Sub-ppm multi gas sensing based on photoacoustic spectroscopy using DFB laser diodes

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Abstract:
Sensitive photoacoustic detection of methane (CH$_4$), hydrogen chloride (HCl) and water vapour (H$_2$O) in the near-infrared range using semiconductor DFB lasers is reported. A detection limit of 0.17 ppm of CH$_4$, 0.2 ppm of HCl and 0.024 ppm of H$_2$O (signal-to-noise ratio = 3) is reached using a properly designed photoacoustic cell operating in its first longitudinal mode.

1. Introduction
The interest for compact and reliable 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 atmospheric researches [1], combustion processes [2], medical diagnostic by breath analysis [3], food industry [4] or pollution monitoring [5]. Industrial process control is also of great importance, as extremely high purity gas mixtures are usually employed and level of impurities or contaminants must be precisely controlled at trace levels. Several types of impurities need to be monitored, such as ammonia (NH$_3$) and acids (HF, HCl, HBr) in semiconductor clean room applications or moisture contamination in the manufacturing of electronics or optical devices, such as laser diodes [6]. Optical fibres manufacturing represents a particular application where different hydrogenated compounds need to be precisely controlled at sub-ppm level in order to enable the fabrication of low-loss fibres with reduced OH$^-$ contaminant content.

Laser-based photoacoustic spectroscopy (PAS) is a very attractive method for trace gas monitoring, due to its simplicity, high sensitivity and selectivity. This technique measures directly the amount of modulated laser radiation absorbed in the analysed sample and converted into pressure energy via non-radiative relaxation processes. The use of semiconductor lasers in PAS presents many advantages such as their compactness, reliability, long lifetime operation and low current consumption. In addition, they are commonly produced in the spectral range of optical
fibres telecommunications (1.3-1.65 µm), where overtone vibration bands of many molecules of interest occur (CO₂, H₂O, NH₃, CH₄, HF, C₂H₂,…). Although laser diodes have much reduced optical power in comparison to mid-infrared gas lasers (typically a ten of mW against several watts), properly designed photoacoustic (PA) systems based on DFB laser diodes have the potential to reach sub-ppm detection limits for many species of interest. The compatibility of near-infrared DFB lasers with standard telecommunications optical fibres is another key advantage of these lasers. The use of optical fibres simplifies the design of a gas sensor, especially in the case of multi-components detection. A simultaneous monitoring of several species with a single instrument usually requires the use of several lasers, as the typical tuning range of a DFB laser is limited to a few nanometres, whereas the separation between absorption bands of different species is generally much higher. Therefore, one laser per substance is usually required. Optical fibres strongly simplify the coupling of the emission of several lasers into a single measurement cell, eliminating the use of expensive transfer optics (lenses, mirrors, beamsplitters).

We report in this paper some results on the development of a multi-gas PA instrument. The interest of this system consists in the possibility to detect several species at trace level with a single instrument. In these experiments, we have been interested in the detection of three hydrogenated compounds, methane (CH₄), water vapour (H₂O) and hydrogen chloride (HCl), using three near-infrared DFB lasers and a resonant PA cell. Theoretical background of PAS is first reviewed and then the realisation of our system is described. Finally experimental results are presented.

2. Theoretical background of photoacoustic spectroscopy

PAS is a calorimetric method in which the optical energy absorbed in a gas sample is directly measured through the heating induced in the medium. It is therefore radically different from conventional spectroscopic techniques based on Beer-Lambert law, in which the energy transmitted through the sample is detected. The conversion from optical energy to heat is induced by molecular absorption of photons of proper wavelength and subsequent non-radiative relaxation of the excited vibrational state (collisional relaxation). The small local temperature variation of the sample is accompanied by 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, generating also a modulation of the sample pressure. This constitutes an acoustic wave (a sound), which can be detected by a miniature microphone. The
amplitude $S_{PA}$ of this acoustic wave is directly proportional to the sample heating, so to the incident optical power $P_0$ and to the molecular absorption coefficient $\alpha$:

$$S_{PA} = C_{cell} \alpha P_0,$$

(1)

where $C_{cell}$ is a proportionality coefficient, called the cell constant, describing the conversion from optical to acoustic energy. This conversion depends not only from the analysed gas, but also from other external parameters, such as the modulation frequency $f$ or the chemical composition of the buffer gas. A $1/f$ dependence of the PA signal occurs as the energy absorbed in a modulation cycle decreases as the inverse of the modulation frequency. The composition of the buffer gas influences also the conversion from optical energy to heat (and therefore to acoustic energy) through several physical parameters, such as the buffer gas density, molar mass and specific heat.

The theory of the generation and detection of the PA signal in a cylindrical cell has been described in detail by several authors (see for example [7-10]). As the generated sound is very weak, resonant configurations are usually used. In such geometries, the PA cell is designed to constitute an acoustic resonator and the laser is modulated at a resonant frequency of this cavity. The acoustic wave is thus amplified by a resonance effect, the enhancement coefficient being the quality factor $Q_j$ of the acoustic resonance. In resonant operation, an acoustic standing wave oscillates in the cavity and the cell constant is given by:

$$C_{cell} = \frac{Q_j (\gamma - 1) I_j L_c}{V_c} p_j(r_M, \omega_j),$$

(2)

where $\gamma = C_p/C_v$ is the ratio of the specific heat at constant pressure and constant volume, $\omega_j$ the angular resonance frequency, $V_c$ the cell volume, $L_c$ the cell length, $p_j(r_M, \omega)$ the value of the normalized acoustic mode at the position $r_M$ of the microphone and $I_j$ is the overlap integral between the laser beam distribution $g(r)$ and the acoustic mode $p_j(r, \omega_j)$ of the cavity:

$$I_j = \frac{1}{L_c V} \int dV g(r) p_j^*(r, \omega_j).$$

(3)

The index $j$ describes the acoustic mode of interest. In a cylindrical resonator, three different kinds of modes occur: longitudinal modes (named by an index $k$), azymuthal modes (index $m$)
and radial modes (index \(n\)), so that \(j = [k, m, n]\). A sensitive PA-based spectrometer aims at maximizing the amplitude of the generated acoustic wave. This can be accomplished by various means. Of course, a strong absorption line and a high power laser are desirable, but for a given absorption feature and laser, the only way of improving the sensitivity consists in an increase of the cell constant and in a reduction of the background noise. A major challenge of PAS is to determine a proper design in order to reach the highest cell constant as possible. The objective is to optimise the cell geometry, choosing the proper type of resonance and suitable cell dimensions, in order to maximize expression (2). Practical considerations must still be taken into account and restrict the choice of the cell dimensions:

- Manufacturing constraints prevent the use of too small cells, as it is necessary to place the microphone or the gas inlet and outlet.
- As the acoustic and electronic noise varies as \(1/f\), the modulation frequency can not be too small. Practically, resonance frequencies lower than approximately 1 kHz should be avoided. The resonant frequencies depend directly on the resonator dimensions:

\[\omega_j = 2\pi f_j = \pi c_s \sqrt{\left(\frac{k}{L_{\text{eff}}}\right)^2 + \left(\frac{\alpha_{\text{mn}}}{R_c}\right)^2}, \quad (4)\]

where \(c_s\) is the sound velocity in the medium, coefficients \(\alpha_{\text{mn}}\) are related to the zeros of the derivatives of Bessel functions and \(L_{\text{eff}}\) is the effective length of the resonator. This parameter differs from the geometrical length \(L_c\) by a correction factor due to boundary effects at the resonator ends [11]:

\[L_{\text{eff}} = L_c + \frac{16}{3\pi} R_c. \quad (5)\]

