New developments in quartz enhanced photoacoustic gas sensing

V. Spagnolo[1], A. Sampaolo[1,2], P. Patimisco[1,2], H. Zengh[2,3], M. Giglio[1], L. Dong[3], Frank K. Tittel[2]

[1]Dipartimento Interateneo di Fisica, University and Politecnico of Bari, CNR-IFN UOS BARI, Bari, Italy

[2]Department of Electrical and Computer Engineering, Rice University, 6100 Main Street, Houston, TX 77005, USA

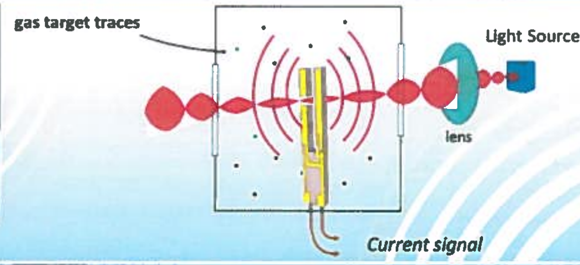
[3]State Key Laboratory of Quantum Optics and Quantum Optics Devices, Institute of Laser Spectroscopy, Shanxi University, Taiyuan 030006, China

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-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 vibration is excited by the sound waves
- The mechanical vibration is converted to an electrical signal via piezoelectric effect
- The trace gas concentration is proportional to the electrical signal



P. Patimisco et al. "Quartz-enhanced photoacoustic spectrophones exploiting custom tuning forks: a review", Advances in Physics X 2, 169-187 2016

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 for several molecule
- Cross sensitivity issues
- Alignment cost (no light hitting 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

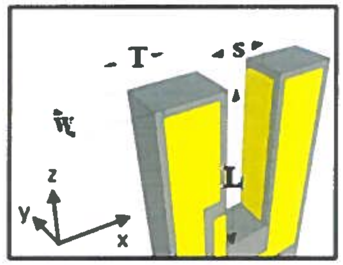
V. Spagnolo et al. Optics Letters 37, 4461-4463 2012
P. Patimisco et al. Quartz-Enhanced Photoacoustic Spectroscopy: a Review, Sensors 14, 6165 2014

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



QEPAS signal: $S \propto P\alpha Q\varepsilon$

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

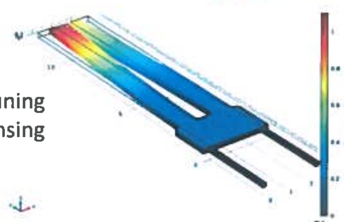
Piezoelectric signal: $I = a\frac{dx}{dt} = \frac{V}{R}$

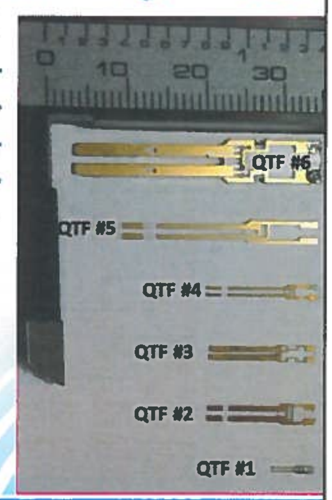
Fork constant: $a = 3d_{11}E \cdot \frac{Tw}{L}$

P. Patimisco et al. Sensors and Actuators B Chemical 227 539-546 2016

Custom tuning forks
Realization

COMSOL MULTIPHYSICS®





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**

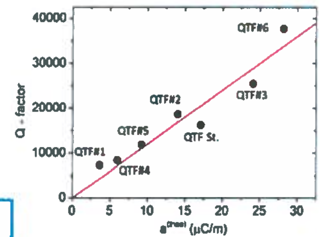
All these figures of merit depend on the tuning fork geometry

