UNIVERSITY OF
CHEMISTRY AND TECHNOLOGY
PRAGUE

ATHENS 2024

Vibrational Nano- and Micro-Spectroscopy

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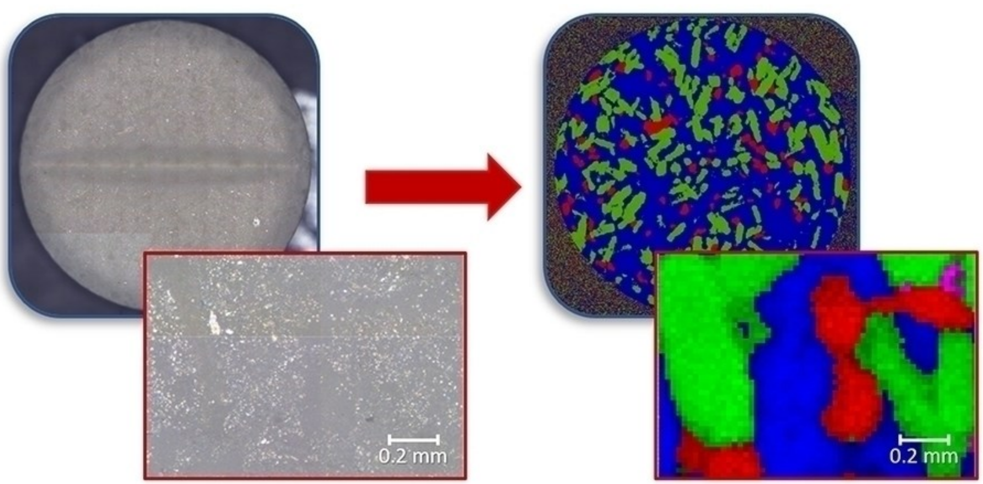
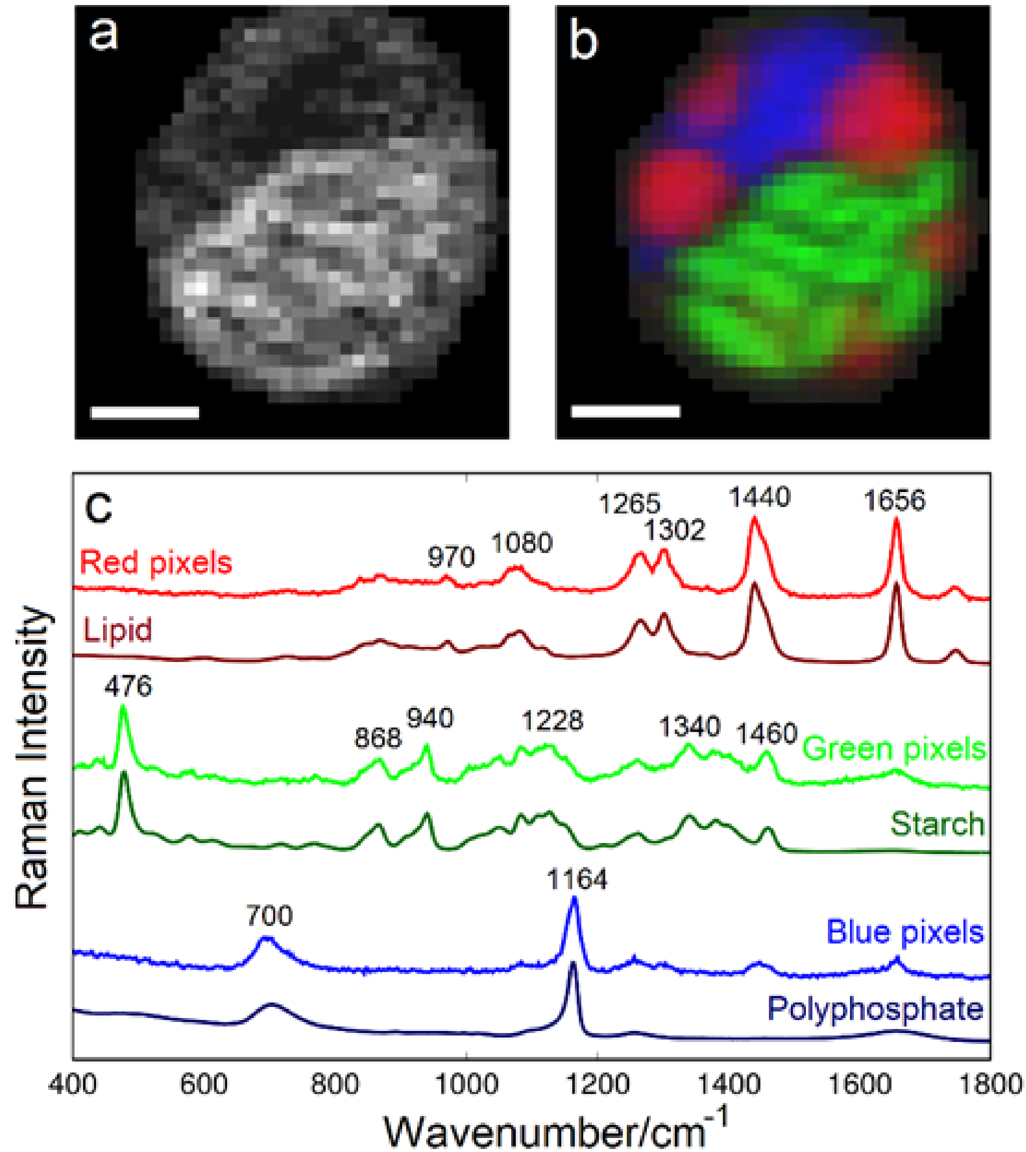
Microspectroscopy

- Detailed chemical information about the sample – **chemical maps**
  - group of points collected over the entire area of interest
  - points can be collected in series (mapping – scanning the surface, single channel detection) or in parallel (imaging – multichannel detection)
- Generate maps from peak heights, areas, peak ratios, correlation, results of principal component analysis etc.
- Monitoring changes in chemical composition in a sample:
  - inhomogeneities, defects, composite materials



Microspectroscopy – Examples

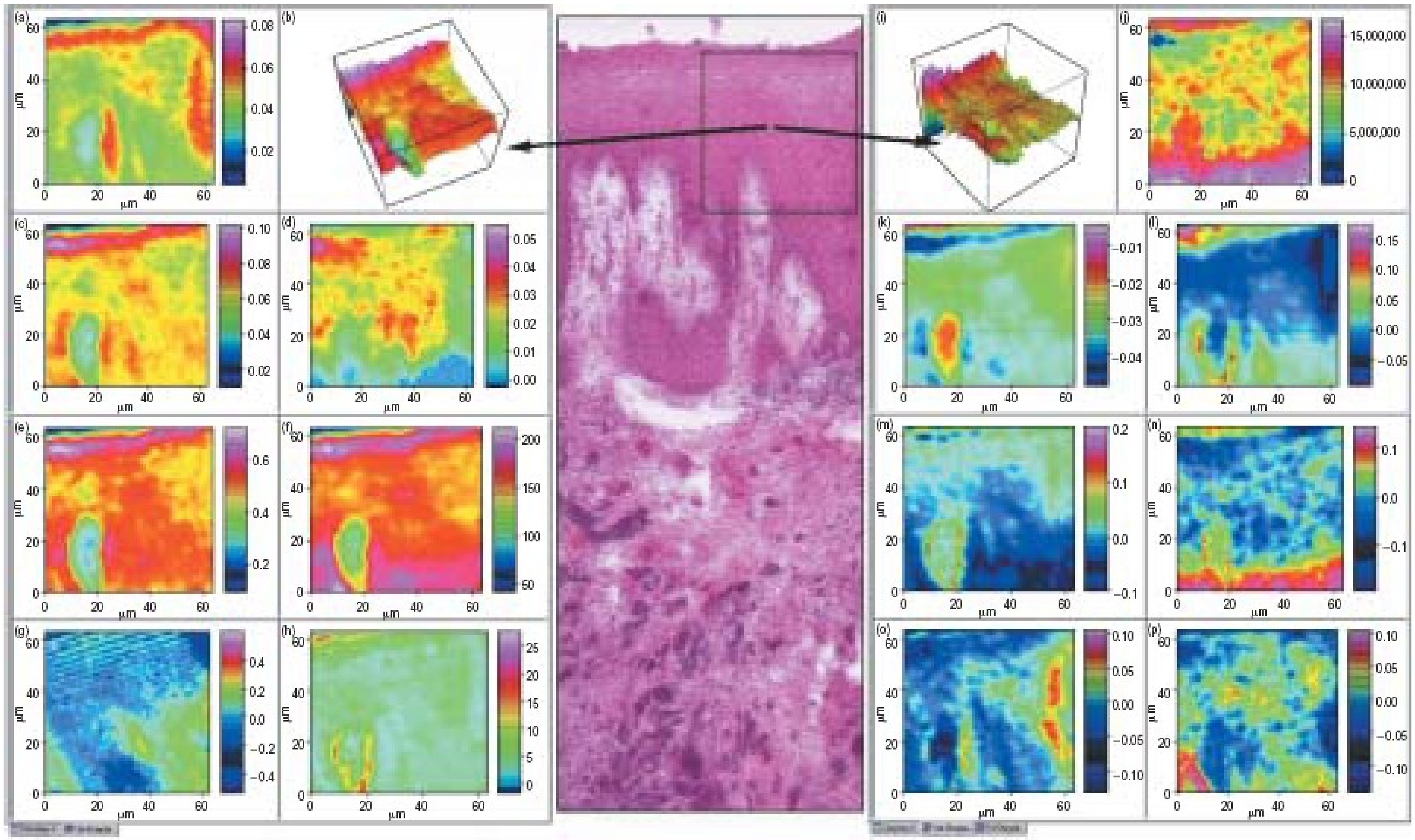
Spectral map generated by database spectral correlation



Microspectroscopy – Examples

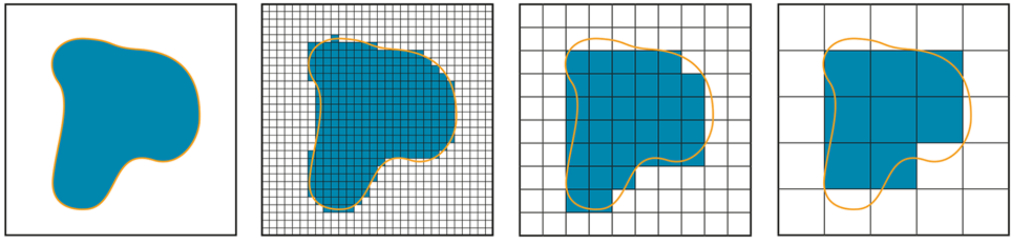
Spectral maps generated by peak height and PCA

<u>Peak height</u> <u>PCA</u>



Microspectroscopy – Resolution

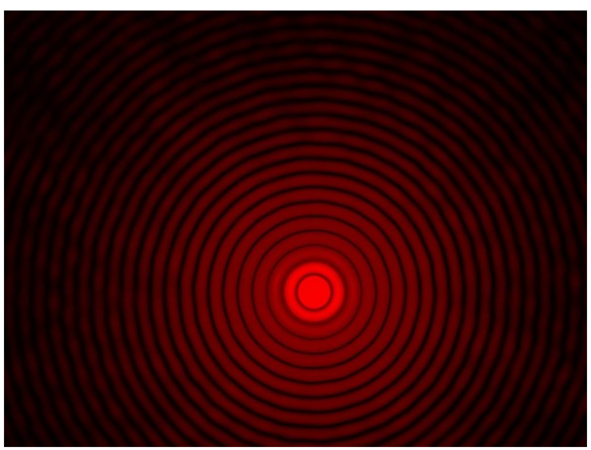
- **Spatial Resolution**
  - the ability to view two closely spaced points as distinct objects
  - limited by diffraction

