Multi-Species, High-Precision MIR Trace Gas Detection for Environmental Applications

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Abstract: MIR spectroscopy using QCLs allows sensitive, selective, and fast detection of gases and their isotopic composition. Recent developments, including dual-wavelength QCLs, create tantalizing options for compact, multi-species analysis in environmental applications.
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1. Introduction

Advances in mid-IR quantum cascade laser (QCL) technology have triggered an impressive progress in instrumental developments. This progress is in line with a continuous quest for high-precision and selective measurements of a large variety of molecular species, as well as for compact, robust, and field deployable gas analyzers. Correspondingly, the applications cover very diverse areas, with deployment in environmental sciences being especially relevant and successful in recent years.

This can be nicely illustrated by numerous contributions from our laboratory, showing many advances and the future potential of direct absorption spectroscopy using QCLs. In the following, we will focus on two fields of applications: (i) the development of mid-infrared spectroscopy for high-precision measurements of stable isotopes of greenhouse gases to elucidate their sources and sinks, and (ii) the use of multi-wavelength QCLs for the simultaneous detection of many different greenhouse gases and air pollutants in a single, compact optical setup.

2. Isotopic Ratio Measurements

The fact that isotope ratios of atmospheric trace gases contain highly valuable information about their sources and sinks triggered various instrumental developments based on QCL spectroscopy. This is because, unlike isotope-ratio-mass-spectrometry (IRMS), laser based methods can deliver real-time, non-destructive analysis at moderate cost and instrument size. To resolve subtle changes in the isotopic composition of ambient trace gases, it is often necessary to reach a precision of 0.1‰ for the isotopic ratio (δ-value). While this is highly demanding, over 10 years of in-situ isotope ratio measurements of CO_2 in the free troposphere at the high-alpine research station Jungfraujoch prove that reliable data can be obtained, even under largely unattended operation. Furthermore, these measurements document the long-term stability of the corresponding DFB-QCL, which, after more than 10 years of nearly uninterrupted operation, is arguably the world's longest running device of its type [1-2].

Laser spectroscopy is inherently specific to structural isomers having the same mass, and opposed to IRMS, it is thus capable to perform site-specific N_2O isotopomer measurements [3]. The coupling of QCL spectroscopy to automated preconcentration units for ambient air has further enhanced the performance of this technique, which has found many applications, including the identification of microbial pathways in soil, or the study and optimization of waste water treatment [4-5]. Recently, we have demonstrated measurements of the very rare, multiply substituted isotopologues of N_2O, i.e. so called clumped isotopes [unpublished]. These contain unique information on production/consumption pathways, reaction conditions and temperature of formation in the corresponding biological or chemical processes.

3. Air Pollutants and Greenhouse Gases

Instrumentation for environmental monitoring of gaseous pollutants and greenhouse gases tends to be complex, expensive, and energy demanding, because every measured compound relies on a specific analytical technique and dedicated analyzer. An exciting alternative approach is based on mid-infrared laser absorption spectroscopy with dual-wavelength distributed-feedback (DFB) quantum cascade lasers (QCLs). The first spectroscopic feasibility studies used pulsed laser designs that were limited in optical power and laser linewidth [6-7]. Recently, we have developed devices that are continuous wave or support long pulses up to 100 μs. These rely on two distinct designs: (i)

Neighbour DFB (NDFB): two single-mode DFB QCLs are fabricated next to each other, with minimal lateral distance, in order to allow simultaneous beam shaping, suitable for long-path optical gas cells, and (ii) devices that rely on the Vernier effect to obtain switchable DFB lasers, with two target wavelengths that are separated by up to 300 cm^{-1} [8].

In our latest instrument, we have combined two dual- and one single-QCL for high-precision measurements of CO, CO_2, NH_3, NO, NO_2, N_2O, and O_3 simultaneously in a compact setup with a single measurement cell and detector. The lasers were driven time division multiplexed in intermittent continuous wave mode [9] with a repetition rate of about 1 kHz for each device. Custom driving electronics and FPGA based data acquisition (125 MS/s, 14 bit) allow a compact design with minimal heat dissipation. The instrument was used for environmental monitoring and benchmarked with established reference instrumentation. The data quality was assessed by Allan-Werle variance analyses and by comparing to standard air quality monitoring equipment [10]. All achieved detection limits are significantly below ppb (parts per billion, 10^{-9}), with the exception of CO_2, which has the highest mol fraction in ambient air, and does thus not require such low detectivity.

In the near future, we will replace the single DFB-QCL at 9.6 μm with a dual-wavelength DFB-QCL adding the frequency around 7.4 to measure CH_4 and SO_2. This would complete the instrument to become a universal environmental monitoring station, opening a wide range of new possibilities in atmospheric sciences by a true all-in-one monitoring solution.

4. References

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