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## Mid-Infrared Semiconductor Laser based Trace Gas Sensor Technologies: Recent Advances & Applications

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OUTLINE

Asia Communications & Photonics Conf. (ACP)

Guangzhou, China

- 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, and $SO_2$
  - Future Directions of Laser Based Gas Sensor Technology and Conclusions

Research supported by NSF ERC MIRTHE, NSF-ANR NexCILAS, the Robert Welch Foundation & Sentinel Photonics via an EPA Phase 1 SBIR Sub-award

## 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 (eg measurement of isotopologues)
  - 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**
- **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)
  - 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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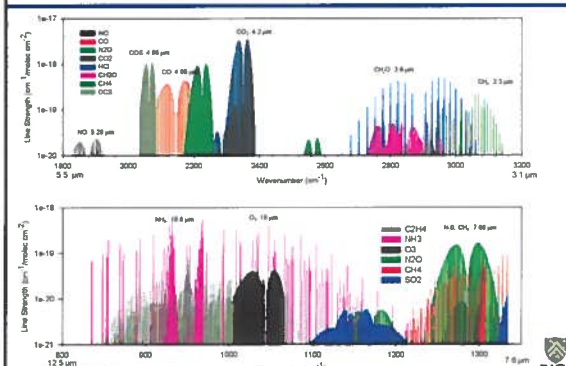
## HITRAN Simulated Mid-Infrared Molecular Absorption Spectra




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 – Oct 2012

- **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
  - ~ 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 (MIOMD-11, NWU, Sept. 2012)**
  - Room temperature pulsed power of > 30 W with 27% wall plug efficiency and CW powers of ~ 5 W with 21% wall plug efficiency
  - > 2W, TEC CW DFB @ 4.6 µm
  - > 600 mW (CW FP) @ RT, wall plug efficiency of ~17 % at 4.6 µm;

4 mm

## 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 $TEM_{00}$ 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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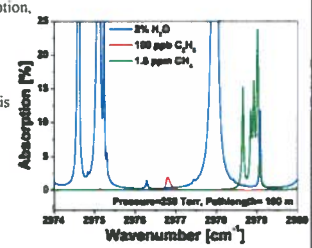
## Motivation for Mid-infrared $C_2H_6$ Detection

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




HITRAN absorption spectra of $C_2H_6$, $CH_4$, and $H_2O$

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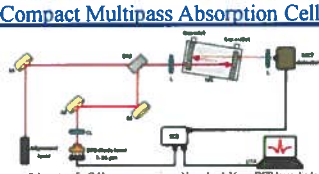
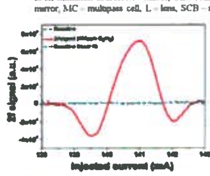
## $C_2H_6$ Detection with a 3.36 μm DFB LD using a Novel Compact Multipass Absorption Cell and Control Electronics



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

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

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

## Motivation for $NH_3$ Detection

- Monitoring of gas separation processes
- Detection of ammonium-nitrate explosives
- Spacecraft related gas monitoring
- Monitoring $NH_3$ concentrations in the exhaust stream of $NO_x$ removal systems based on selective catalytic reduction (SCR) techniques
- Semiconductor process monitoring & control
- Monitoring of industrial refrigeration facilities
- Pollutant gas monitoring
- Atmospheric chemistry
- Medical diagnostics (kidney & liver diseases)

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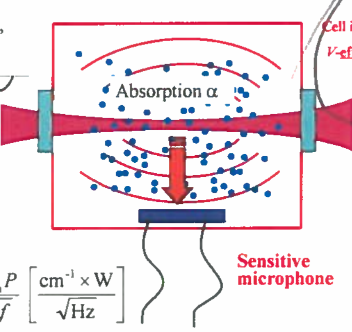
## Conventional PAS

Laser beam, power $P$

Modulated ($P$ or λ) at $f$ or $f/2$




Q>>1000
Cell is OPTIONAL!
V-effective volume

Sensitive microphone

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

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

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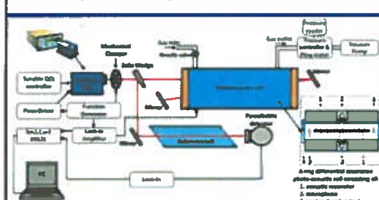
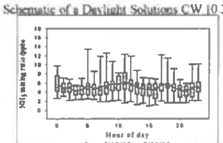
## Atmospheric $NH_3$ Measurements using an EC-QCL PAS Sensor

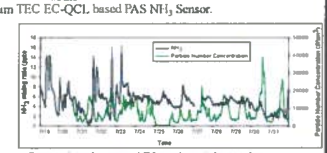


$NH_3$ sensor at the Moody Tower rooftop monitoring site.

