UNIVERSITY OF CHEMISTRY AND TECHNOLOGY PRAGUE

ÚFCH VŠCHT

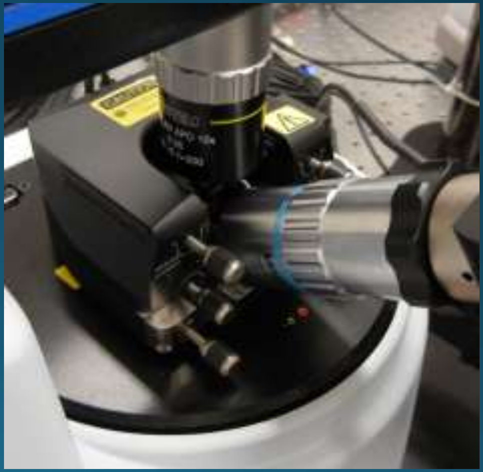
Pavel Matějka

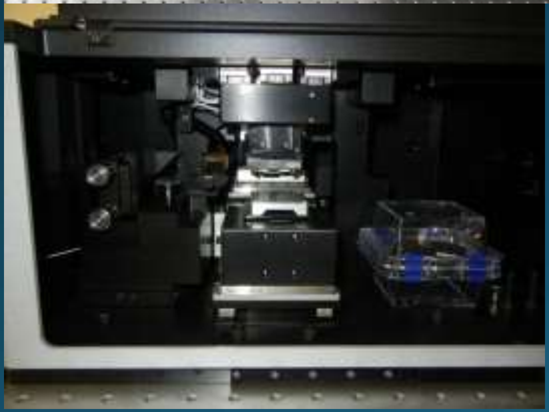
From vibrational spectroscopy to nanoscopy – scanning near-field infrared imaging – tip-enhanced Raman spectrscopy

VŠCHT Praha - A K07 A

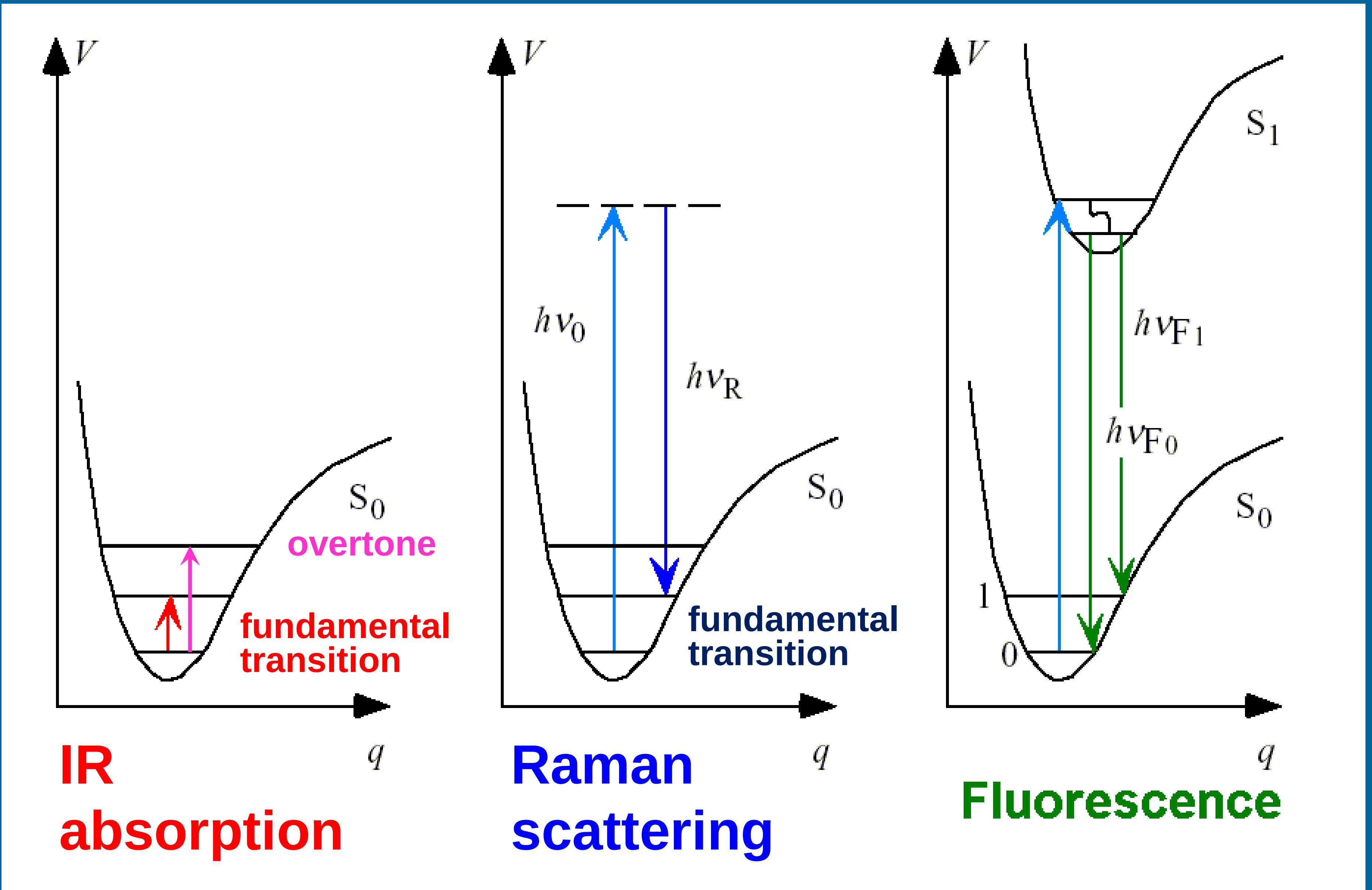
Raman AFM - TERS - Renishaw -

SNIM – NeaSpec – 3 tunable QC lasers





Scheme of levels



Infrared spectroscopy

Fundamental selection rule of infrared absorption

$$\frac{\partial p}{\partial q} \neq 0$$

BAND INTENSITIES PROPORTIONAL TO CHANGES of DIPOLE MOMENT in the course

of VIBRATIONAL MOTION

Raman spectroscopy

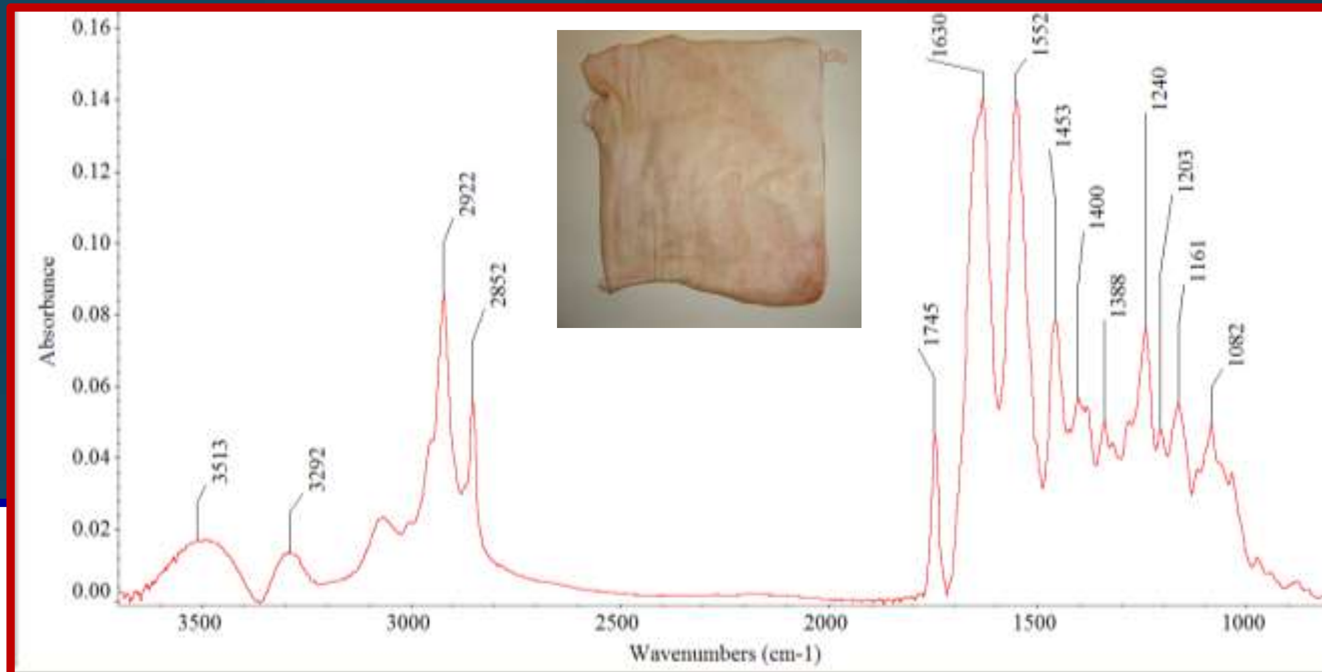
Fundamental selection rule of Raman scattering

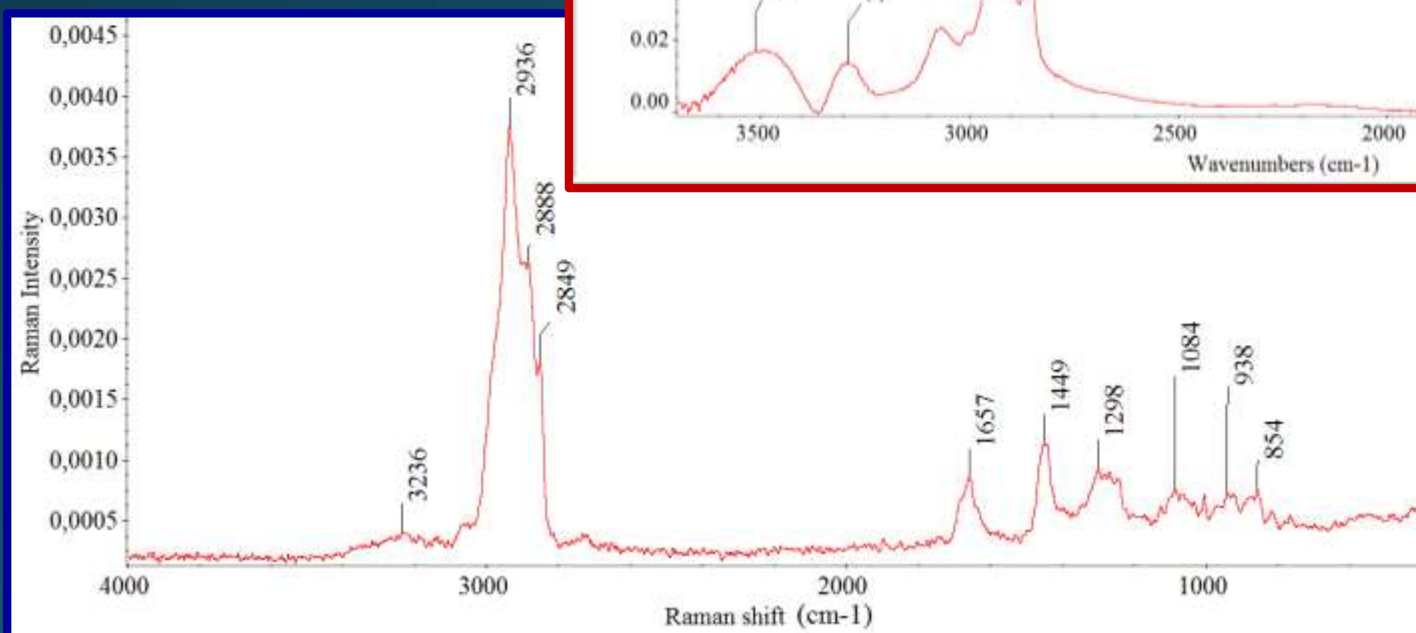
$$\frac{\partial \alpha}{\partial q} \neq 0$$

BAND INTENSITIES PROPORTIONAL TO CHANGES of **POLARIZABILITY**
in the course
of VIBRATIONAL MOTION

IR and Raman spectrum of untreated PS

Strong vibrational bands of **amides, saturated aliphatic skeletons, esters** and **OH-components**