P. Patimisco et al. Sensors and Actuators B Chemical 227 539-546 2016

Custom tuning forks
Fundamental Mode

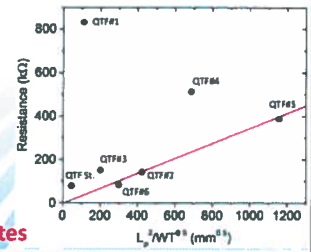
- The Quality Factor scales linearly with the fork constant *a*

$$Q \propto wT/L$$



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

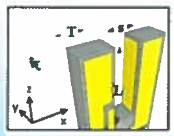
$$R \propto L^2/w\sqrt{T}$$



QTF DESIGN GUIDELINES

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

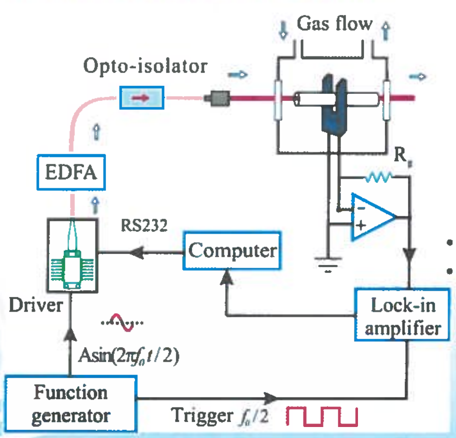
⇒ *w, T* ↑ *L* ↓

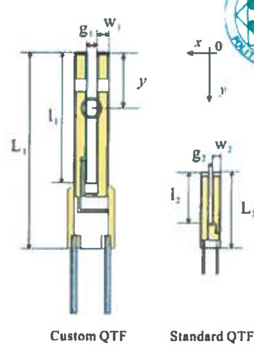


- f ($\propto T/L^2$) < 50 KHz ⇒ **Limit imposed by gas relaxation rates**

P. Patimisco et al., Sensors and Actuators B Chemical, 227, 539-546, 2016

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

⇓

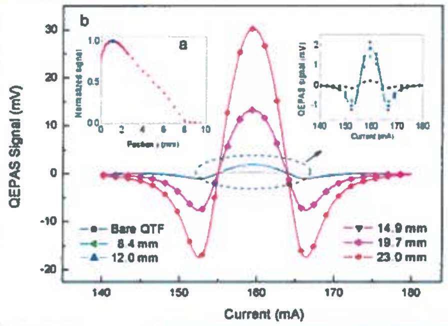
- Custom tuning forks with large prong spacing (700μm) gives low-noise and allow easy alignment

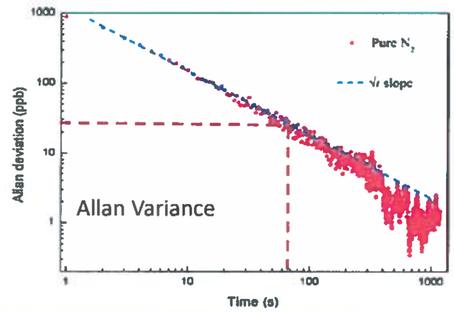
⇓

Gas Target H_2S

H. Wu, A. Sampaolo et al., Applied Physics Letters, 107, 111104, 2015

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

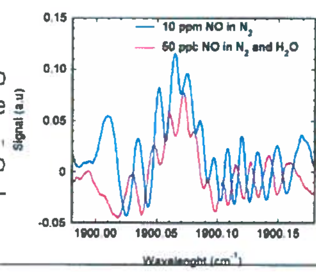
Detection sensitivity @ 60sec: 30 ppb
NNEA: $1.3\cdot10^{-8}$ $cm^{-1}\cdot W/\sqrt{Hz}$

H. Wu, A. Sampaolo et al. Applied Physics Letters 107, 111104, 2015

QEPAS sensors in the THz range

Standard QTFs are characterized by a compact sensitive volume (~0.3×0.3×3 mm^3)

In QEPAS experiments, 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 carries a shifting fringe-like interference pattern.

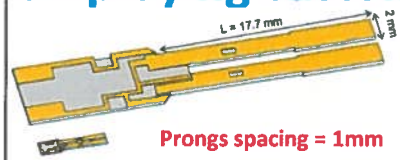


The limited space (300 μm) between the QTF prongs is comparable with the wavelength of THz sources so far has represented the main limitation for the use in QEPAS-based sensor systems in THz range.

