Quantum cascade laser-based multipass absorption system for hydrogen peroxide detection

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ABSTRACT

Hydrogen peroxide (H_2O_2) is a relevant molecular trace gas species, that is related to the oxidative capacity of the atmosphere, the production of radical species such as OH, the generation of sulfate aerosol via oxidation of S(IV) to S(VI), and the formation of acid rain. The detection of atmospheric H_2O_2 involves specific challenges due to its high reactivity and low concentration (ppbv to sub-ppbv level). Traditional methods for measuring atmospheric H_2O_2 concentration are often based on wet-chemistry methods that require a transfer from the gas- to liquid-phase for a subsequent determination by techniques such as fluorescence spectroscopy, which can lead to problems such as sampling artifacts and interference by other atmospheric constituents. A quartz-enhanced photoacoustic spectroscopy-based system for the measurement of atmospheric H_2O_2 with a detection limit of 75 ppb for 1-s integration time was previously reported. In this paper, an updated H_2O_2 detection system based on long-optical-path-length absorption spectroscopy by using a distributed feedback quantum cascade laser (DFB-QCL) will be described. A 7.73-μm CW-DFB-QCL and a thermoelectrically cooled infrared detector, optimized for a wavelength of 8 μm, are employed for the H_2O_2 sensor system. A commercial astigmatic Herriott multi-pass cell with an effective optical path-length of 76 m is utilized for the reported QCL multipass absorption system. Wavelength modulation spectroscopy (WMS) with second harmonic detection is used for enhancing the signal-to-noise-ratio. A minimum detection limit of 13.4 ppb is achieved with a 2 s sampling time. Based on an Allan-Werle deviation analysis the minimum detection limit can be improved to 1.5 ppb when using an averaging time of 300 s.

Keywords: Quantum cascade lasers, multipass absorption cell, wavelength modulation, hydrogen peroxide, minimum detection limit

1. INTRODUCTION

Hydrogen peroxide (H_2O_2) is a relevant species due to the fact that it participates in a variety of oxidative processes in the atmosphere, such as the production of radical species, OH and HO_2, the formation of sulfate aerosol by in-cloud oxidation of S(IV) to S(VI), which is closely related to the phenomena of acid rain and fog[1-3]. In addition to its relevance in atmospheric activities, the concentration levels of H_2O_2 in human breath can be also used as a biomarker for oxidative stress. This is associated with pulmonary conditions such as lung cancer and chronic obstructive pulmonary disease. Therefore, high sensitivity determination of H_2O_2 is of importance in different application fields. The precise detection of H_2O_2 involves practical challenges due to its low atmospheric concentration levels (from sub-ppb to ppb levels).

Traditional methods for H_2O_2 determination are usually based on wet-chemical techniques[4]. In these methods, transfer of H_2O_2 from gas-phase to liquid-phase is required for a subsequent determination via techniques such as fluorescence spectroscopy. Sampling artifacts and interference from other atmospheric species can be introduced in these methods, preventing an accurate determination of H_2O_2 in the atmosphere.

Direct H_2O_2 measurements in the gas-phase based on optical approaches, such as tunable diode laser absorption spectroscopy (TDLAS), provide practical advantages over other methods due to their high sensitivity, selectivity, fast

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response and long- term operation[5-8]. With a 40-m multipass White cell, Slemr et al. reported a H_2O_2 detection limit of 2.9 ppb with a 5-minute averaging time[5]. Lindley et al. obtained a H_2O_2 detection limit of 15 and 3 ppb for walkthrough portal and optical bench top instruments, respectively, using a quantum cascade laser (QCL)-based TDLAS method with a 100-m astigmatic multipass cell[6]. Another TDLAS-based system was demonstrated for H_2O_2 detection with a minimum detection limit of 110 ppt for 1-s integration time by using a long path-length (260 m with 554 passes) multipass cell[7]. Most recently, a H_2O_2 sensor system based on a sensitive quartz-enhanced photoacoustic spectroscopy technique was demonstrated by Ren et al.[8]. Minimum detection limits of 75 ppb and 12 ppb were achieved for 1-s and 100-s integration time, respectively.

Here, we demonstrate a TDLAS-based sensor system for sensitive gas-phase H_2O_2 measurements. A continuous wave (CW) distributed feedback (DFB) QCL operating at room temperature is used as the excitation source to target a strong H_2O_2 absorption line at 1296.2 cm^{-1}. H_2O_2 absorption is enhanced in a commercial multipass cell with an effective path-length of 76 m.

