THz Quartz-enhanced photoacoustic sensor for H_2S trace gas detection

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Abstract: We report on a quartz-enhanced photoacoustic (QEPAS) gas sensing system for hydrogen sulphide (H_2S) detection. The system architecture is based on a custom quartz tuning fork (QTF) optoacoustic transducer with a novel geometry and a quantum cascade laser (QCL) emitting 1.1 mW at a frequency of 2.913 THz. The QTF operated on the first flexion resonance frequency of 2871 Hz, with a quality factor Q = 17,900 at 20 Torr. The tuning range of the available QCL allowed the excitation of a H_2S rotational absorption line with a line-strength as small as $S = 1.13 \cdot 10^{-22}$ cm/mol. The measured detection sensitivity is 30 ppm in 3 seconds and 13 ppm for a 30 seconds integration time, which corresponds to a minimum detectable absorption coefficient $\alpha_{min} = 2.3 \cdot 10^{-7}$ cm^{-1} and a normalized noise-equivalent absorption $NNEA = 4.4 \cdot 10^{-10}$ $W \cdot cm^{-1} \cdot Hz^{-1/2}$, several times lower than the values previously reported for near-IR and mid-IR H_2S QEPAS sensors.

OCIS codes: (280.3420) Laser sensors; (140.5965) Semiconductor lasers, quantum cascade; (300.6390) Spectroscopy, molecular.

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1. Introduction

Recent breakthroughs in photonics and nanotechnology are now enabling terahertz (THz) frequency research to be applied in a widespread range of sensing applications, such as medical diagnostics, global environmental monitoring, homeland security, petrochemical, chemical, industrial process monitoring, as well as noninvasive industrial and food industry inspection. Explosives, narcotics, toxic gases and biomedical compounds have distinct spectral "fingerprints" and strong absorption bands in the THz spectral range. Optical techniques based on absorption processes, compared to electrochemical and analytical techniques, are considerably faster with response times of <1 s, offer high gas specificity, sensitivity and permit real time *in situ* measurements [1]. A number of THz optical sensing systems based on quantum cascade lasers (QCLs) have been proposed for gas sensing or spectroscopy. Several THz spectrometers for high-resolution gas phase spectroscopy based on distributed feedback [2,3] or comb-assisted [4] QCLs have been demonstrated. Recently, gas sensors based on QCL wavelength modulation absorption spectroscopy [5] or saturable absorption spectroscopy [6] for methanol vapors detection have been realized, providing a minimum detectable absorption coefficient normalized to the detection bandwidth of $5.5 \cdot 10^{-6}$ cm^{-1} $Hz^{-1/2}$ and saturation intensity of 25 $\mu W/mm^2$, respectively. Among trace-gas detection techniques, quartz-enhanced photo-acoustic spectroscopy (QEPAS) is capable of record sensitivities using a compact and relatively low-cost acoustic detection module. The key innovation of this method, with respect to the conventional photoacoustic approach [7], is the enhancement of acoustic energy density by a sharply resonant quartz high quality factor tuning fork (QTF) acting as piezoelectric acoustic transducer [8].

Efficient QEPAS sensors have been demonstrated for trace detection of several chemical species with a detection limit of a few parts per trillion in volume [9]. The performance of different types of QEPAS sensors can be compared in terms of the normalized noise equivalent absorption (NNEA), taking into account the available optical laser power, the selected absorption line strength and the integration time (see Fig. 1) [8]. It should be noted that the smallest *NNEA* value is found in the THz region. In fact, rotational levels are mainly

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involved in THz absorption processes and their relaxation rates are up to three orders of magnitude faster with respect to vibrational levels in the mid-IR spectral range, the THz spectral range is the most suitable for the QEPAS technique [10]. In addition, the fast relaxation times characteristic of THz transitions allow low-pressure operation, thereby providing high QTF Q-factors, and large QEPAS signals. The THz region offers advantages in terms of selectivity, because gas molecules have clear spectral "fingerprints" absorption spectra, arising from rotational quantum transitions. These spectra allow unambiguous, more efficient and accurate detection compared to the characteristic ro-vibrational complex structures in the mid-IR. Moreover, an important advantage of the QEPAS techniques is that no optical detection is required, thereby avoiding the need of low-noise but costly, bulky and cryogenic bolometric THz detectors.

