Sensitive detection of nitric oxide using a 5.26 μm external cavity quantum cascade laser based QEPAS sensor

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ABSTRACT

The development and performance of a continuous wave (CW), thermoelectrically cooled (TEC) external cavity quantum cascade laser (EC-QCL) based sensor for quantitative measurements of nitric oxide (NO) concentrations in exhaled breath will be reported. Human breath contains ~ 400 different chemical species, usually at ultra low concentration levels, which can serve as biomarkers for the identification and monitoring of human diseases or wellness states. By monitoring exhaled NO concentration levels, a fast non-invasive diagnostic method for treatment of patients with asthma and chronic obstructive pulmonary disease (COPD) is feasible. The NO concentration measurements are performed with a 2*f* wavelength modulation based quartz enhanced photoacoustic spectroscopy (QEPAS) technique, which is very suitable for real time breath measurements, due to the fast gas exchange inside a compact QEPAS gas cell (<5 mm^3 typical volume). In order to target the optimal interference free NO R (6.5) absorption doublet at 1900.08 cm^{-1} (λ~5.263 μm) a Daylight Solutions Inc. widely tunable, mode-hop free 100 mW EC-QCL was used. The sensor reference channel includes a 10 cm long reference cell, filled with a 0.5% NO in N_2 at 150 Torr, which is used for line-locking purpose. A minimum detection limit (1σ) for the EC-QCL based line locked NO sensor is ~5 ppbv with a 1 sec update time by a custom built control QCL compatible electronics unit.

Keywords: Quartz enhanced photoacoustic spectroscopy, Quantum cascade lasers, Trace gas detection, Exhaled breath analysis, Nitric oxide, Asthma and chronic pulmonary obstructive disease

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, 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 rains and smog [1]. Furthermore, it was found that NO is associated with

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numerous physiological processes in the human body. In particular, NO can be used as a biomarker of asthma and inflammatory lung diseases such as chronic obstructive pulmonary disease [2]. This paper describes development of sensitive and selective sensor technology, capable of detecting and monitoring single ppbV NO concentration levels with a time response of 1 sec, for environmental monitoring and noninvasive exhaled breath analysis [3].

Quartz-enhanced photoacoustic spectroscopy (QEPAS), first reported in 2002, is a gas-sensing technique that features an absorption detection module (ADM) with dimensions of 10-20 mm [4]. QEPAS allows performing sensitive measurement of trace gases in gas sample of a few mm^3 in volume. The QEPAS technique employs a 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. The mechanical deformation of the QTF due to interaction with the acoustic waves results in the generation of electrical charges on its electrode pairs

In order to further enhance the QEPAS signal, a so-called micro-resonator (mR) can be added to the QTF sensor architecture. The mR typically consists of two metallic [4] or glass tubes [5]. The QTF is positioned between the tubes to probe the acoustic waves excited in the gas contained inside the mR. To date, such a configuration has been used in most reported QEPAS based gas sensors [5-11]. Moreover, a recent optimization study revealed that for a 32kHz QTF, two 4.4 mm-long tubes with 0.5-0.6 mm inner diameter yields the highest QEPAS signal-to-noise ratio (SNR) [6]. These optimum tube parameters have been adopted in a near-infrared (NIR) fiber-coupled semiconductor diode laser based QEPAS sensors where the typical size of the NIR beam spot, after using a fiber-coupled optical focuser, is <100 μm. In such systems, a clear NIR beam passage through the ADM is observed, resulting in zero background and excellent detection results [7, 8]. However, these optimum mR tube parameters are not suitable for a free space mid-infrared (MIR) QEPAS sensor configuration due to much more challenging process of focusing a typical ~3 mm-diameter MIR beam through the mR and 300 μm gap between QTF's prongs. In fact, the radiation that is blocked by the mR or QTF or absorbed by the ADM structural elements results in an undesirable non-zero background. This background is usually several times larger than the thermal noise level of QEPAS and carries a shifting fringe-like interference pattern, which limits the detection sensitivity of QEPAS [9].

For a typical QCL beam, short mR tubes with a larger inner diameter are advantageous in facilitating optical alignment of the QCL excitation beam with the mR and the QTF. In this paper, we particularly address this issue by performing experimental measurements using ADMs with different tube sizes so that we were able to determine the optimized geometrical mR parameters to meet sensitivity requirements for a specific QCL based QEPAS application. Subsequently, the optimized mR tubes were applied to the NO detection, using a 5.26 μm, CW, thermoelectrically cooled (TEC), external cavity quantum cascade laser (EC-QCL) commercially available from Daylight Solutions Inc. as an excitation source. We also investigated the effect of different concentrations levels of water vapor in a NO mixture on QEPAS signals, since the presence of water vapor can act as a catalyst for the vibrational energy transfer and therefore enhance measured NO signal amplitude. The effective overall characteristic performance of EC-QCL based NO QEPAS sensor was determined.

