New developments in quartz enhanced photoacoustic gas sensing

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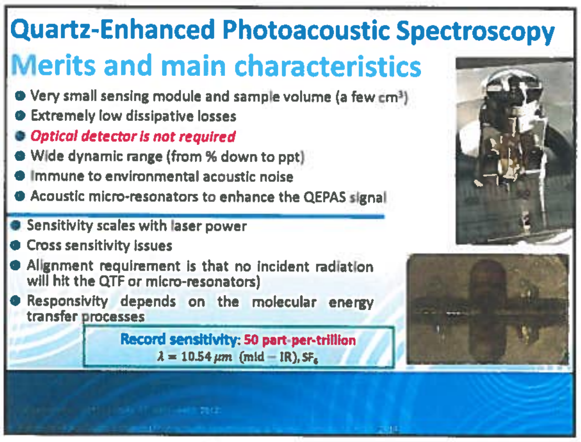


Quartz-Enhanced Photoacoustic Spectroscopy Merits and main characteristics

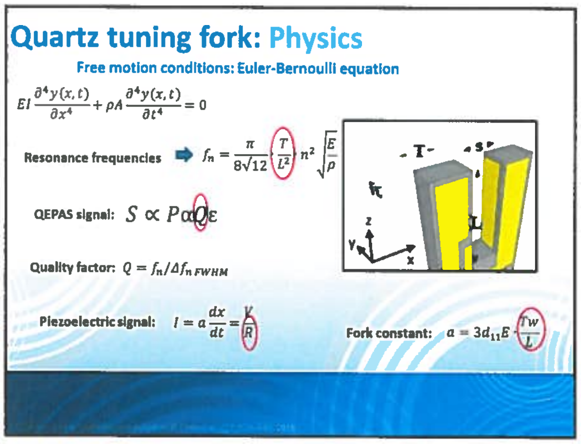
- Very small sensing module and sample volume (a few cm^3)
- Extremely low dissipative losses
- *Optical detector is not required*
- Wide dynamic range (from % down to ppt)
- Immune to environmental acoustic noise
- Acoustic micro-resonators to enhance the QEPAS signal

- 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 processes

Record sensitivity: 50 part-per-trillion
$\lambda = 10.54\,\mu m$ (mid – IR), SF_6

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-antinode excited QEPAS sensor
  - e) Dual-gas QEPAS sensor
  - Future Directions and Conclusions



Quartz tuning fork: Physics

Free motion conditions: Euler-Bernoulli equation

$$EI\frac{\partial^4 y(x,t)}{\partial x^4} + \rho A\frac{\partial^4 y(x,t)}{\partial t^4} = 0$$

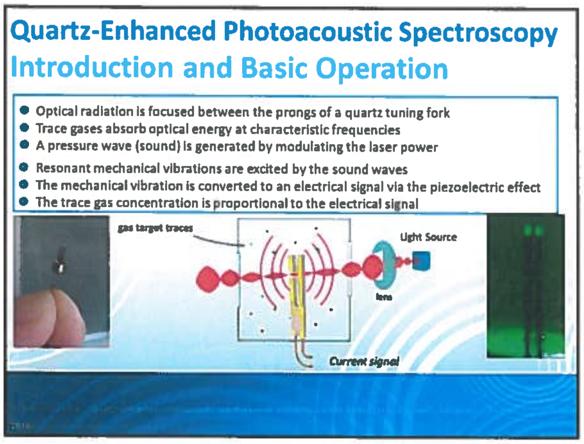
Resonance frequencies ➡ $f_n = \frac{\pi}{8\sqrt{12}}\boxed{\frac{T}{L^2}}n^2\sqrt{\frac{E}{\rho}}$

