



H₂S quartz-enhanced photoacoustic spectroscopy sensor employing a liquid-nitrogen-cooled THz quantum cascade laser operating in pulsed mode

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ABSTRACT

In this work, we report on a quartz-enhanced photoacoustic spectroscopy (QEPAS) sensor for hydrogen sulfide (H₂S) detection, exploiting a liquid-nitrogen-cooled THz quantum cascade laser (QCL) operating in pulsed mode. The spectrophone was designed to accommodate a THz QCL beam and consisted of a custom quartz tuning fork with a large prong spacing, coupled with acoustic resonator tubes. The targeted rotational transition falls at 2.87 THz (95.626 cm⁻¹), with a line-strength of $5.53 \cdot 10^{-20}$ cm/mol. A THz QCL peak power of 150 mW was measured at a heat sink temperature of 81 K, pulse width of 1 μs and repetition rate of 15.8 kHz. A QEPAS record sensitivity for H₂S detection in the THz range of 360 part-per-billion in volume was achieved at a gas pressure of 60 Torr and 10 s integration time.

1. Introduction

Many oil fields, especially mature ones, can produce high levels of Hydrogen Sulfide (H₂S), which is deadly at even low concentrations. H₂S is generally present in raw natural gas reserves in concentrations ranging from parts per million (ppm) to percentage levels [1]. The Occupational Safety and Health Administration (U.S. Department of Labor) lists the acceptable concentration limit for exposure to H₂S at 20 ppm for an eight-hour period, with the maximum peak exposure at 50 ppm for 10 min [2]. A short-term exposure to even 500–1000 ppm of H₂S gas can be life threatening and can cause serious harm. Higher concentration levels can cause instant death [3]. Moreover, due to its highly inflammatory property, an explosive atmosphere may occur when H₂S is combined with air. Also, H₂S combined with air humidity or moisture may corrode metals (such as in pipes, tanks, vessels, etc.) through the formation of sulfuric acid [4]. Due to these risks, several processes in gas refining facilities have been implemented to remove

H₂S from gas streams and it is always crucial to identify a leak when occurs, even in the most challenging conditions [5,6]. Beyond the safety of downstream operation and natural gas handling, the studies on the genesis of hydrogen sulfide are also useful to understand the formation process and the pattern of natural gas reservoir accumulation, which would be helpful to discover more gas reservoirs. The geological genesis of hydrogen sulfide in natural gas includes cracking of sulfur bearing organic matter and its thermal evolution, bacterial sulfate reduction and thermochemical sulfate reduction [1,7]. In this context, isotopic ratio represents a valuable fingerprint and an indicator for many processes involving isotopic fractionations. Therefore, instruments devoted to hydrogen sulfide detection at the well site should be: i) set to measure H₂S and its isotopes in a gas matrix composed of multiple gases, ii) rugged to properly work in harsh environments, iii) fast and responsive to warn people of high concentrations [8,9], but also capable of detection sensitivities of few ppm or less.

Among the typical sensors used so far for H₂S detection in natural gas

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leaks, electrochemical sensors lack resilience in high and low temperatures, are affected by evaporation of electrolytes in dry hot conditions and by reduced response speed in cold conditions, and suffer from the effect of humidity on their performance [10,11]. Such serious limitations make their use in desert and arctic regions not the ideal solution. Metal oxide semiconductor (MOS) and even more nanotube enhanced MOS detectors have a long life compared to electrochemical sensors and continue to operate over a wide-temperature range, particularly high temperatures, as well as in extremely dry conditions. However, similarly to electrochemical detectors, MOS detectors are not fail-safe and a change in oxygen levels may affect their output. Moreover, MOS sensors experience slow H₂S response times (up to 120 s) [12,13].