Larger sized QTFs are mandatory to operate in the THz

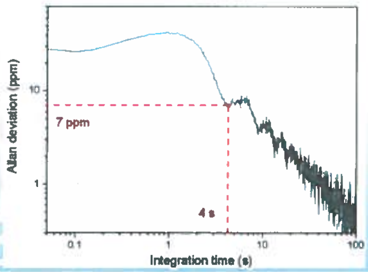
S. Borri et al., Applied Physics Letters, 103, 021105, 2013
P. Patimisco et al., Analyst, 139, 2079-2087, 2014
P. Patimisco et al., "QEPAS Review", Sensors, 14, 6165-6206, 2014

1st THz QEPAS sensor employing custom QTFs

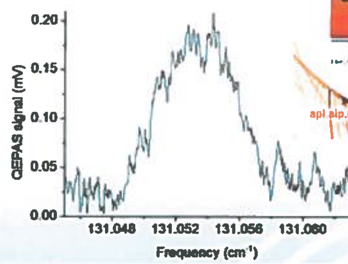


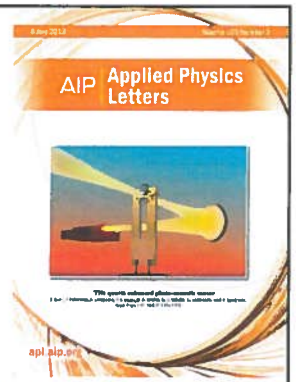
Prongs spacing = 1mm

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 x10^{-10} cm^{-1}W(Hz)$^{-1/2}$

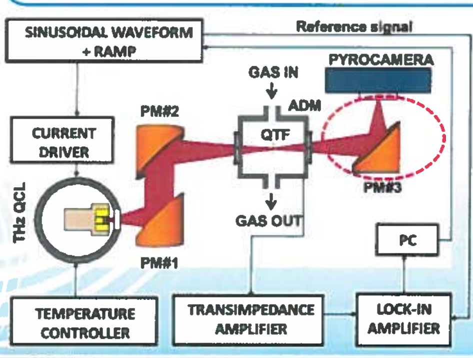
S. Borri et al., Applied Physics Letters, 103, 021105, 2013
P. Patimisco et al., Analyst, 139, 2079-2087, 2014

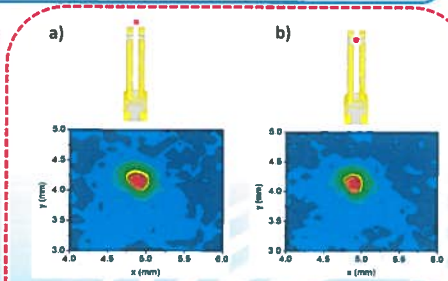
THz QEPAS results employing a Novel Custom QTF

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

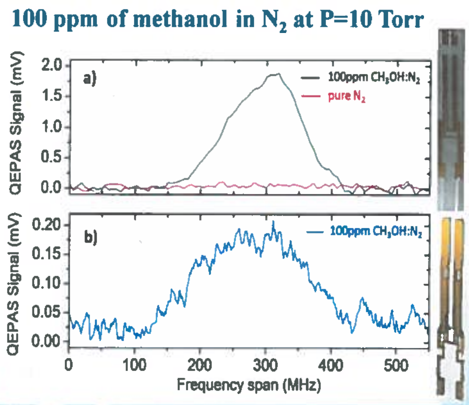




96.4% of the light intensity passes between the QTF prongs

A. Sampaolo et al., Sensors, 16, 439, 2016

THz QEPAS results employing a Novel Custom QTF



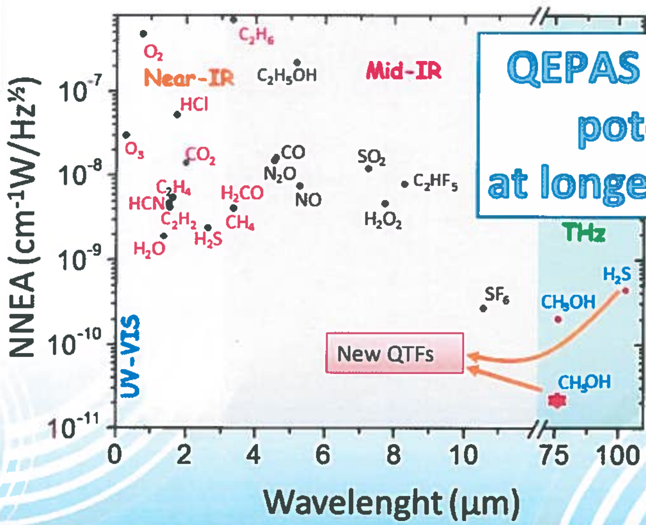
Comparison between QTFs with custom and new geometry