QEPAS signal: $S \propto P\alpha\boxed{Q}\varepsilon$

Quality factor: $Q = f_n/\Delta f_{n\,FWHM}$

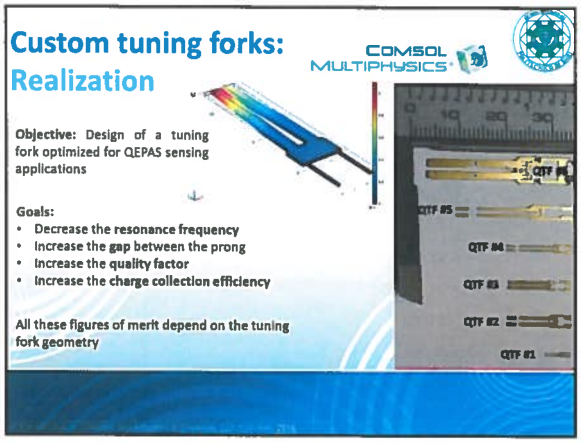
Piezoelectric signal: $I = a\frac{dx}{dt} = \frac{V}{\boxed{R}}$

Fork constant: $a = 3d_{11}E\boxed{\frac{Tw}{L}}$



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

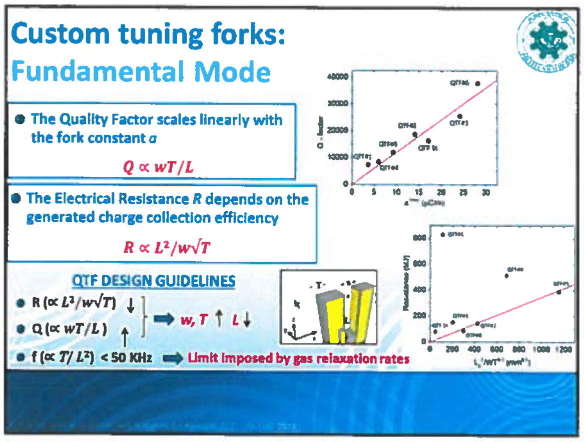


Custom tuning forks: Realization

Objective: Design of a tuning fork optimized for QEPAS sensing applications

Goals:
- Decrease the resonance frequency
- Increase the gap between the prong
- 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

$Q \propto wT/L$

- The Electrical Resistance R depends on the generated charge collection efficiency

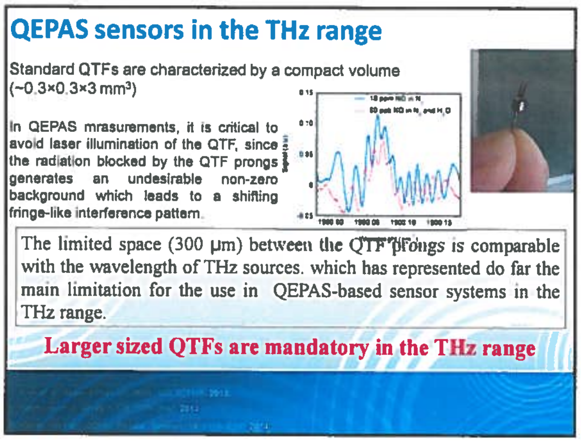
$R \propto L^2/w\sqrt{T}$

QTF DESIGN GUIDELINES

- R ($\propto L^2/w\sqrt{T}$) ↓
- Q ($\propto wT/L$) ↑

$\Rightarrow$ $w, T \uparrow$ $L \downarrow$

- f ($\propto T/L^2$) < 50 KHz ⇒ Limit imposed by gas relaxation rates



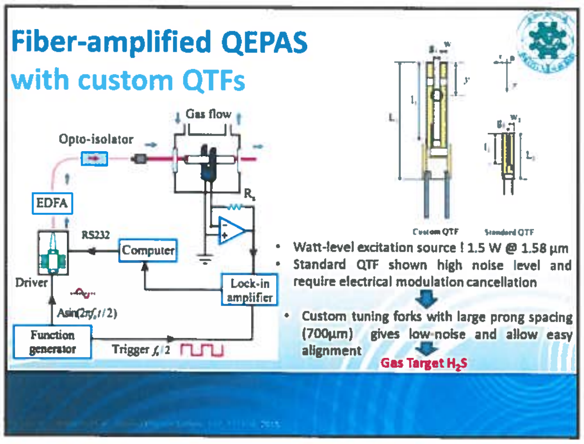
QEPAS sensors in the THz range

Standard QTFs are characterized by a compact volume (~0.3×0.3×3 mm³)

In QEPAS mrasurements, 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 do far the main limitation for the use in QEPAS-based sensor systems in the THz range.

