25ème Forum des microscopies à sondes locales

AFM-IR, spectroscopie et imagerie infrarouge à l'échelle nanométrique : *Principe et applications*

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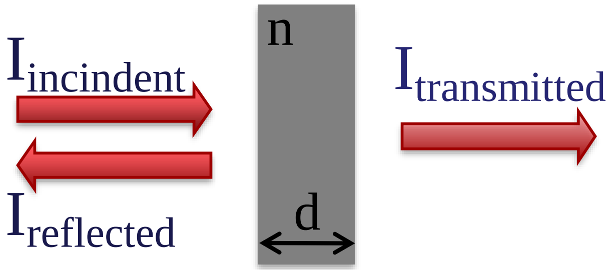
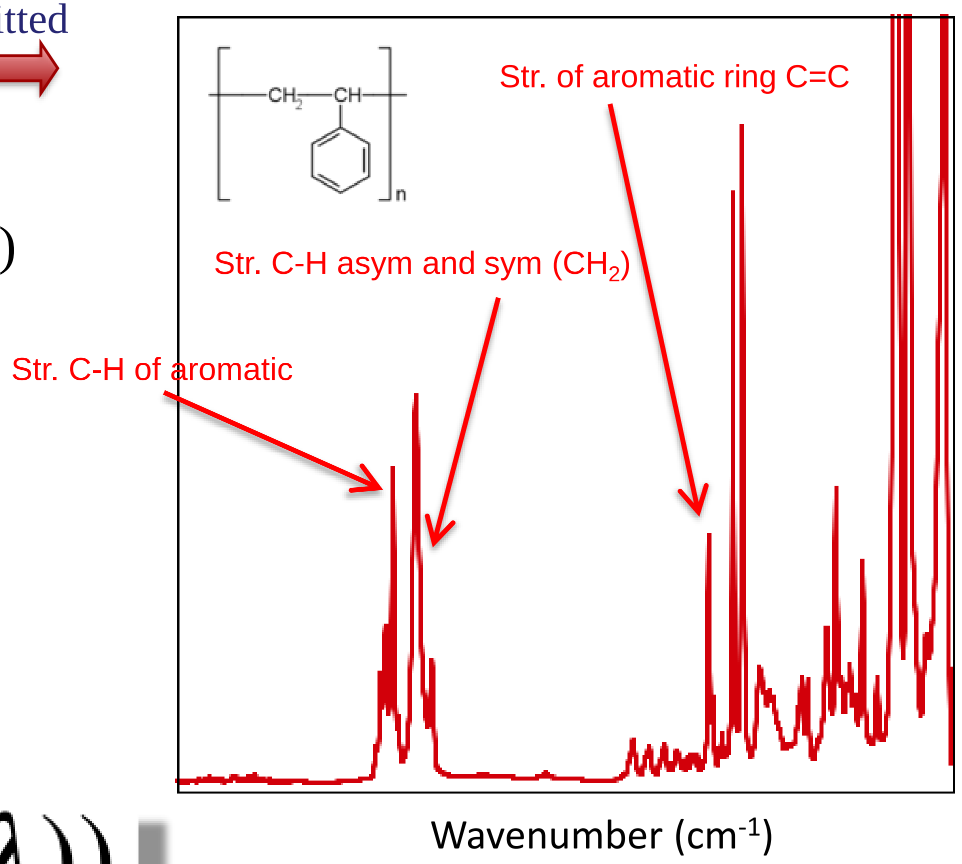
Spectroscopy principle:



(Loi de Beer-Lambert)

Absorbance spectra



Transmittance

$$T = \frac{I_t}{I_{inc}}$$

Absorbance

$$A = Log_{10} \frac{I_{inc}}{I_t} = \frac{1}{\ln 10} \frac{4\pi}{\lambda} n_i d$$

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

Coupling spectrometer and microscope

Mode	Theoretical resolution	Experimental resolution
Transmission	2λ	~10-30 µm
ATR	0.5λ	~3-10 µm

2. AFM-IR theory and concept

AFM (Atomic Force Microscope)

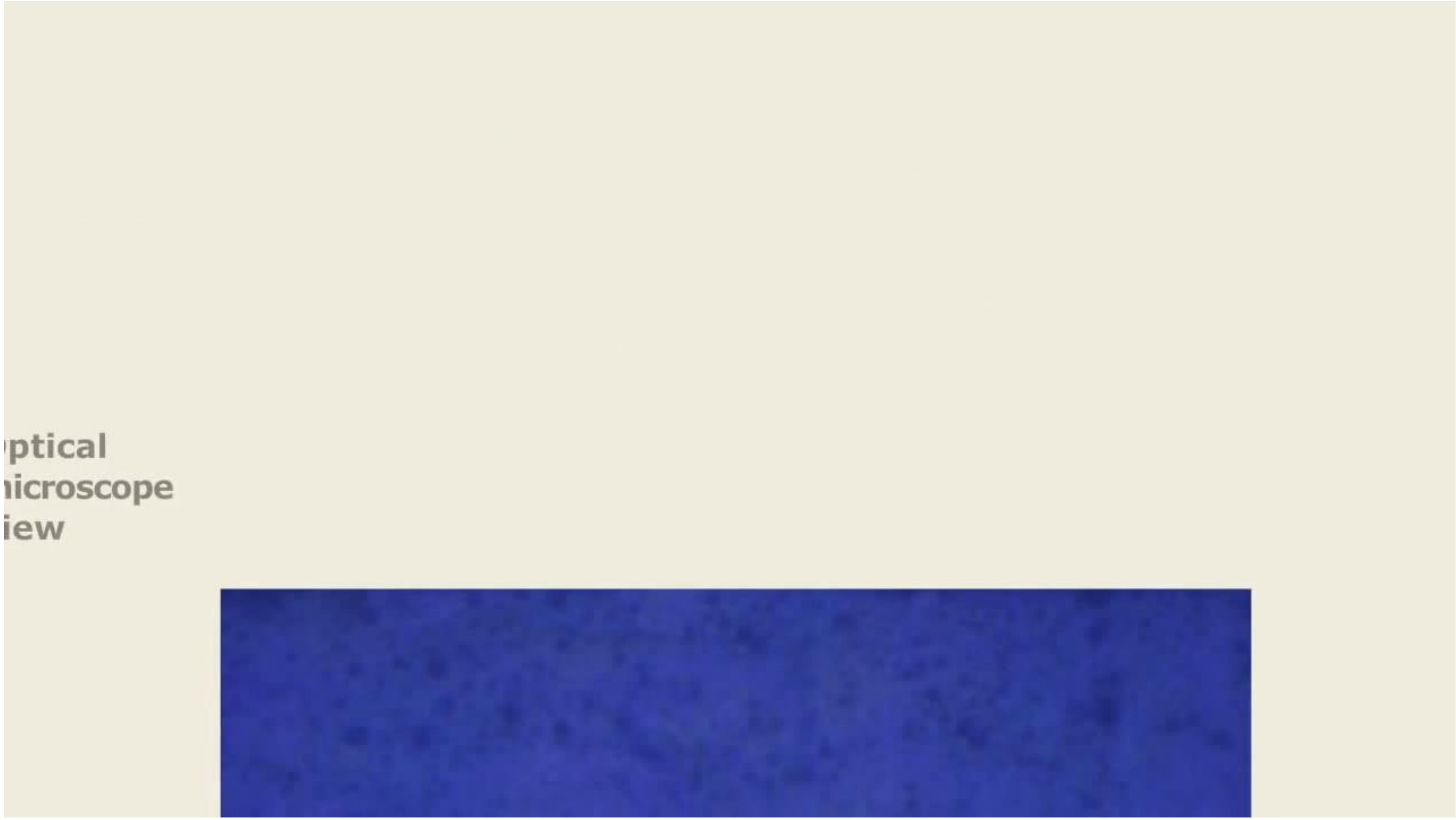
+

InfraRed laser

= AFM-IR

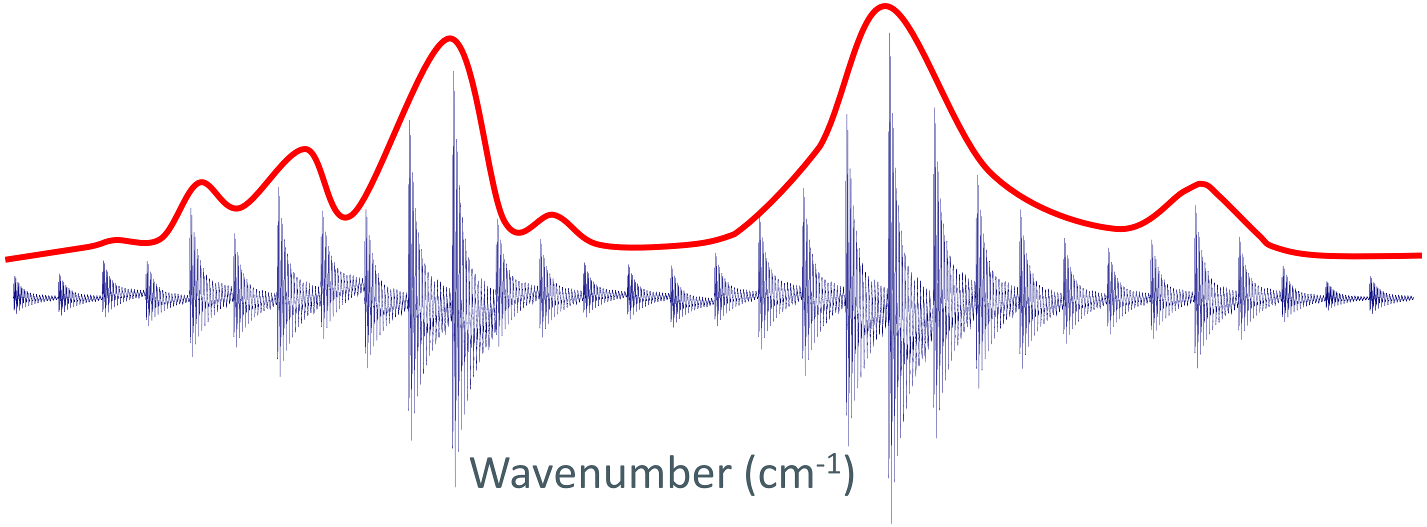
Infrared spectroscopy and imaging at nanometer scale

AFM-IR technique principle

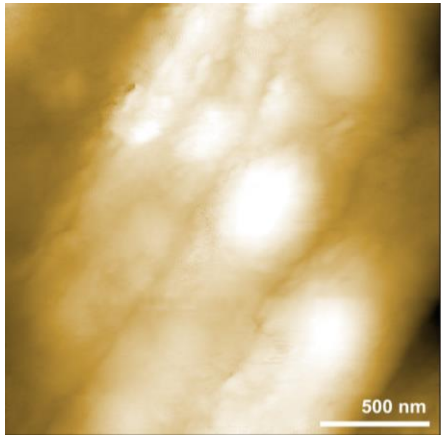


2. AFM-IR theory and concept

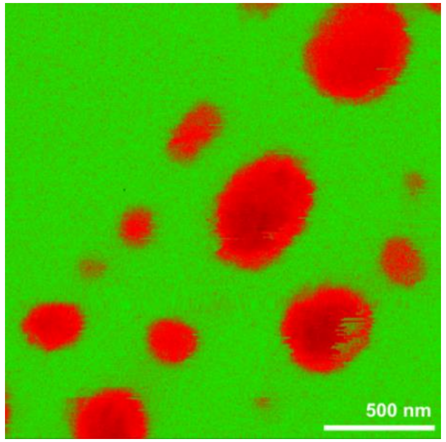
- Absorption Spectrum (fix tip position and scan the wavelength of the laser)



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

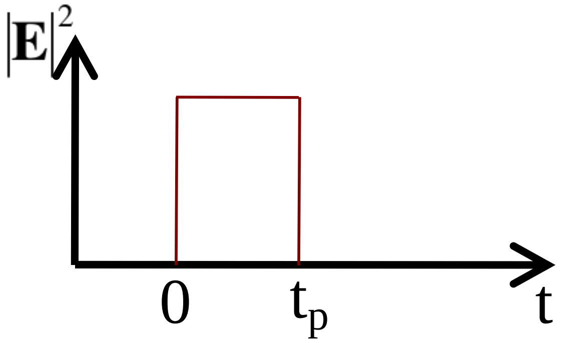


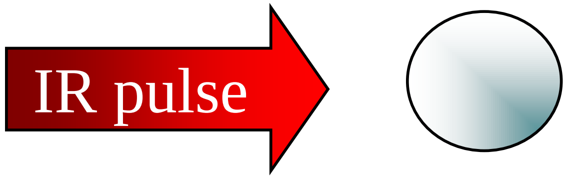
topography



Chemical mapping (λ=5,76µm)

Laser illumination





a sphere radius
V volume
n refractive index

Absorbed power

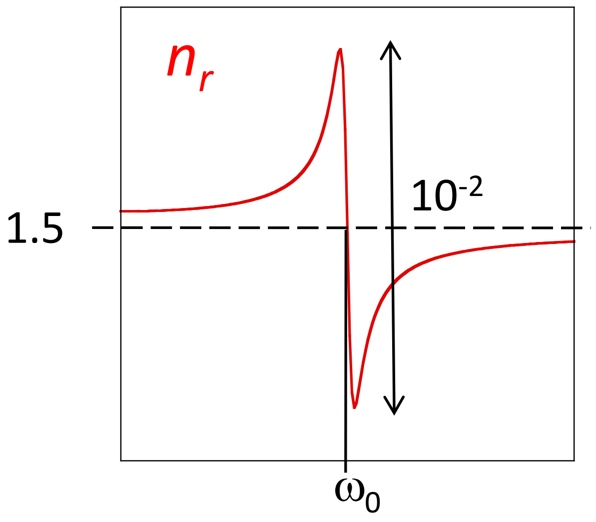
$$P_{abs} = \int_V \frac{\omega\varepsilon_0}{2} \mathrm{Im}\left[n^2(\lambda)\right] |\mathbf{E}_{loc}|^2 dV$$

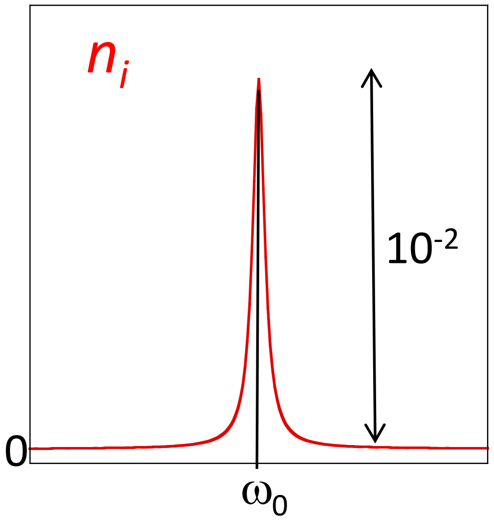
si a << ⌊

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

Organic matter

$n_i << n_r$





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

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

Heat equation:

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

$\rangle$ density, C heat capacity, K thermal conductivity

Temperature evolution of the sphere (a << ⌊)

$$T = \frac{T_{max}}{t_p} t \quad \text{when} \quad 0 \leq t \leq t_p$$

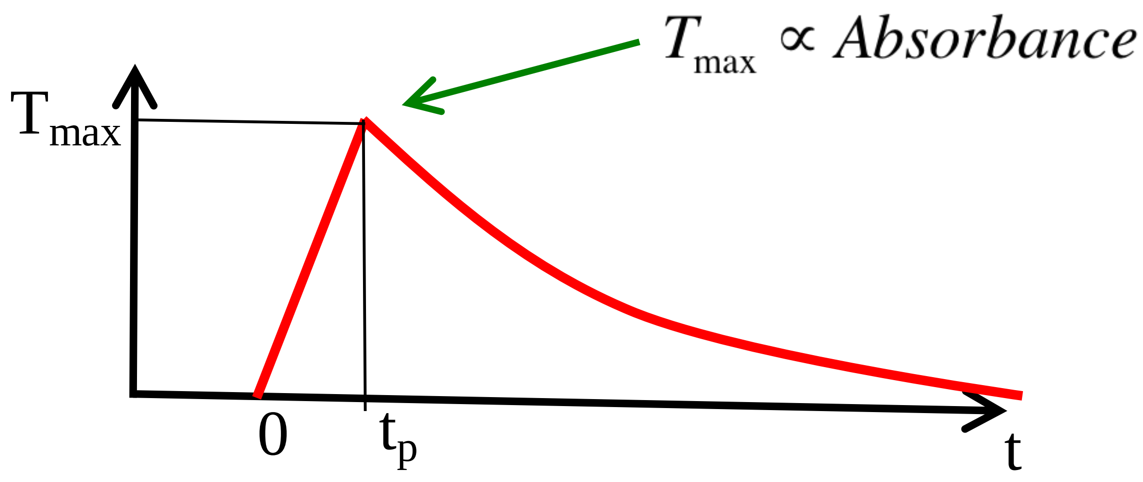
$$T = T_{max} e^{-\frac{(t - t_p)}{\tau_{relax}}} \quad \text{when} \quad t_p \leq t$$

with

$$T_{max} = \frac{P_{abs} t_p}{\rho_{sph} C_{sph} V}$$

$$\tau_{relax} = \frac{\rho_{sph} C_{sph}}{3K_{ext}} a^2$$

Only when $t_p <<$ | relax



JOURNAL OF APPLIED PHYSICS VOLUME 90, NUMBER 10 15 NOVEMBER 2001

Localized photothermal infrared spectroscopy using a proximal probe

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different types of samples (*1–6*). For example, photoacoustic spectroscopy (PAS) (*1–4*) involves the detection with a sensitive microphone of the pressure fluctuations in a gas arising from heat produced by the absorption of radiation from a modulated light beam. This technique has the advantage of not requiring optical detection of transmitted or reflected light, and it can be applied to samples which are difficult to examine by conventional spectroscopic methods. Thermal detection methods also have been suggested for the determination of absolute quantum yields by employing calorimetric techniques which are free from the geometrical correction problems of optical methods (*5–8*). These have also frequently employed microphone detectors (*6*, *8*) or the

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ANALYTICAL

Resolution bigger than a few micrometers !

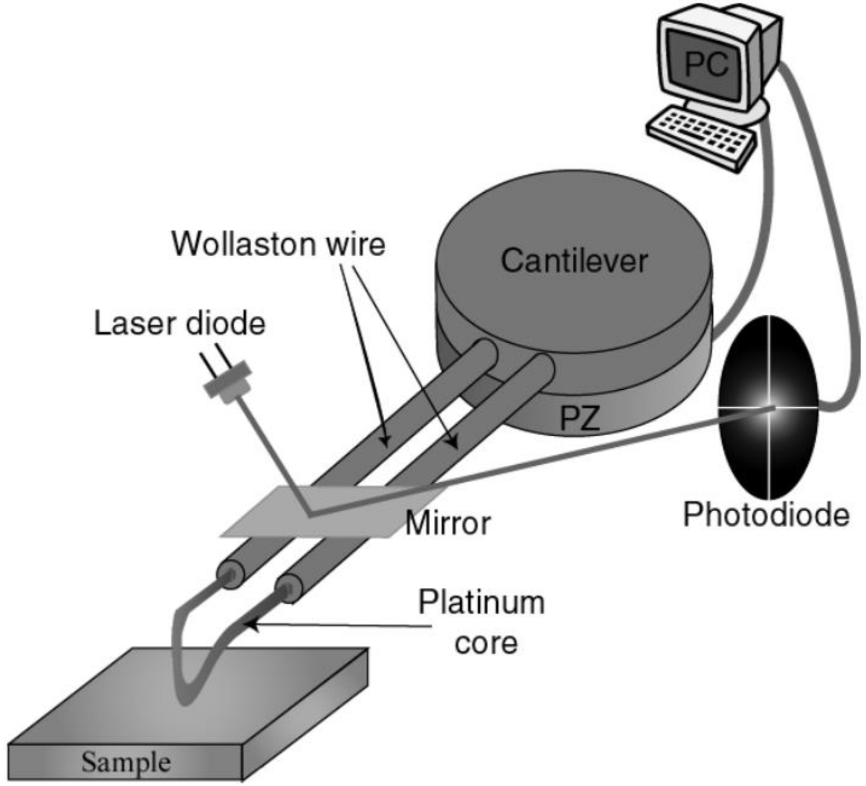
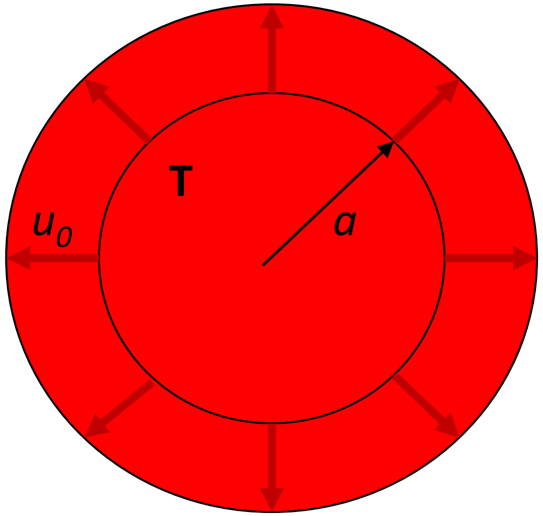


Figure 4: STHM schematic view

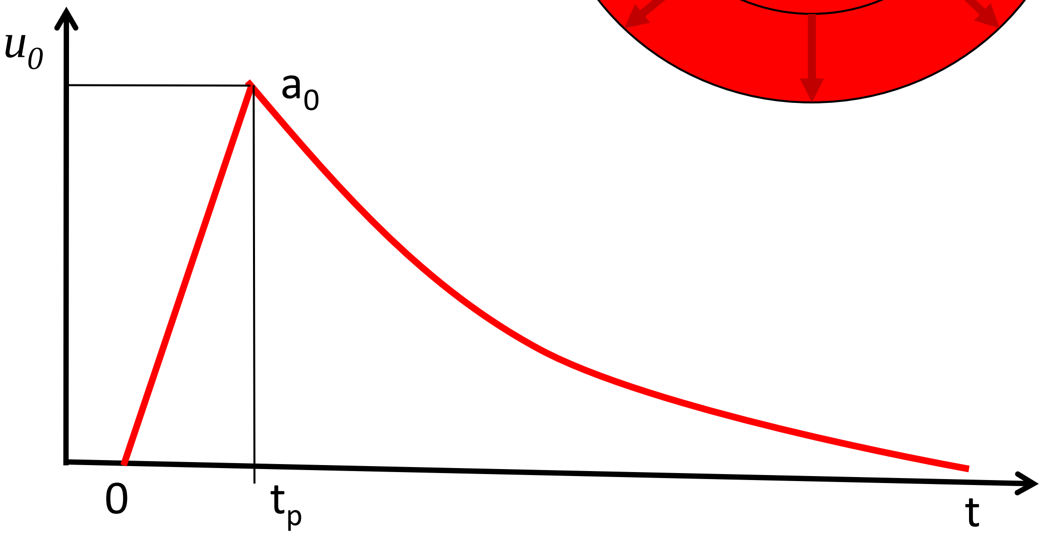
2. AFM-IR theory and concept

Evolution of the sphere deformation



$$(1-2\nu)\nabla^2\vec{u} + \nabla(\nabla\vec{u}) = 2(1+\nu)\alpha_{sph}\nabla T$$

$$\frac{u_0(t)}{a} = \frac{1+\nu}{1-\nu}\frac{\alpha_{sph}}{3}T(t)$$



α_{sph} thermal expansion coefficient

ν Poisson cofficient

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

ART. XXXIV.—*On the Production and Reproduction of Sound by Light*; by ALEXANDER GRAHAM BELL, Ph.D.

[Read before the American Association for the Advancement of Science, in Boston, August 27, 1880.]

IN bringing before you some discoveries made by Mr. Sumner Tainter and myself, which have resulted in the construction of apparatus for the production and reproduction of sound by means of light, it is necessary to explain the state of knowledge which formed the starting point of our experiments.

I shall first describe that remarkable substance "selenium," and the manipulations devised by previous experimenters; but the final result of our researches has widened the class of substances sensitive to light vibrations, until we can propound the fact of such sensitiveness being a general property of all matter.

We have found this property in gold, silver, platinum, iron, steel, brass, copper, zinc, lead, antimony, german-silver, Jenkin's metal, Babbitt's metal, ivory, celluloid, gutta-percha, hard rubber, soft vulcanized rubber, paper, parchment, wood, mica, and silvered glass; and the only substances from which we have not obtained results, are carbon and thin microscope glass.*

* Later experiments have shown that these are not exceptions.

We find that when a vibratory beam of light falls upon these substances *they emit sounds*, the pitch of which depends upon the frequency of the vibratory change in the light. We find farther, that when we control the form or character of the light, vibrations on selenium (and probably on the other substances), we control the quality of the sound, and obtain all varieties of articulate speech. We can thus, without a conducting wire as in electric telephony, speak from station to station wherever we can project a beam of light. We have not had the opportunity of testing the limit to which this photophonic effect may be extended, but we have spoken to and from points 213 meters apart; and there seems no reason to doubt that the results will be obtained at whatever distance a beam of light can be flashed from one observatory to another. The necessary privacy of our experiments, hitherto, has alone prevented any attempts at determining the extreme distance at which this new method of vocal communication will be available.

ACCOUNTS OF CHEMICAL RESEARCH

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The Opto-Acoustic Effect: Revival of an Old Technique for Molecular Spectroscopy

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Over 90 years ago,
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until the present.[1]

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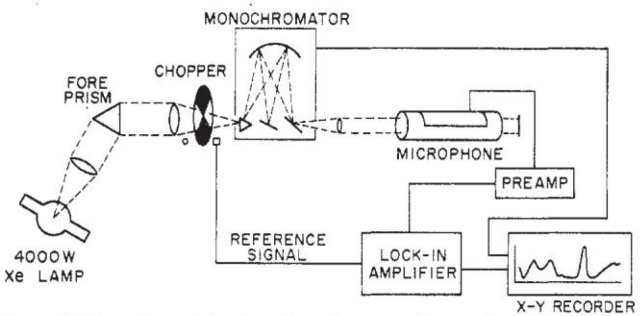


Figure 1. Experimental setup for opto-acoustic spectroscopy.

offers the possibility of observing absorption at the parts per 10^6 level or, for a gas at 1-atm pressure in the cell, the possibility of observing transitions with an oscillator strength of only 10^{-12} or so. This is the feature which first attracted us to the technique, but we have not yet realized the anticipated sensitivity.

