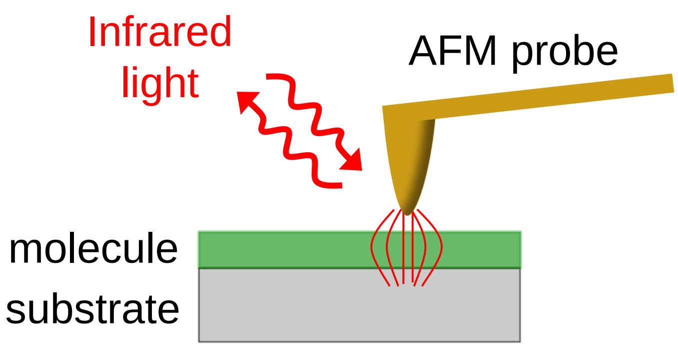
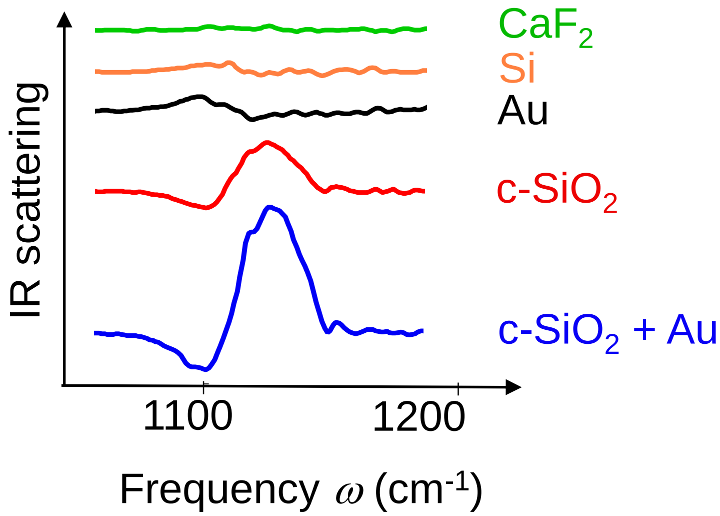
Substrate Matters: Surface-Polariton Enhanced Infrared Nanospectroscopy of Molecular Vibrations

M. Autore, L. Mester, M. Goikoetxea, R. Hillenbrand
CIC nanoGUNE BRTA, Donostia-San Sebastian, Spain

Scattering-type scanning near-field optical microscopy
(S-SNOM & nano-FTIR)





Nano Lett. 2019, 19, 11, 8066-8073

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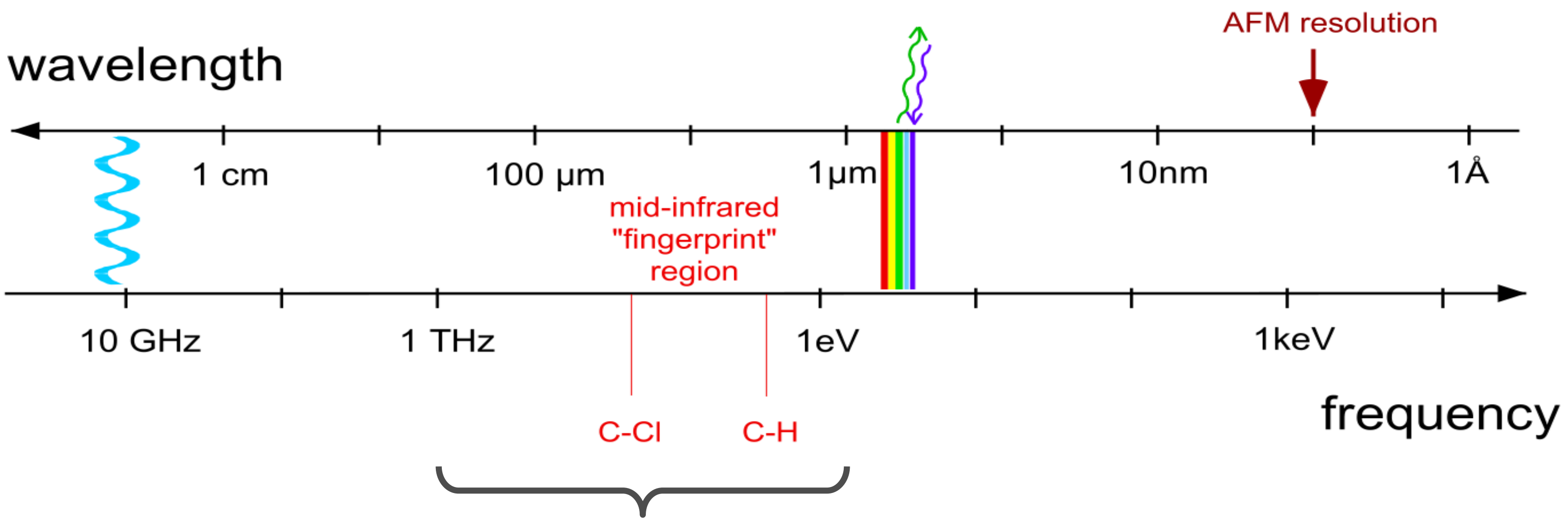
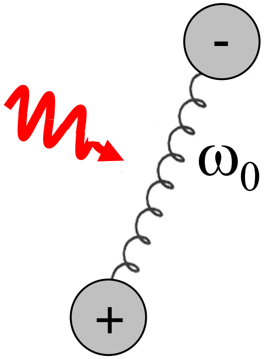
Infrared spectroscopy is a powerful tool for material analysis



Infrared light is highly sensitive to

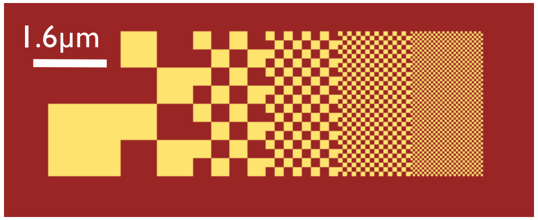
- molecular vibrations → chemical composition
- crystal lattice vibrations → structural properties
- plasmons in doped semiconductors, graphene → electron properties
- …



Chemical mapping is possible, but
spatial resolution is diffraction limited > $\lambda/2 \approx 10 - 100\ \mu m$

Resolution in (far-field) IR spectroscopy is limited

Test Pattern



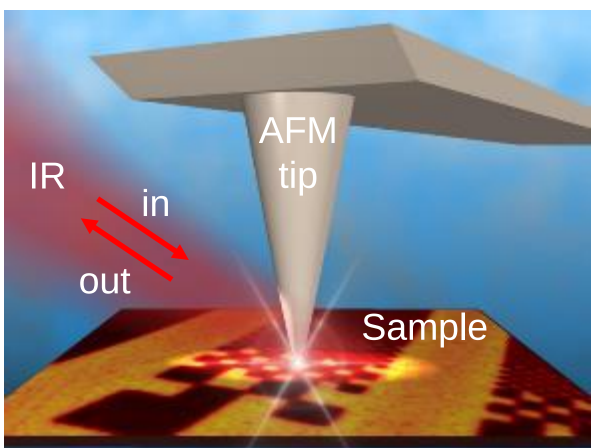
λ = 0.5 µm (visible)

λ = 10 µm (infrared)

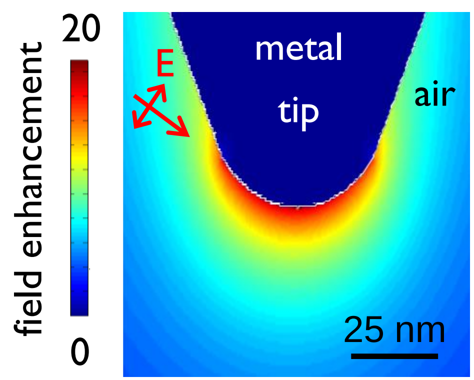
The lateral resolution in (far-field) IR spectroscopy is limited to about λ/2

