

**SCF2023
Congress**

June 26th to 28th, 2023
Cité des Congrès de Nantes

Contact



**General public
week-end**

co-organized by
 Chimie
& Société
June 24th-25th, 2023
Museum de Nantes

Contact

AFM-IR : When AFM meets IR

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Université Paris-Saclay

**université
PARIS-SACLAY**

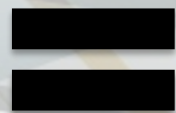


AFM-IR technique

AFM



IR laser



AFM-IR

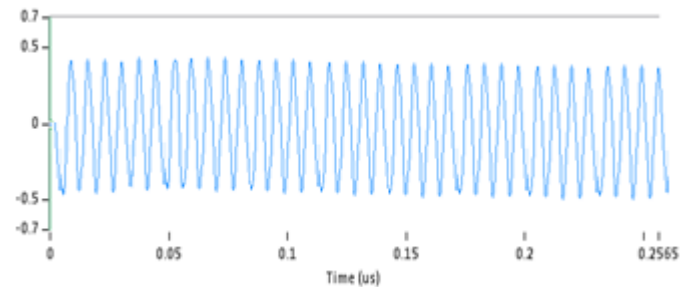
Infrared spectroscopy and imaging at nanoscale

Technique principle

AFM-IR setup

Contact mode

Cantilever deflection detection

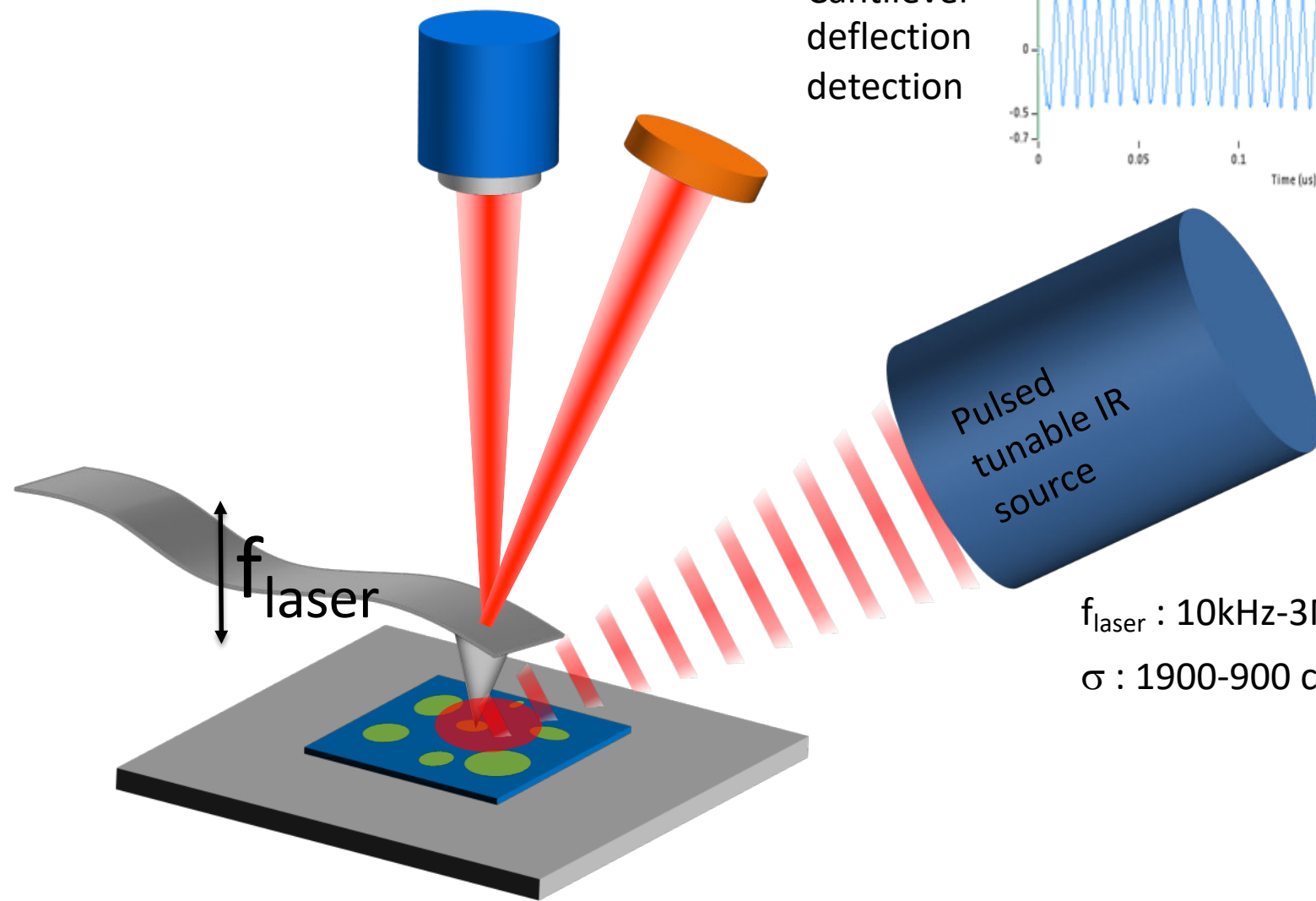


Pulsed tunable IR source

$f_{\text{laser}} : 10\text{kHz}-3\text{MHz}$

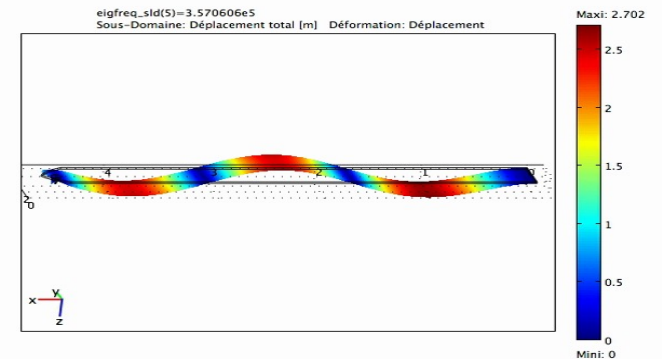
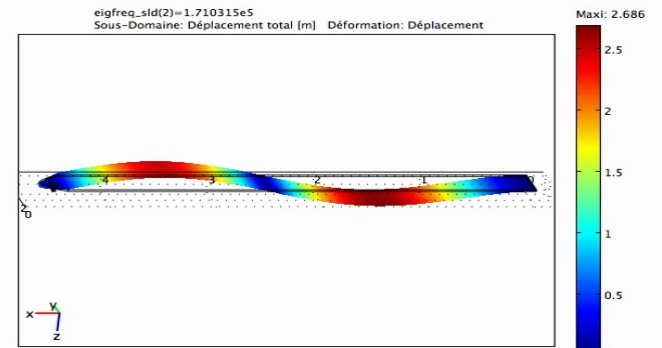
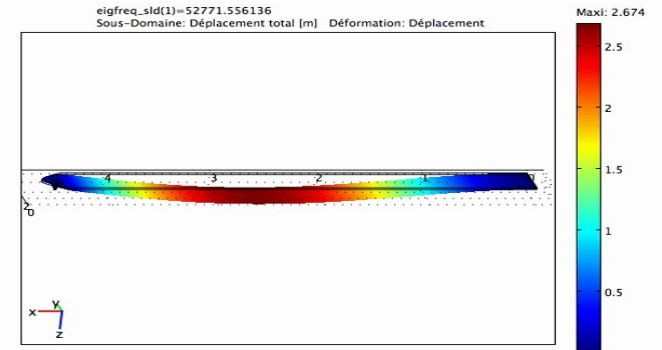
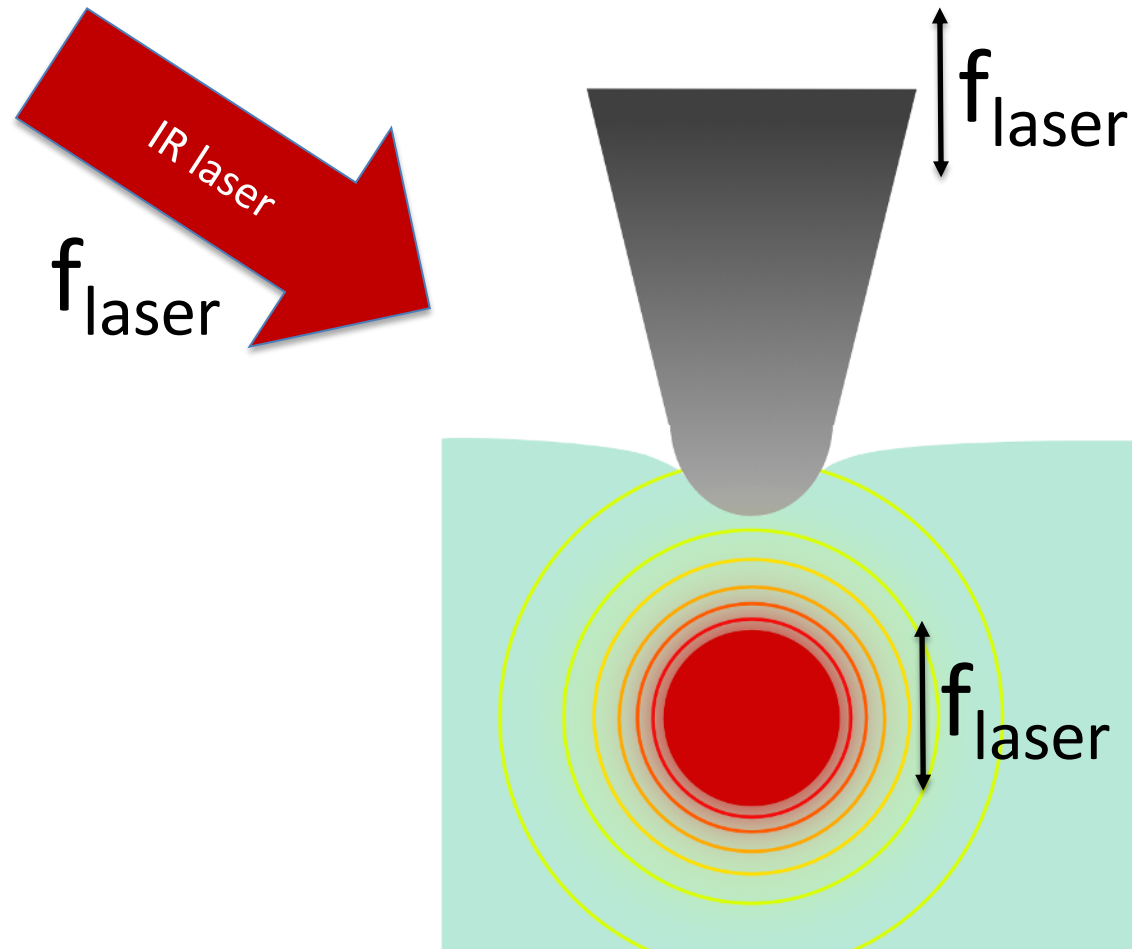
$\sigma : 1900-900\text{ cm}^{-1}$