Under what conditions does absorption lead to a signal at the microphone? In general, following electronic excitation, a molecule has three channels open to it: (i) it may luminesce, leaving little or no heat in

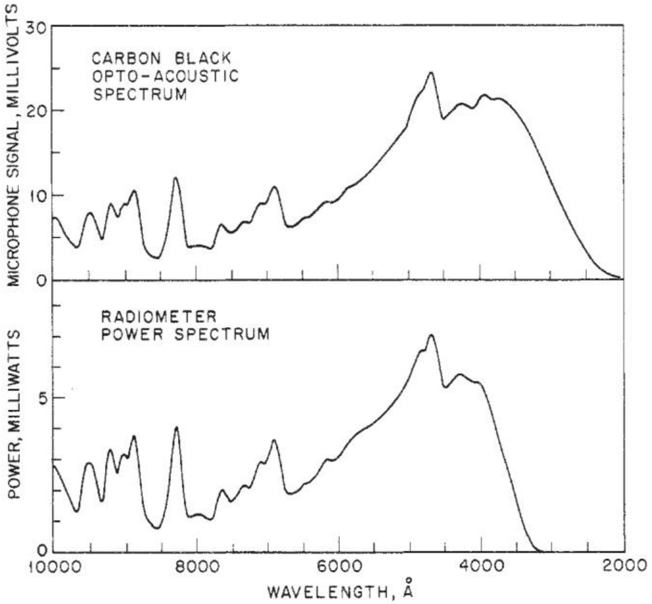


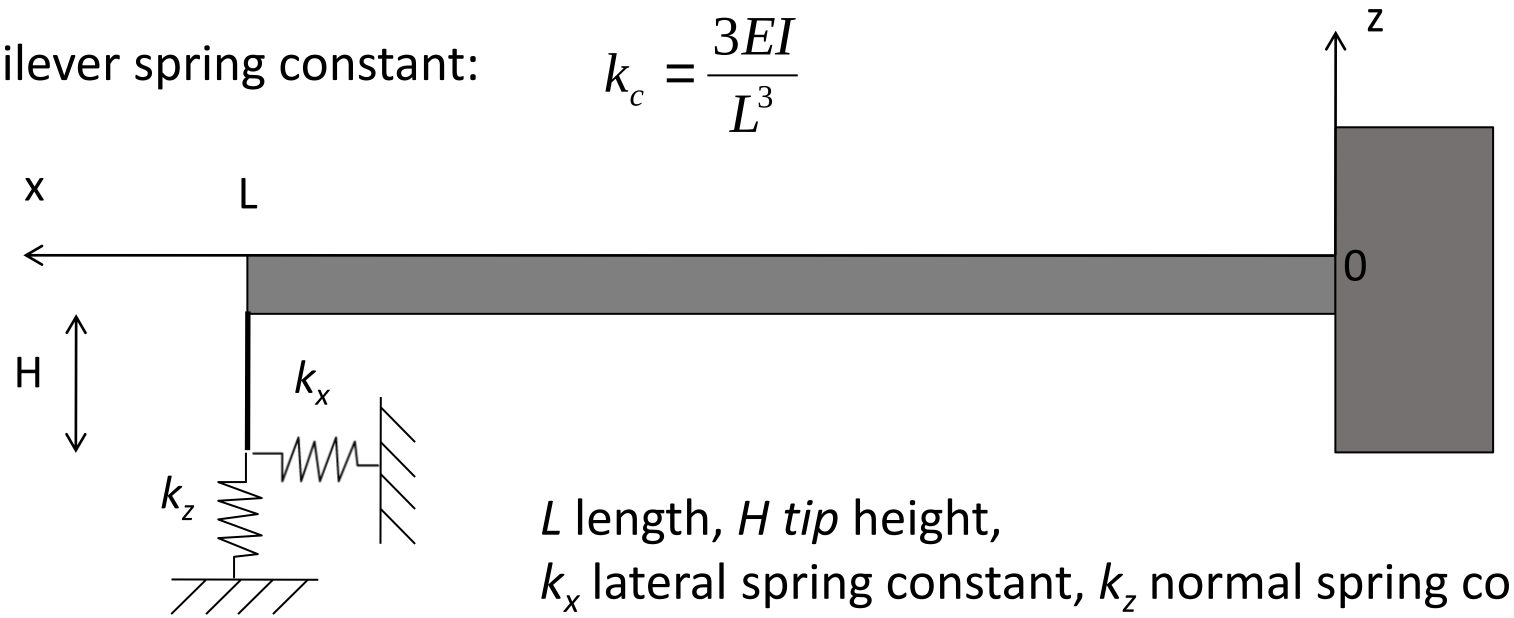
Figure 2. Comparison of the carbon black opto-acoustic spectrum with that of a calibrated radiometer.

Differential equation of cantilever motion :

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

E Young modulus, *I* inertia moment, ρ density, *A* section, κ damping

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



L length, *H tip* height,

k_x lateral spring constant, k_z normal spring constant

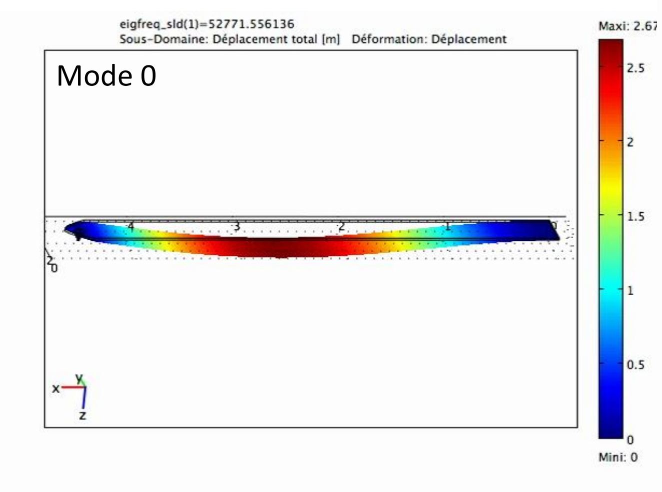
$k_z >> k_c$ **NO indentation**

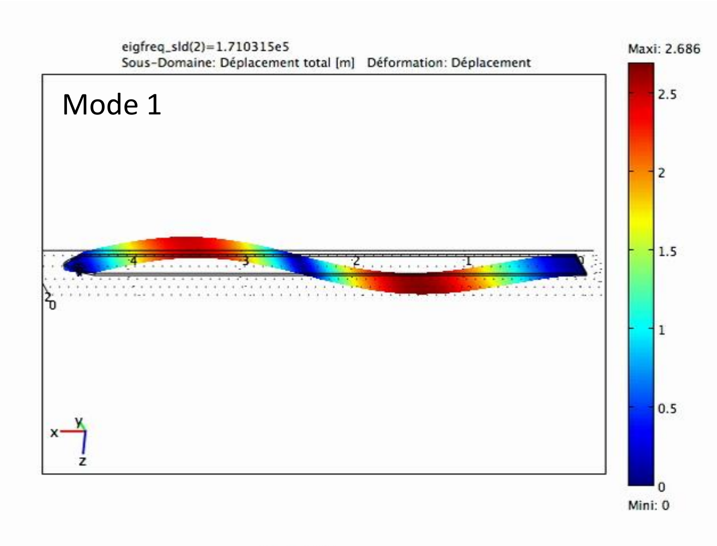
$$-1+\cos X\cosh X - UX(\sin X\cosh X - \cos X\sinh X) = 0$$

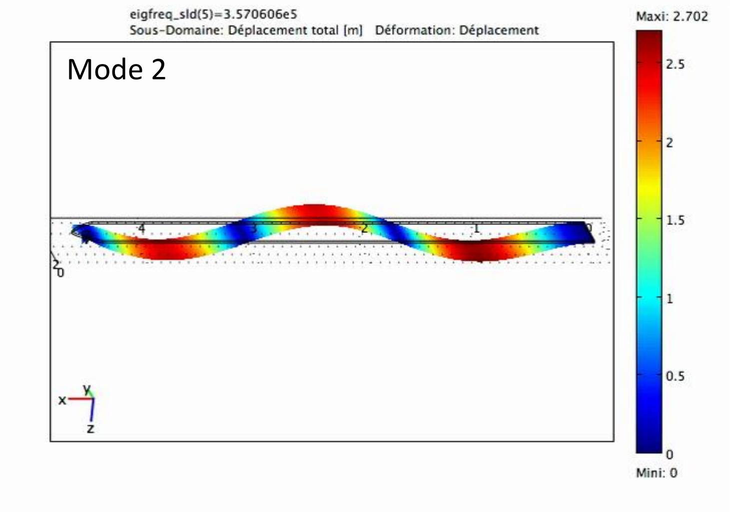
with $U = \dfrac{k_c L^2}{3k_x H^2}, X = \beta L$

Cantilever Si contact

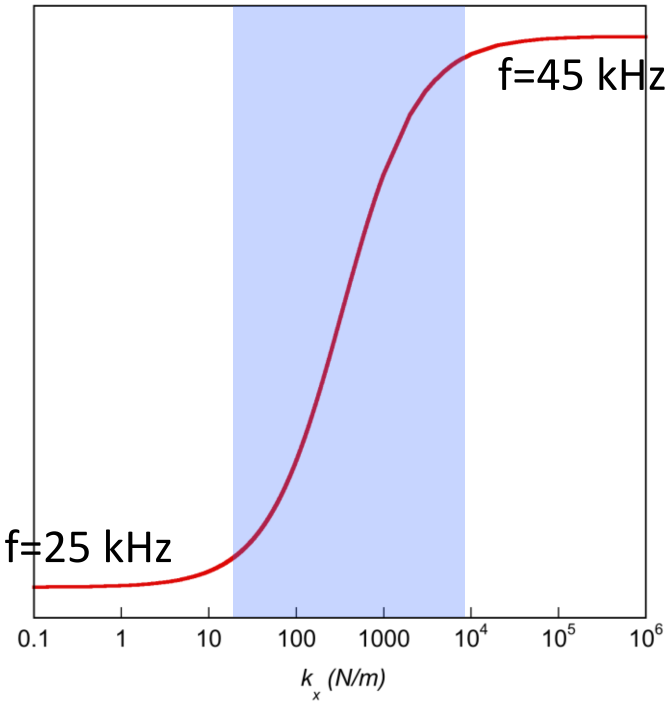
k_x	0 (pure sliding)	∞ (pinned)
Mode	$X_n=\beta_n L$	$X_n=\beta_n L$
0	3.92662	4.73004
1	7.06858	7.8532
2	10.3518	14.1372







Mechanical sensitivity of contact resonance modes



$$f_n = \frac{1}{2\pi}\sqrt{\frac{k_c}{3\rho A L}}\left(\frac{(X_n^p - X_n^f)}{\left(1+\left(\frac{k_c L^2}{3k_x H^2}\right)(a_n X_n^p - X_n^f)\right)} + X_n^f\right)^2$$

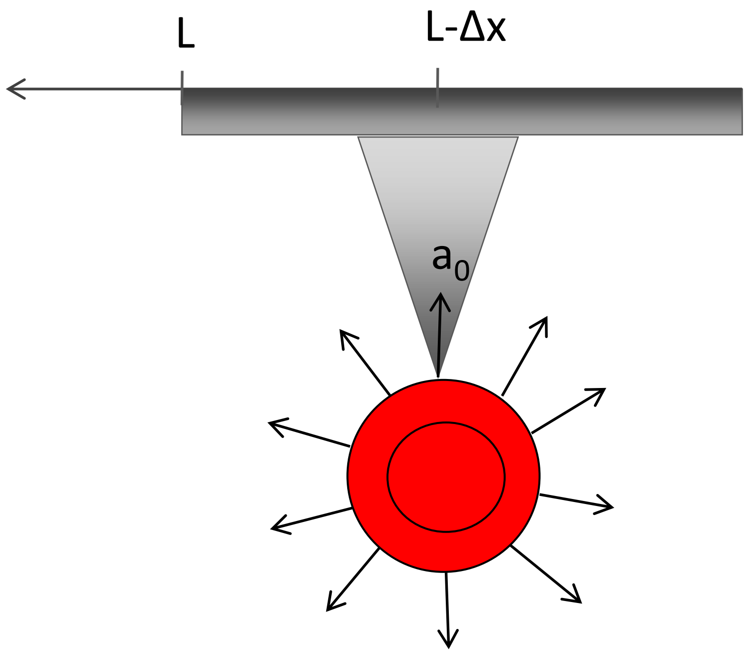
X_n^p pinned,
X_n^f pure sliding,
a_n modal constant

Mode number n	a_n	X_n^p	X_n^f
0	2 .09	4.730040	3.92662
1	2.2524	7.853200	7.06858
2	2.3005	10.99560	10.2102
3	2.3276	14.1372	13.3518

Differential equation of cantilever motion with external force :

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

with $S(x,t)$ external excitation



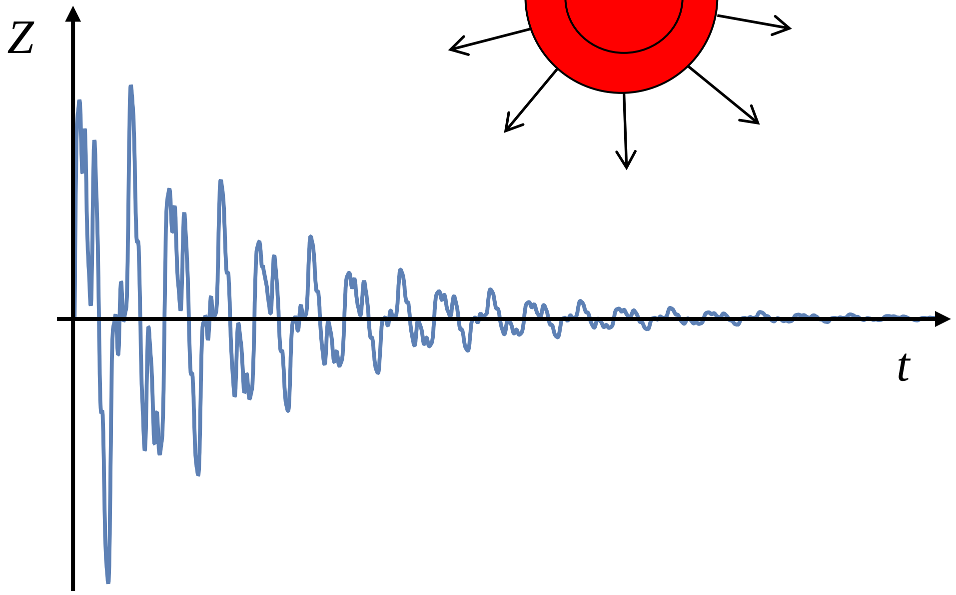
Induced force by the sphere expansion gives :

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

Equation solution becomes :

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

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



2. AFM-IR theory and concept

Fourier transform of Z(t) signal

$$\tilde{Q}(\omega) = \sum_n \tilde{Q}_n(\omega) = \sum_n D|C|\left(\frac{\partial g_n(x)}{\partial x}\right)^2\Bigg|_{x=L} \frac{\left|\tilde{T}_{sph}(\omega)\right|}{\sqrt{\left(\omega_n^2 - \omega^2\right)^2 + \Gamma^2\omega^2}}$$

Mode amplitude

$$\tilde{Q}_n(\omega_n) = H_m H_{AFM} H_{opt} H_{th} \frac{\mathrm{Im}(n(\lambda))}{\lambda}$$

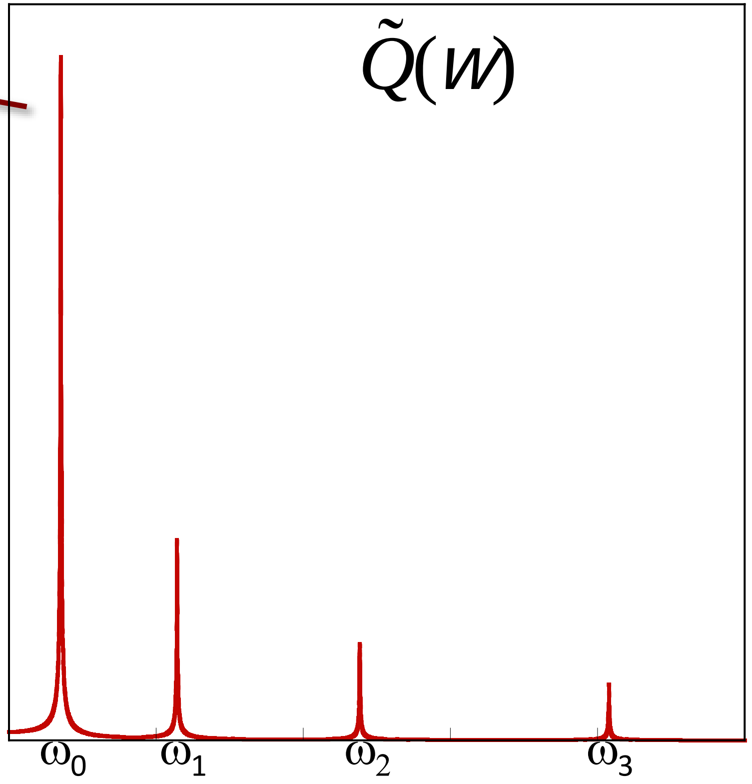
$$H_m = k_z \alpha_{sph} \alpha$$

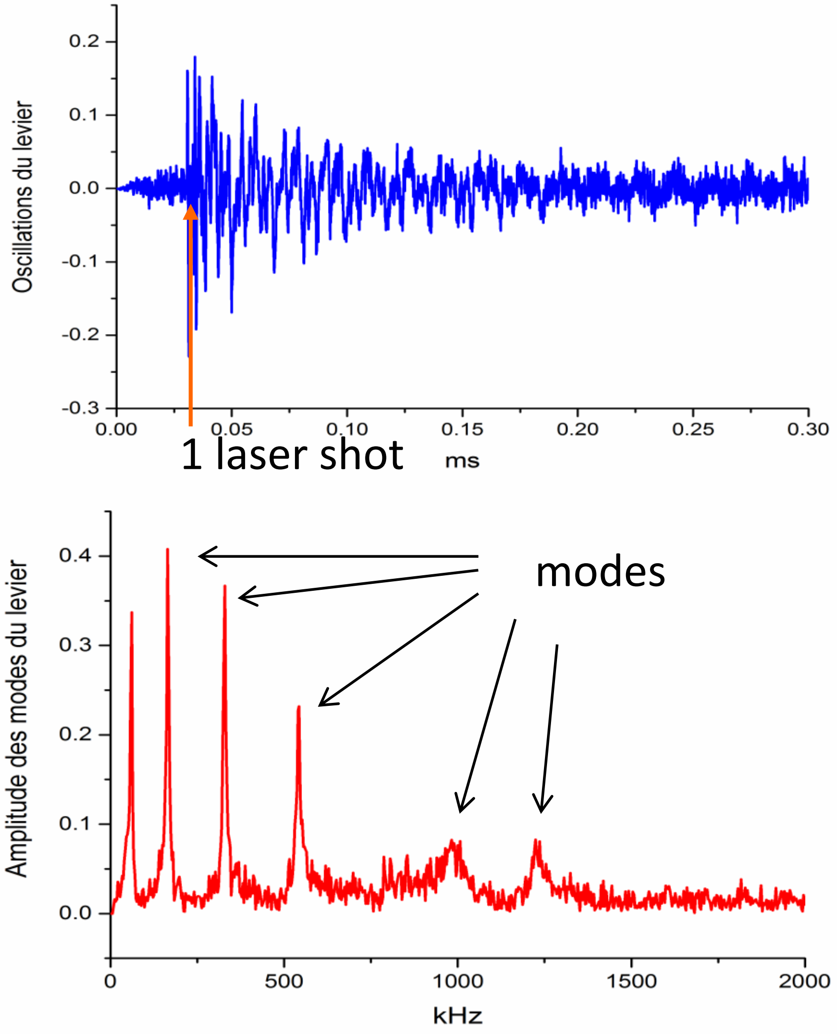
$$H_{AFM} = \frac{1}{\Gamma\omega_n}\left[\cos(\alpha)\delta x + \sin(\alpha)H\right] \frac{D}{m}\left[\frac{\partial g_n(x)}{\partial x}\bigg|_{x=L}\right]^2$$

$$H_{opt} = \frac{\mathrm{Re}(n)}{(\mathrm{Re}(n)^2+2)^2} c\varepsilon_0 |E_{inc}|^2$$

$$H_{th} = \frac{6\pi}{\rho_{sph} C_{sph}} \tau_p \left(\frac{\tau_p}{2} + \tau_{relax}\right)$$

$$\tilde{Q}_n(\omega_n) \propto \frac{\mathrm{Im}(\lambda)}{\lambda} \propto Absorbance$$





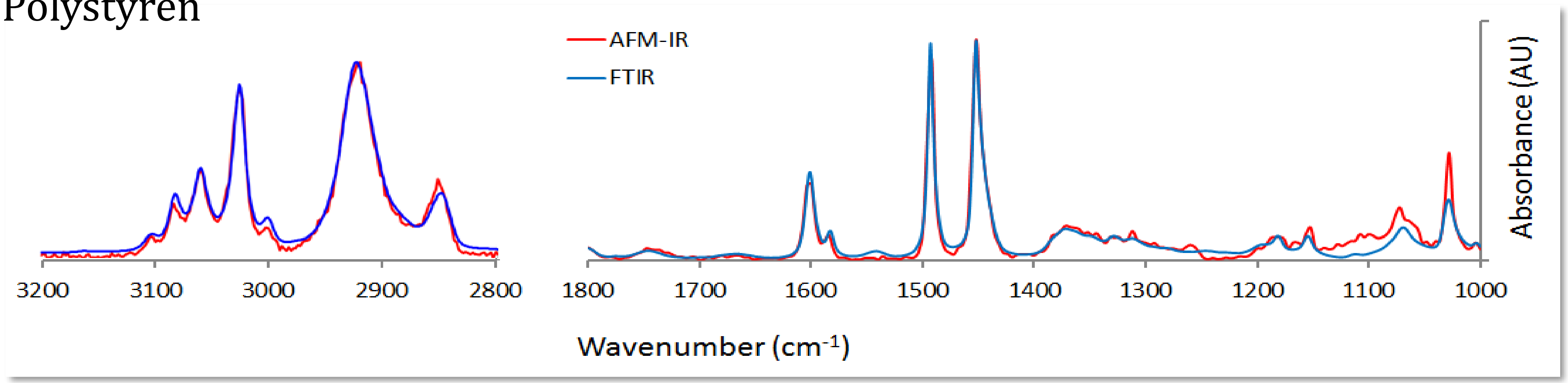
Classical AFM-IR (old version)

Classical AFM-IR

Demonstration that photothermal measurement give a direct estimation of imaginary part of the refractive index.

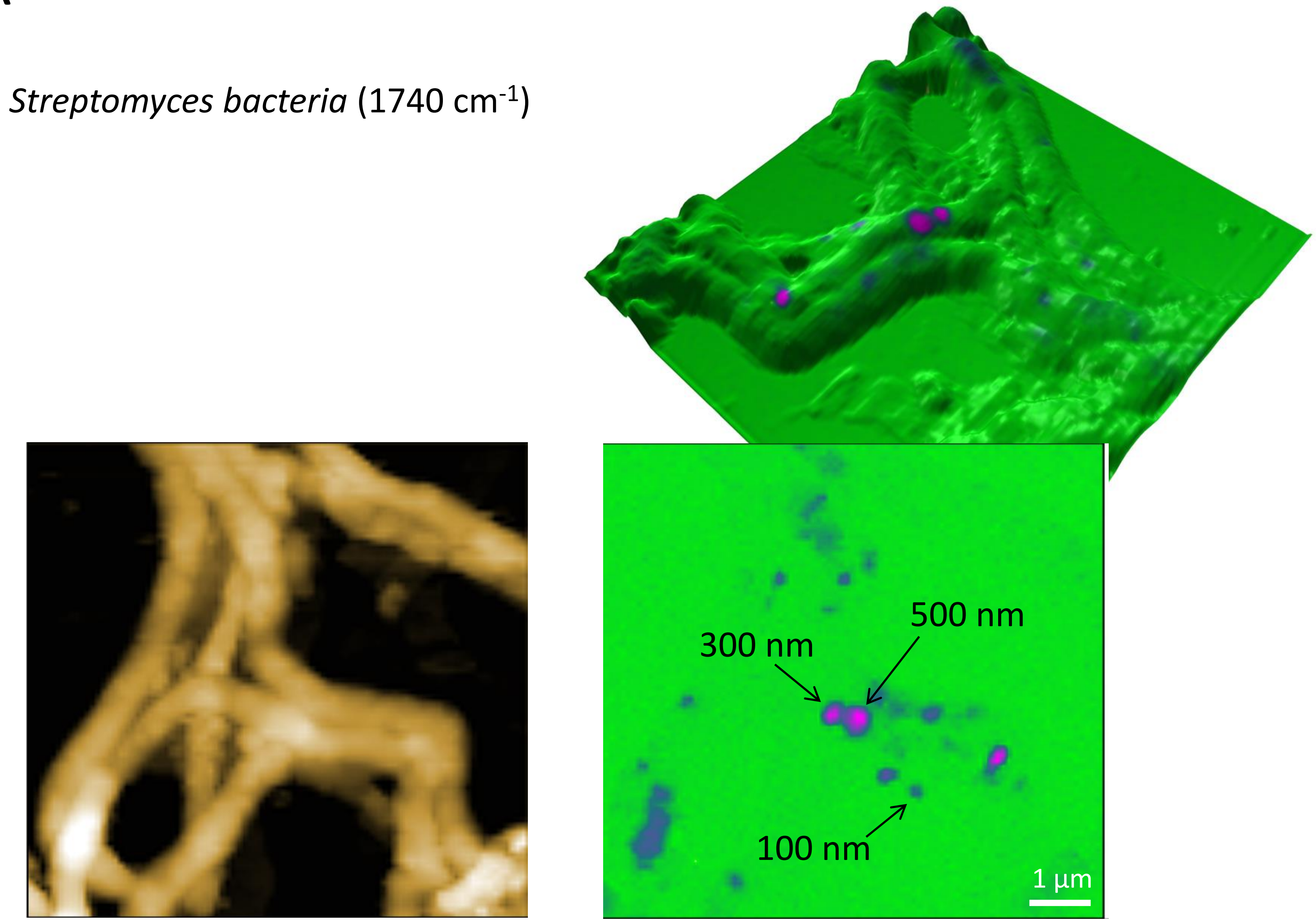
AFM-IR Spectrum similar to those obtained by FTIR

