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Extremely sensitive trace gas analysis with modern photoacoustic spectroscopy

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Abstract

An extremely sensitive approach to detect weak pressure variations has been applied to photoacoustic spectroscopy. A capacitive microphone is replaced with a miniature silicon cantilever, whose displacement is measured with a compact Michelson-type laser interferometer. Major improvements to the sensitivity of photoacoustic detection have been achieved. For example, a sub-ppb detection limit for methane gas has been obtained with a conventional photoacoustic setup in a nonresonant operation mode, using a broadband black body radiator as a source. The new sensing method has also been applied to the detection of carbon dioxide with a distributed feedback diode laser. A noise equivalent sensitivity of 4.6×10^{-9} cm^{-1} WHz$^{-1/2}$ was demonstrated. A novel selective differential method, which combines the photoacoustic detection with long path absorption spectroscopy, is described.

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1. Introduction

Trace gas detection has widespread applications, for example, in biology, medicine, controlling industrial processes and monitoring pollutants or toxic gases [1]. The most critical characteristics of the sensing device are: long-term stability, high signal-to-noise ratio (S/N), i.e., high sensitivity, and good selectivity. Low resolution FTIR spectrometers with a broadband IR source are excellent instruments for multi-component gas analysis although 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 in the sensitivity, 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 Fig. 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 capacitive 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 with semiconductor detectors 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 with a better pressure sensor.

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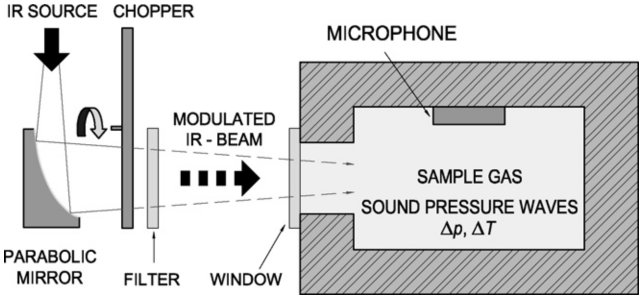

Fig. 1. Conventional photoacoustic measurement setup.

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 condenser, whose capacitance C changes proportionally to the pressure change Δp via the Δh dependencies, i.e.

$$\Delta p \propto \Delta C = -\frac{\varepsilon A}{3h^2}\Delta h \quad (\Delta h \ll h), \tag{1}$$

where A is the common area of the electrodes, and ε is the dielectric constant of the gas between the electrodes. The increase of A and the decrease of h will increase the sensitivity. Still, there is a maximum, which cannot be further improved by this means. This is due to the 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 have replaced the capacitive microphone with a cantilever-type pressure sensor as shown in Fig. 3. The sensor is made out of silicon. A thin (t = 10 μm) cantilever portion moves like a flexible door due to the pressure variations in the surrounding gas. There is a narrow ($\Delta < 5$ μm) gap between the thicker frame and the cantilever on three sides (l = 6 mm, w = 4 mm).

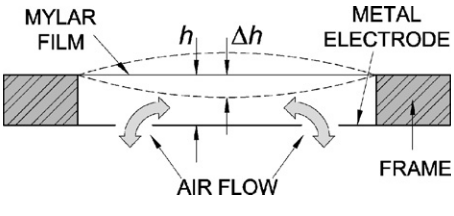

Fig. 2. The structure of a capacitive microphone.

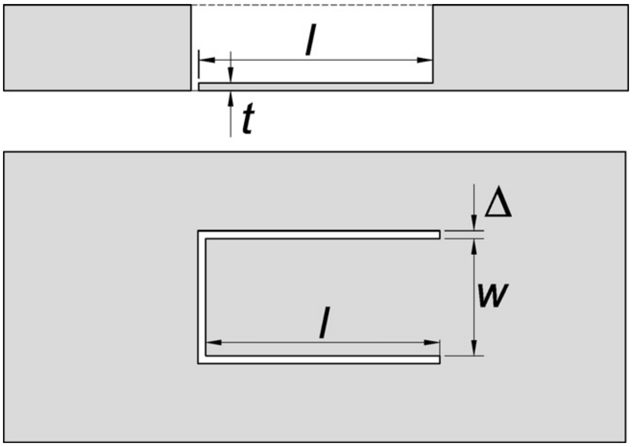

Fig. 3. The dimensions of the silicon cantilever.

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]. It should also be noted that the capacitive microphone measures the average displacement of the membrane not the movement of its middle point.

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:

$$m\ddot{x} + \beta\dot{x} + kx = F_0\cos(\omega t), \tag{2}$$

where m is the mass, β 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 ω_0 is the first resonance frequency. If a uniform cantilever with a rectangular cross-section is used, the first resonance frequency becomes:

$$\omega_{0,\mathrm{cant}} = \frac{(1.875)^2}{l^2}\sqrt{\frac{Et^2}{12\rho}}, \tag{3}$$

where E is Young’s modulus, ρ is the density, l is the length, and t is the thickness of the cantilever [5]. The solution $x(\omega)$ of the Eq. (2) gives the amplitude of the cantilever as:

$$A_x(\omega) = \frac{F_0}{m\sqrt{(\omega_0^2 - \omega^2)^2 + (\omega\beta/m)^2}}. \tag{4}$$

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.

2.4. Interferometric displacement measurement

The displacement of the cantilever is measured via a compact Michelson-type laser interferometer (Fig. 4). The laser