2. OPITIZATION OF QEPAS mR FOR QCL BASED SENSOR APPLICATIONS

To assess the optimum mR performance, the QEPAS SNR must be used as the selection criterion. The amplitude of QEPAS signal is determined by the following five factors: 1. QTF Q factor, 2. enhancement factor of the acoustic mR, 3. peak intensity of the absorption line of the desired trace gas species, 4. vibrational-translational (V-T) relaxation rate of target gas and 5. laser modulation depth. The first four factors depend on pressure, while the fifth factor, the laser modulation depth, must match the pressure dependent absorption line width. In order for the enhancement factor of mR to dominate the amplitude of QEPAS signal, an experimental characterization similar to the one reported in Ref [6] was performed. A C_2H_2 absorption line at 6529.17 cm^{-1} with 6.31×10^{-7} cm^{-1} peak absorption was used as the target line [12]. The C_2H_2 has a fast V-T relaxation rate, 72.8 ns at 25 ℃ [13], which can be considered instantaneous for the $1/f_0$ time scale where f_0 is the resonant frequency of the QTF. The laser modulation depth was set to the optimal value based on different pressures. Thus, at a certain pressure, the influence of factors 3 to 5 on the amplitude of QEPAS signal can be neglected. Since the interaction of sound wave fields in the mR and between the prongs of QTF impacts the QTF's parameters, the QTF's Q factor is not an independent variable. Hence, the factors 1 to 2 can be combined as one factor, which is determined by the geometrical mR parameters.

It has been verified from theoretical and experimental analysis that the primary noise source affecting measured QEPAS signals is the thermal noise associated with the QTF at the resonant frequency f_0. Its root mean square (rms) voltage value can be expressed as [14]:

$$\sqrt{V_{\mathrm{rms}}^2} = R_{\mathrm{g}}\sqrt{\frac{4k_{\mathrm{B}}T}{R}}\sqrt{\Delta f}, \qquad (1)$$

$$R = \frac{1}{Q}\sqrt{\frac{L}{C}}, \qquad (2)$$

where Δf is the detection bandwidth, k_{B} is the Boltzmann constant, T is QTF temperature, R_{g} is the value of the feedback resistor in transimpedance amplifier, and R, L, and C are the electrical parameters of the QTF when it is represented by the equivalent serial resonant circuit.

The results of SNR as a function of pressure measurements obtained for mR tubes of different lengths and internal diameter size are plotted in Fig.1. The results of a bare QTF and a QTF with the NIR optimal mR tubes (4.4 mm-long, 0.6 mm inner diameter) are also shown in Fig.1 as SNR level references. The SNR of the 3.9 mm-long mR tubes are lower but close to that of the NIR optimal length mR tubes, especially at lower pressures. For the pressure ranges between 20 to 100 Torr, the 3.9 mm-long mR tubes with inner diameters of 0.76 mm and 0.84 mm have practically the same SNR as the NIR optimal mR tubes. In the pressure range between 100 to 250 Torr, the 3.9 mm-long mR tubes with 0.76 mm inner diameter results in the same SNR as the NIR optimal mR tubes, while the 0.84 inner diameter tubes have a ~10% lower SNR.

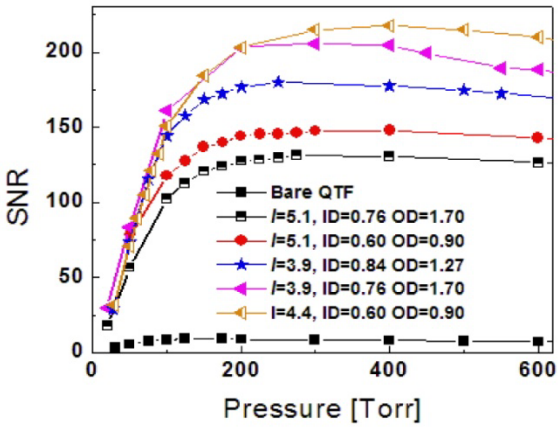

Fig. 1 Signal-to-noise ratio as a function of pressure for mR tubes.of different inner and out diameters; l-length of each mR tube; ID, OD-inner and outer diameter of the mR tube. The data for a bare QTF are shown as a reference.

