

Article Simultaneous Detection of CO₂ and CH₄ Using a DFB Diode Laser-Based Absorption Spectrometer

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Abstract: In this paper, an attractive gas sensing technique based on fiber optical sensing ideal was developed for the detection of multi-gas species simultaneously. Calibration-free laser absorption spectroscopy (LAS) was used and combined with a multi-pass optical absorption cell, two fiber-coupled near-infrared (NIR) distributed feedback (DFB) diode lasers are used and coupled into a single optical path for measuring CO_2 and CH_4 absorption spectra simultaneously. The optimal sampling pressure, laser tuning characteristics, spectral sampling points, and potential optical interference are theoretically and experimentally investigated in detail. The results indicated that the proposed technique has good reliability and has been successfully demonstrated for ambient CO_2 and CH_4 detection by using a single sample cell and detector. An Allan–Werle deviation analysis shows that detection limits of 0.12 ppm for CH_4 and 35.97 ppm for CO_2 can be obtained with an integration time of 181 s and 166 s, respectively. The proposed technique can be expanded to measure more molecules simultaneously by combing laser array and may pave a new way for developing a low-cost and ultra-compact multi-gas laser spectroscopy sensing system.

Keywords: laser absorption spectroscopy; calibration-free; multi-gas detection; CO₂; CH₄

1. Introduction

Laser spectroscopy gas sensing technique plays a key role in various fields such as climate warming, Mars exploration, ocean exploration, bio-medical diagnosis, etc. [1–4]. With the continuous deterioration of global environmental ecology and energy problems, the ability to analyze multiple substances or even unknown components has been a highly technical challenge for developing optical gas sensors, considering the limitations of system volume, weight, power consumption, and cost. Mid-infrared (MIR) external cavity quantum cascade lasers (ECQCLs) are widely attractive for spectroscopic applications, which can be used for simultaneously measuring more than three gas components [5], but they are still not universal due to their high cost. With the development of optical communication technology, near-infrared lasers have been developed more maturely, especially for distributed feedback (DFB) diode lasers, which have been demonstrated for most atmospheric molecules by combing with various spectroscopy techniques, such as direct absorption spectroscopy (DAS), wavelength modulation spectroscopy (WMS), photoacoustic spectroscopy (PAS), off-axis integrated-cavity output spectroscopy (OA-ICOS), cavity ring-down spectroscopy (CRDS), or cavity-enhanced absorption spectroscopy (CEAS) [6–13].

In the case of multi-component analysis, a single broadband laser source or multi-laser array is usually adopted to cover the fingerprint spectral region of interest by combing with multiple photoelectric detectors and the time division multiplexing (TDM) or frequencydivision multiplexing (FDM) technique [14,15]. For example, a single quartz crystal tuning fork (QCTF) detector and multiple diode lasers near 1391, 1574, and 1653 nm based compact multi-gas sensor system was developed for the simultaneous detection of H₂O, CO₂, and



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CH₄, respectively, by Xu et al. [16]. Quartz-enhanced photoacoustic spectroscopy (QEPAS) sensor was reported by Wu et al. for detecting CH₄ and H₂O simultaneously with the FDM technique [17]. Jin et al. reported a robust FDM-based optical sensor for remote multi-species (CH₄ and C₂H₂) detection [18]. By combing the FDM technique with WMS and OA-ICOS techniques, a dual-gas NIR sensor was developed for sensing C₂H₂ and CH₄ molecules simultaneously [19]. As for the TDM detection technique, a TDM-based multi-gas sensor system was developed by combing a single broadband light source and multiple CO, CO₂, and CH₄ pyroelectric detectors by Dong et al. [20]. A multi-channel fiber surface plasmon resonance sensor was proposed by Liu et al. by using the multi-core fiber and TDM technique [21]. Moreover, a hybrid multi-component gas sensing system integrated with NIR diode laser and MIR quantum cascade laser (QCL) was most recently reported for atmospheric CO, N₂O, and CH₄ detection by Liu et al. [22]. Even though, atmospheric trace gases can also be detected by measuring the absorption spectroscopy in either NIR or MIR spectral bands. To meet all the requirements on cost, size, and power permissibility for field applications, the NIR spectral gas sensors are preferred.

