Sulfur Dioxide Detection Using CW-DFB-QCL Based Quartz-Enhanced Photoacoustic Spectroscopy

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Abstract: The development of a sensitive SO_2 QEPAS based sensor platform employing a 140 mW CW-DFB-QCL will be reported. A detection limit of 75 ppbv (3σ) was achieved with a 1-sec averaging time for the 1380.94 cm^{-1} SO_2 absorption line.
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1. Introduction

A sensitive, selective and portable gas sensor based on quartz-enhanced photoacoustic spectroscopy (QEPAS) employing a high power 7.25 µm CW-DFB-QCL was developed for detecting SO_2 at ppbv concentration levels, suitable for environmental and industrial monitoring. SO_2 is a major air pollutant that is mainly released to the atmosphere by industrial combustion processes as well as fuel-based transport activities. SO_2 becomes toxic when its concentration exceeds 1 ppmv in ambient air [1]. In this work the influence of the H_2O presence in the sample gas mixture on the SO_2 sensor performance was investigated.

2. Quartz-enhanced photoacoustic spectroscopy (QEPAS)

QEPAS is a sensitive technique that allows performing measurement of trace gases in an ultra-small absorption detection module (ADM) with a total effective sample volume of a few mm^3 [2]. The technique is based on the use of a 32.768 Hz quartz tuning fork (QTF) as a sharply resonant transducer for acoustic waves, which are induced in an absorbing gas by modulated optical radiation. The QTF is a piezo-electric element which converts its deformation by pressure waves into separation of electrical charges that can be measured as a voltage. 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. Moreover, for slow relaxing molecules, blending the gas mixture with water vapor, which is an efficient catalyst for V-T relaxation processes in the gas phase, can improve the detected QEPAS signal [3].

3. SO_2 QEPAS sensor architecture and performance

The QEPAS based gas sensor architecture is depicted in Fig.1. It employs a CW-DFB-QCL (*Hamamatsu, L10195-7253H*) as mid-IR light source. An anti-reflection coated aspheric collimating lens (*Black Diamond*^{TM}, f=3.05 mm) was used to collimate the laser beam. The laser beam quality was improved by implementing a spatial filter consisting of a plano-convex CaF_2 lens (f=25 mm) and a 300 µm pinhole. The QEPAS ADM consists of the QTF and the mR placed into a gas cell. A reference cell filled with 0.5 % of SO_2 in N_2 at 133 mbar and a pyroelectric detector located after the ADM were used as a reference channel in order to lock the laser frequency to the center of the selected SO_2 absorption line. The sensor platform is based on 2f wavelength-modulation spectroscopy (WMS) and QEPAS detection.

In order to implement the 2f-WM technique the DFB-QCL emission wavelength was tuned across the SO_2 absorption line centered at 1380.94 cm^{-1} by applying a ramp to the laser current and modulating it sinusoidally at half of the QTF resonance frequency ($f_{mod}=f_0/2$=16.384 Hz). 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 (TA) with a 10 MΩ feedback resistor. The amplified QTF signal was demodulated at f_0, using an internal lock-in amplifier with a time constant set to 1 sec.

The presence of H_2O vapor influences the QEPAS response to SO_2 by enhancing the vibrational translational (V-T) energy transfer rate and thus increasing the photoacoustic signal. The optimum working pressure and modulation depth (MD) for dry SO_2 and for moisturized SO_2 (absolute humidity AH=2.3 %) gas mixture was found to be 175 mbar and 9 mA, and 100 mbar and 6 mA, respectively. Fig. 2 shows a QEPAS spectrum of 10 ppm dry and moisturized SO_2 gas mixture. In order to investigate the dependence of H_2O on the response of the QEPAS

based SO_2 sensor the amplitudes of the 2*f* signals were acquired as a function of the H_2O concentration (*p*=100 mbar, *MD*=6 mA). The results demonstrated as an inset to Fig. 2 show that ~3.1 times improvement of the QEPAS signal was observed when the absolute humidity of analyzed gas mixture is 2.3 %. To lock the laser frequency to the center of the SO_2 absorption line in order to perform long term measurements a pyroelectric detector signal, demodulated by a lock-in amplifier at 3*f*, was employed. Fig. 3 shows an example of 2*f* WM QEPAS signals acquired at different concentration levels of dry SO_2 gas.

