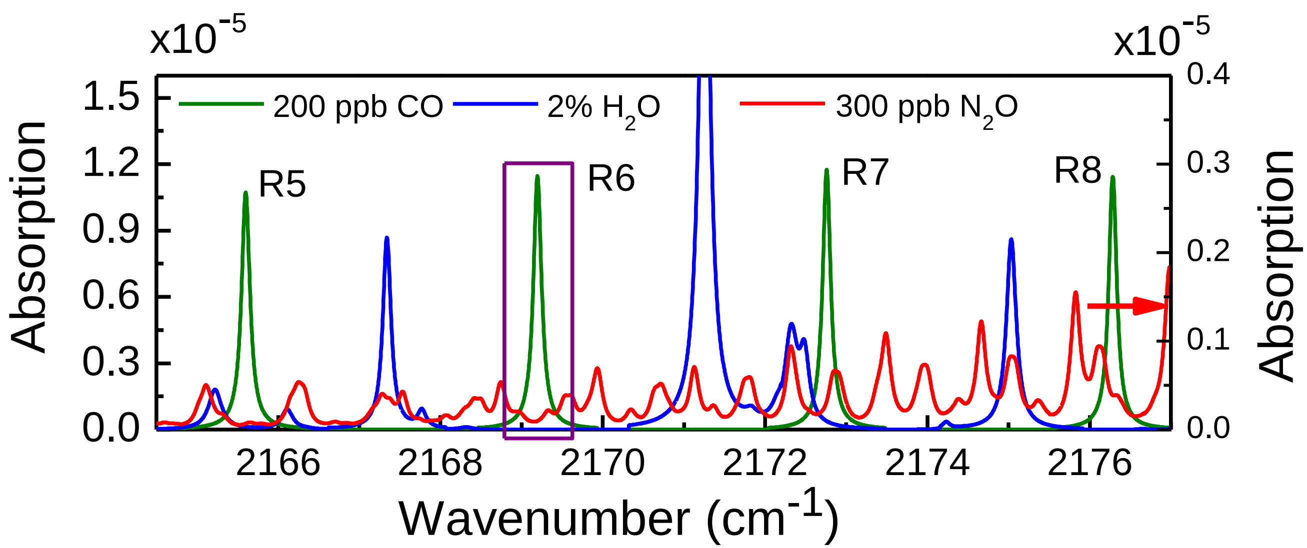
- Atmospheric Chemistry
  - Incomplete combustion of natural gas, fossil fuel and other carbon containing fuels.
  - Major global pollutant. Impact on atmospheric chemistry through its reaction with hydroxyl (OH) for troposphere ozone formation and changing the level of greenhouse gases (e.g. CH_4).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

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





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



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

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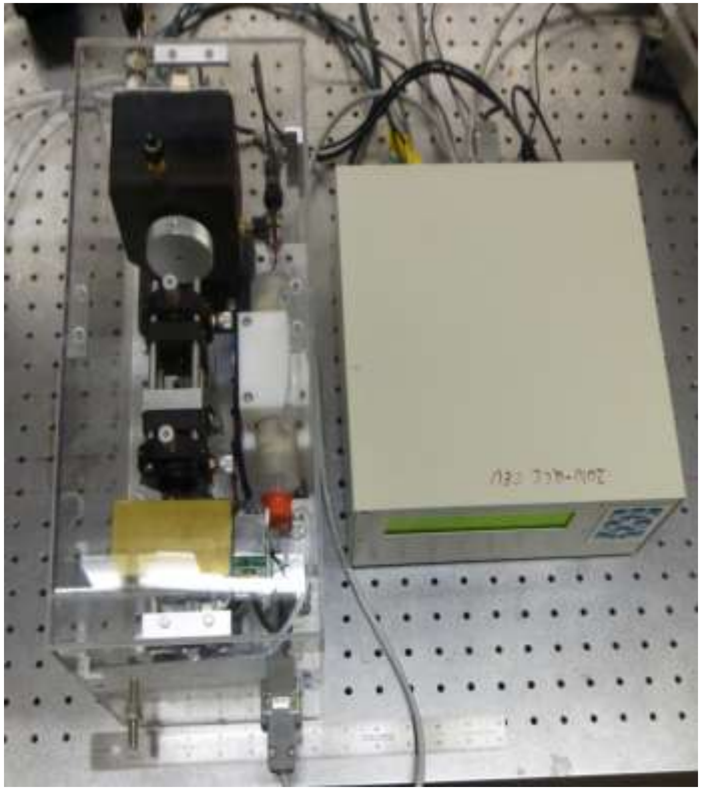
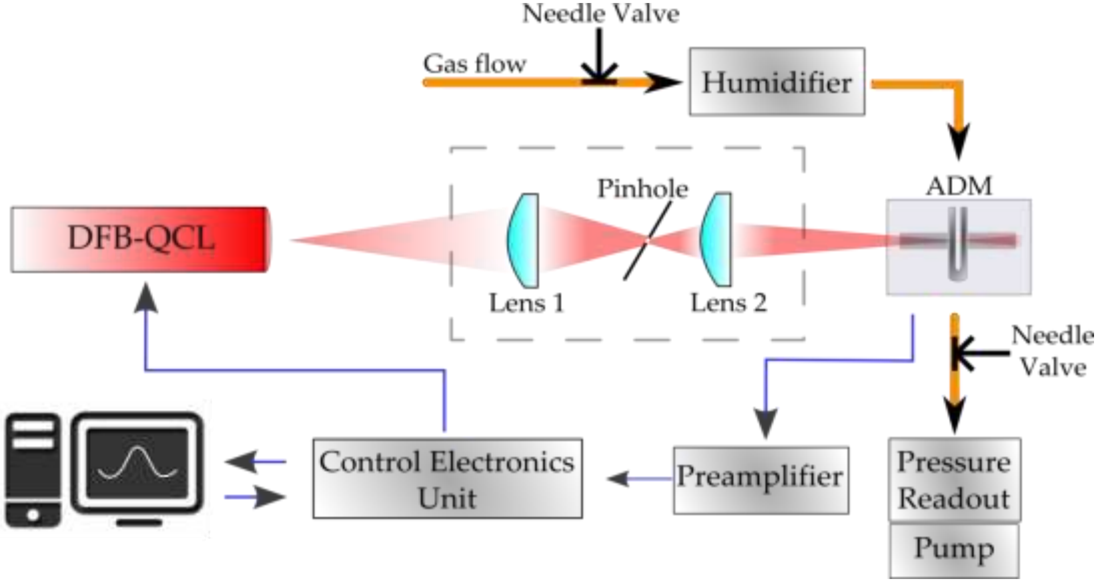
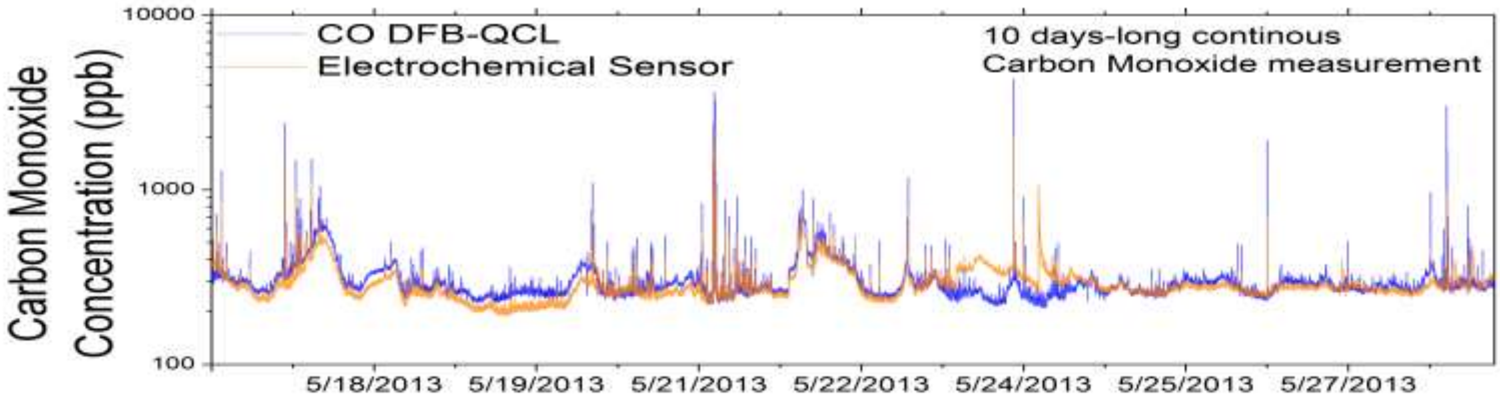
Performance of a NWU 4.61 μm high power CW TEC DFB QCL



