N_2-cooled THz quartz-enhanced photoacoustic (QEPAS) sensor operating in pulsed mode for hydrogen sulfide detection in the part-per-billion concentration range

Andrea Zifarelli[a,d], Angelo Sampaolo[a,d], Pietro Patimisco[a,d], Marilena Giglio[a,d], Chenren Yue[b], Huan Zhu[b], Haiqing Zhu[b], Gaolei Chang[b], Fangfang Wang[b], Jianxin Chen[b], Lianhe Li[c], A. Giles Davies[c], Edmund H. Linfield[c], Li He[b], Tingting Wei[d], Hongpeng Wu[d], Lei Dong[d], Gangyi Xu[b], Frank K. Tittel[e], and Vincenzo Spagnolo[a,d]

[a] *PolySense Lab, Dipartimento Interateneo di Fisica, University and Politecnico of Bari, Via Amendola 173, Bari,70126 Italy*
[b] *Key Laboratory of Infrared Imaging Materials and Detectors, Shanghai Institute of Technical Physics, Shanghai 200083, China*
[c] *School of Electronic and Electrical Engineering, University of Leeds, Leeds LS2 9JT, United Kingdom*
[d] *State Key Laboratory of Quantum Optics and Quantum Optics Devices, Institute of Laser Spectroscopy, Shanxi University, Taiyuan 030006, China*
[e] *Electrical and Computer Engineering Department, Rice University, 6100 Main St., Houston TX, 77005 USA*

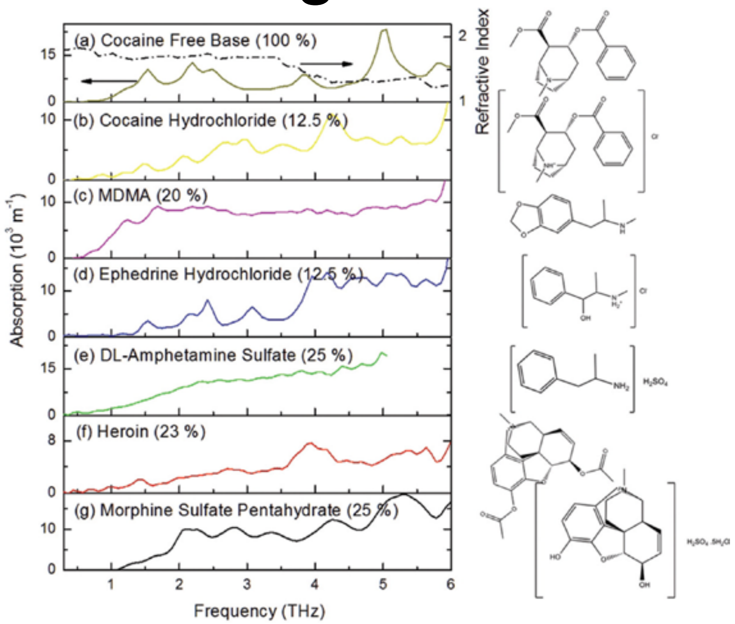
SPIE.
Photonics West 2020
San Francisco, California, USA
2nd - 6th February 2020

Outline

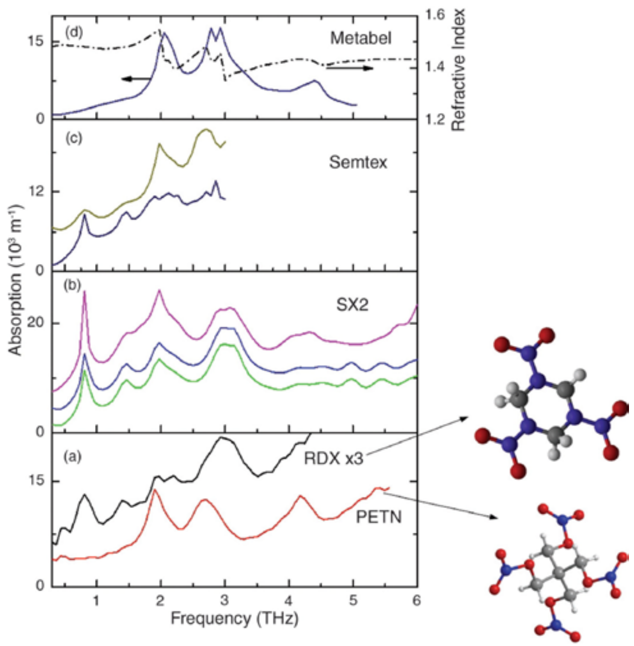
- **THz** spectroscopy for **H_2S detection**
- **QEPAS** for THz sensing applications
- **Nitrogen-cooled pulsed wave** quantum cascade laser (**QCL**)
- **THz-QEPAS sensor** for **H_2S** detection
- **Results** and **performance**
- **Conclusions** and **future perspectives**

THz gas spectroscopy: why?

Drugs

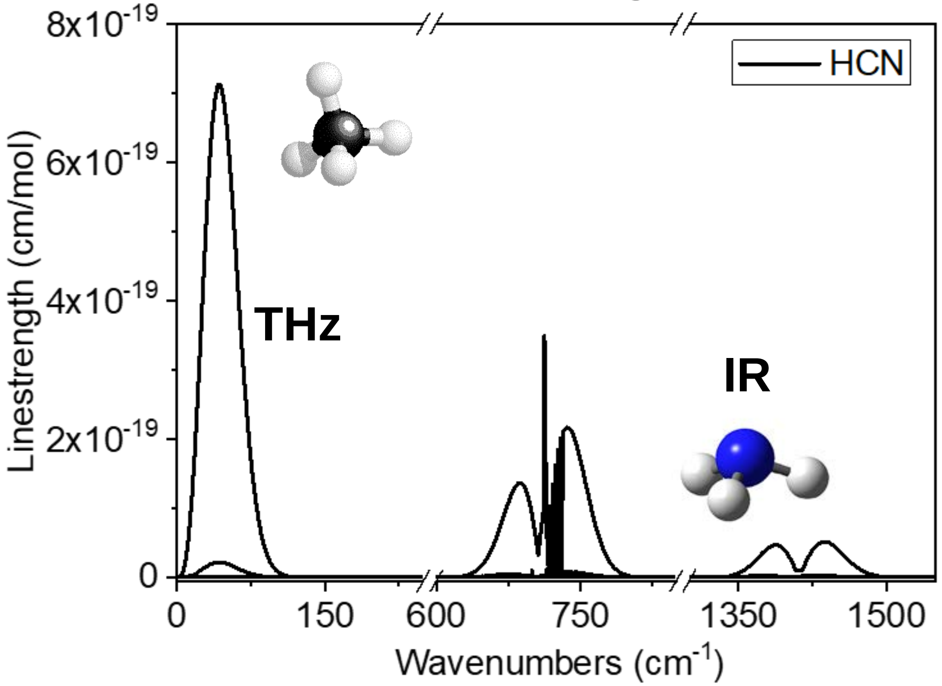


Explosives



Davies, A. G., et al., “Terahertz spectroscopy of explosives and drugs,” Materials Today 11(3), 18–26 (2008)

Harmful gases



- **Fingerprint region** for heavy molecules
- High-intensity **rotational transition**
- **Comb-like** absorption lines

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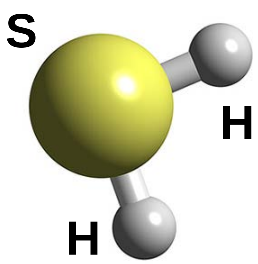
H_2S risks and applications

NIOSH IDLH = 100 ppm

Barsan, M.E. *NIOSH Pocket Guide to Chemical Hazards*; NIOSH Publications, Washington, USA, 2007.

