Faraday rotation spectroscopy of nitrogen dioxide based on a widely tunable external cavity quantum cascade laser

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ABSTRACT

Faraday Rotation Spectroscopy (FRS) is a technique for the sensitive and selective detection of paramagnetic molecules or radicals such as NO, NO_2, O_2 or OH^-. Moreover FRS is suitable for atmospheric measurements due to the insensitivity to non-paramagnetic interfering molecules such as H_2O and CO_2. Experimental results of an FRS sensor for the NO_2 detection employing an external-cavity quantum cascade laser (EC-QCL) are reported. The CW EC-QCL exhibits mode-hop free (MHF) tuning between 1600 cm^{-1} and 1650 cm^{-1}. This allows targeting the optimum $4_{41} \leftarrow 4_{40}$ Q-branch NO_2 transition at 1613.25 cm^{-1}. A rotation of the polarization state of the initially linearly polarized laser light is observed when an AC magnetic field is applied to the NO_2 cell, placed between two nearly crossed Rochon polarizers. This rotation of the polarization state is proportional to the NO_2 concentration and can be determined by a photodetector located after the second polarizer. For long-term continuous measurements a second branch consisting of a detector and reference cell filled with 0.2 % NO_2 in N_2 is used to lock the laser to the selected NO_2 transition. A minimum detection sensitivity (1σ) of 1 parts per billion (ppbv) was obtained for a 1 sec lock-in time constant (TC).

Keywords: Faraday Rotation Spectroscopy, external-cavity quantum cascade laser, nitrogen dioxide, trace-gas detection, paramagnetic molecules, atmospheric measurements, midinfrared

1. INTRODUCTION

NO_2 is a prominent pollutant in the atmosphere and is formed in various combustion devices such as car engines or fuel using power plants. In order to investigate and control the NO_2 formation processes it is important to determine the concentration of the target gas. A suitable technique for this purpose is ultra sensitive and highly selective FRS, which is a technique for the detection of paramagnetic molecules and radicals such as O_2, NO, NO_2 or OH^- [1-3]. Furthermore, FRS can be considered as a background-free detection method due to its insensitivity to non-paramagnetic molecules present in the atmosphere such as H_2O or CO_2. The ro-vibrational transition of a paramagnetic molecule undergoes a splitting due to the Zeeman effect. This leads to a different refractive index for the right- and left-handed circular polarization (LHCP and RHCP) components of an incident laser beam. Therefore, a linearly polarized beam, i.e. a superposition of LHCP and RHCP, experiences a rotation of the polarization axis due to birefringence. The rotation angle is proportional to the concentration of the paramagnetic molecules present in the cell [4]. The optimum FRS signal of NO_2 for our spectroscopic source is induced by the Q-branch transition $4_{41} \leftarrow 4_{40}$.

2. EXPERIMENTAL SETUP

The block diagram of the experimental setup of the FRS system is shown in Figure 1. As a convenient spectroscopic source a widely tunable EC-QCL from Daylight Solutions was employed. The frequency tuning range from 1538.3 cm^{-1} to 1703.3 cm^{-1} is realized by varying the diffraction grating angle of the EC-QCL.

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The MHF frequency tuning range between 1600 cm^{-1} and 1650 cm^{-1} covers the optimum for the Q-branch NO$_2$ transition in the fundamental ν_3 band at 1613.25 cm^{-1}. This is the first time to our knowledge that NO$_2$ was detected at this transition with an EC-QCL based FRS technique.
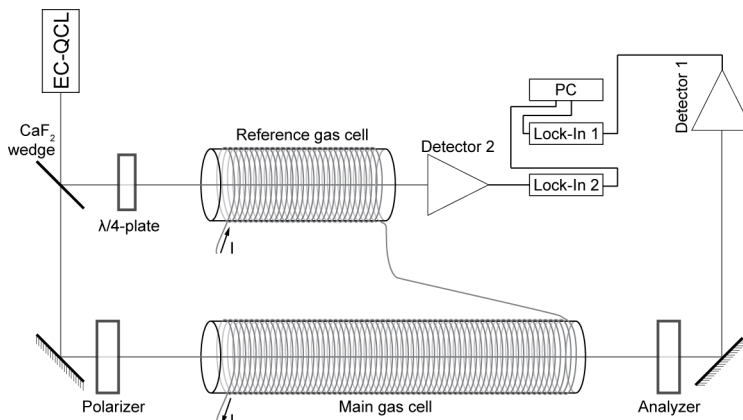

Figure 1: Block diagram of the experimental setup of the FRS system.

