**New developments in quartz enhanced photoacoustic gas sensing**

**OUTLINE**

- Quartz Enhanced Photo-Acoustic Spectroscopy (QEPAS): Basics and merits
  a) Custom QTFs for QEPAS applications
  b) Single tube on-beam QEPAS
  c) QTFs 1st overtone flexural mode
  d) Dual-anode excited QEPAS sensor
  e) Dual-gas QEPAS sensor
- Future Directions and Conclusions

**Quartz-Enhanced Photoacoustic Spectroscopy**

**Merits and main characteristics**

- Very small sensing module and sample volume (a few cm³)
- Extremely low dissipative losses
- Optical detector is not required
- Wide dynamic range (from % down to ppt)
- Immune to environmental acoustic noise
- Acoustic micro-resonators to enhance the QEPAS signal

- Sensitivity scales with laser power
- Cross sensitivity issues
- Alignment requirement is that no incident radiation will hit the QTF or micro-resonators
- Responsivity depends on the molecular energy transfer process

**Quartz tuning fork: Physics**

- Free motion conditions: Euler-Bernoulli equation
- Resonance frequencies
- QEPAS signal: $S \propto P_{BKE}$
- Quality factor: $Q = f_0 / A_{ISR}$
- Piezoelectric signal: $I = a \frac{dV}{dt}$
- Fork constant: $a = \frac{1}{3\pi\lambda}$

**Quartz-Enhanced Photoacoustic Spectroscopy**

**Introduction and Basic Operation**

- Optical radiation is focused between the prongs of a quartz tuning fork
- Trace gases absorb optical energy at characteristic frequencies
- A pressure wave (sound) is generated by modulating the laser power
- Resonant mechanical vibrations are excited by the sound waves
- The mechanical vibration is converted to an electrical signal via the piezoelectric effect
- The trace gas concentration is proportional to the electrical signal

**Custom tuning forks: Realization**

- Objective: Design of a tuning fork optimized for QEPAS sensing applications
- Goals:
  - Decrease the resonance frequency
  - Increase the gap between the prongs
  - Increase the quality factor
  - Increase the charge collection efficiency
- All these figures of merit depend on the tuning fork geometry
Custom tuning forks: Fundamental Mode
- The Quality Factor scales linearly with the fork constant $a$:
  \[ Q \propto \frac{a^2}{L} \]
- The Electrical Resistance $R$ depends on the generated charge collection efficiency:
  \[ R \propto \frac{1}{V/I} \]

QEPAS sensors in the THz range
Standard QTFs are characterized by a compact volume (~3.3x3x3 mm$^3$)
In QEPAS measurements, it is critical to avoid laser illumination of the QTF, since the radiation blocked by the QTF prongs generates an undesirable non-zero background which leads to a shifting fringe-like interference pattern.

The limited space (300 μm) between the QTF prongs is comparable with the wavelength of THz sources, which has represented so far the main limitation for the use in QEPAS-based sensor systems in the THz range.

Larger sized QTFs are mandatory in the THz range

Fiber-amplified QEPAS with custom QTFs
- With-level excitation source (1.5 W @ 4.5 μm)
- Standard QTF shows high noise level and require electrical modulation cancellation
- Custom tuning forks with large prong spacing (700 μm) gives interferometer and allow easy alignment

1st THz QEPAS sensor employing custom QTFs
- QTF with same geometry of standard one (~6x bigger)
- 4 sec Lock-In constant, NIE = 7 ppm [laser power 40 μW]
- NIEA = 3.0 x 10$^{-4}$ cm$^{-1}$ W/$\text{Hz}^{1/2}$

Fiber-amplified QEPAS with custom QTF: Results
- QEPAS detection sensitivity enhanced by a factor of ~60, compared to the case of a sensor using a bare custom QTF
- Detection sensitivity @ 850 ppm: 3 C pm
- NIEA = 1.3 x 10$^{-4}$ cm$^{-1}$ W/$\text{Hz}^{1/2}$

THz QEPAS results employing a Custom QTF
- Prongs spacing > 300 μm
- Wavenumber: 131.054 cm$^{-1}$ (9.58 THz)
- Absorption line strength: 4.28 x 10$^{-15}$ cm/$\text{mol}$
- Optical power: 40 μW
- 96.4% of the light intensity passes between the QTF prongs
THz QEPAS results employing a Custom QTF

Comparison between QTFs with custom and new geometry
- Same noise level
- Improved signal-to-noise ratio (SNR) and sensitivity by better for QEPAS system employing a QTF with new geometry
- 10 sec integration time:
  - Sensitivity 50 ppm
  - Noise 5 × 10⁻¹¹ W/Hz

QEPAS RECORD

Single-tube QEPAS Novel approach: Results

Custom tuning fork 7.3 kHz with larger-prone spacing

Two small slits are cut symmetrically on each side of the tube waist in the middle of the AnR, where the acoustic pressure antinode is located.

QEPAS based gas sensor comparison

QEPAS shows better potentialities at longer wavelengths

Fast energy relaxation rates of the rotational transition allows to operate at low pressure, taking advantage of the high QTF Q-factors and enhanced sensitivity.