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

Focused laser beam illuminates AFM tip

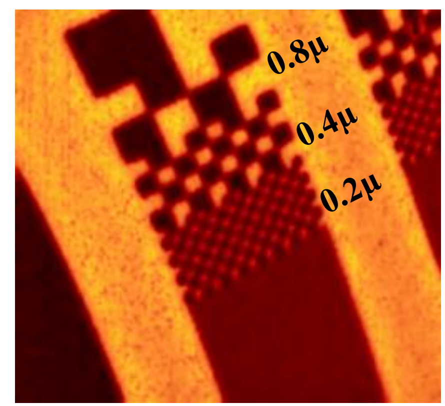


Tip creates nano-focus



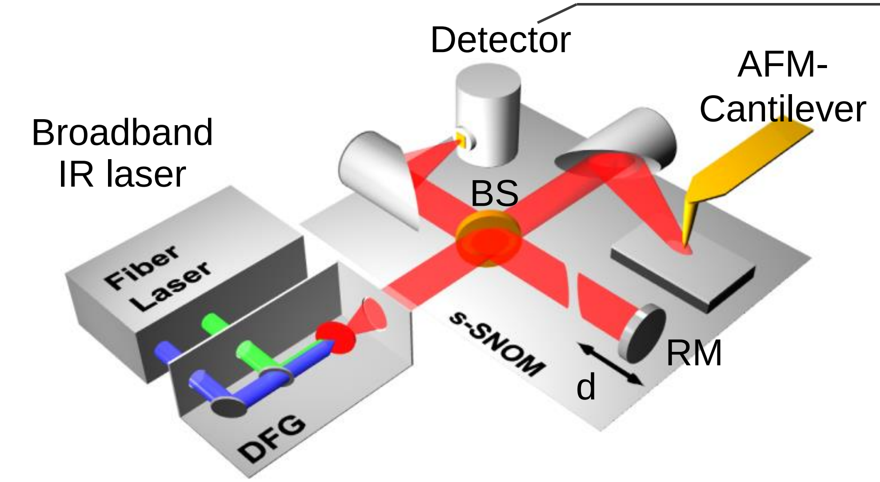
λ ≈ 10 µm

near-field image
λ = 10 µm

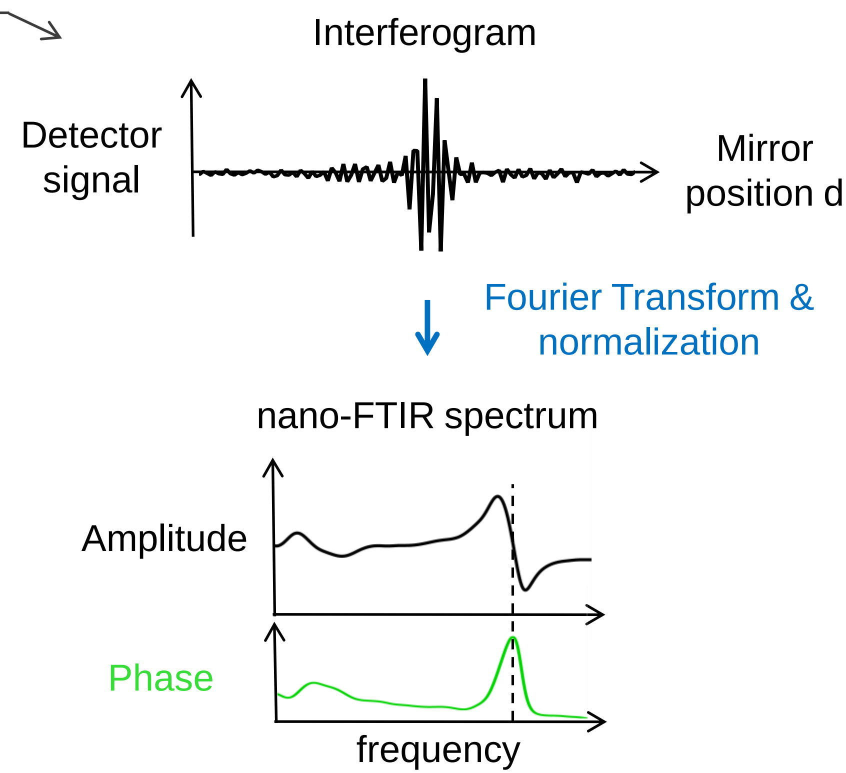


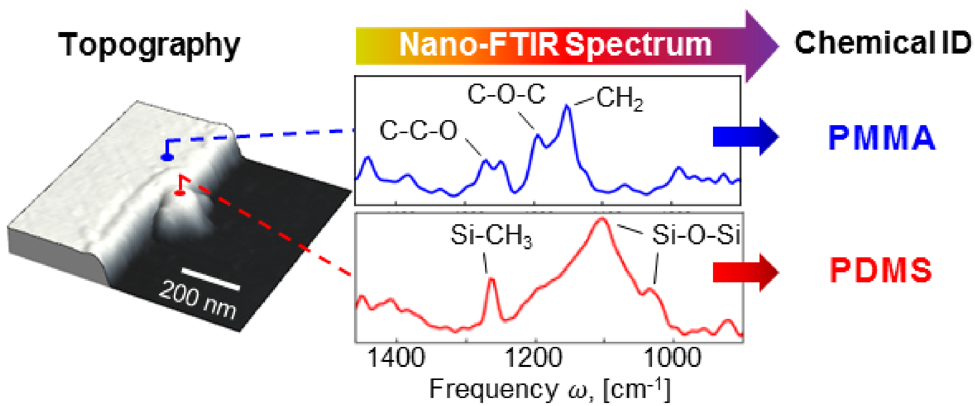
Nature Mat. **3**, 606-609 (2004)

Nanoidentification by infrared s-SNOM and nano-FTIR



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

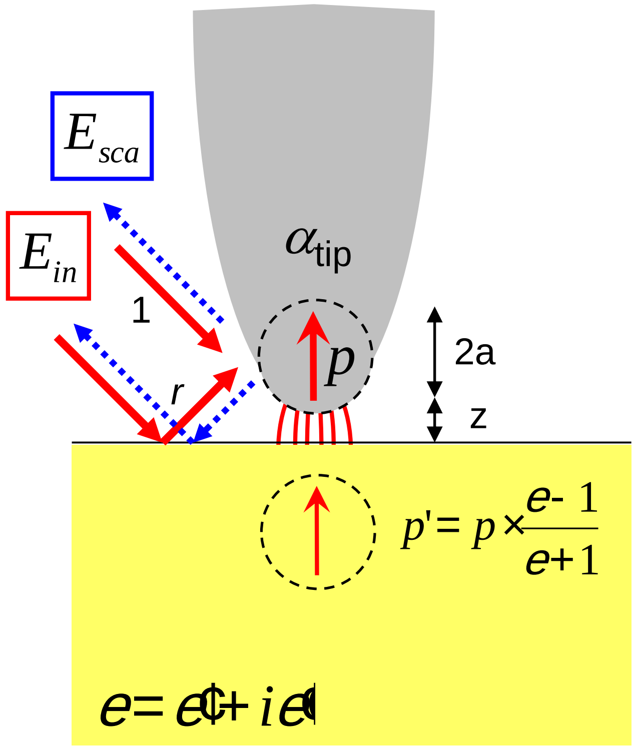




nano-FTIR spectroscopy allows for chemical nanoidentification

F.Huth, *Nano Lett.*, **12**, 3973-3978 (2012)

Quasi-electrostatic dipole model of s-SNOM (bulk samples)



$$E_{sca} = (1+r)^2 \alpha_{eff} E_{in}$$

Far-field contribution: $(1+r)^2$

Near-field contribution: α_{eff}

with effective tip polarizability

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

Approx. for Abs(β) < 1

$$\alpha_{eff} \propto \beta$$

where $\beta = \frac{\varepsilon - 1}{\varepsilon + 1}$ (near-field reflection coefficient)

Keilmann, Hillenbrand, in Nano-Optics and Near-Field Optical Microscopy (Artech House, 2008)

Sample properties are measured via near- and far-field reflection coefficients (β and r)

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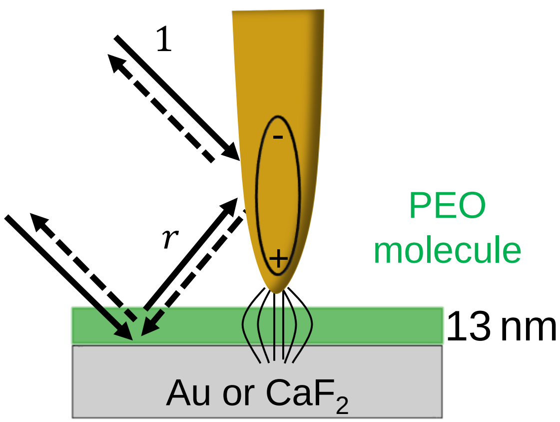
Reflective substrates strongly enhance nano-FTIR signals

