Nano-chemical mapping performed by an AFM-based (“AFMIR”) acousto-optic technique and applications

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Why infrared ?

Many species have a characteristic absorption spectrum
("chemical signature")

-Molecules (vibrations)
-Pseudo-atoms and molecules (defects in solids, nanostructures)
-Elementary excitations in solids (plasmons, Cooper pairs...)

Linear spectroscopy :

Performed with blackbody sources and synchrotron radiation

Non-Linear spectroscopy :

Performed with lasers, particularly pulsed lasers

Microspectroscopy :

Resolution > $\lambda/2$: performed with blackbody sources and synchrotron radiation

Resolution << $\lambda/2$: performed with lasers ➔ tunable IR FEL

Infrared microspectroscopy

The infrared microspectroscopy associates lateral resolution ("microscopy") and IR spectral analysis ("chemical identification")

Classical sources provide lateral resolution > $\lambda/2$

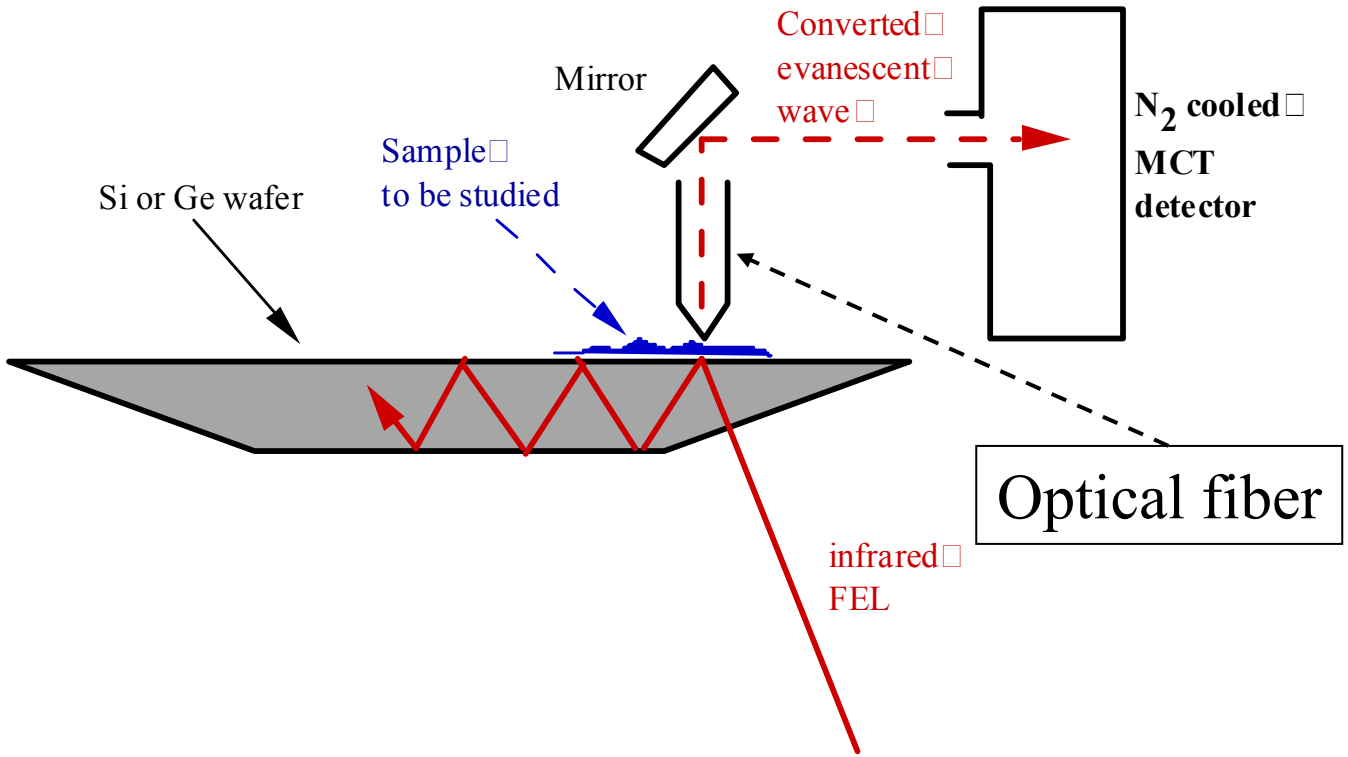
Laser sources + near-field techniques should provide resolution << λ (illumination of small objects requires beam of sufficient brightness)

Near-field techniques :

- Fully optical methods (SNOM, PSTM, apertureless...)

- **New photo-acoustic method ("AFMIR") to overcome the problems encountered with usual means**

Example of a near-field method : the PSTM (photon scanning microscope)



The electric field above the sample is sampled by the tip ($< \lambda$) of an infrared transmitting optical fiber

(1st method used at CLIO in1995)

Disadvantages of all-optical near-field

High spatial resolution (<< λ) requires a very small thickness of the sample (<< λ)

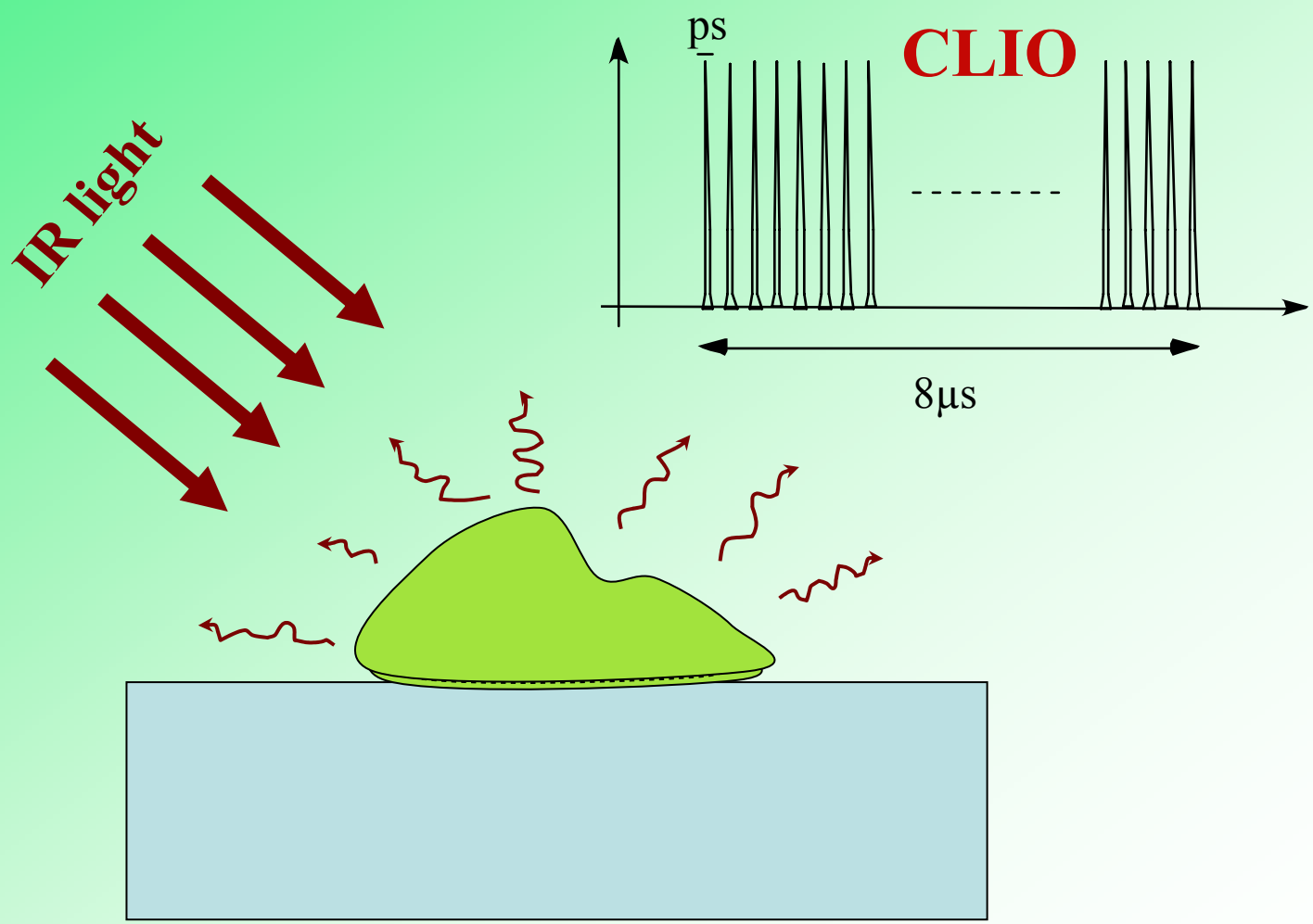
--> Therefore the optical contrast becomes very small (< 1 %)
(necessarily pulsed) tunable lasers do not allow observation of such low contrasts

Moreover, there is no general method to separate the contributions from :

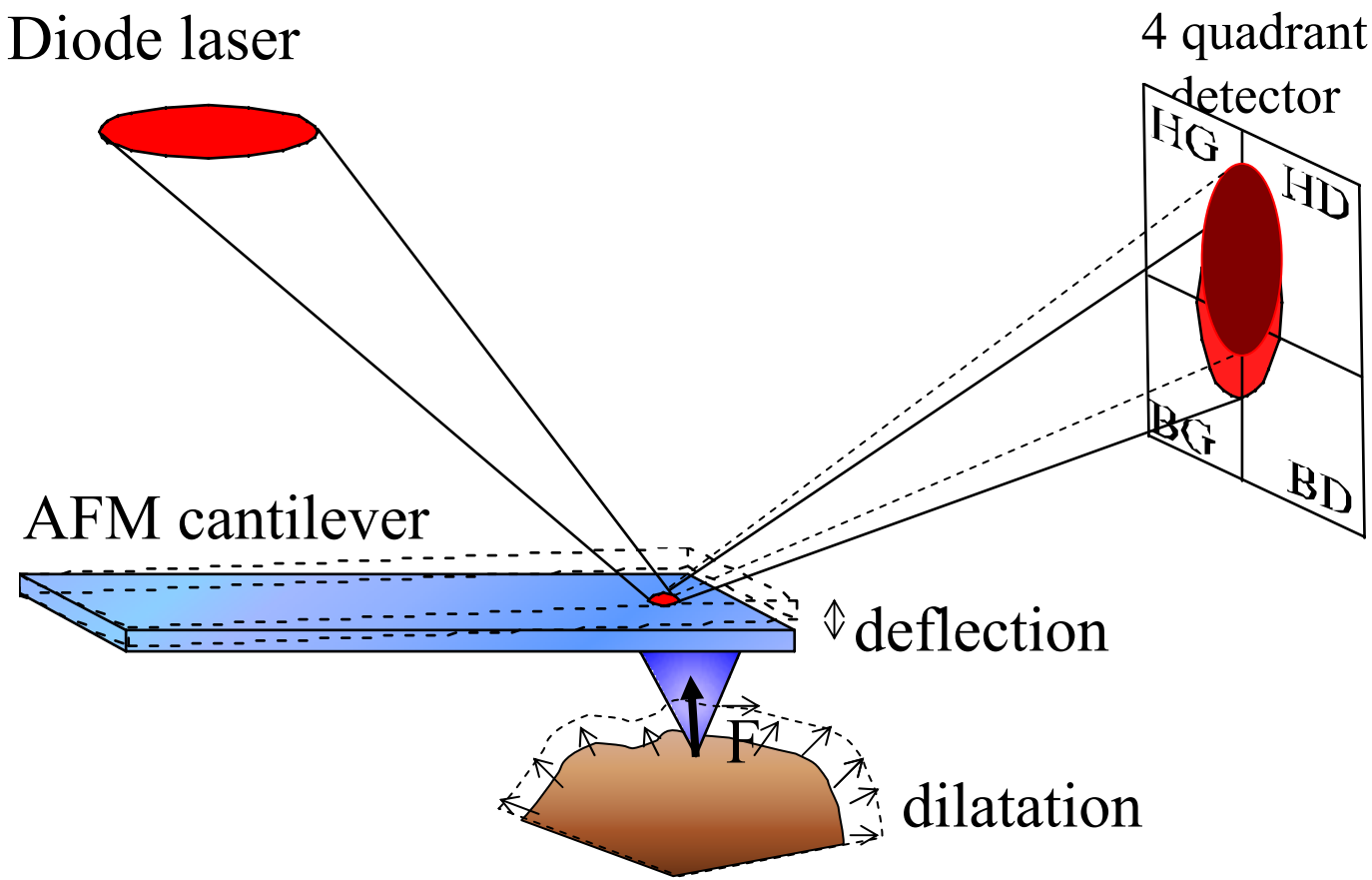
- The real part of n = index of refraction (topography, inhomogeneities)
- The imaginary part of n = optical absorption : **desired quantity**

