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Research Article

Photoacoustic Measurement of Ethane with Near-Infrared DFB Diode Laser

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A compact resonant photoacoustic sensor based on a near-infrared distributed-feedback (DFB) diode laser was developed for detection of ethane (C_2H_6). A DFB laser emission at 5937.25 cm^{-1} with a power of ~5 mW was used as an excitation light source for generating the photoacoustic signal. Wavelength modulation and second harmonic detection scheme were employed. Modulation frequency and modulation amplitude were optimized for getting optimum performance. Performance evaluation based on the linearity response of the PAS sensor system with respect to C_2H_6 concentration levels was performed, and a good linear dependence of the PAS signal on the C_2H_6 concentration was obtained. A minimum detectable concentration of 9 ppmv was achieved for detection of C_2H_6 with a lock-in time constant of 10 ms.

1. Introduction

Ethane (C_2H_6) is the second largest component among natural gases; therefore, detection of C_2H_6 was an effective method for discrimination of CH_4 leakage between natural gas pipe line and biogenic sources of landfills or wetlands. Detection of C_2H_6 is also important in environmental or atmosphere monitoring as C_2H_6 strongly affects both atmosphere chemistry and climate as a most abundant nonmethane hydrocarbon in the atmosphere [1]. In addition, C_2H_6 detection has found applications in breath analysis as a noninvasive method to monitor and identify diseases, such as lung cancer and asthma [2]. Therefore, developing the C_2H_6 sensor has a strong need in industrial, environmental, or medical applications.

Laser spectroscopy-based gas sensors is an effective tool for real time, selective, and sensitive detection of trace gases, which has a wide range of potential applications in environmental monitoring, medical diagnostics, and industrial process control [3, 4]. Photoacoustic spectroscopy, based on the photoacoustic effect which was first discovered by Alexander Graham Bell in 1880 [5], is a sensitive, selective, and well-established method for sensing trace gases that has been successfully employed in numerous applications [6, 7]. The PAS technique offers several practically important advantages, such as high trace gas detection sensitivity with a small sensing module and wide dynamic range and no need for an optical detector such as a photodiode. Unlike spectroscopic techniques, such as integrated cavity output spectroscopy (ICOS) [8], cavity ring down spectroscopy [9], or absorption spectroscopy with multipass cell [10], the PAS is a "zero base line" method. In addition, the amplitude of the photoacoustic signal depends on the power of the exciting light beam. Therefore, the PAS can benefit from using continuous wave infrared laser sources capable of emitting high optical power [11]. To date, there are several PAS techniques including traditional resonant PAS with wideband microphones [12], cantilever-based PAS [13], and quartz-enhanced PAS (QEPAS) [14].

In the present work, we report on our recent efforts in the development of a compact PAS sensor for detection of C_2H_6 by using a distributed-feedback (DFB) diode laser operating at

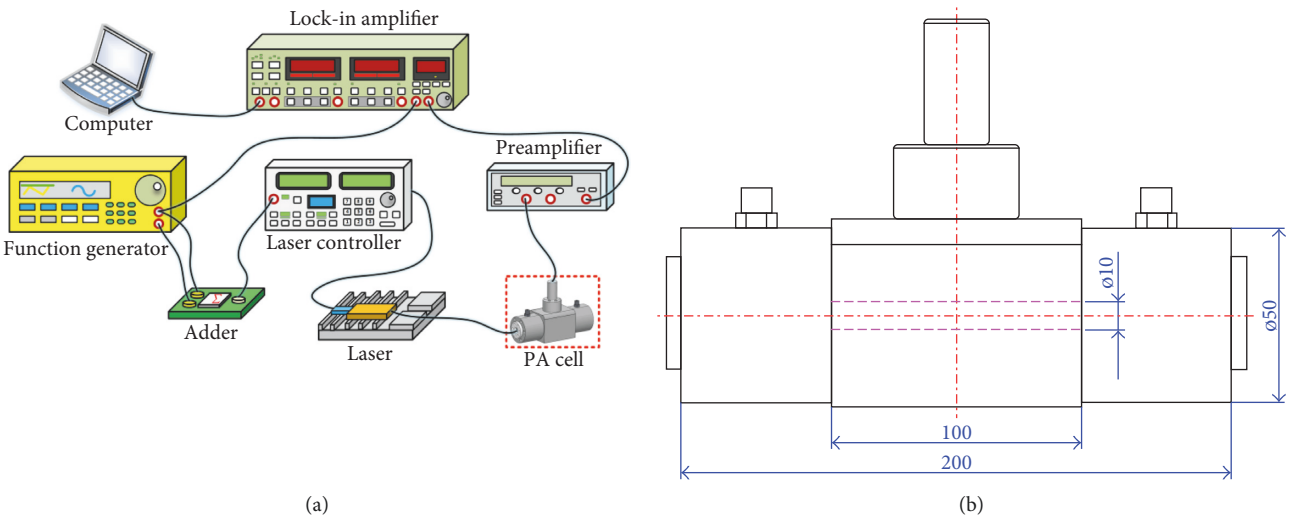

Figure 1: (a) Schematic diagram of the developed C_2H_6 PAS experimental setup and (b) geometric dimension of the PAS cell.