Single-tube QEPAS: Results

Optimization of the AnR

L = 38 mm, improved SNR 128 times
L = 46 mm

Single-tube QEPAS Results

A SNR gain factor of 128 with respect to the base QTF and a gain factor of 4 with respect to the standard on-beam configuration.
- NEA for SO-QEPAS detector is 3.5 times lower than the standard on-beam configuration using a commercial 12 kHz QTF 2.6 × 10⁻¹¹ W/Hz (3.5 kHz)
- Same detection sensitivity for a 46 mm double tube and a 26 mm single tube.
- Mica resonator length for standard 32 kHz QTF is ~12 mm.
Custom tuning forks 1st Overtone Mode

\[
\frac{1}{Q} = \frac{1}{K_s} \left( \frac{1}{Q_{ep}} + \frac{1}{Q_{air}} \right)
\]

**Contribution from resonator**: 
\[ Q_{ep} = \frac{1}{2} \left( \frac{4n_0 l_0^2}{\pi W} \right) \]

At the 3rd harmonic support losses dominate the energy dissipation processes.

- Air losses become important only for QTFs with very thin prongs.

Single-tube approach with QTF overtone mode

- Total length of the micro-resonator tube is inversely proportional to QTF frequency.
- \( f_2 \) is the fundamental frequency.
- \( f_3 \) is the second overtone frequency.

Near-IR SO-QEPAS operating at the QTF 1st overtone

- Excitation source: 365 nm, 33 mW
- Absorption line: 7980.23 cm\(^{-1}\)
- Temperature: 25°C
- Pressure: 760 Torr
- Lock-in amplifier: 101.2 Hz

QEPAS signal profiles \( f_1 \) and \( f_2 \) modes

- Moving the laser spot along the symmetry axis of the prongs, the QEPAS signal follows the mode profile.
- At the higher antennode position, a large part of the sound wave is lost.

Single-tube QEPAS with overtone Results

- A SNR gain factor of 380 with respect to the bare QTF at the fund. mode
- Micro-resonator optimal length of 14.5 mm
- Micro-resonator length for 3200 GHz QTF is 50 mm
Double antinode excited SO-QEPAS operating at the QTF 1st overtone

- A custom-made QTF with a prong length of 17 mm and prong spacing of 700 µm was employed. Target: a gas sensor system sensitive to various gases.
- Gas sensor: reacts at a pressure of 700 torr. Target: a gas sensor system sensitive to various gases.
- Infrared distributed feedback (DFB) laser emitting at 1.3 µm.

Dual-gas QEPAS operating at both the QTF fundamental and 1st overtone

- Two beams from two independently modulated lasers are focused between the prongs of a quartz tuning fork at two different positions to excite both the fundamental and first overtone flexural modes simultaneously.
- Dual-gas quartz-enhanced photoacoustic spectroscopy (QEPAS) sensor system sensitive to frequency division multiplexing applications.

Double antinode excited SO-QEPAS

- The phase difference has to be compensated to maximize the QEPAS signal.
- The single mode fiber was coiled around a piezoelectric transducer serving as a phase compensator.
- A slight gain factor of 500 with respect to the bare QTF operating on the fundamental mode.
- Total micro-resonators optimal length of 12 mm.

Single-tube QEPAS with overtone Results

<table>
<thead>
<tr>
<th>QTF configuration</th>
<th>OD (mm)</th>
<th>ID (mm)</th>
<th>L (mm)</th>
<th>Gain factor</th>
<th>NNEA</th>
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<tbody>
<tr>
<td>Bare QTF</td>
<td>1.5</td>
<td>0.8</td>
<td>15.4</td>
<td>1</td>
<td>1.81 x 10^-1</td>
</tr>
<tr>
<td>Two-tube</td>
<td>1.5</td>
<td>0.8</td>
<td>15.4</td>
<td>1</td>
<td>1.81 x 10^-1</td>
</tr>
<tr>
<td>Curved single-tube</td>
<td>0.9</td>
<td>0.6</td>
<td>12.6</td>
<td>1</td>
<td>1.3 x 10^-4</td>
</tr>
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<td>Single-tube + overtone</td>
<td>0.98</td>
<td>0.62</td>
<td>14.5</td>
<td>30</td>
<td>2.7 x 10^-4</td>
</tr>
<tr>
<td>Double antenna + overtone</td>
<td>1.58</td>
<td>1.3</td>
<td>19</td>
<td>500</td>
<td>173 x 10^-4</td>
</tr>
</tbody>
</table>

(NNEA: normalized noise equivalent absorption coefficient cm^(-1) W^(-1/2))

Conclusions and Future Perspectives

- Demonstration of near-IR and THG QEPAS sensor employing custom QTFs with new geometry and gold contact pattern with improved sensitivity.
- Realization of a novel single-tube microresonator system.
- First-demonstration of QEPAS sensors operating with the 1st overtone.
- Dual-antinode excited QEPAS with QTF operating at the 1st overtone flexural mode.
- Dual gas QEPAS with QTF simultaneously operate at the fundamental and 1st overtone flexural mode.

- Implement single-tube micro-resonators in dual gas QEPAS.
- Design and realize QTFs with optimized geometry for the 1st overtone flexural mode.
- Push QEPAS sensor module towards commercialization level.