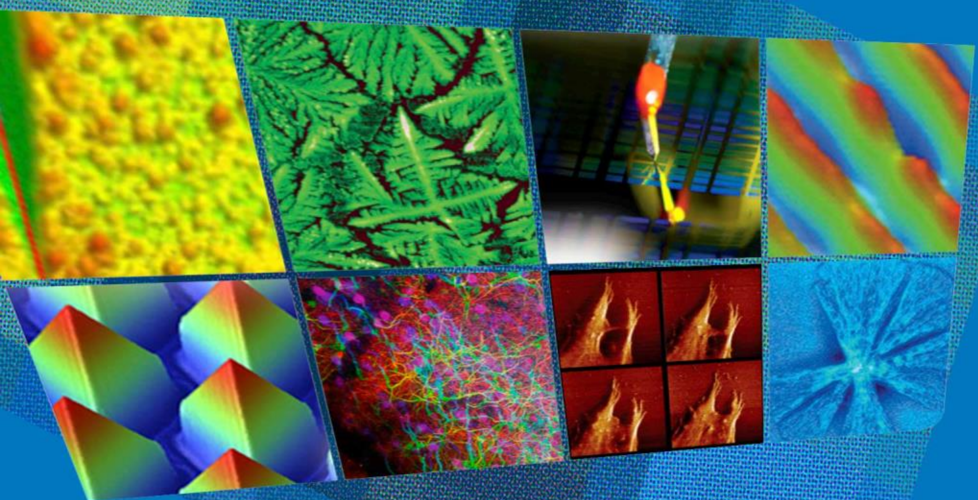
Advanced nanoscale IR spectroscopy and Applications Webinar



Atomic Force Microscopy
3D Optical Microscopy
Fluorescence Microscopy
Tribology
Stylus Profilometry
Nanoindentation

Innovation with Integrity

Bruker Nano Surfaces Division

Advanced nanoscale IR spectroscopy and Applications
Webinar May 21st

Presenter

Professor Alexandre Dazzi,
University Paris-Sud,
Orsay France

Host & Moderator

Dr Curtis Marcott
Light Light Solutions

ANASYS INSTRUMENTS
The nanoscale spectroscopy company

Bruker Nano Acquires Anasys Instruments

Anasys joins Bruker Nano Surfaces Division

Strengthening the world of nanoanalysis and nanomechanical materials characterization- together

- Bruker Nano Surfaces Division acquired Anasys Instruments Corp on April 10th 2018
- All nanoIR products are now integrated into the Bruker Nano Product Support

The leader in nanoscale IR spectroscopy

2010

nanoIR™
1st Generation
AFM-IR

2014

nanoIR2™
2nd Generation AFM-IR
Top Down Configuration &
Resonance Enhanced

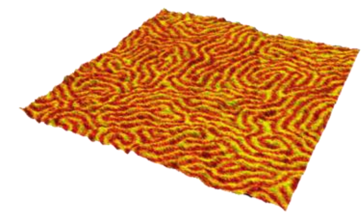
2015

nanoIR2-s™
Combined
IR s-SNOM & AFM-IR

2016

nanoIR2-FS™
3RD Generation
FASTspectra

2017



Tapping AFM-IR
HYPERspectra

2018

NEW
nanoIR3™
Latest Generation
nanoIR platform with
Tapping AFM-**IR**

- History of patented technology for nanoscale IR spectroscopy & materials property mapping
- Ernst Abbe award for Alex Dazzi - Inventor of AFM-IR

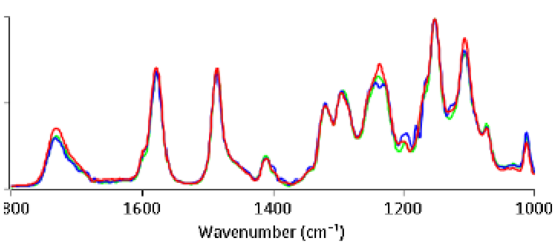
NEW nanoIR3 platform configurations

nanoIR3™ - Latest Generation nanoIR platform with Tapping AFM-IR

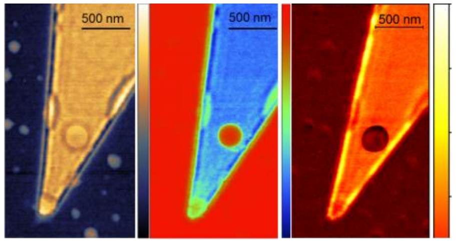
- Highest performance nanoIR spectra with AFM-IR
- Sub-10nm resolution IR chemical imaging with Tapping AFM-IR
- Correlates to FTIR & industry databases
- Easy to use for fast, productive measurements

nanoIR3-s™ High Performance IR nano-spectroscopy

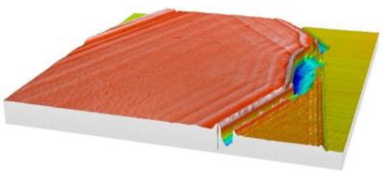
- Complementary sSNOM & Tapping AFM-IR
- Highest Performance IR nano-spectroscopy
- Broadband Spectroscopy & Chemical Imaging
- Nanoscale property mapping
- *Versatility* & Easy to Use



nanoIR Spectroscopy of Polyethersulphone (PES)



Plasmonic Imaging on Graphene with Tapping AFM-IR & s-SNOM



S-SNOM imaging Phase and Amplitude on HbN

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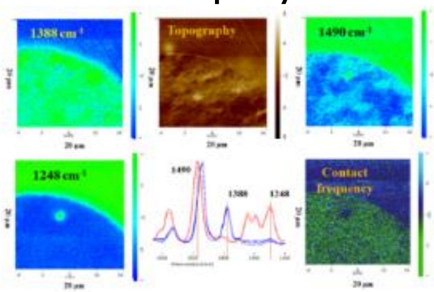
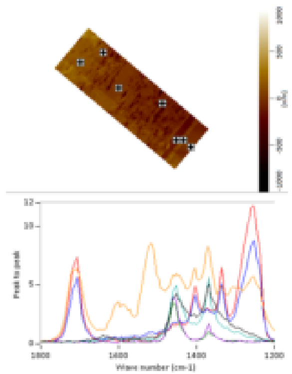
Broad range of nanoIR applications

BRUKER

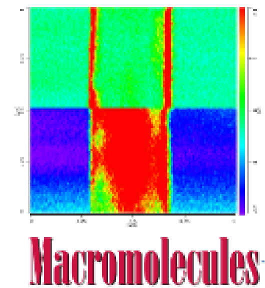
Polymer blends & Block Copolymers



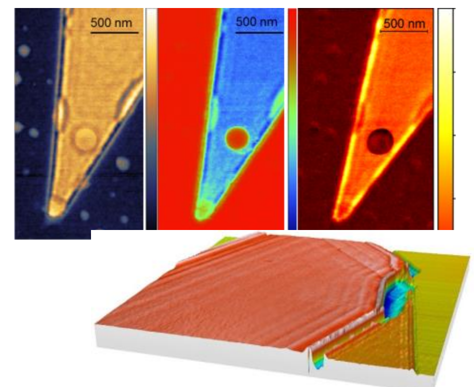
Multilayer films



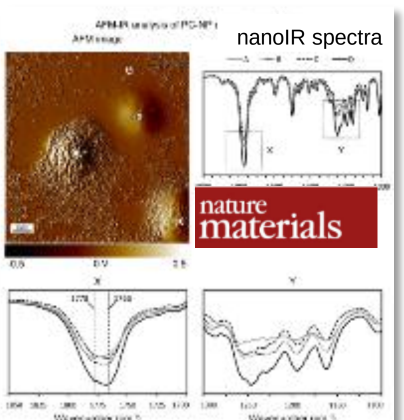
Nanofibers



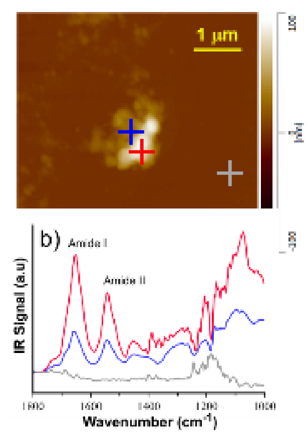
2D Materials/Graphene



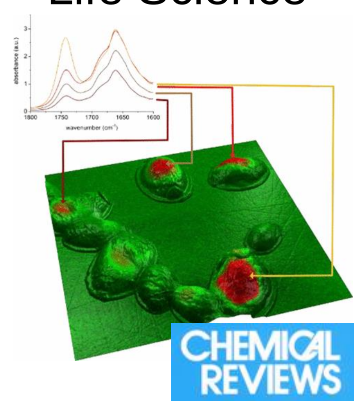
Nano-Composites



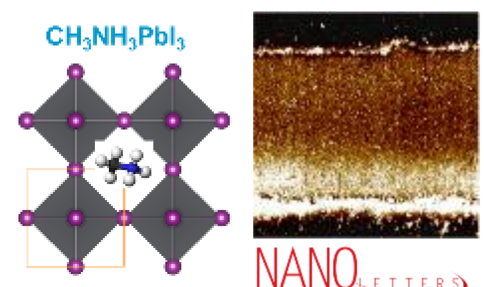
Organic nano Contaminants



Life Science



Perovskites & Solar Cells



ANASYS INSTRUMENTS
The nanoscale spectroscopy company

European Forum on Nanoscale IR Spectroscopy
University of Amsterdam, Sept 11-12th
Co-hosted by University of Amsterdam & Bruker

Select Key Speakers

Professor Alexandre Dazzi

Université Paris-Sud
Laboratoire de Chimie Physique
Batiment 350
91400 Orsay, France

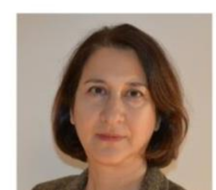
PD Dr. Karsten Hinrichs

Research Group Leader In-Situ-Spectroscopy
Leibniz-Institut für Analytische Wissenschaften – ISAS – e. V.

Simone Ruggeri, PhD.

Research Fellow
Department of Chemistry & Darwin College
University of Cambridge, Cambridge, UK

Dr Lily Poulikakos



Empa
Swiss Federal Laboratories for Materials Science and Technology
Überlandstrasse 129
8600 Dübendorf
Switzerland

Dr. Laurene Tetard

Associate Professor
Physics Department
Nanoscience Technology Center
University of Central Florida

AFM-IR : Advanced nanoscale IR spectroscopy and Applications

Alexandre Dazzi
Laboratoire de chimie physique
Université Paris-Sud

Comprendre le monde, construire l'avenir®

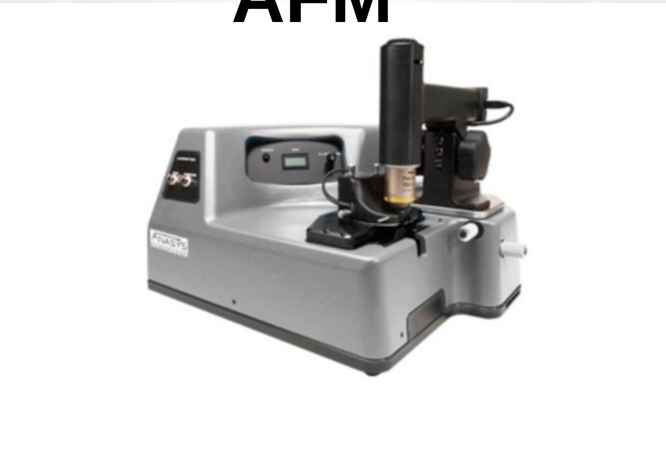
dépasser les frontières

Introduction

ANASYS INSTRUMENTS
The nanoscale spectroscopy company

AFM-IR technique

AFM



+

IR laser

= AFM-IR

Infrared spectroscopy and imaging at nanoscale

AFM-IR technique and microscope evolution

- **2005** : Birth of the technique in UPSud
  - **2007** : Patent with Anasys Instruments

- **2010** : 1st commercial microscop
  The nanoIR1

- **2012** : nanoIR2
- **2014** : nanoIR2s
- **2018** : nanoIR3

NanoIR platform at U-Psud

AFM-IR TEAM

Ariane Deniset-Besseau

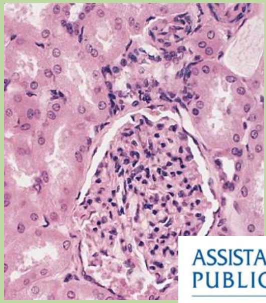
Dominique Bazin

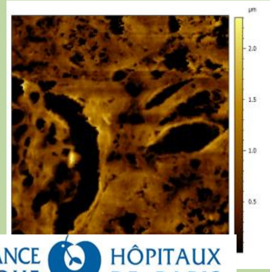
NanoIR2

NanoIR1

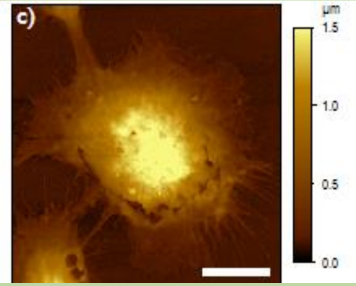
Field of applications - Biology

TISSUE – Human cells





Calcification in human tissues
Extracellular vesicles
Penetration of nanocarriers

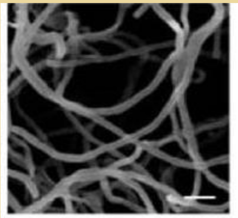


Nanoparticules and cell: macrophage

Fine structure of the hair…

MICRO-ORGANISMS

Accumulation of biopolymer or lipids

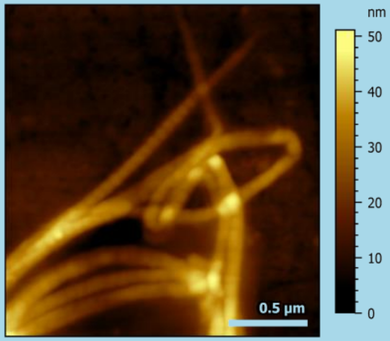


Localisation and quantification

Local composition, TAG, DAG, MAG and FFA differentiation

NANOMETRIC SCALE

Protein assemblies



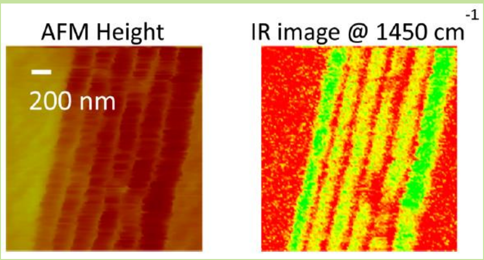
Collagen fibrils denaturation
System complex: Collagen-antibiotic

Bacterial amyloids
Beta structure of amyloids
Prion, lipids bilayer

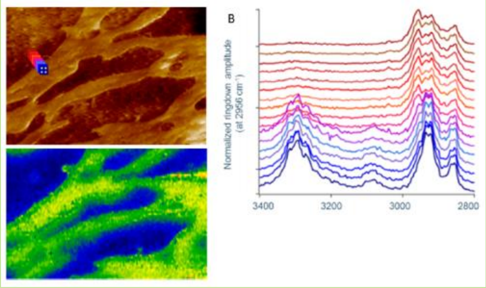
Field of applications

Polymers sciences

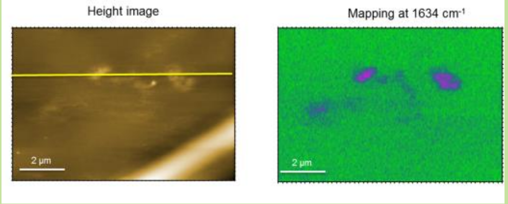
Multilayers: Structure-cristallinity



A Dazzi, Chem Rev, 2016



Trace of adjuvant blooming



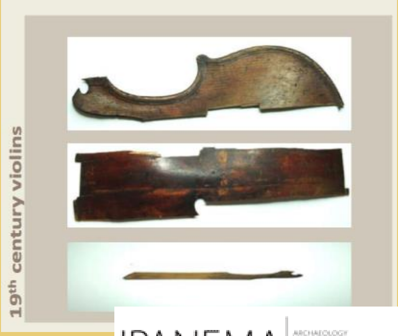
A Dazzi, International journal of pharmaceutics Volume 484, Issues 1–2, 2015

Heritage sciences

G.Latour, Scientific Report, 2016

- Investigate parchments degradation

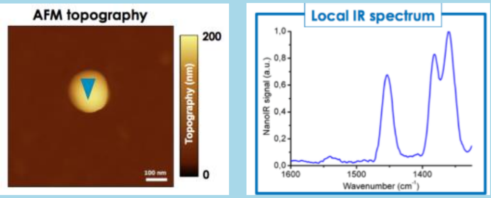
- IR signatures: heterogeneities in ancient tissues or violin sections



