

CW DFB-QCL and EC-QCL based sensor for simultaneous NO and NO₂ measurements via frequency modulation multiplexing using multi-pass absorption spectroscopy

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ABSTRACT

Nitrogen oxides (NO_x), including nitric oxide (NO) and nitrogen dioxide (NO₂) play important roles in determining the photochemistry of the ambient atmosphere, controlling the production of tropospheric ozone, affecting the concentration levels of the hydroxyl radical, and forming acid precipitation. A sensor system capable of simultaneous measurements of NO and NO₂ by using a commercial 76 m astigmatic multi-pass gas cell (MPGC) was developed in order to enable fast-response NO_x detection. A continuous wave (CW), distributed-feedback (DFB) quantum cascade laser (QCL) and a CW external-cavity (EC) QCL were employed for targeting a NO absorption doublet at 1900.075 cm⁻¹ and a NO₂ absorption line at 1630.33 cm⁻¹, respectively. Both laser beams were combined and transmitted through the MPGC in an identical optical path and subsequently detected by a single mid-infrared detector. A frequency modulation multiplexing scheme was implemented by modulating the DFB-QCL and EC-QCL at different frequencies and demodulating the detector signal with two Labview software based lock-in amplifiers to extract the corresponding second-harmonic (2f) components. Continuous monitoring of NO and NO₂ concentration levels was achieved by locking the laser frequencies to the selected absorption lines utilizing a reference cell filled with high concentrations of NO and NO₂. The experimental results indicate minor performance degradation associated with frequency modulation multiplexing and no cross talk between the two multiplexed detection channels. The performance of the reported sensor system was evaluated for real time, sensitive and precise detection of NO and NO₂ simultaneously.

Keywords: quantum cascade laser, nitric oxide, nitrogen dioxide, multi-pass absorption, wavelength modulation spectroscopy, frequency modulation multiplexing, trace gas detection, laser sensors

1. INTRODUCTION

Nitric oxide (NO) and nitrogen dioxide (NO₂), denoted as nitrogen oxides (NO_x), are prominent pollutants in the atmosphere and have impact on public health and natural system significantly [1]. The emission sources of NO_x are mainly from fossil fuel combustion, such as the exhaust from traffic vehicles and electric power plants, and biomass burning events. Since preindustrial period, NO_x emissions due to human activities have increased drastically, especially influencing the air quality in urban areas worldwide. In addition, NO_x are relevant in atmospheric chemistry reactions, involving NO₂ production by reaction of NO with ozone (O₃) and conversion back to NO by photolysis at wavelengths of < 424 nm [2]. Nitrogen oxides also impact the contribution to the hydroxyl radical (OH), acid rain and secondary organic aerosols [3]. Furthermore, NO plays critical role in human and mammalian cells via controlling different biological and pathophysiological processes in, for example, the diameter of blood and the biomarker of many respiratory diseases like asthma or inflammation [4]. The permissible NO₂ exposure of 40 µg/m³ (= 21.3 ppb) for an annual mean and 200 µg/m³ (= 106 ppb) for a 1-hour mean, was set by World Health Organization (WHO) to protect public health [5]. Sensitive and

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selective NO and NO₂ detection is thus useful for environmental monitoring, atmospheric chemistry research, industrial process control and medical diagnostics.

In this manuscript, we report the recent development of two quantum cascade lasers (QCLs) based sensor system for simultaneous measurements of atmospheric NO and NO₂ using a commercial astigmatic multi-pass gas cell (MPGC) with an effective optical path-length of 76 m. A Frequency modulation multiplexing method [6] was implemented to achieve the simultaneous detection by modulating each QCL at a different frequency and demodulating the signals with a pair of Labview-based lock-in amplifiers.

