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Research note

Field detection of CO and CH_4 by NIR 2f modulation laser spectroscopy

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Abstract

A novel compact fiber-coupled NIR system based on a DFB diode laser source is employed as a portable and sensitive gas sensor for trace detection of combustion pollutant molecules. We demonstrate the performance of such an NIR gas sensor by tracing the absorption lines of CO and CH_4 using 2f-WMS technique at moderate temperature of $T \sim 600°C$ in the recuperator channel of an industrial furnace provided by Mobarakeh steel company. This measurement shows the excellent sensitivity of the applied NIR gas sensor to the on-line and in-situ monitoring of such molecular species.

Keywords: wavelength modulation spectroscopy, NIR gas sensor, DFB tunable laser

1. Introduction

Laser spectroscopy is a very efficient technique for measuring molecular pollutants because it is promising for sensitive and selective gas tracing in the infrared spectral region [1]. It is also capable of on-line and in-situ applications in harsh industrial environments [2]. Such applications require tunable as well as narrow linewidth laser sources. Recent developments in MIR laser sources radiating between 3 and 10 microns make those applications even more interesting because nearly all molecules have characteristic absorption band within this fingerprint region [3]. Quantum cascade (QC) laser and Quantum cascade distributed-feed-back laser diodes (QC-DFB) [4, 5] are very promising sources in terms of high spectral purity and wide tuneability**.** The main drawback of QC lasers is that they are still not applicable at room-temperature. Although DFG lasers operate under room-temperature condition, they suffer from low conversion efficiency and setup sensitivity and complexity. However, a compact and wide tunable MIR-DFG spectrometer based on fiber optic sensor as probe is applied to environmental gas monitoring [6, 7]. In contrast, tunable diode laser (TDL) absorption spectroscopy based on overtone excitation of ro-vibrational transitions of various important gases like CO and CH_4 in the near-infrared (NIR) spectral region between 1.5 and 2.5 microns provides a non-intrusive, fast and sensitive technique [8-12].

Diode lasers are known to be efficient and compact. Their comparably low fabrication costs and their compatibility with fiber waveguides offer direct measurement for diagnostics of absorptive species and hence for real-time control of combustion [13-15]. The most common laser sources in the NIR region are found in a spatially periodic modulation structure of the refractive index in the gain medium to form distributed feedback (DFB) lasers [16]. They have been grown at wavelengths as short as 760 nm and are commercially available in InGaAsP devices up to 2 μm and even further. They can be temperature tuned over 3–5 nm around their center wavelength. The long interaction length of the DFB grating provides very narrow linewidth in the order of 10 MHz which is quite responsible for high resolution spectroscopy.

In the case of NIR laser absorption spectroscopy when the concentration of the gas is so weak, wavelength modulation spectroscopy (WMS) can be employed with higher order harmonic detection to improve the absorption sensitivity and accuracy [17]. This technique shifts the detection band to high-frequency region where the $1/f$ laser noise is avoided. WMS can usually be performed in kHz frequencies with conventional lock-in amplifiers used for signal detection. The sensitivity can be significantly improved when the laser is modulated in MHz frequencies [18]. However, depending on the gas concentration and required

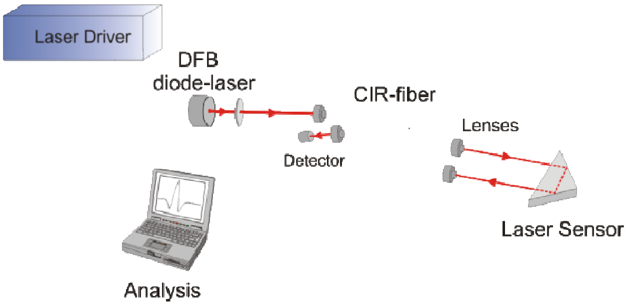

Figure 1. Experimental setup of NIR spectrometer with the components of fiber coupled sensor devices.