IPANEMA ANCIENT MATERIALS RESEARCH PLATFORM

Nanoparticles

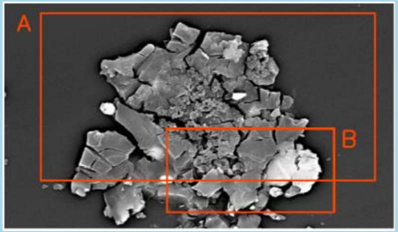
- Polymeric Nps



Mathurin J., 10.1039/C8AN01239C, Analyst, 2018

Astrochemistry

- Investigation of organic matter in micrometeorites



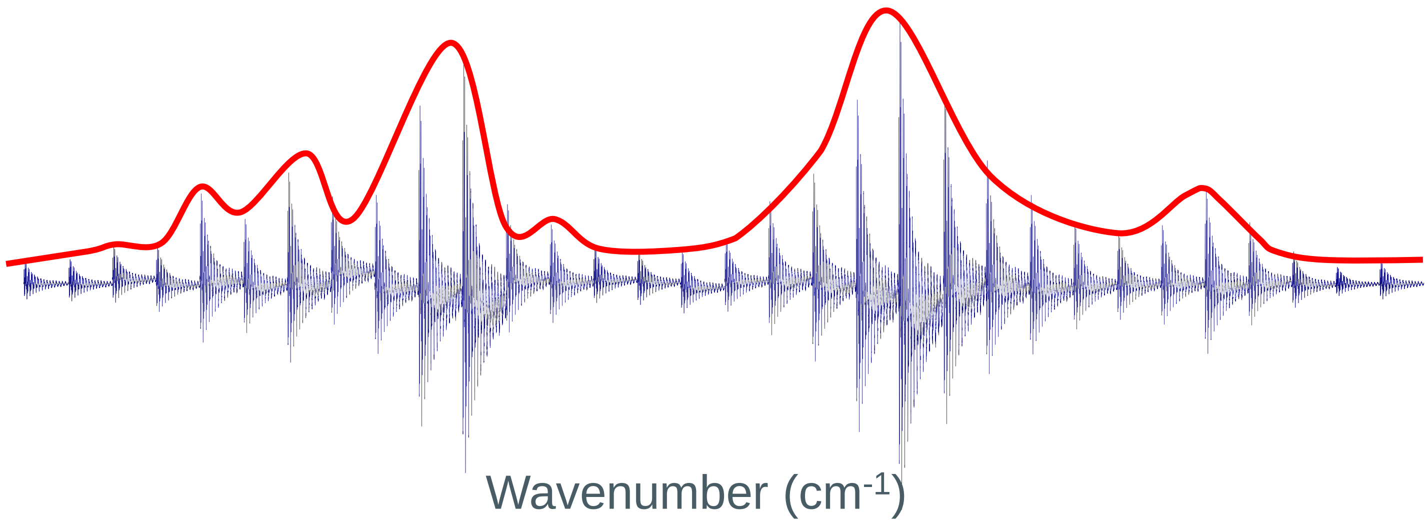
J. Mathurin, A&A, 2019

Technique principle

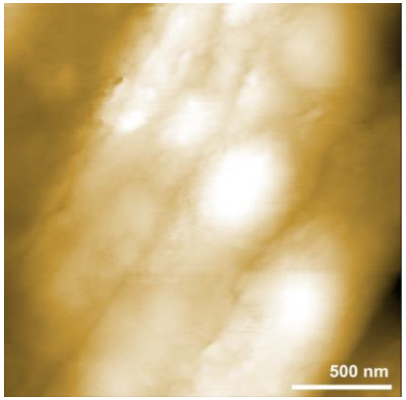
Nanoscale IR spectroscopy

Nanoscale IR spectroscopy

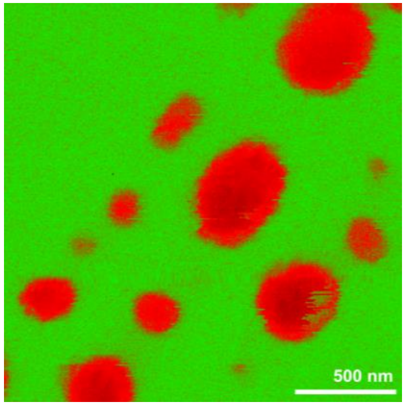
- Absorption Spectrum (fix tip position and scan the wavelength of the laser)



- Chemical mapping (fix the laser wavelength and scan the surface with the tip)



topography

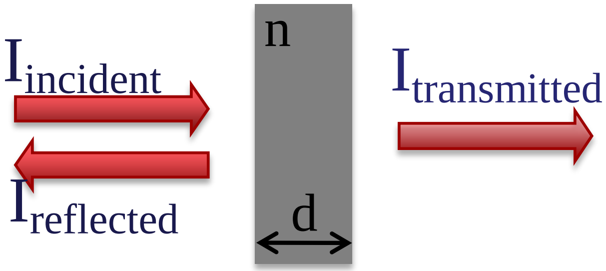


Chemical mapping (λ=5,76µm)

Theoretical concept of AFM-IR

Infrared spectroscopy

Basic principle of spectroscopy :

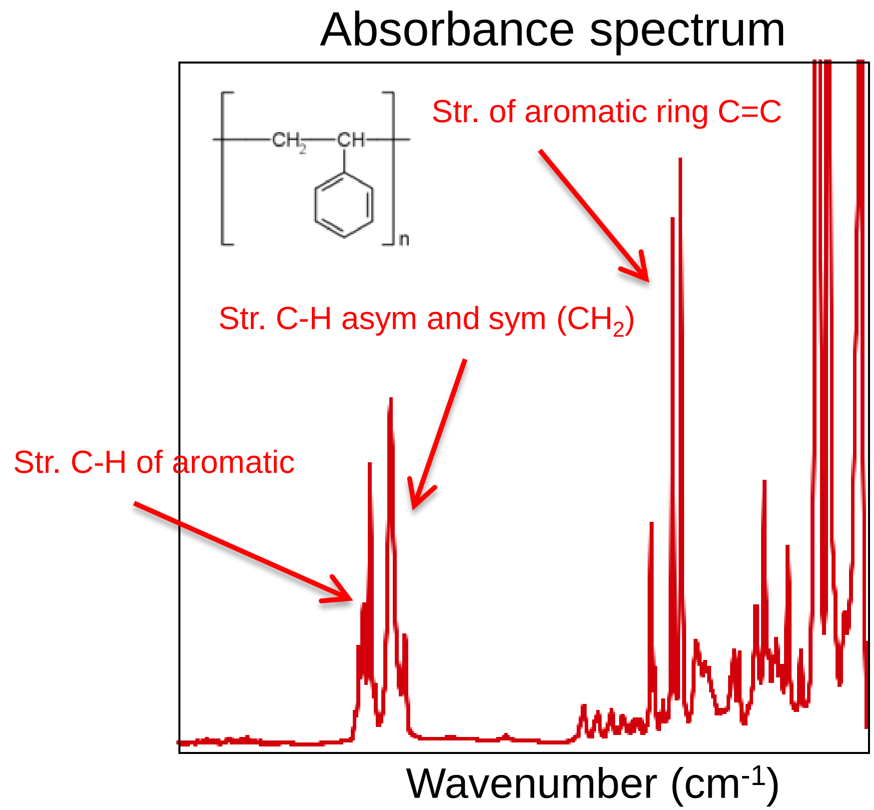


(Beer-Lambert law)

Transmission coefficient

$$T = \frac{I_{transmitted}}{I_{incident}} = \exp(-\frac{4\pi}{\lambda}\mathrm{Im}(n)d)$$

$$\alpha = \frac{4\pi}{\lambda}\mathrm{Im}(n)$$ Extinction coefficient

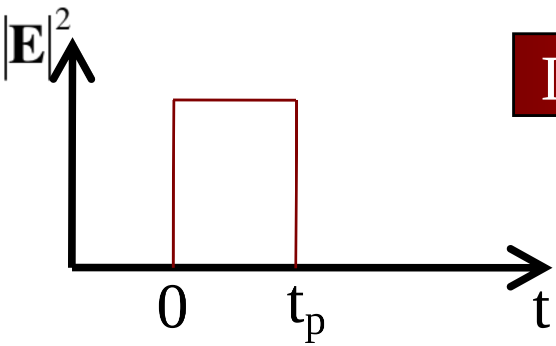


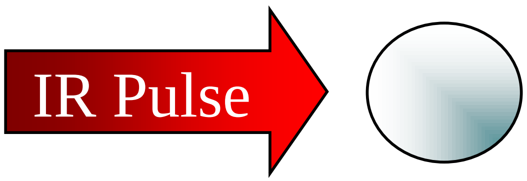
Absorbance

$$Absorbance \propto \frac{\mathrm{Im}(n(\lambda))}{\lambda}$$

Photothermal effect and spectroscopy

Laser Illumination





a sphere radius
V volume
n refractive index

Absorbed power:

$$P_{abs} = \int_V \frac{\omega \varepsilon_0}{2} \mathrm{Im}\left[n^2(\lambda)\right] |\mathbf{E}_{loc}|^2 dV$$

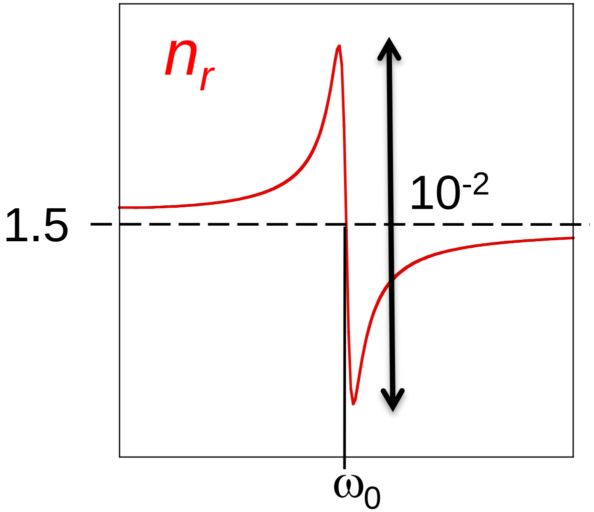
if a << ⌊

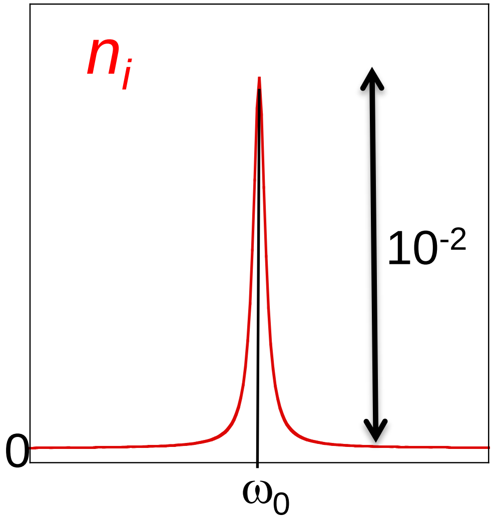
$$P_{abs} = \frac{2\pi}{\lambda} c \varepsilon_0 \frac{9\,\mathrm{Im}(n)\mathrm{Re}(n)}{\left(\mathrm{Re}(n)^2 + 2\right)^2} |E_{inc}|^2 V$$

Photothermal effect and spectroscopy

Weak absorption

$n_i << n_r$





$$P_{abs} = \frac{2\pi}{\lambda} c\varepsilon_0 \,\mathrm{Im}(\alpha) \left|E_{inc}\right|^2 V$$

$$P_{abs} \propto \frac{\mathrm{Im}(n)\,\mathrm{Re}(n)}{\lambda\left(\mathrm{Re}(n)^2 + 2\right)^2} \propto Absorbance$$

Heat Equation:

$$\rho_{sph} C_{sph} \frac{\partial T}{\partial t} = k_{sph} \Delta T + \frac{P_{abs}(t)}{V}$$

〉 density, *C* heat capacity, *k* thermal conductivity

Photothermal effect and spectroscopy

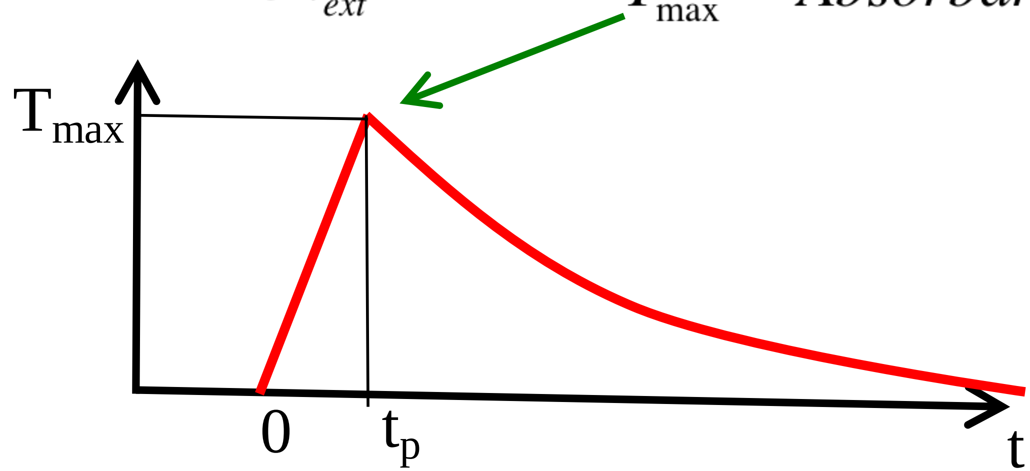
Temperature behavior of the sphere (a << ⎣)

$$T = \frac{T_{\max}}{t_p} t \qquad when \quad 0 \le t \le t_p$$

$$T = T_{\max} e^{-\frac{(t - t_p)}{\tau_{relax}}} \qquad when \quad t_p \le t$$

with $T_{\max} = \frac{P_{abs} t_p}{\rho_{sph} C_{sph} V}$ and $\tau_{relax} = \frac{\rho_{sph} C_{sph}}{3k_{ext}} a^2$

