Simultaneous measurement of NO and NO\textsubscript{2} by dual-wavelength quantum cascade laser spectroscopy

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Abstract: The concept of a multi-wavelength quantum cascade laser emitting at two or more spectrally well-separated wavelengths is highly appealing for applied spectroscopy, as it allows detecting several species with compact and cost-efficient optical setups. Here we present a practical realization of such a dual-wavelength setup, which is based on a room-temperature quantum cascade laser emitting single-mode at 1600 cm\textsuperscript{-1} and 1900 cm\textsuperscript{-1} and is thus well-suited for simultaneous NO and NO\textsubscript{2} detection. Operated in a time-division multiplexed mode, our spectrometer reaches detection limits of 0.5 and 1.5 ppb for NO\textsubscript{2} and NO, respectively. The performance of the system is validated against the well-established chemiluminescence detection while measuring the NO\textsubscript{x} emissions on an automotive test-bench, as well as upon monitoring the pollution at a suburban site.

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secured their leading position for trace gas detection in environmental sciences [6–8], medical based on single-mode quantum cascade (QC) [1–3] or interband cascade (IC) [4, 5] lasers has

1. Introduction

The excellent sensitivity, specificity and speed of state-of-the-art mid-infrared spectrometers based on single-mode quantum cascade (QC) [1–3] or interband cascade (IC) [4, 5] lasers has secured their leading position for trace gas detection in environmental sciences [6–8], medical
The strength of this technique rests upon the availability of distributed feedback (DFB) lasers with extremely narrow spectral emission that can be tailored for any frequency in the entire fingerprint region from 3 to 25 \( \mu \text{m} \). However, one major limitation of using DFB-QC lasers is their rather small spectral coverage of typically 10 \( \text{cm}^{-1} \), which generally leads to one-laser-one-compound measurement strategy.

Much broader single-mode tuning ranges in the order of 100 \( \text{cm}^{-1} \) have been recently achieved using external cavity (EC) configurations [13] or MIR optical combs [14, 15]. In the case of the EC lasers, the large tunable bandwidth is achieved at the expense of a drastic reduction of the measurement rate, which is typically between 1–100 Hz [16] compared to more than 10 kHz with DFB lasers. On the other hand, MIR dual comb spectroscopy realized using novel heterostructure QC lasers [17] give a promise of both, bandwidth and speed, but immaturity of this method still hinders its use in practical application.

Commercial implementations of multi-compound spectrometers therefore rely on multiple DFB laser modules, each selected for a given target gas, whose outputs are combined into a single multi-wavelength beam using macroscopic optical elements, such as beam splitters or dichroics [18], dispersive elements [19] or metallic reflectors [12]. In this way, for instance, up to four QC lasers were combined through a four-face pyramidal mirror to measure five different components of cigarette smoke [18], and highly time-resolved molecular plasma diagnostics was accomplished using three lasers coupled by a series of four off axis parabolic mirrors [12]. All these approaches, however, imply a significant amount of optical elements that are highly sensitive to their alignment. Furthermore, a temperature controller and driving electronics is required for each individual laser, which increases the overall footprint and the cost of the instrument. In this context, it is highly appealing to have a MIR laser source with all advantages of a DFB laser, which emits at two or more wavelengths associated with molecular transitions of different gas species.

In this paper, we demonstrate a dual-wavelength spectrometer, based on a DFB laser emitting sequentially at 1600 \( \text{cm}^{-1} \) and 1900 \( \text{cm}^{-1} \). These two wavelengths were chosen as they coincide with the strongest absorption bands of \( \text{NO}_2 \) and \( \text{NO} \) that are both relevant pollutants and their simultaneous detection is of a great practical interest. Since both frequencies are generated in the same optical waveguide, their emission directions are strictly identical, providing for multi-species detection without the need for multiple laser modules or beam combining optics.

### 2. Dual-wavelength quantum cascade laser

Although hardly achievable in conventional semiconductor diode lasers, multi-wavelength emission, i.e. emission at two or more spectrally well-separated wavelengths from the same active ridge, is feasible with QC lasers. The first working dual-wavelength lasers were demonstrated more than a decade ago [20–22]. However, only due to newly developed predictive physical models [23] and improvements in fabrication technology, designs maintaining good quantum efficiency and gain performance for both lasing wavelengths have been realized.

