European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability - *EuNetAir*

COST Action TD1105

Final Meeting at PRAGUE (CZ), 5-7 October 2016

New Sensing Technologies for Air Quality Monitoring

Action Start date: 01/07/2012 - Action End date: 15/11/2016 - EXTENSION: 15/11/2016

Multilayer graphene cantilever for laser photoacoustic detection

cost
EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

ÚFCH JH

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EuNetAir
European Network on New Sensing Technologies for Air-Pollution Control and Environmental Sustainability

COST is supported by the EU Framework Programme

European Science Foundation
ESF provides the COST Office through a European Commission contract

Scientific context and objectives in the Action

Background / Problem statement

- utilizing microlever physical and mechanical properties of graphene for gas sensing by photoacoustic detection ;
- to test developed sensors in a form of MLG cantilevers/membranes by the laser photoacoustic detection

Brief reminder of MoU objectives:

- development of novel sensors for gas analysis based on micro-cantilever material properties and its utilization for chemical sensing
- combination of sensitive microphones and micromechanical elements with advanced laser techniques - a precise method for the studies of chemical sensing possibilities

- **WG2: Sensors, Devices and Systems for AQC**
- **SIG2: Smart Sensors for Urban Air Monitoring in Cities**

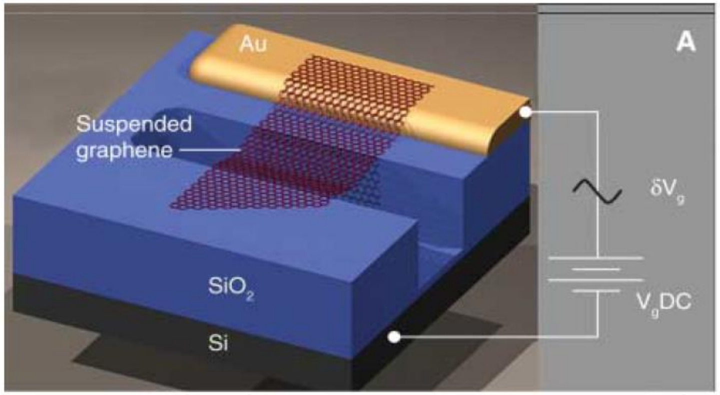
Current research topics at the partner organization / Problem statement:

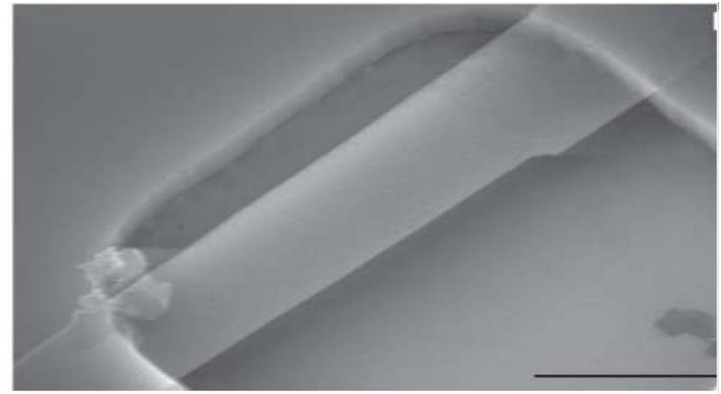
Despite outstanding electromechanical properties of graphene leafs and impressive sensitivity as a mass detector, its utilization as nano/micro-lever sensing devices for chemical analysis is an important challenge:

P. Li, Z. You, T. Cui, “Graphene cantilever beams for nano switches“, *Applied Physics Letters*, **101**, (2012) Issue 9, id. 093111.

main methods to actuate and detect the movement in graphene elements:

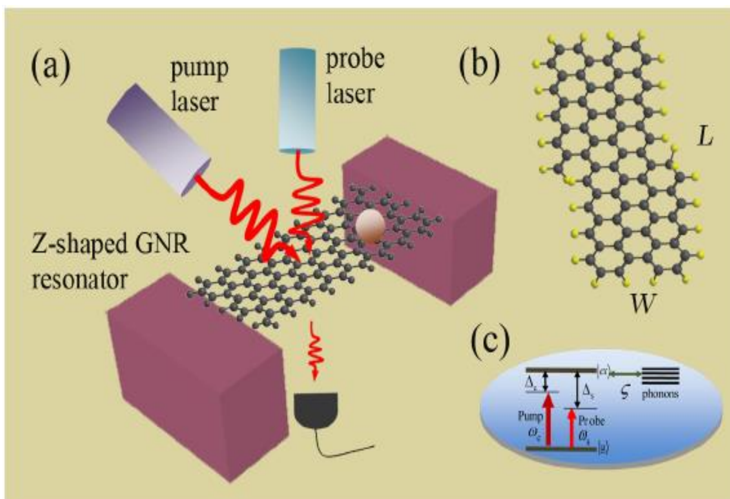
Electrical actuation:





Bunch et. al. Electromechanical Resonators from Graphene Sheets. Science 2007

Optical actuation:

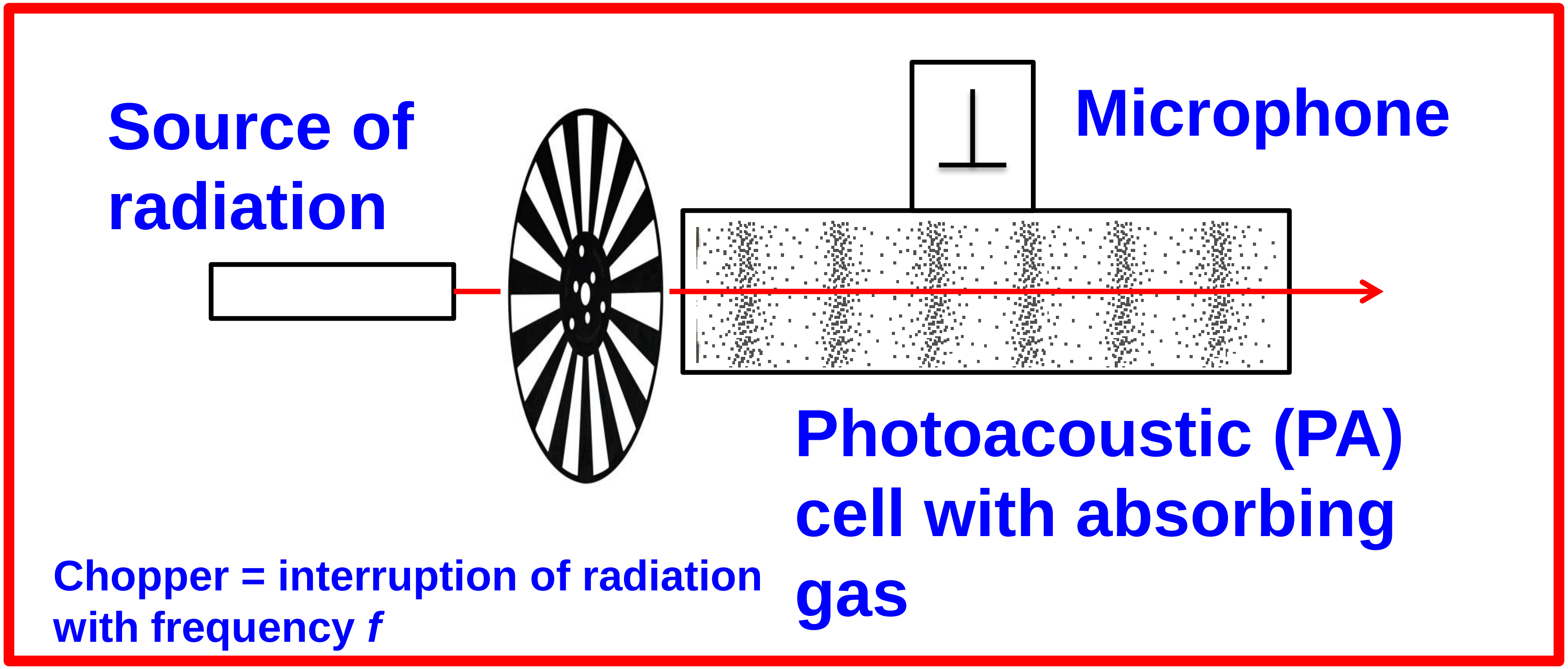


Electrical vs Optical actuation of graphene sheets

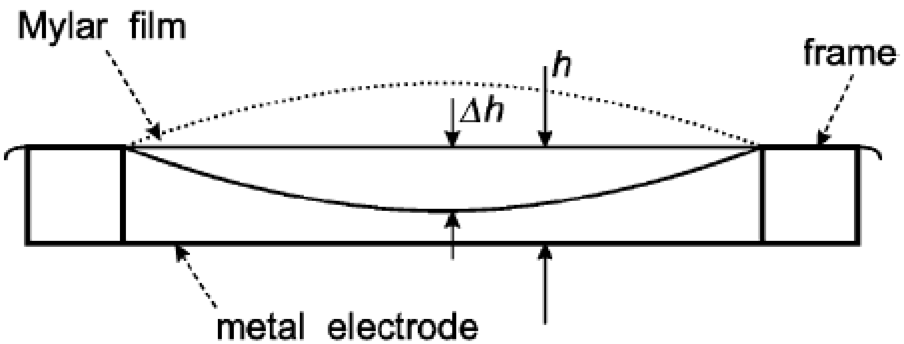
Hua-Jun Chen et. al.Graphene-Based Nanoresonator with Applications in Optical Transistor and Mass Sensing. Sensors 2014

Third method of actuation: **photoacoustic actuation:** → optical microphone

- Direct way of detecting IR radiation
- Detector (a microphone) doesn´t depend on spectral region



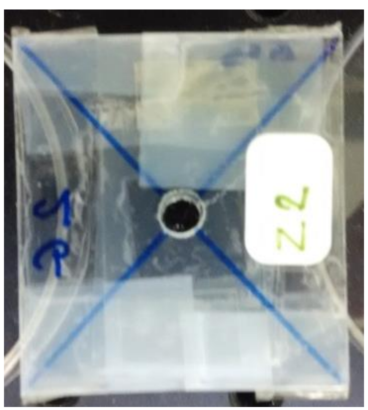
PRESURE SENSORS IN A FORM OF
MEMBRANES OR CANTILEVERS

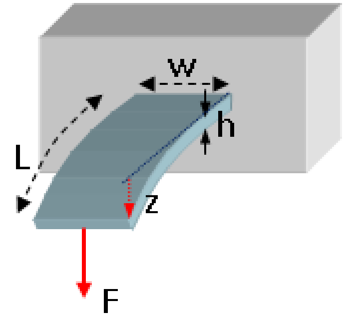


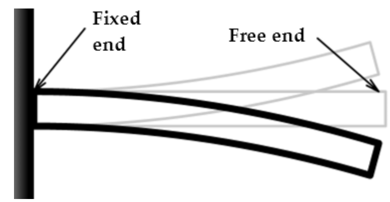
$$C = \frac{\varepsilon A}{h}$$

Sensitivity for membrane:

$$\Delta p \propto \Delta C = -\frac{\varepsilon A}{3h^2}\Delta h \qquad \Delta h \ll h$$



