Mid-infrared detection of atmospheric CH₄, N₂O and H₂O based on a single continuous wave quantum cascade laser

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Introduction: Nitrous Oxide, Methane and Water

NO$_2$, CH$_4$ & H$_2$O are three major atmospheric greenhouse gases contributing to global warming and climate change.

- Nitrous Oxide (N$_2$O)
  - A global warming potential (GWP) of 298
  - A longer atmospheric lifetime than carbon dioxide (CO$_2$)
  - 330 ppbv atmospheric concentration level with an increasing rate of ~0.7 ppbv/yr

- Methane (CH$_4$)
  - A global warming potential of 25
  - A short lifetime (12 yrs) compared with CO$_2$ and N$_2$O
  - 1.8ppm atmospheric concentration level

- Water vapor (H$_2$O)
  - A dominant energy carrier in the atmosphere and regulates planetary temperatures through the absorption and emission of radiation.

A simultaneous detection of NO$_2$, CH$_4$ & H$_2$O's helpful for a better understanding of global warming and climate change

Spectroscopy Fundamentals

Beer's Law: \[ \frac{I_i}{I_0} = \exp(-kL) \]

where: 
- \( I_i \) is transmitted light intensity
- \( I_0 \) is incident light intensity
- \( k \) is absorption coefficient
- \( k_v = S(T)P_x\phi_v \)

WMS-2f detection:
- Ramp (Hz) t to sweep over absorption lines
- Fast sinusoidal modulation f \( \sim \) kHz
- Demodulate at 2f (2nd derivative line-shape)

+ Multipass Gas Cell
Absorption Line Selection

- Most gas species have their strong fundamental absorption lines in the mid-infrared spectral range
- N$_2$O, CH$_4$ and H$_2$O absorption lines occur at wavelengths from 3 to 8.5µm
- The strongest absorption bands are located at 3.3 µm for CH$_4$, 4.5 µm for N$_2$O, and 5.9 µm for N$_2$O
- A relatively strong absorption line at 7.7 µm is a good compromise for the detection of N2O, CH4 and H2O
- Three neighboring absorption lines are well separated from each other occur within a relatively small spectral range of 0.5 cm$^{-1}$

N$_2$O: 1297.05cm$^{-1}$
CH$_4$:1297.486cm$^{-1}$
H$_2$O: 1297.184cm$^{-1}$

QCL Characterization & Performance Evaluation

Corning-Maxion- Thorlabs QCL, 7.73µm center-wavelength

Performance evaluation for a 7.73-µm CW DFB-QCL at different operating temperatures and injection currents. (a) QCL output power response curves; (b) Emission wavenumber curves.
Sensor System Configuration

- Laser source
  - Current: 240 mA
  - Temperature: 15 °C

- Spatial filter two lenses & one pin hole
  - $f_1=50$ mm and $f_2=100$ mm
  - 400 μm pinhole

- Multipass cell
  - Aerodyne Research Inc.
  - 76m effective optical path length
  - 32cm mutipass cell length

Performance Optimization and Assessment for N\textsubscript{2}O Detection

- Optimum operating conditions: 80 Torr and 4 mA
- Good linearity ($R^2=0.9977$)
- 1.7 ppb for a 2s sampling time
- 0.3 ppb for a 100s integration time
Performance Optimization and Assessment for CH₄ Detection

- Optimum operating conditions: 100 Torr and 4 mA
- Good linearity ($R^2=0.997$)
- 8.5 ppb for a 2s sampling time
- 2.5 ppb for a 50s integration time

Performance Optimization and Assessment for H₂O Detection

- Optimum operating conditions: 400 Torr and 5.5 mA
- Good linearity ($R^2=0.997$)
- 16 ppm for a 1s sampling time
- 5 ppm for a 30s averaging time
Simultaneous Detection of CH₄, N₂O and H₂O

(a) Direct output of the mid-infrared detector,
(b) 2f signal of the sensor system for simultaneous three gas species (N₂O, CH₄, and H₂O) detection at a pressure of 100 Torr and a modulation depth of 4 mA.

Laboratory Measurements

(a) Simultaneously measured concentrations of N₂O, CH₄, and H₂O in laboratory ambient air.
(b) Allan deviation of N₂O, CH₄, and H₂O within constant concentration periods.
Atmospheric N$_2$O, CH$_4$ and H$_2$O Concentration Measurements

(a) A CW QCL based N$_2$O, CH$_4$ and H$_2$O sensor system;
(b) Measurement results of simultaneous monitoring of three gas concentrations in the atmosphere for a 6 hour time duration.

Summary and Conclusions

- Development of a 7.73 $\mu$m CW DFB QCL based absorption sensor for simultaneous detection of nitrous oxide, methane, and water vapor using a 76 m commercial optical path length astigmatic multipass Herriott.
- A minimum detection concentrations of 1.7 ppb for N$_2$O, 8.5 ppb for CH$_4$, and 1 ppm for H$_2$O with 2 sec integration time were achieved.
- This single QCL based multi-gas detection system possesses application in environmental monitoring and breath analysis.
Future Outlook of mid-IR Sensor Technologies

Current sensor platform:
- 18 in multipass cell
- 24in x 18in board
- QCL
- High power consumption for current and temperature control

Next generation sensor platform:
- 6.5 in novel multipass cell
- 12.5in x 8in board (folded optical path)
- Interband cascade laser(s)
- Low power consumption for current and temperature control

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Sensor size: 2 in cube

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