

AFM-IR technique

AFM



+

IR laser



=

AFM-IR

Infrared spectroscopy and imaging at nanoscale

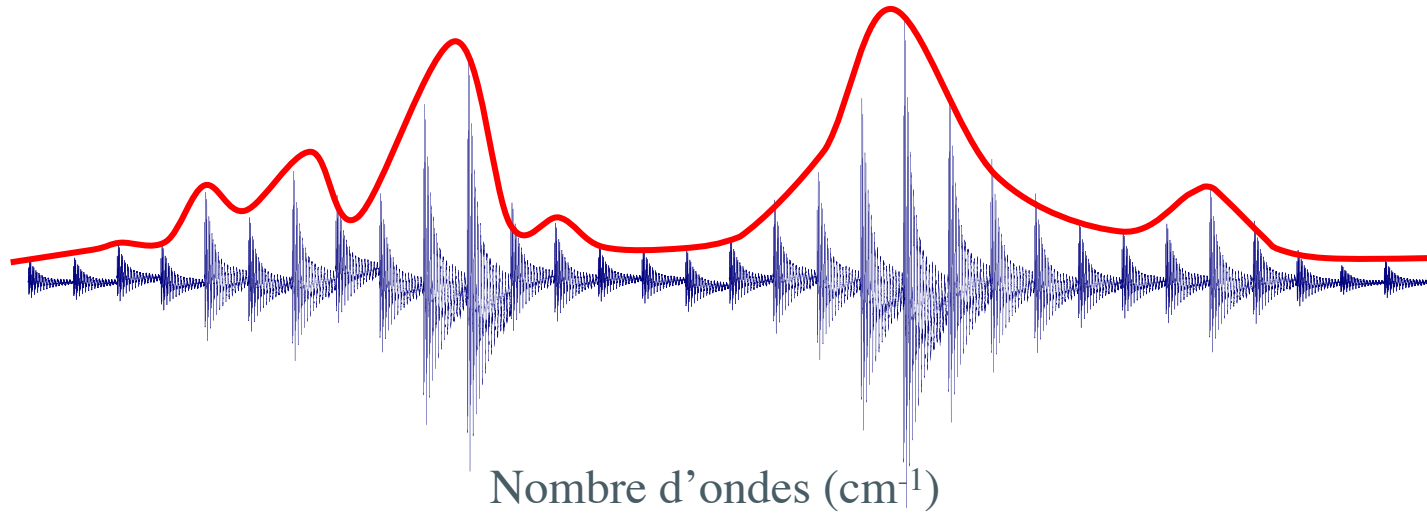
Nanospectroscopie IR

Optical
microscope
view

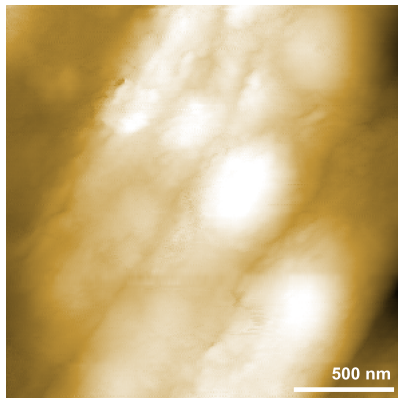


Nanospectroscopie IR

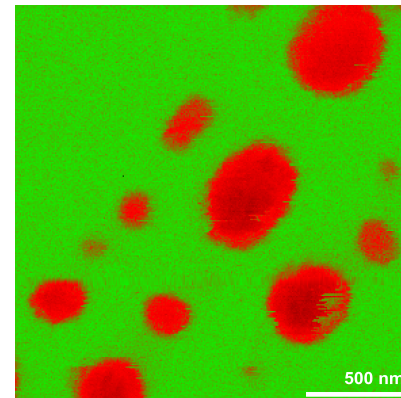
- **Spectre d'absorption** (pointe fixe, scan du laser)



- **Cartographie chimique** (fixe la longueur d'onde du laser et on balaye la pointe)



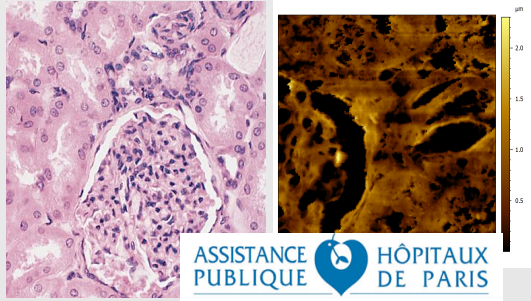
topographie



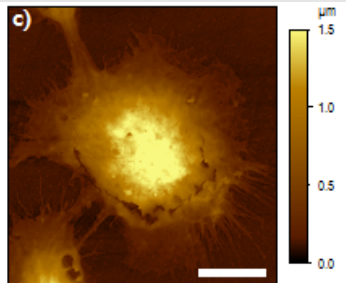
Cartographie ($\lambda=5,76\mu\text{m}$)

Champs d'applications - Biologie

TISSUE – Human cells



Calcification in human tissues
Extracellular vesicles
Penetration of nanocarriers



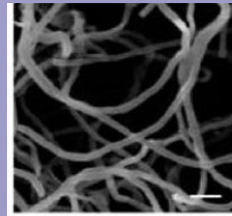
Nanoparticules and cell:
macrophage

Fine structure of the hair...

