Fiber-distributed multi-channel open-path H_2S sensor based on tunable diode laser absorption spectroscopy

Dong Chen (陈 东), Wenqing Liu (刘文清), Yujun Zhang (张玉钧), Jianguo Liu (刘建国), Ruifeng Kan (阚瑞峰), Min Wang (王 敏), Xi Fang (方 曦), and Yiben Cui (崔益本)

Key Laboratory of Environmental Optics & Technology,
Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei 230031

Received October 11, 2006

Tunable diode laser based gas detectors are now being used in a wide variety of applications for safety and environmental interest. A fiber-distributed multi-channel open-path H_2S sensor based on tunable diode laser absorption spectroscopy (TDLAS) is developed, the laser used is a telecommunication near infrared distributed feed-back (DFB) tunable diode laser, combining with wavelength modulation spectroscopy technology, a detection limit of 20 ppm·m is demonstrated. Multi-channel detection is achieved by combining optical fiber technique. An on-board reference cell provides on-line sensor calibration and almost maintenance-free operation. The sensor is suitable for large area field H_2S monitoring application.

OCIS codes: 300.6260, 300.6340, 300.6380, 060.2370.

Hydrogen Sulfide (H_2S) is a highly toxic and flammable gas; it is generated as a common by-product of many industries[1]. Early detection of H_2S at concentration of l0 ppm in air is essential to prevent its toxic influence at higher concentration. Existing detection methods for H_2S rely mainly on non-optical point detectors such as electrochemical and semiconductor devices, while these traditional detectors have adequate low detection limit, they exhibit a cross sensitivity to other chemical species and a tendency to poisoning which are disadvantageous. In addition, a gas has to reach the detector's area (surface) at a concentration high enough to cause an alarm. Gas monitoring is achieved by installing a grid of many "point" type detectors, in a three-dimensional (3D) grid formation and correlating their signals, if monitoring over a large area is required, use of these monitors can be prohibitively expensive. During the last twenty years, the tunable diode laser absorption spectroscopy (TDLAS) technology has been intensively studied and has found broadly applications in the field of environmental monitoring, medical and industrial process[2−5]. Their characteristics like non-intrusive, high selectivity, high sensitivity, and fast response time make them more appealing than conventional point sensors for a reliable H_2S detection. A further advantage of near infrared (IR) TDLAS is its compatibility with optical fibers, this feature extends their potential use to distributed sensing, where many locations, remote from the laser source, can be monitored by one system.

In this letter, a fiber-distributed multi-channel open-path tunable diode laser system for H_2S detection is reported, a near IR InGaAs-InP distributed feed-back (DFB) diode laser emitting at 1.58 μm is used to probe a single absorption line in the $\nu_1 + \nu_2 + \nu_3$ combination band. The emission of diode laser is switched into eight fibers sequentially by an optical fiber switcher, enabling multiple path measurement with a single laser gas analyzer. Combining with wavelength modulation spectroscopy and second harmonic detection technology, the minimum detectivity that we achieved using this sensor is 20 ppm·m for H_2S.

Wavelength modulation spectroscopy is a useful trace gas detection technique. In wavelength modulation spectroscopy, the diode laser is modulated about its centre frequency (ν_c) by overlapping a high frequency (ω) sine waveform signal over the diode laser injecting current, the instantaneous laser frequency, $\nu(t)$, can be represented as

$$\nu(t) = \nu_c + m\delta\nu \cos\omega t, \tag{1}$$

where $\delta\nu$ is the half width at half maximum (HWHM) of the absorption line, m is wavelength modulation index. According to the Beer-Lambert law, the transmitted intensity of monochromatic radiation of frequency ν through optically thin absorption gas medium can be approximately expressed as

$$I(\nu) = I_0(\nu)[1 - \sigma(\nu)CL], \tag{2}$$

where $I_0(\nu)$ and $I(\nu)$ are the laser intensities before and after passing through the absorption medium, $\sigma(\nu)$ is the absorption cross-section of the gas at frequency ν, C is the concentration of the absorption gas, and L is the absorption optical path length. The transmitted laser intensity is a periodic even function, and can be expanded in a Fourier cosine series

$$I(\nu, t) = \sum_{n=0}^{n=+\infty} H_n(\nu_c) \cos n\omega t, \tag{3}$$

where $H_n(\nu_c)$ are the Fourier harmonic components. Neglecting the small amplitude modulation accompanying the wavelength modulation, the harmonic components can be expressed as $(n > 0)$

$$H_n(\nu_c) = \frac{I_0(\nu_c)}{\pi} \int_0^{\pi} [1 - \sigma(\nu_c + m\delta\nu\cos\theta)CL] \cos n\theta \mathrm{d}\theta. \tag{4}$$