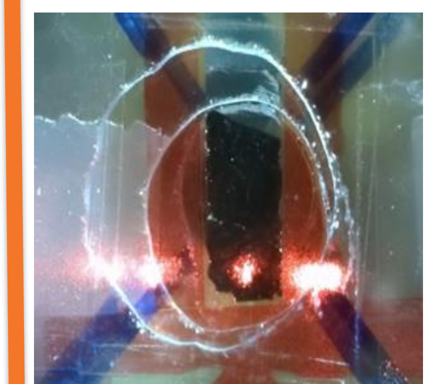


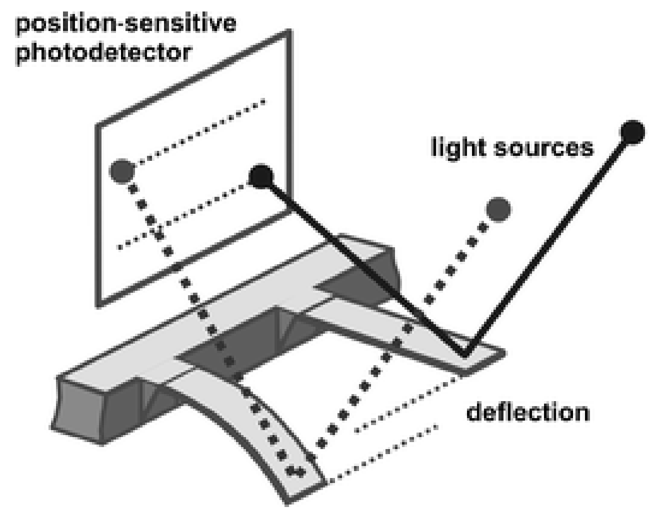


$$k = \frac{2}{3} wY \left(\frac{h}{L}\right)^3$$

Sensitivity for cantilever:

$$\Delta p \propto \frac{L^3}{wYh^3}$$





Theory: Parameters from response to acoustic waves

Two damped harmonic oscillators

$$\ddot{x}_{m(c)} + 2K_{m(c)}\,\dot{x}_{m(c)} + \omega^2_{m(c)}\,x_{m(c)} = F_{m(c)}\,p(t)$$

movement x_m of our *sample* (or movement of the membrane of the microphone)

movement x_c of volume element of gas inside the PA cell

SAMPLE (membrane or cantilever)

$$K_m = \frac{\omega_m}{2Q_m} = \frac{D}{2\sigma_m A_m}$$

$$F_m = \frac{1}{\sigma_m}$$

$$\omega_m^2 = \frac{k}{\rho_0 V}$$

Photoacoustic Cell

$$K_c = \frac{\omega_c}{2Q_c} = \frac{B_c}{2\rho_0 V}$$

$$F_c = \frac{A_c}{\rho_0 V}$$

$$\omega_c^2 = \frac{\chi}{\rho_0 V}$$

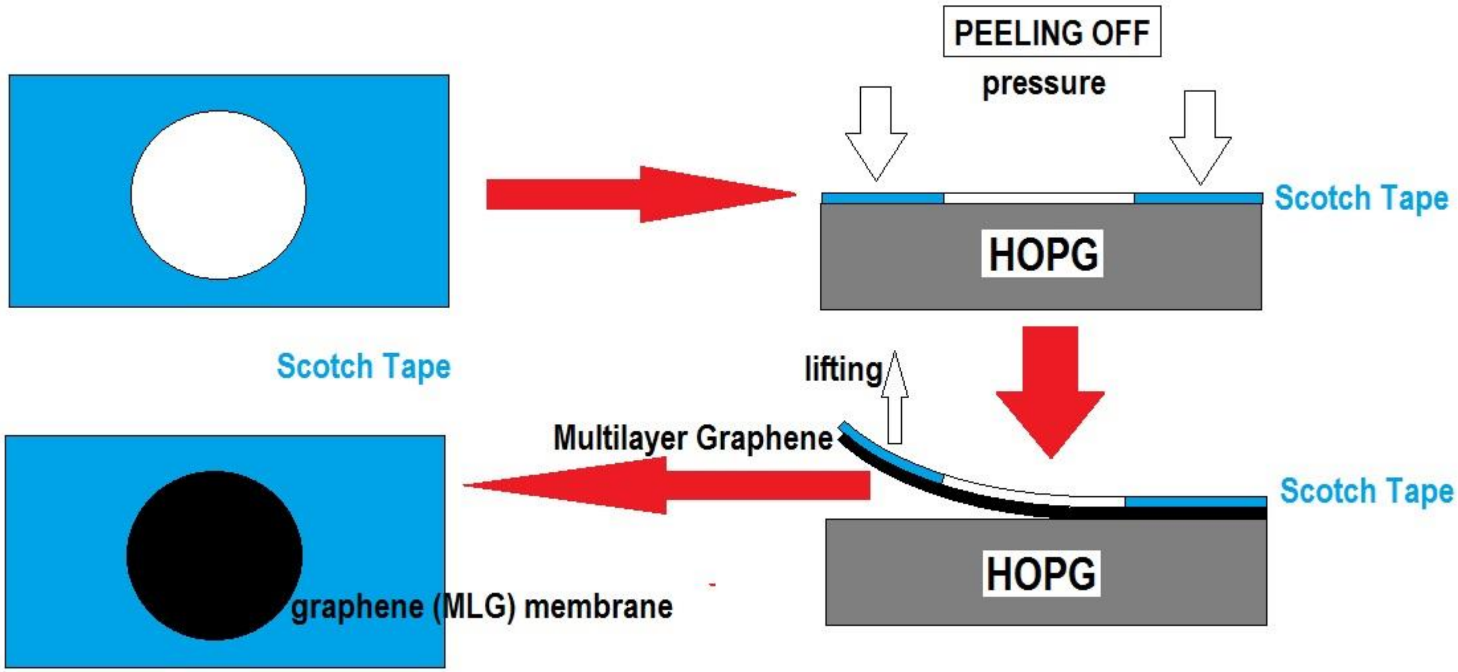
ω_m, ω_c is resonant frequency of a sample, PA cell, respectively,
Q_m , Q_c is quality factor of a sample, PA cell, respectively,
σ_m is surface density of a sample,
A_m is area of a sample,
A_c is inner surface area of PA cell,
χ is spring constant describing behavior of gas inside PA cell,
B_c is damping coefficient describing behavior of gas inside PA cell,
k is spring constant of a *sample* (or microphone membrane),
D is damping coefficient of a *sample* (or microphone membrane),
ρ_0 is density of gas inside PA cell,
V is volume of PA cell