The laser is operated in a CW mode at a temperature of 18 °C and exhibits a maximum optical power of 150 mW within the tuning range. A measurement of the total spectral tuning range and optical power is shown in Figure 2. The collimated EC-QCL beam is delivered to the CaF$_2$-wedge and split into two optical paths. The main path consists of a 50 cm long 1-inch diameter glass cell with wedged CaF$_2$ windows, flushed constantly during the experiment with a calibrated mixture of 2 ppmv NO$_2$ in N$_2$. The gas cell was surrounded by a 44 cm long solenoid coil and placed between two MgF$_2$ Rochon polarizers with an extinction ratio of less than 10^{-5}. The first polarizer maintains the incident horizontal polarization whereas the second polarizer (called analyzer) oriented at almost 90° crossed position with respect to the first polarizer is used to measure the rotation of the polarization axis caused by the presence of NO$_2$ molecules. For small rotation angles, the amplitude of the resulting signal is proportional to the NO$_2$ concentration. The pressure inside the glass cell was controlled by an MKS pressure controller and kept at a lower pressure value in order to minimize the NO$_2$ absorption line broadening effect. The best signal-to-noise-ratio (SNR) for the FRS measurement was obtained with pressures between 25 and 35 Torr.
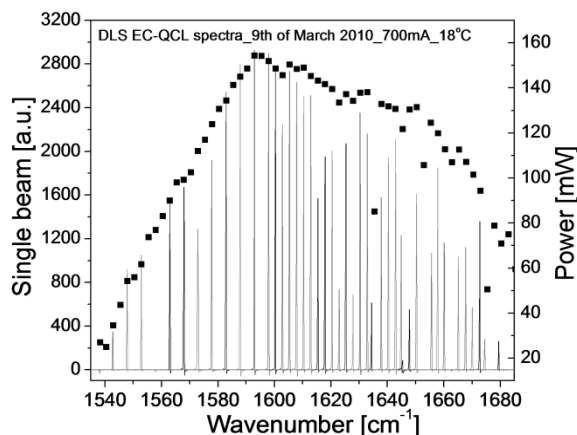

Figure 2: EC-QCL spectrum (lines) and power (squares)

A solenoid was used to produce an AC magnetic field. This solenoid is a part of a series RLC circuit with a resonance frequency of f$_{res}$ = 832 Hz. The sinusoidal signal at f$_{res}$ is generated with a function generator (Stanford Research) which is amplified with a commercial audio amplifier (QSC Model RMX850) and delivered to the solenoid resulting in amplitude modulation of the intensity of the detected EC-QCL radiation. The maximum AC current of the coil of 7 A

(rms) corresponds to an AC magnetic field of 230 Gauss (rms). The FRS signal is detected with a thermoelectrically cooled (TEC) mercury-cadmium-telluride (MCT) detector, pre-amplified with a transimpedance amplifier and demodulated with a phase-sensitive lock-in amplifier.

The second optical path is used as a reference channel to fix the laser frequency at the peak of the selected NO_2 absorption line. A quarter-wave plate is used to convert the linearly polarized EC-QCL radiation into circular polarized light (either LHCP or RHCP depending on the orientation of the quarter-wave plate) for Zeeman modulation spectroscopy. The reference cell filled with 0.2 % NO_2 in N_2 at a pressure of 25 Torr is also enclosed a 10 cm long solenoid connected in series to the solenoid in the main FRS channel. For the maximum current of 7 A (rms) the generated magnetic field is 75 Gauss (rms). Since the radiation in this branch is circular polarized the oscillating magnetic field modulates the absorption via Zeeman detuning of the corresponding transition (either the $\Delta M_J = +1$ or $\Delta M_J = -1$ transition corresponding to the LHCP or RHCP components respectively). The reference beam is detected with a second TEC MCT detector and demodulated with a second lock-in amplifier. The 3rd harmonic of the signal is used to lock the laser at the Q-branch transition frequency of 1613.25 cm^{-1}.

