Recent Advances in Quartz-Enhanced Photoacoustic Spectroscopy for Gas Sensing Applications

Presented by:

OSA Environmental Sensing Technical Group

Environmental Sensing Technical Group

Technical Group Leadership:

Krishnan Parameswaran, Analog Devices Inc., USA

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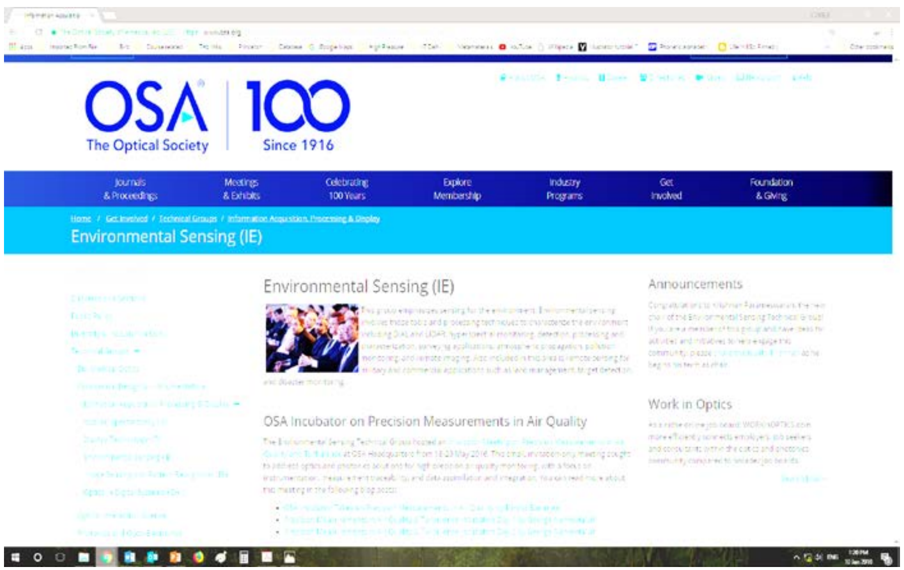
Amartya Sengupta, Indian Institute of Technology Delhi, India

OSA Environmental Sensing Technical Group

Technical Group Website:

www.osa.org/EnvironmentalSensingTG



Over 1,100 Total Members

Scope:

This technical group covers optical tools and techniques used in environmental sensing, including DIAL and LIDAR, hyperspectral monitoring, detection, processing and characterization, surveying applications, atmospheric propagation, pollution monitoring, and remote imaging. Also included in this area is remote sensing for military and commercial applications such as land management, target detection, and disaster monitoring.

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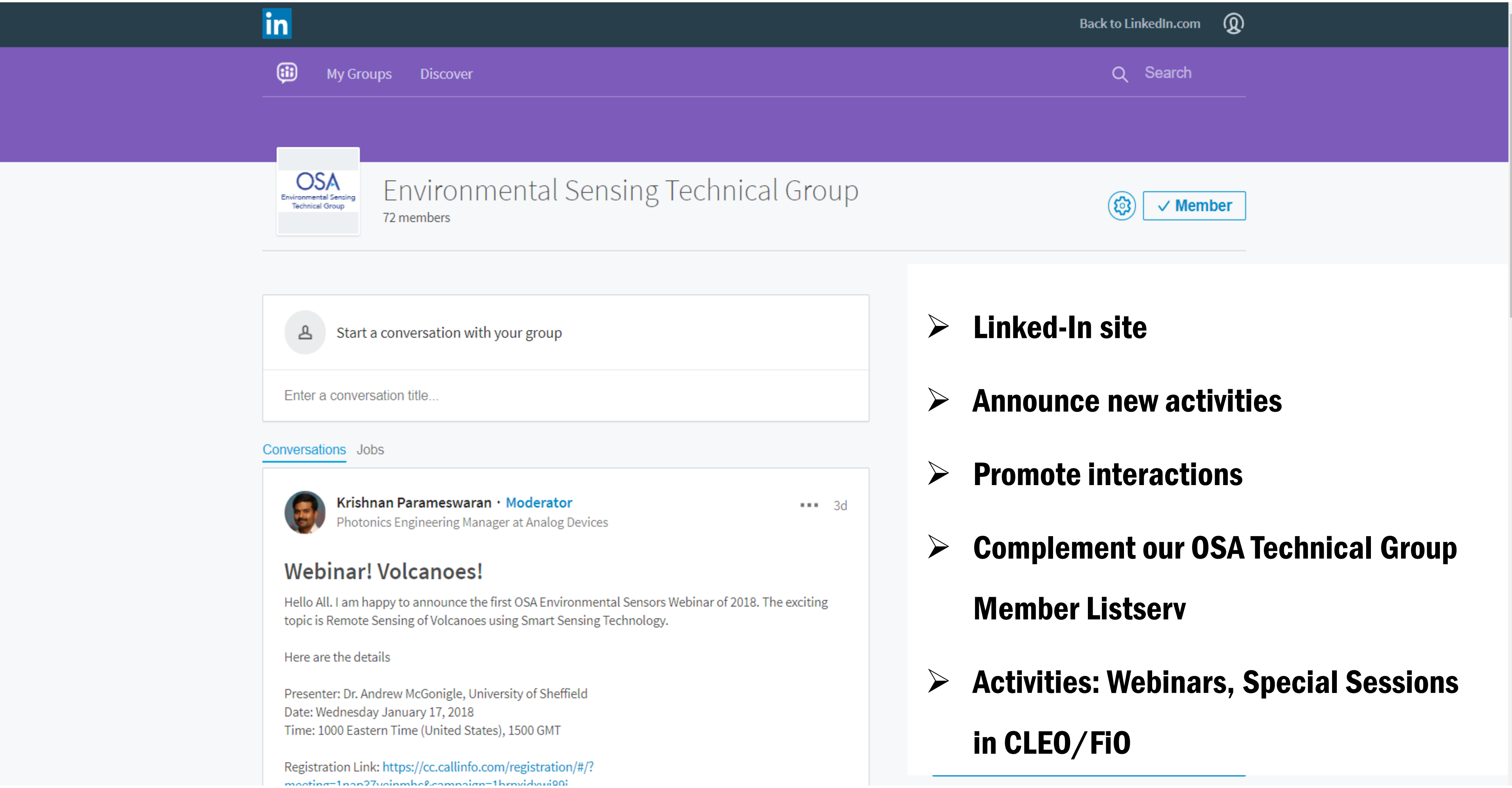


- **Linked-In site**
- **Announce new activities**
- **Promote interactions**
- **Complement our OSA Technical Group Member Listserv**
- **Activities: Webinars, Special Sessions in CLEO/FiO**

OSA INCUBATORS

Collaborate. Innovate. Discover.

OSA Agri-Photonics Incubator

Advanced Spectroscopy in Precision Agriculture

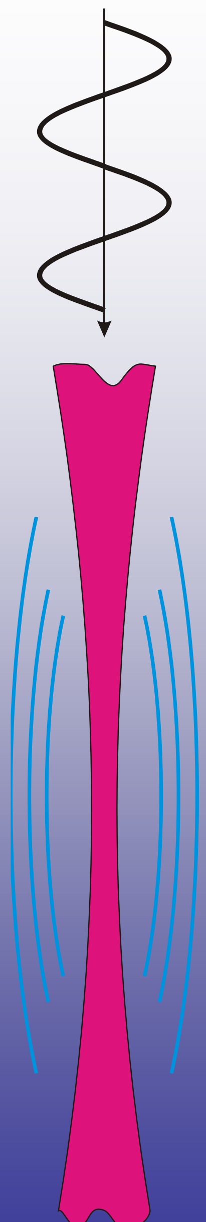
12-14 May 2019, OSA Headquarters, Washington DC

We are excited to share with you that our technical group has been working on planning an OSA Incubator focused on exploring advanced spectroscopy in precision agriculture. Visit www.osa.org/agriphotonicsinc to learn more!

Welcome to Today's Webinar!

OSA Environmental Sensing Technical Group

Vincenzo Spagnolo obtained the PhD in physics in 1994 from University of Bari. From 1997 to 1999, he worked as researcher of the National Institute of the Physics of Matter (INFM). Since 2004, he has been with the Technical University of Bari, formerly as assistant and associate professor and, starting from 2018, as Full Professor of Applied Physics. He is "Hundred Talent" visiting professor as Shanxi University in Taiyuan (China). He is the director of the joint-research lab PolySense created by Technical University of Bari and THORLABS GmbH. His research interests include optoacoustic gas sensing and spectroscopic techniques for real-time device monitoring. His research activity is documented by more than 180 Scopus publications and two filed patents. He has given more than 50 invited/keynote presentations at international conferences and workshops. Prof. Spagnolo is program committee member of several SPIE and OSA conferences. He is editor of Sensors (MPDI), Applied Science (MPDI) and Journal of Sensors (Hindawi). Prof. Spagnolo is senior member of the OSA and senior member of SPIE.

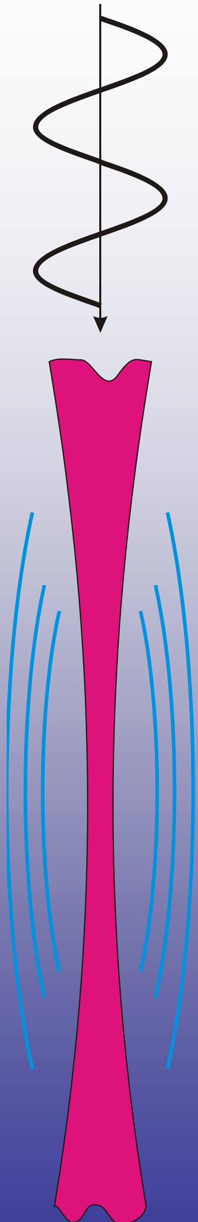


Recent advances in quartz-enhanced photoacoustic spectroscopy for gas sensing applications

Vincenzo Spagnolo

PolySense Lab, Technical University of Bari – Italy

- Motivation for optical Gas Sensing
- Quartz Enhanced Photoacoustic gas detection



Recent advances in quartz-enhanced photoacoustic spectroscopy for gas sensing applications

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- Motivation for optical Gas Sensing
- Quartz Enhanced Photoacoustic gas detection
  - QEPAS: Basic principles and merits
  - QEPAS with custom quartz tuning forks
  - QEPAS in the THZ range
  - Intracavity QEPAS
  - Real word applications
- Future perspectives

PolySense

Main applications of gas sensing

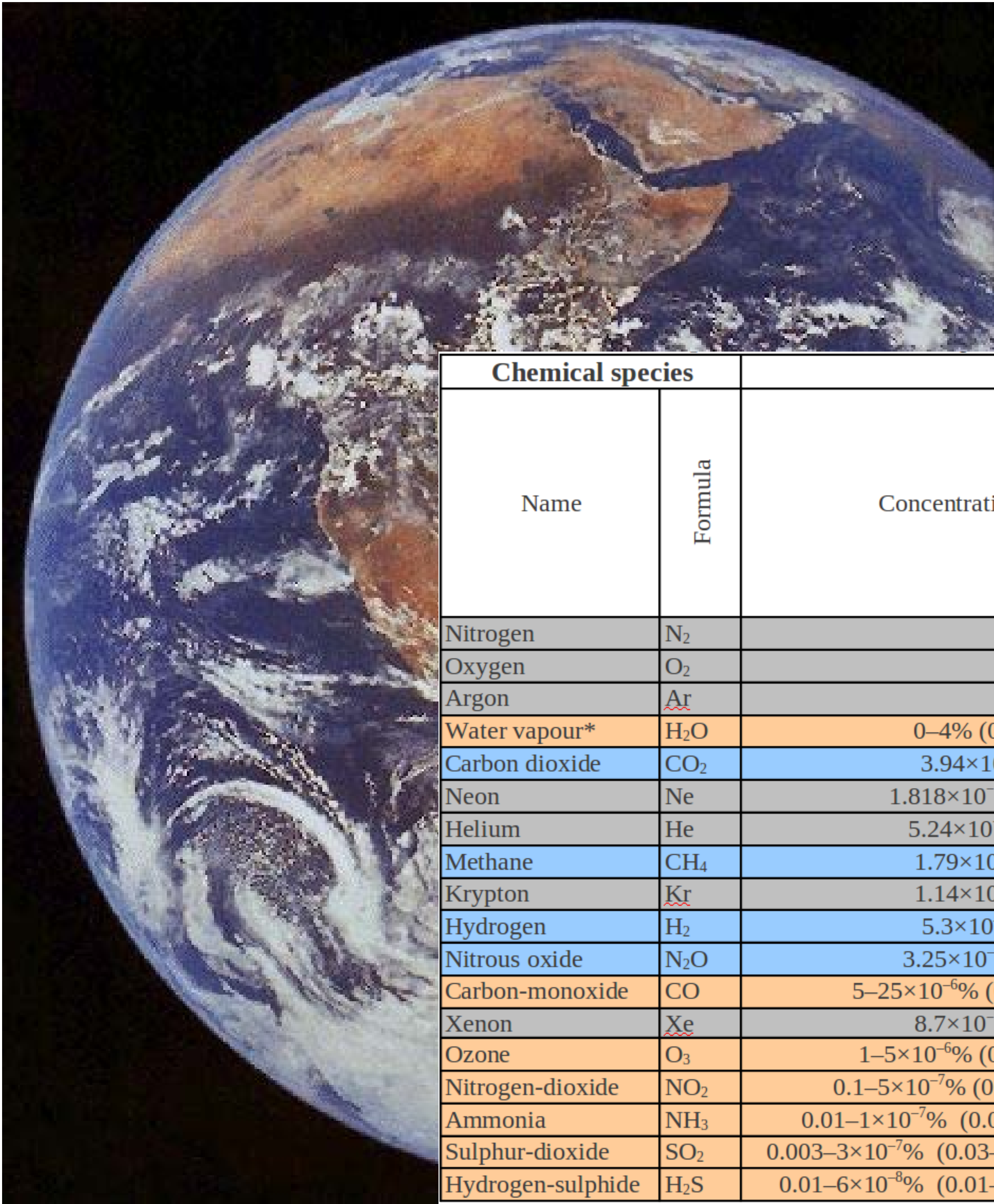
Industrial process control
- Chemical analysis
- Monitoring combustion processes
- Quantification of gas leaks

Health and Life Sciences
- Breath analysis
- Biomedicine

TRACE GAS SENSING APPLICATIONS

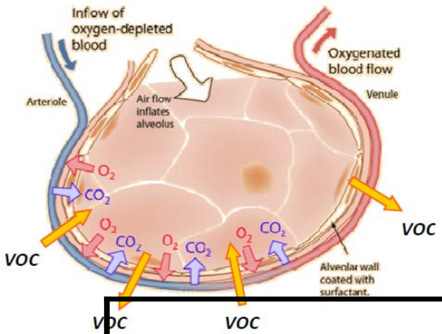
Law Enforcement
- National Security
- Defense

Environmental Monitoring
- Air pollution monitoring
- Detection of toxic gases
- Eco-sustainability



Trace gases in the atmosphere

Chemical species				Sources					
Name	Formula	Concentration	Residence time	Biogenic	Anthropogenic	Photochemical	Volcanic	Radiogenic	Other
Nitrogen	N_2	78.084%	1.6×10^{7} years	✓			✓		
Oxygen	O_2	20.946%	3×10^{3}–10^{4} years	✓					
Argon	Ar	0.934%						✓	
Water vapour*	H_2O	0–4% (0– 40 000 ppm)	10 days	✓	✓		✓		(1
Carbon dioxide	CO_2	3.94×10^{-2}% (394 ppm)	20–150 years	✓	✓		✓		
Neon	Ne	1.818×10^{-3}% (18.18 ppm)					✓?		
Helium	He	5.24×10^{-4}% (5.24 ppm)	10^{7} years					✓	
Methane	CH_4	1.79×10^{-4}% (1.79 ppm)	10 years	✓	✓				
Krypton	Kr	1.14×10^{-4}% (1.14 ppm)						✓	
Hydrogen	H_2	5.3×10^{-5}% (0.53 ppm)	2 years	✓	✓				(2
Nitrous oxide	N_2O	3.25×10^{-5}% (0.325 ppm)	150 years	✓	✓				
Carbon-monoxide	CO	5–25×10^{-6}% (0.05–0.25 ppm)	0.2–0.5 year	✓	✓				
Xenon	Xe	8.7×10^{-6}% (0.087 ppm)							
Ozone	O_3	1–5×10^{-6}% (0.01–0.05 ppm)	weeks - months			✓			
Nitrogen-dioxide	NO_2	0.1–5×10^{-7}% (0.001–0.05 ppm)	8–10 days	✓	✓	✓			
Ammonia	NH_3	0.01–1×10^{-7}% (0.0001–0.01 ppm)	~5 days	✓	✓				
Sulphur-dioxide	SO_2	0.003–3×10^{-7}% (0.03–30×10^{-3} ppm)	~2 days		✓	✓	✓		
Hydrogen-sulphide	H_2S	0.01–6×10^{-8}% (0.01–0.6×10^{-3} ppm)	~0.5 day	✓	✓		✓		

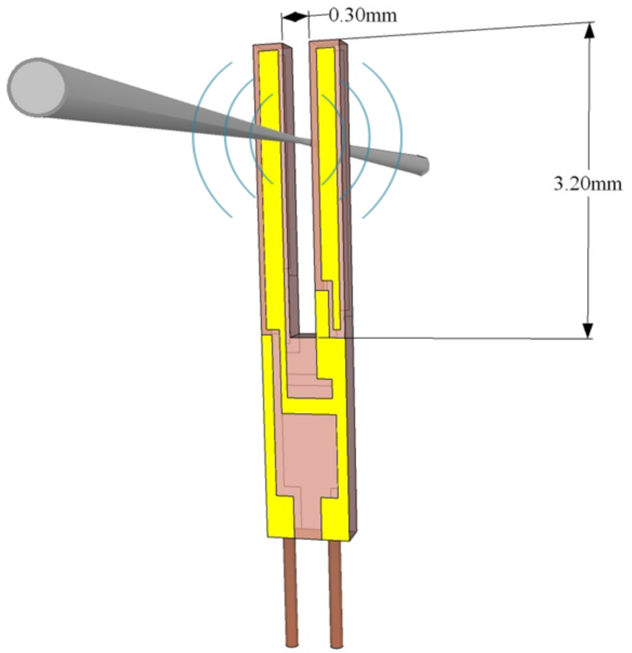


Trace gases in human breath

Molecule	Formula	Biological/Pathology Indication	Center wavelength [μm]
Pentane	C_5H_{12}	Inflammatory diseases, transplant rejection	6.8
Ethane	C_2H_6	Lipid peroxidation and oxidation stress, lung cancer (low ppbv range)	6.8
Carbon Dioxide isotope ratio	$^{13}CO_2/^{12}CO_2$	Helicobacter pylori infection (peptic ulcers, gastric cancer)	4.4
Carbonyl Sulfide	COS	Liver disease, acute rejection in lung transplant recipients (10-500 ppbv)	4.8
Carbon Disulfide	CS_2	Disulfiram treatment for alcoholism	6.5
Ammonia	NH_3	Liver and renal diseases, exercise physiology	10.3
Formaldehyde	CH_2O	Cancerous tumors (400-1500 ppbv)	5.7
Nitric Oxide	NO	Nitric oxide synthase activity, inflammatory and immune responses (e.g. asthma) and vascular smooth muscle response (6-100 ppb)	5.3
Hydrogen Peroxide	H_2O_2	Airway inflammation, oxidative stress (1-5 ppbv)	7.9
Carbon Monoxide	CO	Smoking response, lipid peroxidation, CO poisoning, vascular smooth muscle response	4.7
Ethylene	C_2H_4	Oxidative stress, cancer	10.6
Acetone	C_3H_6O	Ketosis, diabetes mellitus	7.3

OUTLINE

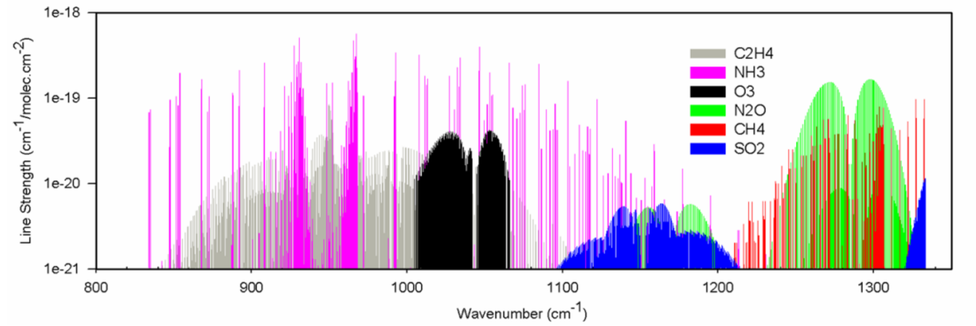
- Motivation for Gas Sensing
- Quartz Enhanced Photoacoustic (QEPAS) trace gas detection
    - Basic principles and merits
    - ....

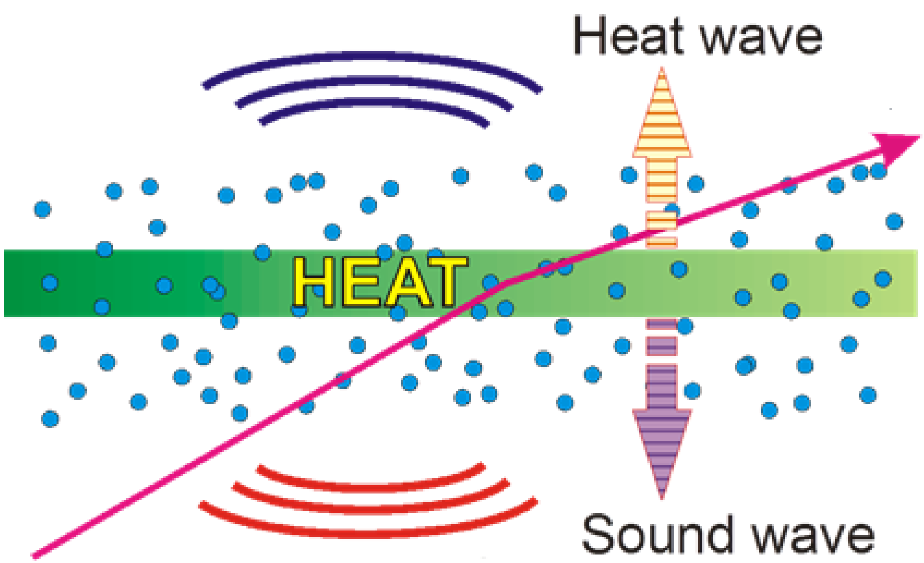


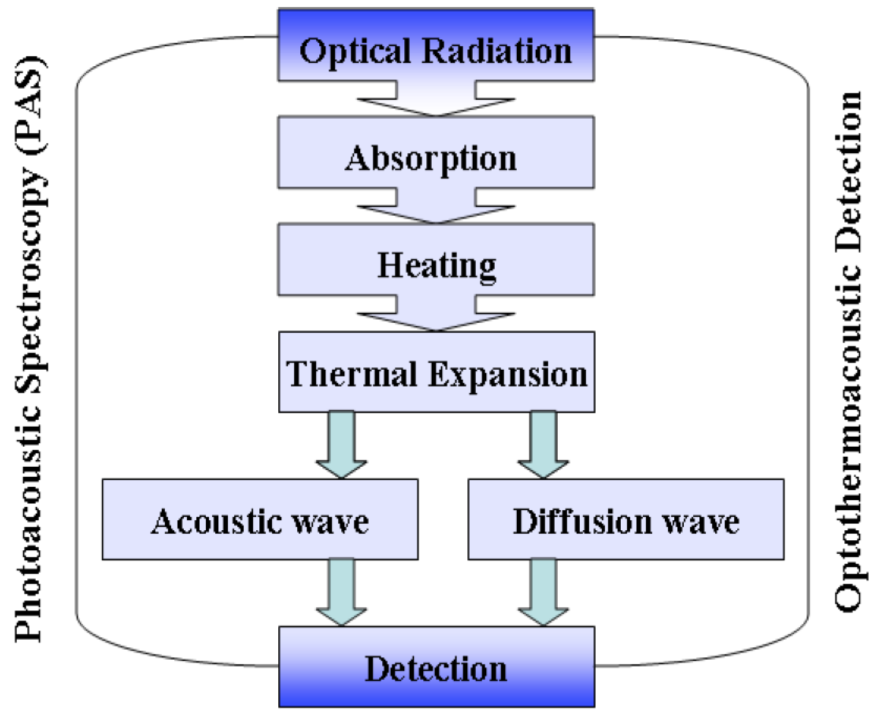
The physics of *opto-acoustic/thermal* trace gas detection