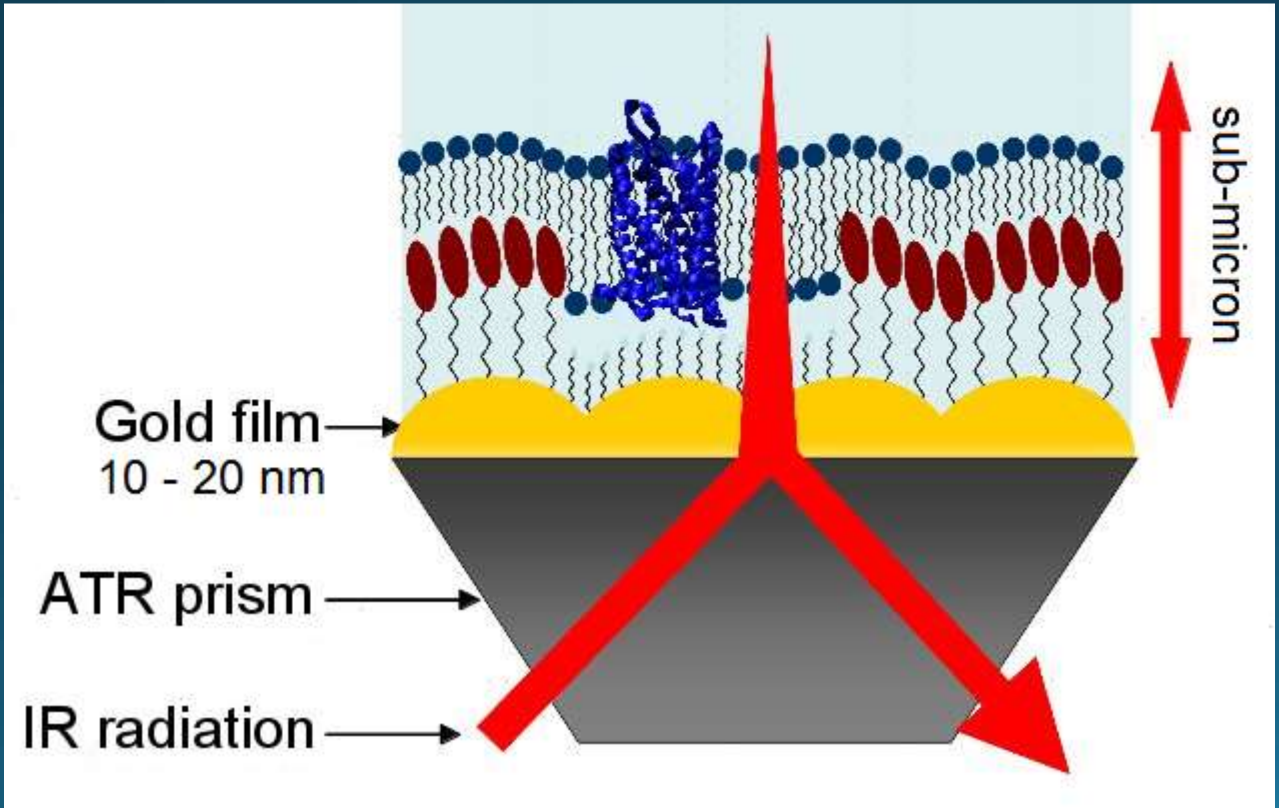




Strong vibrational bands especially of **saturated aliphatic skeletons**

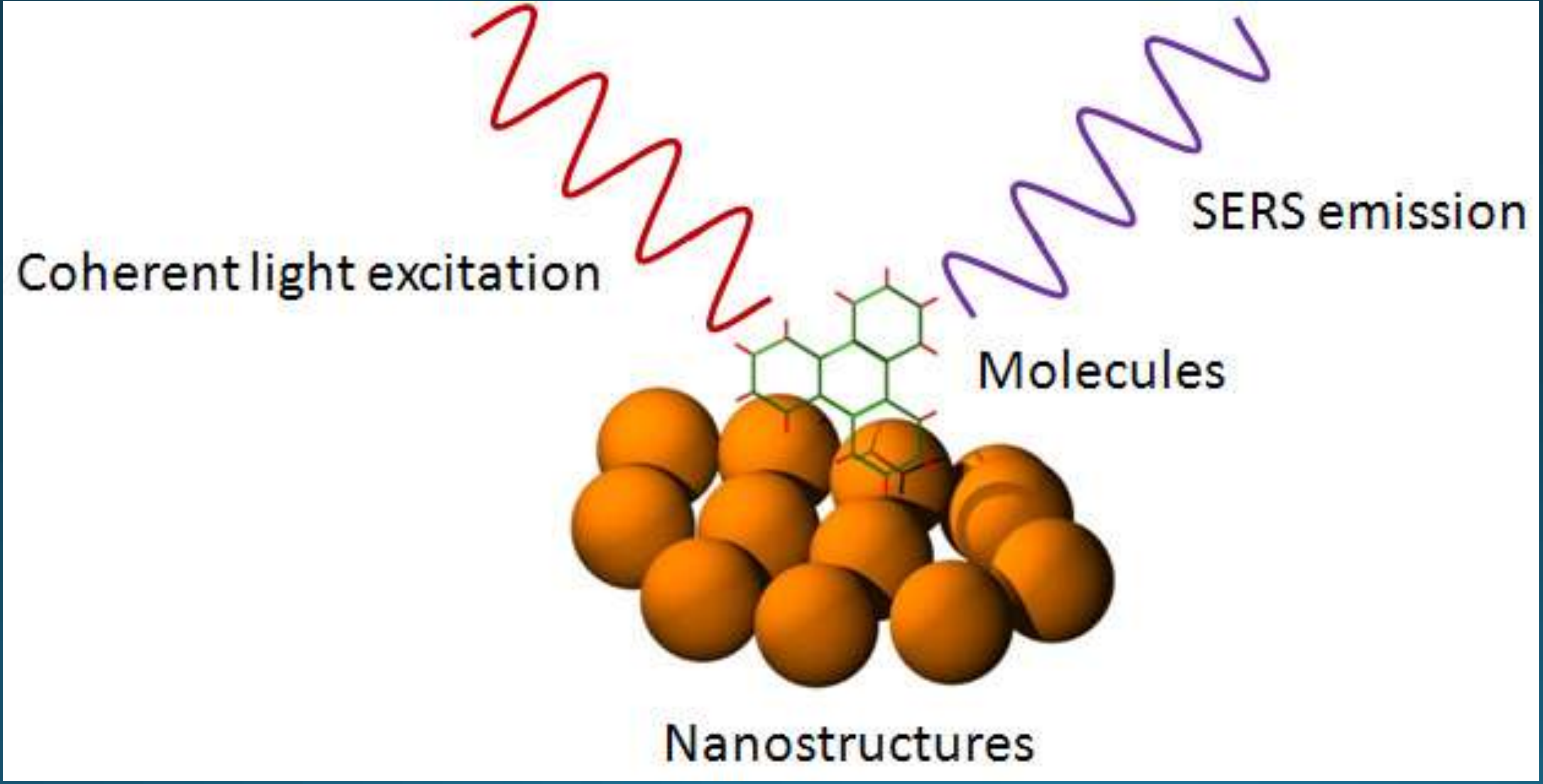
Surface-enhanced infrared absorption – SEIRA /ATR

- Nanoparticles and/or nanostructures are required for signal enhancement

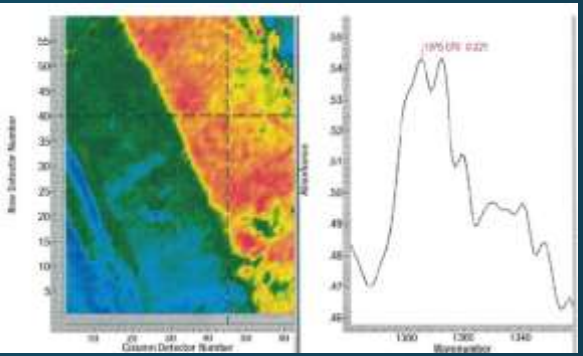


Surface-enhanced Raman scattering

- Nanoparticles and/or nanostructures are required for signal enhancement



Vibrational microscopy



- Chemical images of samples
  - Generate from peak heights, areas, peak ratios, correlation, results of principal component analysis etc.
  - Useful for monitoring changes in chemical composition in a sample
- 2D-images – scanning and mapping
- 3D-images – depth profiling

Microspectroscopy

Diffraction

$$d = \frac{1.22\,\lambda}{\text{NA obj.} + \text{NA cond.}}$$

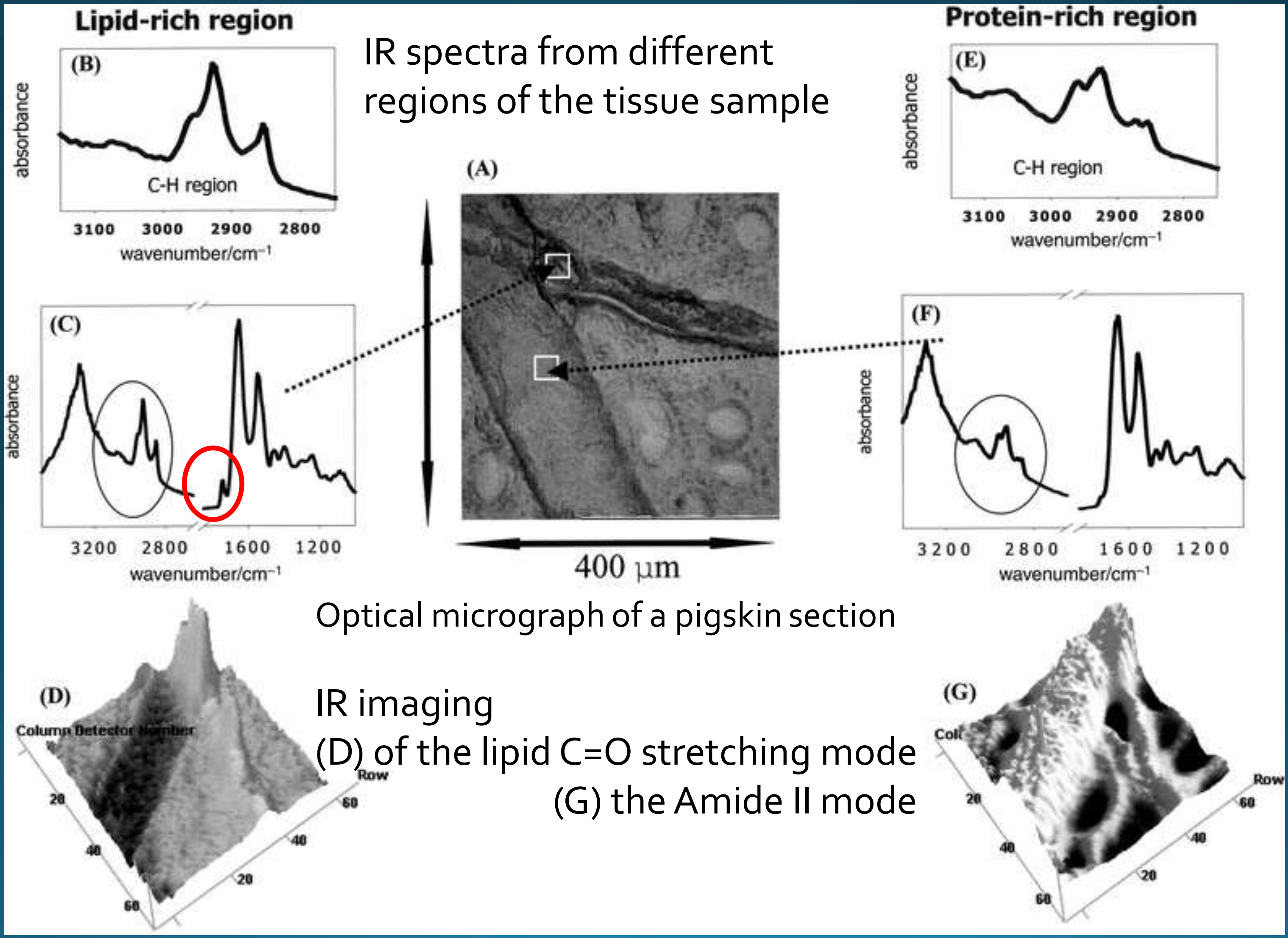
For 1469 cm $^{-1}$,

(1469 cm^{-1} = 6.8 µm)

$$d = \frac{1.22\,(6.8\ \mu m)}{0.58 + 0.71} = 6.4\ \mu m$$

Infrared spectroscopy and microscopic imaging of *stratum corneum* models and skin