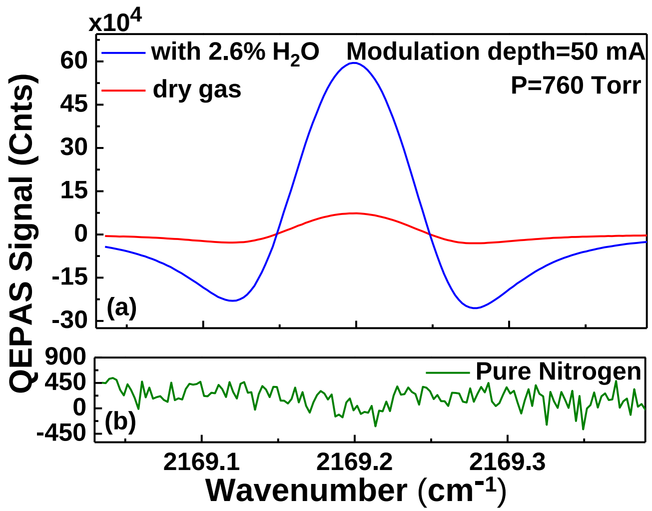


- CO sensor is enclosed in a 6" x 14" x 8" case
- Each 2f scan is completed in ~5s, when operating QCL in a frequency scanning mode
- QCL operating temperature is set to 10°C
- Sensor operates at a pressure of **225 Torr**, which is optimal in terms of signal-to-noise ratio

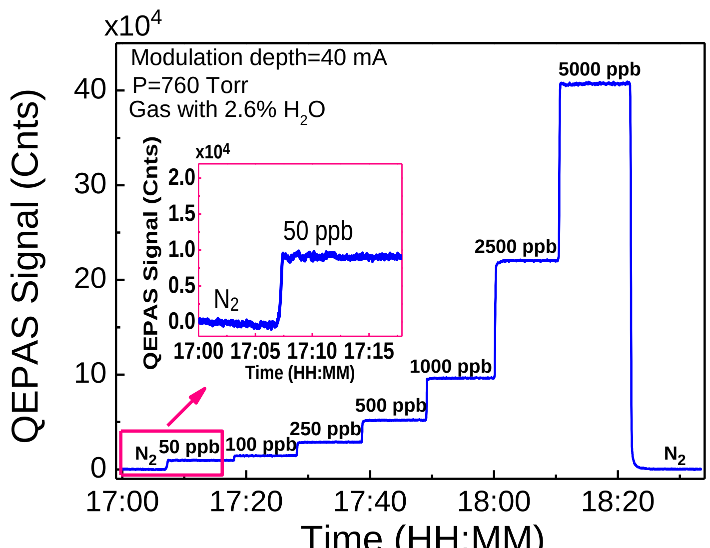
10 days-long continous measurements were performed to determine CO concentration levels on Rice University



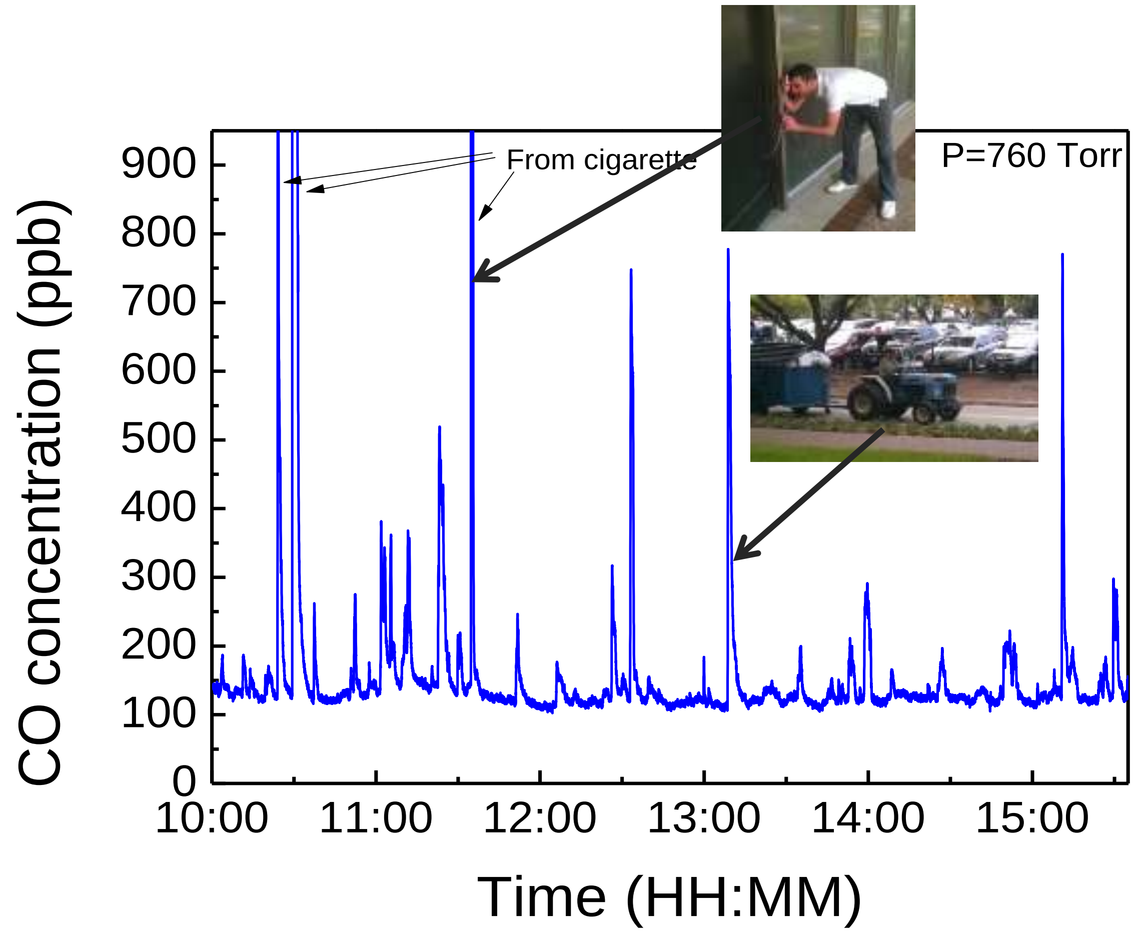
CW DFB-QCL based CO QEPAS Sensor Results



2f QEPAS signal for dry (red) and moisturized (blue) 5 ppm CO:N_2 mixture near **2169.2 cm^{-1}**.



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



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

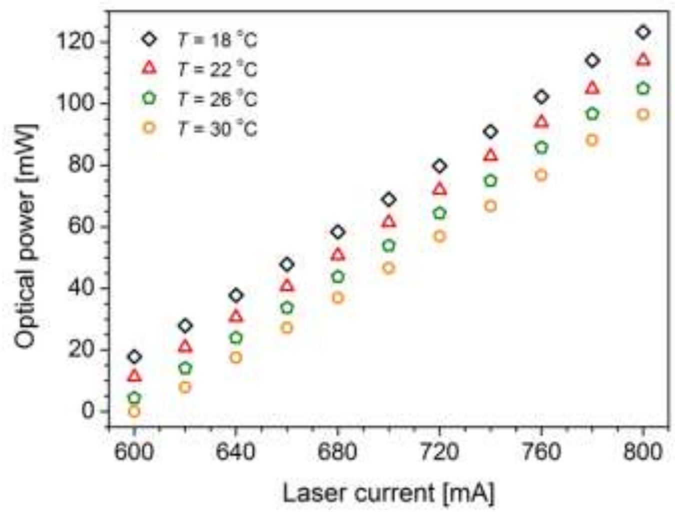
Minimum detectable CO concentration is:

~ 2.5 ppbv (1σ; 1 s time resolution)

