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# Carbon dioxide and ammonia detection using 2 $\mu\text{m}$ diode laser based quartz-enhanced photoacoustic spectroscopy

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Received: 12 September 2006

Published online: 9 November 2006 • © Springer-Verlag 2006

**ABSTRACT** Quartz-enhanced photoacoustic spectroscopy was employed for trace gas concentration measurements of  $\text{CO}_2$  and  $\text{NH}_3$  using a continuous wave thermoelectrically cooled, distributed feedback diode laser operating at 2  $\mu\text{m}$ . A normalized noise equivalent absorption coefficient,  $\text{NNEA}(1\sigma) = 1.4 \times 10^{-8} \text{ cm}^{-1} \text{ W}/\sqrt{\text{Hz}}$  was obtained for  $\text{CO}_2$  using the  $R18$  line of the  $2\nu_1 + \nu_3$  band at  $4991.26 \text{ cm}^{-1}$ . This corresponds to minimum detection limit ( $1\sigma$ ) of 18 parts per million (ppm) for a 1 s lock-in time constant. The influence of the  $\text{H}_2\text{O}$  presence in the sample gas mixture on the  $\text{CO}_2$  sensor performance was investigated. Ammonia detection was performed using the  ${}^P P_6(6)_S$  line of the  $\nu_3 + \nu_4$  band at  $4986.99 \text{ cm}^{-1}$ . A detection limit ( $1\sigma$ ) of 3 ppm for  $\text{NH}_3$  concentration with a 1 s lock-in time constant was achieved. This results in a normalized noise equivalent absorption of  $\text{NNEA}(1\sigma) = 8.9 \times 10^{-9} \text{ cm}^{-1} \text{ W}/\sqrt{\text{Hz}}$ .

PACS 82.80.Kq; 46.62.Fi; 42.55.Px

using a quartz tuning fork (QTF) [9]. The key innovation of this latter method, named quartz enhanced photoacoustic spectroscopy (QEPAS) is to accumulate the acoustic energy in a sharply resonant piezoelectric transducer with a very high quality factor ( $Q$ -factor) of  $> 10\,000$  instead of using broadband microphone and low  $Q$  ( $\sim 200$ ) resonant photoacoustic gas cell. QEPAS employs commercially available 32.8 kHz quartz tuning forks used as a frequency standard in digital clock circuits. Due to their excellent resonant and piezoelectric parameters, QTFs are also used as a shear force detector in near-field scanning [10], atomic force and magnetic force microscope applications [11, 12]. The most important features of QEPAS include a detection sensitivity comparable to traditional laser based PAS, high immunity to environmental acoustic noise, the feasibility to analyze ultra small gas samples (volume of analyzed gas sample is only limited by the dimensions of the QTF, which is  $\sim 1 \text{ mm}^3$ ) and a compact trace gas sensor platform.

The photoacoustic signal measured by QEPAS sensor is proportional to the following:

$$S_0 \sim \frac{\alpha \cdot P \cdot Q}{f_0}, \quad (1)$$

where  $\alpha$  is an absorption coefficient,  $P$  is optical power,  $Q$  is quality factor of the resonator and  $f_0$  is resonant frequency [13].  $Q$ -factor is dependent on pressure ( $Q = \frac{Q_{\text{vac}}}{1 + Q_{\text{vac}} \cdot a \cdot P^b}$ , where  $Q_{\text{vac}}$  is the quality factor in vacuum and  $a$  and  $b$  are parameters dependent on a specific TF design [14]), and pressure has also an influence on molecular relaxation time  $\tau$  of measured species ( $\tau \sim \frac{1}{p}$ ) and the absorption coefficient  $\alpha$ . Therefore it is necessary to select optimum working conditions for a QEPAS based trace gas sensor in order to obtain the best detection sensitivity.

## 2 Experimental details

In this work a continuous wave (CW) distributed feedback diode laser (NTT/NEL KELD1G5B2TA) operating at  $\lambda = 2 \mu\text{m}$  was employed as a spectroscopic light source. This diode laser delivers a power of 6.2 mW at  $T = 25 \text{ }^\circ\text{C}$ . Coarse tuning of this near infrared (NIR) laser in the range from  $4982 \text{ cm}^{-1}$  to  $4993 \text{ cm}^{-1}$  is performed by changing the diode laser temperature from  $41 \text{ }^\circ\text{C}$  to  $12 \text{ }^\circ\text{C}$ , respectively,

## 1 Introduction

Laser photoacoustic spectroscopy (PAS) is a well established method used in trace gas sensing applications, providing high chemical selectivity and sensitivity. Absorption of laser radiation in a gas sample causes a local temperature rise, which results in a pressure change. By using modulated laser radiation at an audio frequency, an acoustic wave is produced. The intensity of an acoustic signal created in this manner reflects the optical absorption of the gas sample. The most common transducer employed to detect a photoacoustic signal is a sensitive microphone [1–3]. Since the photoacoustic signal is proportional to optical excitation power of the light source, it is possible to achieve minimum detectable concentrations at the sub-ppb level [4–6] using high power laser sources such as continuous wave  $\text{CO}_2$  and CO lasers, optical parametric oscillators and fiber amplifiers. In recent years several other methods of PAS signal detection were reported such as, utilization of a silicon cantilever in combination with a compact Michelson-type interferometer [7], an optical cantilever microphone [8] or a technique

while fine tuning is realized by changing the diode laser current with a tuning coefficient of 18.08 nm/A.

