H_2S detection in complex gas matrices

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In this work we report on two quartz-enhanced photoacoustic sensors for H_2S trace detection in natural gas leaks dispersed in air. The challenge for these two spectroscopic approaches consists in avoiding methane interference and detect hydrogen sulfide at the sub-ppm level.

Background – Hydrogen sulfide is a toxic gas and is a threat to human health, since it is rapidly absorbed by the lungs. Exposure to H_2S at high concentration levels will cause unconsciou

sness and death, because of respiratory paralysis and asphyxiation. Thus, due to its toxicity, flammability, and corrosivity, it is extremely important to detect and monitor its presence in situ and real time [1].

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 [2].

Standard photoacoustic and QEPAS sensors for in situ and real-time detection of multiple hydrocarbons in near- and mid-IR were already demonstrated [3], as well as H_2S sensors employing diode lasers in the near- IR [4] and quantum cascade lasers (QCLs) in the mid-IR [5].

The main issue related with H_2S detection consists in the fact that most of the hydrogen sulfide leaks in atmosphere are associated with natural gas leaks. This means that H_2S needs to be detected over a strong background of methane absorption, whose bands are partially or totally overlapping with H_2S bands all over the infrared region.

Methods – The first QEPAS configuration we implemented for H_2S detection within a methane-based gas matrix consists in on-beam sensor employing a custom 12 kHz quartz tuning fork, equipped with resonator tubes. The laser employed is an interband cascade laser emitting at 2636 nm. The main criteria adopted for identifying the optimum spectral conditions in this wavelength range were i) selecting a H_2S absorption line well separated from the surrounding features related to atmospheric absorbers, such water vapor, and from methane, which is the main component in a natural gas leak dispersed in air: the most suitable H_2S feature was found at 3793 cm^{-1}; ii) investigating the trade-off working pressure minimizing the spectral overlap between H_2S absorption line and the absorption background without losing too much in the photoacoustic signal: this value was found at 100 torr.

The sensing system was tested for different gas mixtures containing traces of H_2S in a matrix of i) N_2, ii) N_2 with methane up to percent scale, iii) standard air with methane up to percent scale.

As an alternative to the near-IR QEPAS sensor, we designed and developed a THz sensor based on a pulsed laser emitting at 2.87 THz and exciting a H_2S absorption line falling at 95.63 cm^{-1} [6].

In fact, the smartest approach to detect real-time traces of H_2S in natural gas is to exploit its intense absorption bands in the THz range, where hydrocarbons absorption cross-sections are several orders of magnitude smaller. In the THz region, the absorption lines of H_2S 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. This situation avoids interference effects from hydrocarbons, enables a fast and easy H_2S detection scheme and creates an ideal spectral environment, where H_2S isotopes can be also discriminated and high precision measurements on isotopic ratios can be performed.

The two sensor architectures are shown in Fig. 1.

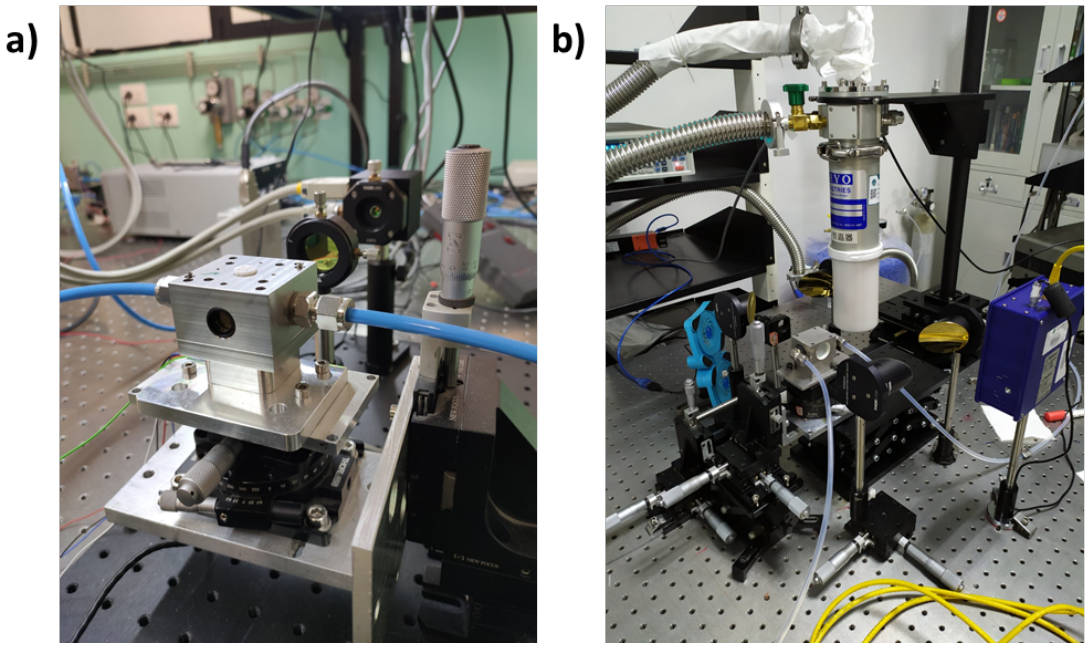

Fig. 1. Picture of the near-IR H_2S QEPAS sensor (a) and of the THz H_2S QEPAS sensor (b).

Results – The near-IR sensor proved to detect hydrogen sulfide at sub ppm level, in mixtures of standard air and methane at the percent concentration, at a working pressure of 100 Torr and an integration time of 10 s. The THz sensor has also demonstrated a sub-ppm sensitivity level in detection of H_2S at an integration time of 10 s and a working pressure of 60 Torr.

Conclusions – In this work we demonstrated two approaches for pursuing hydrogen sulfide detection in a natural gas leak dispersed in air. The sensor implementing the laser diode is a ready-to-use solution for discriminating H_2S presence in a matrix where CH_4 concentration does not exceed the 10%. This is due to a minimal CH_4 absorption background affecting the H_2S detection sensitivity. In the case of H_2S THz detection, there are no restrictions for CH_4 concentration in the matrix, since its absorption cross-sections are ~7 orders of magnitude lower with respect to H_2S. The drawback is that THz sources are still far for commercialization and thus the related gas sensing technology.

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