L'OREAL

MICRO-ORGANISM

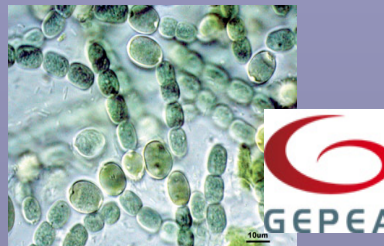
Accumulation of biopolymer or lipids



Localisation and quantification

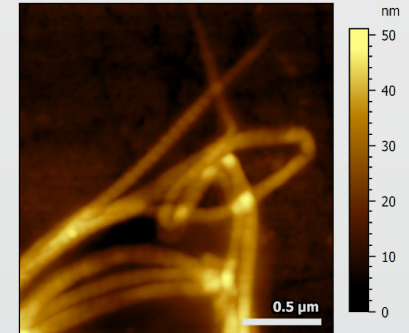


Local composition, TAG, DAG, MAG
and FFA differentiation



NANOMETRIC SCALE

Protein assemblies



Collagen fibrils denaturation
System complex: Collagen-
antibiotic

UPMC
UNIVERSITÉ PARIS SORBONNE UNIVERSITÉS

Bacterial amyloids
Beta structure of amyloids
Prion, lipids bilayer

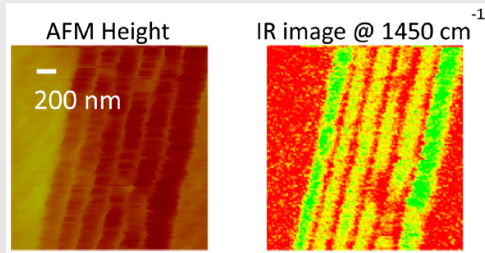
ULB UNIVERSITÉ
LIBRE
DE BRUXELLES

INRA
SCIENCE & IMPACT

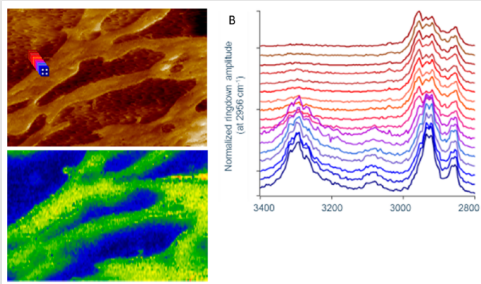
Champs d'applications

Polymers sciences

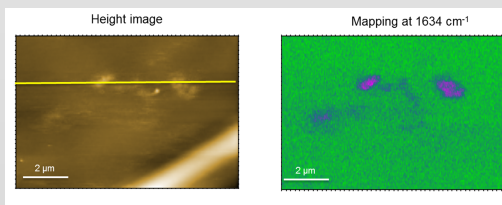
Multilayers: Structure-cristallinity



A Dazzi, Chem Rev, 2016



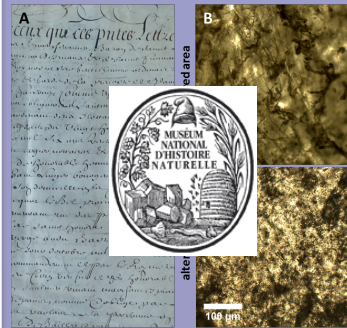
Trace of adjuvant blooming



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

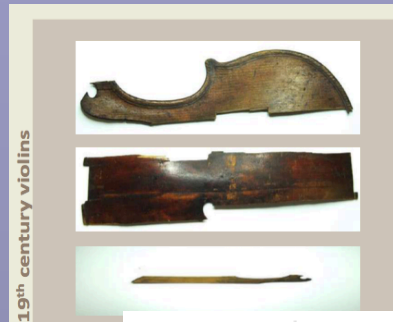
Heritage sciences

- Investigate parchments degradation



G.Latour, Scientific Report, 2016

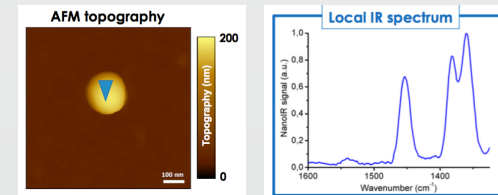
- IR signatures: heterogeneities in ancient tissues or violin sections



IPANEMA ARCHAEOLOGY CONSERVATION SCIENCES PALEONTOLOGY PALAEO ENVIRONMENTS ANCIENT MATERIALS RESEARCH PLATFORM

Nanoparticles

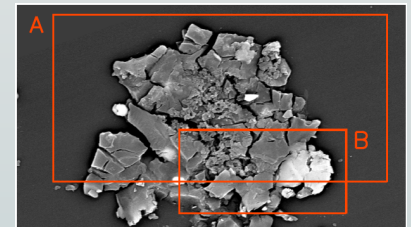
- Polymeric Nps



Mathurin J., 10.1039/C8AN01239C, Analyst, 2018

Astrochemistry

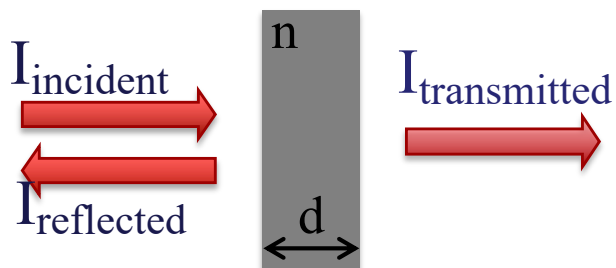
- Investigation of organic matter in micrometeorites



J. Mathurin, A&A, 2019

Infrared spectroscopy

Basic principle of spectroscopy :



(Beer-Lambert law)