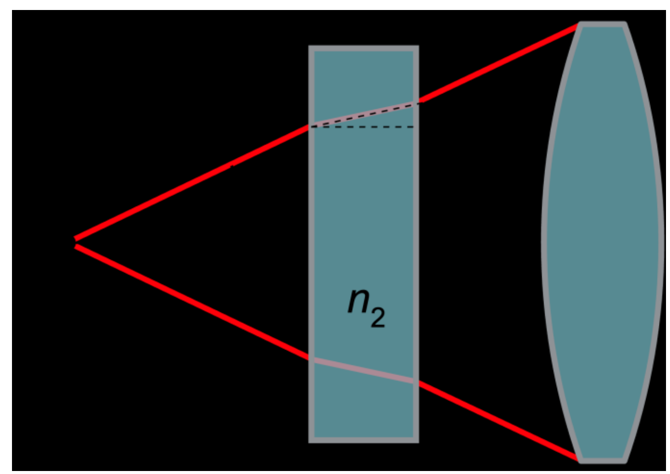


- **Diffraction**
  - the bending (or “scattering”) of light/energy by an opening of an optical element (lens, aperture)
  - the wavelength of the light approaches the size of the opening
  - for infrared spectroscopy ~ 10 µm (1000 cm^{-1} is 10 µm)
  - for Raman spectroscopy better than 1 µm (excitation in visible range)

Microspectroscopy – Resolution

- Abbe diffraction limit: $d = \frac{1.22 * \lambda}{NA_{obj} + NA_{cond}}$
- Numerical aperture: $NA = n * \sin\theta$
  - $\sim$ 1.4–1.6 in modern microscopes
- Approximation: $\mathrm{d} = \frac{\lambda}{2}$
- Circular aperture – Airy disk

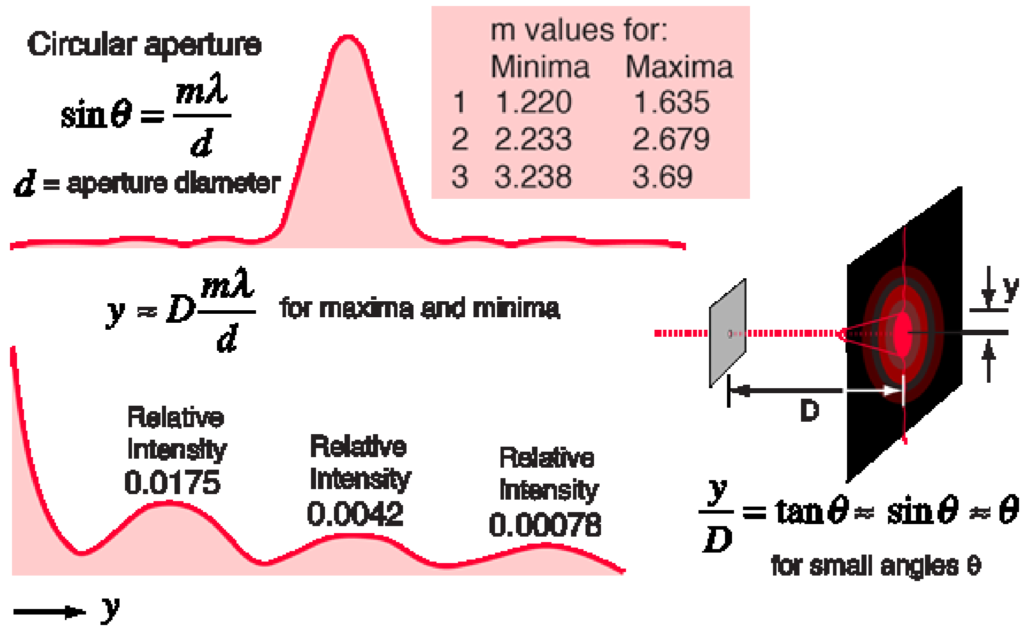




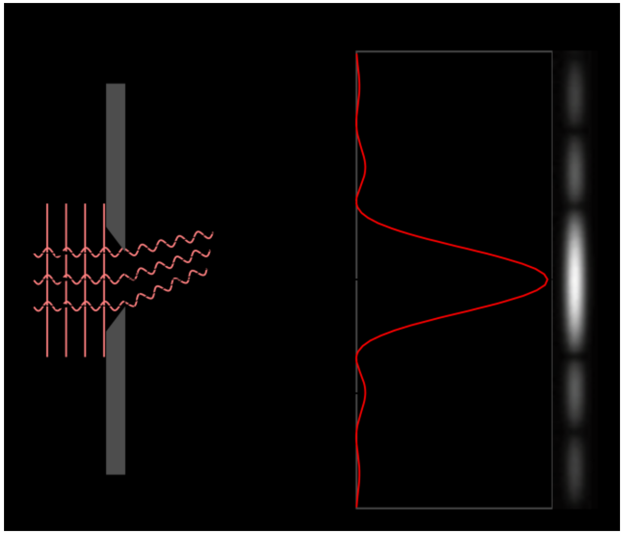
Microspectroscopy – **Resolution**

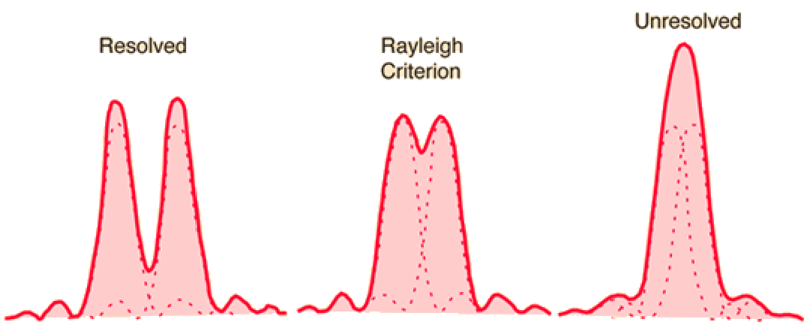
- Rayleigh criterion – generally accepted criterion for the minimum resolvable detail
- Diffraction-limited imaging process – the first diffraction minimum of the image of one source point coincides with the maximum of another

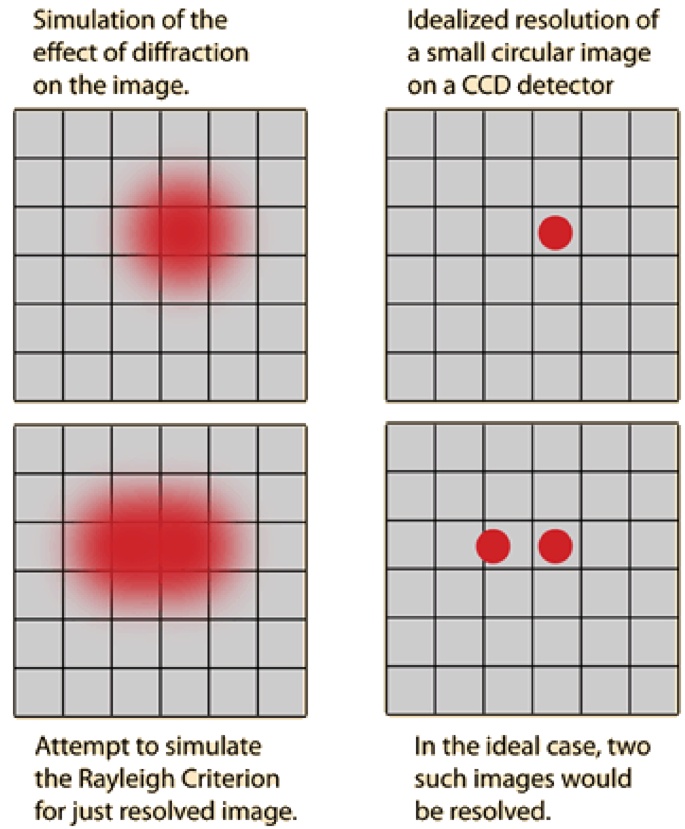
$$d = \frac{1.22 * \lambda}{NA_{obj} + NA_{cond}}$$



Microspectroscopy – Resolution



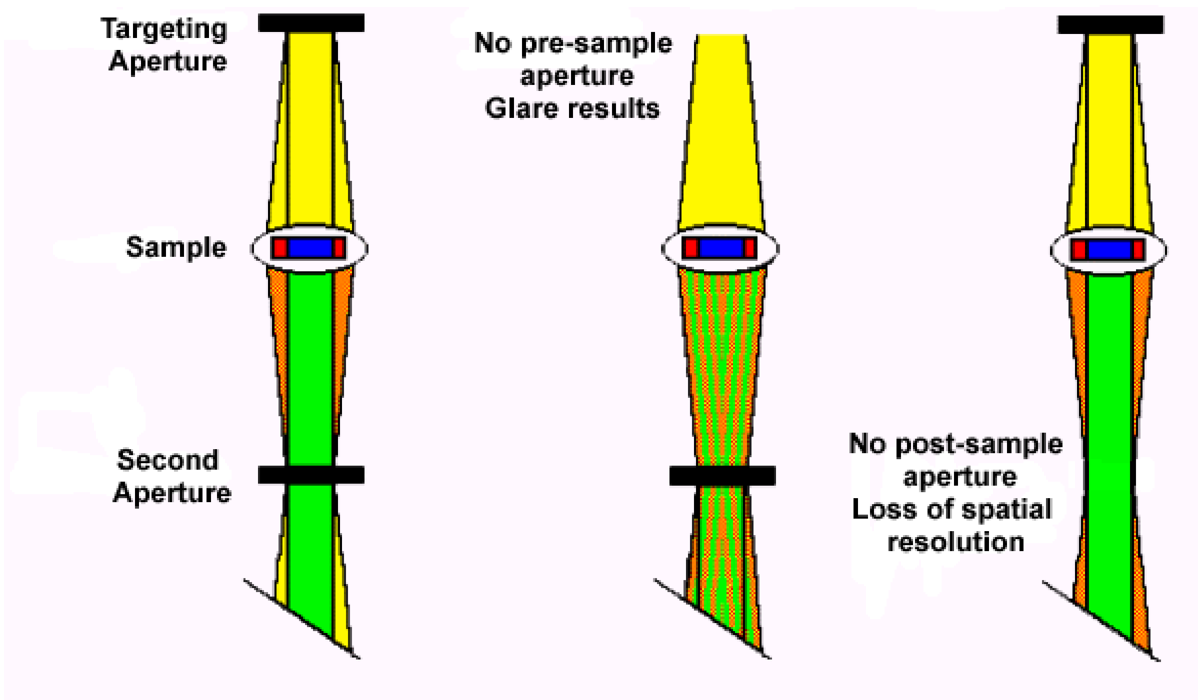




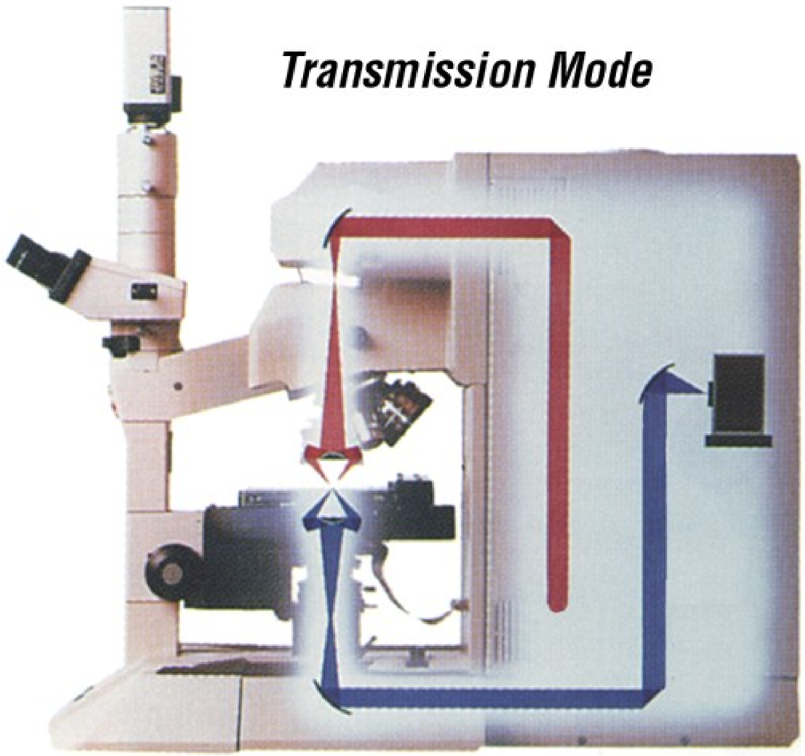
http://hyperphysics.phy-astr.gsu.edu/hbase/phyopt/diflim.html