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

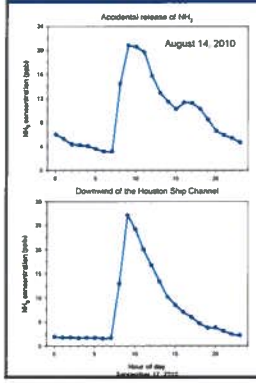



Diurnal profile of atmospheric $NH_3$ levels in Houston, TX.




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

## $NH_3$ Detection due to a Fire resulting from a Truck Collision




A chemical incident occurred at ~ 6 a.m. after two 18-wheelers headed southbound side-by-side collided. 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

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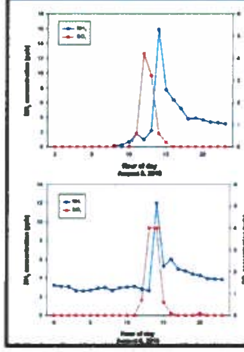
## Sporadic increased $NH_3$ concentration levels related to emissions by the Parish electric power plant, TX



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

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## From Conventional PAS to QEPAS

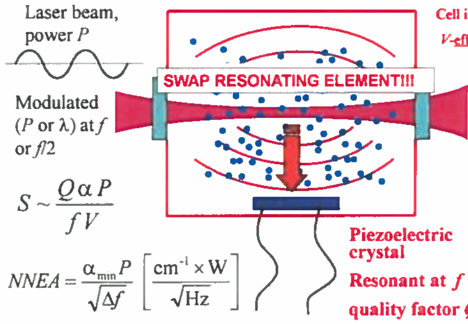
$Q$>>1000

Cell is OPTIONAL!

$V$-effective volume

Laser beam, power $P$

Modulated ($P$ or $\lambda$) at $f$ or $f/2$




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

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

Piezoelectric crystal

Resonant at $f$

quality factor $Q$

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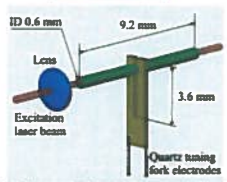
## Quartz Tuning Fork as a Resonant Microphone for QEPAS

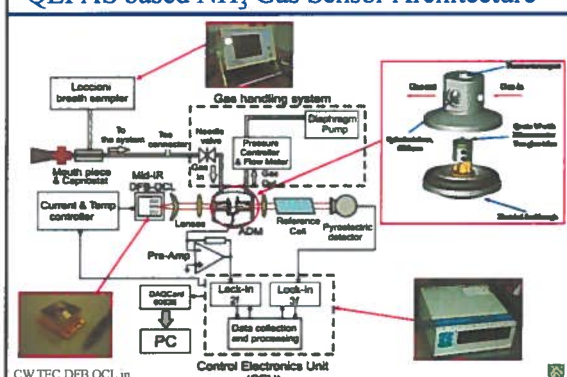

**Unique properties**

- Extremely low internal losses:
  - Q~10 000 at 1 atm
  - Q~100 000 in vacuum
- Acoustic quadrupole geometry
  - Low sensitivity to external sound
- Large dynamic range (~$10^6$) – linear from thermal noise to breakdown deformation
  - 300K noise: $x$~$10^{-11}$ cm
  - Breakdown: $x$~$10^{-2}$ cm
- Wide temperature range: from 1.6K to ~700K

**Acoustic Micro-resonator (mR) tubes**

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

## QEPAS based $NH_3$ Gas Sensor Architecture




CW TEC DFB QCL in HHL package (Hamamatsu)

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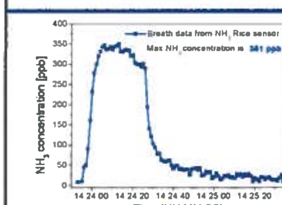
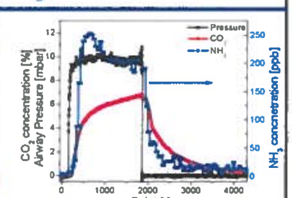
## Real-time exhaled human $NH_3$ Breath Measurements




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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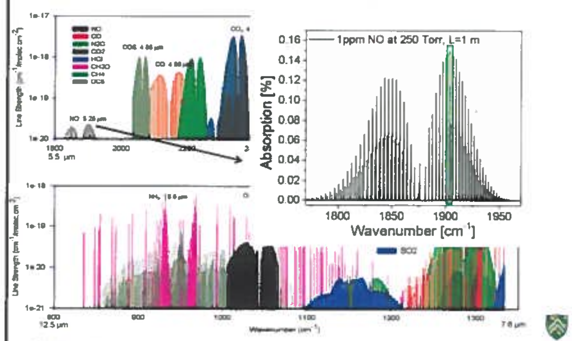
## Motivation for Nitric Oxide Detection