Phys. Chem. Chem. Phys., 2000, 2, 4651-4657



IR spectra from different regions of the tissue sample

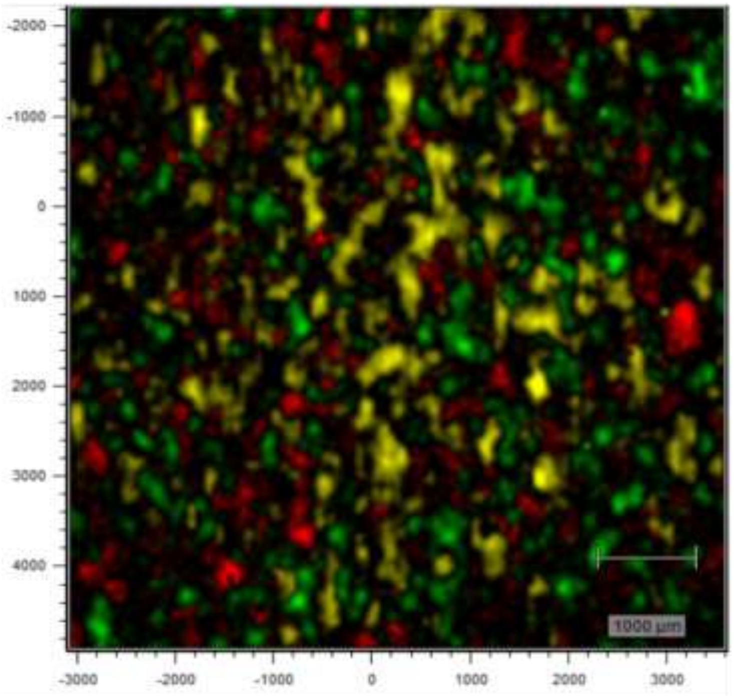
Optical micrograph of a pigskin section

IR imaging
(D) of the lipid C=O stretching mode
(G) the Amide II mode

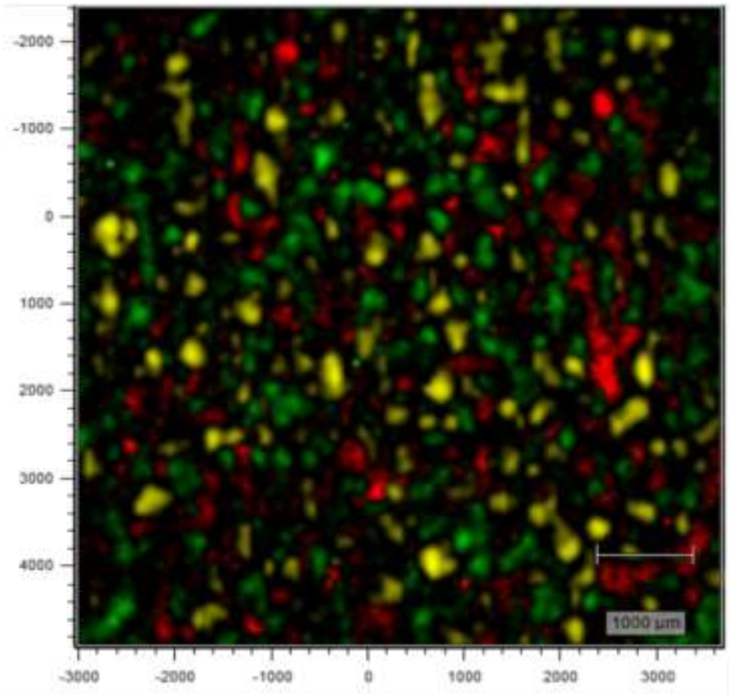
Comparison of the Tablets

Different particle size of API

- Raman chemical maps of cross-sections of tablets



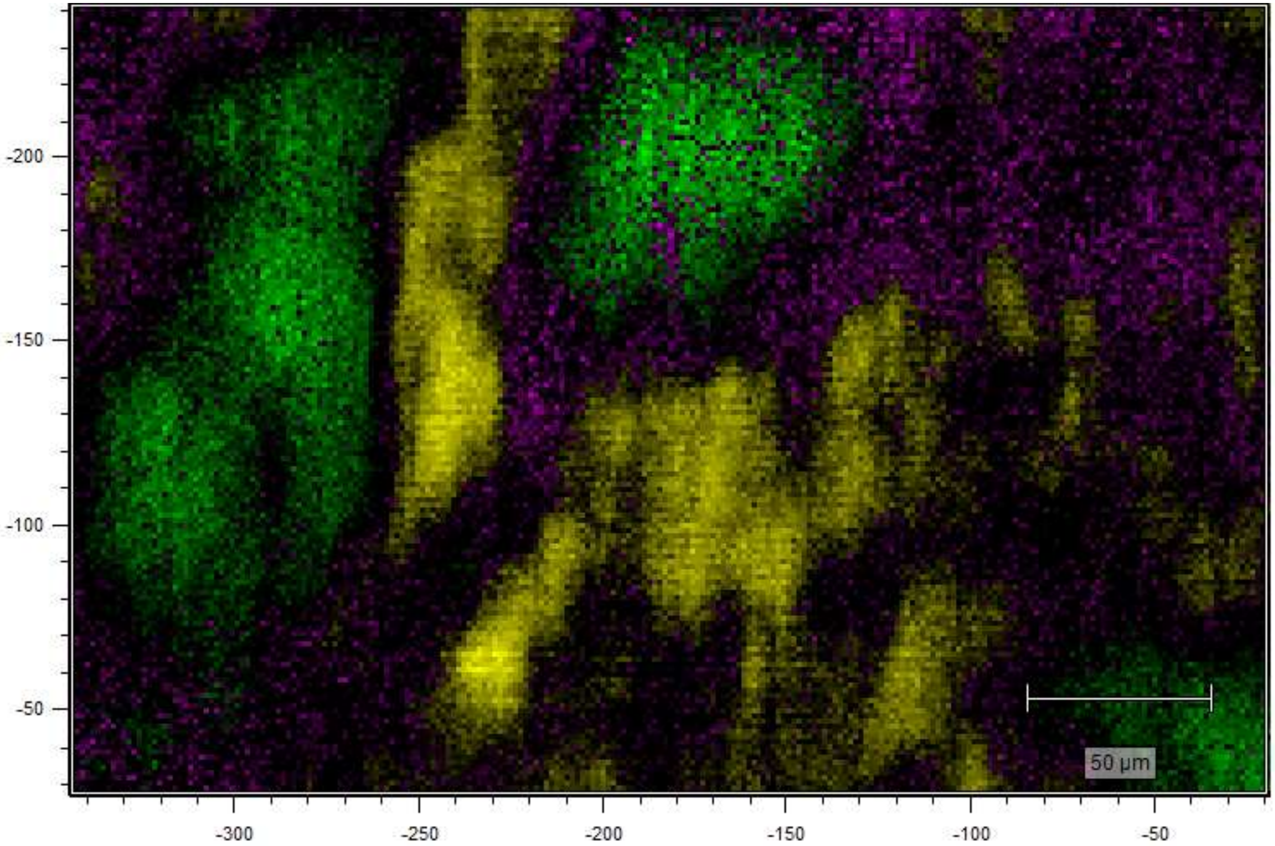
Batch 1
5x objective



Batch 2
5x objective

Tablet / detail

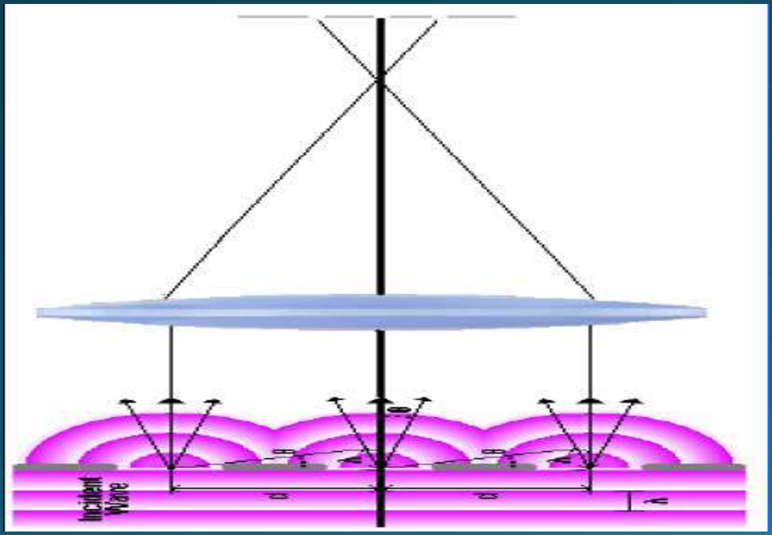
50x objective



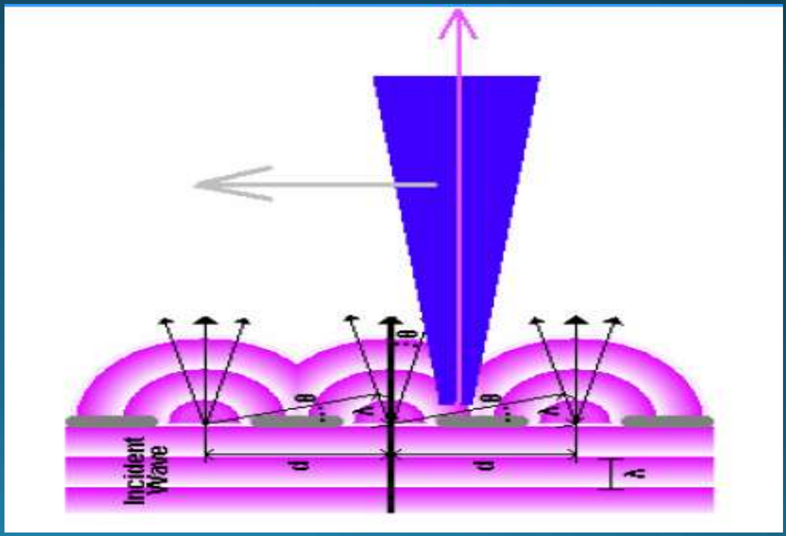
Raman map

Nanospectroscopy vs. microspectroscopy

- **Microspectroscopy** – techniques of far field
  - The maximum spatial resolution in a properly designed microscope is limited by the **diffraction** of light.

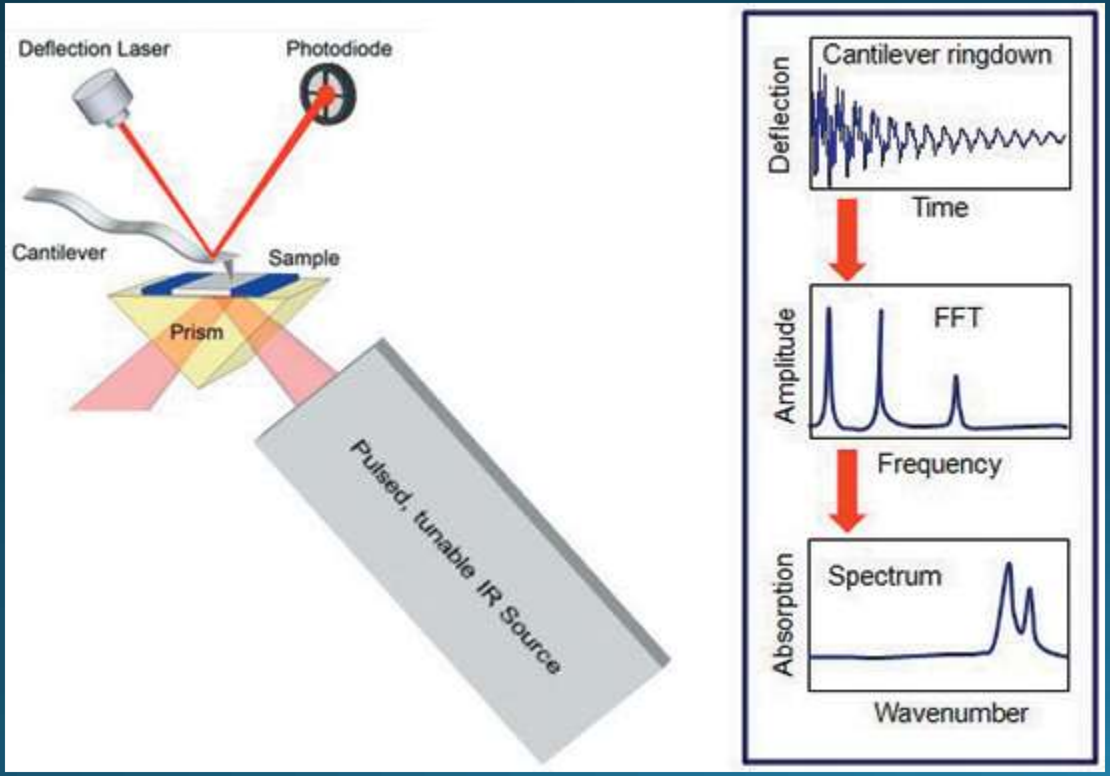


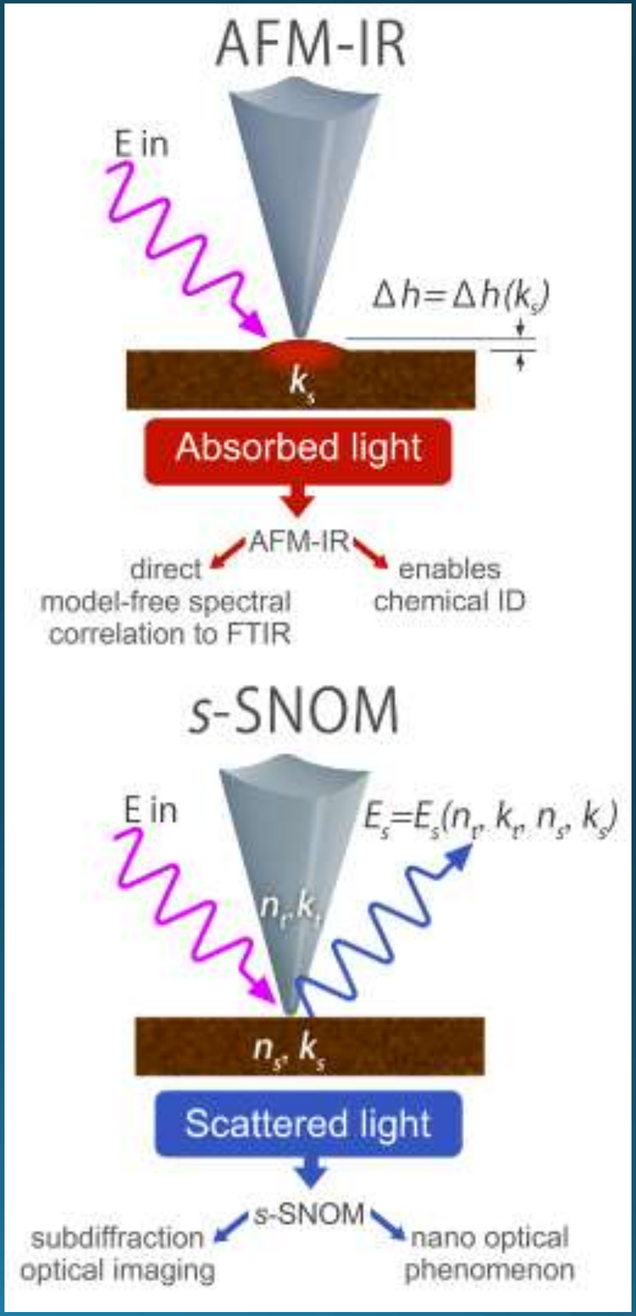
- **Nanospectroscopy** – techniques of near field
  - The maximum spatial resolution is **under diffraction limit**, it is limited mostly **by probe aperture** (probe diameter).