5937.2 cm^{-1} with a power of ~5 mW and an excitation light source to generate the photoacoustic signal. The near-infrared DFB diode lasers that are commercially available offer a robust, relatively inexpensive, and attractive alternative. This low-cost, compact, and sensitive PAS sensor of C_2H_6 is very suitable for various field applications, in particular, for discrimination of CH_4 leakage between natural gas pipe line and biogenic sources of landfills or wetlands [15].

2. C_2H_6 PAS Sensor Configuration

A schematic diagram of the developed C_2H_6 PAS sensor platform is shown in Figure 1(a). A PAS cell built out of aluminum with a central cylinder tube of radius $r = 5$ mm and length of $L = 100$ mm acting as an acoustic resonator was designed. A buffer volume with a radius of 25 mm and length of 50 mm was set at both sides of the cylinder resonator, and the total length of the PAS cell was 200 mm (Figure 1(b)). C_2H_6 shows an unresolvable vibration-rotation absorption band near 1.68 μm [16, 17]. Therefore, a fiber-coupled distributed-feedback (DFB) diode laser (NLK1E5GAAA, NEL) operating at 1.684 μm was used as the excitation light source for generating the photoacoustic signal. The laser current and temperature were controlled by a commercial diode laser controller (ILX Lightwave LDC-3724). Coarse and fine wavelength tuning was performed by changing the laser temperature and current, respectively. Wavelength modulation and second harmonic detection are used in this work. A dual channel function generator was used to provide a voltage ramp for scanning the laser wavelength and a sine wave for modulating the laser wavelength. The voltage ramp and the sine wave were combined with a home-made adder before being fed to the laser driver. The laser current was the sine wave modulated at half the resonant frequency f_0 of the PAS cell. The laser beam was collimated with a fiber-coupled collimator (f ~4.8 mm) and subsequently focused into the PAS cell by using a lens L with a 30 mm focal length. A preamplifier (EG&G, Model 5113) with a gain of 25 and 6 dB bandpass filter (300 Hz–30 kHz) was used for signal

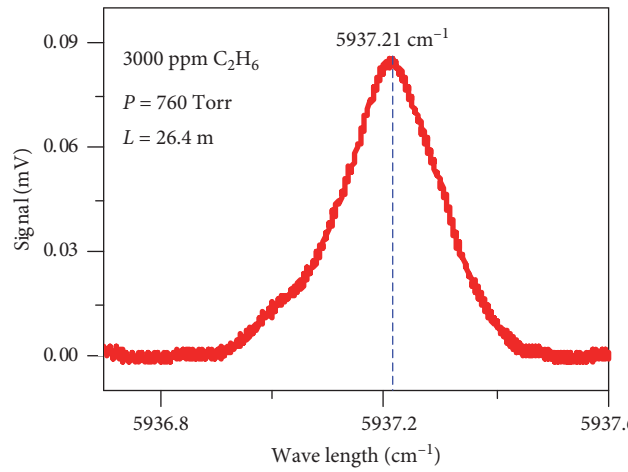

Figure 2: Direct absorption spectroscopy of C_2H_6.

amplification prior to demodulation at f_0 by a lock-in amplifier (Stanford Research Systems, Model SR 830 DSP). The time constant of the lock-in amplifier was set at 10 ms in combination with an 18 dB/octave slope filter (leading to a detection bandwidth of $\Delta f = 9.375$ Hz). The demodulated signal was subsequently digitalized with a DAQ card (NI-USB-6212) and displayed on a laptop via a LabVIEW interface.

3. Results and Discussion

Direct absorption spectroscopy of C_2H_6 was first measured for determining absorption peak. Figure 2 shows a 3000 ppm C_2H_6 absorption spectroscopy that was measured by using a compact multipass absorption cell with an optical path length of 26.4 m [10] at normal atmosphere pressure. The absorption peak was found to be at 5937.21 cm^{-1} and the corresponding laser temperature was 31°C. Therefore, the laser temperature was controlled at 31°C during following measurement.

