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Sensitive detection of methane at 3.3 μm using an integrating sphere and Interband Cascade Laser

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ABSTRACT

Detection of methane at 3.3μm using a DFB Interband Cascade Laser and gold coated integrating sphere is performed. A 10cm diameter sphere with effective pathlength of 54.5cm was adapted for use as a gas cell. A comparison between this system and one using a 25cm pathlength single-pass gas cell is made using direct TDLS and methane concentrations between 0 and 1000 ppm. Initial investigations suggest a limit of detection of 1.0ppm for the integrating sphere and 2.2ppm for the single pass gas cell. The system has potential applications in challenging or industrial environments subject to high levels of vibration.

Keywords: Interband Cascade Laser, integrating sphere, tunable diode laser spectroscopy, TDLS, multipass cell, methane detection

1. INTRODUCTION

Average global concentrations of greenhouse gases are at their highest levels for 11,000 years [1], increasing at a rate of 2.2% per year between 2000 and 2010 [2]. Methane is a colourless, odourless gas that can be found extensively in nature, being the most abundant organic trace gas in the atmosphere [3]. Although the concentration of methane is significantly lower than carbon dioxide (1.8ppm compared with 391ppm), it has a global warming potential 34 times greater than that of CO2 over a hundred year period. As a result, trace detection of methane has attracted significant attention for environmental monitoring.

Sensors based on the use of tunable diode laser spectroscopy (TDLS) provide a high specificity to the target gas, a fast response time, repeatable measurements and provide low limits of detection [4]. However when used outside of laboratory conditions, the effectiveness of TDLS sensors can be reduced by fluctuations in ambient conditions and vibrations, as standard systems require precise optical alignment to provide high quality results.

Interband Cascade Lasers (ICLs) fill an important gap between the wavelength coverage of standard laser diodes and Quantum Cascade Lasers (QCLs), having an operating range between 3 and 6 μm. This presents the opportunity to make measurements at the fundamental absorption bands of a number of C-H, N-H and O-H molecules [4]. Difference Frequency Generation (DFG) sources and QCLs are also available in the mid infrared; however they each have disadvantages compared with ICLs. DFG sources are more complex than ICLs and can be sensitive to misalignment, whilst QCLs are noisier and not currently available in the 3-4μm region.

Originally used for the measurement of the total flux of light sources, integrating spheres have also gained attention as multipass absorption cells. These spheres consist of a hollow container with a diffusely reflective internal surface. Typically, there are two or more ports for light sources and detectors as well as two ports for gas inflow and exhaust. To prevent direct illumination of the detector by the light source, a light barrier (or baffle) is often used. Integrating spheres do not suffer from interference fringes [5] and are also tolerant to misalignment. They have been shown to increase effective pathlength [6], both theoretically and experimentally, within a relatively small volume without the need for precise alignment.

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Here, we analyse the detection of methane at 3.3µm using an ICL and gold coated integrating sphere. A comparison of this setup is made against a conventional single-pass, short pathlength gas cell.

2. PRINCIPLE OF OPERATION

Optical gas detection using TDLS is based on the application of the Beer Lambert Law:

$$\boldsymbol{I = I_0 \exp(-\alpha \ell)} \quad \textbf{(1)}$$

Where I is the light transmitted through the gas cell, I_o is the light incident on the gas cell, α is the absorption coefficient of the sample (typically with units of cm^{-1}) and ℓ is the cell's optical pathlength (typically with units of cm). $\alpha\ell$ is defined as the absorbance, which is unitless but often described in "absorbance units" (AU).

The limit of detection of a target gas species can be quantified as the noise equivalent absorbance (NEA, in AU) or the minimum detectable absorption coefficient (α_{min}, in cm^{-1}), allowing instrumental techniques to be compared without reference to the specific target gas.

When undertaking TDLS measurements, the output of a laser diode is scanned across one or more gas absorption lines in a narrow wavelength range, typically1-2nm wide. This is performed by modulating continuously the injection current of the laser diode, usually with a ramp waveform.

