Real Time Ammonia Detection in Exhaled Human Breath with a Quantum Cascade Laser Based Sensor

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Abstract: Quantum cascade laser based breath sensor platform for medical applications employing a quartz-enhanced photoacoustic spectroscopy technique is reported. The detection sensitivity for exhaled ammonia is at <10 ppbv level with 1 s time resolution.

OCIS codes: (140.5965) Semiconductor lasers, quantum cascade; (300.6360) Spectroscopy, laser; (170.4580) Optical diagnostics for medicine

1. Introduction

This work demonstrates the implementation of a sensitive quantum cascade laser based sensor platform for quantitative measurements of ammonia concentrations in exhaled breath. Exhaled human breath contains ~ 400 different trace gas species, mostly at ultra low concentration levels. Many of these gases can serve as biomarkers for the identification and monitoring of various types of human diseases or wellness states. Typical concentrations of ammonia in healthy human breath may vary from tens to few hundreds ppbv, whereas elevated level (e.g. ≥1 ppmv) may indicate significant pathology. Monitoring of ammonia concentration in exhaled breath using laser spectroscopy techniques provides a fast, non-invasive diagnostic method for patients with a variety of medical conditions, including liver and kidney disorders [1-3], and helicobacter pylori infections [4]. Therefore laser spectroscopy in combination with a mid-infrared, continuous wave, high performance QCL is a promising analytical approach for real time breath analysis and the quantification of breath metabolites [5].

2. Sensor performance

The measurements of exhaled ammonia were performed with quartz enhanced photoacoustic spectroscopy (QEPAS) [6, 7]. The QEPAS technique is very suitable for real time breath measurements due to the fast gas exchange inside the QEPAS gas cell (~5 mm typical dimensions). The layout of the QEPAS-based ammonia sensor platform is schematically shown in Fig. 1a. A widely tunable external cavity quantum cascade laser (EC-QCL) [Daylight Solutions model 21106-MHF] with a center frequency of 943 cm^{-1} (λ~10.6 μm) was employed. The EC-QCL replaced an initially used CW distributed feedback (DFB) quantum cascade laser (Maxion Technologies, Inc., model # DQ-M532P) centered at 1047.2 cm^{-1} (λ=9.55 μm). The implementation of an EC-QCL source for spectroscopic measurements provides more versatility in the optimum NH_3 line selection. The laser is operated in a CW mode at 15°C and delivers a maximum output power of 42 mW. A coarse, single mode frequency tuning from 914 to 972 cm^{-1} (Fig. 1b), with resolution of 0.01 cm^{-1}, can be performed by changing the diffraction grating angle. Continuous mode hop free tuning within 0.6 cm^{-1} range can be obtained by varying the voltage applied to a PZT actuator of the EC-QCL. Strong P and R branch ro-vibrational lines of the ν_2 NH_3 fundamental absorption band are accessible, specifically at 968 cm^{-1}. A reference cell filled with 100 ppmv NH_3 balanced in N_2 was used to lock the laser frequency to the selected target ammonia absorption line. The temperature inside the sensor enclosure was maintained at 45°C in order to minimize the ammonia adsorption effects. The ammonia concentration measurements with EC-QCL based sensor platform were carried out with external amplitude modulation of the laser beam at frequency f=~32 kHz using a quartz tuning fork operating as a mechanical chopper.

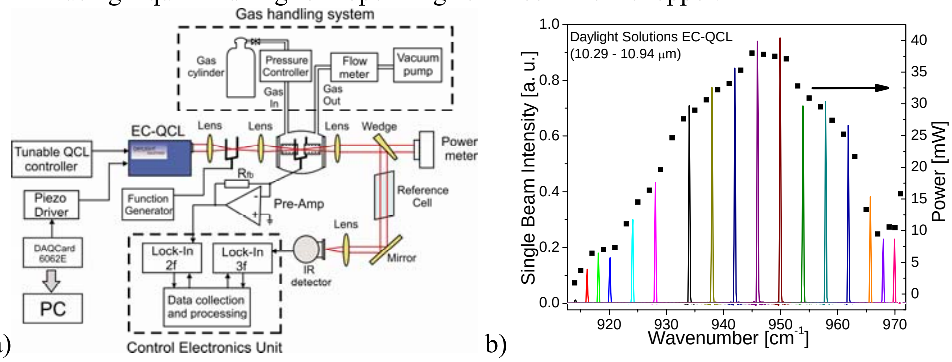

Fig. 1a) Schematic diagram of EC-QCL-based ammonia sensor platform employing quartz enhance photoacoustic spectroscopy. b) Tuning range and output power performance of CW external-cavity quantum cascade laser (Daylight Solutions Model 21106-MHF)

3. Experimental results

First pilot study of exhaled ammonia in human breath was performed with the QEPAS sensor equipped by a CW DFB QCL and using 2f wavelength modulation technique. The DFB QCL operated at 5°C and provided a maximum power of ~30 mW. The tuning range of 4.5 cm^{-1} with injection current enabled monitoring an ammonia line at 1046.4 cm^{-1} (Fig. 2a). Interference from a nearby CO_2 absorption line was effectively eliminated by performing independent CO_2 concentration measurements using a commercial capnograph. An ammonia detection limit of <10 ppbv with 1 s time resolution was achieved. Systematic breath ammonia concentration measurements were performed on a healthy volunteer over a three week period with DFB QCL, and the results are presented in Fig. 2b. Performance characteristics for both the DFB-QCL and the EC-QCL sensor platforms operating with 2f wavelength modulation and 1f amplitude modulation respectively will be reported.

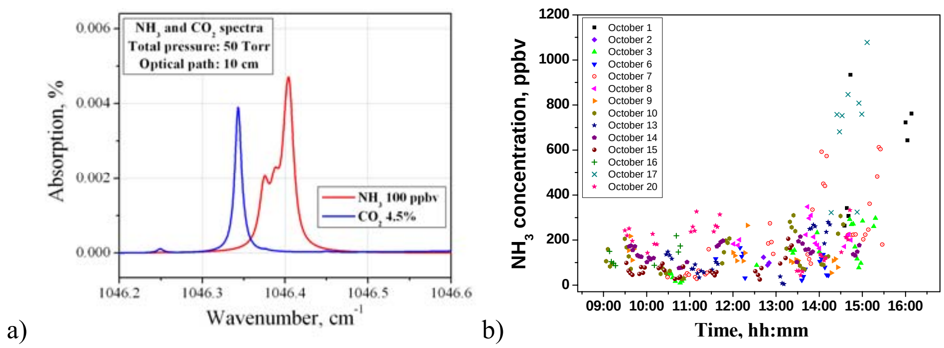

Fig. 2a) HITRAN-based simulation of absorption spectra for NH_3 (100 ppbv) and CO_2 (4.5%) for DFB-QCL; b) systematic exhaled ammonia tests performed on a healthy volunteer.

4. References

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