Mid-Infrared/THz Near-Field Nanoscopy (AFM/SNOM)

Jean-François Lampin

THz Photonics Group

Institute of Electronics, Microelectronics and Nanotechnology

UMR CNRS 8520, Université de Lille, F-59652 Villeneuve d'Ascq, France

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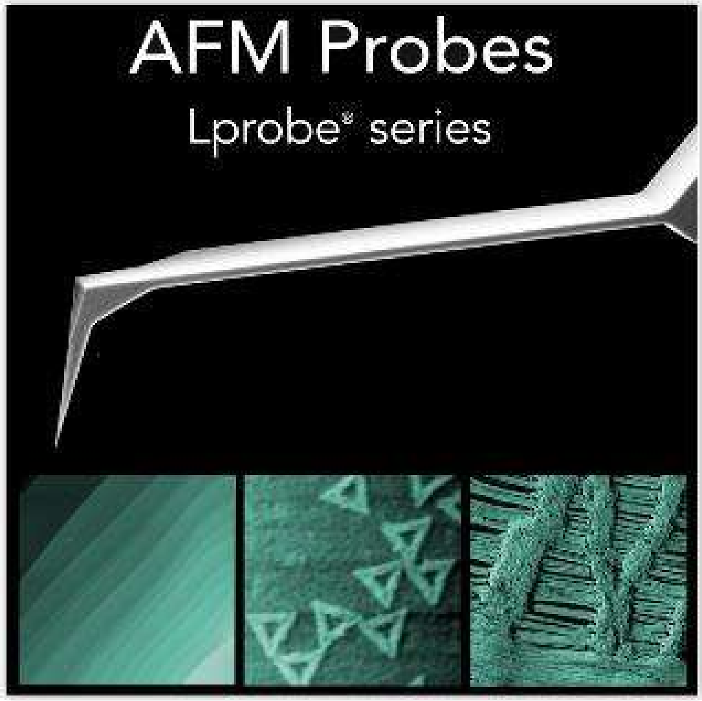
29/08/2019

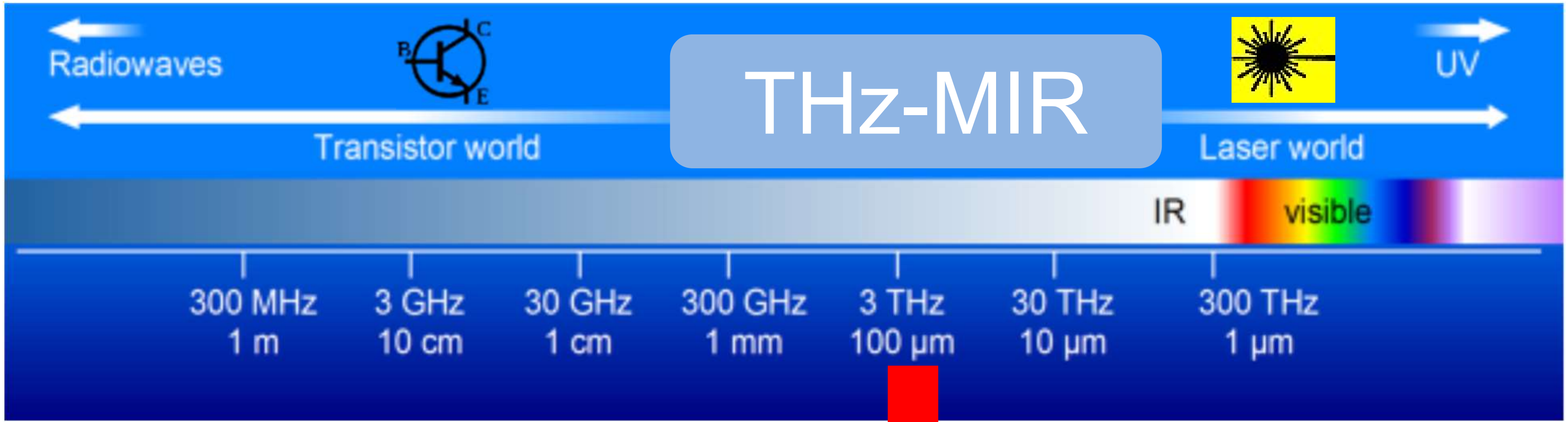
IEMN THz Photonics group

C. N. Santos, T. Hannotte, L. Thomas, S. Eliet, R. Peretti



B. Walter
M. Faucher

Electromagnetic spectrum



$h\nu \ll kT$ $\qquad$ $h\nu \gg kT$

Ranges: (3 decades)

3000 < *Wavelength* < 3 µm
3.3 > *Wavenumber* > 3333 cm^{-1}
0.1 > *Frequency* > 100 THz
0.4 > *Photon energy* > 412 meV
10 < *Period* < 0.01 ps
4.8 > *Temperature* > 4800 K

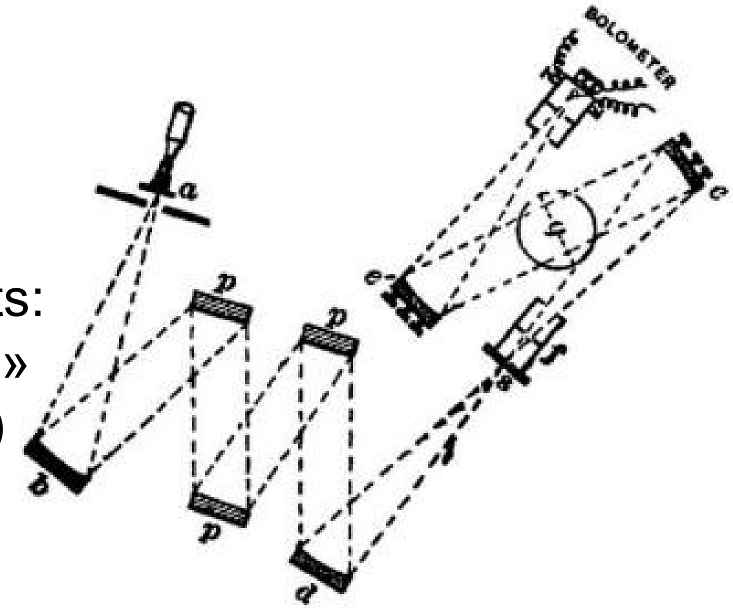
Matter …

Group → / Period ↓	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La *	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac **	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
			*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
			**	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

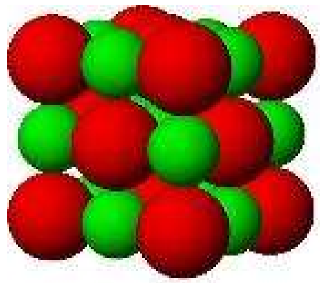
H. Rubens: exploring the long wavelengths

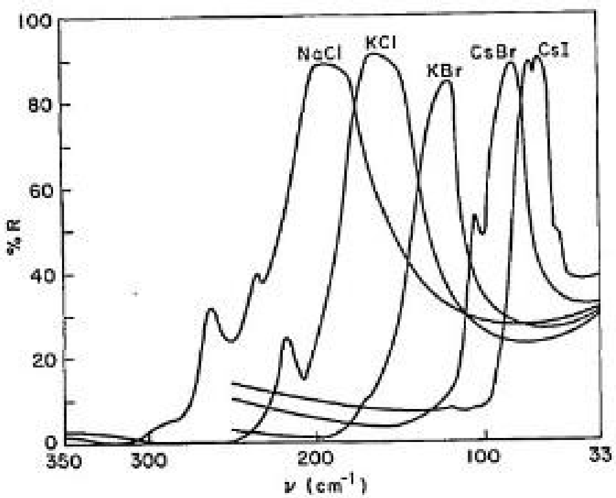
Heinrich Rubens (1865-1922)
(Physical Institute, Berlin Univ.)

MIR experiments:
« Reststrahlen »
(residual rays)



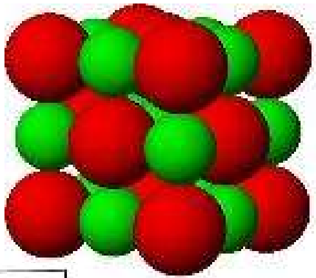
- He fabricated IR spectrometers
- He discovered that crystals have **high reflectivity** bands in the mid-IR

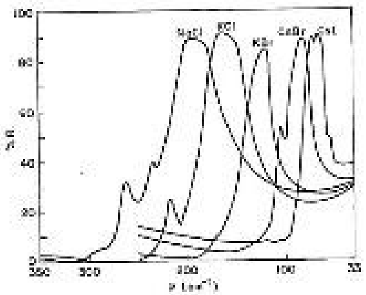


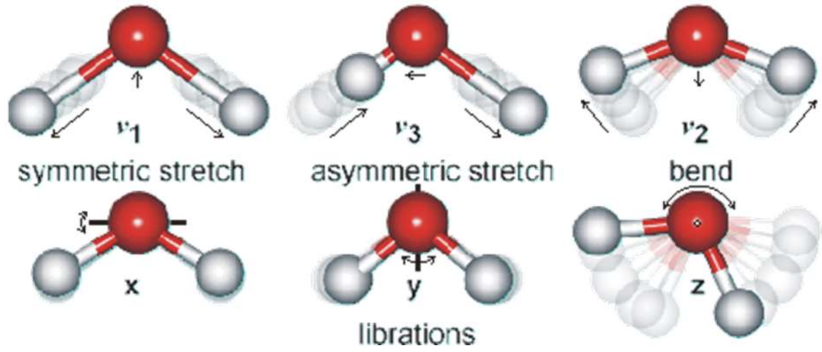


THz-MIR - matter interaction

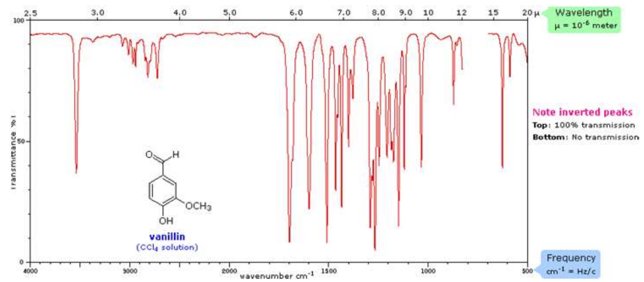
Phonons in crystals







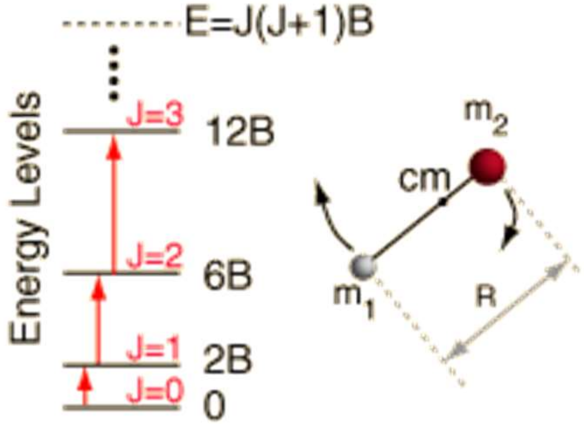
Molecular vibrations



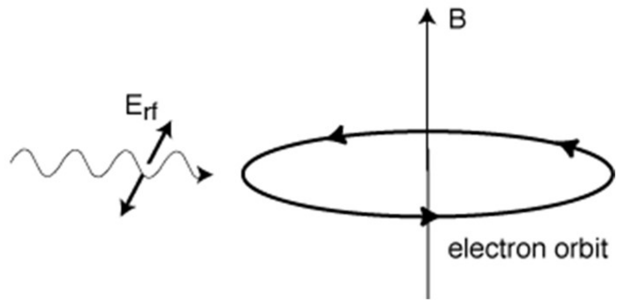
Since a long time MIR/THz range helps to understand **molecular motions**…

FTIR spectrometer is a common instrument in chemistry, biology …

But is it possible to have **nanoscopic resolution** in MIR/THz ?



Molecular rotations



Cyclotron resonnances
Plasmons …

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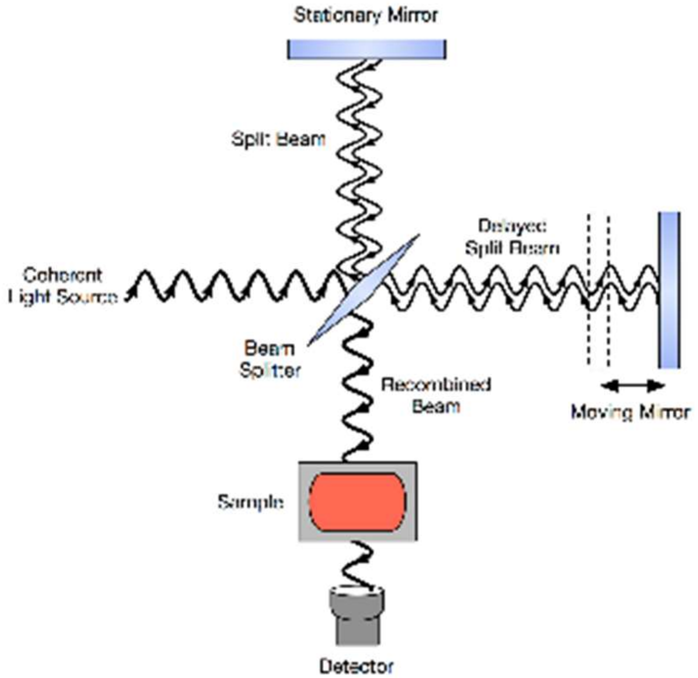
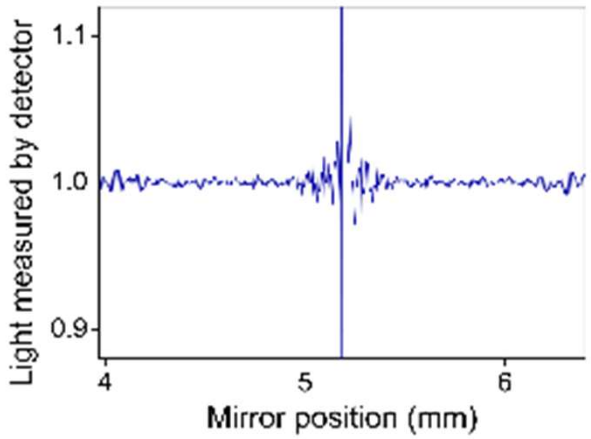
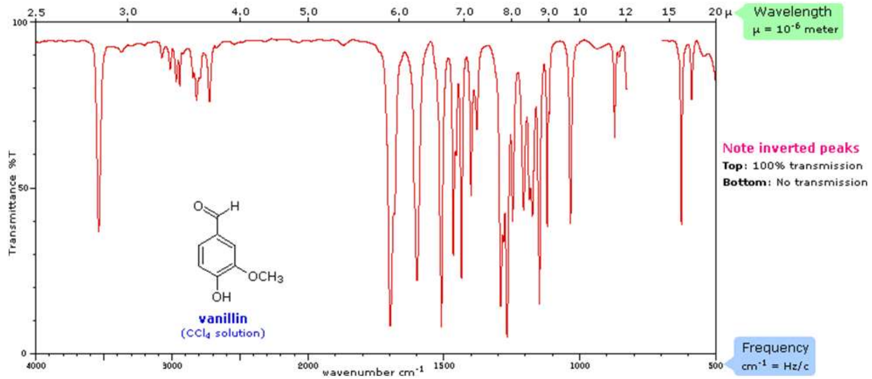
The Fourier Transform Spectrometer

Ideal for infrared !







Used in physics but also in chemistry, biochemistry, agrochemistry …

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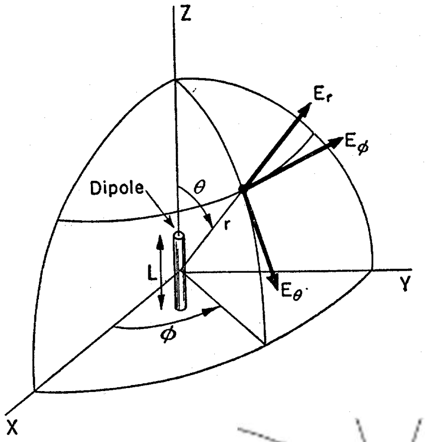
Radiation of dipoles

Oscillated charges: electric dipole



$$A_r = \frac{\mu_0 I_0 L}{4\pi r} e^{j\omega\left(t-\frac{r}{c}\right)} \cos\theta$$

$$A_\theta = -\frac{\mu_0 I_0 L}{4\pi r} e^{j\omega\left(t-\frac{r}{c}\right)} \sin\theta$$

$$A_\varphi = 0$$

$$E_r = \frac{I_0 L \cos\theta}{2\pi\varepsilon_0} e^{j\omega\left(t-\frac{r}{c}\right)} \left(\frac{1}{cr^2} + \frac{1}{j\omega r^3}\right)$$

$$E_\theta = \frac{I_0 L \sin\theta}{4\pi\varepsilon_0} e^{j\omega\left(t-\frac{r}{c}\right)} \left(\frac{j\omega}{c^2 r} + \frac{1}{cr^2} + \frac{1}{j\omega r^3}\right)$$

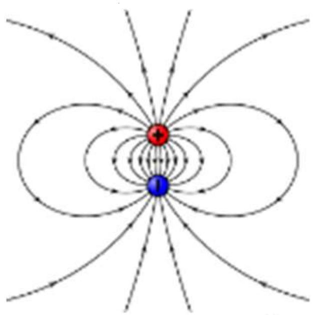
$$E_\varphi = 0$$

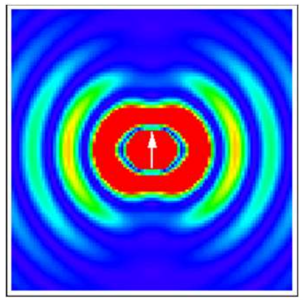
Far-field

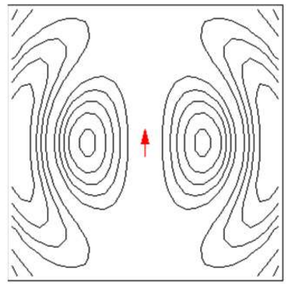
$$H_r = 0$$

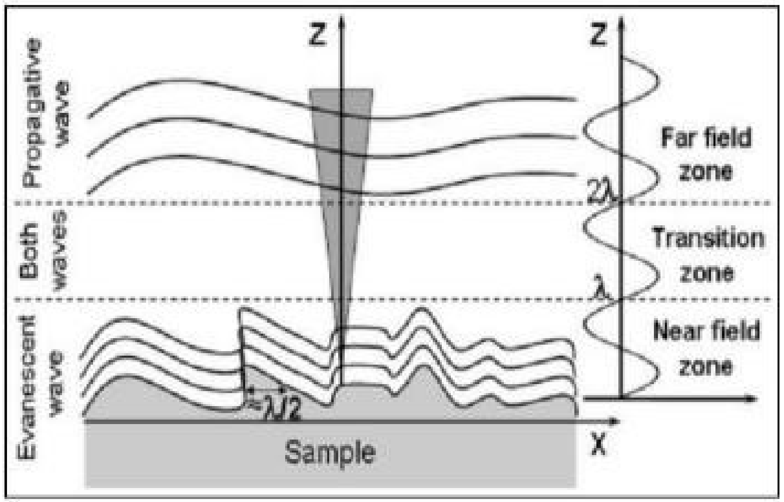
$$H_\theta = 0$$

$$H_\varphi = \frac{I_0 L \sin\theta}{4\pi} e^{j\omega\left(t-\frac{r}{c}\right)} \left(\frac{j\omega}{cr} + \frac{1}{r^2}\right)$$









Optical regions arrangement around the probe

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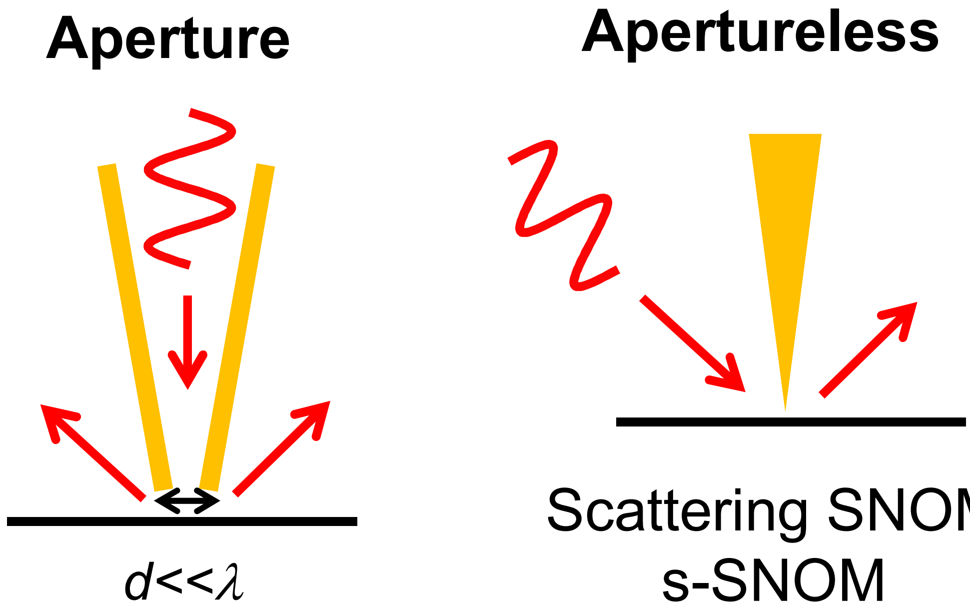
Far-field vs near-field

Microscopy with objectives
Diffraction limited resolution:

$$d = \frac{\lambda}{2NA} = \frac{\lambda}{2n \sin \alpha}$$

In the THz-MIR range:
resolution limited to few **µm or mm** !!

THz-MIR images of **Nano-objects ?**
The ratio *λ/resolution* should be large:
Near-field microscopy

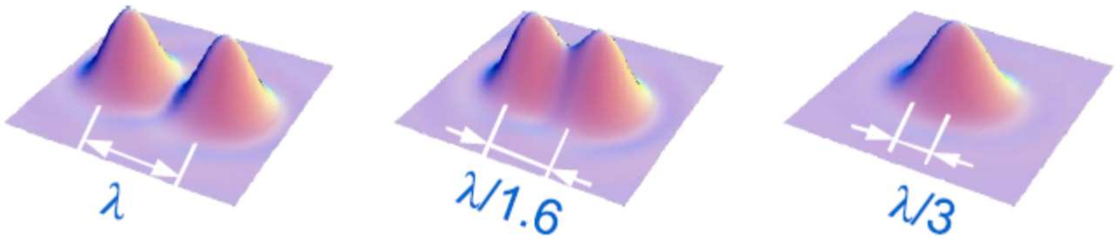


Scanning Near-Field Optical Microscopy (SNOM)
Aperture limited

Scattering SNOM
s-SNOM
Tip limited

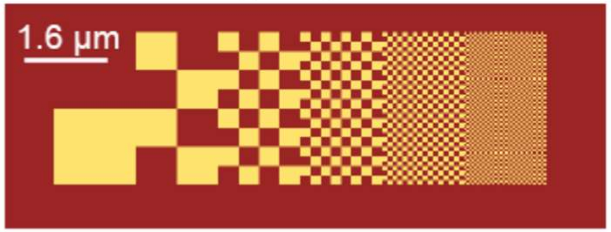
...diffraction prevents optical spectroscopy on the nanoscale

Classical far-field optical microscopy → **Rayleigh resolution criterion**



Cause: Image of a point source is not a point, but a diffraction-limited intensity distribution.