CW DFB-QCL based SO_2 QEPAS Results

Basic Facts & Motivation of Sulfur Dioxide Detection

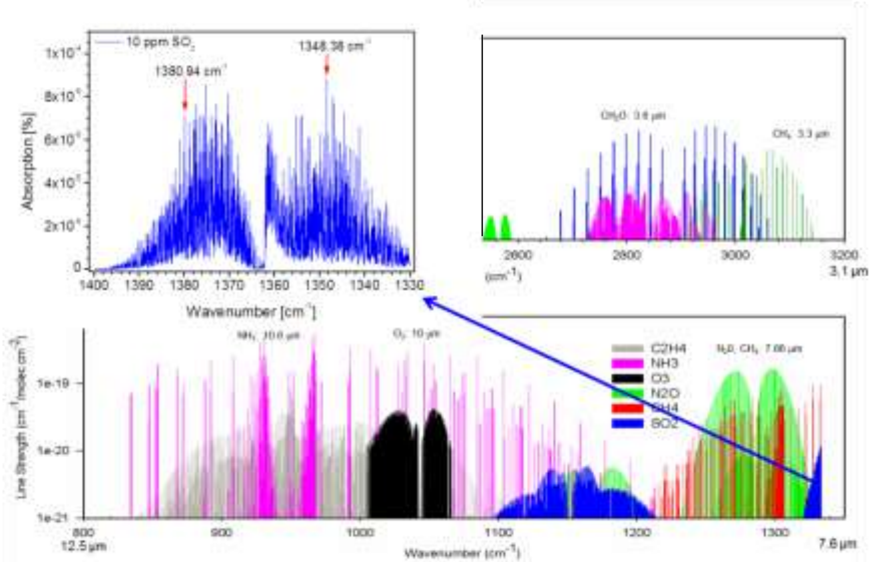
- Prominent air pollutant
- Emitted from coal fired power plants (~73%) and other industrial facilities (~20%)
- In atmosphere SO_2 converts to sulfuric acid primary contributor to acid rain
- SO_2 reacts to form sulfate aerosols
- Primary SO_2 exposure for 1 hour is 75 ppb
- SO_2 exposure affects lungs and causes breathing difficulties
- Currently, reported annual average atmospheric SO_2 concentrations range from ~ 1 - 6 ppb
- Major Sources are motor vehicles exhaust, fuel combustion, and fires.



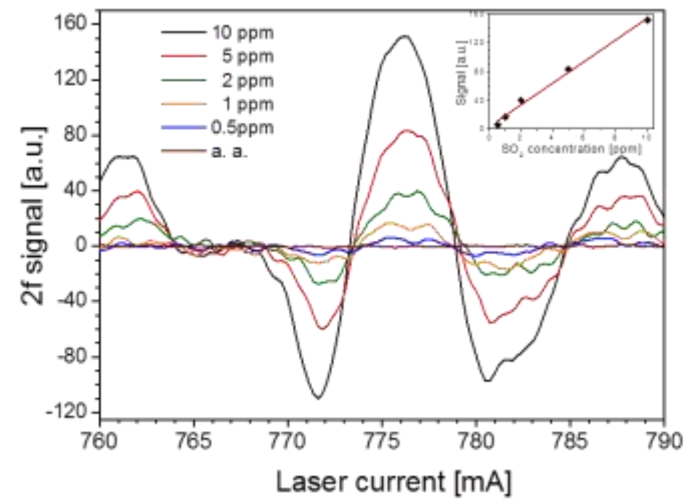
HHL CW DFB QCL

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

SO_2 Absorption Line Selection



Molecular Absorption Spectra within two Mid-IR Atmospheric Windows

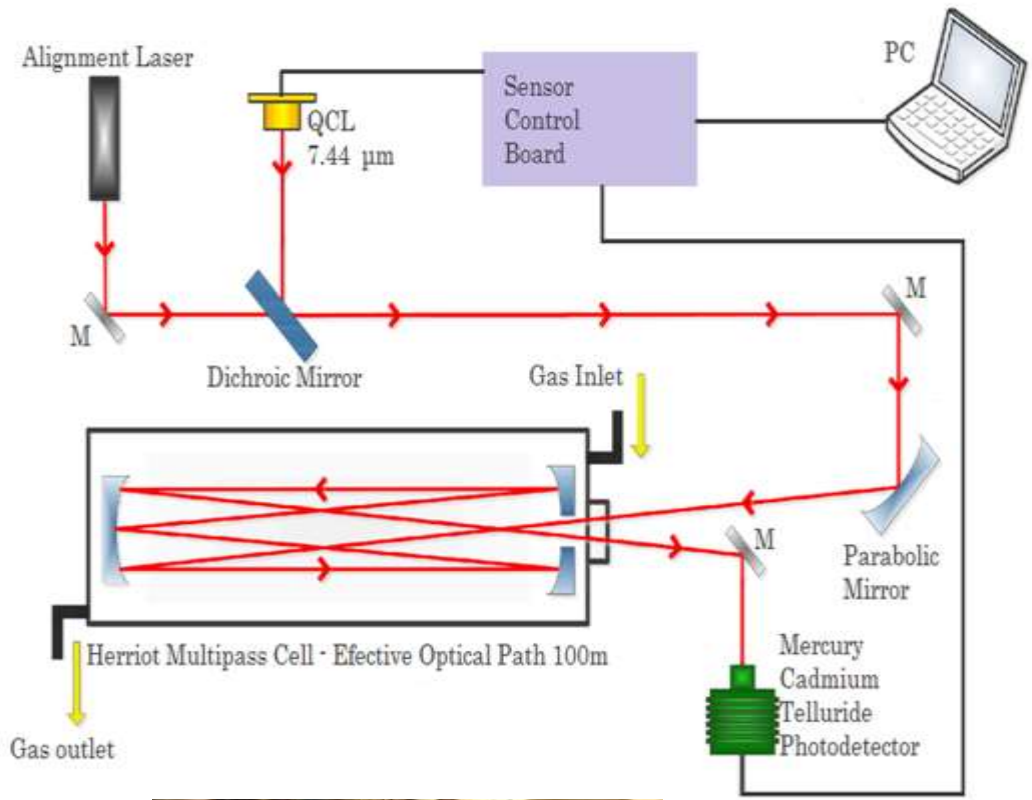


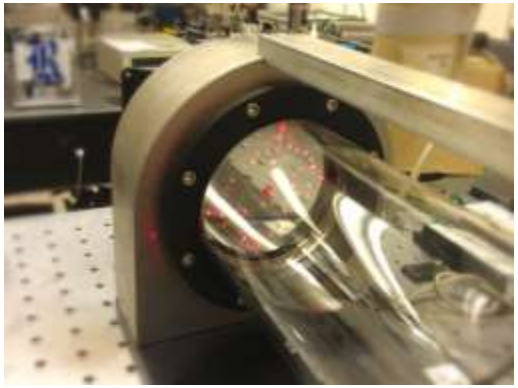
2f WMS QEPAS signals for different SO_2 concentrations when laser was tuned across **1380.9 cm^{-1}** line.

Minimum detectable SO_2 concentration is:

~ 100 ppbv (1σ; 1 s time resolution)

Comparison of SO_2 sensor performance using different techniques





Red beam spot pattern for a 100-m path length Herriott multipass (192 passes)

- Direct absorption open path 2m ~ 1 ppmv[1]
- QEPAS with 180mW laser power ~100 ppbv[2]
- Aerodyne WMS MPC system based on a 76m MPC ~0.5 ppb (projected with HITRAN simulation) [3]
- WMS MPC sensor system ~45 ppbv [4]

