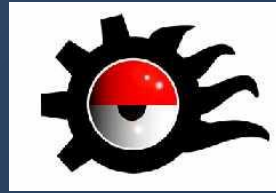# Instituto Politécnico Nacional

**Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada**
*CICATA, Legaria 694. Col. Irrigación, C.P. 11500, México D.F., México*
*http://www.cicata.ipn.mx*

# "BASIC PRINCIPLES OF PHOTOTHERMAL TECHNIQUES AND THEIR APPLICATIONS."

by

## ERNESTO MARÍN MOARES (Ph.D)
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**Winter College on Optics: Advanced Optical Techniques for Bio-Imaging**
**February 13-24, 2017**

# RESEARCH CENTRE ON APPLIED SCIENCE AND ADVANCED TECHNOLOGY (CICATA)
## NATIONAL POLYTECHICAL INSTITUTE (IPN), MEXICO CITY
### http://www.cicata.ipn.mx
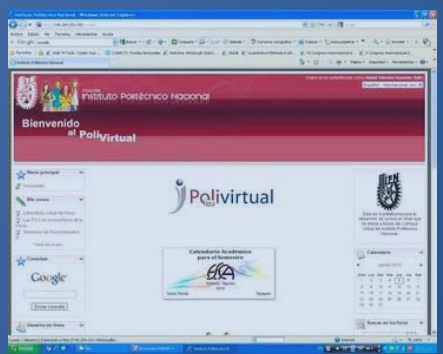
**MASTER AND PHD PROGRAMS IN ADVANCED TECHNOLOGY**

**Research Areas**
1- Nanotechnology and Functional Materials
2- Biomaterials.
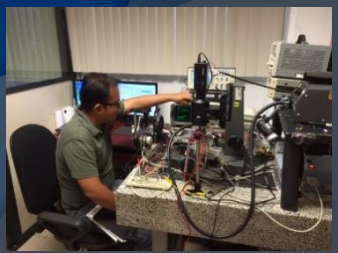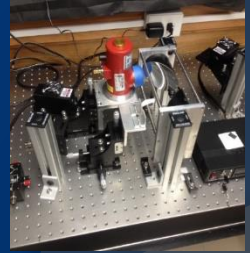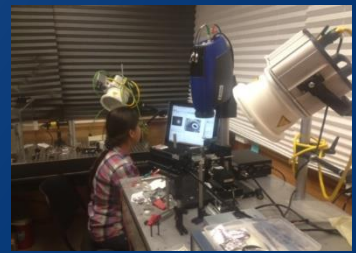2- Instrumentation and Characterization

Since 2011 Graduate Programms of International Competence
PNPC-CONACyT
→ Scholarships (also for foreign students)

**MASTER AND PHD PROGRAMS IN PHYSICS EDUCATION**

**MASTER AND PHD PROGRAMS IN MATHEMATICS EDUCATION**

**PHOTOTHERMAL TECHNIQUES LABORATORY**

**OUTLINE:**

**1.      THE PHOTOACOUSTIC EFFECT**
        - WHY TO USE THE PA EFFECT FOR MATERIALS CHARACTERIZATION ?
        -  HEAT GENERATION AFTER LIGHT ABSORPTION:
        - THE PHOTOACOUSTIC TECHNIQUE: EXPERIMENTAL SET-UP. WHAT IS
MEASURED?

**2.      THERMAL WAVES PHYSICS**
        - OPTICAL ABSORPTION AND LIGHT INTO HEAT ENERGY CONVERSION
        THREE MODES OF HEAT TRANSFER
        - 1 D HEAT CONDUCTION: THE HEAT DIFFUSION EQUATION
        - THERMAL WAVES AND THEIR PROPERTIES

**3.      THE PHOTOTHERMAL TECHNIQUES**
        - BESIDES PHOTOACOUSTICS: HOW TO DETECT?
        - SOME PHOTOTHERMAL TECHNIQUES

**4.       SELECTED APPLICATIONS** :
        - SPECTROSCOPY
        - CALORIMETRY: THERMAL PROPERTIES MEASUREMENT
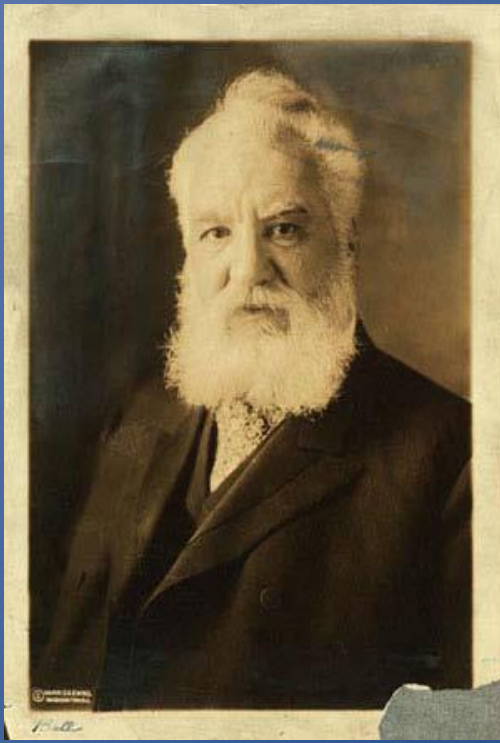        - DEPTH PROFILING
        - IMAGING

A LITTLE BIT OF HISTORY: REDISCOVERING 19 CENTURY DISCOVERIES BY MODERN SCIENCE

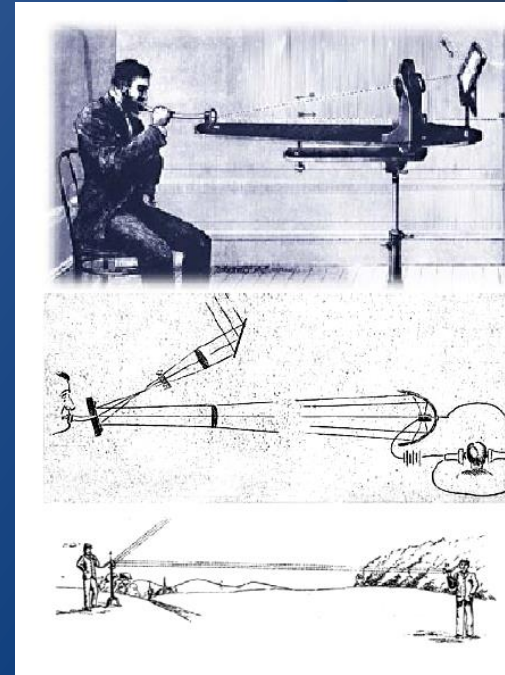# 1ST PART: THE PHOTOACOUSTIC EFFECT

# "HEARING LIGHT"

# 1880: the discovery

Bell, A. G., *Am. J. of Sci.* **20**, 305 (1880).



**Alexander Graham Bell (1847-1922)**

Bell, A. G. y Tainter, S., *Photophone*
United State Patent No. 235, 496, (1880).

*I have heard articulate speech produced by sunlight, I have heard a ray of the sun laugh and cough and sing! I have been able to heard a shadow, and I have even perceived by ear the passage of a cloud across the sun´s disk…can imagination picture what the future of this invention is to be…*

*A. G. Bell. Fragment of 1880´ Brief to Charles Sumner Tainter*

**BELL´S EXPERIMENTAL SET-UP TO STUDY THE PHOTOACOUSTIC EFFECT**
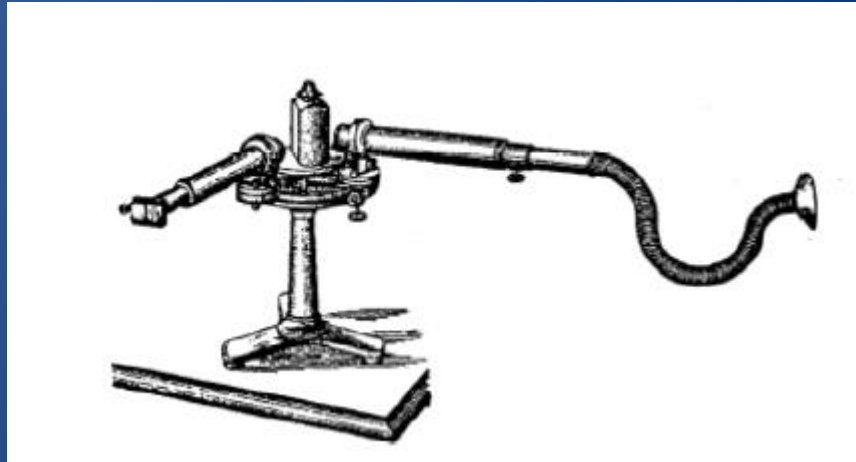


**SPECTROPHONE**

The Manufacturer and Builder Volume 0013 Issue 7 p. 156 (July 1881)

**HOME WORK:**
**DEMONSTRATING THE PHOTOACOUSTIC EFFECT WITH A STETHOSCOPE**

*Lat. Am. J. Phys. Educ. Vol. 2, No. 2, May 2008*

# OTHER "KITCHEN" EXPERIMENTS
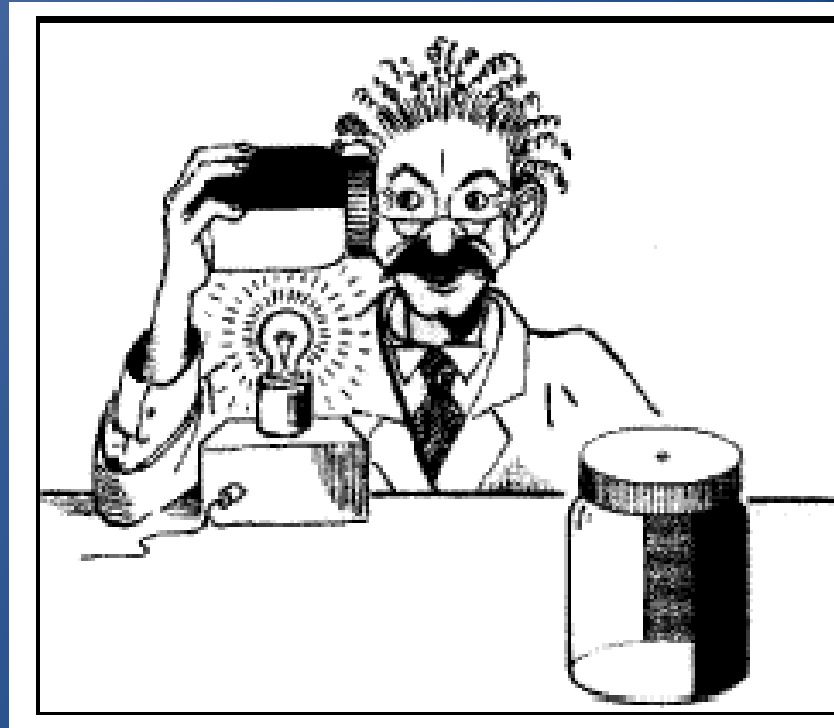


Rush, W. F. and Heubler, E. 1982 *Am. J. Phys.* **50** 669**.**

Campbell, C. and Laherrere 1998 *J. Sci. Am.* **78** 278**.**

Euler, M., Niemann, K. and Müller, A. 2000 *Phys. Teacher* **38** 356

Euler, M., *Phys. Teacher* 2001 **39** 406**.**

**Modulated light beam**

**To hearing tube**

**Stethoscope head**

**Mechanisms involved in the generation of the photoacoustic signal**

| Light absorption | → | Light energy into heat conversion | → | Heat diffusion | → | Sound waves |

↑ | ↑ | ↑ | ↑

| Optical properties | | e.g. Conversion Efficiency | | Thermal properties | | Elastic properties |
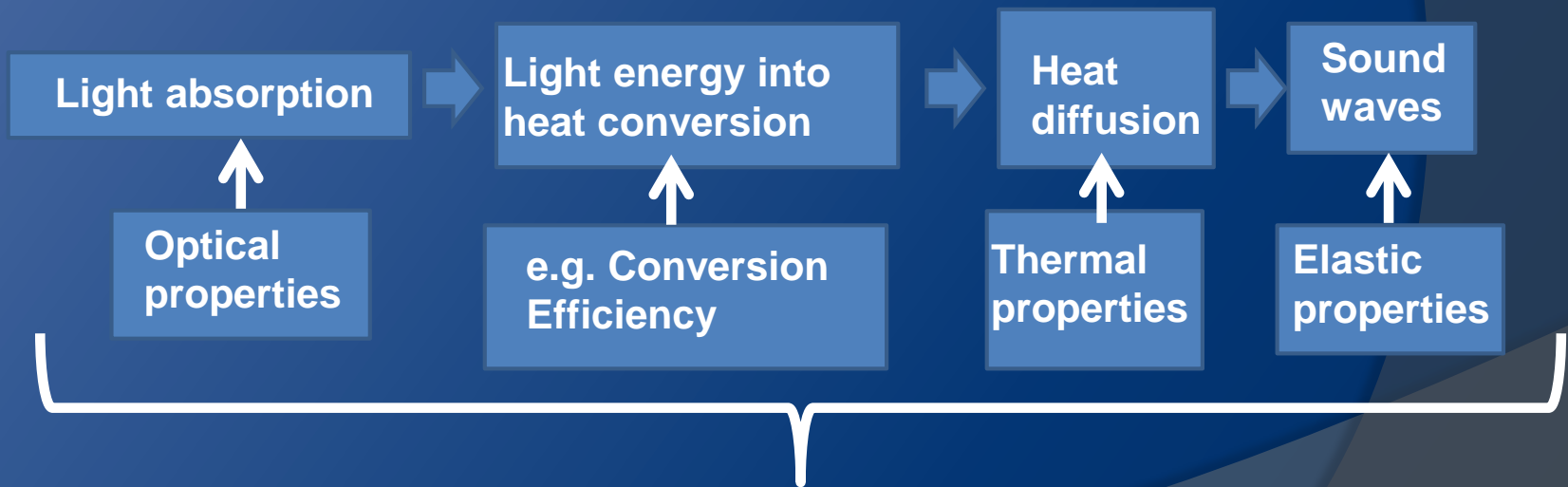
**MOTIVATION:
WHY TO USE SUCH EFFECT FOR MATERIALS CHARACTERIZATION**

# RAW ESTIMATION: ORDERS OF MAGNITUDE

Power: 0.1 mW
Duration: 5.0 ms
$\rightarrow Q = 5.0 \times 10^{-7}$ J

Light pulse

1.0 cm$^3$ of air

$\Delta T = ?$

$Q = m\,c\,\Delta T$
$c_{air} = 1.0$ J/gK
$\rightarrow \Delta T = 4.2 \times 10^{-4}$ K



threshold of pain

music — $4.0 \times 10^{-2}$ Pa

hearing threshold — $\Delta T = 10^{-6}$ K, $3.3 \times 10^{-4}$ Pa

frequency (Hz)

pressure (Pa): 30, 0,3, $3 \times 10^{-3}$, $3 \times 10^{-5}$
20  100  1000  10000

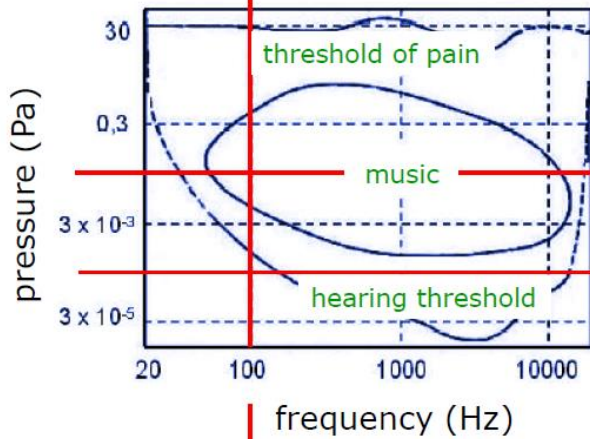5 ms (x 2)

$\Delta P = ?$

Before de light pulse
$P_0 V = nRT_0$

After de pulse
$(P_0 + \Delta P)V = nR(T_0 + \Delta T)$
$\rightarrow \Delta P = P_0 (\Delta T / T_0)$
$\rightarrow \Delta P = 4.0 \times 10^{-2}$ Pa

MOTIVATION:
HOW TO DETECT SO SMALL VARIATIONS IN PRESSURE (OR TEMPERATURE) ?