Optical detectors are a field-proven detection solution in many industrial applications because of the high selectivity provided by the use of lasers as gas target excitation source, and high sensitivity achieved through the implementation of several diverse spectroscopic approaches [14]. TDLAS sensors based on multi-pass cells have been successfully employed in petrochemical applications and environmental monitoring for hydrocarbon and H₂S detection [15–17]. In quartz-enhanced photoacoustic spectroscopy (QEPAS) sensors, quartz tuning forks (QTFs) detect weak sound waves produced by gas molecules excited by modulated light. The laser wavelength is resonant with vibrational or rotational transitions of the target molecule and the QTF can be designed on purpose in terms of size and resonance frequency to match the laser beam dimension and gas target relaxation rate, respectively [18,19]. The quartz tuning fork can properly work over a wide range of pressure and temperatures and can replace piezoelectric and photovoltaic/photoelectric sensors, that are mandatory for multipass cell or cavity enhanced-based techniques [15,20,21].

Standard photoacoustic and QEPAS sensors for in situ and real-time detection of multiple hydrocarbons in near- and mid-IR were already demonstrated, as well as H₂S sensors employing diode lasers in the near-IR [26] and quantum cascade lasers (QCLs) in the mid-IR [23,24]. Helman et al. were able to detect H₂S with a sensitivity of 492 ppb at 1 s of integration time in off-beam configuration [25].

Hydrocarbon QEPAS sensors are undergoing a rapid development phase to transform prototypes into reliable sensors ready for deployment and their operation in mid-IR guarantees excellent levels of sensitivity. The best approach to reveal real-time traces of H₂S in natural gas is to exploit its intense absorption bands in the THz range instead, where hydrocarbons absorption cross-sections are several orders of magnitude smaller. In the THz region, the absorption lines of H₂S are the strongest of the whole infrared spectrum. These optical transitions are divided into three groups, corresponding to energy levels related to the molecule rotation around the three axes and are perfectly spaced of 0.62 THz, 0.54 THz, and 0.28 THz, respectively [26]. This situation avoids interference effects from hydrocarbons, enables a fast and easy H₂S detection scheme and creates an ideal spectral environment, where H₂S isotopes can be discriminated and high precision measurements on isotopic ratios can be performed. Conversely, the most convenient spectral windows in the mid-IR, where in principle the H₂S isotopes could be easily separated and discriminated with fairly high cross-sections, are characterized by strong and broad bands of methane [27].

The technological limits that have so far slowed down the implementation of optical sensors operating with THz QCLs are mainly due to i) the purely prototypal nature of QCL sources emitting in the THz range, ii) the need of continuous wave emission with the consequent use of helium cooling systems, which entails a high cost and size, iii) the low optical powers available and the poor quality of the THz beams [28,29].

In 2015, H₂S detection in the THz range was demonstrated by employing a continuous wave QCL. Due to the relatively weak line-strength ($\sim 10^{-22}$ cm/mol) of the targeted feature and a low QCL optical power (240 μ W), a detection limit of 20 ppm was achieved in 10 s lock-in integration time [30].

In the perspective of developing a new generation of sensors capable of providing a systematic and exhaustive analysis of hydrogen sulfide in

natural gas-like samples, here we demonstrate a nitrogen-cooled THz QEPAS sensor, employing a pulsed QCL to excite a H³²SH rotational transition at 95.626 cm⁻¹ having a line-strength of $5.53 \cdot 10^{-20}$ cm/mol.

2. Experimental apparatus

The custom QTF designed for this sensor is also equipped with resonator tubes. The schematic of the experimental setup is shown in Fig. 1.

The THz QCL was provided by the Shanghai Institute of Technical Physics (SITP). The laser chip was mounted on a cold finger accommodated in a liquid-N₂ cryostat. A TPX cylindrical enclosure was tightly sealed to the cryostat to maximize the collection of the THz beam radiating from the grating coupler and facilitate the setup configuration. The employed laser source is a THz QCL with a grating coupler to efficiently extract the THz radiation and an active distributed Bragg reflector for single-mode operation. The QCL GaAs/Al_{0.15}Ga_{0.85}As active region is based on a bound-to-continuum design, with a thickness of ~ 12 μ m and a metal-metal waveguide [31]. The pulses were generated by means of pulse generator (AVTECH AVR-3HF-B), controlled via a custom LabVIEW software.

