Recent progress of mid-infrared compact, field deployable sensors recent advances and their real world applications in industry, environment and defense

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OUTLINE

• Novel Laser-Based Trace Gas Sensor Technology
  • Mid-IR TDLAS based on a Novel Multipass Gas Cell Design
  • Quartz Enhanced Photoooustic Spectroscopy (QEPAS)
  • Examples of four Mid-infrared Trace Gas Species
    • CH₄, CO₂, H₂O and H₂S
  • Future Directions of QEPAS-Based Trace Gas Sensor Technologies and Conclusions
    • I (intra-cavity) – QEPAS
    • New custom QTFs

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

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 Gas Cell (e.g., White, Herriot, Chemin, Aeries Technologies, and Circular Cylindrical Multipass Cell
  • Cavity Enhanced and Cavity Ringdown Spectroscopy
  • Open Path Monitoring (with retro-reflector or back scattering from topographic target): Standoff and Remote Detection
  • Fiber optic & Wave-guide Evanscent Wave Spectroscopy
• Spectroscopic Detection Schemes
  • Frequency or Wavelength Modulation
  • Balanced Detection
  • Zero-air Subtraction
  • Photoacoustic & Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)

Outline

• Novel Laser-Based Trace Gas Sensor Technology
  • Quartz Enhanced Photoooustic Spectroscopy (QEPAS)
  • Mid-infrared & THz spectral ranges
  • Recent near infrared QEPAS sensor technology
  • Sensor performance improvements resulting from custom QTFs

• Applications of QEPAS based sensor systems
  • Six mid-infrared Trace Gas Species
    • NO, NH₃, CO₂, CO, SF₆, H₂S
  • Two THz Trace Gas Species
    • H₂S and CH₃OH (Methanol)
  • Future Directions of QEPAS-Based Trace Gas Sensor Technologies and Conclusions
    • I (intra-cavity) – QEPAS

Mid-IR Source Requirements for Laser Spectroscopy

<table>
<thead>
<tr>
<th>REQUIREMENTS</th>
<th>IR LASER SOURCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity (% in ppb)</td>
<td>Optimum Wavelength and Power</td>
</tr>
<tr>
<td>Selectivity (Spectral Resolution) or Specificity</td>
<td>Stable Single Mode Operation and Narrow Linewidth</td>
</tr>
<tr>
<td>Multi-gas Components, Multiple Absorption Lines, and Broadband Absorbers</td>
<td>Mode-Hop-Free Wavelength Tunability</td>
</tr>
<tr>
<td>Directionality or Cavity Mode Matching</td>
<td>Beam Quality</td>
</tr>
<tr>
<td>Rapid Data Acquisition</td>
<td>Fast Time Response Time</td>
</tr>
<tr>
<td>Room Temperature Operation</td>
<td>High Wall Plug Efficiency, No Cryogenics or Cooling Water</td>
</tr>
<tr>
<td>Field Deployable in Harsh Environments</td>
<td>Compact and Robust</td>
</tr>
</tbody>
</table>
Key Characteristics of Mid-IR QCL & ICL Sources – April 2016

- **Band-structured engineered devices**: Emissivity wavelength is determined by layer thickness – MEM or MOCVD. QCLs span the 3 to 24 μm spectral range. 
- **Compact, reliable, stable, long-lived, and commercially available**.
- **Fabricated (FE) single mode (QCL) and multi-wavelength devices**

- **Wide spectral tunability range in mid-IR**
  - 1-3 cm⁻¹ tuning operation current control for DFB devices
  - 10-20 cm⁻¹ tuning temperature control for DFB devices
  - >100 cm⁻¹ tuning current and temperature control for QCLs DBR Arrays
  - >525 cm⁻¹ (at 214 K) tuning with external gain element and FETs

- **Output power, optical output power, and electrical bandwidth of QCL and ICL systems**

- **Narrow spectral linewidths**
  - CW: 0.1-3 MHz @ 10kHz with frequency stabilization

- **High pulsed and CW powers of OCLs & ICLs at RT temperature**
  - TDL QCL, pulsed peak power of ~200 W with 10% wall plug efficiency
  - CW QCL, power of ~5 W with 25% wall plug efficiency at 214 K
  - >100 mW CW DFB at TECOR I, wall plug efficiency: 23% at 6 μm
  - >200 mW QCL DFB at 6 μm

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**Motivation for Mid-infrared C₂H₅ Detection**

