TBA

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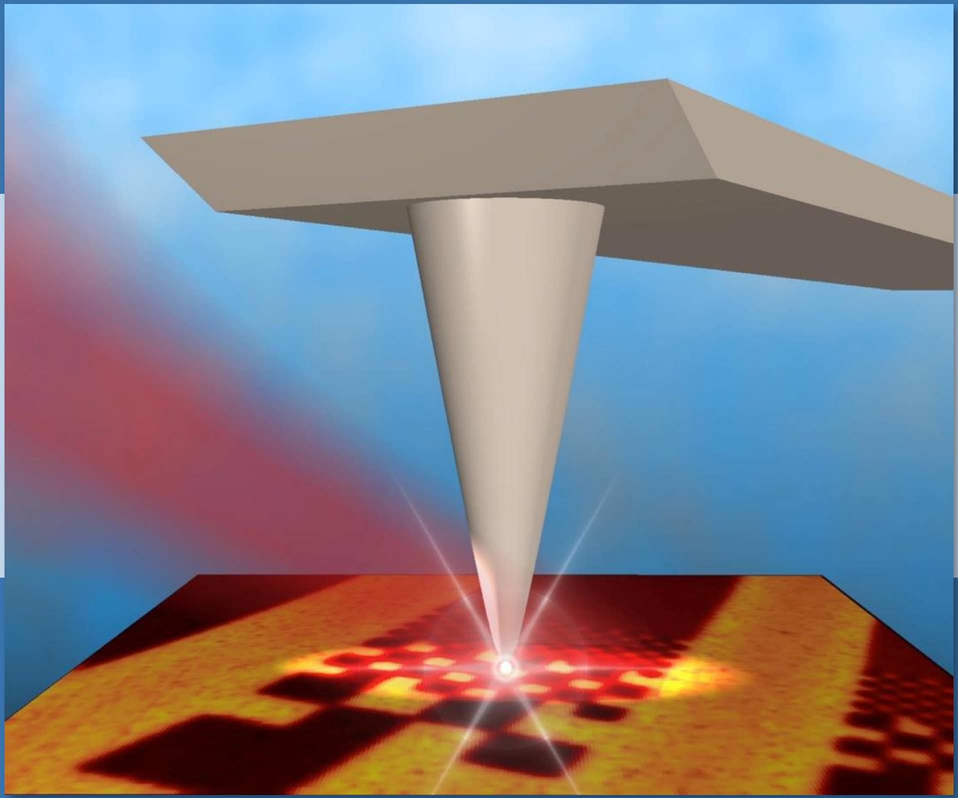
Infrared nanoimaging and nanospectroscopy by near-field optical microscopy



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San Sebastian - Donostia

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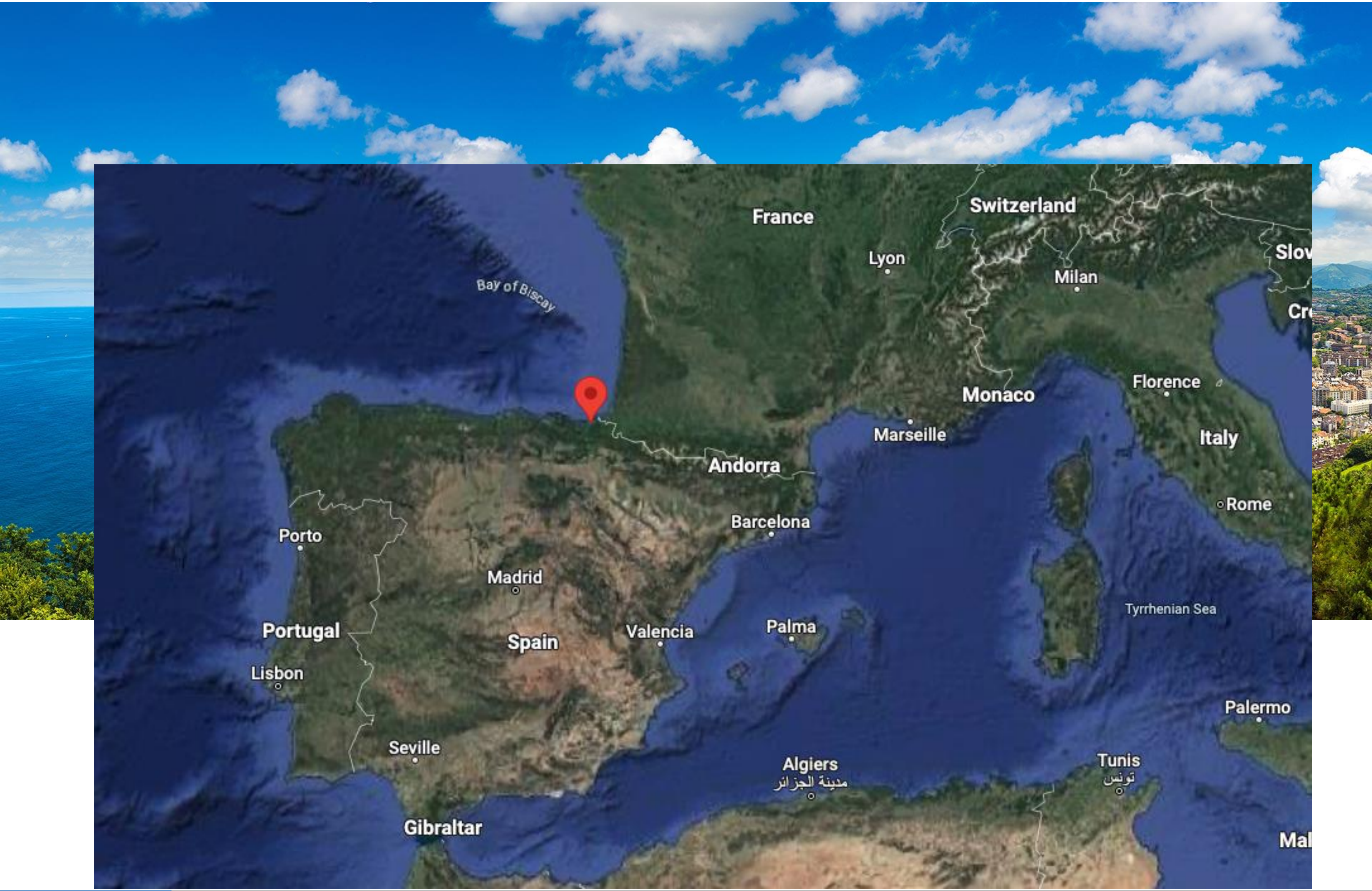
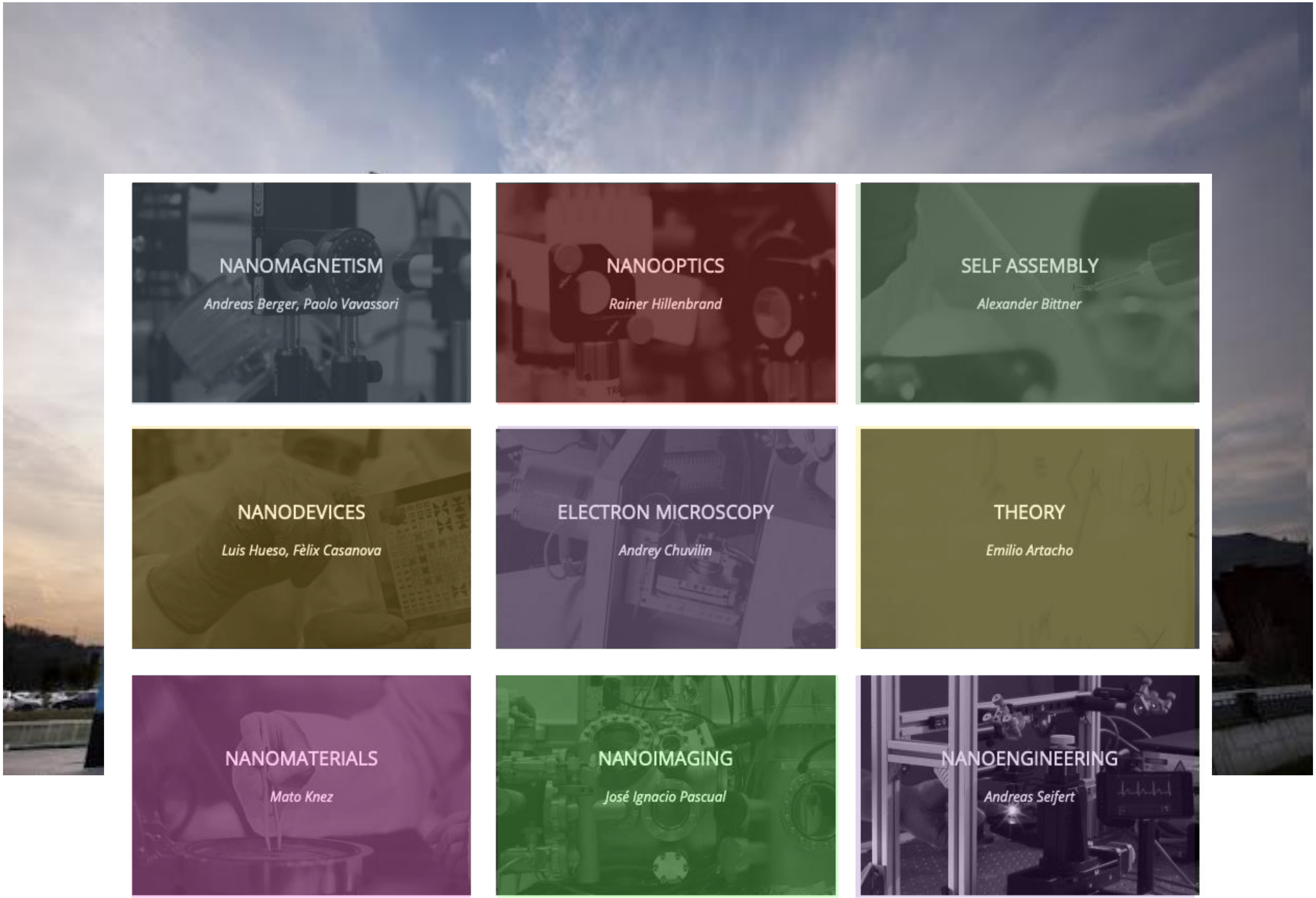


CIC nanoGUNE

https://www.nanogune.eu

CIC nanoGUNE



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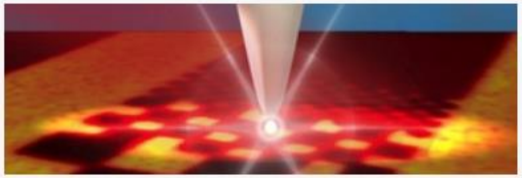
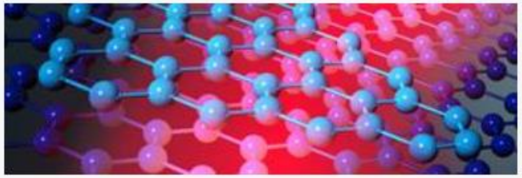
NANOOPTICS group

INSTRUMENTAL DEVELOPMENTS



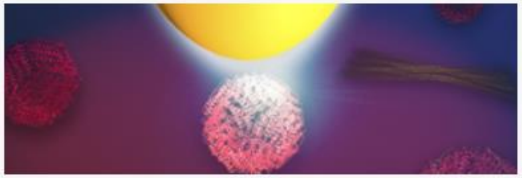
We continuously work on novel instrumental developments, with the goal to push the spatial resolution towards the single molecule level and to enable three-dimensional infrared-spectroscopic nanotomography.

PLASMONICS AND PHONONICS



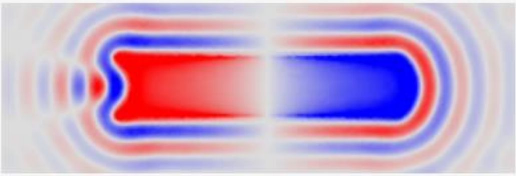
We apply s-SNOM and nano-FTIR to study plasmons in metal and graphene nanostructures, as well as phonons in polar crystals, for the development of ultracompact nanophotonic devices and their application, e.g. in optoelectronics and sensing.

IR NANOSPECTROSCOPY



IR s-SNOM and nano-FTIR are applied for nanoscale mapping of chemical composition of polymers, secondary structure of proteins, carrier distribution in semiconductor nanowires and optoelectronic properties of novel 2D materials.

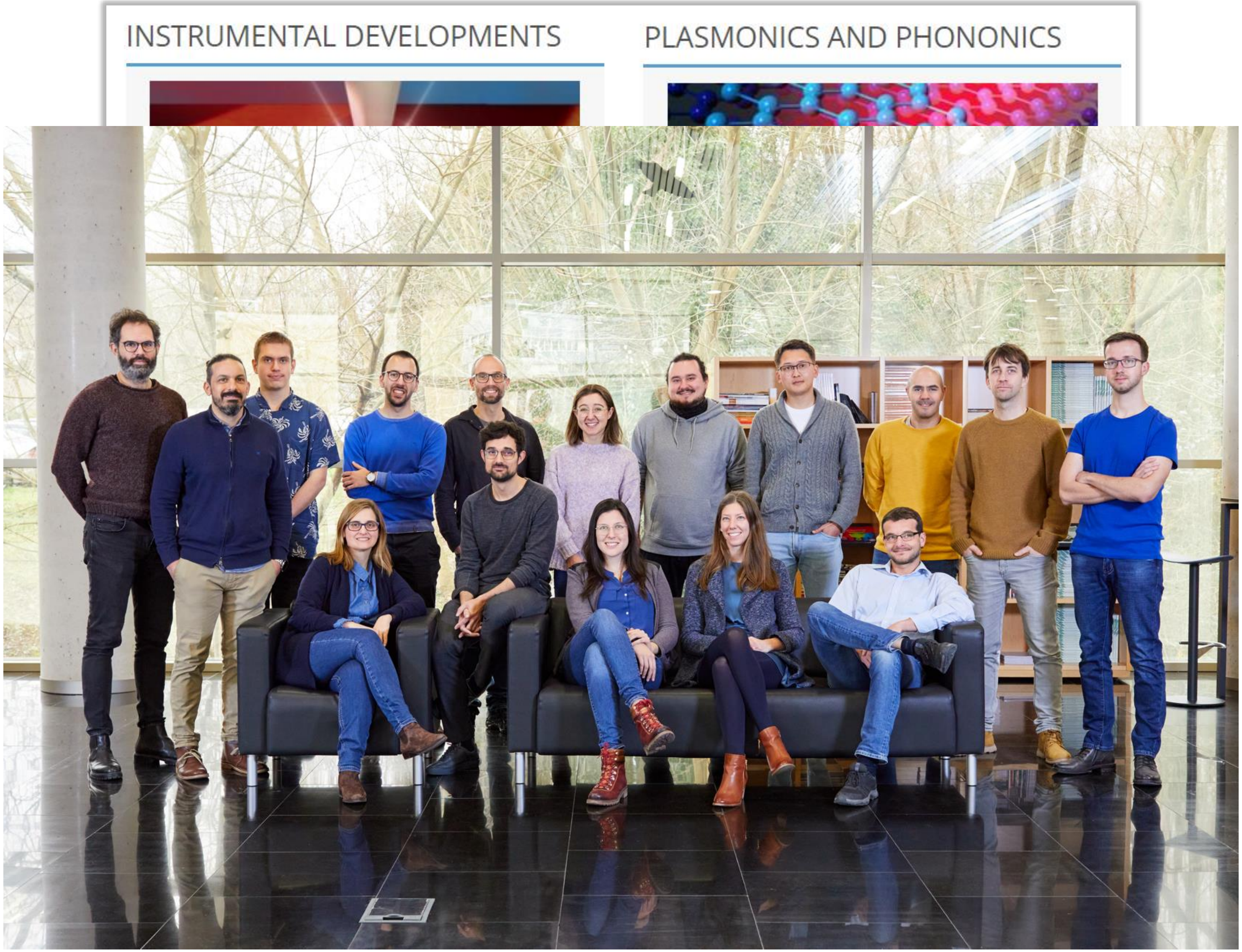
NANOOPTICS THEORY



We develop and apply theory for the propagation and scattering of waves/surface waves in natural, artificial and 2D materials, for modeling near-field spectroscopy, and for reconstruction of material properties from near-field data.

https://www.nanogune.eu/en/research/groups/nanooptics

NANOOPTICS group



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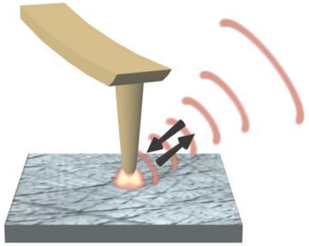
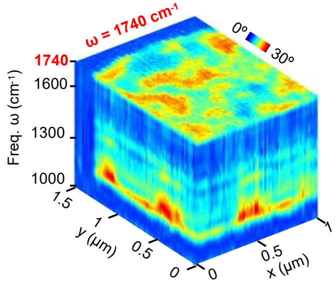
Outline

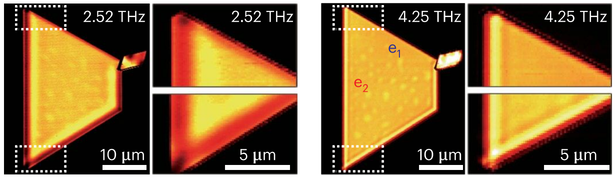
s-SNOM and nano-FTIR techniques

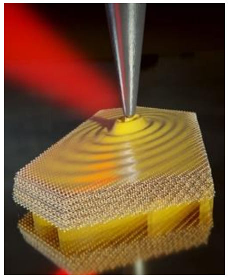




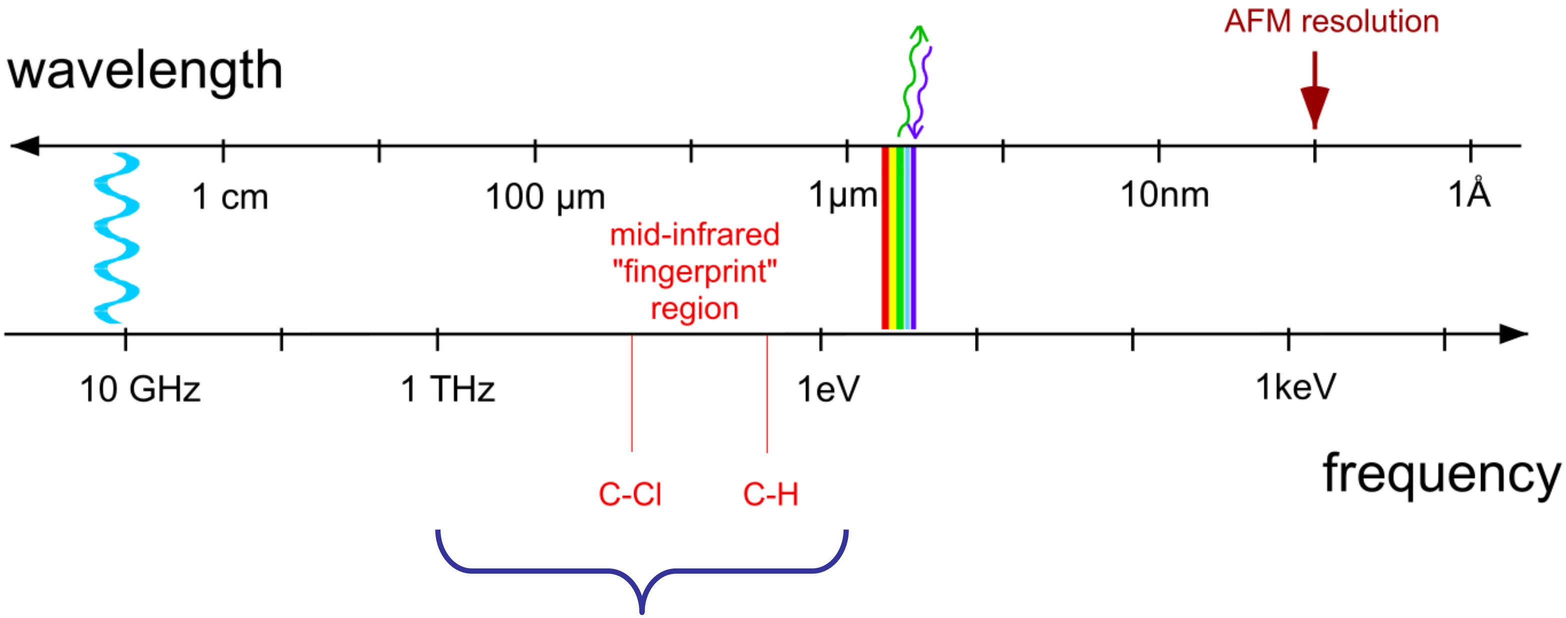
illustrated with materials characterization examples

Imaging anisotropic plasmon polaritons in AgTe by THz s-SNOM



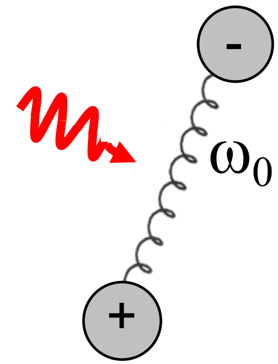


Infrared spectroscopy is a highly sensitive tool for material analysis



IR is highly sensitive to

- molecular vibrations → chemical composition
- crystal lattice vibrations → structural properties
- plasmons in doped semiconductors, graphene → electron properties
- …..

