Optical spectroscopy in materials science 9.
Near-field methods

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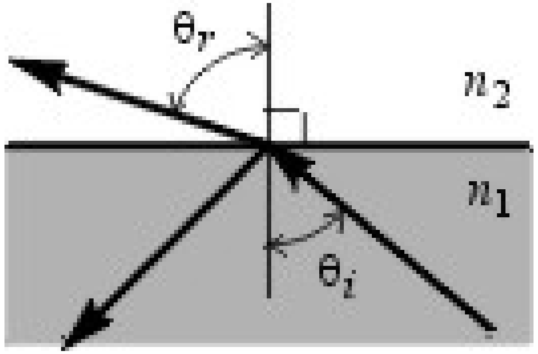
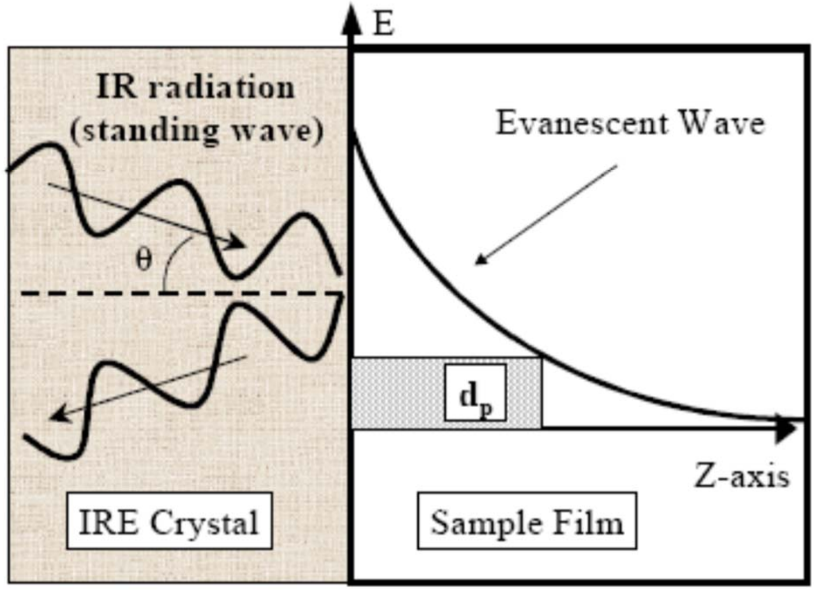
Total reflection



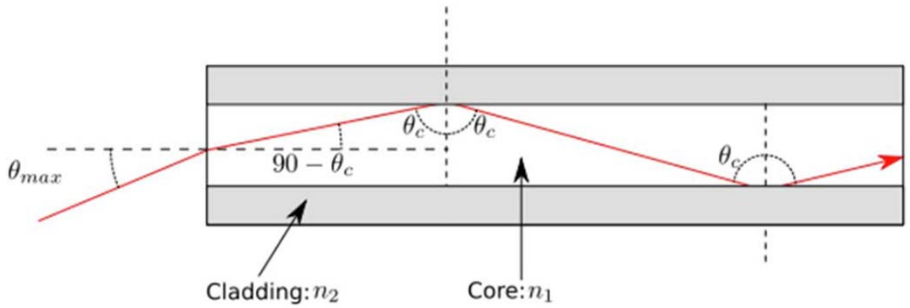
Critical angle of total reflection $\theta_c = \sin^{-1}\left(\frac{n_2}{n_1}\right)$

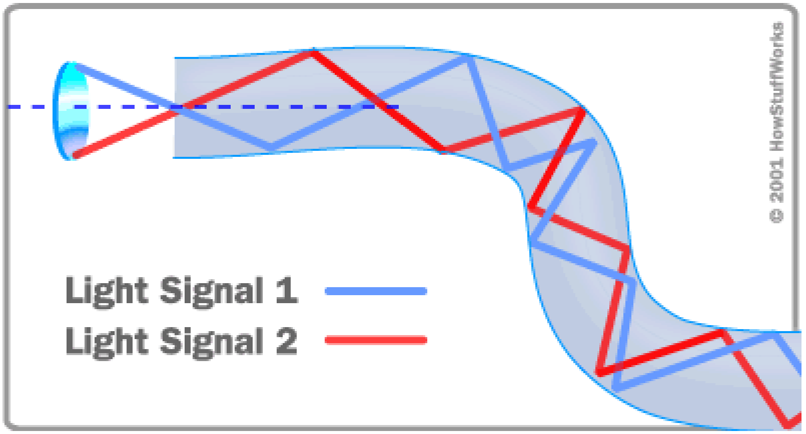
- Nonzero field in the medium with lower refractive index
- Evanescent field – non-transversal wave (vector components in all directions)
- Evanescent field present in the layers close to the boundary and decays fast



$$d_p = \frac{\lambda}{2\pi(n_1^2 \sin^2\theta - n_2^2)^{1/2}}$$

Total reflection
Application: optical fibers

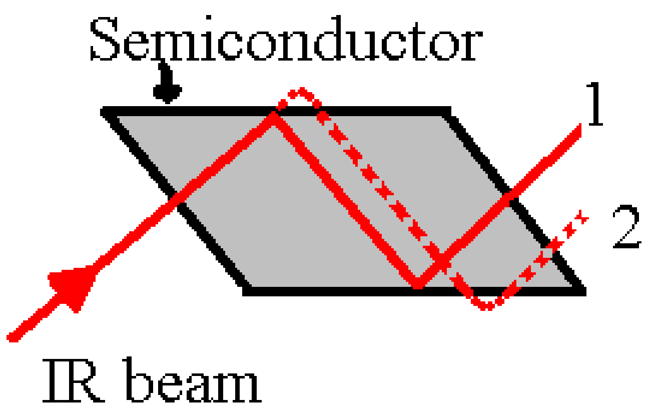


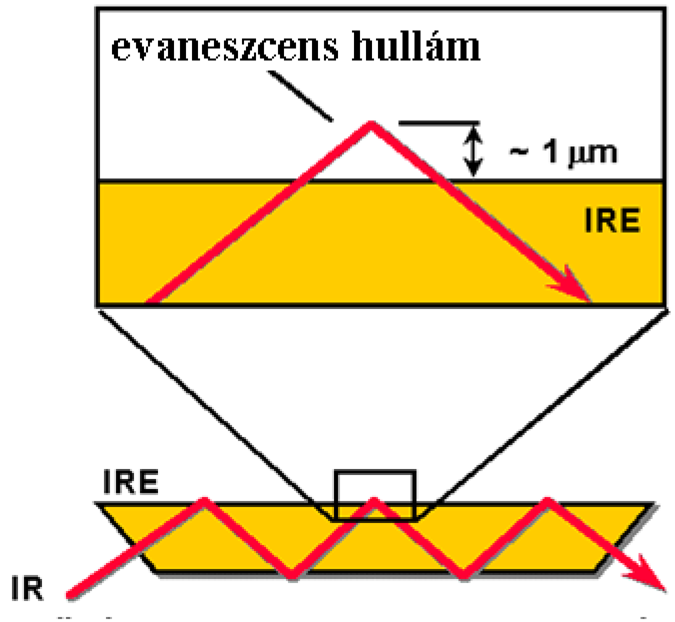


www.physics.rutgers.edu/ugrad/389/FresnelsEqns.ppt

Excitation by evanescent field:
Surface IR spectroscopy

Attenuated total reflection (ATR) spectroscopy
absorption by sample on interface attenuates
evanescent field

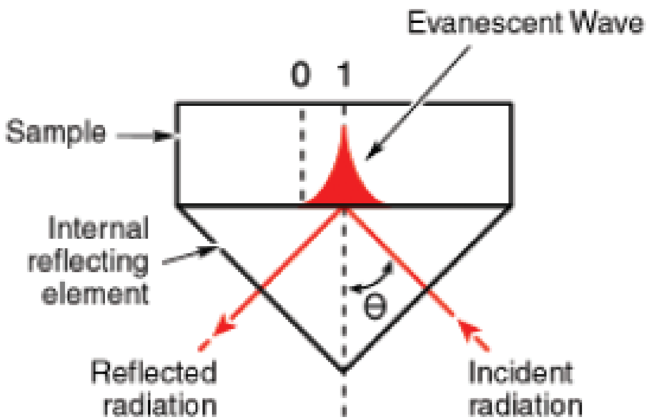




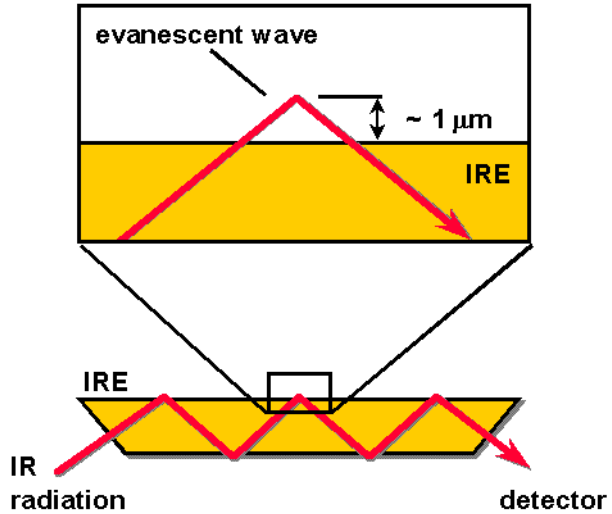
www.piketech.com,

Francis M. Mirabella, Jr. (Ed.)-Internal reflection spectroscopy, Marcel Dekker, Inc. (1993)

ATR methods



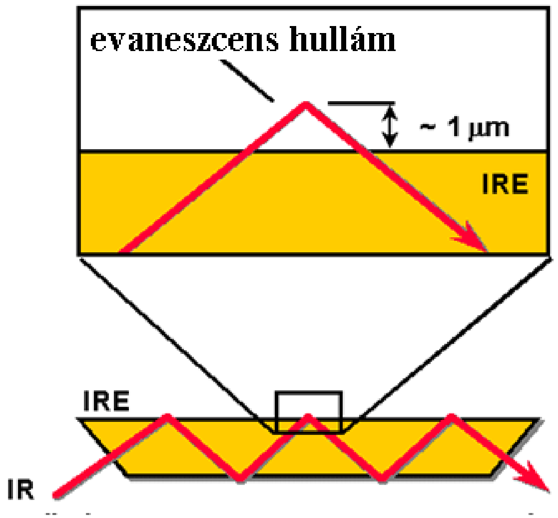
Single-bounce

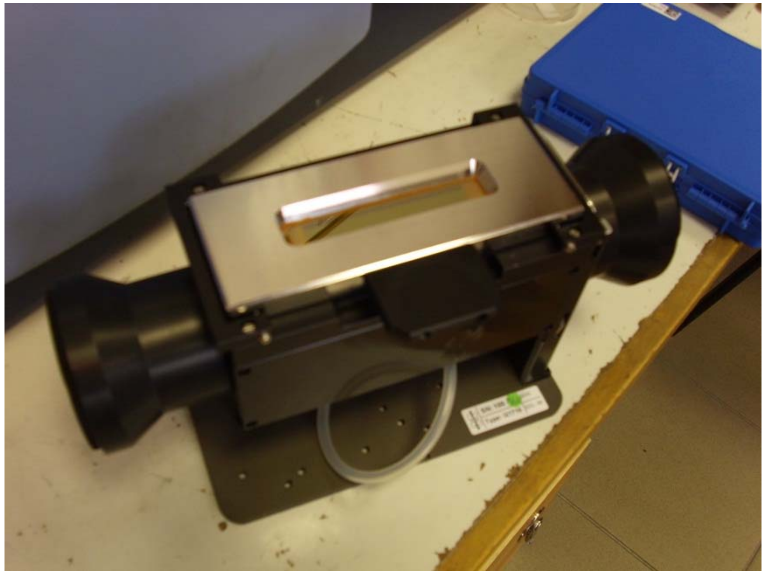


Multibounce

Sample close to interface boundary shows specific absorption

Multi-bounce liquid cell

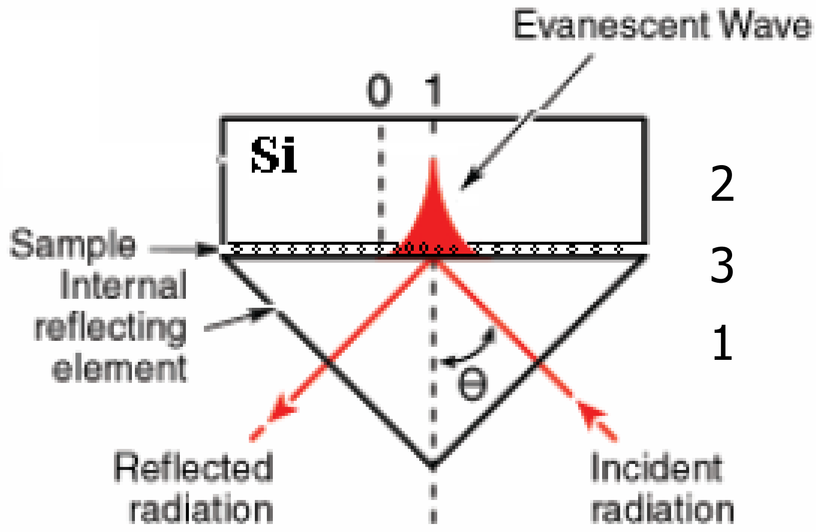




ATR probes a narrow layer close to the surface – solvents with high absorption give measurable signal

