Gas sensing applications of quantum cascade lasers

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● Specific features of the QC lasers
● Spectroscopic detection of trace gases with CW QCs:
  □ multipass cell
  □ cavity ringdown
● Using pulsed QC lasers for trace gas detection
QC-DFB Compared to Diode Lasers
Distributed Feedback QC Laser-Schematic

- Grating selects well defined single wavelength
- Tunable with temperature
<table>
<thead>
<tr>
<th>Compound</th>
<th>N₂O</th>
<th>H₂S</th>
<th>NO₂</th>
<th>NO</th>
<th>C₆H₆</th>
<th>CH₃OH</th>
<th>NH₃</th>
<th>H₂CO</th>
<th>CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<tr>
<td>Spectral Coverage by Diode/QC Lasers</td>
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Trace Gas Detection with a Multipass Cell

1. Pulse generator
2. Laser diode driver
3. Temperature monitor
4. Room air
5. "Zero" air
6. QC laser in dewar
7. Collimating optics
8. Multipass cell
9. To vacuum pump
10. Signal
11. Data Acquisition Card
12. Computer
13. MCT detector
CH$_4$, H$_2$O and N$_2$O Absorption Spectra

Laser frequency

Band centered at ~1500 cm$^{-1}$
IR Absorption Spectrum of Ethanol

QC laser frequency

Frequency, cm\(^{-1}\)

1000  2000  3000
High-resolution IR Ethanol Spectrum

Pure ethanol vapor
P=1 Torr

Ethanol vapor + air
$P_{\text{eth}}=1$ Torr, $P=36.6$ Torr
Reference and Sample Spectra of Ethanol in Air

Sample absorbance vs. Frequency, cm$^{-1}$

- Sample absorbance
- Reference absorbance

$P=37$ Torr
Linear Regression Technique

\[ 1 - D : \quad y_i = a x_i \]

MLR : \[ y_i = \sum_{k=1}^{N} a_k x_{ki} \]
## 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>
Cavity Ring-Down Spectroscopy

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

\[ \tau = \frac{l}{c} \cdot \frac{1}{\alpha l - \ln \sqrt{R_1 R_2}} \]

\[ \alpha = \frac{1}{c} \left( \frac{1}{\tau} - \frac{1}{\tau_{empty}} \right) \]
Optical Cavity Transmission

Laser line

Cavity modes

\[
T \approx \frac{\Delta v_{\text{cavity}}}{\Delta v_{\text{laser}}}
\]

\[
\Delta v_{\text{cavity}} = \frac{c(1-R)}{2\pi d} = \frac{1}{2\pi \tau}
\]

\[
\tau = 3.5\mu s \quad \Rightarrow \quad \Delta v_{\text{cavity}} = 45\text{kHz}
\]
Absorption lines: NO, H$_2$O and CO$_2$
CRDS Gas Sensor

Function Generator
Current Source

Function Generator

PZT Driver

A/D Converter

Trigger Circuit

QCL

Removable mirror

Reference Cell

Ringdown Cell

Gas flow

IR Detectors
Laser Linewidth Estimate

\[ \Delta \nu_{QC}/\text{FSR} = \Delta t(\text{spike})/\Delta t(\text{FSR}) \approx 7.1 \times 10^{-3} \]

FSR = \frac{c}{2l} = 405 \text{ MHz}

\[ \Delta \nu_{QC} \approx 3 \text{ MHz} \]
Recorded Ringdown Events

![Signal vs Time Graph](image)
Distribution of Ringdown Times

\[ \langle \tau \rangle = 3.48 \mu s \]

\[ \frac{\sigma(\tau)}{\langle \tau \rangle} = 2.3 \times 10^{-3} \]

\[ \sigma(\alpha) = \frac{1}{c \tau \langle \tau \rangle} \sigma(\tau) \]

\[ \sigma(\alpha) = 2.2 \times 10^{-8} \text{ cm}^{-1} \]
NO absorption, 60 Torr Total Pressure

\[ \text{NO:N}_2 \]
\[ 620 \text{ ppb} \]
\[ 1921.6 \text{ cm}^{-1} \]

\[ 48.4 \pm 0.7 \text{ ppb} \]
# Pulsed Operation of a QC-DFB Laser

## ADVANTAGES
- Laser can be operated at near-room temperature
- Facilitates temperature control
- No consumables (liquid N\(_2\))
- Compact

