Chemical Sensors using Quantum Cascade Lasers

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- Motivation and Technology Issues
- Infrared QC Laser-based Gas Sensors
  - Pulsed quasi-room temperature sensors
  - CW cryogenically cooled sensors
- Outlook and Summary

Wide Range of Gas Sensor Applications

- Urban and Industrial Emission Measurements
  - Industrial Plants – Fence-line perimeter monitoring
  - Combustion Diagnostics
  - Automobile
- Rural Emission Measurements
  - Agriculture
- Environmental Monitoring
  - Atmospheric Chemistry
  - Volcanic Emissions
- Spacecraft and Planetary Surface Monitoring
  - Crew Health Maintenance & Life Support
- Diagnostic and Industrial Process Control
  - Petrochemical and Sensinghostor Industry
- Medical Diagnostics
  - Fundamental Science-Kinetics and Photochemistry
- Law enforcement and military chemical sensing

Air Composition

<table>
<thead>
<tr>
<th>Main Components</th>
<th>Trace Components</th>
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<tbody>
<tr>
<td>Nitrogen</td>
<td>Methane</td>
</tr>
<tr>
<td>78%</td>
<td>1.7 ppm</td>
</tr>
<tr>
<td>Oxygen</td>
<td>CO</td>
</tr>
<tr>
<td>21%</td>
<td>0.4 ppm</td>
</tr>
<tr>
<td>Water</td>
<td>N₂O</td>
</tr>
<tr>
<td>0.8%</td>
<td>0.3 ppm</td>
</tr>
<tr>
<td>CO₂</td>
<td>O₃</td>
</tr>
<tr>
<td>0.03%</td>
<td>0.03 ppm</td>
</tr>
<tr>
<td></td>
<td>H₂CO</td>
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<tr>
<td></td>
<td>0.001 ppm</td>
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Existing Methods for Trace Gas Detection

Non-Optical
- Mass Spectroscopy
- NMR
- Chemical
- Electro Chemical
- Galvanic
- Fourier Transform
- Gas Filter Correlation

Optical
- Non-Dispersive
- Gas Chromatography
- Dispersive
- Microwave Spectroscopy
- Laser Spectroscopy

Absorption Spectroscopy

Beer-Lambert’s Law

\[ I = I_0 e^{-\alpha v L} P_0 \]

\( \alpha(v) \): absorption coefficient \( \text{cm}^{-1} \text{cm}^{-1} \)
\( v \): frequency \( \text{cm}^{-1} \)
\( L \): path length \( \text{cm} \)

Molecular Absorption Coefficient

\[ \alpha(v) = \frac{c S g(v-v_0)}{P_0} \]

\( c \): total number of molecules of absorbing gas \( \text{cm}^{-3} \)
\( S \): molecular line intensity \( \text{cm}^{-1} \text{ molecule}^{-1} \)
\( g(v-v_0) \): normalized line-shape function \( \text{cm}^{-1} \) (Gaussian, Lorentzian, Voigt)

IR Source Requirements for Spectroscopy

- Sensitivity
- Specificity
- Multi-gas Components
- Directionality
- Rapid Data Acquisition
- Room Temperature

SOURCE
- Power
- Line Width
- Tunable
- Beam Quality
- Response
Spectral Coverage by Diode & QC Lasers

<table>
<thead>
<tr>
<th>Wavelength, μm</th>
<th>NH3</th>
<th>H2O</th>
<th>NO</th>
<th>N2</th>
<th>O2</th>
<th>CH3OH</th>
<th>CH3SH</th>
<th>CH4</th>
<th>NH3</th>
<th>CH3</th>
<th>H2O</th>
<th>CO2</th>
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[Graph showing spectral coverage by diode and QC lasers]

Sensitivity Enhancement Techniques

- Optimum Absorbing Transition
- Overtone or Combination Band
- Fundamental Band
- Long Pathlength
- Multi-pass Cell
- Cavity Enhanced, Cavity Ringdown
- Open Path with retro-reflector
- Fiber optic Evanescent Wave Spectroscopy
- Detection Schemes
  - Frequency Modulation, Wavelength Modulation
  - Two-tone frequency modulation
  - Balanced Detection
  - Zero-air Subtraction

