### Advanced Infrared Semiconductor Laser based Chemical Sensing Technologies: Opportunities and Challenges

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- Motivation: Wide Range of Chemical Sensing
- Fundamentals of Laser Absorption Spectroscopy
- New Laser Sources and Sensing Technologies
- Selected Applications of Trace Gas Detection
  - Nitrogen Oxide Detection (Faraday Rotation Spectroscopy, Remote Sensing & Cavity Enhanced Spectroscopy)
- Future Directions and Conclusions

### Air Composition

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<th>Main Components</th>
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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 Health and Life Sciences
- Technologies for Law Enforcement and National Security
- Fundamental Science and Photochemistry

### Worldwide Megacity Megacities

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Fundamentals of Laser Absorption Spectroscopy

Mid-IR Source Requirements for Laser Spectroscopy

**REQUIREMENTS** | **IR LASER SOURCE**
--- | ---
Sensitivity (% to ppt) | Wavelength, Power
Selectivity (Spectral Resolution) | Single Mode Operation and Narrow Linewidth
Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers | Tunable Wavelength
Directionality or Cavity Mode Matching | Beam Quality
Rapid Data Acquisition | Fast Time Response
Room Temperature Operation | No Consumables
Field deployable | Compact & Robust

Molecular Absorption Spectra within the two Mid-IR Atmospheric Windows

IR Laser Sources and Wavelength Coverage

Key Characteristics of mid-IR QCLs and ICL Sources-2008

- **Band – structure engineered devices**
  - Terahertz wavelengths: 4000 μm (infrared) – 400 cm⁻¹.
  - MIR or MOCVD
  - 400 cm⁻¹ (mid-infrared)
  - 5 cm⁻¹ (far-infrared)
  - Compact, reliable, stable, long lifetime, and commercial availability.
  - Fiber (Bragg)
  - Single mode (DFB) and multi-wavelength

- **Spectral tuning range in the mid-IR**
  - 400 cm⁻¹ (laser)
  - 5 cm⁻¹ (absorption)
  - 5 cm⁻¹ (spectral resolution)
  - 200 cm⁻¹ (temperature control)
  - 50 cm⁻¹ (using external cavity elements and heterogeneously fabricated devices)

- **Narrow spectral linewidth**
  - 400 cm⁻¹ (bandwidth)
  - 5 cm⁻¹ (frequency stability)
  - 50 cm⁻¹ (linear accuracy)

- **High power and CW sources of QCLs at room temperature**
  - 50 W, high temperature operation: 250 W
  - Average power levels: 1400 mW (laser) and 20 mW (CW, Absorption)

- **Antimonide-MCT**
  - 400 cm⁻¹ (bandwidth)
  - 5 cm⁻¹ (frequency stability)
  - 200 cm⁻¹ (temperature control)

- **Linewidth**
  - 400 cm⁻¹ (bandwidth)
  - 5 cm⁻¹ (frequency stability)
  - 200 cm⁻¹ (temperature control)

Widely Tunable, CW, TEC Quantum Cascade Lasers
Tunable external cavity QCL based spectrometer

- Fine wavelength tuning
- PZT controlled EC-length
- PZT controlled grating angle
- OCL current control
- Motorized coarse grating angle tuning
- Vacuum light QCL enclosure with built-in 3D lens positioner (TEC laser cooling + optional chilled water cooling)

Wide Wavelength Tuning of a 5.3μm EC-QCL

- Coarse wavelength tuning of 155 cm⁻¹ is performed by varying diffraction grating angle
- Power output is ~ 11mW
- Access to Q(32) transition of NO at 1876.8 cm⁻¹ for LMR spectroscopy

Performance of 8.4 μm cw EC-QCL Spectroscopic Source

Tunability 182 cm⁻¹ @8.4 μm; (1100 to 1280 cm⁻¹); λ=15%
AR coating: $P_{\text{EC-QCL}}$: ~ 50 mW @ -30°C; also 103 mW @ 8.3 μm & -25°C; ~700mA; 2007 QCL technology

Quartz Enhanced Photoacoustic Spectroscopy

From conventional PAS to QEPAS

Laser beam, power $P$

Modulated (P or φ) at f or $f/2$

\[ S = \frac{Q}{f} \frac{\alpha P}{V} \]

Cell is OPTIMUM!

Effective volume

Resonating ELEMENT!

