Simultaneous Measurement of NO andNO_2 using a Dual-Wavelength Quantum Cascade Laser

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Abstract: We demonstrate a sequentially operating dual-wavelength QCL, emitting single-mode at 5.26 and 6.25 μm, and its spectroscopic application on an automotive test-bench, and for air pollution monitoring reaching over 10 Hz and sub-ppb detection.
OCIS codes: (300.6190) Spectrometers; (300.6360) Spectroscopy, laser; (140.3070) Infrared and far-infrared lasers; (140.5965) Semiconductor lasers, quantum cascade; (280.1740) Combustion diagnostics; (280.1120) Air pollution monitoring.

1. Introduction

Simultaneous detection of multiple gas species using mid-IR laser spectroscopy is highly appealing for a large variety of applications ranging from air quality monitoring or medical breath analysis to industrial process control. However, state-of-the-art distributed-feedback (DFB) mid-IR lasers are usually tunable only within a narrow spectral range, which generally leads to a one-laser-one-compound measurement strategy. Thus, multi-species detection involves several lasers and elaborate beam combining solutions [1]. This makes them bulky, costly, and highly sensitive to optical alignment, which limits their field deployment.

1. Dual-wavelength quantum cascade laser

In this paper, we explore an alternative measurement concept based on a dual-wavelength quantum cascade laser (DW-QCL) [2]. This laser emits at two spectrally distinct wavelengths using a succession of two DFB gratings with different periodicities and a common waveguide to produce one output beam (Fig. 1). The laser design was optimized for NO_x measurements and correspondingly emits single-mode at 5.26 and 6.25 μm. Electrical separation of the respective laser sections makes it possible to address each wavelength independently. Thereby, it is possible to detect both NO and NO_2 with a single device using the same optical path, without any beam combining optics, i.e. in a compact and cost-efficient single-path optical setup.

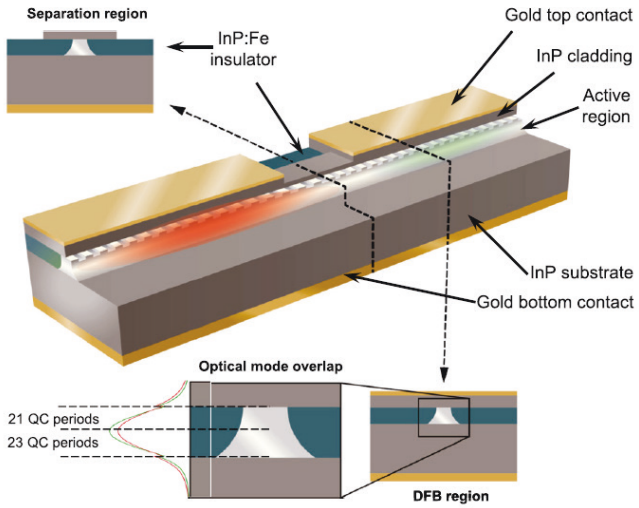

FIG. 1. Schematic drawing of the dual-wavelength laser with cross-sectional views of the injection and the separation regions. Calculated mode profiles of the fundamental TM modes supported by the active waveguides at 5.25 μm (green) and 6.25 μm (red) are also shown. [2]

The laser operates in pulsed mode in a wide temperature range up to 30 °C. As a result of accurate active region design, the threshold current is similar for both emission wavelengths, i.e. 0.8 A (3.6 $kAcm^{-2}$) and 1.0 A (4.4 $kAcm^{-2}$) at 1900 cm^{-1} and 1600 cm^{-1}, respectively, allowing to operate both laser sections at the same driving conditions. The laser linewidth at both emission frequencies is primarily determined by the thermal chirp, which scales with the pulse duration and the magnitude of the injection current. In order to achieve a spectrally narrow emission, both laser sections were driven with equally short pulses of 5 ns and an injection current of 1.1 A. The laser emission linewidths retrieved from low pressure gas spectra measurements are 0.025 cm^{-1} at 1600 cm^{-1} and 0.030 cm^{-1} at 1900 cm^{-1}, respectively, comparable to conventional pulsed QC lasers.

2. Setup and applications

The dual-wavelength QCL was used in a direct absorption spectroscopic setup using a pulse normalization technique to account for pulse to pulse variations. The laser beam was collimated and directed into an astigmatic mirror Herriott multipass gas cell with an optical path of 36 m (Aerodyne Research, USA). The beam leaving the cell was refocused onto a fast thermoelectrically cooled MCT detector (Vigo SA, Poland). A set of 44 spectra of each gas were acquired and averaged at a rate of 10 Hz.

The spectrometer was successfully deployed for fast (10 Hz) detection of NO and NO_2 emissions after an exhaust gas treatment system of a heavy duty diesel engine (Fig. 2). Results were in excellent agreement with a standard CLD analyzer, which however only yields NO_x (NO + NO_2) data. Emission limit regulations ask for continuous reduction of oxides of nitrogen NO_x, i.e. the sum of NO and NO_2. This is achieved through elaborate exhaust gas treatment systems, often consisting of several catalysts and a particle filter. Because of the complex chemistry involved, optimization of the exhaust gas treatment would largely profit from the selective detection of NO and NO_2, as opposed to measuring their sum, as is usually done using certified chemiluminescence NO_x detectors.