Infrared nanoscopy

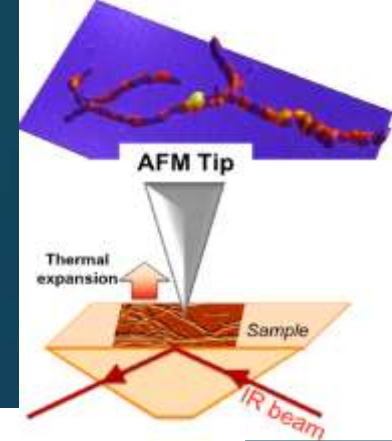
- AFM-IR - PTMS
- IR SNOM – SNIM – mainly sSNIM/sSNOM

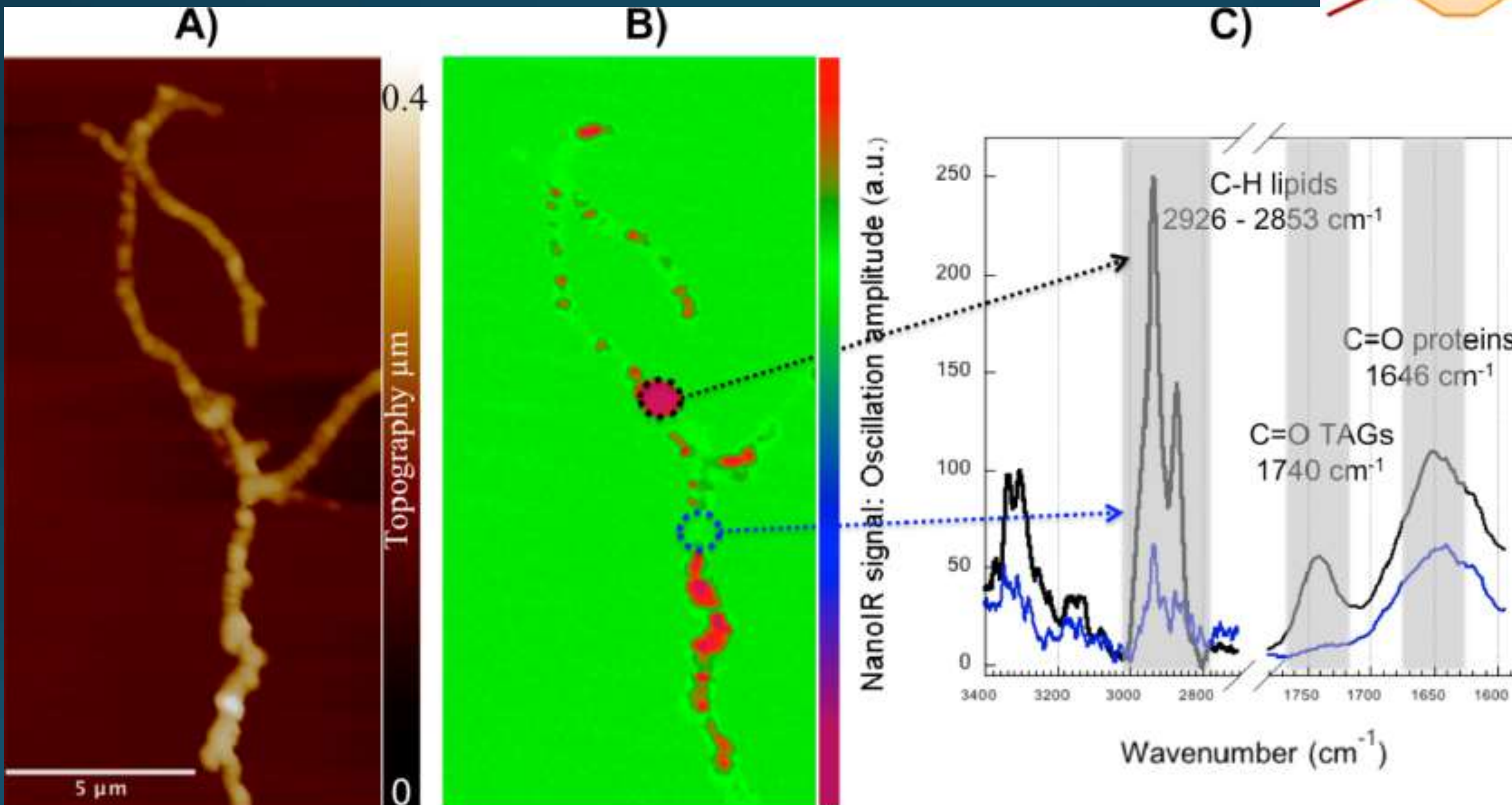




Infrared nanoscopy

Monitoring TriAcylGlycerols Accumulation by Atomic Force
Microscopy Based Infrared Spectroscopy in *Streptomyces* Species

