

Infrared Dual-Gas CH₄/C₂H₆ Sensor Using Two Continuous-Wave Interband Cascade Lasers

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Abstract—An infrared dual-gas sensor system for the simultaneous detection and monitoring of methane (CH₄) and ethane (C₂H₆) at parts-per-billion by volume (ppbv) concentration levels was developed using two room temperature, distributed feedback (DFB) interband cascade lasers (ICLs) and two miniature multipass cells with an effective absorption length of 54.6 m. Laser direct absorption spectroscopy (LDAS) was used to detect CH₄ utilizing the 3038.5 cm⁻¹ absorption line, and second-harmonic wavelength modulation spectroscopy (2f-WMS) method was used to detect C₂H₆ using the 2996.88 cm⁻¹ absorption line. The 1σ CH₄ detection limit is ~ 2.7 ppbv with a 1 s averaging time and exhibits a minimum value of ~ 1.7 ppbv for a 9 s averaging time; the 1σ C₂H₆ detection limit is ~ 2.6 ppbv with a 3.4 s averaging time and shows an optimum averaging time of 65 s corresponding to a stability of ~ 0.36 ppbv. Using the dual-gas sensor system, 48 hours' monitoring of the two atmospheric gases was performed in the Greater Houston area, TX, USA.

Index Terms—laser sensors, spectroscopy, infrared, Semiconductor lasers, quantum cascade

I. INTRODUCTION

METHANE (CH₄) is a main contributor to the greenhouse effect and a safety hazard in the production of chemicals.

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Hence the monitoring of CH₄ concentration levels is critical in urban or rural areas [1,2]. Ethane (C₂H₆) [3,4] is the second-largest component of natural gas after CH₄, which is mainly used in the chemical industry. Simultaneous detection of C₂H₆ and CH₄ is an effective method to discriminate CH₄ origin between thermogenic (e.g. natural gas production) and biogenic sources (e.g. landfills, wetlands). Therefore, a dual-gas sensor should be developed to perform the detection of CH₄ at an atmospheric level of ~ 2 parts-per-million by volume (ppbv) ppm and C₂H₆ from several parts-per-billion by volume (ppbv) to tens of ppbv.

Laser direct absorption spectroscopy (LDAS) is an increasingly important method for trace gas detection [5, 6]. In LDAS, either a near-infrared or a mid-infrared semiconductor laser source can be used. Commercially obtainable quantum cascade lasers (QCLs) are limited to wavelengths above 4 μm [7], which cannot be used for targeting the strongest absorption lines of CH₄ and C₂H₆ at ~ 3.3 μm. Interband cascade lasers (ICLs) can provide continuous-wave (CW) radiation in the 3.0–4.0 μm spectral region at room temperature [8]. ICLs also possess an intrinsic distributed feedback (DFB) structure, which permits CW tuning with spectral linewidths of < 10 MHz. Therefore, the combination of LDAS and ICL provides ultra-high sensitive detection on CH₄ and C₂H₆ in the 3.0 – 4.0 μm spectral region. LDAS technique was used for CH₄ detection, which is simple to realize and sufficient for measuring the light intensity directly using a novel, compact, multipass gas cell (MPGC) with an effective 54.6 m absorption length and a strong absorption line at 3038.5 cm⁻¹. However, the ppb-level detection of C₂H₆ required second-harmonic wavelength modulation spectroscopy (2f-WMS).

II. SENSOR STRUCTURE AND DESIGN DETAILS

A. Absorption Line Selection

HITRAN absorption spectra of 2% H₂O, 10 ppbv C₂H₆, 1.8 ppmv CH₄, calculated at 700 Torr gas pressure and a 5460 cm effective optical path length are depicted in Fig. 1(a). A single CH₄ line which is located at 3038.5 cm⁻¹ was selected as the target line. A H₂O absorption line at 3038.75 cm⁻¹ is observed, which will affect the CH₄ detection especially at higher H₂O concentration levels. Therefore, a drier must be used to filter H₂O during CH₄ detection. Similarly, HITRAN absorption spectra of 2% H₂O, 10 ppbv C₂H₆, 1.8 ppmv CH₄ calculated at 100 Torr gas pressure and a 5460 cm effective optical path length are depicted in Fig. 1(b) within the range of 2996-2998

cm^{-1} . An interference free C_2H_6 absorption line centered at 2996.88 cm^{-1} was selected as the optimum target line. Such a low pressure also avoids the interference from CH_4 absorption at $\sim 2997 \text{ cm}^{-1}$ by suppressing the broadening of this line.