Classical microscopy images (simulated)

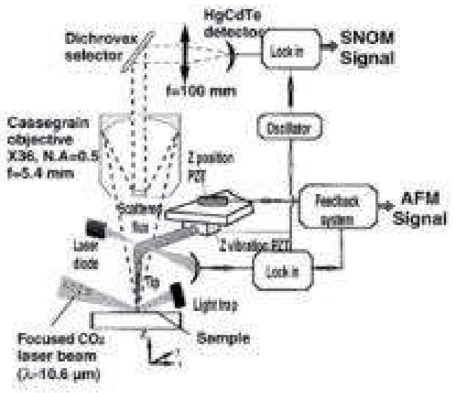
original pattern	visible	mid-infrared
		
λ = "0"	λ ≈ 0.5μm	λ ≈ 10μm

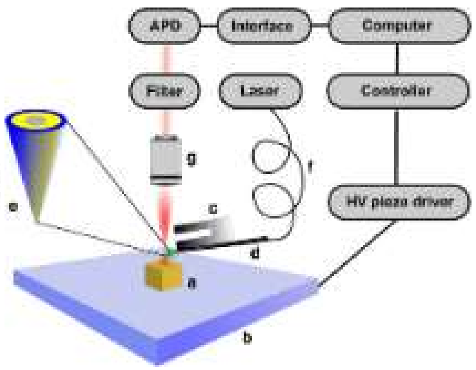
Scanning near-field optical microscope (SNOM)

Short history:

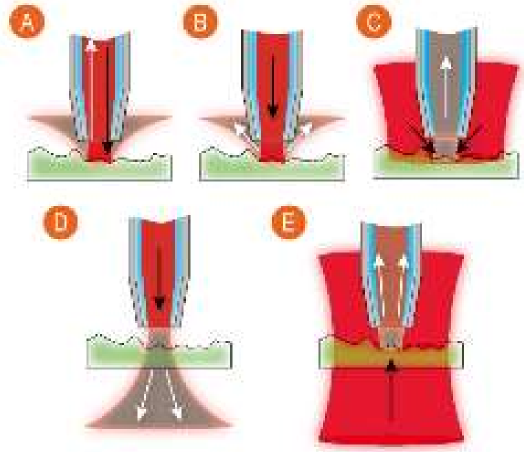
- Proposed by Singe in 1928
- Ash & Nichols (1972): $\lambda/60$ microwaves
- 1980’s: several groups on visible SNOM
- 2000’s: First IR images

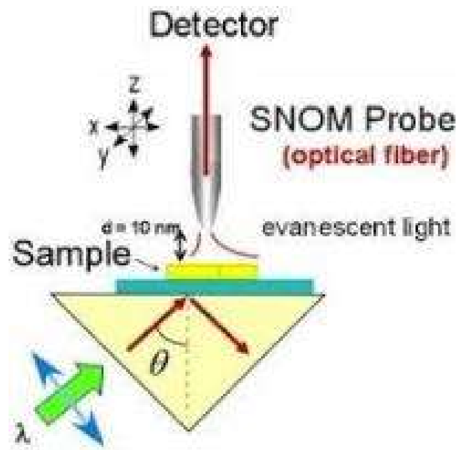
Various approaches:



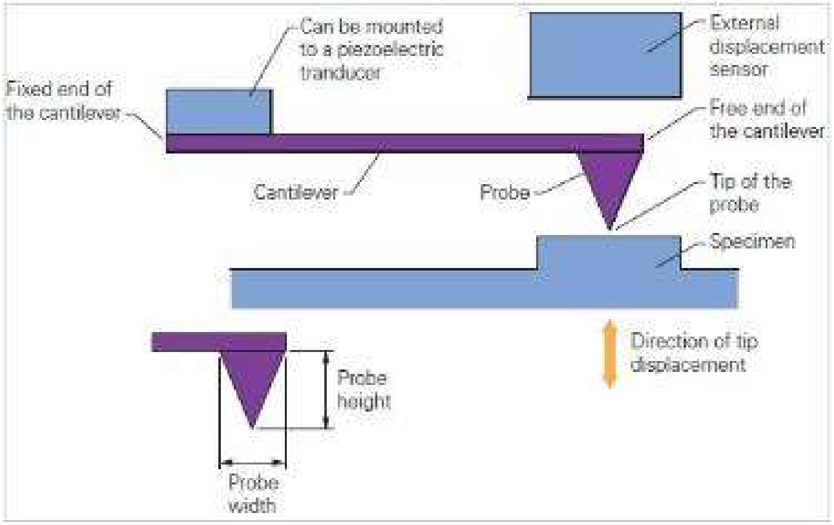


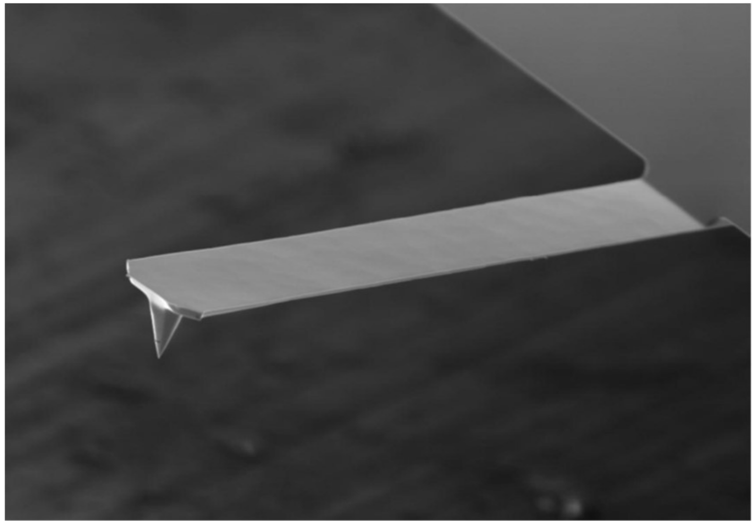
- Illumination from above
- Illumination from the backside
- Use of optical fibers
- Use of microscope objective
- Use total internal reflection (TIR)
- …

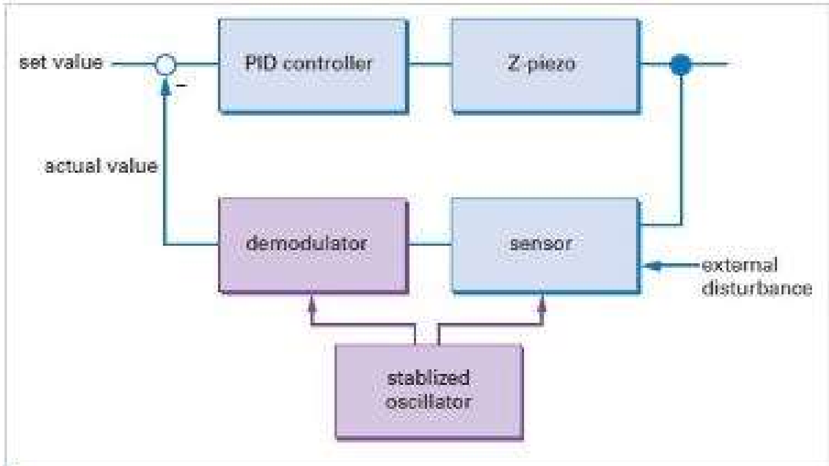




The Atomic Force Microscope (AFM)



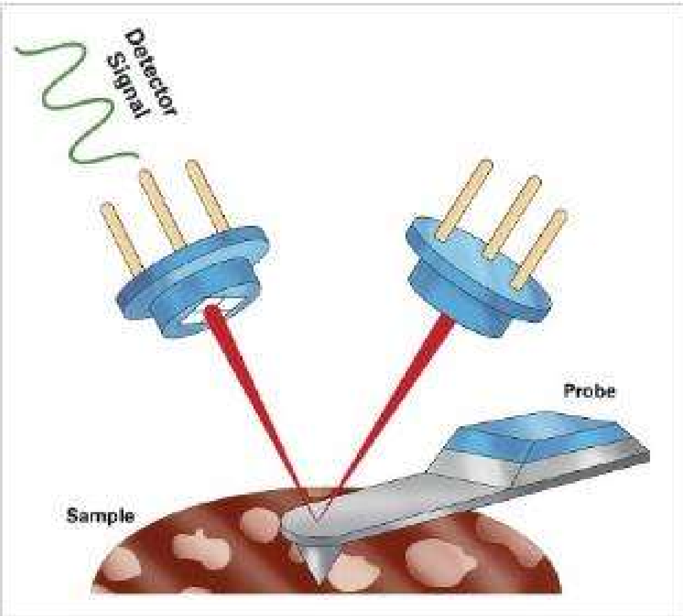


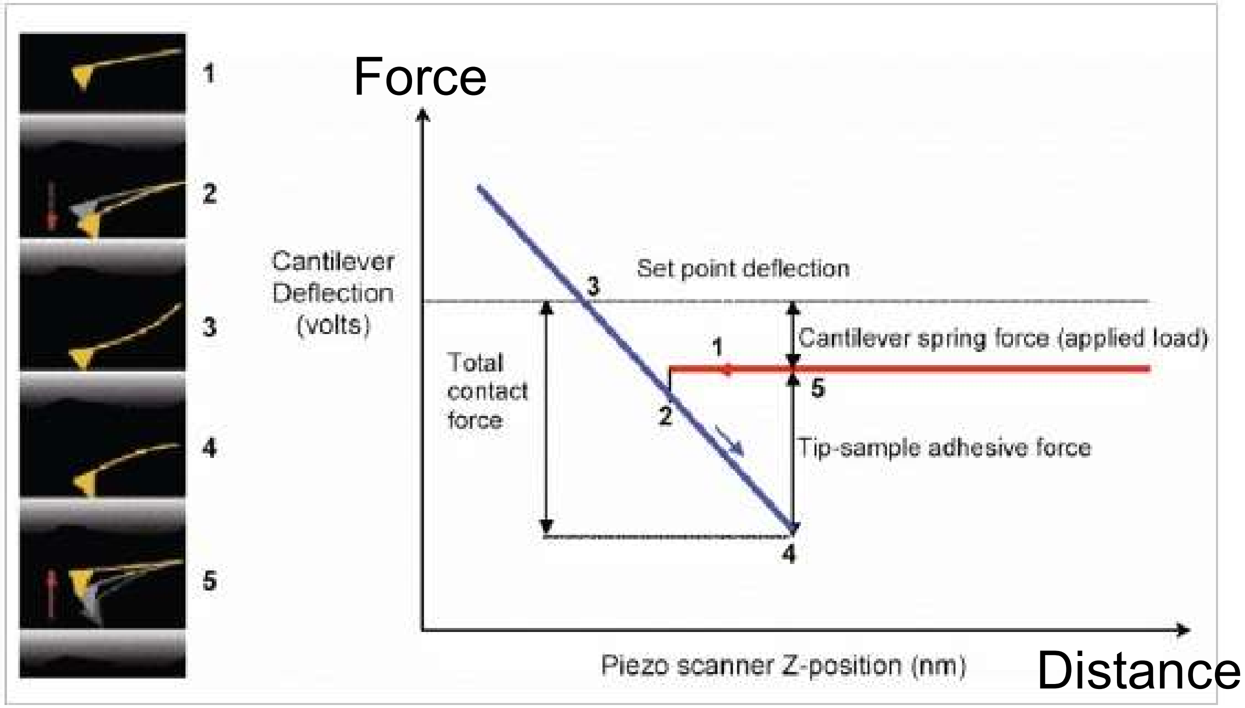


Two main modes :

- Contact mode
- Tapping mode
- …

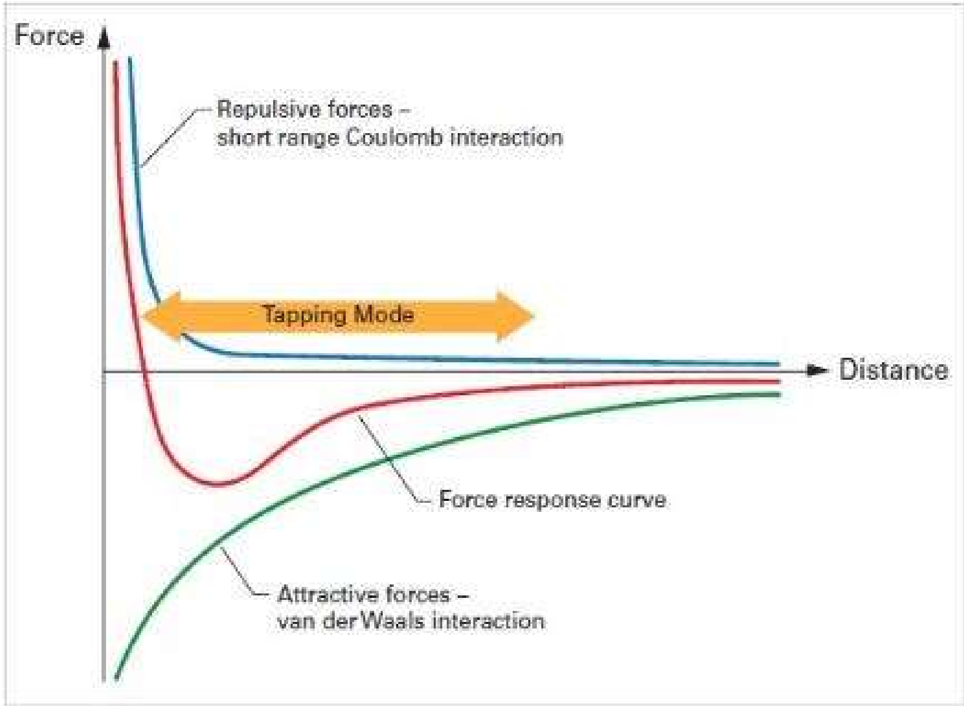
The contact mode

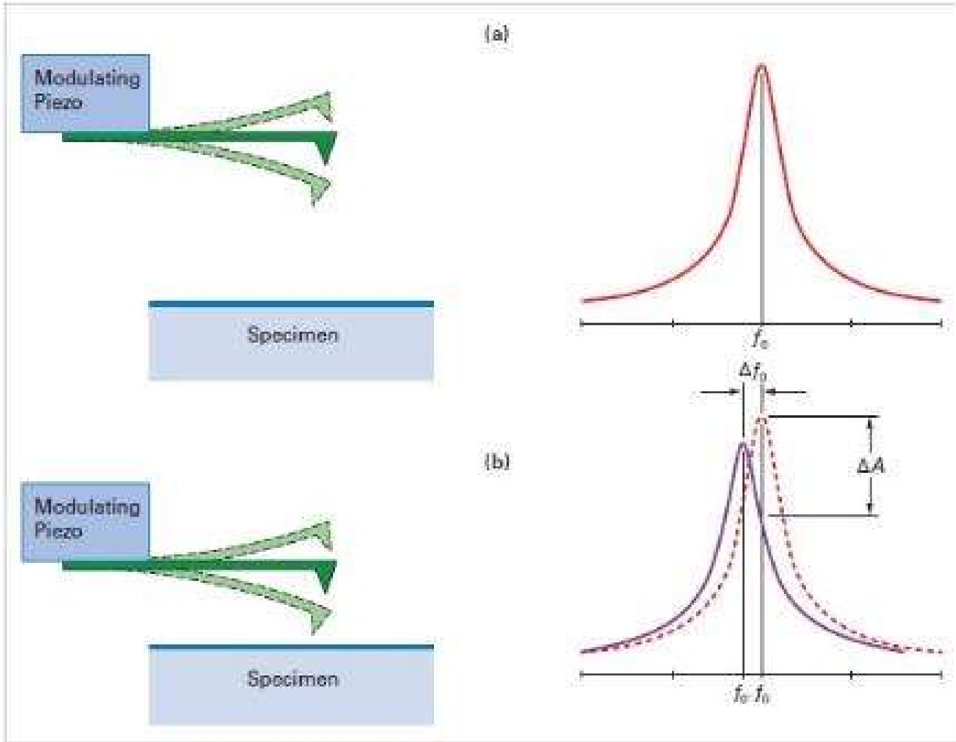




- Hysteresis: adhesion informations
- Tip wear
- Sample damages if the force is too high

The tapping mode





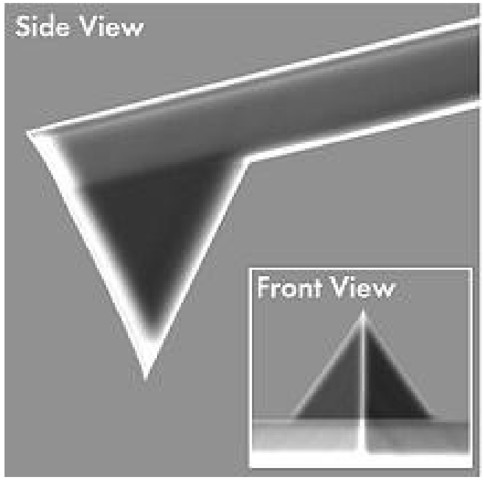
- Lock-in detection
- Force is not directly measured
- Short « touch » $\Rightarrow$ less tip wear

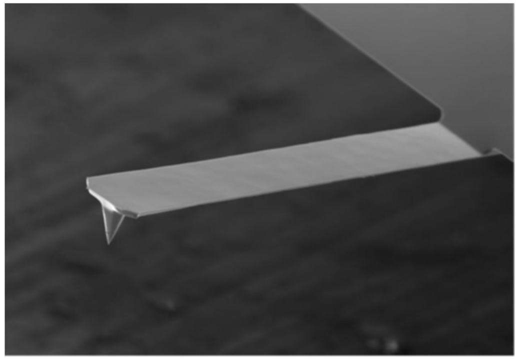
AFM probes

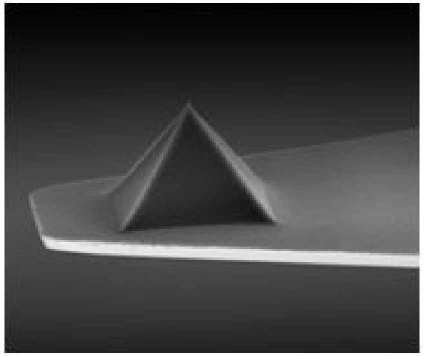
Generally Si, SiN, glass
Can be coated (metal, diamond…)

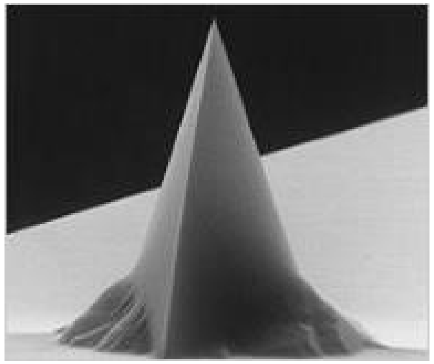
Parameters:

- Resonance frequency (kHz)
- Force constant (N/m)
- Radius of curvature
- Q factor
- …



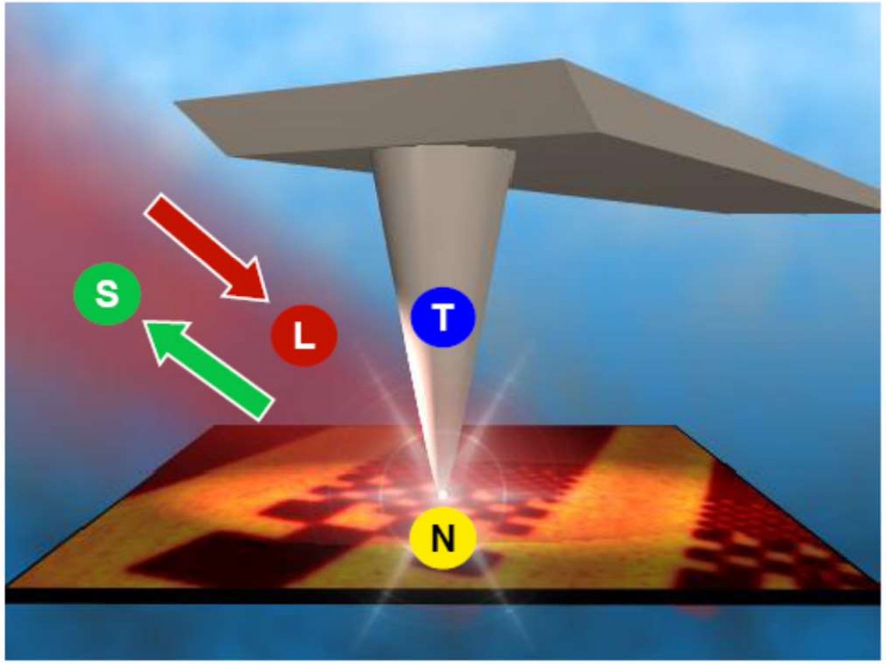






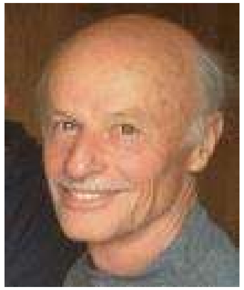
Apertureless Scanning Near-field Optical Microscopy employs a nanofocus for imaging

Simultaneous measurement of mechanical topography and optical near-fields



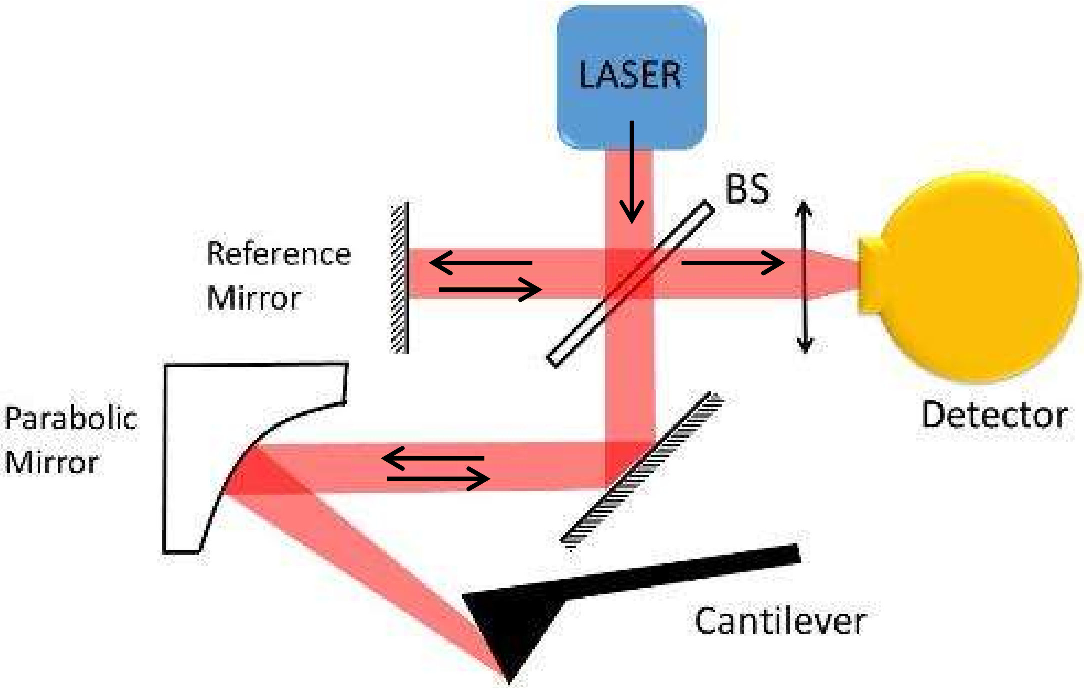
- A focused laser-beam **L** illuminates a commercial AFM tip **T**
- The tip generates a nano-focus **N** about the size of the tip-radius of 10 nm (Lightning Rod Effect)
- The near-field interaction between the tip and the sample modifies the back-scattered light **S**
- By scanning the sample surface with the tip, an optical image with 10nm spatial resolution is created