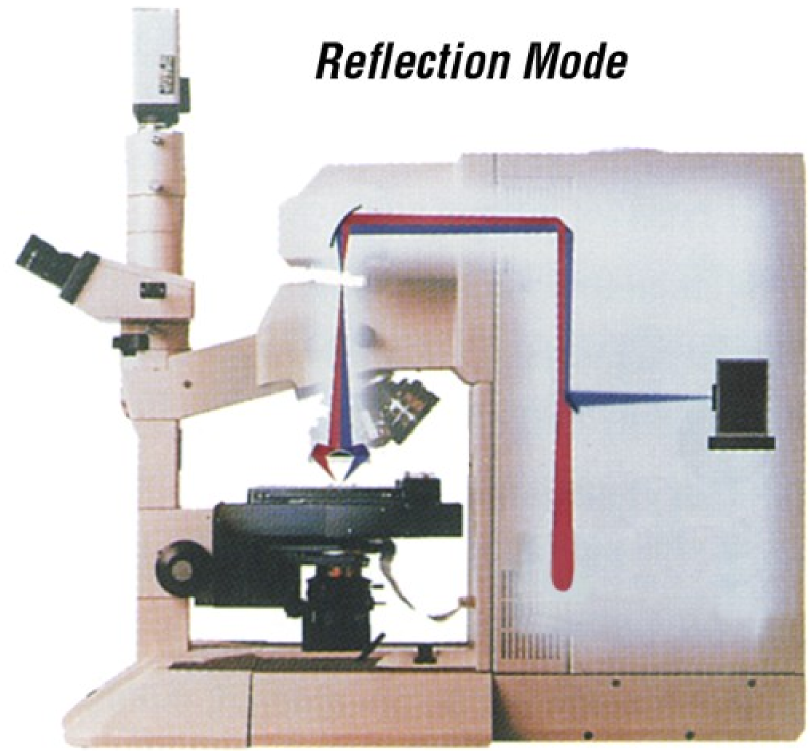
Microspectroscopy – Resolution

- Dual remote aperture
  - first aperture placed between infrared source and sample – limits beam to desired sample area
  - second aperture placed between sample and detector – reduces amount of diffracted light detected



IR Microspectroscopy Sampling Modes





IR Microspectroscopy Sampling Modes

Transmission

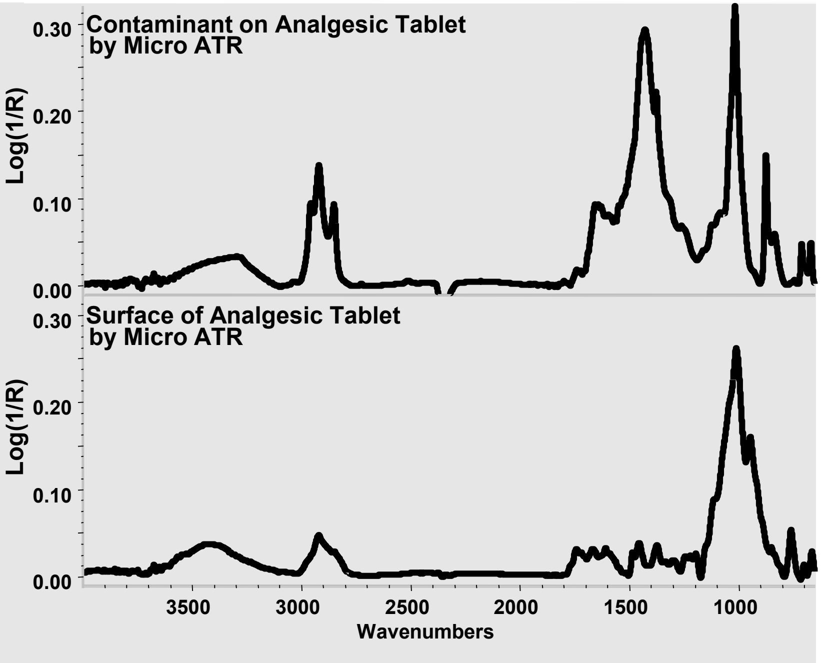
- transparent samples
- thin layers
    - 5–15 µm thickness
    - large and uniform surface
- compression cells

Reflection

- non-transparent samples
- ATR – attenuated total reflection
- specular reflection
- grazing angle

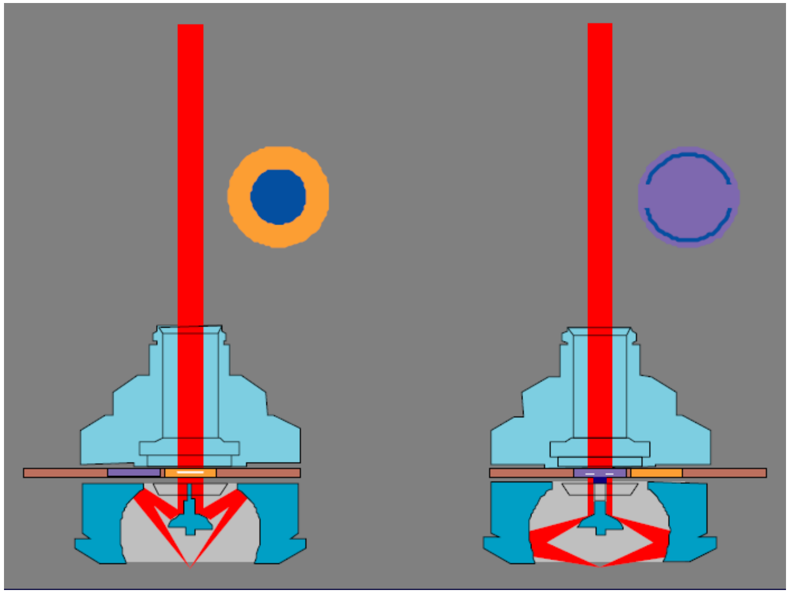
IR Microspectroscopy Sampling Modes

- Attenuated Total Reflection – ATR
  - simplifies sample preparation
  - solves sample thickness problem (0.4–2.0 µm penetration depth)



IR Microspectroscopy Sampling Modes

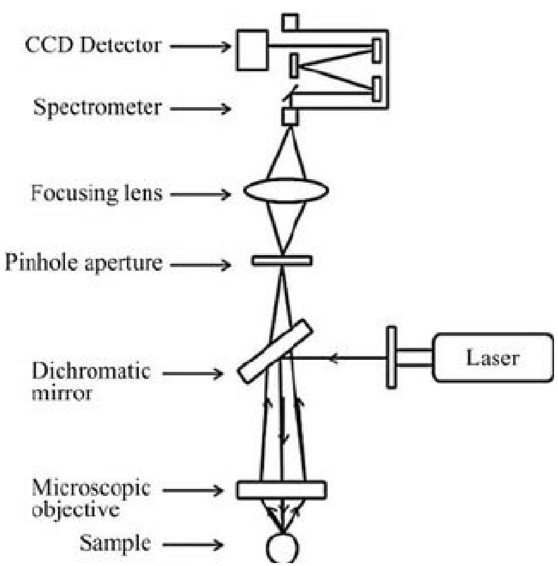
- Reflection – grazing angle microscope, angle of incidence: 55–85°
- Different lenses/modes – glass lenses for viewing, reflection for measurement



Raman Microspectroscopy Modes

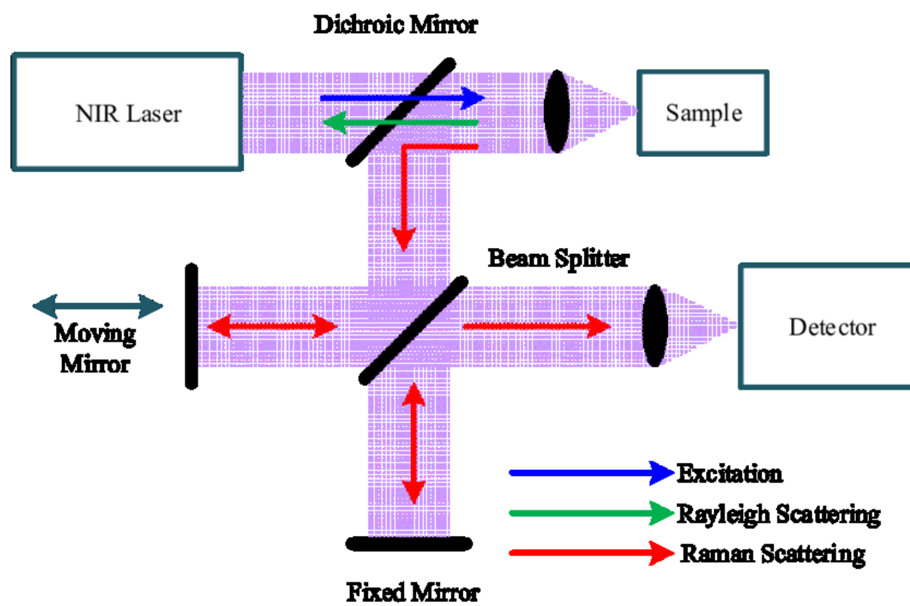
Dispersive

- visible excitation
- higher spatial resolution
- higher Raman signal
- possibility of confocal mode to enhance depth resolution



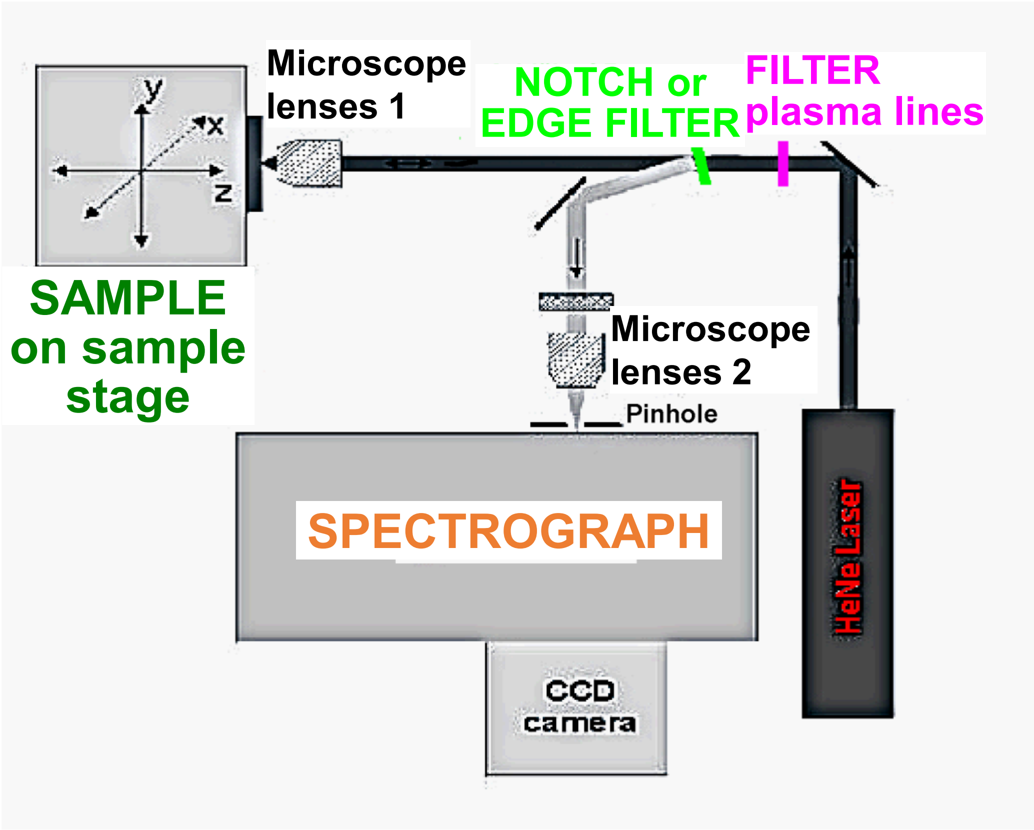
Fourier-Transform

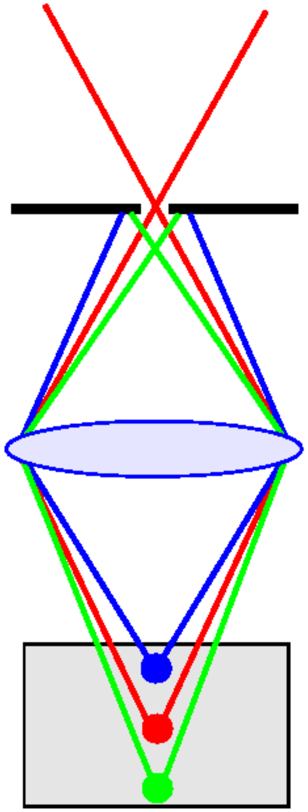
- near-infrared excitation
- lower spatial resolution
- lower risk of damaging the sample



