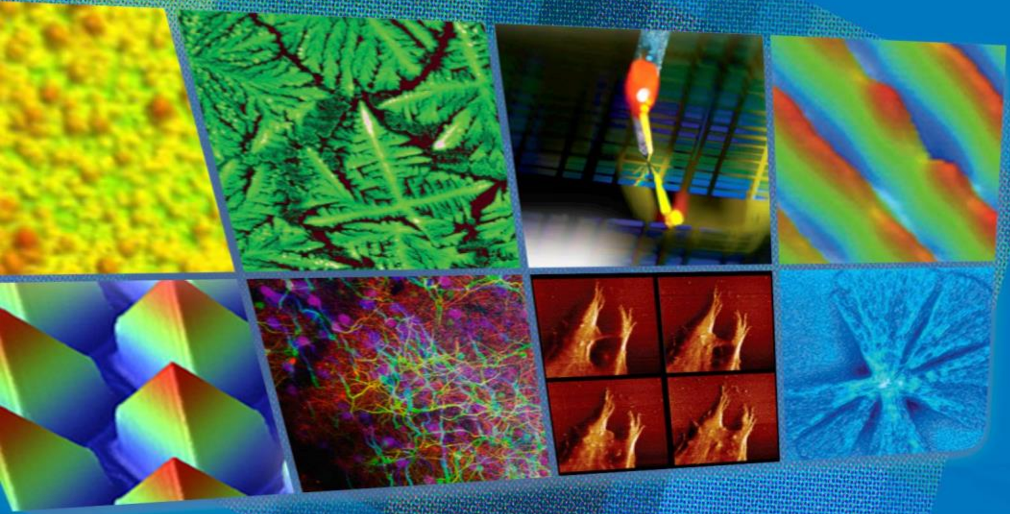
Recent Advancements in Nanoscale IR Spectroscopy and Imaging

Anirban Roy, Qichi Hu, Honghua Yang, Miriam Unger and Curtis Marcott



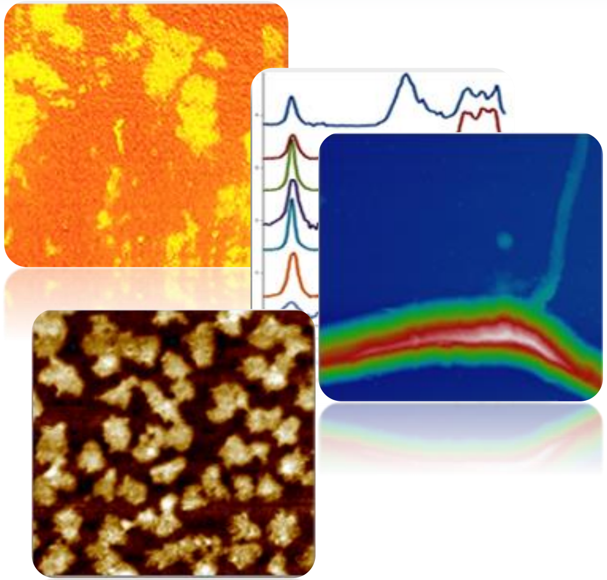
Atomic Force Microscopy
3D Optical Microscopy
Fluorescence Microscopy
Tribology
Stylus Profilometry
Nanoindentation

Bruker Nano Surfaces Division

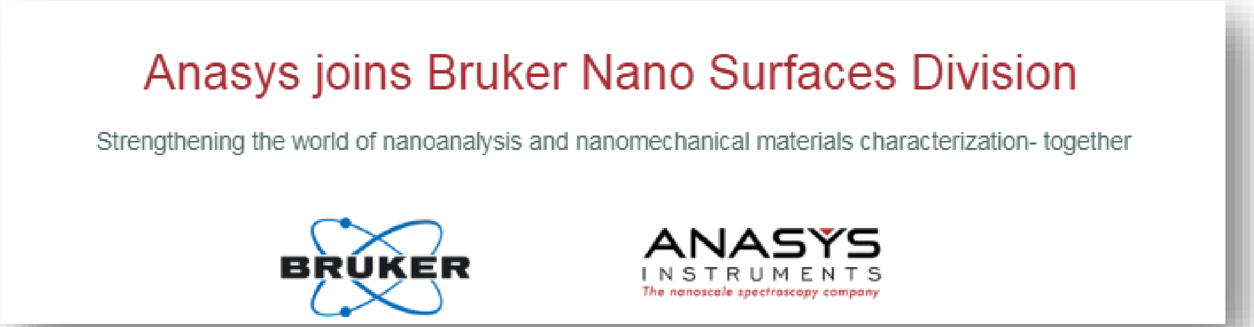
Innovation with Integrity

Outline

- Company Background
- Introduction to AFM-IR
- Latest AFM-IR Advancements
    - Resonance Enhanced AFM-IR
    - HyperSpectral Imaging/Spectroscopy
    - Tapping AFM-IR Imaging/Spectroscopy
        - Technical Overview
        - Applications
- s-SNOM Technology and Applications
- Tunable IR Laser Options
- Summary



Bruker Nano Acquires Anasys Instruments



Anasys joins Bruker Nano Surfaces Division

Strengthening the world of nanoanalysis and nanomechanical materials characterization- together

- Bruker Nano Surfaces Division acquired Anasys Instruments Corp on April 10th 2018
- All nanoIR products are now integrated into the Bruker Nano Product Support

Nanoscale IR spectroscopy

2010

nanoIR™
1st Generation
AFM-IR

2014

nanoIR2™
2nd Generation AFM-IR
Top Down Configuration &
Resonance Enhanced

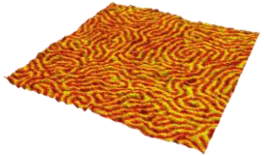
2015

nanoIR2-s™
Combined
IR s-SNOM & AFM-IR

2016

nanoIR2-FS™
3RD Generation
FASTspectra

2017

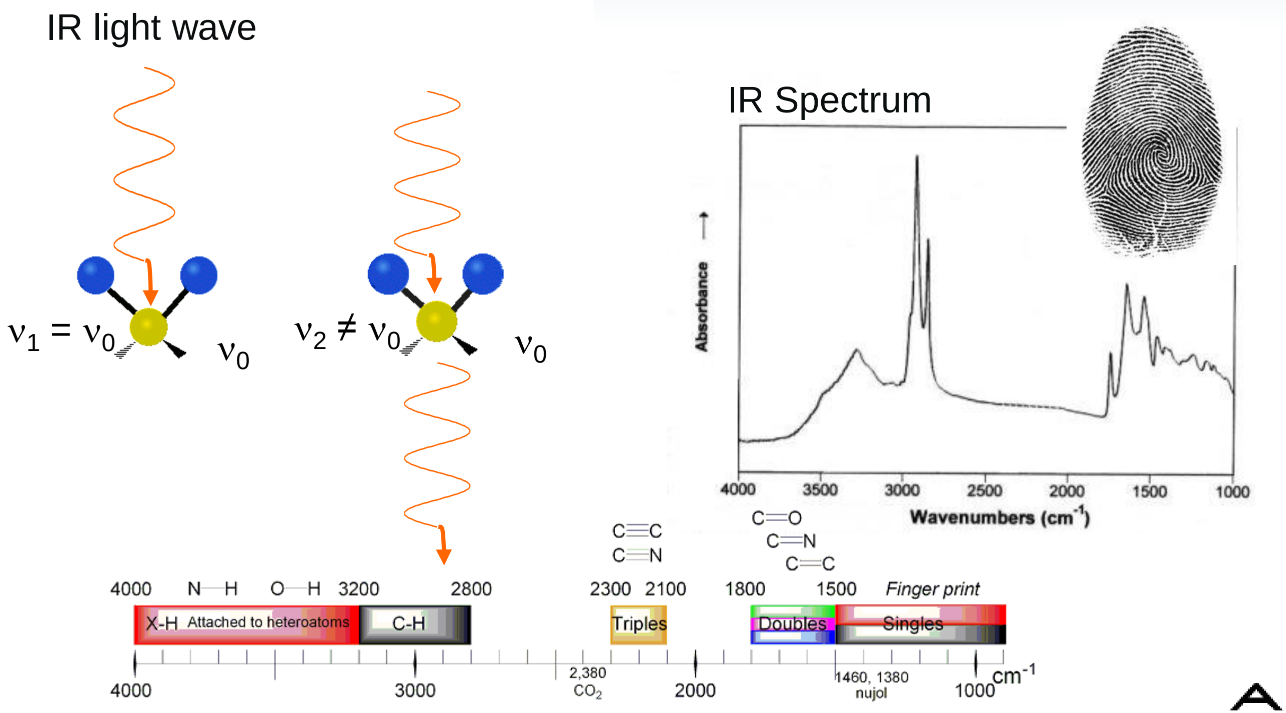


Tapping AFM-IR
HYPERspectra

2018

NEW
nanoIR3™
Latest Generation
nanoIR platform with
Tapping AFM-**IR**

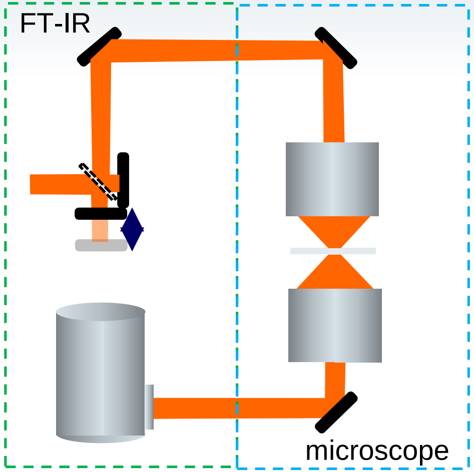
Infrared Spectroscopy Introduction



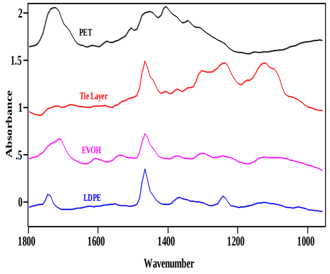
Source: Wikipedia

The nanoscale spectroscopy company

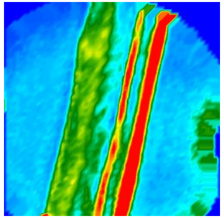
Power and Limitations of Infrared Microspectroscopy



IR spectra



Chemical Image

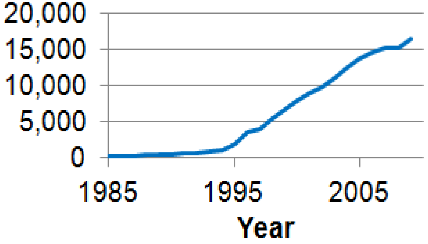


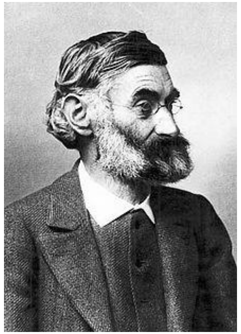
Multilayer film, courtesy of Dr. Curtis Marcott

IR microspectroscopy applications

- Materials Science
- Consumer products
- Pharmaceuticals
- Life sciences
- Health & beauty
- Forensics

IR microspectroscopy annual publications

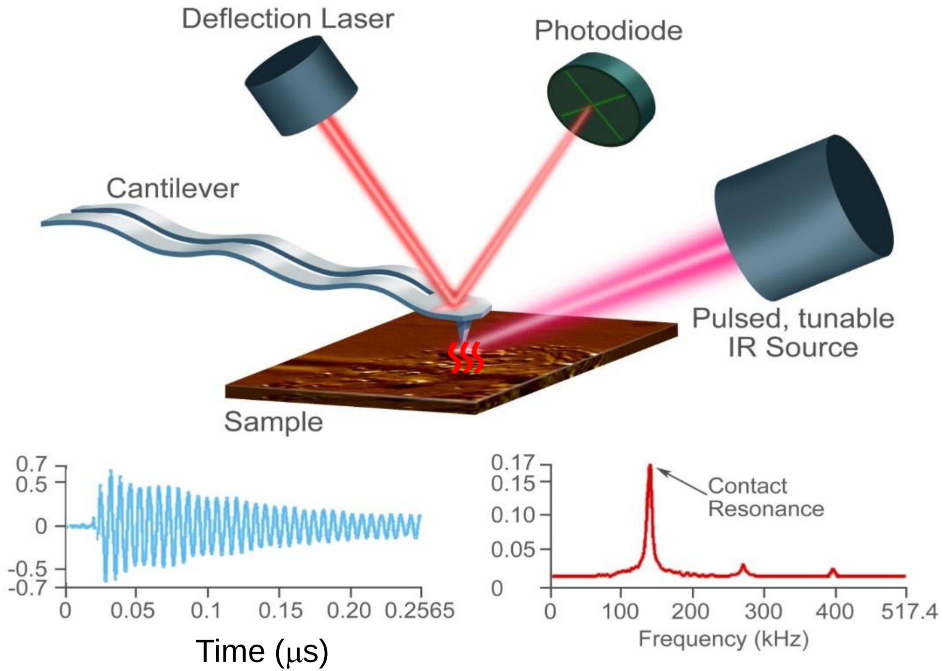




Sampling Method	Diffraction limited resolution*	Practical resolution limit
Transmission	2λ	~10-30 µm
ATR	0.5λ	~3-10 µm

Abbe diffration limit:
Practical resolution many microns

AFM-Based IR Spectroscopy (AFM-IR)



Dazzi, A.; Prazeres, R.; Glotin, F.; Ortega, J.M.; *Opt. Lett.* 2005, *30*, 2388-2390.

