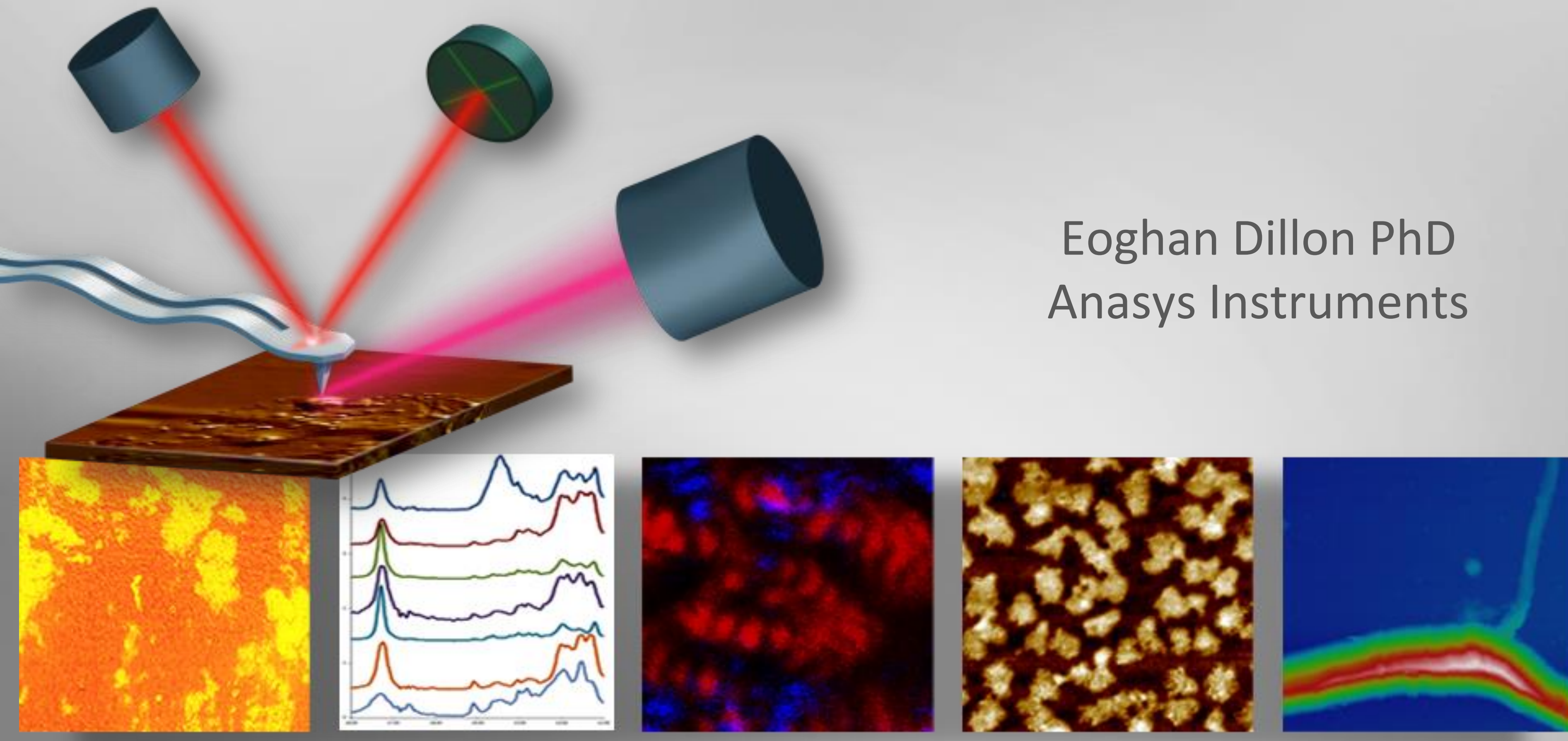
# AFM-based IR spectroscopy—nanoscale chemical analysis with monolayer sensitivity

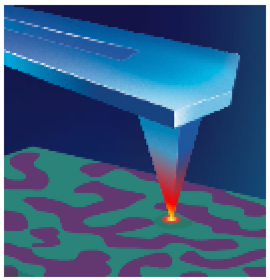



Eoghan Dillon PhD
Anasys Instruments

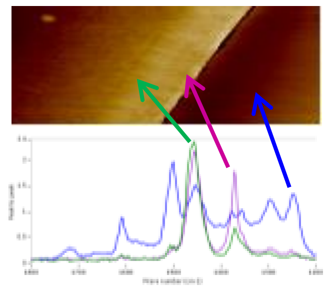
# About Anasys Instruments

## Pioneering nanoscale materials characterization

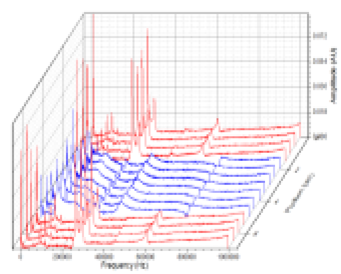
### AFM + Thermal Analysis

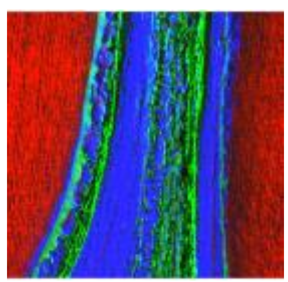


### AFM + IR Spectroscopy

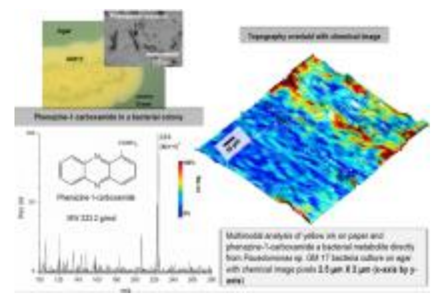


### AFM + Mechanical Spectroscopy

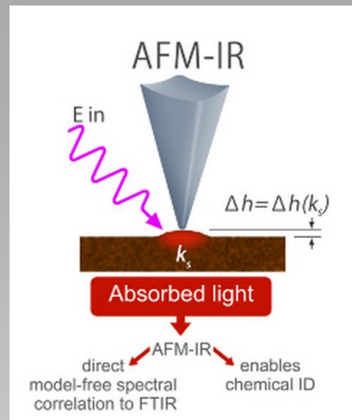


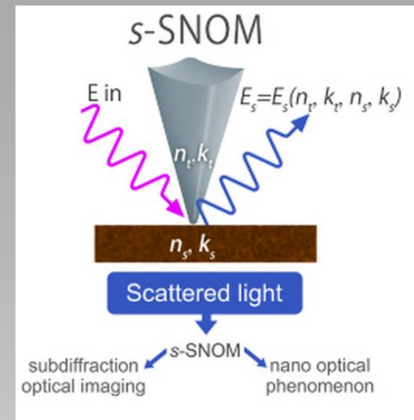


### AFM + Mass Spectrometry



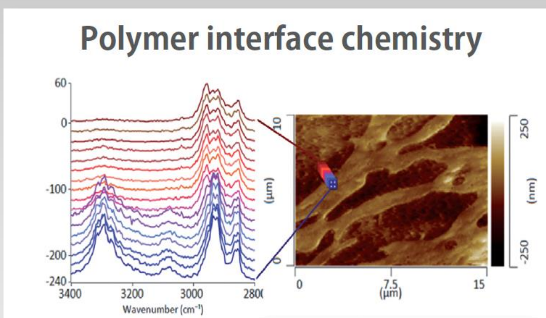
# nanoIR2-s: One platform, two complementary techniques