The dual-wavelength QC laser employed in the present work is a single-mode, room-temperature device based on a common active waveguide (see Fig. 1), which allows for sequential operation at two, spectrally well-separated wavelengths. The option of sequential operation is a necessary prerequisite for use in laser spectrometers, since it prevents any overlaps and cross-talks between absorption signals from the two spectral ranges. Detailed description of the active region design, the QC layer structure as well as the laser processing is reported elsewhere [24].

The laser operates in pulsed mode in a wide temperature range with an upper limit of 30 \( ^{\circ} \text{C} \). Figure 2(a) shows the peak output power versus the injection current at the heatsink tempera-
Fig. 1. Schematic drawing of the dual-wavelength QC laser. The active waveguide is formed by a stack of two different single-wavelength active regions optimized for emission at 1600 cm$^{-1}$ and 1900 cm$^{-1}$. Along the propagation direction, it is divided into two electrically separated DFB sections, which provide for single-mode, separately addressable lasing at the two targeted frequencies. Inset: gain curve retrieved from the experimental electroluminescence spectra (gray) overlaid with the single-mode emission defined by the front (red) and the back (green) DFBs.

ture of 0 °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$^{-1}$, which is comparable to conventional pulsed QC lasers [25].

Despite similar lasing thresholds, the peak output powers from the front and the back laser sections differ considerably. This is mainly due to poor light extraction from the strongly over-coupled back DFB resonator, which could be corrected by shortening its length. Furthermore, the non-reciprocal laser geometry negatively affects the emission from the back section as the light first passes the unbiased front laser section where it gets attenuated due to absorption and scattering. As depicted in Fig. 2(b), simultaneous subthreshold driving of the inactive section can compensate for this effect and increase the emitted power from the back section by as much as a factor of three. Nevertheless, the 2.3 mW output power at 1.6 A acquired from the back laser without subthreshold driving is largely sufficient when using state-of-the-art TE-cooled MIR detectors.

2.1. Spectral considerations

Spectral simulations of NO$_2$ absorption along with other species such as water and methane reveal that the absorption lines at 1900.08 cm$^{-1}$ and 1599.91 cm$^{-1}$ are best suited for the detection of NO and NO$_2$ [26]. The challenge when working with a dual-wavelength laser is to simultaneously match, at the same heatsink temperature, the laser emission frequencies to these absorption lines for both wavelengths.

Careful active region design and thorough numerical simulation of the whole laser structure resulted in a device tunable between 1597.7 – 1602 cm$^{-1}$ and 1888.8 – 1894 cm$^{-1}$ by decreas-
Fig. 2. (a) Voltage and peak optical power at 1600 cm$^{-1}$ (red) and 1891 cm$^{-1}$ (green) plotted versus the injection current. The optimal operating point of the laser for inter-pulse spectroscopy is indicated by arrows. (b) Increase of the optical power emitted from the back laser section (1891 cm$^{-1}$) when simultaneously injecting into the front section; more than three-fold power increase from 2.3 mW to 7.8 mW at $I_{\text{back}} = 1.6$ A is observed just before the front section starts simultaneously lasing at $I_{\text{front}} = 0.77$ A.

Fig. 3. Transmission spectrum of NO$_2$, NO and water simulated using the HITRAN database overlaid with the emission spectrum of the dual wavelength laser at the heatsink temperatures of -20 °C, 0 °C and 20 °C (front DFB section: red line, back DFB section: green line). The targeted transmission peaks of NO$_2$ at 1599.14 cm$^{-1}$ and NO at 1890.71 cm$^{-1}$ are indicated (blue arrows) and their position within the electrically tunable range of both laser sections at 0 °C (gray shaded region) is depicted.
ing the heatsink temperature from 20 °C to -20 °C. Figure 3 shows the tunable wavelength range superimposed with the absorption spectra of NO and NO₂ calculated using the molecular parameters from the HITRAN database [27]. While the spectral emission of the front laser is in perfect agreement with the design, a slight mismatch for the 1900 cm⁻¹ section prevents us from reaching the ideal 1900.08 cm⁻¹ NO line. Nevertheless, the heatsink temperature of 0 °C gives simultaneous access to a strong absorption doublet of NO at 1890.71 cm⁻¹ and to a NO₂ absorption line at 1599.14 cm⁻¹. Being weaker only by a factor of 1.3 and 2.5, respectively, these lines are of a comparable intensity as the originally targeted lines and exhibit a relatively small overlap with other interfering gases, in particular water. Fast electric tuning over these lines is achieved by applying subthreshold current ramp of 0 to 100 mA.

