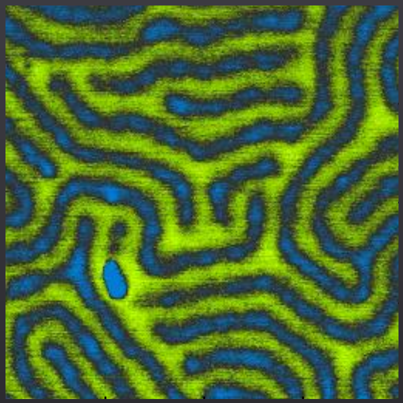
molecular VISTA
www.molecularvista.com



Nanoscale Chemical Imaging by Photo-induced Force Microscopy (PiFM)

D. Nowak, W. Morrison, T. R. Albrecht, K. Park, and S. Park

Molecular Vista, Inc., San Jose, CA, USA

NCCAVS February 23, 2017

Chemical Mapping: Elemental Analysis via Electron Microscopy

Atomic Resolution Elemental Mapping on SrTiO3 crystal by Super X EDS (EDX) system on Titan 80-300 Aberration Corrected Scanning Transmission Electron Microscope

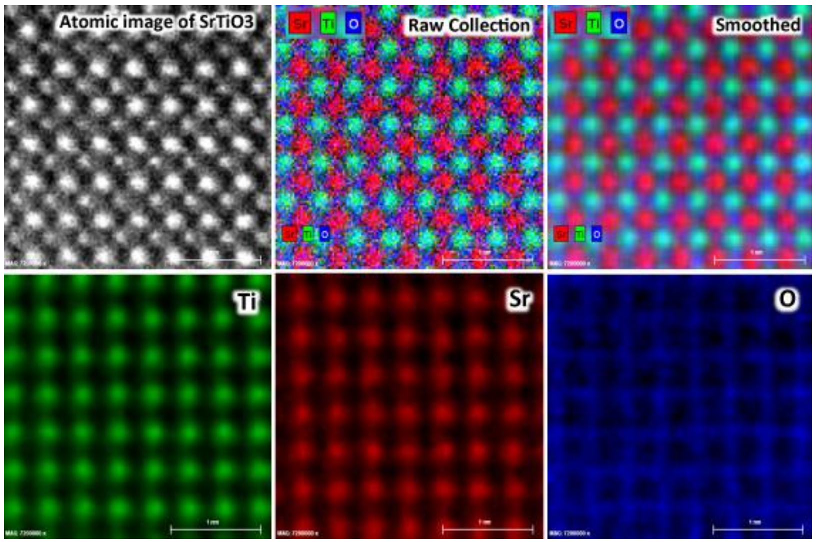


Image credit: North Carolina State Univ. Analytical Instrumentation Facility

https://www.aif.ncsu.edu/tem-lab/

Elemental mapping of a device structure by EDS (EDX)

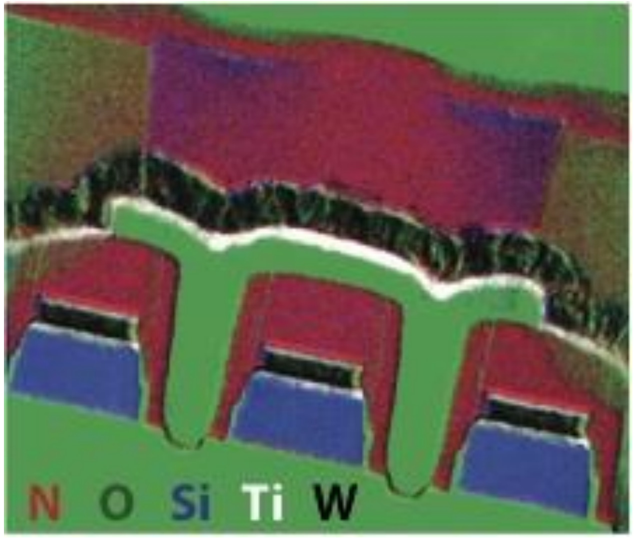


Image credit: Nanolab Techologies

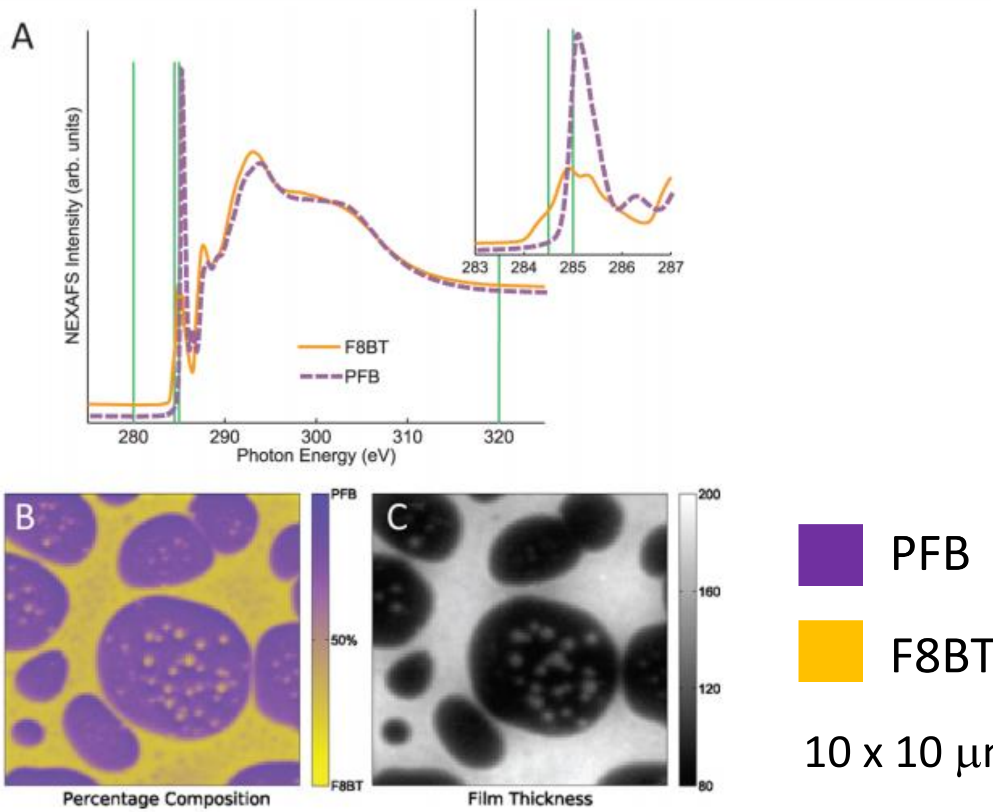
http://www.nanolabtechnologies.com/TEM-STEM-EELS-EDS

- Advanced capability for elemental mapping (but not for organics)
- Atomic-scale resolution in certain circumstances

Chemical Mapping of Molecular Materials via X-Rays, Neutrons

- X-ray Techniques
  - Wide-Angle X-ray Scattering (WAXS)
  - Small-Angle X-ray Scattering (SAXS)
  - Resonant Soft X-ray Scattering (r-SoXS)
- Neutron Techniques

Scanning Transmission X-ray Microscopy (STXM)



10 x 10 μm

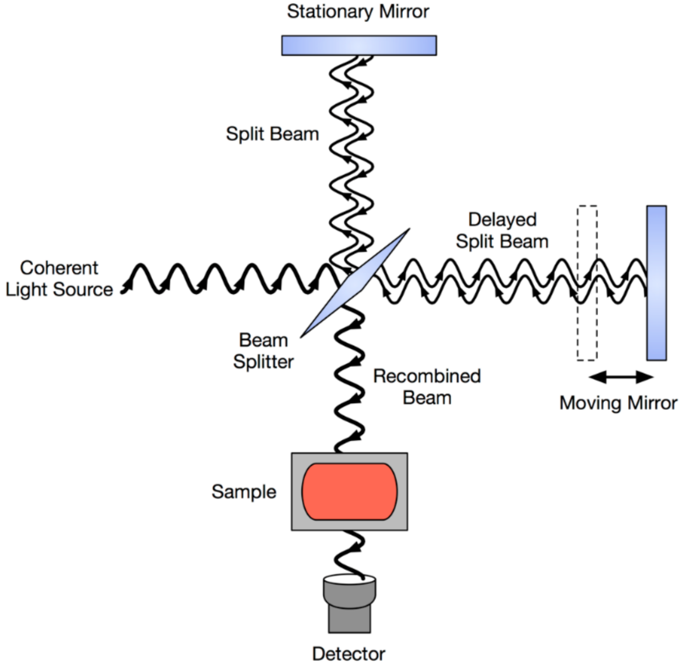
Image credit:

Watts, B.; McNeill, C. R.; Raabe, J. Synth. Met. 2012, 161, 2516.

- Polymers prone to damage to X-ray
- Synchrotron sources are not easily accessible

FTIR: Infrared Absorption "Chemical Fingerprint" Spectrum

FTIR apparatus



Detailed absorption spectrum – chemical "fingerprint"

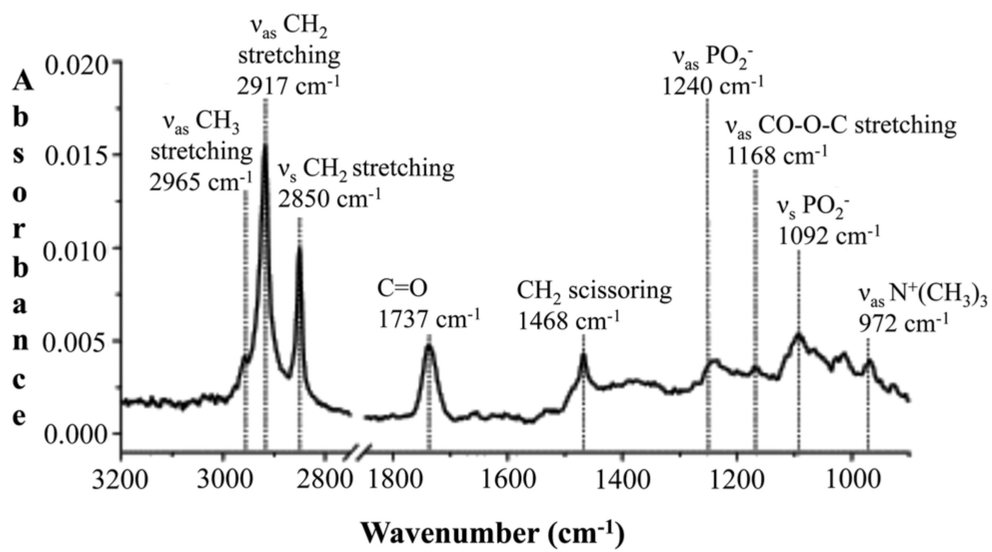


Image credit: Wikipedia

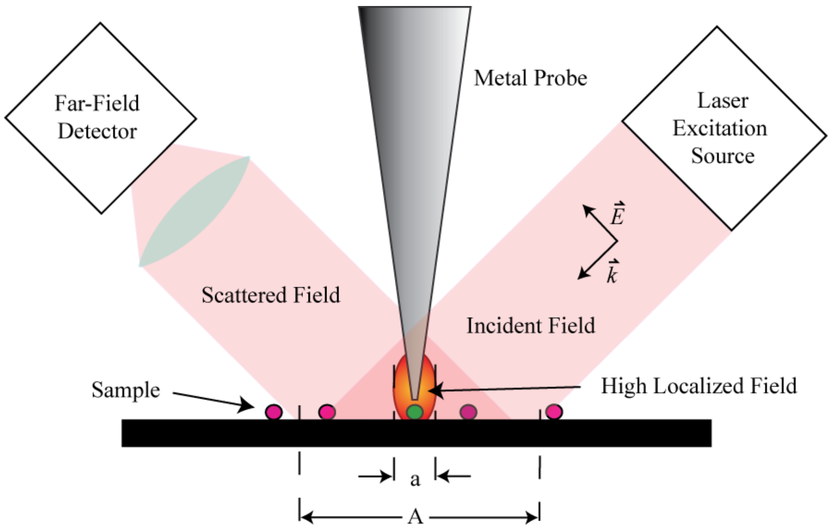
https://en.wikipedia.org/wiki/Fourier_transform_infrared_spectroscopy#/media/File:FTIR_Interferometer.png

Image credit: Mudunkotuwa et al., Analyst 139, 870-881 (2014).