Raman Microspectroscopy Confocal Mode

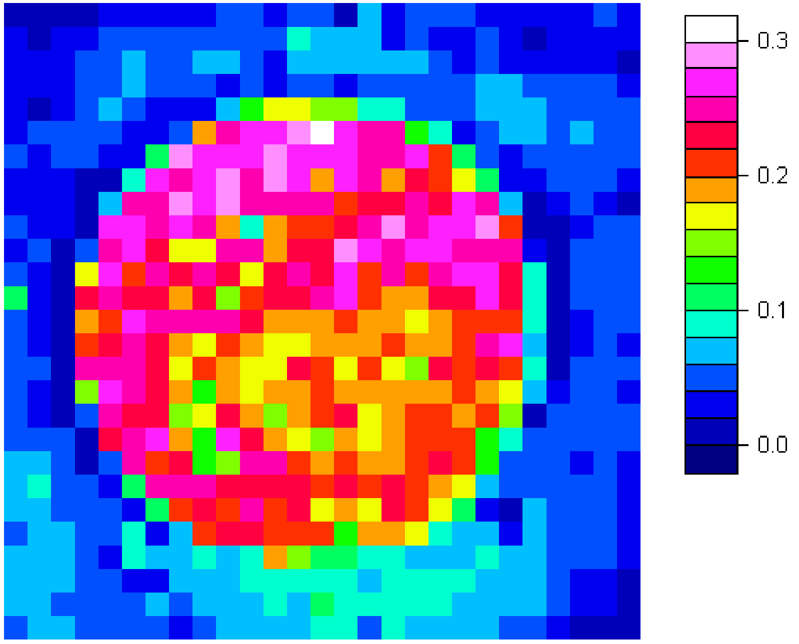
- Confocal microscope – uses a very narrow pinhole to greatly improve the depth resolution



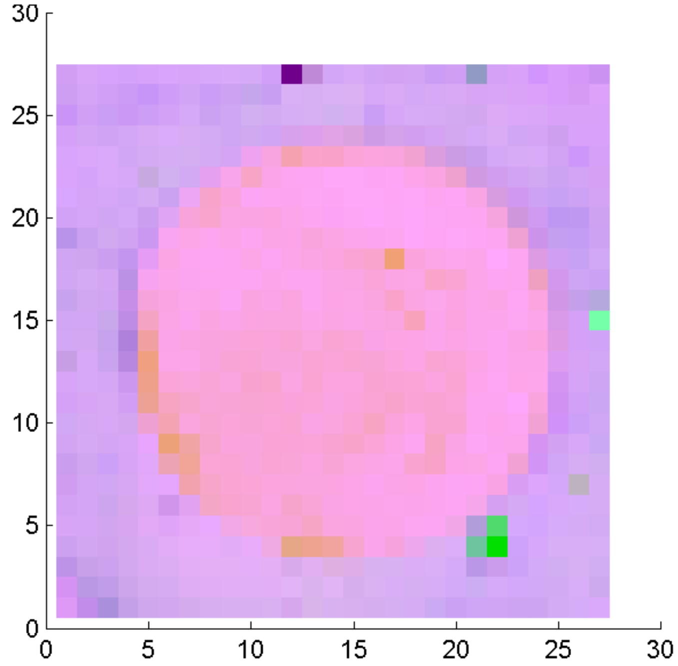


Raman Microspectroscopy – Examples

Medicine – tablets

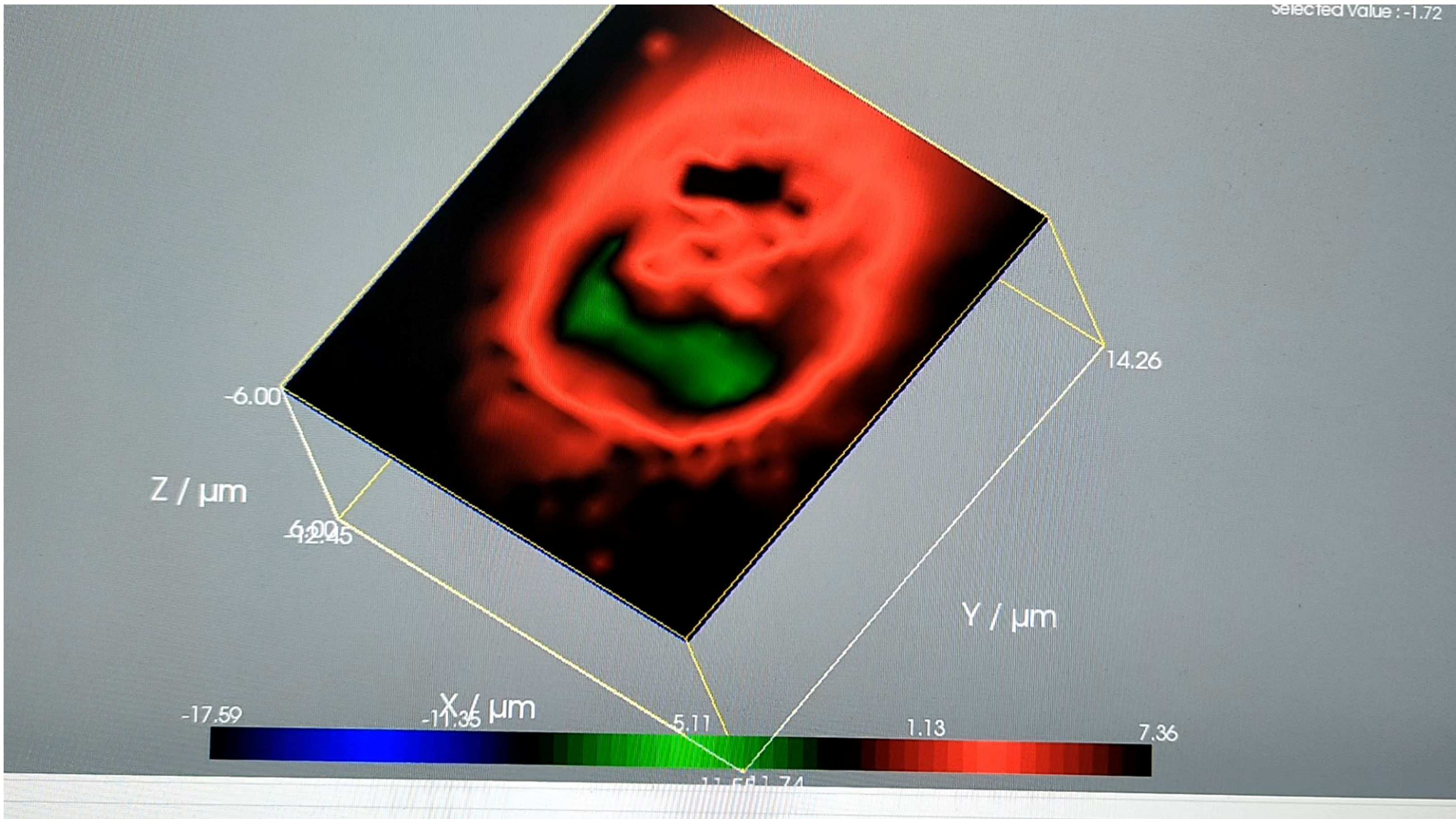


PCA



Raman Microspectroscopy – Examples

Life science – Cells, 3D volume scan, PCA



Microspectroscopy – Applications

- Small samples
- Large Samples
- Plastics
- Packaging materials
- Pharmaceuticals
- Fibers
- Trace evidence
- Contaminants
- Forensic analysis
- Failure analysis
- Coatings & inks
- Electronic materials
- Migration, diffusion and aging studies
- Reverse engineering
- Art conservation
- Geology
- Archeology

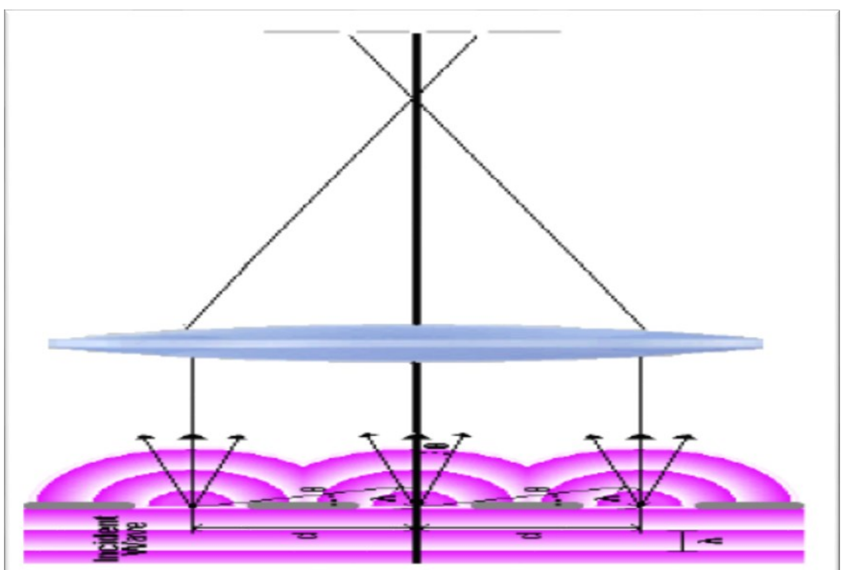
Microspectroscopy vs. Nanospectroscopy

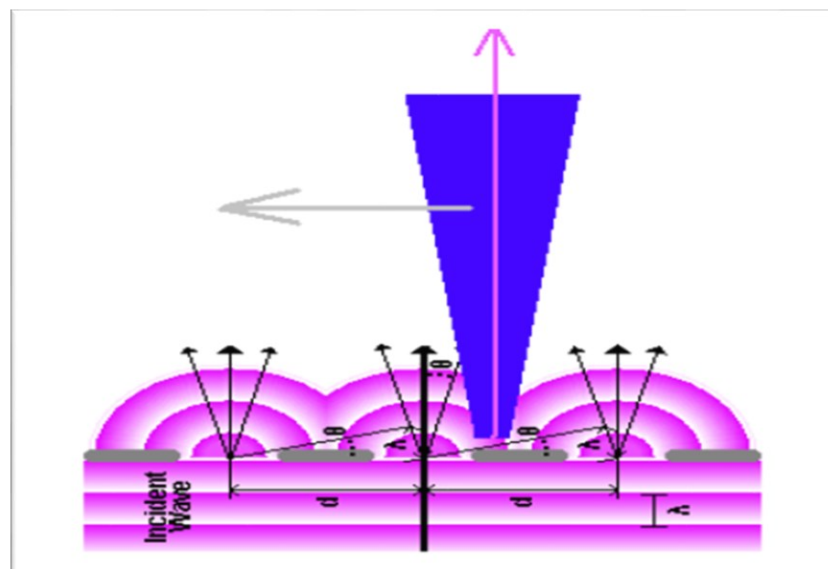
Microspectroscopy

- techniques of far field
- averaged signal over a large area
- spatial resolution limited by the diffraction of light