- Sewers and swamps
- Human exhalate
- Natural gas extraction



Lack of real-time, in situ detection

Laser-based absorption spectroscopy!

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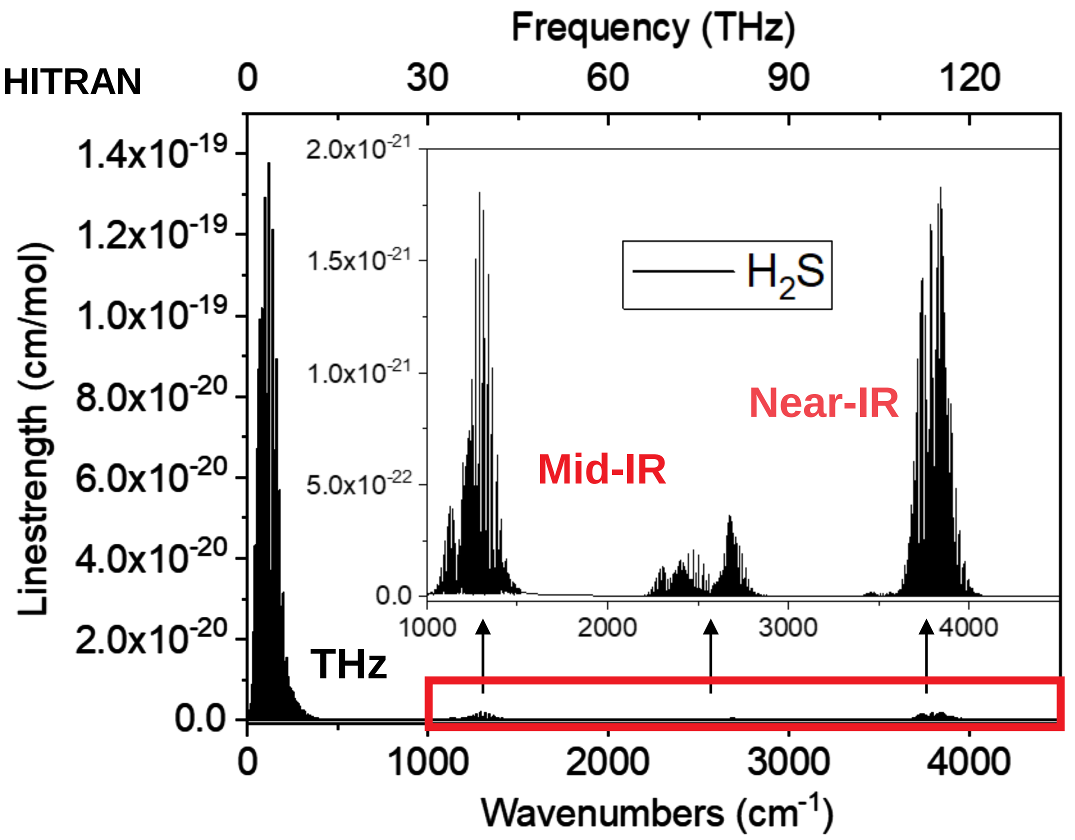
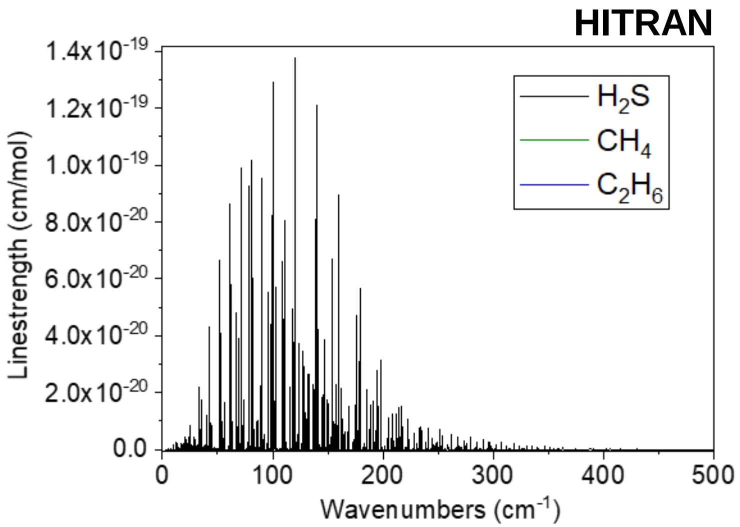
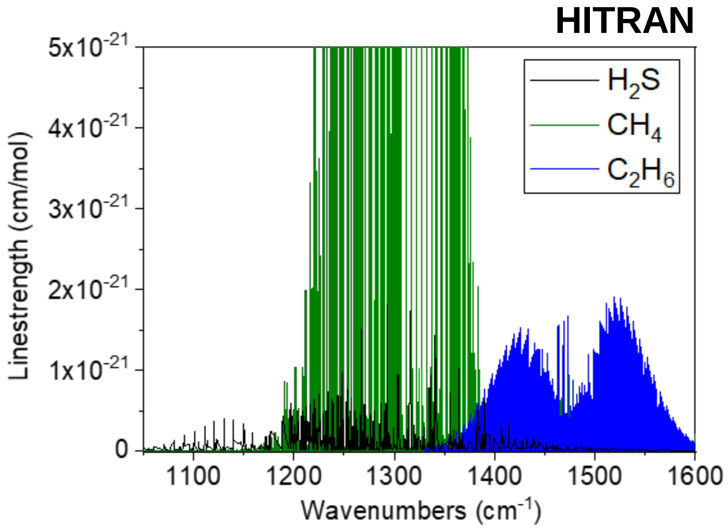
H_2S absorption spectrum

Absorption spectroscopy → Which line to target?







