

Step-Scan Tuning of Vernier Quantum-Cascade Lasers for Rapid Detection of Volatile Organic Molecules

Raphael Brechbühler*, Miloš Selaković*,[†], Philipp Scheidegger*, Herbert Looser*,
André Kupferschmid*, Lukas Emmenegger*, and Béla Tuzson*

* Laboratory for Air Pollution / Environmental Technology, Empa, Ueberlandstrasse 129, 8600 Dübendorf, Switzerland

[†] Department of Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich, Switzerland
bela.tuzson@empa.ch

Abstract: We demonstrate a fast and flexible driving scheme that fully exploits the potential of extended-tuning quantum-cascade lasers (QC-XT). Integrated in a spectroscopic setting, it enables the sensitive and selective detection of volatile organic molecules. © 2022 The Author(s)

1. Introduction

Laser-absorption spectroscopy is an established technique to detect and quantify molecular species based on their absorption fingerprints. Conventional distributed-feedback (DFB) quantum-cascade lasers (QCLs) are ideally suited light sources to probe the distinct and spectrally narrow absorption features of small, inorganic compounds. However, their narrow tuning range significantly limits extending this method toward the detection of volatile organic compounds (VOCs), which exhibit broad and spectrally overlapping ro-vibrational absorption features (*cf.* Fig. 1a, bottom). Although mid-infrared technologies with much broader tuning ranges exist, *e.g.* external-cavity QCLs, they suffer from mechanical instabilities, mode hopping, and high costs. Furthermore, commonly applied wide-tuning schemes do not provide enough spectral resolution to fully exploit fine-structure details in the absorption spectra of gas-phase VOCs, which might allow for more selective and sensitive measurements [1].

Extended-tuning quantum-cascade lasers (QC-XT) are electrically tunable multi-wavelength lasers using the Vernier effect that have the potential to combine rapid, high-resolution spectral scanning with a broad coverage [2]. While such lasers have been developed and commercialized, their potential has not yet been fully explored in previous implementations [3] because a dedicated driving scheme and the corresponding hardware were missing.

In this work, we demonstrate an efficient laser-driving scheme for the QC-XT and its application for high-precision measurements of VOCs in gas-phase mixtures.

2. Methodology

For developing our driving concept, we use a prototype QC-XT (Alpes Lasers, Switzerland) emitting at 1080 cm^{-1} . Using the Vernier effect, its emission wavelength can be switched between six single-mode lasing clusters distributed over $\sim 40\text{ cm}^{-1}$ (Fig. 1a, top) by electrically driving integrated micro heaters located along the front and back distributed Bragg reflectors [2].

Fig. 1b shows our proposed step-scan driving scheme that maximizes the operation duty cycle of the Vernier laser. In one measurement cycle of this scheme (typically 360 ms), the laser is subsequently switched between and tuned within the six Vernier clusters. Steps in the heater currents correspond to switching between Vernier clusters, each emitting at a different wavelength, and were typically performed every 60 ms. During the entire cycle, the laser is driven in the intermittent-continuous-wave (iCW) regime [4] and performs one spectral scan per laser pulse in the momentary cluster (typically ~ 3300 scans/s). Hence, our approach involves multiple laser scans in each cluster before switching (typically 200 scans/cluster) to minimize idle time due to thermal effects in the laser device after a heater-current step. Spectra obtained from the first few scans in a cluster are discarded and then a co-averaging process is started (shown as colored laser pulses in Fig. 1b). This significantly reduces the data load for data transfer, storage, and post-processing.

The driving scheme was realized with custom-developed, low-noise driving electronics and an FPGA-based triggering and data-acquisition system, building on our modular laser-driving platform [4, 5].

3. Spectroscopic System for VOC Detection

The laser and the driving electronics were integrated into a compact spectrometer. To enhance the instrument sensitivity, we employ an optical multi-pass cell with 76 m of optical path (AMAC-76, Aerodyne Research, Inc., USA). The high spectral resolution ($< 0.005 \text{ cm}^{-1}$) reveals, especially at decreased gas pressures, significant fine-structure features in the infrared fingerprints of our benchmark compounds, facilitating sensitive and selective measurements. Since such high-resolution spectral absorption data are not available for most VOCs, we created our own reference spectra and developed a dedicated concentration-retrieval algorithm using these custom-made spectral templates. To increase the sensitivity and selectivity for mixtures of multiple compounds, a global spectral fitting routine was implemented, taking into account all spectral information available from multiple Vernier clusters. For this method, the rapid cycling between the Vernier channels provided by our driving scheme is critical, especially in situations where the gas concentration varies dynamically.

