Extreme Sensitivity in Photoacoustics by Using Optical Cantilever-type Microphone

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Low resolution Fourier Transform infrared (FTIR) spectrometers are known to be the best instruments for gas analysis, when a broadband black body radiation source and a normal absorption technique is used. However, modern spectrometers are developed very close to their theoretical performance limits. Thus, in order to significantly enhance the sensitivity, one has to find new techniques, still unrestricted by any fundamental law of physics. A modern photoacoustic detection system is a that kind of technique. Currently, photoacoustic gas analysis systems are known to be more sensitive than FTIR spectrometers only if a laser source is used. However, the microphone sets the limit of the sensitivity on the whole photoacoustic system. Thus, a major improvement can be achieved with a new pressure sensing technique. A recently introduced optical microphone has shown to improve orders of magnitude the sensitivity of a conventional photoacoustic system. The pressure sensing element is a thin silicon cantilever with a narrow gap to its frame and it is located between two chambers like a door in a wall. The displacement of the free end of the cantilever is continuously measured with a compact Michelson interferometer. By using a preliminary prototype of the proposed photoacoustic gas detector, equipped with a black body radiation source and an optical filter, a detection limit in the sub-ppb range was obtained for e.g. methane gas. The limit, obtained in non-resonant operation mode, is very close to the best results achieved with powerful laser sources and by exploiting the cell resonances.

1 Introduction

Trace gas detection has widespread applications for example in biology, medicine, controlling industrial processes and monitoring pollutants or toxic gases [1]. An ideal trace gas measurement system has to fulfill various requirements:

1. ability to measure different substances with a single device;
2. high selectivity, when the sample consists of several substances;
3. high sensitivity, the detection limits of concentrations on the level of ppb (10\(^{-9}\)) or ppt (10\(^{-12}\));
4. possibility for field measurements, easy to transport and not vulnerable to the ambient noise;
5. good time resolution, which enables real time measurements;
6. rapid sample generation or capability for in situ measurements;
7. automatic operation and remote controlling.

Low resolution FTIR spectrometers with a broadband IR source are excellent instruments for multi-component gas analysis, but in several applications they are not sensitive enough. It is also very difficult to further improve e.g. the radiation source, the throughput of the optics or the semiconductor IR detectors. Thus, in order to gain significant improvement, some part(s) of the spectrometer must be changed dramatically.

2 Photoacoustic detection

2.1 Basic photoacoustic spectroscopy

Photoacoustic spectroscopy (PAS) is recognized as a sensitive, zero background method for trace gas analysis. A conventional gas measurement setup is shown in Figure 1. As the IR beam penetrates the sample cell, the absorption of the radiation heats up the gas increasing both the temperature and the pressure. Thus, the IR radiation modulated by a chopper with a certain frequency will create temperature and pressure variations in the sample gas with the same frequency. These variations form a sound wave, which is usually measured with a capacitative microphone. The selectivity is achieved by using an optical filter or a laser with a certain wavelength.

Even though almost ppt-level concentrations can be detected with efficient and complicated laser setups, PAS is known to be less sensitive than FTIR spectrometers if a broadband radiation source is used. Fortunately, the sensitivity of the whole photoacoustic system is limited by the pressure sensor i.e. the microphone. Thus, major enhancements could be achieved by replacing the capacitive microphone.
2.2 Capacitive microphone

The vibrating element in a capacitive microphone (Fig. 2) is a conducting, flexible membrane, which deforms due to the pressure variations in the surrounding gas. The membrane is separated from a fixed metal electrode by distance \( h \). Thus, they form a condencor, whose capacitance \( C \) changes proportionally to the pressure change \( \Delta p \) via the \( \Delta h \) i.e.

\[
\Delta p \propto \Delta C = -\frac{\varepsilon A}{3h^2} \Delta h \quad (\Delta h \ll h),
\]

where \( A \) is the common area of the electrodes, and \( \varepsilon \) is the dielectric constant of the gas between the electrodes. The increase of \( A \) and the decrease of \( h \) will increase the sensitivity. But there is a maximum, which cannot be further improved by this mean. This is due to so called ‘breathing effect’: the air flow in and out of the gap between the electrodes requires energy, and therefore creates a strong damping on the film. This effect increases as \( A \) and \( h \) increases and decreases, respectively. [2]

2.3 Cantilever-type optical microphone

Microphones, where the flexible membrane is strained over a frame, are not very sensitive and their response is not perfectly linear. This is due to the fact, that the material has to stretch out radially under the pressure variations. The sensitivity of the membrane depends also on its tension, which is a function of the temperature. Thus, the thermal stability of a capacitive microphone is not very good.

