

Recent advances of mid–infrared compact, field deployable sensors and their real world applications in the petrochemical industry, atmospheric chemistry and security

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Abstract: Development of trace gas sensors based on mid-infrared interband cascade lasers and quantum cascade lasers as well as their applications will be reported. The sensor technology will use both laser absorption and quartz enhanced photoacoustic spectroscopy.

OCIS codes: 280.4788 Optical sensing and sensors; 300.6360 Spectroscopy, laser; 280.3420 Laser sensors

1. Introduction

The recent development of compact interband cascade lasers (ICLs) and quantum cascade lasers (QCLs) based trace gas sensors will permit the targeting of strong fundamental rotational-vibrational transitions in the mid-infrared which are one to two orders of magnitude more intense than transitions in the overtone and combination bands in the near-infrared. This has led to the design and fabrication of mid-infrared compact, field deployable sensors for use in the petrochemical industry, environmental monitoring, atmospheric chemistry, life sciences, medical diagnostics, defense and security. Specifically, the spectroscopic detection and monitoring of four molecular species, methane (CH_4) [1-4], ethane (C_2H_6), formaldehyde (H_2CO) [5-6] and hydrogen sulphide (H_2S) [7-8] will be described.

2. Measurement Techniques

CH_4 , C_2H_6 and H_2CO can be detected using two detection techniques: mid-infrared tunable laser absorption spectroscopy (TDLAS) using a compact multi-pass gas cell and quartz enhanced photoacoustic spectroscopy (QEPAS) (Fig. 1a). Both techniques utilize state-of-the-art mid-IR, continuous wave (CW), distributed feedback (DFB) ICLs and QCLs. TDLAS was performed with an ultra-compact 54.6m effective optical path length innovative spherical multipass gas cell capable of 435 passes between two concave mirrors separated by 12.5 cm. QEPAS used a small robust absorption detection module (ADM) which consists of a quartz tuning fork (QTF), two optical windows, gas inlet/outlet ports and a low noise frequency pre-amplifier. Wavelength modulation and second harmonic detection were employed for spectral data processing.

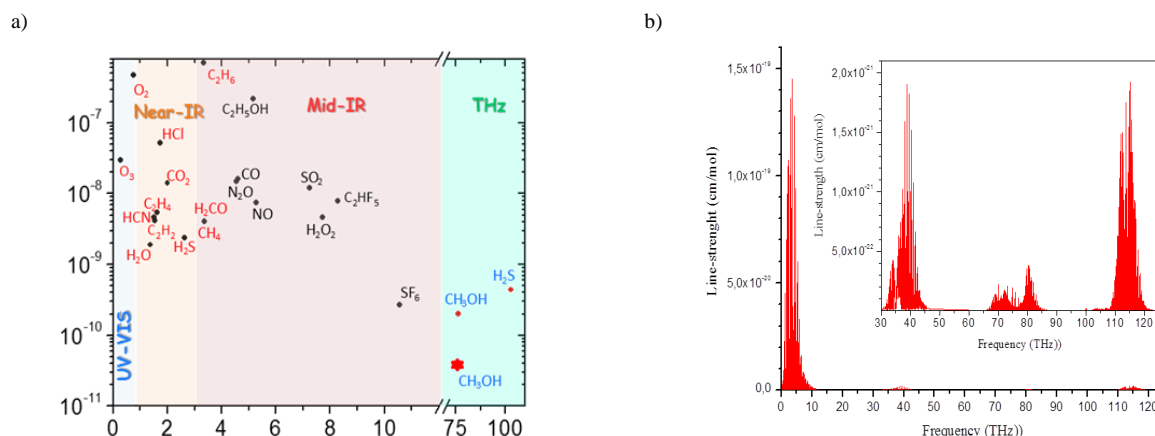


Fig. 1. (a) Normalized noise equivalent absorption coefficients (NNEA) results (vertical scale) obtained with QEPAS sensors for trace gas species versus wavelengths (horizontal scale in μm) in the UV-Vis, near-IR, mid-IR and THz spectral ranges of commercially available mid-IR laser sources. The red star symbol (*) marks the result obtained with the custom QTF with new geometry. (b) Stick H_2S spectrum as obtained from the HITRAN database [9].

TDLAS and QEPAS can achieve minimum detectable absorption losses in the range from 10^{-8} to $10^{-11} \text{ cm}^{-1}/\text{Hz}^{1/2}$. Several recent examples of real world applications of field deployable gas sensors will be described. For example, an ICL based TDLAS sensor system is capable of detecting CH_4 and C_2H_6 concentration levels of 1 ppb in a 1 sec. sampling time, using an ultra-compact, robust sensor architecture. H_2S detection (Fig. 1b) was realized with a THz QEPAS sensor system using a custom quartz tuning fork (QTF) with a new geometry and a QCL emitting at 2.913 THz [7].