The QEPAS-based gas sensor architecture is depicted in Fig. 1. The  $Q$  factor of the tuning fork used in this work is  $\sim 21\,000$  at 50 Torr and decreases to 12 500 at atmospheric pressure, with resonant frequencies of  $f_0 = 32\,762$  Hz and  $f_0 = 32\,756$  Hz, respectively. The  $\lambda = 2\ \mu\text{m}$  DFB diode laser beam is collimated by a 8 mm focal length aspherical Corning glass lens (Thorlabs, model C0550). Subsequently the laser beam is focused between TF prongs by using a 1-inch diameter BK7 lens with a 75 mm focal length.

As reported in [12] an acoustic micro-resonator can enhance the QEPAS signal, and hence increase the detection sensitivity up to 10 times. Therefore glass tubes with a length of 2.45 mm each and inner diameter of 0.4 mm were mounted on both sides of the QTF. The total length of the micro-resonator, which includes length of the tubes, the QTF thickness (0.34 mm) and the 0.06 mm gaps on each side of the QTF, was adjusted to match  $\frac{1}{2}$  of the acoustic wavelength in air at  $\sim 32.76$  kHz.

A  $2f$  wavelength modulation technique was implemented by applying a sinusoidal modulation of the diode laser current at half of the QTF resonance frequency ( $f = f_0/2 \sim 16.38$  kHz) and detecting the QTF response at  $2f$  by means of a lock-in amplifier. The highest amplitude of the  $2f$  harmonic component  $A(2f)$  achieved at the absorption line center is generally lower than the highest amplitude of the first component  $A(f)$ . Assuming the Lorentzian absorption line shape and using the equations from [15] (Sect. 3.III, "Wavelength and Amplitude Modulation of the Excitation Source"), it can be calculated that  $A(2f)/A(f) \approx 0.7$ . However the residual amplitude modulation (RAM) signal created at  $1f$  during the laser current modulation is strongly suppressed at higher harmonics. For an ideal diode laser where the output power is linear with injection current the RAM is zero for  $2f$  and higher-harmonic detection [16]. Therefore second harmonic detection is ideally a zero-background technique. This minimizes the influence of adjacent broad absorption tails on the measured QEPAS signal. Besides, second harmonic always reaches its maximum value at the absorp-

tion line center, thus allowing locked-to-line sensor operation mode.

The QTF-micro resonator assembly is placed in a sealed enclosure. Such an assembly together with a low noise transimpedance preamplifier is called an absorption detection module (ADM). The incident laser beam passes through the microresonator and between the QTF prongs. The pressure and the flow of the sample gas within the ADM are controlled and maintained at the optimum level using a pressure controller (MKS Instruments Type 640) and a ball flow meter (Key Instruments). The flow of the gas mixture was always at a constant rate of 50 ml/min. The power of the laser radiation that exits the ADM is monitored with a power meter for normalization of QEPAS signals. A part of the emitted laser power is lost when the beam passes through two sapphire windows (transmittance of the sapphire for  $2\ \mu\text{m}$  is  $\sim 85\%$ ). Therefore this must be taken into account in order to determine the optical power present between the prongs of the QTF.

A piezoelectric current generated in the TF is amplified by a custom designed transimpedance amplifier (feedback resistor  $R_{fb} = 10\ \text{M}\Omega$ ). Subsequently the signal is demodulated by a lock-in amplifier (Signal Recovery Model 7265) and delivered to a data acquisition card (National Instruments DAQCard AI-16XE-50), which is connected to a personal computer. The lock-in amplifier and a function generator (Stanford Research Systems Model DS345) are controlled through a serial communications port (RS232) using LabVIEW-based software. The time constant of the lock-in amplifier was set to 1 s for all QEPAS-based measurements performed in this work.

### 3 Experimental results and discussion

The main objective for this work was improving the detection sensitivity of  $\text{CO}_2$  and  $\text{NH}_3$  as compared to that previously reported [17] for a QEPAS-based gas sensor. Several  $\text{CO}_2$  lines from the  $R$  branch of the  $2\nu_1 + \nu_3$  band can be reached within the spectral tuning range of the  $2\ \mu\text{m}$  diode laser (see Fig. 2 taken from HITRAN96 database [18]). The best lines for  $\text{CO}_2$  detection in this spectral region are the lines  $R16$  and  $R18$ , which have the highest line intensity and the least interference from  $\text{H}_2\text{O}$ . In order to perform the direct sensitivity comparison to the results presented in [17], the  $R18$  line at  $4991.26\ \text{cm}^{-1}$  is selected, which has a line intensity of  $1.302 \times 10^{-21}\ \text{cm}^{-1}/\text{mol cm}^{-2}$ . The laser radiation was at resonance with this absorption line at the laser diode current of 80 mA when its temperature was set to  $19.1\ ^\circ\text{C}$ . In addition to the  $\text{CO}_2$  absorption lines several  $\text{NH}_3$  lines from the combination band  $\nu_3 + \nu_4$  can be targeted (see also Fig. 2). The strongest and interference free line is the  ${}^P P_6(6)_S$  transition at  $4986.99\ \text{cm}^{-1}$  with a line intensity of  $7.703 \times 10^{-21}\ \text{cm}^{-1}/\text{mol cm}^{-2}$ .

