A NOVEL LARGE AREA IMAGING NEXAFS SPECTROMETER FOR COMBINATORIAL CHEMICAL AND STRUCTURAL ANALYSIS

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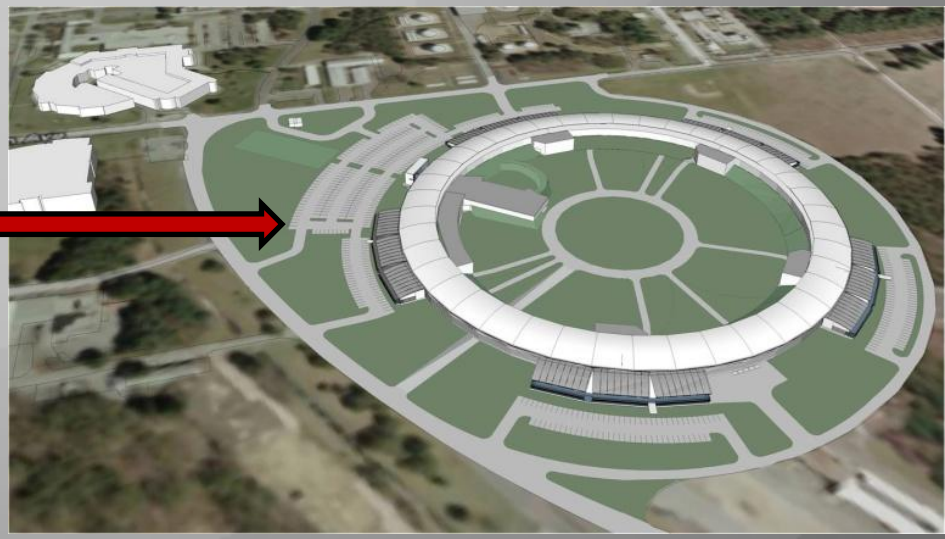
LARIAT NEXAFS Imaging Spectrometer

Where Does It Live?

Synchrotron Methods and Measurements

Current home of LARIAT MKI
NSLS I
BNL
Beamline U7A
(commissioned July 2008)

Future home of LARIAT MK II
NSLS II
BNL
(2012-2013)



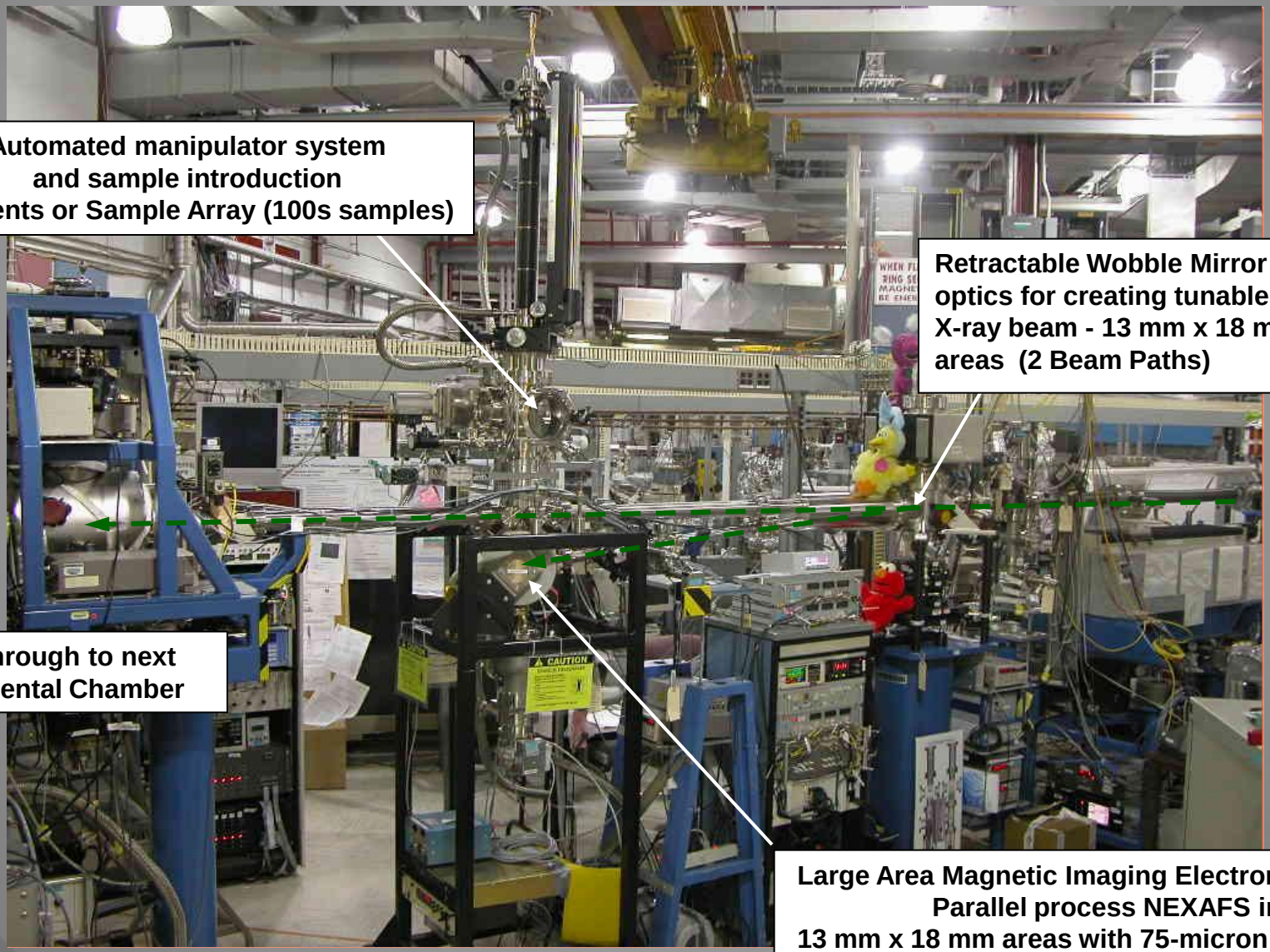
LARIAT NEXAFS Imaging Spectrometer

Brookhaven National Laboratory

Beamline U7A

Synchrotron Methods and Measurements

New automated endstation for full field NEXAFS imaging (parallel process)



Automated manipulator system and sample introduction Gradients or Sample Array (100s samples)

Retractable Wobble Mirror optics for creating tunable Soft X-ray beam - 13 mm x 18 mm areas (2 Beam Paths)