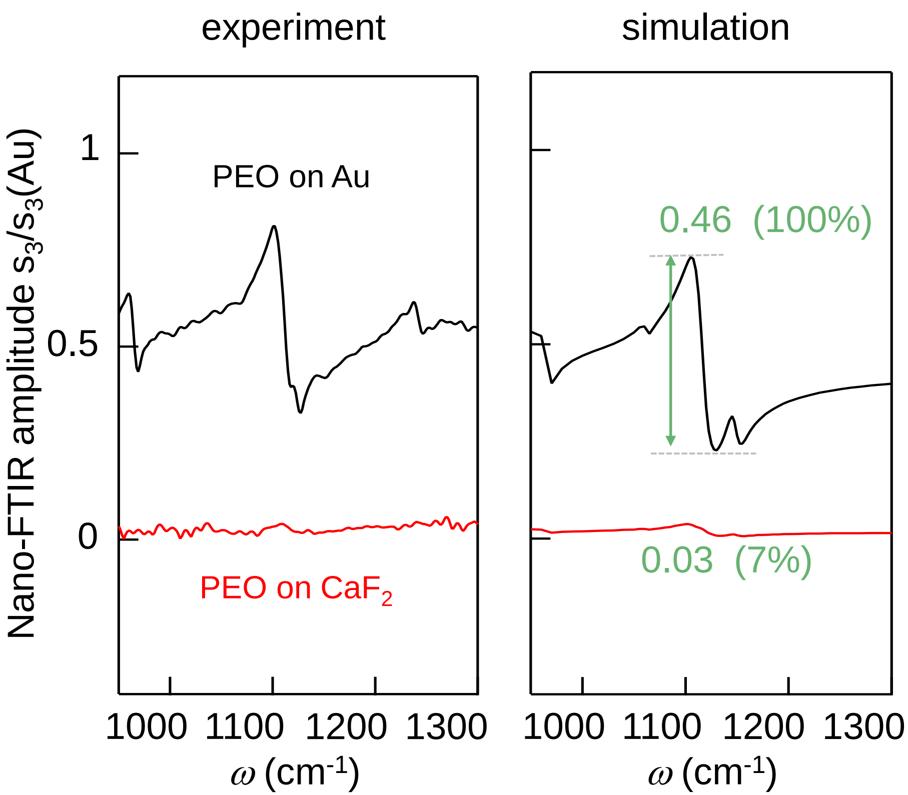
Sketch of experiment

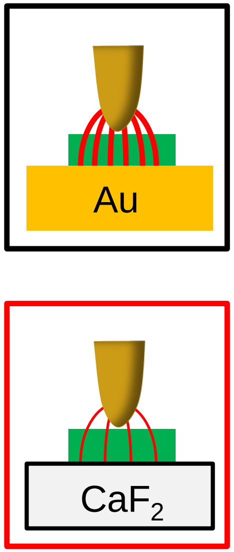


Sustrate reflectivities

$r_{Au} = 1$ $\beta_{Au} \approx 1$

$r_{CaF2} = -0.06$ $\beta_{CaF2} \approx 0.3$





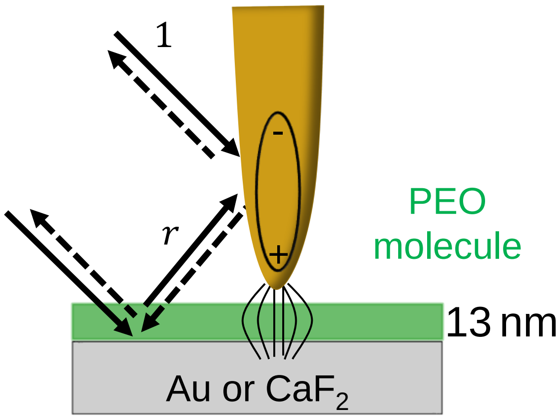
Nano-FTIR amplitude essentially probes near-field reflection of PEO

14x signal enhancement

by using a highly reflective Au substrate compared to CaF_2

Reflective substrates strongly enhance nano-FTIR signals

Sketch of experiment



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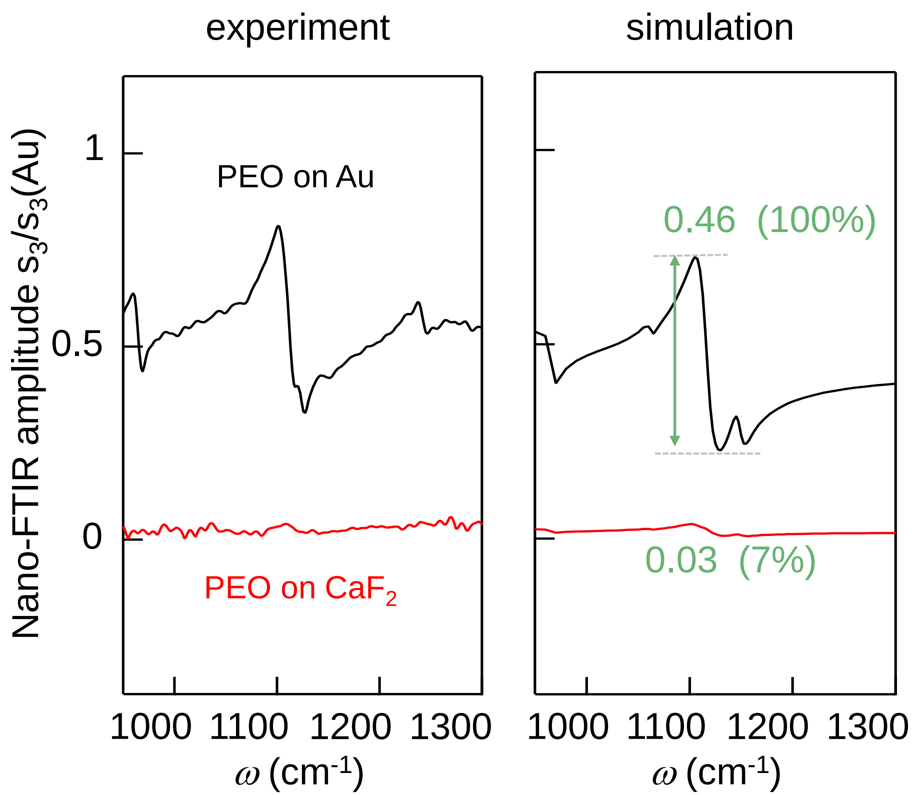
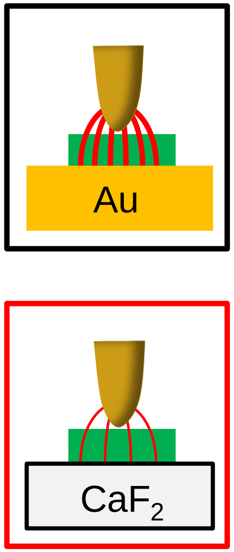




Nano-FTIR amplitude essentially probes near-field reflection of PEO

Increased tip-substrate coupling

Incident and scattered light reflected via substrate

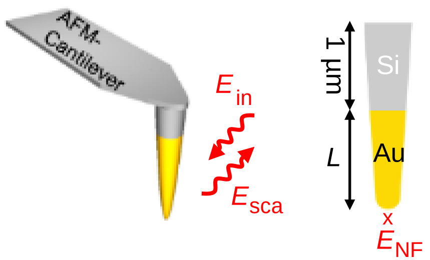
14x signal enhancement
by using a highly reflective Au substrate compared to CaF_2

Resonant enhancement of near-fields at the tip apex

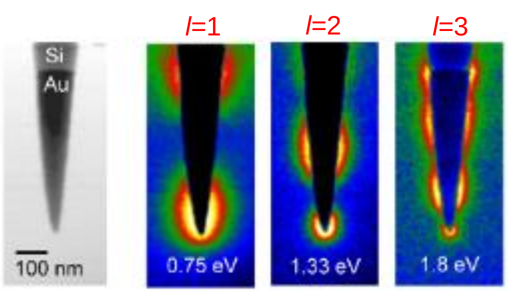
Strong field-enhancement can be provided e.g. by:

Resonant S-SNOM tips

e.g. tailored probe tip length



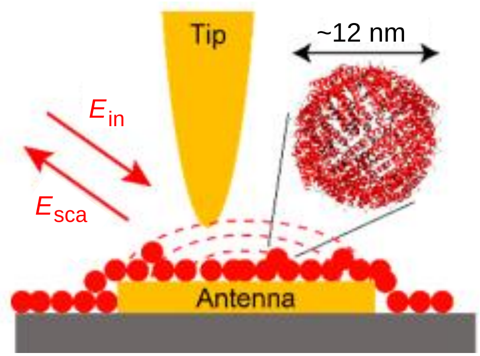
Electron energy loss spectroscopy maps



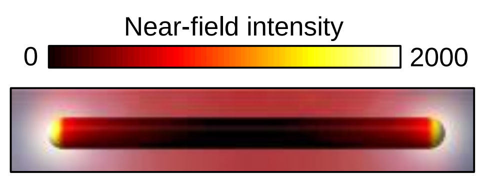
Huth, *Nano Lett.* 2013, 13, 1065-1072

Resonant tip-antenna coupling

e.g. in plasmon-resonant gold nanowire



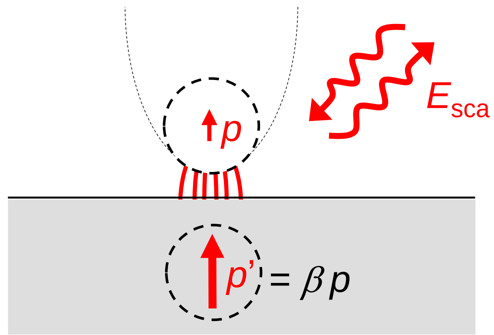
O'Callahan, *J. Phys. Chem. C* 2019, 123, 17505-17509



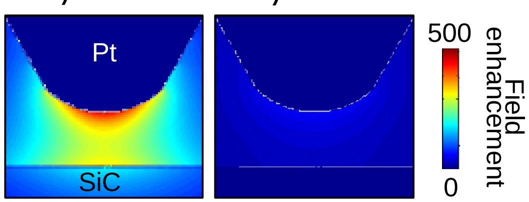
Neubrech, *PRL* 101, 157403 (2008)

Resonant tip-substrate coupling

e.g. phonon- or plasmon-polariton resonance



e.g. polar crystal SiC



Calculations J. Aizpurua (DIPC, Spain)

- Sophisticated fabrication

- Sophisticated fabrication
- Localized hotspots on sample

+ flat surface
+ simple (no fabrication required)
+ hotspot independent of position

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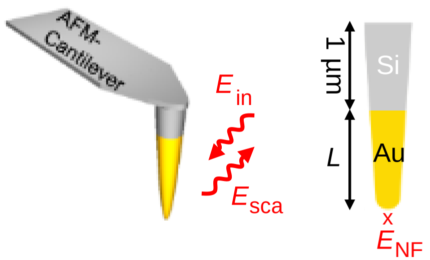

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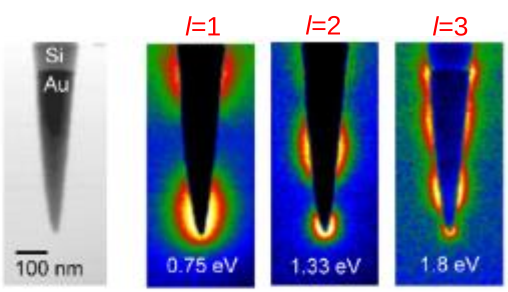

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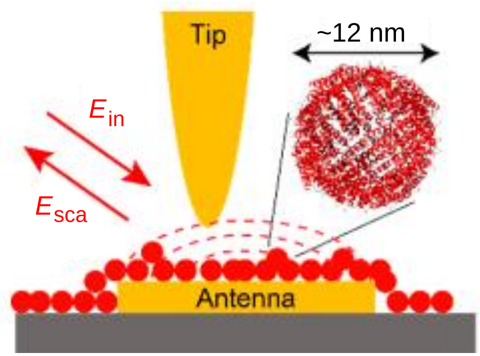

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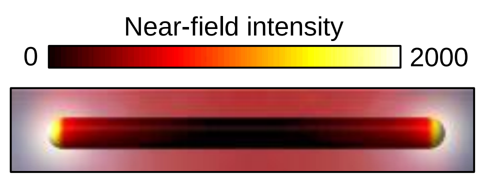

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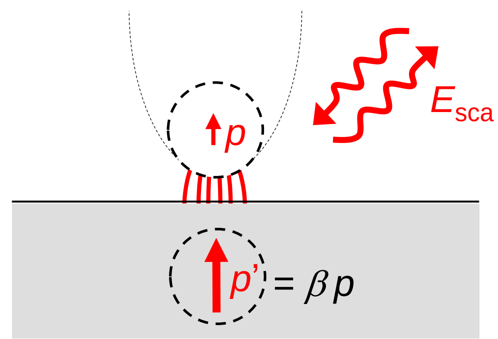

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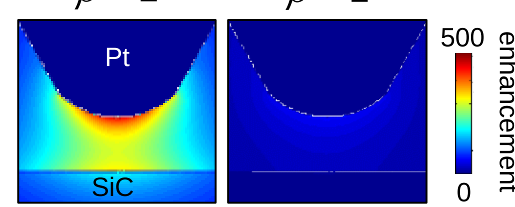

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Resonant tip-substrate coupling (here SiC substrate)

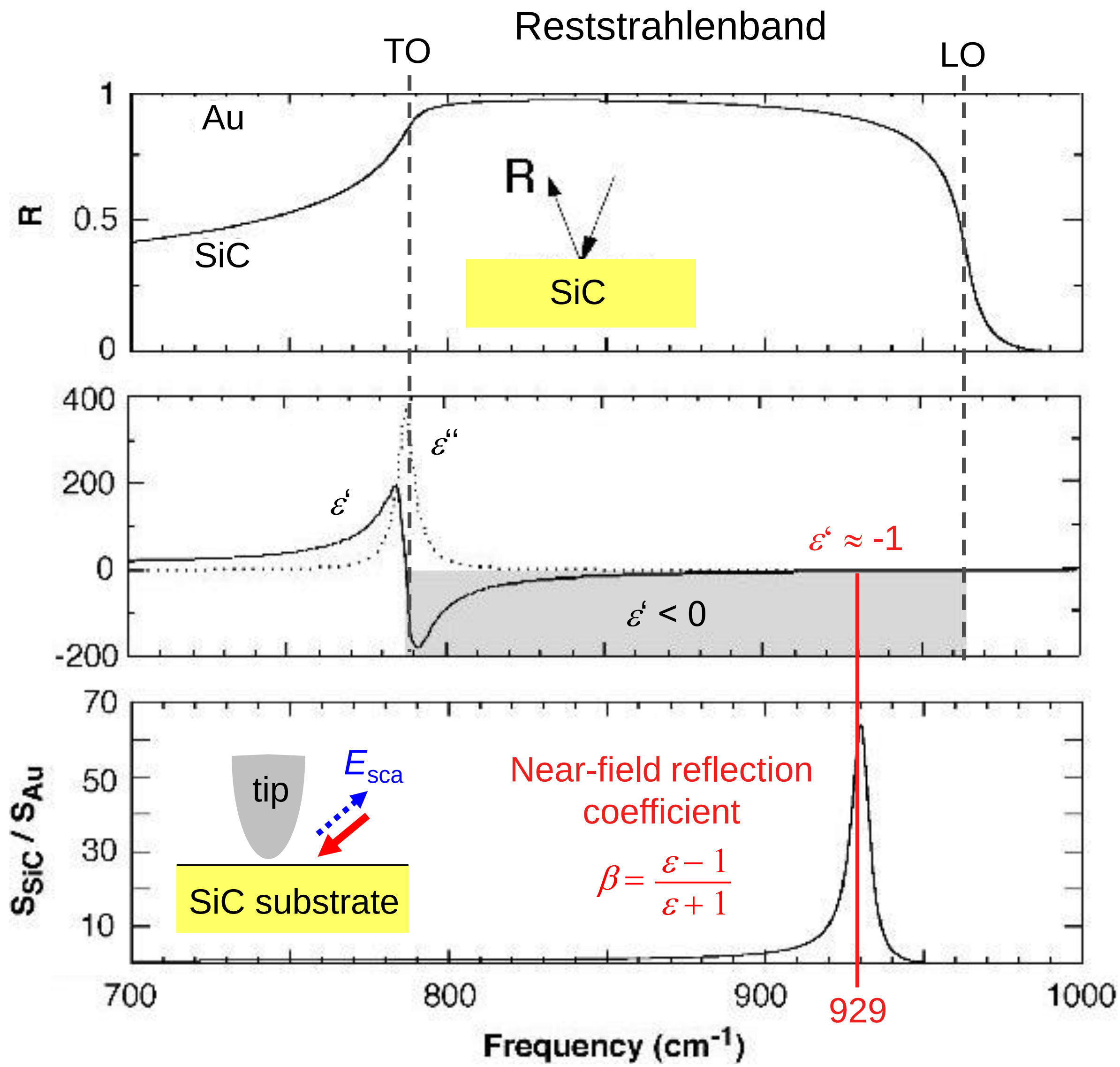
Far-field reflectivity

Dielectric function of SiC-sample

$$\varepsilon = \varepsilon' + i\varepsilon''$$

Near-field spectrum dipole model

$S = E_{sca}^2$



Hillenbrand, *Nature* **418**, 159-162 (2002)