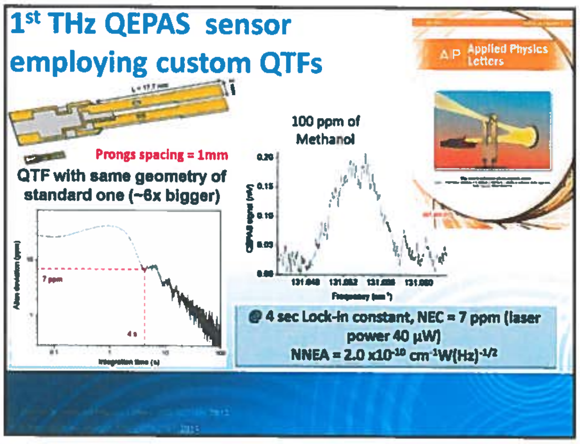
Larger sized QTFs are mandatory in the THz range



Fiber-amplified QEPAS with custom QTFs

- Watt-level excitation source ! 1.5 W @ 1.58 μm
- Standard QTF shown high noise level and require electrical modulation cancellation
- Custom tuning forks with large prong spacing (700μm) gives low-noise and allow easy alignment

Gas Target H_2S



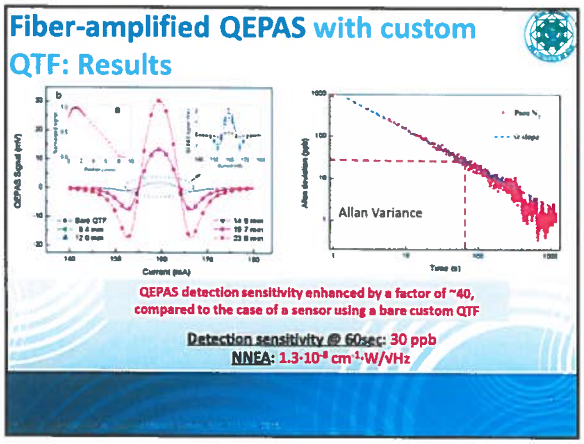
1st THz QEPAS sensor employing custom QTFs

Prongs spacing = 1mm

QTF with same geometry of standard one (~6x bigger)

100 ppm of Methanol

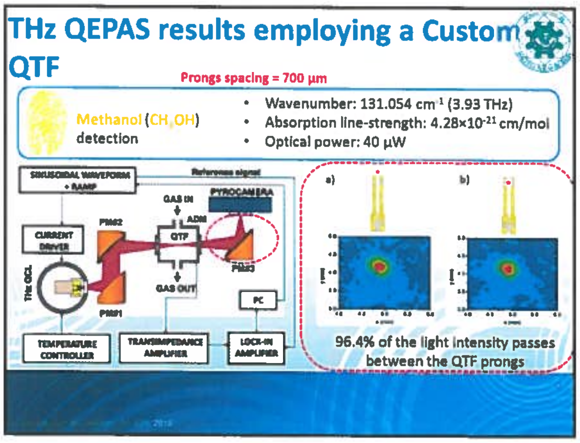
@ 4 sec Lock-in constant, NEC = 7 ppm (laser power 40 μW)
NNEA = 2.0×10^{-10} cm^{-1}W(Hz)$^{-1/2}$



Fiber-amplified QEPAS with custom QTF: Results

QEPAS detection sensitivity enhanced by a factor of ~40, compared to the case of a sensor using a bare custom QTF

Detection sensitivity @ 60sec: 30 ppb
NNEA: $1.3 \cdot 10^{-8}$ cm^{-1}·W/√Hz



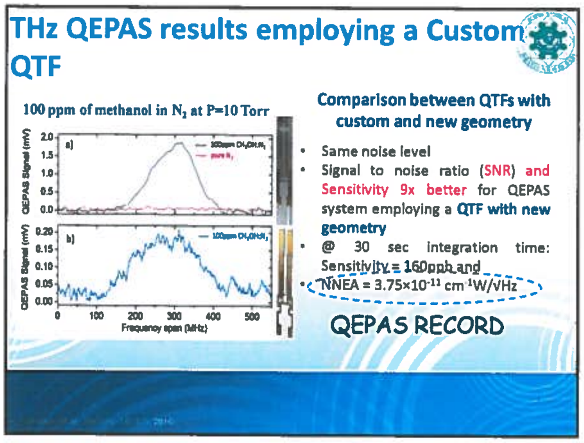
THz QEPAS results employing a Custom QTF