- **Higher linestrengths** compared to IR
- No hydrocarbons interference

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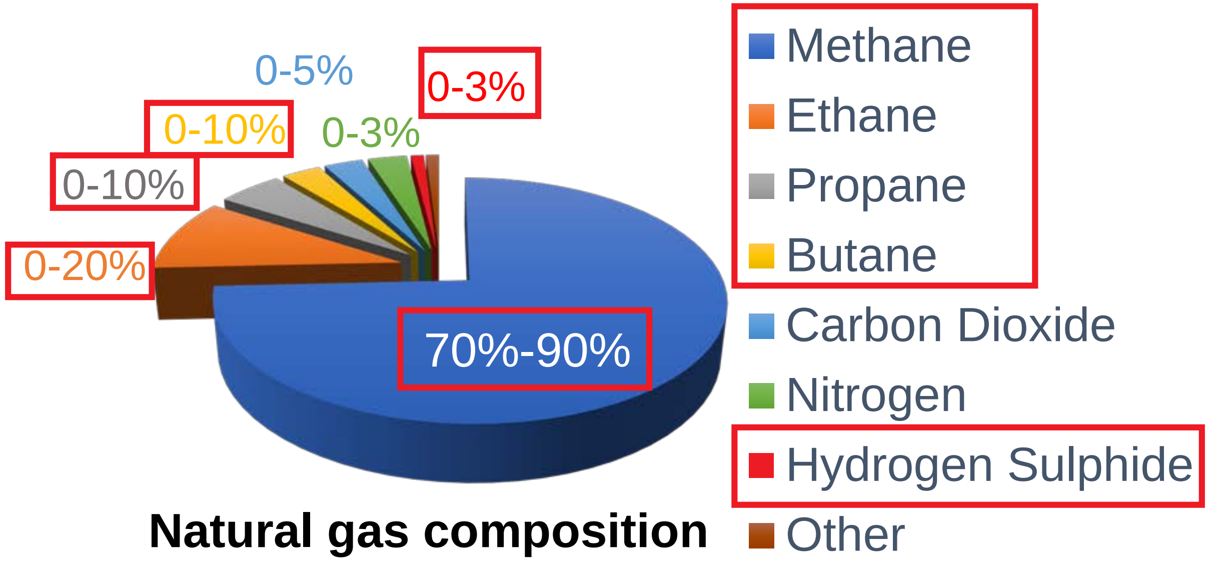
Application: H_2S detection in natural gas

H_2S detection in natural gas deposits needs:

- Real-time monitoring
- In-situ detection

Perfect matching for THz spectroscopy!



Natural gas composition

- **Higher linestrength** compared to IR
- No hydrocarbons interference

Which technique has to be chosen?

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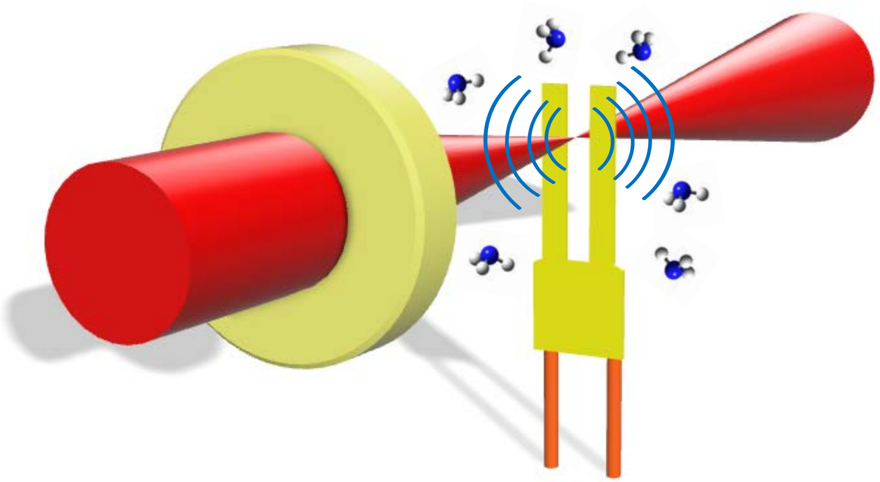
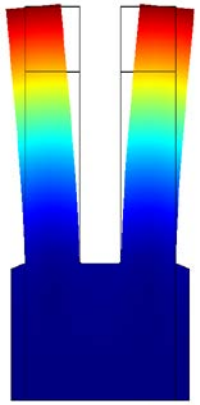
Basics of QEPAS

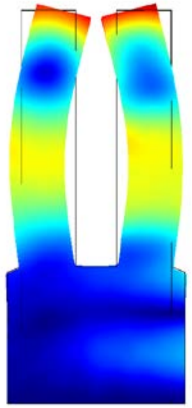


- Laser light **resonant** with **gas target transitions** hits the sample
- **Modulated absorption** induces an **acoustic wave**
- Incident beam is focused between prongs of a quartz tuning fork (**QTF**), used as a **resonant acoustic transducer**
- **Resonant mechanical vibration** is excited by the pressure waves and converted in an electrical signal, via **piezoelectric effect**
- **Resonator tubes** used to enhance the pressure waves amplitude

Fundamental resonance mode



First overtone resonance mode



Laser power Q-factor

$$\text{QEPAS signal} \propto P \cdot \alpha \cdot Q \cdot \varepsilon$$

Gas absorption Radiation-to-sound ...iency

- **No optical detector required**
- **Wavelength independent**

Patimisco et al., "Recent advances in quartz enhanced photoacoustic sensing", Applied Physics Review, 5(1):011106, **2018**

QEPAS exploiting THz sources

THz QCL sources:

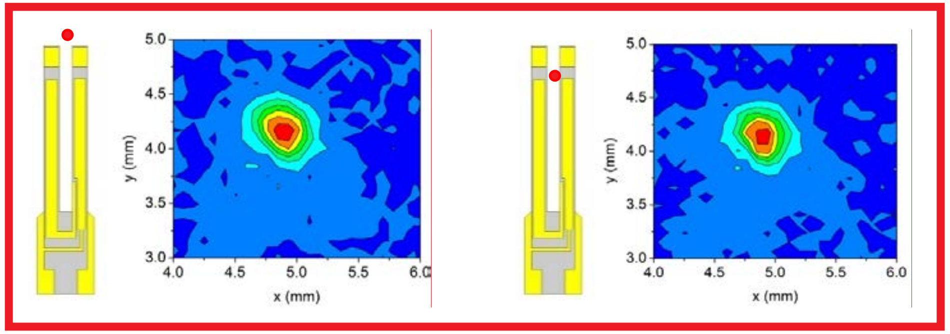
- Low output optical power
- Poor beam spatial quality
- Highly-divergent output angles

Standard QTF

Prong spacing (300 μm) **comparable** to THz source **beam dimensions**

Custom QTF

Larger prong spacing prevent the laser **beam** to **hit the QTF prongs**



Reduced background noise
Improved detection sensitivities

Gas target	Wavenumber (cm^{-1})	Frequency (THz)	Absorption linestrength (cm/mol)	Optical power (μW)	MDL @30 s	NNEA ($cm^{-1}W/\sqrt{Hz}$)	Ref.
CH_3OH	131.054	3.93	4.28×10^{-21}	40	160 ppb	4.3×10^{-11}	[1]
H_2S	97.08	2.91	1.13×10^{-22}	240	13 ppm	4.4×10^{-10}	[2]

[1] Sampaolo et al., “Improved Tuning Fork for Terahertz Quartz-Enhanced Photoacoustic Spectroscopy,” Sensors **16**(4), 439 (2016).
[2] Spagnolo et al., “THz Quartz-enhanced photoacoustic sensor for H_2S trace gas detection,” Opt. Express **23**(6), 7574 (2015).