- Detailed spectra for analysis and identification of molecular materials
- Spatial mapping resolution limited by optical diffraction limit (~ 1 μm)

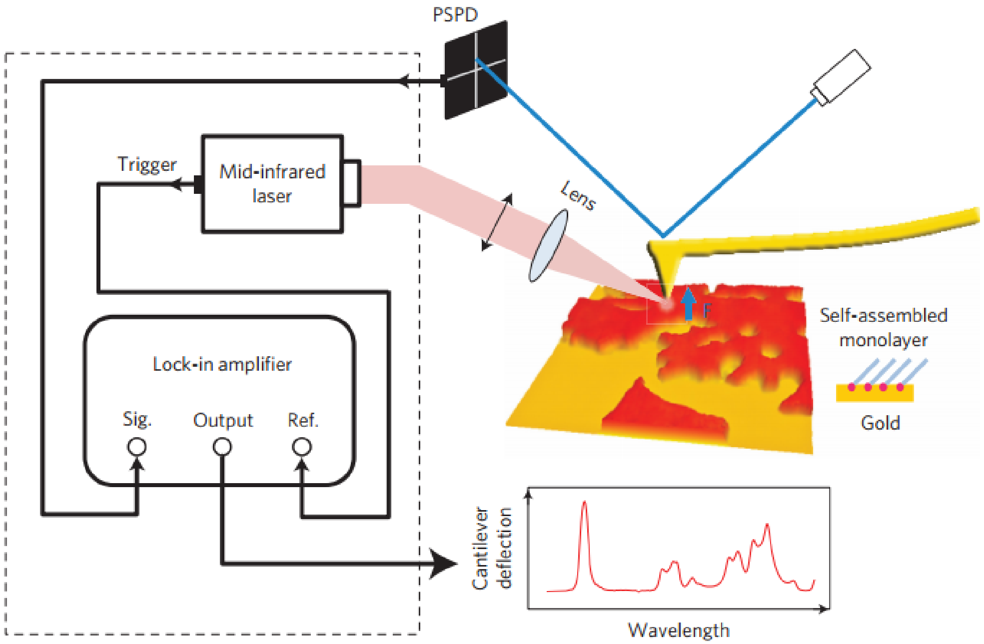
Existing IR-NF Probe Techniques: Optical vs. Mechanical Detection

Scattering techniques (sSNOM or TERS)



D. Nowak thesis

Photothermal imaging (PTIR)



Lu, Jin, and Belkin, Nature Photonics 8, 307-312 (2014)

- Interaction region confined by enhanced fields at sharp tip
- Far-field collection of scattered photons (low efficiency/sensitivity)
- Smooth samples preferred (background scattering concern)

- Material specific λ-selective absorption
- Local sensing of thermal expansion
- Tip in hard contact with sample
- ~100 nm resolution
- Strongly affected by sample thickness and substrate

Photo-induced Force Microscopy (PiFM)

- Mechanical detection
- Dipole-dipole forces between sample and tip

Photo-induced Force Microscopy (PiFM)

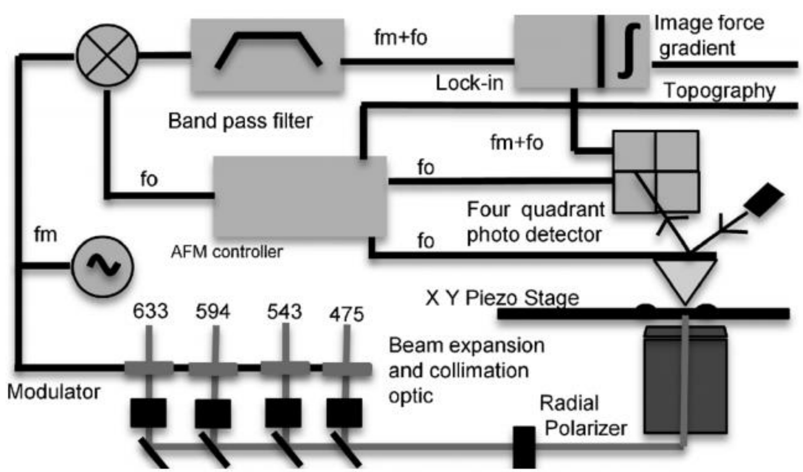
APPLIED PHYSICS LETTERS **97**, 073121 (2010)

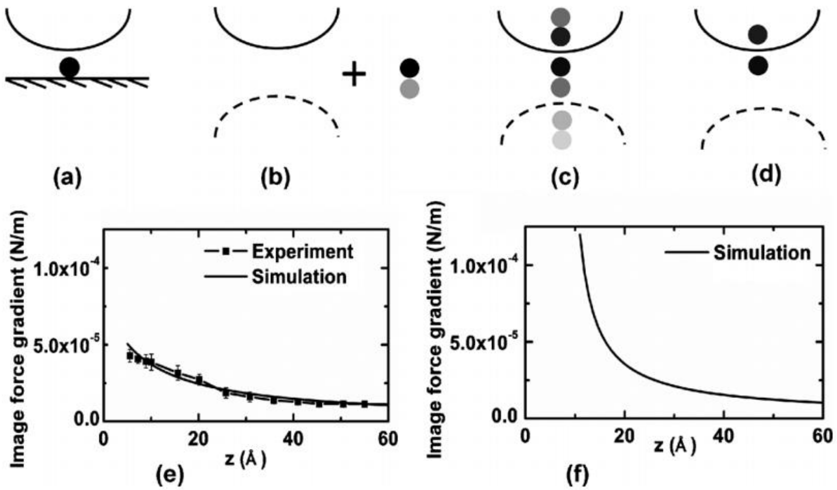
Image force microscopy of molecular resonance: A microscope principle

I. Rajapaksa, K. Uenal, and H. Kumar Wickramasinghe[a)]
Department of Electrical Engineering and Computer Science, University of California, Irvine, California 92697, USA

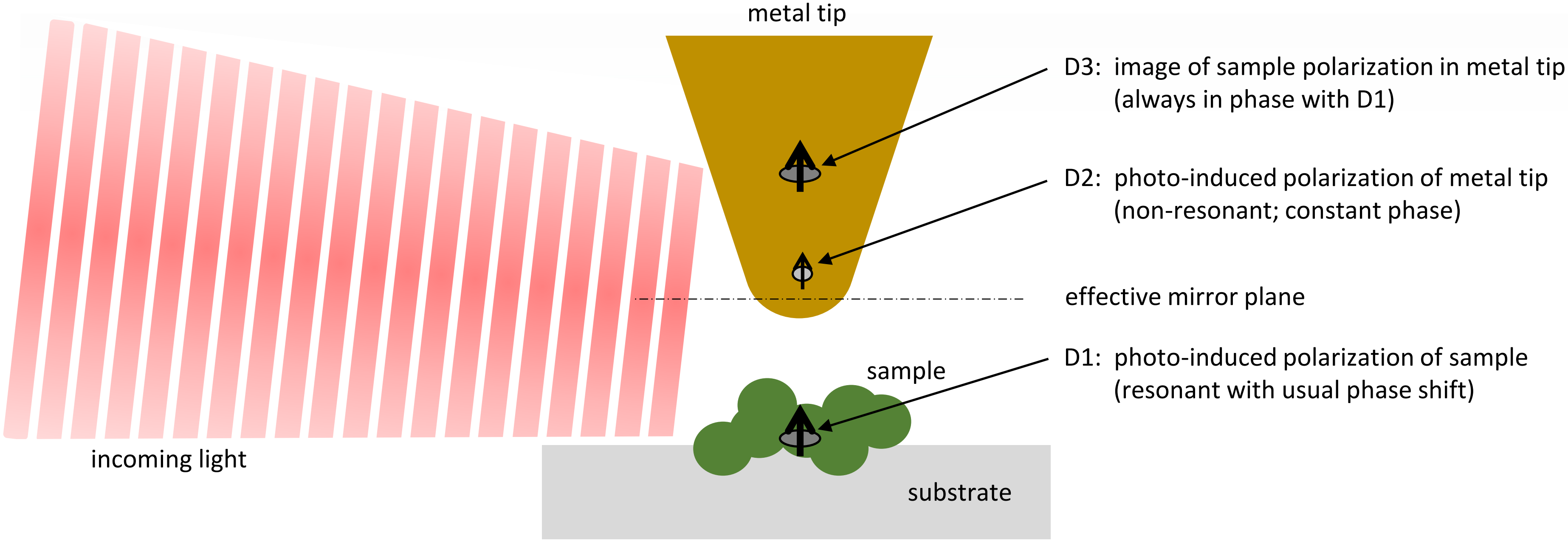
(Received 3 June 2010; accepted 12 July 2010; published online 20 August 2010)

We demonstrate a technique in microscopy which extends the domain of atomic force microscopy to optical spectroscopy at the nanometer scale. We show that molecular resonance of feature sizes down to the single molecular level can be detected and imaged purely by mechanical detection of the force gradient between the interaction of the optically driven molecular dipole and its mirror image in a platinum coated scanning probe tip. This microscopy and spectroscopy technique is extendable to frequencies ranging from radio to infrared and the ultraviolet. © *2010 American Institute of Physics*. [doi:10.1063/1.3480608]





Origin of the Photo-Induced Force (Image Force)

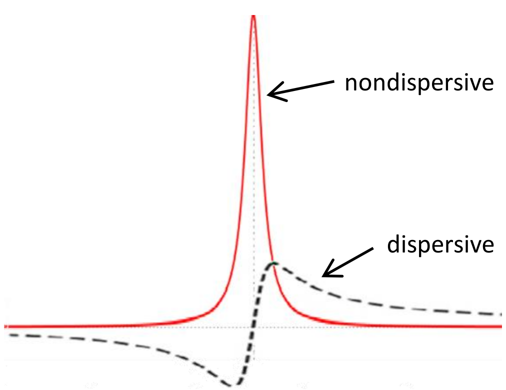


<u>PHOTO-INDUCED FORCE:</u>

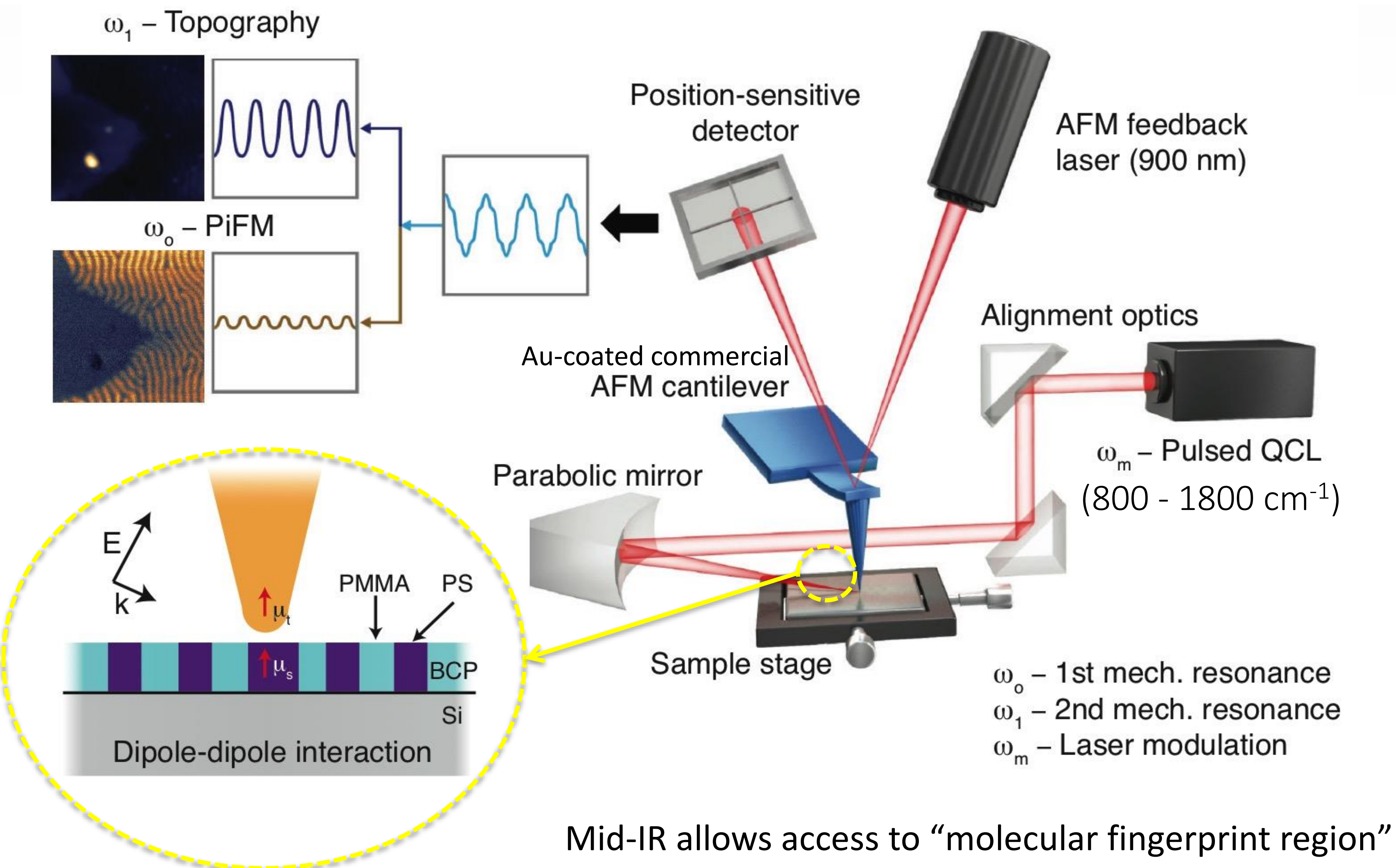
- D1↔D2: direct interaction (dispersive peak shape; weak in IR)
- D1↔D3: "image force" (nondispersive peak shape; strong in IR)