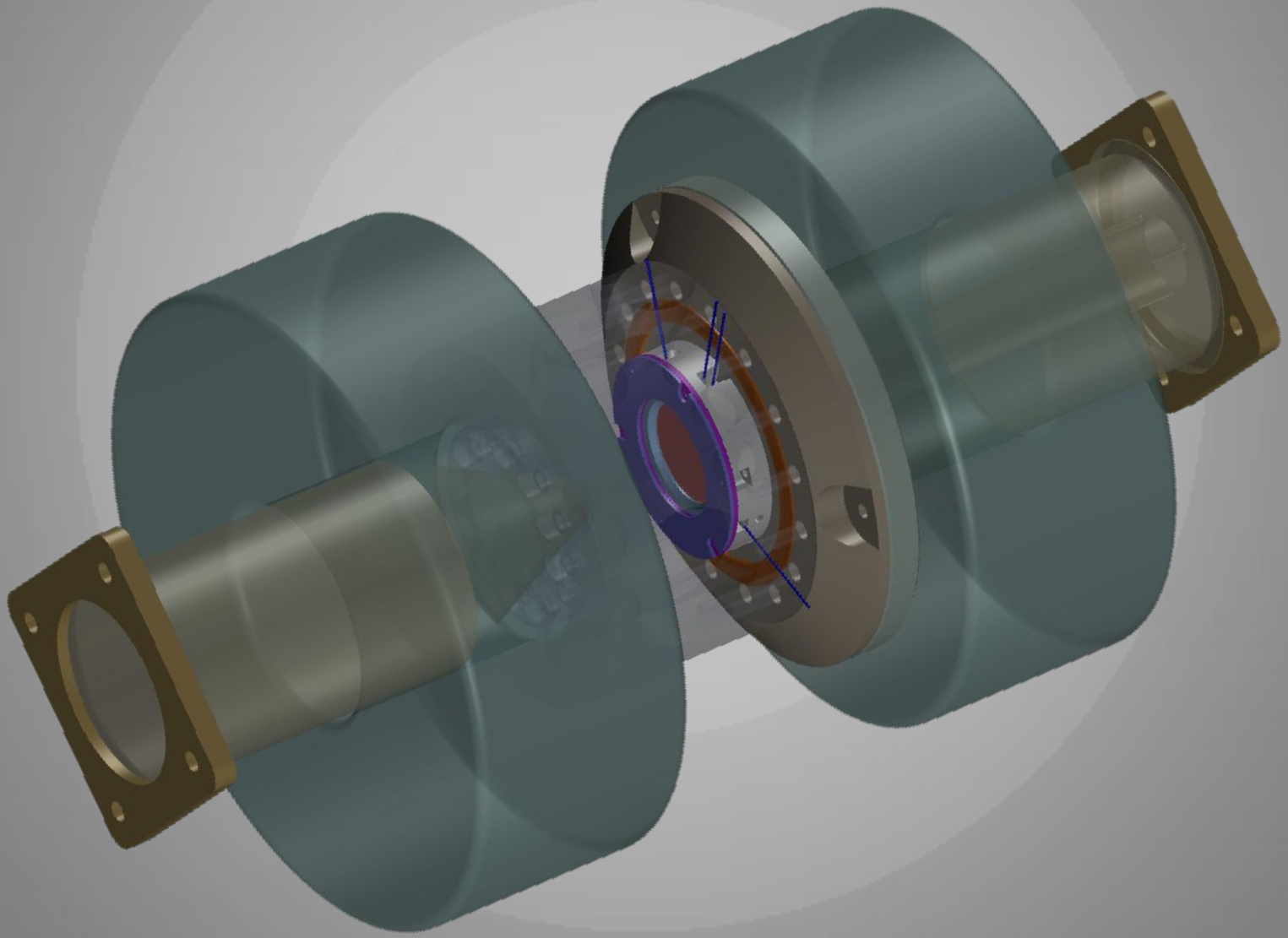
Pass Through to next Experimental Chamber

Large Area Magnetic Imaging Electron Energy Ana
Parallel process NEXAFS imaging
13 mm x 18 mm areas with 75-micron spatial resol

LARIAT NEXAFS Imaging Spectrometer

Brookhaven National Laboratory
Beamline U7A

Spectrometer Overiew



LARIAT NEXAFS Imaging Spectrometer: Principle of Operation

NIST SBIR Phase II Awarded to E. L. Principe & Assoc. (Imaging NEXAFS detector)

"Large Area Imaging Two-Dimensional Electron Energy Analyzer"

Synchrotron Methods and Measurements

- Cyclotron Radius determines resolution*.

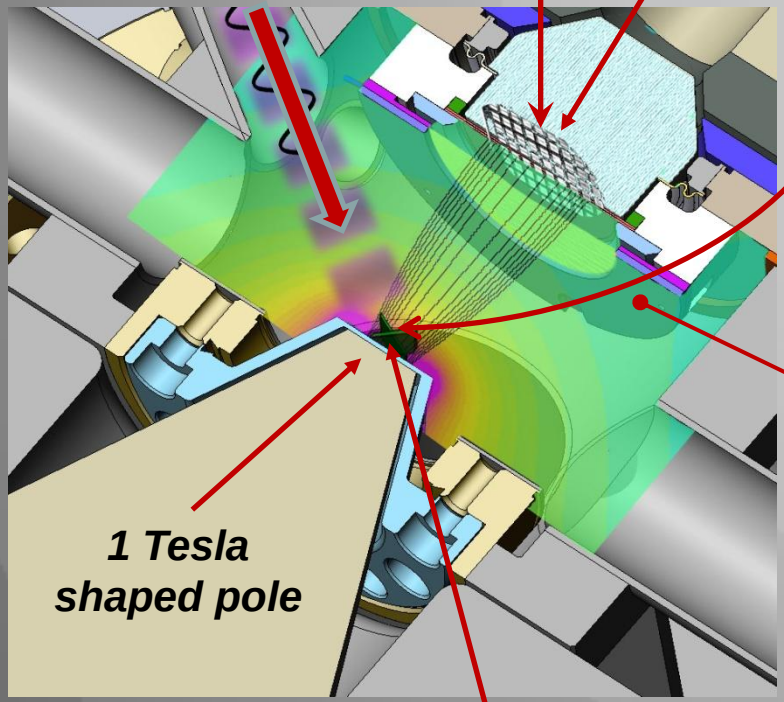
$$CR_{max} = \frac{3.4 \times \sqrt{(E_T)}}{B}$$

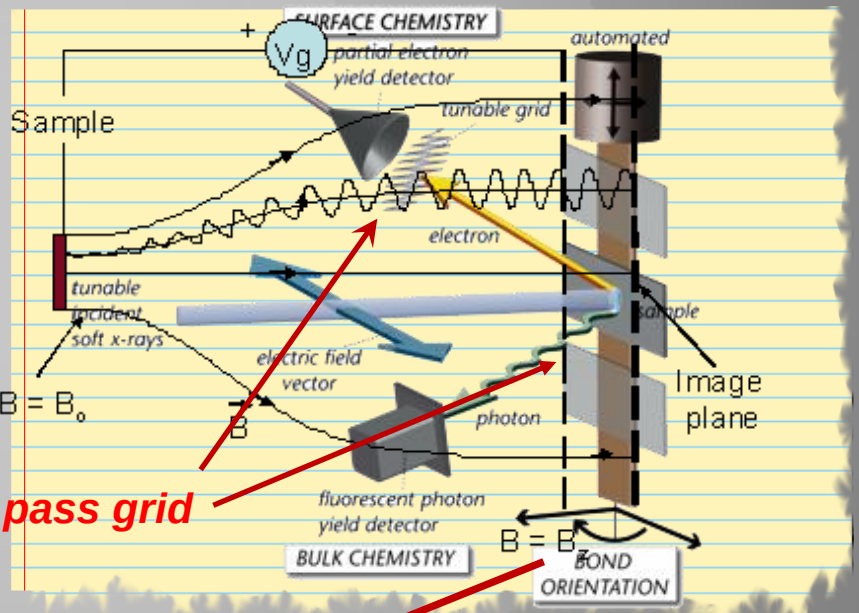
For electron energies in electron volts where CRmax is in microns

$$Mag = \sqrt{\frac{B_0}{B}} \cong 2$$

NEXAFS Image

Soft x-ray beam
15 mm x 20 mm





High pass grid

- Diverging magnetic field converts transverse energy into energy along B field lines.
- If field decreases from B_0 to B, transverse energy decreases from E_t to $E_t(B/B_0)$