- 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

V. Spagnolo et al., Sensors, 16, 439, 2016

QEPAS sensors comparison

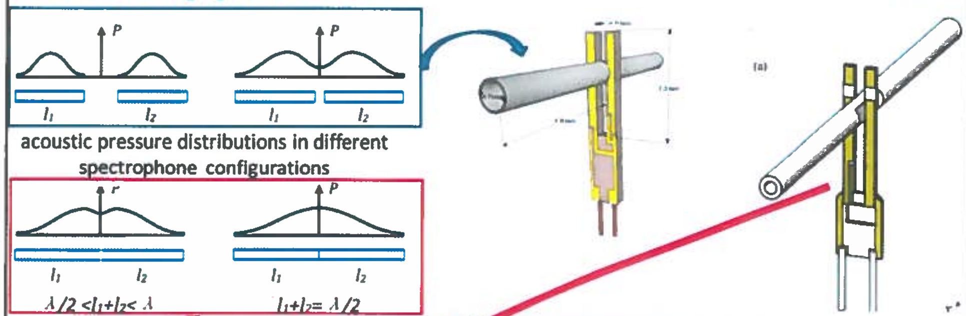


QEPAS shows better potentialities at longer wavelenghts

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.

V. Spagnolo et al., Optics Express, 23, 7574-7582, 2015

Single-tube micro-resonator QEPAS
Novel approach

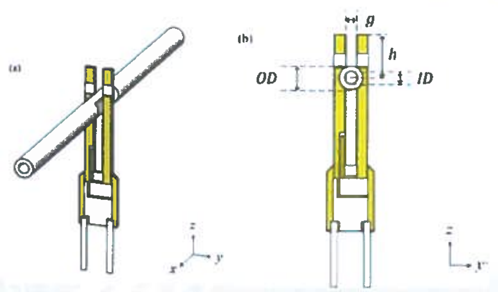


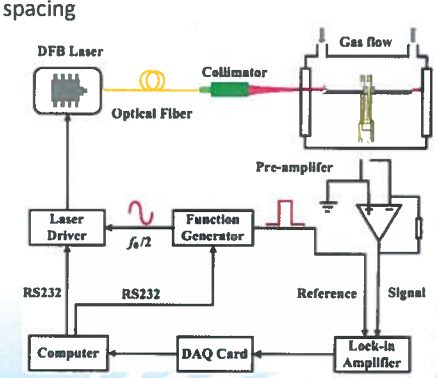
Two small slits are cut symmetrically on each side of the tube waist in the middle of the AmR, where the acoustic pressure antinode is located.

P. Patimisco et al., Advances in Physics X 2, 169-187, 2016
H. Zheng, L. Dong, A. Sampaolo et al. Optics Letters 41, 978-981, 2016

Single-tube QEPAS Novel approach: Results

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



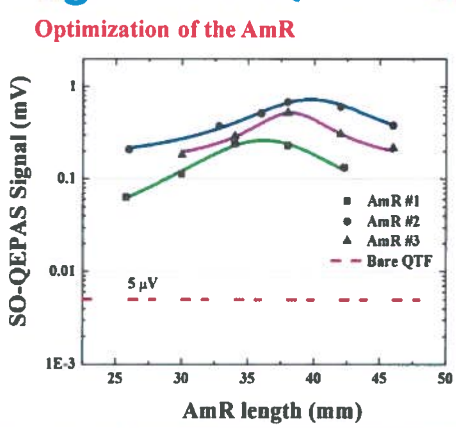


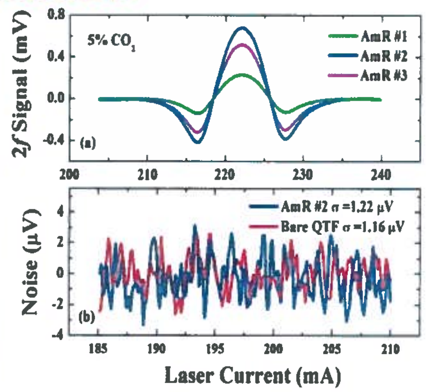
Two small slits are cut symmetrically on each side of the tube waist in the middle of the AmR, where the acoustic pressure antinode is located.

