Recent Developments of Chemical Sensors based on Quartz Enhanced Photoacoustic Spectroscopy


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• Motivation: Wide Range of Chemical Sensing
• Fundamentals of QE Photoacoustic Spectroscopy
• Selected Applications of QEPAS
  ▪ NH₃ Detection with 1.5 µm RT cw DFB Diode Laser
  ▪ H₂CO Detection with 3.5 µm LN₂ cw DFB interband cascade laser
  ▪ N₂O Detection with 4.6 µm LN₂ cw DFB quantum cascade laser
• Merits, Summary and Outlook for QEPAS

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Gas sensing: wide range of applications

- Urban and Industrial Emission Measurements
  - Industrial Plants
  - Combustion Sources and Processes
  - Automobile
- Rural Emission Measurements
  - Agriculture
- Environmental Monitoring
  - Atmospheric Chemistry
  - Volcanic Emissions
- Chemical Analysis and Industrial Process Control
  - Chemical, Pharmaceutical & Semiconductor Industry
- Spacecraft and Planetary Surface Monitoring
  - Crew Health Maintenance & Life Support
- Medical Applications
- Law enforcement
- Fundamental Science and Photochemistry
Existing Methods for Trace Gas Detection

Non-Optical
- Mass Spectroscopy
  - Gas Chromatography
  - Chemical
    - Electro Chemical
      - Chemiluminescence
        - Fourier Transform
          - Gas Filter Correlation
            - Microwave Spectroscopy
              - Laser Spectroscopy
  - Non-Dispersive
    - Dispersive

Optical
Direct Laser Absorption Spectroscopy

Beer-Lambert’s Law of Linear Absorption

\[ I(\nu) = I_0 \cdot e^{-\alpha(\nu) \cdot P_a \cdot L} \]

\( \alpha(\nu) \) - absorption coefficient \([\text{cm}^{-1} \text{ atm}^{-1}]\); \( L \) – path length [cm]

\( \nu \) - frequency \([\text{cm}^{-1}]\); \( P_a \) - partial pressure \([\text{atm}]\)

\[ \alpha(\nu) = C \cdot S(T) \cdot g(\nu - \nu_0) \]

\( C \) - total number of molecules of absorbing gas/atm/cm\(^3\) \([\text{molecule} \cdot \text{cm}^{-3} \cdot \text{atm}^{-1}]\)

\( S \) - molecular line intensity \([\text{cm} \cdot \text{molecule}^{-1}]\)

\( g(\nu - \nu_0) \) - normalized lineshape function \([\text{cm}]\), (Gaussian, Lorentzian, Voigt)
Sensitivity Enhancement Techniques

- **Optimum Molecular Absorbing Transition**
  - Overtone or Combination Bands (NIR)
  - Fundamental Absorption Bands (MID-IR)

- **Long Optical Pathlength**
  - Multipass Absorption Cell (White, Herriott)
  - Cavity Enhanced and Cavity Ringdown Spectroscopy
  - Open Path Monitoring (with retro-reflector)
  - Fiberoptic Evanescent Wave Spectroscopy

- **Spectroscopic Detection Schemes**
  - Frequency or Wavelength Modulation
  - Balanced Detection
  - Zero-air Subtraction
  - **Photoacoustic Spectroscopy**
  - Noise Immune Cavity Enhanced-Optical Heterodyne Molecular Spectroscopy (NICE-OHMS)
Resonant photoacoustic spectroscopy

Laser beam, power $P$

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

$S \sim \frac{Q \alpha P}{fV}$

Sensitivity $[k] = \frac{cm^{-1} \times W}{\sqrt{Hz}}$

Piezoelectric crystal

Resonant at $f$

Q $\gg$ 1000

Cell is OPTIONAL!

$V$-effective volume
Quartz Tuning Fork as a Resonant Microphone

- Miniature size, 0.3 mm$^3$ detection volume
- Dimensions in mm: l = 3.8, g = 0.3, t = 0.3, w = 0.58
- Piezo-active material
- Signal currents \( \approx \) pA
- Intrinsically high \( Q \) factor, \( \sim 10,000 \) at ambient conditions; \( Q_{\text{vacuum}} \sim 125,000 \)
Equivalent circuit of a quartz TF

\[ \omega_0 = \sqrt{\frac{1}{LC}} \]
\[ Q = \frac{1}{R} \sqrt{\frac{L}{C}} \]
\[ \sqrt{\langle I_N^2 \rangle} = \sqrt{\frac{4k_BT}{R}} \]
Noise analysis