Thin films
(atomic monolayers)

$$\theta_{12} = \sin^{-1} n_{21}$$
$$\theta_{13} = \sin^{-1} n_{31}$$

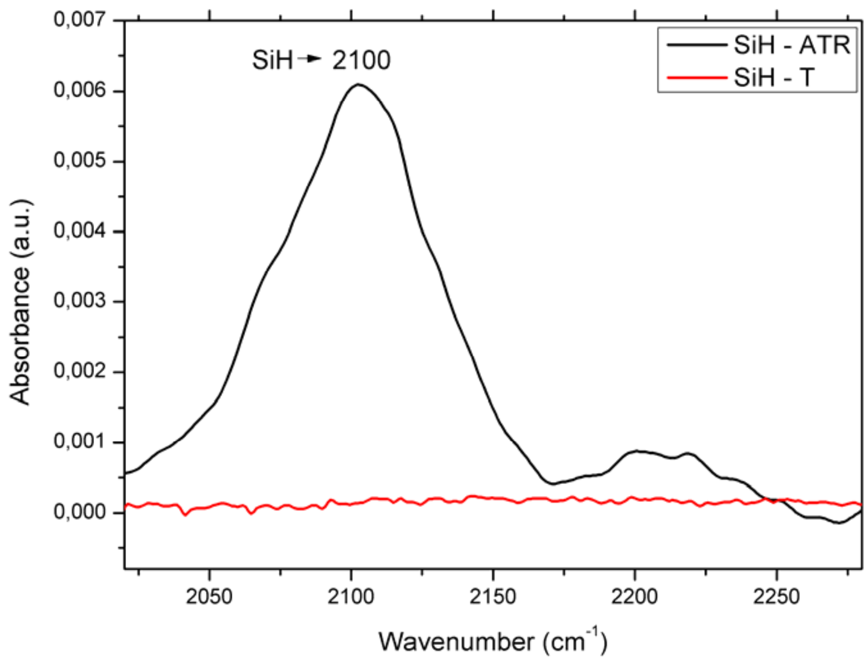


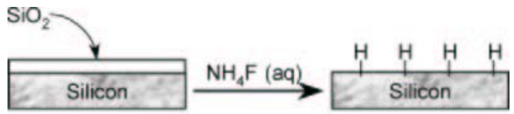
Condition of observation: $\theta > \theta_{13}$
Samples with higher index of refraction can be measured

if $d > d_p$ signal comes only from sample, if $d < d_p$ substrate has to be taken into account

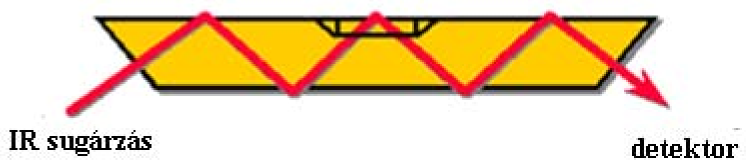
Francis M. Mirabella, Jr. (Ed.)-Internal reflection spectroscopy, Marcel Dekker, Inc. (1993)

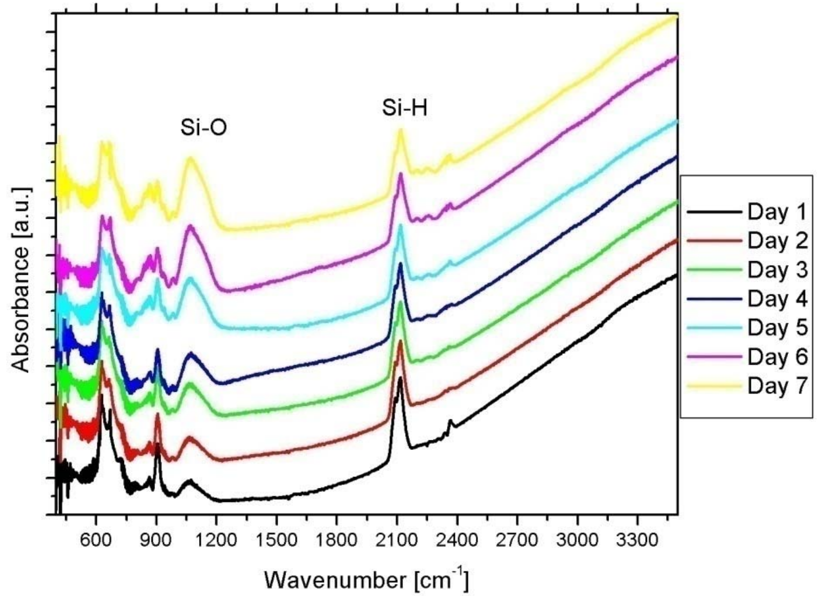
Study of adsorbed hydrogen monolayers on silicon by multi-bounce ATR





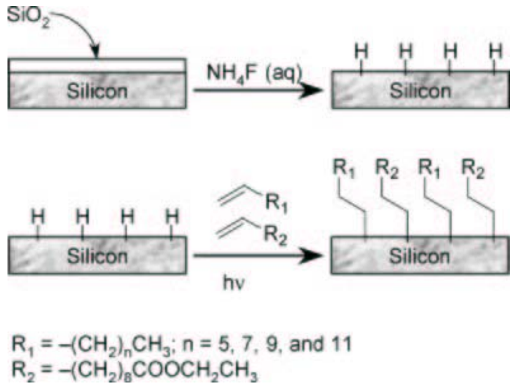
Szekrényes Zsolt, 2008



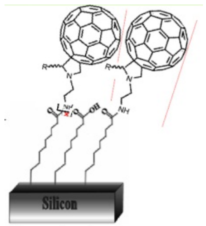


A.E. Pap, Cs. Dücső, K. Kamarás, G. Battistig, I. Bársony: *Mat. Sci. Forum* **573-574**, 119-131 (2008)

Complex molecules on Si substrate

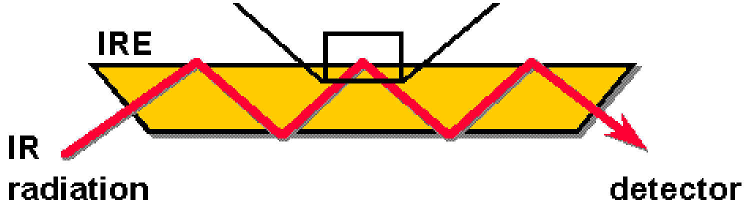


Y.-J. Liu, N.M. Navasero, H.-Z. Yu:
Langmuir **20**, 4039 (2004)



C_{60} – silicon hybrid materials
F. Cattaruzza, M. Prato et al.

Substrate: ATR crystal

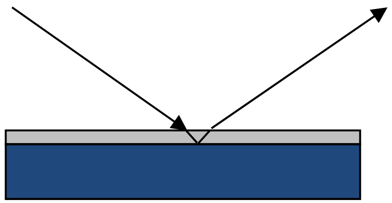


ATR crystal properties

	n_1	ATR Range, cm^{-1}	d_p, for $n_2 = 1.5$ $\lambda = 1000$ cm^{-1}	Water Solubility, g/100g	pH Range	Hardness, Kg/mm
AMTIR	2.5	11,000-625	1.70	Insoluble	1-9	170
Diamond/ZnSe	2.4	30,000-525	2.01	Insoluble	1-14	5,700
Diamond/KRS-5	2.4	30,000-250	2.01	Insoluble	1-14	5,700
Germanium	4.0	5,500-780	0.66	Insoluble	1-14	550
KRS-5	2.37	17,900-250	2.13	0.05	5-8	40
Silicon	3.4	8,900-1,500	0.85	Insoluble	1-12	1150
Silicon/ZnSe	3.4	8,900-525	0.85	Insoluble	1-12	1150
ZnS	2.2	17,000-850	3.86	Insoluble	5-9	240
ZnSe	2.4	15,000-525	2.01	Insoluble	5-9	120

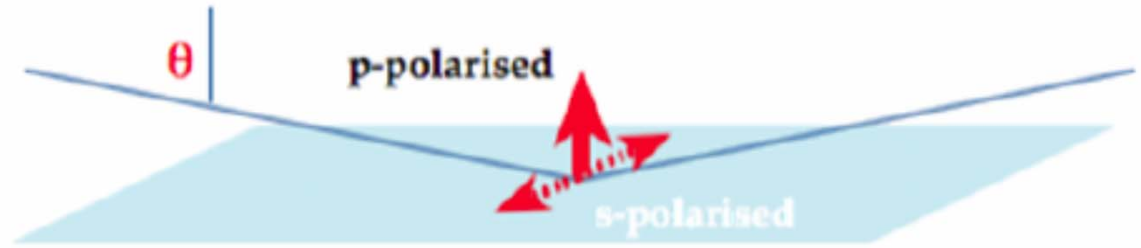
Absorption by crystal (mostly multiphonon) can limit useful frequency range

RAIRS, IRRAS – Reflection-absorption IR spectroscopy



Reflecting substrate

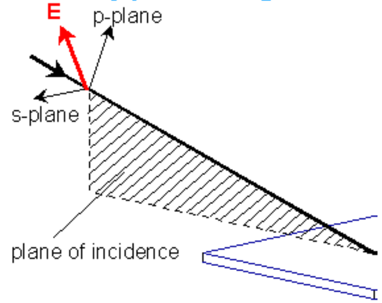
Dipole scattering on metallic surface
External reflection, non-normal incidence



Metal surface screening

Metal surface dipole selection rule

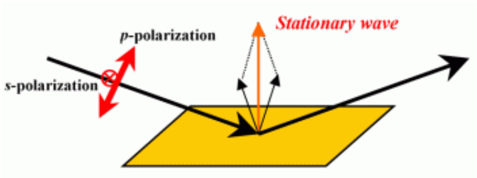
On metal surfaces, due to the screen effects of free electron in the substrate, the dynamic dipole parallel to the substrate is cancelled by its image, while the dynamic dipole perpendicular to the surface is enhanced by its image. Therefore, only the vibration modes with component along the surface normal can be measured in RAIRS.