Prongs spacing = 700 μm

Methanol (CH_3OH) detection

- Wavenumber: 131.054 cm^{-1} (3.93 THz)
- Absorption line-strength: 4.28×10^{-21} cm/mol
- Optical power: 40 μW

96.4% of the light intensity passes between the QTF prongs



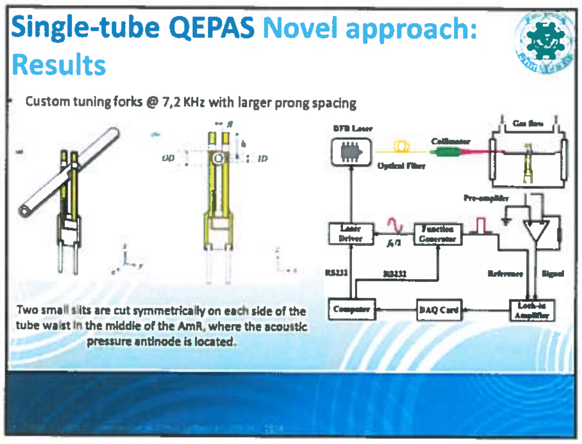
THz QEPAS results employing a Custom QTF

100 ppm of methanol in N_2 at P=10 Torr

Comparison between QTFs with custom and new geometry

- Same noise level
- Signal to noise ratio (SNR) and Sensitivity 9x better for QEPAS system employing a **QTF with new geometry**
- @ 30 sec integration time: Sensitivity = 160ppb and
- NNEA = 3.75×10^{-11} $cm^{-1}W/\sqrt{Hz}$

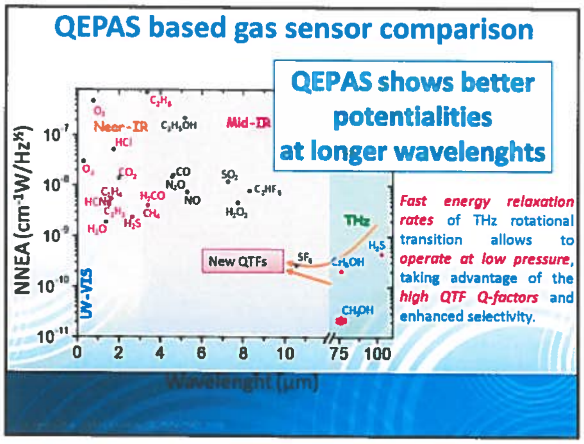
QEPAS RECORD



Single-tube QEPAS Novel approach: Results

- Custom tuning forks @ 7,2 KHz with larger prong spacing

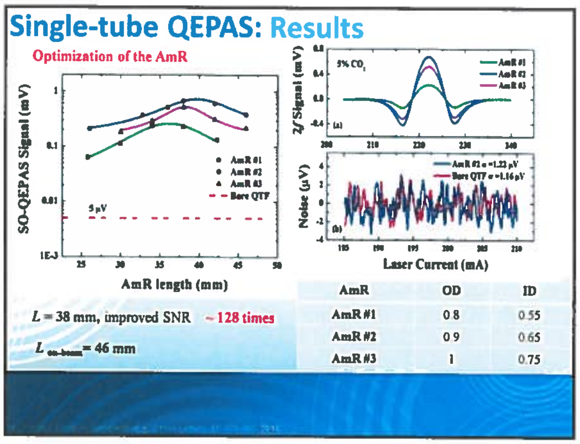
Two small slits are cut symmetrically on each side of the tube waist in the middle of the AmR, where the acoustic pressure antinode is located.