Pulse frequency and width were set on an external waveform generator driving the pulser (not shown in figure). Both the polarization current and voltage of the laser were measured by means of a probe directly connected to the device and read on the oscilloscope, while the operating temperature was controlled using a Lakeshore Model 335. A Microtech Golay Cell was used to measure the optical power for alignment purpose. QCL emission spectra were recorded using a Fourier-transform interferometer (Bruker 80 V) with a resolution of 0.1 cm⁻¹. According to the acquired spectra, at 81 K and injected current of 3.25 A, the THz QCL emission wavelength peaks at 95.626 cm⁻¹, resonant with a H₂S rotational transition having a line-strength of $5.53 \cdot 10^{-20}$ cm/mol [27] (see Fig. 2). By varying the injected current in the 3 A – 3.9 A range, a linear tuning of the emission wavenumber was observed, with a tuning coefficient of 0.07 cm⁻¹/A, as shown in the inset of Fig. 2.

The divergent light beam with a full width half maximum $\sim 7^\circ \times 33^\circ$ was first collected and collimated using a 2-inch diameter, gold-coated 90° off-axis parabolic mirror with focal length $f_1 = 50$ mm and then focused between the QTF prongs by a 2-inch 90° off-axis parabolic mirror with focal length $f_2 = 150$ mm. The QEPAS Acoustic Detection Module (ADM) implements a custom QTF with a resonance frequency is 15.8 kHz, properly designed to operate with THz QCL sources. Indeed, the prongs spacing is 1.5 mm, more than doubled with respect to the custom QTF employed in ref [30] and allowing the implementation of large size resonator tubes (length of 9.5 mm and internal diameter of 2.4 mm) to enhance the sound wave amplification [32]. These represent the largest values of prongs spacing and resonator tube sizes implemented so far for QEPAS sensing and permit to operate with laser beams of large waist and poor spatial characteristics, typical of THz QCL sources. In this experiment, the ADM was equipped with TPX windows with a power transmittivity of the incident light $> 90\%$. Before entering the ADM, the beam was spatially filtered using a pinhole (not shown in Fig. 1). The piezo-current generated by the QTF was converted into a voltage signal by means of a transimpedance amplifier ($R_{fb} = 10$ M Ω) and then fed to a Stanford Research SR830 lock-in amplifier to be demodulated. The lock-in time constant was set to 300 ms for all measurements reported in this work. The collected signal was recorded by a LabVIEW-based acquisition program and visualized on a personal computer.

A certified 100 ppm H₂S:N₂ mixture and a cylinder of pure N₂ were used to obtain different concentrations of H₂S by means of an MCQ Instruments gas blender, model GB100. The pressure inside the gas delivery line was controlled by the combined action of an MKS pressure controller and a pump.

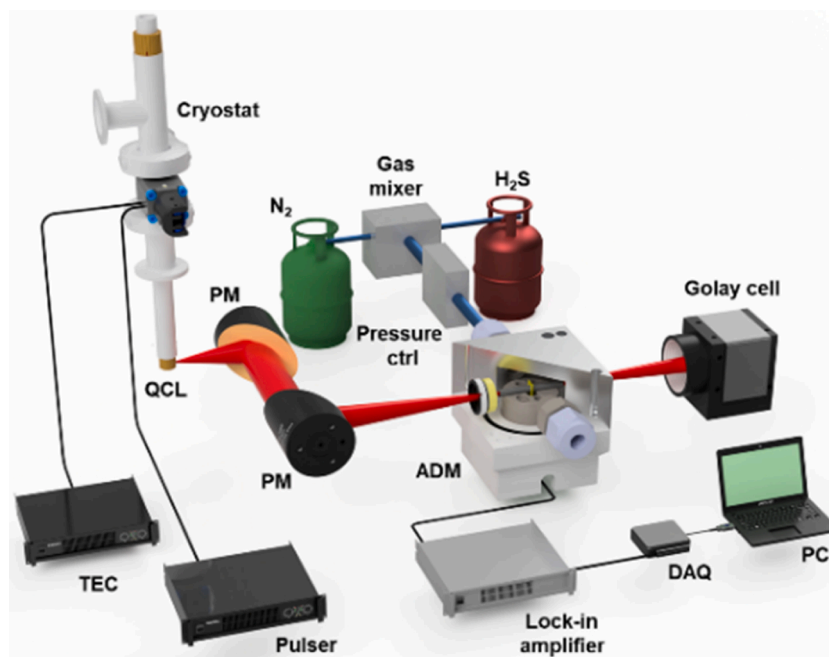


Fig. 1. Schematic of the QEPAS sensor. QCL, quantum cascade laser; TEC, thermo-electric cooler; Pressure ctrl, pressure controller; PM, parabolic mirror; ADM, acoustic detection module; DAQ, data acquisition board; PC, personal computer.