sensitivity of measurement it can be further increased to GHz ranges. The choice of the frequency of modulation which usually ranges from kHz to MHz strongly depends on the absorption linewidth and limits with the detector bandwidth [18, 19]. The sensitive detection can be performed at modulation frequency or second harmonic (2f) of the modulated signal. In this paper, we develop a compact and automated fiber-coupled NIR system based on DFB diode laser source and WMS technique for CO and CH_4 detection in harsh industrial environment provided by Mobarakeh steel complex (MSC) located in Isfahan, Iran. The experiment was performed in the λ = 2.3 µm band with a ceramic open path probe as gas sensor which was designed for high temperature operation. Before being used in combustion experiments, the system is validated in a laboratory room-temperature absorption cell filled with pure CO and natural CH_4 gas.

2. An introduction to WMS basics

Absorption spectroscopy is based on the Lambert-Beer's law which can be written for weak absorption lines in the following form

$$I(\nu) = I_0(\nu)\left[1-\alpha(\nu)L\right], \qquad (1)$$

where $\alpha(\nu)$ denotes the frequency dependent absorption coefficient of the medium. To enable TDL at harmonic signals (e.g. 2f signal), a sinusoidal modulation of frequency is directly superimposed upon the diode laser current and the diode laser frequency will be changed during the time as

$$\nu(t) = \bar{\nu} + \beta\cos\omega t\,, \qquad (2)$$

where mean frequency $\bar{\nu}$ is the unmodulated laser frequency and β is the modulation index while ω is the frequency of modulation. The treatment of WMS follows the definition of dimensionless parameters x and m in terms of absorption half-width, $\Delta\nu_{1/2}$ of the desired absorption molecule as

$$x = \frac{\nu-\nu_0}{\Delta\nu_{1/2}},$$

$$m = \frac{\beta}{\Delta\nu_{1/2}}. \qquad (3)$$

Therefore the absorption coefficient is modulated in the following form

$$\alpha(x,m) = \frac{1}{1+(x+m\cos\omega t)}. \qquad (4)$$

The best performance of WMS is characterized for $x \ll 1$ and the optimum 2f signal is obtained for a value of $m = 2.2$ [12].

3. Fiber coupled NIR laser spectrometer as gas sensor

The schematic setup of the NIR spectrometer is shown in figure 1.

The spectrometer consists of three dependent parts: laser source, laser sensor and the detection system. The laser source is provided by a DFB continuous wave single mode laser (nanoplus GmbH) operating at center wavelength of 2.33 µm with the maximum output power of 3 mW. Its wavelength can be tuned over the overtone ro-vibrational absorption lines of CO molecule at the tuning rate of 0.02 (nm/mA) and of 0.2 (nm/K). The typical linestrength of these overtone band are in the order of ~ 10^{-21} cm^{-1}/(molecule.cm^{-2}) [3] which provides a very weak signal at low concentration levels. This laser can also be used to detect a rotational line of CH_4 centered within the emission band of the applied laser. The laser radiation is then coupled into a chalcogenid infrared (CIR) fibers to make one-or multi-pass absorption probe together with a 45° sapphier prisms. The probe was made of ceramic arms and a platinum plate to stand at elevated temperatures (e.g. at T = 1500°C) and to fix the reflecting prisms.

Three sapphier prisms are located at two ends of the probe to increase the absorption path length up to about 60 cm. The absorbed light is then imaged on a high speed FGA20 InGaAs (Thorlabs GmbH) photodiode with the spectral response from 1200 to 2600 nm and maximum spectral responsivity at 2.2 µm provided by the manufacturer. A special window was programmed and designed in the LabView software to record the absorbed signal and to adjust and control the required parameters of the laser and electronics directly on the screen of a laptop.

The system enable for either direct measurement of absorptive spices by periodically chopping the laser beam at several kHz or by 2f detection which were recordable by a lock-in amplifier and associated circuits.

4. CO tracing

Fig.2. shows the spectral lineshape of the CO rotational line at 4291.4994 cm^{-1} [linestrength: 3.074×10^{-21} cm^{-1}/(molecule.cm^{-2})] [3] as measured in a 10 cm single pass absorption cell at room temperature. The measurement is performed for either direct measurement or 2f measurement by using WMS technique.