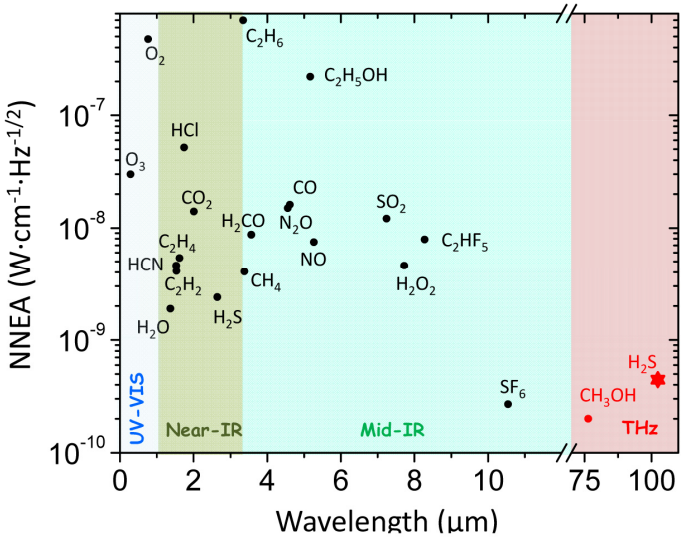

Fig. 1. NNEA results obtained with QEPAS sensor for the gas species reported *versus* employed laser wavelength, in the UV-Vis, near-IR, mid-IR and THz spectral ranges. The red symbol (*) marks the result of present work.

Since the sensitivity of QEPAS technique is ultimately limited by the available optical power, QCLs represent the most promising THz light sources for QEPAS applications. Recently, by exploiting suitably designed custom QTFs and THz QCLs we have reported the first demonstration of QEPAS sensor operating in the THz range [11,12].

In this paper, we report on the design and realization of a THz QEPAS sensor for the detection of hydrogen sulfide (H_2S) traces. H_2S is a toxic gas present in oil, natural gas (up to 90%), volcanoes, hot springs, well water (often because of the action of sulphate-reducing bacteria) and food [13]. H_2S is produced in large quantities from natural gas drilling and refining operations, wastewater treatment, tanneries and landfills [14]. H_2S is also a threat to human health since it is rapidly absorbed by the lungs. Exposure to H_2S at high concentration levels will cause unconsciousness and even death as a result of respiratory paralysis and asphyxiation [15].

H_2S QEPAS near-IR [16] and mid-IR [17] sensors with detection limits of 500 part per billion (ppb) for 1-minute integration and 330 ppb for integration time of 30 seconds, respectively, have been recently demonstrated. The interest for exploring the QEPAS in the THz range is related to the strengths of H_2S absorption lines that can increase by two orders of magnitude with respect to the mid-IR, as shown in Fig. 2. However, in order to fully exploit the increased line strength advantage, THz sources with suitable tuning range must be used.

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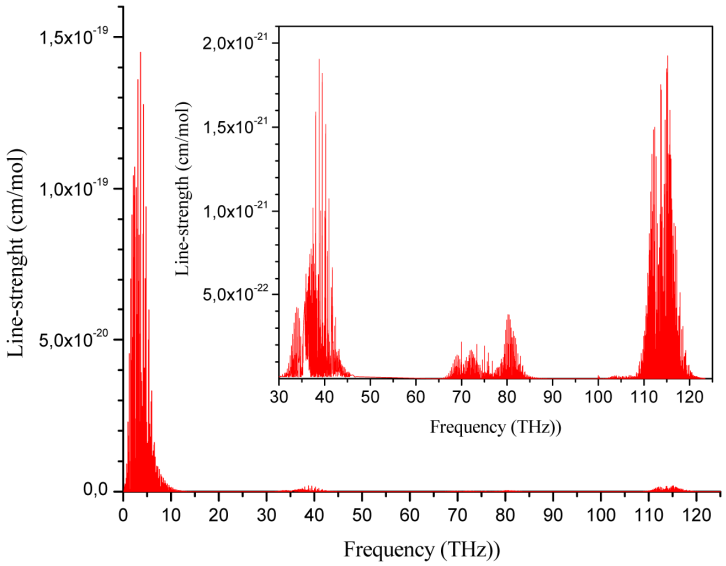