- Magnitude: F_{PIFM} ~ (sample polarization)^2 / z^4

- Very high resolution limited by tip radius
- Minimal thermal contribution



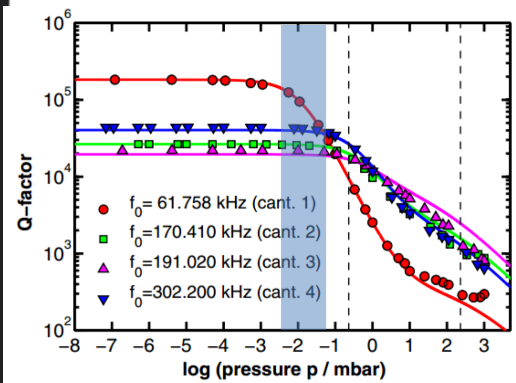
PiFM Apparatus



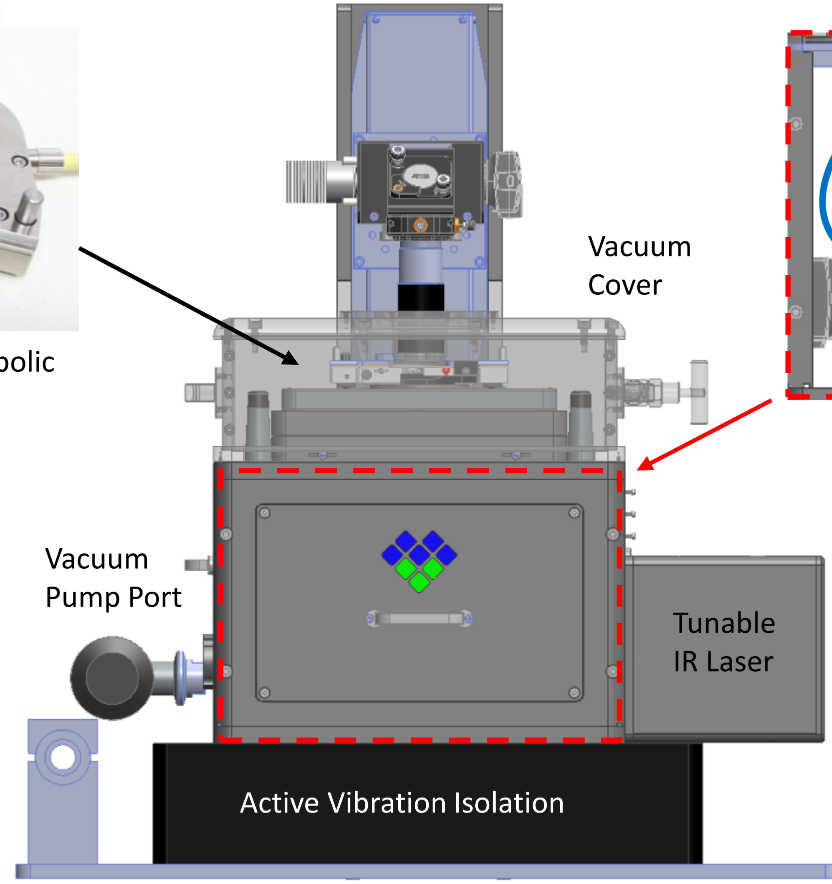
Mid-IR allows access to "molecular fingerprint region"

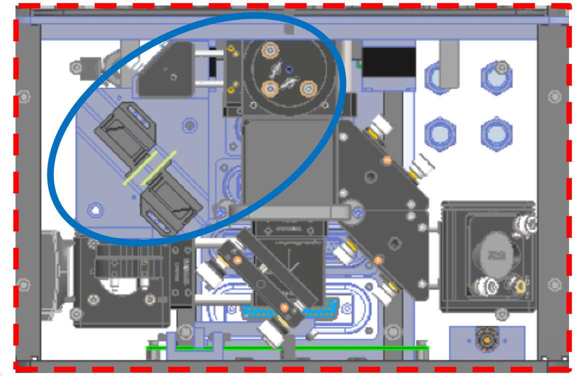
The Instrument: "Vista IR"

AFM head with integrated parabolic mirror on 3D piezo motor



Meas. Sci. Technol. 22, 055501 (2011)



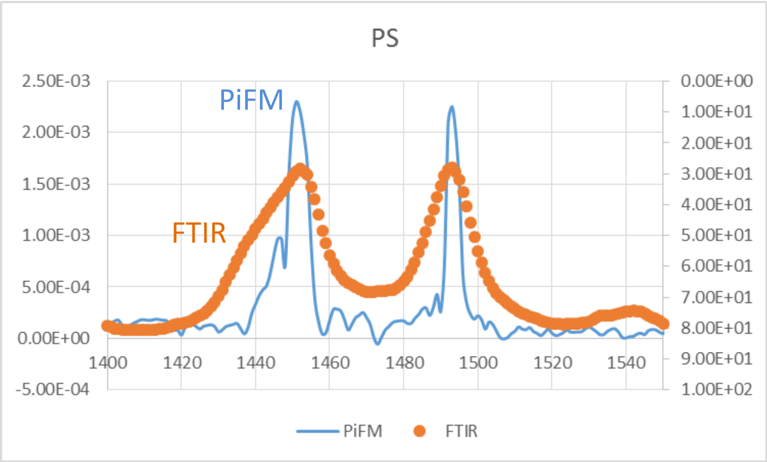


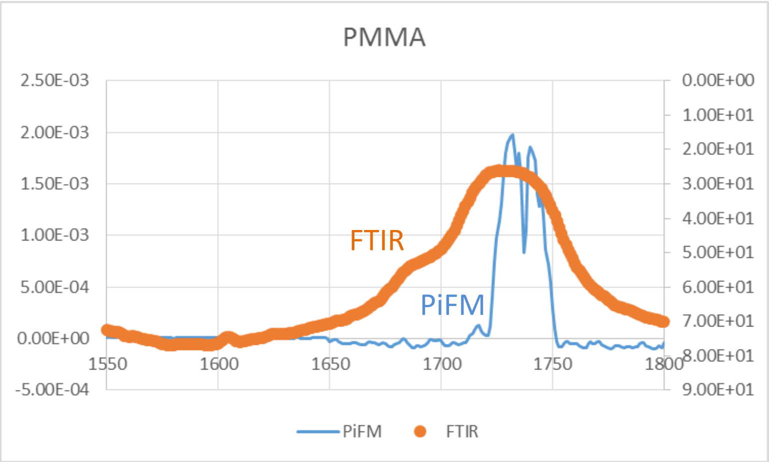
Cover removed showing the optical layout (shown with optional Michelson interferometer for scattering SNOM)

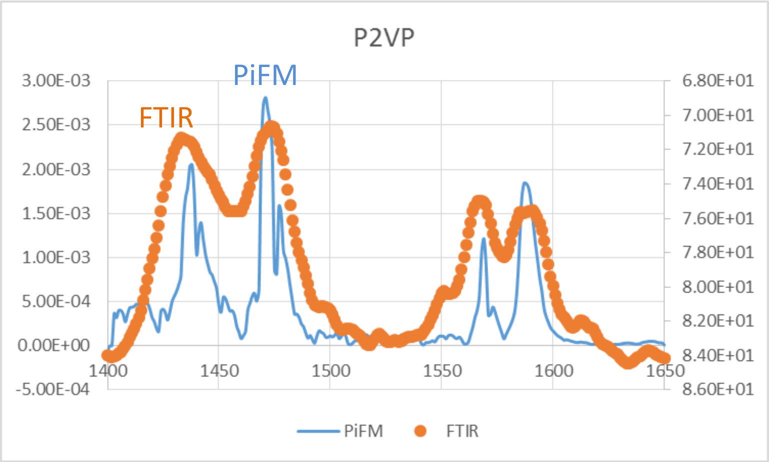
- Everything needed for PiFM built in
- sSNOM option available
- Controlled atmosphere or low vacuum
- Multiple optical ports provided for customization of research

PiFM Results

Point Spectroscopy with PiFM (Homopolymers)





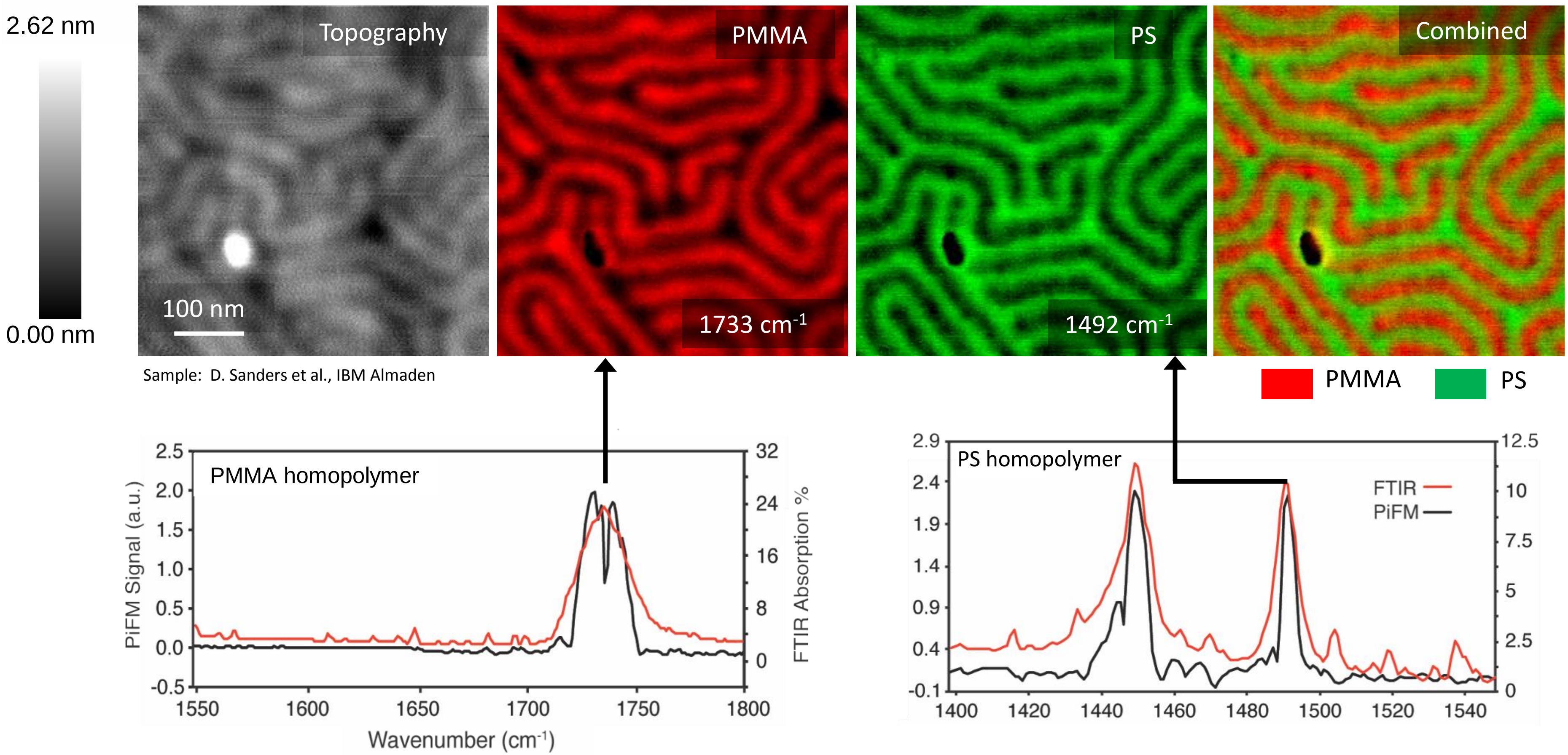


- PiFM spectra on 30 nm thick homopolymer films on Si, with no special preparation. (~20 sec acquisition time)
- FTIR absorption curve on bulk samples of polymers
- Significant correlation to FTIR
- Selection rules and water vapor providing additional peak structure *(per discussion with Warren Vidrine)*

Nowak et al., Science Advances Vol. 2, no. 3, e1501571 (2016)

PiFM of PS-*b*-PMMA Block Copolymer: ~10 nm Lateral Resolution

(40 nm pitch “fingerprint” patterns)

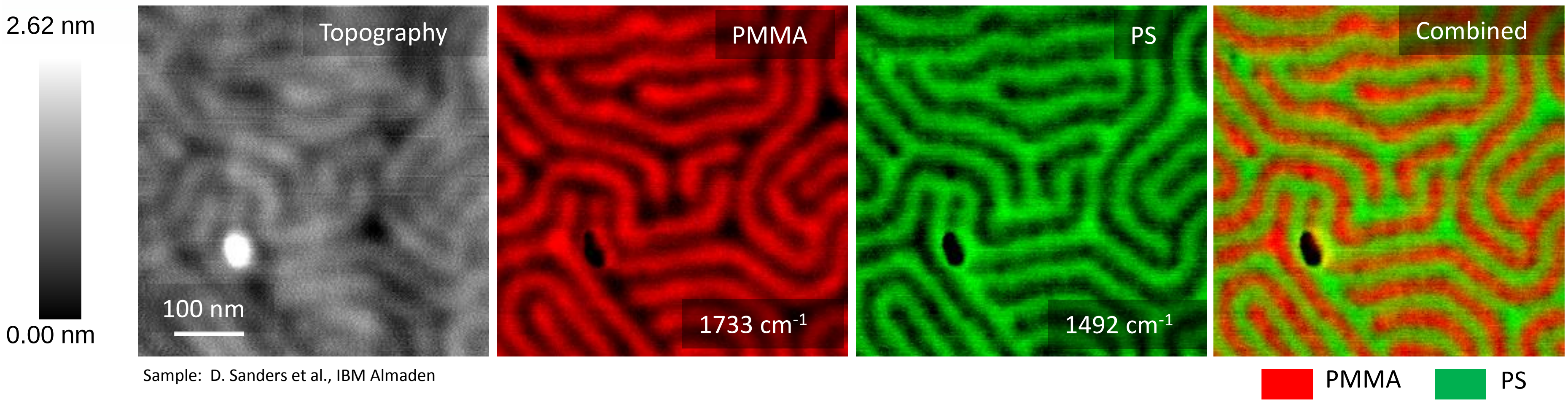


Sample: D. Sanders et al., IBM Almaden

Publication: “Nanoscale chemical imaging by photoinduced force microscopy,” D. Nowak et al., *Science Advances* 25 Mar 2016: Vol. 2, no. 3, e1501571 DOI: 10.1126/sciadv.1501571

Is PIFM responding to AFM Phase?

