Optical Engineering

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Michal Nikodem, Karol Krzempek, Dorota Stachowiak, Gerard Wysocki, “Quantum cascade laser-based analyzer for hydrogen sulfide detection at sub-parts-per-million levels,” *Opt. Eng.* **57**(1), 011019 (2017), doi: 10.1117/1.OE.57.1.011019.

Optical Engineering 57(1), 011019 (January 2018)

Quantum cascade laser-based analyzer for hydrogen sulfide detection at sub-parts-per-million levels

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Abstract. Due to its high toxicity, monitoring of hydrogen sulfide (H_2S) concentration is essential in many industrial sites (such as natural gas extraction sites, petroleum refineries, geothermal power plants, or waste water treatment facilities), which require sub-parts-per-million sensitivities. We report on a quantum cascade laser-based spectroscopic system for detection of H_2S in the midinfrared at ~7.2 μm. We present a sensor design utilizing Herriott multipass cell and a wavelength modulation spectroscopy to achieve a detection limit of 140 parts per billion for 1-s integration time. [DOI: 10.1117/1.OE.57.1.011019]

Keywords: molecular spectroscopy; laser spectroscopy; wavelength modulation spectroscopy; quantum cascade laser; hydrogen sulfide.

Paper 170917SS received Jun. 14, 2017; accepted for publication Sep. 21, 2017; published online Oct. 11, 2017.

1 Introduction

Hydrogen sulfide (H_2S) is frequently found in the vicinity of industrial sites such as petroleum refineries, natural gas plants, or waste water treatment facilities. Due to its high toxicity, recommended exposure limits are typically between 10 and 20 ppmv (parts per million by volume). In this respect, its detection with sensitivities at or below ppmv levels is critical for safety reasons. Optical spectroscopy enables fast and highly selective detection and quantification of H_2S. So far, laser-based H_2S sensors typically relied on near-infrared wavelengths and could achieve adequate sensitivities only with appropriate signal enhancement methods. A photoacoustic spectroscopy-based system operating at 1.57 μm was used to achieve minimum detectable concentration of 2 ppmv (1σ) (for integration time of 10 s).[1] A quartz-enhanced photoacoustic spectroscopy (QEPAS) operating roughly at the same wavelength (1580 nm) was implemented with a powerful laser source (1250-mW excitation power) to further improve the detection limit down to ~1.5 ppmv with a 1-s averaging time.[2] Minimum detectable concentration of ~220 ppbv (1σ) for a 2-s averaging time was obtained through the application of an off-axis integrated cavity output spectroscopy (OA-ICOS) at 1571.6 nm.[3] Several groups also performed studies of stand-off detection of H_2S in this spectral region by implementing wavelength modulation spectroscopy (WMS) at 1.59 μm (Ref. 4) with a detection limit at 50 ppmv × m level at 1-s integration time, or chirped laser dispersion spectroscopy (CLaDS) at 1574.5 nm with a detection limit at ~225 ppmv × m (tested with an open-path multipass cell).[5] By moving to longer wavelengths, stronger H_2S transitions can be targeted[6–8] and the target sensitivity could be achieved with less complex and more robust spectroscopic systems. Viciani et al.[9] explored the H_2S absorption band around 2.6 μm, and a QEPAS arrangement achieved sensitivity of 4 ppmv in 1 s with only 3 mW of optical power. As with the most molecules, optical spectroscopy in the midinfrared spectral region is a powerful tool to further increase the detection limits by targeting even stronger fundamental molecular vibration bands. In the case of H_2S detection, the most interesting wavelength range spans between 7 and 8.2 μm and provides from 5 to 10 times stronger absorption lines comparing to the near-infrared wavelengths while still offering relatively low interference from other species (mainly water vapor and methane) absorbing in this region. This wavelength region can be conveniently accessed with quantum cascade lasers (QCLs). With currently available thermoelectrically cooled, continues wave QCLs and thermoelectrically cooled photodetectors, high-sensitivity absorption spectrometers can be achieved in robust and compact instrumental form factors. Some early studies in the ~8.1-μm region were performed using ring-cavity surface-emitting QCL in Ref. 10, which enabled H_2S sensing with a detection limit of 500 ppbv (1σ) using a 100-m Herriott multipass cell. An external cavity QCL was used to target H_2S transition at ~7.89 μm with detection limit of 0.45 ppmv for 3.5-s integration time achieved using QEPAS system.[11] Another QEPAS setup with an external cavity QCL was presented and detection limit of 492 ppbv (1-s integration time, 118 mW of optical power) was achieved.[12]

In this work, we present a setup that uses a distributed feedback (DFB) QCL source near 7.2 μm to target the H_2S transition at ~1389.3 cm^{-1} and achieve the desired sub-ppm detection limit using a multipass cell-based WMS spectrometer arrangement. A system design and its performance evaluation are demonstrated in this work.