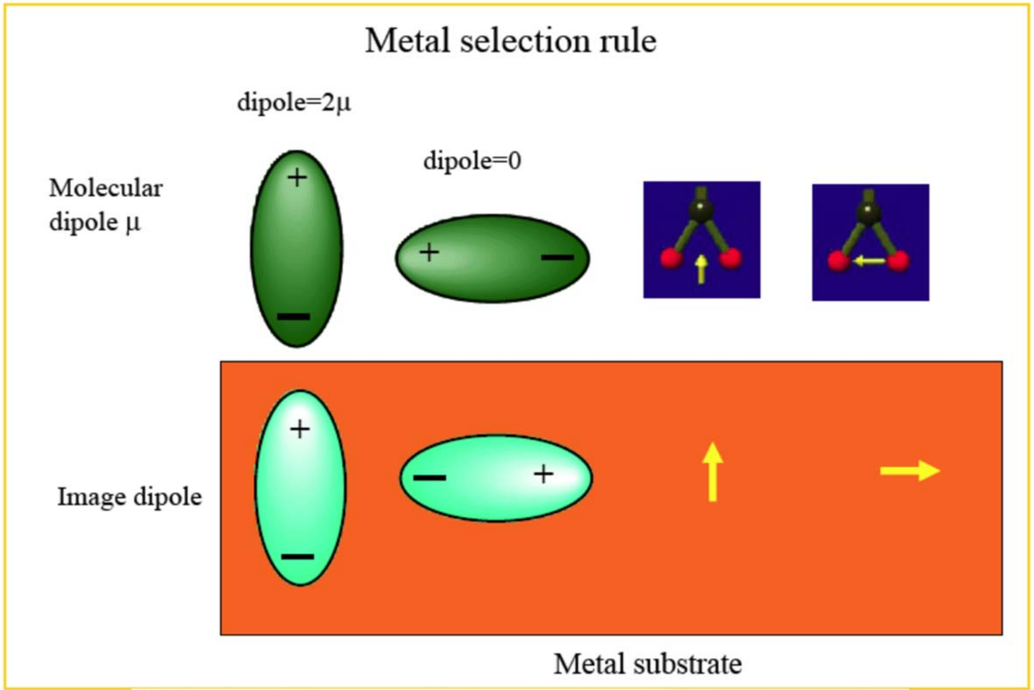


p = parallel
s = perpendicular
(senkrecht)
to plane of incidence

http://www.sussex.ac.uk/Users/qc25/

IRRAS surface selection rules



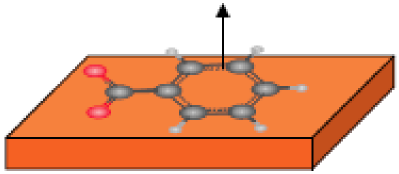


Determination of surface orientation

RAIRS of benzoate on Cu(110) as a function of surface coverage

Determine the polar orientation

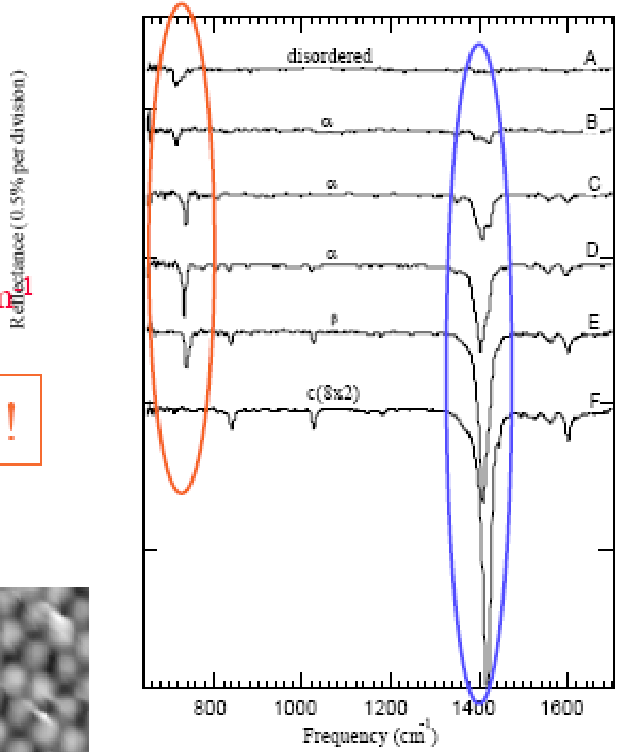
$<1000 cm^{-1}$



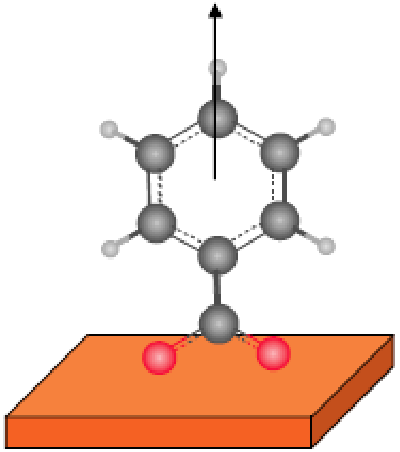
Surface IR active modes

CH out-of-plane bending at $770 cm^{-1}$

Flat-lying molecule!!



$>1000 cm^{-1}$

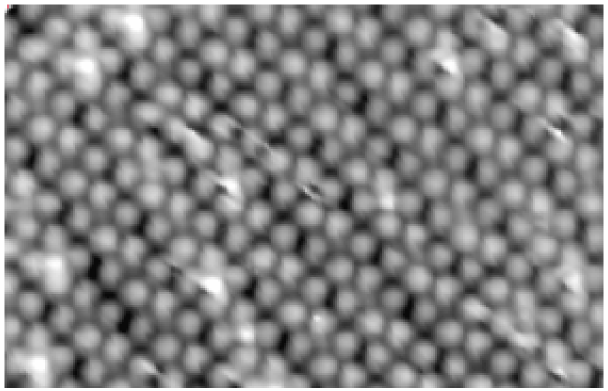


Surface IR active modes

C-C stretch

CO_2 symmetry stretch at $1420 cm^{-1}$

Up-right molecule!!



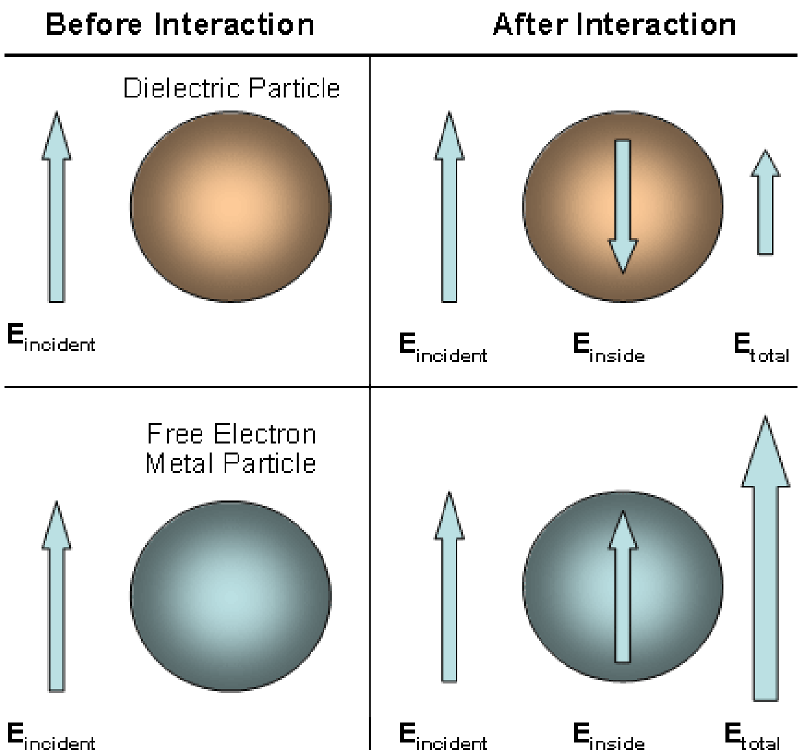
http://www.sussex.ac.uk/Users/qc25/

Surface-enhanced Raman spectroscopy (SERS)

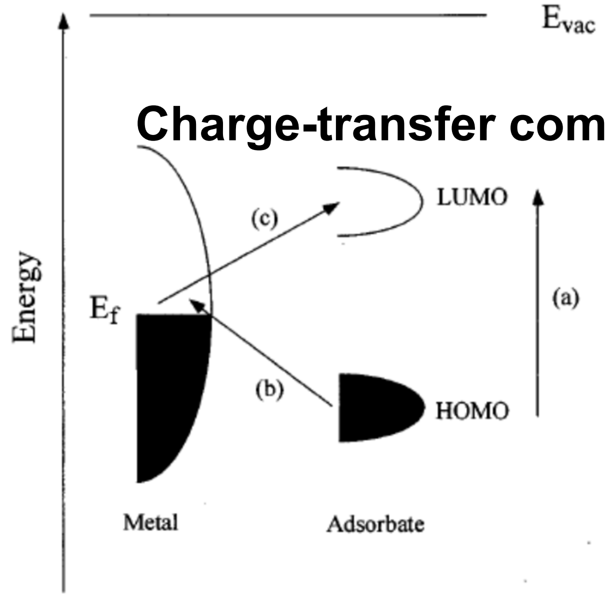
Tarczay György – Rezgési spektroszkópia, ELTE

Fleischman and Van Duyne 1970-s: surface of **Ag** electrodes

Electromagnetic enhancement



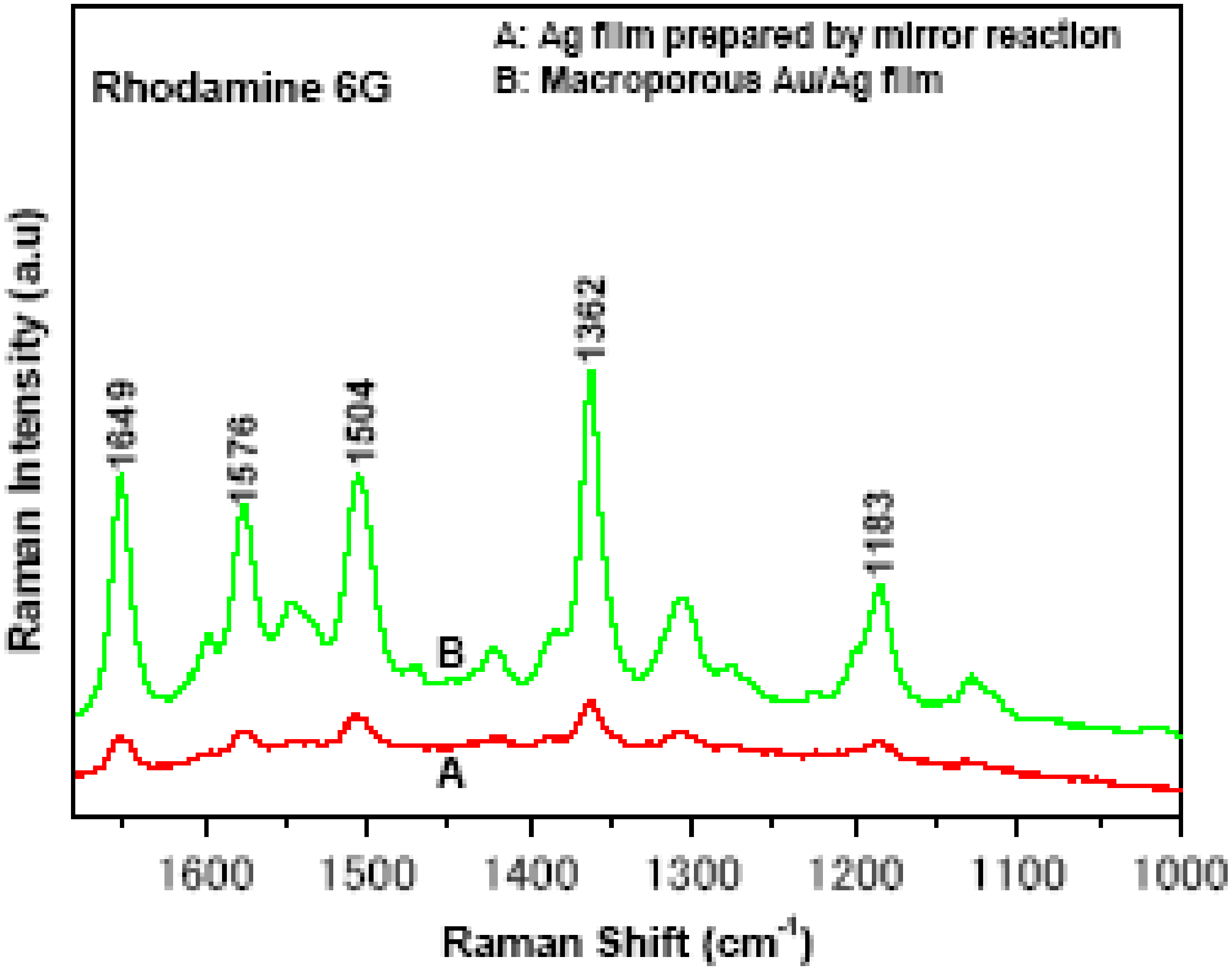
Chemical enhancement



Charge-transfer complexes

Fig. 1 Typical energy level diagram for a molecule adsorbed on a metal surface. The occupied and unoccupied molecular orbitals are broadened into resonances by their interaction with the metal states; orbital occupancy is determined by the Fermi energy. Possible charge transfer excitations are shown.

