Fibre-coupled photoacoustic sensor for sub-ppm methane monitoring

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ABSTRACT

Sensitive photoacoustic detection of methane with a fibre-coupled 1.65-μm laser is reported. A sensitivity of 0.18 parts-per-million (signal-to-noise ratio = 3) is achieved using a properly designed photoacoustic cell operating on its first longitudinal mode.

Keywords: Photoacoustic spectroscopy; DFB laser; Trace gas monitoring.

1. INTRODUCTION

The interest for reliable and compact trace gas sensors has considerably increased in recent years. A precise monitoring of a large variety of species in different gas mixtures and at various concentration levels, ranging from parts-per-billion (ppb) to several hundreds of parts-per-million (ppm), is required in various fields of applications, such as combustion processes [1], atmospheric researches [2], pollution monitoring [3] and industrial process control [4]. Laser-based photoacoustic spectroscopy (PAS) is a well-established technique for trace gas monitoring, thanks to its simplicity, high sensitivity and large dynamic range. This method consists schematically in the generation of an acoustic wave in a sample excited by a modulated laser beam at proper wavelength and in the detection of this sound using a sensitive microphone.

The development of a photoacoustic (PA) sensor for sub-ppm methane detection is reported in this paper. The sensor uses a distributed feedback (DFB) laser in the 1650 nm range in order to excite methane molecules to the $2\nu_3$ vibrational state. The use of a fibre-coupled laser simplifies the coupling of the laser emission into the measurement cell and reduces the dimensions of the system. It also opens the possibility to realize multi-species detection systems [5].

2. BASICS OF PHOTOACOUSTIC SPECTROSCOPY

PAS is a calorimetric method, in which the optical energy absorbed in a gas sample is directly measured through the heating produced in the medium. The conversion from optical energy to heat is induced by molecular absorption of photons at proper wavelength and subsequent non-radiative relaxation of the excited state (collisional relaxation). The small local temperature variation in the sample is associated to a pressure variation. When the deposited optical energy is modulated (for example by an intensity or wavelength modulation of the laser), a periodic heating is produced, thus generating a modulation of the sample pressure. This results in an acoustic wave, which can be detected using a miniature microphone. The amplitude S_{PA} of this acoustic wave can be significantly enhanced using an acoustic resonator configuration. In such a case, the PA cell is designed to be acoustically resonant and when the laser modulation frequency is adjusted on a resonance frequency of the cavity, an amplified standing wave is created in the cell. The amplitude of this wave depends linearly on the laser power P_0, the molecular absorption coefficient α and on a parameter characterizing the geometry of the PA cell, the cell constant C_{cell}: $S_{PA} = C_{cell}\ \alpha\ P_0$.

3. DESIGN OF THE PHOTOACOUSTIC SENSOR

Our home-made PA cell has been optimised to be operated on its first longitudinal mode [5]. It is built out of stainless steel and consists in two large buffer volumes and a central cylindrical tube of radius $R_c = 3$ [mm] acting as an acoustic resonator (see Figure 1). An optical telecommunications DFB laser diode emitting at 1651 nm is used for the detection of methane. The laser is fibre-coupled and the optical fibre ends with a beam collimator directly mounted on the face of the first buffer volume of the PA cell, which facilitates the light coupling into the cell. Each of the buffer volumes was

Second European Workshop on Optical Fibre Sensors, edited by
José Miguel López-Higuera, Brian Culshaw, Proceedings of SPIE Vol. 5502
(SPIE, Bellingham, WA, 2004) 0277-786X/04/$15 · doi: 10.1117/12.566792

built with a movable piston, enabling to easily adjust its length and to study its influence on the coupling between the ambient acoustic noise and the resonator. The laser beam goes across the cell on its axis in order to efficiently excite the first longitudinal mode of the resonator. The generated sound wave was detected with an electret microphone located at the centre of the resonator, i.e. at the maximum of the acoustic standing wave. The signal amplitude is measured using a lock-in amplifier, with a time constant usually set to 10 s. A 28-fold amplification of the PA signal is achieved in the present resonant configuration, as shown in Figure 2. An electronic module controls the laser modulation and processes the data. This DSP-based electronics completely and autonomously controls the measurement and computes the methane concentration.