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2 System Design

The target line selection is depicted in Fig. 1. The ν_2 rovibrational band between 1100 and 1450 cm^{-1} is the second strongest midinfrared band and offers access to H_2S transitions that are not affected by the strong water or carbon dioxide absorption in this region (in contrast to band between 3700 and 3900 cm^{-1}). The specific frequency range between 1389 and 1390 cm^{-1} explored in this work contains two closely spaced H_2S absorption lines that do not overlap with water vapor (H_2O) transitions and have only small interferences from weaker methane (CH_4) lines.

The optical layout of the system is shown in Fig. 2. A continuous wave DFB QCL (from AdTech Optics) was used as the source. Laser temperature was stabilized at 31°C by a thermoelectric cooler (TEC) driven by a temperature controller (Arroyo, model TECPak 585-05-12). The laser current was controlled by a current driver (Wavelength Electronics, model QCL500) and could be modulated with an external function generator (laser threshold and maximum currents were 230 and ~460 mA, respectively, tuning rate of ~5.7 cm^{-1}/A at low frequency). Beam emitted from the laser source was collimated and directed through a 76-m path-length astigmatic Herriott multipass cell (Aerodyne Research, AMAC-76, volume of 500 ml). After passing through the cell, the beam was focused using a 3″ focal length off-axis parabolic mirror onto a two-stage TEC-cooled mercury–cadmium–telluride photodetector (Vigo Systems, model PVMI-2TE-8). The system could be set to detect direct absorption (with a Sawtooth modulation of the laser injection current) or WMS signal (with a sinewave modulation and subsequent lock-in detection).

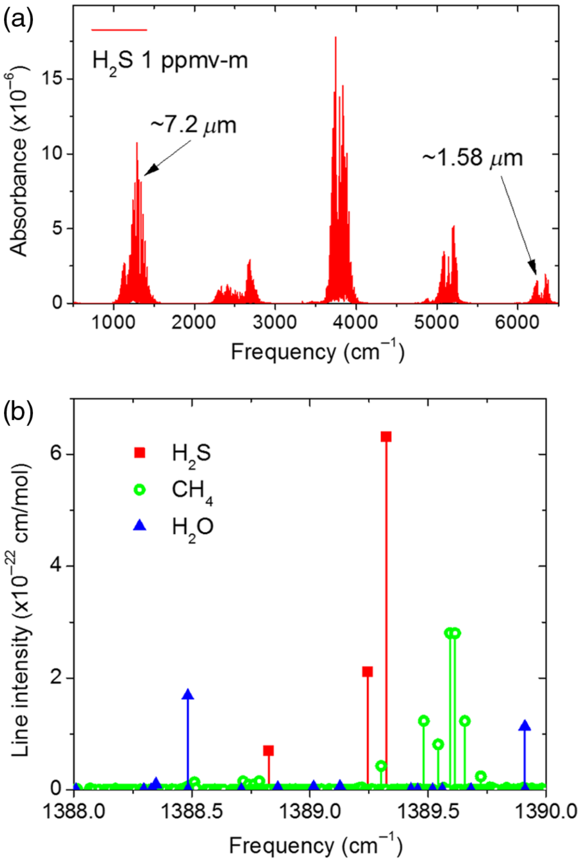

Fig. 1 (a) Infrared absorption spectrum of H_2S based on HITRAN database. Near-infrared band (typically used for optical-based H_2S detection) and spectral region explored in this work (at ~7.2 μm) are indicated. (b) Line intensities for three molecules: hydrogen sulfide, methane, and water vapor. The chosen transition at ~1389.3 cm^{-1} is ~4 to 5 times stronger comparing to absorption lines in the near-infrared and has relatively small interference from other gases.

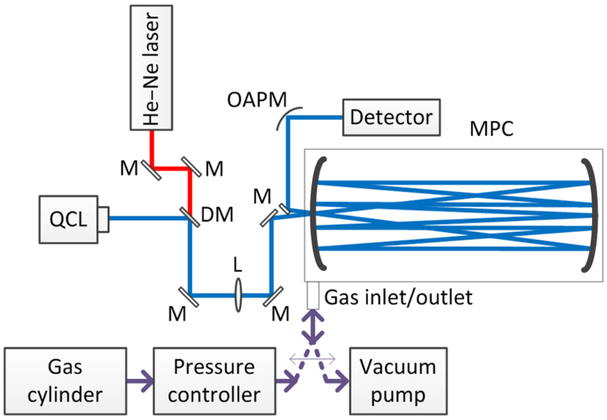

Fig. 2 Schematic diagram of the setup. M, mirror; DM, dichroic mirror; OAPM, off-axis parabolic mirror; L, lens (500-mm focal length); and MPC, multipass cell. He–Ne laser was used for system alignment.

