**Mid-Infrared Quantum Cascade Laser based Trace Gas Sensor Technologies: Recent Advances and Applications**


Rice University, Houston, TX.

* Motivation: Wide Range of Chemical Sensing
* Fundamentals of Laser Absorption Spectroscopy
* New Mid-IR Sensing Technologies
* Laser Absorption Spectroscopy of UF₆ at 7.8, 12.2 and 16μm
* NH₃ Sensor Technology for Urban Environmental Monitoring at 10.3μm
* Future Directions and Conclusions

Work supported by NSF ERC, NASA, DOE, and the Robert Welch Foundation

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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
  - 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 Biomedical and the Life Sciences
- Technologies for Law Enforcement and National Security
- Fundamental Science and Photochemistry

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**Methods for Trace Gas Detection**

- Mass Spectroscopy
- Gas Chromatography

**Non-Optical**

- Chemical
- Electro Chemical
- Chemiluminescence

**Optical**

- Back Body Sources
- Fourier Transform
- NDIR Analyzer
- Coherent Sources
- Microwave Spectroscopy
- Laser Spectroscopy

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**Sensitivity Enhancement Techniques for Laser Spectroscopy**

- Optimum Molecular Absorbing Transition
  - Overtone or Combination Bands (NIR)
  - Fundamental Absorption Bands (MID-IR)
- Long Optical Pathlength
  - Multipass Absorption Cell (White, Herriot, Chemin)
  - Cavity Ringdown and Cavity Enhanced Spectroscopy
  - Open Path Monitoring (with & without retro-reflector): Standoff and Remote Detection
  - Fiberoptic Evanescent Wave Spectroscopy
- Spectroscopic Detection Schemes
  - Frequency or Wavelength Modulation
  - Balanced Detection
  - Zero-air Subtraction
  - Photoacoustic Spectroscopy (PAS and QEPAS)
  - Laser Induced Breakdown Spectroscopy (LIBS)

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**Simulated Mid-Infrared Molecular Absorption Spectra**

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**CW IR Source Requirements for Laser Spectroscopy**

<table>
<thead>
<tr>
<th>REQUIREMENTS</th>
<th>IR LASER SOURCE</th>
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<tbody>
<tr>
<td>Sensitivity (% relative to ppt)</td>
<td>Optimum Wavelength, Power</td>
</tr>
<tr>
<td>Selectivity (Spectral Resolution)</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</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 &amp; Robust</td>
</tr>
</tbody>
</table>
**UF₆ mid-infrared absorption bands**

Absorption spectrum of UF₆ is broadband with unresolved rotational-vibrational spectral covering several tens of wavenumbers (cm⁻¹).


**Key Characteristics of mid-IR QCL and ICL Sources – Jan ’11**

- **Band – structure engineered devices**
  - Emission wavelength determined by laser dichroic – MBE or MOCVD.
  - Mid-infrared QCLs operate from 3 to 21 μm (AM840/GaSb).
  - Compact, reliable, stable, long lifetime, and commercial availability.
  - 'Piezo' QCL with single mode (21 μm) and multi-wavelength devices.

- **Widescalar tuning ranges in the mid-IR**
  - 2.5 - 3.5 μm for QC laser (e.g. InAs/GaSb DFB) and GaSb based QC lasers.
  - 1.5 - 10 μm using injection current control for DFB devices.
  - 0.5 - 20 μm using temperature control for DFB devices.
  - 10 - 30 μm using external etalon cavity doped PDAs with injection current and temperature control, and QCL, DFB Array.

- **Narrow spectral linewidths**
  - CW, 0.1 - 2 MHz & <100 kHz with frequency stabilization (0.0005 cm⁻¹).
  - Pulse ~ 200 MHz.

- **High output and cw powers of QCLs at 3.2 μm**
  - CW, 50 μW, TEC CW DFB at 3 μm.
  - ~600 μW (CW PDAs) at RT, with wall plug efficiency of ~17% at 3.6 μm.

**Motivation for High Wall Plug Efficiency**

- High WPE essential for applications limited by:
  - Electrical power (Battery Capacity)
  - Thermal Control
  - Size
  - Weight
- CW, RT QC laser state of the art:
  - 2006: ~1%
  - 2008: ~12%
  - 2016: ~17%

**Strategies for Improving WPE**

- **Voltage Efficiency:**
  - Lower voltage detect
  - Reduce contact resistance

- **Extraction Efficiency:**
  - Implement high reflection (HR) and anti-reflection (AR) coatings
  - Employ low loss waveguides
  - Optimize cavity length

- **Internal Efficiency:**
  - Reduce thermoelectric emission
  - Improve heat removal from active core
  - Optimize injector barriers