For pressures above 250 Torr, the 3.9 mm-long mR tubes with 0.76 mm inner diameter result in a 10% decrease of the SNR compared to the SNR for NIR optimal mR tubes. For the 0.84 mm inner diameter tubes, the decrease of the SNR can be up to 20% SNR. When determining the optimum MIR mR parameters, a major design rule is that tubes with wider inner diameter are preferable provided that the SNR does not decrease significantly. Therefore, based on the sensor operating pressure, the geometrical mR parameters can be optimized to achieve MIR SNR values that are close to NIR optimal mR tubes.

3. EXPERIMENTAL SETUP AND OPTIMIZATION OF NO QEPAS DETECTION

A schematic of the QEPAS sensor for NO detection is depicted in Fig. 2. The sensor platform is based on a 2*f* wavelength-modulation spectroscopy (WMS) and QEPAS-detection approach. A widely tunable CW EC-QCL (Daylight Solutions Inc., model 21052-MHF) served as the excitation source for generating the QEPAS signal. The EC-QCL frequency tuning was achieved by applying a voltage to the piezoelectric translator that controls a diffraction grating angle. A continuous spectral tuning range from 1763 to 1949 cm^{-1} was obtained at a QCL operating temperature of 16.5 °C and a maximum QCL current of 450 mA. The diameter of collimated EC-QCL output beam was ~3 mm. Two 25 mm focal length plano-convex Ge lenses with broadband antireflection (AR) coating were used to focus the laser radiation through the mR and the prongs of QTF and to re-collimate the laser beam upon exiting the ADM. A beam diameter of ~20 μm at the center of the prongs of QTF was obtained from a theoretical calculation using the above-mentioned two lenses. Since previous results showed that the optimal pressure range for NO detection is from 150 and 250 Torr [9], an acoustic mR consisting of two hypodermic tubes, each 3.9 mm long with 0.84 mm inner diameter, was mounted on both side of the QTF. These mR tube parameters result in an optical power transmission of 99% through the mR and the QTF. A beam splitter was inserted, which directs a portion of the EC-QCL radiation to a reference channel consisting of 10 cm

long reference cell, filled with a 0.5% NO in N_2 at 150 Torr and a pyroelectric detector (InfraTec, LIE-332f-63). The beam splitter allowed most of the laser radiation to pass and provides convenient monitoring of the EC-QCL output with a power meter (Ophir, 3A-SH). The QTF was connected to an ultra-low noise transimpedance amplifier with a 10 MΩ feedback resistor that converted the current generated by QTF into a voltage.

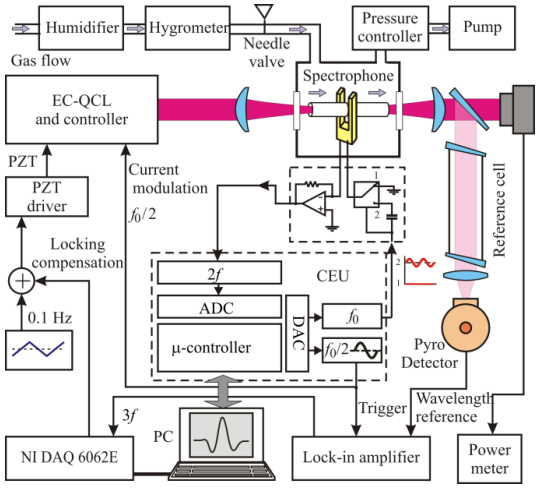

Fig. 2 Schematic of an EC-QCL based NO sensor system

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This voltage was directed to a custom made control electronics unit (CEU) [15], which was employed to realize three functions: 1. to measure three QTF parameters, i.e. the resonant frequency f_0, quality factor Q and resistance R of the QTF, 2. to modulate the laser current at the frequency $f = f_0/2$, and 3. to measure the $2f$ harmonic component generated by the QTF. The CEU converted the measured current to QEPAS signal counts (1 cnt = 6.67×10^{-16}A). A notebook PC computer communicating with the CEU via a RS232 serial port collected the $2f$ harmonic data. The QTF and mR were enclosed inside a gas enclosure with AR coated ZnSe windows. A pressure controller (MKS Instruments, Inc.,Type 640) and an oil free vacuum pump were placed downstream to control and maintain the NO sensor system pressure. A Nafion humidifier (PermaPure) and a hygrometer (DewMaster, EdgeTech) were connected to the upstream side of the ADM gas cell to add water vapor to the gas mixture and monitor the water content, respectively. A needle valve was employed to set the gas flow to a constant rate of 100 scc/min.

