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Sub-ppb detection of nitrogen dioxide with an external cavity quantum cascade laser

Rafał Lewicki [a*], Kun Liu[a,b], Timothy Day[c], and Frank K. Tittel[a]

[a]Rice University, ECE Dept, 6100 Main St., Houston, TX 77005, USA
[b]Environmental Spectroscopy Laboratory, Anhui Institute of Optics & Fine Mechanics, Chinese Academy of Sciences, Hefei, 230031, People Republic of China
[c]Daylight Solutions Inc., 15378 Avenue of Science, Suite 200, San Diego, CA 92128, USA

ABSTRACT

Ultra-sensitive detection of nitrogen dioxide (NO_2) in the ν_3 fundamental band of NO_2 using Faraday Rotation Spectroscopy (FRS) based optical sensor platform is reported. The FRS technique is well suited for selective trace gas measurements of paramagnetic species including the prominent air pollutants such as NO or NO_2. In this paper a widely tunable external cavity quantum cascade laser (EC-QCL) is employed as an excitation source. The available EC-QCL mode-hop free tuning range between 1600 cm^{-1} and 1650 cm^{-1} allows to access the optimum for FRS technique 4_{41}<-4_{40} Q-branch NO_2 transition at 1613.2 cm^{-1} with an optical power of ~135 mW. In order to improve detection sensitivity and reduce size of the sensor platform, a custom made 22.47 cm long Herriott multipass gas cell (MPC) with a total effective optical path of 10.1 m was implemented. For a MPC configured NO_2 FRS sensor operating in line-scanning mode a minimum detection limit of 1.6 ppbv (1σ) and 0.15 ppb (1σ) is achieved for a 1 sec and 100 sec averaging time, respectively. Preliminary results for long term measurements of atmospheric NO_2 for the FRS sensor operating at an optimal pressure of 30 Torr and magnetic field of 200 $Gauss_{rms}$ were demonstrated.

Keywords: Faraday rotation spectroscopy, external cavity quantum cascade laser, atmospheric trace gas detection, nitrogen dioxide.

1. INTRODUCTION

For the past few years an atmospheric pollution has became serious problem for highly developed urban environments especially, due to the recent dramatic growth in human population and industrial activities, along with an intensified usage of fossil fuels. In the United States one of the six principal pollutants in the atmosphere, next to ozone, carbon monoxide, sulfur dioxides, lead, and particulate matter are nitrogen oxides, among which the nitrogen dioxide (NO_2) is of greatest interest. NO_2 is mainly present in emitted fumes from cars, trucks and buses, coal-fired power plants, but also from space heaters, fireplaces, or tobacco smoke. In addition nitrogen dioxide contributes to the formation of

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[*] Rafal.Lewicki@rice.edu; phone 1 713 348-2614; fax 1 713 348-5686; http://www.ece.rice.edu/lasersci/

ground-level ozone (photochemical smog) and corrosive nitric acid, which can have significant impacts on environment and human health [1]. Moreover NO_2 is respiratory irritant and can reduce lung function causing asthma and other respiratory diseases [2-3]. Therefore, there is an increasing demand for highly sensitive and selective instrumentation capable of detecting NO_2 at low ppb (parts per billion) or even sub- ppb levels.

One of many laser based spectroscopic approaches to perform quantitative detection of nitrogen dioxide molecules at trace gas concentration levels is Faraday rotation spectroscopy (FRS). The FRS was first reported by G. Litfin et al. in 1980 year [4] and since then it has been recognized as a sensitive and zero background technique for sensitive measurements of the paramagnetic molecules such as NO, NO_2, O_2, or OH^-[5-8]. Moreover the FRS technique offers high selectivity during atmospheric measurements because contribution to absolute FRS signal from interfering non-paramagnetic species, such as water and carbon dioxide, is effectively eliminated.

In the FRS technique a longitudinal magnetic field is used to split the ro-vibrational transitions of a paramagnetic molecule into $\Delta M_J = +1$ and $\Delta M_J = -1$ components that interact with right-hand circularly polarized (RHCP) and left-hand circularly polarized (LHCP) light, respectively. These two opposite circularly polarized light components have different wavelength dependent propagation constants due to different refractive indexes for the RHCP and LHCP light. Therefore, when linearly polarized light, which is considered as a superposition of RHCP and LHCP light, is propagating through the paramagnetic medium a rotation of the initial polarization plane will be observed as a result of above mentioned magnetic circular birefringence. The rotation angle Θ can be calculated as $\Theta = \Delta n L \pi / \lambda$, where $\Delta n = n_R - n_L$ is the difference between refractive index for RHCP (n_R) and LHCP (n_L) respectively, L is propagation distance through a paramagnetic molecules, and λ is wavelength of the light. The modulation of the laser beam is achieved by continuously alternating magnetic field, and thus rotating plane of polarization of the transmitted light. The light that is delivered to the detector, after passing through almost totally crossed polarizer (also called analyzer), is proportional to the concentration of the paramagnetic molecules in the analyzed medium.