Polystyren

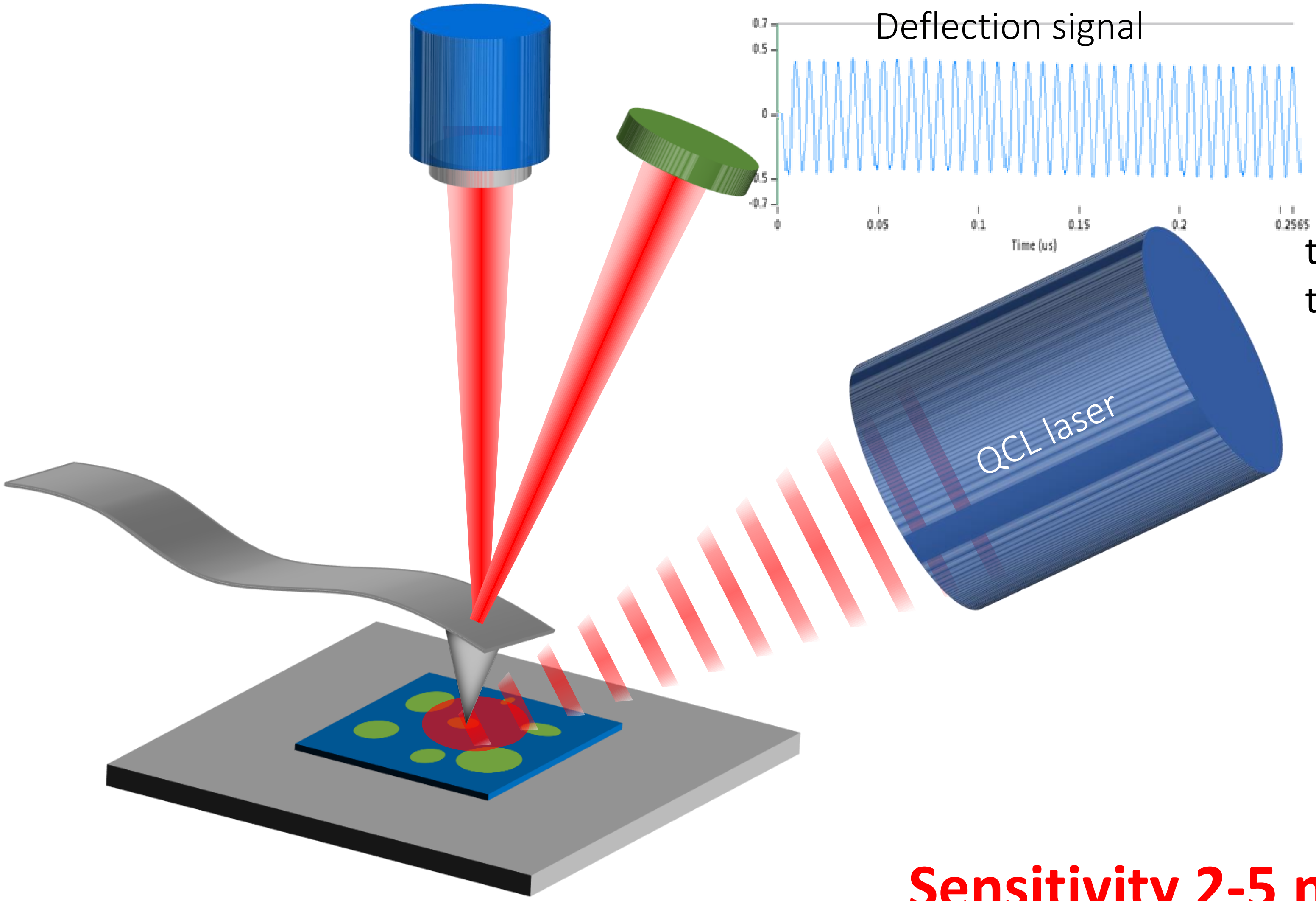


Classical AFM-IR

Detection of lipid vesicles in *Streptomyces bacteria* (1740 cm^{-1})



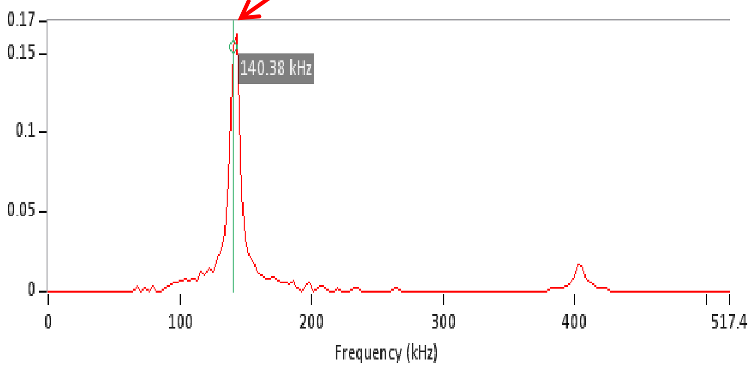
AFM-IR imaging mode : contact resonance mode



QCL laser (Quantum Cascade Laser)

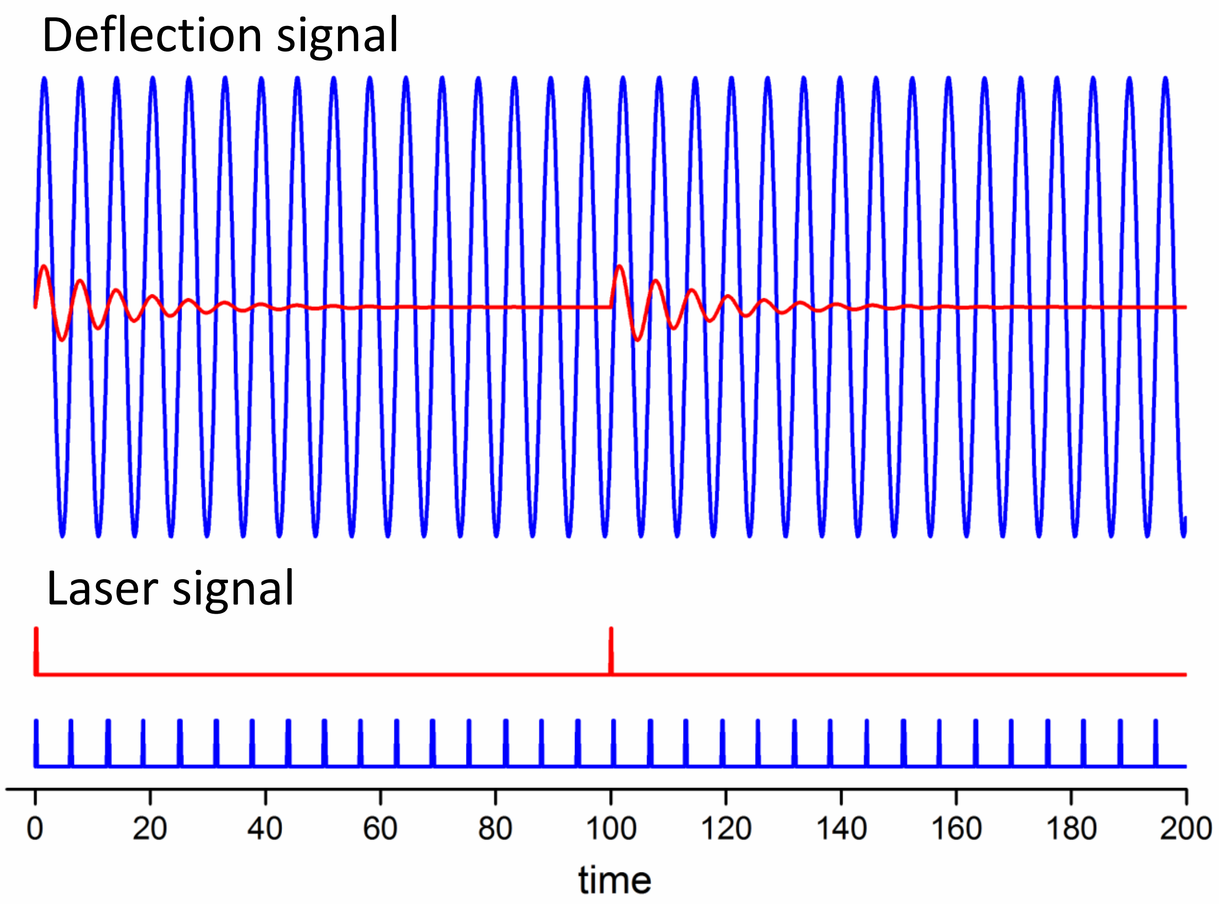
tunable in wavenumber (1900-900 cm^{-1})
tunable repetition rate (0-3000 kHz)

contact
resonance mode

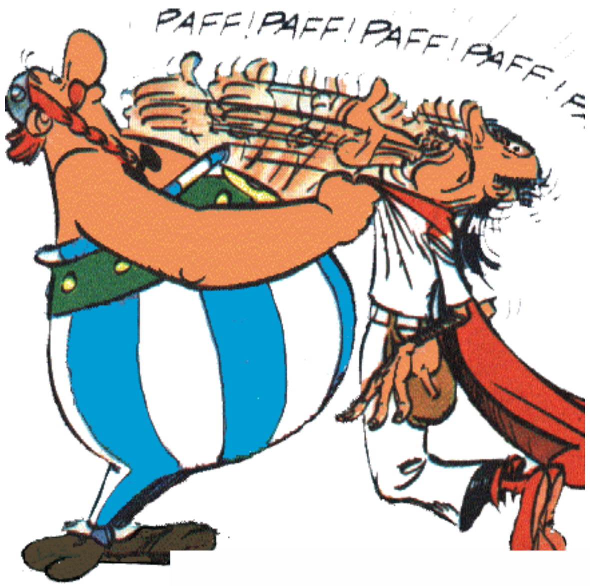


Sensitivity 2-5 nm

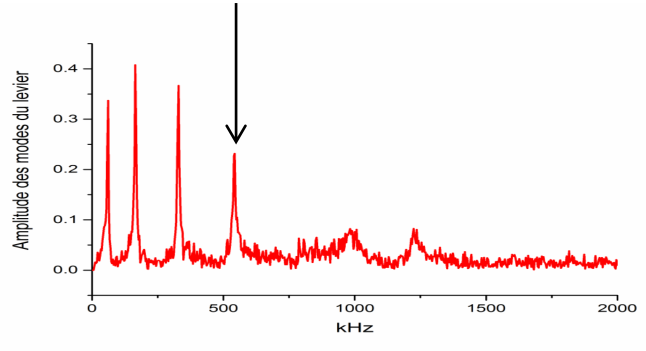
AFM-IR imaging mode : contact resonance mode

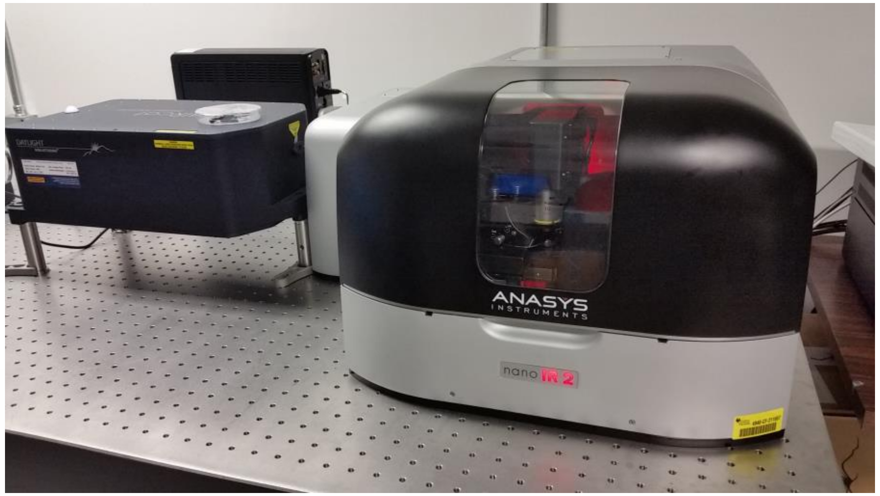


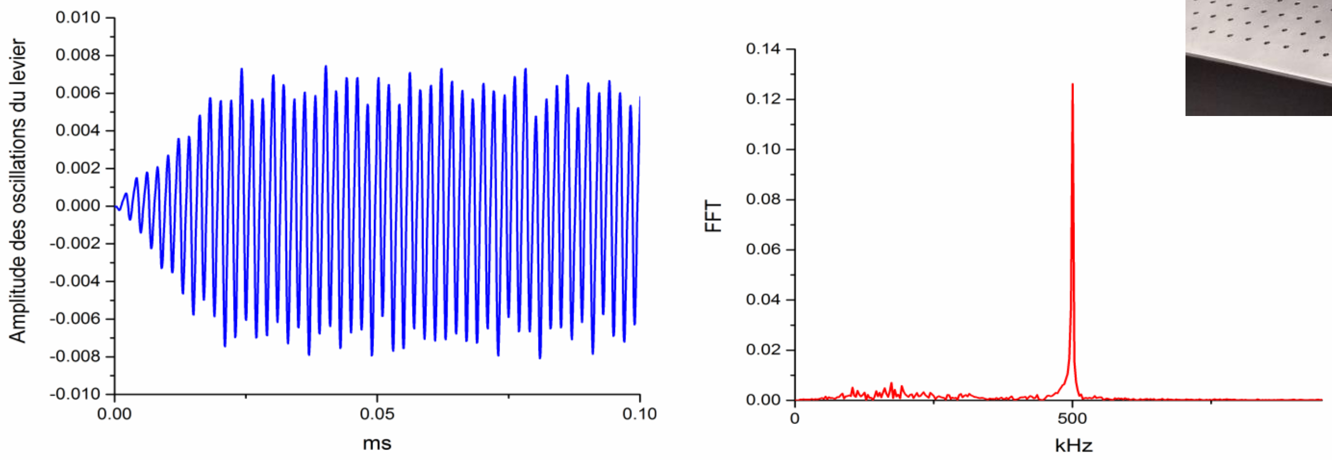
Enhanced resonance leads to have a better sensitivity and then better resolution



Laser repetition rate







2. AFM-IR theory and concept

Deflection for 1 pulse (OPO)

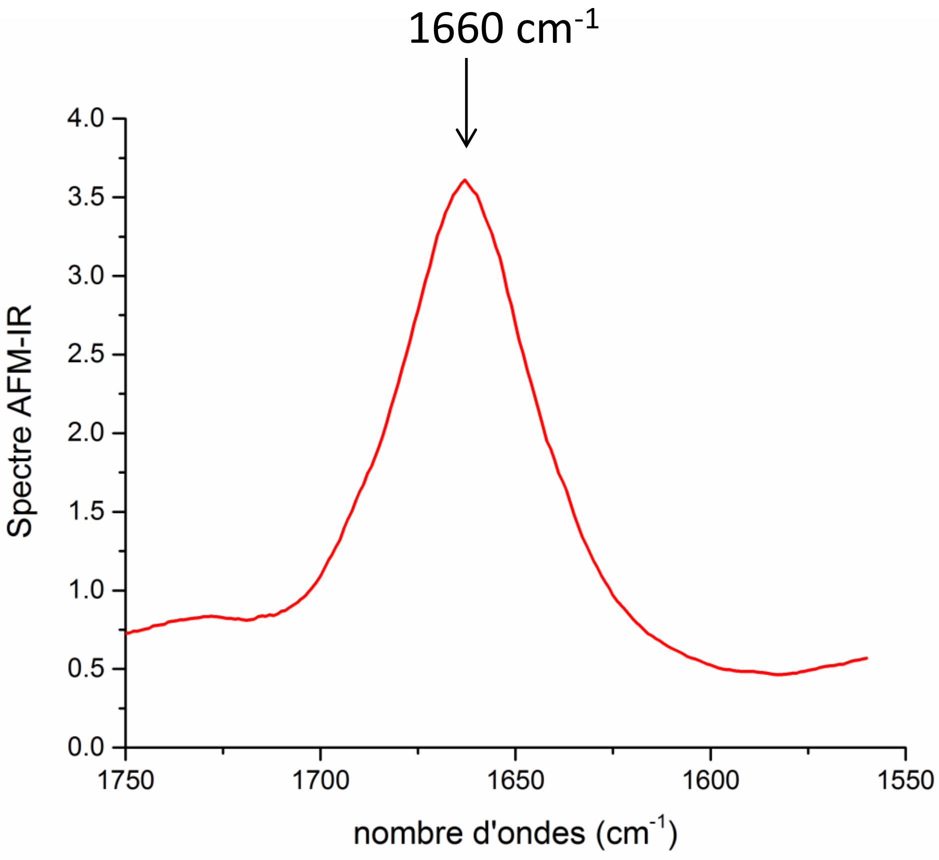
$$Z(t) = \sum_n \frac{K k_z D \delta_x}{\rho S L} \left(\frac{\partial g_n}{\partial x} \bigg|_{x=L} \right)^2 \frac{\left(\frac{t_p}{2} + \tau_{relax} \right)}{\omega_n} \sin(\omega_n t)\, e^{-\frac{\Gamma}{2} t}\, a_0$$

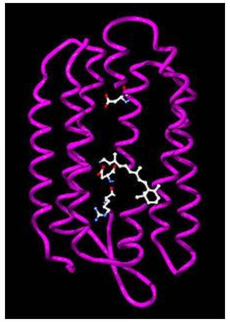
Deflection when repetiton rate = contact resonance mode (QCL)

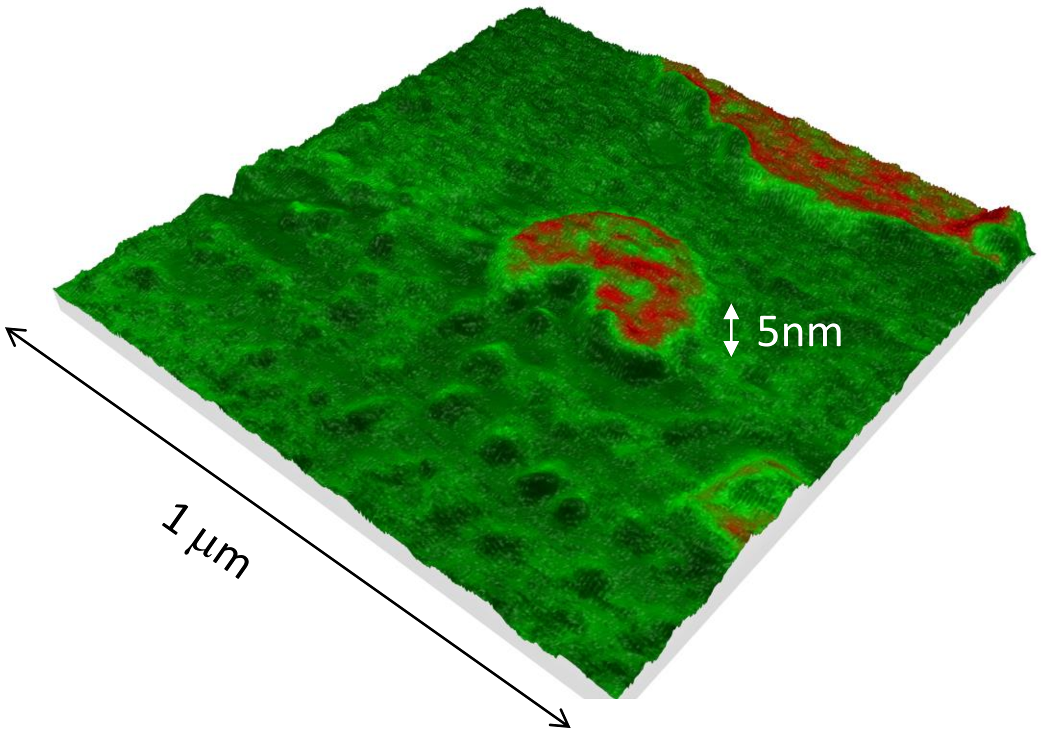
$$Z(t) = \frac{K k_z D \delta_x}{\rho S L} \left(\frac{\partial g_n}{\partial x} \bigg|_{x=L} \right)^2 \frac{\left(\frac{t_p}{2} + \tau_{relax} \right)}{\omega_n} \frac{Q_n}{\pi} \sin(\omega_n t)\, a_0$$

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

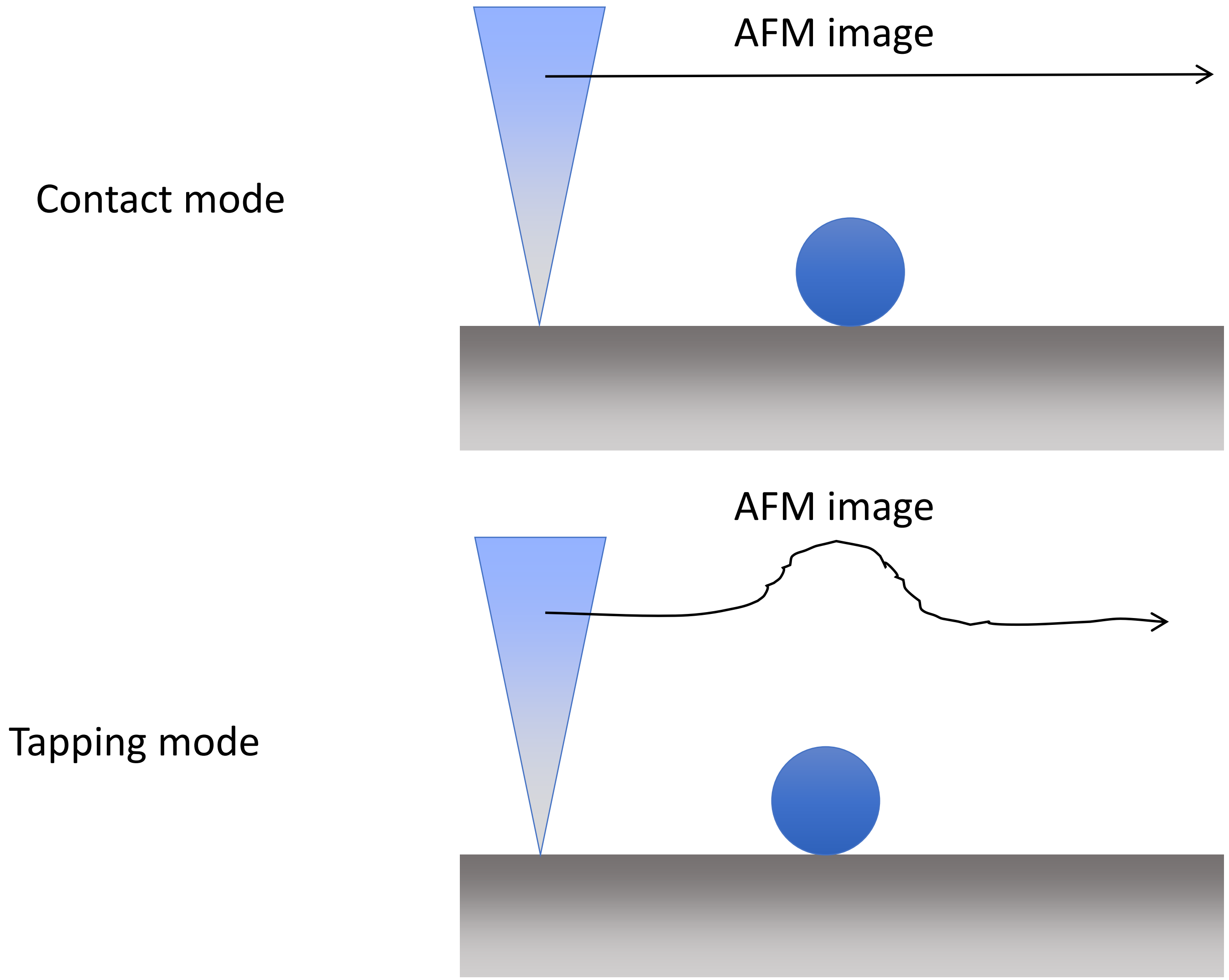
Bacteriorhodopsin detection inside a purple membrane







AFM-IR imaging mode : tapping AFM-IR

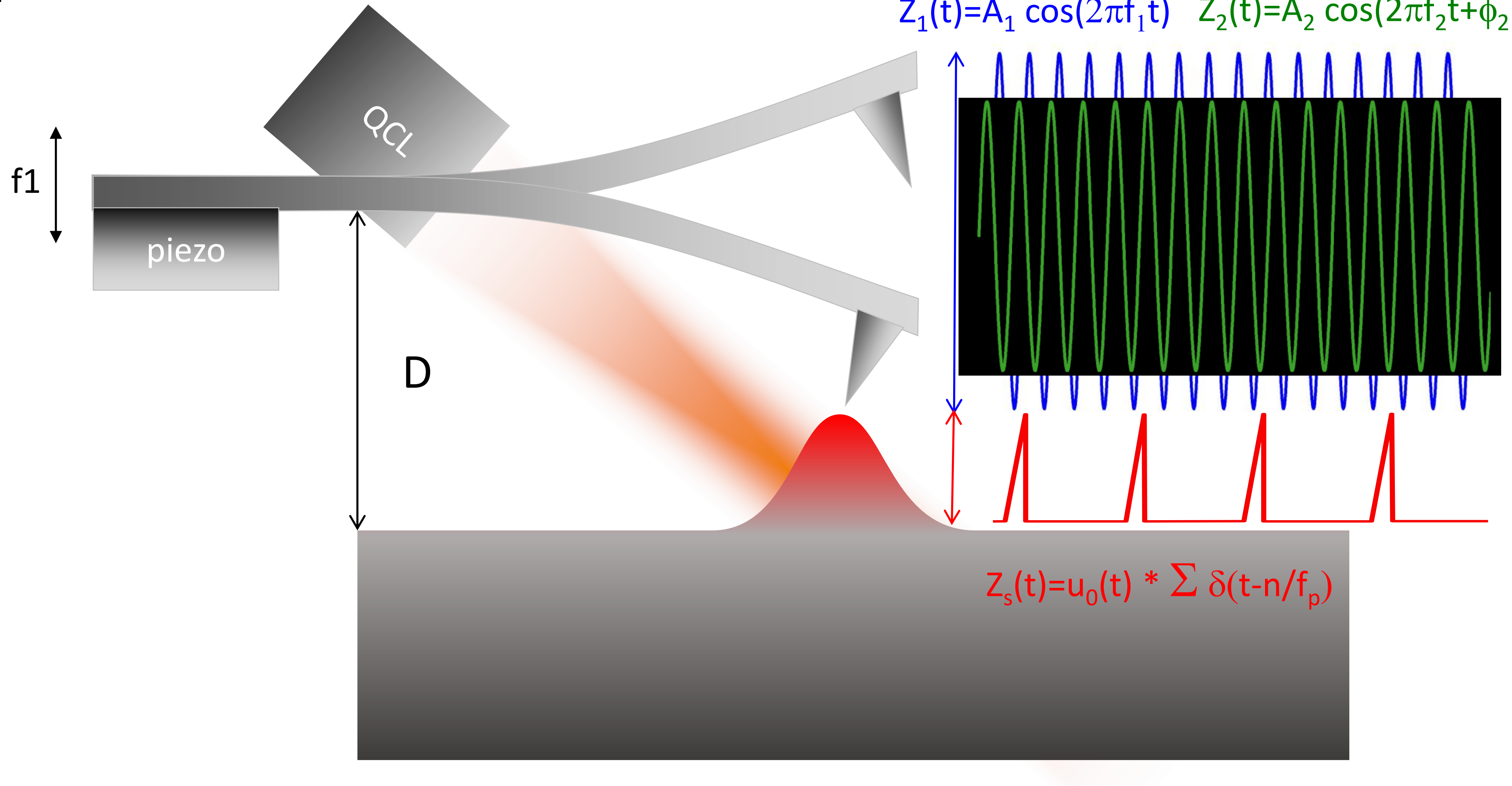


Tapping AFM-IR principle

If non linear interaction then: $f_2=f_1+f_p$ ou $f_2=f_1-f_p$

f_1= drive frequency of tapping mode
f_p = QCL laser frequency

$Z_1(t)=A_1\cos(2\pi f_1 t)$ $Z_2(t)=A_2\cos(2\pi f_2 t+\phi_2)$



$Z_s(t)=u_0(t) * \Sigma\, \delta(t-n/f_p)$

2. AFM-IR theory and concept

Differential equation of motion for the mode f2 :