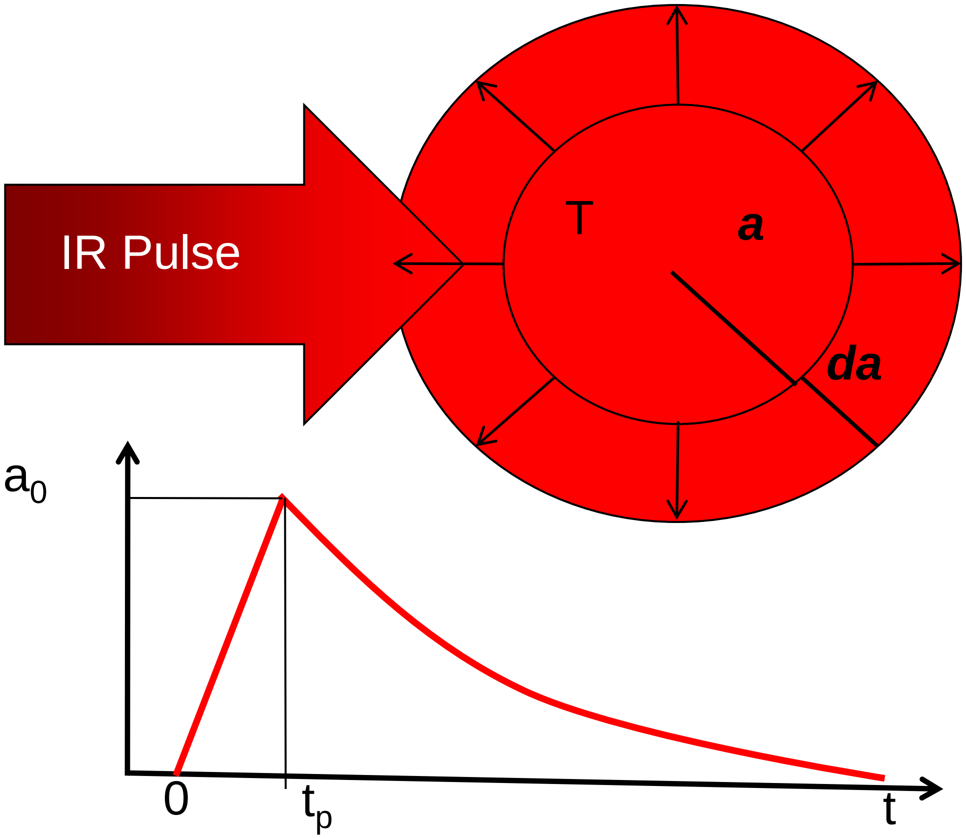
$T_{\max} \propto Absorbance$



Only for t_p << |$_{relax}$

Photoacoustic effect and spectroscopy

Thermoelastic effect



$$\frac{da(t)}{a} = \frac{1+\nu}{1-\nu}\frac{\alpha_{sph}}{3}T(t)$$

α_{sph} thermal expansion coefficient

ν Poisson coefficient

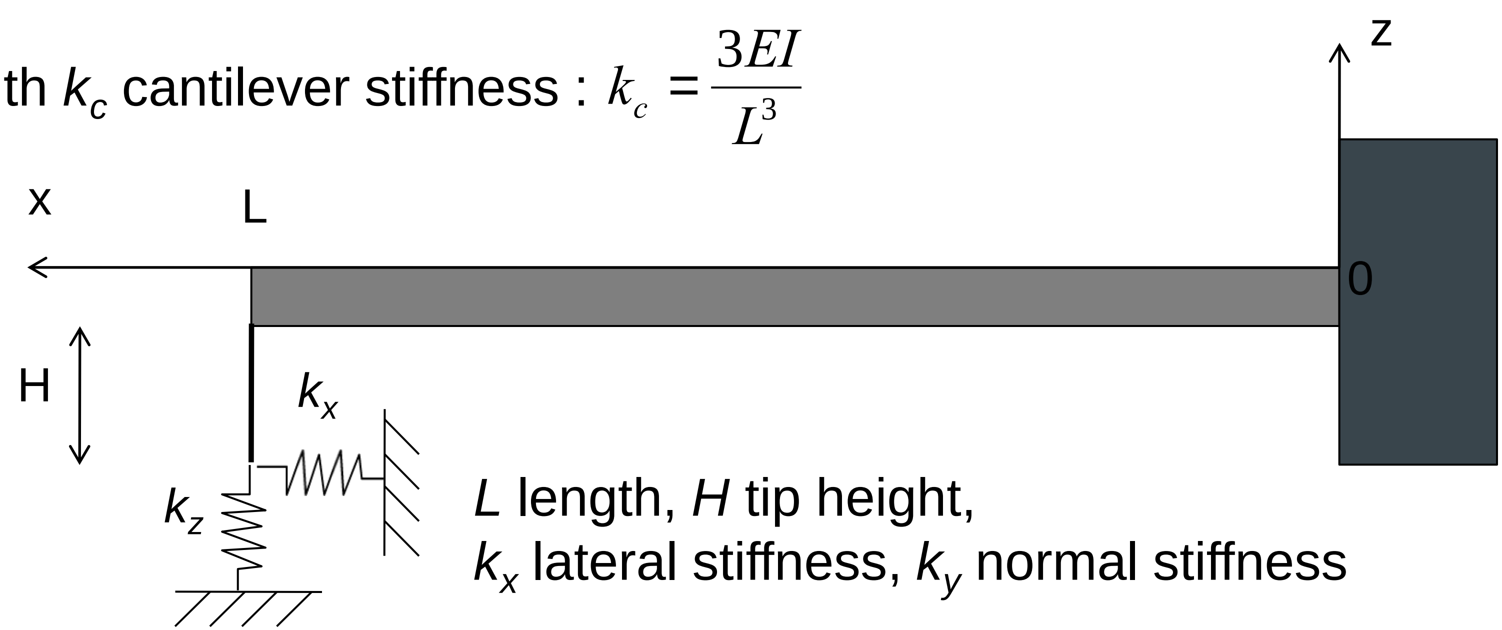
$$a_0 = \frac{1+\nu}{1-\nu}\frac{a}{3}\alpha_{sph}T_{\max} = \frac{1+\nu}{1-\nu}\frac{a\alpha_{sph}P_{abs}t_p}{3\rho_{sph}C_{sph}V} \propto Absorbance$$

Motion equation of the cantilever

$$EI\frac{\partial^4 z}{\partial x^4}+\rho A\frac{\partial^2 z}{\partial t^2}+\kappa\frac{\partial z}{\partial t}=0$$

E Young modulus, *I* inertial momentum, ρ density, *A* section, κ Cantilever damping

with k_c cantilever stiffness : $k_c = \frac{3EI}{L^3}$



L length, *H* tip height,
k_x lateral stiffness, k_y normal stiffness

$k_z >> k_c$ **NO indentation**

AFM-IR, a new tool for nanoscale IR spectroscopy

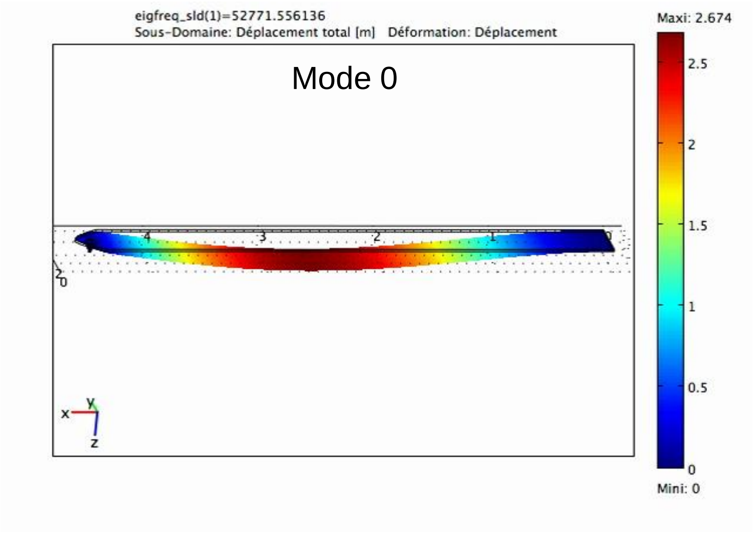
Eigenvalues equation :

$$-1 + \cos X \cosh X - UX(\sin X \cosh X - \cos X \sinh X) = 0$$

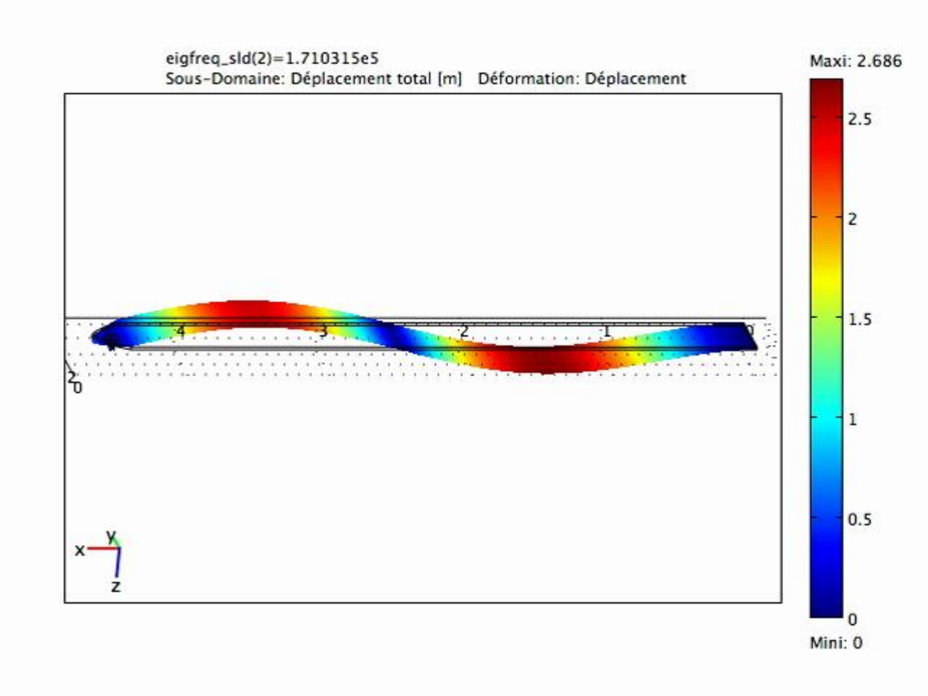
with $$U = \frac{k_c L^2}{3 k_x H^2}, X = bL$$

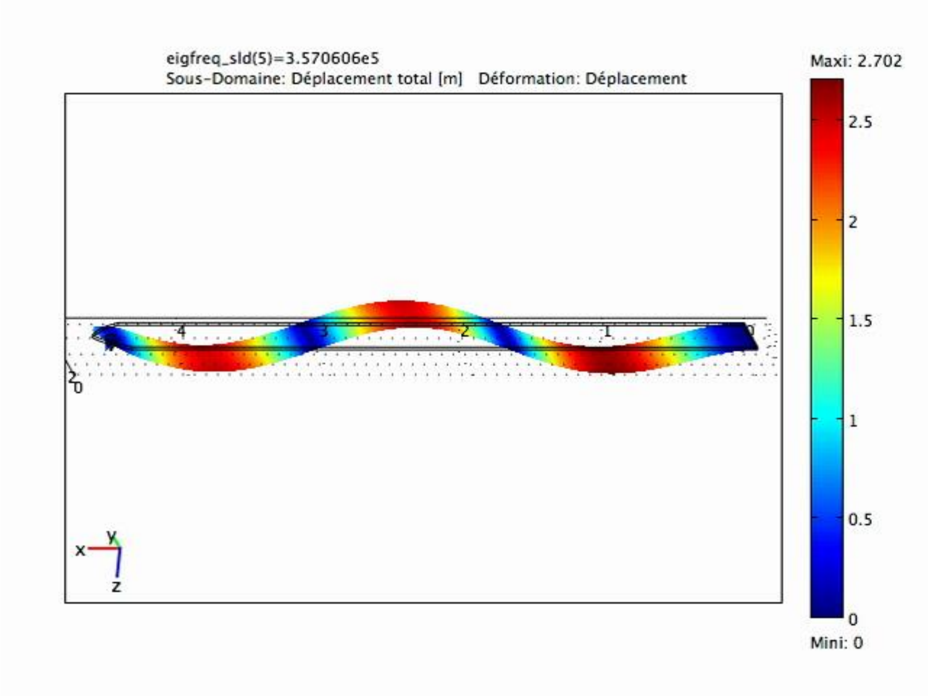
Si Cantilever in contact

k_x	0 (slipping)	∞ (pinned)
Mode	$X_n=\beta_n L$	$X_n=\beta_n L$
0	3.92662	4.73004
1	7.06858	7.8532
2	10.3518	14.1372



AFM-IR, a new tool for nanoscale IR spectroscopy

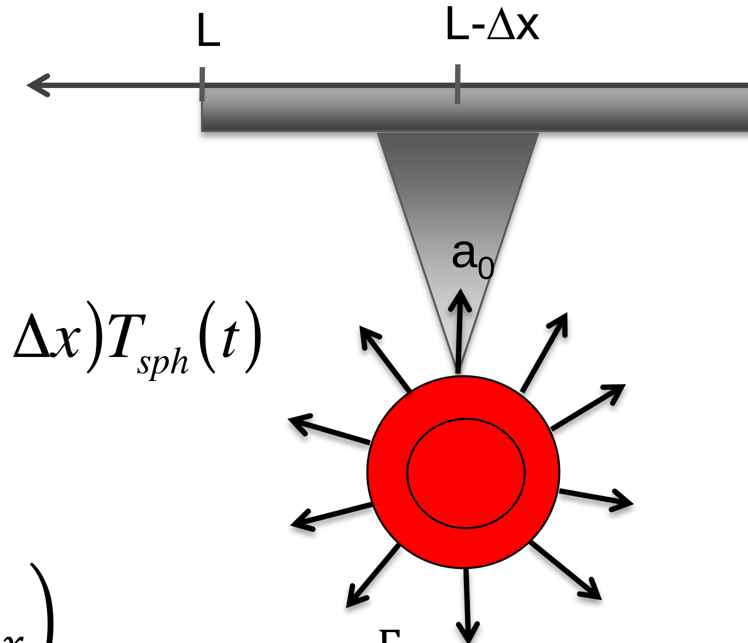




Detection by AFM

Motion equation with external excitation

$$EI\frac{\partial^4 z}{\partial x^4} + \rho A\frac{\partial^2 z}{\partial t^2} + k\frac{\partial z}{\partial t} = S(x,t)$$



with $S(x,t)$ external excitation

<u>Excitation expression for a photothermal expansion :</u>

$$S(x,t) = \delta(x - L + \Delta x)F(t) = B\delta(x - L + \Delta x)T_{sph}(t)$$

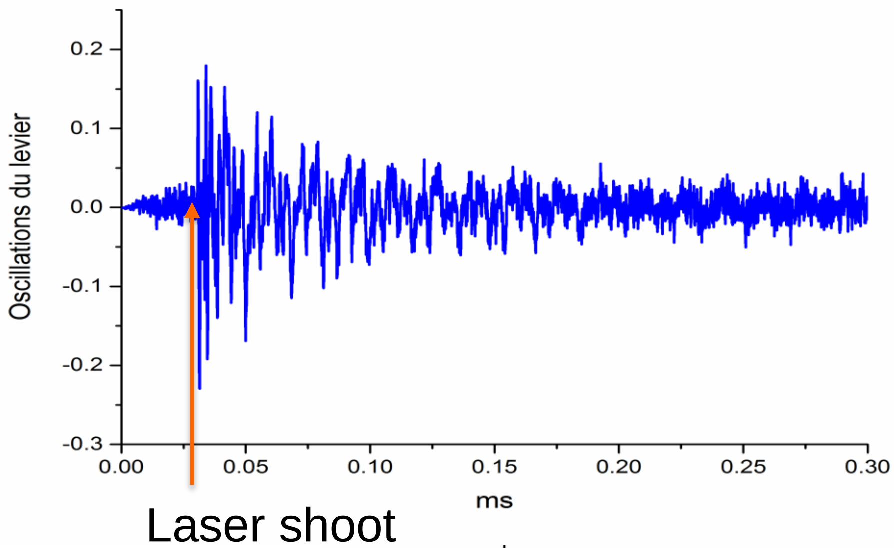
<u>Solution expression of the cantilever motion :</u>

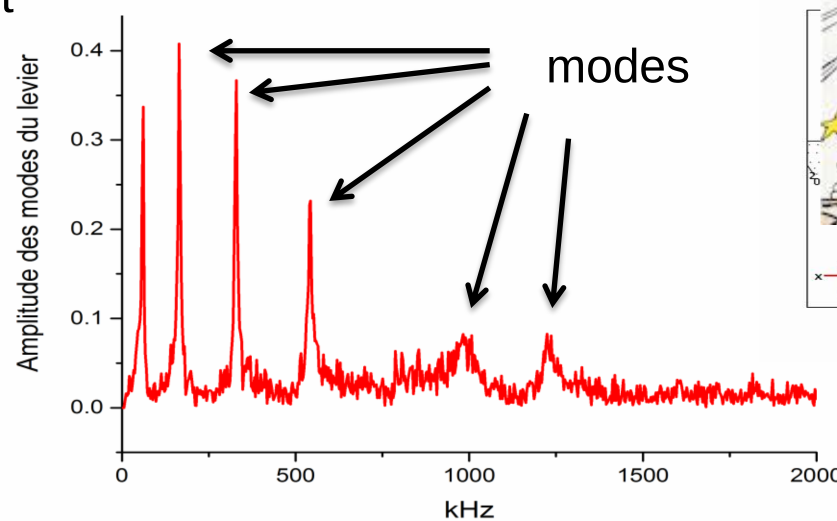
$$Z(t) = \sum_n \frac{Kk_z D\delta_x}{\rho SL}\left(\frac{\partial g_n}{\partial x}\bigg|_{x=L}\right)^2 \frac{\left(\frac{t_p}{2} + \tau_{relax}\right)}{\omega_n} \sin(\omega_n t)\, e^{-\frac{\Gamma}{2}t}\, a_0$$

