Ultrathin Mica and Graphite Cantilevers Enhanced Photoacoustic Spectroscopy – towards Modelling of Acoustomechanical Properties

Suchánek Jan¹, Dostál Michal¹, Janda Pavel¹, Zelinger Zdeněk¹, Chalupský Jaromír², Wild Jan³

¹J. Heyrovsky Institute of Physical chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic
²Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic
³Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic

Abstract. In this article, we present the concept of probing of the acousto-mechanical properties (e.g. spring constant, resonator quality factor) of thin 2D or 2D like samples (i.e., samples with one dimension at least 2 orders of magnitude smaller than the others). Samples prepared from highly ordered pyrolytic graphite and muscovite with thickness under 1 μm and other dimensions in the mm range are used for this purpose. These samples are employed in photoacoustic spectroscopy as the pressure sensitive elements and its movement is monitored by a He-Ne laser beam reflected from the surface of these samples onto a position sensitive detector. The concept includes the following steps: 1) development of the method of preparation of thin samples from layered materials 2) development of the experimental approach for data collection 3) derivation of theoretical behavior of photoacoustic response of the samples and 4) development and application of a model on experimentally acquired data.

1. Introduction
Micro and nanomechanical 2D materials show extreme sensitivity to mass and surface changes and can thus be exploited as sensitive chemical and biological sensors with the ultimate sensitivity down to individual molecules. Such materials can be used as nanomechanical resonators with resonance frequencies above 1 GHz and with high quality factors (10³ - 10⁵) [1,2]. Its supreme sensitivity to mass was exploited for the measurement of physical quantities [3–5] Beside ultrasensitive mass detection, resonators with high resonance frequencies can be applied in signal processing and communication technologies.

Layered materials such as highly ordered pyrolytic graphite (HOPG) and multilayer muscovite (mica, MLM) are ideal starting materials for the preparation of ultrathin (down to single layer) 2D materials. Its thickness can be simply reduced by exfoliation of the basal planes. Bunch et. al. demonstrated methods for the characterization of mechanical properties (resonance frequency, spring constant, quality factor) for nanoresonators prepared from graphene sheets [6]. The resonators are actuated either optically or electrically and are detected optically by interferometry. High quality factors were
demonstrated for these nanoresonators with resonant frequencies in the MHz range. Recently, frequency tracking through resonant frequency comb was reported [7]. The extreme sensitivity of nano/micromechanical elements to external force can be exploited in photoacoustic spectroscopy (PAS). PAS is very sensitive detection method, where the periodically interrupted radiation is converted to heat when absorbed by a substance (gas, solid or liquid) and subsequently converted to acoustic waves, which can be detected by a microphone. An optical microphone was proposed by de Paula et.al. – a pressure sensitive element which motion can be sensed optically with a position sensitive detector [8]. Wilcken and Kauppinen demonstrated a 5 micrometer thin silicon cantilever used as an optical microphone and showed both theoretically and experimentally that such microphone exceeds conventionally used (electret and condenser) highest-class microphones [9]. Cantilever enhanced photoacoustic spectroscopy (CEPAS) is very promising sensitive trace gas detection method [10–12].

In our previous work, we suggested that thin graphite and multilayer graphene sheets can be utilized in PAS as pressure sensitive elements – optical microphones [13–15]. In our first work on this topic [13], we tested multilayer graphene sheets prepared from multilayer graphene through the micromechanical cleavage of basal plane highly ordered pyrolytic graphite. The sheets with thickness ~ 100 nm were glued to a glass substrate with a circular opening (r ~ 1 mm). We showed the feasibility of using these elements for PAS, although the sensitivity was inferior to a commercial highest-class microphone. Through the development of the preparation method, we prepared a multilayer graphene with cantilever-like geometry that surpassed the conventional microphone [15]. Nevertheless, we have found that the non-uniform structure of the cantilever caused by the presence of grain boundaries of the graphene sheets limits its elastic properties and thus its performance as an acoustic resonator. Next, we focused on multilayer mica as starting material for cantilever preparation [16]. It seems that the structure of mica sheets prepared by exfoliation of basal planes is more uniform when compared to the graphene sheets prepared by the same method from HOPG. Thanks to the progress in cantilever preparation, the sensitivity was further increased, although the cantilevers suffered from long term instabilities when used as a part of an optical microphone.

We have also suggested, that PAS can serve as a method for probing the mechanical properties of thin samples like graphene and mica sheets and cantilevers [14]. In this article, we explore this idea into more depth.

