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Mid-Infrared Laser based Gas Sensor Technologies for Environmental Monitoring, Medical Diagnostics, Industrial and Security Applications

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OUTLINE

TERA-MIR 2012 Workshop

Cesme, Izmir Turkey

Nov. 3-6, 2012

- 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 I 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 (e.g. 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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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)

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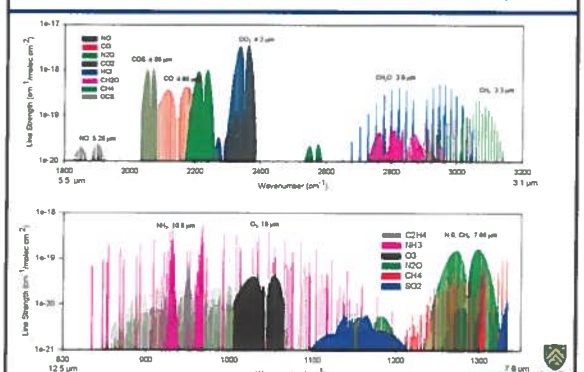
HITRAN Simulated Mid-Infrared Molecular Absorption Spectra



Source: HITRAN 2000 database

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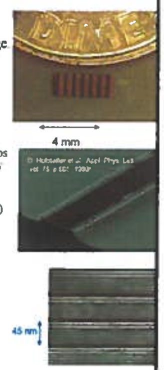
Mid-IR Source Requirements for Laser Spectroscopy

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, Packaging, Low Noise

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;



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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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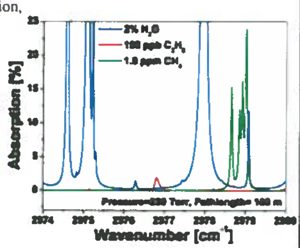
Motivation for Mid-infrared C_2H_6 Detection

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



HITRAN absorption spectra of C_2H_6, CH_4, and H_2O

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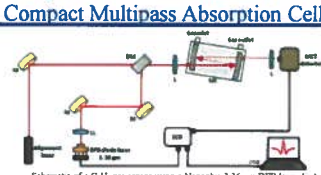
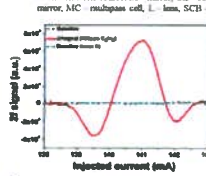
C_2H_6 Detection with a 3.36 µm DFB LD using a Novel Compact Multipass Absorption Cell and Control Electronics

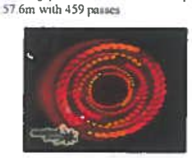


Schematic of a C_2H_6 gas sensor using a Nanoplus 3.36 µm DFB laser diode as an excitation source. M – mirror, CL – collimating lens, DM – dichroic mirror, MC – multipass cell, L – lens, SCB – sensor control board.

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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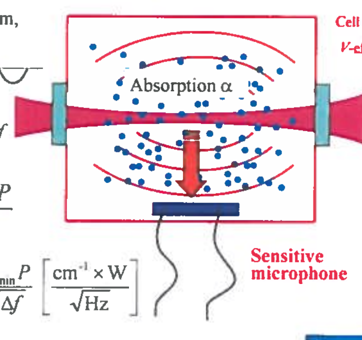
Conventional PAS

Laser beam, power *P*

Modulated (*P* or λ) at *f* or *f*/2



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

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

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

Sensitive microphone

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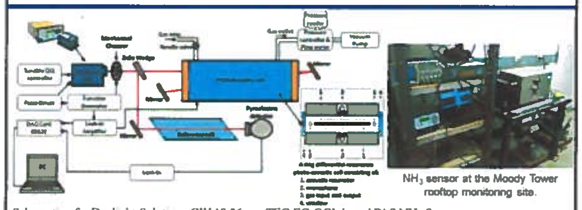
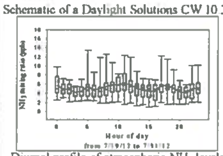
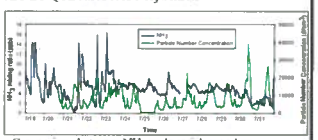
Atmospheric NH_3 Measurements using an EC-QCL PAS Sensor



