Mid-Infrared Laser based Trace Gas Sensor Technologies: Recent advances and Applications

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ABSTRACT

The recent development of interband cascade lasers (ICLs) and quantum cascade lasers (QCLs) based trace gas sensors enables the targeting of strong fundamental rotational-vibrational transitions in the mid-infrared, This has led to the development of mid-infrared compact, field deployable sensors based on two sensor system platforms, laser absorption and quartz enhanced spectroscopy. These sensor platforms are applicable for environmental monitoring, atmospheric chemistry and for use in the petrochemical industry. The spectroscopic detection and monitoring of methane (CH_4) and ethane (C_2H_6) [1-4], as well as carbon dioxide (CO_2) [5-7] will be described.

INTRODUCTION

Trace gas sensors based on laser absorption spectroscopy (LAS) can achieve low minimum detection limits (MDL) and high selectivity. Techniques for improving LAS detection sensitivity are based on multipass gas cells or optical resonators (cavities) in order to increase the effective optical path length. LAS can be described by Lambert-Beer's law,

$$I(\lambda) = I_0(\lambda)\exp\left[-\alpha(T,\lambda)L\right], \tag{1}$$

where $I_0(\lambda)$ is the intensity of the incident radiation, α denotes the absorption coefficient of the targeted trace gas, L is the length of the optical path in the absorbing sample and T is the temperature of the sample. When the wavelength of the incident radiation is matched to an absorption line of the sample, the optical path increases and results in a higher difference between $I_0(\lambda)$ and $I(\lambda)$. An improved MDL can be achieved due to an increase in the signal-to-noise ratio.

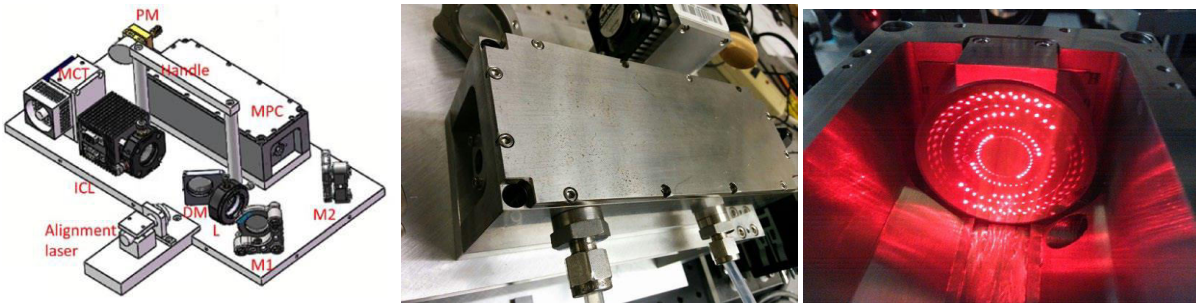
Wavelength modulation (WM) and frequency modulation (FM) are used to achieve this goal. These methods are applicable for interband cascade lasers (ICLs) and quantum cascade lasers (QCLs) based absorption spectroscopy (LAS-WM/FM) due to their spectral tunability. ICLs and QCLs possess a distributed feedback (DFB) structure and hence emit a single axial mode output. The wavelength of the probing laser is modulated over the absorption line by a sinusoidal signal of frequency. As a result, the light intensity transmitted through the LAS multipass gas cell and the signal at the detector has a time-dependent form. The signal can be detected by means of a lock-in amplifier. A slow change of the mean laser frequency provides the opportunity to record the first or the second derivative of the absorption spectrum, depending on the demodulation frequency. The advantage of wavelength modulation spectroscopy (WMS) is that it is proportional to the output signal derivative of the targeted absorption line. As a result, harmonic signals reach a maximum value when absorption is the greatest and the odd harmonic signals pass through zero. Therefore, second harmonic (i.e., *2f* detection) measurements are usually performed, while the first or the third harmonics are used to stabilize the operating point of the laser excitation source.

SENSOR PLATFORMS BASED ON LASER ABSORPTION SPECTROSCOPY

Optical methods based on infrared laser absorption spectroscopy (LAS) [1-4] are advantageous in terms of size, cost and requiring no pretreatment and accumulation of the concentration of the targeted gas samples in comparison with mass spectrometry or gas chromatography. Furthermore, optical methods provide high-precision remote sensing capabilities and fast

response. LAS enables non-contact measurements and has proven to be an excellent tool for trace gas detection in various applications. LAS requires a tunable laser exhibiting single frequency emission and a narrow linewidth at the targeted absorption line of a gas molecule in order to achieve high detection sensitivity and selectivity in the near and mid-infrared spectral range. Quantum cascade lasers (QCLs) in the 4−12 µm spectral range and interband cascade lasers (ICLs) in the 2.5−4 µm spectral range with low power-consumption are lasers of optimum choice in LAS, because they provide advantages of continuous-wave (CW) output power levels (up to ~hundreds of mW for QCLs and ~tens of mW for ICLs).