The signals from both the main and reference optical paths are recorded with a personal computer using a National Instrument data acquisition card and LabView software. The FRS NO_2 system is operated both in the line-scanning or real-time monitoring mode.

3. RESULTS

3.1 Line Scanning FRS Results

The upper plot in Figure 3 shows the FRS signal for the calibration mixture of 2 ppmv NO_2 in N_2 at 30 Torr. The analyzer angle is set to 2° from the totally crossed position. The laser frequency was tuned over ~0.8 cm^{-1} by applying 1 mHz sine wave with an amplitude of 60.5 V to the EC_QCL piezo element. The spectrum is recorded with a lock-in amplifier TC set to 1 sec. The lower plot shows a HITRAN based simulation of the absorption spectrum under the same conditions of pressure, concentration and path length.
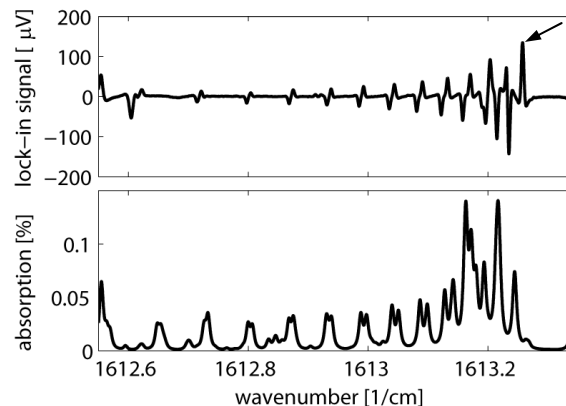

Figure 3: FRS signal of 2 ppmv NO_2 in N_2 at the optimum transition of 1613.25 cm^{-1} at 30 Torr (upper plot) and the result of the corresponding HITRAN based simulation for the same parameters (lower plot).

The mismatch of the transition frequencies between simulated and measured spectrum is caused by a slight non-linearity in the frequency tuning of the EC-QCL. In Figure 4 the FRS signal of NO_2 at the optimum $4_{41} \leftarrow 4_{40}$ transition (1613.25 cm^{-1}) is depicted over a narrow frequency spectral range of ~0.04 cm^{-1}.
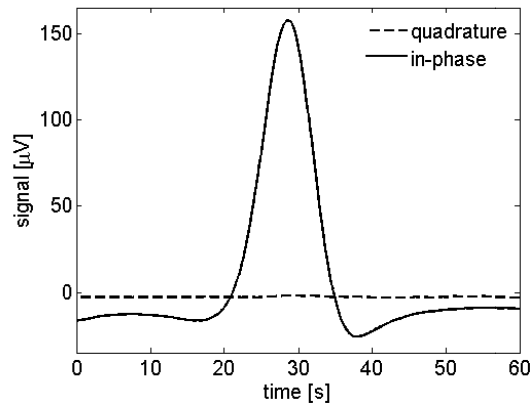
Figure 4: Narrow frequency scan over the optimum Q-branch $4_{41} \leftarrow 4_{40}$ NO_2 transition for the FRS technique. This transition corresponds to the one marked with an arrow in Figure 3.