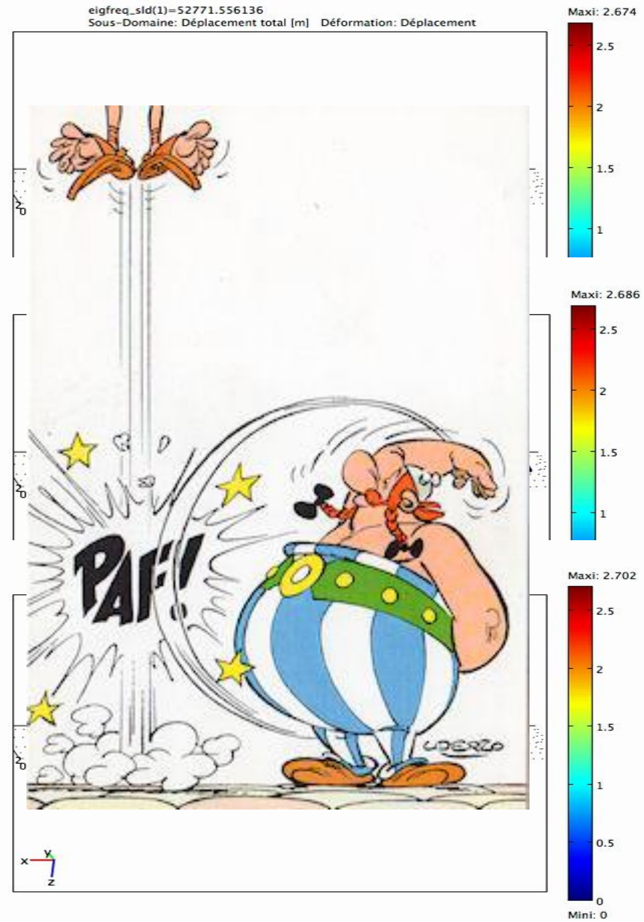
$$Z(t) \propto a_0 \propto Absorbance$$

AFM-IR Technique

Classic measurement

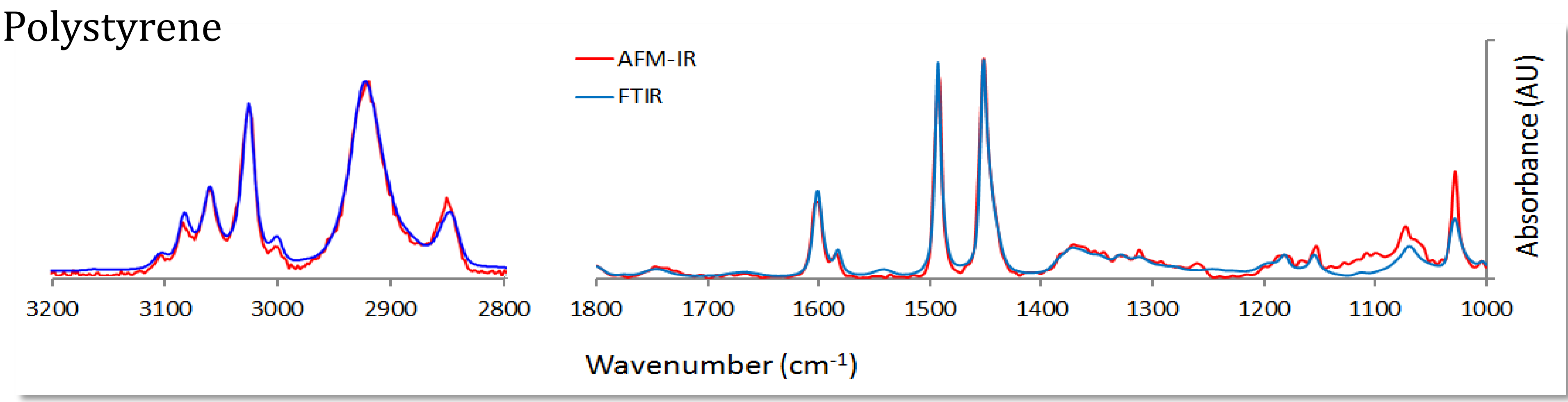






AFM-IR and spectroscopy

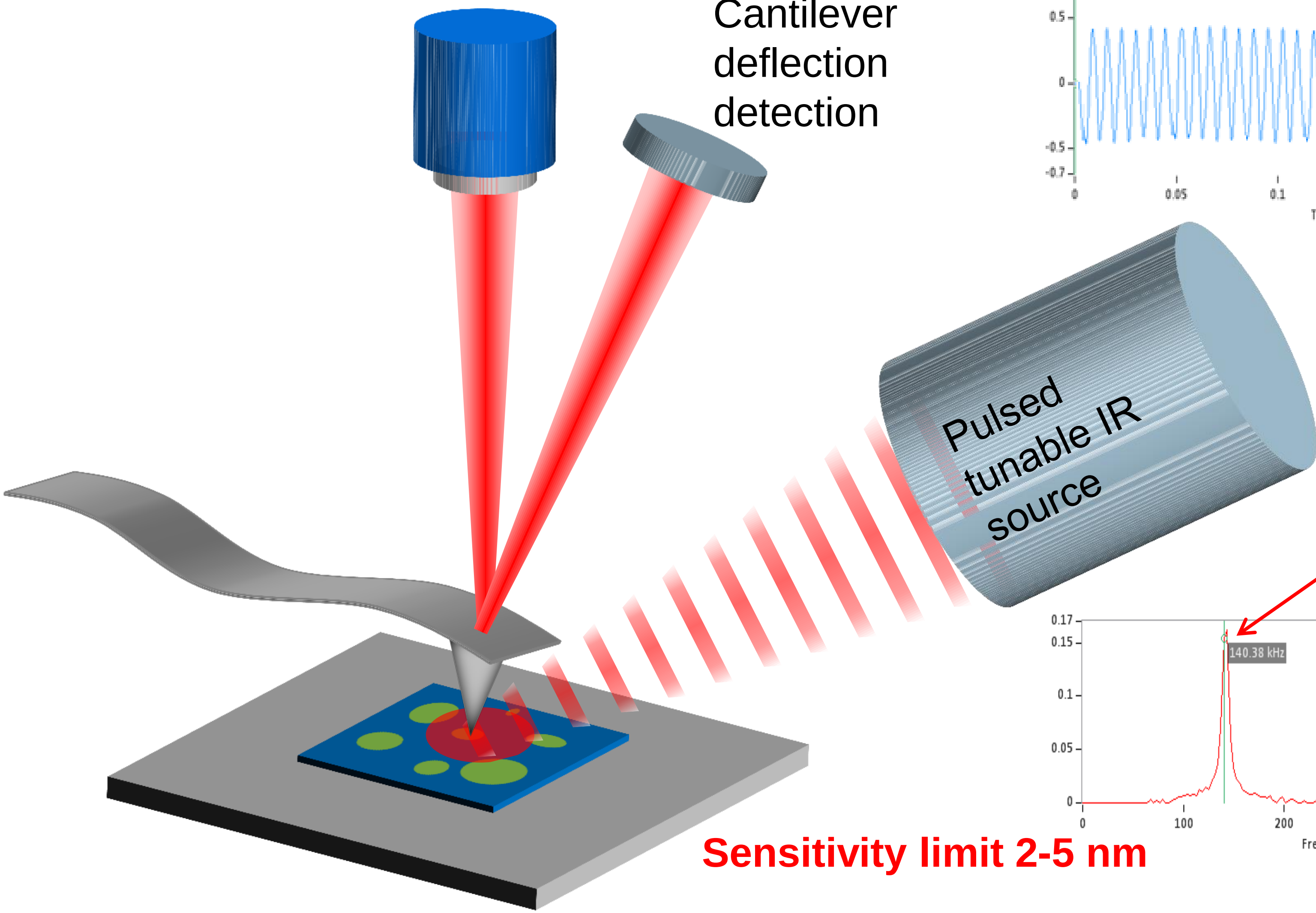
Photothermal approach gives a direct measurement of the Imaginary part of the index

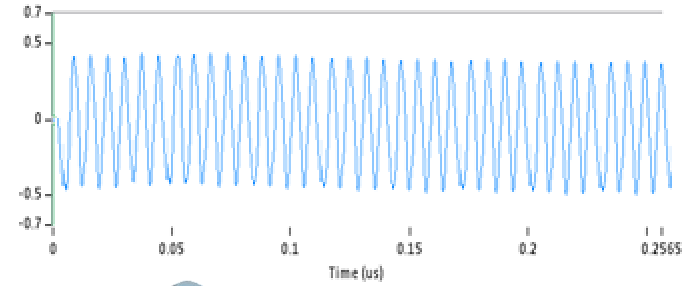


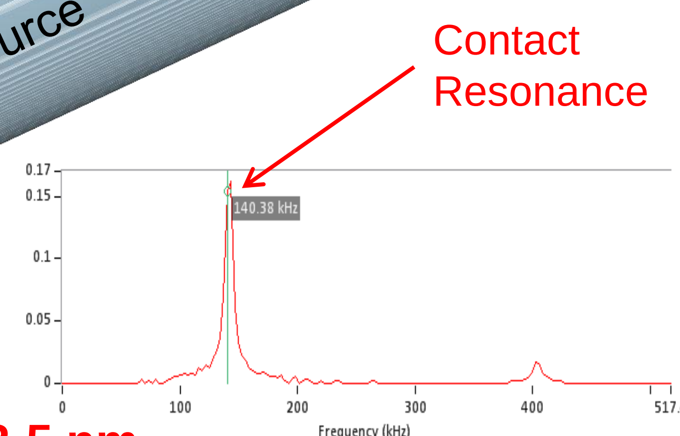
Resonance Enhanced mode

Resonance enhanced AFM-IR

- **Demonstrated by Pr. Belkin team in 2011 (Opt. Express)**



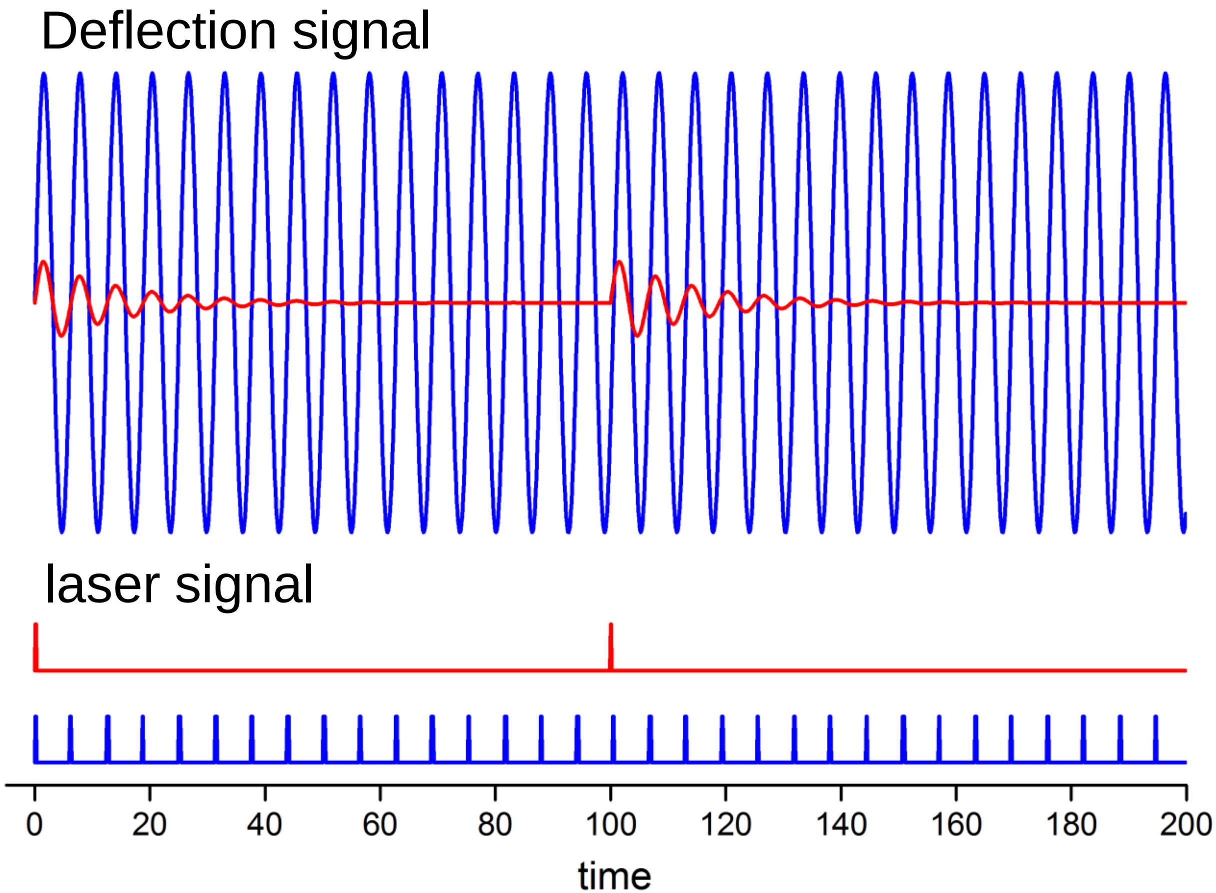




Sensitivity limit 2-5 nm

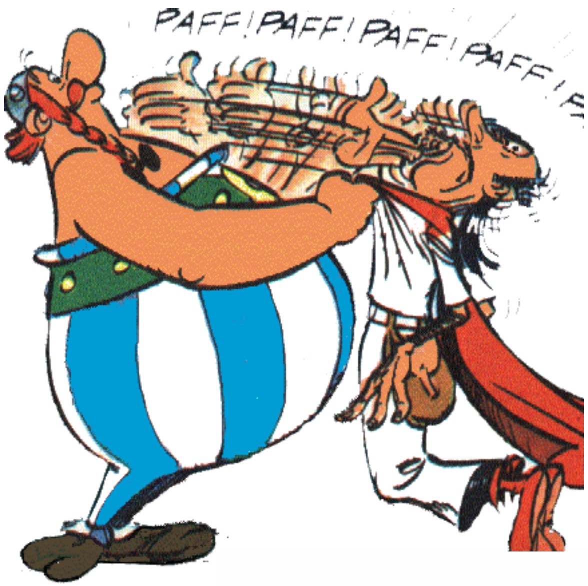
Resonance enhanced AFM-IR

Resonance Enhanced Mode

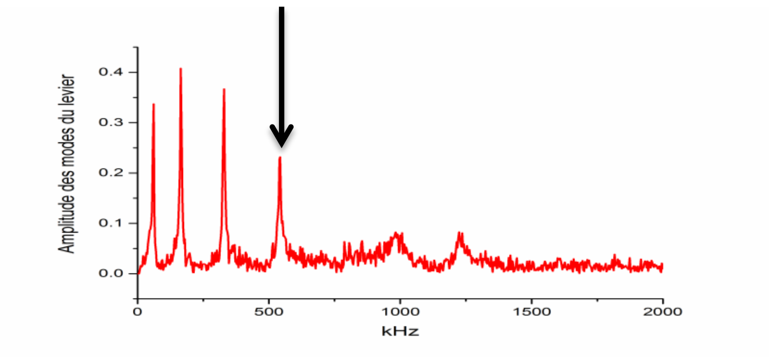


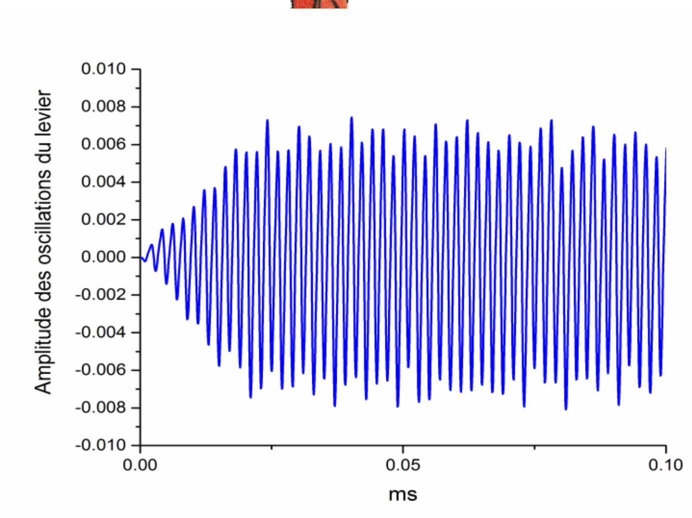
Resonance enhanced AFM-IR

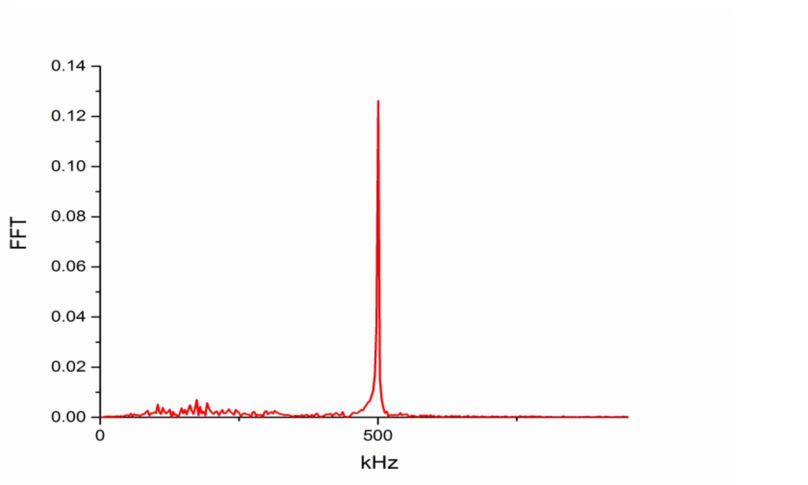
Forced resonance makes AFM-IR more sensitive