We propose a cantilever-type pressure sensor [3] as shown in Fig. 3. The sensor is made out of silicon. An extremely thin \((t = 5 \mu m)\) cantilever portion moves like a flexible door due to the pressure variations in the surrounding gas. The frame around the silicon cantilever is thick \((380 \mu m)\) and there is a narrow \((\Delta = 30 \mu m)\) gap between the frame and the cantilever on three sides \((l = 4 mm, w = 2 mm)\).

As the pressure varies the cantilever only bends but it does not stretch. Therefore, the movement of the cantilever’s free end can be about two orders of magnitude greater than the movement of the middle point of a tightened membrane under the same pressure variation [3]. Notice also, that the capacitive microphone measures rather the average displacement of the membrane than its middle point movement.

The motion of the cantilever can be described with a point mass model using a harmonic oscillator, because we are only interested in the region below the first resonance frequency. Therefore, the equation of motion becomes:

\[
m \ddot{x} + \beta \dot{x} + kx = F_0 \cos(\omega t),
\]

where \( m \) is the mass, \( \beta \) is the damping constant, \( k \) is the string constant of the vibrating element, \( x \) is the displacement from the equilibrium, and \( F_0 \cos(\omega t) \) is the external force. The string constant is defined as \( k = m\omega_0^2 \), where \( \omega_0 \) is the first resonance frequency. If a uniform cantilever with a rectangular cross-section is used, the first resonance frequency becomes:

\[
\omega_{0,\text{cant}} = (1.875)^2 \sqrt{\frac{E l^2}{12 \rho}},
\]

where \( E \) is Young’s modulus, \( \rho \) is the density, \( l \) is the length, and \( t \) is the thickness of the cantilever.[4] The solution \( x(\omega) \) of eq. (2) gives the amplitude of the cantilever as:

\[
A_x(\omega) = \frac{F_0}{m \sqrt{\omega_0^2 - \omega^2 + (\beta/\omega m)^2}}.
\]

The dynamic range of the cantilever is exceptionally large, and the response is extremely linear, when the displacement of the tip of the cantilever is less than ten microns.
3 New photoacoustic measurement system

3.1 Setup

Fig. 4 shows our proposed photoacoustic measurement system using an optical cantilever-type sensor. Both chambers are filled with the sample gas to be measured. The diameter, length and the volume of the sample cell are \( 2r, d \) and \( V = d\pi r^2 \), respectively. The silicon cantilever is located between the two chambers (like a door in a wall). The absorption cell is a inside polished brass tube, and the cantilever and its frame act like a mirror reflecting the IR beam back. By this way, the absorption path length can be doubled to \( (2d)/\cos\Theta \).

![Figure 4: The structure of the first prototype of the proposed system](image)

3.2 Interferometric displacement measurement

The displacement of the cantilever is measured with a compact Michelson interferometer (Fig. 4). The laser beam is directed towards the free end of the cantilever and focused very close to it. Both arms of the interferometer are set to equal and the reference mirror is adjusted in such a way that there is a half of an interference fringe over the photodiodes \( D_2 \) and \( D_3 \). When the cantilever moves, the signals from the photodiodes have a 90° phase difference between one another. Note, that the phase difference between \( D_1 \) and \( D_3 \) is exactly 180°. Using these three signals we are able to continuously calculate the phase of the interferometer even though it changes over \( 2\pi \), which corresponds to the displacement of \( \lambda/2 \) of the cantilever.

3.3 Photoacoustic signal

A photoacoustic signal is generated by the absorption of energy from the modulated IR beam. This energy produces a periodically varying heat source that acts as a source of sound. If the dimensions of the gas cell are much smaller than the wave length of the sound wave, then the temperature, the total pressure and the density of the gas have constant values without any dependence on the location inside the sample cell. In these conditions, it is justifiable to use the equation of the state of an ideal gas to derive equations for the force amplitude \( F_0 \) and the resonance angular frequency \( \omega_0 \) in eq. (4). This derivation (presented in detail elsewhere [2]) gives an expressions for the \( F_0 \):

\[
F_0 = \frac{A(\gamma - 1)\alpha_x p_x \frac{2d}{\cos\Theta}P_0}{\omega},
\]

where \( A, V, \) and \( d \) are the area of the cantilever, the volume and the length of the sample cell, respectively, \( P_0 \) is the power of the IR beam, \( \alpha_x \) is the absorption coefficient, \( p_x \) is the partial pressure and \( \gamma = C_p/C_V \) is the specific heat ratio. Substitution of this in eq. (4) leads to the following expression for the amplitude of the cantilever inside the sample cell:

\[
A_x(\omega) = \frac{A(\gamma - 1)\alpha_x p_x \frac{2d}{\cos\Theta}P_0}{\omega \sqrt{(\omega^2 - \omega_0^2)^2 + (\omega/\gamma m)^2}}.
\]