f_{laser}



AFM-IR setup

Photothermal excitation and photoacoustic detection



Resonance enhanced AFM-IR

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

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

Amplitude(Z) \propto thermal expansion(a₀) \propto absorbance

J. Mathurin, A. Deniset-Besseau, D. Bazin, E. Dartois, M. Wagner, A. Dazzi, *J. Appl. Phys.* 131, 010901, 2022.

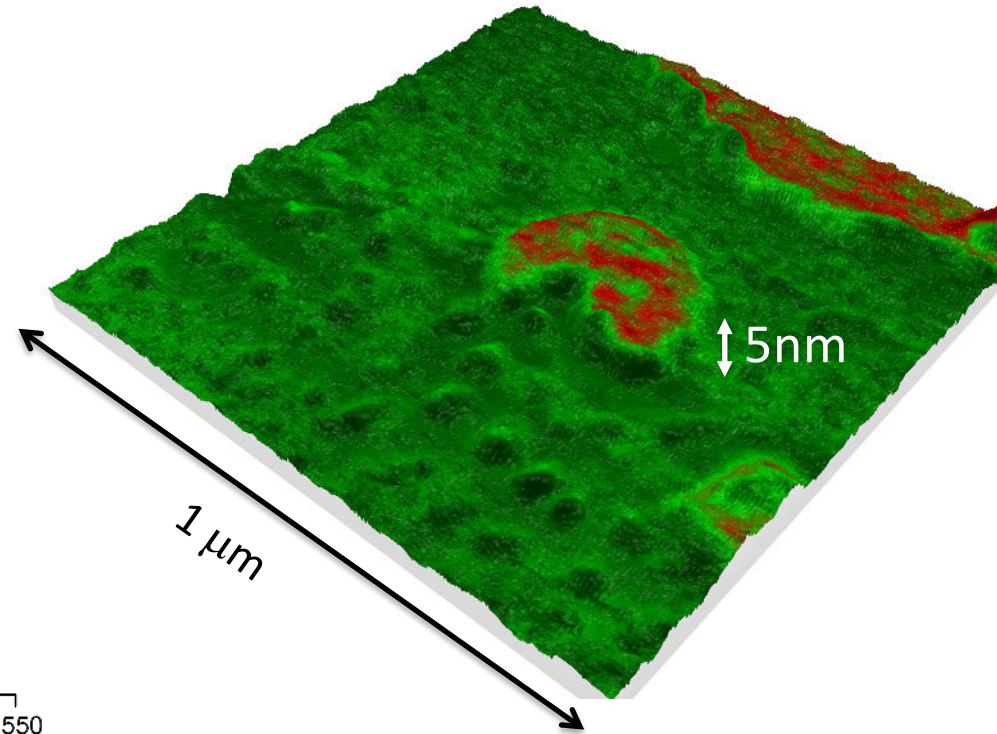
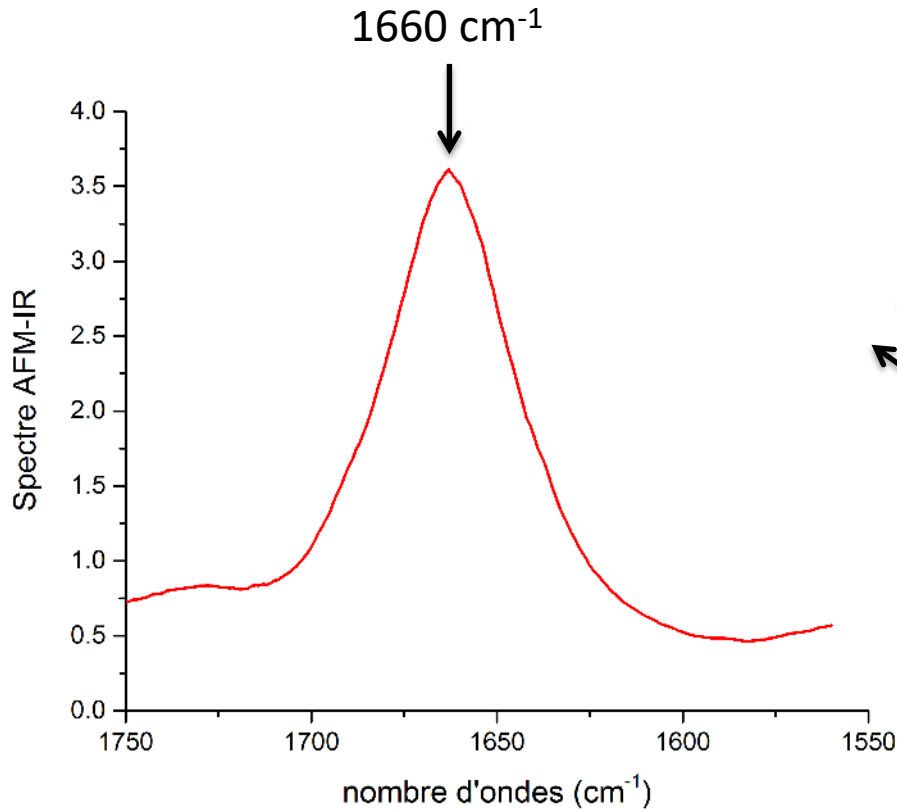
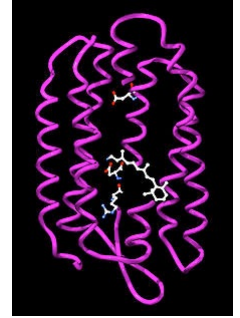
D. Kurouski, A. Dazzi, R. Zenobi, A. Centrone, *Chem. Soc. Rev.* 49, 3315-3347, 2020.

J. Mathurin, E. Pancani, A. Deniset-Besseau, K. Kjoller, C.B. Prater, R. Gref, A. Dazzi, *Analyst*, 143, 5940-5949, (2018).