# EARLY WORKS

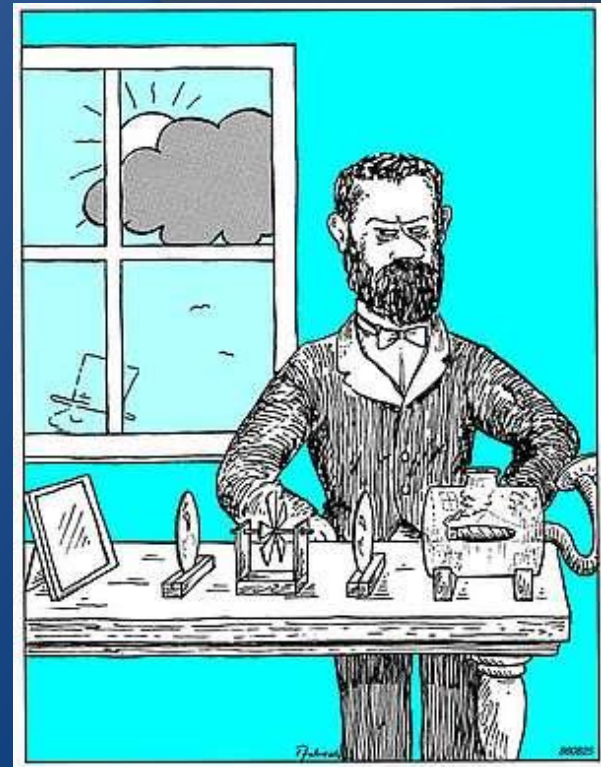Bell A G 1881 *Nature* **24** 42

Tyndall J 1881 *Proc. R. Soc. Lond.* **31** 307

Roentgen W 1881 *Phil. Mag.* **11** 308

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Viengerov, M. L. 1938 *Dokl. Akad. Nauk. SSSR* **19** 687

Luft K F 1954 *C. R. Hebd. Seances Acad. Sci.* **238** 1651

**PHOTOACOUSTIC SPECTROSCOPY**

→ **First theoretical model**          → **First applications**
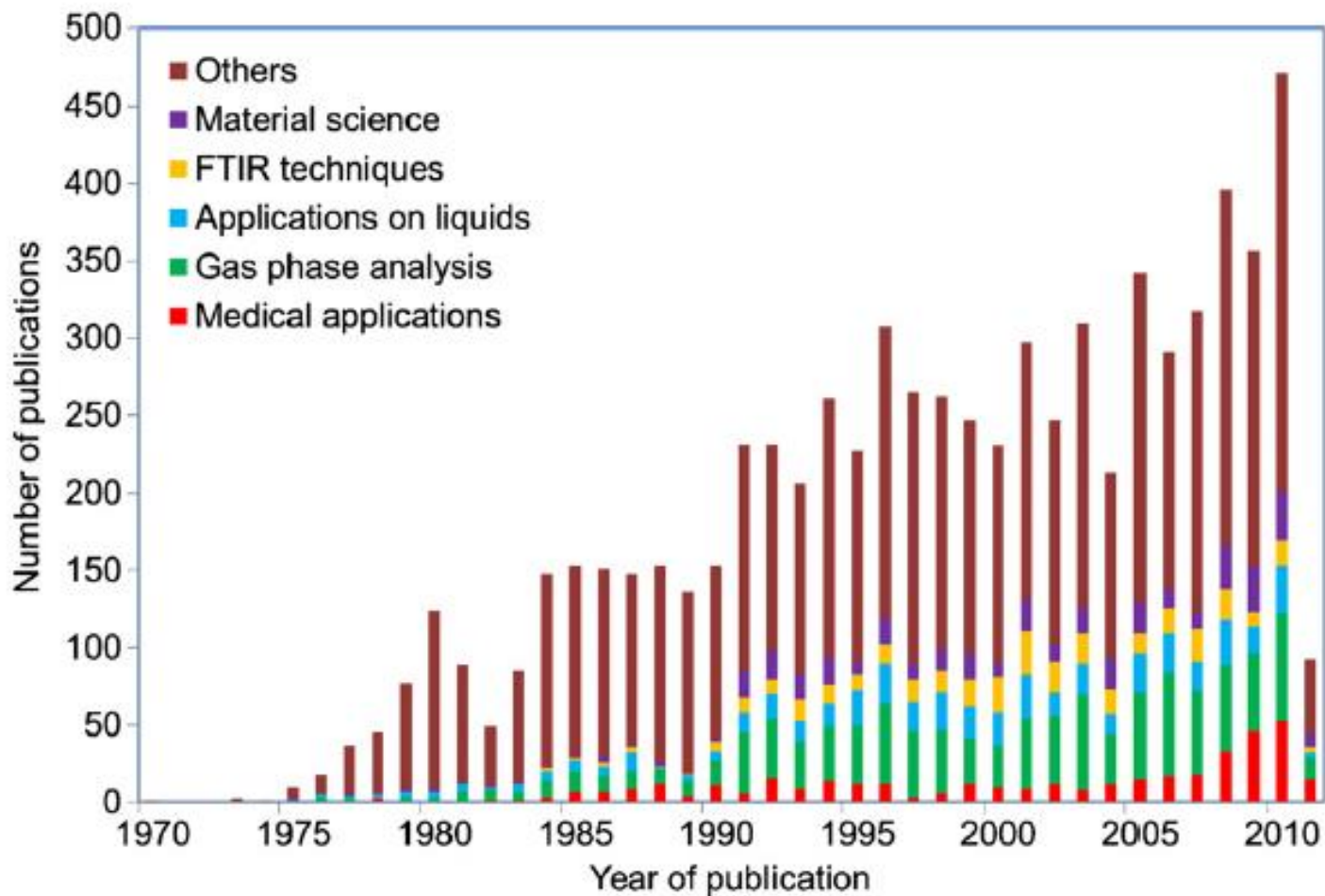
Number of publications on different fields of PA applications according to the ISI web of science statistics.
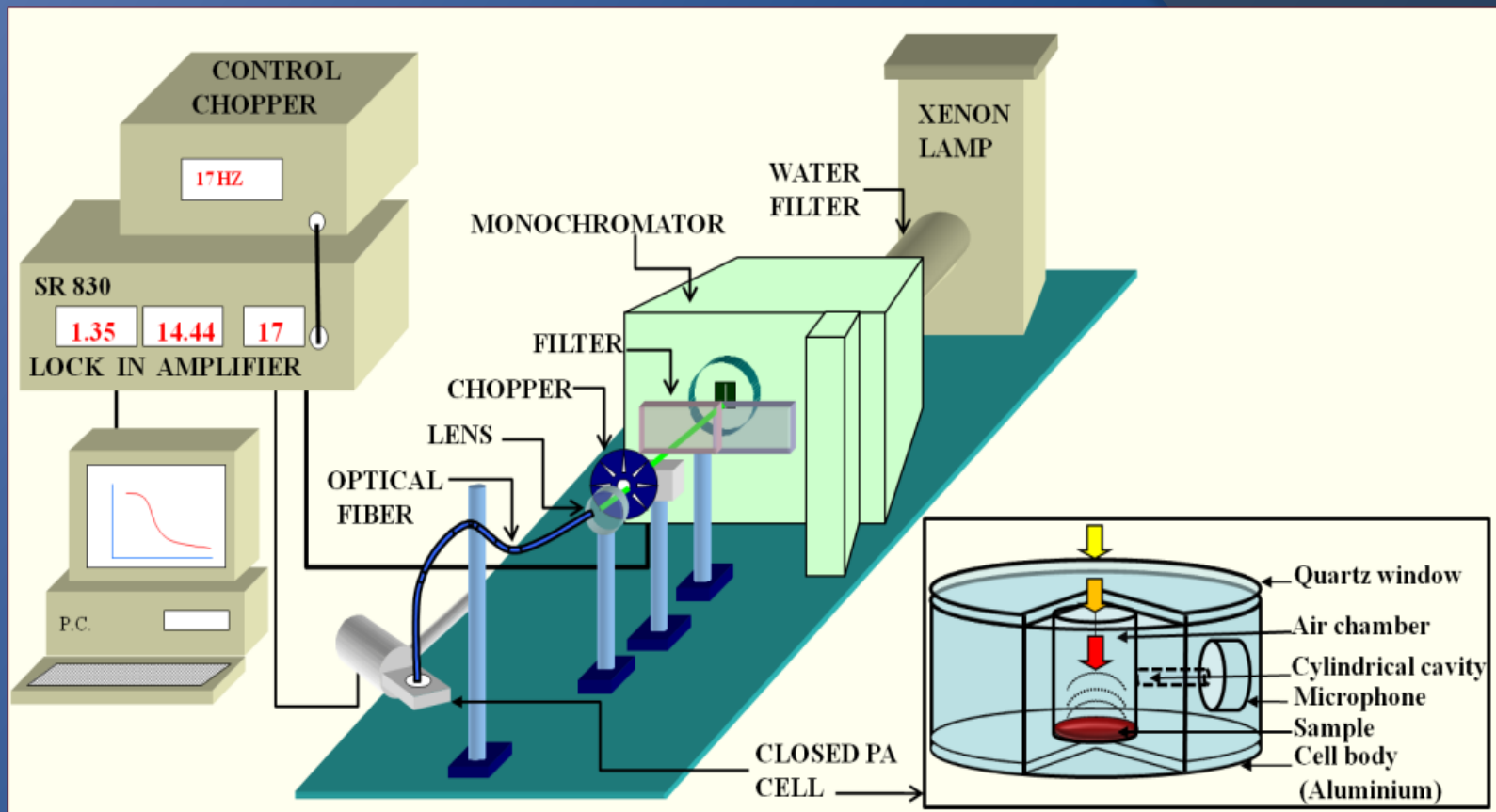
## Schema of a typical experimental set-up

F. Gordillo Delgado, 2011 "Photoacoustic technique applied to the strengthening of clean agriculture"
*Ph. D. Thesis*, CICATA-Legaria México D.F.

## LIA in a Nut Shell

$S = A \cos (\omega t + \varphi) + n$
 signal to be measured

A: signal amplitude;
$\varphi$: signal phase
$\omega = 2\pi f$: angular frequency
n: noise at f
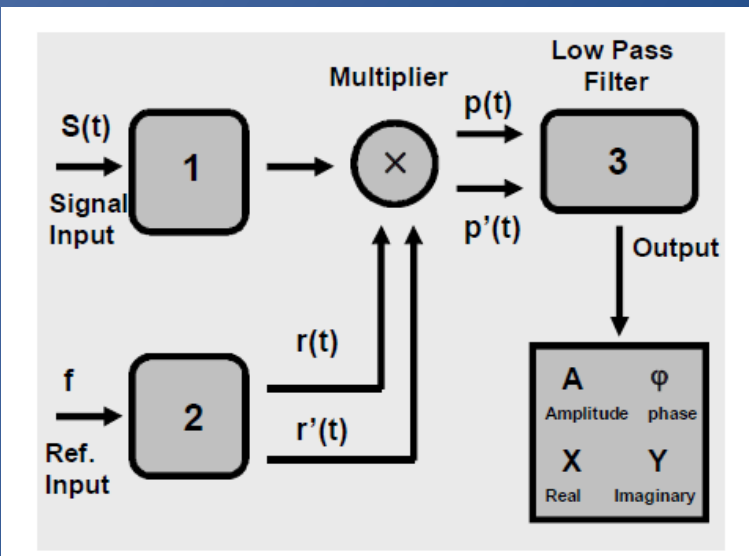


r = 2 cos ($\omega$t)
r' = 2 sin ($\omega$t)

$p = S \times r = A \cos (\varphi) + A \cos (2\omega t + \varphi) + 2n \cos (\omega t)$

$p' = S \times r' = A \sin (\varphi) + A \sin (2\omega t + \varphi) + 2n \sin (\omega t)$

X and Y real (<u>in-phase</u>) and imaginary (<u>quadrature</u>) parts of the complex number A exp (i$\varphi$) ; i = (-1)$^{1/2}$

$A = (X^2 + Y^2)^{1/2}$
$\varphi = \text{atan} (Y/X)$

$X = A \cos(\varphi)$
$Y = A \sin(\varphi)$



SR810 LIA from Stanford Research Systems
~ $ 4000



CICATA-FPGA LIA
Field Programmable Gate Array FPGA Spartan-3E
~ $ 400

Fig. 1 A comparison between the optical properties obtained from PAS (circles) and conventional optical transmission (squares) measurements for a CdS sample (2 µm of thickness) grown by CSVT on glass substrates. The light modulation frequency used for PAS was 17 Hz

J Mater Sci (2007) 42:7176–7179

**Wavelength ($\lambda$)-resolved experiments (PA-spectroscopy)($f$-fixed)**

**Time-resolved (both $f$ and $\lambda$ fixed) Monitoring of dynamic processes**



○ TiO$_2$ + *Burkholderia unamae* (Strain TATI-371)
▼ *Burkholderia unamae* (Strain TATI-371)
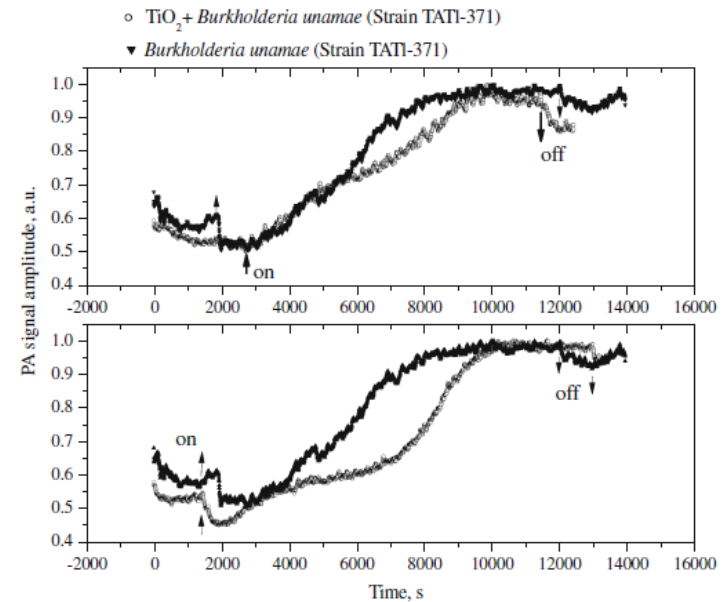
Fig. 2 PA signal amplitude as a function of time. *Triangles* correspond to the PA response of *B. unamae* (Strain TATI-371) and the *circles curve* corresponds to the PA response including the photobaric effect due to the photocatalytic activity of TiO$_2$ film on this same bacteria. The *up* and *down arrows* indicate the time instants at which a non-modulated white light Xe lamp, used to induce the photocatalytic process, is turned on and off, respectively. Both curves correspond to scans of two samples of the same culture

**Modulation frequency ($f$)-resolved ($\lambda$ fixed) Determination of transport parameters**



FIG. 4. (Color online) The amplitude (a) and the phase (b) of the PA signal as the function of the modulation frequency. Circles: correspond to samples where the CdS layers were grown by CSVT and the CdTe film by CSVT. Squares: S/Cd=2.5. Up-triangles: S/Cd=6. Down-triangles: S/Cd=5. The solid line is the result of the best fit using the theoretical model.