Fig. 2. Stick H_2S spectrum as obtained from the Hitran database [20].

One of the most important potential applications for H_2S sensing is in the petrochemical industry. Natural gas contains H_2S concentration levels. Due to its toxicity, flammability, and corrosivity, H_2S is an extremely important component to control at all stages of natural gas handling, from wellhead to the customer. The destructive effects of H_2S on equipment and pipelines along with the constant threat to personnel safety justify major investment in H_2S sensing technology. Such measurements cannot be performed using near or mid-infrared optical sensors, due to the ambiguity related to the dense absorption spectra of the buffer natural gas mixture (ethane, methane, propane and other hydrocarbons), while the THz range offers a spectral region of simplified absorption features and hence leads to a potential solution for sensitive H_2S detection in natural gas.

2. Experimental setup

The THz laser source employed in this work is a single-mode bound-to-continuum QCL emitting at 2.91 THz (~97.11 cm^{-1}), operated in a continuous wave (CW) mode and mounted on the cold finger of a continuous-flow cryostat equipped with polymethylpentene (TPX) windows. The CW light-current-voltage (L-I-V) characteristics, measured at a heat sink temperature of 15 K are shown in Fig. 3a. The threshold current is I_{th} = 550 mA, with a maximum collected peak optical power P_o ~1.1 mW. We performed a preliminary investigation of the QCL emission frequency under pulsed excitation. Representative spectra measured at 15 K (with 250 ns pulse-width and 20 kHz repetition rate) are shown in Fig. 3b.

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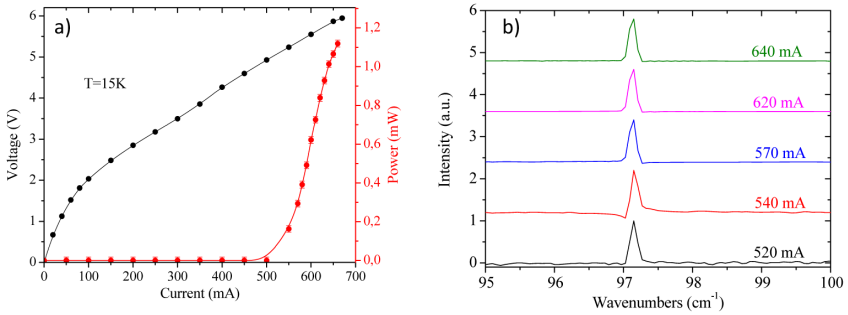

Fig. 3. a) Voltage as a function of current measured at a heat sink temperature of 15 K. The QCL was driven in a CW mode at 15 K. The solid lines are guides for the eye. b) Emission spectra recorded for different values of current at 15K.

These spectra have been recorded using a Fourier-transform interferometer in rapid-scan mode with a resolution of 0.125 cm^{-1} and an f/2 off-axis parabolic mirror coated with gold for light collection. The QCL shows a stable single mode emission in the investigated current range.

A schematic of the gas QEPAS based sensor is shown in Fig. 4.