Differential methods are needed : photoacoustics

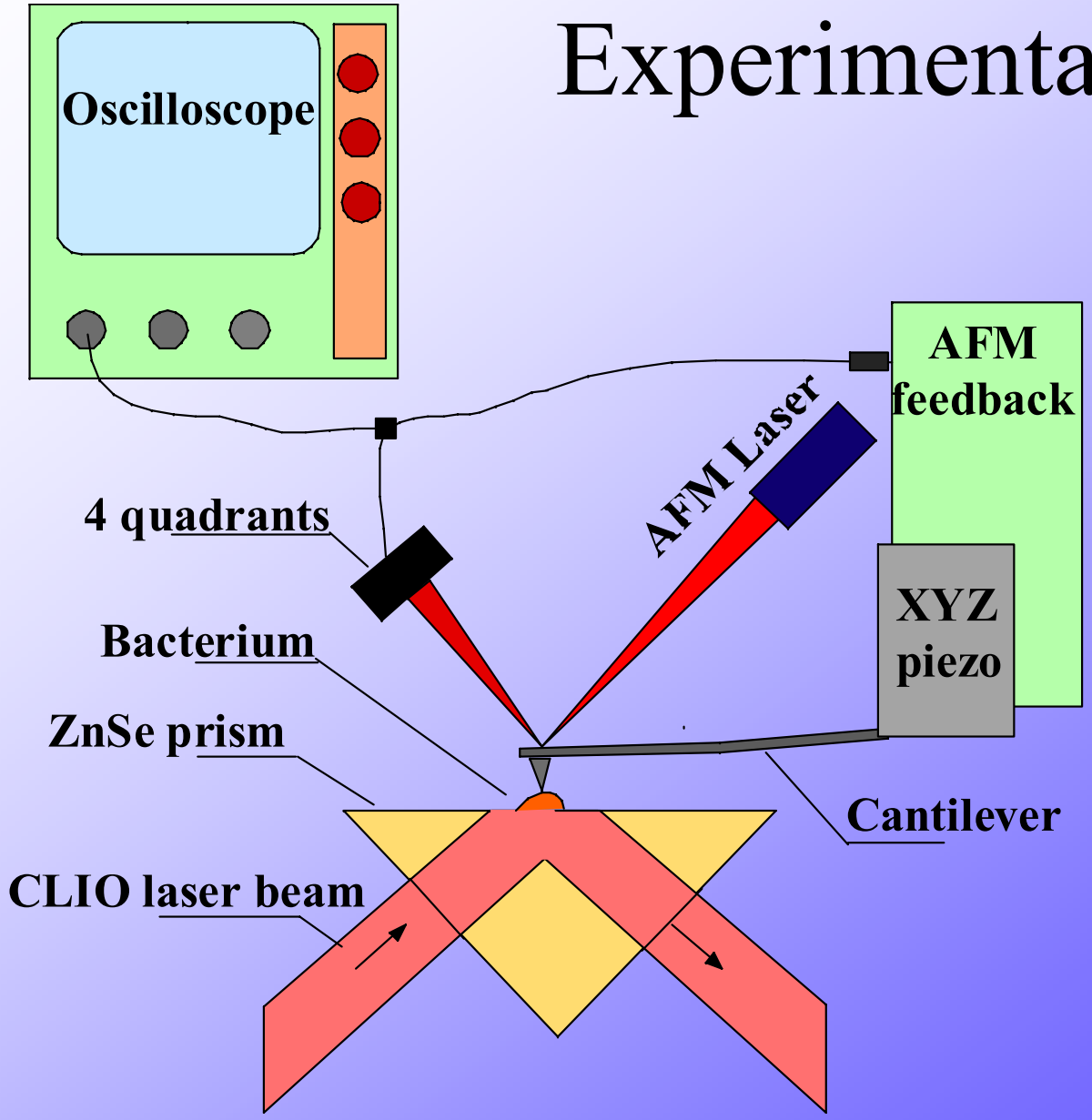
The photothermal effect



Detection of dilatation



Experimental setup



A new method : « AFMIR »

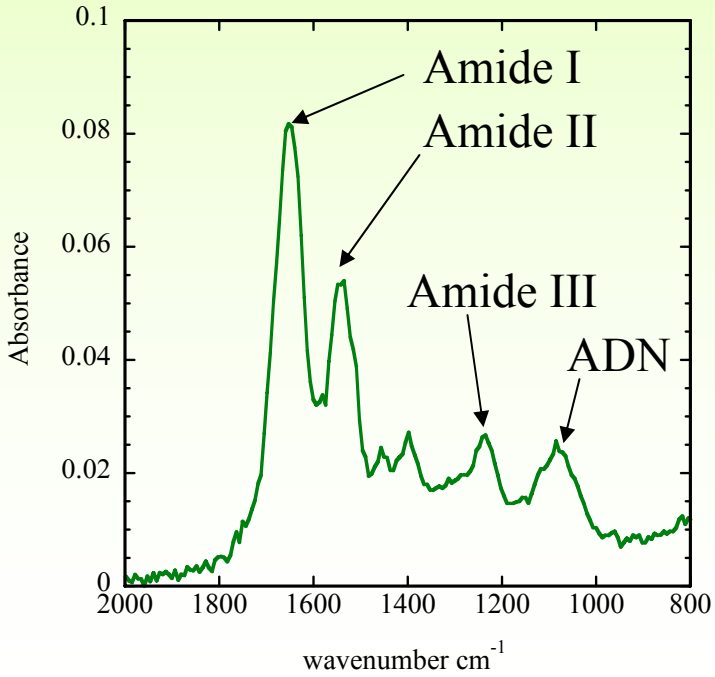
- A commercial AFM is used
- The sample is irradiated in PSTM configuration
- An IR absorption results in a local dilatation
- This dilatation is recorded by optical detection of the tip motion
- The transient character of the dilatation (due to the pulsed nature of the laser) ==> spatial resolution
- The topography is recorded at the same time