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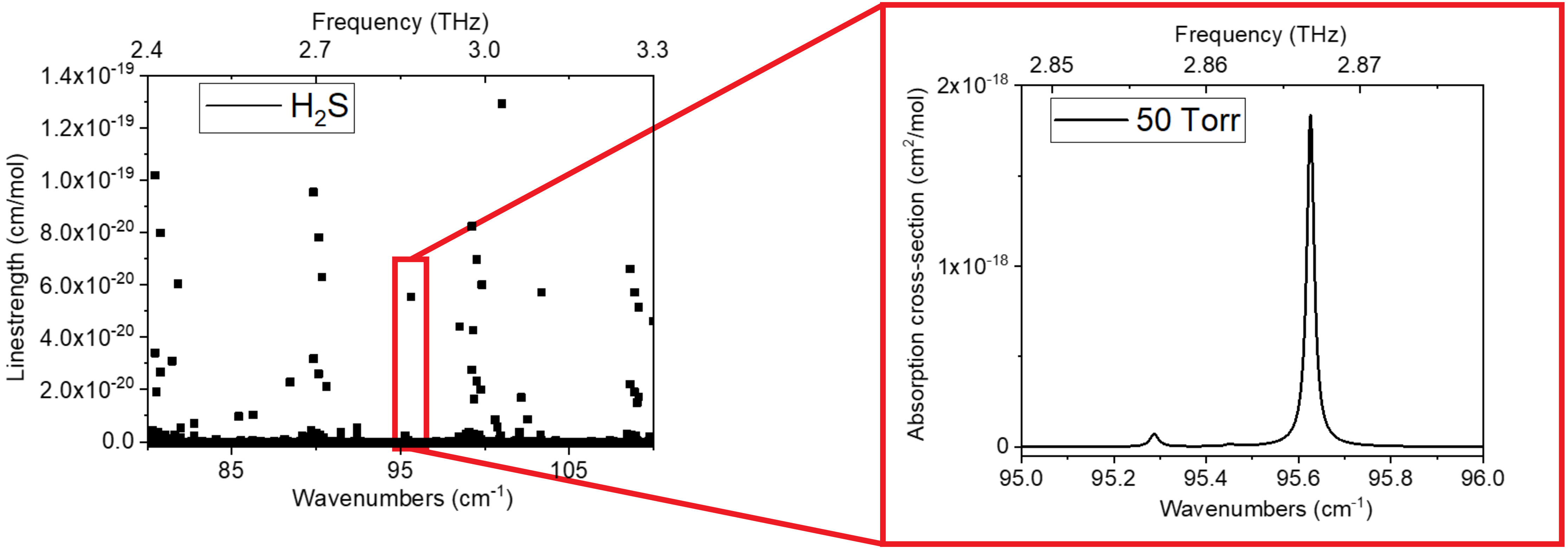
H_2S absorption line selection

Need for a high-intensity, well-isolated absorption line to target



H_2S line @ 95.62 cm^{-1}

S = 5.5×10^{-20} cm/mol

500x higher than previous QEPAS experiment

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N_2-cooled PW QCL source

Continuous Wave

- **Helium cooling**
- Large size
- High cost

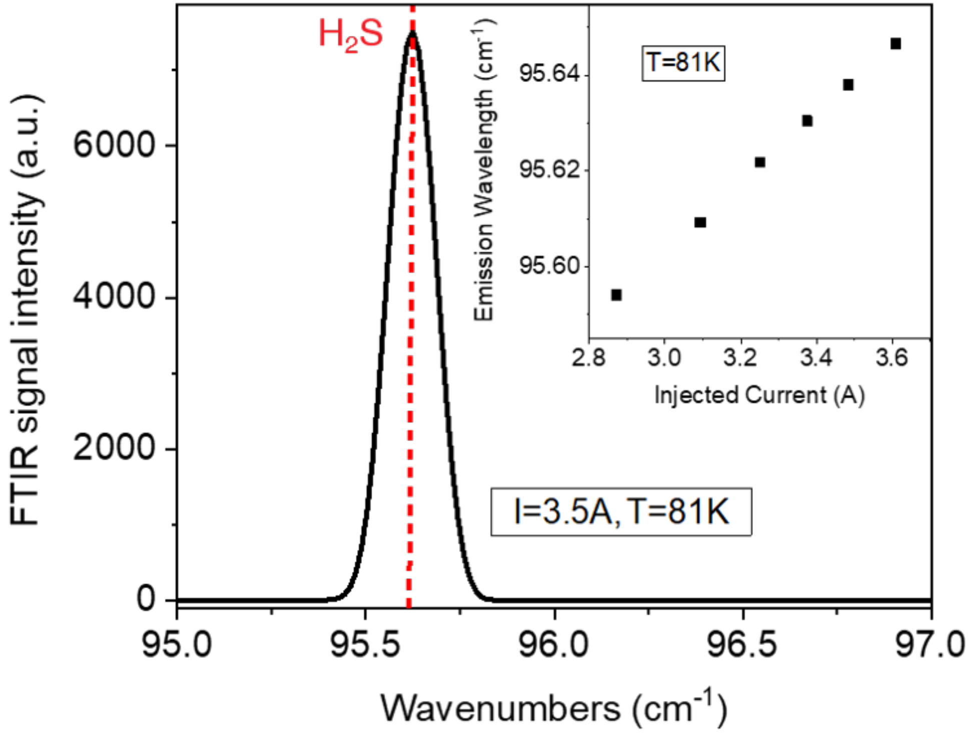
Pulsed Wave

- **Nitrogen cooling**
- Reduced size
- Low cost

SITP

Faby-Perot THz-QCL with graded metal-metal (MM) waveguide

Yu, C. et al., "Highly efficient power extraction in terahertz quantum cascade laser via a grating coupler," Applied Physics Letters 113(12), (2018)



- Repetition rate = 15 kHz
- Pulse width = 1 µs
- **Peak power = 150 mW**

- FTIR resolution = 0.25 cm^{-1}
- Emitted beam with 20°×30° divergence
- **Emission wavelength linearly proportional to injected current**

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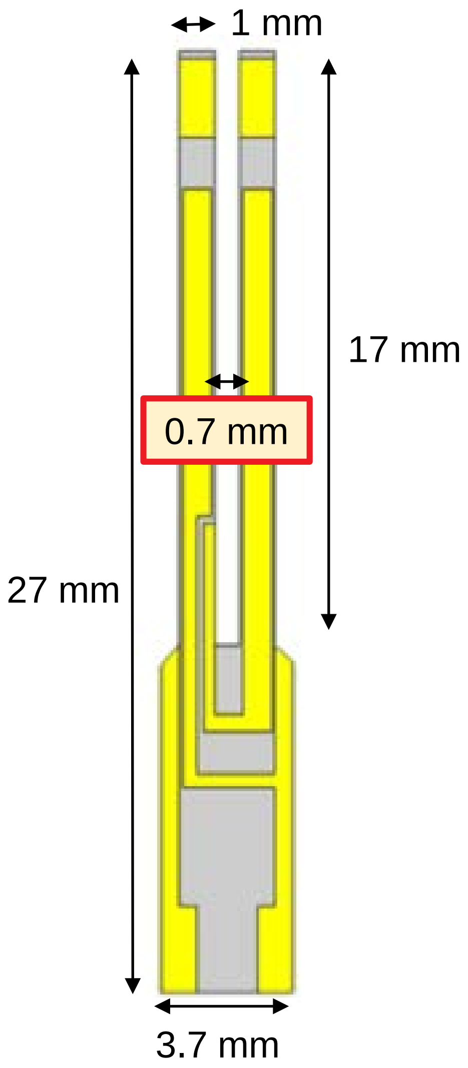
QEPAS spectrophone