2. EXPERIMENTAL

2.1 Characterization of CW QCL

A 7.73 µm CW DFB-QCL (Corning Corp., now ThorLabs) with its tuning range overlapping a strong H_2O_2 absorption band in the mid-infrared is selected as the excitation source for H_2O_2 absorption. The emission wavenumbers of the laser were tested at different laser temperature and injection current to verify the QCL wavelength tunability. The results are depicted in Fig. 1 and show an approximately linear dependence of the QCL wavenumber on laser temperature and injection current, with linear coefficients of -0.09 cm^{-1}/°C and -0.014 cm^{-1}/mA, respectively.
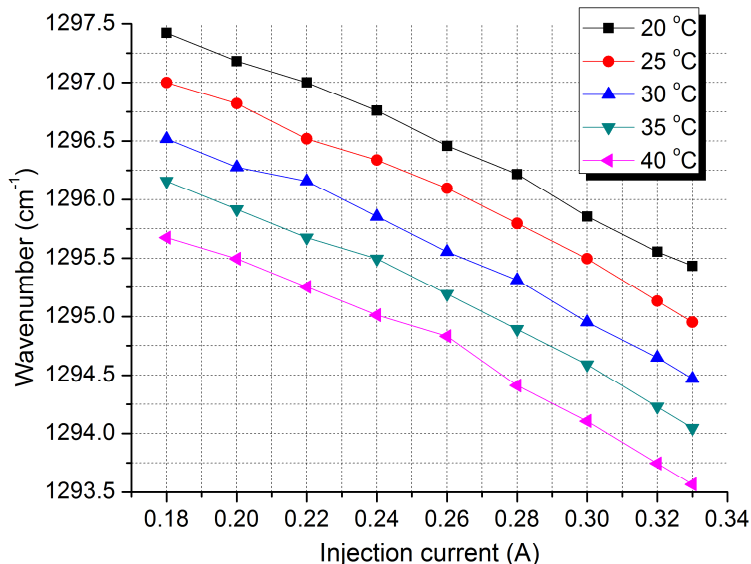

Figure 1. Spectral response of 7.73 µm CW DFB-QCL at different laser temperatures and injection currents.

2.2 Schematic of sensor system

The H_2O_2 sensor system based on a multipass gas absorption cell is depicted in Fig. 2. A CW DFB-QCL with its emission beam collimated served as the light source. The wavelength of the QCL was controlled by a temperature controller (TED 200C, Thorlabs, Inc.) and a current controller (LDX 3232, ILX Lightwave). A mixed current signal containing both a sawtooth wave and a sinusoidal wave from a function generator (AFG 3102, Tektronix, Inc.) was sent to the current controller in order to realize simultaneous laser wavelength scanning and modulation. The QCL beam after passing through a wedged beam splitter was optimized and focused into the multipass cell (AMAC-76, Aerodyne Research, Inc.) using three plano-convex lenses (f_1=50 mm, f_2=100 mm and f_3=250 mm) and a pinhole spatial filter (D=400 µm). After 238 passes in the multipass cell (resulting in an effective path-length of 76 m), the exit beam was collected by an infrared (IR) detector (PVMI-3TE-8, Vigo System S.A.) via a fourth plano-convex lens (f_4=20 mm). The detected signal was demodulated by a lock-in amplifier for second harmonic (2f) signal acquisition. The reflected beam

