

Continuous Monitoring of Nitric Oxide at 5.33 μm with an EC-QCL based Faraday Rotation Spectrometer: Laboratory and Field System Performance

Gerard Wysocki^{*1}, Rafal Lewicki², Xue Huang¹, Robert F. Curl², and Frank K. Tittel²

¹Electrical Engineering Department, Princeton University, Princeton, NJ 08544, USA

²Rice Quantum Institute, Rice University, 6100 Main St., Houston, TX 77005, USA

Abstract (100 words): Nitric oxide detection with Faraday rotation spectroscopy offers excellent sensitivity and high specificity together with outstanding long term system performance. Development of a transportable, cryogen-free, prototype field instrument based on mode-hop-free external cavity quantum cascade laser targeting the optimum NO Q(3/2) transition at 1875.8 cm^{-1} is reported. The system shows a minimum detection limit of 5.4 ppb with a 1sec. lock-in time constant. Continuous, unattended NO monitoring with >1 hour white noise limited averaging times is reported.

Keywords: nitric oxide, quantum cascade laser; laser spectroscopy, Faraday effect, trace-gas detection,

1. INTRODUCTION

Detection of nitric oxide (NO) is of importance in a number of applications including environmental pollution monitoring, or medical diagnostics (e.g. in exhaled breath by asthma patients). By targeting fundamental ro-vibrational transitions of NO at 5.3 μm sensitive concentration measurements can be performed using spectroscopic methods [1, 2]. Faraday rotation spectroscopy (FRS) is an extremely sensitive technique for the detection of paramagnetic species [3-5]. Under influence of a magnetic field the NO transitions undergo Zeeman splitting, which causes a rotation of the polarization of linearly polarized light interacting with the molecules. The best sensitivity for FRS NO detection can be obtained using the Q(3/2) transition at 1875.8 cm^{-1} [5]. This method is intrinsically background free and shows high immunity to the spectral interference from other diamagnetic species. Quantum cascade laser (QCL) based FRS systems have been employed to monitor NO concentrations previously [5, 6], but to our best knowledge by employing a widely tunable external cavity (EC) QCL as a spectroscopic source it is the first time that the most optimum Q(J=3/2) molecular transition at 1875.8 cm^{-1} could be

* gwysoc@princeton.edu; phone 609-258-8587; fax 609-258-2158

used. A transportable, cryogen-free, prototype instrument based on a mode-hop-free EC-QCL will be described.

2. EXPERIMENTAL DETAILS

The experimental setup of the FRS platform is schematically shown in Fig.1. A tunable EC-QCL based on a Littrow configuration with a center radiation frequency at 1890 cm^{-1} ($\lambda \sim 5.3\text{ }\mu\text{m}$) was used as a spectroscopic source. The details of the EC-QCL configuration and performance are described in Ref. [7]. The total EC-QCL frequency tuning range from 1825 to 1980 cm^{-1} allows access to almost entire fundamental absorption band of NO at $5.2\text{ }\mu\text{m}$ as shown in Fig. 2a.