(40 nm pitch “fingerprint” patterns)



Sample: D. Sanders et al., IBM Almaden

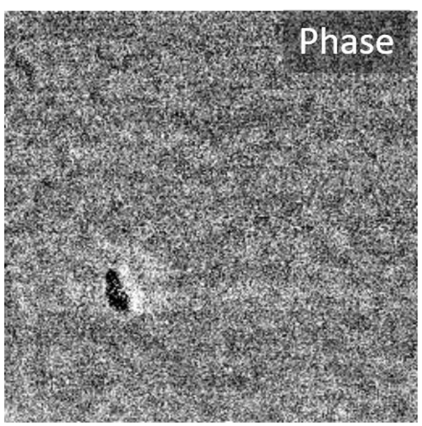
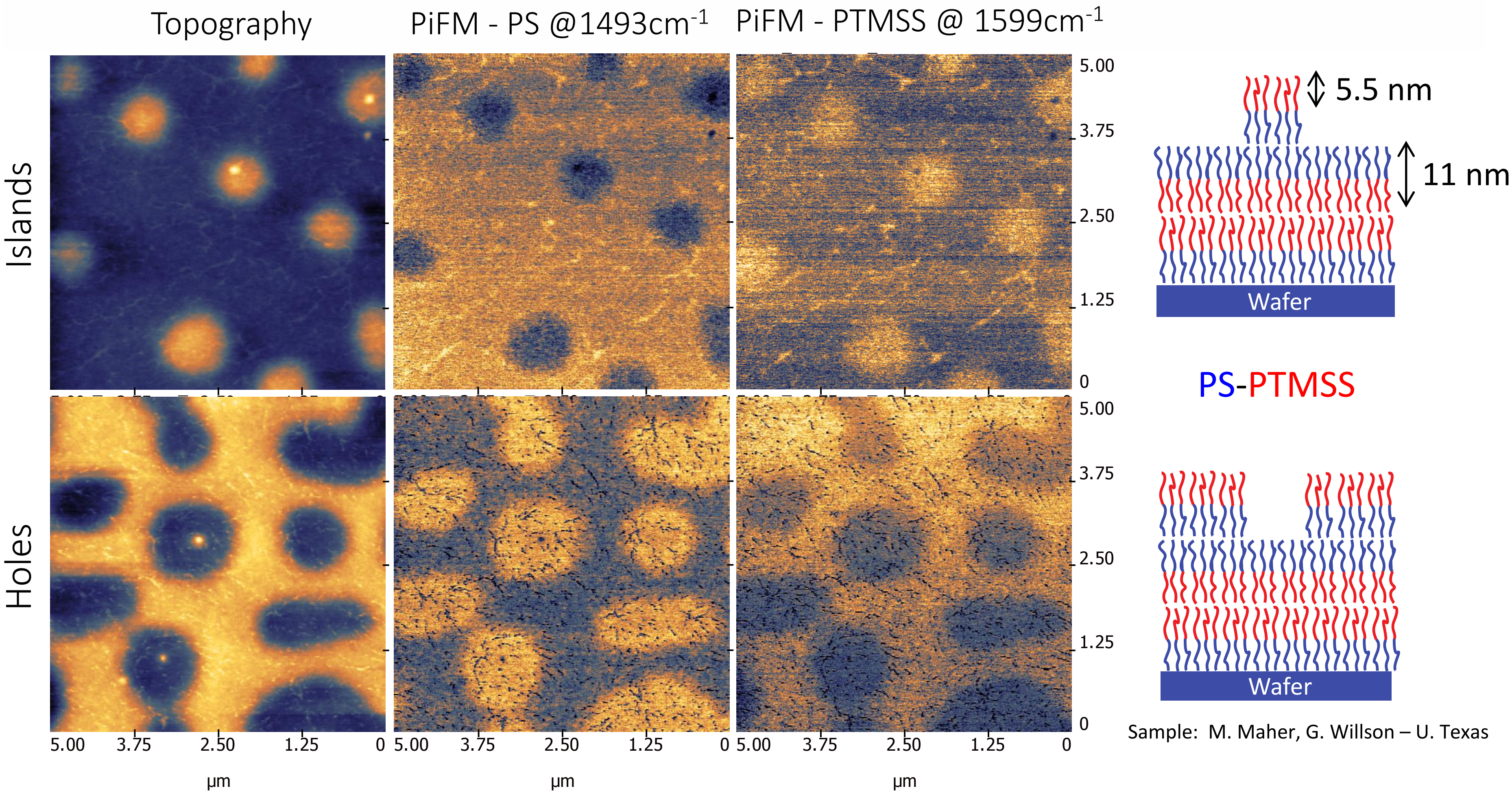


Photo-induced force imaging is completely unrelated to AFM phase imaging

Surface Sensitivity: PiFM of PS-*b*-PTMSS Block Copolymer

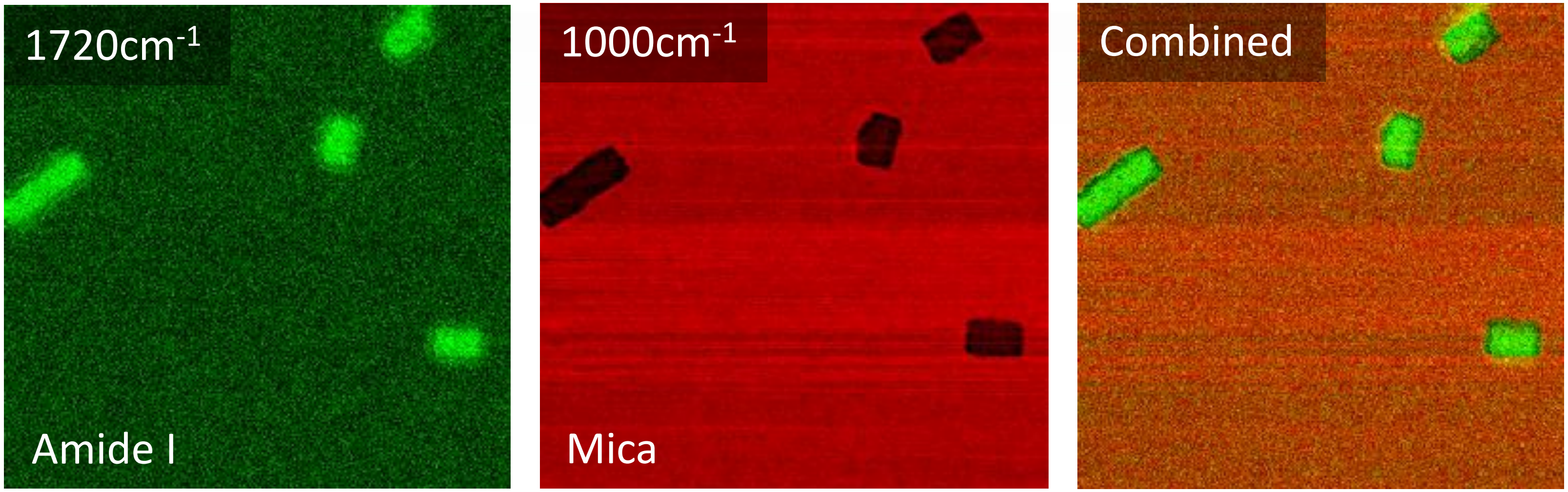
Horizontal lamellae – quantized thickness “island / hole” formations

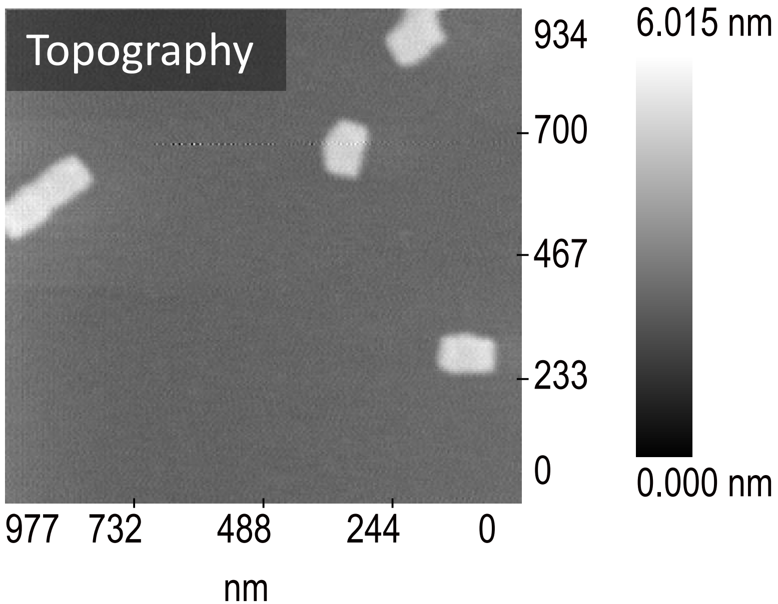


Sample: M. Maher, G. Willson – U. Texas

Surface material has stronger response – penetration depth is several nanometers

DNA Origami





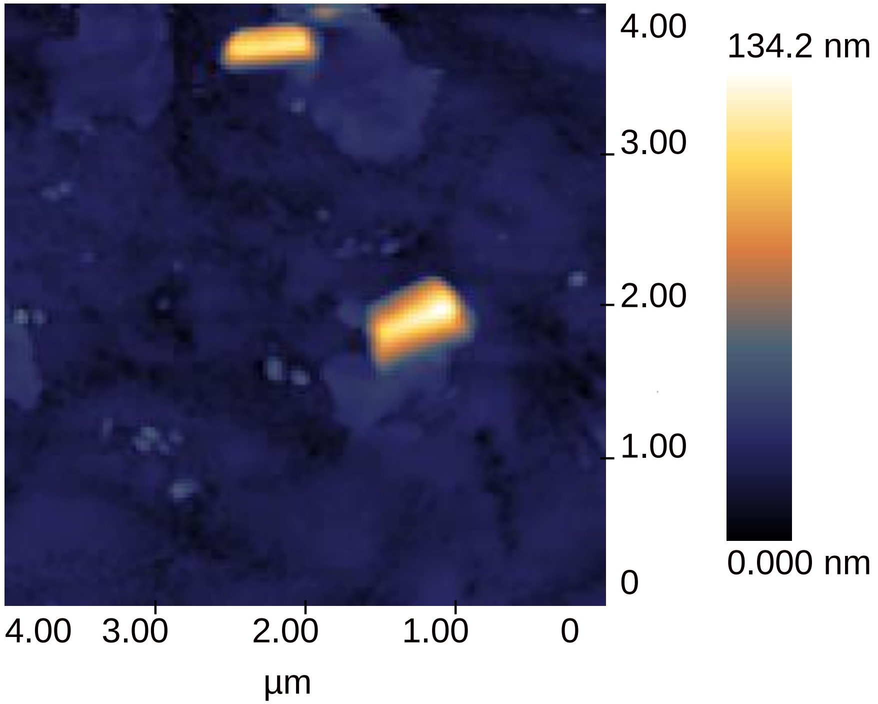
DNA structures only 2-3 nm thick

Sample provided by:
R. Berger
Max Planck Institute

“Hyperspectral” Image of 2D Perovskite

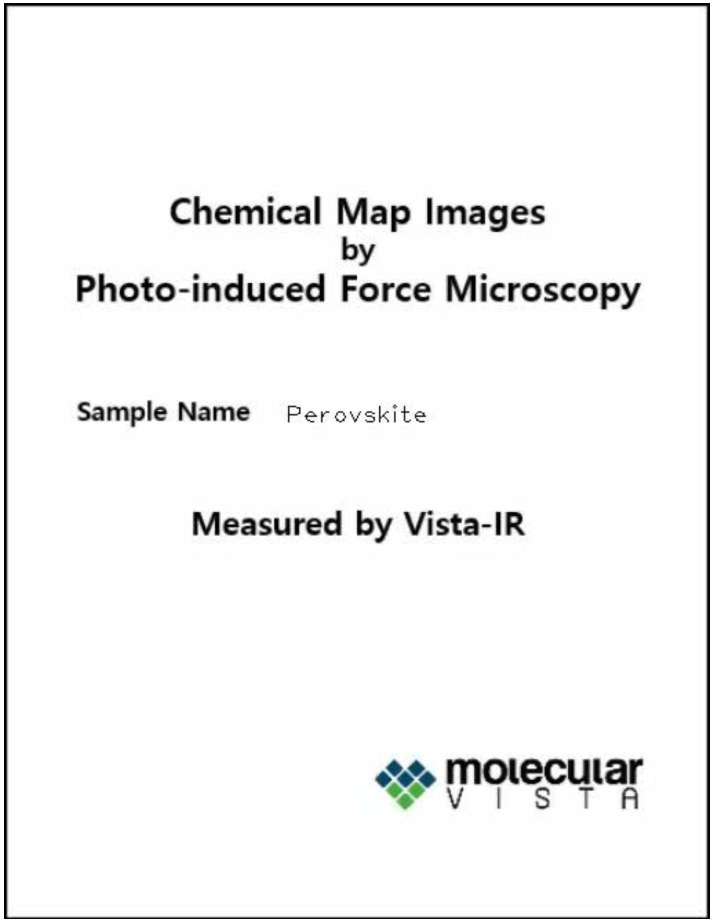
“Hyperspectral” or “hyPIR” image = full spectrum at every pixel

