Nitrogen Dioxide Detection by use of Photoacoustic Spectroscopy with a High Power Violet-Blue Diode Laser

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Abstract: A nitrogen dioxide (NO_2) sensor based on conventional photoacoustic spectroscopy and a 3.5 W multimode violet-blue diode laser was designed and demonstrated. The photoacoustic cell uses a construction with differential resonators to reduce the impact from ambient acoustic noise. A minimum detection limit of ~ 54 pptv was obtained with a 1 s integration time, corresponding to a 1 σ noise equivalent absorption coefficient of 1.583×10^{-9} cm^{-1} $W/Hz^{1/2}$. Such a sensor system will allow continuous monitoring of atmospheric NO_2 concentration.

OCIS codes: (300.6360) spectroscopy, laser; (280.3420) Laser sensors; (280.4788) optical sensing and sensors.

1. Introduction

Nitrogen oxides (NO & NO_2) play a vital role in many aspects of atmospheric chemistry. This comes from natural lightning and anthropogenic combustions, contributing to acid precipitation and atmospheric oxidants such as nitrate radicals. Of the above oxides, nitrogen dioxide (NO_2) is one of the most prevalent air pollutants causing photochemical smog and acid rain. The average mixing ratio of NO_2 in the atmosphere is ~ 5–30 part per billion by volume (ppbv), but can be even several orders higher when being closer to its source. There is considerable interest in the development of high precision, compact, robust and cost-effective NO_2 sensors. Photoacoustic spectroscopy (PAS) is one of the most effective approaches to detect trace gases because of its sensitive and selective characteristics. [1-4] One of advantages of the PAS is that its sensitivity is proportional to the excitation laser power and thus the performance of PAS-based sensors can benefit from the high output power levels achieved as a result of technology developments in the semiconductor industry. [5] In this work, we report sensitive NO_2 detection based on a 3.5W CW violet-blue diode laser operating at 447 nm.

2. Differential photoacoustic cell and NO_2 absorption spectrum

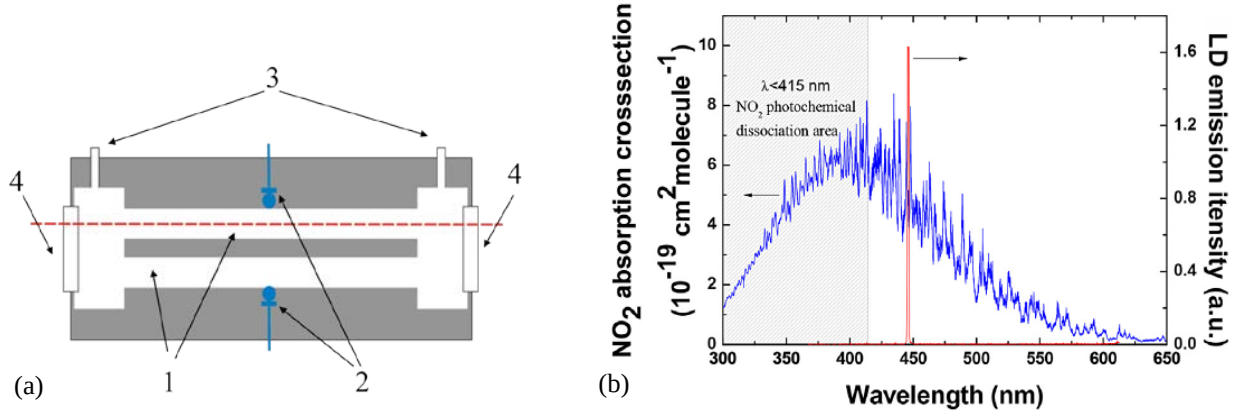

Fig. 1 (a) Differential photoacoustic cell. 1. acoustic resonators, 2. microphones, 3. gas inlet-outlet, 4. windows. (b) NO_2 absorption cross section as a function of wavelength, LD emission spectrum and photochemical dissociation area.

