## A sensitive CW DFB quantum cascade laser based QEPAS sensor for detection of SO<sub>2</sub>

\*<sup>2</sup>J. P. Waclawek, <sup>1</sup>R. Lewicki, <sup>1</sup>M. Jahjah, <sup>1</sup>Y. F. Ma, <sup>2</sup>E.t.H. Chrysostom, <sup>2</sup>B. Lendl and <sup>1</sup>F. K. Tittel 

<sup>1</sup>Rice University, Electrical & Computer Engineering Department, MS-366; 6100 Main St. Houston, TX, 77005

<sup>2</sup>Institute of Chemical Technologies and Analytics, Vienna University of Technology, Getreidemarkt 9/164 AC, 1060 Vienna

\*johannes.waclawek@tuwien.ac.at; Rafal.lewicki@rice.edu

**Abstract:** The development of a sensitive SO<sub>2</sub> QEPAS-based sensor platform employing a CW DFB-QCL will be reported. A detection sensitivity of 100 ppbv was achieved with a 1-sec averaging time for the 1380.94 cm<sup>-1</sup> SO<sub>2</sub> line.

**OCIS** codes: (140.5965) Semiconductor lasers, quantum cascade; (300.6340) Spectroscopy, infrared; (280.4788) Optical sensing and sensors.

## 1. Introduction

This presentation will describe the development of a sensitive, selective and compact sensor platform, capable of detecting and monitoring  $SO_2$  at single ppbv concentration levels with a time response of 1-sec, suitable for environmental and industrial monitoring.  $SO_2$  is a major air pollutant. The major sources of  $SO_2$  emission into the atmosphere are associated with industrial combustion processes as well as automobile, truck, aircraft and marine transport emissions.  $SO_2$  becomes toxic when its concentration exceeds 1 ppmv in ambient air [1]. In this work a 7.25  $\mu$ m, 140 mW CW-DFB QCL operating at 20.5°C was used as a convenient excitation source for a compact quartz-enhanced photoacoustic spectroscopy (QEPAS) based sensor architecture.

2. Quartz-enhanced photoacoustic spectroscopy

OEPASis a sensitive technique that allows performing measurement of trace gases in an ultra-small absorption detection module (ADM) where the total volume of the analyzed gas sample is ~ 4 mm<sup>3</sup> [2]. The QEPAS technique employs a 32 kHz quartz tuning fork (QTF) as a sharply resonant acoustic transducer with a high quality factor (Q-104), instead of a broadband electric microphone as used in conventional photoacoustic spectroscopy. The QTF is a piezo-electric element, capable of detecting weak acoustic waves generated when the modulated optical radiation interacts with a trace gas. This interaction results in an acoustically modulated pressure wave, which is subsequently converted to a QTF deformation. This deformation causes a separation of electrical charges on the tuning fork electrodes that can be measured as either a current or voltage by using an ultra-low noise pre-amplifier and lock-in detection electronics [3]. An enhancement of the QEPAS signal can be achieved when two metallic tubes acting as a micro-resonator (mR) are added to the QTF sensor architecture. In a typical QEPAS configuration the QTF is positioned between the mR tubes to probe the acoustic waves excited in the gas contained inside the mR. An optimization study of the geometrical mR parameters showed that the highest QEPAS signal-to-noise ratio (SNR) is achieved for two 4.4 mm-long and 0.5-0.6 mm inner diameter mR tubes [4]. The presence of these tubes decreases the Q-factor of the QTF, due to the acoustic coupling between the micro-resonator and the piezoelectric OTF. This can lead to significant improvement of the QEPAS sensor detection sensitivity of up to 30 fold [4]. Furthermore, an additional enhancement of the SO<sub>2</sub> QEPAS signal amplitude can be obtained by blending an analyzed mixture with water vapor, which is known to be an efficient catalyst for V-T relaxation processes in the

3. SO<sub>2</sub> QEPAS sensor architecture and performance

The QEPAS based chemical sensing platform (as depicted in Fig. 1) consists of a CW-DFB-QCL, an aspheric black diamond collimating lens with an effective focal length of f=4 mm, two plano-convex germanium lenses (f=25 mm) with broadband antireflection (AR) coatings and a 150  $\mu$ m pinhole used as a spatial filter in order to improve the laser beam quality. The QEPAS spectrophone consists of the QTF and the mR placed into a gas cell. The sensor platform is based on 2f wavelength-modulation spectroscopy (WMS) and QEPAS-detection.