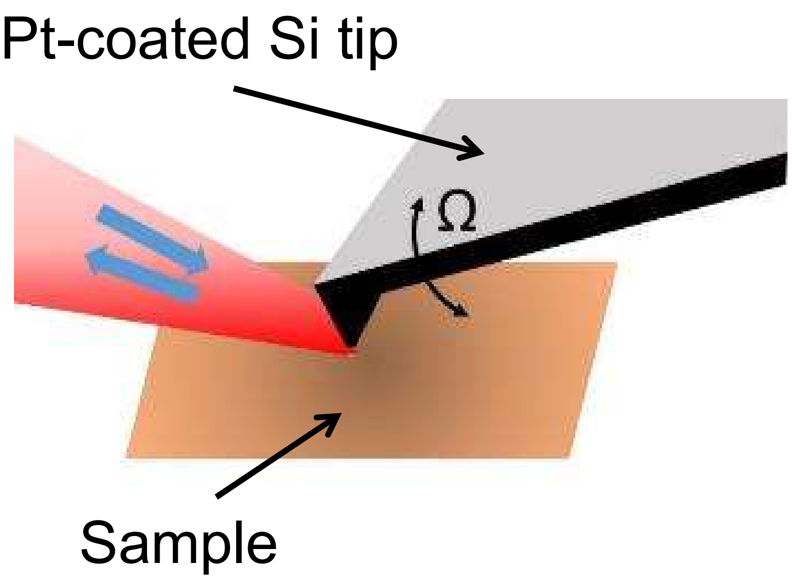
Wavelenght independant spatial resolution of 10nm – In the visible, infrared and THz spectral regime



F. Keilmann

Principle of s-SNOM



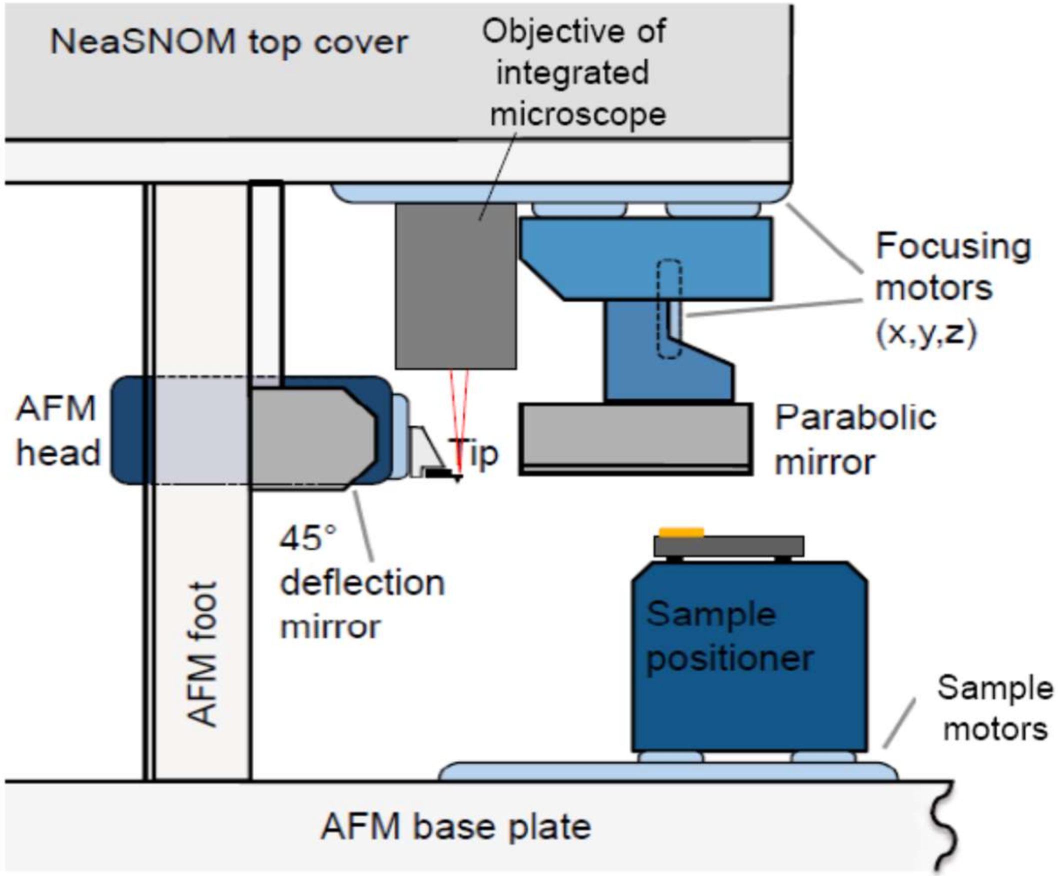


A Michelson interferometer:
one arm is illuminating an AFM cantilever oscillating at Ω (tapping mode)

The sample is scanned ! (keeps optical alignment)

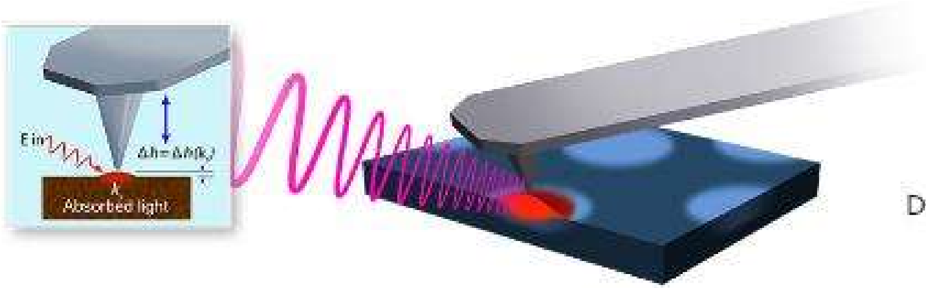
- Y. De Wilde, F. Formanek, L. Aigouy, Rev. Sci. Instrum. 74, 3889 (2003).
- F. Keilmann, R. Hillenbrand, "Near-field microscopy by elastic light scattering from a tip", Phil. Trans. Roy. Soc. London, vol. A362, pp. 787–805, April 2004.

NeaSNOM features standard AFM technology



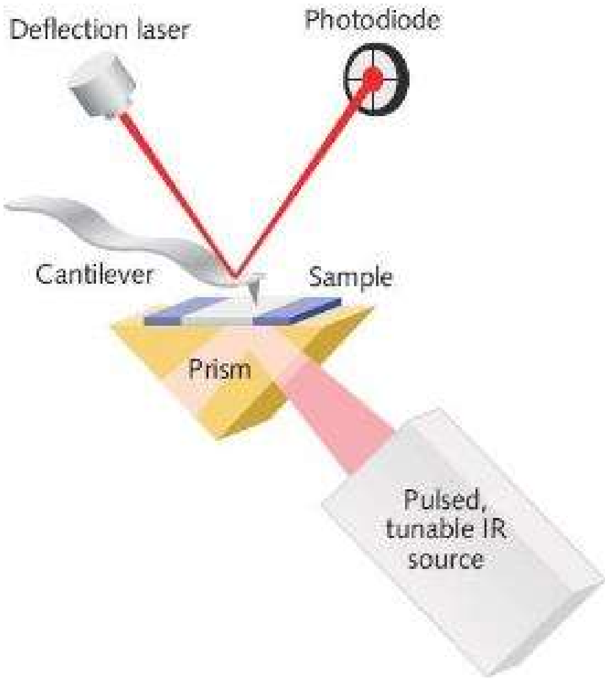
- 3D positioning of parabolic mirror
- Operation mode: intermittent contact mode
- Optical read-out of cantilever deflection
- Oscillation amplitude based tip-sample distance regulations
- Integrated optical (conventional) Microscope (resolution of ca. 0.8µm)
- Sample scanner (coarse and fine positioning)

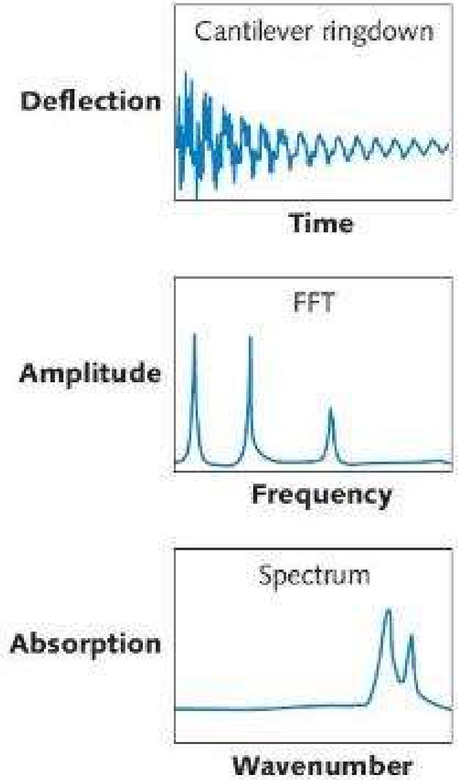
AFM-IR

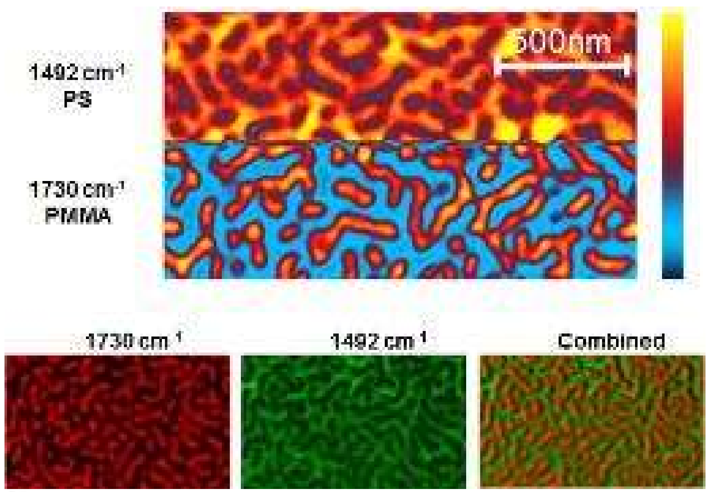


- Photothermal expansion
- No IR detector !

(Anasys Instruments, Bruker, Molecular Vista)







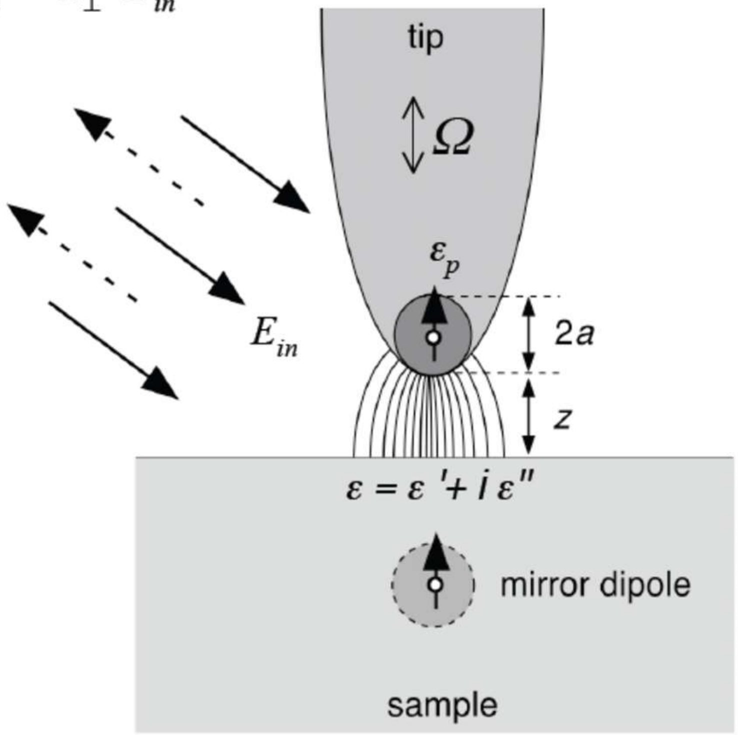
PI

Analytical model of s-SNOM

Simple model: apex dipole interacts with **mirror** dipole in the sample

measured far-field:

$$E_{sca} \propto \alpha_{\perp}^{eff} E_{in}$$



polarizability of tip dipole:

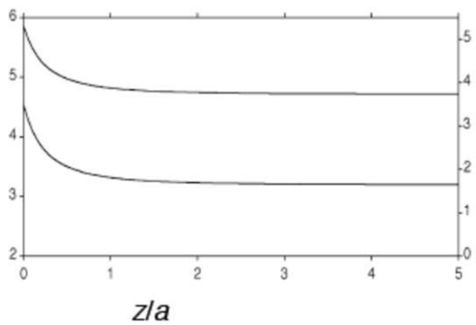
$$\alpha = 4\pi a^3 \frac{(\varepsilon_p - 1)}{(\varepsilon_p + 2)}$$

effective polarizability of tip and sample:

$$\alpha_{\perp}^{eff} = \frac{\alpha(1+\beta)}{1 - \dfrac{\alpha\beta}{16\pi(z+a)^3}}$$

with $\beta = \dfrac{(\varepsilon - 1)}{(\varepsilon + 1)}$

nonlinear characteristic



B. Knoll *et al.*, Nature **399** p. 134 (1999)

Near-field interaction: **nonlinear** in *z* (harmonic components)

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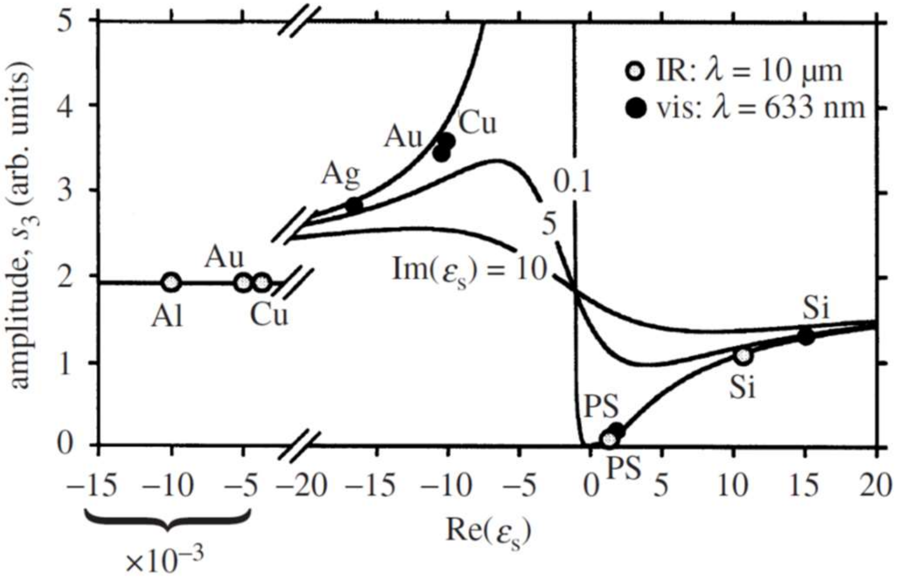
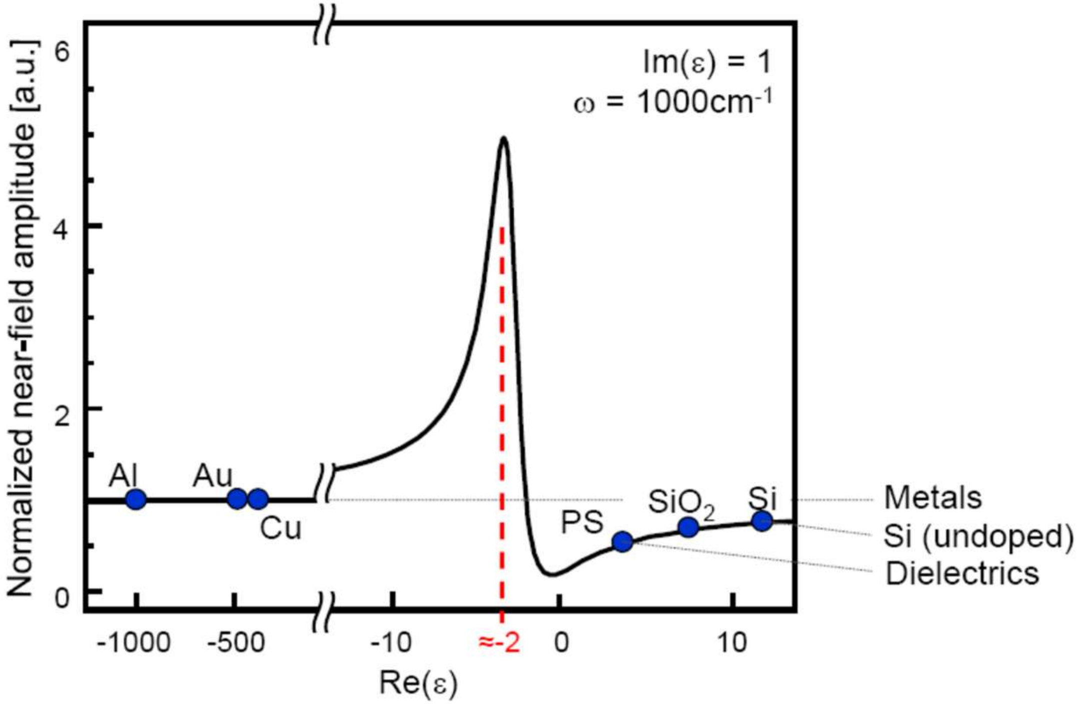
Signal vs sample permittivity

$$\beta = \frac{\varepsilon - 1}{\varepsilon + 1}$$

Complex ε determines scattered amplitude & phase

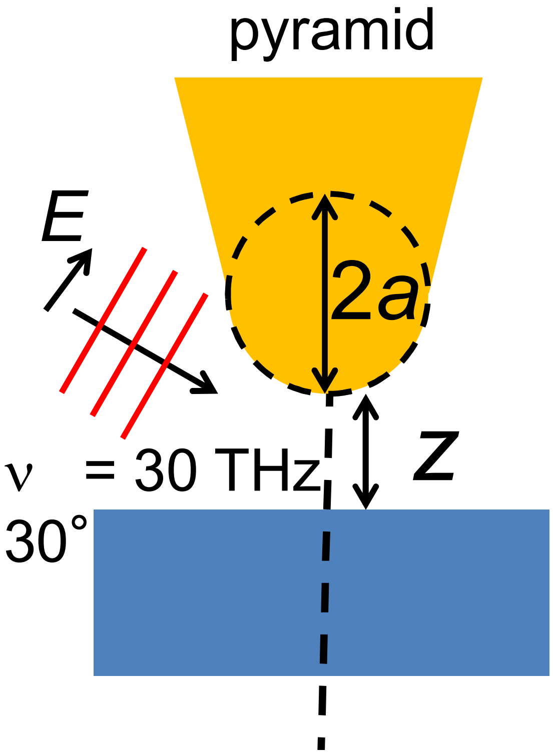


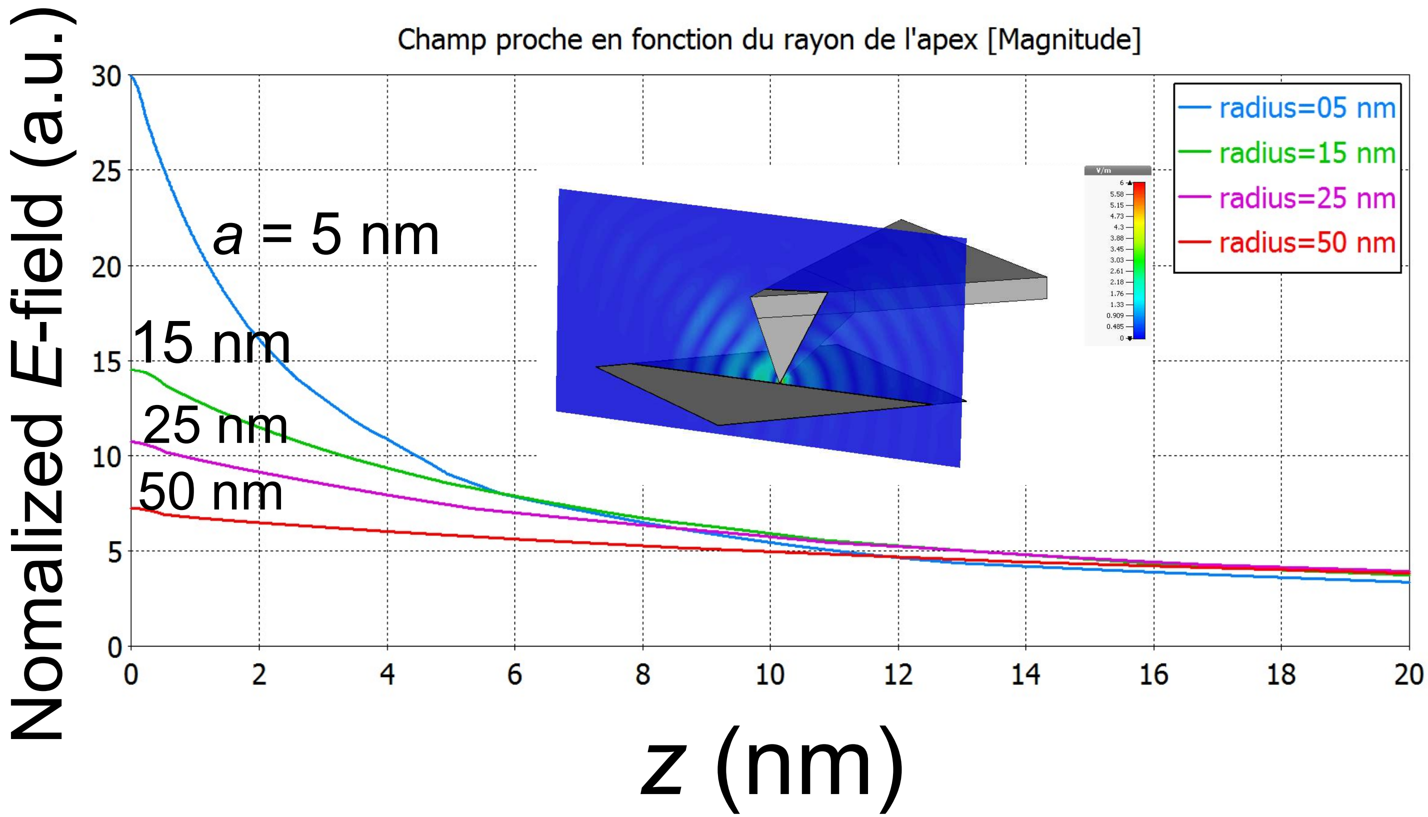


F. Keilmann, R. Hillenbrand, Phil. Trans. R. Soc. Lond. A **362**,787-805 (2004)

Electromagnetic simulations

Simulations with CST (3D EM software)





Smaller apex radius: *E*-field more confined (better resolution)

"Near-field microscopy: from MIR to THz", G. Moreno, A. Pagies, D. Ducatteau, N. Clément, T. Akalin, M. Vanwolleghem, J.-F. Lampin, Proceedings of the joint 25th Conference of the Condensed Matter Division of the European Physical Society, and 14èmes Journées de la Matière Condensée, CMD25-JMC14, Paris, France, (August 24-29, 2014).