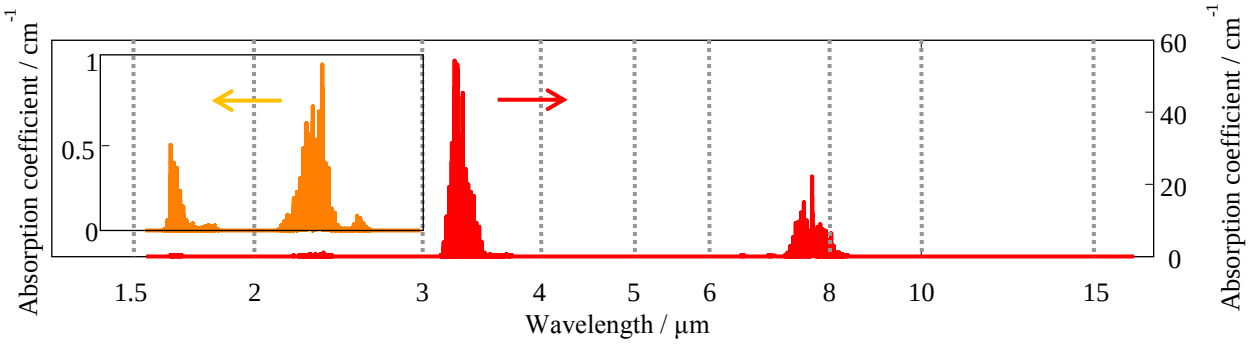

Figure 1 Comparison of methane absorption line strength in the near (inset) and mid infrared

A comparison of the absorption bands for methane in the near and mid infrared are shown in Figure 1. One of the most common absorption lines targeted for analysis using TDLS is at 1651nm due to the ease of getting lasers and detectors that operate in this region. Although this line is the strongest in its respective absorption band, it has an absorption coefficient approximately 100 times smaller than those seen at the fundamental band at 3.3µm. As ICLs are now commercially available, it has now become possible to target methane lines in this fundamental region. It is important to note, however, that there are strong water absorption lines in this region that overlap with a number of the methane absorption lines. As such, it is imperative that when choosing an absorption line to be used for environmental sensing, a line must be chosen that does not have a water line either overlapping or in close enough proximity that it could influence that detection. Following this principle, a methane line at 3313nm was chosen as the target for this experiment, due to it being one of the strongest methane lines not influenced by a water absorption line.

3. EXPERIMENTAL

A diagram of the optical setup is shown in Figure 2. Light from a 3313nm ICL (Nanoplus) was collimated into a gas cell, initially a 25cm single pass cell before being switched for a 10cm diameter integrating sphere with effective pathlength of 54.5cm. The ICL current was driven with a sawtooth waveform at a frequency of 1kHz. The beam was then detected with a cooled MCT (mercury-cadmium-telluride) detector (Hamamatsu P3981), with the signal amplified through a variable gain transimpedance amplifier (Femto DLPCA-200). The output was then fed to a computer-based data acquisition system implemented in Labview via an analogue-to-digital converter (ADC). The instrument was tested with different gas concentrations using a bank of mass flow controllers to provide a series of dilutions of methane in hydrocarbon-free air.

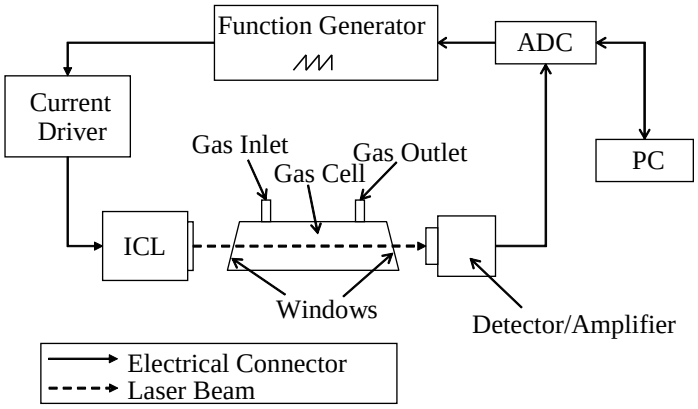

Figure 2 Initial configuration for methane detection using tunable diode laser spectroscopy

4. RESULTS

Figure 3 shows an example of raw data collected directly from the detector, for both a signal in the absence of any gas and a methane concentration of 1010ppm using the standard gas cell. In the absence of gas, the reference signal showed an increase in output intensity as the current increased, as expected. With methane present, a dip corresponding to the target gas absorption lines was observed.