A. Dazzi, C.B. Prater, *Chem. Rev.*, 117, 7, 5146–5173, (2017)

Resonance enhanced AFM-IR

Bacteriorhodopsin protein
Detected inside a purple membrane



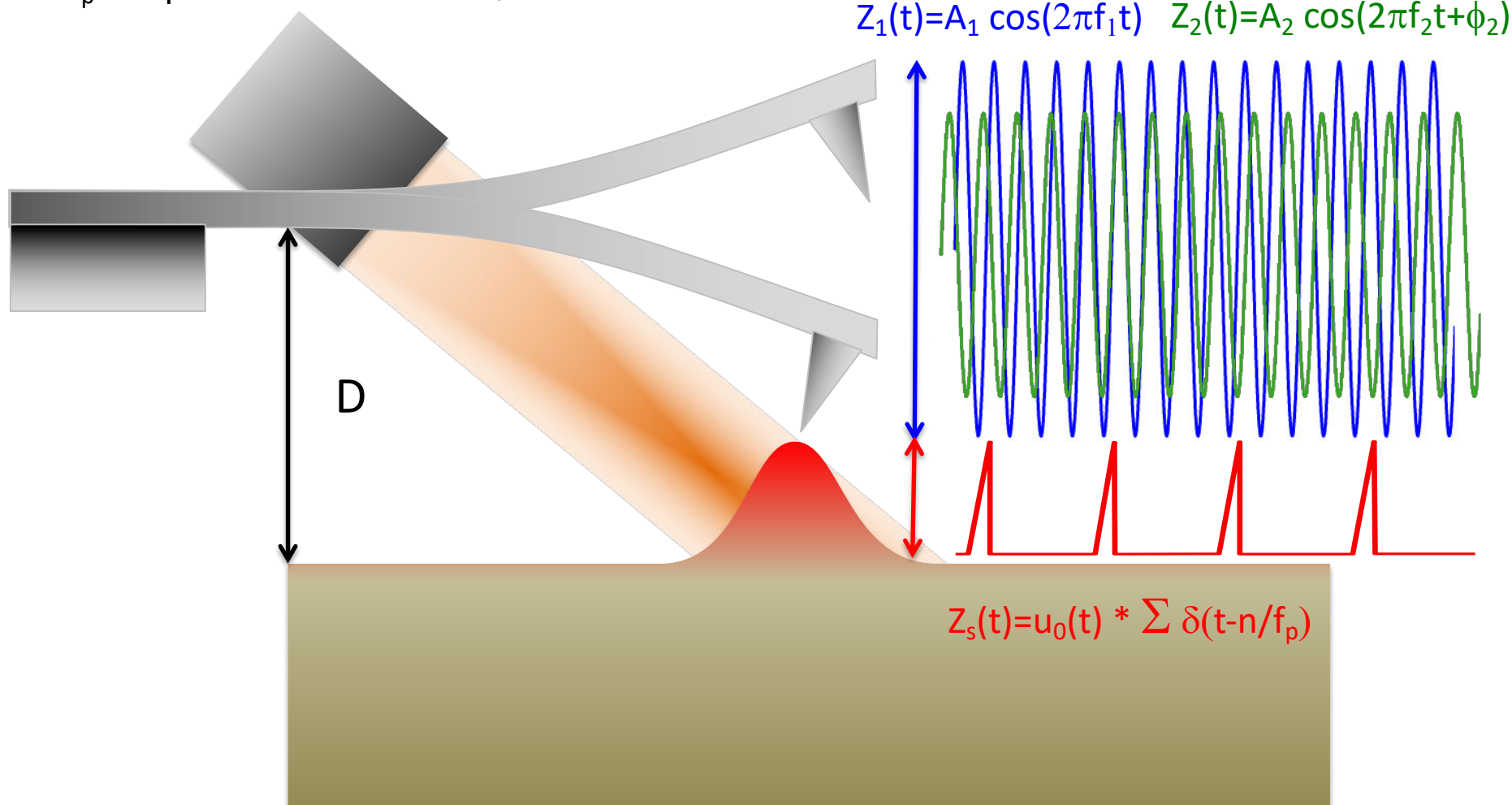
Tapping AFM-IR

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

Amplitude of the second mode f_2

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

Non linear elasticity contact coefficient

Setpoint

Laser pulse

Cantilever parameters

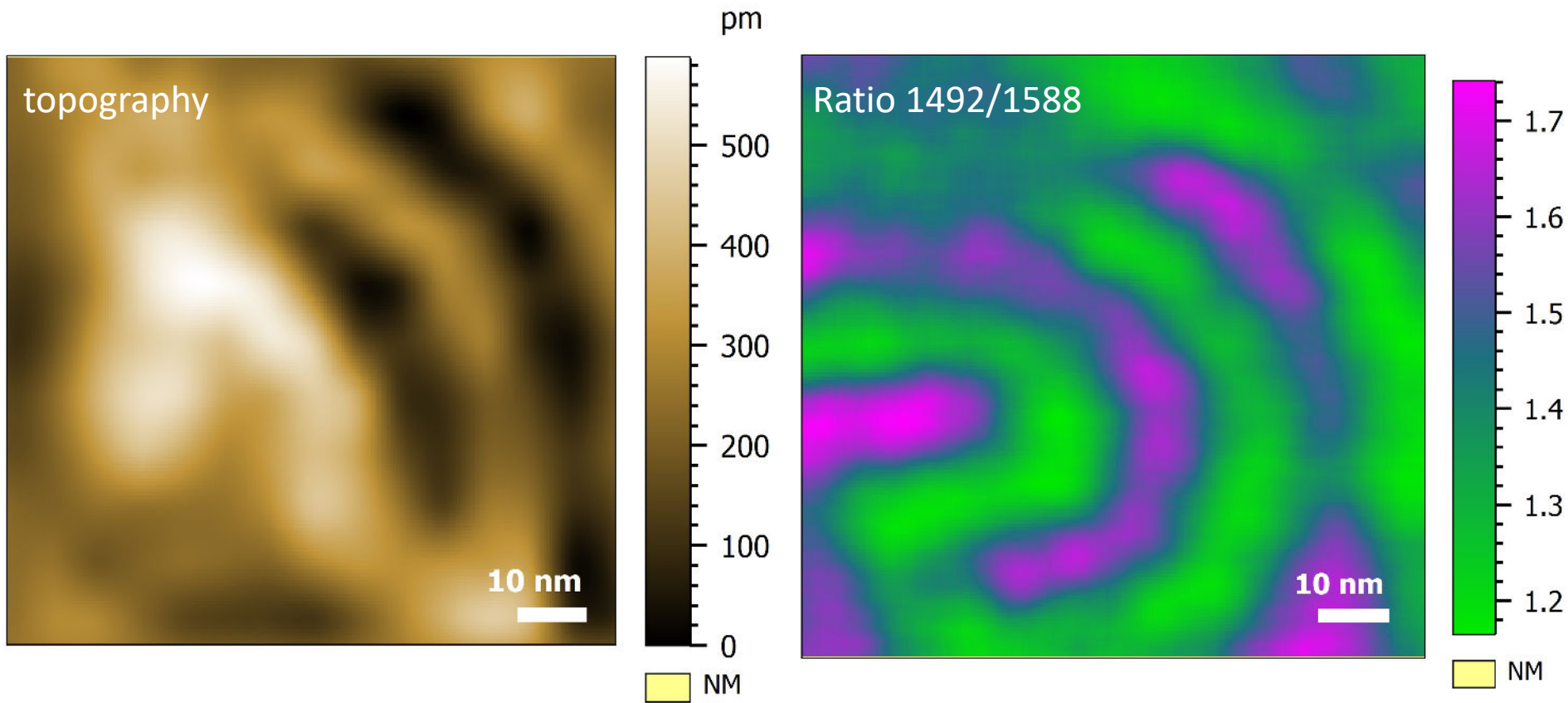
Driving amplitude

**Thermal expansion
 α Absorbance**

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

Tapping AFM-IR

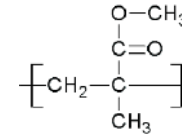
PS-b-P2VP lamellar polymer



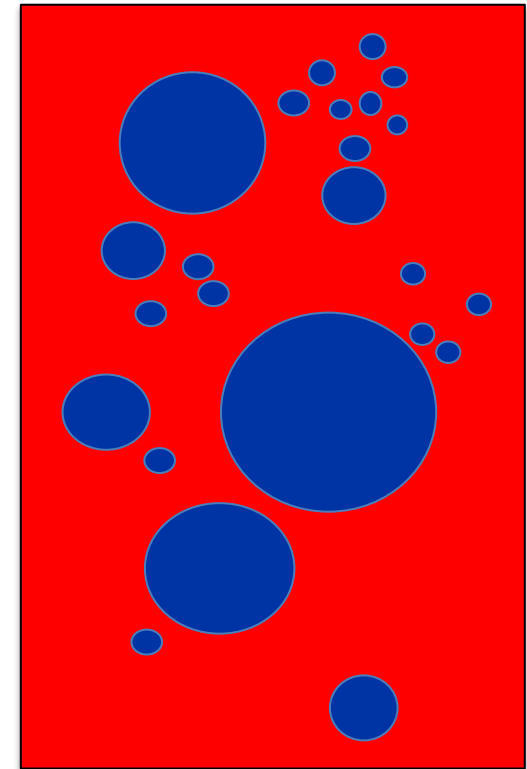
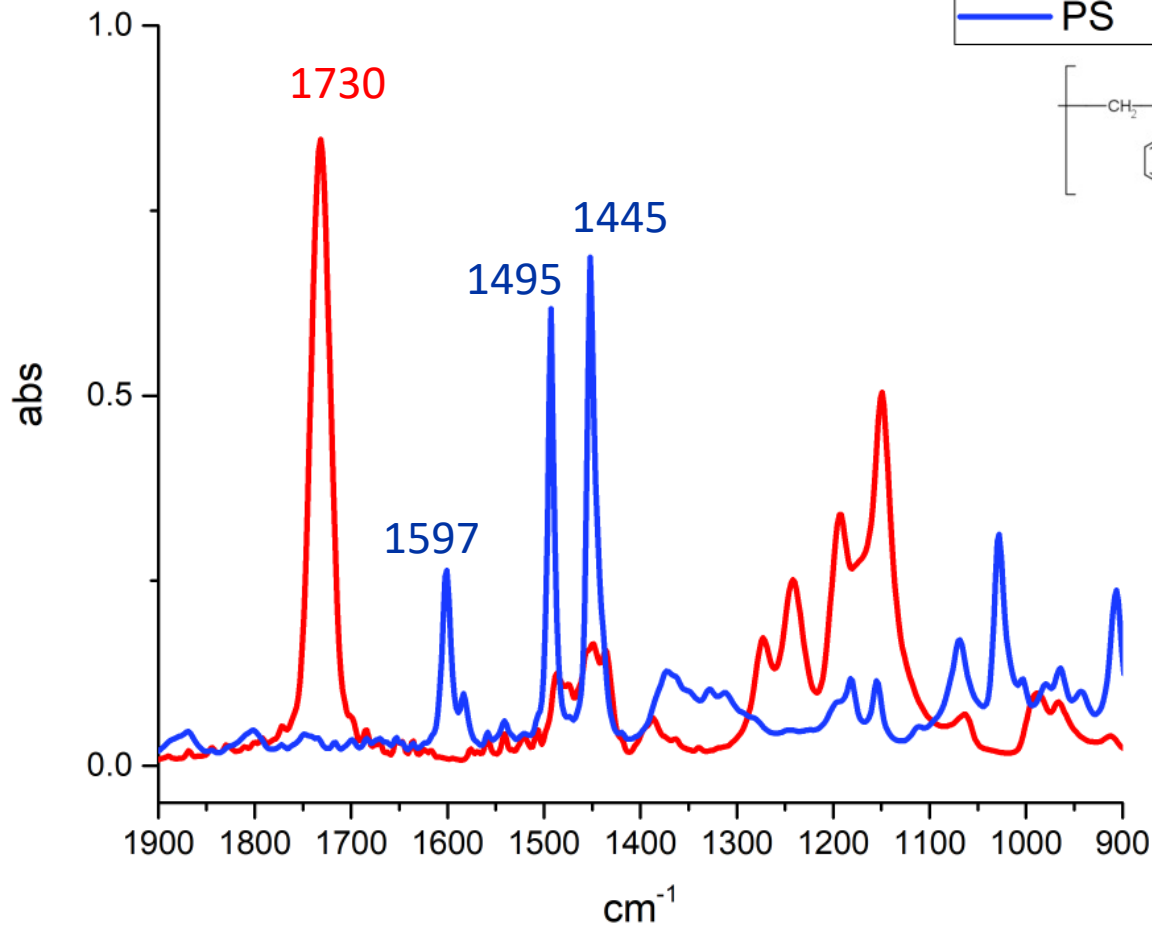
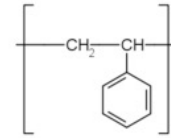
Exemples of Applications