1. Wilson T. *et al.*
2. Waclawek J. *et al.*
3. Rodrigo J. *et al.*
4. *Tarka J. et. al.*

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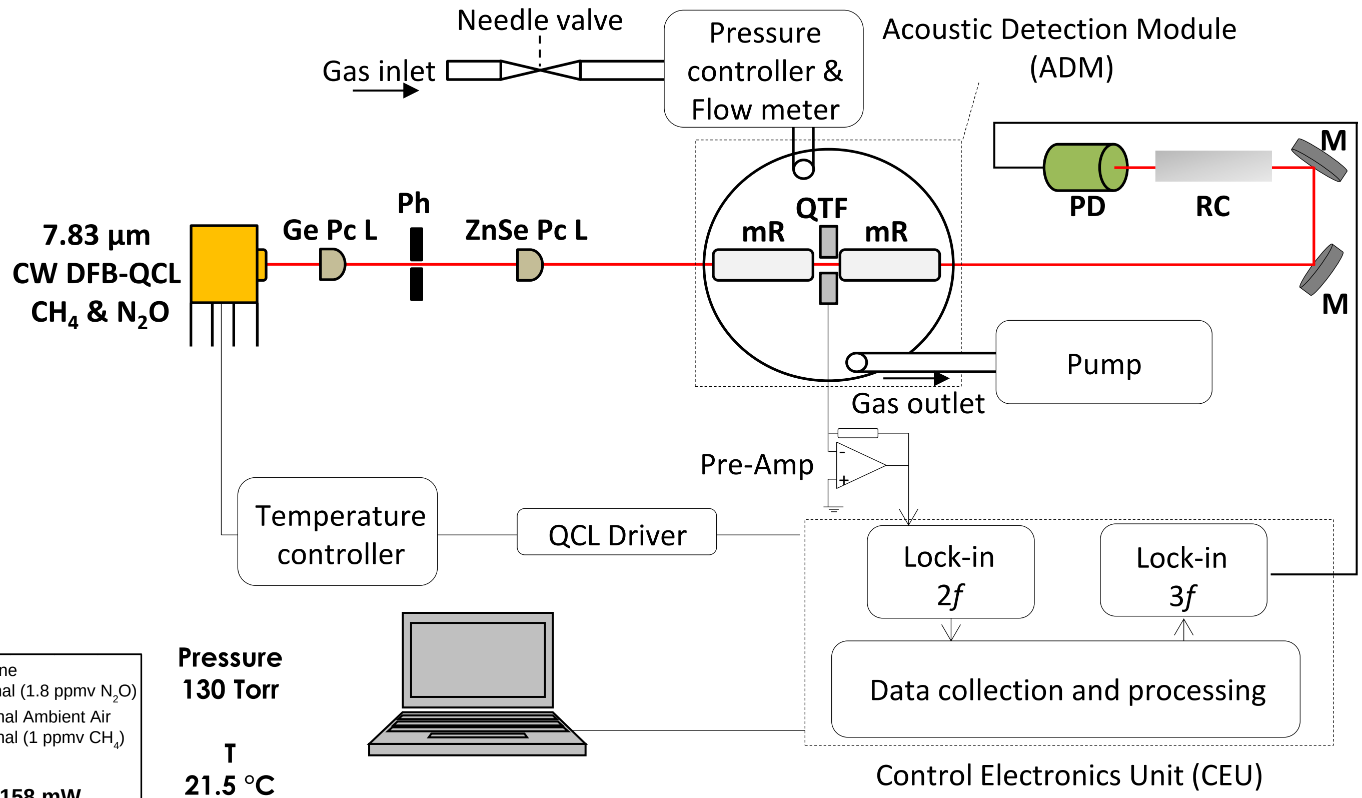
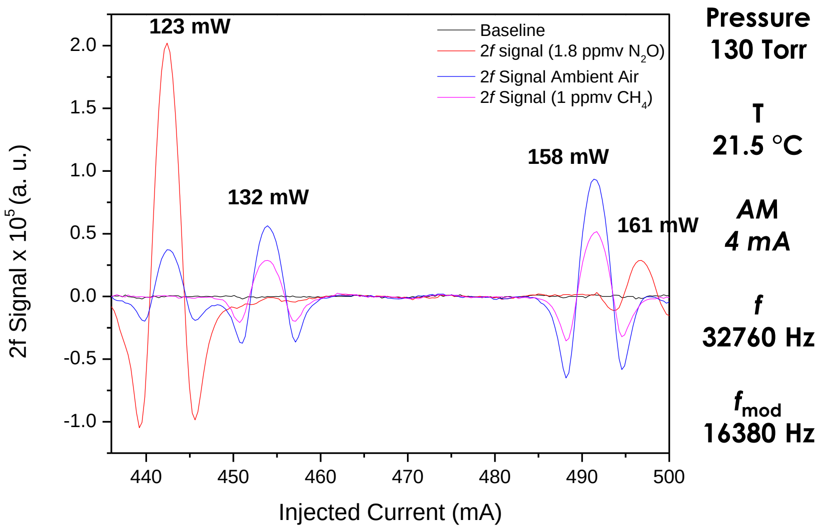
QEPAS based CH_4 and N_2O Gas Sensor

Motivation for CH_4 and N_2O Detection

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





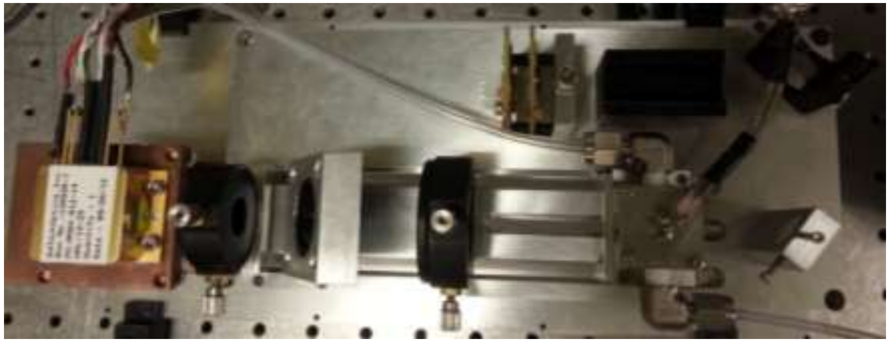
Detection Limit (1σ) with a **1-sec** averaging time

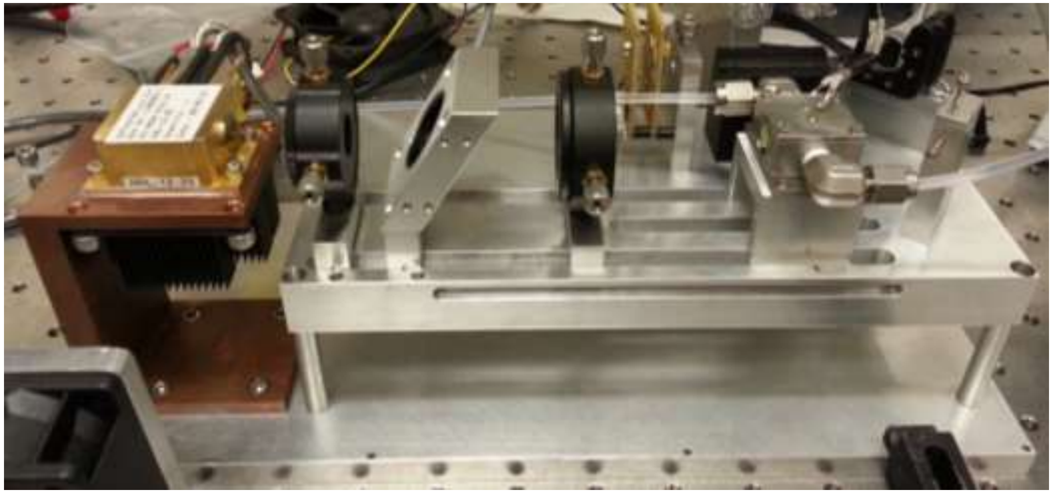
Methane (CH4) (1275.04 cm^{-1}) **13 ppbv**

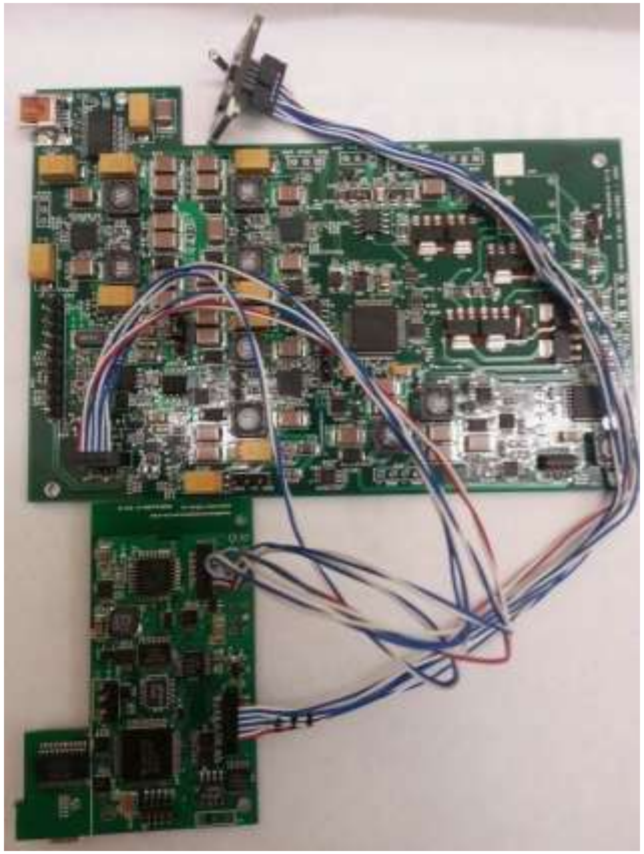
Nitrous Oxide (N_2O) (1275.5 cm^{-1}) **6 ppbv**