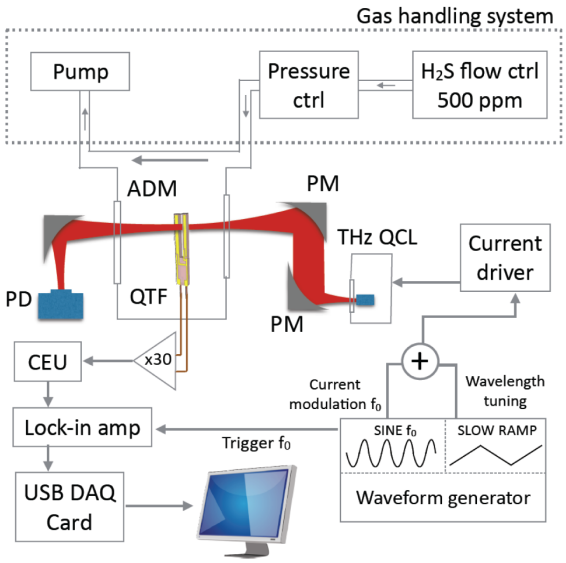

Fig. 4. Schematic of a QEPAS based trace gas sensor using a THz QCL as an excitation source. CEU – Control Electronic Unit; PM – Parabolic mirror; ADM – Acoustic detection module; USB DAQ – Universal serial bus data acquisition system; PD – Pyroelectric detector.

We employed a QTF with a new geometry, having 1.7 cm long prongs and a thickness of 250 µm. The width of the QTF prongs was reduced from 2.5 mm to 1 mm with respect to the QTFs employed in [11,12] in order to make them more flexible. Furthermore, the prongs spacing was reduced from 800 µm to 700 µm in order to increase the acoustic wave deflection effects. We also used a new design for the gold pattern in order to optimize the piezoelectric charge collection. The QTF first flexion resonance is f_0 = 2871 Hz at 20 Torr. The QTF resonant frequency f_0 changes with a slope of $-6 \cdot 10^{-4}$ Hz/Torr in the pressure range 10-760 Torr. At atmospheric pressure, we measured a resonance quality factor Q = 5,900, which increases to a value Q ~30,000 under vacuum conditions.

The THz laser beam was focused between the QTF prongs by using two 2-inches diameter, 90° off-axis parabolic aluminum reflectors. We employed a collecting mirror with

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f/# = 2 and a focusing mirror with f/# = 5. The QTF is housed in an acoustic detection module (ADM) with TPX input and output windows. The THz laser beam exiting the ADM was re-collimated onto a pyroelectric detector (Ophir, 3A-P-THz) by means of an additional aluminum parabolic mirror. The 3D laser beam profile and the corresponding 1D profile measured at the QTF focal plane using a pyroelectric camera (mod. Spiricon Pyrocam III-C) is shown in Fig. 5a and Fig. 5b, respectively. A full-width-half-maximum (FWHM) of 460 μm, ~65% smaller than the QTF gap size of ~700 μm was extracted from a Gaussian fit of the beam profile. This was also confirmed by measuring the power transmitted between the QTF prongs with the pyroelectric detector by a careful alignment of the QTF with respect to the focused beam. The measured beam waist is limited by diffraction and the ratio between the focal lengths of the focusing (f = 12.5 cm) and collecting (f = 5 cm) off-axis parabolic mirrors. This choice for the focal lengths arises from the trade-off between several, optical (e.g efficient light collection from our highly divergent source) and practical geometrical parameters (e.g. cryostat and gas cell sizes). With the best alignment conditions, it is possible to achieve 96.4% transmission of the incident THz laser beam between the QTF prongs. This is a crucial point to minimize the noise related with the direct illumination of QTF prongs by the laser beam [18,19].