The detection of trace gases is based on the interaction between

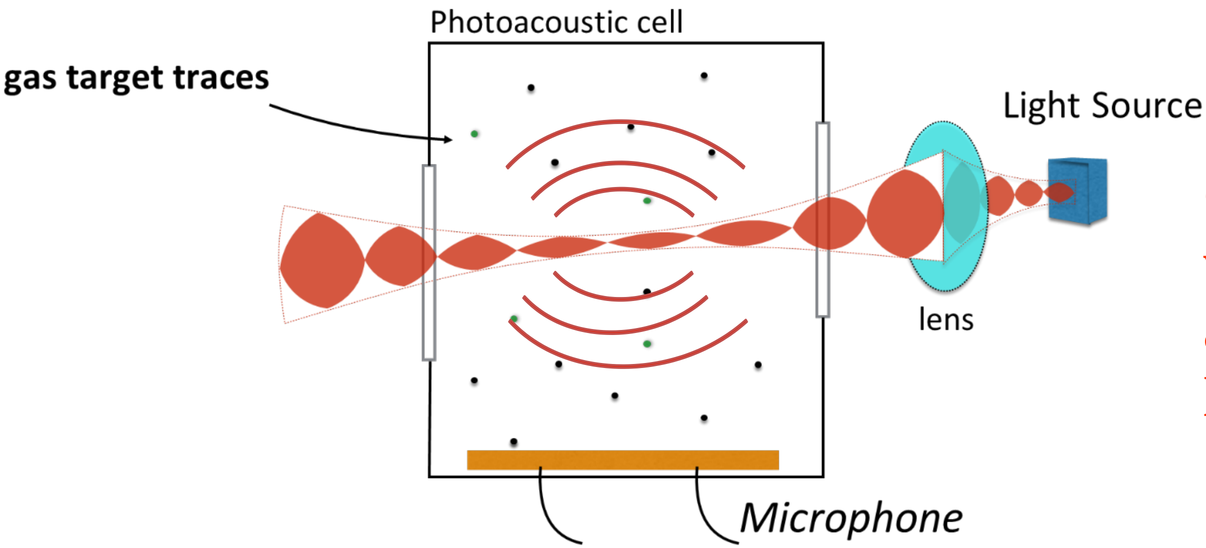
- **optical radiation**: a laser source
- **gas molecules**: absorb light only at certain wavelengths







The PA effect - Principle



Alexander Bell, 1880

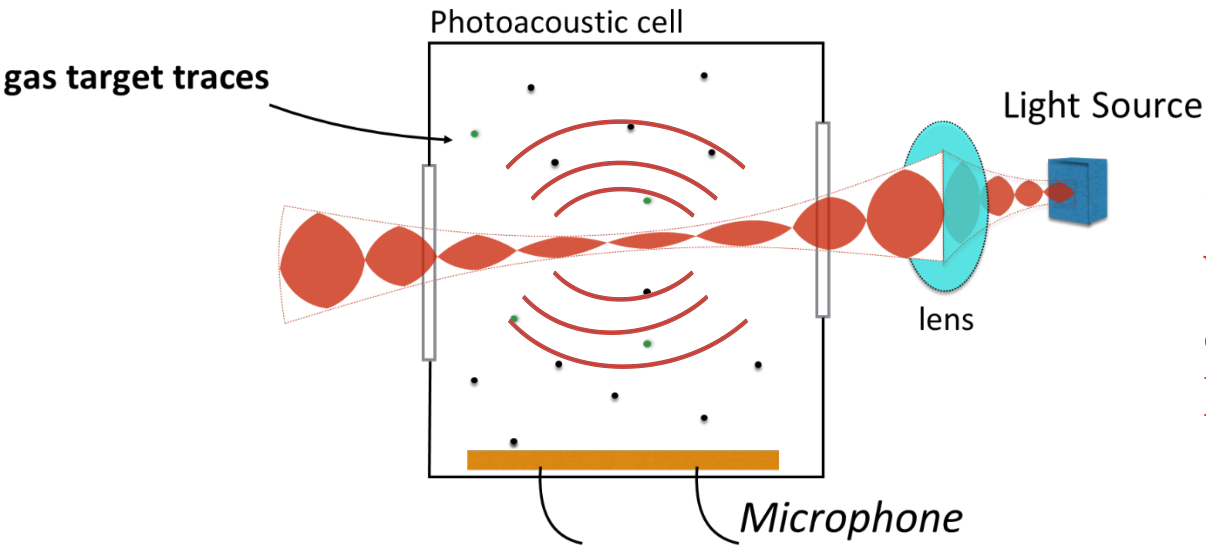
Generation of an acoustic wave in a sample due to the absorption of a modulated laser beam

$$S = C \times P \times \alpha \qquad \alpha = N\sigma c$$

S = photoacoustic signal C = Instrumental constant
P = (laser) power α = Absorption coefficient

→ the intensity of the sound is proportional to the concentration of absorbing molecules

The PA effect - Principle



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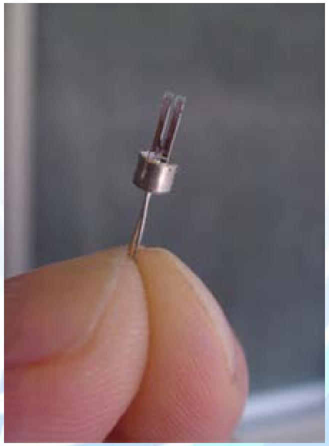
Why use the photoacoustic technique?

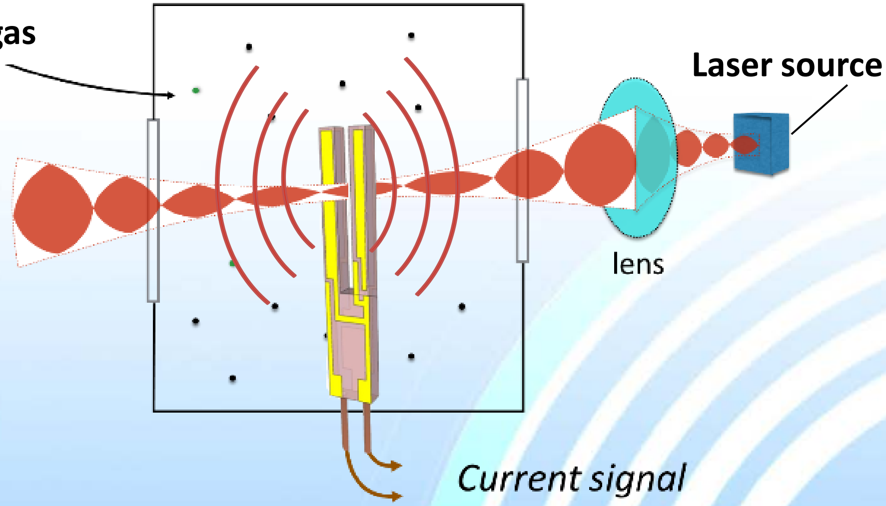
- Excellent sensitivity up to ppq with high power lasers
- Large dynamic range: linearity over a range of 10^6
- High resolution
- Fast measurements
- Capability of *in situ* detection
- Feasible costs, compact set-up, *coupled with semiconductor lasers*

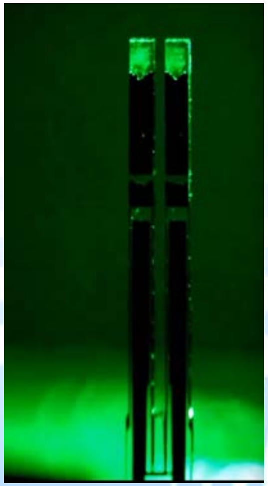
Quartz-Enhanced Photoacoustic Spectroscopy

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 (sound) wave 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 the piezoelectric effect
- The trace gas concentration is proportional to the electrical signal







P. Patimisco A. Sampaolo, L. Dong, F.K. Tittel, V. Spagnolo, Appl. Phy
P. Patimisco A. Sampaolo, H. Zheng, L. Dong, F.K. Tittel, V. Spagnolo
P. Patimisco, G. Scamarcio, F.K. Tittel and V. Spagnolo,, Sensors 14, 6

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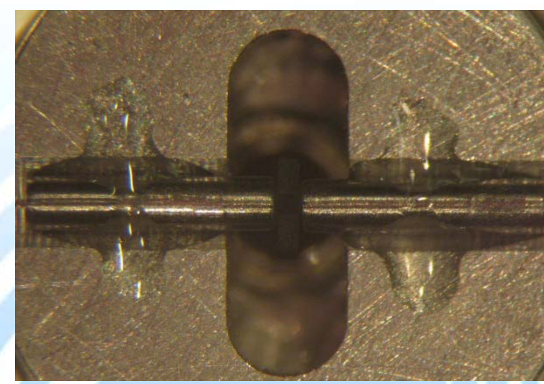
Quartz-Enhanced Photoacoustic Spectroscopy

Merits and main characteristics

- Small sensing module and sample volume (a few cm^3)
- Wavelength independent
- ***Optical detector is not required***
- Wide dynamic range (from % to ppt)
- Immune to environmental acoustic noise
- Acoustic micro-resonator(s) to enhance the QEPAS signal



P. Patimisco, et al., Applied Physics Review, 5, 011106, 2018
P. Patimisco et al., Sensors 14, 6165, **2014**
V. Spagnolo et al., Optics Letters, 37, 4461–4463, **2012**

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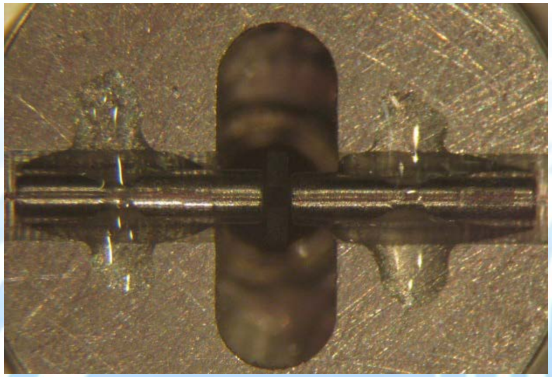
- Sensitivity scales with laser power
- Cross sensitivity issues
- Alignment (no light must hit the QTF or micro-resonators)
- Responsivity depends on the molecular energy transfer processes

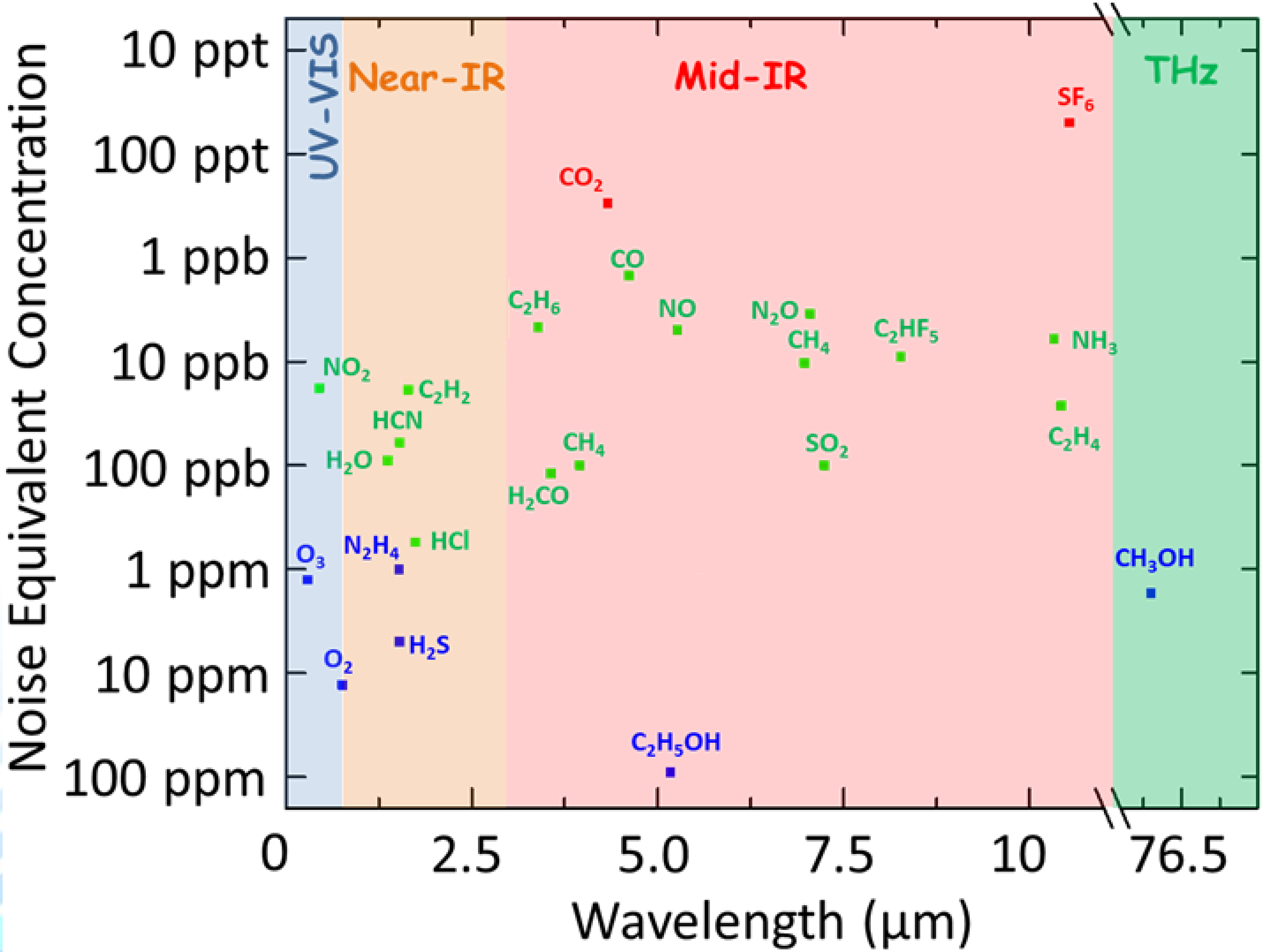


Record sensitivity: **50 part-per-trillion**

$\lambda = 10.54\ \mu m$ (mid – IR), SF_6

P. Patimisco, et al., Applied Physics Review, 5, 031106, **2018**
P. Patimisco et al., Sensors 14, 6165, **2014**
V. Spagnolo et al., Optics Letters, 37, 4461–4463, **2012**

QEPAS gas sensing performance

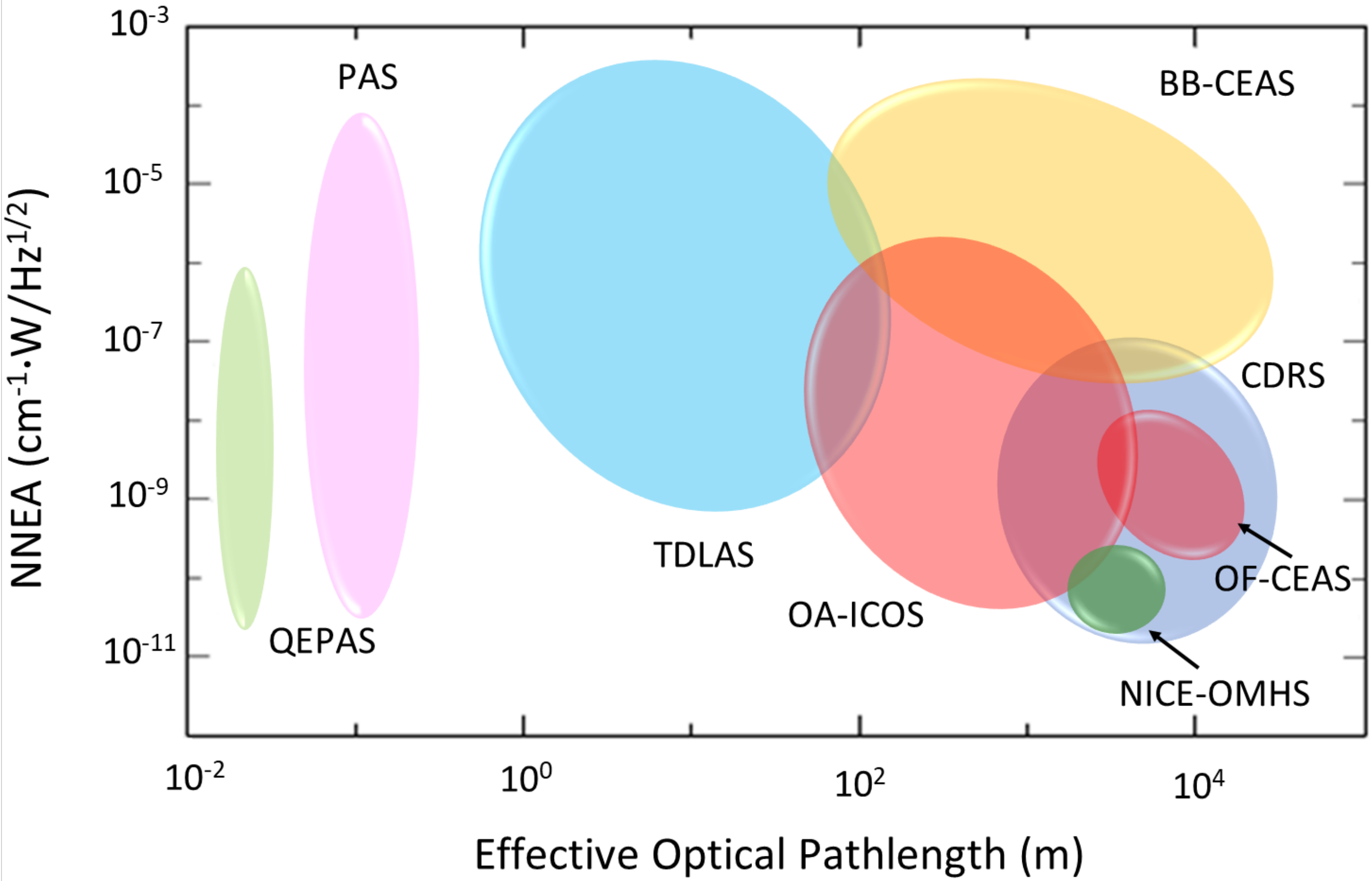


P. Patimisco, et al., Applied Physics Review, 5, 011106, **2018**.

P. Patimisco et al., "Sensors, 14, 6165–6206, **2014**.

Gas sensing techniques performances (Mid-IR)

P. Patimisco, G. Scamarcio, F.K. Tittel and V. Spagnolo, **"Quartz-enhanced photoacoustic spectroscopy: a review",** *Sensors, 14, 6165-6206 (2014)*



NNEA for categories of gas detection techniques as a function of optical path-length. Key: BB-CEAS—broadband cavity-enhanced spectroscopy, CRDS—cavity ring-down spectroscopy, OA-ICOS—off-axis integrated cavity output spectroscopy, OF-CEAS—optical feedback cavity-enhanced absorption spectroscopy, NICE-OHMS—noise-immune cavity-enhanced optical heterodyne spectroscopy, PAS photoacoustic spectroscopy, QEPAS—Quartz-enhanced photoacoustic spectroscopy.

OUTLINE

- Motivation for Gas Sensing
- Quartz Enhanced Photoacoustic Gas Detection
- QEPAS: Basic principles and merits
- QEPAS with custom quartz tuning forks (**2nd Generation)**
- ………

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Quartz tuning fork

Gas absorption coefficient

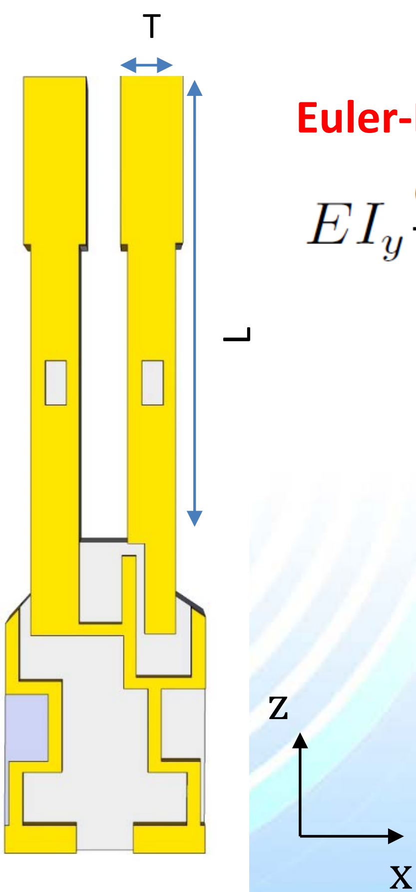
QTF-dependent

$$\textbf{\textit{QEPAS Signal}} \propto P \cdot \alpha \cdot Q \cdot \varepsilon$$

Conversion efficiency: optical power → sound

Laser power

QTF Q-factor



Euler-Bernoulli beam theory

$$EI_y \frac{d^4 X}{dz^4} + \rho S \frac{d^2 X}{dt^2} = 0$$

Resonance Frequency, in-plane flexural modes

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

$$\boldsymbol{n_{fund}} = 1.19$$
$$\boldsymbol{n_{overt}} = 3$$

P. Patimisco, et al., Analyst 139, 2079, **2014**.
A. Sampaolo, et al., Appl. Phys. Lett.,107, 231102, **2015**.
P. Patimisco et al., Sens. Act, B Chem. 227, 539, **2016**.

Quartz tuning fork

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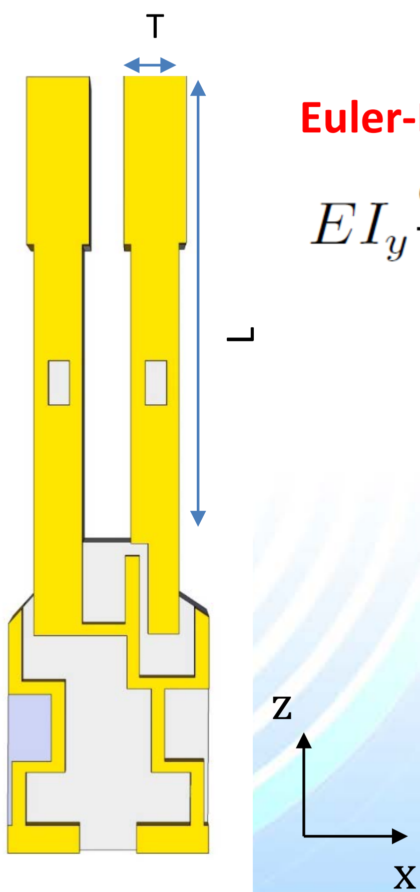

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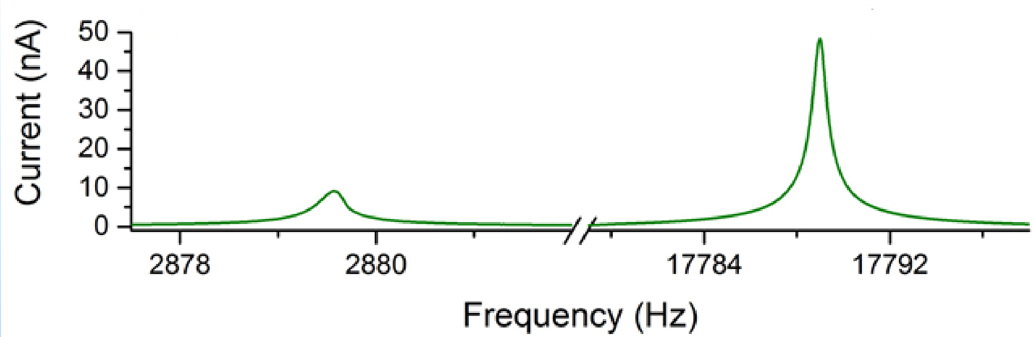
Resonance Frequency, in-plane flexural modes

$$\boldsymbol{n_{fund}} = 1.19$$
$$\boldsymbol{n_{overt}} = 3$$

$$f_{1st\ overtone} \sim \mathbf{6.2} \cdot f_{fundamental}$$



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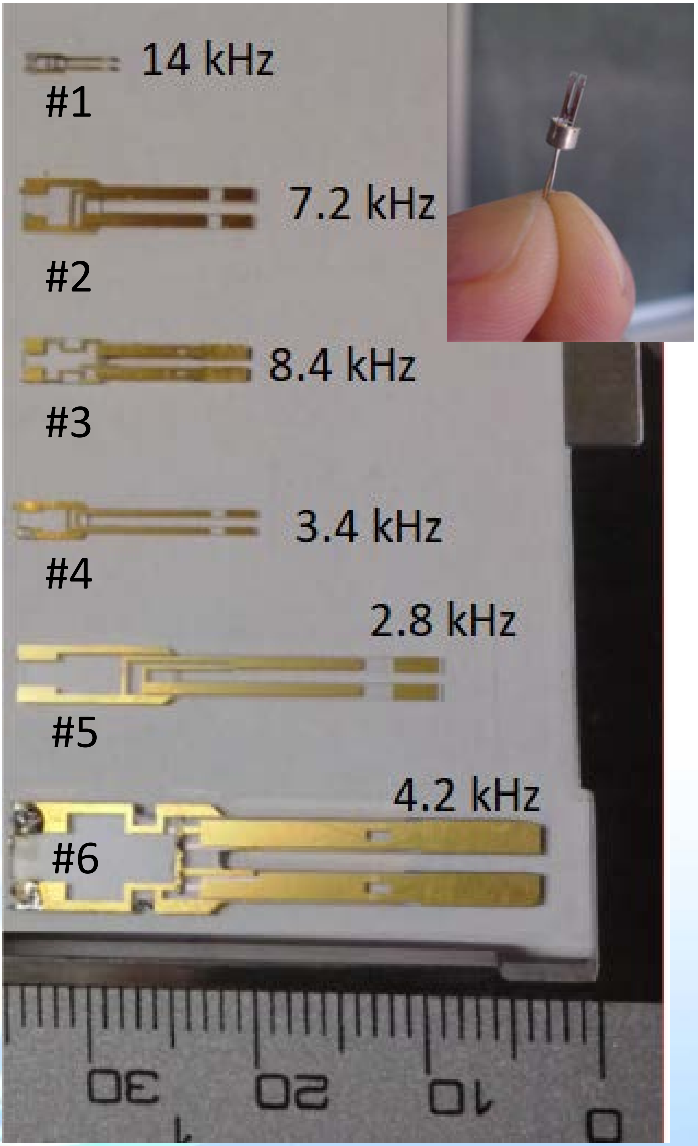
Custom QTF 2nd generation