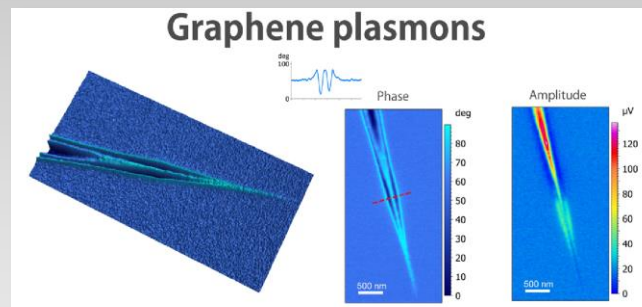



Analogous to Transmission FTIR

Analogous to ellipsometry




Direct IR absorption spectroscopy & chemical imaging

Highly interpretable spectra

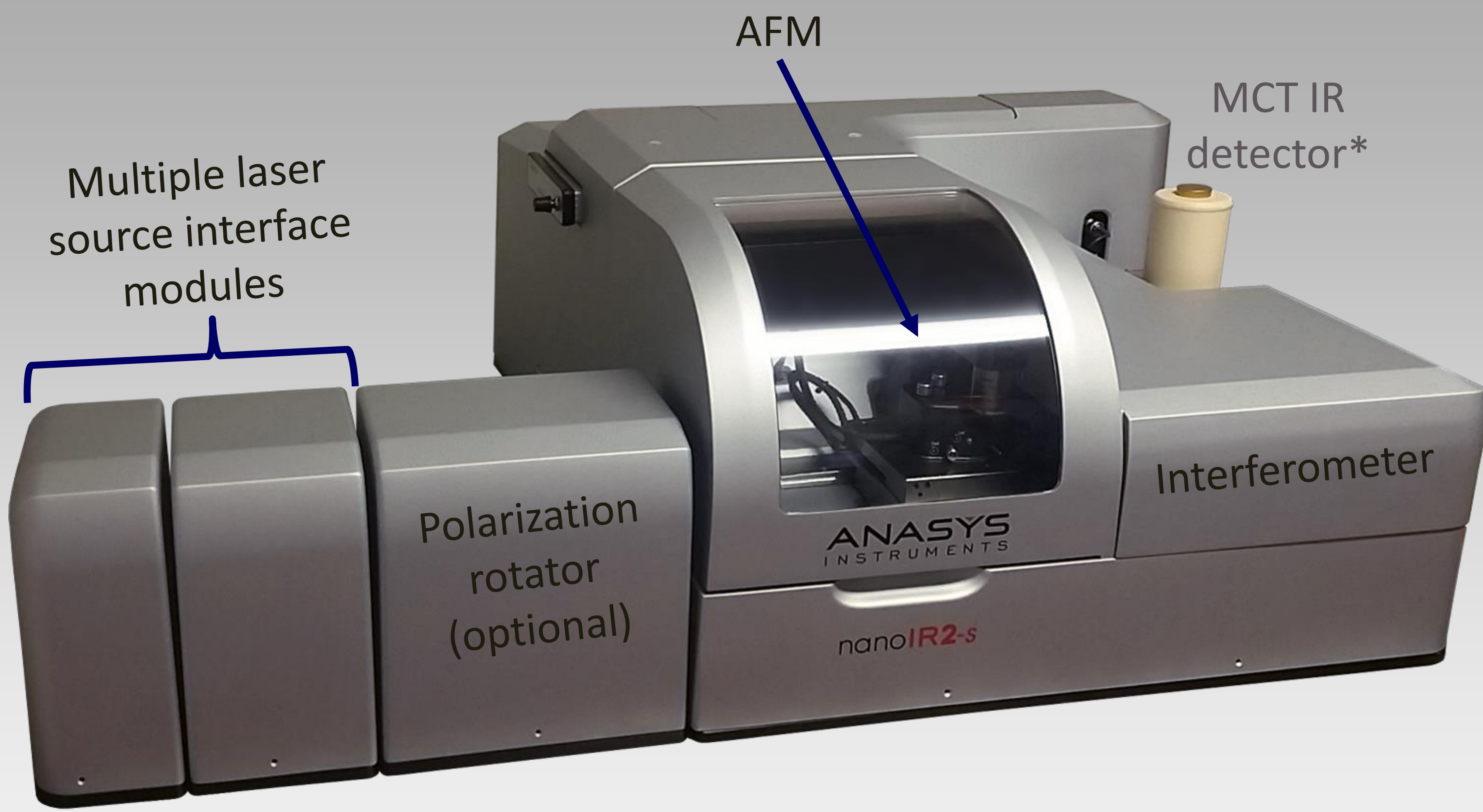
Excels for polymers, life sciences

Sub-20 nm optical microscopy

Mapping of complex optical properties

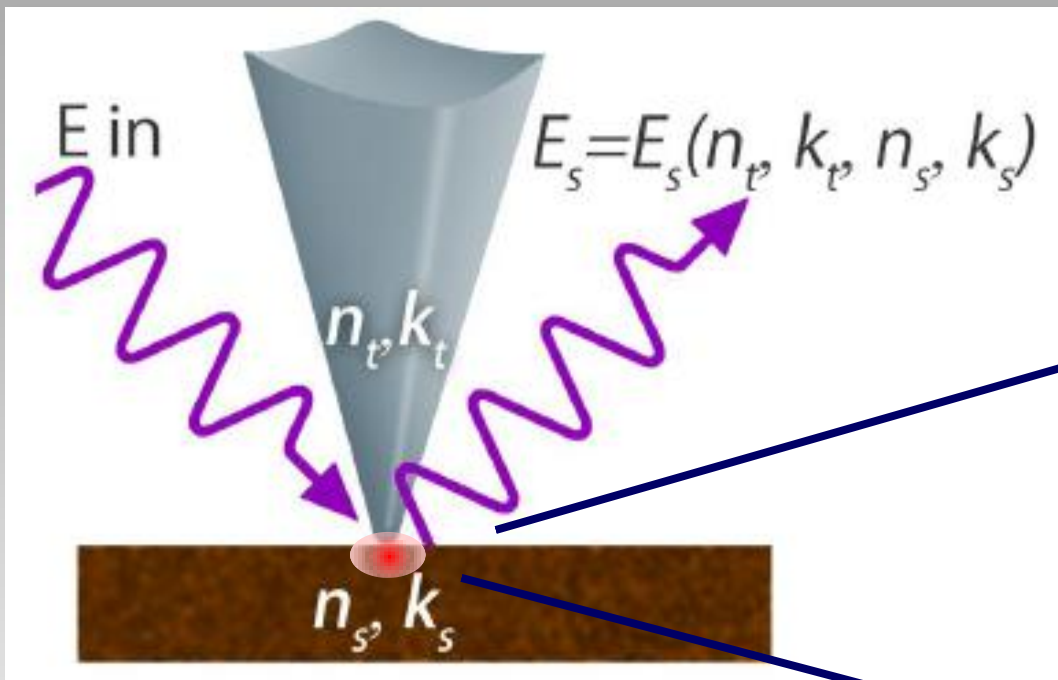
Excels for inorganics, 2D materials, photonics