1671-7694/2007/020121-04

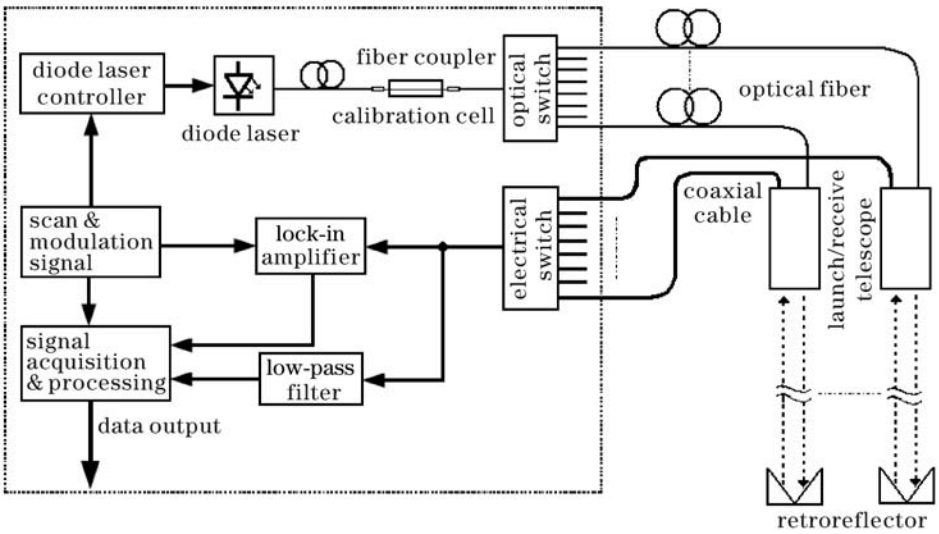

Fig. 1. Schematic of the multi-channel H_2S sensor.

Although each harmonic component is proportional to the gas concentration, the second harmonic component ($2f$) of the transmitted light intensity is generally used as detection signal[2−4]. A lock-in amplifier can be used to isolate the $2f$ signal, the demodulated $2f$ signal can be approximately expressed as

$$I_{2f} \propto I_0(\nu)\alpha(\nu)CL. \quad (5)$$

The near IR spectrum of H_2S has been the subject of many high resolution studies[6,7], the most strong absorption band lies in 1.6 μm region, this band actually composes of several overlapping combination and overtone bands, primarily is $\nu_1+\nu_2+\nu_3$ band which centered at 1.59 μm. This band can be readily accessible with telecommunication L-band DFB diode laser and recommended by many authors for gas sensing[7−9]. Figure 1 shows a schematic of the multi-channel fiber distributed open-path H_2S sensor based on the TDLAS. The system can be divided into two parts: central unit module and multi-channel open-path optics. The central unit contains the laser, laser temperature and current controller, signal generator, lock-in amplifier, multiplexing and data processing components. The optics consists of an integrated transmitter/receiver telescope and a remote, retro-reflector array for each detection channels. The maximum optical path length can extend up to 500 m. The diode laser employed for this study is a commercially available fiber pigtailed near-infrared DFB laser from NEL NTT Electronic Corporation. The laser output wavelength can be coarsely tuned by temperature controlling and fine tuned by injection current controlling. In order to achieve the expected sensitivity, a double modulation was applied to the laser diode. The laser wavelength is slowly scanned through the absorption line by a sawtooth waveform at frequency of 100 Hz and simultaneously modulated by a sinusoidal waveform at frequency of 10 kHz. The laser light is first fed into a 1:8 optical multiplexer and then sequentially switched on to 8 different optical paths with a scan cycle of 24 s. Fiber-optic cable carries the laser light to transmitter heads in the fields, which direct the beam along a path to a reflector. The return light is collected and focused onto a non-biased photo-detector housed in the telescope. The transmitter heads are therefore intrinsically safe. The photo current is returned to the central unit using coaxial cable. An 8:1 electrical multiplexer that operates synchronously with the optical multiplexer is used to coordinate the return electronic signals. The return electronic signal is then divided into two parts, one is sent to the lock-in amplifier to get the $2f$ absorption signal, and the other passing through a low-pass filter and linearly fitted to obtain a caliber for the laser intensity, the detected signal was then normalized by the fitted laser intensity to eliminate the influence of the laser intensity fluctuation arriving at the detector[10]. The normalized $2f$ signal is coadded and averaged for 100 times to give a measurement absorption spectrum.