QEPAS based gas sensor comparison

QEPAS shows better potentialities at longer wavelenghts

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



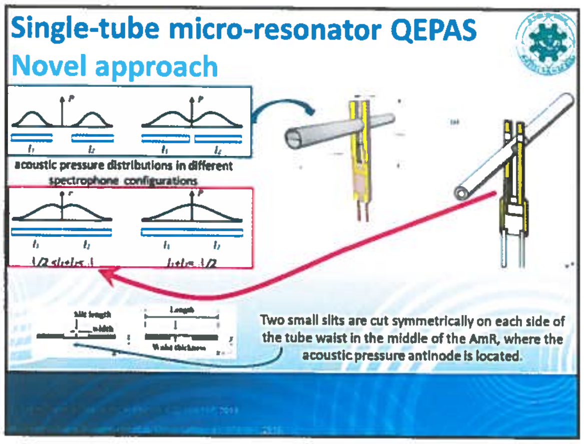
Single-tube QEPAS: Results

Optimization of the AmR

L = 38 mm, improved SNR ~128 times

L on-beam = 46 mm

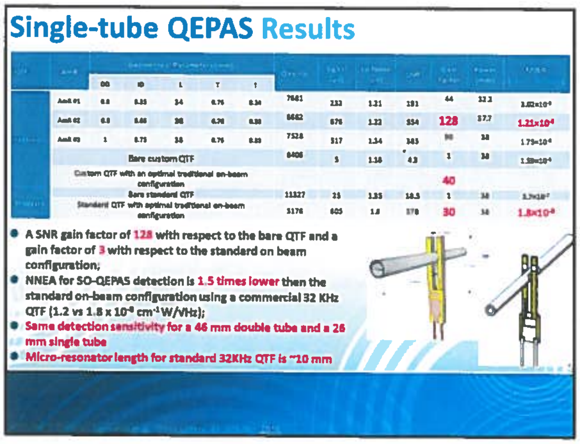
AmR	OD	ID
AmR #1	0.8	0.55
AmR #2	0.9	0.65
AmR #3	1	0.75



Single-tube micro-resonator QEPAS Novel approach

acoustic pressure distributions in different spectrophone configurations

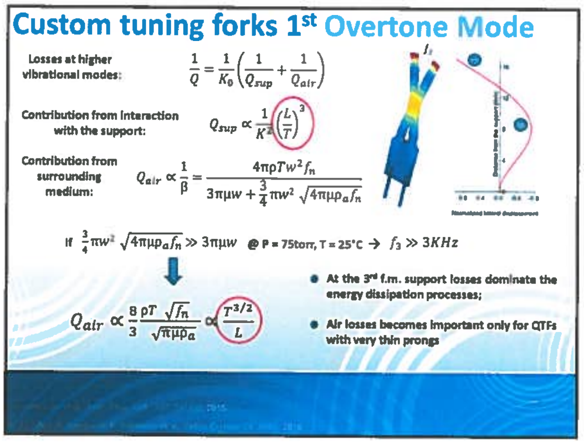
Two small slits are cut symmetrically on each side of the tube waist in the middle of the AmR, where the acoustic pressure antinode is located.



Single-tube QEPAS Results

[illegible]	[illegible]	OD	ID	L	T	t	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	AmR #1	0.8	0.55	34	0.76	0.14	7681	232	1.21	191	44	12.2	1.02×10⁻⁸
	AmR #2	0.9	0.65	38	0.76	0.10	6662	676	1.22	554	128	17.7	1.21×10⁻⁸
	AmR #3	1	0.75	38	0.76	0.10	7528	317	1.34	385	[illegible]	38	1.79×10⁻⁸
	Bare custom QTF						6406	5	1.16	4.3	1	38	1.59×10⁻⁸
	Custom QTF with an optimal traditional on-beam configuration										40		
[illegible]	Bare standard QTF						11327	25	1.35	18.5	1	38	1.7×10⁻⁷
	Standard QTF with optimal traditional on-beam configuration						3176	605	1.8	178	30	38	1.8×10⁻⁸

- A SNR gain factor of 128 with respect to the bare QTF and a gain factor of 3 with respect to the standard on beam configuration;
- NNEA for SO-QEPAS detection is 1.5 times lower then the standard on-beam configuration using a commercial 32 KHz QTF (1.2 vs 1.8 x 10^{-8} $cm^{-1}W/\sqrt{Hz}$);
- Same detection sensitivity for a 46 mm double tube and a 26 mm single tube
- Micro-resonator length for standard 32KHz QTF is ~10 mm



Custom tuning forks 1st Overtone Mode

Losses at higher vibrational modes: $\frac{1}{Q} = \frac{1}{K_0}\left(\frac{1}{Q_{sup}} + \frac{1}{Q_{air}}\right)$