Polymer science

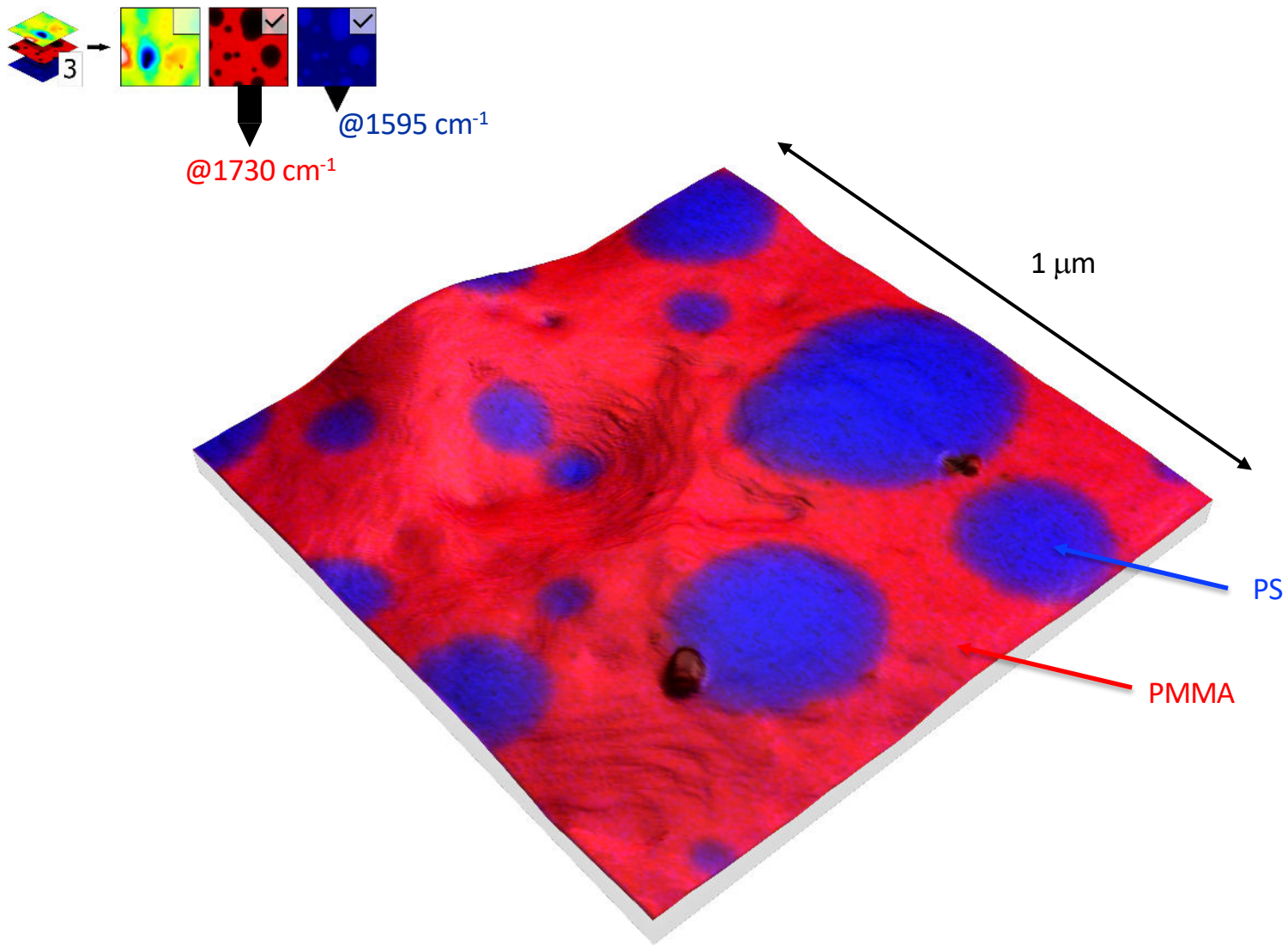
PMMA-PS polymer blend 1-1



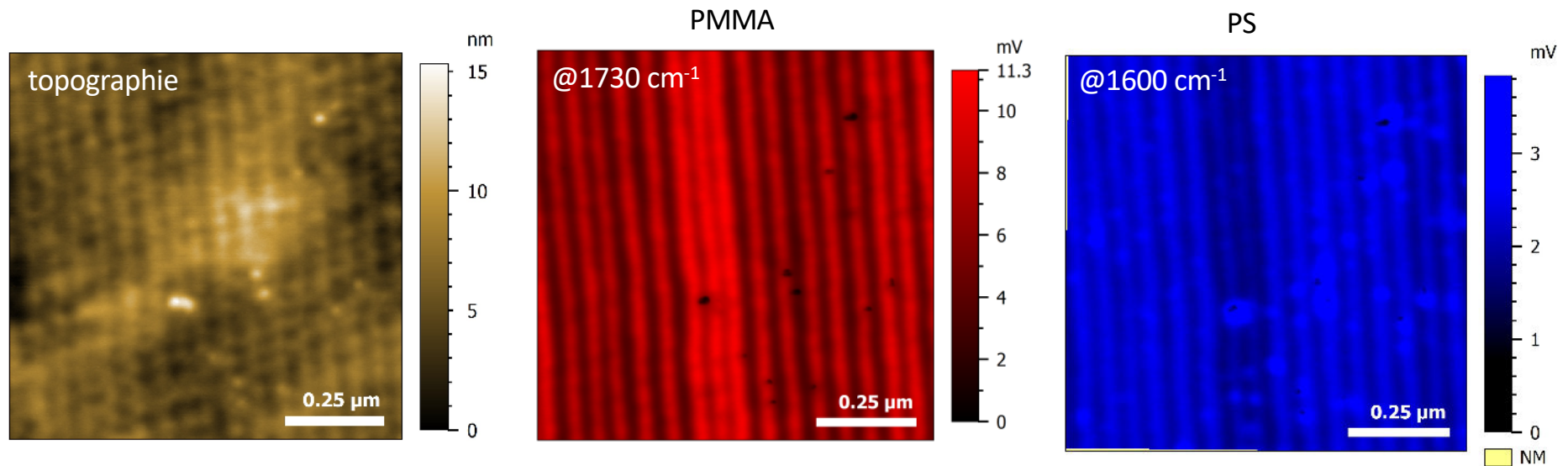
— PMMA
— PS



Polymer science

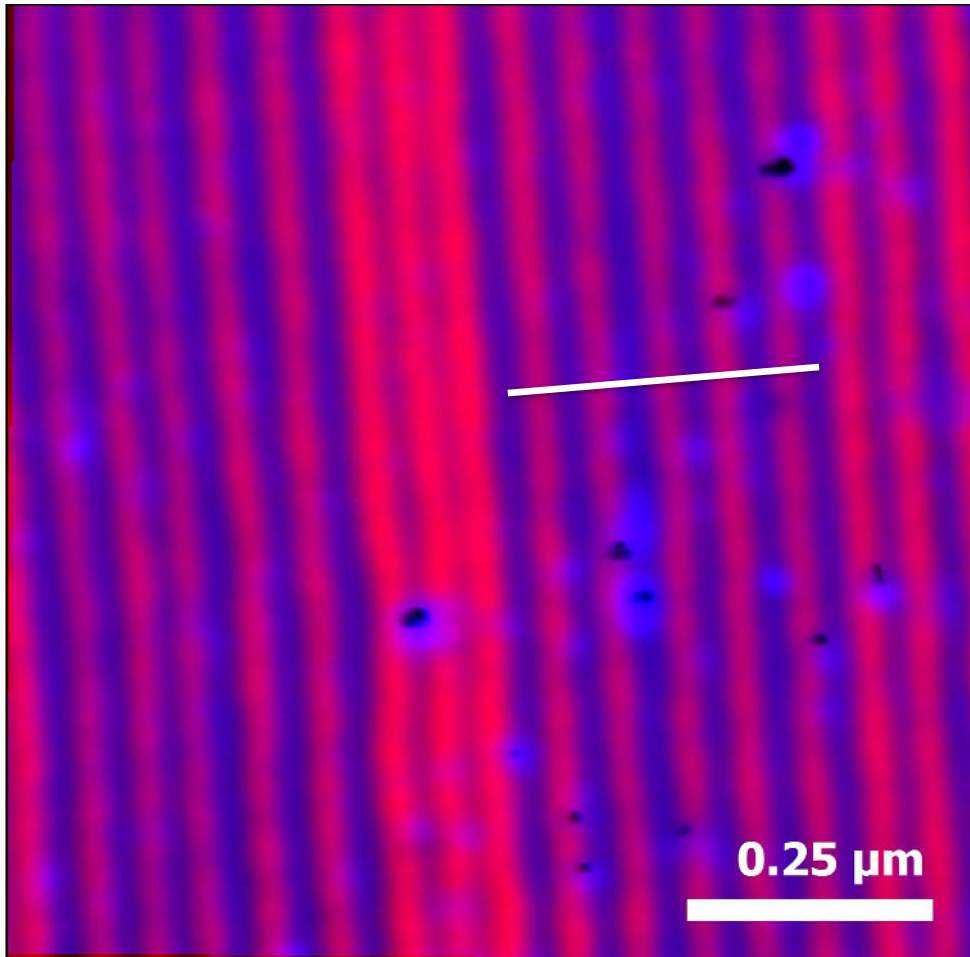


PS-PMMA multilayers film

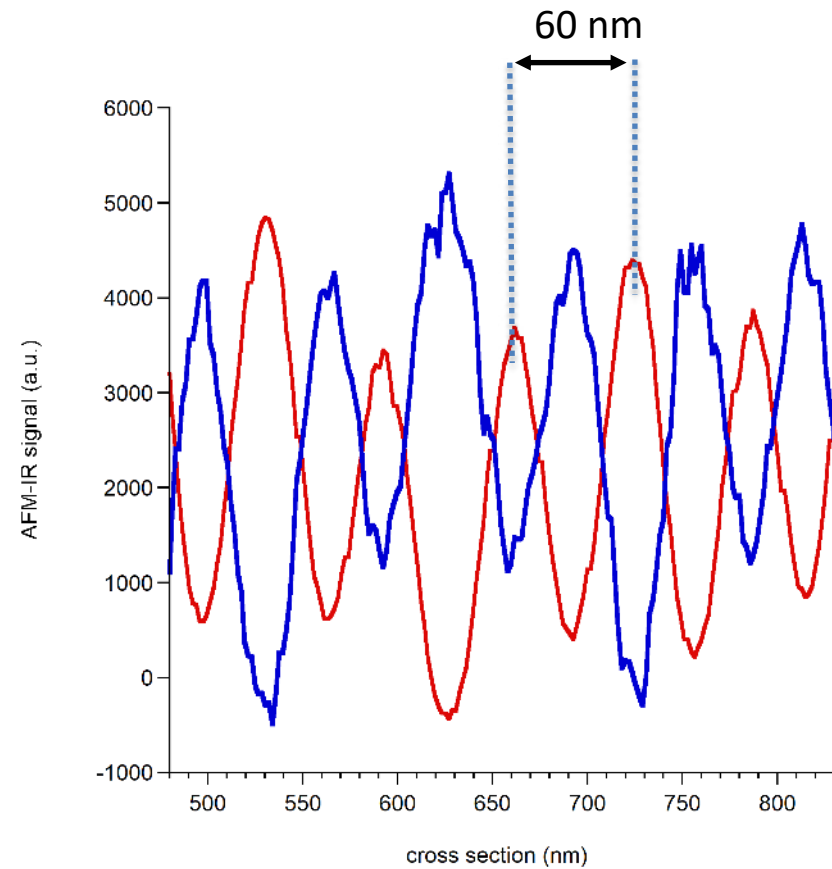


Polymer science

Overlay (1730/1600)