2. THE FRS SENSOR ARCHITECTURE

Ultra sensitive nitrogen dioxide sensor platform based on Faraday Rotation Spectroscopy is schematically shown in Fig. 1. This platform is an improved version of the double pass configured NO_2 FRS system that was reported in Ref. [9]. As a spectroscopic source widely tunable, water cooled, continuous wave external cavity quantum cascade laser (EC-QCL) from Daylight Solutions, operating at a temperature of 18 °C and providing a maximum optical power of 152 mW, is employed. Total EC-QCL frequency tuning from 1538.3 cm^{-1} to 1703.3 cm^{-1} covers an entire fundamental ν_3 band of nitrogen dioxide, centered at ~1600 cm^{-1}. With the available mode-hop free (MHF) frequency tuning, between 1600 cm^{-1} and 1650 cm^{-1}, the optimum for the FRS experiment 4_{41}<-4_{40} Q-branch NO_2 transition at 1613.25 cm^{-1} is accessed. An optical power profile within the EC-QCL tuning range and preferable NO_2 transitions for FRS are illustrated in Fig. 2. The optical power drop recorded for the laser frequency of ~1635 cm^{-1} was caused by a strong atmospheric water absorption line.

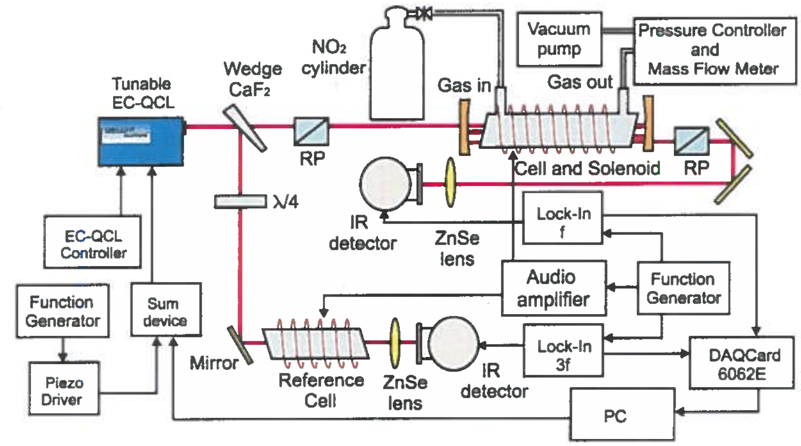


Fig.1 Ultra sensitive nitrogen dioxide sensor based on Faraday rotation spectroscopy.

The collimated EC-QCL beam is split by the CaF_2 wedge into two optical paths. The main path consists of a custom made multipass gas cell (MPC) that has total effective optical pathlength of 10.1 m for 22.47 cm separation between the multipass mirrors. The MPC is surrounded by a 15 cm long air core solenoid and placed between two MgF_2 Rochon polarizers (RP) with an extinction ratio of less than 10^{-5}. The first polarizer is used to maintain horizontal polarization of the light when the analyzer, usually oriented at small angle from the crossed position, is used to pass only this portion of light that undergo a rotation of the polarization plane as result of the interaction with paramagnetic molecule of NO_2. The rotated light is detected by a thermoelectrically cooled mercury-cadmium-telluride (MCT) IR detector (Vigo, model PDI-2TE-5). The measured signal from the detector was pre-amplified with a transimpedance amplifier and then demodulated with a phase-sensitive lock-in amplifier. The pressure inside the MPC was controlled by an MKS pressure controller and kept at an optimum level of 30 Torr.