2. EXPERIMENTAL METHOD AND DESIGN

2.1 Absorption lines selection

The NO molecule has a strong fundamental vibrational band near $\lambda = 5.2 \mu\text{m}$ and the most intense line is the NO R(6.5) absorption doublet, which is a superposition of two lambda coupling components centered at 1900.075 cm^{-1} . Fig. 1(a) shows a HITRAN based simulation of 20 ppb NO and standard air (1.2% water vapor, 380 ppm CO₂, 2 ppm CH₄, 320 ppb N₂O and 10 ppb NH₃) at 40 Torr, 296 K and 76 m path-length in the spectral range of $1899.5\text{-}1900.5 \text{ cm}^{-1}$. The absorption doublet is free from interference of other atmospheric species due to a flat absorption background. The peak absorption in the entire NO₂ R-branch of fundamental ν_3 vibration occurs at 1630.33 cm^{-1} [7]. As shown in Fig. 1(b), the quasi-interference-free absorption line at 1630.33 cm^{-1} is well resolved, with the same conditions of Fig. 1(a) described above, in the spectral region from 1629.8 to 1630.8 cm^{-1} . Therefore, the optimum choices for NO and NO₂ absorption detection are at 1900.075 cm^{-1} and 1630.33 cm^{-1} , respectively, and selected in the development of our NO_x sensor system.

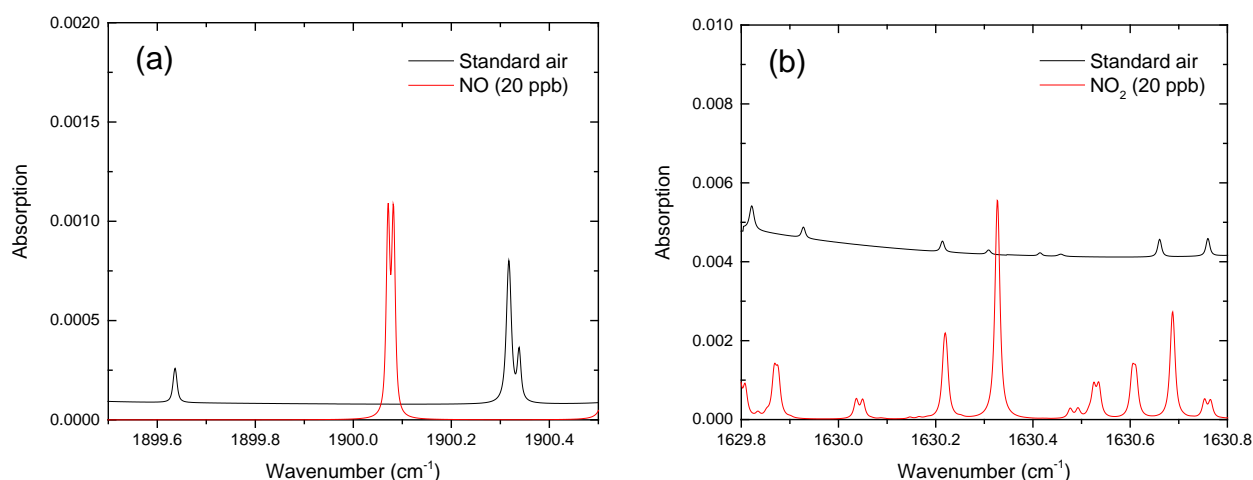


Figure 1. HITRAN simulation of absorption spectra of standard air with (a) 20 ppb NO and (b) 20 ppb NO₂, in the ambient condition of 40 Torr, 296 K and 76 m path-length.

2.2 Sensor design

In our study, a thermoelectrically cooled (TEC), continuous wave (CW), distributed-feedback (DFB) QCL (Hamamatsu Photonics, LE0178) emits at $\sim 5.26 \mu\text{m}$ was used to cover the target NO absorption feature. A water-cooled CW external-cavity (EC) QCL (Daylight Solutions, Model 21062-MHF) with a spectral tuning range from 1535 to 1640 cm^{-1} (mode-hop-free range of $1580\text{-}1635 \text{ cm}^{-1}$) operates to probe the NO₂ absorption line at 1630.33 cm^{-1} . The optical layout of the NO_x sensor system is depicted in Fig. 2. The dash and dot traces plotted in Fig. 2 represent light paths traveled by DFB-QCL and EC-QCL beams, respectively. The solid trace represents a co-aligned light path traveled by a visible alignment laser (Coherent, $\lambda = 630 \text{ nm}$) beam and the dual QCL split beams. The divergent output light from the DFB-QCL was collimated by a high NA = 0.56 antireflection coated aspheric lens (Thorlabs, C028TME-E) with a focal length of $f = 5.95 \text{ mm}$. The output beam from EC-QCL passed through a spatial filter consisting of two CaF₂ plano-convex lenses (the former