- **Current Efficiency:**
  - Design high gain, low loss structures
  - Lower threshold currents

**Resonant Photoacoustic Spectroscopy (PAS)**

- **Conventional PAS:** Resonance in the gas cell
- Modulated radiation
- (I or λ)

- **DEPAS:** Resonance in the microphone
  - Signal proportional to the absorbed power, hence to the (trace) gas concentration
  - 2002 (Rice LSC)

**Traditional and Quartz Enhanced Photoacoustic Spectroscopy**
Quartz Tuning Fork as a Resonant Microphone

**Unique properties**
- Extremely low internal losses
- Q~10^8 at 1 mm
- Q~100,000 in vacuum
- Acoustic quadrupole geometry
- Low sensitivity to external sound
- Large dynamic range (>10^5) - linear from thermal noise to breakdown deformation
- 350K, normal x~10^-7 cm
- Breakdown: ~10^-7 cm
- Wide temperature range: from 1.3K (superfluid helium) to ~700K
- Low cost (<$1)

**Other parameters**
- Resonant frequency ~32.8 kHz
- Force constant ~25000 N/m
- Electromechanical coefficient ~7.30 x 10^-11 cm

QEPAS spectrophone (QTF & Micro-resonator)

**Micro-resonator (mR) tubes**
- Must be close to QTF but not touch QTF (25-50 µm gaps).
- Optimum inner diameter: 0.6 mm
- Optimum micro-resonator tubes are 4.4 mm long (~λ/4<λ/2 for sound at 32.8 kHz)
- Maximum SNR of QTF with mR tubes: ×30 (depending on gas composition and pressure)

Comparison of State-of-the-Art CPAS & QEPAS Detection Modules

<table>
<thead>
<tr>
<th>CPAS</th>
<th>QEPAS</th>
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<tbody>
<tr>
<td>Acoustic resonance, 2 MHz</td>
<td>Micro-resonator, 3 GHz</td>
</tr>
<tr>
<td>Gas inlet/outlet, 4 Windows</td>
<td>Gas inlet/outlet, 4 Windows</td>
</tr>
<tr>
<td>1.56 mm, 656.5 mm</td>
<td>2.5 mm, 656.5 mm</td>
</tr>
<tr>
<td>Resonator: 4500 mm</td>
<td>Resonator: 4500 mm</td>
</tr>
<tr>
<td>Optical path: 90 mm</td>
<td>Optical path: 90 mm</td>
</tr>
<tr>
<td>f=1790 Hz in N_2</td>
<td>f=1790 Hz in N_2</td>
</tr>
<tr>
<td>Q=49 in N_2</td>
<td>Q=49 in N_2</td>
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</tbody>
</table>

Comparison of CPAS vs. QEPAS: C_2H_2 and CO_2 Sensitivity Comparison

<table>
<thead>
<tr>
<th>C_2H_2: absorption line at 6529.3 cm^-1, 10 ppmv</th>
<th>CO_2: 6361.25 cm^-1, 100%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 ppmv (C_2H_2), ln N_2</td>
</tr>
<tr>
<td>QEPAS</td>
<td>CPAS</td>
</tr>
<tr>
<td>Signal, µV</td>
<td>6280</td>
</tr>
<tr>
<td>Noise, µV</td>
<td>53</td>
</tr>
<tr>
<td>SNR</td>
<td>119</td>
</tr>
<tr>
<td>Laser Power, mW</td>
<td>37.2</td>
</tr>
<tr>
<td>NNEA, cm^-1/W/Hz</td>
<td>4.1 x 10^-10</td>
</tr>
</tbody>
</table>

NNEA: normalized noise-equivalent absorption coefficient

| QEPAS Performance for 15 Trace Gas Species (Jan. '11) |

**Merits of QEPAS based Trace Gas Detection**
- Very small sensing module and sample volume (a few mm^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_B T energy in the TF symmetric mode
- Absence of low-frequency noise: SNR scales as 1/τ, up to c/3 hours as experimentally verified

**QEPAS: some technical challenges**
- Responsivity depends on the speed of sound and molecular energy transfer processes
- Sensitivity scales with laser power
- Effect of H_2O
- Cross-sensitivity issues
- Alignment costs

**QEPAS**
Groups working on Quartz Enhanced Photoacoustic Spectroscopy

- Rice University
- UMBC, Baltimore, MD
- Savannah River National Laboratory, Aiken, SC
- Pacific Northwest National Laboratory, Richland, WA
- NASA-JSC, Houston, TX
- JPL, Pasadena, CA
- Woods Hole Oceanographic Institution, MA
- United States Naval Academy, Annapolis, MD
- Daylight Solutions Inc., San Diego, CA
- NKT Flexibles, Copenhagen, Denmark
- University of Bari, Italy
- TU Clausthal, Germany
- TU Vienna, Austria
- University of Montpellier, France
- Institute of Spectroscopy, Troitsk, Russia
- University of Littoral, Dunkerque, France
- Ahsan Institute of Optics and Fine Mechanics, Hefei, China
- Zhejiang University, Hangzhou, China

Recent Applications of Mid-Infrared Laser based Trace Gas Sensors

UF₆ mid-infrared Absorption Bands

Absorption spectrum of UF₆ is broadband with unresolved rotational-vibrational spectral features spanning several tens of wavenumbers (cm⁻¹).