# nanoIR2-s key elements

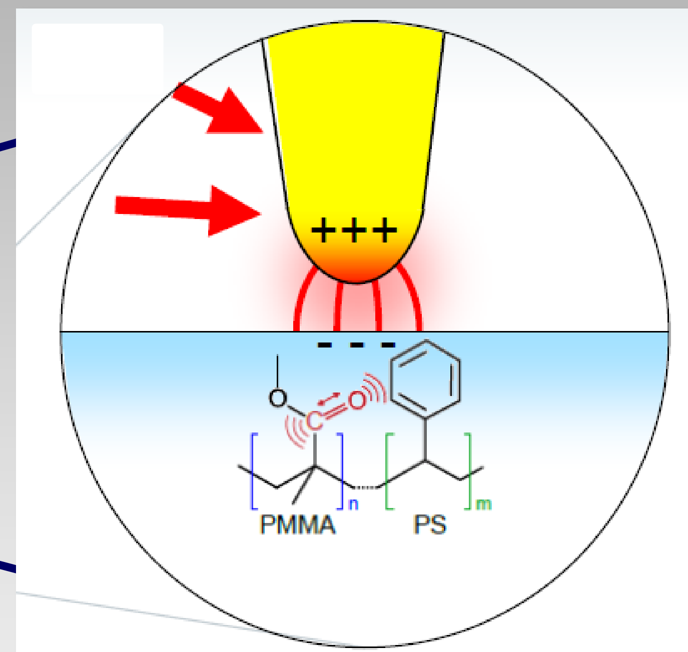



*easily exchangeable for other wavelengths

# s-SNOM principle




Tip localizes the field



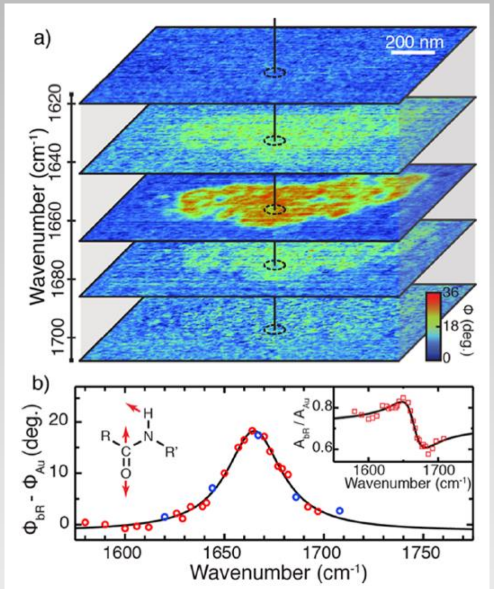

Spatial resolution set by tip radius

Best ~10 nm, typical 20-30 nm

# Previous: Spatio-spectral imaging & broadband spectroscopy

1) Accumulate many images at different wavelengths

2) Construct spectra from image stack

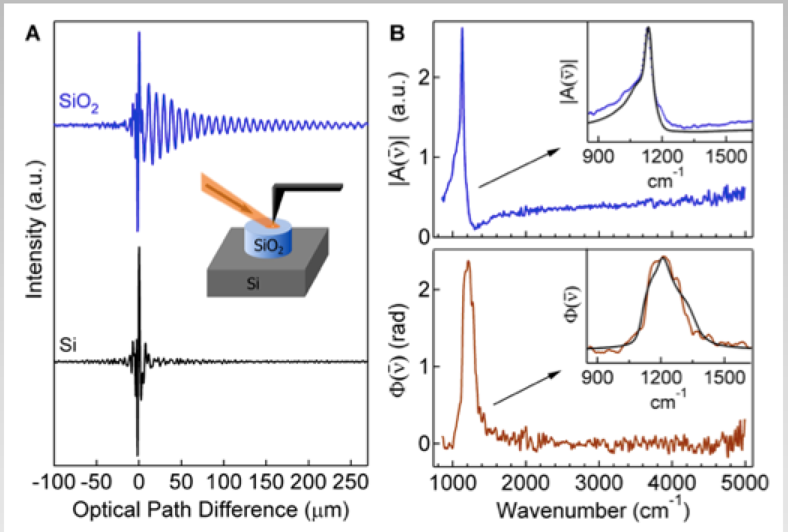



*J. Am. Chem. Soc.*, **2013**, *135*, 18292

Disadvantages: slow, limited spectral resolution

1) Use broadband light source with long travel interferometer

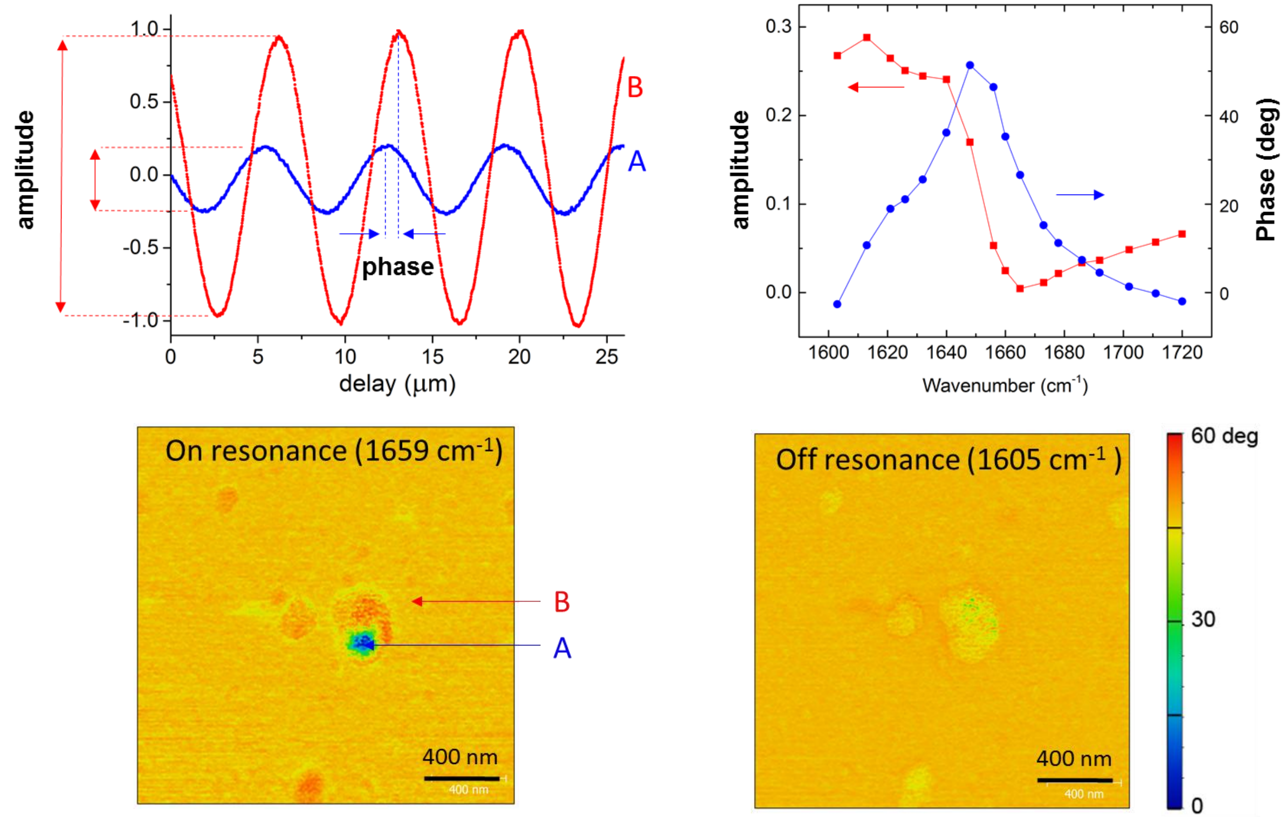
2) Construct spectra from FFT of interferogram




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

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

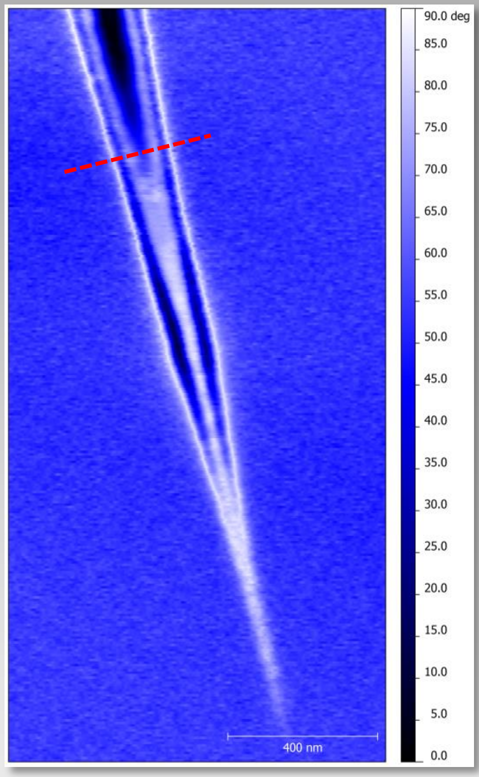
# New from Anasys:
# Point spectroscopy with s-SNOM

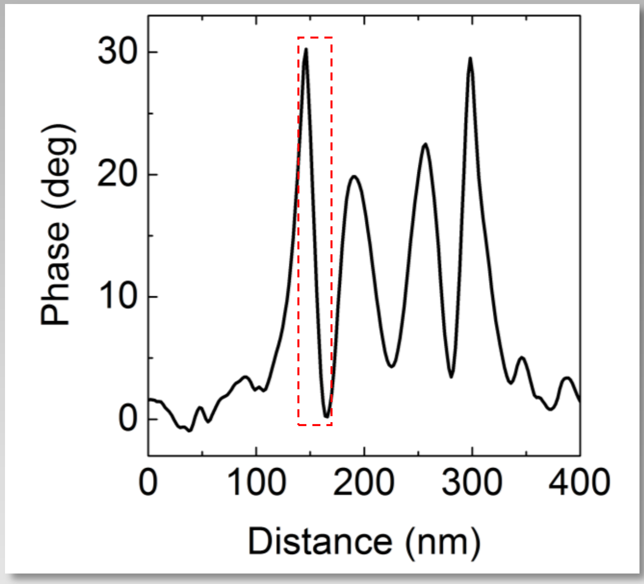


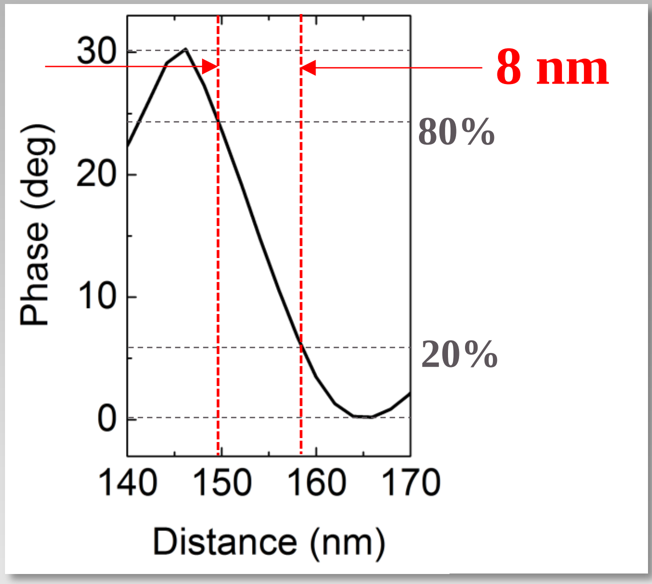

**Benefits:**

- Spectra can be created quickly at <u>any</u> point
- Same laser source can be used for <u>both spectroscopy and imaging</u>.