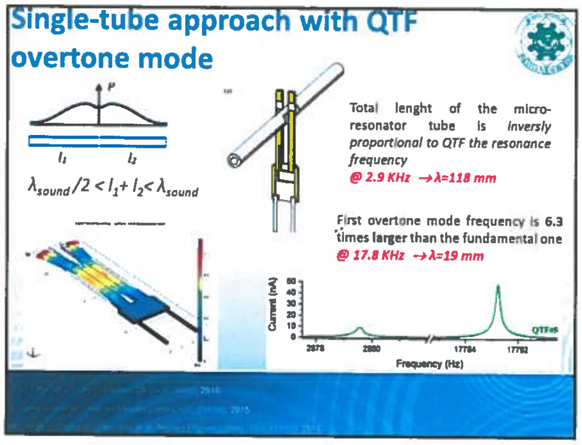
Contribution from interaction with the support: $Q_{sup} \propto \frac{1}{K^2}\boxed{\left(\frac{L}{T}\right)^3}$

Contribution from surrounding medium: $Q_{air} \propto \frac{1}{\beta} = \frac{4\pi\rho T w^2 f_n}{3\pi\mu w + \frac{3}{4}\pi w^2\sqrt{4\pi\mu\rho_a f_n}}$

If $\frac{3}{4}\pi w^2\sqrt{4\pi\mu\rho_a f_n} \gg 3\pi\mu w$ @ P = 75torr, T = 25°C → $f_3 \gg 3KHz$

$$Q_{air} \propto \frac{8}{3}\frac{\rho T\sqrt{f_n}}{\sqrt{\pi\mu\rho_a}} \propto \boxed{\frac{T^{3/2}}{L}}$$

- At the 3rd f.m. support losses dominate the energy dissipation processes;
- Air losses becomes important only for QTFs with very thin prongs

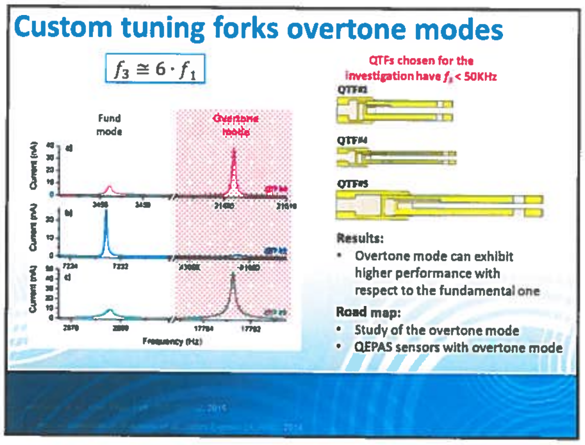


Single-tube approach with QTF overtone mode

$\lambda_{sound}/2 < l_1 + l_2 < \lambda_{sound}$

Total lenght of the micro-resonator tube is *inversly proportional to QTF the resonance frequency*
@ 2.9 KHz →λ=118 mm

First overtone mode frequency is 6.3 times larger than the fundamental one
@ 17.8 KHz →λ=19 mm



Custom tuning forks overtone modes

$f_3 \cong 6 \cdot f_1$

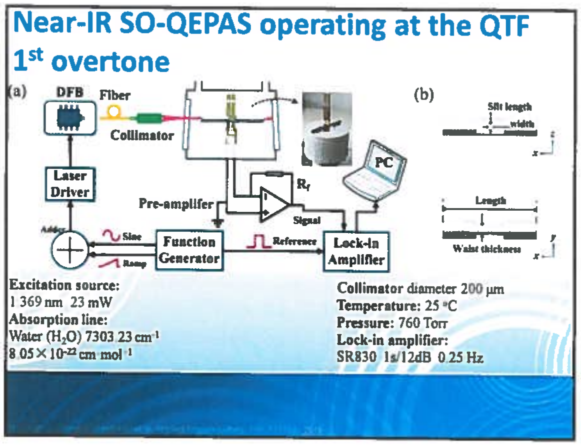
QTFs chosen for the investigation have f_3 < 50KHz

Results:

- Overtone mode can exhibit higher performance with respect to the fundamental one

