Sensitive detection of ethane using tunable laser diode absorption spectroscopy near 3.3 μm

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Abstract: A spectroscopic trace-gas sensor employing a continuous wave, thermoelectrically cooled distributed feedback laser diode and a 100 m optical pathlength astigmatic Herriott cell for sensitive and selective detection of ethane near 3.3 μm is reported.

OCIS codes: (300.6340) Spectroscopy, infrared; (140.2020) Diode lasers; (120.6200) Spectrometers and spectroscopic instrumentation

1. Introduction

Trace gas optical sensors employing tunable laser diode absorption spectroscopy (TDLAS) have proven to be an excellent tools for fast, selective, in situ, and real time detection of molecular species [1,2]. For highly sensitive detection of hydrocarbons an attractive spectral region is located between 3 and 4 μm where several important hydrocarbons such as methane, ethane, acetone, formaldehyde, and butane have their fundamental absorption bands. In this work the major emphasis was focused on ethane (C_2H_6) detection, which is the most abundant hydrocarbon in the atmosphere after the methane (CH_4). The prominent sources of methane and ethane emission to the atmosphere are mostly associated with fossil fuel and biofuel consumption, biomass burning process, vegetation/soil or natural gas loss [3, 4]. Therefore, monitoring atmospheric concentration levels of both with sub-ppb resolution is important in finding a correlation between these two molecules and to determine their role in atmospheric chemistry and climate changes. Furthermore, ultra-sensitive detection of ethane is of interest 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 [5], schizophrenia [6], or lung cancer [7]. In addition breath ethane has been used as a biomarker of vitamin E deficiency and therapy in children with chronic liver disease [8].
In this work sensitive, sub-ppb detection of C_2H_6 concentration levels was performed using a GaSb based, continuous wave(CW), and thermoelectrically cooled (TEC) distributed feedback (DFB) laser diode, emitting radiation in the ν_7 fundamental band of C_2H_6 located at ~ 3.36 μm (2977 cm^{-1}).

2. Sensor configuration

The architecture of the C_2H_6 sensor based on a CW TEC DFB laser diode (nanoplus GmbH) is illustrated in Fig.1. Single mode frequency tuning of the laser diode from 2975.3 to 2978.9 cm^{-1} is well suited for sensitive C_2H_6 detection, because it covers one of the strongest rotational-vibrational absorption line of ethane. Moreover the DFB laser diode, packaged in a TO-5 can and attached to an aluminum heatsink, was designed to operate at temperatures between 6 ^oC and 21 ^oC, without the need of water or air cooling. A maximum optical power of 1.75 mW was obtained when the laser diode operating temperature and current were set to 6 ^oC and 170 mA, respectively.

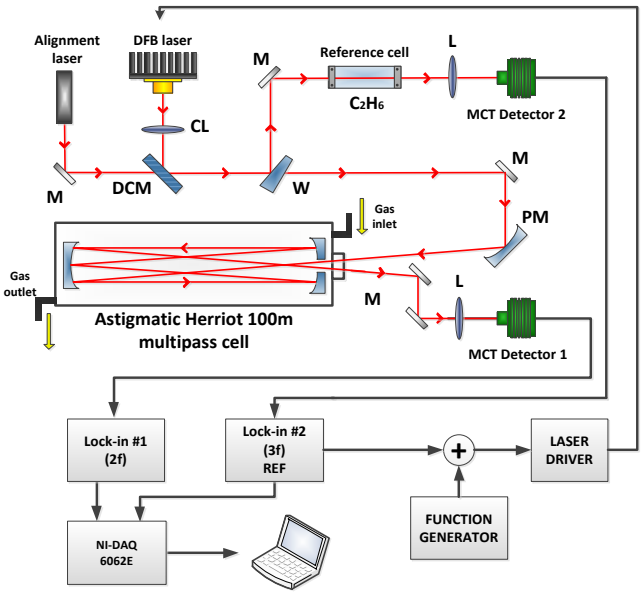
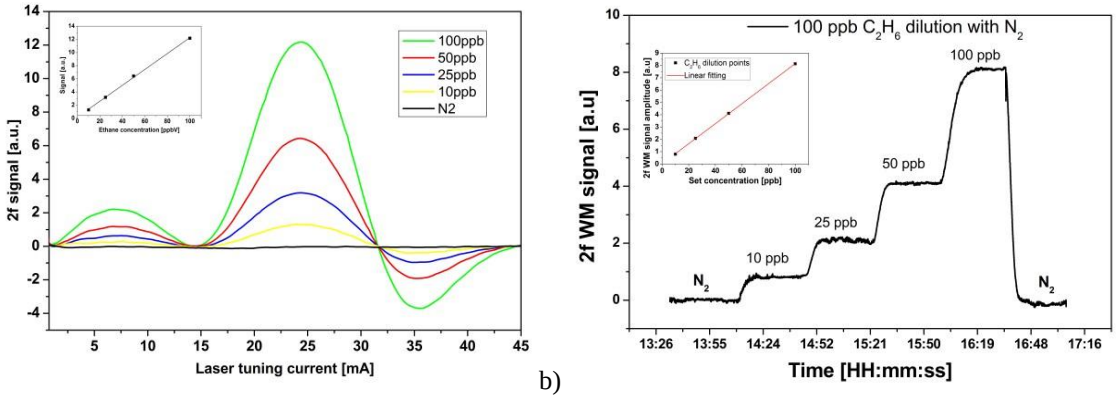