Intensity AND frequency change!


Rhodamine 6G
A: Ag film prepared by mirror reaction
B: Macroporous Au/Ag film
1649
1576
1504
1362
1183
B
A
1600
1500
1400
1300
1200
1100
1000
Raman Shift (cm-1)
Raman Intensity (a.u)

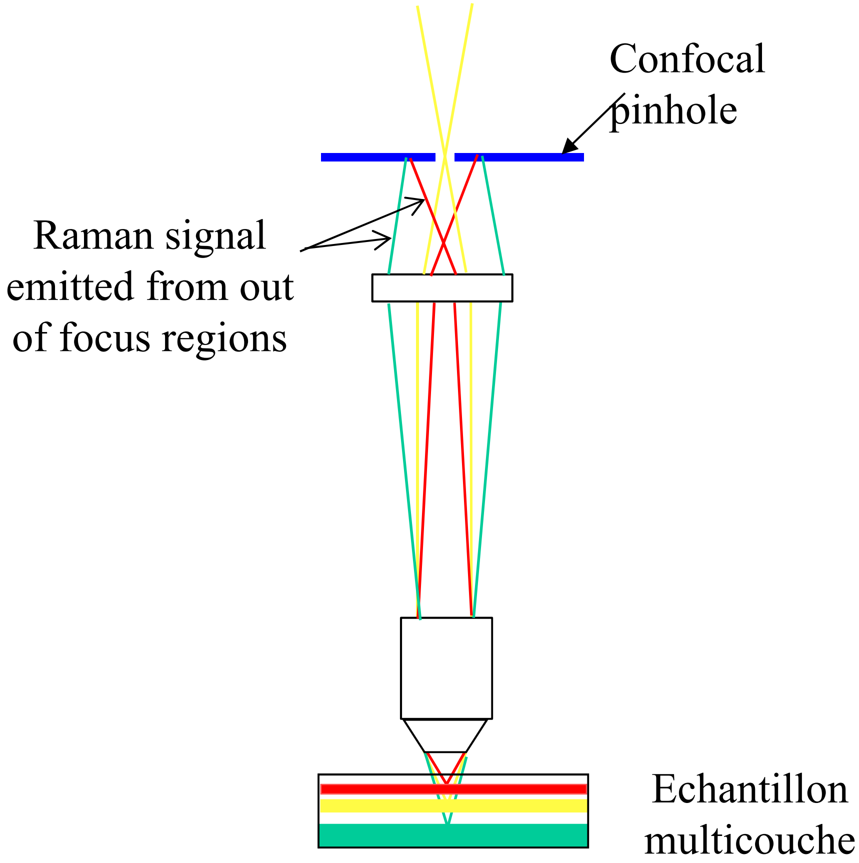
Increasing spatial resolution

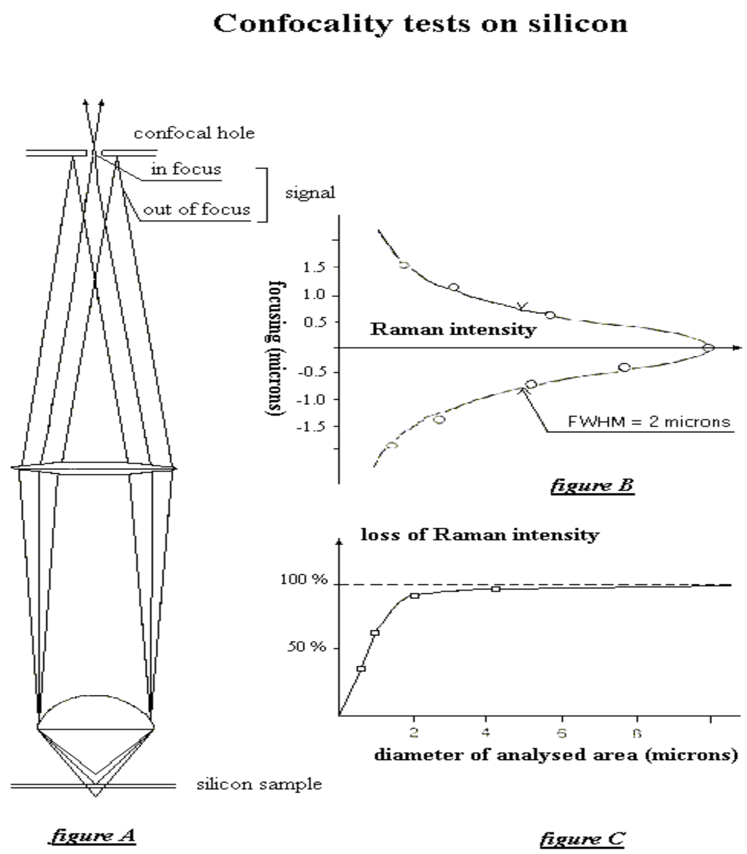
Optical microscope

- Far field: Diffraction limit ~ λ/2 lateral resolution
  Infrared: ~ 5 μm, Raman: ~ 200 nm
  axial resolution can be increased by confocal arrangement
  Raman: selective resonance

- Near field: SNOM (scanning near-field optical microscopy)
  TERS (tip-enhanced Raman spectroscopy)

Confocal Raman microscope





The confocal pinhole acts as an adjustable spatial filter allowing a precise selection of the analysed volume

Horiba Jobyn-Yvon

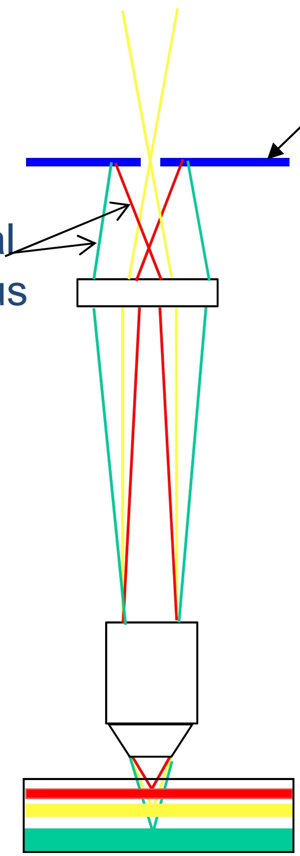
Advantages of confocal Raman

- Tremendous improvement of the axial resolution (~2 μm)
- Better lateral resolution (<1μm)
- Efficient reduction of fluorescence interference

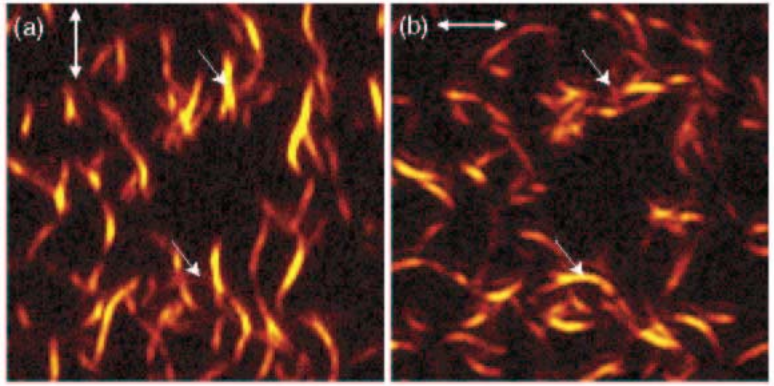
Expanding Raman Applications

- Minute samples quantities – micron and sub-micron particles
- Thin films and multilayer samples
- Inclusions in matrices
- IMAGING : phases and components distribution (copolymers, composite materials…etc

Confocal Raman microscopy – axial and lateral resolution



Source: Horiba Jobin-Yvon



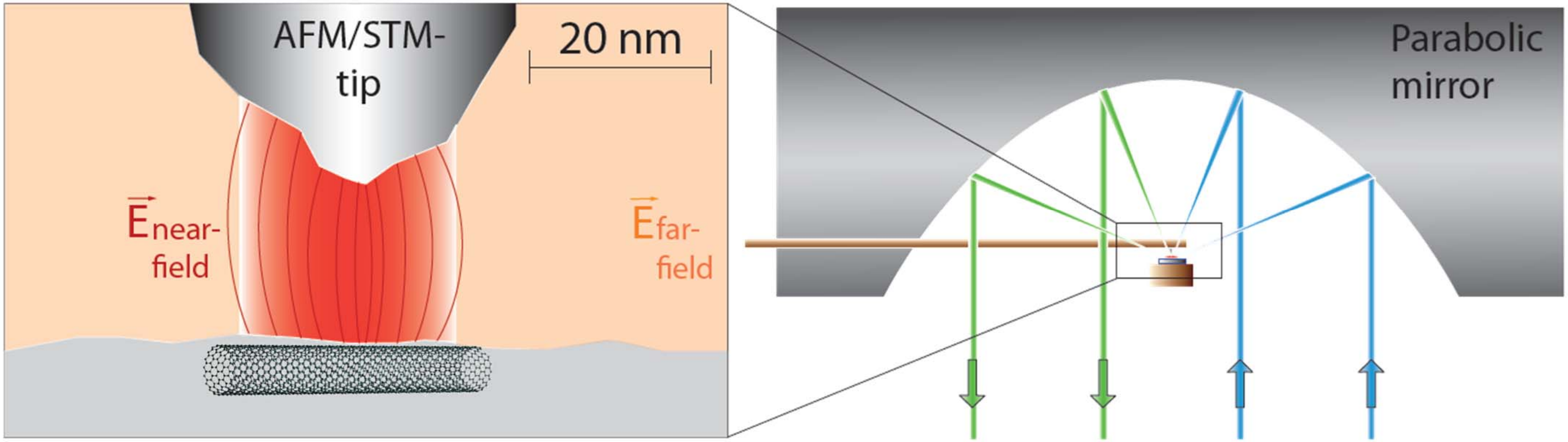
Confocal Raman image of carbon nanotube bundles

A. Hartschuh, E.J. Sánchez, X.S. Xie, L. Novotny:
Phys. Rev. Lett. **90**, 095503 (2003)

Confocal aperture acts as a spatial filter – measured volume can be limited

Tip-enhanced Raman spectroscopy (TERS)

