Ammonia sensor for environmental monitoring based on a 10.4 μm external-cavity quantum cascade laser

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Abstract: An EC-QCL based sensor employing photo-acoustic spectroscopy as a detection technique for monitoring of atmospheric ammonia will be reported. For the NH_3 absorption line at 965.35 cm^{-1} a detection limit of 3.3 ppbv was obtained.

OCIS codes: (300.6340) Spectroscopy, infrared; (010.1120) Air pollution monitoring; (140.5965) Semiconductor lasers, quantum cascade

1. Introduction

Ammonia (NH_3) is normally present in the atmosphere at trace concentration levels and like other nitrogen-containing trace gases, such as N_2O, NO, NO_2 and HNO_3 plays an important role in atmospheric chemistry. The total estimated global emission of NH_3 to the atmosphere, as a result of natural biochemical and chemical processes, is approximately 45 TgN/year. The largest emission of ammonia is caused by anthropogenic sources such as animal waste, poultry, mineral fertilizers, agricultural crops or biomass burning. Other significant sources of ammonia emission are natural sources such as animals, oceans, vegetation, and the decomposition of plants [1]. In urban areas, an additional increase of atmospheric ammonia concentration levels results from industrial and motor vehicular activities. In the atmosphere ammonia reacts with different acid pollutants to produce acid salts like ammonium bisulfate (NH_4HSO_4), ammonium sulfate ($(NH_4)_2SO_4$) and ammonium nitrate (NH_4NO_3). These acid salts, which are corrosive solids in atmospheric aerosols, comprise a portion of atmospheric particulate matter. Moreover, for low SO_2 environments ammonia is a potential source of atmospheric NO and N_2O. In order to perform real-time detection and monitoring of atmospheric NH_3 at trace concentration levels, researchers often preferentially use field deployable optical spectroscopic sensors rather than non-optical devices or techniques (gas or ion chromatography, wet collection technique). For an industrial and urban area such as the greater Houston area, where data regarding atmospheric ammonia concentration are limited, data obtained from an optical sensor will be informative. Generally, the atmospheric NH_3 concentrations for urban areas vary between 0.1 and 10 ppbv, depending on the proximity to the source [2]. Based on summer 2000 year average observational data and photochemical modeling analyses, the modeled ammonia concentration for Houston area was estimated to range between 1 and 15 ppb [3].

2. Sensor configuration and results

The ammonia sensor architecture is depicted schematically in Fig. 1. As a spectroscopic source a commercially available cw tunable Fabry Perot QCL in external cavity (EC) configuration (Daylight Solutions, Model 21106-MHF) was employed. The EC-QCL emits an ~3 mm in diameter collimated beam with a maximum optical power of 27mW (Fib. 1b). Coarse, single mode frequency tuning from 935 to 989 cm^{-1} (Fig. 1b), with minimum step size of 0.01 cm^{-1}, can be performed by rotation of the diffraction grating. In order to perform high resolution spectroscopy, a sinusoidal voltage, with a maximum amplitude of 75V, was applied to a piezo element enabling mode hop free tuning within ~0.7 cm^{-1}. To monitor the NH_3 trace gas concentration, an amplitude modulated photo-acoustic spectroscopy (AM-PAS) technique was employed. As a photo-acoustic detector, two balanced electret microphones placed in the 9.1 cm long differential resonant photo-acoustic cell were used [4]. The amplitude modulation of the laser beam was performed by a mechanical chopper wheel operating at 1.754 kHz to match the resonance frequency of the

PA cell at a selected working pressure of 200 Torr. In order to improve the detection sensitivity of the AM-PAS technique, the optical beam passes through the PA cell twice. A pyroelectric detector placed after a 10 cm long reference cell, filled with 0.2% of NH_3 at 200 Torr, was used for compensating the possible EC-QCL wavelength drift as well as for monitoring its power. The pressure inside the system was kept at 200 Torr while the flow was maintained at 150 ml/min. For sensor calibration, a certified mixture of 2ppm of NH_3 in nitrogen was used. In order to minimize the ammonia adsorption to surfaces and to prevent water vapor condensation in the sensor, the sensor enclosure was heated to +42°C.

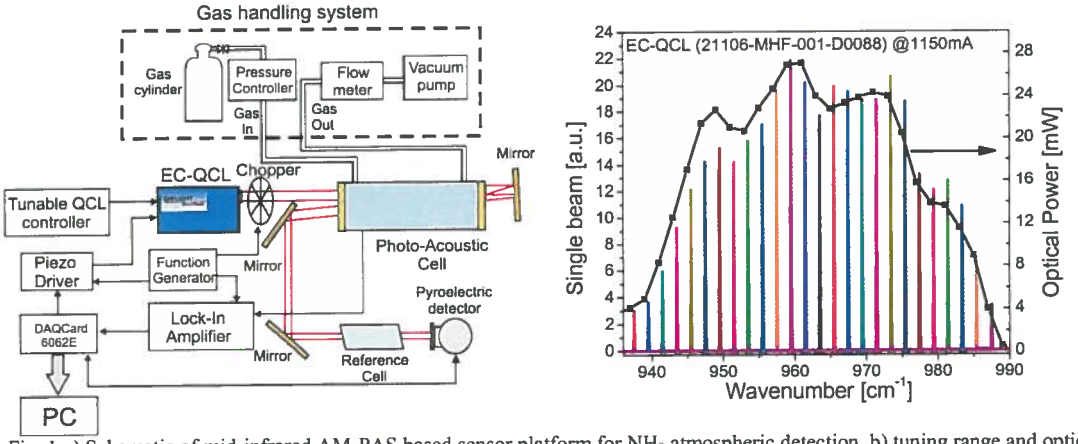

Fig. 1 a) Schematic of mid-infrared AM-PAS based sensor platform for NH_3 atmospheric detection, b) tuning range and optical power profile for a mid infrared CW EC-QCL laser system.