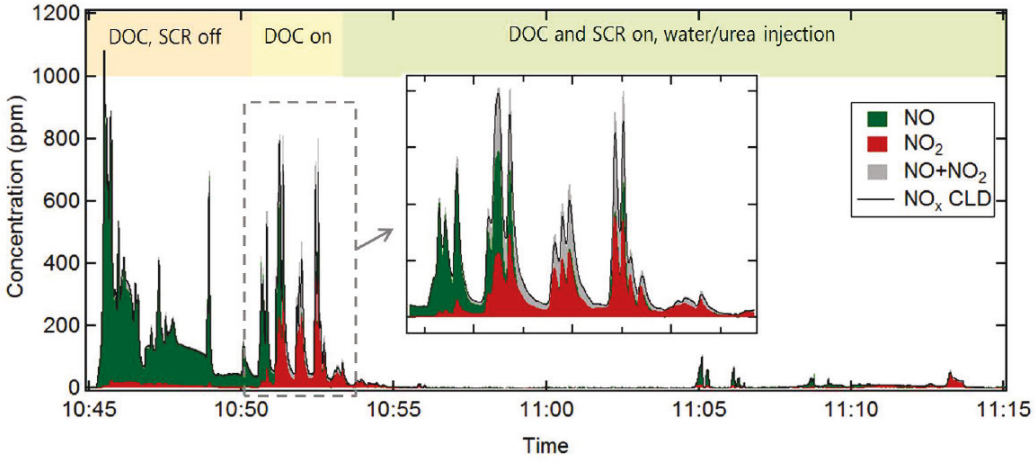

FIG. 2. NO_2 (red) and NO (green) emissions measured after the exhaust gas treatment system of a heavy-duty diesel engine during a WHTC test. Comparison of their sum (gray) with the NO_x concentration measured by an automotive CLD (black line) is shown in the inset. [3]

While automotive emission measurements require high measurement rates and linearity in a large concentration range, the main challenge for atmospheric research is reaching the necessary sensitivity. This has been investigated by continuously measuring the ambient NO and NO_2 concentrations at the Empa campus site in Dübendorf, Switzerland (Fig. 3). For these measurements, outdoor ambient air was continuously sampled through the multipass cell at 1 slpm and 80 hPa. Every hour, a zero-point measurement was performed during 180 s to account for instrumental drifts, taking advantage of the excellent 1s-detection limit of 0.5 and 1.5 ppb after 100 s of averaging. A commercial dual channel CLD (APNA360, Horiba, Japan) measuring both NO and NO was employed as a reference.

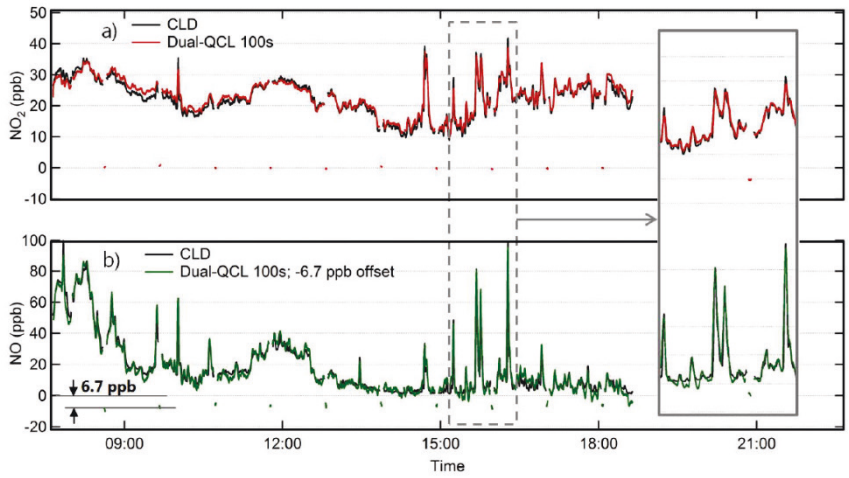

FIG. 3. NO_2 (red) and NO (green, –6.7 ppb offset) emissions in ambient air at the Empa site in Dübendorf, Switzerland. For both datasets, a direct comparison with a chemiluminescence ambient air monitor (black) is shown. A small systematic offset of 6.7 ppb present in the NO measurement is due to independent zero calibration of the instruments. [3]

3. Conclusions and outlook

The present work is a successful demonstration of sensitive and specific multi-species detection performed with a novel dual-wavelength QC laser. Emitting at two, spectrally largely distinct (300 cm^{-1}) frequencies, this laser provides for simultaneous detection of NO and NO_2 down to ppb levels. Very recently, the laser design has been further improved, currently allowing for continuous wave operation at room temperature. This enhances the spectroscopic performance further, likely triggering a new trend in multi-species laser spectrometer development.

4. References

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[3] Jágerská, J., P. Jouy, B. Tuzson, H. Looser, M. Mangold, P. Soltic, A. Hugi, R. Brönnimann, J. Faist and L. Emmenegger. "Simultaneous measurement of NO and NO_2 by dual-wavelength quantum cascade laser spectroscopy." Optics Express 23, 1512-1522 (2015).