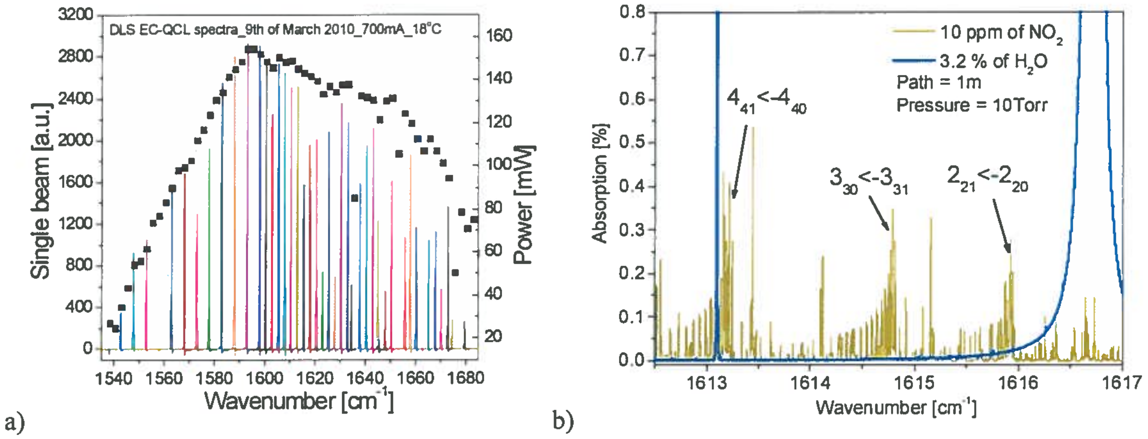


Fig. 2 a) An optical power profile within the EC-QCL tuning range and b) preferable NO_2 transitions for FRS.

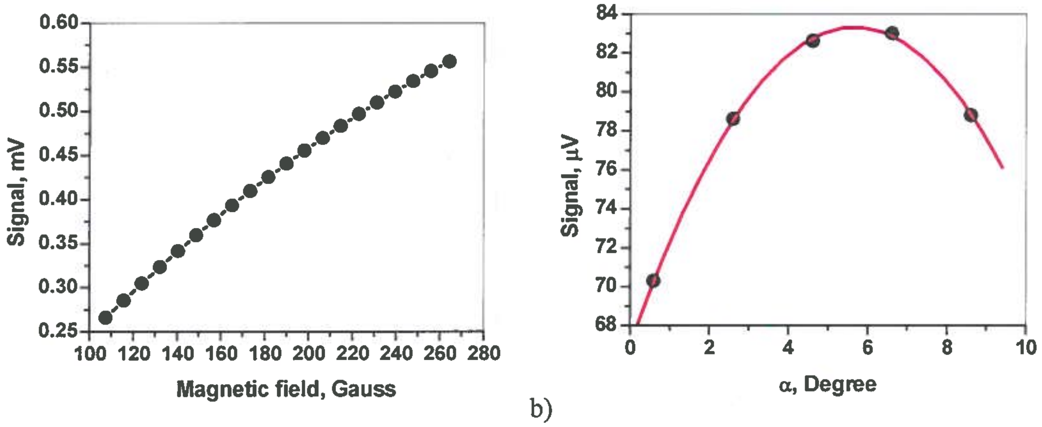
The second optical path is used as a reference channel to control frequency of the EC-QCL. In this channel a linearly polarized EC-QCL light after passing trough a quarter-wave plate is converted into circularly polarized light (either LHCP or RHCP depending on the orientation of the quarter-wave plate). The reference cell, filled with a 0.5 % NO_2 in N_2 at 25

Torr, is surrounded by a 10 cm long solenoid which is connected in series to the solenoid in the main sensor path. Two solenoids together with a 1 µF capacitor form a series RLC resonant circuit with a resonance frequency of f_{res} = 1971 Hz. Therefore, to create an alternating magnetic field, a sine wave signal at f_{res} from a function generator (Stanford Research model SR830), after amplifying with a commercial audio amplifier (QSC Model RMX850), was delivered to the both solenoids. In the reference channel the Zeeman modulation signal, resulting from magnetic circular dichroism, is detected by a thermoelectrically cooled MCT IR detector (Vigo, model PDI-2TE-5) and demodulated by a lock in amplifier (Signal Recovery model 7265) at second harmonic of f_{res}. Both signals from the main and reference optical paths are recorded with a personal computer using a National Instruments data acquisition card and LabView software.

In all measurements the EC-QCL was operated in line-scanning mode where a frequency of the laser is tuned back and forth across the selected $4_{41}<-4_{40}$ NO_2 transition by applying a sine wave signal to the laser piezo element which is resposible for the frequency tunning. To control EC-QCL frequency a peak position of the 2f reference signal was continuously monitored. In case of any frequency shift from the original position a correction signal from the LabView software based PID controller was applied to the EC-QCL piezo element. The quantitative measurements of NO_2 concentration level at fix laser frequency that corresponds to the highest detected FRS signal for selected NO_2 transition were abandoned due to the significant long term drift of the baseline caused by fluctuation of the magnetic field.