Transmission coefficient

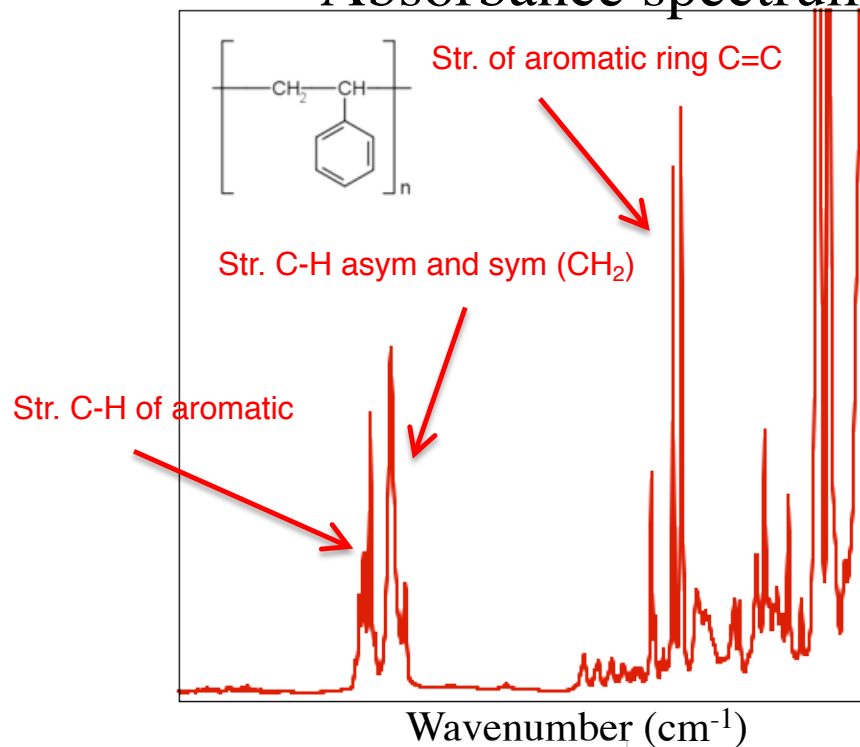
$$T = \frac{I_{\text{transmitted}}}{I_{\text{incident}}} = \exp\left(-\frac{4\pi}{\lambda} \text{Im}(n)d\right)$$

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

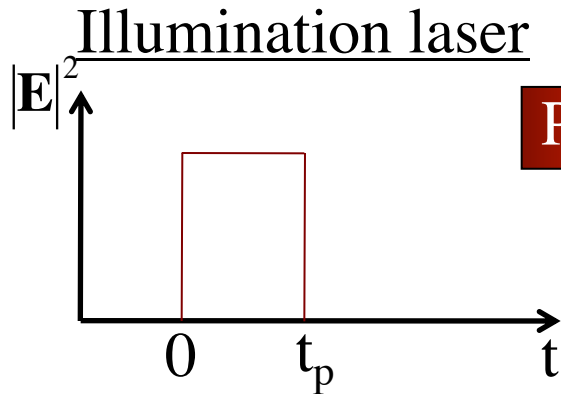
Absorbance

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

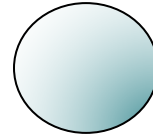
Absorbance spectrum



Effet photothermique



Pulse IR



a rayon

V volume

n indice de réfraction

Puissance absorbée: if $a \ll \lambda$

$$P_{abs} = \int_V \frac{2\pi\omega\epsilon_0}{c\epsilon_0} \frac{9 \operatorname{Im}(n) \operatorname{Re}(n)}{2 \left(\operatorname{Re}(n)^2 + 2 \right)} \left\| \frac{\mathbf{E}_{\text{ind}}}{\mathbf{E}_{\text{inc}}} \right\|^2 dV$$

Faible absorption

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

Equation de la chaleur:

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

ρ densité, C capacité calorifique, k conductivité thermique

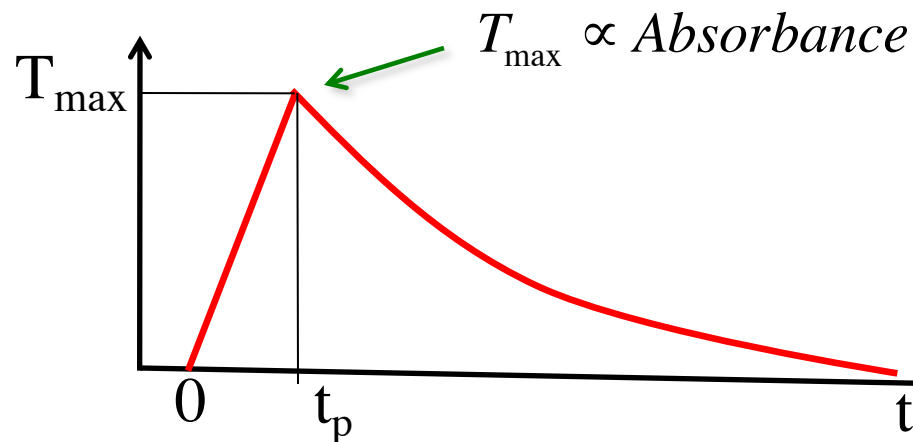
Comportement en température de la sphère

$$t_p \ll \tau_{\text{relax}} \text{ (ns OPO IR)}$$

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

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

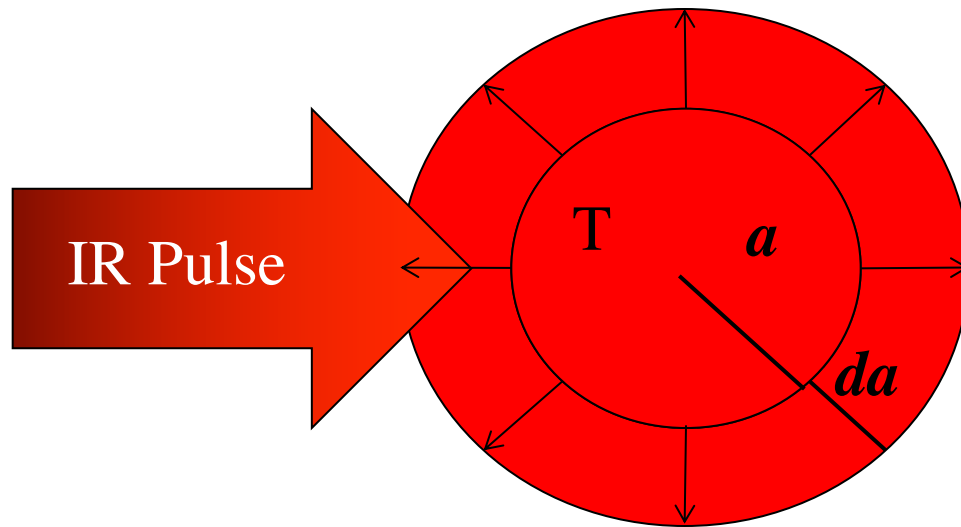
$$\text{avec } T_{\text{max}} = \frac{P_{\text{abs}} t_p}{\rho_{\text{sph}} C_{\text{sph}} V}$$