The calibration of the system is achieved through an on-board 10-cm long calibration gas cell filled with standard high concentration H_2S sample gas in the optical beam path. The absorption signal generated by the calibration cell is additive to the field absorption signal. For the species of interest, the measured path-integrated concentration will increase by an amount proportional to the concentration of the gas contained in the calibration cell. The response calibration factors for individual species are set through comparison of the actual and expected concentration changes with the calibration cell in place. The calibration factors for the instrument are optimized in the laboratory and verified in the field.

The diode laser used here has a nominal operating wavelength of 1575.4 nm and can be temperature tuned nearly 6 nm. Figure 2 shows the high-resolution absorption spectrum of H_2S at atmospheric pressure in the wavelength region of 1573.2—1578.7 nm obtained by wavelength modulation spectroscopy, the spectrum is recorded by a simplified single-pass optical setup using a 10-cm absorption cell filled with 5% standard H_2S sample buffered by nitrogen gas. There are several relatively strong absorption lines of H_2S within the tuning range of the diode laser of which the line at 1576.3 nm is the best choice for the study.

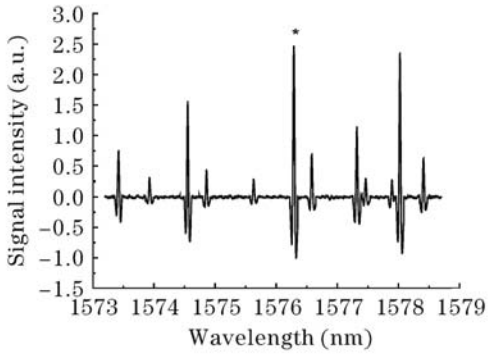

Fig. 2. High-resolution absorption spectrum of H_2S in the wavelength region of 1573.2—1578.7 nm.

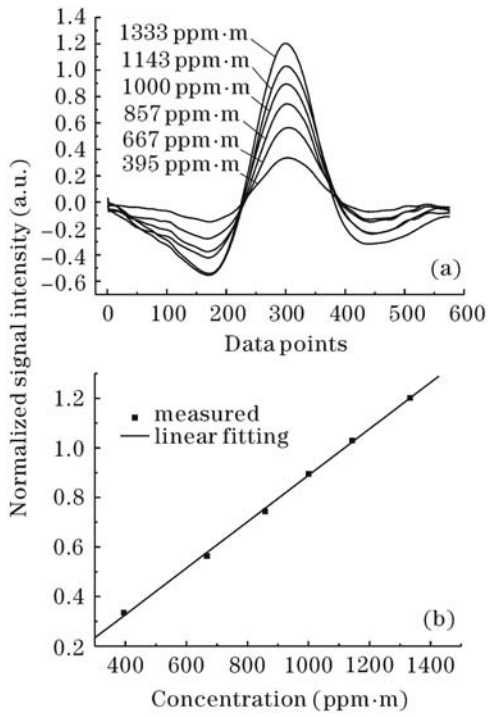

Fig. 3. (a) Normalized second harmonic signals of H_2S at different concentrations and (b) the linear relation between the measured and expected concentration values.

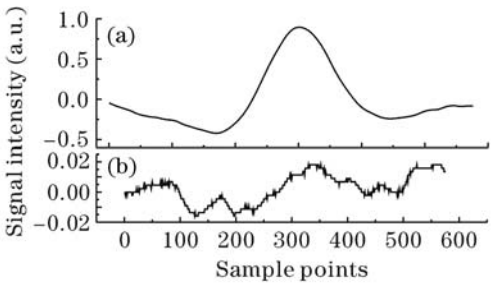

Fig. 4. (a) Normalized second harmonic signal of H_2S at concentration of 1000 ppm·m and (b) corresponding noise signal.

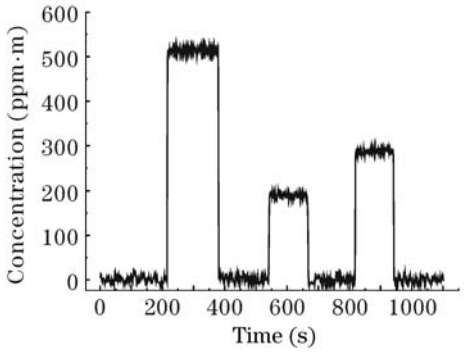

Fig. 5. Measured gas concentrations for different H_2S gas samples.

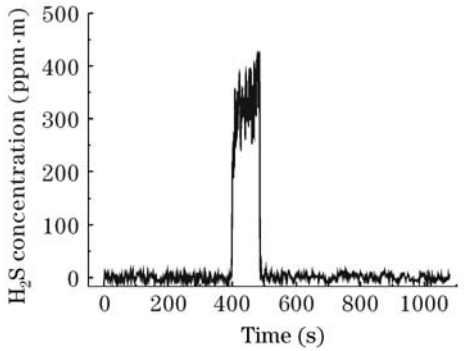

Fig. 6. Simulated gas leakage detection by the tunable diode laser based H_2S sensor.