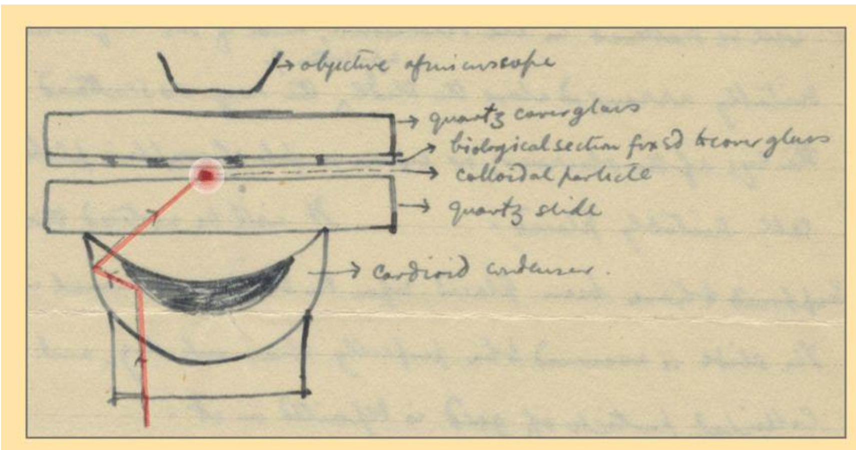


BUT: spatial resolution is diffraction limited

Edward Hutchinson Synge's idea

Idea for super-resolution imaging was conceived as early as in 1928

Original idea (1928)



L. Novotny, "From near-field optics to optical antennas," 6 (n.d.).

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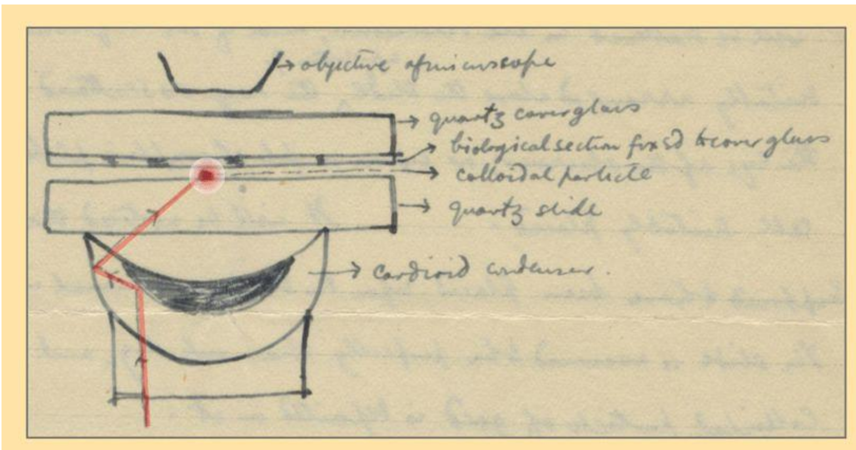

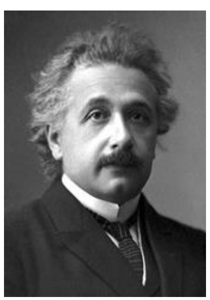

"As far as this goes, I agree. However, your method of implementation appears to be fundamentally unusable to me"
1928 – Albert Einstein

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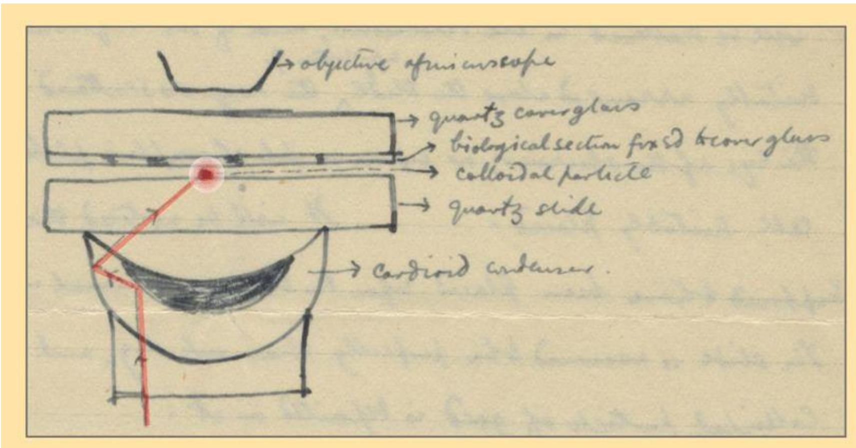
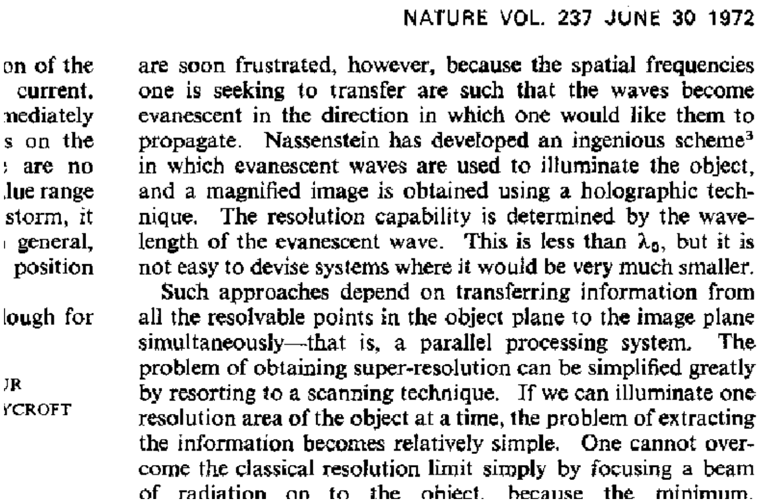


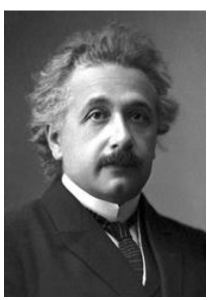
First super-resolution imaging (1972)


NATURE VOL. 237 JUNE 30 1972

are soon frustrated, however, because the spatial frequencies one is seeking to transfer are such that the waves become evanescent in the direction in which one would like them to propagate. Nassenstein has developed an ingenious scheme[3] in which evanescent waves are used to illuminate the object, and a magnified image is obtained using a holographic technique. The resolution capability is determined by the wavelength of the evanescent wave. This is less than λ_0, but it is not easy to devise systems where it would be very much smaller.

Such approaches depend on transferring information from all the resolvable points in the object plane to the image plane simultaneously—that is, a parallel processing system. The problem of obtaining super-resolution can be simplified greatly by resorting to a scanning technique. If we can illuminate one resolution area of the object at a time, the problem of extracting the information becomes relatively simple. One cannot overcome the classical resolution limit simply by focusing a beam of radiation on to the object, because the minimum

E.A. Ash, G. Nicholls, Nature 237, 510 (1972)



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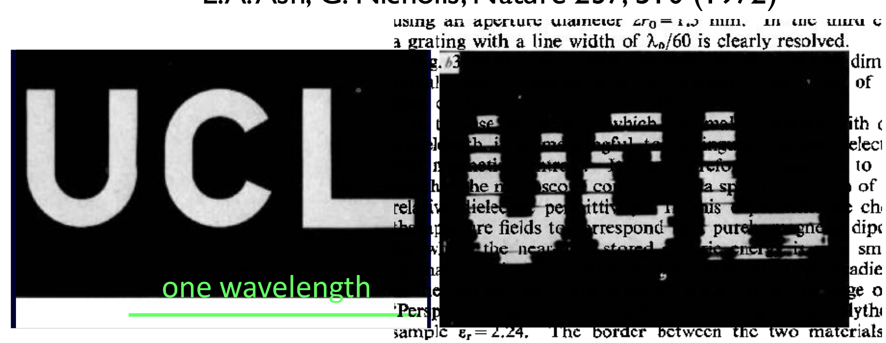


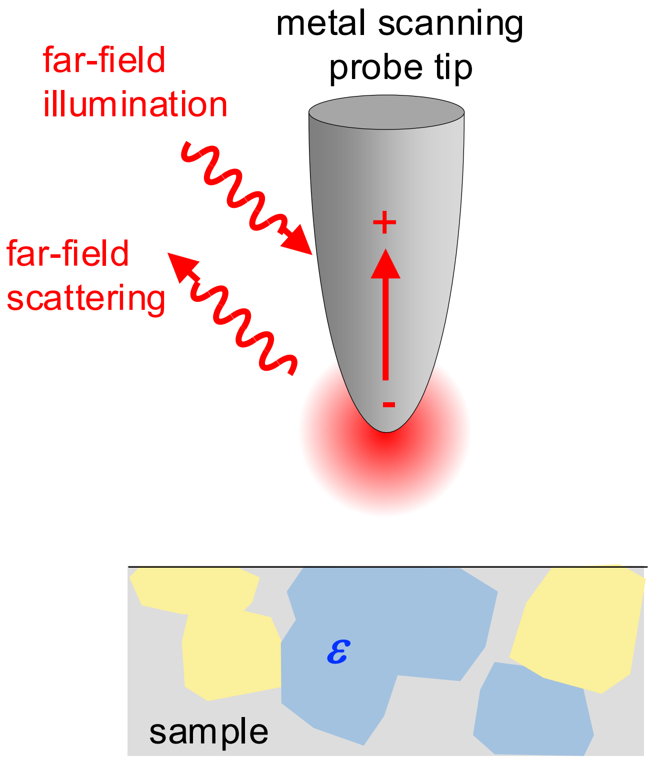
Resolution of 1/60 of the wavelength

L. Novotny, "From near-field optics to optical antennas," 6 (n.d.).

Modern s-SNOM

(scattering-type scanning near-field optical microscopy)

A sharp metal tip replaces the particle in Synge's idea



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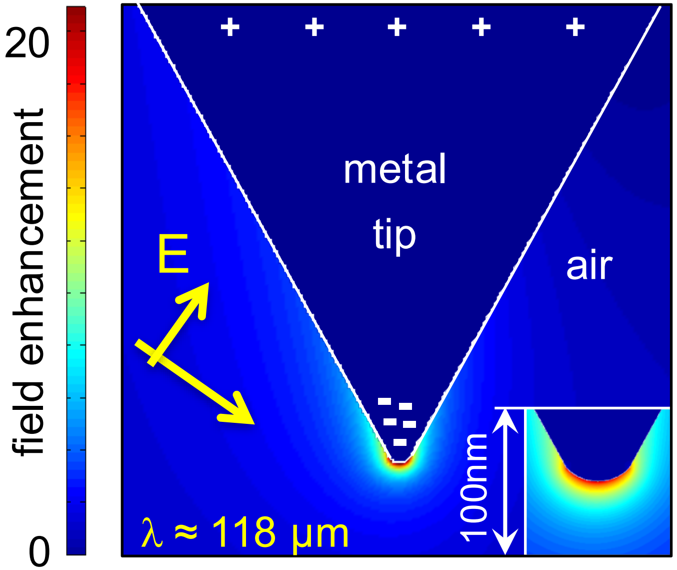
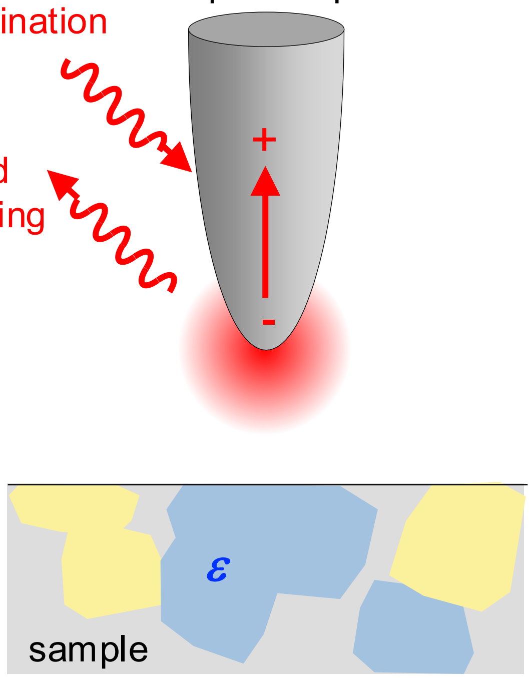
Strong optical near-fields at a metal tip with apex diameter << λ

(numerical calculation)



Optical field confinement on the scale of the tip apex d << λ



A.J. Huber, F. Keilmann, J. Wittborn, J. Aizpurua, R. Hillenbrand, *Nano Lett.* **8**, 3766 (2008)

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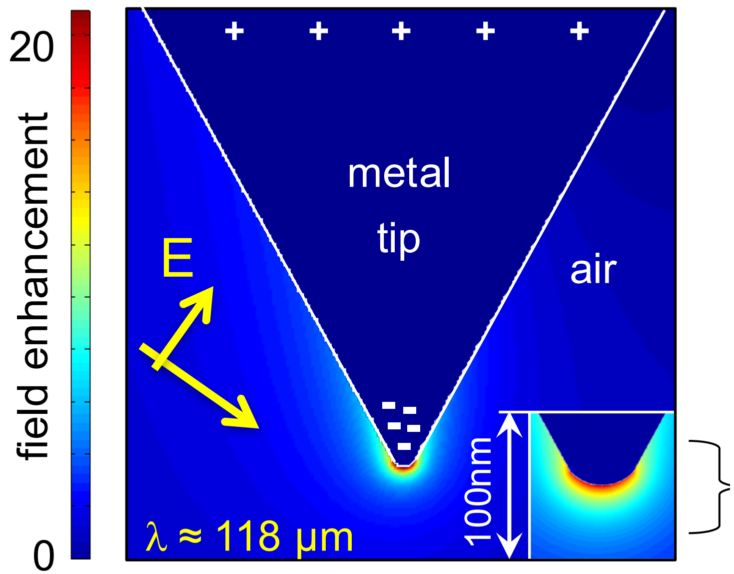

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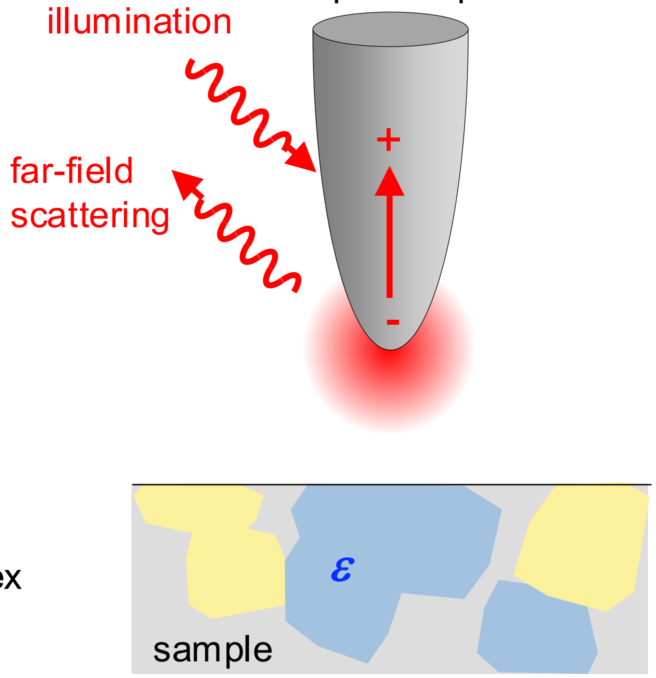
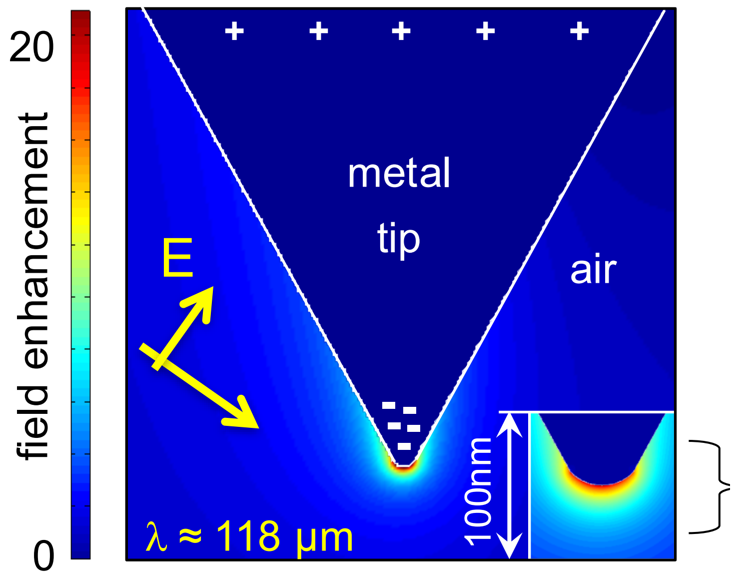


Near-field optical excitation of the sample yields

- **Elastic scattering (vis, IR, THz,…)**
- Inelastic scattering (e.g. Raman → TERS)
  [Novotny, Deckert, Hartschu, Kawata, Raschke]
- SHG, SFG,…

Reflection of near field leads to addition scattering form the tip depending on sample properties

Strong optical near-fields at a metal tip with apex diameter << λ
(numerical calculation)



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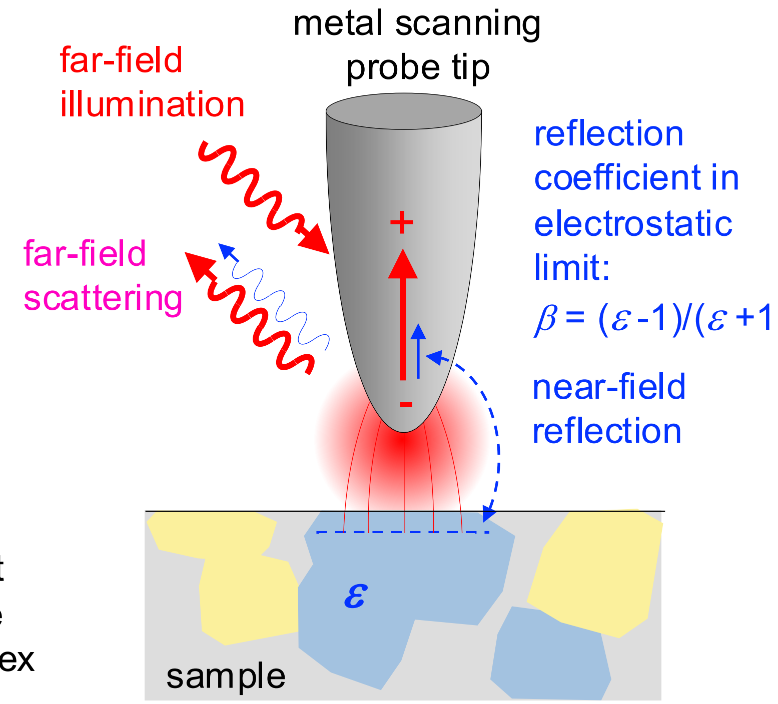