Alexandre Dazzi
2014 Ernst Abbe Award

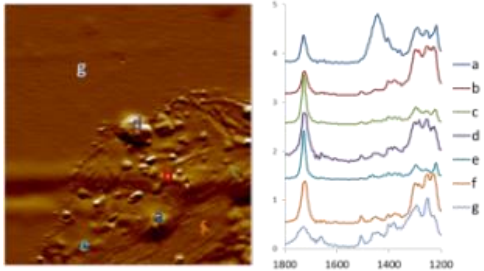
Ernst Abbe

ANASYS INSTRUMENTS
The nanoscale spectroscopy company

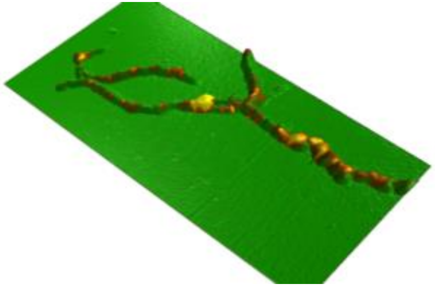
Nanoscale IR Spectroscopy

nanoscale infrared imaging & spectroscopy capabilities

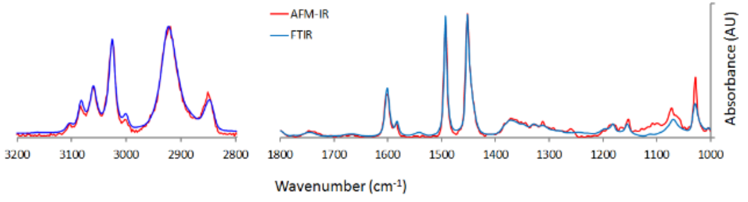
Nanoscale IR
chemical analysis



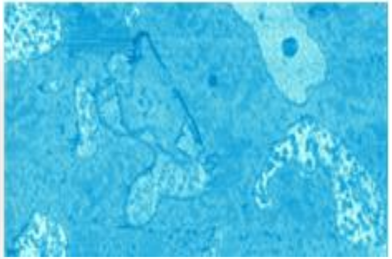
Chemical composition &
nanoscale property mapping



Rich, interpretable
spectra
directly correlates to FTIR



Monolayer sensitivity &
high spatial resolution



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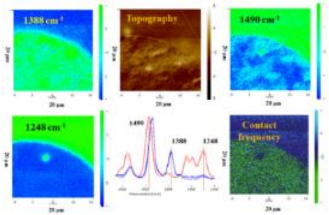
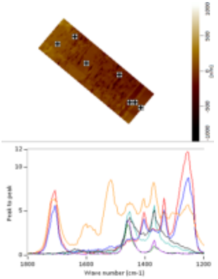
Broad range of nanoIR applications

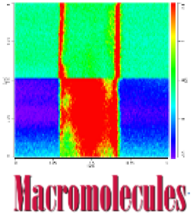
Polymer blends & Block



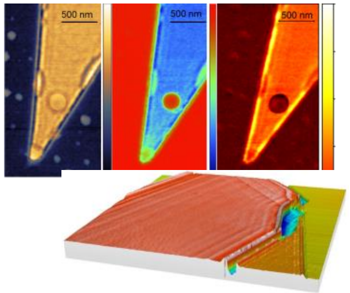
Multilayer films



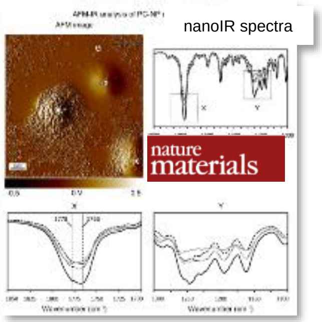
Nanofibers



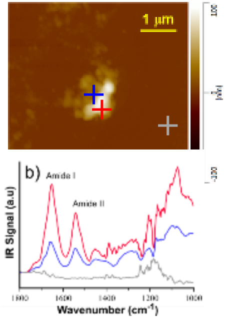
2D Materials/Graphene



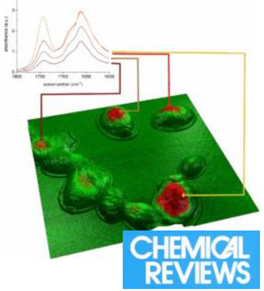
Nano-Composites



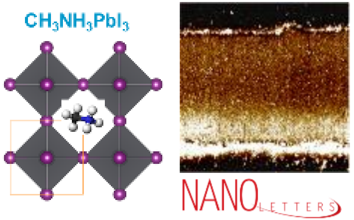
Organic nano Contaminant



Life Science

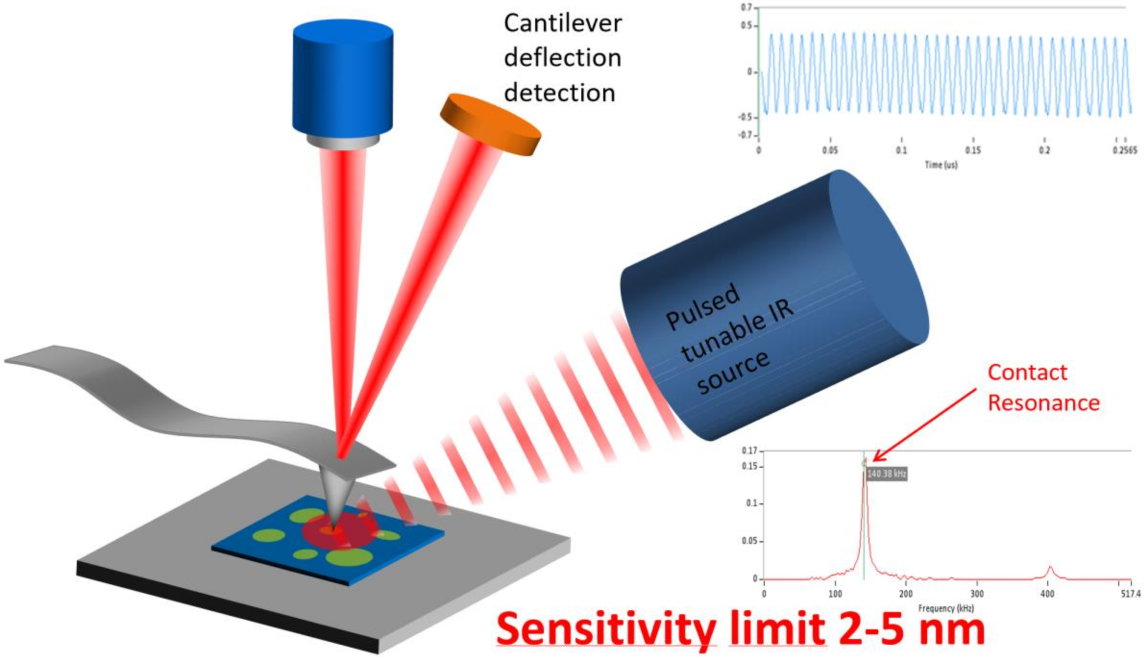


Perovskites & Solar Cells



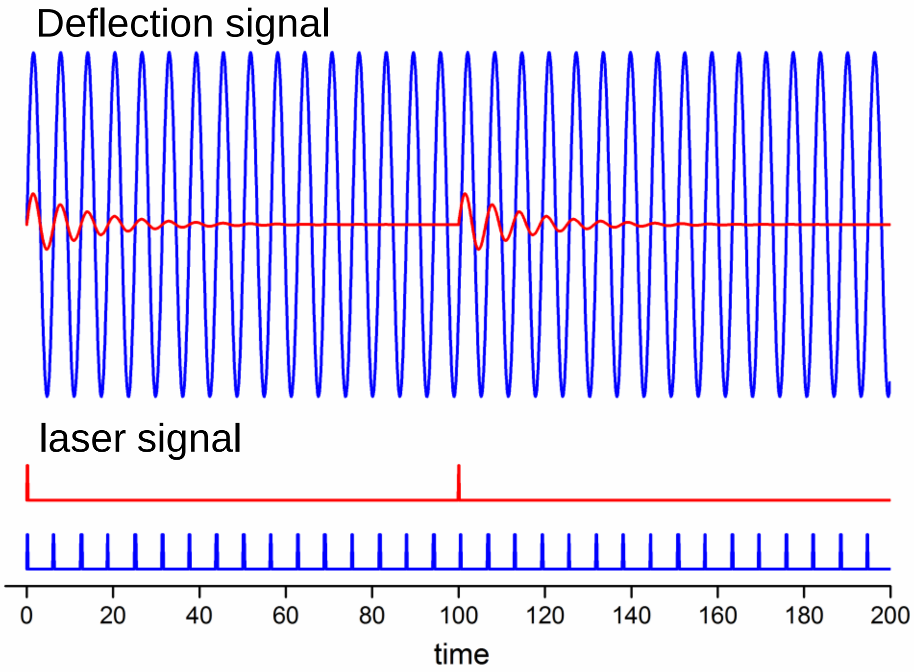
Resonance Enhanced Mode

- **Demonstrated by Pr. Belkin team in 2011 (Opt. Express)**



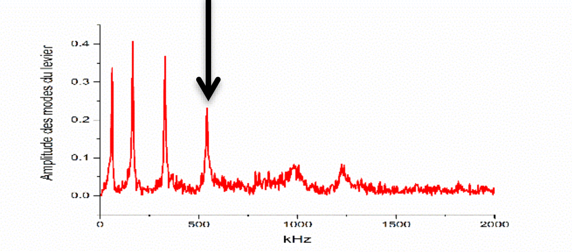
Sensitivity limit 2-5 nm

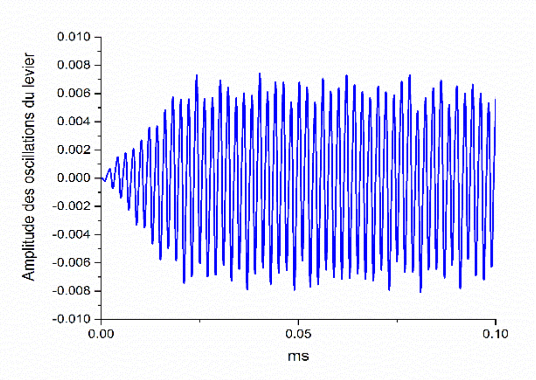
Resonance Enhanced Mode

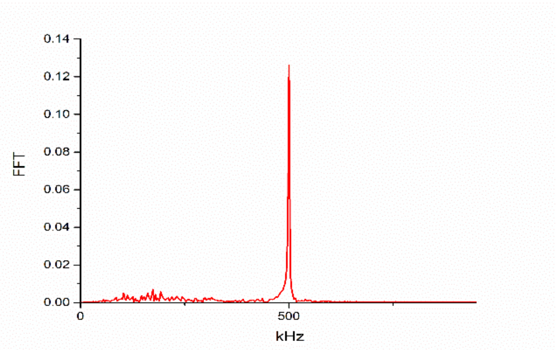


Forced resonance makes AFM-IR more sensitive

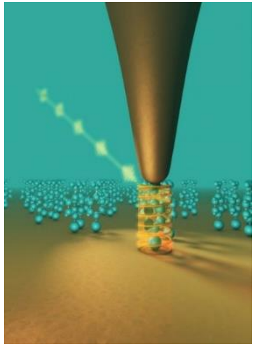
Laser repetition rate

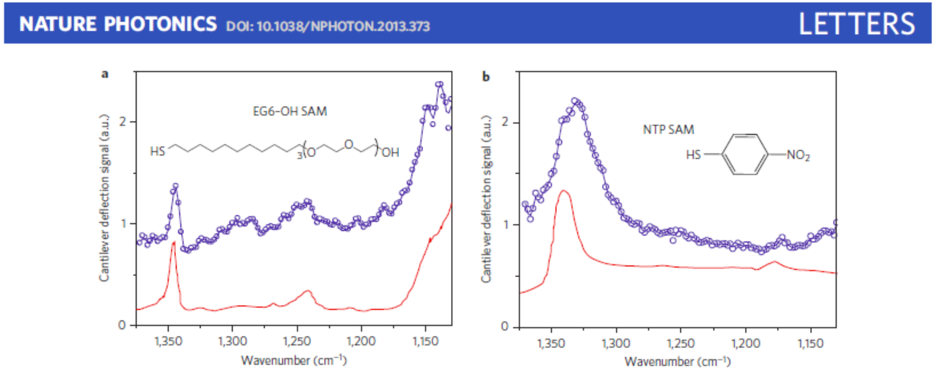






Single Monolayer Sensitivity

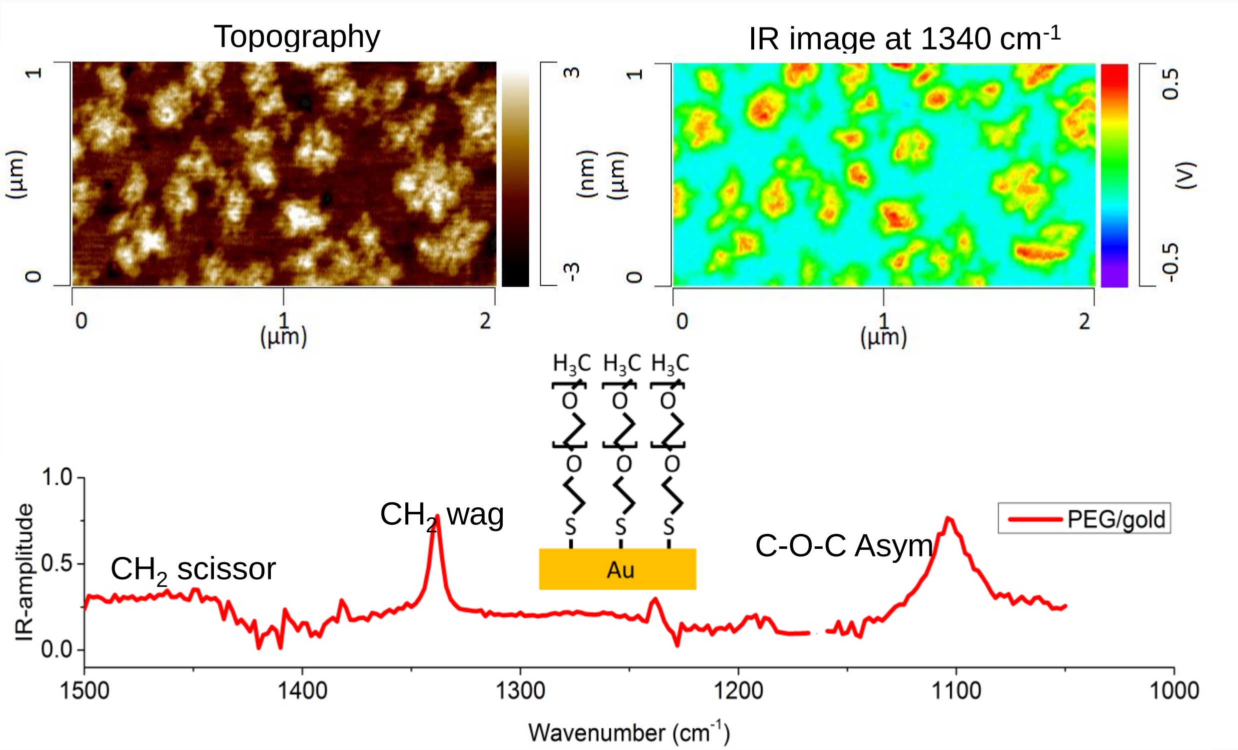




NATURE PHOTONICS DOI: 10.1038/NPHOTON.2013.373 LETTERS

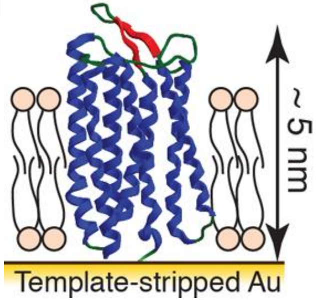
F. Lu, M. Jin, and M.A. Belkin, *Nat. Photonics* **8**, 307–312 (2013).