- Atmospheric chemistry and climate
- Fossil fuel and biofuel consumption
- Biomass burning
- Vegetation/soil
- Natural gas loss
- Application in medical breath analysis
- Asthma
- Schizophrenia
- Lung cancer
- Vitamin E deficiency

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**NOAA Monitoring & Sampling: Alert, Nunavut, Canada**

- General View on the Facility
- Latitude: 82.4650° North
- Longitude: 62.5099° West
- Elevation: 200.00 m

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**C₂H₅ Detection with a 3.36 μm CW DFB LD using a Novel Compact Multipass Absorption Cell and Control Electronics**

- Schematic diagram of the gas cell set-up
- CW DFB laser diode
- Multipass cell
- Photodetector
- Control electronics

- Minimum detectable C₂H₅ concentration: ~768 μm (1 minute time resolution)
- Distance between MOCs: 32.5 cm

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**From Conventional PAS to Quartz Enhanced PAS (QEPAS)**

- Laser beam, power \( P \)
- Modulated \((P' or \lambda) \) at \( f \) or \( f/2 \)
- \( S' = Q \alpha P \)
- \( \frac{NNEA}{\sqrt{A}} = \frac{\alpha P}{\sqrt{A}} \)

- **QEPAS** cell is **optional**!

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**Quartz Tuning Fork as a Resonant Microphone for QEPAS**

- **Unique Properties**
  - Extremely low internal losses
  - \( Q \sim 10^8 \) at 1 atm
  - \( Q \sim 10^6 \) in vacuum
  - Acoustic quadrupole geometry
  - Low sensitivity to external sound
  - Large dynamic range (~10⁹) – linear from thermal noise to breakdown deformation
  - 300 kHz noise: \( x \times 10^{-5} \) cm
  - Breakdown: \( x \times 10^{-3} \) cm
  - Wide temperature range: 1.6K to ~700K

- **Acoustic Micro-resonator (aRM)**
  - Optimum inner diameter: 0.6 mm, μQTF gap in 25-50 μm
  - Optimum MFP tubes must be ~4.4 mm long (~34±0.25) for sound at 32.3 kHz
  - SNR of QTF with μQTF tubes: 30 (depending on gas composition and pressure)
Motivation for Nitric Oxide Detection

- NO in medicine and biology
  - Important signaling molecule in physiological processes in humans and mammals (1998 Nobel Prize in Physiology/Medicine)
  - Treatment of asthma, chronic obstructive pulmonary disease (COPD) & lung rejection
- Environmental pollutant gas monitoring
  - Ozon depletion
  - Precursor of smog and acid rain
  - NO_x monitoring from automobile exhaust and power plant emissions
- Atmospheric Chemistry

HITRAN Simulated Mid-Infrared Molecular Absorption Spectra

Emission spectra of a 1900 cm\(^{-1}\) TEC DFB QCL and HITRAN simulated spectra of NO, H_2O & CO_2

Performance of a 5.26 μm CW HHL TEC DFB-QCL

CW TEC DFB QCL based QEPAS NO Gas Sensor

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

Minimum detectable NO concentration is:
- 3 ppbv (1σ; 1 x time resolution)
Motivation for NH₃ Detection

- Medical diagnostics
  - Kidney disease
  - Liver failure and Cirrhosis
  - Brain Cells dysfunction
  - Drowsiness and Coma
- Atmospheric chemistry
- Pollutant gases monitoring
- Monitoring NH₃ concentrations in the exhaust stream of NOₓ removal systems based on selective catalytic reduction (SCR) techniques associated with electric power plants
- Spacecraft related trace gas monitoring

Ammonia Leaks from ISS May 2013

Atmospheric NH₃ Measurements using an EC-QCL PAS Sensor

Schematic of a Delft SF Solutions 1034-nm CW VCSEL EC-QCLS based PAS 195 Sensor

Dermal profile of atmospheric NH₃ levels in Houston, TX

Comparison between NH₃ and particle number concentration time series from 10/12 to 6/12 2012

NH₃ Detection due to a Fire resulting from a Truck Collision

A chemical incident occurred at ~4 a.m. after two trucks collided on 5-9. Both trucks caught fire. [www.chem.com]

Estimated toxicity: NH₃ emissions from the Houston Ship Channel area is about 0.25 ton. Mellenet et al., 2001). Fed. Regist., U.S. EPA, 66(51)