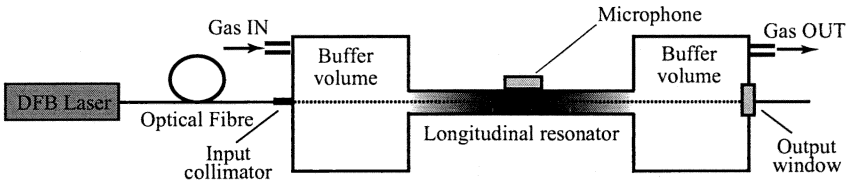

Figure 1: Schematic representation of the PA sensor based on a DFB laser and a PA cell operated in its first longitudinal mode. The laser emission is directly launched into the PA cell using a fibre collimator.

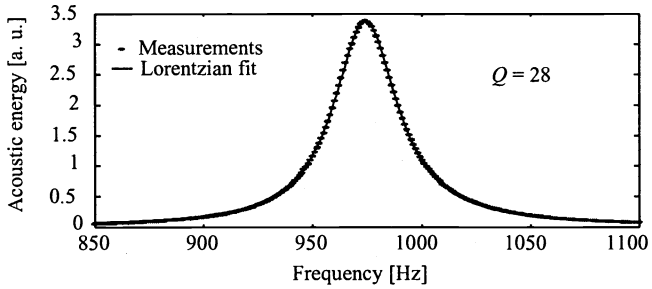

Figure 2: First longitudinal acoustic resonance of the PA cell. Circles are experimental points and the curve is the result of a fit by a Lorentzian distribution. The amplification factor of the photoacoustic signal is given by the quality factor Q of the resonance, which corresponds to the resonance frequency divided by the full width at half maximum of the acoustic energy distribution. A quality factor Q = 28 is achieved in our set-up.

4. EXPERIMENTAL

The PA spectrum of methane has been measured by tuning the laser temperature and modulating its intensity, via a modulation of the injection current at a frequency corresponding to the first longitudinal resonance of the acoustic resonator (around 1 kHz). The measured spectrum is shown in Figure 3 and is compared with the absorption spectrum calculated from HITRAN database [6]. A good agreement is obtained between PA measurement and calculated spectrum. However, a slightly reduced spectral resolution is achieved experimentally, as some weak lines are not completely resolved in the measurement. This is probably due to a shift of the laser wavelength during the current pulses, induced by a heating of the laser.

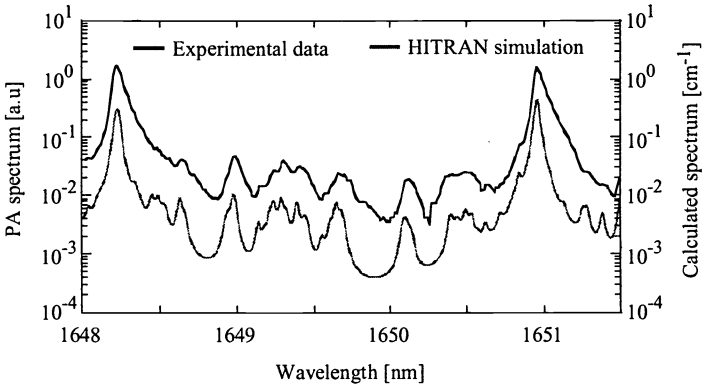

Figure 3: CH_4 PA spectrum measured with our experimental set-up. Black curve shows experimental data and the grey line represents the corresponding absorption spectrum calculated from HITRAN database.

The strongest CH_4 absorption line at 1650.96 nm has then been selected for methane monitoring. The laser temperature has been tuned to reach the appropriate wavelength and the current modulation amplitude has been optimised to achieve the strongest PA signal (see Figure 4). The current modulation produces a combined frequency- and intensity-modulation of the laser, but the frequency modulation is dominant for the optimal modulation depth. The PA signal obtained when the laser is scanned through the methane absorption line thus looks like a derivative of the absorption feature [7]. This is no longer the case at high modulation depths, where intensity modulation becomes dominant and the measured PA signal is directly proportional to the absorption line.