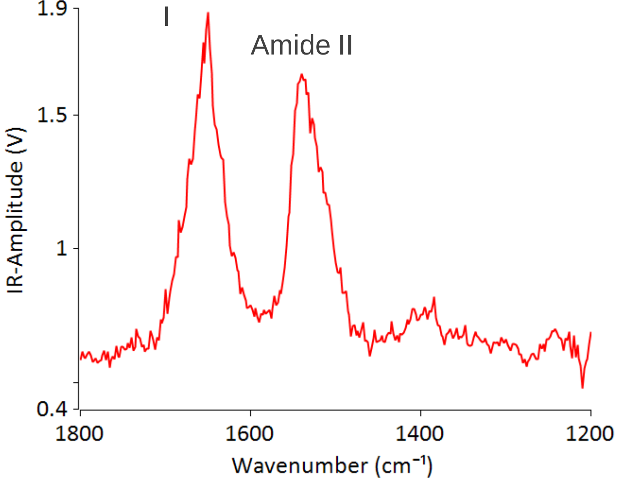
Resonance enhanced AFM-IR of PEG monolayer

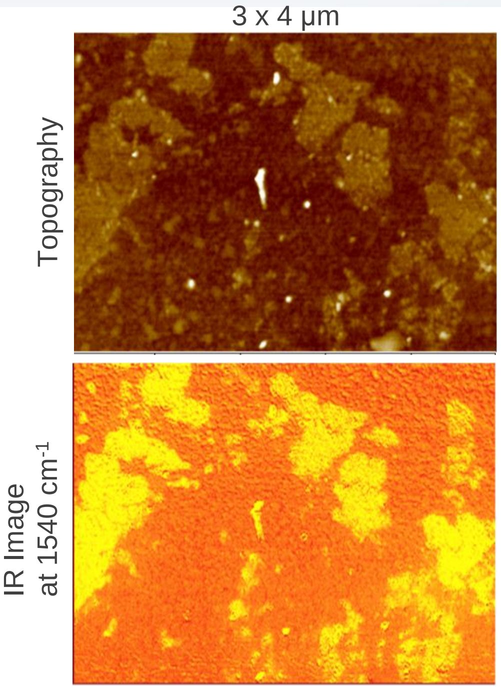


Purple Membrane (Resonance Enhanced AFM-IR)

Halobacterium Salinarum deposited on a Au substrate







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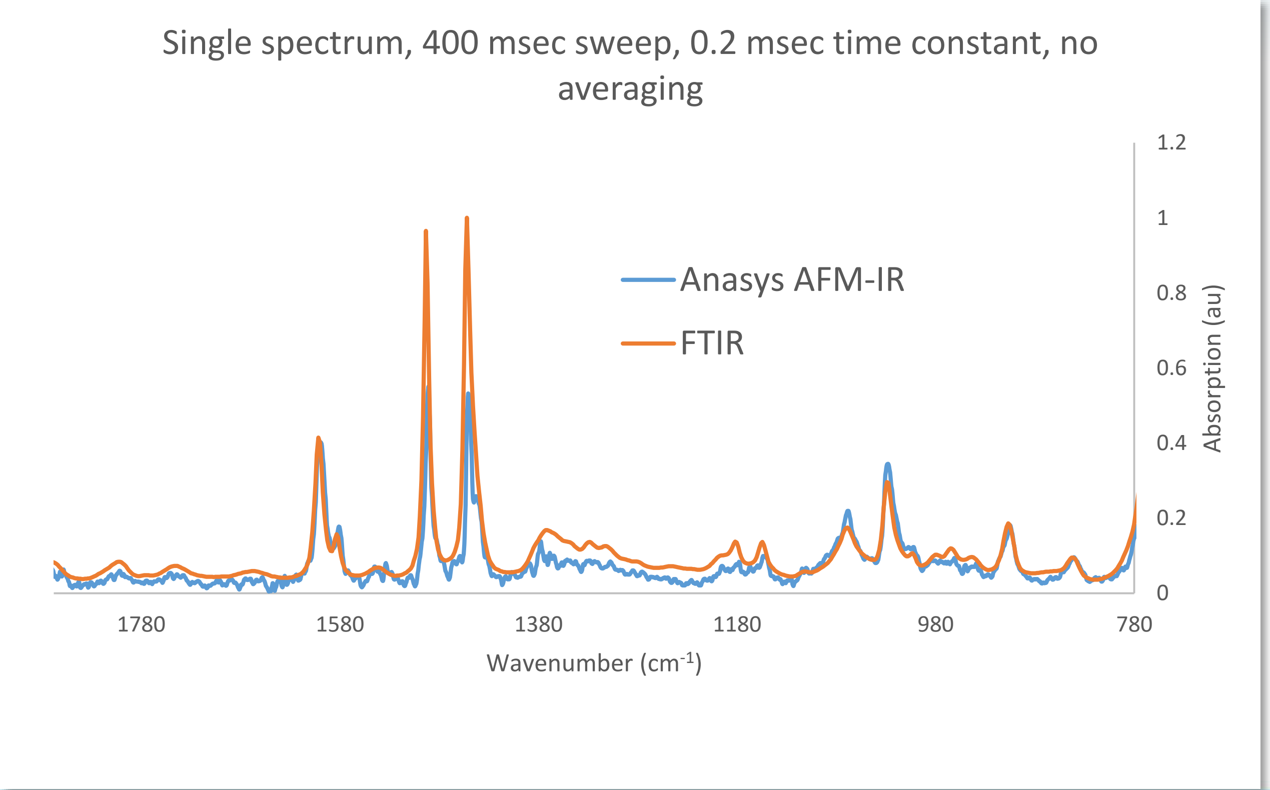
QCLs are getting faster!



Faster Scanning Enables Hyperspectral Imaging

Hyperspectral image cube

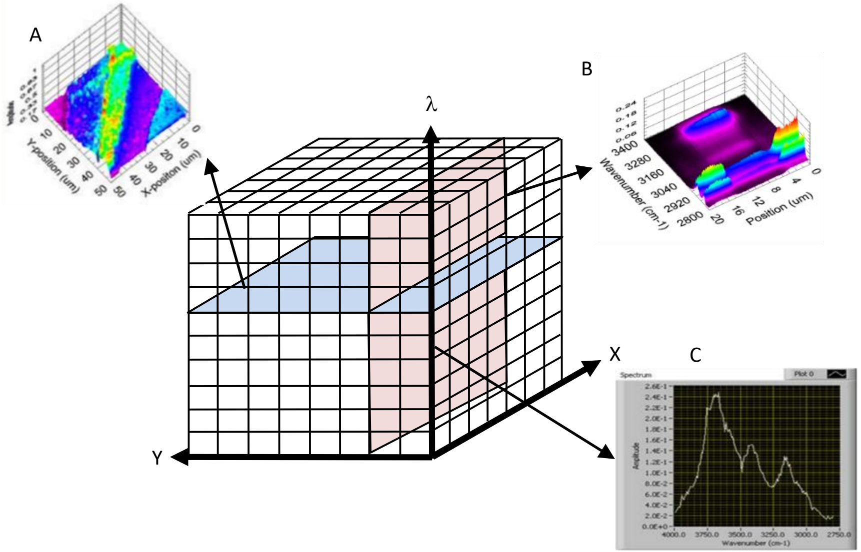
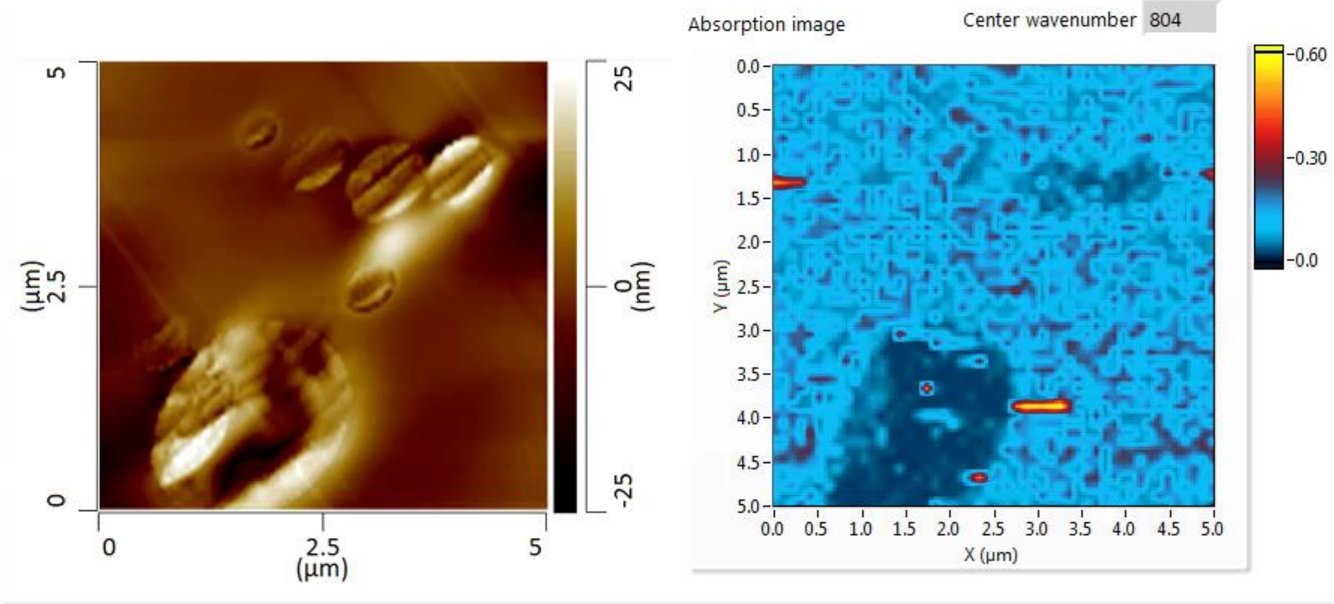


Figure 5. Illustration of the hyperspectral image cube. High speed AFM-based IR spectroscopy allow for the first time practical hyperspectral imaging, i.e., where spectra are mapped at matrix of XY points. One can extract segments of the hyperspectral cube to obtain (A) chemical maps that show spatial variation in absorption at a given wavelength, (B) spectral line maps showing the variation in spectra in one direction, or (C) individual spectra at any X,Y location.

Hyperspectral animation

5-μm x 5-μm, 50 x 50 spectrum array on PS/PMMA/epoxy blend

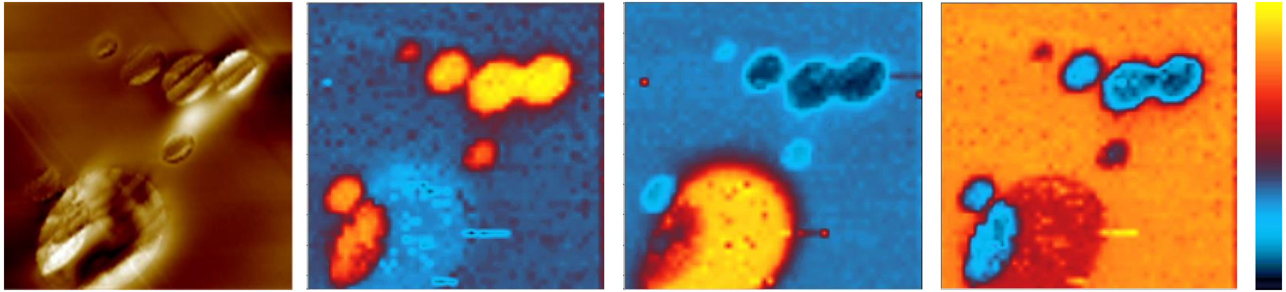


Center wavenumber 804

Move cursor onto above image and click on arrow to start animation

Hyperspectral array PCA weight maps

5-μm x 5-μm, 50 x 50 spectrum array on PS/PMMA/epoxy blend

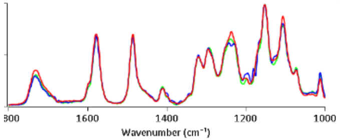

AFM image PS PMMA Epoxy

- New hyperspectral imaging provides point by point spectra over a large number of data points to provide an array of spectra and chemical images at specific wavenumbers
- Principle component analysis can be applied to identify specific chemical components and their spatial distribution

NEW nanoIR3 platform configurations

nanoIR3™ - Latest Generation nanoIR platform with Tapping AFM-IR

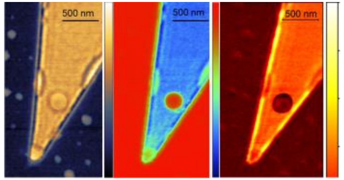
- Highest performance nanoIR spectra with AFM-IR
- Sub-10nm resolution IR chemical imaging with Tapping AFM-IR
- Correlates to FTIR & industry databases
- Easy to use for fast, productive measurements



nanoIR Spectroscopy of Polyethersulphone (PES)

nanoIR3-s™ High Performance IR nano-spectroscopy

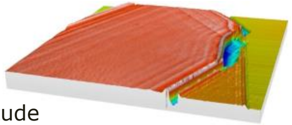
- Complementary s-SNOM & Tapping AFM-IR
- Highest Performance IR nano-spectroscopy
- Broadband Spectroscopy & Chemical Imaging
- Nanoscale property mapping
- *Versatility* & Easy to Use



Plasmonic Imaging on Graphene with Tapping AFM-IR & s-SNOM

nanoIR3-s™ **S-SNOM** - High Performance s-SNOM Imaging

- IR s-SNOM platform for optical & chemical Imaging
- Supports multiple laser types, visible, nearIR
- Electrical nanoscale property mapping
- Upgradeable to nanoIR-spectroscopy

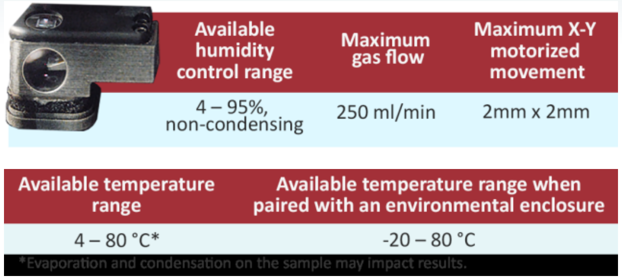


s-SNOM imaging
Phase and Amplitude
on HbN

Sample Environmental Control

Humidity control & heater & cooler

- For control of humidity/gas & temperature for in-situ AFM-IR
- 4% to 95% non condensing
- 4°C to 80°C heating and cooling



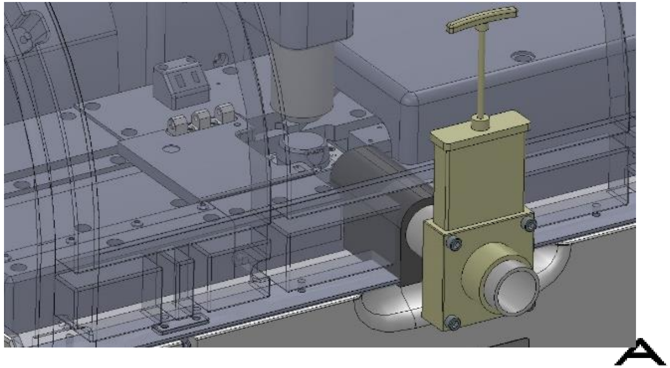
Available humidity control range	Maximum gas flow	Maximum X-Y motorized movement
4 – 95%, non-condensing	250 ml/min	2mm x 2mm

Available temperature range	Available temperature range when paired with an environmental enclosure
4 – 80 °C*	-20 – 80 °C

*Evaporation and condensation on the sample may impact results.