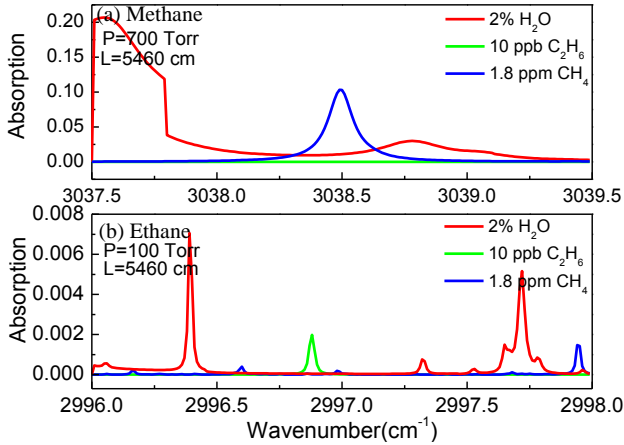


Fig. 1. HITRAN-based absorption spectra of H_2O (2%), C_2H_6 (10 ppbv) and CH_4 (1.8 ppmv) in a narrow spectral range. The lines of H_2O , C_2H_6 and CH_4 are shown in red, green and blue, respectively. (a) Wavenumber range from 3037.5 cm^{-1} to 3039.5 cm^{-1} for a 5460 cm path length at a pressure of 700 Torr . (b) Wavenumber range from 2996.0 cm^{-1} to 2998.0 cm^{-1} for a 5460 cm path length at a pressure of 100 Torr

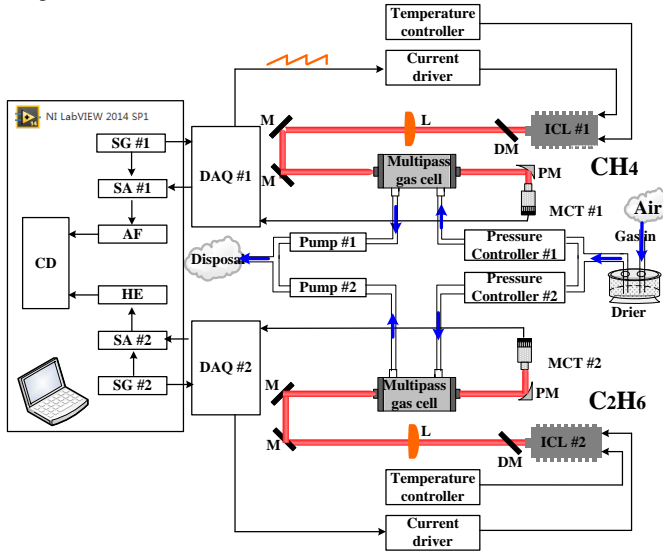


Fig. 2. Block diagram of the dual-gas $\text{CH}_4/\text{C}_2\text{H}_6$ sensor system. SG: signal generation; SA: signal acquisition; AF: absorption fitting; HE: harmonic extraction; CD: concentration decision

