Applications of near and mid-infrared semiconducotor laser based trace gas sensors

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- Motivation: Wide Range of Chemical Sensing
- Fundamentals of Laser Absorption Spectroscopy
- New Laser Sensing Technologies
- Selected Application of Trace Gas Detection
- Quartz Enhanced L-PAS (NH₃, Freon 125 & acetone)
- Future Directions and Conclusions

Wide Range of Trace Gas Sensing Applications

- Urban and Industrial Emission Measurements
- Agricultural 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
- Petroleum, 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

Fundamentals of Laser Absorption Spectroscopy

Key Characteristics of mid-IR QCLs and ICL Sources

- Band - structure engineered devices
  - Laser wavelength is determined by laser design - MIR or MOCVD
  - No need for QC laser diodes (excitation)
- Compact, reliable, stable, long lifetime, and commercial availability
- Facile, P-type FET, simple mode (DMR) and multi-wavelength
- Spectral tuning range in the mid-IR
  - 4-5 cm⁻¹ (IR DFB) and 2-3 cm⁻¹ (EAM) at R = 10 GHz
  - 1.5 cm⁻¹ using injection current control
  - 10-20 cm⁻¹ using temperature control
  - 200 cm⁻¹ with an external grating element and with homogeneous modal active region design
- Nanosecond spectral linewidth
  - > 1 cm⁻¹ (< 1 ns, high frequency stabilization @ 1000 cm⁻¹); pulsed ~ 300 MHz (chirp from heating)
- High pulsed and cw powers at TEC/RINT temperatures
  - Pulsed peak power > 1.0 W; high temperature operation >250K
  - Average power levels: 1-300 mW (current wall plug = 5mW)
  - > 50 mW, TEC CW DFB at 1 and 305 AlGaAs, Proportion.
  - 300 mW (< 1 mm, conduction cooling)
  - ~ 300 mW (4.1 mm, conduction cooling, width)
  - > 300 mW (< 1 mm,版权声明,及商规)
- Q-factor of ~ 1000, ~ 150 mW/W (DFB) & 200 K, (Nazaretti)

Quartz Enhanced Photoacoustic Spectroscopy

From conventional PAS to QEPAS

Laser beam, power \( P \)

Modulated \((P \text{ or } \lambda) \text{ at } S \text{ or } f'\)

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

\[ NNEA = \frac{a_{\text{max}} P}{\sqrt{f}} \left[ \frac{\text{cm}^{-1} \times W}{\text{Hz}} \right] \]

Resonant at \( f \)

Quality factor \( Q \)
**Quartz Tuning Fork (TF) as a Resonant Microphone**
- Resonant frequency $f=32.8$ kHz
- Low loss, high $Q$ factor $Q_f=125000$
- Piezoelectric required no transducer
- Miniature size
- Mass produced for cheap — low cost

**Absorption Detection Module for QEPAS based Gas Sensor**
- $\varnothing 0.41$ mm
- 10 mm
- Lens
- Excitation laser beam
- Quartz tuning fork electrodes

**Alignment-free QEPAS Absorption Detection Module**
- Quartz tuning fork
- Acoustic micro resonator

**Merits of QE Laser-PAS based Trace Gas Detection**
- 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
- Rugged and low cost (compared to other optical sensor architectures)

**Trace Gas Sensing Examples**

**Motivation for NH$_3$ Detection**
- Monitoring of gas separation processes
- 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 dysfunctions)
Infrared NH₃ Absorption Spectra

QEPAS based Gas Sensor Architecture

Calibration and Linearity of QEPAS based NH₃ Sensor

NH₃ Measurements at an Oklahoma State University Research Feedyard

Biomarkers Present in Exhaled Human Breath

QCL based Quartz-Enhanced Photoacoustic Gas Sensor

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

Noise-equivalent absorption (NEA) coefficient δ=7.2×10⁻⁹ cm⁻¹/WHz⁻¹/²

NO (Wysocki)
**QEPAS based Freon 125 and Acetone concentration measurements with a tunable 8.4 μm CW-EC-QCL**

**QEPAS concentration measurement of a Freon 125 (upper traces) and acetone mixture (lower traces) using 8.4 μm tunable gas sensors.**

*Minimum detection limit (1σ) of ~5 g/L was obtained for Freon 125 with an average laser power of 0.5 mW.*

Wide tunable enables excellent molecular selectivity for broad band absorbers.

**CW DFB QCL based QEPAS Ammonia Sensor operating at 1046.4 cm⁻¹**

**Future of Chemical Trace Gas Sensing**

**Wireless Sensor Networks for Gas Sensing**

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

**Miniature LAS CO₂ Sensor Board**

USB

Detector

10 cm path

Laser Driver Board

Network Core

Sensor Core

1.3A Li-Ion Battery

(Attached to bottom)
Summary & Future Directions of QCL based Gas Sensor Technology

- Quantum and Interband Cascade Laser based Trace Gas Sensors
  - Compact, tunable, and robust
  - High sensitivity (×10^5) and selectivity (3 to 500 MHz)
  - Capable of fast data acquisition and analysis
  - Detected 13 trace gases to date: NH₃, CH₄, H₂O, CO₂, CO, NO, H₂-O, COS, C₂H₂, H₂S, CO₂, C₂H₆, CH₃OH, C₂H₄, and several isotopic species of C, O, N, and H

- New Applications of Trace Gas Detection
  - Environmental Monitoring (urban quality - H₂-O and isotopic ratio measurement of CO₂ and CH₄; fine detection and quantification of engine exhausts)
  - Industrial process control and chemical analysis (NO, NH₃, H₂O, and H₂S)
  - Medical & biomedical diagnostics (NO, NH₃, N₂-O, H₂CO and CH₁₂COCH₂)
  - Hand-held sensors and sensor network technologies (CO₂)

- Future Directions and Collaborations
  - Improve endurance of the existing sensing technologies using novel, thermoelectrically cooled, cw, high power, and broadband wavelength tuning mid-IR interband and interband quantum cascade lasers
  - Utilize novel broadly wavelength tunable quantum cascade lasers based on heterogeneous EC-QCLs (i.e. sensitive, concentration measurements of broadband absorbers; in particular VOCs, HCl and multi-species detection)
  - Development of optically gas sensor networks based on QEPAS and LAS