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RAPID COMMUNICATION

Continuous wave, distributed feedback diode laser based sensor for trace-gas detection of ethane

K. Krzempek · R. Lewicki · L. Nähle · M. Fischer · J. Koeth · S. Belahsene · Y. Rouillard · L. Worschech · F.K. Tittel

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Abstract The development of a continuous wave (CW), thermoelectrically cooled (TEC), distributed feedback (DFB) laser diode based spectroscopic trace-gas sensor for ultra-sensitive and selective ethane (C_2H_6) concentration measurements is reported. The sensor platform used tunable diode laser absorption spectroscopy (TDLAS) based on a 2f wavelength modulation (WM) detection technique. TDLAS was performed with a 100 m optical path length astigmatic Herriott cell. For an interference free C_2H_6 absorption line located at 2976.8 cm^{-1} a 1σ minimum detection limit of 240 pptv (part per trillion by volume) with a 1 second lock-in amplifier time constant was achieved. In addition, reliable and long-term sensor performance was obtained when operating the sensor in an absorption line locked mode.

K. Krzempek
Laser & Fiber Electronics Group, Wroclaw University of Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland

R. Lewicki · F.K. Tittel (✉)
Department of Electrical and Computer Engineering, Rice University, 6100 Main Street, Houston, TX 77251, USA
e-mail: fkt@rice.edu
Fax: +1-713-3485686

L. Nähle · M. Fischer · J. Koeth
Nanoplus GmbH Oberer, Kirschberg 4, 97218 Gerbrunn, Germany

S. Belahsene · Y. Rouillard
Institut d'Electronique du Sud, UMR 5214 CNRS, Université Montpellier 2, 34095 Montpellier, France

L. Worschech
Technische Physik, University of Würzburg, Am Hubland, 97074 Würzburg, Germany

1 Introduction

Tunable laser diode absorption spectroscopy (TDLAS) has proven to be an excellent tool for trace gas detection in environmental [1–3], biomedical [4–10], industrial [11, 12] and national security [3] applications, providing fast, in situ, and real time, ultra-sensitive detection and monitoring, with an ability of being highly selective, precise and accurate [13]. In this work we focused on ethane detection, which along with methane, is one of the most abundant hydrocarbons in the atmosphere that strongly affect both atmospheric chemistry and the climate [14, 15]. Similar to methane the major sources of ethane in the atmosphere are related to fossil fuel and biofuel consumption, biomass burning process, vegetation/soil or natural gas loss. Oil and gas prospecting has been explored based on naturally occurring ethane seepages that accompany hydrocarbon reservoirs in desert environments [16, 17]. Furthermore, ultra-sensitive detection of ethane has found application in medical breath analysis. Monitoring elevated levels of ethane in exhaled human breath can be used as a non-invasive method to identify and monitor different diseases, such as asthma [18], schizophrenia [19], or lung cancer [20]. In addition breath ethane has been used as a biomarker of vitamin E deficiency and therapy in children with chronic liver disease [21]. In the mid-infrared (mid-IR) spectral region, a C_2H_6 strong fundamental absorption band is located at ∼3.36 μm (2977 cm^{-1}). Moreover, the entire spectral region between 3 μm and 4 μm is attractive because several important hydrocarbons such as methane, acetone, formaldehyde, and butane have their fundamental absorption bands in this region. This spectral range can be targeted with different types of short wavelength mid-IR, continuous wave (CW) or pulsed room-temperature laser source such as nonlinear frequency conversion based mid-IR lasers [22], quantum cascade or interband cascade lasers [23–32] and