The 2f spectrum is obtained by ramping the laser current at a frequency of several hertz and the sinusoidal modulation at a frequency of about 30 kHz which was imposed on the voltage ramp signal for 2f measurement.

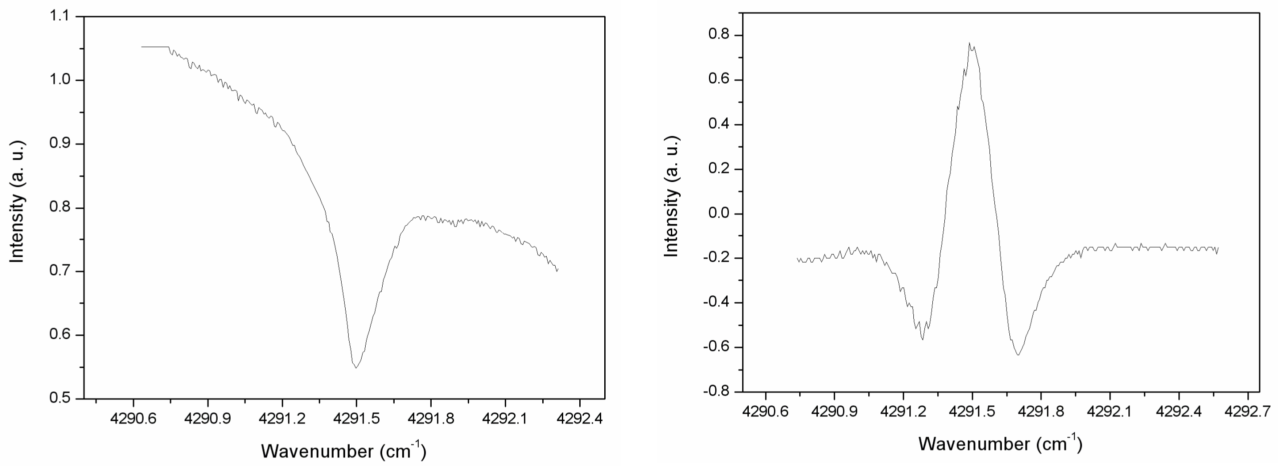

Figure 2. Direct measurement (top) and 2f signal (bottom) of CO absorption line at 4291.4994 cm^{-1} for p_{CO}=50 mbar in a 10 cm absorption cell and room-temperature condition. The wavenumber axes are arbitrarliy scaled.

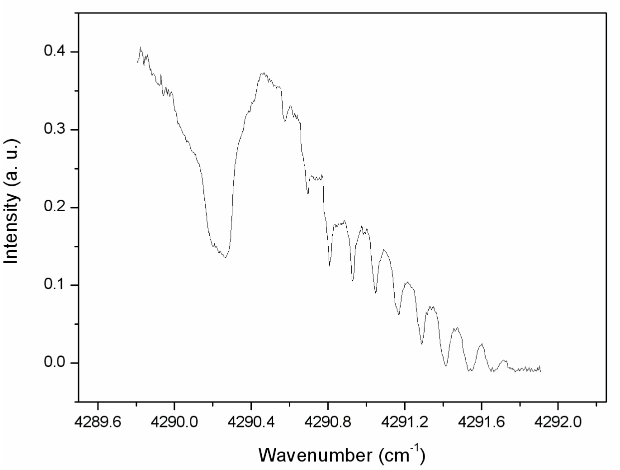

Figure 3. Absorption spectra of the CH_4 rotational line at 4290.2307 cm^{-1} detected in an open laboratory cell at atmospheric pressure. The wavenumber axis is arbitrarily scaled. The obtrusive peaks are interferometric patterns which are formed by the absorption cell.

