Quantum cascade laser-based photoacoustic sensor for environmental pollution monitoring

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Outline

- Motivations
- QCLs
- Photoacoustic spectroscopy (PAS)
- Results with the H-Cell for NO and CH₂O
- Fiber-Coupled PAS T-Cell
- Results with the T-Cell for CH₂O
- Conclusions and Prospective
Increasing awareness and new regulations for safety and emission control have created a strong demand for compact/portable low-cost, reliable trace gas sensors (ppb/ppt concentration)

- Urban and Industrial Emission Measurements
  - Industrial work areas
  - Combustion Processes (early fire sensing)
  - Vehicle Exhaust Emissions
- Rural Emission Measurements
  - Agriculture
- Environmental Monitoring
  - Atmospheric Chemistry
  - Volcanic Emissions
- Chemical Analysis and Industrial Process Control
  - Chemical, Pharmaceutical, Food
  - Semiconductor Industry
- Medical Diagnostics (e.g. breath analysis)
- Toxic Chemicals, Explosives, and Biological Agents
- Fundamental Science
Quantum Cascade Laser

- Band-structure engineered devices
  - Quantum well nanostructures
  - Cascading (each electron creates N laser photons and the number of periods N determines laser power)
- QCLs operate in the range 3 - 200 µm
- Compact, reliable, stable, long lifetime, commercial availability
- High output powers
  - Pulsed peak powers of 10 W;
  - High temperature operation ~ 425 K
  - Average power levels up to 600 mW
- Broad spectral tuning range in the mid-IR (4-24 µm)

MID-IR frequency range
- “fingerprint region”,
- fundamental roto-vibrational transitions,
- atmospheric windows
**The PA effect - Principle**

**Generation of an acoustic wave in a sample due to the absorption of a modulated laser beam**

\[ S = C \times P \times \alpha \]

\[ \alpha = N \sigma c \]

- \( S \): photoacoustic signal
- \( C \): Instrumental constant
- \( P \): (laser) power
- \( \alpha \): Absorption coefficient

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**Why the photoacoustic technique**

- Excellent sensitivity up to ppt with high power lasers
- Large dynamic range: linearity over a range of \( 10^6 \)
- High resolution
- Fast measurements
- Capability of *in situ* detection
- Feasible costs, compact set-up, *coupling with QCLs*
Why monitoring NO?

- **Environmental monitoring:**
  - Control of NO emissions from vehicles

- **Atmospheric pollution monitoring:**
  - Depletion of the Earth’s ozone layer
  - Generation of photochemical smog and acid rains

- **Non-invasive medical diagnostics:**
  - Human breath analysis
NO infrared spectrum

Selected line:
- @ 1871.06 cm$^{-1}$
- intensity $0.8 \times 10^{-20}$ cm/molecule

(HITRAN database)
Why monitoring formaldehyde?

- Atmospheric CH₂O is a key hydrocarbon oxidation product which leads to the photochemical generation of ozone and release of hydrogen radicals.

- Toxic pollutant due to: incomplete fuel combustion processes; cigarette smoke; fermental processes of organic materials.

- Potential trace contaminant in industrial manufactured products. Urea-formaldehyde and phenol-formaldehyde resins are used in foam insulations, as adhesives in the production of particle board and plywood, and in the treating of textiles.

Carcinogen

The USA Occupational Safety and Health Administration (OSHA) set standards for formaldehyde exposure limits: 0.75 parts per million in volume (ppmv) for long-term exposure (8-hour time weighted average) and 2 ppmv for short-term exposure (15 min).
ABSORPTION SPECTRA $\text{CH}_2\text{O}$

- Commercial available QCLs operating @RT
- $\{v_2\}$ 5.7 μm C=O stretching mode
- $\{v_1, v_5\}$ 3.6 μm
- ICL or lead salt laser
- $\text{H}_2\text{O}$ interference

Formaldehyde ($\text{H}_2\text{CO}$)

Assorbance (u.a.)

Wavenumber (cm$^{-1}$)

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Absorbance (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1759.2</td>
<td>0.3</td>
</tr>
<tr>
<td>1767.7</td>
<td>0.3</td>
</tr>
<tr>
<td>1776.7</td>
<td>0.3</td>
</tr>
<tr>
<td>1786.5</td>
<td>0.3</td>
</tr>
</tbody>
</table>

$\text{C}=\text{O}$ stretching mode

$\{v_2\}$ 5.7 μm

$\{v_1, v_5\}$ 3.6 μm

ICL or lead salt laser

$\text{H}_2\text{O}$ interference
H-Cell photoacoustic sensor

- LASER SOURCE DFB-QC (Alpes Lasers)
  - Emission 5.3 µm or 5.6 µm
  - Average optical power: 2-10 mW
  - Duty cycle: 1.4-2.0 %
  - TE cooling, RT operation