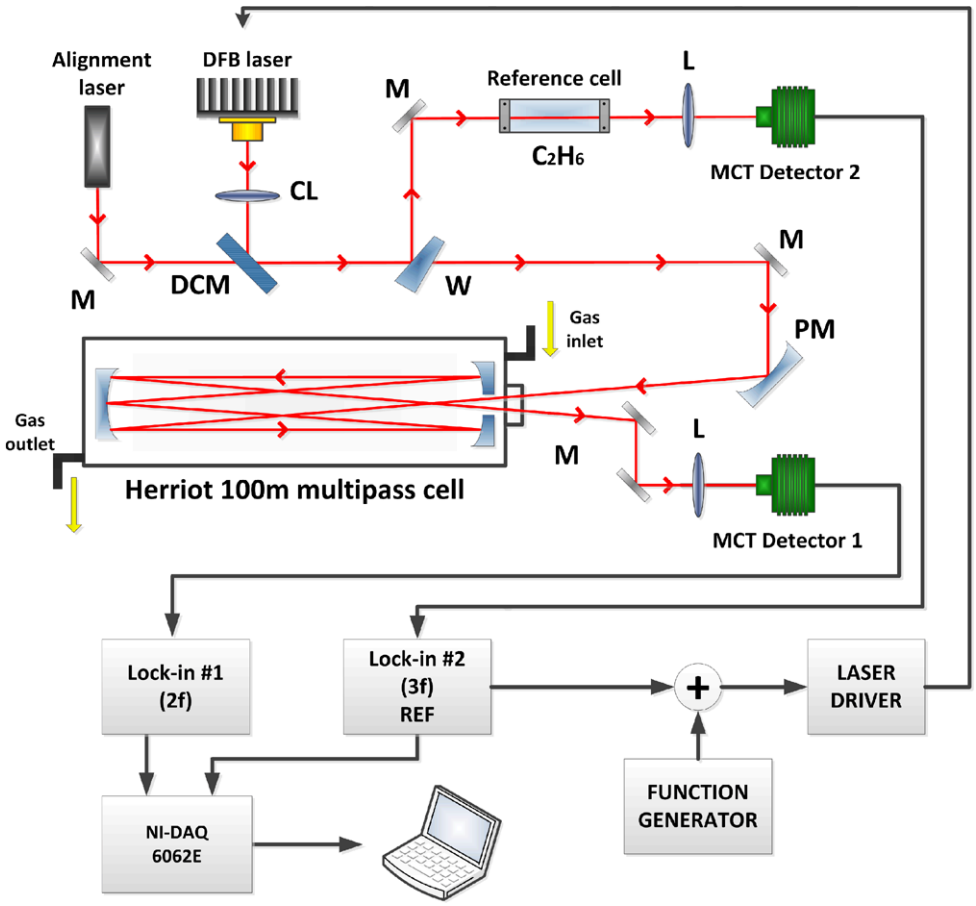

Fig. 1 Schematic of a C_2H_6 gas sensor employing a 3.36 μm DFB laser diode as a spectroscopic source. CL—collimating lens; L—CaF_2 lens; M—mirror; DCM—dichroic mirror; W—CaF_2 glass wedge; MCT—mercury–cadmium–telluride photodetector; PM—parabolic mirror

semiconductor laser diodes [33–37]. In this work a CW, GaSb based, TEC DFB semiconductor laser diode, with type-I transitions was used as the excitation source for the sensitive detection of sub-ppb C_2H_6 concentration levels.

2 Experimental details

2.1 DFB laser diode sensor platform

The C_2H_6 sensor architecture is depicted in Fig. 1. A thermoelectrically cooled DFB laser diode (nanoplus GmbH), emitting single frequency CW radiation at 2977 cm^{-1} (3.36 μm), was employed as a spectroscopic source. This laser diode was packaged in a TO-5 can and attached to an aluminum heatsink in order to remove heat dissipated from the hot side of the TEC and the diode laser structure. The laser diode was driven by a commercial current source (ILX, model LDX-3220). The current was modulated at 16.3 kHz in order to perform wavelength modulation spectroscopy. The operating temperature of the laser diode was set and controlled at 10°C using a temperature controller (Wavelength Electronics Inc., FFT-2000). The laser diode beam was collimated with a 6.5 mm in diameter antireflection coated BlackDiamond™ aspheric lens (Thorlabs, model C036TME-E). To simplify the alignment process of the mid-IR optical sensor components, a semiconductor laser diode, emitting radiation at $\lambda = 630$ nm, was used as a reference beam. Both laser diode beams, visible and mid-IR, were combined by means of a dichroic mirror (ISO Optics, model BSP-DI-25-3). A CaF_2 wedged window, acting as a ~95/5 beamsplitter, placed after the dichroic mirror, was employed in order to split the laser diode beam into the TDLAS signal and a reference channel. In the main channel the laser diode beam was coupled into a 100 m optical path length astigmatic Herriott multipass gas absorption cell (Aerodyne Research, Inc.) by using a 500 mm focal length concave mirror. The concave mirror had its focusing point in the center of the multipass cell in order to obtain a nearly collimated output beam. The beam exiting the multipass gas cell was focused onto a TEC, mercury-cadmium-telluride (MCT) detector (Vigo, PVI-2TE-5) using a 75 mm focal length CaF_2 lens. The reference channel was used to lock the laser frequency to the peak of the selected C_2H_6 absorption line. Hence, the laser beam was passed through a reference cell, filled with a 25 ppm ethane in N_2 mixture at 50 Torr, and then detected by a second TEC MCT detector. The TDLAS signal and reference channel MCT detector signals were amplified by transimpedance preamplifiers