J. Appl. Phys. **107**, 123701 (2010)

2/5/2017

◉16

# 2ND PART: THERMAL WAVE PHYSICS

# OPTICAL ABSORPTION

## Lambert-Beer law
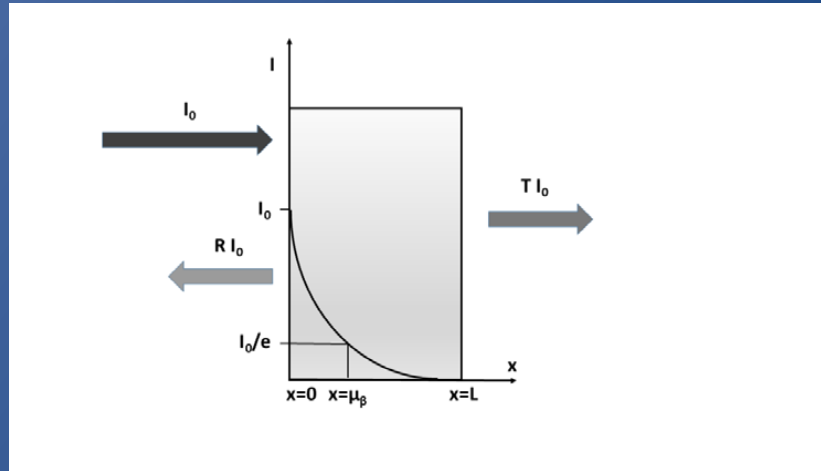


Light Intensity [$Wm^{-2}$] $\longrightarrow$ $I = I_0 \exp(-\beta x) = I_0 \exp(-x/\mu_\beta)$

I (x=0)   Optical absorption coefficient

Light penetration depth = $1/\beta$

**Absorbance**

Molar Concentration [M]

$A = \chi L C_m$   *

Molar Absorptivity Coefficient [$M^{-1}m^{-1}$]
($\lambda$-dependent)

$A = -\ln(T) = \ln(I_0/I) = \beta L$   * *

$T = I/I_0$   Transmitance

Reflectance

*   +   * *   $\rightarrow$   $\beta = \chi C_m$

$A = R + T$

# LIGHT INTO HEAT ENERGY CONVERSION

amount of heat generated per volume unit of the sample in an element of thickness *dx* at depth *x*

$$dQ = -\eta(1-R)(dI/dx)dx \quad + \quad I = I_0 \exp(-\beta x) \quad \rightarrow \quad dQ = \eta(1-R)I_0\beta\exp(-\beta x)dx$$

quantum efficiency for heating
= produced heat / incident energy

# THREE MODES OF HEAT TRANSFER

## 1- Convection

Heat flux density [W/m$^2$]

$$\Phi_{conv} = q_{conv}/A = h conv \Delta T$$

Convection heat transfer coefficient

Newton's law

## 2- Radiation

$$\Phi_{rad} = q_{rad}/A = \sigma e (T_0^4 - T^4)$$

Stefan-Boltzmann law

The spectral intensity as a function of wavelength for a black body

T-T$_0$ << T$_0$ →

$$\Phi_{rad} = 4 \sigma e T_0^3 (T - T_0) = h_{rad} \Delta T$$

Radiation heat transfer coefficient

$$h_{rad} = 4 \sigma e T_0^3$$

## 3- Conduction

$$\Phi_{cond} = q_{cond}/A = -k \nabla T$$

Fourier´s law
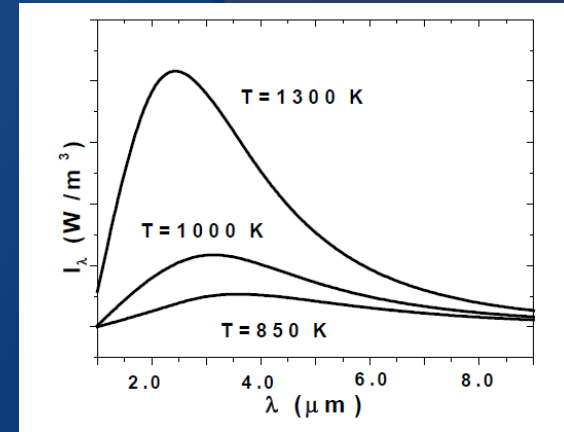
1D, homogeneous and isotropic samples, → ∇T small

$$\Phi_{cond} = k \frac{T_2 - T_1}{x_2 - x_1} = \frac{K \Delta T}{L} = h_{cond} \Delta T$$

Conduction heat transfer coefficient

$$h_{cond} = k/L$$

$$\Phi_{cond} = k\frac{T_2 - T_1}{x_2 - x_1} = \frac{K\Delta T}{L} = h_{cond}\Delta T \quad \rightarrow \quad q_{cond} = \frac{KA\Delta T}{L} = \frac{\Delta T}{R_{cond}}$$

Ohm´s law for thermal conduction

$$R_{cond} = \frac{L}{Ak} = \frac{1}{Ah_{cond}}$$

<u>Thermal resistance</u>
(against conduction)

$$H = h_{conv} + h_{cond} = 1/(AR)$$

R: resistance
(against convection-radiation)

$$B_i = \frac{H}{h_{cond}} = \frac{R_{cond}}{R}$$

Biot´s number : fraction of material's thermal resistance that oposses to convection-radiation heat losses

# FOURIER´S LAW + ENERGY CONSERVATION LAW → HEAT DIFFUSION EQUATION



$$\frac{\partial U}{\partial t} = -q_{net}$$

*
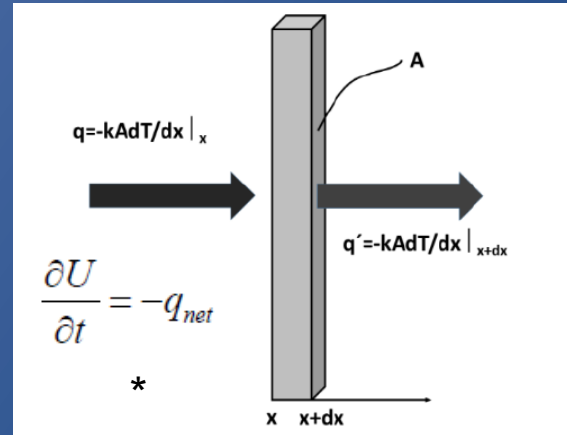
First law of thermodynamics

$$(dx = \delta x, \text{ where } \delta x \to 0)$$

$$m = \rho \delta V = \rho A \delta x$$

$$q_{net} = -kA \left\{ \frac{\partial T}{\partial x}\bigg|_{x+\delta x} - \frac{\partial T}{\partial x}\bigg|_{x+dx} \right\} = -kA \left\{ \frac{\frac{\partial T}{\partial x}\big|_{x+\delta x} - \frac{\partial T}{\partial x}\big|_{x+dx}}{\delta x} \right\} \delta x = -kA \frac{\partial^2 T}{\partial x^2} \delta x \qquad **$$

$$\frac{\partial U}{\partial t} = mc \frac{\partial T}{\partial t} \qquad ***$$

* + ** + *** →   $$\nabla^2 T - \frac{1}{\alpha} \frac{\partial T}{\partial t} = 0$$   Heat diffusion equation

$$\alpha = k/\rho c$$

Thermal diffusivity
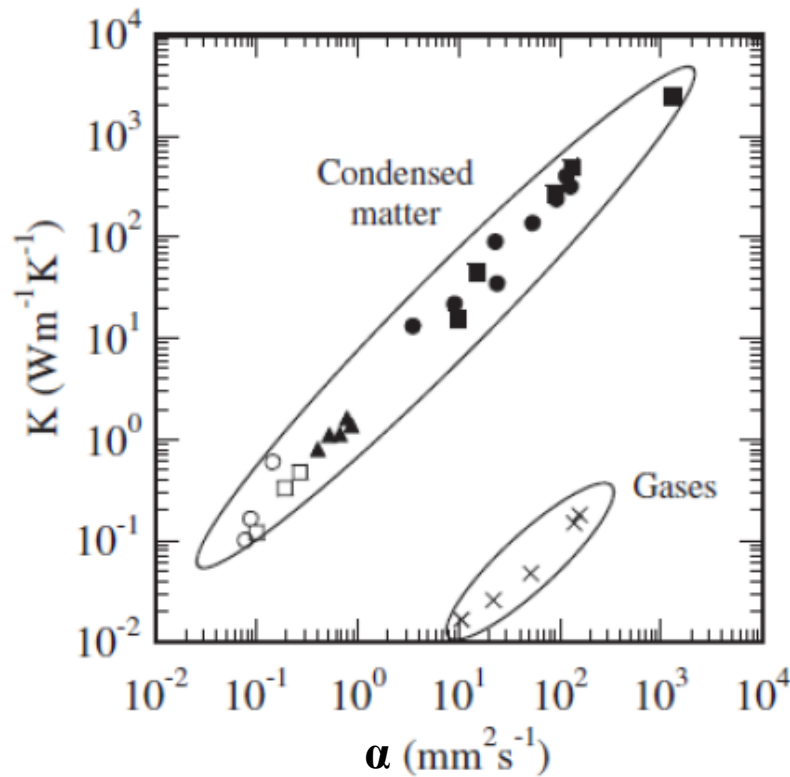
$$\alpha = k/\rho c$$

$$k = C\alpha$$

$$C = \rho c$$

**Thermal conductivity versus thermal diffusivity**
Closed circles: metals; squares: ceramics; triangles: glasses; open squares: polymers; open circles: liquids; crosses: gases

Slope $\sim \rho C = k / \alpha \sim 3 \times 10^6$ Jm$^{-3}$ K$^{-1}$

# THERMAL WAVES AND THEIR PROPERTIES

[Almond and Patel, 1996] Almond, D. P. and Patel, P. M. 1996, "Photothermal Science and Techniques" in "Physics and its Applications, 10", E.R. Dobbs and S.B. Palmer (Eds), Chapman and Hall, London.

Isotropic and homogeneus semi-infinite solid + Superficial uniform light absorption (1D) + $\eta = 1$ + R=0 + neglecting heat losses (with H

)

$$\frac{\partial^2 T(x,t)}{\partial x^2} - \frac{1}{\alpha}\frac{\partial T(x,t)}{\partial t} = 0 \quad , \quad x > 0 \, , \quad t > 0$$

HDE

$$-k\left.\frac{\partial T(x,t)}{\partial x}\right|_{x=0} = \frac{I_0}{2}Re[(1 + \exp(i\omega t))]$$

BC

$$T(x,t) = \theta(x)exp(i\omega t) \rightarrow$$

$$\frac{\partial^2 \theta(x,t)}{\partial x^2} - q^2\theta(x) = 0$$

$$-k\left.\frac{\partial \theta(x,t)}{\partial x}\right|_{x=0} = Re\left[\frac{I_0}{2}exp(i\omega t)\right]$$

$$q = \sqrt{\frac{i\omega}{\alpha}} = \frac{(1+i)}{\mu}$$

$$\mu = \sqrt{\frac{2\alpha}{\omega}}$$

Wave number     Thermal diffusion length

$$T(x,t) = \frac{I_0}{2\varepsilon\sqrt{\omega}}exp(-qx)exp\left[-i\left(\omega t + \frac{\pi}{4}\right)\right] = \frac{I_0}{2\varepsilon\sqrt{\omega}}exp\left(-\frac{x}{\mu}\right)exp\left[-i\left(\frac{x}{\mu} + \omega t + \frac{\pi}{4}\right)\right]$$

## THERMAL WAVE EQUATION

Thermal properties determination is possible !

$$\varepsilon = k/\alpha^{1/2} = (Ck)^{1/2}$$

$$C = \rho c$$

Thermal effusivity ~ *k* because the almost constancy of *C*

$$T(x,t) = \frac{I_0}{2\varepsilon\sqrt{\omega}} exp(-qx) exp\left[-i\left(\omega t + \frac{\pi}{4}\right)\right] = \frac{I_0}{2\varepsilon\sqrt{\omega}} exp\left(-\frac{x}{\mu}\right) exp\left[-i\left(\frac{x}{\mu} + \omega t + \frac{\pi}{4}\right)\right]$$

Amplitude         Phase

$$\Delta\phi = x/\mu + \pi/4$$

$T_0$

$$T_0 \exp\left(-\frac{x}{\mu}\right)$$

$$\mu = \sqrt{\frac{2\alpha}{\omega}}$$

$\dfrac{T_0}{e}$

0   μ      $l$    x
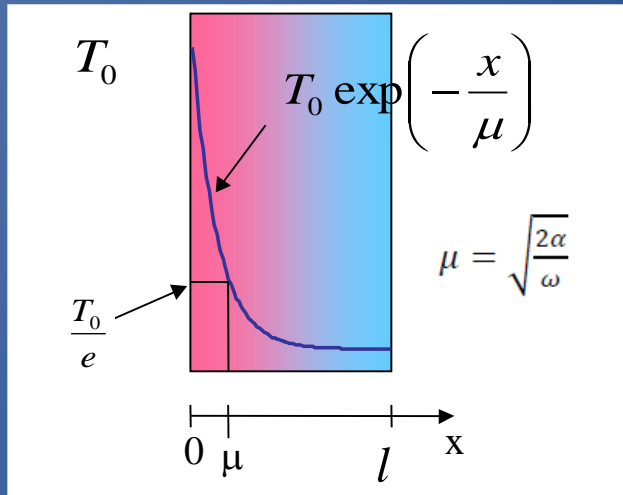
Thermal diffusion length

$$Z_t = \frac{T(x=0,t) - T_{amb}}{-k\frac{dT(x,t)}{dx}\Big|_{x=0}}$$

$$Z_t = \frac{1-i}{\varepsilon\sqrt{\omega}} = \frac{1}{\varepsilon\sqrt{\omega}} exp\left(-i\frac{\pi}{4}\right)$$

