Sensitive Detection of CO and N_2O using a High Power CW 4.61 μm DFB-QCL Based QEPAS Sensor

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Abstract: A high power CW DFB-QCL based CO and N_2O QEPAS sensor demonstrating the MDL of 1.5 ppbv and 23 ppbv, respectively was developed. Continuous monitoring of atmospheric CO and N_2O concentration levels were performed.

OCIS codes: (140.5965) Semiconductor lasers, quantum cascade; (280.4788) Optical sensing and sensors; (300.6340) Spectroscopy, infrared.

1. Introduction

Carbon monoxide (CO) is one of the major air pollutants globally. The major sources of CO emission into atmosphere result from a variety of incomplete combustion activities, including the burning of fossil fuel, natural gas, and other carbon containing fuels. CO has an important impact on atmospheric chemistry due to its reaction with hydroxyl for troposphere ozone formation and also can change the level of greenhouse gases (e.g. CH_4) [1]. Furthermore, CO is extremely dangerous to human life even at a low concentration and therefore it must be accurately and precisely monitored in real time. Currently nitrous oxide (N_2O) is the single most important ozone-depleting substance emitted through human activities as a byproduct of industrial processes, agricultural fertilization, and from natural microbial processes in soil [2].

2. Quartz-enhanced photoacoustic spectroscopy

Quartz-enhanced photoacoustic spectroscopy (QEPAS) technique was first reported in 2002 [3]. This technique uses a commercially available mm sized piezoelectric quartz tuning fork (QTF) as an acoustic wave transducer. A high Q-factor and a ~32.7 kHz resonance frequency of the QTF improve QEPAS selectivity and immunity to environmental acoustic noise. Moreover a typical QEPAS detection module has a very small gas sample volume of ~ 4 cm^3 which significantly reduces the overall size of a sensor platform. A significant 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. Like conventional photoacoustic spectroscopy, QEPAS does not require optical detectors. This feature is especially attractive for gas sensing in the 5-20 μm region, where the availability of high-performance optical detectors is limited, and cryogenic cooling is often required. The QEPAS technique also benefits from the high optical power of employed laser source in order to achieve minimum detectable concentration at ppb or sub-ppb level.

3. QEPAS sensor architecture and performance

A 4.61 μm high power, continuous wave (CW), distributed feedback quantum cascade laser (DFB-QCL) was employed as an excitation source [4]. The temperature of the DFB-QCL was controlled at 10 °C resulting in emitted optical power of 987 mW when the laser current was set to 1250 mA. The DFB-QCL current and temperature were set and controlled by control electronics unit which is also employed to modulate the laser current, to lock the laser frequency to the selected absorption line, and to measure the current generated by QTF in response to the photoacoustic signal.

For sensitive CO and N_2O concentration measurements a wavelength modulation spectroscopy (WMS) with 2nd harmonic detection was utilized. To improve the CO and N_2O vibrational-translational relaxation processes an external humidifier was added at the inlet to the QEPAS system. The addition of 2.6 % H_2O to certified 5 ppm CO:N_2 gas mixture results in ~8 times improvement of the measured CO QEPAS signal when compared with the result obtained for the dry mixture. For the targeted R(6) CO absorption line, located at 2169.2 cm^{-1}, a minimum detection limit (MDL) of 1.5 ppbv was achieved for moisturized (2.6% H_2O) mixture analyzed at atmospheric pressure using a 1-sec acquisition time when the modulation depth was 0.325 cm^{-1}. For N_2O concentration

measurements, a P(41) N_2O absorption line located at 2169.6 cm^{-1} was selected. For this line a MDL of 23 ppbv was obtained when the same 2.6% water vapor concentration was added to the gas mixture and the gas pressure was set to be 100 Torr. A 3f pyroelectric detector signal with a zero crossing point at the maximum of the 2f WM QEPAS signal was used as the signal reference for the line-locking technique. An amplitude of 2f QEPAS signal when the DFB-QCL frequency is tuned across and locked to the R(6) CO absorption line is depicted in Fig. 1(a). An Allan deviation analysis was performed to investigate a long term stability and precision of the CO QEPAS sensor when pure N_2 was passed through the system. From the Allan deviation plot shown in Fig. 1(b) the optimum averaging time for the CO sensor is found to be 500 sec, which results in a MDL of 340 pptv.