# 8 nm spatial resolution achieved

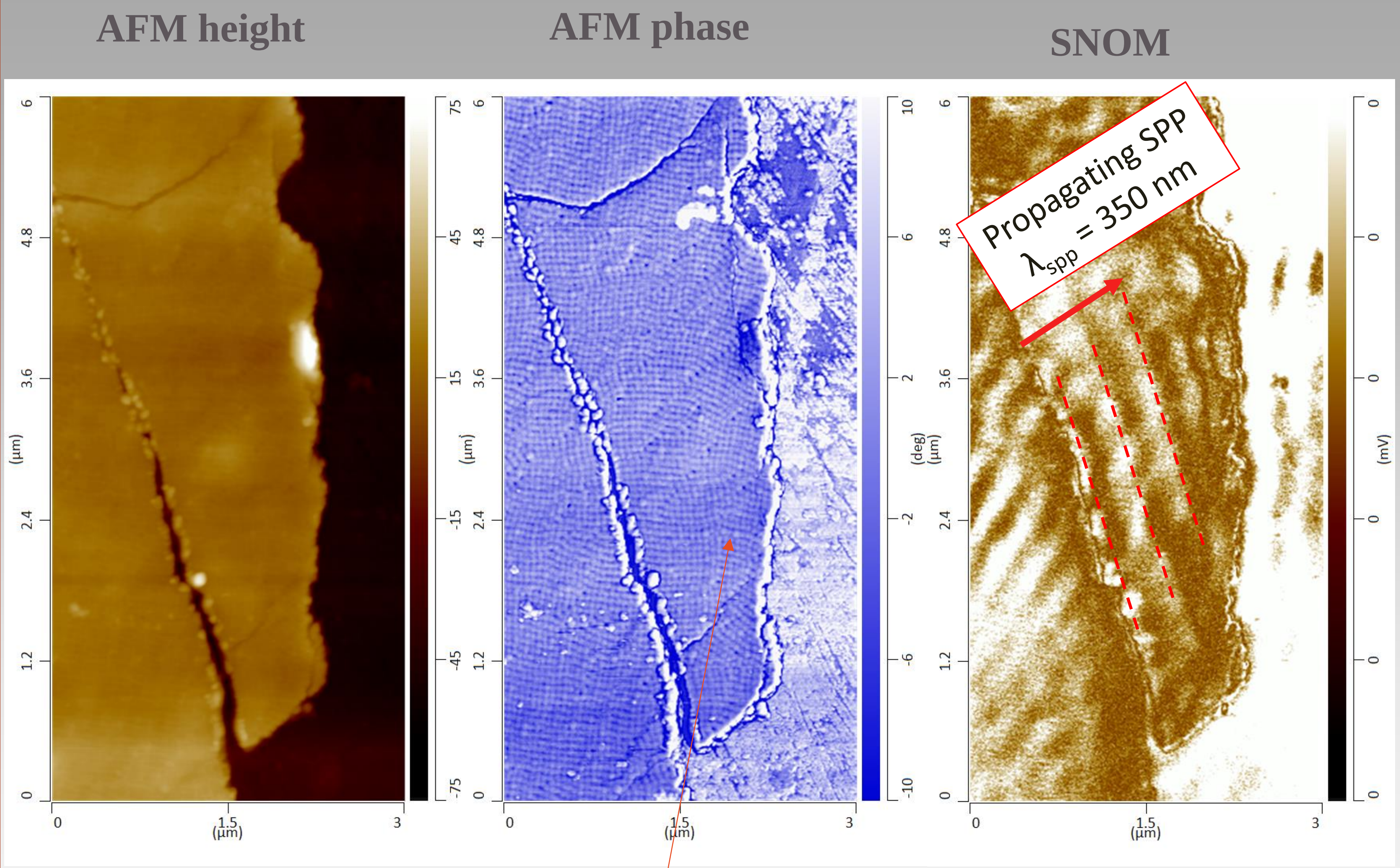



~λ/1300 spatial resolution

# Surface plasmon polaritons, visible illumination

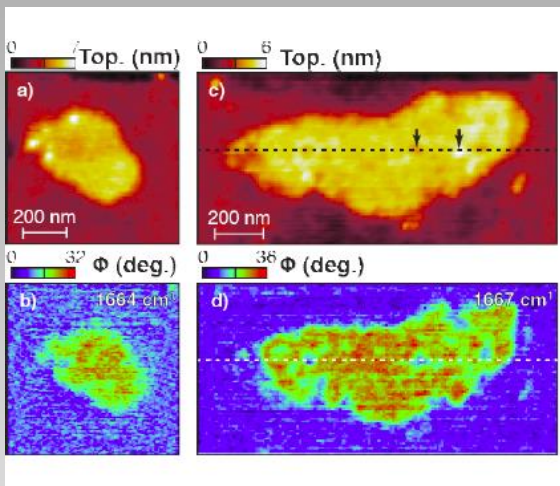



Note Au rhombic dodecahedral lattices

# Biological membrane: purple membrane

## nanoIR2-s measurement

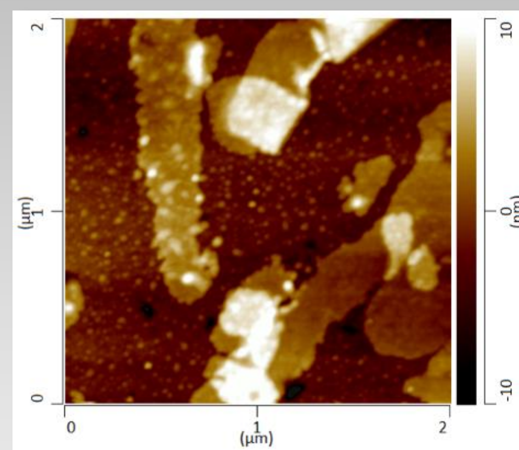
### Example from literature



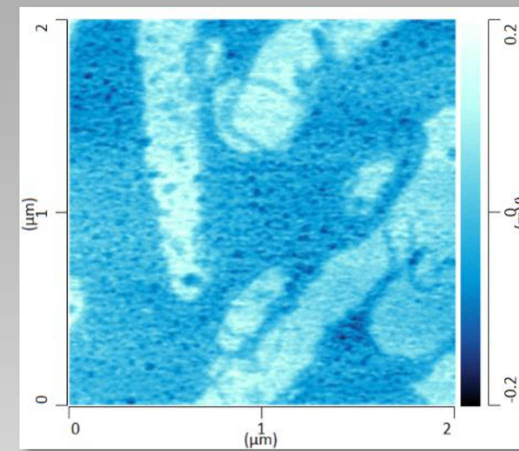

Berweger et al (2013) JACS 135 (49), 18292-18295.