## DISADVANTAGES
- Broader linewidth (~300 MHz)
- Reduced average power
- More sophisticated electronics for driving QC laser and data acquisition are required
Pulsed QC-DFB Laser Housing
Manipulating the Pulsed QC Laser Frequency

1. Fast scanning of the laser frequency with a subthreshold current
   
   \[ v_0 \rightarrow v_1 \rightarrow v_2 \rightarrow \ldots \rightarrow v_N \]

2. Fast cycling of the laser frequency with a subthreshold current and slow scanning with temperature (wavelength modulation)

   \[ v_-(T) \quad v_0(T) \quad v_+(T) \]

   \[ T \]

   \[ \ldots \]
Pulsed QC-DFB Spectrometer

- Temperature controller
- QC-DFB laser housing
- Detector
- "Zero air"
- "20 kS/s"
- R1
- R2
- Pulse generator
- Gated integrator
- DaqCard-1200
- High current pulser
Linearization of Fast Frequency Scan

FSR = 0.027 cm\(^{-1}\)

Acquisition rate \(\frac{1}{2} \times 20\,\text{kS/s}\)
Spectral Shape of a Pulsed QC Laser Line

- Measured lineshape
- Simulated: FT of a 3.1 ns rectangular pulse convolved with an absorption line envelope

FWHM of peak (deconvolved)
9.6×10^{-3} \text{ cm}^{-1}
(290 MHz)

75\% of energy is in the FT limited spectrum

Laser threshold
5 \text{ ns FWHM}

Current pulse
“Fast Scan” Detection of Trace Gases in Air

Pathlength: 100 m (multipass cell)

Pressure: 85 Torr
Extracting the Concentration

ACQUIRED DATA

LASER LINE SHAPE

SIMULATED SPECTRUM

DERIVATIVE

CONVOLUTION

DERIVATIVE

LINEAR REGRESSION

\[ y = kx \]

\[ c_{sample} = kc_{sim} \]
## Results of the Data Analysis

<table>
<thead>
<tr>
<th>Molecular species</th>
<th>CH$_4$</th>
<th>HDO</th>
<th>N$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration assumed in simulations, ppm</td>
<td>1.7</td>
<td>2.408</td>
<td>0.32</td>
</tr>
<tr>
<td>Simulated peak absorption</td>
<td>4.58%</td>
<td>0.29%</td>
<td>2.15%</td>
</tr>
<tr>
<td>Number of scans</td>
<td>1000</td>
<td>1000</td>
<td>200</td>
</tr>
<tr>
<td>Linear regression slope</td>
<td>1.195±0.005</td>
<td>1.78±0.05</td>
<td>0.998±0.014</td>
</tr>
<tr>
<td>Resulting concentration, ppm</td>
<td>2.032±0.009</td>
<td>4.28±0.12</td>
<td>0.319±0.004</td>
</tr>
</tbody>
</table>
NH$_3$ Sensor Based on Pulsed 10.05 $\mu$m laser

One IR detector
Sensitivity $\sim$0.3 ppm
Ammonia Spectrum at 993 cm\(^{-1}\)

6.7 ppm
1m pathlength
Two-Channel Data Acquisition

Diagram showing the connections and components involved in a two-channel data acquisition system, including a function generator, pulse generator, high current pulser, gated integrators, data acquisition card, and temperature controller.
CO Absorption: Ambient Air Sample

- Measured concentration: 780 ppb
- Total pressure: 95 Torr
- Pathlength: 1m
- Two IR detectors
- Sensitivity ~10 ppb
- Frequency, cm$^{-1}$: 2158.300 cm$^{-1}$

Fractional absorption vs. Frequency, cm$^{-1}$
CO Concentration Measurements

CO concentration, ppm

Time, hrs:min:sec (March 8, 2001)
Summary and Future Outlook

• A variety of approaches can be used for QC-DFB laser based spectroscopic detection of trace species;
• Molecules detected with QC lasers at sub-ppm levels in the Rice Laser Science group: CH$_4$, N$_2$O, NH$_3$, CO, NO, H$_2$O, C$_2$H$_5$OH

Future developments
♦ Make compact gas sensors based on pulsed thermoelectrically cooled QC-DFB lasers, short optical path and two-channel detection
♦ Wider range of molecules, including bigger organic molecules
♦ Compact cavity ringdown sensors when thermoelectrically cooled CW QC lasers become available