H. Zheng, L. Dong, A. Sampaolo et al. Optics Letters 41, 978-981, 2016

Single-tube QEPAS: Results

Optimization of the AmR





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

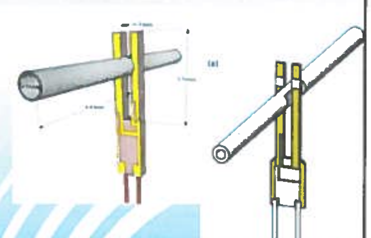
L = 38 mm, improved SNR ~ 128 times

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

Single-tube QEPAS: Results

QTF	AmR	Geometrical Parameters (mm)					Q factor	Signal (μV)	1σ Noise (μV)	SNR	Gain Factor	Power (mW)	NNEA
		OD	ID	L	T	I							
Custom	AmR #1	0.8	0.55	34	0.76	0.24	7681	232	1.21	191	44	32.2	3.02×10^{-8}
	AmR #2	0.9	0.65	38	0.76	0.33	6682	676	1.22	554	**128**	37.7	**1.21×10^{-8}**
	AmR #3	1	0.75	38	0.76	0.33	7528	517	1.34	385	90	38	1.75×10^{-8}
	Bare custom QTF						8406	5	1.16	4.3	1	38	1.59×10^{-6}
	Custom QTF with an optimal traditional on-beam configuration										**40**		
Standard	Bare standard QTF						11327	25	1.35	18.5	1	38	3.7×10^{-7}
	Standard QTF with optimal traditional on-beam configuration						5176	605	1.6	378	**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/√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**

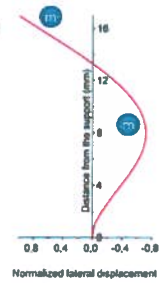


Custom tuning forks 1st Overtone Mode

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 QTF support: $Q_{sup} \propto \frac{1}{K^2}\left(\frac{L}{T}\right)^3$

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 → $f_3 \gg 3KHz$

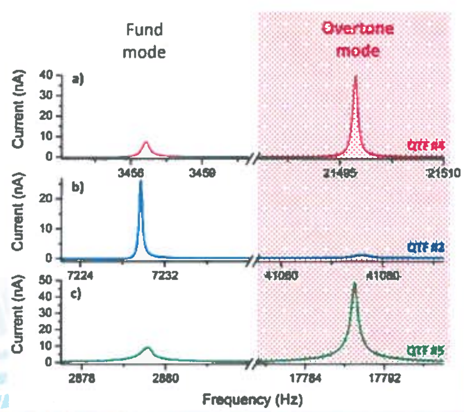
$$Q_{air} \propto \frac{8}{3}\frac{\rho T}{\sqrt{\pi\mu\rho_a}}\sqrt{f_n} \propto \frac{T^{3/2}}{L}$$

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

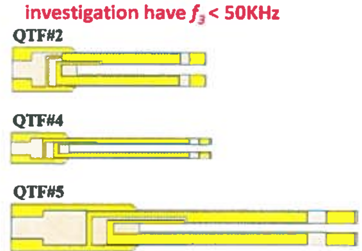
A. Sampaolo et al. Appl. Phys. Lett. 107, 231102, 2015
F. K. Tittel, A. Sampaolo, P. Patimisco et al. Optics Express 24, A682, 2016

Custom tuning forks overtone modes

$$f_3 \cong 6 \cdot f_1$$



QTFs chosen for the investigation have f_3 < 50KHz



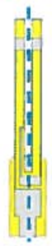
Results:
- Overtone mode can exhibit higher performance with respect to the fundamental one