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

QEPAS based CH_4 and N_2O Gas Sensor







QEPAS Sensor Control Board

QCL Current and TEC Driver, Performing wavelength modulation, Data acquisition, Applying continuous saw-tooth current ramping at 8 Hz, Testing QTF and low noise pre amplifier

QCL based QEPAS Performance for10 Trace Gas Species (June 19 2013)

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
C_2H_5OH (N_2)**	1934.2	770	2.2×10^{-7}	10	$9\text{x}10^{4}$
NO (N_2+H_2O)	1900.07	250	7.5×10^{-9}	100	3.6
SO_2 (N_2+2.4%H_2O)	1380.94	100	2.0×10^{-8}	40	100
N_2O (air)	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
SF_6***	943.73	75	2.7×10^{-10}	40	5×10^{-2}

* - Improved microresonator
** - Improved microresonator and double optical pass through ADM
*** - With amplitude modulation and metal microresonator

NNEA – normalized noise equivalent absorption coefficient.
NEC – noise equivalent concentration for available laser power and τ=1s time constant, 18 dB/oct filter slope.

For comparison: conventional PAS 2.2 (2.6)×10^{-9} $cm^{-1}W/\sqrt{Hz}$ (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; *** - V. Spagnolo, et al. University and Politecnico of Bari, Italy

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Merits of QEPAS based Trace Gas Detection

- Very small sensing module and sample volume (a few mm^3 to ~$2cm^2$)
- Extremely low dissipative losses
- Optical detector is not required
- Wide dynamic range
- Frequency and spatial selectivity of acoustic signals
- Rugged transducer – quartz monocrystal; can operate in a wide range of pressures and temperatures
- Immune to environmental acoustic noise, sensitivity is limited by the fundamental thermal TF noise: $k_B T$ 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_2O
- Responsivity depends on the speed of sound and molecular energy transfer processes
- Cross sensitivity issues

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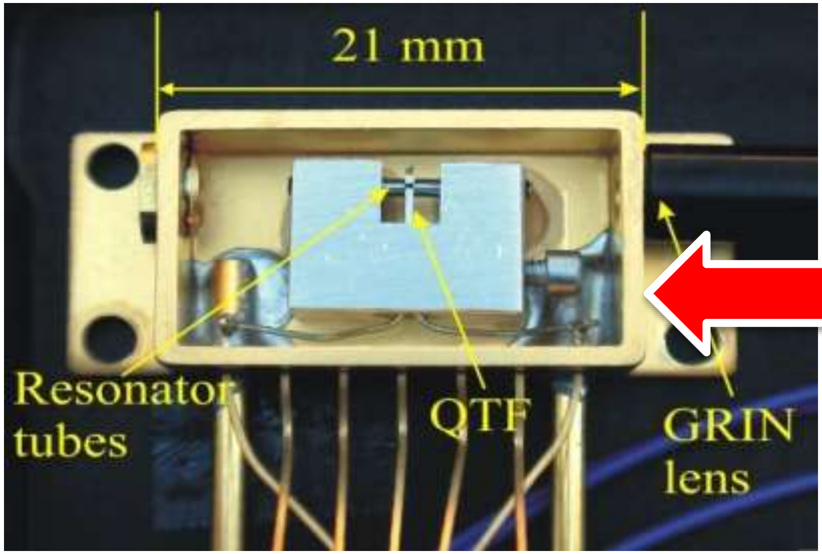
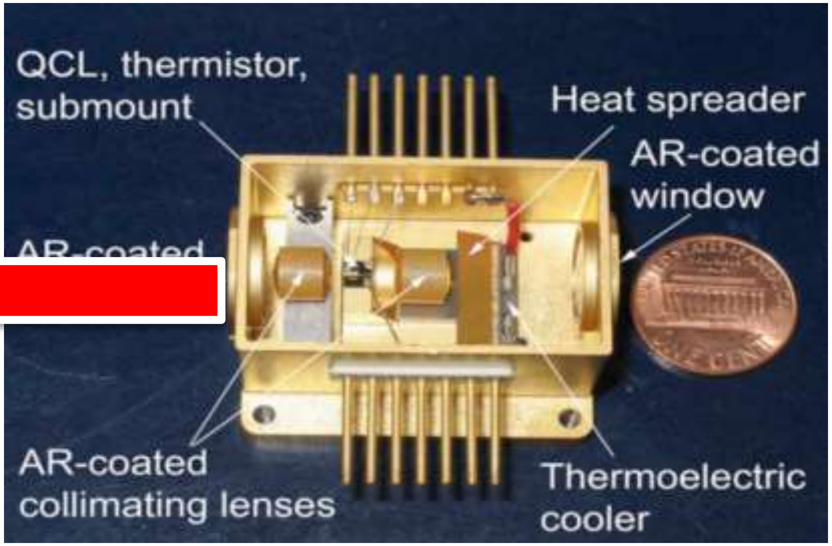
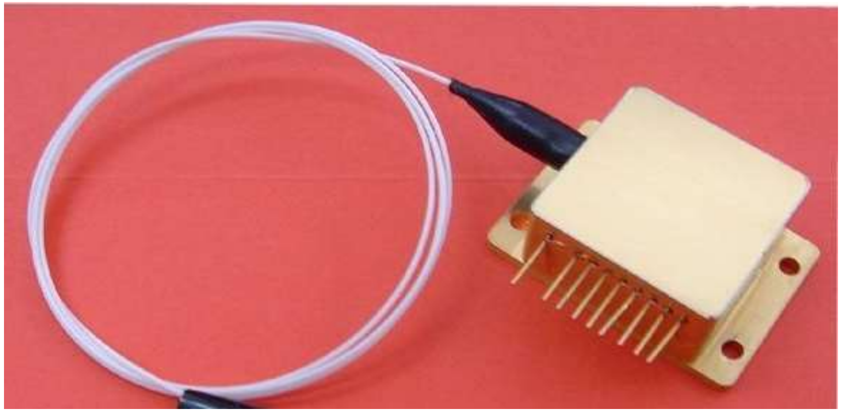
Potential Integration of a CW DFB- QCL and QEPAS Absorption Detection Module



