Ppb-level mid-infrared ethane detection based on three measurement schemes using a 3.34-µm continuous-wave interband cascade laser

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Abstract A ppb-level mid-infrared ethane (C_2H_6) sensor was developed using a continuous-wave, thermoelectrically cooled, distributed feedback interband cascade laser emitting at 3.34 μ m and a miniature dense patterned multipass gas cell with a 54.6-m optical path length. The performance of the sensor was investigated using two different techniques based on the tunable interband cascade laser: direct absorption spectroscopy (DAS) and second-harmonic wavelength modulation spectroscopy (2f-WMS). Three measurement schemes, DAS, WMS and quasi-simultaneous DAS and WMS, were realized based on the same optical sensor core. A detection limit of ~7.92 ppbv with a precision of ± 30 ppbv for the separate DAS scheme with an averaging time of 1 s and a detection limit of ~1.19 ppbv with a precision of about ± 4 ppbv for the separate WMS scheme with a 4-s averaging time were achieved. An Allan-Werle variance analysis indicated that the precisions can be further improved to 777 pptv @ 166 s for the separate DAS scheme and 269 pptv @ 108 s for the WMS scheme, respectively.

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For the quasi-simultaneous DAS and WMS scheme, both the 2f signal and the direct absorption signal were simultaneously extracted using a LabVIEW platform, and four C_2H_6 samples (0, 30, 60 and 90 ppbv with nitrogen as the balance gas) were used as the target gases to assess the sensor performance. A detailed comparison of the three measurement schemes is reported. Atmospheric C_2H_6 measurements on the Rice University campus and a field test at a compressed natural gas station in Houston, TX, were conducted to evaluate the performance of the sensor system as a robust and reliable field-deployable sensor system.

1 Introduction

Ethane (C_2H_6) is the second largest component of natural gas after methane (CH_4). C_2H_6 is used in the production of ethylene (C_2H_4) as well as in the manufacture of other commodity chemicals. C_2H_6 is also an explosive when mixed with 3–12.5 % volume of air. C_2H_6 occurs as a trace gas in the atmosphere at concentration levels of several ppbv. In fact, C_2H_6 is the most abundant non-methane hydrocarbon in the atmosphere that strongly affects both atmosphere chemistry and climate [1, 2]. Hence, the detection of C_2H_6 , at low concentration levels (i.e., ppbv), is important in environmental monitoring [3, 4]. Furthermore, ultra-sensitive C_2H_6 detection has found applications in human breath analysis as a noninvasive method to monitor and identify different diseases, such as lung cancer and asthma [5–7].

There are two typical techniques used in the detection of trace-level gases based on infrared absorption spectroscopy. The first technique is direct absorption spectroscopy (DAS), in which excitation sources such as near- and mid-infrared lasers or an incandescent light source [8, 9] can be used. An advantage of DAS is its ability to offer quantitative concentration

measurements of trace gas species without sensor calibration as the concentration can be calculated from the relative change of the intensity according to Beer-Lambert's law. On the other hand, wavelength modulation spectroscopy (WMS) [10-12]enables non-contact trace gas concentration measurements. In WMS, the spectral signal is shifted to the high-frequency region to minimize low frequency noise, referred to as 1/f noise. This procedure can improve the measurement precision. Therefore, WMS has proven to be an excellent tool for trace gas detection in environmental [13–15], biomedical [16–18], industrial [19, 20] and national security [15] applications. WMS requires a tunable laser capable of single-frequency emission and a narrow linewidth at the targeted absorption line of a gas molecule. To meet this requirement, several laser sources are commercially available, e.g., difference-frequency generation (DFG) [21] and optical parameter oscillators (OPO) [22]. In recent years, quantum cascade lasers (QCLs) [23] in the 4- to 12-µm spectral range and interband cascade lasers (ICLs) in the 3- to 6-µm range, capable of operating with low electrical power consumption [24], provide continuous-wave (CW) output power levels of >5 mW. For example, the development of WMS based on CW, thermoelectrically cooled (TEC), distributed feedback (DFB) diode lasers for C_2H_6 detection was reported in [25, 26].

In this manuscript, a mid-infrared C₂H₆ sensor based on a compact multipass gas cell (MPGC) with a 54.6-m effective absorption length and a room-temperature CW, TEC, DFB ICL centered at 2996.88 cm⁻¹ was experimentally demonstrated. The reported C2H6 sensor describes improvements in terms of the optical sensor core design, operating schemes and sensor application compared to a previously CH4 sensor based on a similar MPGC and an ICL [27]. A second-generation optical sensor core with a single-floor structure (see Fig. 2e) was developed based on the two-floor optical sensor core described in Ref. [27]. The single-floor design provides better mechanical stability without compromising the sensor-system footprint. Furthermore, three measurement schemes (DAS, WMS and quasi-simultaneous DAS and WMS) were realized, compared with only the DAS scheme used in Ref. [27]. In addition, an atmospheric C₂H₆ measurement campaign on the Rice University campus and a field test at a compressed natural gas (CNG) station in Houston, TX, were conducted to evaluate the performance of the sensor system as a robust and reliable field-deployable sensor system.