A continuous-wave (CW) ICL based mid-infrared sensor system was demonstrated for simultaneous detection of atmospheric methane (CH_4) and ethane (C_2H_6) [1-4]. A 3.337 µm CW ICL with an emitting wavenumber range of 2996.0−3001.5 cm^{-1} was used to simultaneously target two absorption lines, C_2H_6 at 2996.88 cm^{-1} and CH_4 at 2999.06 cm^{-1}, respectively [1]. The sensor performance was first evaluated for single-gas detection by only targeting the absorption line of one gas species (Figures 1 and 2). Allan deviations of 11.2 parts per billion in volume (ppbv) for CH_4 and 1.86 ppbv for C_2H_6 with an averaging time of 3.4 s were achieved for the detection of these two gases. Dual-gas detection was realized by using a long-term scan signal to target both CH_4 and C_2H_6 absorption lines. Measurements for both indoor and outdoor concentration changes of CH_4 and C_2H_6 were conducted.



(a) (b) (c)

Figure 1. (a) A CAD image of compact optical sensor core with dimensions of length (35.5 cm), width (18 cm) and a height (8 cm); (b) A photograph of the miniature MPGC; and (c) The mode pattern inside the MPGC obtained with a red diode alignment laser.

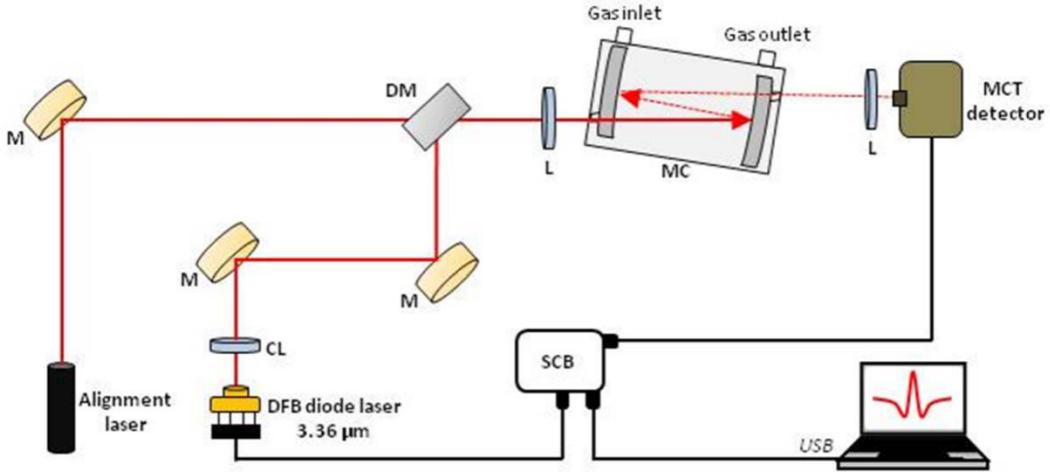


Figure 2. Schematic of a C_2H_6 gas sensor using a Nanoplus 3.36 µm DFB laser diode. M – mirror, CL – collimating lens, DM – dichroic mirror, MC – multipass cell, L – lens, SCB – sensor control board.

SENSOR PLATFORMS BASED ON PHOTOACOUSTIC SPECTROSCOPY AND QUARTZ-ENHANCED PHOTOACOUSTIC SPECTROSCOPY

Trace gas sensor systems based on PAS are effective tools for trace gas sensing and are characterized by a compact, cost-effective and robust architecture that require no detector. Sensitive microphones are used to detect the conversion of laser light matched to the targeted absorption line in the trace gas sample. The main disadvantage of PAS sensors is their sensitivity to mechanical and acoustic vibrations. A much improved sensor performance can be achieved by replacing the microphone with a commercially available, inexpensive quartz tuning fork (QTF).

