

# Sensitive and Fast Gas Sensor for Wide Variety of Applications Based on Novel Differential Infrared Photoacoustic Principle

Zahlreiche neue Anwendungen durch hochempfindlichen und schnellen IR photoakustischen Gassensor mit neuartigem differentiellen Messprinzip

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**Summary** A modular sensor concept for various gas measurement applications requiring high sensitivity and fast response time is presented. The proposed differential photoacoustic detection combines the selectivity of the traditional absorption method and the high sensitivity of the novel cantilever enhanced photoacoustic detector. High precision is achieved using short optical path length resulting in fast response time and wide dynamic measurement range. An example realization for greenhouse gas flux measurement is presented. ▶▶▶

**Zusammenfassung** Für verschiedenartige Gasmessungen,

die hohe Empfindlichkeiten und schnelle Reaktionszeiten erfordern, wird ein modulares Sensorkonzept vorgestellt. Das dabei verwendete differentielle photoakustische Messprinzip kombiniert die Selektivität konventioneller Absorptionsmethoden mit der hohen Empfindlichkeit neuartiger photoakustischer Detektion mittels Schwingbalken. Hohe Messgenauigkeit wird durch eine kurze optische Weglänge erzielt und resultiert in schneller Reaktionszeit und hoher Dynamik. Als Beispielanwendung wird die Flussmessung von Treibhausgasen beschrieben.

**Keywords** Photoacoustic, gas detection, greenhouse gas flux, cantilever sensor, leak detection ▶▶▶

**Schlagwörter** Photoakustik, Gasetektion, Treibhausgas, Schwingbalkensensor, Leckdetektion

## 1 Introduction

With the increase in the emission of gases from the industries and vehicles, there is a strongly growing need of a solution to monitor the emissions in order to have a cleaner and a greener atmosphere. Furthermore, a fast and sensitive gas sensor with compact size is needed in several applications such as greenhouse gas flux measurements, breath measurements in medical diagnostics, tail pipe measurements in engine development, leak de-

tection and homeland security. There exist a lot of gas measurement solutions, but they do not satisfy the demand of the growing global warming effect. Moreover the existing technologies are not sensitive, fast, compact, and cost efficient enough.

The ultimate aim of the research is to develop and demonstrate a versatile and miniaturized gas sensor subsystem that has the capability to detect greenhouse gases along with explosive gases, medical markers and chemical

agents with orders of magnitude better sensitivity than prior optical measurement methods at the same package volume.

## 2 Photoacoustic Gas Measurement

The photoacoustic effect is the process of acoustic wave generation in a sample resulting from the absorption of photons. This process was invented already at the end of the 19th century [1], but first real applications were introduced not until the 1960's [2]. The photoacoustic method has since been used to study various chemical and physical phenomena in number of fields. Some of the applications are trace gas analysis, spectroscopy of weak optical transitions, and probing of optically thick samples. To date photoacoustic spectroscopy is widely used in many areas of research and applications [3;4].

The basic theory behind photoacoustic detection is rather simple. Light absorbed in a sample will excite a small fraction of the ground state molecular population to higher energy levels. These excited states will subsequently relax through a combination of radiative and non-radiative pathways. The non-radiative part of the excitations will finally generate heat in the localized region of the light beam and produce a pressure wave, which propagates away from the source. This pressure wave can be then detected with a suitable sensor such as a microphone. Photoacoustic detection is a unique method since it is a direct monitor of the non-radiative relaxation channel and thus it complements spectroscopic techniques based on absorption and fluorescence. The photoacoustic method is also an extremely sensitive technique, with the ability to detect highly forbidden optical transitions and trace components in a mixture of gases.

The essential components of the apparatus used for photoacoustic gas analysis or spectroscopy are a source of modulated light, a sample cell, a sensor for detecting the acoustic signals, and the signal processing system.