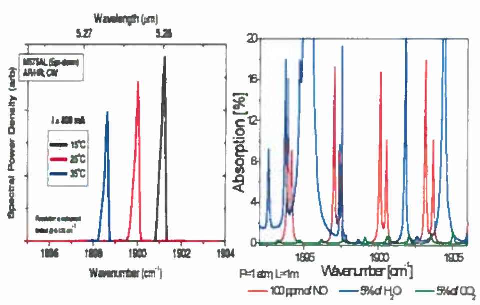
- Atmospheric Chemistry
- Environmental pollutant gas monitoring
  - $NO_x$ monitoring from automobile exhaust and power plant emissions
  - Precursor of smog and acid rain
- Industrial process control
  - Formation of oxynitride gates in CMOS Devices
- NO in medicine and biology
  - Important signaling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



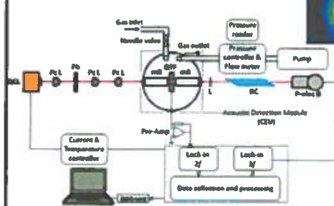

Source: HITRAN 2000 database

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




Output power: 117 mW @ 25 C

## QCL based WMS QEPAS NO Gas Sensor Platform

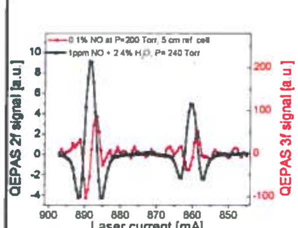


Schematic of a QCL QEPAS based Gas Sensor. M – mirror, PcL – plano-convex lens, Ph – pinhole, QTF – quartz tuning fork, mR – acoustic micro-resonator, RC – reference cell.

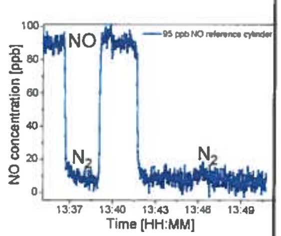
CW HHL TEC DFB-QCL package and IR camera image of the laser beam at 630 mA and 20.5 deg C through tubes after ADM

Compact Prototype NO Sensor (September 2012)

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




2f QEPAS signal (navy) and reference 3f signal (red) when laser was tuned across $1900.08\ cm^{-1}$ line.



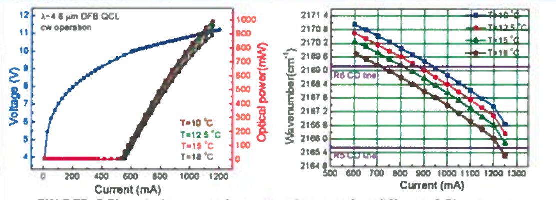

2f QEPAS signal amplitude for 95 ppb NO when laser was locked to the $1900.08\ cm^{-1}$ line.

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

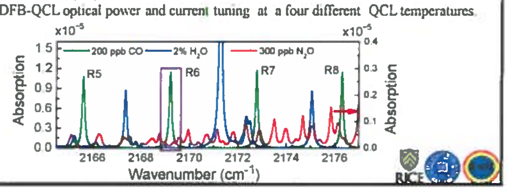
## Motivation for Carbon Monoxide Detection

- 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. $CH_4$).
- Public Health
  - Extremely dangerous to human life even at a low concentrations. Therefore CO must be carefully monitored at low concentration levels.
- CO in medicine and biology
  - Hypertension, neurodegenerations, heart failure and inflammation have been linked to abnormality in CO metabolism and function.

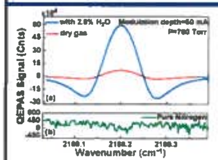
## Performance of a NWU 4.6 μm high power CW TEC DFB QCL



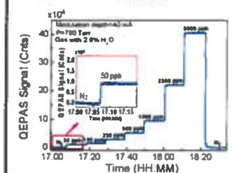

CW DFB-QCL optical power and current tuning at a four different QCL temperatures



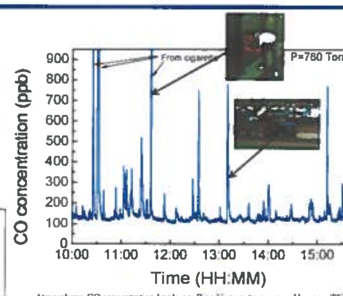

## CW DFB-QCL based CO QEPAS Sensor Results




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 ppbv (1σ; 1 s time resolution)**

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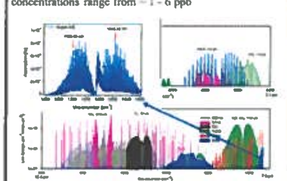
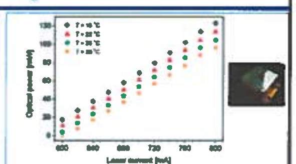
## CW DFB-QCL based $SO_2$ QEPAS Results