The most important parameters

$$K_m = \frac{\omega_m}{2Q_m} = \frac{D}{2\sigma_m A_m} \qquad F_m = \frac{1}{\sigma_m} \qquad \omega_m^2 = \frac{k}{\rho_0 V}$$

ω_m	**Resonant frequency**
Q_m	**Quality factor of sample**
σ_m	**Surface density of the sample**
k	**Spring constant of sample**

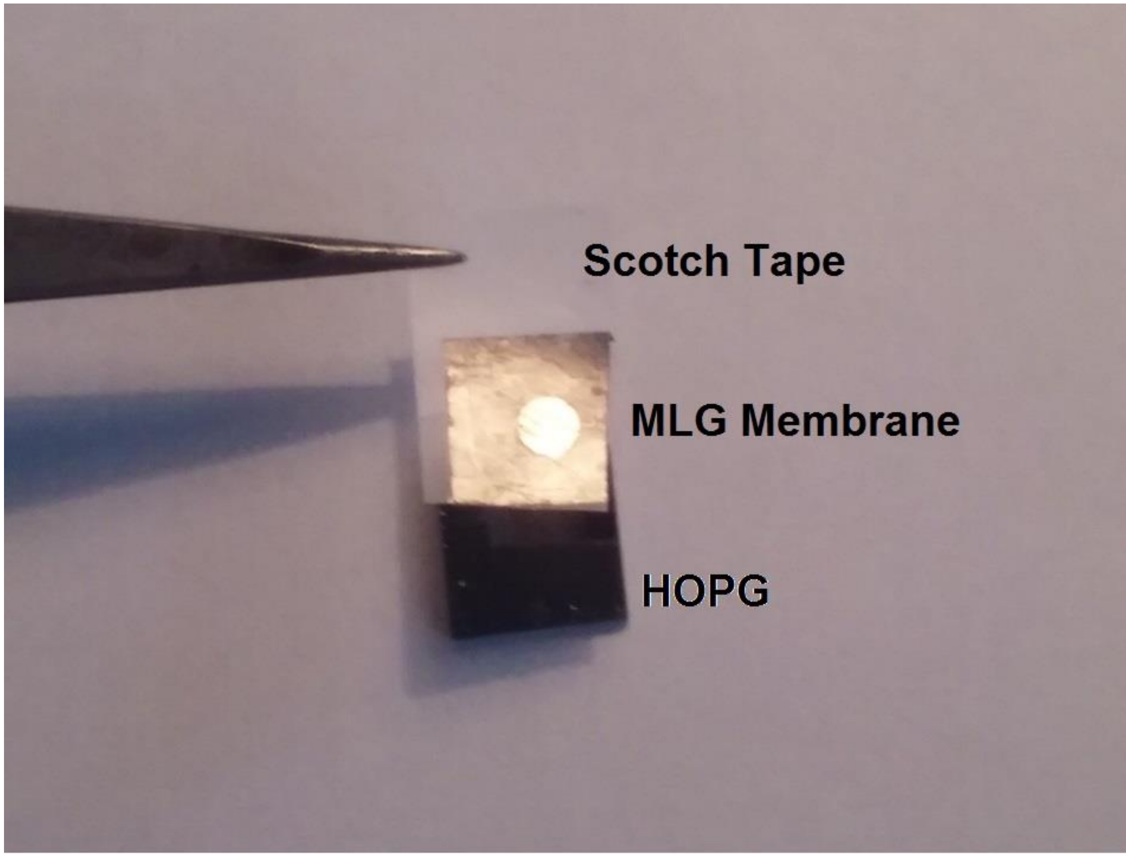
Preparation of the Samples

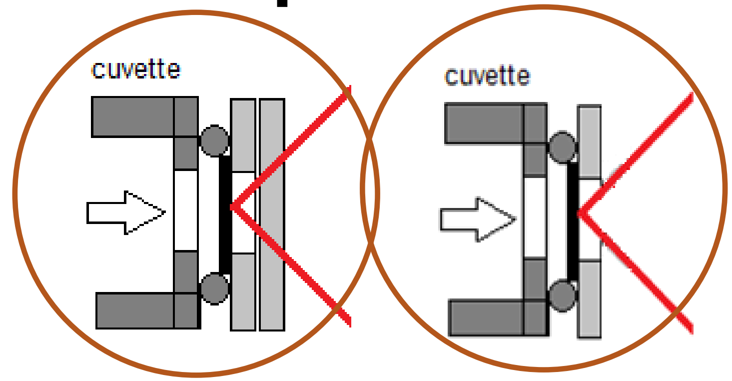


micromechanical cleavage of basal plane
Highly Ordered Pyrolytic Graphite (HOPG)