Botka Bea

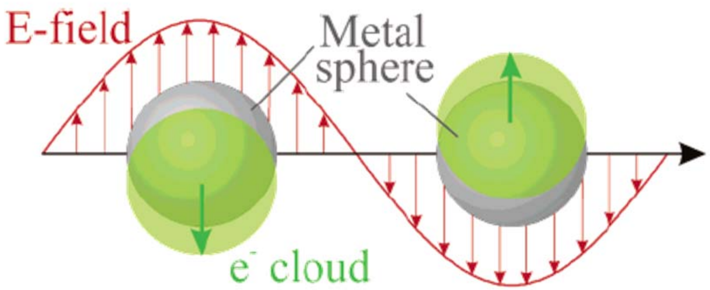


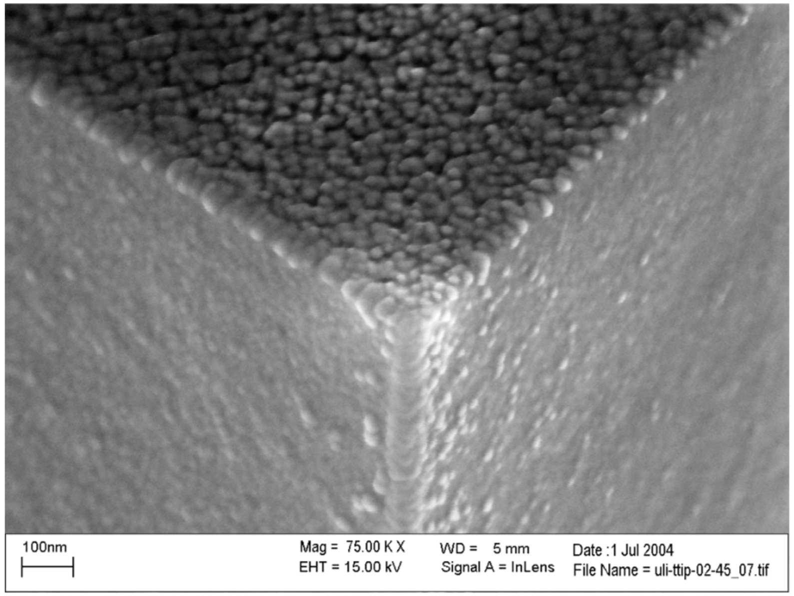
Walther-Meissner Institute, Garching, Germany

N. Chelwani, D. Hoch, D. Jost, B. Botka, J.-R. Scholz, R. Richter, M. Theodoridou, F. Kretzschmar, T. Böhm, K. Kamarás, R. Hackl: *Appl. Phys. Lett.* **110,** 193504-193507 (2017)

Enhancement mechanism

$\lambda_{light} >> d_{particle}$



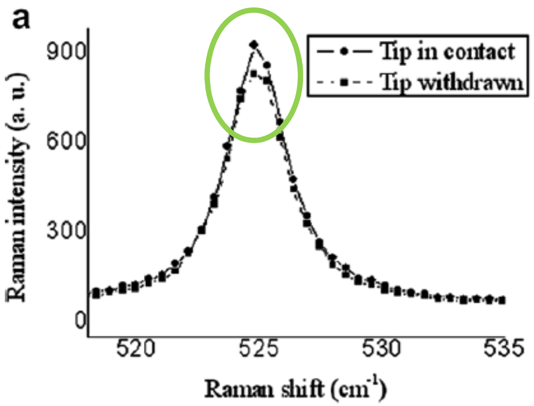


surface plasmon: collective electron excitation

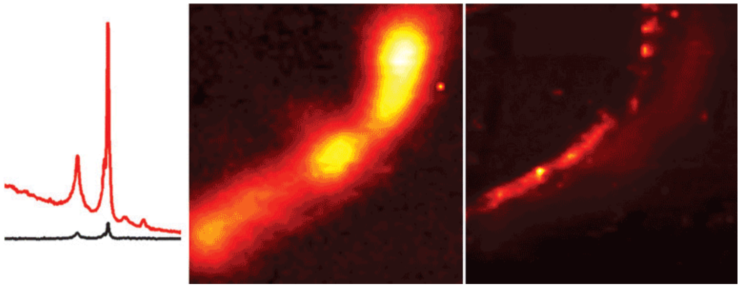
electrostatic lightning rod effect

Enhancement and contrast

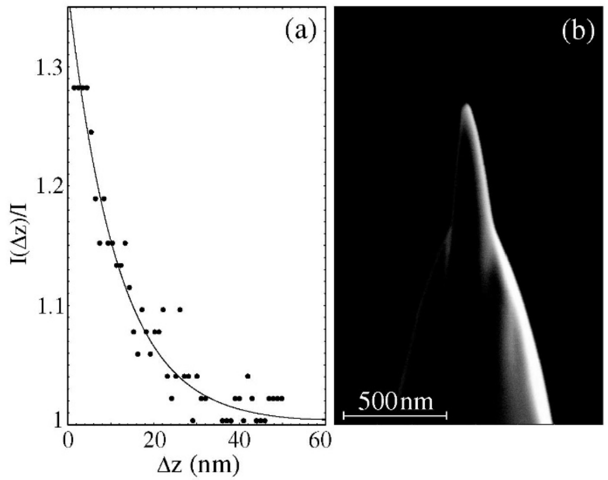
- contrast: $I_{near\ field} / I_{far\ field}$
- enhancement: contrast weighted by illuminated area
- contrast determined by focus area

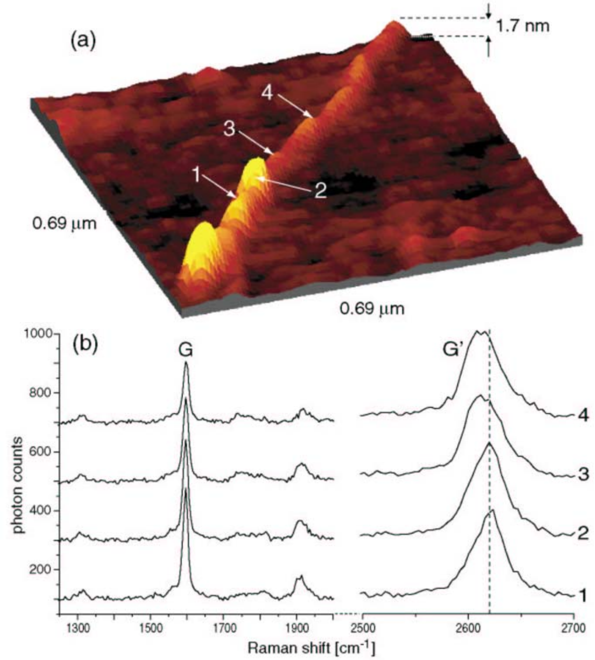


Example: carbon nanotubes



Tip-enhanced Raman spectroscopy on carbon nanotubes





A. Hartschuh, E.J. Sánchez, X.S. Xie, L. Novotny: *Phys. Rev. Lett.* **90**, 095503 (2003)

ATR-IR based tip enhancement

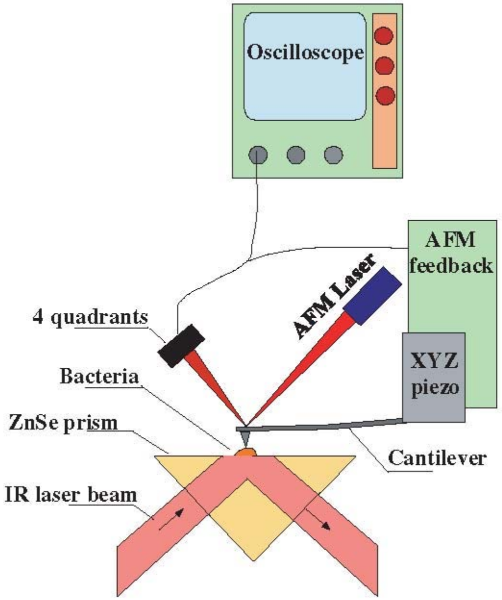
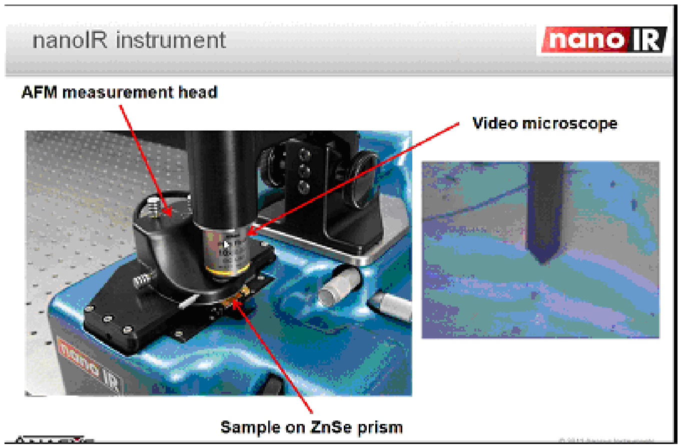


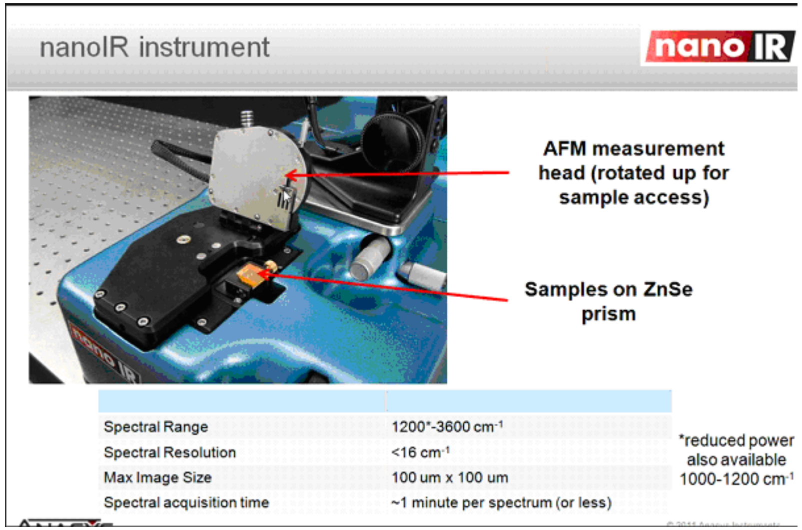
Fig. 1. Experimental setup of the AFMIR.