For a 2 ppmv of NO_2 concentration at 30 Torr a minimum detection sensitivity is found to be 3.5 ppbv (1σ). In order to optimize the FRS sensor performance the optimum selection for the analyzer angle, gas pressure value and magnetic field strength was performed. As mentioned above, the optimum pressure with respect to highest SNR was experimentally found to be between 25 and 35 Torr. Therefore, a pressure of 30 Torr was selected for most of the FRS measurements. Figure 5a illustrates how the measured sensitivity of the FRS sensor depends upon the analyzer angle. The optimum angle was found to be at 3° with respect to the crossed position. For analyzer angles smaller than 3° less optical power is transmitted through the analyzer resulting in a lower signal on the photodetector. For higher analyzer angles a reduction in the SNR value is observed due to an increase of the source noise received by the photodetector. The level of this noise scales proportionally with the intensity transmitted by the analyzer. Therefore, an optimum angle is expected to exist due to the trade-off between higher signal on the detector and higher noise transmitted by the analyzer simultaneously. In addition, a too intense laser beam will saturate the MCT detector which reduces the FRS signal. The measured NO_2 sensitivity as a function of the magnetic field strength produced by the solenoid in the main branch is shown in Figure 5b. The optimum field is ~200 Gauss (rms) corresponding to a current through the coil of ~6 A (rms). It is interesting to note that the sensitivity mainly depends on the noise level rather than on the signal strength. The difference in the refractive indices for the LHCP and RHCP only slightly increases with increasing magnetic field above ~180 Gauss (rms). The FRS signal is proportional to this difference in the refractive indices which explains the slow increase for increasing magnetic fields. On the other hand, the electronic noise of the system (produced by the RLC circuit and detection equipment) has a minimum for a magnetic field of ~200 Gauss. Since the analyzer angle used in Figure 5b is small (2°) the optical noise has an insignificant effect.
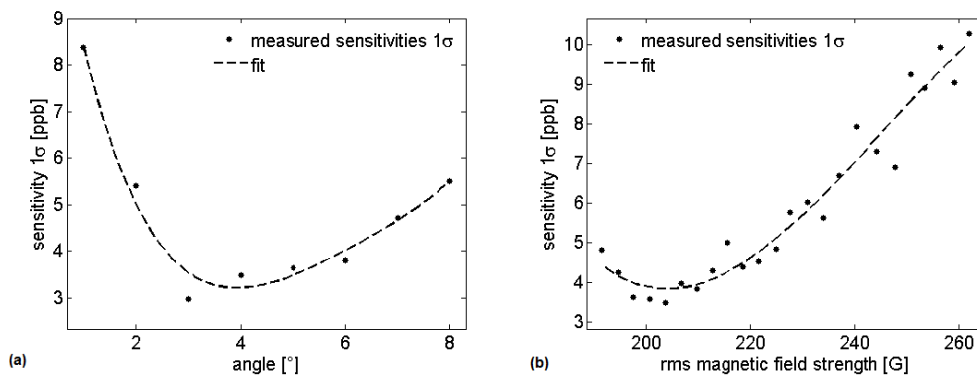

Figure 5: Optimization of the analyzer angle (a) and the applied magnetic field (b) with respect to maximum NO_2 detection sensitivity.

Improvement in the SNR can be achieved either by the reduction of the system noise, mostly related to the applied magnetic field, by using better quality polarizers or more sensitive potodetectors. Reducing the system noise and electromagnetic pick-up is a time consuming and not necessarily trivial task. However an improved detection limit of the FRS signal can be achieved by increasing the active pathlength.
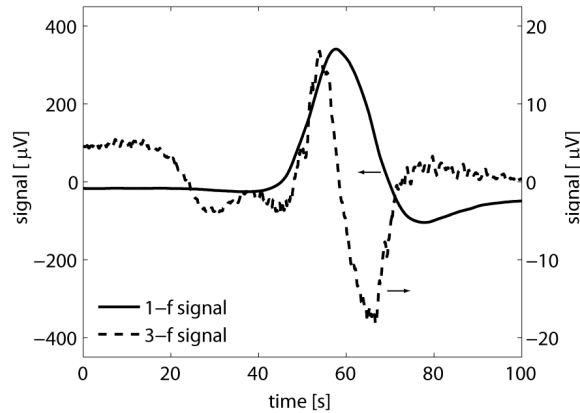

Figure 6: Scan over the optimum transition at 1613.25 cm^{-1}; solid line: the 1-f FRS signal from the main gas cell filled with the 2 ppmv NO_2 mixture; dashed line: 3-f signal induced by the 0.2 % NO_2 mixture present in the reference cell.

By implementing a double pass configuration by adding a concave mirror after the main gas cell an increase of the FRS signal by a factor of two is obtained, which is shown in Figure 6 for 2 ppmv NO_2 in N_2 mixture at 30 Torr. With this modification a significant improvement of the maximum sensitivity to 1 ppbv (1σ) for a 1 sec lock-in TC was achieved.