3 System Performance

3.1 *Direct Absorption Measurements*

Direct absorption measurements were performed solely for system diagnostic purposes and identification of spectral region containing target H_2S transitions. For direct absorption measurement, the laser injection current was modulated with a Sawtooth signal (10 Hz) and detected signal was recorded with a digital oscilloscope. Multipass cell was filled with a gas mixture of 200 ppmv of H_2S balanced with nitrogen. Two spectral scans (after baseline subtraction), recorded at two different gas pressures of 750 and 100 Torr, respectively, are shown in Fig. 3. In case of the reduced pressure measurement, the two separate transitions marked in Fig. 1(b) are clearly visible. At atmospheric pressure, the transitions

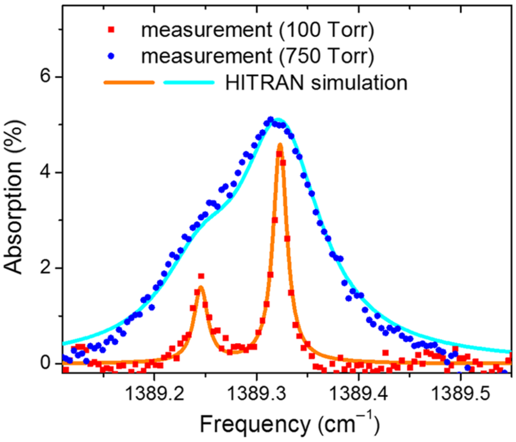

Fig. 3 H_2S spectra recorded for pressures of 100 and 750 Torr (sample is 200 ppmv of H_2S balanced in nitrogen, 76-m path length). In both cases, good agreement with HITRAN-based simulation is obtained.

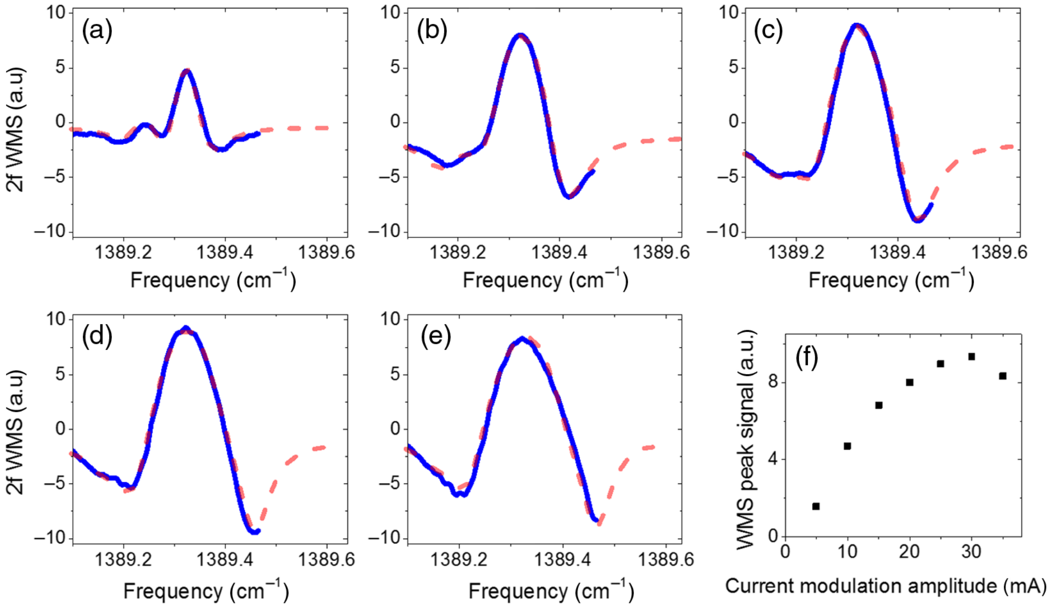

Fig. 4 (a)–(e) 2f WMS spectra recorded for different amplitudes of current modulation (5, 15, 25, 30, and 35 mA). Blue solid line, measured signal; dashed red line, HITRAN-based simulation (for large modulation amplitudes part of the spectrum was not recorded due to limited tuning range of the source); (f) 2f WMS amplitude at the transition center plotted in function of current modulation amplitude.

merge into one absorption feature, with full-width at half-maximum of ∼4.2 GHz. In both cases, recorded spectra are in very good agreement with simulation based on HITRAN database.[8]