Sample transfer port for nanoIR3-s

- Protects sample in controlled gas environment from glove box to nanoIR system to protect
- includes integrated humidity sensor with optional high sensitivity humidity and oxygen sensors

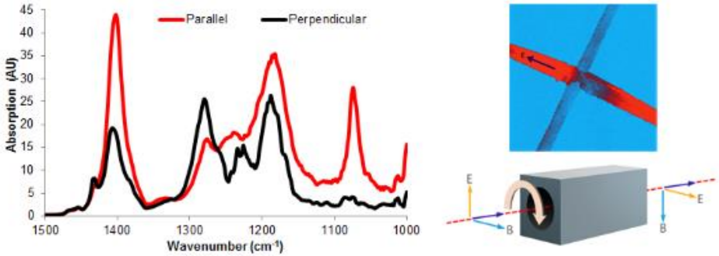


IR Polarization Control & extended IR range

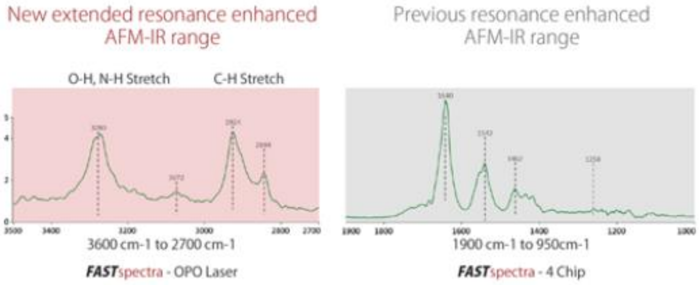
Polarization control

Allows users to study molecular orientation with nanoscale spatial resolution by changing the input polarization of the IR light while studying the associated changes in the nanoscale IR spectra and/or chemical maps at a certain wavenumber.

Polarizer Option
Optional & upgradeable



(L) AFM-IR spectra on electrospun PVDF fibers under two different IR polarizations (R) IR absorption image at 1404 cm-1 of crossed PVDF fibers under polarized illumination. (polarization direction shown by arrow)



Nylon 12 nanoIR spectrum measured with both the new FASTspectra OPO and FASTspectra QCL lasers. Important C-H stretch, N-H stretch and OH regions are now enabled with rich interpretable data

FASTspectra™ OPO mid-IR laser

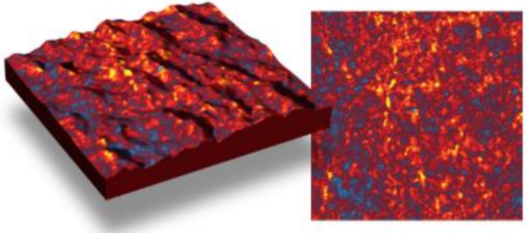
The new high pulse rate OPO laser extends the wavelength range of Resonance Enhanced AFM-IR to cover the 2700 to 3600cm^{-1} wavenumbers, extending capability to important spectroscopic regions and addressing wider range of applications, while still providing direct correlation to FTIR at the nanoscale.

nanoIR nanoscale property mapping modes

Conducting AFM (CAFM):

(Application Module)

Allows the user to obtain simultaneous height and current flow maps of the sample surface. Available on all Anasys systems.

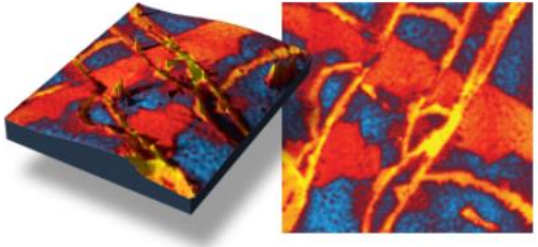


Height (Left) and Conductivity (Right) images of a nanocomposite polymer.

Kelvin Probe Force Microscopy (KPFM)

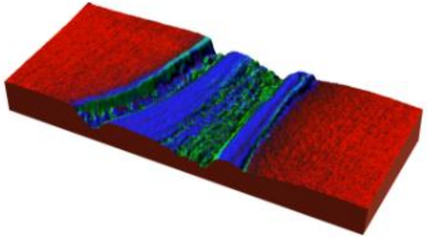
(Application Module)

Allows the user to obtain surface potential measurements. Available on all Anasys systems.



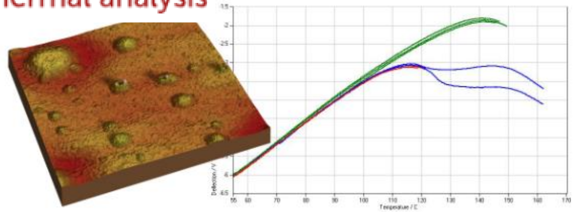
Height (Left) and Surface Potential (Right) images of a nanocomposite polymer.

Lorentz Contact Resonance mode



LCR composite image made by overlying the LCR amplitudes collected at three different contact resonances. These resonances were selected to highlight the varying ratios of the lignin and cellulose which compose the sample.

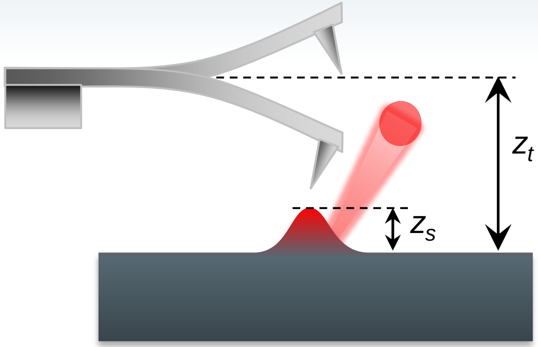
Nano thermal analysis



Nanoscale thermal analysis of a PS-PMMA blend deposited on glass. A scan (left) shows indents in the surface caused by temperature ramps (right). The data from the PS (red) and PMMA (green) clearly differentiate the two materials. Also shown is data from a thin film of PS on PMMA (blue) showing the initial penetration of the PS followed by the melting of the PMMA.

Tapping AFM-IR: Technical Overview

Concept



Z_t : Distance of the Tip
Z_s : Sample expansion (photothermal)
k/γ : Linear/non-linear force constant
a_s: Absorption coefficient
a_t: Tip oscillation amplitude
ω_p: Laser pulse rate
ω_n: cantilever eigen mode frequency (n=1,2,3…)

$$F = k \cdot (z_t - z_s) + \boxed{\gamma \cdot (z_t - z_s)^2}$$

$$z_s = a_s(\lambda)\cos(\omega_p t)$$

$$z_t = a_t\cos(\omega_n t)$$

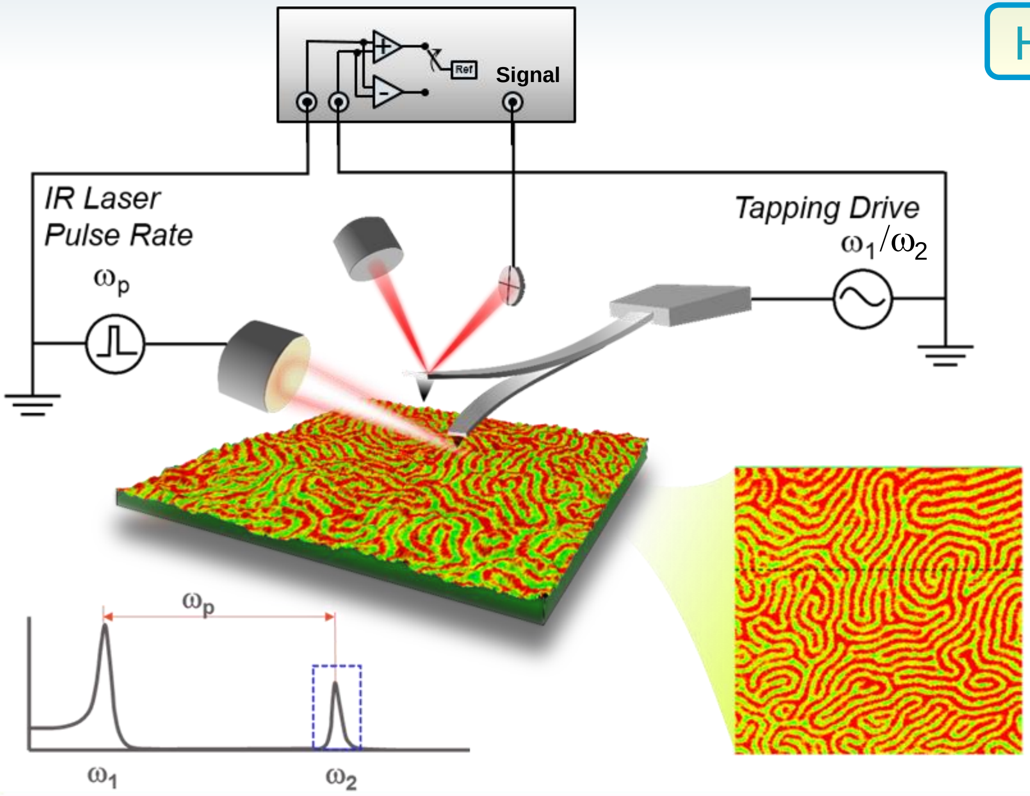
$$F \sim 2\gamma a_t a_s(\lambda)\cos(\omega_n t)\cos(\omega_p t)$$

$$F \sim \gamma a_t a_s(\lambda)\left[\underbrace{\cos(\omega_n + \omega_p)t}_{\text{Sum frequency}} + \underbrace{\cos(|\omega_n - \omega_p|)t}_{\text{Diff. frequency}}\right]$$

Resonance Condition: $\overset{\text{Fundamental mode}}{\omega_1} + \overset{\text{Pulse rate}}{\omega_p} = \overset{\text{2nd Eigen mode}}{\omega_2}$

Tapping AFM-IR: Technical Overview

Schematic

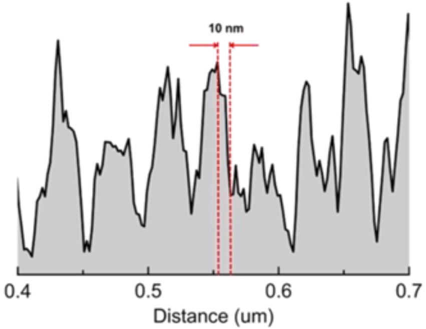


Heterodyne Force Microscopy

M.T. Cuberes, J. Nanomater., 2009

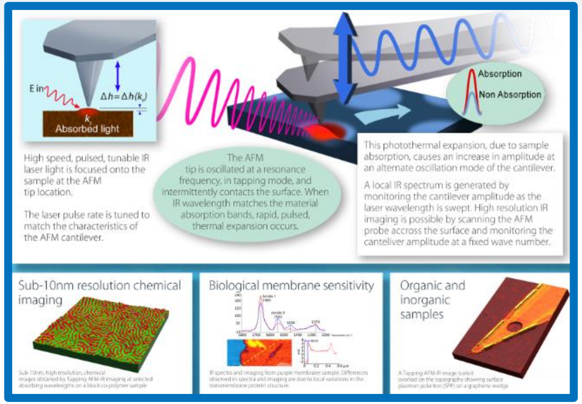
Resonance Condition:

$$\omega_1 + \omega_p = \omega_2$$



Tapping AFM-IR: Key features

- **Broad Application range:**
  - Hard/soft sample, Adhesives, Membranes, Particulates
  - Minimal sample/tip degradation due to absence of lateral forces
- **Improved Sensitivity:**
  - Sensitivity enhanced by cantilever Q-factor – new probes
  - AFM detector with higher sensitivity
  - Efficient optical beam delivery optics with minimal loss
- **High Spatial Resolution:**
  - Spatial resolution extends to ~10 nm or better
- **Multimodal Imaging:**
  - Simultaneous chemical and viscoelastic property (Tapping Phase) imaging



High speed, pulsed, tunable IR laser light is focused onto the sample at the AFM tip location.

The laser pulse rate is tuned to match the characteristics of the AFM cantilever.

The AFM tip is oscillated at a resonance frequency, in tapping mode, and intermittently contacts the surface. When IR wavelength matches the material absorption bands, rapid, pulsed, thermal expansion occurs.

This photothermal expansion, due to sample absorption, causes an increase in amplitude at an alternate oscillation mode of the cantilever.

A local IR spectrum is generated by monitoring the cantilever amplitude as the laser wavelength is swept. High resolution IR imaging is possible by scanning the AFM probe accross the surface and monitoring the canteliver amplitude at a fixed wave number.

Sub-10nm resolution chemical imaging

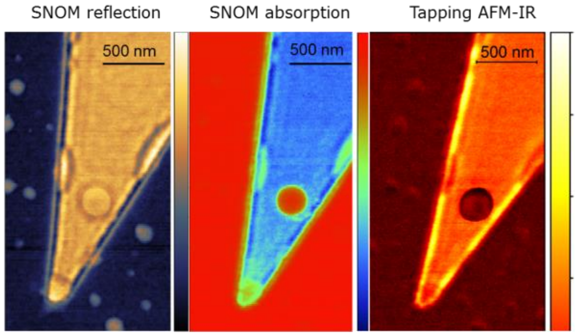
Sub-10nm, high resolution, chemical images obtained by Tapping AFM-IR imaging at selected absorbing wavelengths on a block co-polymer sample

Biological membrane sensitivity

IR spectra and imaging from purple membrane sample. Differences observed in spectra and imaging are due to local variations in the transmembrane protein structure.

