# Trace gas spectroscopy using state-of-the-art mid-infrared semiconductor laser sources: progress, status 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, which are one to two orders of magnitude more intense than transitions in the near-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 three molecular species, methane ($CH_4$), ethane ($C_2H_6$) [1], formaldehyde ($H_2CO$) [2] and hydrogen sulphide ($H_2S$) [3] will be described.

**Keywords:** Trace gas sensors; interband cascade lasers; laser absorption spectroscopy, quartz-enhanced photoacoustic spectroscopy;

## 1. 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,

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

where $I_0(\lambda)$ is the intensity of the incident radiation, $\alpha$ 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 sample TDLAS 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.

## 2. SENSOR PLATFORMS BASED ON LASER ABSORPTION SPECTROSCOPY (LAS)

In comparison with mass spectrometry or gas chromatography, optical methods based on infrared laser absorption spectroscopy (LAS) [1,2] are advantageous in terms of size, cost and requiring no pretreatment and accumulation of the concentration of the targeted gas samples. In addition, 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]. 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. The sensor performance was first evaluated for single-gas detection by only targeting the absorption line of one gas species. 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. The reported single ICL based dual-gas sensor system has the advantages of reduced size and cost compared to two separate sensor systems.

## 3. SENSOR PLATFORMS BASED ON PHOTOACOUSTIC SPECTROSCOPY (PAS) AND QUARTZ-ENHANCED PHOTOACOUSTIC SPECTROSCOPY (QEPAS)

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). 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 $mm^3$ [3].

An intracavity I-QEPAS sensor platform based on a combination of QEPAS and an optical resonator was first reported by S. Borri et al. [3]. I-QEPAS achieves an extremely low MDL, because the QEPAS signal amplitude is

directly proportional to the available laser excitation power. The target trace gas was carbon dioxide and a $CO_2$ detection sensitivity of 300 ppt for a 4 s integration time was achieved.

In this paper we will report the application of the I-QEPAS sensor platform to fast measurements of nitric oxide (NO) trace concentrations The motivation for developing an I-QEPAS NO sensor is that NO is a toxic gas, the concentration of which is strongly related to meteorological conditions and emission sources. Furthermore, NO is produced during combustion of fossil fuels in power plants and automobile engines as well as during lightning in thunderstorms. Droplets and vapor of nitric acid are removed from the atmosphere in rain or dry precipitation of aerosols. During daytime, there is a correlation between the concentration of $NO_x$ and $NO_2$, and during night-time between $NO_x$ and NO. Nitric oxide is also a characteristic decomposition compound of specific explosive materials. Furthermore, NO plays an important role in numerous functions in the human body where it is produced in inflammatory processes. In 1998, three US scientists, R F. Furchgott, L J. Ignarro and F. Murad, received the Nobel Prize in Physiology or Medicine for their discoveries concerning the role of "nitric oxide as a signaling molecule in the cardiovascular system" [4]. Real-time concentration measurements of short-lived NO are important in many applications. At present, most common commercially available NO analyzers, which offer concentration measurements at the ppb level, are based on chemiluminescence. Such analyzers detect the UV radiation produced in the reaction of NO with ozone [5,6]. 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.

NO has a strong absorption band in the mid-infrared spectral range located at a wavelength of 5.263 μm (1900.08 $cm^{-1}$). The NO concentration measurements were performed with wavelength modulation (WM) using a *2f* detection scheme. The WM technique suppresses background noise originating from spectrally non-selective absorbers (such as the resonator walls, QTF electrodes, and MPGC elements). A diagram of the I-QEPAS sensor platform is shown in Figures 1 and 2. A room-temperature, continuous-wave (cw), distributed-feedback (DFB) QCL (Hamamatsu Photonics) emitting at 5.263 μm wavelength enclosed in a High Heat Load (HHL) package was used as the excitation source. The linewidth of a DFB QCL is narrow and mainly limited by the noise of the QCL current and temperature controllers.

