Trace gas sensing using quantum cascade lasers and a fiber-coupled optoacoustic sensor: application to formaldehyde

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Abstract. We will report here on the design and realization of an optoacoustic sensor for the detection of formaldehyde. The sensor consists of a commercial QCL and a resonant PA cell. Two different cell configurations have been investigated: a “standard” H cell and an innovative T-cell with an optical fiber directly inserted into. Two different type of sound detector have been employed: electret microphones and optical MEMS-based microphone. As possible applications, we will describe the results obtained in the detection of formaldehyde (CH\textsubscript{2}O), a gas of great interest for industrial processes and environmental monitoring.

1. Introduction

The detection and quantification of trace chemical species in the gas phase is of great interest in a wide range of applications such as environmental monitoring, industrial process control and medical diagnostics. Increasing awareness and new regulations for safety and emission control have created a strong demand for compact/portable, low-cost, reliable trace gas sensors. Quantum-cascade lasers (QCLs) have given new impulse to the development of optical gas sensors thanks to their tunability in the region from 3 to 20 µm (fingerprint region). QCLs show excellent properties in terms of narrow linewidth, average power (up to few W) and room temperature operation \cite{1}. In combination with these laser sources, photoacoustic spectroscopy (PAS) offers the advantage of high sensitivity, down to part per billion in volume (ppbv) detection limits, compact set-up, fast time-response and simple optical alignment \cite{2}, if compared with multipass absorption spectroscopy. We will describe here an optoacoustic sensor designed for the detection of formaldehyde (CH\textsubscript{2}O).

CH\textsubscript{2}O is often considered as one of the most dangerous chemicals that can be found in living space. It is known as an ubiquitous component of both the remote and urban atmospheres. The CH\textsubscript{2}O concentrations in polluted cities are on the order of 10–20 ppbv; in more remote locations concentrations from 0.01 to 10 ppbv have been observed \cite{3}. Moreover, CH\textsubscript{2}O is a chemical widely used in the manufacture of building materials and many household products like foams, consumer paints and polymer products. Out gassing of formaldehyde from these materials may lead to elevated indoor air levels. CH\textsubscript{2}O causes health problems and may be associated with various diseases, such as
bronchial asthma, atopic dermatitis and sick building syndrome. Therefore, the World Health Organization recommends that the human permissible exposure level of formaldehyde to a limit of 0.08 ppmv (0.096 mg/m3) with an average time of 30 minutes.

2. Optoacoustic sensor

The optoacoustic sensor consists of a resonant cell and a commercially available distributed feedback quantum cascade laser source (QC-DFB). The light source was supplied by Alpes Laser with drive electronics for pulsed operation. A Peltier cooled housing held the laser device at a constant temperature between –35 °C and +65 °C. Two types of cell configuration have been investigated.

2.1. H-Cell

The resonant photoacoustic (PA) cell is characterized by a H geometry and consists of a cylindrical stainless steel resonator of 120 mm length and 4 mm radius with two 60 mm (λ/4) long buffer volumes connected to its endings in order to reduce by destructive interference the background signal due to the heating of the two ZnSe windows, sealing the cell at its ends. To reduce the influence of adsorption/desorption processes at the inner surfaces of adhesive molecules, such as CH₂O, we realize a PA cell with gold coated inner walls cell. The resonator, placed in a massive aluminum housing to minimize sensitivity to external noises, was designed to be excited in its first longitudinal mode at 1380 Hz; it was equipped with 4 electret microphones (Knowles EK 3024) with sensitivity of Sₘ=20 mV/Pa, placed on the antinode of the acoustic mode to increase the signal-to-noise ratio. The electrical signal, fed by the microphones, was pre-amplified and then measured by a digital lock-in amplifier (EG&G Instruments) with a 10 s integration time constant. The laser radiation was collected with an AR coated ZnSe lens (2.54 cm focal length, f/1) and collimated by a beam condenser (0.2X) to avoid reflections on the cell walls. In Figure 1 is show a schematic of the H-cell setup.

![FIG.1 Schematic diagram of the H-Cell photoacoustic sensor.](image)

In order to measure the resonance frequency and the quality factor (Q), we measure the response of the cell in air using white noise as source. In Fig 2, the frequency response of the H-cell is reported, for our experiments we select the first longitudinal mode at 1380 Hz, showing a Q-factor of 45.