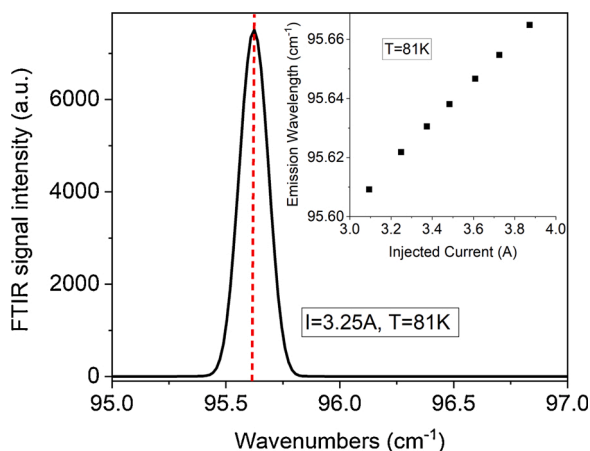


Fig. 2. Emission of the THz QCL at $I = 3.25$ A and $T = 81$ K, resonant with the H_2S line falling at 95.626 cm^{-1} (red dashed line). The repetition rate of the pulses was set to 15 kHz while the pulse width was 1 μs . In the inset the wavelength tuning over the QCL dynamic range at $T = 81$ K is shown.

3. Results

At 60 Torr, a QTF resonance frequency f_0 of 15831.1 Hz with a quality factor $Q = 25400$ was measured. Thus, the repetition rate of current pulses was set as the resonance frequency of the QTF. When the QCL operates in pulsed mode with repetition rate equal to the QTF resonance frequency, the photoacoustic signal is generated by the intensity modulation. Consequently, the $1f$ -QEPAS spectra signal show the line-shape typical of a direct absorption signal [33]. The peak signal was obtained at a laser current of 3.5 A, different from what expected (3.25 A), however the difference in wavelength estimated by the FTIR is ~ 0.01 cm^{-1} , well below its resolution.

The influence of pressure on the photoacoustic signal represents a crucial point, especially in the THz spectral region, since the typically involved absorption features are related to rotational transitions, characterized by very fast energy relaxation rates [18]. This leads to a higher

radiation-to-sound conversion efficiency that usually requires working pressures in the order of few tens of Torr to maximize the photoacoustic response. This is also beneficial for the quality factor of the resonator and in turn on the generated piezo-current. In order to identify the optimum working pressure, a first set of measurements was performed by operating the QCL at 81 K in pulsed mode with an injected current fixed at 3.5 A, ranging the gas pressure from 30 to 90 Torr. The highest $1f$ -QEPAS signal was recorded at 60 Torr, for a pulse duration of 1 μs . The QCL peak power measured outside the cryostat is 150 mW.

Once determined the optimal operating conditions, the linear response and the detection stability of the sensor were investigated. By spanning the laser current from 3 to 4.1 A, corresponding to an overall wavelength tuning of ~ 0.07 cm^{-1} , a full scan of the $1f$ -QEPAS signal across the H_2S absorption line was acquired. Five different concentrations of H_2S in N_2 were analyzed, including the certified concentration of