Topography:

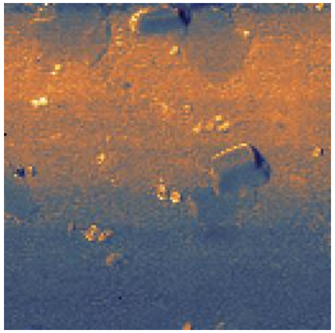


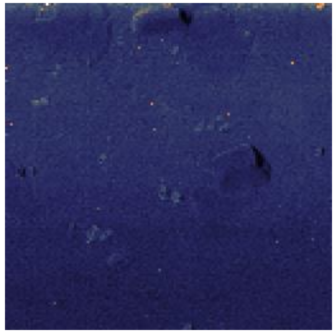
Sample: David Ginger, Raj Giridharagopal, Alex Jen - Univ. of Washington

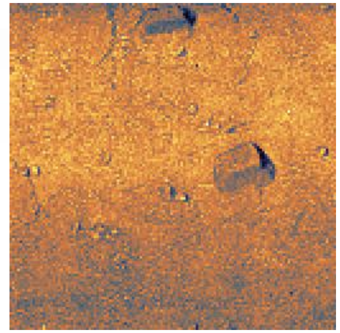
Hyperspectral image video:

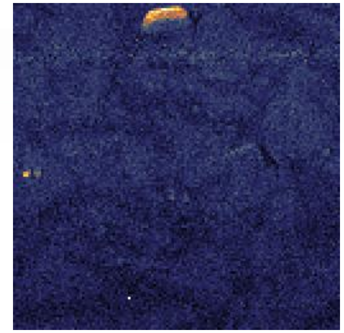


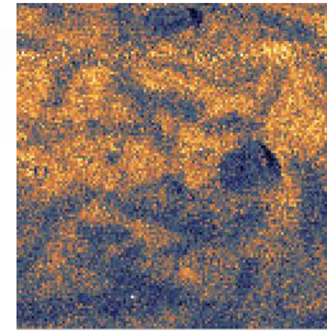
Hyperspectral Image of 2D Perovskite

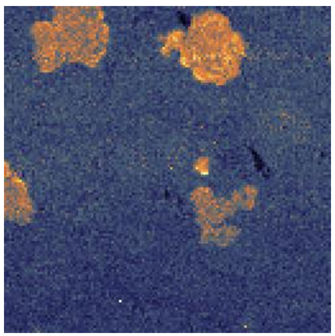

1761 cm^{-1}

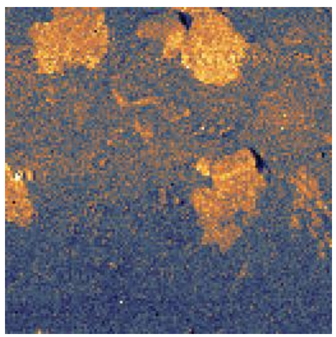

1738 cm^{-1}

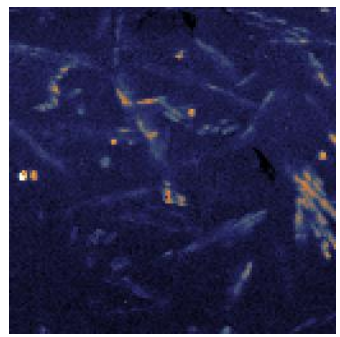

1682 cm^{-1}

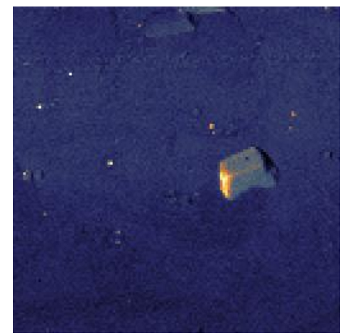

1581 cm^{-1}

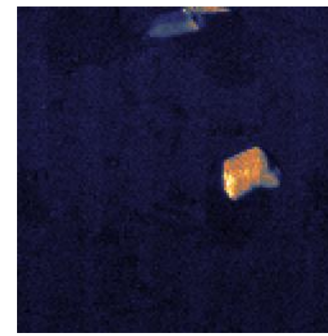

1566 cm^{-1}

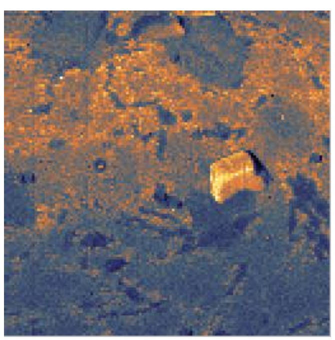

1529 cm^{-1}

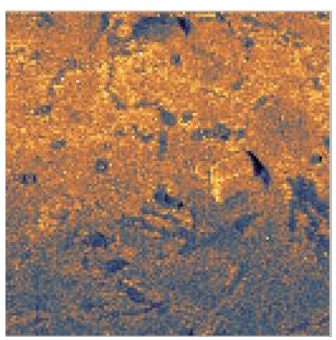

1515 cm^{-1}

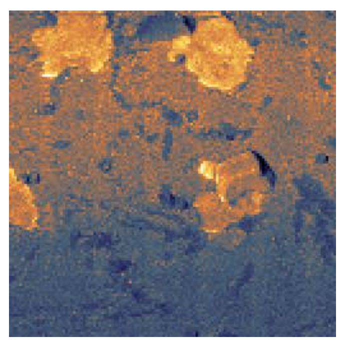

1496 cm^{-1}

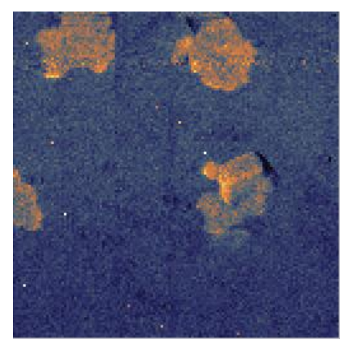

1481 cm^{-1}

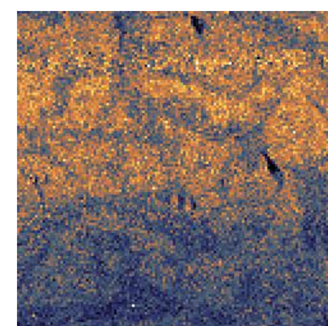

1474 cm^{-1}


1467 cm^{-1}


1466 cm^{-1}


1463 cm^{-1}


1458 cm^{-1}

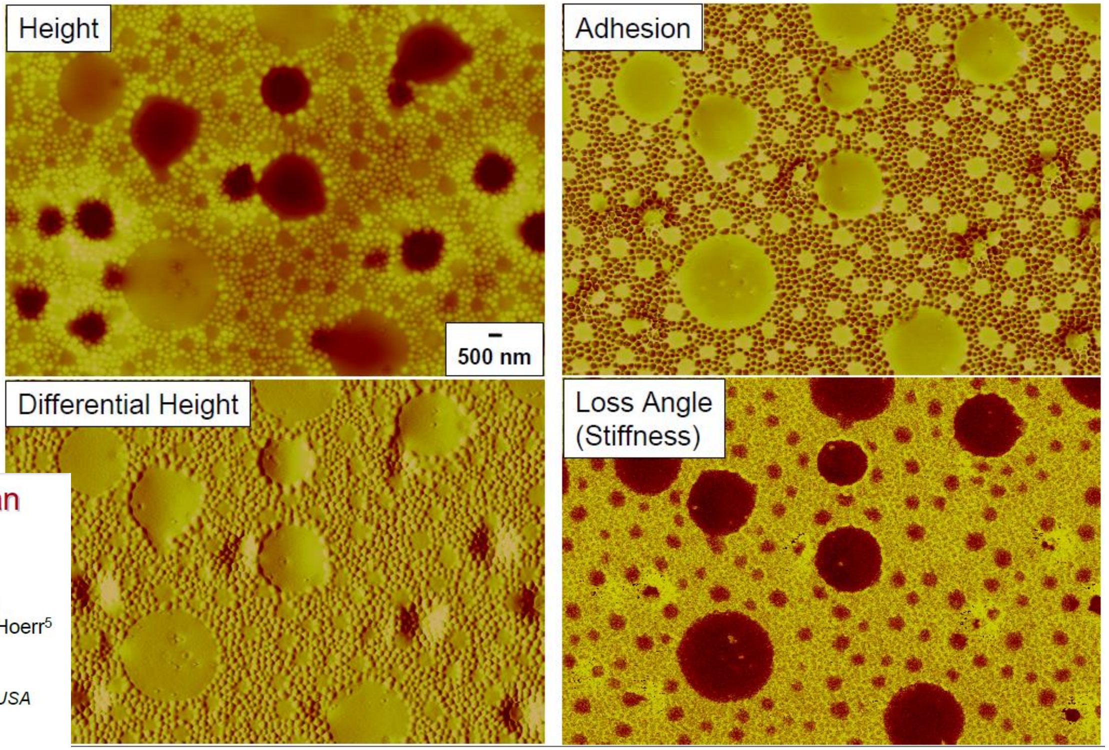

1387 cm^{-1}

PBMA/PLMA/Dexamethasone (Pharmaceutical Composite)

Sample provided by:
Greg Haugstad (PhD),
Characterization Facility - University of Minnesota

In collaboration with:
Dr. Klaus Wormuth, Surmodics, Inc.

Spin-coated PBMA / PLMA / dexamethasone (43.5:13:43.5)

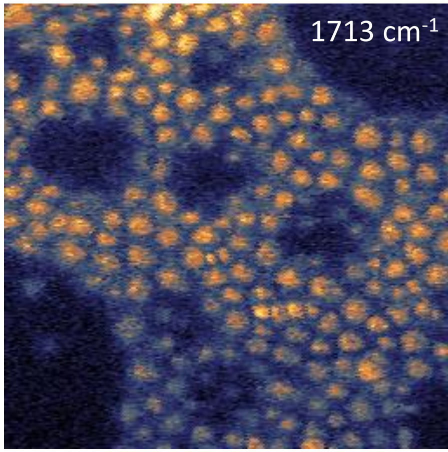


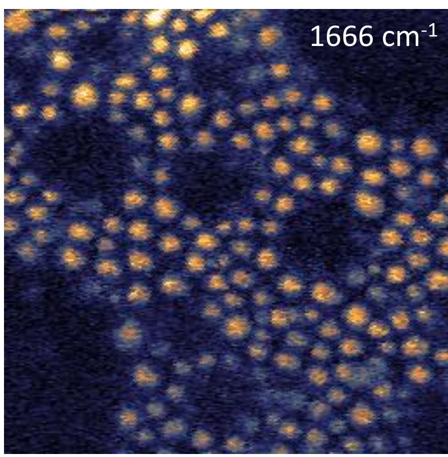
Environmental Atomic Force and Confocal Raman Microscopies in Pharmaceutical Science

Greg Haugstad,[1] Klaus Wormuth,[3] Jinping Dong,[1] Dabing Chen[2] and Raj Suryanarayanan,[2] Eric Vandre,[1] Jeannette Polkinghorne,[4] John Foley,[5] Robert Hoerr[5]

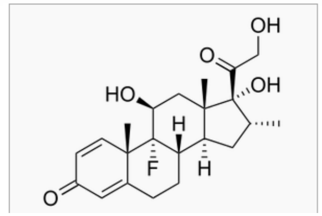
[1]*Characterization Facility, University of Minnesota, Minneapolis, Minnesota, USA*
[2]*Department of Pharmaceutics, University of Minnesota, Minneapolis, Minnesota, USA*
[3]*Surmodics, Eden Prairie, Minnesota, USA*
[4]*Boston Scientific, Maple Grove, Minnesota, USA*
[5]*Nanocopoeia, St. Paul, Minnesota, USA*

Dexamethasone PiFM Mapping (5 x 5 µm Image)