P. Patimisco, et al., Applied Physics Review, 5, 011106; **2018**

P. Patimisco et al., Sensors and Actuators B Chemical,

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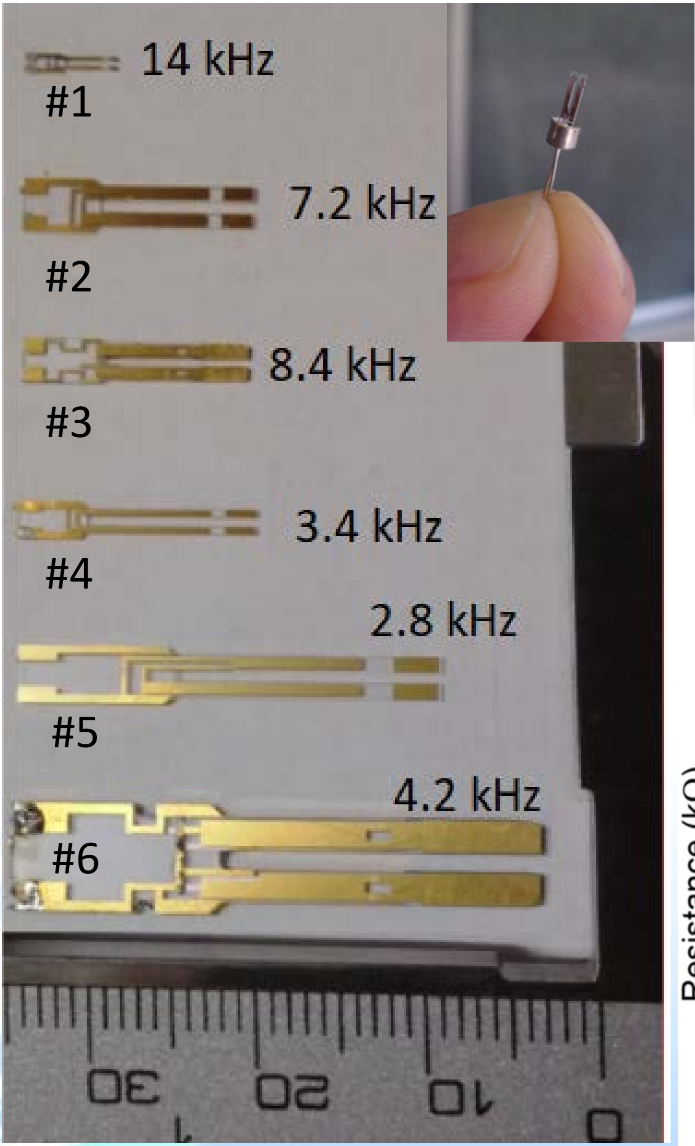
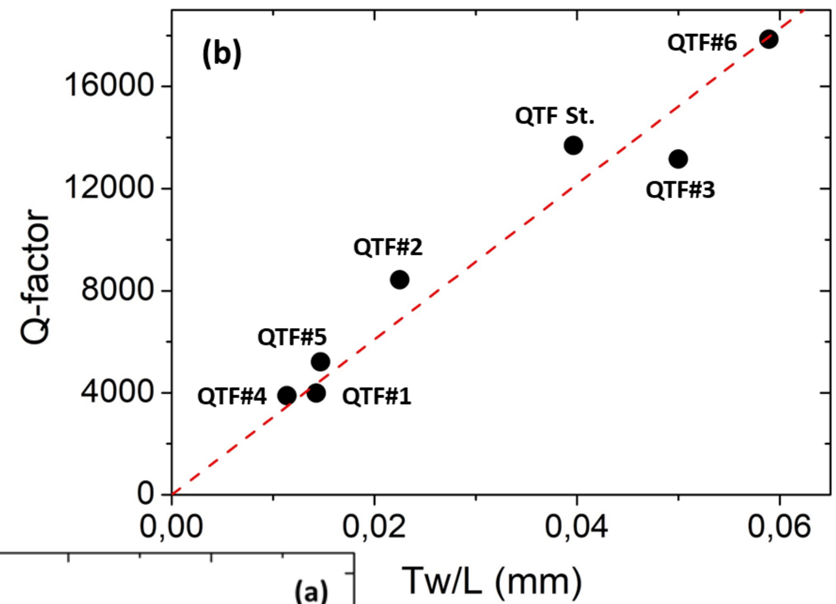
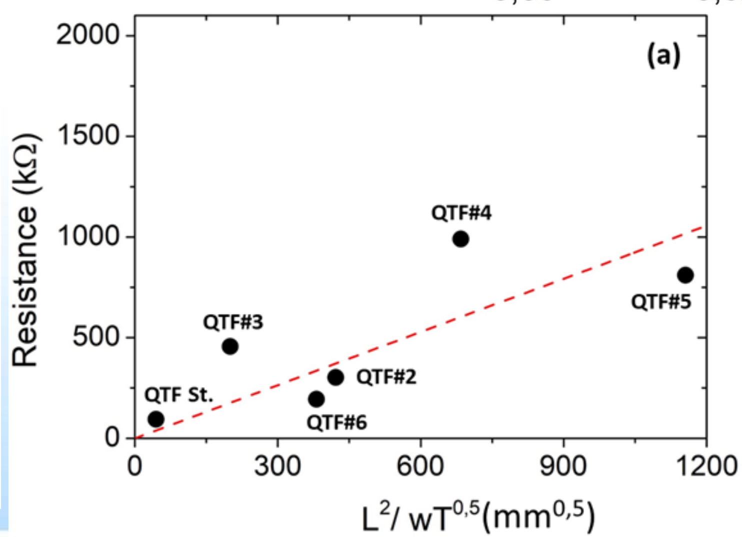


$Q \propto wT/L$





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

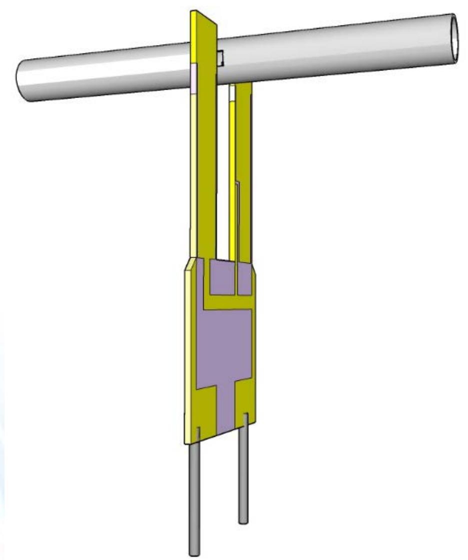
QTF DESIGN GUIDELINES

P. Patimisco, et al., Applied Physics Review, 5, 011106; **2018**

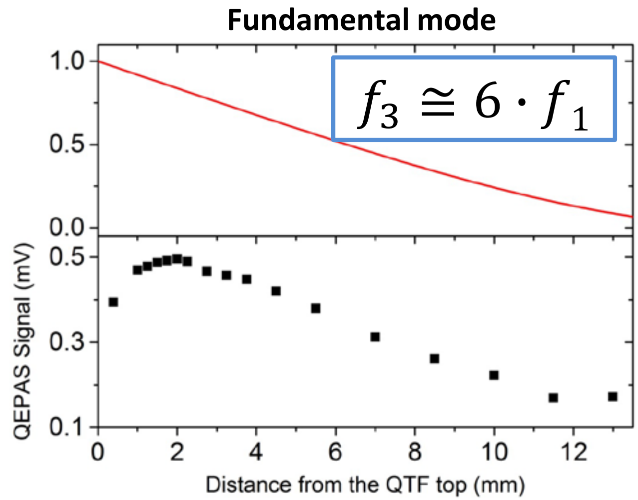
P. Patimisco et al., Sensors and Actuators B Chemical,

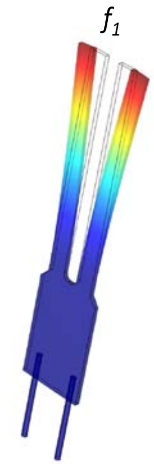
2nd generation main results

Single–tube microresonator



1st Overtone modes





P. Patimisco, et al., Applied Physics Review, 5, 011106, **20**

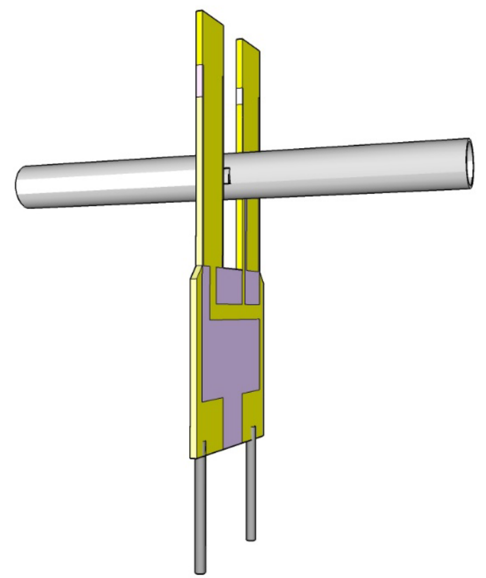
H. Zengh, L. Dong, P. Patimisco et al, Applied Physics Letters 110, 021110, **2017**

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

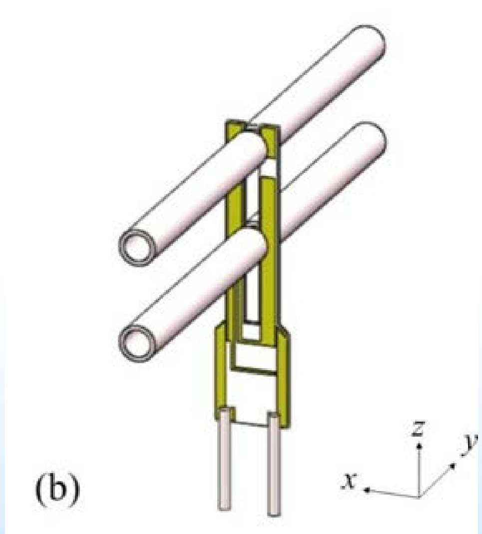
F. K. Tittel , A. Sampaolo, P. Patimisco et al., Optics

2nd generation main results

Single–tube microresonator

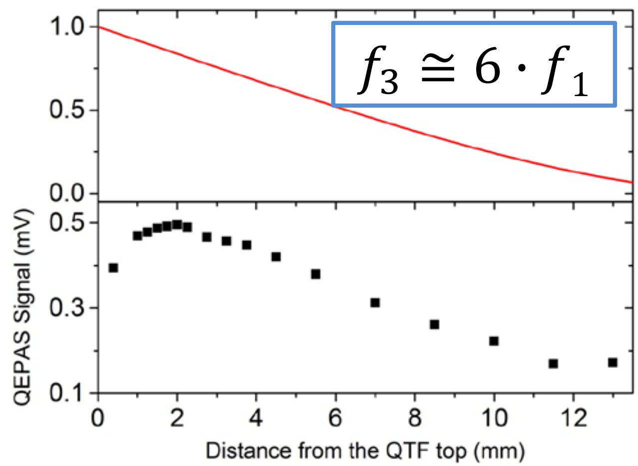


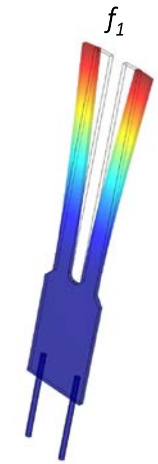
Double antinode excited SO-QEPAS



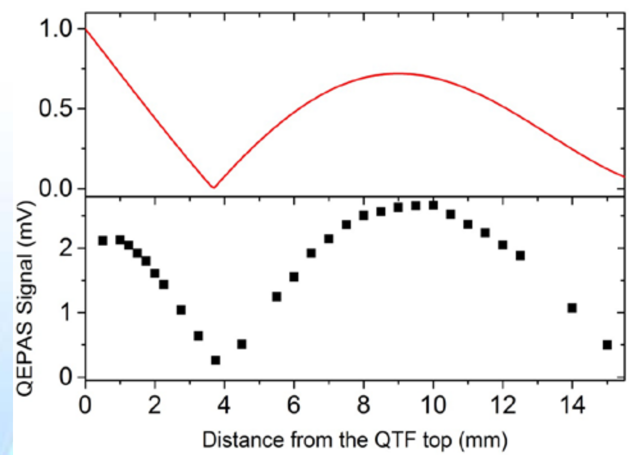
1st Overtone modes

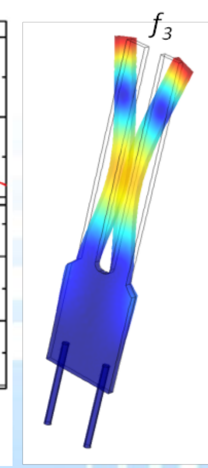
Fundamental mode





Overtone mode





A SNR gain factor of 500 with respect to the bare QTF operating in the fundamental mode

P. Patimisco, et al., Applied Physics Review, 5, 011106, **20**
H. Zengh, L. Dong, P. Patimisco et al, Applied Physics Letters 110, 021110, **2017**
H. Zengh, L. Dong, A. Sampaolo et al, Applied Physics Lette... **2016**
F. K. Tittel , A. Sampaolo, P. Patimisco et al., Optics

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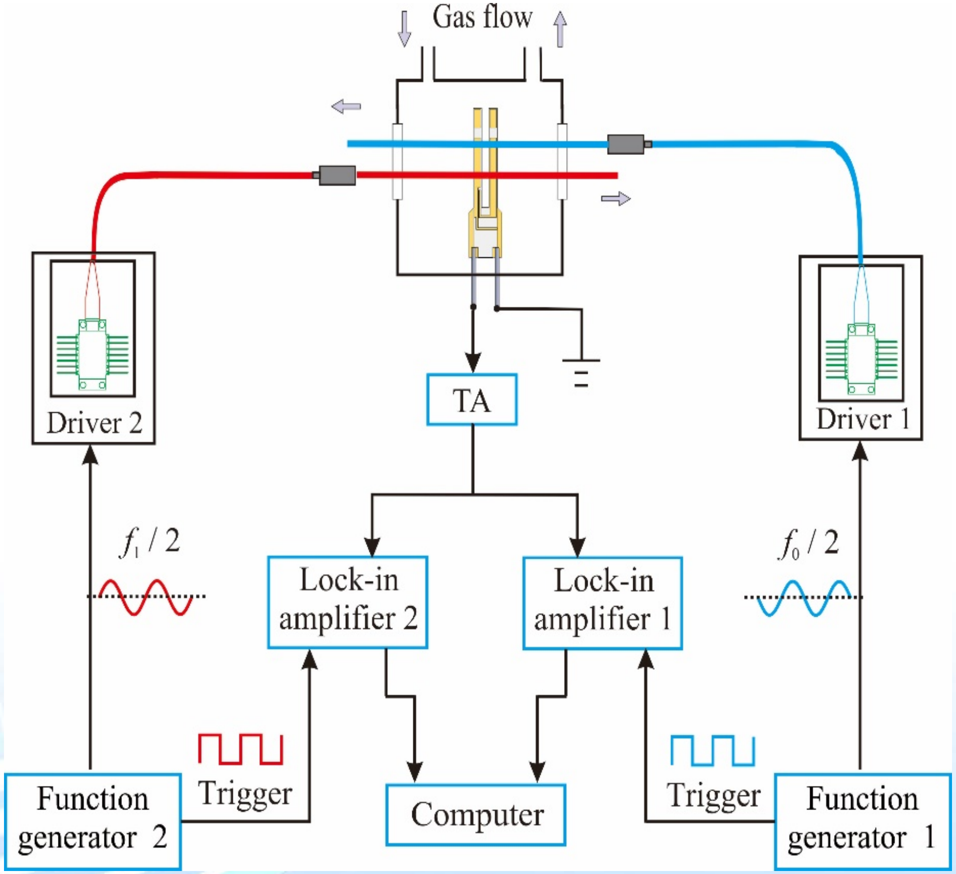
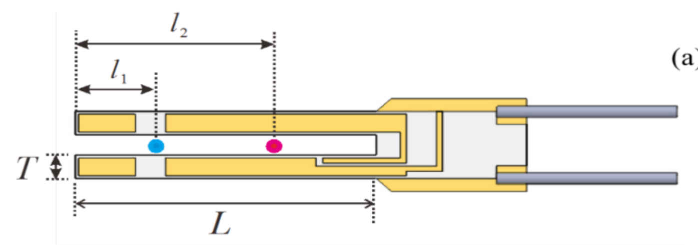
Dual-gas QEPAS operating at both the QTF fundamental and 1st overtone



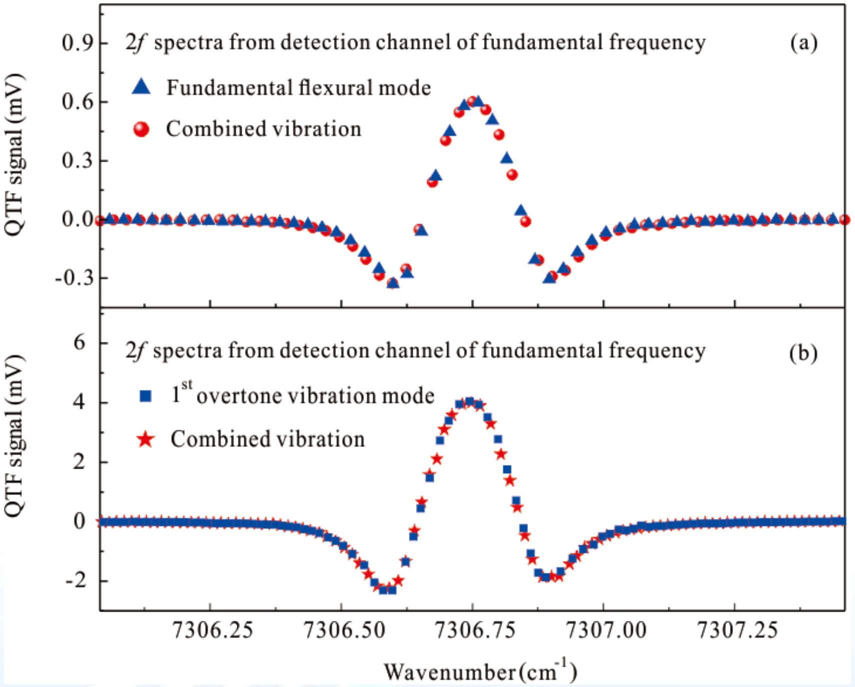


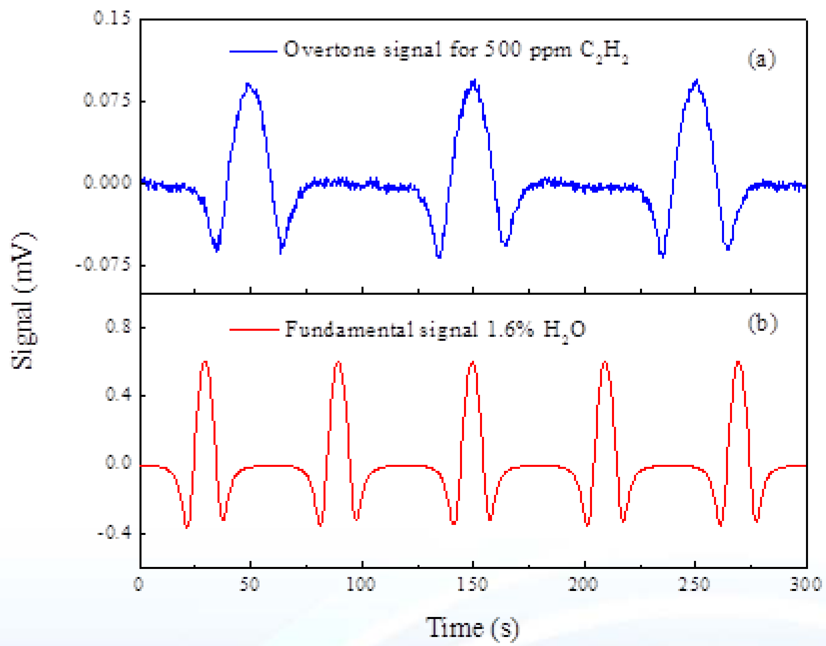
Two beams from two independently modulated lasers are focused between the prongs of a quartz tuning fork at two different positions to excite both the fundamental and first overtone flexural modes simultaneously

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., *110, 121104,*

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





- **No cross-talk between fundamental and 1st overtone**
- **Simultaneously dual-gas detection (eg. C_2H_2 and H_2O)**
- **Future improvements using single-tube resonators**
- **Applications include: industrial process control, isotope ratio measurements, breath analysis**

H. Wu, X, Yin, L. Dong, K. Pei, A. Sampaolo, P. Patimisco et al, Appl. Phys. Lett., *110, 121104,* **2017**

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OUTLINE

- Motivation for Gas Sensing
- Quartz Enhanced Photoacoustic Gas Detection
- QEPAS: Basic principles and merits
- QEPAS with custom quartz tuning forks
- QEPAS in the THZ range
- ....

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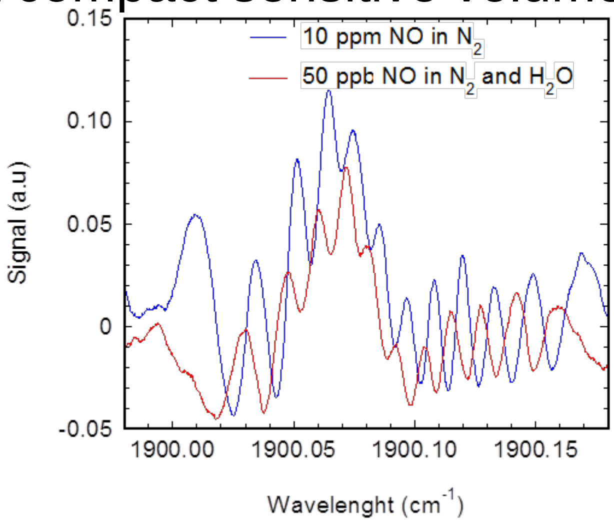
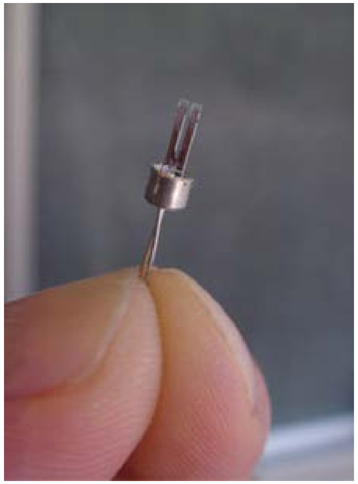
QEPAS sensors in the THz range

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.



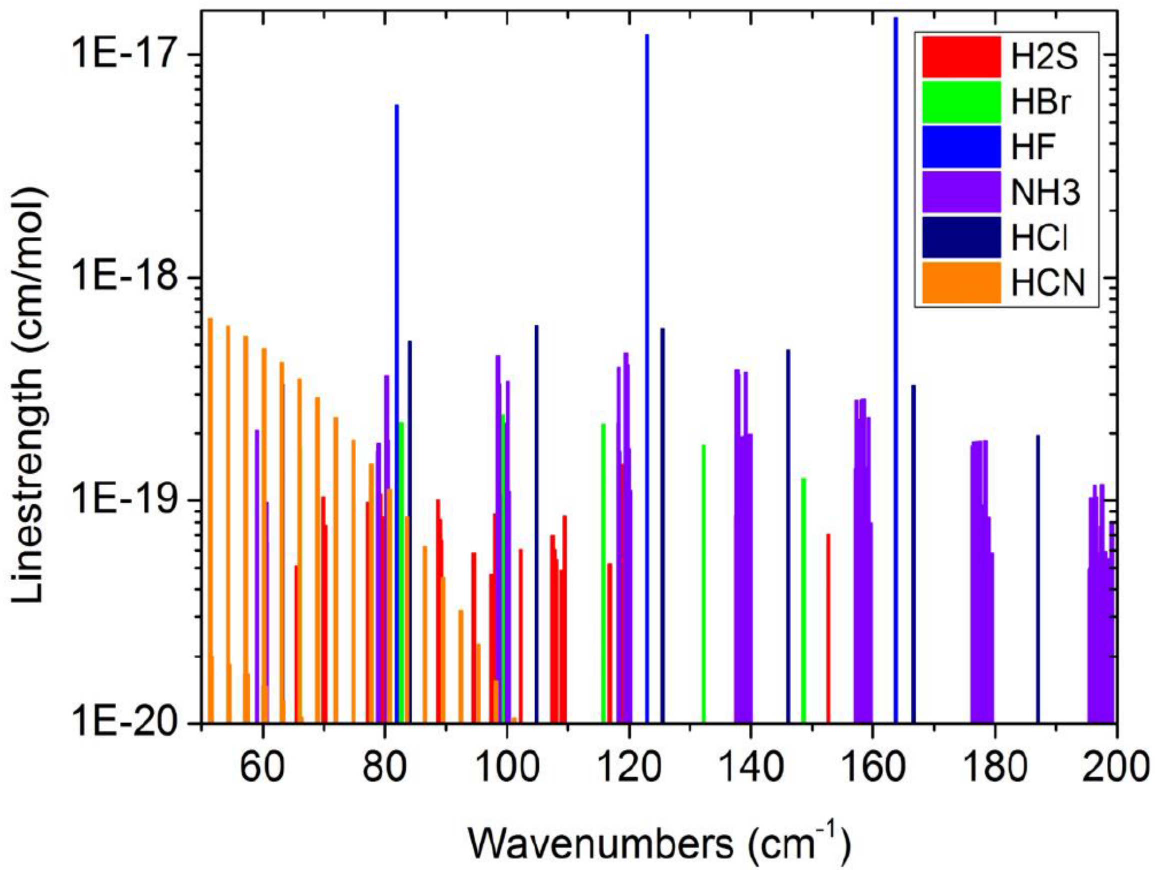


The limited space (300 μm) between the QTF prongs is comparable with the wavelength of THz sources so far has represented the main limitation for the use in QEPAS-based sensor systems in the THz range.