A schematic of the differential photoacoustic cell is shown in Fig. 1 (a). The differential photoacoustic cell consists of two identical resonators, gas inlet and outlet, two acoustic filters and two windows. Each resonator is composed of a cylindrical channel and a miniature microphone, which is installed in the middle of the channel and 4 mm far from the center axis. The maximum acoustic wave oscillations are detected, as shown in Fig. 1 (a). According to the

HITRAN2008 database [6] NO_2 exhibits a broadband absorption from 300 nm to 650 nm with a maximum cross-section of 7.4×10^{-19}cm^2/molecular at 414 nm as depicted in Fig. 1 (b). Photochemical dissociation occurs below 415 nm, lowering the photoacoustic signal intensity, as shown in Fig. 1 (b). Therefore a commercial high stability multimode violet-blue diode laser emitting at 447 nm (Changchun New Industries Optoelectronics, model MDL-F-447) was selected as the laser excitation source for the PAS based senor system.

3. Experimental setup and results

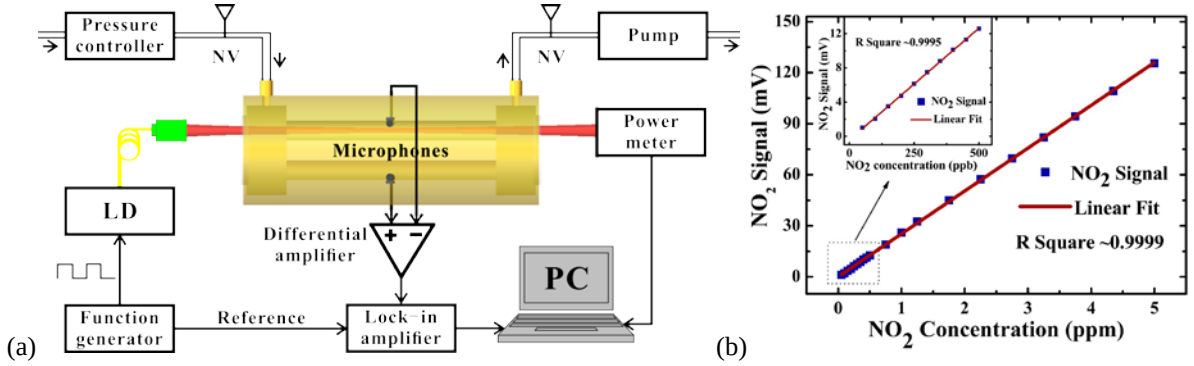

Fig. 2. (a) Experimental setup of differential resonator PAS based sensor for NO_2 detection. LD: 447 nm laser diode; NV: needle valve; PC: personal computer. (b) Linearity of the NO_2 signal as a function of NO_2 concentration obtained with the differential resonator PAS based sensor system.

A schematic of the differential resonator PAS based sensor for NO_2 detection is depicted in Fig. 2 (a). A function generator (Agilent, Model 33500B) was employed to generate a square signal with a duty cycle of 50% and to scan the laser diode. The TTL modulated laser beam irradiated only one of the two resonators of the differential photoacoustic cell and its power was monitored by a power meter. After signal detection both output signals of the microphones were differentially amplified and demodulated by a lock-in amplifier, which was set to a 12 dB/oct filter slope, 1 s a time constant and 1-*f* mode, corresponding to a detection bandwidth of Δf= 0.25 Hz. All of the data acquisition and processing was controlled by a computer based LabVIEW program. A noise equivalent concentration (NEC) of ~ 54 pptv with a 1 s integration time was achieved. With an effective absorption cross section of 4.4699×10^{-19} cm^2/molecular [7], a 1 σ normalized noise equivalent absorption coefficient (NNEA) of 1.583×10^{-9} cm^{-1} W/Hz$^{1/2}$ was obtained. The linearity assessment of the NO_2 signal as a function of NO_2 concentration is depicted in Fig. 2 (b). The obtained *R* square value of 0.9999 confirms the excellent linearity of this sensor's response to NO_2 in a concentration range of >3 orders of magnitude. Long term, continuous, real-time monitoring of atmospheric NO_2 concentration levels will also be reported.

4. Conclusions

A differential resonator PAS based NO_2 sensor using a high power violet-blue diode laser as the excitation source was demonstrated. The minimum detection limit of ~ 54 pptv was obtained at 1 s integration time, corresponding to a 1 σ NNEA of 1.583×10^{-9} cm^{-1} W/Hz$^{1/2}$. An excellent linearity of the NO_2 signal as a function of NO_2 concentration covering >3 orders of magnitudes was observed. The use of high power multimode diode lasers to trace gas detection reduces sensor system cost.

5. References

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