The DFB-QCL emission wavelength was tuned across the SO<sub>2</sub> absorption line centered at 1380.94 cm<sup>-1</sup> (as shown in Fig. 2) by applying a slow frequency ramp ( $f_{\text{ramp}}$ =0.06 Hz) to the external modulation input of the laser current drive. In addition the laser current was modulated sinusoidally at half of the QTF resonance frequency ( $f_{\text{mod}}$ = $f_0$ /2=16.375 kHz) in order to implement a 2f-WM technique. Once the optical energy is absorbed by the gas, the acoustic wave is generated and detected by the QTF. The induced QTF piezoelectric signal was enhanced by an ultra- low noise trans-impedance amplifier with a 10 M $\Omega$  feedback resistor. The amplified QTF signal was demodulated at  $f_0$ , using an internal control electronics unit lock-in amplifier with a time constant set to 1 sec. Measurements were performed to investigate the sensitivity and linear response of the QEPAS based SO<sub>2</sub> sensor.

Measurements were performed to investigate the sensitivity and linear response of the QEPAS based SO<sub>2</sub> sensor. Different SO<sub>2</sub> concentrations (0.1, 1, 2, 5 and 10 ppmv) were detected using a SO<sub>2</sub>: N<sub>2</sub> calibration mixture and 2.4 % water vapor concentration at a pressure of 100 Torr. Figure 3 represents the measured 2f QEPAS signals

corresponding to different  $SO_2$  concentrations and the linearity of the QEPAS sensor (see inset). The noise level was determined from the baseline recorded for the ADM filled with ambient air. Good linearity between signals amplitudes and  $SO_2$  concentrations was observed for the QEPAS based sensor. For a certified mixture of 10 ppm  $SO_2$  in  $N_2$  the calculated QEPAS SNR is 100, which yields a minimum detection limit (1 $\sigma$ ) of 100 ppbv.

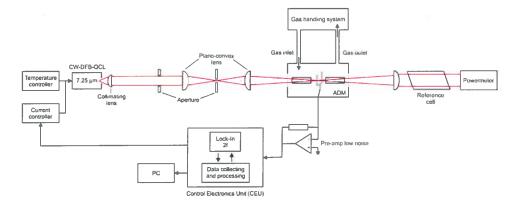


Fig. 1 Block diagram of the QEPAS based SO<sub>2</sub> gas sensor employing a 7.25 μm CW-DFB-QCL.

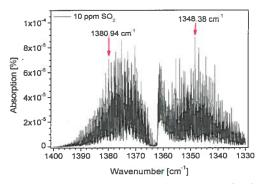


Fig. 2 HITRAN simulated absorption spectrum of a 10 ppm  $SO_2$  (for p=100 Torr, l=1 cm). The targeted  $SO_2$  absorption line is located at 1380.94 cm<sup>-1</sup> whereas the strongest  $SO_2$  absorption line is located at at 1348.94 cm<sup>-1</sup>. maximum power at this wavelength.

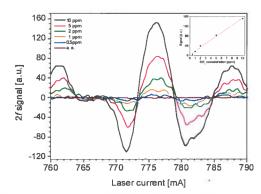


Fig.3 2f wavelength modulation QEPAS signals acquired at different  $SO_2$  concentration levels; Inset: Dependence of measured 2f signals as a function of  $SO_2$  concentrations.

ruture measurements will employ a reference channel (shown in Fig. 1), in order to lock the laser frequency to the center of the absorption line and perform long term measurements as well as using a QCL operating at 1348 cm<sup>-1</sup>.

## 4. Acknowledgement

JPW, EtHC and BL acknowledge financial support provided by the Austrian research funding association under the scope of the COMET program within the research network "Process Analytical Chemistry" (contract # 825340) RL, MJ, YM, FKT acknowledge financial support provided by NSF ERC MIRTHE and NSF NexCILAS

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