Key Characteristics of Quantum Cascade Lasers

- Laser wavelengths cover entire range from 3.5 to 66 μm determined by layer thickness of same material
- Intrinsically high power lasers (determined by number of stages)
  - CW: ~100 mW @ 80 K, mW's @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 - 330 MHz)
- Wavelength tunable by current or temperature scanning
- High reliability: low failure rate, long lifetime, robust operation and reproducible wavelength

QC-DFB Laser: Pulsed vs. CW

<table>
<thead>
<tr>
<th>ADVANTAGES</th>
<th>SPECIFIC ISSUES</th>
</tr>
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<tbody>
<tr>
<td>Laser can be operated at near-room temperature (i.e., cooling)</td>
<td>Broad asymmetric line width (&lt;100 MHz FWHM) related to heating during the pulse</td>
</tr>
<tr>
<td>Facilitates temperature control</td>
<td>How to tune the frequency</td>
</tr>
<tr>
<td>No consumables (liquid N2)</td>
<td>Reduced average power</td>
</tr>
<tr>
<td>Unattended remote monitoring</td>
<td>More sophisticated electronics are required for driving QC laser and data acquisition are required</td>
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<tr>
<td>Decreased instrument size &amp; weight</td>
<td></td>
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Simulated v2 NH3 Absorption Spectrum

[Graph showing simulated v2 NH3 absorption spectrum]

Pulsed QC Laser Based Gas Sensor

[Diagram of pulsed QC laser based gas sensor]

[Graph comparing QC-DFB laser properties]

[Diagram showing sensitivity enhancement techniques]
Absorption Spectrum of Room Air

Trace Reactive Gases As Physiological Messengers
- NO production is tied to numerous physiological processes in human
  - vasorelaxation, inflammation, thrombosis, immunity
  - reduced NO production associated with atherosclerosis and ulcers
  - enhanced NO production associated with asthma, endotoxin shock, diabetes, and edema
- CO production is important in vascular muscle cell physiology and platelet aggregation
- Trace levels of these and other breath species are associated with numerous physiological pathologies
- Typical endogenous production rates are 10 pmol/min requiring trace gas detection levels in the range of 1 to 10 ppbv.

Cavity Ring-Down Spectroscopy

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

\[ R > 0.999... \]

\[ \tau = \frac{1}{c} \frac{1}{\alpha} \ln \left( \frac{R}{R_2} \right) \]

CRDS Based Gas Sensor

Laser-Cavity Resonances (spikes)

NO absorption, 60 Torr Total Pressure
Tuning Range of Broadly λ-Tunable ECDL

ECDL Configuration for Pulsed QC Laser

Laser Spectrum of Ultra-Broadband QC Laser

Photoacoustic Spectroscopy with a Solid State Resonator

Close-up of QEPAS sensor

CH₄ Spectrum Acquired with QEPAS
Summary

- Quantum Cascade and Diode Laser Based Trace Gas Sensors
  - Compact, tunable, robust, fieldable
  - High sensitivity (~2 x 10^-9 to 10^-8) and selectivity (10-300 MHz)
  - Fast data acquisition and analysis
  - Detected trace gases: NH3, CH4, H2CO, NO2, N2O, H2O, CO2, CO, NO, HCl, SO2, C2H5OH, isotopic species of NGC, NO2, NOCl

- Applications in Trace Gas Detection
  - Environmental monitoring and atmospheric chemistry: H2CO, CH4, CO, CO2, CH3 (NASA, NCAR, NOAA, EPA)
  - Industrial process and chemical analysis: NO
  - Medical diagnostics: NO, CO, CO2

- Future Directions
  - Longer and shorter IR wavelengths with improved QC lasers
  - QC amplifiers and broadly tunable QC lasers
  - Cavity enhanced and cavity ringdown spectroscopy