3.2 *Wavelength Modulation Spectroscopy Measurements*

WMS mode of operation is planned to be used for routine H_2S monitoring. WMS offers simplicity in terms of data acquisition electronics (lock-in detection), linear response (for peak absorption up to ∼10%), and possibility of continuous monitoring with an even further simplified system operating in a line-locked mode, which is ultimately preferred for future industrial monitoring applications. In this work, the WMS absorption signal retrieval was performed by modulation of laser injection current using a 1-kHz sinewave followed by a lock-in detection (with data acquisition rate of 100 Hz). A digital lock-in amplifier (Signal Recovery, model 7265) was used to retrieve the second harmonic (2f) component of the photodetector signal. No baseline subtraction was used in all presented WMS measurements. A set of 2f WMS spectral scans recorded for different modulation amplitudes is shown in Figs. 4(a)–4(e) (additional 100-mHz ramp signal was used to sweep the laser wavelength across the transition; gas was at room temperature and pressure was 750 Torr). The dependence of the WMS signal peak (at the transition center) on modulation amplitude is presented in Fig. 4(f). Modulation amplitude of 30 mA (peak–peak) was found to provide maximal 2f WMS signal and was used in subsequent H_2S measurements.

To analyze the system detection limit and stability, an Allan deviation analysis was performed.[13] Laser was tuned to the center of the transition by adjusting a bias current to 330 mA (no active frequency stabilization was performed to test the worst-case scenario expected in the line-locked mode of operation). For this injection, current emitted optical power was ∼21 mW. With the current modulation amplitude set to 30 mA (peak–peak), the 2f WMS signal amplitude was recorded for ∼500 s and was used to calculate Allan deviation shown in Fig. 5. For integration times of 1 and 5 s, the detection limit reaches 140 and 80 ppbv, respectively. Longer averaging does not improve system performance, which is most likely due to drifts of the laser emission wavelength. This can be improved by applying active laser stabilization using a reference gas cell and 3f stabilization (similar to presented in Refs. 14–17). Figure 5 also shows modified, two-point deviation (defined in Ref. 18) that provides an information on the system precision and the actual system accuracy at any given time after calibration. It shows that for the presented system after 1000 s precision stays below 400 ppbv (for integration time of 1 s).

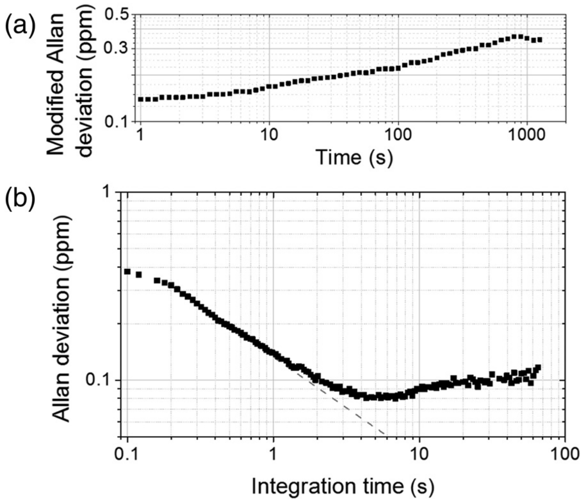

Fig. 5 (b) Allan deviation and (a) modified, two-point Allan deviation measured when laser wavelength was adjusted to target center of H_2S transition.

4 Conclusions

In this paper, a WMS-based setup with a 76-m astigmatic Herriott multipass cell for H_2S detection was demonstrated. DFB QCL operating at 7.2 μm enables targeting strong mid-infrared H_2S transitions, resulting in a 1-s detection limit of 140 ppbv. This sensitivity is from 2 to 10 times better comparing to results reported for near-infrared systems that use QEPAS, integrated cavity output spectroscopy, WMS, or CLaDS.[2–5] It outperforms most previously demonstrated setups that also use QCLs in 7- to 8.2-μm range[10–12] and is comparable to a recently demonstrated system operating at 8.018 μm.[19] Modified two-point deviation analysis reveals that a basic WMS system with no active line-locking can achieve better than 400 ppbv accuracy over extended operation times spanning above 1000 s, which is an ideal solution for a cost-effective technology required for industrial safety monitoring applications. The system was characterized using gas mixture of 200 ppmv H_2S balanced in nitrogen at 750 Torr.

Application to open-path measurements would require further studies on cross interference between target H_2S line and adjacent methane transitions. Fortunately, even when larger than ambient concentrations of methane are expected, several other H_2S lines with similar or even larger line strength are also available in the spectral region between 7 and 8.2 μm. With careful selection of target transition, reduced interference from other species can be obtained,[10,19] allowing for highly accurate open-path H_2S detection at sub-ppm levels with compact optical design and simple data processing.

Acknowledgments

This work was supported by the National Centre for Research and Development (NCBiR) award LIDER/023/379/L-5/13/NCBR/2014. M.N. acknowledges a scholarship for young scientists from the Polish Ministry of Science and Higher Education. G.W. acknowledges partial funding of his research effort by the Advanced Research Projects Agency-Energy (ARPA-E), U.S. Department of Energy, under Award Number DE-AR0000540. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

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