**Motivation for Sulfur Dioxide Detection**

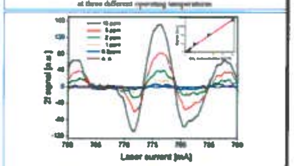
- Prominent air pollutant
- Emitted from coal fired power plants (~73%) and other industrial facilities (~20%)
- In atmosphere $SO_2$ converts to sulfuric acid → primary contributors to acid rain
- $SO_2$ reacts to form sulfate aerosols
- Primary $SO_2$ exposure for 1 hour is 75 ppb
- $SO_2$ exposure affects lungs and causes breathing difficulties
- Currently, reported annual average atmospheric $SO_2$ concentrations range from ~1 - 6 ppb



Molecular Absorption Spectra within two Mid-IR Atmospheric Windows

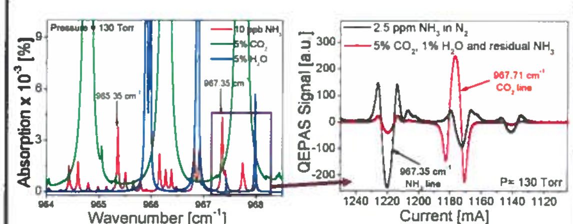



7.24 μm CW DFB-QCL optical power and current tuning at three different operating temperatures




2f WMS QEPAS signals for different $SO_2$ concentrations when laser was tuned across 1380.9 cm$^{-1}$ line.
Minimum detectable $SO_2$ concentration is:
100 ppbv (1σ; 1 s time resolution)

## 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 $v_2$ R band.

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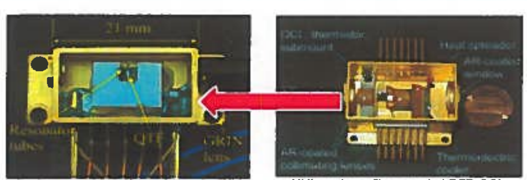
## Potential Integration of a CW DFB- QCL and QEPAS Absorption Detection Module




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)

## Summary and Outlook

- Laser spectroscopy with a mid-infrared, room temperature, continuous wave, DFB laser diodes and high performance DFB QCL is a promising analytical approach for real time atmospheric measurements and breath analysis.
- 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
  - $SO_2$ at ~7.24μm with a detection limit of 100 ppbv
  - CO at ~4.61μm with minimum detection limit of 2 ppbv
  - $CH_4$ and $N_2O$ at ~7.28 μm currently in progress with detection limits of 20 and 7 ppbv, respectively
- New target analytes such as OCS, $CH_2O$, HONO, $H_2O_2$, $C_2H_4$, $C_3H_8$, and $C_6H_6$
- Monitoring of broadband absorbers: acetone and $UF_6$
- Compact, robust sensitive and selective single frequency, mid-infrared sensor technology is capable of performing precise and accurate concentration measurements of trace gases relevant in environmental, biomedical, industrial monitoring and national security.

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## Merits of QEPAS based Trace Gas Detection

- Very small sensing module and sample volume (a few $mm^3$ to ~$2cm^3$)
- 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: $k_BT$ 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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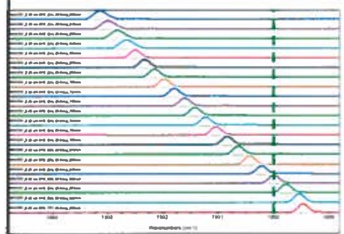
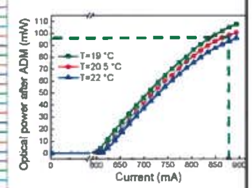
## Performance of a 5.26 μm CW HHL TEC DFB-QCL



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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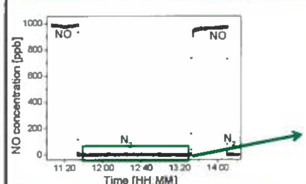
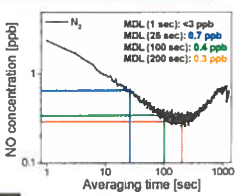
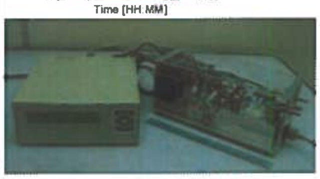
## Long Term Stability of QEPAS based Sensor for NO Concentration Measurements in Exhaled Breath



2012 QEPAS Mid-IR sensor technology

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

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## Future Directions and Outlook

- New target analytes such as OCS, $CH_2O$, HONO, $H_2O_2$, $C_2H_4$, $C_3H_8$, and $C_6H_6$
- Ultra-compact, low cost, robust sensors (e.g. $C_2H_6$, NO, CO……)
- Monitoring of broadband absorbers: acetone, TATP acetone peroxide, $UF_6$
- Optical power build-up cavity designs
- Development of trace gas sensor networks

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