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Multiplexed gas spectroscopy using tunable VCSELs

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ABSTRACT

Detection and identification of gas species using tunable laser diode laser absorption spectroscopy has been performed using vertical cavity surface emitting lasers (VCSEL). Two detection methods are compared: direct absorbance and wavelength modulation spectroscopy (WMS). In the first, the output of a DC-based laser is directly monitored to detect for any quench at the targeted specie wavelength. In the latter, the emission wavelength of the laser is modulated by applying a sinusoidal component on the drive current of frequency ω , and measuring the harmonics component (2 ω) of the photo-detected current. This method shows a better sensitivity measured as signal to noise ratio, and is less susceptible to interference effects such as scattering or fouling. Gas detection was initially performed at room temperature and atmospheric conditions using VCSELs of emission wavelength 763 nm for oxygen and 1392 nm for water, scanning over a range of approximately 10 nm, sufficient to cover 5-10 gas specific absorption lines that enable identification and quantization of gas composition. The amplitude and frequency modulation parameters were optimized for each detected gas species, by performing two dimensional sweeps for both tuning current and either amplitude or frequency, respectively. We found that the highest detected signal is observed for a wavelength modulation amplitude equal to the width of the gas absorbance lines, in good agreement with theoretical calculations, and for modulation frequencies below the time response of the lasers (<50KHz). In conclusion, we will discuss limit of detection studies and further implementation and packaging of VCSELs in diode arrays for continuous and simultaneous monitoring of multiple species in gaseous mixtures.

Keywords: Vertical Cavity Surface Emitting Lasers, multiplexing, wavelength modulation spectroscopy, oxygen, water

1. INTRODUCTION

Gas composition analysis is needed in a wide variety of settings that include environmental as well as industrial processes monitoring [1]. In this study we carried on experiments for the detection of oxygen and water, two common components found in atmospheric environments [2, 3]. The detection of both gas and vapor species was carried on using current tunable VCSELS emitting near 763nm[4] and 1392 nm.

The detection of dipolar gas species (e.g. molecules composed of atoms with different electro-negativity) relies on strong absorption of infrared light (0.75-10 μ m) over an optical path containing the analyzed gas [2, 5]. Our approach is to vary the emission wavelength of infrared VCSEL devices to scan absorption lines. For monolithic devices the tuning is realized by changing the drive current that changes the device temperature through heat dissipation. Thermal expansion of the laser microcavity affects the longitudinal optical modes and shifts the emission to longer wavelengths. For the devices considered, the scanning range is about 4-10 nm, significantly larger than the absorption line widths of the gases considered, approximately 100 pm. Typical VCSEL parameters are 0.6 nm/mA and 0.06 nm/K for current and thermal tuning coefficients, and devices are driven with currents up to 10 -15 mA[6].

In the following we describe in more details our results on optimized detection using WMS along with concentration studies and integration arrangements for multiplexed detection of gas mixtures.

2. RESULTS

2.1 WMS vs. Direct Absorbance

Two methods were employed for detection. In the first one, direct absorbance spectroscopy, the emission wavelength of the laser was scanned by adjusting the tuning current in the device and the power measured after light propagation over a fixed length was recorded (Figs. 1a and 1c). Because the emission profile from the lasers has a divergence of about 30 degrees), a 20 cm focal length mirror was used to focus the light on the photodetector (Fig. 1g). The signal depends on the light-current characteristics of the device as well as the absorbance characteristics of the gas along the optical pathway.

Although oxygen is a diatomic molecule and does not have an electric dipole moment, it does have a magnetic dipole which exhibit the strongest signature absorption lines in the near infrared region around 763 nm or 13000 cm-1. Based on published spectroscopy literature data (HITRAN database), the strongest absorption lines are plotted in Fig. 1c. The 763 nm VCSEL devices (ULM Photonics) were characterized by taking the LIV (light-current-voltage) curves, also shown in Fig. 1a. The device exhibit a threshold current of approximately 0.5 mA and a power roll off around 4 mA. Devices were not driven over 7.5 mA to avoid irreversible damage. Absolute power measurements were calculated by calibrating the silicon photodetector with a Newport 1930C power meter for a responsivity of 0.525 A/W. For the oxygen detection experiments the laser beam was focused on a silicon photodetector over a double pass optical path of 40 cm. The wavelength domain was scanned over a 3 nm range containing three pairs from the oxygen P-branch of the A-band absorption. In the measurements shows here the current driver resolution is 1 uA and the integration time 0.4 s.

Water detection [7, 8] was performed in open atmosphere under conditions similar to the ones described earlier for oxygen sensing. The used laser device emitted around 1390 nm showing a good overlap with the absorption spectrum of water. In these experiments we used a gallium arsenide biased photo-detector since silicon photo-detectors have a detection cutoff wavelength around 1100 nm. As previously, the optical path was about 80 cm, and the atmospheric water concentration was estimated to be about 1%, corresponding to 50% humidity measured with a hygrometer. In Figs. 1d and 1e we show the detection results using the 1392 nm VCSEL. Very strong absorption lines are observed due to a combination of factors: high absorption strength lines as well as high water concentration. We also show a very good agreement of this measurement with indexed lines from HITRAN database (Fig. 1f).