Sporadic increase in NH₃ concentration levels related to emissions by the Parish Electric Power Plant, TX

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

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

Eagle Mountain Lake continuous ambient monitoring station (CAMS75), operated by Texas Commission on Environmental Quality (TCEQ)
Instrumentation available at CAMS 75 & TCEQ monitoring site

- **NH₃**, Thermo Electron Corp. (Gas Analyzer) (FTIR Spectroscopy)
- **NO**, Thermo Electron Corp. (GC/MS) (Gas Chromatography)
- **NO₂**, Thermo Electron Corp. (GC/MS) (Gas Chromatography)
- **CO**, Thermo Electron Corp. (GC/MS) (Gas Chromatography)
- **H₂S**, Thermo Electron Corp. (GC/MS) (Gas Chromatography)
- **SO₂**, Thermo Electron Corp. (GC/MS) (Gas Chromatography)
- **H₂O**, Thermo Electron Corp. (GC/MS) (Gas Chromatography)
- **VOCs**, Thermo Electron Corp. (GC/MS) (Gas Chromatography)
- **PM₁₀**, Thermo Electron Corp. (GC/MS) (Gas Chromatography)
- **PM₂.₅**, Thermo Electron Corp. (GC/MS) (Gas Chromatography)

**NH₃** Source Attribution & Temperature Variations

- 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%; heavy duty vehicles: 4.4%)
- Livestock might account for approximately 66.4% of total **NH₃** emissions
- Increased contribution from industry (29.9%)

Motivation for Carbon Monoxide Detection

- **CO** in Medicine and Biology
  - Hypertension and abnormality in heme metabolism
- **Public Health**
  - Extremely dangerous to human health even at low concentrations. Therefore CO must be carefully monitored at low concentration levels (<35 ppm).
- **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).

Performance of a 4.61μm high power CW TEC DFB QCL

- CW DFB-QCL based CO QEPAS Sensor Results
  - Minimum detectable CO concentration: -2 ppb (1σ)
  - Integration time: 1 sec
  - Normalized Noise Equivalent Absorption: NREA = 7.5x10⁻⁶ cm⁻¹[W(Hz)⁻¹/²]
Motivation for NH₃ Detection

- Medical diagnostics
  - Kidney disease
  - Liver failure and Cirrhosis
  - Brain Cells dysfunction
  - Drowsiness and Coma
- Atmospheric chemistry
- Pollutant gases monitoring
- Monitoring NH₃ concentrations in the exhaust stream of NOx removal systems based on selective catalytic reduction (SCR) techniques associated with electric power plants
- Spacecraft related trace gas monitoring

Important Breath Molecules

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Formula</th>
<th>Biological/Pathological Indication</th>
<th>Center Wavenumber [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>CH₂O</td>
<td>Carcinogenic lung cancer (145-185 nm)</td>
<td>9.7</td>
</tr>
<tr>
<td>Persistent</td>
<td>NO</td>
<td>Nitric oxide synthase, inflamatory and immune responses (8-18 µm)</td>
<td>9.2</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td>H₂O₂</td>
<td>Artery inflammation, oxidative stress (4-6 µm)</td>
<td>7.4</td>
</tr>
<tr>
<td>Ethylene</td>
<td>C₂H₄</td>
<td>Oxidative stress, cancer</td>
<td>10.0</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>C₂H₄O</td>
<td>Diabetes mellitus</td>
<td>7.5</td>
</tr>
</tbody>
</table>

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

- Simulated HITRAN high resolution spectra at 130 Torr indicating two NH₃ absorption lines of interest
- No overlap between NH₃ and CO₂ absorption lines was observed for the selected 967.35 cm⁻¹ NH₃ absorption line in the ν₃ R-bands

Real-time exhaled human NH₃ Breath Measurements

- Airway pressure, CO₂, CO, and NH₃ (mean profiles of a single breath exhales lasting 45s)
- Successful testing of a 2nd generation breath analyser device installed in a clinical environment (Johns Hopkins, Baltimore, MD and St. Luke's Hospital, Philadelphia, PA)
- Minimum detectable concentration of NH₃ in 6 µM (at 967.35 cm⁻¹: 4 s time resolution)

Motivation for SF₆ Detection

Industrial and semiconductor processes
- SF₆ is used in semiconductor manufacturing for plasma etching of metal silicides, nitrides and oxides
- SF₆ is an insulating material used as a dielectric in electrical transformers
- SF₆ is a tracer gas for leak detection