As discussed in [17] the  $\text{H}_2\text{O}$  vapor presence influences the QEPAS response to  $\text{CO}_2$  by enhancing the vibrational translational ( $V-T$ ) energy transfer rate and thus increasing the PAS signal. However, the  $[\text{H}_2\text{O}]$  variation from 1.5% to 3.1% corresponding to the relative humidity of 48% and 100%, respectively, at  $+25\ ^\circ\text{C}$  and 760 Torr increases the sensor response by only 5%. Therefore, we carried out a se-

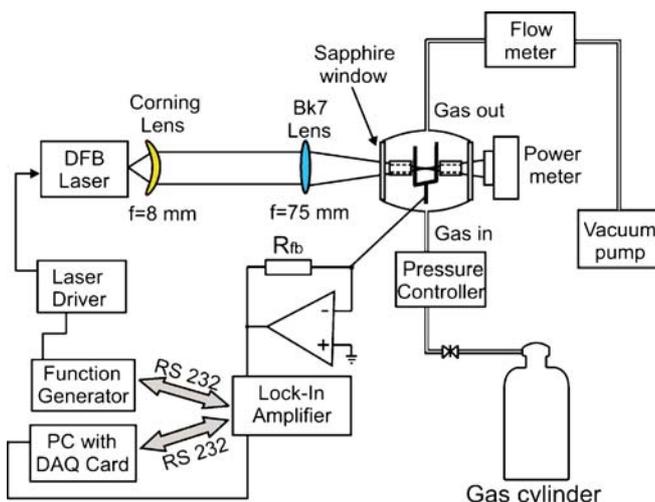
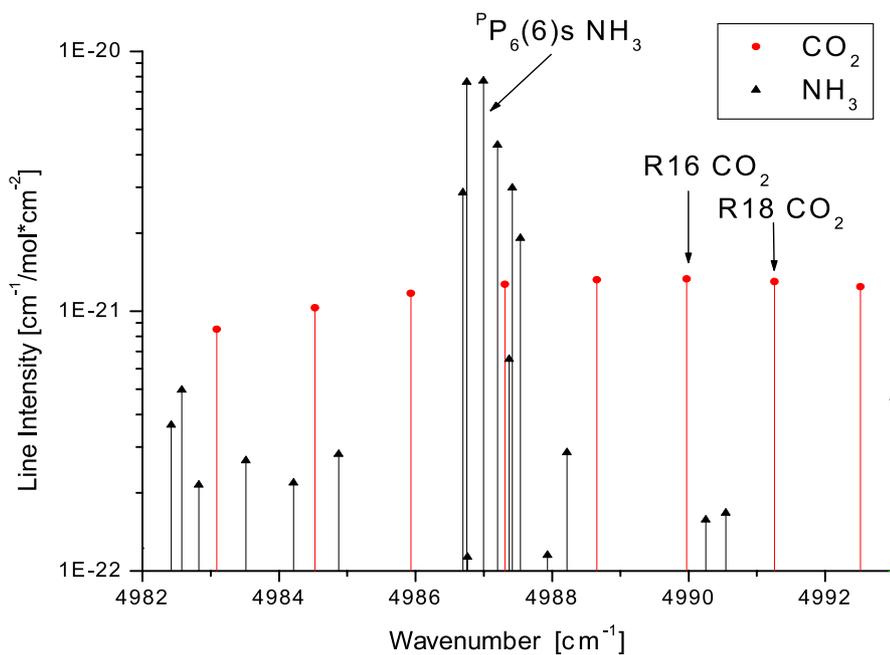


FIGURE 1 Schematic of a  $2\ \mu\text{m}$  DFB diode laser based QEPAS trace gas sensor



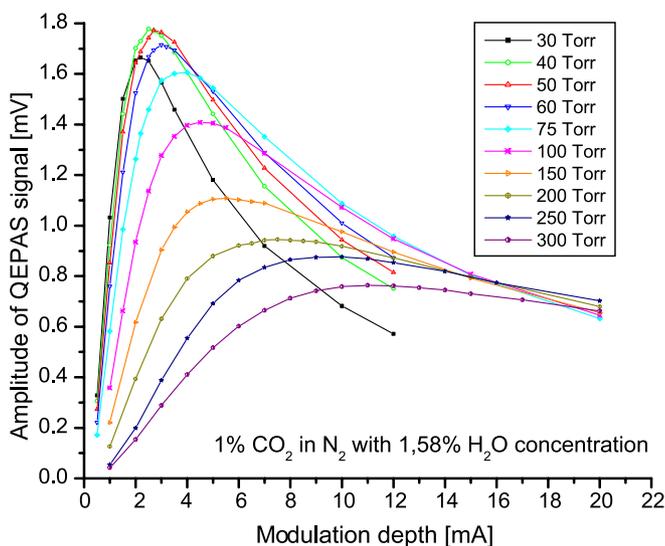
**FIGURE 2** Simulated intensity of  $\text{CO}_2$  and  $\text{NH}_3$  absorption lines (HITRAN96 database) [11], which can be accessed within the spectral tuning range of the 2  $\mu\text{m}$  DFB laser