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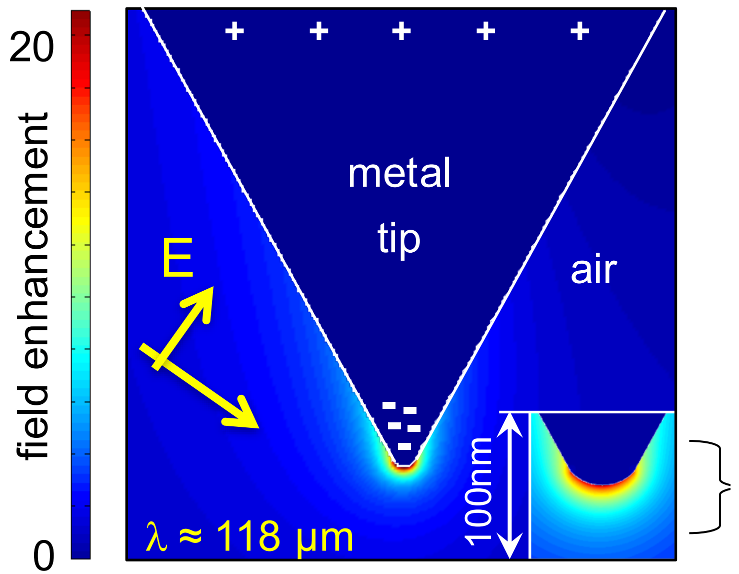

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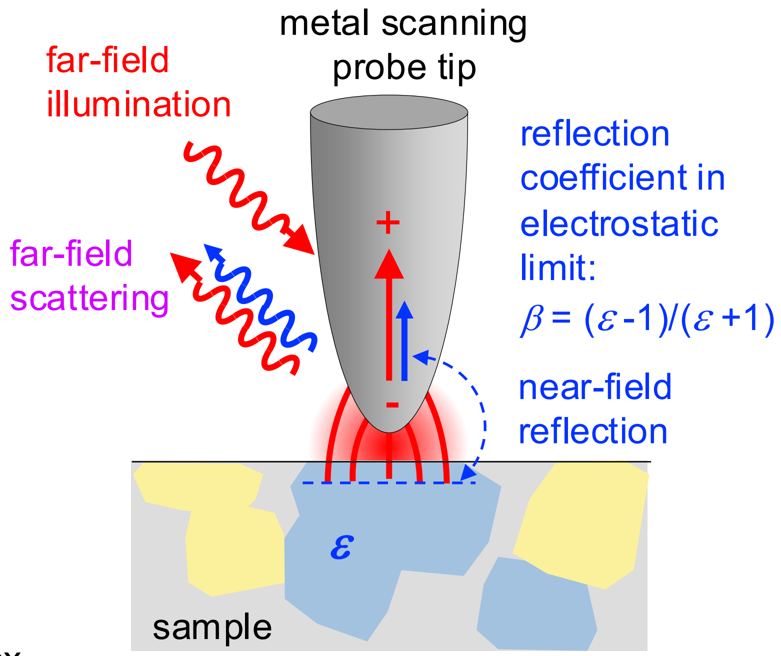

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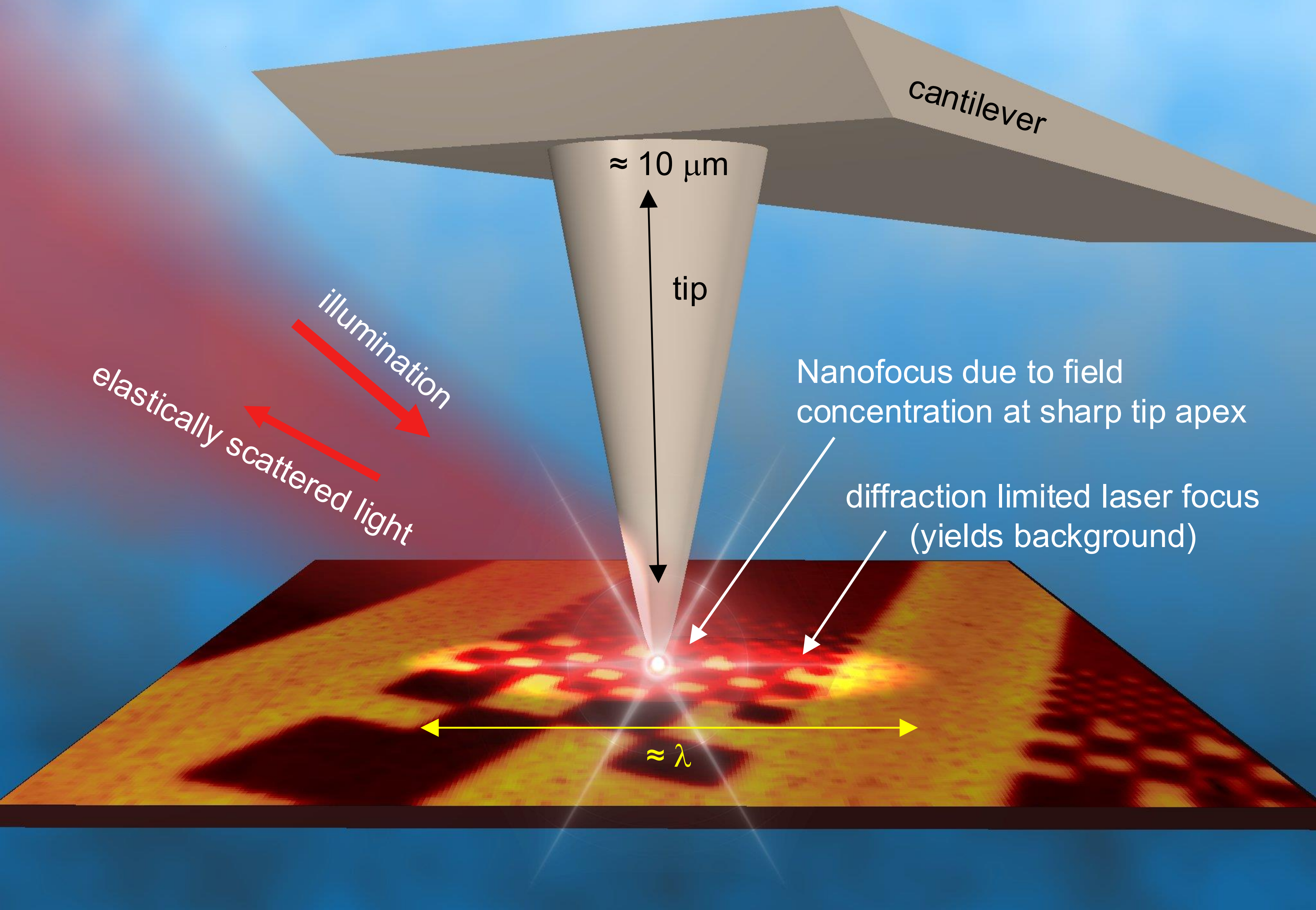
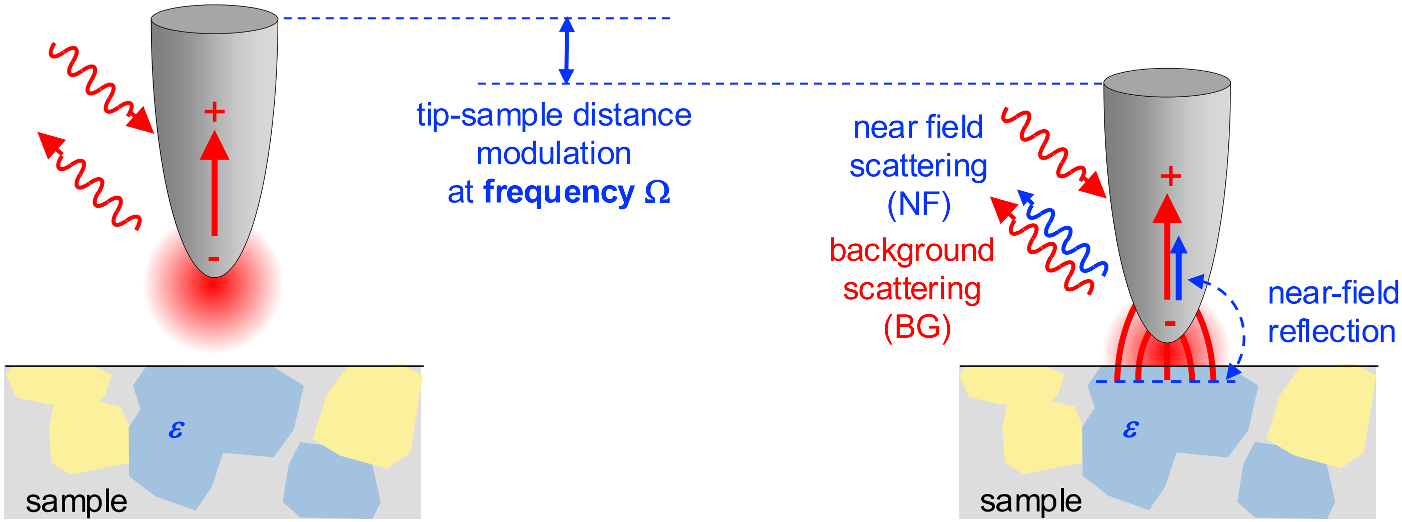
- SHG, SFG,…

Breaking the diffraction barrier by light scattering at a sharp tip



Modulation of tip-sample distance yields higher near-field signal harmonics



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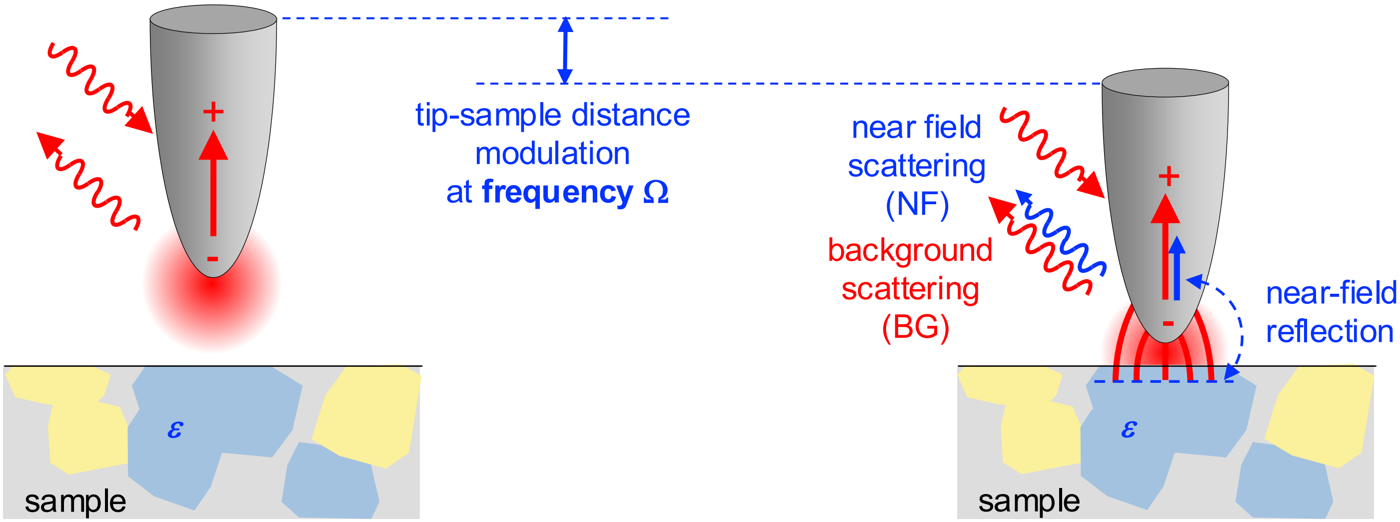
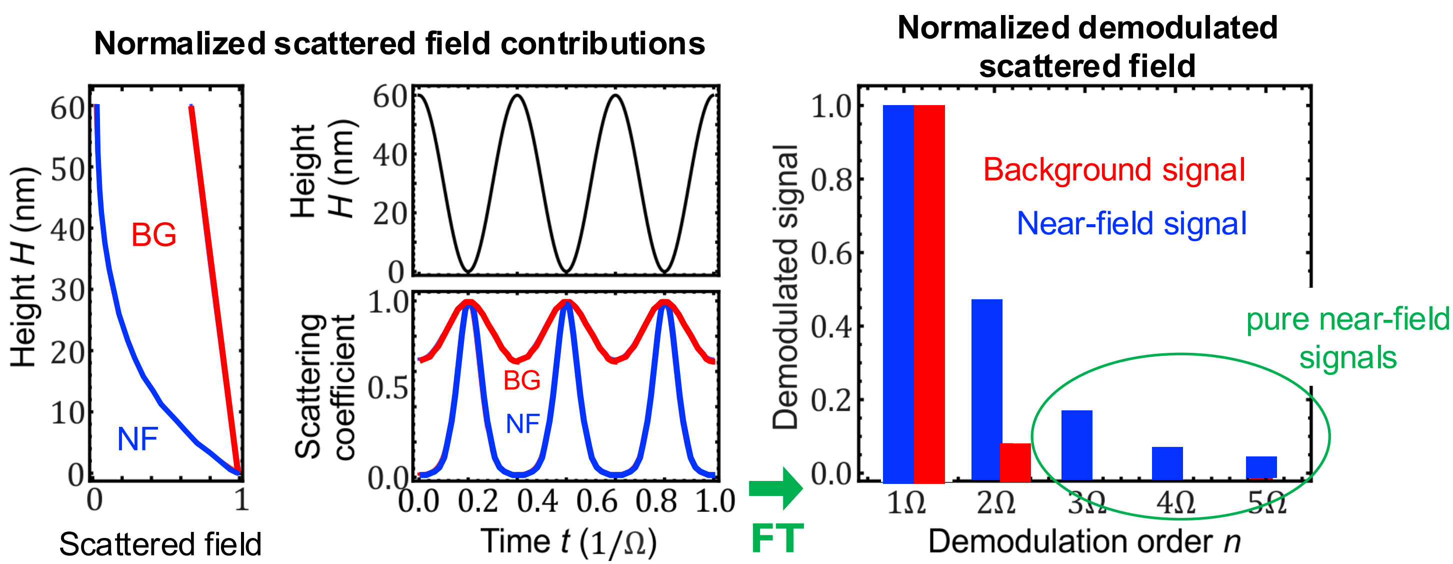
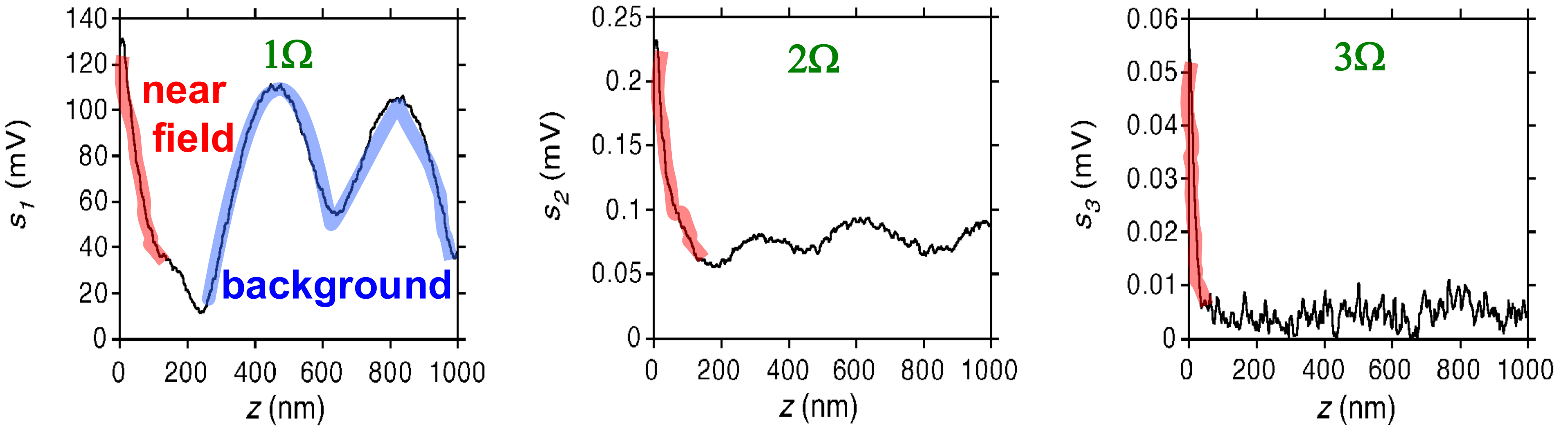




Modulation of tip-sample distance yields higher near-field signal harmonics

s_n = signal demodulated at tapping frequency $n\Omega$ λ = 633 nm



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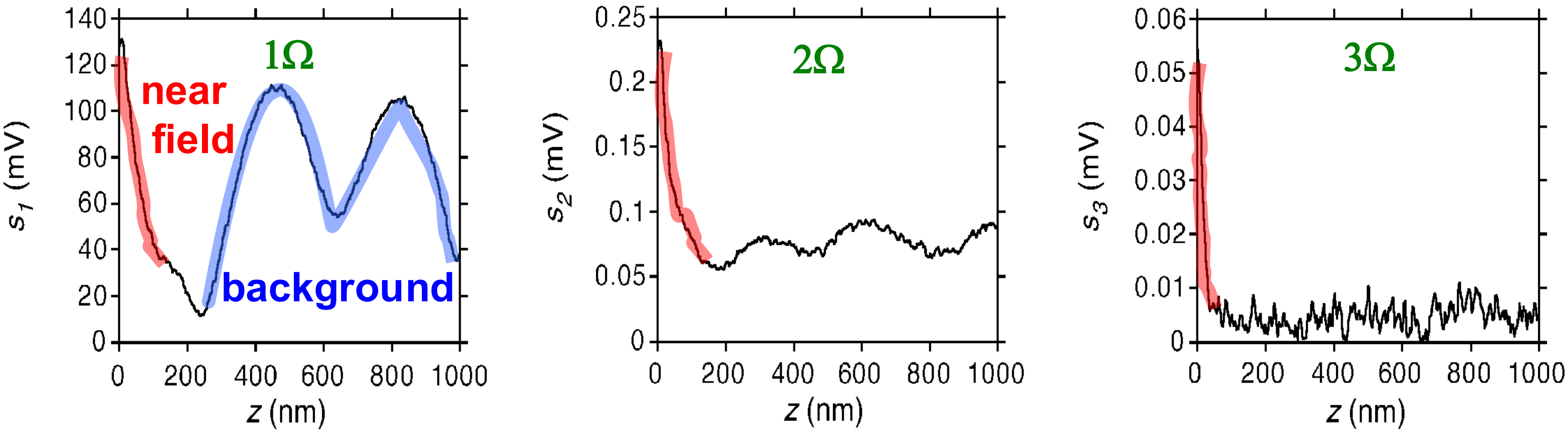
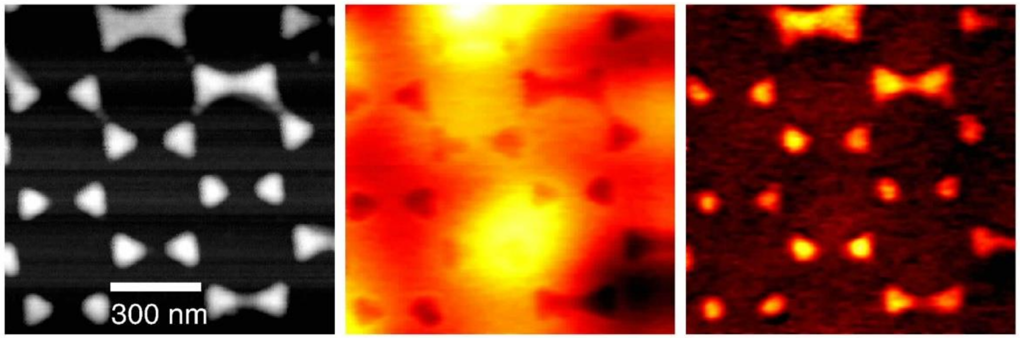
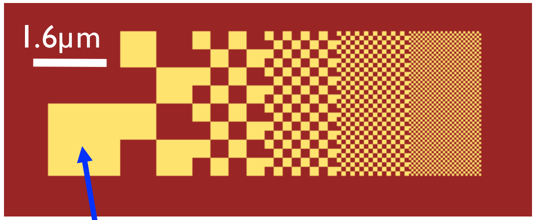


Au islands on Si surface



s-SNOM beats the diffraction limit by orders of magnitude

Test Pattern



highly
reflective material

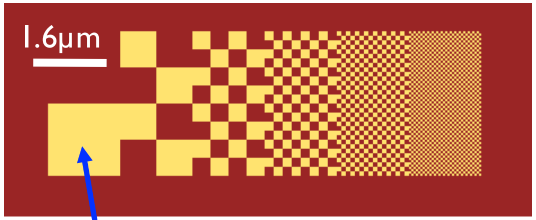
Reflection image
λ = 0.5 µm (visible)