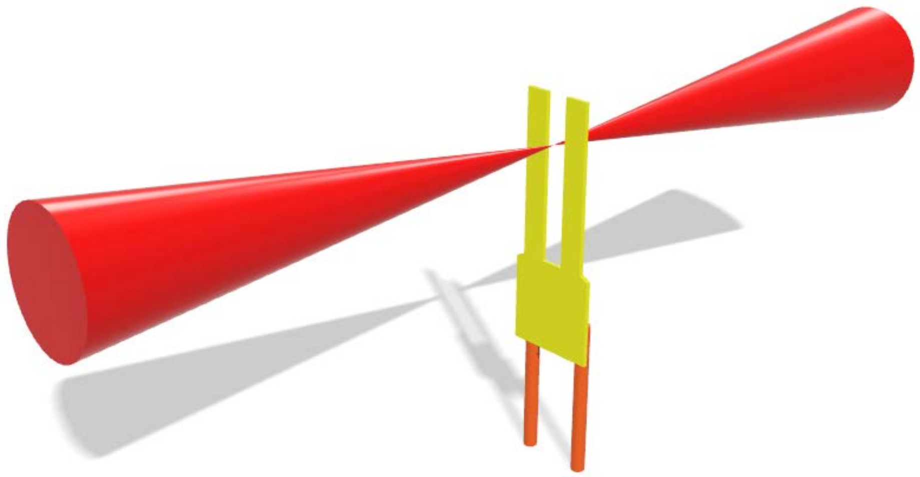
First custom QTF employed for H_2S THz detection (2014)



Performance at atmospheric pressure

- f = 2.8 kHz
- Q-factor = 5650

2x larger prongs spacing compared to standard tuning forks



Bare QTF configuration

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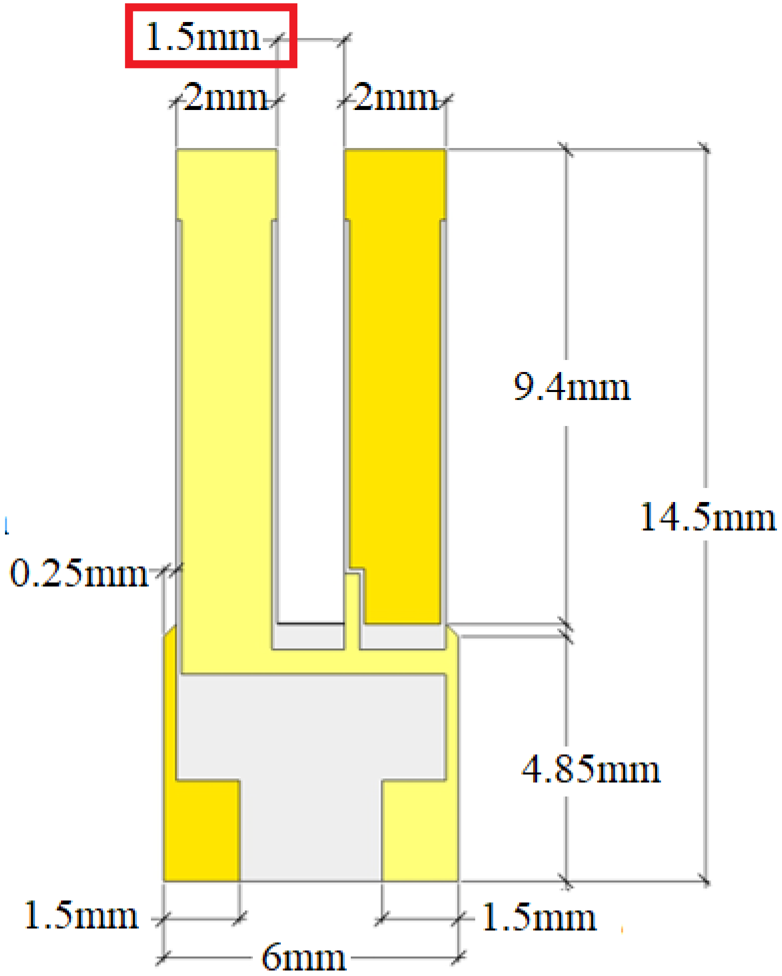
Sampaolo et al., "Improved Tuning Fork for Terahertz Quartz-Enhanced Photoacoustic Spectroscopy," Sensors **16**(4), 439 (2016)

QEPAS spectrophone

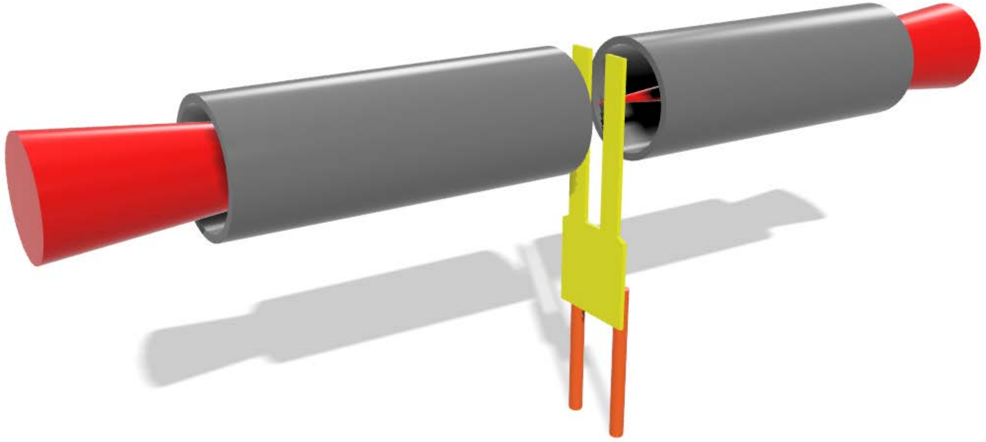
New design of custom QTFs for H_2S THz detection (2019)