2. Experimental

2.1. Photoacoustic spectroscopy setup

A modified setup for photoacoustic spectroscopy was developed to test ultrathin samples (Fig. 1). A quantum cascade (QC) laser emitting between 7.996 – 8.009 μm / 1249 - 1251 cm⁻¹ (QD4580, Thorlabs, USA) was used as an excitation source for PA signal generation. The QC laser was installed in a laser mount with temperature stabilization (Arroy 242, Arroyo Instruments, USA) and controlled by a laser current/temperature controller (ITC4005QCL, Thorlabs, USA). The laser beam was collimated by an aspheric lens, periodically interrupted by a chopper and focused inside a custom-made photoacoustic cell with inner diameter of 6 mm and a length of 245 mm (length can be adjusted via changeable arms). Part of the laser beam was reflected by a beam splitter onto nitrogen cooled InSb detector with preamplifier (Graseby Infrared) to monitor the laser beam. The photoacoustic cell is an important part of the setup and was designed to enable easy exchange of tested materials (graphene/mica membranes and cantilevers). The samples were placed on a glass substrate. The movements of the cantilever ends induced by acoustic waves were actuated by a He–Ne laser beam that was reflected from the cantilever ends onto a quadrant detector (a red-enhanced quad-cell silicon photodiode, SD 085-23-21-021, Laser Components). The PA cell has a place for mounting both the samples and conventional microphone and is made symmetrical, so the comparison of the samples and the microphone (Brüel and Kjaer, condenser microphone, type 4144) is possible. There is a small opening in the middle of the cell leading to the microphones. The detail of the custom-made PA cell can be found in the paper [16]. The signals (waveforms) from the quadrant cell (mica and graphite
cantilever), microphone, InSb detector (QC laser - excitation source of photoacoustic signal) were collected via 4-channel digital oscilloscope (DSO5054A, Agilent Technologies, USA).

2.2. Cantilever preparation
The preparation of multilayer graphene/muscovite cantilever is described in detail in our previous paper [16]. Briefly, the sample was prepared by the Scotch tape method (by peeling the basal planes) and then cutting them to desired shape. The surface was covered by thin Au film (50 – 100 nm) for better reflectiveness. The cantilever was circular with 13 mm diameter and thickness under 1 μm.

![The photoacoustic experimental setup.](image)

3. Results and discussion

3.1. Experimental approach for data collection
To get the relevant inputs for a photoacoustic model, the experimental approach described above was developed. This setup enables the collection of the signals from a) the 4-quadrant detector (i.e. – the cantilever/membrane movement) b) the microphone c) an optical detector (profile of the excitation laser beam) and d) reference signal from the chopper control unit (information about phase shift). The example of collected signals is on Fig. 2.
Figure 2. Typical experimental results. 9 Hz modulation. Cantilever movement (red), condenser microphone movement (blue), excitation laser profile (black dash) and chopper reference signal (green).

To test the developed (acousto-mechanical) models thoroughly, the response of the samples (cantilevers, membranes) to photoacoustic pressure can be tested at various conditions. The change of carrier gas influences the sound velocity and thus the PA cell resonant frequencies, which can be monitored by changing the modulation frequency of the source of radiation. The acoustic properties of the PA cell can be varied (different PA cell length, closed/open gas inlet and outlet arrangement).

3.2. Derivation of theoretical photoacoustic behavior

This section describes the theoretical aspects of PA signal behavior, as derived by the authors. The derivation are not shown here in full details, as it is beyond the scope of this article, but only the main starting points and results are highlighted. For more details, please see [17][10]

When investigating the process of acoustic wave formation in a PA cell, it is necessary to observe all influences on the volume element of the gas inside the cell. Pressure changes caused by the absorption of laser radiation create an acoustic field inside the PA cell.

Photoacoustic signal generation can be divided into these steps: 1) periodic vibration/electronic excitation of molecules into higher state by radiation source - 2) vibrational-transational relaxation followed by heating of the gas and finally 3) the formation of acoustic wave. The acoustic and thermal wave generation inside of the PA cell can be modelled by applying the laws of thermodynamics a fluid mechanics. The time-dependent pressure changes inside the PA cell can be theoretically expressed as follows:

\[
\frac{dP}{dt} = \frac{2}{3} h \nu \frac{n_1}{\tau_c} \left( P - P_0 \right) / \tau_1
\]

where \( P_0 \) is the equilibrium pressure inside the cell without radiation, \( h \) is the Planck-constant, \( \nu \) is the frequency where the sample absorbs, \( n_1 (m^{-3}) \) is the number of molecules in unit volume in higher energetic state with absorption frequency equal to the frequency of the radiation, \( \tau_c \) is the collision-controlled lifetime of the higher energy state and \( \tau_1 \) is the time of photoacoustic delay which depends on the thermal properties of the gas.