Nanospectroscopy

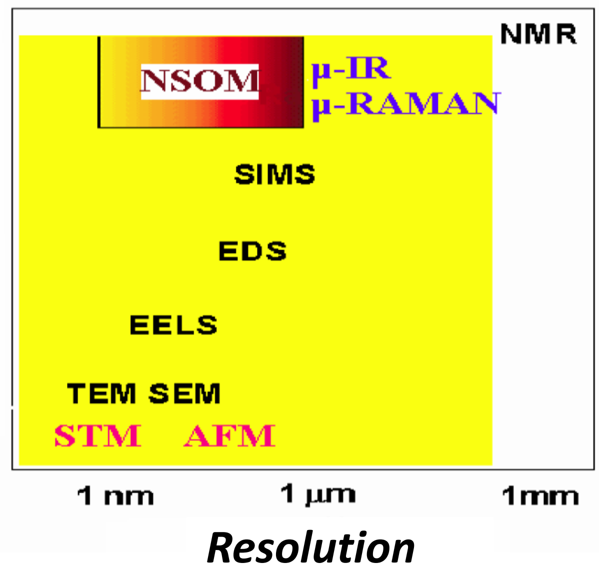
- techniques of near field
- „coupling“ of a probe and surface
- spatial resolution limited by probe aperture





Vibrational Nanospectroscopy

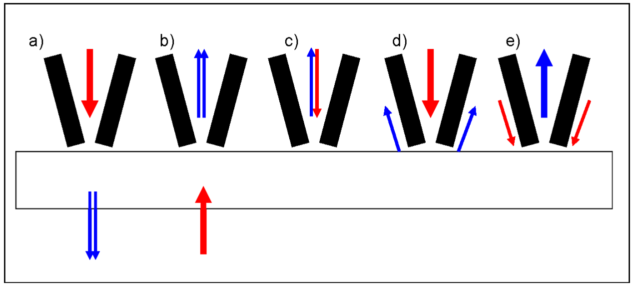
- based on scanning probe microscopy (SPM) – AFM, STM, …
- probe near the surface („near-field techniques“)
- probe–sample distance lower than used wavelength
- „non-destructive“ approach
- easy sample preparation
- vacuum is not required (compared to SEM)



Vibrational Nanospectroscopy

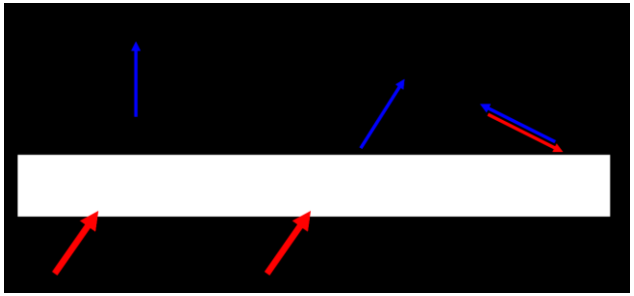
SNOM (NSOM)

- scanning near-field optical microscopy, hollow optical fibre with miniature aperture (aperture mode)
- IR-SNOM
- Raman-SNOM



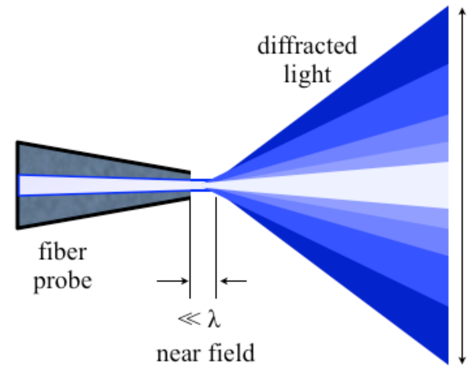
s-SNOM

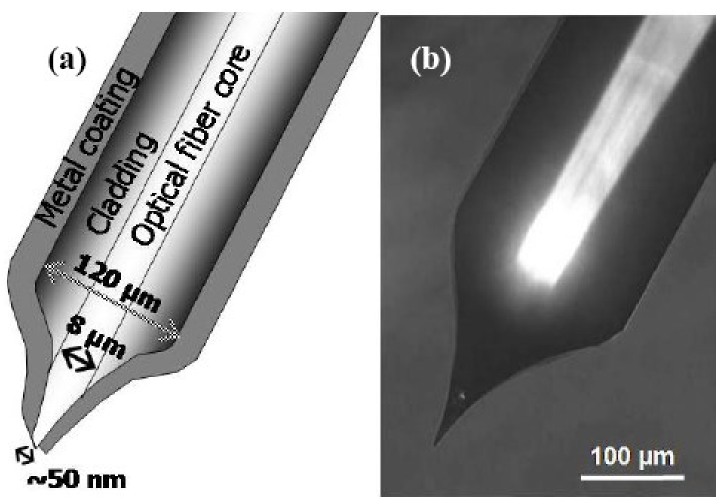
- „scattering reflection“ SNOM, „full“ SPM tip interferes with and modulates the incoming radiation (apertureless mode)
- SNIM (IR-sSNOM) – scanning near-field infrared microscopy
- nano-FTIR
- TERS – tip-enhanced Raman spectroscopy

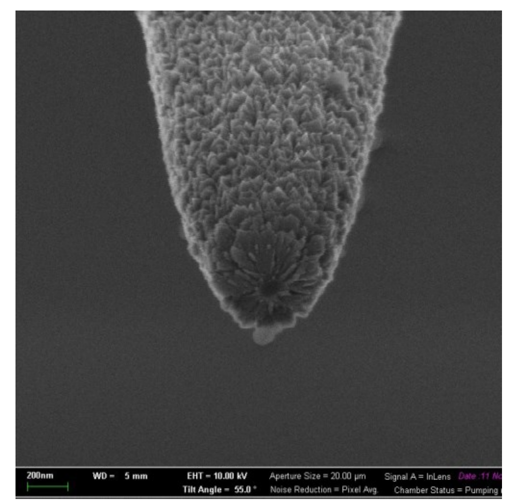


IR-SNOM

- near-field technique
- construction of spectroscopic image by scanning of the surface
- probe scans the surface – point by point
- critical parameters – probe aperture (smaller than used wavelength) and its distance from surface

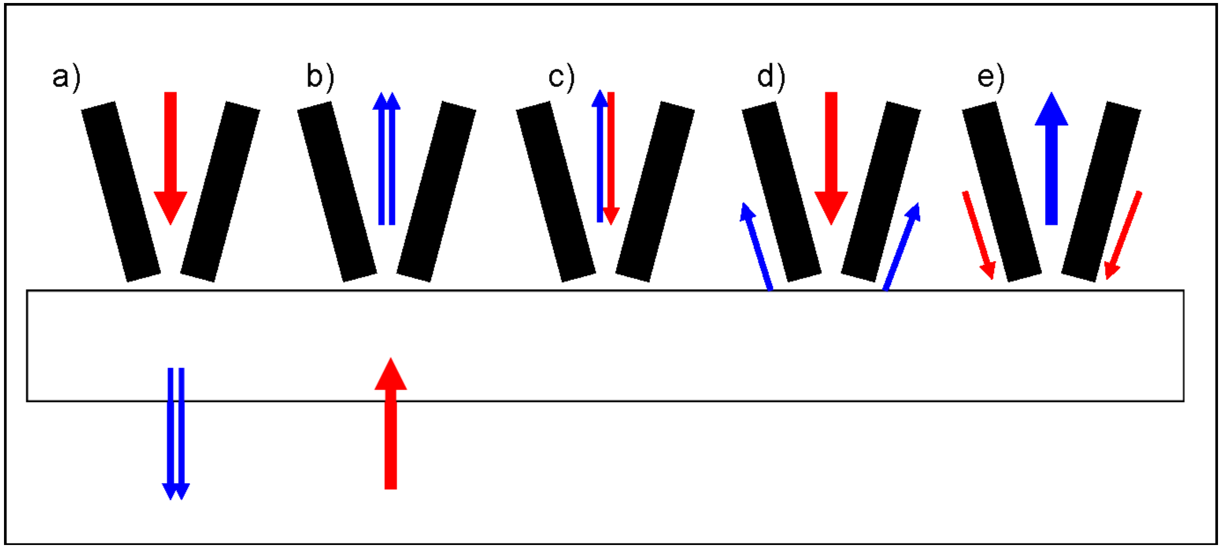




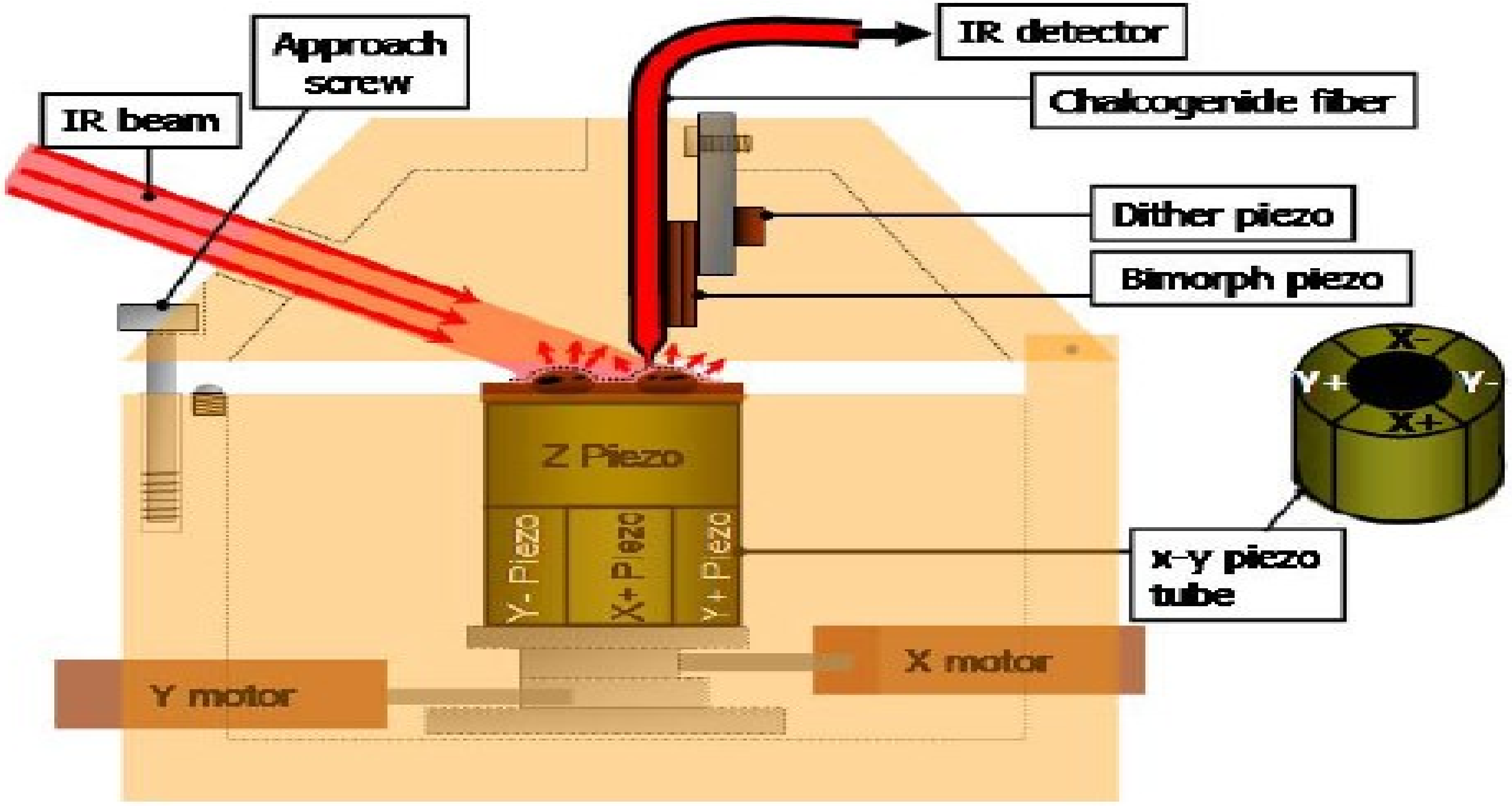


IR-SNOM

- distance of probe ≈ 10 nm
- aperture of probe 10–100 nm
- optical coupling of the tip of the probe and the sample surface
- the probe responses on changes of dielectric function in its surroundings
- optical modes of spectra collection
  - transmission (only for transparent samples) – transmitter, receiver
  - reflection – transmitter, receiver, both