Line Selection Criteria for QEPAS:
1. High absorption strength
2. Well resolved spectral absorption features
3. Selected line far from interfering gases such as CO₂ and H₂O

Due to the fast vibrational-translation relaxation rate of SF₆, it is possible to work at low pressures (~100 Torr) and take advantage from the typically high quality factor Q of the QTF (~20,000) at these conditions

THz absorption line selection for SF₆

- Selected line
  - Working Conditions
    - λₓₒ = 948.66 cm⁻¹
    - V = 26 - 45 V
    - t = 5 mms
    - t (lock-in) = 100 ms
    - t (max view) = 300 ms

- Main absorption lines for SF₆ in the range 947-950 cm⁻¹ corresponding to the ν₃ band (from the HITRAN database)
**QEPAS SF₆ Sensor Platform**

- Laser emission: 10.54 μm
- Power: 40 mW
- CW operation @ RT
- Hollow Fiber
- QCL

**SF₆ QEPAS sensor performance assessment and linearity**

- Allan Plot
- NNEA = 6.7x10⁻¹¹ cm³/W·(Hz)⁻¹/₂

**Motivation for Sulfur Dioxide Detection**

- Prominent air pollutant
- Annual SO₂ concentrations range from ~1 - 6 ppb
- SO₂ is emitted from coal fired power plants (~73%) and other industrial facilities (~20%)
- In atmosphere, SO₂ converts to sulfuric acid and is a primary contributor to acid rain
- SO₂ reacts to form sulfate aerosols
- SO₂ exposure affects lungs and causes breathing difficulties

**QEPAS based NH₃ Gas Sensor Architecture**

- Control Electronics Unit (CEU)
- CW-TEC DFB QCL in ASIC, package (Harmanation)
- Gas handling system
- Cold mirror beam sampler
- Gas selection through gas handling system

**SO₂ Line Selection for a 7.24 μm CW RT DFB-QCL**

- Estimated HITRAN absorption spectra of 10 ppm SO₂ and 1% water vapor (P=10 Torr, P=20% R, 1.1 atm).

**QEPAS Performance for Trace Gas Species (April 2016)**

<table>
<thead>
<tr>
<th>Species</th>
<th>Sensitivity</th>
<th>Precision</th>
<th>NNEA</th>
<th>Parts Per Trillion</th>
<th>Parts Per Billion</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>1000 PPM</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>1000</td>
</tr>
<tr>
<td>CH₄</td>
<td>2000 PPM</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>2000</td>
</tr>
<tr>
<td>NO</td>
<td>500 PPM</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>500</td>
</tr>
<tr>
<td>NO₂</td>
<td>200 PPM</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>200</td>
</tr>
<tr>
<td>SO₂</td>
<td>50 PPM</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>50</td>
</tr>
</tbody>
</table>

For comparison: conventional PAS 2.2 *10⁻⁶ cm³/W·(Hz)⁻¹/₂ for NH₃.
Oil in Water Detection

- Produced water
  - legislation: < 15 ppm
- Injection water
  - economic reasons
  - target value: < 5 ppm or lower

A North Dakota Oil Facility in 2016.

Typical Oil & Gas Production Site near Houston, TX

This figure depicts the result of a sequence of four fracking injections obtained by directional drilling which creates horizontal production in the target strata.

A proposed DOE-ARPA-E methane detection project at 3.327 μm will start in 2016 at various Texas locations wellpad sites (typically 10 m x 10 m with 0.1 m spatial resolution).

CH₄ and N₂O Measurements performed with a DFB-QCL based QEPAS Sensor installed in a mobile laboratory operated by Aerodyne, Inc (Sept 7, 2013)

CH₄ mixing ratios

Comparison of proposed Rice CH₄ Sensor System and current commercially available CH₄ Platforms