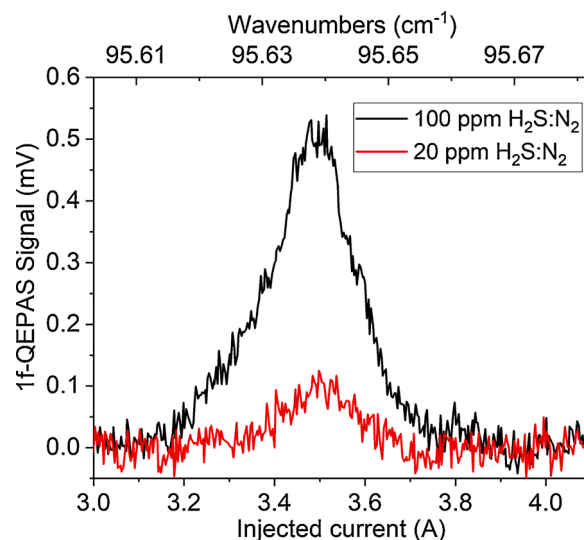


Fig. 3. $1f$ -QEPAS Signals for a mixture of 100 ppm and 20 ppm of H_2S in pure N_2 .

100 ppm and a gas sample of pure N_2 , with a constant flow of 30 standard cm^3 per minute (sccm) for the whole set of measurements. Fig. 3 shows the signal obtained for 20 ppm and 100 ppm $H_2S:N_2$.

Stepwise concentration acquisitions were performed to evaluate the stability in time of the 1-f-QEPAS signal. The injected current was fixed at 3.5 A and the signal related to each analyzed mixture was acquired for about 30 min, as shown in Fig. 4.

By extracting the mean value of the 1-f-QEPAS signal for each H_2S concentration, a linear response of the sensor was obtained with a negligible intercept and a slope of $5.14 \mu V/ppm$. For the 20 ppm $H_2S:N_2$ mixture, the mean value of the signal was calculated to be $\sim 103 \mu V$ while the $1-\sigma$ standard deviation was $\sim 13 \mu V$, corresponding to a signal to noise ratio of ~ 8 . This results in a minimum detection limit of ~ 2.5 ppm at 300 ms lock-in integration time. To determine how the sensitivity of the QEPAS sensor improves as the integration time increases, an Allan-Werle deviation analysis was performed, as reported in Fig. 5 [34].

The laser current was firstly locked to 3.5 A, which corresponds to a laser emission resonant with the H_2S absorption line. The QEPAS signal was then acquired as a function of the time, while a mixture of 100 ppm of $H_2S:N_2$ was flowing through the cell at a constant rate of 30 sccm.

The plot closely follows a $1/\sqrt{t}$ dependence over the entire duration of the measurement series without a base line or a sensitivity drift up to ~ 300 s, indicating that QTF thermal noise is the dominant noise source. At 10 s integration time, a detection limit of ~ 360 ppb was achieved. The normalized noise equivalent absorption (NNEA) can be calculated considering the actual optical peak power available between the prongs of the QTF, i.e. a peak power of ~ 100 mW, averaged over a duty cycle of $\sim 1.6\%$. Thus, the NNEA results $\sim 3 \cdot 10^{-8} cm^{-1}W/Hz^{1/2}$.

4. Comparison with previous H_2S QEPAS sensors and perspectives

In Table 1 the main characteristics, the minimum detection limit and the NNEA of the most performing H_2S QEPAS sensors operating in the near-IR, mid-IR and THz spectral range are summarized. In the last two columns, the comparison between the first THz sensor operating in continuous wave (CW) [30] and the sensor presented in this work is highlighted.

It is worth noting that the best minimum detection limit (MDL), i.e. 40 ppb at 10 s of integration time, was achieved with the mid-IR QEPAS sensor in off-beam configuration demonstrated by Helman et al. [25]. The near-IR sensor also reached sub-ppm detection limit, exploiting the very high power provided by the erbium doped fiber connected to the

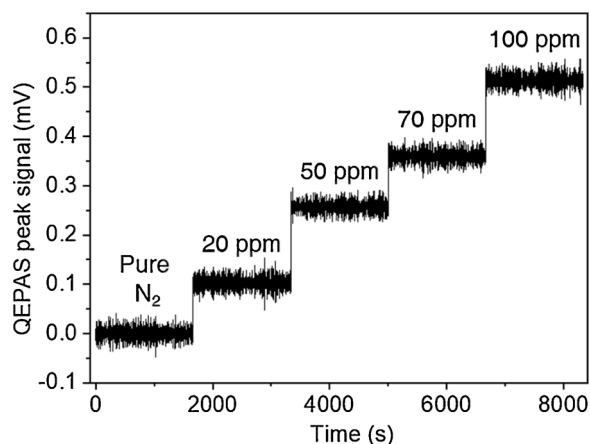


Fig. 4. Stepwise concentration measurements for gas mixtures with increasing concentration of H_2S from zero (pure N_2) up to a certified concentration of 100 ppm in N_2 . The peak signal related to each mixture was acquired for almost 30 min.

