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Scannig Probe Microscopy (SPM)

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Microscopic metods by resolution

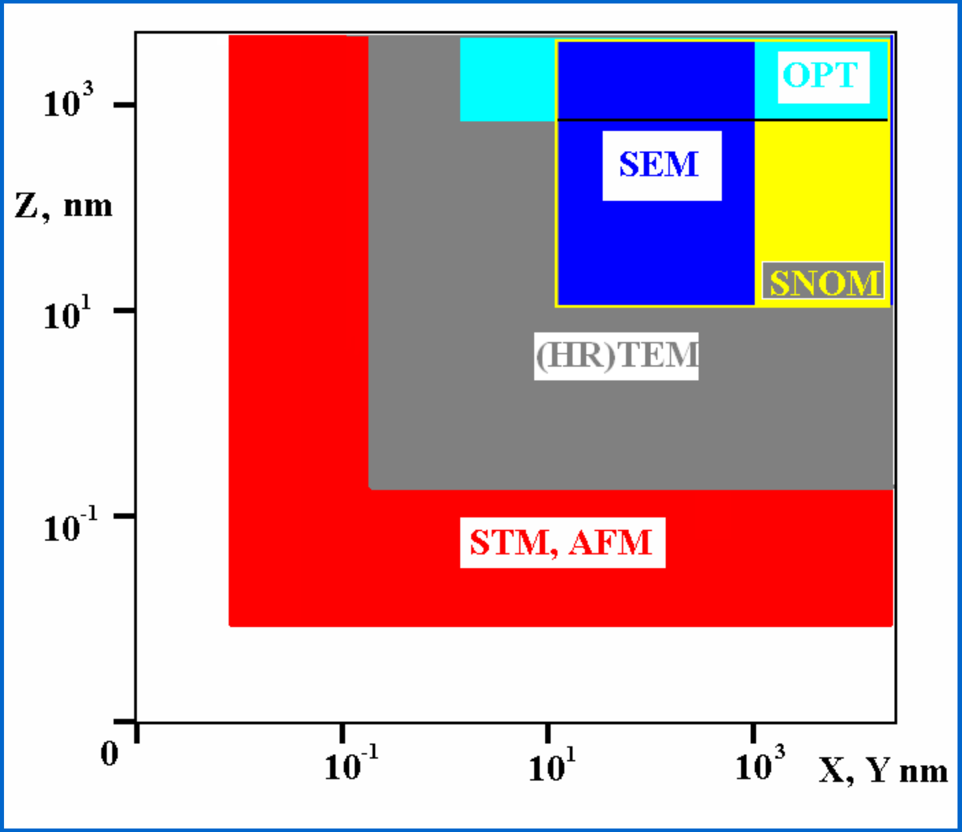
OPT: optical microscopy

SNOM: scanning near-field optical microscopy

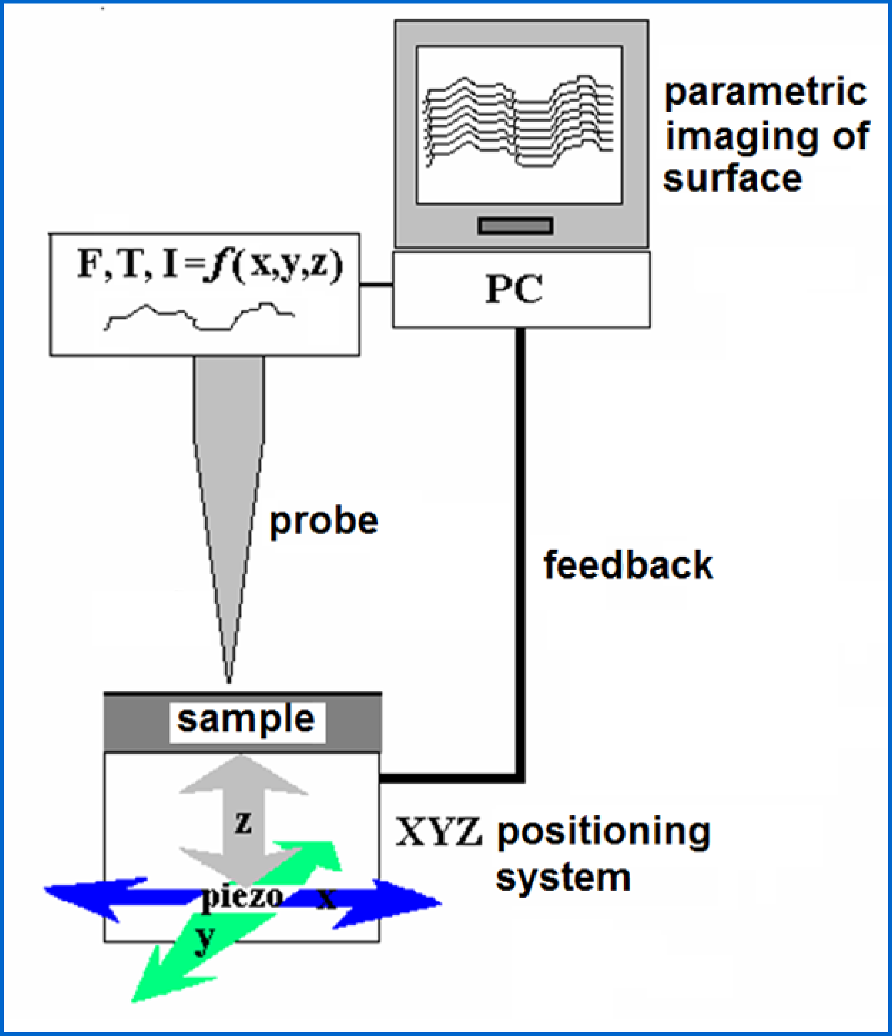
SEM: scanning electron. microscopy

HRTEM: high resolution transmission el. microscopy

STM,AFM:
tunneling microscopy,
atomic force microscopy



Scanning Probe Microscopy
Arrangement



SPM methods by information acquired

Charge Transfer

Electrons - **STM**

Ions - electrochemical microscopy **ECM**

Force interaction - AFM

Long range: magnetic, coulombic

Medium range: van der Waals (dipole-dipole, dipole-non-polar., capillary forces: liquid-probe...)

Short range: bonding interaction (attractive)
repulsive (deformation)

Electromagnetic radiation

-IR - Thermal microscopy **ThM**

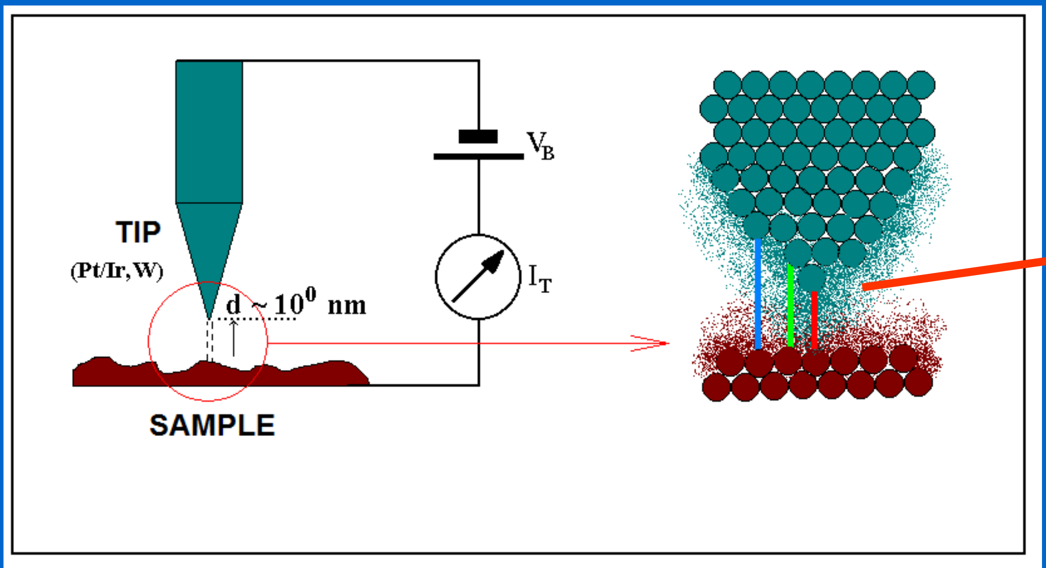
-UV/Vis/IR - optical microscopy/spectr. Near-field **SNOM**

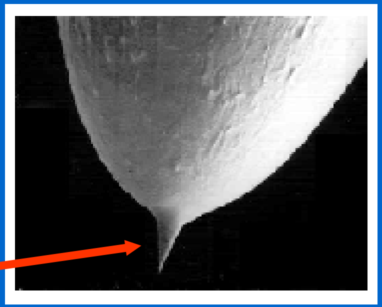
-Tip-enhanced optical microscopy/spectr**.** **TERS/TEFS**

Scanning Tunneling Microscopy,
Scanning Tunneling Spectroscopy

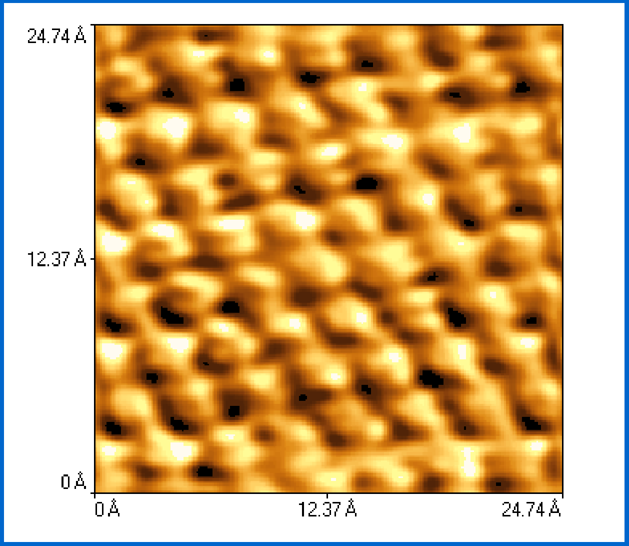
Tunneling microscopy

Binning, Rohrer, IBM, 1981, Nobel Prize 1986





Pt/Ir tip



Au(111)

Approximation of tunneling current

$$I_T \sim V_B\, f_{mTS}(V_B)\, \exp\left[-2z\sqrt{(2m\Phi_{ST}/\hbar^2)}\right]$$

$\hbar = h/2\pi$, $f_{mTS}(V_B)$...reduced Planck.const.
dependence $I_T = f(V_B)$ is given by e-structure of tip and sample
z...distance tip-sample (~ 10^{-1} nm), V_B up to ±1-2 V, I_T ~ nA - pA

Barrier/Distance Tunneling Spectroscopy
(*barrier properties of tunneling gap*)

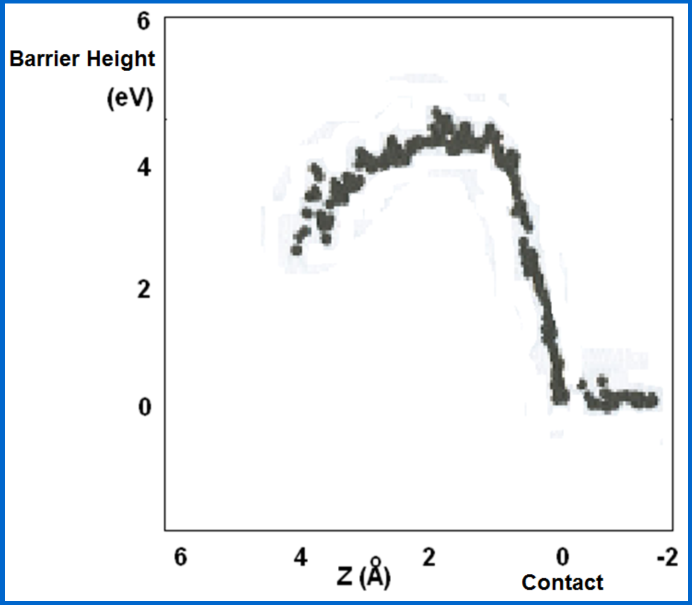
Barrier (distance) spectroskopy

For low V_B is $(dI_T/dZ)/I_T \sim (2\sqrt{2m_e})/\hbar \sqrt{(\Phi_S + \Phi_T)}$

where **Φ_S , Φ_T local work function**, I_T tunneling current, Z tip-sample distance, m_e e-mass

Instrumental arrangement: **modulation VVVVV Z-piezzo, acquired function dI_T/dZ => $\Phi_{Sample,Tip}$ Barrier height**

Simplification: $\Phi_T \approx$ const., lateral variation in measured barrier height ~ local Φ_S



Si-surface, Tungsten-tip

D.A. Bonnel: Scanning Tunneling Microscopy and Spectroscopy VCH 1993

Tunneling voltage spectroscopy
(*mapping e-density of states*)

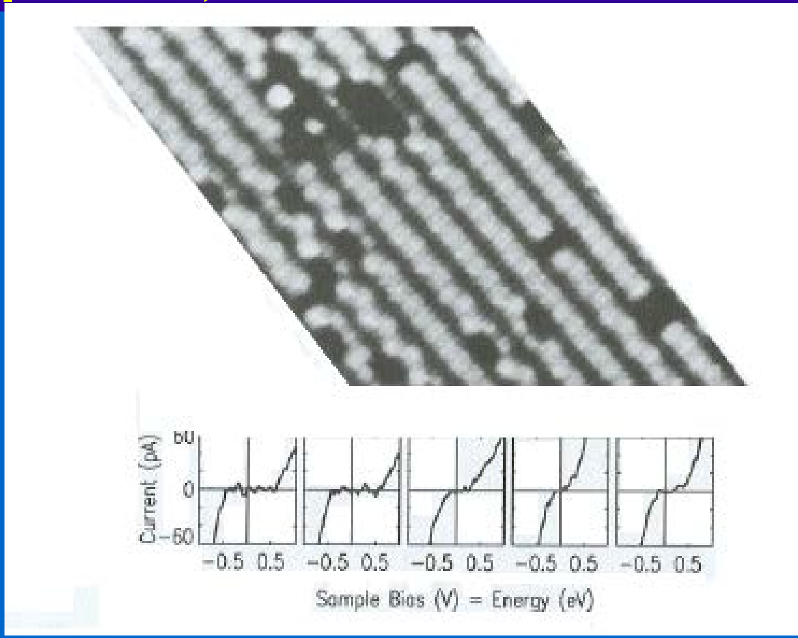
Voltage spectroscopy :

For V_B < work function of tip and sample (typically 10 mV),

dI_T/dV_B ~ local surface density of states (real or from local band structure of sample)

Instrumental arrangement: Modulation VVVVV V_B, acquiring I_T-V_B curve, usually as $d(\log I_T)/d(\log V_B)$ vs V_B

Information obtained: map of surface states (UHV) images states filling, ad-atoms and dangling bonds ...

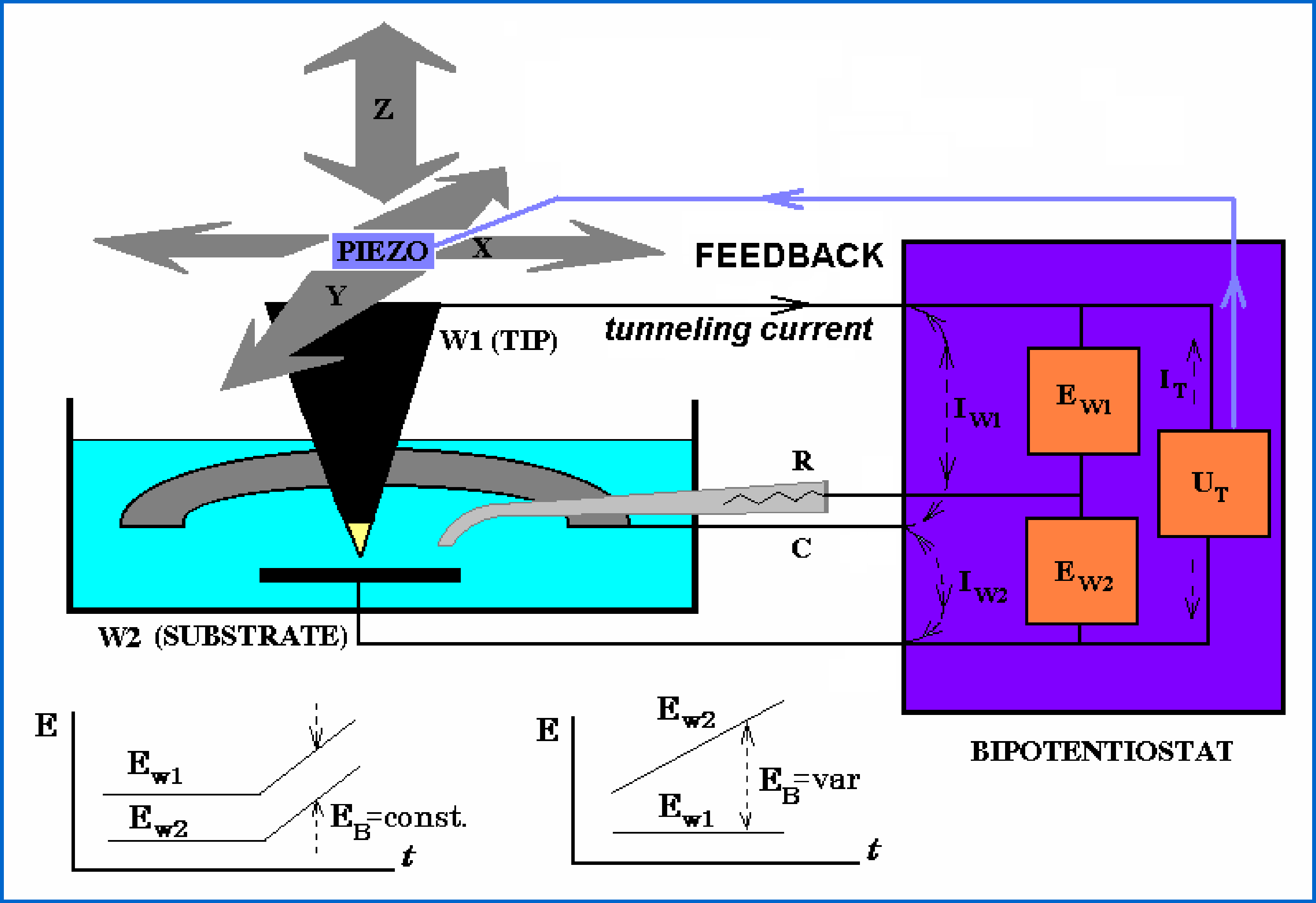


I_T-V_B curves on single-cryst. Si (UHV) (tip passage over defects)

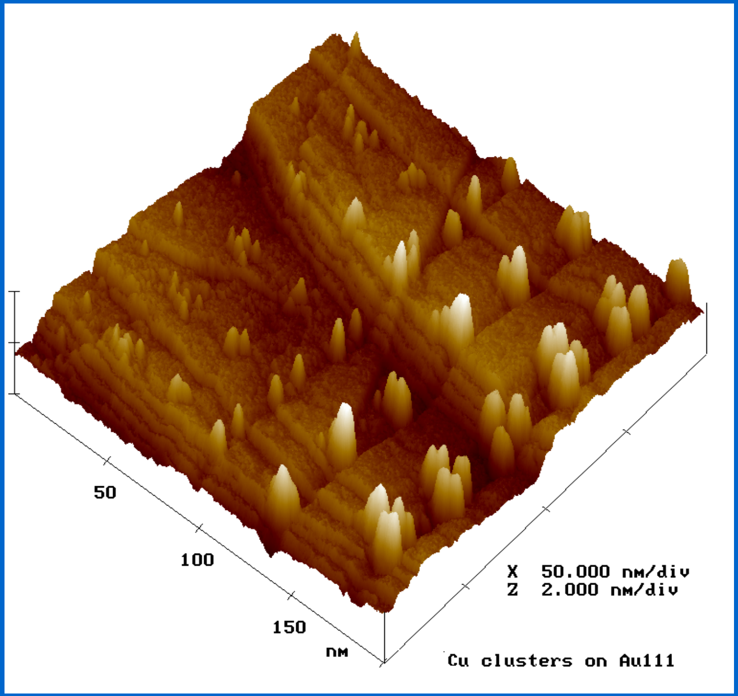
[B. Persson, A. Baratoff, Phys.Rev.Lett. 59, 339]

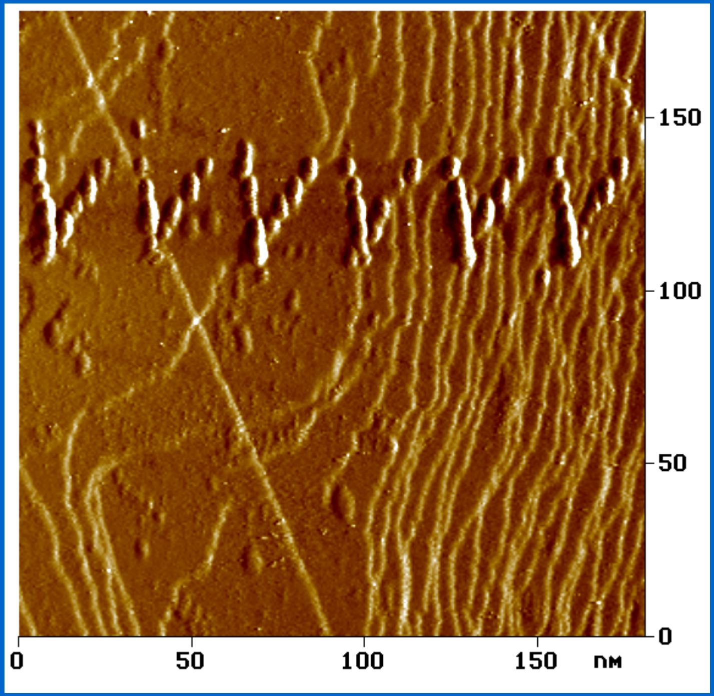
Electrochemical Scanning Tunelling Microscopy
EC STM

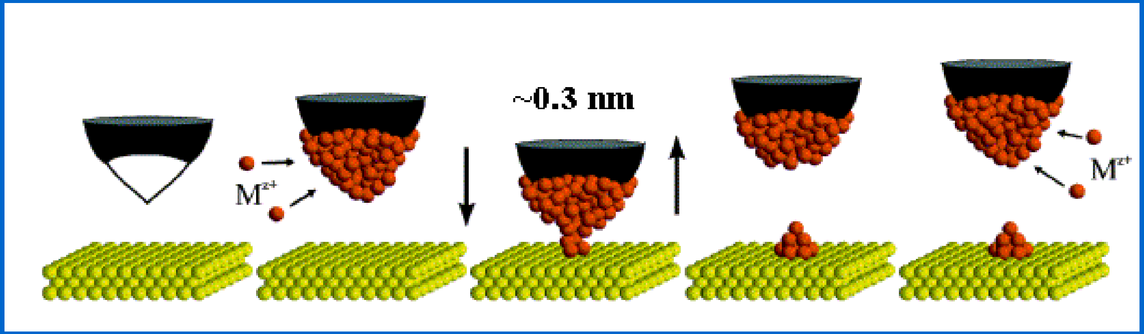
EC STM – arrangement
detection of tunneling currents in electrolyte



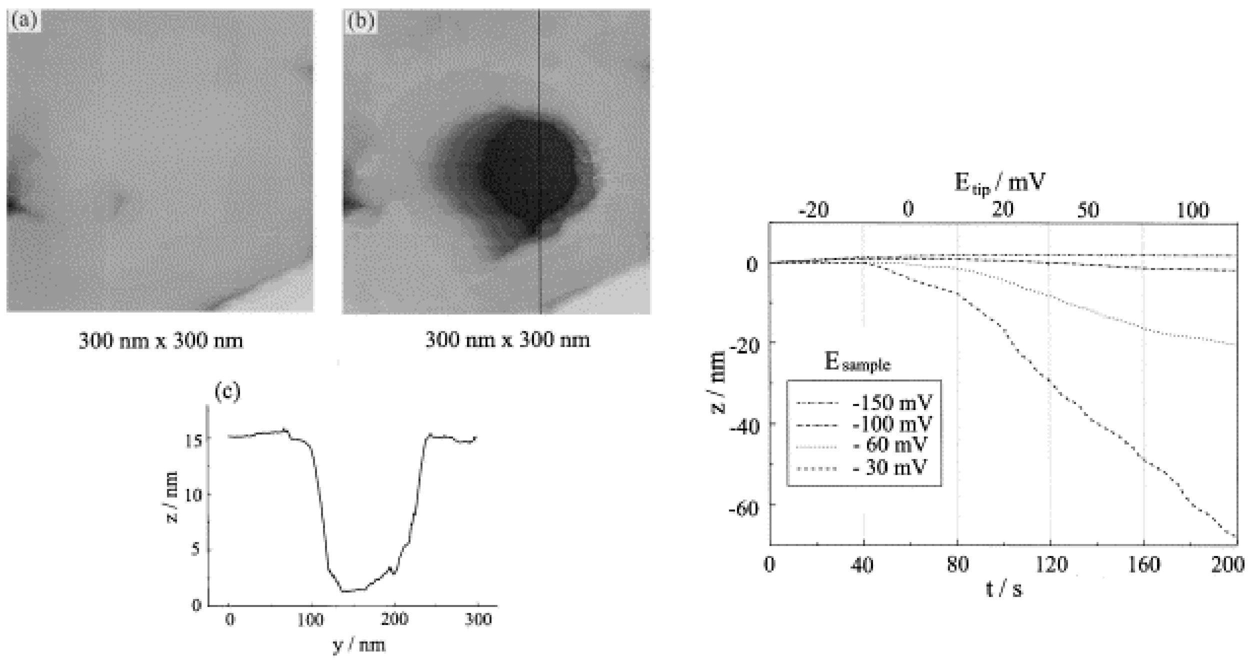
„Nanoprint“: nanoparticle Ø~8 nm, height < 1 nm