Organic and inorganic samples

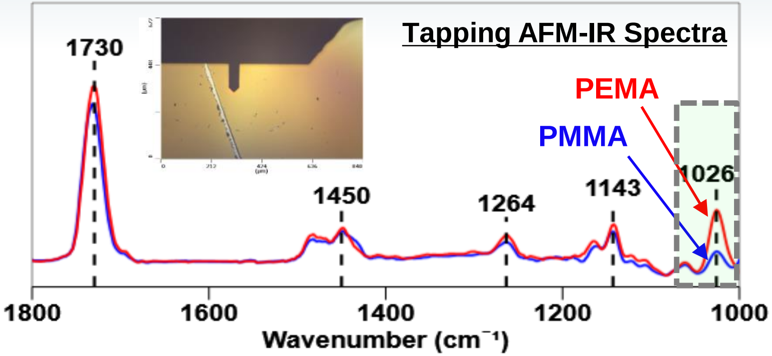
A Tapping AFM-IR image (color) overlaid on the topography showing surface plasmon polariton (SPP) on a graphene wedge

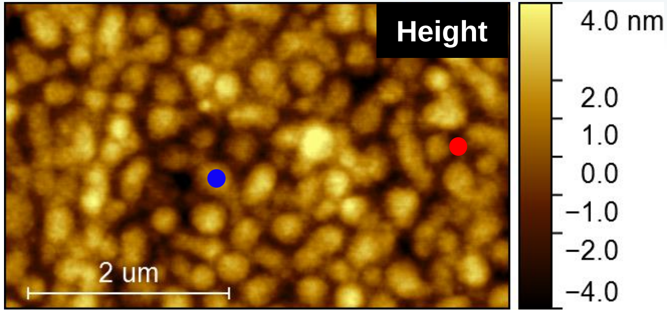


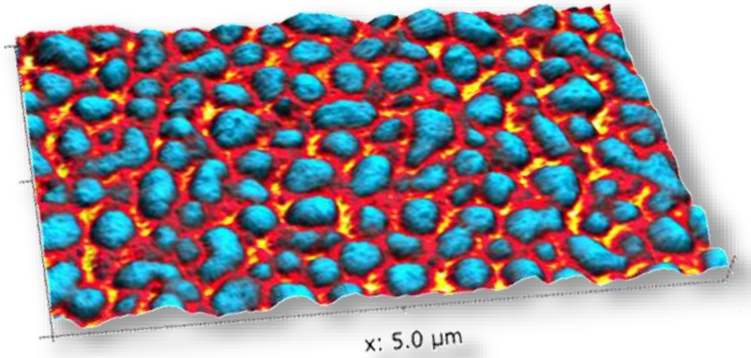
Measurement of graphene wedge on silicon with s-SNOM and Tapping AFM-IR show plasmonic effects at the edge

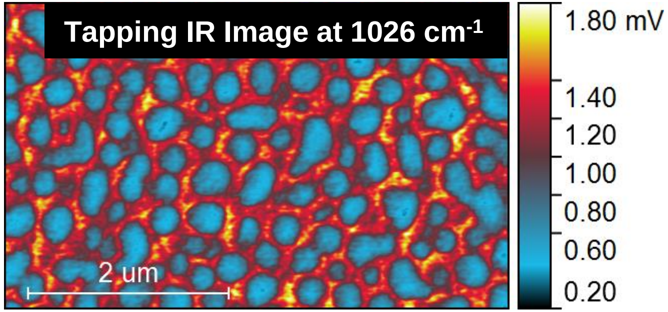
Tapping AFM-IR: Applications

Polymer 01: PEMA/PMMA Blend





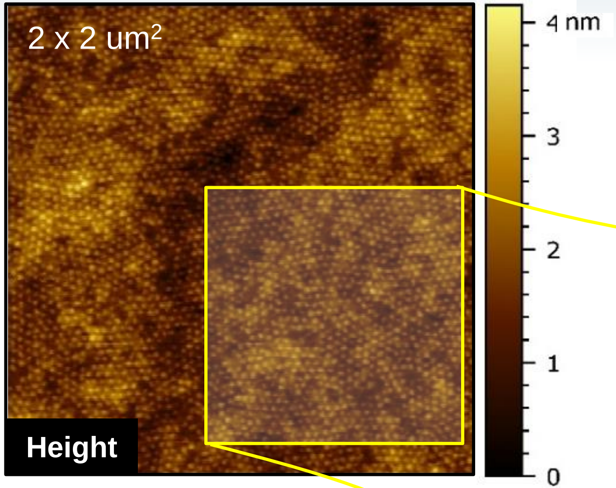




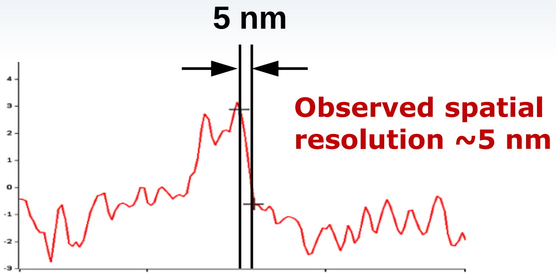
Sample courtesy: University of Minnesota

Tapping AFM-IR: Applications

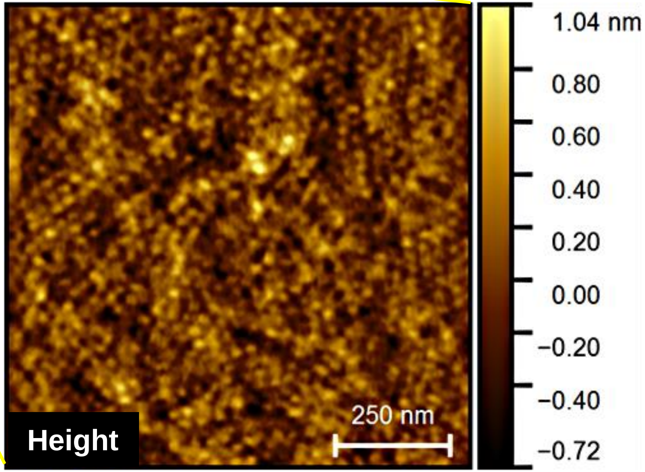
Polymer 02: PS/PMMA block copolymer

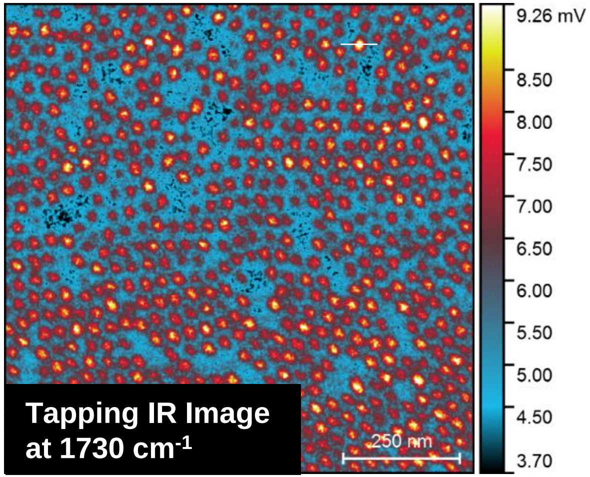


Tapping AFM-IR image at 1730 cm^{-1} highlights PMMA spheres embedded in PS matrix



Observed spatial resolution ~5 nm

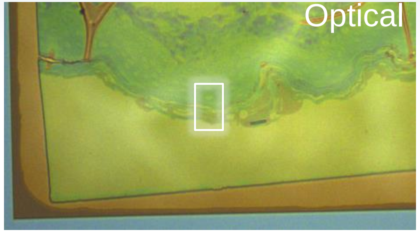


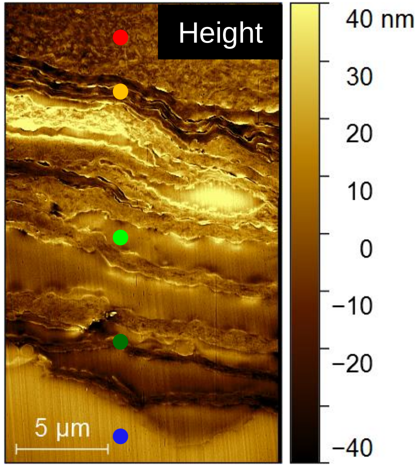


Sample courtesy: CEA-Leti

Tapping AFM-IR: Applications

Bio-pharmaceuticals 01: Skin/Dexamethasone



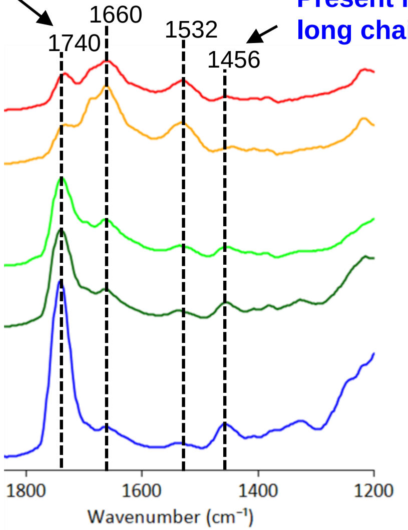


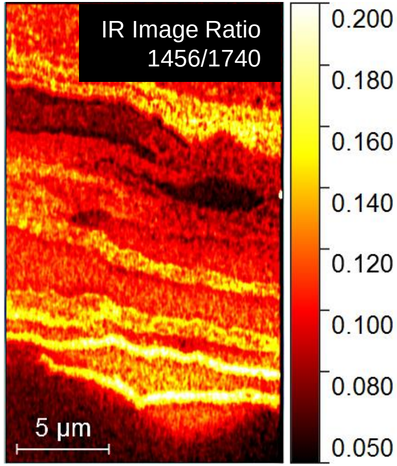
- Tapping AFM-IR image ratio at 1456/1740 cm^{-1} highlights the relative abundance of the drug in the lipophilic regions (bright yellow)

Ester C=O in the lipids

Amide I & II bands from Proteins

$-CH_2$ bending Present in both drug and long chain lipids

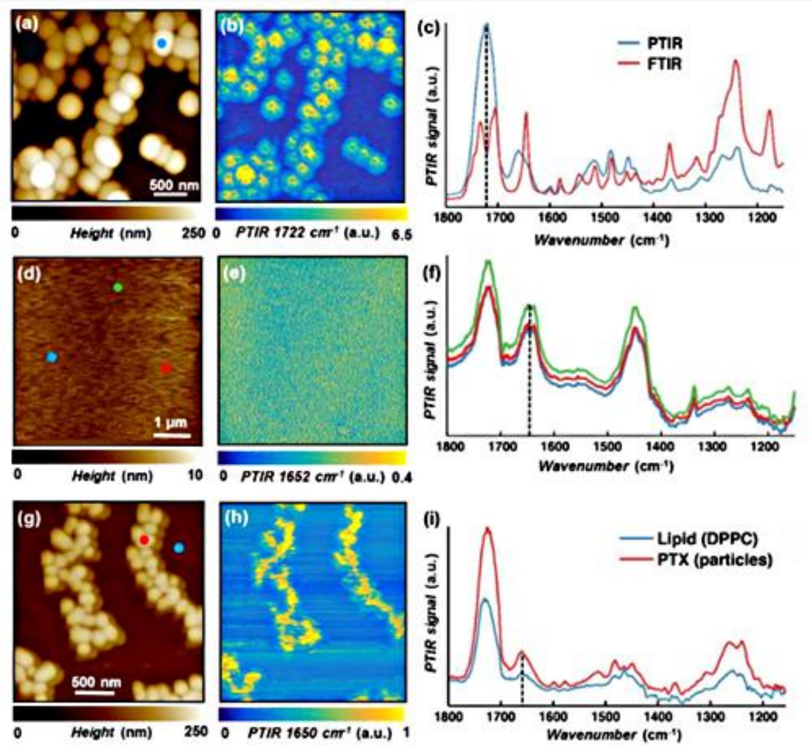




Sample courtesy: FU Berlin

Tapping AFM-IR: Applications

Bio-pharmaceuticals 02: Anti-cancer drug delivery



- Paclitaxel, a power anti-cancer drug, suffers from low efficacy and side effects due to low water solubility/recrystallization

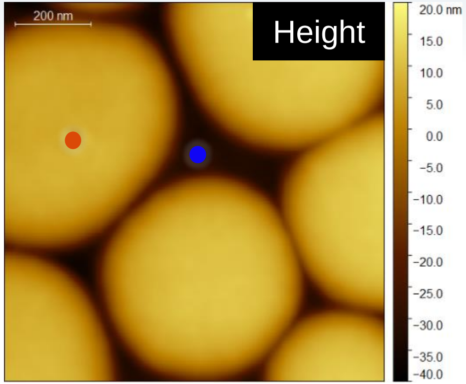
- Recent study by Centrone and coworkers highlights the use of Tapping AFM-IR technology to explore the effect of different encapsulations in drug delivery

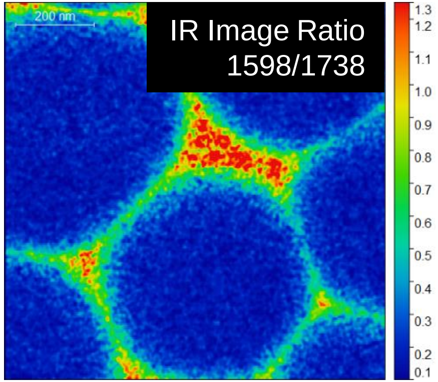
- High resolution compositional sensitivity of this technique unfolds new developments of lipid-polymer hybrid films in drug delivery applications

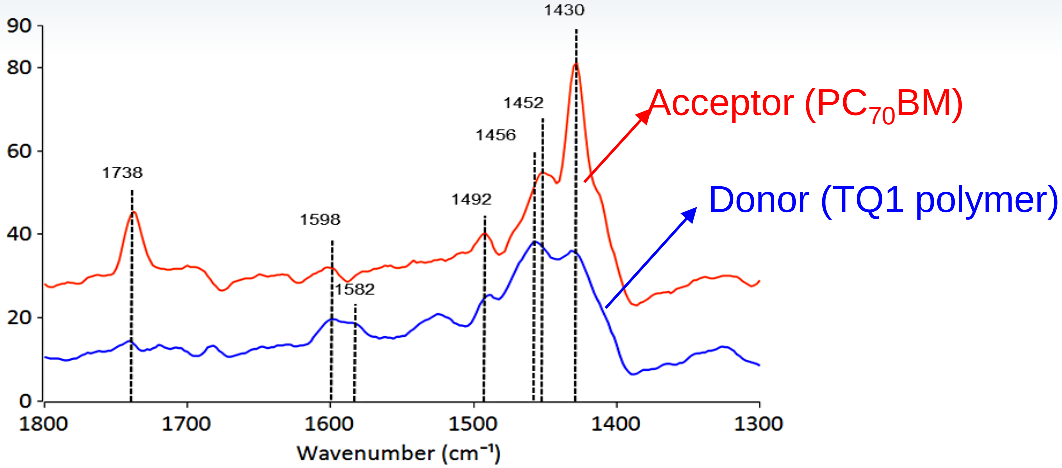
Centrone et al., ***Analyst,*** *2018,* ***143,*** *3808-3813*