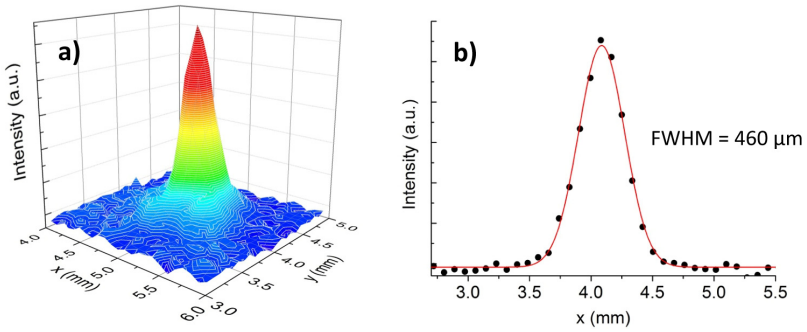

Fig. 5. a) Three-dimensional beam profile of the THz-QCL at the focal point of the QTF, b) the corresponding two-dimensional profile on a log scale (●) and the related Gaussian fit (solid red line).

Data acquisition and real-time analysis were performed using a lock-in amplifier (Stanford Research Model SR830) and a function generator (Tektronix model AFG3102) controlled by a Labview-based software. QEPAS measurements were performed by applying a sinusoidal dither at frequency f_0 to the QCL current, while detecting the QTF response at the same frequency by means of the lock-in amplifier [12]. A slow voltage ramp allows scanning of the THz laser wavelength through one H_2S absorption band for line-shape analysis. The QTF signal is processed by a transimpedance amplifier (30x) and a control electronic unit (CEU) before demodulation by a lock-in amplifier (see Fig. 4). The CEU also provides the QTF electromechanical parameters: its dynamic resistance R, quality factor Q, and resonant frequency f_0.

3. H_2S concentration measurements

The main requirement for QEPAS based field measurements is to avoid interference effects arising from other gas species, typically present at high concentration levels in ambient air, such as H_2O, CO_2, CH_4 which can strongly deteriorate the sensitivity and reproducibility performance of a H_2S sensor. To verify that this condition is fulfilled in the reported experiments, we simulated the absorption spectra for a gas mixture of standard air and 10 part per million (ppm) of H_2S at 20 Torr pressure using the HITRAN database. The absorption profile and the line-strengths of the main H_2S transitions within the spectral tuning range of the THz QCL are shown in Fig. 6.

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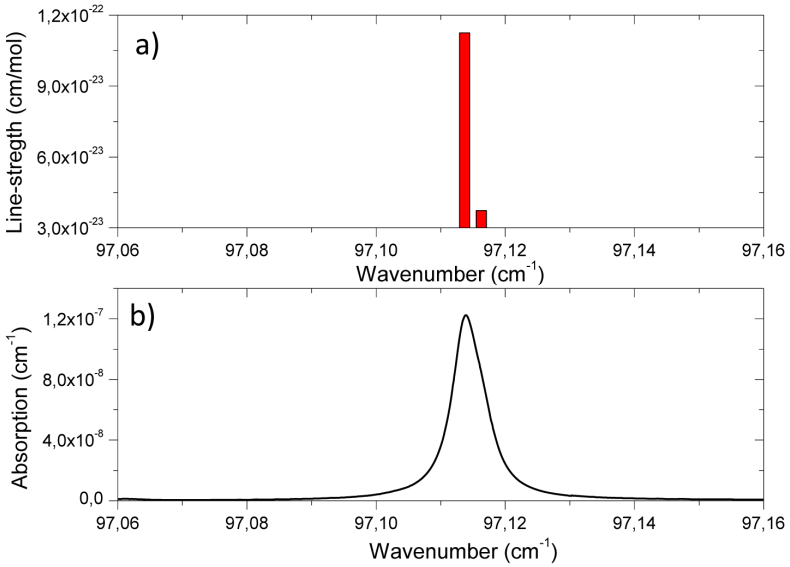

Fig. 6. a) Line-strengths of the main H_2S transitions (vertical bars), as reported in the Hitran database [20]. b) Simulation of direct absorption spectrum of a gas sample composed of 10 ppm H_2S in ambient air, with 2.0% water vapor. The sample pressure was set to 20 Torr, the same as used in our measurements. The absorption path was (arbitrarily) set to 10 cm. At 20 Torr pressure, the nearest water line at 97.27 cm^{-1} does not affect the H_2S peak absorption.