\[ S_1 = \sqrt{4k_BT R_g} \quad R_g = 10 \text{ M\Omega} \Rightarrow S_1 = 4.1 \cdot 10^{-11} \text{ Hz}^{1/2} \]

\[ S_2 = \sqrt{\frac{4k_BT}{R}} R_g \quad R = 100 \text{k\Omega} \Rightarrow S_2 = 4.1 \cdot 10^{-10} \frac{\text{Hz}^{1/2}}{(\text{at 760 Torr})} \]

\[ S = \sqrt{S_1^2 + S_2^2} \approx S_2 \quad \text{(at resonance)} \quad \text{Noise goes up as } \sqrt{Q}. \]
Typical QTF resonance curves

\[ Q = \frac{f_0}{\Delta f_{\sqrt{2}}} \]

- Air, 760 Torr \( Q = 13\,270 \)
- Vacuum \( Q = 93\,500 \)
Quartz Enhanced PAS ADM

Active mode – symmetric vibration
Acoustic quadrupole! ⇒ Noise immunity

Laser radiation

Acoustic microresonator

Quartz tuning fork

5 mm

Acoustic micro-cavity is added to enhance sensitivity
## NASA Target Gas Opportunity Matrix

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Detection Limit (ppb)</th>
<th>QEPAS detectable?</th>
<th>1.3-1.7 μm</th>
<th>2-5 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>10</td>
<td>No</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>20</td>
<td>Experiments required</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>100</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>1000</td>
<td>Probably not</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Hydrogen cyanide</td>
<td>100</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>&lt;2%</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Nitrogen dioxide</td>
<td>100</td>
<td>Probably not</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>HF</td>
<td>100</td>
<td>Experiments required</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acrolein (2-Propenal)</td>
<td>5</td>
<td>Unlikely</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water vapor</td>
<td>10-90%</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

**X – Demonstrated**

**X – Highly expected based on the existing technology level**

**X – Expected with the technology advance**
Motivation for NH$_3$ Detection

- Spacecraft related gas monitoring
- Monitoring NH$_3$ concentrations in the exhaust stream of NO$_x$ removal systems based on selective catalytic reduction (SCR) techniques
- Semiconductor process monitoring & control
- Monitoring of industrial refrigeration facilities
- Pollutant gas monitoring
- Atmospheric chemistry
- Medical diagnostics (kidney & liver dysfunctions)
Molecular absorption spectra: NH$_3$
QEPAS fiber based gas sensor architecture

Diagram showing the flow of light from a laser through a beam splitter, fiber amplifier, and two cells (Ref Cell and PD). The output is processed through DC, 3f, and 2f stages before being sent to a data collection and processing module with the output labeled as CONCENTRATION.
Ammonia Detection using a 1.53 μm Telecom Diode Laser

Spectral simulations based on data from Webber et al., APPLIED OPTICS 40, 2031-2042 (2001)

QEPAS spectra at different pressures of NH₃:N₂ gas mixture; t=0.3s, 38 mW diode laser excitation power at 6529 cm⁻¹

Applied Optics 43, 6213-6217, 2004
Pressure Dependence of QEPAS Sensitivity

- Peak optical absorption varies with pressure
- Q-factor decreases at higher pressure
- V-T relaxation is faster at higher pressure
- Acoustic resonator enhancement factor changes with pressure

[Graph showing NH₃:N₂ ratio with varying pressures and modulation levels.]
Calibration and Linearity of QEPAS based NH\textsubscript{3} Sensor

$6.5$ ppmy for $38$ mW excitation

$\text{(NEC)}$ for $T=1$ s, time constant is $1$ s

\begin{align*}
\text{Signal, a.u.} & \\
\text{Time, s} & \\
\text{[NH}_3\text{]} \text{ ppm} & \\
0 & 1000 2000 3000 4000 5000 6000 7000 8000 9000 10000 12000
0 & 20 & 40 & 60 & 80 & 100 & 120
\end{align*}

$y = 0.093226 + 0.1096x$, $R = 0.99977$
Case study: NH₃ (100 ppb target)

Presently demonstrated sensitivity – NIR: 490 ppb

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Now</th>
<th>Modified</th>
<th>Scaling</th>
<th>Expected sensitivity, ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>τ</td>
<td>1s</td>
<td>10s</td>
<td>3.2</td>
<td>155</td>
</tr>
<tr>
<td>W</td>
<td>38 mW</td>
<td>60 mW</td>
<td>1.6</td>
<td>100</td>
</tr>
<tr>
<td>f</td>
<td>32.7 kHz</td>
<td>10 kHz</td>
<td>3.2</td>
<td>35</td>
</tr>
</tbody>
</table>