Test experiment

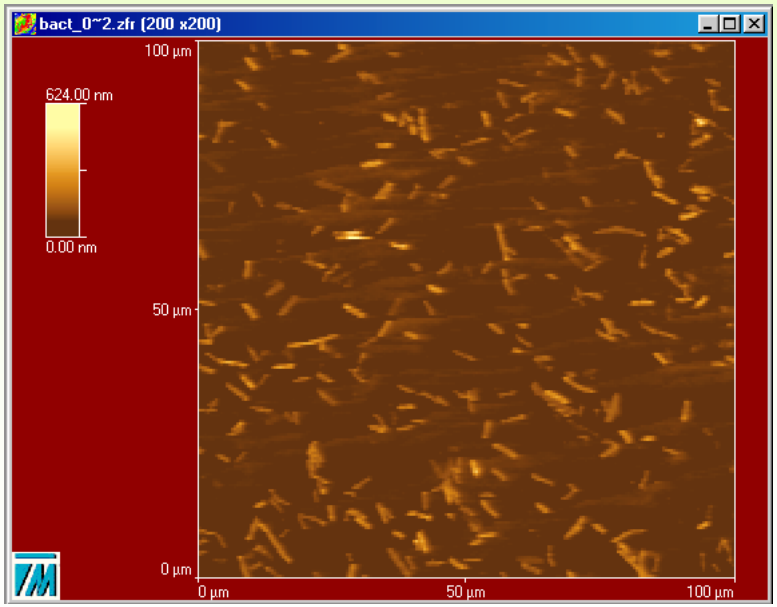
Bacteria Escherichia coli

Typical size : 2-6 µm long 1-2 µm large and 500 nm height

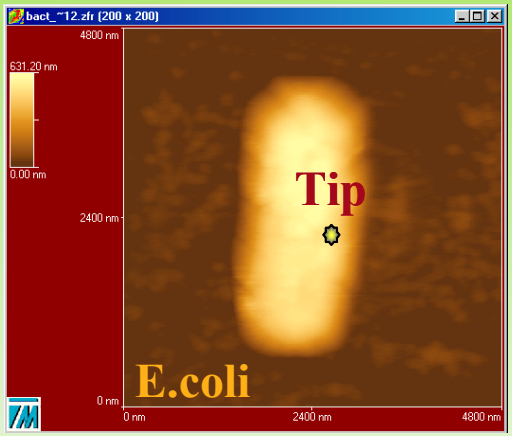
FT-IR spectrum

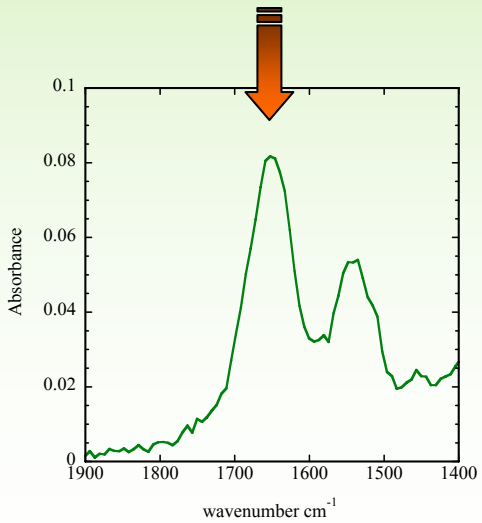


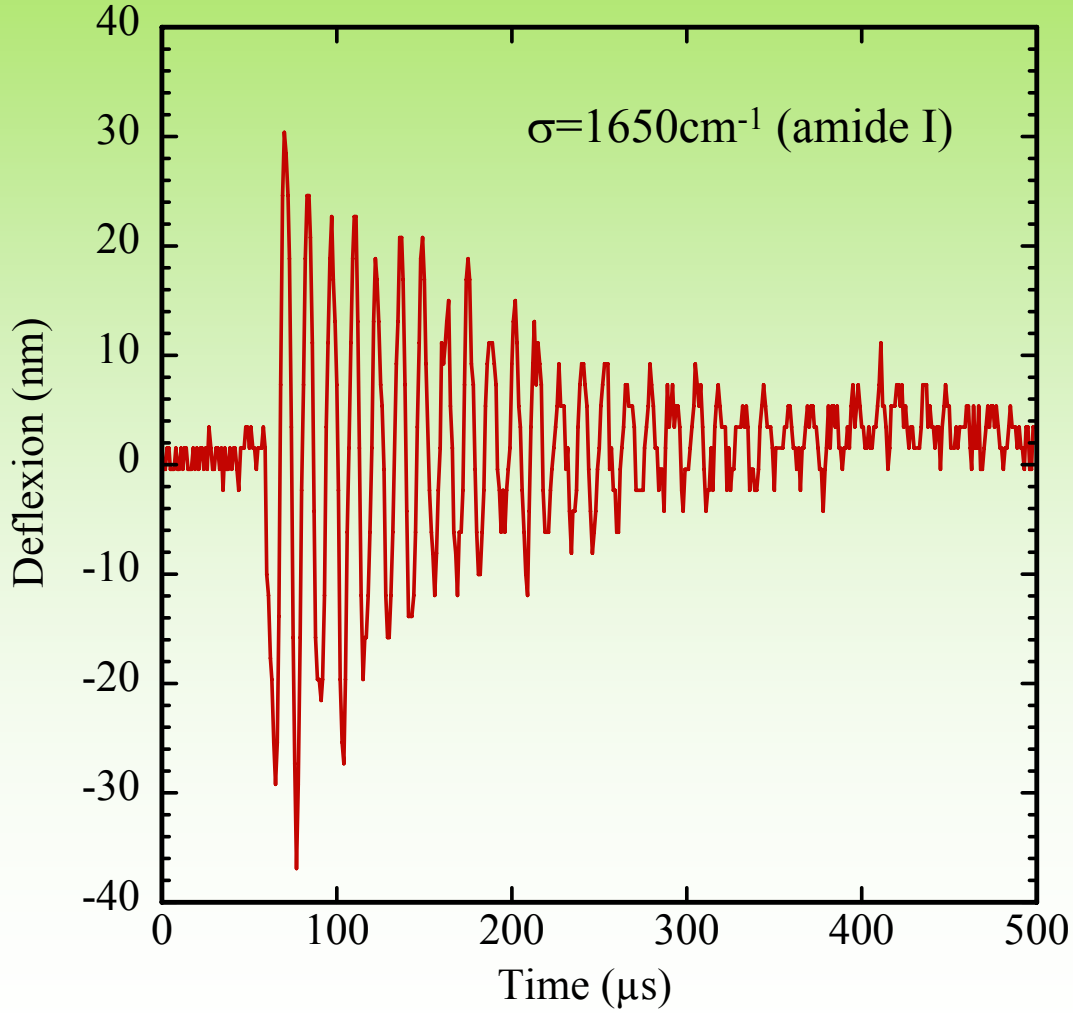
AFM microscopy



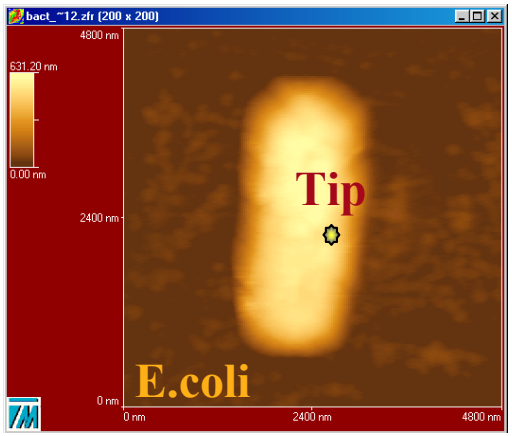
Temporal response

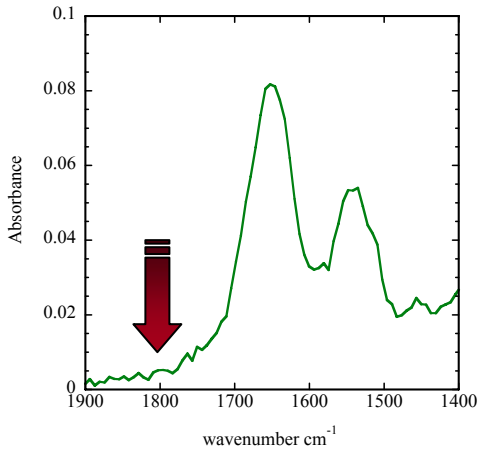


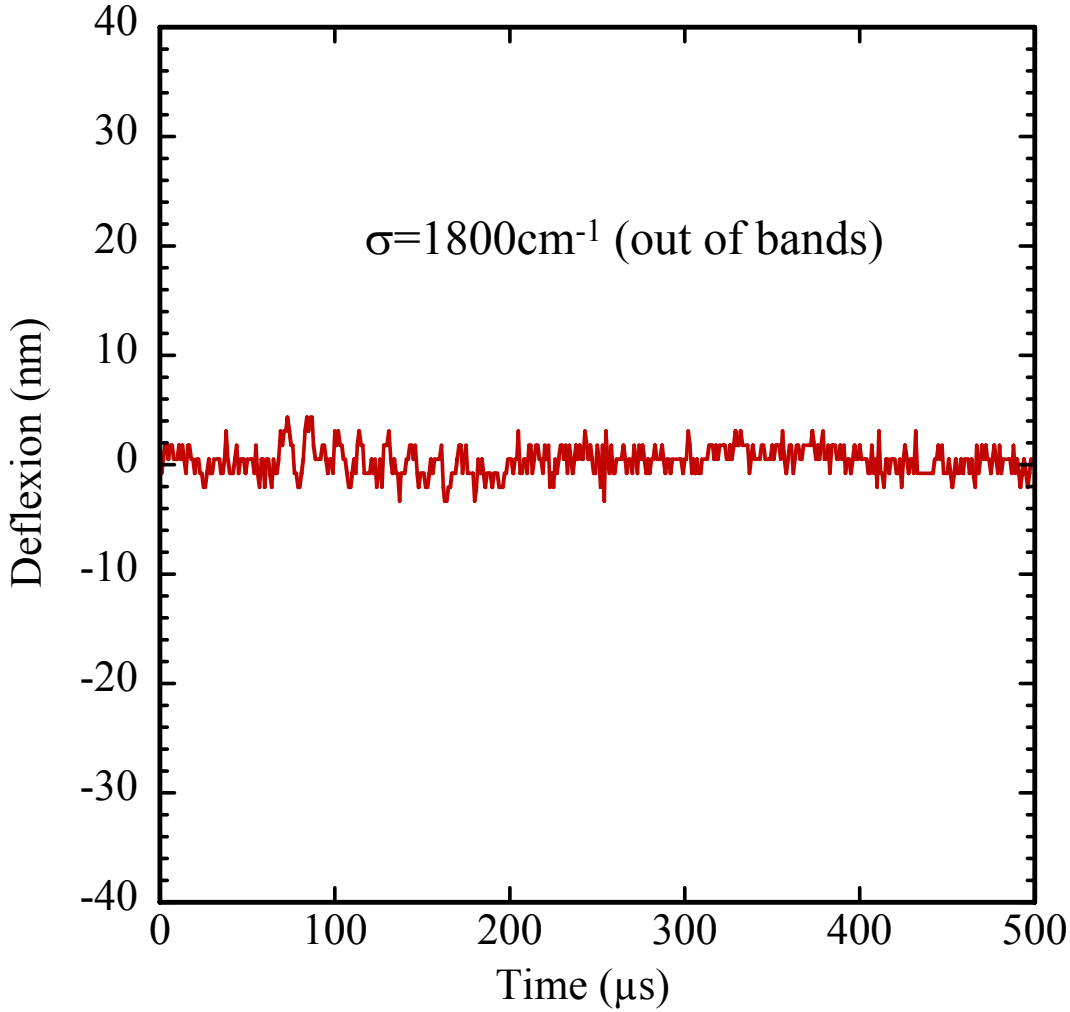