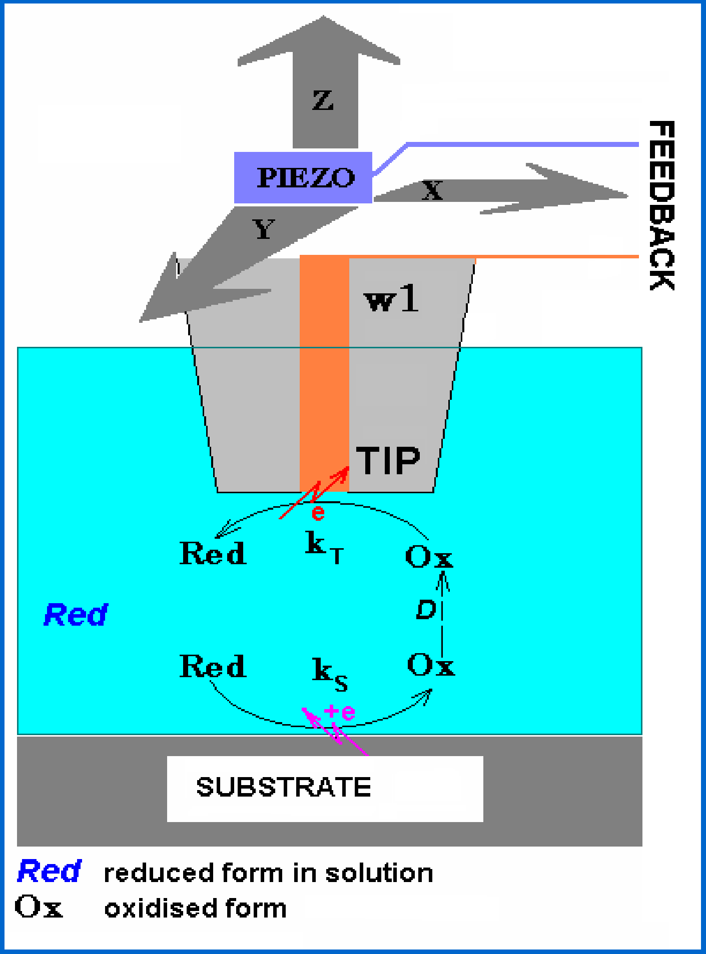
Tip -induced dissolution



Z. X. Xie, D. M. Kolb: J.Electroanal.Chem. 481 (2000), 177.

SECM – detection of Farad. current

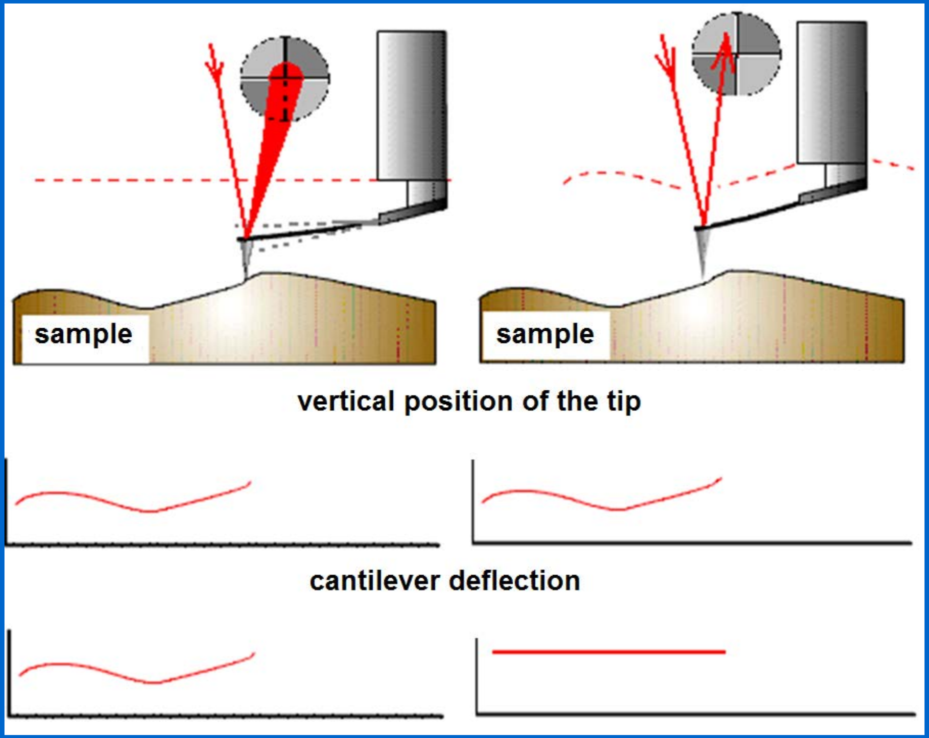
Detection of substrate catalytic activity

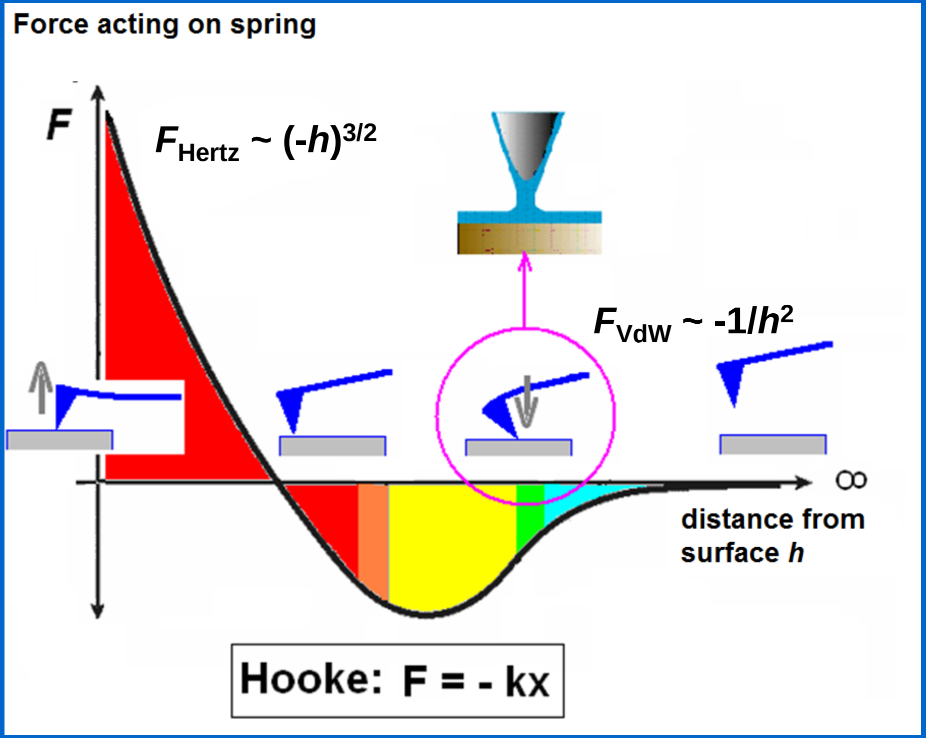


Substrate: generation
Tip: detection

Atomic Force Microscopy
AFM

AFM: Fundamentals/Force Curve

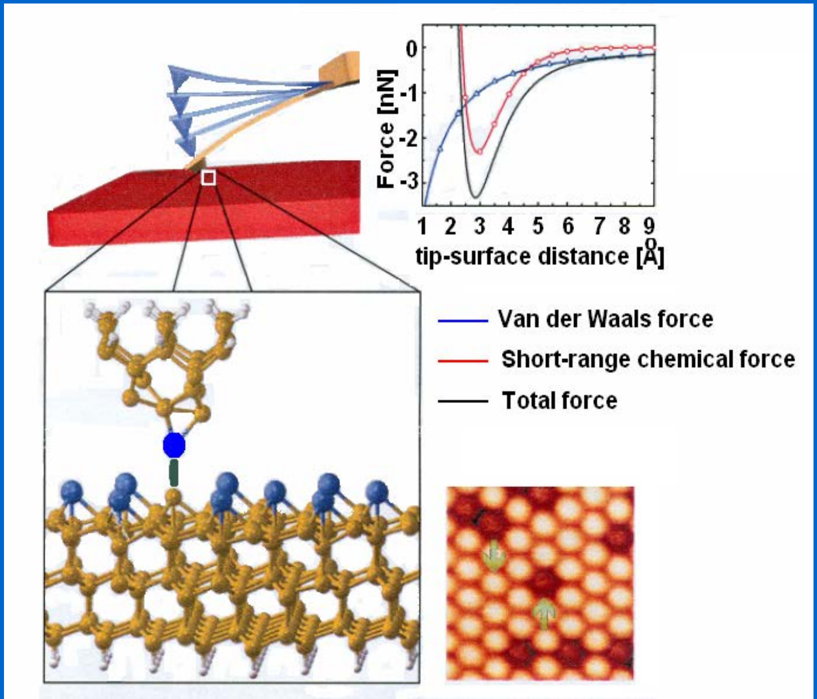


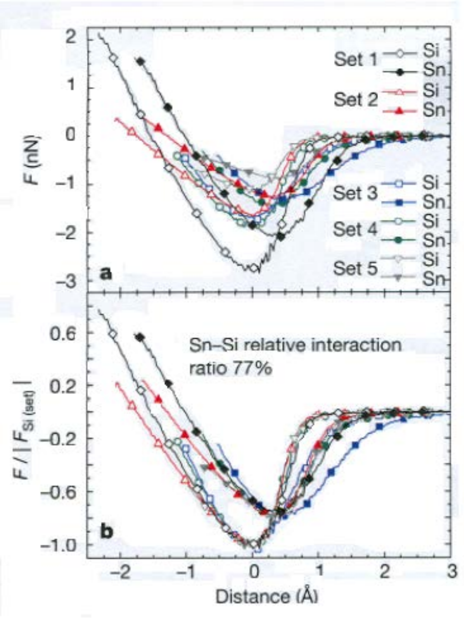


k…spring const. 0,01-1 N/m (cantilever)

Modes:
Contact semicontact noncontact

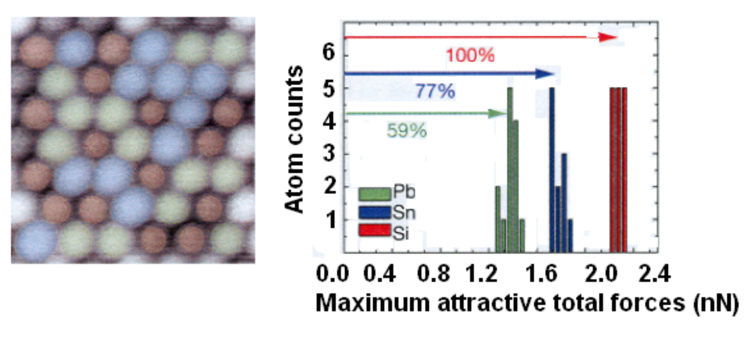
AFM Semicontact mode:
Chemical identification of atoms





Force curve before normalization

Curve normalized to maximum interaction of system substrate-tip

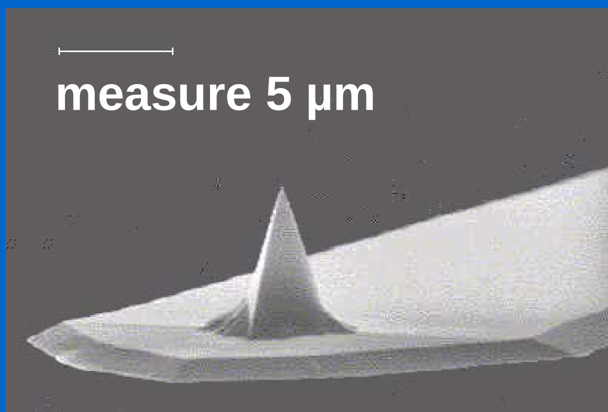


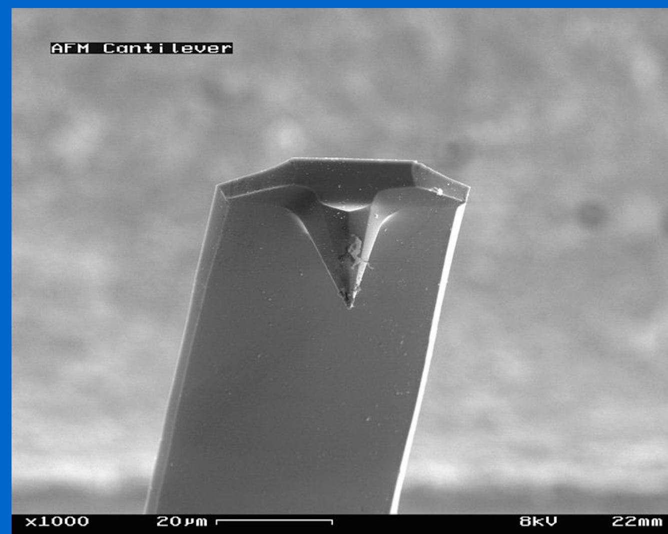
Dynamic Force Spectroscopy

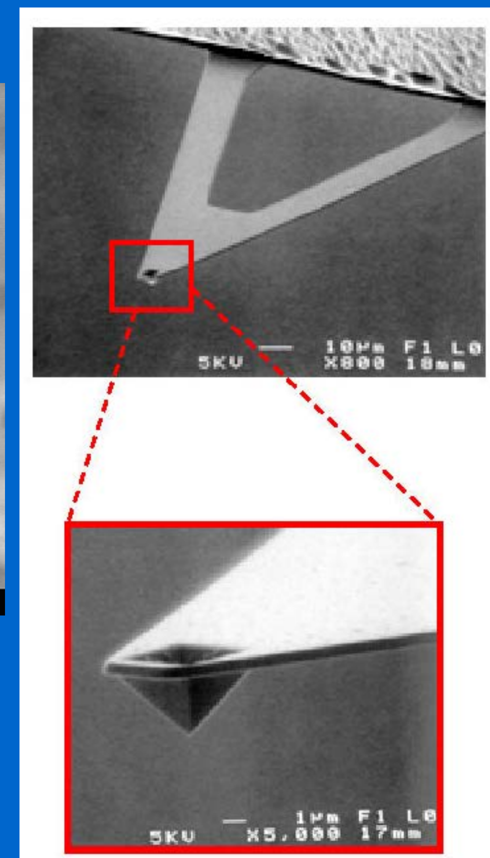
Short range forces – chemical interaction

Yoshiaki Sugimoto, Pablo Pou, Masayuki Abe, Pavel Jelinek, Rubén Pérez, Seizo Morita & Óscar Custance: Nature Letters Vol. 446 March 2007

AFM
tip and microspring (*cantilever*)

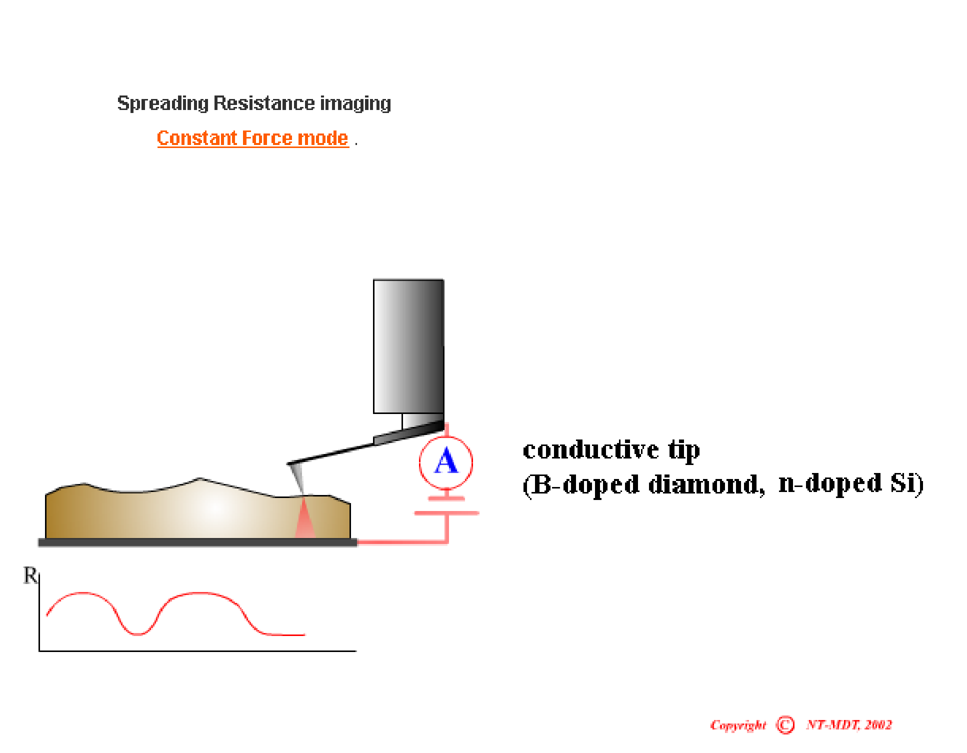


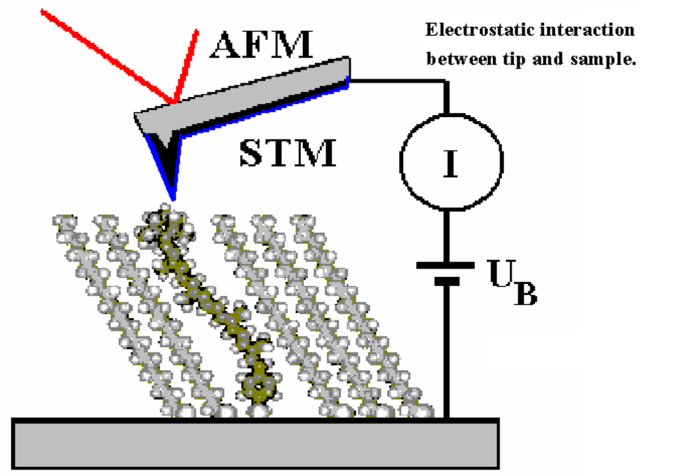




material of tip and cantilever: Si, Si_3N_4

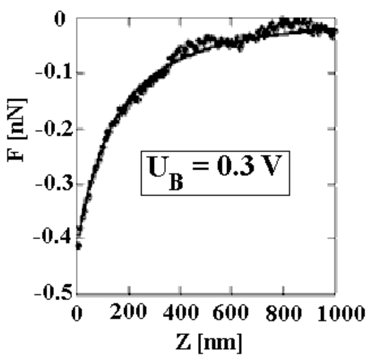
Conductive AFM

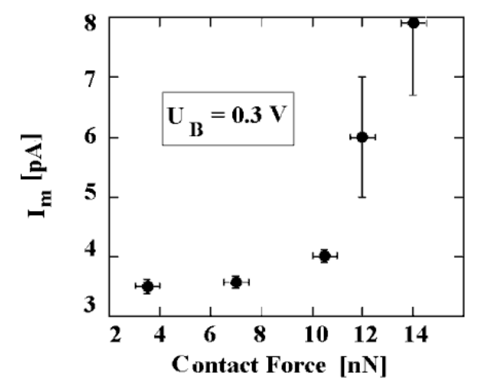




Carotenoid embedded in 1-docosanethiol attached to Au.
Current measured between biased Pt-coated AFM cantilever and Au substrate.
Maximum current (I_m) vs. contact force.

[*J. Phys. Chem. B* **103** 4006-4010 (1999)]