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**.

Why THz QEPAS Spectroscopy?



Several gas species such as HF, OH, HCN, HCl, HBr, NH_3, H_2O_2, H_2S, H_2O, explosive (vapour phase) etc. show strong absorption bands in the THz spectral range.

⇩

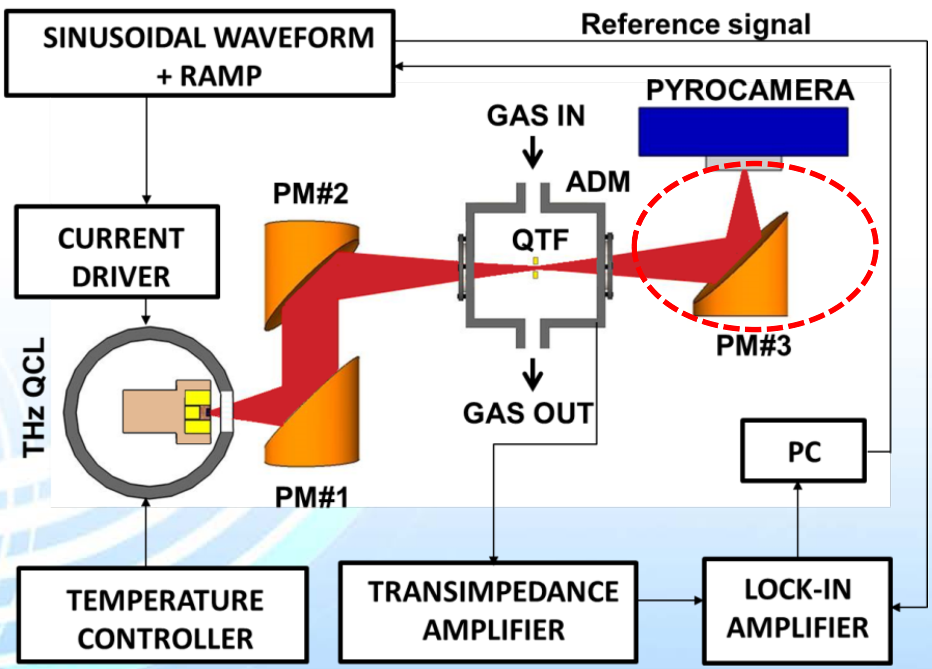
Mainly rotational levels are involved in THz absorption processes and rotational-translational (R-T) relaxation rates are ***up to three order of magnitude faster*** with respect to vibrational-translational (V-T).

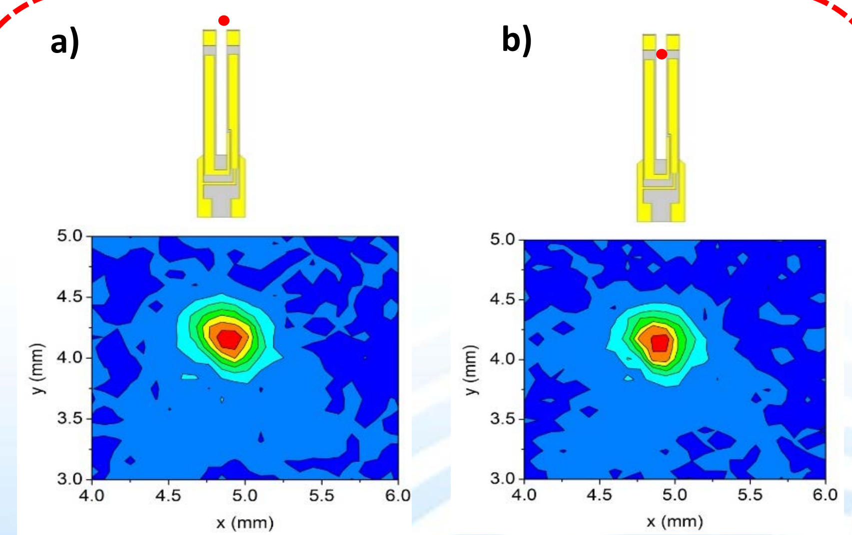
S. Borri et al., Applied Physics Letters 103, 021105, **2013**
P. Patimisco et al., Analyst 139, 2079-2087, **2014**
V. Spagnolo et al., Optics Express 23, 7574–7582, **2015**.

THz QEPAS results employing a Novel Custom QTF

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



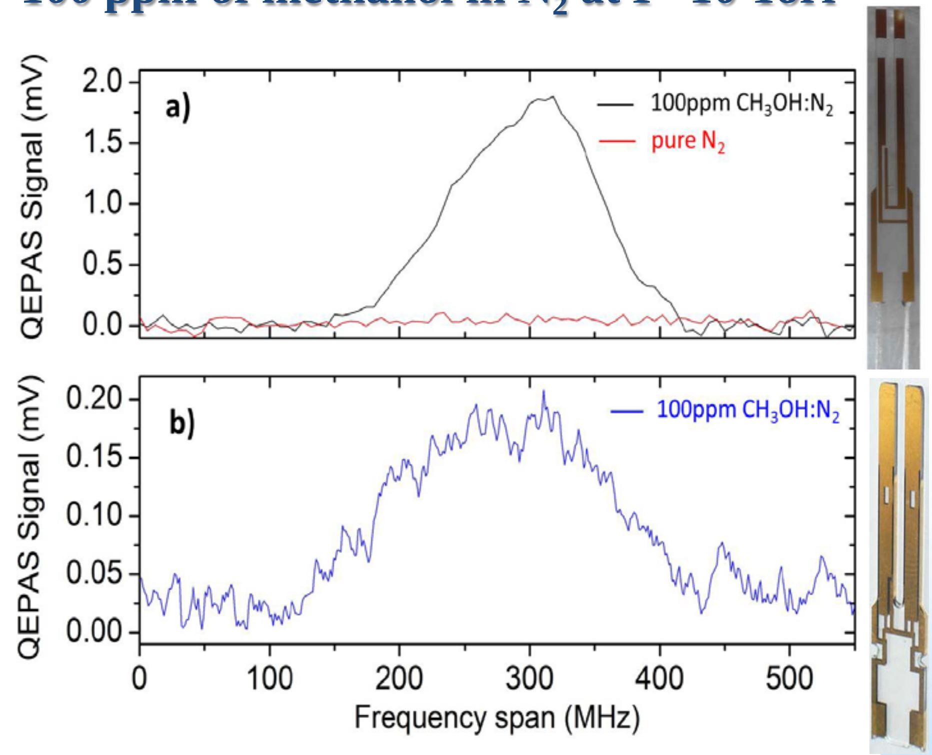


96.4% of the light intensity passes between the QTF prongs

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

THz QEPAS results employing a Novel Custom QTF

100 ppm of methanol in N_2 at P=10 Torr



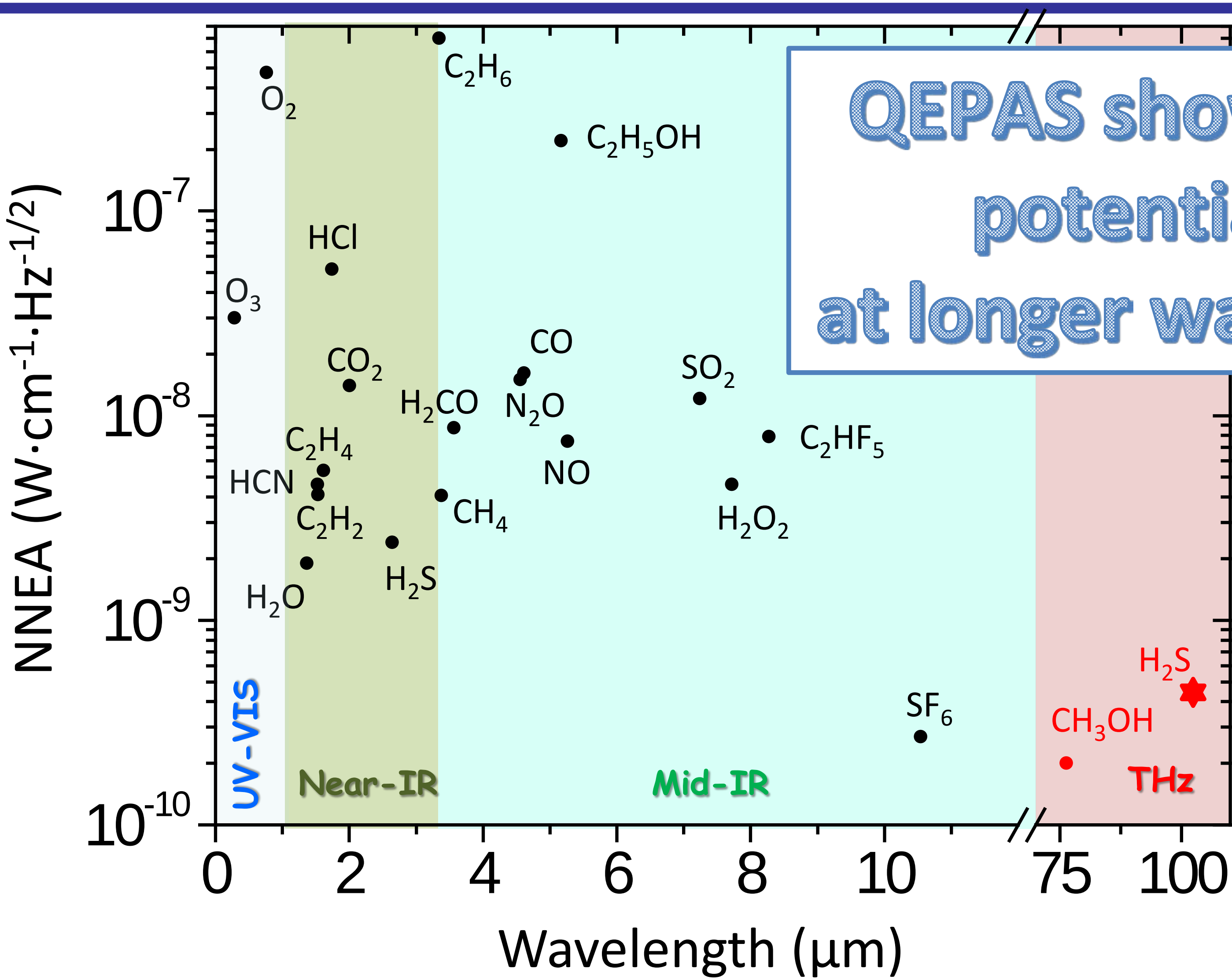
Comparison between QTFs with custom and new geometry

- 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

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

QEPAS Performance for Trace Gas Species: NNEA vs λ



QEPAS shows better potentialities at longer wavelenghts

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

Intracavity QEPAS
Basics

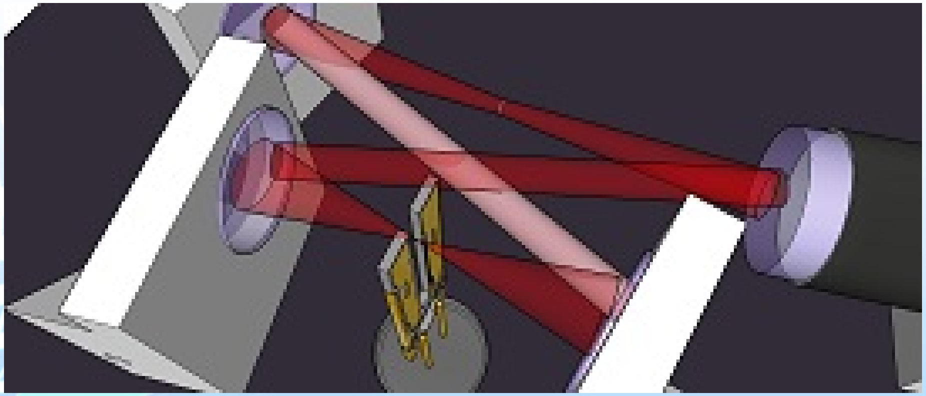
Three main criteria drive the development of high-sensitivity optical sensors:

i) Selection of optimal molecular transition in terms of absorption strength

ii) Long optical absorption length and/or use of buildup optical cavity;

iii) Efficient spectroscopic detection schemes, e.g. photoacoustic spectroscopy (PAS)

QEPAS sensitivity scale with optical power



Cavity-**E**nhanced **A**bsorption

+

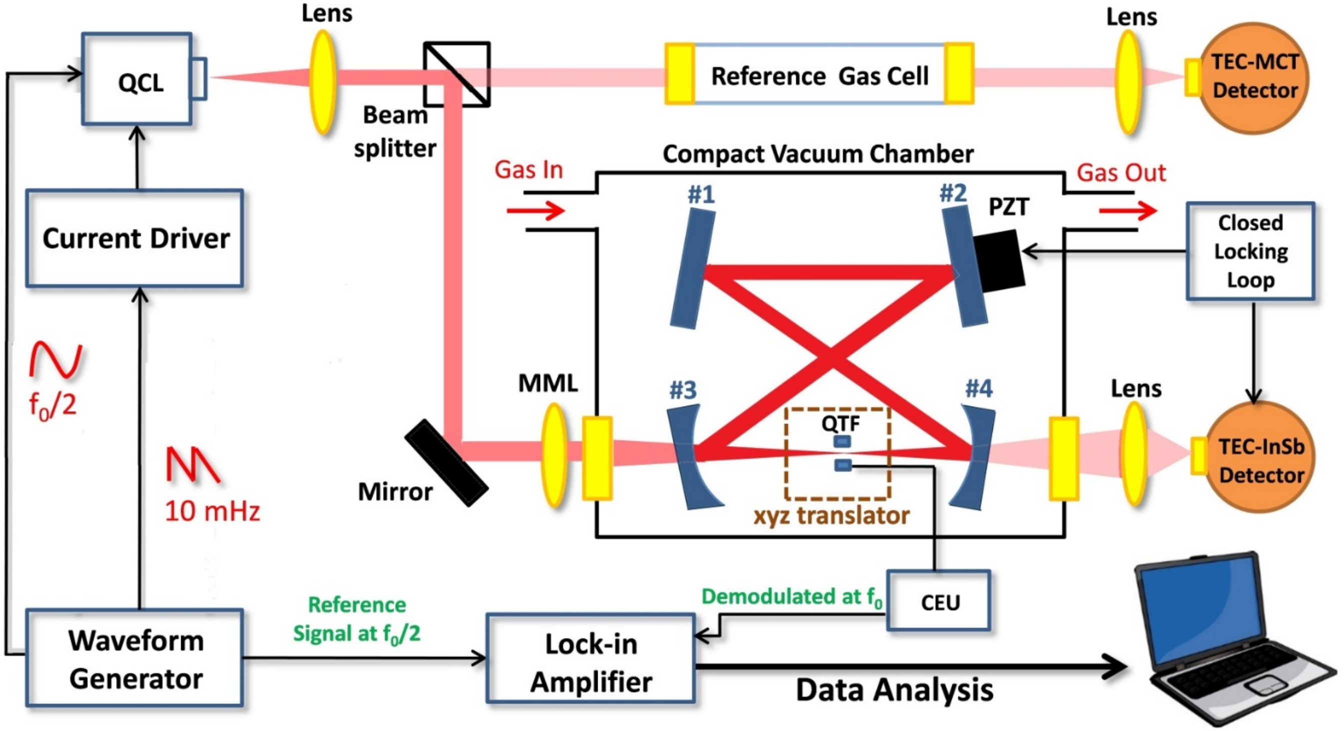
QEPAS

=

Intra-cavity **QEPAS**

S. Borri et al., Applied Physics Letters, 104, 09114, **2014**
P. Patimisco et al., Analyst, 140, 736-743, **2015**

Intracavity-QEPAS setup

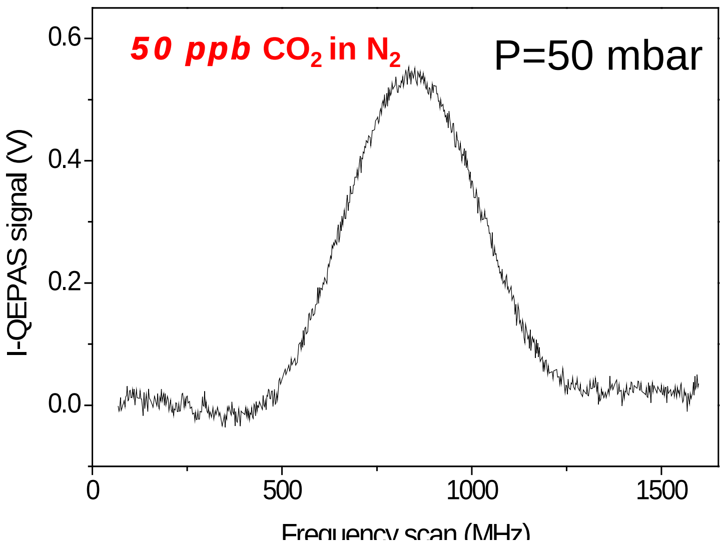


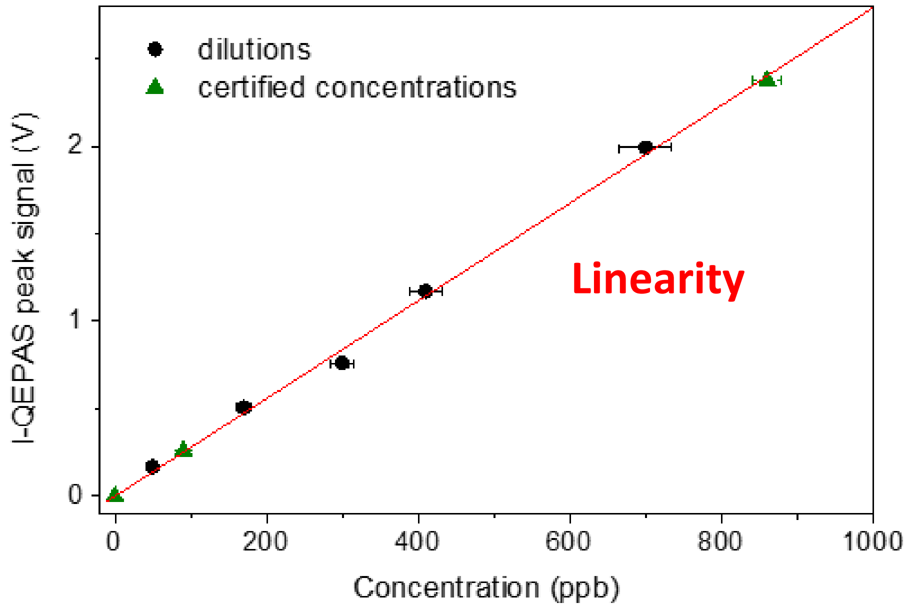
- RT CW DFB **Q**uantum **C**ascade **L**aser λ = 4.33 μm (P = 3mW)
- Home-made low-noise current driver → laser linewidth $\sim 1\ MHz$
- Bow-tie cavity → 4 high reflectivity mirrors, $R = 99.9\%$
- Electronic control-loop + PZT motor lock cavity resonant frequency to the laser one

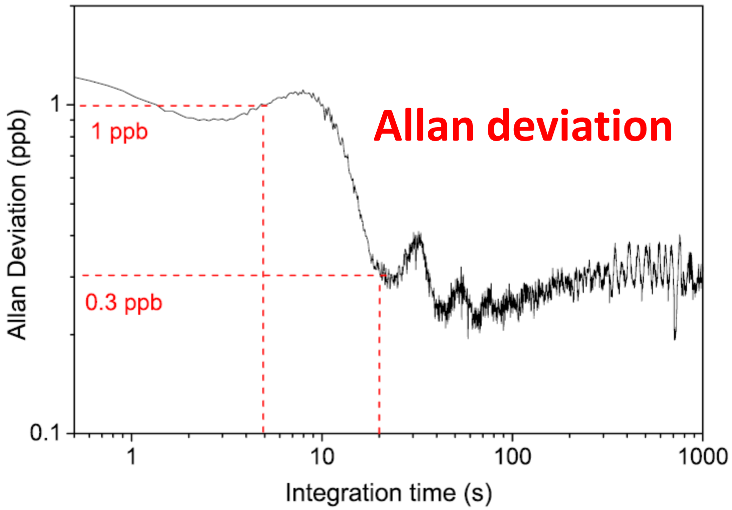
Intracavity optical power enhancement factor = 240

S. Borri et al., Applied Physics Letters, 104, 09114, **2014**
P. Patimisco et al., Analyst, 140, 736-743, **2015**

Performance and long term stability







Noise **E**quivalent **C**oncentration:

NEC = 300 ppt @ 20sec integration time

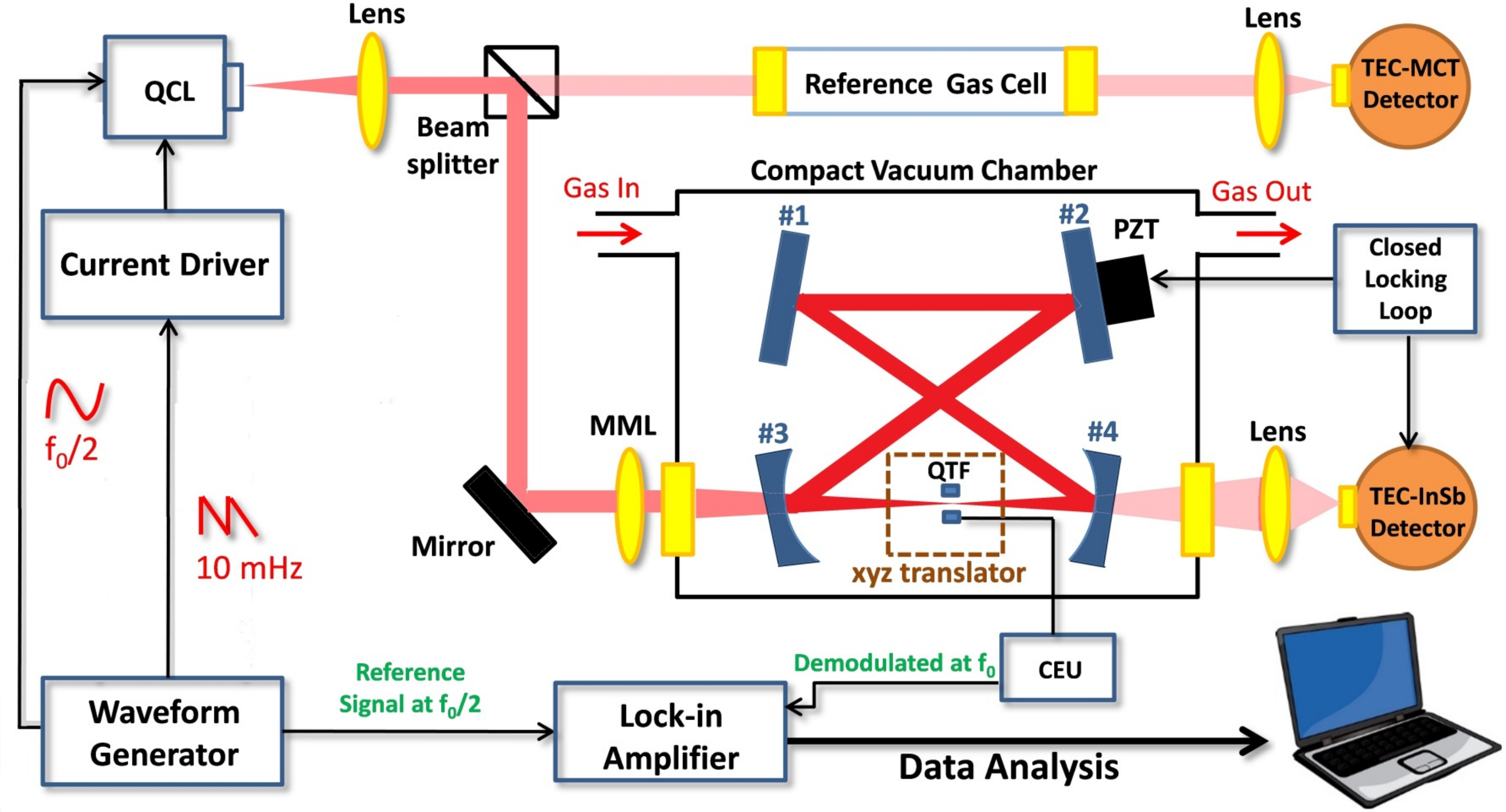
(4sec lock-in time constant)

Absorption Coefficient Normalized to detection bandwidth and optical power:

NNEA = 3.2×10^{-10} $cm^{-1}W(Hz)^{-1/2}$

S. Borri et al., Applied Physics Letters, 104, 09114, **2014**
P. Patimisco et al., Analyst, 140, 736-743, **2015**

“Single-pass” QEPAS setup

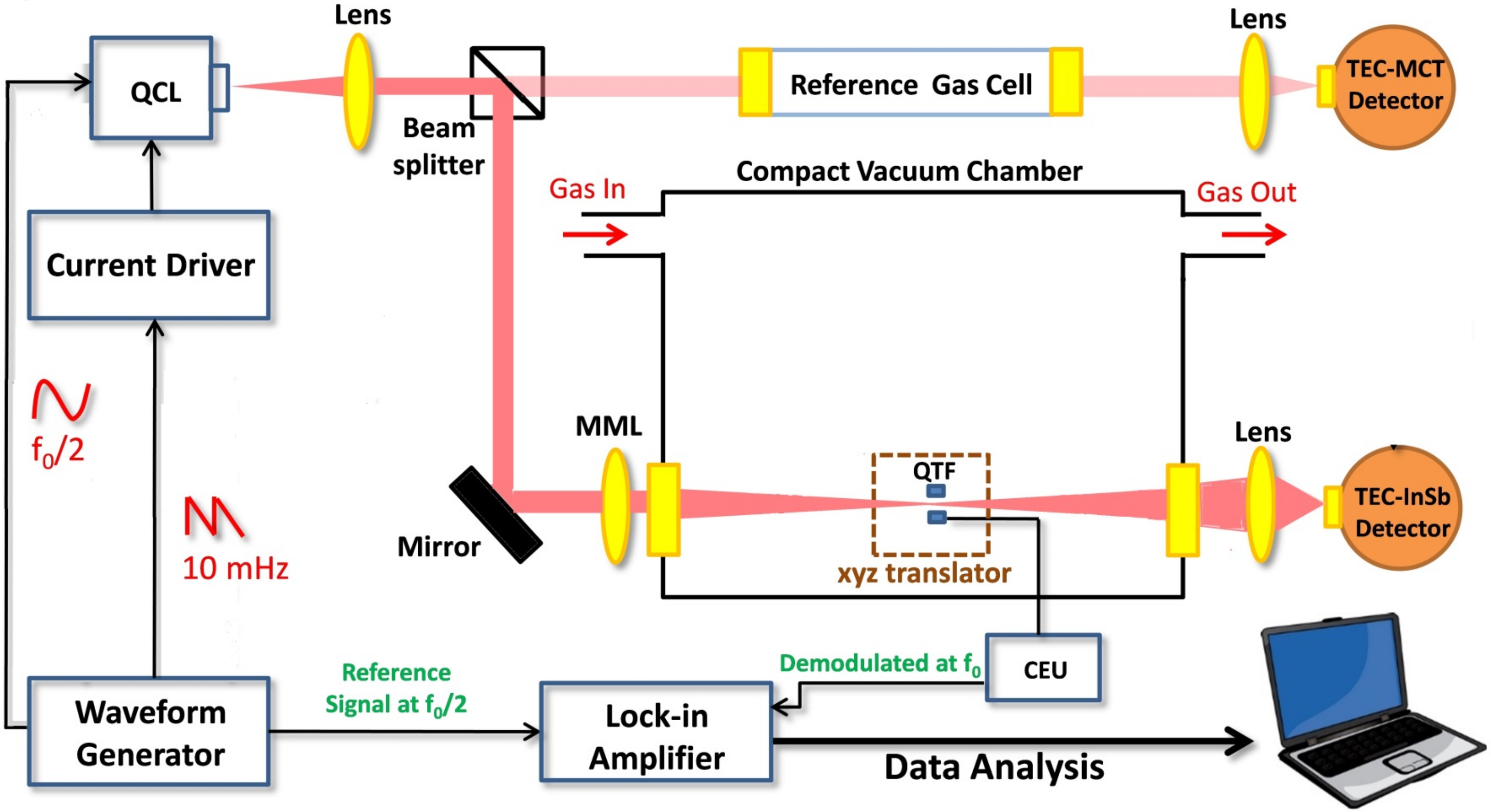


Optical power build-up cavity removed

- Same optical power $3\ mW$
- Same gas pressure in the chamber $50\ mbar$
- Wavelength modulation approach and f_0 detection

S. Borri et al., Applied Physics Letters, 104, 09114, **2014**
P. Patimisco et al., Analyst, 140, 736-743, **2015**

"Single-pass" QEPAS setup



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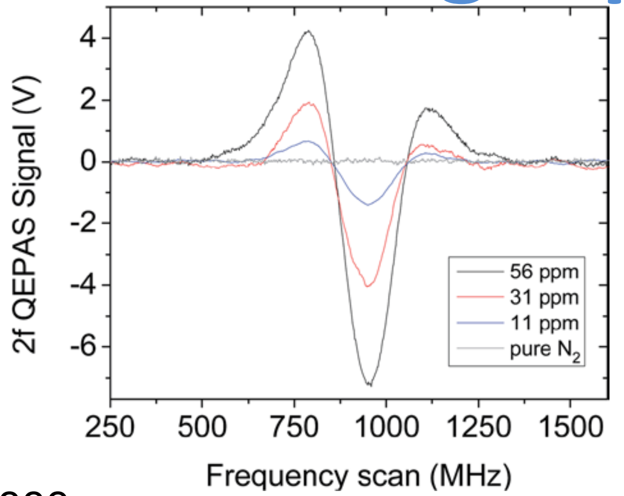
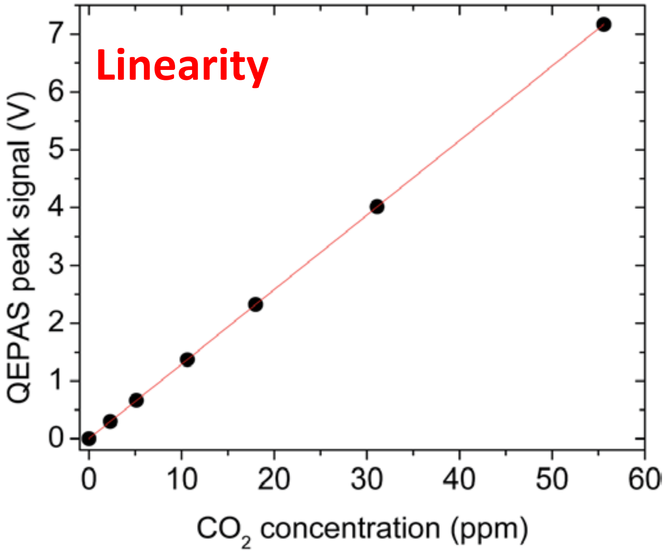
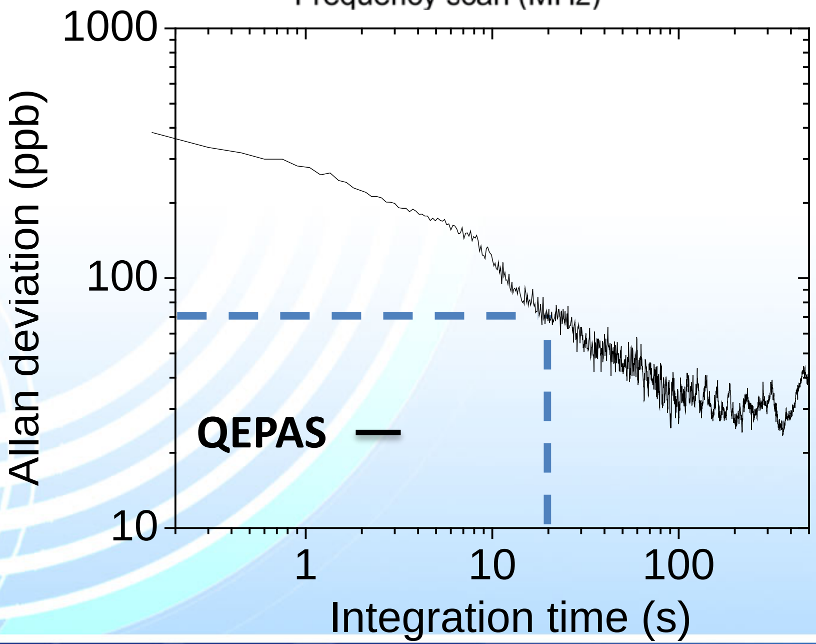
S. Borri et al., Applied Physics Letters, 104, 09114, **2014**
P. Patimisco et al., Analyst, 140, 736-743, **2015**

Standard single-pass QEPAS performances





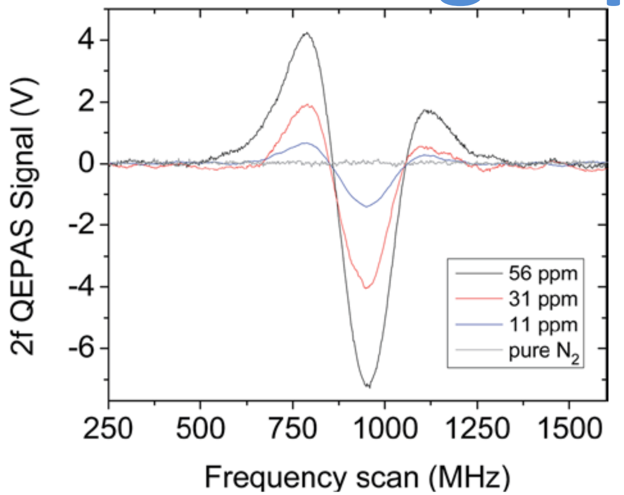


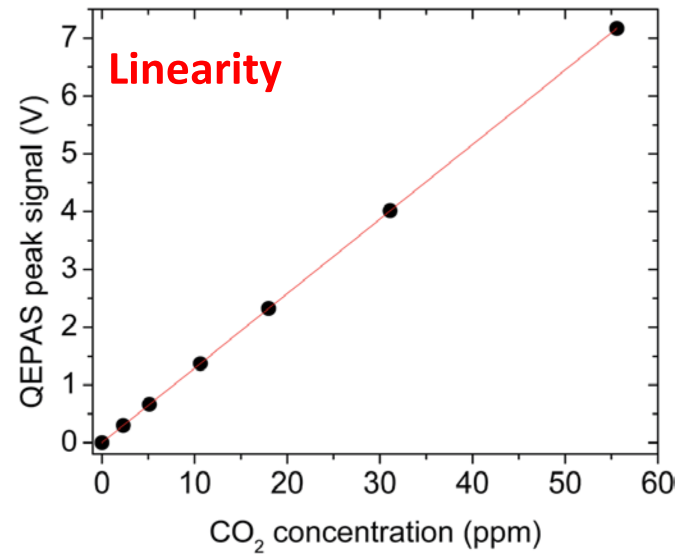
NEC = 70 ppb @ 20sec integration time

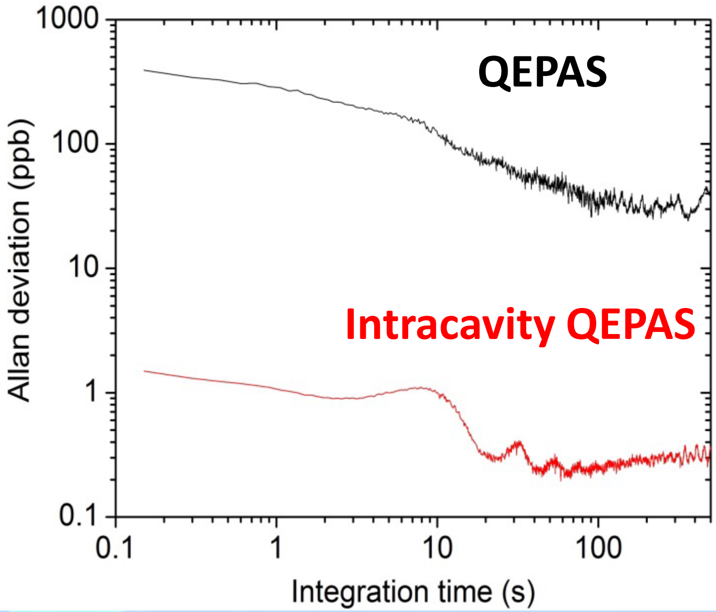
NNEA = $7{,}5 \times 10^{-8}\ cm^{-1}W(Hz)^{-1/2}$

S. Borri et al., Applied Physics Letters, 104, 09114, **2014**
P. Patimisco et al., Analyst, 140, 736-743, **2015**

Standard single-pass QEPAS performances







NEC = **72 ppb** @ 20sec integration time

NNEA = **$7{,}5 \times 10^{-8}$ $cm^{-1}W(Hz)^{-1/2}$**

A factor **234** bigger than **I-QEPAS**

Comparable with intracavity enhancement : 240

S. Borri et al., Applied Physics Letters, 104, 09114, **2014**
P. Patimisco et al., Analyst, 140, 736-743, **2015**

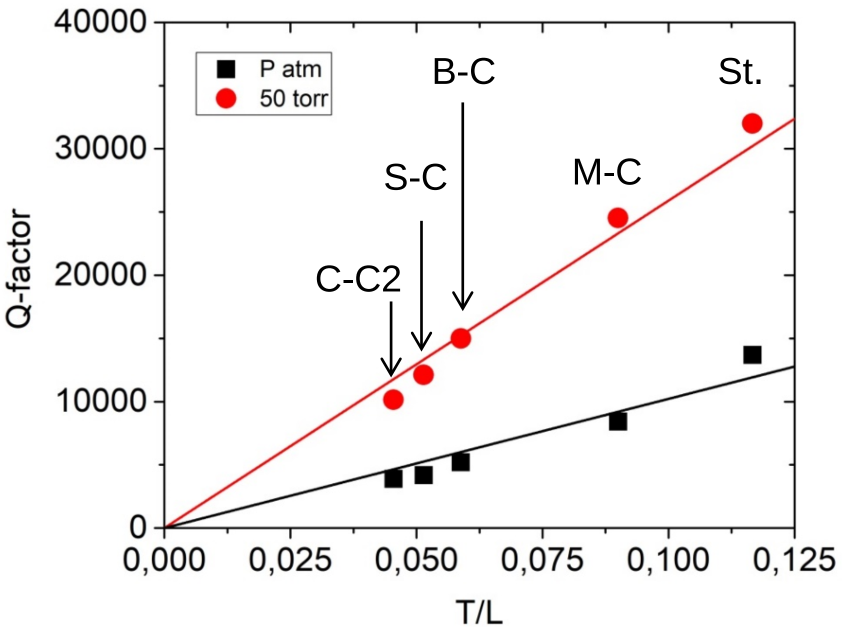
OUTLINE

- Motivation for Gas Sensing
- Quartz Enhanced Photoacoustic Gas Detection
- QEPAS: Basic principles and merits
- QEPAS with custom quartz tuning forks (3rd **Generation)**
- ……….

3rd generation of custom QTFs

Objective: Design of QTFs with a **high Q-factor** and resonant frequency in the range 15-17 kHz

Starting from QTFs 2nd generation



Air damping dominates

$$Q \propto \frac{T}{L}$$

P. Patimisco et al, Optics Express *27, 1401-1415,* **2019.**

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3rd generation of custom QTFs

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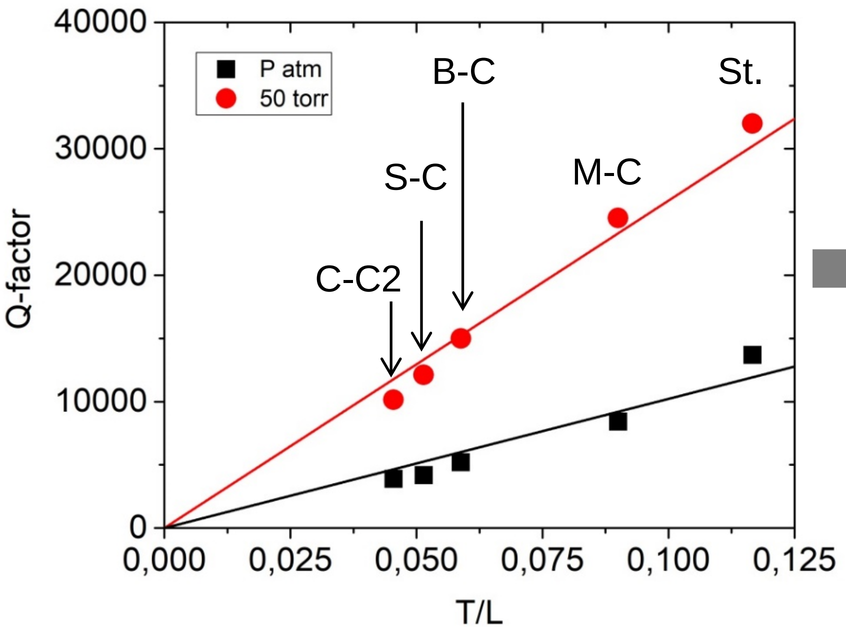
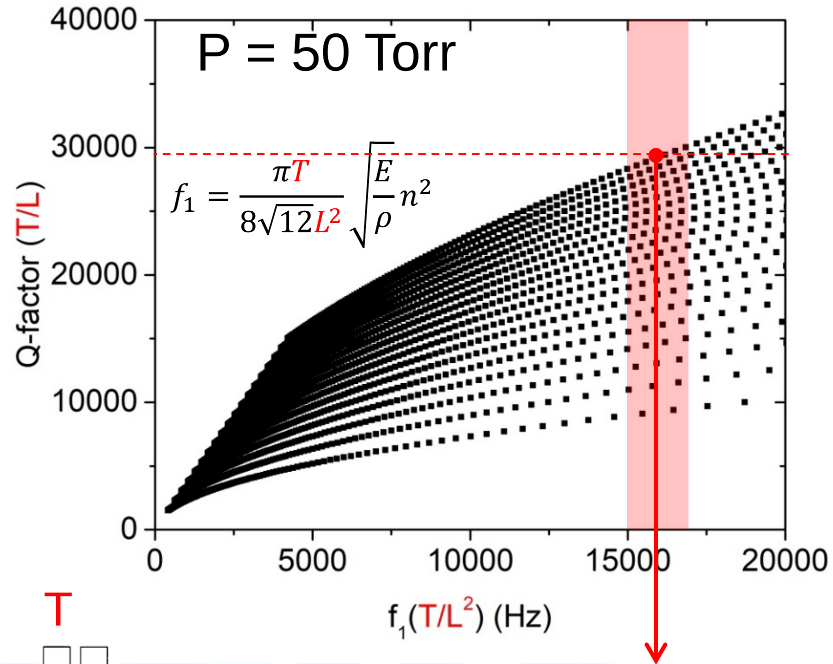
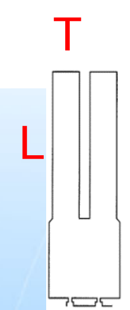


Air damping dominates

$$Q \propto \frac{T}{L}$$

Simulation





Selected design:

L = 9.4 mm

T = 2 mm

Q ~ 30000 @ 50 Torr

Q ~ 10000 @ Atm P.

P. Patimisco et al, Optics Express *27, 1401-1415,* **2019.**

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3rd generation of custom QTFs

Goal: Realize custom quartz tuning forks, targeting: i) reduction of the resonance frequency; 2) maintenance of a high the Q-factor; 3) optimized electrode layout for overtone flexural mode

5 NEW DESIGNS

QTF S08
(prongs spacing 0.8 mm)

QTF S08 - G
(prongs spacing 0.8 mm)

QTF S08 – TOP
(prongs spacing 0.8 mm)

QTF S15
(prongs spacing 1.5 mm)

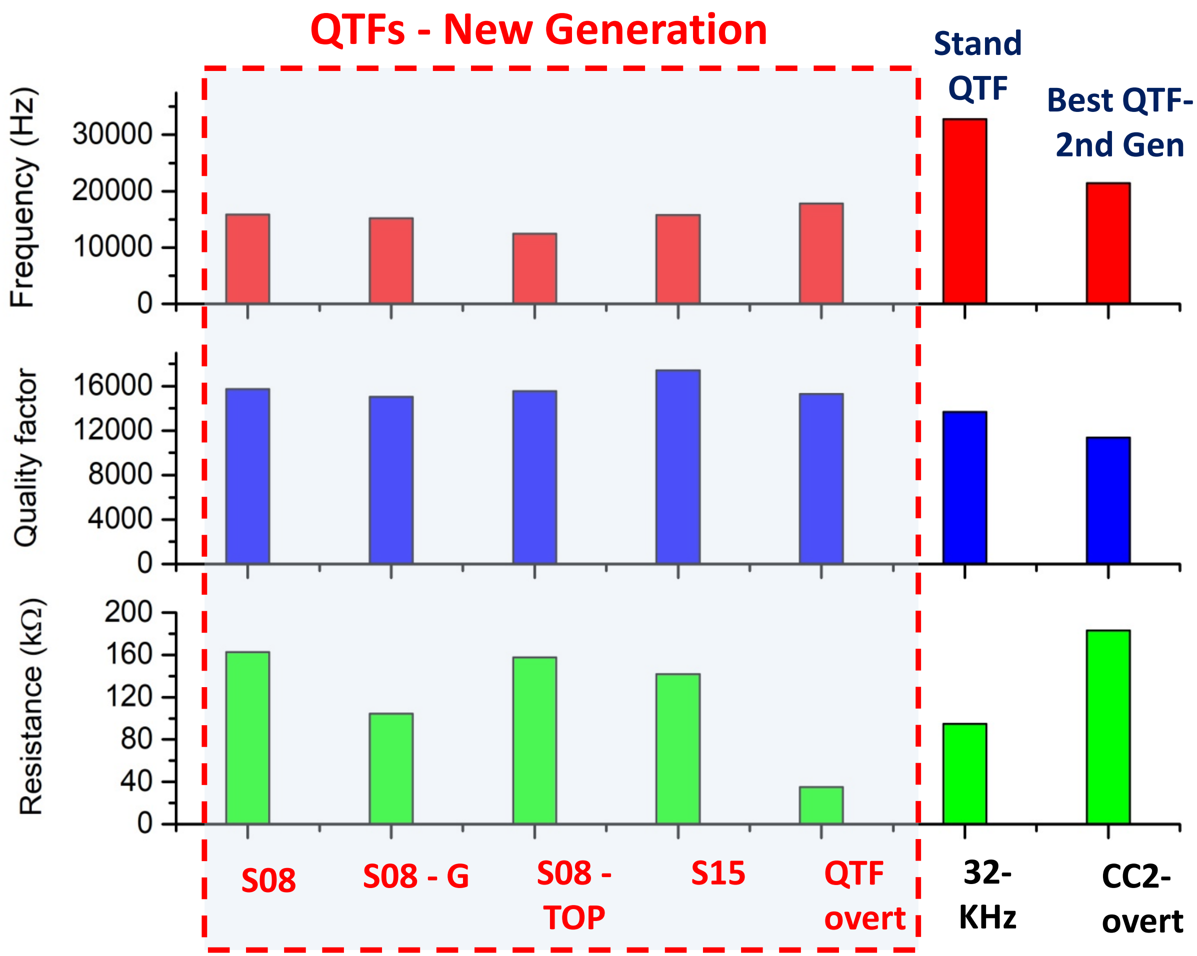
QTF-Overtone
(prongs spacing 0.7 mm)

- QTF S08: Reducing air damping while keeping f_0 15-17 kHz
- QTF S08 - G: Grooves engraved on both sides of the QTF prongs
- QTF S08 – TOP: Wider top end on both prongs
- QTF S15: Increased prong spacing of 1.5 mm to facilitate optical alignment of the focused laser beam
- QTF-Overtone: Enhanced overtone mode operation @ 17 kHz with an optimized electrode layout design

All these QTFs have the same prong length and thickness

P. Patimisco et al, Optics Letters *43, 1854-1857,* **2018**
P. Patimisco et al, IEEE T. Ultr. Ferr. 65, 1951-1957,

3rd gen. QTFs Electrical Characterization



Results are compared with a *standard 32 kHz*-QTF and the best QTF of the 2nd generation (*C-C2, overtone*)

- The **frequency was decreased by a factor of 2** with respect to the 32 KHz-QTF achieving **higher quality Q-factors.**

P. Patimisco et al, IEEE T. Ultr. Ferr., 65, 1951-1957, **2018**

P. Patimisco et al, Optics Express *27, 1401-1415,*

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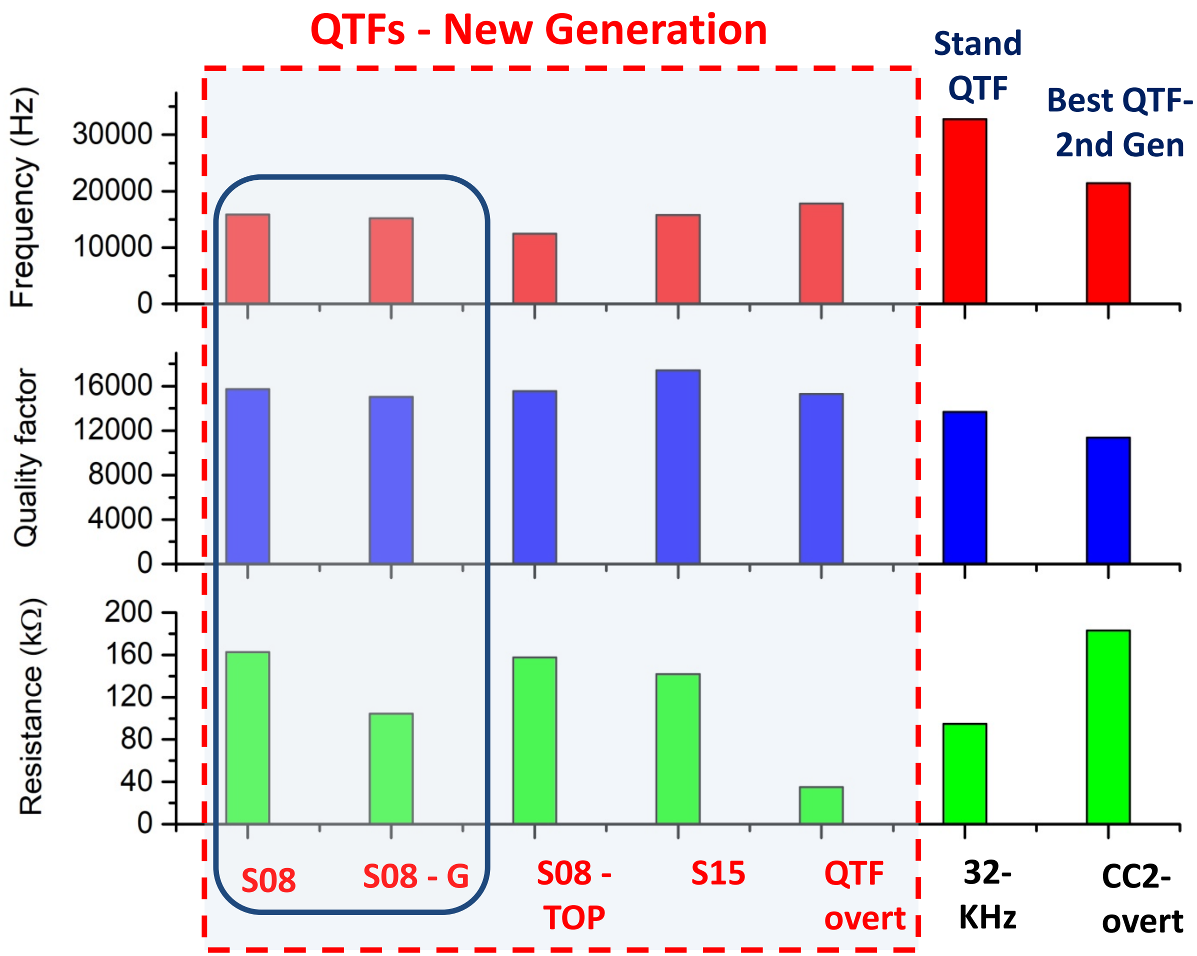
3rd gen. QTFs Electrical Characterization



Results are compared with a *standard 32 kHz-Q*TF and the best QTF of the 2nd generation (*C-C2, overtone*)

- The **frequency was decreased by a factor of 2** with respect to the 32 KHz-QTF achieving **higher quality Q-factors.**
- Engraving **grooves** on the prongs surface **decreased the QTF electrical resistance by a factor of 2** (see **S08-G vs S08**).