Characteristics of the acoustic resonator were experimentally investigated to determine the specific resonant

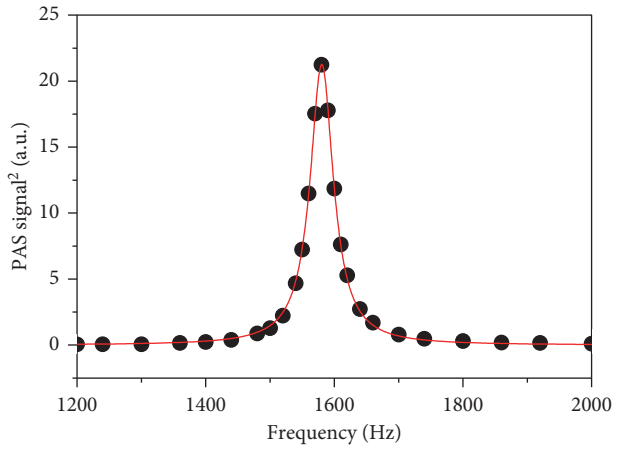

Figure 3: Square of the PAS signals amplitude as a function of frequency. The data are fitted with a Lorentz profile.

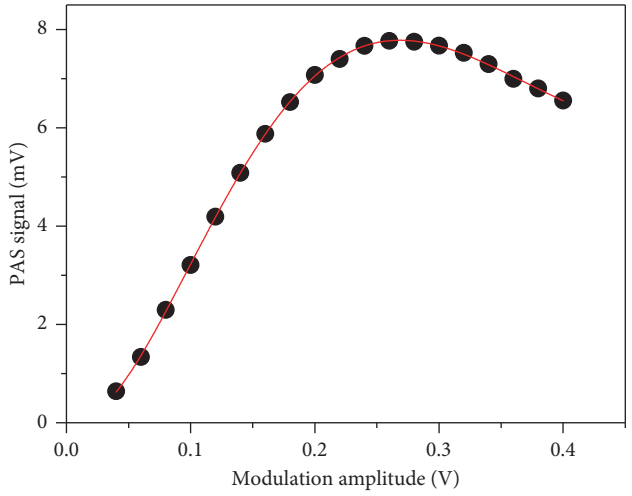

Figure 4: C_2H_6 PAS signals as a function of modulation amplitude.

frequency of the resonator in an atmospheric environment. Measurements of the C_2H_6 PAS signal with constant concentration of 5000 ppm at different modulation frequencies were performed for this study. Figure 3 shows the square of the signal amplitude as a function of frequency. The data were fitted to a Lorentz contour, which describes power in a classical driven oscillator as a function of frequency. From the results shown in Figure 3, optimum resonant frequencies $f_{10} = 1580$ Hz were found for the resonator. This value corresponds to the first longitudinal resonant mode of the resonator [18]. Therefore, the laser wavelength was modulated at a frequency of 790 Hz.

The C_2H_6 PAS sensor system was designed to operate in a wavelength modulation mode, which can effectively suppress the background noise. However, wavelength modulation of the PAS signal is dependent on modulation amplitude. Therefore, the laser frequency modulation amplitude was also to be optimized to get an optimum PAS signal. Figure 4 shows the measured PAS signal as a function of the modulation amplitude. The measurements were carried out under normal atmospheric conditions. As can be seen in Figure 4, the

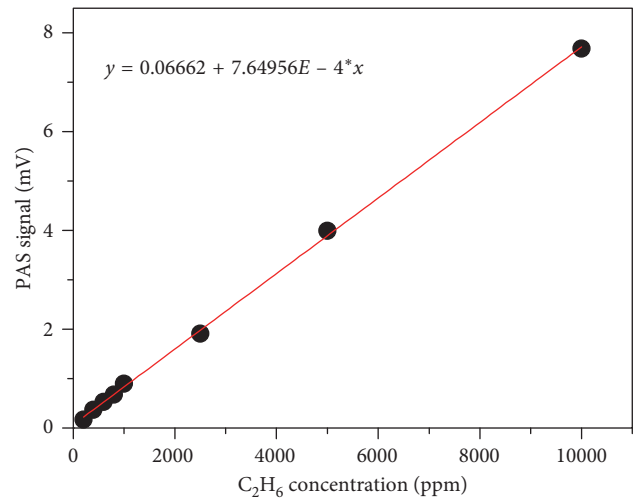

Figure 5: Linear response of the PAS signals to C_2H_6 concentration.