* To 1st order

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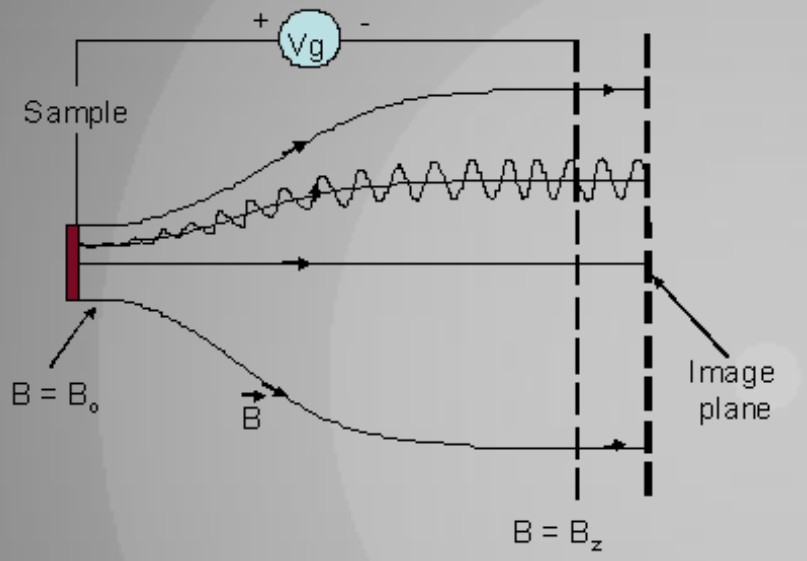
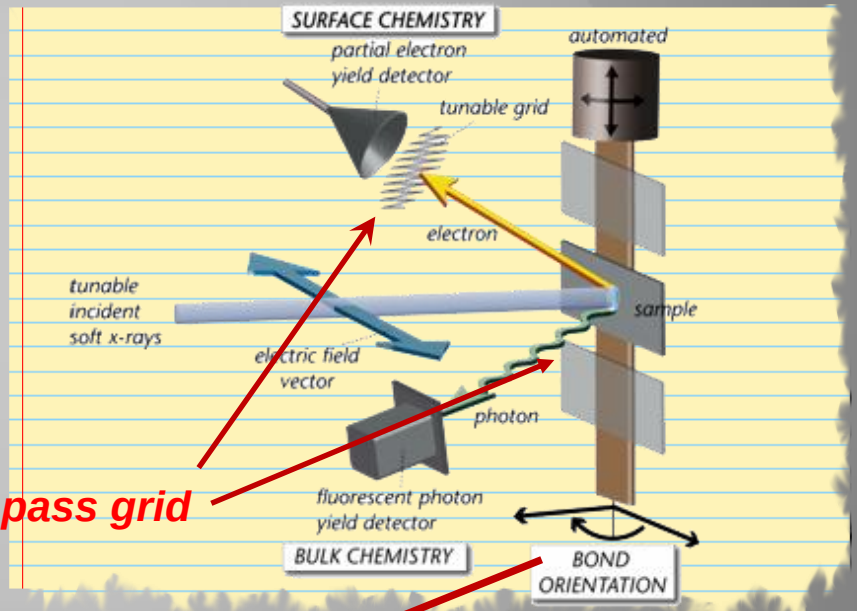
Synchrotron Methods and Measurements





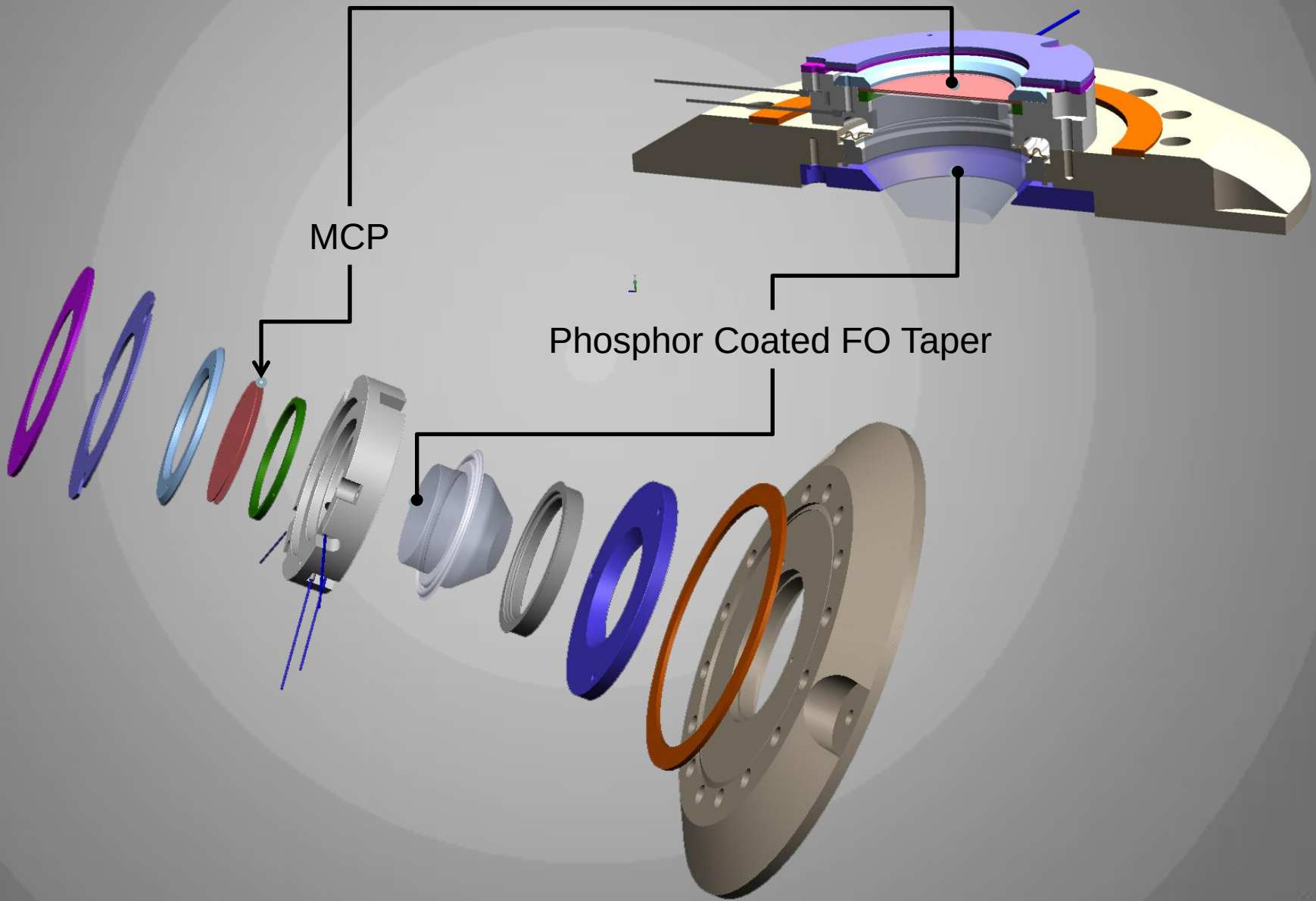
High pass grid

- Diverging magnetic field converts transverse energy into energy along B field lines.
- If field decreases from B_o to B, transverse energy decreases from E_t to $E_t(B/B_o)$