P. Patimisco et al, IEEE T. Ultr. Ferr., 65, 1951-1957, **2018**
P. Patimisco et al, Optics Express *27, 1401-1415,*

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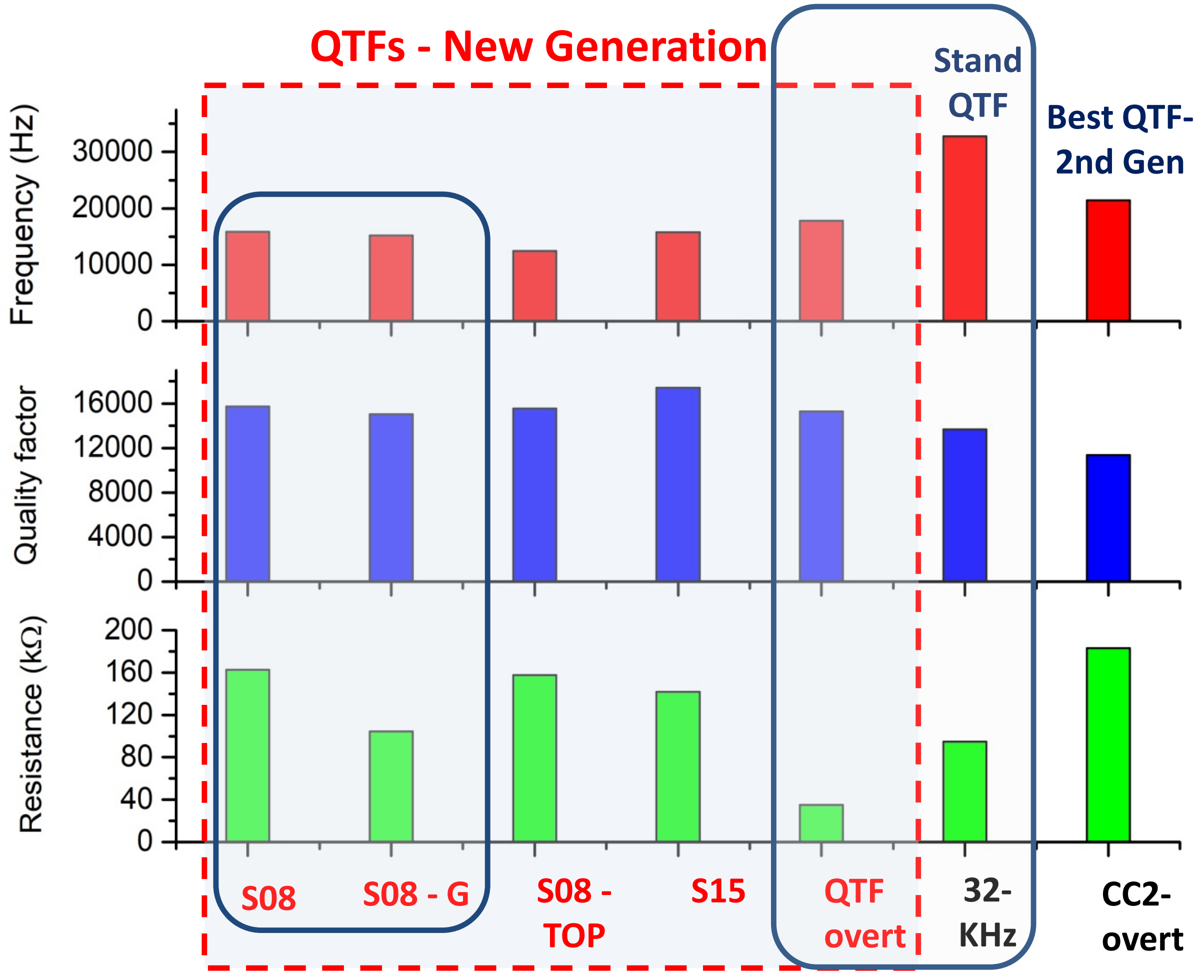

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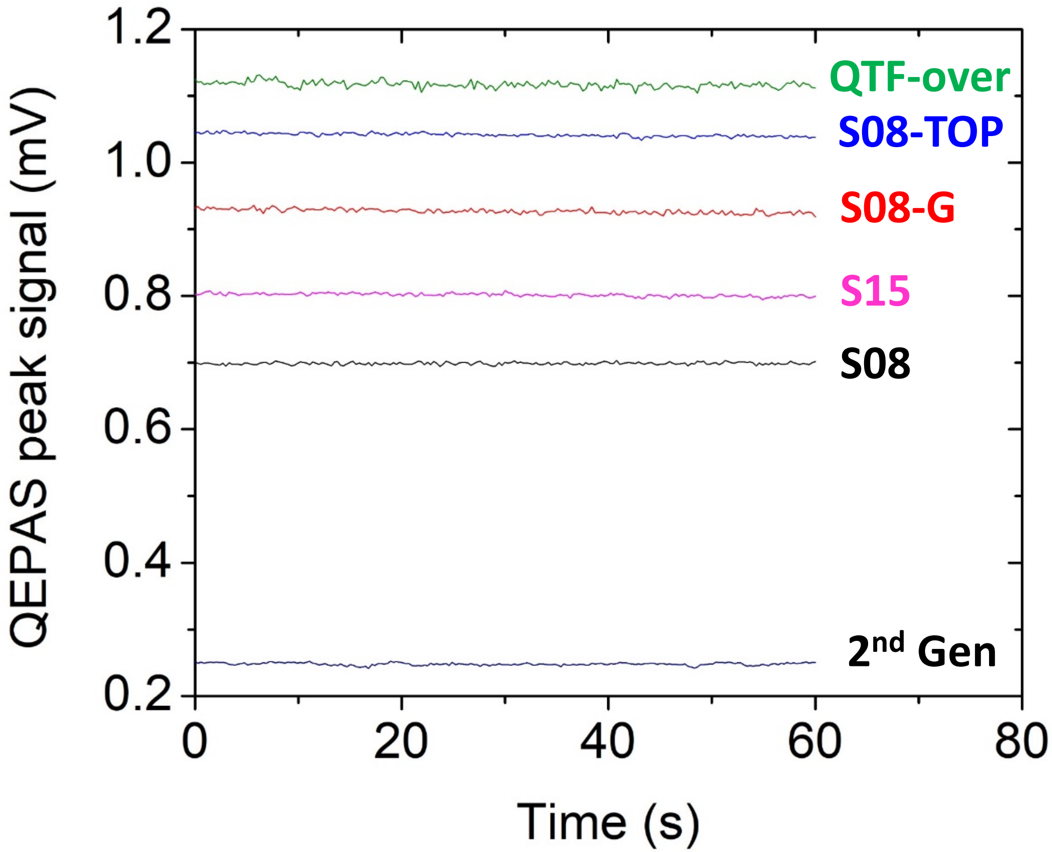
- Engraving **grooves** on the prongs surface **decreased the QTF electrical resistance by a factor of 2** (see **S08-G vs S08**).
- The **QTF operating in the overtone mode** (**QTF-overt**) exhibits a **lower electrical resistance** than a 32KHz-QTF.

3^{rd} gen. QTFs –Photoacoustic performances

Detection of a water line @7.7 µm, atm pressure

QEPAS line-locking measurements



All new QTFs show <u>**higher QEPAS signals**</u> than the 2^{nd} generation.

The **noise level is nearly the same** for all QTFs except for QTF-overtone, due to its narrower prongs spacing (700 µm).

P. Patimisco et al, Optics Express *27, 1401-1415,* **2019.**

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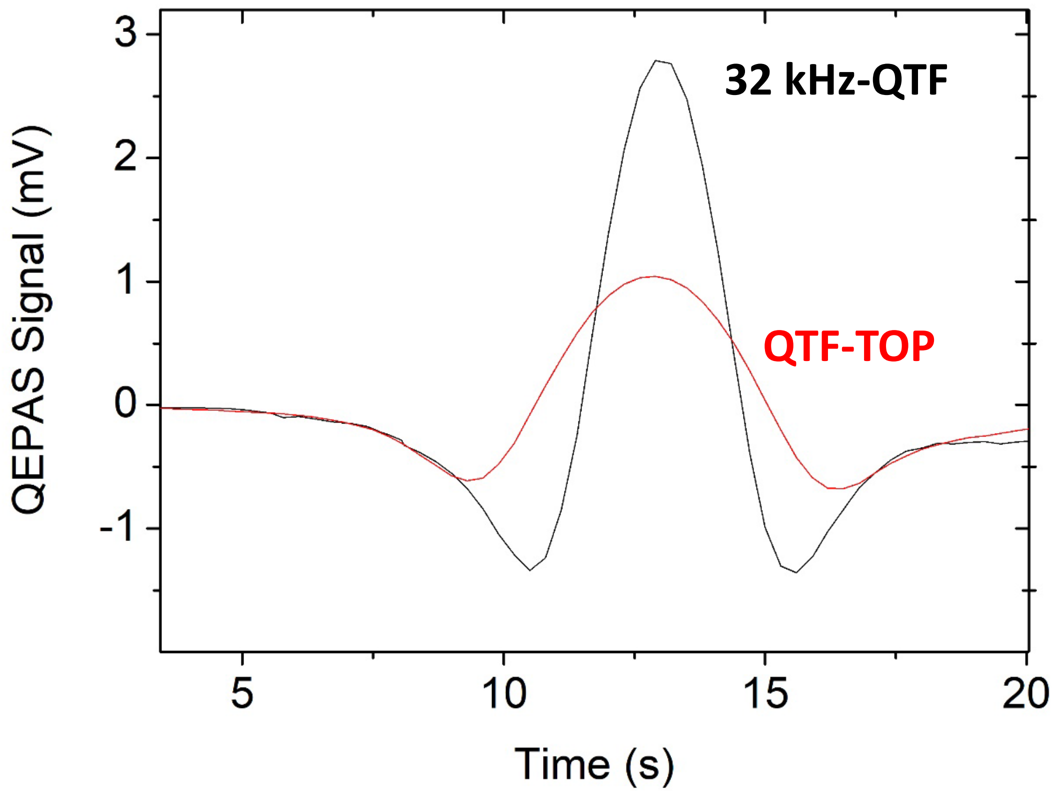
3rd gen. QTFs – Comparison with 32 kHz-QTF

Detection of a water line @7.7 µm, atm pressure

QEPAS spectral scan measurements

32 kHz-QTF exhibits a **higher signal**



P. Patimisco et al, Optics Express *27, 1401-1415,* **2019.**

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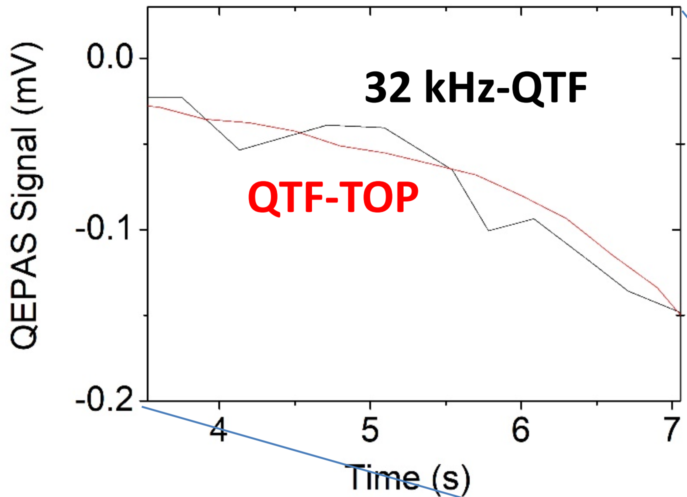
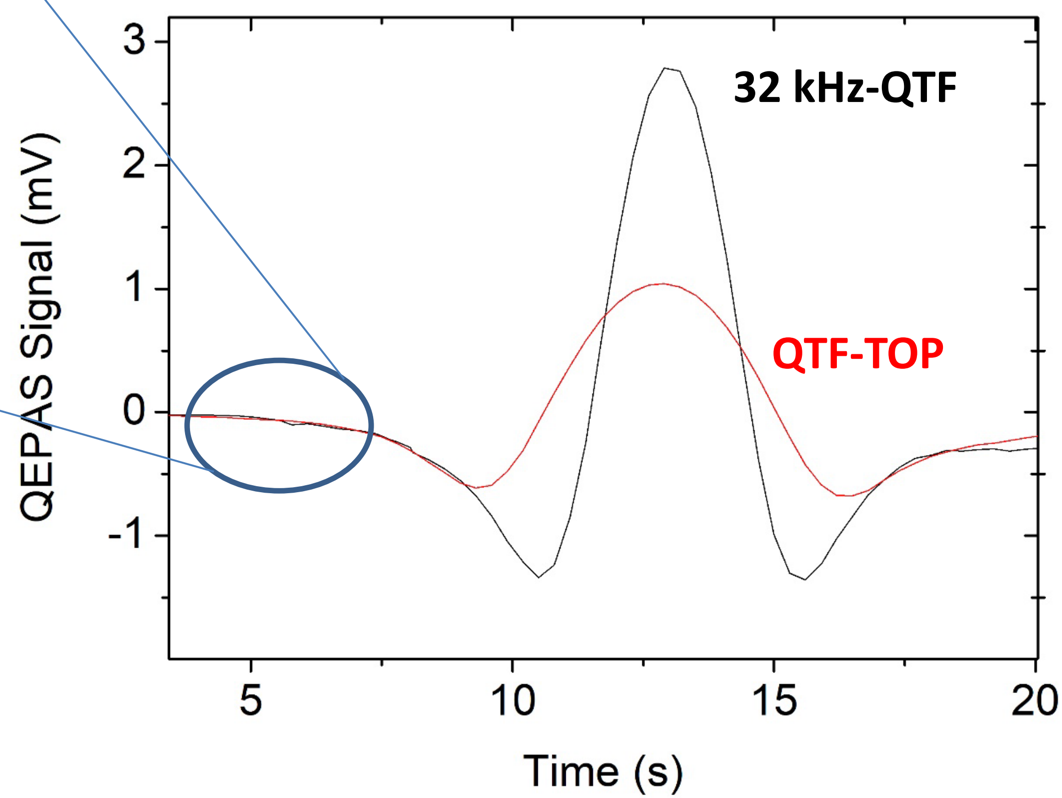
3rd gen. QTFs – Comparison with 32 kHz-QTF

Detection of a water line @7.7 µm, atm pressure



QEPAS spectral scan measurements



32 kHz-QTF exhibits a **higher signal**

but also a **higher noise background**

P. Patimisco et al, Optics Express *27, 1401-1415,* **2019.**

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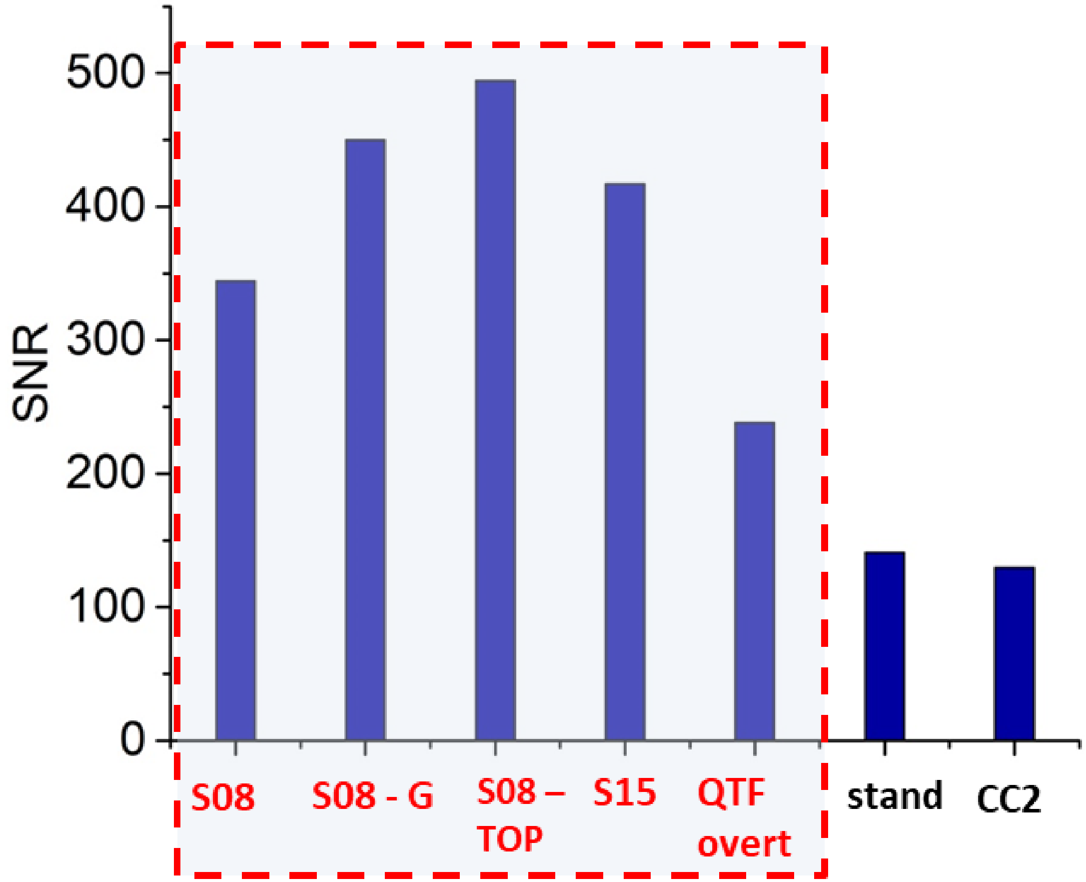
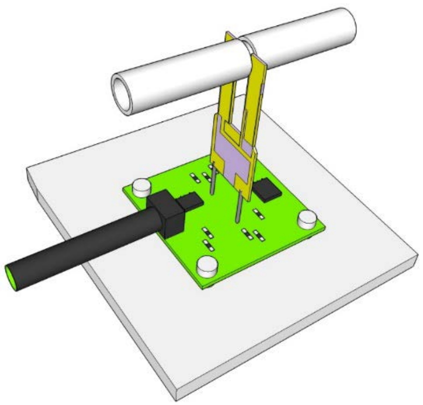
3rd gen. QTFs –SNR performances

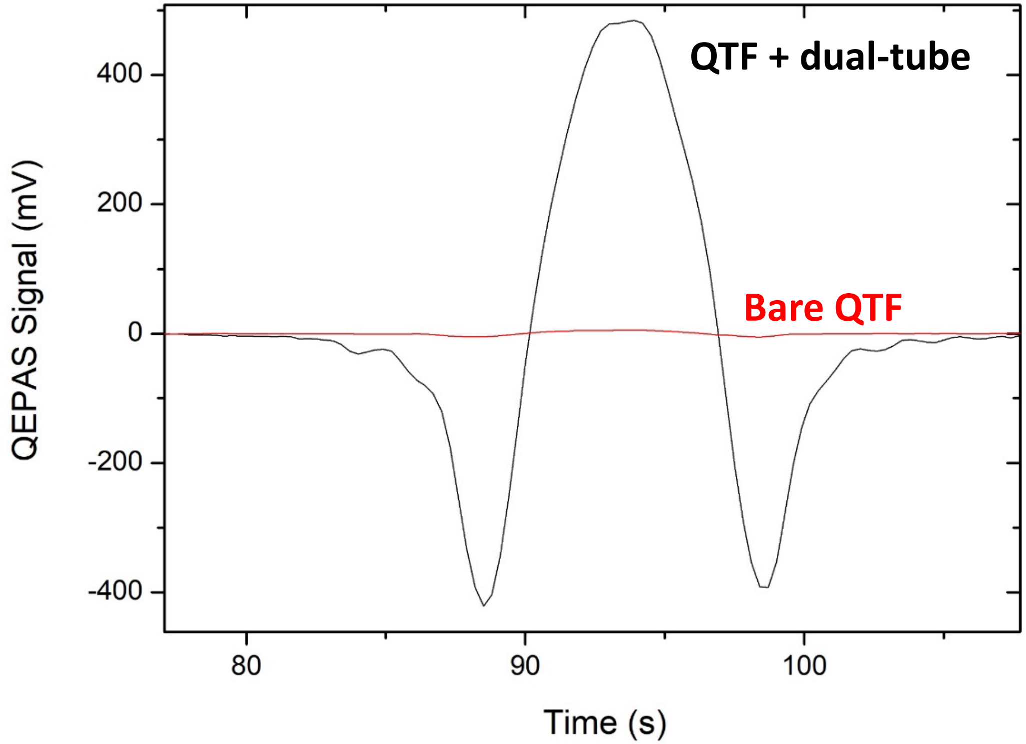


All 3rd gen. QTFs exhibit **higher performance (SNR)** with respect to the 2nd gen. QTFs and the standard 32kHz QTF.