Road map:

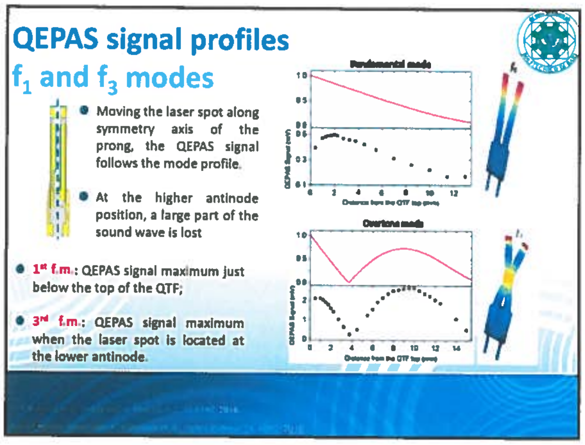
- Study of the overtone mode
- QEPAS sensors with overtone mode



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

Excitation source:
1 369 nm 23 mW
Absorption line:
Water (H_2O) 7303 23 cm^{-1}
8 05 × 10^{-22} cm mol^{-1}

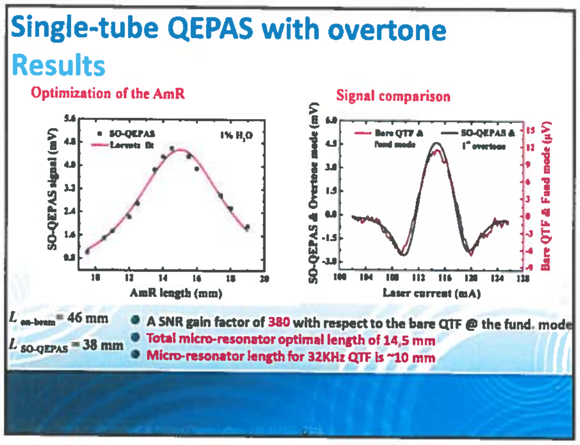
Collimator diameter 200 μm
Temperature: 25 °C
Pressure: 760 Torr
Lock-in amplifier:
SR830 1s/12dB 0 25 Hz



QEPAS signal profiles

f_1 and f_3 modes

- Moving the laser spot along symmetry axis of the prong, the QEPAS signal follows the mode profile.
- At the higher antinode position, a large part of the sound wave is lost
- 1st f.m.: QEPAS signal maximum just below the top of the QTF;
- 3rd f.m.: QEPAS signal maximum when the laser spot is located at the lower antinode.



Single-tube QEPAS with overtone

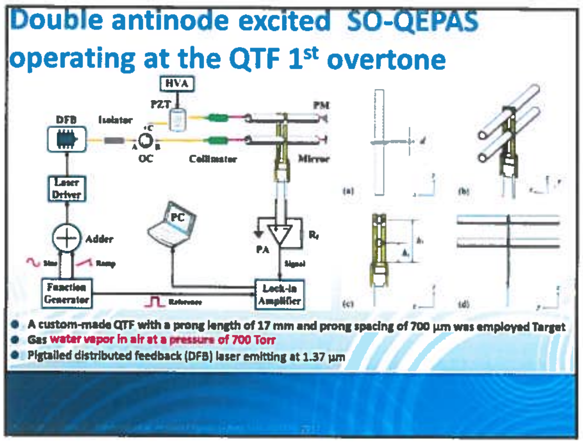
Results

Optimization of the AmR

Signal comparison

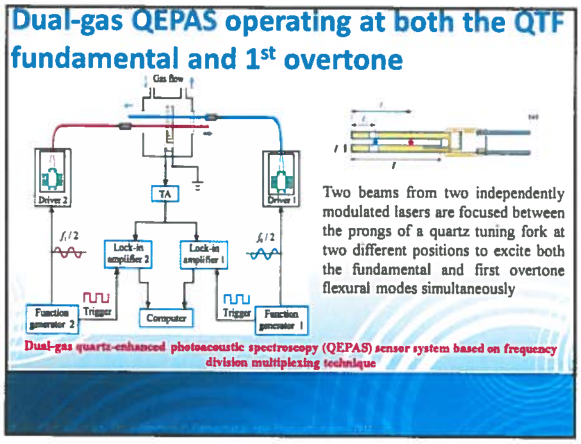
$L_{on\text{-}beam}$ = 46 mm
$L_{SO\text{-}QEPAS}$ = 38 mm

