A Compact CW Quantum Cascade Laser based QEPAS Sensor for Sensitive Detection of Nitric Oxide

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Abstract: The development of a compact NO QEPAS-based sensor platform employing a CW DFB-QCL will be reported. A detection sensitivity of 4 ppbv wass achieved with a 1-sec averaging time for the 1900.08 cm-1 NO line

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1. Introduction

The capability of detecting and quantifying nitric oxide (NO) at ppbv (parts per billion by volume) concentration levels has an important impact in diverse fields of applications including environmental monitoring, industrial process control and medical diagnostics. The major sources of NO emission into the atmosphere are associated with industrial combustion processes as well as automobile, truck, aircraft and marine transport emissions. Long term, continuous and reliable NO concentration measurements in ambient air are important because of NO's role in the depletion of earth's ozone layer and in the formation of acid rain and smog [1]. Furthermore, NO is associated with numerous physiological processes in the human body and particularly it can be used as a biomarker of asthma and inflammatory lung diseases such as chronic obstructive pulmonary disease [2]. This report will describe the development of sensitive and selective sensor technology, capable of detecting and monitoring NO at single ppbv concentration levels with a time response of 1-sec, for environmental monitoring and noninvasive exhaled breath analysis [3].

2. Quartz-enhanced photoacoustic spectroscopy

Quartz-enhanced photoacoustic spectroscopy (QEPAS), first reported in 2002, is a sensitive technique that allows performing measurement of trace gases in an ultra small absorption detection module (ADM) where the total volume of the analyzed gas sample is ~4 mm^3 [4]. The QEPAS technique employs a 32 kHz quartz tuning fork (QTF) as a sharply resonant acoustic transducer, instead of a broadband electric microphone used in conventional photoacoustic spectroscopy (CPAS). The QTF is a piezo-electric element, capable of detecting weak acoustic waves generated when the modulated optical radiation interacts with a trace gas, and converting its deformation into a separation of electrical charges. An enhancement of the QEPAS signal can be achieved when two metallic tubes acting as a micro-resonator (mR) are added to the QTF sensor architecture. In a typical QEPAS configuration the QTF is positioned between the mR tubes to probe the acoustic waves excited in the gas contained inside the mR [5-9]. A recent optimization study of the geometrical mR parameters showed that the highest QEPAS signal-to-noise ratio (SNR) is achieved for two 4.4 mm-long and 0.5-0.6 mm inner diameter tubes [6]. However for a typical QCL beam, short mR tubes with a larger inner diameter are advantageous in facilitating the optical alignment of the QCL excitation beam with the respect to the mR and the QTF. Therefore for the DFB-QCL based NO QEPAS measurements a length and an inner diameter of the mR tubes of 4.0 mm and 0.84 mm, respectively were selected. Furthermore, an additional enhancement of the NO QEPAS signal amplitude can be achieved by blending an analyzed mixture with water vapor, which is known to be an efficient catalyst for V-T relaxation in the gas phase.

3. Sensor architecture and optimization of NO QEPAS detection

A prototype NO QEPAS-based sensor installed on a 12 x 5 inches platform is depicted in Fig. 1. A CW Maxion Technologies/Physical Sciences Inc. DFB-QCL was employed to target the 1900.08 cm^{-1} (5.26 μm) NO doublet absorption line of the NO fundamental band. The high heat load (HHL) packaged DFB-QCL emitted ~100mW optical power at an operating temperature of 19 °C. For sensitive NO concentration measurements a 2f wavelength-modulation (WM) technique was used.

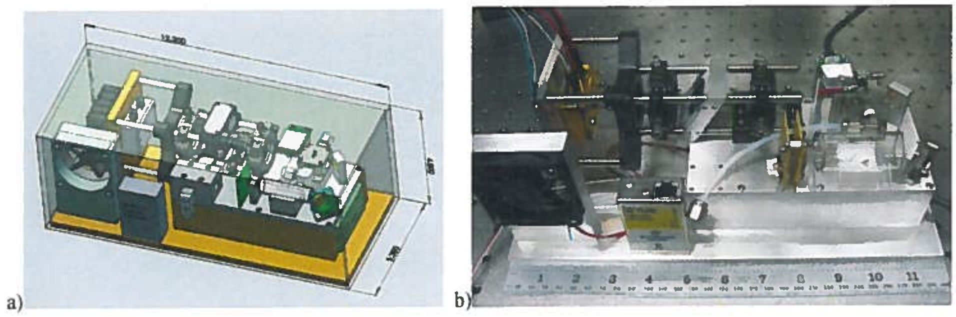

Fig 1 Schematic (a) and completed design (b) of a compact room temperature, CW, DFB QCL based NO Sensor platform.

In order to improve the quality of the QCL beam two 25 mm focal length plano-convex Ge lenses with broadband antireflection (AR) coatings and 150 μm pinhole are used as a special filter. The second lens is used to direct the laser radiation through the mR and between the prongs of QTF mounted inside the ADM with a transmission efficiency of 98%. The exiting QCL beam from the ADM is directed to 5 cm long reference cell, filled with a 0.11% NO in N_2 mixture at 175 Torr and a pyroelectric detector (InfraTec, LIE-332f-63). A 3f pyroelectric detector signal with a zero crossing point at the maximum of the 2f WM QEPAS signal was used as the sig reference for the line-locking technique. All the measurements were performed at a gas pressure of 250 Torr which according to previous experimental results is within the optimal pressure range for QEPAS based NO detection [9].

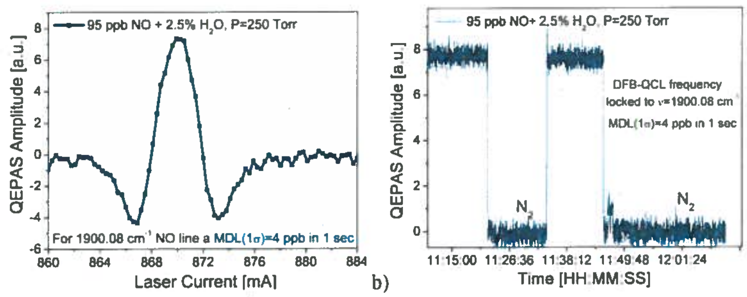

Fig 2. 2f QEPAS signal amplitude when QCL frequency is tuned across (a) and locked (b) to the NO doublet absorption line at 1900.08 cm^{-1}.

An amplitude of 2f QEPAS signal when the DFB-QCL frequency is tuned across and locked to the H_2O and CO_2 interference-free NO doublet absorption line at 1900.08 cm^{-1} is depicted in Fig. 2a and 2b, respectively. For a 95 ppb NO in N_2 calibrated mixture and 2.5 % water vapor concentration the calculated noise-equivalent (1σ) concentration of NO with a 1s averaging time is 4 ppbv at gas pressure of 250 torr. The corresponding absorption coefficient normalized to the detection bandwidth and optical power is 6.2×10^{-9} $cm^{-1}W/Hz^{1/2}$. With a detection sensitivity of single ppb concentration levels this compact, portable NO QEPAS sensor is suitable for applications in environmental monitoring, industrial processing, and medical diagnostics of human diseases .

4. References

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