Recent Advances and Applications of Semiconductor Laser based Gas Sensor Technology

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- Motivation: Wide Range of Chemical Sensing
- Fundamentals of Laser Absorption Spectroscopy
- Selected Applications of Trace Gas Detection
- LAS with a Multispectra absorption cell (NH₃, H₂CO)
- Quartz Enhanced Laser PAS (H₂CO)
- OA-ICOS NO based Sensor Technology
- Outlook and Conclusions

Motivation: Wide Range of Gas Sensing Applications

- Urban and Industrial Emission Measurements
  - Industrial Plants
  - Combustion Sources and Processes (e.g. early fire detection)
  - Automobile and Aircraft Emissions
- Rural Emission Measurements
  - Agriculture and Animal Facilities
  - Environmental Gas Monitoring
  - Atmospheric Chemistry (e.g., ecosystems and airborne)
  - Volcanic Emissions
- Chemical Analysis and Industrial Process Control
  - Chemical, Pharmaceutical, Food & Semiconductor Industry
  - Toxic Industrial Chemical Detection
- Spacecraft and Planetary Surface Monitoring
  - Crew Health Maintenance & Advanced Human Life Support Technology
  - Biomedical and Clinical Diagnostics (e.g., breath analysis)
  - Forensic Science and Security
  - Fundamental Science and Photochemistry

Trace Gas Monitoring in a Petrochemical Plant

University of Szeged, Hungary

Worldwide Megadirty Mega Cities

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NASA-JSC Human-Rated Simulation Chamber
Existing Methods for Trace Gas Detection

- **Non-Optical**
  - Mass Spectroscopy
  - Chemical
  - Electro Chemical

- **Optical**
  - Non-Dispersive
  - Dispersive
  - Microwave Spectroscopy
  - Laser Spectroscopy

Fundamentals of Laser Absorption Spectroscopy

- **Optimum Molecular Absorbing Transition**
  - Overtones or Combination Bands (OVB)
  - Fundamental Absorption Bands (MABs)

- **Laser/Photoluminescence**
  - Multipass Absorption Cell
  - Cavity Ringdown & Littrow Spectroscopy

  - Optical Pathlength
  - Cavity Ringdown & Monochromatic Spectroscopy

  - Échelle Spectroscopic Monitoring (Versa & waveguide)

Spectroscopic Detection Schemes

- Frequency or Wavelength Modulation
- Balanced Detectors
- Zero-air Substitution

Photometric Spectroscopy

Mid-IR Source Requirements for Laser Spectroscopy

<table>
<thead>
<tr>
<th>REQUIREMENTS</th>
<th>IR LASER SOURCE</th>
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<tr>
<td>Sensitivity (%i to ppi)</td>
<td>Power</td>
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<tr>
<td>Selectivity</td>
<td>Single Mode Operation and Narrow Line Width</td>
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<td>Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers</td>
<td>Tunable Wavelengths</td>
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<td>Directionality or Cavity Mode Matching</td>
<td>Beam Quality</td>
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<tr>
<td>Rapid Data Acquisition</td>
<td>Fast Time Response</td>
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<tr>
<td>Room Temperature Operation</td>
<td>No Consumables</td>
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<tr>
<td>Field deployable</td>
<td>Compact &amp; Robust</td>
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</table>

IR Laser Sources and Wavelength Coverage

Quantum and Interband Cascade Laser: Basic Facts

- Solid-state engineered devices (emission wavelength is determined by layer thickness – MBE or MOCVD QCLs operate from 4 to 160 μm limit by MBE CAVAR on the short wavelength side)
- Unpolar devices
- Cavity-enhanced emission of InP lasers and the number of modes determines laser power
- Compact, reliable, stable, long lifetime, commercial availability
- Fabry-Perot (FP) or single mode (DFB)
- Broad spectral gain range in the mid-IR (4.2-2.4 μm for QC-CL and 3.5 μm for ICL)
- 1.3 cm⁻¹ tuning range
- 10-20 cm⁻¹ using temperature
- > 100 cm⁻¹ using an external grating element
- Narrow spectral linewidth 0.01 - 3 MHz & ~10kHz with frequency stabilization
- Linewidth is ~ 200 MHz of pulsed QCLs (cavity from heater)
- High output powers in several amperes
  - Pulsed pulse power is 8 W, high temperature operation ~ 250 K
  - Average power levels 1-400 mW
  - ~ 50 mW: TEC, 12°C DFB at 5 and 10 microns (AlGaAs-DL time)
- ~400 mW (CW FF) and ~150 mW (CW DFB) at 250 K
- Continuous
Motivation for NH₃ Detection