2 Sensor configuration

2.1 Absorption line selection of C_2H_6 at 3.34 µm

 C_2H_6 possesses strong fundamental absorption lines in the mid-infrared spectral range centered at 3.34 μ m, which



Fig. 1 HITRAN-based absorption lines of CH₄, C₂H₆ and H₂O in **a** a spectral range from 2992 to 2999 cm⁻¹ and **b** a narrow range from 2996.8 to 2997.0 cm⁻¹. C₂H₆, CH₄ and H₂O absorption lines are shown in *red*, *blue* and *purple*, respectively. The *inset* in Fig. 1b shows the HITRAN absorption spectra of 10 ppb C₂H₆ and 1.8 ppm CH₄ calculated at 100 Torr (*solid line*) and 1 atm (*dashed line*) gas pressure and a 5460-cm effective optical path length

allows sensitive and selective atmospheric gas detection in this spectral range. HITRAN absorption lines of CH_4 , C_2H_6 and H_2O within the range of 2992–2999 cm⁻¹ are depicted in Fig. 1a. An ICL can be current-tuned to target the strong C_2H_6 absorption line at 3336.8 nm (2996.88 cm⁻¹), which is free from spectral interference of H_2O . A detailed illustration of the absorption lines within the range of 2996.8– 2997.0 cm⁻¹ is shown in Fig. 1b. Several CH₄ absorption lines near 2997 cm⁻¹ may interfere with C_2H_6 concentration measurements. A HITRAN spectral simulation of 10 ppbv C_2H_6 and 1.8 ppmv CH₄ (atmospheric concentration level) at 100-Torr gas pressure and a 5460-cm effective optical path length (see the solid lines in the inset in Fig. 1b) indicates that atmospheric CH₄ has almost no



Fig. 2 a Schematic of the C_2H_6 optical sensor core using a multipass gas cell (MPGC) and a 3.337- μ m CW, DFB, ICL excitation source. **b** Electrical part of the sensor based on direct absorption spectroscopy (DAS). **c** Electrical part of the sensor based on wavelength modulation spectroscopy (WMS). **d** Electrical part of the sensor based on quasi-simultaneous DAS and WMS. **e** A CAD image of compact opti-

cal sensor core with dimensions of length (35.5 cm), width (18 cm) and a height (8 cm). **f** A photograph of the miniature MPGC. **g** The mode pattern inside the MPGC obtained with a red diode alignment laser. *ICL* interband cascade laser, *DM* dichroic mirror, *L* lens, *M* plane mirror, *PM* parabolic mirror, *MCT* mercury-cadmium-telluride detector

effect on C_2H_6 detection. However, at 760 Torr pressure, the 2996.88-cm⁻¹ C_2H_6 line overlaps with the 2997-cm⁻¹ CH_4 line (see the dashed lines in the inset of Fig. 1b). Hence, the pressure inside the MPGC was controlled experimentally below 150 Torr in order to avoid the broadening of adjacent CH_4 lines, especially the absorption line at ~2997 cm⁻¹. Below 150 Torr, the absorption line at 2996.88 cm⁻¹ is the optimum choice for C_2H_6 detection (Fig. 2).

2.2 Sensor configuration based on three measurement schemes

The C_2H_6 sensor architecture is depicted in Fig. 2. An optical sensor core with a single-floor structure was developed, whose schematic and computer-aided design (CAD) image is shown in Fig. 2a, e, respectively. All the components were placed on an aluminum plate, which provided good mechanical stability and small footprint. A Nanoplus CW, TEC, DFB ICL was employed as the mid-infrared laser excitation source. The current and temperature wavelength-tuning coefficients for this ICL were measured to be $-0.141528 \text{ cm}^{-1}/\text{mA}$ and $-0.30138 \text{ cm}^{-1}/\text{o}C$. An ICL