- Size
- L/R
- Power
- Dim
- Weight
- Cost

<table>
<thead>
<tr>
<th>Name</th>
<th>L/R</th>
<th>Power</th>
<th>Dim</th>
<th>Weight</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice</td>
<td>48×50×70</td>
<td>200W</td>
<td>200W</td>
<td>40 kg</td>
<td>40-50K USD</td>
</tr>
<tr>
<td>ABB-LGR I</td>
<td>48×50×70</td>
<td>200W</td>
<td>200W</td>
<td>40 kg</td>
<td>40-50K USD</td>
</tr>
<tr>
<td>ABB-LGR II</td>
<td>48×50×70</td>
<td>200W</td>
<td>200W</td>
<td>40 kg</td>
<td>40-50K USD</td>
</tr>
<tr>
<td>Aerodyne</td>
<td>48×50×70</td>
<td>200W</td>
<td>200W</td>
<td>40 kg</td>
<td>40-50K USD</td>
</tr>
</tbody>
</table>
Motivation for Carbon Dioxide 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).
- CO in Medicine and Biology
- Indoor Air Quality
- Beverage Carbonation
- Industrial process monitoring
  - Hypertension and abnormality in heme metabolism
  - CO in Medicine and Biology
  - Hypertension and abnormality in heme metabolism

Schematic of single pass QEPAS CO₂ Detection

Optical power build up cavity can provide:
- Raman shift in the cavity
- QCL laser
- Optical power at 2 mW
- Gas absorption in the cavity
- Wavelength modulation approach and Z direction

Development of a novel I-QEPAS based sensor design: Initial performance evaluation of LOEPAS based on CO₂ detection

At the same conditions of pressure and optical power:
- Optical power build up cavity can provide:
  - Same as cavity at high reflecting mirrors, 30% R

Optical properties of bow-tie cavity-I

- Voltage ramp + modulation dither applied to QCL
- Cavity length: 174 nm
- FSR = c/λ = 1.725 GHz
- ΔV(FWHM) = 1.15 kHz
- F = FSR/ΔV = 1505
- G = 1/ΔV = 480
- Mode matching 50%
- Intracavity optical power enhancement factor = 240

Optical properties of bow-tie cavity-II

- Voltage ramp + modulation dither applied to QCL
- under vacuum
- locking loop ON
- The close-coupled loop works on the PTZ tuning the cavity length
- It was not fast enough to follow the fast dither at f/2 = 16 kHz
- It maintains the optical cavity resonant with the laser frequency at the center of the fast dither
- Mechanical chopper at f₀

I-QEPAS Performance in locked mode and long term stability

- Optimal sensitivity at high concentration
- Linearity
- NEC ~ 300 ppm
- QEPAS lock-in time constant
- NNEA ~ 3.2 x 10⁻⁴ cm⁻³ W(Hz)⁻¹/₂

A factor >20 higher than I-QEPAS
- Identically to the intracavity optical power enhancement factor (240)

Further Development of a novel I-QEAPAS based Sensor Design

Computer Visualization of an Intra-Cavity Quartz Enhanced Photoacoustic Spectroscopy Optical Resonator

- Tess: cavity resonator consists of 4 high reflectivity mirrors, R=99.9%
- Electronic Control Loop + PZT driver for locking of the cavity resonant frequency to the frequency of the laser excitation source

Comparison of I-QEAPAS with Other Trace Gas Sensing Techniques

- NNEA (cm⁻³·W·Hz⁻¹)
- Optical pathlength (m)

Custom fabricated QTFs with new Shapes and Dimensions optimized for mid-IR and THz QEAPAS

- Standard photolithographic techniques were used to etch custom QTFs. Chromium/gold layer was deposited on both sides of the custom QTFs for electrical contacts.
- New generation of custom QTFs behave similar to "standard" QTFs in terms of their vibrational mode(s)

Comparison between fundamental and the first overtone QTF flexural modes for QTF#5 - Electrical Characterization

- Golden coated electrode pattern was optimized for the fundamental vibrational mode, resulting in an enhanced piezo-charge collection for the 1st overtone flexural mode.

Comparison between fundamental and first overtone QTF flexural modes for QTF#5 - QEAPAS Characterization

- 1st detection of a fixed H₂O concentration

- Comparison between the 1st overtone (180Ghz) and fundamental (30Ghz) flexural modes of the B-C QTF @ 75Torr:
  - The signal for the 3rd flexural mode is ~5 times higher.
  - The two vibrational modes differ in the stress profile.
  - A larger charge is generated for the high order modes.

In-plane view of designs of three types of tuning forks realized in this work. The size scale is shown on the right bottom.
Why QEPAS sensors have not been developed in the THz range to-date?

Standard QTFs are characterized by a very small sensitive volume ($\sim 0.3 \times 0.3 \times 3$ mm$^3$).

In QEPAS experiments, it is critical to avoid laser illumination of the QTF since the radiation blocked by the QTF prongs results in an undesirable non-zero background which is associated with a shifting fringe-like interference pattern.