from the beam splitter is passed through a reference cell (1% N_2O at 150 Torr) and detected by a pyroelectric detector (LIE-332f, InfraTec) for wavelength locking. Gas flow into/out of the multipass cell was controlled by a pressure controller and an oil-free vacuum pump to maintain a suitable pressure inside the multipass gas cell.
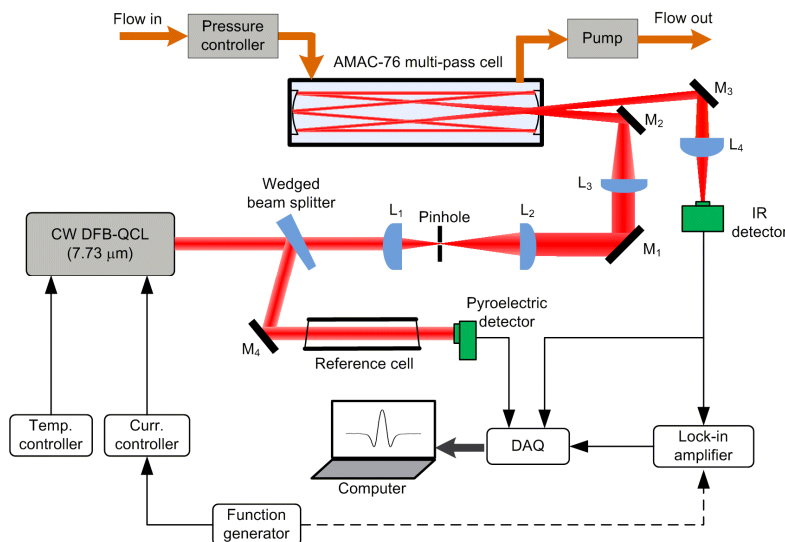

Figure 2. Schematic of the H_2O_2 TDLAS based sensor system. L: plano-convex lens, M: mirror, DAQ: data acquisition.

3. H_2O_2 LINE SELECTION AND OPTIMIZATION

3.1 Selection of optimum H_2O_2 absorption line

The sensitive and selective detection of H_2O_2 requires the selection of the optimum H_2O_2 absorption line. Fig. 3(a) shows the absorption spectra of 1 ppm H_2O_2 and air within the tuning range of the 7.73 μm QCL based on the HITRAN database with a path-length of 76 m at 30 Torr. For comparison, the experimental $2f$ signals for H_2O_2, air and pure N_2 are provided in Fig. 3(b) for the same spectral range. Two groups of strong H_2O_2 lines, marked as single-peak and double-peaks, are easily distinguished in both figures, with minor overlaps with CH_4 and N_2O absorption lines in air. Therefore, these two groups of H_2O_2 lines are selected as the potential target lines for the reported H_2O_2 measurements.
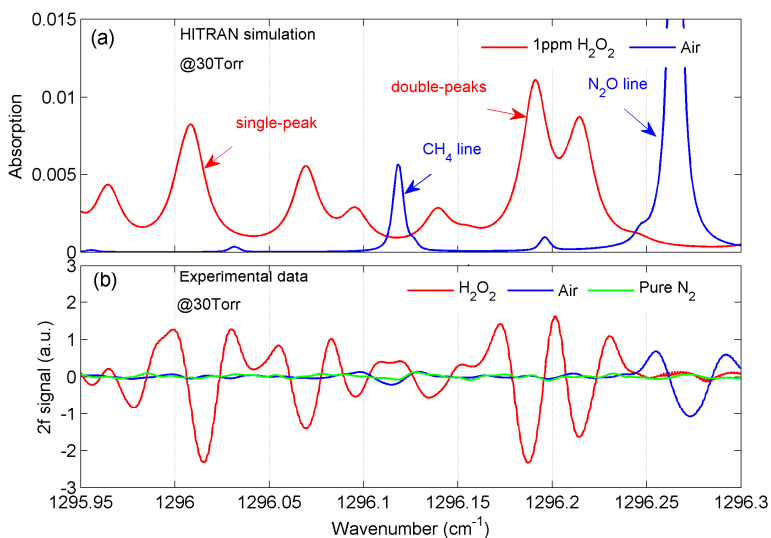

Figure 3. (a) Simulation results of absorption spectra for 1 ppm H_2O_2 and air based on HITRAN database; (b) experimental results of $2f$ signals for H_2O_2 vapor, air and pure N_2, respectively, when the QCL wavelength was swept across the spectral range from 1295.95 to 1296.3 cm^{-1}. The pressure was set to 30 Torr and the absorption length is 76 m.

