Photoacoustic measurements of ammonia by a telecommunication diode laser

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Abstract:

A distributed-feedback (DFB) telecommunication diode laser radiating at 1.53 µm was used for photoacoustic (PA) detection of ammonia molecules in the gas phase. The wavelength of the diode laser was adjusted to an absorption line of ammonia at 6528.8 cm^{-1}. For photoacoustic signal generation, the laser current was modulated by the first longitudinal resonant frequency of the cylindrical resonator of the photoacoustic cell (3.8 kHz). This frequency was superposed with a lower frequency for wavelength modulation. The photoacoustic signal was recorded with a 12-bit A/D-card and a lock-in (2f) was simulated in a personal computer. For noise reduction a differential method with two acoustic resonators was used. To increase the Q factor of the cell, the resonators consisted of electro-polished stainless steel. However, for reducing the adsorption problem of the polar ammonia molecule, the remaining surface of the cell was covered with a 30 µm Teflon coating.

With this small system, fast trace gas measurement of ammonia up to the parts per million (ppmV) is possible. The sensitivity of the photoacoustic cell could be determined to 3.29×10^{-9} Wcm^{-1} ($S/N = 3$).

Introduction

The development of molecule-specific spectroscopic detection methods for real-time monitoring of pollutants in biology, medicine, and the environment (e.g. traffic, industrial production) is getting more and more attention, as the environmental problems are increasing.

Thereby the pollution by ammonia plays a basic role in the acid-base equilibrium of the soil in adjacencies of the emission source, because most part of the emitted ammonia is converted rapidly into ammonium [1]. Since the average value of the retention period of ammonia is only about several hours in the atmosphere, real-time concentration monitoring is getting more and more important.

Ammonia is basically emitted by animal production facilities, application of mineral fertilizers, automobile traffic and combustion of fossil fuels.

Measurement setup

The photoacoustic (PA) measurements of mixtures with traces of ammonia were performed with the setup shown schematically in Fig.1. As light source a fiber-pigtailed butterfly laser diode (~9.5 mW) radiating at 1.53 µm was used. The light absorption was monitored by a differential PA detector.

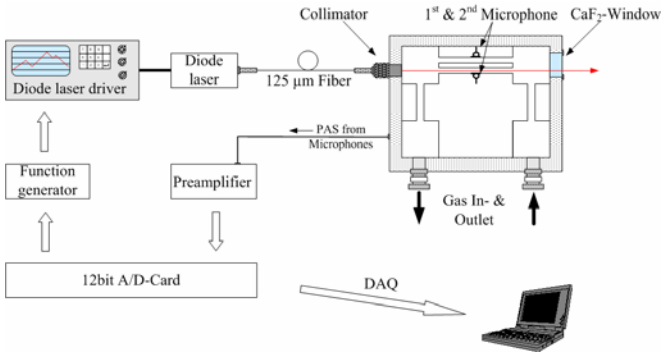

Figure 1: Schematic drawing of the measurement setup

This PA detector consisted of a Teflon-coated aluminium case for reduction of adsorption and two identical 40 mm long acoustic resonator tubes for differential measurement. For additional noise reduction the cell had two acoustic λ/4-filters. The PA signal was generated in one of the resonators by modulating the laser radiation. Thereby the first longitudinal acoustic mode (~3.82 kHz) was excited (Q-factor ~31) [2].

The beam quality of the used fiber-pigtailed diode laser can be seen in Fig. 2. The beam diameter was determined to 0.55 mm (1/e Gaussian) at a distance of 4 cm from the collimator, according to the location of the center of the resonator tube with an inner diameter of 5.5 mm in the measurement setup.

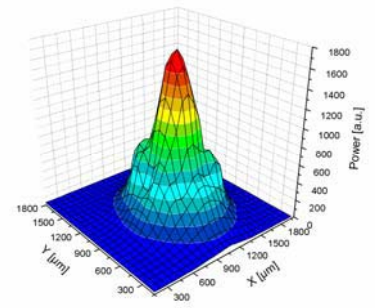

Figure 2: Beam profile of the fiber-pigtailed laser by using a fiber collimator. The beam profile was measured at a distance of 4 cm from the collimator.

For spectral measurements the amplitude modulation (AM) method was used for generating PA the signal. Thereby the current of the diode laser was modulated with a sine function and the spectrum scan was performed by changing the laser diode temperature from -2 °C to 30 °C in 0.1 K steps. For noise reductions a digital lock-in amplifier (Stanford SR850) was employed for data acquisition.