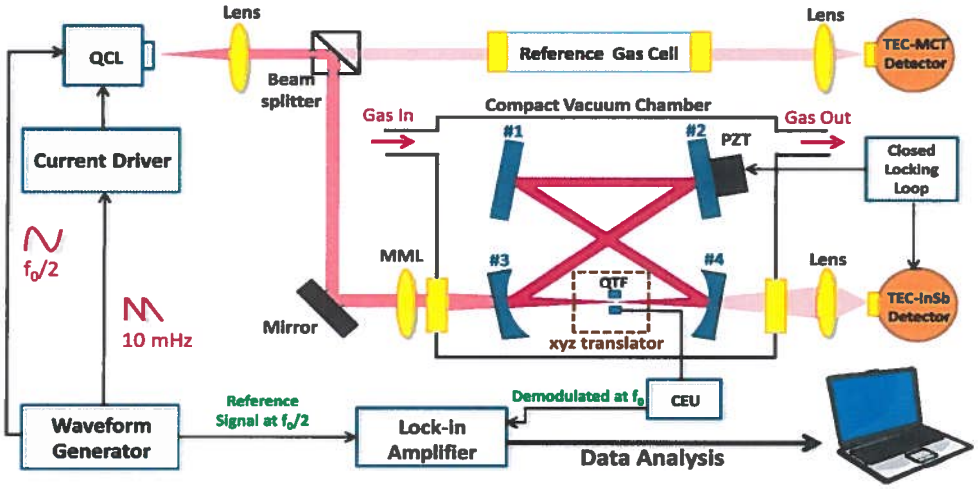
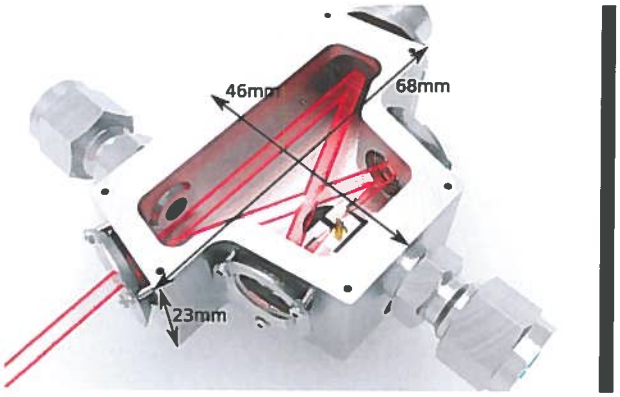



Figure 1. Development of a novel I-QEPAS based sensor design: Initial performance evaluation of I-QEPAS based on $CO_2$ detection




(a) (b)

Figure 2. (a) Optical cavity 3D design; and (b) photo of a novel and compact bow-tie resonator for an I-QEPAS sensor system

| Molecule (Host) | Frequency, $cm^{-1}$ | Pressure, Torr | NNEA, $cm^{-1}W/Hz^{½}$ | Power, mW | NEC (t=1s), ppbv |
|---|---|---|---|---|---|
| $O_3$ (air) | 35087.70 | 700 | $3.0\times10^{-8}$ | 0.8 | 1,270 |
| $O_2$ ($N_2$) | 13099.30 | 158 | $4.74\times10^{-7}$ | 1228 | 13,000 |
| $C_2H_2$ ($N_2$)* | 6523.88 | 720 | $4.1\times10^{-9}$ | 57 | 30 |
| $NH_3$ ($N_2$)* | 6528.76 | 575 | $3.1\times10^{-9}$ | 60 | 60 |
| $C_2H_4$ ($N_2$)* | 6177.07 | 715 | $5.4\times10^{-9}$ | 15 | 1,700 |
| $CH_4$ ($N_2$+1.2% $H_2O$)* | 6057.09 | 760 | $3.7\times10^{-9}$ | 16 | 240 |
| $N_2H_4$ | 6470.00 | 700 | $4.1\times10^{-9}$ | 16 | 1,000 |
| $H_2S$ ($N_2$)* | 6357.63 | 780 | $5.6\times10^{-9}$ | 45 | 5,000 |
| HCl ($N_2$ dry) | 5739.26 | 760 | $5.2\times10^{-8}$ | 15 | 700 |
| $CO_2$ ($N_2$+1.5% $H_2O$) * | 4991.26 | 50 | $1.4\times10^{-8}$ | 4.4 | 18,000 |
| $C_2H_6$ | 2976.8 | 200 | | 1.8 | .74 |
| $CH_2O$ ($N_2$:75% RH)* | 2804.90 | 75 | $8.7\times10^{-9}$ | 7.2 | 120 |
| CO ($N_2$ +2.2% $H_2O$) | 2176.28 | 100 | $1.4\times10^{-7}$ | 71 | 2 |
| CO (propylene) | 2196.66 | 50 | $7.4\times10^{-8}$ | 6.5 | 140 |
| $N_2O$ (air+5%$SF_6$) | 2195.63 | 50 | $1.5\times10^{-8}$ | 19 | 7 |
| $C_2H_5OH$ ($N_2$)** | 1934.2 | 770 | $2.2\times10^{-7}$ | 10 | 90,000 |
| NO ($N_2$+$H_2O$) | 1900.07 | 250 | $7.5\times10^{-9}$ | 100 | 3 |
| $H_2O_2$ | 1295.6 | 150 | $4.6\times10^{-9}$ | 100 | 12 |
| $C_2HF_5$ ($N_2$)*** | 1208.62 | 770 | $7.8\times10^{-9}$ | 6.6 | 9 |
| $NH_3$ ($N_2$)* | 1046.39 | 110 | $1.6\times10^{-8}$ | 20 | 6 |
| $SF_6$ | 948.62 | 75 | $2.7\times10^{-10}$ | 18 | 0.05 (50 ppt) |