Performance at atmospheric pressure

- f = 15.8 kHz
- Q-factor = 15500

5x larger prongs spacing compared to standard tuning forks

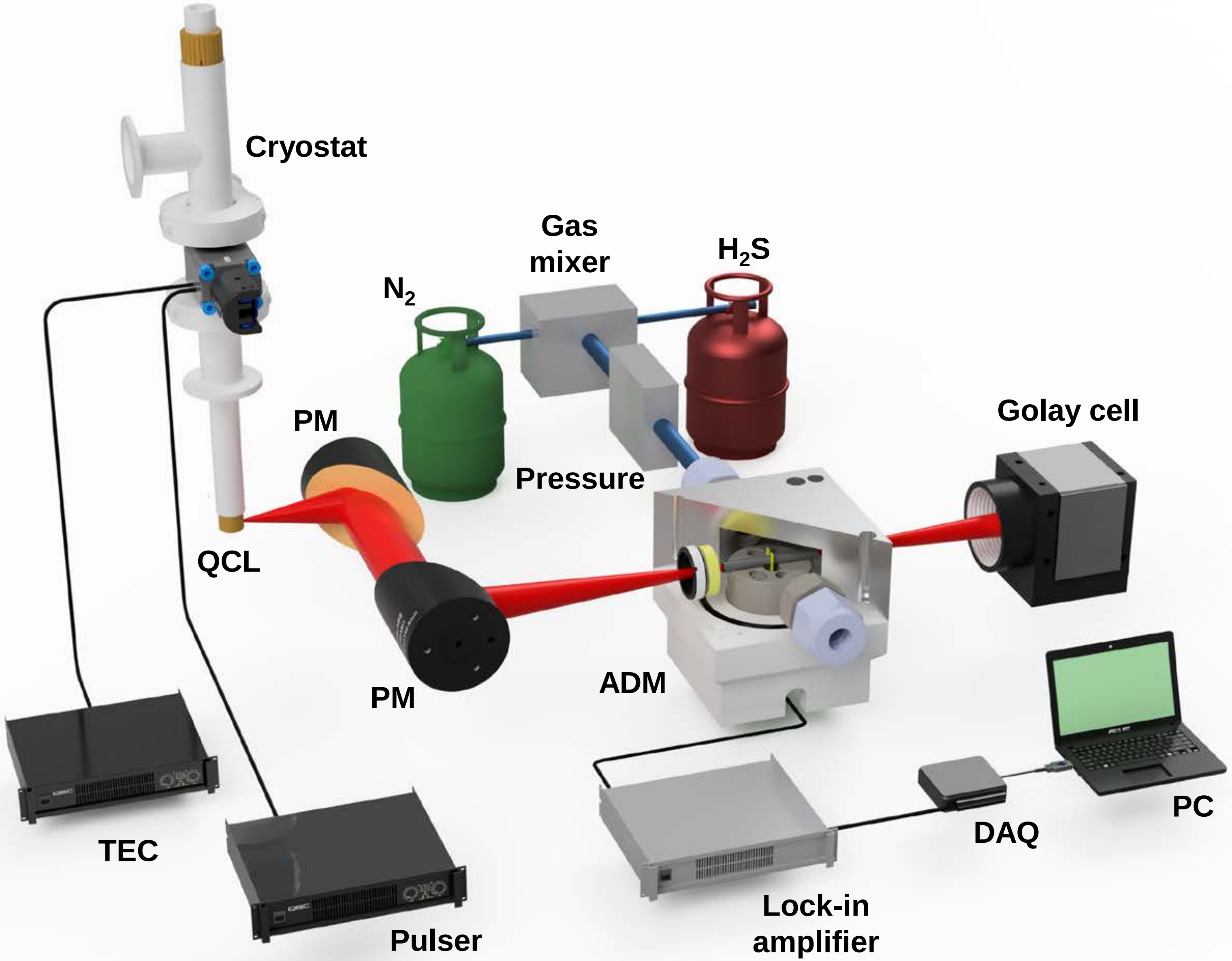


Dual-tube configuration

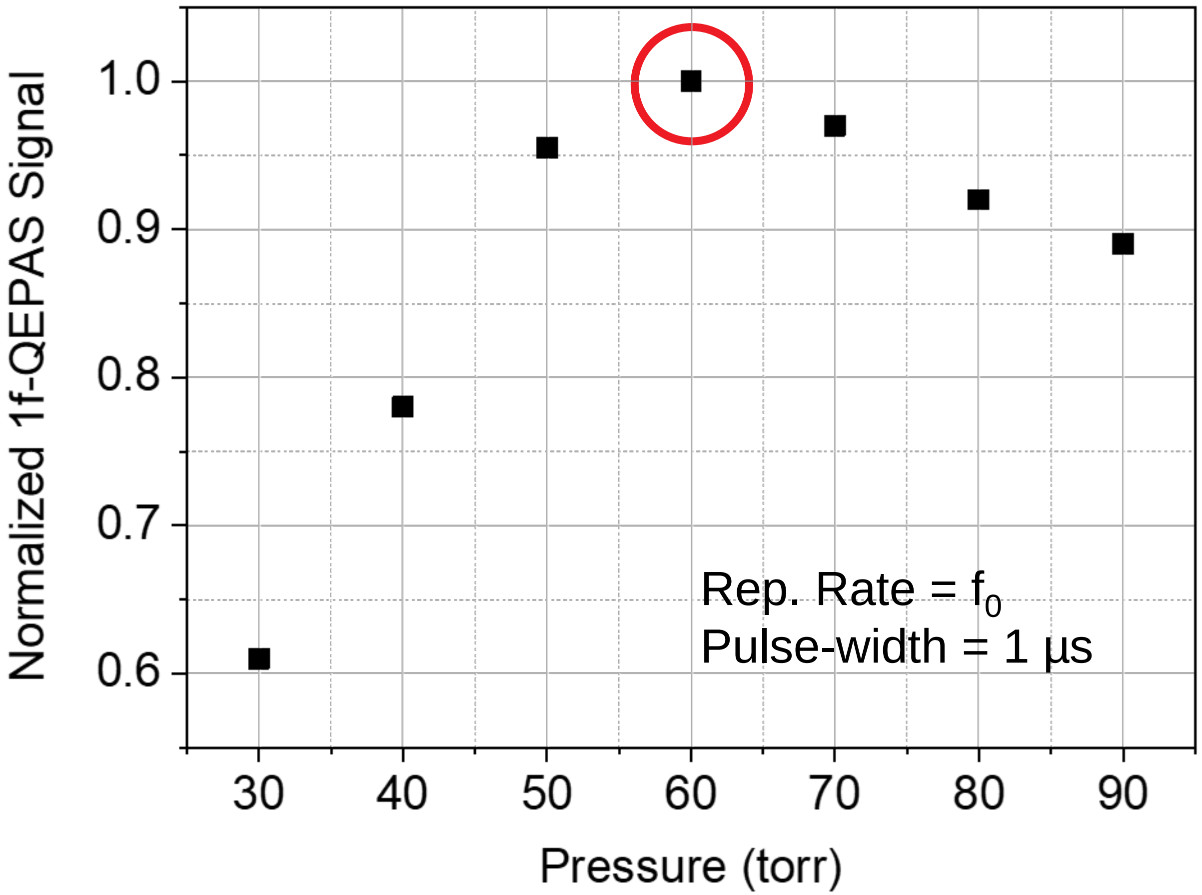
L = 9.5 mm
ID = 2.4 mm

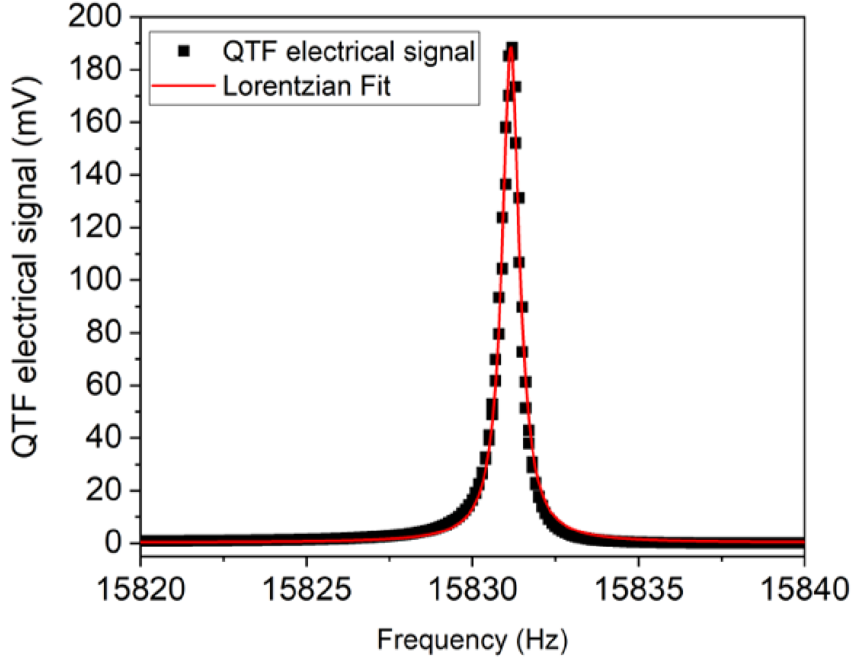