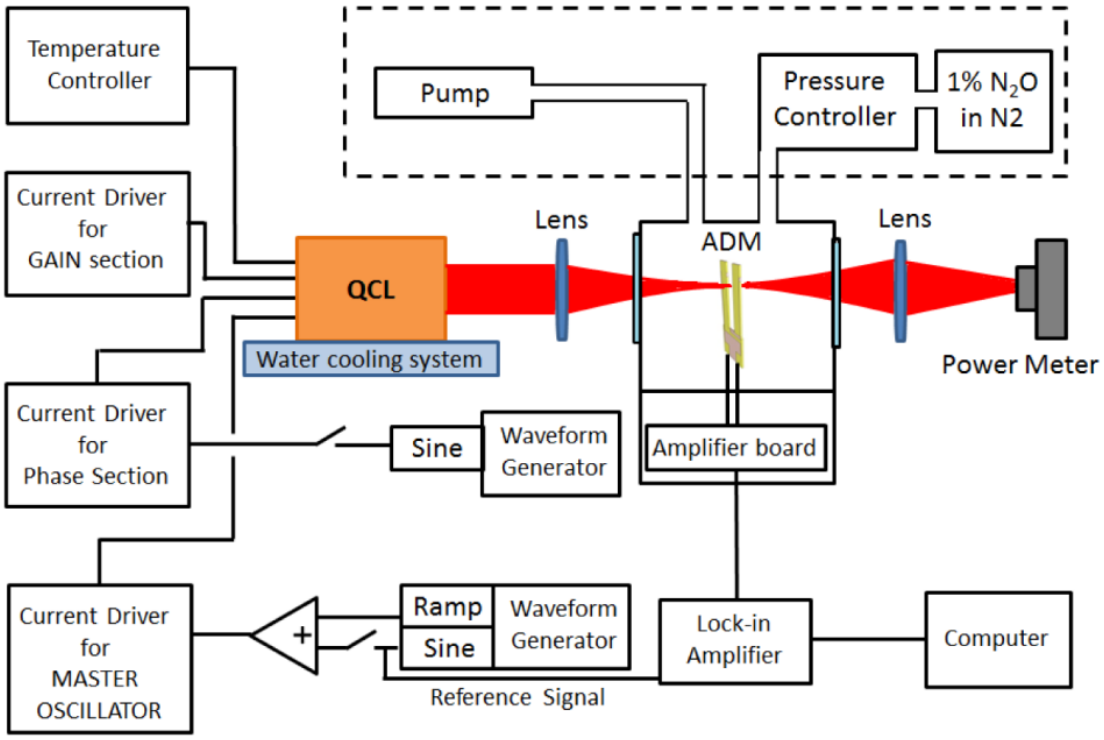


Figure 3. Schematic of the QEPAS experimental setup employed for the detection of N_2O in a gas mixture composed of 1% N_2O in pure N_2, at a pressure of 85 Torr. QCL – Quantum Cascade Laser. ADM – Acoustic Detection Module.

Such a technique is called quartz-enhanced photoacoustic spectroscopy (QEPAS). QTFs have a resonant frequency of ~32.8 kHz and a Q-factor of ~10^5 in vacuum and ~10^4 at 760 Torr. Furthermore, only the symmetric vibration of a QTF is piezo-electrically active, which makes QEPAS immune to environmental acoustic noise and is applicable over a wide range of pressures and is capable of analyzing trace gas samples as small as ~3 mm^3 [6-7].

I-QEPAS achieves an extremely low MDL, because the QEPAS signal amplitude is directly proportional to the available laser excitation power [9]. The target trace gas was carbon dioxide and a CO_2 detection sensitivity of 300 ppt for a 4 s integration time was achieved (Figures 4 and 5).

In this paper we report the application of the I-QEPAS sensor platform to fast measurements of carbon dioxide (CO_2) trace concentrations [7]. The motivation for developing an I-QEPAS CO_2 sensor is that a low CO_2 concentration level leads to hypocapnia which constricts blood vessels and leads to a decreased profusion of vital organs, the concentration of which is strongly related to meteorological conditions and emission sources. Furthermore, CO2 is a greenhouse gas having a global average concentration of 404ppm. In addition the monitoring of CO_2 is important in agricultural and biological applications since plants require CO_2 to conduct photosynthesis; for example, the atmosphere of commercial greenhouses must be enriched with additional CO_2 to sustain and increase the rate of plant growth. Carbon dioxide is also used in enhanced oil recovery, where it is injected into or adjacent to producing oil wells, when it becomes miscible with the oil. This approach increase original oil recovery by reducing residual oil saturation by between 7% and 23% additional to primary extraction. Lastly, liquid and solid CO_2 are important refrigerants, especially in the food industry where they are employed in the transportation and storage of

frozen foods. Another approach consists of measuring the change in the ozone concentration instead of the UV intensity. Furthermore, the I-QEPAS–based sensor technology is equally applicable to other trace gas species.