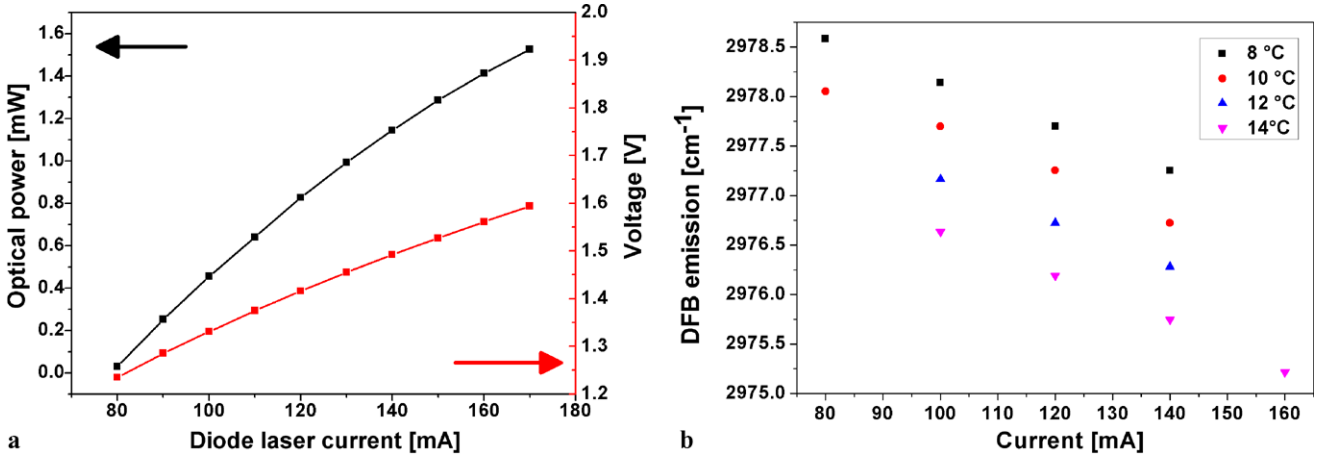

Fig. 2 (**a**) LIV curve for the 3.36 μm CW TEC DFB laser diode operating at 10°C; (**b**) temperature and current tuning characteristics of CW TEC DFB laser diode

and delivered to two lock-in amplifiers (Signal Recovery model 7265) for further data processing. The signal lock-in amplifier was set to measure a 2f signal, whereas the reference lock-in amplifier was set to measure a 3f signal (see Fig. 1). In-phase and quadrature signal components of both lock-in amplifiers were acquired by a data acquisition card (National Instruments, model NI-DAQ 6062E) and stored on a laptop computer operated by a LabView program. The pressure inside the multipass gas was controlled by a pressure controller (MKS Instruments model 649) at 250 Torr, whereas the flow was adjusted by a needle valve from 200 to 1000 ml/min.

2.2 CW TEC DFB laser diode parameters

A novel CW GaInAsSb/AlGaInAsSb DFB laser diode was designed to emit single-mode radiation near 2977 cm^{-1} (3.36 μm) in order to target a selected rotational-vibrational C_2H_6 absorption line. The TO-5 mounted TEC laser diode can be operated at temperatures between 6°C and 21°C, without the need of water or air cooling. A maximum power of 1.75 mW of the collimated laser diode beam was measured, when the laser diode operating temperature and current were set to 6°C and 170 mA, respectively. The measured LIV curve at the selected laser operational temperature of 10°C is shown in Fig. 2a. Experimentally determined current and temperature tuning coefficients of the DFB laser diode structure are -0.022 cm^{-1}/mA and -0.26 cm^{-1}/°C, respectively. For the available temperature and current ranges, the DFB laser diode is tunable between 2975.3 cm^{-1} and 2978.9 cm^{-1} (shown in Fig. 2b) in a single frequency mode. This spectral range is well suited for sensitive C_2H_6 detection, because it covers one of the strongest absorption lines in the ν_7 fundamental band of ethane.

