Mid-Infrared Quantum Cascade Laser based Trace Gas Sensor technologies: Recent Advances and Applications

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***Abstract*— Recent advances in the development of trace gas sensors based on the use of quantum cascade lasers (QCLs) for the sensitive, selective detection, quantification and monitoring of small molecular gas species with resolved spectroscopic features will be described. High detection sensitivity at ppbv and sub-ppbv concentration levels requires detection sensitivity, enhancement schemes such as multipass absorption cells, cavity enhanced absorption techniques, or quartz enhanced photo-acoustic absorption spectroscopy (QEPAS).**

I. Introduction And Background

THIS presentation will focus on recent advances of mid-infrared quantum cascade laser based sensors for the detection, quantification, and monitoring of trace gas species as well as their applications to environmental monitoring and medical diagnostics. The development of compact trace gas sensors, in particular those based on quantum cascade lasers (QCL) and interband cascade lasers (ICL), permits the targeting of strong fundamental rotational-vibrational transitions in the mid-IR [1]. Trace gas detection at ppbv (parts per billion in volume) and sub-ppbv concentration levels requires sensitivity enhancement schemes such as a multipass optical cell, a cavity absorption enhancement technique, or quartz enhanced photo-acoustic absorption spectroscopy (QEPAS) [1,2]. These three spectroscopic methods can achieve minimum detectable absorption losses in the range from 10^{-8} to 10^{-11} $cm^{-1}/\sqrt{Hz}$. Two recent examples of real world applications of field deployable PAS and QEPAS based gas sensors will be reported, namely the monitoring of atmospheric ammonia (NH_3) in urban environments and nitric oxide (NO) concentrations in exhaled human breath. To-date, seven chemical species have been detected using QCL based QEPAS. Table 1 lists the optimum wave number and pressure as well as the normalized noise equivalent absorption coefficient (NNEA) and the noise equivalent concentration (NEC) for the available QCL power for a 1 sec data acquisition time.

Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, $cm^{-1}W/Hz^{½}$	Power, mW	NEC (τ=1s), ppmv
CH_2O (N_2:75% RH)	2804.90	75	8.7×10^{-9}	7.2	0.12
CO (N_2+ 2.2% H_2O)	2176.28	100	1.41×10^{-8}	71	0.002
CO (propylene)	2196.66	50	7.4×10^{-8}	6.5	0.14
N_2O (air+5% SF_6)	2195.63	50	1.5×10^{-8}	19	0.007
NO (N_2+ H_2O)	1900.07	250	7.5×10^{-9}	100	0.003
C_2H_5OH (N_2)	1934.2	770	2.2×10^{-7}	10	90
C_2HF_5 (N_2)	1208.62	770	7.8×10^{-9}	6.6	0.009
NH_3 (N_2)	1046.39	110	1.6×10^{-8}	20	0.006

Table 1. QCL based QEPAS Performance for 7 Trace Gas Species (2011)

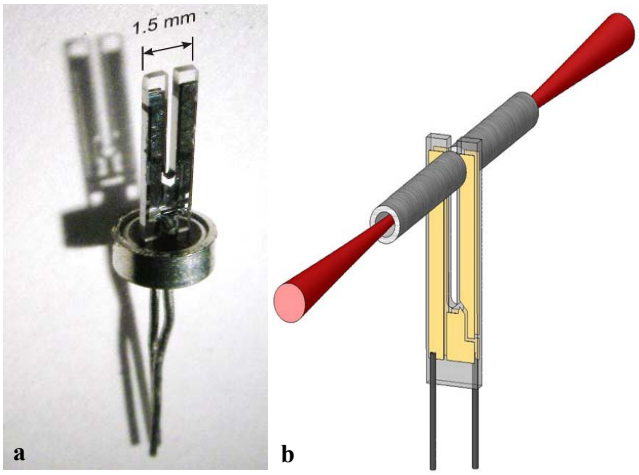

Fig. 1 a) A typical QTF geometry used in QEPAS based trace gas measurements; and b) an enhanced QTF configuration with an acoustic resonator formed by two pieces of rigid tubing.