Temps de relaxation τ_{relax} d'une sphère de PMMA :
$$\rho = 1200 \text{ kg m}^{-3}, C = 1420 \text{ J kg}^{-1} \text{ K}^{-1} \tau_{relax} = \frac{\rho_{sph} C_{sph}}{3k_{ext}} a^2$$

$k_{ext} \backslash a$	10 μm	1 μm	100 nm	10 nm
air 0.025 $\text{Wm}^{-1}\text{K}^{-1}$	2.3 ms	22.7 μs	227 ns	2.3 ns
eau 0.58 $\text{Wm}^{-1}\text{K}^{-1}$	98 μs	980 ns	9.8 ns	98 ps
verre 1.38 $\text{Wm}^{-1}\text{K}^{-1}$	41 μs	411 ns	4 ns	41 ps
or 317 $\text{Wm}^{-1}\text{K}^{-1}$	0.18 μs	1.8 ns	18 ps	0.18 ps

Effet thermoélastique



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

α_{sph} coefficient d'expansion thermique

ν coefficient de Poisson

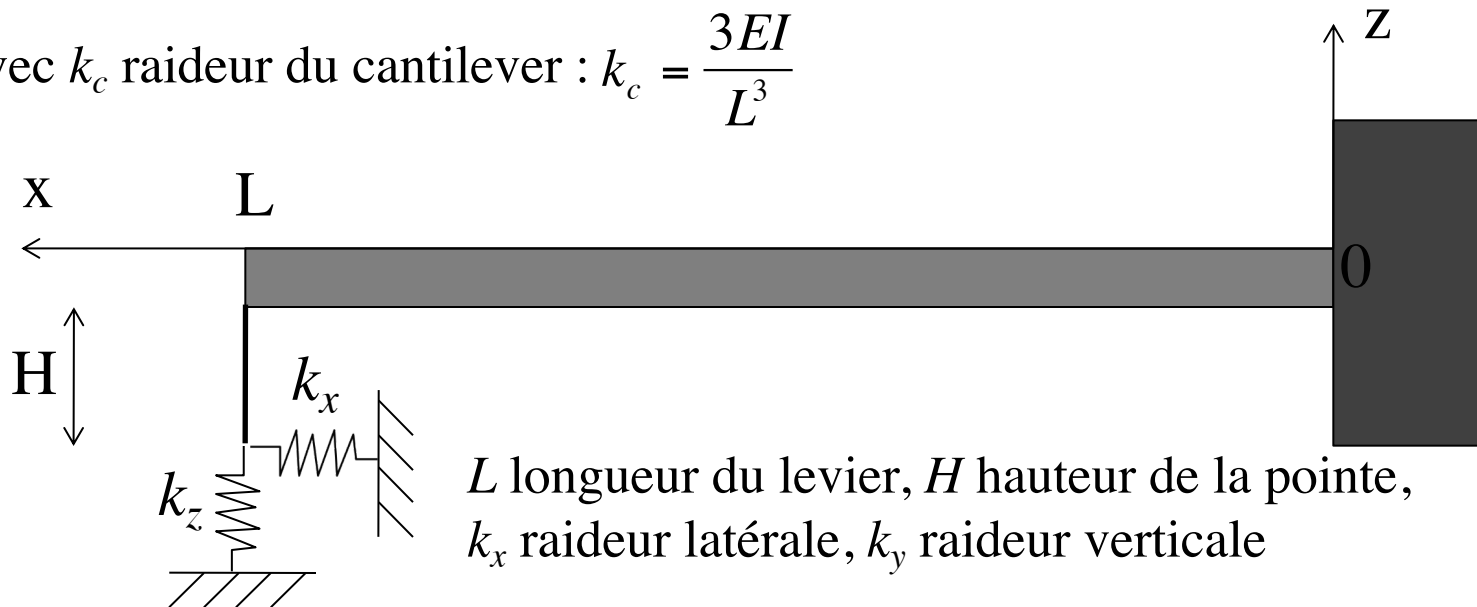
$$da_{\max} = \frac{1 + \nu}{1 - \nu} \frac{a}{3} \alpha_{sph} T_{\max} = \frac{1 + \nu}{1 - \nu} \frac{a \alpha_{sph} P_{abs} t_p}{3 \rho_{sph} C_{sph} V} \propto Absorbance$$

Equation dynamique du 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 module d'Young, I moment d'inertie, ρ densité, A section, κ Amortissement du levier

Avec k_c raideur du cantilever : $k_c = \frac{3EI}{L^3}$



L longueur du levier, H hauteur de la pointe, k_x raideur latérale, k_y raideur verticale