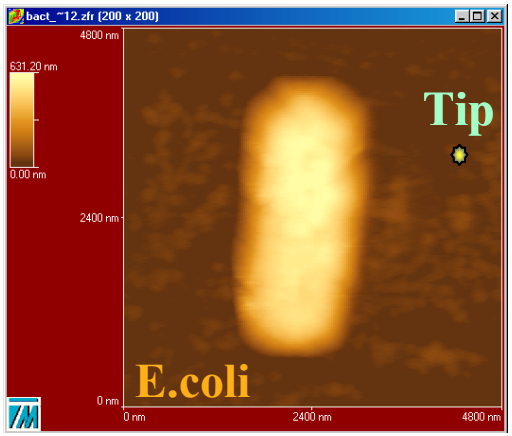
Temporal response

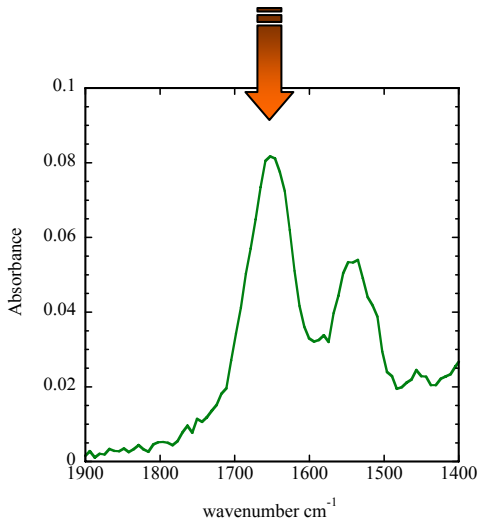


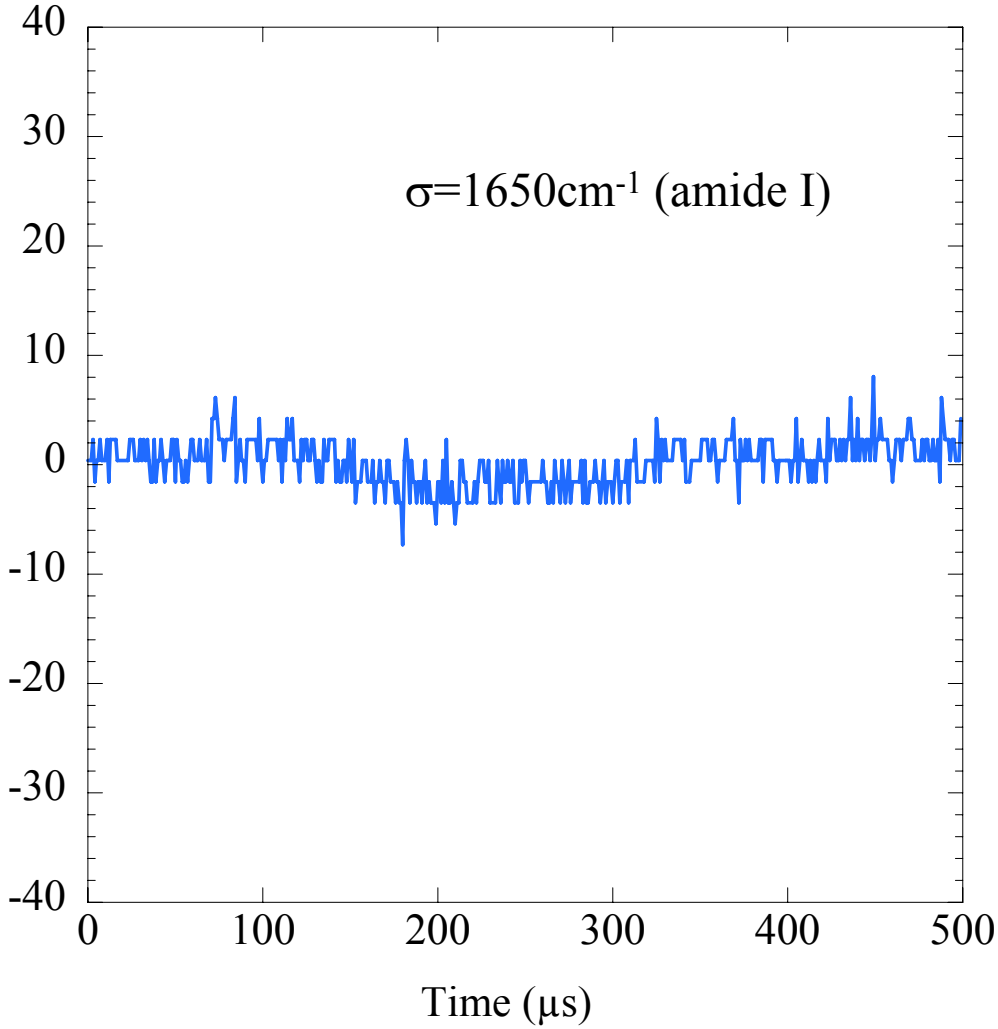




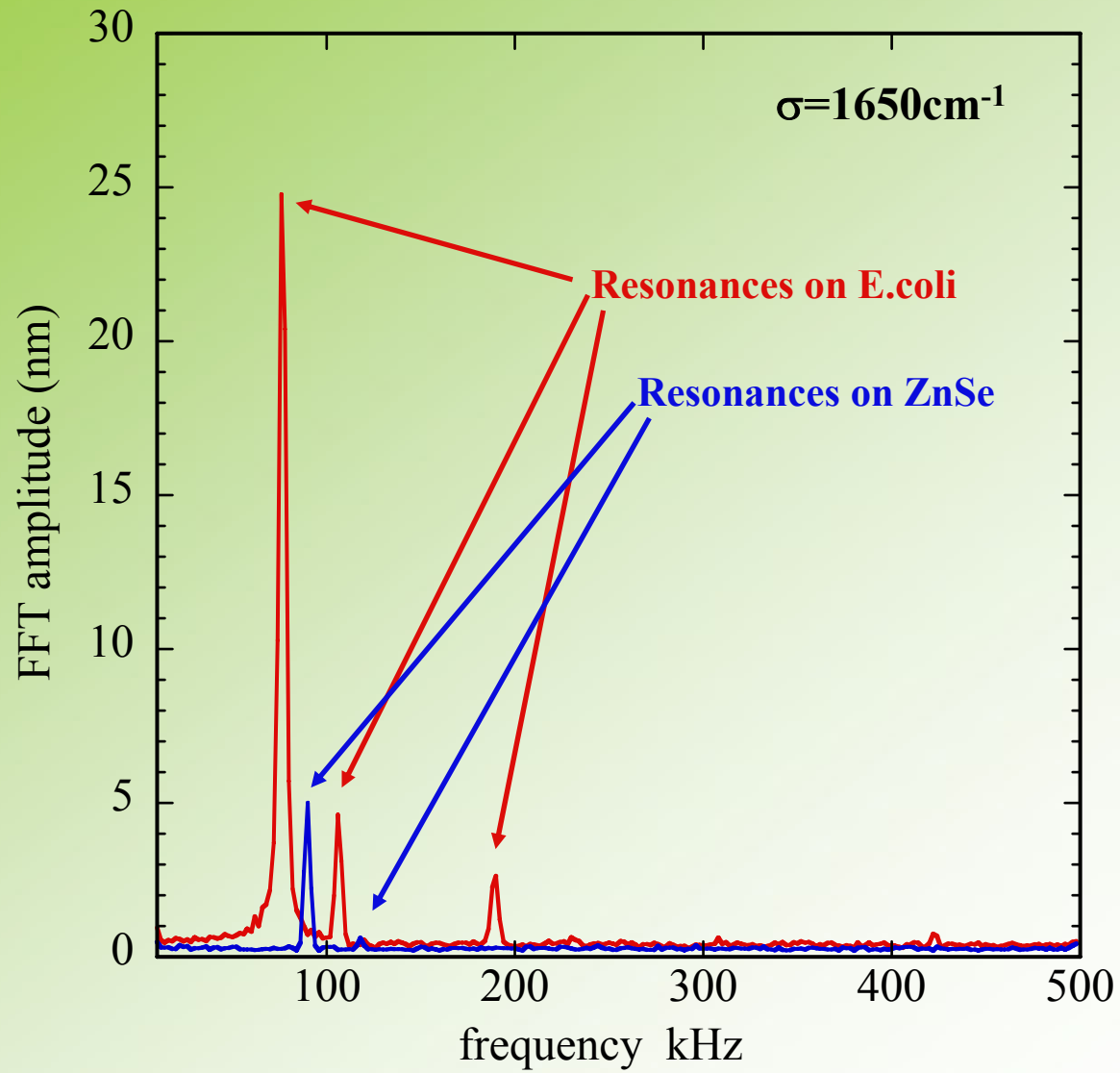
Temporal response





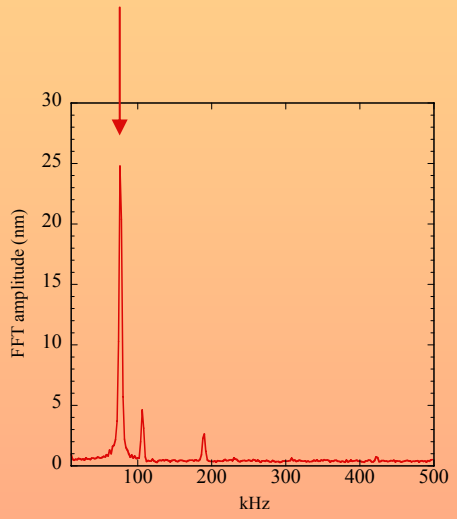


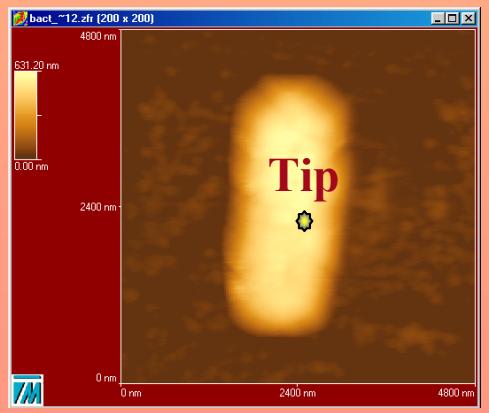
Fourier analysis

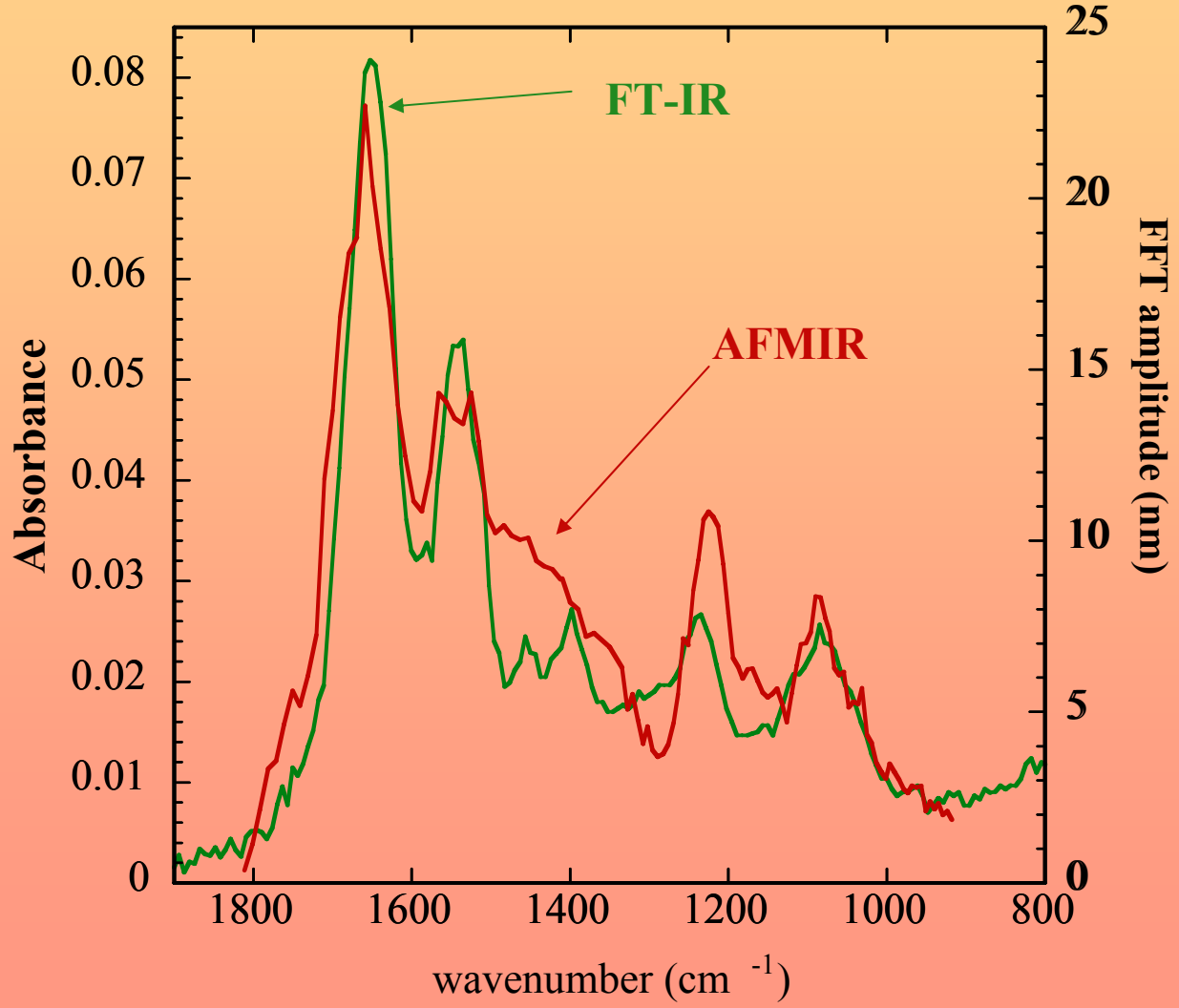


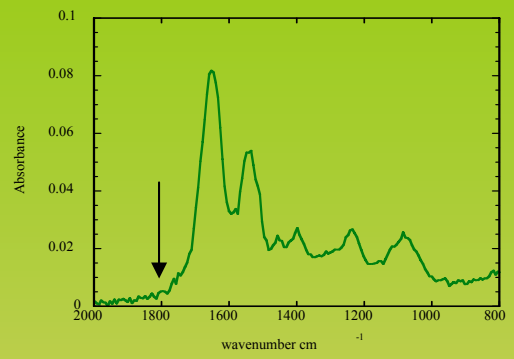
Localised spectroscopy

66 kHz

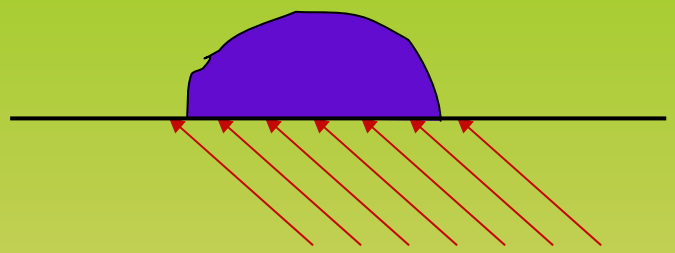