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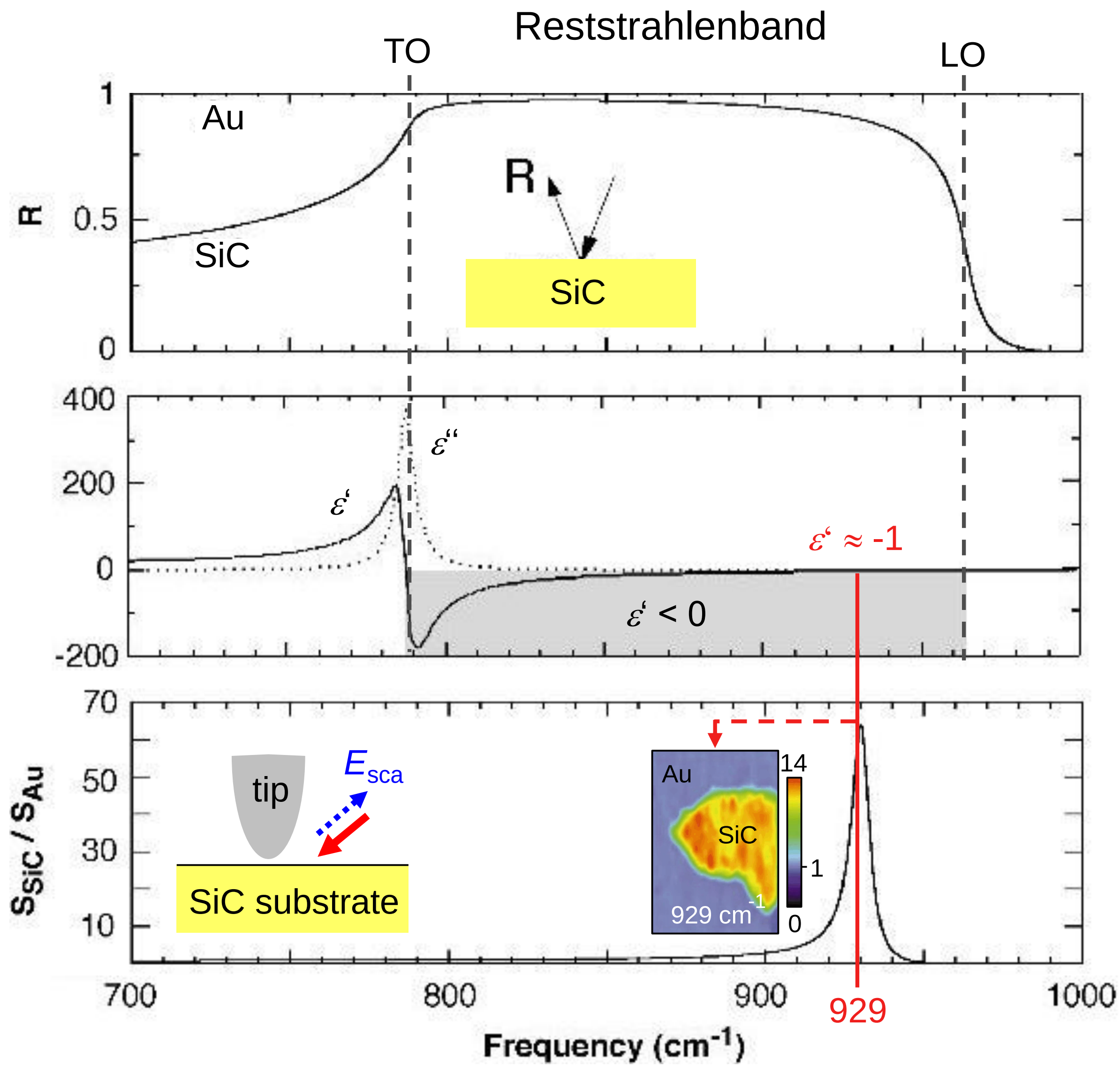

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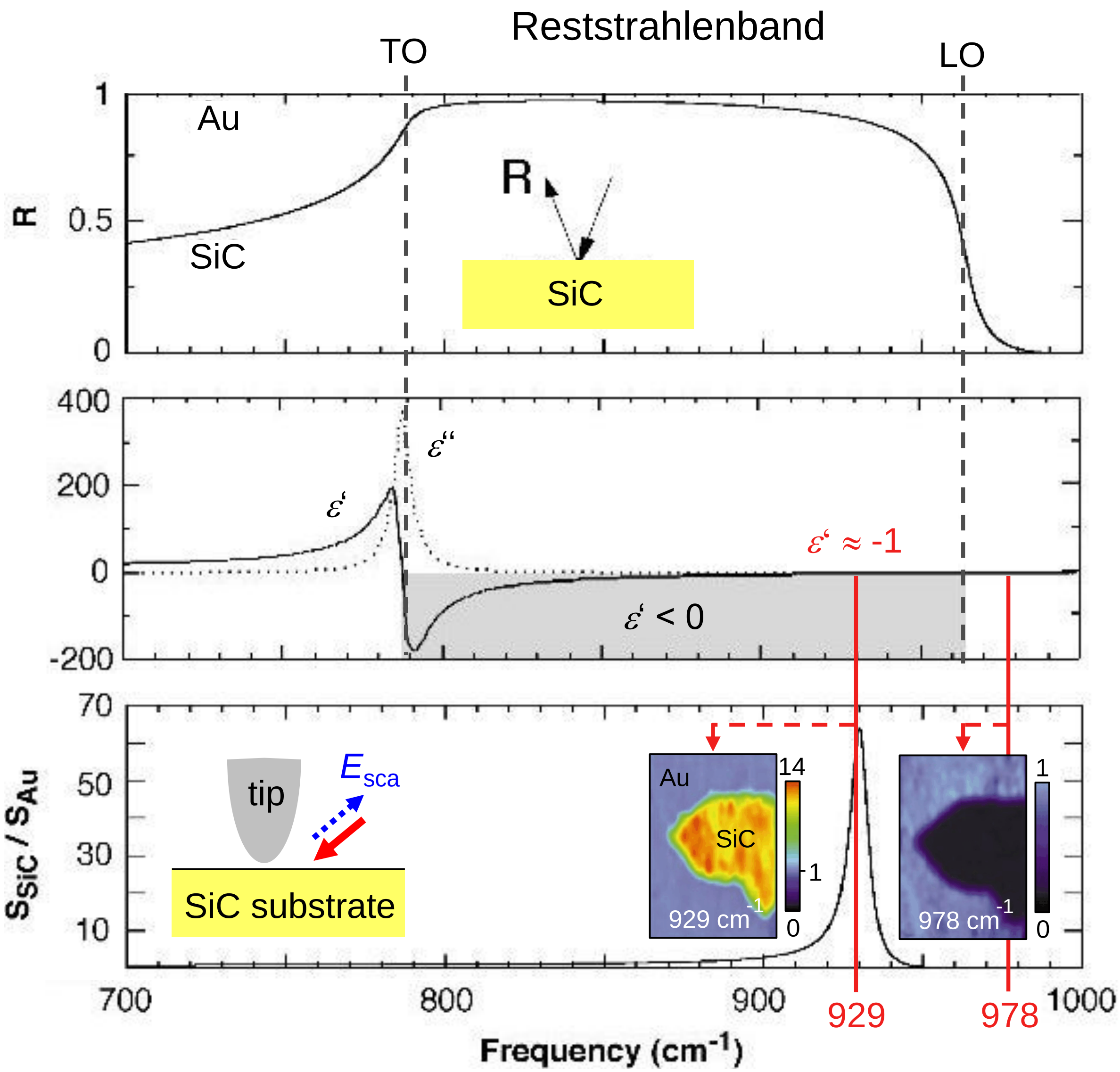

