Quantum Cascade Lasers for Trace Gas Sensing

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- Motivation and Technology Issues
- Mid-IR QC Laser based Gas Sensors
  - Pulsed quasi-room temperature sensors
  - CW cryogenically cooled sensors
- Selected Applications of Trace Gas Detection
- Outlook and Summary

Wide Range of Gas Sensor Applications

- Urban and Industrial Emission Measurements
  - Industrial Plants
  - Combustion Sources and Processes
  - Automobile
- Rural Emission Measurements
  - Agriculture
- Environmental Monitoring
  - Atmospheric Chemistry
  - Volcanic Emissions
- Chemical Analysis and Industrial Process Control
  - Chemical, Pharmaceutical, & Semiconductor Industry
- Spacecraft and Planetary Surface Monitoring
  - Crew Health Maintenance & Life Support
- Medical Applications
- Fundamental Science and Photochemistry

Existing Methods for Trace Gas Detection

Non-Optical
- Mass Spectroscopy
- Chemical
- Electro Chemical
- Classical Sources
- Gas Filter Correlation
- Microwave Spectroscopy
- Laser Spectroscopy
- Coherent Sources

Optical
- Spectroscopic Detectors
- Fourier Transform

Direct Laser Absorption Spectroscopy

\[ \alpha(v) = \frac{C \cdot S(T) \cdot g(v - v_0)}{L} \]

- Laser Source
- Absorber
- Gas, Liquid or Solid
- Detector

Been-Lambert's Law of Linear Absorption

\[ F_{\lambda} = \frac{1}{P_{\lambda}} \Rightarrow P_{\lambda} \cdot L \]

- Frequency [cm\(^{-1}\)]
- Partial pressure [atm]
- Path length [cm]
- Absorption coefficient [cm\(^{-1}\) atm\(^{-1}\)]
- Total number of molecules of absorbing gas

Sensitivity Enhancement Techniques

- Optimum Molecular Absorbing Transition
  - Overtones or Combination Bands (NIR)
  - Fundamental Absorption Bands (MID-IR)
- Long Optical Pathlength
  - Multipass Absorption Cell (White, Herriot)
  - Cavity Enhanced and Cavity Ringdown Spectroscopy
  - Open Path [with retro-reflector]
  - Fiber optic Evanescent Wave Spectroscopy
- Spectroscopic Detection Schemes
  - Frequency or Wavelength Modulation
  - Balanced Detection
  - Zero-air Subtraction
  - Photoacoustic Spectroscopy
  - Noise Immune Cavity Enhanced Optical Heterodyne Molecular Spectroscopy (RICE-OHME)

CW IR Source Requirements for Spectroscopy

<table>
<thead>
<tr>
<th>REQUIREMENTS</th>
<th>SOURCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity</td>
<td>Power</td>
</tr>
<tr>
<td>Selectivity</td>
<td>Line Width</td>
</tr>
<tr>
<td>Multi-gas Components</td>
<td>Tunable ( \lambda )</td>
</tr>
<tr>
<td>Directionality</td>
<td>Beam Quality</td>
</tr>
<tr>
<td>Rapid Data Acquisition</td>
<td>Fast Response</td>
</tr>
<tr>
<td>Room Temperature</td>
<td>No Consumables</td>
</tr>
</tbody>
</table>
Spectral Coverage by Diode & QC Lasers

Key Characteristics of Quantum Cascade Lasers
- QC laser wavelengths cover entire range from 3.5 to 66 μm determined by thickness of the quantum well and barrier layers of the active region
- Intrinsically high power lasers (determined by number of stages of injector-active quantum well gain regions)
  - CW: 100 mW @ 80°K, mWs @ 300 °K
  - Pulsed: 1 W peak at room temperature, ~50 mW avg. @ 0 °C (up to 80% duty cycle)
- High Spectral purity (single mode: <kHz - 330MHz)
- Wavelength tunable by current or temperature scanning
- High reliability: long lifetime, robust operation and reproducible emission wavelengths