2.2. Laser driving

Taking advantage of the fact that both laser sections can be operated at the same driving conditions, the laser is driven using a single pulser unit combined with a radio-frequency compatible switch to time-multiplex the laser sections. Compared to the option of driving the respective sections with two laser drivers, our approach has the advantage of reduced hardware cost, but involves a custom solution for switching short and high-current driving pulses.

The pulser generates both the pulses (5 ns width and 1 MHz repetition rate) and the subthreshold current ramp (0.025 to 0.065 A, 10 kHz) for fine frequency tuning. The latter is optimized to sweep only a narrow spectral region around the targeted absorption lines in order to densely sample the absorption features and thus increase the precision of the measurement. The pulser output is fed into a switch based on reed-relays, which is characterized by a low capacitive coupling between the output channels even for 5-ns short laser pulses. The drawback is a rather long down-time of the switch of 300 µs that clearly hinders switching between subsequent spectral scans. An effective solution to overcome this issue while maintaining both high data rates and a thermal equilibrium of the system is to record several spectra while the switch is in a given position. However, the switching speed must still be faster than the thermal relaxation of the system, i.e. the laser heat sink must remain at an apparently constant temperature despite the fact that the heat dissipation in the respective laser sections may differ. Based on these considerations, an optimal switching rate of 100 Hz was identified. The first three spectra after each switching event are discarded due to thermal stabilization of the active region, which yields 44 spectra that are recorded within 5 ms for each laser section (Fig. 4(a)).

3. Spectroscopic setup

The experimental setup is schematically shown in Fig. 4(b). The highly divergent output beam from the QC laser is collimated by a high NA = 0.56 antireflection coated aspheric lens and passed through a 1 mm-thick sapphire window. The latter acts as an optical short-pass filter with a soft cutoff at 6 µm, reducing the power from the stronger front laser section (1600 cm⁻¹) by a factor of 5. The power-equalized laser beam is then directed into an astigmatic mirror Herriott multipass gas cell (AMAC-36, Aerodyne Research, Inc., USA), where it undergoes 182 reflections corresponding to an optical path of 36 m. The nearly parallel beam leaving the cell is then refocused onto a fast thermoelectrically cooled MCT detector with a 10 MHz bandwidth and a noise-equivalent power of 1 pW Hz⁻¹/² (PVI-4TE-6, Vigo SA, Poland).

Pulsed operation of QCL typically exhibit pulse-to-pulse amplitude variations of few percents [25] that mainly reflect the current fluctuations of the driving electronics. In order to compensate for such amplitude variations, we employ the technique of pulse normalization using a reference optical path with temporal gating as proposed by [25]. The 120 ns time delay due to the 36 m path difference makes it possible to temporally resolve and normalize the reference and the signal pulses using a single detector, thus reducing the signal noise by as much
as an order of magnitude.

The transmission signal is acquired by a high-speed digitizer card (NI PCI-5124, National Instruments Corp., USA) with 50 MS/s rate that is synchronized with the laser pulser. As the digitizer does not allow for real-time streaming, the 44 spectra of each gas are acquired and sent to the computer at a maximum rate of 10 Hz. The data are averaged and processed online using a custom-written LabView-based program, which also controls the laser and monitors the system parameters such as gas pressure and temperature. A separate module of the program provides for real-time fitting of the absorption spectra using molecular parameters from the HITRAN database.

3.1. Instrument performance

The instrument sensitivity, linearity and long term stability were determined using calibration gas cylinders with mixing ratios of 90 ppm NO in N₂ and 90 ppm NO₂ in synthetic air. They were supplied at 1 slpm (standard liter per minute) into the multipass cell and measured at a pressure of 80 hPa.