A. Dazzi, R. Prazeres, F. Glotin, J.M. Ortega:
Infr. Phys. Techno. **49,** 113 (2006)

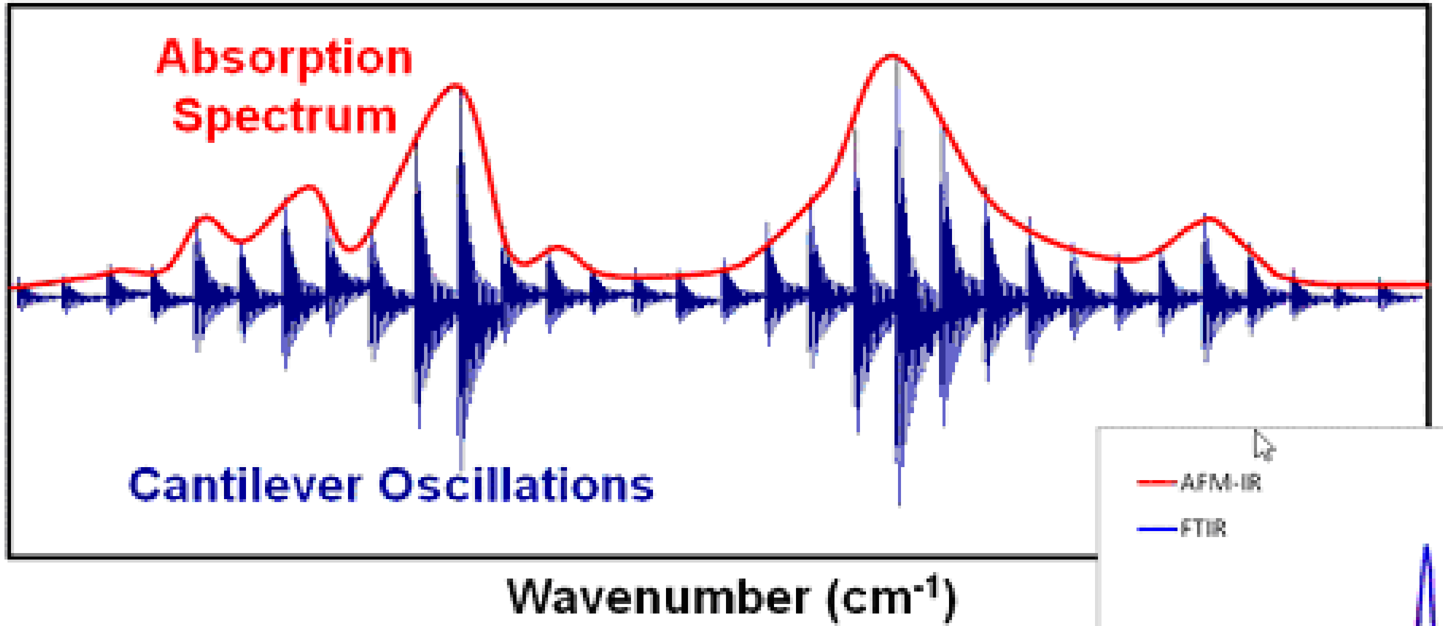
ATR crystal
short IR laser pulse
heating – acoustic wave
detection by metal-coated AFM tip

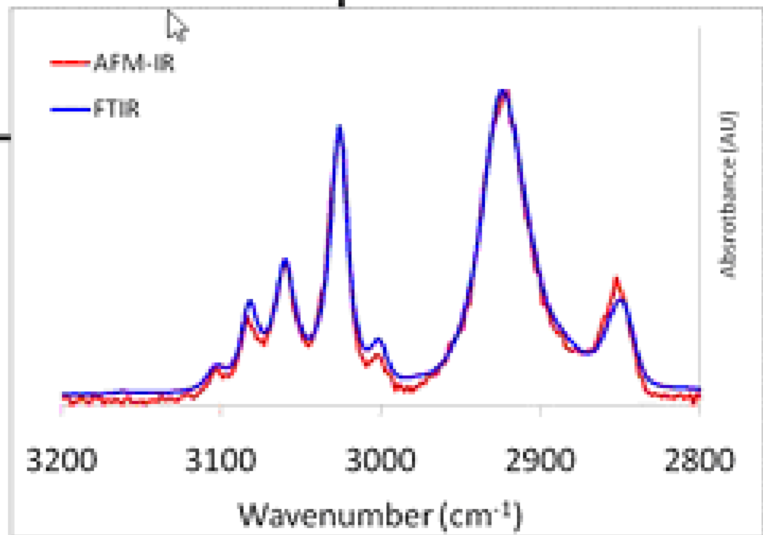


http://www.anasysinstruments.com/



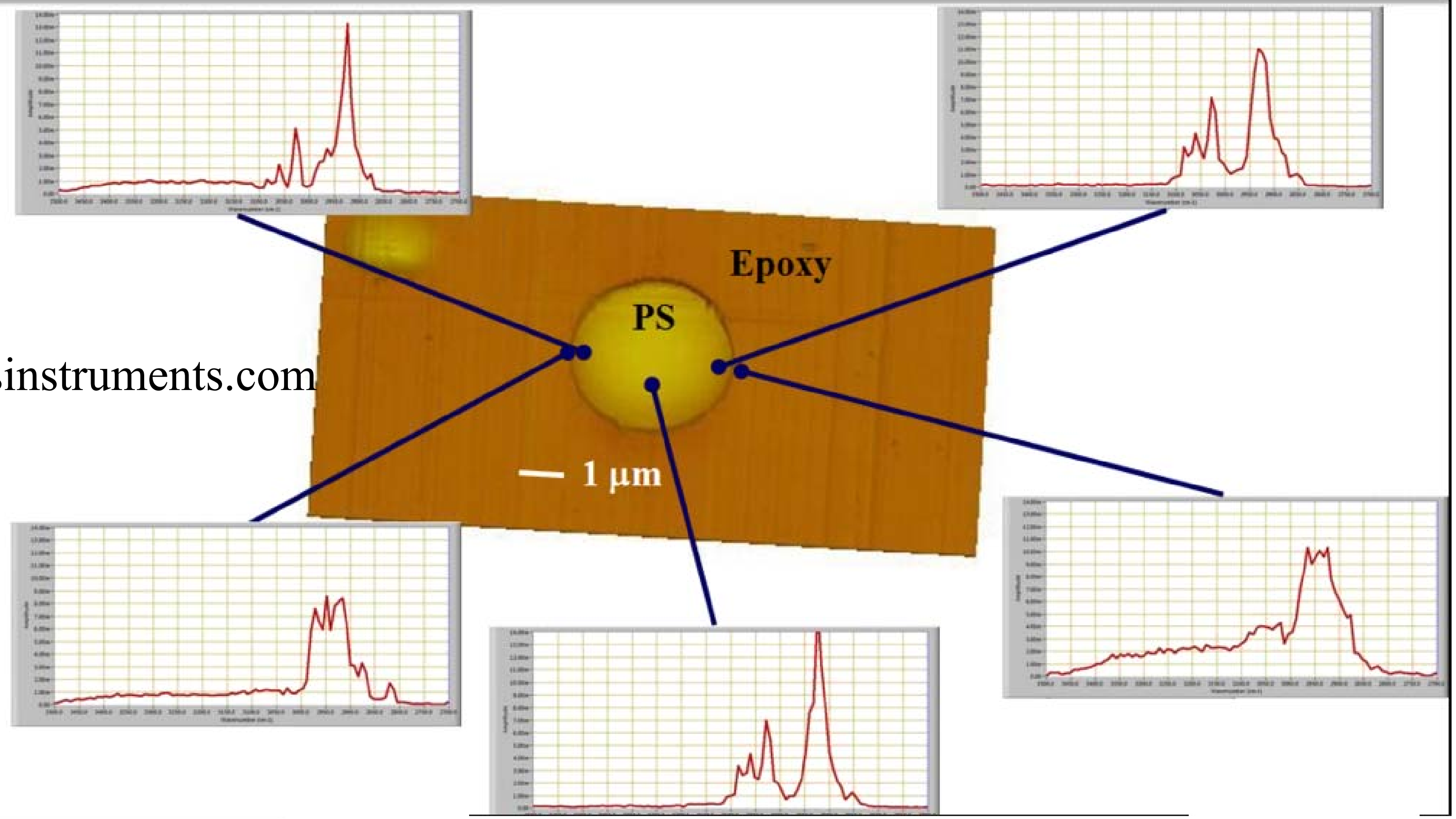
Generating a spectrum from sequential ringdowns



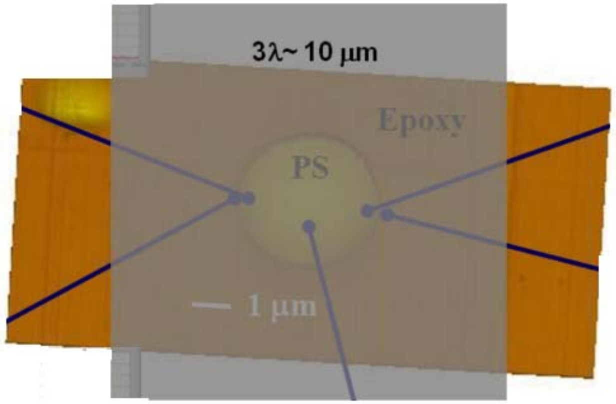


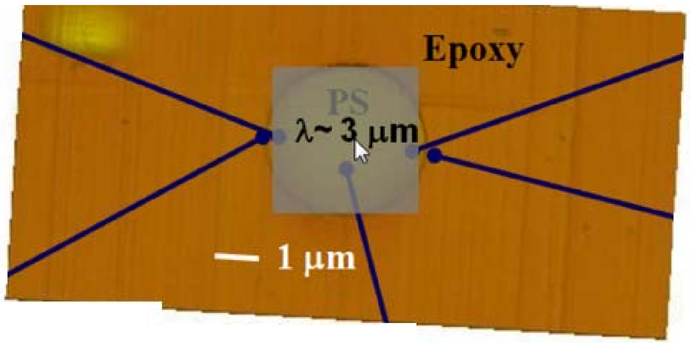
AFM contact mode

Interface mapping--PS/Epoxy Composite

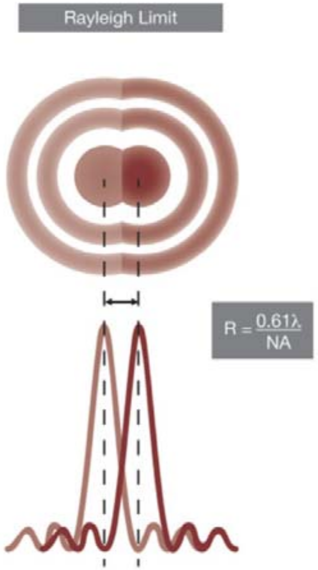


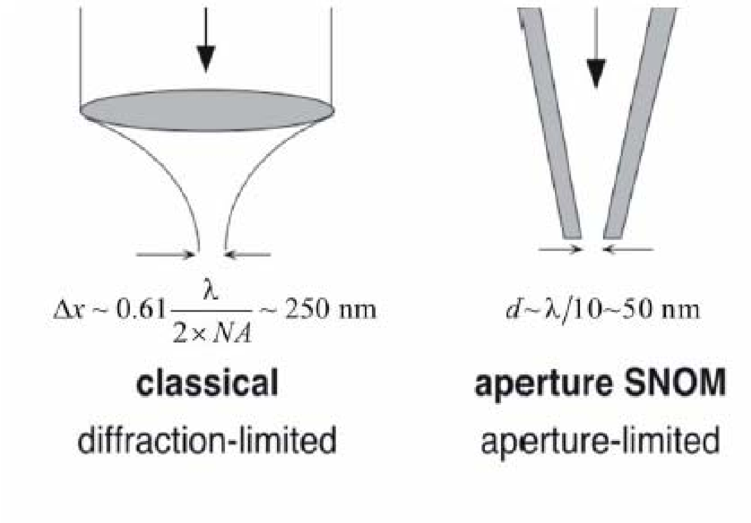
www.anasysinstruments.com

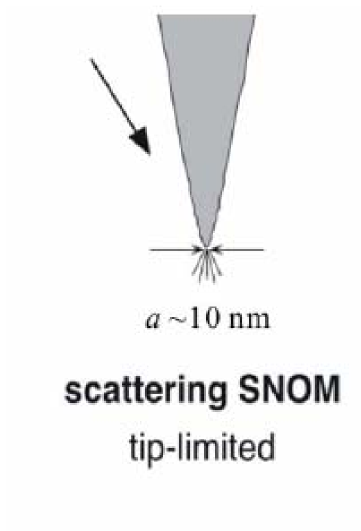




Resolution in classical microscopy and SNOM (scanning near-field optical microscopy)







$$\Delta x = \frac{0.61\lambda}{n sin(\theta)} \approx 200 - 400nm$$

- metal coated optical fiber

$d < \frac{\lambda}{2}$ - drastic decrease in T

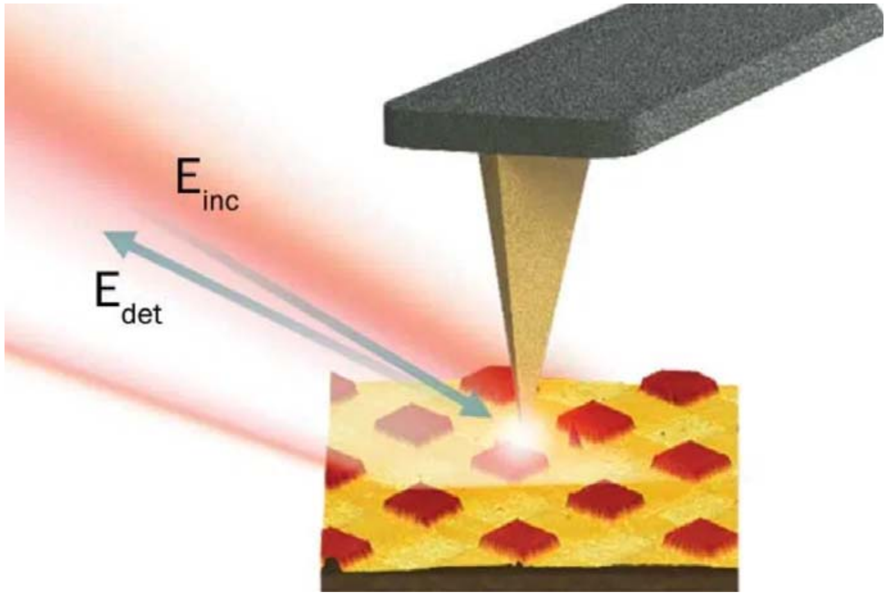
E.g. $\lambda \approx 10\mu m \quad d = 100nm$