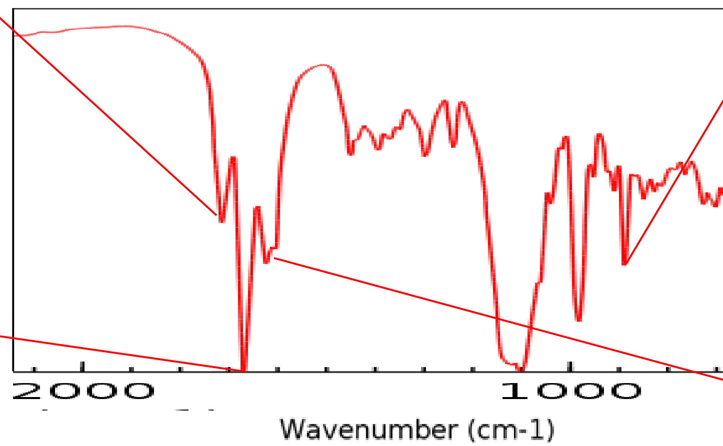




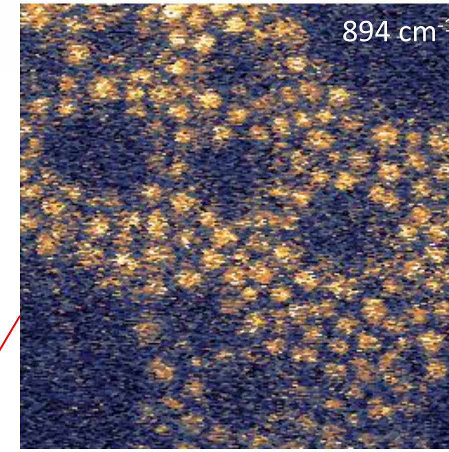
Dexamethasone

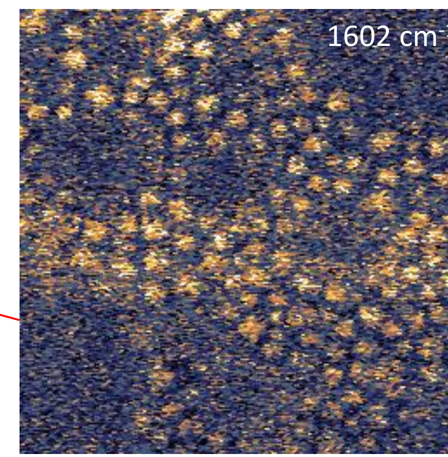


DEXAMETHASONE, DISODIUM PHOSPHATE
INFRARED SPECTRUM

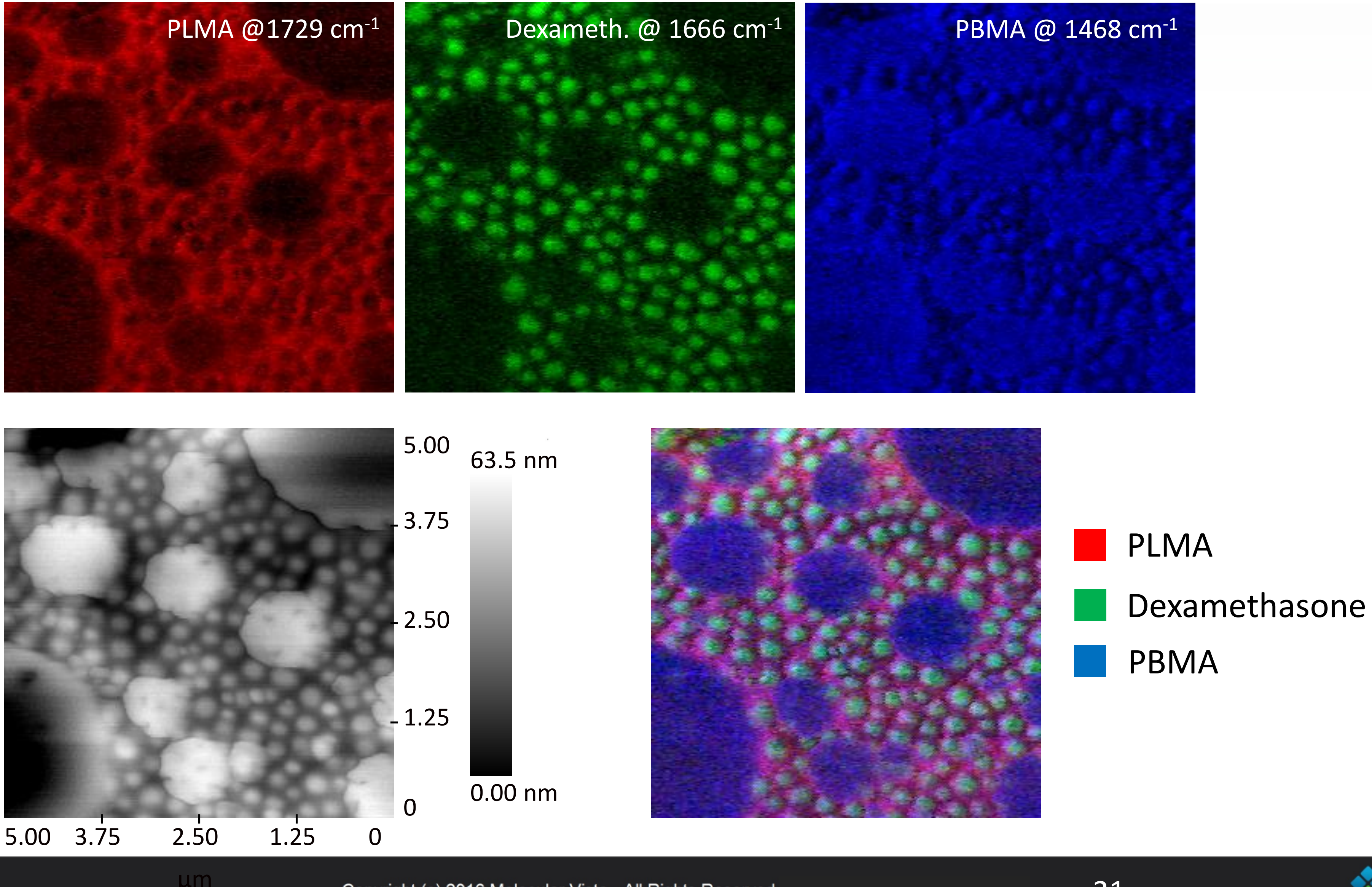


Chemistry WebBook (http://webbook.nist.gov/chemistry)





PBMA/PLMA/Dexamethasone (Pharmaceutical Composite)

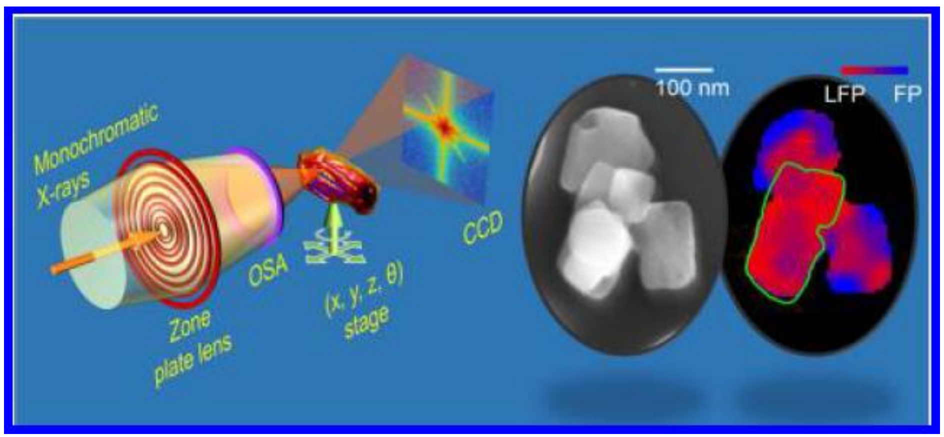


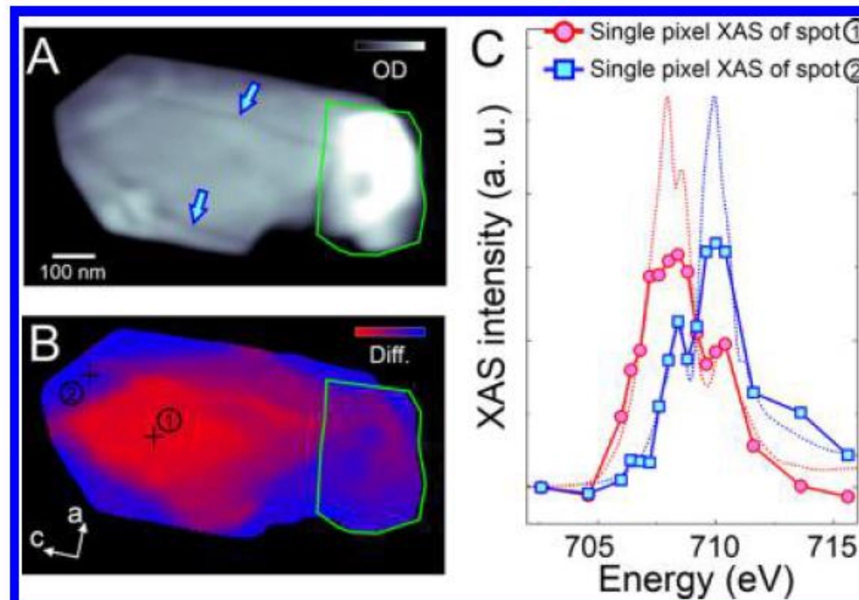
Li_xFePO_4 Battery Electrode Material

NANO LETTERS
Letter
pubs.acs.org/NanoLett

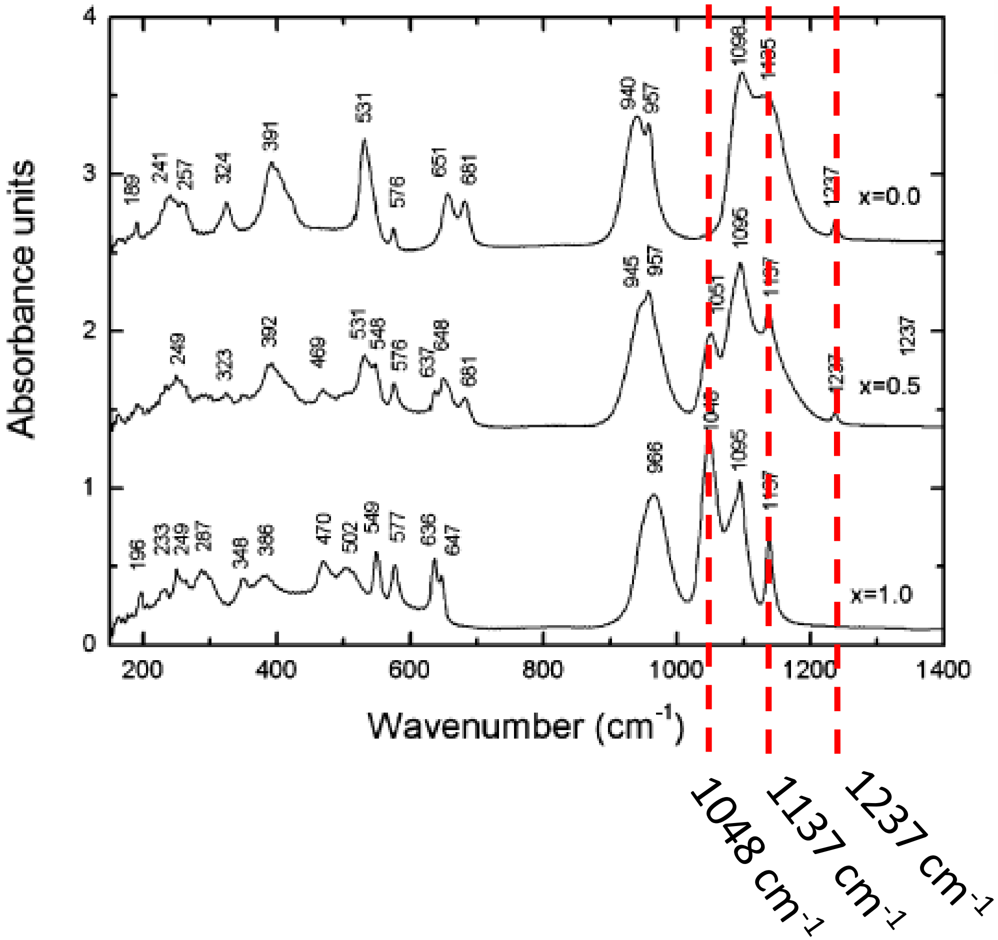
Dependence on Crystal Size of the Nanoscale Chemical Phase Distribution and Fracture in Li_xFePO_4

Young-Sang Yu,[†,‡,§,∥] Chunjoong Kim,[†] David A. Shapiro,[‡] Maryam Farmand,[‡] Danna Qian,[§] Tolek Tyliszczak,[‡] A. L. David Kilcoyne,[‡] Rich Celestre,[‡] Stefano Marchesini,[‡] John Joseph,[⊥] Peter Denes,[‡] Tony Warwick,[‡] Fiona C. Strobridge,[#] Clare P. Grey,[#,∇] Howard Padmore,[‡] Ying Shirley Meng,[§] Robert Kostecki,[∥] and Jordi Cabana*[,†]