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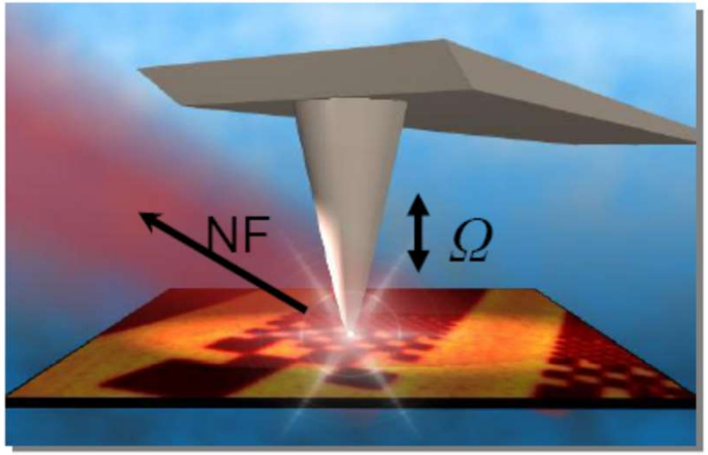
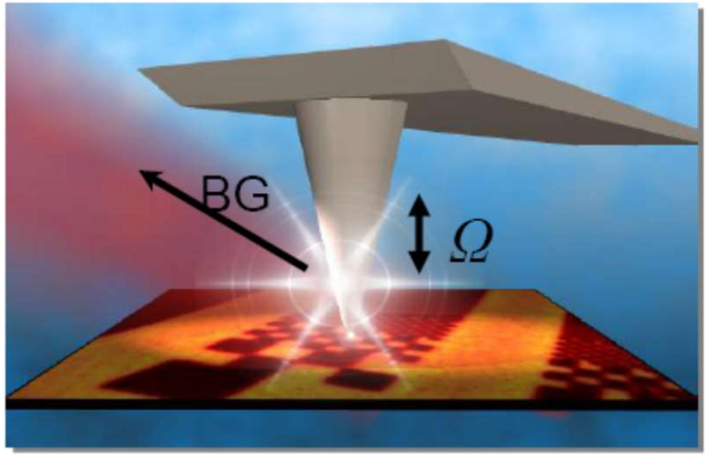
Apertureless Near-field Optical Microscopy requires efficient background suppression



1% near-field signal …

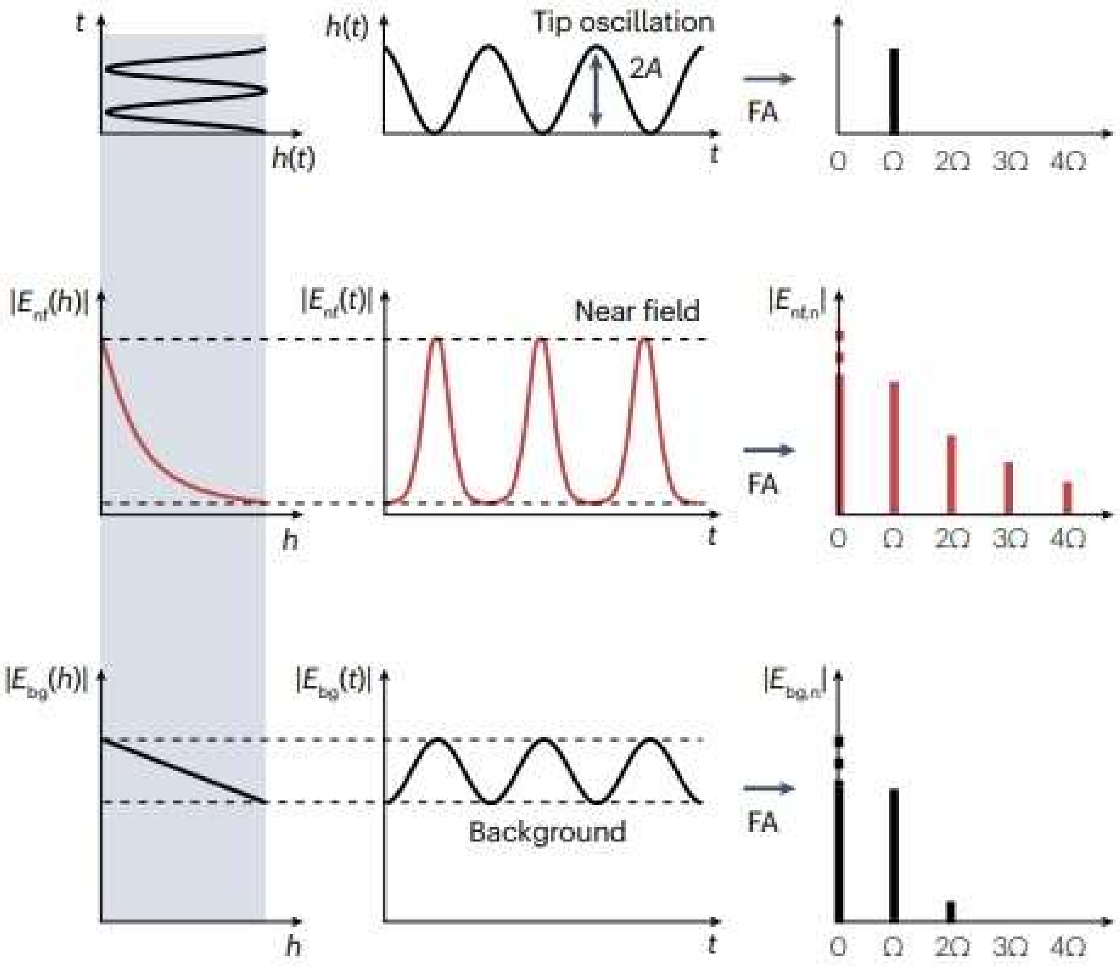
- Is generated by near-field interaction between probe and sample
- Is highly localized
- Is predictable by analytic or numeric calculations



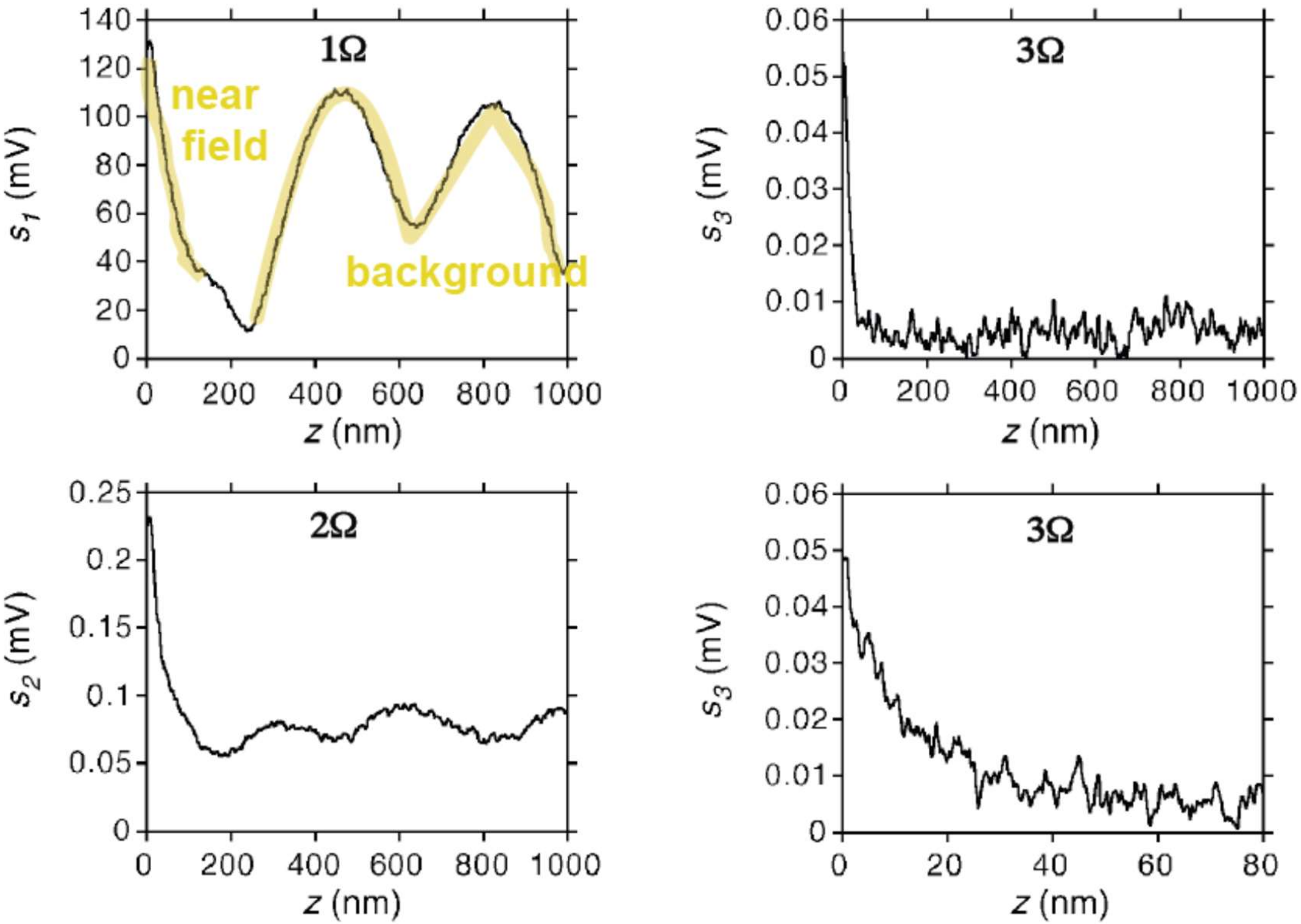
99% background signal

- By scattering and reflections by tip & sample
- Is poorly confined
- Is unpredictable due to diffraction and topography

Removing the background



Harmonic signal demodulation



F. Keilmann, R. Hillenbrand, Phil. Trans. R. Soc. Lond. A **362**,787-805 (2004)

2Ω and 3Ω signals are almost **free from background** !

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Harmonic signal demodulation

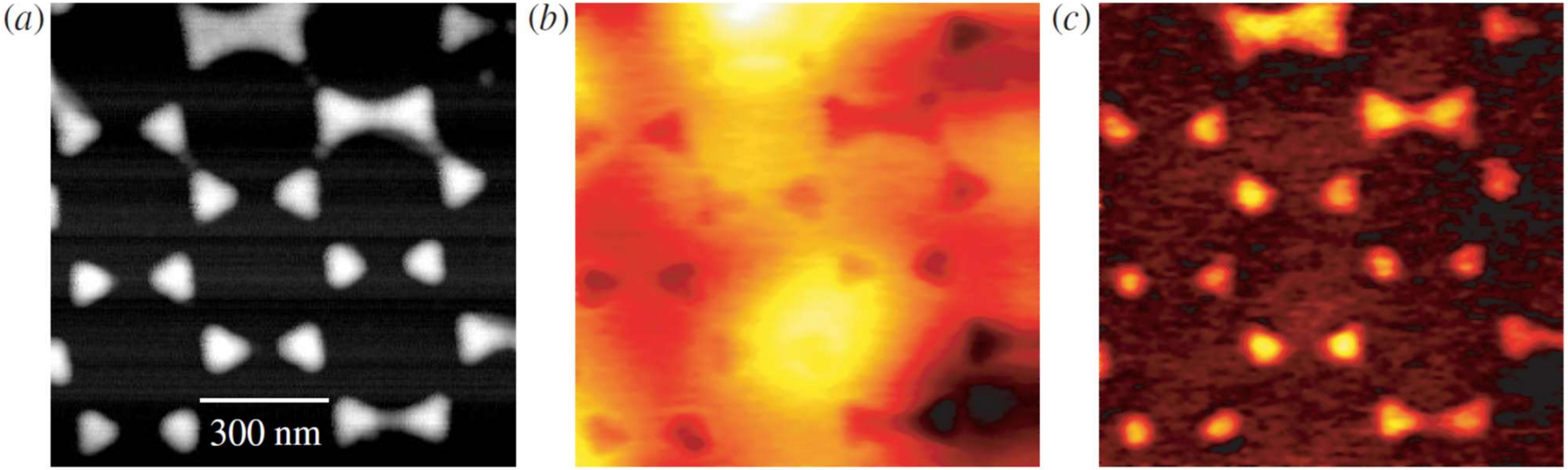
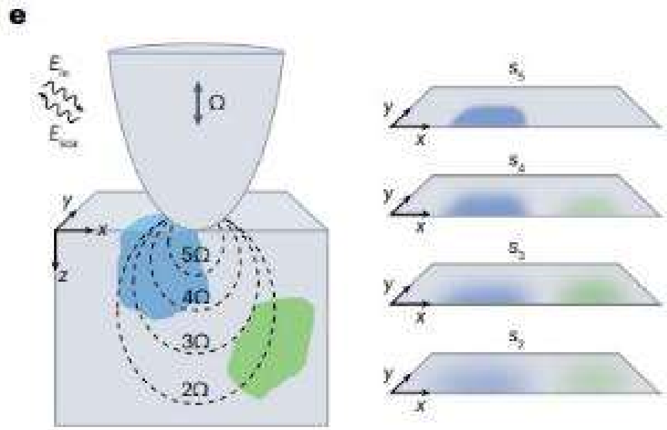
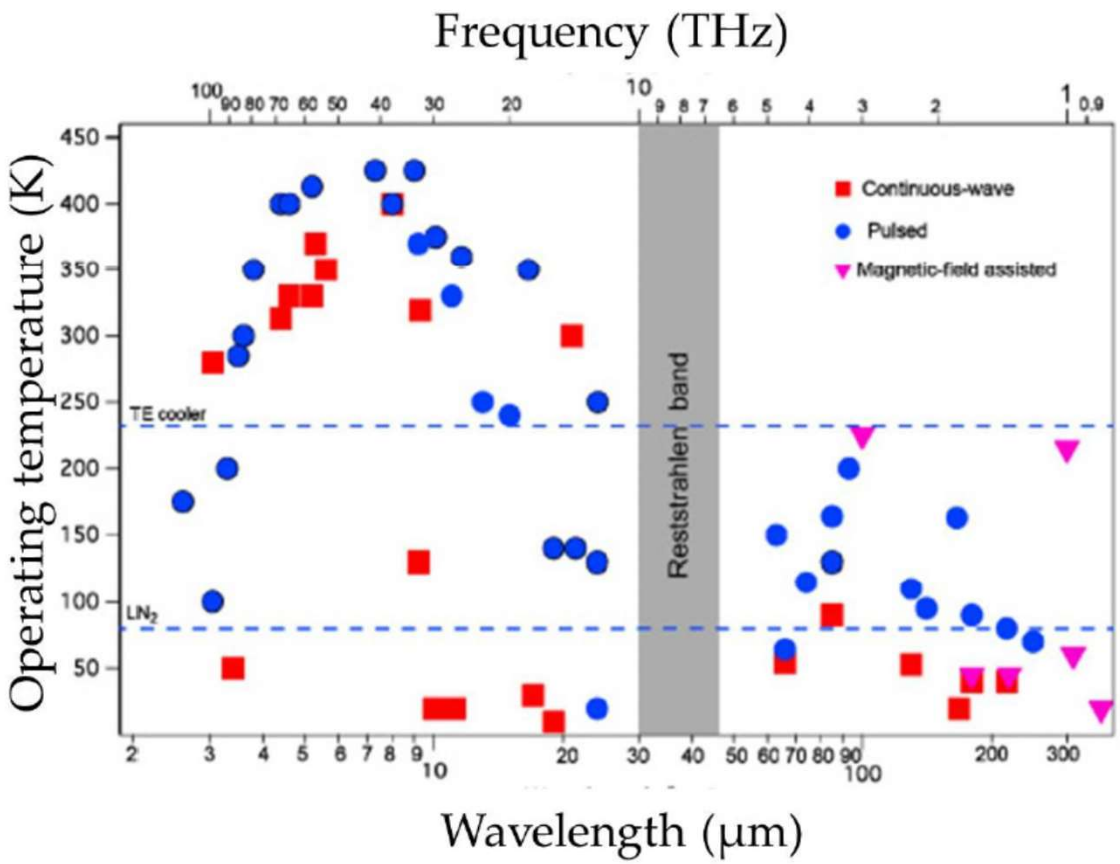
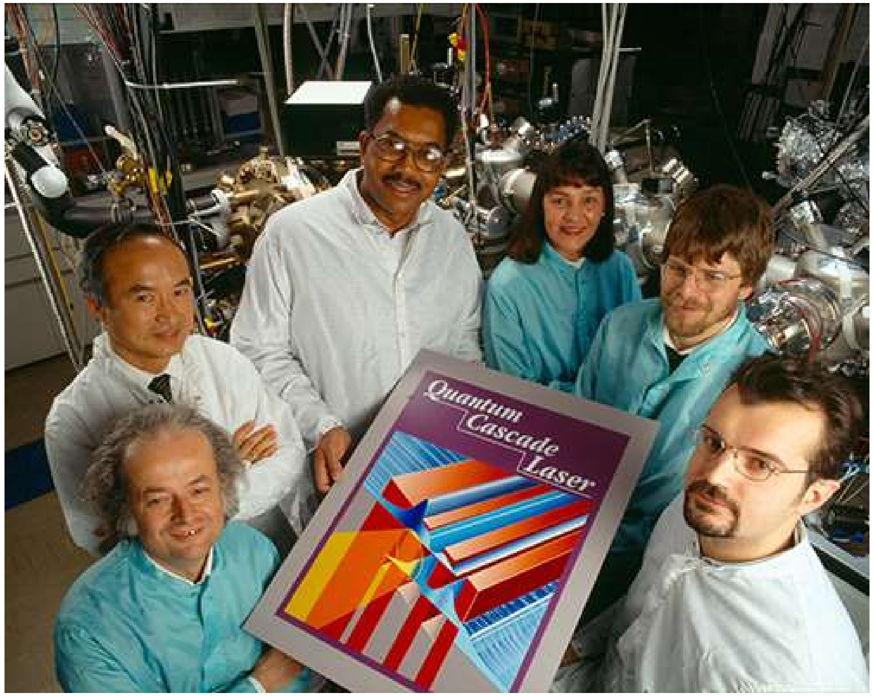


Figure 7. Experimental s-SNOM images of 20 nm high Au islands on Si. (a) Topography, (b) optical amplitude s_1 showing residual background scattering, and (c) optical amplitude s_3 showing pure near-field response.



A revolution in the IR world: QCLs !

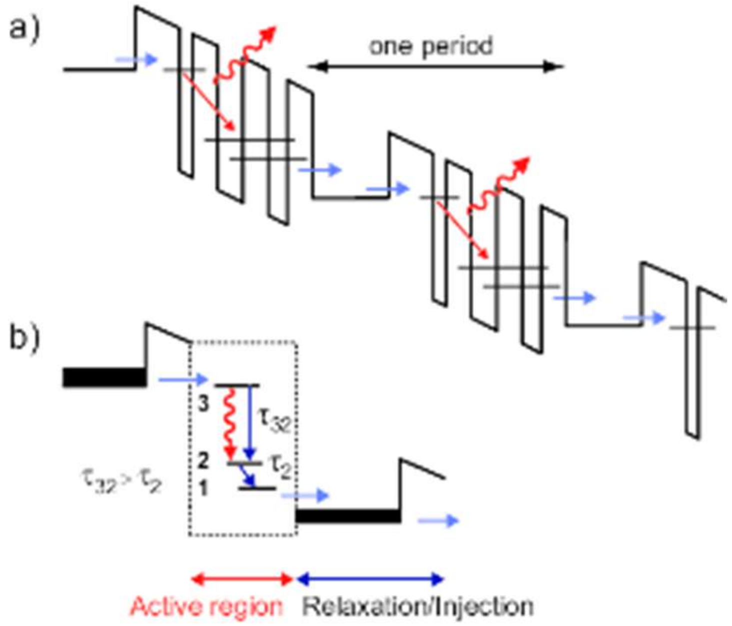


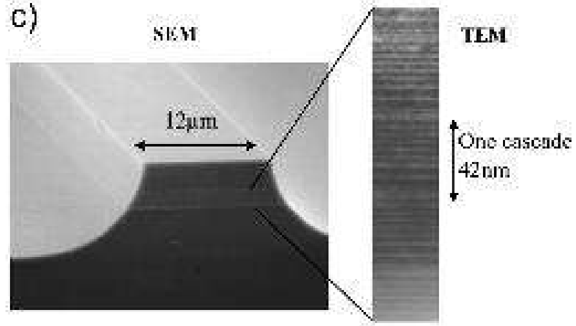


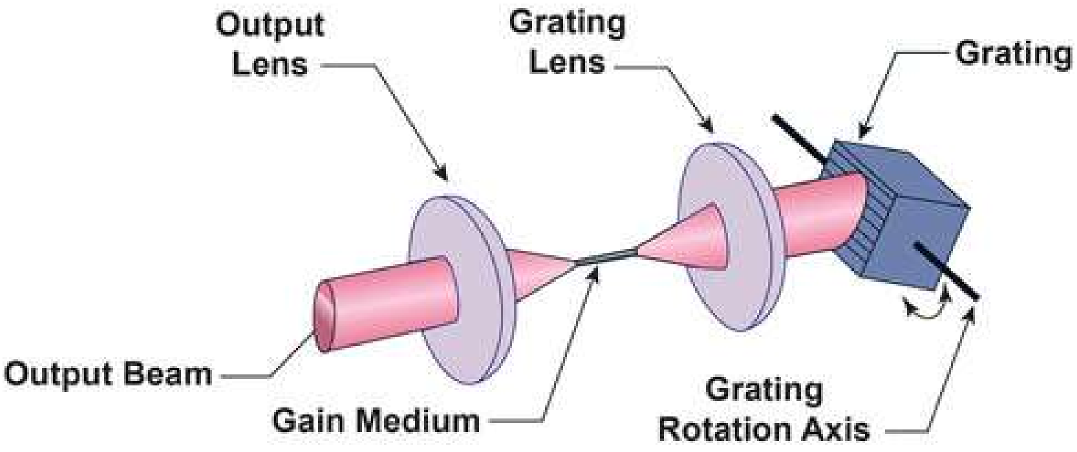
Faist *et al.*, Science (1994)

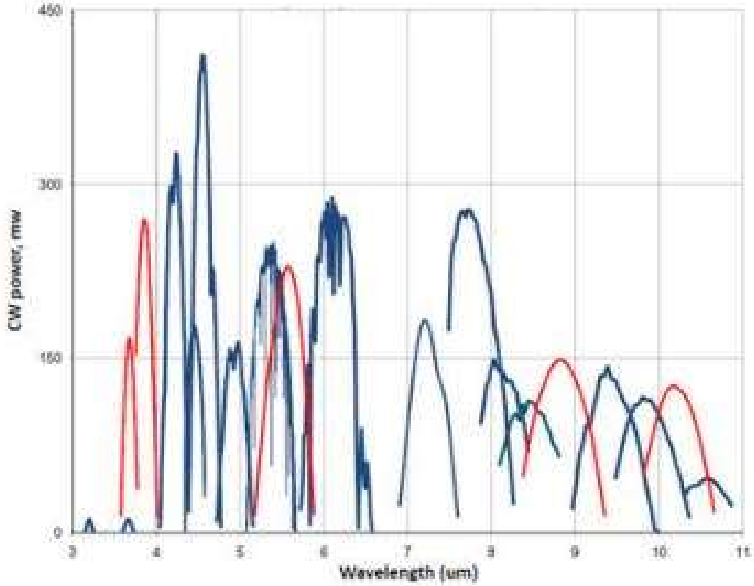
- Monomodes CW and pulsed QCL: external cavity, DFB
- Commercially available with 100’s mW