The light source of the photoacoustic detection system is either a broadband IR-source (blackbody radiator), a continuous wave or a pulsed laser. When using an IR-source the radiation must be fed to the sample cell through a narrow band-pass filter or monochromator. With conventional lamps it is very simple to generate large enough infrared power (total power can be several watts), but the modulation of the infrared source is clumsy, in practice the only method is to use a mechanical chopper although small-power semiconductor infrared emitters, which can be modulated by current, are already available. Unfortunately, the output power of these sources is quite low and the highest modulation frequency is very limited. With lasers the amplitude and especially frequency modulation is easily performed. However, the suitable wavelengths needed for molecular excitations can be difficult to realize when using laser sources. Infrared light emitting diodes (IR-LED) are interesting alternatives. They are not as broadband sources as blackbody radiators since typical spectral width is 1/10 of the centre

wavelength, and therefore, in some applications they can be used without any optical filter. The output power of IR-LEDs is still very low, clearly less than 1 mW, and they are available on the wavelength range of (2...7)  $\mu\text{m}$ . The amplitude modulation of IR-LEDs is easy to accomplish and the modulation frequency can be very high.

The sample cell design depends on the type of the light source, but always the main target is to generate acoustic waves and couple the sensor to acoustic excitations as efficiently as possible. All sample cells can be used either in the non-resonant or resonant mode of operation. If the modulation frequency is much lower than the lowest acoustical resonance frequency, the cell is operated in a non-resonant mode. In this case the sound wavelength is much larger than the cell dimensions, thus sound cannot propagate and standing waves cannot form, and the average pressure in the cavity will oscillate along with the modulation frequency.

## 3 Condenser and Cantilever Microphones

The device coupling to the acoustic field and converting pressure changes to voltage a signal is the most critical part of the apparatus when looking for the best sensitivity in trace gas analysis. Microphones normally used in photoacoustic applications can be divided to two main categories: capacitive and optical. Capacitive microphones are either condenser or electret microphones. Optical sensors are based on measuring the movements of either elastic membranes or silicon cantilevers using optical beam deflection methods or interferometers [5].

Both condenser and electret microphones have some fundamental limitations, which cannot be overcome. First, to increase the sensitivity of the microphone the gap between the elastic membrane and the back plate cannot be decreased below a certain limit. If the gap is very narrow, the gas between the membrane and plate cannot flow freely because of viscous effects and therefore membrane movements are restricted. Secondly, the tension of the membrane cannot either decrease too much: if the membrane is very flexible the dynamic range of the sensor is extremely small. The response of the membrane on the external pressure is also nonlinear due to the fact that the material has to stretch out radially under pressure variations. Finally, the output impedance of condenser and electret microphones is very high, especially at low frequencies, necessitating the use of very high input impedance amplifier for further signal processing. In practice, the noise of best available amplifiers usually exceeds the noise generated from the transducer itself, thus there are no possibilities to further increase the sensitivity of the microphone.

A cantilever does not have the same mechanical restrictions as a membrane when using it for pressure wave detection in photoacoustic applications. A cantilever has two main benefits. First, the spring constant of the vibrating cantilever can be quite easily 2 or 3 decades smaller than that one of the membrane and it can be very easily

adjusted by changing the dimensions of the cantilever. Secondly, the dynamical range of the cantilever is very large compared to the one of the membrane, i.e., the cantilever can bend even tens of micrometers without any nonlinear effects or restricting effects while the smallest detectable bending is below 1 pm. The bending can be measured either using an optical beam or an interferometer. If a large dynamical range is needed the optical beam method is not applicable and an interferometer should be used. The interferometric measuring has inherently infinite range of dynamics since the bending can be determined over as many wavelengths of the laser as is needed. This large dynamic range is directly related to the concentration range of the trace gas, which can be measured. This is an important feature of any gas detection and measuring system.

#### 4 Differential Measuring Concept

In the long path absorption spectroscopy the light beam penetrates through the sample gas, and the absorption at two or more wavelengths are measured and compared. The sensitivity of this kind of method depends mainly on the absorption length, output power of the light source and the response of the detector. In practice the absorption path length cannot be increased too much since then, because of the exponential decreasing of the signal, the signal-to-noise ratio would be very small, and with e.g. wet gases the water absorption can be a serious problem.

