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A novel methane detection system based on InGaAsP distributed feedback laser

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The authors report a novel methane detection system based on InGaAsP DFB (distributed feedback) laser using the WMS-2*f* (wavelength modulation spectroscopy) to prompt the sensitivities of TDLAS (tunable diode laser absorption spectroscopy) measurement technology at the *R*(3) transition of the $2\nu_3$ band of methane. The system employs a novel signal processing to cancel emitter-amplitude variations as well as changes in the optical transmission not due to the target gas. High accuracy and low detecting limit (about 1 ppm) are achieved at normal air pressure and room temperature. Excellent stability and fast response are also found based on the detection system in 30 days. These results suggest that our system is a good candidate for CH_4 detectors.

Keywords: optical sensor, methane, distributed feedback (DFB) laser.

1. Introduction

Trace gas detection has attracted much attention because of its wide applications in air quality control, environmental protection and healthcare as well as security [1–3]. Among these detection systems, CH_4 detection systems have gained special focus due to their extreme importance for safety reasons in oil and coal industries, water treatment plants, landfill sites and commercial or domestic environments [4–8]. CH_4 is the main component of harsh gases, and is inflammable and explosive, with a lower explosion limit (LEL) of 5% and an upper explosion limit of 15% [9]. Detecting its concentration in time safely and reliably has an important effect on the safe operation of industrial mines. Tragedies of CH_4 explosions worldwide in recent years reinforce the importance of recognizing the potential hazards in underground coal mining. On the other hand, if inhaled, CH_4 molecules effectively replace the oxygen in the body, causing suffocation and death. Therefore, new technologies are needed to detect CH_4 for occupational safety and health [10, 11].

Optical sensors based on semiconductor sources have the potential advantages of: *i*) being intrinsically safe, *ii*) showing ability to detect a specific gas by selection of appropriate wavelengths, *iii*) ability to operate in zero-oxygen environment (*e.g.*, for

purging of pipe lines), and *iv*) low cost of ownership [12–14]. The infrared laser spectroscopy sensors are typically based on absorption spectroscopy of fundamental bands in the range of 3–25 μm spectral region and near-IR vibrational overtone and combination bands from 1 to 3 μm [15]. CH_4 has a rich spectrum in the near-IR region. In the spectral range from 1610 to 1750 nm (~5500–6180 cm^{-1}), MARGOLIS have identified and assigned more than 2000 methane absorption lines of rotational–vibrational transitions in the band of $2\nu_3$ [16]. SCHÄFER *et al*. examined these lines for interferences and pointed out the best lines for monitoring purposes [17].

Herein, we demonstrate a CH_4 detection system by WMS-2*f* measurement based on a 1654 nm near-infrared (InGaAsP) distributed feedback (DFB) laser diode. Compared with the sensing systems without this signal process, the sensing system with WMS-2*f* measurement exhibits good sensing properties such as high sensitivity, quick response, good linear dependence and excellent stability. These experimental results provide a good basis for the development of practical systems.

2. Experiment

2.1. Theoretical principles

In the limit of low absorption, the Beer–Lambert law can be approximated as:

$$I(\nu) = I_0(\nu)\left[1 - \alpha(\nu)CL\right] \tag{1}$$

where $I(\nu)$ is the transmitted light intensity of monochromatic radiation at frequency ν passed through an absorbing gas of concentration C, $I_0(\nu)$ is the input intensity, L is the length of optical path, ν is the radiation frequency, and $\alpha(\nu)$ is the absorption cross-section.

When WMS is referred to, the diode laser injection current is sinusoidally modulated with angular frequency $\omega = 2\pi f$ to produce laser frequency modulation (FM), and the light intensity is simultaneously modulated (IM) as well as the wavelength:

$$I_0(\nu(t)) = I_0\left[1 + i_0\cos(\omega t + \varphi_1) + i_2\cos(2\omega t + \varphi_2)\right] \tag{2}$$

$$\nu(t) = \nu_0 + \Delta\nu_m\cos(\omega t) \tag{3}$$

in which I_0 is the laser frequency without modulation, $\Delta\nu_m$ is the amplitude of the frequency modulation, i_0 and i_2 are coefficients to fit the observed intensity--frequency relationship for the specific laser used, normalized by the average laser intensity at ν_L, with φ_1 and φ_2 being the linear and nonlinear FM/IM phase shifts.