* To 1st order

LARIAT NEXAFS Imaging Spectrometer: Detection System

MCP / Phosphor / Optical taper / CCD Camera

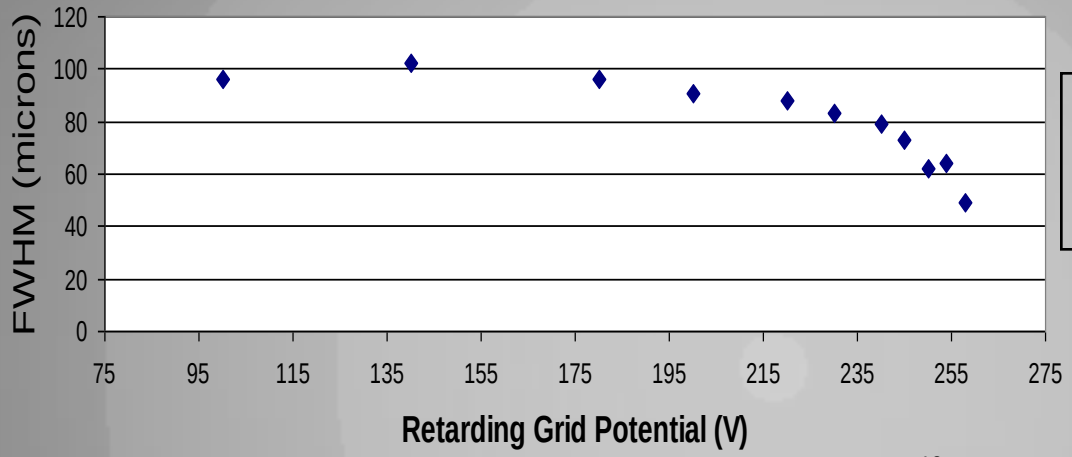


LARIAT NEXAFS Imaging Spectrometer: Results

Spatial Resolution ~ 50 microns at high retarding grid bias

Synchrotron Methods and Measurements

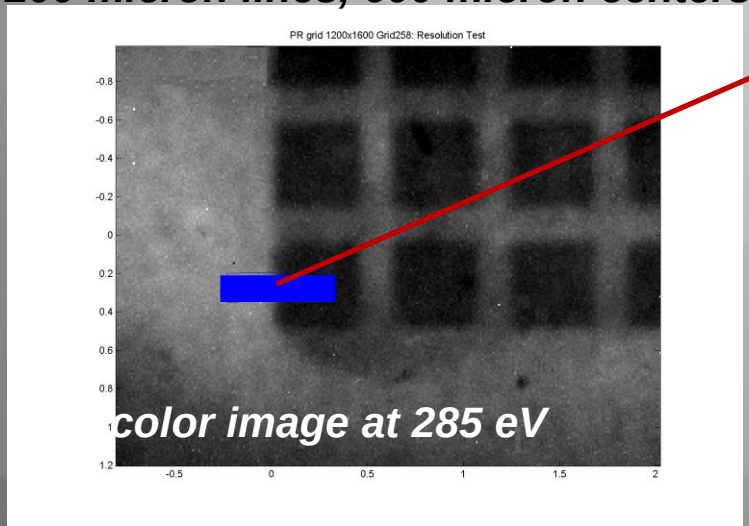
Electrons with axial energy below the grid potential are rejected

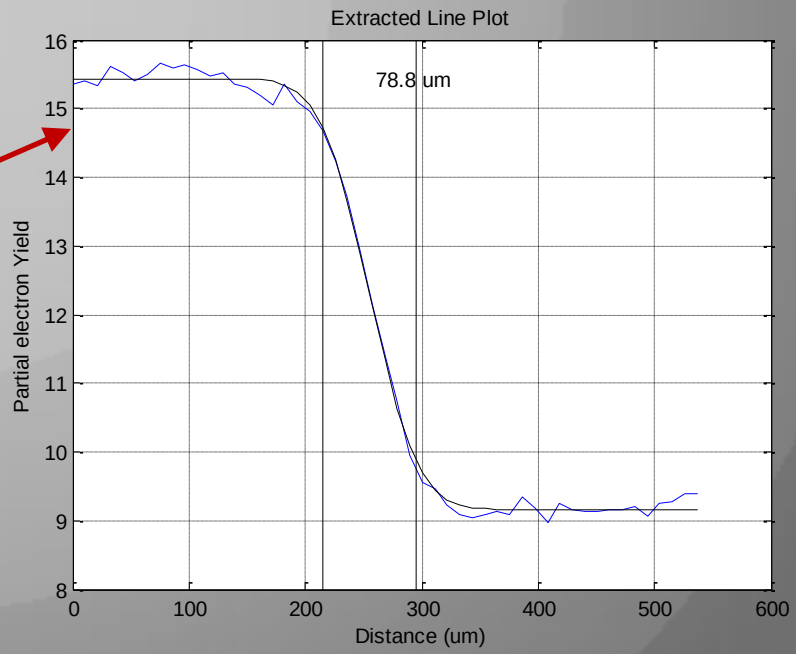


Carbon NEXAFS images
13.5 mm x 18 mm = 600x800
i.e. ~ 22.5 microns / pixel

78 microns at 240 volts

Photoresist grid on Si
200 micron lines, 600 micron centers



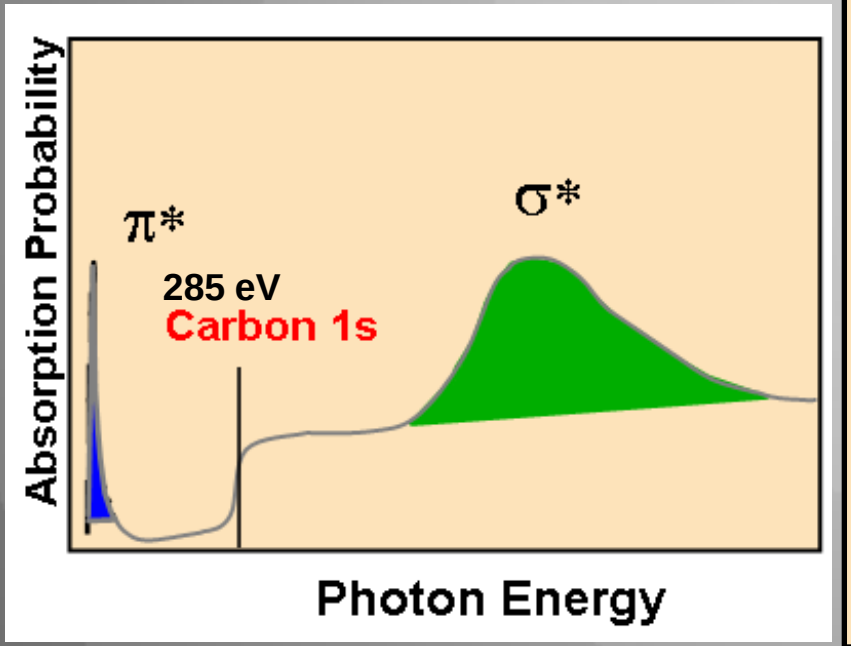


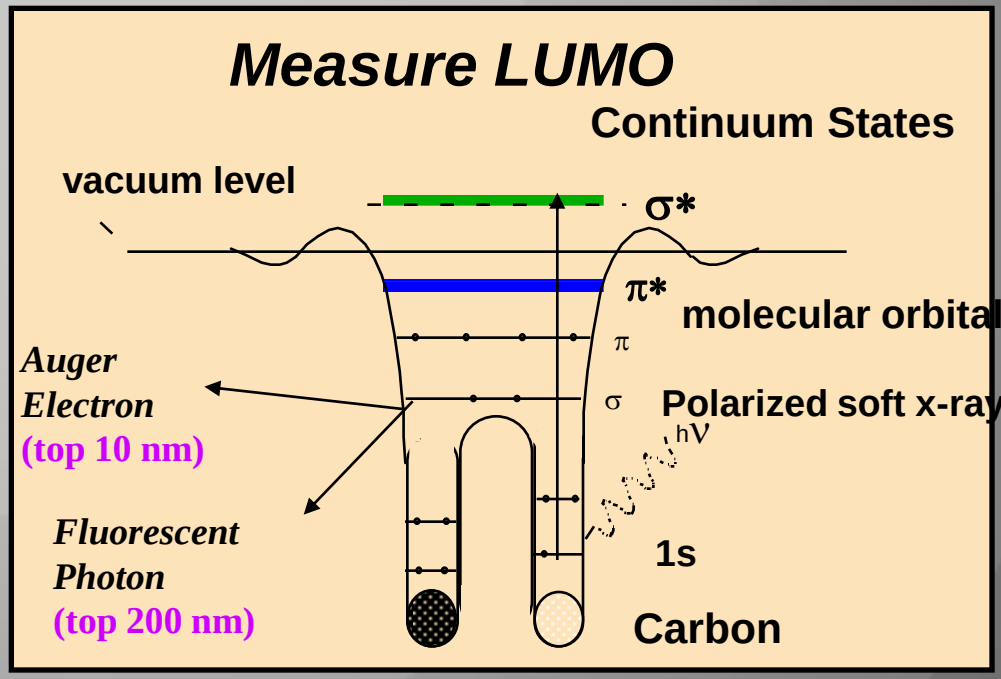
High Throughput NEXAFS: Soft Matter Structure and Chemistry

Synchrotron Methods and Measurements

Near Edge X-ray Absorption Fine Structure (NEXAFS) ***Soft X-rays 175 – 1300 eV***

Photon energy scanning	⟷	• Elemental selectivity
Resonance/Final State/Orbital	⟷	• **Chemical bond sensitivity**
Electric field vector incidence	⟷	• **Orientation Information**
Adjusting the Grid Voltage	⟷	• Depth selectivity

