Quantum Cascade Laser Sources: Recent Advances and Applications

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- Motivation: Wide Range of Gas Sensing Applications
- Key Characteristics of QC Lasers: October 2009
- Selected Applications of Trace Gas Detection
  - NH₃ Detection for Environmental and Health Applications
  - Nitric Oxide Detection
- Future Directions and Outlook
  - Fiber coupled CW EC-QCL Nitric Oxide Detection System
  - Detection of Broadband Molecular Absorbers
  - Development of QC Laser Arrays
  - Ultra-compact QCL based Analyzers

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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 the Life Sciences**

- **Technologies for Law Enforcement and National Security**

- **Fundamental Science and Photochemistry**
Existing Methods for Trace Gas Detection

Non-Optical

Chemical

Electro Chemical

Black Body Sources

Optical

Coherent Sources

Mass Spectroscopy

Gas Chromatography

Chemiluminescence

Fourier Transform

Gas Filter Correlation

Microwave Spectroscopy

Laser Spectroscopy
Basics of Optical Trace Gas Analyzers

**Optimum Molecular Absorbing Transition**
- NIR Overtone or Combination Bands
- MIR Fundamental Absorption Bands
- Long Optical Pathlengths
  - Multipass Absorption Cell (White, Herriott)
  - Cavity Enhanced, Cavity Ringdown & Intracavity Spectroscopy
  - Open Path Monitoring (with retro-reflector); Standoff and Remote Detection
  - Fiberoptic evanescent wave Spectroscopy

**Spectroscopic Detection Schemes**
- Wavelength or Frequency Modulation
- Balanced Detection
- Zero-air Subtraction
- Photoacoustic Spectroscopy (PAS or QEPAS)
- Laser Induced Breakdown Spectroscopy

**Key Requirements:** Sensitivity, specificity, rapid data acquisition and multi-species detection

**Beer-Lambert's Law of Linear Absorption**
\[ I(\nu) = I_0 e^{-\alpha(\nu) P_a L} \]

- \( \alpha(\nu) \) - absorption coefficient [cm\(^{-1}\) atm\(^{-1}\)]; \( L \) – path length [cm]
- \( \nu \) - frequency [cm\(^{-1}\)]; \( P_a \) - partial pressure [atm]

\[ \alpha(\nu) = C \cdot S(T) \cdot g(\nu - \nu_0) \]

- \( C \) - total number of molecules of absorbing gas/atm/cm\(^3\) [molecule \cdot cm\(^{-3}\) \cdot atm\(^{-1}\)]
- \( S \) – molecular line intensity [cm \cdot molecule\(^{-1}\)]
- \( g(\nu - \nu_0) \) – normalized spectral lineshape function [cm], (Gaussian, Lorentzian, Voigt)
Molecular Absorption Spectra within the two Mid-IR Atmospheric Windows

Source: HITRAN 2000 database
## Mid-IR Source Requirements for Laser Spectroscopy

<table>
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<tr>
<th>REQUIREMENTS</th>
<th>IR LASER SOURCE</th>
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<tr>
<td>Sensitivity (% to ppt)</td>
<td>Optimum Wavelength, Power</td>
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<td>Selectivity (Spectral Resolution)</td>
<td>Single Mode Operation and Narrow Linewidth</td>
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<td>Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers</td>
<td>Tunable Wavelength</td>
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<td>Directionality or Cavity Mode Matching</td>
<td>Beam Quality</td>
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<td>Rapid Data Acquisition</td>
<td>Fast Time Response</td>
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<td>Room Temperature Operation</td>
<td>No Consumables</td>
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<td>Field deployable</td>
<td>Compact &amp; Robust</td>
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Key Characteristics of mid-IR QCL and ICL Sources-2009

- **Band – structure engineered devices**
  (Emission wavelength is determined by layer thickness – MBE or MOCVD); mid-infrared QCLs operate from 3 to 24µm (AlInAs/GaInAs)

- Compact, reliable, stable, long lifetime, and commercial availability

- Fabry-Perot (FP), single mode (DFB) and multi-wavelength

- **Broad spectral tuning range in the mid-IR**
  (4-24µm for QCLs and 3-5µm for ICLs and GaSb diodes)
  - 1.5 cm⁻¹ using injection current control for DFB devices
  - 10-20 cm⁻¹ using temperature control for DFB devices
  - > 430 cm⁻¹ using an external grating element and FP chips with heterogeneous cascade active region design; also QCL DFB r array

- **Narrow spectral linewidth**
  - CW: 0.1 - 3 MHz & <10Khz with frequency stabilization (0.0004 cm⁻¹)
  - Pulsed: ~ 300 MHz

- **High pulsed and cw powers of QCLs and ICLs at TEC/RT temperatures**
  - Pulsed and CW powers of ~ 1.5 W; high temperature operation ~300K
  - >50 mW, TEC CW DFB @ 5 and 10 µm
  - > 600 mW (CW FP) @ RT; wall plug efficiency of ~15 % at 4.6µm;
Quantum Cascade (QC), Interband (IC) and GaSb Laser Availability in October 2009

• Commercial Sources
  ▪ Adtech, CA
  ▪ Alpes Lasers, Switzerland & Germany
  ▪ Alcatel-Thales, France
  ▪ Corning, NY
  ▪ Hamamatsu, Japan
  ▪ Physical Sciences, Inc (Maxion Technologies, Inc
  ▪ Nanoplus, Germany