Reflection image
λ = 10 µm (infrared)

Diffraction prevents to resolve the of smallest structures

s-SNOM beats the diffraction limit by orders of magnitude

Test Pattern



highly
reflective material

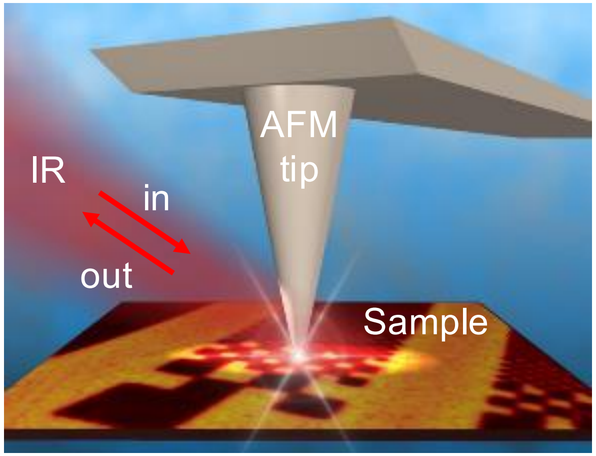
Reflection image
λ = 0.5 µm (visible)

Reflection image
λ = 10 µm (infrared)

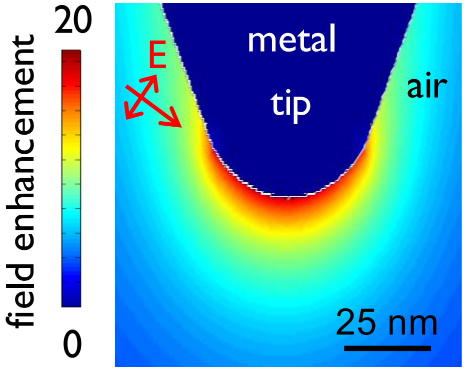
Diffraction prevents to resolve the of smallest structures

Near-field IR microscopy (s-SNOM or nano-FTIR) overcomes diffraction limit by orders of magnitude

Focused laser beam
illuminates AFM tip

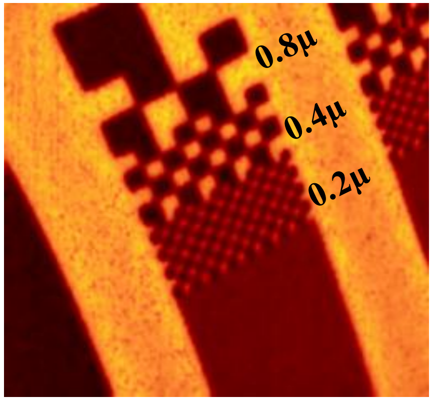


Tip creates nano-focus



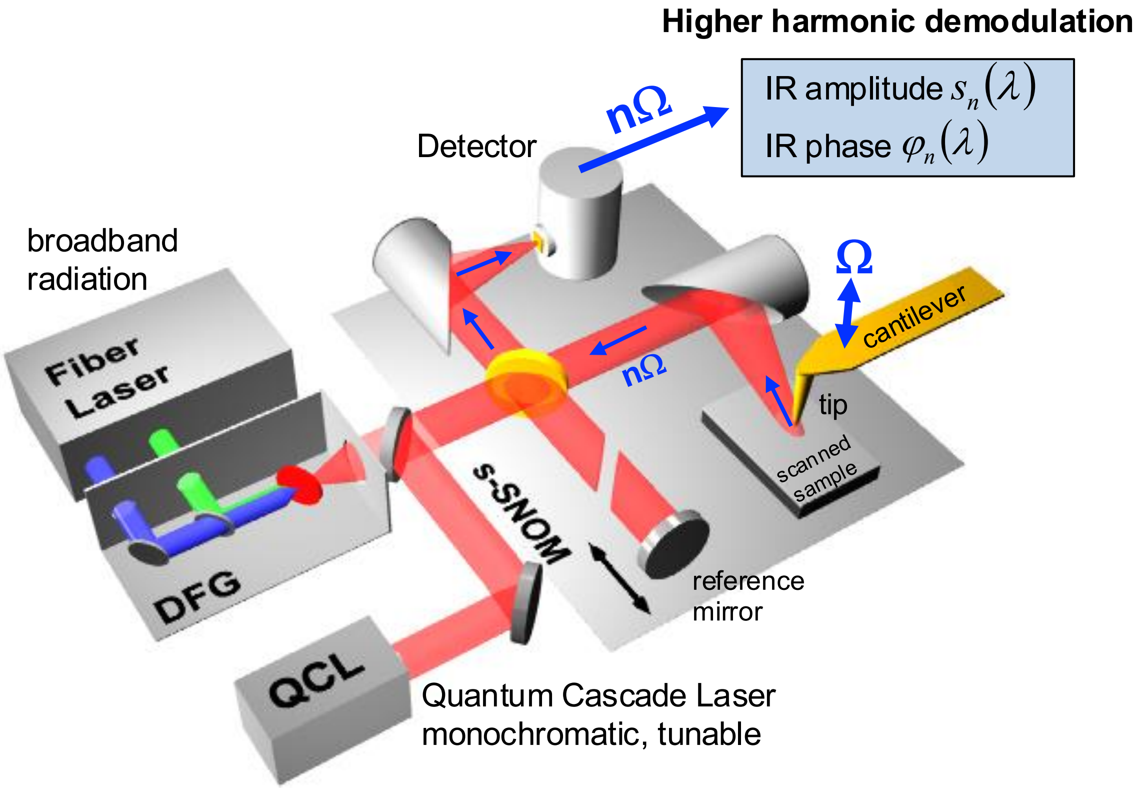
λ ≈ 10 µm

Recorded tip-scattered field yields
near-field image; λ = 10 µm

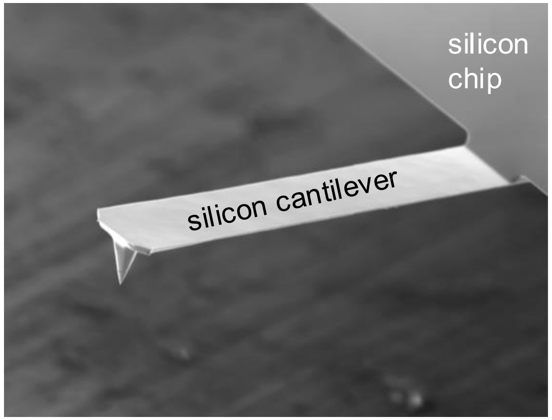


Nature Materials **3**, 606 (2004)

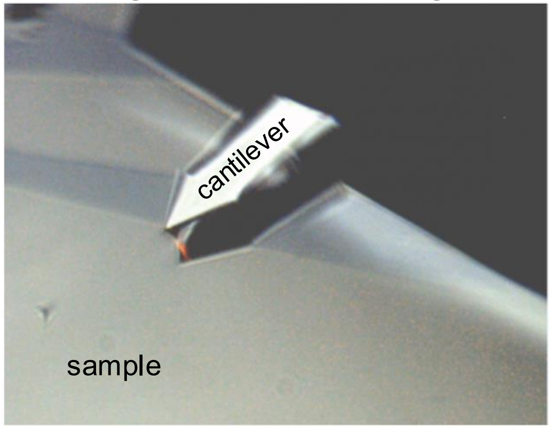
Typical setup of interferometric s-SNOM/nano-FTIR



Electron microscope image



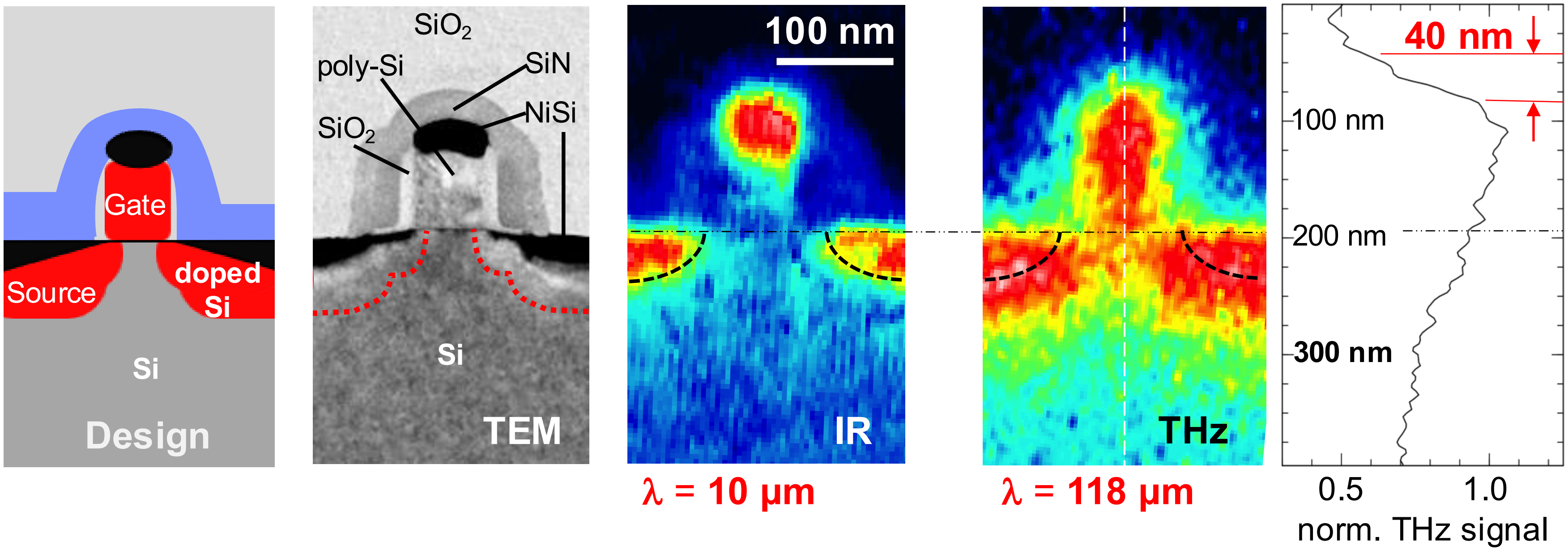
Light microscope image



- Accessible wavelength range 0.5 – 500 µm
- Higher harmonic demodulation + interferometric detection scheme yields background-free, spectroscopic near-field signals

Pseudoheterodyne detection: N. Ocelic, A. Huber, R. Hillenbrand, *Appl. Phys. Lett.* **89**, 101124 (2006)
nano-FTIR spectroscopy: F. Huth, et al. *Nano Lett.* **12**, 3973 (2012)

IR/THz s-SNOM can map materials and free-carriers with nanoscale resolution



λ = 10 µm

λ = 118 µm

⇒ substructure of single 65 nm-transistor can be characterized with IR-THz s-SNOM

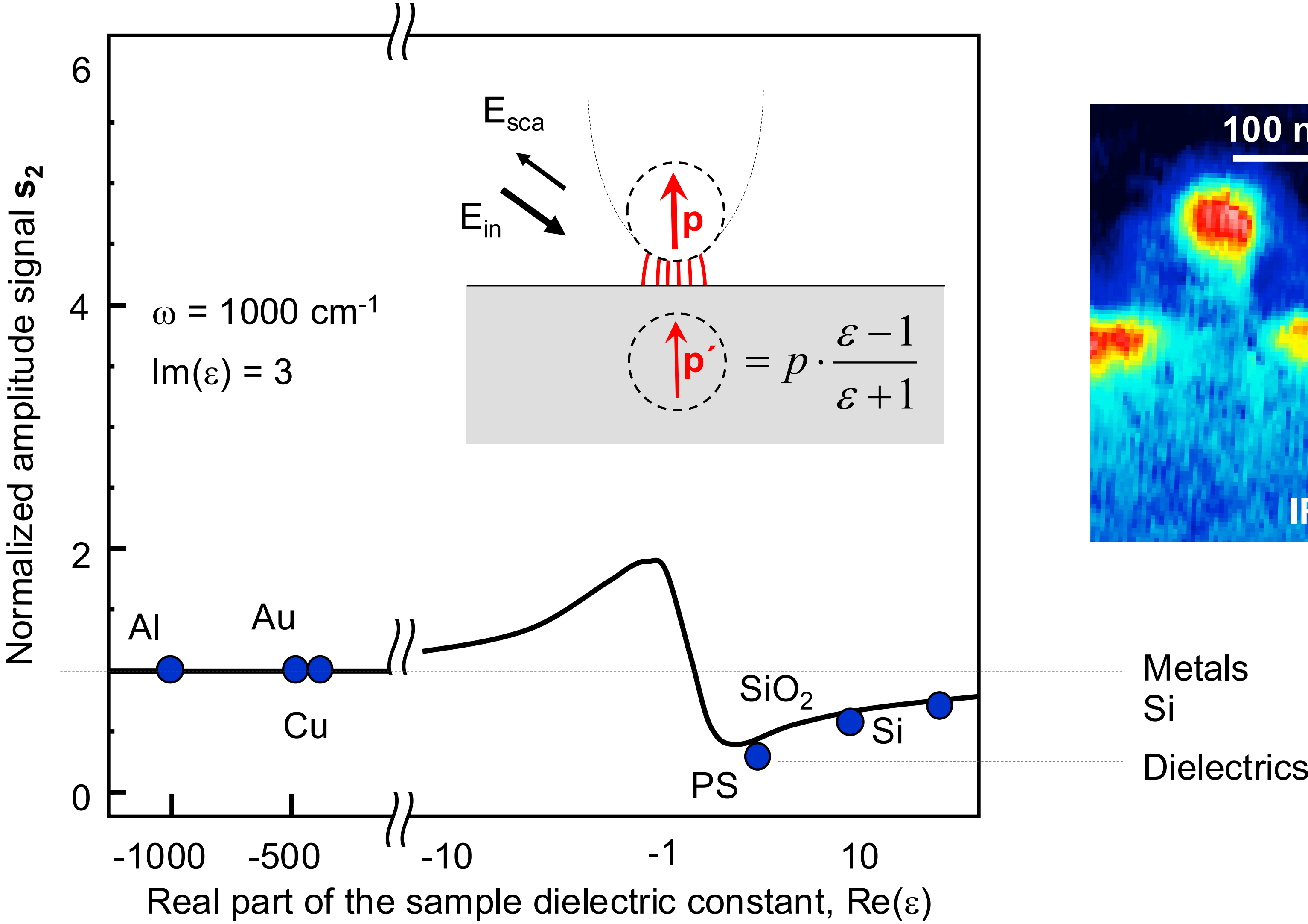
⇨ s-SNOM offers nanoscale spatial resolution at IR and THz frequencies

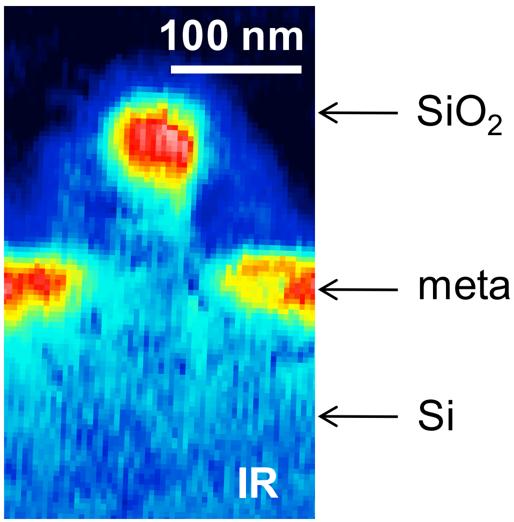
⇨ We already achieve **40 nm** resolution at **118 µm (= λ/3000)**

⇨ Enables quantitative and nanoscale resolved mapping of free carriers

A. Huber, F. Keilmann, J. Wittborn, R. J. Aizpurua, R. Hillenbrand, *Nano Lett.* **8**, 3766 (2008)

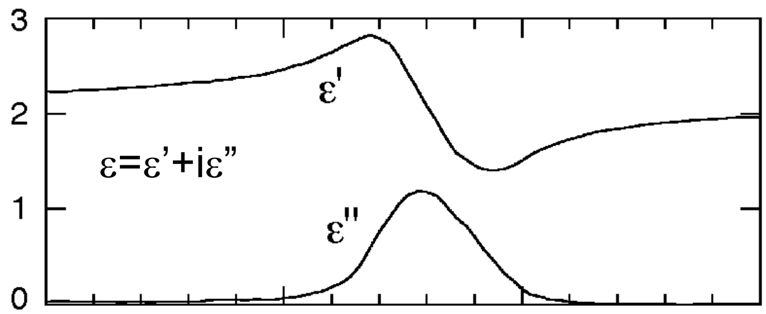
Dipole model describes material contrast based on tip-sample near-field interaction



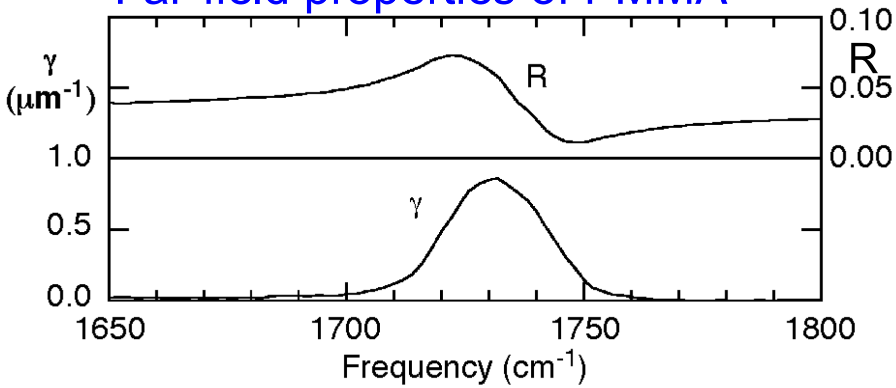


Far-field vs. s-SNOM spectra

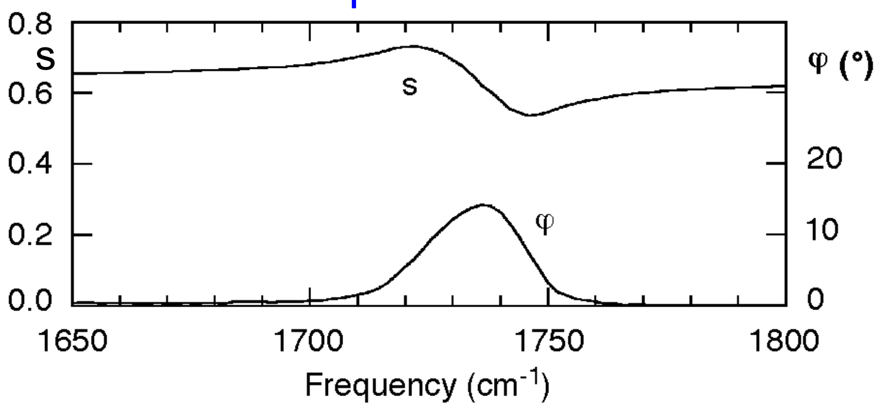
Dielectric function of PMMA



Far-field properties of PMMA



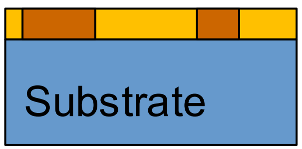
s-SNOM response of PMMA

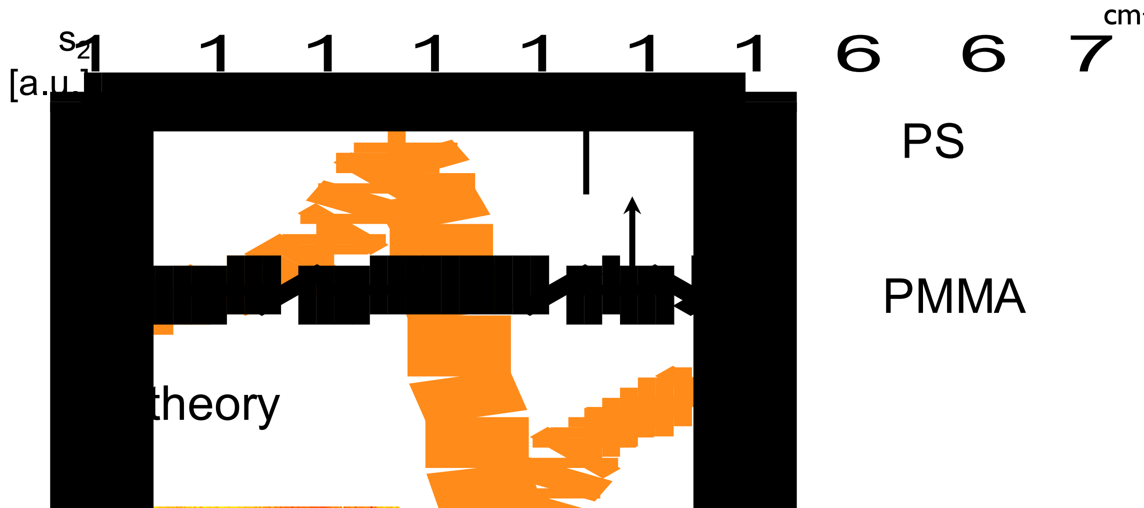


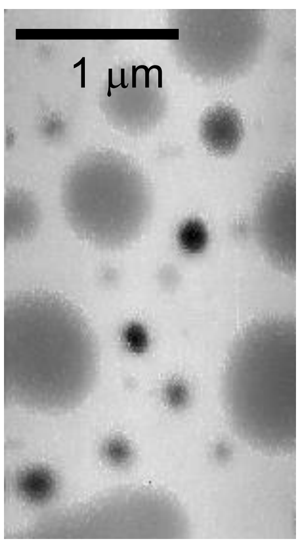
→ Near-field amplitude behaves much like far-field reflectivity
Near-field phase behaves much like far-field absorption