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

Interaction force between tip and sample surface

$$F_{ts}(t) = K(A_1 \cos(\omega_1 t) - D - u_0(t))^{3/2}$$

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

f_1 f_p $2f_1$ $2f_p$

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

τ Is the contact time led by f_1

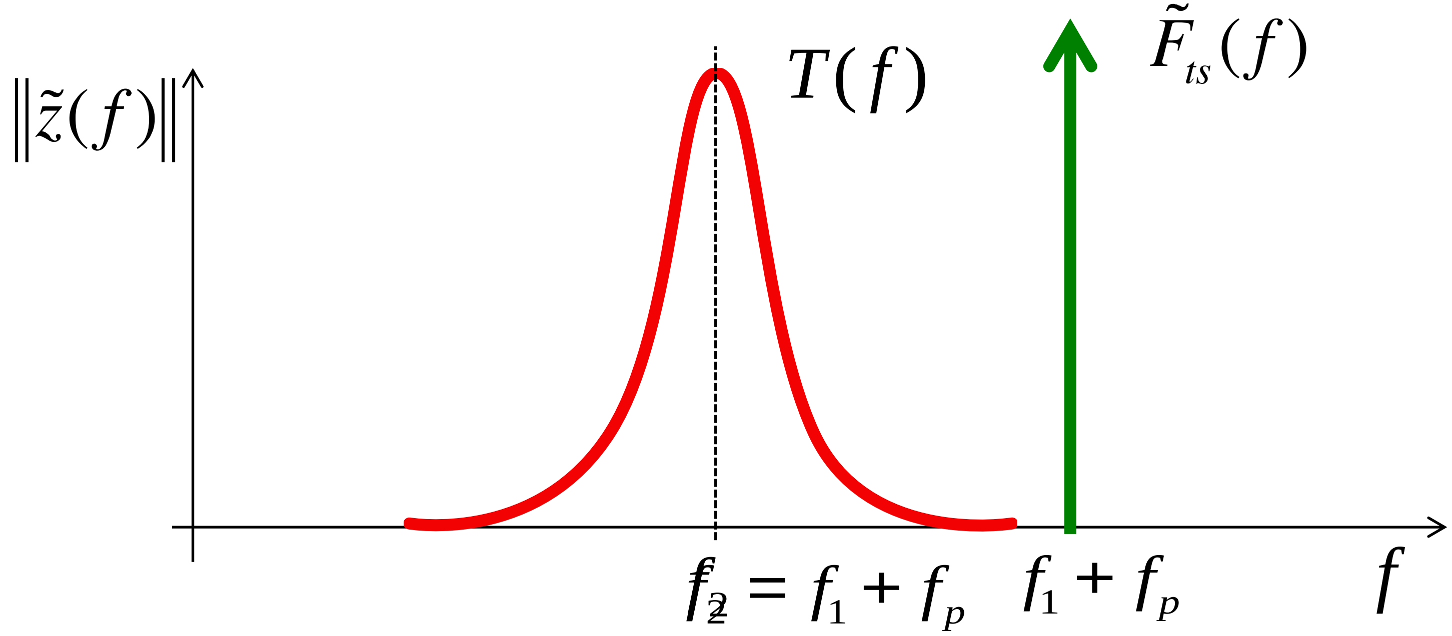
2. AFM-IR theory and concept

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

Fourier transform

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

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



Mode f2 ($f_2=f_1+f_p$) amplitude give :

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

non linear elasticity coefficient

Pulse duration

Tapping setpoint

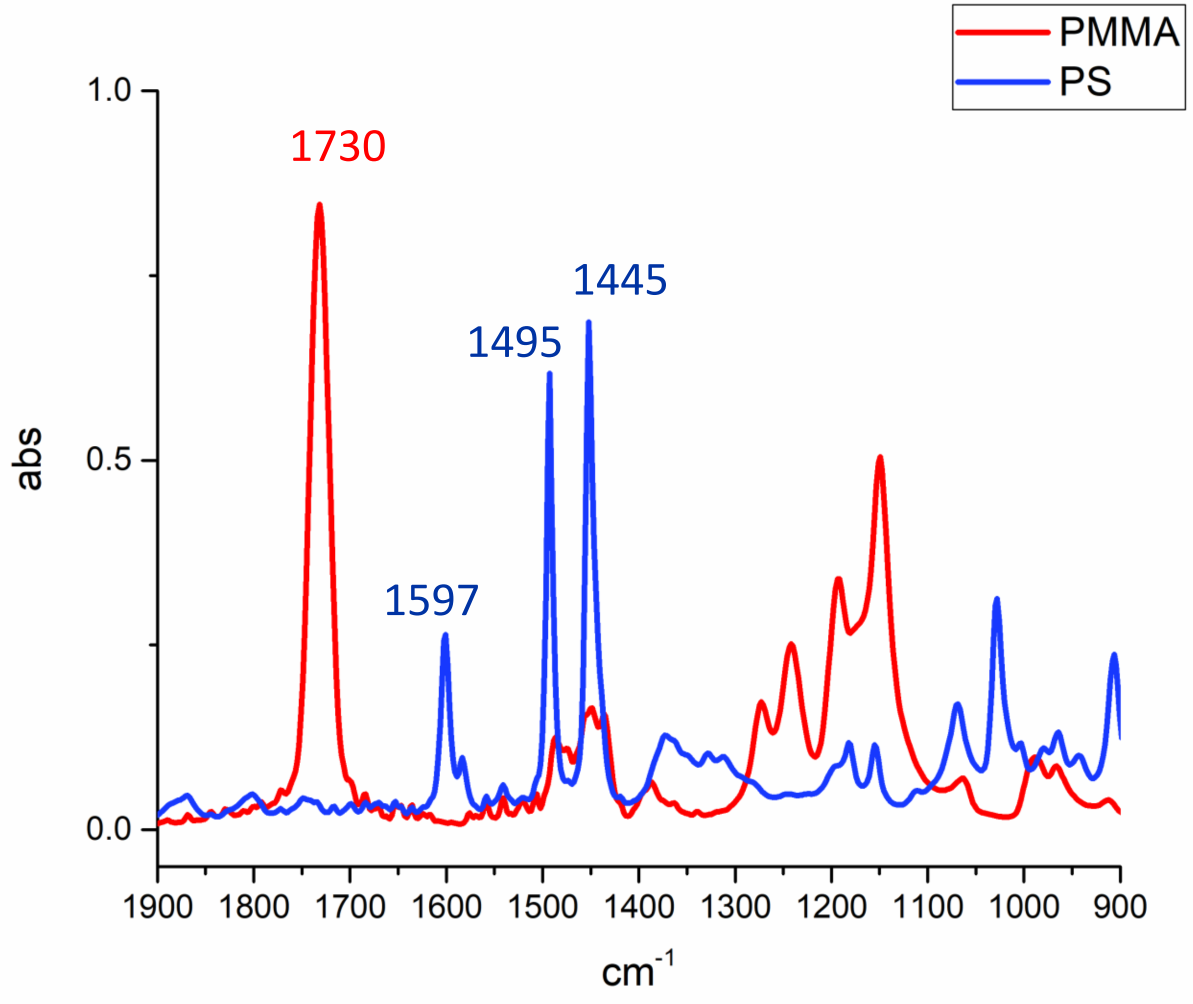
Tapping amplitude

Cantilever modes

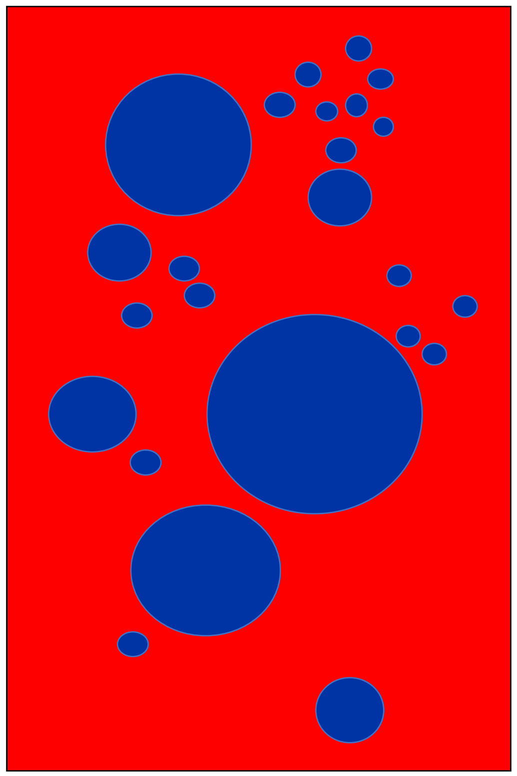
Thermal expansion
α absorbance

Tapping AFM-IR signal is proportional to the **absorbance** (even if non linear)

Examples of tapping AFM-IR results

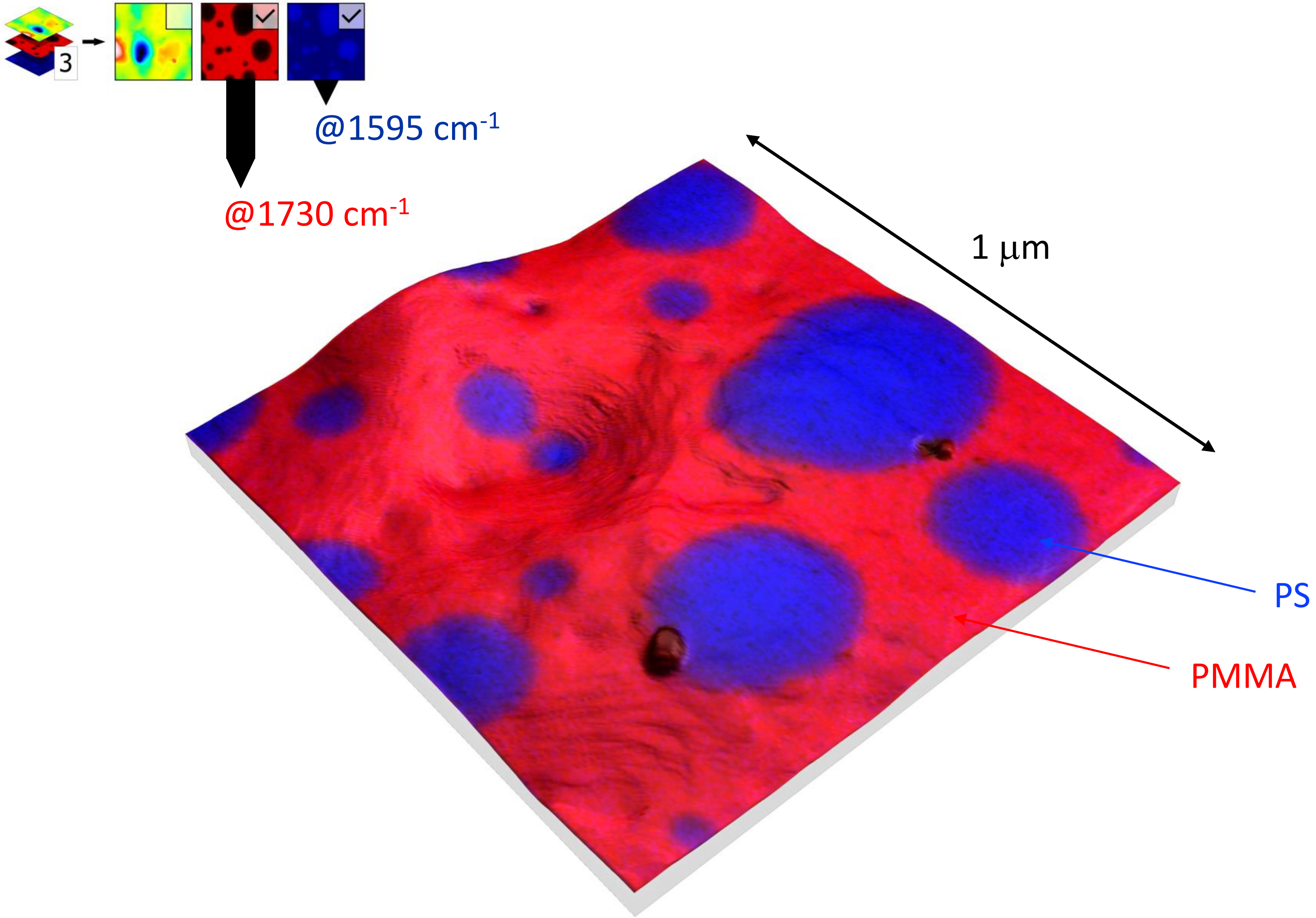


PMMA-PS polymer blend 1-1



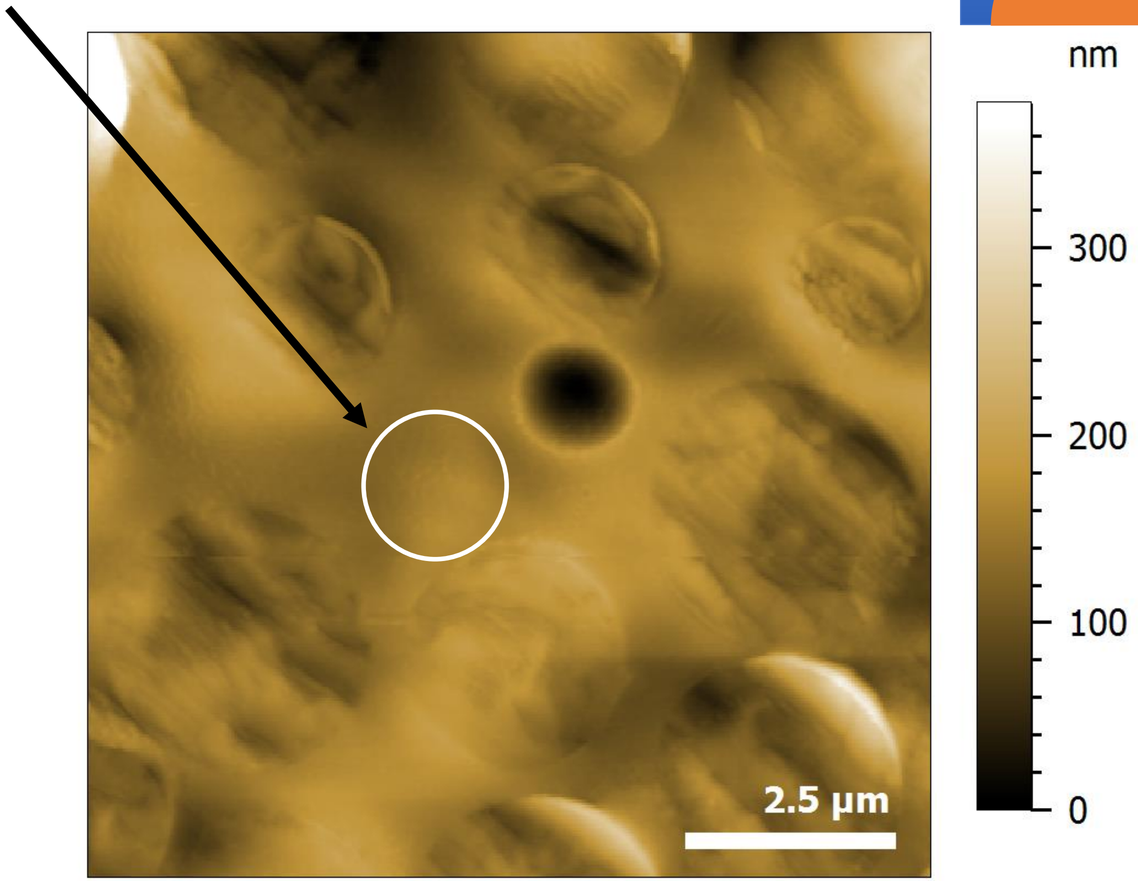
Collab. Philippe Leclere U-Mons

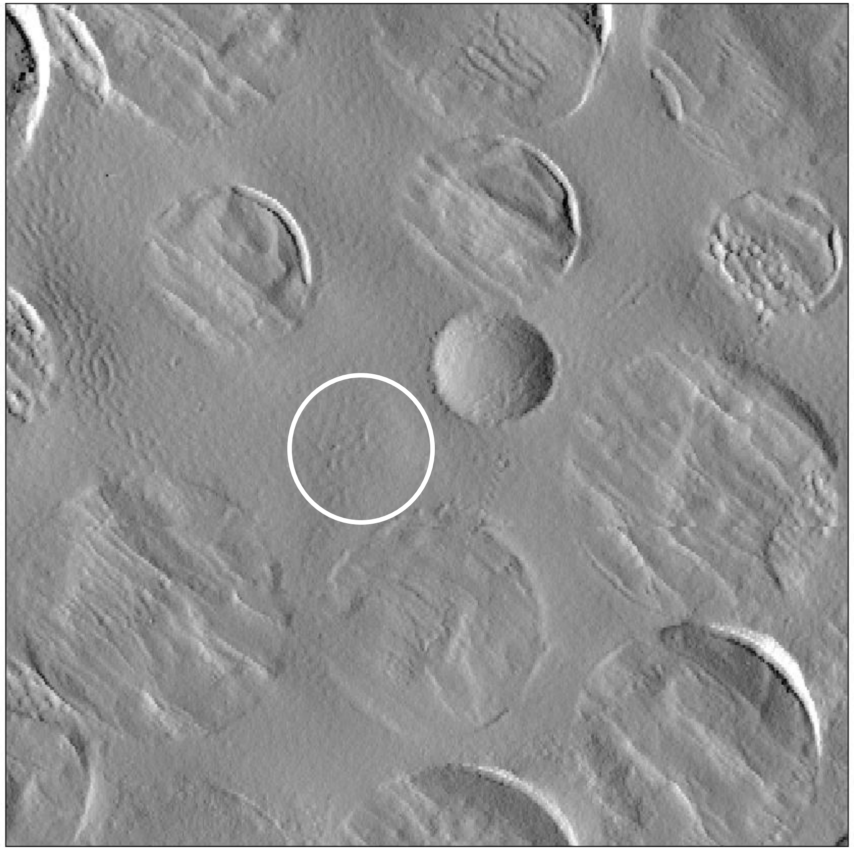
2. AFM-IR theory and concept



Probing depth of AFM-IR ?