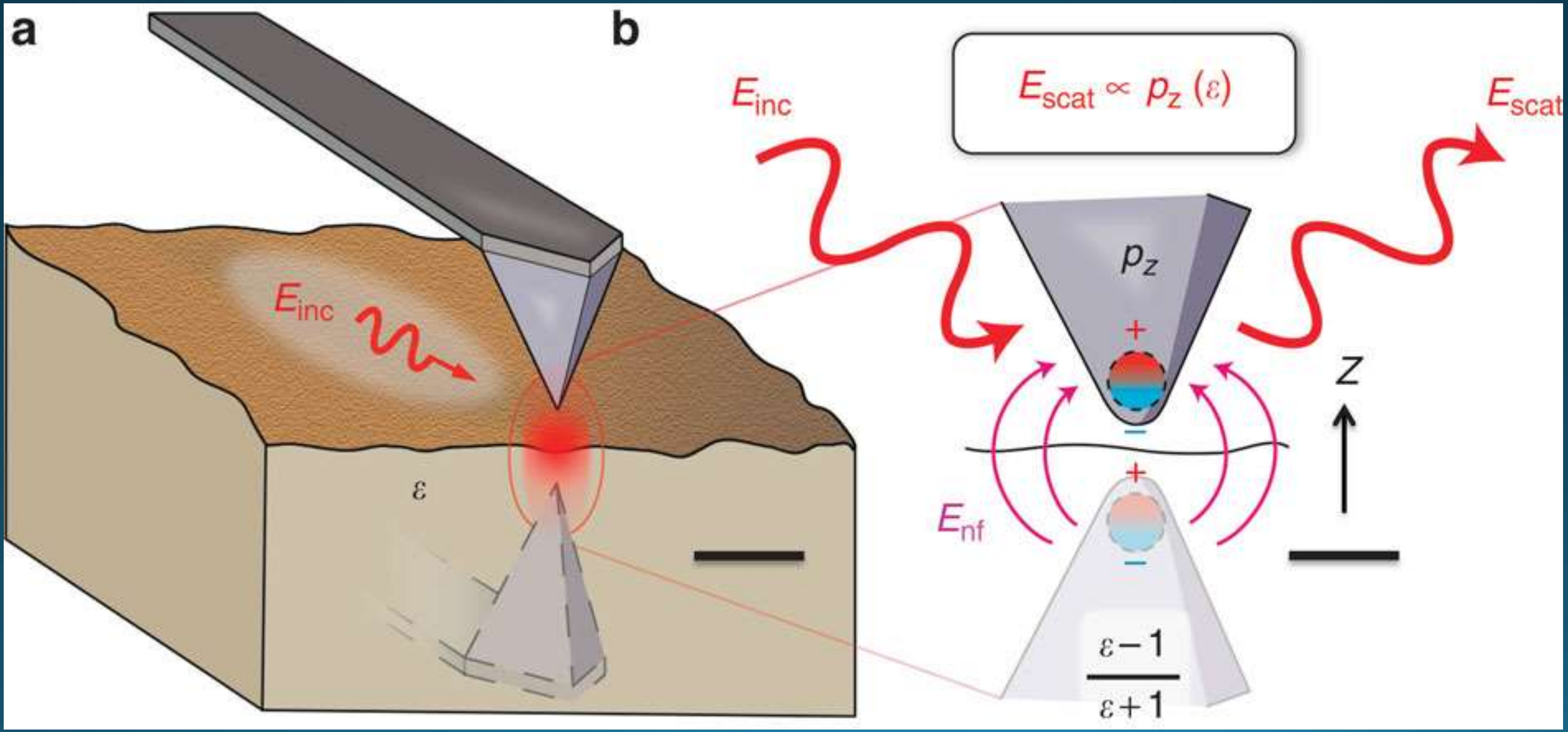




(A) AFM topography (B) chemical mapping (C) local IR spectra

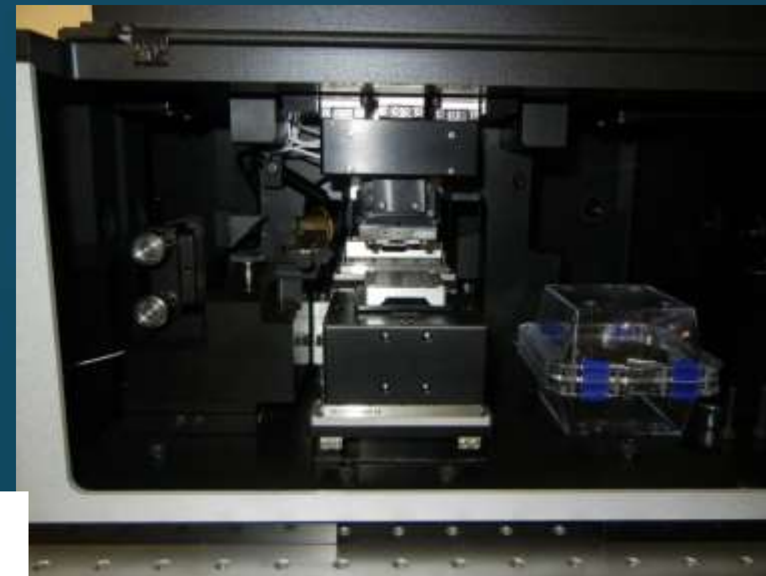
Infrared nanoscopy

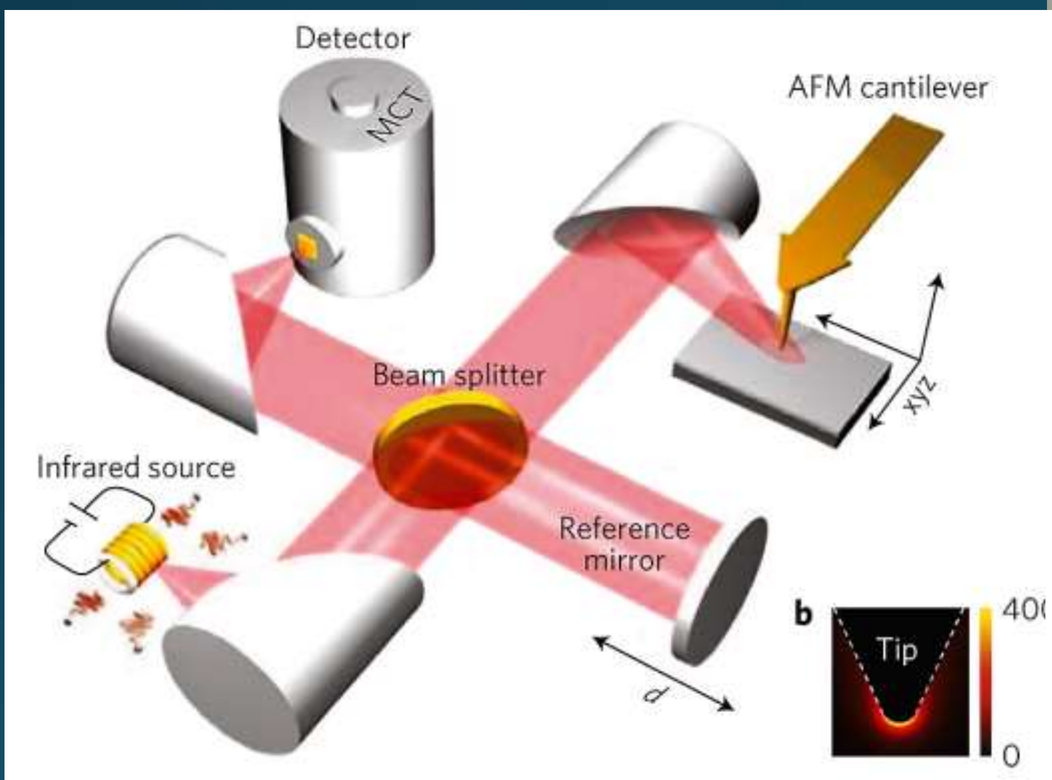
- IR SNOM – sSNIM

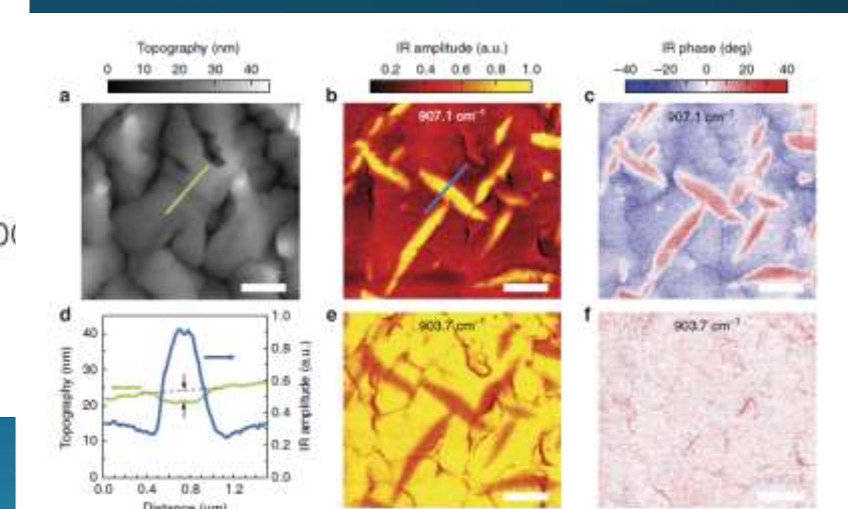


Infrared nanoscopy

- IR SNOM – sSNIM

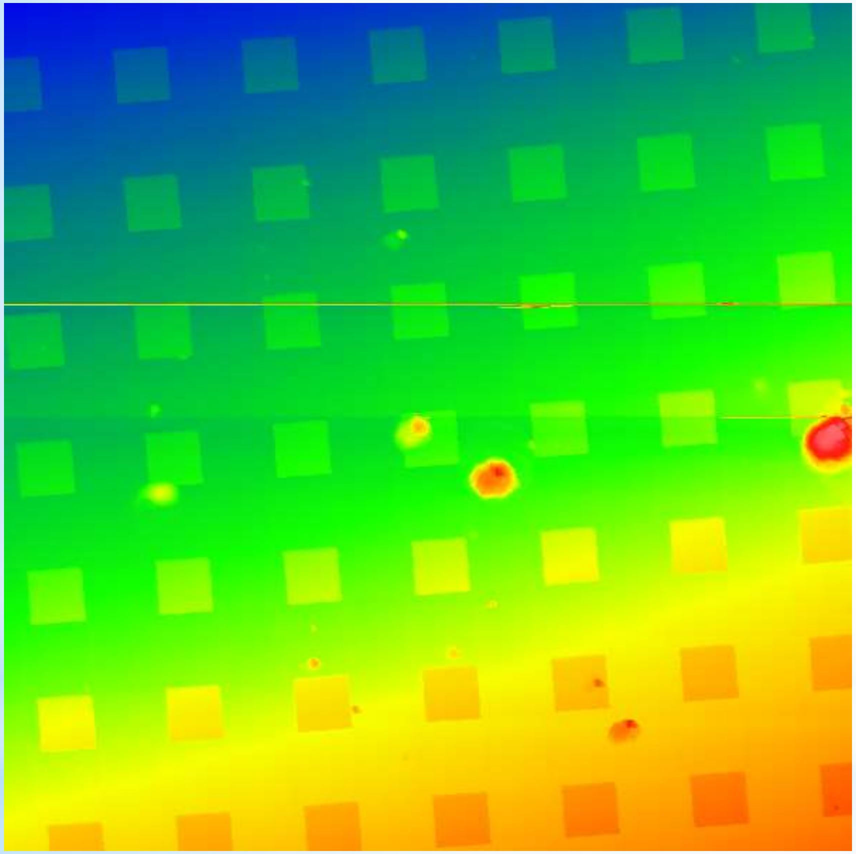




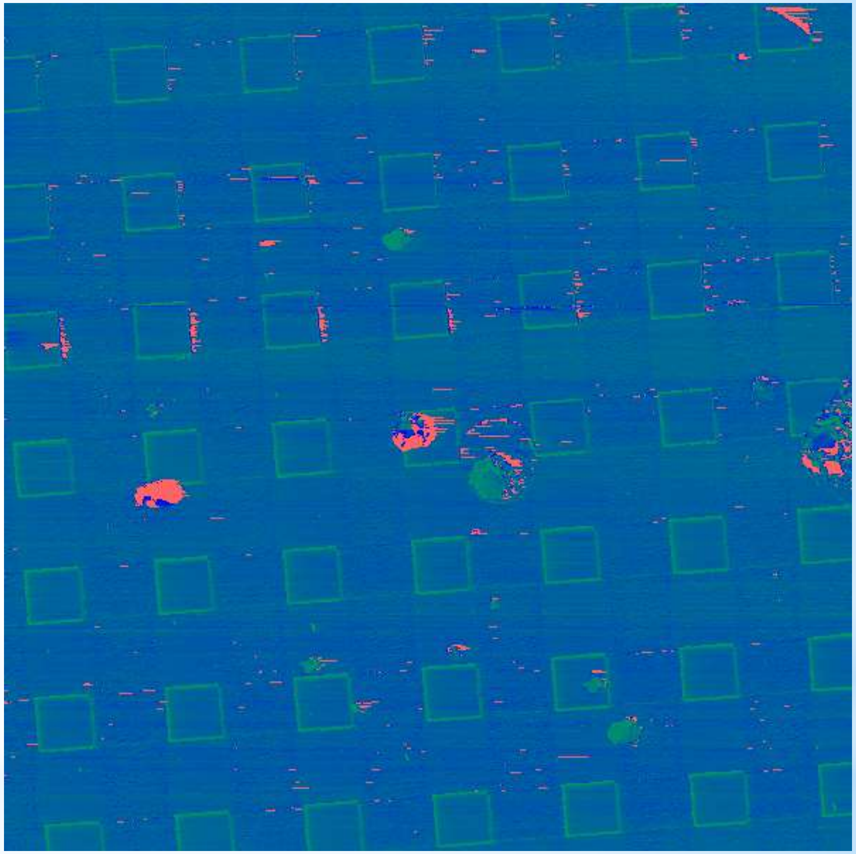


UCT Prague - A K07 A

SNIM - NeaSpec   Micrometer squares, height 20 nm – IR images

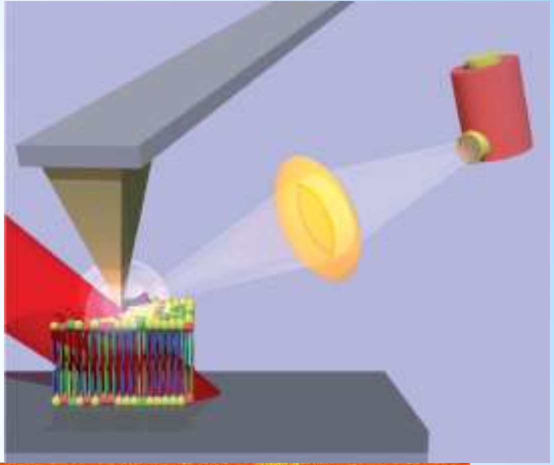


Intensity image



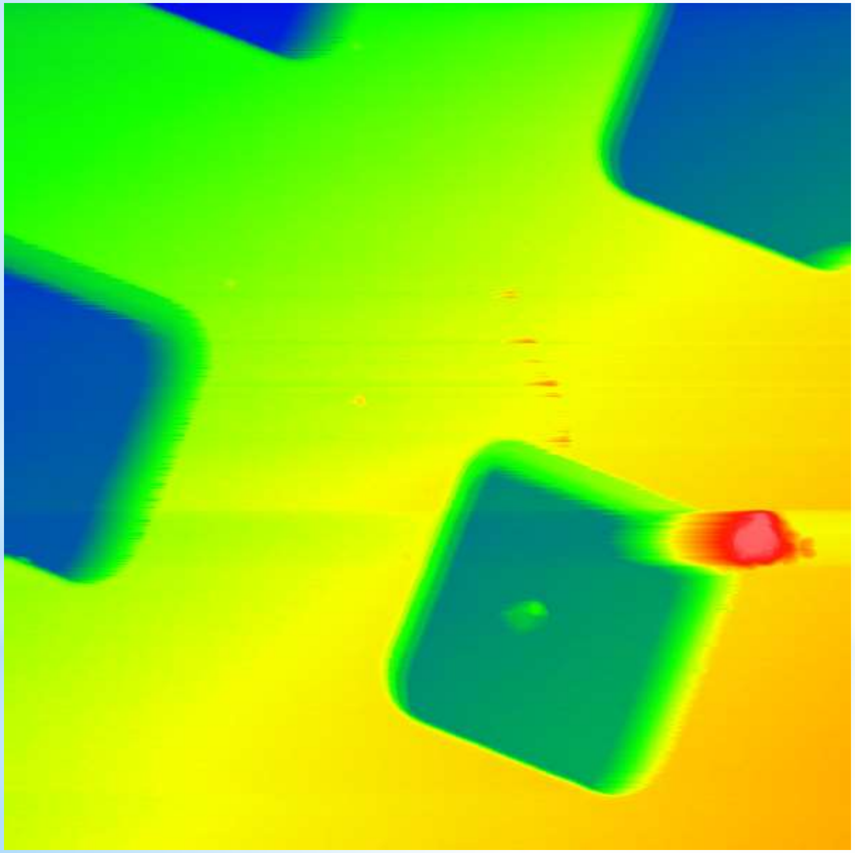
Phase image

UCT Prague - A K07 A

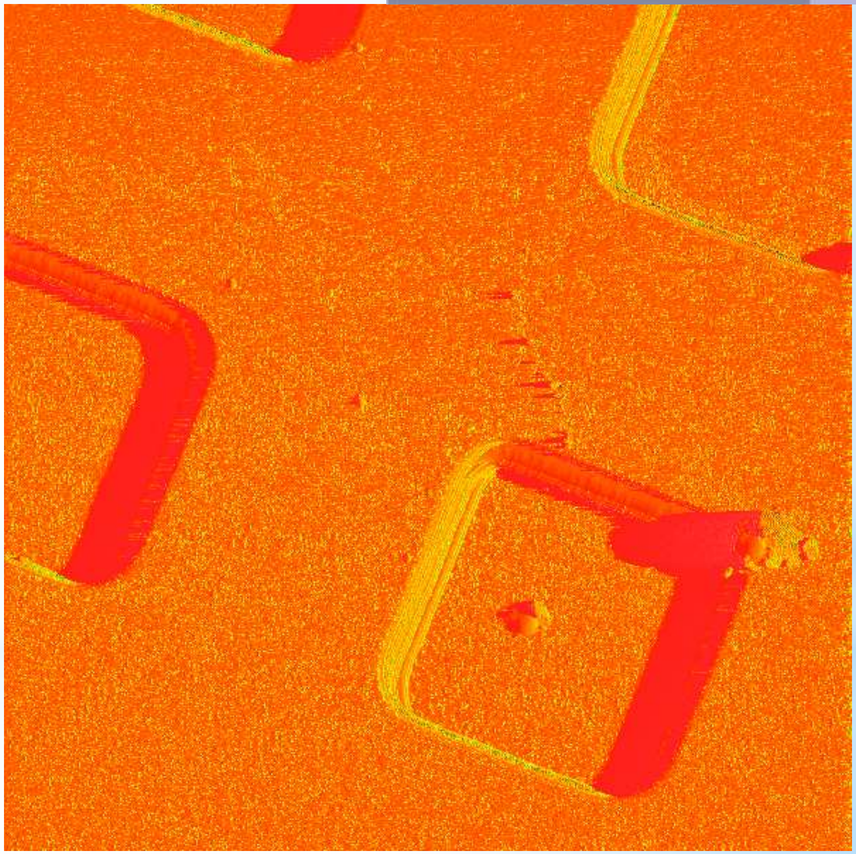


SNIM - NeaSpec

Micrometer squares – height 20 nm - IR images



Intensity image



Phase image

Infrared nanoscopy

- IR SNOM – sSNIM

ChemComm

COMMUNICATION

Synthesis and deposition of a Tröger's base polymer on the electrode surface for potentiometric detection of a neuroblastoma tumor marker metabolite†