Thermal impedance

$$T(x,t) = \frac{I_0}{2} Z_t exp\left(-\frac{x}{\mu}\right) cos\left(\frac{x}{\mu} + \omega t\right)$$

$\lambda = 2\pi\mu$     Wave-length

$v_f = f\lambda = (\omega/2\pi)(2\pi\mu) = \mu\omega\mu = (2\,\alpha\omega)^{1/2}$     $v_g = 2v_f$

Phase velocity           Group velocity

# THERMAL WAVES AND THEIR PROPERTIES

Behavior at interfaces (normal incidence)
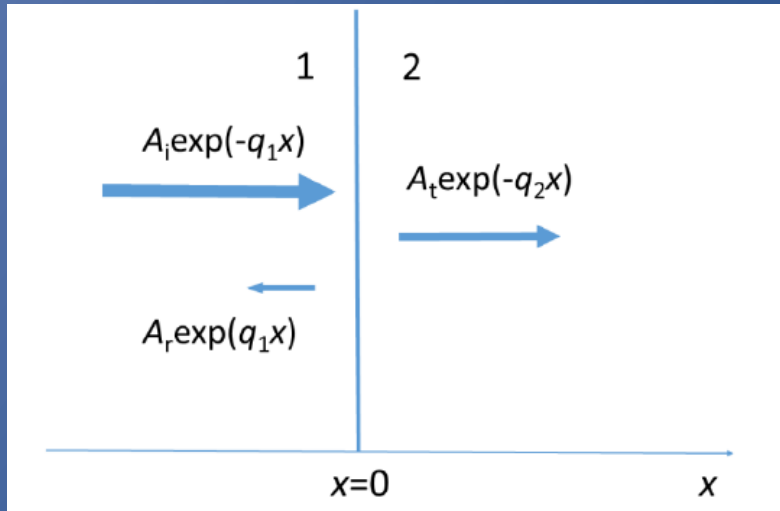
$$T(x,t) = \begin{cases} A_i e^{-q_1 x} + A_r e^{q_1 x} & x < 0 \\ A_t e^{-q_2 x} & x > 0 \end{cases}$$



1    2

$A_i \exp(-q_1 x)$

$A_t \exp(-q_2 x)$

$A_r \exp(q_1 x)$

$x=0$    $x$

$$A_j = (I_0 / 2\varepsilon \omega^{1/2}) \exp[i(\omega t - \pi/4)]$$

$$(j = i, r, t)$$

Temperature continuity at x=0
(negligible interfacial termal resistance)    →    $A_i + A_r = A_t$

Heat flux continuity at x=0
(see Fourier´s law)    →    $A_i - A_r = (k_2 q_2 / k_1 q_1) A_t$

$$A_t = 2 A_i / [1 + k_2 q_2 / k_1 q_1]$$

$$A_r = A_i [(1 - k_2 q_2 / k_1 q_1) / (1 + k_2 q_2 / k_1 q_1)]$$

Reflection and transmission coefficients

$$R_{12} = \frac{A_r}{A_i} = \frac{b_{12} - 1}{b_{12} + 1}$$

$$b_{12} = \frac{\varepsilon_1}{\varepsilon_2}$$

$$T_{12} = \frac{A_t}{A_i} = \frac{2 b_{12}}{1 + b_{12}}$$

# THERMAL WAVES AND THEIR PROPERTIES

Depth profiling and imaging are posible !

$$\mu = \sqrt{\frac{2\alpha}{\omega}}$$

## Orders of magnitude

$\lambda = 2\pi/k_w = 2\pi\mu$  Wave-length ($k_w$ is the wave-number)

**!TWs are fully damped within one wave-length!**

$v = \omega/k_w = \sqrt{2\alpha\omega}$ phase velocity

Typical solid material ($\alpha \approx 10^{-4}$ m$^2$/s)

For $f$=10 kHz

$\mu \approx 10$ μm $\lambda \approx 30$ μm $v \approx 0.1$ m/s

!The wave-length of acoustic waves at $f$=1 kHz is $\lambda_{aw} = v_{aw}/f$

$\approx$1cm, where $v_{aw} \approx 1000$m/s is the sound velocity!

©HKUST Library

THÉORIE
ANALYTIQUE
DE LA CHALEUR,
PAR M. FOURIER.

A PARIS,
CHEZ FIRMIN DIDOT, PÉRE ET FILS,
LIBRAIRES POUR LES MATHÉMATIQUES, L'ARCHITECTURE HYDRAULIQUE
ET LA MARINE, RUE JACOB, N° 24.
1822.
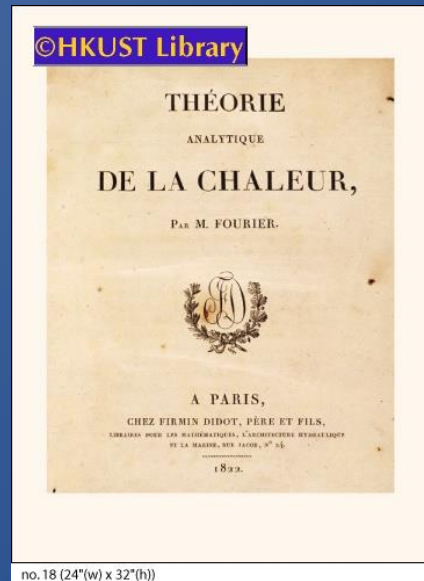
no. 18 (24"(w) x 32"(h))

**Jean Baptiste Joseph Fourier (1768-1830)**

"*The problem of the earth crust temperature is one of the most beatifull applications of the heat transfer theory*"
J. B. J. Fourier

Home work: A very simple
photothermal experiment

REVISTA MEXICANA DE FÍSICA E **52** (1) 21–27
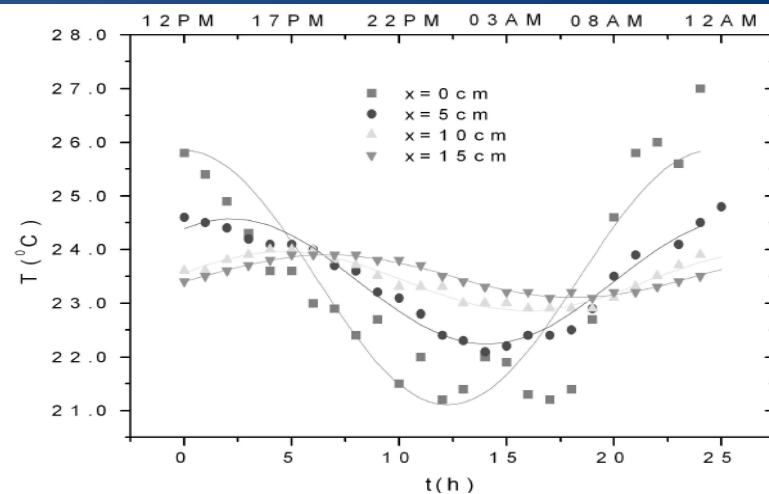
FIGURE 4. Soil Temperature as a function of time at different
depths beneath the earth's surface and hourly air temperature. The
solid curves represent best fits to Eq. (14) The air temperature (x=0)
versus time curve is also represented for comparison.

(1822´s Théorie Analytiqúe de la chaleur was first developed in 1807
under the name Théorie de la propagation de la Chaleur dans les Solides)



Adrien Marie Legendre (left) and **Joseph Fourier** (right)

Boilly, Julien-Leopold. (1820). *Album de 73 Portraits-Charge Aquarelle's des Membres de l'Institute* (water colour portrait #29).
Biliotheque de l'Institut de France.

T. N. Narasimhan 1999 Fourier´s heat conduction equation: History, influence, and connections. *Reviews of Geophysics* **37** 151

**Anders Jöns Ångström
(1814-1874)**



Figure 10. (a) Diagram of the measurement system. (b) Detail of the measurement cell, showing the spreading of the thermocouples along the thermometric region.



Figure 12. Experimental results obtained for an aluminum sample of 40 cm thickness, for $z = 0$ cm (solid line), 8 cm (dashed line) and 16 cm (dotted line).

Eur. J. Phys. **33** (2012) 135–148
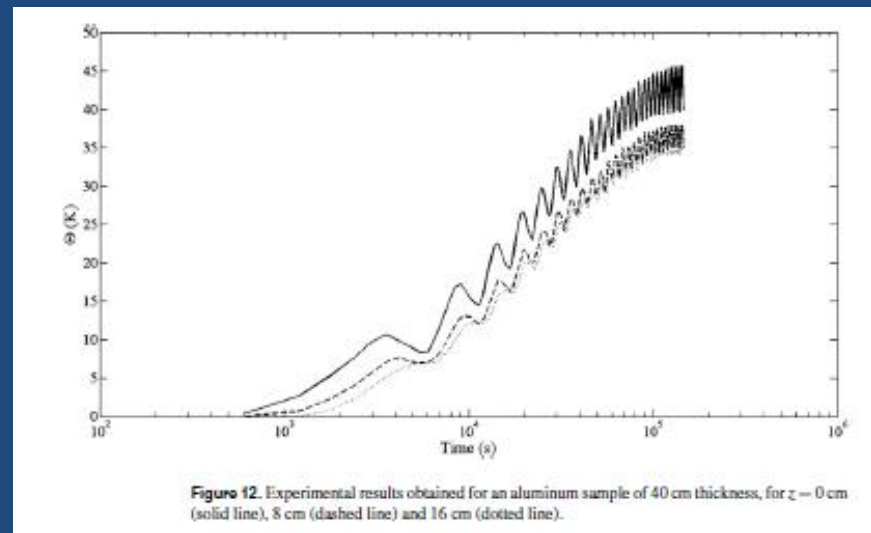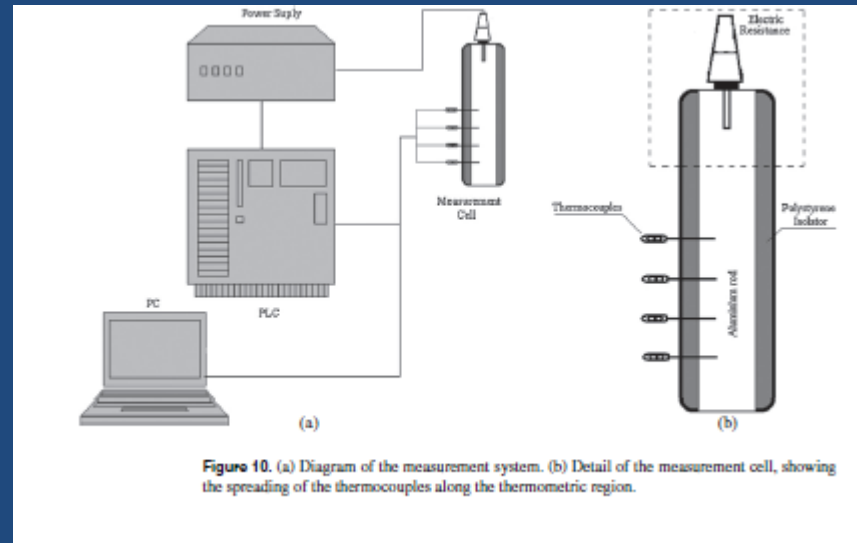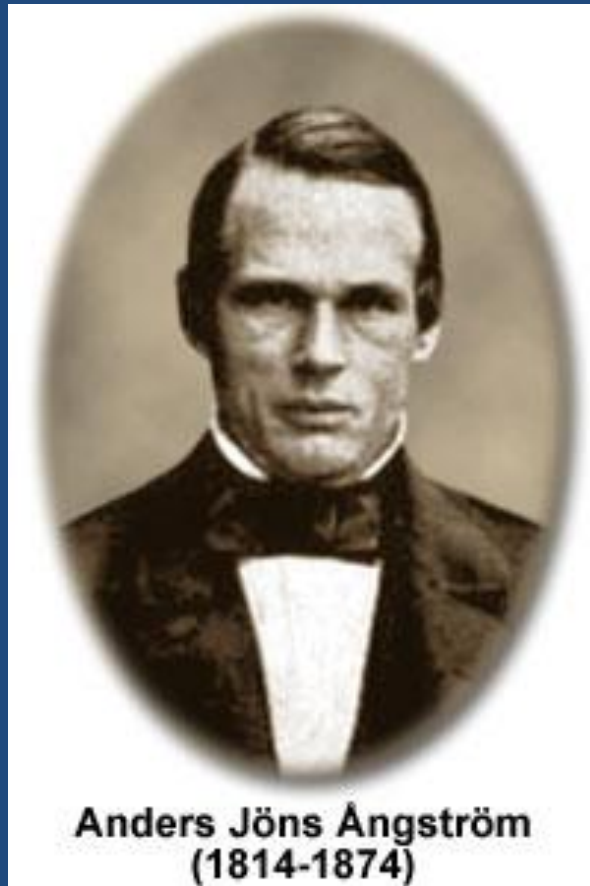
# THERMAL WAVES (with distributed heat source)

Isotropic and homogeneus semi-infinite solid + <u>Bulk</u> uniform light absorption (1D) + <u>$\eta \neq 1$</u> + <u>$R \neq 0$</u> + neglecting heat losses

amount of heat generated per volume unit of the sample in an element of thickness *dx* at depth *x*

$$dQ = \eta(1-R)I_0\beta\exp(-\beta x)dx$$

$$T(x,t) = \frac{I_0\eta(1-R)\beta}{2\varepsilon\sqrt{\omega}}\int_x^{x+dx}\exp(-\beta x')\,exp(-qx')dx' \times exp\left[-i\left(\omega t + \frac{\pi}{4}\right)\right]$$

$$T(x,t) = \frac{I_0\eta(1-R)}{2\varepsilon\sqrt{\omega}}\frac{\beta}{\beta+q}\exp[-(\beta+q)x]exp\left[-i\left(\omega t + \frac{\pi}{4}\right)\right]$$

$\beta\,(\lambda) \rightarrow$ Spectroscopy is possible !