Furthermore, two new approaches aimed to achieve enhanced detection sensitivities with QEPAS based sensing can be realized. The first method will make use of a compact optical power buildup cavity (see Fig. 2), which achieves significantly lower minimum detectable trace gas concentration levels of < 10 pptv. The second approach will use custom fabricated QTFs capable of improved detection sensitivity [10].

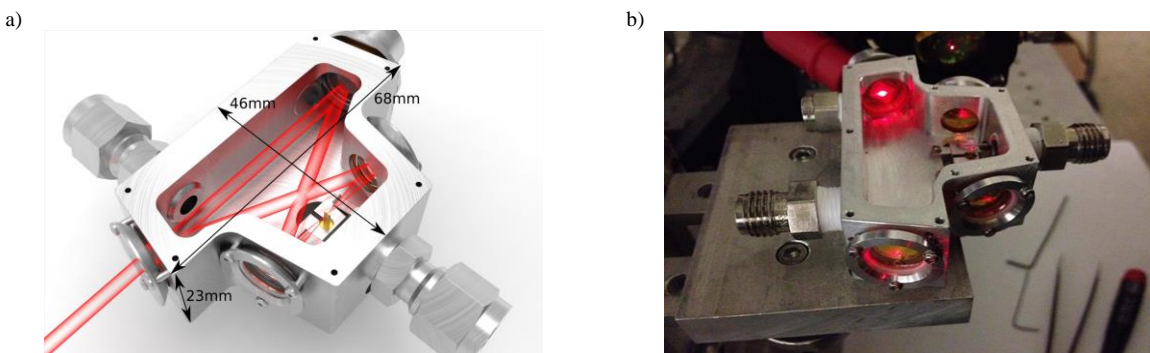


Fig. 2. (a) Compact intra cavity QEPAS stainless ADM module, resulting in a ~ 5000 fold power enhancement. (b) A red diode laser beam was used for alignment of the mid-IR ICL and QCL pump beams.

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4. References

- [1] P. Patimisco, G. Scamarcio, F.K. Tittel, and V. Spagnolo, "Quartz-enhanced photoacoustic spectroscopy: a review" *Sensor: Special Issue "Gas Sensors-2013"*, 14, 6166206 (2014).
- [2] W. Ren, W. Jiang, and F.K. Tittel, "Single-QCL based absorption sensor for simultaneous trace-gas detection of CH_4 and N_2O " *Appl. Phys B* 117, 245-251 (2014).
- [3] Y. Cao N. P. Sanchez, W. Jiang, R. J. Griffin, F. Xie, L. C. Hughes, C. Zah and F. K. Tittel "Simultaneous atmospheric nitrous oxide, methane and water vapor detection with a single continuous wave quantum cascade laser" *Opt. Ex.* 23, 2121-2132 (2014).
- [4] L. Dong, C. Li, N. P. Sanchez, A. K. Gluszek, R. Griffin and F. K. Tittel; "Compact CH_4 sensor system based on a continuous-wave, low power consumption, room temperature interband cascade laser", *Appl. Phys Lett.* 108, 011106 (2016).
- [5] L. Dong, Y. Yu, C. Li, S. So, and F.K. Tittel, "Ppb-level formaldehyde detection using a CW room-temperature interband cascade laser and a miniature dense pattern multipass cell" *Optics Express*; 23, 19821-19830 (2015).
- [6] W. Ren, L. Luo, F. K. Tittel, "Sensitive detection of formaldehyde using an interband cascade laser near $3.6 \mu\text{m}$ ", Elsevier, *Sensors and Actuators B: Chemical*; 221, 1062-1068 (2015).
- [7] V. Spagnolo, P. Patimisco, R. Pennetta, A. Sampaolo, G. Scamarcio, M. Vitiello, and F.K. Tittel, "THz Quartz-enhanced photoacoustic sensor for H_2S trace gas detection", *Opt. Exp.* 23, 7574-7582 (2015).
- [8] H. Wu, L. Dong, H. Zheng, X. Liu, X. Yin, W. Ma, L. Zhang, W. Yin, S. Jia, F. K. Tittel, "Enhanced near-infrared QEPAS sensor for sub-ppm level H_2S detection by means of a fiber amplified 1582 nm DFB laser" *Sensors and Actuators B:Chemical* 221, 666-672 (2015).
- [9] L.S. Rothman, et al "The HITRAN 2012 molecular spectroscopic database," *J. Quant. Spectrosc. Radiat. Transfer* 130, 4-50 (2013).
- [10] A. Sampaolo, P. Patimisco, L. Dong, A. Geras, S. G. Scamarcio, T. Starecki, F.K Tittel, V. Spagnolo; "Quartz-Enhanced Photoacoustic Spectroscopy exploiting tuning fork overtone modes", *Appl. Phys Lett.* 107, 231102 (2015).