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

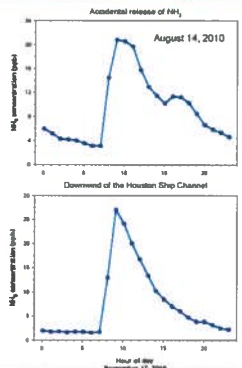


Diurnal profile of atmospheric NH_3 levels in Houston, TX.



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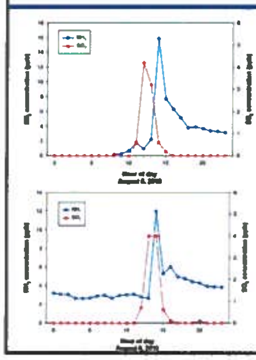
Sporadic increased NH_3 concentration levels related to emissions by the Parish electric power plant, TX



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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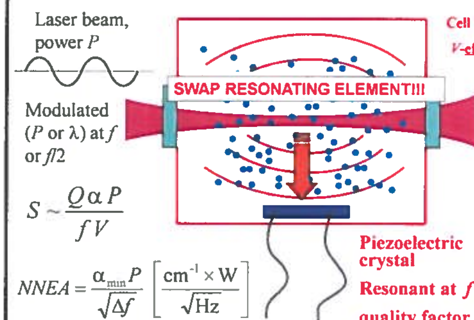
From Conventional PAS to QEPAS

Laser beam, power P

Modulated (P or λ) at f or $f/2$



Q>>1000

Cell is OPTIONAL!

V-effective volume

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

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

Piezoelectric crystal

Resonant at f

quality factor Q

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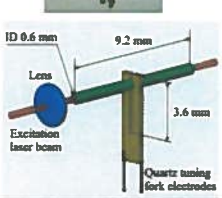
Quartz Tuning Fork as a Resonant Microphone for QEPAS



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 (~λ/4<l<λ/2 for sound at 32.8 kHz)
- SNR of QTF with mR tubes: ×30 (depending on gas composition and pressure)

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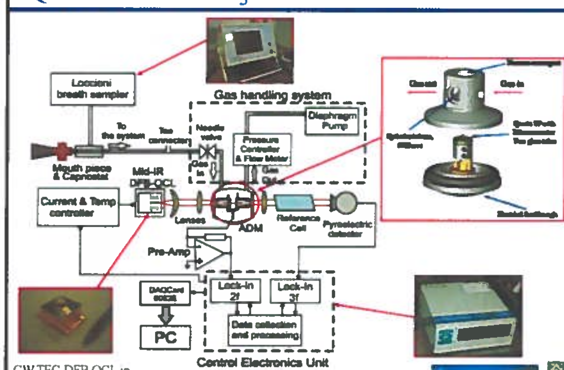
QEPAS based NH_3 Gas Sensor Architecture



CW TEC DFB QCL in HHL package (Hamamatsu)

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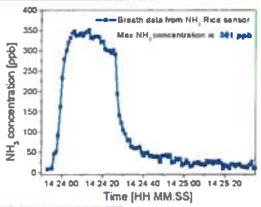
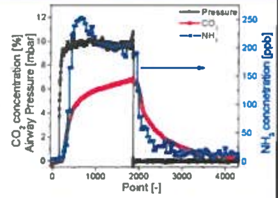
Real-time exhaled human NH_3 Breath Measurements





Airway pressure (black), CO_2 (red), and NH_3 (blue) profiles of a single breath exhalation lasting 40sec.