ries of measurements to optimize the sensor performance at  $[\text{H}_2\text{O}] \sim 1.5\%$ . A certified gas mixture of 1%  $\text{CO}_2$  in  $\text{N}_2$  humidified by adding 1.58% of  $\text{H}_2\text{O}$  to the sample gas (51% of relative humidity at atmospheric pressure and 25  $^\circ\text{C}$ ) was used. Moisturizing was performed by passing the calibration gas through a  $\text{H}_2\text{O}$  bath at a temperature of 14.1  $^\circ\text{C}$  stabilized by a water chiller (Lauda RM6, Brinkmann). The flowing gas becomes saturated with water vapor and the concentration can be calculated using the published  $\text{H}_2\text{O}$  saturation vapor pressure data. The  $\text{H}_2\text{O}$  concentration was verified using another NIR diode laser and measuring the strength of  $\text{H}_2\text{O}$  absorption line at 7306.736  $\text{cm}^{-1}$ . Calibration curves for optimization of the QEPAS detection were acquired. The results presented in Fig. 3 depict the influence of pressure and laser modulation

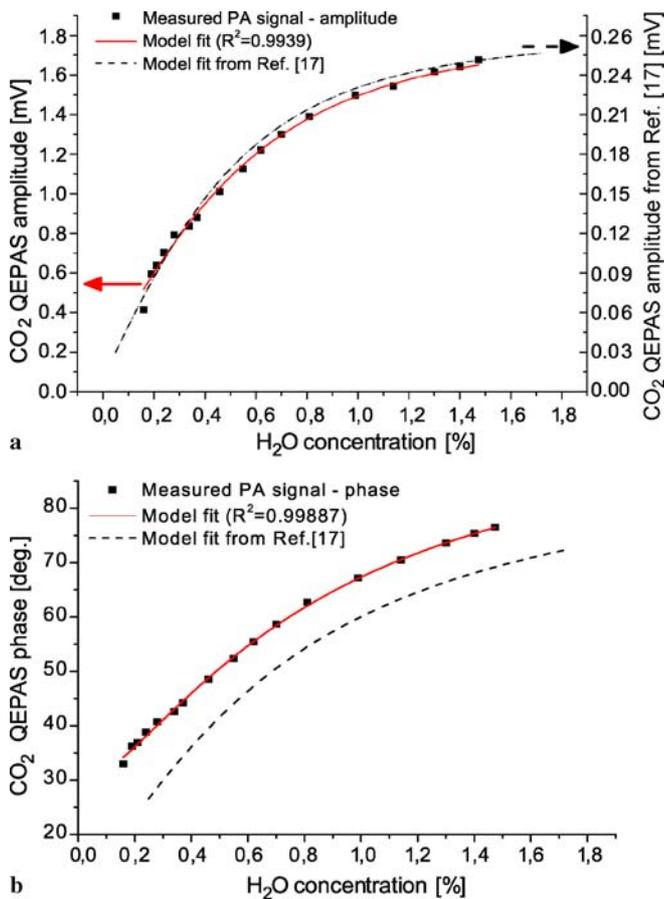
depth on the QEPAS signal amplitude. The optimum sensor operating conditions were found at a pressure of 50 Torr with a modulation depth of the diode laser current of 2.7 mA (3.4% of DC).

In order to vary the water content in the measured gas sample the humidified gas mixture was diluted by a dry gas mixture delivered directly from a reference gas cylinder using a custom built diluter. By changing the dilution ratio, the  $\text{H}_2\text{O}$  concentration in the produced mixture could be adjusted to the required level. The results illustrating the behavior of the  $\text{CO}_2$  QEPAS signal as a function of water concentration at different pressures are presented in Fig. 4.

The relaxation time for  $\text{CO}_2$  is dependent on the presence of other molecules and intermolecular interactions. The QEPAS measurements that are performed at the modulation frequency of  $f = 16.38$  kHz are more sensitive to the vibrational relaxation rate compared to the conventional PAS, which is commonly performed at  $< 4$  kHz frequency. In case of a slow  $V-T$  relaxation with respect to the modulation frequency ( $\omega\tau_{VT} \gg 1$ , where  $\omega = 2\pi f$ ), the translational gas temperature cannot follow fast changes of the laser induced molecular excitation rate. Thus the generated photoacoustic wave is weaker than it would be in case of instantaneous  $V-T$  energy equilibration. In a dry  $\text{CO}_2$ - $\text{N}_2$  mixture the vibrational energy can be transferred during collisions between  $\text{CO}_2$  and  $\text{N}_2$  molecules (the background gas) and also between  $\text{CO}_2$  molecules themselves.  $\text{CO}_2$ - $\text{CO}_2$  collisions at  $[\text{CO}_2] < 1\%$  do not accelerate the relaxation processes significantly. However, water addition to such a gas mixture makes the ( $V-T$ ) relaxation of excited  $\text{CO}_2$  molecules considerably faster. This likely occurs due to a strong dipole moment of the  $\text{H}_2\text{O}$  molecule. Water vapor is known to be an efficient catalyst for the vibrational energy transfer reactions in gas phase [19]. In the gas system studied in this work  $\text{H}_2\text{O}$  is a relaxation promoter for the energy stored in relatively slow relaxing  $\text{CO}_2$  vibrational states or trapped in a long living  $\text{N}_2(v=1)$  vibrational state [20, 21]. Therefore increasing water concen-