In the differential photoacoustic detection [6] the selectivity of the traditional absorption method and the

high sensitivity of the photoacoustic detector are combined. The basic structure of this system is shown in Fig. 1 (top). The device consists of three cells: the sample cell containing the unknown concentration of the gas to be detected, the reference cell filled with pure nitrogen and the differential photoacoustic cell containing high concentration of the analysed gas. The differential cell is divided into two equal parts and the cantilever is between them, and the bending of the cantilever is measured by using the interferometer. If there is a pressure difference over the cantilever it bends proportionally to that difference, i.e., it acts like a highly sensitive differential pressure sensor. The infrared radiation is directed to the sample and reference cell with an equal power. From these cells the radiation enters to the both parts of the differential cell. The pressure difference can be generated only if the light absorption is different on the both sides of the cantilever, and this is possible only if there have been some absorption of light in the sample cell at the same wavelength specific to the analysed gas. Thus the pressure difference and the bending of the cantilever are directly related to the concentration of the gas.

The differential setup is very flexible. First, the selectivity of the method over various gases is achieved by using suitable gas in the differential cell. Even gas mixtures are possible, and then the output signal depends on the total concentration of these gases in the sample cell. There are several alternatives for the infrared light source, as shown in Fig. 1. When using blackbody radiator the beam must

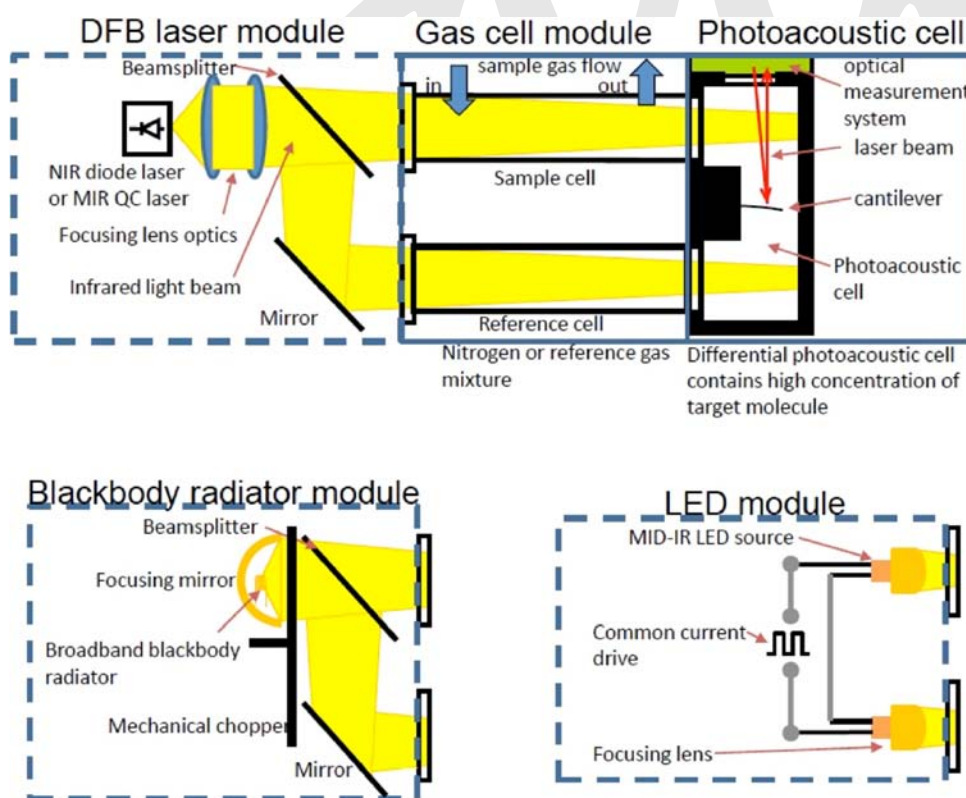


Figure 1 Modular concept of the proposed differential infrared photoacoustic gas sensor.