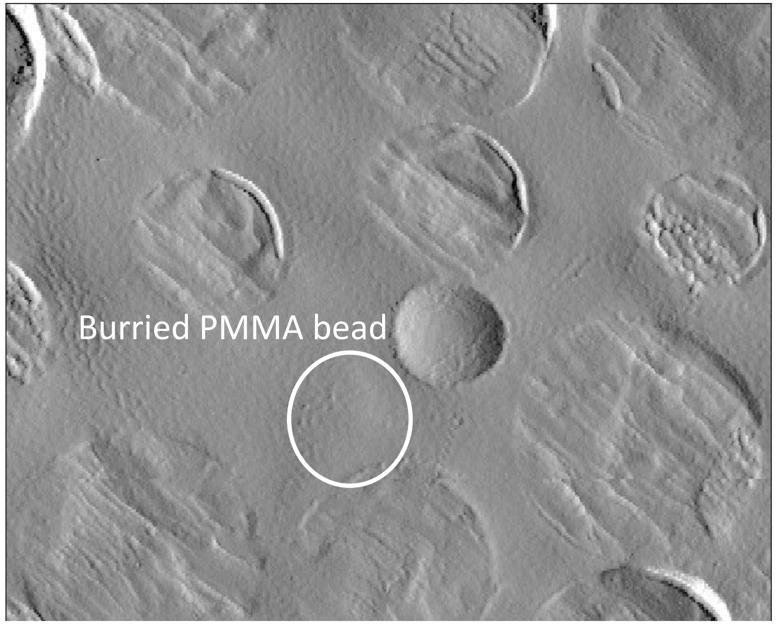
Burried PMMA bead

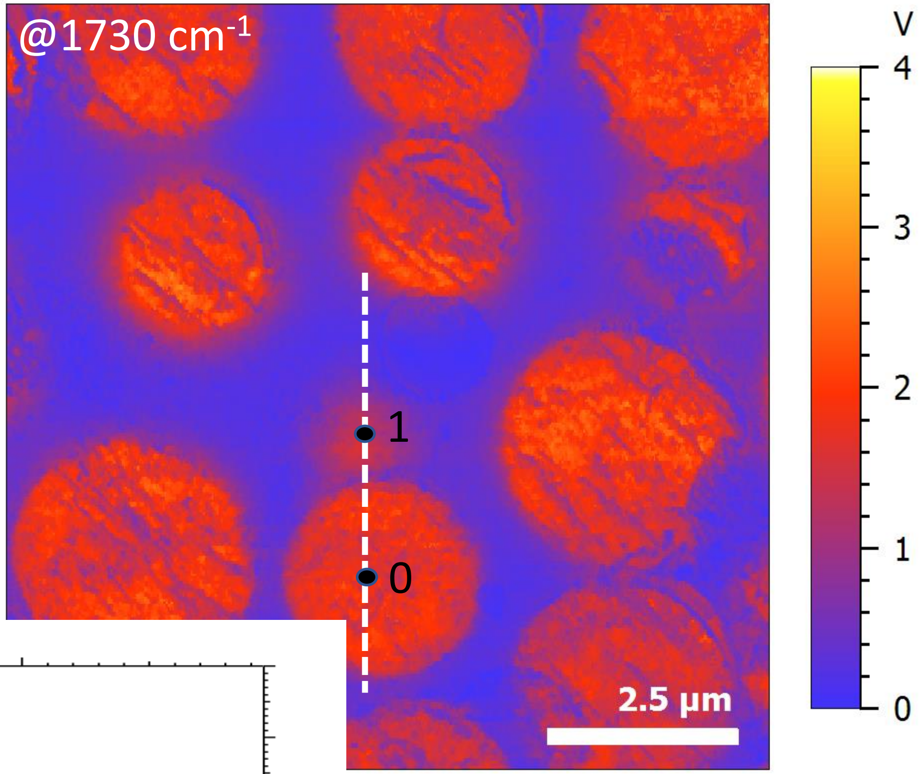


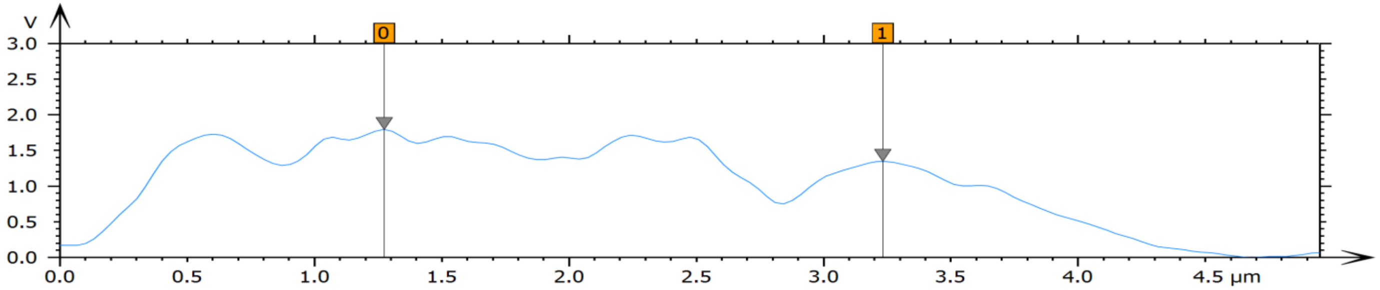


Probing depth of contact resonance AFM-IR

f_{laser} = 205 kHz



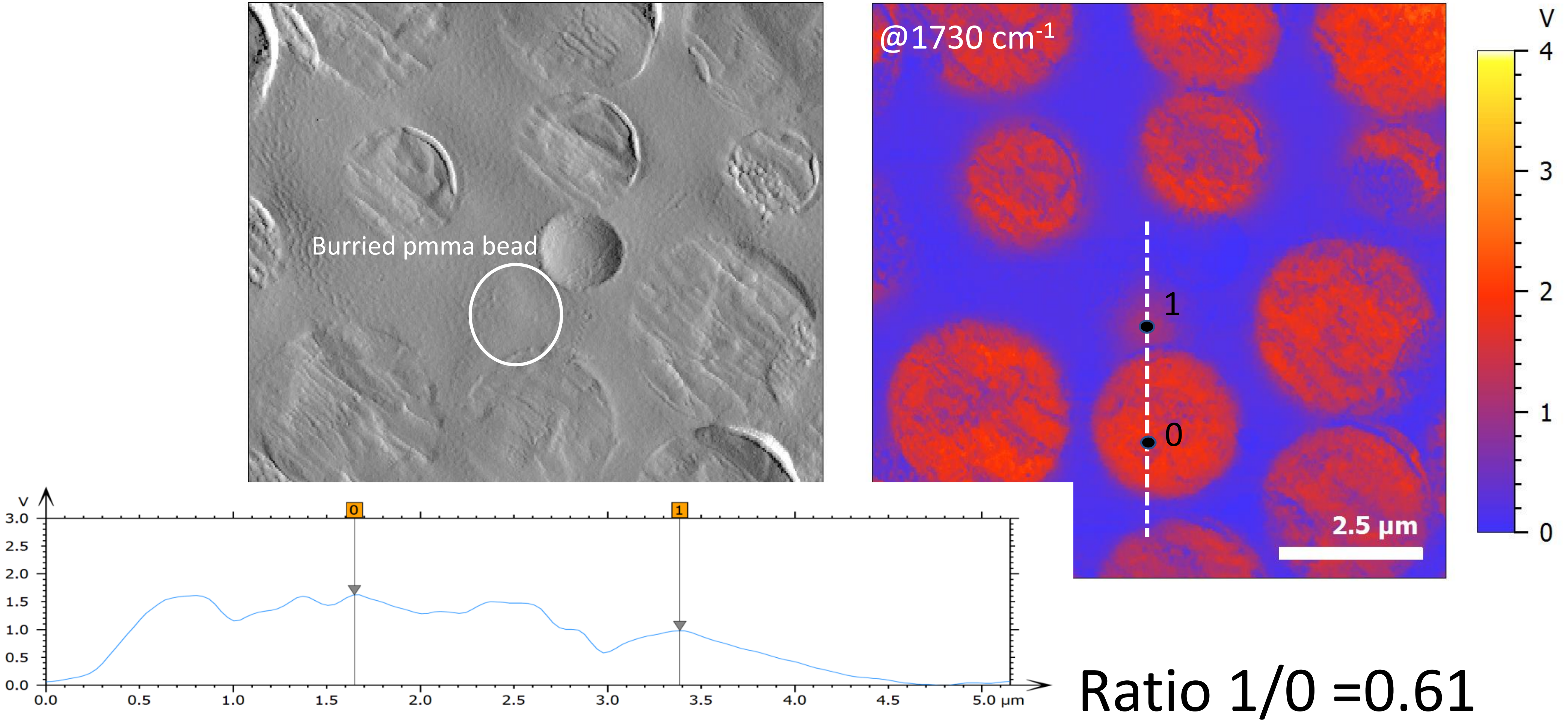




Ratio 1/0 =0.75

Probing depth of contact resonance AFM-IR

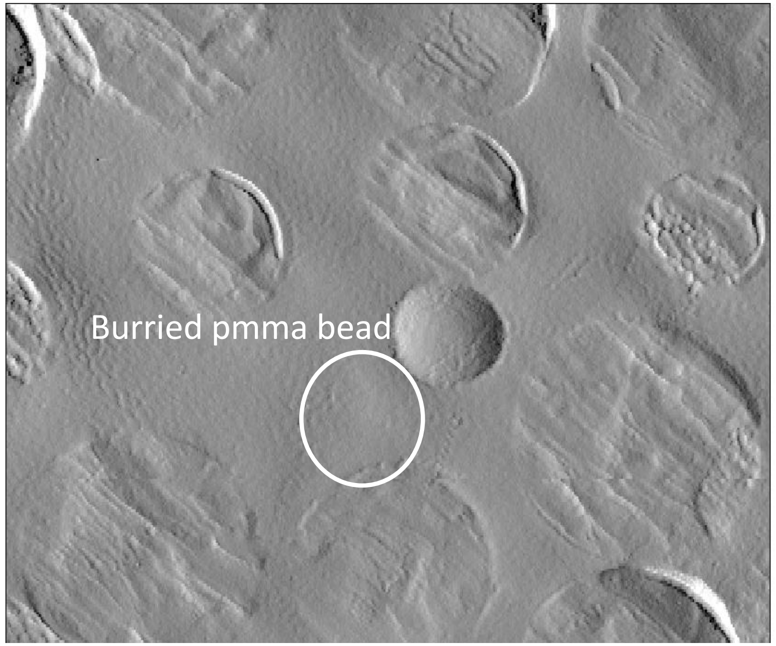
$$f_{laser} = 550\ kHz$$

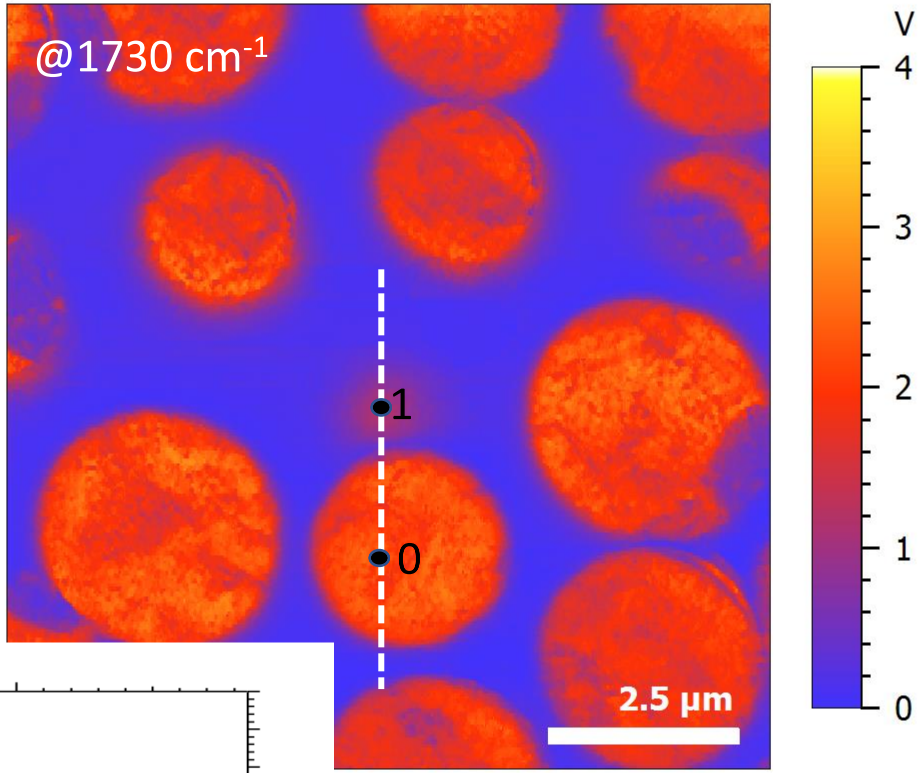


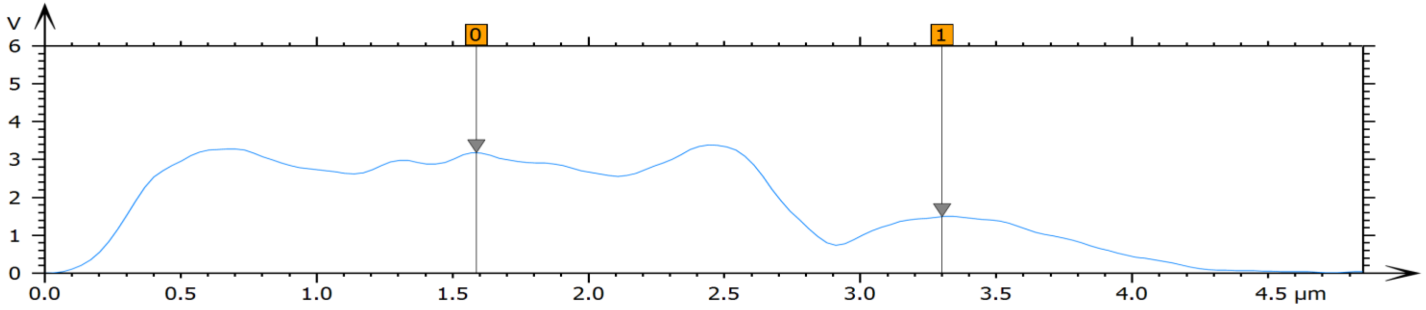
Ratio 1/0 =0.61

Probing depth of contact resonance AFM-IR

$f_{laser} = 1250$ kHz



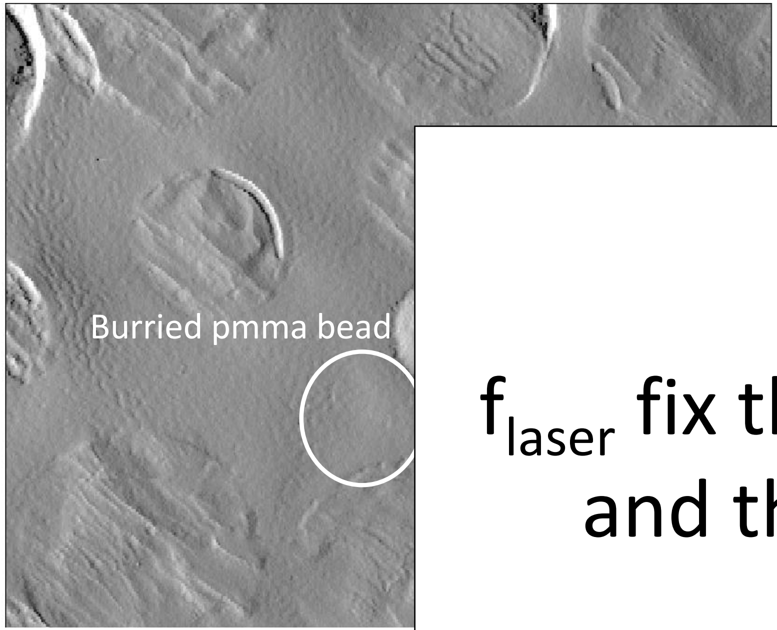


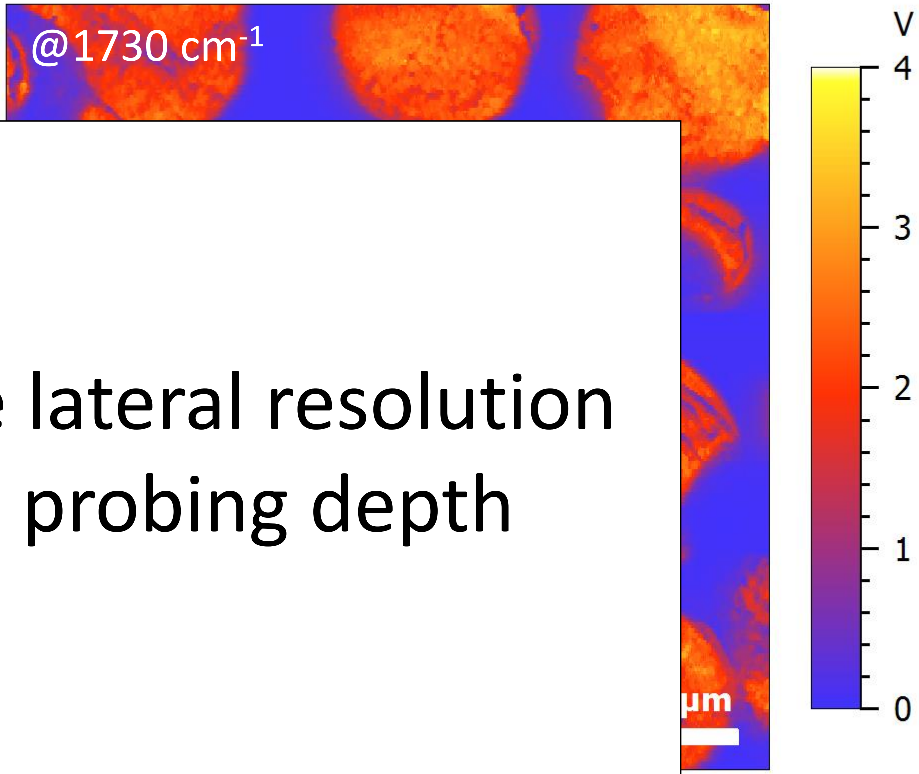


Ratio 1/0 =0.47

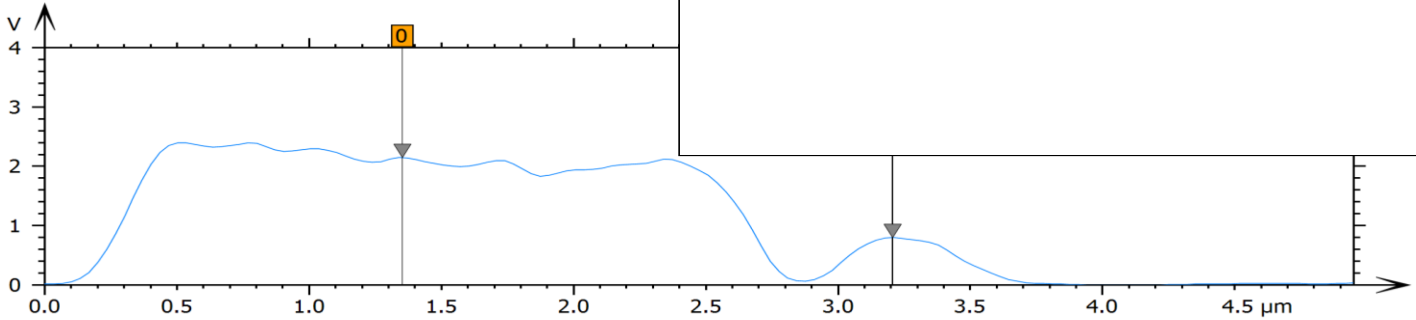
Probing depth of contact resonance AFM-IR

f_{laser} = 1750 kHz



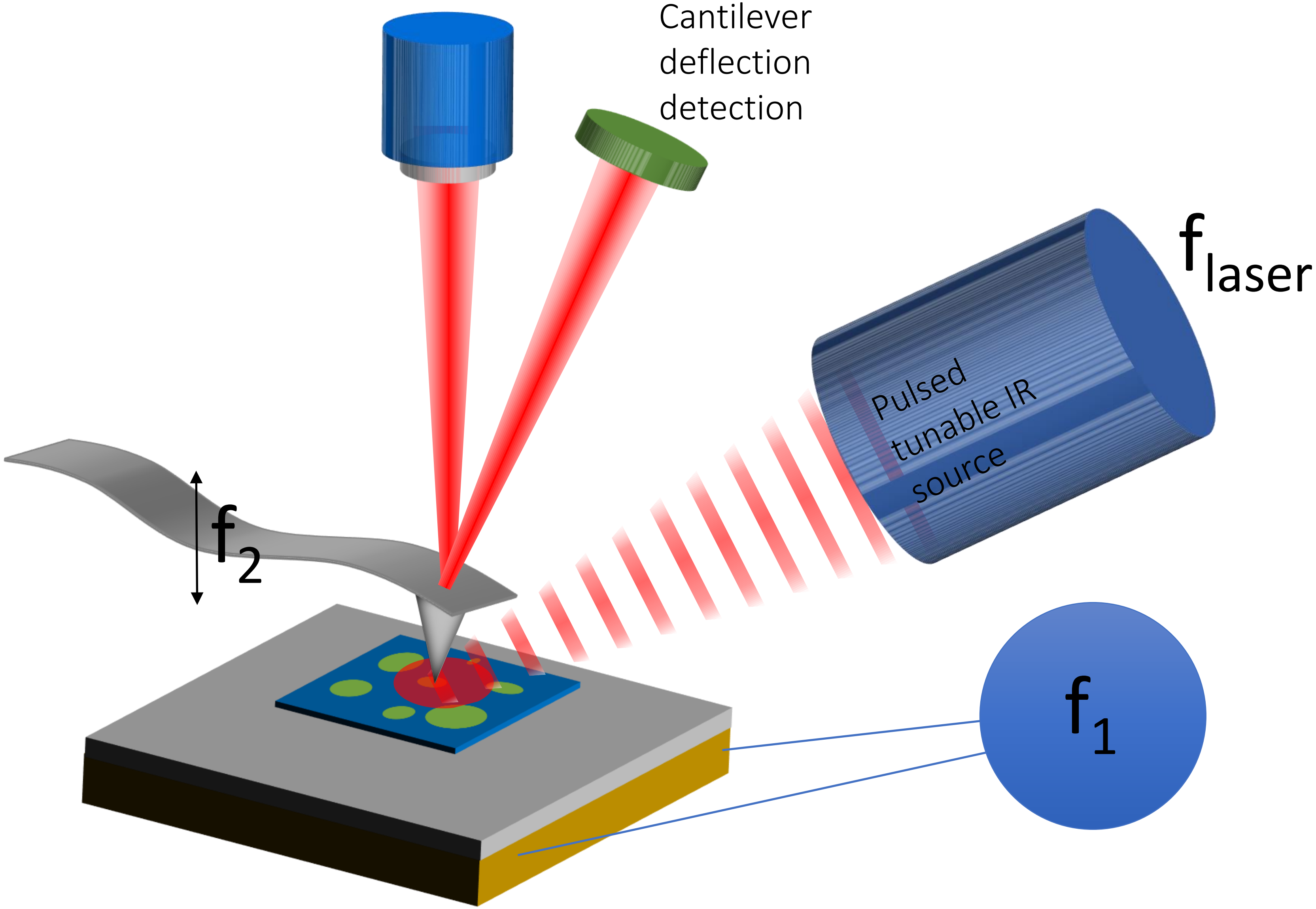


f_{laser} fix the lateral resolution and the probing depth



Ratio 1/0 =0.37

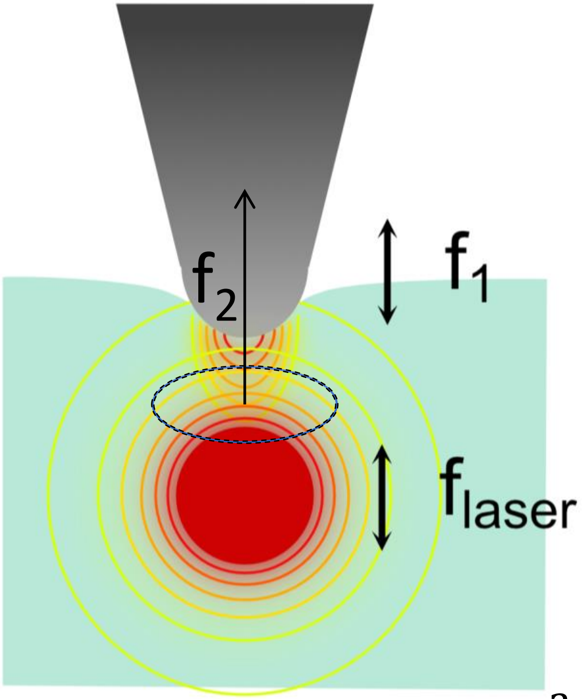
Surface sensitive AFM-IR setup



2. AFM-IR theory and concept

Motion equation of the cantilever mode

$$\ddot{z}_2 + \Gamma \dot{z}_2 + (2\pi f_2)^2 z_2 = \frac{1}{m^*} F_{int}(t)$$



$$F_{int}(t) = k_z(\delta_0 + A_1 \sin(2\pi f_1 t) - a(f_{laser}; t))^{3/2}$$

$$= k_z\left(\delta_0 + A_1 \sin(2\pi f_1 t) - a(f_{laser}; t)\right) + \chi_z\left(\delta_0 + A_1 \sin(2\pi f_1 t) - a(f_{laser}; t)\right)^2 + \cdots$$

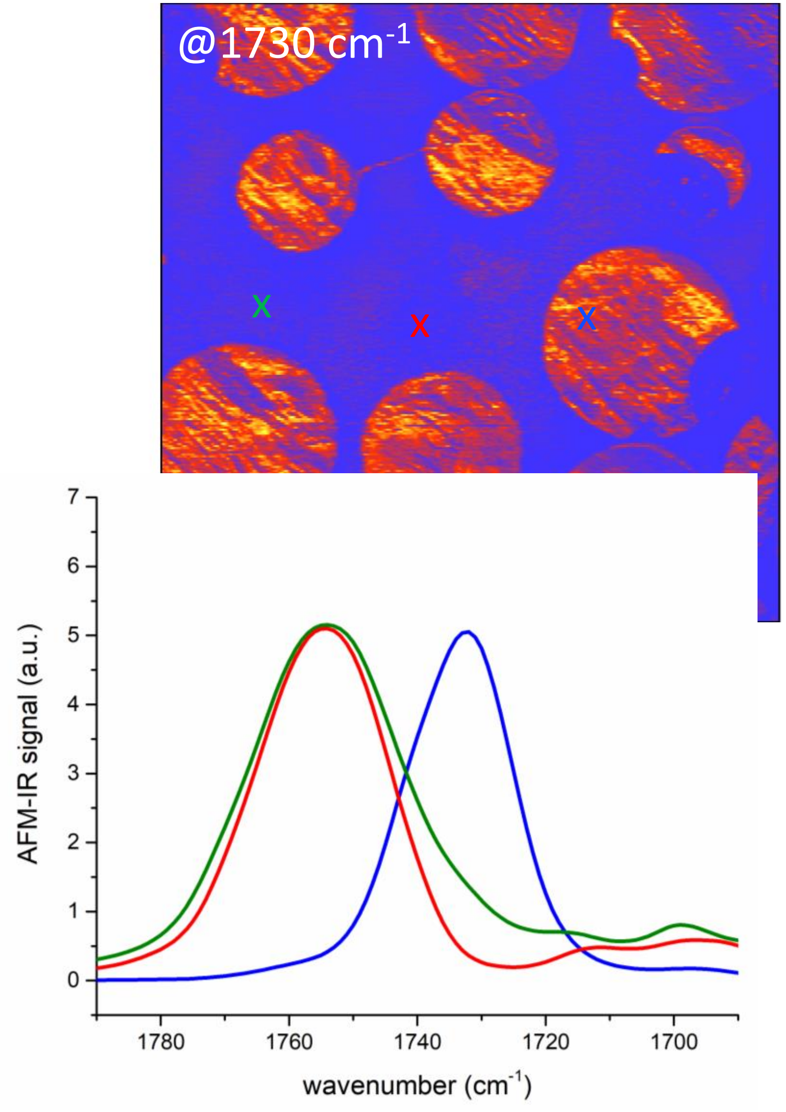
$$= 2\chi_z A_1 \sin(2\pi f_1 t) a(f_{laser}; t) \longrightarrow \begin{matrix} \cos(2\pi(f_1 - f_{laser})t) \\ \cos(2\pi(f_1 + f_{laser})t) \end{matrix}$$

Only if $f_1 + f_{laser} = f_2$ or $f_1 - f_{laser} = f_2$

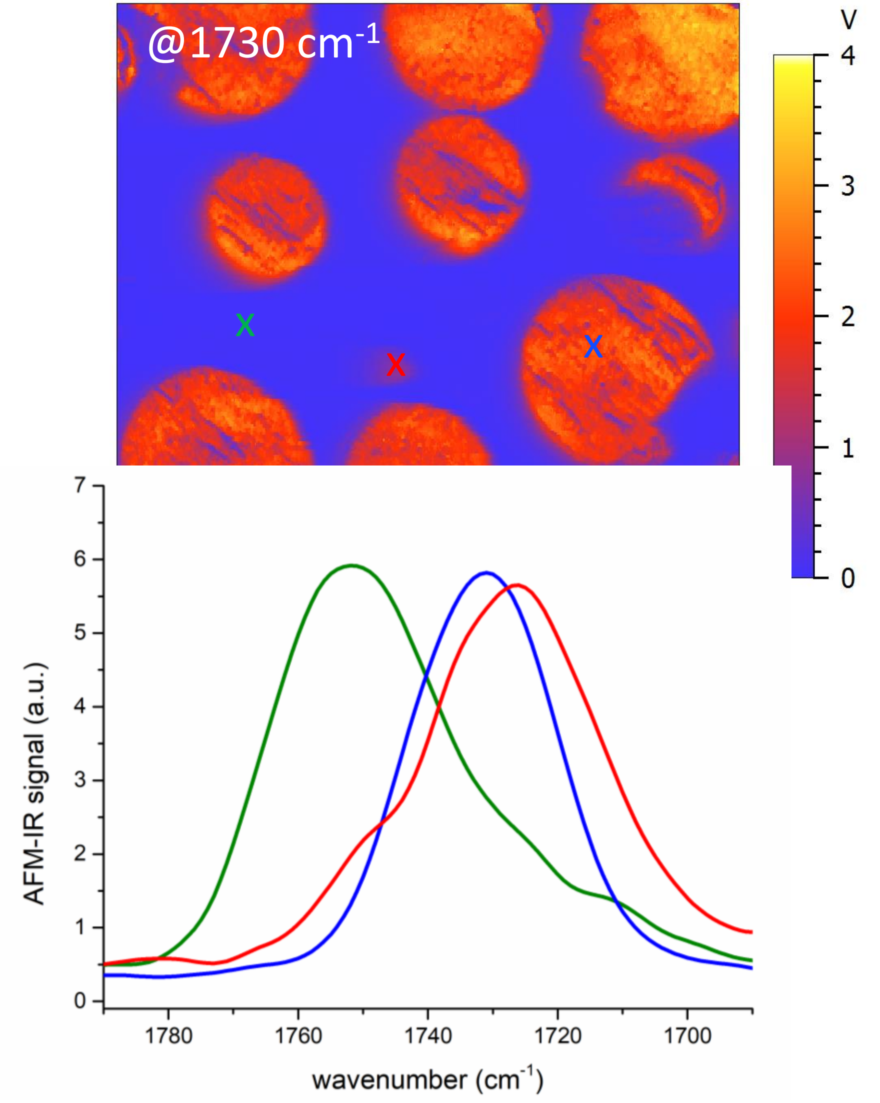
$$z_2 = 2\pi^2 \chi_s \frac{Q_2}{k_c} A_1 f_{laser} t_p a_0$$ μ absorbance

2. AFM-IR theory and concept

Surface sensitive mode
(f_1=2130kHz ; f_{laser}=1650 kHz)



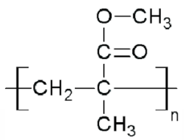
Resonance enhanced mode
(f_{laser}=1750 kHz)