A fiber multiplexer splits the beam into two beams with a power ratio of 1:1, and an insertion loss of less than 4%. $I(\nu)$ can be obtained on a detector receiving an optical beam that has encountered gas absorption on the optical path, which will be called $I_s(t)$, and on a detector receiving a signal that has not crossed the gas, which will be called $I_r(t)$.

$$I_s(\nu(t)) = \frac{1}{2}K_s m_s I_0\left[1 + i_0\cos(\omega t + \varphi_1) + i_2\cos(2\omega t + \varphi_2)\right] \times \times \left[1 - \alpha\left(\nu_0 + \Delta\nu_m\cos(\omega t)\right)CL\right] \quad (4)$$

$$I_r(\nu(t)) = \frac{1}{2}K_r m_r I_0\left[1 + i_0\cos(\omega t + \varphi_1) + i_2\cos(2\omega t + \varphi_2)\right] \quad (5)$$

where K_s, K_r are the optical-electronic gains of detector 1, detector 2, and m_s, m_r are the transmittances. Adjust K_s and K_r until $K_s \times m_s$ is equal to $K_r \times m_r$, the signal processing then consists of a subtraction stage where (4) subtracted from (5) gives (6) to obtain the optical intensity change quantity caused by gas absorption but not the optical intensity itself. The output of this subtraction stage is

$$I_L(\nu(t)) = I_r(\nu(t)) - I_s(\nu(t)) = = \frac{1}{2}K_s m_s I_0\left[1 + i_0\cos(\omega t + \varphi_1) + i_2\cos(2\omega t + \varphi_2)\right] \times \times \left[\alpha\left(\nu_0 + \Delta\nu_m\cos(\omega t)\right)CL\right] \quad (6)$$

Then the $I_L(\nu(t))$ is divided by the $I_r(\nu(t))$ in a divider stage to cancel such factors as laser intensity, optical-electronic gain and transmittance

$$I_F(\nu(t)) = \alpha\left(\nu_0 + \Delta\nu_m\cos(\omega t)\right)CL = CL\sum_j S_j(T)\hbar_j \quad (7)$$

where $S_j(T)$ is line strength of the transition j and $\hbar_j$ is the line shape function of the transition j. It is a periodic even function in ωt and can be expanded in a Fourier cosine series:

$$F\left(\nu_0 + \Delta\nu_m\cos(\omega t)\right) = \sum_{n=0}^{\infty}\tau_n(\nu_0, \Delta\nu_m)\cos(n\omega t) \quad (8)$$

where the components $\tau_n(\nu_0, \Delta\nu_m)$ can be described as

$$\tau_0(\nu_0, \Delta\nu_m) = \frac{CL}{2\pi}\int_{-\pi}^{\pi} S_j\,\hbar_j(\nu_0, \Delta\nu_m)\cos(\theta)\,\mathrm{d}\theta \quad (9)$$

$$\tau_n(\nu_0, \Delta\nu_m) = \frac{CL}{\pi}\int_{-\pi}^{\pi} S_j\,\hbar_j(\nu_0, \Delta\nu_m)\cos(n\theta)\,\mathrm{d}\theta \quad (10)$$

The magnitude of the absorption-based WMS-2f signal, $S_{2f}(\nu_0)$ measured by a lock-in amplifier can be reduced as follows

$$S_{2f}(\nu_0) = \frac{CL}{2\pi}\int_{-\pi}^{\pi} S_j \hbar_j(\nu_0, \Delta\nu_m)\cos(2\theta)\,\mathrm{d}\theta \tag{11}$$

The $2f$ signal has its maximum value at the absorption center, and the maximum value can be converted to the methane concentration using a known analytical relationship between them [18, 19].

2.2. Line selection

For the detection of CH_4, the $R(3)$ transition of the $2\nu_3$ band (the wavelength is about 1653.72 nm and the corresponding frequency is about 6046.96 cm^{-1}) was chosen for its high average absorption coefficient [20]. Figure 1 shows the CH_4 spectral line intensity at different frequencies. The strongest CH_4 absorption line accessible with

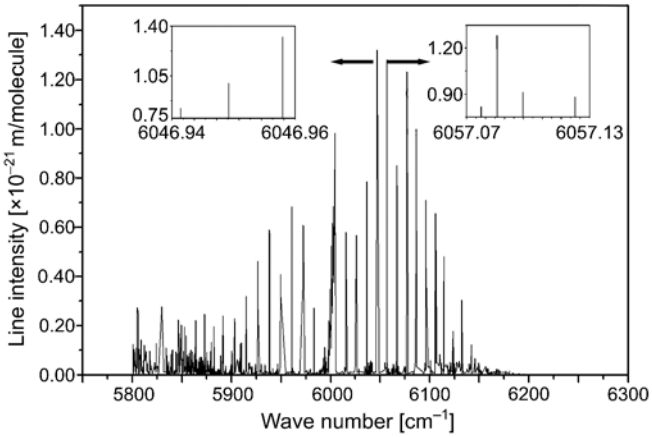

Fig. 1. CH_4 spectral line intensity at different frequencies.

