

MIR Spectroscopy beyond trace levels - environmental and industrial applications

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Abstract: MIR spectroscopy using QCL allows sensitive, selective and fast gas detection. This is illustrated by many environmental and industrial applications. Recent developments show significant advances towards portable, high-sensitivity sensors for multiple components.

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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, including environmental sciences and industrial process control. Examples can be found from many research groups and manufacturers world-wide. This contribution focuses on work from our own laboratory, illustrating recent advances and the future potential of direct absorption spectroscopy using QCLs.

2. Environmental and industrial applications

Monitoring of trace gases is widely used to establish trends, and to improve our understanding of their global cycles and their influence on the earth's climate. Most air pollutants affect human health and influence chemical processes in the atmosphere at even very low abundances (ppb or ppt mixing ratios). Nitrogen dioxide (NO₂) is one of the most prominent examples. QC laser based trace gas analysis is well suited for remote locations with very low NO₂ mixing ratios. Using an astigmatic Herriott sample cell with 200 m optical path length, a precision of 3 ppt and 10 ppt for NO₂ and NO, respectively was obtained in a three month field campaign under predominantly free tropospheric air conditions [1].

The fact that isotope ratios of atmospheric trace gases contain highly valuable information about their sources and sinks triggered numerous instrumental developments based on QCL spectroscopy, because, unlike isotope-ratio-mass-spectrometry (IRMS), laser based methods can deliver real-time data at moderate cost and instrument size. Furthermore, laser spectroscopy is inherently specific to structural isomers having the same mass, and opposed to IRMS, it is thus capable to perform site-specific N₂O isotopomer measurements [2-3]. To resolve subtle changes in the isotopic composition of ambient trace gases, it is most often necessary to reach a precision of 0.1‰. While this is highly demanding, over 5 years *in-situ* isotope ratio measurements of CO₂ in the free troposphere at the high-alpine research station Jungfraujoch prove that reliable high-precision data can be obtained, even under largely unattended operation [4-6].

For measurements that require high temporal resolution, such as industrial process monitoring or flux measurements by the eddy covariance method, optical detection is in many aspects the first choice. This is illustrated by a prototype analyzer for leak detection of aerosol can propellants. The instrument allows detecting with high speed (< 10 ms) and sensitivity (1 ppm) propane, butane, and other carbohydrates that are used as propellants in aerosol cans. Its performance is evaluated with an industrial demonstrator for aerosol cans leak testing, confirming that, in compliance with international directives, it can detect leaks of 1.2×10^{-4} slpm at an unprecedented rate of 750 cans per minute [7].

3. Multi-species detection

Simultaneous detection of multiple gas species using MIR laser spectroscopy is highly desired for numerous applications. Typically, it is not possible to address the spectra of different gases with a single laser. Here, we explore the concept of “multi-color” spectroscopy based on a dual-wavelength QCL [8]. The active region of the laser consists of two different active layers stacked on top of each other, optimized for a broadband emission at 1600 cm⁻¹ and 1900 cm⁻¹, while single-mode emission at the desired wavelengths is ensured by a succession of two

distributed-feedback (DFB) gratings with different periodicities. The two wavelengths are ideally suited for the detection of nitrogen oxide (NO) and nitrogen dioxide (NO₂). A prototype spectrometer was successfully tested for fast (10 Hz) operation during automotive exhaust emission measurement and for ambient air monitoring in a suburban environment [9].

4. Portable QCL spectrometry

There is an increasing need for compact instrumentation. We report on the development of the first fully quantum cascade technology based, laser absorption spectrometer employing a cw-QCL emitting at 2310 cm⁻¹, and a quantum cascade detector (QCD) optimized for this spectral range [10]. In this configuration, the concentrations of the three most abundant, stable CO₂ isotopes can be simultaneously analyzed. The small footprint of the optical set up (30×13 cm²), was achieved by designing and developing a novel multipass cell, which consists of a diamond turned, copper cylinder with a toroidal inner surface [11]. This surface assures a minimal aberration of the laser beam, a freely adjustable optical path from 16 cm to more than 4 m, while the cell geometry allows for a small detection volume of 40 ml. A precision below 0.1 ‰ for δ¹³C and δ¹⁸O measurements has been demonstrated. Further compactness was obtained by developing a fully integrated, largely analog, yet flexible laser driver that eliminates the need for any external electronics for current modulation, lowers the demands on power supply performance, and allows shaping of the tuning current in a wide range. Along with intermittent scanning of cw-QCLs, the overall heat dissipation of the laser is significantly reduced and thus opens the way to very compact and portable sensors based on QCLs [12].

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