IR-SNOM setup



IR-SNOM

ADVANTAGES

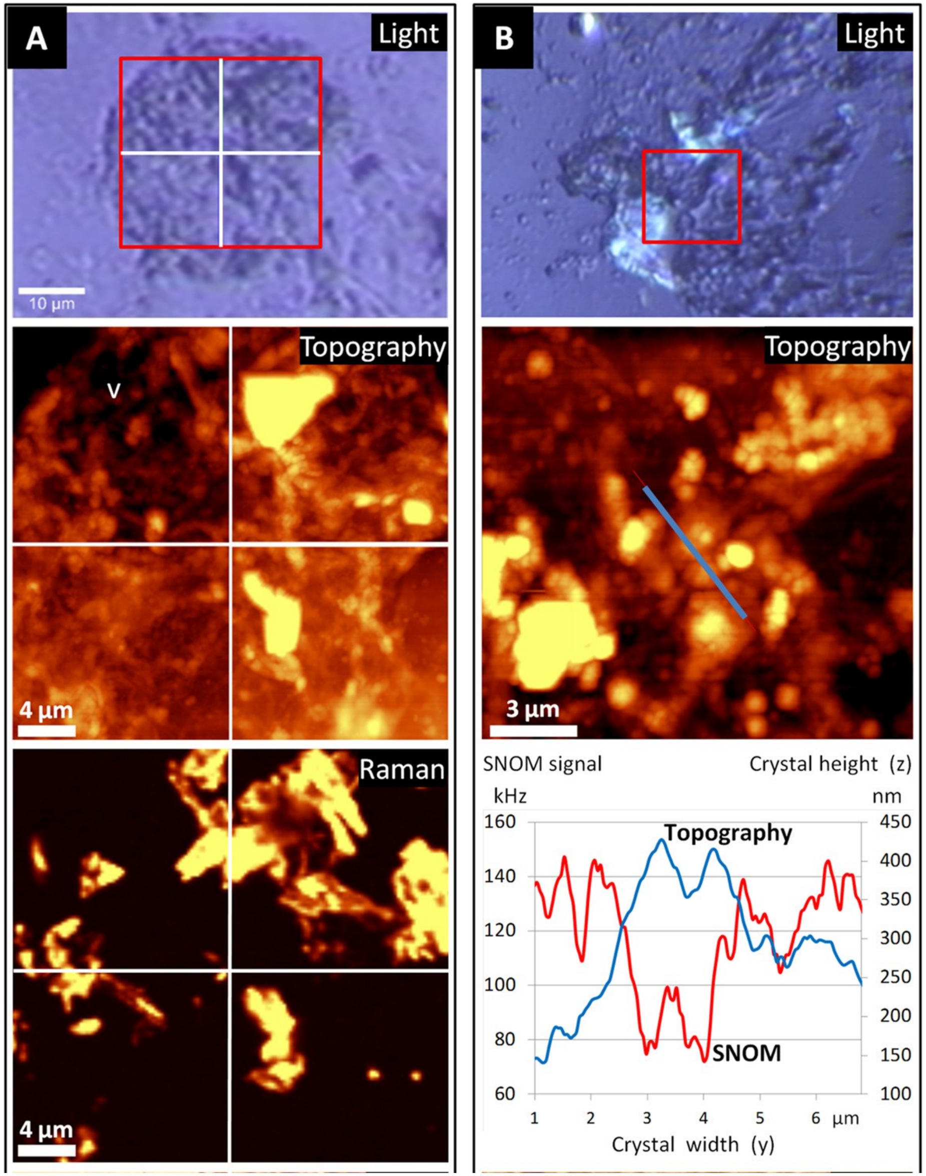
- overcome the diffraction limit – „nanoresolution“
- chemical information based on IR spectra
- non-destructive method
- flexible modes of data collection

DISADVANTAGES

- technological demands on design and construction of SNOM probe
- low intensity of detected radiation
- demands on sensitivity of the detector

Raman SNOM – Example

Model carrot cell with carotenoid crystals



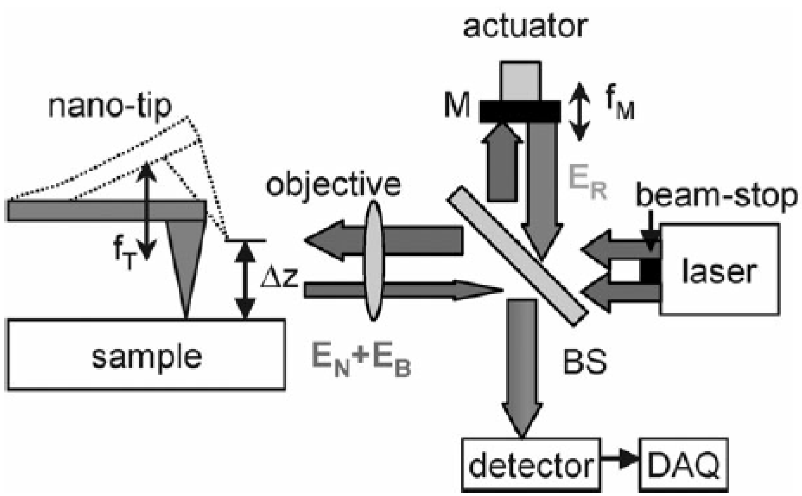
SNIM – scattering reflection IR-sSNOM

REVIEW www.rsc.org/annrepc | Annual Reports C

SNIM: Scanning near-field infrared microscopy

Erik Bründermann*[a] and Martina Havenith*[b]

DOI: 10.1039/b703982b



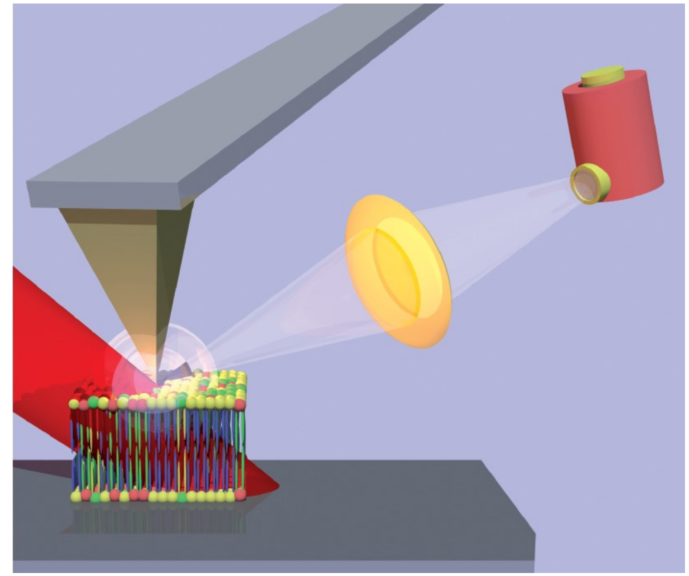
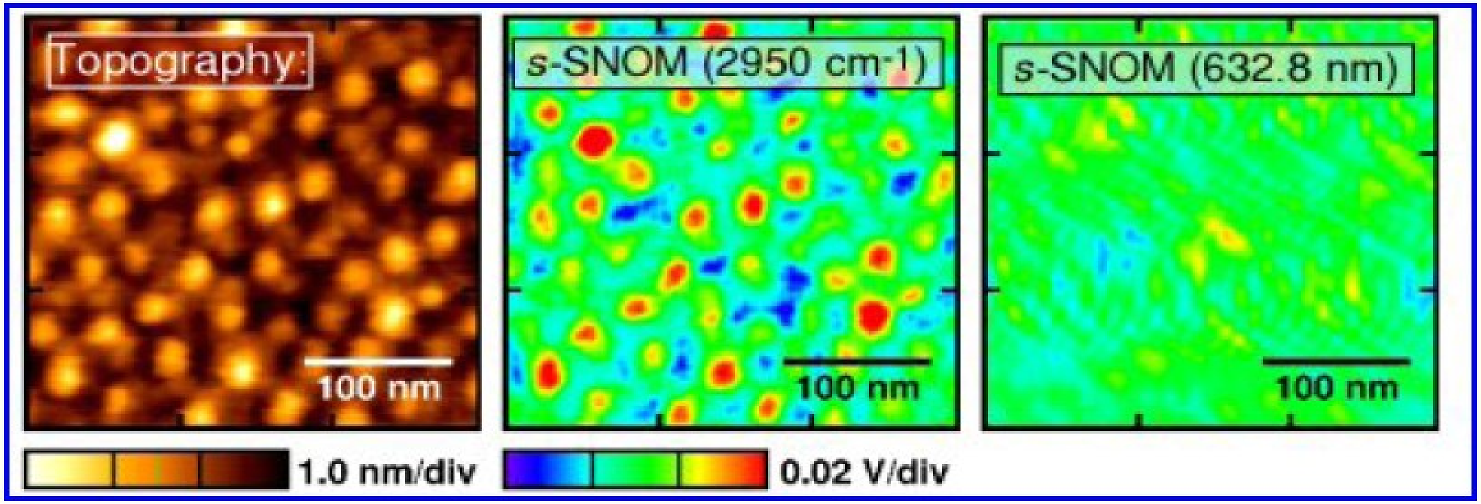
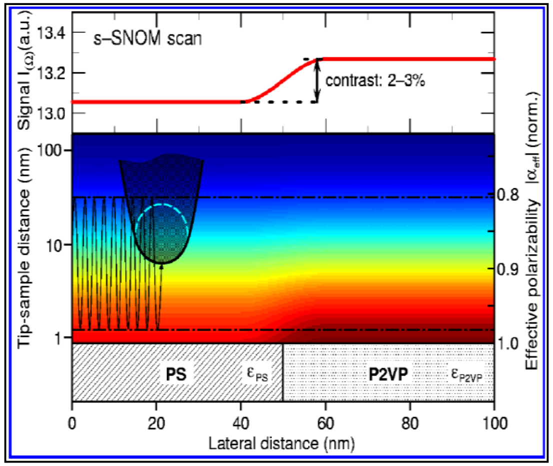


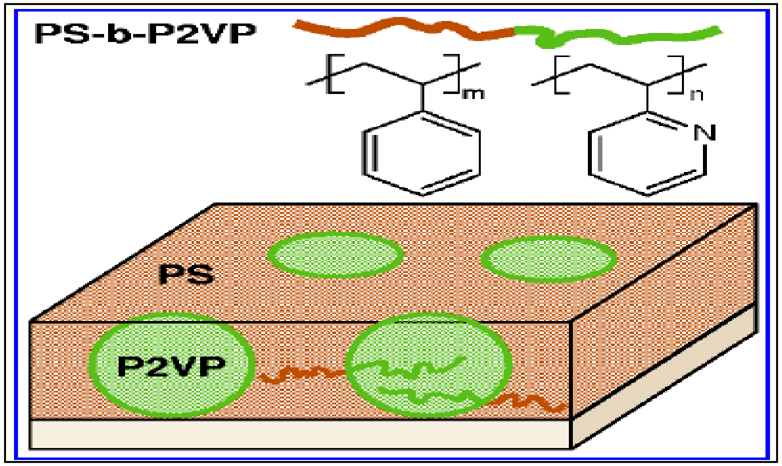
Fig. 3 (Online in colour): Experimental set-up for the detection of near-field signals. The nano-tip oscillates with a frequency f_T which leads to a modulation of the sample-tip distance of $z = \Delta z(1 + \cos(2\pi f_T t))/2$. Using an interferometer for detection, the laser beam is separated with a beam splitter (BS) into two beams. One beam is reflected at a mirror (M). If this mirror is placed on an actuator, *e.g.* piezoelectric actuator, the mirror can oscillate at a frequency f_M for phase modulation of the reference beam (E_R). The remaining laser light is focused *via* an objective on the tip–sample region. The background field (E_B) and the near-field (E_N) contribution of the scattered light are both reflected at the probe. The interference of both fields with the reference beam is recorded at the detector. The detector signal is then processed during the data acquisition (DAQ).