3. **Design of the photoacoustic sensor**

In order to amplify the photoacoustic signal, a resonant configuration is used. In our experiments a resonator made out of stainless steel has been optimised to be excited in its first longitudinal mode around 1 KHz in air [11]. Buffer volumes with variable length are built to create a standing wave in the resonator. The adjustable length is used to determine the best acoustic filter between the external noise and the longitudinal tube (Figure1). The dimensions of the tube are chosen to obtain the best photoacoustic signal and have in this case a length of \(l=170\) mm and a radius of \(r=3\) mm. Two telecommunications DFB laser diodes were used for the detection of
methane around 1651 nm and water vapour around 1369 nm. These lasers are 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. The detection of hydrogen chloride around 1742 nm is made with a non-fibred DFB laser used in a free-space configuration. The laser was mounted on micrometer linear stages in order to enable a precise alignment of the beam into the PA cell. In addition, a collimating lens of short focal length and numerical aperture of 0.5 was used to collimate the diverging laser emission. In order to generate the PA signal, the injection current of the laser is modulated at a frequency corresponding to the first longitudinal resonance of the acoustic cavity and the generated sound wave is detected with an electret microphone located at the centre of the resonator where the maximum of the acoustic wave occurs. The signal amplitude is measured using a lock-in amplifier with a time constant set to 10 s. The acoustic resonance measured with this configuration in a CH$_4$-N$_2$ mixture is presented in Figure 2. An electronic module controls the measurement and computes the concentrations of the different gases.

**Fig. 1:** Schematic representation of the PA sensor based on DFB lasers and a PA cell operated in its first longitudinal mode.

**Fig. 2:** First longitudinal acoustic resonance of the PA cell. Circles are experimental points and the curve is the result of a lorentzian fit.
4. Experimental results

PA spectra of methane, water vapour and hydrogen chloride have been measured by tuning the lasers temperature and by recording the generated PA signals. They are shown in Figure 3 and are compared with the absorption spectra calculated from Hitran database [12]. A good agreement is obtained between PA measurements and calculated spectra. However, a slightly reduced spectral resolution is achieved experimentally, as some weak lines in the methane and water spectra are not completely resolved in the measurements. This is probably due to a shift of the laser wavelength during the current pulses, induced by a heating of the laser. The HCl experimental spectrum is also fairly noisy, as it has been measured with a less sensitive acoustic resonator, with a low laser power, a weak HCl concentration and in a rather noisy acoustic environment.

**Fig. 3:** PA spectra measured with our experimental set-up. Black curves show experimental data and the grey lines represent the corresponding absorption spectrum calculated from HITRAN database. (a) CH$_4$; (b) H$_2$O; (c) HCl

The response of the system to methane, water vapour and hydrogen chloride concentration is shown in Figure 4. The temperature of each laser is tuned to reach the appropriate absorption line and the amplitude of the laser current modulation is optimised to achieve the strongest PA
signal. Different gas mixtures are obtained from certified concentrations diluted with mass flow controllers. An excellent linearity is obtained, particularly for methane, which has been measured over more than 4 orders of magnitude. The flow rate used in each measurement was 1 l/min, which is the maximum before increasing the noise level. The detection limit for each gas has been determined from the noise level of the sensor. By taking a signal-to-noise ratio $SNR = 3$ a sensitivity of 0.17 ppm of methane, 0.20 ppm of hydrogen chloride and 0.024 ppm of water vapour is obtained. The dominant sources of noise are the intrinsic noise of the microphone and the ambient noise.

![Graph](image)

**Fig. 4:** Response of the system as a function of CH$_4$, H$_2$O and HCl concentrations

5. **Conclusion**

Multi-hydrogenated compounds detection has been performed by resonant PAS. The reported system is based on a PA cell operated in its first longitudinal mode and three DFB lasers for the detection of CH$_4$ at 1651 nm, H$_2$O at 1369 nm and HCl at 1742 nm. A detection limit of 0.17 ppm of methane, 0.2 ppm of hydrogen chloride and 0.024 ppm of water vapour is achieved (for $SNR = 3$).

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