lens with a focal length of $f_1 = 40$ mm and the latter one with $f_2 = 50$ mm) and a pinhole with a diameter of $400 \mu\text{m}$. The beam quality can be optimized with the spatial filter mounted. A pair of beam splitters separated each laser beam in two different paths, one for the main beam for the gas sample and the second one as the reference beam for wavelength locking. The main beam, co-aligned by both laser beams, was coupled into a 76 m astigmatic Herriott multi-pass gas cell (MPGC) (Aerodyne Research Inc., AMAC-76). The beam exiting the MPGC was focused onto a TE-cooled mercury-cadmium-telluride (MCT) detector (Vigo System S.A., PVMI-3TE-8) using a 40 mm focal length plano-convex lens. The reference beam of each laser was directed through a reference gas cell by a group of mirrors and subsequently collected by a second mid-infrared detector (Vigo System S.A., PVM-10.6). The reference cell contains high concentration samples of NO and NO₂ at a pressure of ~ 30 Torr. Both electrical signals from the two mid-infrared detectors were acquired by a data acquisition card (National Instruments, USB-6361) and then analyzed by a Labview program in a laptop. Each QCL was tuned at a low frequency of 1 Hz to perform a wavelength scan that covers the absorption line of interest. In addition to the slow scan, the wavelength was modulated by sinusoidal waveform at 19 kHz for DFB-QCL and 40 kHz for EC-QCL. The frequency modulation multiplexing scheme was realized by demodulating the laser signals to extract the corresponding second-harmonic (2f) components using custom-made Labview-based lock-in amplifiers. The system pressure was maintained at 40 Torr by pressure controller (MKS Instruments, Type 640) and an oil free vacuum pump (Varian, DS102). More details about EC-QCL operation can be found in [8].

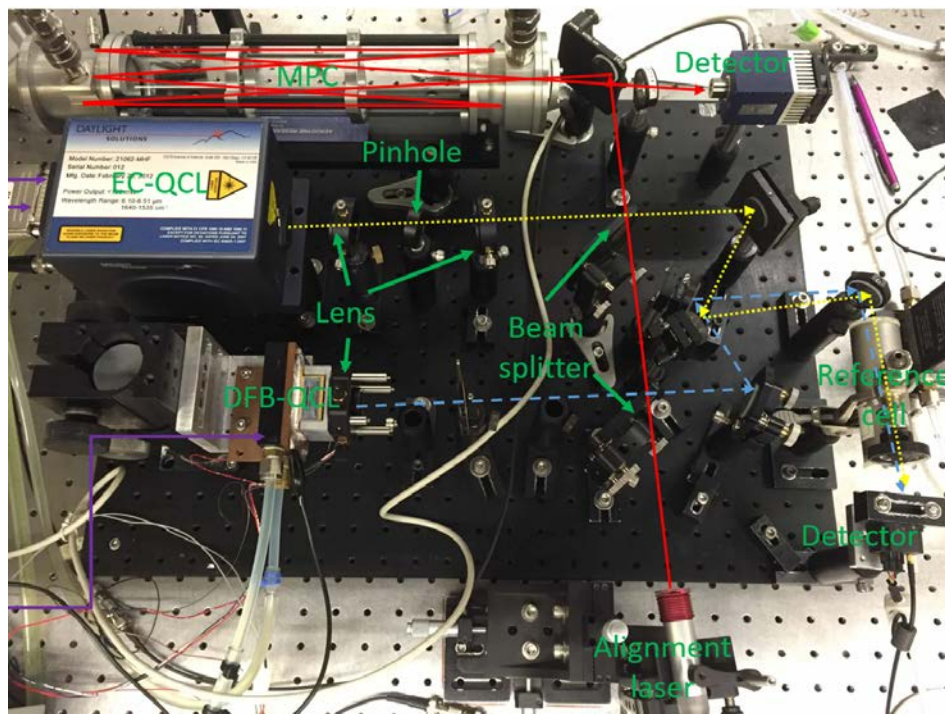


Figure 2. Optical layout of a dual QCL based sensor system for simultaneous NO and NO₂ detection. The dash and dot traces represent paths traveled by DFB-QCL and EC-QCL beams, respectively. The solid trace represents a co-aligned path traveled by an alignment laser beam and the dual QCL split beams.

3. RESULT

3.1 Sample signals

As displayed in Fig. 3, the output results from the two lock-in amplifiers were acquired simultaneously with NO and NO₂ samples co-existing in the MPGC. No cross talk appeared during the two gas species measurements.