P. Patimisco et al, IEEE T. Ultr. Ferr., 65, 1951-1957, 2018;
P. Patimisco et al, Optics Express *27, 1401-1415,* 2019

QTF-S08-TOP with dual-tube resonator
ID = 1.59 mm and L = 12.4 mm





SNR Enhancement x60 (new QEPAS record)

P. Patimisco et al, Optics Express *27, 1401-1415,* **2019.**

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New QEPAS Acoustic Detection Module with 3rd gen. QTF–available in the market in 2019

THORLABS

OUTLINE

- Motivation for Gas Sensing
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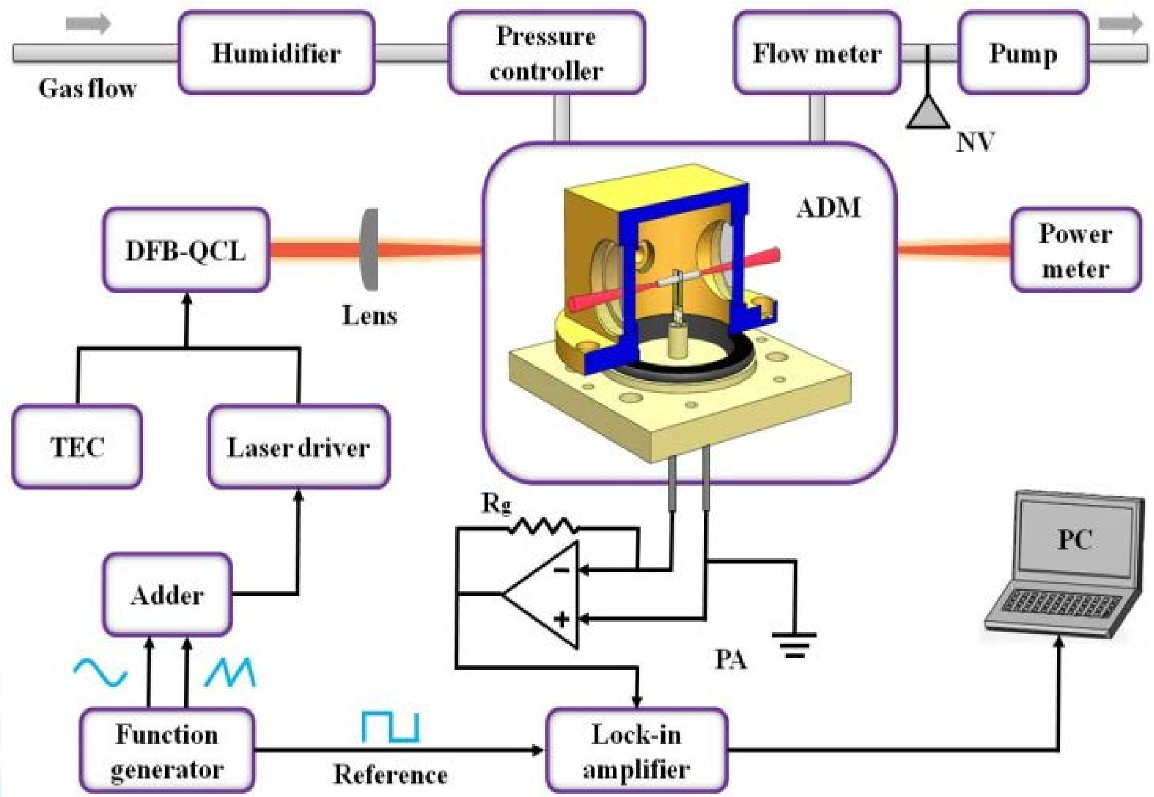
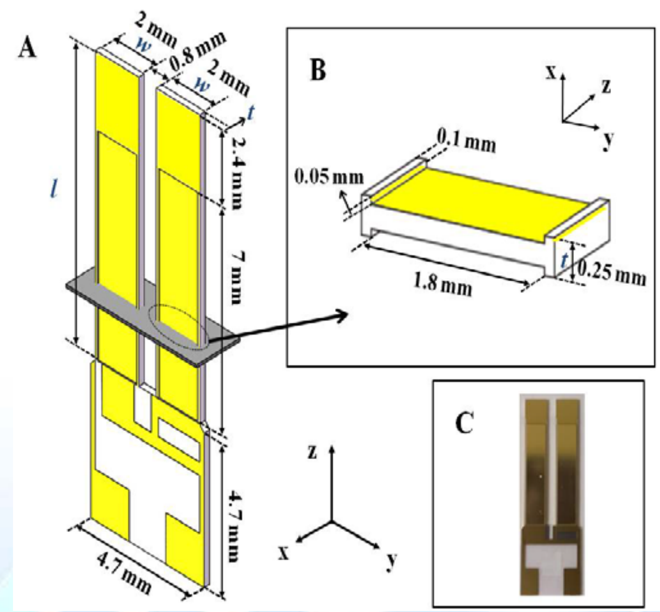
- QEPAS: Basic principles and merits
- QEPAS with custom quartz tuning forks
- QEPAS in the THZ range
- Real world applications

Carbon Oxide detection with 3rd gen QTF



QTF-S08-G



DFB-QCL emitting @ 4.61 μm
Optical power: 21 mW
Absorption line-strength: 4.5·10^{-19} cm/mol

S. Li, L. Dong, H. Wu, A. Sampaolo, P. Patimisco, V. Spagnolo, F.K. Tittel, ACS Analytical Chemistry, *submitted 2019*

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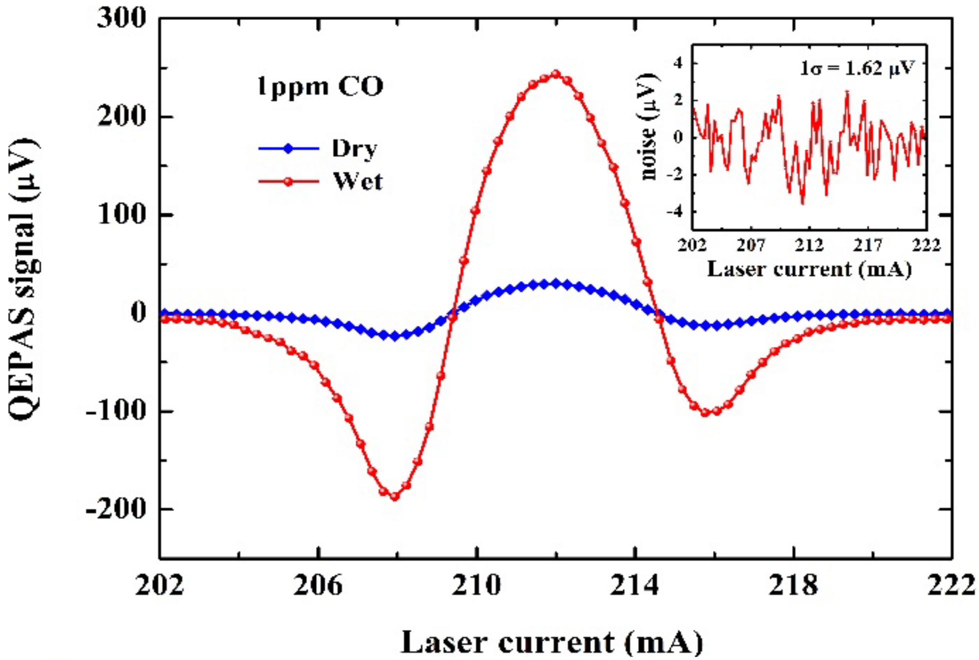
CO QEPAS Sensor calibration and detection limit

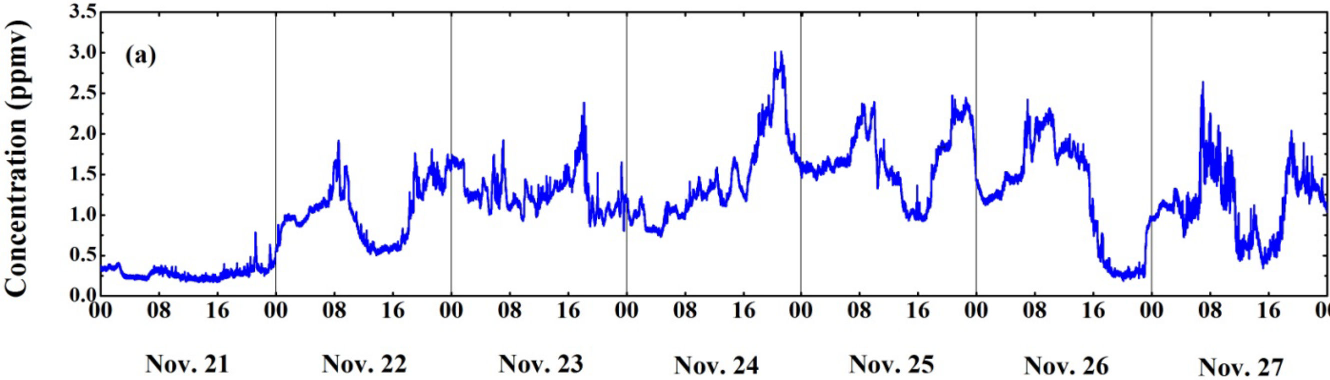


MDL: 7 ppb
with a 1 s integration time

QEPAS record for CO!

NNEA: 8.7·10^{-9} cm^{-1}W /√Hz

Continuous monitoring of atmospheric carbon oxide concentrations measured for a 7-day period in Nov. 2018 at Shanxi University, China



S. Li, L. Dong, H. Wu, A. Sampaolo, P. Patimisco, V. Spagnolo, F.K. Tittel, ACS Analytical Chemistry, *submitted 2019*

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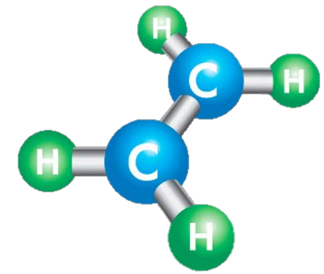
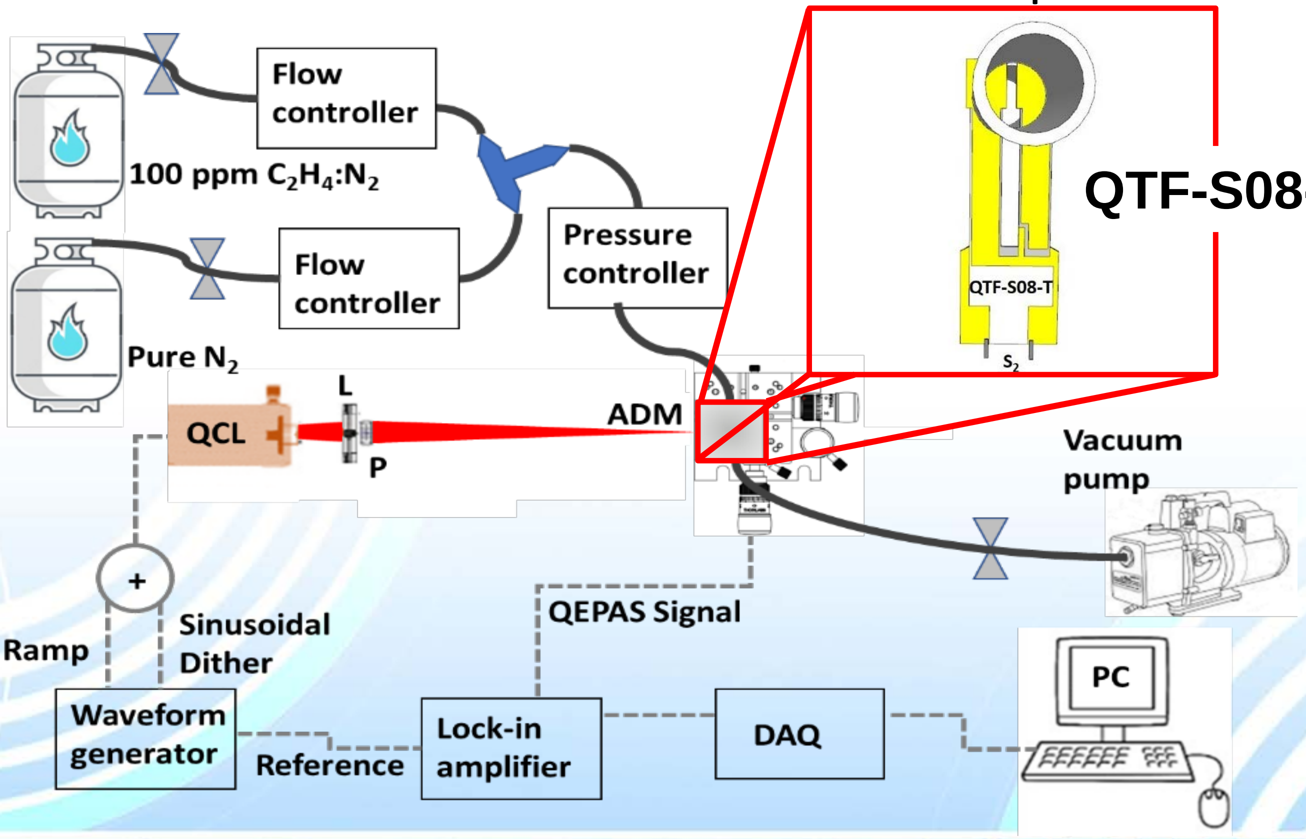
Ethylene detection with 3rd gen QTF

- In chemistry, C_2H_4 is the basic building block for **hydrocarbons**
- **Breath biomarker** for bacterial infections
- **Plant hormone** associated with cellular respiration in fruits





DFB-QCL emitting @
10.34 µm

Optical power:
61.6 mW

Absorption line strength:
$2.21 \cdot 10^{-20}$ cm/mol

G. Marilena et al, Optics Express 27, 4271-4280, **2019**

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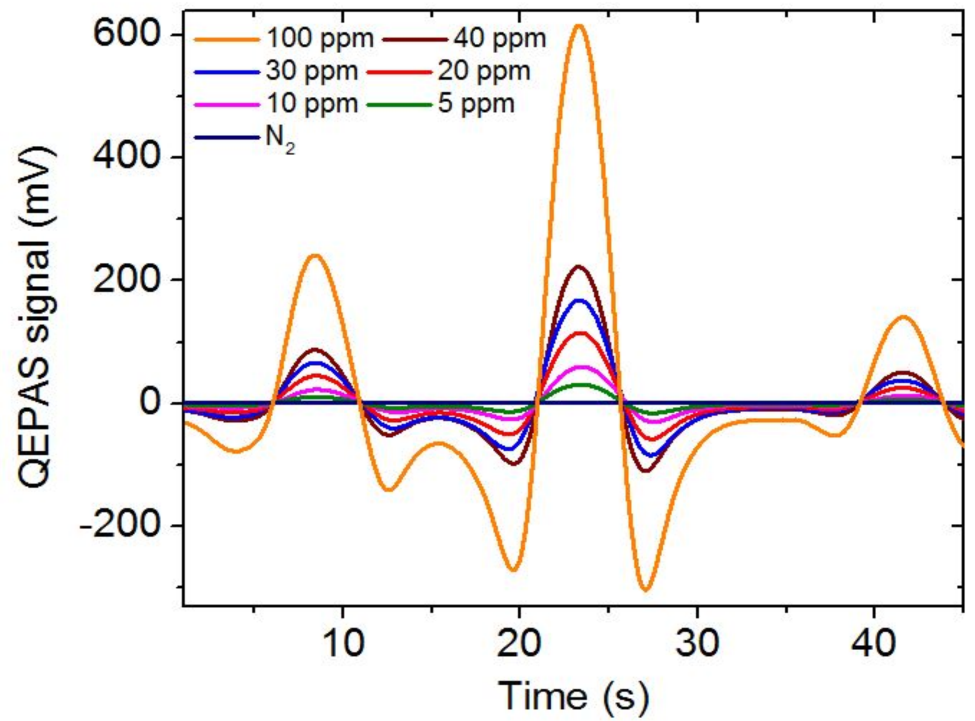
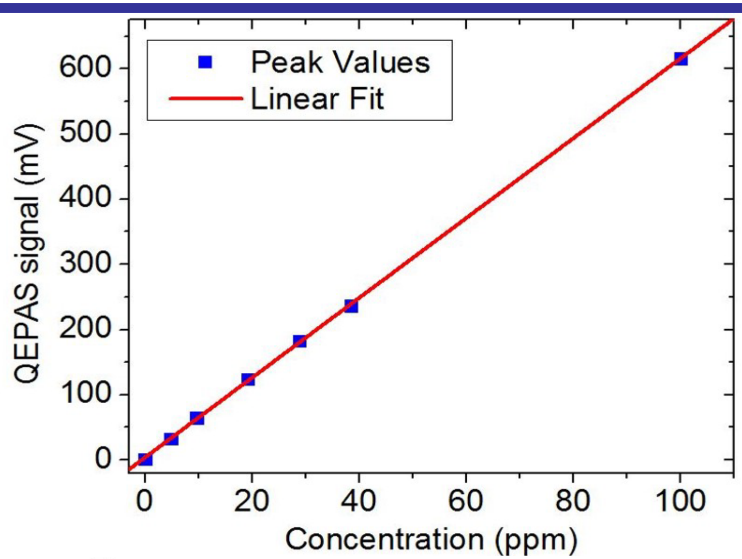
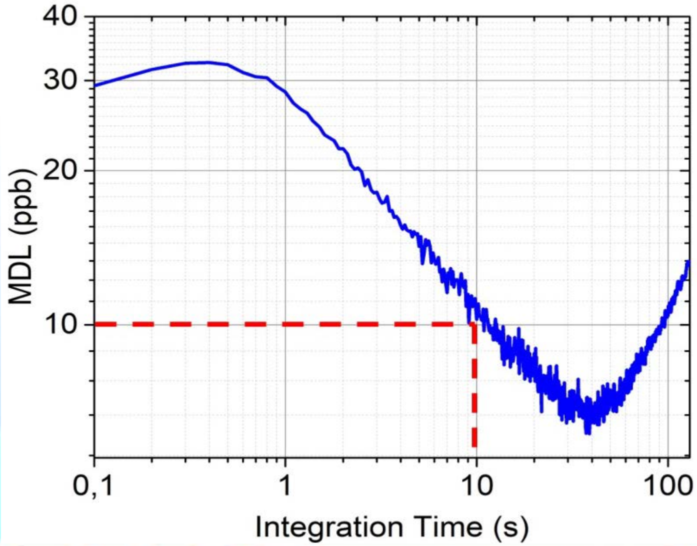
C_2H_4 QEPAS Sensor calibration and detection limit







MDL: 29 ppb
with 100 ms integration time

MDL: 10ppb
with 10 s integration time
QEPAS record for C_2H_4!

G. Marilena et al., Optics Express 27, 4271-4280, **2019**

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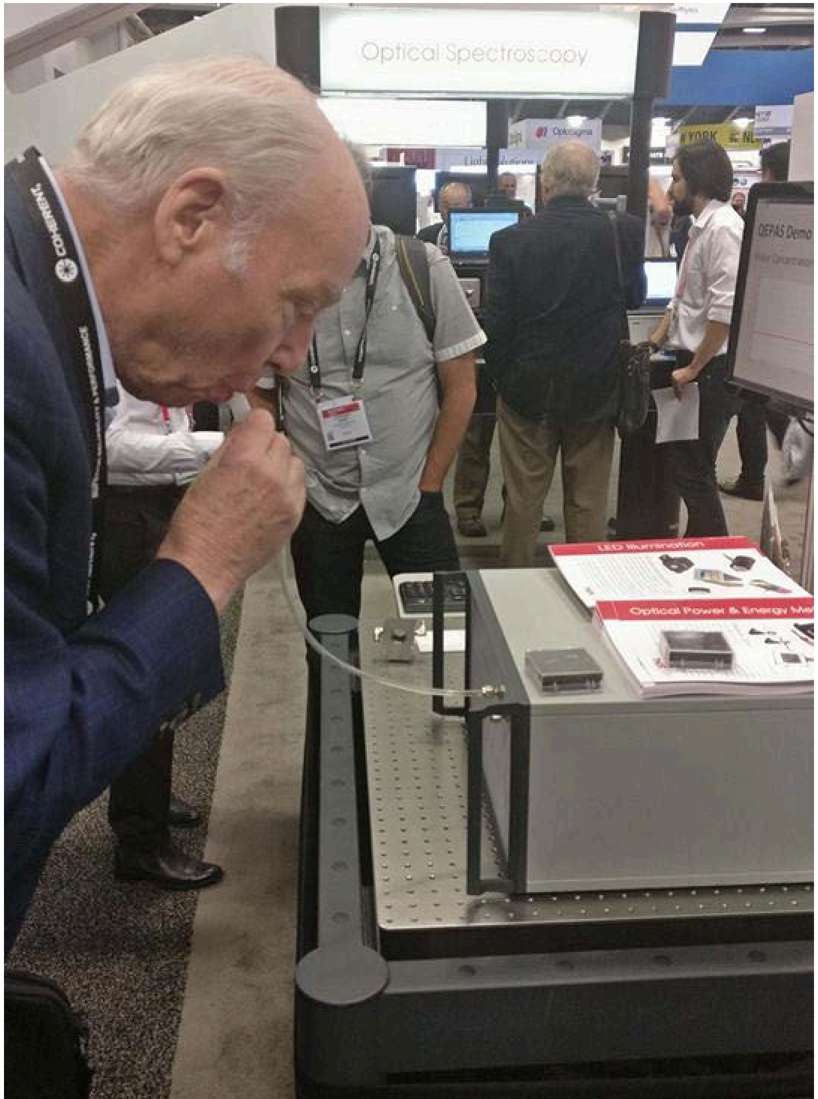
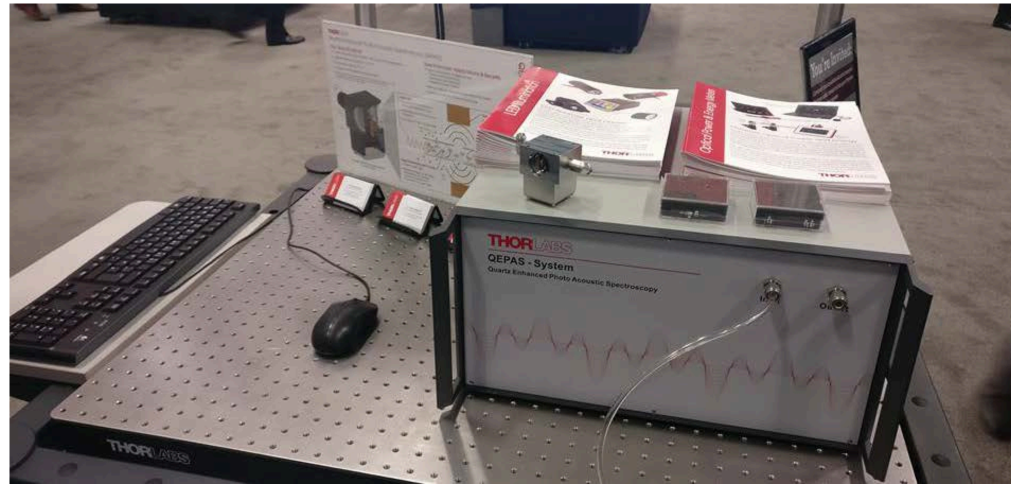
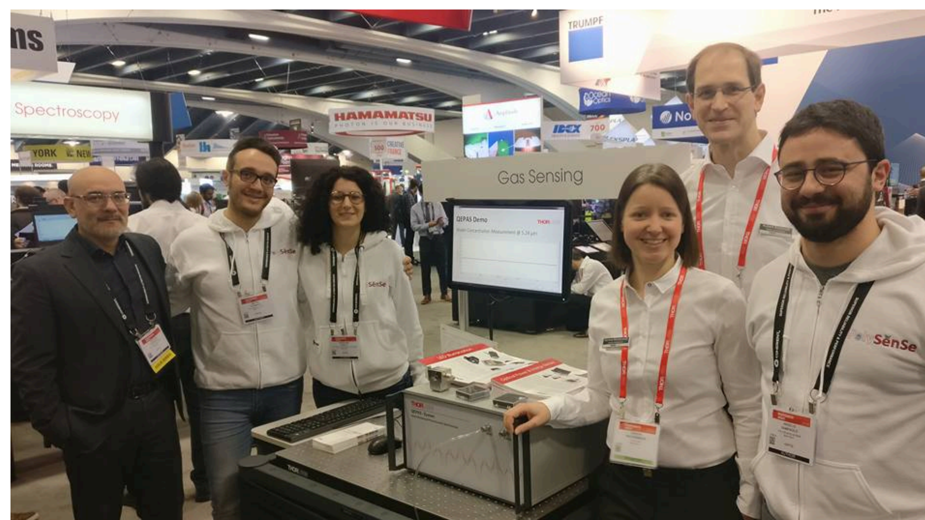
First commercial Ethylene QEPAS prototype
Thorlabs Booth at Photonics West Feb. 2018



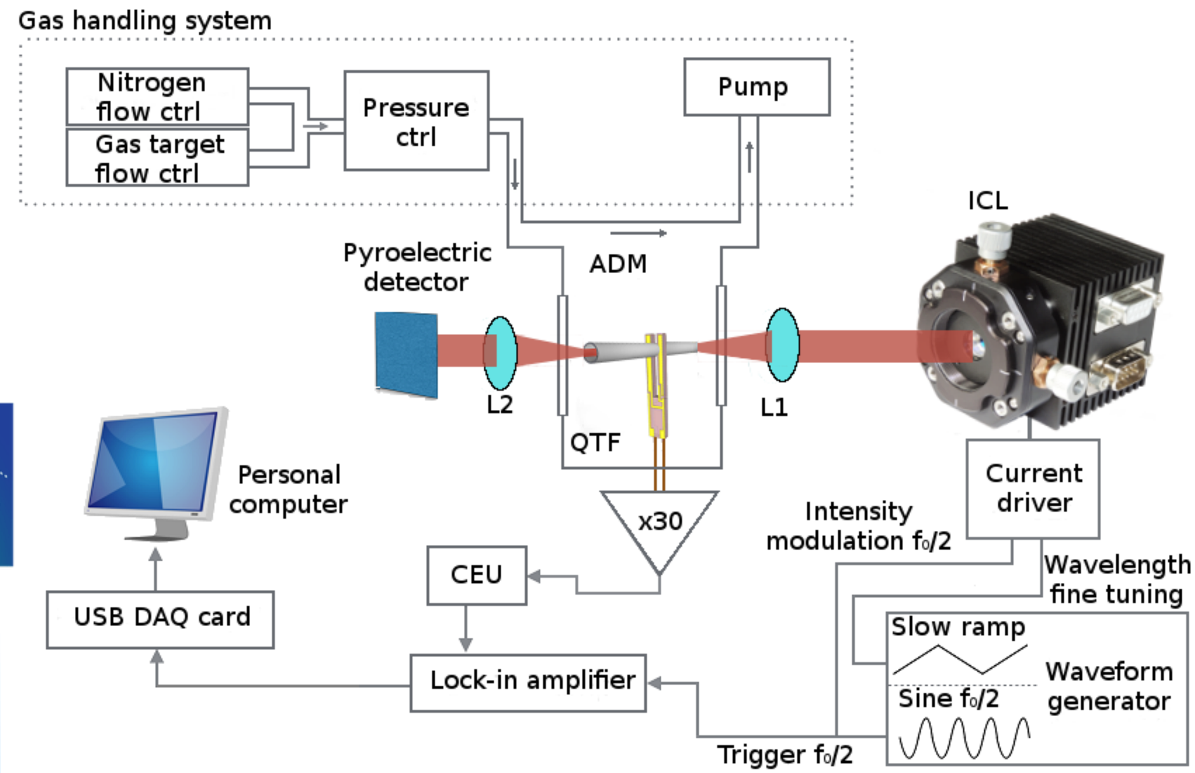




QEPAS Sensor setup for C1-C2-C3 detection

ILC characteristics

- $\lambda_{emission}$: **3345 nm**
- Tuning range: **12 nm**
- Optical Power: **12 mW**



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Spectroscopic technique

- **2f wavelength modulation**: laser current modulated at the half of the QTF resonance frequency and QEPAS signal demodulated by lock-in amplifier at the QTF resonance frequency → **background free detection**