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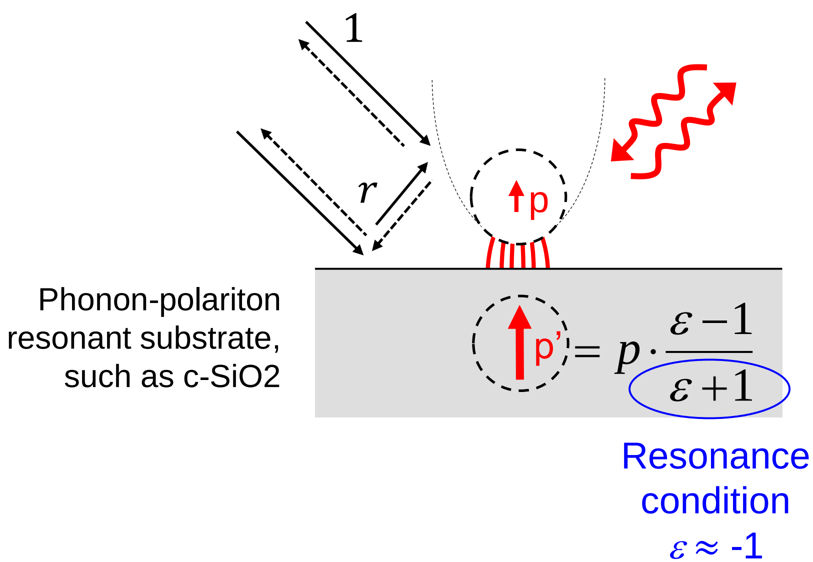
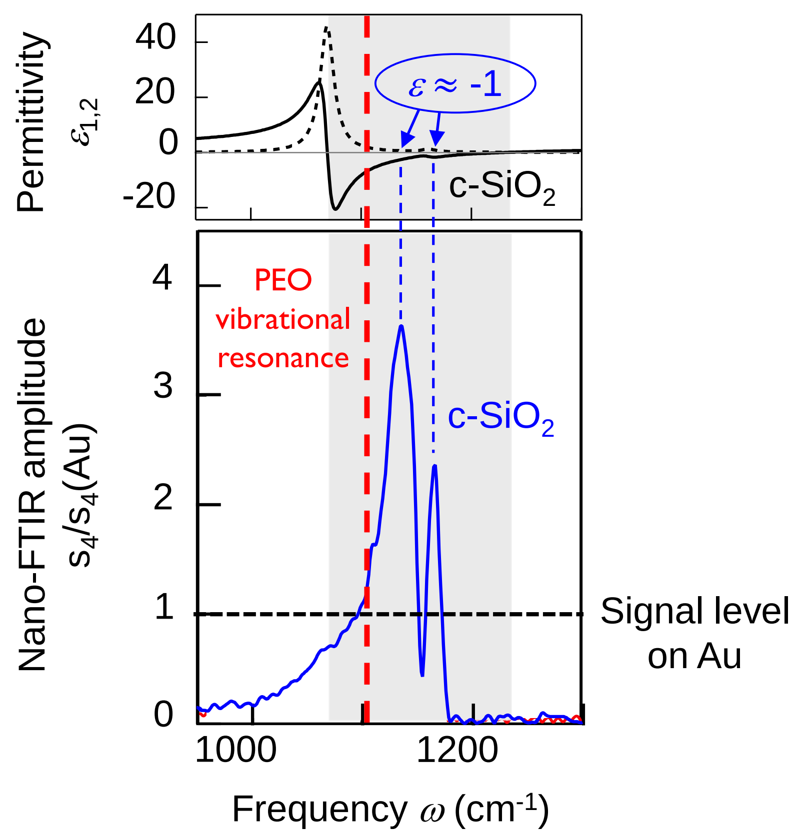
Tip-substrate resonance of quartz matches PEO's vibrational resonance

Resonant tip-substrate coupling
provides large (additional) field enhancement



Localized phonon-polariton
resonance in quartz



→ We aim to exploit polariton-resonance to further increase nano-FTIR signals of PEO

Autore, *Nano Lett.* **19**, 11, 8066-8073 (2019)

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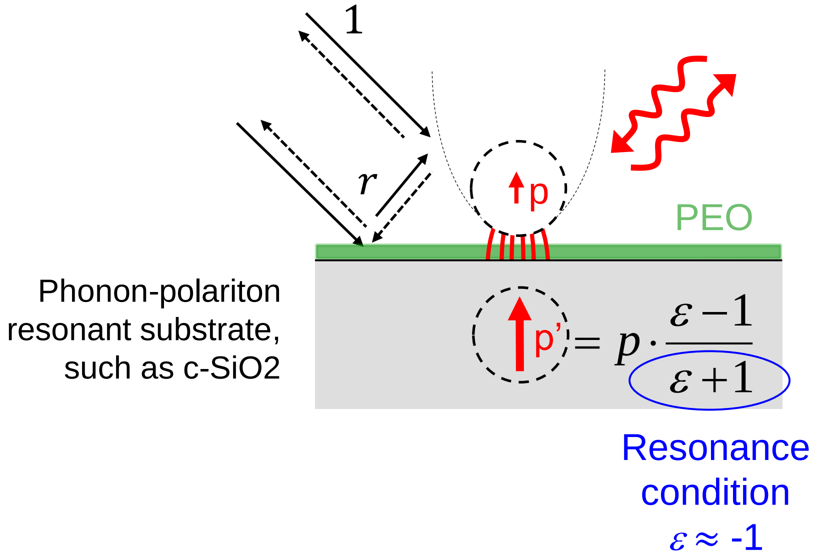

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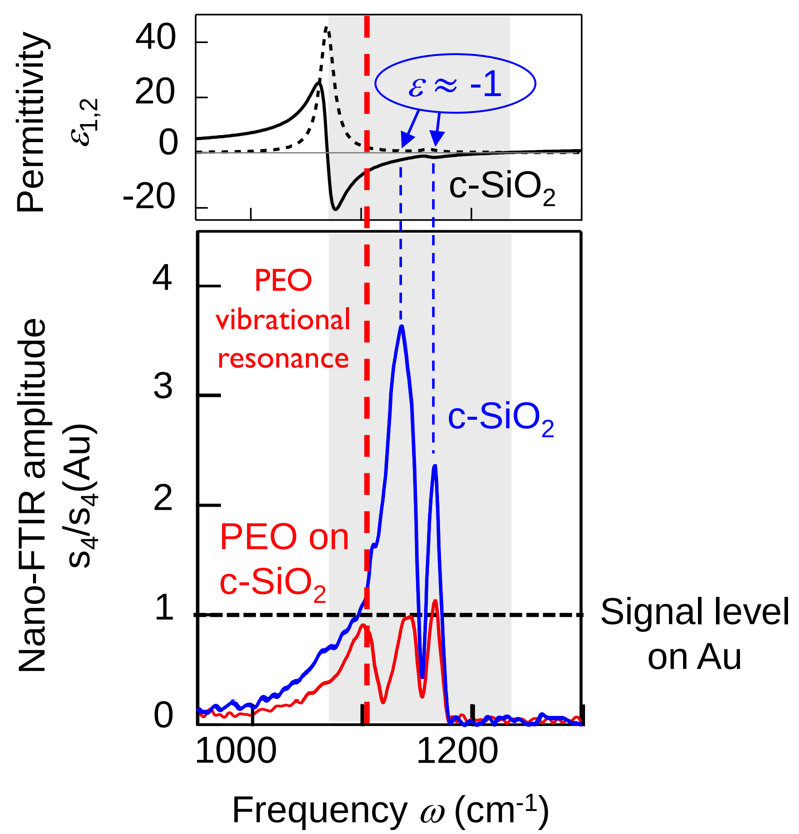