Laser repetition rate







Resonance enhanced AFM-IR

Deflection expression for 1 single pulse (OPO)

$$Z(t) = \sum_{n} \frac{K k_z D \delta_x}{\rho S L} \left(\frac{\partial g_n}{\partial x} \bigg|_{x=L} \right)^2 \frac{\left(\frac{t_p}{2} + \tau_{relax} \right)}{\omega_n} \sin(\omega_n t)\, e^{-\frac{\Gamma}{2} t}\, a_0$$

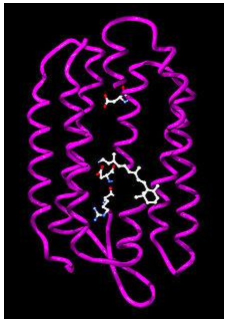
Deflection expression when the repetition rate = contact resonance (QCL)

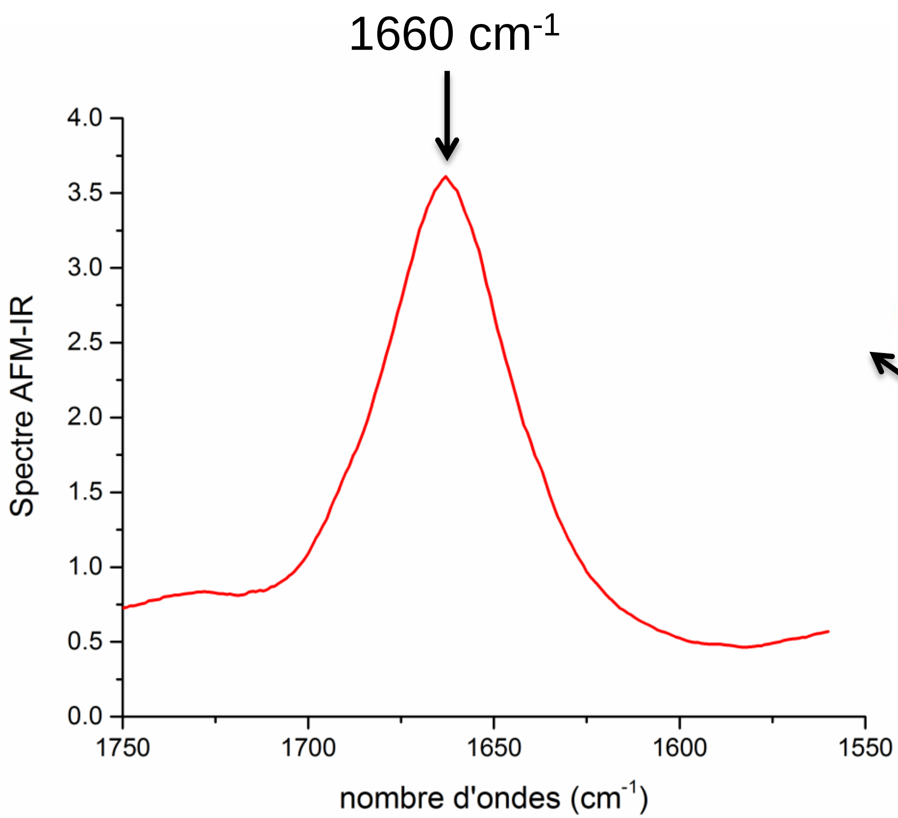
$$Z(t) = \frac{K k_z D \delta_x}{\rho S L} \left(\frac{\partial g_n}{\partial x} \bigg|_{x=L} \right)^2 \frac{\left(\frac{t_p}{2} + \tau_{relax} \right)}{\omega_n} \frac{Q_n}{2\pi} \sin(\omega_n t)\, a_0$$

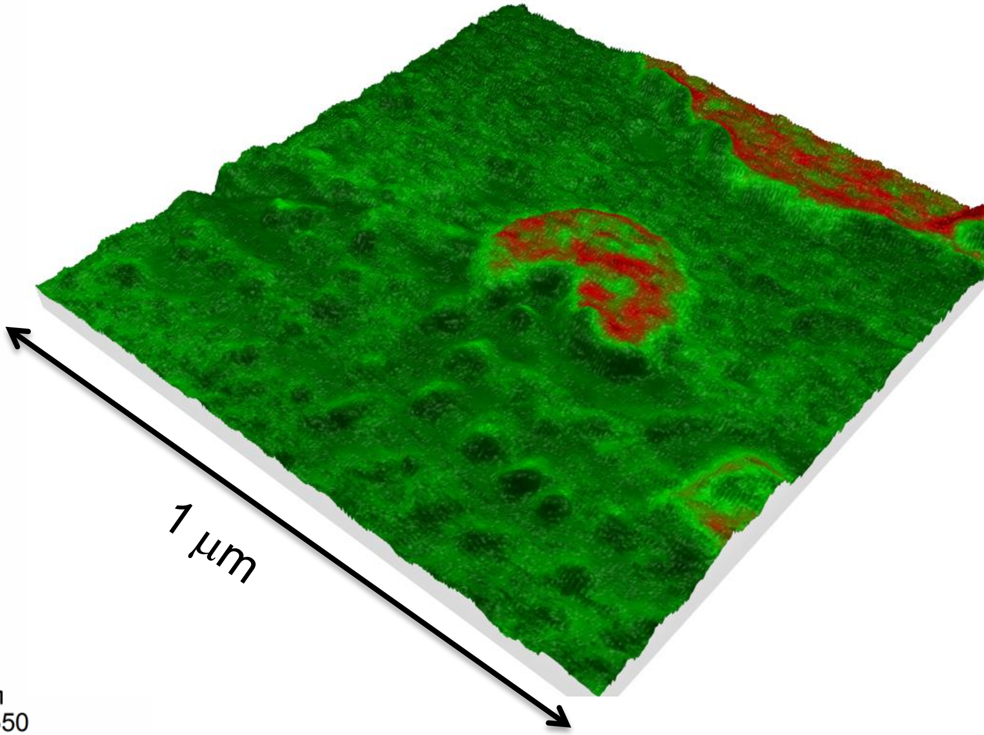
Amplitude(Z) µ thermal expansion(a_0) µ absorbance

Improving the sensitivity and resolution…

Bacteriorhodopsin protein
Detected inside a purple membrane



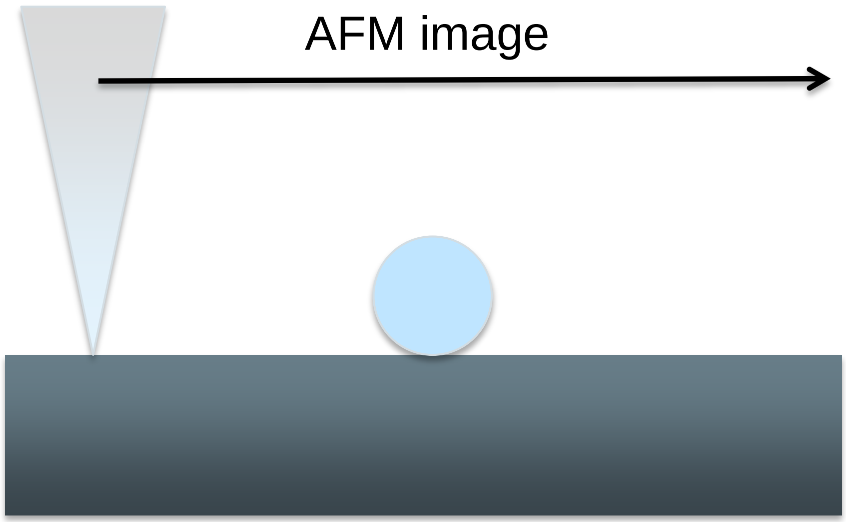




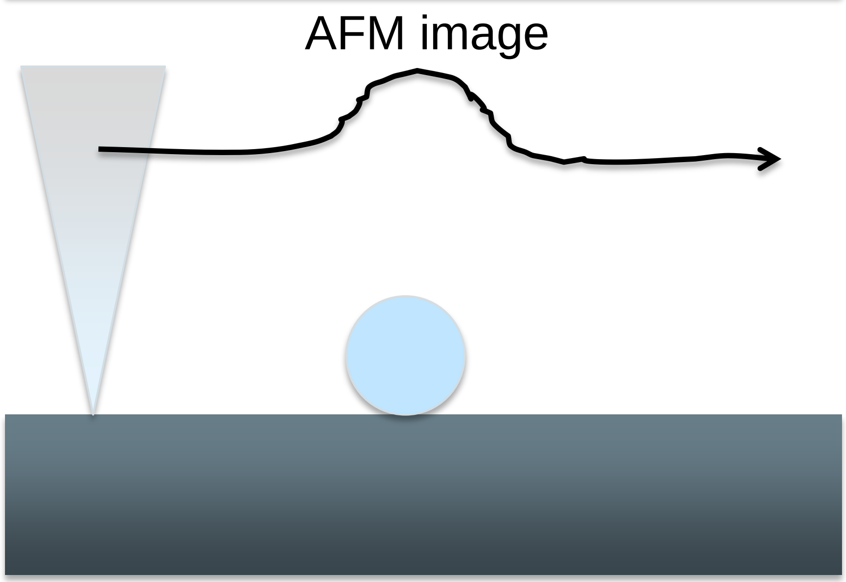
Tapping AFM-IR

IMAGING MODE IN AFM

CONTACT MODE



TAPPING MODE

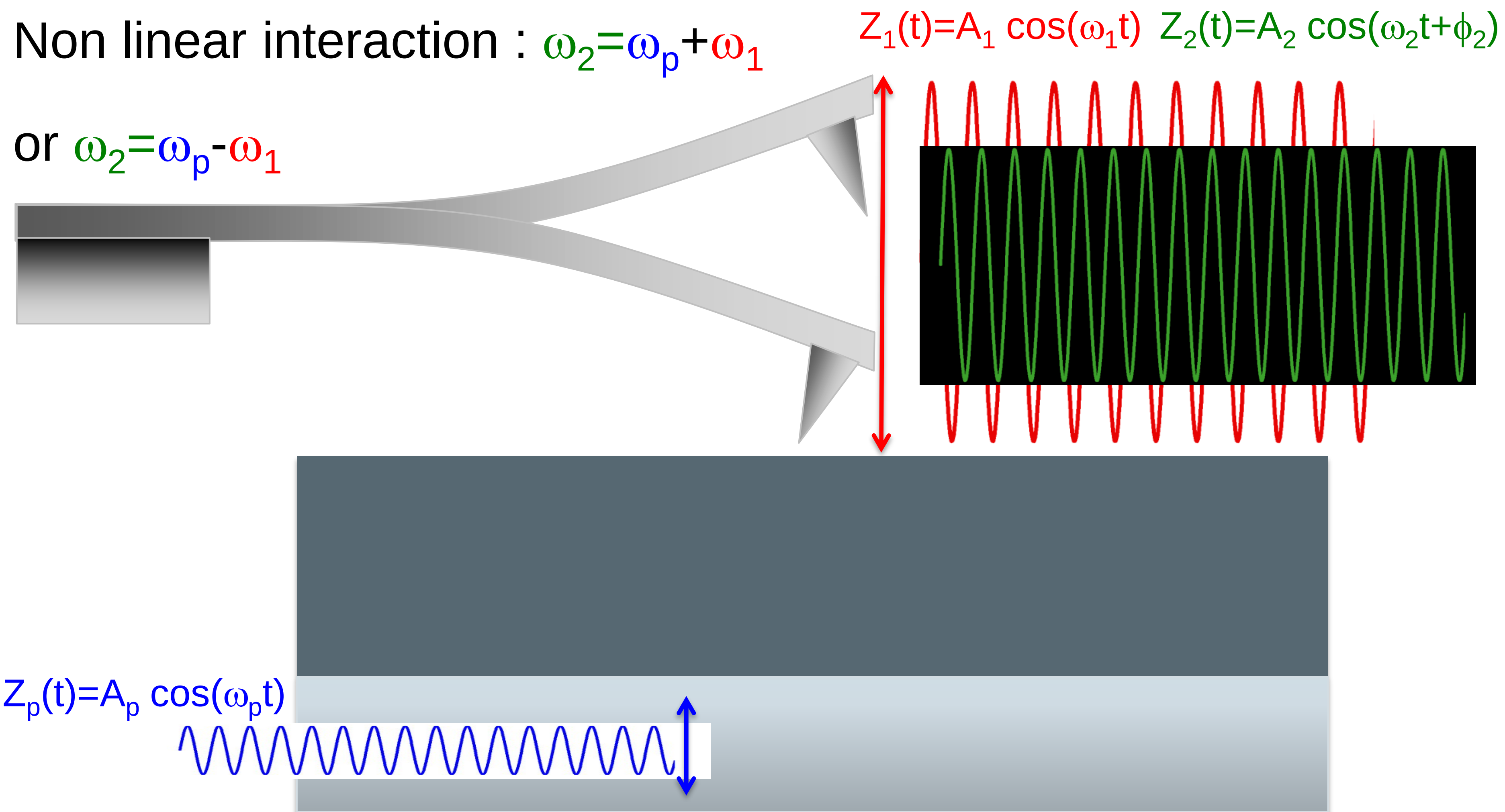


Heterodyne force detection

M.T. Cuberes et al J.Phys.D:Appl.Phys. 2000

Non linear interaction : $\omega_2=\omega_p+\omega_1$

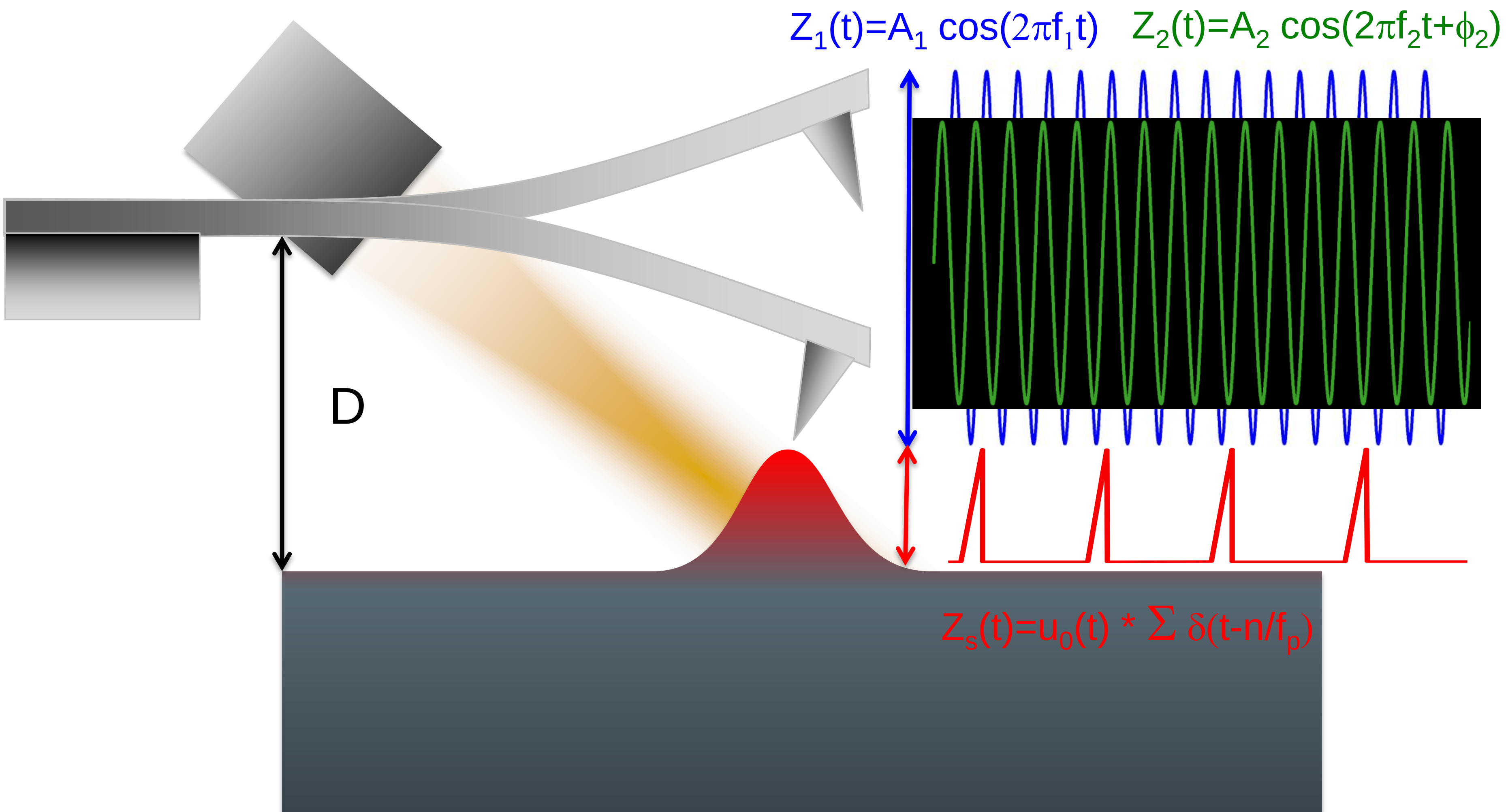
or $\omega_2=\omega_p-\omega_1$



Tapping AFM-IR configuration

f_1= Driving frequency of the tapping mode
f_p = repetition rate of the QCL laser