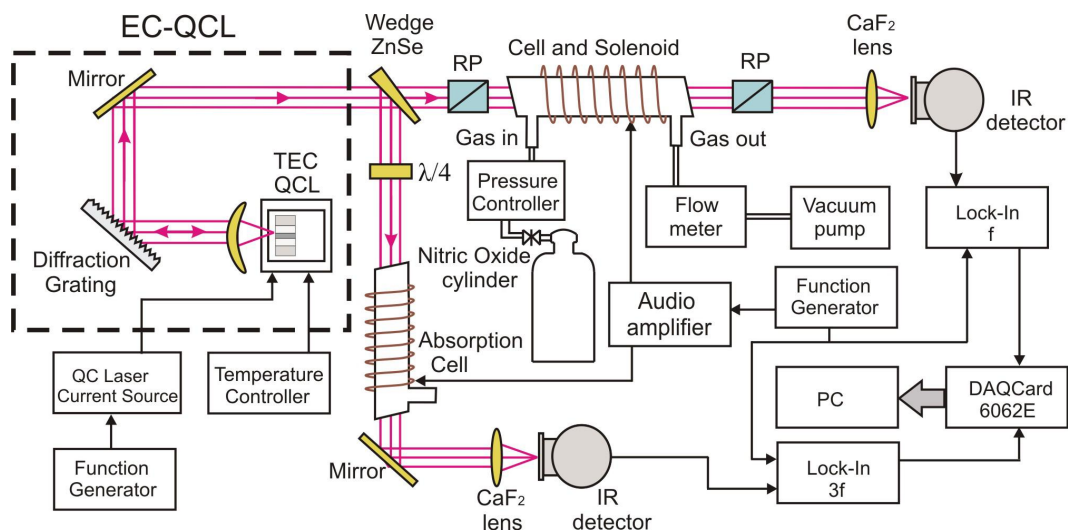


Fig. 1 Schematic diagram of experimental setup for EC-QCL based magnetic rotation spectroscopy. RP – Rochon polarizer, $\lambda/4$ – quarter wave plate, PC – personal computer.

In this work the laser was operated in a CW mode at -20°C and provided a maximum output power of 5 mW at the wavelength coinciding with the target NO line. Fine mode-hop-free tuning of up to 2.5 cm^{-1} enabled by this EC-QCL technology allows for high resolution spectroscopy anywhere within the tuning range and it has been critical to perform active frequency locking to achieve long-term unattended operation of the FRS system.

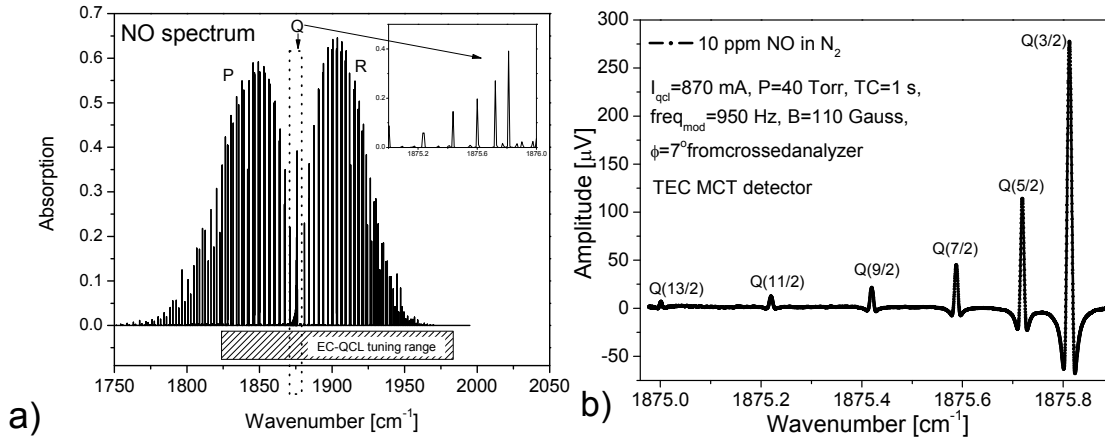


Fig. 2 a) NO absorption spectrum at $5.2\mu\text{m}$ simulated using HITRAN 2004 database. The EC-QCL tuning range is shown for reference. The inset shows the absorption lines in the Q-branch targeted by the FRS sensor system. B) FRS spectrum of the NO Q-branch measured for 10 ppm NO in N_2 mixture at 40 Torr and with 42 cm active optical path length.