- Monitoring of gas separation processes
- 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 dysfunctions)

Fundamentals of Laser Absorption Spectroscopy

Optimum Molecular Absorbing Transition
- Overtones or Combination Bands (OCS)
- Fundamental Absorbing Bands (H₂O, CO₂)

Lange Optical Pathlength
- Multipass Absorption Cell
- Cavity Enhanced, Cavity Ringdown & Intensity Spectroscopy
- Open Path Monitoring (fibers & waveguides)
- External Field Monitoring (fibers & waveguides)

Spectroscopic Detection Schemes
- Frequency or Wavelength Modulation Balanced Detection
- Zero-que Subtraction
- Photoacoustic spectroscopy

Pulsed QC Laser Based Gas Sensor
Ammonia Absorption Spectrum @ 993 cm⁻¹

6.7 ppm, precision: 0.3 ppm
lm pathlength
95 Torr

y=CE⁻¹-x
y: absorption
C: concentration
x: peak shift

Frequency, cm⁻¹

Wavelength Modulation Spectroscopy of NH₃

- QCL Drive Current: Quasi CW + Wavelength modulation

- Calibration with a 1038 ppm NH₃:N₂ mixture
  - 1σ extrapolated sensitivity
  - 82 ppb.m/√Hz

=> Improvement by a factor of 3 compared to direct absorption spectroscopy

Motivation for Precision Monitoring of H₂CO

- Pollutant due to incomplete fuel combustion processes
- Potential trace contaminant in industrial manufactured products
- Precursor to atmospheric O₃ production
- Medically important gas

Mid-IR DFG Based H₂CO Sensor

Advanced DFG System for H₂CO Detection

Laser₁, Laser₂
Laser₁ = 1560 nm
Laser₂ = 1083 nm
λ_{DFG} = 2831.6417 cm⁻¹

A. Fried et al. Development of DFG source in progress
HITRAN Based Simulation of a H₂CO-H₂O-CH₄ Spectrum in Tuning Range of a 3.53 μm IC Laser

- H₂CO: 10 ppb
- H₂O: 3% relative humidity
- CH₄: 2 ppm
- Optical path: 100 m
- Total pressure: 30 Torr

IC Laser based Formaldehyde Calibration Measurements with a Gas Standard Generator

- H₂CO absorption frequency: 2835.3 cm⁻¹
- Lock-in time constant: 10 s
- QEPAS parameters:
  - Resonance frequency: 32.768 KHz
  - Q-factor: 175
  - Pressure: 20 Torr
  - Gas Flow: 75 sccm
  - IC laser power: 6 mW

QEPAS Performance for 10 Trace Gas Species (Dec’05)

<table>
<thead>
<tr>
<th>Molecule (Host)</th>
<th>Frequency, cm⁻¹</th>
<th>Pressure, Torr</th>
<th>NNEA, cm⁻¹·cm⁻³</th>
<th>Power, µW</th>
<th>NEC (μA)</th>
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<td>H₂CO (air)</td>
<td>1713.17</td>
<td>40</td>
<td>0.2×10⁻³</td>
<td>3.6</td>
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<td>CH₃OH (air)</td>
<td>6252.47</td>
<td>80</td>
<td>2×10⁻³</td>
<td>39</td>
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<td>CO₂ (pure)</td>
<td>5541.25</td>
<td>50</td>
<td>0.5×10⁻³</td>
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<td>H₂O (air-H₂O)</td>
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<td>50</td>
<td>3.6×10⁻³</td>
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- Improved memorization
- Multiple gas exposures with different pressures and temperatures
- NNEA - normalized noise equivalent absorption coefficient
- NEC - noise equivalent concentration for available laser power and 1 s time constant.

Merits of QE Laser-PAS based Trace Gas Detection

- High sensitivity (ppm to ppb gas concentration levels) and excellent dynamic range
- Immunity to ambient and flow acoustic noise, laser noise and crosstalk effects, which allows applications that involve harsh operating environments
- Required sample volume is very small. The volume is ultimately limited by the gap size between the TF prongs, which is less than 1 mm² for the presently used QTFs
- No spectrally selective elements are required
- Applicable over a wide range of pressures, including atmospheric pressure
- Sensitive to phase shift introduced by vibrational to translational (V-T) relaxation processes and hence the potential of concentration measurements of spectrally interfering species
- Ultra-compact, rugged and low cost compared to LAS that requires a multipass absorption cell and infrared detector(s)
- Potential for optically multiplexed concentration measurements

