Signal processing strategies for liquid phase sensors based on external cavity quantum cascade lasers

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Introduction

Due to the spectral properties and the high emission power, Quantum Cascade Lasers (QCLs) are nowadays a powerful source for mid-infrared radiation. QCLs are available in various modifications concerning the laser type. Distributed Feedback-QCLs (DFB-QCLs) are ideally suited for spectroscopy of gases as they offer mode-hop free emission. However, they can be tuned over a few wavenumbers only. In contrast, External Cavity-QCLs (EC-QCLs) are optimized for a tuning range of over several hundred wavenumbers and are therefore well suited for liquid phase spectroscopy (broad absorption bands). For application to liquid phase solutions the high-power QCLs permit the use of considerable pathlengths (up to 200 μm) despite the strong water absorption in the carbohydrate region (around 10,000 cm⁻¹).

Signal handling and data processing are both crucial parts for achieving measurement results with sufficient reproducibility. One way of improving such an experimental setup is, for example, to increase the tuning range and/or the laser’s intensity which usually means the acquisition of a new laser. A way to circumvent this rather costly undertaking is to optimize the peripheral devices and the software. Here we report on efficient ways of improving the signal of a pulsed EC-QCL. Furthermore, we present a modular and user-friendly software-tool for controlling the laser, managing the data acquisition and a sequential injection autosampling system.

Experimental Setup

An EC-QCL (Daylight Solutions, CA, USA) tunable in the range between 1030 cm⁻¹ and 1230 cm⁻¹ is combined with a MCT-detector (thermoelctrically cooled to -70°C). The collimated laser beam gets focused by a parabolic mirror and before arriving at the detector, it passes a flowcell (Capillary, 135 μm) filled with a glucose solution.

The amplified detector-signal is connected to an in-house developed Boxcar-system (see below). The generated DC-voltage-signal proportional to the sensed radiation intensity, is digitalized by a 24-bit ADC (NI-9239, National Instruments, TX, USA).

Measurement times of less than 10 s are achieved by using the scan mode of the laser which is realized by moving a built-in grating (External Cavity Design). The synchronization with the ADC is done with the NI-9239 Module. Sample injection is achieved by a 14 port-valve and a syringe-pump in a Sequential Injection Analysis (SIA) modification. Fig. 1 shows the according setup-scheme.

Boxcar WT

One approach of acquiring the transient detector signal is triggering an ADC with a certain time delay. Problems arise if mode hopping occurs during a single sample pulse and the digitalisation point is close to it. One solution for that is averaging over a defined adjustable period during a pulse. This processing is performed by a Boxcar integrator (see Fig. 3).

Commercially available devices (e.g. SR830, Stanford Research Systems, CA, USA) are usually based on the scheme shown in Fig. 4. This way of building a Boxcar integrator leads to a very flexible tool but its signal-to-noise ratio (SNR) of around 11 bit is not satisfying for applications in the field of high-precision measurements.

As sample/injection elements have very similar characteristics to a gated integrator in the range between 20 and 200 ns, the integrator can be bypassed and the following average-filter can be software-implemented (see Fig. 5).

Results

Different Methods of Data Acquisition

The graphs in Fig. 9 represent 100% lines of deionized water whereas five are the result of the new Boxcar WT and the other five were recorded with a triggered ADC. Each line is calculated by averaging five scans from 1030 cm⁻¹ to 1230 cm⁻¹ and then building the absorption. An ideal measurement system without noise would lead to a perfect line at 0 mAU and therefore the quality of a setup can be estimated very simple.

Influence of Sample Injection

Another fact, that has to be considered in evaluating the setup’s performance, is the influence of changing the liquid in a flowcell. Fig. 10 shows ten 100% lines where half of the spectra were recorded without changing the liquid in the flowcell. The remaining spectra were obtained with changing the liquid between two single beams. One can recognize a considerable influence by the sample injection. This can be ascribed to very small changes in the flowcell’s optical path length, which leaded to measureable changes in the intensity because of the strong water absorption.

Calibration Curve (Glucose)

One key application for a broadly tunable EC-QCL in the range between 1030 cm⁻¹ and 1230 cm⁻¹ is the quantification of glucose in aqueous solution (e.g. serum) [2]. Therefore, a number of glucose solutions at various concentrations were measured and a linear regression was performed. For a comparitively large range from 10 mg/dl to 500 mg/dl [4], [3] a R²=0.99988 was achieved. Fig. 12 shows a selection of the spectra for calculating the calibration curve.

Software Control

Advanced Total Lab Automation System (ATLAS) [1]

The intended liquid phase sensor application of the EC-QCL required an efficient software control handling all hardware components including data acquisition and automatic sample handling. For this purpose the software control ATLAS was developed. It is a software project based on LabVIEW (National Instruments, TX, USA) and supports a flexible way of controlling different kinds of devices.

As shown in Fig. 7, TCP/IP-connections are used to distribute the operations that have to be executed. The high flexibility of ATLAS is achieved by an user-friendly and easy to modify scripting language. The graphs in Fig. 9 represent 100% lines of deionized water whereas five are the result of the new Boxcar WT and the other five were recorded with a triggered ADC. Each line is calculated by averaging five scans from 1030 cm⁻¹ to 1230 cm⁻¹ and then building the absorption. An ideal measurement system without noise would lead to a perfect line at 0 mAU and therefore the quality of a setup can be estimated very simple.

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