Pulsed QC Laser Based CO Gas Sensor

TEC cooled QC Laser Housing

CO Absorption: Ambient Air Sample

CO Concentration Measurements
- Measured concentration: 782 ppb
- Total pressure: 85 Torr
- Pathlength: 1 m

Sensitivity ~7 ppb

Frequency, cm⁻¹

Time, hrs:min:sec (March 8, 2001)
Motivation for NH₃ Detection

- 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
- Spacecraft related gas monitoring
- Pollutant gas monitoring
- Atmospheric chemistry
- Medical diagnostics (kidney & liver dysfunctions)

Infrared NH₃ Absorption Spectra

Ammonia Absorption Spectrum @ ~10μm

Frequency, cm⁻¹

6.7 ppm
1 m pathlength
95 Torr

Important Biomedical Target Gases

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Formula</th>
<th>Trace Concentration in Blood (ppb)</th>
<th>Biological/Pathology Indication</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitric Oxide</td>
<td>NO</td>
<td>6 - 100</td>
<td>Inflammatory and immune response (e.g., asthma) and vascular smooth muscle response</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>CO</td>
<td>400 - 3000</td>
<td>Smoking response, CO poisoning, vascular smooth muscle response, platelet aggregation</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td>H₂O₂</td>
<td>1 - 5</td>
<td>Airway inflammation, Cotton wool spots</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>CCl₄</td>
<td>100 - 1000</td>
<td>Liver disease and acute allograft rejection in long-term transplant recipients</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>HCHO</td>
<td>400 - 1500</td>
<td>Cns neurotoxic, breast cancer</td>
</tr>
</tbody>
</table>

Cavity ring-down spectroscopy

\[
I = I_0 \exp \left( - \frac{t}{\tau} \right)
\]

\[
T = \frac{1}{c \cdot \alpha \cdot \ln(R/R_0)}
\]

\[
\alpha = \frac{1}{c \left( \frac{1}{\tau} + \frac{1}{\tau_{empty}} \right)}
\]

CRDS Based Gas Sensor

Function Generator
Current Source
PC
Function Generator
TFT Display
Residual
Detector
A/D Converter
Infrared Co2
Gas Flow
Infrared Co2
NO absorption in Nitrogen

Absorption spectrum of NO in N2 at 1920.7 cm⁻¹

- NO: N2 Calibration mixture: 100 Torr
- NO concentration: 490 ppm
- Effective optical path ~ 70 m (1350 passes)
- Detection sensitivity: 1.0×10⁻⁷ cm³ Hz⁻¹/² (NE: sensitivity: 9 ppm)

Novel compact gas cell design for Off-Axis ICOS

- Adjustment screws are utilized to make spherical mirror astigmatic

Exhaled Carbonyl Sulfide

- A 2001 study by the T. H. Risby group at John Hopkins University demonstrated that elevated levels of COS could have a diagnostic role in the detection of acute allograft rejection in lung transplant recipients

Measured with gas chromatography and flame ionization detection

COS Spectra for 13-ppm
2-Tunable Pulsed QC Laser GCEC Architecture

Photoacoustic Spectroscopy with a Solid State Resonator

QEPAS based Gas Sensor Assembly

Measured and Simulated CH₄ Spectrum

Laser Spectrum of Ultra-Broadband QC Laser

Summary and Future Directions

- Quantum Cascade Laser based Trace Gas Sensors
  - Compact, tunable, and robust
  - High sensitivity (<10⁻⁶) and selectivity (3 to 300 MHz)
  - Fast data acquisition and analysis
  - Detected trace gases: NH₃, CH₄, N₂O, CO₂, CO, NO, H₂O, OCS, CH₂O, C₂H₅OH and nitric species
- Applications in Trace Gas Detection
  - Industrial process control and chemical analysis
  - Environmental monitoring (NASA, NCAR, NOAA, EPA)
  - Medical Diagnostics (NO, CO)
- Future Directions
  - Thermoelectrically cooled, cw quantum cascade lasers and amplifiers
  - Cavity ring down and QEPAS spectroscopy
  - Near IR and Far-IR wavelengths quantum cascade lasers