Ultra-sensitive detection of Nitric Oxide at 5.33 μm using an External Cavity QCL based Faraday Rotation Spectroscopic Sensor Platform

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Abstract: Magnetic rotation spectroscopy of nitric oxide at most favorable Q(3/2) transition at 1875.8 cm^{-1} is reported. Detection limit (1σ) at 5ppb level was obtained for a ~44cm long active optical path with 1s lock-in time constant.

OCIS codes: (140.5965) Semiconductor lasers, quantum cascade; (300.6360) Spectroscopy, laser

1. Introduction

Magnetic Rotation Spectroscopy (MRS) based on the Faraday effect is well known as an extremely sensitive spectroscopic technique for detection of paramagnetic molecules like nitric oxide, oxygen or hydroxyl radicals [1-4]. An additional advantage of this method is its high selectivity only to molecules exhibiting paramagnetic properties, which is very desirable in atmospheric measurements of free radicals [5] or in medicine application for breath analysis, where interference from water and carbon dioxide is eliminated. Linearly polarized light can be considered as a superposition of right handed and left handed circularly polarized electromagnetic waves. Under the influence of an axial magnetic field each circularly polarized wave will experience a different complex propagation constant originating from the interaction with either ΔM = +1 or the ΔM = -1 NO transition components. This is observed as a rotation of the polarization axis of the initially linearly polarized light. After passing through a nearly crossed second polarizer, this polarization rotation state is detected as a change in the intensity of the transmitted light with a photodetector. MRS provides a significant reduction of source noise [6] limited only by the quality of the polarizers used. Amplitude modulation of the magnetic field makes MRS a zero background technique, where ultimate sensitivity is often limited by detector noise. For the case of NO the Q(3/2) fundamental transition at 1875.8 cm^{-1} is the most optimum for MRS detection of nitric oxide due to its highest magnetic modulation sensitivity [1].

2. MRS experimental setup and results

A schematic view of the experimental setup for MRS is presented in Fig. 1. A Fabry Perot quantum cascade laser operating in external cavity configuration (EC-QCL) at 5.2 μm was employed [7,8] as a spectroscopic source. The EC-QCL source is capable of coarse single mode tuning over 155 cm^{-1} by changing the diffraction grating angle. For high resolution spectroscopy, mode hop free tuning in a range of 2 cm^{-1} can be performed anywhere between 1825 and 1980 cm^{-1}. The laser was operated at –30°C with a maximum output power of 11 mW. The collimated output laser beam (3 mm in diameter) is split by ZnSe wedged window into two independent pathways in order to obtain a reference channel used for EC-QCL control purposes. The main laser beam after passing through first MgF_2 Rochon polarizer (extinction ratio below 10^{-5}) is directed into 50cm absorption gas cell placed inside a 44 cm solenoid then passed through a second MgF_2 Rochon polarizer and detected by a thermoelectrically cooled MCT detector.

The MRS experiment is performed using phase sensitive lock-in detection scheme, where sinusoidally modulated magnetic field at 950Hz is demodulated by lock-in amplifier at 1st harmonic and recorded by personal computer. The detected signal originates from the magnetic circular birefringence and is proportional to the first derivative of a dispersion line shape. The optimum signal-to-noise ratio is obtained by selection of a sample gas pressure, magnetic field strength and analyzer offset angle. First measurements were performed using a certified mixture of 10 ppm NO balanced with nitrogen. The MRS spectrum presented in Fig. 2 was recorded at pressure of 35 Torr with a longitudinal alternating magnetic field of 110

Gauss (rms). It was found that in our optical system the offset angle of 6° from perfectly crossed analyzer position results in a minimum detection limit of 5.4 ppb with a 1 sec lock-in time constant.

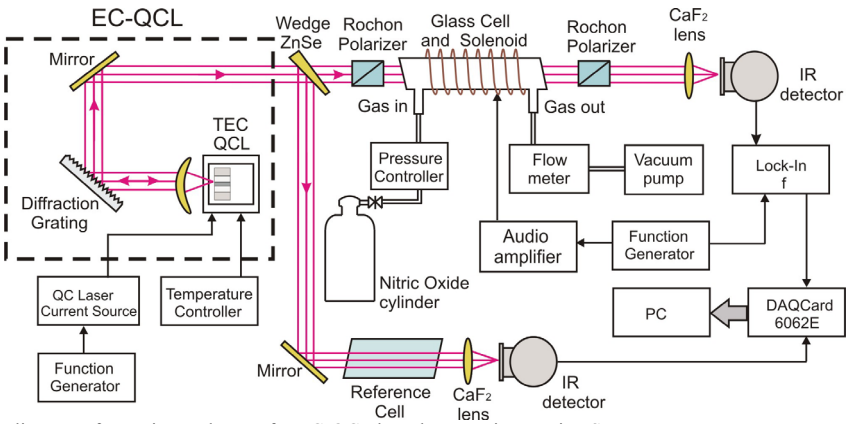

Fig. 1 Schematic diagram of experimental setup for EC-QCL based Magnetic Rotation Spectroscopy.

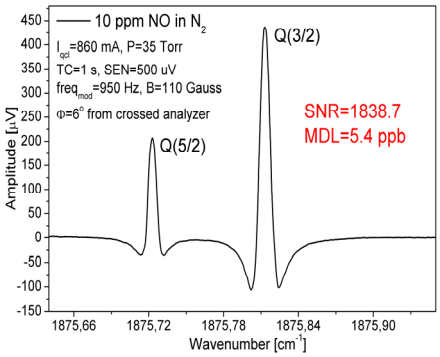

Fig. 2 Magnetic rotation spectrum of Q(3/2) and Q(5/2) transitions of nitric oxide.

3. Conclusion

The results obtained to-date show an excellent potential of this highly sensitive spectroscopic technique in combination with high power liquid nitrogen free QCLs to perform sensitive quantification of paramagnetic molecular species.

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