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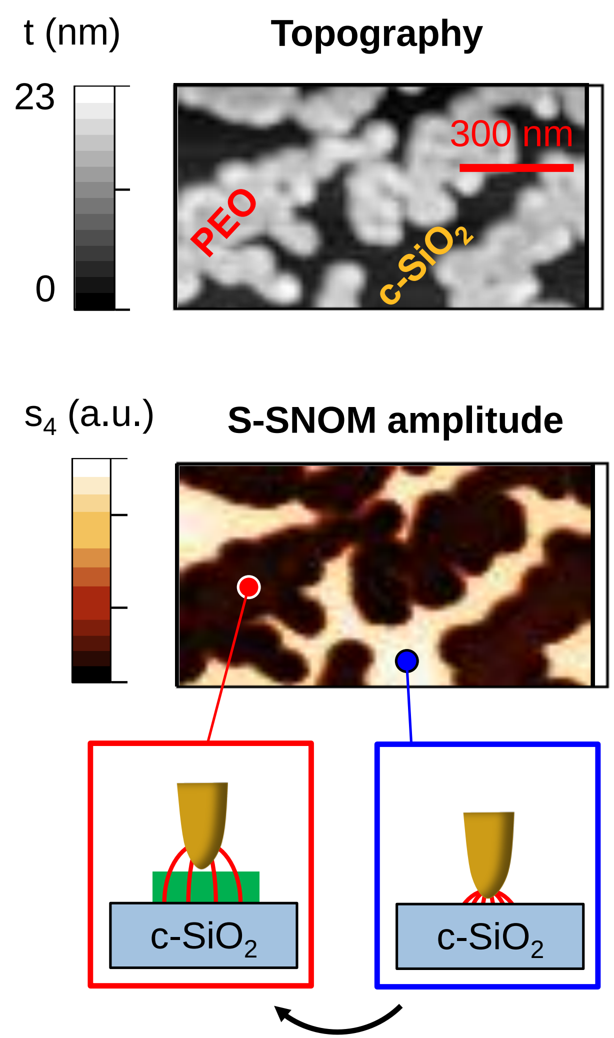
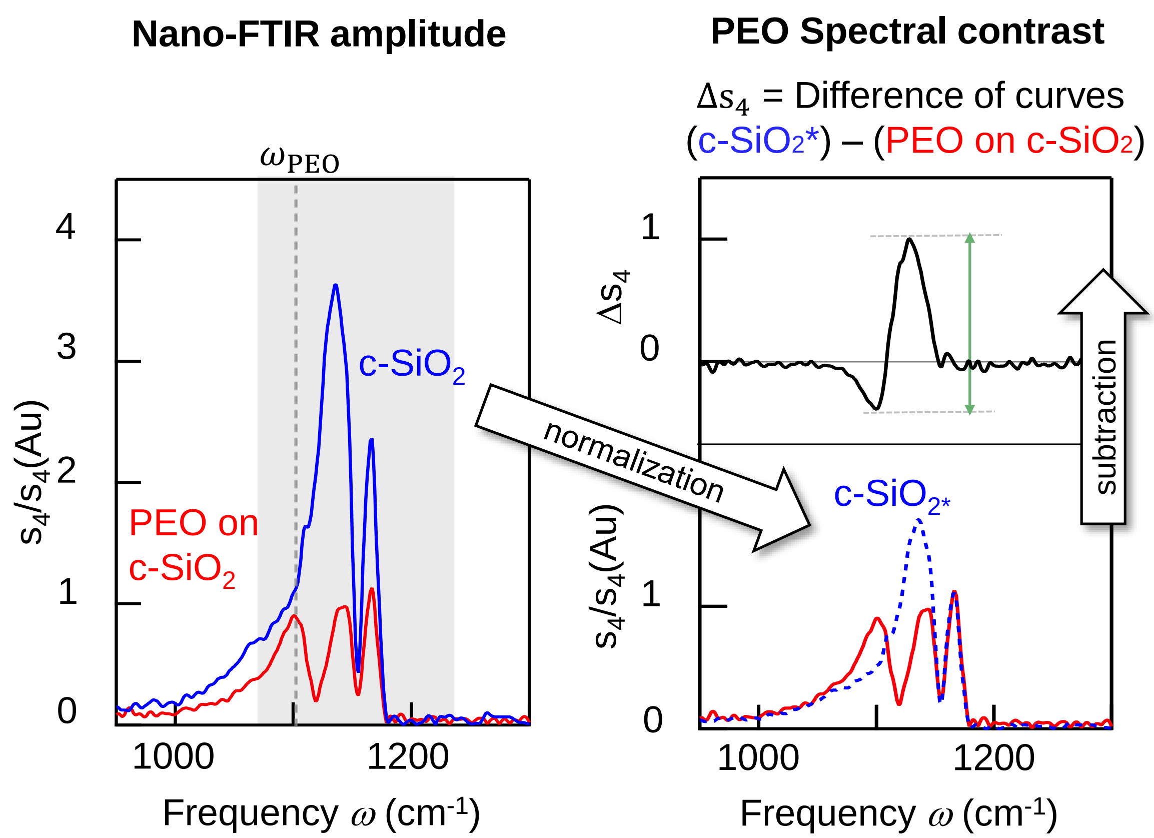
Autore, *Nano Lett.* **19**, 11, 8066-8073 (2019)

Resonant tip-substrate coupling boosts nano-FTIR signal beyond Au



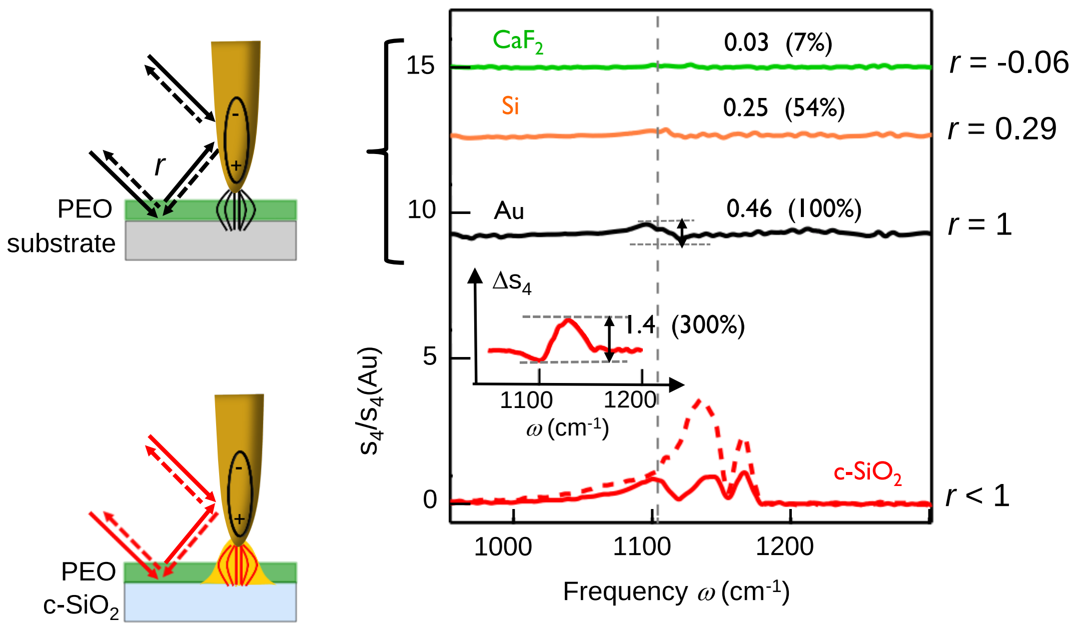
Increased tip-substrate distance reduces tip-substrate coupling



Dip in resonance indicates large coupling between molecule and tip-induced phonon-polariton

(Analog to SEIRA effect, but in near-field microscopy)