B. Sensor Structure and Configuration

Fig. 2 shows the diagram of the dual-gas sensor system, where the upper part is the CH_4 sensor system and the lower part is the C_2H_6 sensor system. Two Nanoplus, CW, DFB ICLs mounted in TO66 headers emitting single-mode radiation at a center wavelength of 3291 nm (ICL #1) and 3337 nm (ICL #2) were employed. Detailed parameters of the two ICLs are shown in Table I. The two optical sensor systems possess similar designs. The infrared laser beam and a visible alignment beam (not shown) were combined by means of a dichroic mirror (DM, ISO optics, model BSP-DI-25-3). The combined beams were coupled into a MPGC using a mode matching lens (L) with 200-mm focal length. Two plane mirrors (M) fold the necessary optical path into a reduced space. An effective optical path

length of 54.6 m was obtained after 435 beam passes. The exiting ICL beam from the MPC was focused onto a mercury-cadmium-telluride (MCT) detector (Vigo, PVI-4TE-4) using a 35-mm focal length parabolic mirror (PM).

For the CH_4 sensor, a laptop equipped with a DAQ card (NI, model 6062E) with similar parameters used in Ref. [2] was used to generate a 500 Hz sawtooth scan signal (2.1 V bias, 0.4 V amplitude). The ICL temperature was set to $30.95 \text{ }^\circ\text{C}$ using an onboard temperature controller. The sensing signal was supplied to DAQ card (#1) for data processing with a sampling rate of 500 ksp .

For the C_2H_6 sensor, the same laptop equipped with a second DAQ card (NI, model USB6356) was used to generate a 0.3 Hz triangular wave with a peak-peak amplitude of 0.2 V as well as a 5 kHz modulation signal with a peak-to-peak amplitude of 0.026 V . The two signals were superimposed on each other and supplied to the commercial ICL current driver (Thorlabs, model LDC202C) with a bias current of 47 mA . The ICL temperature was set to $10 \text{ }^\circ\text{C}$ using a commercial temperature controller (Wavelength Electronics, model LFI-3751). The sampling rate of the DAQ card, including the DAC and ADC module, was set to 300 kHz , resulting in 10^6 data points per triangular period. The $2f$ signal was obtained from a LabVIEW-based lock-in amplifier (see Fig. 3), whose amplitude was used to determine C_2H_6 concentration. The total power consumption of the dual-gas sensor system was $\sim 500 \text{ W}$, including $\sim 200 \text{ W}$ for the two vacuum pumps (KNF Neuberger Inc, model N 813.5 ANE/AF), $\sim 100 \text{ W}$ for the ICL driver and temperature controller, and $\sim 60 \text{ W}$ for the laptop.

TABLE I
KEY PARAMETERS IN CH_4 AND C_2H_6 DETECTION

	ICL #1	#2
Center wavelength	3291 nm	3337 nm
Operation temperature	$30.95 \text{ }^\circ\text{C}$	$10 \text{ }^\circ\text{C}$
Temperature tuning coefficient	$-0.240 \text{ cm}^{-1}/^\circ\text{C}$	$-0.301 \text{ cm}^{-1}/^\circ\text{C}$
Current tuning coefficient	$-0.232 \text{ cm}^{-1}/\text{mA}$	$-0.142 \text{ cm}^{-1}/\text{mA}$
Target absorption line	3038.5 cm^{-1}	2996.88 cm^{-1}
Detection pressure	700 Torr	100 Torr
Technique	LDAS	$2f$ -WMS
Target gas	CH_4	C_2H_6

C. LabVIEW-Based Data-Processing System

Data sampling and processing were realized on a LabVIEW-based platform, whose function diagram is shown in Fig. 3. For CH_4 detection, we used a similar but simpler technique as compared with Ref. [2]. After normalization of the absorption signal, a Lorentzian fitting was performed on the normalized absorption signal without using any spectral data from HITRAN for absorption fitting. Fig. 4(a) shows the Lorentzian fitting curves at different concentration levels of 1.0 , 1.2 , 1.4 , 1.6 and 2.1 ppmv . The raw data (red dots) of the normalized absorption at 2.1 ppmv CH_4 was shown in Fig.3(a).

For C_2H_6 detection, the output signal from the detector as well as two frequency-doubled orthogonal signals synchronized by the modulation signal was sent to a lock-in module. A “R” signal with a positive bias was generated. For data processing, we removed the baseline from the “R” signal

via a subtraction operation, and obtained a $2f$ signal biased at zero. The $2f$ signals at different C_2H_6 concentration levels from 10-100 ppbv are shown in Fig. 4(b).