2.3 Experimental results

HITRAN absorption spectra of 100 ppb ethane, 1.8 ppm methane, and 2% water simulated for 250 Torr gas pressure and a 100 m effective optical path length are depicted in Fig. 3. This spectral simulation shows that the ethane absorption line located at 2976.8 cm^{-1} is interference free from other molecules that are normally present in the atmosphere (such as H_2O, CO_2, and CH_4). A 2f WMS detection technique was employed in order to perform sub-ppb C_2H_6 concentration measurements. When using WMS the laser diode frequency was scanned across the selected C_2H_6 absorption line ($\sim$0.5 cm^{-1}) by applying a 100 mHz saw-tooth ramp to the external modulation input of the laser diode current driver. Furthermore, a 16.3 kHz sinusoidal signal, with an amplitude of 9 mA superimposed on the saw-tooth ramp, was applied to the laser diode. This amplitude represents an optimum modulation depth resulting in the highest measured 2f C_2H_6 signal at 250 Torr. Several 2f WM scans, acquired at different C_2H_6 concentration levels, are shown in Fig. 4. The minimum detectable C_2H_6, concentration determined was 290 pptv (1σ) for a 1 sec time constant of the lock-in amplifier, when the laser diode was operated in a scan mode. In addition a linear dependence of the detected 2f signal as a function of ethane concentration was observed and illustrated as an insert in Fig. 4.

A line-locking technique was implemented in order to acquire C_2H_6 concentration data only at a single laser diode frequency that corresponds to the peak of the selected C_2H_6 absorption line. With this technique the reference channel 3f signal, with a zero crossing point at the maximum of the main channel 2f signal, was monitored by LabView (National Instruments, Inc.) software. Therefore, any CW TEC DFB laser diode frequency drift, caused either by laser diode temperature or current fluctuations, will introduce a non-zero offset to the measured reference 3f signal value. This

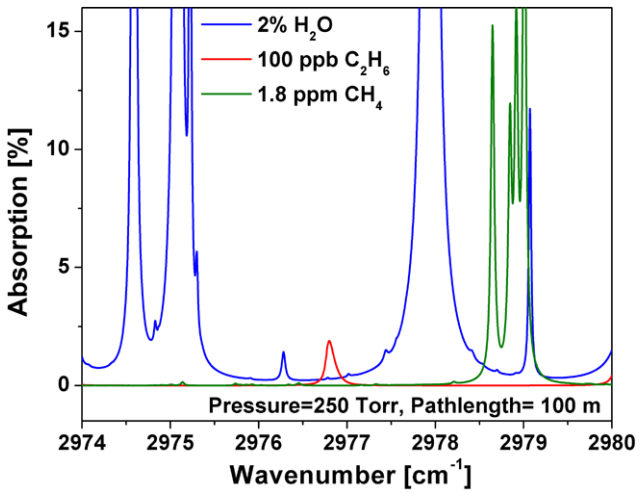

Fig. 3 HITRAN absorption spectra of 100 ppb ethane, 1.8 ppm methane, and 2% water simulated for a 250 Torr gas pressure and a 100 m effective optical path length