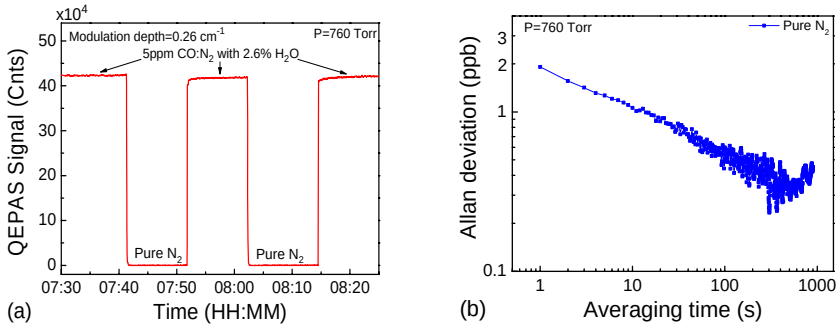

Fig. 1. (a) QEPAS signal using line locking mode for moisturized 5 ppmv CO:N_2 and pure N_2; (b) Allan deviation plot for time series measurements of pure N_2 for the QEPAS based CO sensor system.

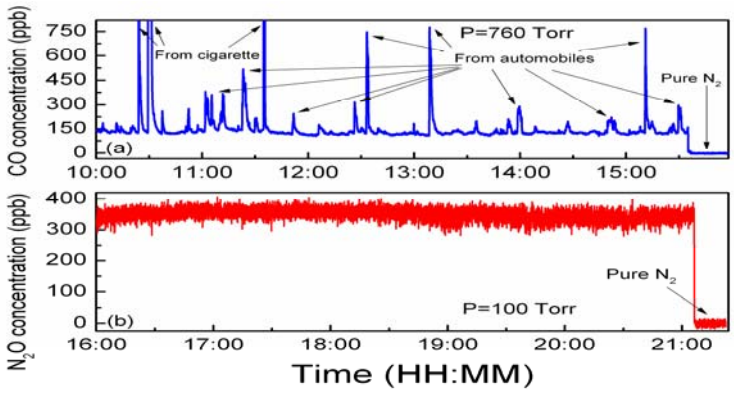

Fig. 2. Continuously measured CO and N_2O concentration levels from air sampled on Rice University campus, Houston, TX , USA (a):CO concentration measurement; (b): N_2O concentration measurement

For ambient CO and N_2O concentration measurements, an inlet tube of the QEPAS sensor was placed outside the laboratory and the atmospheric air was pumped into the sensor. The results of continuous measurements of atmospheric CO and N_2O concentration levels for a 5 hour period are shown in Fig. 2(a) and (b), respectively. The highest CO concentration spikes are caused by cigarette smoke when a smoking person breathe into the tube directly whereas all other less intense spikes, recorded on top of the CO atmospheric background of ~130 ppbv, are due to automobile emissions coming from traffic on Rice University campus road ~ 20 meters away from the sensor sampling inlet. The mean atmospheric concentration of N_2O was calculated to be 350 ppbv. Due to a long atmospheric residence time, the N_2O concentration is well mixed in the lower atmosphere and therefore its atmospheric concentration level is relatively stable as can be seen from Fig. 2(b).

With detection sensitivity at single ppb concentration levels the reported CO and N_2O QEPAS based sensor is suitable for applications in environmental monitoring, atmospheric chemistry, industrial chemical analysis and medical and biomedical diagnostics as well as in law enforcement.

4. References

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