However, the FDM technique is commonly combined with the WMS detection method because of the dependence of WMS on light intensity variation, which requires frequent corrections to ensure accuracy for real-time measurement applications [23]. Obviously, the TDM-based multi-laser array technique has one of the disadvantages of decreasing time resolution, while the simultaneous usage of multiple detectors or gas cells and other additional devices makes the gas sensor system more complicated. To resolve these issues mentioned above, a novel gas detection technique based on fiber optical sensing ideal and calibration-free DAS spectroscopy analysis technique is proposed for the detection of multicomponent gas molecules simultaneously. To explore the characteristics of the proposed gas detection technique, two fiber-coupled NIR DFB diode lasers emitting near 1574 nm and 1653 nm, respectively, are used and coupled into a single optical path for simultaneously measuring CO_2 and CH_4 absorption spectra. The optimal sampling pressure, laser tuning characteristics, spectral sampling points, and potential optical interference are theoretically and experimentally investigated in detail. Finally, the developed sensor system is evaluated for ambient atmospheric measurement.

2. Theory Analysis

2.1. Absorption Spectroscopy Theory

The interaction between light and gas medium can be described by the well-known Lambert–Beer law, which is suitable for all electromagnetic radiation and absorbing medium, including gases, solids, liquids, molecules, atoms, and ions. Assuming a laser beam has a wavelength of λ and a light intensity of I_0 , and after passing through a homogeneous medium, the output light intensity is *I*. The change of the light intensity after passing through the medium will satisfy the Beer–Lambert law

$$I(\lambda) = I_0(\lambda)e^{-\alpha(\lambda)L}$$
(1)

when it passes through a non-uniform gaseous medium, in addition to the absorption process of the interaction between light and matter, the change in light intensity will also be affected by other factors, such as scattering effects and instrument response characteristics, so the generalized Beer–Lambert law can be expressed as:

$$I(\lambda) = I_0(\lambda) e^{[-\alpha(\lambda)L + \beta(\lambda)L + \gamma L + \delta]A(\lambda)}$$
(2)

where $I(\lambda)$ and $I_0(\lambda)$ are the transmitted and initial light intensity, $\beta(\lambda)$ and γ are the Rayleigh scattering coefficient and Mie scattering coefficient, respectively, δ is the influencing factor of other effects, and $A(\lambda)$ is the response function of the instrument. Since the main medium studied in this paper is a gas molecule, the gas molecule can default to a uniform medium, so the interaction process between light and gas molecules is mainly absorption. The absorption coefficient $\alpha(\lambda)$ of gas molecules is related to the absorption line-

shape, line strength, and molecular number of molecules, and the absorption of individual lines can be expressed as:

$$\alpha(\lambda) = \phi(\lambda - \lambda_0) \cdot S(T) \cdot N(T, P)$$
(3)

where S(T) is the molecular absorption line strength, N(T, P) is the molecular number density, $\phi(\lambda - \lambda_0)$ is an absorption line type centered on wavelength λ_0 , and usually satisfies the normalization condition as follows:

$$\int_{-\infty}^{\infty} \phi(\lambda - \lambda_0) d\lambda = 1 \tag{4}$$

The number density of molecules is a function of temperature *T* and pressure *p*, which can be expressed as:

$$N(T,P) = \frac{P}{P_0} \cdot N_0 \cdot \frac{T_{ref}}{T}$$
(5)