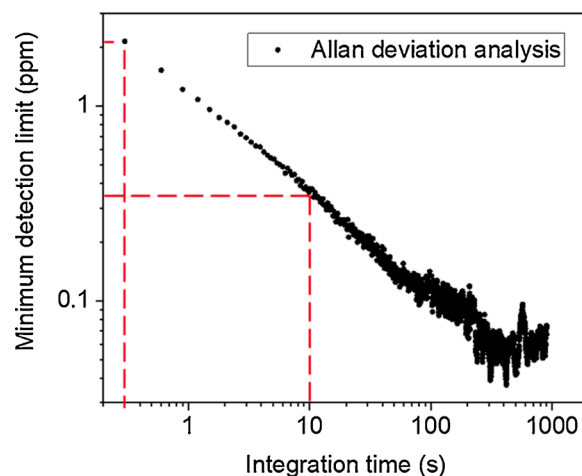


Fig. 5. Allan-Werle deviation analysis. At 10 s of integration time, the calculated detection limit is 360 ppb.

laser diode. Indeed, the 1.5 W of output power helps in balancing the weak line-strength of the absorption feature targeted, which is more than one order of magnitude lower with respect to the mid-IR sensor. However, the photothermal noise induced by the high-power tails of the laser beam mode irradiating the spectrophone, affects the NNEA which results $\sim 10^{-8} cm^{-1} \cdot W/\sqrt{Hz}$. The best NNEA, $4.4 \cdot 10^{-10} cm^{-1} \cdot W/\sqrt{Hz}$, was measured for the THz sensor operated with a CW QCL whose beam was focused between the prongs of a bare custom tuning fork. In this case, the resonator tubes were not implemented to keep the photothermal contribution to the noise negligible [30]. On the other hand, the MDL achieved represents the worst sensitivity value and this is mainly due to the low optical power available in continuous wave. The THz QCL employed in this work is resonant with a $H^{32}SH$ rotational transition having an intense line-strength of $5.53 \cdot 10^{-20} cm/mol$. This, together with the signal-to-noise ratio enhancement provided by the implementation of a dual tube resonator system, contributed to achieve an MDL almost two orders of magnitude better than the one reached in the CW QEPAS THz sensor [30].

In terms of NNEA, the pulsed THz QEPAS sensor is comparable with the near-IR sensor, reflecting one more time the detrimental effect of the poor spatial quality laser beams on the resonator background noise. Moreover, differently from a sinusoidal wavelength modulation, in which the spectrum of the generated acoustic signal consists in the modulation frequency f_{mod} and its weak subharmonics, the acoustic spectrum of a train of pulses with fast rise and decay time is composed of numerous odd harmonics of f_{mod} . These harmonics arise due to the shape and duration of the single pulse and by the cylindrical shape of the laser beam with a finite radius r (~ 0.75 mm in this experiment). If we suppose to divide the cross section of the beam in a series of concentric thin rings, each ring generates an outgoing cylindrical shell of sound and each shell reaches the QTF prongs at different times. Thus, the duration T_S of the resulted primary sound pulse at the QTF prong is $T_S = T_H + r/v_s$, where T_H is the duration of the heat pulse ($> 1 \mu s$ in our experiments) and v_s the sound speed (~ 340 m/s) [35]. The strongest harmonic component f_{max} would be found at $\sim (T_H + r/v_s)^{-1}$. A rough calculation gives $f_{max} \sim 300$ kHz, which does not contribute to the overall QEPAS signal. For laser repetition rates in the order of kHz, only a small part of the total sound pressure contributes to the fundamental component, affecting thus the radiation to sound efficiency.