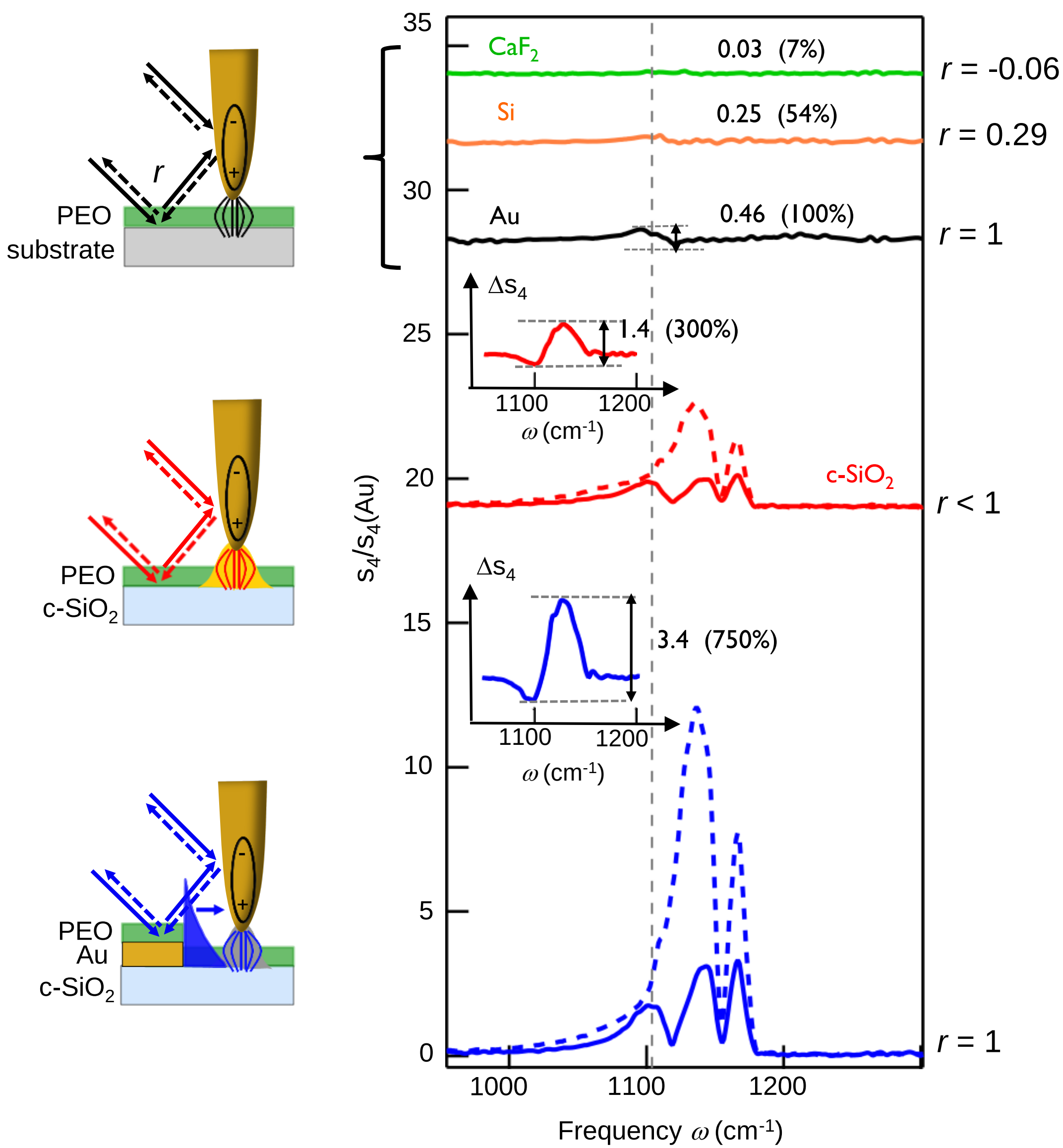
Comparison of substrate-enhancements



Metal substrate yields
14x higher spectral contrast than CaF2

Polariton-resonant substrate yields
further 3x enhancement

Comparison of substrate-enhancements



Metal substrate yields
14x higher spectral contrast than CaF2

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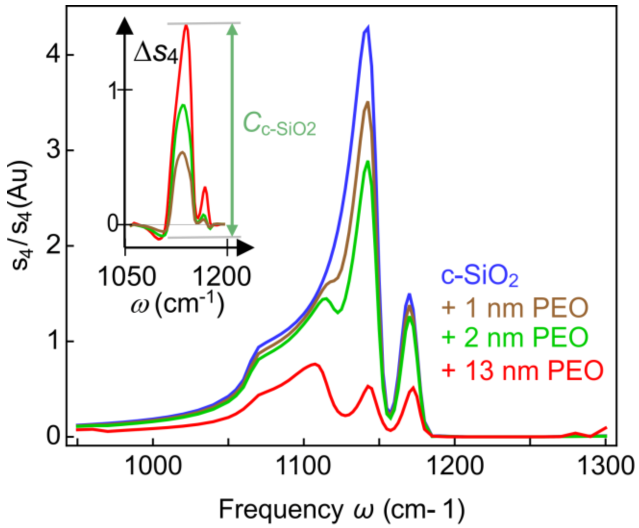
further 3x enhancement

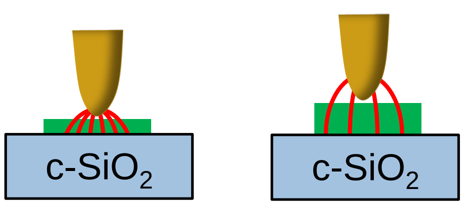
Polariton-resonant substrate
+ illumination of tip via gold surface
(+ illumination via propagating SPhP) yields
two orders of magnitude enhancement
(compared to CaF2)

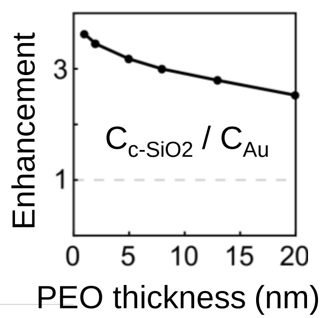
Outlook

Strong spectral contrast Δs_4 predicted even for nm-thin molecular layers



Tip-substrate coupling increases for thin molecular layers

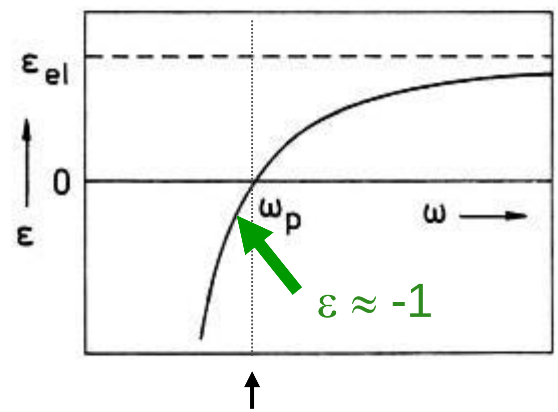




Wide range of materials host polariton resonances that can enhance sensing ($\varepsilon \approx -1$)

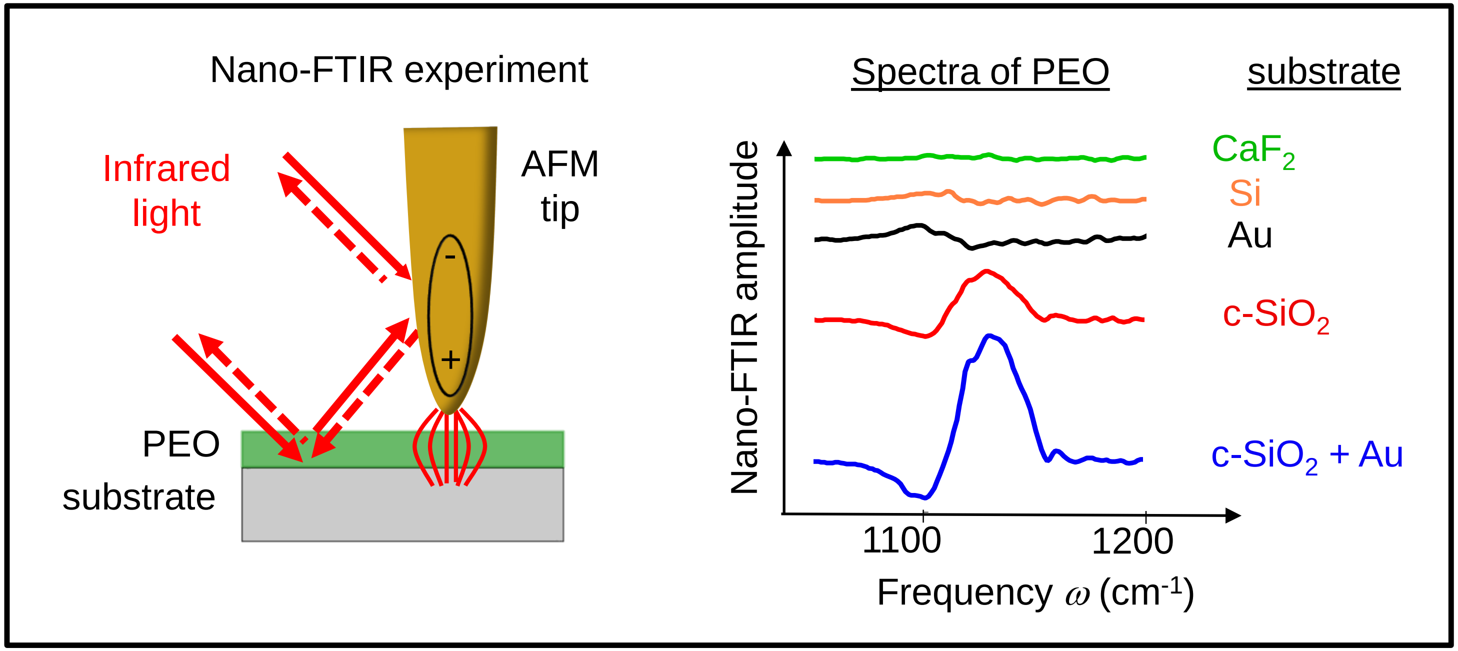
Polar crystals
strong lattice vibrations (phonons)
e.g. SiO_2, SiC, Al_2O_3, …

Metals / doped semiconductors
collective free electron oscillations (plasmons)



plasma frequency
(longitudinal oscillation)

Summary



Non-resonant tip-substrate coupling (e.g. Au substrate) → 14x enhancement compared to CaF_2

Phonon-resonant tip-substrate coupling (e.g. Quartz substrate) → further 3x enhancement

Resonant tip-substrate coupling (Quartz) + efficient tip illumination (via Au)
→ 7.5x enhancement compared to Au
→ 14x enhancement compared to Silicon

Autore, *Nano Lett.* 2019,**19**,11, 8066-8073

Acknowledgements

Autore, *Nano Lett.* 2019,**19**,11, 8066-8073

M. Autore

M. Goikoetxea

R. Hillenbrand

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