**FIGURE 3** QEPAS signal amplitude measured for  $\text{CO}_2$  as a function of diode laser modulation depth acquired at different pressures for a  $\text{CO}_2$ : $\text{N}_2$ : $\text{H}_2\text{O}$  mixture



**FIGURE 4** Dependence of the amplitude (a) and phase (b) of the measured photoacoustic CO<sub>2</sub> signal as a function of the H<sub>2</sub>O concentration. Data measured by QEPAS sensor (squares) are fitted with the calculated model curves (solid lines) and compared with model curves from [17] (dashed lines)

tration in the studied gas mixture causes increase of the detected CO<sub>2</sub> QEPAS signal amplitude and a simultaneous decrease of the photoacoustic signal phase lag ( $\varphi$ ). Experimental study and theoretical analysis of  $V$ - $T$  relaxation processes in a CO<sub>2</sub>:N<sub>2</sub>:H<sub>2</sub>O gas mixture by means of QEPAS is described in more detail in [17].

The above mentioned phase lag ( $\varphi$ ) introduced in part due to slow  $V$ - $T$  relaxation is monitored by lock-in amplifier and is used to determine the actual phase value of the photoacoustic signal ( $\Theta = \varphi_0 - \frac{\pi}{2} - \varphi$ ), where  $\varphi_0$  is the instrumental phase shift which has to be found out. When the modulation is slow in comparison to the  $V$ - $T$  relaxation time ( $\omega \cdot \tau \ll 1$ ), the  $\Theta$  value is close to  $\varphi_i = \varphi_0 - \frac{\pi}{2}$  [15]. This quasi-instantaneous relaxation is a good approximation of the CO<sub>2</sub> relaxation in the presence of a high concentration of H<sub>2</sub>O in the analyzed gas. On the other hand, when  $\omega \cdot \tau \gg 1$ , the phase lag is strongly increasing. This condition is satisfied in the dry CO<sub>2</sub>:N<sub>2</sub> mixture and results in a small photoacoustic signal amplitude. Due to such a strong influence of water vapor on the CO<sub>2</sub> relaxation, the gas mixture humidity should be monitored. At high CO<sub>2</sub> levels ( $> 0.05\%$ ) the H<sub>2</sub>O concentration can be estimated via the phase of the photoacoustic CO<sub>2</sub> signal as measured by means of QEPAS.

The measured amplitude and phase of the photoacoustic signal as a function of the humidity content in the gas are

shown in Fig. 4. For comparison, fitting curves from [17] describing the behavior of these parameters when measured with a QEPAS sensor without a microresonator are also plotted. The dependence of the PAS signal amplitude on the water content shown in Fig. 4 displays the same behavior independently of the presence of a microresonator, whereas the phase of the PAS signal shows a constant shift of  $\sim 7.5$  degrees within the entire range of the H<sub>2</sub>O contents.

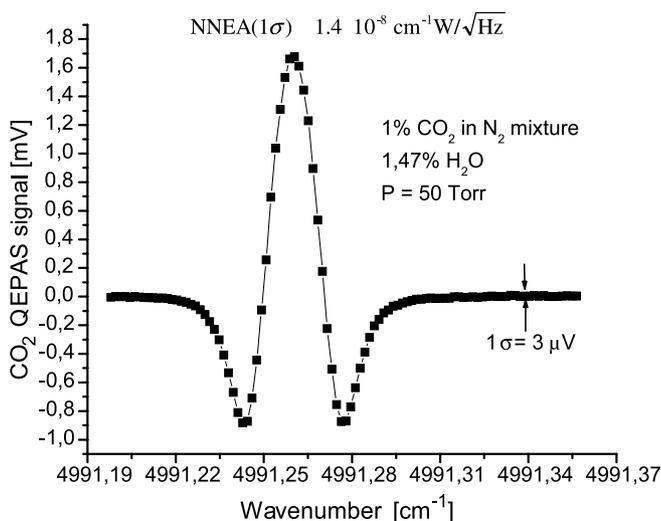
The mismatch between the absolute phase values observed in [17] and this work can be caused by the following reasons:

1. The optimum gas sample pressure was 60 Torr in [17] and 50 Torr in this work;
2. The carrier gas used in this study was N<sub>2</sub> as compared to air in [17];
3. The presence of the microresonator introduces a phase shift that is discussed in detail in [22].