Tapping AFM-IR: Applications

Organic Photovoltaics: TQ1/PC$_{70}$BM Blend







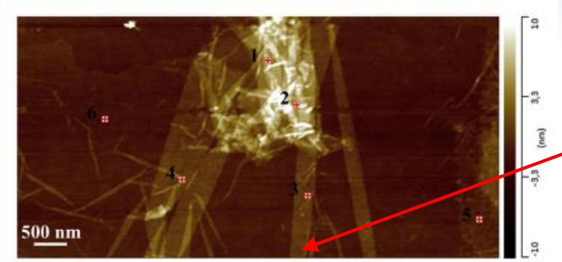
- Tapping AFM-IR spectra and images highlights the polymer rich matrix and PC$_{70}$BM rich domains

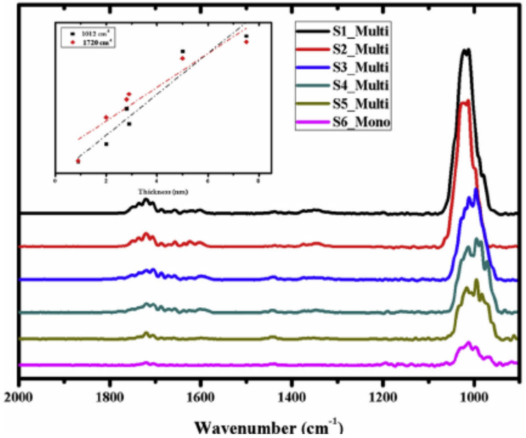
Sample courtesy: Karlstad University

Tapping AFM-IR: Applications

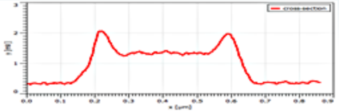
2D Materials: Graphene/Graphene Oxide

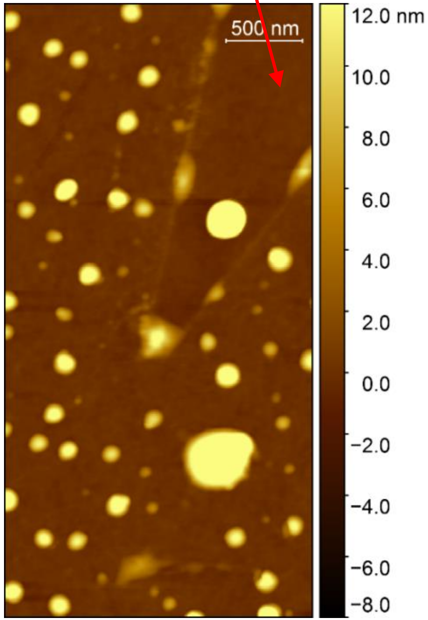
- Tapping AFM-IR spectra and images show sensitivity to monolayer Graphene and Graphene Oxide

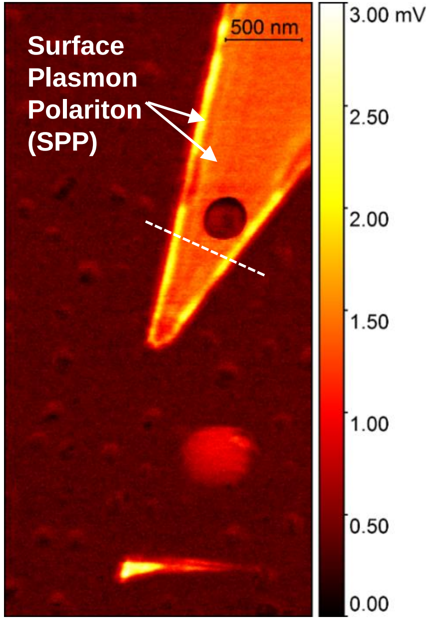




Liu et al., ***Carbon***, 2018, **127**, 141-148





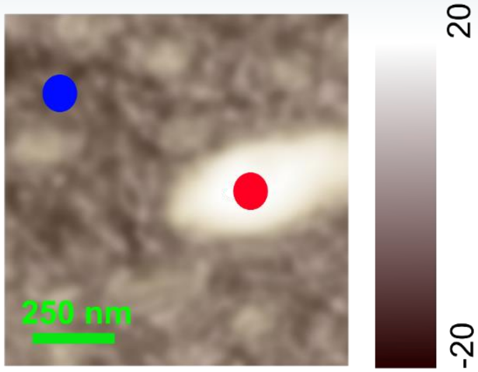


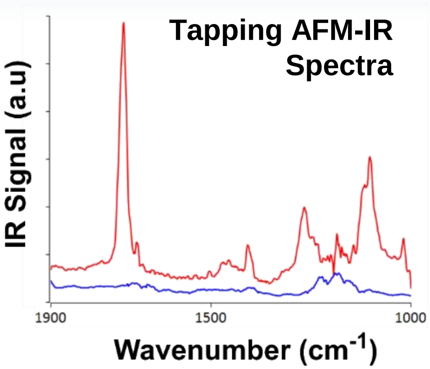
Surface Plasmon Polariton (SPP)

Manuscript in prep

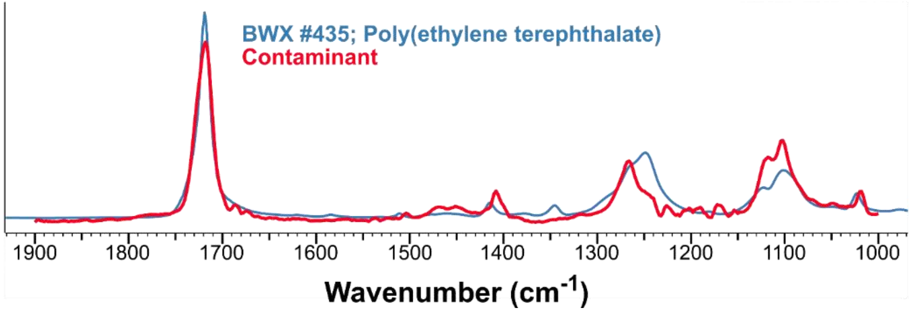
Tapping AFM-IR: Applications

Failure Analysis: Organic Nanocontaminations





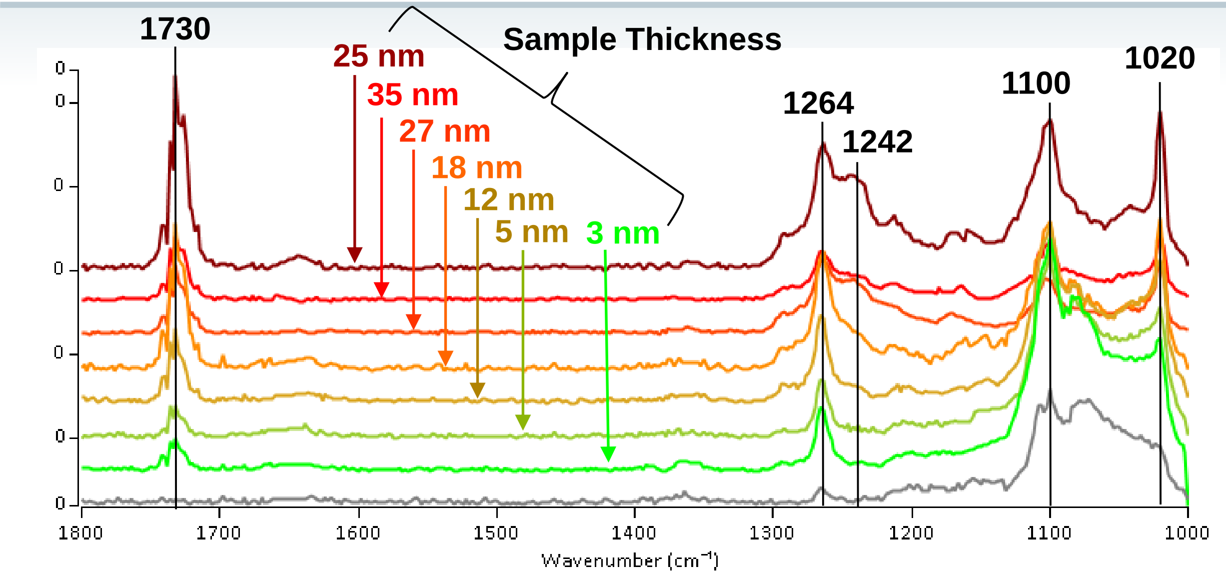
FTIR Library Search

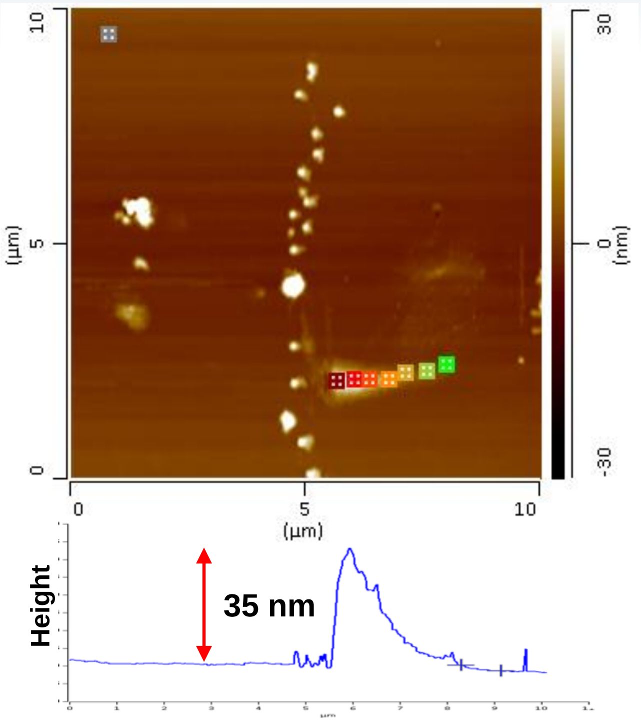


> ***"…Knowing why devices fail is a must when designing next-generation products.."***
>
> ***V. Lakshminarayanan***
> ***www.rfdesign.com, 2011***

- AFM-IR technology complements traditional analytical tools used for failure analysis in nanoscale semiconductor devices/architectures
- Enhanced sensitivity extends to samples with thickness <20 nm
- Tapping AFM-IR technology demonstrates positive identification of nanoscale organic contaminants on Silicon wafer

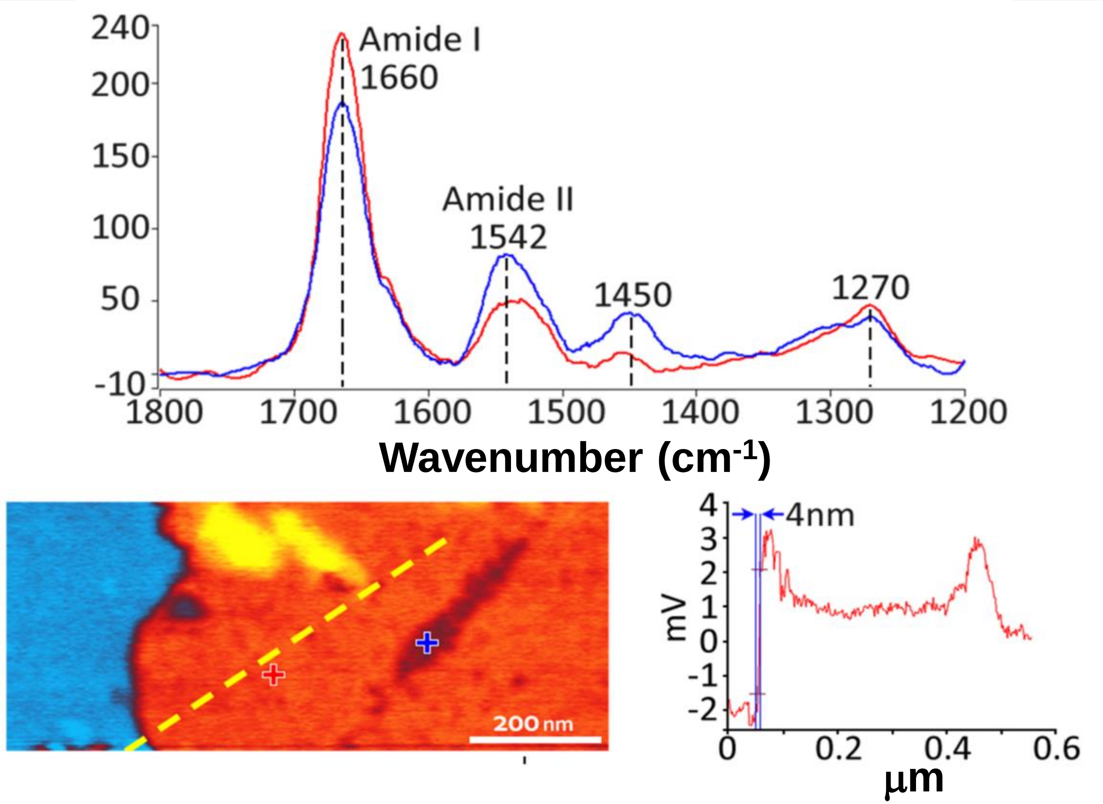
Tapping AFM-IR Measurements on nanocontaminant sample



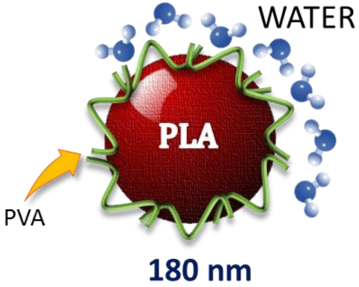


- Each spectrum is an average of 5 measurements, **NOT** smoothed
- Tapping AFM-IR spectra show absorption bands consistent with earlier measurements performed onsite – contamination is most likely synthetic polyester (PET/PBT)
- IR signal **sensitivity goes down to 3 nm thick residue** (bright green)