From microphone crystal

Resonant at $f$

quality factor $Q$

Quartz Tuning Fork (TF) as a Resonant Microphone

- Resonant frequency $\nu$ ~ 32.8 kHz
- Intrinsic high $Q$ factor $Q_{\text{water}}$ ~ 12,000
- $Q_{\text{water}}$ ~ 10,000 at ambient conditions;
- Resonator requires no transducer
- Minimum size
- Mass produced for clocks – low cost
QEPAS Signal Detection

![QEPAS Signal Detection Diagram](image)

Absorption Detection Module for QEPAS based Gas Sensor

![Absorption Detection Module Diagram](image)

Comparative Size of Absorption Detection Modules (ADM)

- Optical multipass cell (100 m): ~10 cm, I=1000 cm^2
- Resonant photoreactive cell (1000 Hz): ~30 cm, I=60 cm^2
- QEPAS spectrophotometer: ~1 m, I=40 cm^2

Alignment-free QEPAS Absorption Detection Module

High Performance 4.6 μm CW, RT QC Laser - 2008

- High sensitivity (ppm to ppb gas concentration levels) and excellent dynamic range
- Immune to ambient and flow acoustic noise, laser noise and etalon effects
- Significant reduction of sample volume (< 1 mm^3)
- Applicable over a wide range of pressures
- Temperature, pressure and humidity insensitive
- Ultra-compact, rugged and low cost (compared to other laser based sensor architectures)
Trace Gas Sensing Examples

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

QEPAS based Gas Sensor Architecture

Calibration and Linearity of a 1.53 μm QEPAS based NH₃ Sensor

Infrared NH₃, HCN and C₂H₂ Absorption Spectra

Noise-equivalent concentration (NEC) for t=1s time constant is 0.06 ppm for 60mW excitation power at 6538 76 cm⁻¹

Noise-equivalent absorption (NEA) coefficient k=3.1×10⁻⁵ cm⁻¹ WHz⁻¹
QEPAS based Multi-Gas Sensor Architecture

Biomarkers Present in Exhaled Human Breath

More than 400 different molecules in breath; many with well defined biochemical pathways

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<tr>
<th>Compound</th>
<th>Concentration</th>
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Mid-IR QEPAS based NH3 Gas Sensor Architecture

Breath Collection Interface to Trace Gas Sensor

Ammonia Sensor

1. Critical orifice
2. Measurements made (10 times)
3. Raw data processed controlled

Real Time Exhaled NH3 Sensor Response from a Healthy Volunteer

For the available QCL the presence of CO2 in breath (~4% - 4.5%) contributes to the sensor signal. This fact has to be taken into account in the quantification of the exhaled ammonia concentration.

NH3 Measurements at an Oklahoma State University Research Feedyard
**Commercial widely tunable cw EC-QCL**

- Mid-IR Lasers From Daylight Solutions

**Motivation for Nitric Oxide Detection**

- Atmospheric Chemistry
- Environmental pollutant gas monitoring
  - NOx 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 (TNT)

**Laser-based ICOS Nitric Oxide Sensor**

- Online NO concentration measurements at 32mbar exhaust.
- Interoperability of ICOS and commercial chemiluminescence sensor (ICOS + solid time)

**High resolution spectroscopy with a 5.3µm EC-QCL**

- Mode hop free scan of up to 2.5 cm⁻¹ with a resolution <0.001 cm⁻¹
- (300 MHz) can be performed anywhere within the tuning range

**QCL based Quartz-Enhanced Photoacoustic Gas Sensor**

- QEPAS characteristics:
  - High sensitivity (ppm to ppt)
  - Excellent linear range
  - Immune to environmental noise
  - Ultra-small sample volume (~ milliliter)
  - Sensitivity is limited by the fundamental thermal T Foucault
  - Compact, rugged and low cost
  - Potential for trace gas sensor networks

**High resolution EC-QCL based QEPAS**

- External Amplitude Modulation
  - QTF is used as a mechanical chopper at f~320Hz
  - High resolution mode-hop-free tuning is possible
EC-QCL based Magnetic Rotation Spectroscopy

Magnetic rotation spectrum of Q(3/2) and Q(5/2) transitions of nitric oxide

Magnetic Rotation Spectroscopy of Nitric Oxide

Allan Plot of EC-QCL based MRS NO Sensor

EC-QCL based MRS NO Sensor for IAP, Beijing

National Stadium, Beijing, July-Sept. 2008
Design of an EC-QCL Based Remote Sensing System