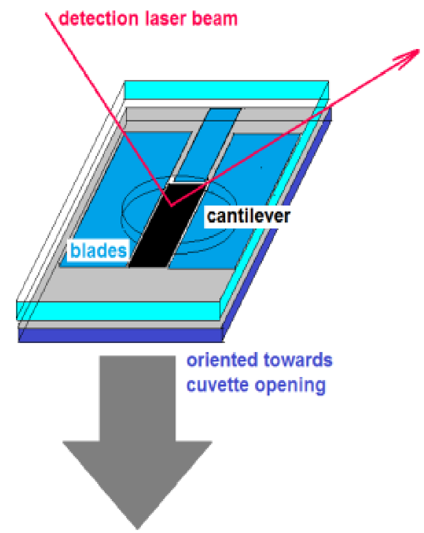
Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. (2004). "Electric Field Effect in Atomically Thin Carbon Films". Science 306 (5696): 666–669.

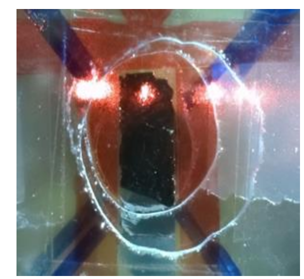
Preparation of the Samples





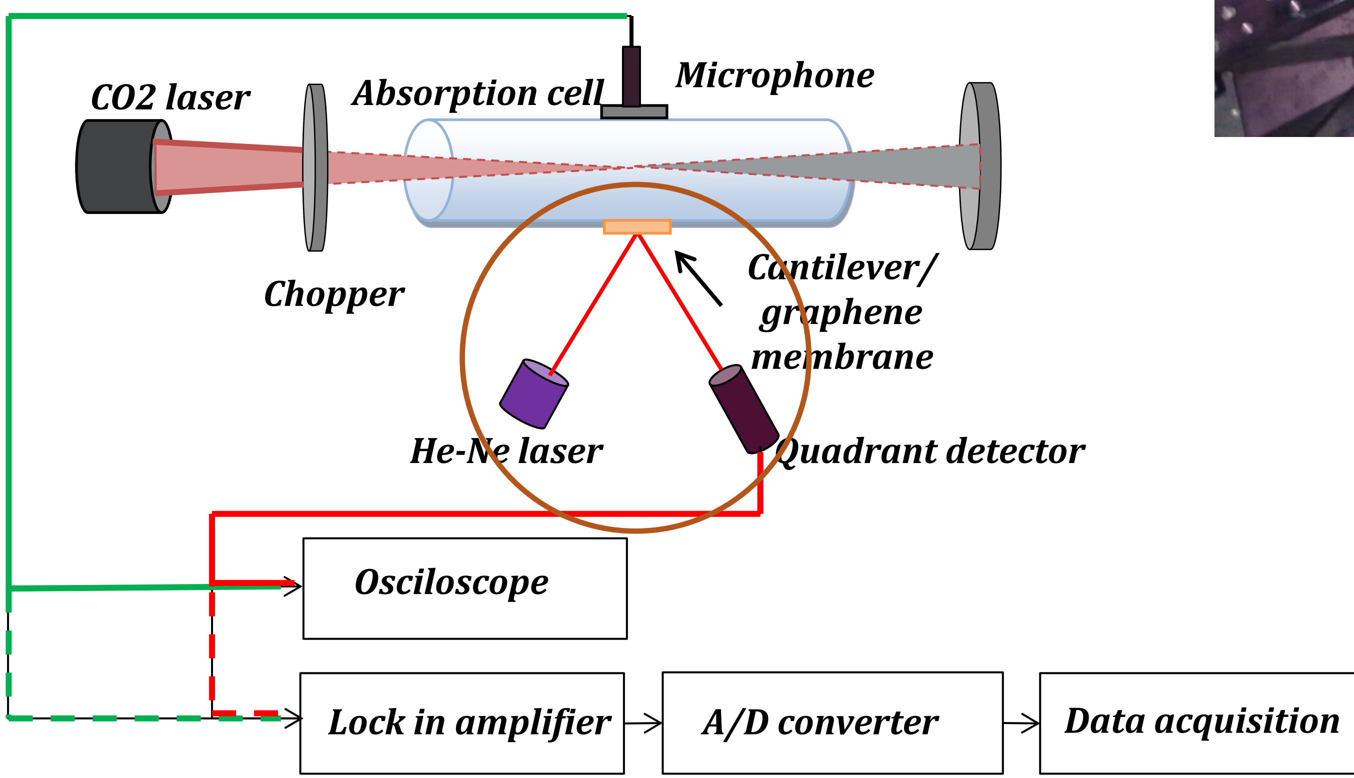
Circular membrane (diameter ~ 4 mm), thickness ~ 100 nm