IR s-SNOM allows for nanoscale chemical mapping of polymer blends

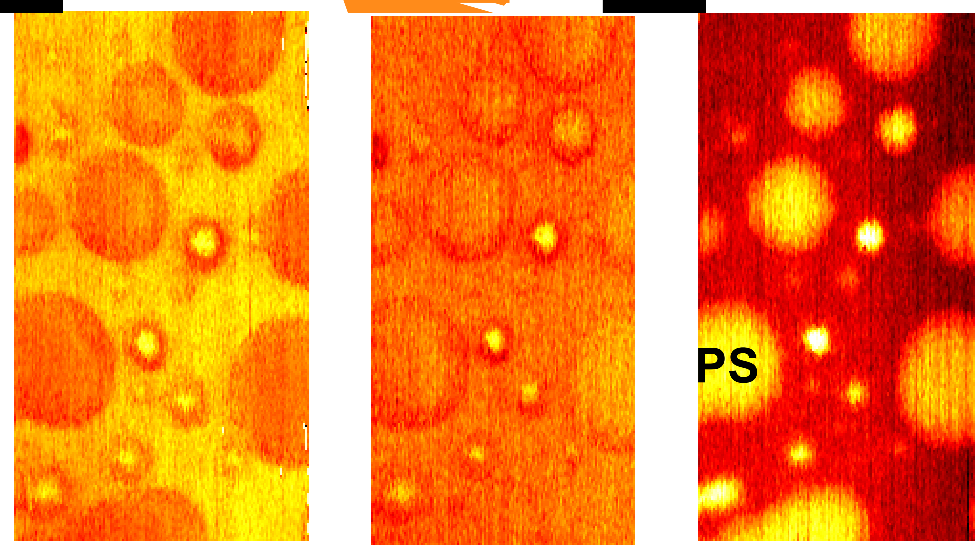
70 nm thick film of PS/PMMA polymer blend on Si suface







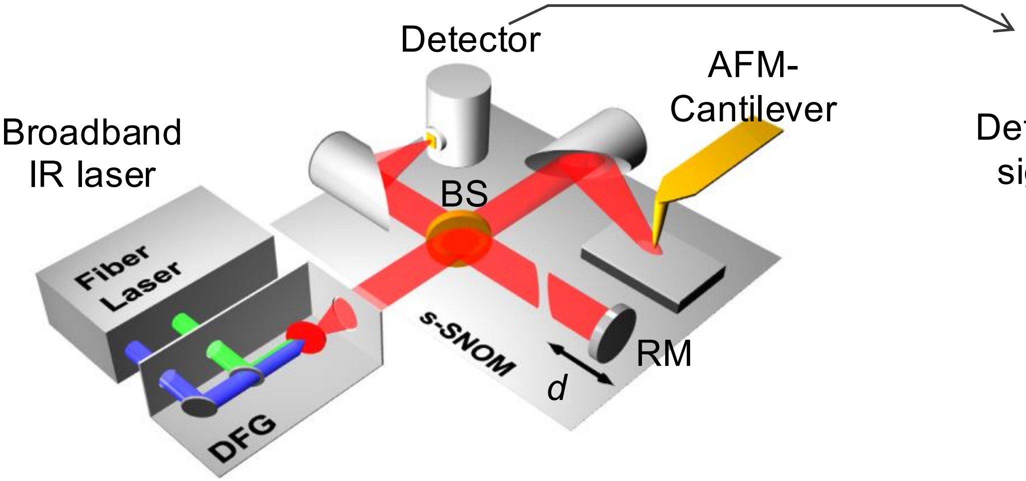
topography

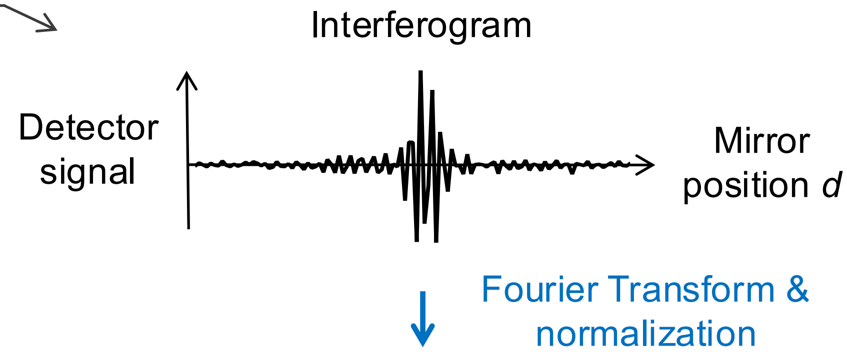


IR:1725 cm^{-1} 1732 cm^{-1} 1750 cm^{-1}

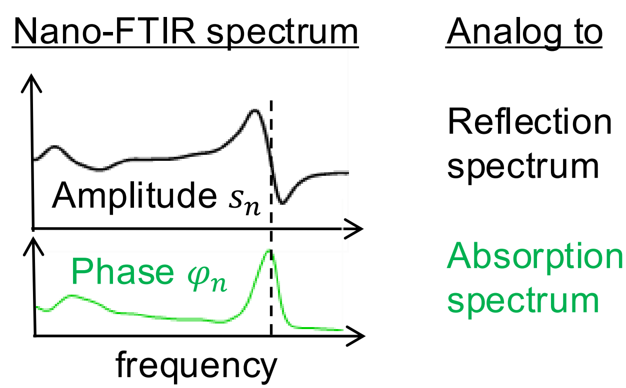
T. Taubner, R. Hillenbrand, F. Keilmann, *Appl. Phys. Lett.* **85**, 5064 (2004)

Nanoidentification by infrared s-SNOM and Nano-FTIR

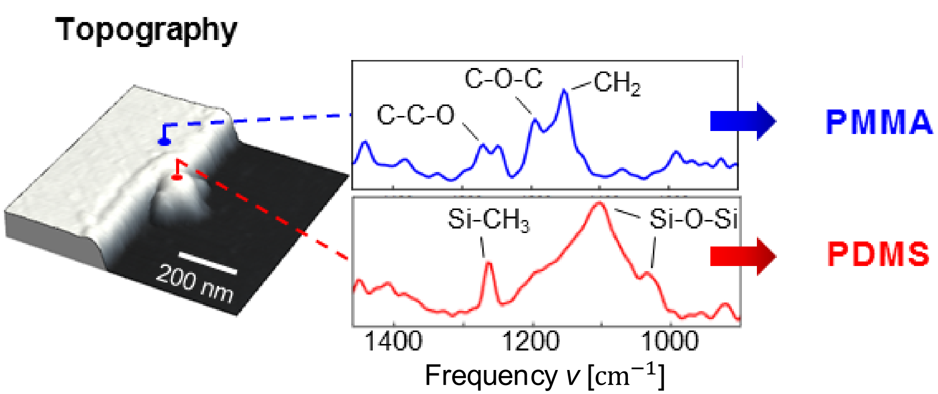




s-SNOM is based on **atomic force microscopy** and **interferometric detection of the tip-scattered light.**



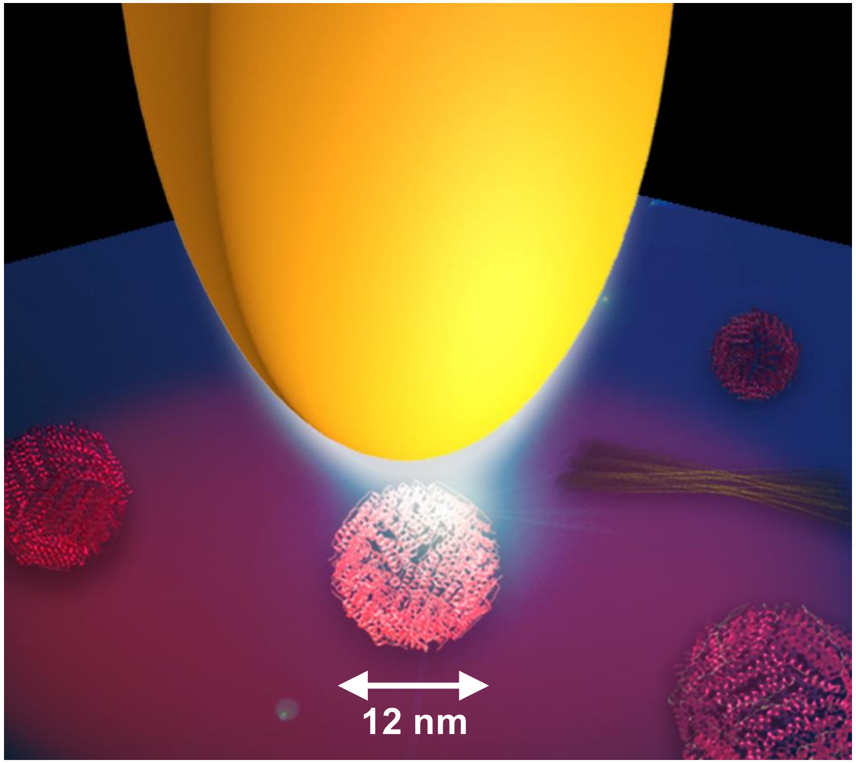
Nano-FTIR spectroscopy allows for chemical nanoidentification

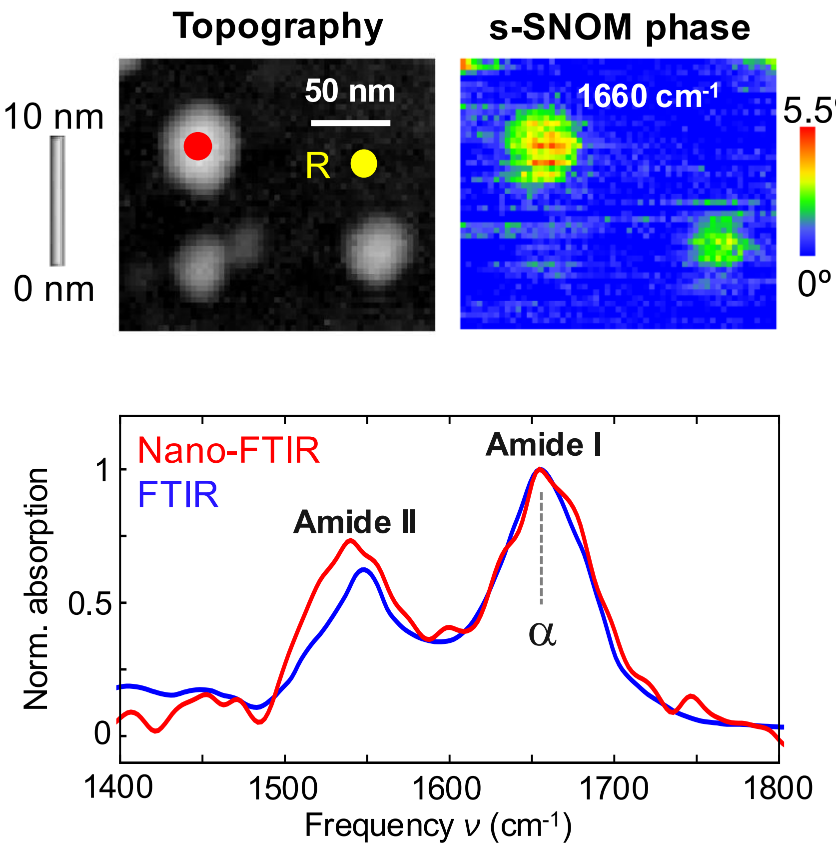


F. Huth, *Nano Lett.*, **12**, 3973 (2012)

Example of s-SNOM imaging and nano-FTIR spectroscopy

We can measure single protein complexes





Ferritin characteristics:

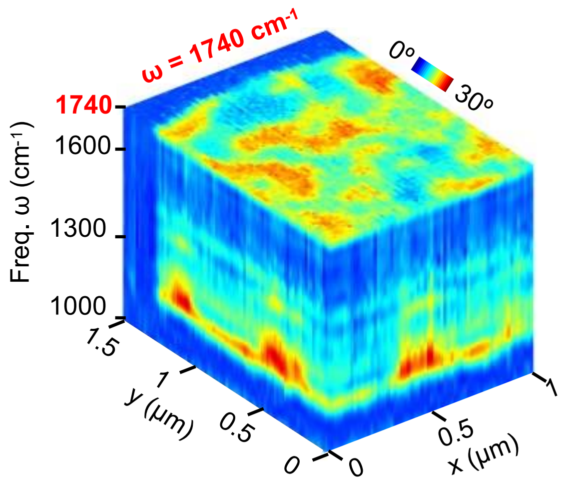
- 24 proteins/subunits
- 5000 C=O bonds
- 1 attogram mass

However: Signal-to-noise-ratio goes down
(23 min / spectrum, limited by signal-to-noise level)

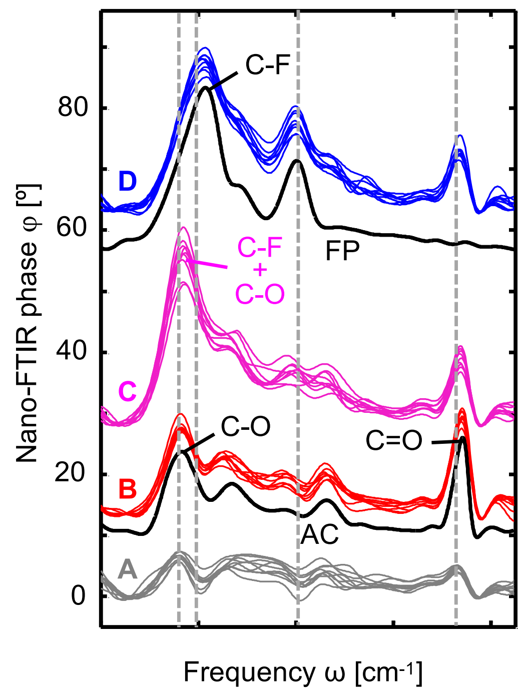
I. Amenabar et al, Nature Comm. **4**, 2890 (2013)

Hyperspectral imaging and multivariate analysis yields maps of chemical composition and interaction

Hyperspectral data cube of three-component polymer blend

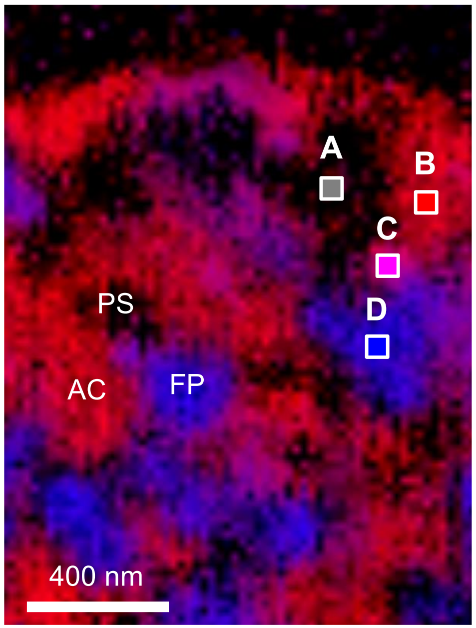


Analysis



fluorine copolymer (FP)
acrylic copolymer (AC)
polystyrene (PS)

Compositional map



Purple spectra cannot be composed of the components´spectra

Areas of chemical interaction

I. Amenabar et al.,
Nat. Commun. **8**, 14402 (2017)

Nano-FTIR application examples

Nano-FTIR is ready for applications … … and many more to come!

… in organic electronics

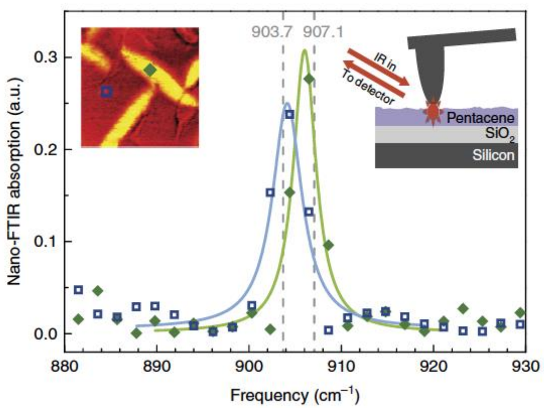
nature COMMUNICATIONS

ARTICLE

Received 28 Feb 2014 | Accepted 13 May 2014 | Published 11 Jun 2014 DOI: 10.1038/ncomms5101 OPEN

Sub-micron phase coexistence in small-molecule organic thin films revealed by infrared nano-imaging

Christian Westermeier[1,2], Adrian Cernescu[1,3], Sergiu Amarie[3], Clemens Liewald[1], Fritz Keilmann[1] & Bert Nickel[1,2]



… in bio-chemistry

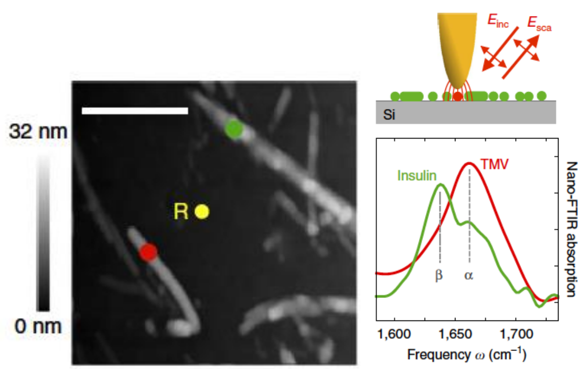
nature COMMUNICATIONS

ARTICLE

Received 12 Jul 2013 | Accepted 7 Nov 2013 | Published 4 Dec 2013 DOI: 10.1038/ncomms3890 OPEN

Structural analysis and mapping of individual protein complexes by infrared nanospectroscopy

Iban Amenabar[1], Simon Poly[1], Wiwat Nuansing[1], Elmar H. Hubrich[2], Alexander A. Govyadinov[1], Florian Huth[1,3], Roman Krutokhvostov[1], Lianbing Zhang[1], Mato Knez[1,4], Joachim Heberle[2], Alexander M. Bittner[1,4] & Rainer Hillenbrand[1,4]