At high H<sub>2</sub>O concentrations, the relaxation process of CO<sub>2</sub> molecules is dominated by CO<sub>2</sub>-H<sub>2</sub>O collisions. Therefore an increase of H<sub>2</sub>O concentration beyond a certain level has a small effect on the PAS signal. By using model fit (Fig. 4a) performed for the present system an increase of the water content from 1.47% to 3.1% ( $\sim 47\%$  and 100% relative humidity at atmospheric pressure and 25 °C), causes a 6.2% increase of the photoacoustic signal amplitude, thus having little impact on the sensor calibration.

The measured amplitude ( $A$ ) and phase ( $\Theta$ ) of the QEPAS signal for different water concentrations was approximated by the same equations as derived in [17]. From the best fit parameters acquired for both the amplitude and phase model fit it is possible to determine the relaxation times for CO<sub>2</sub> ( $\tau_1$ ) and for H<sub>2</sub>O ( $\tau_3$ ) molecules in a CO<sub>2</sub>:H<sub>2</sub>O:N<sub>2</sub> gas mixture. The calculations yield  $\tau_1 = 3.53 \mu\text{s atm}$  and  $\tau_3 = 0.08 \mu\text{s atm}$ . In comparison to the previously obtained results, the CO<sub>2</sub> relaxation rate corresponding to dry gas is almost 3 times faster in the system with the microresonator. We assume that the main reason for such a reduced value of  $\tau_1$  is a CO<sub>2</sub> molecules relaxation due to collisions with the microresonator walls. We calculated the diffusion length for CO<sub>2</sub> molecules ( $L = \sqrt{2 \cdot D \cdot \tau}$ ) in order to check if they are able to reach the tube walls within a modulation period  $T = \frac{1}{f_0}$ . For our measurement conditions ( $P = 50$  Torr) and for a CO<sub>2</sub> diffusion coefficient of  $D = 1.43 \times 10^{-4} \frac{\text{m}^2}{\text{s}}$ , the calculated diffusion length value is  $L = 93.45 \mu\text{m}$ . This corresponds to  $\sim 0.5$  of the microresonator tube radius ( $r_{\text{res}} = 200 \mu\text{m}$ ). By taking also into account the  $\sim 100 \mu\text{m}$  diameter of the laser beam which fills the microresonator tube, it is clear that some CO<sub>2</sub> molecules excited by the laser radiation will reach the microresonator walls and can release their vibrational energy in the collision event.

For the sensitivity evaluation, a photoacoustic  $2f$  signal of a 1% CO<sub>2</sub> in nitrogen containing 1.47% of H<sub>2</sub>O was acquired using a 1 s lock-in time constant (Fig. 5). A single point noise was calculated as the standard deviation of the measured data points in the wing of the targeted absorption line, which yields a value of  $1\sigma = 3 \mu\text{V}$ . This value matches the thermal noise level of the QTF at its resonance frequency, which is the dominating noise source limiting the device sensitivity. This yields a minimum detection limit ( $1\sigma$ ) of 17.8 ppm

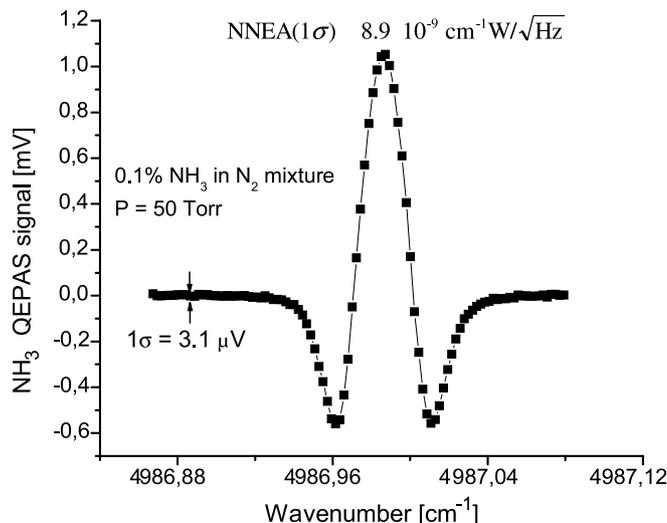


**FIGURE 5** Amplitude of PAS signal for 1%  $\text{CO}_2$  in dry nitrogen at 50 Torr with a 1.47% of  $\text{H}_2\text{O}$  concentration in the QEPAS system

for  $\text{CO}_2$  concentration measurements at  $4991.26 \text{ cm}^{-1}$ . By normalization to the corresponding bandwidth of  $0.318 \text{ Hz}$  and an optical power of  $4.4 \text{ mW}$  between the prongs of the QTF a normalized noise equivalent absorption coefficient,  $\text{NNEA}(1\sigma) = 1.4 \times 10^{-8} \text{ cm}^{-1} \text{ W}/\sqrt{\text{Hz}}$  is obtained.