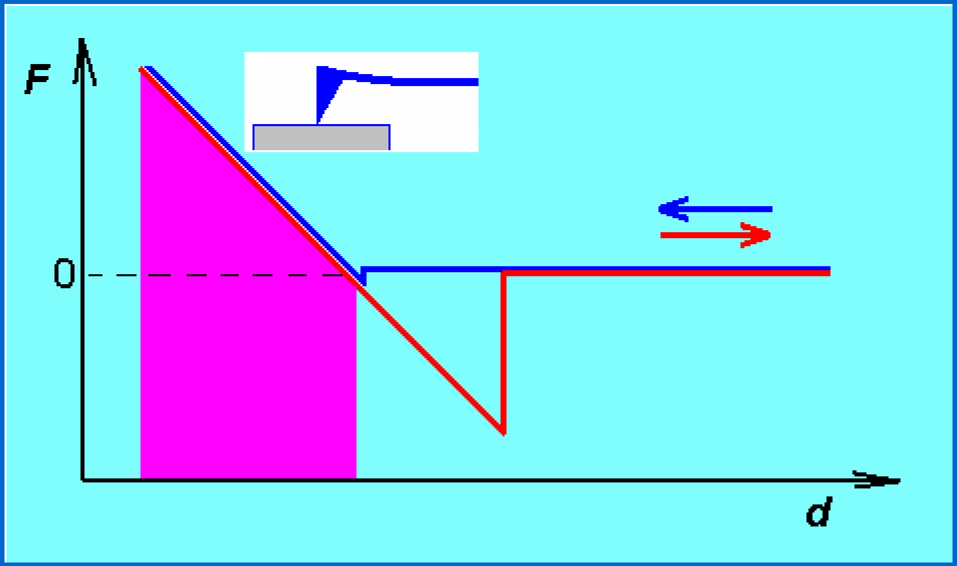


AFM

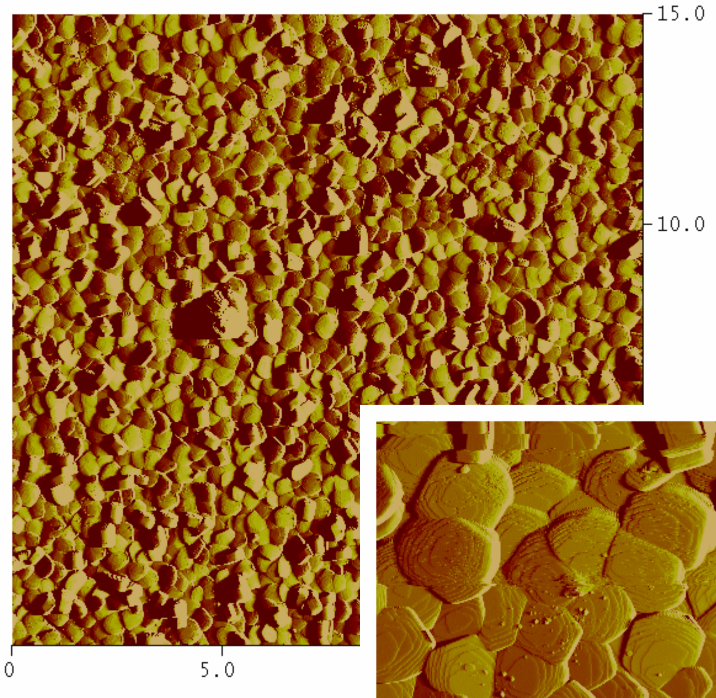
20 cm

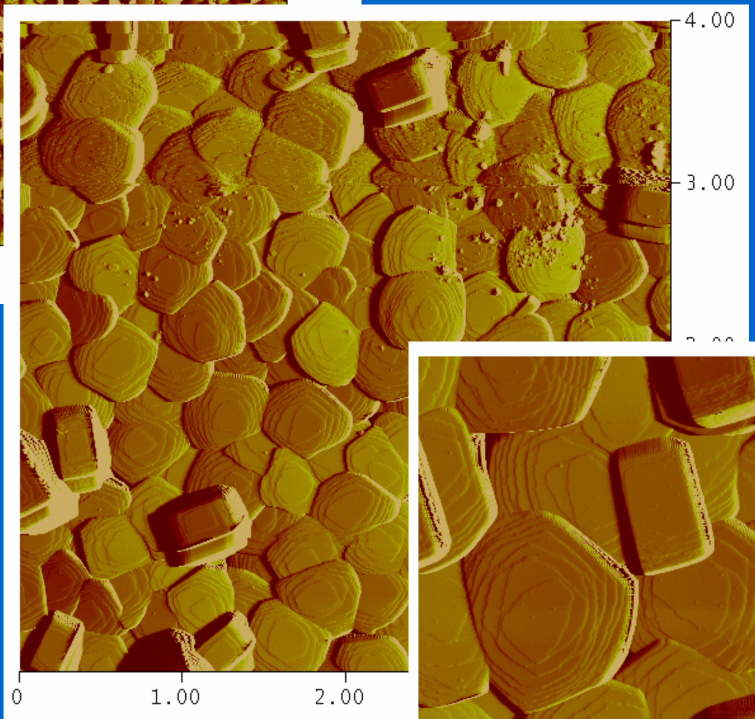
Bruker

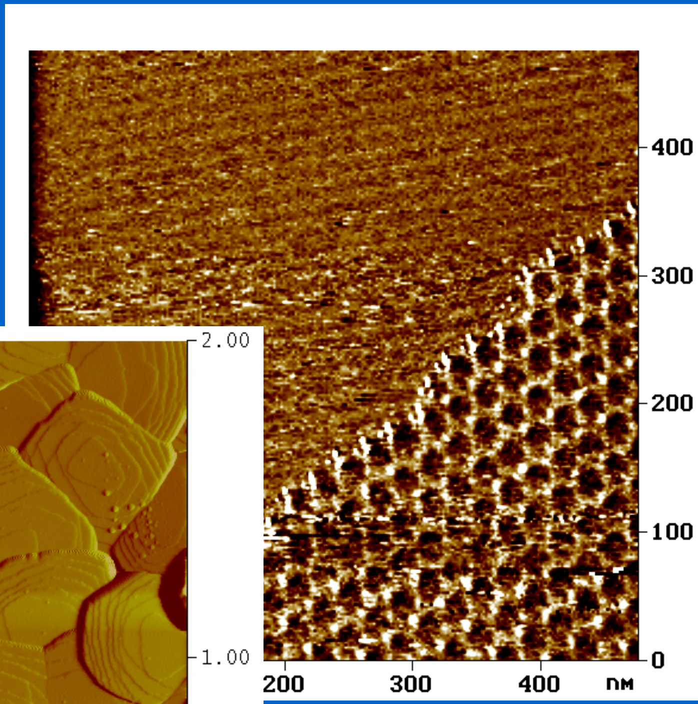
AFM Repulsive forces: Contact mode

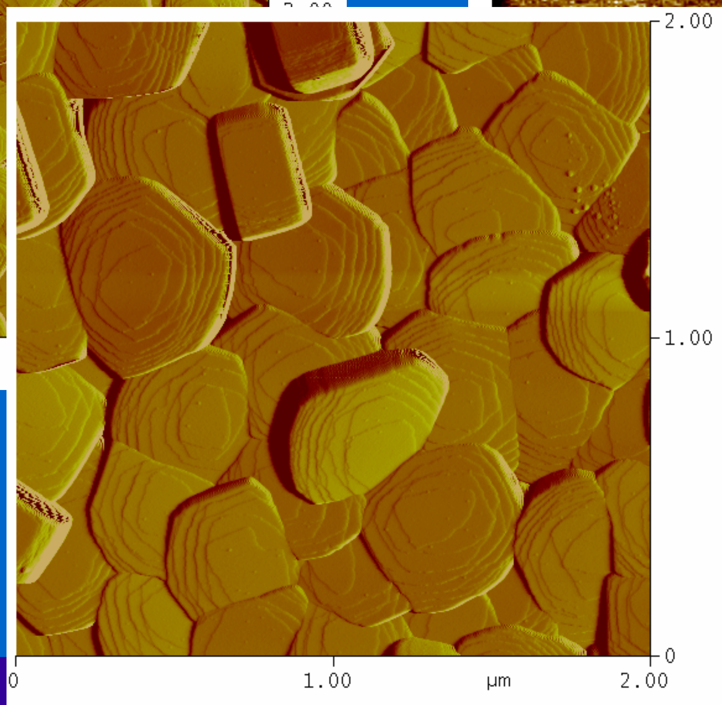


AFM Contact mode



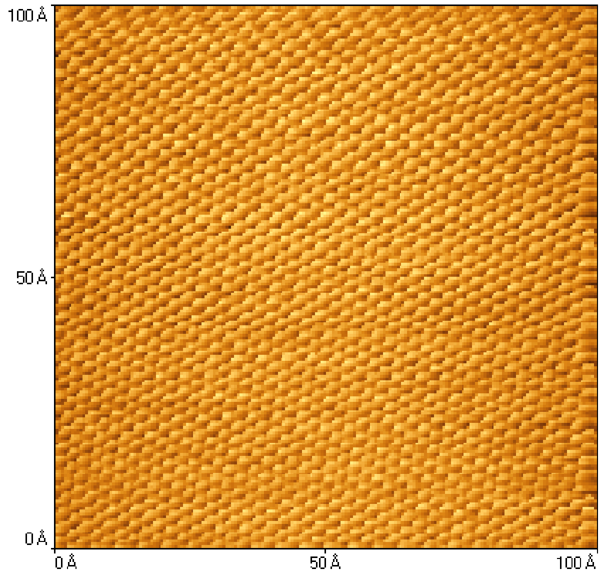


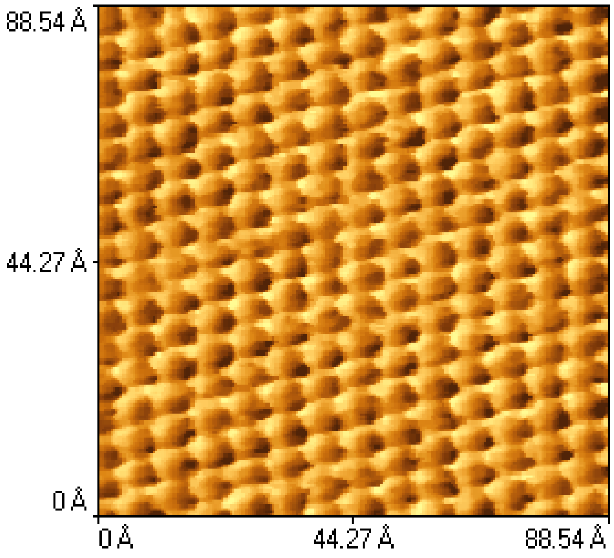




Zeolite crystals

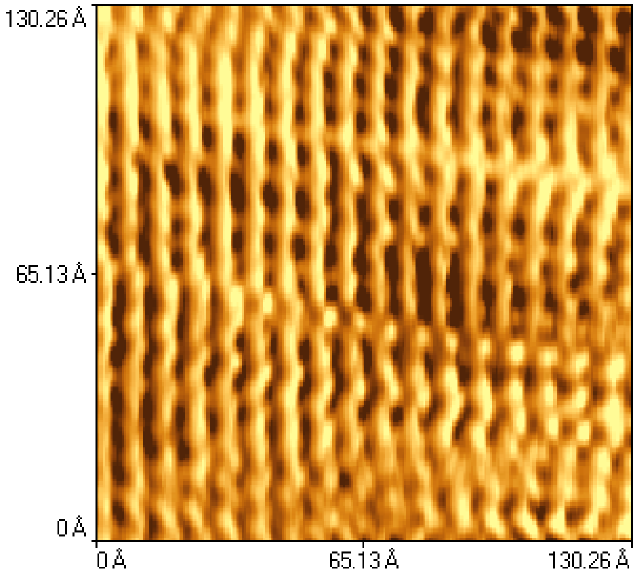
AFM Contact mode





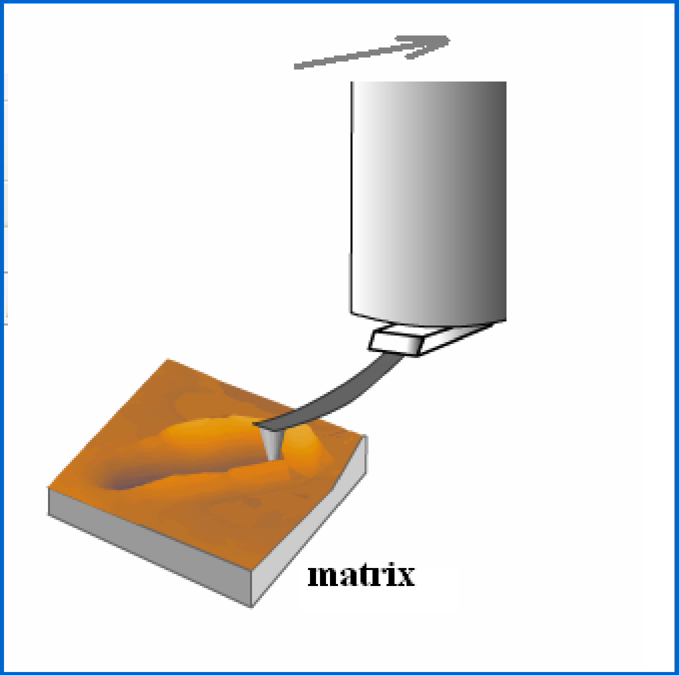
Graphite

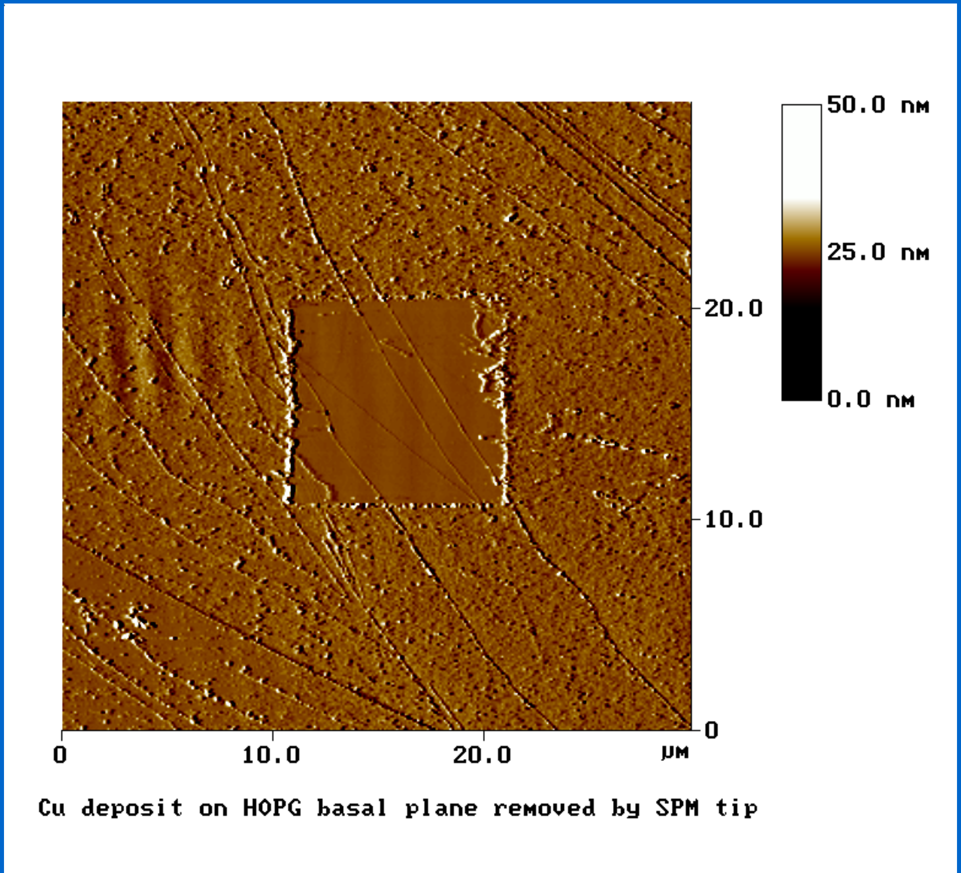
Muscovite (mica)



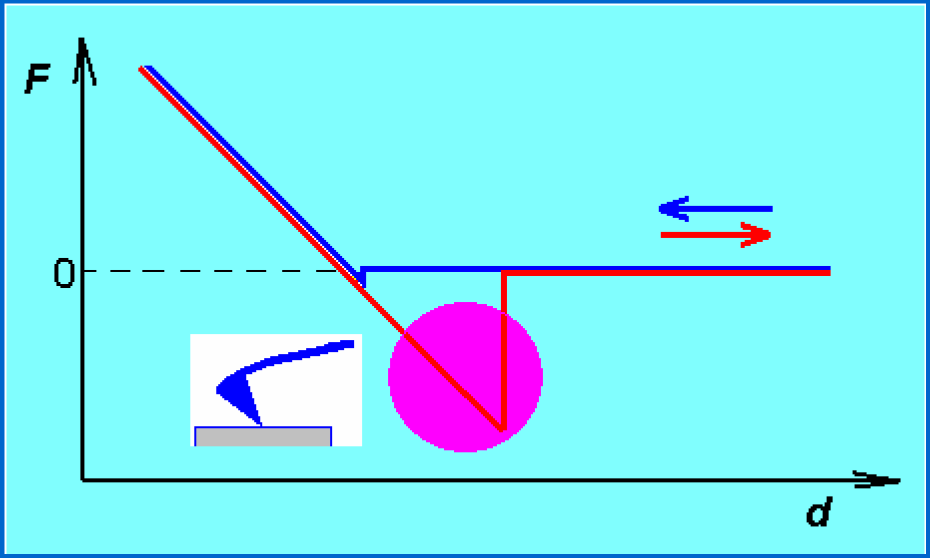
Oriented PTFE (Teflon) molecules

Nanolithography

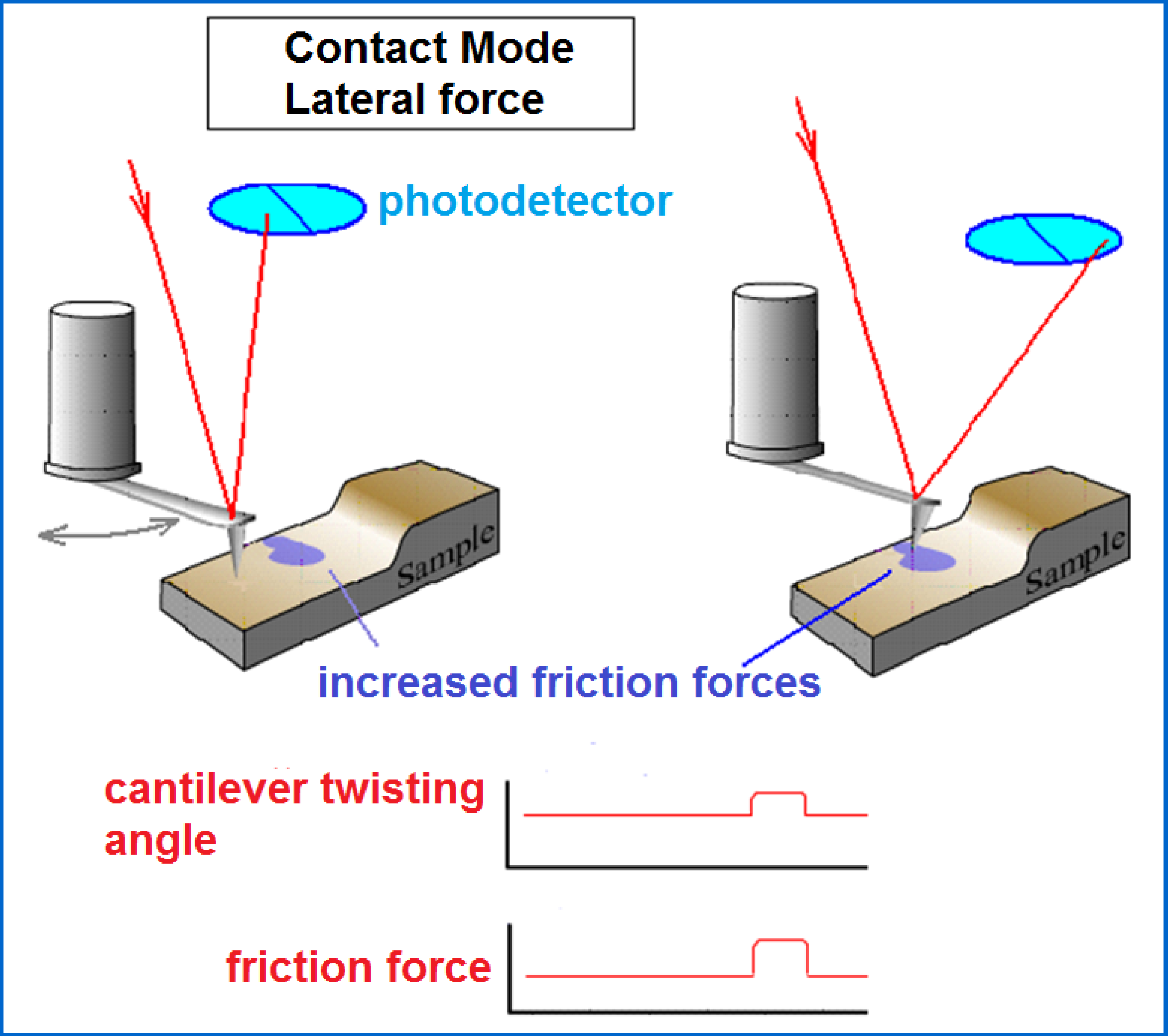




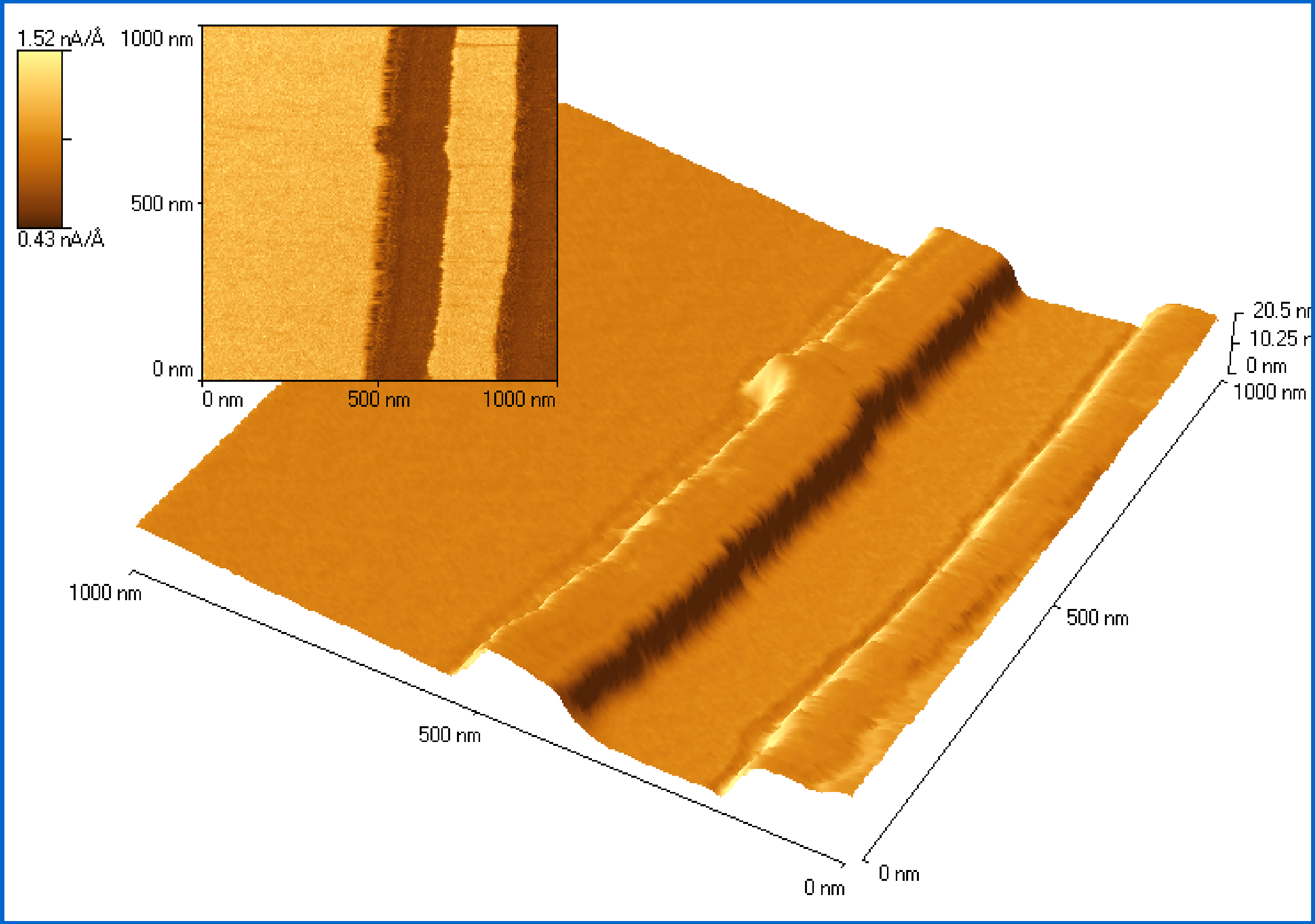
AFM attractive forces (adhesion, bonding interaction)



Microscopy of adhesive (lateral) forces (LFM)

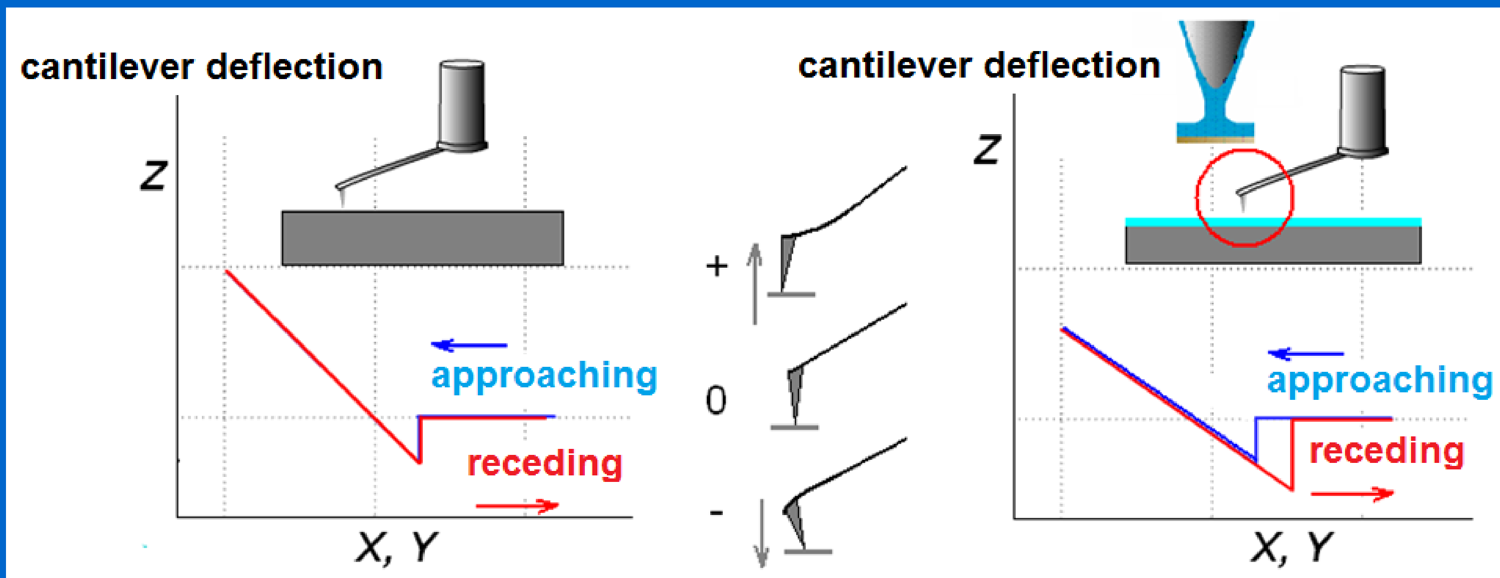


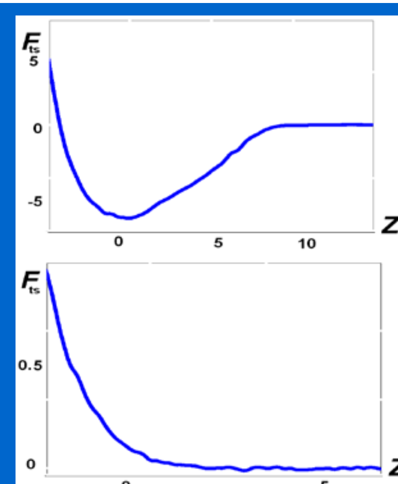
Microscopy of lateral forces (LFM)