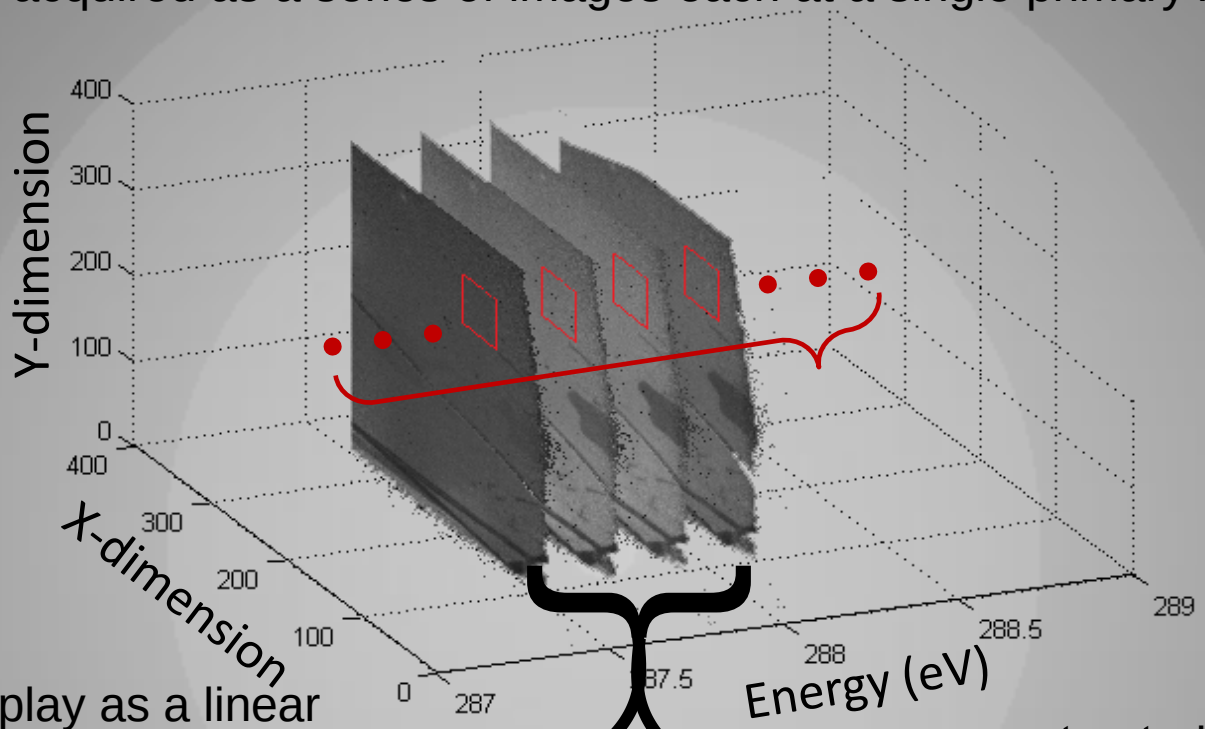




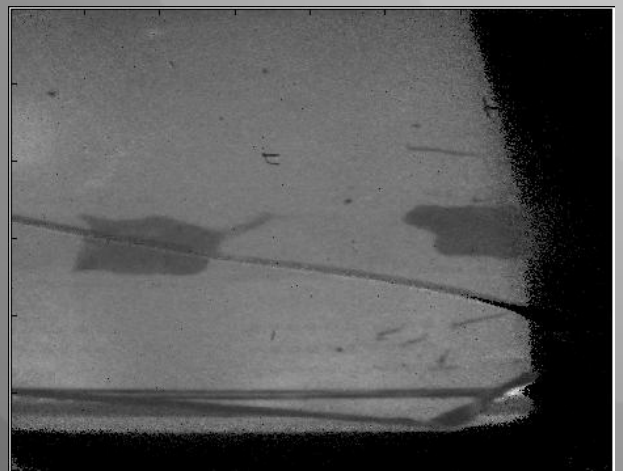
LARIAT NEXAFS Imaging Spectrometer: Data Reduction

Hyperspectral Imaging Acquisition and Analysis Package

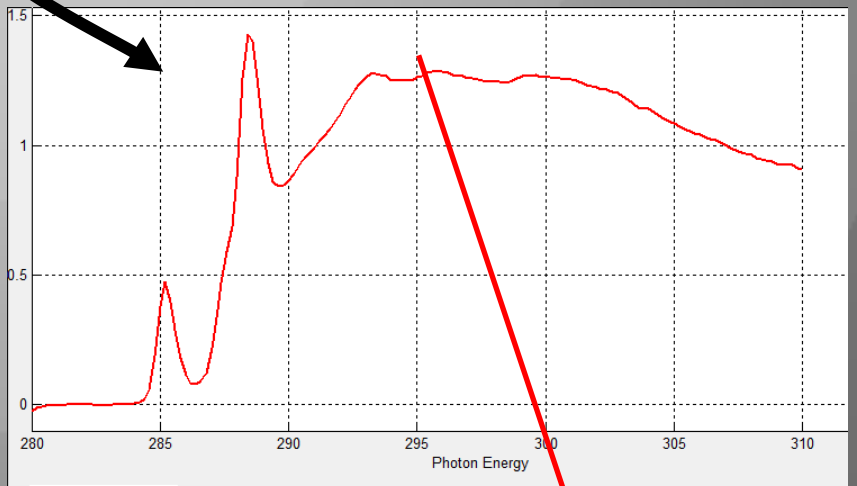
Data is acquired as a series of images each at a single primary x-ray energy



And display as a linear combination of images…



…or extracted spectra

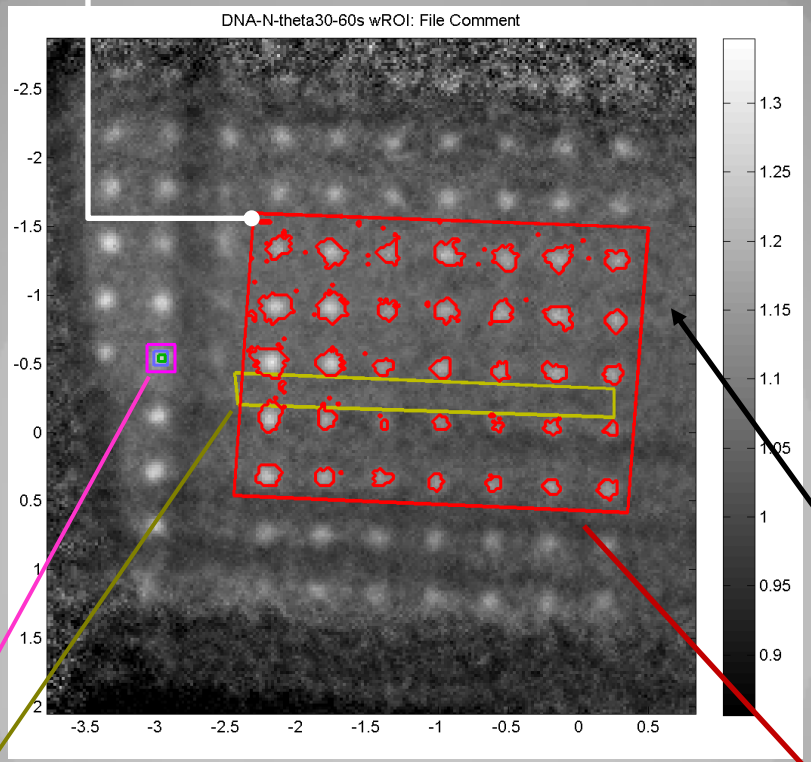


LARIAT NEXAFS Imaging Spectrometer: Data Reduction

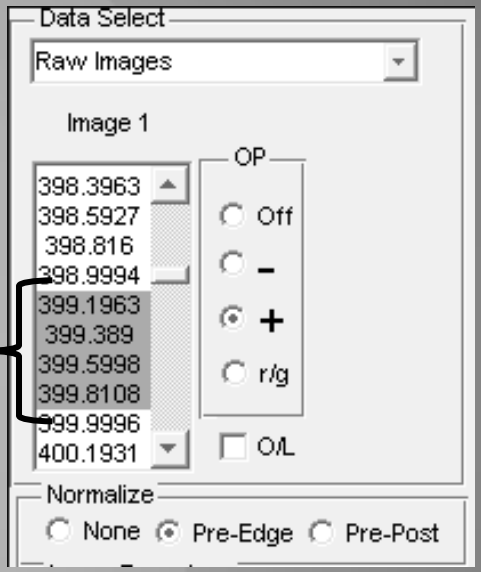
Hyperspectral Imaging Acquisition and Analysis Package