injection current of 47 mA combined with a 10 °C operating temperature was selected for C2H6 concentration measurements at the interference-free absorption line of 2996.88 cm^{-1} . For beam tracing purposes, a visible diode laser beam was used for alignment of the mid-infrared ICL beam. The alignment laser beam was coupled to a 54.6-m MPGC using a dichroic mirror (ISP Optics, model BSP-DI-25-3), a CaF₂ lens (d = 25 mm, f = 200 mm) and two adjustable plane mirrors. By careful adjustment of each optical element, the ICL beam entering into the MPGC at the correct position and angle will be reflected 453 times internally prior to exiting. The exiting beam is focused onto a TEC mercury-cadmium-telluride (MCT) photodetector (VIGO System, model PVI-4TE-3.4) using a parabolic mirror (d = 25 mm, f = 35 mm). A photograph of the used miniature MPGC is shown in Fig. 2f, whose dimension is $17 \times 6.5 \times 5.5$ cm³. The mode pattern obtained with red diode alignment laser inside the MPGC is shown in Fig. 2g. The current and temperature of the ICL were set using a commercial current driver (ILX, model LDX-3220) and a temperature controller (Wavelength Electronics, model LFI-3751), respectively. A pressure controller (MKS, Type

649) is connected with the MPGC inlet and a vacuum pump (KNF Neuberger, Type N831.5 ANE/AF) that is attached to the MPGC outlet to regulate the pressure inside the MPGC.

Two different techniques (DAS and WMS) were adopted for the detection of C_2H_6 , and three measurement schemes were realized via the same optical sensor core: DAS, WMS and quasi-simultaneous DAS and WMS. These three schemes require different electronic modules, drive signals and data-processing methods.

- DAS scheme (Fig. 2b). A data acquisition (DAQ) unit (NI, model USB6356) was used to generate a triangular signal for tuning the laser wavelength, and the output signal from the detector was applied directly to the DAQ for data acquisition. A LabVIEW laptop computer platform was used for scan-signal generation and absorption-signal extraction.
- 2) WMS scheme (Fig. 2c). A triangular signal produced by function generator 1 (Stanford, model DS345) combined with a small-amplitude sinusoidal wave from function generator 2 (Stanford, model DS345) via an electrical adder was applied to the current driver to scan and modulate the ICL wavelength. A lock-in amplifier (Stanford, model SR830) was used to demodulate the signal from the MCT when operated in the 2*f* mode and used a sync signal from function generator 2. A DAQ card was used to acquire the second-harmonic spectra from the lock-in amplifier. A LabVIEW platform was used for the 2*f* signal acquisition.
- 3) Quasi-simultaneous DAS and WMS scheme (Fig. 2d). A triangular drive signal was used to realize this scheme. The first half-period of this signal (for WMS operation) was a rising ramp signal for wavelength scanning combined with a sinusoidal wave signal for wavelength modulation. The second half-period (for DAS operation) was a falling ramp signal for wavelength scanning. For simplifying the sensor design, signal generation, data acquisition and processing were all conducted by a DAQ unit as well as a laptop. In order to decide the C_2H_6 concentration simultaneously, a LabVIEW-based lock-in amplifier was employed to

extract the 2f signal from the first half-period of the detector output signal, and a data-processing procedure was adopted to extract the laser absorption signal during the second half-period of the output signal from the detector.

3 Sensor performances using a separate DAS scheme

3.1 Measurement formulation

The periodic triangular signal u_{tri} generated by the DAQ unit is used to tune the ICL frequency to scan the selected C_2H_6 absorption line, which can be expressed in one period as

$$u_{\text{tri}}(t) = \begin{cases} -A_{\text{tri}}/2 + (2A_{\text{tri}}/T_{\text{tri}})t, 0 \le t \le T_{\text{tri}}/2\\ 3A_{\text{tri}}/2 - (2A_{\text{tri}}/T_{\text{tri}})t, -T_{\text{tri}}/2 \le t \le T_{\text{tri}} \end{cases}$$
(1)

where A_{tri} and T_{tri} are the amplitude and the period of the triangular signal, respectively. The variation of emitting wavelength leads to a change of the absorption coefficient $\alpha_{das}(t)$. Without absorption, the light intensity received by the MCT detector is given by

$$I_{\rm s}(t) = I_0[1 + m u_{\rm tri}(t)]$$
⁽²⁾

where *m* and I_0 are the light intensity modulation coefficient and the original ICL intensity, respectively. After the ICL light propagation through a C₂H₆ sample with a concentration of *C* for a length of *L*, the light will be received by the detector. Through an optical-to-electrical conversion and amplification, an electric signal, $u_r(t)$, is obtained

$$u_{\rm r}(t) = KD_{\rm oe}I_{\rm s}(t)\exp[-\alpha_{\rm das}(t)LC]$$

$$\approx KD_{\rm oe}I_0[1 + mu_{\rm tri}(t)][1 - \alpha_{\rm das}(t)LC]$$
(3)