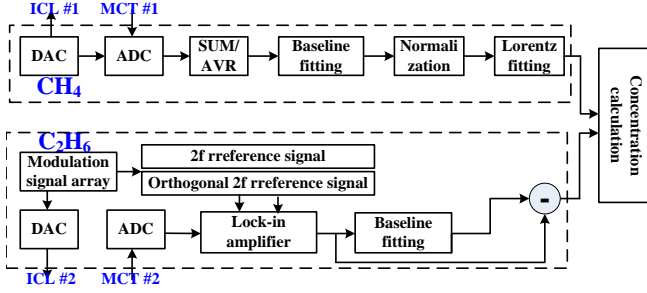


Fig. 3. Function diagram of the LabVIEW-based data-processing system. DAC: digital-to-analog converter; ADC: analog-to-digital converter

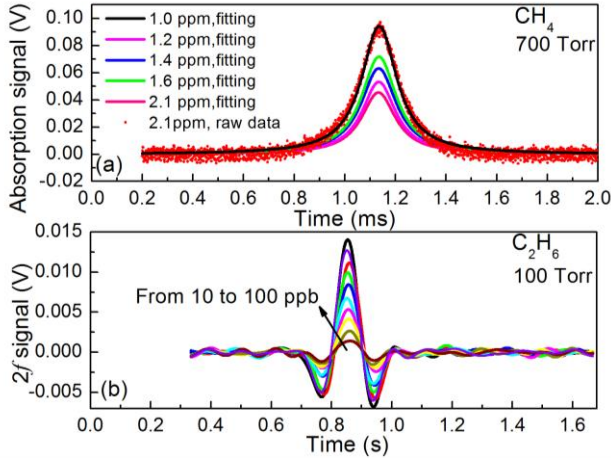


Fig. 4. (a) Lorentzian fitting curves at five CH_4 concentration levels of 1.0, 1.2, 1.4, 1.6, and 2.1 ppmv. (b) The recorded $2f$ signal at ten different C_2H_6 concentration levels of 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 ppbv. The integral time of the LabVIEW-based lock-in amplifier was set at 16 ms, and the modulation frequency was 5 kHz. Note that some data points were removed during the data-processing of the CH_4 and C_2H_6 spectra

III. PERFORMANCE OF SENSOR SYSTEMS

A. CH_4 Sensor

Four CH_4 samples with concentration levels of 1.0, 1.2, 1.4, 1.6 ppmv were generated by diluting a 2.1 ppmv CH_4 sample balanced by N_2 using an Environics dilution system (Series 4040). The concentration levels of the four samples were measured using the CH_4 sensor, as shown in Fig. 5(a). The sensor readings performed linearly in agreement with the theoretical value. Measurements of the standard CH_4 sample with a 2.1 ppmv concentration over a period of ~ 10 minutes were performed with a sampling period of 1 s. Fig. 5(b) exhibits the measured concentration levels as a function of time t , which shows a range of $2.11\text{ppm} \pm 10\text{ppbv}$. Fig. 5(c) shows the Allan-Werle deviation as a function of averaging time τ , based on the data depicted in Fig. 5(b). The 1σ detection limit is ~ 2.66 ppbv with a 1 s averaging time. Fig. 5(c) also shows an optimum averaging time of 9 s corresponding to a limit of ~ 1.66 ppbv.