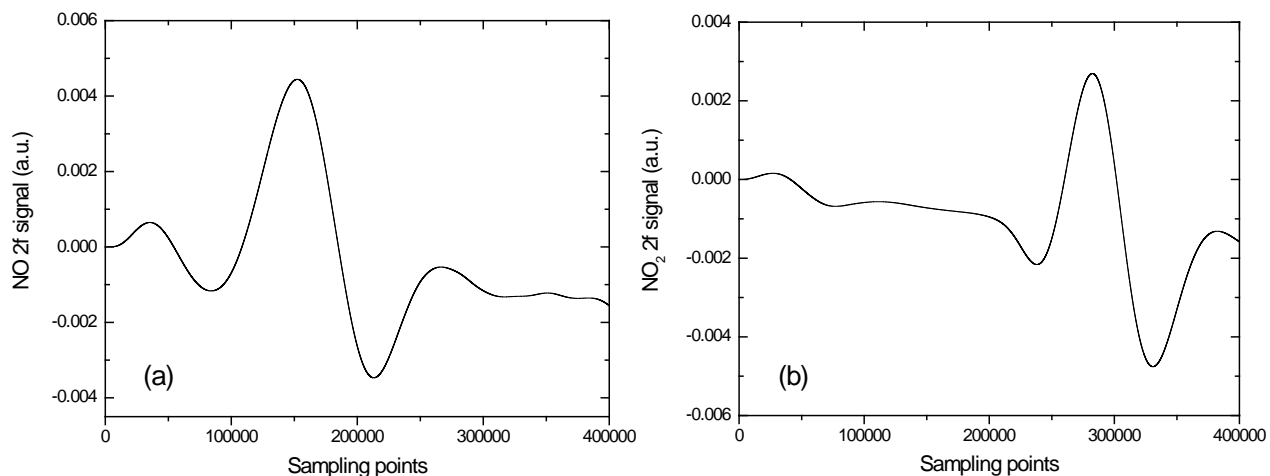


Figure 3. (a) NO and (b) NO₂ spectra simultaneously acquired with frequency modulation multiplexing.

3.2 Allan deviation

The noise level analysis of the NO_x sensor system was determined by flowing pure nitrogen through the MPGC and acquiring the 2f signals in terms of NO and NO₂ in a 2.2 hour period with 1 sec time intervals. An Allan-Werle deviation analysis (Fig. 4) indicated that minimum detection limits of ~4 ppb for NO and ~9 ppb for NO₂ were achieved with a 1 sec integration time. The optimum detection limits were estimated to be ~0.8 ppb for NO and NO₂ with integration times of 100 sec and 250 sec, respectively.