where *K* and D_{oe} are an amplifying factor and an opticalto-electrical conversion coefficient, respectively, and $exp[-\alpha_{das}(t)LC] \approx 1 - \alpha_{das}(t)LC$ for $\alpha_{das}(t)LC \approx 0$ is used in Eq. (3). For each period of the triangular signal, it is necessary to consider only the first half-period (rising part). Each time *N* frames of $u_r(t)$ (rising part) were sampled by means of the DAQ card and averaged as

$$u_{\rm r, \, avr}(t) = \frac{1}{N} \sum_{i=1-N} u_{\rm r, \, i}(t) = \frac{1}{N} K D_{\rm oe} I_0 \left\{ \underbrace{\sum_{i=1-N} [1 + m u_{\rm tri, \, 1^{\rm st} \, \rm half}(t)]}_{\rm background} - \underbrace{\sum_{i=1-N} [1 + m u_{\rm tri, \, 1^{\rm st} \, \rm half}(t)] \alpha_{\rm das, \, 1^{\rm st} \, \rm half}(t) L C}_{\rm absorption} \right\}$$
(4)

Once $u_{r, avr}(t)$ is obtained, data fitting based on LabVIEW (results are reported in "Results and discussion" section) is used to obtain the background signal

$$u_{\rm r, \, bac}(t) = \frac{1}{N} K D_{\rm oe} I_0 \underbrace{\sum_{i=1-N} [1 + m u_{\rm tri, \, rising}(t)]}_{\text{background}}$$
(5)

Furthermore, the following processing is performed to eliminate the background signal

$$u_{\mathrm{r,\,final}}(t) = \frac{u_{\mathrm{r,\,bac}}(t) - u_{\mathrm{r,\,avr}}(t)}{u_{\mathrm{r,\,bac}}(t)} = \left[\sum_{i=1-N} \alpha_{\mathrm{das,\,1^{st}\,half}}(t)\right] LC$$
(6)

Therefore, the amplitude of $u_{r, \text{ final}}(t)$ is proportional to the concentration *C*

$$\operatorname{Amp}\left[u_{\mathrm{r,\,final}}(t)\right] = \operatorname{Amp}\left[\sum_{i=1-N} \alpha_{\mathrm{das,\,1^{st}\,half}}(t)\right] LC \tag{7}$$

Such a curve can be achieved by means of a calibration experiment with standard C_2H_6 samples.

3.2 Experiment details

The mid-infrared C₂H₆ sensor system in DAS mode described in "Sensor configuration based on three measurement schemes" section was operated at a drive current and temperature of 47 mA and 10 °C, respectively. The pressure in the MPGC was set to 100 Torr in order to avoid spectral interference from CH₄. A triangular scan signal with a frequency of 250 Hz and a peak-topeak amplitude of 200 mV was used. The sampling rate of the DAO card was set to 250 kHz, and therefore, each triangular period (including two C₂H₆ spectra) contains 1000 data points. Data sampling was triggered by the triangular signal to realize the complete sample of the first half-period of the sensing signal, which contains 500 points. Each time, N = 80 frames were sampled, which required ~1 s plus the data-processing time. All the data were recorded by a Dell computer (model # PP04X) for processing and postanalysis. Furthermore, a standard gas generator (Environics, Series 4040) was used for the performance assessment of the C₂H₆ sensor. A 1.14-ppmv [balanced by nitrogen (N_2)] C_2H_6 cylinder and a pure N_2 cylinder were used as input to the gas generator for the preparation of C₂H₆ samples with different concentrations at ppbv levels. The same method was used to prepare C₂H₆ samples in all of the following experiments except for atmospheric C₂H₆ measurements. Our data-processing routine was based on LabVIEW.



Fig. 3 a Typical example of the fitting strategy for C_2H_6 laser absorption spectra at five different concentration levels of 30, 200, 300, 400 and 500 ppbv, where the balance gas was N₂. **b** Experimental data and fitting curves of the normalized absorption signal $u_{r,final}(t)$ for five C_2H_6 concentration levels

3.3 Results and discussion

Figure 3a shows the measured absorption signal after spectral averaging of five different C2H6 concentration levels (30, 200, 300, 400 and 500 ppbv and background information), where the balance gas was N₂. For each absorption signal in the first half-period with 500 data points, the last 50 data points were deleted due to the fact that they corresponded to a decrease of the triangular wave. In order to remove the effect of power variations caused by current changes, the two wings of the spectrum were extracted (including the first 50 points and the last 200 points from the 450 points) and polynomial fitting was applied to obtain the C_2H_6 spectral baseline $u_{r, bac}$ (representing the intensity I_0), as shown in Fig. 3a (solid line). Subsequently, the background signal was removed from the absorption signal by obtaining a differential signal. The ratio between this differential signal and the background signal was obtained (see Eq. (6)) to eliminate the background effect. The normalized