# 3$^{RD}$ PART: THE PHOTOTHERMAL TECHNIQUES
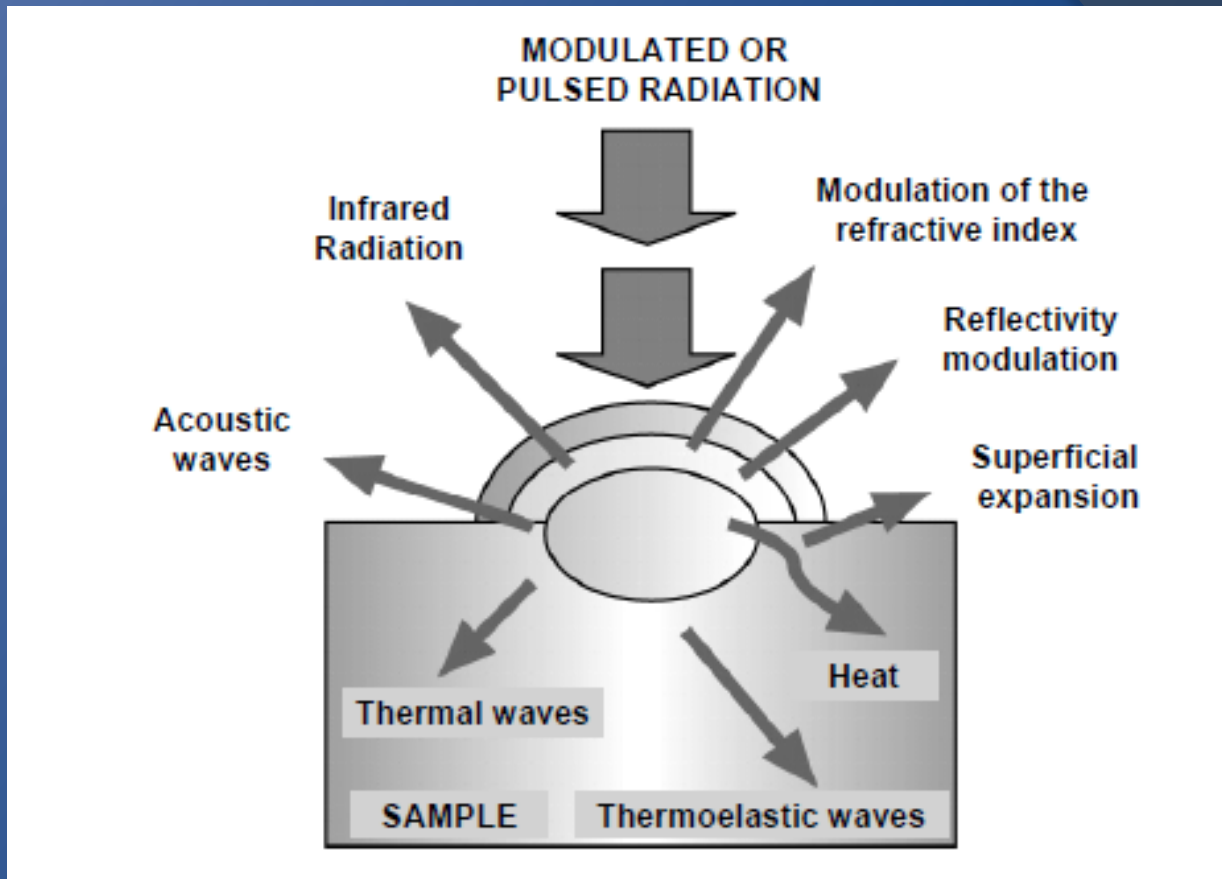
**PRINCIPLES OF PHOTOTHERMAL TECHNIQUES**

# Photothermal techniques available at Photothermal Techniques Laboratory, CICATA-Legaria



Thermal lens and photothermal modulated photoreflectance microscopy



Thermal lens spectroscopy



Photothermal Infrared thermography



Photoacoustic spectroscopy
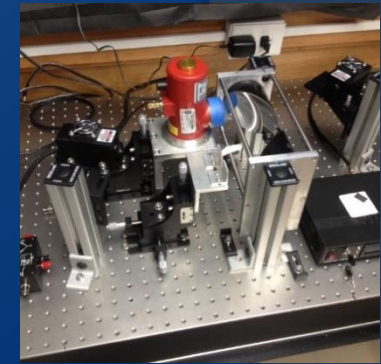


Photothermal Infrared radiometry
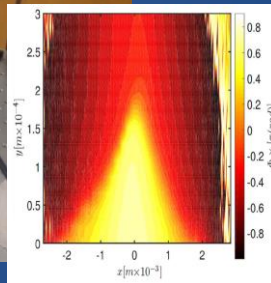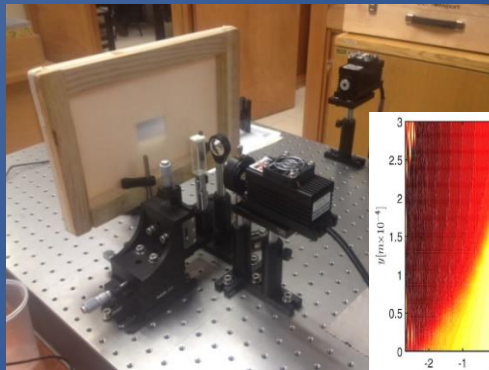


Photothermal (multi) beam deflection and photothermal lock-in shadowgraphy



Photopyroelectric technique



Photopyroelectric/acoustic microscopy

# Another example of a photothermal technique:
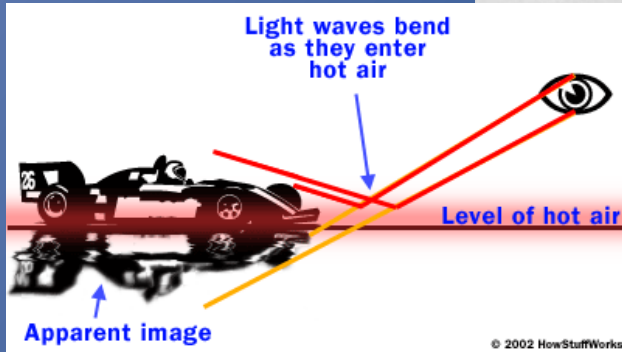


Mirage effect (BEAM DEFLECTION)
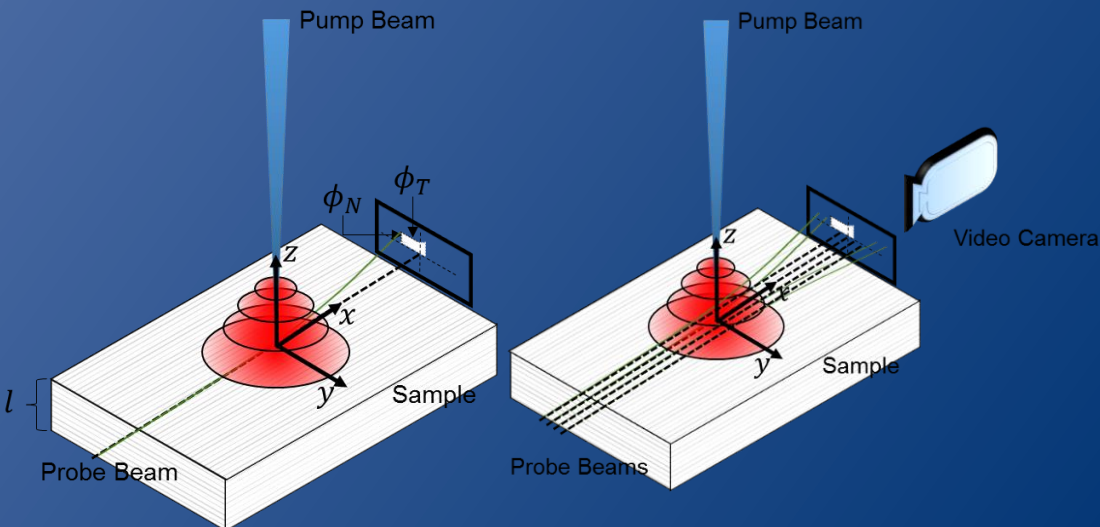


Wednesday 9.00 h Photothermal digital lock-in shadowgraph technique for materials thermal characterization (signal and image digital processing) ( Leonardo Building - Budinich Lecture Hall ) !!

# 4<sup>TH</sup> PART: SELECTED APPLICATIONS
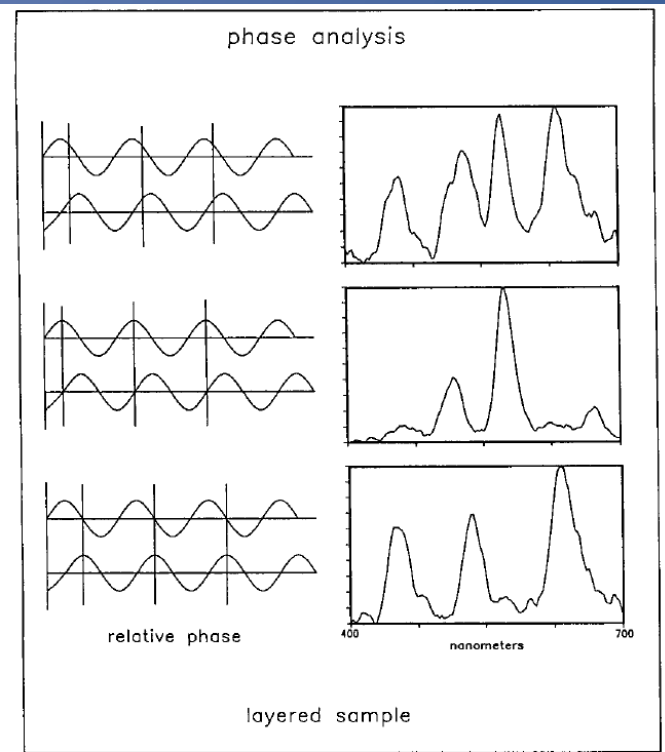
FIG. 6. An illustration of selective depth profiling using phase sensitive detection at a modulation frequency, *f*, of 13 Hz and corresponding thermal diffusion length of 37 μm: (a) both layers contribute to the total photoacoustic signal; (b) maximization of the contribution from the surface layer; (c) maximization of the contribution from the interior layer.
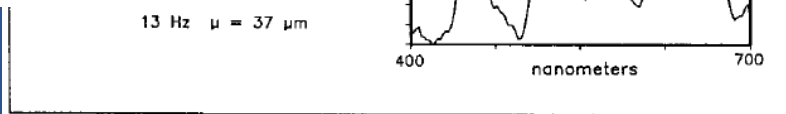
FIG. 4. An illustration of depth profiling by variation of the modulation frequency using the layered sample: (a) modulation frequency, *f*, 208 Hz; thermal diffusion length, μ, 9 μm; (b) *f*, 26 Hz; μ, 26 μm; (c) *f*, 13 Hz; μ, 37 μm.
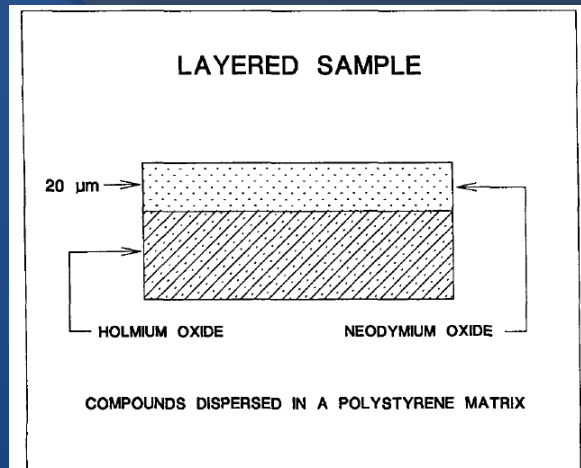
FIG. 2. Schematic diagram for the layered sample consisting of a thin (20 μm) surface layer of neodymium oxide on a thick (2.5 mm) interior layer of holmium oxide.
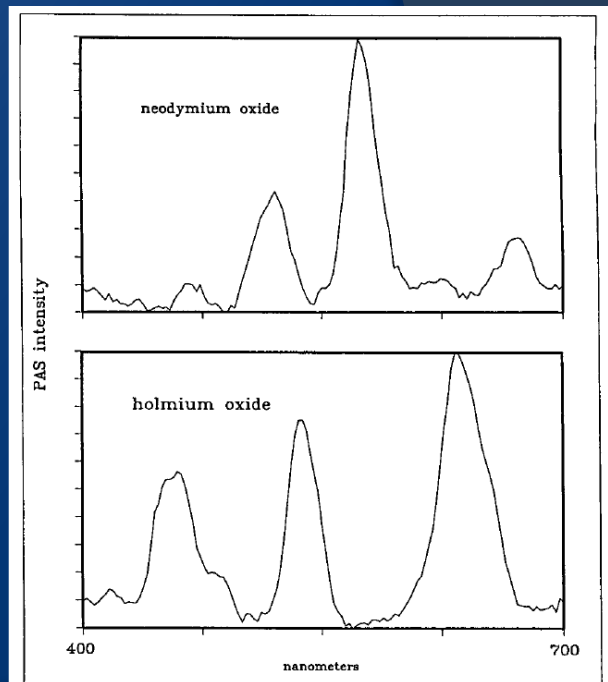
FIG. 5. Visible Hadamard transform photoacoustic spectra of neodymium oxide and holmium oxide.

**More Spectroscopic Applications:**
Thermal lens spectroscopy:
Prof. A. Marcano, Wednesday 15 and Thursday 16, 11.00 h

Thermal lens microscopy:
Prof. M. Franko Monday 20 and Tuesday 21, 11.00 h

**+ some experimental sessions**

# THERMAL CHARACTERIZATION BY SLOPE METHOD

$$T(L, t) = \frac{I_0}{2\varepsilon\sqrt{\omega}} exp(-qL)exp\left[-i\left(\omega t + \frac{\pi}{4}\right)\right] = \frac{I_0}{2\varepsilon\sqrt{\omega}} exp\left(-\frac{L}{\mu}\right) exp\left[-i\left(\frac{L}{\mu} + \omega t + \frac{\pi}{4}\right)\right]$$

Amplitude        Phase

$$\mu = \sqrt{\frac{2\alpha}{\omega}}$$

$$\Delta\phi = L/\mu + \pi/4$$

LOG (AMPLITUDE × $\omega^{1/2}$ ) VERSUS $\omega^{1/2}$

PHASE VERSUS $\omega^{1/2}$

⎫ STRAIGH LINE WITH SLOPE = L /$(2\alpha)^{1/2}$

FREQUENCY DEPENDENT INSTRUMENTAL FACTOR
CAN AFFECT BOTH AMPLITUDE AND PHASE
→ NORMALIZATION PROCEDURES, EXPERIMENTAL ARTIFACTS, ETC

LOG (AMPLITUDE ) VERSUS L

PHASE VERSUS L

⎫ STRAIGH LINE WITH SLOPE = $(\omega/2\alpha)^{1/2}$
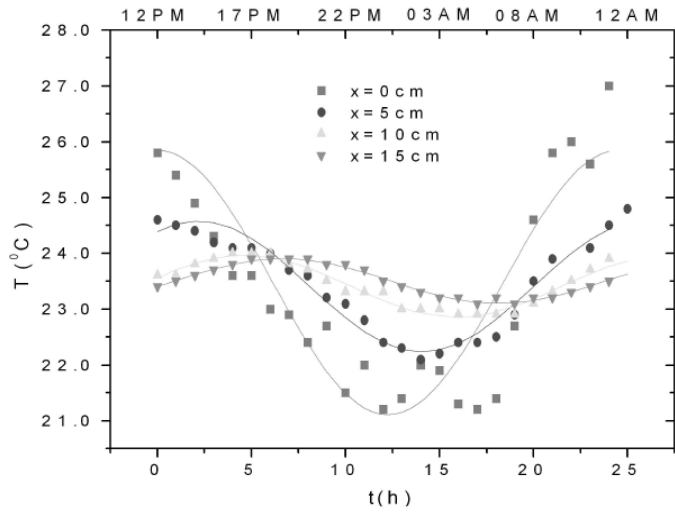
STRAIGHFORWARD PROCEDURES

FIGURE 4. Soil Temperature as a function of time at different depths beneath the earth's surface and hourly air temperature. The solid curves represent best fits to Eq. (14) The air temperature (x=0) versus time curve is also represented for comparison.