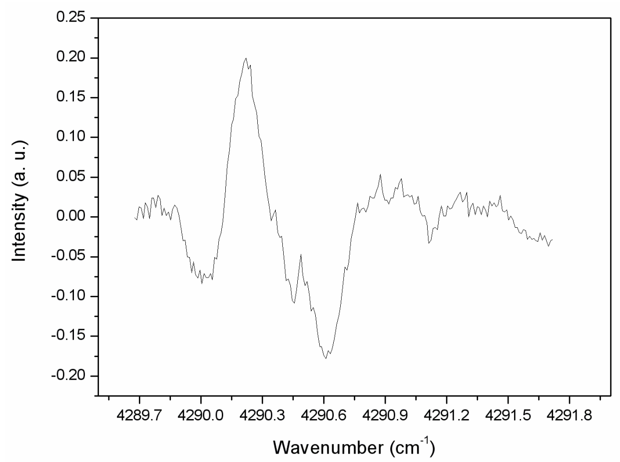

Figure 4. WMS-2f spectra of the CH_4 rotational line at 4290.2307 cm^{-1} detected in an open laboratory cell at atmospheric pressure. The wavenumber axis is arbitrarily scaled.

5. CH_4 tracing

To indicate the further performance of the system and the fabricated ceramic probe, CH_4 rotational line at 4290.2307cm^{-1} [linestrength: 1.409×10^{-21}cm^{-1}/(molecule.cm^{-2})] [3] was also measured in the atmospheric pressure when a gas was flowed in an open laboratory cell. The detected CH_4 absorption line is shown in figure 3.

The same measurement is performed for WMS-2f detection of CH_4 in the same open cell under similar condition. The result is shown in figure 4.

As shown, the results confirm the utility and ability of the built fiber-coupled NIR gas sensor for the tracing of molecular species such as CO and CH_4 in a normal laboratory situation.

6. Field detection of CO and CH_4

Isfahan is an industrial city. Most of the mother industries such as Mobarakeh steel company and power plants factory are placed in the suburbs of Isfahan. They are using huge gas-fired furnaces at elevated temperatures e.g. T = 1500-2500^{o}C. They are the major sources of pollutants and therefore the possibility of in-situ combustion diagnostics using NIR laser absorption spectroscopy offers several advantages over conventional chemical analysis in terms of less susceptibility to handling errors and delays. Mobarakeh steel company was chosen for the application of the fiber-coupled NIR system in an industrial environment. The experiment was performed in the atmosphere of the industrial natural gas-fired furnace where the iron bars were pre-heated up to 1500°C for rolling process. The CO measurement in their combustion provides many advantages to optimize the combustion process and to avoid the formation of the toxic gases. On the other hand, annually, the company spends a huge budget for natural CH_4 gas preparing and therefore sensitive measurement of unburned CH_4 in their combustion leads to saving a huge amount of energy and money. During the measurement the system was placed in an air-cooled aluminum box (50×70×90 cm) to protect the system from the hot surrounding atmosphere (T~ 40°C) on the factory roof beside the recuperator channel of the furnace.