Fig. 4 a Measured values of $\text{Amp}[u_{r,\text{final}}(t)]$ versus calibration time *t* for 0, 50, 100, 200, 300, 400 and 500 ppbv C_2H_6 concentration levels, where the balance gas was N₂. **b** Experimental data and fitting curve of C_2H_6 concentration values as a function of $\text{Amp}[u_{r,\text{final}}(t)]$

absorption signals $u_{r, \text{final}}^{\exp}(t)$ for the five concentrations levels are shown in Fig. 3b. The infrared absorption line, $u_{r, \text{final}}^{\exp}(t)$, follows a Lorentzian lineshape function. Hence, the experimental data were fitted using the Lorentzian lineshape function, $u_{r, \text{final}}^{\text{fit}}(t) = \frac{A}{\pi \gamma \left[1 + \left(\frac{t-t_0}{\gamma}\right)^2\right]}$, for each con-

centration, where A, γ and t_0 were obtained by data fitting. The amplitudes of the fitting curves $(u_{r, \text{final}}^{\text{fit}}(t))$ were used to represent C₂H₆ concentrations, which are more accurate than those obtained by using the amplitude of $u_{r, \text{final}}^{\text{fit}}(t)$ due to signal fluctuations.

Figure 4a shows a time series of the concentration measurements at seven different flow rates, which correspond to C_2H_6 concentrations of 0, 50, 100, 200, 300, 400 and 500 ppbv with N₂ as the balance gas. For each C_2H_6 concentration level, a measurement was taken lasting ~5 min. The measured amplitudes of the normalized absorption signal $u_{\rm r, final}^{\rm fit}(t)$ for each concentration were



Fig. 5 a Measured C_2H_6 concentration levels using DAS by passing pure N₂ into the MPGC for zero concentration. **b** Allan–Werle deviation plot as a function of the averaging time, τ , based on the data shown in Fig. 5a

averaged and plotted as a function of $\operatorname{Amp}\left[u_{r,\,\text{final}}^{\text{fit}}(t)\right]$ as shown in Fig. 4b. A linear relation can be found between them, which is represented by the following fitting curve:

$$C = 7110 \operatorname{Amp} \left[u_{r, \text{ final}}^{\text{fit}}(t) \right] - 14.69$$
(8)

The C₂H₆ concentration can be determined from the measured value of Amp $\left[u_{r, \text{ final}}^{\text{fit}}(t)\right]$.

A C_2H_6 concentration measurement of the sample with zero concentration (pure N₂) was performed for a time period of ~1.7 h. The total variation range of the measured concentration is ~ ±30 ppbv for an observation time of ~1000 s, as shown in Fig. 5a. An Allan– Werle analysis was utilized to evaluate the stability of the C_2H_6 sensor system based on the measured data. The Allan–Werle deviation was plotted on a log–log scale versus the averaging time, τ as shown in Fig. 5b. The plot indicates a measurement precision of ~7.92 ppbv with a 1-s averaging time. With increasing averaging time, the Allan–Werle plot shows an optimum averaging time of ~166 s, corresponding to a precision of ~777 pptv. However, as the averaging time continues, the Allan–Werle derivation increases again, which shows that sensor-system drift becomes the dominant factor and decreases the sensor-system stability. The red solid line (which is proportional to the sqrt(1/ τ)) indicates that the theoretically expected behavior of the sensor system drifts start to occur.

4 Sensor performance using separate WMS scheme

4.1 Measurement formulation

In the case of WMS, the electrical drive signal of the DFB ICL is

$$u_{\rm wms}(t) = u_{\rm tri}(t) + u_{\rm sin}(t) \tag{9}$$

where $u_{tri}(t)$ is given by Eq. (1), and $u_{sin}(t) = A_{sin} \sin(\omega_{sin}t)$ is a modulation signal with A_{sin} and ω_{sin} as its amplitude and angular frequency, respectively. Hence a variation, $u_{WMS}(t)$, of the ICL leads to a change of the absorption coefficient, expressed as $\alpha_{wms}(t)$. As a result of optical-toelectrical conversion and amplification, an electrical signal is also obtained, which can be written as

$$u_{\rm r}(t) = KD_{\rm oe}I_0[1 + mu(t)][1 - \alpha_{\rm wms}(t)LC]$$
(10)