The system performance was test by insertion a 10-cm reference cell flushed with standard H_2S gas sample; the $2f$ signals were normalized by the fitted light intensity to eliminate the influence of laser intensity fluctuation through detection region. Figure 3 shows the normalized $2f$ signals at different H_2S gas concentrations and the fitted linear relation between the measured and expected H_2S concentrations. The good linear character shows the bright promise for the field use of the laser based H_2S sensor.

Because H_2S is affinity for water vapor and tends to adsorb onto the gas cell surface, it is difficulty for accurately calibrating of low H_2S concentration levels when admitted to the gas sample cell. So the system detection limit was not directly measured, but extrapolated from the magnitude of the absorption signal obtained with a known high concentration and the corresponding signal noise ratio (SNR). Figure 4 shows the absorption $2f$ signal of H_2S with a path integrated concentration of 1000 ppm·m and the corresponding noise level; the calculated SNR is approximate 50. Hence the system minimum detection limit can be calculated to be 20 ppm·m. Therefore, only a path length of 2 m is needed to provide the 10-ppm detection sensitivity. Figure 5 shows the measured H_2S concentrations when flushed the reference cell with different standard H_2S gas samples.

To demonstrate the time response of the system, a simulated gas leakage measurement was conducted in an open area. The optical path length is 20 m. A cylinder containing 1% H_2S was attached to a hand-held welder's nozzle. The nozzle is mounted 30 cm below the optical path and flow rate is set at 1 L/min. Figure 6 shows the measurement results of the simulated gas leakage by the diode laser based H_2S sensor. The figure shows the immediate response of the system, which is important for safe alarming gas sensing.

In summary, detectors based on TDLAS have many advantages over established gas detection techniques in process, quality, safety and environmental monitoring. They are not prone to poisoning and do not suffer from

interferences. They provide fast response and can measure a wide range of concentration values. In this letter, a fiber-distributed multi-channel open-path H_2S sensor based on tunable diode laser absorption spectroscopy is reported, a telecommunication near IR InGaAs-InP DFB tunable diode laser is used to detect a single rovibrational line around 1576.3 nm, the detection limit of 20 ppm·m is achieved through wavelength modulation spectroscopy combining with second harmonic signal detection, eight optical paths measurement by one system is realized through optical fiber switcher technology. This sensor is ideally suitable for large scale field trace gas detection in petrochemical industry for safety and environmental monitoring.

This work was supported by the National Natural Science Foundation of China (No. 50534050), and the Funds of the Chinese Academy of Sciences for Key Topics in Innovation Engineering (No. KJCX2-SW-W27). D. Chen's e-mail is chendong@aiofm.ac.cn.

References

1. N. S. Lawrence, J. Davis, and R. G. Compton, Talanta **52,** 771 (2000).
2. P. Werle, F. Slemr, K. Maurer, R. Kormann, R. Mücke, and B. Jänker, Optics and Lasers in Engineering **37,** 101 (2002).
3. M. Wang, Y. Zhang, J. Liu, W. Liu, R. Kan, T. Wang, D. Chen, J. Chen, X. Wang, H. Xia, and X. Fang, Chin. Opt. Lett. **4,** 363 (2006).
4. R. Kan, W. Liu, Y. Zhang, J. Liu, F. Dong, M. Wang, S. Gao, and D. Chen, Acta Opt. Sin. (in Chinese) **26,** 67 (2006).
5. R. Kormann, H. Fischer, C. Gurk, F. Helleis, Th. Klüpfel, K. Kowalski, R. Königstedt, U. Parchatka, and V. Wagner, Spectrochimica Acta Part A **58,** 2489 (2002).
6. I. Meusel, B. Sumpf, and H.-D. Kronfeldt, J. Mol. Spectrosc. **185,** 370 (1997).
7. L. Lechuga-fossat, J.-M. Flaud, and C. Camy-peyret, Mol. Phys. **61,** 23 (1987).
8. L. R. Brown, O. V. Naumenko, E. R. Polovtseva, and L. N. Sinitsa, Proc. SPIE **5311,** 59 (2004).
9. J. O'Gorman, V. Weldon, D. McDonald, J. J. Perez-Camacho, B. Corbett, and J. Hegarty, Proc. SPIE **3105,** 301 (1997).
10. R. Kan, F. Dong, Y. Zhang, J. Liu, C. Liu, M. Wang, S. Gao, and J. Chen, Chin. Phys. **14,** 1904 (2005).