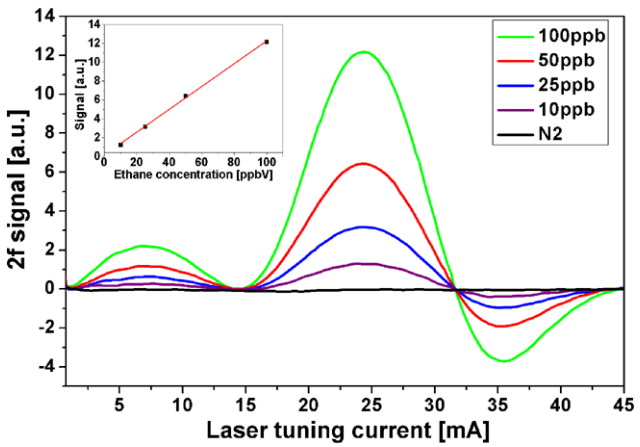

Fig. 4 2f WMS scans, acquired at different C_2H_6 concentration levels, using a 100 m astigmatic Herriot multipass cell filled at a gas pressure of 250 Torr. *The inset* shows the linear dependence of measured 2f signal as a function of the C_2H_6 concentration

offset was eliminated by adding a LabView based PID controller correction signal to the external modulation input of the laser diode current driver.

Long-term continuous operation of the C_2H_6 sensor was tested with the laser diode operating in a line locked mode at 2976.8 cm^{-1}. To determine the minimum detection limit of the sensor an ultra high purity (UHP) nitrogen was flushed into the astigmatic Herriott multipass gas absorption cell and replaced with a certified mixture of 100 ppbv C_2H_6 in N_2. For a 100 m effective optical path length, a target gas pressure of 250 Torr and 1 sec lock-in amplifier time constant the calculated signal to noise ratio was ~420. This results in a measured minimum 1σ C_2H_6 detection sensitivity of 240 pptv.

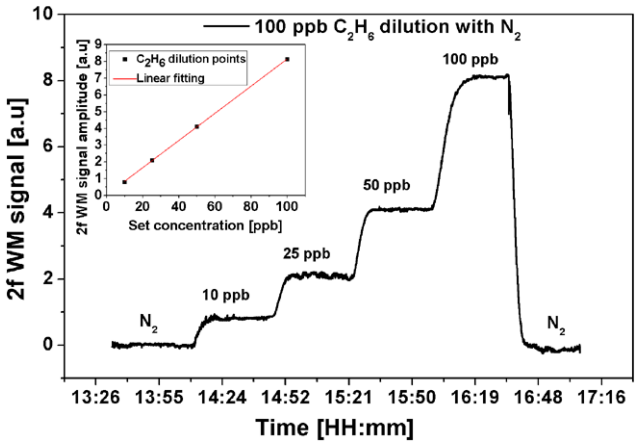

Fig. 5 2f WMS signal measurements for different ethane concentration levels acquired at a gas pressure of 250 Torr. *The insert* depicts the measured 2f WM signal amplitude as a function of the C_2H_6 concentration

The linear response of the ethane sensor was also verified in the line locking mode by diluting the certified mixture of 100 ppbv C_2H_6 in N_2 with UHP nitrogen. The results of 2f WMS signal amplitude measurements for different diluted ethane concentrations are shown in Fig. 5. The inset shows the linear dependence. The intervals between each C_2H_6 concentration value applied to the sensor were set to 35 min in order to reach a stable level of the measured signal. The N_2 signal levels, recorded at the beginning and at the end of the measurement, indicate that no significant drift in the baseline level occurred during the entire measurement period of 3.5 hours.

3 Conclusions

A 3.36 μm CW TEC DFB laser diode has proven to be an excellent compact spectroscopic source for ultra-sensitive and highly selective C_2H_6 concentration measurements. A TDLAS using 2f wavelength modulation technique was employed in order to perform sub-ppb C_2H_6 concentration measurements. The laser diode frequency was scanned across an interference free C_2H_6 absorption line located at 2976.8 cm^{-1} by applying both a saw-tooth ramp and a sinusoidal signal to the external modulation input of the laser diode current driver. A 1σ minimum detection limit of 240 pptv with a 1 second lock-in amplifier time constant was achieved at a gas pressure of 250 Torr.

A significant decrease in sensor platform size will be accomplished by replacing the 1 m long astigmatic Herriott multipass gas absorption cell with a miniaturized multipass cell as well as adopting an ultra-compact electronics controller [38] that will eliminate the need for commercially available laser diode and TEC drivers as well as two lock-in amplifiers. Further improvements in sensor detection limit

can also be obtained by using a more sensitive mid-IR detector. In addition the reported sensor platform is capable of using other compact mid-IR laser sources, making the reported sensor architecture a versatile platform for trace-gas analysis in the mid-infrared region.

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