3. THE FRS SENSOR OPTIMIZATION

In order to optimize the FRS sensor performance, the optimum selection for the magnetic field amplitude, the gas sample pressure, and the analyzer angle has to be performed. The measured FRS signal levels for different amplitudes of the magnetic field, when the reference mixture of 500 ppb NO_2 in N_2 was filling the MPC, are illustrated on Fig. 3. For the purpose of stable and long term operation of the FRS sensor platform, a 200 Gauss$_{rms}$ amplitude of magnetic field, which corresponds to a 5 A$_{rms}$ of AC current flowing through the solenoids, was selected. Higher values for the magnetic field can cause thermal runaway in the high power RLC circuit, frequent shut downs of the audio amplifier due to overheat effect, and increase detectors noise level due to electromagnetic pickup between solenoids and detectors.



a) b)

Fig. 3 FRS signal amplitude versus magnetic field (a) and analyzer angle (b).

The optimum pressure, with respect to the highest SNR, was experimentally determined to be 30 Torr. For the laser beam exiting a MPC the optimum analyzer angle (α) of 5° from the crossed position was found to be a trade-off between detector signal and noise level transmitted by the analyzer. The results of FRS signal levels for different analyzer angles (α), which were measured when a 100 ppb NO_2 in N_2 mixture at optimal pressure of 30 Torr filled the MPC, are illustrated in Fig. 3. For analyzer angles α larger than 5 degree a decrease in FRS signal level is observed due to a MCT saturation effect. Detailed analysis on signal to noise ratio (SNR) relation to the angle of analyzer can be found in Ref. [5].

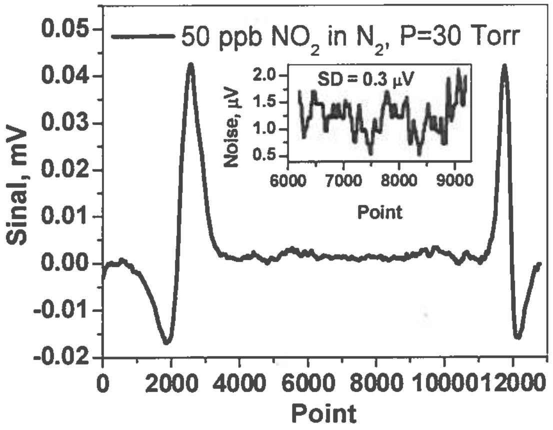


Fig.4 FRS signal of NO_2 at the optimum $4_{41} \leftarrow 4_{40}$ transition at 1613.25 cm^{-1} (6.2 μm).

The NO_2 FRS signal at the optimum $4_{41} \leftarrow 4_{40}$ transition (1613.25 cm^{-1}) for MPC configured sensor platform was illustrated in Fig. 4. For an optimum system pressure of 30 Torr and the 5° analyzer offset angle from the crossed position, a minimum sensitivity for reference mixture of 50 ppb NO_2 in N_2 was found to be 0.4 ppbv (1σ) for a 1 sec lock-in time constant. The laser frequency was mod-hop free tuned over a narrow frequency spectral range of ~0.04 cm^{-1} by applying a 1 mHz sine wave to the piezo element of the EC-QCL head.

4. THE FRS SENSOR PERFORMANCE

A linear response of the FRS sensor for different NO_2 concentration levels was investigated. For this purpose a certified gas mixture of 2 ppm NO_2 in N_2 was diluted with ultra high purity N_2 by using a MKS flow meters based custom dilution system. From the obtained results for detected FRS signal as a function of NO_2 concentration, a perfect linear relationship with $R^2=1$ was observed.

Fast response of the FRS sensor platform during the atmospheric measurements was obtained when the laser frequency scanning rate was set to 1 Hz and both lock-in amplifiers time constants were adjusted to 10 ms. Each acquired every 1 sec atmospheric Faraday spectrum is compared with reference spectrum of 100 ppb NO_2 in N_2 by using a LabView based general least square linear fitting procedure. After a comparison process a fitting coefficient with its value directly proportional to the monitored concentration level of NO_2 is obtained. The calculated NO_2 concentration levels are subsequently averaged over 10, 100, and 300 sec and then plotted in the real time on screen of a laptop computer.