500nm

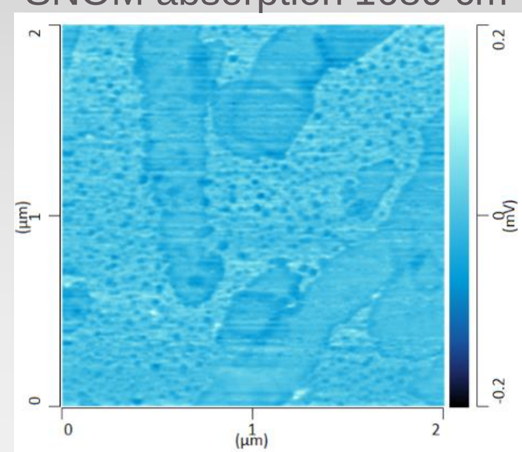
AFM height




SNOM absorption 1660 cm$^{-1}$

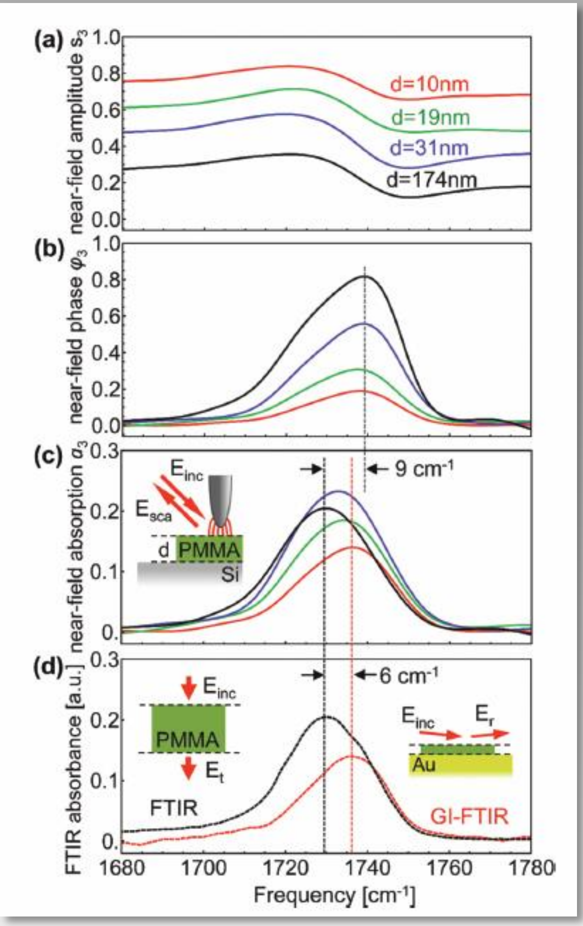



SNOM absorption 1689 cm$^{-1}$



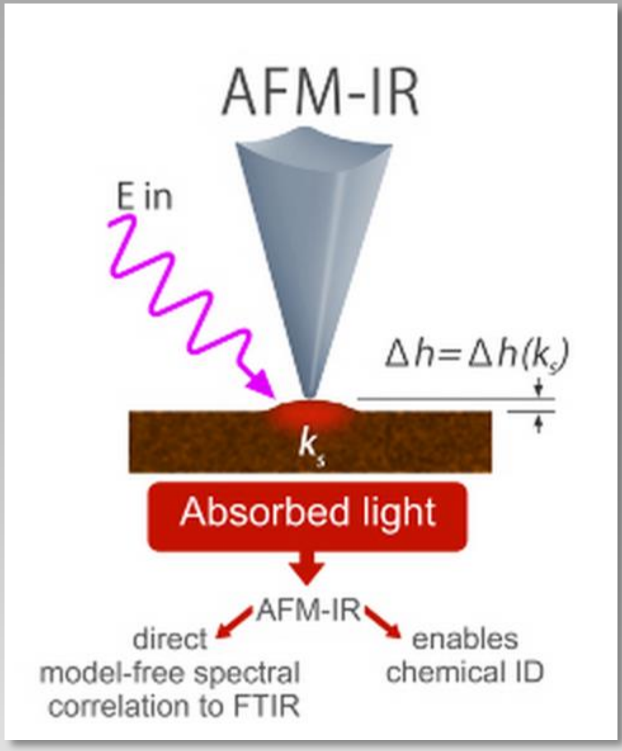
# Spectral shifts issue with thin samples

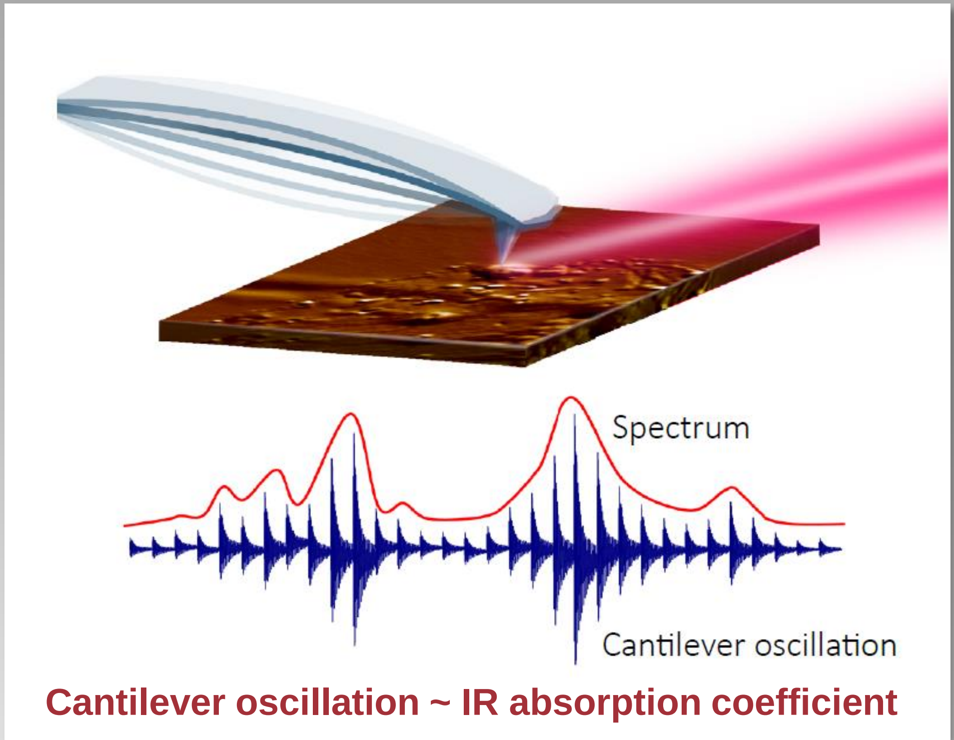
s-SNOM peak positions can depend on tip, substrate and sample thickness