$k_z \gg k_c$ **PAS d'indentation**

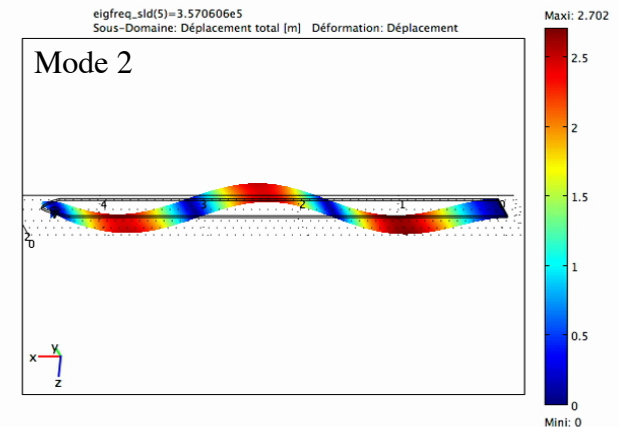
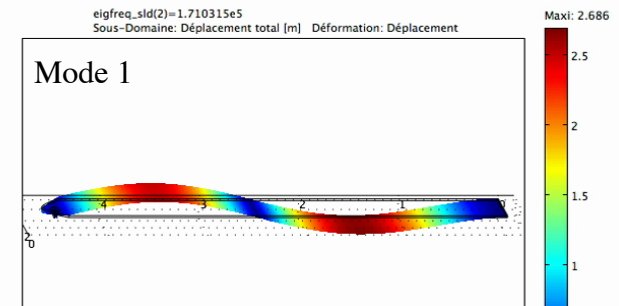
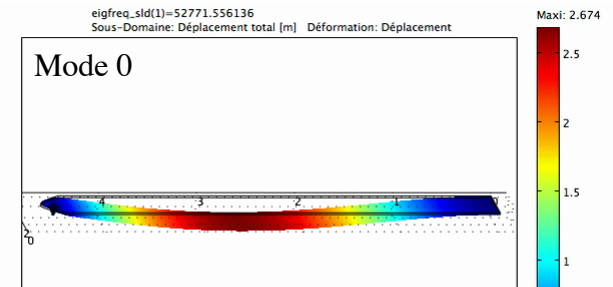
Equation aux valeurs propres des modes:

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

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

Cantilever Si contact

k_x	0 (glissement)	∞ (encasté)
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



Equation dynamique du cantilever sous excitation extérieure

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

Avec $S(x, t)$ excitation extérieure

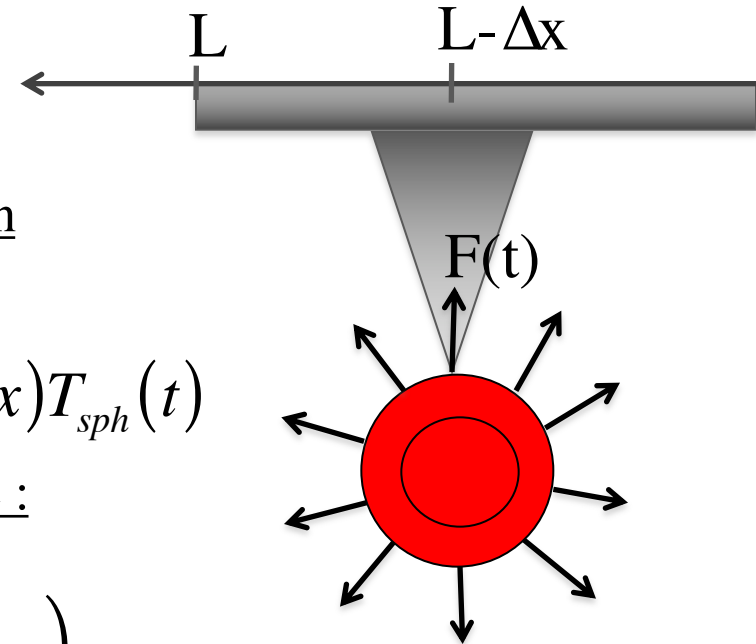
Expression de l'excitation dans le cas de la dilatation photothermique :

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

Solution des oscillations dans le cas photothermique :

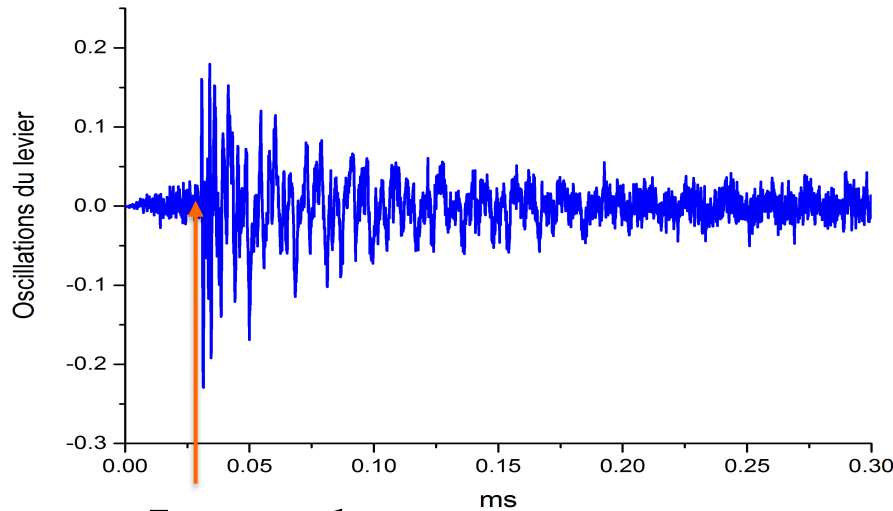
$$Z(t) = \sum_n \frac{K k_z D \delta_x}{\rho S L} \left(\frac{\partial g_n}{\partial x} \Big|_{x=L} \right)^2 \frac{\left(\frac{t_p}{2} + \tau_{relax} \right)}{\omega_n} \sin(\omega_n t) e^{-\frac{\Gamma}{2} t} a_0$$