Transmission 10^{-25}

Best: $\Delta x > \frac{\lambda}{10} \approx 1 - 2\ \mu m$

What is near field? How do we apply it for detection?

- Non-radiating part of an optical field, decays faster than 1/r
- Directly not detected, still interacts with matter, if it is close enough
- Interaction modifies scattered field of metallic probe antenna
- Challenge: isolate the part of the field, that corresponds to the near field spot



$$E_N = \sigma_N E_I$$

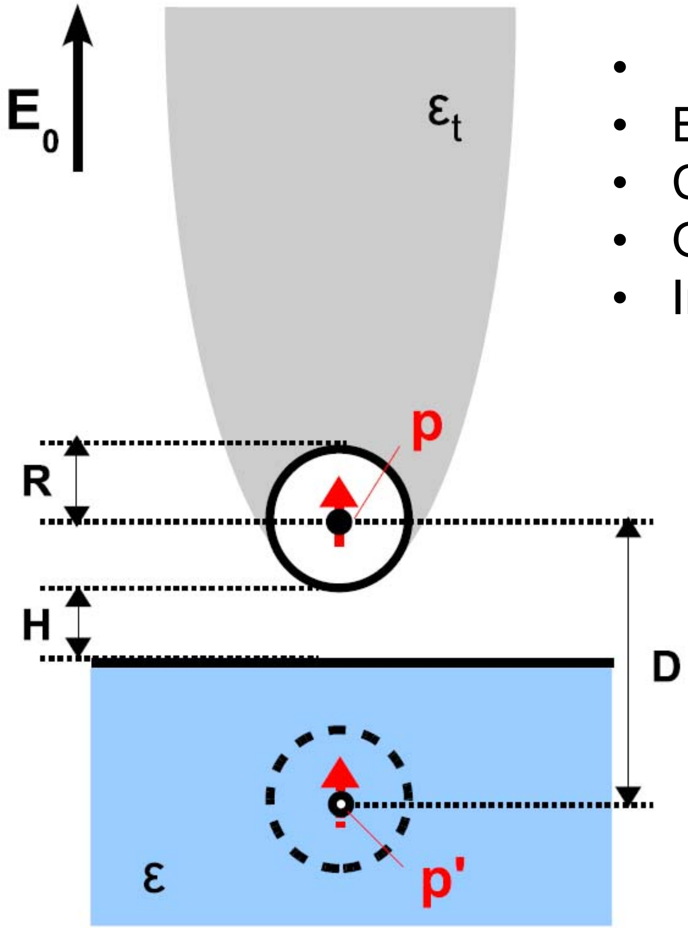
$$\sigma_N = s_N e^{i\varphi_N}$$

σ_N scattering coefficient

Near-field infrared imaging

Neaspec_NeaSNOM_sSNOM_ANSOM_principle.flv

Model for near-field detection



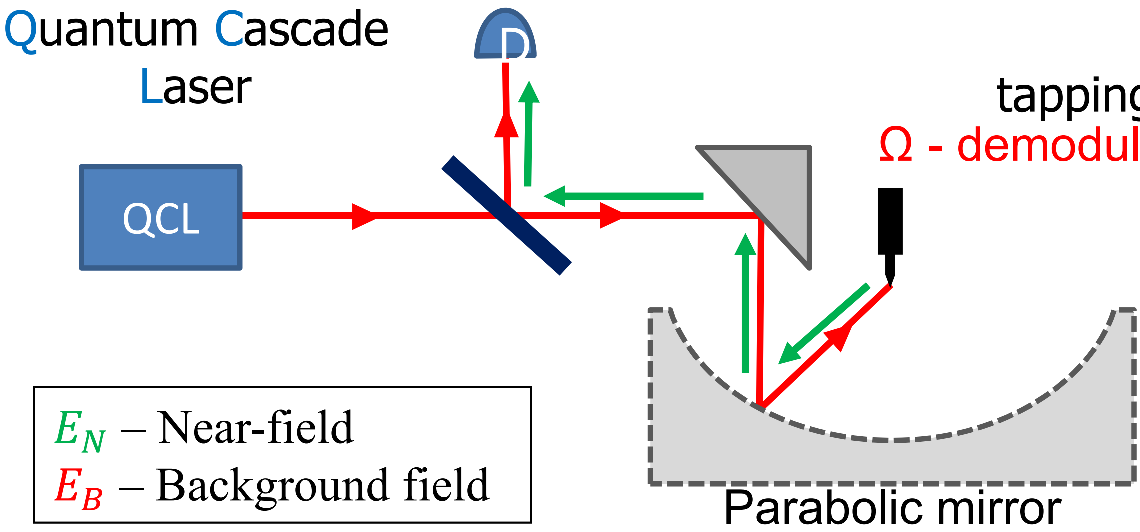
- Metal-coated AFM tip
- Evanescent electric field at tip apex
- Close to sample
- Optical near field polarizes the sample
- Interaction with near field –> scattered light

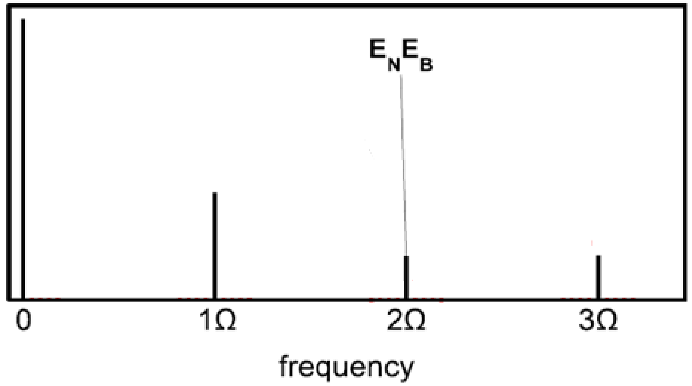
Detecting scattering from near field spot

Aim is material specific detection, no geometric artefacts

$$E_N = \sigma_N E_I$$

$$\sigma_N = s_N e^{i\varphi_N}$$



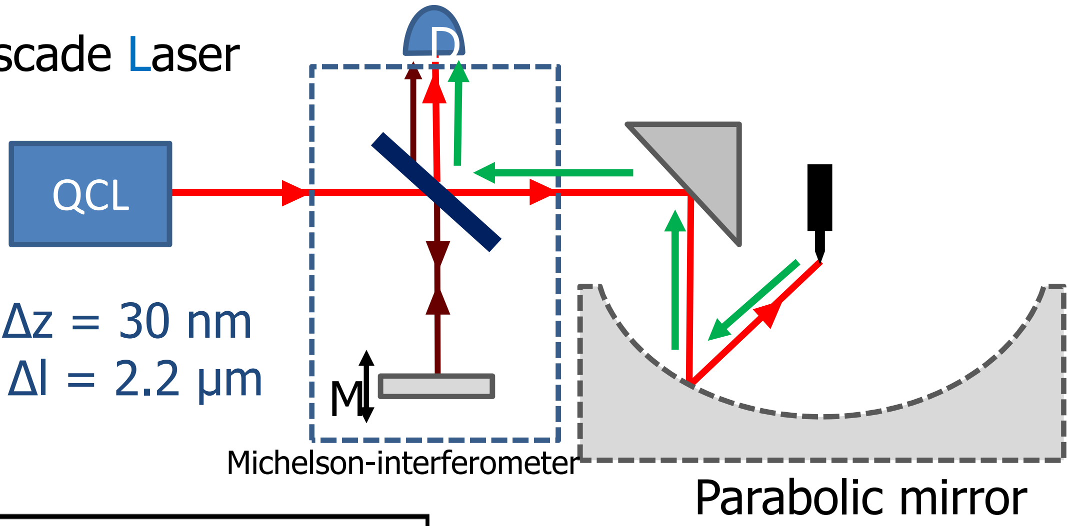


$$I = |E_B + E_N|^2 \Rightarrow E_B^2 + E_N^2 + 2E_N E_B$$

Still contains background electric field

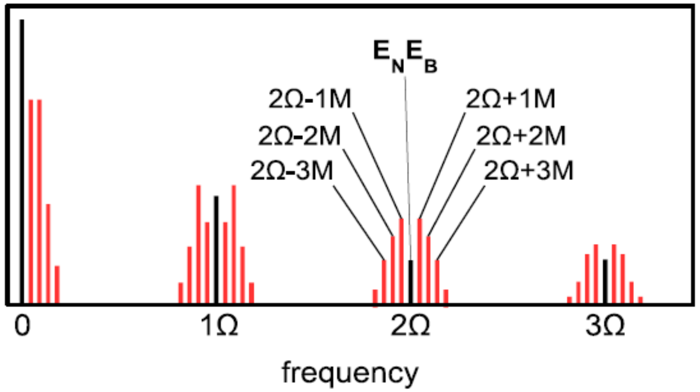
Eliminating the background: Pseudo-heterodyne detection