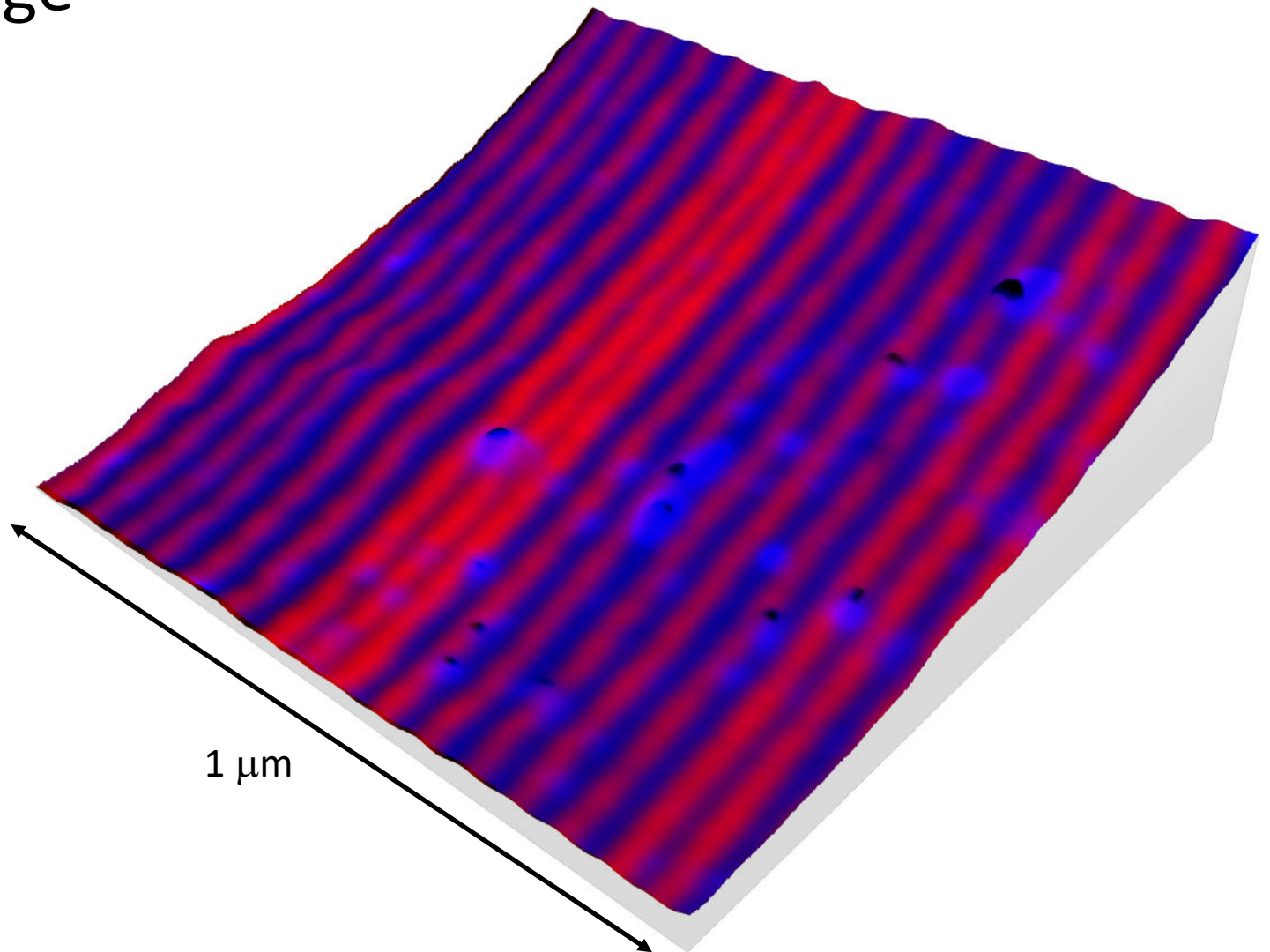


Cross section



Polymer science

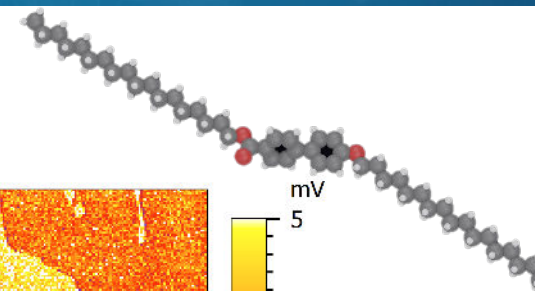
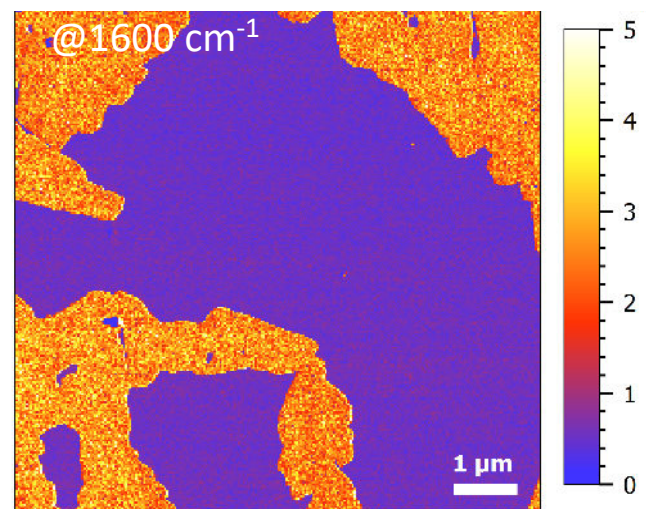
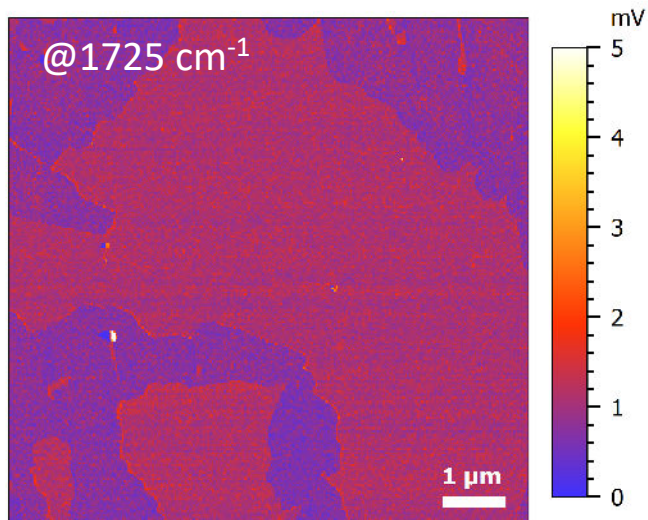
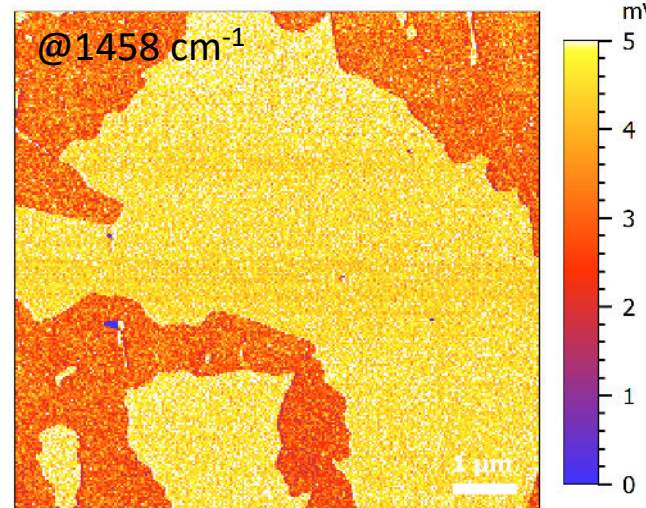
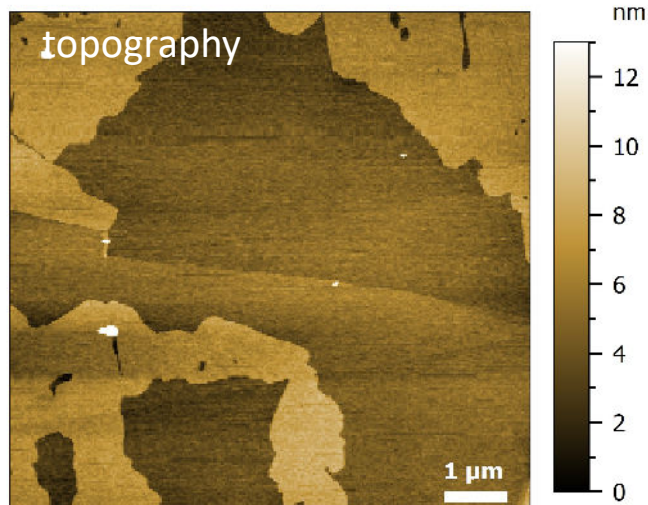
3D image