Cite this: DOI: 10.1039/c6cc06203b

Received 27th July 2016, Accepted 6th September 2016

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www.rsc.org/chemcomm

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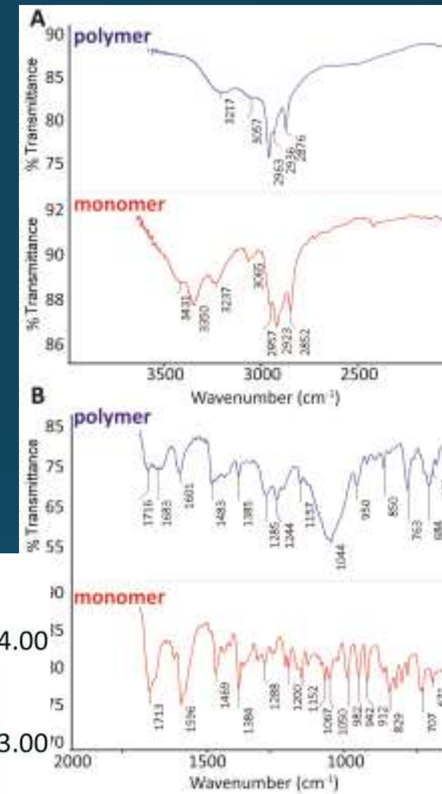
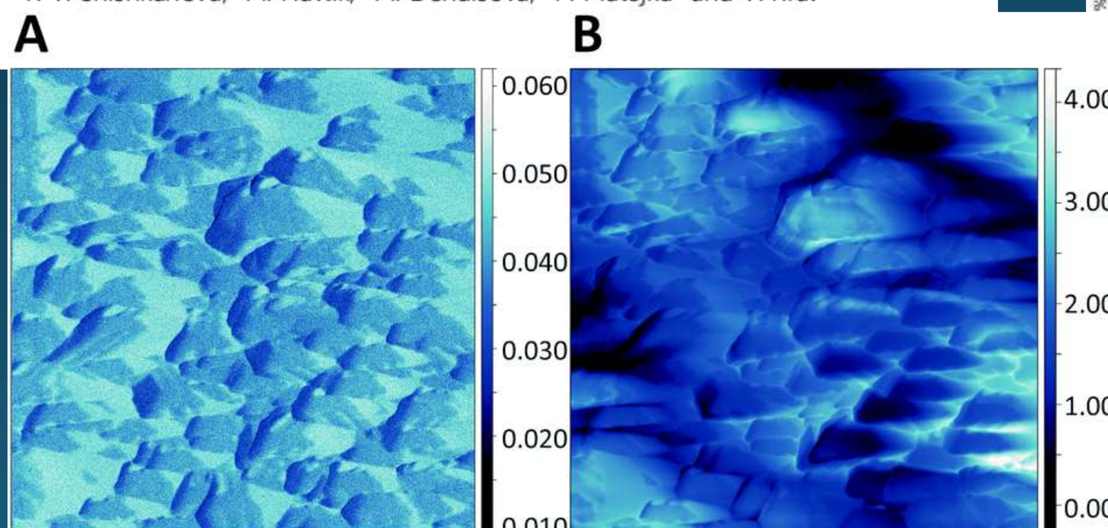
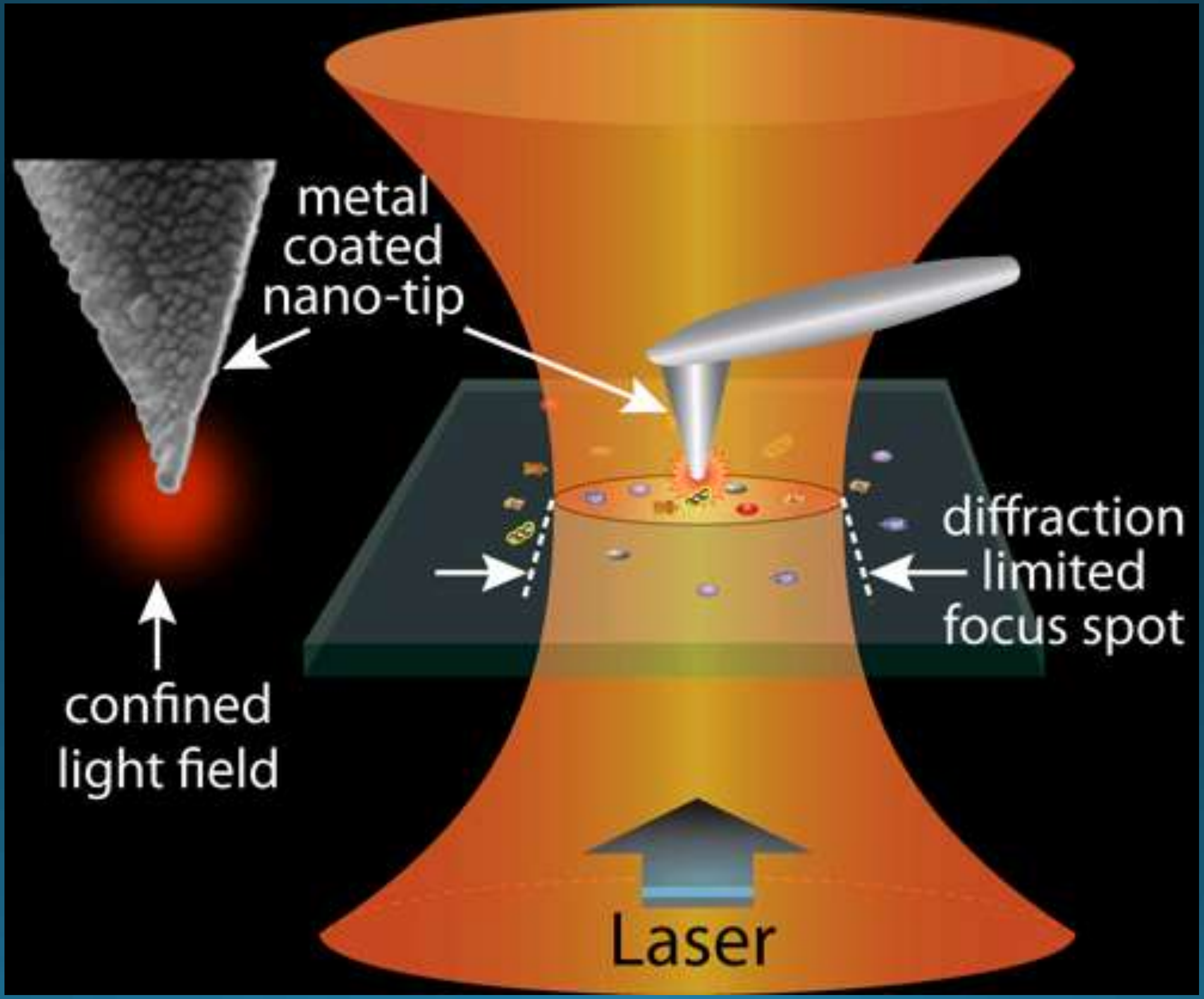




SNIM images 5x5 µm of the Au electrode surface. Mechanical amplitude signal (A) and optical signal (B).

Raman nanoscopy

- TERS spectroscopy and imaging



TERS – LOCAL FIELD

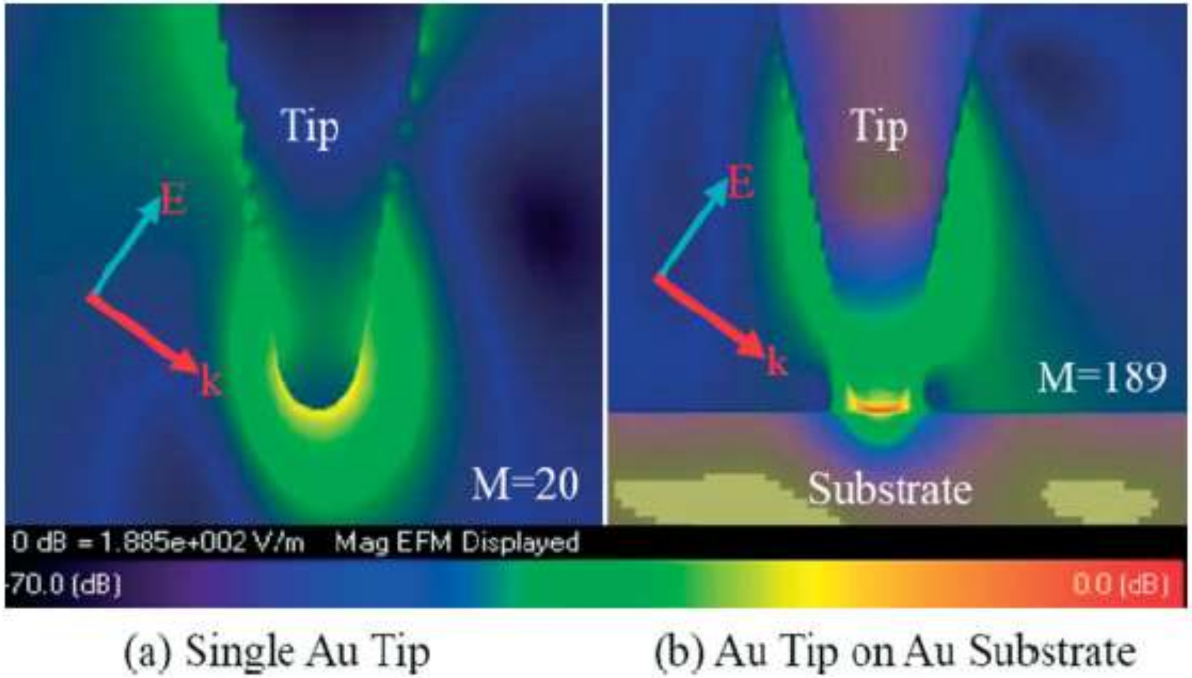
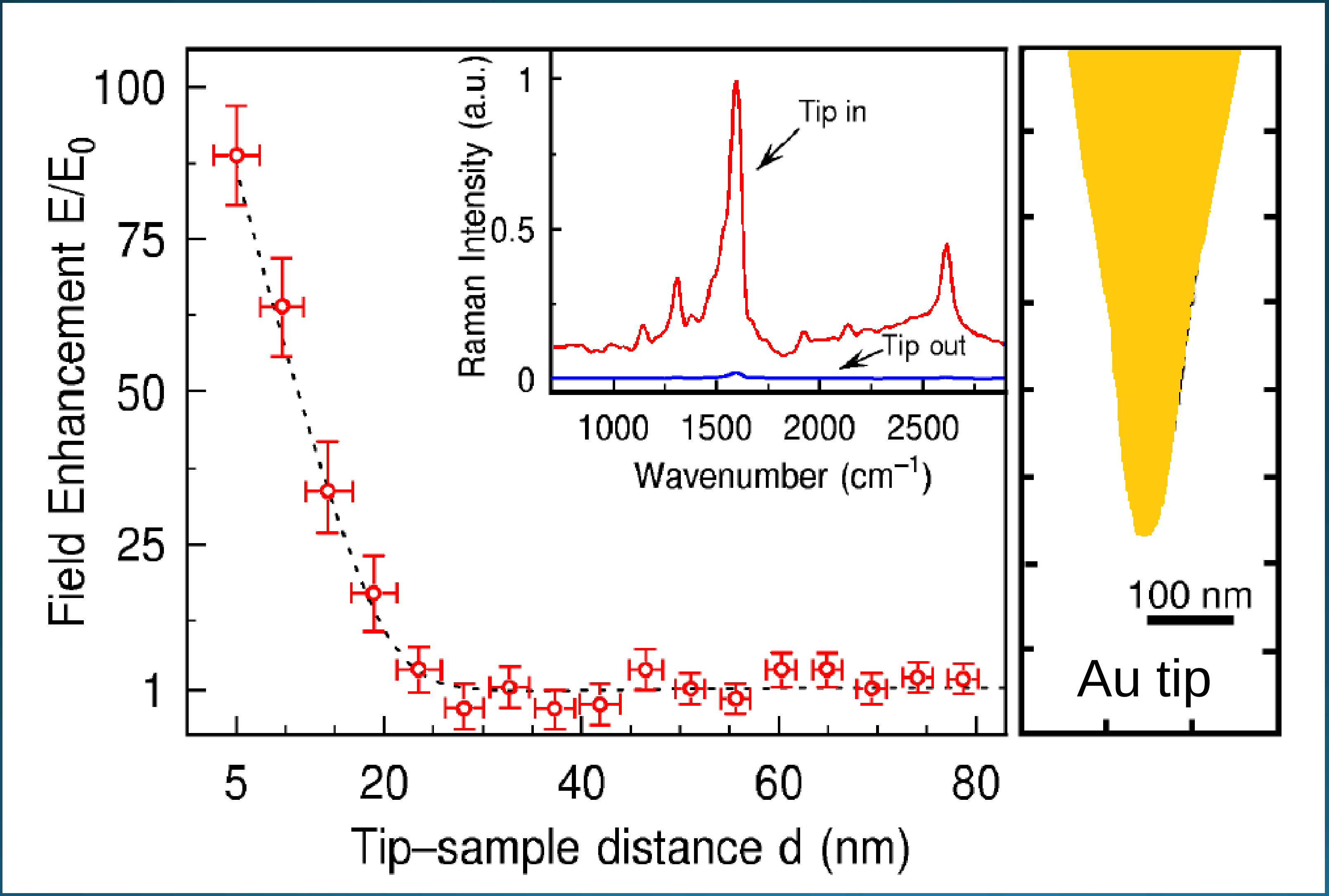


Figure 2. FDTD simulations of the electric field distribution for a single Au tip (a), and a gold tip held at distance $d = 2$ nm from a gold substrate surface. The polarization E and wave vector k of the incoming light are displayed in the schematics. *M* stands for the maximum.