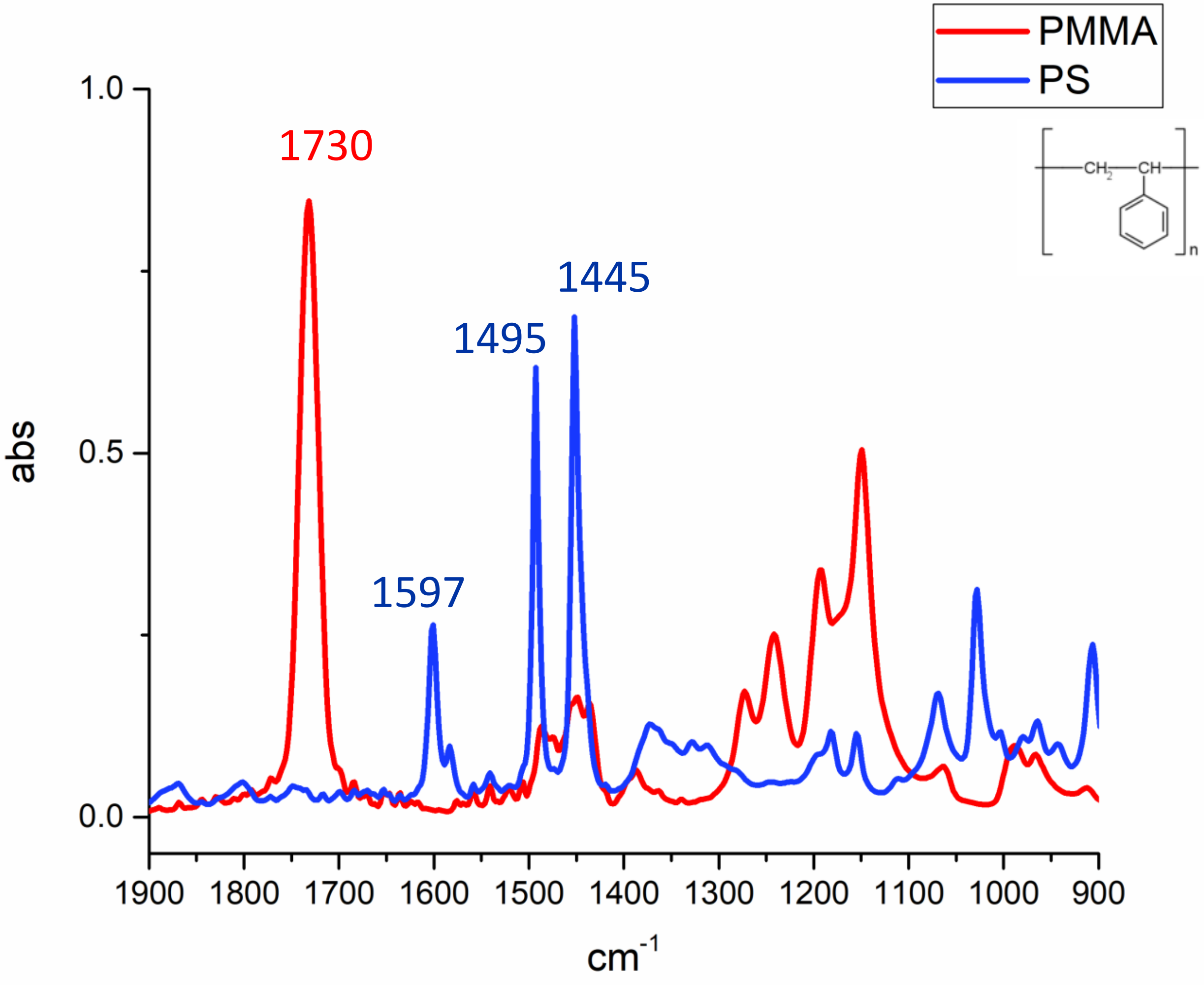


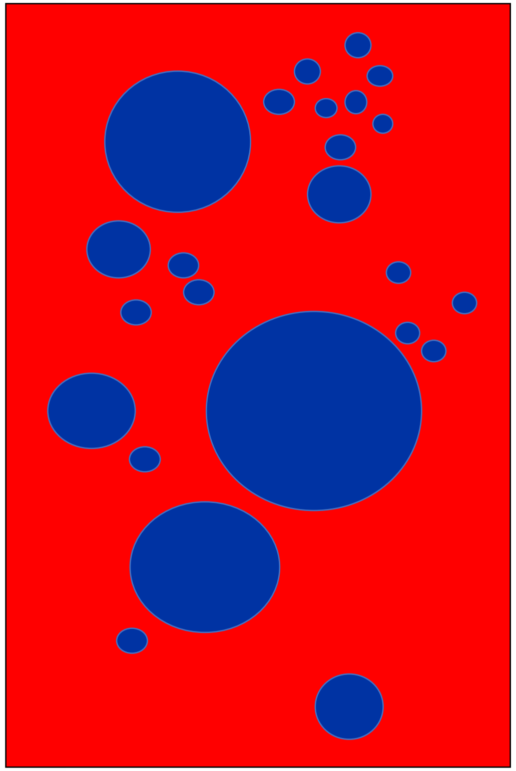
2. AFM-IR theory and concept

PMMA-PS polymer blend 1-1

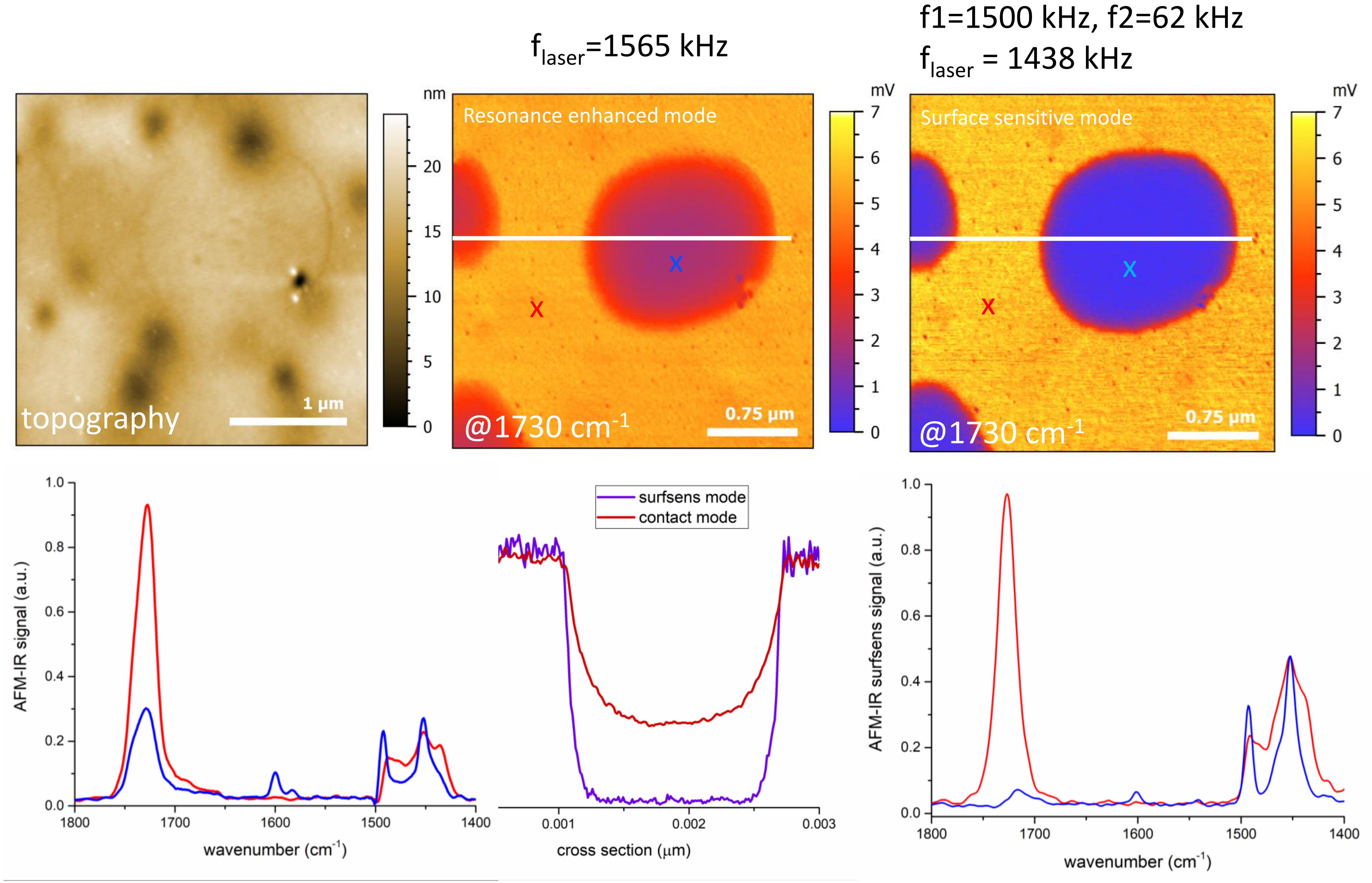
(Philippe Leclere , Université de Mons, Belgique)





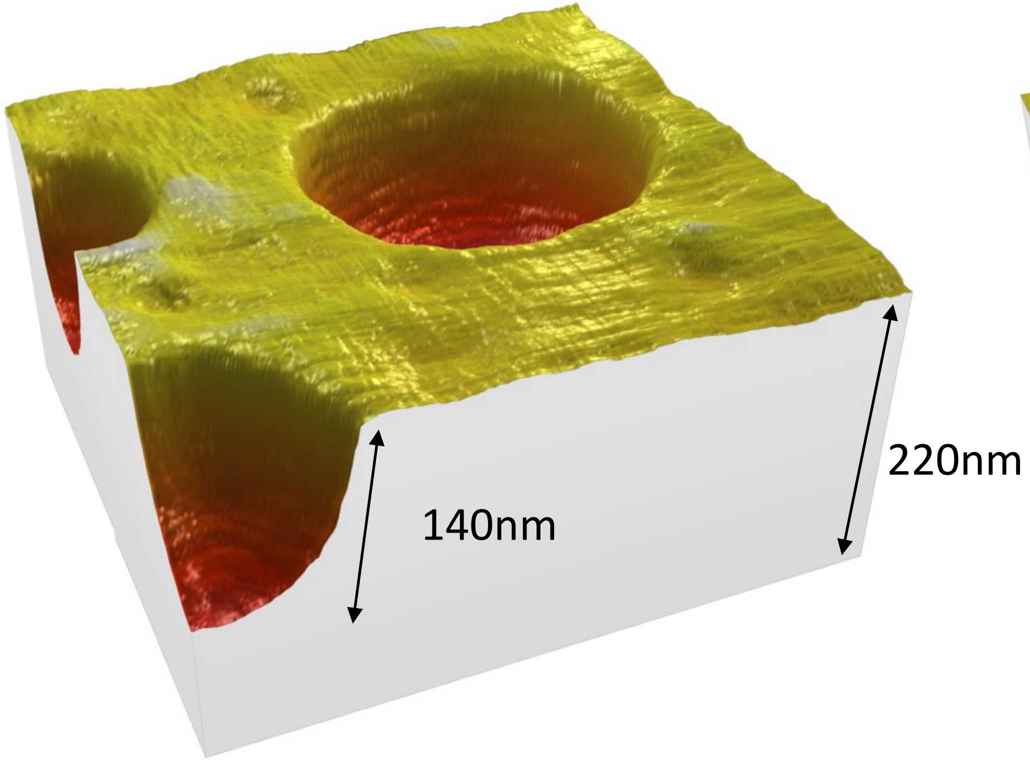


2. AFM-IR theory and concept

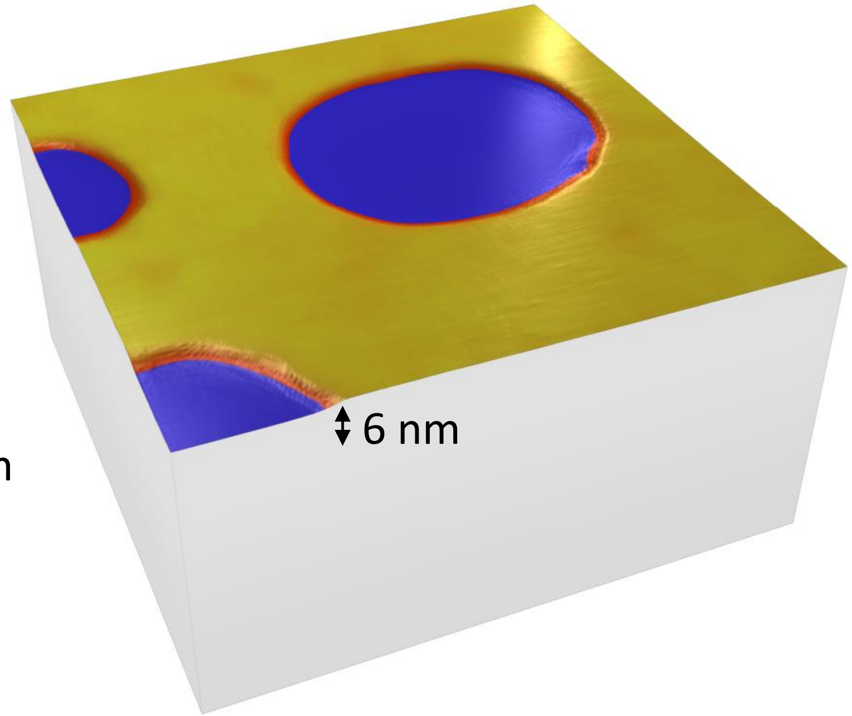


PMMA-PS blend

Resonance enhanced mode



Surface sensitive mode



APPLICATIONS EXAMPLES:

from bio to space via polymer and surface chemistry

« when ICON makes AFM-IR more powerfull»

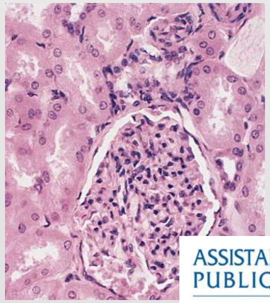
- Quality of electronics
- Mechanical and acoustic stability
- Minimum thermal drift (0.5 nm/min)

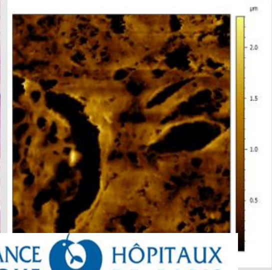
↓

Lead to have a PLL working very well and able to correct perfectly the mechanical change during IR mapping
Better data quality with better S/N ratio, get rid of most of the artifacts, reproducability of IR maps.

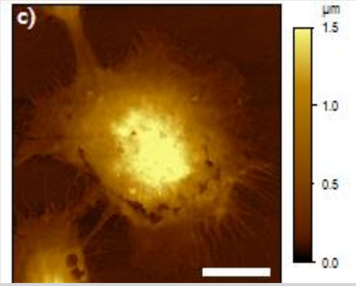
Field of applications - Biology

TISSUE – Human cells





Calcification in human tissues
Extracellular vesicles
Penetration of nanocarriers

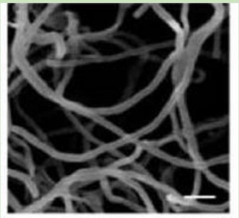


Nanoparticules and cell: macrophage

Fine structure of the hair…

MICRO-ORGANISMS

Accumulation of biopolymer or lipids

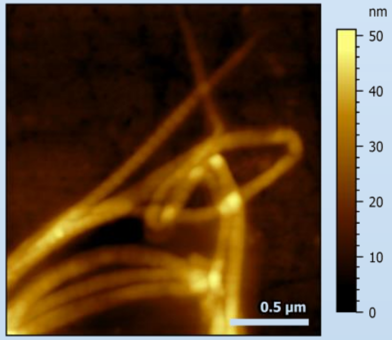


Localisation and quantification

Local composition, TAG, DAG, MAG and FFA differentiation

NANOMETRIC SCALE

Protein assemblies



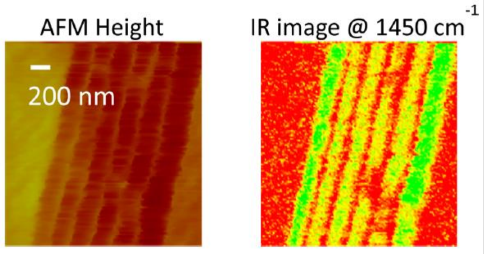
Collagen fibrils denaturation
System complex: Collagen-antibiotic

Bacterial amyloids
Beta structure of amyloids
Prion, lipids bilayer

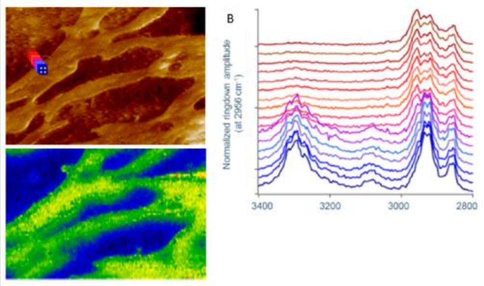
Field of applications

Polymers sciences

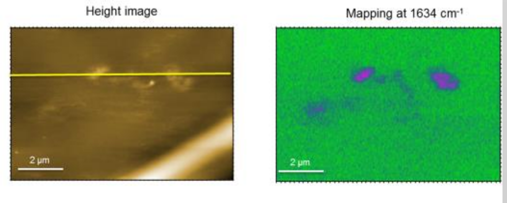
Multilayers:
Structure-cristallinity



A Dazzi, Chem Rev, 2016



Trace of adjuvant blooming



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

Heritage sciences

- Investigate parchments degradation

ÉCOLE POLYTECHNIQUE UNIVERSITÉ PARIS-SACLAY

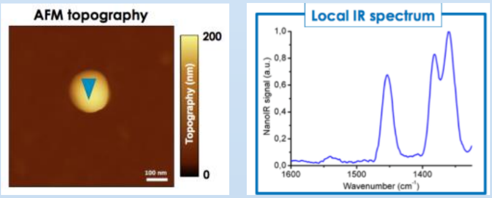
G.Latour, Scientific Report, 2016

- IR signatures: heterogeneities in ancient tissues or violin sections

IPANEMA ARCHAEOLOGY CONSERVATION SCIENCES PALAEONTOLOGY PALAEO-ENVIRONMENTS ANCIENT MATERIALS RESEARCH PLATFORM

Nanoparticles

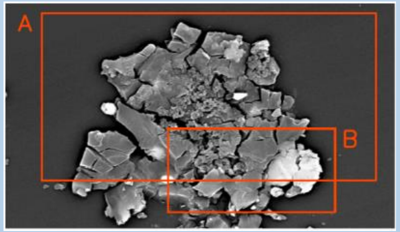
- Polymeric Nps



Mathurin J., 10.1039/C8AN01239C, Analyst, 2018

Astrochemistry

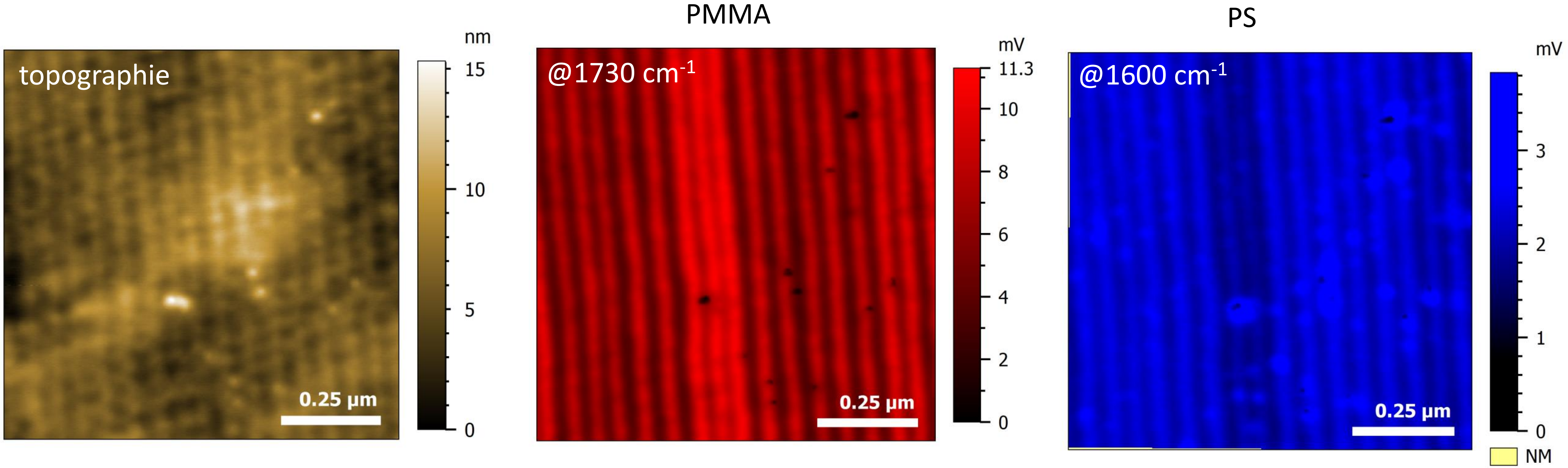
- Investigation of organic matter in micrometeorites



CSNSM

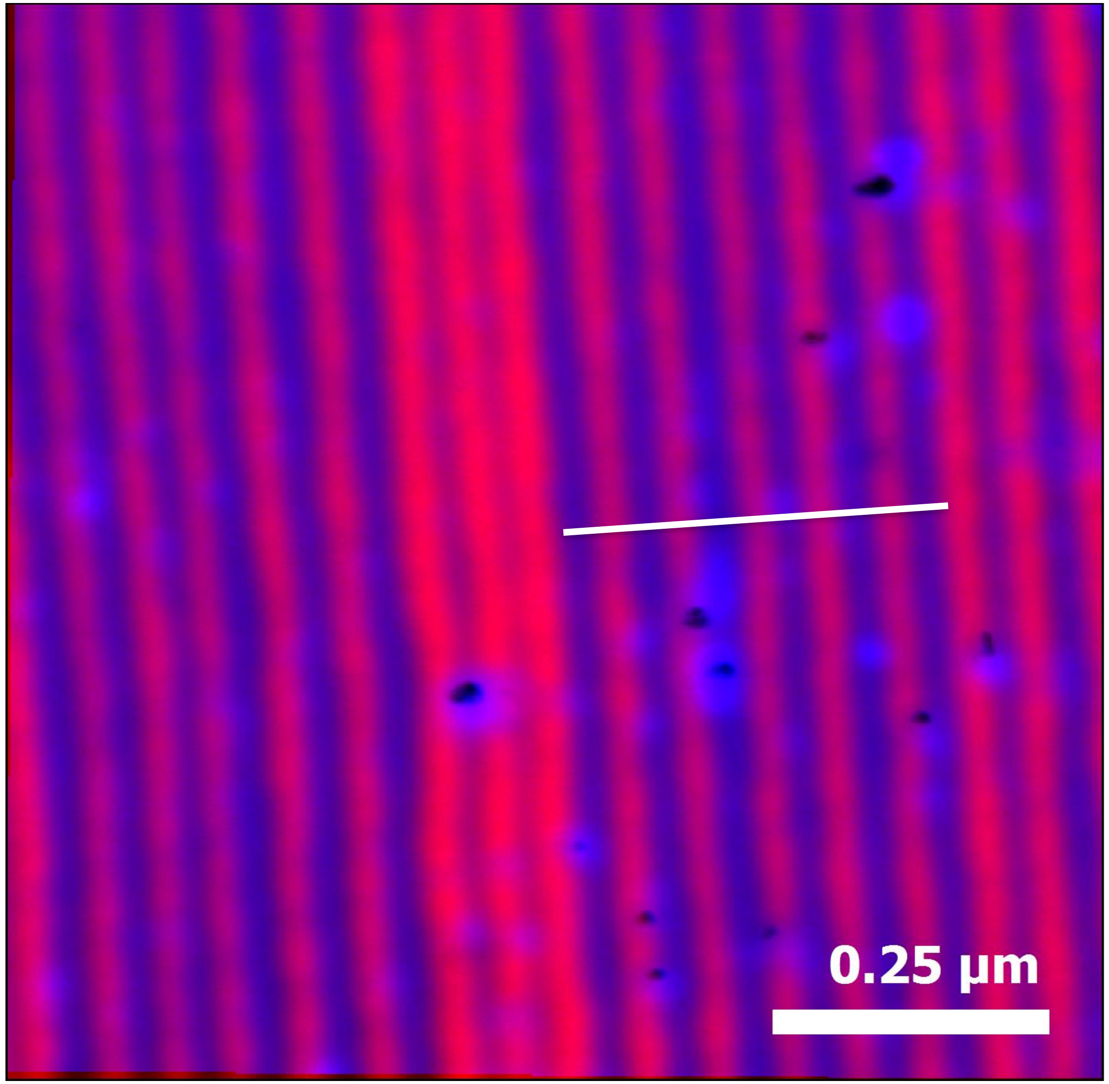
J. Mathurin, A&A, 2019

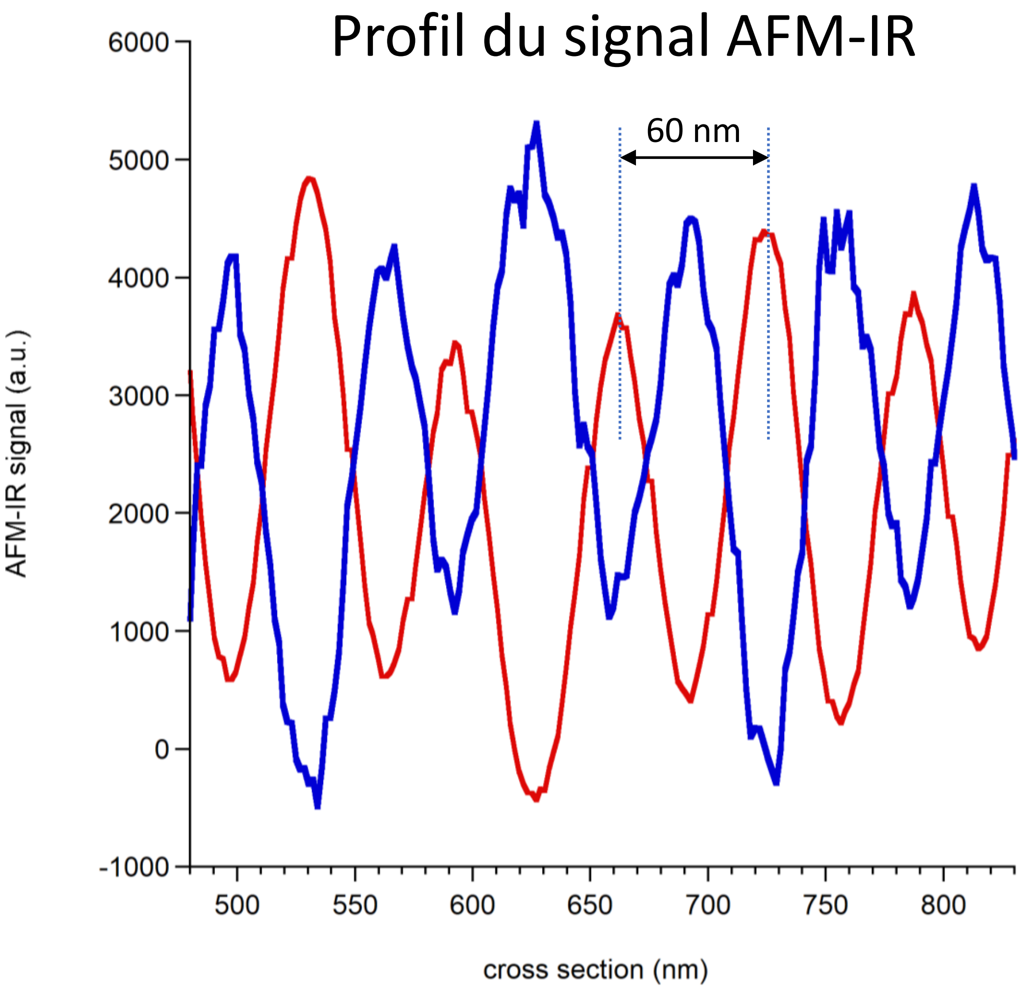
PS-PMMA multi-layers film



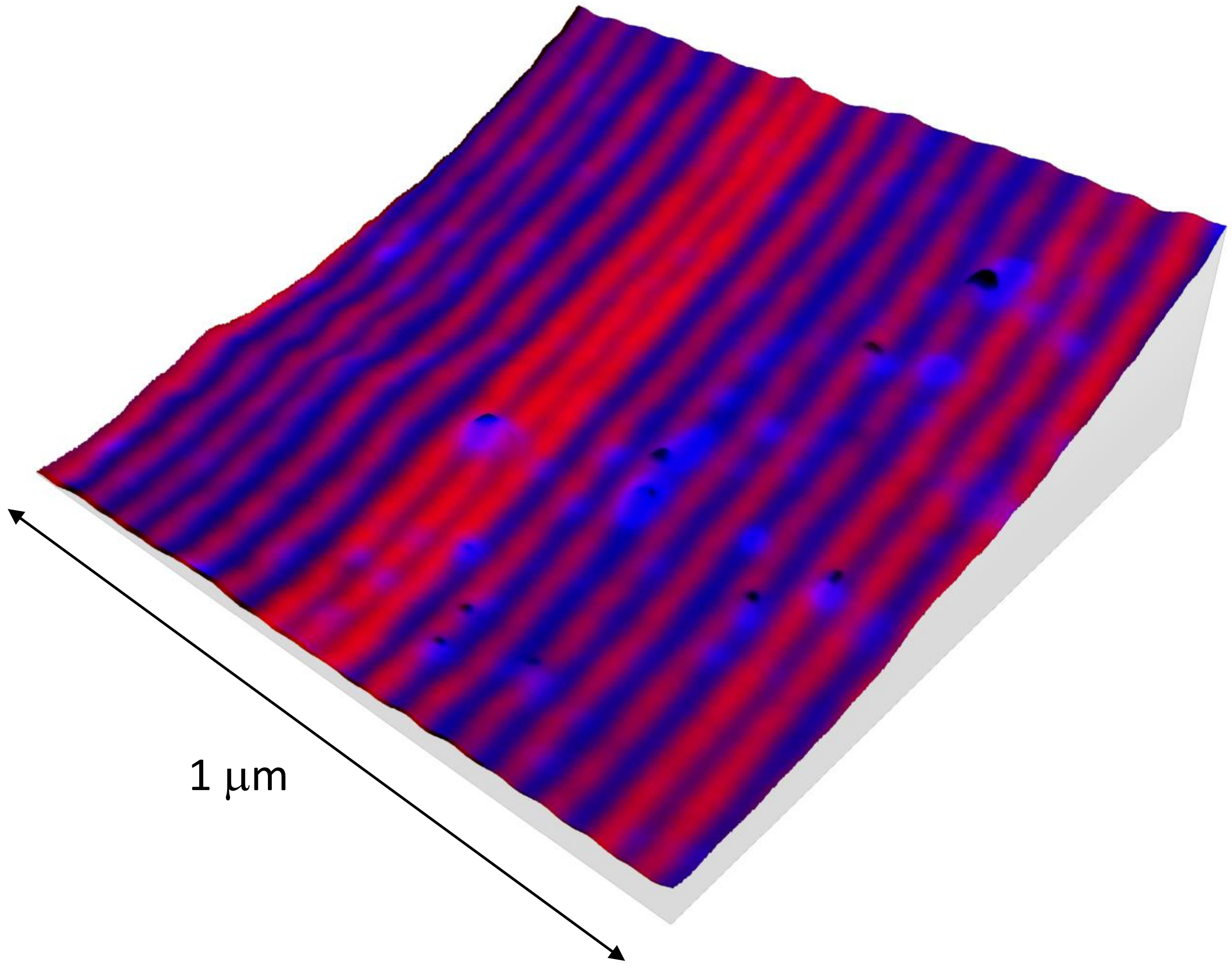
Collab. G. Miquelard-Garnier CNAM

Overlay imaging (1730 and 1600)