Tunable QCLs



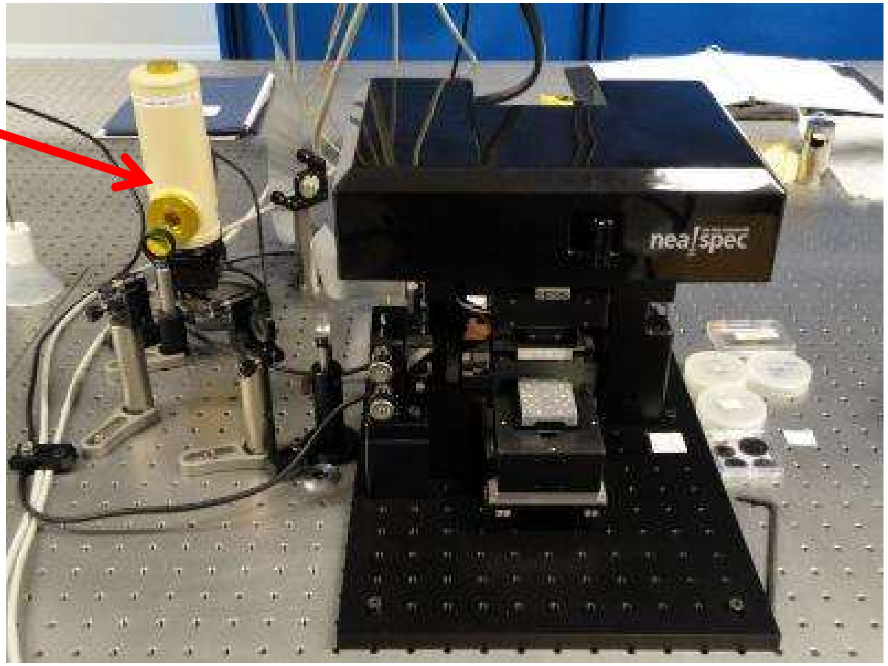






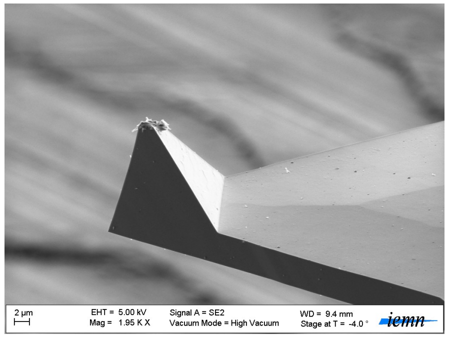
Experimental set-up

HgCdTe
Detector
LN_2 cooled
3-12 µm



s-SNOM based on an AFM with parabolic mirror (NeaSPEC)

10-10.5 µm Quantum Cascade Laser (100 mW)



Typical Probe
Ω = 280 kHz

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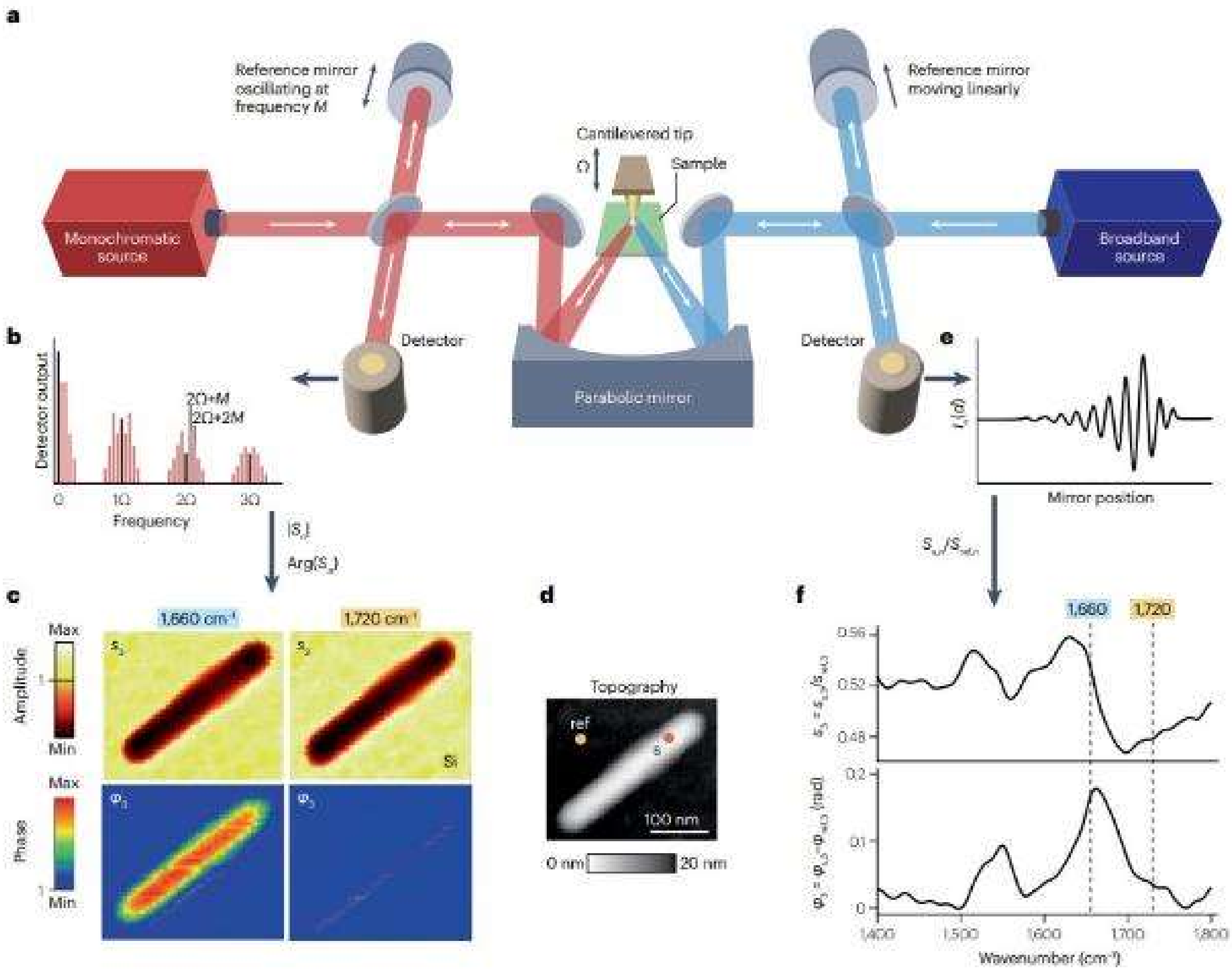
Dual source configuration



R. Hillenbrand *et al.*
Nature Rev. Mat.
2025

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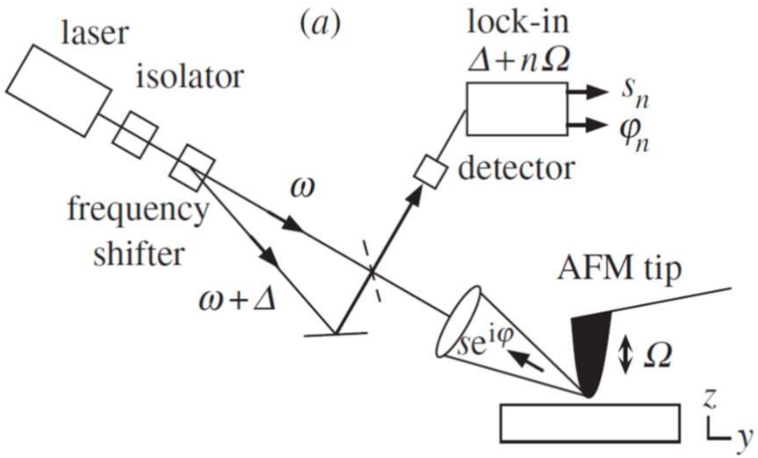
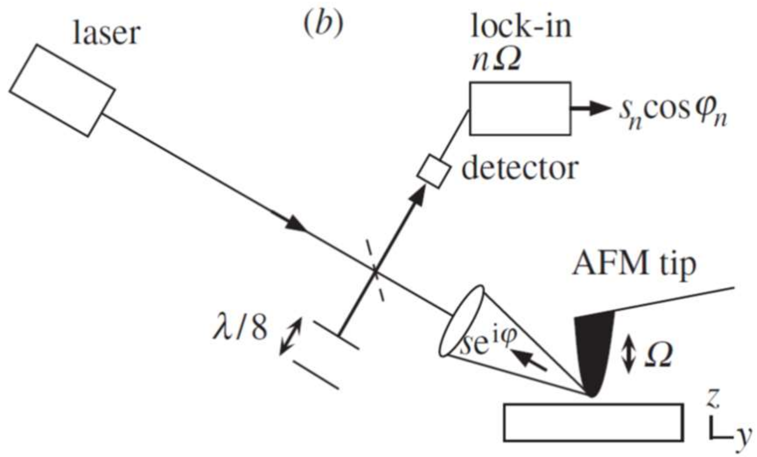
Interferometric SNOM

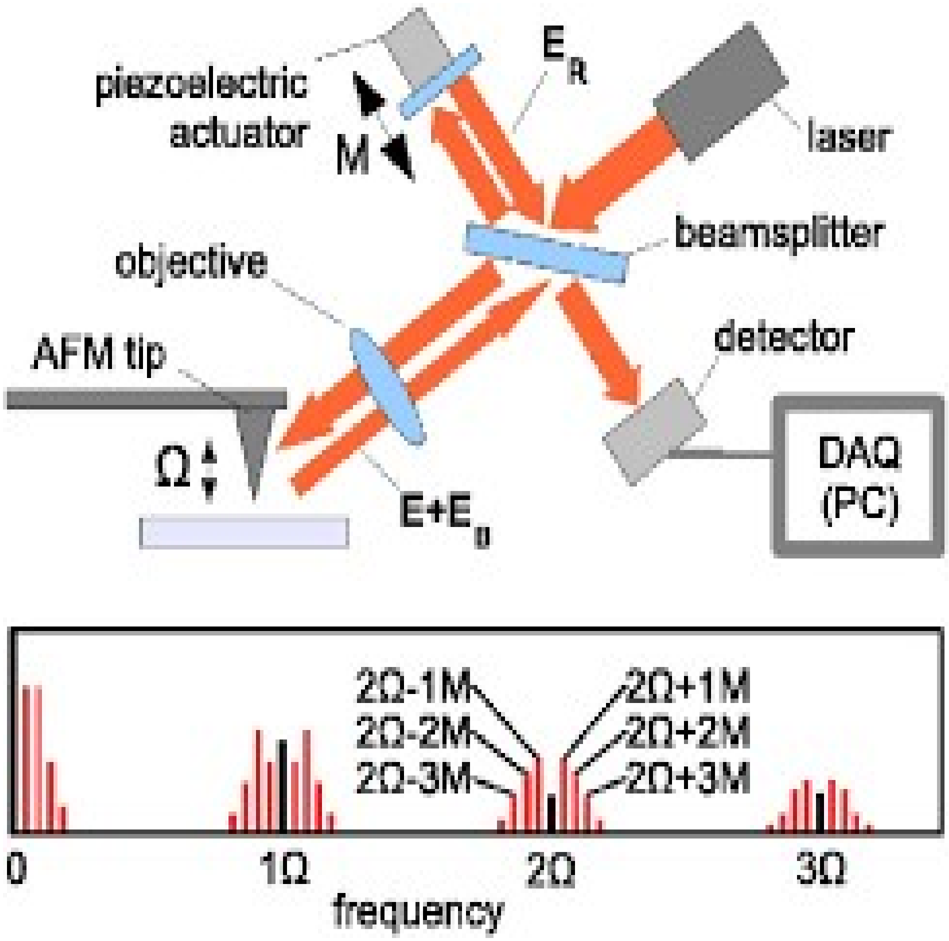




Heterodyne scheme
Δ=80 MHz (acousto-optics shifter)

Homodyne scheme
(based on Michelson interferometer)
Phase alternated between 0° and 90°

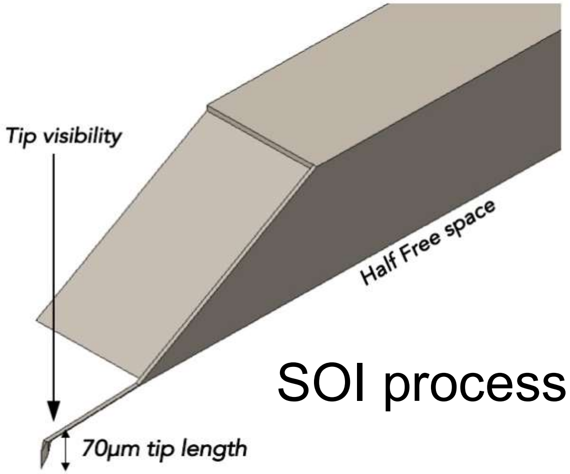
Pseudo-heterodyne detection



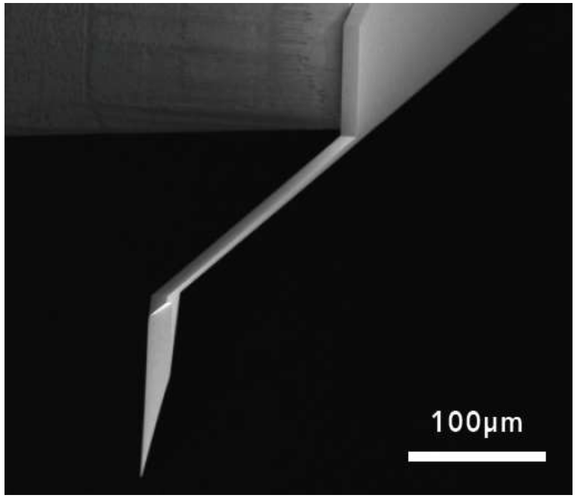
- Pseudoheterodyne detection
- Based on Michelson interferometer
- Background suppression
- Near-field amplitude and phase measurements

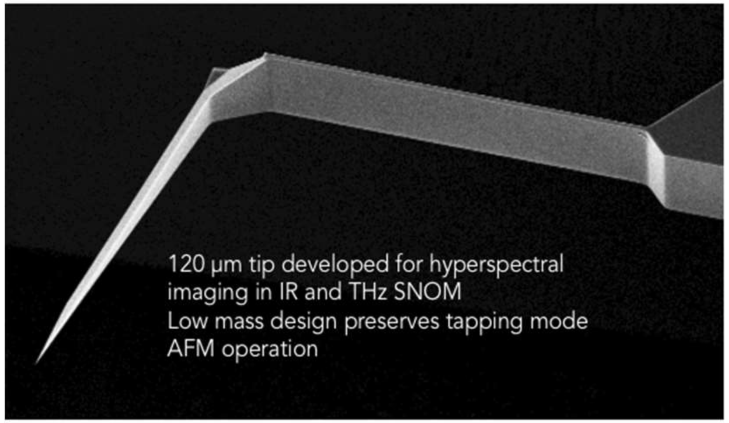
N. Ocelic et al., APL **89**, 101124 (2006)

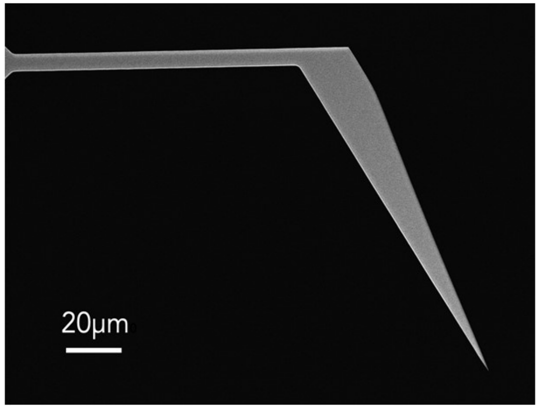
THHz probes for s-SNOM



SOI process



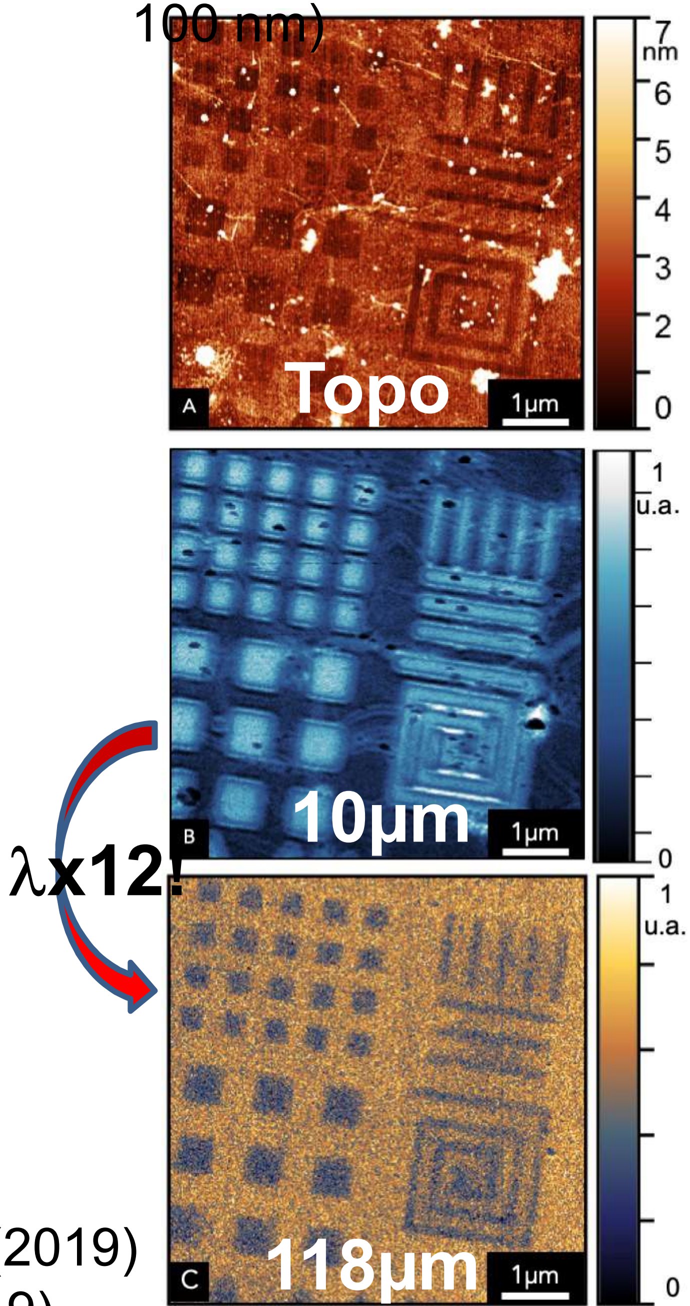




Pt-metallized tip for THz s-SNOM
220 kHz – 20 N/m

B. Walter *et al.*, 44th IRMMW-THz, Paris (2019)
B. Walter *et al.*, MARSS'19, Helsinki (2019)

Etched graphene sample on SiO_2 (lines: 100 nm)

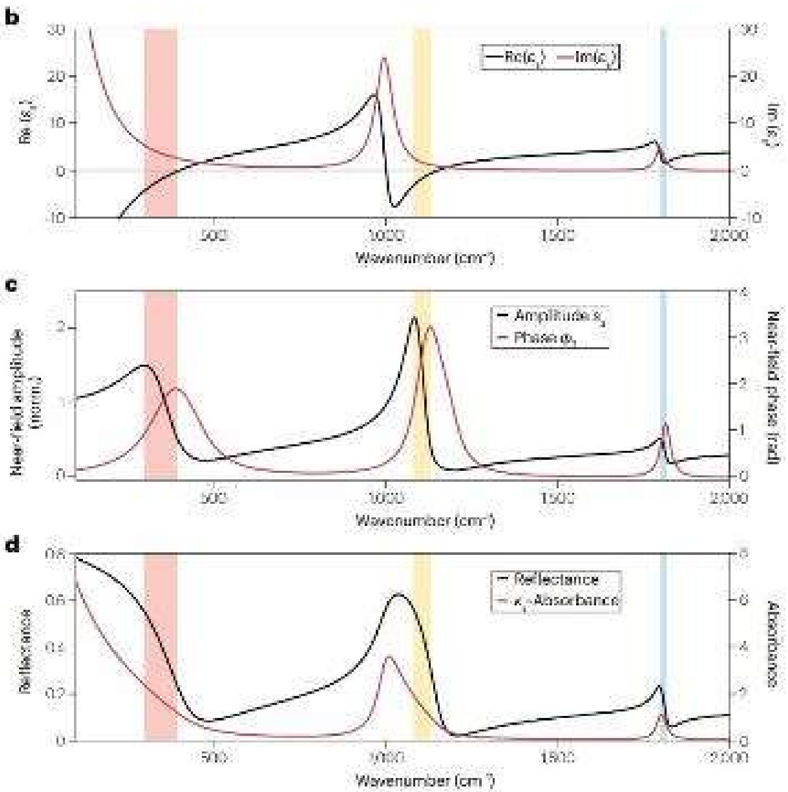


Images

Origin of contrast : oscillators

Oscillators	Charge carriers	Phonons	Molecular vibrations	Excitons
Materials	Organic and inorganic (semi)metals, semiconductors	Polar crystals, oxides, minerals	Polar organic and inorganic molecules	Organic and inorganic semiconductors
Spectral range	THz–Vis	THz–mid-IR	THz–mid-IR	THz–Vis

	Drude term	Lorentz oscillator strong	Lorentz oscillator weak
$\varepsilon_s = \varepsilon_{s,\infty}$	$\left(1-\frac{\omega_p^2}{\omega^2+i\omega\gamma_p}\right)$	$+\frac{A_{ph}^2}{\omega_{ph}^2-\omega^2-i\omega\gamma_{ph}}$	$+\frac{A_m^2}{\omega_m^2-\omega^2-i\omega\gamma_m}$