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

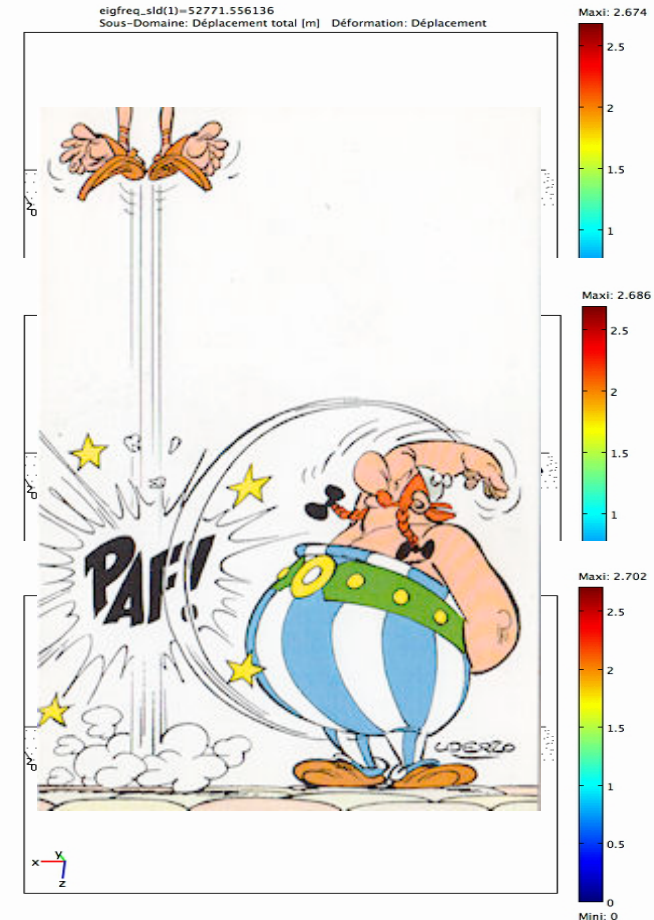
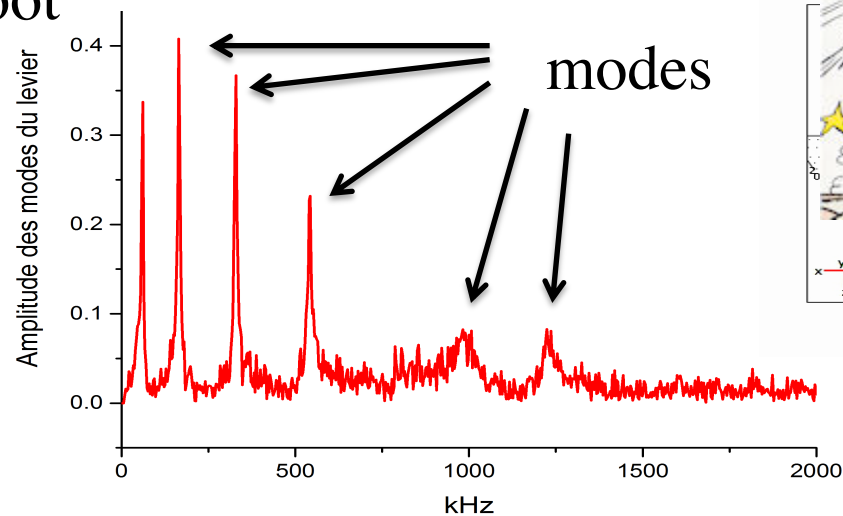