• Research Groups
  ▪ Harvard University
  ▪ Fraunhofer-IAF, Freiburg, Germany
  ▪ NASA-JPL, Pasadena, CA
  ▪ Naval Research Laboratories, Washington, DC
  ▪ Northwestern University, Evanston, IL
  ▪ Princeton University (MIRTHE), NJ
  ▪ State University of New York
  ▪ Technical University, Zuerich, CH
  ▪ University of Montpelier, France
  ▪ UK: Sheffield
Recent Applications of QCL based Trace Gas Sensors
Motivation for NH$_3$ Detection

- Monitoring of gas separation processes
- Detection of ammonium-nitrate explosives
- 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 diseases)
Noise–equivalent concentration (NEC) is 6 ppb for a 1s time constant and 20mW excitation power at 1046.4 cm\(^{-1}\) (110 Torr)
Real-time Breath Monitor Interface

- Controlled flow
- Continuous control of mouth pressure
- Continuous monitoring of CO₂ concentration (capnograph) and its use in QEPAS data processing
Motivation for Nitric Oxide Detection

• Environmental pollutant
  ▪ Product of fossil fuel combustion process (automobile and power plant emissions)
  ▪ Precursor of smog and acid rain
Faraday Rotation Spectroscopy of Nitric Oxide

- Amplitude [mV]
- Wavenumber [cm\(^{-1}\)]

96 ppb NO on N\(_2\)

- \(I_{qcl}=850\) mA, \(P=40\) Torr
- \(TC=1\) s, \(SEN=2\) mV
- \(freq_{mod}=950\) Hz, \(B=110\) Gauss
- \(\Phi=3^\circ\) from crossed analyzer
- LN cooled InSb detector

\(Q(3/2)\): SNR=253, MDL(1\(\sigma\))=380 ppt

\(Q(5/2)\): \(1\sigma=4.325\) \(\mu\)V
Future Directions and Outlook of Chemical Trace Gas Sensing Technology
High power fiber-coupled QCL for NO detection

- LASER SOURCE EC-QCL (Daylight Solutions, Inc)
  - Tuning range 5.13-5.67 µm
  - Maximum tuning Rate 38 nm/sec
  - Highest optical power: ~250 mW
  - TE cooling, RT operation

Collaboration with: V. Spagnolo Politecnico Bari and CNR-LIT³
Fiber coupled QCL and QEPAS detection system

- High coupling efficiency of laser output to fiber
- Beam size matching to QEPAS after collimation
- Aspheric lenses for both coupling and re-collimating.
- **86% coupling efficiency**

**FIBER**

- Material: AsSe$_3$
- 22 µm core diameter
- Single mode operation
- FC-PC termination
- AR Coated.

Collaboration with: V. Spagnolo, Politecnico Bari and CNR-LIT$^3$
Monitoring of Broadband Absorbers

- **Freon 125 (C$_2$HF$_5$)**
  - Refrigerant (leak detection)
  - Safe simulant for toxic chemicals, e.g. chemical warfare agents
- **Acetone (CH$_3$COCH$_3$)**
  - Recognized biomarker for diabetes
- **TATP (Acetone Peroxide, C$_6$H$_{12}$O$_4$)**
  - Highly Explosive
- **Uranium Hexafluoride (UF$_6$)**
DFB QCL array performance

Emission spectrum of a DFB-QCL array
Pulsed operation (80kHz, 50ns) at room temperature
Grating coupling strength, $|\kappa L| \approx 10$

Lee, Belkin, et al., APL 2007
Summary & Future Directions of Laser based Gas Sensor Technology

• **Semiconductor Laser based Trace Gas Sensors**
  - Compact, tunable, and robust
  - High sensitivity (<10⁻⁴) and selectivity (3 to 500 MHz)
  - Capable of fast data acquisition and analysis
  - Detected 14 trace gases to date: NH₃, CH₄, N₂O, CO₂, CO, NO, H₂O, COS, C₂H₄, H₂S, H₂CO, SO₂, C₂H₅OH, C₂HF₅, TATP and several isotopic species of C, O, N and H.

• **New Applications of Trace Gas Detection**
  - Environmental Monitoring (urban quality – NH₃, H₂CO, NO, isotopic ratio measurements of CO₂ and CH₄, fire and post fire detection; quantification of engine exhausts)
  - Industrial process control and chemical analysis (NO, NH₃, H₂O, and H₂S)
  - Medical & biomedical non-invasive diagnostics (NH₃, NO, N₂O and CH₃COCH₃)
  - Ultra-compact, low cost, robust sensors (CO and CO₂)

• **Future Directions and Collaborations**
  - Improvements of the existing sensing technologies using novel, thermoelectrically cooled, cw, high power, and broadly wavelength tunable mid-IR intersubband and interband quantum cascade lasers
  - Further development of spectraphone technology
  - New applications enabled by novel broadly wavelength tunable quantum cascade lasers based on heterogeneous EC-QCL (i.e sensitive concentration measurements of broadband absorbers, in particular HCs, UF₆ and multi-species detection)
  - Development of optically gas sensor networks based on QEPAS and LAS