… in astro-geo-physics

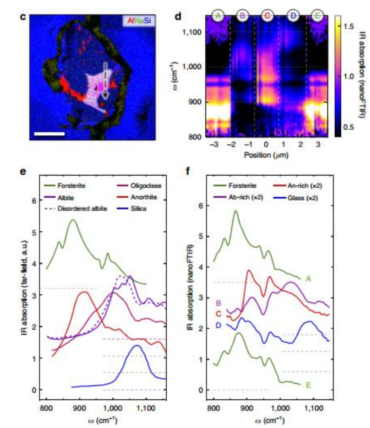
nature COMMUNICATIONS

ARTICLE

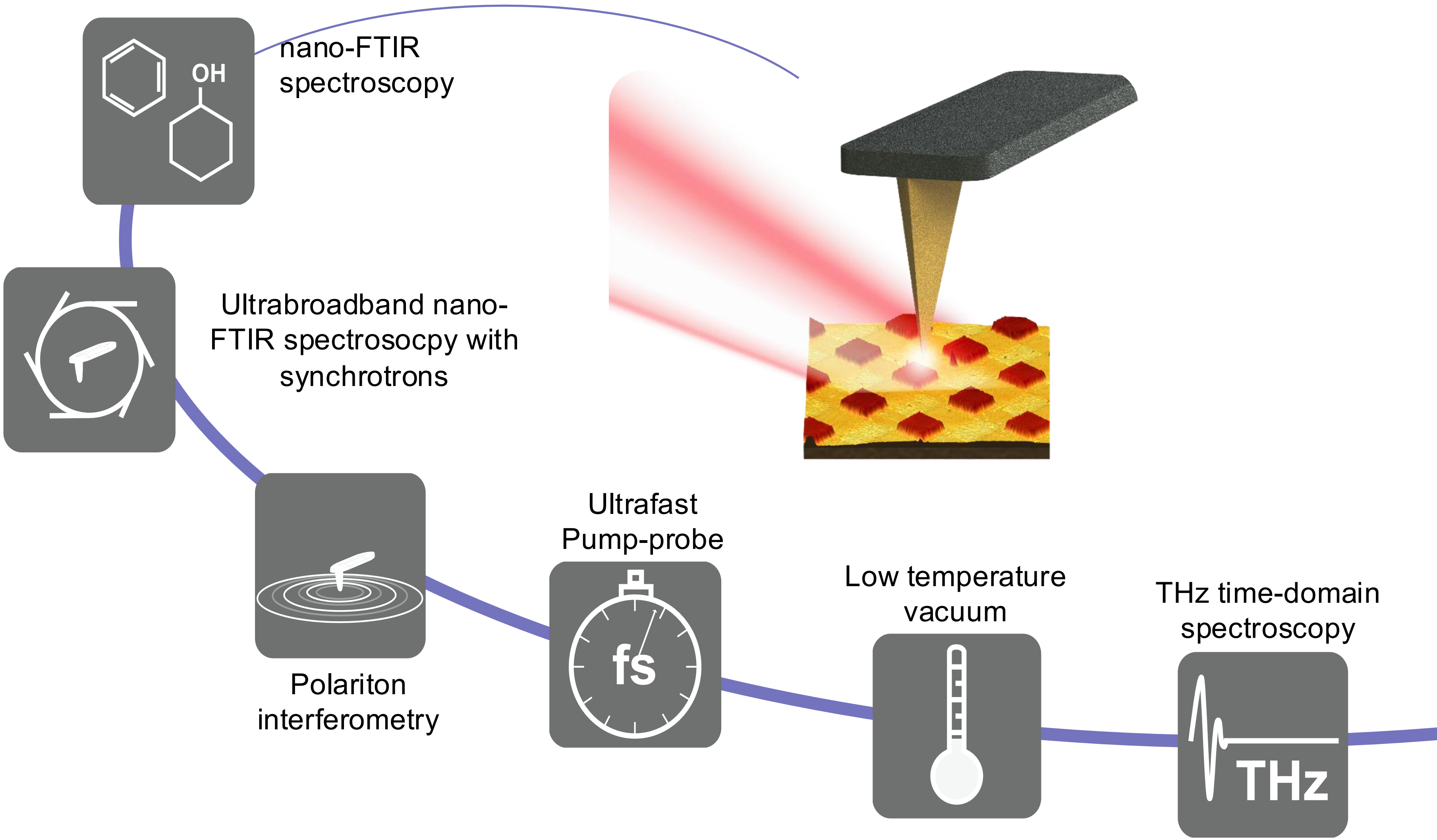
Received 3 Apr 2014 | Accepted 2 Oct 2014 | Published 9 Dec 2014 DOI: 10.1038/ncomms6445

Nanoscale infrared spectroscopy as a non-destructive probe of extraterrestrial samples

Gerardo Dominguez[1,2,*], A.S. Mcleod[3,*], Zack Gainsforth[4], P. Kelly[3], Hans A. Bechtel[5], Fritz Keilmann[6], Andrew Westphal[4], Mark Thiemens[2] & D.N. Basov[3]

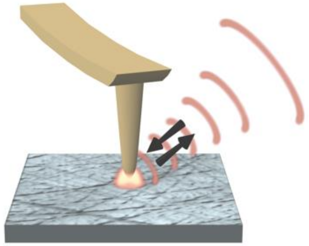


Emerging trends

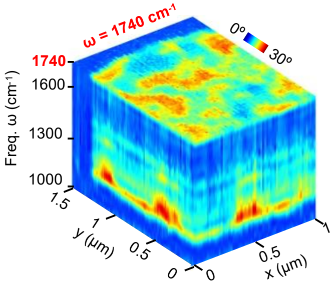


Outline

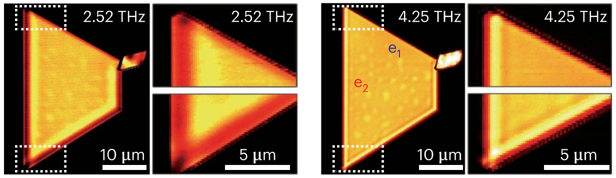
s-SNOM and nano-FTIR techniques

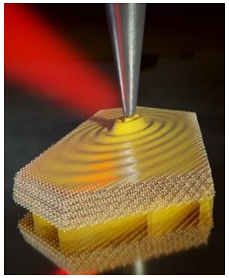


illustrated with materials characterization examples

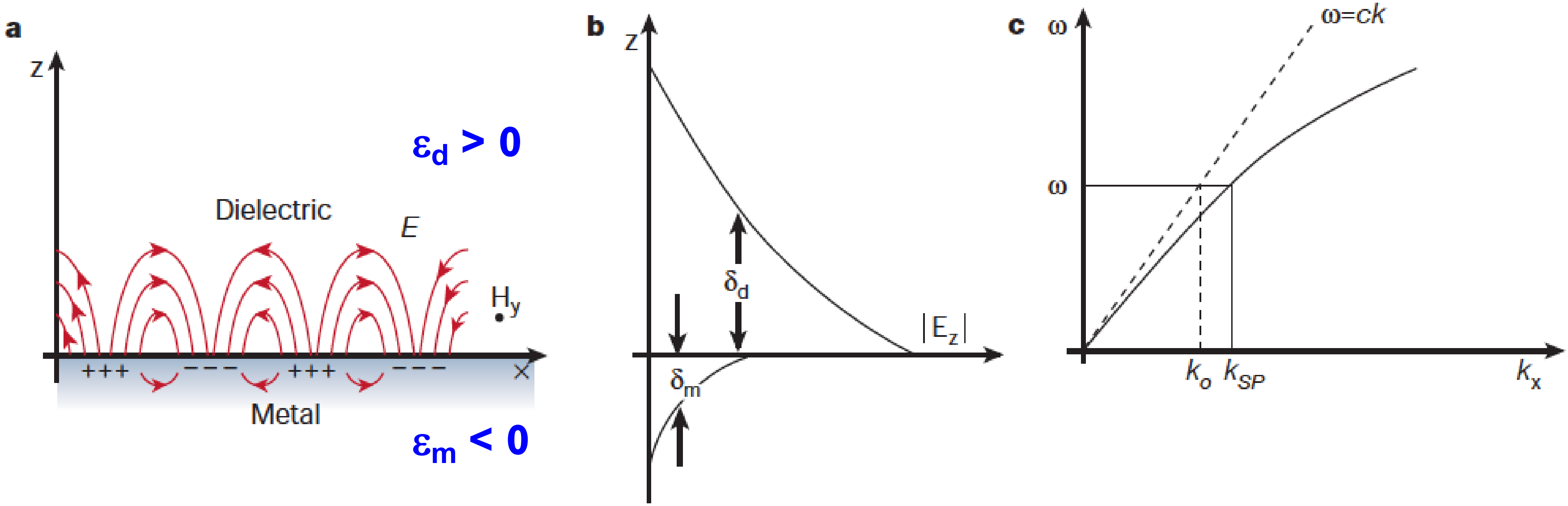


Imaging anisotropic plasmon polaritons in AgTe by Thz s-SNOM





Propagating surface plasmon polaritons (SPPs) at the metal/dielectric interface



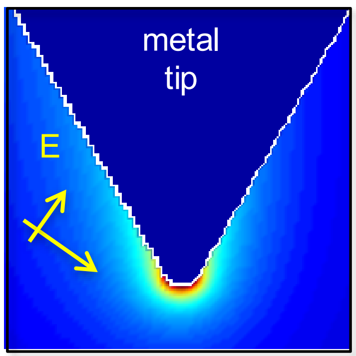
TM surface wave of combined electromagnetic and surface charge character

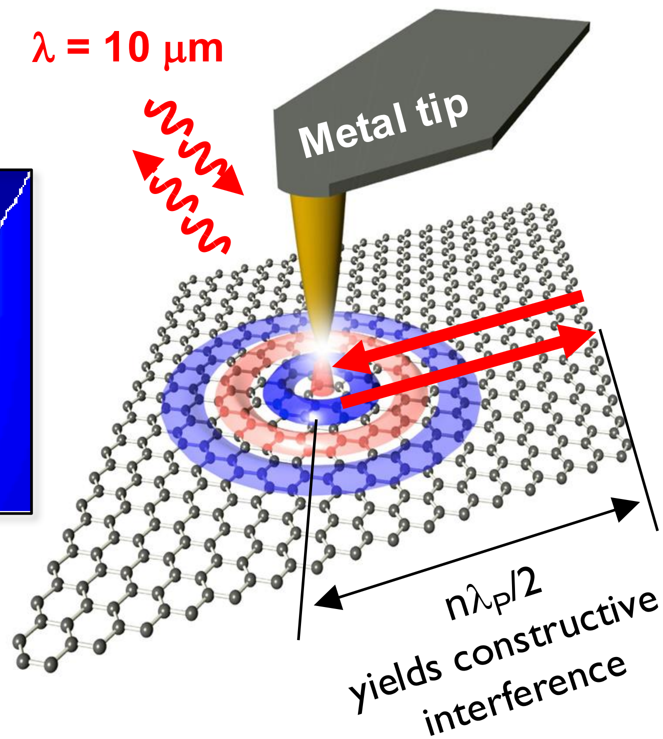
Field perpendicular to surface decays exponentially (evanescent field)

Dispersion curve shows that SPP has momentum greater than free space photon of the same frequency

Barnes, Dereux, Ebbesen, Nature **424,** 824 (2003)

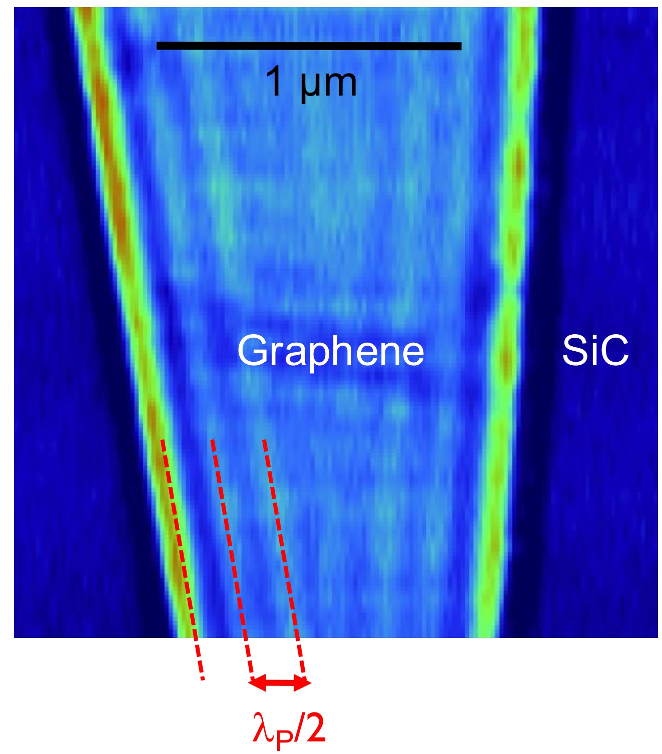
Tip-enhanced near-field mapping of mid-IR plasmons in graphene (near-field plasmon interferometry)





IR s-SNOM image

ω = 1087 cm^{-1}, λ = 9200 nm



$\lambda_P \approx 230$ nm $= \lambda/40$

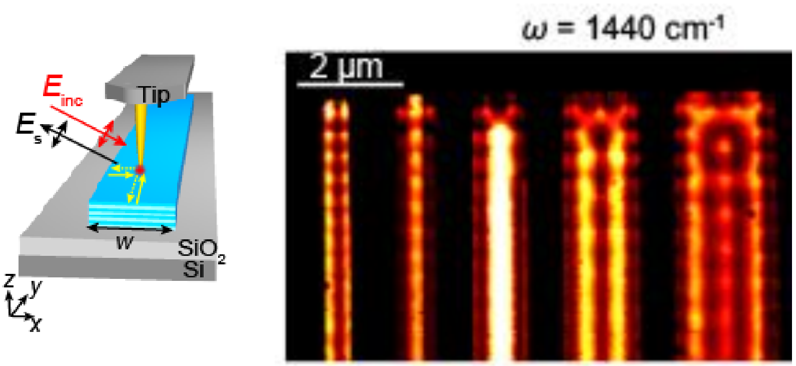
The plasmon wavelength on graphene is dramatically shorter than the free-space wavelength.

Chen et al., *Nature* **487**, 77 (2012)
Fei et al., *Nature* **487**,82 (2012)

PPs are an interesting platform for infrared nanophotonics

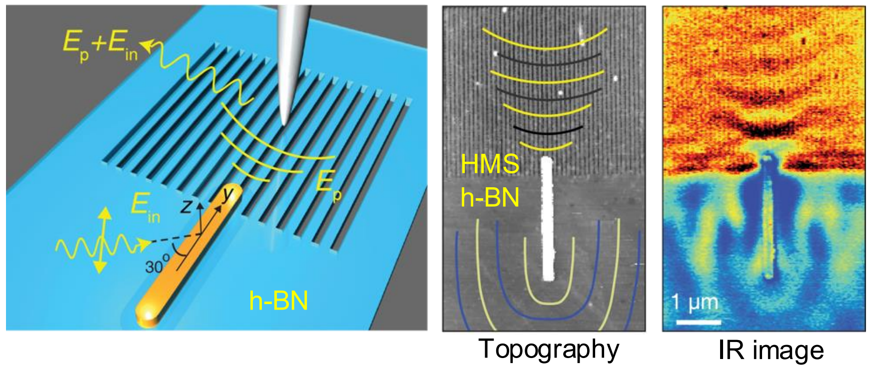
Some examples from our studies

Nanoscale guiding of mid-infrared light



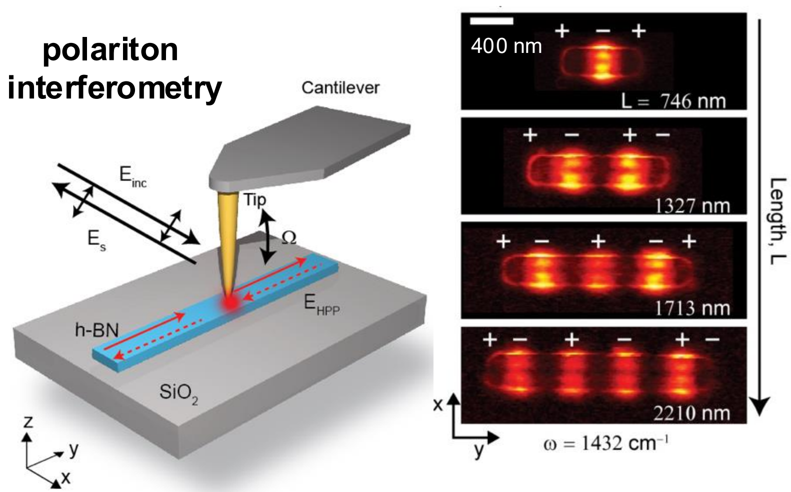
I. Dolado, et al. *Adv. Mater.* 1906530 (2020)

Anomalous wavefronts



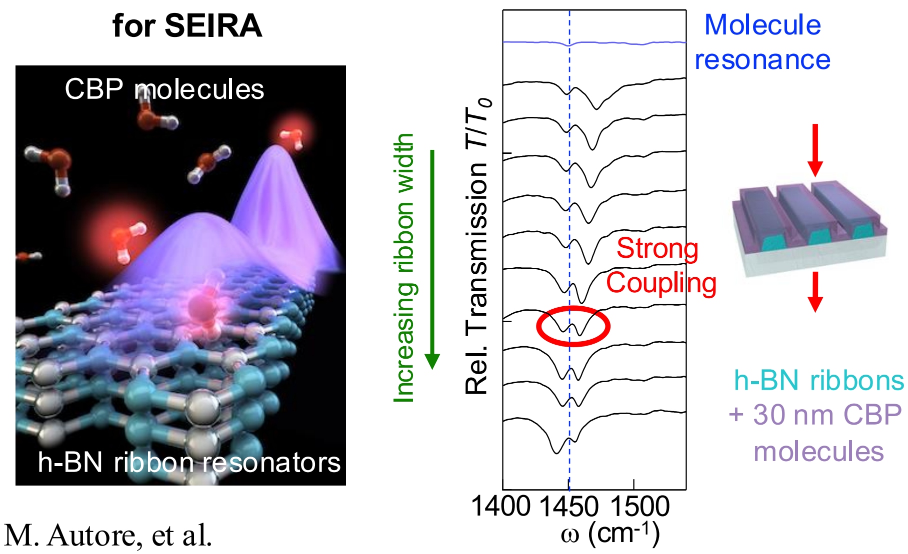
P. Li, I. Dolado, et al., *Science* **359**, 892 (2018)

PP resonators



F.J. Alfaro-Mozaz et al., *Nat. Comm.* **8**, 15624 (2017)

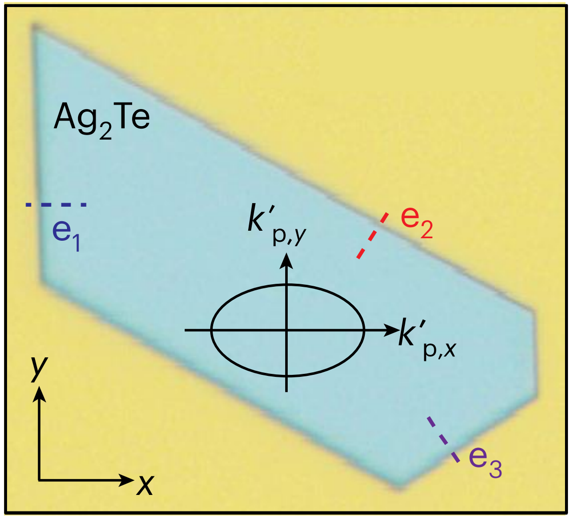
for SEIRA



M. Autore, et al.
Light Sci. Appl. **7**, 17172 (2018); *Adv. Optical Mater.* 9, 2001958 (2021)

Ag_2Te : a biaxial narrow bandgap semiconductor

Ag_2Te



Optical microscope image

Single crystal platets grown by chemical vapour deposition

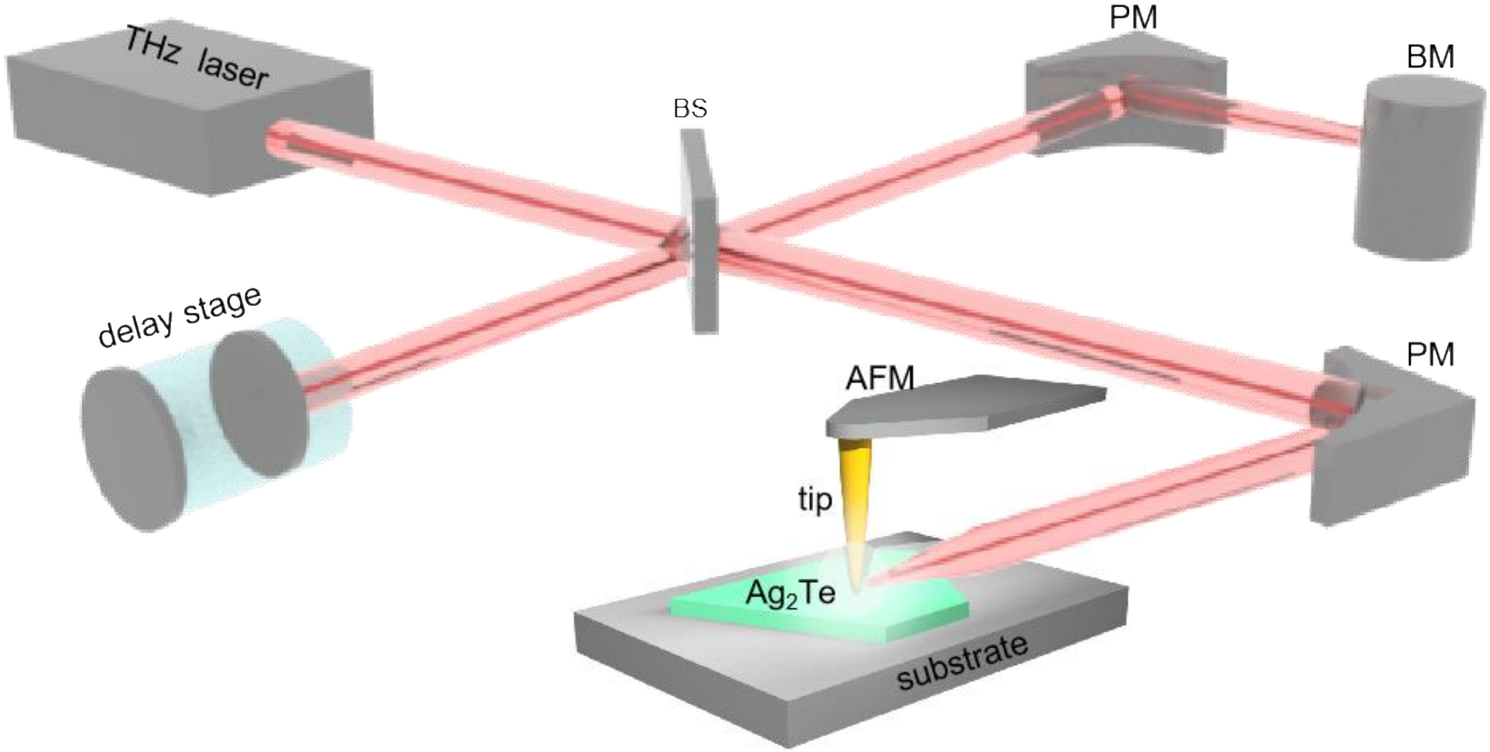
Narrow-bandgap (0.06eV)
electron concentrations 10^{18} cm^{-3} at T_{room}