AFMIR Technique

Mesure classique



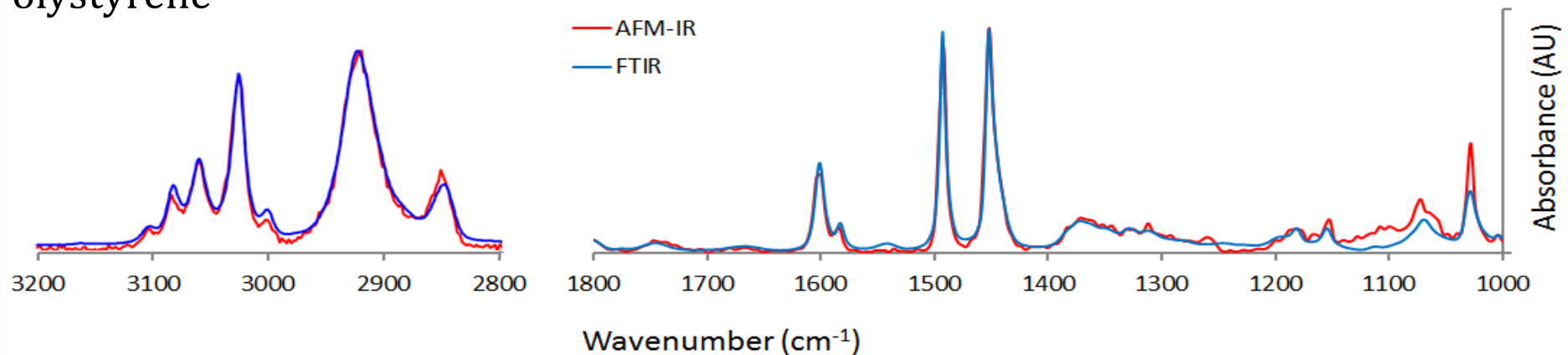
Laser shoot



AFMIR et spectroscopie

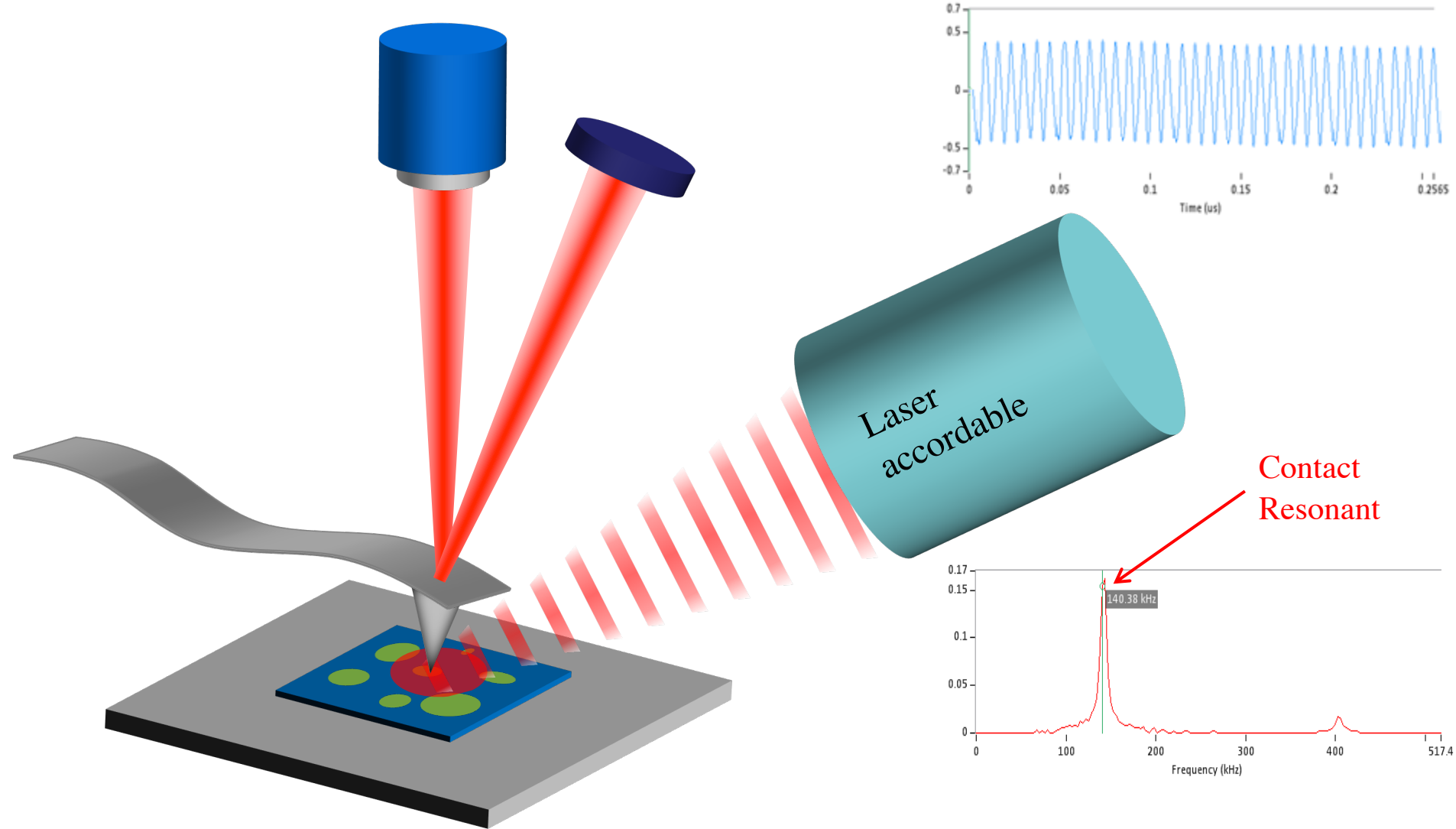
Les spectres AFM-IR sont identiques à ceux obtenus en FTIR