The 2f signal can be extracted from the orthogonal output of the lock-in amplifier, which is given by

$$A_{2f}(t) = \sqrt{(A_{2f,\perp})^2 + (A_{2f,\parallel})^2}$$
(11)

where

$$A_{2f,\perp}(t) = \int_{t-T_{\text{int2}}}^{t} u_r(\tau) \sin(2\omega_{\sin}\tau) d\tau, \ A_{2f,\parallel}(t)$$

$$= \int_{t-T_{\text{int2}}}^{t} u_r(\tau) \cos(2\omega_{\sin}\tau) d\tau$$
(12)

are two orthogonal components and T_{int2} is an integrationtime factor determined by the cutoff frequency of a related low-pass filter. The peak amplitude of the 2*f* signal corresponding to the peak absorption wavelength of C₂H₆ as max[$A_{2f}(t)$] is proportional to the C₂H₆ concentration, as

$$\max \left| A_{2f}(t) \right| = F(C) \tag{13}$$



Fig. 6 Measured 2f signal and scan signal for a ~100-ppbv C_2H_6 concentration, where the balance gas was N_2

where the expression of F can be determined experimentally by means of calibration of the C₂H₆ sensor system.

4.2 Experimental details

The ICL driver current, laser temperature and the pressure in the MPGC were the same as those used in the separate DAS scheme. The scan signal was a triangular signal with a frequency of 0.3 Hz and a peak-to-peak amplitude of 200 mV. The modulation signal was a sinusoidal signal of 5 kHz and an optimized amplitude of 0.026 V, resulting in a modulation depth of 0.074 cm⁻¹. The integration time of the lock-in amplifier was 10 ms, and its input sensitivity was 50 mV. The sampling rate of the DAQ card was set to 1 kHz. As a result, each triangular period (including two C_2H_6 spectra) contains 3333 data points. Data sampling was triggered by the triangular signal at the peak position of the 2*f* signal, denoted by max[$A_{2f}(t)$], as depicted in Fig. 6. The data of max[$A_{2f}(t)$] were recorded by the Dell laptop computer for subsequent processing and analyzing.

4.3 Results and discussion

A measured 2f signal and scan signal over one spectral scan for a 100-ppbv C₂H₆ concentration are depicted in Fig. 6, where the balance gas was N₂. A maximum amplitude max[$A_{2f}(t)$] = 20.71 mV was measured. The 2*f* signal was influenced by the presence of optical fringes, which affected the C₂H₆ minimum detection limit (MDL). The amplitude of the noise and MDL were estimated to be 1.58 mV and 100 ppbv/(20.71/1.58 mV) = 7.6 ppbv, respectively.

 C_2H_6 samples using N₂ as the balance gas different concentration levels from 0 to 100 ppbv were prepared with the standard gas generator as described in "Experiment details"



Fig. 7 a Measured 2*f* waveforms for ten C_2H_6 concentration levels of 100, 90, 80, 70, 60, 50, 40, 30, 20 and 10 ppbv, where the balance gas was N_2 . **b** Experimental data and fitting curve of C_2H_6 concentration levels (ppbv) versus max[$A_{2f}(t)$] (mV)

section. The 2f waveforms acquired at different concentrations are shown in Fig. 7a. The value of $\max[A_{2f}(t)]$ increases as the concentration level increases due to the increased absorption at the peak absorption wavelength. For a 10-ppbv concentration, a well-defined 2f signal can still be observed, which indicates a MDL of <10 ppbv. A sensor-system calibration was obtained by filling the MPGC with different gas samples for measuring the amplitude of the 2f signal. Each sample was tested for ~7 min. The measured data of $\max[A_{2f}(t)]$ for each concentration were averaged and plotted against the nominal concentration as shown in Fig. 7b. A linear relation was observed between $\max[A_{2f}(t)]$ and C. The fitting curve is given by

$$C = 4.737 \max[A_{2f}(t)] + 2.429 \tag{14}$$



Fig. 8 a Measured concentration using 2*f*-WMS for pure N₂ inside the MPGC to establish zero background C₂H₆ concentration condition. **b** Allan–Werle deviation plot as a function of averaging time, τ , based on the data shown in Fig. 8a

where C is in ppbv and $\max[A_{2f}(t)]$ is in mV.

Measurements of the C_2H_6 sample with 0 ppbv (pure N_2) over a period of ~2 h were taken, and the measured concentrations were recorded. An Allan–Werle analysis was utilized to assess the stability and precision when using this technique. Figure 8a exhibits the measured concentration versus time *t*, and Fig. 8b shows the Allan–Werle deviation as a function of averaging time τ . The Allan deviation is ~1.19 ppbv with a 4-s averaging time and also shows an optimum averaging time of 108 s corresponding to a stability of ~299 pptv. The decreasing red solid line indicates the theoretical expected behavior, which is proportional to sqrt($1/\tau$) of a sensor system dominated by white noise.