* - Improved microresonator

** - Improved microresonator and double optical pass through ADM

*** - With amplitude modulation and metal microresonator

NNEA – normalized noise equivalent absorption coefficient.

NEC – noise equivalent concentration for available laser power and t=1s time constant, 18 dB/oct filter slope.

**For comparison: conventional PAS 2.2 $\times10^{-9}$ $cm^{-1}W/\sqrt{Hz}$ for $NH_3$**

Figure 3. QEPAS Performance for Trace Gas Species (July 2017)

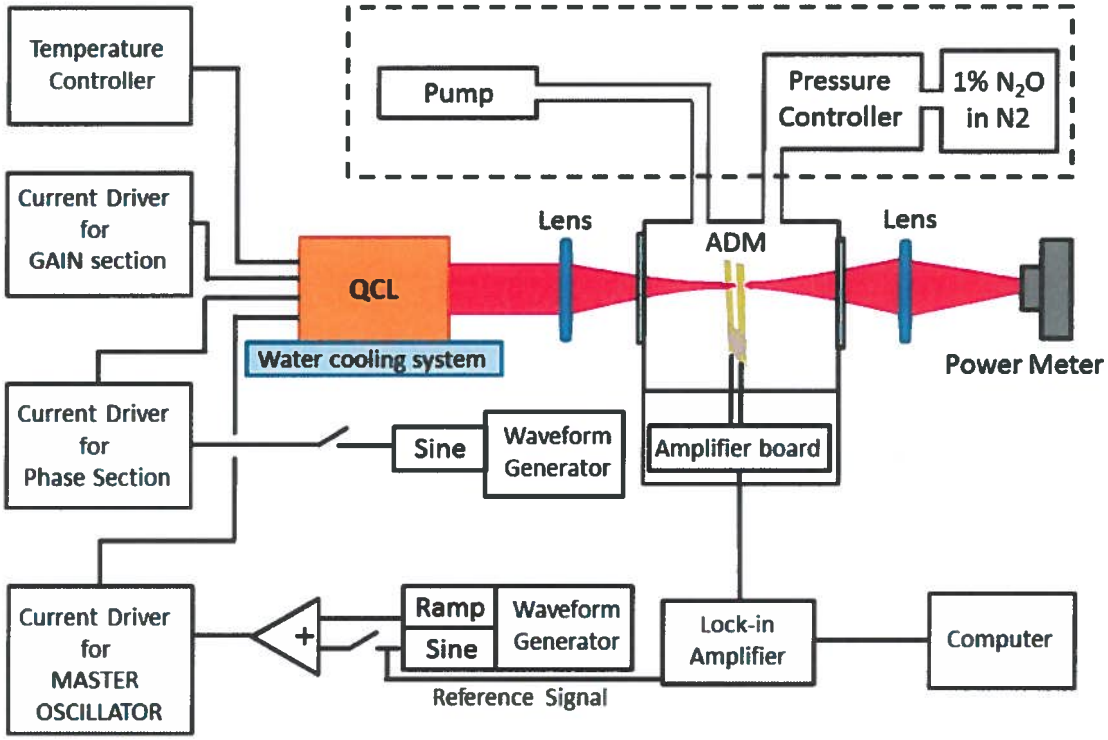