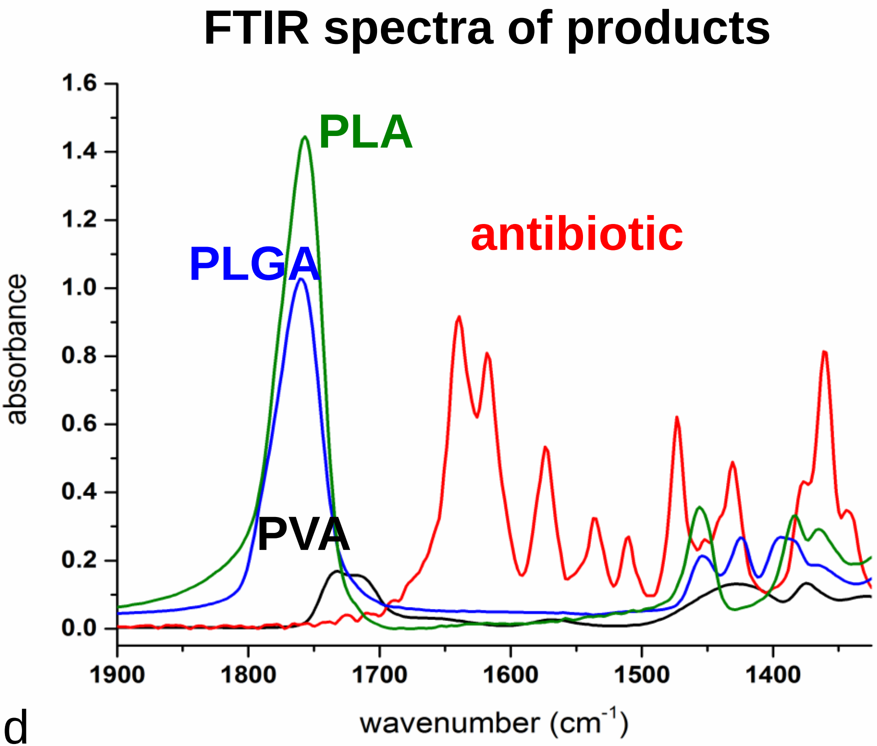
Tapping AFM-IR of a Biological Membrane



Polymeric Nanoparticles for drug delivery



Antibiotic = pipemidic acid

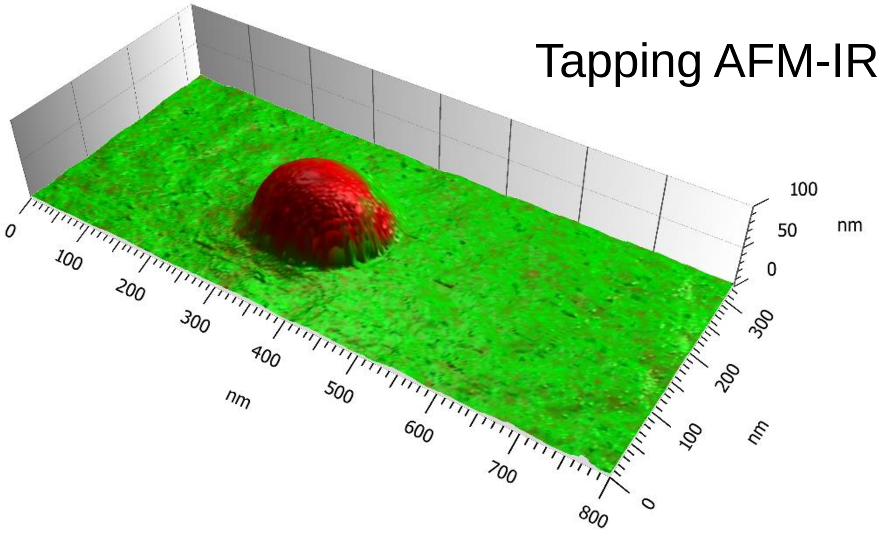


Polymeric Nanoparticles for drug delivery

PLA/PVA nanoparticle

Mapping at 1760 cm^{-1} center on ester carbonyl band of PLA

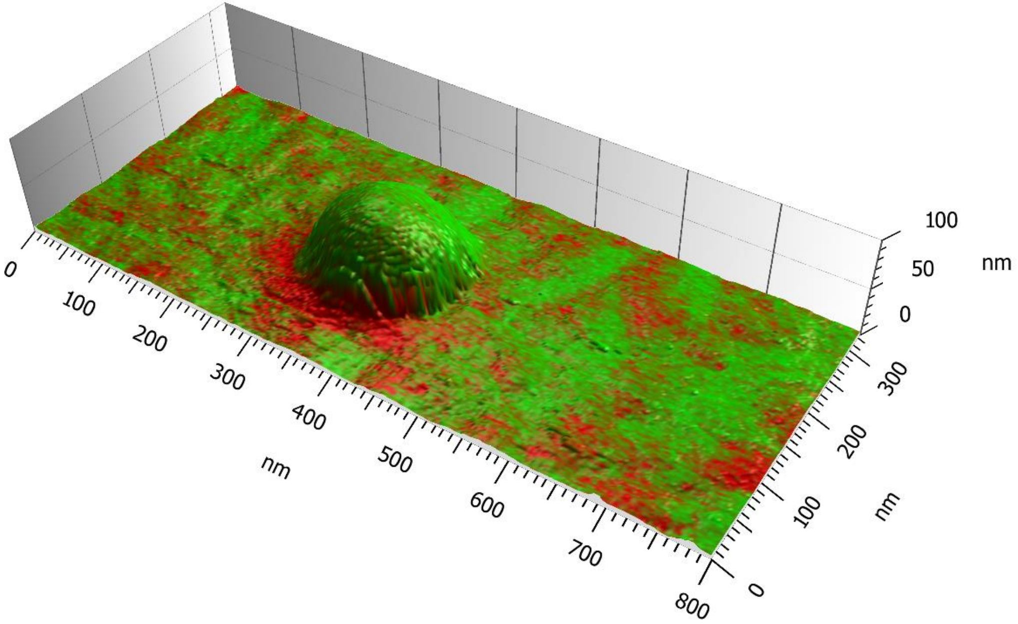
Tapping AFM-IR ode



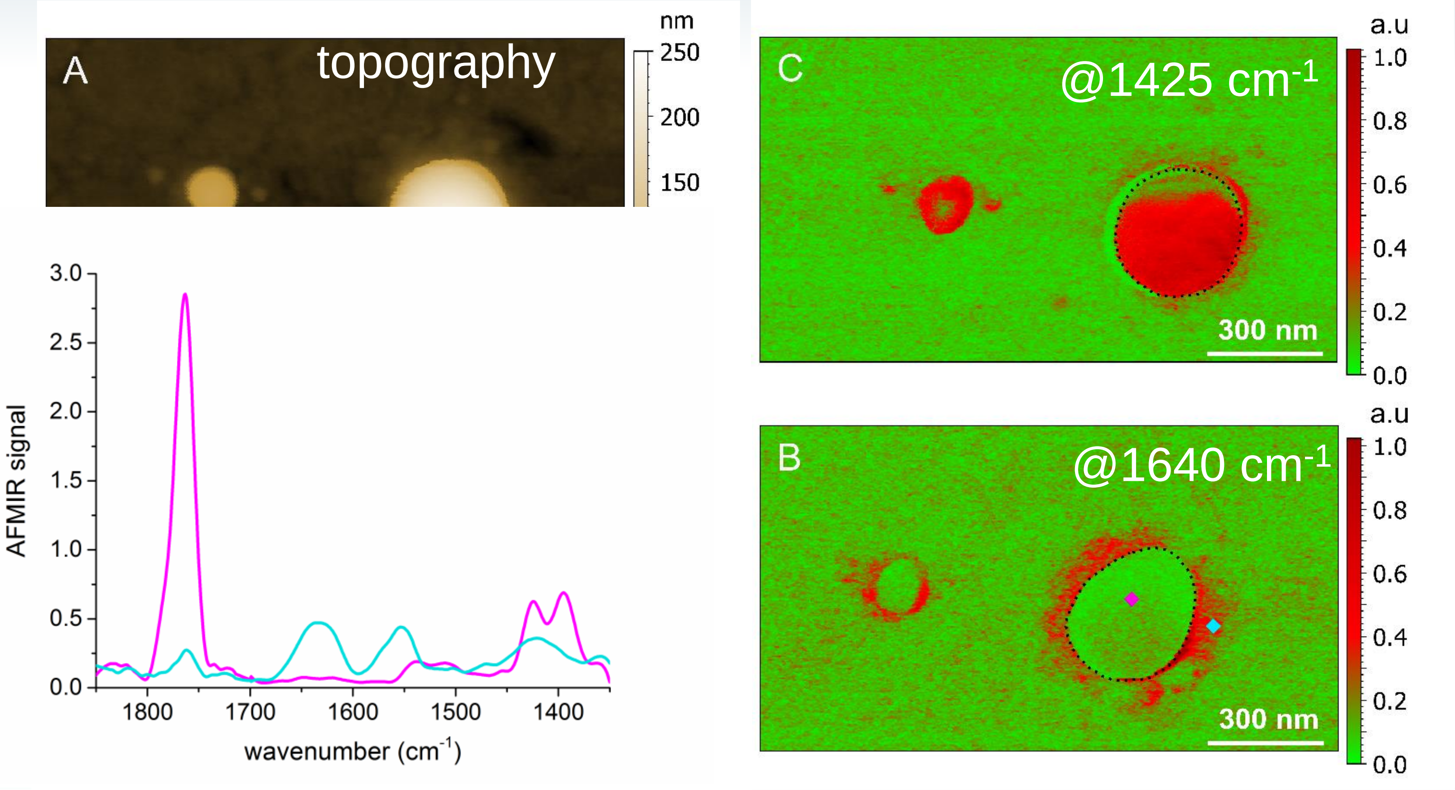
Polymeric Nanoparticles for drug delivery

PLA/PVA nanoparticle

Mapping at 1425 cm^{-1} center on absorption band of PVA



PLGA/PVA nanoparticles with antibiotic

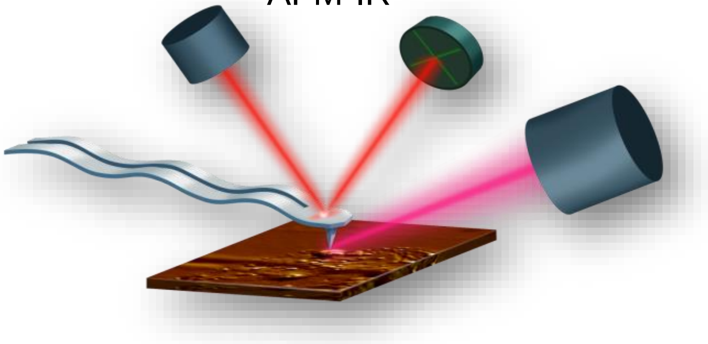


Benefits of Tapping AFM-IR approach

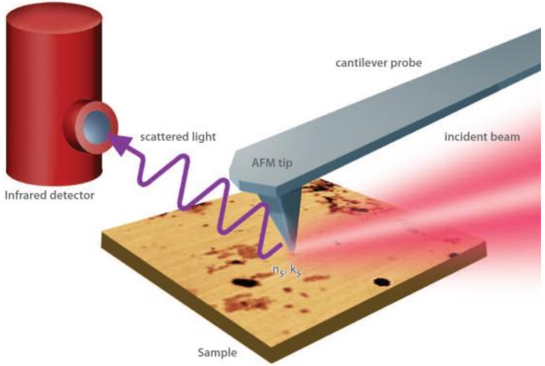
- **Better spatial resolution/softer samples via tapping AFM**
- **Improved chemical imaging via heterodyne detection**
  - **Insensitive to non-local background forces**
- **Material selectivity via resonance tuning**

Complementary: AFM-IR and s-SNOM
scattering scanning nearfield optical microscopy

AFM-IR



s-SNOM

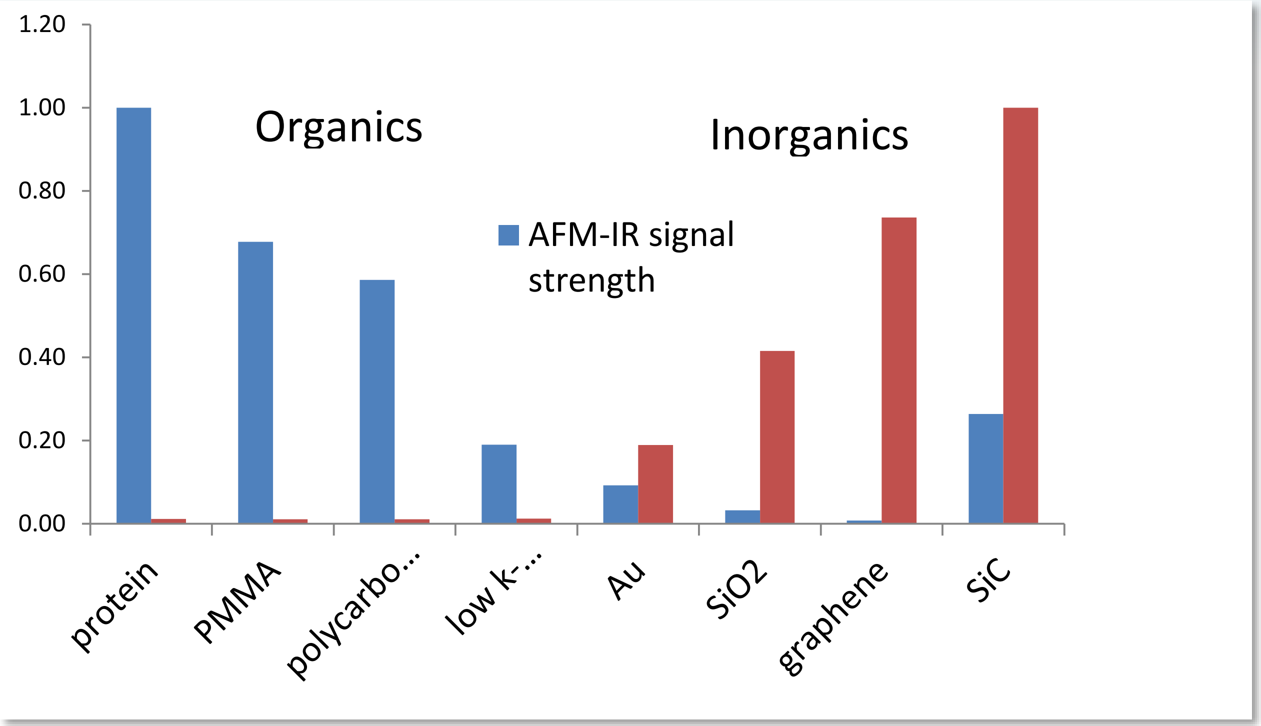


Thermal expansion proportional to absorption and thermal expansion coefficients

Scattered light depends on complex optical constants

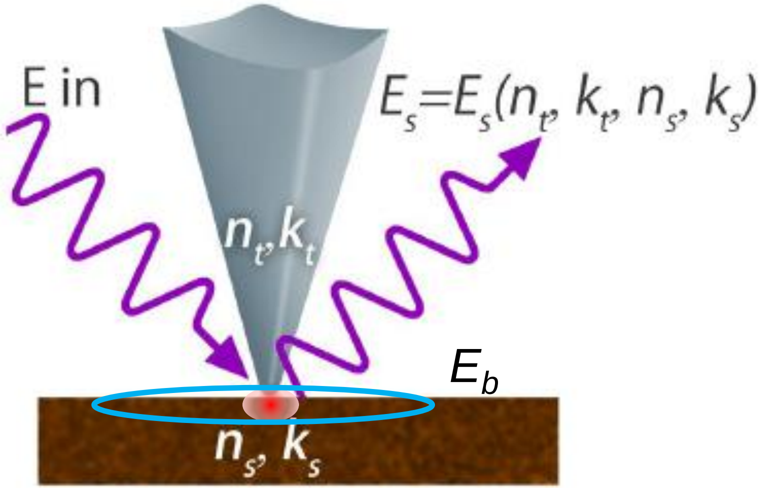
ANASYS INSTRUMENTS
The nanoscale spectroscopy company

Sensitivity of AFM-IR and s-SNOM



s-SNOM: complex optical property

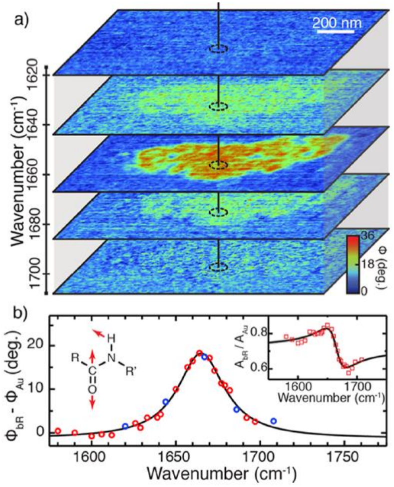
Metal coated tip acts like an antenna to enhance and localize the light.