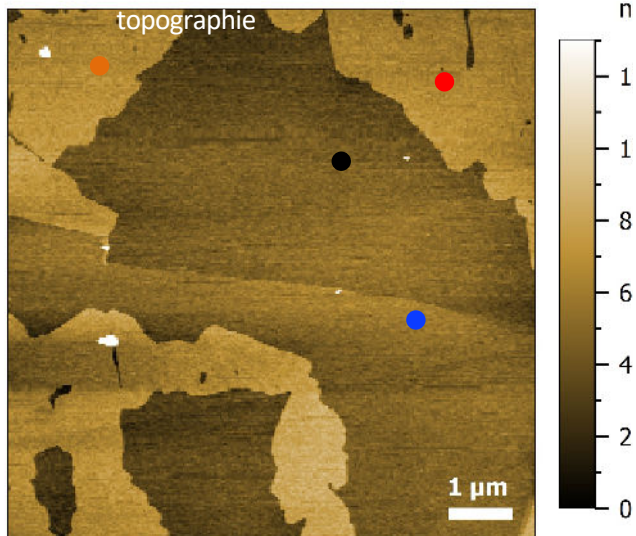
2D chemistry science

Organic molecule self-assembly on HOPG

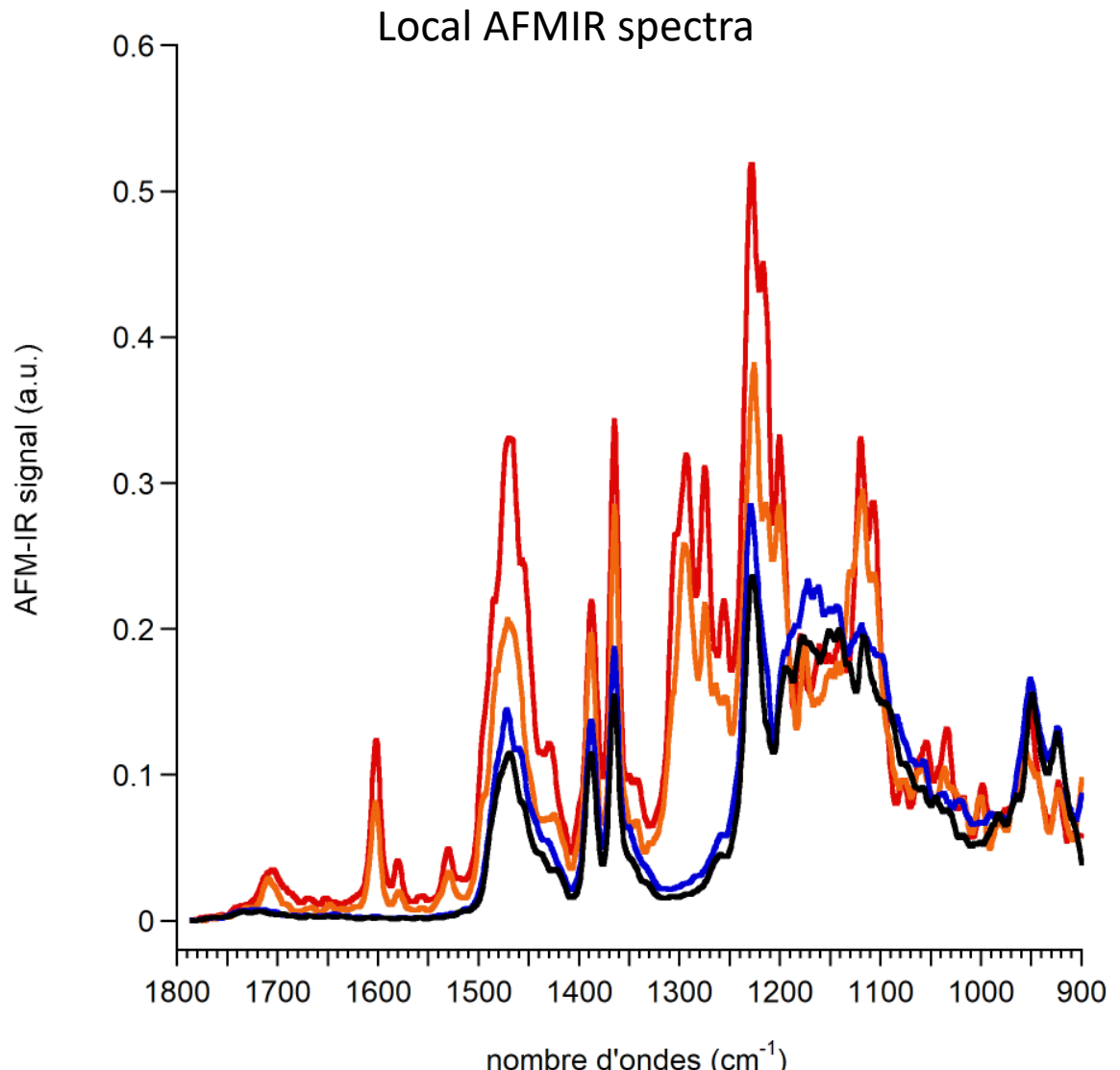
(4'-octadecyloxy-4-biphénylcarboxyloate d'octadecyle)



2D chemistry science



Polarisation of the incident light
is perpendicular to the surface



Astrochemistry

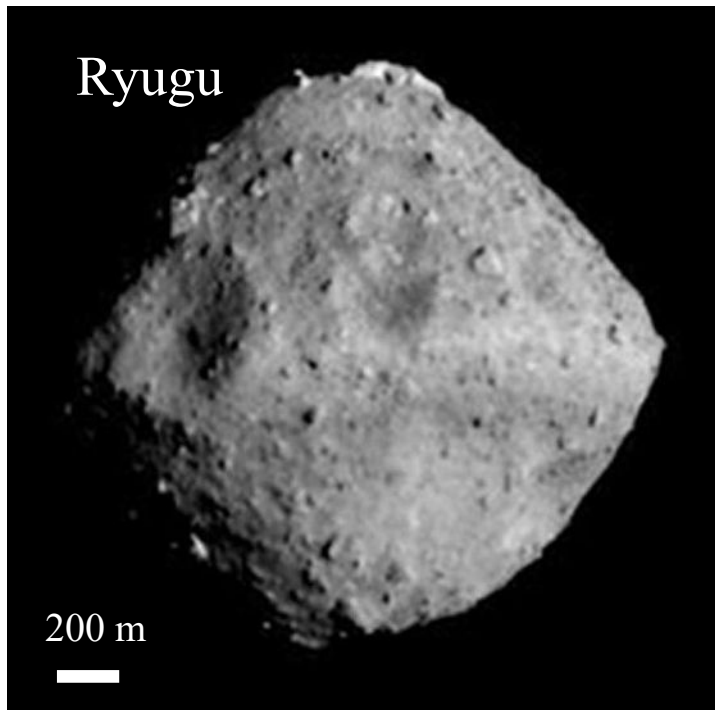


Wednesday 28 June 2023