. Sampaolo et al, Sensors and Actuators B. hem 282 952-960 2019

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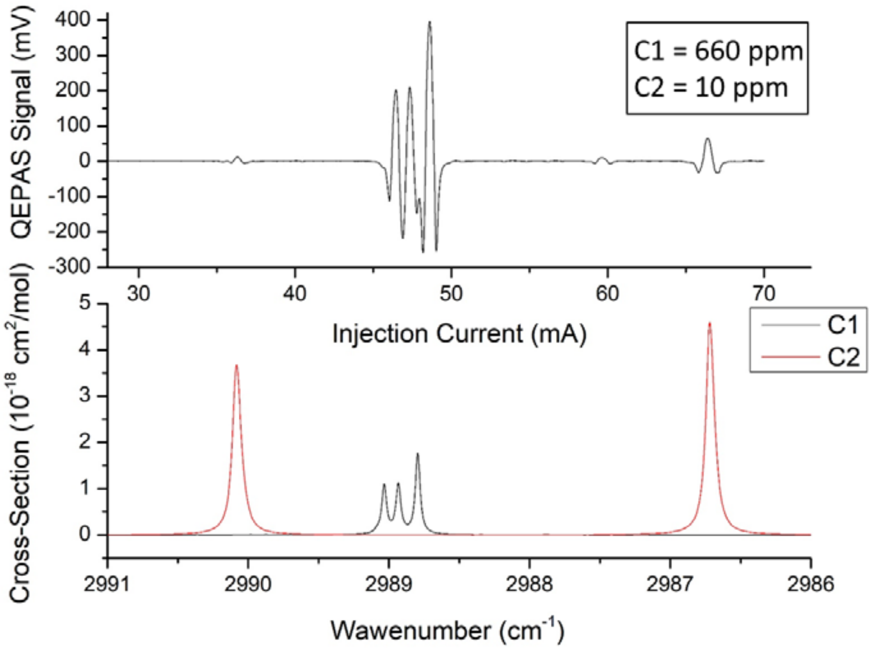
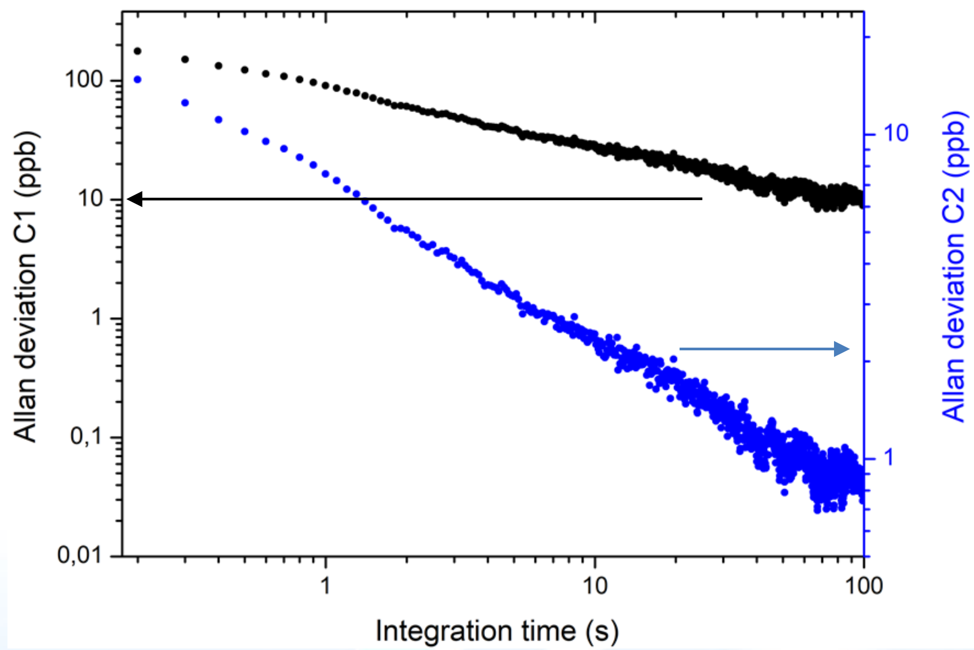
Hydrocarbons QEPAS Sensor
C1-C2 detection

Aramco Services Company





- Detection limit C1: **90 ppb** @ integration time **1 s**
- Detection limit C2: **7 ppb** @ integration time **1 s**,

RECORD for QEPAS technique

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Hydrocarbons QEPAS Sensor

C2-C3 detection

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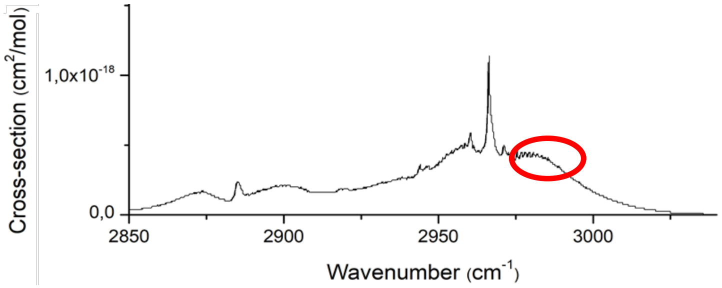
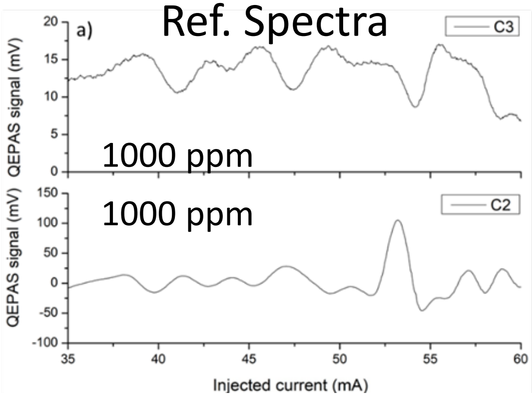
Propane absorption



$$Y(\lambda) = \sum_{i=0}^{n} A_i \, X(\lambda)_i \; = A_2 \, X(\lambda)_{C2} + A_3 \, X(\lambda)_{C3}$$



a)2f-signal for 1000 ppm-C3 and 1000 ppm-C2 respectively in pure N_2

. Sampaolo et al, Sensors and Actuators B. hem., 282, 952-960, 2019

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Hydrocarbons QEPAS Sensor

C2-C3 detection

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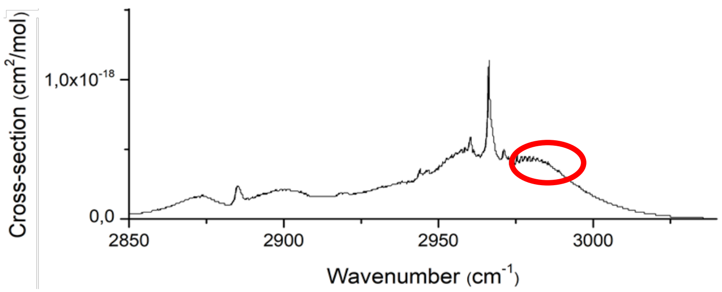
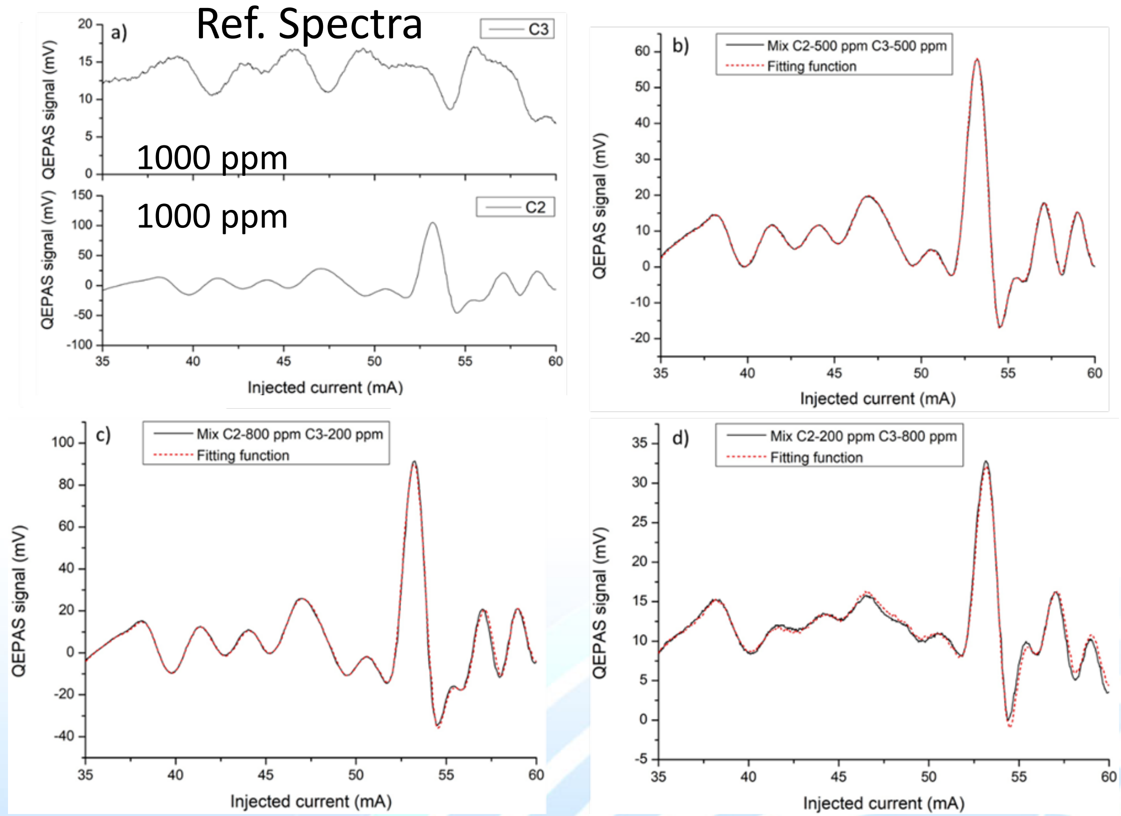
Propane absorption



$$Y(\lambda) = \sum_{i=0}^{n} A_i\, X(\lambda)_i \; = A_2\, X(\lambda)_{C2} + A_3\, X(\lambda)_{C3}$$

Mix	Actual C2 concentration [ppm]	Actual C3 concentration [ppm]	Calculated C2 concentration [ppm]	Calculated C3 concentration [ppm]
1	500	500	487.02 (±1.4)	520.00 (±2.5)
2	800	200	828.98 (±3.8)	208.01 (±6.8)
3	200	800	199.98 (±1.7)	831.47 (±2.9)

C3 detection limit @ 1s for peak at 5°C is 3 ppm



a)2f-signal for 1000 ppm-C3 and 1000 ppm-C2 respectively in pure N_2 b)2f-signal for a dry mixture containing 500 ppm of C2 and 500 ppm of C3, in pure N_2; c) 2f-signal for a dry mixture containing 800 ppm of C2 and 200 ppm of C3 in pure N_2; d) 2f-signal for a dry mixture containing 200 ppm of C2 and 800 ppm of C3 in pure N_2.

. Sampaolo et al, Sensors and Actuators B.
hem , 282, 952-960, 2019

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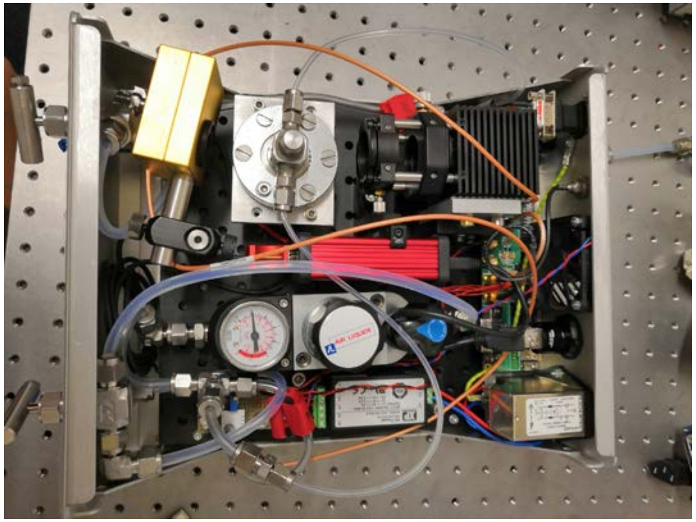
New QEPAS sensor system for hydrocarbon (C1, C2, C3) detection to be tested in Dahran Spring 2019



2 kg

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aramco

30cm x 10cm x 20cm

. Sampaolo et al, Sensors and Actuators B.
hem. 282, 952-960, 2019

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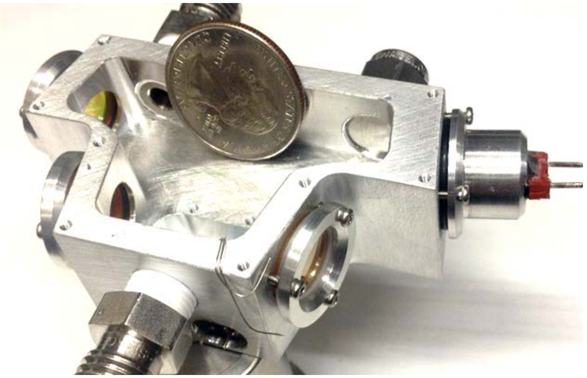
Future Perspectives

➢ Realization of *QTFs 3rd generation*

➢ Develop ultra compact I-QEPAS sensors for high-sensitive detection



➢ Develop QEPAS sensors for mainstream, upstream and downhole petrochemical applications

➢ Develop QEPAS-on drone sensing systems

➢ Push QEPAS sensor systems development for *real-world applications* and *commercialization*

THORLABS PolySenSe Aramco Services Company

Thank You

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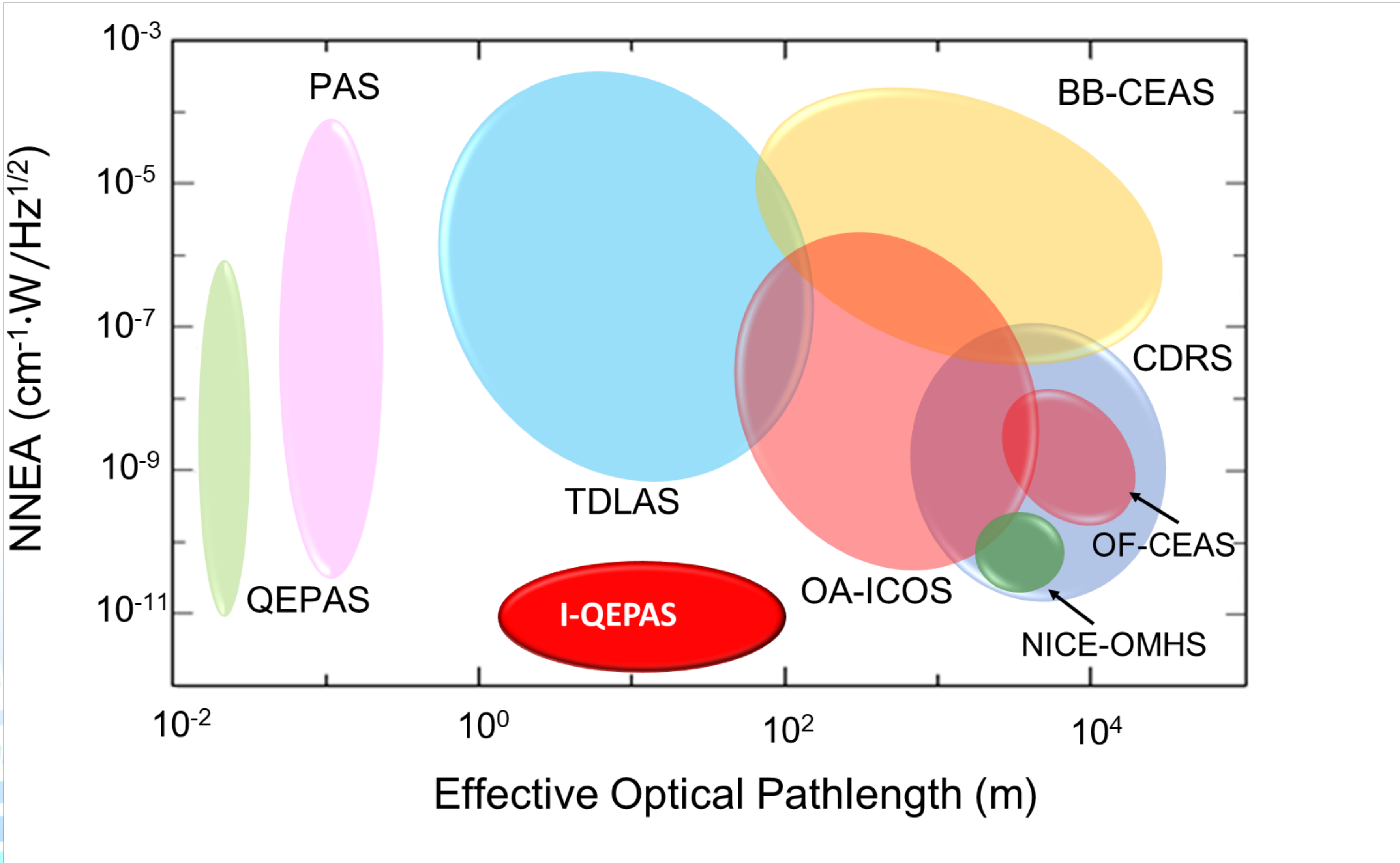
Aramco Services Company

Max Deffenbaugh
Sebastian Csutak

I-QEPAS vs Other Techniques



P. Patimisco et al., "QEPAS Review", Sensors, 14, 6165–6206, **2014**.

Design considerations for:

QTF-S15

Same geometry as QTF S08

Increased prong spacing up to 1.5 mm to:

- **Facilitate the optical alignment** of the focused laser beam
- Employ laser source with **poor spatial beam** quality or emitting in the **THz range**
- Implement micro-resonator tubes with **large inner diameters**
- **Investigate** of the influence of the **prongs spacing** on the QEPAS signal

QTF S15

(prongs spacing 1.5 mm)

P. Patimisco et al, IEEE T. Ultr. Ferr., 65, 1951-1957, **2018**

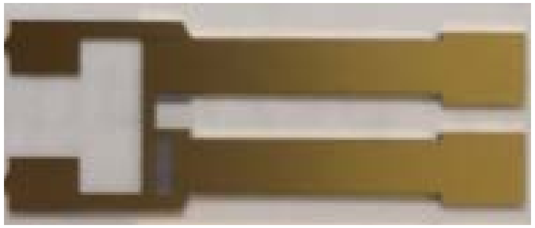
P. Patimisco et al, Optics Express, *submitted*,

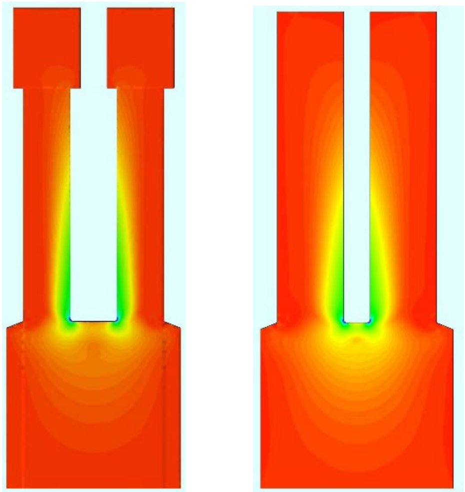
PolySenSe

Design considerations for:

QTF-S08-TOP

Same geometry as QTF S08 but with a **wider top end** of on both prongs to **better distribute the stress** field along the prongs and increase the **generated piezo-charges**





QTF S08 TOP

QTF S08

QTF-S15

Same geometry as QTF S08

Increased prong spacing up to 1.5 mm to:

- **Facilitate the optical alignment** of the focused laser beam
- Employ laser source with **poor spatial beam** quality or emitting in the **THz range**
- Implement micro-resonator tubes with **large inner diameters**
- **Investigate** of the influence of the **prongs spacing** on the QEPAS signal

QTF S15
(prongs spacing 1.5 mm)

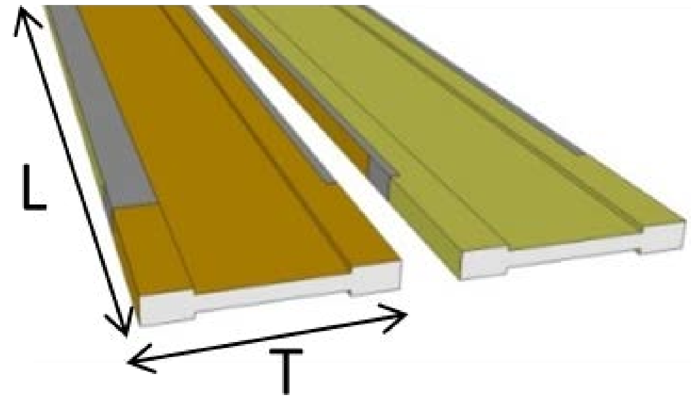
P. Patimisco et al, IEEE T. Ultr. Ferr., 65, 1951-1957, **2018**

P. Patimisco et al, Optics Express, *submitted,*

PolySenSe

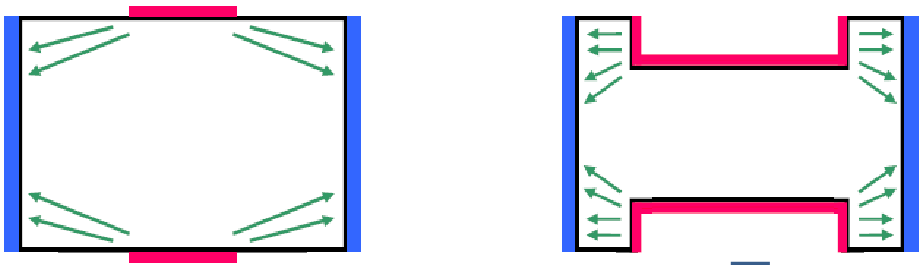
Design considerations for QTF S-08-G

Same geometry of QTF S-08, but **with grooves** engraved on both surfaces of **the prongs** to reduce the electrical resistance



Top view of one prong

QTF S-08 **QTF S-08-G**



■ Positive Electrode
■ Negative Electrode
→ Electrical Field

QTF capacitance increases

$$C = \frac{1}{2\pi Q R f}$$

Q and **f** depend on T and L

Not affected by grooves

R should be reduced

Higher **QEPAS signal**

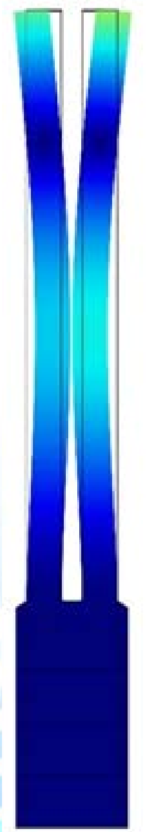
P. Patimisco et al, IEEE T. Ultr. Ferr., doi:10.1109/TUFFC.2018.2853404
P. Patimisco et al, Optics Express, *submitted*,

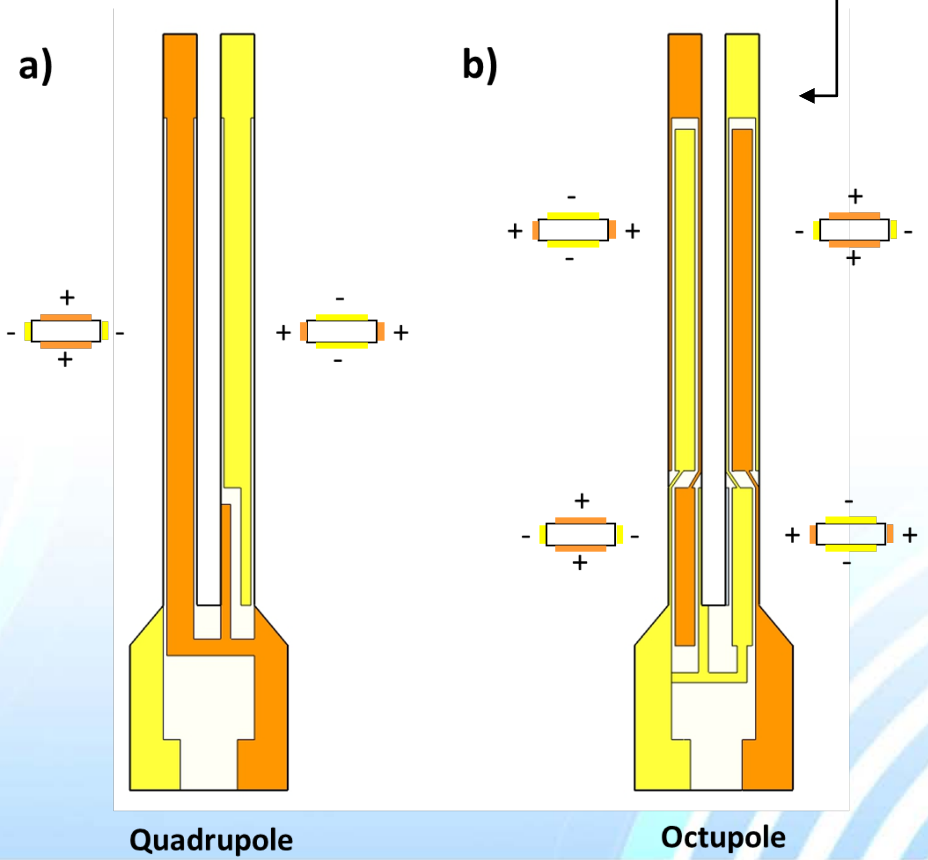
PolySenSe

Design considerations of QTF-overtone

QTF design optimized for **overtone mode** operation @ 17 kHz
Electrode layout designed to efficiently collect the **generated piezo-charges** (octupole configuration)

QTF-overtone
(prongs spacing 0.7 mm)





P. Patimisco et al, Optics Letters, *43, 1854-1857,* **2018**

PolySenSe