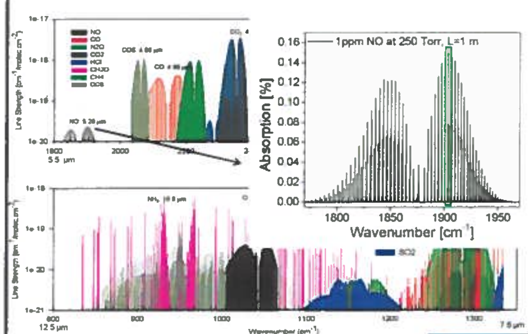
Successful testing of a 2nd generation breath ammonia monitor installed in a clinical environment.(Johns Hopkins, Baltimore, MD and St. Luke's Hospital, Bethlehem, PA)

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

Motivation for Nitric Oxide Detection

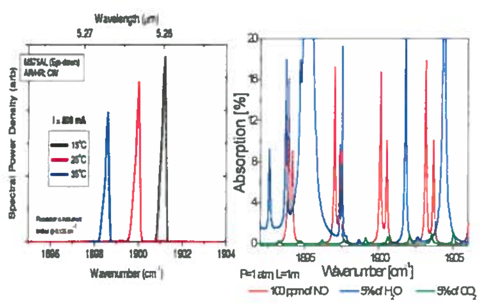
- Atmospheric Chemistry
- Environmental pollutant gas monitoring
  - NO_x monitoring from automobile exhaust and power plant emissions
  - Precursor of smog and acid rain
- Industrial process control
  - Formation of oxynitride gates in CMOS Devices
- NO in medicine and biology
  - Important signaling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



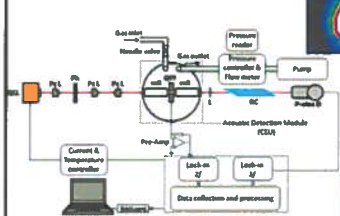
Source: HITRAN 2000 database

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

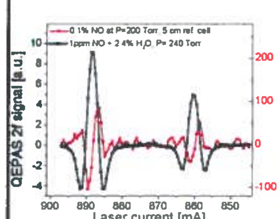


Schematic of a QCL QEPAS based Gas Sensor. M – mirror, PcL – plano-convex lens, Ph – pinhole, QTF – quartz tuning fork, mR – acoustic micro-resonator, RC – reference cell.

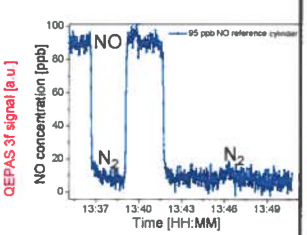
CW HHL TEC DFB-QCL package and IR camera image of the laser beam at 630 mA and 20.5 deg C through tubes after ADM

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.

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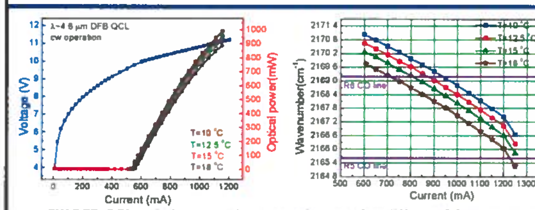
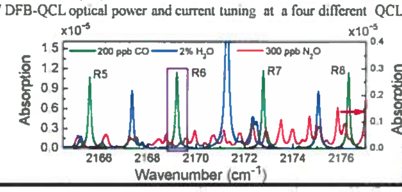
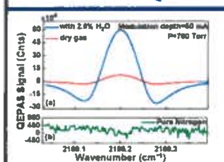
Performance of a NWU 4.6 μm high power CW TEC DFB QCL



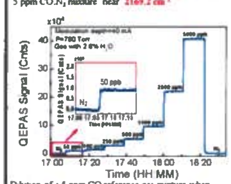
CW DFB-QCL optical power and current tuning at a four different QCL temperatures.