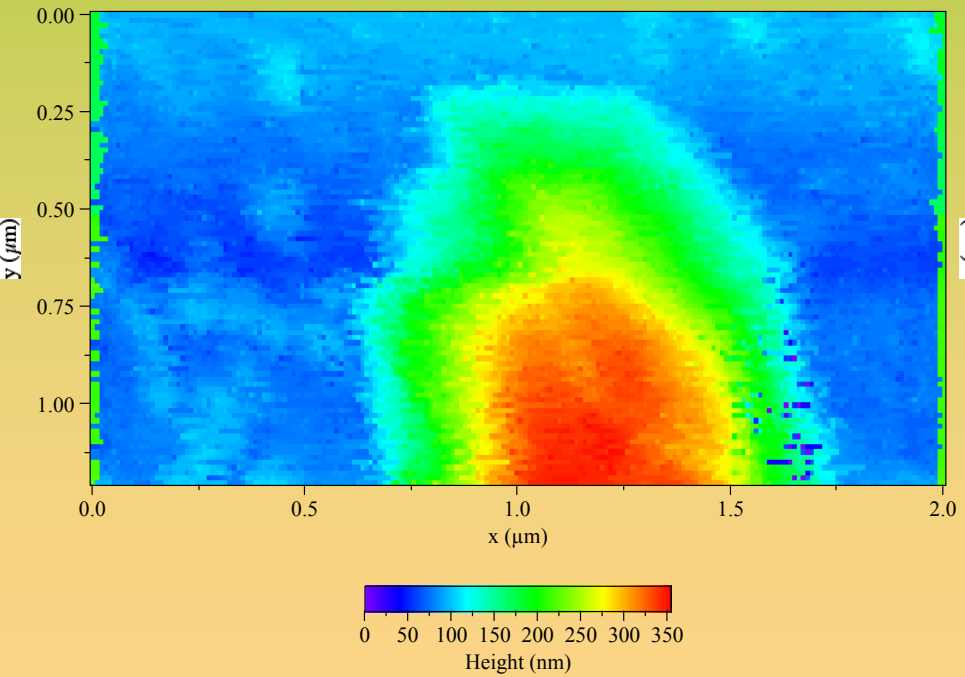


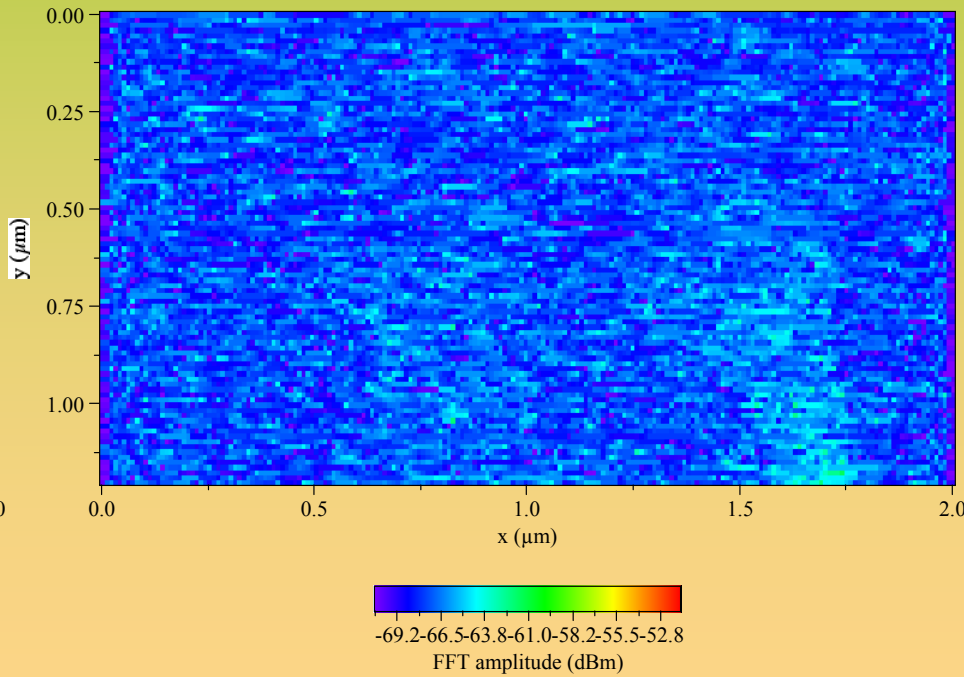




σ=1800 cm^{-1}

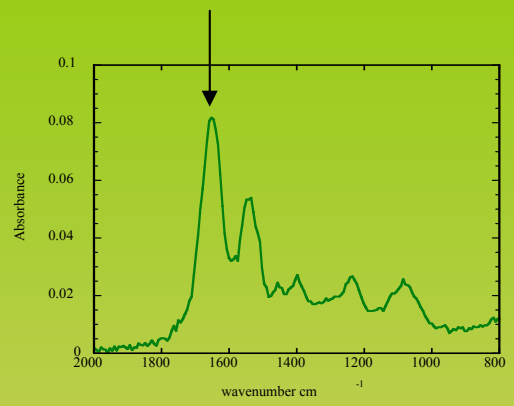




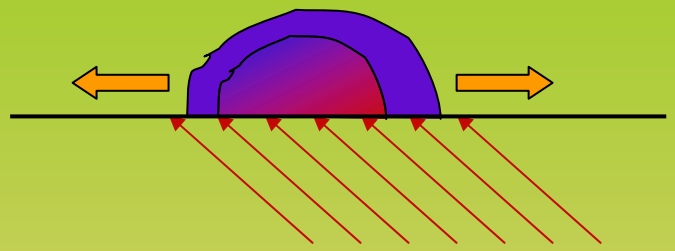


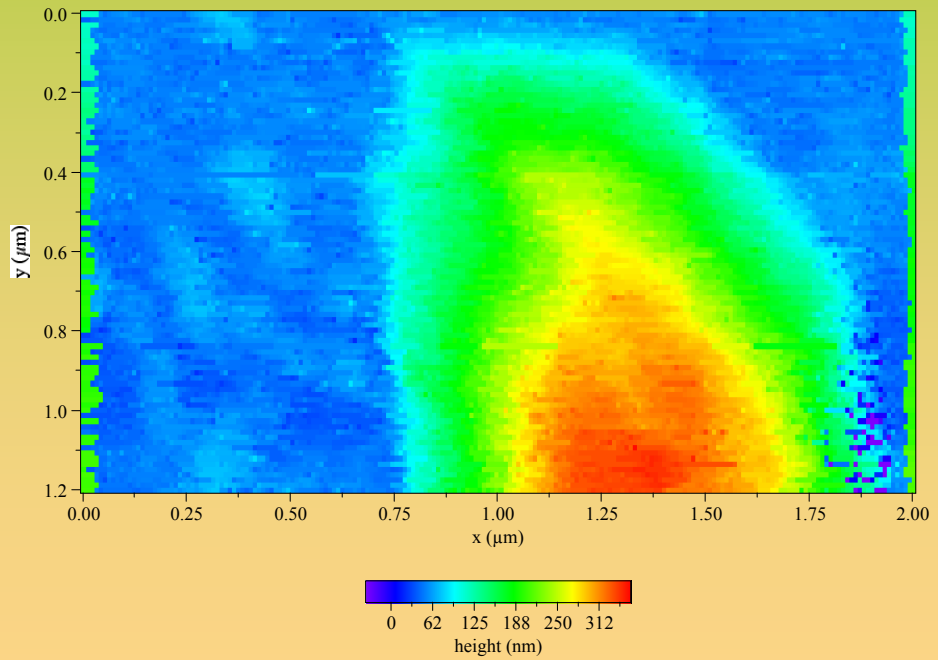
AFM topography

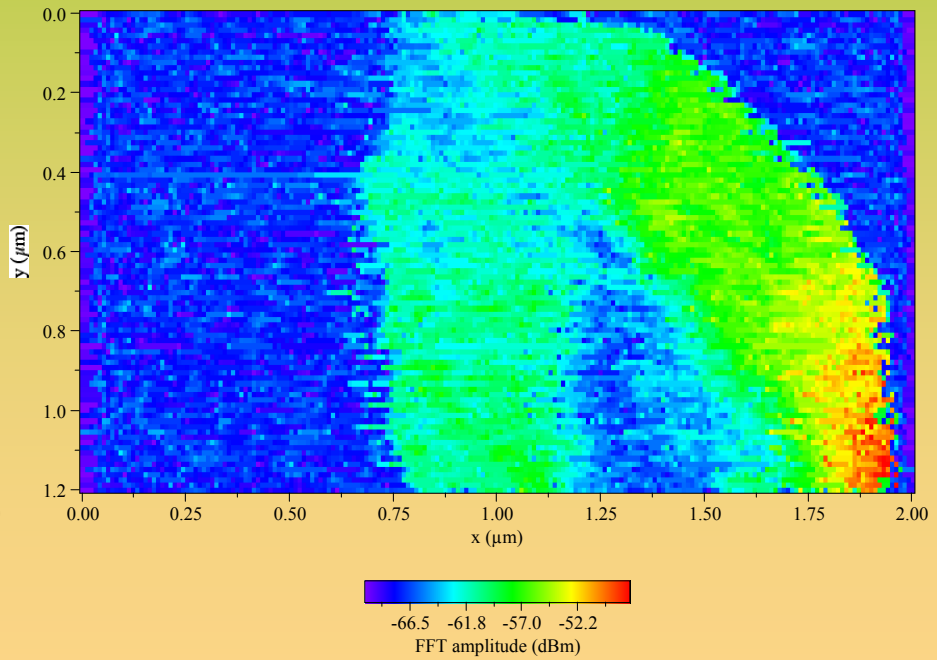
Chemical mapping



σ=1650 cm^{-1}







AFM topography

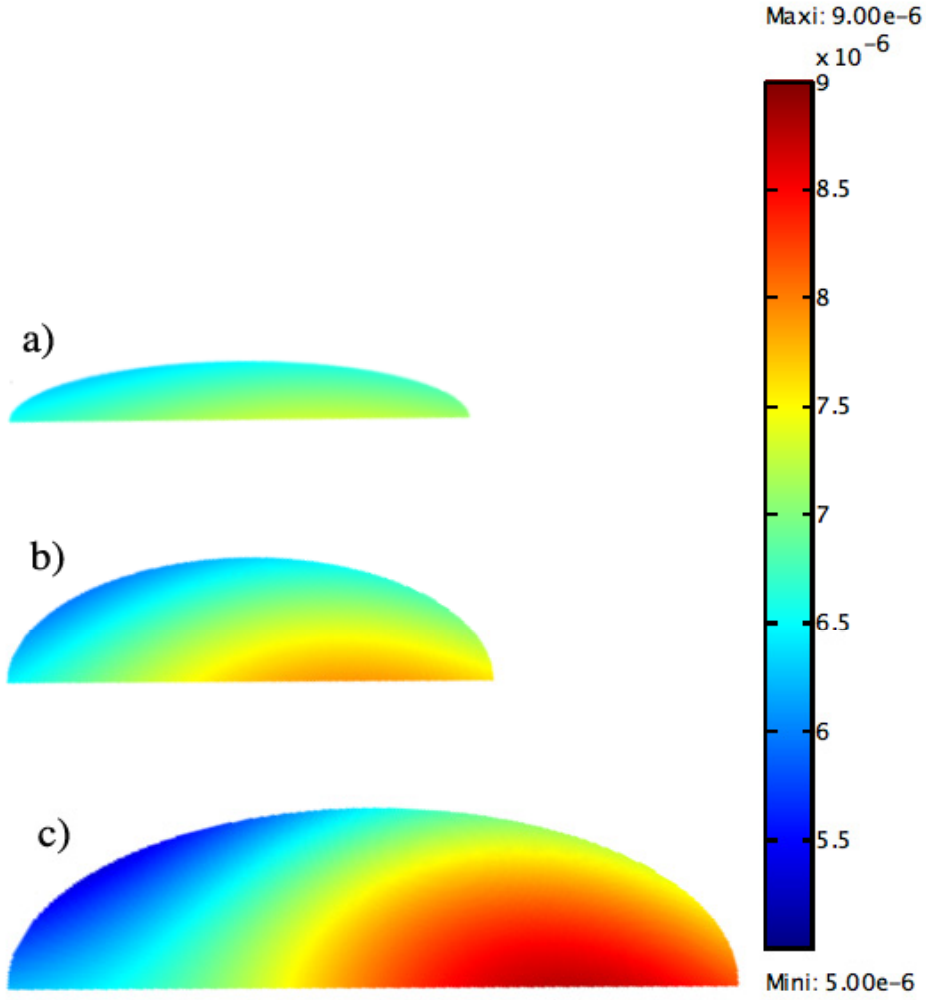
Chemical mapping

Example of light distribution in tree different bacteria :