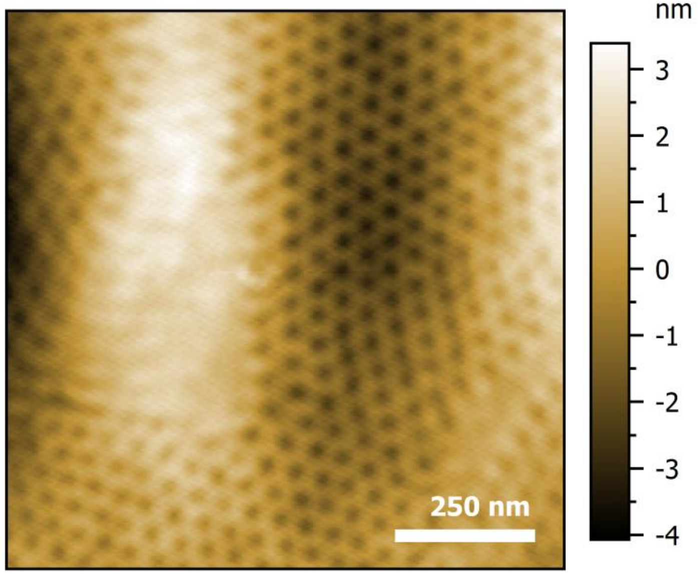
3D overlay imaging

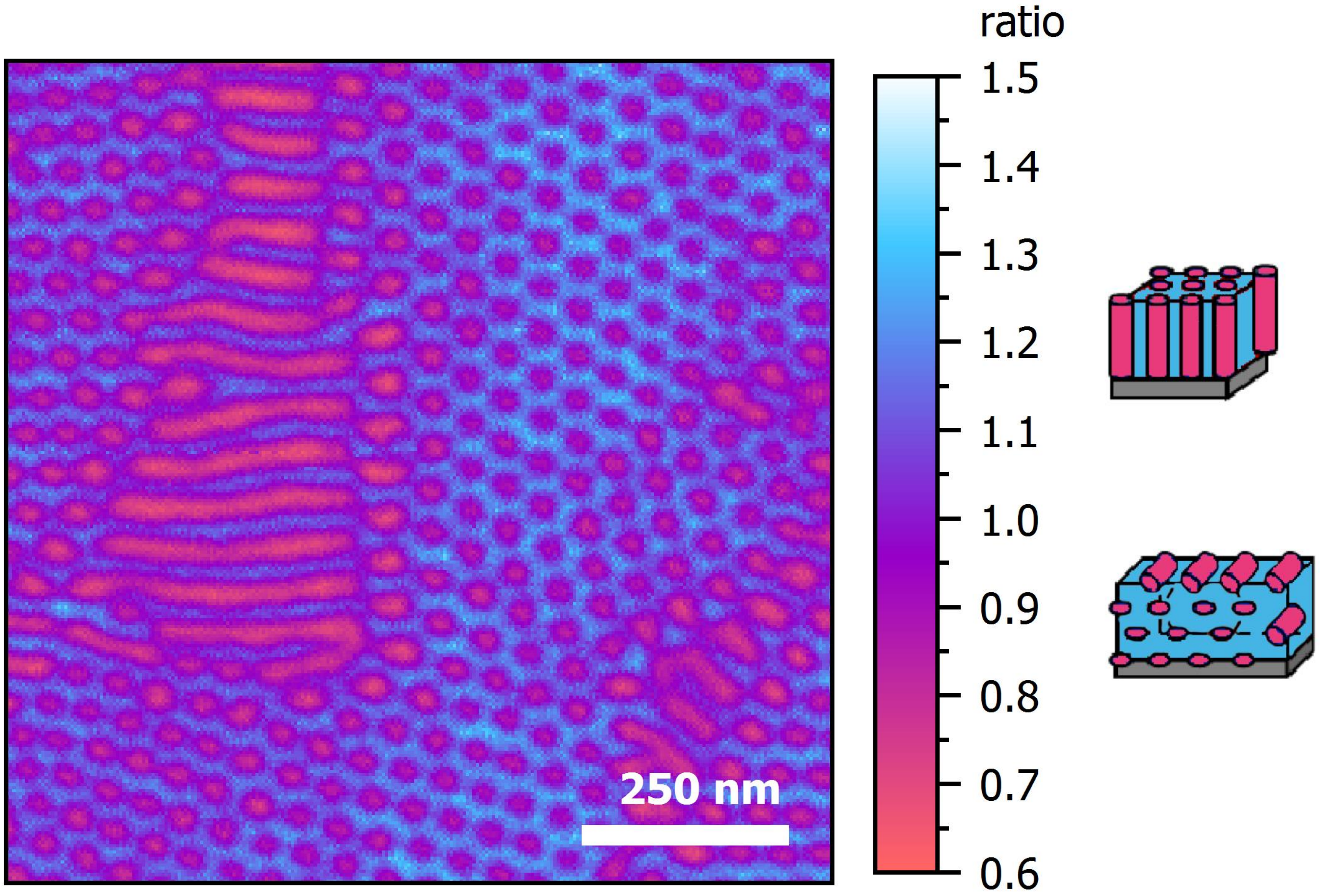


3. Applications examples

Structuration of PLA/PS copolymer

topography





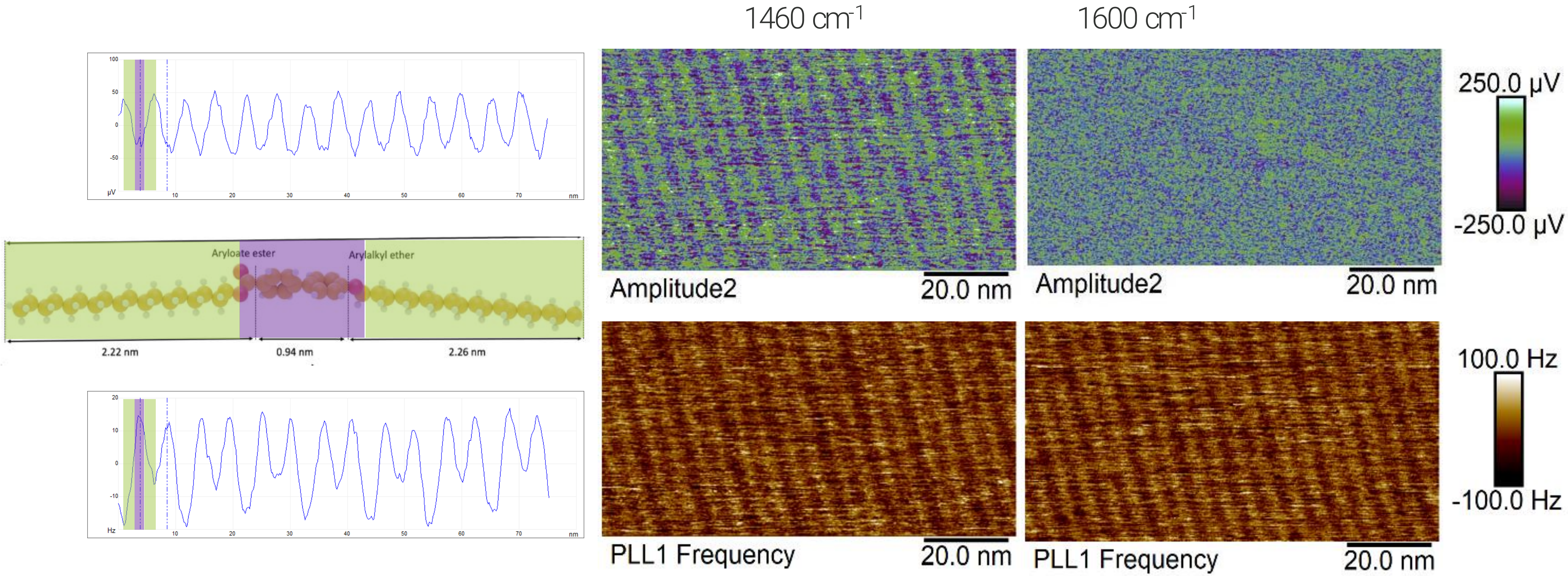
Molecular monolayer (OC18) on HOPG

octadecyl 4’-octadecyloxy-4-biphenylcarboxyloate

11h00 Ali HAMADEH
Toward conformational identification of molecules in 2D and 3D self-assemblies on surfaces

Collab. F.Palmino et F.Cherioux institut FEMTO-ST

3. Applications examples



- Resolution: **1-2 nm** (10-90% 'level')
- Monolayer (0.8 nm) sensitivity on HOPG
- Low drift: < 0.2 nm/min

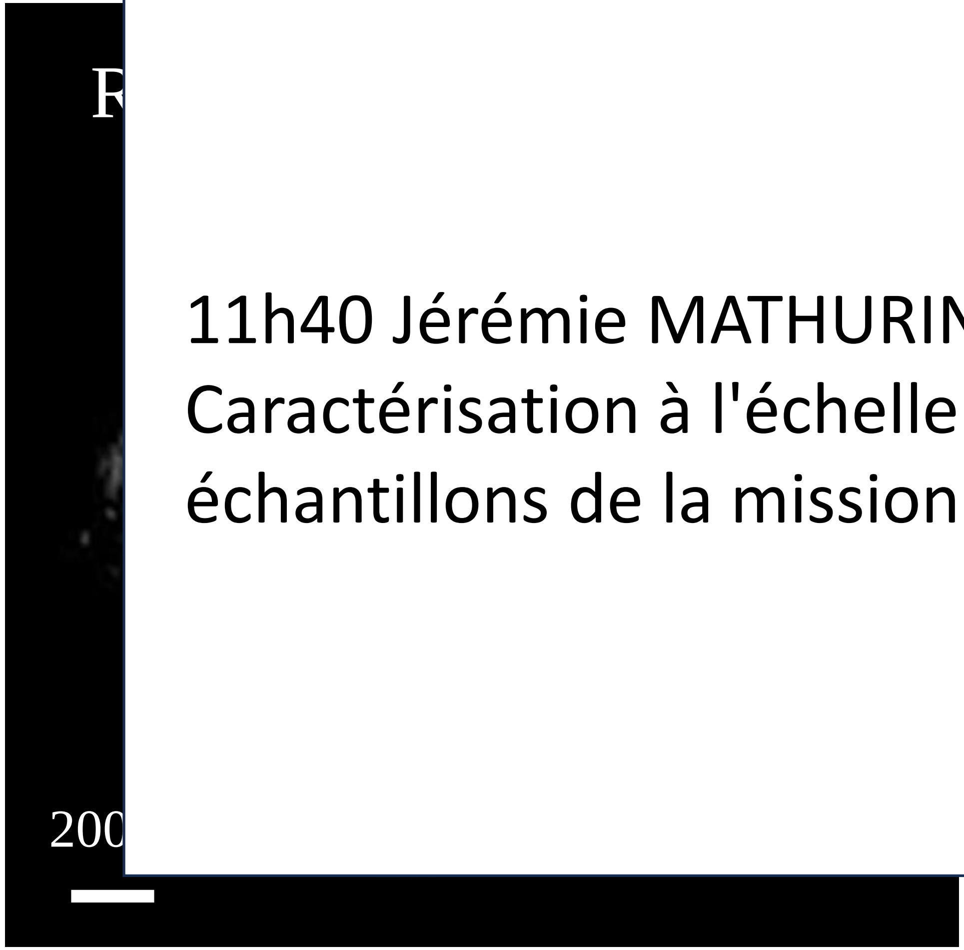
Collaboration with

- Dr. Peter Dewolf (Bruker)
- Pr. Frank Palmino (Université de Franche-Comté, FEMTO-ST)
- Dr. Frédéric Chérioux (CNRS, FEMTO-ST)

Hayabusa2 spatial mission

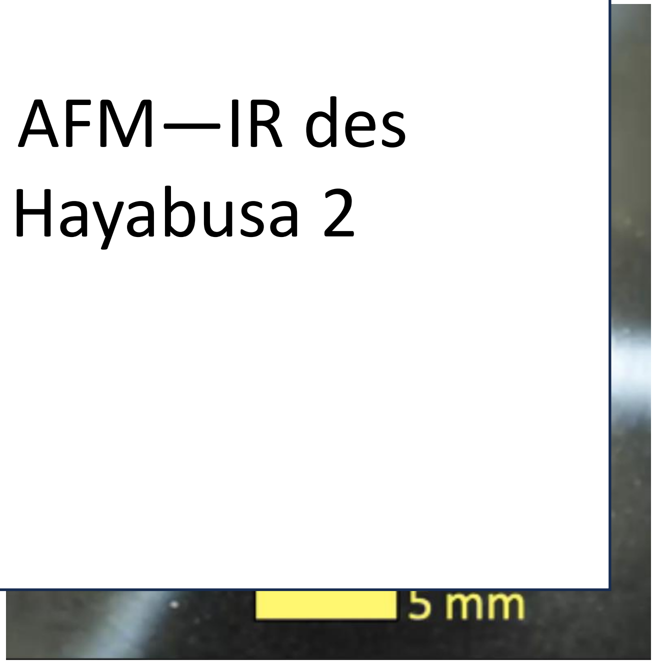
20

atter,



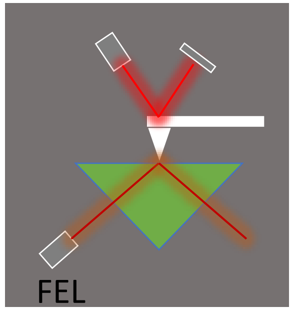
11h40 Jérémie MATHURIN

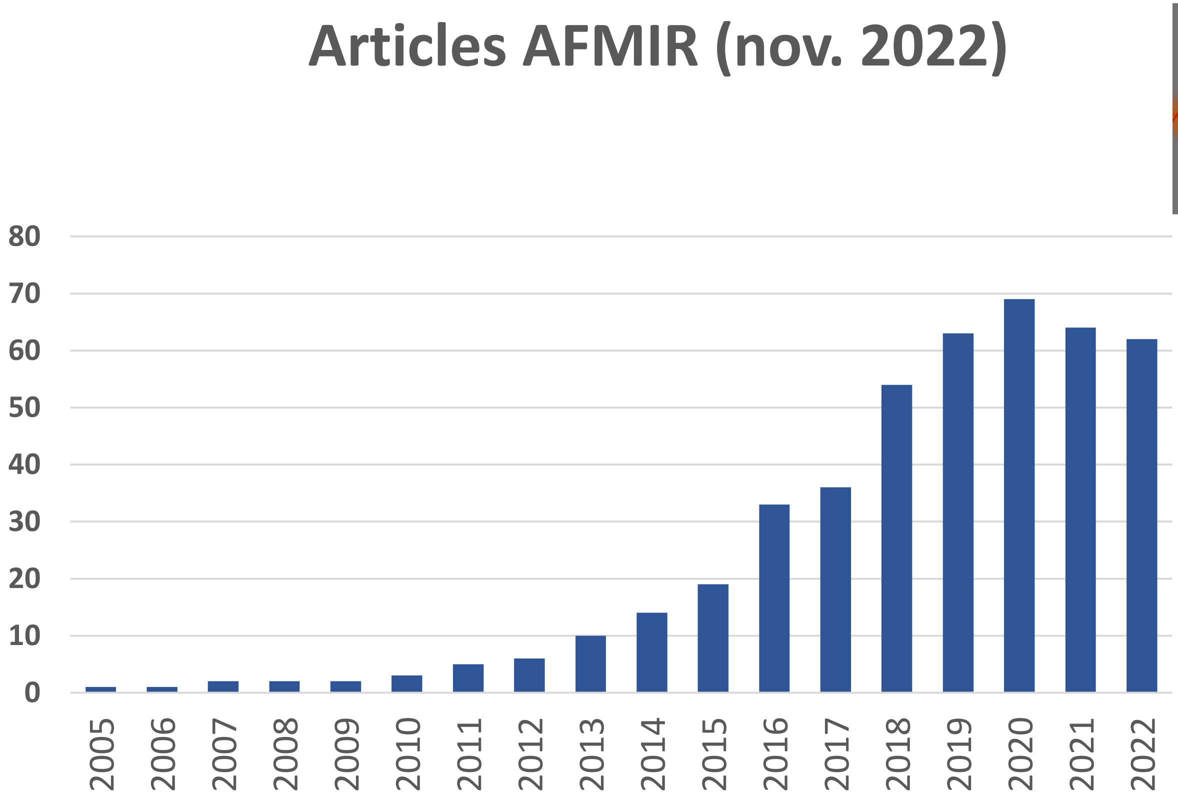
Caractérisation à l'échelle nanométrique par AFM—IR des échantillons de la mission spatiale japonaise Hayabusa 2

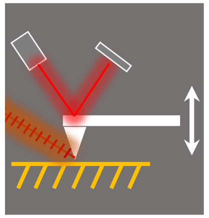


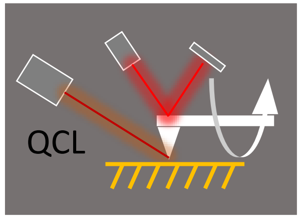
4. Evolution of the AFM-IR technique

contact	brevet	Mode contact	Mode résonant	Peakforce tapping IR	tapping AFM-IR	Surface sensitive	ForceVolume-IR
2004	2007	2010	2011	2017	2018	2022	2024







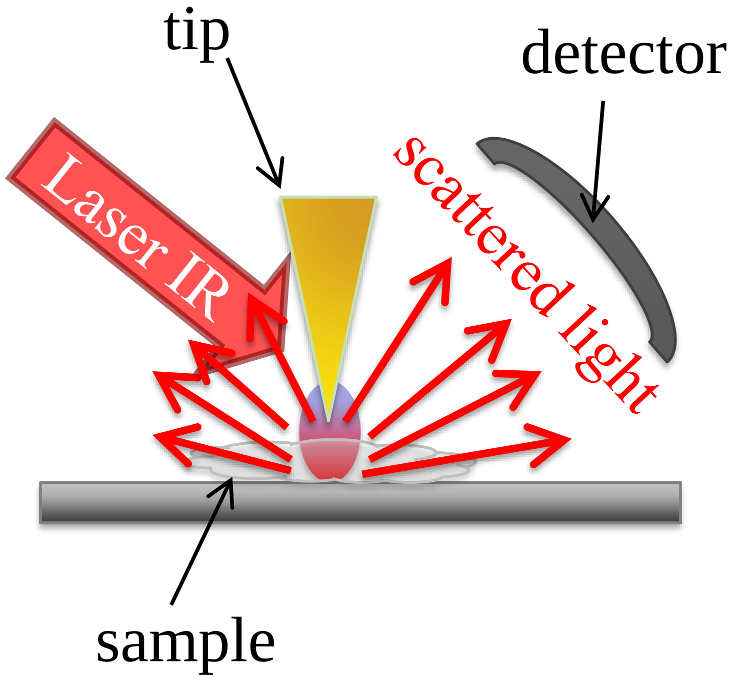


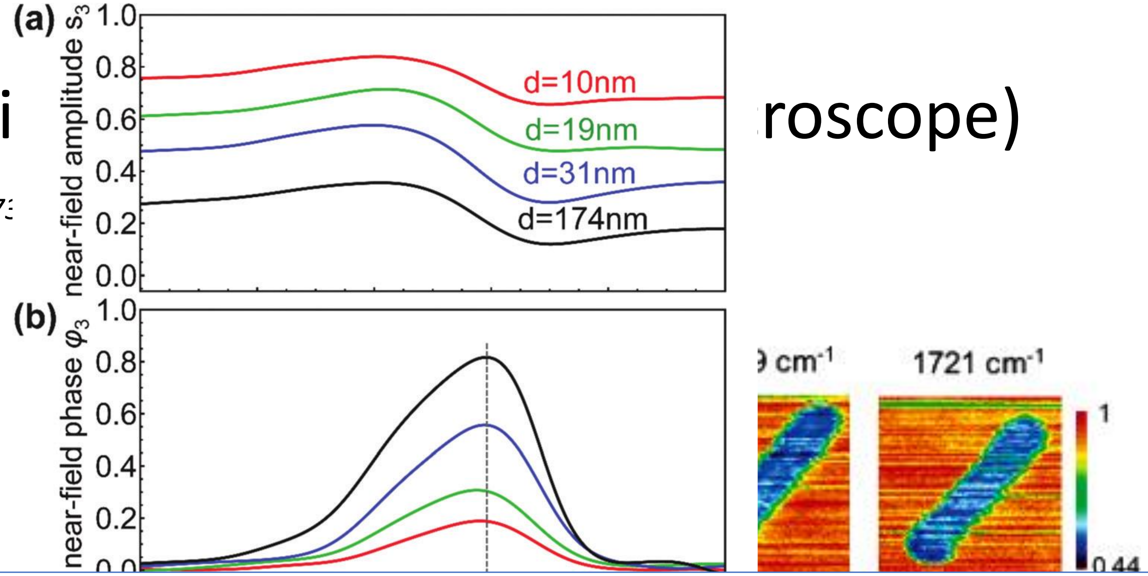
80% of nanoIR paper

5. Comparison with competitors

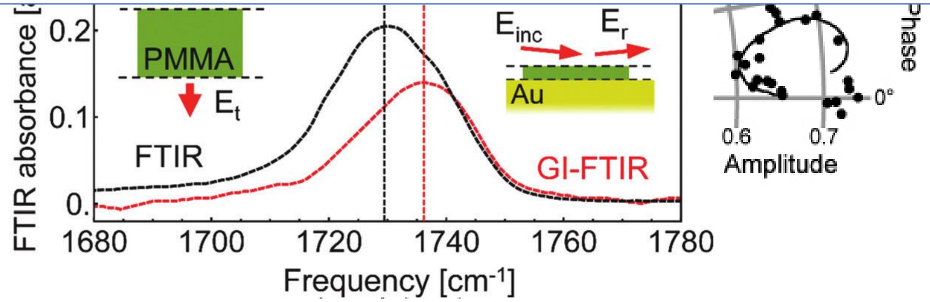
- Scattering SNOM (Scanni... roscope)

B. Knoll and F. Keilmann, Nature, Volume 399, Issue 67...



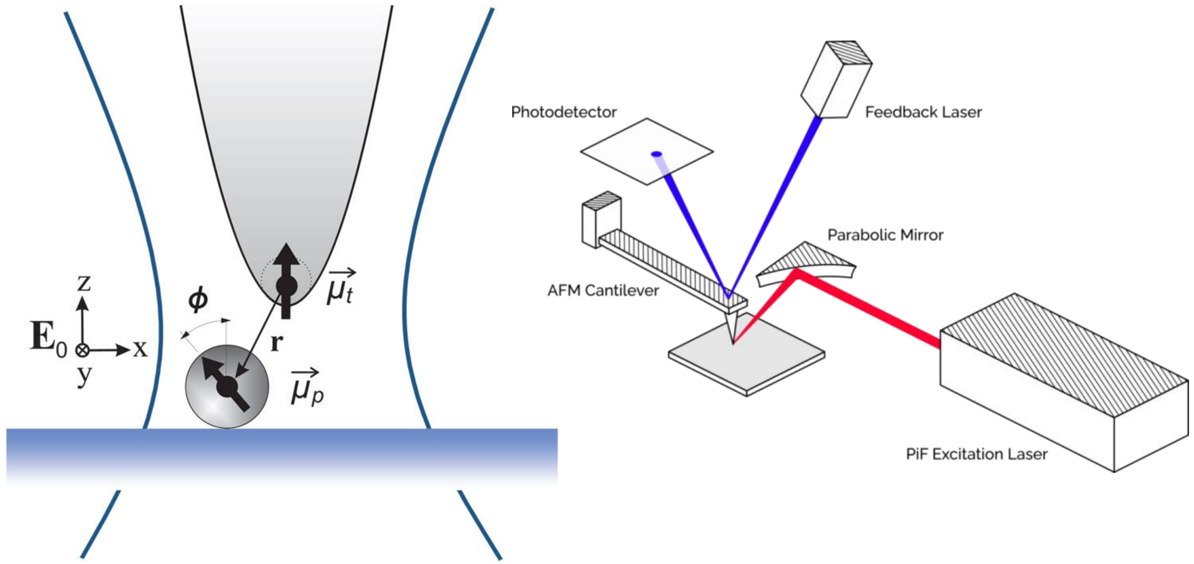


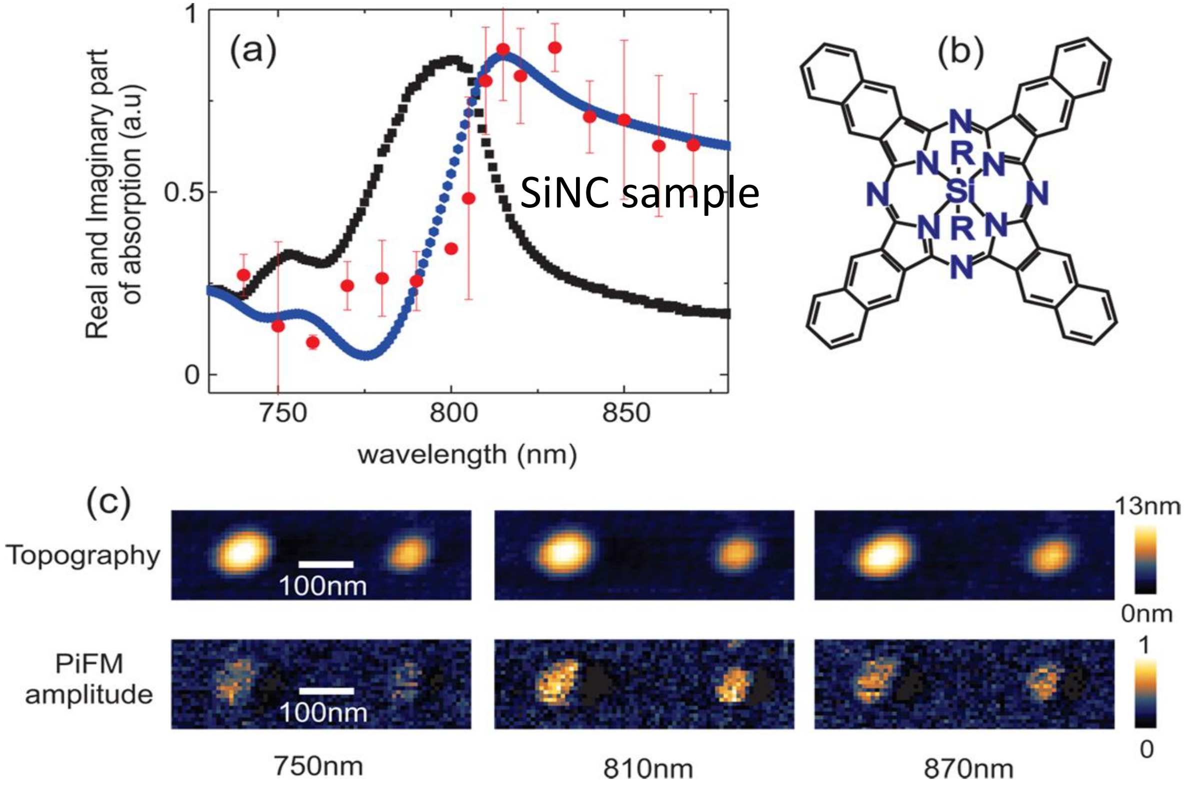
$$\text{Signal}(x,y) = \alpha(x,y)Re(n) + \beta(x,y)Im(n)$$