be first divided into two equal parts and then amplitude modulated by a mechanical chopper (Fig. 1, bottom left). Similar optical design is needed when using laser sources (Fig. 1, top). IR-LEDs as a source are the most compact solution since then it is possible to use two LEDs and balance the system by adjusting the currents of the LEDs (Fig. 1, the lower right panel). In the case of laser sources (and partially also with IR-LEDs) the selectivity is mainly set by the choice of the wavelength of the source, thus the differential setup does not produce any additional benefits on this feature. However, the sample cell is not part of the photoacoustic system and, therefore, it can be in open path operation mode. If a closed sample cell is used the gas can be changed very fast since there is no risk to damage the microphone as in the photoacoustic cell. In practice this means that the response time of the overall system can be very short.

### 5 Example Systems

One realization of the modular differential system is presented in Fig. 2. The diode lasers and beam splitter are assembled in source module, sample and reference cells are in the second module, and the photoacoustic cell with the optical cantilever microphone in the third mod-

ule. The volume of the sample cell is only 5.6 ml and the absorption path length amounts to 20 cm. Photoacoustic cell diameter and length are 2 mm and 25 mm, respectively. Cantilever dimensions in the example system are: length 2 mm, width 0.8 mm, thickness 4  $\mu\text{m}$ , and gap between cantilever and its frame 1  $\mu\text{m}$ . Mirrors are mounted at the end of the photoacoustic cell. Two diode lasers were integrated into this system in order to perform simultaneous measurement of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The lasers were focused to the photoacoustic cell using lens system made of IR-graded fused silica.

In MINIGAS-project (EC FP7 Program # 224625) another realization of the modular differential photoacoustic system is developed. For a miniaturized solution to methane leak detection an infrared (IR) light-emitting diode (LED) [7] will be designed and utilized resulting in a packaging volume of 5  $\text{cm}^3$  of the sensor sub-module leading to a below-ppm detection limit in 1 s measurement time. The gas cell itself is a flow-through cell with a volume of a few milliliters providing the possibility for fast response time. The mechanical design of the device is based on LTCC (Low Temperature Cofired Ceramics) technology, which will be used both for the cell structures and the readout interferometer (Fig. 3).

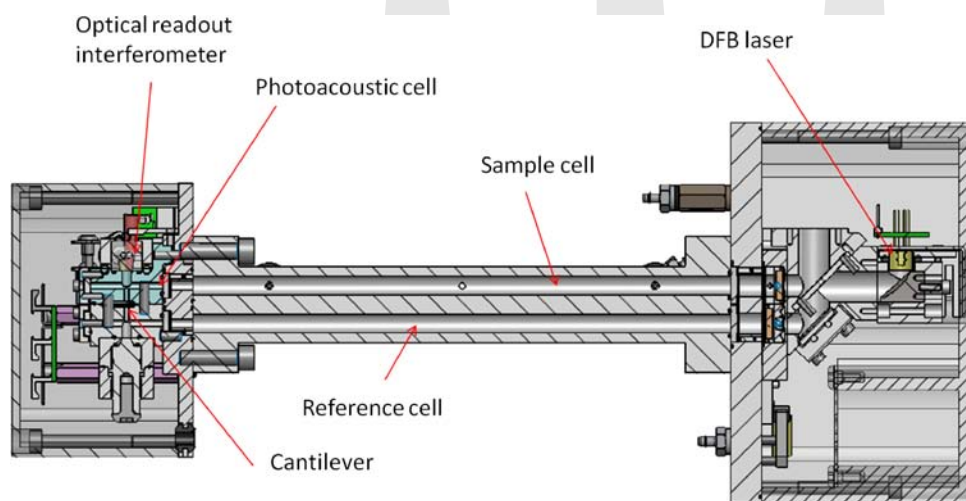


Figure 2 Mechanical structure of the differential system designed for  $\text{CO}_2$  flux measurements.

