Monitoring of atmospheric ammonia in the greater Houston area using a 10.4 µm external-cavity quantum cascade laser

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Abstract: Amplitude modulated photo-acoustic spectroscopy using a 10.4 µm EC-QCL source, targeting the NH_3 absorption line at 965.35 cm^{-1}, resulted in a sub-ppb ammonia detection limit. Atmospheric ammonia concentration levels from our study will be reported.

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 a significant role in atmospheric chemistry. The largest emission of NH_3 to the atmosphere is caused by anthropogenic sources such as animal waste, poultry, mineral fertilizers, agricultural crops, and biomass burning. Other significant sources of NH_3 emission are natural, including animals, oceans, vegetation, and the decomposition of plants [1]. Moreover, for highly developed urban areas, an additional increase of atmospheric NH_3 concentration levels can be observed as a result of industrial and motor vehicle activities.

From the perspective of environmental concern, NH_3 is a precursor of particulate matter due to its chemical reaction with sulfuric and nitric acids to produce different ammonium salts such as ammonium sulfate ($(NH_4)_2SO_4$), ammonium nitrate (NH_4NO_3), and ammonium bisulfate (NH_4HSO_4). As a result, the abundance of NH_3 in the atmosphere has a great impact on aerosol nucleation and composition. Moreover, for low SO_2 environments, oxidation of NH_3 is a potential source of atmospheric NO and N_2O.

Despite the importance of NH_3 in atmospheric chemistry, it currently is not regulated by the U.S. Environmental Protection Agency (EPA) as an air pollutant. In addition, there are not any governmental air quality monitoring network sites to regularly measure ambient NH_3 concentration levels. The atmospheric NH_3 concentrations for urban areas vary between 0.1 and 10 ppbv, depending on the proximity to the source [2]. For the Houston area the modeled NH_3 concentration is estimated to range between 1 and 15 ppbv [3].

2. Sensor configuration and results

Environmental determination of ammonia concentration levels was performed with a 10.4-µm external cavity quantum cascade laser (EC-QCL)-based sensor platform employing an amplitude modulated photo-acoustic spectroscopy (AM-PAS) technique (see Fig. 1a). A CW TEC EC-QCL system from Daylight Solutions (Model 21106-MHF) can be tuned from 933 to 1006 cm^{-1}, emitting a maximum optical power of 72 mW. Within the EC-QCL tuning range an optimum NH_3 absorption line in the ν_2 fundamental absorption band of NH_3 at 965.35 cm^{-1} 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 by a mechanical chopper 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 [4]. 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 monitoring the QCL power.

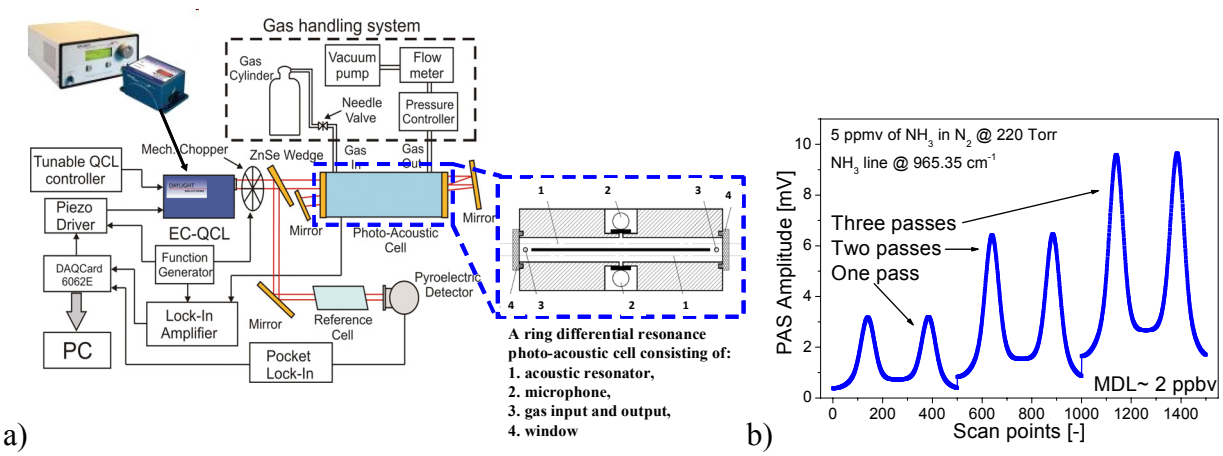

Fig. 1 a) Mid-infrared AM-PAS-based sensor platform for NH_3 atmospheric detection, b) AM-PAS signal for reference mixture of 5 ppmv NH_3 in N_2 after one, two, and three laser beam passes through the photoacoustic cell.

The pressure inside the system was kept at 220 Torr while the flow was maintained at 150 ml/min. In order to minimize NH_3 losses to surfaces and to prevent water vapor condensation in the sensor, the sensor enclosure was heated to 38°C. The minimum detectable concentration of NH_3 for the sensor, when the laser beam passes three times through the photo-acoustic cell, was ~ 2 ppbv for a 5-second data acquisition time (Fig. 1b). After averaging the data over 100 seconds, a sub-ppbv NH_3 concentration level of ~0.6 ppbv was achieved.

To improve our understanding of the dynamics of NH_3 in an industrial and urban area such as Greater Houston, where atmospheric NH_3 data are limited, the EC-QCL-based NH_3 sensor platform was deployed on the roof of the 60 m high North Moody Tower, located on the University of Houston main campus, between November 2009 and October 2010. This experimental location is a perfect sampling site due to proximity to potential NH_3 emission sources such as the Houston Ship Channel and several highways (I-610, US 59, I-45). In addition our atmospheric NH_3 data will be compared directly with data simultaneously acquired by other advanced gas sensing instruments also installed at the Moody Tower air quality monitoring site.

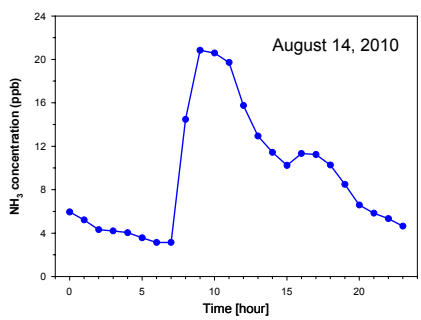

Fig. 2 Accidental ammonia release from a chemical fire resulting from a collision of 18-wheeler trucks on the Houston-Gulf Freeway (I-45) only 2 miles from the sampling site.

Fig. 2 shows a long-lasting increase of the NH_3 concentration (~21 ppb) on August 14, 2010, when a major accident occurred during the same time period on the Houston-Gulf Freeway (I-45) only two miles from the sampling site. The elevated concentration levels are assumed to be associated with NH_3 generation from a chemical fire resulting from a collision of two 18-wheeler trucks, one of which was carrying both a powdery marine pollutant and a liquid pesticide called dimethylamine. Several other unexpected events of high NH_3 concentrations levels were observed during the 2010 Moody Tower NH_3 sensor deployment and will be described.

3. References

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