

Mid-Infrared Quantum Cascade Laser based Trace Gas Technologies: Recent Progress and Applications in Health and Environmental Monitoring

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Abstract: This talk will focus on recent advances in the development of sensors based on mid-infrared (mid-IR) semiconductor lasers for the detection, quantification and monitoring of trace gas species as well as their applications to medical diagnostics, environmental monitoring, industrial process control, and security. The development of compact trace gas sensors, in particular based on quantum cascade (QC) and interband cascade (IC) lasers, permits the targeting of strong fundamental rotational-vibrational transitions in the mid-IR, that are one to two orders of magnitude more intense than overtone transitions in the near-IR.

1. Introduction

Trace gas detection at ppbv (parts per billion in volume) and sub-ppbv concentration levels requires sensitivity enhancement schemes such as a multi-pass optical cell, a cavity absorption enhancement technique, or quartz enhanced photo-acoustic absorption spectroscopy (QEPAS) [1-4]. These three spectroscopic methods can achieve minimum detectable absorption losses in the range from 10^{-8} to 10^{-11} $\text{cm}^{-1}/\sqrt{\text{Hz}}$. 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, $\text{cm}^{-1}\sqrt{\text{W/Hz}}^{-1/2}$	Power, mW	NEC ($\tau=1\text{s}$), 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
$\text{C}_2\text{H}_5\text{OH}$ (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)

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 NH₃ during morning rush hours in summer. There was a large amount of variability, particularly in summer, with several episodes of elevated NH₃ mixing ratios that could be linked to industrial facilities. A considerable discrepancy in NH₃ mixing ratios existed between weekdays and weekends. This study suggests that NH₃ mixing ratios in Houston occasionally 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 NH₃ absorption line at 965.35 cm^{-1} in the ν_2 fundamental absorption band of NH₃ was selected in terms of available laser power, absorption coefficient, and lack of interfering species such as CO₂ and H₂O. 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 NH₃ detection at single ppbv concentration levels, which is required for sensitive atmospheric measurements, the optical beam was passed through the cell three times. A pyroelectric detector placed after a 10-cm reference cell, filled with 0.2% of NH₃ at 30 Torr, was used for frequency locking as well as the monitoring of the QCL power.

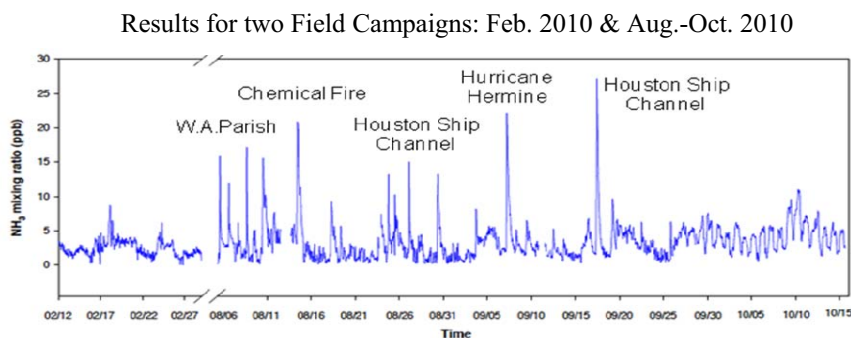


Fig. 1. Monitoring of Atmospheric Ammonia in Houston, TX

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, NH₃ 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 NH₃ 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 NH₃ 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 device, the CO₂ 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.

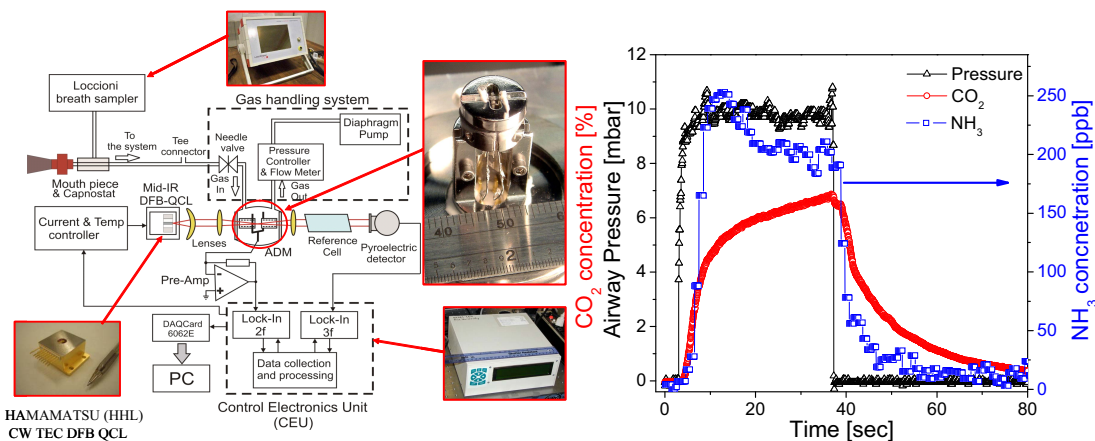


Fig 2. LHS: Block diagram of ammonia breath sensor architecture; RHS: CO₂ concentration [%], airway pressure [mbar] and NH₃ concentration [ppb] profiles of the same single breath exhalation

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, CO₂, CH₄ and H₂CO 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, CO₂, NH₃, C₂H₆ and CH₃COCH₃). 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.

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