FTIR of Li_xFePO_4 from Literature

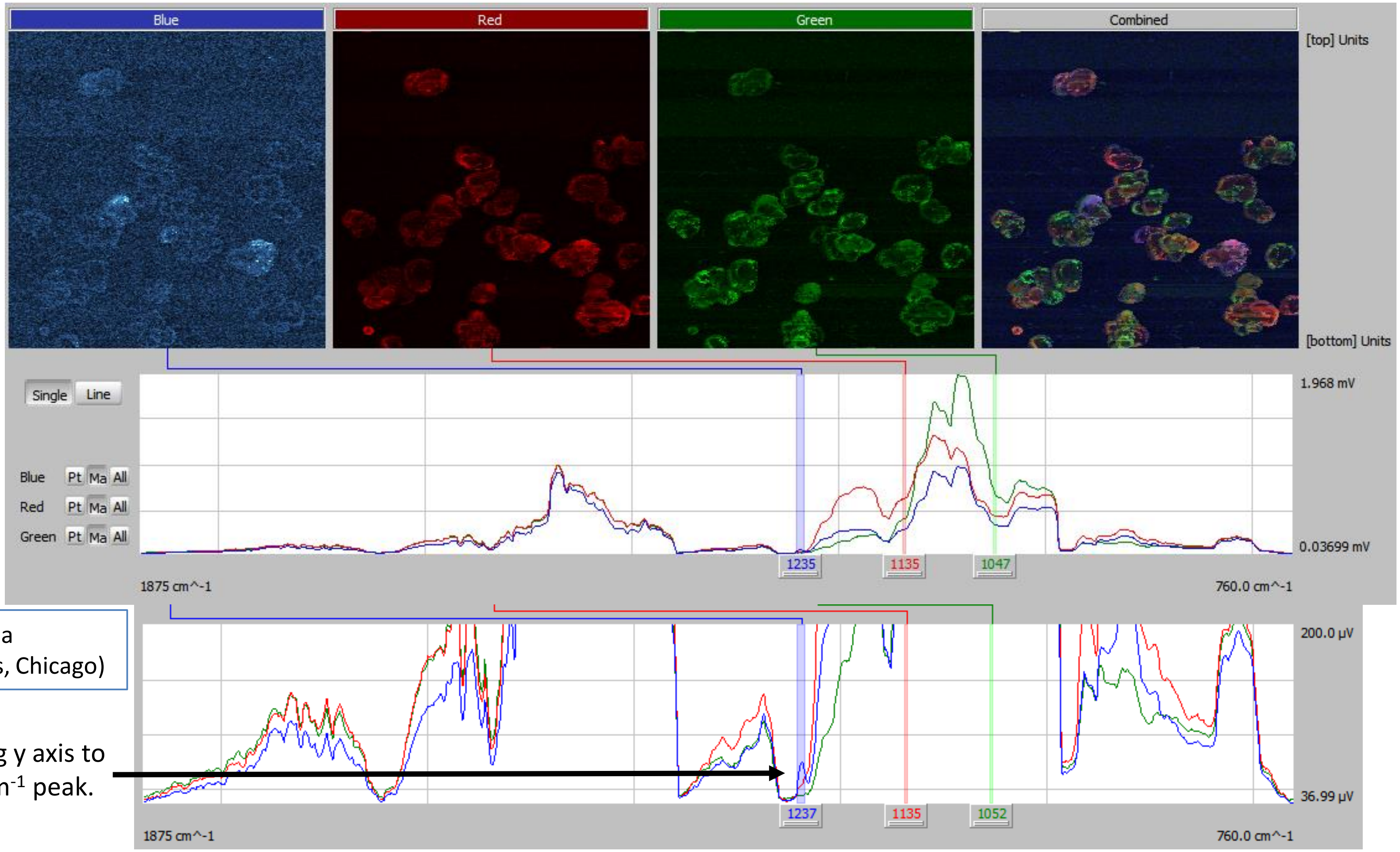


FTIR spectra of the three Li_xFePO_4 samples defined by their concentration of x in lithium

Absorption lines: 1048, 1137, and 1237 wavenumbers are of particular interest, as they vary the most based on lithium concentration.

Spectrochimica Acta Part A 65 (2006) 1007–1013

PiFM of Li_xFePO_4



Sample: Jordi Cabana
(University of Illinois, Chicago)

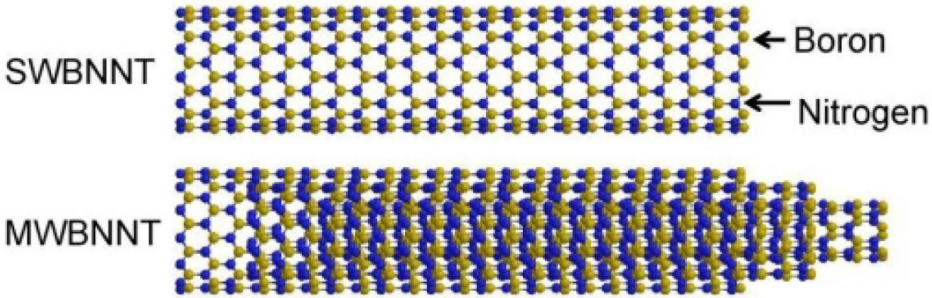
Zoom in along y axis to show 1235 cm^{-1} peak.

❖ Based on the FTIR information for Li_xFePO_4 we believe that the blue channel (1235 cm^{-1}) are areas of lowest Li_x concentration, green channel (1047 cm^{-1}) the highest concentration, and the red channel (1135 cm^{-1}) is in between.

BNNT Surface Phonon Polaritons (SPhP) - Background

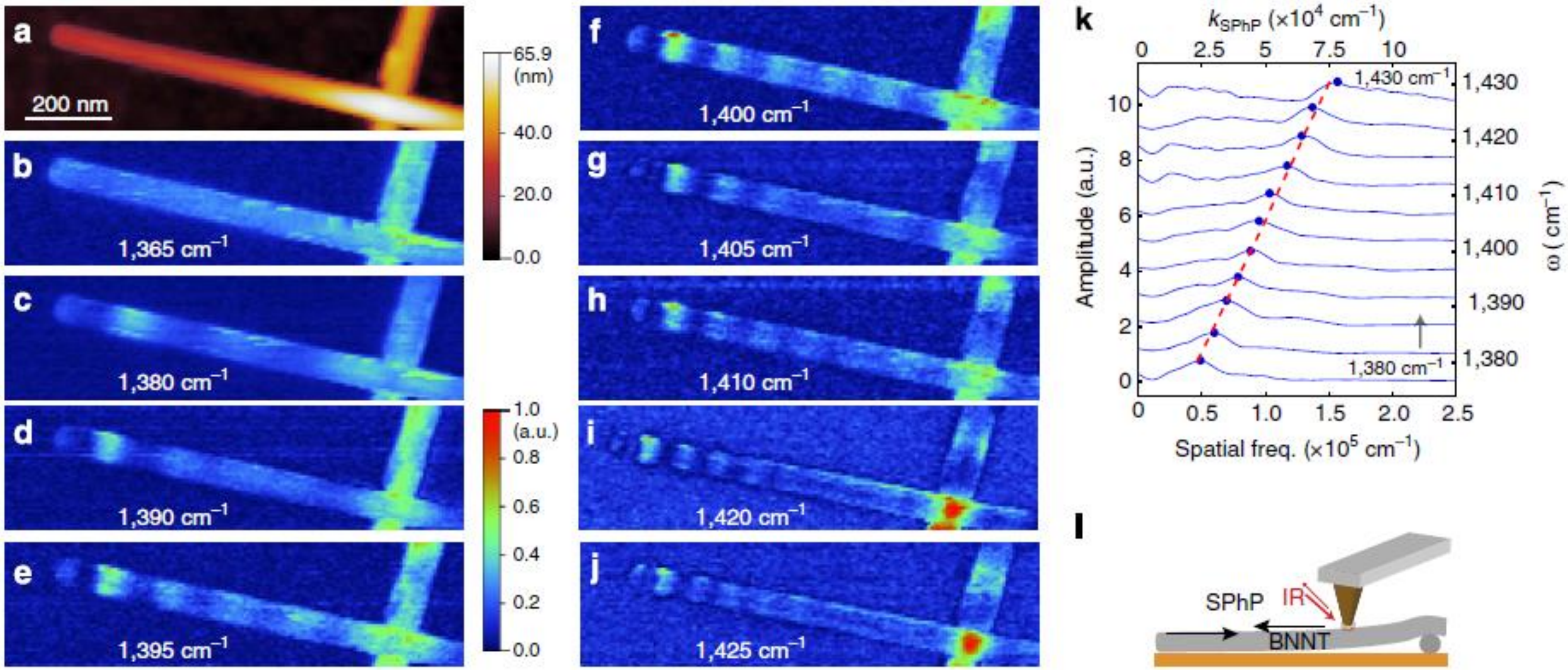
Structure of boron nitride nanotubes

Zhenghong Gao *et al.*, Nanobiomedicine **1** 7 (2014)

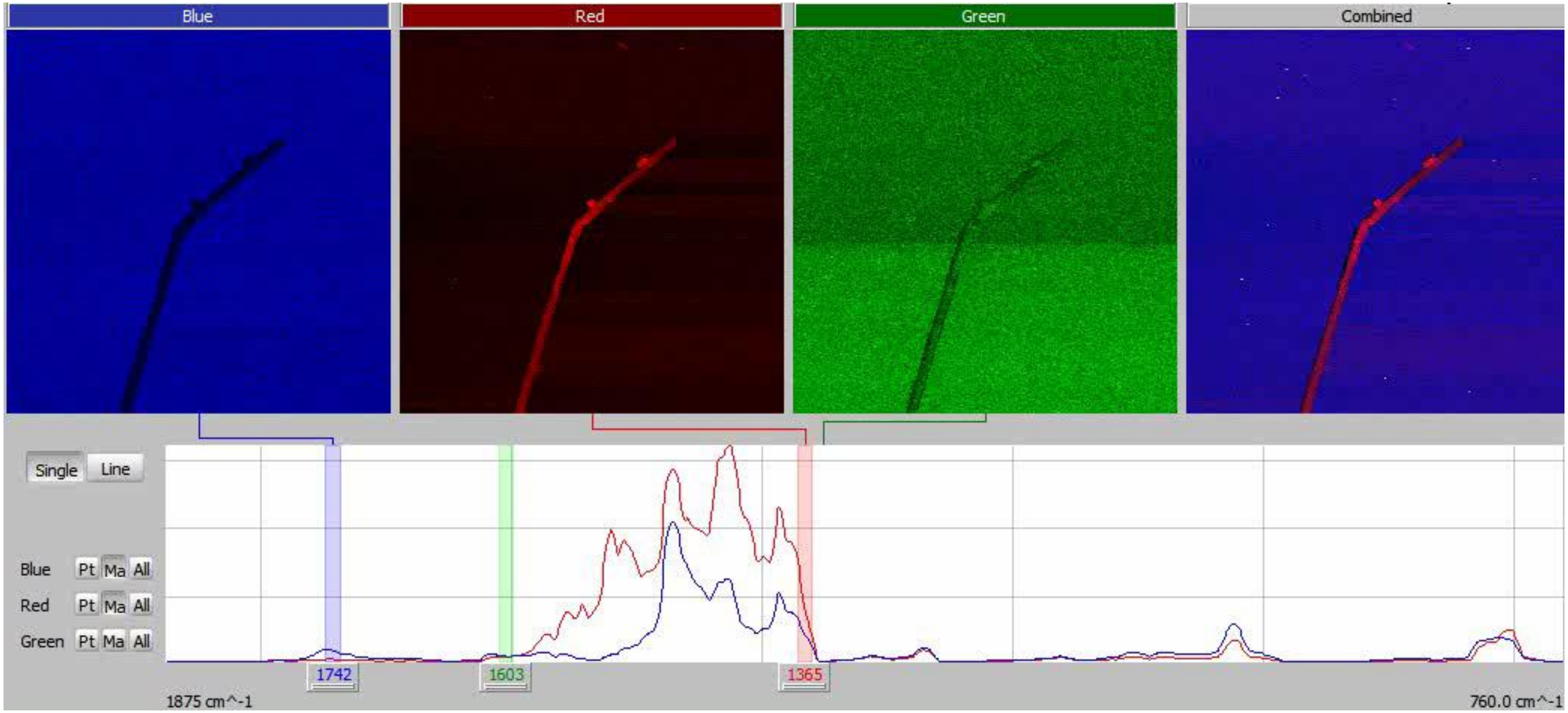


sSNOM of SPhP (images at multiple wavenumbers)

Xiaoji G. Xu *et al.*, Nature Comm., **1** 7 (2014)