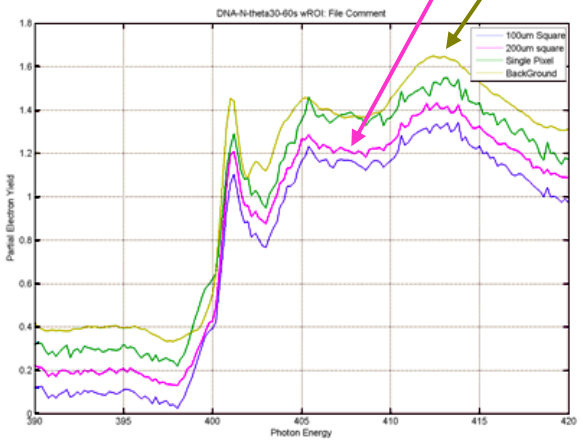
Threshold selection ROI

- "Regions of Interest" – aggregations of pixels used to define spectra can be defined in multiple ways including arbitrary polygons, squares of fixed size and positive of negative thresholds



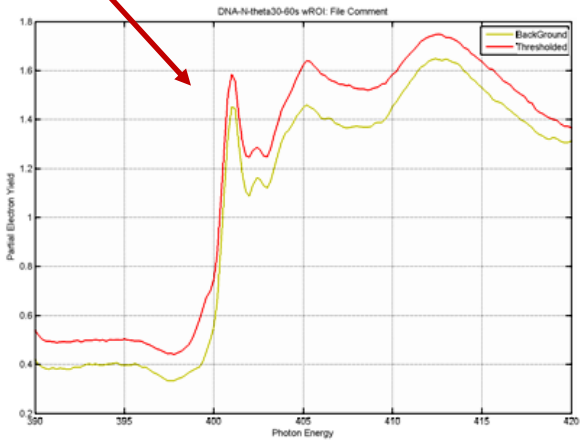
Composite is sum of normalized images at energies 399.2 : 399.8eV





Spectra can be extracted from areas as small as single pixels….

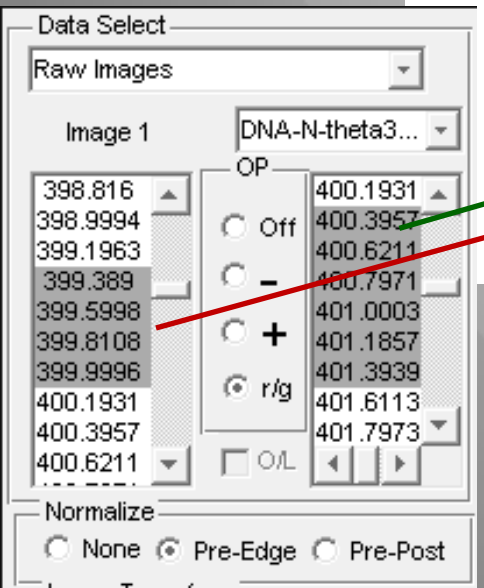
……or aggregated from multiple areas for improved S/N

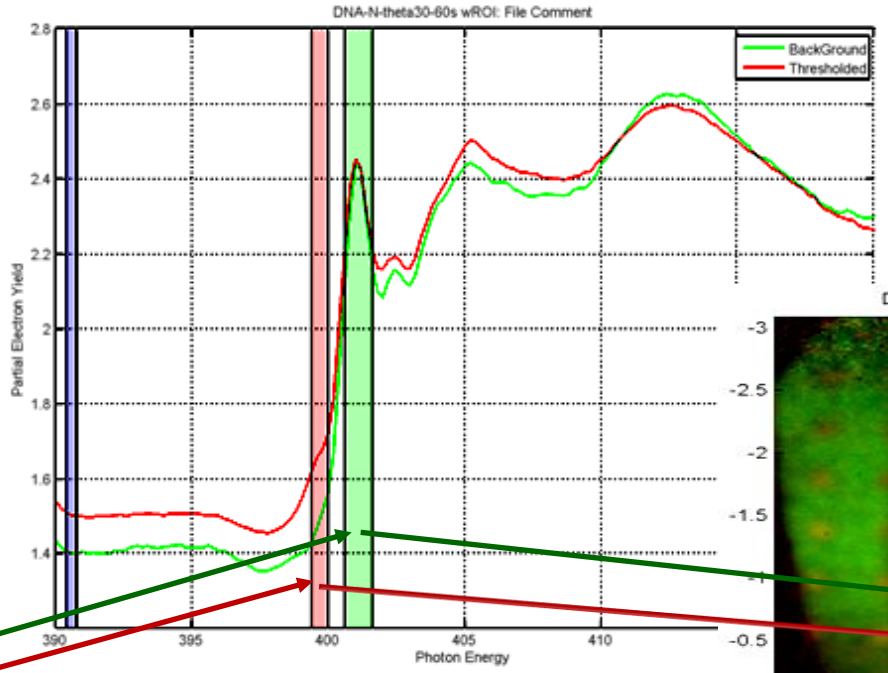


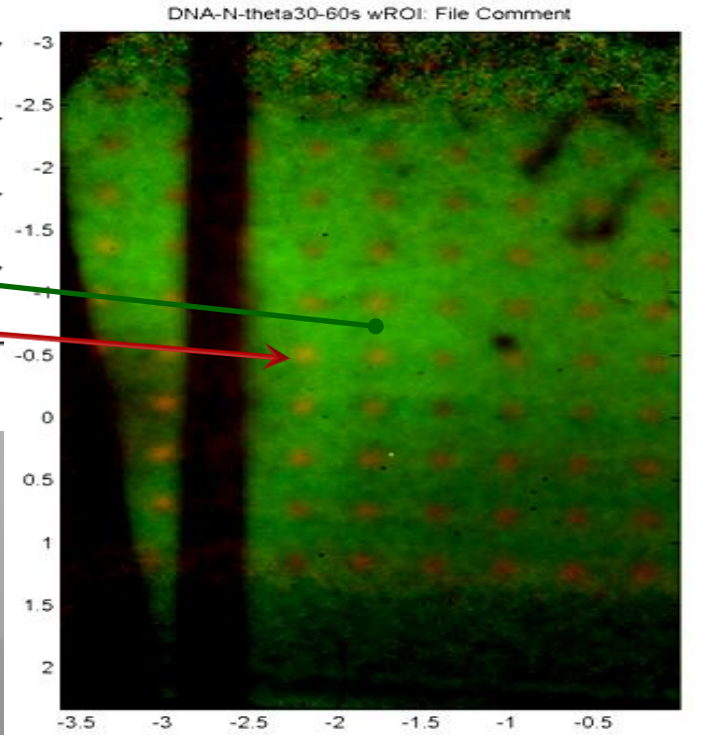
LARIAT NEXAFS Imaging Spectrometer: Data Reduction

Hyperspectral Imaging Acquisition and Analysis Package

Images are constructed from portions of the spectra to show spatial distribution of chemical information