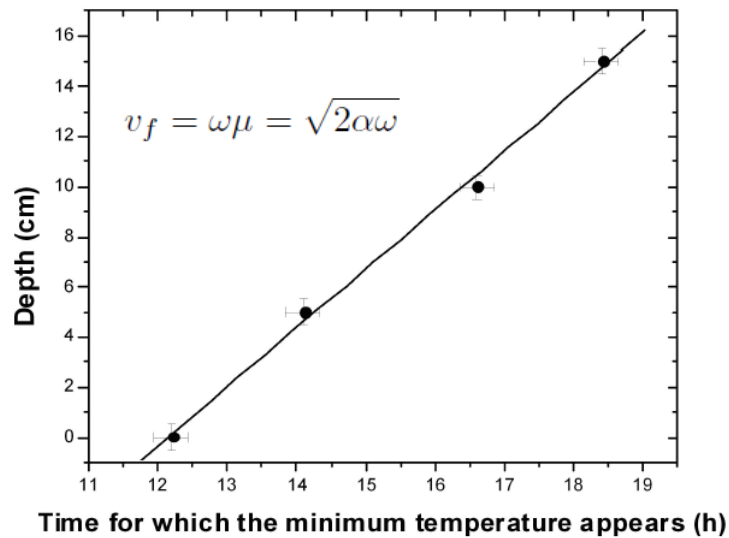$$v_f = \omega\mu = \sqrt{2\alpha\omega}$$

FIGURE 5. Depth at which the measurements were performed at a function of time at which the minimum temperature appears. The solid line is the best linear fit for the data.
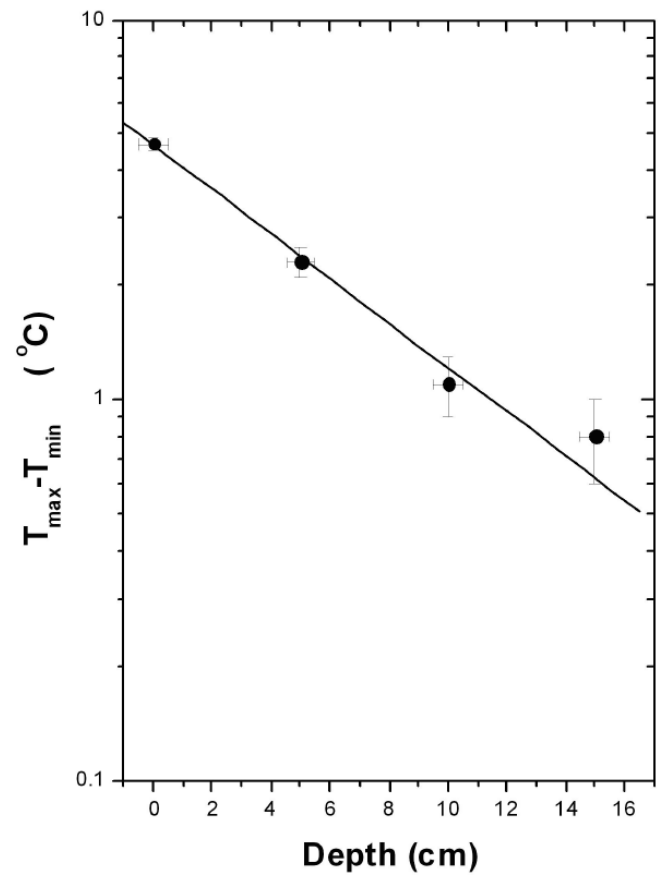


FIGURE 6. Logarithm of the thermal waves amplitudes as a function of depth. The solid line is the best linear fit for the data.
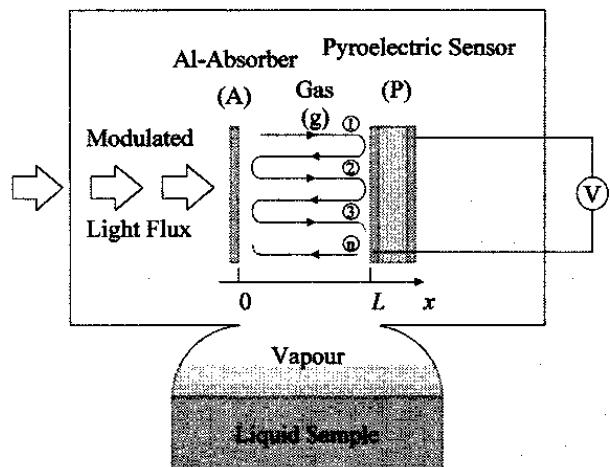
FIG. 1. Schematic view of the thermal wave resonator cavity sensor described in the text.
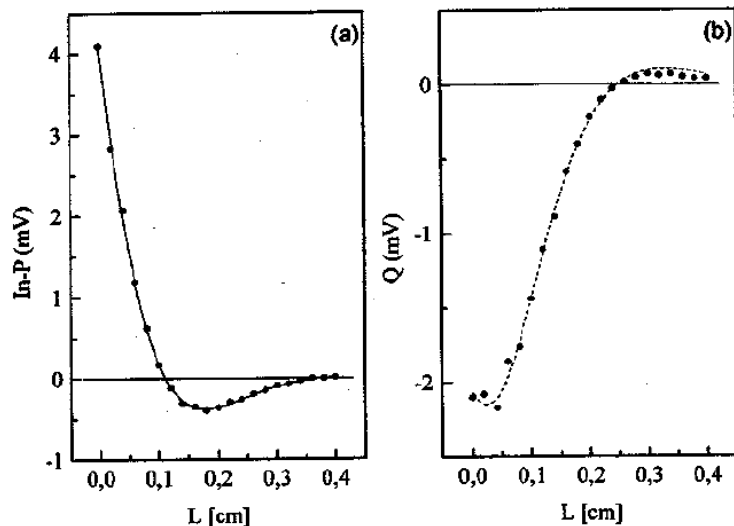


FIG. 2. In-phase (a) and quadrature (b) signals measured for air. The solid curves are the best-fit results to the real and imaginary parts of Eq. (6), respectively.
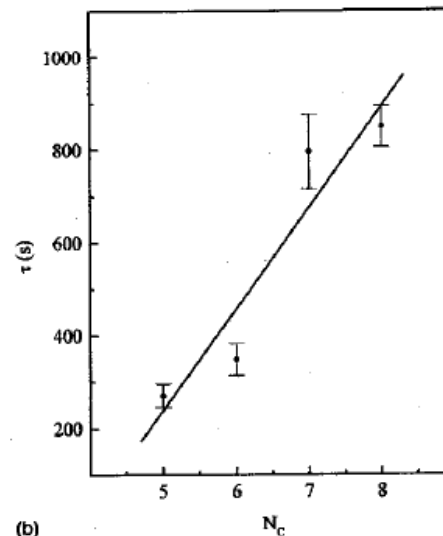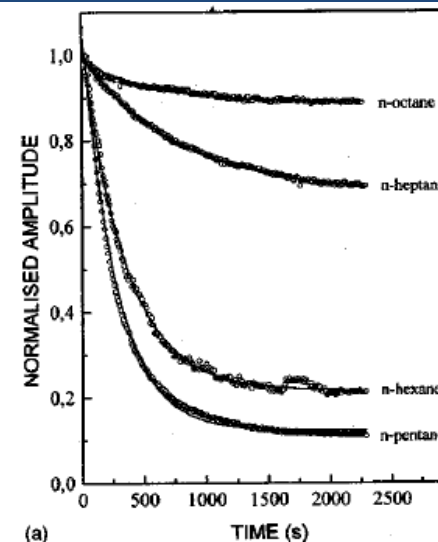


FIG. 3. (a) Time evolution (normalized signal as a function of time) of the TWRC signal corresponding to different hydrocarbon samples. The solid curves are the best-fit result of the data to an exponential decay law. (b) Decay time obtained from the fits represented in (a) as a function of the number of carbon atoms in the linear chain.
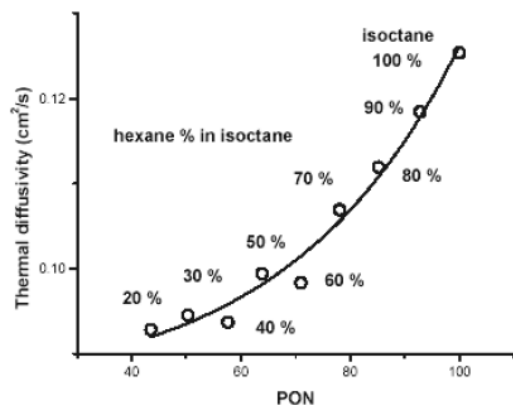
Cardoso, S.L, da Silva, M.G., Lima, J.A.P. Sthel, M.S., Marin, E. and Vargas, H. 2001 Anal. Sc. 17, 479.



**Figure 10.** Thermal diffusivity versus Pump Octane Number for different concentrations of (liquid) *n*-hexane in isooctane. The solid curve is the best fit to an exponential growth function. (Taken from Ref. [76]).

Lima, J.A.P., Massunaga, M.S.O., Vargas, H. and Miranda, L.C.M. 2004, Anal. Chem. 76, 114.
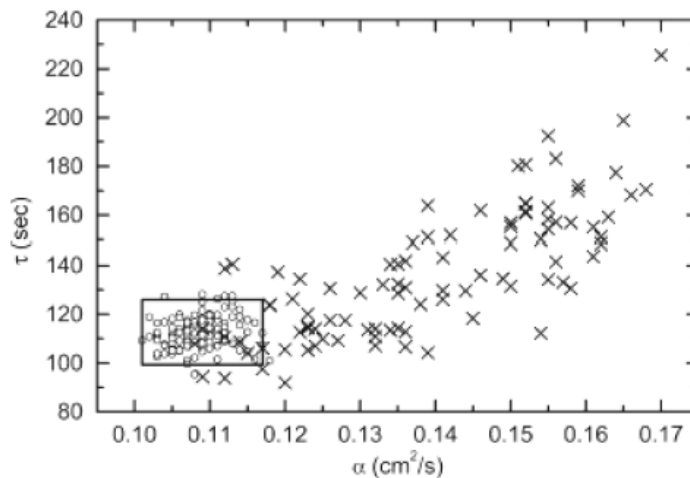


**Figure 11.** Correlation between the characteristic decay time and the thermal diffusivity for the 210 gasoline samples. The solid rectangle represents the conformity grid. Measurements were performed at $23^0$C , at $f$=10 Hz and $L$=2mm (Reprinted in part with permission from Ref. [41]. Copyright 2004 American Chemical Society).

# Thermal characterization of thin filaments



**Spider silk ties scientists up in knots**

Two years ago, researchers published a study which concluded that spider silk conducts heat as well as metals. Now scientists have repeated the experiment and the results throw this discovery into question.

http://www.sciencedaily.com/releases/2014/01/14012209173 2.htm

**ADVANCED MATERIALS**
www.advmat.de

*Materials Views*
www.MaterialsViews.com

**New Secrets of Spider Silk: Exceptionally High Thermal Conductivity and Its Abnormal Change under Stretching**

*Xiaopeng Huang, Guoqing Liu, and Xinwei Wang*

Materials Letters 114 (2014) 1–3

Contents lists available at ScienceDirect

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Revising the exceptionally high thermal diffusivity of spider silk

Raquel Fuente, Arantza Mendioroz, Agustín Salazar *

Departamento de Física Aplicada I, Escuela Técnica Superior de Ingeniería, Universidad del País Vasco UPV/EHU, Alameda Urquijo s/n, 48013 Bilbao, Spain
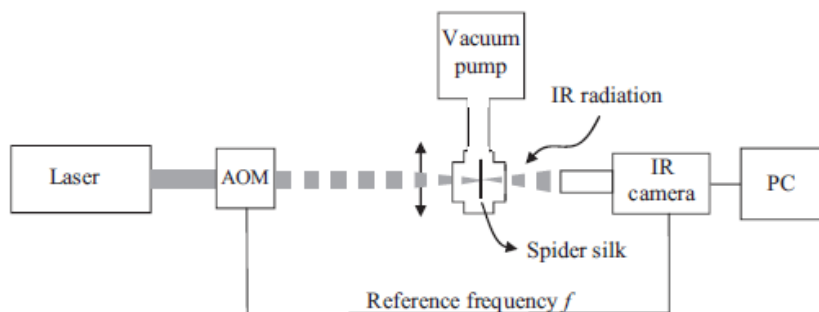
Fig. 1. Diagram of the experimental setup. The intensity of the laser is modulated by an acousto-optic modulator (AOM) and focused onto the spider silk filament. Then, IR radiation is emitted from the sample and detected by the IR camera, which processes the signal at the frequency reference ($f$) and sends the information to the PC for further analysis.
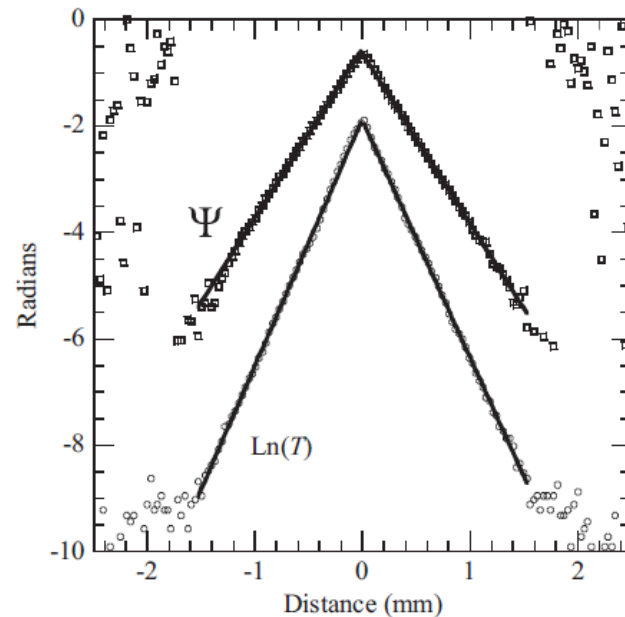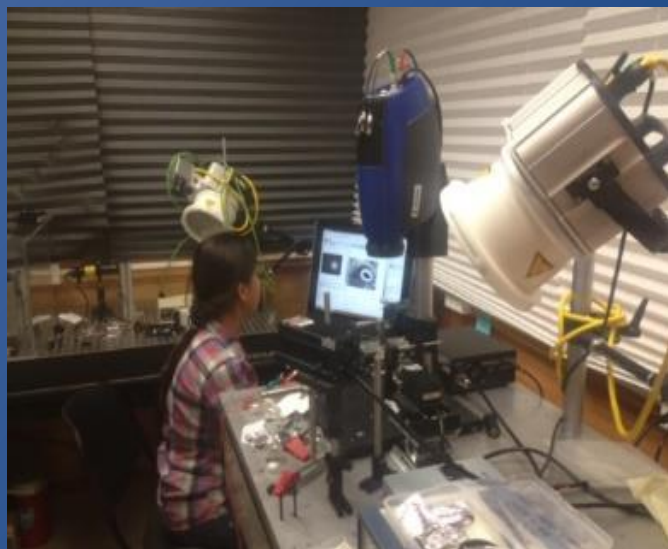


Fig. 2. Phase ($\psi$) and natural logarithm of the amplitude ($Ln(T)$) of a spider dragline silk temperature as a function of the distance to the heating spot, at $f=0.914$ Hz. Symbols correspond to experimental data and continuous lines to the linear fittings.



