Recent Developments of Quantum Cascade Laser based Trace Gas Sensor Technology: Opportunities and Challenges

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- Motivation: Wide Range of Chemical Sensing Applications
- Fundamentals of Quantum Cascade Laser Spectroscopy
- Comparison of QEPAS to L-PAS
- Selection of Applications of QE-PAS
  - N₂O and CO Detection with a 4.6 μm LN₂-CW DFB Quantum Cascade Laser
  - H₂O and CO Detection with a 3.5 μm LN₂-CW DFB Interband Cascade Laser
  - NH₃ Detection with a 3 μm RT-CW DFB Dioded Laser
- Conclusions and Outlook

Motivation: Wide Range of Gas Sensing Applications

- Urban and Industrial Emission Measurements
- Industrial Plants
- Combustion Sources and Processes (e.g., fire sensing)
- Automobile and Aircraft Emissions
- Rural Emission Measurements
- Agriculture and Animal Facilities
- Environmental Monitoring
- Atmospheric Chemistry (e.g., ecosystems and airbone)
- Volcanic Emissions
- Chemical Analysis and Industrial Process Control
- Chemical, Pharmaceutical, Food & Semiconductor Industry
- Spacecraft and Planetary Surface Monitoring
- Crew Health Maintenance & Human Life Support Program
- Medical Diagnostics (e.g., breath analysis)
- Biohazard and Toxic Chemical Detection
- Fundamental Science and Photochemistry

Fundamentals of Laser Absorption Spectroscopy

Optimum Molecular Absorbing Transition
- Transition of Combination Bands (NIR)
- Fundamental Absorption Band (UV-IR)

Long Optical Pathlengths
- Multipass Absorption Cells
- Cavity Enhanced and Ringdown Spectroscopy
- Open Path Monitoring (with retro-reflector)

Spectroscopic Detection Schemes
- Frequency or Wavelength Modulation
- Balanced Detection
- Zero-Offset Absorptiometry
- Photoacoustic Spectroscopy

IR Laser Sources and Wavelength Coverage

Resonant Photoacoustic Spectroscopy

Laser beam, power $P$

Modulated frequency ($P$ or $\lambda$) at $f$ or $f/2$

Sensitivity $S = \frac{Q\alpha P}{fV}$

Cavity, resonant at $f$, volume $V$, quality factor $Q$
Quartz-Enhanced Photoacoustic Spectroscopy (QEPAS)

Laser beam, power $P$

Modulated ($P$ or $\lambda$) at $f$ or $f/2$

Sensitivity $S_{\text{QEPAS}} = \frac{Q \alpha P}{f}$

Piezoelectric quartz crystal (instead of microphone)

Resonant at $f$, quality factor $Q$ is $10,000$ instead of $20-200$ for PAS.

Comparative Size of Absorbance Detection Modules (ADM)

Optical multipass cell (100 m)
1-75 cm, 1-3000 cm$^3$

Resonant photoacoustic cell (1000 Hz)
1-60 cm, 1-50 cm$^3$

Equivalent Electrical Circuit of a Quartz TF

$\omega_0 = \frac{1}{\sqrt{LC}}$

$Q = \frac{L}{R \sqrt{C}}$

$\sqrt{\phi_0^2} = \frac{4kT}{R}$

TF & Trans-impedance Amplifier Noise Analysis

$S_T = \sqrt{4kT R_s^2}$

$R_s = 10 \, \text{M} \Rightarrow S_T = 4.1 \times 10^{-3} \frac{V}{\sqrt{Hz}}$

$S_T = \frac{4kT}{R_s}$

$R_s = 100 \, \text{k} \Rightarrow S_T = 4.1 \times 10^{-3} \frac{V}{\sqrt{Hz}}$ (at 760 Torr)

$S = \sqrt{S_T^2 + S_s^2}$ (at resonance)

Noise goes up as $\sqrt{Q}$.

Quartz TF Resonant Response in Air

Amplitude $A$

Frequency, Hz

Pressure dependence of $Q$ factor of a Typical TF

$Q_T = \frac{1}{Q} \Rightarrow \frac{1}{Q} = Ap^m$

$Q_T = 126000$, $m = 0.44$

$A = 3.7 \times 10^{-4}$ (p in Torr)

SNR $\sim \sqrt{Q}$

Pressure, Torr
**QCL based Quartz-Enhanced Photoacoustic Sensor**

**N₂O Detection in Ambient Air at 4.55 μm (2195.6 cm⁻¹)**

Noise-equivalent absorption coefficient $\kappa = 1.5 \times 10^{-4}$ cm$^{-1}$ W Hz$^{-1/2}$ for 5% SF$_6$

**QEPAS based N₂O Concentration Measurements**

11 ppb N₂O in an ultra-pure gas mixture: N₂ = 5% SF$_6$ for QCL locked to 2195.6 cm⁻¹

Detuned QCL wavelength

![Chart showing QEPAS based N₂O concentration measurements](chart)

**HITRAN Based Simulation of a H₂CO-H₂O-CH₄ Spectrum in Tuning Range of a 3.53 μm IC Laser**

- H₂CO: 10 ppb
- H₂O: 5%
- CH₄: 3 ppm
- Optical path: 100 m
- Total pressure: 760 Torr

![Chart showing HITRAN spectrum](chart)