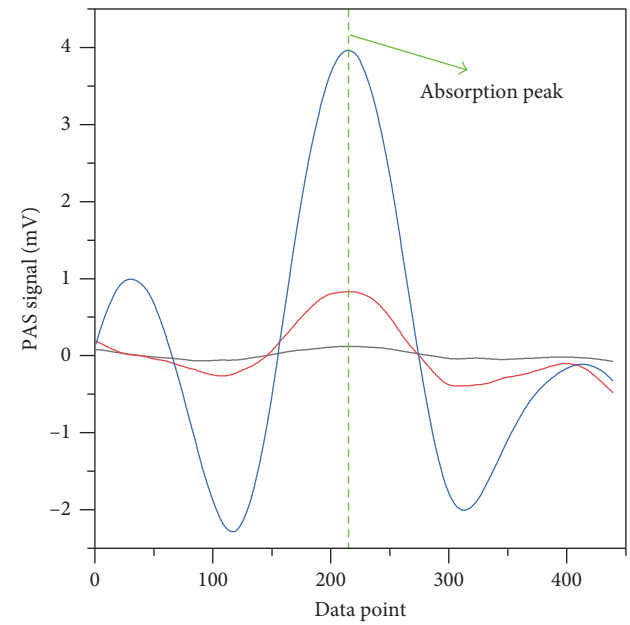

Figure 6: C_2H_6 PAS signals obtained with 100 ppmv, 1000 ppmv, and 5000 ppmv C_2H_6 samples, respectively. The dotted line position corresponds to the absorption peak of Figure 2.

optimum modulation amplitude of the sine wave for PAS detection of C_2H_6 was found to be 0.25 V which was then used in the following measurements.

A performance evaluation based on the linearity response with optimized parameters of the C_2H_6 PAS sensor system with respect to C_2H_6 concentration levels was performed. A calibrated standard gas mixture consisting of 10,000 ppm C_2H_6:N_2 was employed and diluted with pure N_2 by using a commercial gas dilution system (Environics, S4000). As expected, a linear dependence of the PAS signal on the C_2H_6 concentration was found. The measured PAS signals and the fitted straight line are shown in Figure 5.

As an example, Figure 6 depicts the PAS 2*f*-signals of C_2H_6 with a concentration of 100 ppmv, 1000 ppmv, and

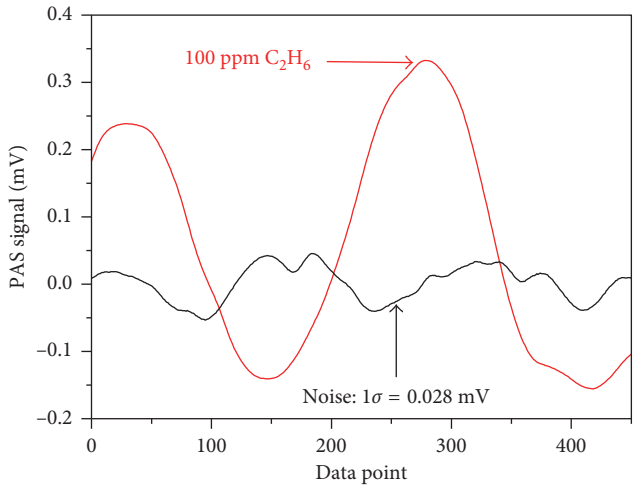

Figure 7: PAS signal of 100 ppmv C_2H_6 and noise obtained in air.

5000 ppmv, respectively. The corresponding signal (the peak value at the dotted line) was 0.12 mV, 0.83 mV, and 3.96 mV, respectively. For evaluation of the minimum detection limit of the C_2H_6 PAS sensor, the PAS signal in air, as the noise level, was measured. Figure 7 shows the PAS noise obtained in air and the 100 ppmv C_2H_6 PAS signal for comparison. The noise level (1σ) defined as standard deviation was found to be 0.028 mV. Taking into account the PAS signal of 0.33 mV obtained with 100 ppmv C_2H_6, the signal to noise ratio was then found to be 11. Therefore, the minimum detection limit was estimated to be 9 ppmv for C_2H_6 detection.

4. Conclusion

A PAS sensor for detection of C_2H_6 was developed. Using wavelength modulation and second harmonic detection scheme, combined with optimization of modulation frequency and modulation amplitude, good performance was achieved for detection of C_2H_6. Good linear dependence of the PAS signal on the C_2H_6 concentration was obtained. A minimum detectable concentration of 9 ppmv was achieved for detection of C_2H_6 with a lock-in time constant of 10 ms and optical power of 5 mW. The developed C_2H_6 PAS sensor could be applied in monitoring the natural gas pipe line leakage or industrial process control.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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