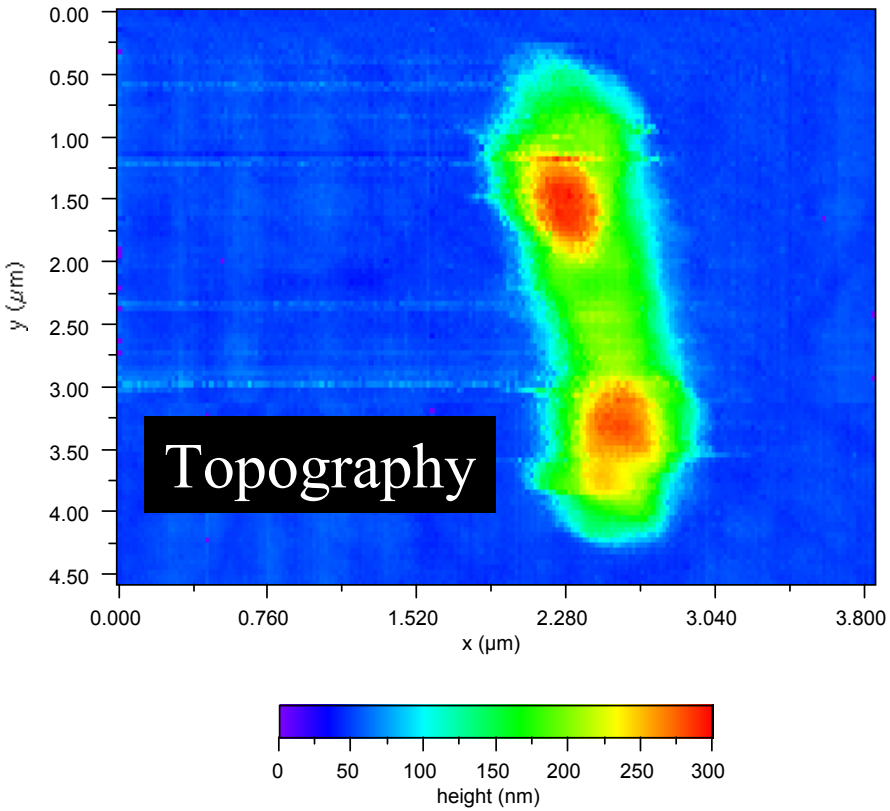
a) height=100 nm width = 1.5µm

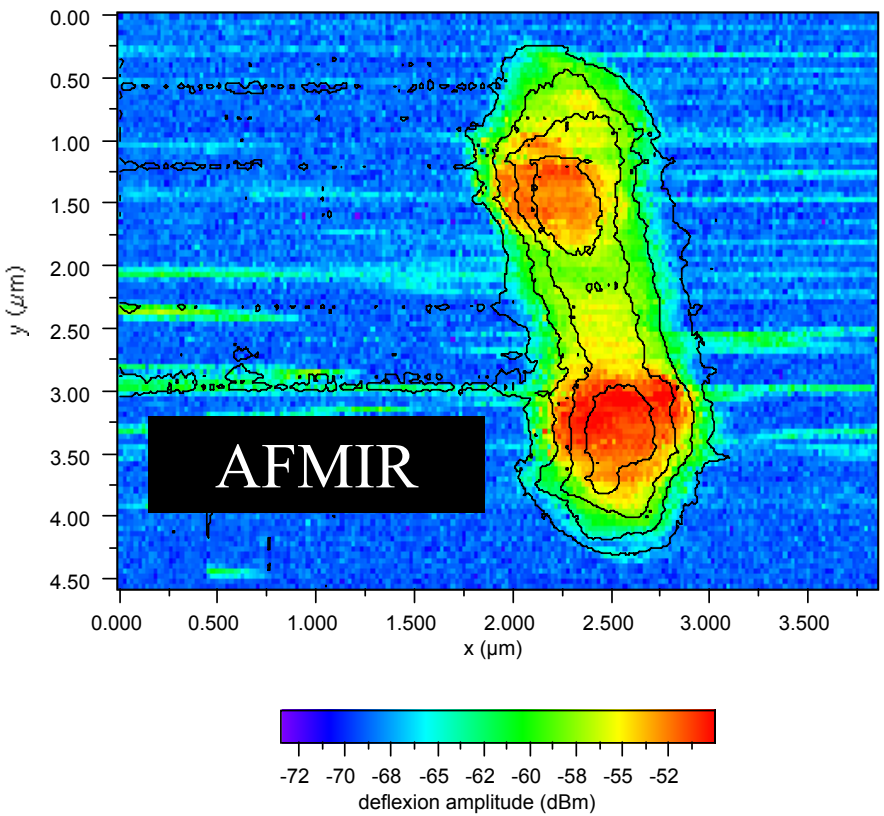
b) height=210 nm width = 1.5µm

c) height=450 nm width = 2µm



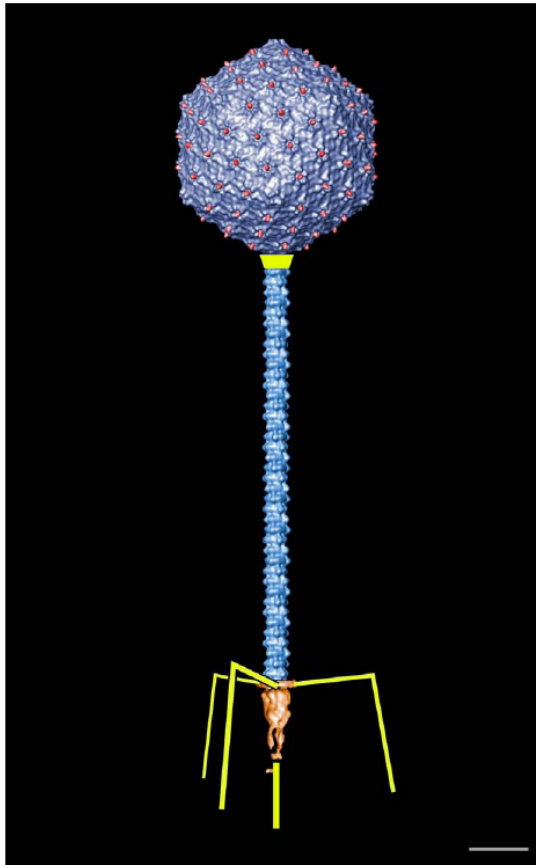
Mapping of amide I on a thin spectrally homogeneous sample (nearly homogeneous lighting)





Virus T5 infecting E. Coli bacteria

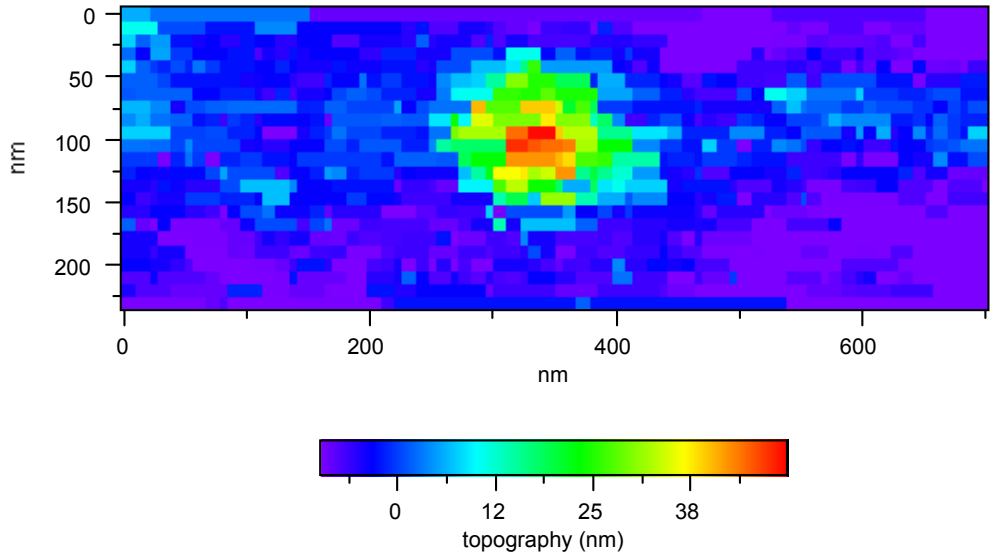
- Most of its weight is constituted by DNA
- It has a protein envelope : capsid
- The virus injects its DNA in the bacterium through its tail
- The DNA is replicated inside the infected cell
- New capsids are synthesized
- The process can be stopped at any stage
- Cells were dried in this experiment



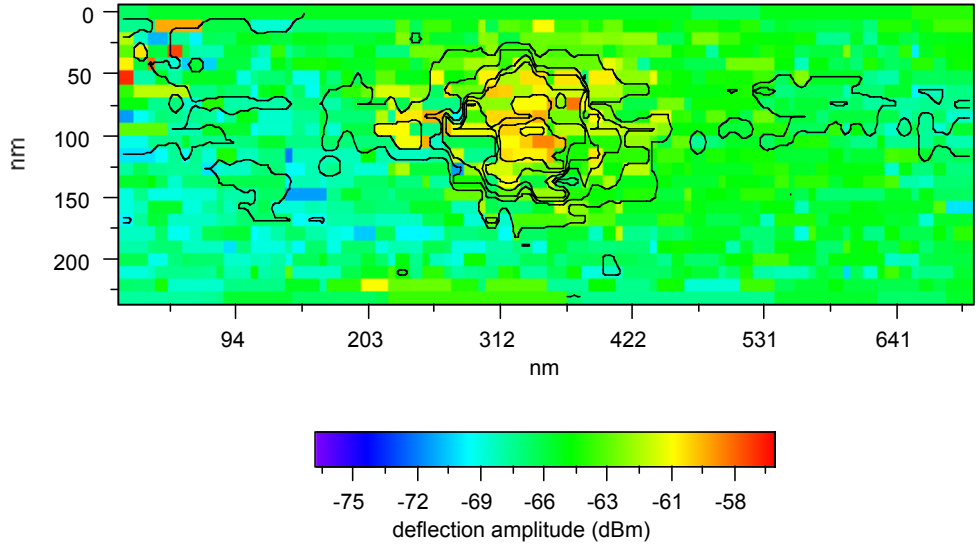
Observation of an isolated virus T5

(Amide I band at 1650 cm^{-1} : capsid)

AFM



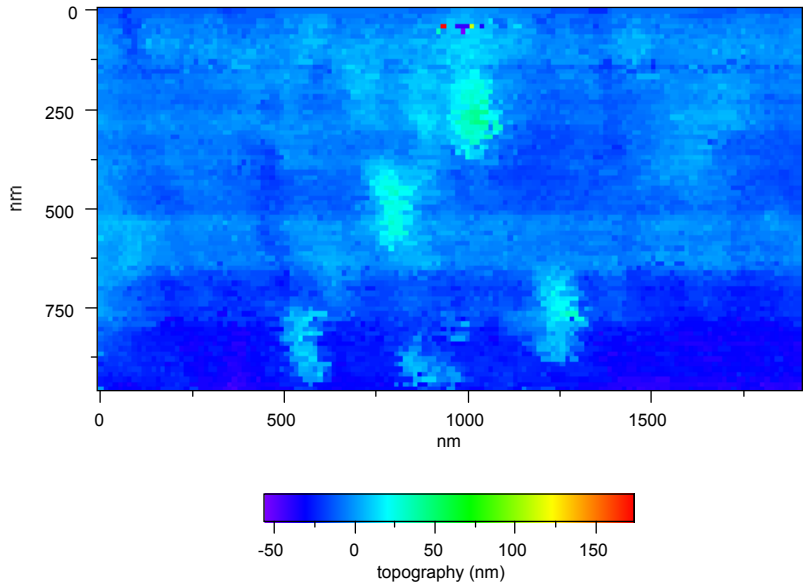
AFMIR



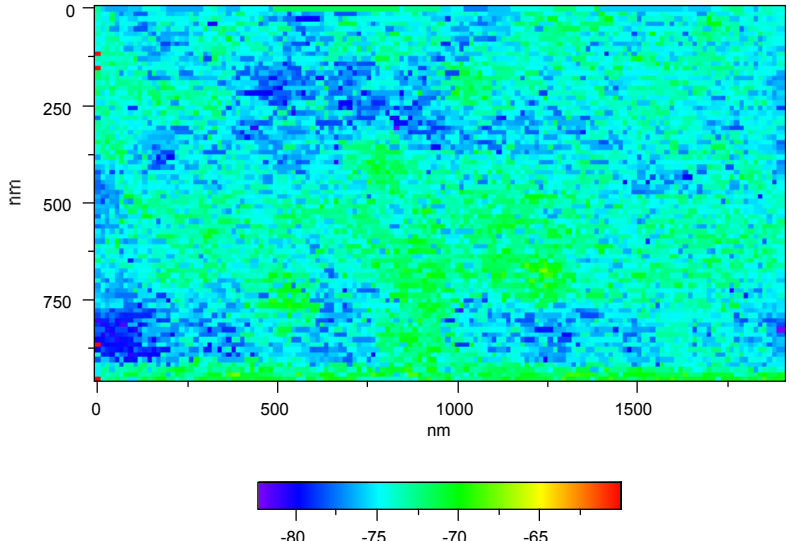
Observation of isolated virus T5

(DNA band at 1050 cm^{-1} : the dried virus has expelled its DNA and looks diluted)