**IC Laser based Formaldehyde Calibration Measurements with a Gas Standard Generator**

- H₂CO absorption frequency: 2832.4 cm⁻¹
- Lock-in time constant: 10 s
- QEPAS parameters:
  - Resonance frequency: 3.3 GHz
  - Q factor: 1030
  - Pressure: 300 Torr
  - Gas flow: 75 sccm
  - IC laser power: 6 mW

Sensitivity: $2.2 \times 10^{-6}$ cm$^3$ STP ppm$^{-1}$

![Chart showing IC laser based formaldehyde calibration measurements](chart)
Merits of QE Laser-PAS based Trace Gas Detection

- High sensitivity (ppm to ppb gas concentration levels) and excellent dynamic range
- Immune to ambient and flow acoustic noise, laser noise and etalon effects
- Significant reduction of sample volume (<1 mm³)
- Applicable over a wide range of pressures
- Temperature, pressure and humidity insensitive
- Rugged and low cost compared to LAS that requires a multipass absorption cell and infrared detector(s)
- Potential for optically multiplexed concentration measurements

QEPAS versus Traditional PAS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Traditional PAS</th>
<th>QEPAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>f, Hz</td>
<td>100 to 4000</td>
<td>Presently ~32 760</td>
</tr>
<tr>
<td>Q</td>
<td>20 to 200</td>
<td>10 000 to 30 000</td>
</tr>
<tr>
<td>Q vs. pressure</td>
<td>INCREASES</td>
<td>DECREASES</td>
</tr>
<tr>
<td></td>
<td>(high spectral resolution is problematic)</td>
<td>(high spectral resolution is achievable)</td>
</tr>
<tr>
<td>Sample volume</td>
<td>&gt;10 cm³</td>
<td>&lt;1 mm³</td>
</tr>
<tr>
<td>Sensitivity to ambient acoustic and flow noise</td>
<td>Usually high</td>
<td>None observed</td>
</tr>
<tr>
<td>Pathlength involved</td>
<td>~10 cm</td>
<td>(a) 0.3mm, (b) 3mm</td>
</tr>
</tbody>
</table>

QEPAS Performance for 7 Trace Gas Species

<table>
<thead>
<tr>
<th>Molecule (Host)</th>
<th>Frequency, cm⁻¹</th>
<th>Pressure, Torr</th>
<th>NNEA, cm⁻¹ W⁻¹ Hz⁻¹</th>
<th>Power, mW</th>
<th>NEC (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃ (N₂)</td>
<td>6528.76</td>
<td>60</td>
<td>7.2 x 10⁻⁴</td>
<td>38</td>
<td>0.65</td>
</tr>
<tr>
<td>H₂O (exhaust air)</td>
<td>6041.29</td>
<td>90</td>
<td>8.0 x 10⁻⁴</td>
<td>31</td>
<td>1.10</td>
</tr>
<tr>
<td>CO₂ (exhaust air)</td>
<td>5542.51</td>
<td>90</td>
<td>1.5 x 10⁻⁴</td>
<td>31</td>
<td>0.67</td>
</tr>
<tr>
<td>CH₄ (air)</td>
<td>2196.66</td>
<td>50</td>
<td>3.3 x 10⁻⁴</td>
<td>13</td>
<td>0.5</td>
</tr>
<tr>
<td>CO (propylene)</td>
<td>2196.50</td>
<td>50</td>
<td>7.4 x 10⁻⁴</td>
<td>6.5</td>
<td>0.14</td>
</tr>
<tr>
<td>CH₃OH (air)</td>
<td>2732.48</td>
<td>200</td>
<td>2.3 x 10⁻⁴</td>
<td>3.4</td>
<td>0.55</td>
</tr>
</tbody>
</table>

NNEA = normalized noise equivalent absorption coefficient.
NEC = noise equivalent concentration for available laser power and τ = time constant.
Presently achieved QEPAS NH₃ sensitivity is 5.4 x 10⁻⁴ cm⁻¹ W⁻¹ Hz⁻¹ (32 760 Hz).
For comparison: conventional PAS 2.2 x 10⁻⁴ cm⁻¹ W⁻¹ Hz⁻¹ (1 800 Hz).

Conclusions and Future Directions

- Laser based Trace Gas Sensors
  - Compact and robust sensors based on QEP L-PAS and QCL-PAS
  - QCL-PAS is immune to ambient noise.
  - TF sensitivity is limited by thermal excitation of symmetric mode
  - Best demonstrated minimum detectable absorption coefficients is 5.4 x 10⁻⁴ cm⁻¹ W⁻¹ Hz⁻¹
  - Dramatic reduction of sample volume (~0.2 mm³) with QEP L-PAS
  - Demonstrated trace gases: NH₃, CH₄, N₂O, CO₂, CO, NO, H₂O, COS, CH₃O, C₂H₅, C₃H₇OH, SO₂, NO and several isotopic species of C, O, N & H
- Applications in Trace Gas Detection
  - Environmental & Spacecraft Monitoring (NH₃, CO, CH₄, N₂O, CO₂, H₂CO)
  - Medical Diagnostics (NO, CO, CO₂, COS, C₂H₅, C₃H₇OH)
  - Industrial process control and chemical analysis (NO, NH₃)
- Future Directions and Collaborations
  - QEP-L-PAS and Cavity enhanced (ICUSP) and spectroscopy based applications using novel thermoelectrically cooled c-w and broadly wavelength tunable quantum cascade lasers
  - Applications using near IR interfered and far IR intersub-band quantum cascade lasers

QEPAS based CO signal in C₃H₇OH before and after Phase Rotation