Road map:
- Study of the overtone mode
- QEPAS sensors with overtone mode

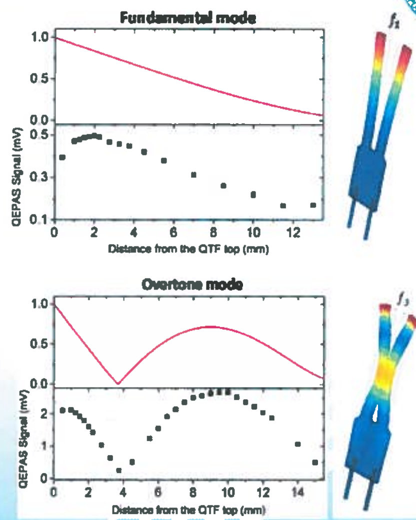
A. Sampaolo et al. Appl. Phys. Lett. 107, 231102, 2015
F. K. Tittel, A. Sampaolo, P. Patimisco et al. Optics Express 24, A682, 2016

QEPAS signal profiles:

f_1 and f_3 modes



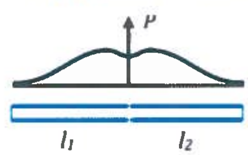
- Moving the laser spot along symmetry axis of the prong, the QEPAS signal follows the mode profile.
- At the higher antinode position, a large part of the sound wave is lost



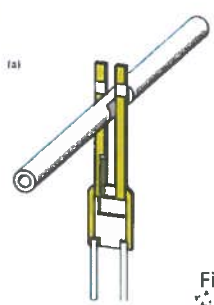
- **1st f.m.**: QEPAS signal is a maximum just below the top of the QTF;
- **3rd f.m.**: QEPAS signal maximum when the laser spot is located at the lower antinode.

P. Patimisco et al., Advances in Physics X 2, 169-187, 2016
F. K. Tittel, A. Sampaolo, P. Patimisco et al., Optics Express 24, A682, 2016

Single-tube approach with QTF overtone mode



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

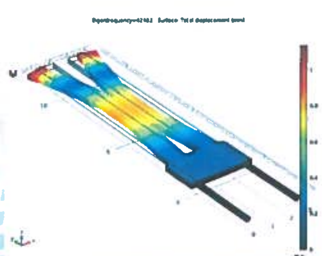


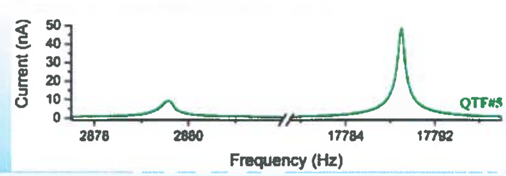
Total length of the micro-resonator tube is *inversely proportional to the QTF the resonance frequency*

@ 2.9 KHz →λ=118 mm

First overtone mode frequency is **6.3** times **larger** than the fundamental one

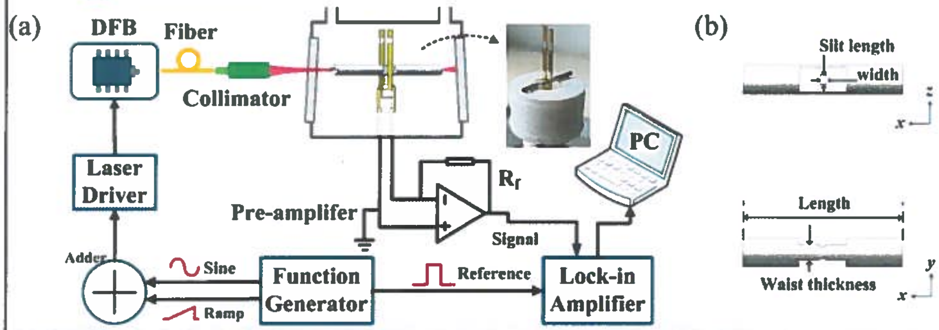
@ 17.8 KHz →λ=19 mm





F. K. Tittel et al., Optics Express 24, A682-A692, 2016
A. Sampaolo et al., Applied Physics Letters 107, 231102, 2015
H. Zheng, L. Dong, A. Sampaolo et al., Applied Physics Letters, 109, 111103, 2016