- An upgraded version of a four-laser pulsed OCL system
- The optical set-up, electronics and control software modified for CW-QCL operation
- First tests performed with a QFB CW-QCL operating at ~5.5 μm

Outdoor Open Path Measurements
(Influence of Atmospheric Transmission)

Monitoring of broadband absorbers

- Freon 125 (C₂H₂F₆)
  - Refrigerant (leak detection)
  - Safe simulant for toxic chemicals, e.g., chemical warfare agents
- Acetone (CH₃COCH₃)
  - Recognized biomarker for diabetes
- TATP, Acetone Peroxide (C₆H₁₂O₄)
  - Highly Explosive

QEPAS based Freon 125 and Acetone concentration measurements with a tunable 8.4 μm CW EC-QCL

- Minimum detection limit (1σ) of ~4.5 ppb was obtained for Freon 125 with an average laser power of 6.6 mW
- Wide tunability enables excellent molecular selectivity for broadband absorbers

TATP Absorption Spectrum

Applications of Efficient Mid-Infrared 9.6 μm QCL

- FTIR analysis of the broadband output from FP QCL, ~85% efficiency from uncoated chip
- Wavelength using Characteristics and FTIR spectrum
**Applications of Efficient Mid-Infrared 9.6µm QCLs**

- Measured QCL-PAS spectrum of H₂S
- Measured QCL-PAS spectrum of CO₂
- Measured QCL-PAS spectrum of H₂ liquid

**Future of Chemical Trace Gas Sensing**

**QEPAS Performance for 12 Trace Gas Species (July '08)**

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<td>CH₄</td>
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<td>70</td>
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<td>80</td>
<td>40</td>
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**Conceptual Design of Ultra-compact QCL Trace Gas Sensor**

**New design of fast broadly tunable EC-QCLs (2008)**

- New optical configuration
- Folded cavity (configuration #1)
- Fast tuning capabilities:
  - Coarse Broadband Tuning
  - High resolution mode-hop free tuning

**Proposed QEPAS-OPBC Sensor Configuration**

- DFB diode laser
- High reflectivity dielectric mirrors
- Photodiode
- PZT
- Feedback electronics
Wireless Sensor Networks for Trace Gas Sensing

- Each point called "mote"
- Advantages?
  - Spatial resolution
  - Measure fluxes
- What is needed?
  - Low power
  - Low cost
  - Ultra miniature
  - Replicable
  - Autonomy

H₂CO Concentration (ppb) Versus Wind Direction

Mean H₂CO concentration versus wind direction at sampling site (time in ppb)

Major ethylene sources in Harris County

PHOTONS v4.0 - 2.7μm CO₂ Direct Absorption Based Sensor

- Small size
- Retain very low cost
- High efficiency switching power supplies
- PWM Pellet cooler driver
- 0.2W control system power consumption
- Detection sensitivity of CO₂ 1 ppm with 1 sec. lock-in time constant
- Over 100× improvement in sensitivity possible @ -4.5μm

LAS based CO₂ Spectrum at 2.7 μm

Ambient CO₂ (380ppm)

Summary & Future Directions of QCL based Gas Sensor Technology

- Quantum and Interband Cascade Laser based Trace Gas Sensors
  - Compact, reliable, and robust
  - High sensitivity (<10⁻⁹) and selectivity (1 to 500 MHz)
  - Capable of fast data acquisition and analysis
  - Detected 13 trace gases (O₃, N₂O, H₂O, CO₂, NO, CH₄, C₂H₆, H₂CO, SD, C₃H₄, C₂H₂, and H₂S) and several isotopic species of C, O, N and H.

- New Applications of Trace Gas Detection
  - Environmental Monitoring (urban air quality, H₂ and CO₂, and isotope ratio measurements of CO₂ and CH₄)
  - Industrial process control and chemical analysis (NO, NH₃, H₂O, and H₂S)
  - Medical & biomedical diagnostics (NO, NH₃, N₂O, O₂, CO₂, and CH₃OH)
  - Hand-held sensors and sensor network technologies (CO₂)

- Future Directions and Collaborations
  - Improvements of the existing sensing technologies using new, thermoelectrically cooled, cw, high power, and broadly wavelength tunable mid-IR semiconductor quantum cascade lasers
  - New applications enabled by use of broadly wavelength tunable quantum cascade lasers based on heterogenous EC-QCL in e.g. semiconductor concentration measurements of broad band absorbers, in particular VOCs, HC's and multi-species detection
  - Development of optically gas sensor networks based on OEPAS and LAS