As mentioned previously, it is also possible to detect several absorption lines of ammonia ( $\text{NH}_3$ ) molecule from its  $\nu_3 + \nu_4$  band within the tuning range of our diode laser, from  $4982 \text{ cm}^{-1}$  to  $4993 \text{ cm}^{-1}$ . To determine of the system sensitivity to  $\text{NH}_3$ , a calibration mixture of 1000 ppm of  $\text{NH}_3$  in  $\text{N}_2$  was used. A strong and interference free  $\text{NH}_3$  line at  $4986.99 \text{ cm}^{-1}$  was selected for  $\text{NH}_3$  concentration measurements. The desired wavelength could be reached by changing temperature of the laser from  $19.1 \text{ }^\circ\text{C}$  ( $\text{CO}_2$  line) to  $32.5 \text{ }^\circ\text{C}$  for the same value of laser current ( $I_0 = 80 \text{ mA}$ ). The intensity of the selected  $\text{NH}_3$  line ( $7.703 \times 10^{-21} \text{ cm}^{-1}/\text{mol cm}^{-2}$ ) is about 6 times higher than the measured  $R18 \text{ CO}_2$  line of  $2\nu_1 + \nu_3$ . Similarly to the  $\text{CO}_2$  measurements, an optimization of the photoacoustic signal was performed. The best result was obtained at a pressure of 50 Torr and for a modulation amplitude of  $3.2 \text{ mA}$ . Ammonia is known to exhibit fast  $V-T$  relaxation. Therefore the photoacoustic signal is efficiently generated even at relatively high laser modulation frequency ( $f_0/2 \sim 16.38 \text{ kHz}$ ). Furthermore, the photoacoustic signal for ammonia molecules is independent from the concentration of water present in the gas mixture, which we experimentally verified. However, it should be mentioned that ammonia is readily adsorbed on the surfaces. This requires careful gas handling to avoid measurement errors associated with adsorption and desorption processes involving the system walls. Therefore  $\text{NH}_3$  concentrations should be measured for stable gas flow conditions.

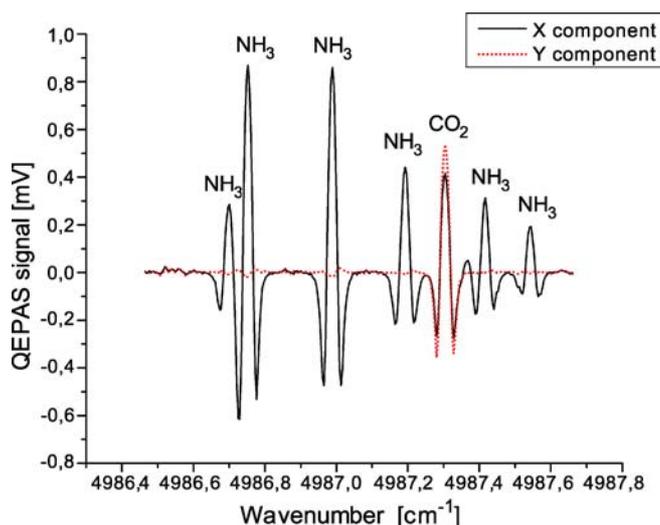
The photoacoustic signal acquired at optimal operating conditions for the  $\text{NH}_3$  line at  $4986.99 \text{ cm}^{-1}$  is shown in Fig. 6. The noise level determined as a standard deviation during the scan was  $1\sigma = 3.1 \mu\text{V}$ , in agreement with the  $\text{CO}_2$  results presented in Fig. 5. The signal-to-noise ratio for these data was found to be  $\text{SNR} = 340$ . Therefore it is possible to perform  $\text{NH}_3$  concentration measurements



**FIGURE 6** Amplitude of PAS signal for 0.1%  $\text{NH}_3$  in dry nitrogen at a pressure of 50 Torr

with a minimum detection limit ( $1\sigma$ ) of 3 ppm. For a  $1 \text{ s}$  time constant of the lock-in amplifier and a laser power of  $3.9 \text{ mW}$  between the prongs of the QTF, the acquired normalized noise equivalent absorption coefficient is  $\text{NNEA}(1\sigma) = 8.9 \times 10^{-9} \text{ cm}^{-1} \text{ W}/\sqrt{\text{Hz}}$ .

All the strong  $\text{NH}_3$  lines present within the tuning range of the diode laser used in this work can be accessed in a single wavelength scan by laser current modulation. For such measurements, the wavelength of the laser was tuned from  $4986.46 \text{ cm}^{-1}$  to  $4987.66 \text{ cm}^{-1}$  by varying the laser current from  $108 \text{ mA}$  to  $78.5 \text{ mA}$ , respectively. Within such a tuning range the  $\text{CO}_2 \text{ R12}$  line at  $4987.3 \text{ cm}^{-1}$  can also be used for  $\text{CO}_2$  concentration monitoring. The line strength of the  $\text{CO}_2 \text{ R12}$  is only 2.5% smaller than line strength of the optimum  $R18$  line used in this work for  $\text{CO}_2$  detection. An example of such a scan depicting all  $\text{NH}_3$  lines as well as a single  $\text{CO}_2$  line is shown in Fig. 7. The spectrum was acquired using a gas cylinder with 1% of  $\text{CO}_2$  in dry  $\text{N}_2$  connected to the QEPAS