Polystyrene

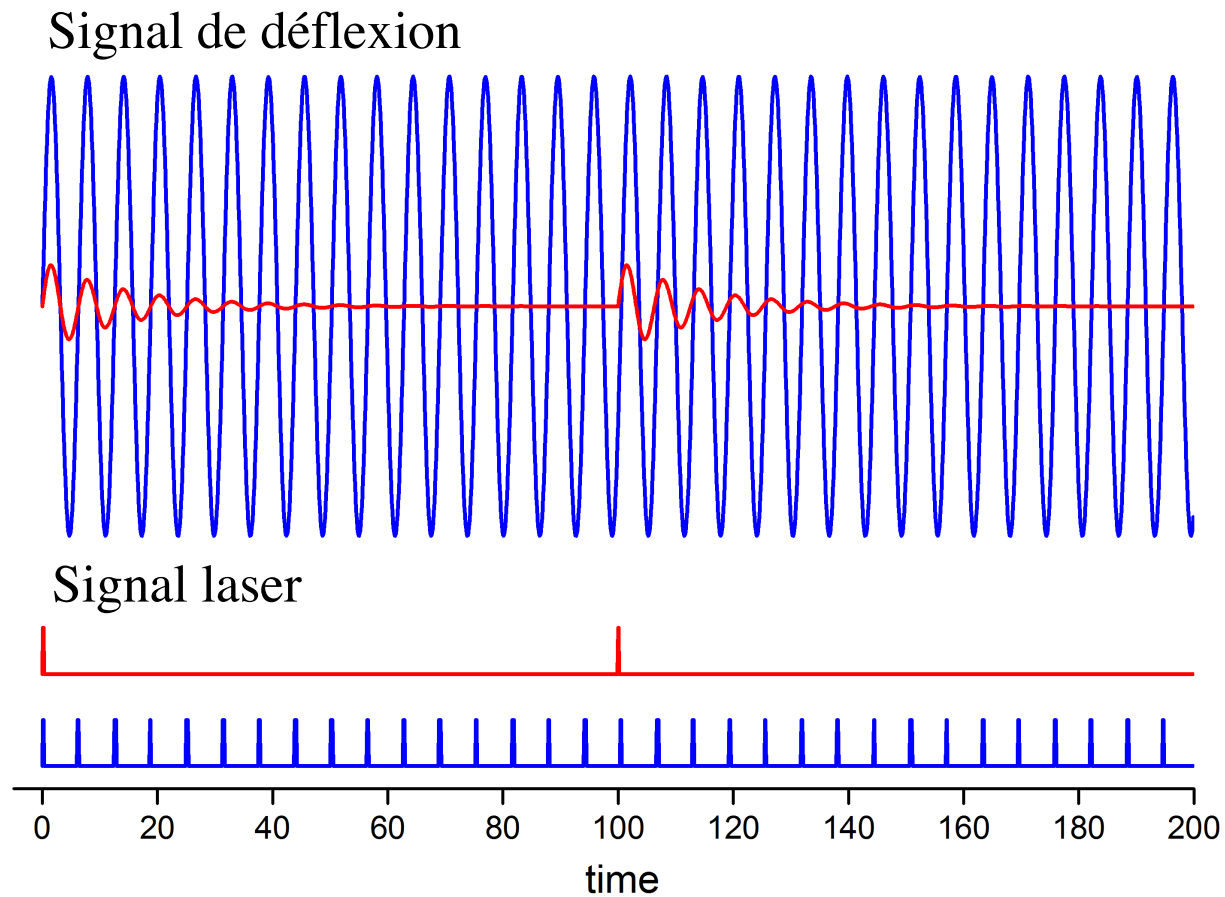


Mode resonant AFM-IR

➤ Démontré par Pr. Belkin en 2011 (Opt. Express)

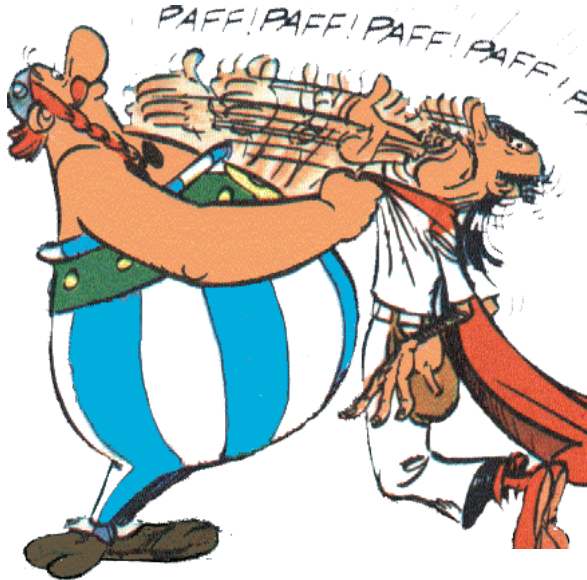


Mode resonant AFM-IR

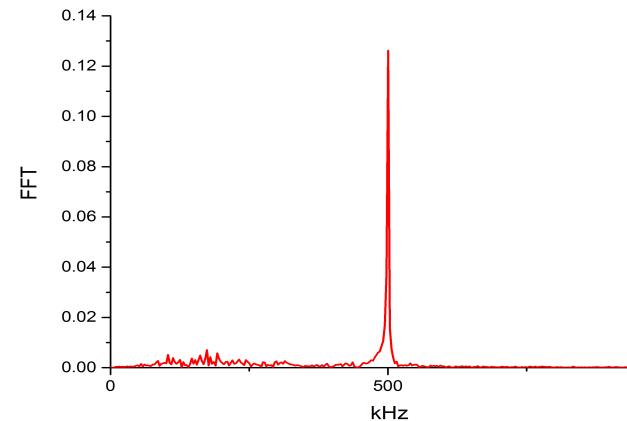
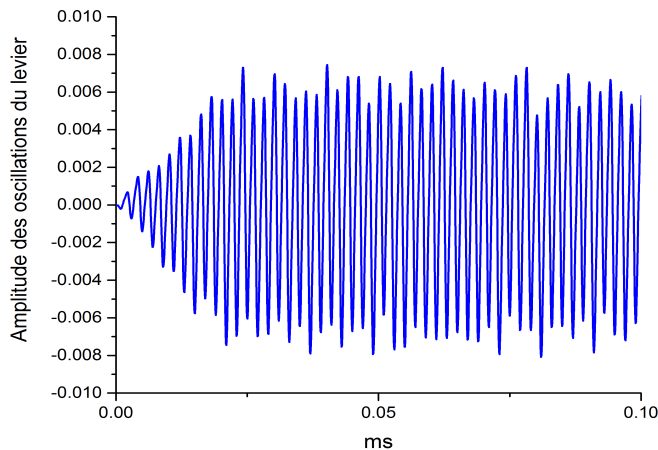
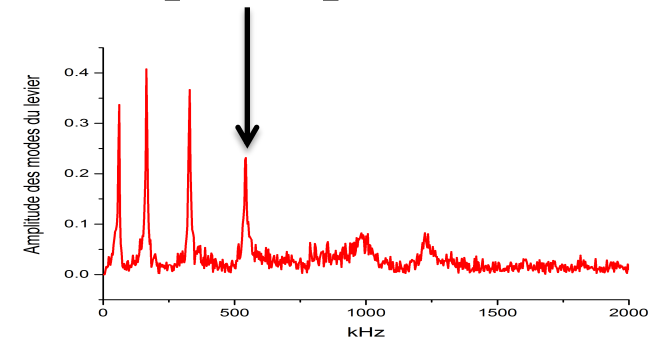


Mode resonant AFM-IR

L'AFM-IR en resonance forcée est plus sensible



Freq de répétition



Mode resonant AFM-IR

Expression pour 1 tir laser (OPO)

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

Expression quand le fréquence de répétition laser = mode de contact (QCL)

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

amplitude(Z) $\propto$ expansion thermique $\propto$ (a_0) absorbance

AFM-IR en mode résonant

Détection de Bacteriorhodopsin

