Mid-Infrared Semiconductor Laser Based Trace Gas Sensor Technologies: Recent Advances and Applications

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Introduction

Recent advances in the development of sensors based on infrared semiconductor lasers has led to a wide range of trace gas sensing applications, such as urban, industrial and rural emission measurements, environmental monitoring, chemical analysis and industrial process control as well as applications in biomedical, medical diagnostics and the life sciences [see: www.ece.rice.edu/lasersci].

The development of compact trace gas sensors, in particular based on quantum cascade and interband cascade lasers permit the targeting of strong fundamental rotational-vibrational transitions in the mid-infrared. Two laser based sensor technologies, Quartz-Enhanced Photo-Acoustic Spectroscopy (QEPAS) and TDLAS based on an innovative, compact multi-pass absorption cell will be described. Four examples of recent mid-infrared sensor architectures, which include NO, SO$_2$, NH$_3$ and C$_2$H$_6$ have undergone detailed performance evaluation.

The future direction of our research includes improved and novel sensor architectures as well as detection of additional atmospheric trace gases, such as CH$_4$, N$_2$O, HONO and H$_2$O$_2$.
Quartz Tuning Fork as a Resonant Microphone for QEPAS

**Unique properties**

- Extremely low internal losses:
  - $Q \sim 10,000$ at 1 atm
  - $Q \sim 100,000$ in vacuum
- Acoustic quadrupole geometry
  - Low sensitivity to external sound
- Large dynamic range ($\sim 10^6$) – linear from thermal noise to breakdown deformation
  - 300K noise: $x \sim 10^{-11}$ cm
  - Breakdown: $x \sim 10^{-2}$ cm
- Wide temperature range: from 1.6K to $\sim 700$K

**Acoustic Micro-resonator (mR) tubes**

- Optimum inner diameter: 0.6 mm; mR-QTF gap is 25-50 $\mu$m
- Optimum mR tubes must be $\sim 4.4$ mm long ($\sim \lambda/4 < l < \lambda/2$ for sound at 32.8 kHz)
- SNR of QTF with mR tubes: $\times 30$ (depending on gas composition and pressure)
Merits of QEPAS based Trace Gas Detection

- Very small sensing module and sample volume (a few mm\(^3\) to \(\sim 2\text{ cm}^2\))
- Extremely low dissipative losses
- Optical detector is not required
- Wide dynamic range
- Frequency and spatial selectivity of acoustic signals
- Rugged transducer – quartz monocrystal; can operate in a wide range of pressures and temperatures
- Immune to environmental acoustic noise, sensitivity is limited by the fundamental thermal TF noise: \(k_B T\) energy in the TF symmetric mode
- Absence of low-frequency noise: SNR scales as \(\sqrt{t}\), up to \(t=3\) hours as experimentally verified

QEPAS: some challenges

- Cost of spectrophone assembly
- Sensitivity scales with laser power
- Effect of H\(_2\)O
- Responsivity depends on the speed of sound and molecular energy transfer processes
- Cross sensitivity issues
## Mid-IR QEPAS Performance for 8 Trace Gas Species (Sept 2012)

<table>
<thead>
<tr>
<th>Molecule (Host)</th>
<th>Frequency, cm⁻¹</th>
<th>Pressure, Torr</th>
<th>NNEA, cm⁻¹W/Hz¹⁄₂</th>
<th>Power, mW</th>
<th>NEC (τ=1s), ppmv</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O (N₂)**</td>
<td>7306.75</td>
<td>60</td>
<td>1.9×10⁻⁹</td>
<td>9.5</td>
<td>0.09</td>
</tr>
<tr>
<td>HCN (air: 50% RH)*</td>
<td>6539.11</td>
<td>60</td>
<td>4.6×10⁻⁹</td>
<td>50</td>
<td>0.16</td>
</tr>
<tr>
<td>C₂H₂ (N₂)*</td>
<td>6523.88</td>
<td>720</td>
<td>4.1×10⁻⁹</td>
<td>57</td>
<td>0.03</td>
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<tr>
<td>NH₃ (N₂)*</td>
<td>6528.76</td>
<td>575</td>
<td>3.1×10⁻⁹</td>
<td>60</td>
<td>0.06</td>
</tr>
<tr>
<td>C₂H₄ (N₂)*</td>
<td>6177.07</td>
<td>715</td>
<td>5.4×10⁻⁹</td>
<td>15</td>
<td>1.7</td>
</tr>
<tr>
<td>CH₄ (N₂+1.2% H₂O)*</td>
<td>6057.09</td>
<td>760</td>
<td>3.7×10⁻⁹</td>
<td>16</td>
<td>0.24</td>
</tr>
<tr>
<td>CO₂ (breath ~50% RH)</td>
<td>6361.25</td>
<td>150</td>
<td>8.2×10⁻⁹</td>
<td>45</td>
<td>40</td>
</tr>
<tr>
<td>H₂S (N₂)*</td>
<td>6357.63</td>
<td>780</td>
<td>5.6×10⁻⁹</td>
<td>45</td>
<td>5</td>
</tr>
<tr>
<td>HCl (N₂ dry)</td>
<td>5739.26</td>
<td>760</td>
<td>5.2×10⁻⁸</td>
<td>15</td>
<td>0.7</td>
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<tr>
<td>CO₂ (N₂+1.5% H₂O)*</td>
<td>4991.26</td>
<td>50</td>
<td>1.4×10⁻⁸</td>
<td>4.4</td>
<td>18</td>
</tr>
<tr>
<td>CH₂O (N₂:75% RH)*</td>
<td>2804.90</td>
<td>75</td>
<td>8.7×10⁻⁹</td>
<td>7.2</td>
<td>0.12</td>
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<tr>
<td>CO (N₂ +2.2% H₂O)*</td>
<td>2176.28</td>
<td>100</td>
<td>1.4×10⁻⁶</td>
<td>71</td>
<td>0.002</td>
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<tr>
<td>N₂O (air+5%SF₆)</td>
<td>2195.63</td>
<td>50</td>
<td>1.5×10⁻⁸</td>
<td>19</td>
<td>0.007</td>
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<tr>
<td>NO (N₂+H₂O)</td>
<td>1900.07</td>
<td>250</td>
<td>7.5×10⁻⁹</td>
<td>100</td>
<td>0.003</td>
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<tr>
<td>C₂H₅OH (N₂)**</td>
<td>1934.2</td>
<td>770</td>
<td>2.2×10⁻⁷</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>SO₂ (N₂ +2.4% H₂O)*</td>
<td>1380.94</td>
<td>100</td>
<td>2.0×10⁻⁸</td>
<td>40</td>
<td>0.1</td>
</tr>
<tr>
<td>C₂HF₅ (N₂)**</td>
<td>1208.62</td>
<td>770</td>
<td>7.8×10⁻⁹</td>
<td>6.6</td>
<td>0.009</td>
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<tr>
<td>NH₃ (N₂)*</td>
<td>1046.39</td>
<td>110</td>
<td>1.6×10⁻⁸</td>
<td>20</td>
<td>0.006</td>
</tr>
</tbody>
</table>