the commercial DFB laser is near 6046 cm^{-1} [21]. The line strengths in the $R(3)$ transition are 1.320×10^{21}, 1.000×10^{21} and 8.170×10^{21} cm/molecule. The corresponding absorption coefficient for the lines calculated are about 0.003022, 0.003700 and 0.004884 cm^{-1} at 10000 ppmv, respectively [22].

2.3. Instrument details

The experimental set up used to demonstrate the application of DFB laser diodes in gas sensing is shown in Fig. 2. Figure 2**a** is the optical schematic of CH_4 detection

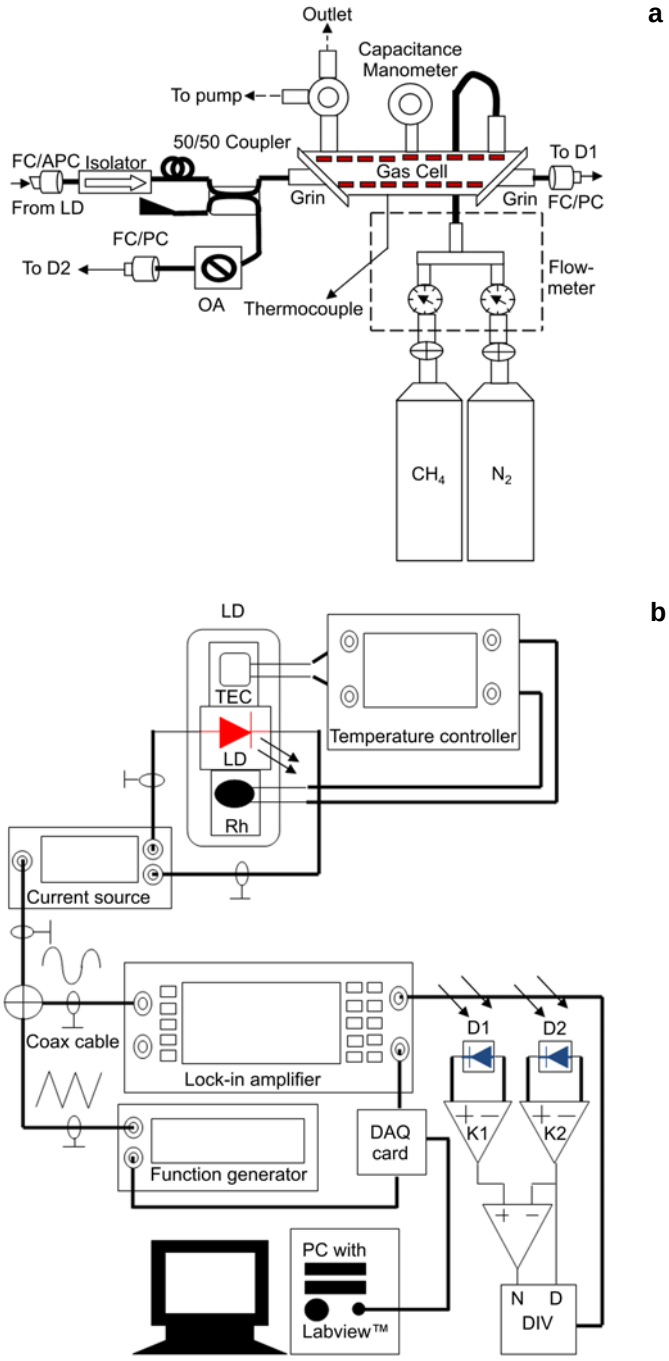

Fig. 2. Optical (**a**) and electronic (**b**) schematic of CH_4 detection system based on WMS-2f technology.