5 Sensor performances using a quasi-simultaneous DAS and WMS scheme

5.1 Experimental details

For this measurement scheme, the parameters of the ICL were the same as those in the previous two schemes. An

asymmetric drive signal with a frequency of 0.3 Hz was used, its first half-period was a rising ramp signal (peakto-peak amplitude: 200 mV) combined with a sinusoidal wave signal (frequency: 5 kHz; amplitude: 0.026 V), and its second half-period was only a falling ramp signal (peak-topeak amplitude: 200 mV). A LabVIEW-based platform on a laptop was modified, and its function diagram is shown in

Measurement scheme	Scan/modulation fre- quency	Allan deviation ^a	Primary technology	Advantages and disadvan- tages
Separate DAS	250 Hz/unused	7.92 ppbv (@ 1 s) 777 pptv (@ 166 s)	Background/absorption fit- ting based on LabVIEW	Simple, limited sensitivity
Separate WMS	0.3/5 kHz	1.19 ppbv (@ 4 s) 299 pptv (@ 108 s)	Harmonic extraction based on SR830	Complex, high stability
Quasi-simultaneous DAS and WMS	0.3/5 kHz	5.4 ppbv (@ 7 s) for DAS	Background/absorption fit- ting based on LabVIEW	Simple, low sensitivity
		2.9 ppbv (@ 7 s) for WMS	Harmonic extraction based on LabVIEW	Complex, high stability

Table 1 Intercomparison of C_2H_6 sensor-system performance obtained with three measurement schemes, separate DAS, separate WMS and quasi-simultaneous DAS and WMS

^a Allan deviation listed in the table is either the value obtained at the minimum averaging time of a sensor or the minimum value of the Allan deviation plot of a sensor

Fig. 9a. The sampling rate of digital to analog conversion (DAC) was 300 kHz, and there were 1000-k data points for each period of the drive signal. The sampling rate of analog to digital conversion (ADC) was also 300 kHz, which resulted in 1000-k data points for each period of the sampled signal. A typical frame of the sampled signal output from the detector is shown in Fig. 9b, where the C_2H_6 concentration was 90 ppbv with N₂ as the balance gas. Ethane absorption occurred both in the rising part and in the falling part of the absorption spectra signal.

After data sampling of a whole period (1000-k data points), the first 500-k data points were sent to an orthogonal lock-in amplifier, which was realized by LabVIEW software. Two orthogonal sinusoidal wave signals with 500-k data points were used as reference signals for extracting the two orthogonal components from the absorption signal, and details of this procedure are shown in Fig. 9a. The last 500-k data points were processed following a similar method adopted in the separate DAS scheme (see "Sensor performances using a separate DAS scheme" section). This method provided background fitting, background elimination, low-pass filtering (LPF, cutoff frequency: 10 Hz) and absorption line fitting. A 2f signal extracted from the first half-period and an absorption signal extracted from the second half-period were merged together. Typically, the 2f signal and the filtered/fitted absorption signals for a 90-ppbv C₂H₆ concentration level with N₂ as the balance gas are shown in Fig. 9c.

5.2 Measurements and results

The concentration levels of four C_2H_6 samples with N_2 as the balance gas of 0, 30, 60 and 90 ppbv, respectively, were measured. The measurement results based on DAS and WMS are shown in Fig. 9d, e, respectively. The average sampling period was ~7 s, which included a data sampling time (~3.4 s) as well as a data-processing time (e.g.,

lock-in time). As shown in the insets of Fig. 9d, e, the Allan deviations of the measurement results for the 0-ppbv C₂H₆ sample are 2.9 and 5.4 ppbv (@ 7 s) for WMS and DAS, respectively. These two values differ slightly from the Allan deviations, 1.2 ppbv (@ 4 s) for the separate WMS and 7.9 ppbv (@ 1 s) for the separate DAS. For WMS, this difference results from the use of a different signal generator and processing unit, e.g., a commercial SR830 lock-in amplifier for WMS and a LabVIEW-based lock-in amplifier for the quasi-simultaneous scheme. For DAS, the difference mainly arises from different scan-signal frequency and data-processing procedures, e.g., 250-Hz scan frequency and averaging of 80-frame spectra for a separate DAS mode, a scan 0.3-Hz scan frequency and no averaging of the absorption spectra for the quasi-simultaneous scheme.