where $N_0 = 2.6875 \times 10^{19} \text{ (mol/cm}^3)$ is the molecular density of an ideal gas at a reference temperature $T_{ref} = 296 \text{ K}$ and a reference pressure $P_0 = 1$ atm. The strength of the molecular absorption process is usually measured by the absorption coefficient of the molecule and the product of the absorption path, that is, the absorption depth $\alpha(\lambda)L$. In summary, the integral area of a single absorption line of a molecule can be expressed as:

$$A = \int_{-\infty}^{\infty} \alpha(\lambda) L dv = \int_{-\infty}^{\infty} \phi(\lambda - \lambda_0) \cdot S(T) \cdot N(T, P) \cdot L dv$$
(6)

since the lineshape function satisfies the normalization condition, thus *A* can be simplified into:

$$A = S \cdot N \cdot L \tag{7}$$

Once the relevant experimental conditions (such as temperature, pressure, optical path, and spectral line parameters) are known, the number or concentration of the absorbing molecule is calculated by measuring the integral absorption area of the molecule, i.e., Equation (7). Conversely, the spectral line parameters of the interested molecule (e.g., line strength) can also be calculated.

2.2. Detection Principle

The illustration of three different detection schemes is presented and compared in Figure 1 in the time domain. The main principle of the multi-gas TDLAS sensor system based on the traditional time division multiplexing (TDM) technique is that different gas molecules are measured by driving each laser source successively, this approach presents a significant time lag in the time domain, as shown in Figure 1a. In the case of a frequency division multiplexing (FDM) detection scheme (Figure 1b), the key principle is combing modulation and demodulation techniques with a different frequency to realize signal separation, i.e., WMS detection, which deprives the most critical advantage of calibration-free nature. For these issues mentioned above, a new detection scheme was proposed for calibration-free detection of multi-gas species without any time lag in this study. The proposed detection scheme (Figure 1c) is based on calibration-free direct absorption spectroscopy and an effective combination of pressure broadening effect, laser tuning characteristics, and data acquisition mode. The fast current tuning characteristics and wide tuning range of diode lasers enable simultaneous measurement of multiple absorption peaks. Generally, the atmospheric small molecular absorption profile can be fully recovered using data sampling points less than 10³. Obviously, as the sampling pressure decreases, the absorption profile will be narrower, the fewer sampling points are needed. Note that it is meaningless to record too much non-absorptive baseline background in the absorption spectrum. Moreover, the fewer sampling data points, the better for improving measurement time resolution. Due to the relatively high concentration of water vapor (H₂O) in ambient and strong NIR absorption characteristics (i.e., absorption saturation effect), H₂O detection is not experimentally demonstrated for the developed long path gas cell-based TDLAS sensor system. More details of theoretical simulation and experimental investigation will be described in the next section.



Figure 1. Illustration of different detection schemes: (**a**) Traditional TDM, (**b**) Traditional FDM, (**c**) The proposed detection scheme in this work.

3. Experimental Details

3.1. Absorption Line Selection

Atmospheric carbon dioxide (CO₂) and methane (CH₄) are two very important greenhouse gases, which play a key role in global warming and climate change. Therefore, the multi-gas sensing system was evaluated for simultaneous measuring CH₄ and CO₂ using a single photoelectric detector. Figure 2 shows the simulated absorption spectral line intensity (@296 K) of each molecule in the NIR spectral region (between 1 μ m and 2.5 μ m) based on the HITRAN database. For this mission, two NIR DFB diode lasers with a center wavelength near 1574 and 1653 nm are selected as excitation light sources, respectively. Table 1 summarizes the spectral parameters of the selected CH₄ and CO₂ molecular selection lines.