system based on WMS-2f technology. The laser source is a DFB quantum well diode laser with a power of 10 mW supplied by the Institute of Semiconductors, Chinese Academy of Sciences, emitting single mode at 1654 nm (25 °C, 30 mA). The laser device is integrated with the Peltier thermoelectric cooler in a butterfly package together to stabilize the laser emission. The pig-tail of the laser diode is connected to a commercial fiber multiplexer, which divides the beam into two beams with a ratio of 1:1. The signal beam was propagated through a 200 mm electro-polished, brass absorption cell that had antireflection-coated sapphire windows. After exiting the cell, the beam was refocused onto a thermoelectric-cooled InGaAs detector (Judson Inc., J23-18I-R01M), marked as detector 1. Similarly, the reference beam was propagated through a reference optical path and then refocused onto another InGaAs detector (detector 2). To avoid notorious etalon fringes related to residual reflections, all fiber connections are either fusion-spliced or made with angle-polished FC/APC connectors. These measurements are performed after accurate purging of the cell to prevent interference from adsorbed–desorbed molecules at normal air pressure (1.01×10^5 Pa) and room temperature (296 K).

Figure 2**b** is the electronic schematic of CH_4 detection system based on WMS-2f technology. A modular laser controller (Newport Inc., model 500B) provides the working current of laser diode with ripple noise smaller than 1 μA (~1% duty factor), thus the frequency fluctuations of the laser line that are due to current noise can be neglected (<1 MHz). The laser wavelength is driven by a 10 Hz triangle ramp (generated by Agilent Inc., model 33120A) summed by an adder with a 10 kHz sine wave to provide the wavelength modulation. The sine signal is generated by a lock-in amplifier (Signal Recovery Inc., model 7265), and it is also the reference signal. The laser temperature was controlled to within 0.5 °C, near 20 °C by a thermoelectric current driver (Newport Inc., model 300B). The electrical signal from detector 1 was first subtracted by the electrical signal from detector 2, then the remainder was divided by the electrical signal from detector 2. The quotient signal was demodulated by lock-in amplifier to recover the 2f signal with a time constant of 20 μs and filter slope of 24 dB/oct, which leads a noise equivalent bandwidth of the low pass filter to be 26 Hz. The final demodulated signal from LIA is sent to a PC via the DAQ (data acquisition) card (National Instruments Inc., model PCI 6221).

It is also noted that by changing the modulation depth, the peak value varies. Using software simulation, we can find that the peak value of the 2nd harmonic is going through its maximum while the ratio of $\Delta\nu_m$ and $\Delta\nu_\nu$ is about 2.2, here $\Delta\nu_\nu$ is the half width at half maximum (HWHM) of the target spectral line. In the experiment, the optimal modulation index is set to 2.3, which is slightly higher than the theoretical value.

3. Results and discussion

Figures 3**a** to 3**d** show the experimental data and fitted line of 2f signals with different concentrations of methane (from 50 ppm to 200 ppm, diluted by N_2) under