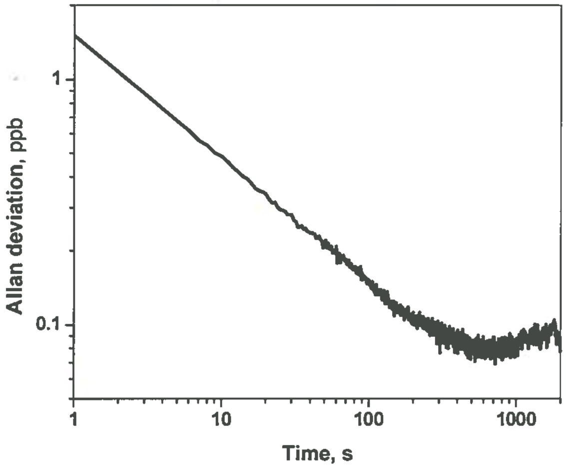


Fig. 5 Allan deviation calculated as a function of the measurement time.

The long term stability of a FRS gas sensor platform was investigated by performing Allan variance analysis [10]. The illustrated on Fig. 5 Allan deviation plot, which was calculated as square root of the Allan Variance, shows that minimum detection limit of 80 ppt can be achieved for NO_2 concentration measurements after averaging data over 600 sec. For 1, 10, 100, and 300 seconds averaging time the minimum detection limit for NO_2 is 1.5 ppb, 500 ppt, 150 ppt and 95 ppt, respectively.

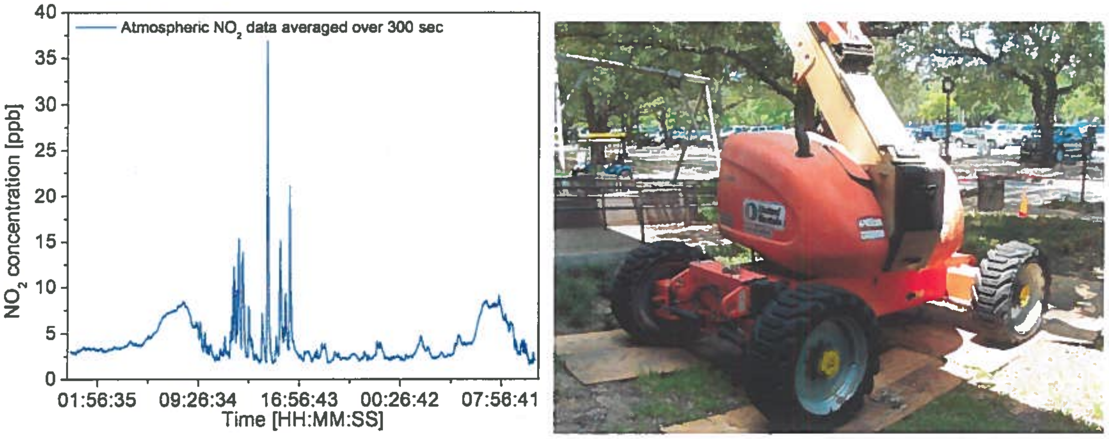


Fig. 6. Preliminary results for continuous monitoring of atmospheric NO_2 using FRS.

Fig. 6 depicts an example of continuous NO_2 concentration monitoring from the outdoor air outside the Laser Science Group laboratory at Rice University, Houston, TX. During several hours of FRS sensor operation several sharp peaks, having up to 40 ppb of detected NO_2 concentration levels for 300 seconds averaging time (up to 300 ppb for 1 sec averaging time) , were observed. Such high concentration levels of NO_2 were found to be emitted from the exhaust of a mobile crane operating outside the laboratory. Moreover, in the morning a strong decrease of NO_2 concentration due to photolysis was also observed. Recently a portable FRS NO_2 optical sensor platform version was installed on 18" by 24" optical board and deployed on the roof of the 60 meters high Moody Tower located at the University of Houston.

5. CONCLUSIONS

Ultra sensitive and highly selective Faraday rotation spectroscopy based sensor platform employing a 6.4 µm EC-QCL as a spectroscopic source was demonstrated. In order to improve the sensitivity and reduce the total size of the NO_2 sensor, a custom made 22.47 cm long Heriott multipass gas cell (MPC) providing an effective optical path of 10.1 m was implemented. For the NO_2 FRS sensor operating in line-scanning mode a minimum detection limit of 1.6 ppbv (1σ) was achieved for a 1 sec averaging time. The FRS sensor performance was optimized with respect to sensitivity by selecting optimum values for the amplitude of magnetic field, the sample gas pressure, and the polarization analyzer angle. Further improvement in the SNR value can be achieved by using better quality polarizers, more sensitive photodetectors, or by reducing system noise.

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