For single compounds, the performance of the QC-XT-based approach, with a precision of $\sim 10 \text{ ppb}$ for 20 s averaging time at VOC concentrations of 200 ppm, is on a par with our previously reported DFB-QCL-based spectrometer for ethanol [1]. Additionally, the significantly extended tuning range of QC-XTs offers clear advantages for more complex gas matrices, relevant for a large variety of environmental, industrial, and medical sensing applications. In particular, our system will be further developed toward a breath analyzer in the framework of Zurich Exhalomics.

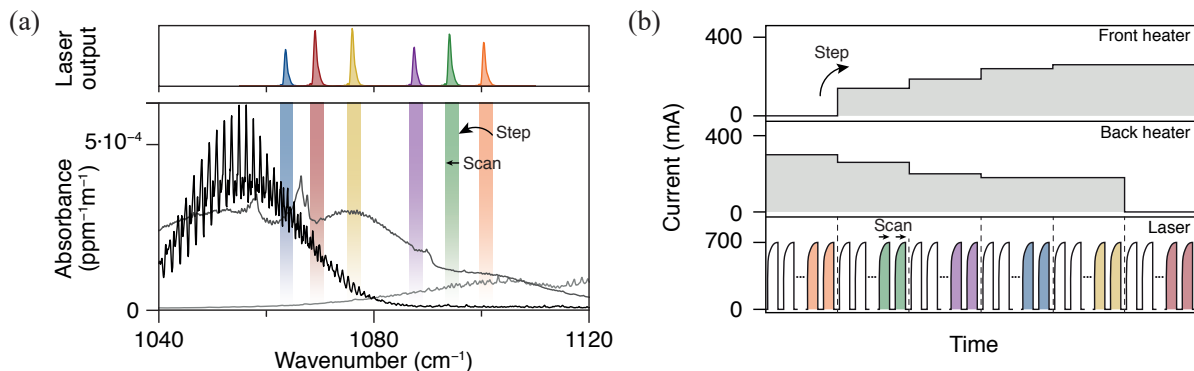


Fig. 1. (a) Top: Output frequencies of the QC-XT at different heater configurations, measured with a table-top Fourier-transform infrared spectrometer (FTIR). The spectral asymmetry stems from tuning of the laser within each Vernier cluster. Bottom: Broad and overlapping absorption spectra of methanol (black), ethanol (dark gray), and acetaldehyde (light gray), obtained from Ref. [6] (FTIR data). The six Vernier clusters, each with a coverage comparable to an individual DFB QCL, are highlighted as colored areas. (b) Proposed driving scheme of the QC-XT. The emission frequency of the laser is switched at every heater-current step, while the laser is repeatedly tuned within these Vernier clusters using the iCW driving scheme.

References

1. O. Aseev, B. Tuzson, H. Looser, P. Scheidegger, C. Liu, C. Morstein, B. Niederhauser, and L. Emmenegger, "High-precision ethanol measurement by mid-IR laser absorption spectroscopy for metrological applications," *Opt. Express* **27**, 5314 (2019).
2. Y. Bidaux, A. Bismuto, C. Tardy, R. Terazzi, T. Gresch, S. Blaser, A. Muller, and J. Faist, "Extended and quasi-continuous tuning of quantum cascade lasers using superstructure gratings and integrated heaters," *Appl. Phys. Lett.* **107**, 221108 (2015).
3. S. Freitag, M. Baer, L. Buntzoll, G. Ramer, A. Schwaighofer, B. Schmauss, and B. Lendl, "Polarimetric Balanced Detection: Background-Free Mid-IR Evanescent Field Laser Spectroscopy for Low-Noise, Long-term Stable Chemical Sensing," *ACS Sensors* **6**, 35–42 (2021).
4. M. Fischer, B. Tuzson, A. Hugi, R. Brönnimann, A. Kunz, S. Blaser, M. Rochat, O. Landry, A. Müller, and L. Emmenegger, "Intermittent operation of QC-lasers for mid-IR spectroscopy with low heat dissipation: tuning characteristics and driving electronics," *Opt. Express* **22**, 7014 (2014).
5. C. Liu, B. Tuzson, P. Scheidegger, H. Looser, B. Bereiter, M. Graf, M. Hundt, O. Aseev, D. Maas, and L. Emmenegger, "Laser driving and data processing concept for mobile trace gas sensing: Design and implementation," *Rev. Sci. Instruments* **89**, 065107 (2018).
6. I. Gordon *et al.*, "The HITRAN2016 molecular spectroscopic database," *J. Quant. Spectrosc. Radiat. Transf.* **203**, 3–69 (2017).