Quantum Cascade Laser



Ω = 30 kHz, Δz = 30 nm
M = 400 Hz, Δl = 2.2 μm

E_N – Near-field
E_B – Background field
E_R – Reference field



$$\sigma_N = s_N e^{i\varphi_N}$$

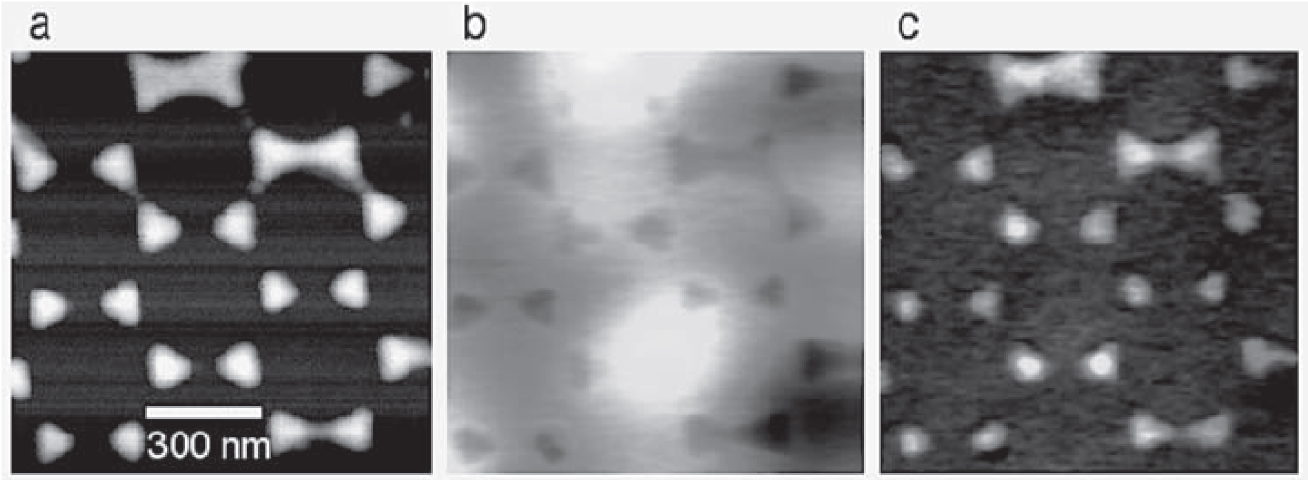
$$s_n = \sqrt{|C_{n\Omega+M}|^2 + |C_{n\Omega+2M}|^2}$$

$$\varphi_n = \arctan\frac{|C_{n\Omega+M}|}{|C_{n\Omega+2M}|}$$

Based on scattering theory:
A ~ $Im(\sigma_n)$
R ~ $Re(\sigma_n)$

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

Demodulation at higher harmonics



AFM topography (20 nm high Au islands)

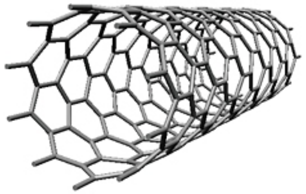
O1 (strong background scattering)

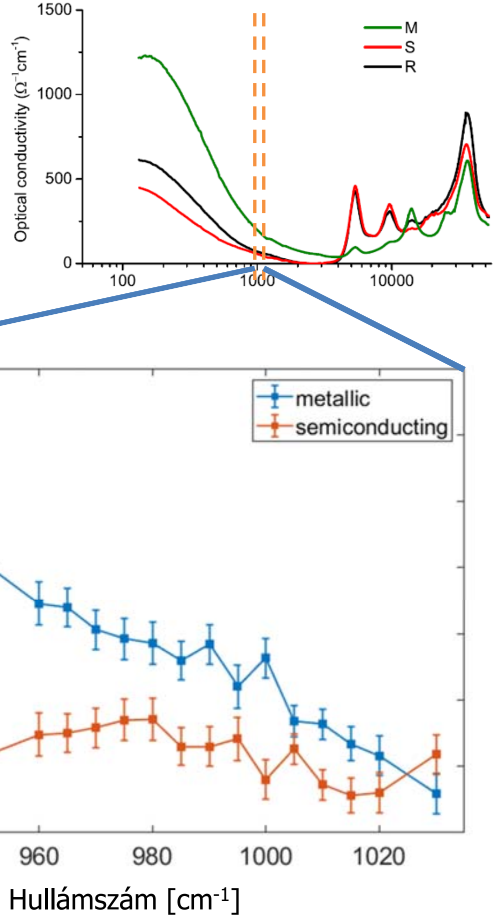
O3 (clear near-field)

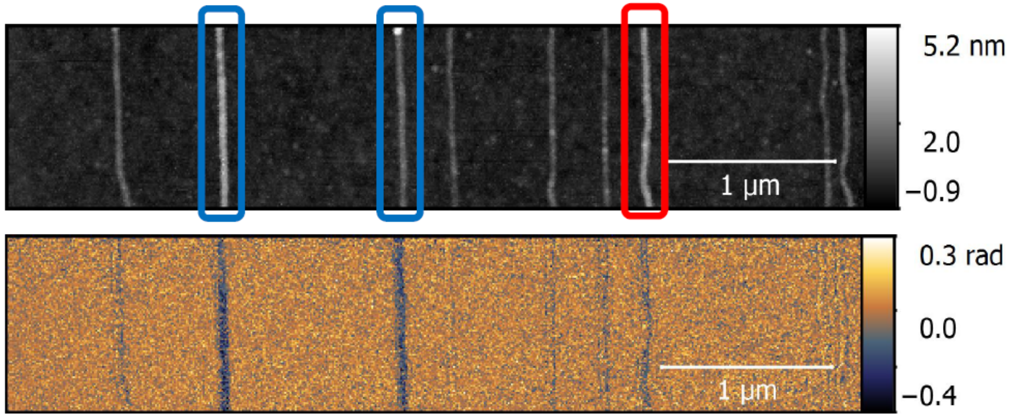
Hillenbrand, R., B. Knoll, and F. Keilmann. "Pure optical contrast in scattering-type scanning near-field microscopy." *Journal of microscopy* 202, no. 1 (2001): 77-83.

Single-walled carbon nanotubes

- Individually grown nanotubes
- Diameter: 0.8 – 3 nm
- metallic and semiconducting





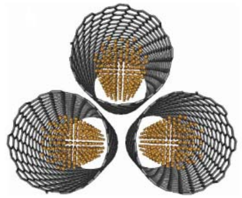


G. Németh et al., physica status solidi (b), 253 (12), 2413-2416 (2016)

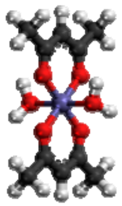
G. Németh et al., Physica status solidi (b), 254(11), 1700433 (2017)

Metals give stronger contrast

Carbon nanotube hybrid systems

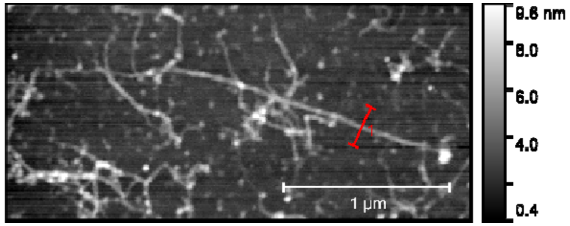


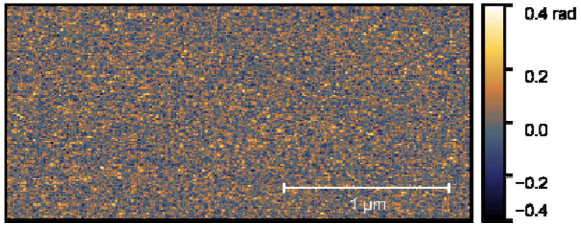
Ni(II)-acetylacetonate encapsulation
and reaction due to heating



Gergely Németh

Before heating

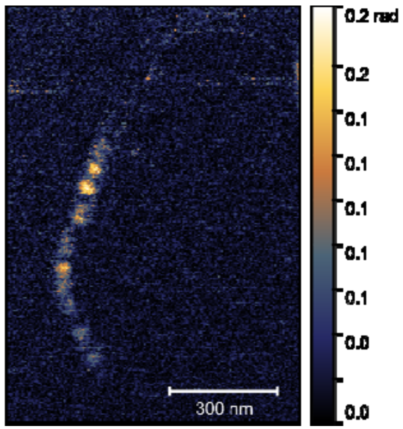


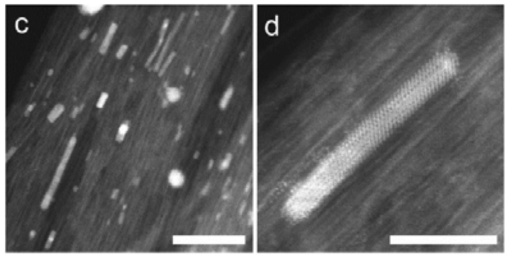


After heating

Ni metal clusters
give strong IR contrast

Detection limit
~ 700 atoms

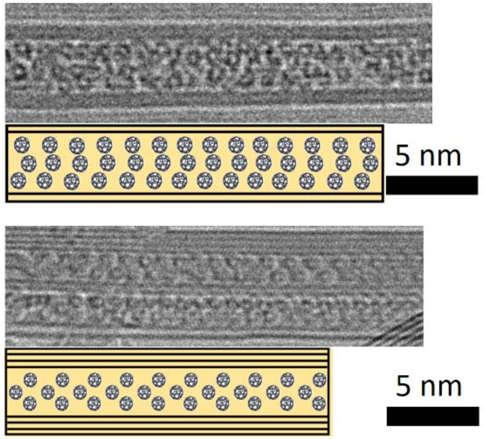


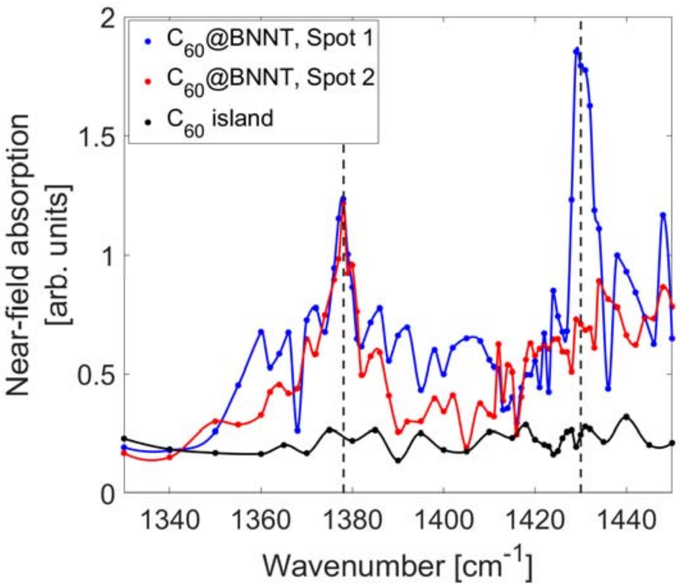


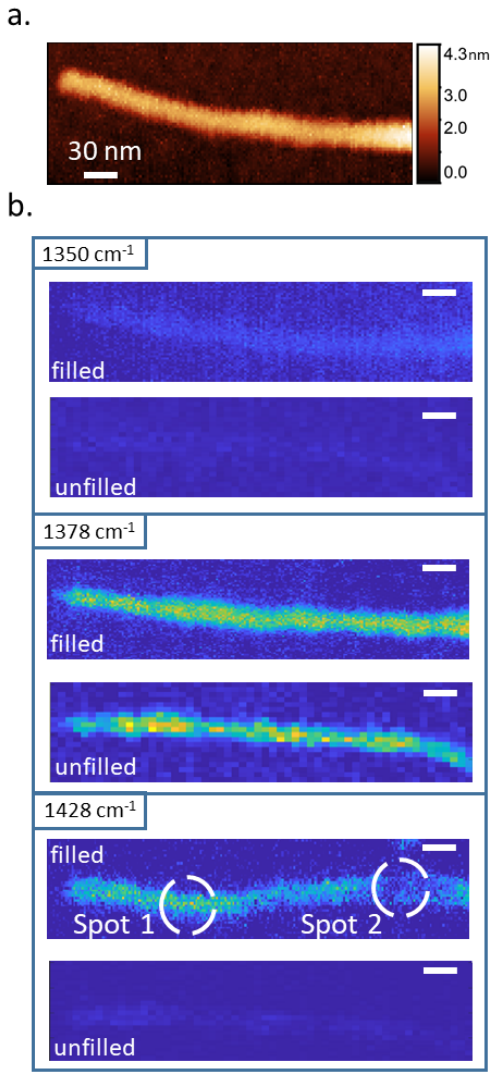
TEM by Béla Pécz

G. Németh et al., RSC Adv., 59, 34120-34124 (2019)

Boron nitride nanotube hybrid systems: C_{60}@BNNT







Dániel Datz

Detection limit
~ 160 C_{60} molecules

http://arxiv.org/abs/2008.06521
D. Datz et al.: ACS Appl. Nano Mater.,
doi=10.1021/acsanm.1c00064