II. EC-QCL PAS BASED ATMOSPHERIC AMMONIA SENSOR

In order to improve the current understanding of the dynamics of ammonia (NH_3) in a major industrial and urban area, intensive measurements of atmospheric NH_3 were conducted in Houston during two sampling periods in 2010 using a 10.4-µm external cavity quantum cascade laser (EC-QCL)-based sensor employing conventional photo-acoustic spectroscopy (See Fig.1). The mixing ratio of NH_3 ranged from 0.1 to 8.7 ppb with a mean of 2.4±1.2 ppb in winter and ranged from 0.2 to 27.1 ppb with a mean of 3.1±2.9 ppb in summer. The larger levels in summer probably are due to higher ambient temperature. A notable morning increase and a mid-day decrease were observed in the diurnal profile of NH_3 mixing ratios. Motor vehicles were found to be major contributors to the elevated levels during morning rush hours in winter. However, changes in vehicular catalytic converter performance and other local or regional emission sources from different wind directions governed the behavior of NH_3 during morning rush hours in summer. There was a large amount of variability, particularly in summer, with several episodes of elevated NH_3 mixing ratios that could be linked to industrial facilities. A considerable discrepancy in NH_3 mixing ratios existed between weekdays and weekends. This hat NH_3 mixing ratios in Houston occasionally

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exceeded previous modeling predictions when sporadic and substantial enhancements occurred, potentially causing profound effects on particulate matter (PM) formation and local air quality.

The environmental determination of ammonia concentration levels was performed with a commercial, continuous wave (CW), thermoelectrically cooled (TEC) 10.4-µm external cavity quantum cascade laser (EC-QCL)-based sensor employing an amplitude modulated photo-acoustic spectroscopy (AM-PAS) technique. The CW TEC EC-QCL system from Daylight Solutions (Model 21106-MHF) can be tuned from 933 to 1006 cm^{-1} and emits a maximum optical power of 72 mW. Within this EC-QCL tuning range the optimum NH_3 absorption line at 965.35 cm^{-1} in the ν_2 fundamental absorption band of NH_3 was selected in terms of available laser power, absorption coefficient, and lack of interfering species such as CO_2 and H_2O. The laser beam was modulated at 1.8 kHz, and a 9.1 cm long differential resonant photo-acoustic cell, with two balanced electret microphones, was used as the state-of-the-art photo-acoustic detector [5]. In order to achieve NH_3 detection at single ppbv concentration levels, which is required for sensitive atmospheric measurements, the optical beam was passed through the cell three times. A pyro-electric detector placed after a 10-cm reference cell, filled with 0.2% of NH_3 at 30 Torr, was used for frequency locking as well as the monitoring of the QCL power.

Results for two Field Campaigns: Feb. 2010 & Aug.-Oct. 2010

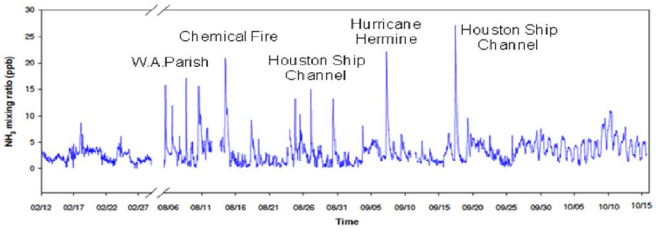

Fig. 1. Monitoring of Atmospheric Ammonia in Houston, TX

III. REAL-TIME DETECTION IN EXHALED HUMAN BREATH USING A QCL BASED SENSOR

Exhaled breath is a mixture of more than four hundred molecules, some of which are present at parts per billion (ppb) or even as low as parts per trillion (ppt) concentration levels [6]. For example, NH_3 monitoring in exhaled human breath using a laser spectroscopic technique can provide fast, non-invasive diagnostics for patients with liver and kidney disorders [7]. Exhaled NH_3 concentration measurements are obtained with a QEPAS based sensor system, shown in Fig 2 using a Hamamatsu CW, TEC, DFB QCL mounted in a high heat load (HHL) photonics package. The QEPAS technique is very suitable for real time breath measurements due to the fast gas exchange inside an ultra-compact gas cell.