Figures 5(a) and 5(b) show the recorded 10 Hz spectra (average of 44 scans) obtained by sampling the diluted calibration gases; the frequency scale is determined from a germanium etalon with free spectral range of 0.0244 cm⁻¹. The absolute gas concentrations were obtained using a reference chemiluminescence detector (CLD; APNA360, Horiba).

The time series of the concentration data measured at 10 Hz rate over a 16 min period are shown in Figs. 5(c) and 5(d). The associated Allan-deviation plots [28] indicate a 10 Hz precision of 10 and 30 ppb for NO₂ and NO, respectively, as well as a 1σ-detection limit of 0.5 and 1.5 ppb after 100 s of averaging. These values are about factor 5 inferior to the best performing single-species spectroscopic systems based on pulsed QC lasers [6], however, this is expected due to the shorter optical pathlength, the compromise in the absorption line selection, and the slower data acquisition rate of our prototype setup.

As indicated by fit residuals in Figs. 5(a) and 5(b), the measured line profiles are slightly deviating from a true Voight shape. This deviation originating from the thermal chirp of the laser emission induces a slight offset in the Voigt fit parameters and prevents us, in particular at higher concentrations, from determining the exact gas quantity from the fit directly. Therefore, calibration in the range of 0-45 ppm NO and NO₂ was performed, where the spectroscopically retrieved values are validated against the pre-defined mixing ratios obtained by dilution of the 90 ppm calibration gases. The calibration shows that for both gases the measurement is linear to about 7 ppm, while beyond this value, a nonlinear correction must be applied in order to
extend the dynamic range of the instrument.

4. Field applications

4.1. Automotive emission measurement

The dual-wavelength spectrometer was successfully deployed for fast detection of NO and NO\textsubscript{2} emissions after an exhaust gas treatment system of a heavy duty diesel engine. Emission limit regulations ask for the continuous reduction of oxides of nitrogen NO\textsubscript{x}, i.e. the sum of NO and NO\textsubscript{2} [29]. 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\textsubscript{2}, as opposed to measuring their sum, as is usually done using certified chemiluminescence NO\textsubscript{x} detectors.

The exhaust gas was sampled directly after the treatment system consisting of a Diesel Oxidation Catalyst (DOC), a Diesel Particle Filter (DPF), a Selective Catalytic Reduction (SCR) and a Clean-up Catalyst. Selective catalytic reduction of NO\textsubscript{x} is performed by the injection of a urea/water solution before the catalyst, which is then thermolysed/hydrolysed to ammonia as the reducing agent. The engine was operated on an engine test bench during 30 minutes in the cold-started World Harmonized Transient Cycle (WHTC), which is a certification test for on-road heavy duty engines. The hot and humid exhaust gas was diluted at a ratio of 1:15 with dry pressurized air and was drawn through the multipass cell using a scroll vacuum pump (TriScroll 600, Varian Inc., USA), achieving a gas exchange rate of 15 Hz, comparable to the 10-Hz measurement rate of the spectrometer. Prior to the measurement, the whole system was...
Fig. 6. 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.

Fig. 7. Quantitative comparison of the NO$_x$ data measured by the dual-wavelength laser spectrometer (already rescaled to pre-dilution values) and the reference CLD. The first 30 seconds after the engine start were not considered due to initial fluctuations of the dilution ratio. Shown in the plot is the 1:1 line (red). Using a linear regression, the data would be best represented by $y = 0.77 + 1.007x$, with $R^2$ of 0.998.

calibrated for zero and span using 90 ppm NO and NO$_2$ calibration gases, that were introduced upstream of the dilution system. Considering the dilution ratio 1:15, the effective concentration of the gases upon calibration was 6 ppm, i.e. the span was determined within linear measurement range of the instrument. A posteriori, nonlinear correction was applied to the measured data in order to extend the dynamic range to high NO and NO$_2$ concentrations as mentioned above. In addition, an automotive emission bench (Mesa 7500 DEGR, Horiba, Japan) equipped with a NO$_x$ chemiluminescence analyzer (CLA 755A, Horiba, Japan) was run in parallel as a reference.