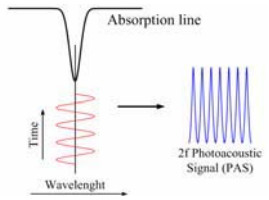

Figure 3: Schematic showing how modulation of an optical source wavelength across the center of a molecular absorption feature produces a PA signal at twice the modulation frequency.

For calibration measurements the wavelength modulation (WM) technique was applied (Fig. 3). WM was achieved by superimposing the above mentioned sine-like function (3.82 kHz) with a second sine function (0.37 Hz). With this new generated function the laser current was modulated. The second modulation is responsible for changing the average current and thereby the wavelength of the laser. To reduce the hereby generated AM, the PA signal was normalized during data acquisition by measuring the laser power with a built-in photodiode in real-time. The wavelength of the laser was adjusted to the absorption line of ammonia at 6528.79 cm^{-1} (25.67 °C). After the determination of the background with pure nitrogen, the ammonia concentration was increased from 1 ppmV to 40 ppmV in eleven steps. The PA signal was amplified and recorded by a 12-bit A/D-card. A lock-in device at 2f was simulated with Labview software.

For gas supply a certified mixture of 50 ppmV NH_3 in nitrogen (Air Liquide) was diluted with nitrogen (Air Liquide) by means of mass flow controllers (Tylan FC 260, 300 and 500 sccm (standard cubic centimeters per minute) full range) to produce concentrations of the investigated species in the 1 ppmV–50 ppmV range. The constant flow velocity of the diluted gas through the PA cell was 250 sccm. The pressure at the outlet of the PA cell was kept at that of the ambient air.

Results

A spectrum of 50 ppmV ammonia in the range between 6527 cm^{-1} and 6541 cm^{-1} was obtained by using AM and normal lock-in technique (Fig. 4). The power of the laser diode was determined to be about 9.5 mW. Additional to this spectrum an absorption spectrum of ammonia (1 ppmV, 1 atm) from the Northwest-Infrared-Database [3] is shown in the figure.

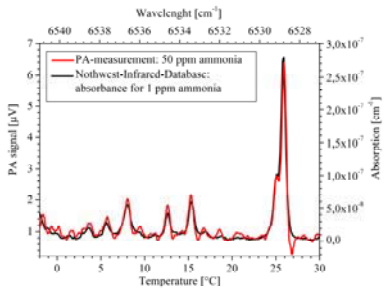

Figure 4: Measured PA spectrum (using AM and lock-in technique with t=3s time constant) in comparison with the ammonia spectrum of the Northwest-Infrared-Database.

The agreement, which implies the peak intensities and the peak width between both spectra, is good.

The result of the calibration measurement by using WM method is shown in Fig. 5. For calibration measurements this kind of modulation was chosen, as it has the advantage to be an example of "derivate spectroscopy", which means that the measurement is highly sensitive to the shape and width of the trace gas absorption feature. Noise from windows and other broadband absorbers have small derivatives and vanish, resulting in a better signal-to-noise ratio. Nevertheless to achieve WM, the current of the laser had to be modulated with an additional lower frequency and data acquisition was performed with A/D-card after adjusting the wavelength of the laser to the absorption line of ammonia at 6528.79 cm^{-1} (25.67 °C). Each data point of this calibration curve consists of 25 single measurements each with 64.8 seconds data acquisition time. The linearity of the calibration curve is good; the curve can be approximated to a background noise of ~16 nV.

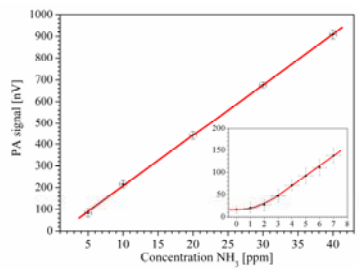

Figure 5: Calibration measurement by using WM technique. Each data point consists of 25 measurements, each with a data acquisition time of 64.8 sec.

The same calibration measurements were also performed with AM method and lock-in amplifier with a lock-in time of 3 s. The sensitivities of both kinds of measurements were comparable, indeed the background noise for AM is about 20 times larger than for WM. Though for the same sensitivity a 20 times longer data acquisition is necessary, the system could be strongly simplified by using an A/D-card for data acquisition.

Conclusion

In this work an economic, small, and easy to handle setup for ammonia trace gas measurements down to the ppm-level could be realized. By using a commercially available telecommunication diode laser with new development evaluation software, measurements with wavelength modulation by simultaneously suppressing amplitude modulation are now possible. Besides this mean advantage, an expensive lock-in amplifier is no longer necessary, as the lock-in technique is simulated in the software.

References

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