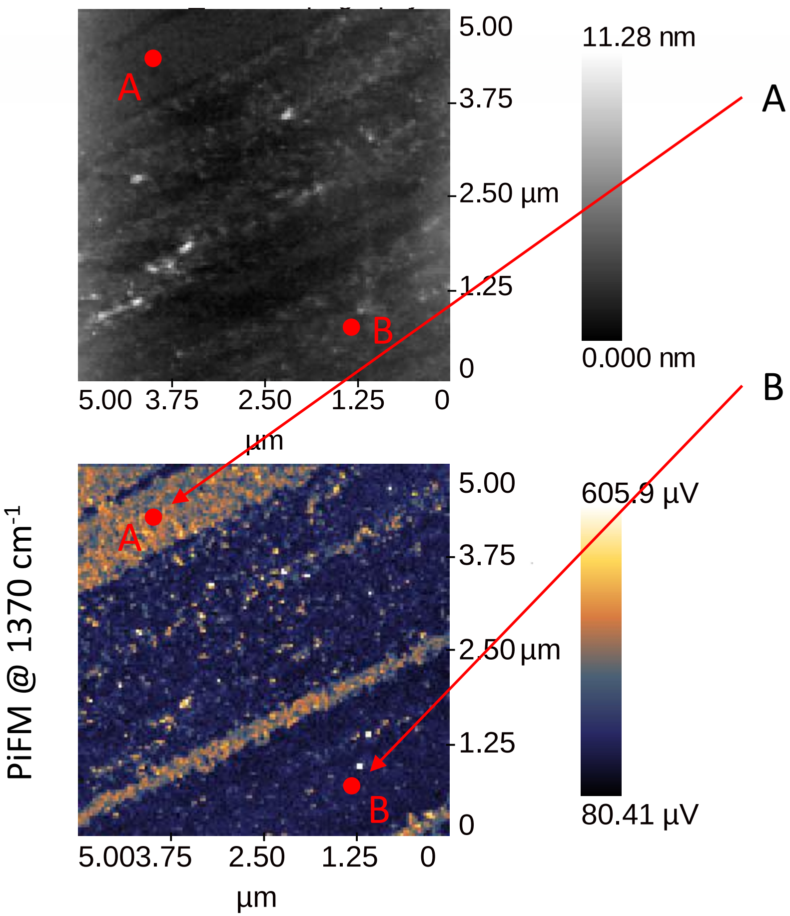


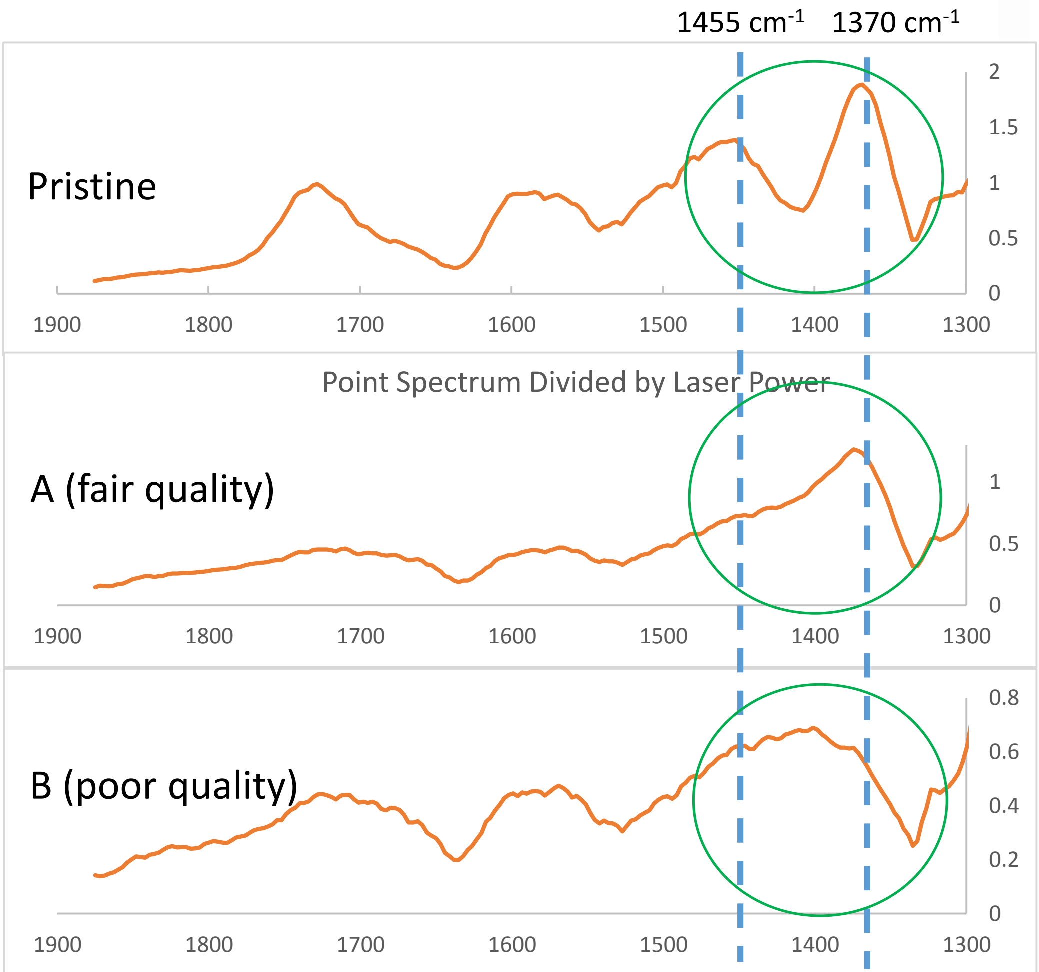
BNNT SPhP: 1603 – 1365 cm^{-1}



- ~100 nm diameter MWBNNT
- Absorption resonance at 1365 cm^{-1} (per literature)
- IR frequency-dependent crest/node patterns at frequencies above resonance
- Response similar to that observed by sSNOM (Xu et al.)

Hexagonal Boron Nitride (damaged by processing)

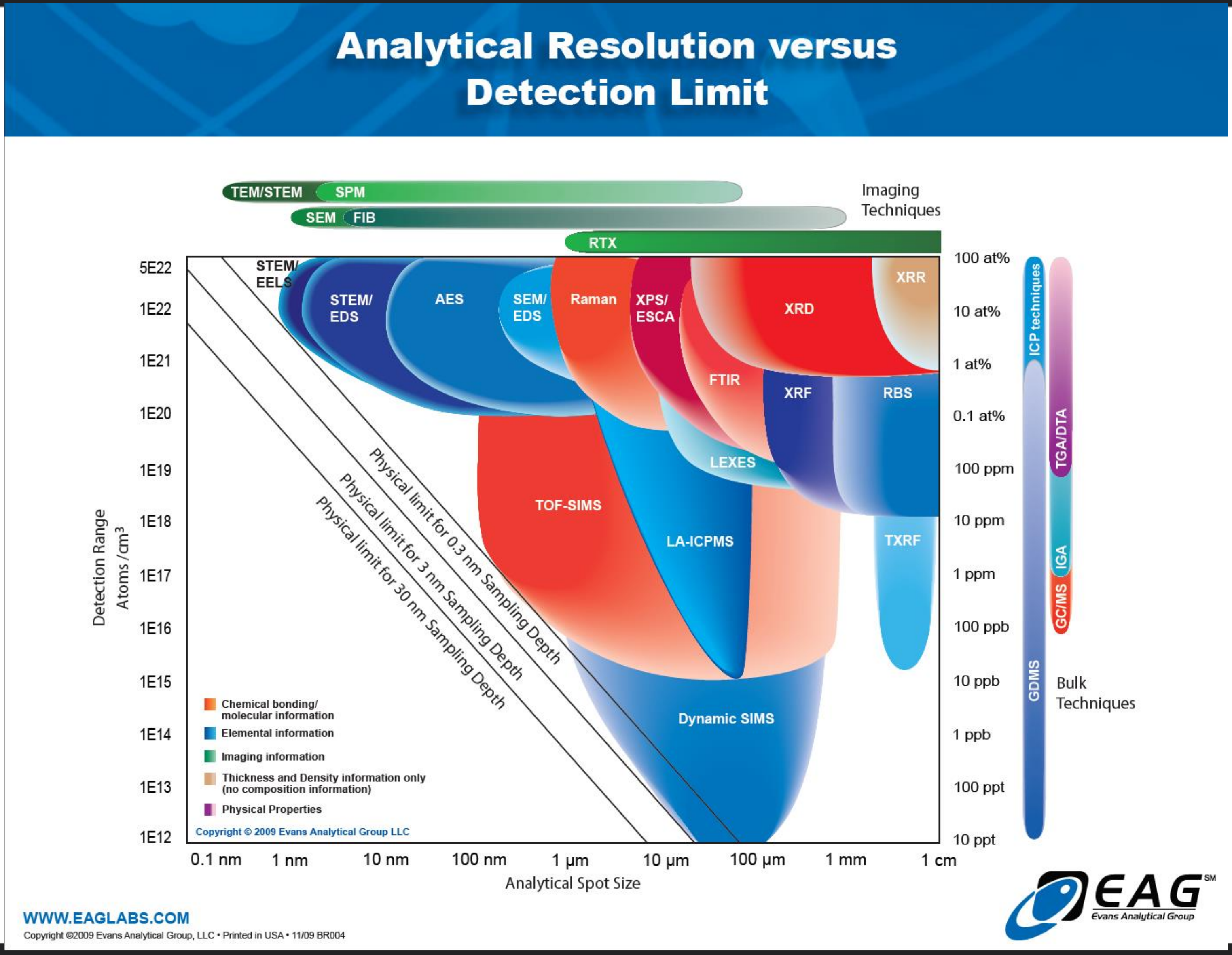




Some regions (A) retain a minimal peak at $1370\ cm^{-1}$ whereas some regions (B) do not.

Sample: UNIST, S. Korea

PiFM: A New Standard Chemical Mapping Technique



PiFM: A New Standard Chemical Mapping Technique

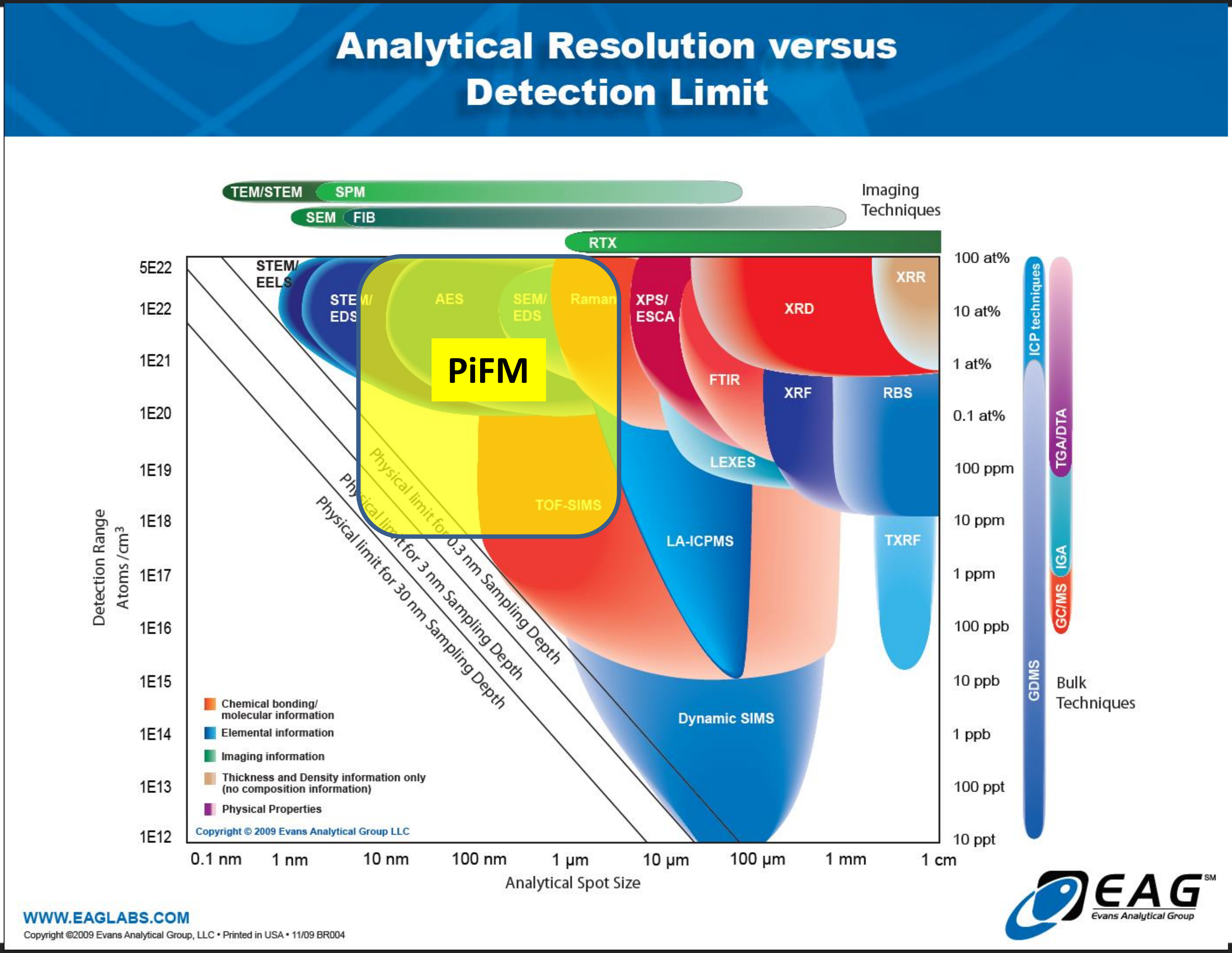


Photo-induced Force Microscopy: Summary

- **PiFM generates IR spectra with nm-scale spatial resolution**
  - Robust, high-SNR technique for nm-scale IR spectroscopy (easy!)
  - Ideal for chemical mapping of molecular materials, including organics
  - Mechanical detection of dipole forces eliminates background scattering effects
  - Resolution unaffected by sample thickness or thermal properties
  - A significant step forward in IR spectroscopic microscopy

- **Hyperspectral imaging is a powerful PiFM mode which generates and stores a full spectrum at each image pixel**
  - Individual chemical species “light up” at specific wavelengths, depending on each material’s IR absorption spectrum

- **Sample results shown here include:**
  - Chemical mapping of self-assembled block copolymer patterns
  - Chemical mapping of three-component pharmaceutical composite
  - Viewing of wavelength-dependent surface phonon polariton crest/node patterns on boron nitride nanotube

- **PiFM may become a standard analytical chemical mapping technique for use in industry/academia**