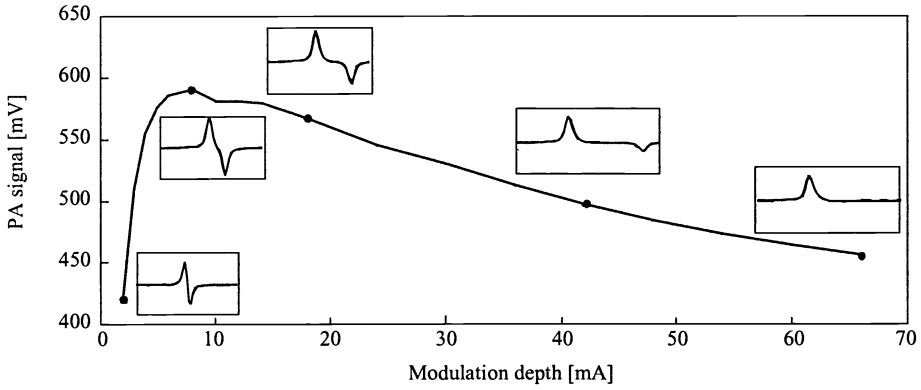

Figure 4: Amplitude of the PA signal detected for the strong CH_4 line at 1650.96 nm as a function of the laser current modulation depth. The shape of the PA signal obtained when the laser is swept through the absorption feature is also shown for some modulation depths indicated by circles on the curve.

The response of the sensor as a function of the methane concentration has been measured using various CH_4 concentrations generated from two certified gas mixtures (4930 ppm of CH_4 in N_2 and 99.9 ppm of CH_4 in N_2) diluted in nitrogen using mass flow controllers. Calibration gas concentrations ranging from 5000 ppm CH_4 down to 0.5 ppm have been generated. For each concentration, the PA signal has been recorded during two minutes and the average value and standard deviation have been measured. The response of the sensor, illustrated in Figure 5, is linear with respect to the CH_4 concentration over several orders of magnitude. The ultimate detectivity is limited by the noise of the system. The zero concentration background level has been measured when pure nitrogen was flown through the sensor. The predominant noise source in the actual set-up is ambient acoustic noise and microphone intrinsic noise. The noise level is equivalent to a CH_4 concentration of 60 ppb. Flow rates up to 200 ml/min have been used without enhancement in this level. A detection limit of 0.18 ppm of CH_4 is thus achieved for a signal-to-noise ratio $S/N = 3$.

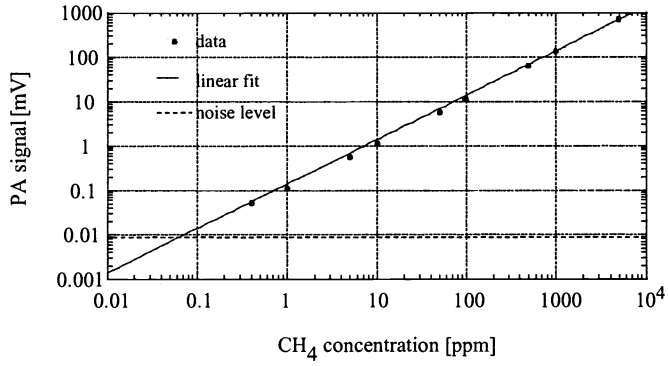

Figure 5: Response of the system as a function of the CH_4 concentration. The noise level, equivalent to 60 ppb CH_4 is also indicated.

5. CONCLUSION

Methane monitoring has been performed by resonant photoacoustic spectroscopy. The developed sensor is based on a PA cell operated in its first longitudinal mode and a DFB laser emitting at 1651 nm. The use of a fibre-coupled semiconductor laser facilitates the coupling of the laser emission into the acoustic resonator. It also makes possible the development of multi-species PA sensors using several lasers at different wavelengths, which may be coupled in a single resonator using fibre couplers. A methane detectivity of 0.18 ppm has been reached ($S/N = 3$) with an average

laser power of 10 mW. Sensitivity improvements are still expected to be achieved by reducing the acoustic noise coupled into the resonator and by increasing the laser power.
In addition to its high sensitivity, the main advantage of this sensor is also its capability to perform continuous and on-line monitoring of methane. A dedicated DSP-based electronics developed for the processing of the acoustic signal and the computation of the methane concentration makes the system totally self-operating. The sensor is thus able to perform unattended automatic measurement of methane concentration and finds application in various domains, such as pollution monitoring and industrial process control.

AKNOWLEDGEMENTS

The authors would like to acknowledge the Commission of Technology and Innovation of the Swiss Government for the financial support and companies Omnisens SA and Daetwyler Fiber Optics SA for their technical and financial contributions.

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