TERS



100
75
50
25
1
Field Enhancement E/E0
5
20
40
60
80
Tip–sample distance d (nm)
Raman Intensity (a.u.)
1
0.5
0
Tip in
Tip out
1000
1500
2000
2500
Wavenumber (cm−1)
100 nm
Au tip

VÝVOJ EXPERIMENTÁLNÍCH METODIK PRO HROTEM ZESÍLENOU RAMANOVU SPEKTRSKOPII

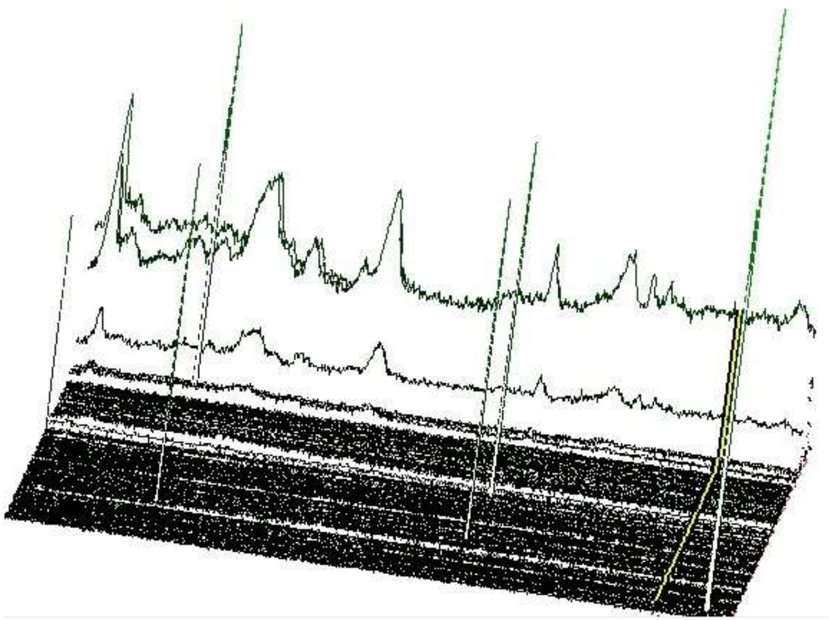
- BAKALÁŘSKÁ PRÁCE 2015/16

Martin Král
Ústav fyzikální chemie VŠCHT Praha

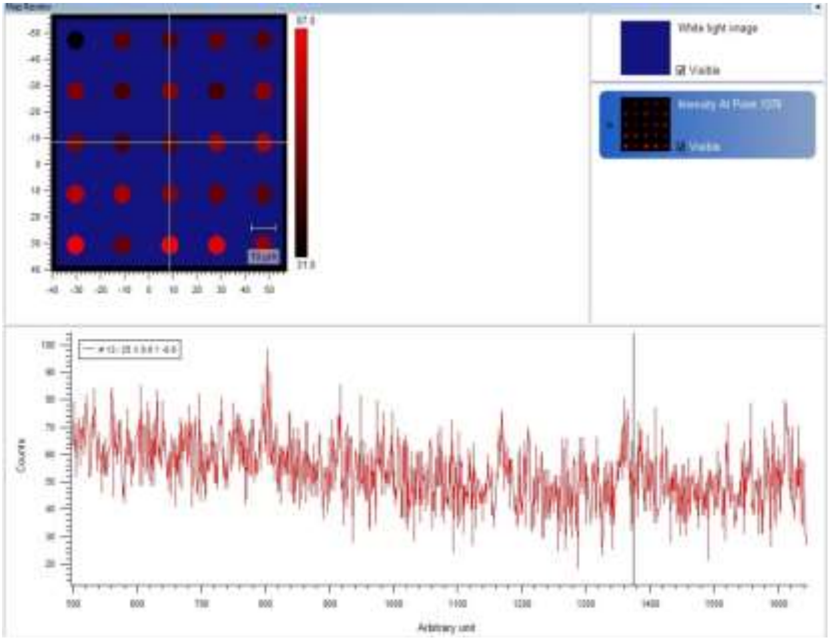
VYSOKÁ ŠKOLA CHEMICKO-TECHNOLOGICKÁ V PRAZE

TERS s STM

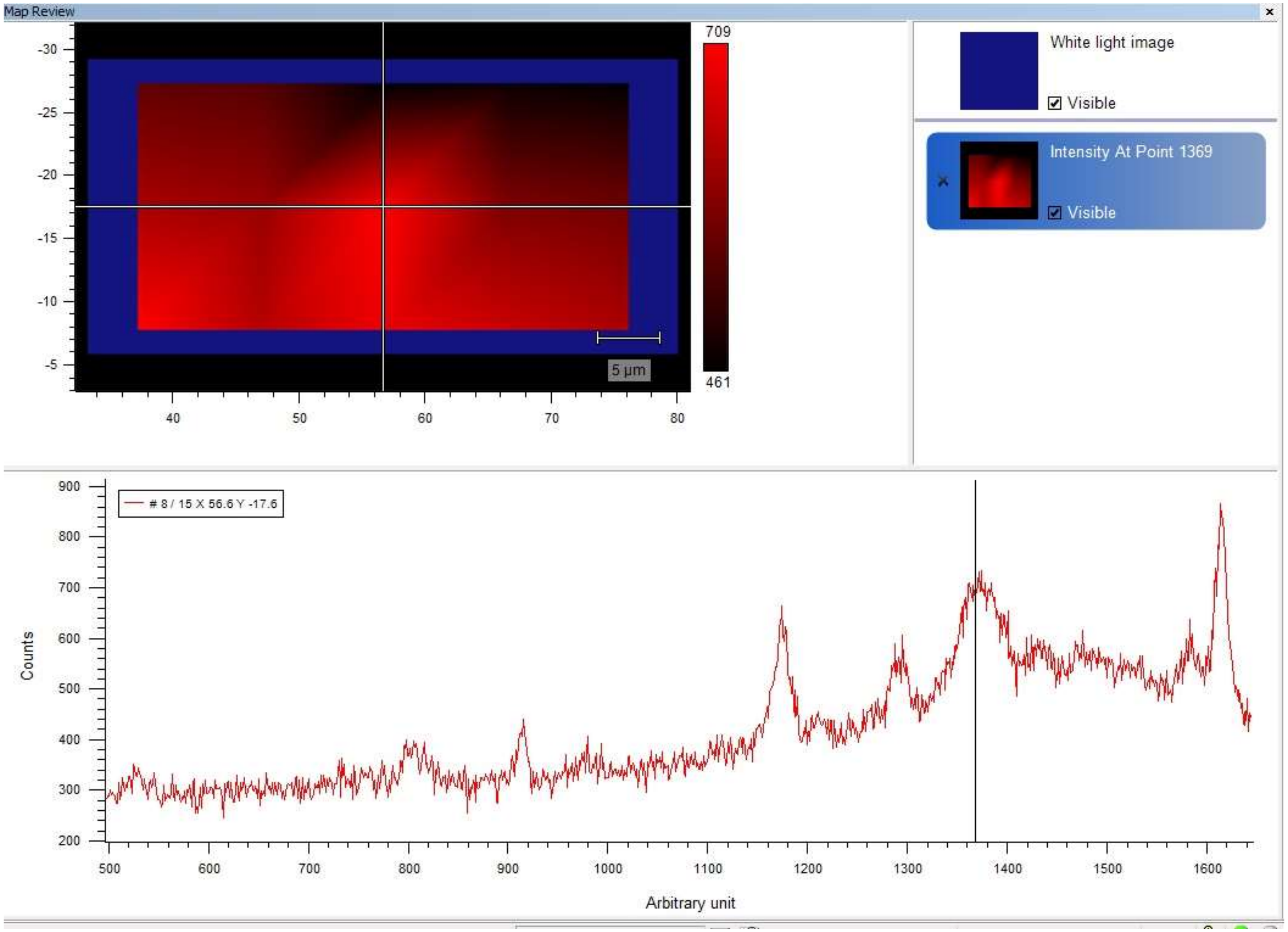
Hotspot



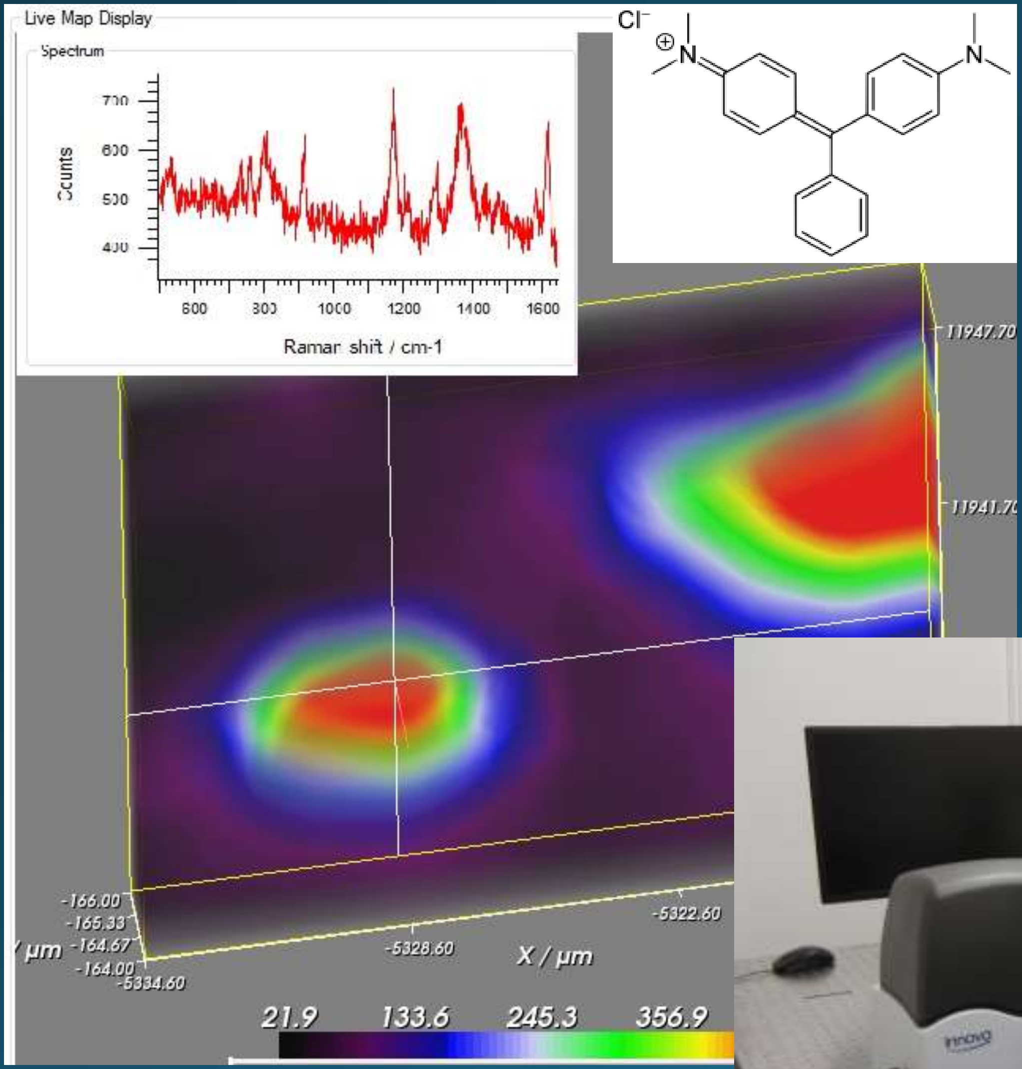
Mapování při 1376 cm^{-1}

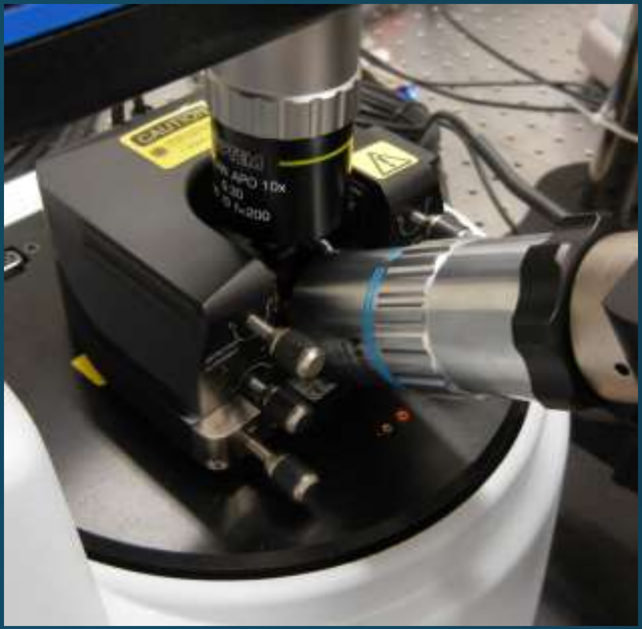


TERS s mikroskopií střižných sil



TERS


Live Map Display
Spectrum
700
600
500
400
800
1000
1200
1400
1600
Raman shift / cm-1
Cl⁻
N
N
11947.70
-166.00
-165.33
-164.67
-164.00
-5334.60
-5328.60
-5322.60
X / µm
21.9
133.6
245.3
356.9




RENISHAW
innova

Advances in TERS (tip-enhanced Raman scattering) for biochemical applications

Regina Treffer*, René Böhme†, Tanja Deckert-Gaudig*, Katherine Lau*[1], Stephan Tiede‡, Xiumei Lin* and Volker Deckert*†[2]