Measurements were then taken of the target absorption lines between 0 and 1010ppm methane concentrations. These measurements were averaged over a 1 second period to reduce noise levels. Using equation (1), values for the absorbance for each of these concentrations were calculated, an example of which is shown in Figure 4. When compared with data taken from the HITRAN database, also shown in Figure 4, it can be seen that the detected methane absorption correlates strongly with this data. The peak absorbances could then be plotted against their corresponding concentration, as seen in Figure 5. This was then repeated using the integrating sphere, for methane concentrations between 0 and 250 ppm, as shown in Figure 6.

Calculations for the NEA for both the standard cell and integrating sphere were then performed, resulting in a standard deviation of 1.8×10^{-3} AU and 1.6×10^{-3} AU respectively. From this, a limit of detection for each system could be calculated by comparing it to the absorbance strength at 50ppm in each cell: 2.2ppm for the standard cell and 1.0ppm for the integrating sphere.

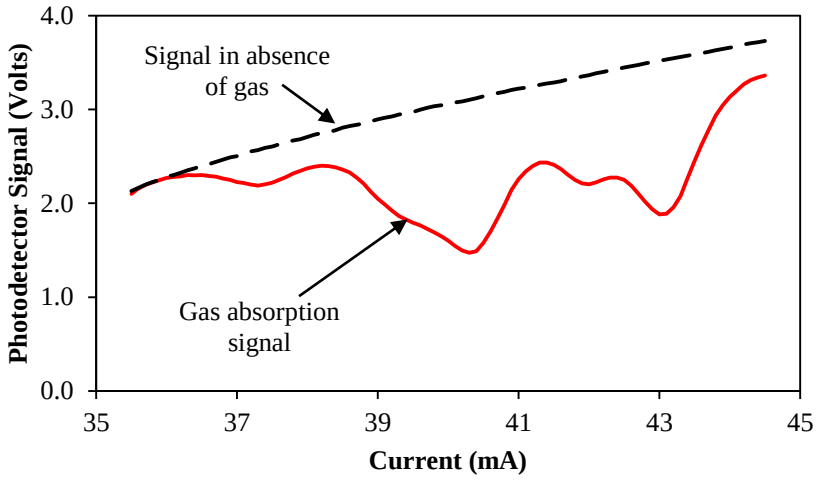

Figure 3 Comparison between collected data for the system with and without methane

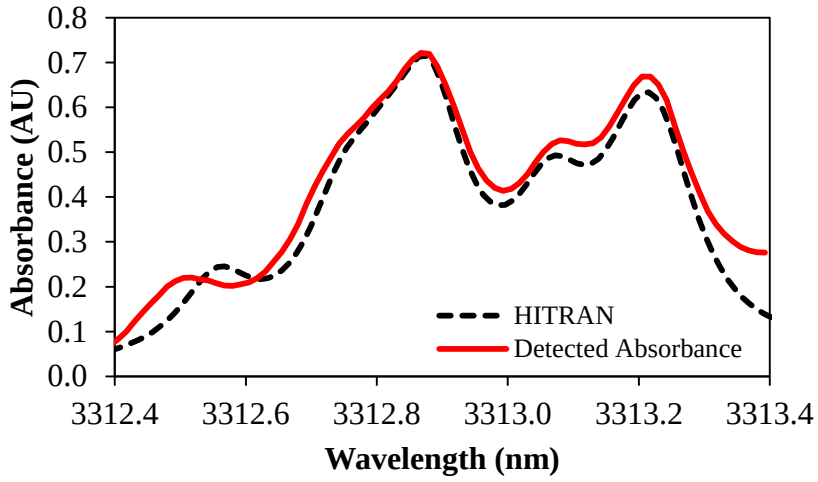

Figure 4 Comparison between detected methane absorbance at 1010ppm and 3313nm (25cm cell) and data from HITRAN at atmospheric pressure for the same concentration and pathlength [7]

