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

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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

Elemental mapping of a device structure by EDS (EDX)

- 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**

Image credit:

- Polymers prone to damage to X-ray
- Synchrotron sources are not easily accessible
FTIR: Infrared Absorption “Chemical Fingerprint” Spectrum

- Detailed spectra for analysis and identification of molecular materials
- Spatial mapping resolution limited by optical diffraction limit ($\sim 1 \, \mu m$)

Detailed absorption spectrum – chemical “fingerprint”

Image credit: Mudunkotuwa et al., Analyst 139, 870-881 (2014).
Existing IR-NF Probe Techniques: Optical vs. Mechanical Detection

**Scattering techniques (sSNOM or TERS)**

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

**Photothermal imaging (PTIR)**

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

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D. Nowak thesis
Photo-induced Force Microscopy (PiFM)

- Mechanical detection
- Dipole-dipole forces between sample and tip
Photo-induced Force Microscopy (PiFM)

Image force microscopy of molecular resonance: A microscope principle

I. Rajapaksa, K. Uenal, and H. Kumar Wickramasinghe
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(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)

**PHOTO-INDUCED FORCE:**
- **D1↔D2:** direct interaction (dispersive peak shape; weak in IR)
- **D1↔D3:** “image force” (nondispersive peak shape; strong in IR)
- **Magnitude:** \( F_{PIFM} \sim (\text{sample polarization})^2 / z^4 \)
- Very high resolution limited by tip radius
- Minimal thermal contribution
Mid-IR allows access to “molecular fingerprint region”
The Instrument: “Vista IR”

AFM head with integrated parabolic mirror on 3D piezo motor

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)

PiFM of PS-\textit{b}-PMMA Block Copolymer: \textasciitilde10 nm Lateral Resolution

(40 nm pitch “fingerprint” patterns)

Sample: D. Sanders et al., IBM Almaden

PMMA homopolymer

PS homopolymer

Is PIFM responding to AFM Phase?

(40 nm pitch “fingerprint” patterns)

Topography

PMMA

PS

Combined

2.62 nm

0.00 nm

100 nm

Sample: D. Sanders et al., IBM Almaden

1733 cm\(^{-1}\)

1492 cm\(^{-1}\)

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

Topography

<table>
<thead>
<tr>
<th>Islands</th>
<th>PiFM - PS @ 1493 cm(^{-1})</th>
<th>PiFM - PTMSS @ 1599 cm(^{-1})</th>
</tr>
</thead>
</table>

| Holes   | | |
|---------| | |
|         | | |

Surface material has stronger response – penetration depth is several nanometers

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

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DNA Origami

Sample provided by: R. Berger
Max Planck Institute

1720 cm\(^{-1}\) Amide I

1000 cm\(^{-1}\) Mica

Combined

Topography

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:

Hyperspectral image video:

Chemical Map Images by Photo-induced Force Microscopy

Sample Name: Perovskite

Measured by Vista-IR

Sample: David Ginger, Raj Giridharagopal, Alex Jen - Univ. of Washington
Hyperspectral Image of 2D Perovskite
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 Chen2 and Raj
Suryanarayanan,2 Eric Vandre,1 Jeannette Polkinghome,4 John Foley,5 Robert Hoerr5

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2Department of Pharmaceutics, University of Minnesota, Minneapolis, Minnesota, USA
3Surmodics, Eden Prairie, Minnesota, USA
4Boston Scientific, Maple Grove, Minnesota, USA
5Nanocopeia, 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)

PLMA @ 1729 cm\(^{-1}\)
Dexameth. @ 1666 cm\(^{-1}\)
PBMA @ 1468 cm\(^{-1}\)

[Image of molecular structures and spectra]

- Red: PLMA
- Green: Dexamethasone
- Blue: PBMA
Li$_x$FePO$_4$ Battery Electrode Material

Dependence on Crystal Size of the Nanoscale Chemical Phase Distribution and Fracture in Li$_x$FePO$_4$

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

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FTIR of $\text{Li}_x\text{FePO}_4$ from Literature

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

FTIR spectra of the three $\text{Li}_x\text{FePO}_4$ samples defined by their concentration of $x$ in lithium
PiFM of Li$_x$FePO$_4$

Based on the FTIR information for Li$_x$FePO$_4$ 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.

Sample: Jordi Cabana (University of Illinois, Chicago)
BNNT Surface Phonon Polaritons (SPhP) - Background

Structure of boron nitride nanotubes
Zhenghong Gao et al., Nanobiomedicine 17 (2014)

sSNOM of SPhP (images at multiple wavenumbers)
Xiaoji G. Xu et al., Nature Comm., 17 (2014)
• ~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.

Pristine

Point Spectrum Divided by Laser Power

A (fair quality)

B (poor quality)

Sample: UNIST, S. Korea
PiFM: A New Standard Chemical Mapping Technique
PiFM: A New Standard Chemical Mapping Technique

Analytical Resolution versus Detection Limit

EAG Labs

WWW.EAGLABS.COM

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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**