In-plane anisotropy: $\varepsilon_x \neq \varepsilon_y$

THz plasmon

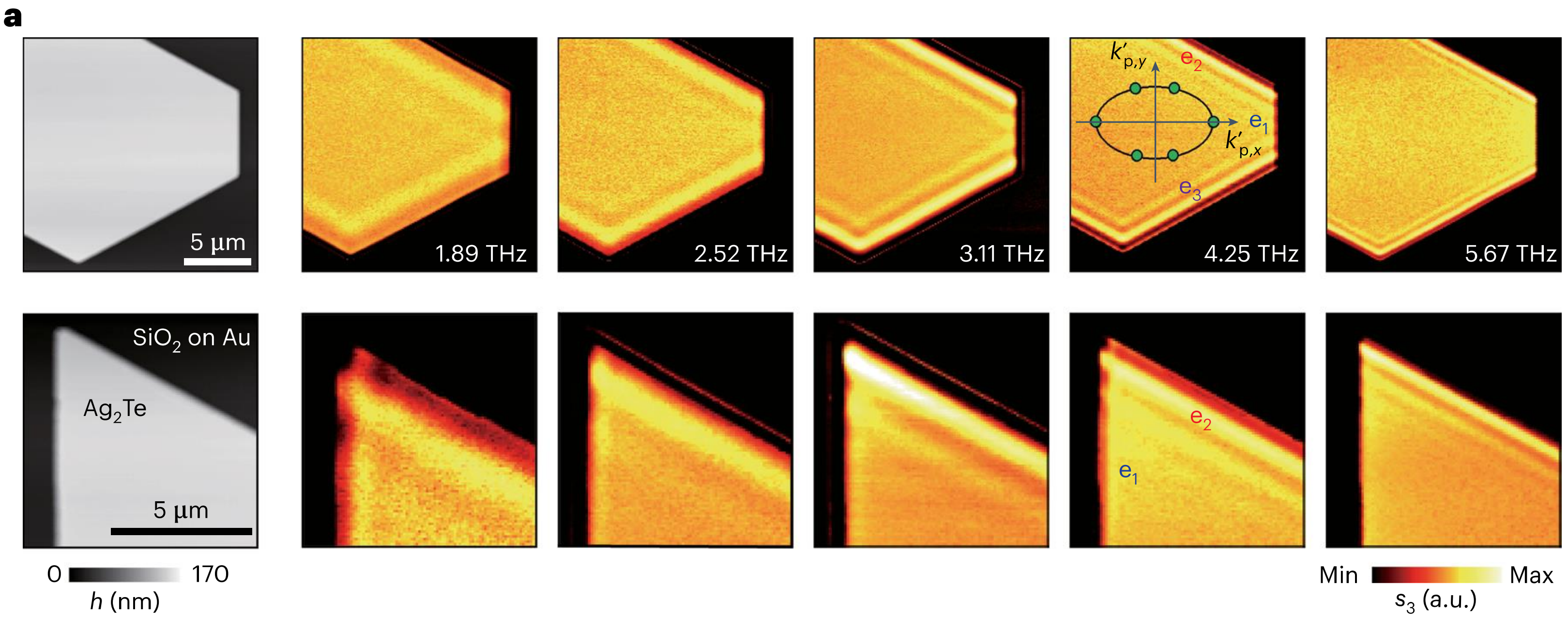
S. Chen, Nat. Mater. 22, 860 (2023)

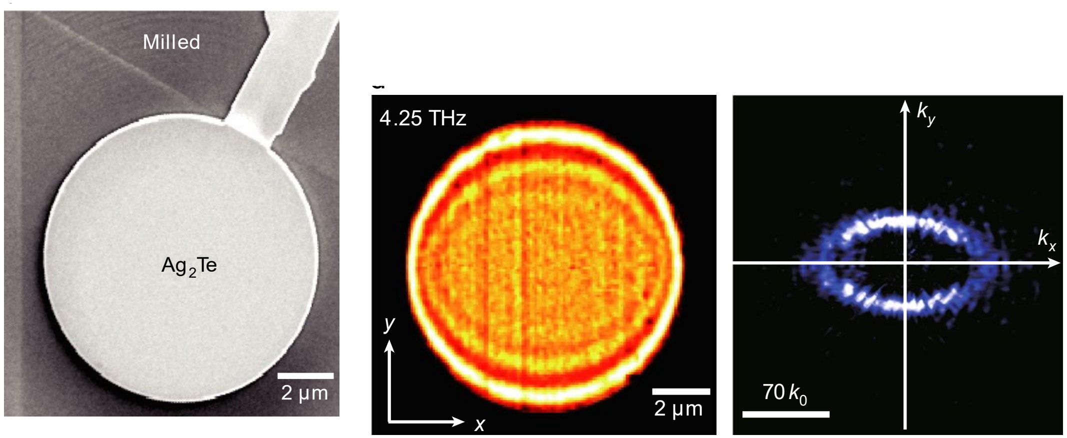
THz plasmon polaritons setup



S. Chen, Nat. Mater. 22, 860 (2023)

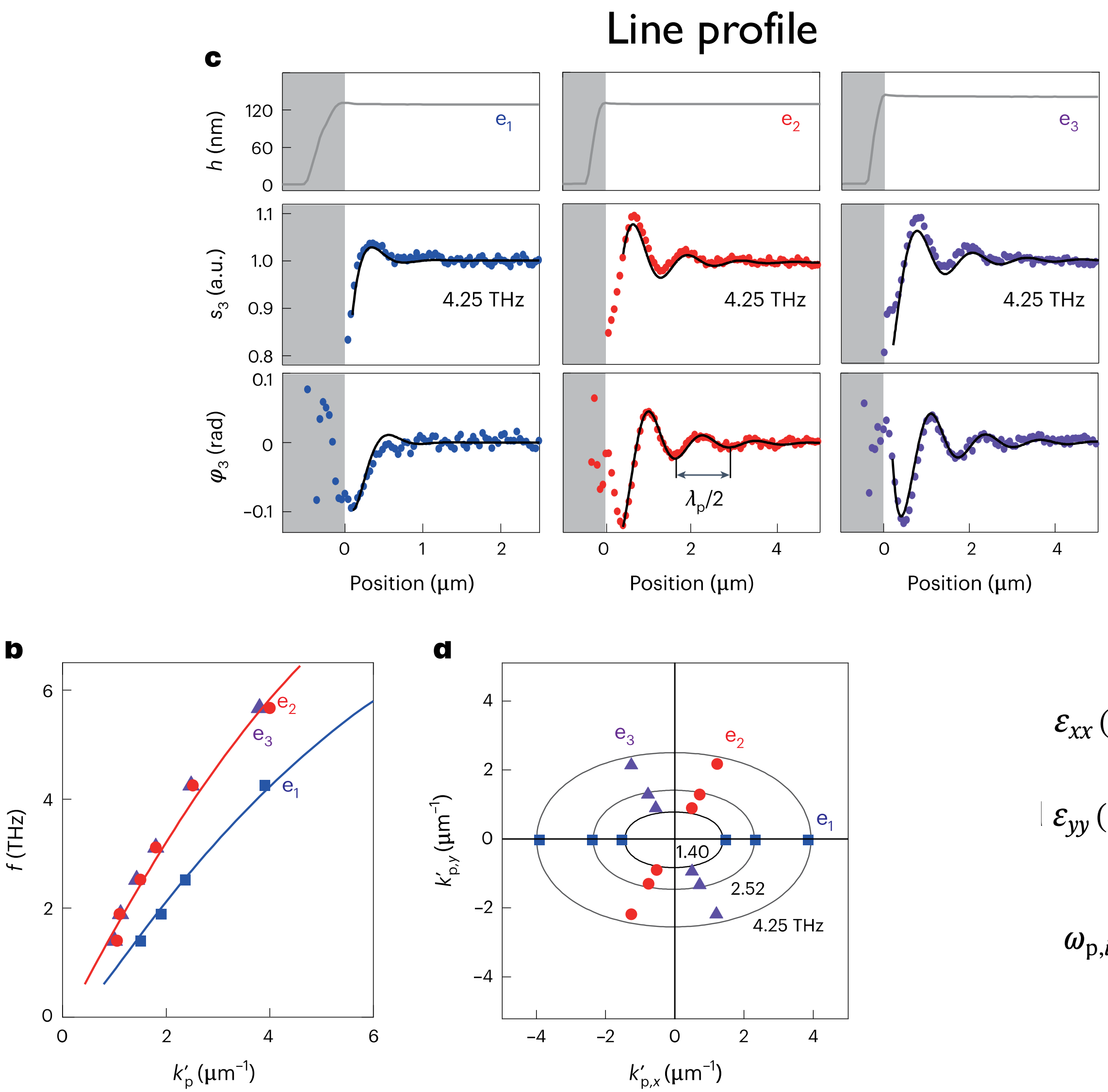
THz plasmon polaritons in a Ag_2Te slab





S. Chen, Nat. Mater. 22, 860 (2023)

THz plasmon polaritons in a Ag_2Te slab



$$\varepsilon_{xx}(\omega) = \varepsilon_{\mathrm{IR},x} - \frac{\omega_{\mathrm{p},x}^2}{\omega^2 + \mathrm{i}\gamma_x\omega}$$

$$\varepsilon_{yy}(\omega) = \varepsilon_{\mathrm{IR},y} - \frac{\omega_{\mathrm{p},y}^2}{\omega^2 + \mathrm{i}\gamma_y\omega},$$

$$\omega_{\mathrm{p},i} = 2\pi f_{\mathrm{p},i} = \sqrt{\frac{ne^2}{m_{\mathrm{eff},i}\varepsilon_0}}$$

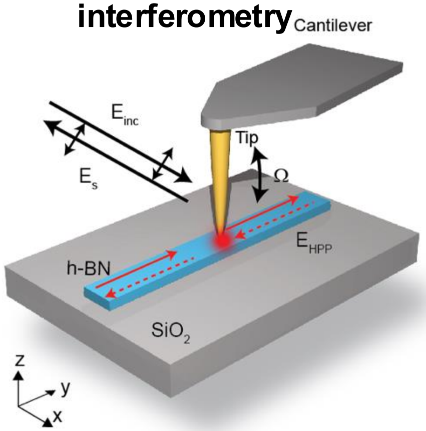
S. Chen, Nat. Mater. 22, 860 (2023)

PPs are an interesting platform for infrared nanophotonics

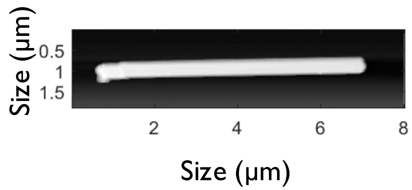
What next?