The collimated EC-QCL beam (4 mm in diameter), is split by a CaF_2 wedged window into two independent optical paths. In the main path the laser beam propagates through a 50 cm long optical gas cell, which is located inside 44 cm long solenoid. The gas cell was placed between two nearly crossed MgF_2 Rochon polarizers (extinction ratio for both polarizers is $<10^{-5}$). When a longitudinal magnetic field is applied, the linearly polarized QCL beam experiences a Faraday rotation of the plane of polarization as a result of interaction with paramagnetic NO molecules. The light passing through a second polarizer is detected by a mid-infrared thermoelectrically cooled mercury-cadmium-telluride (MCT) photodetector. For small rotation angles the detector signal is directly proportional to the NO concentration inside cell. The current in the solenoid is modulated at $f_m=950$ Hz using a commercial high power audio amplifier (QSC audio model: RMX850), which results in the amplitude modulation of the intensity of the detected radiation. Since the signal exists only when the NO molecules are present, the FRS is considered an optical zero background technique. The NO LMR spectrometer uses a phase sensitive lock-in detection scheme, which demodulates the sinusoidally modulated FRS signal at the frequency f_m . An optimum magnetic field of 110 Gauss required for the FRS signal was produced using an AC current of 3.5A. The detected signal, which is proportional to the difference between two frequency shifted dispersion line shapes, was recorded by a personal computer. For calibration of the FRS spectrometer two calibrated

mixtures of 10 ppm and 96 ppb NO in nitrogen (N₂) were used respectively. The system gas flow was set to ~200 ml/min. An example FRS measurement of the Q-branch of the NO fundamental ro-vibrational band is depicted in Fig. 2b.

The second optical channel of the sensor is used as a reference channel for frequency control of the EC-QCL. The initial linear polarization of the laser radiation is transformed into circular polarization by a quarter wave plate ($\lambda/4$). The beam is directed through a 20 cm absorption gas cell filled with high concentration (5%) NO mixture with air at 25 Torr total pressure. The reference absorption cell was placed inside a 10 cm long magnetic coil. This solenoid was a part of the series RLC circuit formed with the main solenoid and supplied from the same power amplifier. In the presence of alternating magnetic field the signal of Zeeman modulation is observed as a result of interaction between circularly polarized light and NO molecules. The Zeeman modulated reference signal was recorded by a thermoelectrically cooled MCT photodetector and demodulated by a second lock-in amplifier at the 3rd harmonic of f_m . The zero-crossing of the 3rd harmonic signal was used to implement line locking of the EC-QCL to the optimum Q(3/2) molecular transition of NO at 1875.8 cm⁻¹.

3. MEASUREMENT RESULTS

The ultra-sensitive NO detection using the FRS technique at the Q(3/2) molecular transition (1875.8cm⁻¹) requires a careful optimization to obtain the best signal-to-noise ratio (SNR). A series of experiments were performed to determine the optimum sample gas pressure, magnetic field intensity and the analyzer offset angle. The optimum FRS SNR was obtained at a total pressure of 40 Torr and with the magnetic flux density of $B_{rms}=110$ Gauss, measured inside the main magnetic coil. In the reference cell the magnetic flux density was $B_{rms}=33$ Gauss. With a thermoelectrically cooled MCT photodetector with a detectivity of $D^* \approx 1 \cdot 10^{10}$ cm·Hz^{1/2}/W the best SNR is primarily limited by the thermal detector noise. The optimum measurement conditions were obtained for an analyzer offset angle of 7 deg. from its crossed position. The example spectrum of two strongest Q(3/2) and Q(5/2) molecular transitions at 1875.82 cm⁻¹ and 1875.71 cm⁻¹ respectively recorded with the FRS system for a mixture of 96 ppb of NO

in N_2 is shown in Fig. 3. The SNR determined from the standard deviation of the measurement points far from the absorption line yielded minimum detection limit of $MDL=4.3$ ppb. The inset in this Fig. 3 shows similar spectrum recorded for 10 ppm in N_2 mixture. The 100 times higher concentration of NO measured by the system with comparable MDL of 5.4 ppb demonstrates the high dynamic range of the developed technology.

