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Ammonia, carbon dioxide and water vapor detection based on tunable fiber laser photoacoustic spectroscopy

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ABSTRACT

Tunable laser photoacoustic spectroscopy is attracted as a powerful tool for trace gas detection in environmental applications. A photoacoustic gas sensor using a near-infrared tunable fiber laser and based on wavelength modulation spectroscopy is developed. Continuous measurements of ammonia, carbon dioxide and water vapor in gas mixtures are achieved at atmospheric pressure. The minimum detection limits (signal-to-noise ratio = 1) of 6 ppb of ammonia, 5 ppm of carbon dioxide and 29 ppm of water vapor have been demonstrated with the sensor. Ammonia, carbon dioxide and water vapor in ambient air are measured by the sensor.

1. Introduction

Multi-gas sensing is required in medical diagnosis, various industrial and environmental applications [1–3]. Laser photoacoustic spectroscopy (PAS) is a well established method used in multi-gas sensing applications [4–6]. In recent years, near-infrared (IR) tunable lasers based photoacoustic (PA) sensors have attracted many interests as their excellent performance in sensing sensitivity, multi-gas sensing and long life time [7]. The near-IR tunable lasers show good promise for fiber-optic telecommunications applications, high-resolution spectroscopy and gas sensors. The developments of tunable lasers provide new opportunities for PA gas detection [8,9].

PAS is an absorption-based technique. When a wavelength or intensity modulated light beam goes through a PA cell, the gas which absorbs the laser radiation will be heated up periodically at the modulation frequency. Periodic pressure variation will be produced in the PA cell, and the PA signal, which is proportional to the target gas concentration, is generated. Since PA signals depend on the intensity of the excitation light source, high power light sources are generally required for high sensitivity. In mid-IR, the sensitivities at parts per billions (ppb) levels have been achieved using gas lasers (CO and CO_2 lasers) and Quantum cascade lasers (QCLs) [10,11]. In near-IR, tunable diode lasers in combined with fiber amplifier based PAS have also been implemented [12,13]. The detection of multi-species trace gas over broad spectral bandwidth is desirable for many applications ranging from industrial applications to environmental monitoring. However, the use of multiple lasers makes the PA sensor too complicated and expensive. The near-IR tunable lasers have created new opportunity for spectroscopic gas sensing, owing to their low cost and unique combination of continuous tunability and broadband wavelength coverage, where overtone vibration bands of many molecules of interest occur (CO_2, CO, H_2O, NH_3 etc). These features enable spectral signatures of multi-species trace gas to be detected continuously. The near-IR tunable lasers will become very promising spectroscopic sources for multi-gas sensing applications.

In this paper, a multi-gas PA sensor based on a tunable erbium-doped fiber laser (TEDFL) in combination with a fiber amplifier is developed. The performance of this sensor is demonstrated by the measurements of H_2O, CO_2 and NH_3 in atmospheric environment.

2. Experimental setup

The configuration of multi-gas PA sensor is depicted in Fig. 1. The light source consists of a TEDFL in combination with an

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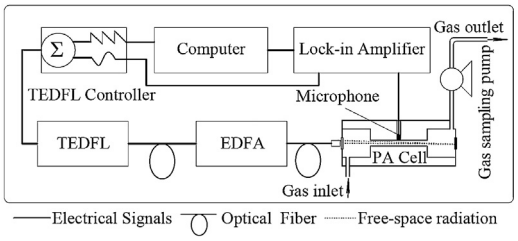

Fig. 1. Schematic representation of the PA sensor.

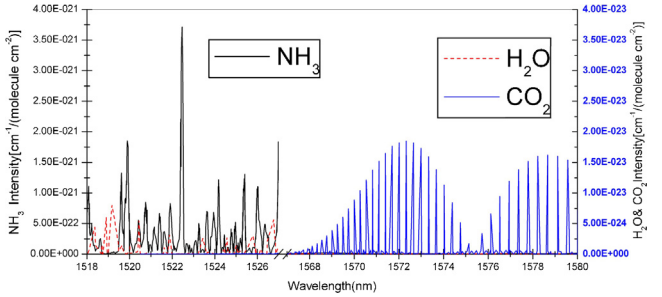

Fig. 2. H_2O and CO_2 spectra obtained from the HITRAN database [15] and NH_3 spectrum obtained from the PNNL database [16], NH_3 transition at 1522.4 nm is isolated from interference from typical background constituents CO_2 and H_2O.

erbium-doper fiber amplifier (EDFA, Amonics, AEDFA-27-BFA). The EDFA is used to amplify the TEDFL output power up to 500 mW. The configuration of TEDFL has been described elsewhere in detail [14], so we only give a brief introduction. The output wavelength of TEDFL is controlled by a TEDFL controller. The operation wavelength of the TEDFL can be continuously scanned with different scan rate from 1520 nm to 1610 nm. Wavelength modulated light from the TEDFL is amplified by the EDFA and coupled into the PA cell with a double-pass configuration through a fiber collimator.