- A SNR gain factor of 380 with respect to the bare QTF @ the fund. mode
- Total micro-resonator optimal length of 14,5 mm
- Micro-resonator length for 32KHz QTF is ~10 mm



Double antinode excited SO-QEPAS operating at the QTF 1st overtone

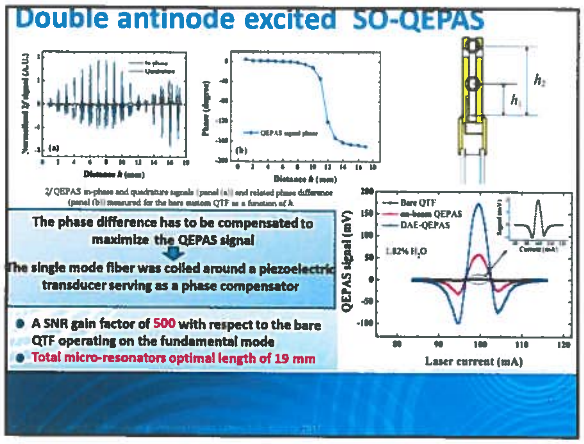
- A custom-made QTF with a prong length of 17 mm and prong spacing of 700 μm was employed Target
- Gas water vapor in air at a pressure of 700 Torr
- Pigtailed distributed feedback (DFB) laser emitting at 1.37 μm



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 based on frequency division multiplexing technique



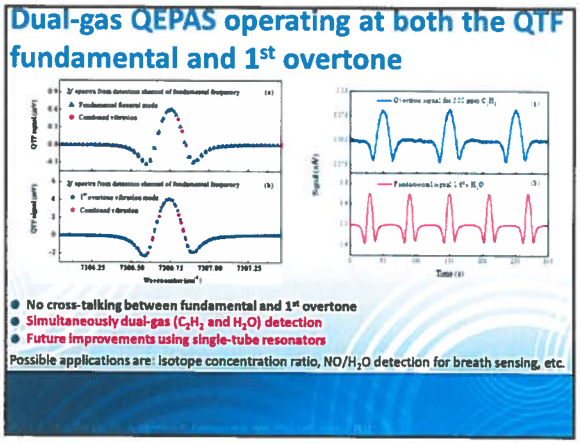
Double antinode excited SO-QEPAS

2f QEPAS in-phase and quadrature signals (panel (a)) and related phase difference (panel (b)) measured for the bare custom QTF as a function of h.

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 SNR gain factor of 500 with respect to the bare QTF operating on the fundamental mode
- Total micro-resonators optimal length of 19 mm



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

- No cross-talking between fundamental and 1st overtone
- Simultaneously dual-gas (C_2H_2 and H_2O) detection
- Future improvements using single-tube resonators

Possible applications are: isotope concentration ratio, NO/H_2O detection for breath sensing, etc.

Single-tube QEPAS with overtone Results

Performances comparison:

QTF	configuration	OD (mm)	ID (mm)	L_a (mm)	Gain factor	NNEA
Custom	bare QTF				1	$1.59 \cdot 10^{-6}$
	two-tubes	1.5	1.3	46	40	$4.0 \cdot 10^{-8}$
	single-tube	0.9	0.65	38	128	$1.21 \cdot 10^{-8}$
	Single-tube+overtone	0.98	0.62	14.5	380	**$2.76 \cdot 10^{-9}$**
	Double antinode + overtone	1.58	1.3	19	500	$1.73 \cdot 10^{-9}$
Standard	bare QTF				1	$3.7 \cdot 10^{-7}$
	on-beam	1.24	0.8	10.0	30	**$1.8 \cdot 10^{-8}$**

(NNEA: normalized noise equivalent absorption coefficient $cm^{-1} \cdot W/\sqrt{Hz}$)

The sensitivity enhancement factor is ~10 times higher than that attained by a conventional QEPAS spectrophone based on commercial 32 kHz QTF

Conclusions and Future Perspectives

- Demonstration of *near-IR and THz 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