In the second set of experiments (Figs. 1b and 1e) we employed wavelength modulation spectroscopy (scheme in Fig 1h) in which the driving signal on the VCSELs has and constant and a sinusoidal component of frequency ω [9-11]. Similarly to the direct absorbance method, the constant part is tuning the emission wavelength along the spectral range that contains the gas lines. The lorentzian dependence of the absorbance lines can be decomposed in a Fourier series with the basis an integer multiple of ω , and the first component, A ω leads to a photodetector signal of double frequency, 2 ω . While it is possible to use higher harmonics (e.g. 2 ω , 3 ω , 4 ω , etc) to measure the signal due to gas absorbance lines, we found that the second harmonic is optimal since it has high signal amplitude, low noise, and no background. All wavelength modulations spectroscopy measurements performed in this study are for the second harmonic. The modulation was optimized by performing a VCSEL tuning current sweep at fixed frequency. The optimal amplitude that maximized the 2 ω signal was observed for modulation amplitude that was close to the width of the absorption lines. While a higher modulation frequency is desired for better signal to noise, the optimal value is influenced by the switching characteristics of the devices considered. Slow devices cannot track the modulation signal such that the applied sinusoidal current will not correspond to a sinusoidal time dependence of the emission wavelength. We found that a modulation frequency of 5 kHz is a good compromise between the two trends.

Also the wavelength modulation spectroscopy measurements were related to data from HITRAN database, and a good agreement was observed for both detected species (Figs. 1c, and 1f).



Figure 1. Light current curves for 763 nm (1a) and 1392 nm (1d) VCSELs,. A decrease in emission corresponding to oxygen and water absorption is compared to the wavelength modulation spectroscopy signal (1b and 1e) along with the line strength from HITRAN database (1c and 1f). Schematic of the open space measurement setup (1g) the WMS scheme (1h).

2.2 Concentration Studies

Concentration dependent studies were performed for oxygen in a White multi-pass cell (Figs 2d, 2e, 2f) with an equivalent optical path of 2.6 m for a total of 27 passes. The multi-pass cell was integrated with a flow cell with gas

inlets, and specific concentrations of oxygen were delivered by adjusting the settings of two mass flow controllers that directed the flow of each pure component of the mixture, oxygen and nitrogen. In Fig. 2a we present representative wavelength modulation spectroscopy lines for one absorption line for oxygen at concentration of 10, 50, and 100%. Furthermore, the oxygen concentration in the multi pass cell was varied from 0 to 100% in 1% increments (Fig. 2b). Horizontal cutouts from the color plot correspond to the graphs presented in 2a. The concentration dependence of the second harmonic signal is plotted in Figure 2.c using the maximum value. For low oxygen absorbance the dependence is linear, while for concentrations approaching 100% a sub-linear trend is observed due to the exponential dependence of absorbance on concentration. Preliminary estimations for the limit of detection are based on the observation of ¹⁶O isotope resonance lines place a lower bound on the order of 100 ppm.



Figure 2. (a) Wavelength modulation spectroscopy signals for a 763 nm VCSEL for a 2.6 m optical path with oxygen in concentrations of 10, 50, and 100%. (b) Two dimensional plot of the second harmonic wavelength modulation signal for oxygen concentrations varying from 0 to 100% in 1% steps. (c) Relation between the oxygen concentration and the maximum of the second harmonic is following an approximately linear dependence. The red line represents a linear fit of the first ten data points that highlight the sub-linear dependence at higher concentrations; (d-e) top view and central mirror view of bean propagation and spots distribution in the White Gas Cell (Fraunopher Institute) and (f) illustrations in the ZMAx model.

2.3 Multiplexing

The multiplexed detection of both species was implemented using a printed circuit board loaded with electronic switches that routed the measurement circuitry to either of the oxygen or water sensing devices. The measurements were performed in open atmosphere using a 20 cm focal length mirror that focused the emission of each laser to its corresponding photodetector. Three device circuits considered were the laser drive, the thermistor, and the thermoelectric circuits. In addition, a set of switches controlled the photodetector signal route to the lock in amplifier from either a silicon or a gallium arsenide device that measured the light from the 763 and 1392 nm VCSELS. A digital output data acquisition powered and signaled the device be addressed on the switch board. The multiplexed gas analysis experiment mimicked a surveillance situation in which gas analysis was performed over 24 hours with measurements being taken every 8 hours. At initial time the water spectrum was acquired, followed by that of oxygen half an hour later, after which this cycle was repeated periodically.



Figure 3. Multiplexed detection of oxygen and water. A picture of the multiplexing board showing the main components (3a). Both species were detected on the same board using a series of binary electronic switches. The water measurements were performed at 0, 8, 16, and 24 hours, while the oxygen measurements were performed with 0.5 hours delay (3b and 3c).

Although a loss in sensitivity was observed for the oxygen sensing laser driven on the board the data indicated sufficient sensitivity for taking concentration measurements bellow 1%. Further work needs to be conducted to identify the origin of the change in the overall shape of the wavelength modulation spectroscopy scans as well as the relative amplitude of the second harmonic lines.

3. DISCUSSION

In this work we investigated the use of VCSELs for detection of oxygen and water using both direct absorbance and wavelength modulation spectroscopy. The direct absorbance method has the disadvantage of a having a non-zero background as well as lower signal to noise if we assume an inversely proportional dependence between noise and

measurement frequency. Both detection methods correlate well with the expected location and strength of the absorption lines tabulated in the HITRAN database.

The concentration measurements related the fraction of oxygen present in a multi pass White cell with the amplitude of the 2^{nd} harmonic signal and a linear dependence was observed between the two at low concentrations.

Multiplexed measurements of the two analyzed species were performed using an array of solid state switches that cycled the active devices between the 763 and 1392 nm VCSELs as well as between their corresponding photodetectors. While a degradation in the shape of the light current curves for the oxygen detection laser was noticeable, the approach is still functional with respect to line identification and concentration quantization.

Further investigation are needed for a more precise determination of the limit of detection for both water and oxygen as well as for other analyte targets of interest, carbon monoxide, carbon dioxide, methane and nitrous oxide. On the multiplexing side a more compact integration of the laser diodes within a muti-pass flow cell is needed for a smaller footprint of the gas analyzer.

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