3.2 Optimization of pressure and modulation depth

For optimum performance of the sensor system, the 2*f* signals at both single-peak and double-peaks were recorded for a constant H_2O_2 concentration at different pressures (from 30 Torr to 250 Torr) and modulation depths (from 1 mA up to 10 mA), and plotted in Fig. 4. The curves with open circles and solid dots represent the data for single-peak and double-peaks, respectively. The results show that as the pressure increases to above 100 Torr, signals for the double-peaks exceed those for a single-peak, which can be explained by line broadening of the double-peaks. The optimum operating conditions of the sensor system were determined to occur at a pressure of 150 Torr and a modulation depth of 8 mA for the double-peaks.
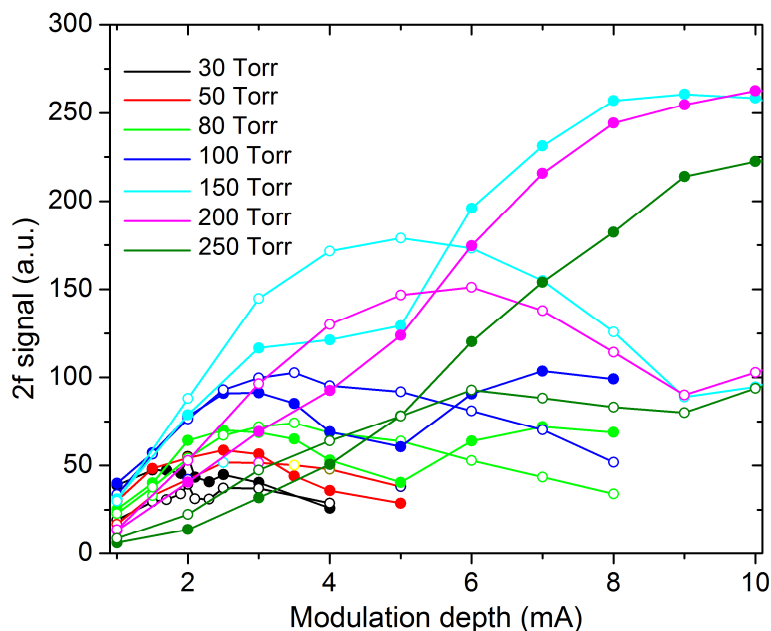

Figure 4. 2*f* signals for a constant H_2O_2 concentration at different pressures and modulation depths. The open circles and solid dots represent the results for the H_2O_2 single-peak and double-peaks, respectively.

4. SENSOR CALIBRATION AND EVALUATION

The H_2O_2 sensor calibration was performed by mixing the H_2O_2 vapor produced by the flow of pure N_2 passing over a container filled with a 10% H_2O_2 solution (w/w). Due to the sticky nature of H_2O_2, it usually takes up to 1 minute before the H_2O_2 reaches a stable concentration in the multipass cell. Therefore, during this H_2O_2 concentration stabilization process, both the direct absorption signals from the IR detector and the 2*f* signals from the lock-in amplifier were recorded at several discrete times. The H_2O_2 concentrations in the multipass cell can then be estimated by fitting the direct transmission curves with HITRAN database, while the 2*f* signals are plotted in Fig. 5(a) at these discrete times. The dependence of peak 2*f* signals on H_2O_2 concentrations is plotted in Fig. 5(b). A linear relationship between the 2*f* signal and the H_2O_2 concentration is observed from the fitting curve, resulting in a sensitivity of 0.93 mV/ppm.