The narrow space (300 $\mu$m) between the QTF prongs is comparable with the wavelength of THz sources, which has so far represented the main limitation preventing the use of QEPAS system in THz range.

Hence, larger sized QTFs are required for operating in the THz regime.

Schematic of the QEPAS trace gas sensor using a THz Quantum Cascade Laser (THz QCL) as the excitation source

Two-dimensional beam profile of the THz-QCL acquired by means of an IR pyrocamera after mirror PM#3 (see Fig. 2) when the beam is focused out the N-QTF

(a) or between the two prongs (b). Both beam profiles are shown together with an illustration representing the position of the focused THz beam (red spot) with respect the N-QTF.

NNEA results obtained with QEPAS sensor for the gas species reported versus employed laser wavelength, in the UV-Vis, near-IR, mid-IR and THz spectral ranges

The red symbol (*) marks the result of present work.

THz QEPAS H$_2$S Sensor employing QTF#5

THz QEPAS H$_2$S Sensor Performance Assessment and Linearity

No signal changes with a few % of H$_2$O

Absorption coefficient normalized to a detection bandwidth (0.00566 Hz) and an optical power (240 $\mu$W);

NNEA = 4.05x10^{-10} cm$^{-1}$ W/(Hz)$^{1/2}$
**Summary, Conclusions and Future Work**

- Development of robust, compact, sensitive, selective mid-IR trace gas sensor technology based on RT, CW high performance DFB ICLs & QCLs for environmental monitoring and medical diagnostics.
- ICLs and QCLs were used in TDLAS and PAS/QEPAS based sensor platforms.
- Performance evaluation of seven target trace gas species were reported. The minimum detection limit (MDL) with a 1 sec sampling time were:
  - CO: MDL of 24 ppbv at -4.35 μm, CH₂: MDL of 15 ppbv at -4.38 μm, NO: MDL of 6 ppbv at -7.28 μm.
- I-QEPAS demonstration resulted in a factor of 240 increase in detection sensitivity.
  - CO₂: MDL of 300 ppbv at 50 nmol was achieved for a 20 sec integration time.
- THz-QEPAS H₂S sensing demonstration using a custom QTF resulted in a NNEA of 10⁻⁸ cm³(STP)/mL. The MDL was 13 ppbv for a 30 sec integration time.
- Novel implementation of QTF 1st overtone flexural mode for QEPAS sensing.
- Development of “active” I-QEPAS system for CO and NO detection in the ppt range.
- Future development of trace gas sensors for monitoring of broadband absorbers acetone (C₂H₅O), propane (C₃H₈), benzene (C₆H₆), acetone peroxide-TATP (C₄H₅O₆).
- Future development of mid-IR electrically pumped interband cascade optical frequency combs (QECs) with JPL, Pasadena, CA, USA. 

**Comparison of three QEPAS based sensors for H₂S detection operating in the near-IR, mid-IR and THz spectral ranges.**
Companies Offering Infrared Laser Based Sensors

- Thorlabs, Newton, NJ
- Daylight Solutions Inc., San Diego, CA
- Neomonitor, Loerenkog, Norway
- Siemens, Goteborg, Sweden
- Focused Photonics, Hangzhou, China
- Yokogawa USA, Houston, Texas
- Cascade Technologies, Sterling, UK
- Aerodyne Research Inc., Billerica, MA
- Physics Sciences Inc., Andover, MA
- California Analytical Instruments Inc., Orange, CA
- Gasera Ltd., Turku, Finland
- Vista Photonics Inc., Santa Fe, NM
- Southwest Sciences Inc., Santa Fe, NM
- Spectra Sensors, Houston, TX
- Boreal Laser Inc., Spruce Grove, Alberta, Canada

**CW DFB-QCL based SO₂ QEPAS Results**

Motivation for Sulfur Dioxide Detection

- Present in coal fired power plants (70%) and other industrial facilities (20%)
- Its atmosphere SO₂ converts to sulfuric acid in primary constituents in acid rain
- SO₂ reacts to form sulfate aerosols
- Primary SO₂ exposure for 1 hour is 30 μg
- SO₂ exposure affects lungs and causes breathing difficulties
- Currently, reported normal average atmospheric SO₂ concentrations range from 1-6 ppb

![Graphs showing CW DFB-QCL absorption and response time for different operating temperatures.](image)

*Graphs showing CW DFB-QCL absorption and response time for different operating temperatures.*