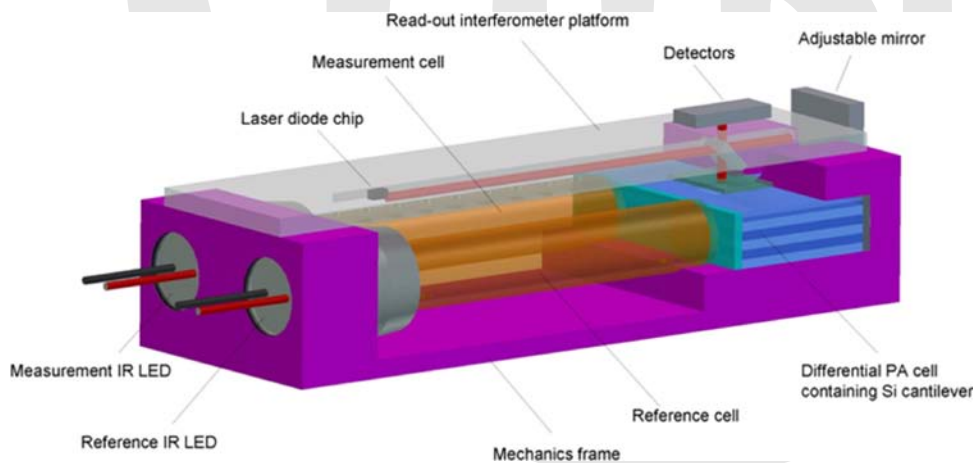


Figure 3 MINIGAS methane leak detector.

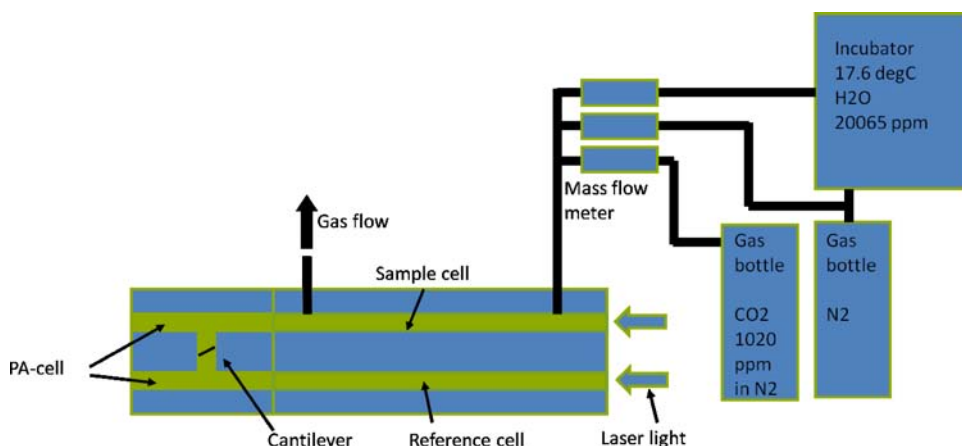


Figure 4 Gas exchange to the sample cell.

## 6 Experiments

Experiments have been carried out with the system shown in Fig. 2 for H<sub>2</sub>O and CO<sub>2</sub> gas flows using a DFB lasers with a center wavelengths of 2702.86 nm and 0.5 mW power for CO<sub>2</sub> and 1877.09 nm with 2 mW output power for H<sub>2</sub>O. Lasers were wavelength-modulated using 70 Hz frequency. The signal was measured in the second harmonic frequency at 140 Hz. The differential photoacoustic cell was filled with a gas mixture of 50%CO<sub>2</sub> + 50%Xe + 2%H<sub>2</sub>O, and the total pressure was 120 mbar. Absorption path length in the cell was 20 cm. The sample was filled in by using mass flow meter for controlling the CO<sub>2</sub> and H<sub>2</sub>O concentrations. CO<sub>2</sub> concentration was changed in 10 ppm steps between 460 ppm and 390 ppm. H<sub>2</sub>O concentration were 2%, 1% and 0.5%, respectively. The different CO<sub>2</sub> concentrations were diluted to N<sub>2</sub> from a standardized gas bottle having 1020 ppm ( $\pm 2\%$ ) of CO<sub>2</sub> concentration. Water samples were created by using incubator and saturated water vapor pressure (20 065 ppm) at 17.6 °C. The sampling setup is shown in Fig. 4. The flow was set to 1000 ml/min in the sample cell and the reference cell was filled with pure nitrogen. The CO<sub>2</sub> and H<sub>2</sub>O measurement results are presented as a function of time in Figs. 5 and 6, respectively. The sampling rate was 10 Hz. It can be seen that the measured CO<sub>2</sub> concentration changed very well