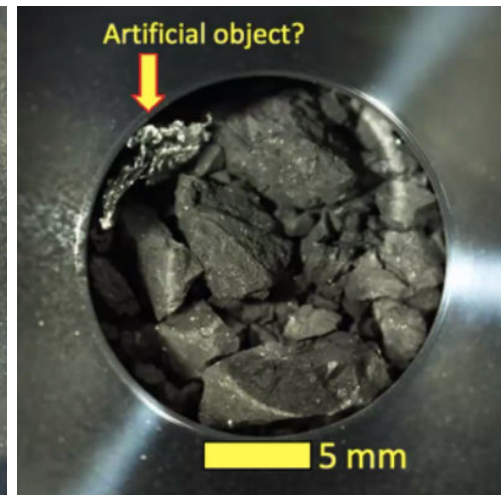
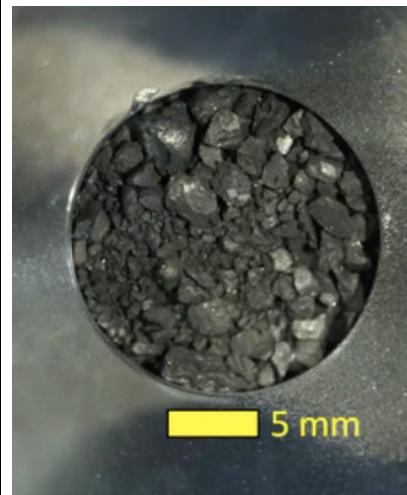
Physical Chemistry 7
ROOM 300

11:15 - 330 | NANOSCALE INFRARED CHARACTERIZATION OF
EXTRATERRESTRIAL RYUGU SAMPLES RETURNED BY THE HAYABUSA 2
SPACE MISSION

MATHURIN Jérémie - ICP, UPSACLAY, CNRS - FR

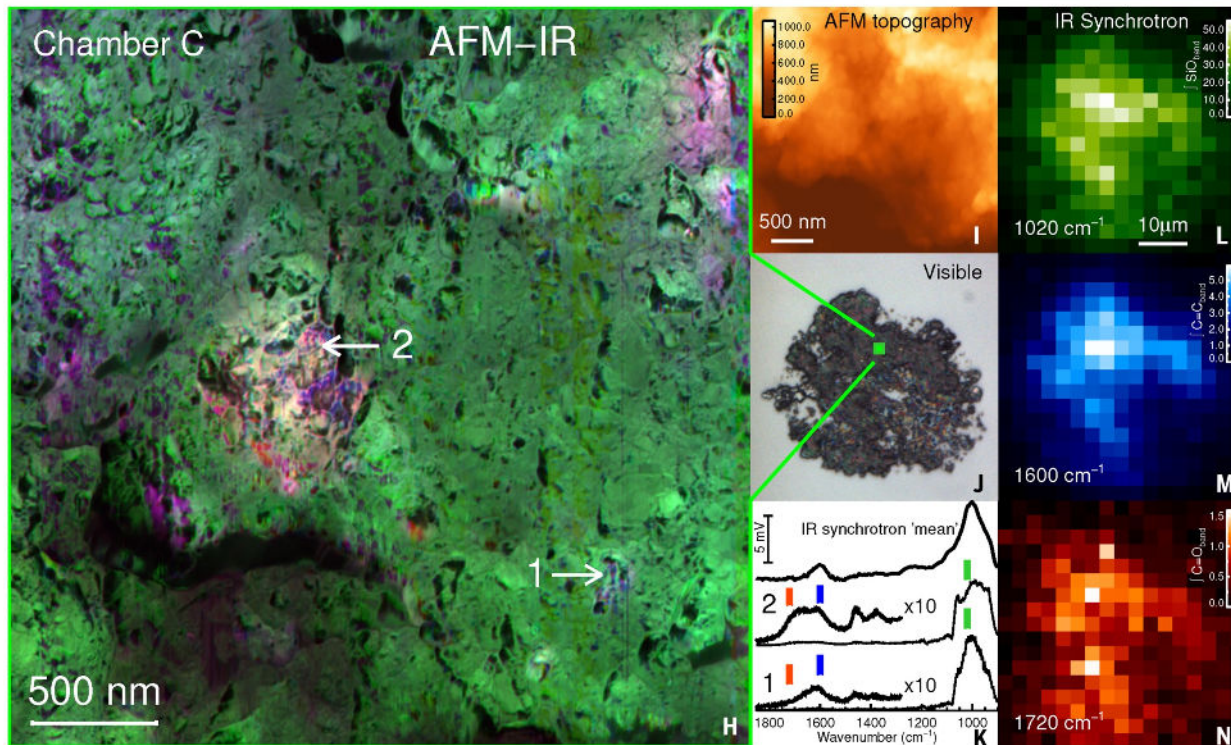
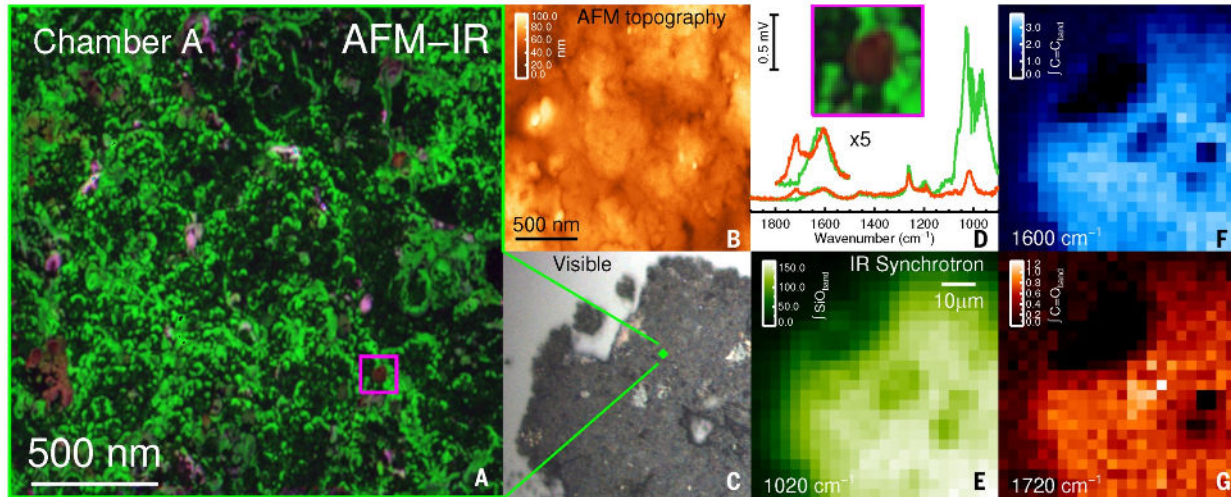