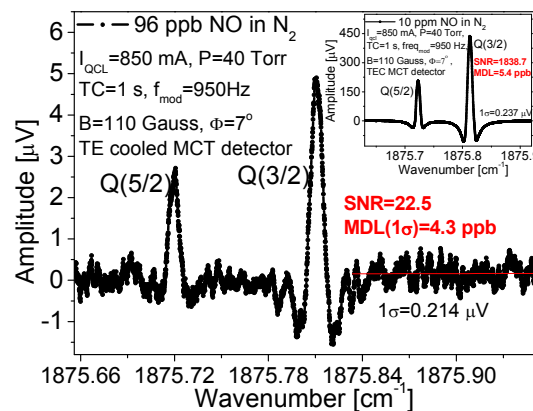


Fig. 3 Magnetic rotation spectrum of Q(3/2) and Q(5/2) transitions of nitric oxide centered at 1875.8 cm^{-1} measured with a thermoelectrically cooled MCT photodetector.

An active wavelength control of the EC-QCL was applied in order to perform continuous, autonomous operation of NO sensor platform. A computer controlled active feedback loop was implemented to lock the laser operating frequency to the target NO Q(3/2) transition at 1875.8 cm^{-1} . The signal measured in the reference channel was used as an error signal for the PID controller, which sets the operating wavelength of the EC-QCL at the peak of the desired absorption line. For system performance evaluation a long time (over 10 hours) measurement series was acquired for a zero-gas preceded and followed by a calibrated mixture of 96 ppb NO in N_2 as shown in Fig. 4a. The Allan variance plot calculated for this data set is shown in Fig. 4b together with a reference plot for an ideal white noise limited system performance. The precise line locking technique results in exceptional system stability allowing averaging times of up to $\sim 4,000$ sec with near the fundamental white noise limited performance.

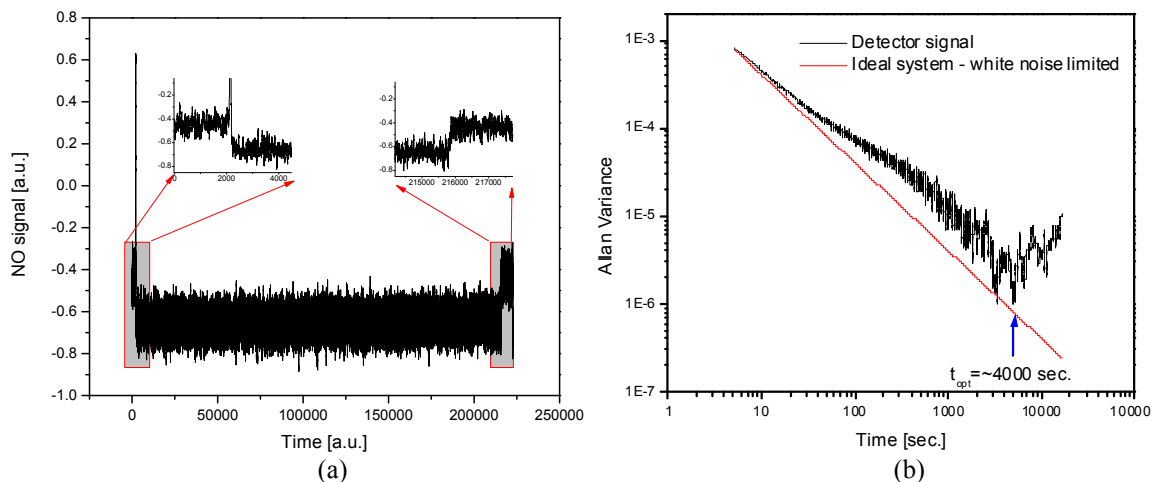


Fig. 4 a) Continuous measurement of NO concentration performed with a FRS sensor system. The time series shows a measurement of zero-gas preceded and followed by a calibrated mixture of 96ppb NO in N_2 .
 b) The Allan plot calculated for the measurement series shown in a).

The capability of continuous unattended operation with an ultra-sensitive detection at the single ppb level enables the application of the EC-QCL based FRS system as a field deployable spectroscopic sensor instrument. A fully automatic prototype sensor system was configured as a transportable platform with an optical setup placed on a 60 cm by 90 cm optical breadboard and with standard laboratory equipment such as lock-in amplifiers, signal generators, power supplies etc. used as system components. A photograph of the system is shown in Fig. 5. The prototype FRS sensor was tested in the field and showed similar performance as in the laboratory.



