Resonant photoacoustic spectroscopy

- Laser beam, power $P$
- Modulated ($P$ or $\lambda$) at $f$ or $f/2$
- $S \sim \frac{Q\alpha P}{fV}$
- Sensitivity $[k] = \frac{cm^{-1} \times W}{\sqrt{Hz}}$
- Cavity, resonant at $f$, volume $V$, quality factor $Q$
- Microphone

Photoacoustic spectroscopy with a resonant microphone

- Laser beam, power $P$
- Modulated ($P$ or $\lambda$) at $f$ or $f/2$
- $S \sim \frac{Q\alpha P}{f}$
- Sensitivity $[k] = \frac{cm^{-1} \times W}{\sqrt{Hz}}$
- Absorption $\alpha$
- Piezoelectric crystal
- Resonant at $f$, quality factor $Q$
- Cell is OPTIONAL

A readily available solution – wrist-watch tuning fork

- WATCH CRYSTAL TUNING FORKS
- Frequency: 32,768kHz
- Operating temperature: –20°C to 60°C
- Price: 1-50 $0.32 ea (Newark Electronics)
- QUANTITY DISCOUNTS AVAILABLE

Wrist-watch tuning fork

Typical tuning fork (TF) dimensions (mm)

- Gap volume < 0.35 mm³
Pressure dependence of Q factor of a typical TF

Tested QEPAS configurations

(a) Simplest configuration

(b) Acoustic microcavity added to enhance sensitivity

QEPAS vs. traditional PAS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Traditional PAS</th>
<th>QEPAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>fkHz</td>
<td>100 to 4000</td>
<td>~37 kHz</td>
</tr>
<tr>
<td>Q</td>
<td>20 to 300</td>
<td>10 000 to 10 000</td>
</tr>
<tr>
<td>Q vs. pressure</td>
<td>Increase</td>
<td>Decrease</td>
</tr>
<tr>
<td>Sample volume</td>
<td>&gt;10 cm³</td>
<td>&lt;1 cm³</td>
</tr>
<tr>
<td>Sensitivity to ambient</td>
<td>Usually high</td>
<td>None observed</td>
</tr>
<tr>
<td>and flow rates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pulsing length involved</td>
<td>~10 cm</td>
<td>(a) 0.3 mm, (b) 5 mm</td>
</tr>
</tbody>
</table>

Laboratory setup for QEPAS based gas sensor evaluation

Gas cell for QEPAS experiments

Gas cell for QEPAS experiments

Bottom part with a mounted TF

Assembled cell with a pressure sensor mounted on top
An example of QEPAS data

Optimum pressure: C2H2 signal

NH3-N2 sensitivity test

QEPAS gas sensor architecture

Summary and Outlook

Packaged QEPAS control unit (v. 1.0)

*QEPAS is immune to ambient noise. Experimentally measured noise level coincides with theoretical limit.

* Required sample volume is very small. It is ultimately limited by the gap size between the TF prongs, which is 0.15 mm for the presently used TF

* The best experimentally demonstrated sensitivity of QEPAS approach to date is $8.8 \times 10^{-9}$ cm$^3$/s/WHz

* The achieved sensitivity corresponds to a NH3 detection limit (SNR=5) of 1.7 ppm with commercially available NIR DFB lasers (40 mW at 1.53 µm) with $\tau=1$ ms time constant, or 0.9 ppb with 5 min acquisition time ($\tau=600$ s)

* A new advanced version of a compact dedicated control unit for an autonomous QEPAS sensor is currently under development

NEXT STEPS:

* Optimize acoustic microresonator design (geometry and material)

* Investigate TFs with lower resonant frequencies

* Combine QEPAS with mid-IR laser sources (e.g., QC lasers) for improved gas sensing (ammonia, <200 times stronger absorption line)