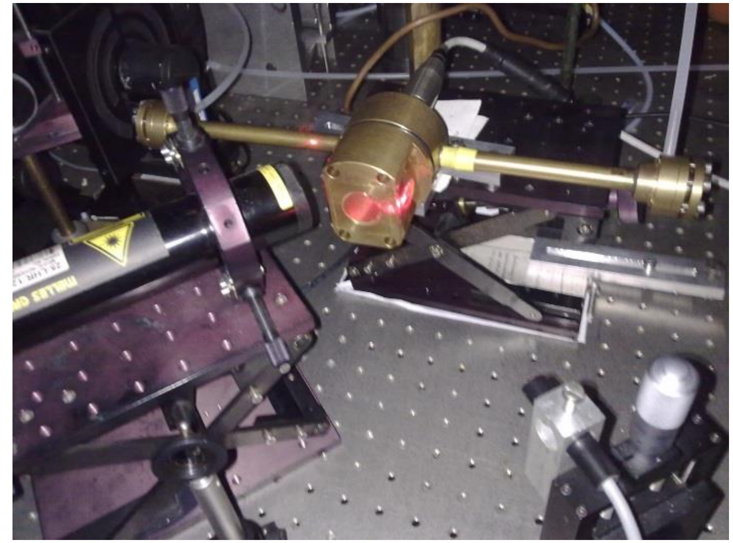




Cantilever 6 x 3 mm, t = 50 μm

Experimental set-up





PA CELL

Current research activities of the Partner

Brief list of ongoing research topics of the Partner:

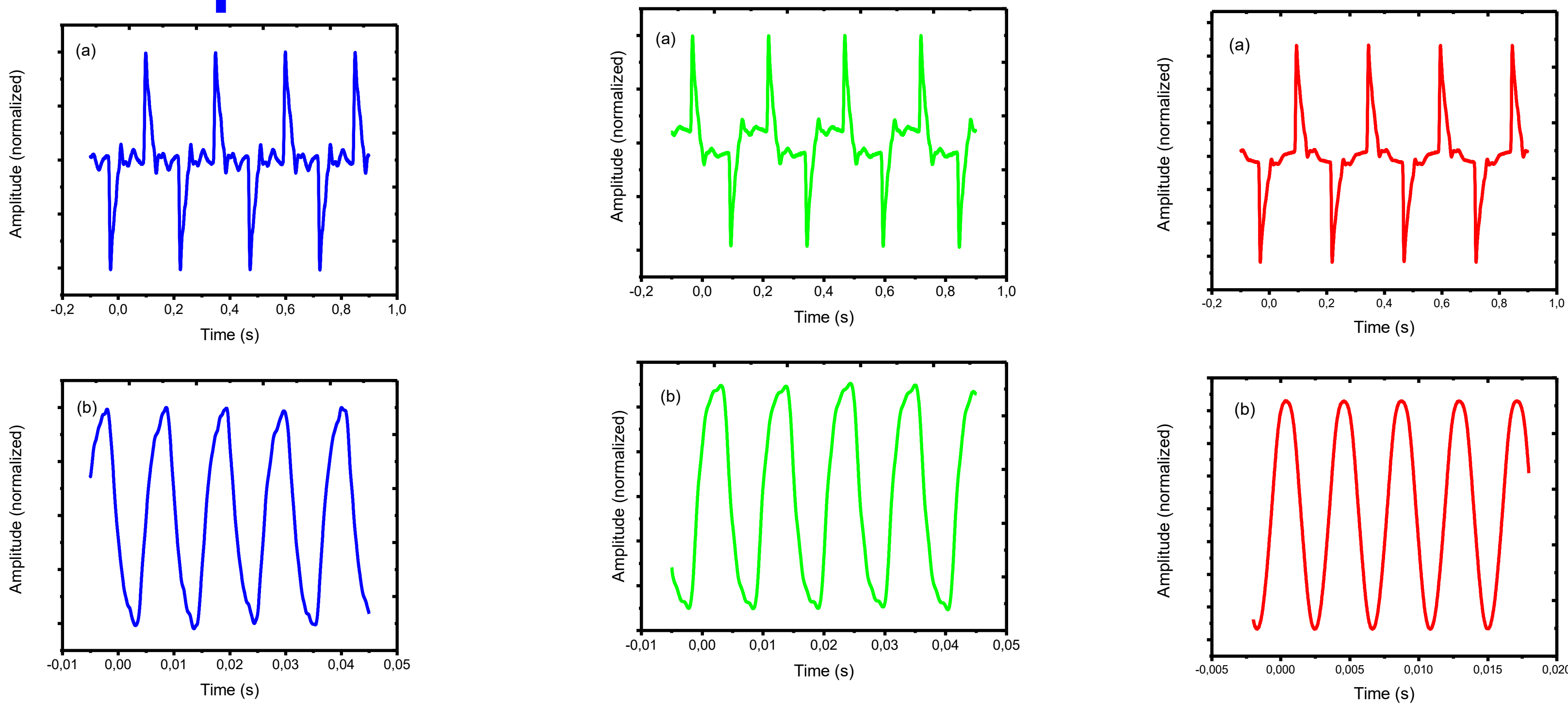
- Investigation of mechanical behavior of multilayer graphene (MLG) membranes and cantilevers for sensitive detection of acoustic waves in gases
- To test developed sensors in a form of cantilevers or membranes by the laser photoacoustic detection
- Actuation of the MLG cantilever/membrane movements by pressure waves triggered by the absorption of the CO_2 laser pulse in the gas-filled photoacoustic cell and its detection by a He-Ne laser beam reflected from the cantilever/membrane to a position sensing detector (optical microphone)
- The utilization of MLG for the construction of a cantilever for photoacoustic detection with enhanced sensitivity and comparison with both the MLG membrane and current top condenser microphone