SNIM – Examples

Nanocomposite organic materials – polystyrene and poly-2-vinylpyridine

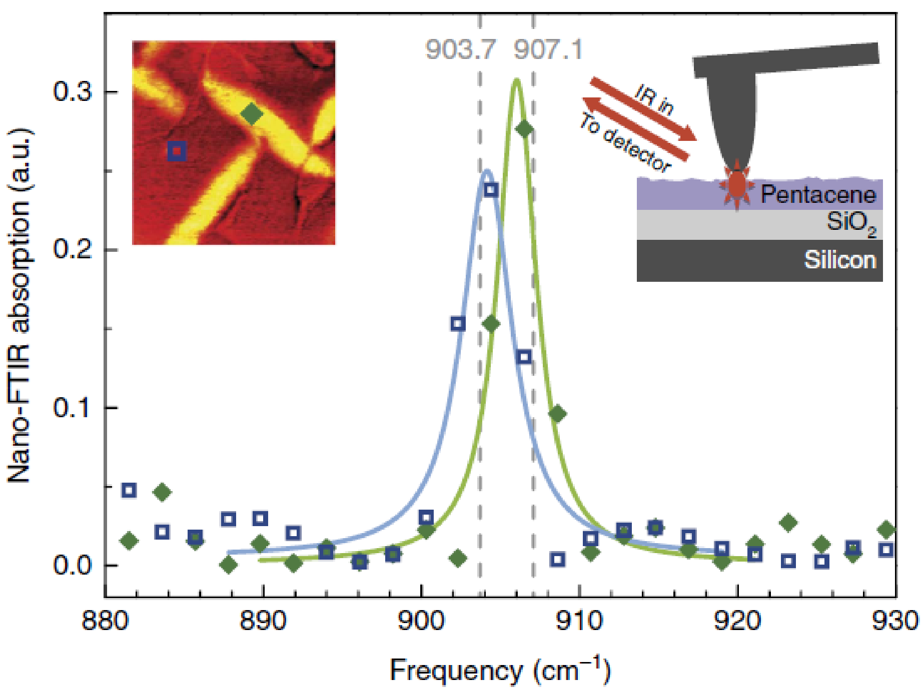






SNIM – Examples

Pentacene – two coexisting phases → slight shift in peak position



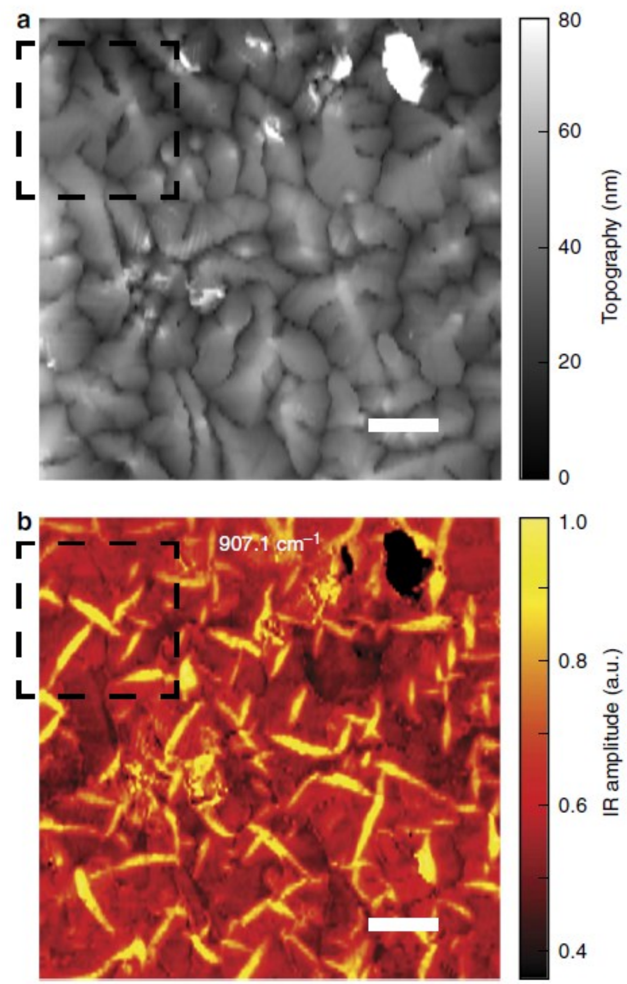
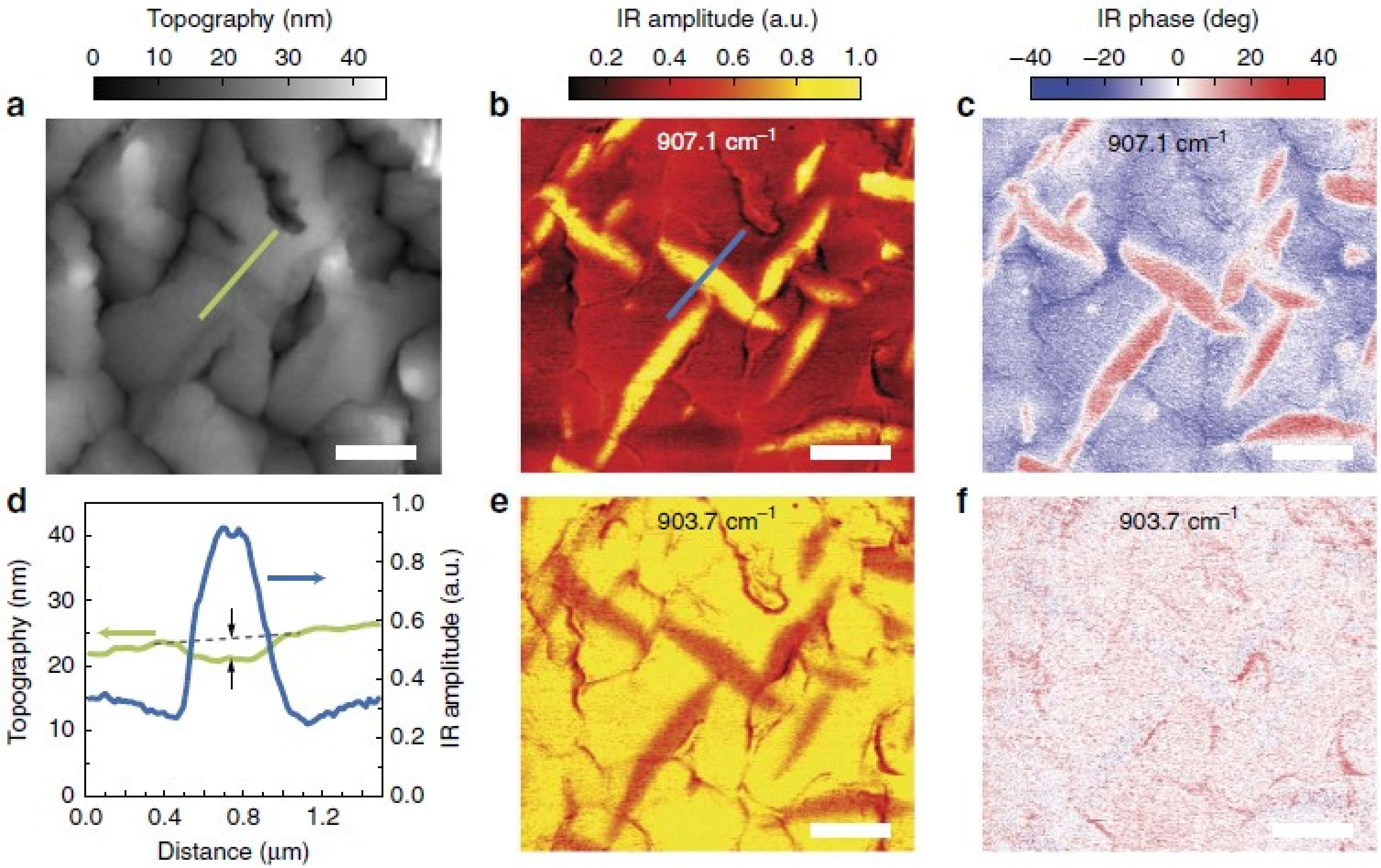


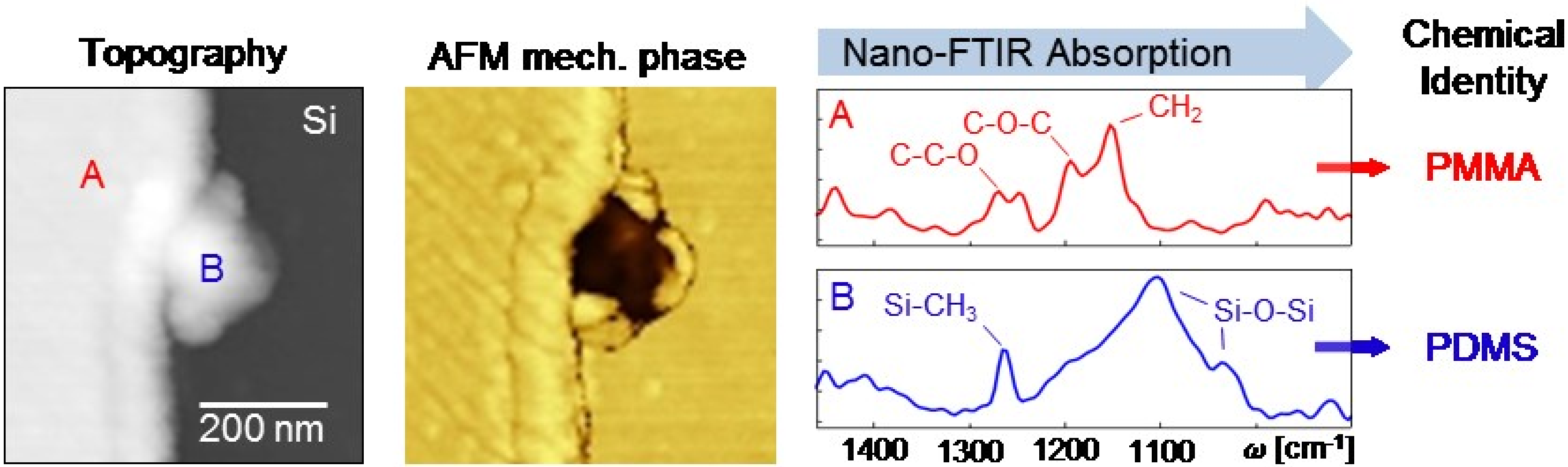
Figure 2 | Grain morphology and lateral distribution of two coexisting phases. (**a**) AFM topography (13.5 µm × 13.5 µm) showing a 40-nm thick pentacene film on SiO_2/Si substrate, after storage at room temperature for 20 months. (**b**) s-SNOM amplitude image at 907.1cm $^{-1}$, recorded simultaneously, proves the coexistence of two phases of pentacene, which obviously persist across grain boundaries. The dashed square marks the section shown in Fig. 4. Scale bar, 2 µm.