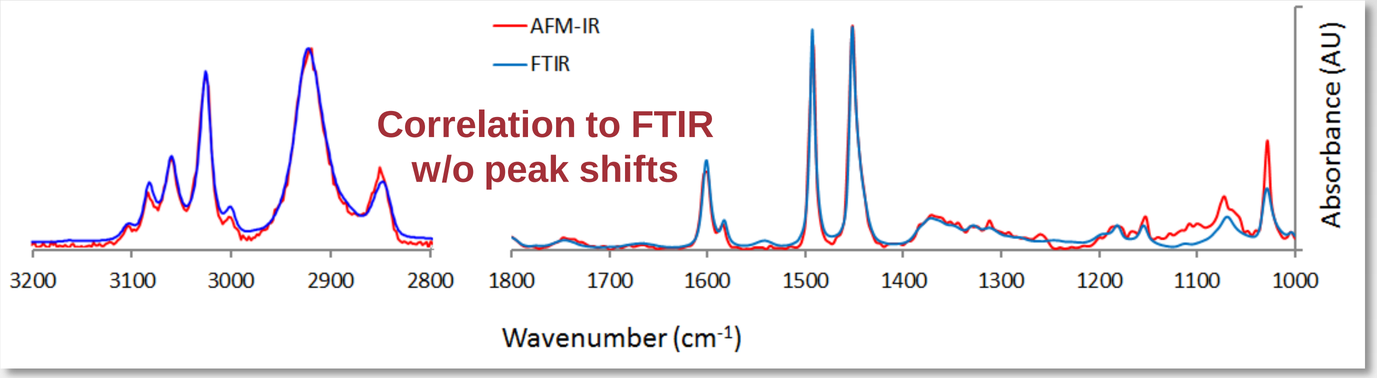



**Ranier Hillenbrand et al., APL 106, 023113 (2015)**

# AFM-IR: Measurement of IR absorption



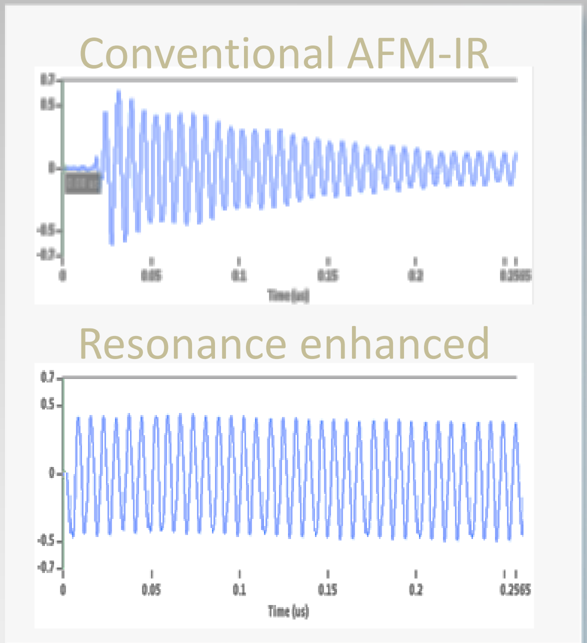



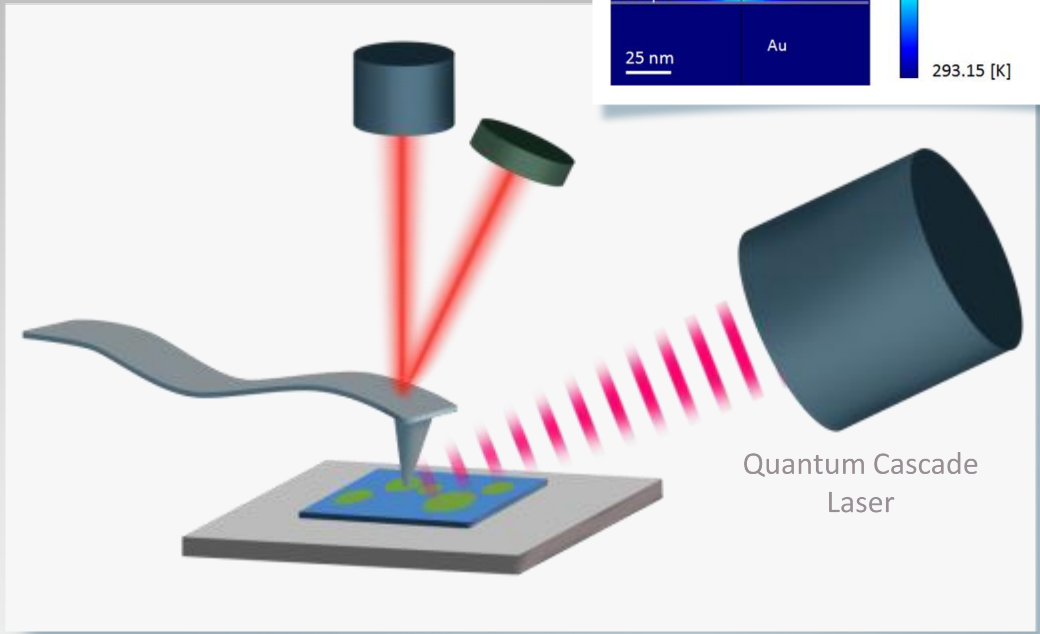

# Improved sensitivity-Resonant Enhanced AFM-IR

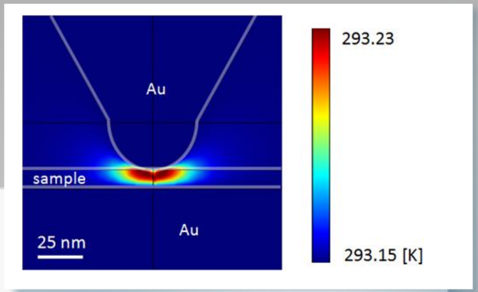
Pulse IR source at contact resonant frequency of cantilever

Continuous oscillation

Sample thickness down to single monolayers



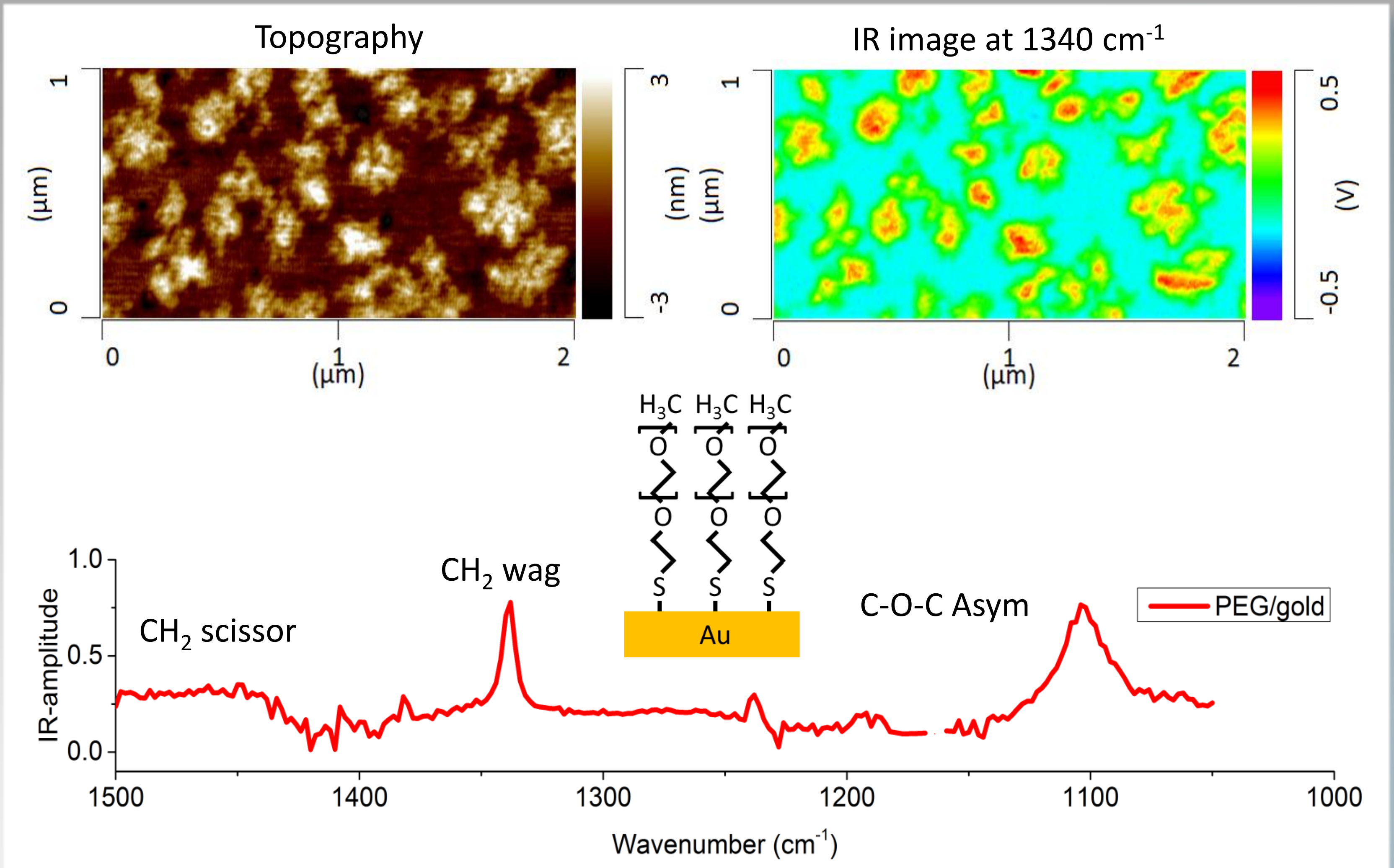





Lu, F.; Belkin, M. *Opt. Exp*. 2011, 19, 19946.

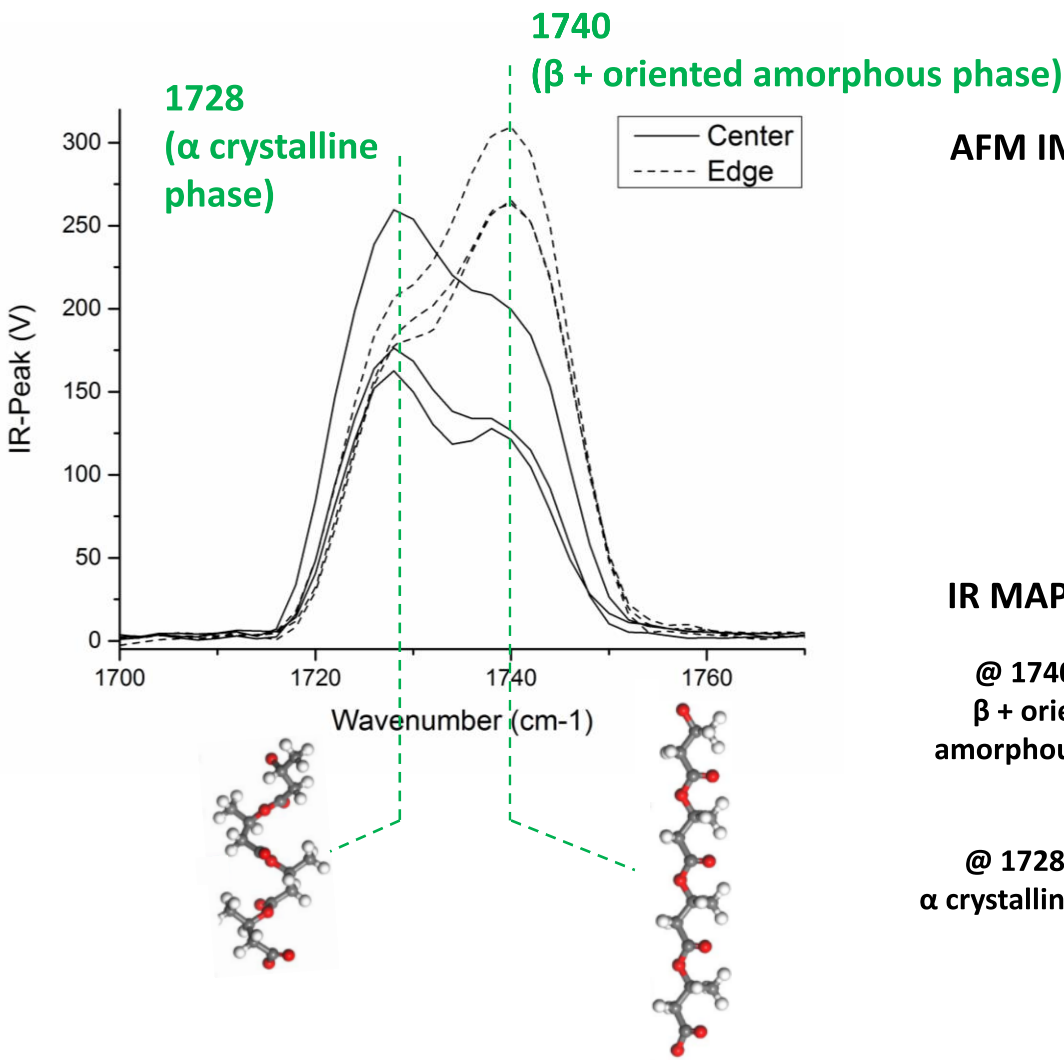
F. Lu, M. Jin, M.A. Belkin, Nat. Photon. 8 307 (2014)