In order to eliminate the signal variations induced by absorption changes in the multipass cell, a long-term sensor performance evaluation was carried out by passing pure N_2 over the multipass cell and recording the signal in terms of H_2O_2 concentration based on the above calibrated sensor sensitivity. The results for a continuous measurement over ~3 hours are shown in Fig. 6(a). An Allan-Werle deviation plot[9] is performed for this measurement and shown in Fig. 6(b) to analyze the noise limited minimum detectable H_2O_2 concentrations. A minimum detection limit (1σ) of 13.4 ppb was achieved for H_2O_2 with a 2-s sampling time. With an increased optimum averaging time of 200 s, the detection limit can be improved to 1.5 ppb (blue lines in Fig. 6(b)).
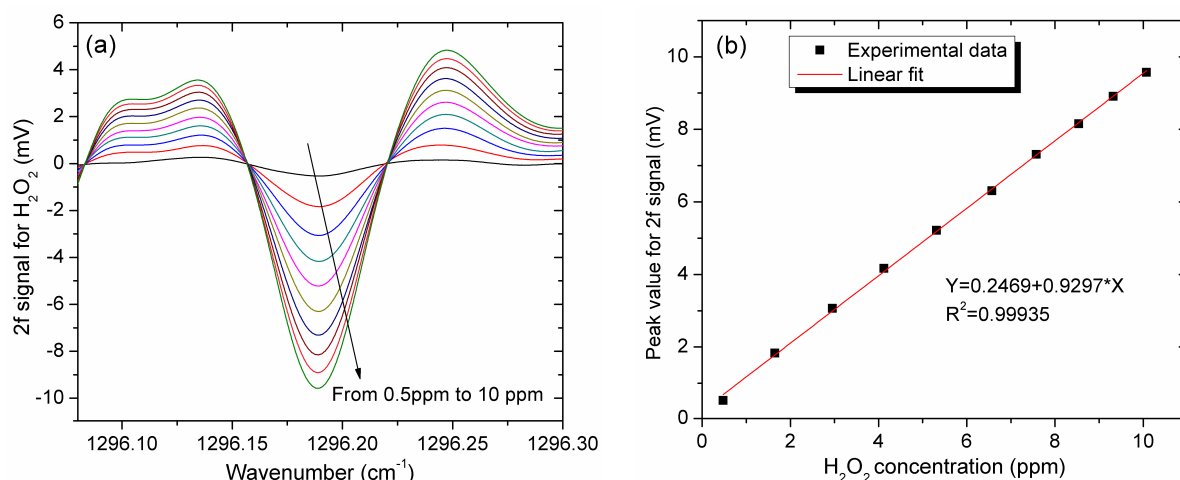
Figure 5. H_2O_2 sensor system calibration. (a) $2f$ signals across the double-peaks position for H_2O_2 concentrations from 0.5 ppm to 10 ppm; (b) peak values for data in Figure 5(a) at different H_2O_2 concentration levels.
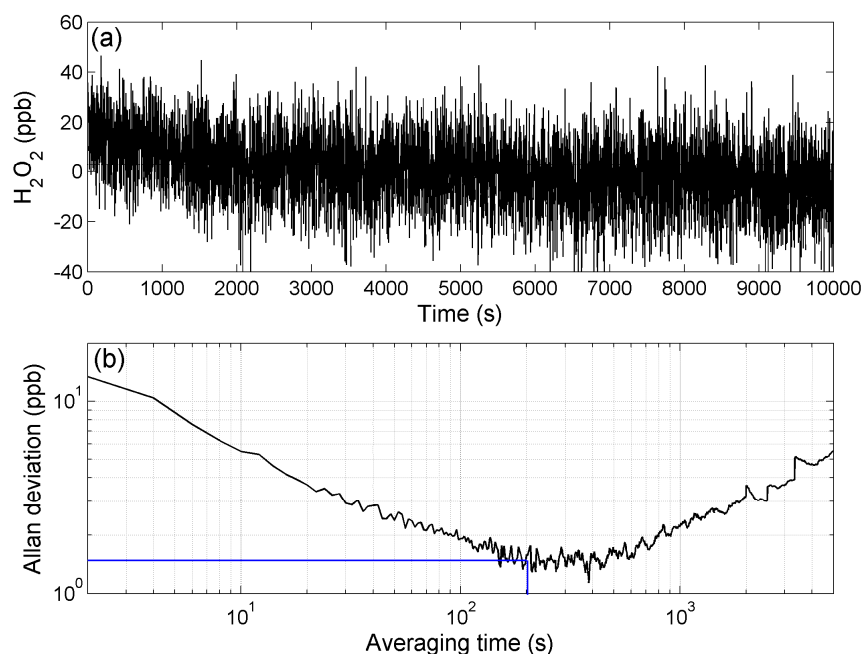

Figure 6. (a) H_2O_2 concentration signals for a measurement period of ~3 hours as pure N_2 passes through the sensor system; (b) Allen-Werle plot of the data in Figure 6(a). The blue lines indicate a minimum optimum detection limit of 1.5 ppb with a 200-s integration time.

5. CONCLUSIONS

In conclusion, we have demonstrated a sensitive H_2O_2 detection system based on multipass absorption spectroscopy. A CW DFB-QCL with a wavelength of ~7.73 µm was used to target a strong H_2O_2 line at 1296.2 cm^{-1}. The gas absorption is enhanced in a commercial multipass Herriott cell with an effective optical path-length of 76 m. The system shows a H_2O_2 detection limit of 13.4 ppb for a 2-s sampling time with optimized parameters for the $2f$-WMS method. This detection limit can be further improved to 1.5 ppb with an optimum integration time of 200 s based on an Allan-Werle deviation plot[10].

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