3.2 Continuous Monitoring Results

Continuous monitoring of the NO_2 concentration was achieved by locking the laser frequency to the NO_2 transition at 1613.25 cm^{-1}. For this purpose a LabView software based PID controller correction signal was applied to the EC-QCL piezo element which is responsible for the laser frequency control. Figure 7 shows the results for the dilution of a certified mixture of 2 ppmv NO_2 in pure N_2 diluted by a factor of 100, 40, 20, 10, 4 and 2 times, respectively.
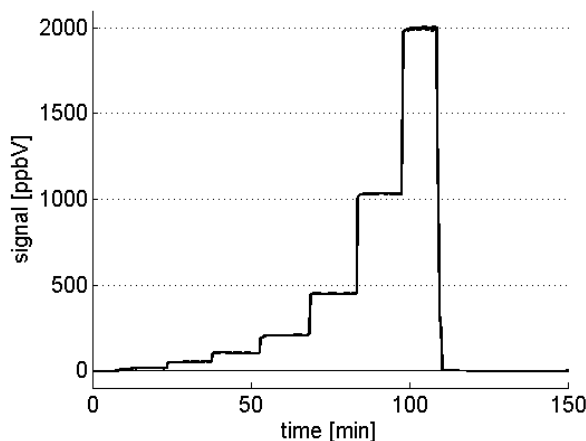

Figure 7: FRS signal for NO_2 diluted to different concentrations (see Table 1); other parameters are a TC of 1 sec, a pressure of 30 Torr, a magnetic field of 180 G (rms) and a one pass gas cell configuration.

In Table 1 the measured vs. targeted concentrations are presented. The linear response of the sensor on the NO_2 concentration is obtained with ~10 % error. The mismatch between measured and targeted NO_2 concentrations results from the reactive nature of the NO_2 and its adsorption to the metal components of the FRS system. Reasonably fast response time in the order of 10 sec (limited by the strength of the pump) is achieved by keeping the tubing length as short as possible.

Targeted	20	50	100	200	500	1000	2000
Measured	16.5	53.6	105	207	450	1030	2000 (cal.)

Table 1: NO_2 concentrations as measured in the continuous measurement mode (see Figure 7).

To estimate the long-term stability of the FRS system the signal of ultra high purity N_2 was recorded for a period of >30 hours (see Figure 8). Slow drift and fluctuations on a time-scale of several hours limit the maximum sensitivity of the one pass system to ~5 ppbv. We expect electrical noise generated in our system (ground loops and electromagnetic coupling between coil and detector) to be responsible for these fluctuations since the FRS system is insensitive to optical noise and no additional background signal is present. As for the line scanning operation mode an improvement of the maximum sensitivity is expected by using a two pass cell configuration. However, strong interferences due to etalon effects within the gas cell destabilize the system and lead to an SNR much lower than the one obtained with the single pass cell.
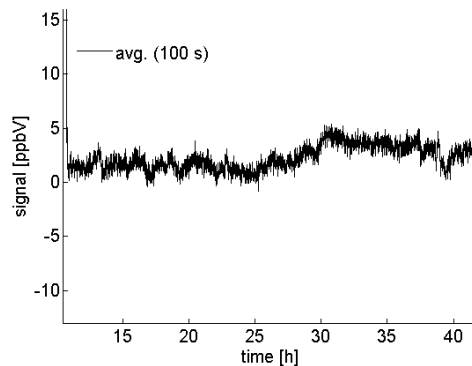

Figure 8: Long-term FRS measurements of purified N_2; fluctuations on the timescale of several hours limit the sensitivity to 5 ppbv.

4. CONCLUSION AND OUTLOOK

An EC-QCL based FRS system for NO_2 detection providing high selectivity and dynamic range of the measurements is demonstrated. A maximum NO_2 sensitivity of 1 ppbv (1σ) concentration level for a 1 sec lock-in TC was achieved with the FRS sensor. The sensor is optimized with respect to sensitivity by an independent analysis of the system pressure, the analyzer angle and magnetic field strength. A frequency control loop is implemented allowing the continuous monitoring of NO_2 with a maximum sensitivity of 5 ppbv. To enable real-time detection of atmospheric NO_2 the detection sensitivity must be improved since typical concentrations range from 1 to 20 ppbv. In order to achieve sub-ppbv NO_2 detection a multi-pass scheme can be adapted to the FRS technique. Another option is to operate the laser in a fast line-scanning mode (e.g. at one scan per second) and use line-fitting software to estimate the NO_2 concentration. Future work upon achieving single ppbv sensitivity in the real-time detection mode will include environmental field studies. Miniaturization of the FRS system will be another future task.

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