Fig. 5 A transportable prototype FRS NO sensor system

4. CONCLUSIONS

A sensitive and selective detection of NO was demonstrated using EC-QCL based FRS sensor system. The FRS based spectrometers offer an effective method for the detection of atomic and molecular species with permanent magnetic dipole moment such as oxygen, nitrogen dioxide or hydroxyl radical. With further increasing tuning capabilities of the QCL gain media [8] the developed system offers an attractive solution for multispecies detection using single laser source that allows for most optimum absorption line selection within the EC-QCL tuning range. The results obtained with the FRS and only 44 cm optical pathlength demonstrate detection limit to NO at single ppb level (thermal detector noise limited), which is significantly better than other sensitive spectroscopic techniques in mid-IR [9, 10]. The technique is sensitive only to the paramagnetic species which assures an excellent selectivity of the sensor system. The FRS technique can be further enhanced by increasing the effective optical length within the sample e.g. by means of a multi pass configuration. Future work will focus on the development of a compact, robust and portable QCL based FRS sensor for environmental and biomedical applications.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support from a NSF ERC MIRTHE, a sub-contract from a DoE STTR grant from Aerodyne Research Inc., and the Robert Welch Foundation.

REFERENCES

- [1] J. B. McManus, D. D. Nelson *et al.*, "Comparison of cw and pulsed operation with a TE-cooled quantum cascade infrared laser for detection of nitric oxide at 1900 cm⁻¹", *Applied Physics B: Lasers and Optics* **85**, 235 (2006).
- [2] B. W. M. Moeskops, S. M. Cristescu *et al.*, "Sub-part-per-billion monitoring of nitric oxide by use of wavelength modulation spectroscopy in combination with a thermoelectrically cooled, continuous-wave quantum cascade laser", *Opt. Lett.* **31**, 823 (2006).
- [3] G. Litfin, C. R. Pollock *et al.*, "Sensitivity enhancement of laser absorption spectroscopy by magnetic rotation effect", *The Journal of Chemical Physics* **72**, 6602 (1980).

- [4] R. J. Brecha, L. M. Pedrotti *et al.*, “Magnetic rotation spectroscopy of molecular oxygen with a diode laser”, *J. Opt. Soc. Am. B* **14**, 1921 (1997).
- [5] H. Ganser, W. Urban *et al.*, “The sensitive detection of NO by Faraday modulation spectroscopy with a quantum cascade laser”, *Molecular Physics* **101**, 545 (2003).
- [6] T. Fritsch, M. Horstjann *et al.*, “Magnetic Faraday modulation spectroscopy of the 1–0 band of 14NO and 15NO”, *Applied Physics B: Lasers and Optics* **93**, 713 (2008).
- [7] G. Wysocki, R. Lewicki *et al.*, “Widely tunable mode-hop free external cavity quantum cascade lasers for high resolution spectroscopy and chemical sensing”, *Applied Physics B: Lasers and Optics* **92**, 305 (2008).
- [8] A. Wittmann, A. Hugi *et al.*, “Heterogeneous High-Performance Quantum-Cascade Laser Sources for Broad-Band Tuning”, *Quantum Electronics, IEEE Journal of* **44**, 1083 (2008).
- [9] G. Wysocki, A. Kosterev *et al.*, “Spectroscopic trace-gas sensor with rapidly scanned wavelengths of a pulsed quantum cascade laser for in situ NO monitoring of industrial exhaust systems”, *Applied Physics B: Lasers and Optics* **80**, 617 (2005).
- [10] M. R. McCurdy, Y. Bakhirkin *et al.*, “Performance of an exhaled nitric oxide and carbon dioxide sensor using quantum cascade laser-based integrated cavity output spectroscopy”, *Journal of Biomedical Optics* **12**, 034034 (2007).