Teflon on glass:
-AFM topography
-mapping of friction forces (left insert)

AFM of adhesive (axial) forces

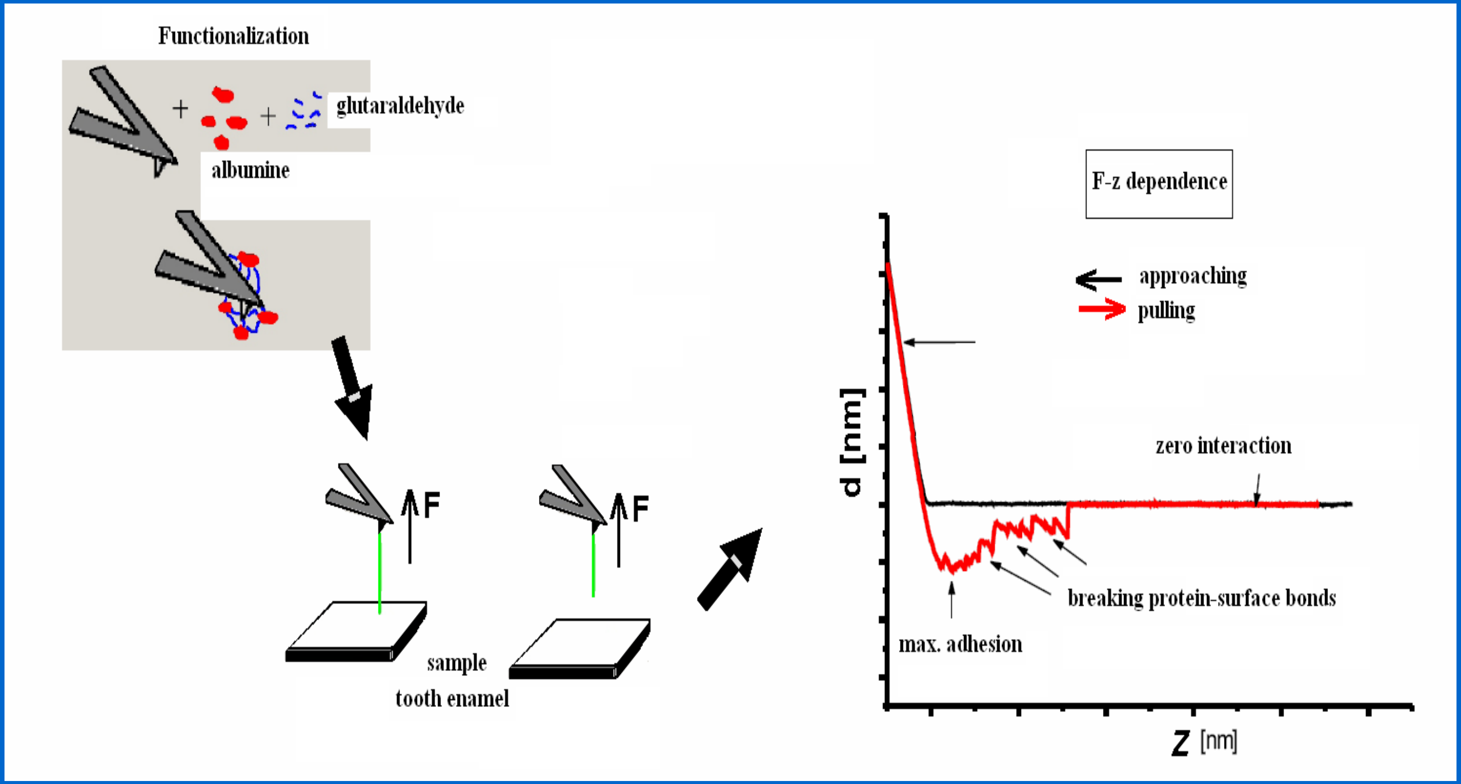


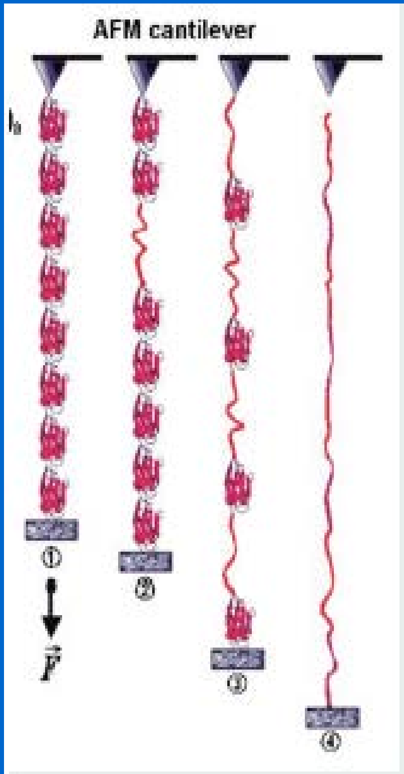


$F_{ts}(Z)$
(Si/SiO_2)/air

water

Protein adsorption on tooth enamel



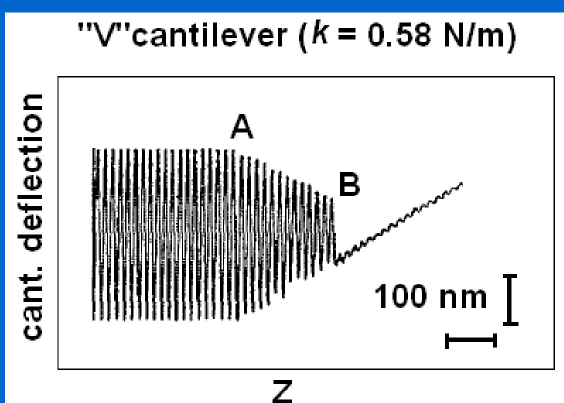


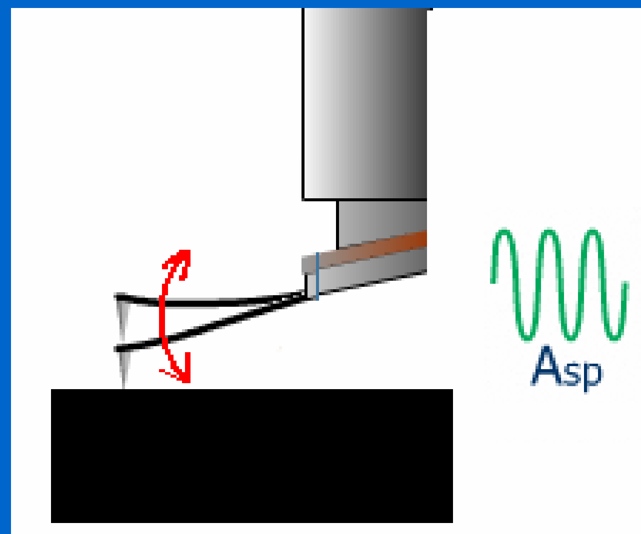
N. Schwender , M. Mondon , K. Huber , M. Hannig , C. Ziegler Department of Physics, University of Kaiserslautern, Department of Operative Dentistry and Periodontology, Saarland University

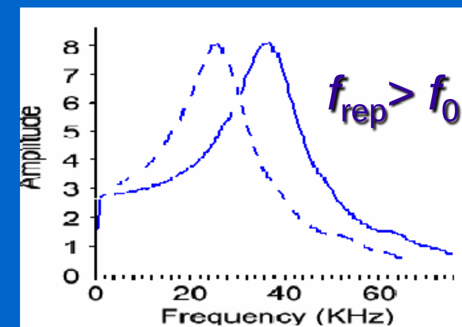
Semicontact mode (tapping)   Acoustic /mgt. excitation

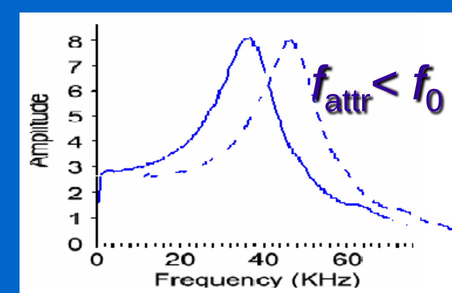
mechanical oscillator
in resonance
input parameters:
***f_{rez}*, *A_{sp}* (~ 20 nm)**

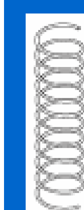
output parameters
***A*, *Δf*, *Δθ*, *d* (deflection)**







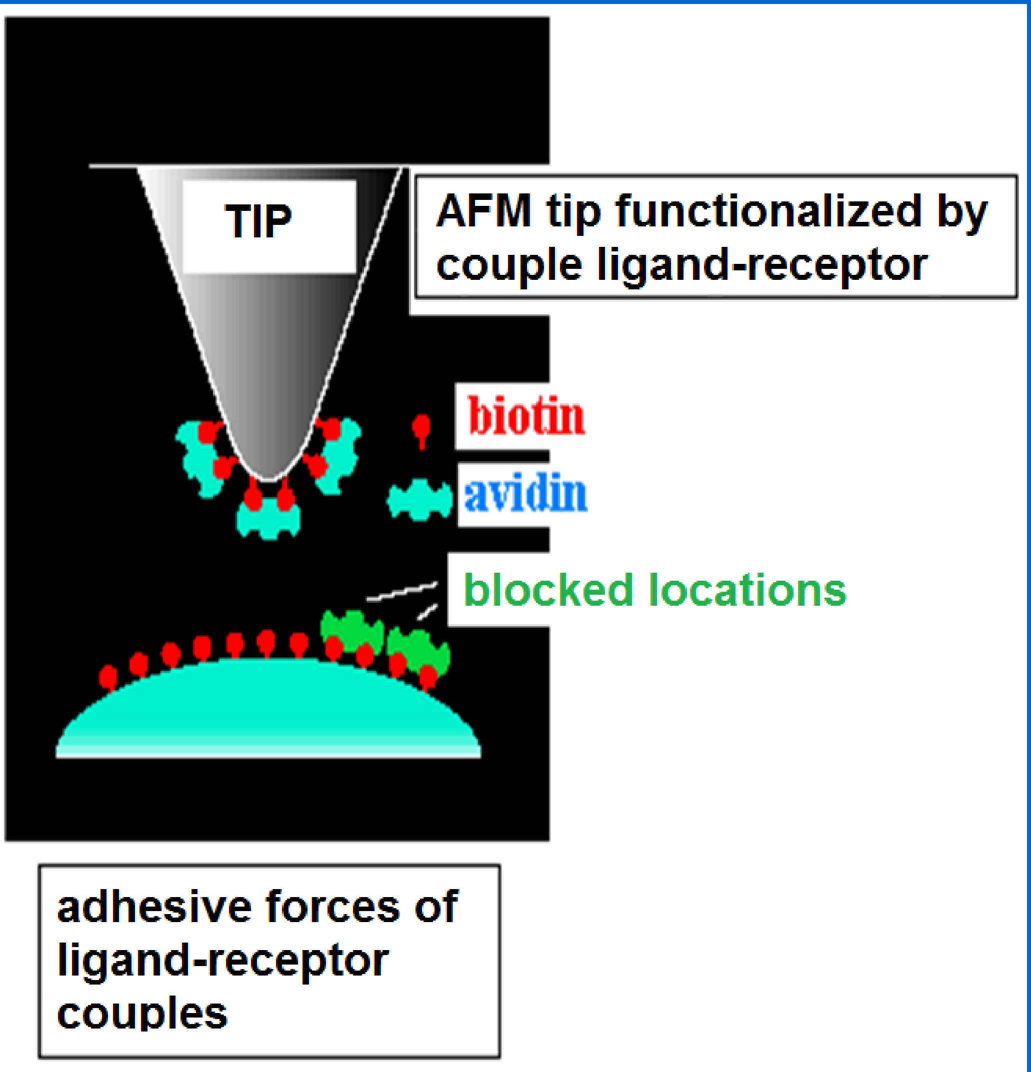


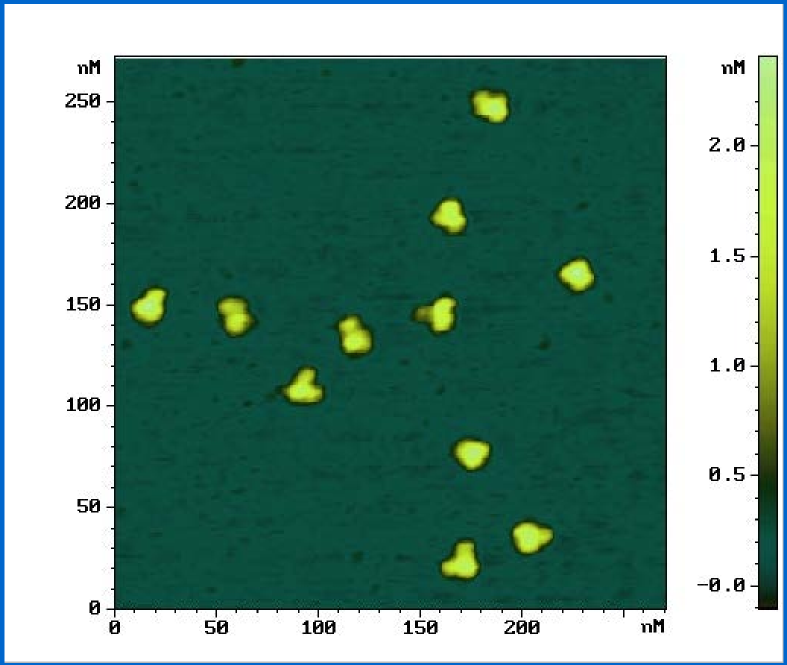


$md^2z/dt^2 = -kz - (m\omega_0/Q)dz/dt + F_{ts} + F_d\cos\omega t$ piezo (drive) $\omega_0 = \sqrt{k/m}$

Hook   Dissipation E.   Tip-Surf. interaction

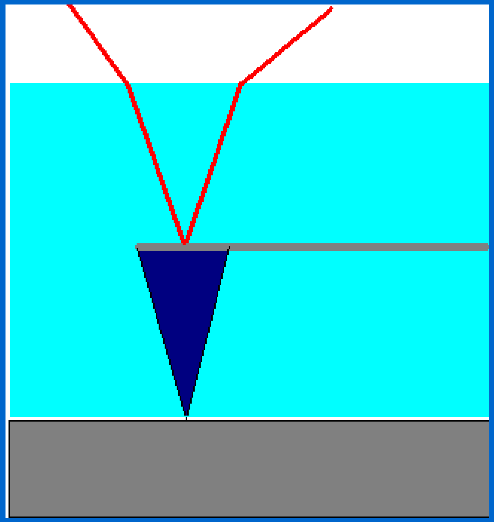
AFM with modified tip
Semicontact mode (tapping): Bonding interactions

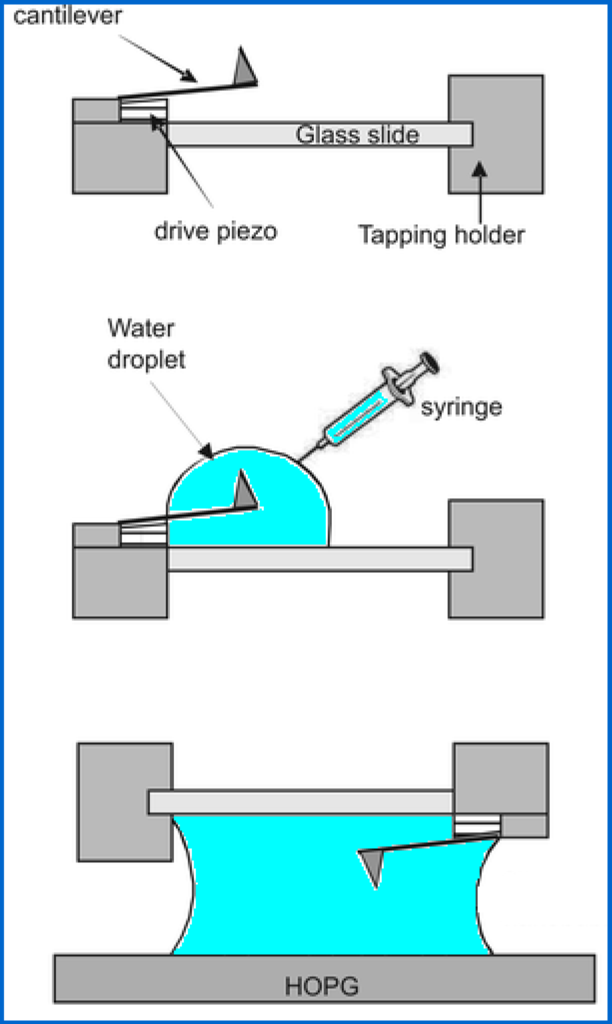


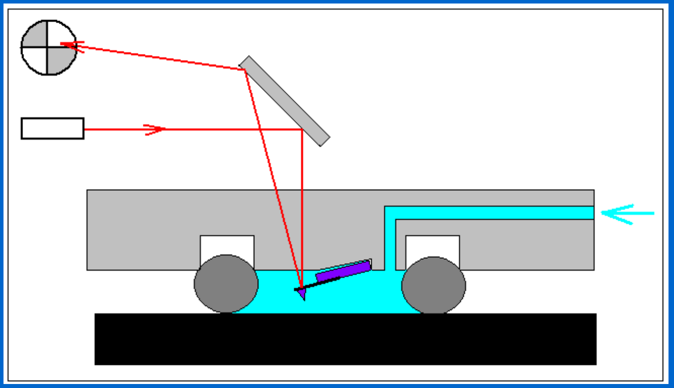


Monoclonal antigen 1RK2 to A-chain of ricine (tip-IgG1).
Visible is Y-structure of antigene.
AFM-semicontact mode on air. [*Veeco*]

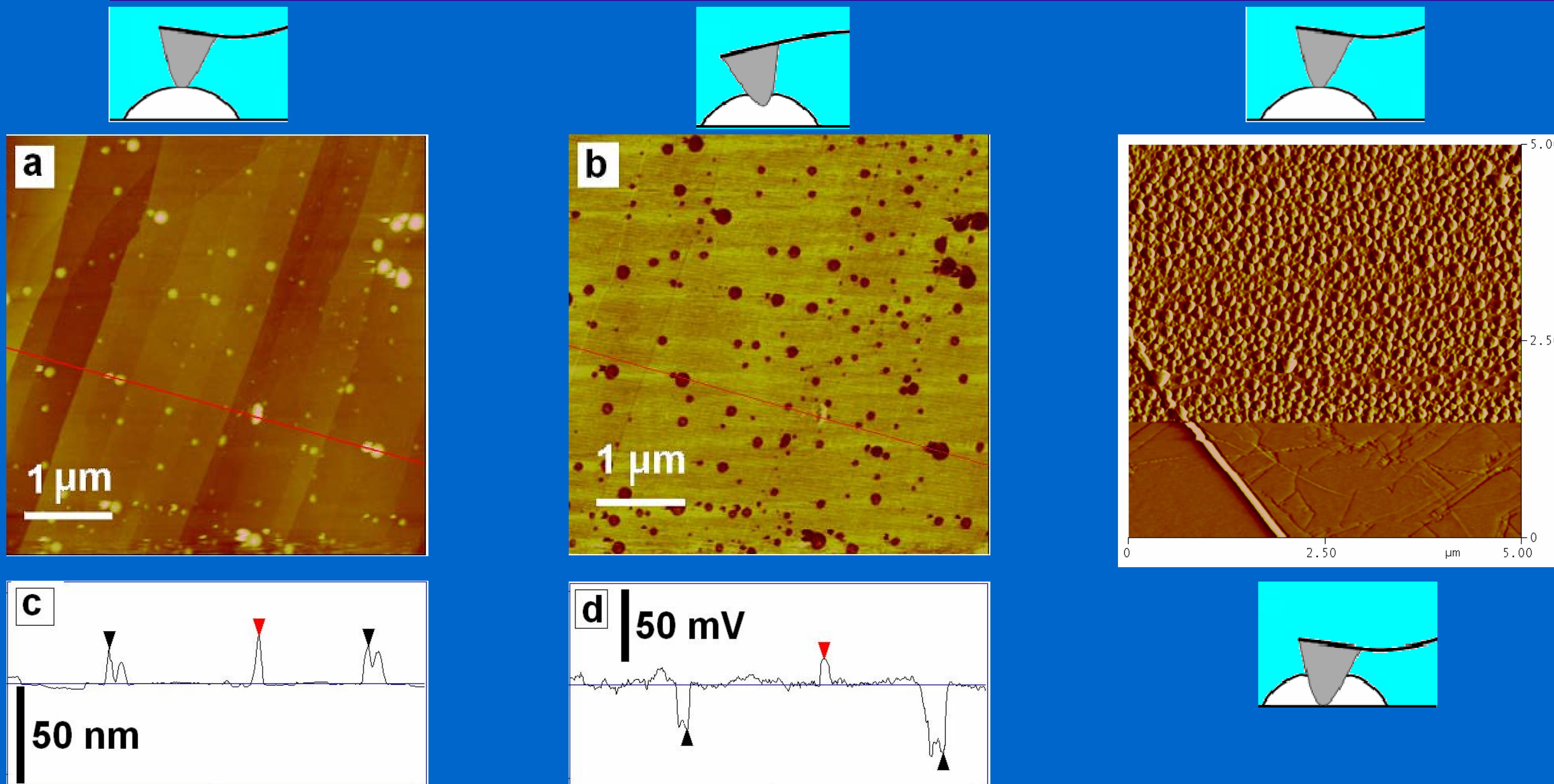
AFM in liquids







Nanobubbles at the immersed interface (liquid/solid)

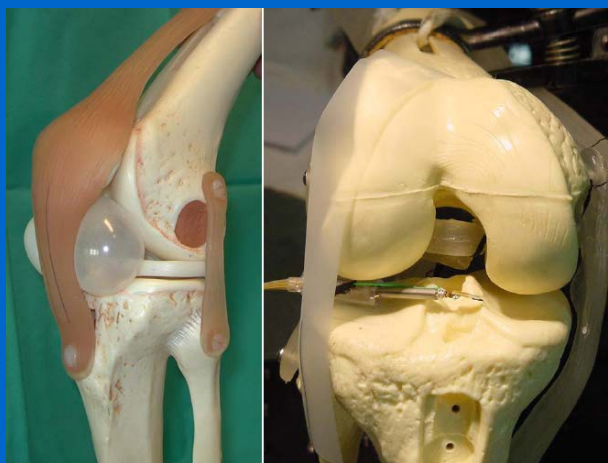


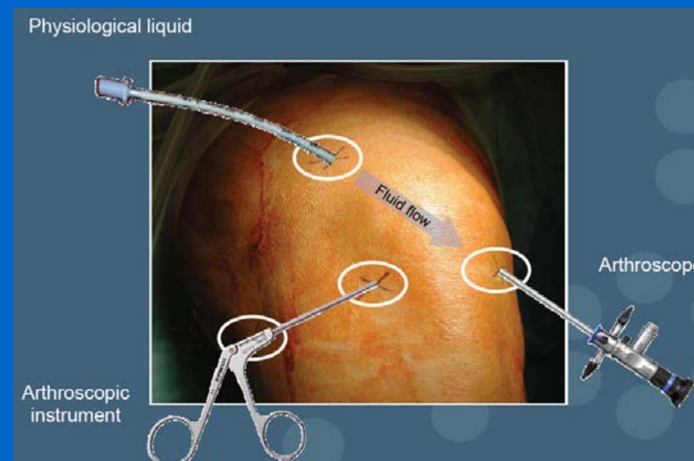
Topography

Cantilever deflection

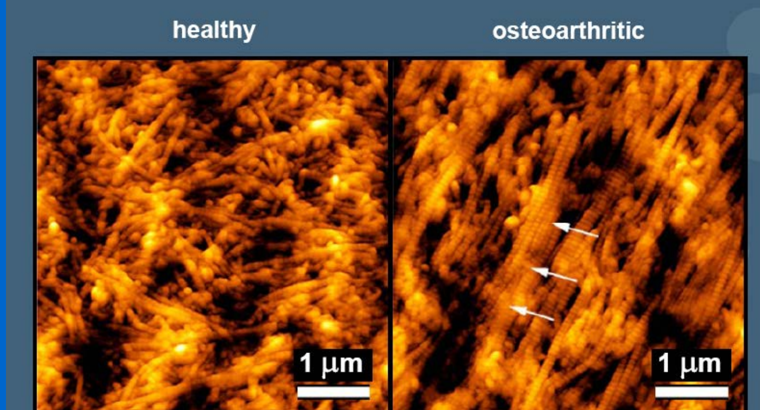
P. Janda, O. Frank, Z. Bastl, M. klementová, H. Tarábková, L. Kavan : Nanotechnology 21 (2010) 095707