![FIG.2 .Response of the H-cell photoacoustic sensor to a white noise source. From the fit of the data (dotted line) we extract the resonance frequency and the relate Q-factor.](image)
2.2. T-Cell

The resonant PA T-cell is characterized by a T geometry consisting of two intersecting volumes: an optical absorption volume and an acoustical resonance cylinder. At the end of the resonance cylinder the microphone is mounted. The internal walls of the optical cavity have been shaped in order to produce multiple light reflection and subsequent focusing in the cavity center. We can change the resonator length and radius using a mechanical system in a range between 60-113 mm for the cylinder length and 8-12 mm for the internal radius. This design allows to use of a mid-IR optical fiber to couple the laser source and the PA cell thus eliminating any optical alignment issue. The optical fiber is directly inserted in the PA cell using a SMA hermetic feedthrough connector, so no input windows are required. The inner walls are gold coated in order to reduce adsorption/desorption effects of adhesive and highly polar molecules, such as CH₂O. Two different type of sound detector have been employed: electret microphones (Knowles EK 3024) and optical MEMS-based microphone. The electrical signal was pre-amplified and measured by a digital lock-in, with a 10 s integration time constant.

In Figure 3a is show a schematic of the T-cell setup.

![Schematic diagram of the T-cell photoacoustic sensor](image)

**FIG.3** a) Schematic diagram of the T-cell photoacoustic sensor, b) Response of the T-cell photoacoustic resonator to a white noise source, for different longitudinal resonator length (L). From the fit of the data we extract the resonance frequency and the related Q-factor.

We have studied the response of the T-cell in air using as source white noise, as a function of the resonator length L. In Figure 3b are reported three representative frequency response of the T-cell. The fundamental resonance frequency can be varied in the range 660-1100 Hz. In our experiment we used the first longitudinal mode at 830 Hz, obtained for a cylinder length of 88 mm and a radius of 12 mm, showing a Q-factor of 10. This results the best resonance configuration, in terms of quality factor (Q), PA signal and immunity to external noise sources.

2.3. Experimental results

Both the two PA sensors have been fully calibrated in terms of sensitivity, detection limit and minimum detectable absorption coefficient. We selected the CH₂O absorption line at 1778.9 cm⁻¹ for PA detection, where we have a small overlap with water lines. This line is characterized by a strength
of 5.68×10^{-20} \text{ cm/molecule} \ [4]. The lasing emission has been fixed over this line by setting the temperature of our QC laser at T=13.7 °C. A certified 99.8-ppmv CH\_2O in N\_2 mixture was used to obtain known concentrations of the investigated gas in the 0.1–10 ppmv range via two mass flow controllers (Brooks Instrument). We use a chemical trap (Entegris mod. 35KF) to reduce the water vapour concentration in the certified mixture down to 0.1 ppb. The pressure in the PA cell was kept at that of the ambient air. The magnitude of the photoacoustic signal was measured by the lock-in amplifier. The background signal was measured by filling the PA cell with pure nitrogen and the electronic noise, due to electromagnetic noises and mainly uncorrelated with the modulation frequency, was detected with the laser beam off. Each measurement was performed after an accurate purging of the cell to avoid contributions from adsorbed-desorbed molecules. We observe a linear correlation between the PA signal and the CH\_2O concentration \ [5]. From the experimental data we can extract the sensor detection limit and minimum detectable absorption coefficient, normalized to power and detection bandwidth. In Table I the H- and T-cell sensor performances are summarized.

### Table I. Summary of the sensors performances.

|                   | H-Cell     | T-Cell     |
|-------------------|------------|------------|
| \(P_0\) (mW)      | 4          | 4          |
| \(S_m\) (mV/Pa)   | 20         | 20         |
| \(\tau_m\) (s)   | 10         | 10         |
| \(a_{\text{min}}\) (cm\(^{-1}\)) | 6.6×10^{-7} | 1.4×10^{-7} |
| \(D\) (W\cdot\text{cm}^{-1}\cdot\text{Hz}^{-1/2}) | 2.0×10^{-8} | 4.3×10^{-9} |
| Detection limit (ppbv) | 150        | 30         |

Both the detection limit and the minimum detectable absorption coefficient extracted for the T-cell configuration are about five times better than that measured for the H-cell. This is mainly due to the improved laser-optical cavity coupling in the T configuration in terms of absorption path length (due to the light multi-reflection and focusing) and the reduction of background noise (due to the absence of input optical windows). The T-cell sensor results also more compact and portable.

Future developments to improve the obtained performances will be the implementation of: an inter-cascade laser operating at room temperature in continuous mode in the first absorption range of CH\_2O (around 3.5 \text{ µm}), in order to increase the gas absorption coefficient, eliminate the thermal chirping of pulsed operation and increase the sensor selectivity.

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