The emission spectrum of the tunable EC-QCL accesses the ro-vibrational NH_3 lines in the ν_2 fundamental absorption band of ammonia (Fig. 2a). For a photo-acoustic detector, configured for environmental monitoring, the 965.35 cm^{-1} absorption line of NH_3 was selected. This frequency was the optimum selection for AM-PAS technique in terms of laser power, NH_3 absorption strength and H_2O and CO_2 interferences.

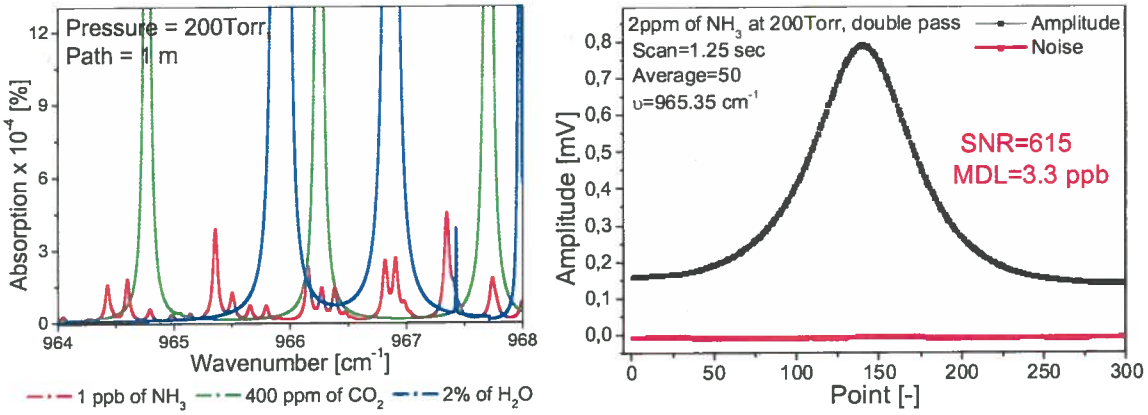

Fig. 2 a) Absorption spectrum of NH_3 including interference from CO_2 and H_2O molecules. The target NH_3 line is at 965.35cm^{-1}, b) AM-PAS signal for 2ppm of NH_3 after 50 averages (P=200 Torr, f_{rep} =1.745 kHz, double pass).

To detect an ammonia signal the EC-QCL was scanned back and forth across the selected NH_3 absorption line with a frequency of f=0.8 Hz. The laboratory results for the sensor performance showed that the minimum detection limit for ammonia concentration is ~20 ppbv in 1.25 sec. However for a scan averaged 50 times (data acquisition time = 62.5 sec), the NH_3 sensitivity improved to 3.3 ppbv (see Fig. 2b). To investigate the long term stability of the ammonia sensor a data set was acquired while pure nitrogen was supplied to the sensor and an Allan variance analysis was performed. The Allan deviation plot depicted in Fig.3, defined as the square root of the Allan variance, shows that the measurement accuracy improves with

averaging time. After 120 sec of the averaging time, the Allan deviation value corresponds to an improved NH_3 minimum detectable concentration of ~2ppbv (red dashed line of Fig. 3). Therefore for the environmental monitoring purpose, where sensor time response is not a critical parameter, the measured ammonia signal can be averaged with even a longer period of time allowing a detection limit of NH_3 ~1 ppbv.

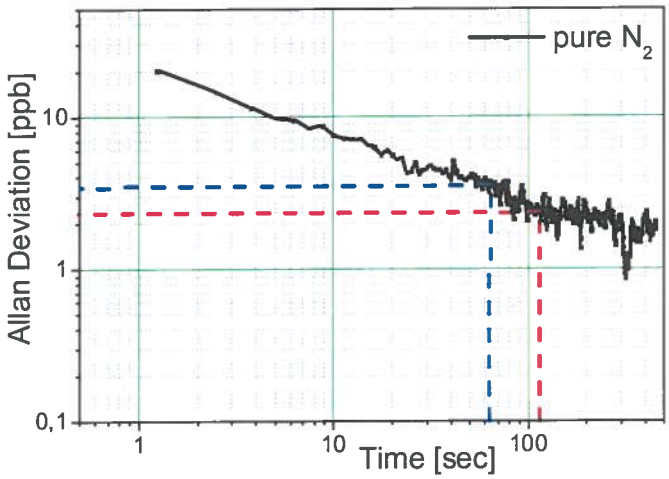

Fig. 3 Allan deviation calculated for a period of steady pure nitrogen. Blue and red lines show the improved NH_3 detection sensitivity after 62.5 sec and 120 sec of the averaging time, respectively.

Starting in October 2009, the described sensor will be employed for atmospheric NH_3 monitoring on the roof of a 100-m building located on the University of Houston campus, which is proximate to both industrial and motor vehicular emissions. This is the same location where members of our group performed successful field measurements of H_2CO as a part of the Texas Air Quality Study II air campaign (TexAQS II) in 2006 [5]. Atmospheric NH_3 data will be analyzed simultaneously with data acquired by other advanced gas sensing instruments at the same location. This will allow for determination of the implications of NH_3 with respect to atmospheric chemistry and air quality in Houston.

3. References

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