Figure 4. Schematic of the QEPAS experimental setup employed for the detection of $N_2O$ in a gas mixture composed of 1% $N_2O$ in pure $N_2$, at a pressure of 85 Torr. QCL – Quantum Cascade Laser. ADM – Acoustic Detection Module.

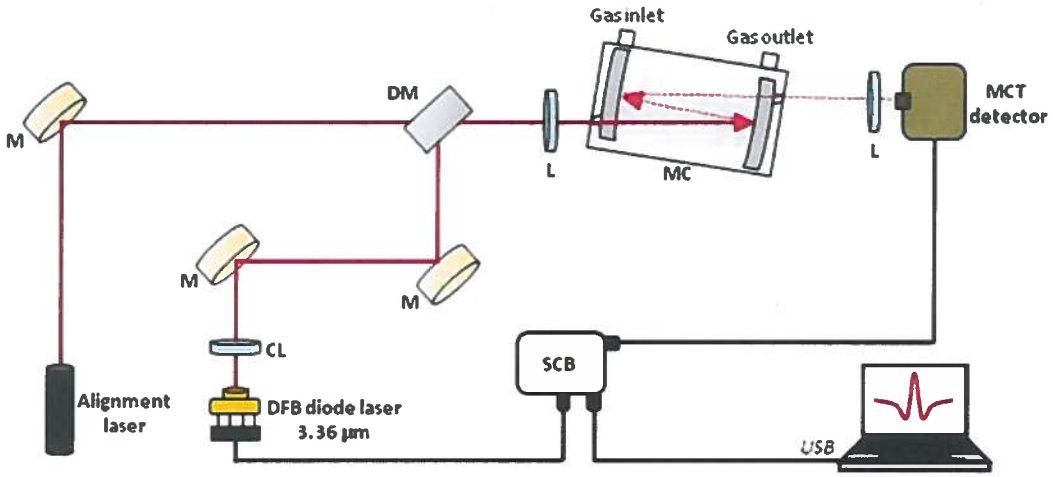
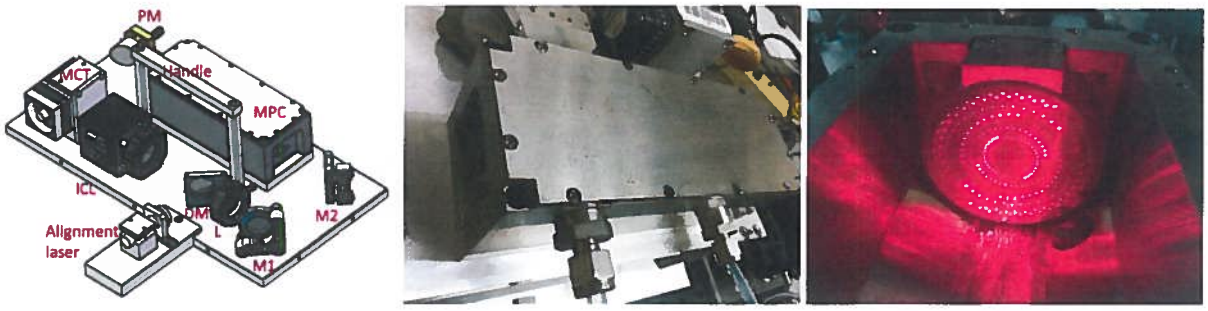



Figure 5. Schematic of a $C_2H_6$ gas sensor using a Nanoplus 3.36 µm DFB laser diode. M – mirror, CL – collimating lens, DM – dichroic mirror, MC – multipass cell, L – lens, SCB – sensor control board.




(a) (b) (c)

Figure 6. (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.

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