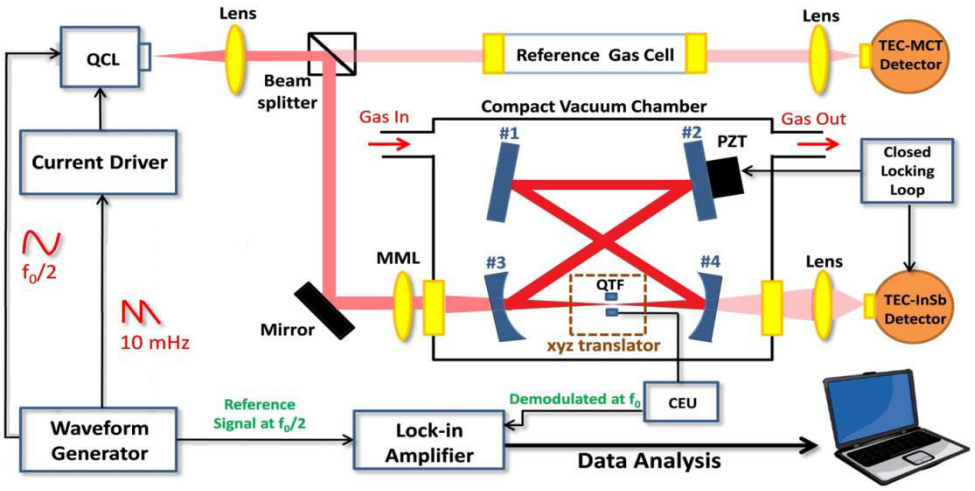
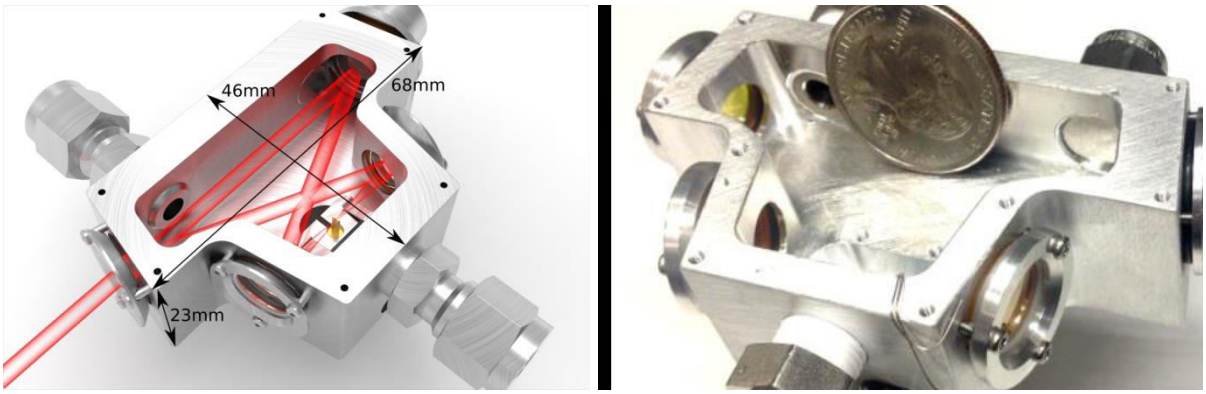


Figure 4. Development of a novel I-QEPAS based sensor design: Initial performance evaluation of I-QEPAS based on CO_2 detection



(a) (b)

Figure 5. (a) Optical cavity 3D design; and (b) photo of a novel and compact bow-tie resonator for an I-QEPAS sensor system [9]

To date we have used QEPAS to detect ten target analytes in the mid-infrared, which include C_2H_6, CO, CH_2O, N_2O, C_2H_5OH, NO, H_2O_2, C_2H_5, and NH_3 at frequencies between 2976.8 cm^{-1} and 1046.39 cm^{-1}, at pressures ranging between 50 Torr and 770 Torr, with excitation powers of 1.8 mW and 100 mW yielding noise equivalent concentrations (NEC) of 2 to 90,000 ppbv, with a data acquisition time of 1 second. For comparison, the normalized noise equivalent absorption coeefficient (NNEA) for conventional PAS was 2.2 x $10^{-9}$$cm^{-1}$W/Hz for NH_3.

Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, $cm^{-1}W/Hz^{½}$	Power, mW	NEC (t=1s), ppbv
C_2H_6	2976.8	200		1.8	.74
CH_2O (N_2:75% RH)*	2804.90	75	8.7×10^{-9}	7.2	120
CO (N_2 +2.2% H_2O)	2176.28	100	1.4×10^{-7}	71	2
CO (propylene)	2196.66	50	7.4×10^{-8}	6.5	140
N_2O (air+5%SF_6)	2195.63	50	1.5×10^{-8}	19	7
C_2H_5OH (N_2)**	1934.2	770	2.2×10^{-7}	10	90,000
NO (N_2+H_2O)	1900.07	250	7.5×10^{-9}	100	3
H_2O_2	1295.6	150	4.6×10^{-9}	100	12
C_2HF_5 (N_2)***	1208.62	770	7.8×10^{-9}	6.6	9
NH_3 (N_2)*	1046.39	110	1.6×10^{-8}	20	6
SF_6	948.62	75	$2.7\text{x}10^{-10}$	18	0.05 (50 ppt)

Figure 6. QEPAS Performance for Trace Gas Species (August 2017)

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KEY WORDS

Trace gas sensors; interband cascade lasers; quartz-enhanced photoacoustic spectroscopy.