Materials Letters 114 (2014) 1–3

**Thermal properties characterization:**
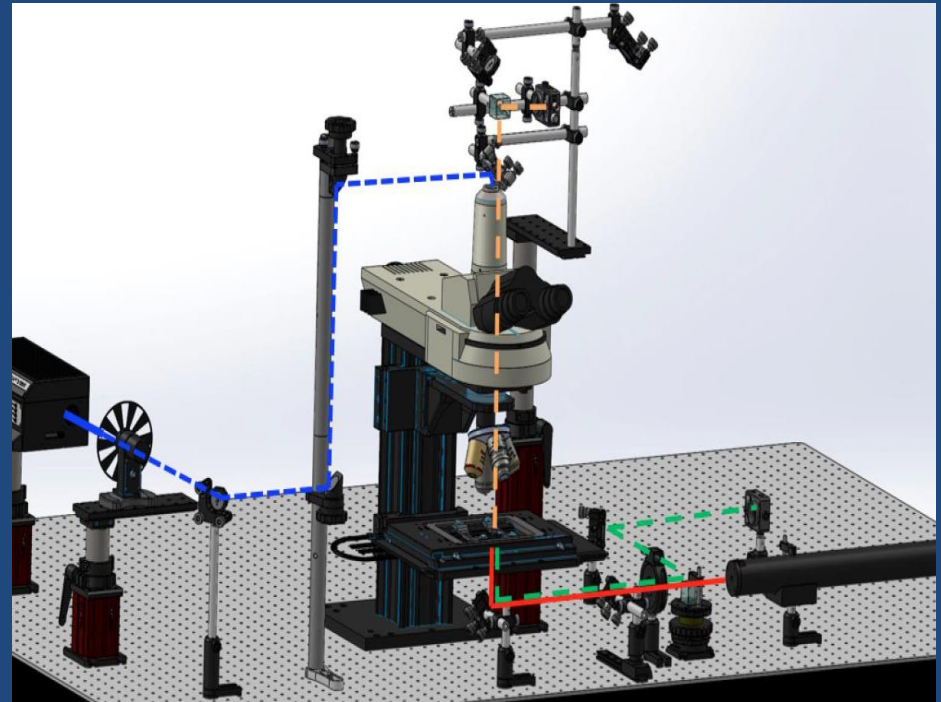Photothermal shadowgraph technique:
Prof. E. Marin, Wednesday 15, 9.00 h

+ SOME EXPERMENTAL SESSIONS

**Photothermal pump-probe optical methods are very useful for both spectroscopy and thermal characterization, e.g. thermal lens technique**

$$\frac{\Delta\eta}{\eta_0} = \frac{1}{\eta_0}\frac{d\eta}{dT}\Delta T$$

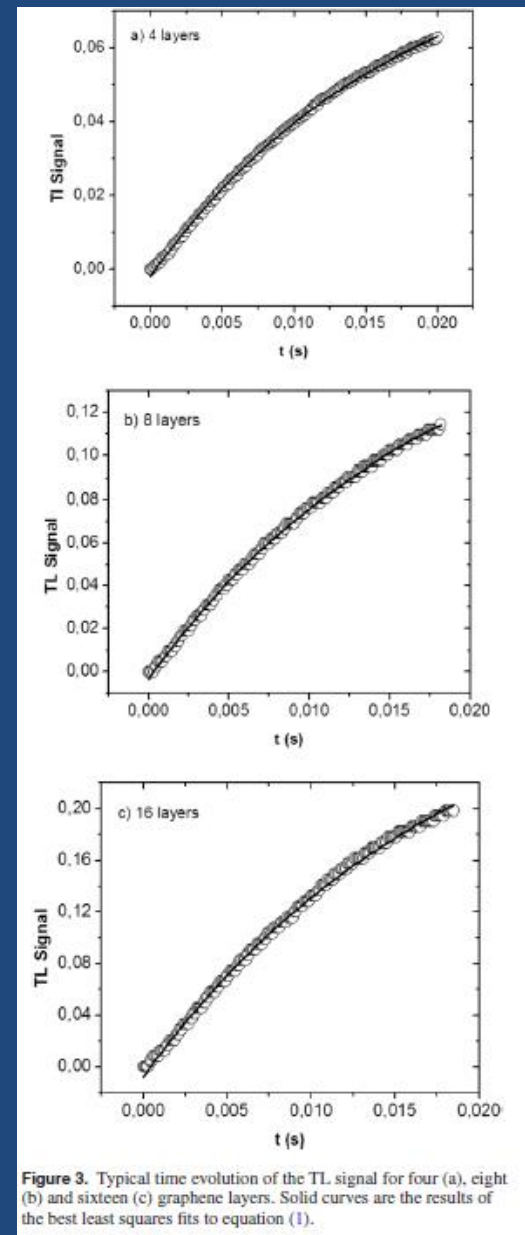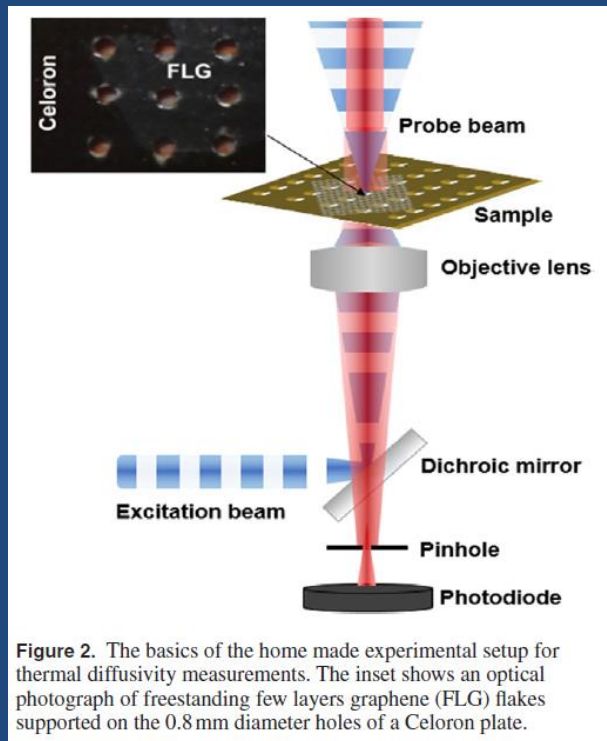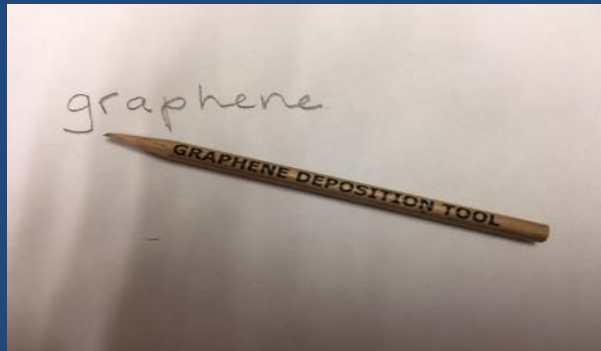**Thermal lens spectroscopy (see Franko and Marcano forthcoming courses)**

Graphene: 2D (semi) metal: a lattice of hexagonally arranged carbon atoms. The potential to produce graphene using a super abundant chemical element, and the possibility of its functionalization, make it a particular laboratory for basic research in 2D systems.





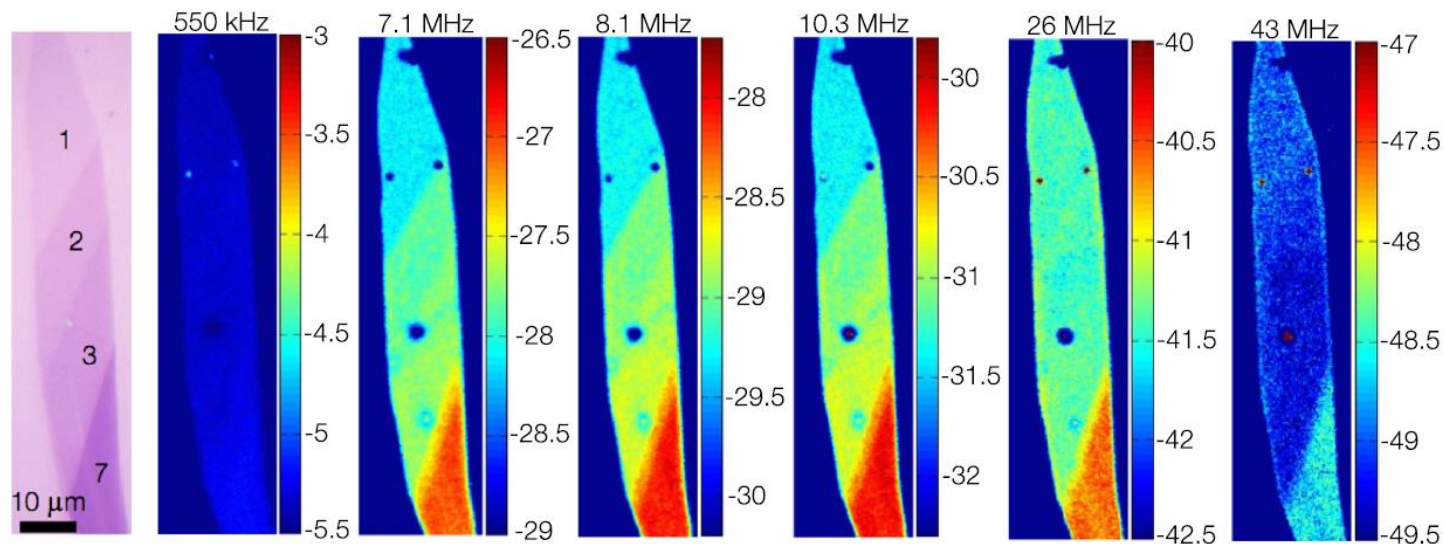**Figure 2.** The basics of the home made experimental setup for thermal diffusivity measurements. The inset shows an optical photograph of freestanding few layers graphene (FLG) flakes supported on the 0.8 mm diameter holes of a Celoron plate.



**Figure 3.** Typical time evolution of the TL signal for four (a), eight (b) and sixteen (c) graphene layers. Solid curves are the results of the best least squares fits to equation (1).

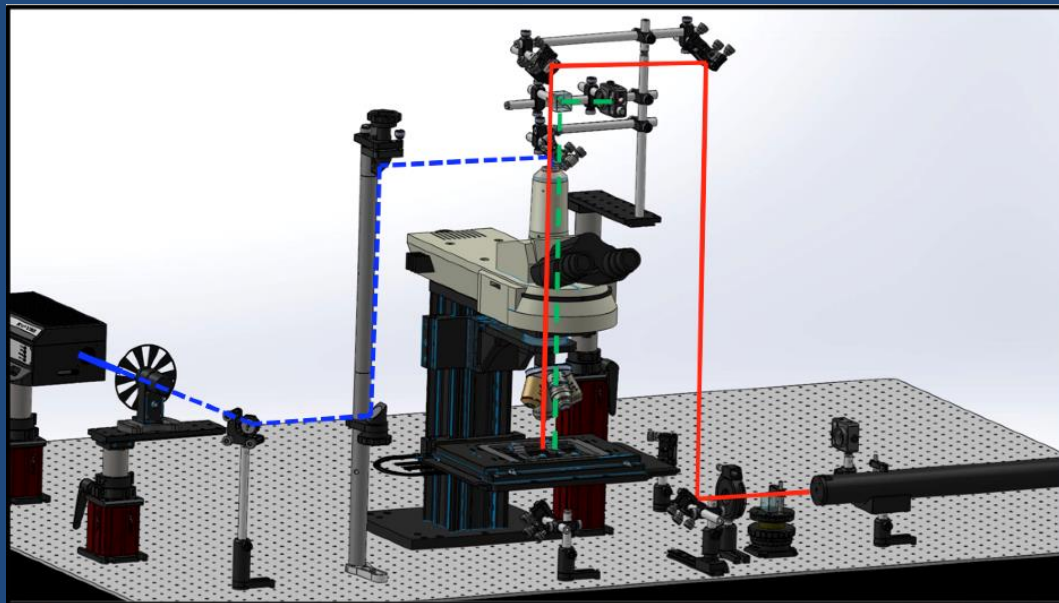Signal ~ number of layers
→ imaging

FIG. 6. Phase images of flake 1 acquired simultaneously at six frequencies: 550 kHz, 7.1 MHz, 8.1 MHz, 10.3 MHz, 26 MHz, and 43 MHz. The image contrast between the layers follows the sensitivity to $G_{\parallel}$ shown in Fig. 5(e).