Absorption spectrum of gas mixtures under investigation and observed spectral features (cm⁻¹).

Opto-mechanical Platform for Evaluation of CW TEC FP QCL Gain Chips

FP-QCL in quasi-Littrow configuration:
- Feedback to the front facet (diffraction grating)
- Back facet radiation analyzed by FTIR

Design schematic of FP-QCL optical mechanical evaluation platform

Laser parameters that are investigated:
- Wavelength tunability
- Optical power
- Threshold value

Spectrum and Tuning Range of a 7.74 μm CW TEC FP-QCL @ -20°C

Resistors & R = 540Ω
Threshold with grating I_th = 543mA
Threshold without grating I_th = 568mA

HR coated CW 7.74 μm FP-QCL in EC-configuration @ -30°C

 Resistance @ RT is R = 560Ω
Threshold with grating I_th = 301.5mA
Threshold without grating I_th = 350mA
Simulant molecules for UF₆

Single mode spectral frequency tuning range of the tested FP-QCLs cover the ν₁ + ν₃ UF₆ combination band centered at ~1291 cm⁻¹ (7.745 µm) and several methane (CH₄) and acetylene (C₂H₂) absorption lines.

Preliminary Results of LAS for CH₄ detection

A 7.74 µm DFB-QCL for AM-QEPAS detection technique

Laser Spectra of a pulsed 14 µm QCL

Long-wavelength Quantum Cascade lasers
Pulsed Light-Current-Voltage (LIV) Characteristics

L = 2.8 mm long, 38μm wide, 100 ns pulse width, ~335 mW avg. power

Threshold Current Density of a 14 μm QCL

38μm wide, 2.8 mm long laser with HR coated back facet

Electroluminescence Spectrum of a 16 μm QC Laser Structure

Preliminary results: Wavelength shifted to 16 μm (625 cm⁻¹)

Motivation for NH₃ Detection

- Monitoring of gas separation processes
- Detection of ammonium-nitrate explosives
- Spacecraft related gas monitoring
- Monitoring NH₃ concentrations in the exhaust stream of NOₓ 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)

Infrared NH₃ Absorption Spectra

Mid-IR EC-QCL based AM-PAS Sensor Architecture for Atmospheric NH₃ Detection
PAS based NH₃ Measurements with a 10.34μm DLS EC-QCL Spectroscopic Source

NH₃ Sensor Deployment at the 60 m high Moody Tower Rooftop Site (U of H campus)

Data of Atmospheric NH₃ Concentration Levels for Houston

NH₃ detection due to fire resulting from truck collision

Increased NH₃ Concentrations related to Traffic Emissions during Houston, TX Rush Hour

Sporadic increased NH₃ Concentration Levels related to Emissions by Parish Electric Power Plant, TX
Outlook of future optical Chemical Sensor Technology

- Improvements of mid-infrared QCL and ICLs in areas such as wall plug efficiency, temperature performance, beam shape, packaging and price reduction
- Improvements of the existing sensing technologies (LAS, CES, QEPAS, EWS) using novel, thermoelectrically cooled, cw, distributed feedback (DFB), high power and broadly wavelength tunable mid-IR QCLs and ICLs.
- New applications enabled by novel broadly wavelength tunable and ultra-compact single frequency quantum cascade lasers (especially sensitive concentration measurements of broadband absorbers, in particular, UF₆, VOCs and HCs)

Performance evaluation of UF₆ Detection with a 16 μm LIDAR using Reflection from a topographic Target

**Ideal conditions:**
- Light source: 100 mW CW RT DFB QCL at 16 μm (625 cm⁻¹)
- Collection mirror: 10" in diameter
- Photodetector: Hamamatsu MCT photovoltaic detector, tuned to the peak sensitivity at 16 μm, Detector area: 1.3 × 1.3 mm², D^* = 10⁷ cm Hz^0.5 W⁻¹, NEP = 10⁻⁷ W Hz⁻¹.
- Distance between source/receiver to target: 200 m
- Diffuse reflectivity from target: <10%
- Neglecting scattering and background absorption.
- Neglecting turbulence

**Potential problems:**
- Background absorption of water, CO₂, and O₂
- Concentration of UF₆ in air is unknown. It can be low due to the reaction of UF₆ with water. This will require a special investigation.
- Differential reflectivity of natural targets at 16 μm is unknown. May impact detectivity. Investigation is required.