2012 QEPAS ADM

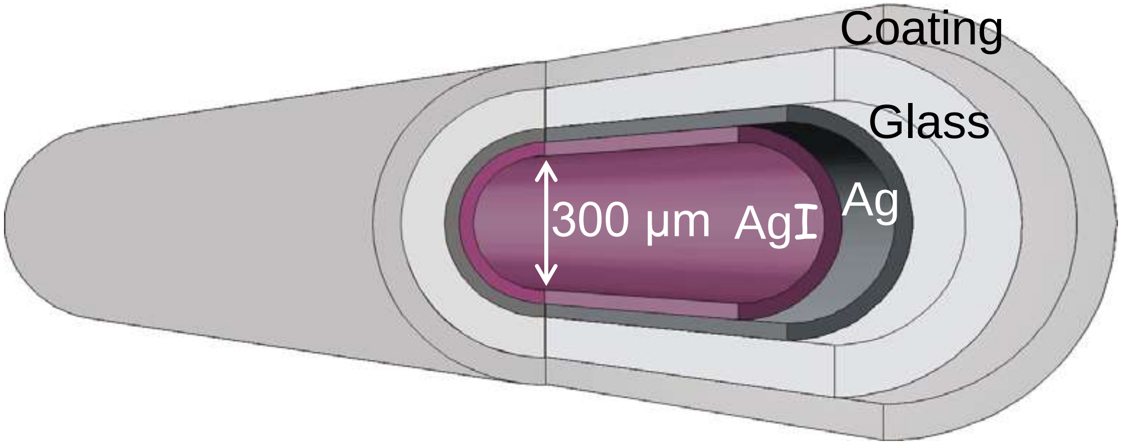


HHL package fiber coupled DFB-QCL

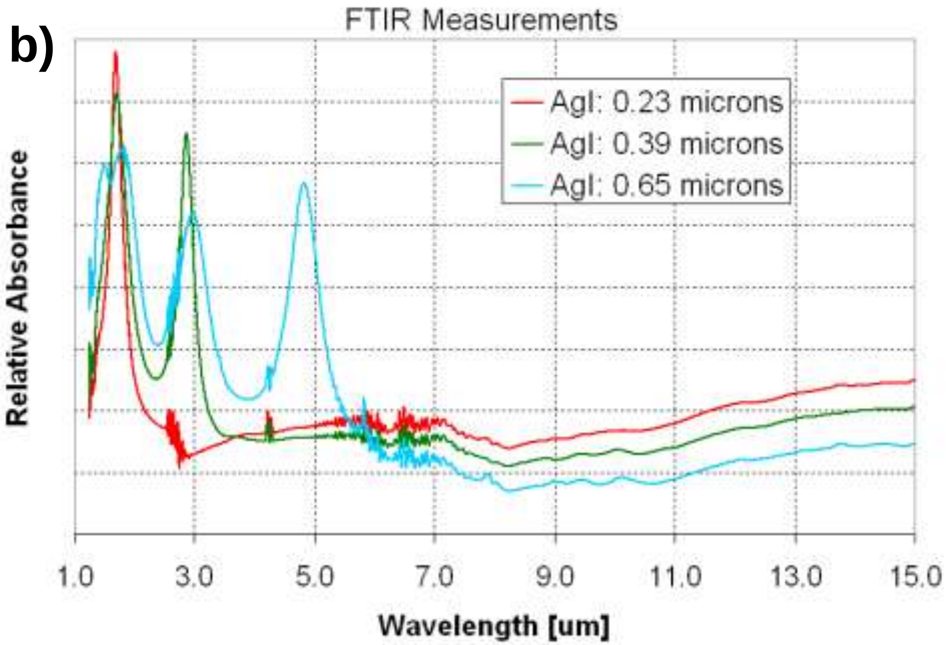


A. Lyakh, et al "1.6 W high wall plug efficiency, continuous-wave room temperature quantum cascade laser emitting at 4.6 μm", Appl. Phys. Lett. **92**, 111110 (2008)

Hollow core waveguide



b)



Hollow Core Glass Waveguides:

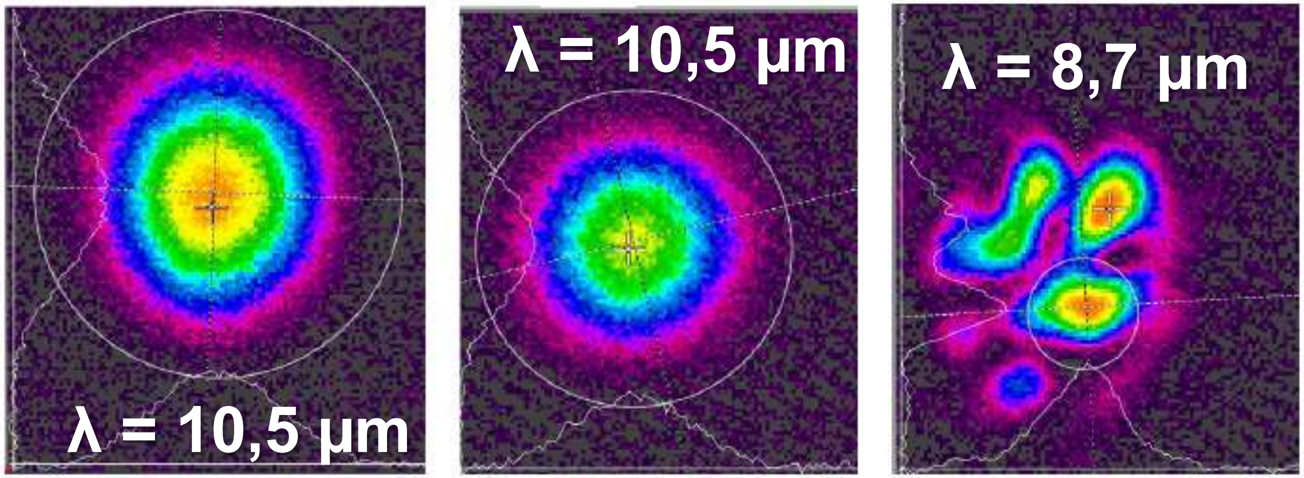
- Excellent Infrared transmission out to 20 µm
- Proven single mode delivery for bore size ~ 30λ
- No end reflections
- High damage threshold
- Very Robust
- 20+ years of experience at Rutgers

Bending loss is the primary concern

OKSI OPTO-KNOWLEDGE SYSTEMS INC.

QCL-fiber beam profile and losses

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



(a) No fiber (b) Single-mode fiber (c) Multi-mode fiber

Beam Profiling measurement setup and sample beam profiles

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

Future Directions and Outlook

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

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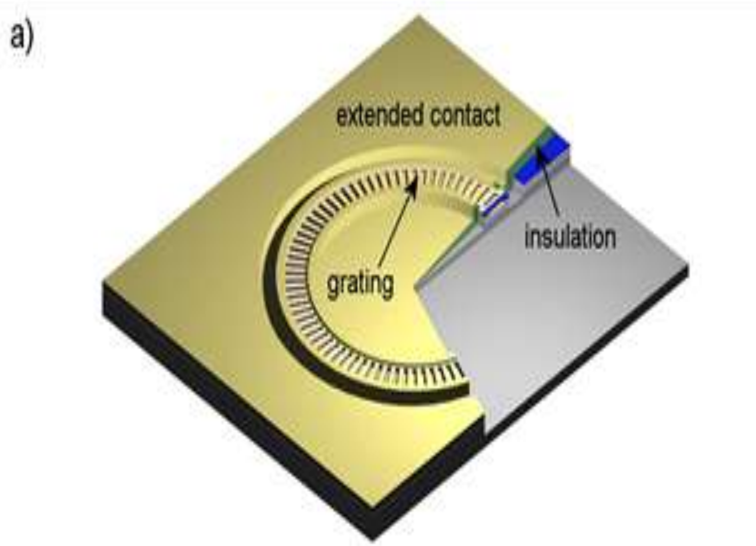
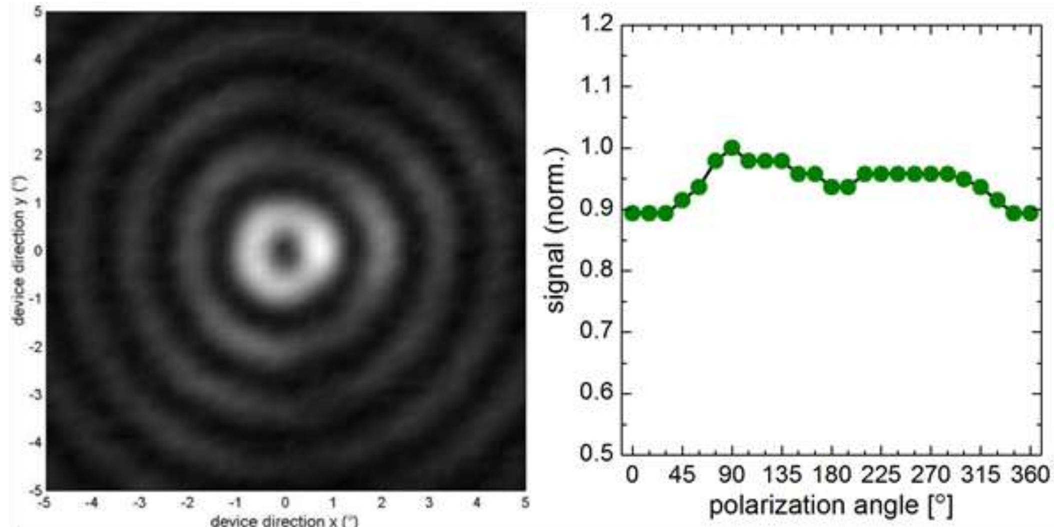
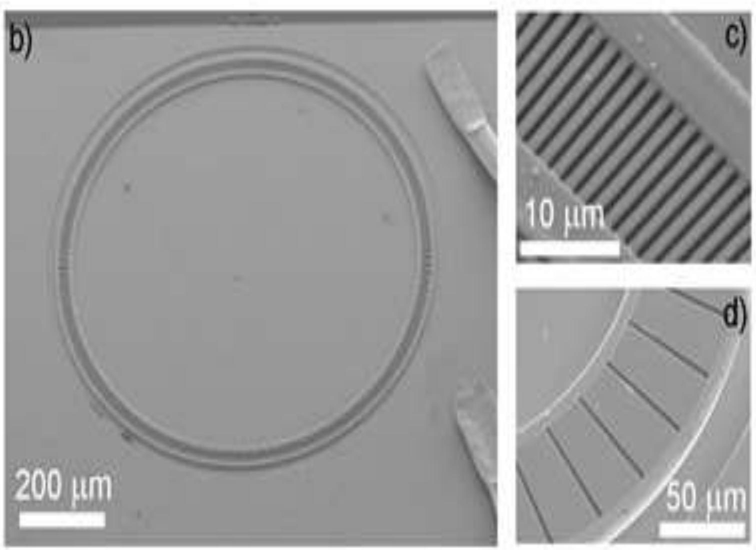
Mid- IR and THz Ring Cavity Surface Emitting QCLs