Species	Wavelength (nm)	Wavenumber (cm ⁻¹)	Line Intensity (cm/mol.)	γ_{air} (cm $^{-1}$ ·air $^{-1}$)	γ_{self} (cm $^{-1}$ ·air $^{-1}$)
CO ₂	1574.03395	6353.10312	1.122×10^{-23}	0.0822	0.112
CH_4	1653.72254 1653.72582 1653.7283	6046.96359 6046.9516 6046.9425	$\begin{array}{c} 1.455 \times 10^{-21} \\ 9.277 \times 10^{-22} \\ 7.877 \times 10^{-22} \end{array}$	0.0578 0.0774 0.0651	0.079



Figure 2. Spectral characteristic simulation of CH₄ and CO₂ based on HITRAN database.

3.2. DFB Diode Laser Characteristics

In general, the emitting wavelength of a diode laser can be tuned by scanning its operating temperature or driving current. For precisely controlling the laser wavelength and achieving coverage of the absorption spectra of the two analytes of interest, the characteristics of the two DFB lasers selected in this study were initially investigated. In this work, the relationship between the laser wavelength and driving voltage is recorded with a high-precision wavelength meter (HighFinesse GmbH, Tubingen, Germany, WS6-200) at a fixed operating temperature, as shown in Figure 3. According to the calibrated results, the operating temperature of the laser was determined at 30 °C, and the absorption line near 1574.03 nm for CO_2 and the absorption line near 1653.72 nm for CH_4 were finally selected, respectively.



Figure 3. Wavelength tuning characteristic of the diode laser as a function of its operating temperature and driving voltage.

3.3. Sensor Platform Design and Data Processing

The configuration of the developed multi-gas sensor system is shown in Figure 4, which mainly consists of the following parts: optical module, system control, and data acquisition units. In the optical module, two fiber output DFB diode lasers with central wavelengths near 1574 nm and 1653 nm, respectively, are directly coupled into a single beam through a 2 × 1 fiber coupler and an optical fiber collimator, and the laser beam is carefully adjusted to enter a multi-pass gas sample Herriott cell (AMAC-76, Aerodyne Research Inc., Billerica, MA, USA). After exiting from the long-path gas cell, it was focused on a photodetector (InGaAs detector, New Focus 2053, Santa Clara, CA, USA) by a gold-plated parabolic mirror. All optical elements are mounted on an aluminum breadboard. The gas handling module mainly consists of an oil-type diaphragm pump, several two-way and three-way valves, two flow meters (MCR-2000 slpm ALICAT), and a pressure meter (PC3-Series ALICAT), several standard gas cylinders for system calibration. A personal computer (PC) and a data acquisition (DAQ) I/O card (National Instruments, Austin, TX, USA, NI USB-6259) were used for system control and data acquisition. Real-time signal processing and analysis were performed by a LabVIEW-based digital lock-in amplifier.



Figure 4. Configuration of the developed multi-component gas synchronous detection system.

3.4. Optimal Sampling Pressure

The key issue for simultaneous detection of multiple molecules is to ensure that there is no crosstalk effect (i.e., absorption overlapping interference between each molecule). Generally, diode lasers can be tuned with 3 cm^{-1} at a fixed operating temperature. The individual absorption profile for typical atmospheric molecules commonly covers 1 cm⁻¹ even under the pressure of 1 atm. By decreasing gas sampling pressure, the molecular absorption profile can be significantly narrowed. However, the optical absorption depth will also gradually decrease with the decrease of gas pressure at a constant concentration, since the molecule number of the absorption medium is reduced, as demonstrated in Figure 5. Therefore, a trade-off should be carefully considered between sampling pressure, the number of analytes, and effective sampling points of the absorption spectrum for each analyte. To explore the capabilities of the proposed multi-gas detection technique, a theoretical simulation was first performed. For the CH_4 absorption line at 6046.9 cm⁻¹ and CO_2 absorption line at 6353.1 cm⁻¹, 500 data sampling points are enough to cover individual spectral profiles (including absorption lineshape and non-absorption baseline) at a total pressure of 1 atm, as shown in Figure 5a, 1000 sampling points are selected for laser scanning ramp. By analogy, 300 data sampling points can be realized for simultaneous measuring three molecules (such as CH_4 , CO_2 , CO, or other atmospheric species) with a sampling pressure of less than 600 mbar. For more molecular analysis simultaneously, the related parameters should be carefully selected according to the available experimental conditions, especially for the selection of molecular absorption fingerprint spectral region and laser tuning characteristics, etc.