R. Hillenbrand *et al.*
Nature Rev. Mat.
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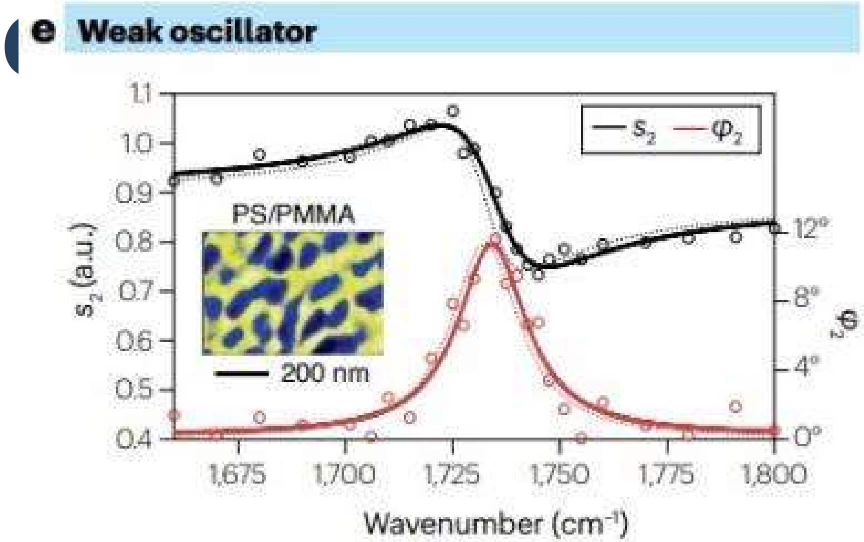
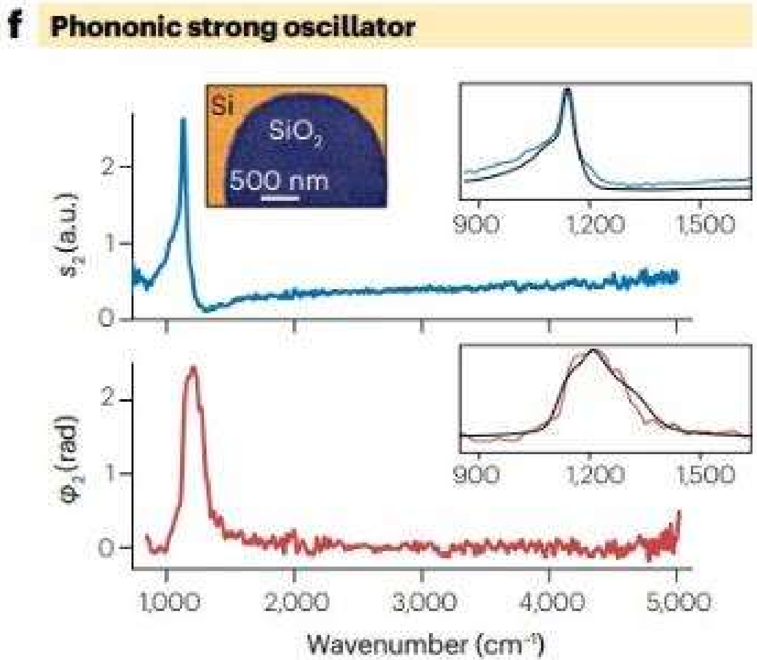
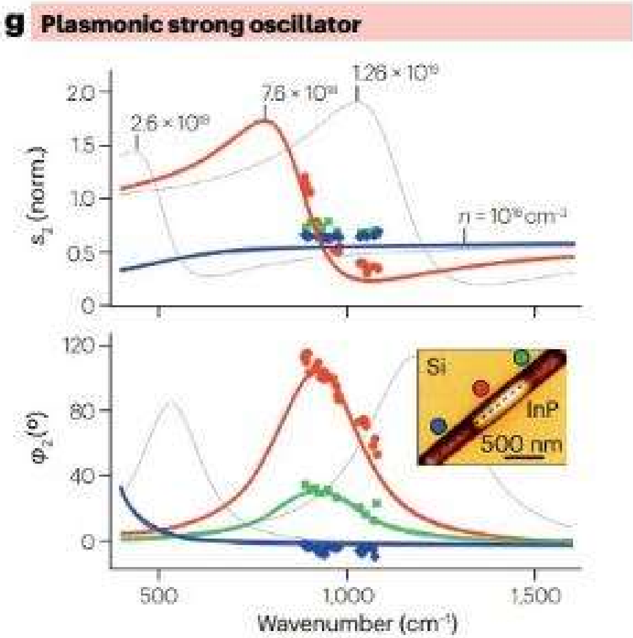
Origin of contrast: various oscillators







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2025

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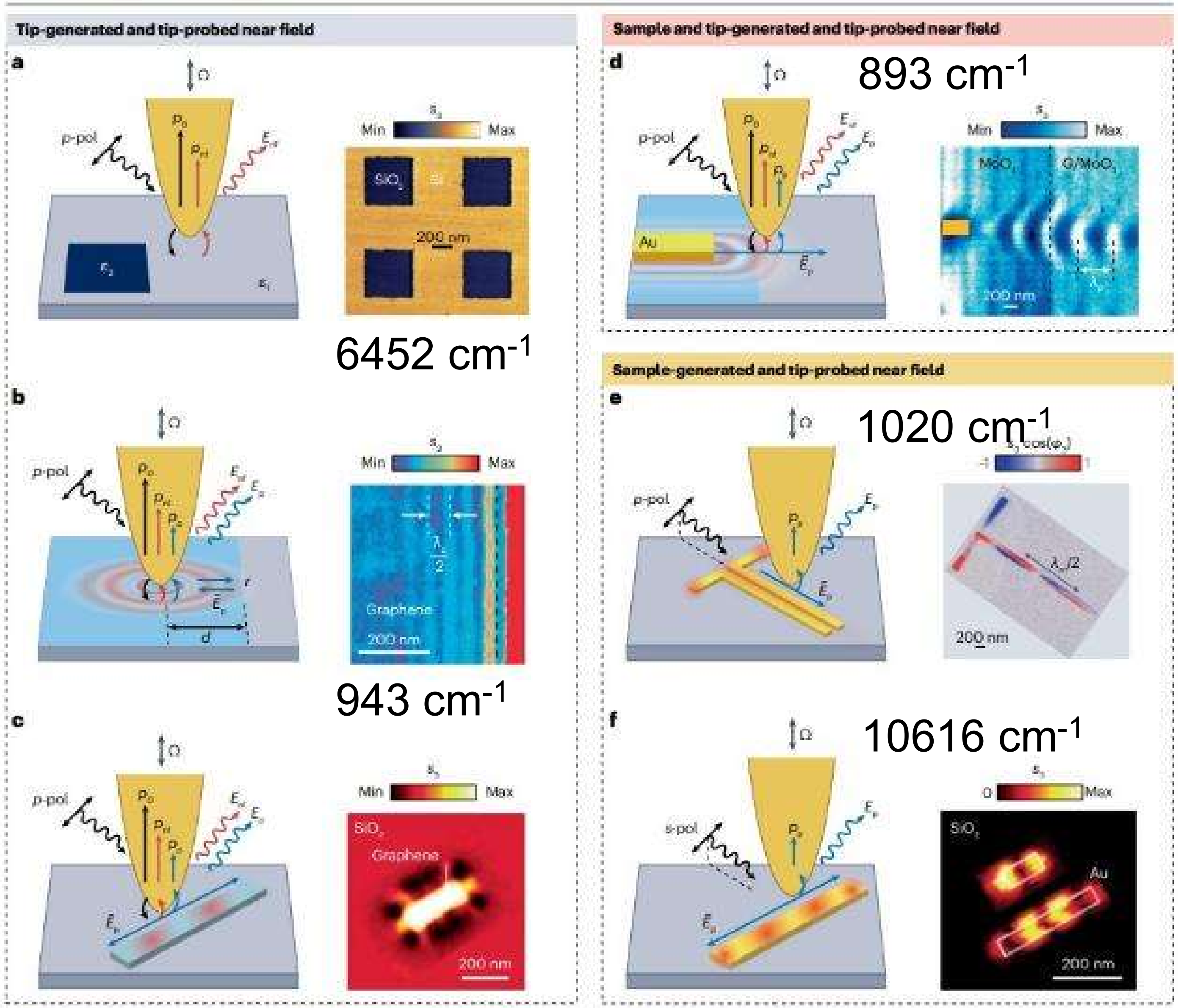
Various near-fields



884 cm^{-1}

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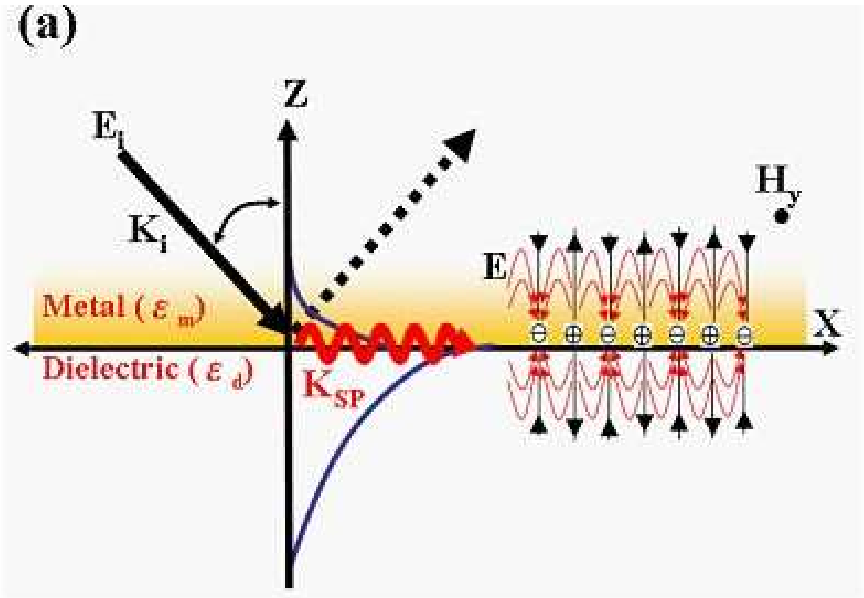
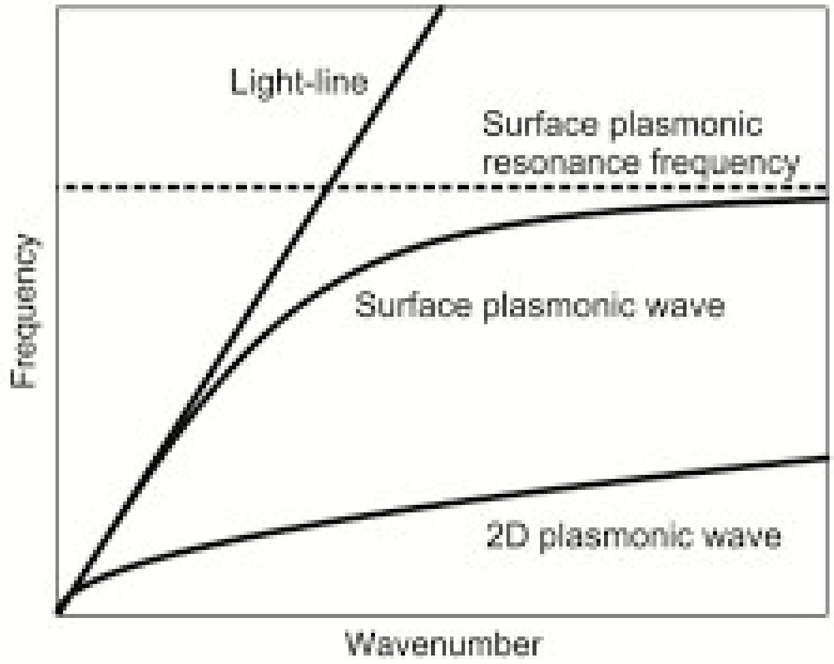
Surface plasmons-polaritons

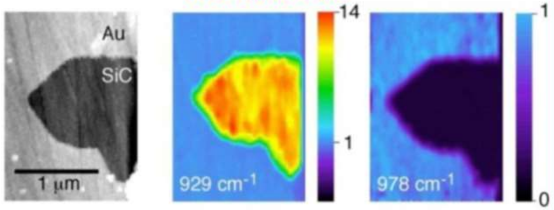




NeaSNOM enables chemical identification on the nanoscale

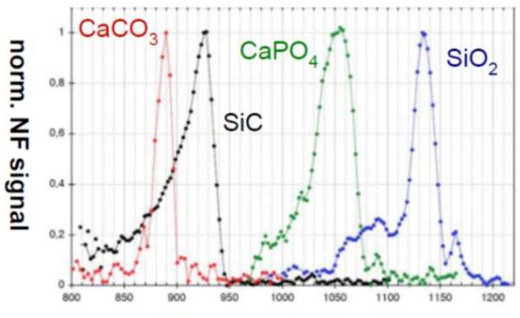
Of Crystals

Au and SiC



Topography **Near-field amplitude images**

IR-active materials

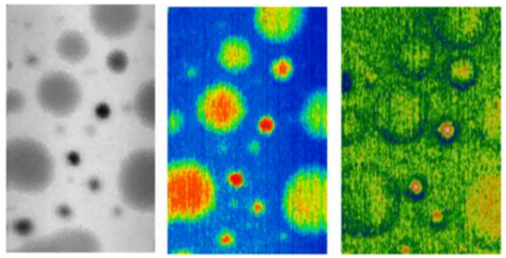


Spectroscopic identification of crystals

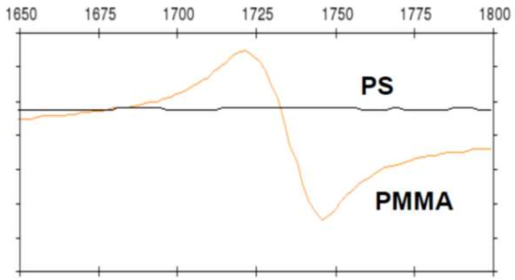
R. Hillenbrand et al., Nature 418, 159 (2002)

Of Polymers

PMMA / PS polymer blend



Topography **Near-field at 1750 cm-1** **Near-field at 1732 cm-1**

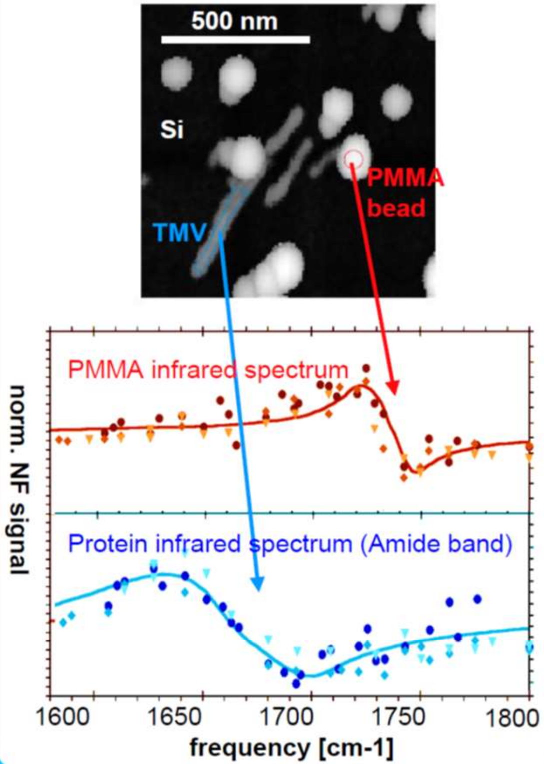


Near-field vibrational fingerprints

T. Taubner et al., APL 85, 5064 (2004)

Of Biological Material

Tobacco mosaic virus (TMV)

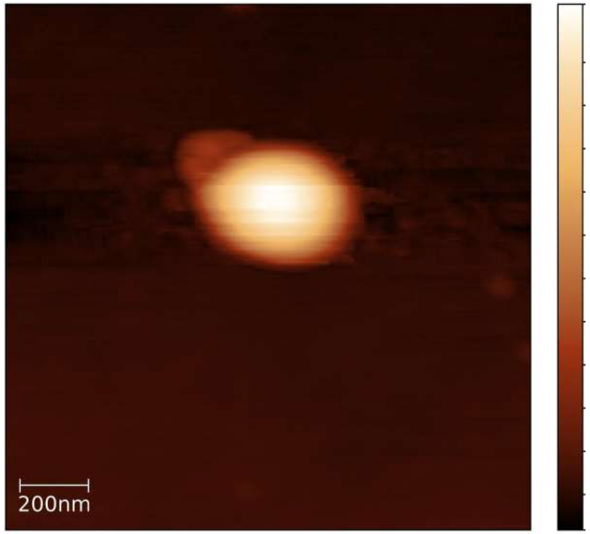


M. Brehm et al., Nano Lett. 6, 1307 (2006)

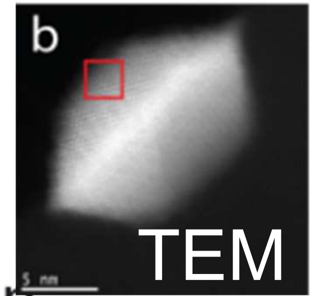
Images of organic molecules

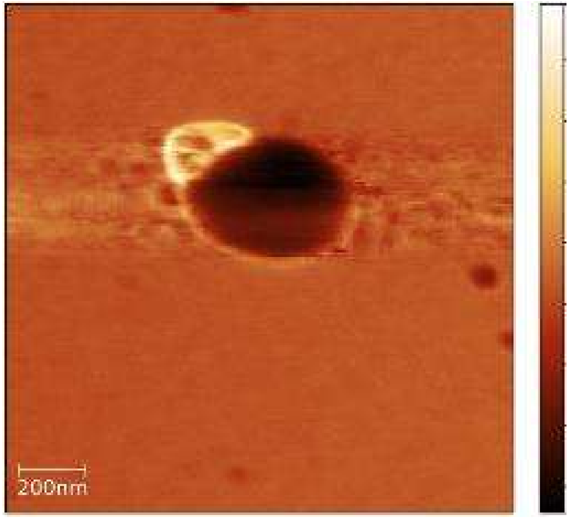
Collab. with N. Clément et al. (IEMN)

200 nm Au nanoparticule with grafted **organic molecules**



AFM (topography)
2 structures are visible





s-SNOM
λ = 10 µm, 2nd harmonic
Interesting contrast: Au is brighter, molecules are darker than Si substrate

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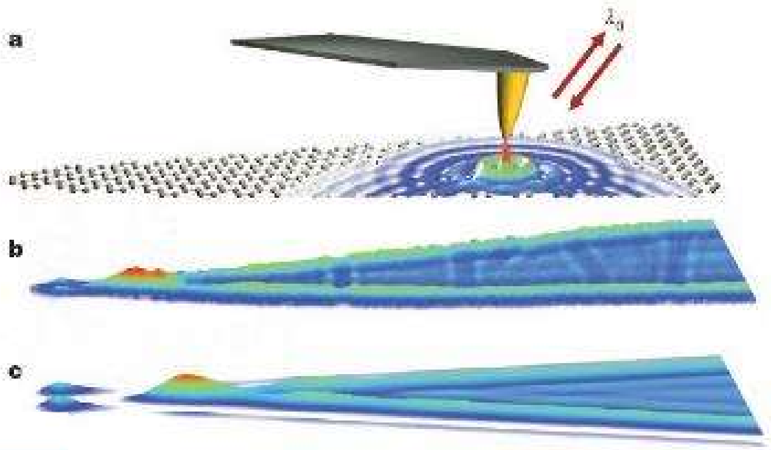
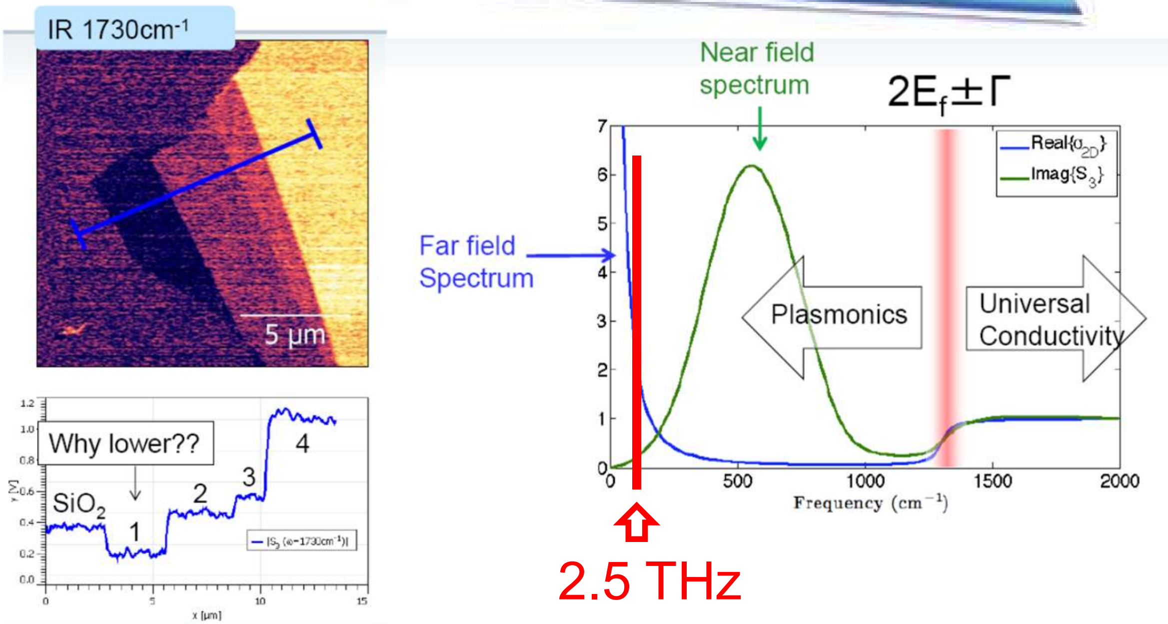
s-SNOM on graphene

Excitation of plasmons in tapered Graphene nanostructures

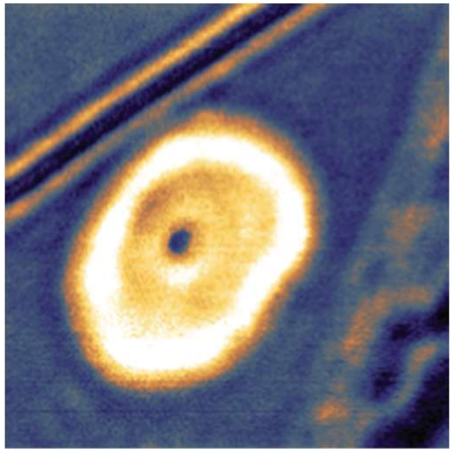
J. Chen et al., Nature 487, p. 77 (2012)

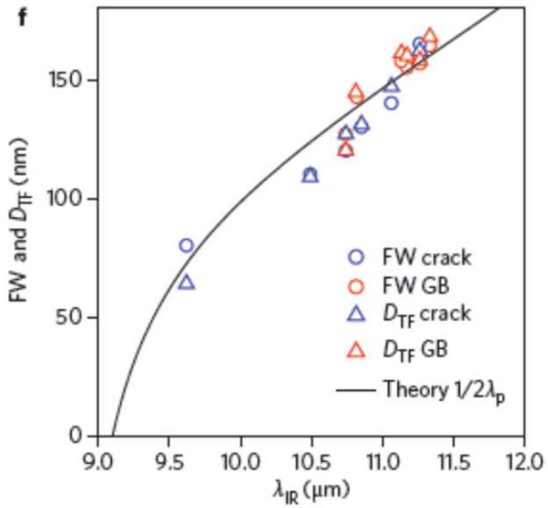




G. Andreev, Brüker Nano

Plasmons at grain boundaries (CVD graphene)





Z. Fei et al., Nature Nanotechnology 8, p. 821 (2013)

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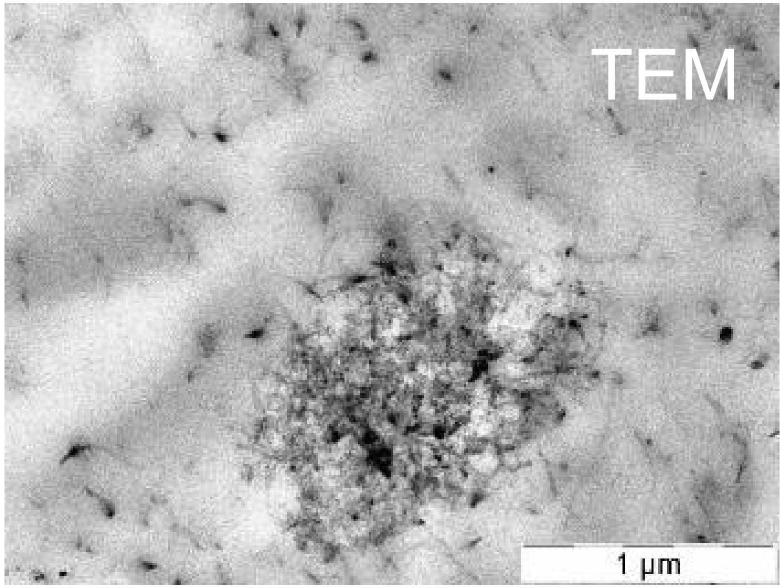
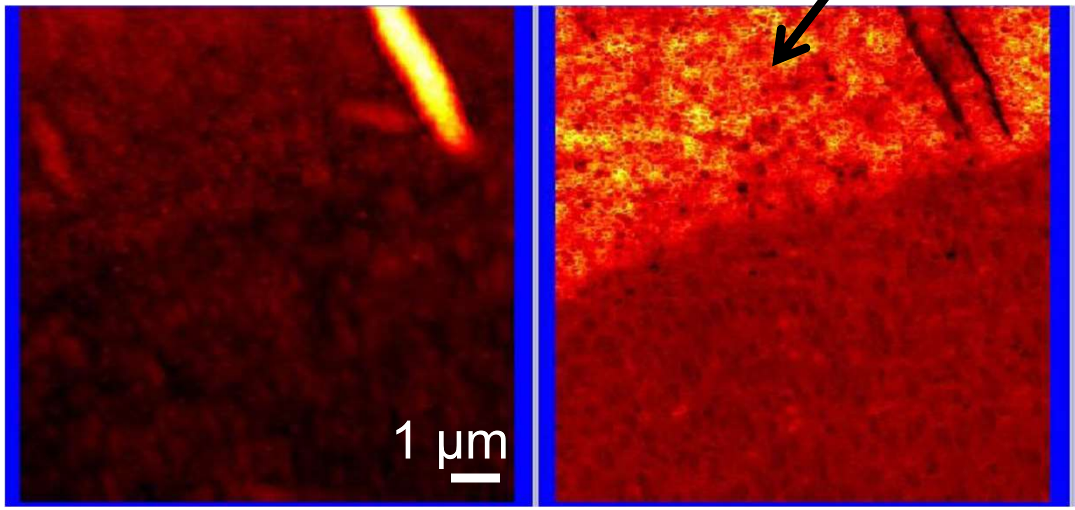
Images of CNT

Collab. with I. Huynen and A. Emplit (UCL)

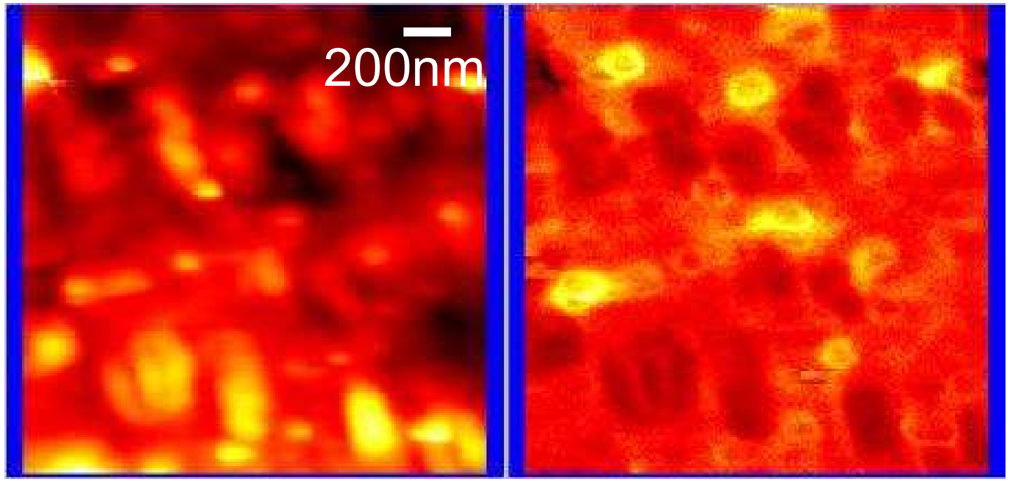


Aggregate



Topography

s-SNOM
λ = 10 µm, 2nd harm.