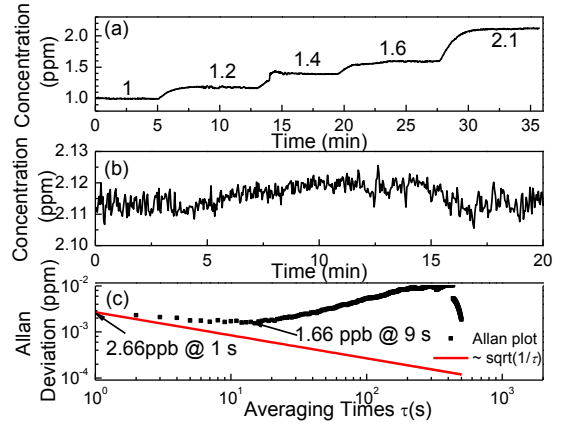


Fig. 5. (a) Time series of the measured concentration of 5 CH_4 samples. (b) Measured concentration of the standard 2.1 ppm CH_4 sample for 600 s with an averaging time is 0.1 s. (c) Allan-Werle deviation plot as a function of averaging time, τ , based on the data shown in Fig. 5(b)

B. C_2H_6 Sensor

Six C_2H_6 samples with concentration levels of 0, 10, 30, 50, 70, and 90 ppbv were generated by diluting a 1.14 ppmv C_2H_6 sample balanced by N_2 . Their concentrations were measured using the calibrated C_2H_6 sensor, as shown in Fig. 6(a). The sensor shows a good linear relation between the concentration reading and the theoretical value. Measurements of the C_2H_6 sample with a concentration of 30 ppbv over a period of ~ 0.5 hour were carried out with a sampling period of 3.4 s, as shown in Fig. 6(b). The variation range of the measured concentration was within $-4 - 4$ ppbv. Fig. 5(b) shows the Allan deviation as a function of averaging time τ . The Allan deviation is ~ 2.6 ppbv with a 3.4 s averaging time. Fig. 5(b) also shows an optimum averaging time of 65 s corresponding to a detection limit of ~ 359 parts-per-trillion by volume (pptv).

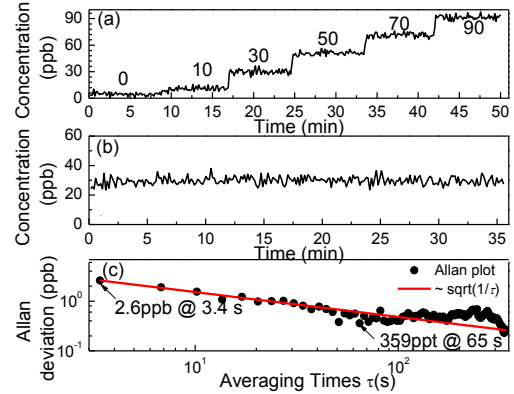


Fig. 6. (a) Time series of the measured concentration of six C_2H_6 samples. (b) Measured concentration of a diluted 30 ppbv C_2H_6 sample for over half an hour. (c) Allan deviation plot as a function of averaging time, τ , based on the data shown in Fig. 6(b)

C. Dual-Gas Detection Using Diluted Gas Samples

The detection characteristic of the dual-gas sensor was further assessed using five generated C_2H_6 samples (200, 90, 50, 10, and 0 ppbv) using an Environics gas dilution system (Environics, Series 4040) and the standard 2.1 ppmv CH_4 sample. The results are shown in Fig. 7, where the time recording period for acquiring both a CH_4 and a C_2H_6 concentration is ~ 8 s. The CH_4 and C_2H_6 gas streams were

switched using two valves to change the $\text{CH}_4/\text{C}_2\text{H}_6:\text{N}_2$ mixing ratio in the MPGC. These results demonstrate the operation of the dual-gas sensor for monitoring both CH_4 and C_2H_6 simultaneously.

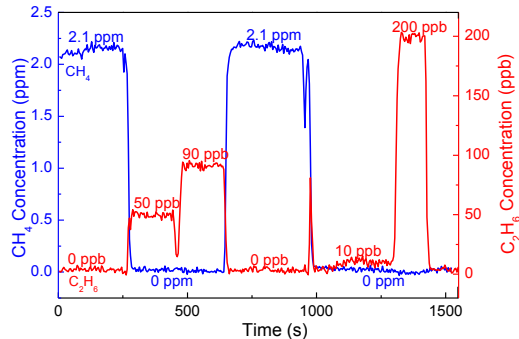


Fig. 7. Concentration measurements on $\text{CH}_4/\text{C}_2\text{H}_6:\text{N}_2$ mixtures using the dual-gas sensor system