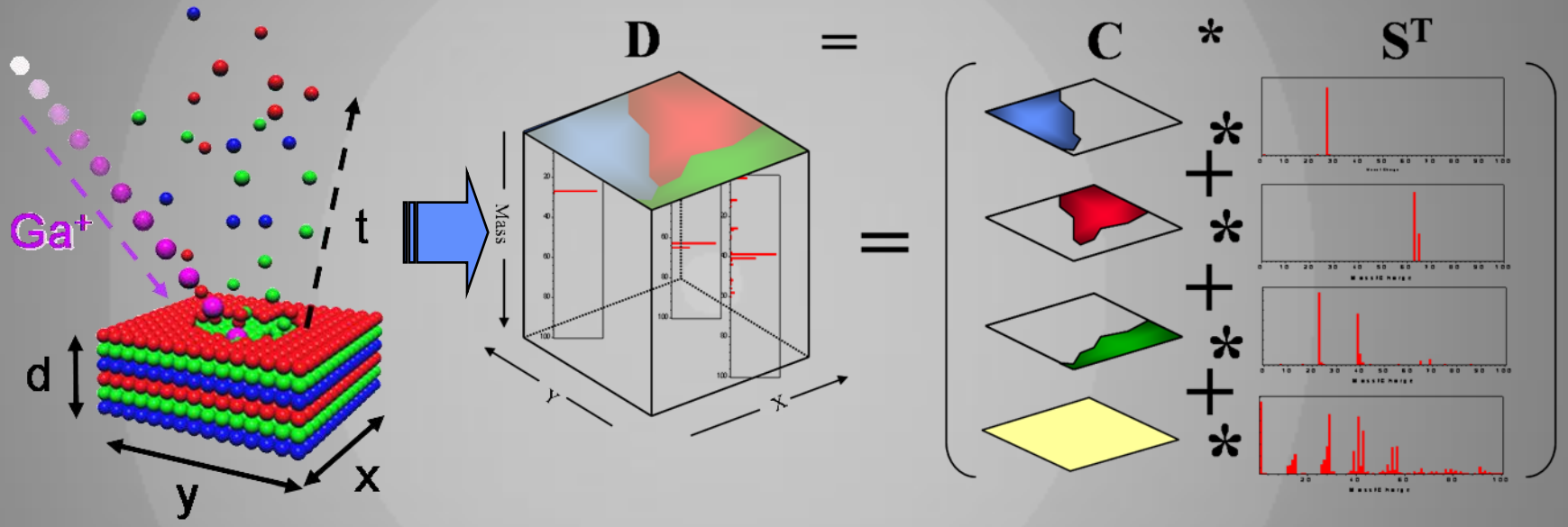
LARIAT NEXAFS Imaging Spectrometer: Data Reduction

Hyperspectral Imaging Acquisition and Analysis Package

Synchrotron Methods and Measurements

Multivariate Analysis of NEXAFS Spectrum Images of ssDNA Chips

AXSIA – Automated eXpert Spectral Image Analysis



Reduces thousands of spectra to a few, with no loss of chemical information.

Uses information from all pixels to improve the spectral signal/noise.

No user bias or assumptions required for component identification*.

****Other than non-negativity, linear additive model and Poisson noise characteristics***

Rapidly finds the small, hidden features of the chemistry or microstructure.

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Tony Ohlhausen

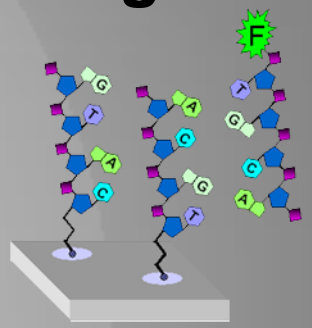
Sandia National Laboratories

LARIAT NEXAFS Imaging Spectrometer: Data Reduction

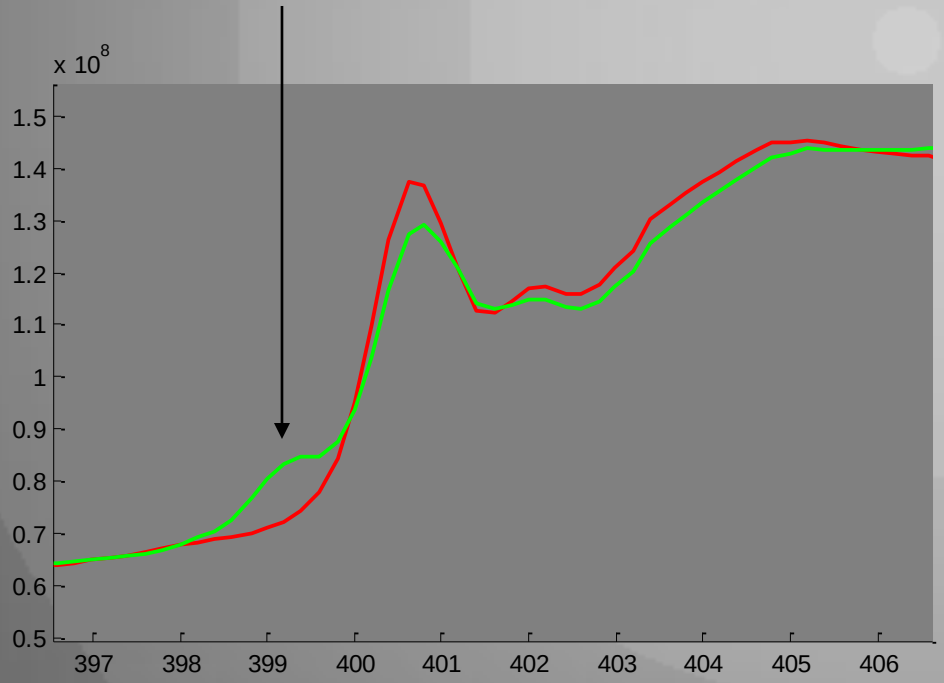
Hyperspectral Imaging Acquisition and Analysis Package

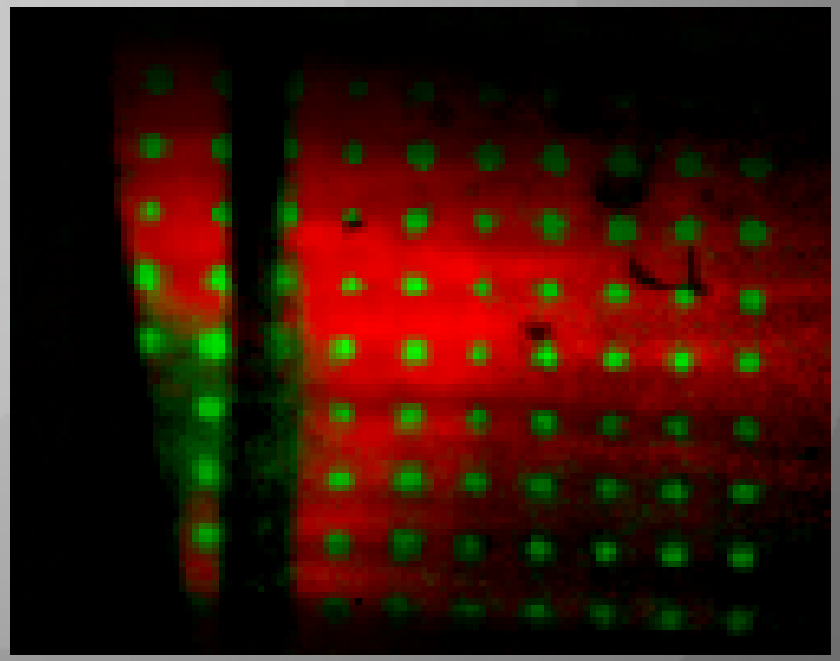
Synchrotron Methods and Measurements

Nitrogen K edge NEXAFS 300 image stack
AXSIA Multivariate Analysis reduces to single image
Identify N chemistry in ssDNA chips
from N chemistry in substrate



Adenine π* N=C *Low Noise Spectra and Images*

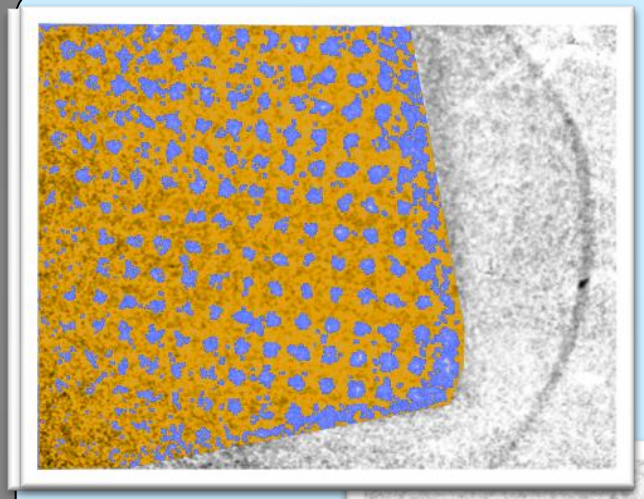




Organic bulk heterojunction Photo Voltaic improvements

***Patterned SAM induces lateral PCBM segregation**; P3HT skin found*

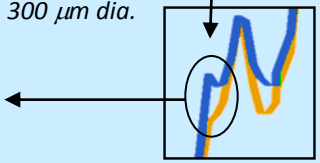
Depth Contrast using retarding grid voltage - 3D imaging