SNIM – Examples



Nano-FTIR spectroscopy

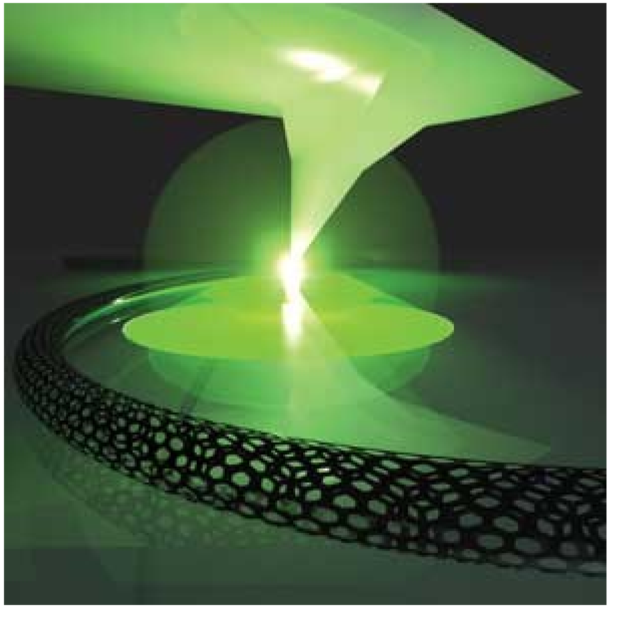
dx.doi.org/10.1021/nl301159v | Nano Lett. 2012, 12, 3973−3978



Chemical identification of nanoscale sample contaminations with nano-FTIR. In the topography image (left), a small sample contaminant (B) can be found next to a thin film of PMMA (A) on a Si substrate (dark region). In the mechanical phase image (middle) the contrast already indicates that the particle consists of a different material than the film and the substrate. Comparing the nano-FTIR absorption spectra at the positions A and B (right panel) with standard IR databases reveals the chemical identity of the film and the particle. Each spectrum was taken in 7 min with a spectral resolution of 13 cm^{-1}.

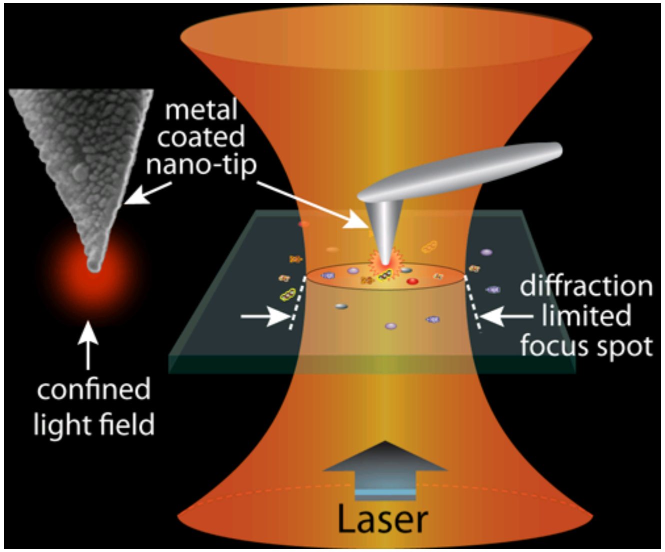
Tip-Enhanced Raman Spectroscopy – TERS

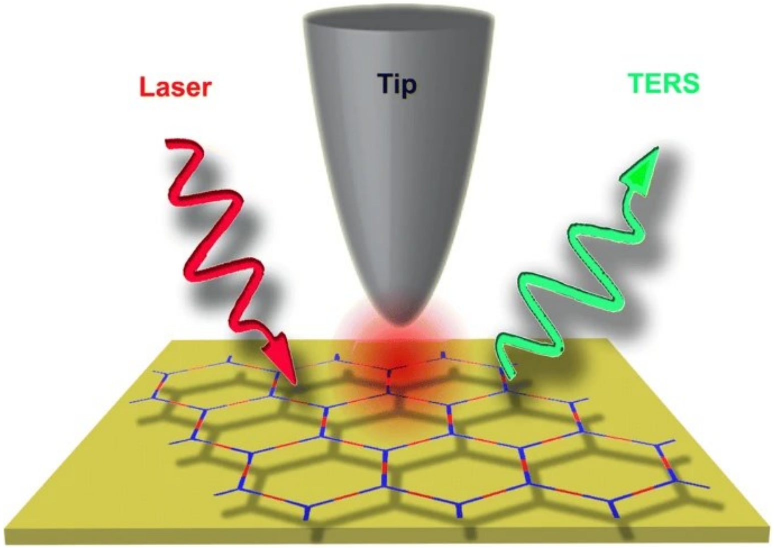
- scanning probe microscopy (AFM, STM) + surface-enhanced Raman spectroscopy (SERS)
- spatial resolution below diffraction limit – defined by the tip diameter
- enhanced sensitivity and lower detection limits (vs. Raman)
- „non-destructive“ analysis
- no vacuum required



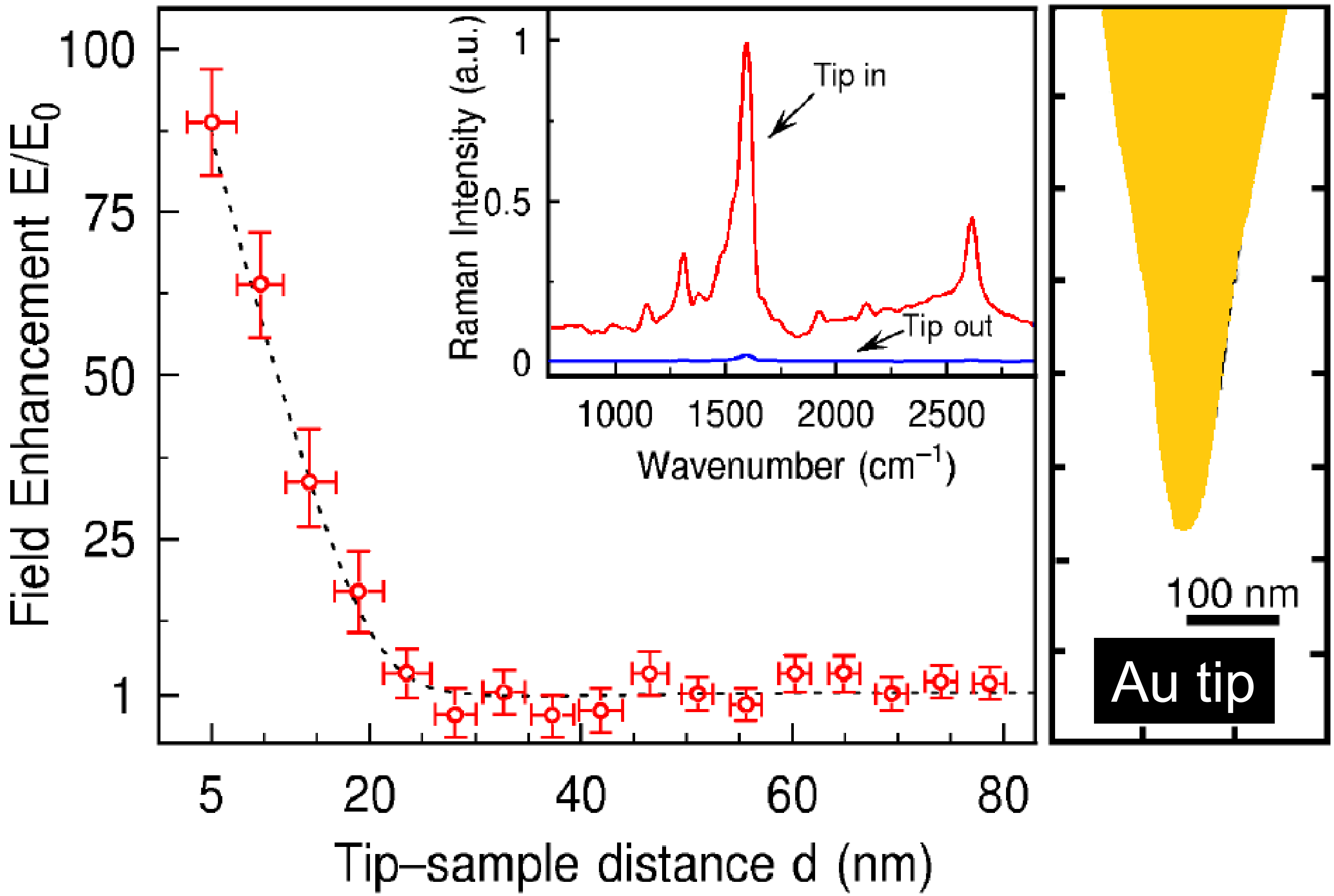
Tip-Enhanced Raman Spectroscopy – TERS

- nanometre-sized plasmonic tips + plasmonic substrate → localized, strong EM field
- commonly used plasmonic metals – Au, Ag
- important tip parameters: sharpness and purity





Tip-Enhanced Raman Spectroscopy – TERS



Tip-Enhanced Raman Spectroscopy – TERS

- Finite-difference time-domain simulations → the enhancement and distribution of the EM field around the metalic tip or between the tip and substrate

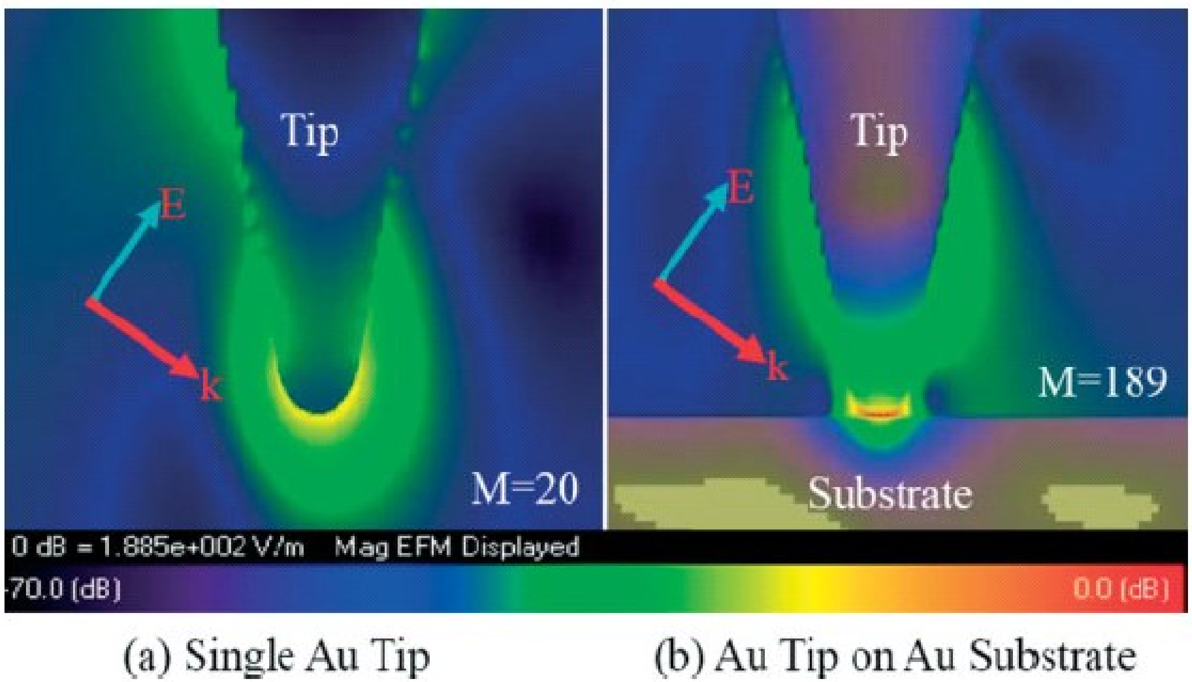


Figure 2. FDTD simulations of the electric field distribution for a single Au tip (a), and a gold tip held at distance $d = 2$ nm from a gold substrate surface. The polarization E and wave vector k of the incoming light are displayed in the schematics. *M* stands for the maximum.

Summary

Microspectroscopy

- spectral maps – points collected in series (mapping – single channel detection) or in parallel (imaging – multichannel detection)
- diffraction limited resolution: $\mathrm{d} = \frac{\lambda}{2}$
- IR – transmission/reflection – ATR, specular reflection, grazing angle
- Raman – usually reflection mode
  - dispersive – lower wavelength, higher spatial resolution (confocal mode)
  - FT – higher wavelength, lower spatial resolution, lower risk of damage

Nanospectroscopy

- based on scanning probe microscopy – resolution limited by aperture or tip diameter (sharpness)
- non-destructive, no high vacuum or cryogenic temperatures
- aperture mode – SNOM – IR, Raman, visible, fluorescence, …
- apertureless mode – s-SNOM – SNIM, nano-FTIR, TERS