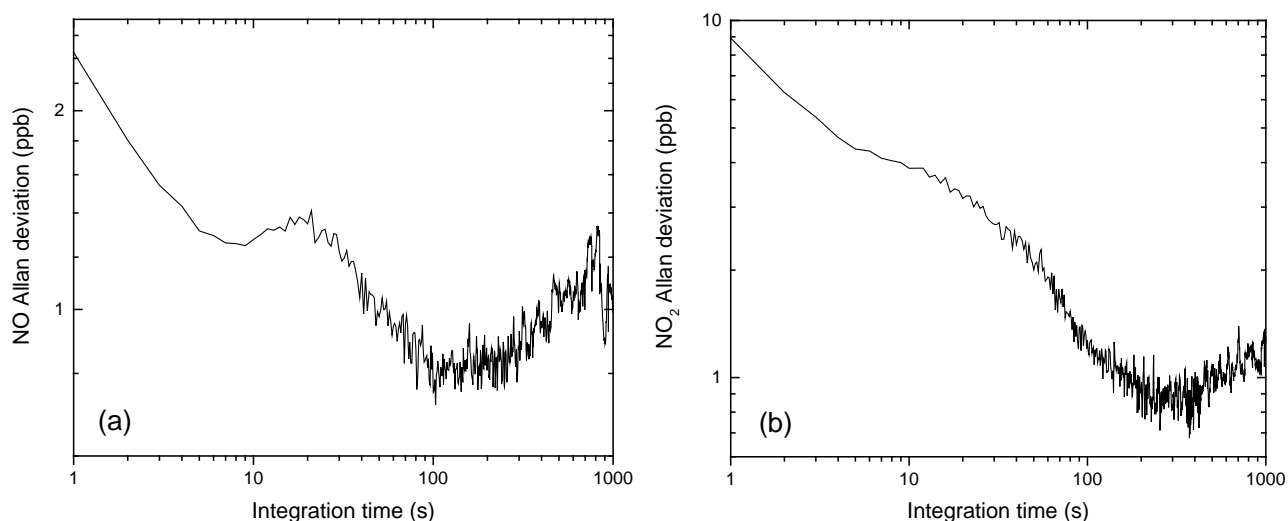


Figure 4. Allan deviation plots of NO and NO₂ concentration as a function of integration time.

3.3 Atmospheric NO_x measurements

The suitability of the sensor system for simultaneous NO and NO₂ detection was evaluated by conducting a continuous sampling campaign on the Rice University campus. The 2 min averaged time series of NO_x concentration levels measured from 12:00 CDT on Aug. 28 to 21:00 CDT on Aug. 29, 2016, were depicted in Fig. 5.

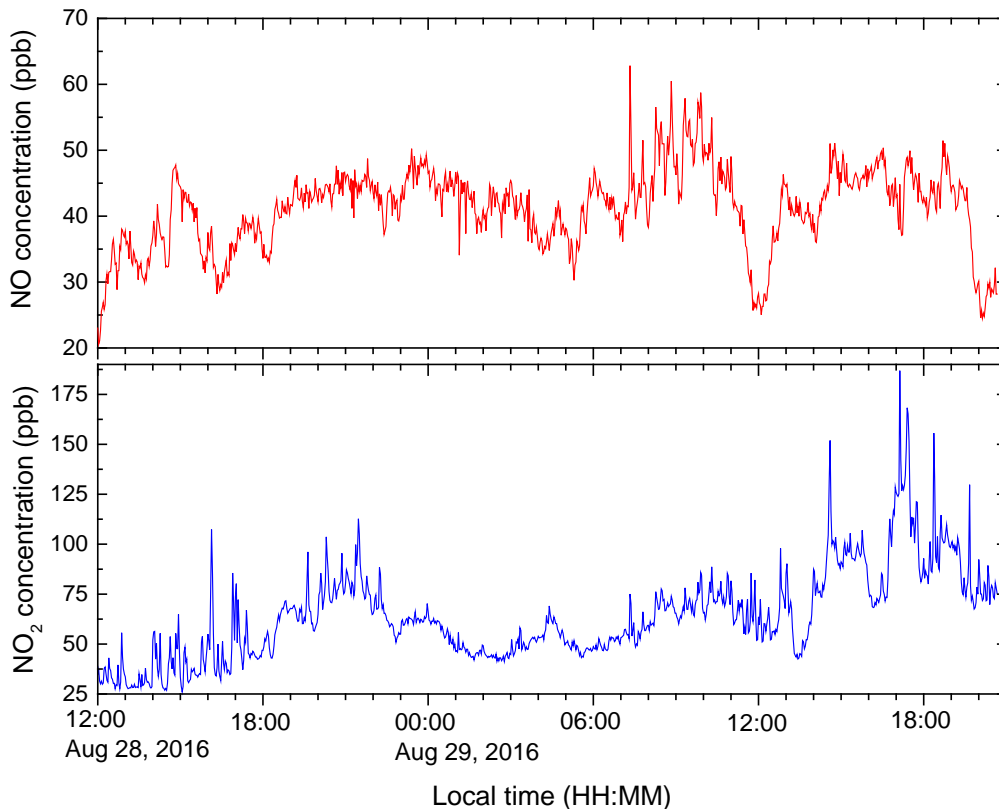


Figure 5. 2 min averaged time series of NO and NO₂ mixing ratios monitored on the Rice University campus.

4. CONCLUSIONS

A CW, DFB-QCL and EC-QCL based sensor system for simultaneous detection of atmospheric NO and NO₂ was demonstrated using a 76 m MPGC from Aerodyne Research. Frequency modulation multiplexing strategy was implemented by modulating dual laser wavelengths and demodulating the corresponding laser signals by custom-made Labview-based lock-in amplifiers. The optimum detection limits were estimated to be ~0.8 ppb for NO and NO₂ with integration time at 100 sec and 250 sec, respectively, according to an Allan-Werle deviation analysis.

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