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



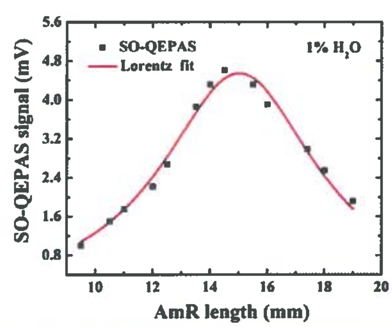
Excitation source:
1.369 nm 23 mW
Absorption line:
Water (H_2O) 7303.23 cm^{-1}
8.05 × 10^{-22} cm·mol^{-1}

Collimator diameter 200 μm
Temperature: 25 °C
Pressure: 760 Torr
Lock-in amplifier:
SR830 1s/12dB 0.25 Hz

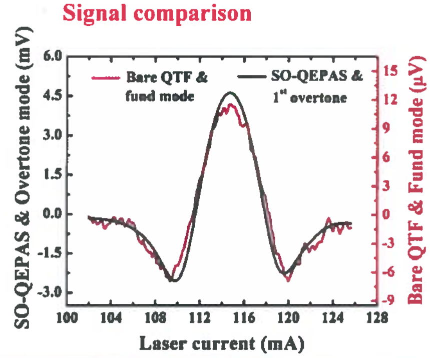
H. Zengh, L. Dong, A. Sampaolo et al. Applied Physics Letters 109, 111103 2016

Single-tube QEPAS with overtone: Results

Optimization of the AmR



Signal comparison

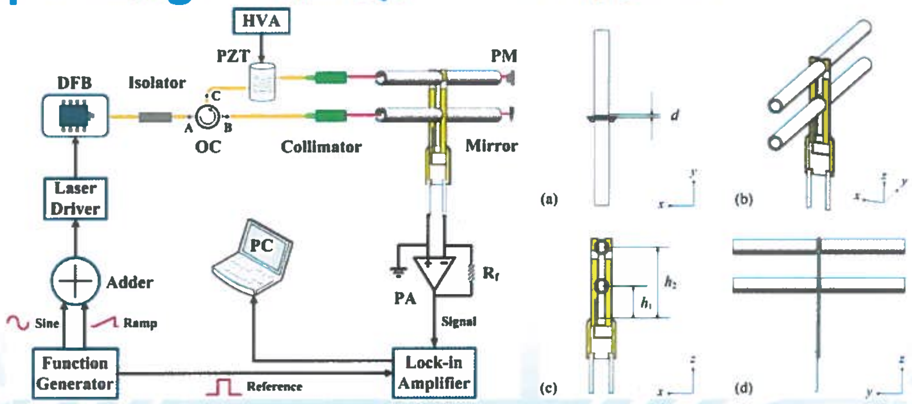


$L_{on\text{-}beam}$ = 46 mm
$L_{SO\text{-}QEPAS}$ = 38 mm

- 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

H. Zengh, L. Dong, A. Sampaolo et al. Applied Physics Letters 109, 111103 2016

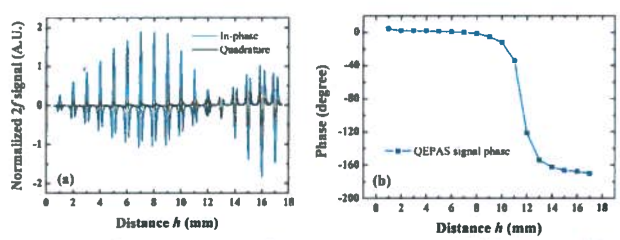
Double antinode excited SO-QEPAS operating at the QTF 1st overtone



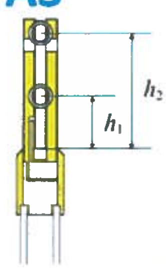
- A custom-made QTF with a prong length of 17 mm and a prong spacing of 700 µm was employed Targe
- Target Gas: water vapor in air at a pressure of 700 Torr
- Pigtailed distributed feedback (DFB) laser emitting at 1.37 µm

H. Zheng, L. Dong, P. Patimisco et al. Applied Physics Letters 110, 021110 2017

Double antinode excited SO-QEPAS



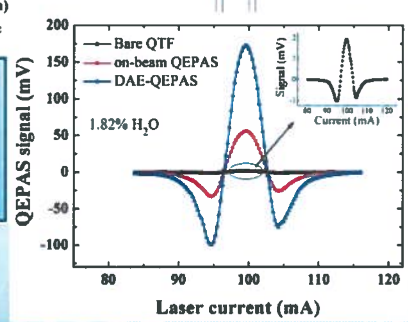
2f QEPAS in-phase and quadrature signals (panel (a)) and related phase difference (panel (b)) measured for the bare custom QTF as a function of h.