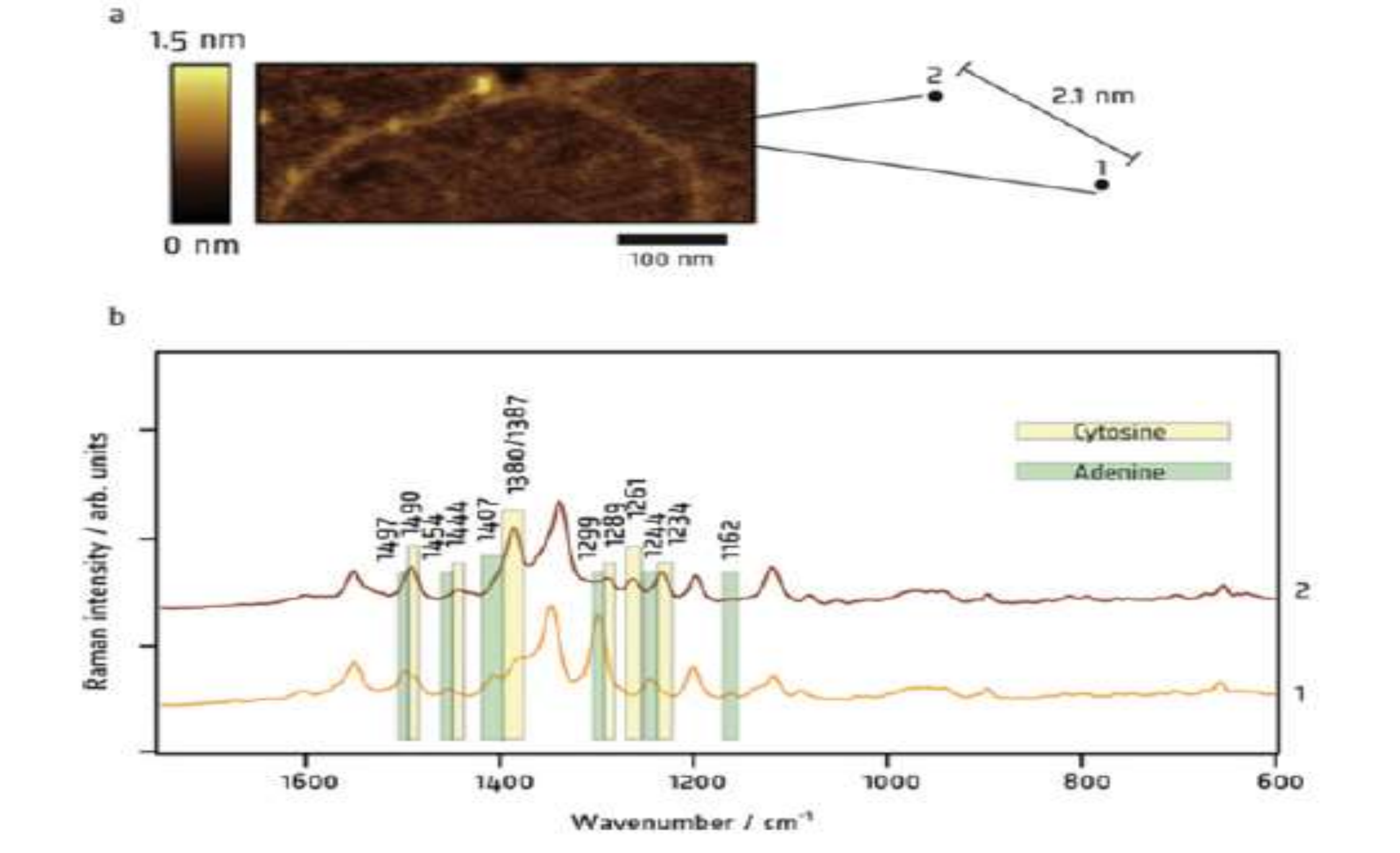


Figure 3 | TERS on a single DNA strand
(**a**) AFM topography image of a $(A_{10}C_{15})_8$ DNA single strand and schematic depiction of the measurement points of the TERS experiment. (**b**) The corresponding TERS spectra; important marker bands are highlighted.

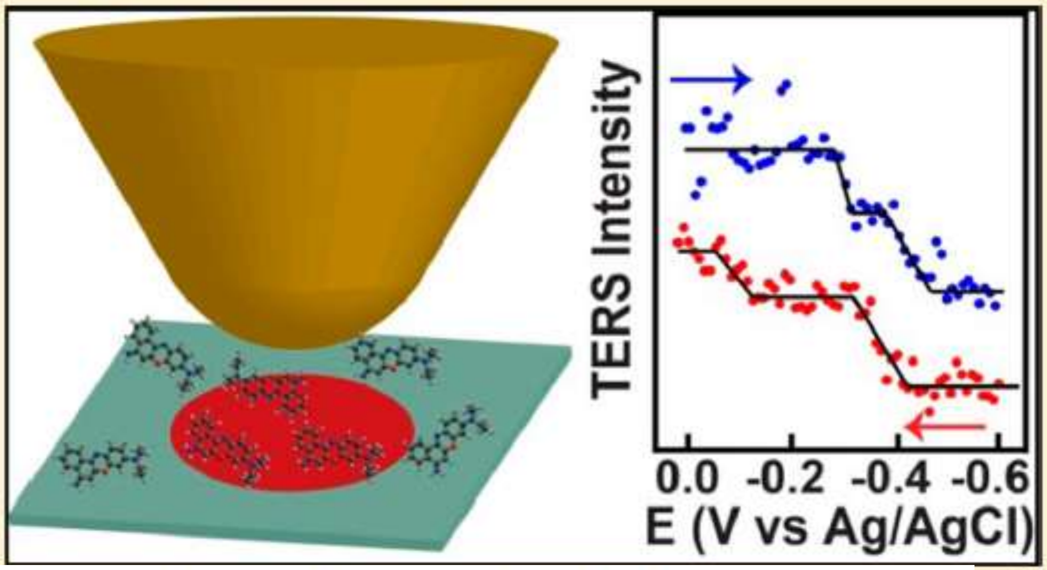
NANO LETTERS
Letter
pubs.acs.org/NanoLett

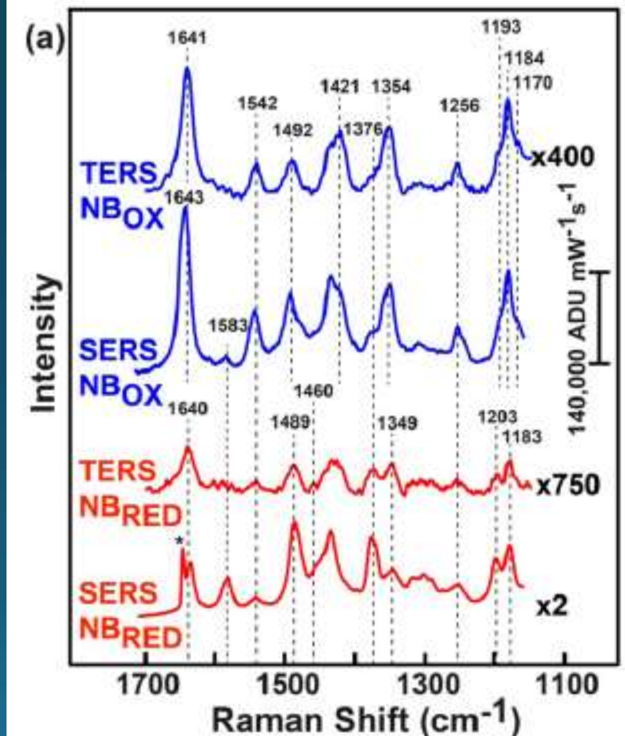
Probing Redox Reactions at the Nanoscale with Electrochemical Tip-Enhanced Raman Spectroscopy

DOI: 10.1021/acs.nanolett.5b04177
Nano Lett. 2015, 15, 7956−7962

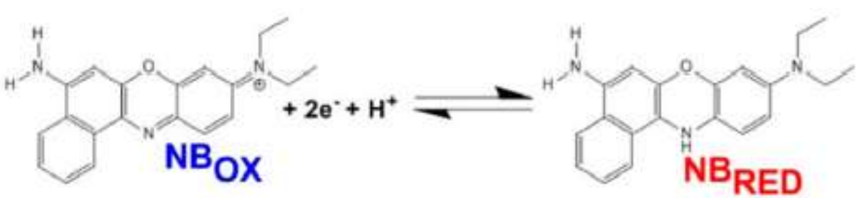
Dmitry Kurouski,[†] Michael Mattei,[†] and Richard P. Van Duyne*,[†,‡]

[†]Department of Chemistry and [‡]Applied Physics Program, Northwestern University, Evanston, Illinois 60208, United States





Scheme 1. Redox Reaction of NB at pH > 6



KEYWORDS: *Tip-Enhanced Raman Spectroscopy (TERS), Nanoscale Electrochemistry, Cyclic Voltammetry (CV)*

FINAL REMARKS TO „MATERIAL"

In the material sciences,
TERS and IR nanoscopy are gaining attention as appropriate non-destructive and high-resolution (molecular dimension) technique.

The **spatial nano-resolution** and **chemical specificity**

- structural and chemical properties of nanocomposites ?
- behavior of molecules on surface of nanostructured material?

FINAL REMARKS TO „BIO“

In the life sciences,
TERS and IR nanoscopy are gaining attention as appropriate label-free and high-resolution (molecular dimension) technique.

The **spatial nano-resolution** and **chemical specificity**

- structural properties on cell membranes, polypeptides, fibrils?
- interactions between the human *stratum corneum* and topically applied liposomal systems?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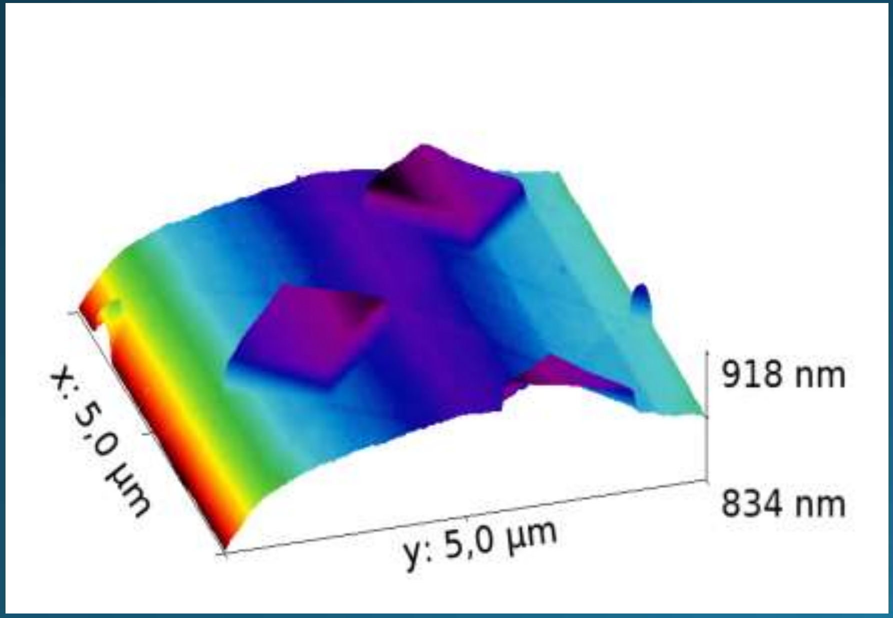
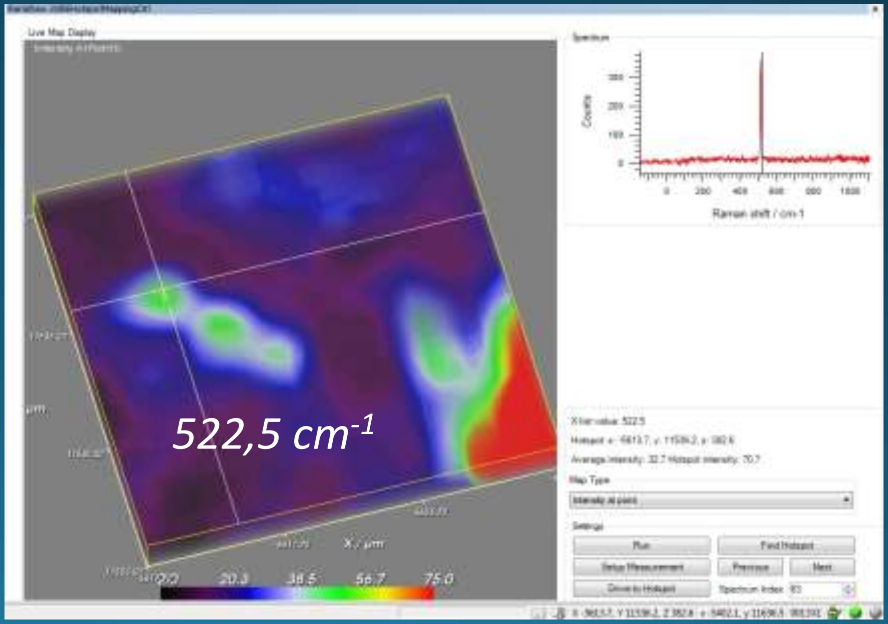

918 nm
834 nm
x: 5,0 µm
y: 5,0 µm


522,5 cm-1
Raman shift / cm-1