Similar considerations apply to low SNR enhancement recorded for the resonator tubes that, according to ref [32], were supposed to provide a signal enhancement of ~ 15 when the laser is operated in CW. Still, for a periodic pulse train, each pulse excites plenty of resonances in the resonator tube. Some of the decaying signals overlap in-phase, therefore these components will be amplified, meanwhile other components will

Table 1

Comparison among high-performing H₂S QEPAS sensors, from near-IR to THz. CW – continuous wave, NNEA – normalized noise equivalent absorption, MDL – minimum detection limit.

Spectral Range	Near-IR [22]	Mid-IR [25]	THz [30]	THz [this work]
Laser source & Power	Fiber amplified Laser Diode, 1500 mW, CW	External Cavity QCL, 118 mW, CW	Fabry-Perot QCL, 0.24 mW, CW	Fabry-Perot QCL, 150 mW, pulsed
ADM configuration	7.2 kHz Custom QTF, on-beam	32 kHz Standard QTF, off-beam	2.8 kHz Custom QTF, bare	15.8 kHz Custom QTF, on-beam
Wavelength (μm)	1.5	8.1	103 (2.91 THz)	104.6 (2.87 THz)
Line-strength (cm/mol)	1.15·10 ⁻²³	7.77·10 ⁻²²	1.13·10 ⁻²²	5.53·10 ⁻²⁰
NNEA (cm⁻¹·W/√Hz)	1.3·10 ⁻⁸	3.05·10 ⁻⁹	4.4·10 ⁻¹⁰	3.1·10 ⁻⁸
MDL @ 10 s	150 ppb	40 ppb	20 ppm	360 ppb

be attenuated or even suppressed. This effect mixes up with i) a non-zero background and increased signal fluctuations due to the low intensity tails of the beam hitting the spectrophone structural elements, and ii) a significant electrical noise component introduced into the system by the strong pulses (in the order of 100 V) used to implement the on-off modulation. All these factors determined an overall reduction of the SNR enhancement factor down to ~ 3 .

Nevertheless, the main improvements provided by the present work are: i) sub-ppm detection limit in THz range; ii) power consumptions as low as 0.45 W, thanks to a pulsed operation duty cycle of $\sim 1.6\%$, and almost one order of magnitude lower than THz CW sensor (~ 4 W), iii) possibility to stabilize a working temperature of 81 K by using a liquid nitrogen cooling system, instead of more expensive liquid Helium with its bulky cooling system. These new achievements, after about a decade of spectroscopic research spent in envisioning only potential developments, can finally trace a roadmap of affordable technological targets to be implemented, with the final goal of creating a generation of portable THz QEPAS sensors for in-situ applications.

In Fig. 6 a THz QCL system developed by the Shanghai Institute of Technical Physics, Chinese Academy of Sciences is displayed [31]. The laser is cooled by a liquid nitrogen dewar (210 × 100 × 100 mm) with a working time before refill of ~ 8 h. The power supply (20 × 11 × 9 cm) is custom designed and provides current pulses from 0 to 10 A, with pulse widths from 100 ns to 10 μs and external modulation frequency in the range 1–200 kHz. Low power consumption, small volume and light-weight represent solid starting points for developing THz QEPAS sensors capable of detecting H₂S isotopes in natural gas streams at the well site. In Fig. 7 is shown a Hitran simulation in the THz spectral window 100.5 – 101 cm⁻¹ of the cross-sections related to the isotopes H³²SH, H³³SH and H³⁴SH for a total H₂S concentration of 1000 ppm, simulated in a gas mixture at 10 Torr together with 85 % of methane and 14.9 % of N₂. The 85 % CH₄ concentration is representative of an average methane-based gas matrix for a natural gas sample.