**Conclusion:** QEPAS provides adequate sensitivity to NH₃ with NIR telecom lasers. Power consumption by the 63 mW JDS-Uniphase laser is (only) ~1W.
Motivation for Precision Monitoring of $\text{H}_2\text{CO}$

- Potential trace contaminant in industrial manufactured products
- Precursor to atmospheric $\text{O}_3$ production
- Pollutant due to incomplete fuel combustion processes
- Medically important gas
QCL based Quartz-Enhanced Photoacoustic Sensor
2f - QEPAS based $\text{H}_2\text{CO}$ signal at 3.53 $\mu$m (2832.48 cm$^{-1}$)

- [H$_2$CO]: 13.27 ppm
- Sensitivity: $2.2 \times 10^{-8}$ cm$^{-1}$ W/√Hz
- QEPAS NE sensitivity for NH$_3$:
  - 7.2$ \times 10^{-9}$ cm$^{-1}$ W/√Hz
- Sensitivity: $2.2 \times 10^{-8}$ cm$^{-1}$ W/√Hz
  For comparison:
  - Sensitivity for NH$_3$:
  - 7.2$ \times 10^{-9}$ cm$^{-1}$ W/√Hz
N₂O Detection in Ambient Air at 4.55 μm (2195.6 cm⁻¹)

Noise-equivalent absorption coefficient is $1.5 \times 10^{-8}$ cm⁻¹W/Hz¹/² for 5% SF₆ with a noise equivalent concentration of 4 ppbv for $\tau = 3$ sec

QEPAS based $N_2O$ Concentration Measurements

$\tau = 3 \text{ s}$

$\sigma = 0.4 \mu\text{V}$

$1.1 \pm 0.02 \mu\text{V}$

$-0.1 \pm 0.04 \mu\text{V}$

11 ppb $N_2O$ in an ultra-pure gas mixture: $N_2 + 5\% SF_6$ [for QCL locked to 2195.6 cm$^{-1}$]

Detuned QCL wavelength
# QEPAS performance for various species

<table>
<thead>
<tr>
<th>Molecule (Host)</th>
<th>Frequency, (\text{cm}^{-1})</th>
<th>Pressure, Torr</th>
<th>NNEA, (\text{cm}^{-1}\text{W/Hz}^{1/2})</th>
<th>Power, mW</th>
<th>NEC ((\tau=1\text{s})), ppmv</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{NH}_3) (N(_2))</td>
<td>6528.76</td>
<td>60</td>
<td>(5.4\times10^{-9})</td>
<td>38</td>
<td>0.65</td>
</tr>
<tr>
<td>(\text{H}_2\text{O}) (exhaled air)</td>
<td>6541.29</td>
<td>90</td>
<td>(8\times10^{-9})</td>
<td>5.2</td>
<td>580</td>
</tr>
<tr>
<td>(\text{CO}_2) (exhaled air)</td>
<td>6514.25</td>
<td>90</td>
<td>(1.0\times10^{-8})</td>
<td>5.2</td>
<td>890</td>
</tr>
<tr>
<td>(\text{N}_2\text{O}) (air+5%SF(_6))</td>
<td>2195.63</td>
<td>50</td>
<td>(1.5\times10^{-8})</td>
<td>19</td>
<td>0.007</td>
</tr>
<tr>
<td>(\text{CO}) (N(_2))</td>
<td>2196.66</td>
<td>50</td>
<td>(5.3\times10^{-7})</td>
<td>13</td>
<td>0.5</td>
</tr>
<tr>
<td>(\text{CO}) (propylene)</td>
<td>2196.66</td>
<td>50</td>
<td>(7.4\times10^{-8})</td>
<td>6.5</td>
<td>0.14</td>
</tr>
<tr>
<td>(\text{CH}_2\text{O}) (air)</td>
<td>2832.48</td>
<td>200</td>
<td>(2.2\times10^{-8})</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 \(\tau=1\text{s}\) time constant.

Presently achieved QEPAS \(\text{NH}_3\) sensitivity is \(5.4\times10^{-9}\ \text{cm}^{-1}\text{W/}\sqrt{\text{Hz}}\) (32,760 Hz)

For comparison: conventional PAS \(2.2\times10^{-9}\ \text{cm}^{-1}\text{W/}\sqrt{\text{Hz}}\) (1,800 Hz)*