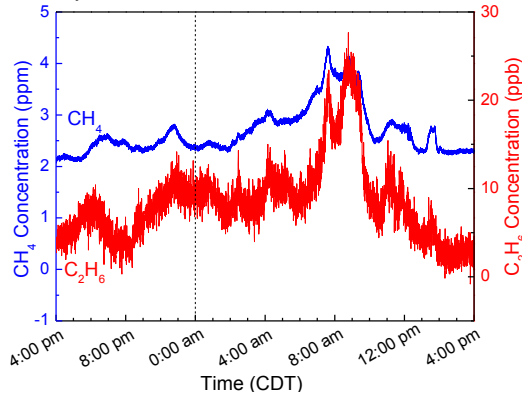


Fig. 8. Monitoring on atmospheric CH_4 and C_2H_6 for 48 hours' period in the Greater Houston area

D. Atmospheric CH_4 and C_2H_6 Monitoring

The sensor system was evaluated for simultaneous detection of atmospheric CH_4 and C_2H_6 on the Rice University campus. The outside air was pumped into the gas cell using a long sampling line. The measured concentrations are plotted in Fig. 8. The experiment was conducted for ~ 24 hours. Fluctuations in concentration levels were observed during the atmospheric monitoring of CH_4 and C_2H_6 . The C_2H_6 concentration ranged between 0 and 27.6 ppbv, with an average value of 8.4 ± 4.6 ppbv. The CH_4 concentration varied from 2.1 to 4.4 ppmv, with an average value of 2.7 ± 0.5 ppmv. The detected CH_4 concentration levels exhibited a typical hourly profile expected for this gas species, which is in agreement with previous research work [1]. This behavior is related to boundary layer dynamics and the extent of atmospheric mixing. C_2H_6 concentration levels peaked during early morning hours resembling diurnal trends observed for CH_4 . Furthermore, point emission sources of CH_4 and C_2H_6 in the Greater Houston area are responsible for minor concentration peaks observed during the monitoring period.

IV. DISCUSSIONS AND CONCLUSIONS

Table II lists the performance of several reported laser based trace sensors and the reported dual-gas sensor. Since the sensors used different absorption lines and pressures, the detection limits (DLs) are also different for the same gas

species. A relatively low DL (ppb level) for both gas species was achieved by the reported sensor as compared with other laser based sensors.

TABLE II
COMPARISON AMONG SEVERAL CH_4 AND C_2H_6 SENSORS

Ref.	Gas	Laser	EPL	DL	Pressure
[6]	C_2H_6	Diode (2976.8 cm^{-1})	100 m	240 pptv @ 1 s	250 Torr
[9]	CH_4	QCL (1281.61 cm^{-1})	57.6m	24.0 ppbv @ 1 s	40 Torr
[10]	CH_4	QCL (1297.486 cm^{-1})	76 m	8.5 ppb @ 2s	100 Torr
This	C_2H_6	ICL (2996.88 cm^{-1})	54.6 m	1.7 ppbv @ 3.4s	100 Torr
	CH_4	ICL (3038.5 cm^{-1})	54.6 m	2.7 ppbv @ 1 s	700 Torr

In conclusion, we demonstrated the development and performance evaluation of a dual-gas sensor system using TLAS technique based on two ICLs. The 1σ detection limit of CH_4 is ~ 2.7 ppbv with a 1 s averaging time and reaches a minimum value of ~ 1.7 ppbv with a 65 s averaging time. The 1σ detection limit of C_2H_6 is ~ 2.6 ppbv with a 3.4 s averaging time and shows an optimum averaging time of 65 s corresponding to a concentration of ~ 359 pptv. Long-term monitoring of these two atmospheric gases was performed in the Greater Houston area. The sensor shows potential application in environmental monitoring, medical diagnostics and industrial process control.

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