AFM *in vivo*: Scanning Force Endoscope

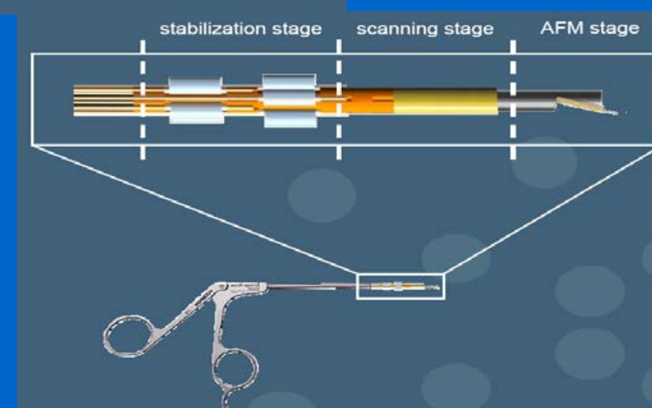




Diagnosing cartilage diseases at an early stage



M. Stolz *et al.*, Biophys. J. 2004; 86 3269-3283



Institute of Microtechnology
University of Neuchâtel

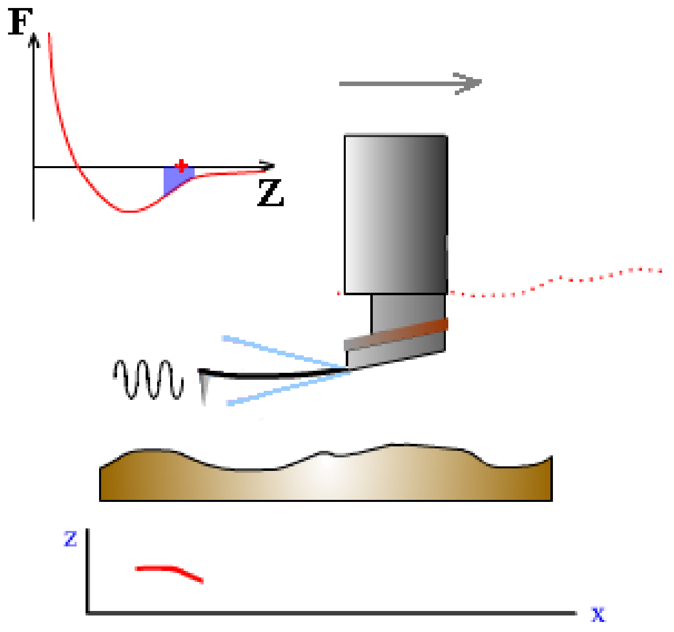
R. Imer
T. Akiyama
N.F. de Rooij
U. Staufer

M.E. Müller Institute (MSB)
Universtiy of Basel

M. Stolz
U. Aebi

AFM: Noncontact Mode

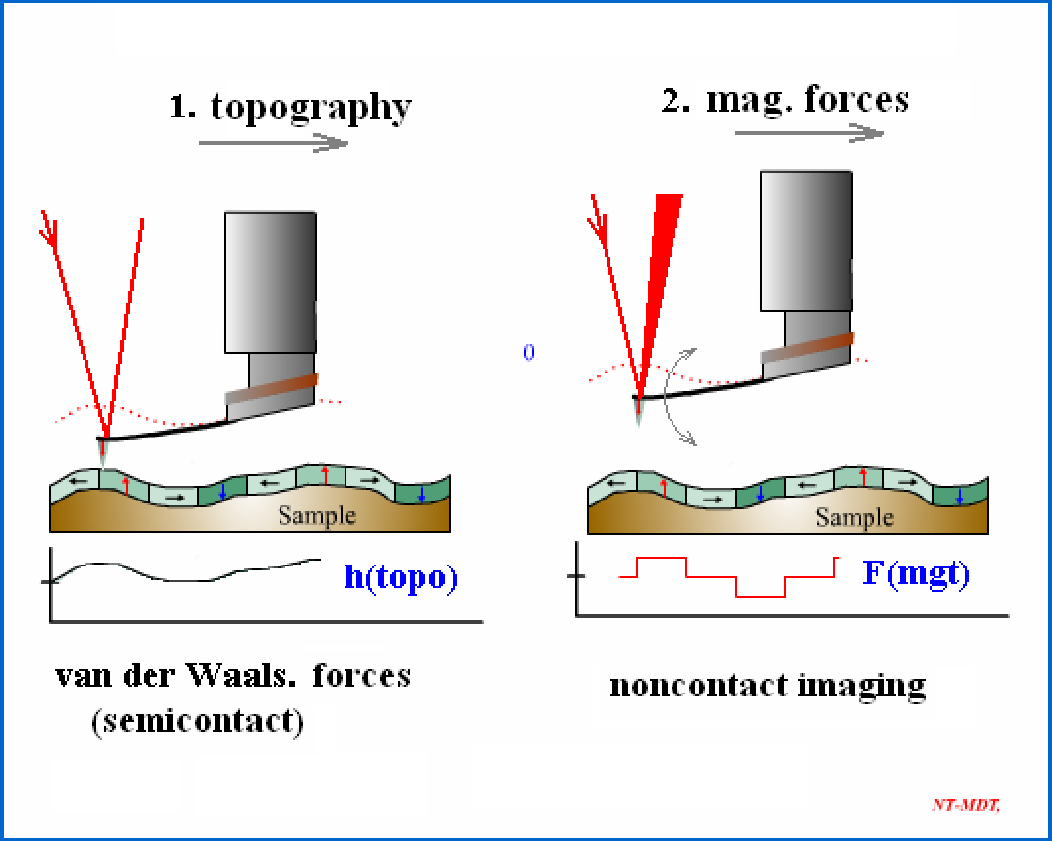
AFM: Noncontact mode

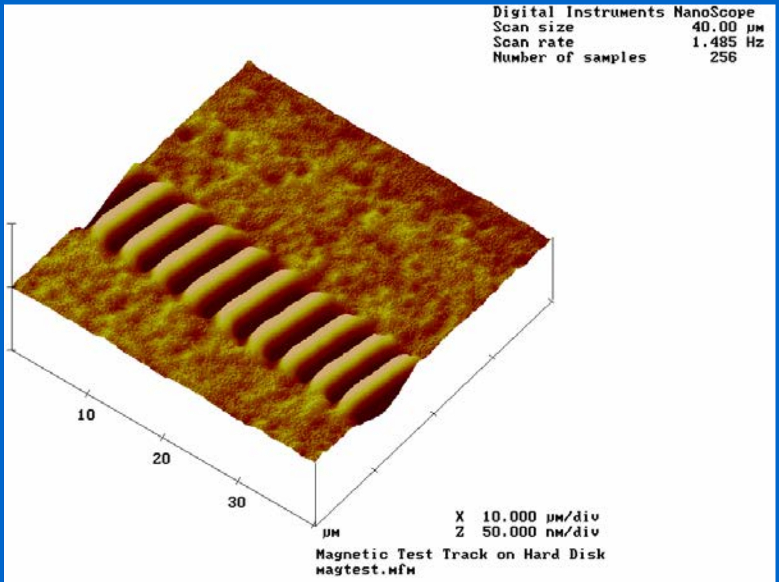


$$f_{eff} = f_o(1 - F(z)/k_o)^{1/2}$$

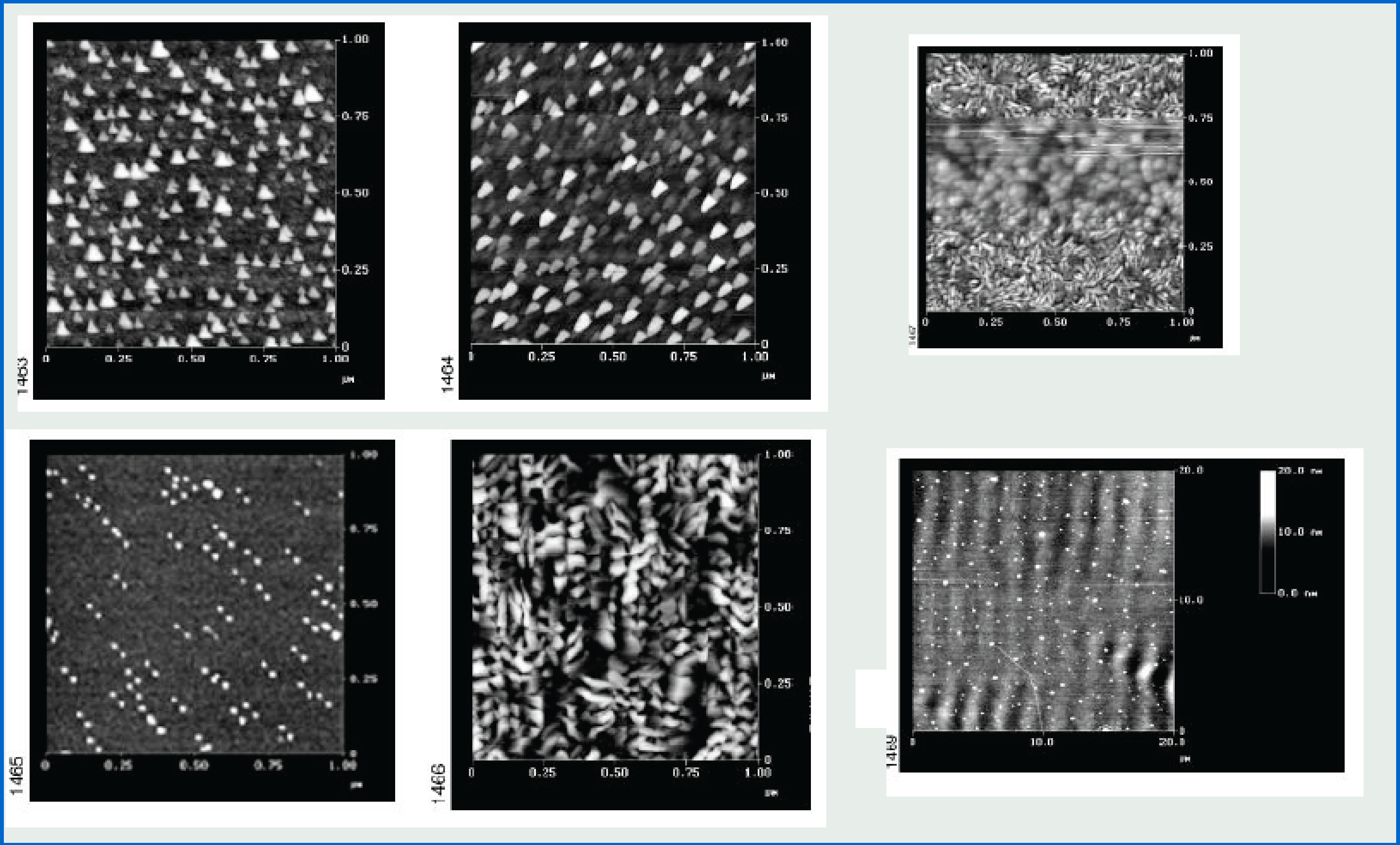
$df = f_o - f_{eff}$ $\quad$ F...gradient

Noncontact AFM:
Magnetic Force Microscopy





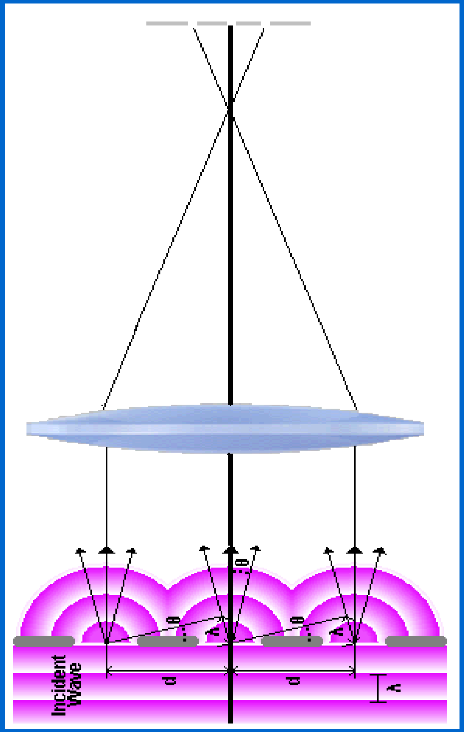
AFM: Artefacts



Scanning Near-field Optical Microscopy/Spectroscopy
SNOM

Far-Field Microscopy

Near-Field Microscopy



$d = \lambda / (\theta \sin \alpha) \approx \lambda / N_a$

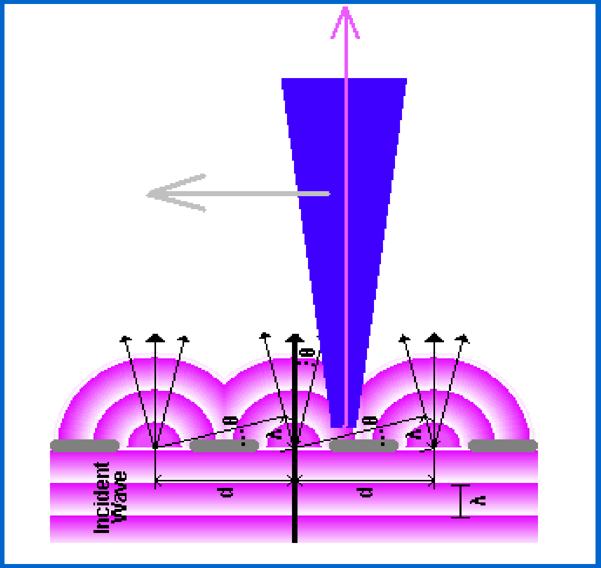
λ...wavelength

α...incident angle

N_a...numeric aperture

Θ...refraction index

d...resolution

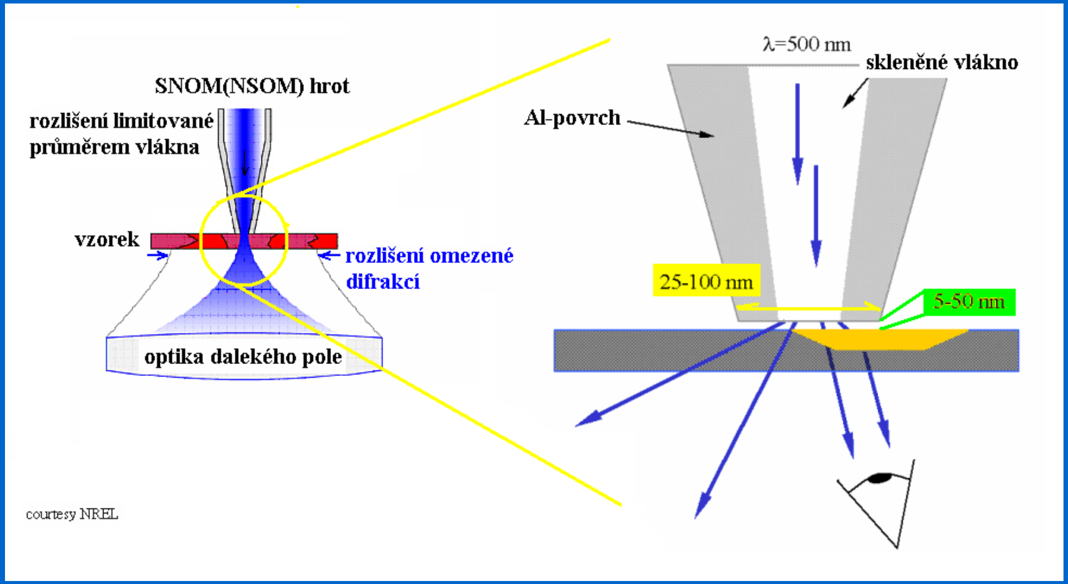


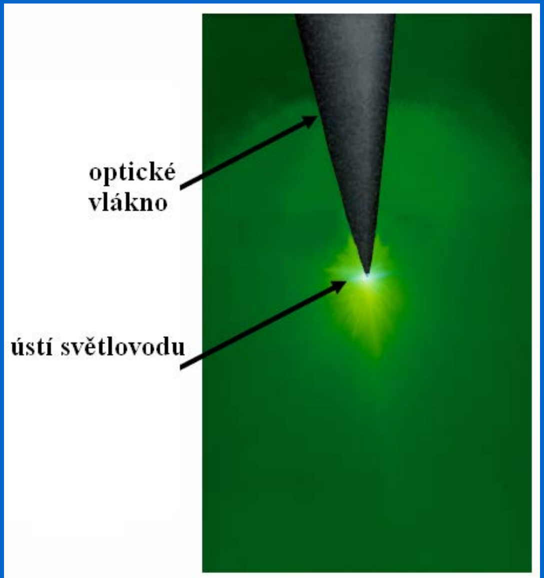
Resolution ⇒
Abbe, Rayleigh **criterion**
Refraction index, incident angle, diffraction limit

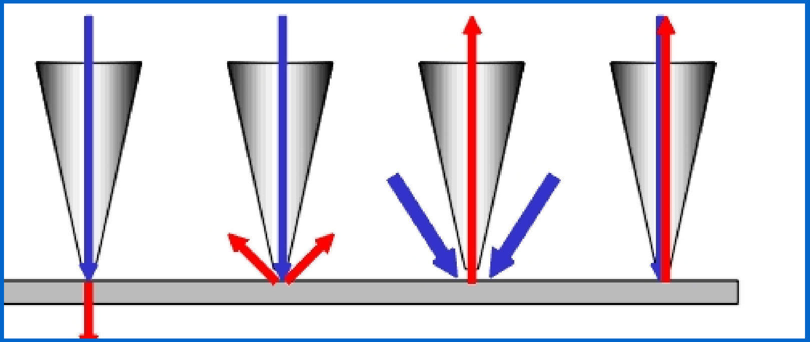
Image reconstruction point by point from wavefront fragments

Resolution ⇒ Probe aperture & Distance from the sample

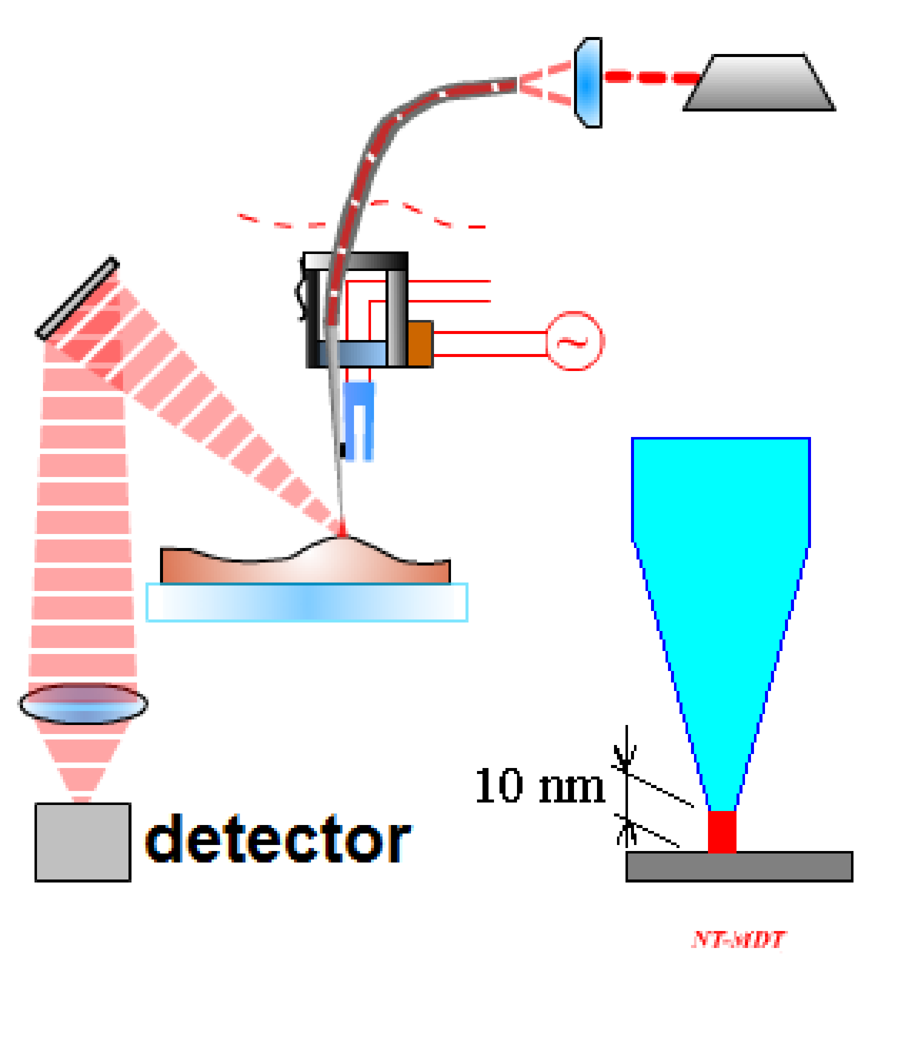
Near-Field Optical Microscopy/Spectroscopy