The PA cell sealed with a quartz window and a gold coated mirror consists of a central cylindrical acoustic resonator (diameter = 10 mm, length = 100 mm) and two buffer volumes (length = 50 mm). For this cell, the resonant frequency of its first longitude mode is 1632 Hz. An optimal modulation depth of 18 mV is determined for this PA sensor. The target gas was introduced into the PA cell by the gas sampling pump. A sensitive microphone is placed in the middle of the PA cell resonator. The PA signal is fed into the lock-in amplifier (Stanford Research Systems, SR830), and then transmitted to the computer where a computer program controls the data acquisition and processing.

3. Experimental methodology

3.1 Wavelength modulation photoacoustic spectroscopy

The theory of wavelength modulation PAS has been described in detail by several authors [12,17]. Here we only give a brief description for the multi-gas PA measurement. The mechanism of multi-gas PA detection is based on different infrared spectrum features of different gas molecules and employing principle of measuring in turn by numbers of laser spectral lines, which can realize a quantitative measurement of concentration of each gas component through building a calibration model [18]. The PA signals can be described by following equation:

$$S_j = S_m P_j F \sum_{i=1}^{n} C_i \alpha_{ij} \quad (1)$$

where S_m is the sensitivity of the microphone, in units of Volts per Pascal; the subscript j represents the jth laser wavelength being used; P_j is the power of the incident laser radiation, with units of Watt; F is the cell-specific constant, with units of Pascal centimeters per Watt; α_{ij} is the absorption coefficient of the ith gas species for jth operating laser line, in wavenumber (cm^{-1}); C_i is the concentration of the ith gas component being measured, in units of ppm (by volume) and n is the number of mixed gas species.

One of the most effective techniques for eliminating the background noise is applying the wavelength modulation spectroscopy (WMS) for PA measurement [19]. For WMS, the laser wavelength can be described by

$$\lambda_j(t) = \lambda_{cj} + a\cos(2\pi f t) \quad (2)$$

here $\lambda_j(t)$ is the instantaneous wavelength of the laser, λ_{cj} is the central wavelength of the jth laser line, a is the modulation depth and f is the sinusoidal modulation frequency.

In wavelength modulation spectroscopy the laser frequency is modulated at a frequency f about the center of the absorption transition, and the background noises occur at the same frequency. However the PA signals are analyzed at the frequency $2f$. Thus, by demodulating the microphone signal at $2f$, the acoustic signal from window absorption and other broadband background absorbers can be avoided. And then, signal-to-noise ratio (SNR) and the sensitivity can be improved effectively.

3.2. Wavelengths selection

It is important for accurate measurement to select the absorption lines at which the three species trace gases have little even no overlapping. The TEDFL is operated in wavelength-modulation mode, whereby it is scanned by a combined sawtooth and sinusoidal waveform. It is tuned to cover a spectral range from 1518 nm to 1576 nm with the operational range of an EDFA. The NH_3 absorption line near 1522.4 nm was selected because of its isolation from H_2O and CO_2 interferences. By the same token the H_2O absorption line near 1519.2 nm and CO_2 absorption line near 1572.6 nm were selected (see Fig. 2).

4. Results and discussions

Multi-gas PA sensing is based on different infrared spectrum features of various gas molecules and employing principle of measuring in turn by numbers of spectral lines of laser. It can realize quantitative measurement the gas of concentration through building calibration model. This sensor was operated according to the optimum design conditions. The TEDFL is tuned continuously from 1518 nm to 1576 nm to ensure NH_3, CO_2 and H_2O detection. The sensor performance was checked by measuring NH_3, CO_2 and H_2O mixtures of different concentrations which were obtained by diluting 1.2% H_2O (44% relative humidity at 20 °C), 20 ppm NH_3 and 2% CO_2 with synthesized N_2. The continuously measured second harmonic signal of 2000 ppm H_2O, 0.2 ppm NH_3 and 350 ppm CO_2 mixture under the background of synthesized N_2 is shown in Fig. 3. In order to separate the PA signal generated by the different species, a PA signal extracting process is used, Input 1519.2 nm, 1522.4 nm and 1572.6 nm, respectively, corresponding to output different measuring result. The background noise is estimated to be the standard deviation of the PA signal ($1\sigma = 1.33\ \mu V$) at optimum conditions ($P = 500$ mw, double-pass, $p = 1$ atm, $\tau = 100$ ms, $V_{mod} = 18$ mV). The experimental results show the SNR of H_2O is 68, the SNR of NH_3 is 34, and the SNR of CO_2 is 66, which indicates that the 1σ noise-limited detection limit of the sensor for H_2O, NH_3 and CO_2 is respectively about 29 ppm, 6 ppb and 5 ppm.