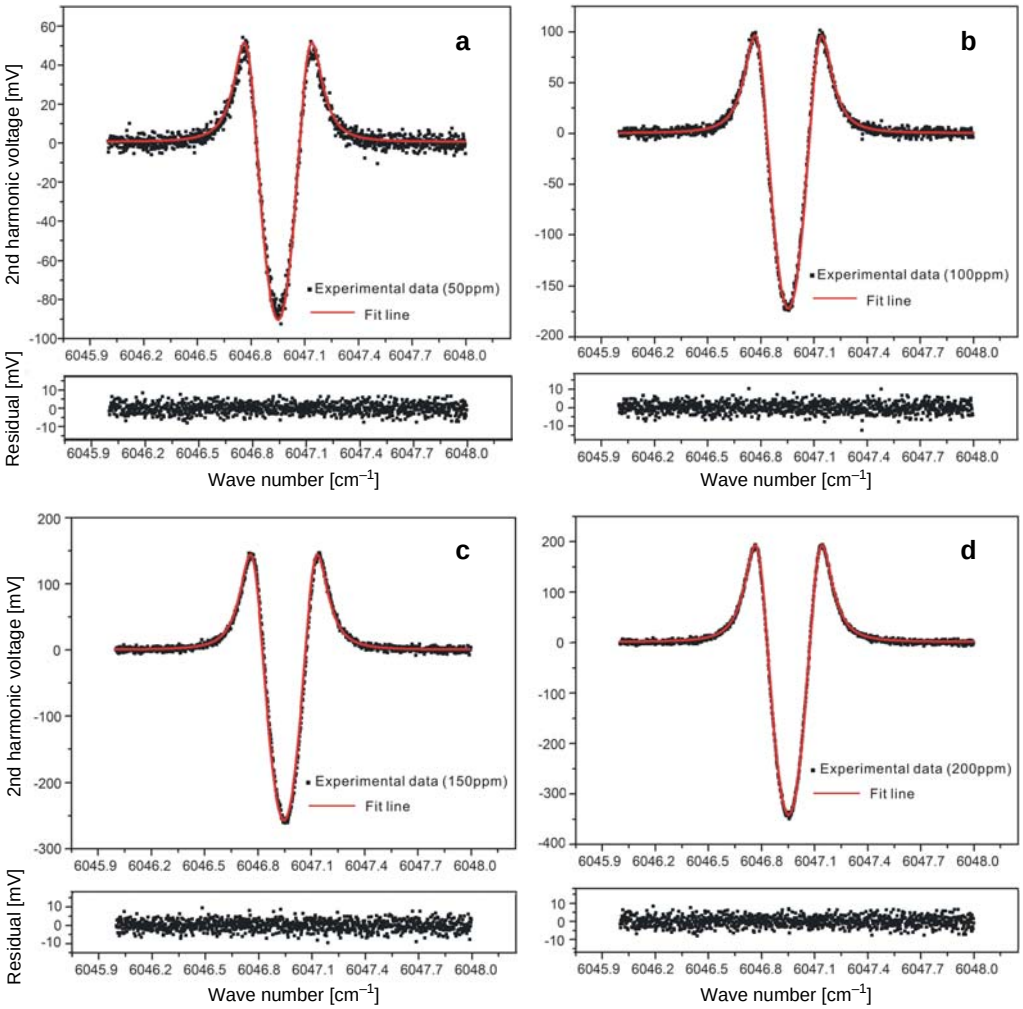

Fig. 3. Voltage of 2*f* signal (50 ppm – **a**, 100 ppm – **b**, 150 ppm – **c**, 200 ppm – **d**) near 6046.96 cm^{-1}.

experimental condition of 1.01×10^5 Pa and 296 K. The sub-panels of the figure show the residual noise. In fact, the residual noise is a system noise, which can neither be averaged out, nor attributed to the absorption feature itself. This noise is, hence, the limiting noise for gas detection. With a CH_4 concentration of 50 ppm, the noise signal shown in the sub-panel of Fig. 3**a** is about 2.82 mV and the peak value of 2*f* signal is about 85.475 mV, from which we inferred a SNR (signal-to-noise ratio) of 30.3. Similarly, the SNRs calculated from Figs. 3**b**, 3**c** and 3**d** are 59.8, 91.2, and 119.5, with the different CH_4 concentrations at 100, 150, and 200 ppm, respectively. Moreover, compared with the absorption spectrum, the peak of 2*f* signal has no offset regardless of the amplitude modulation of the laser output, which is in accordance with the result of novel signal processing.

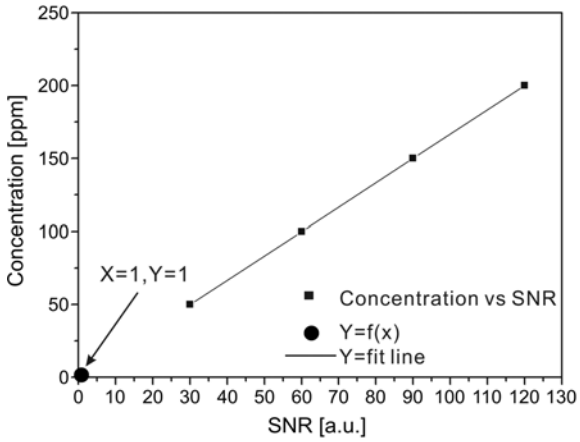

Fig. 4. SNR of 2*f* signal as a function of CH_4 concentration.

Figure 4 shows the SNR of 2*f* signal as a function of CH_4 concentration from 200 to 50 ppm reduced in steps. The solid line is the linear fit of the background-divided data, which shows a strong linear relationship between the SNR and the CH_4 concentration. When SNR is 1, one can clearly see that the ultimate sensitivity of the system is 1 ppm. Excellent stability and fast response (about 5 s) are also found based on the system in 30 days.

4. Conclusions

The demonstration of a novel CH_4 detection system based on WMS-2*f*, using tunable DFB diode laser in the near-infrared region is reported. The signal processing system of our detection system performs one subtraction and one division to extract the 2nd harmonic. The observed 2*f*-WMS spectra were analyzed as a function of the gas concentration. As can be seen in the experiment results, there is no observable distortion of the 2nd harmonic feature, neither the peak shift of the 2nd harmonic from absorption line center has been found. The lowest sensitivity down to 1 ppm is obtained through the lines scanning. The results suggest that the system is a good candidate for high performance sensing applications in the area of gas monitoring and detecting.

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