The QEPAS based NO concentration measurements were carried out in two operational modes. In a scan mode a 0.1 Hz triangular wave with amplitude of 25.5 V_{pp} was applied to the piezoelectric translator of the EC-QCL resulting in mode-hop-free QCL frequency tuning over the targeted absorption line. In a locked mode the QCL frequency was initially set to the center of the absorption line. The $3f$ component from the pyroelectric detector was measured by a lock-in amplifier (Stanford Research systems, SR830), subsequently regulated by a Labview-software based proportional-integral-derivative (PID) controller, and finally directed to an electronic adder. The PID controller compensates any laser frequency shift by generating a correction signal to keep the laser frequency always at the center of the absorption line.

The electronic adder combined the PID compensation signal and the DC voltage setting the QCL frequency to the center of absorption line, and then directed feed-back to the PZT of the EC-QCL.

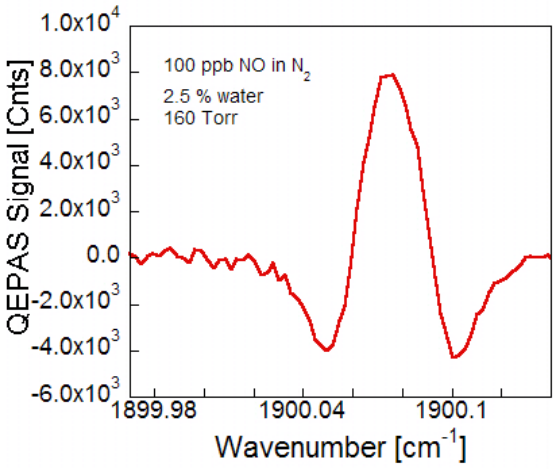

Fig.3 A QEPAS spectrum of the NO absorption doublet at 1900.08 cm^{-1}. The QEPAS signal is recorded in terms of internal CEU units, where 1cnt=6.67×10^{-16}A

The H_2O and CO_2 interference-free NO doublet absorption lines centered at 1900.08 cm^{-1} were found to be optimal for QEPAS based NO detection [11]. A spectral scan of a 100 ppb NO sample at 160 Torr is depicted in Fig. 3. In this scan, there was no background subtraction performed. Compared to Ref [9], no fringe-like interference pattern was observed in Fig. 3, which is the result of using mR tubes with optimal dimensions. The two lines in the doublet are so close that they are unresolved even at low pressure conditions. To optimize NO QEPAS detection performance, both the gas pressure and the wavelength modulation depth must be appropriately chosen. Based on the data in Fig. 3, the NO concentration that results in a noise-equivalent (1σ) concentration with a 1s averaging time is ~5 ppbv. The corresponding absorption coefficient normalized to the detection bandwidth and optical power is 5.6×10^{-9} $cm^{-1}W/Hz^{1/2}$.

4. CONCLUSIONS AND FUTURE OUTLOOK

Monitoring of nitric oxide concentration in exhaled breath using laser spectroscopy techniques provides a fast, noninvasive, diagnostic method for human subjects. The achieved minimum detection limit (1σ) for CW TEC EC-QCL NO sensor operating in line scanning and line locked modes at the NO R (6.5) absorption doublet centered at 1900.08 cm^{-1} (λ~5.263 μm) is ~5 ppbv with a 1 sec update time by a custom built control QCL compatible control electronics unit [16]. This sensitivity is sufficient for detecting exhaled breath nitric oxide concentrations, which are estimated to be between 0 and 100 ppb in healthy humans. The QEPAS sensor technology has been demonstrated to be a robust technology for the development of sensitive, compact sensor systems that can be used in a doctor's office for noninvasive verification of a human subject's medical condition. The same platform is suitable for environmental monitoring and industrial process analysis using not only NO as the target analyte, but will be used to detect, monitor and quantify atmospheric SO_2, CO and NH_3. Recently a 5.26 μm, 100mW CW Maxion Technologies/Physical Sciences

Inc. air-cooled DFB-QCL mounted in a high heat load (HHL) package and operating at 19 °C, was employed in order to significantly reduce size of the NO QEPAS-based sensor platform to ~12.3x5.3x4.8 in.

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