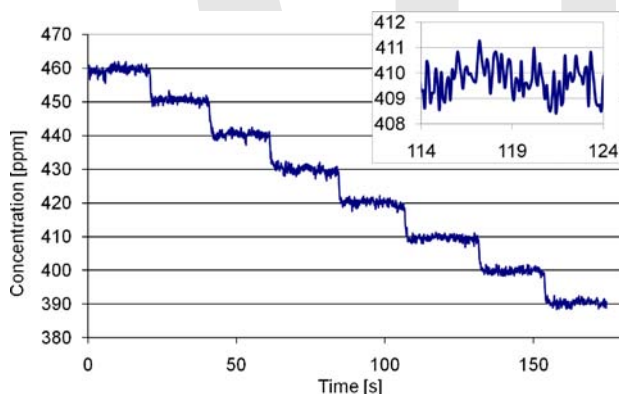


Figure 5 Calibrated differential signal of carbon dioxide in the concentrations between 460 ppm and 390 ppm with 0.1 s integration time.

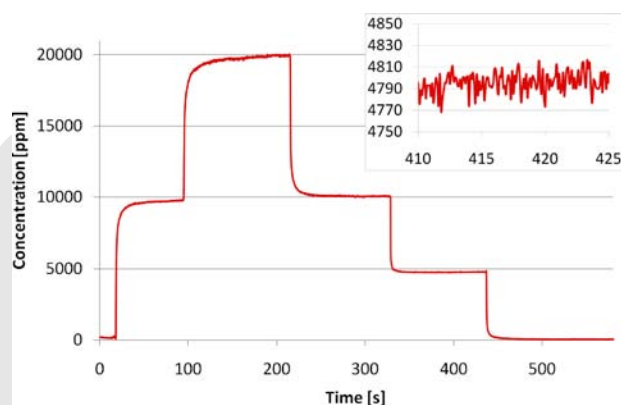


Figure 6 Calibrated differential signal of water vapor between 0 ppm and 20000 ppm with 0.1 s integration time.

with only 0.1 s response time (see the inserted figure in Fig. 5). The precision ( $1\sigma$ ) of the CO<sub>2</sub> concentration with 0.1 s measurement time was 570 ppb. With 5 s measurement time the precision was estimated to be better than 90 ppb. For H<sub>2</sub>O the precisions were 9 ppm with 0.1 s measurement time and 1.3 ppm with 5 s measurement time.

## 7 Conclusions

The differential photoacoustic system utilizing the novel optical cantilever microphone gives high performance. It can be easily scaled to many different applications and price ranges by changing the light source and the gas inside the photoacoustic gas cell.

High sensitivity of the cantilever sensor enables low detection limits using a short optical path length in the sample cell. Several benefits are gained from the short path length namely the size of the system, wide dynamic measurement range and fast response time. The performance of a fast response system with a short path sample cell is demonstrated with a DFB laser setup measuring carbon dioxide and water vapor.

The estimated precision value of 90 ppb for carbon dioxide and 1.3 ppm for water vapor in 5 s measurement time with a 20 cm absorption path length in the sample cell are already comparable e. g. to cavity ringdown with

several kilometer absorption path length and other commercially available flux measurement systems [8–10]. The dynamical measurement range of different concentration can be extremely wide in the proposed system due to the short absorption path length.

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