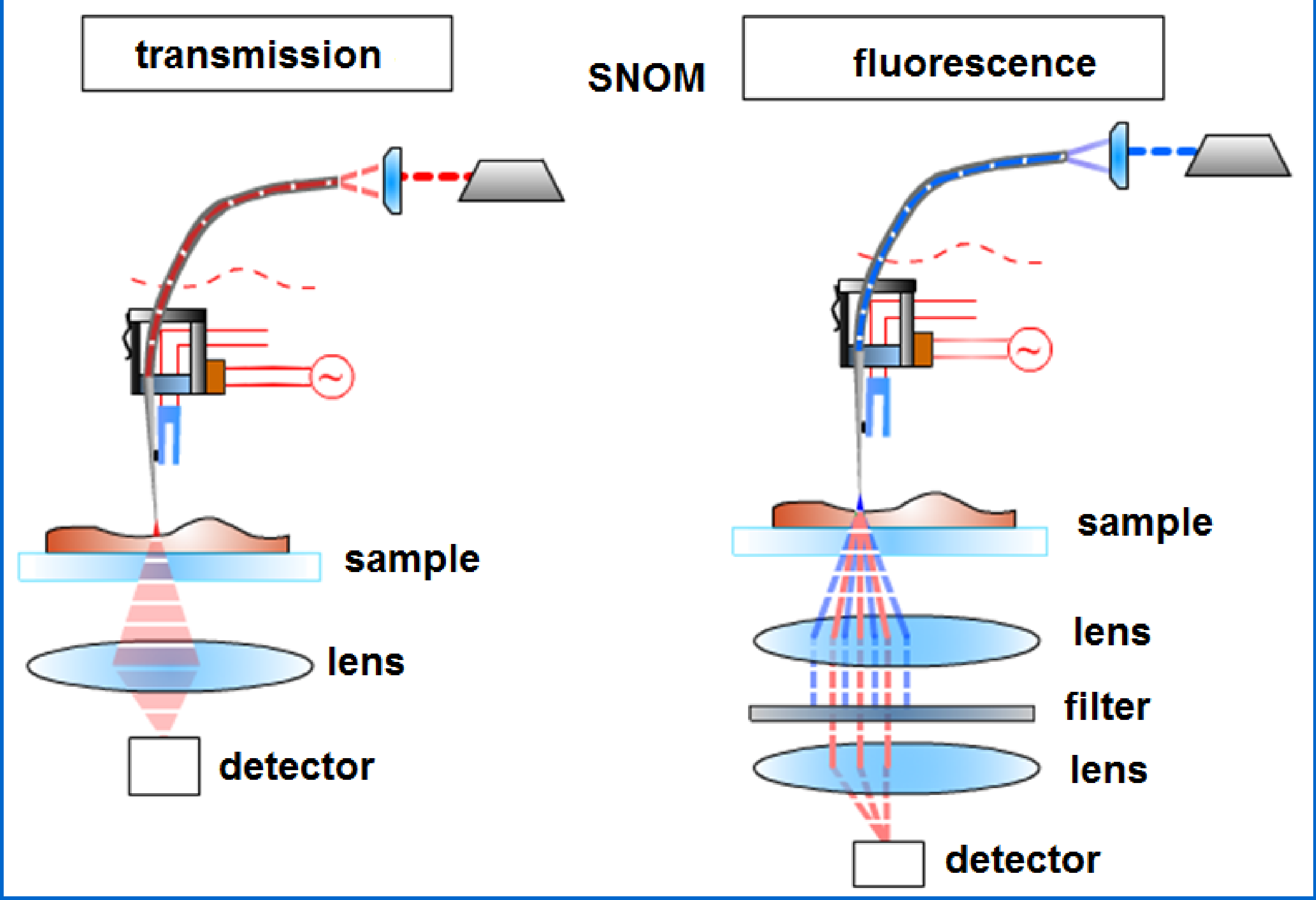


Reflection SNOM

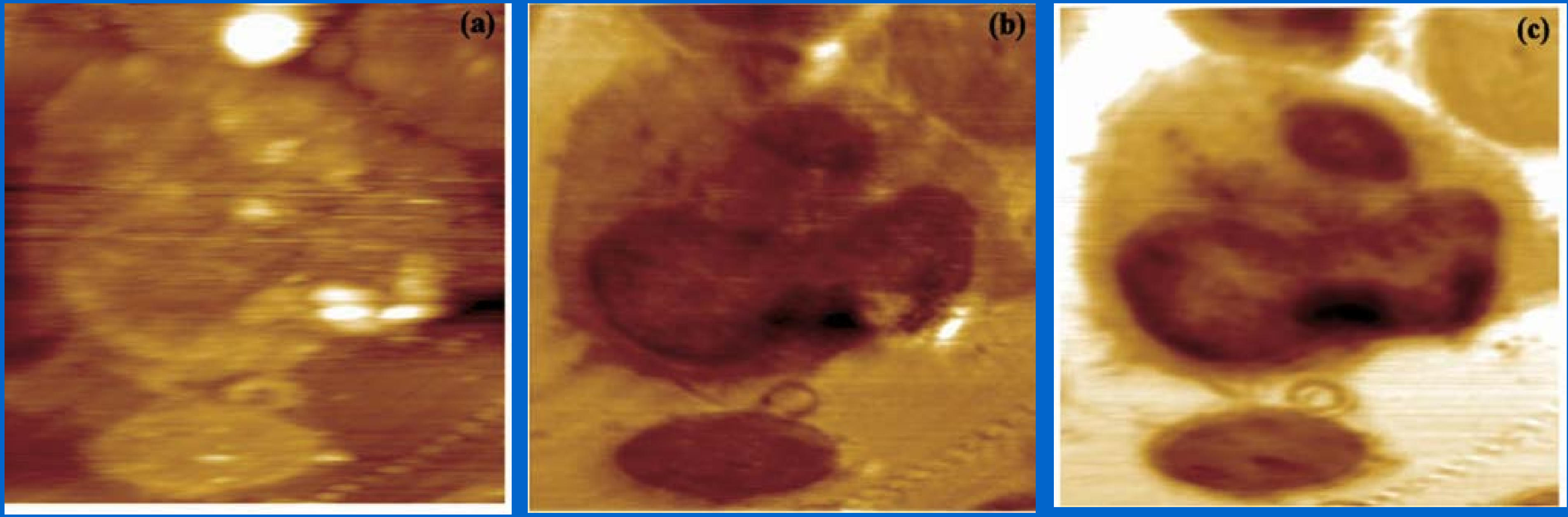


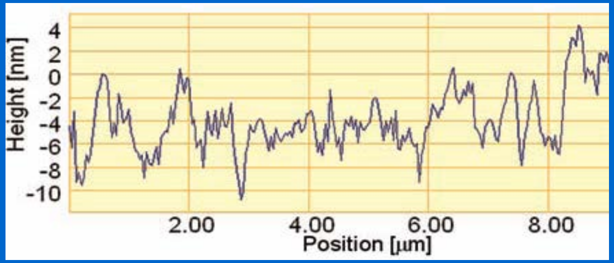
NT MDT

Transmission Fluorescence SNOM



Combined SPM Image: AFM - SNOM





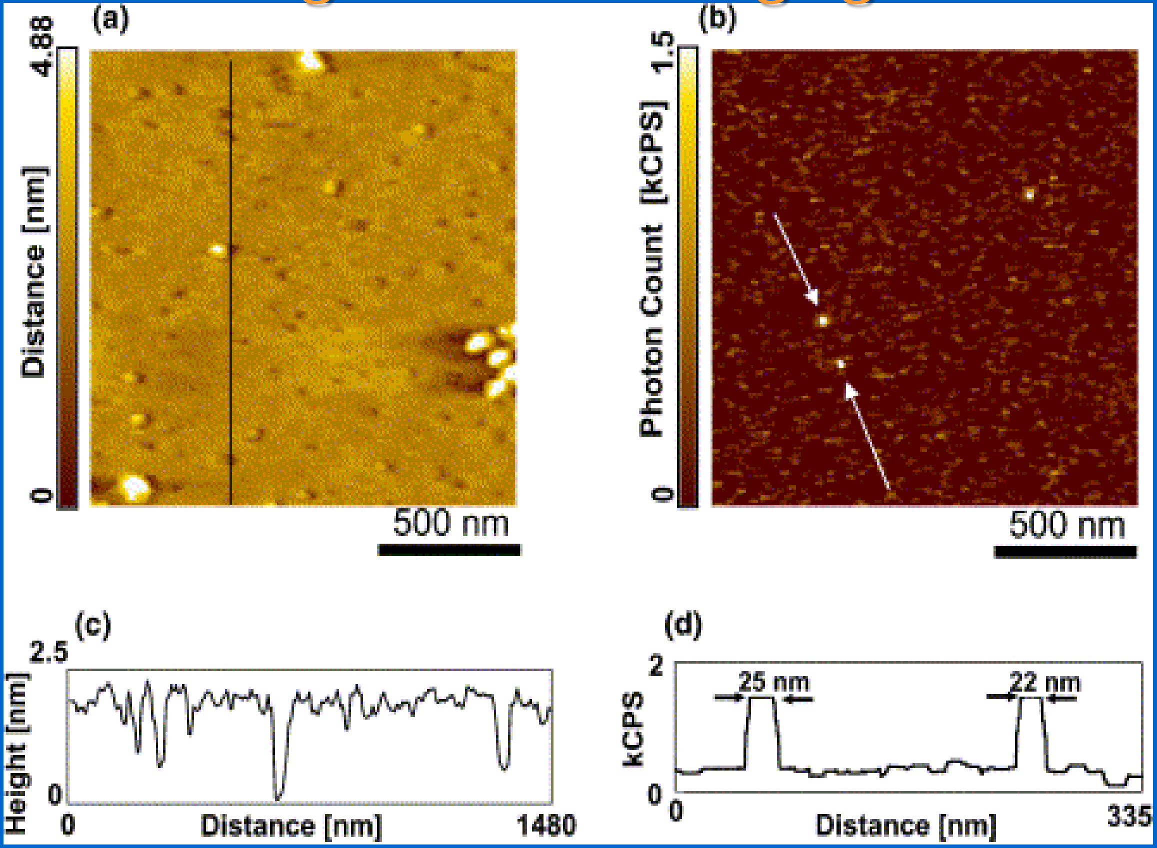
AFM topography (a) and SNOM (b,c) images on ultrathin sections of apoptotic Jurkat cells embedded in araldite resin: SNOM reflection (b)
SNOM transmission (c).
Scan area 25 × 25 µm.

M. ZWEYER *ET AL. Journal of Microscopy*, 229 (2008) 440–446

Fluorescence SNOM

Single molecule imaging

AFM Topography

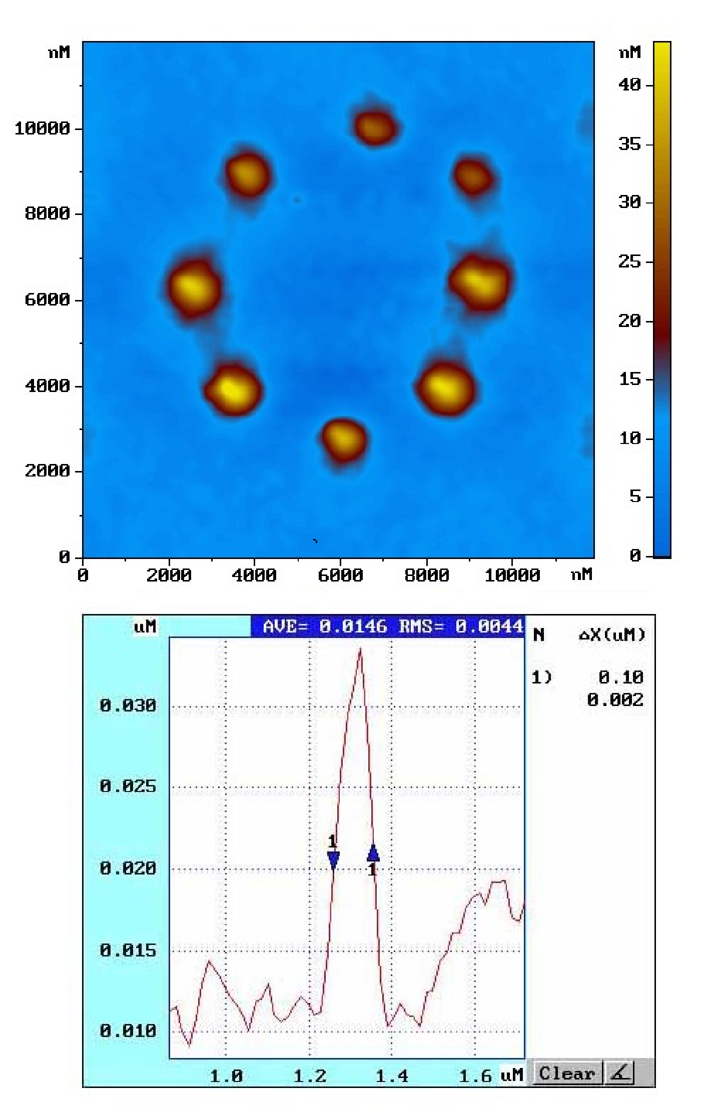


SNOM

Alexa 532 (Exmax 532 nm/Emmax 554 nm, Molecular Probe Inc) v PMMA

H. Muramatsu: Surface Science , Vol. 549, 273, 2004

SNOM lithography



Zdroj: *Veeco*

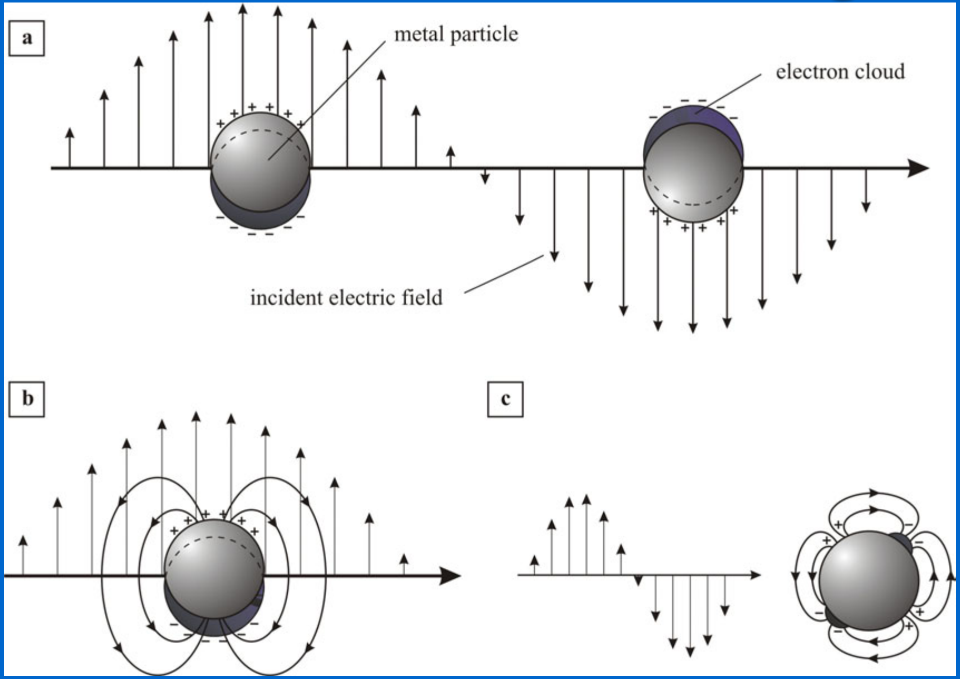
Nanoparticle light amplifier

Plasmon resonant amplification

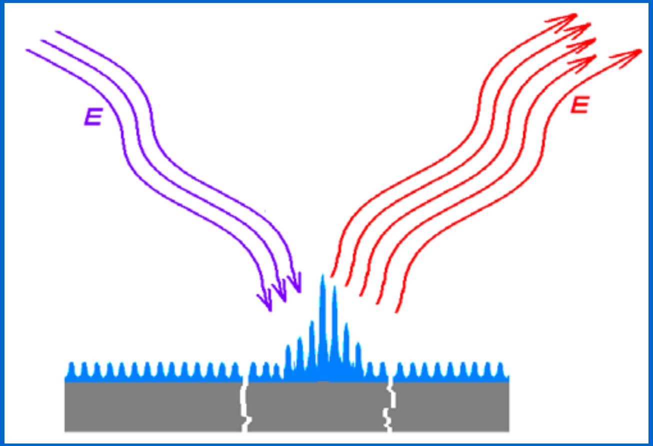
Surface-Enhanced Raman Spectroscopy
SERS

Tip Enhanced Raman Spectroscopy
(Microscopy)
TERS

Metal nanoparticle = Plasmon resonator
light amplifier



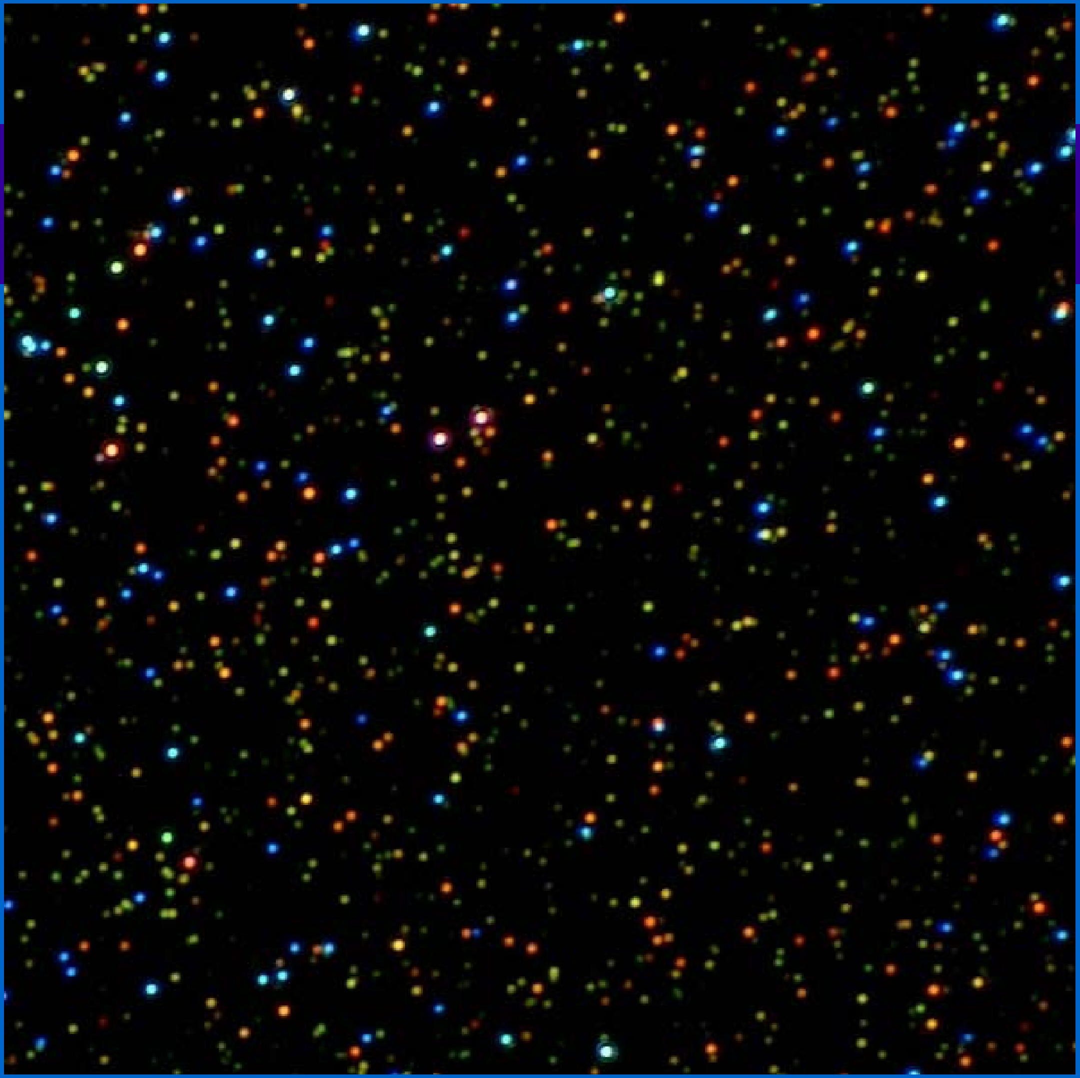
Nanoparticle plasmon:
Min. dimension: > 2 nm
=> non-localised energetic levels
(band/cloud)



Interaction with light => excitation of e$^-$cloud oscillation
Small particles: dipole radiation (a, b) => emission
Large particles: quadru-/n-pole radiation => emission is suppressed (c)

$$\omega_P \sim \sqrt{(n\, e^2/\varepsilon_0\, m^*)}$$

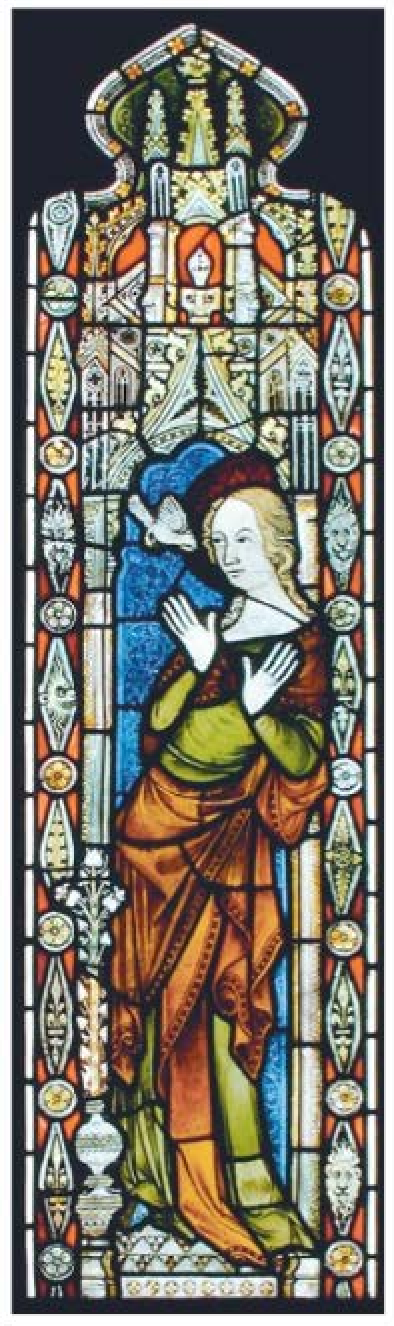
ω_P **plasmon. freq.**
m^* **eff.mass. of conduct.e$^-$**
ε_0 **permitivity**

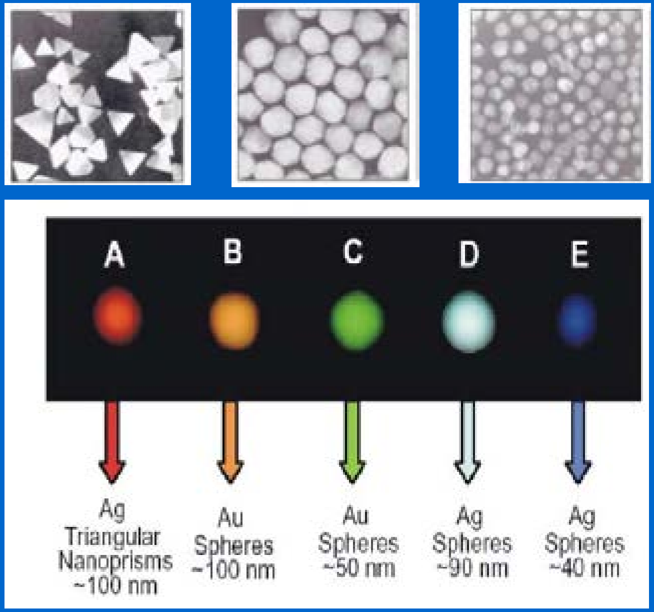


Optical microscopic image (dark field) of light dispersed by nanoparticles:
Ag (nanospheres)   Au (nanospheres)   nanorods

C. Soennischen: *Plasmons in metal nanostructures*. Thesis. L.-M. Universiat Munich 2001

Utilization of plasmon resonance





Ag, Au nanoparticles

70% Ag + 30% Au

Stained Glass

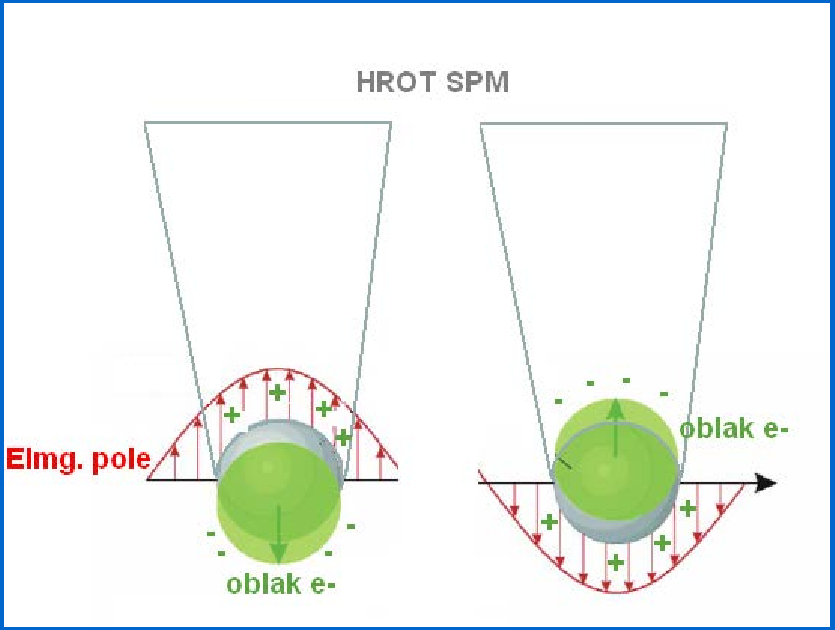
The Lycurgus Cup, Roman (4th century AD), British Museum (www.thebritishmuseum.ac.uk)
R. Jin, Y. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz and J. G. Zheng, Science 294, 1901 (2001).