* - Improved microresonator  
** - Improved microresonator and double optical pass through ADM  
*** - With amplitude modulation and metal microresonator  

NNEA – normalized noise equivalent absorption coefficient.  
NEC – noise equivalent concentration for available laser power and τ=1s time constant, 18 dB/oct filter slope.

For comparison: conventional PAS 2.2 (2.6)×10⁻⁹ cm⁻¹W/√Hz (1,800; 10,300 Hz) for NH₃*, (**)  
Motivation for Nitric Oxide Detection

- Atmospheric Chemistry
- Environmental pollutant gas monitoring
  - NO\textsubscript{X} monitoring from automobile exhaust and power plant emissions
  - Precursor of smog and acid rain
- Industrial process control and analysis
- NO in medicine and biology
  - Important signaling molecule in physiological processes in humans and mammals (1998 Nobel Prize in Physiology/Medicine)
  - Treatment of asthma, COPD, acute lung rejection

Minimum detectable NO concentration is:

\( \sim 3\ \text{ppbv} \) (1\( \sigma \); 1 s time resolution)
Motivation for Sulfur Dioxide Detection

- Prominent air pollutant
- Emitted from coal fired power plants (~73%) and other industrial facilities (~20%)
- In atmosphere SO$_2$ converts to sulfuric acid → primary contributors to acid rain
- SO$_2$ reacts to form sulfate aerosols
- Primary SO$_2$ exposure for 1 hour is 75 ppb
- SO$_2$ exposure affects lungs and causes breathing difficulties
- Currently, reported annual average SO$_2$ concentrations range from ~1 - 6 ppb

Molecular Absorption Spectra within two Mid-IR Atmospheric Windows

2f QEPAS signals for different SO$_2$ concentrations when laser was tuned across 1380.9 cm$^{-1}$ line.

Minimum detectable SO$_2$ concentration is: ~100 ppbv (1σ; 1 s time resolution)
Mid-Infrared ppbV Detection of NH$_3$(10.36µm) and C$_2$H$_6$(3.36µm)

Innovative long path, small volume multipass gas cell: 57.6 m with 459 passes

MGC dimensions: 17 x 6.5 x 5.5 (cm)
Distance between the MGC mirrors: 12.5 cm

10.36µm EC-QCL based AM-PAS Sensor Platform for Atmospheric NH$_3$ Detection

Diurnal profile of atmospheric NH$_3$ levels

Correlation between NH$_3$ and SO$_2$

Minimum detectable C$_2$H$_6$ concentration is:
~ 130 pptv (1σ; 1 s time resolution)
Potential Integration of a CW DFB- QCL and QEPAS Absorption Detection Module (ADM)

Summary and Outlook

- A 5.26 µm and 7.24 µm CW TEC HHL packaged DFB-QCL based QEPAS sensor for NO and SO₂ detection was demonstrated.
- For interference free NO absorption line located at $1900.08 \text{ cm}^{-1}$ a 1σ minimum detection limit (MDL) of 3 ppbv was achieved at a gas pressure of 240 Torr and sampling time of 1 sec.
- A 1σ MDL of 100 ppbv was achieved at a gas pressure of 100 Torr and sampling time of 1 sec for a SO₂ absorption line at 1380.94 cm⁻¹.
- Addition of water vapor to NO and SO₂ trace gas mixture results in an improved QEPAS signal of > 100 and 3 times, respectively.
- An AM-PAS technique was employed to monitor NH₃ with a 65 mW, 10.34 µm CW TEC EC-QCL. MDL obtained for an absorption line at 965.35 cm⁻¹ was ~0.7 ppbv for a 300 sec averaging time.
- For an interference free C₂H₆ absorption line located at 2976.8 cm⁻¹ a MDL of 130 pptv with a 1 second lock-in amplifier time constant was achieved using a novel multi-pass gas absorption cell.
- Next objective will be CH₄ and N₂O detection with a high power 7.23 µm CW TEC HHL packaged DFB-QCL based QEPAS sensor platform.
- Compact, robust sensitive and selective mid-IR based QEPAS sensor technology permits sensitive, selective, real-time environmental, biomedical and industrial emission measurements.