Non linear interaction : $f_2=f_1+f_p$



Tapping AFM-IR

Motion equation of the second mode f2 :

$$\ddot{z}_2 + \Gamma \dot{z}_2 + \left(2\pi f_2\right)^2 z_2 = \frac{F_{ts}(t)}{m^*}$$

$$F_{ts}(t) = k_s\left(A_1\cos(\omega_1 t) - u_0(t)\right) + c_s\left(A_1\cos(\omega_1 t) - D - u_0(t)\right)^2 + \ldots$$

f_1 f_p $2f_1$ $2f_p$

$$F_{ts}(t) = -2c_s\left(A_1\cos(2\pi f_1 t)\Pi(\tau) * \sum_m \delta(t - m/f_1)\right)\left(u_0(t) * \sum_n \delta(t - n/f_p)\right)$$

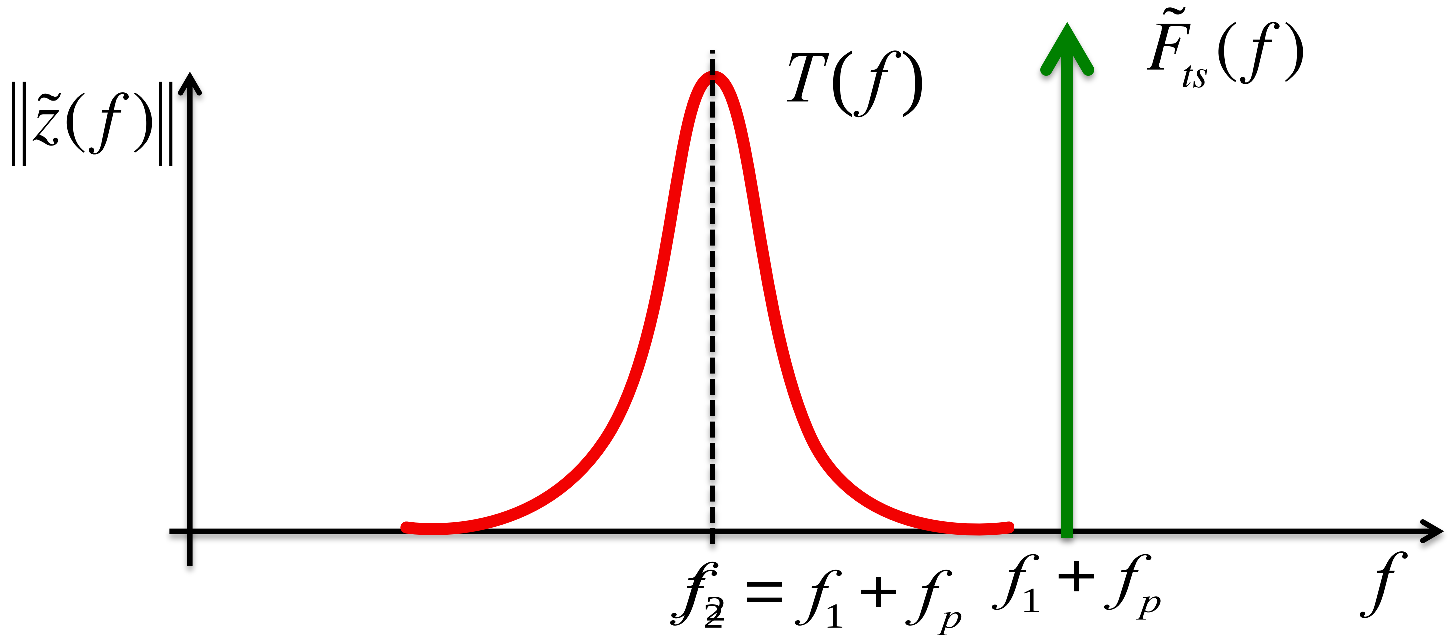
τ is the time of contact driven by the f_1

Tapping AFM-IR

Fourier Transform of equation :

$$\tilde{z}_2(f) = \frac{T(f)\tilde{F}_{ts}(f)}{m^*}$$

$$\tilde{F}_{ts}(f) = -\left(\chi_{ts}\pi A_1 a_0 t_p \tau\omega_1\omega_p\right)\delta(\omega-(\omega_1+\omega_p))$$



Tapping AFM-IR

Amplitude of the second mode f_2

$$\left\|\tilde{z}_2\right\| = \frac{\chi_{ts} Arc\cos(D / A_1)}{2} t_p \frac{(f_2 - f_1)}{m^* f_2^2} Q_2 (A_1 - D) a_0$$

Non linear elasticity contact coefficient

Laser pulse

Setpoint

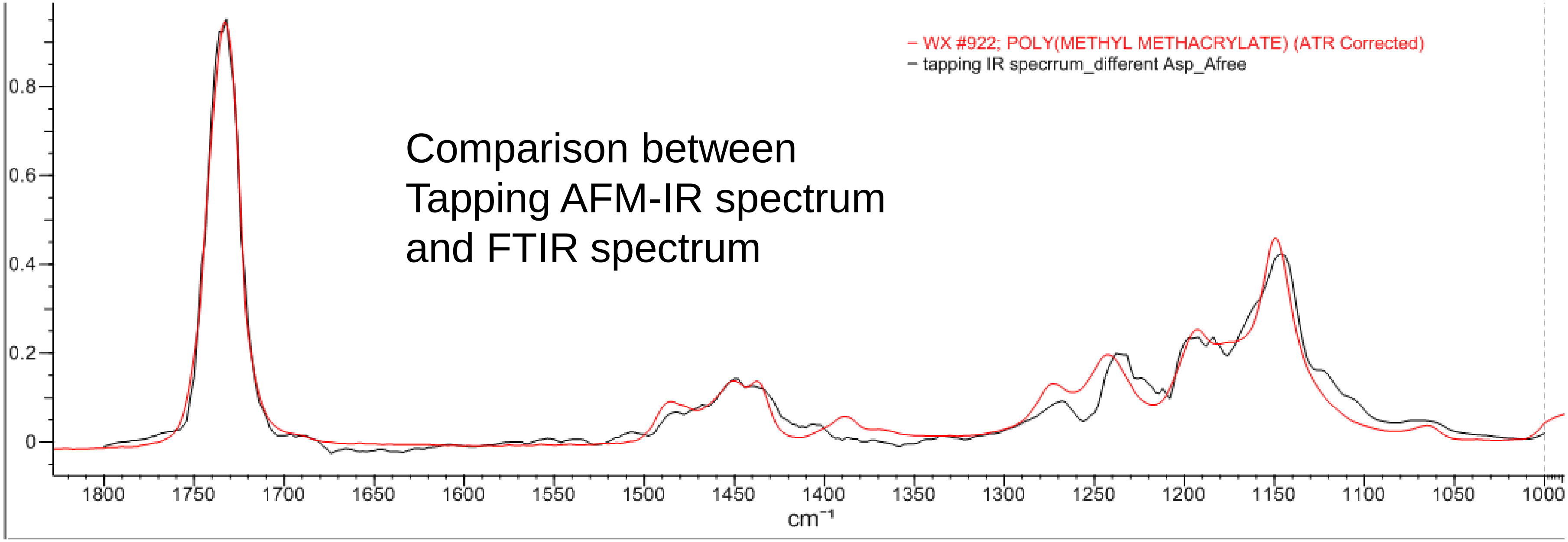
Driving amplitude

Cantilever parameters

Thermal expansion
α Absorbance

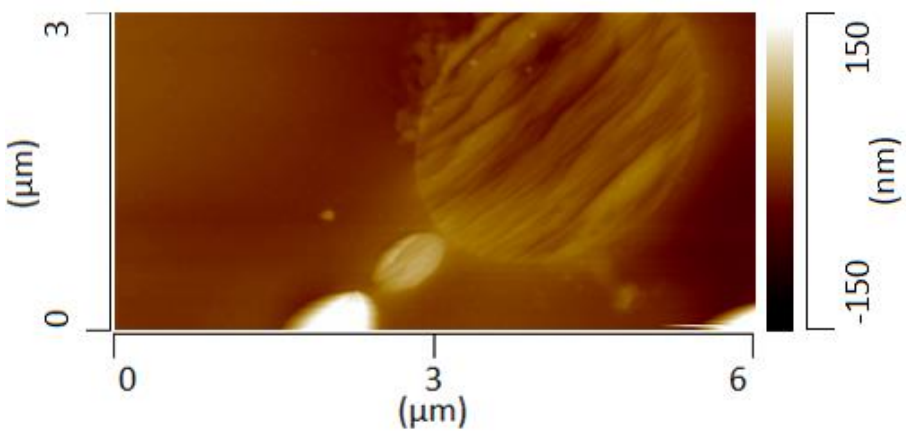
Tapping AFM-IR signal is proportional to **absorbance**

Tapping AFM-IR

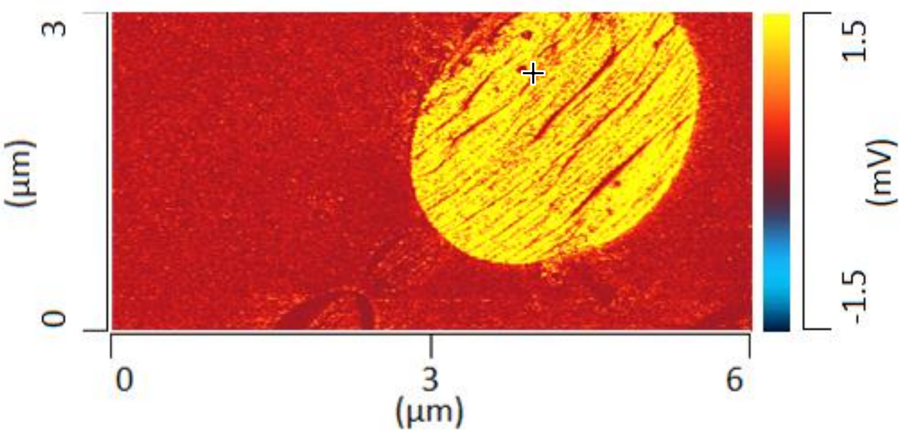


Comparison between Tapping AFM-IR spectrum and FTIR spectrum

Height



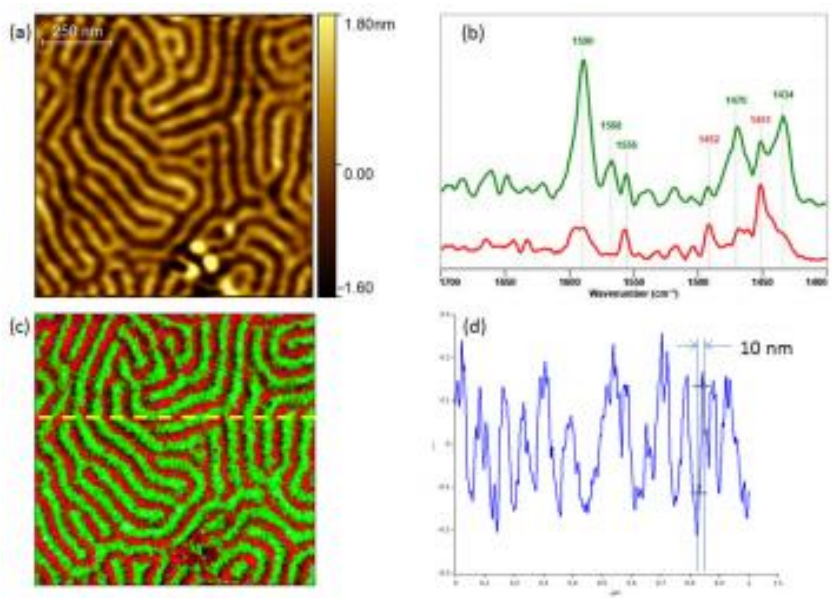
IR Image at 1730 cm^{-1}



Tapping AFM-IR

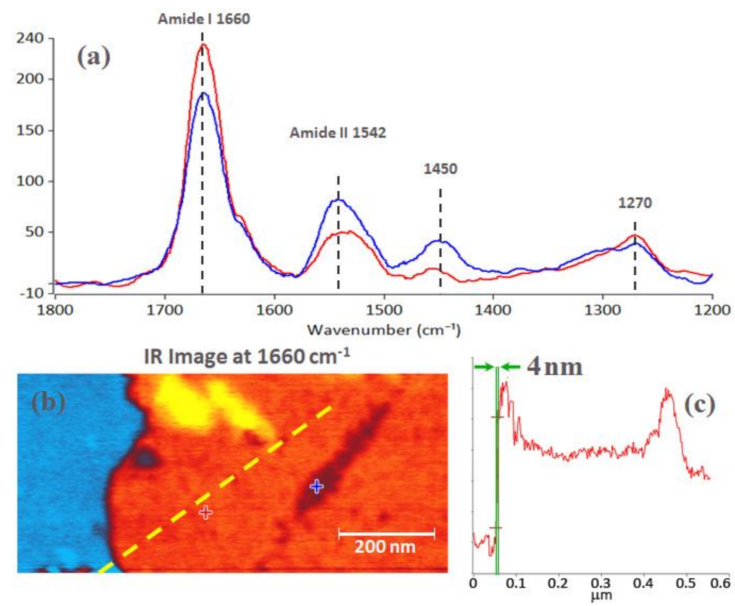
Sub-10nm chemical Imaging & Monolayer Sensitivity with Tapping AFM-IR

Block Co-polymer



Chemical characterization of PS-P2VP block co-polymer sample by Tapping AFM-IR
(a) Tapping AFM height image.
(b) Tapping AFM-IR spectra clearly identifying each chemical component.
(c) Tapping AFM-IR overlay image highlighting both components (PS@ 1492 and P2VP@ 1588).
(d) Profile cross section highlighting the achievable spatial resolution, 10 nm. Sample courtesy of Dr. Gilles Pecastaings and Antoine Segolene at University of Bordeaux