# Resonant enhanced AFM-IR of PEG monolayer



# Electrospun Polymer Fibers

New Publication



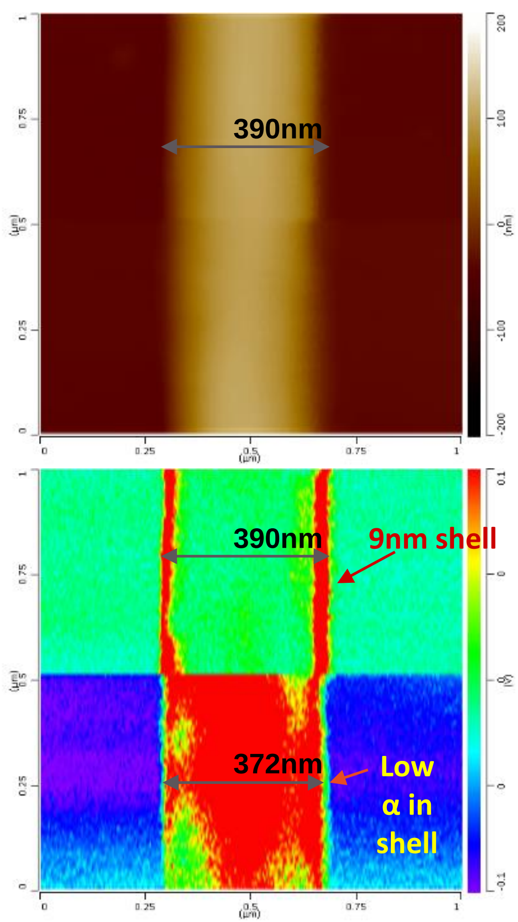

PHBHx nanofibers

AFM IMAGE

IR MAPPING

@ 1740cm$^{-1}$
β + oriented amorphous phase

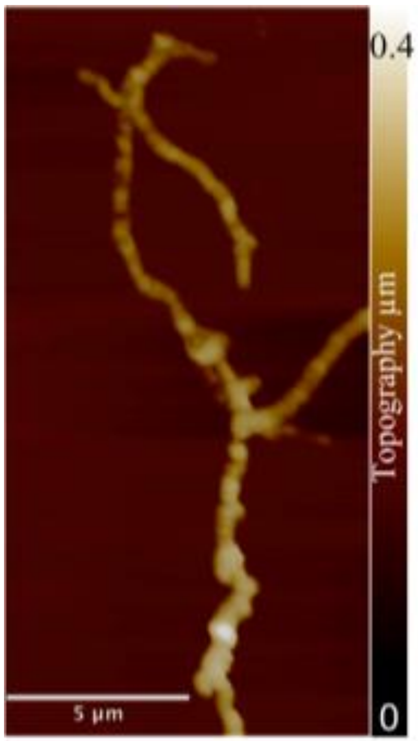
@ 1728cm$^{-1}$
α crystalline phase



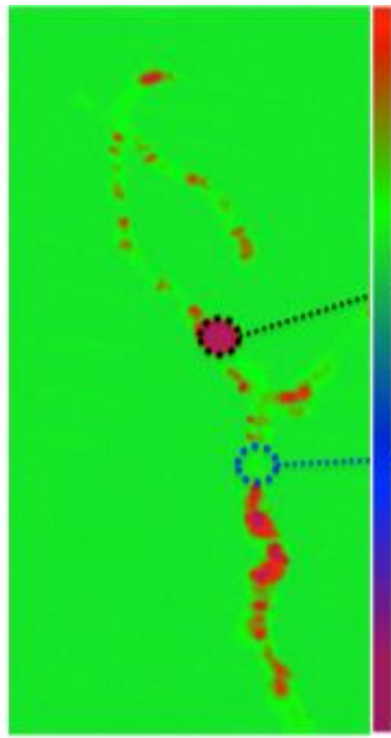

Liang Gong et al Macromolecules, 2015, 48 (17), pp 6197–6205

ANASYS INSTRUMENTS
The nanoscale analysis company

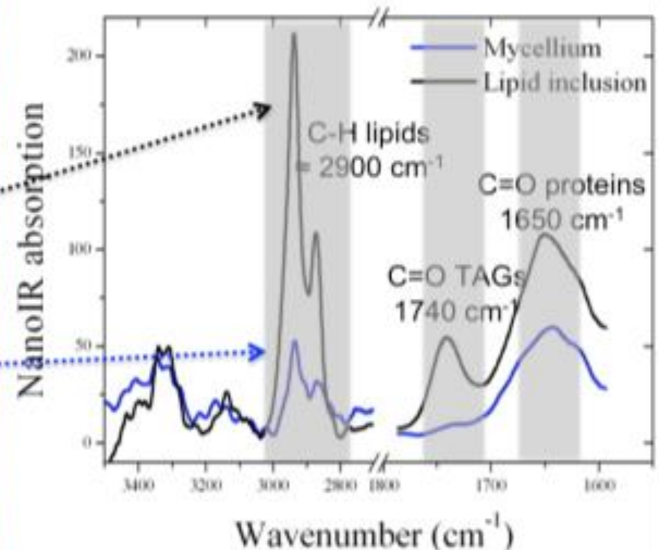
# Biodiesel: Lipid Vesicles in Streptomyces Bacteria

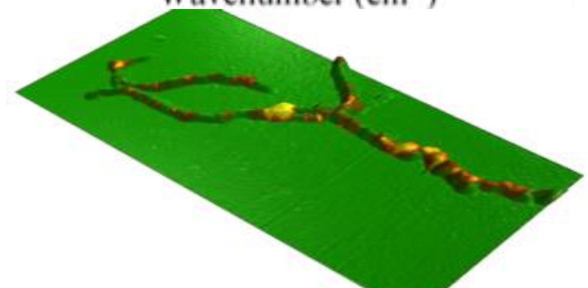



Topography



1740 $cm^{-1}$
(triglyceride)



Deniset-Besseau, et al, The Journal of Physical Chemistry Letters, 5 (4) 654–658 (2014)

# New Publications

New Publication

Go There

http://www.anasysinstruments.com/publications/

| Title | Authors | Journal | Technology |
|---|---|---|---|
| Assessing Chemical Heterogeneity at the Nanoscale in Mixed-Ligand Metal–Organic Frameworks with the PTIR Technique | Dr. Aaron M. Katzenmeyer, Dr. Jerome Canivet, Glenn Holland, Dr. David Farrusseng, Dr. Andrea Centrone | Angewandte Chemie International Edition, 53 (11) 2852-2856 (2014) | AFM-IR |
| Monitoring TriAcylGlycerols Accumulation by Atomic Force Microscopy Based Infrared Spectroscopy in Streptomyces Species for Biodiesel Applications | Ariane Deniset-Besseau, Craig B. Prater, Marie-Joëlle Virolle, Alexandre Dazzi | The Journal of Physical Chemistry Letters, 5 (4) 654–658 (2014) | AFM-IR |
| Nanoscale spatially resolved infrared spectra from single microdroplets | Thomas Müller, Francesco Simone Ruggeri, Andrzej J. Kulik, Ulyana Shimanovich, Thomas O. Mason, Tuomas P. J. Knowles, Giovanni Dietler | **Lab on a Chip** (web) January 29, 2014 | AFM-IR |
| Tip-enhanced infrared nanospectroscopy via molecular expansion force detection | Feng Lu, Mingzhou Jin, Mikhail A. Belkin | **Nature Photonics** (web) January 19, 2014 | AFM-IR |
| PEDOT nanostructures synthesized in hexagonal mesophases | Srabanti Ghosh, Hynd Remita, Laurence Ramos, Alexandre Dazzi, Ariane Deniset-Besseau, Patricia Beaunier, Fabrice Goubard, Pierre-Henri Aubert, Francois Brisset, Samy Remita | **New Journal of Chemistry** 38, 1106-1115 (2014) | AFM-IR |
| Atomic Force Microscope Infrared Spectroscopy of Griseofulvin Nanocrystals | Aaron J. Harrison, Ecevit A. Bilgili, Stephen P. Beaudoin, Lynne S. Taylor | **Analytical Chemistry** (Web): October 31, 2013 | AFM-IR |
| Molecular Architecture of Plant Thylakoids under Physiological and Light Stress Conditions: A Study of Lipid-Light-Harvesting Complex II Model Membranes | Ewa Janik, Joanna Bednarska, Monika Zubik, Michal Puzio, Rafal Luchowski, Wojciech Grudzinski, Radoslaw Mazur, Maciej Garstka, Waldemar Maksymiec, Andrzej Kulik, Giovanni Dietler, Wieslaw Gruszecki | **Plant Cell** 25 (6) 2155-2170 (2013) | AFM-IR |
| Improved atomic force microscope infrared | Hanna Cho, Jonathan R Felts, Min-Feng Yu, | **Nanotechnology** 24, 444007 (2013) 8pp | AFM-IR |