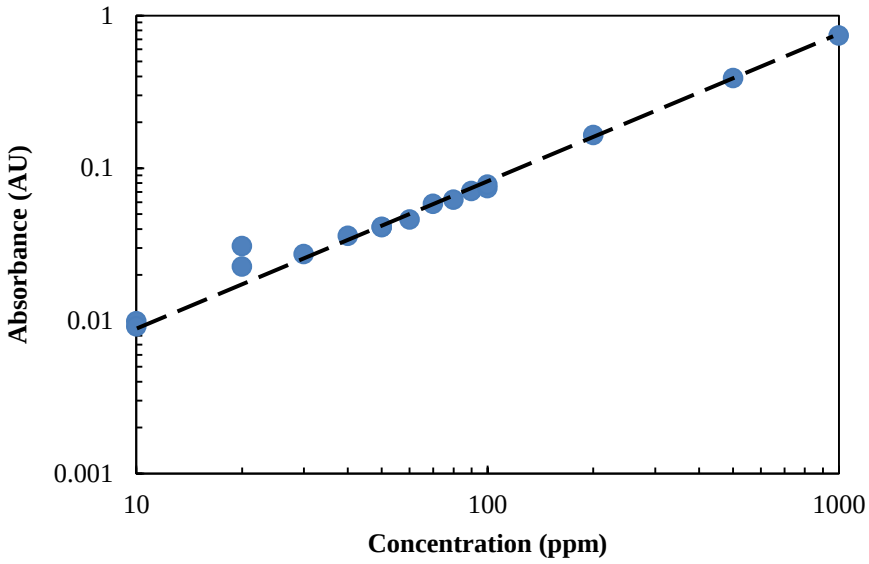

Figure 5 Absorbance of different methane concentrations using standard 25cm pathlength gas cell

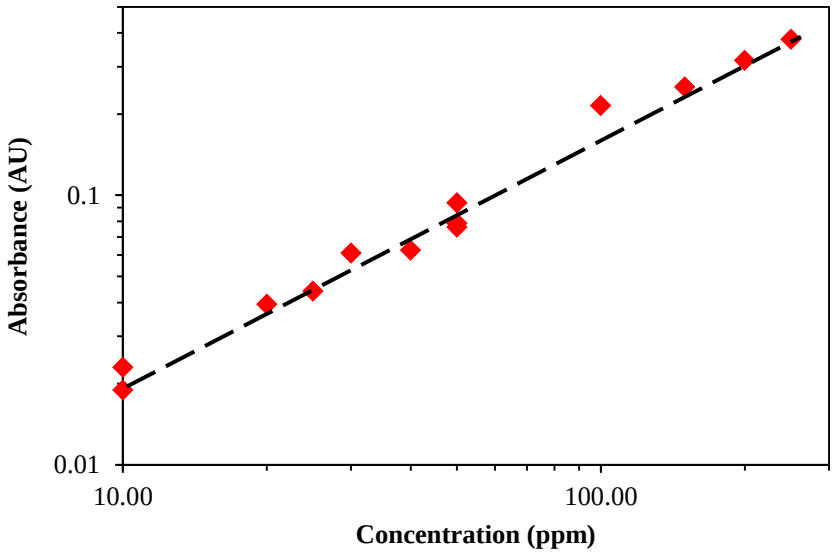

Figure 6 Absorbance of different methane concentrations using 54.5cm pathlength integrating sphere as a gas cell

5. DISCUSSION AND CONCLUSIONS

Measurements of methane were made using tunable diode laser spectroscopy at 3.3µm using an interband cascade laser. Readings were taken initially using a standard single-pass, 25cm pathlength gas cell, before switching to an integrating sphere with effective pathlength of 54.5cm. Detections were made of methane concentrations between 0 and 1010ppm, with concentration curves being produced for both gas cells. Limits of detection of 2.2ppm and 1.0ppm were calculated for the standard cell and integrating sphere respectively.

The performance of the integrating system is limited by the reflectivity of the interior coating of the sphere and by the noise levels detected. The reflectivity of the coating used, Infragold®, is limited to between 94 and 95% in the mid infrared, limiting the theoretical maximum for the effective pathlength. Any slight reduction in the reflectivity caused by dust, grime or tarnishing can cause a large reduction in this pathlength.

Future work will concentrate on improving the limits of detection for each system through the use of line fitting techniques. This method involves producing a curve that models the target absorption lines, then applying the curve to the measured data. The stronger the measured data correlates to the line fit, the higher the concentration of the target gas is present.

To conclude, it has been shown that a 10cm diameter, gold coated integrating sphere provides an improvement in limit of detection when compared with a standard, single-pass gas cell. To the authors knowledge this is the first time that an integrating sphere has been used in conjunction with an ICL for the purpose of gas detection. Integrating spheres also provide easier alignment than found in standard cells. While standard TDLS systems require precise alignment of the laser, cell and detector to achieve high quality measurements, the laser and detector in an integrating sphere system merely need to be directed at the port openings for measurements to be made.

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