Images taken with a modulated thermoreflectance set-up

# Modulated optical reflectance microscopy

$$\frac{\Delta R}{R_0} = \frac{1}{R_0}\frac{dR}{dT}\Delta T$$

# Thermoacoustic and thermoreflectance imaging of biased integrated circuits: Voltage and temperature maps
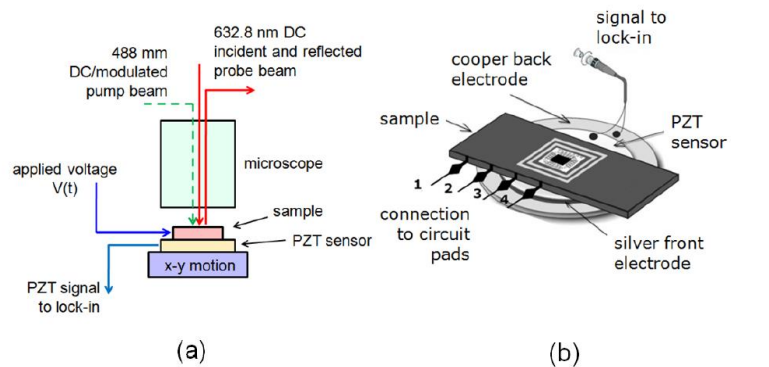
**Figs. 3.1.** (a) Block diagram of the experimental setup; (b) detailed view of the sample and PZT sensor.
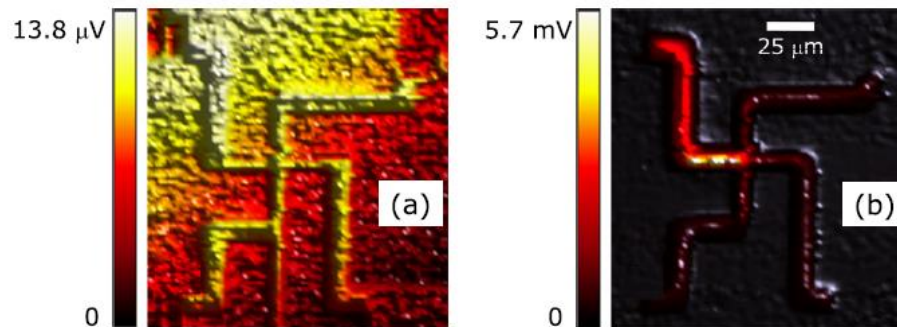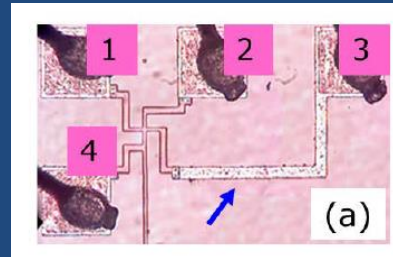


FIG. 3. (a) PZT and (b) thermoreflectance 2nd harmonic signal amplitude maps under modulated voltage excitation. Scanned area: $162\,\mu m \times 173\,\mu m$; modulated voltage: $V_0 = 4.0\,V$, $f = 25\,kHz$.
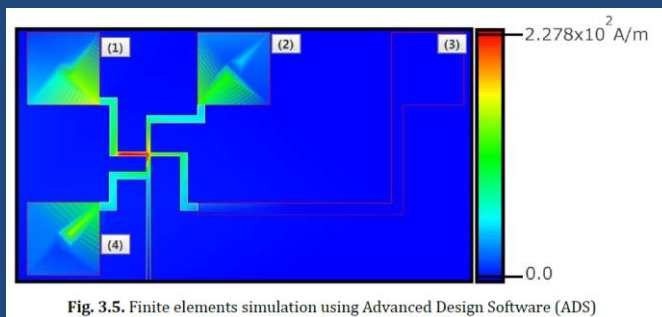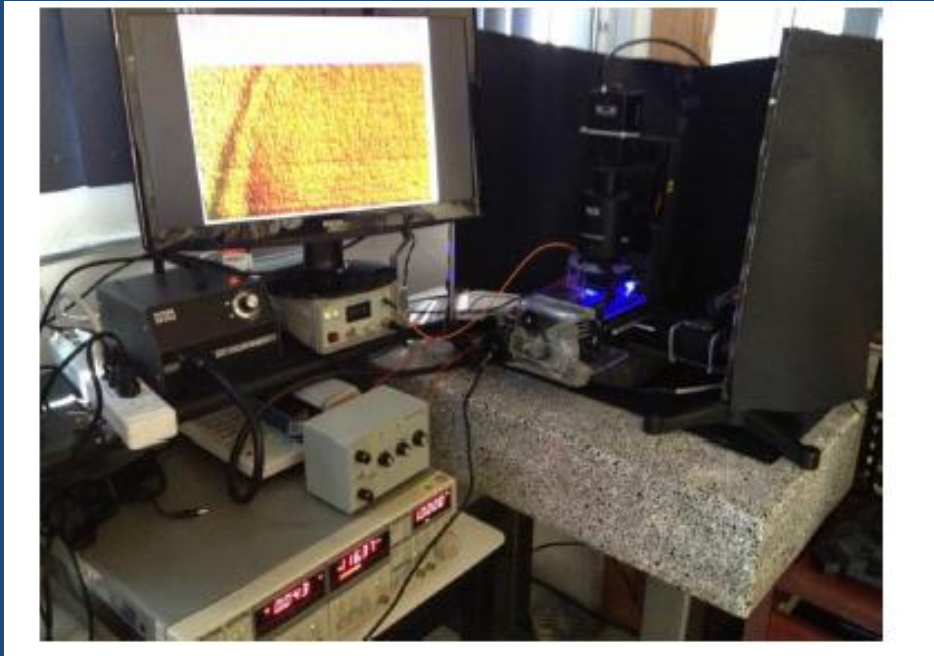


**Fig. 3.5.** Finite elements simulation using Advanced Design Software (ADS)

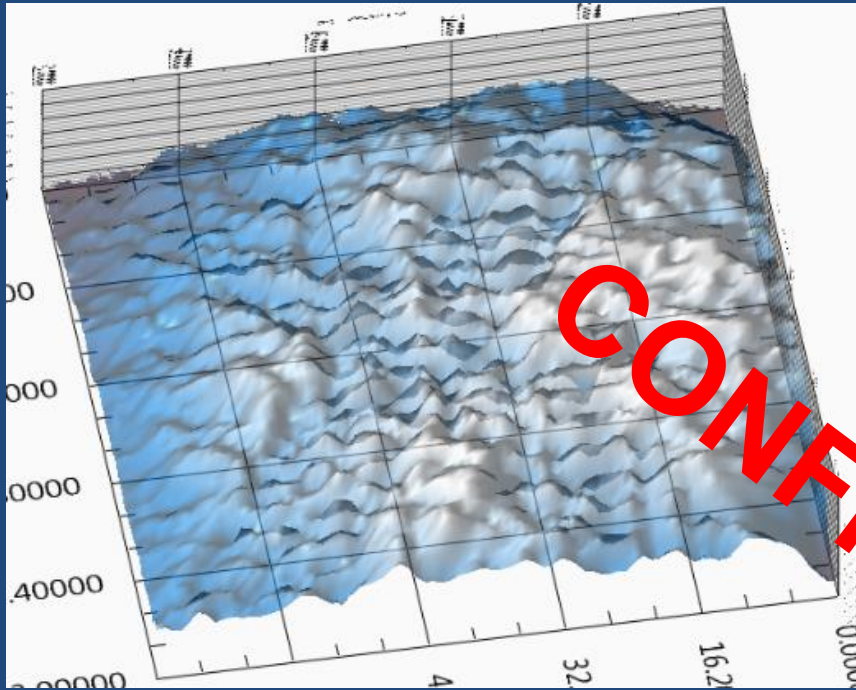E. Hernández Rosales *et al* in preparation

# Imaging

## A photothermal microscope at CICATA-Legaria.
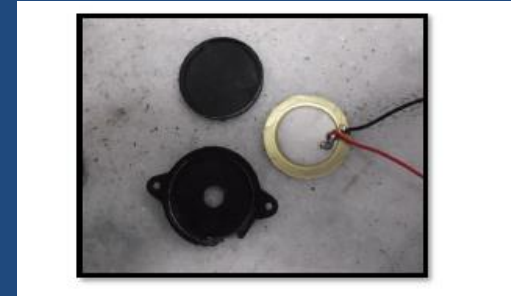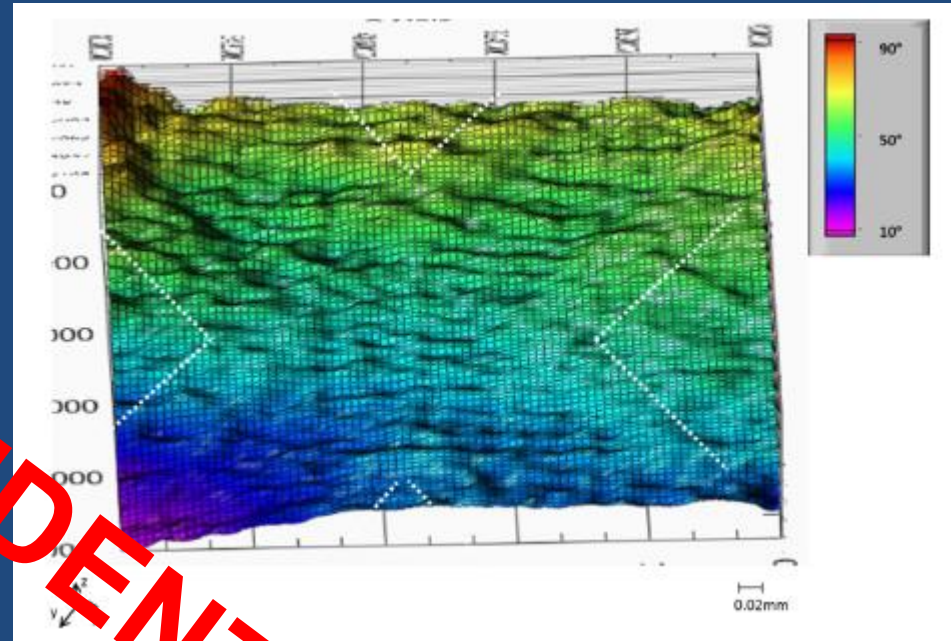




The sensor:
A PZT from a commercial buzzer

E. Cedeño, Master Thesis, CICATA-IPN, México, August 2013
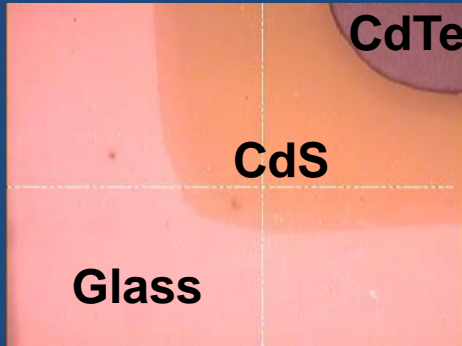
# Imaging



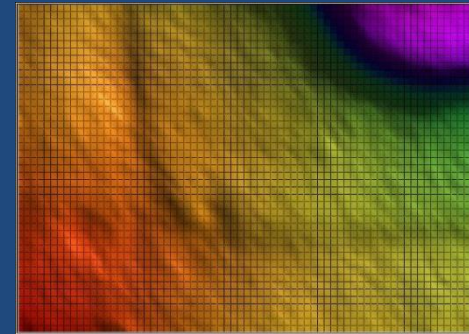Amplitude image



Phase image



Optical image

f=6 kHz
Resolution 0.02 mm
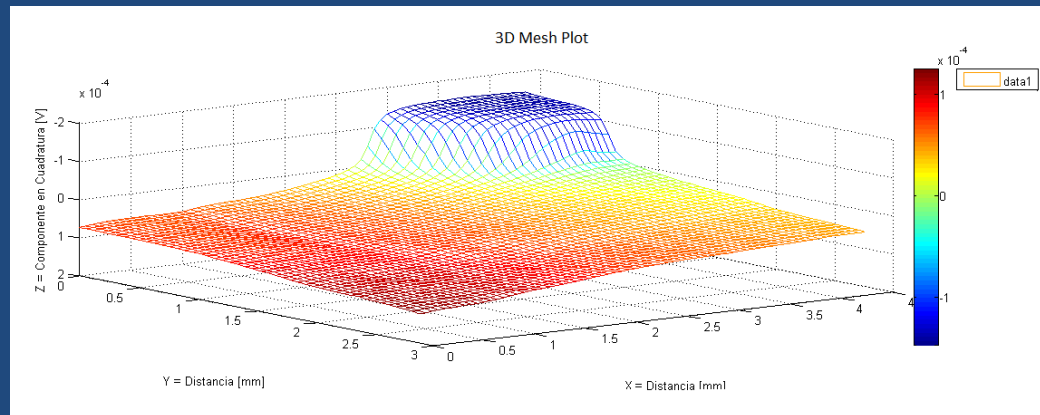(7533 pixels)

Lottery Ticket "Raspe y Gane"
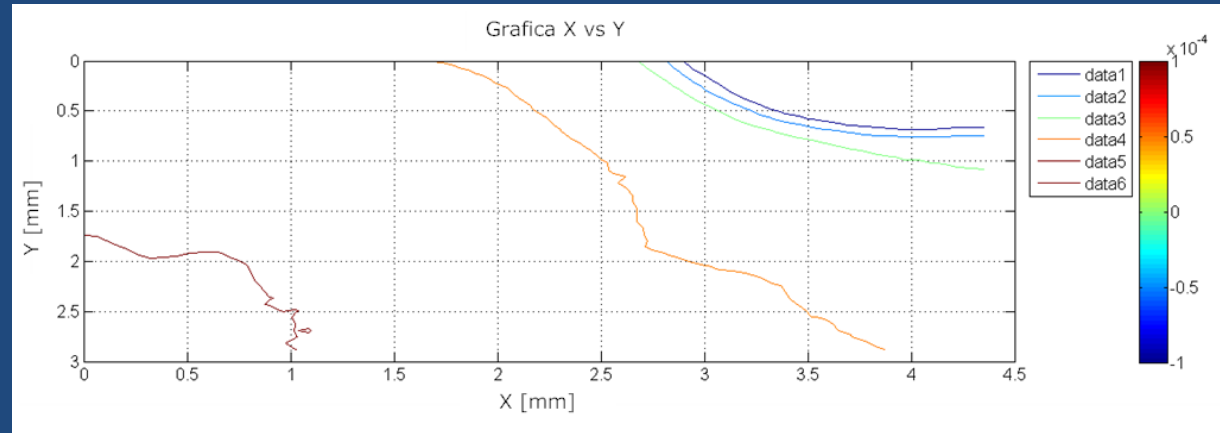
# Imaging
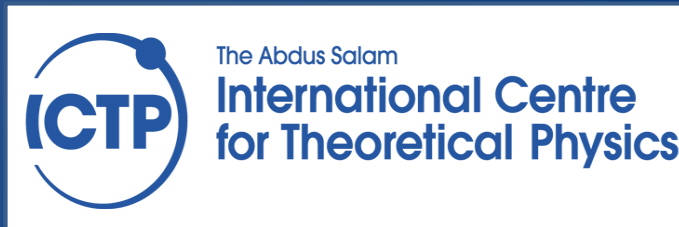
CdTe

CdS
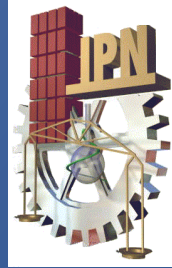
Glass

**Optical**

CdTe/CdS/Glass

**Photoacoustic**

# ACKNOWLEDGEMENTS

INSTITUTIONS:

COLLABORATORS:
MANY COLLEAGUES (IN MEXICO AND ABROAD) AND STUDENTS

# Thank you!