Fundamentals of Laser Absorption Spectroscopy

- Gas-Laser Interactions
- Laser Properties
- Line Shape
- Line Shape Fitting
- Optical Pathlength
- Interferograms
- Spectroscopic Parameters
- Spectroscopic Transition Probabilities
- Frequency Multiplication
- Frequency Synthesis
- Frequency Stabilization
- Frequency Modulation
- Fundamental Absorption Band (Fundamental Band)

Optimum Molecular Absorption Transitions

- | Molecule | Transition | Standard Absorption Band | Energy Level | Intensity |

Laser Optical Pathlengths

- Multipass Absorption Cell
- Cavity Enhanced, Cavity Ringdown & Intersweep Spectroscopy
- Open Path Monitoring (with cavity-enhanced)
- Transient Field Monitoring (short & microwave)
- Spectroscopic Detection Schemes
- Frequency or Wavelength Modulation
- Balanced Detection
- Zero-Point Spectroscopy
- Photonic Spectroscopy
Off-Axis Integrated Cavity Output Spectroscopy (ICOS) Based Gas Sensor

2f NO Absorption Signal at 1835.57 cm⁻¹

ICOS vs. CRDS

External Cavity QCL Based Spectrometer

Mid-IR NO Absorption Spectra Acquired with a Tunable TEC QCL
Important facts of novel EC-QCL Technology

- Laser spectroscopy provides superior resolution compared to other techniques e.g. FTIR
- Single mode operation of the laser is required
- Wavelength tunability of single mode (DFB) mid-IR semiconductor lasers is \( \sim 10 \text{cm}^{-1} \)
- Demonstrated wavelength tunability of the Rice EC QCL is \( \sim 35 \text{ cm}^{-1} \) (limited by the gain chip properties and not by the designed EC configuration)
- Gain chips, which can provide tunability of >200 cm\(^{-1}\) are already reported in the literature

Sensor control and data processing

- Computer control of a laser-based spectroscopic sensor using PC (Windows, LabView) is convenient but not reliable and often does not allow to achieve the optimum sensor performance
- Reliable systems such as NI Real-Time devices are expensive, in part because of their multifunctional abilities
- Dedicated electronic modules for autonomous sensor control and data processing are reliable, small, and consist of inexpensive part
- Today’s technology such as DSP and FPGA offers convenience and flexibility of design

Dedicated DSP-based electronics for trace gas sensing using a pulsed QC laser

Pulsed laser requires high speed pulsed processing system for minimum detection limits

Concept of a ultra-miniature QEPAS gas sensor

Conclusions and Future Directions

- Laser based Trace Gas Sensors
  - Ultra compact (\( \sim 0.2 \text{ mm}^3 \)), robust & low cost sensors based on QE L-PAS
  - QEPAS is immune to ambient solar. The measured noise level coincides with the thermal noise of the QTF
  - Best to date demonstrated QEPAS sensitivity is \( 2.1 \times 10^5 \text{ cm}^{-1} \text{ W} \cdot \text{m}^{-1} \) for \( \text{H}_2\text{O} \), \( \text{N}_2\text{O} \)
  - QEPAS exhibits a low \( 1/2 \) noise level, allowing data averaging for more than 3 hours
  - Detected 14 trace gases to date: \( \text{NH}_3, \text{CH}_4, \text{N}_2\text{O}, \text{CO}_2, \text{CO}, \text{NO}, \text{H}_2\text{O}, \text{CO}_2, \text{HCN}, \text{C}_2\text{H}_2, \text{C}_2\text{H}_4\text{OH}, \text{SO}_2, \text{H}_2\text{O}, \text{H}_2\text{CO} \) and several isotopic species of C, O, N & H
- Applications in Trace Gas Detection
  - Environmental & Spacecraft Monitoring (\( \text{NH}_3, \text{CO}, \text{CH}_4, \text{C}_2\text{H}_2, \text{N}_2\text{O}, \text{CO}_2, \text{H}_2\text{O} \))
  - Medical Diagnostics (\( \text{NO}, \text{CO}, \text{CO}_2, \text{NH}_3, \text{C}_2\text{H}_4 \))
  - Industrial process control and chemical analysis (\( \text{NO}, \text{NH}_3, \text{H}_2\text{O} \))
- Future Directions and Collaborations
  - QEPAS based applications using novel thermoelectrically cooled cw and broadband wavelength tunable quantum and interband cascade lasers
  - Investigate QTFs with lower resonant frequencies
  - Investigate amplitude modulation QEPAS potential and limitations
  - New target gases, in particular VOCs and HCs
  - Development of optically multiplexed gas sensor networks based on QE L-PAS

NASA Atmospheric & Mars Gas Sensor Platforms
OA-ICOS based CO Concentration Measurements at 2196.66 cm⁻¹

FT-IR survey absorption spectrum of benzene vapor (C₆H₆)