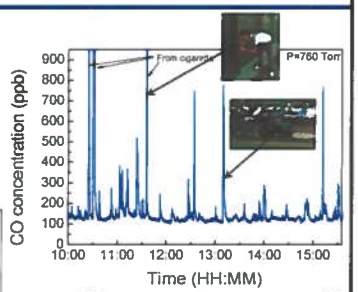
CW DFB-QCL based CO QEPAS Sensor Results



2f QEPAS signal for dry (red) and moisturized (blue) 5 ppm CO:N₂ 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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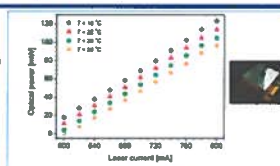
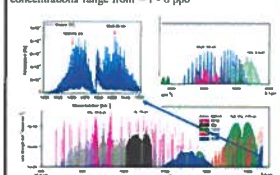
CW DFB-QCL based SO_2 QEPAS Results

Motivation for Sulfur Dioxide Detection

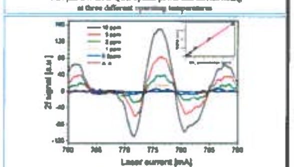
- Prominent air pollutant
- Emitted from coal fired power plants (~73%) and other industrial facilities (~20%)
- In atmosphere SO_2 converts to sulfuric acid → primary contributors to acid rain
- SO_2 reacts to form sulfate aerosols
- Primary SO_2 exposure for 1 hour is 75 ppb
- SO_2 exposure affects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



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



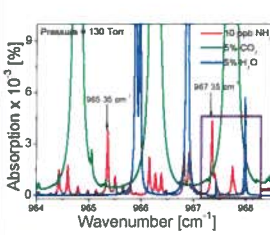
Molecular Absorption Spectra within two Mid-IR Atmospheric Windows



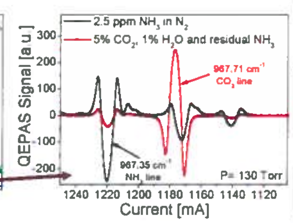
2f WMS QEPAS signals for different SO_2 concentrations when laser was tuned across 1380.9 cm⁻¹ line

Minimum detectable SO_2 concentration is:

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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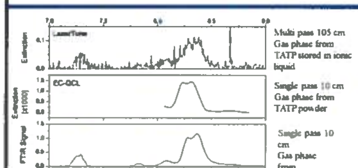
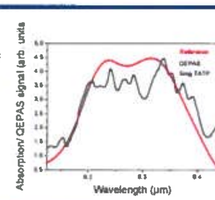
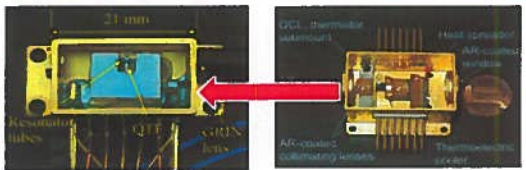
QEPAS Based TATP Detection





DIEHL BGT Defence   TU Clausthal   RICE

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

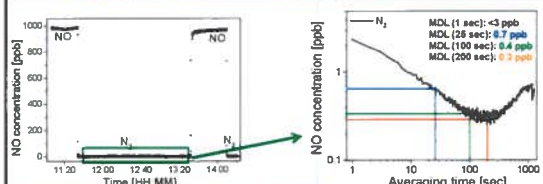
Merits of QEPAS based Trace Gas Detection

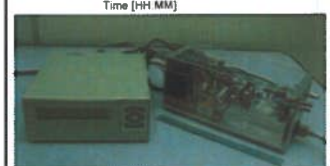
- Very small sensing module and sample volume (a few mm^3 to ~2cm^2)
- Extremely low dissipative losses
- Optical detector is not required
- Wide dynamic range
- Frequency and spatial selectivity of acoustic signals
- Rugged transducer – quartz monocrystal; can operate in a wide range of pressures and temperatures
- Immune to environmental acoustic noise, sensitivity is limited by the fundamental thermal TF noise: k_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

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)

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