Figure 6 shows the measured NO and NO$_2$ concentrations together with the NO$_x$ values
from the reference chemiluminescence detector. During the first 5 minutes, i.e. during engine warm-up phase, the engine emits significant amounts of NO, which is neither oxidized nor eliminated. Afterwards, the DOC becomes sufficiently hot to catalyze the oxidation of NO, which is reflected in the increase of NO₂. In about 8 minutes, the SCR catalyst is warm enough so that urea/water injection is activated, and the overall NOₓ emissions are drastically reduced. As depicted in Fig. 7, we found an excellent agreement between the sum of NO and NO₂ measured with the dual-wavelength laser spectrometer and NOₓ determined by the reference detector in a wide range of concentrations from 0.5 to 1000 ppm. In addition, the laser based system was able to resolve, in contrast to the employed chemiluminescence detector, both NO and NO₂, thus providing direct information on the status and efficiency of each stage of the exhaust gas treatment process.

4.2. Ambient air monitoring

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 NO₂ concentrations in January 2014 at the Empa campus site in Dübendorf, Switzerland.

During the measurement, outdoor ambient air was continuously sampled using 6 mm (outer diameter) Teflon tubing and drawn through the multipass cell at 1 slpm and 80 hPa. Every hour, a zero-point measurement was performed during 180 s by passing the air through an activated charcoal and Purafil® filter to remove all nitrogen oxides, and thus account for possible instrumental drifts. A commercial dual channel CLD (APNA360, Horiba, Japan) measuring both NO and NOₓ was employed as a reference during the whole measurements. Both instruments were brought to the same NOₓ scale by one-point calibration using diluted calibration gases.

Figure 8 shows the 100-s averaged data that were acquired during a period of 10 hours, plotted together with the CLD measurement. The 1σ measurement precision of 0.5 and 1.5 ppb for
NO\textsubscript{2} and NO, respectively, has proven to be sufficient to closely reproduce the concentration variations of both pollutants. Dübendorf is a suburban site in a densely populated area, dominated by industrial and commercial buildings and a dense road network. The highest NO and NO\textsubscript{2} levels were measured in early morning due to rush-hour traffic and accumulation in the low mixing layer, typically found during the winter months. After about 8:30, the concentration of NO gradually decreased to values often not exceeding a few ppb, with isolated peaks that can be attributed to transient pollution events. These events are much more pronounced for NO than for NO\textsubscript{2} because NO is directly emitted during combustion processes, while NO\textsubscript{2} is mainly a secondary pollutant formed during atmospheric transport through the oxidation of NO. Therefore, NO\textsubscript{2} is more representative of the urban background and shows much less variations than NO. During the observed measurement period, NO\textsubscript{2} concentrations were always above 15 ppb with a second rise after 16:00, indicating the evening traffic increase. The measured concentrations of both nitrogen oxides were rather low for an urban site in winter season, with NO\textsubscript{2} well below the Swiss legal daily limit value of 80 µg/m\textsuperscript{3} (42 ppb).

5. Conclusion

The present work is a successful demonstration of sensitive and specific multi-species detection performed with a recently developed dual-wavelength QC laser. Emitting at two, spectrally largely distinct (300 cm\textsuperscript{-1}) frequencies, this laser provides for simultaneous detection of NO and NO\textsubscript{2} down to ppb levels. Moreover, operated using a single laser driver and requiring no beam combining optics, it considerably reduces the footprint, complexity and power consumption of the instrument, compared to systems based on multiple laser modules. As such, it is particularly suitable e.g. for portable NO and NO\textsubscript{2} automotive emission measurements systems (PEMS).

While the current laser prototype still operates in a pulsed mode and is not fully matched to the best-suited absorption features for NO and NO\textsubscript{2} detection, the second generation dual-wavelength lasers promises continuous emission at exactly the targeted wavelengths of 1900 cm\textsuperscript{-1} and 1600 cm\textsuperscript{-1}. Further advances in the laser design and fabrication shall include the extension of the active region design to new spectral regions, which is likely to trigger a new trend in multi-species laser spectrometer development.

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