- PIFm (Photo-Induced Force microscope)

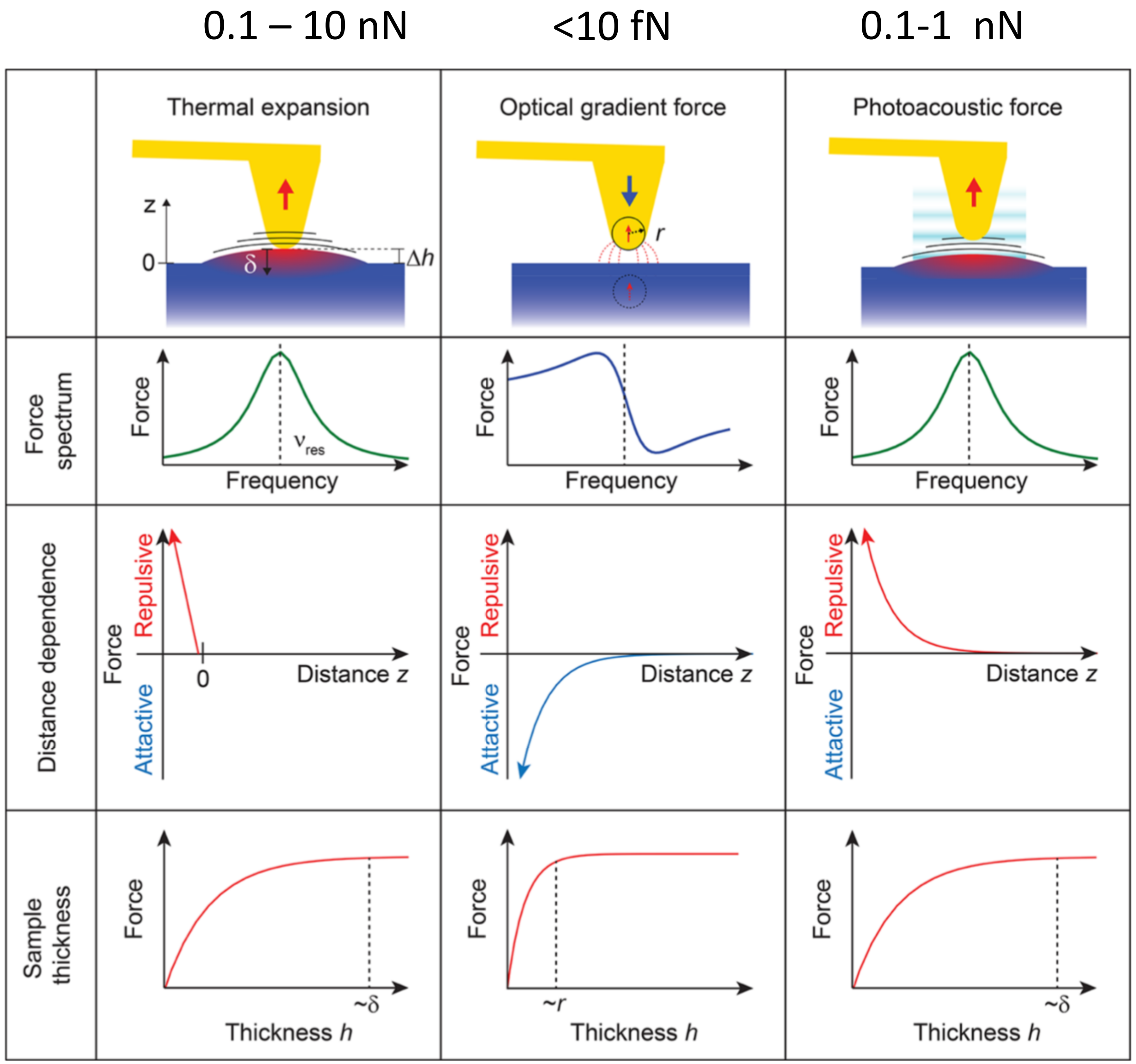
J. Jahng et al. *Acc. Chem. Res.* , 48, 2671−2679, **2015**





$$F \propto \frac{1}{z^4} Re(\alpha_t) Re(\alpha_s)\, {E_0}^2 \propto Re(n)$$

5. Comparison with competitors



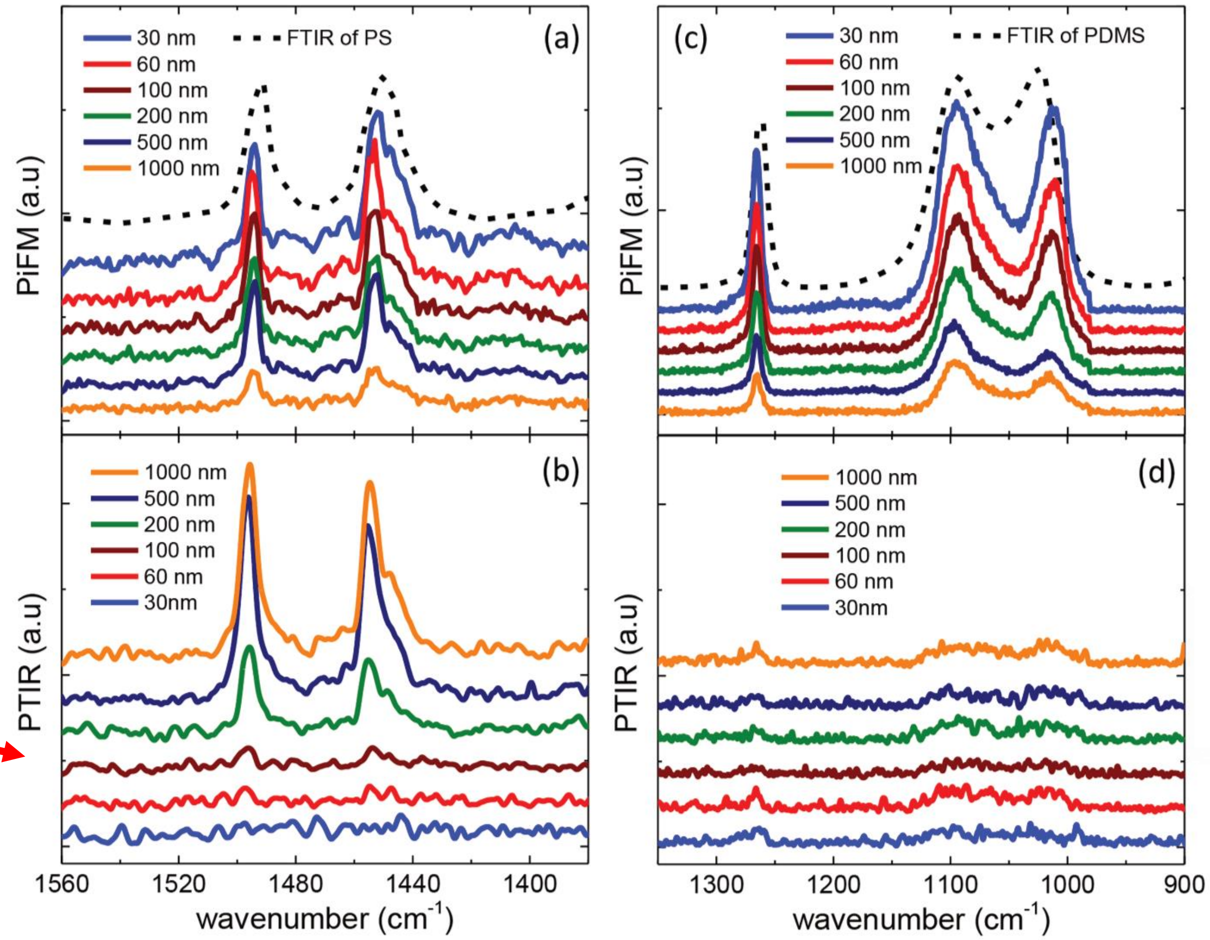
Brian T. O' Callahan et al. Nano Lett. 2018, 18, 9, 5499-5505

- PIFm (Photo-Induced Force microscope)

When conflict of interest (business) meets science

PiFm =Absorbance !?

What a joke ?



J. Jahng et al. Anal. Chem. 2018, 90, 18, 11054–1106

CONCLUSION and PERSPECTIVES

- AFM-IR is the only technique that allows a direct measurement of the imaginary part of the refractive index. IR spectrum are comparable to FTIR for amorphous materials.
- Lot of imaging modes : contact resonance, tapping, peakforce, surface sensitive, ForceVolume that allow us to choose the best investigating mode for specific sample and to suit in an optimum way.
- The advantage of AFM versatility open the door to numerous applications in a wide range of scientific domains
- Technique is still evolving : liquid, tomography, controlled environment
- AFMIR community increases each year that stimulate discussion and exchange between scientists

MUSIICS Platform

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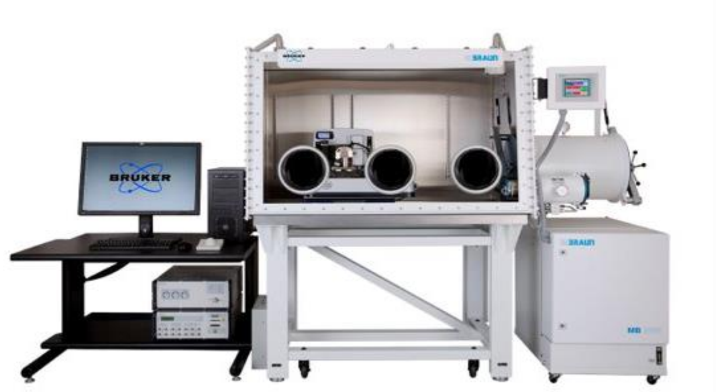

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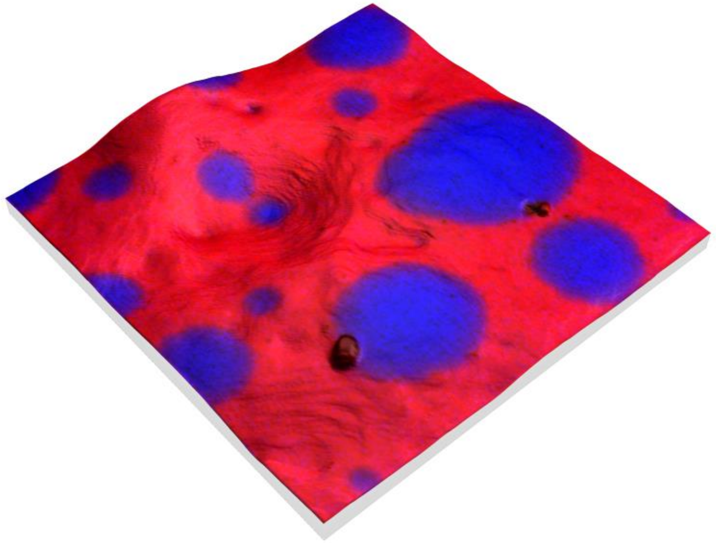
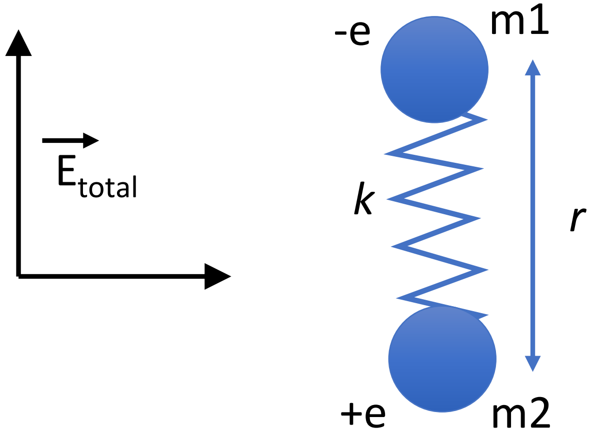


1. Conventional IR spectroscopy and imaging

Polarisation is defined by:

$$P = Np = N\alpha_p E_{total} = \varepsilon_0 \chi E$$

where N number of bonds, α_p polarisability,
ε_0 vaccum permittivity and χ dielectric susceptibility



Refractive index can be expressed by:

$$n^2 = 1 + \chi = 1 + \chi_0 + \frac{3N\alpha_p}{3\varepsilon_0 - N\alpha_p}$$

$$\omega_0 = \sqrt{k/m}$$

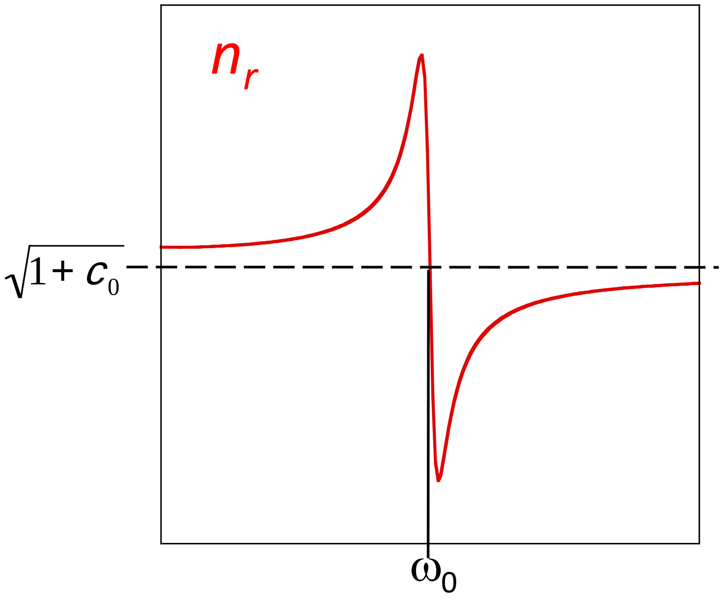
$$\frac{1}{m} = \frac{1}{m_1} + \frac{1}{m_2}$$

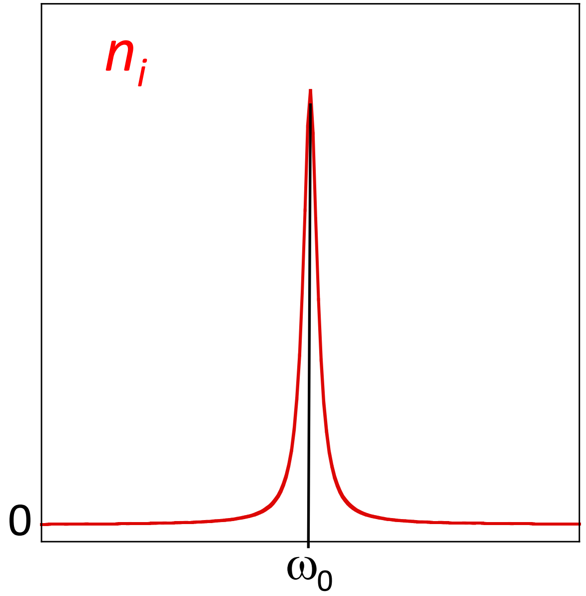
1. Conventional IR spectroscopy and imaging

Refractive index expression can be written :

$$n^2 = n_r^2 - n_i^2 + i2n_r n_i = 1 + \chi_0 + (N/\varepsilon_0)\frac{(e^*)^2/m(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + (\omega\gamma/m)^2} + i(N/\varepsilon_0)\frac{\gamma\omega(e^*/m)^2}{(\omega_0^2 - \omega^2)^2 + (\omega\gamma/m)^2}$$

Considering organic material, then imaginairy part of the index is always smaller than real part ($n_i << n_r$).
This approximation allow to have a simple expression of n_i represented by a Lorentzian function





$$n_i = \frac{(N/\varepsilon_0)}{2\sqrt{1+\chi_0}}\frac{\gamma\omega(e^*/m)^2}{(\omega_0^2 - \omega^2)^2 + (\omega\gamma/m)^2}$$

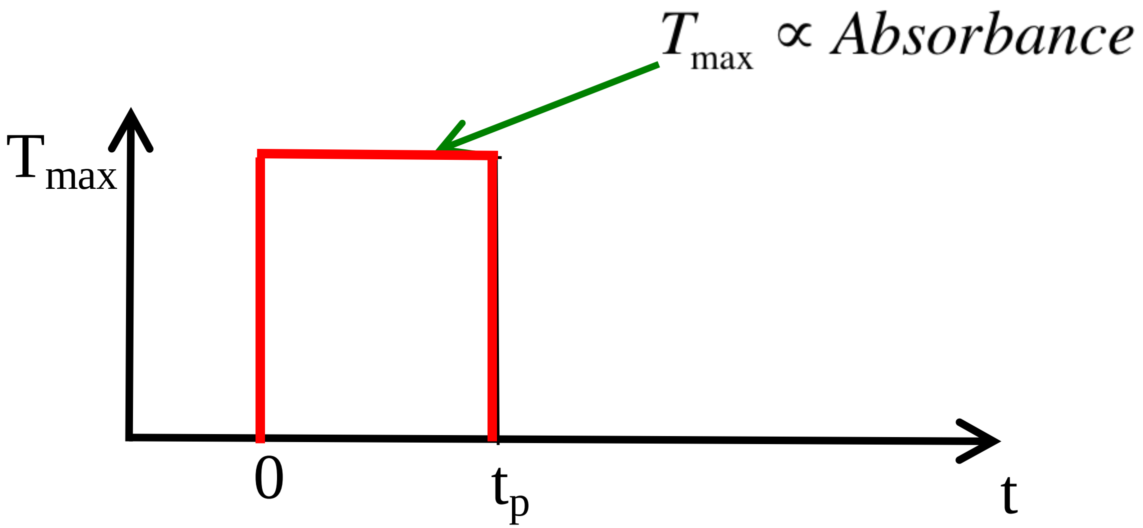
2. AFM-IR theory and concept

Temperature evolution of the sphere (a << ⌊)

when t_p >> | relax

$$T(t) = T_{max} = \frac{P_{abs}}{4\pi a K_{sph}} \quad when\ 0 \leq t \leq t_p$$

$$T(t) = 0 \quad when\ t_p < t$$



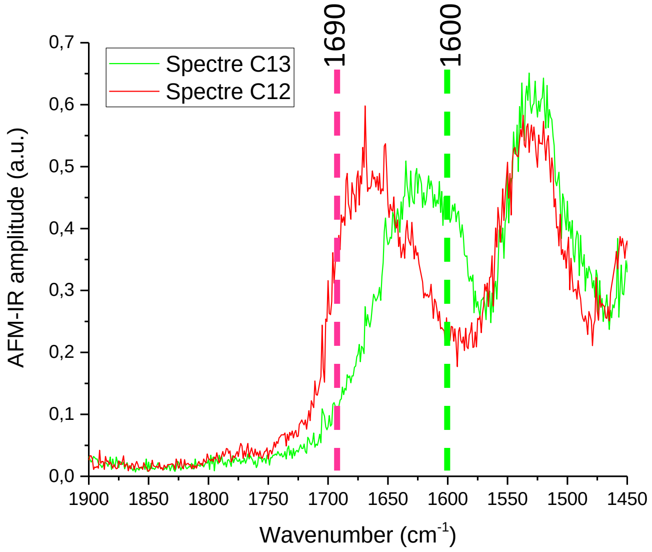
Relaxation time τ_{relax} exemple for polymer sphere (PMMA):

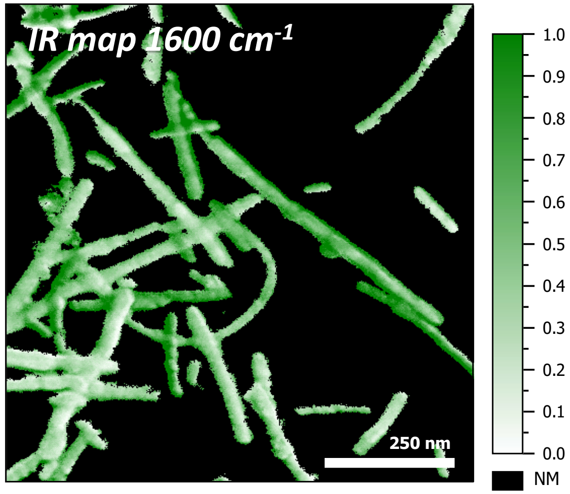
K_{ext} \ a	10 µm	1 µm	100 nm	10 nm
air 0.025 $Wm^{-1}K^{-1}$	2.3 ms	22.7 µs	227 ns	2.3 ns
water 0.58 $Wm^{-1}K^{-1}$	98 µs	980 ns	9.8 ns	98 ps
silica 1.38 $Wm^{-1}K^{-1}$	41 µs	411 ns	4 ns	41 ps
gold 317 $Wm^{-1}K^{-1}$	0.18 µs	1.8 ns	18 ps	0.18 ps

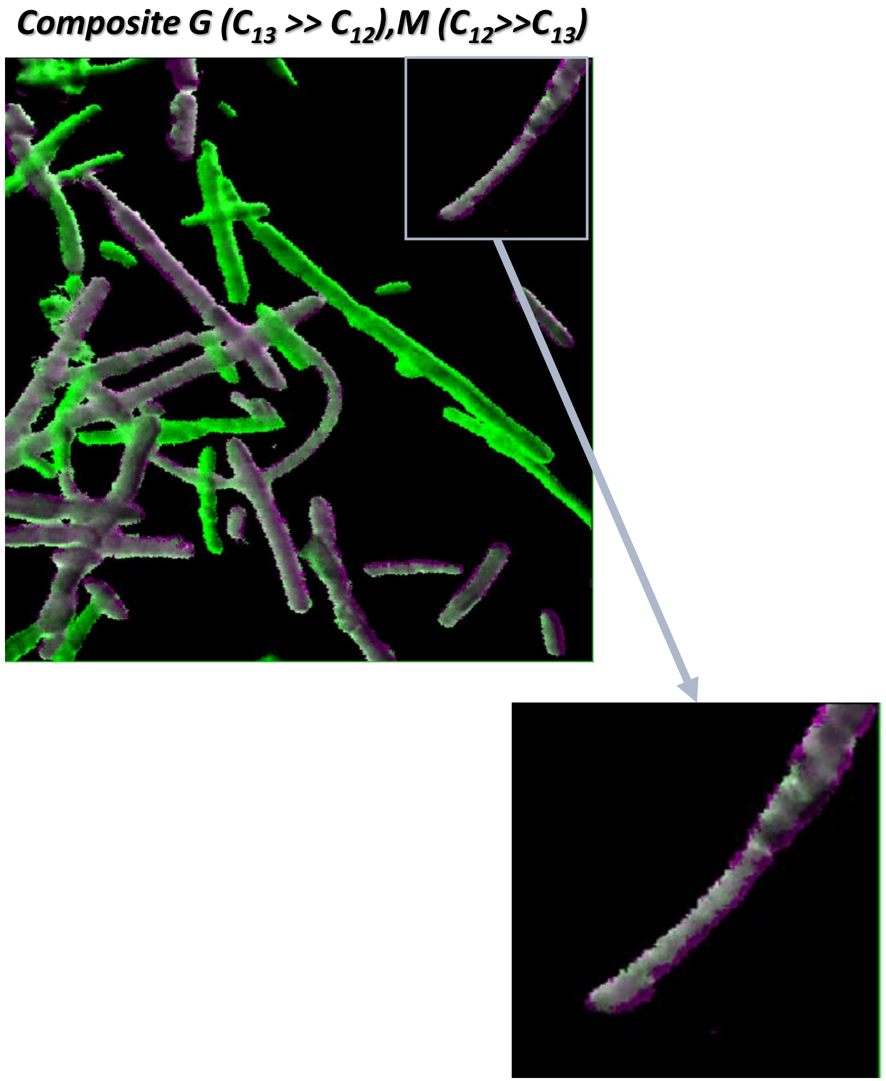
$$\tau_{relax} = \frac{\rho_{sph} C_{sph}}{3K_{ext}} a^2$$

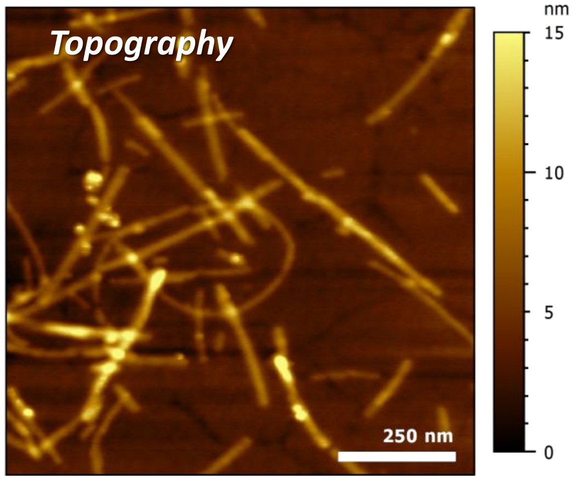
ρ= 1200 kg m^{-3}, C = 1420 J kg^{-1} K^{-1}

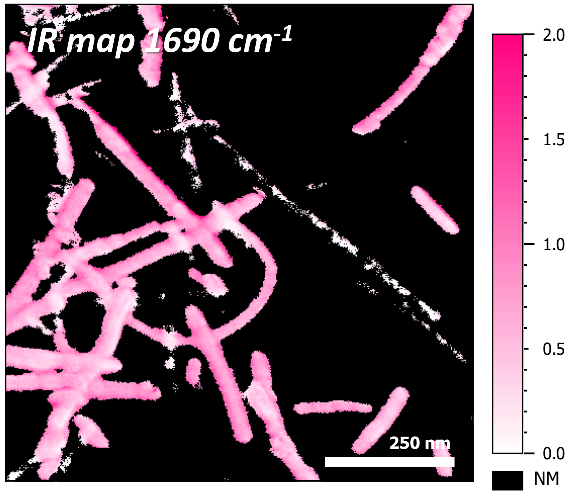
Prions amyloïd fibers analysis











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Silica beads in polystyren film