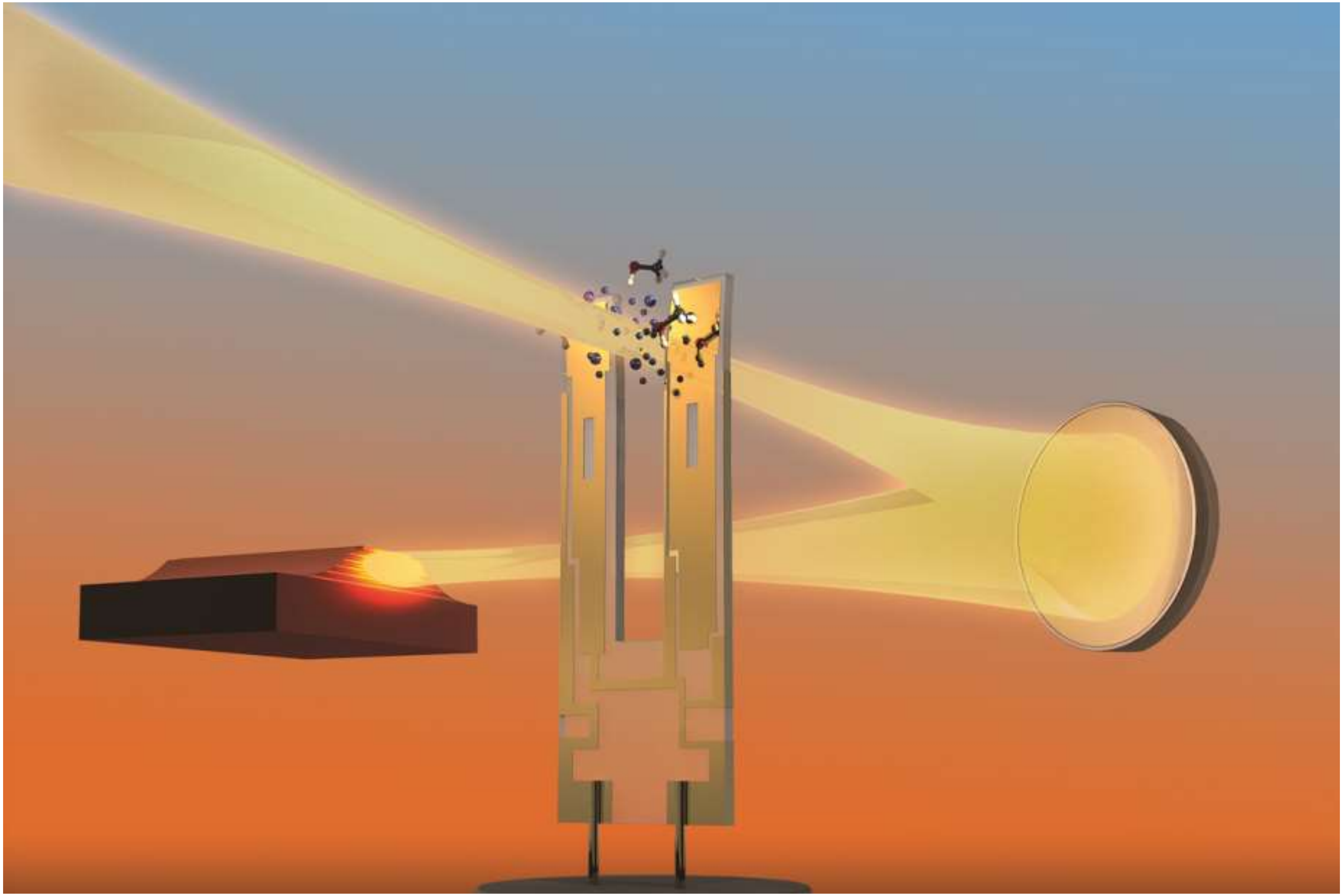




(a) Two-dimensional far-field plot emanating from a MIR RCSE-QCL and recorded with a micro-bolometer camera in a distance of 40 mm. (b) Polarization dependent intensity measurement.

(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.

THz based QEPAS



V. Spangolo et. al. , APL(appear), July (2013)

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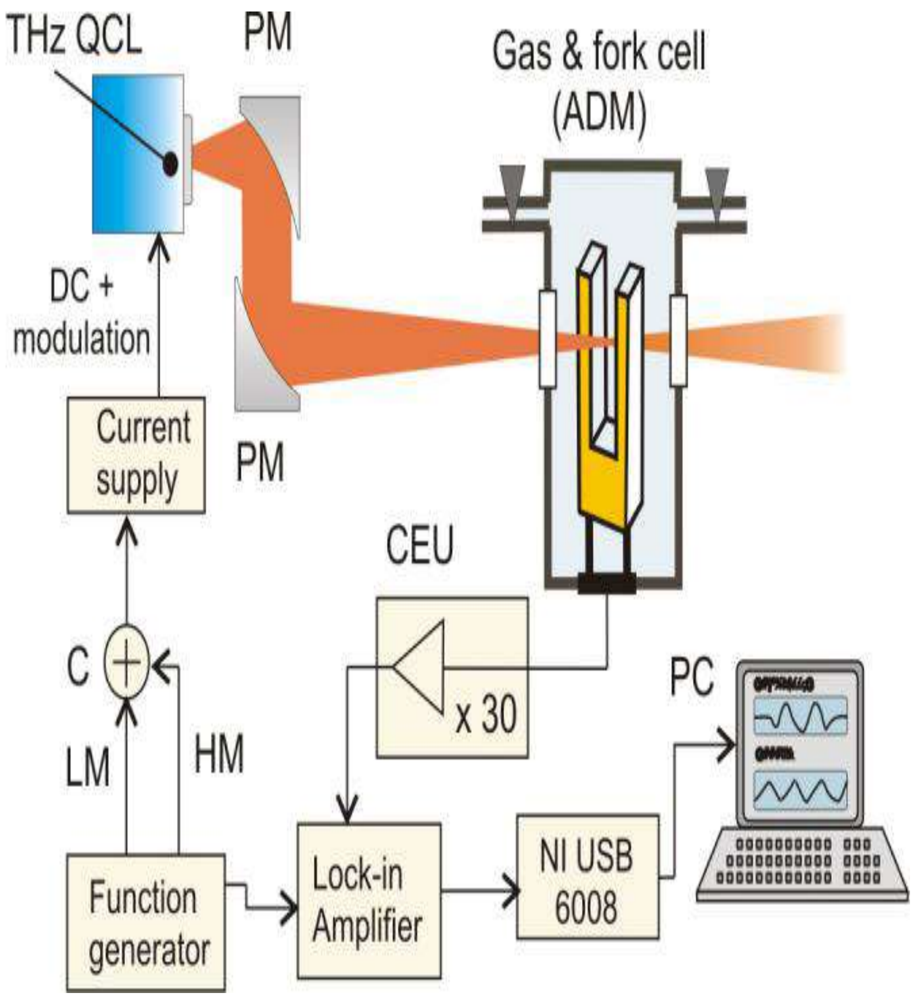
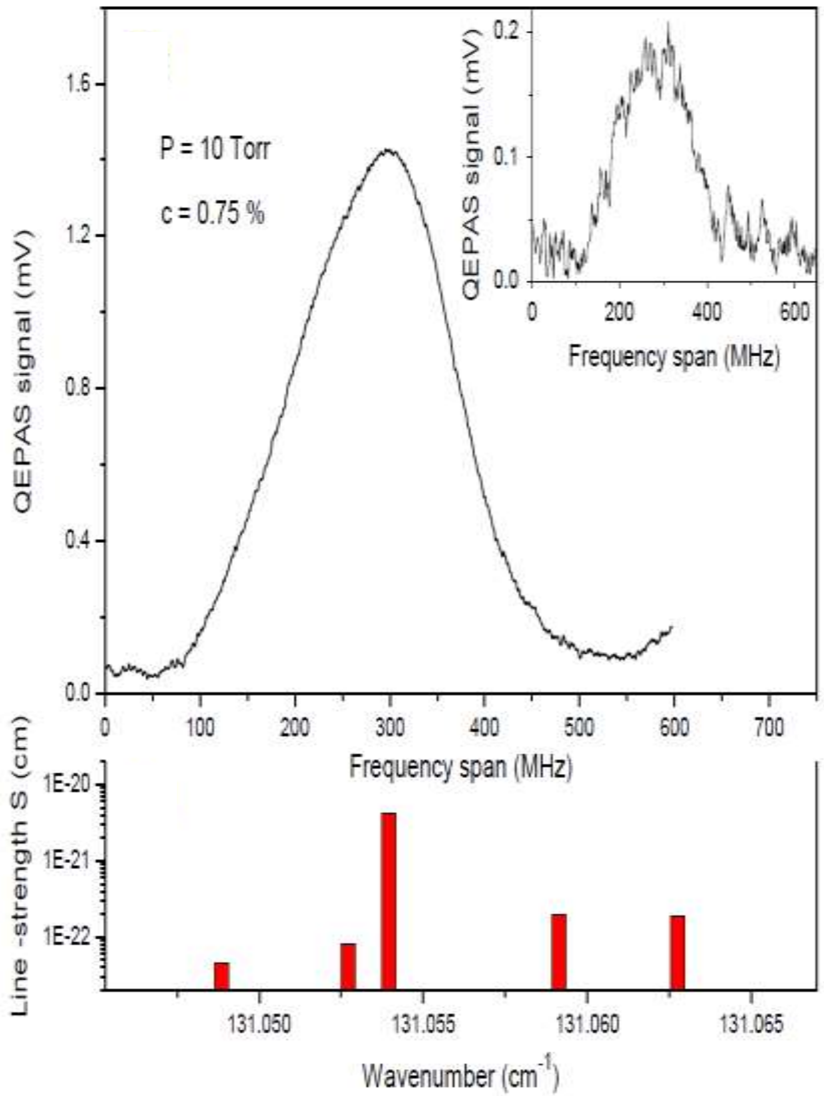
THz based QEPAS