Figure 5. (a) Simulated CH_4 and CO_2 transmitted spectra under different pressures and (b) the optical density at absorption center as function of sample total pressure.

4. Results and Discussion

4.1. Stability Assessment

The proposed detection scheme was initially evaluated using a gas cylinder with known CH₄ (360 ppm) and CO₂ (29,270 ppm) concentrations before practical application. An alternate measurement between an individual laser and a dual laser was carried out to evaluate the potential crosstalk effect under the optimal sampling pressure of 200 mbar and a total of 1000 sampling points. First, the individual CH₄ laser is only coupled into a gas cell, and continuous measurements of CH₄ absorption spectral signal are made; for example, the normalized CH_4 absorption spectra are shown in Figure 6a. Then, the individual CO_2 laser is coupled into a gas cell without the CH₄ laser, and similar procedures are applied to CO₂ spectral signal measurements, as shown in Figure 6b. Finally, both lasers are coupled into a gas cell for recording CH_4 and CO_2 absorption signals simultaneously, as shown in Figure 6c. For comparison, the simultaneously measured CH₄ and CO₂ absorption signals are plotted in Figure 6c,d together with the manually superimposed spectrum from two individual CH_4 and CO_2 absorption signals. To evaluate the repeatability and stability of the sensor system, the experimental procedure described above was repeated several times. From this figure, a good agreement was obtained between the individual laser mode and dual laser measuring mode.

For quantitative comparison, the optical absorption depth for CH_4 and CO_2 are calculated from the continuous measurement of both spectral data, as demonstrated in Figure 7. The statistical standard deviations (1 σ) with two successive cycles of alternating measurements are presented in the insert. The results indicated that the standard deviations for CH_4 are 0.002 and 0.0016, and the standard deviations for CO_2 are approximate 0.00052 and 0.00053, which shows good stability and repeatability for the proposed detection technique.



Figure 6. (**a**,**b**) CH_4 and CO_2 transmission spectra measured individually, (**c**,**d**) CH_4 and CO_2 transmission spectra measured simultaneously and the manually synthesized signals using individually measured spectra.



Figure 7. Experimentally measured absorption depth for CH₄ and CO₂ with two successive cycles.

4.2. Linear Calibration

Based on the optimal experimental conditions determined above, the concentration response characteristics of the gas sensor system were further investigated. Two gas cylinders with a certified concentration of 9000 ppm CH_4 and pure CO_2 were used and diluted with high pure nitrogen (N₂). The optical absorbances were extracted from measured CH_4 and CO_2 spectra to check their linear response. The relationship between absorbance and CH_4 and CO_2 concentrations was analyzed using a linear regression algorithm, shown in Figure 8. From this figure, we can see that good linearity with regression coefficients R^2 of 0.997 for CH_4 and 0.999 for CO_2 , respectively, were obtained.



Figure 8. Measured absorption depth with different concentration gradients for (**a**) CH_4 and (**b**) CO_2 and linear calibrations (**c**,**d**).

4.3. Allan Deviation Analysis

Allan deviation analysis method was used to determine the sensitivity and long-time stability of the developed multi-gas sensing system. CH₄ and CO₂ standard cylinder gases with certified concentrations of 249 ppm and 120,600 ppm were measured continuously for 2 h. The time series concentration data are provided in Figure 9a,b. During the entire observation process, the CH₄ concentration varied in the range of 246 to 252 ppm, and the CO₂ concentration changed from 119,600 to 121,600 ppm. The Allan deviations were plotted on a log–log scale versus signal average time, as shown in Figure 9c,d, the results indicate that detection limits at a 1-second average time are 0.82 ppm for CH₄ and 447.68 ppm for CO₂, respectively. The measurement sensitivity can be improved to 0.12 ppm for CH₄ at an optimal averaging time of 181 s and 35.97 ppm for CO₂ at an optimal averaging time of 166 s. The results of Allan variance show that the gas sensing system has good stability.