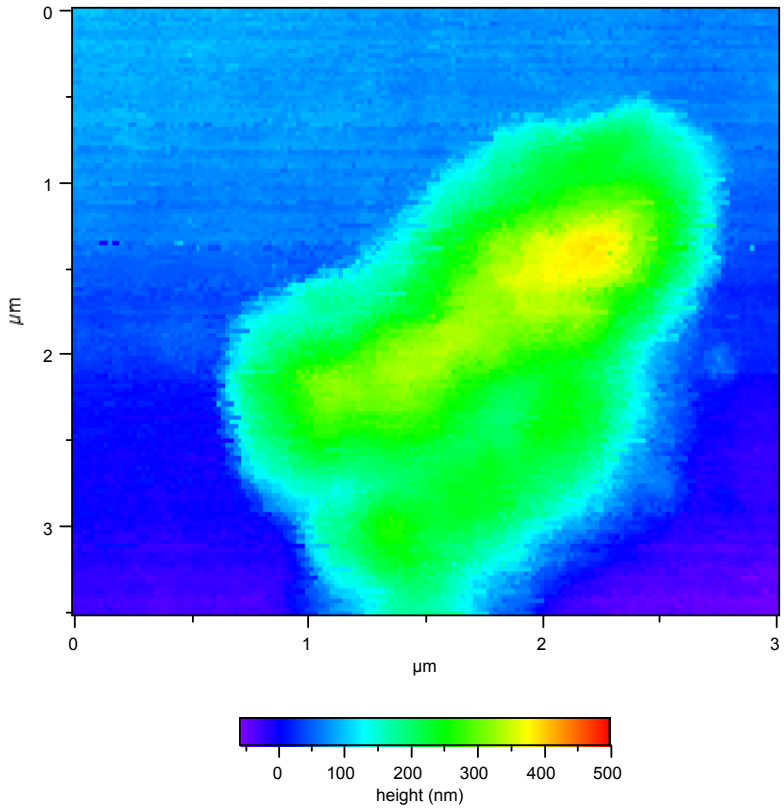
AFM



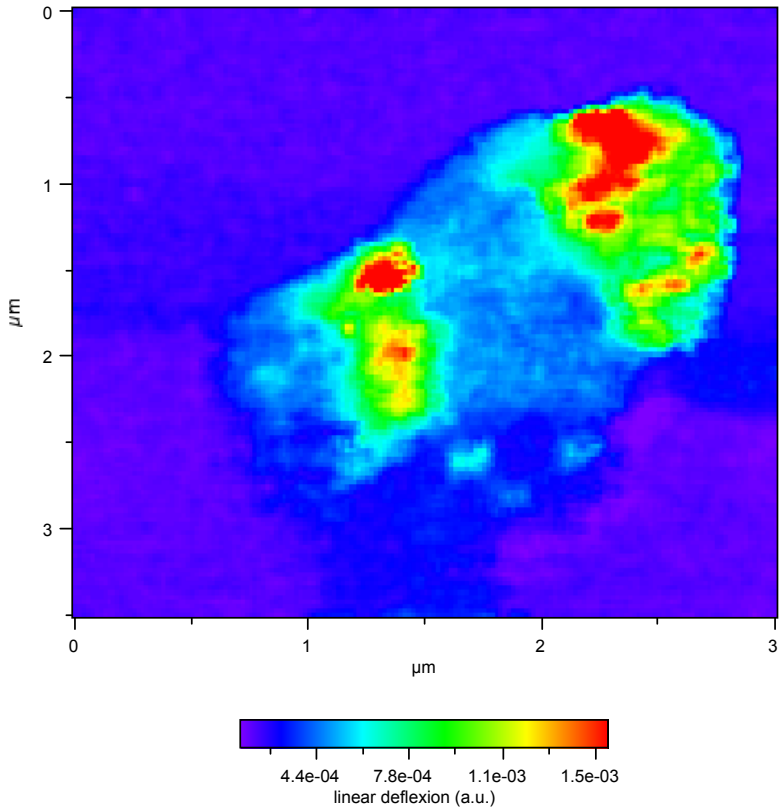
AFMIR



Observation of an heavily infected bacterium

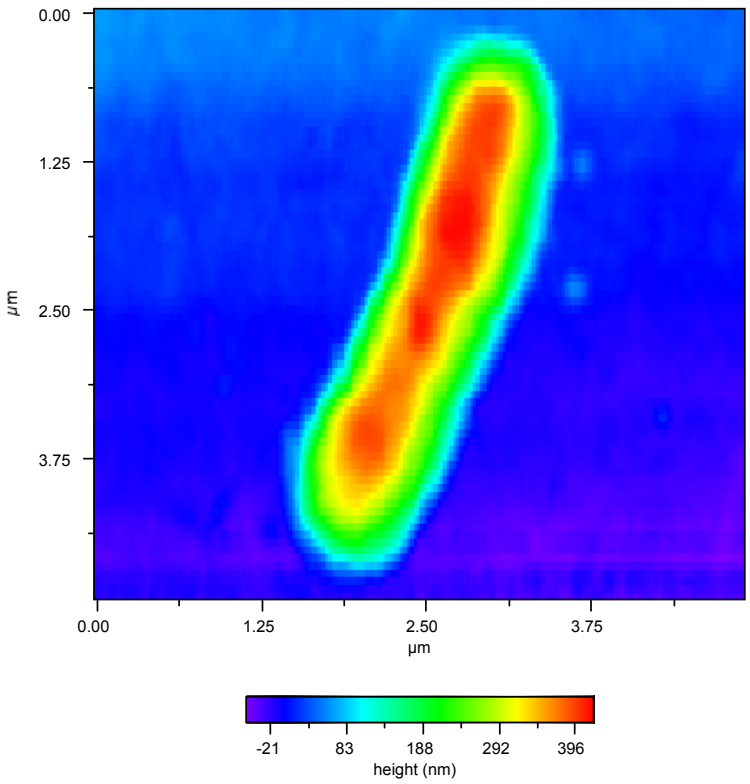


Topography
(AFM)

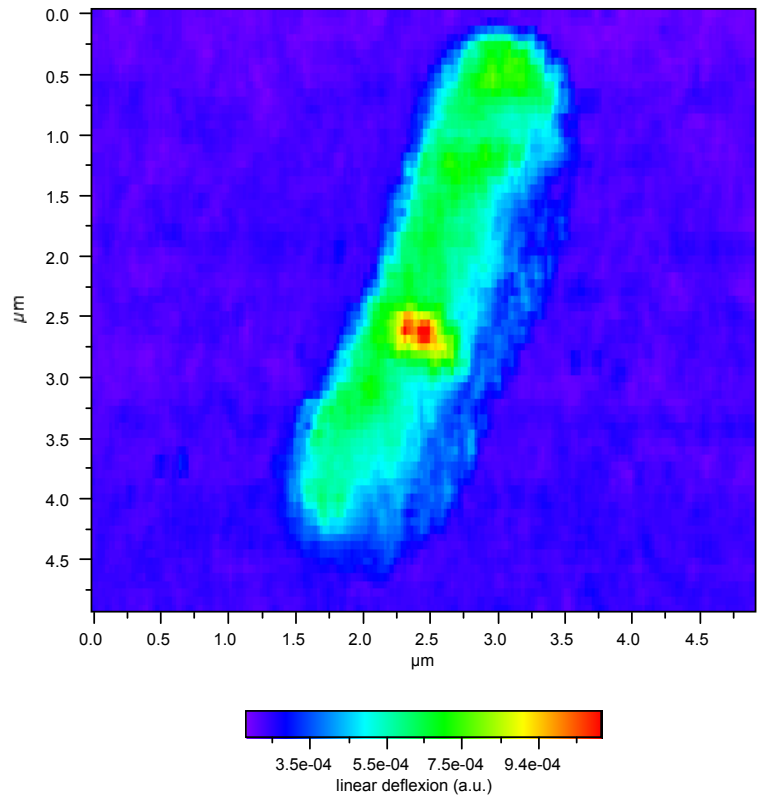


AFMIR
(bande de l'ADN)

Observation of a single virus infecting a bacterium



Topographie
(AFM)



AFMIR
(ADN bande)

Zooming on the single virus

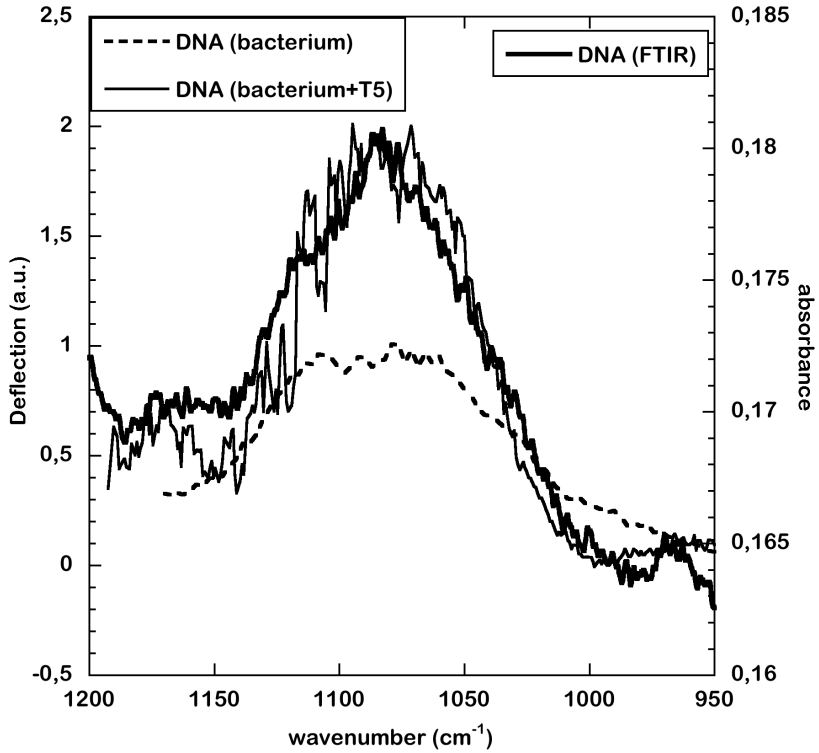
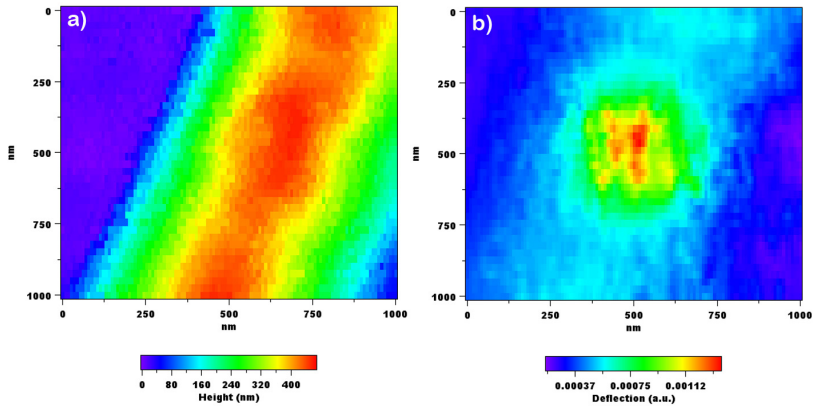
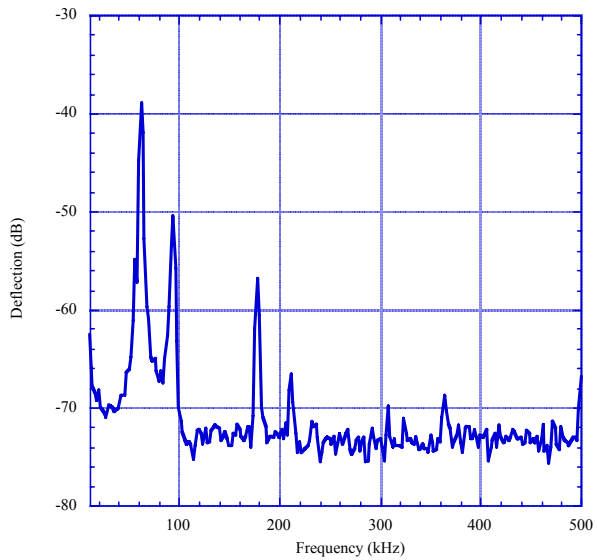


figure 12

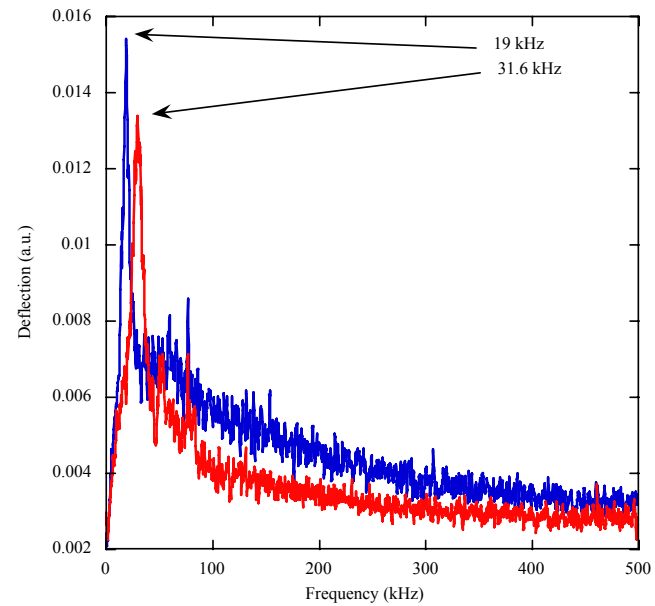


First experiments living cells (in water)
(on candida albicans cells)

Frequency response of the cantilever :



On the cell in air



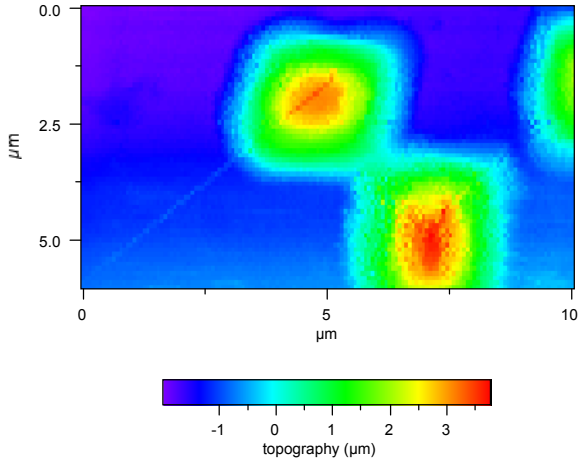
In water : on the cell (red)
on substrate (blue)