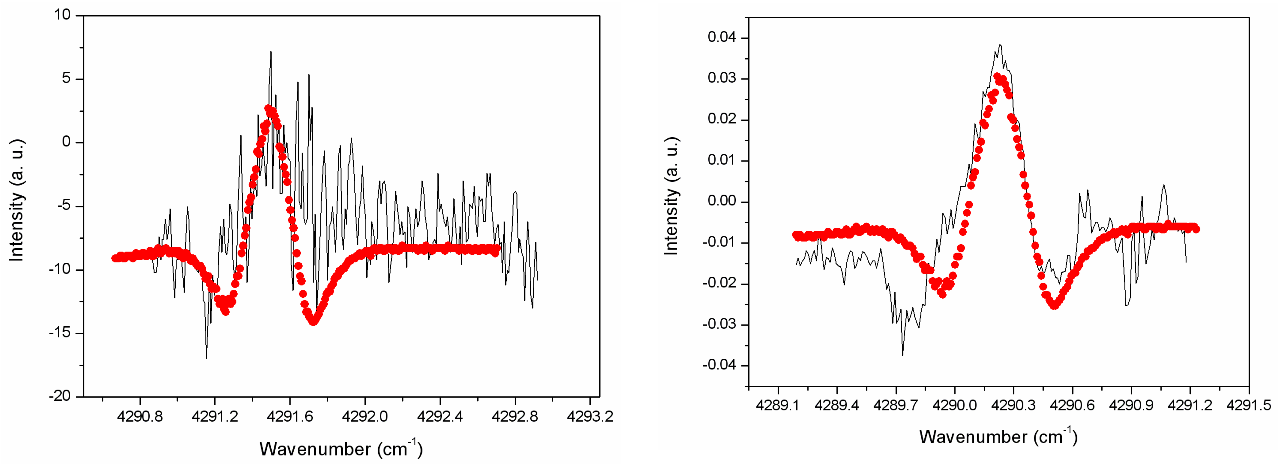

Figure 5. 2f-WMS absorption spectra of the CO rotational line at 4291.4994 cm^{-1} recorded with the ceramic open pass probe in the recuperator channel of the pre-heated furnace (top) and cold-rolling mill (bottom) located at Mobarakeh steel company. Dots: 2f signal of detected CO in the reference cell, solid line: 2f signal of detected CO in the channel. The wavenumber axes are arbitrarily scaled.

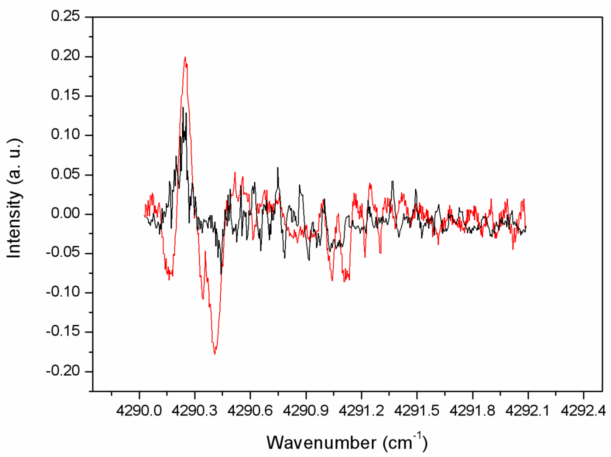

Figure 6. 2f-WMS absorption spectra of the CH_4 rotational line at 4290.2307 cm^{-1} recorded with the ceramic open pass probe in the recuperator channel of the pre-heated furnace located at Mobarakeh steel company. Red line: 2f signal of detected CH_4 in the reference cell, black line: 2f signal of detected CH_4 in the channel of the furnace. The wavenumber axis is arbitrarily scaled.

The temperature inside, the box was stabilized at approximately T~18°C which enabled the diode laser temperature to be set between T~(26±0.01)°C and T~(22±0.01)°C as necessary for CO and CH_4 detection, respectively. The temperature inside the channel was measured T~600°C automatically. The probe ceramic sensor was placed into a predicted cavity on the stack of the furnace and the diode laser was scanned over the absorption line of the CO and CH_4 by fixing the temperature of the DFB diode laser at the desired points. Figure 5 illustrates the 2f-WMS result for the CO absorption line as detected in the recuperator channel of the pre-heated furnace.

In figure 6, the 2f-WMS signal of the detected CH_4 absorption line in the atmosphere of the pre-heated furnace is depicted.

7. Conclusion

Tunable diode laser (TDL) based on fiber-coupled open path probe in the NIR spectral region provides a non-intrusive, fast, and sensitive method for reliable detection of combustion-generated species such as CO and CH_4**.** Our results indicate that the measurement of such pollutant molecular species in harsh industrial environment is promising for absorption spectroscopy in the NIR region. Even though the absorption lines of the most molecular species in the NIR are so weak, the WMS technique can be applied to increase the sensitivity of the detection process. Compared to other conventional gas sensor technology, fiber-coupled NIR spectrometer application offers many economic and ecological benefits because of its potential for monitoring gas formations nonintrusively and on-line, and therefore this technique can be applied for industrial process control.

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