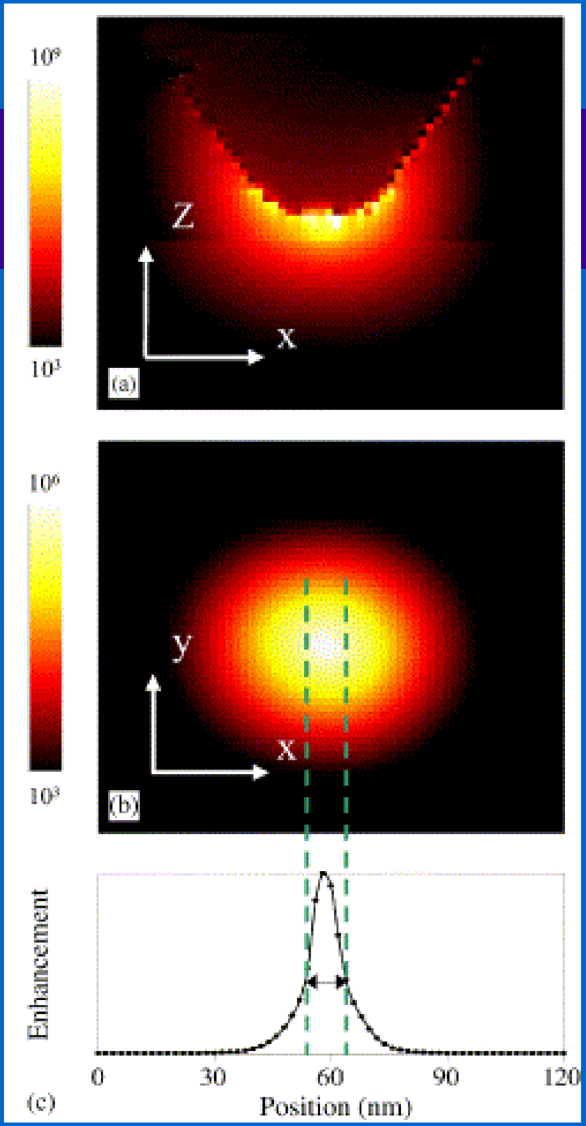
Utilization of plasmon resonance

- Increasing sensitivity of spectroscopic techniques
  fluorescence, Raman spectroscopy ...
  (surface enhancement of Raman spectroscopy ~ $10^{14} – 10^{15}$x allows identification of single molecule)

-resonance shift due to adsorption on the interface
-measurement of adsorbed layer thickness, binding constants

Tip-Enhanced Raman Spectroscopy



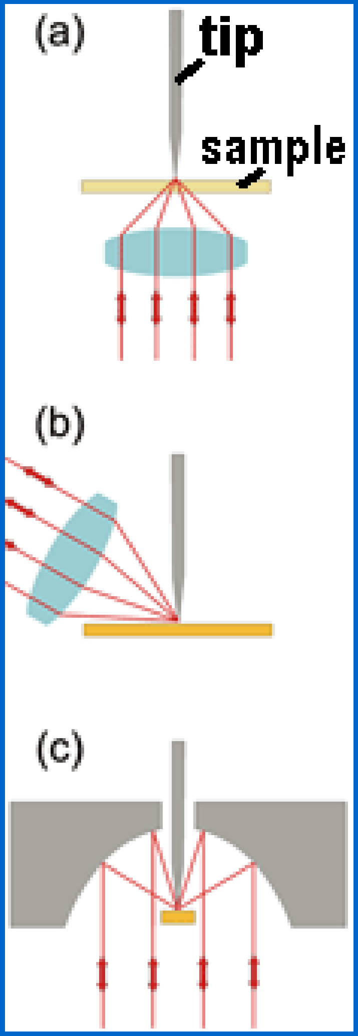


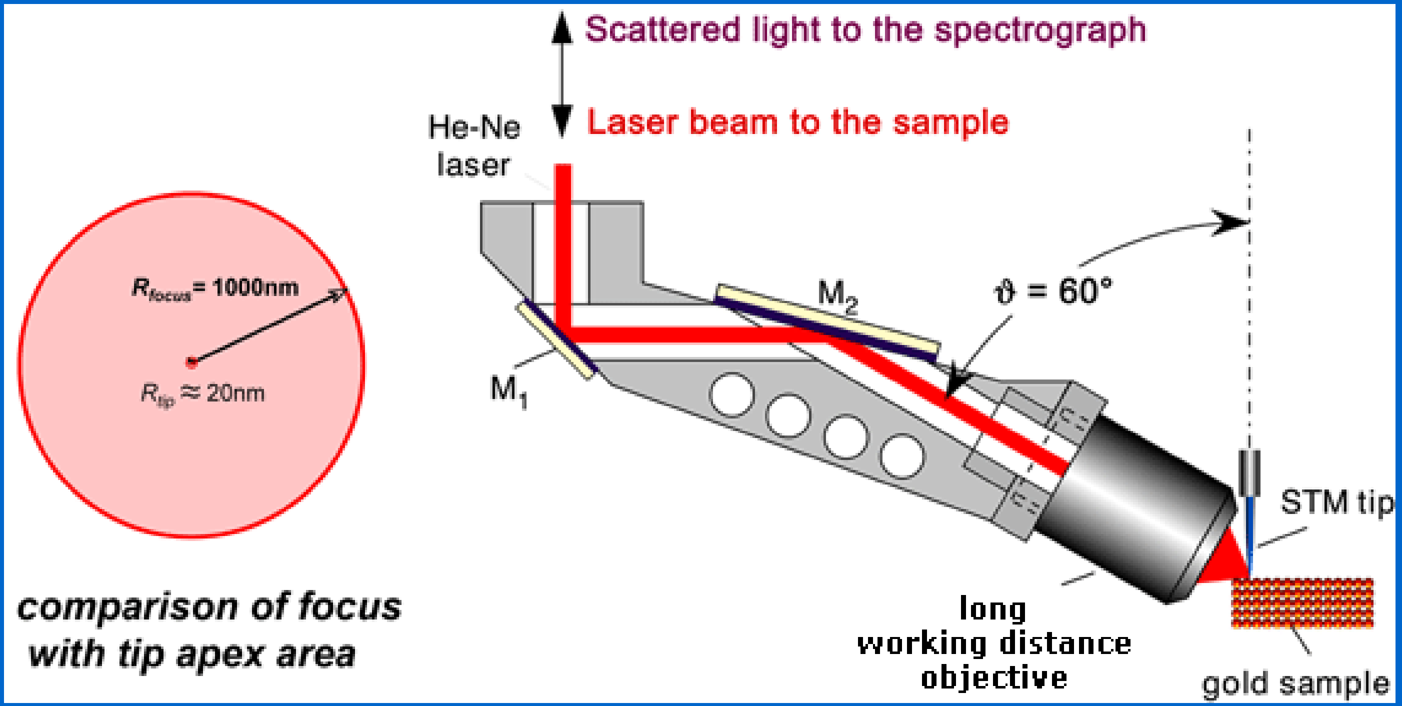
From nanoparticle plasmon resonance (SE) to Tip Enhancement (TE)

P. Hewageegana, M. I. Stockman: Plasmonics enhancing nanoantennas Infrared Physics & Technology 50 (2007) 177–181

TER(S) area ($A = I_{RT}/I_{R0}$)
λ = 541 nm, $d_{T\text{-}S}$ = 4 nm

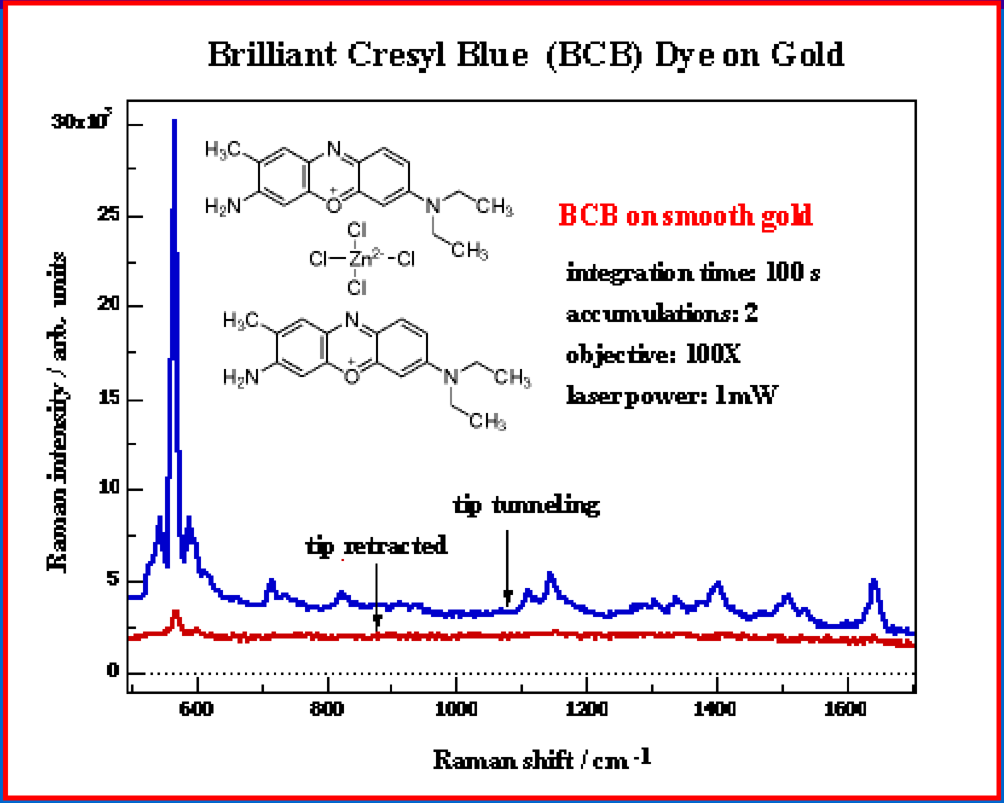
TERS instrumentation





He-Ne laser (632.8 nm) ~0.3 mW on sample

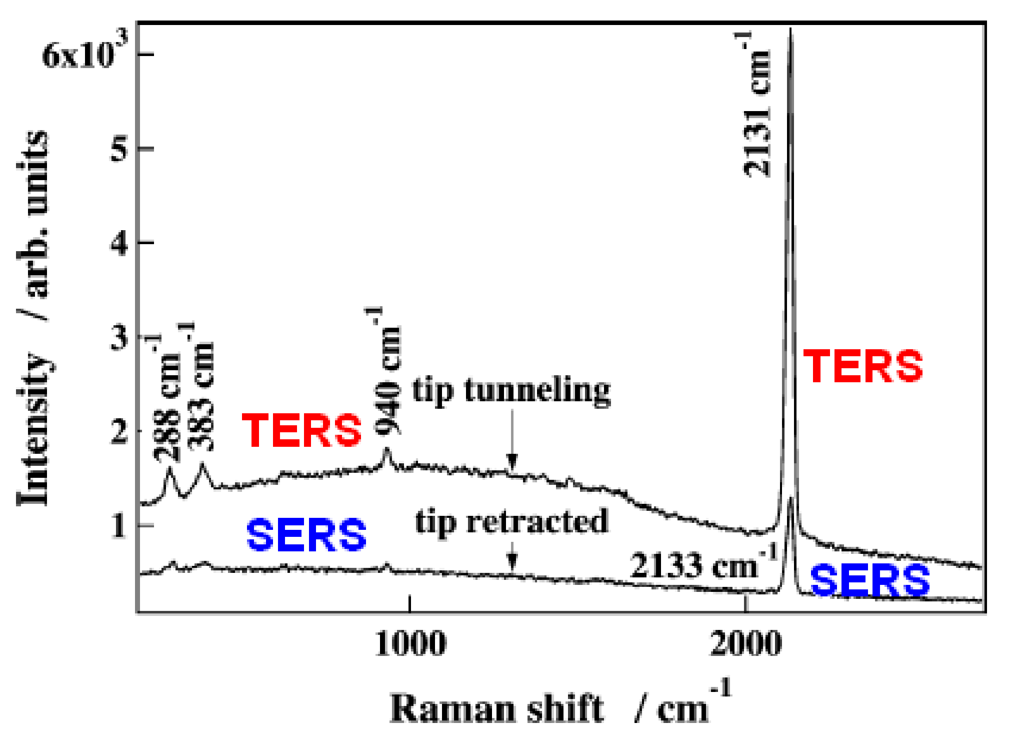
TERS Examples



Monolayer of adsorbate
on Au film, STM Ag-tip

G. Picardi, K. Domke, D.Zhang, B. Ren, J. Steidtner
B. Pettinger Fritz-Haber-Institut der Max-Planck-Gesellschaft

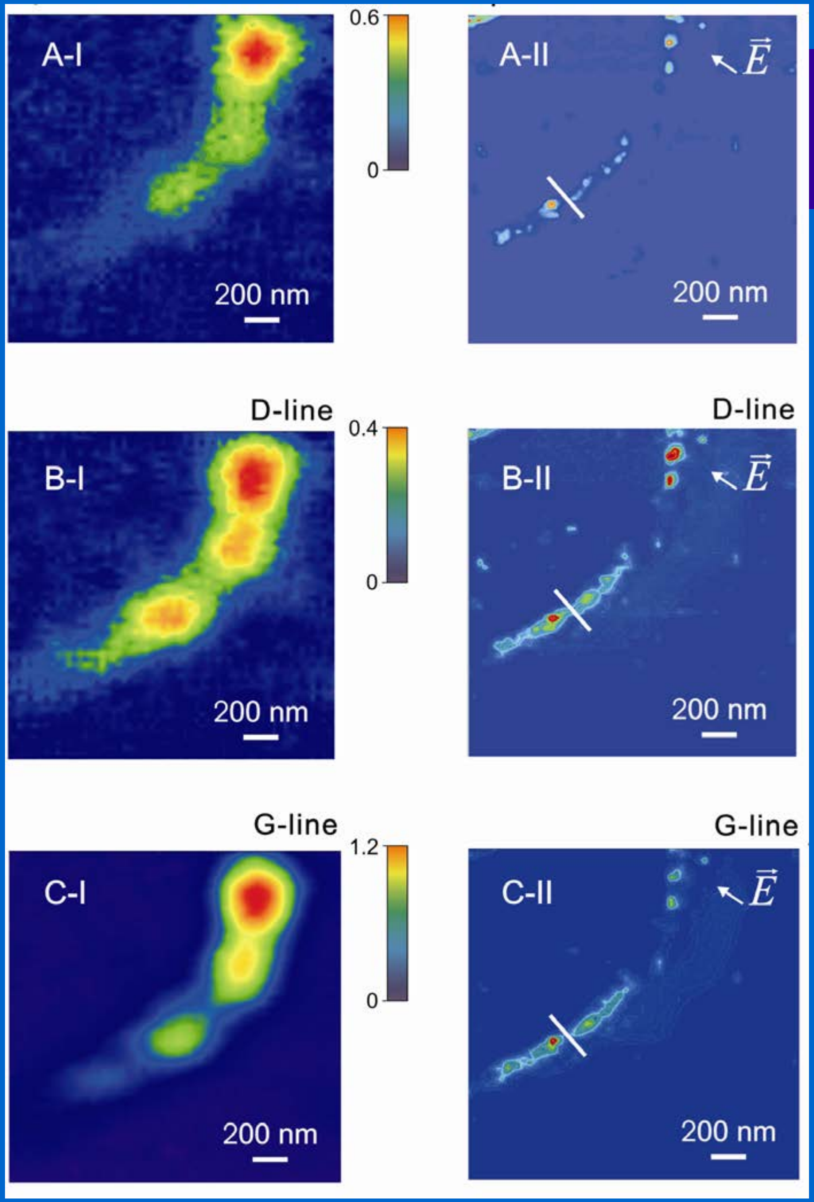
Comparison SERS and TERS



SERS (rough Au surface) a
TERS (same + Au-Tip)/ads. CN^-
Integration time 1sec, laser 5 mW

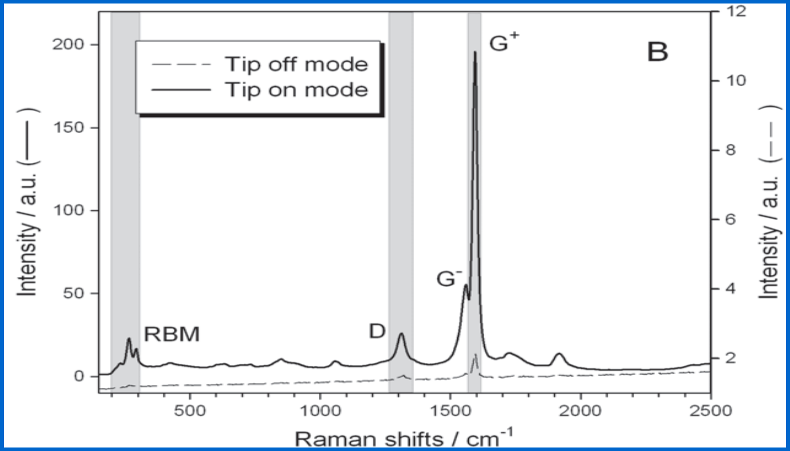
B. Pettinger et al. / Journal of Electroanalytical Chemistry 554–555 (2003) 293–299

TERS Imaging



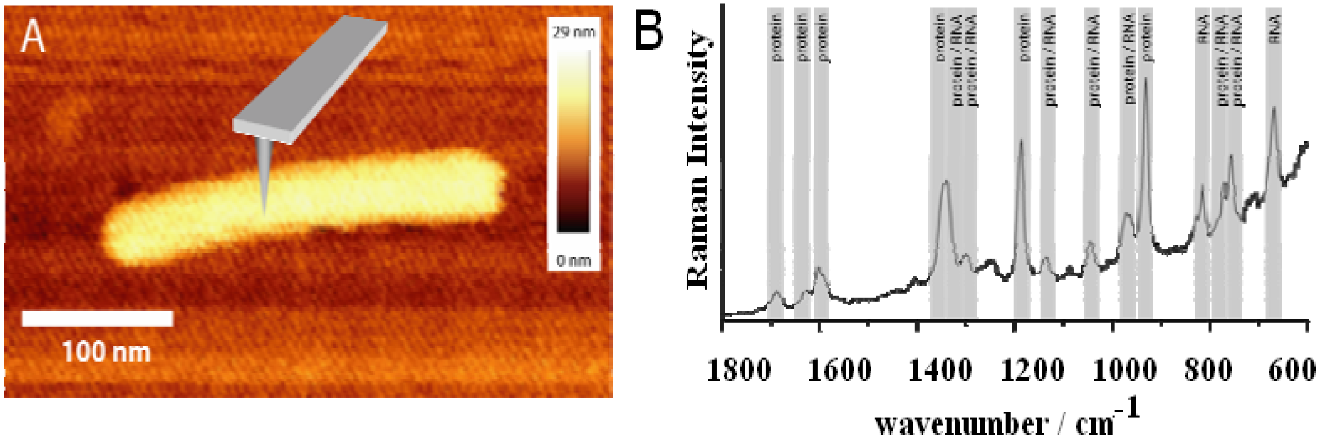
Imaging bundle SWCNT in vibrational modes
RBM (290 cm^{-1})
D („disorder“ 1300 cm^{-1})
G+ tangential C-C stretching (1594 cm^{-1})

I... „tip off“ („far-field“ confocal)
II... „tip on“ (TERS)

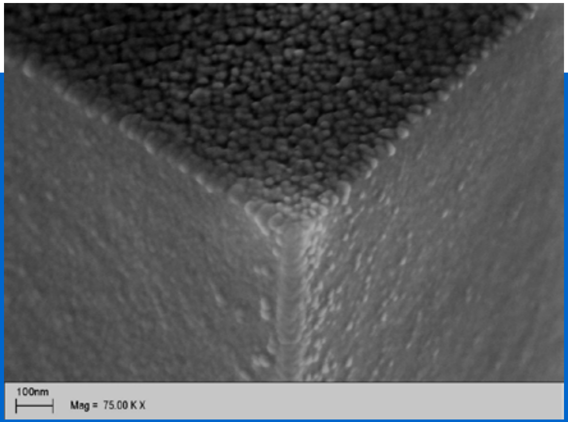


Nanotechnology 18 (2007) 315502

AFM-TERS: Imaging + Analysis



TERS spectroscopic examination of a single tobacco mosaic virus. (A) Before each TERS measurement, an AFM scan with the silver coated AFM tip is performed in order to position the AFM tip directly on a virus. (B) The TERS spectroscopic fingerprint of a tobacco mosaic virus shows that all TERS bands can be assigned protein and RNA contributions.



Metallized (Au) AFM Tip for TERS/AFM

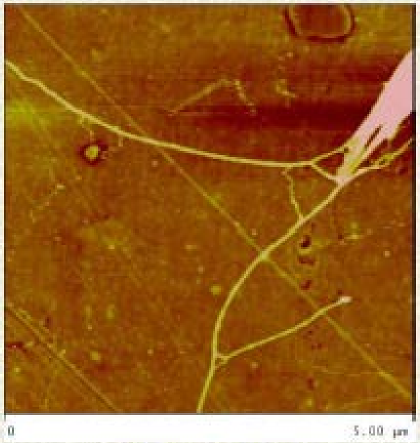
D. Ciala et al

SPM Nanomanipulation & Nanopatterning

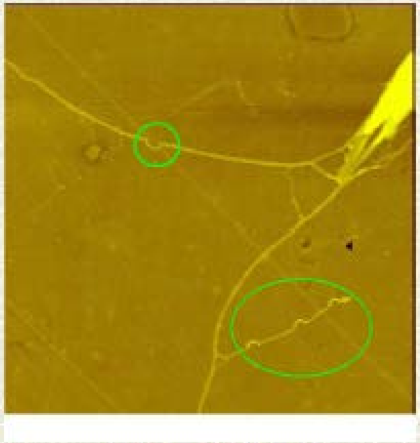
Manipulation on Molecular Level

Contact: Manipulation, Semicontact: Imaging

DNA Manipulation: Pushing

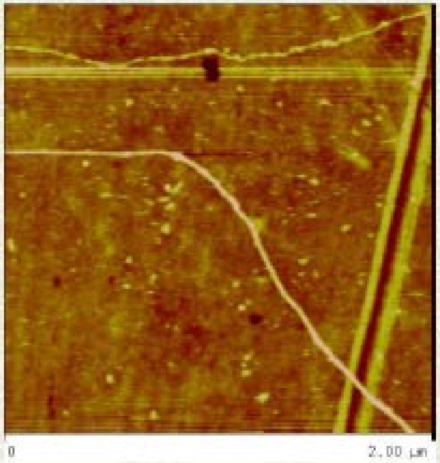


Before pushing

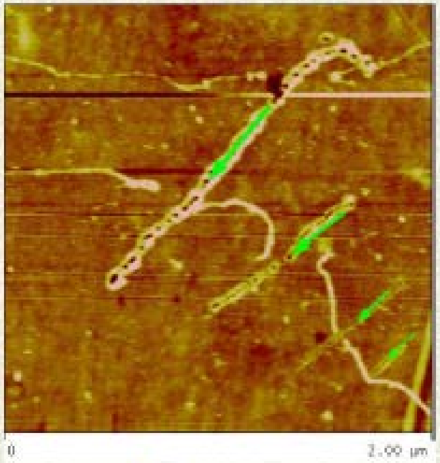


After pushing

DNA Manipulation: Cutting



Before cutting



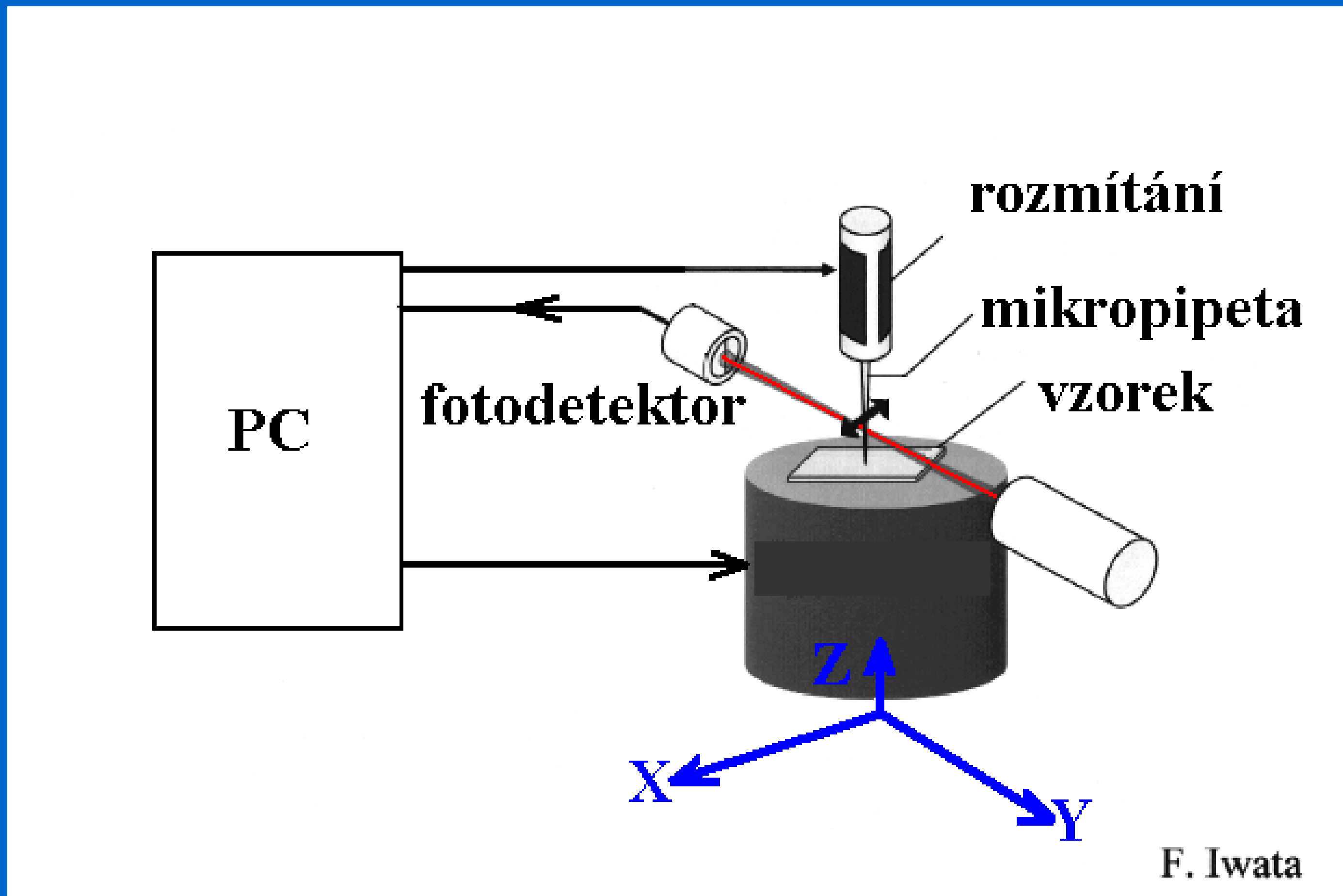
After cutting

Ning Xi

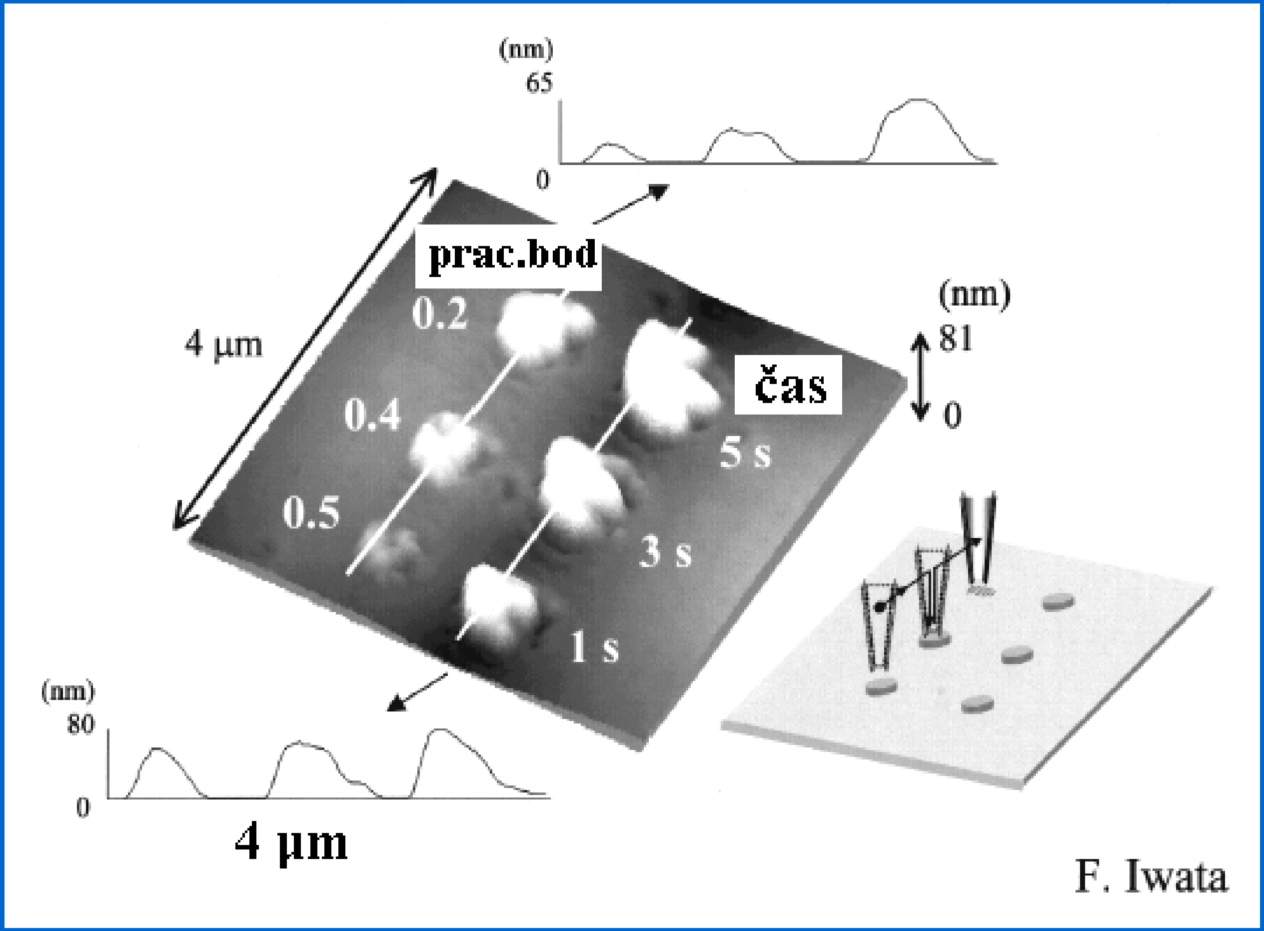
Department of Electrical and Computer Engineering