The minimum detectable NH_3 concentration that is achieved with a 24mW, CW,TEC, DFB QCL operating at 10.34 µm (965.35 cm^{-1}) is ~ 6 ppbv (with a 1 sec time resolution). This sensitivity is sufficient for detecting exhaled breath ammonia concentrations, which are estimated to be between 0.01 and 1 ppm in healthy humans. A fast sensor response time was obtained by shortening the length of the breath sampler tube and by keeping the metal components of the sensor heated to 38°C in order to minimize ammonia adsorption effects. By using a commercial breath sampler (Loccioni, Italy) with a built-in capnograph, the CO_2 concentration measurements can be performed independently. In addition, the breath sampler helps to standardize the breath collection process by monitoring and maintaining the pressure of exhaled breath within a certain acceptable range.

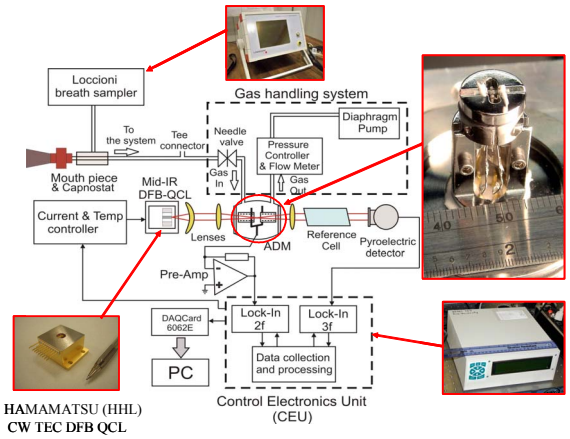

Fig 2. Block diagram of ammonia breath sensor architecture

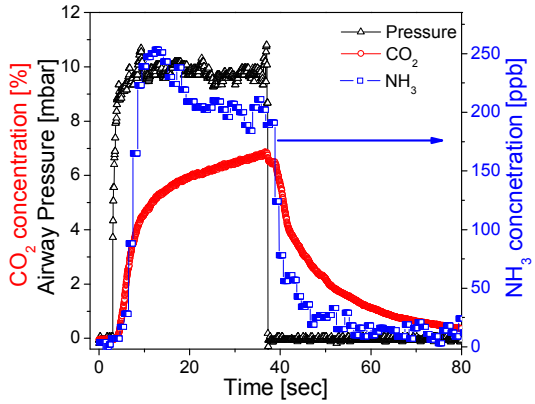

Fig.3. CO_2 concentration [%], airway pressure [mbar] and NH_3 concentration [ppb] profiles of the same single breath exhalation

IV. CONCLUSIONS AND FUTURE TRENDS

Compact, reliable, real time, sensitive (<10^{-4}), and highly selective (< 3 to 500 MHz) gas sensors based on quantum cascade lasers have been demonstrated to be effective in numerous real world and fundamental science applications. These include such diverse fields as atmospheric chemistry and environmental monitoring (e.g. CO, CO_2, CH_4 and H_2CO are important carbon gases in global warming), ozone

depletion studies, acid rain, photo smog formation), industrial emission measurements (e.g. quantification of smokestack emissions, fence line perimeter monitoring by the petrochemical industry, down hole gas monitoring, gas pipeline and industrial plant safety), urban (e.g. automobile, truck, aircraft, marine and electrical power generation) and agricultural emissions. Furthermore sensors are used in chemical analysis and process control for manufacturing processes (e.g. petrochemical processing and exploration) and applications in biomedical and the life sciences, such as non-invasive medical diagnostics that involves the detection and monitoring of exhaled breath biomarkers (e.g. NO, CO, CO_2, NH_3, C_2H_6 and CH_3COCH_3). In addition, EC-QCL and DFB-QCL based spectroscopic methods and instruments for sensing of toxic gases and explosives relevant to law enforcement, national security and defense, as well as spacecraft habitat air-quality and safety (e.g. fire and post fire detection). With the development of efficient mid-infrared lasers [1] we envision a significantly improved performance coupled with a reduction in size and cost of thermoelectrically cooled QCL and ICL based trace gas monitors that will lead to the implementation of sensor networks. Sensor networks based on laser absorption spectroscopy and QEPAS will enable large-area detection of trace-gas fluxes, mapping and localization of emission sources, as well as the identification of unknown natural gas sinks.

ACKNOWLEDGMENT

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