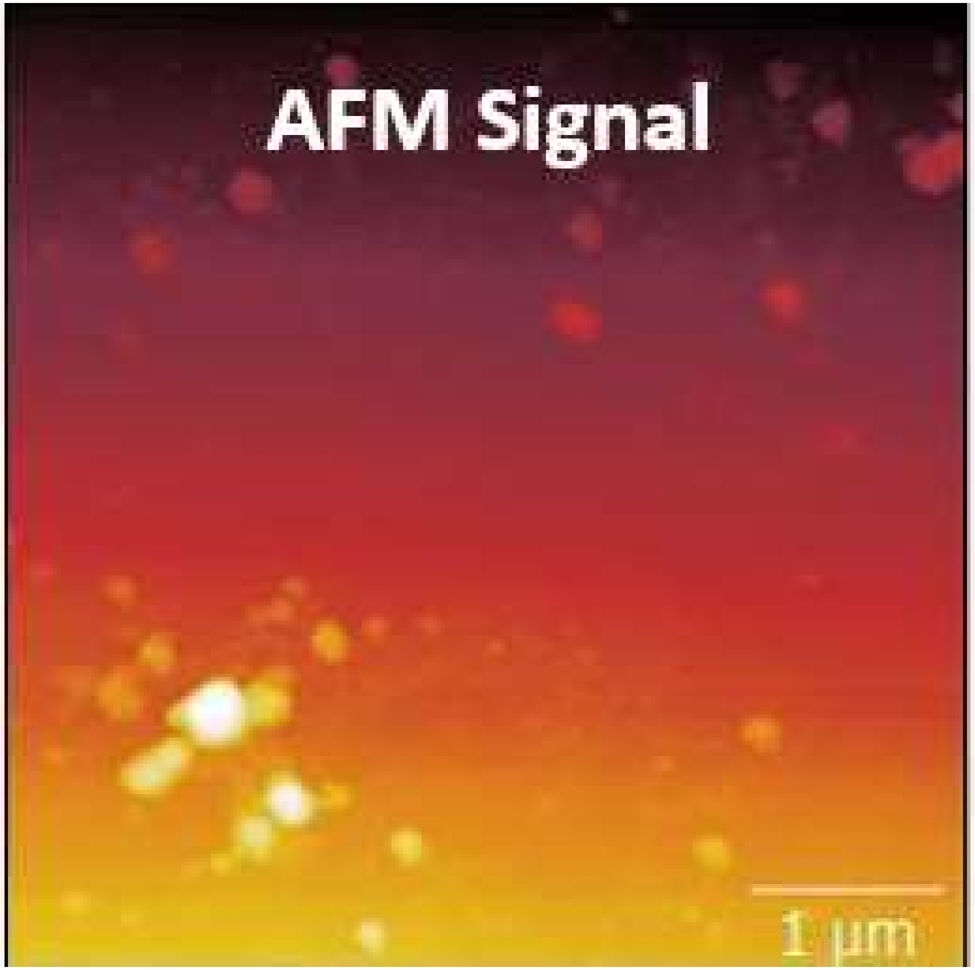
Multiwall CNT dispersed in a polymer matrix
→ Aggregates of CNT

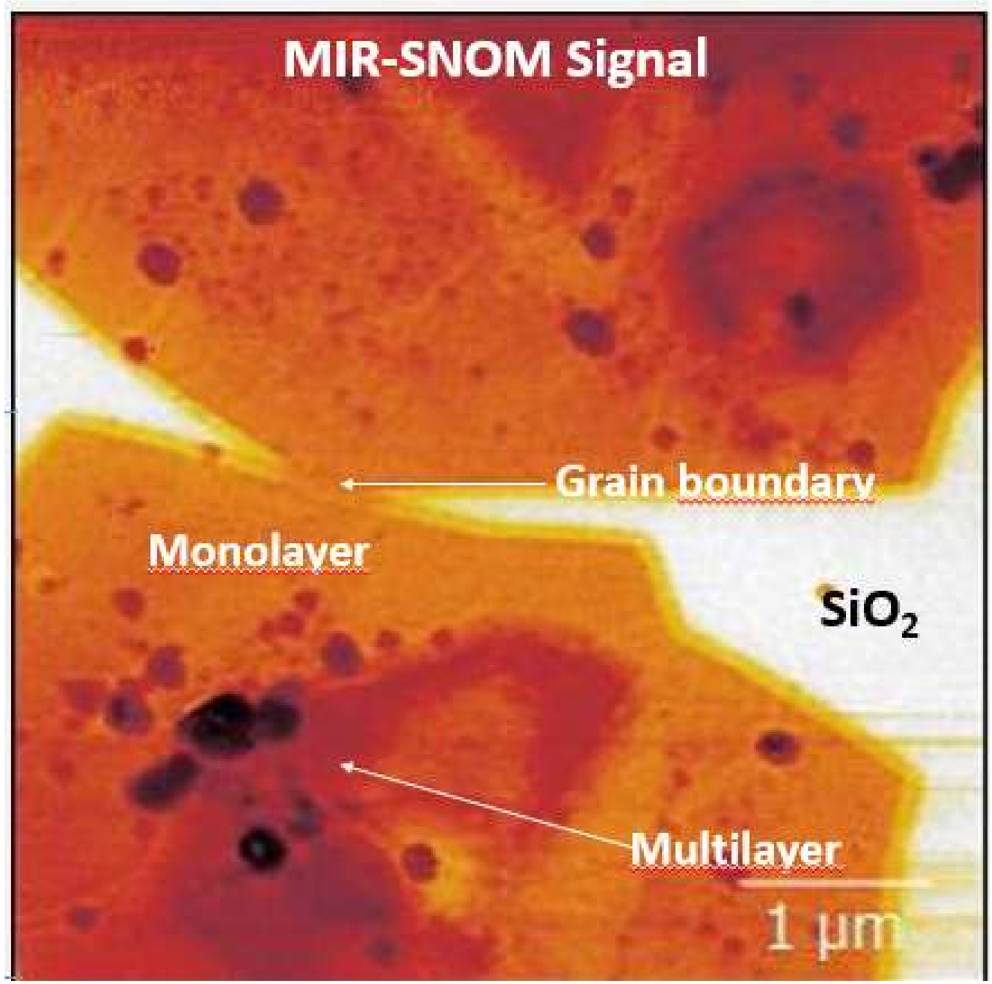
"Mid-infrared near-field nanoscopy of organic and inorganic samples: a valuable tool for the nanoscale", A. Pagies, G. Moreno, D. Ducatteau, N. Clément, T. Akalin, and J.-F. Lampin, A. Emplit, I. Huynen, Proceedings of the 4th International conference on Manipulation, Manufacturing and Measurement on the Nanoscale, 3M-Nano 2014, Taipei, Taiwan (October 27-31, 2014).

Cryo-µtome

MIR images of graphene

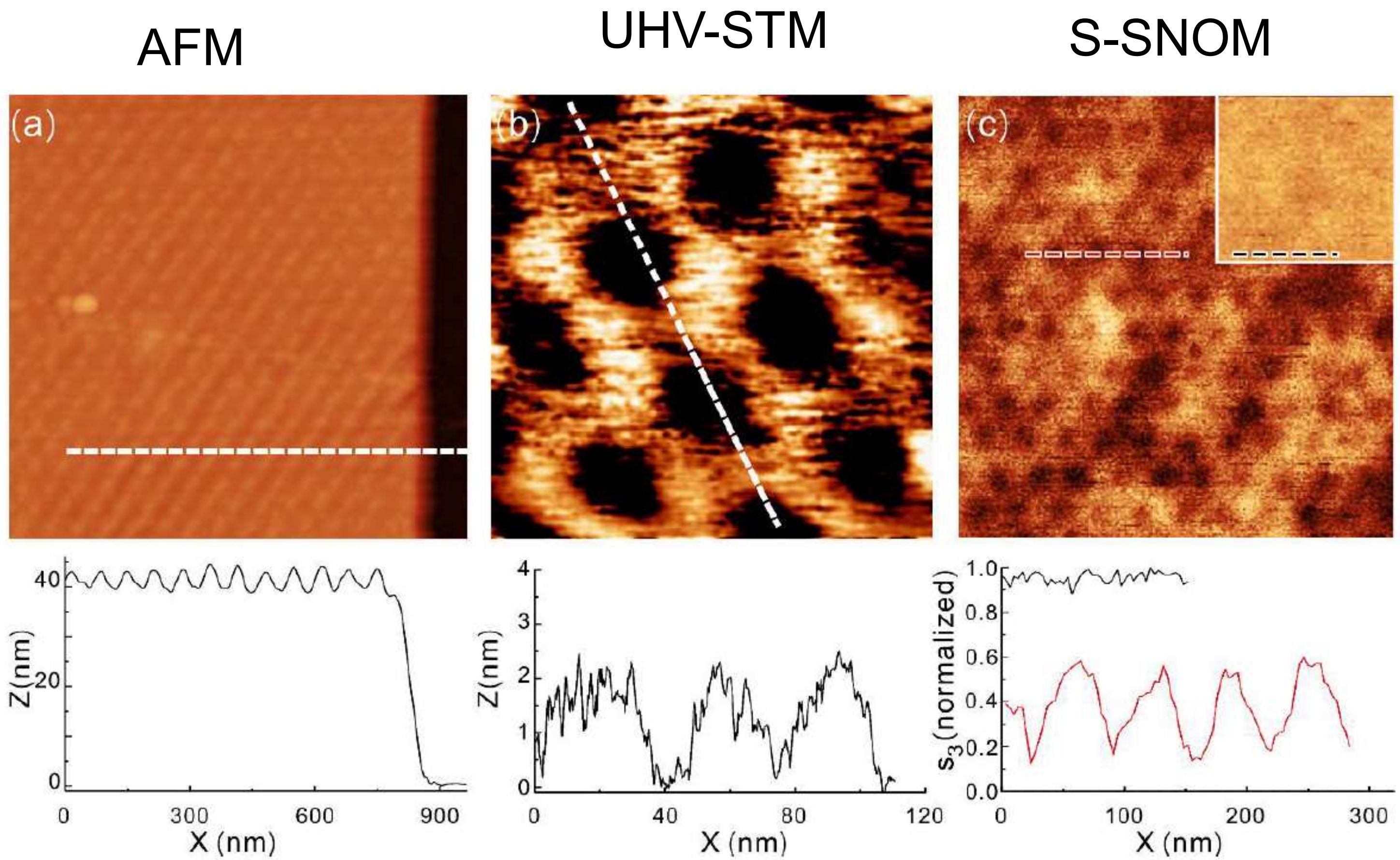
Collab. with Dominique Vignaud (IEMN)





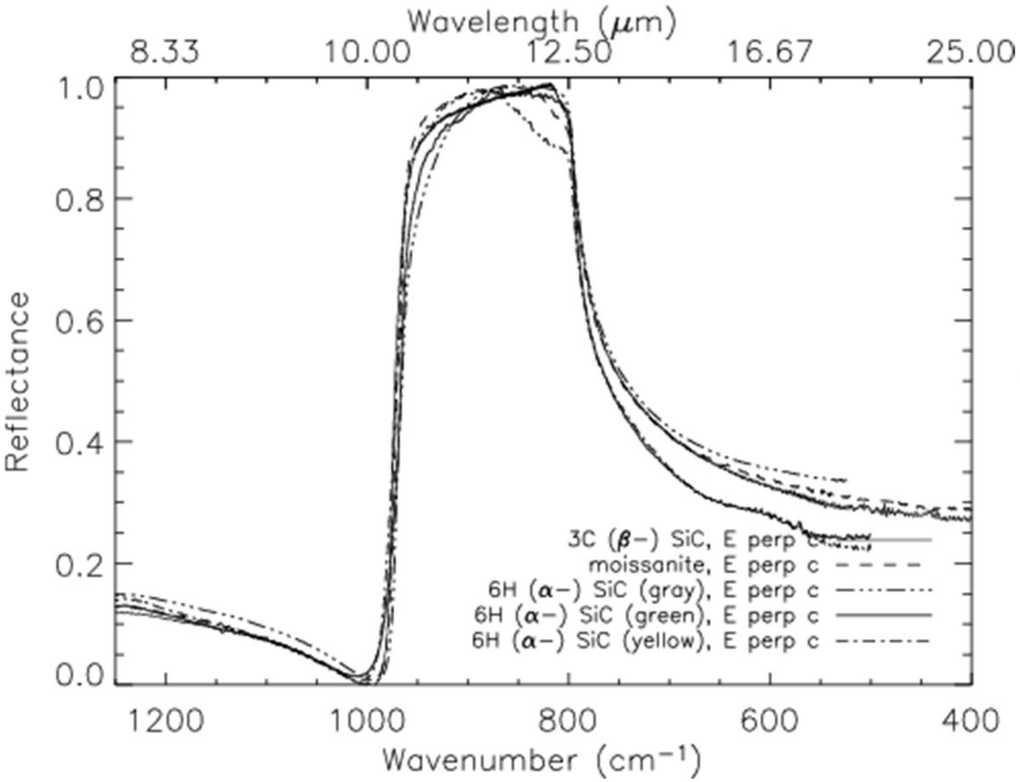
Graphene suspend on SiO2 nanopillars:Comparative studies about : Transport mechanisms in a puckered graphene-on-lattice

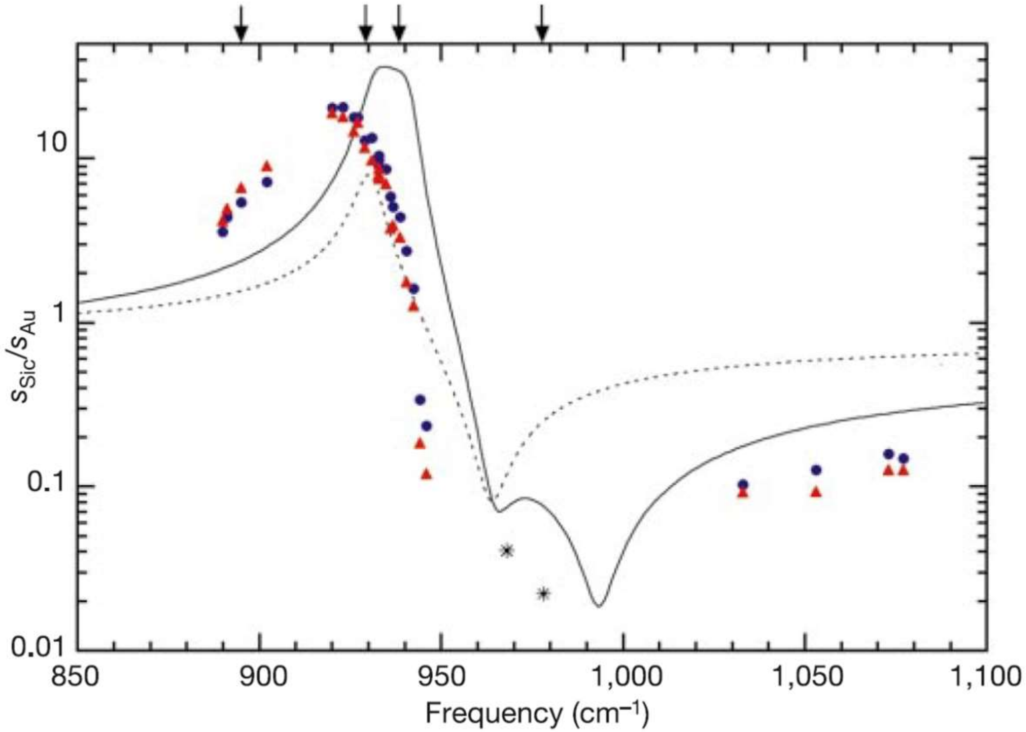
Collab. With Tao Xu (Shangaï University) et al.



Periodic variation due to the **local change of the density of the mobile carriers** and their scattering rate at MIR frequencies that are both involved in the reflection coefficient of the IR light

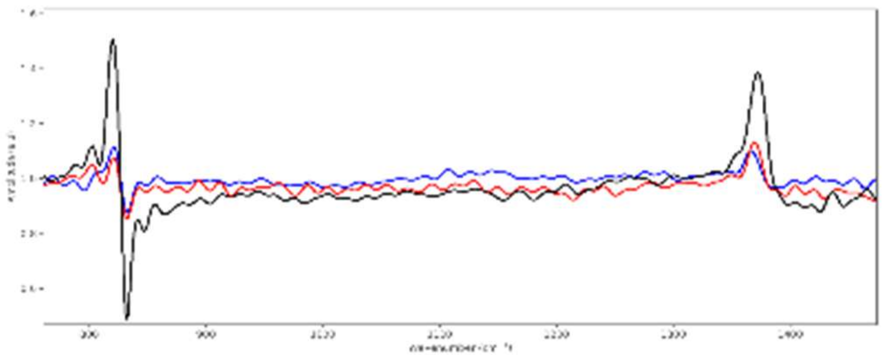
SNOM on phonons-polaritons

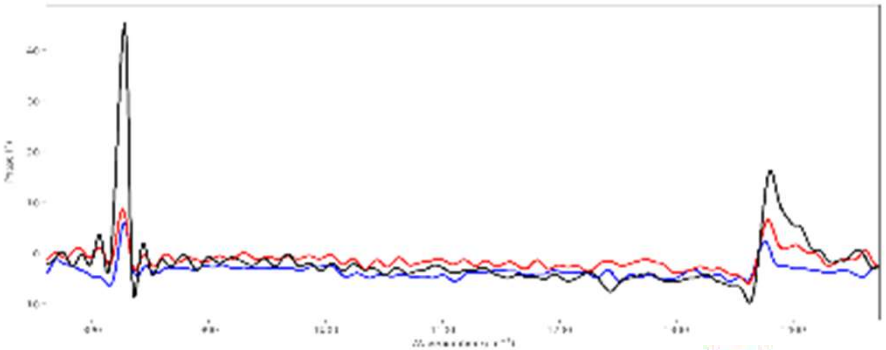


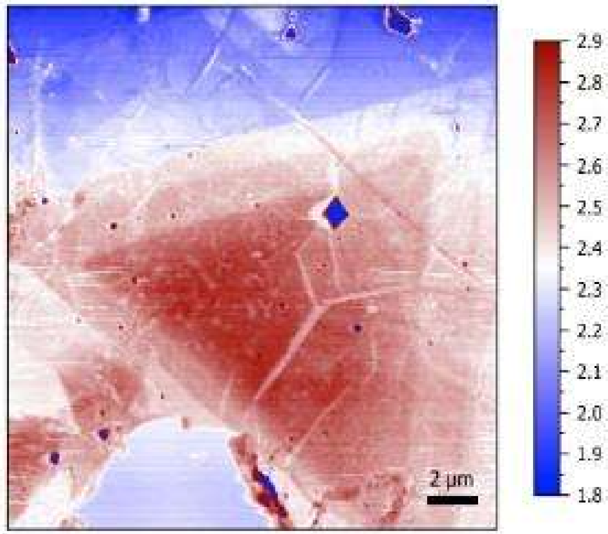


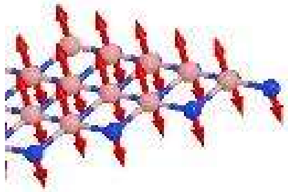
s-SNOM @ SMIS (SOLEIL)

Study on BN (J.-F Lampin, D. Vignaud)