Michigan State University

Microscopy by Scanning Micropipette



Nanolithography: SPM with scanning μ-pipette



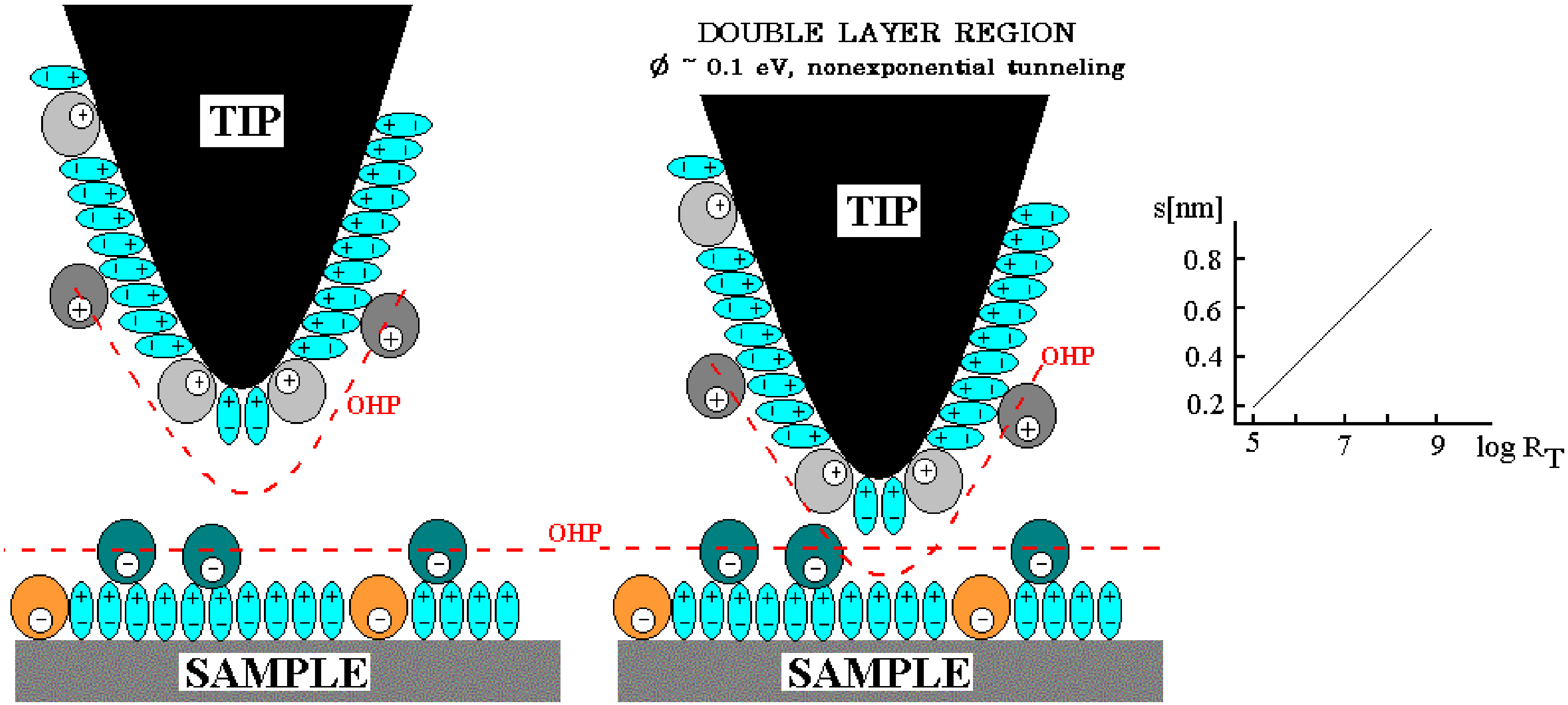
J. Heyrovský Institute of Physical Chemistry, ASCR v.v.i.
Dolejškova 3, 182 23 Praha 8

Laboratory of Scanning Probe Microscopy

AFM/STM Nanoscope IIIa Multimode
In gasses and liquids
Resolution ~ 0.1 nm

AFM/STM TopoMetrix TMX 2010
AFM Dimension Icon
In gasses and liquids
Resolution~ 0.1 nm

http://www.jh-inst.cas.cz/
http://www.jh-inst.cas.cz/~janda
pavel.janda@jh-inst.cas.cz



Halbritter resonant (intermediate) states (n) oriented dipoles HOH-OH,
specif. adsorbed ions/molecules (shape resonances)
parallel along layer of oriented dipols d(eff)=d/(n+1) => ϕ(eff)=ϕ/(n+1)

Toney structural changes in layers of water molecules near the electrode

Kaukonen formation of clusters of water molecules in gap

Ramanova spektroskopie

Elastický rozptyl světla na molekulárních/atomárních strukturách: $\lambda_{rozptyl} = \lambda_{dopad}$

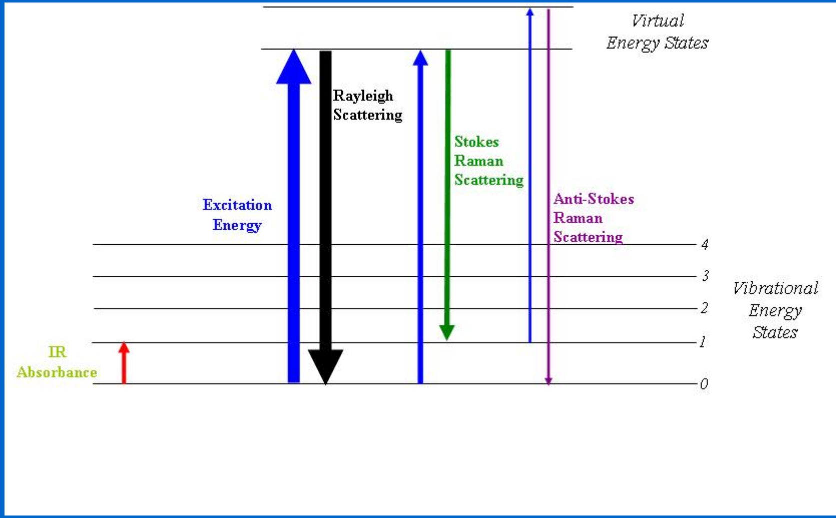
Neelastický rozptyl (malá část ~ $1/10^6$) => posun λ: $\lambda_{rozptyl} \neq \lambda_{dopad}$

=> excituje **vibrační/rotační** a elektronické stavy

Vibrační/rotační excitace (posun λ) **& změna polarizovatelnosti** (intenzita) (deformace e-oblaku vzhledem k vibračním koordinátám) => **Ramanův posun**

molekula absorbuje energii – ***Stokesův rozptyl*** – *„red shift"*: $\lambda_{\mathbf{rozptyl}} > \lambda_{\mathbf{dopad}}$

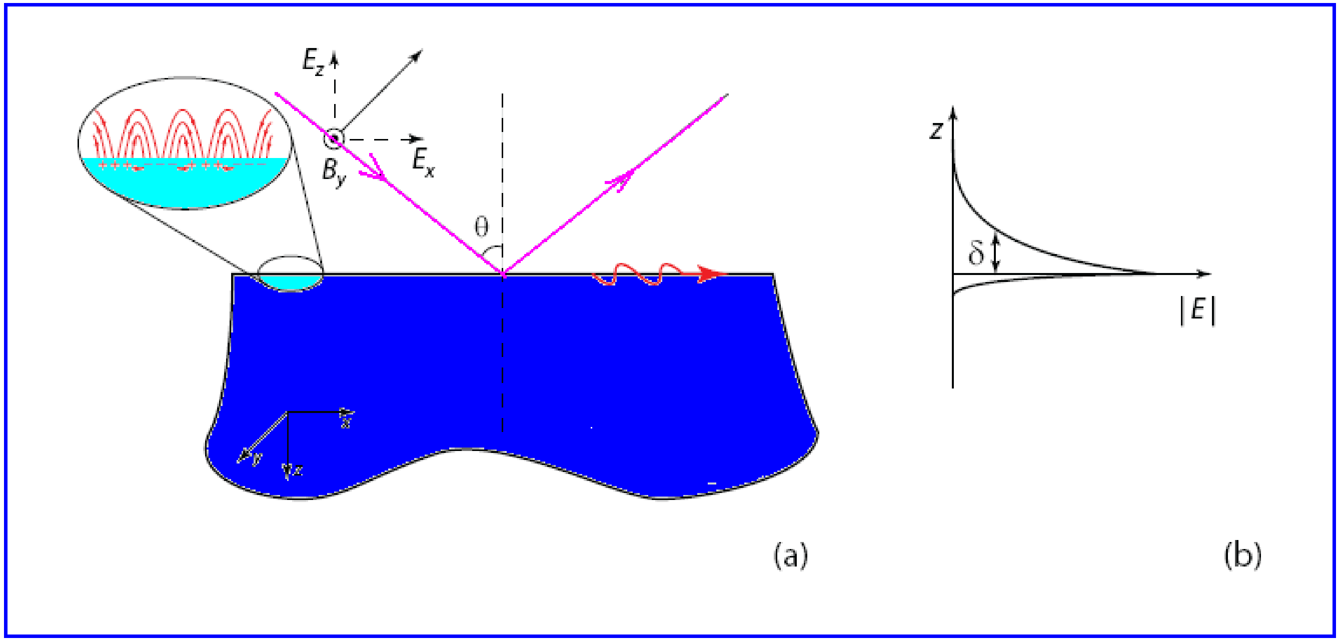
molekula (na vyšší energetické hladině) ztratí energii – ***anti-Stokesův rozptyl*** – *„blue shift"*: $\lambda_{\mathbf{rozptyl}} < \lambda_{\mathbf{dopad}}$



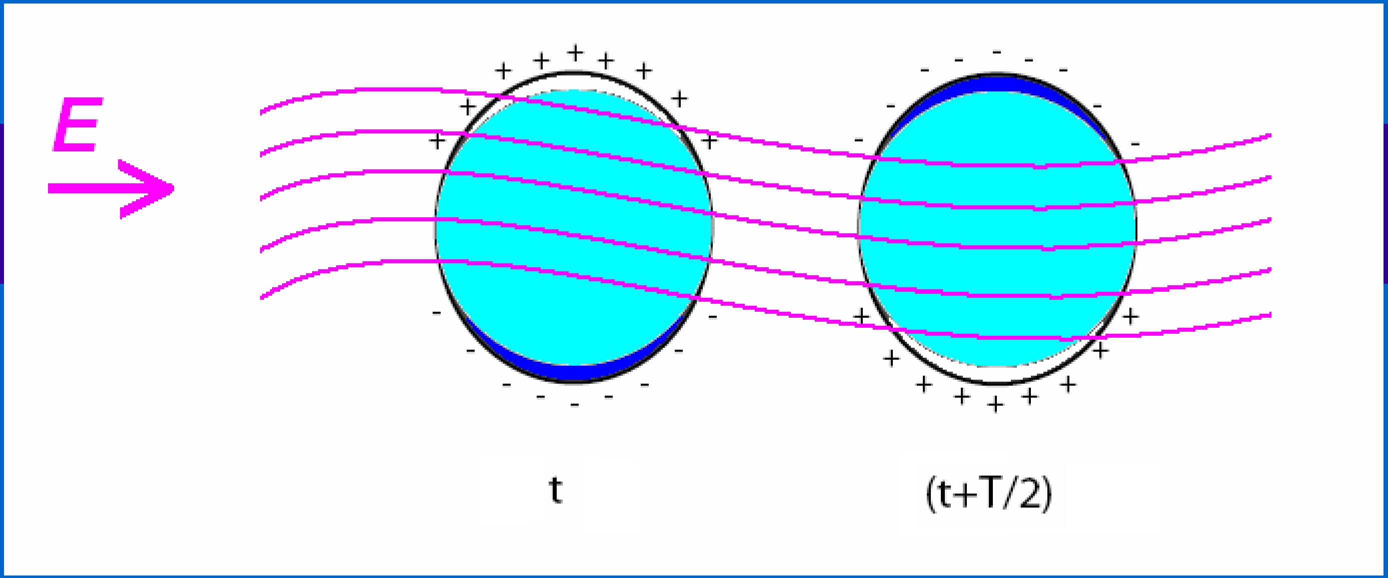
Resonanční Raman:

$\lambda_{\mathbf{dopad}} = \lambda_{\mathbf{excit.e}}$

=> zesílení intenzity vibrač.módu odpovídajícího excit.**e**-hladiny the p-polarized electromagnetic field (i.e. field, which has its electric component parallel to the plane of incidence) propagating towards the boundary of two media at angle of incidence θ.



(a) Excitation of a plasmon on the metal-dielectric interface with p-polarized light, propagating at angle of incidence θ greater than the angle of total internal reflection. Inset illustrates the surface charges. (b) Plasmon-induced field intensity at the interface.



Dopadající světlo λ (***hν***) excituje oscilace oblaku elektronů vodivostního pásu s následným zesílením elmg. pole na fázovém rozhraní (povrchu)

v resonanci absorpce světla λ_{SPEC} vzroste o několik řádů

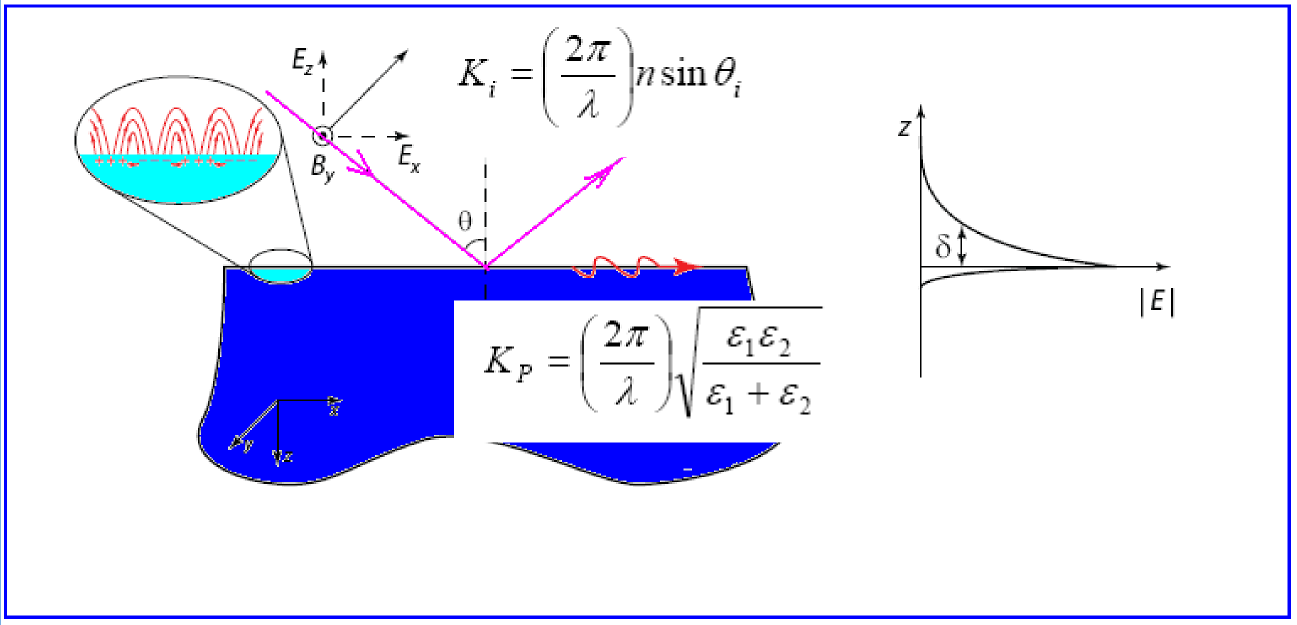
= **povrchová plasmonová resonance**

Kovová nanostruktura funguje jako anténa.

$\boldsymbol{\varepsilon_0}$ and $\boldsymbol{\varepsilon}(\omega)$ are dielectric functions of the surrounding medium and nanoparticle respectively. It can be easily shown that the condition for the resonance is that $\varepsilon'(\omega) = -2\varepsilon_0$.

Interakce s elmg. polem:
Povrchový plasmon a plasmonová resonance

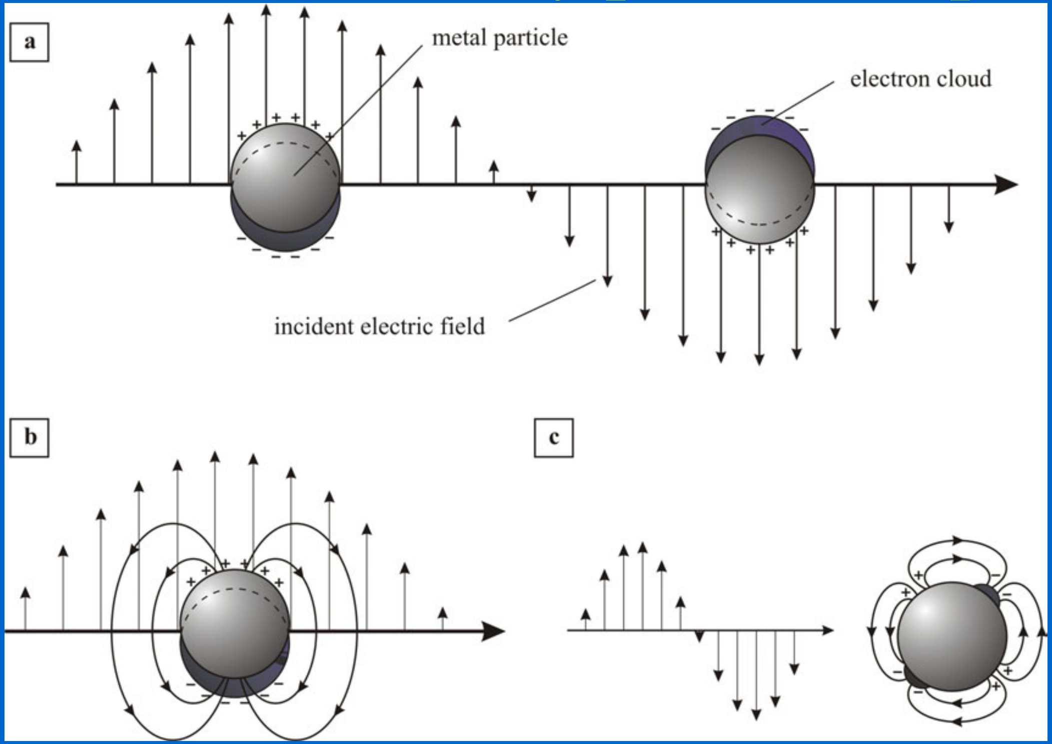
E_p elmg. pole: el. složka polarizovaná paralelně s mezifázím,
$\theta_{dopad} > \theta_{odraz}$. K_i, K_p vlnové vektory dopadajícího pole a plasmonu.



Resonanční podmínka: $K_i = K_p$

absorpční maximum E_p ($\varepsilon_{1,2}$..dielektr.permitivity kovu a prostředí)

Interakce s elmg. polem: Nanočásticový plasmon a plasmonová resonance



Nanočásticový plasmon:
Min. rozměr částic: > 2 nm
=> neexistují lokalizované energetické hladiny
(pás/oblak)

$$\omega_P \sim \sqrt{(n\, e^2/\varepsilon_0\, m^*)}$$

ω_P plasmonová frekvence
m^* ef.hmota vodiv.e^-
ε_0 permitivita prostředí

Interakce se světlem => excitace oscilací e-oblaku => polariton (el.polarizace)
Interakce malé nanočástice se světlem => **dipólová radiace** (**a**, **b**) **emise *hν***
větší nanočástice => kvadrupólová radiace (**c**)

Povrchově zesílená Ramanova spektroskopie
Surface Enhanced Raman Spectroscopy

Max. zesílení - dopadající i rozptýlené světlo - (Raman)
jen pro frekvence s minimálním posunem
(velmi posunuté nemohou být obě v rezonanci => menší zesílení)

kombinuje výhody
fluorescence => vysoký světelný zisk
+
Ramanovy spektroskopie => strukturní informace

-nanostruktury Au, Ag, Cu (NIR-Vis) -„
-Hot-Spots“ (signál není reprezentativní vzhledem k povrchu)

význam TERS

+ **Plasmonová resonance lokalizovaná na povrchu kovového hrotu** (anténa, max.intenzita el.pole na hrotu) => hrot funguje jako téměř ideální bodový zdroj světla.
+ **Mobilní „hot spot“** – snímání reprezentativního signálu z celého povrchu vzorku
+ Proces může být laděn (z/do resonance) vkládáním napětí na hrot
+ umožňuje práci ***in situ***
+ zesílení ~ 10^7

- Vývojové stadium, neúplně definované podmínky: vliv tvaru hrotu, složení hrotu, elektrolytu...

Surface-enhanced and STM-tip-enhanced Raman Spectroscopy at Metal Surfaces
Bruno Pettinger, Gennaro Picardi, Rolf Schuster, Gerhard Ertl
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany
Single Molecules, Volume 3, Issue 5-6 , Pages 285 - 294

S. Kuwata: Near Field Optics and Surface Plasmon Polariton
Springer Verlag, 2001