==> selecting the peak frequency (31,6 MHz) allows to image the cell

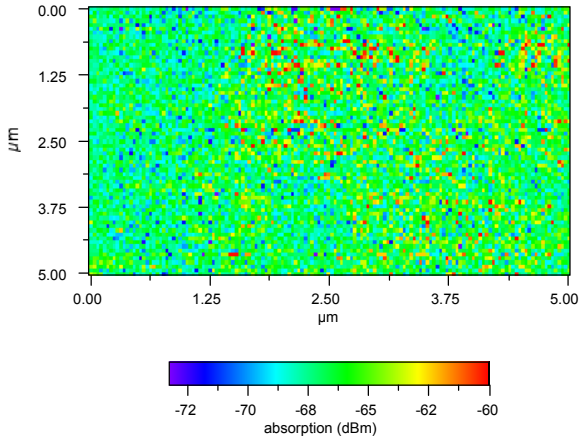
Mapping in water
of living cells
(candida albicans
glued on the substrate)

Wavelength : 1080 cm^{-1}

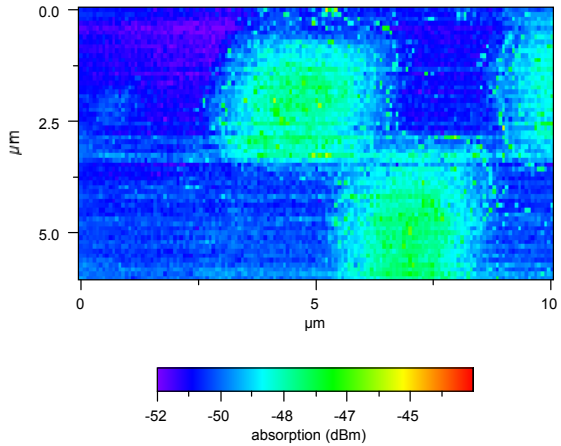
AFM
topography



AFMIR
Topography
at 80 kHz



AFMIR
Topography
at 31.6 kHz



Why is the observed spatial resolution so good ?

- AFMIR spatial resolution is < 100 nm

limited by tip size, sample characteristics, S/N ratio

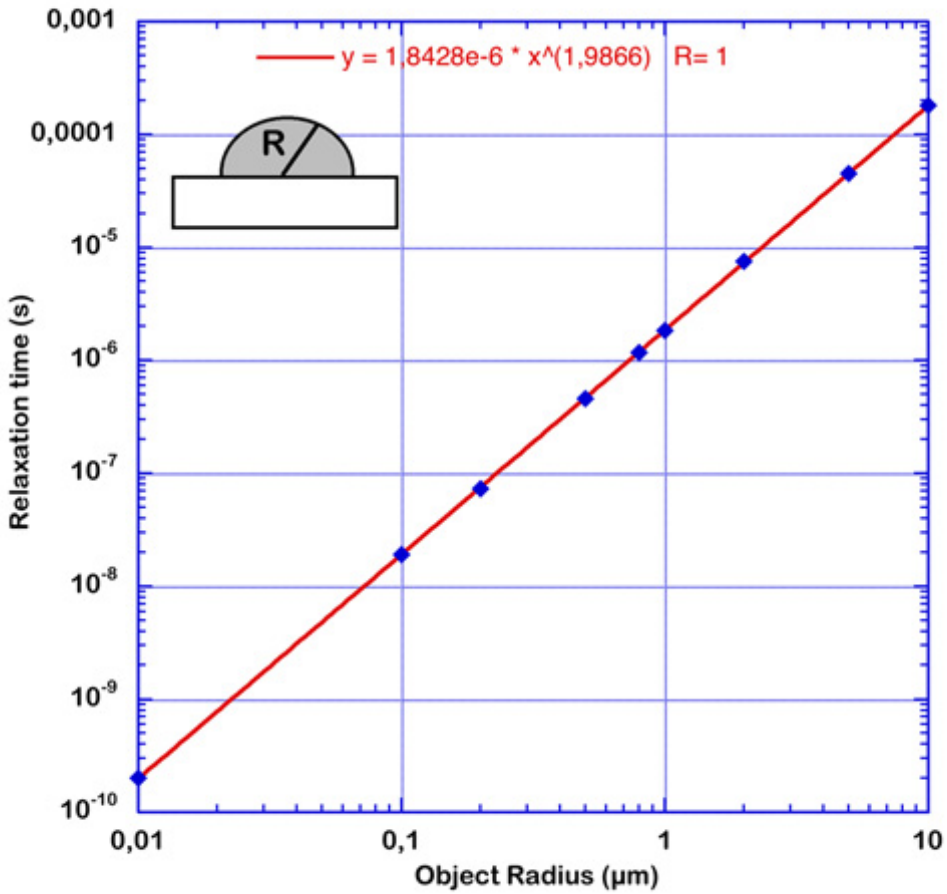
- One expect heat diffusion of ≅1 μm/μs (speed of sound)
- Measurement is done in more than tens of μs

  ===> surprising that resolution << 1 μm
- Simulations show that the heat is diluted in

  the substrate and in air

  ===> Almost no signal outside the absorbing zone

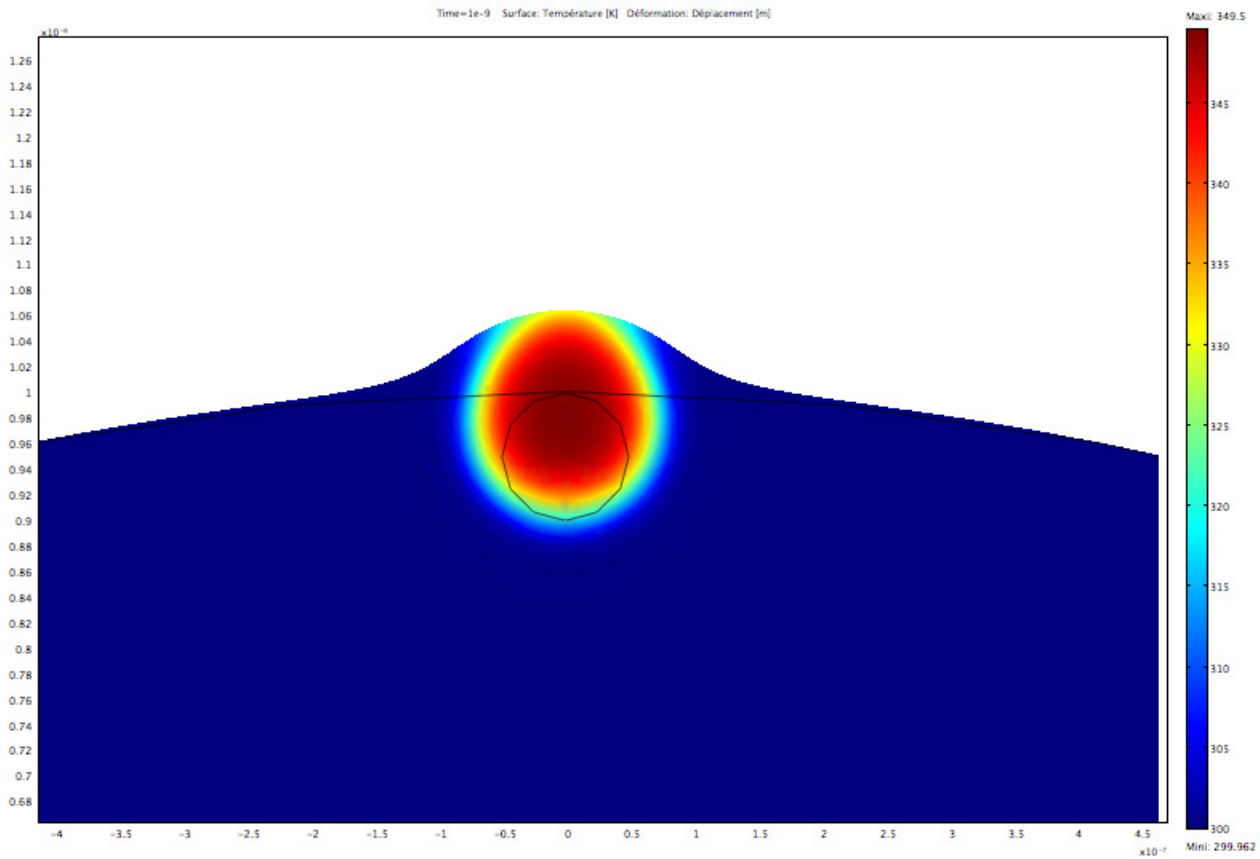
COMSOL simulation of cooling of an hemispherical object



==> After excitation of the cantilever vibration,
the heat is diluted extremely rapidly in the substrate

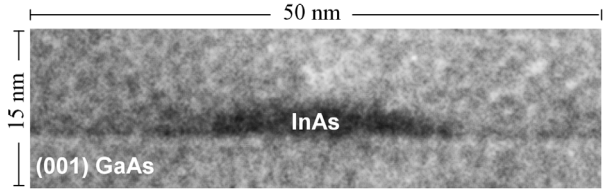
(but too many excited samples on the substrate can “pollute” the signal”)

COMSOL simulation of transient dilatation around the virus



The spatial resolution is limited at ≅ 200 nm in the case of the « buried » virus

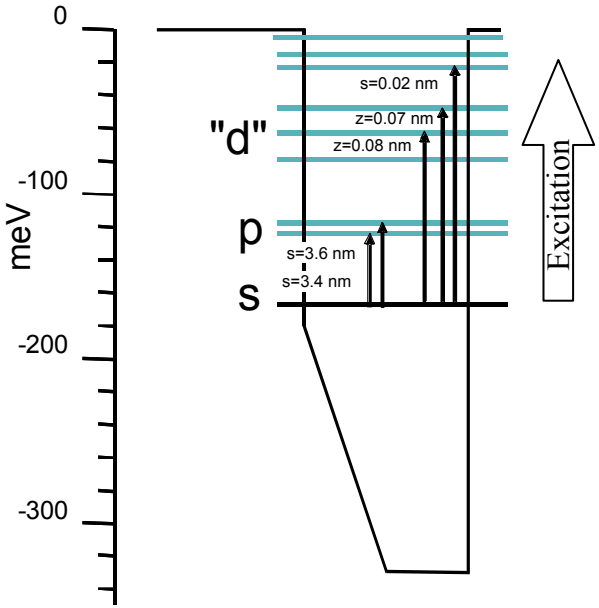
Application : absorption nanospectroscopy of a single quantum dot

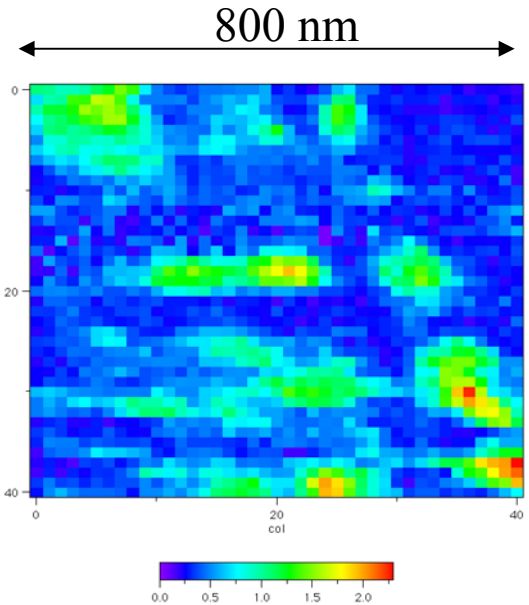


InAs/GaAs self-assembled quantum dot

Quantum dots are "buried" and cannot be observed by AFM

Density : 400 dots per μm^2
20 nm diameter
n-type doping
Resonant absorption in the mid-infrared





Single quantum dot absorption @ room temperature

$\lambda_{exc} = 9.6\ \mu m$
Measurement performed with CLIO + AFMIR

Spatial resolution ~ 80 nm

J. Houel, S. Sauvage, P. Boucaud

Conclusion:
AFMIR + CLIO/OPO capabilities

- Powerful tool to measure local relative absorption
- Good spectral resolution (fit well FT-IR spectrum)
- High spatial resolution (< 100 nm $<< \lambda_{infrared}$)
- Various applications underway