Dello Russo et al., “Acoustic Coupling between Resonator Tubes in Quartz-Enhanced Photoacoustic Spectrophones Employing a Large Prong Spacing Tuning Fork,” Sensors 19 (2019)

Experimental setup



Optimum operating pressure



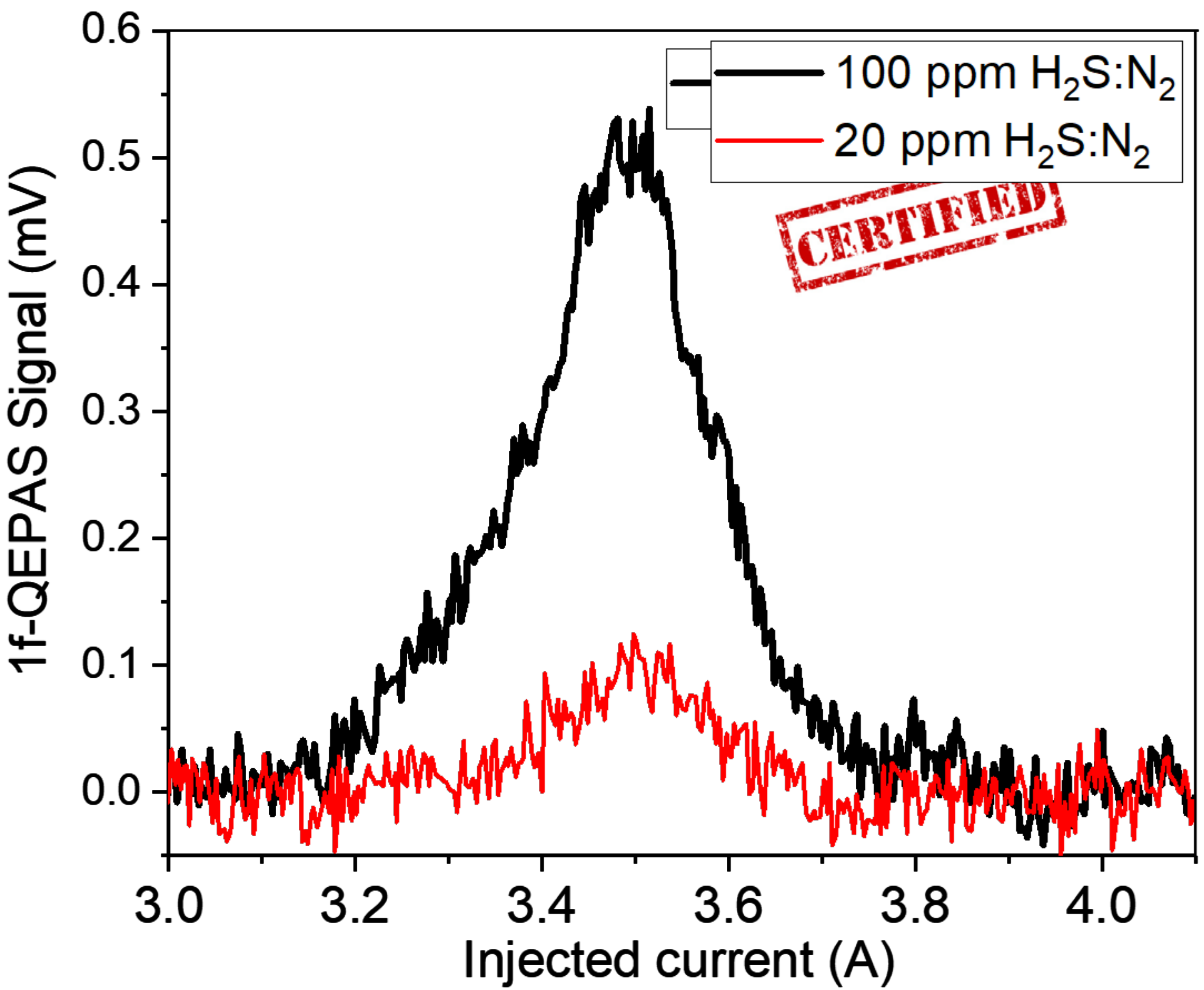


P = 60 Torr:

- f_0 = 15831 Hz
- Q-factor = 25400

QEPAS signal affected by pressure waves generation and QTF performances

QEPAS sensor results



Gas sample parameters

Pressure: 60 Torr

Flow: 30 sccm

Selected absorption line

Wavenumber: 95.62 cm^{-1}

Frequency: 2.866 THz

Linestrength: 5.5×10^{-20} cm/mol

Laser setpoints

Current: 3.5 A

Temperature: 81 K

Modulation parameters

Frequency: 15831 Hz

Pulse width: 1 µs

1-f WM

Integration time: 300 ms

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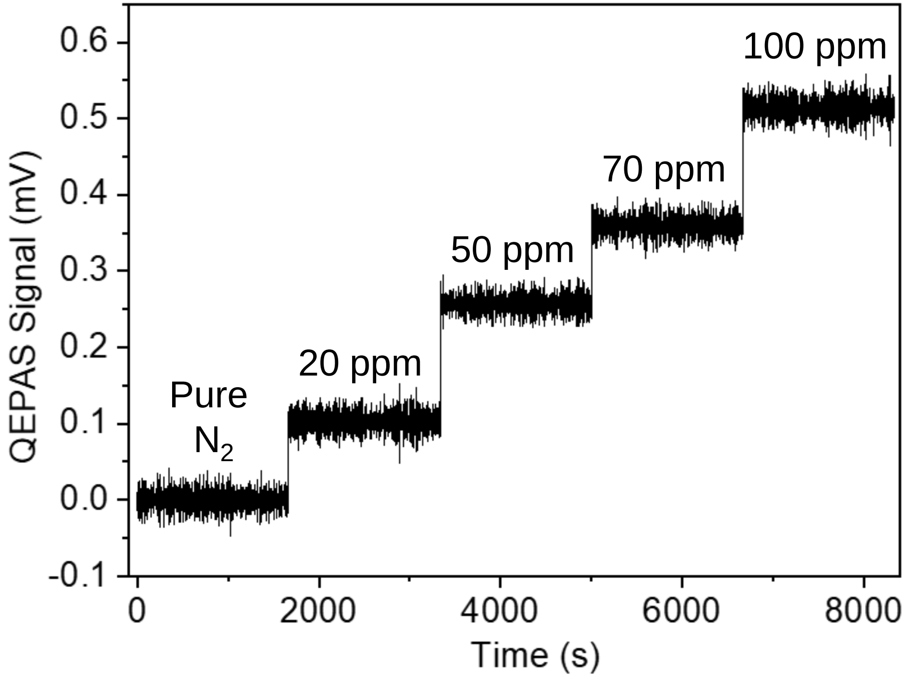
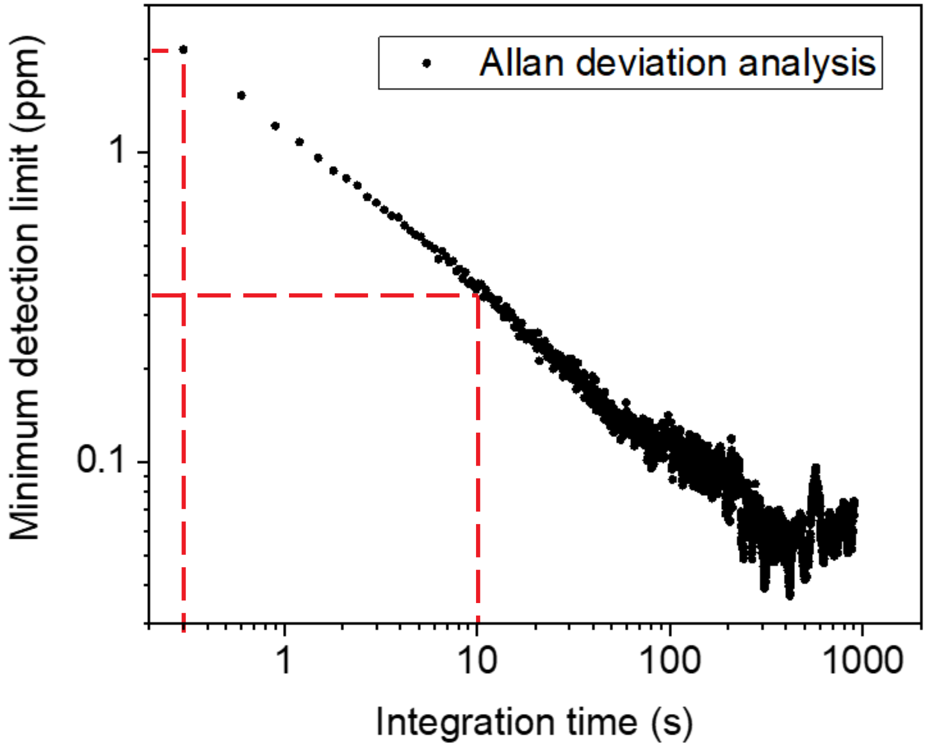
Sensor linearity and detection limits





Stepwise calibration

- 30-minutes-long acquisitions

Sensor linear response

- Slope: 5.14 µV/ppm

Minimum detection limit @ 300 ms: 2.3 ppm

Minimum detection limit @ 10 s: 360 ppb

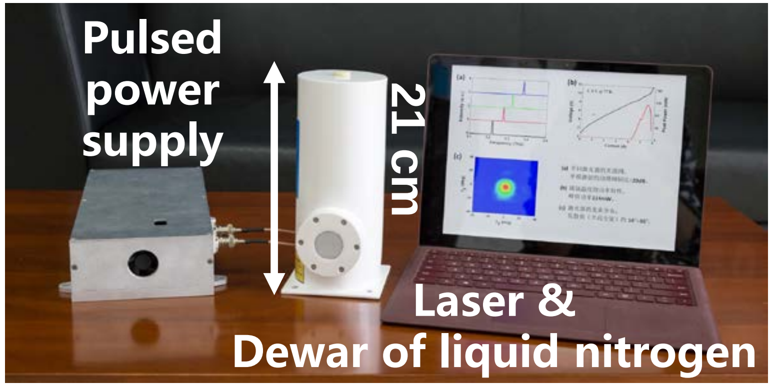
Almost two orders of magnitude lower than previous experiment

Giglio, M. et al., "Allan Deviation Plot as a Tool for Quartz-Enhanced Photoacoustic Sensors Noise Analysis," IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control **63**(4), 555–560 (2016)

Conclusions and future perspectives

- Nitrogen-cooled THz QEPAS sensor for H_2S detection
- Pulsed-wave THz QCL source with peak power of 150 mW
- Custom tuning fork with large prongs spacing coupled with resonator tubes as acoustic transducer
- Minimum detection limit of 2.3 ppm at 0.3 s and 360 ppb at 10 s

- Portable, low power consumption THz-QEPAS sensor for in-situ and real-time detection of H_2S
- Analysis of H_2S photoacoustic behaviour in natural gas matrix



Conclusions and future perspectives

- Nitrogen-cooled THz QEPAS sensor for H_2S detection
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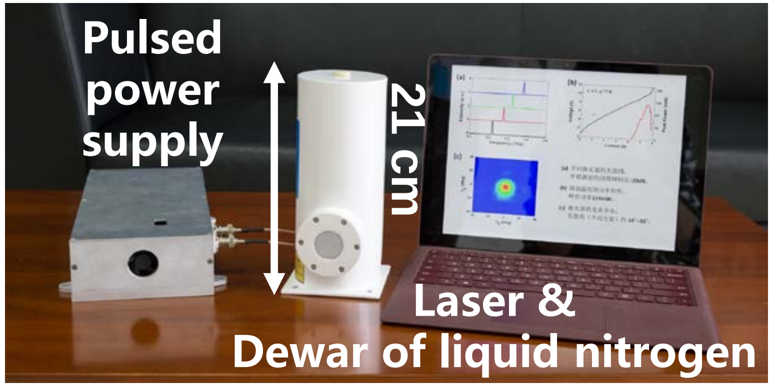
- … QEPAS s… …detection of H_2S
- Ar… …photoacoustic behaviour in nat… …matrix

THANK YOU



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