To investigate the sensitivity and linear response of the QEPAS sensor quantitative measurements of SO_2 were performed using a dry and moisturized SO_2 gas mixture. Different SO_2 concentration levels within the range of 0 to 10 ppm were achieved by diluting 50 ppm SO_2:N_2 calibration mixtures. The inset in Fig. 3 shows the linear response of the QEPAS sensor for different SO_2 concentrations for dry and moisturized gas at optimum sensor operating conditions in each case. The noise level was determined from the baseline recorded for the ADM filled with nitrogen. Good linearity between signals amplitude and SO_2 concentrations was observed for the QEPAS based sensor (dry gas: R^2=0.9998, humidified gas: R^2=0.9996). The determined QEPAS detection limit (3σ) is 75 ppbv for dry and 110 ppbv for moisturized SO_2 gas, respectively.

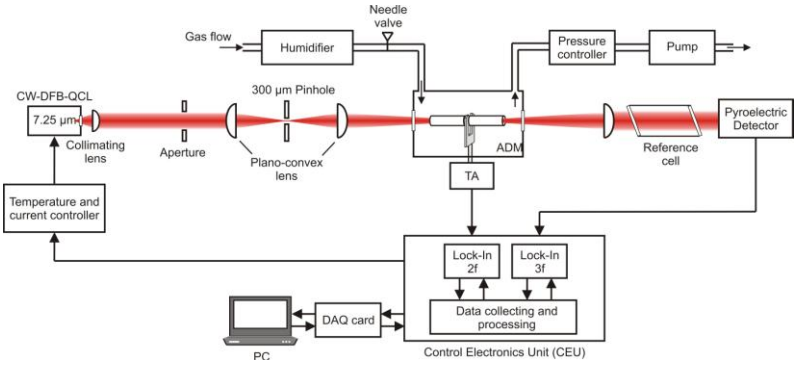

Fig. 1 Schematic diagram of the QEPAS based SO_2 gas sensor platform employing a 7.25 µm CW-DFB-QCL.

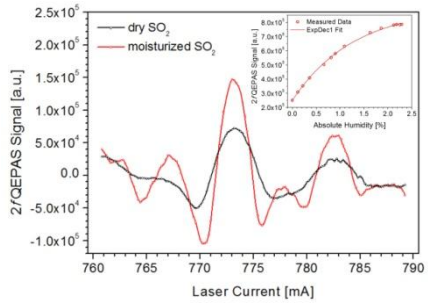

Fig. 2 2*f* WM QEPAS signals for 10 ppm dry SO_2 gas (black) and moisturized with 2.3 % H_2O (black) when laser was tuned across absorption line located at 1380.94 cm^{-1} (optimum conditions for each: *p*=175 mbar, *MD*=9 mA and *p*=100 mbar, *MD*=6 mA, repectively); Inset: Amplitude of the 2*f* WM QEPAS signal as a function of H_2O concentration (50 ppm SO_2, *p*=100 mbar, *MD*=6 mA).

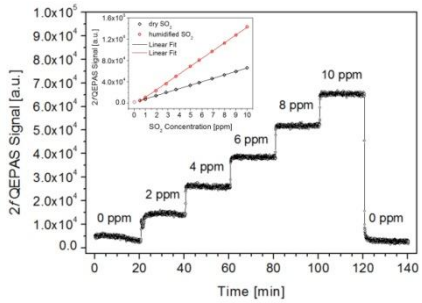

Fig.3 2*f* WM QEPAS signals acquired at different concentration levels of dry SO_2 gas (*p*=175 mbar, *MD*=9 mA). Inset: Dependence of measured 2*f* signals as a function of SO_2 concentrations (black: dry SO_2 gas, red: moisturized SO_2 gas, *AH*=2.3 %).

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