Trace gas detection in ambient air using a 7.9 µm QC-DFB laser

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- Background and Motivation
- Detection of simple molecules in air, cw laser operation
- Detection of ethanol and linear regression data analysis
- Pulsed operation based laser spectrometer
- Summary and future outlook
### Spectral Coverage by Diode/QC Lasers

<table>
<thead>
<tr>
<th>Compound</th>
<th>Coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td></td>
</tr>
<tr>
<td>H₂S</td>
<td></td>
</tr>
<tr>
<td>NO₂</td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td></td>
</tr>
<tr>
<td>C₆H₆</td>
<td></td>
</tr>
<tr>
<td>CH₃OH</td>
<td></td>
</tr>
<tr>
<td>NH₃</td>
<td></td>
</tr>
<tr>
<td>H₂CO</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td></td>
</tr>
</tbody>
</table>
Motivation for CH\textsubscript{4} and N\textsubscript{2}O Detection

- Contribution to global warming
- Important in tropospheric and stratospheric chemistry
- Emitted by agricultural sources
- CH\textsubscript{4} leaks from gas pipelines
Sources of atmospheric CH$_4$

- Landfills
- Enteric Fermentation
- Natural Gas Systems
- Coal Mining
- Manure Management
- Rice Cultivation
- Stationary Sources
- Petroleum Systems
- Mobile Sources
- Wastewater Treatment
- Petrochemical Production
- Agricultural Residue Burning
- Silicon Carbide Production

http://www.epa.gov
Sources of atmospheric N$_2$O

- Agricultural Soil Management
- Mobile Sources
- Stationary Sources
- Adipic Acid
- Nitric Acid
- Manure Management
- Human Sewage
- Agricultural Residue Burning 0.1
- Waste Combustion 0.1

http://www.epa.gov
CH$_4$, H$_2$O and N$_2$O Absorption Spectra

Frequency, cm$^{-1}$

Laser frequency

Band centered at $\sim$1500 cm$^{-1}$
Trace Gas Detection with a Multipass Cell

Pulse generator

Laser diode driver

Temperature monitor

Room air

"Zero" air

QC laser in dewar

Collimating optics

Multipass cell

MCT detector

Data Acquisition Card

Computer

Trigger

Signal

To vacuum pump
Absorption Spectrum of Room Air

- Absorption, %
- Frequency, cm$^{-1}$

Peaks at:
- 1259.0, 1259.5, 1260.0, 1260.5, 1261.0

Species:
- HDO
- CH$_4$
- N$_2$O
- H$_2^{18}$O
- CH$_4$ N$_2$O N$_2$O
Detection of $^{13}$CH$_4$ in Ambient Air

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**Absorption, %**

**Frequency, cm$^{-1}$**

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$^{13}$CH$_4$
IR Absorption Spectrum of Ethanol

Frequency, cm$^{-1}$

QC laser frequency
High-resolution IR Ethanol Spectrum

Pure ethanol vapor
P=1 Torr

Ethanol vapor + air
P_{eth}=1 Torr, P=36.6 Torr
Linear Regression Technique

$1-D : \quad y_i = ax_i$

$MLR : \quad y_i = \sum_{k=1}^{N} a_k x_{ki}$
# Results of the Linear Regression Analysis

<table>
<thead>
<tr>
<th>Species</th>
<th>Measured concentration – sample 1</th>
<th>Measured concentration - sample 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MLR</td>
<td>1-D regression</td>
</tr>
<tr>
<td>C₂H₅OH</td>
<td>11.60×10⁻⁶</td>
<td>12.12×10⁻⁶</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.72×10⁻⁶</td>
<td>-</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.302×10⁻⁶</td>
<td>-</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.72×10⁻³</td>
<td>-</td>
</tr>
</tbody>
</table>
# Pulsed Operation of a QC-DFB Laser

## ADVANTAGES
- Laser can be operated at near-room temperature
- Easy temperature handling
- No consumables (liquid N₂)
- Compact

## DISADVANTAGES
- Broader linewidth (~400 MHz)
- Less average power
- More sophisticated electronics for driving QC laser and data acquisition
Pulsed QC-DFB Spectrometer

- DAQCard-1200
- Pulse generator
- High current pulser
- Gated integrator
- Low impedance stripline
- QC-DFB laser on thermoelectric cooler (in vacuum)
- Temperature controller
- 20 kS/s
- 4 ns
- 3-10 A
- Gas cell
- IR detector
- 20 kS/s
Pulsed QC Laser Housing
Tuning of the Pulsed QC-DFB Laser

\[ \Delta v = -0.084 \text{ cm}^{-1} \times \Delta T \]
Lineshape dependence on electric coupling

With 7.9Ω coupling resistor

Without coupling resistor

~0.015 cm⁻¹
Summary and Future Outlook

• A cw QC-DFB laser based gas sensor at 7.9 µm was designed and tested for methane, nitrous oxide, water and ethanol detection in ambient air; a detection limit of 2.5 ppb for CH₄, 1.0 ppb for N₂O, 60 ppb for H₂O and 125 ppb for C₂H₅OH was achieved

• A new technique for processing congested spectra of VOC was developed and applied to ethanol detection

• A spectrometer based on the near-RT operated pulsed QC-DFB laser was designed and tested

Future development

♦ Medical applications - NO detection (~5 µm)
♦ Field applications
♦ Development of cavity-enhanced detection methods