Monolayer Sensitivity

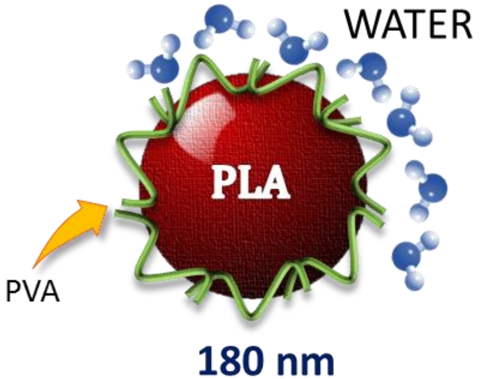


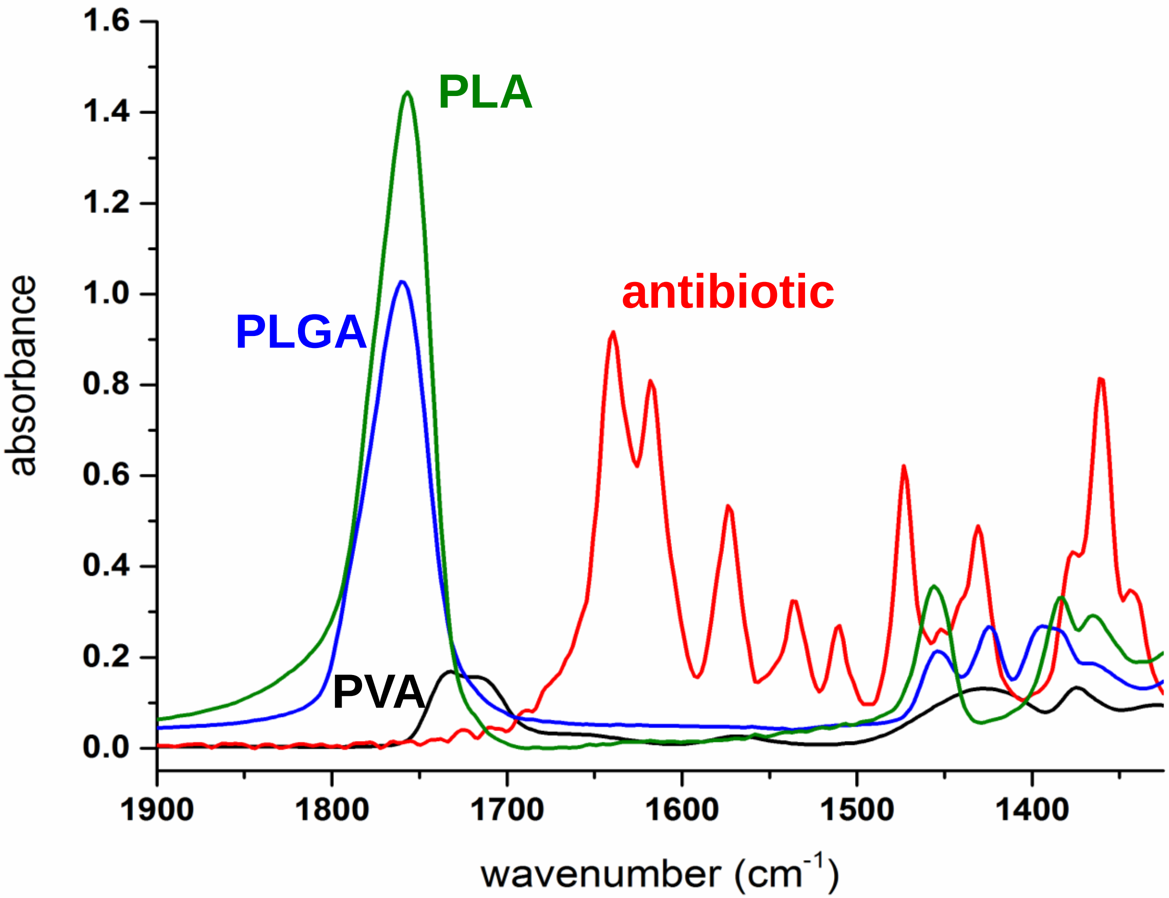
(a) AFM-IR spectra of various locations on a monolayer bacterial membrane
(b) Tapping AFM-IR collected at the amide 1 band showing variations in protein orientation due to the polarization dependent absorption of the incident light
(c) Profile cross section highlighting achieved spatial resolution, 4nm

Polymeric NPs for drug delivery

(coll. R.Gref, ISMO, U-Psud France)

FTIR spectra of products



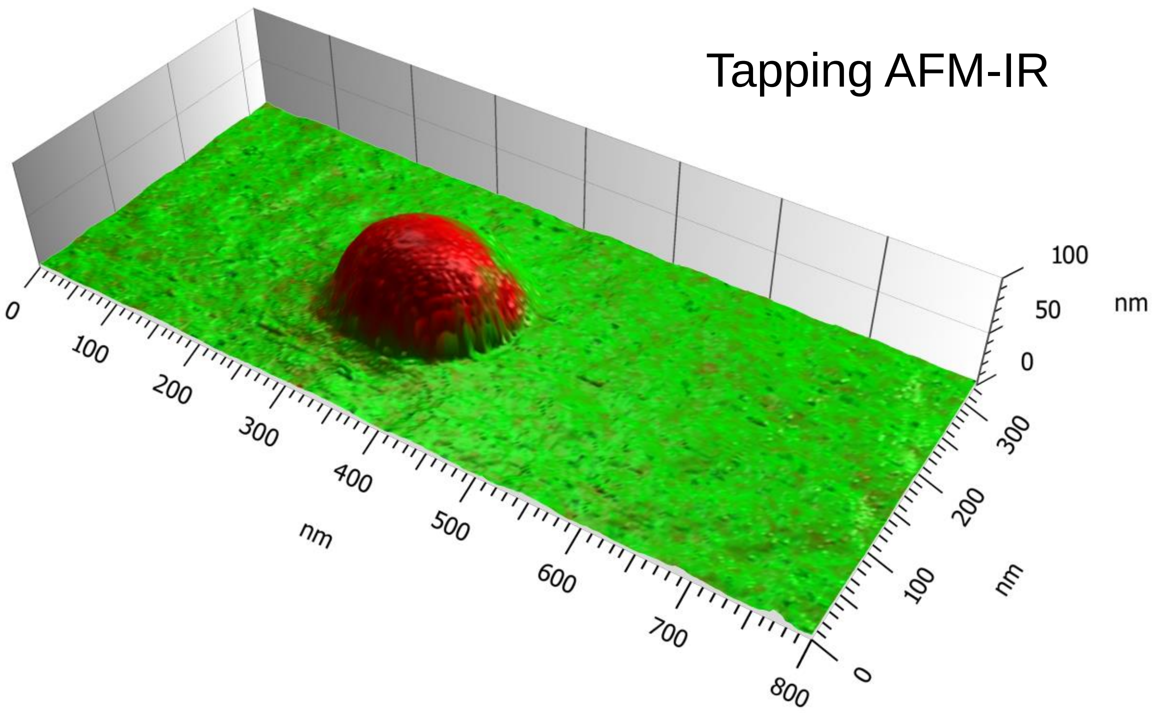


Antibiotic = pipemidic acid

Polymeric NPs for drug delivery

PLA/PVA nanoparticle

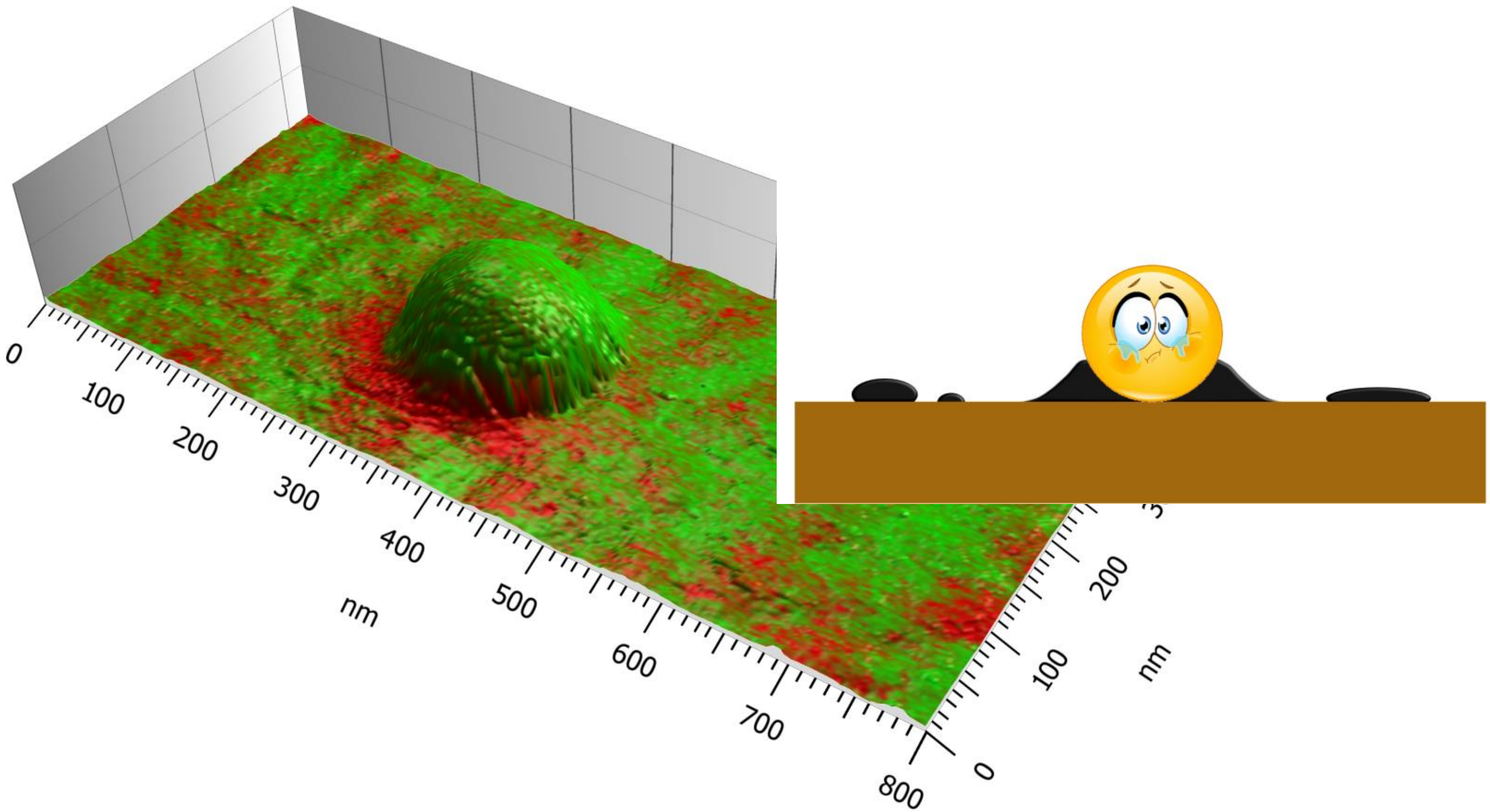
Mapping at 1760 cm^{-1} center on ester carbonyl band of PLA