http://www.anasysinstruments.com/event/webinar/

# Collaborator Acknowledgement

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College of Engineering
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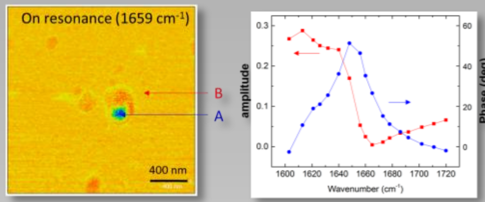
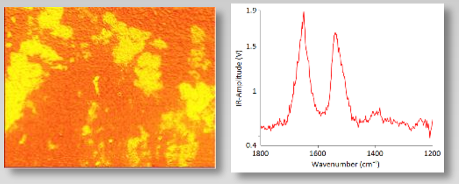
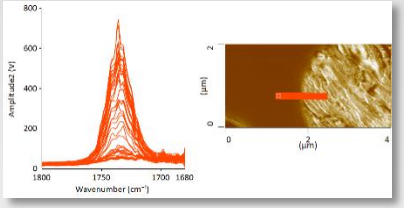
# Summary

- New nanoIR2-s platform combines complementary techniques AFM-IR and s-SNOM
- S-SNOM excels for complex optical property mapping, especially for photonic materials
- AFM-IR excels provide direct, true, model-free IR absorption spectroscopy, especially for polymers and life sciences
- Anasys is leading innovations in both fields, including:
    - Resonance enhanced AFM-IR with sub-monolayer sensitivity
    - ultra fast AFM-IR spectroscopy
    - Efficient s-SNOM point spectroscopy and imaging with a single laser source
- Power and productivity for your research, without compromises

nanoIR2-s

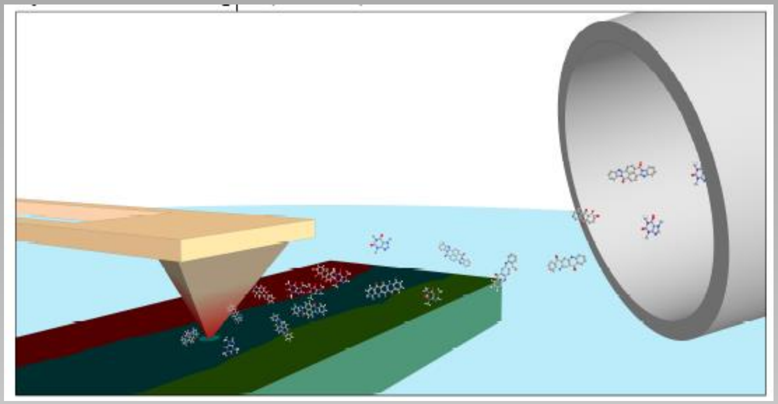


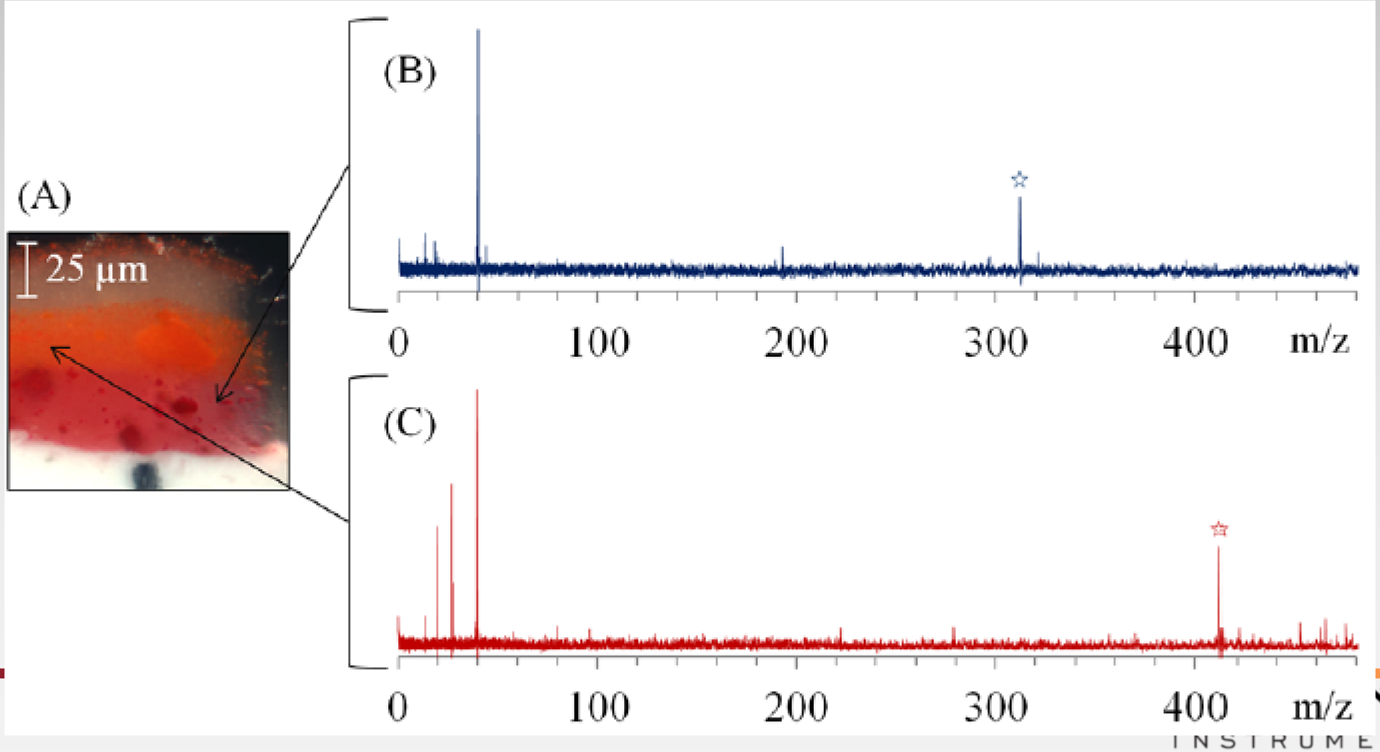
# Questions ?

# New Technology Development AFM-MS



Analytical Methods

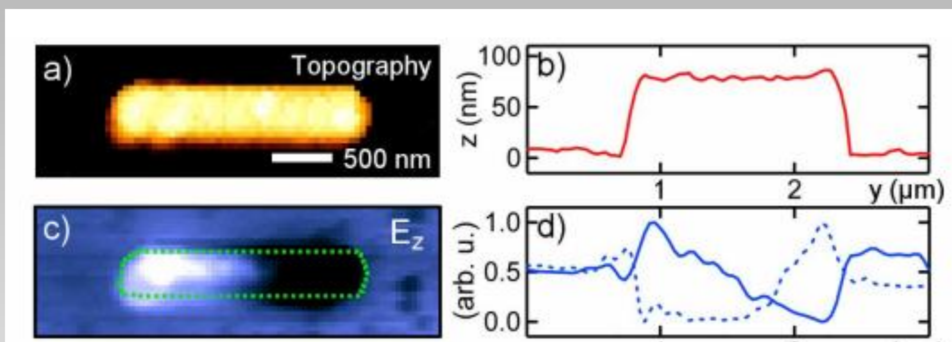
Owens, Shawn; University of California Santa Barbara, Chemistry
Berenbeim, Jacob; University of California Santa Barbara, Chemistry
Patterson, Catherine; Getty Conservation Institute,
Dillon, Eoghan; Anasys Instruments,
de Vries, Mattanjah; University of California Santa Barbara, Chemistry



# Nanoantennas

Enhancement/scattering from resonant nanostructures

Example from literature




Olmon et al, Optics Express 16 20299 (2008)

nanoIR2-s measurement