Fig. 1. Schematic of a C_2H_6 gas sensor employing a 3.36 μm DFB laser diode as a spectroscopic source. CL - collimating lens; L - CaF_2 lens; M - mirror; DCM - dichroic mirror; W - CaF_2 wedge window; MCT – mercury-cadmium-telluride photodetector; PM – parabolic mirror.

The laser diode beam was collimated with a 6.5 mm in diameter anti-reflection 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) and then split by a CaF_2 wedged window into the TDLAS signal and a reference channel. In the signal channel the laser diode beam was coupled into a 100 m optical pathlength astigmatic Herriott multipass gas absorption cell (Aerodyne Research, Inc.) by using a 500 mm focal length concave mirror. 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 including a reference cell and another TEC MCT detector was used to lock the laser frequency to the peak of the selected C_2H_6 absorption line. A 10 cm long reference cell was filled with a 25 ppm ethane in N_2 mixture at 50 Torr. The TDLAS signal and reference channel MCT detector signals were amplified by transimpedance preamplifiers 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). 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. Moreover, to perform wavelength modulation spectroscopy the laser diode current, supplied from the ILX laser diode current source, was additionally modulated at 16.3 kHz. The operating temperature of the laser diode was set and controlled at 10 ^oC using a Wavelength Electronics temperature controller.

3. Experimental results

High resolution spectroscopic measurements of C_2H_6 were performed by targeting the 2976.8 cm^{-1} ethane absorption line, which was found to be interference free from other molecules that are normally present in the atmosphere (such as H_2O, CO_2, and CH_4). In order to perform sub-ppb C_2H_6 concentration measurements 2f wavelength modulation spectroscopy (WMS) was selected as the detection technique of choice. Several 2f WM scans, acquired at 250 Torr for different C_2H_6 concentration levels, are shown in Fig. 2a. The minimum detectable C_2H_6, concentration was determined to be 290 pptv (1σ) for a 1 sec time constant of the lock-in amplifier and an optimum modulation depth of 9 mA. For these measurements a linear dependence of the detected 2f signal as a function of ethane concentration is depicted as an insert to Fig. 2a.



a) b)

Fig. 2a) 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; b) 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 C_2H_6 concentration data acquired at a single laser diode frequency that corresponds to the peak of the selected C_2H_6 absorption line will be also reported. The 2f WMS signal amplitudes for different diluted ethane concentrations, when the C_2H_6 sensor was continuously operating in a line locked mode at 2976.8 cm^{-1}, are shown in Fig. 2b. The intervals between each C_2H_6 concentration value applied to the sensor were set to 35 min. in order to reach a stable measured signal level. 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. The linear response of the line locked ethane sensor is illustrated as an inset to Fig. 2b. For a 100 m effective optical pathlength astigmatic Herriott absorption cell, a target gas pressure of 250 Torr and an 1 sec lock-in amplifier time constant the measured minimum detection sensitivity (1σ) of C_2H_6 was 240 pptv.

The reported sensor platform is capable of using other compact mid-IR laser sources, making this system a universal spectrometer for analysis of different trace-gas species. As an example some experimental results for methane detection obtained with a 3.26 μm ($3070cm^{-1}$) external cavity laser diode will be also discussed. A significant decrease in sensor size will be further addressed by replacing the 100 m long astigmatic Herriott absorption cell by a more compact multipass cell [9] as well as adopting a miniaturized electronics controller that will eliminate the need for commercially available external laser diode and TEC drivers and two lock-in amplifiers [10].

3 References

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