The main H_2S absorption line in the considered spectral range occurs at 97.113 cm^{-1} with a line-strength $S = 1.13 \cdot 10^{-22}$ cm/mol (HITRAN units [20]). The closest water absorption line at ~97.27 cm^{-1} has no interference with the selected H_2S line at the experimental pressure. No other spectral features are present nearby.

To determine the optimal operating condition in terms of the QEPAS signal-to-noise ratio, we investigated the effects of gas pressure and of laser modulation amplitude. The gas pressure influences the QEPAS signal since the *Q*-factor decreases at higher pressures and the rotational-translational relaxation rate is faster at higher pressures, resulting in more efficient sound excitation. The optimal sensor operating conditions were found to occur at a gas pressure of 20 Torr and a modulation voltage of 300 mV peak-to-peak. For sensor validation, we used a trace gas standard generator to produce H_2S concentrations in the range 0-500 ppm, using N_2 as the diluting gas and starting from a certified 500 ppm H_2S in N_2 mixture.

Figure 7 shows a selection of QEPAS scans measured at different H_2S concentrations using a lock-in integration time of 3 s. We employed a sampling time of 9 sec and the total time required to scan the H_2S peak shown in Fig. 7 is ~600 sec. However, for sensing operation, it is not necessary to scan the H_2S absorption line. Typically, measurements are performed with line-locking conditions, i.e., keeping the THz laser frequency fixed and resonant with the selected H_2S absorption line. The QEPAS peak signals corresponded to a THz laser power of 0.24 mW focused between the two QTF prongs located in the ADM. A fringe-like interference pattern is barely visible; this is due to the small portion (~3%) of THz optical power incident on the QTF. A 1σ detection limit of 30 ppm was extracted from the analysis of the signal-to-noise ratio. A spectral scan obtained for pure N_2 under the same operating conditions is also shown for comparison.

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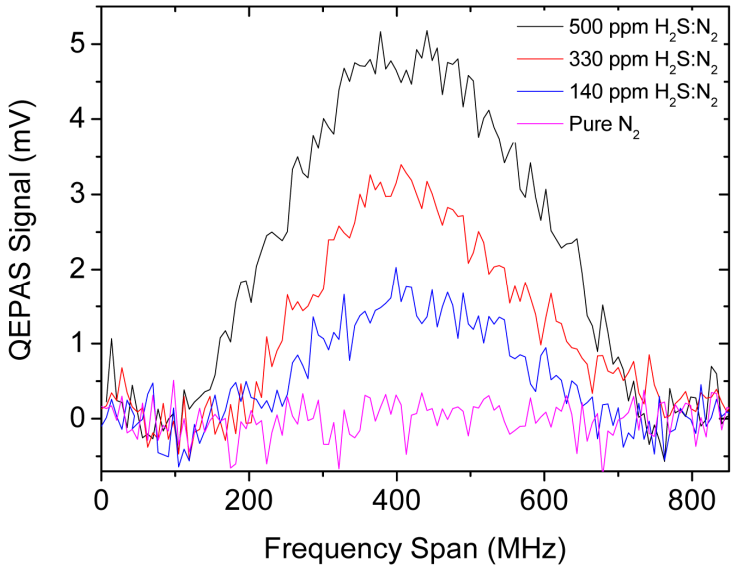

Fig. 7. QEPAS spectral scans of gas mixtures containing 500 ppm, 330 ppm and 140 ppm of H_2S in N_2 at P = 20 Torr, acquired with 3 second lock-in integration time. The spectral scan obtained for pure N_2 under the same operating conditions is also reported (purple curve).