Hayabusa2 : December 2014 – December 2020
Ryugu : Cb-type asteroid, contain organic matter,
CI-like chemical composition



Astrochemistry

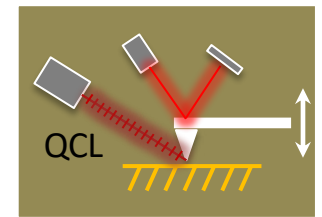
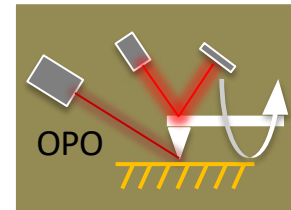
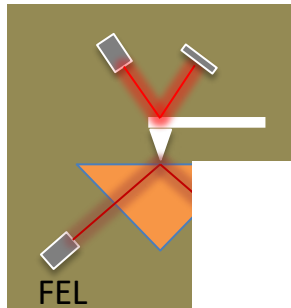
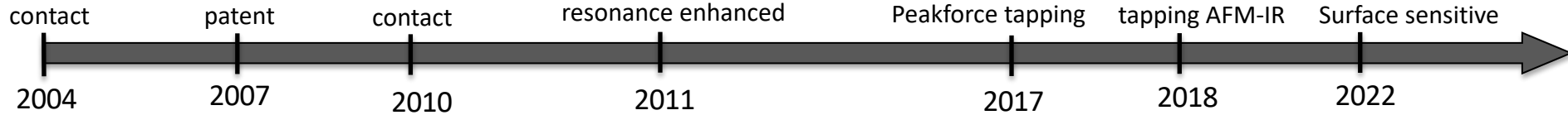
H Yabuta et al. *Science* (162173), 2023.



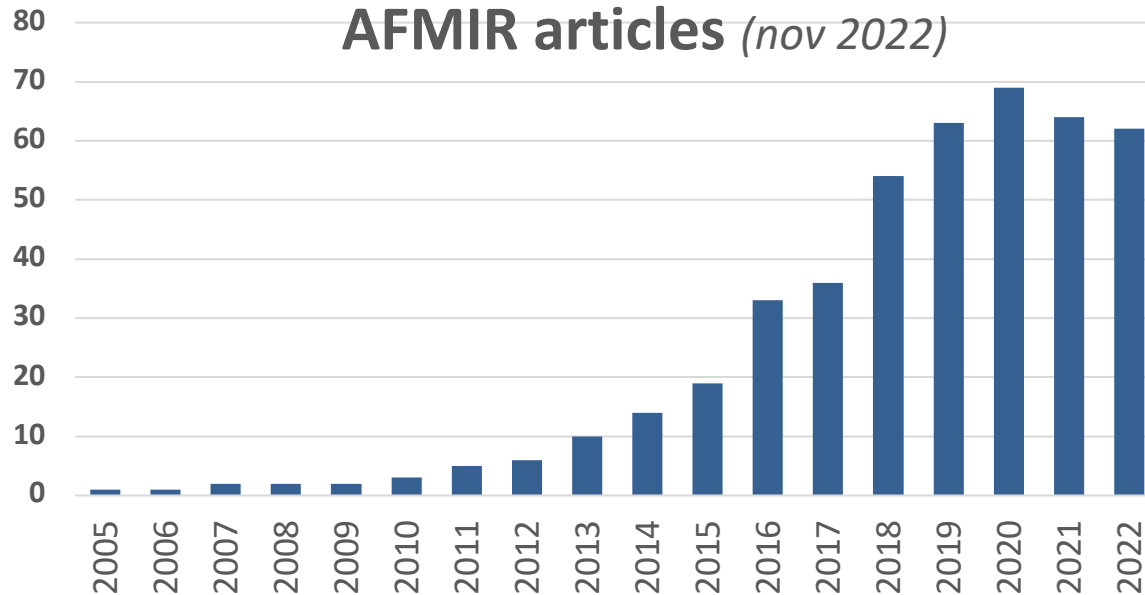
Technique evolution

AFM-IR Technology evolution

OPERATING MODES



AFMIR articles (nov 2022)

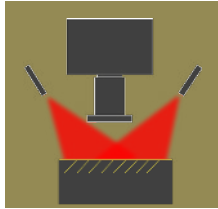


MUSIICS

MUtiScale Infrared ImAGING platform for COMplex Systems

- IR users facility.
- Proposal submission each year
- 2 sites (ICP and IPANEMA)
- Financements : Région, Département de l'Essonne, Labex nanoSaclay, ANR, Université Paris-Saclay, PEPR Origines

- Large scale analysis



(en développement)

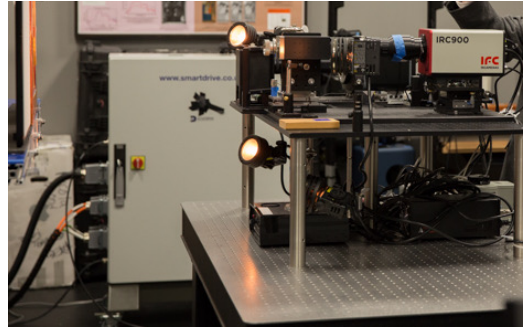


Image : 10 cm
Résolution : 100 μm

- Microscale and sub-microscale analysis



Image : 1 mm
Résolution : 10 μm

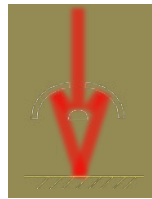
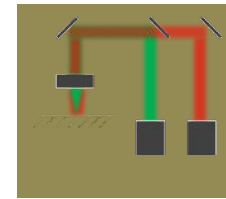


Image : 200 μm
Résolution : 500 nm



• Nanoscale Analysis

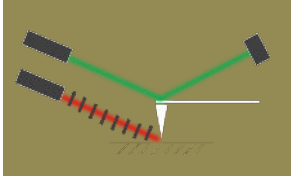
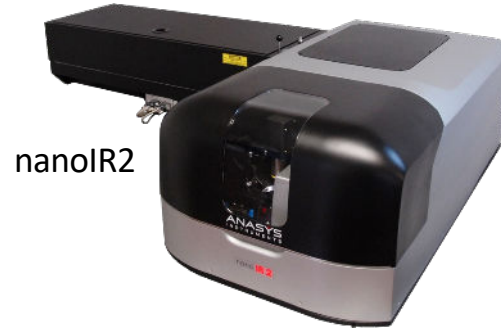


Image : 80 μm
Résolution : 10-20 nm



nanoIR1



nanoIR2



nanoIR2s

Image : 80 μm
Résolution : 1-5 nm



IconIR

COMING SOON !

Icon-IR environnemental



Conclusion

- AFM-IR is the only technique allowing to have a direct measurement of the local absorbance, leading to reliable spectra and comparable to FTIR.
- Tapping AFM-IR is a big improvement that allows to study new kind of organic samples (soft, non adhesive) with a resolution around 10 nm.
- Resonance enhanced and tapping modes allow now to have a huge range of applications (organic or inorganic material).
- New operating mode : Peakforce tapping IR and surface sensitive.

Thanks to



AFM-IR team:

A. Deniset-Besseau

J. Mathurin

D. Bazin

M. Petay (PhD)

L. Bejach (PhD)