4.4. Real-Time Measurement of Ambient CO₂ and CH₄

Finally, the developed dual-gas sensor system was applied for ambient CO_2 and CH_4 simultaneously. Lab indoor air was continuously sampled with a flow rate of 100 sccm and gas cell pressure of 200 mbar. The spectra for ambient CO_2 and CH_4 are repeatedly scanned one after the other at a total rate of 100 Hz and are subsequently averaged in 2 s to improve the signal-to-noise ratio. The finally measured CO_2 and CH_4 concentrations for several hours are shown in Figure 10. The result indicated that CO_2 concentration is stationary with an average of about 570 ppm within lunch break (13:30:00–14:30:00), after then the concentration showed an obviously increasing trend, with a maximum over 1000 ppm as shown in Figure 10a, which is mainly due to entry of laboratory personnel. In the case of CH_4 , its concentration shows a stable during the entire measurement period as shown in Figure 10b, which indicated no correlation with human activity. The calculated average concentration of CH_4 is approximate 1.3 ppm, which is approximately consistent with its average atmospheric concentration level.



Figure 9. (a) and (b) Time series concentrations of CH_4 and CO_2 continuously measured standard gas samples, (c) and (d) Allan deviation of CH_4 and CO_2 , respectively.



Figure 10. Time series of (a) CO_2 and (b) CH_4 were measured by using the gas sensing system from the indoor air for ~ 5 h on 13 April 2022.

For detailed analysis, the histogram analysis of the experimental data is also performed, as illustrated in Figure 11. The histogram plot of CO_2 is made from the relatively stable concentration intervals, as labeled with a rectangle in Figure 10a, while all data in Figure 10b were used for CH_4 histogram analysis. The results indicated that the full width half maximum (FWHM) of the Gaussian profile corresponds to the measurement precision of 76.73 ppm and 0.84 ppm for CO_2 and CH_4 , respectively. The histogram plot analysis shows a good Gaussian distribution, which indicates that the developed dual-gas sensor system is mainly dominant with white noise.



Figure 11. Histogram plot analysis of (a) CO₂ and (b) CH₄ concentration (details see text).

5. Conclusions

In this paper, an attractive gas sensing technique was proposed for the detection of multi-gas species simultaneously, which is based on the fiber optical sensing ideal. The details of parameters optimization of optimal sampling pressure, laser tuning characteristics, and spectral sampling points were theoretically and experimentally investigated. Two typical atmospheric greenhouse gases $(CH_4 \text{ and } CO_2)$ are selected as the analyte for simultaneous calibration-free gas detection without time delay, and two fiber-coupled NIR DFB diode lasers are used and coupled into a single optical path for measuring CO_2 and CH₄ absorption spectra simultaneously. The results indicated that the developed laser spectroscopy sensor has good reliability and has been successfully demonstrated for ambient CO_2 and CH_4 detection using a single detector without any time lag. The Allan–Werle deviation analysis indicated that detection limits at a 1-second averaging time are 0.82 ppm for CH_4 and 447.68 ppm for CO_2 , respectively. The measurement sensitivity can be improved to 0.12 ppm for CH_4 at an optimal averaging time of 181 s and 35.97 ppm for CO_2 at an optimal averaging time of 166 s. detection limits of 0.12 ppm for CH₄ and 35.97 ppm for CO_2 can be obtained with an integration time of 181 s and 166 s, respectively. The proposed technique can be expanded to measure more molecules simultaneously by combing a laser array and may pave a new way for developing a low-cost and ultra-compact multi-gas laser spectroscopy sensing system.

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