V. Spangolo et. al. , APL(appear), July (2013)

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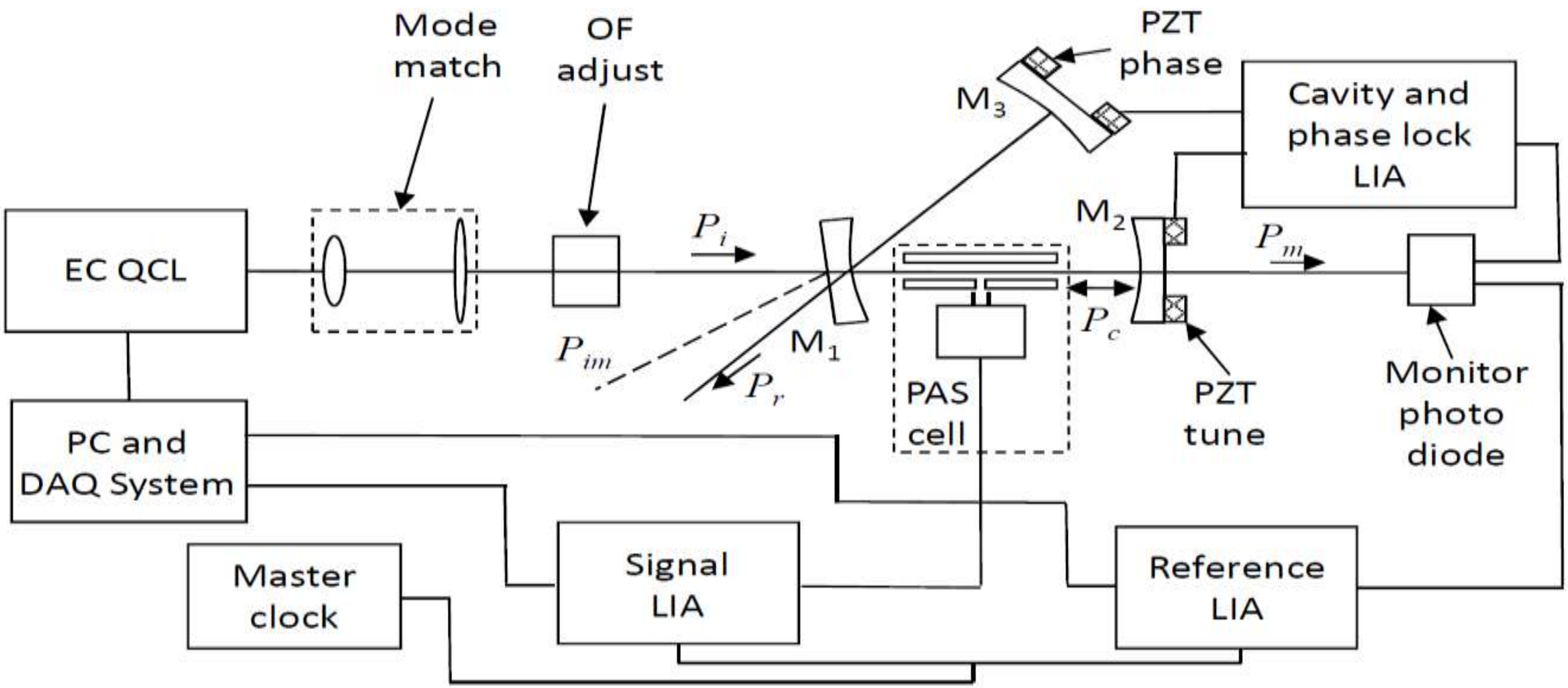
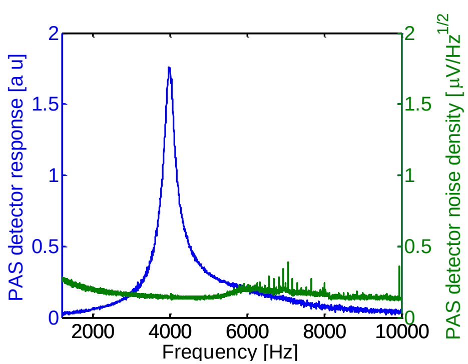
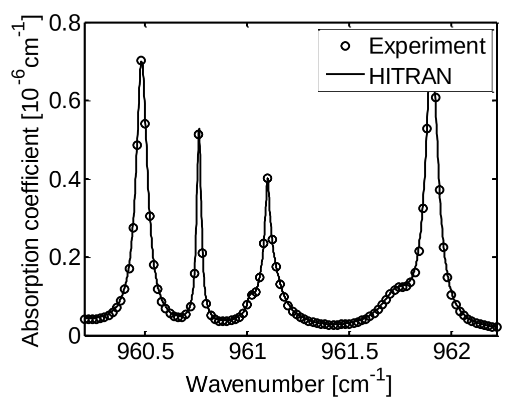
Intracavity NH_3 based QEPAS







A. Kachanov , S. Koulikov, F.K. Tittel , Appl. Phys. B 110: 47-56 (2013)

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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 ~ 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
  - CO at ~ 4.61µm with minimum detection limit of 2.5 ppbv
  - SO_2 at ~7.24µm with a detection limit of 100 ppbv
  - CH_4 and N_2O at ~7.28 µm currently in progress with detection limits of 20 and 7 ppbv, respectively.
- New target analytes such as OCS, CH_2O, HONO, H_2O_2, C_2H_4,
- Monitoring of broadband absorbers such as acetone, C_3H_8, 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.

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