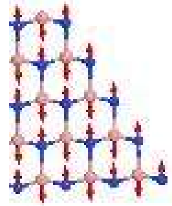








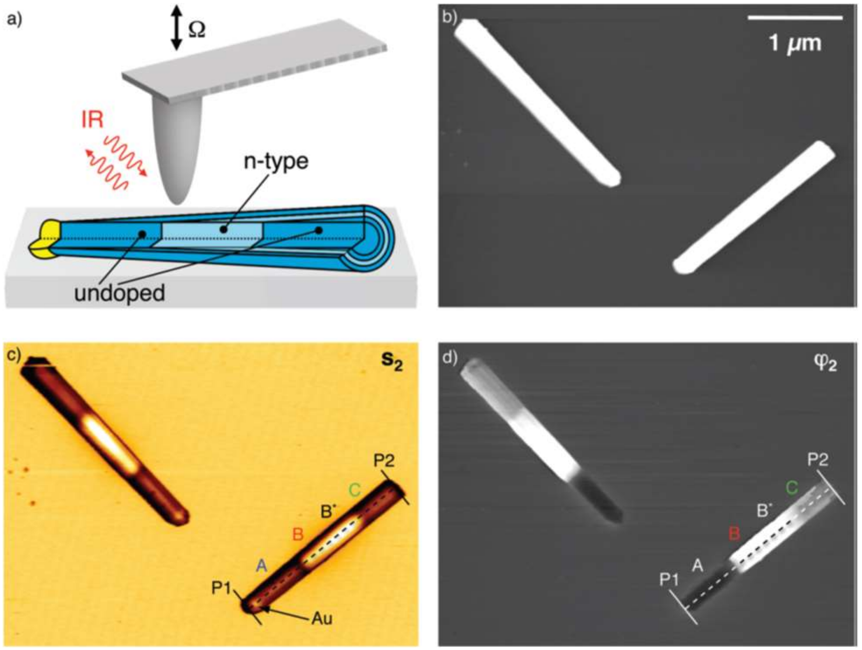
Phonon hors plan

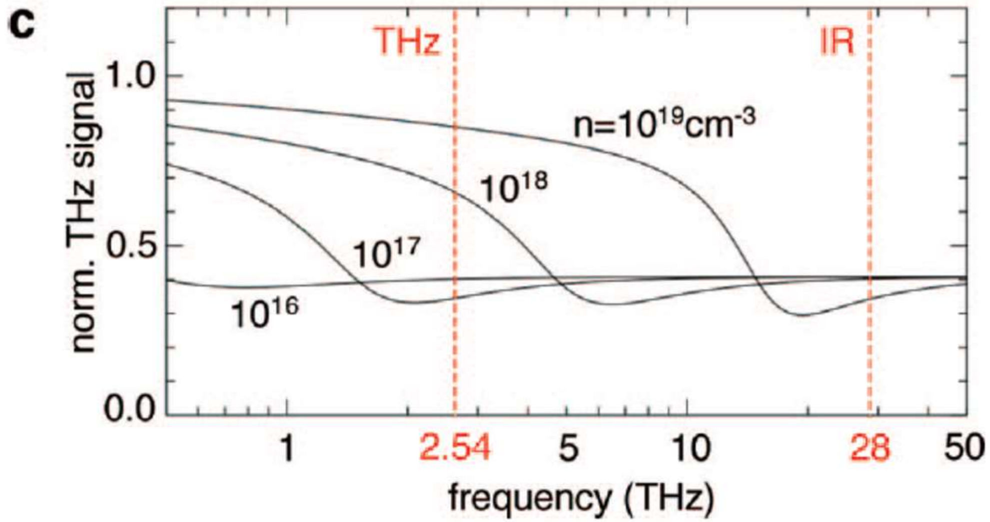


Phonon dans le plan

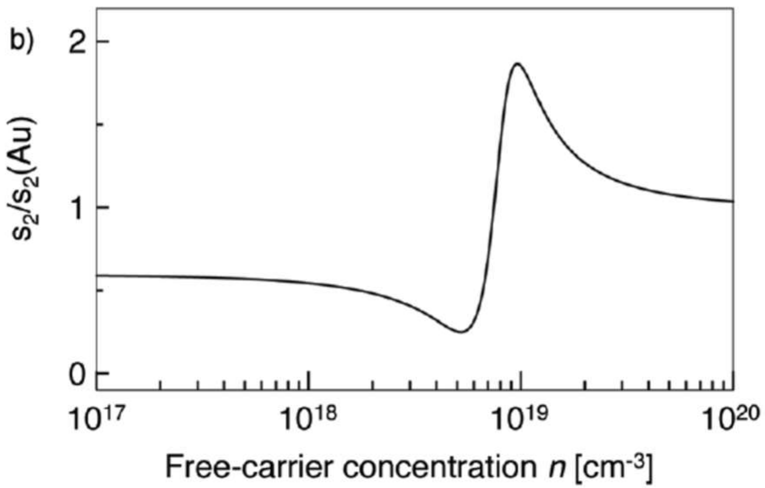
Near-field THz imaging

Why THz ?





Low doping, high resolution: few carriers !



n-doped InP nanowires @ 11.2 µm

J. M. Stiegler *et al.*, Nanoletters **10**, 1387 (2010)

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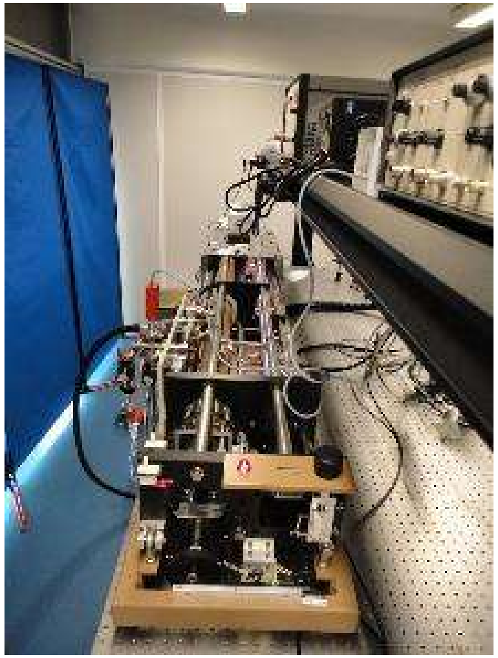
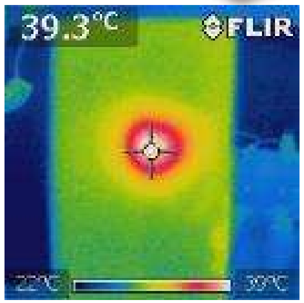
THz SNOM

THz source: CO_2 pumped THz gas laser





Beam @ 2.5 THz

InSb bolometer
3.5 K
(He closed cycle)

THz SNOM:

- Beam path OK
- Signal transmission through microscope OK
- images soon (probes/samples)

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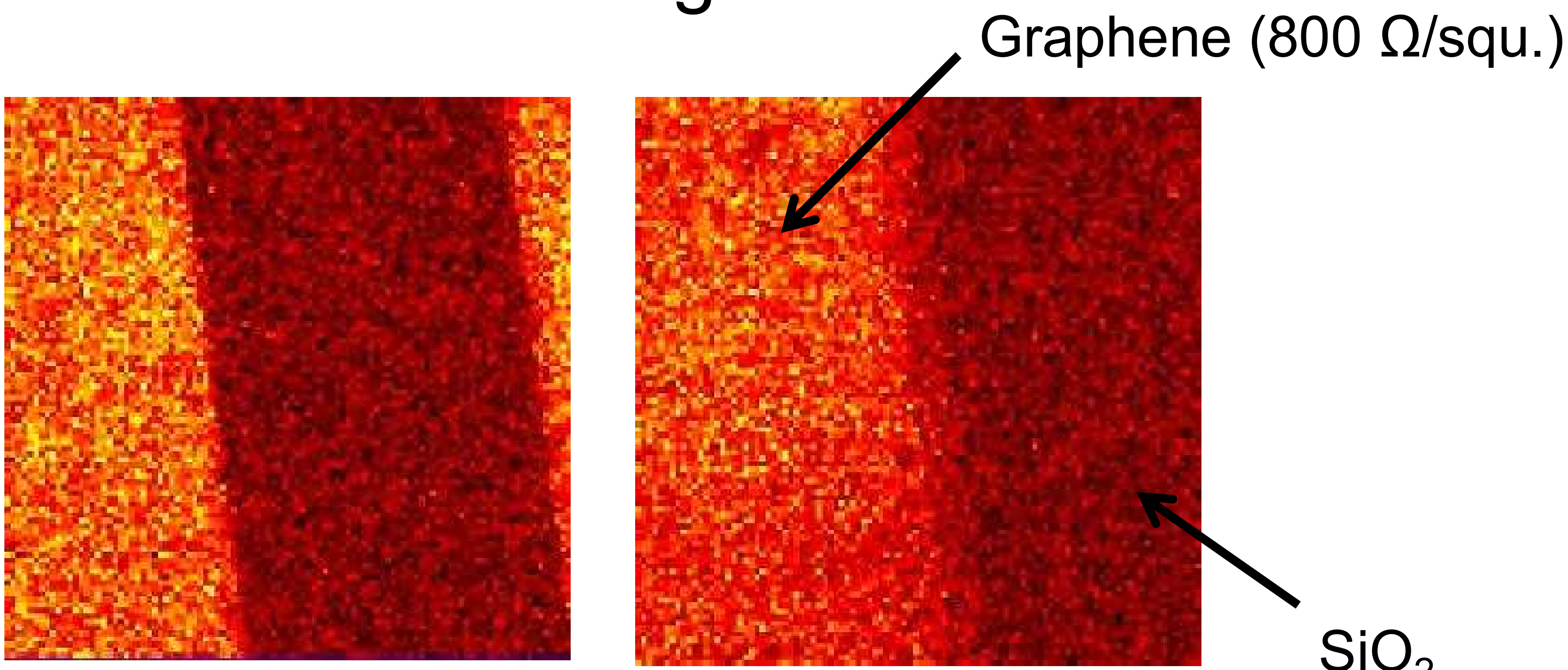
THz s-SNOM: 1st images on graphene

THz 2 Ω signals:



$20x20\ \mu m^2$ $3x3\ \mu m^2$

1st images of a graphene <u>monolayer</u> @ 2.5 THz (λ = 118 µm) !

Pagies et al., IRMMW-THz 2015

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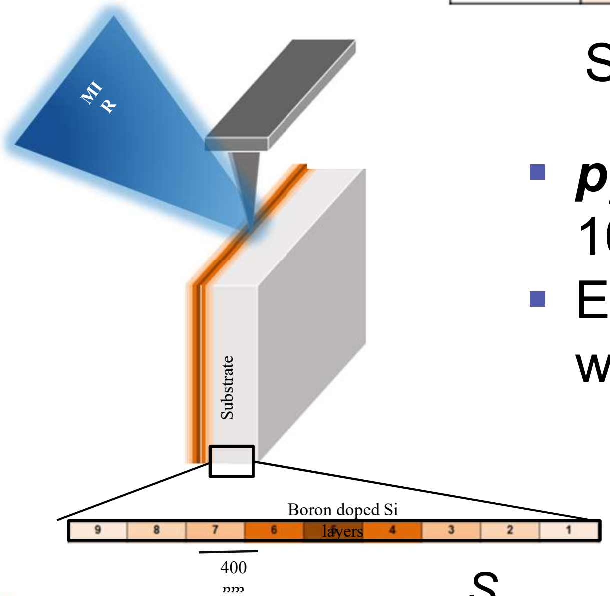
s-SNOM on doped Si layers

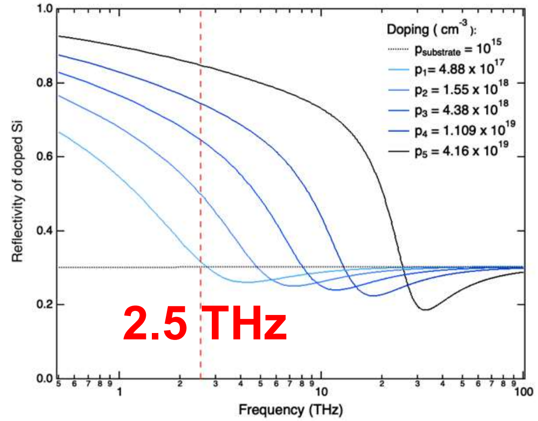
# Area	9	8	7	6	5	4	3	2	1
Doping (cm^{-3})	4.96 x 10^{17}	1.71 x 10^{18}	4.4 x 10^{18}	1.1 x 10^{19}	4.16 x 10^{19}	1.109 x10^{19}	4.38 x 10^{18}	1.55 x 10^{18}	4.88 x 10^{17}

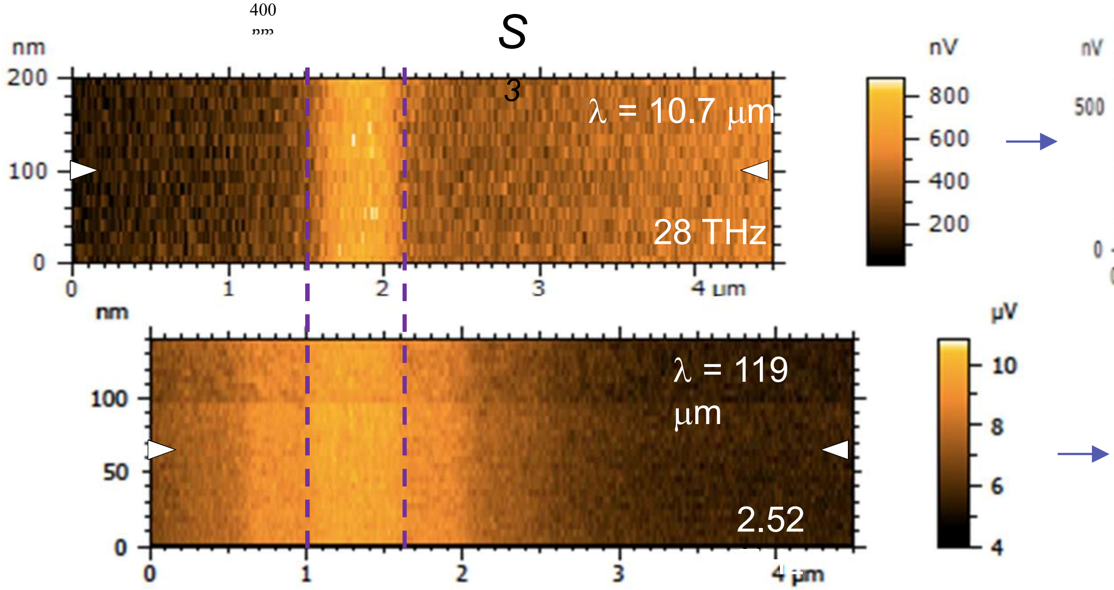
400 nm

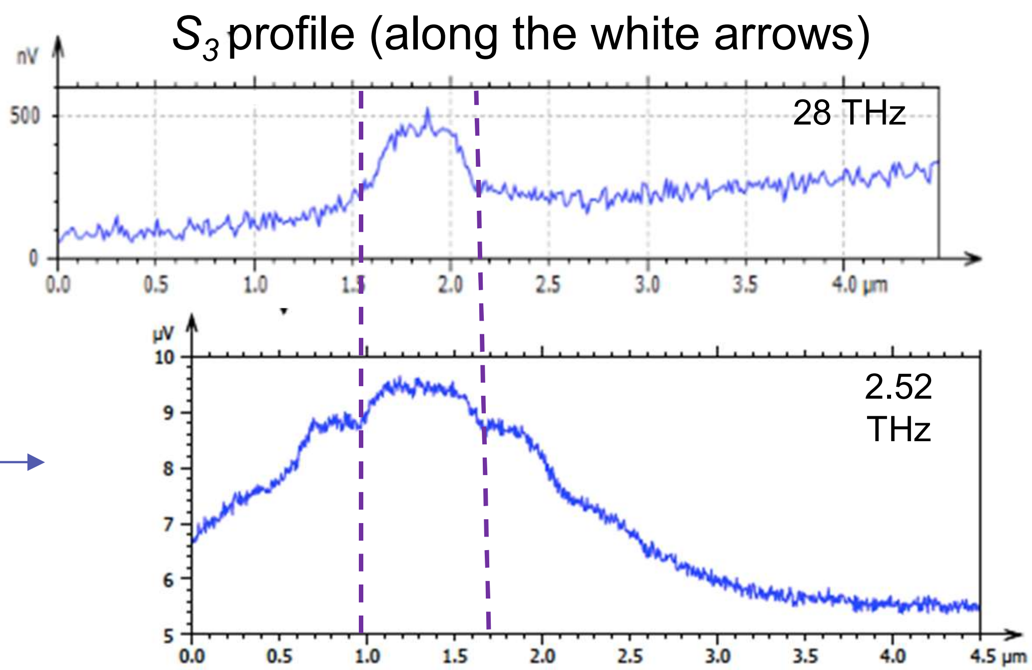
Sample Maya: CVD grown *p*-doped Si layers



- p_i ranges from ~ 4.9x 10^{17} - 4.2x10^{19} cm^{-3}
- Each p_i layer has a width of 400 nm

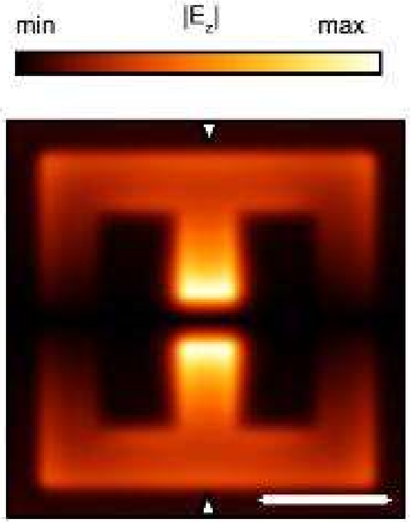




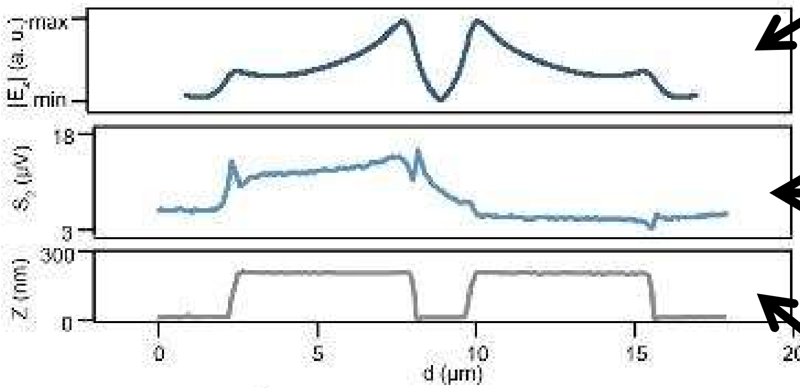


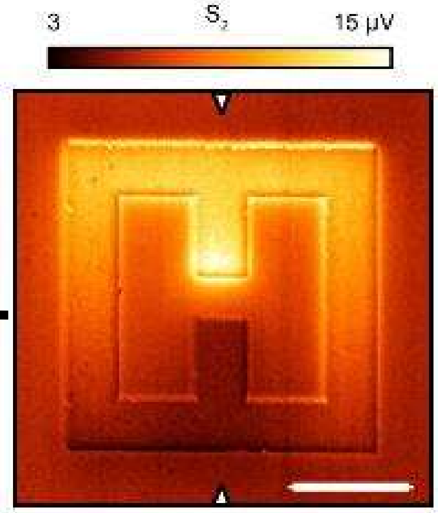
C. N. Santos, IRMMW-THz 2023

s-SNOM on a THz SRR

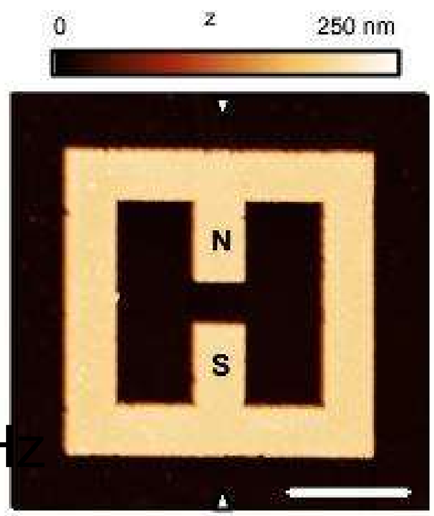


Normal electric field
EM simulation
FDTD Lumerical





2nd harmonic
s-SNOM signal
Tuned @ 2.5 THz



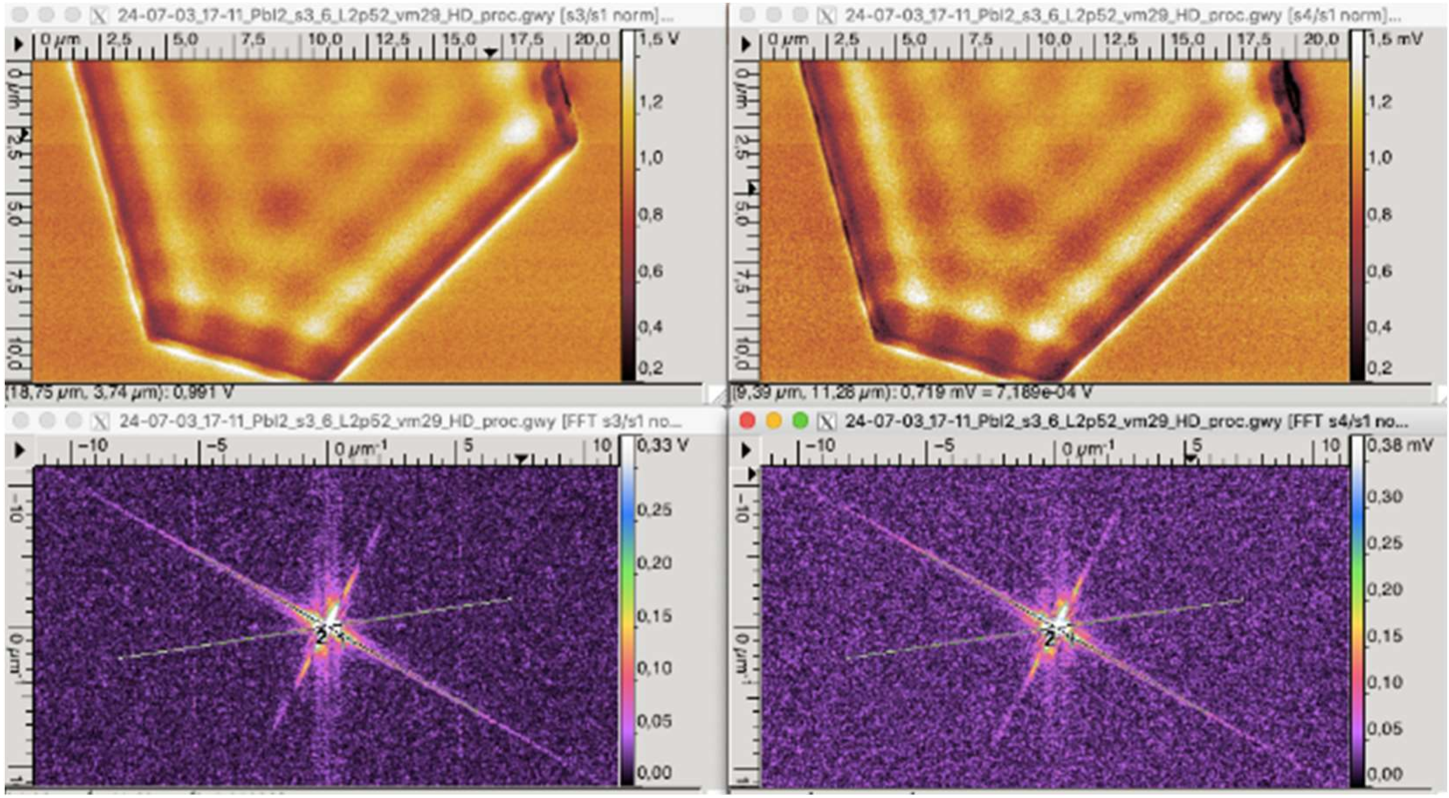
Topography
Scale bar: 5 µm

2nd harmonic
s-SNOM signal
Detuned @ 2.5 THz

L. Thomas *et al.*, ACS AMI, 2022

THz phonon-polariton

2.5 THz



Conclusion & outlook

- AFM + s-SNOM : **fantastic tool** for material identification using MIR-THz properties
- Relatively **simple** set-up & sample preparation
- 30-40 nm resolution with standard probes

Future:

- New dedicated **probes** (EM simulations)
- Dedicated **sources** (MIR & THz)

$\rightarrow$ **Nanoscope with chemical identification, free carrier sensitivity etc…**