If we consider the time dependence of \( n_1 \) in eq. 1 (not shown here), we can write the pressure inside closed (non-flow) PA cell as a function of time:
where $A$ and $B$ are parameters. The pressure changes corresponding to the first harmonic in the Fourier series, which represents the time dependence of the pressure change, are most pronounced when interacting with the pressure sensor. If we take the Fourier series of eq. 2 and take into account its first harmonic frequency and simplify it, we get to eq. (3)

$$S_i(\omega) = \frac{\sqrt{2}}{\pi^2} (\gamma - 1) \frac{NW\sigma}{R^2(1+\alpha^2\tau_1^2)} Q_c(\omega) c_i$$

This equation describes the dependence of PA signal on the concentration of absorbing molecules $N$, on the radiation source power $W$, on the absorption cross-section $\sigma$ of the absorbing molecules, on the time-delay of PA response $\tau_1$, on the modulation frequency $\omega=2\pi f$, on the PA cell radius $R$ and on the PA cell quality factor $Q_c$.

The movement of the pressure actuator (i.e. membrane, cantilever) can be described by the second order one-dimensional eq. (4):

$$\sigma_m A_m \frac{d^2 x_m}{dt^2} + D \frac{dx_m}{dt} + Gx_m = A_m p_+$$

where $\sigma_m$ is the area density of the actuator, $x_m$ is the displacement of the actuator from equilibrium, $p_+$ is the actuating pressure, $A_m$ is the area of the actuator, $D \frac{dx_m}{dt}$ is the damping force and $Gx_m$ is the restoring force acting on the actuator.

The behavior of the gas inside of the cell can be approximated by the equation of forced damped harmonic oscillator. Its main characteristics are the spring constant $k$, the damping constant $B_c$ and mass (of the gas inside of the cell) $-\varepsilon$ - equation 5.

$$\rho_c V \frac{d^2 x_c(t)}{dt^2} = -kx_c(t) - B_c \frac{dx_c(t)}{dt} + \frac{2}{3} \nabla (\psi - \psi_0)$$

where $V$ is the volume of the PA cell and $x_c(t)$ is the displacement of the volume element inside of the cell from equilibrium, $\psi$ is the average transitional energy of the molecules in unit volume and $\psi_0$ is the equilibrium value of $\psi$.

In case of the connection of the PA cell with flow system (which is the common case for photoacoustic setup), we have derived following equation:

$$p_+ = p_{id} \left[ 1 - 2c_i e^{-c_i^2} I_1(t) \right]$$

By substitution of the eq. 6 into equations 4 and 5, it is possible to get the second order inhomogeneous equation that describes the time dependence of the PA signal:

$$\dot{x}_m + 2k_m \dot{x}_m + \omega_m^2 x_m = F_m p_+ (t)$$

$$\dot{x}_c + 2k_c \dot{x}_c + \omega_c^2 x_c = F_c p_+ (t)$$

where
The equations derived above were used to model the acoustic behavior of the system – i.e. PA cell and cantilever/membrane. The model consists of two coupled forced oscillators, which represent both the generation of acoustic waves in the space of the PA cell and the interaction of pressure changes with the sensor. To evaluate the model, the experimentally acquired photoacoustic signals (Fig. 3) are compared to the simulated data using the model (Fig. 4).

At a given stage of the model development, the model is able to simulate a PA signal for different PA cell configurations and pressure sensors. This helps to interpret the process of generating of PA signals. The next planned stage of the model development is to fit the theoretical data with the experimental data to obtain data on acousto-mechanical parameters of the materials used.

$$k_m = \frac{\omega_m}{2Q_m}; k_c = \frac{\omega_c}{2Q_c}; F_m = \frac{1}{\sigma_m}; F_c = \frac{A_c}{\rho_0 V}; \omega_m = 2\pi V_m$$

$$k_m = \frac{D}{2\sigma_m A_m}; \omega_m^2 = \frac{G}{\rho_0 V}; k_c = \frac{B_c}{2\rho_0 V}; \omega_c^2 = \frac{\kappa}{\rho_0 V};$$

$$\omega_c = 2\pi V_c$$

and $\omega_m$ and $\omega_c$ is the resonance frequency of the actuator and the cell, respectively, $Q_m$ and $Q_c$ is the quality factor of the actuator and cell, $\sigma_m$ is the area density of the actuator and $A_c$ is the inner area of the PA cell. Through the superposition of the displacement of the volume elements in PA cell $x_c$, caused by the oscillating pressure $p_\sim(t)$ and the response of the pressure actuator $x_m$, we can derive the time dependent displacement of the photoacoustic response:

$$x(t) = x_m + x_c$$ (10)
Figure 4. Simulated data of experimental signal.

4. Conclusion
We have developed and tested the approach (both experimental and theoretical) to get the material information related to micro-mechanical levers applicable in photoacoustic spectroscopy. It includes the development of a method for the preparation of thin samples from carbon and mica layered materials, the development of an experimental approach to data collection using laser photoacoustic detection and the use of the optical microphone and cantilever principle, the derivation of the theoretical behavior of photoacoustic response of samples based on formulation of processes during radiation absorption, generation of thermal changes and creation of acoustic field inside PA cell, further development and application of the model to experimentally obtained data, where the core of the model lies in the coupling of two forced oscillators describing the dynamics of pressure changes in the PA cell space and the interaction with the pressure sensor.

5. References
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