Trace gas sensing applications of quantum cascade lasers

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• Background and motivation
• Specific issues related to pulsed QC-DFB lasers
• Spectroscopic gas sensing with pulsed QC-DFB lasers
• CRDS with a CW QC-DFB laser
• Summary and future developments
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 Semiconductor Industry

• Medical Diagnostics

• Fundamental Science-Kinetics and Photochemistry
Absorption spectroscopy

\[ I(\nu) = I_0(\nu) \times \exp\left[-\alpha(\nu) \cdot nL\right] \Rightarrow n = -\ln\left(\frac{I(\nu)}{I_0(\nu)}\right) \cdot \frac{1}{\alpha(\nu)L} \]
Molecular absorption and laser sources

QC lasers (pulsed with TEC, CW with cryogenic cooling*; high output power)

Diodes + PPLN, P~1-10 μW
DFG and OPO
Room temperature

QPM GaAs (available in future)

DIODE LASERS

Cryogenic (P<1 mW)

To 24 μm

Wavelength, μm
QC laser with distributed feedback (QC-DFB)

- Grating selects well defined single wavelength
- Tunable with temperature
QC-DFB compared to FP diode laser

FP modes

Single Bragg mode
Pulsed QC-DFB lasers

- **Advantages:**
  - Wider availability – full wavelength coverage
  - Thermoelectric cooling
  - Lower power consumption

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QC-DFB laser line broadening mechanisms

\[ \Delta \nu = \frac{2}{\tau} \]
## Pulsed QC-DFB lasers

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QC-DFB laser tunability vs. wavelength

![Graph showing QC-DFB laser tunability vs. wavelength. The graph plots tunability (cm⁻¹/°C) against laser wavelength (µm) for various gases, including CO₂, NO, CH₄, N₂O, NH₃, and C₆H₆.]
Record narrow linewidth of pulsed QC Laser

\[ \tau = 17 \text{ ns} \]
\[ I = 9A \left( I_{th} + 5\% \right) \]
\[ \Delta \nu_l \approx 200 \text{ MHz} \]

CO\textsubscript{2}, 1.3 Torr
45 cm

DOI: 10.1007/s00340-002-0963-z
Pulsed QC laser wavelength scanning

Solution: Sub-threshold current

Synchronous digitally synthesized steps of tuning current (enables linearization of scan)

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

Pulsed QC laser housing

- Vacuum valve
- Output window (tilted 5° in horizontal plane)
- Low-impedance stripline feedthrough
- Adjustment screws for precise positioning of collimating lens
- 9-pin electric feedthrough; 4 pins are used for temperature monitoring and control
Two-channel data acquisition

- Function generator
- Reference detector
- Gated measurements
- 5 ns current pulse
- Temperature controller
- Data acquisition card
- Gated integrator 1
- Gated integrator 2
- Pulse generator
- High current pulser
CO absorption: ambient air sample

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

Fractional absorption

Frequency, cm\(^{-1}\)
CO concentration in two gas cylinders

CO concentration, ppb

Time, hh:mm

UHP nitrogen

173±12 ppb

Colorado mountain air

359±12 ppb
Longer wavelength: QC-DFB laser at $\lambda = 15.5 \, \mu m$

- Fast sensitive detectors are not available
- Quantum detectors are expensive and LN2 cooled

! What about a thermal detector?
Pyroelectric detector and preamplifier

Detector/preamplifier band: 8 to 1150 Hz
Sensitivity: 3.84 V/mW

18300 Hz
Pyroelectric detector noise and detectivity

IF:
\[ f = 200 \text{ Hz} \]
\[ \Delta f = 1 \text{ Hz} \]
\[ W = 100 \mu \text{W} \]

THEN:
\[ \text{SNR} = 38,000 \]
Detectable absorption \(<3 \times 10^{-5}\)
Longer wavelength: QC-DFB laser at $\lambda=15.5 \, \mu\text{m}$

- Operation current $\sim 10\text{A}$, peak thermal dissipation $\sim 300\text{W}$
  - Average dissipation $>5\text{W}$ at 1 MHz repetition rate
- Low thermal tunability coefficient

! Alternative tuning method required
Frequency tuning of pulsed QC laser by using repetition rate modulation
16 µm QC laser based gas sensor
Fast wavelength scan by repetition rate modulation

![Graph showing signal and repetition rate over time. The graph indicates a fast wavelength scan by repetition rate modulation. The signal reaches a maximum power of 130 µW.](image)
Calibration of fast wavelength scan

\[ \text{Relative wavenumber, cm}^{-1} \]

\[ \text{Repetition rate, kHz} \]

\[ 6.83 \times 10^{-4} \text{ cm}^{-1}/\text{kHz} \]
Ambient air absorption – 45 cm path, 1 atm

100 scans averaged

CO₂: 465 ppmv

H₂O: 5.1 Torr

(25% humidity - ???)

Purely rotational line

Laser line shape
Are CW QC lasers better?

Of course they are!

• Narrow linewidth without effort
• High average power

Can be used for such techniques as:

• Cavity ring-down spectroscopy
• Nonlinear (saturation) spectroscopy
• Photoacoustic spectroscopy
Cavity ring-down spectroscopy

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

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

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

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

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

\[ \tau = 3.5 \mu s \quad \Rightarrow \quad \Delta v_{\text{cavity}} = 45 \text{ kHz}; \quad T = \frac{45 \text{ kHz}}{3 \text{ MHz}} = 1.5\% \]
NO absorption, 60 Torr total pressure

- NO:N₂
- 620 ppb
- 1921.6 cm⁻¹

- 48.4±0.7 ppb

Relative frequency, cm⁻¹

$\frac{1}{\tau}, \mu s^{-1}$
Summary

• QC-DFB lasers are powerful and robust sources for spectroscopic chemical detectors

• To date, commercially offered QC-DFB lasers are designed for pulsed operation mode with thermoelectric cooling

• Pulsed operation imposes specific limitations to the laser linewidth, noise, and power, which can be addressed by proper sensor design.

• CW QC-DFB lasers have better performance characteristics and allow the use of a wider range of high-sensitivity spectroscopic methods. However, most SW QC lasers require cryogenic cooling, and their availability is presently limited.

   **TE cooled CW QC-DFBs are coming!!!**