The spring constant \( K \) for the cantilever inside the cell is given by

\[
K = k + \gamma \frac{A^2 p}{2.5V},
\]

where the last term is due to the gas spring in a closed cell. This leads to the following equation for the resonance frequency:

\[
\omega_0^2 = \frac{K}{m} = k + \gamma \frac{A^2 p}{2.5V}.
\]

In practise, the measurements are done below the resonance frequency (\( \omega \ll \omega_0 \)), so that eq. (4) reduces to the expression given by

\[
A_x(\omega) = \frac{F_0/m}{\omega^2} = \frac{A(\gamma - 1)\alpha_x p_x \frac{2d}{\cos\Theta}I_0}{\omega(k + \gamma p_x^2/2.5V)} \quad (\omega \ll \omega_0),
\]

where \( I_0 \) is the average amplitude of the intensity \( (P_0/\pi r^2) \) of the modulated light going into the cell.

4 Experiments

4.1 Amplitude response

Following measurements were used to test the accuracy of the derived theoretical frequency response of the cantilever, given by equation (6). The chambers were filled with gas (\( N_2, CO_2, CH_4 \) or air) to several different pressures. The signal was produced either by changing the
modulation frequency in the photoacoustic method, or by using an external loudspeaker connected to a signal generator. Fig. 5 shows the measured values in a case of air at normal pressure. As we can see, the theoretical curve (solid line) fits extremely well to the measured values (circle markers).

![Figure 5: The amplitude response of the cantilever inside the sample cell](image)

### 4.2 Gas spring

When the cantilever moves back and forth, the volume of the sample cell changes. Therefore, the cantilever has to compress the gas around it and this will create an additional term to the spring constant according to equation (7). In small sample cells this gas spring has a remarkable effect to the resonance of the cantilever. To test eq. (8), we have measured the resonance frequencies of the cantilever inside the cell, which volume could be altered. The measured values support the theoretical results as shown in Figure 6.

### 4.3 Sensitivity

Methane gas was used to estimate the sensitivity of our proposed detector. Figure 7 illustrates the Fourier transform of the measured cantilever signal (0.74 seconds measurement time). The modulating frequency $\omega/(2\pi)$ accomplished by using a mechanical chopper was 118 Hz. The whole measurement system was filled with a mixture of $N_2$ and $CH_4$, where the concentration of $CH_4$ was $10 \pm 2$ ppm and the total pressure was 0.6 atm. Curve A shows the amplitude of the cantilever as a function of $\omega$ without an optical filter and curve B shows the amplitude profile, when an optical bandpass filter was used (Fig. 8). The cut-on and cut-off wave numbers of the filter were 2500 cm$^{-1}$ and 3500 cm$^{-1}$, respectively. As a reference we analyzed the gas mixture with GASMET gas analyzer. The spectrum showed one methane band at 3000 cm$^{-1}$ between weaker water absorptions on both sides (all the gas samples in practice include a small amount of water) and the other methane band at 1300 cm$^{-1}$. The curve B in Fig. 7 is lower biased due to the optical bandpass filter. Both curves A and B show weak regular maxima (1,2,3...) with an interval of 118/10 Hz. These weak peaks are due to the fact that the 10 blades of the chopper used in the measurements are not exactly identical. This irregularity of the chopper blades generates frequency modulation sidebands.

![Figure 6: The effect of the gas spring on the resonance frequency of the cantilever inside the sample cell](image)

![Figure 7: Photoacoustic signal due to 10 ppm of methane](image)
measurement time to 100 seconds (S/N ≈ 11625) we get an estimation of the detection limit, which is 10 ppm /(S/N) = 0.8 ppb (ppb = 10^-9). Since we measured the displacement of the end of the cantilever interferometrically it is accurately given in laser wavelengths. In this experiment the smallest detectable displacement was about 2 \cdot 10^{-12} m, which is roughly equal to the noise amplitude. The amplitude of the cantilever due to methane at 10 ppm was about 25 nm, which means that the response is absolutely linear in this range. In fact, the detection system is linear upto 5000 ppm due to Beer’s absorption law. If we use root mean square (RMS) noise to derive the detection limits, we result in detection limit of methane better than 0.2 ppb.

5 Summary

In this paper, we have represented a novel photoacoustic IR-detection method, which bases on the use of a cantilever-type optical microphone. This method has been shown to overcome the limitations in the capacitive microphone technology. We have constructed a preliminary prototype of the new measurement system and obtained a detection limit of 0.8 ppb for methane when estimating a peak-to-peak noise and using a black body radiation source. The detection limit is better than 0.2 ppb when using RMS noise.

References