10cm x 5cm x 5cm
Cylindrical stainless steel resonator (L = 120 mm, R = 8 mm)
- Resonant on the first longitudinal mode → Q factor = 36
- Resonance frequency = 1372 Hz
- λ/4 buffer volumes on each side
- closed by antireflection coated ZnSe windows

MICROPHONES

EK-3024 (Knowles Electronics)
- Electret microphones
- Sensitivity ~ 20 mV/Pa
- Low noise
- Miniaturized
Calibration Measurements of the PAS NO sensor
Elia et al. Sensors 9, 3337-3356, (2009)

- NO absorption frequency: 1871.06 cm\(^{-1}\)
- Lock-In time constant: 10 s
- Cell parameters:
  - Resonance frequency: 1372 Hz
  - Q Factor: 36
  - Pressure: 1 atm
- QCL operating conditions:
  - PW = 42 ns
  - duty cycle 1.4%
  - P \sim 2 mW

Detection limit: 150 ppbv
Minimum detectable absorption coefficient: \(2.0 \times 10^{-9} \text{ cm}^{-1} \text{W/Hz}^{1/2}\)
\(\alpha_{\text{min}} = 1.3 \times 10^{-7} \text{ cm}^{-1}\)
Calibration Measurements of the PAS CH$_2$O sensor
Elia et al. Sensors 9, 2697-2705 (2009)

- Lock-In time constant: 10 sec.
- QCL operating conditions: PW= 42 ns, duty cycle 1.4% , P ~ 4 mW
- Gold coated PA cell
- Water interferences --> filters

Detection limit: 150 ppbv
Minimum detectable absorption coefficient: $2.0 \times 10^{-8}$ cm$^{-1}$W/Hz$^{1/2}$
$\alpha_{\text{min}} = 6.6 \times 10^{-7}$ cm$^{-1}$
State of Art Results

Needs a non-diverging laser beam

Alignment Optical System

Not portable System

Alignment-free setup
QCL- PAS CELL coupling via OPTICAL FIBRE “CIR” and “PIR”
(Set-up more compact and handy)

PHOTOACOUSTIC CELL WITH T-GEOMETRY

Acoustical resonance cylinder
Optical cavity

independent optimization of the key parameters affecting the signal strength
Photoacoustic T-Cell

- Cylindrical resonator (L = 60-110 mm, R = 4-6 mm)
- Resonant on the first longitudinal mode: 660-1100 Hz
- Closed by antireflection coated ZnSe window
- Gold Coated
**CH\textsubscript{2}O absorption frequency**: 1778.90 cm\textsuperscript{-1}

- **Lock-In time constant**: 10 sec.
- **QCL operating conditions**: PW= 42 ns, duty cycle 1.4%, P \sim 4 mW
- **Resonance Frequency**: 660 Hz

\[ Y = 0.77 X \quad r^2 = 0.995 \]

<table>
<thead>
<tr>
<th>CH\textsubscript{2}O</th>
<th>T-cell</th>
<th>H-cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detection limit (ppbv)</td>
<td>15</td>
<td>150</td>
</tr>
<tr>
<td>Min. det. abs. coefficient (cm\textsuperscript{-1}W/Hz\textsuperscript{1/2})</td>
<td>1.6\times10^{-9}</td>
<td>2.0\times10^{-8}</td>
</tr>
<tr>
<td>( \alpha_{\text{min}} ) (cm\textsuperscript{-1})</td>
<td>5.2\times10^{-8}</td>
<td>6.6\times10^{-7}</td>
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OPTICAL MICROPHONES

- HIGH Sensitivity (5 V/Pa) : a factor 10 larger than electrets microphones (20 mV/Pa)

- Immunity from electromagnetic noise

CW DFB-QCLs

PAS sensor for N₂O detection

Larger Optical Power and narrow linewidth

Higher sensitivity and selectivity
CONCLUSIONS and PROSPECTIVES

DEMONSTRATED DETECTION OF NO and CH$_2$O TRACES
BY A QUANTUM CASCADE LASER-BASED PHOTOACOUSTIC SENSOR
WITH A DETECTION LIMIT DOWN TO FEW TENS OF PPB

IMPROVEMENTS:

CONTINUOUS-WAVE LASER DFB-QCL (larger optical power)
OPTICAL FIBER (avoid optical alignment systems)
OPTICAL MICROPHONES (higher sensitivity)
NEW PA CELL GEOMETRY

- May lead to detection limits one or two order of magnitude better
  with a more compact and handy set-up