Properties of UF₆ absorption band at 16 μm

- Very large absorption coefficients, peak fractional absorption k-L for a roundtrip path L = 400 m and a 1 ppbv concentration is 3.5 × 10⁻³
- Absorption feature is too broad for wavelength modulation spectroscopy. An External Cavity QCL with a tuning range of ~30 cm⁻¹ will be needed.
- High value of absorption permits using a compact QEPAS sensor


Potential LIDAR System Layout and Performance

![Diagram of LIDAR system layout](image)

The power T_p, transmitted by a target (DLIDAR configuration)

\[ T_p = T_i \times e^{-\alpha d} \times \frac{A_0}{A} \times \frac{1}{\eta} \times \frac{1}{\sigma} \times \frac{1}{\Delta \lambda} \]

**Parameters:**
- Transmitter laser power: \( P_i \)
- Target absorber: \( \Delta \lambda \)
- Detector area: \( A_0 \)
- System optical efficiency: \( \eta \)
- Attenuation due toabsciss and absorption: \( \alpha \)
- Distance to target: \( d \)
- \( C \) is the analytic absorption coefficient and concentration

**Results:**
- Received power \( T_p \): 20 mW
- With detector NEP of 10 ppb V Hz⁻0.5
- Noise equivalent UF₆ concentration: 140 ppb V Hz⁻0.5

**16 μm (625 cm⁻¹) UF₆ LIDAR Summary**

- LIDAR performance assuming ideal conditions and a QCL power of 100 mW allows a detection of 140 ppbv of UF₆ at a distance of 200 m from the target
- Absorption bands of atmospheric water and carbon dioxide overlap strongly with the 16 μm absorption band of UF₆ at 16 μm
- With a broadband and rapidly tunable (>30 cm⁻¹ and >1000 Hz) 100 mW EC-QCL it may be possible to detect UF₆ concentrations in air of ~1 ppbv
- Strong UF₆ absorption may permit a design of an ultra-compact, portable QEPAS detector with a detection sensitivity of ~1 ppbv using the effect of the QEPAS signal phase shift difference of UF₆ and interfering gases (see A. Kosterev et al. “Photonic phase shift as a chemically selective spectroscopic parameter” Applied Physics B 78, 673-676, 2004)

Challenge: Atmospheric Water and CO₂

Transmission spectra for 200 m roundtrip of atmospheric water (50% relative humidity @ 25°C) and carbon dioxide with the overlap of the 16 μm 16₂ absorption band of 100 ppb UF₆ (blue spectrum)

![Transmission spectra](image)

16 μm (625 cm⁻¹) UF₆ LIDAR Summary

Future Directions and Outlook of Chemical Trace Gas Sensing Technology

Proposed QEPAS-OPBC Sensor Configuration

- DFB diode laser
- High reflectivity dielectric mirrors
- Photodiode
- PZT
- QTF
- Feedback electronics

Circulating power = Source power / (1-R)
Very conservatively, ×100

Alex Kabanov, Skymon Research R&D

QEPAS MDAL Comparison with CRDS, ICOS & TDLAS

Minimum Detectable Absorption Loss (MDAL) [cm⁻¹/Hz] can be used for comparison of different techniques:

- Cavity Ring Down Spectroscopy (CRDS): ~ 3x10⁻¹⁴
- Integrated Output Spectroscopy (ICOS): ~ 3x10⁻¹⁴
- Multipass Gas Cell based TDLAS: ~ 2x10⁻¹⁴
- QEPAS (Sept 2009) MDAL (DFB 100mW): 1.9x10⁻⁸
- QEPAS-OPBC MDAL (DFB 20 mW): 3.2x10⁻¹⁰
- QEPAS-OPBC + micro-resonator (estimated): ~ 7x10⁻¹²

QEPAS-OPBC can be as sensitive as CRDS, ICOS and TDLAS and retain most of the performance metrics of QEPAS

Wireless Sensor Networks for Trace Gas Sensing

- Advantages?
  - Spatial resolution
  - Measure fluxes
  - Detect spike before diffusion
- What is needed?
  - Ultra low power
  - Fast duty cycling capability
  - Low cost, Replicable
  - Ultra miniature
  - Autonomy (no consumables; auto-processing; auto start)

Ultra-compact Diode Laser based Trace Gas Sensor

König, 2008/09 01 53