Finally, we performed an Allan-Werle variance analysis (see Fig. 8), measuring and averaging the QEPAS signal for pure N_2 at 20 Torr pressure, in order to determine the QEPAS sensor best achievable detection sensitivity. For this analysis, the laser frequency was set to the H_2S absorption line at 97.113 cm^{-1} and pure carrier gas N_2 was introduced into the ADM. For a 30 seconds lock-in integration time (and a bandwidth of 0.00556 Hz) we extracted a minimum detection sensitivity of 13 ppm, corresponding to a minimum detectable absorption coefficient $\alpha_{min} = 2.3 \cdot 10^{-7}$ cm^{-1} and a NNEA = $4.4 \cdot 10^{-10}$ $cm^{-1}W/Hz^{½}$.

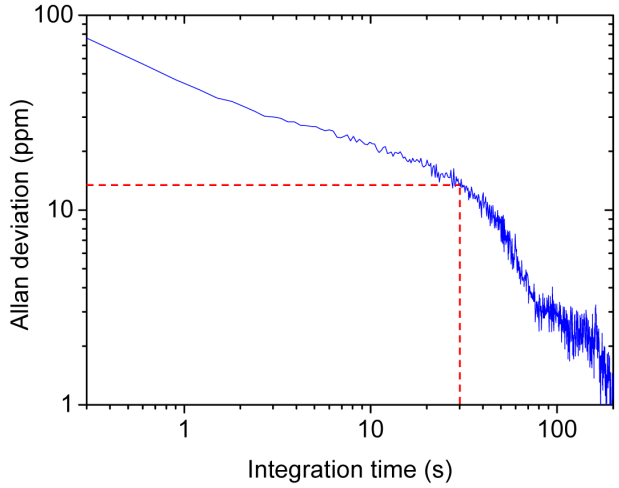

Fig. 8. Allan-Werle deviation in ppm of the QEPAS signal as a function of the lock-in integration time. The curve was calculated by analyzing 120 minute-long acquisition period of the signal with the lock-in set to a 100 ms integration time, measured for pure N_2 at 20 Torr.

A comparison with QEPAS results in the near-IR and in the mid-IR [16,17] is reported in Table 1.

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Table 1. Comparison of three QEPAS based sensors for H_2S detection operating in the near-IR, mid-IR and THz spectral ranges

	Near-IR [16]	Mid-IR [17]	THz [this work]
Frequency (cm^{-1})	3788.56	1266.93	97.113
Laser power (mW)	3	45	0.24
Line strength (cm/mol)	$1.67 \cdot 10^{-21}$	$1.51 \cdot 10^{-21}$	$1.13 \cdot 10^{-22}$
NNEA ($cm^{-1} \cdot W/\sqrt{Hz}$)	$2.4 \cdot 10^{-9}$	$7.3 \cdot 10^{-9}$	$4.4 \cdot 10^{-10}$
Detection sensitivity @ 30s lock-in integration time	750 ppb	330 ppb	13 ppm

The NNEA value measured in the THz is several times lower than those observed in the near-IR and mid-IR ranges. A significant enhancement of the signal-to-noise ratio by more than two orders-of-magnitude and a detection limit of < 100 ppb is expected in the case of stronger absorbing H_2S lines (e.g. the line at 95.626 cm^{-1} with a line-strength of $5.83 \cdot 10^{-20}$ cm/mol). However, due to the inherently small tuning range of THz QCLs (~0.03 cm^{-1}), it was not possible to excite this line with the available THz laser source. This is an important issue for the development of THz spectroscopic techniques based on QCL sources.

4. Conclusions

In this work, we reported the realization of a THz QEPAS sensor for H_2S trace gas detection. The measured value of the normalized noise equivalent absorption coefficient is several times lower than the best result obtained for H_2S in the mid and near-IR. Operating in the THz range has a distinct advantage in terms of sensor selectivity, due to the simpler spectral features of the targeted gas species. The measured detection sensitivity is 30 ppm in 3 seconds and 13 ppm for a 30 seconds integration time. The THz-QEPAS minimum detection limit can be further improved by employing QCLs with higher emission power and with emission frequencies in resonance with stronger H_2S absorption lines potentially achieving a QEPAS H_2S detectivity of a few tens of ppb.

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