Ag_2Te plasmon polariton resonators

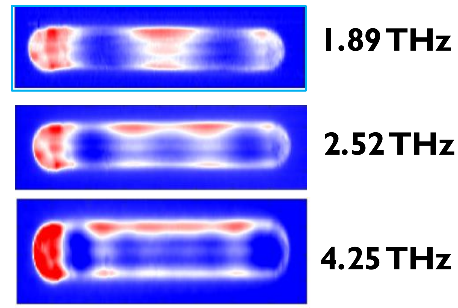
polariton interferometry



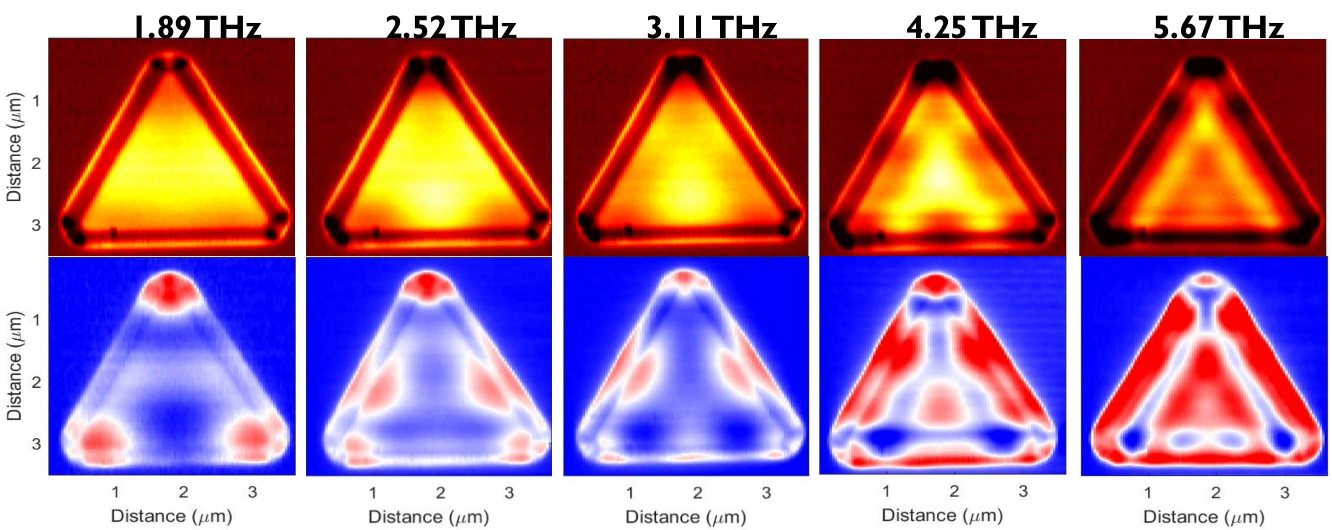
Linear resonators



6um x 0.5um x 0.2um



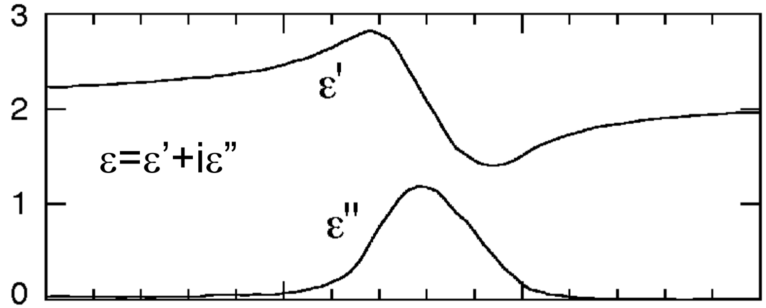
Triangular resonators



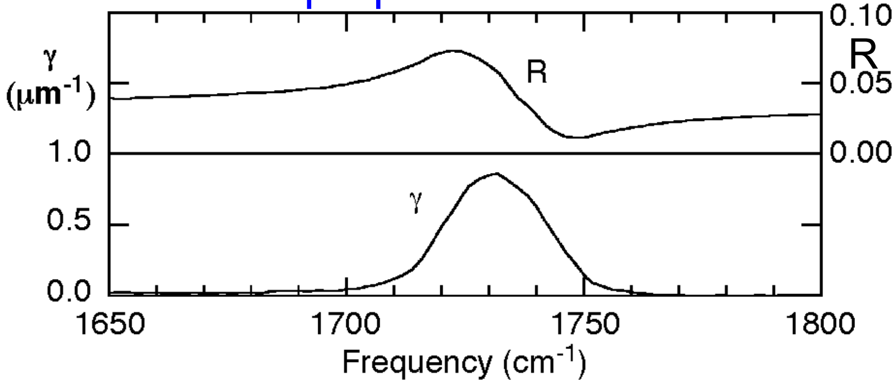

Thank you for the attention

Molecular vibrations: Far-field spectra

Dielectric function of PMMA



Far-field properties of PMMA



complex refractive index

$$n + i\kappa = \sqrt{\varepsilon' + i\varepsilon''}$$

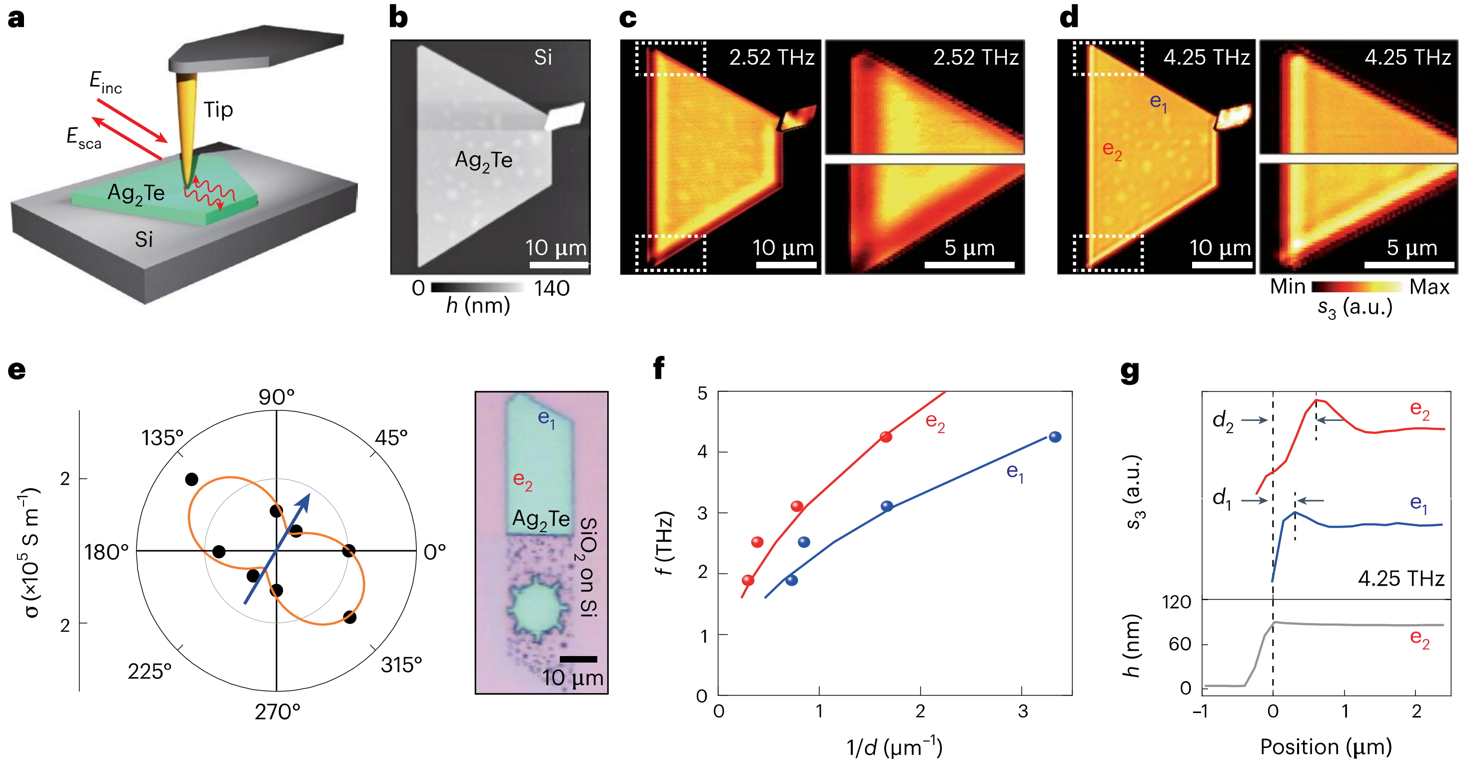
far-field reflectivity

$$R = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2}$$

absorption

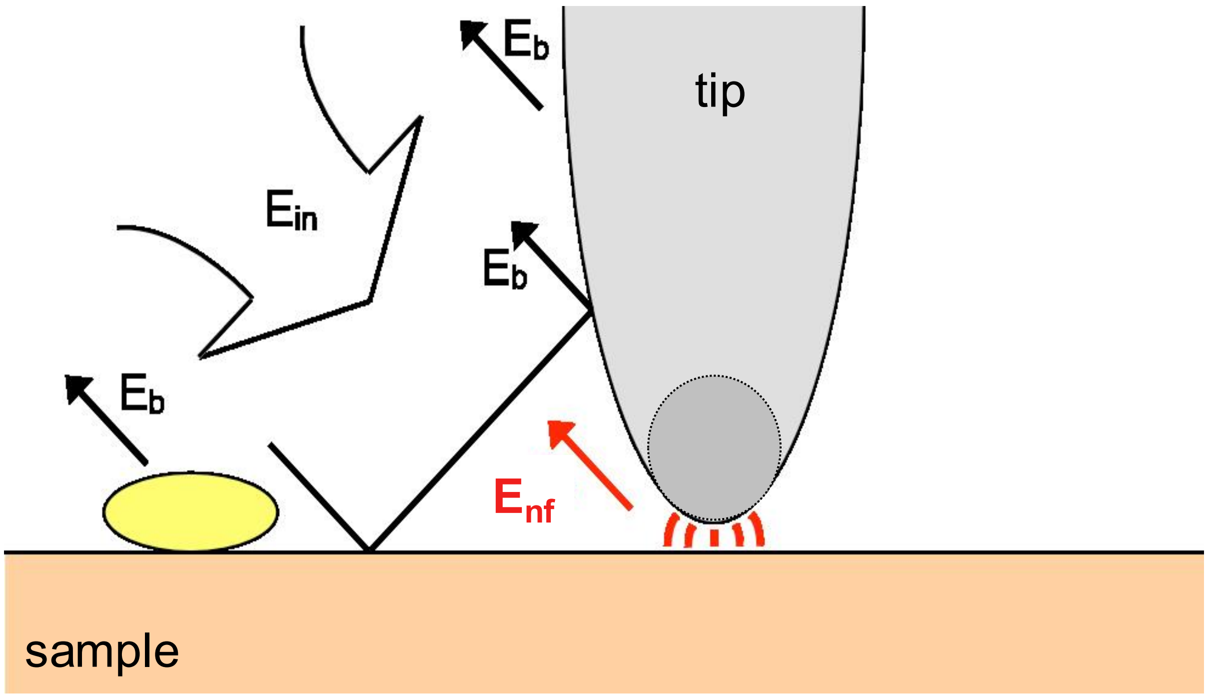
$$\gamma = \frac{4\pi\kappa}{\lambda}$$

THz plasmon polaritons in a AgTe slab



S. Chen, Nat. Mater. 22, 860 (2023)

Scattering sources

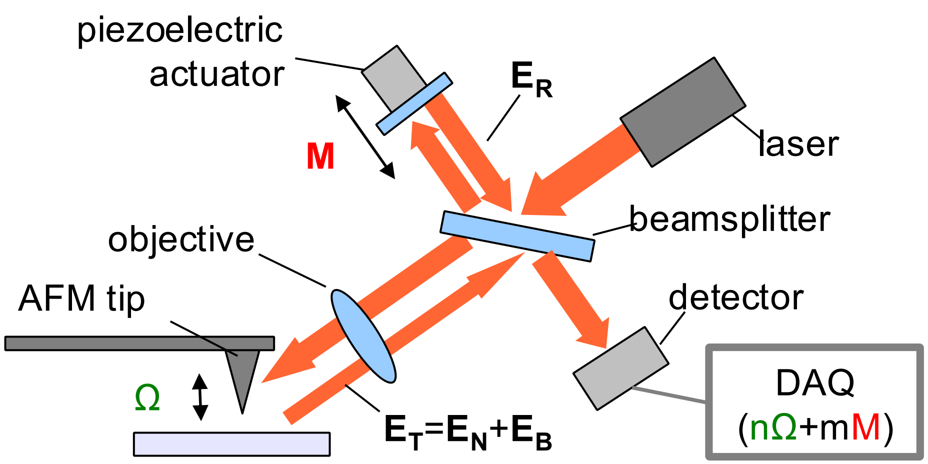


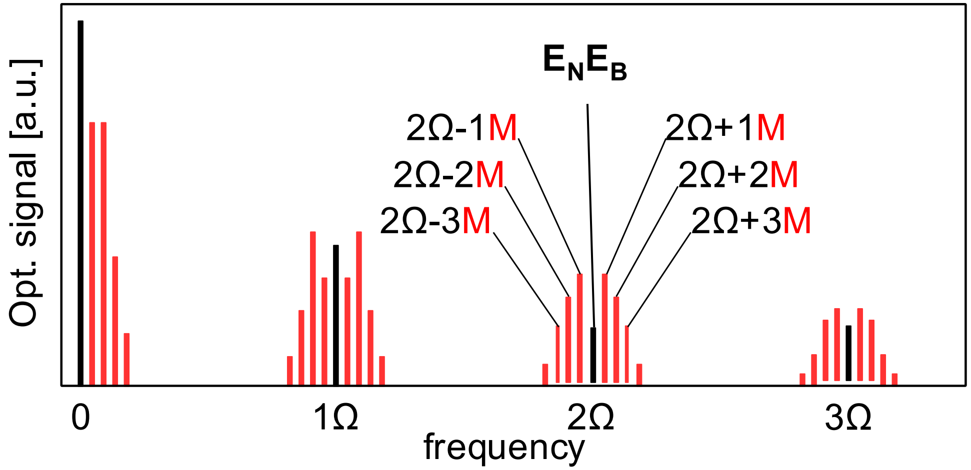
E_{in} : incident light

E_{nf} : scattered light of near-field interaction

E_b : background scattered light

Pseudo-heterodyne detection for simultaneous amplitude and phase mapping





- Additional modulation of reference mirror with frequency M (amplitude ca. 0.21λ) => generation of sidebands
- Sidebands are used to calculate near-field amplitude and phase

$$s_n \propto \sqrt{|U_{n\Omega+M}|^2 + |U_{n\Omega+2M}|^2}$$

$$\phi_n = \tan^{-1}\frac{|U_{n\Omega+M}|}{|U_{n\Omega+2M}|}$$

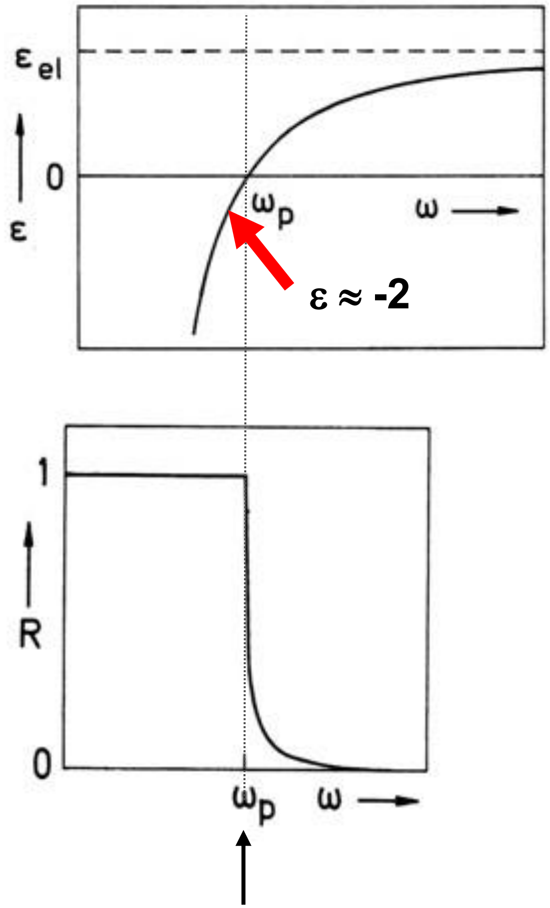
- Features:
  - broad spectral range
  - any coherent source
  - sequential spectroscopy
- Fast data acquisition

N. Ocelic, A. Huber, R. Hillenbrand, Appl. Phys. Lett. **89**, 101124 (2006)

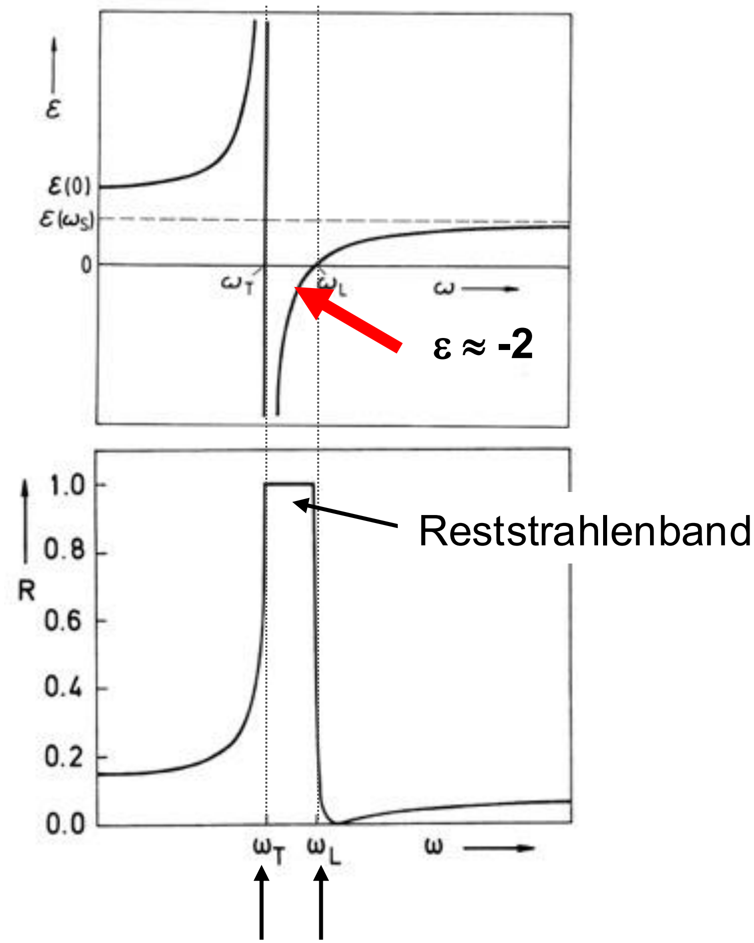
Dielectric function of metals and polar crystals

Metals / doped semiconductors
collective free electron oscillations (**plasmons**)

Polar crystals
strong lattice vibrations (**phonons**)



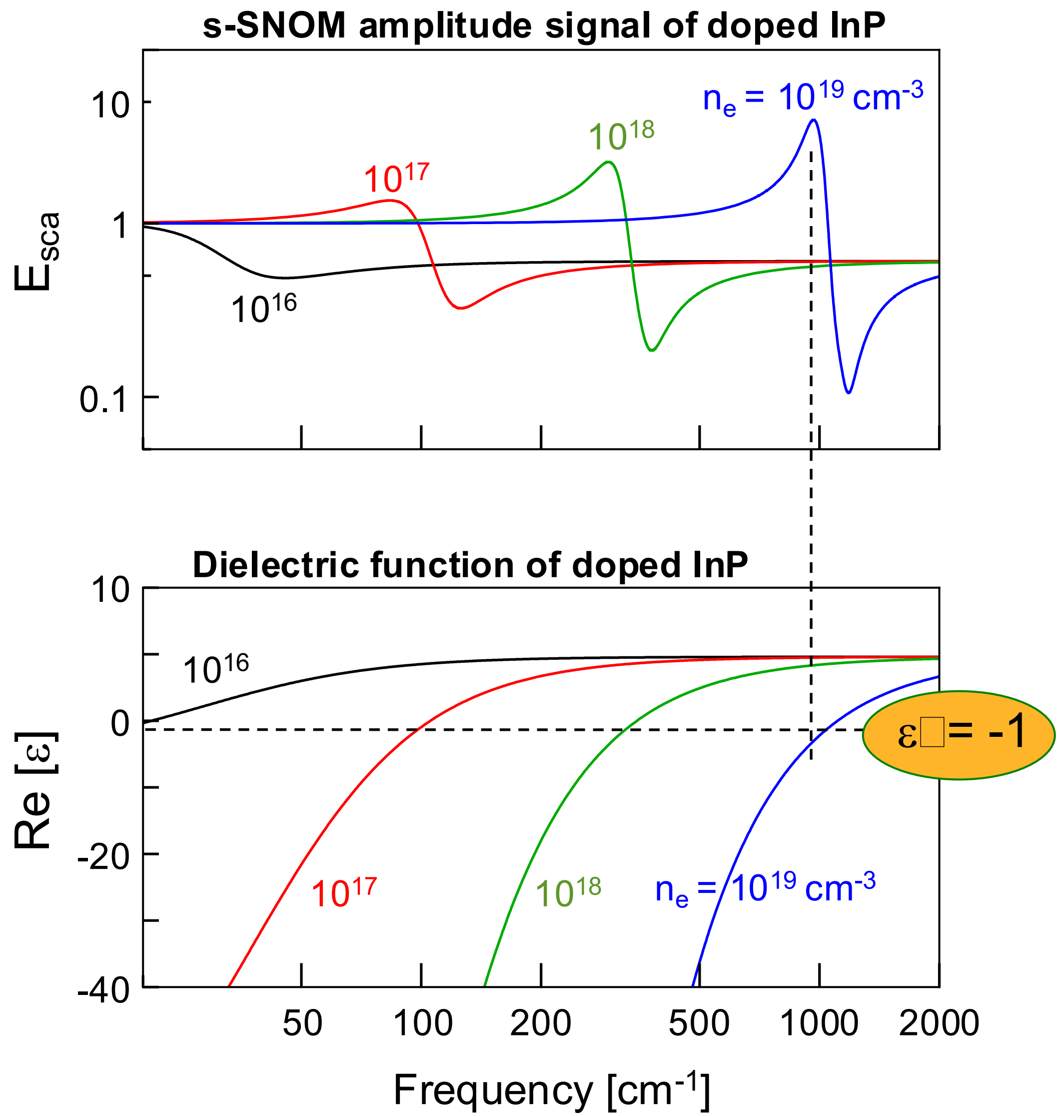
plasma frequency
(longitudinal oscillation)

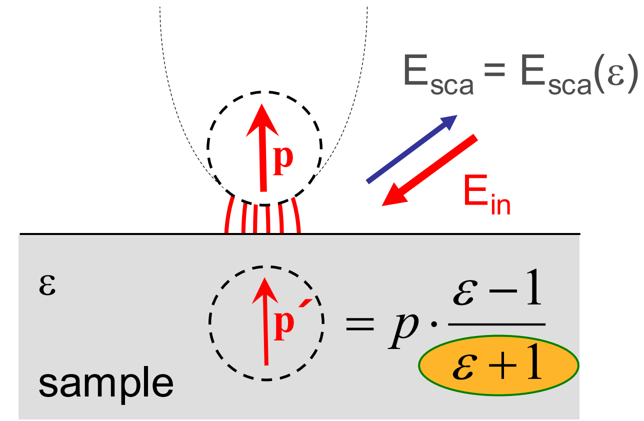


transversal optical
phonon frequency, TO

longitudinal optical
phonon frequency, LO

Near fields at the tip apex induce a local plasmon resonance in semiconductor samples





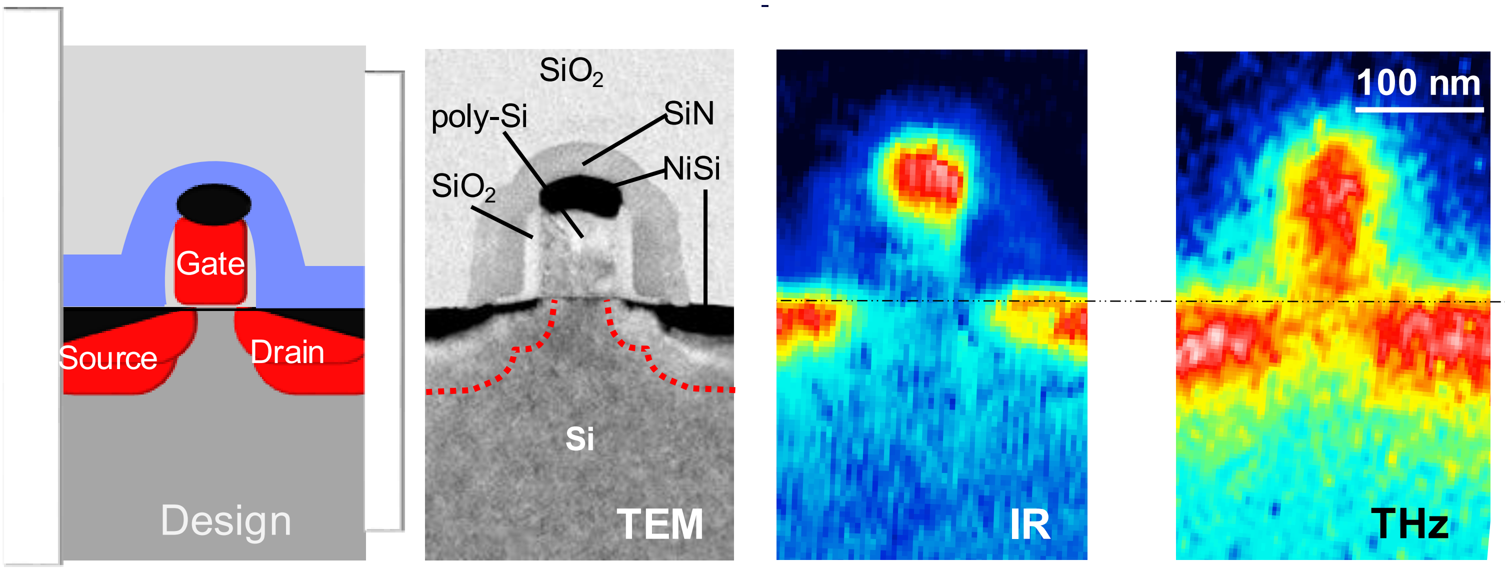
$$p' = p \cdot \frac{\varepsilon - 1}{\varepsilon + 1}$$

Dielectric function $\varepsilon(\omega)$ is determined by plasma frequency ω_P and damping γ:

$$\varepsilon(\omega) = \varepsilon_\infty \left(1 - \frac{\omega_P^2}{\omega^2 + i\gamma\omega} \right)$$

with $$\omega_P^2 = \frac{n_e e^2}{\varepsilon_0 \varepsilon_\infty m \cdot m_0}$$

THz s-SNOM reveals free carriers in single 65-nm-transistor



highly doped Si, n = 10^{19} cm^{-3}

For doped silicon $\varepsilon(\omega)$ depends on the free-carrier concentration n:

$$\varepsilon(\omega) = \varepsilon_{\infty}\left(1 - \frac{\omega_P^2}{\omega^2 + i\gamma\omega}\right)$$

with $$\omega_P^2 = \frac{n\, e^2}{\varepsilon_0 \varepsilon_{\infty} m^* m_0}$$

calculated s-SNOM signal