Behavior of samples in PA cell

microphone | **MLG membrane** | **MLG cantilever**

Low modulation frequency

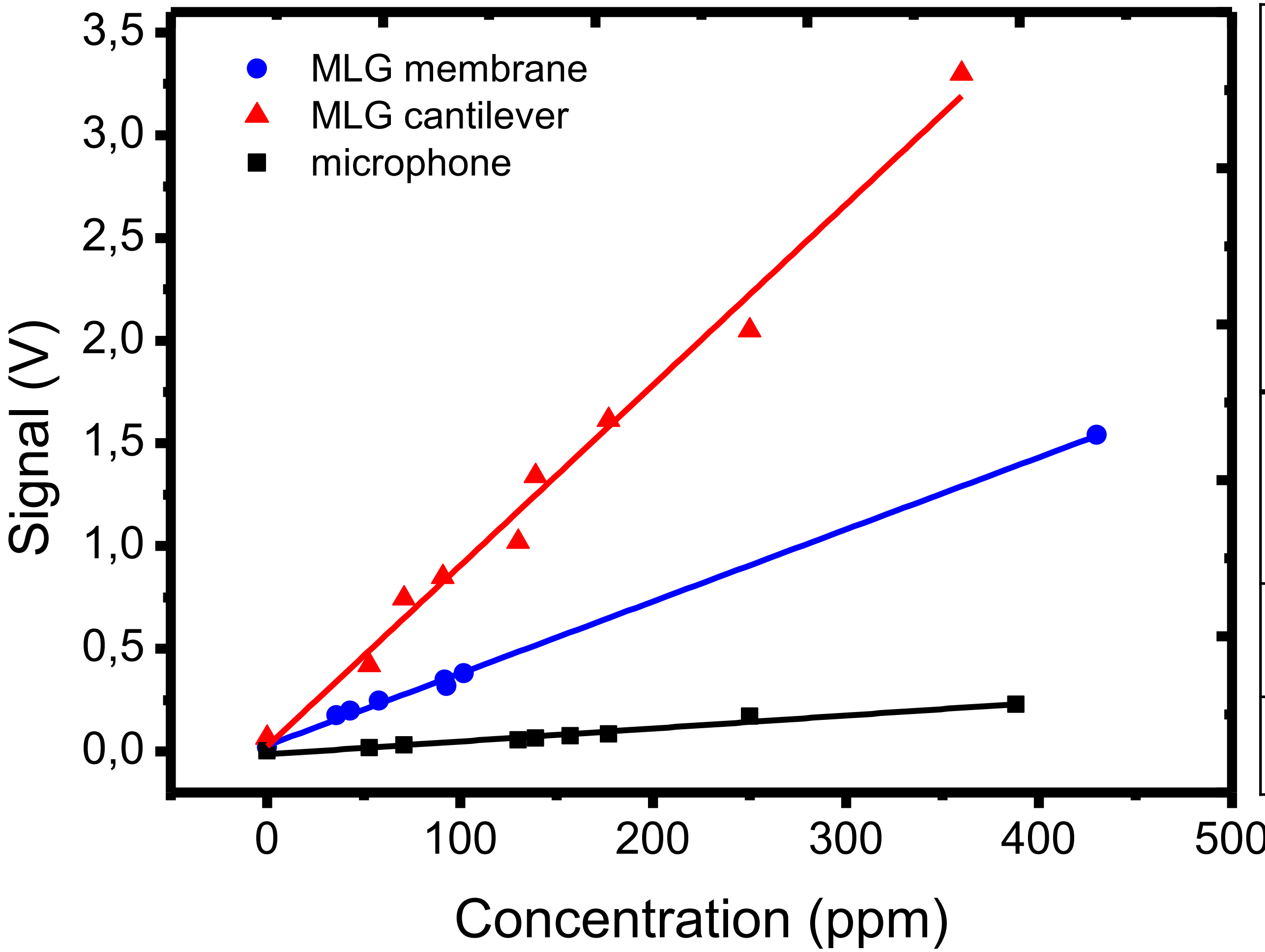
high modulation frequency



$$A(\omega) = \frac{(\gamma - 1)}{\omega} \frac{\alpha W L}{V_c}$$

the signal amplitude $A(\omega)$ of the pressure generated inside of the cell,
γ is the ratio of the specific heat of the gas at a constant pressure to that at a constant volume,
α is the absorbance of gas inside the photoacoustic cell,
W is the total light beam power,
L is the length of the photoacoustic cell,
V_c is the volume of the photoacoustic cell,
ω is the modulation frequency of the laser radiation

Sensitivity testing



	Limit of detection[e], c_L [ppm]
Condenser microphone	**0.75**
MLG membrane	**0.42**
MLG cantilever	**0.33**

- Source: CO_2 laser, 9.5 µm, ~ 160 mW
- Tested gas: Methanol vapors

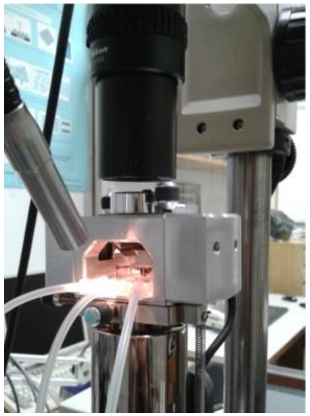
Research Facilities available for the Partner

Research Facilities:

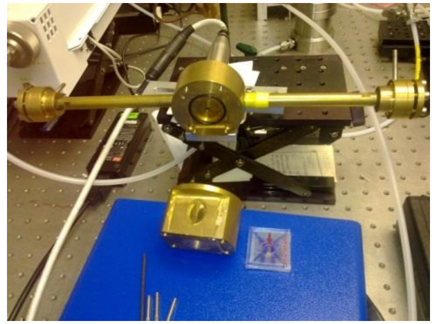
- all scanning probe microscopy (SPM) measurements - STM/AFM both ex-situ and in-situ - research related to carbon nanostructures – fullerenes and nanotubes
- STM/AFM and AFM instrumentation Multimode Nanoscope IIIa extended for low-current (picoamp)
- STM/AFM and Dimension Icon (both Bruker, USA) capable to work in liquids as well
- UV-Vis and FTIR spectroscopy
- Raman spectrometer (LabRam HR Horiba Jobin Yvon, France, interfaced to Olympus BX41 and InVia Reflex spectrometer Renishaw) excited at 633 and 785 nm, respectively, allowing microraman
- excimer and dye laser (Lambda Physik) for pulsed irradiation (193 - 790 nm, pulse length ~28 ns)
- laser kinetic spectrometer (Applied Photophysics) for measurement of time-resolved emission and absorption spectra (200 - 900 nm)
- tunable CO_2 lasers
- laser-diode spectrometers for NIR and IR regions
- Fourier transform spectrometer Bruker IFS 120 HR with high spectral resolution limited by Doppler broadening (0.002 cm^{-1}) and with broad spectral range 500-10000 cm^{-1}

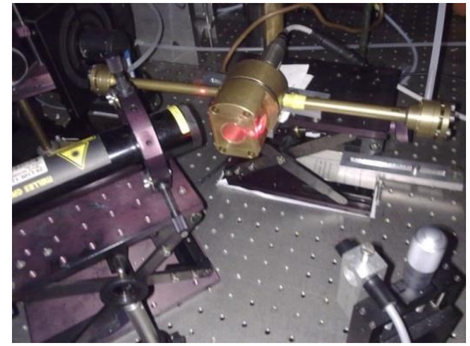
AFM

Scanning Probe Microscopy in situ



graphene cantilevers employed in and studied by photoacoustic spectroscopy

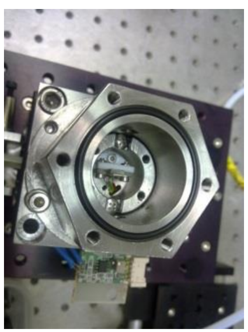


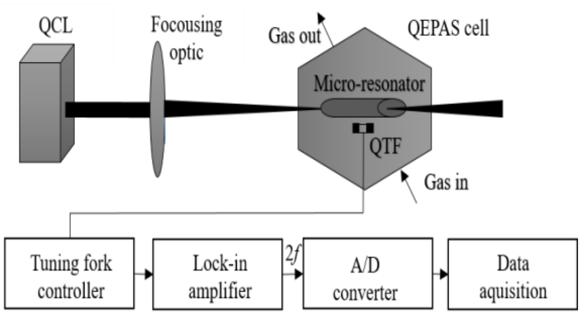


Poster no. P13

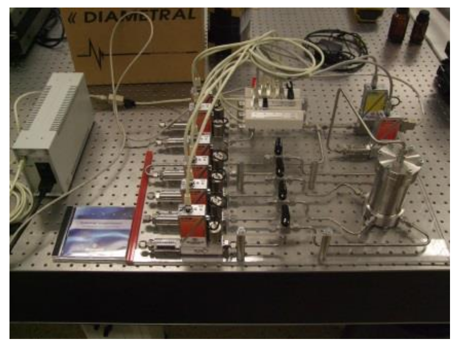
Poster no. P11

Quartz enhanced photoacoustic spectroscopy





Gas mixing systém [1]



Poster no. P10

[1] HELWIG, Nikolai, Marco SCHÜLER, Christian BUR, Andreas SCHÜTZE AND Tilman SAUERWALD. Gas mixing apparatus for automated gas sensor characterization. *Measurement Science and Technology*. 2014, Vol. 25, No. 5, p. 055903.

Conclusion

- Thin MLG membranes/cantilevers have been prepared by cleavage of basel plane HOPG
- Samples employed as an optical microphone in PAS
- Model of mechanical response based on influence of the sample itself + the acoustic properties of the cell => **possible extraction of material properties**
- Sensitivity testing shows promising results – exceeding the top class microphone
- The response of MLG cantilevers and MLG membranes were tested for photoacoustic detection of methanol vapours
- First application of MLG membranes/cantilevers for laser photoacoustic detection
- The sensitivity of MLG cantilevers was more than one order of magnitude higher in comparison with a top class microphone with signal-to-noise ratio and detection limit of 70 and 0.33 ppm, respectively

Suggested **R&I Needs** for future research

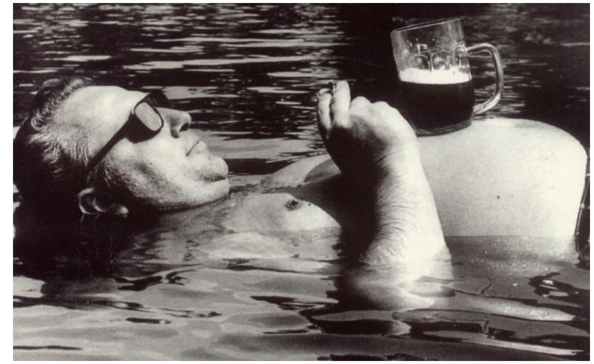
- Focusing on layered materials - decreasing cantilever thickness by stripping surface layers.

- Stripping - straightforward process removing layers of material bonded by van der Waals forces and allows repeating this process down to thickness of nm-level.

- Thus besides graphene (MLG), layered silicates (Muscovites) will be employed as well.

- Prospective study - a special kind of cantilevers, represented by nanoscroll, which response manifested by scrolling and unscrolling, detected by their radial compression and expansion.

Co-workers



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Acknowledgement

The authors are grateful for the financial support via the project No. 14-14696S funded by Czech Science Foundation and via the project no. LD14022 within the COST action TD 1105 funded by the MEYS CR.

Thank you for your attention