Spatial resolution: tip radius 10~20 nm

Previous: Spatio-spectral Imaging & Broadband Spectroscopy

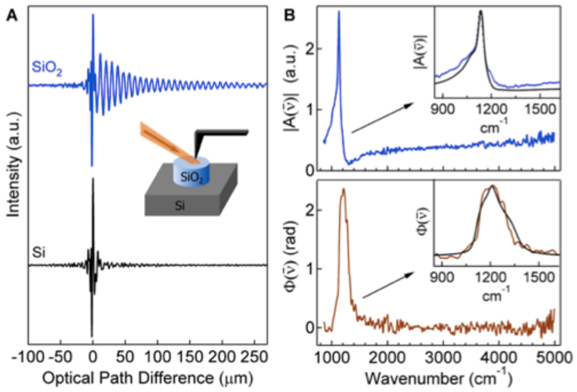
Spatio-spectral Imaging



J. Am. Chem. Soc., 2013, *135,* 18292

Disadvantages: slow, limited spectral resolution

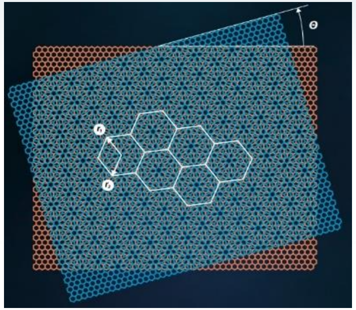
Broadband Spectroscopy

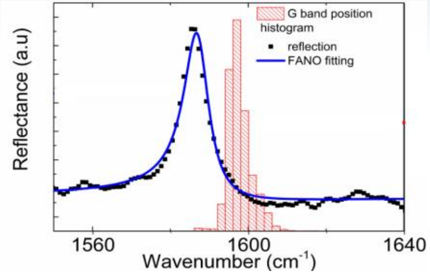


Proc. Natl. Acad. Sci. 111, 7191 (2014)

Disadvantages: can't do narrowband imaging (e.g. for compositional mapping)

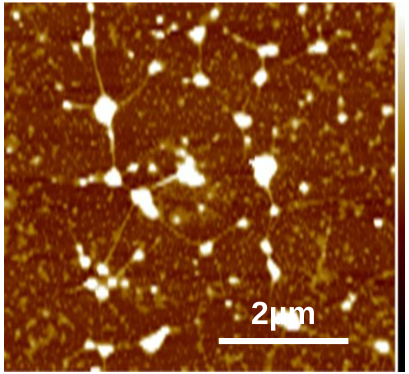
Application: Fano-resonance Bilayer Graphene



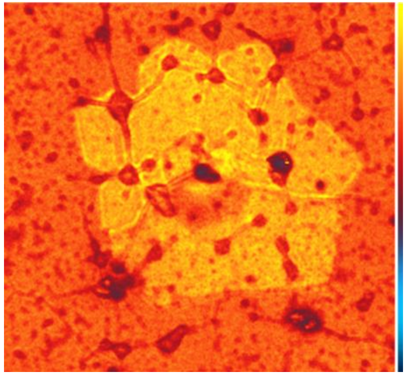


Graphene 2, 38727 (2013)

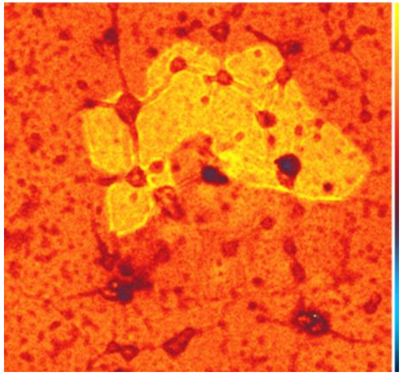
AFM height



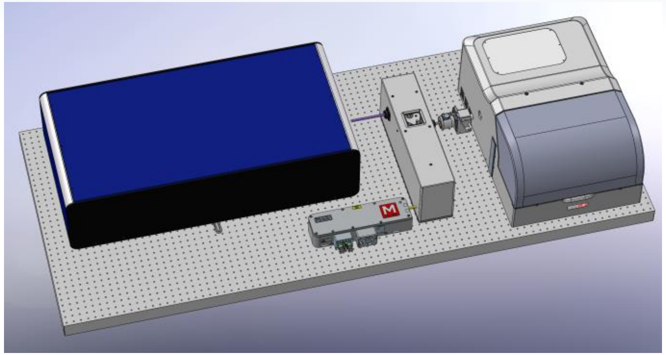
sSNOM 1580cm^{-1}

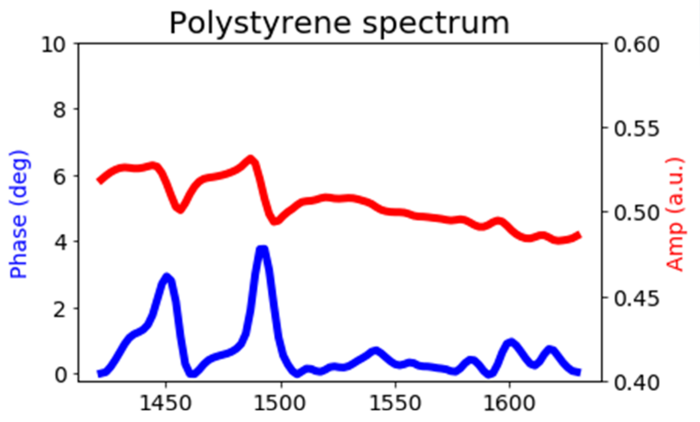


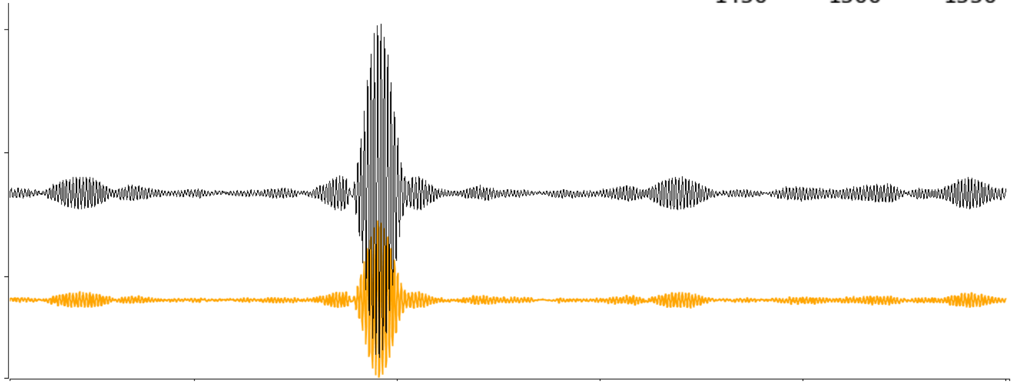
sSNOM 1600cm^{-1}



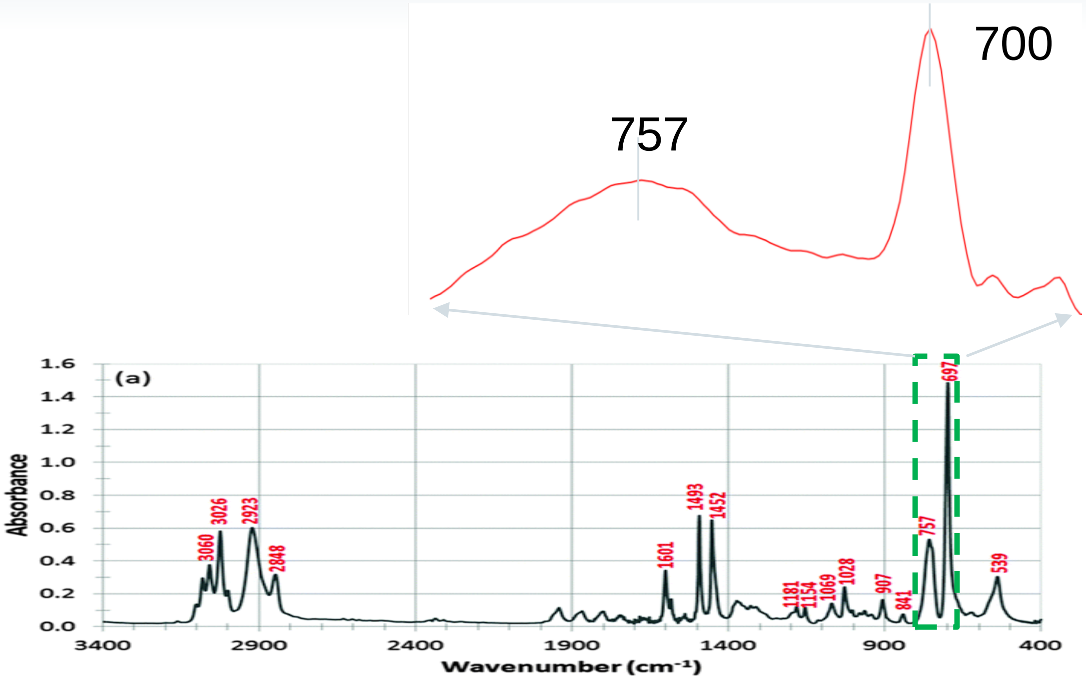
s-SNOM with a broadband laser source




Polystyrene spectrum



s-SNOM spectrum of polystyrene below 800 cm^{-1}

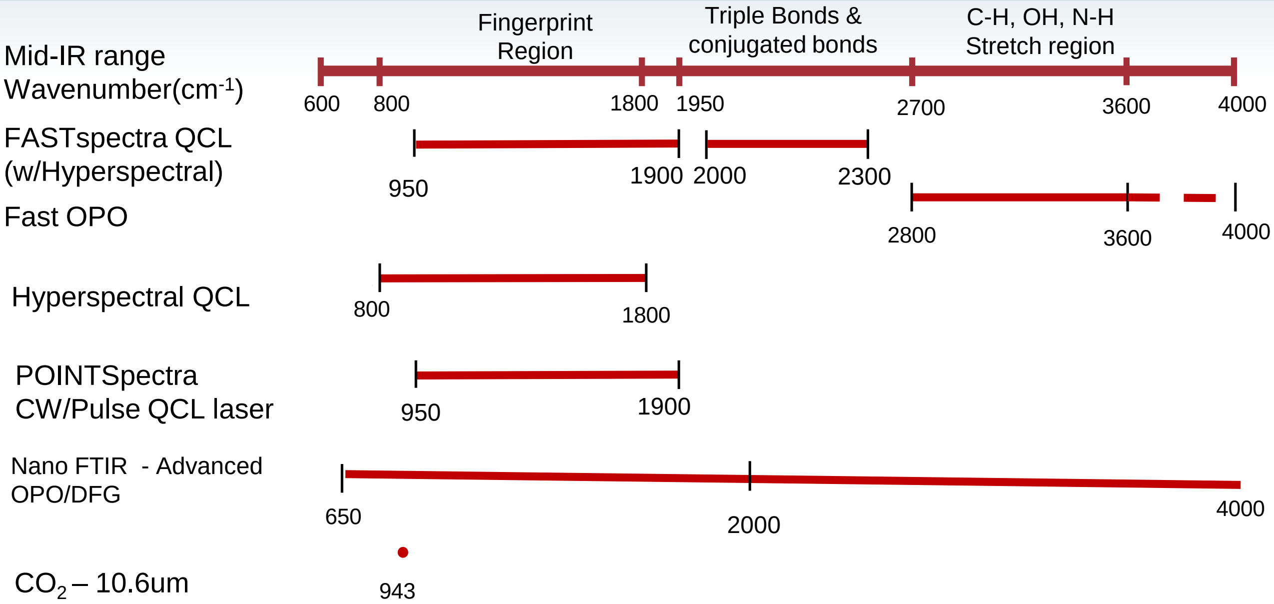


SNOM
phase spectrum

15 µm

FTIR
spectrum

nanoIR Laser Options



- AFM-IR lasers (Pulsed tunable OPO & QCL) can provide both spectroscopy & wavelength specific imaging
- Only CW/P QCL (tunable) lasers provide spectroscopy & wavelength specific imaging for s-SNOM
- nanoFTIR lasers only provide spectroscopy & imaging capabilities (AFM-IR&s-SNOM)

Additional Applications – from 2017-2018 publications

- Life Science
  - Recent paper in Cell – Simone Ruggeri, Tuomas Knowles (Cambridge)
  - AFM-IR in Fluid – Andrea Centrone (NIST)
  - Malaria Infected Red Blood Cells – Bayden Wood (Monash)
  - *In vivo* AFM-IR of Bacteria – Bayden Wood (Monash)
- Materials Science
  - Deuterium-labeled polyolefin copolymer blend - Dow
  - Core/Shell effect in electrospun PHB copolymer fibers – Delaware
  - Functionalized graphene - Manchester
  - h-BN – Photothermal AFM-IR of 2D Materials - Harvard
  - Geoscience - Schlumberger & USGS

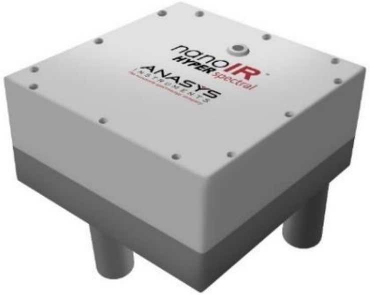
Additional Applications (continued)

- Atmospheric Aerosols – Mark Banaszak Holl (Michigan/Monash)
- Polarized AFM-IR – Karsten Hinrichs (ISAS)

Summary

Recent Technological Advancements in nanoscale IR Technology offers

- Unmatched sensitivity for nanoIR spectroscopy & chemical imaging
- <10nm resolution chemical imaging
- Point spectroscopy in 1-2 secs
- HYPERspectral imaging/Spectroscopy for robust statistical analysis
- Easy to use, high performance AFM imaging with improved noise and sensitivity



www.bruker.com