Polymeric NPs for drug delivery

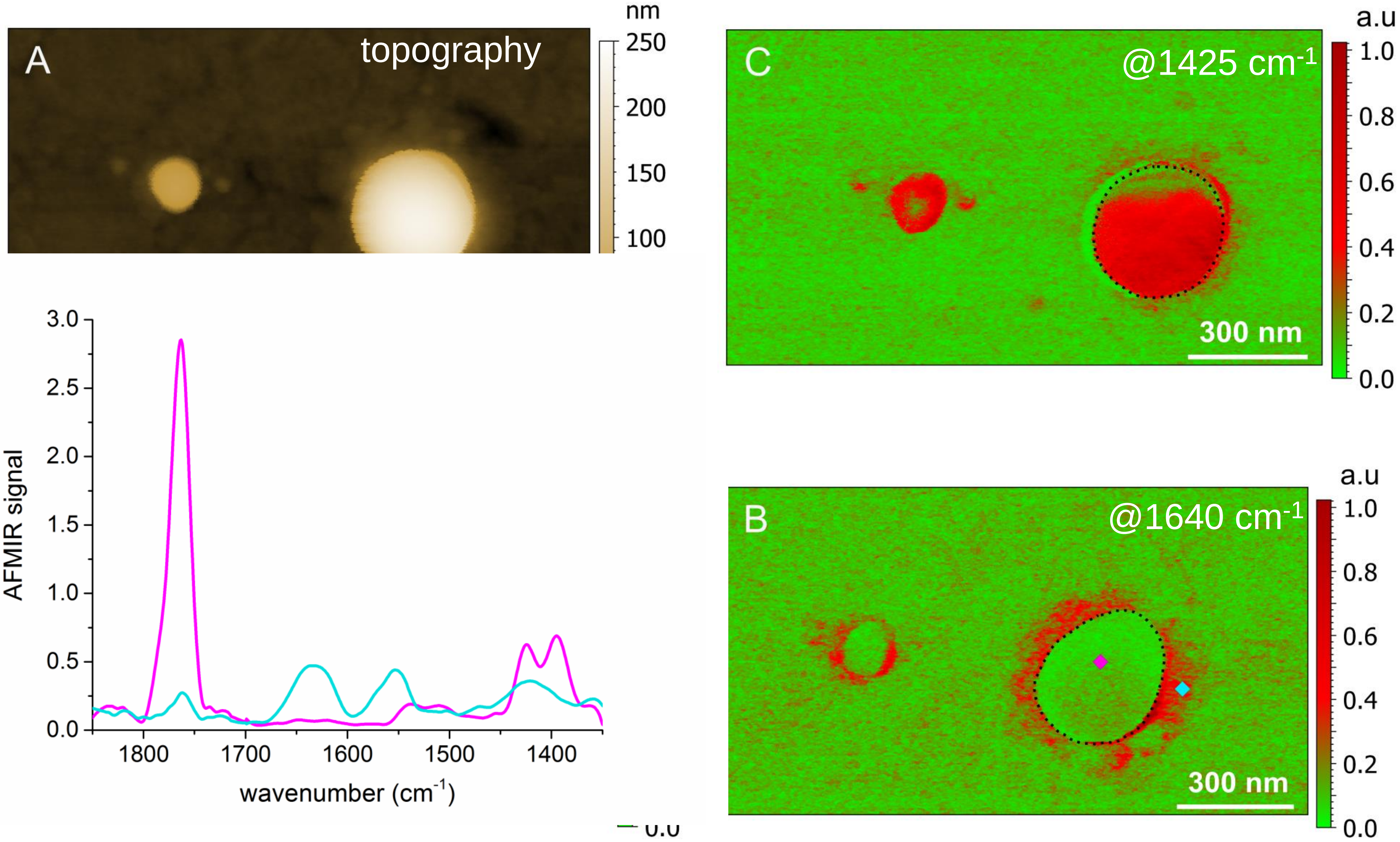
PLA/PVA nanoparticle

Mapping at 1425 cm^{-1} center on absorption band of PVA



Polymeric NPs for drug delivery

PLGA/PVA nanoparticles with antibiotic

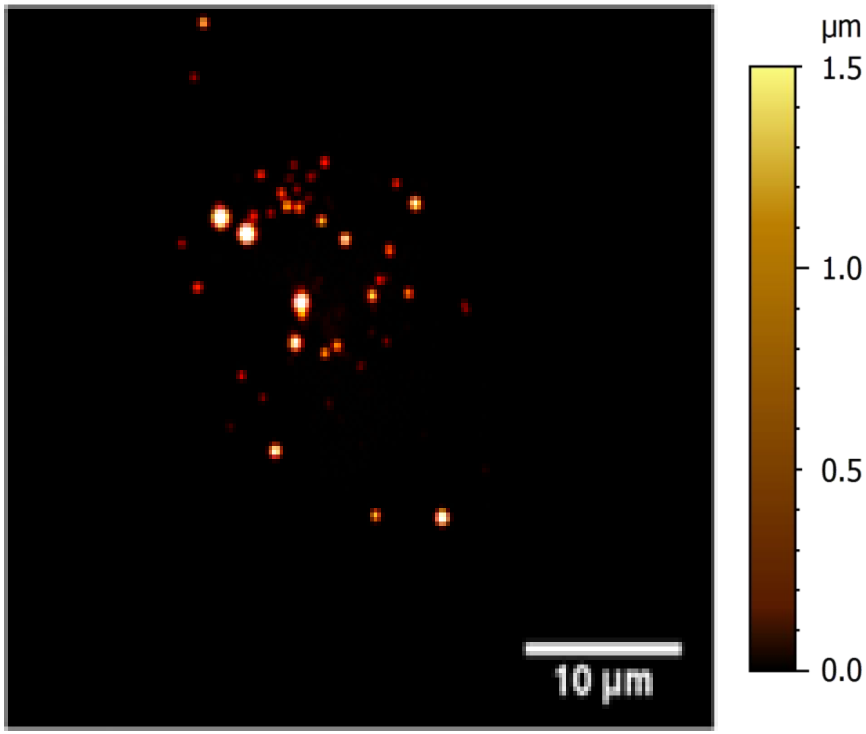


CORRELATIVE IMAGING

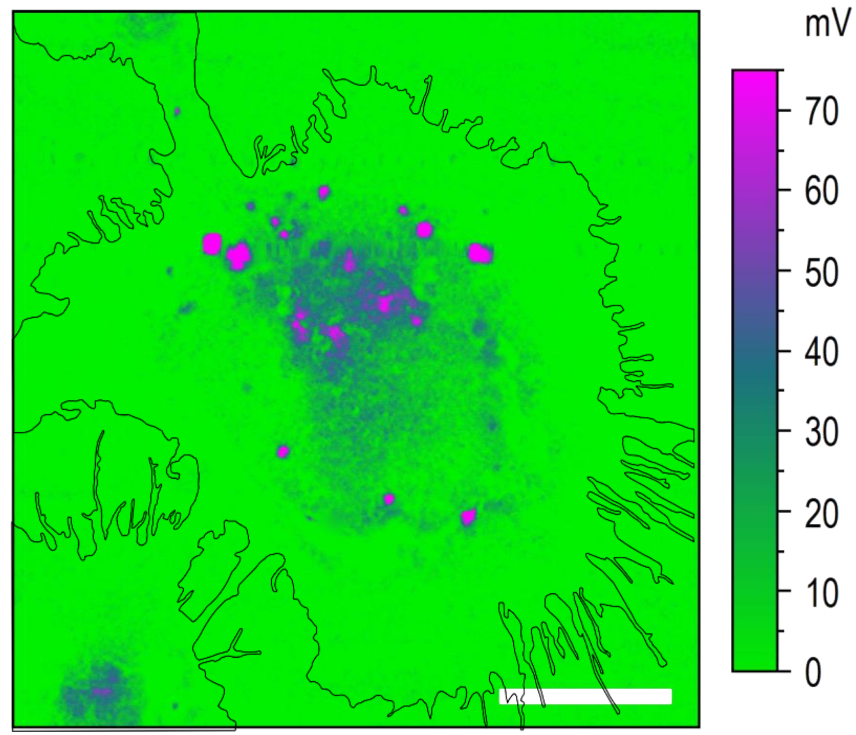
AFM-IR and Fluorescence analysis of NPs

E.Pancani et al. Part. Part. syst. Charact 2018

AFM-IR chemical mapping of fixed macrophage



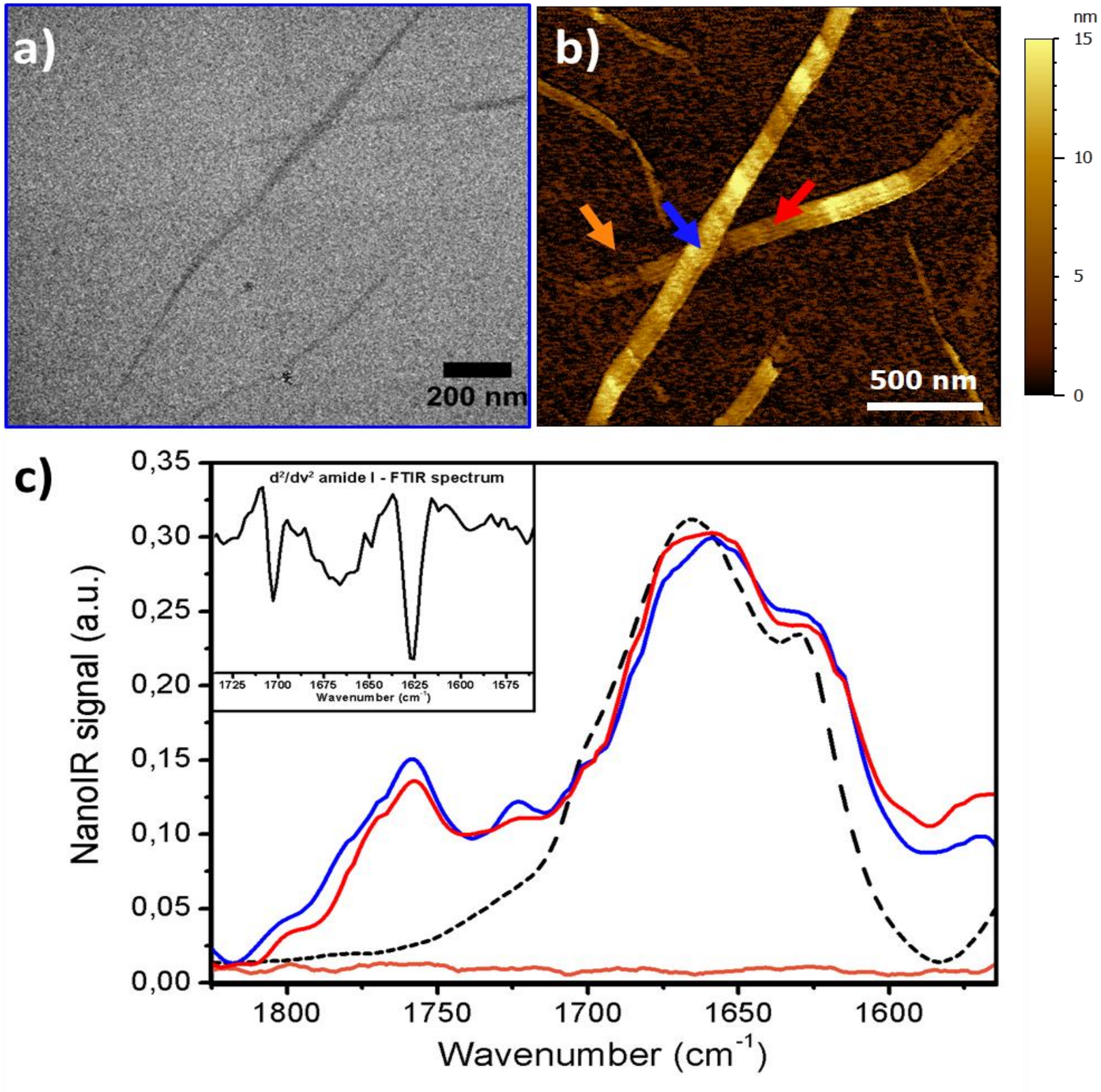
AFM topography
Fluo imaging



IR absorption at 1770cm^{-1}

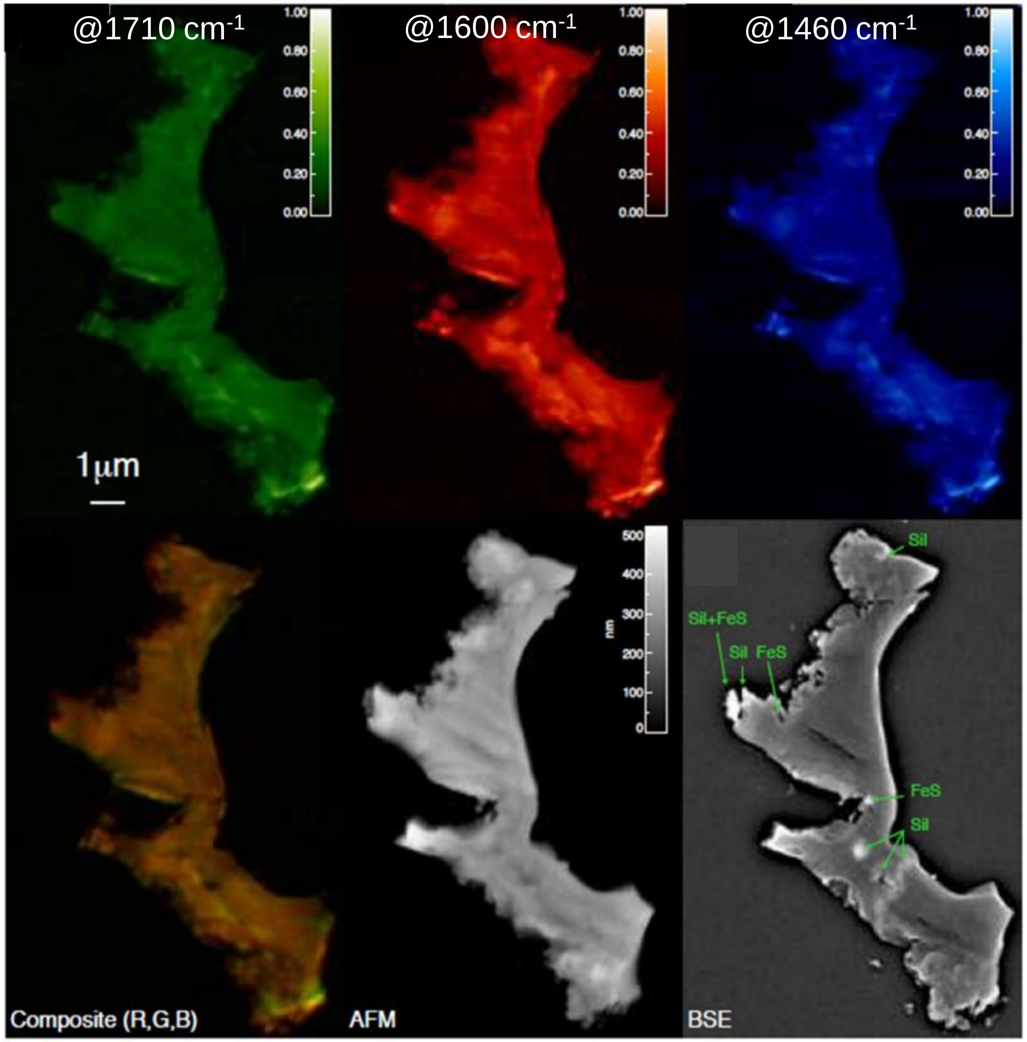
AFM-IR and TEM analysis of Hfq fibrils

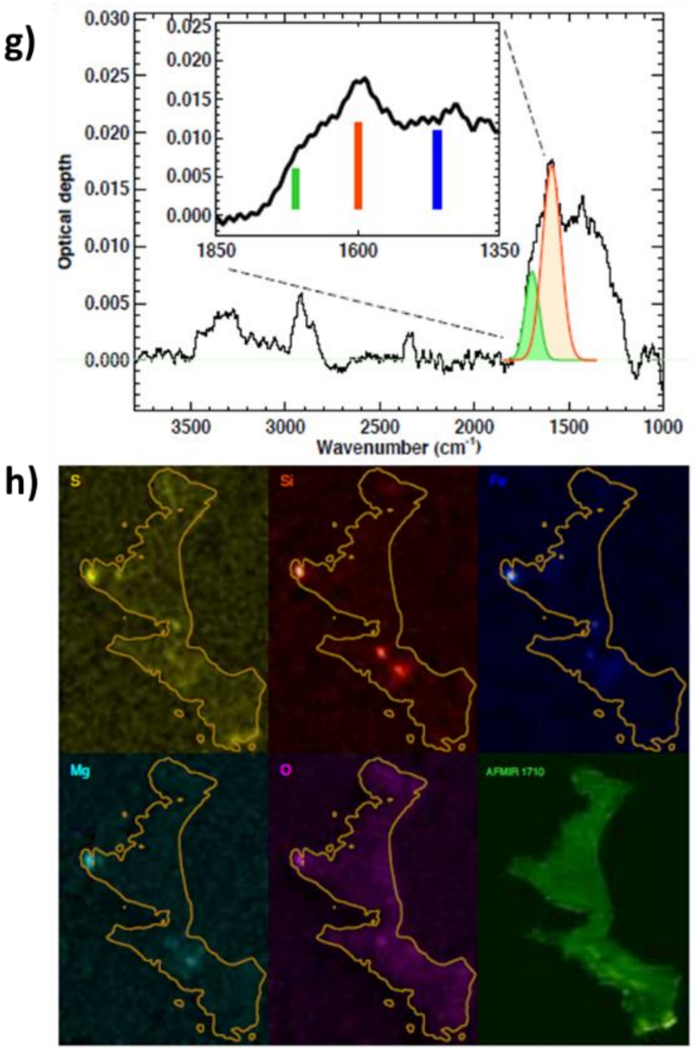
D.Partouche et al. J. Microsc. 2019



AFM-IR and SEM-EDX analysis of UCAMMs

J.Mathurin et al. A&A 2018





Conclusion

- AFM-IR is the only technique allowing to have a direct measurement of the Imaginary part of the refractive index. Leading to reliable spectra and comparable to FTIR.

- Tapping AFM-IR is a big improvement that allows to study new kind of samples (soft, non adhesive).

- Resolution expected to be better than tapping as it is a nonlinear interaction (down to 10 nm).

- Open to correlative imaging

UNIVERSITÉ PARIS SUD

Thanks to

LCP

Laboratoire de Chimie Physique

BRUKER

AFM-IR team:

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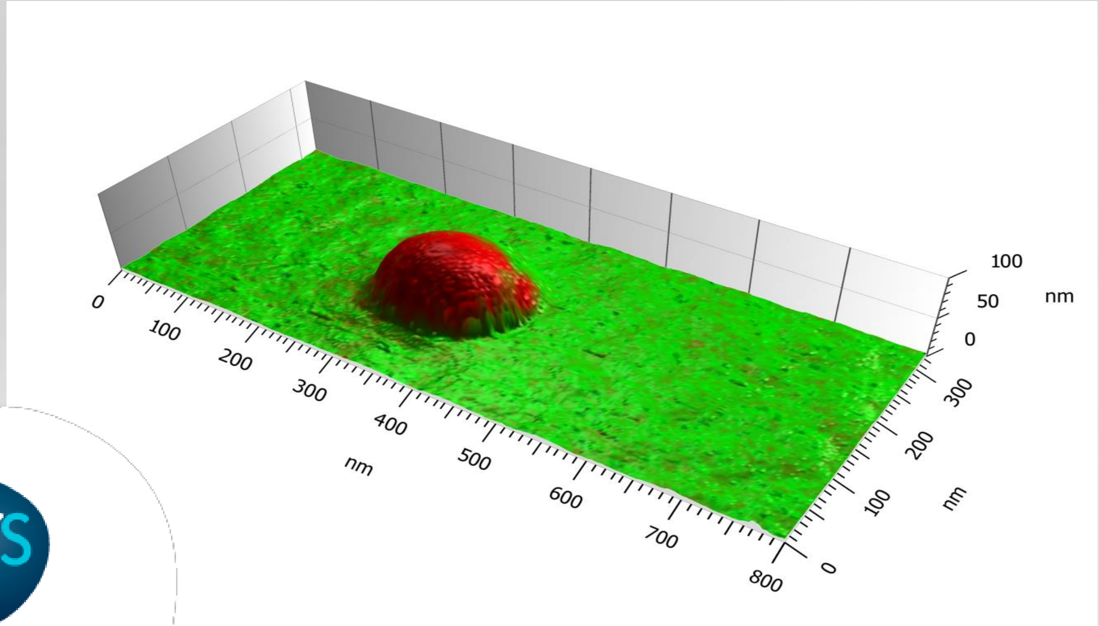
D.Bazin

J.Mathurin

J.Waytens



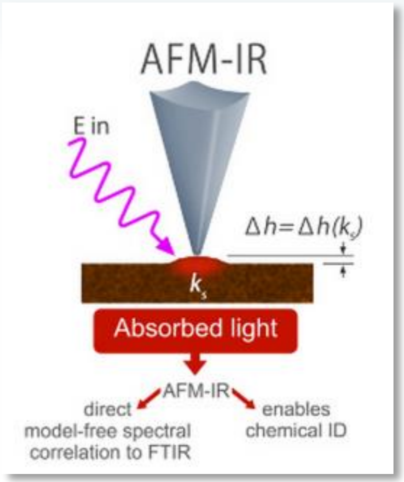
cnrs

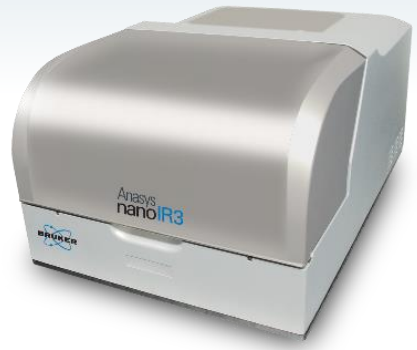
dépasser les frontières

Digital Surf

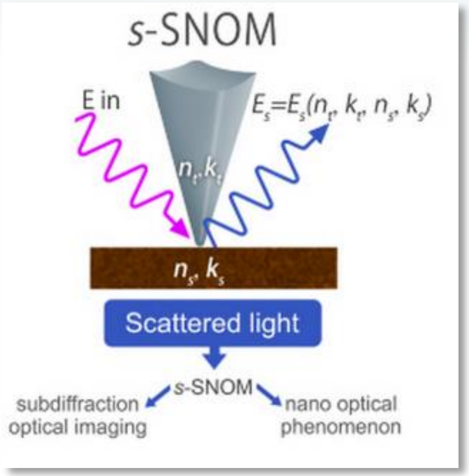
Surface Intelligence

QUESTIONS





nano**IR3-s**™
Latest Generation
nano**IR** platform with Tapping AFM-**IR** &
Scattering SNOM



www.Bruker.com/nanoIR

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