The phase difference has to be compensated to maximize the QEPAS signal

A 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-resonator optimal length of 19 mm



H. Zheng, L. Dong, P. Patimisco et al. Applied Physics Letters 110, 021110 2017

Single-tube QEPAS with overtone: Results

Performance comparisons:

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

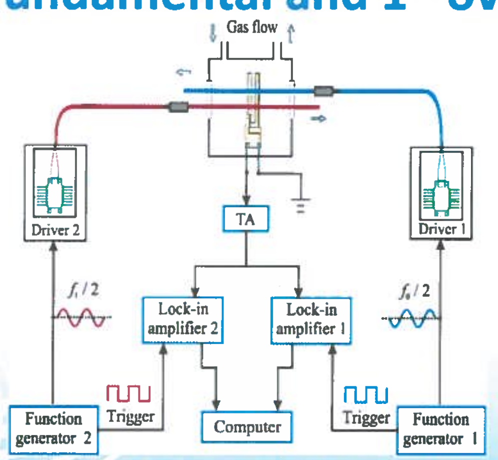
(NNEA: normalized noise equivalent absorption coefficient $cm^{-1} \cdot W/\sqrt{Hz}$)

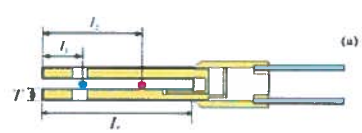
Sensitivity enhancement factor is >10 times higher than that attained by a conventional QEPAS spectrophone based on commercial 32 kHz QTF

P. Patimisco et al. Advances in Physics X 2, 169-187, 2016

H. Zheng, L. Dong, A. Sampaolo et al. Applied Physics Letters 110, 021110, 2017

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



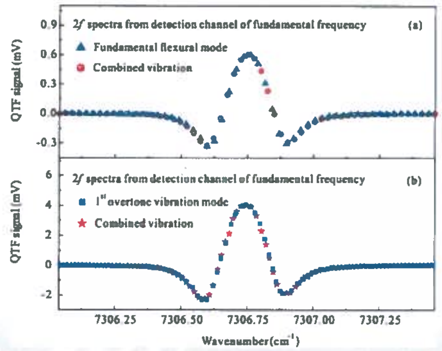


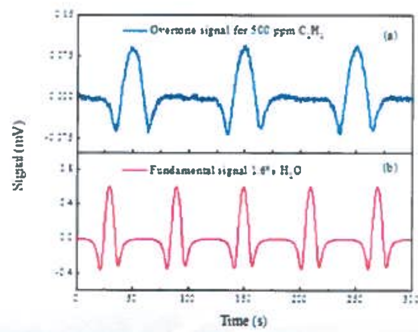
Two beams from two independently modulated lasers are focused between the prongs of a quartz tuning fork at two different positions to excite both the fundamental and first overtone flexural modes simultaneously

Dual-gas quartz-enhanced photoacoustic spectroscopy (QEPAS) sensor system based on a frequency division multiplexing technique

H. Wu, X. Yin, L. Dong, K. Pei, A. Sampaolo, P. Patimisco et al. Appl. Phys. Lett. in press 2017

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





- **No cross-talk between fundamental and 1st overtone modes**
- **Simultaneously dual-gas (e.g C_2H_2 and H_2O) detection**
- **Future improvements using single-tube resonators**

Possible applications are: isotope concentration ratios or NO/H_2O detection for breath sensing

H. Wu, X. Yin, L. Dong, K. Pei, A. Sampaolo, P. Patimisco et al. Appl. Phys. Lett. in press 2017

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 operating at the fundamental and 1st overtone flexural modes

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