It can be noticed the absence of any interference effect from methane

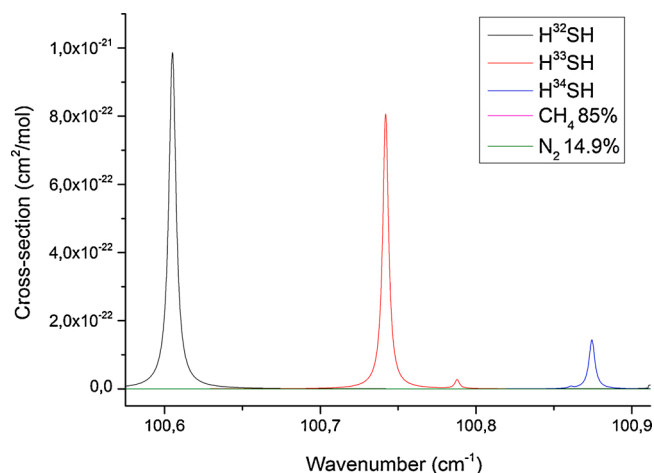


Fig. 7. Cross-sections of a mixture composed of 1000 ppm H₂S, 85% of CH₄ and 14.9% of N₂.

on H₂S isotopes discrimination. This condition cannot be achieved in the mid-IR and near-IR spectral ranges. Thereby, highly selective detection of H₂S in natural gas with sub-ppm precision could allow a smart and effective in-situ evaluation of the sample composition and origin based on the hydrogen sulfide components [36], a killer application for THz sensing.

5. Conclusions

In conclusion, a liquid nitrogen-cooled THz QEPAS sensor operated in pulsed mode for H₂S detection was demonstrated. The possibility to employ a pulsed THz QCL allowed working at 81 K, using a liquid N₂-based cooling system. Moreover, the implementation of a custom tuning

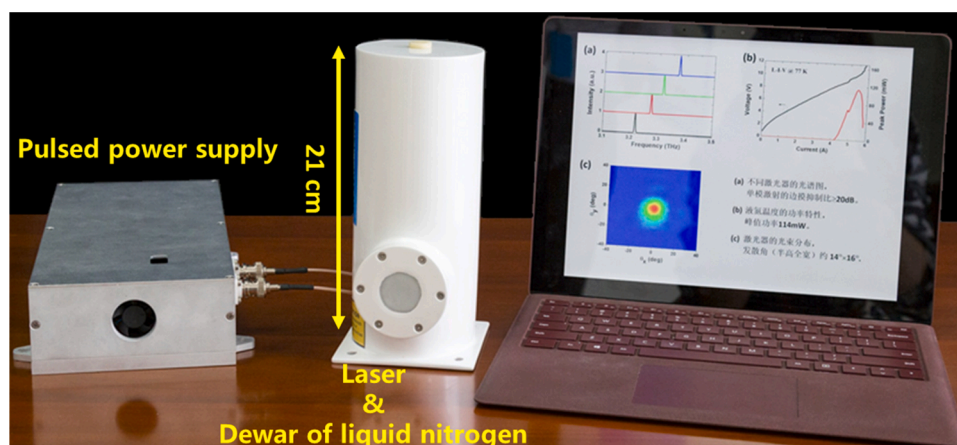


Fig. 6. Portable liquid-N₂ dewars and compact pulsed power supply units.

fork equipped with resonator tubes in a THz QEPAS setup, combined with a line-strength of $5.53 \cdot 10^{-20}$ cm/mol of the targeted absorption feature, provided a minimum detection limit of 360 ppb at 10 s of lock-in integration time. This result is a record value for H₂S QEPAS detection and almost two orders of magnitude better with respect to the previous H₂S THz QEPAS demonstration [30]. The next step will be testing the developed sensor system for the H₂S detection in a natural gas matrix. Finally, the availability of portable liquid-N₂ dewars [37] and compact pulsed power supply units [38] can open the way to design portable, lightweight, low power consumptions THz QEPAS sensors for in-situ and real-time detection of H₂S.

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Declaration of Competing Interest

The authors declare that there are no conflicts of interest.

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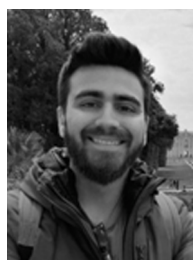
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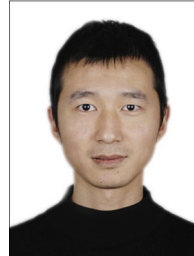
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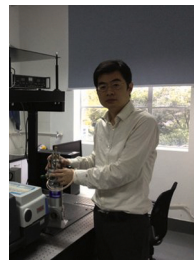
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