6 Intercomparison and atmospheric C₂H₆ measurements

6.1 Intercomparison among the three schemes

 C_2H_6 concentration measurements were realized by using three different schemes, DAS, WMS and quasi-simultaneous DAS and WMS, using the same sensor platform. A comparison of the sensor-system performances among the three measurement schemes is listed in Table 1. Generally, it is simple to use DAS for the C_2H_6 concentration measurement, which only requires a triangular signal and fitting of the background for minimizing noise. The WMS detection technique requires both a scan and a modulation signal and a lock-in amplifier to extract harmonic signals. For WMS, the background noise can be minimized, and both precision and stability can be improved compared with DAS. As shown in Table 1, the Allan–Werle deviation is decreased by a factor of ~7–8 times (from 7.92 ppbv @ 1 s to 1.19 ppbv @ 4 s) in the case of a WMS scheme. A similar behavior can be found between DAS and WMS in the quasi-simultaneous DAS and WMS scheme, subject to some differences in the Allan deviation because of different software and hardware for the three schemes. Hence, these three detection schemes can be applied in different applications, depending upon the requirement of the sensor-system performance.

6.2 Atmospheric C₂H₆ measurement at Rice University, Houston, TX

The sensor system was located in the Space Science and Technology building on the Rice University campus. An oil-free pump (KNF Neuberger, Type N831.5 ANE/AF) was used to sample air from outdoors, and the pressure inside the MPGC was set to 100 Torr. Atmospheric C₂H₆ concentration levels were measured for 2 days of continuous monitoring (from 05:00 pm, February 17, 2016, to 05:00 pm, February 19, 2016, CDT), as shown in Fig. 10. The data-recording period of the WMS-based sensor system was set to ~4 s. The diurnal profile of the C₂H₆ concentration shows an increase during the early morning between 01:00 and 08:30 am. The early morning peak and the diurnal trends observed for the C2H6 mixing ratio were the same for the 2 days. On February 18, a sharp increase of C_2H_6 concentration of ~30 ppbv was observed at 8:00 am. At other time periods, the C_2H_6 concentration levels were below 5 ppbv. Basically, the MDL of the reported C_2H_6 sensor is ~ three times the Allan deviation (1.19 ppbv) and is estimated to be ~4 ppbv. Hence, the reported sensor system can monitor >4 ppbv atmospheric C_2H_6 concentration levels.

6.3 Field test of the C₂H₆ sensor at a CNG facility located in Houston, TX

The C_2H_6 sensor system based on the single-floor optical core and the separate WMS scheme was deployed in a rental vehicle to evaluate its performance for atmospheric C_2H_6 monitoring in a comprehensive field campaign. The car was driven from the Rice University campus monitoring C_2H_6 for a distance of ~21 miles to a commercial CNG station. Figure 11 shows C_2H_6 concentration levels detected at the Freedom Energy CNG station (located at 7155 High Life Drive, Houston, TX, with Globe Positioning Satellite (GPS) coordinates: 29°56′39″N, 95°31′21″W). The data-recording period of the reported field test was ~8 s, because of the associated GPS data processing. The vehicle remained at two locations for ~70 min from 11:30 am to 12:40 pm, respectively, on March 15,



Fig. 10 Monitoring of atmospheric C_2H_6 for a 48-h period using the reported sensor system based on WMS



Fig. 11 a Photograph of the vehicle with the WMS-based C_2H_6 sensor system parked at a Freedom Energy Compressed Natural Gas (CNG) station operated by O'Rourke in Houston, TX. **b** C_2H_6 concentrations measured at the Freedom Energy CNG O'Rourke Station for a ~70-min sampling period

2016. Several peaks in the C_2H_6 mixing ratios compared with observed background levels (~4 ppbv) were observed, while our vehicle was stationary at these locations. C_2H_6 concentrations as high as ~12 ppbv were detected at the Freedom Energy CNG station when a gas truck appeared for refueling. This field test verified that our reported sensor system can be used effectively to monitor C_2H_6 at the ppb levels which were above the MDL of the sensor.

7 Conclusions

A CW, TEC, DFB ICL-based mid-infrared sensor was developed for ppb-level C₂H₆ detection using an absorption line at 2996.88 cm⁻¹ and operating at <100 Torr pressure. A dense patterned MPGC can provide a 54.6-m optical path length with a small sampling volume of 220 ml to facilitate a fast gas exchange demonstrating the potential of compact, sensitive trace gas sensor technology. Three measurement schemes based on two different techniques were employed to assess the C_2H_6 sensor performance. MDLs of ~7.92 ppbv for an averaging time of 1 s for the separate DAS scheme and ~1.19 ppbv @ 4 s for the separate WMS scheme were obtained. MDLs of 299 pptv for an averaging time of 108 s using separate WMS scheme compared to 777 pptv @ 166 s using separate DAS scheme were realized. Similar sensor performance was demonstrated in the quasi-simultaneous DAS and WMS scheme. Atmospheric C_2H_6 measurements at Rice University and a field test at a commercial CNG station in Houston, TX, were conducted using the sensor system based on the WMS scheme. The reported sensor system can be adapted to other trace gas species by using an ICL or QCL with the appropriate central wavelength.

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