**FIGURE 7** Scan of all ammonia lines detected as well as a single  $\text{CO}_2$  line at  $4987.3 \text{ cm}^{-1}$  in the  $2 \mu\text{m}$  spectral region

sensor just after the  $\text{NH}_3$  measurements. The  $\text{NH}_3$  removal time is relatively long and therefore both molecules ( $\text{NH}_3$  desorbing from the system walls and  $\text{CO}_2$  from cylinder) are simultaneously present in the system. From these experimental data and using the earlier sensor calibration the  $\text{NH}_3$  concentration is estimated to be 0.08%, based on  $\text{NH}_3$  line at  $4986.99 \text{ cm}^{-1}$ .  $\text{CO}_2$  concentration based on line  $4987.3 \text{ cm}^{-1}$  is calculated to be 1%, confirming validity of the earlier calibration. The reference frame for data presentation is selected so that the quadrature component of the photoacoustic signal for  $\text{NH}_3$  is nulled (the small  $1f$ -like residual is due to the RAM). An essentially nonzero quadrature component in the  $\text{CO}_2$  produced signal clearly indicates different phase of this signal. The phase lag, ( $\tan \varphi = \omega \cdot \tau$ , where  $\omega$  is modulation frequency and  $\tau$  is  $V$ - $T$  relaxation time) [22], confirms that  $V$ - $T$  relaxation of  $\text{CO}_2$  molecules (phase lag  $\varphi = 52^\circ$ ) is considerably slower in comparison to  $\text{NH}_3$  molecules ( $\varphi = 0^\circ$ ), and this difference in the photoacoustic phase can be used to improve the molecular selectivity of the instrument.

In addition to the  $\text{NH}_3$  and  $\text{CO}_2$  absorption lines there are several weak  $\text{H}_2\text{O}$  absorption lines within the tuning range of the  $2 \mu\text{m}$  diode laser. The minimum detectable  $\text{H}_2\text{O}$  concentration for the best accessible line at  $4988.79 \text{ cm}^{-1}$  is 550 ppm ( $\tau = 1 \text{ s}$ ). This enables simultaneous monitoring of the  $\text{H}_2\text{O}$  content at levels when its influence on the QEPAS-based  $\text{CO}_2$  quantification is essential, and perform the corresponding sensitivity assessment, without the need to employ an additional humidity detection system.

#### 4 Conclusions

The results reported in this paper show that a  $2 \mu\text{m}$  thermoelectrically cooled DFB diode laser-based QEPAS sensor offers a sensitivity sufficient for a number of practical applications. Adding an acoustic microresonator resulted in  $\sim 6.8$  times better sensitivity to  $\text{CO}_2$  in comparison with the results previously demonstrated by our group [17]. The minimum detection limit for  $\text{CO}_2$  concentration measurements was achieved at a level of 18 ppm ( $\tau = 1 \text{ s}$ ), which corresponds to a normalized noise equivalent absorption of  $\text{NNEA}(1\sigma) = 1.4 \times 10^{-8} \text{ cm}^{-1} \text{ W}/\sqrt{\text{Hz}}$ . The same system can be used to perform ammonia concentration measurements with a detection limit of 3 ppm ( $\tau = 1 \text{ s}$ ), which correspond to  $\text{NNEA}(1\sigma) = 8.9 \times 10^{-9} \text{ cm}^{-1} \text{ W}/\sqrt{\text{Hz}}$ . The difference in NNEA reflects faster  $V$ - $T$  energy transfer for ammonia. The ability to detect both  $\text{CO}_2$  and  $\text{NH}_3$  extends the range of practical applications for the reported sensor architecture. For example, such a QEPAS gas sensor is suitable for hazardous area monitoring and could be used in biological studies (microbiology, fermentation), medical (noninvasive human breath analysis, cellular respiration) and environmental applications (measurements of air pollution, volcanic emission detection). The average  $\text{CO}_2$  concentration in the atmosphere is presently  $\sim 380$  ppm, and thus the  $2 \mu\text{m}$  sensor can be employed also in atmospheric research. A further increase of the detection sensitivity can be realized by reflecting the laser beam back to the ADM and letting it pass again between

prongs of the QTF. This approach in its simplest configuration employs a concave mirror placed after ADM that results in an enhancement of the photoacoustic signal by a factor of two [23]. However, the diode laser used in this work is not equipped with an in-line optical isolator and thus any feedback to the laser results in unstable operation. A fiber-coupled  $2 \mu\text{m}$  diode laser with an inline isolator is presently commercially available from NEL/NTT. A further increase in  $\text{CO}_2$  detection sensitivity can be realized by using either commercially GaInAsSb diode lasers in the  $\nu_1 + \nu_3$  ro-vibrational band at  $2.7 \mu\text{m}$  ( $3700 \text{ cm}^{-1}$ ) or quantum cascade lasers in the  $\nu_3$  fundamental band at  $4.3 \mu\text{m}$  ( $2300 \text{ cm}^{-1}$ ).

**ACKNOWLEDGEMENTS** Financial support of the work performed by the Rice group was provided by the National Aeronautics and Space Administration (NASA), DARPA via a subaward from Pacific Northwest National Laboratory (PNNL), Richfield, WA, the Robert Welch Foundation, the Texas Advanced Technology Program and the Office of Naval Research via a subaward from Texas A&M University.

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