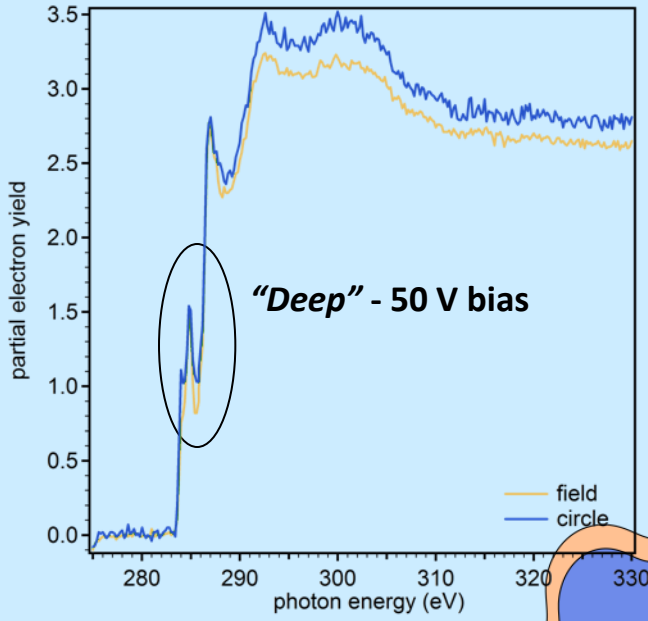


PCBM segregation
("Deep" - 50 V bias)

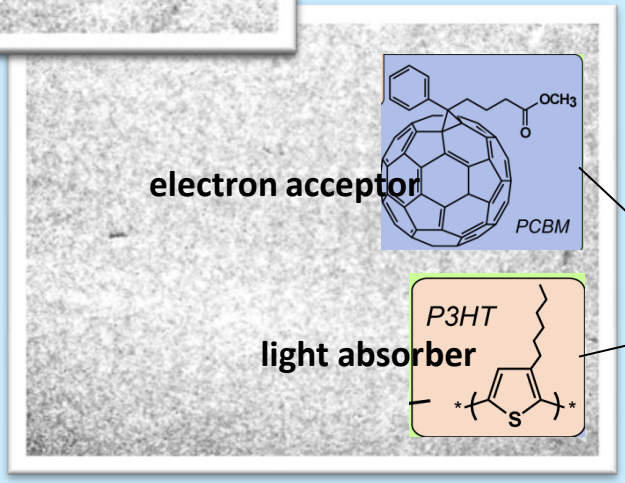
C-60 π* peak

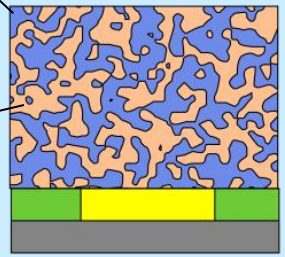
circle stamp
300 μm dia.



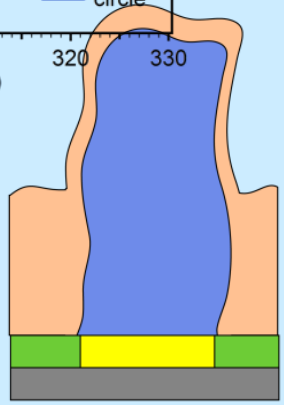


P3HT skin found
"Shallow"
(-200 V bias)





Δ



stamp: acid
backfill: alcohol

w/ U.W. (Ginger)

(Dean Delongchamp NIST/MSEL/ Polymers Div.)

Characteristics of LARIAT NEXAFS Spectrometer

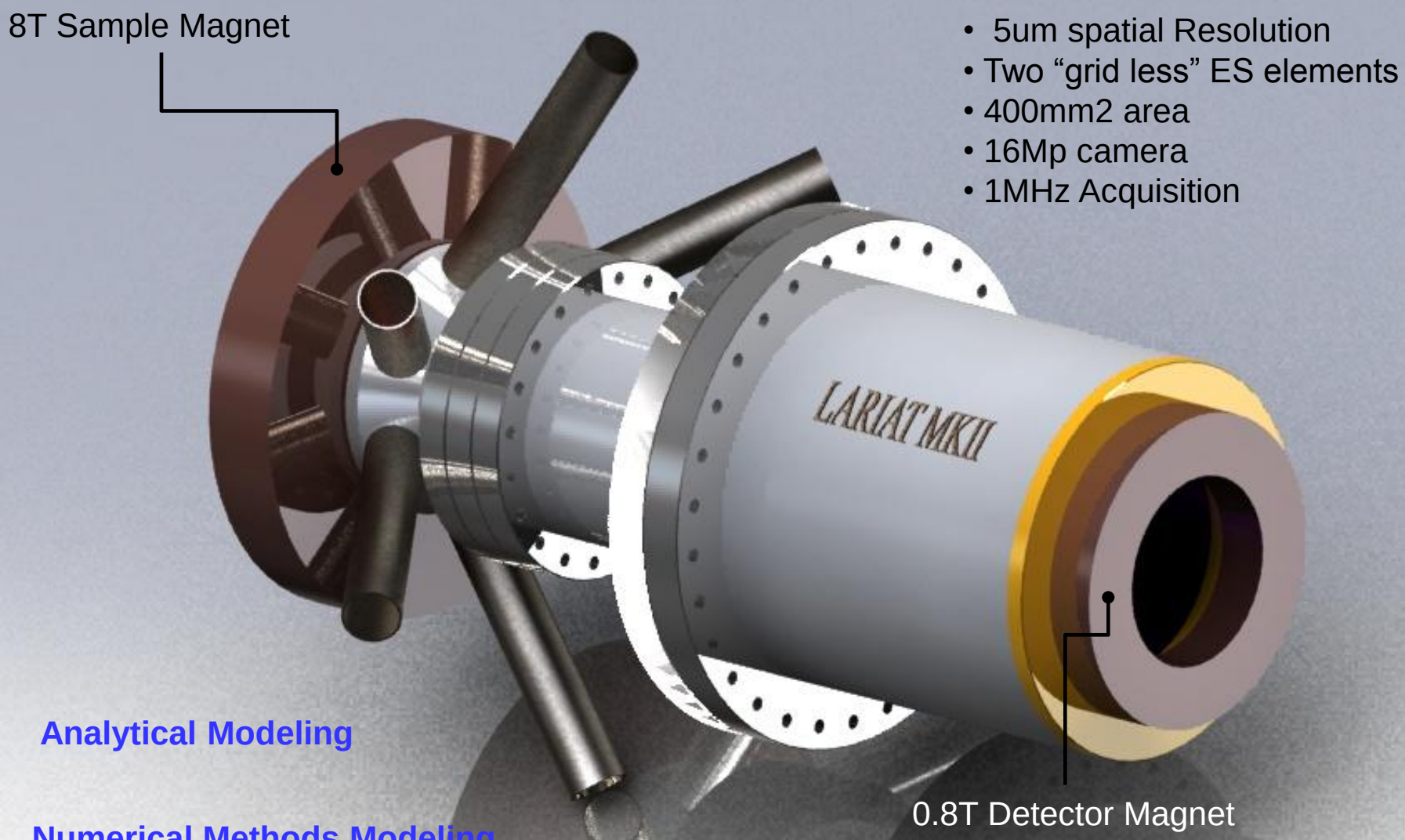
Features

- Magnetic projection electron imaging
  - Electrons follow B field lines to form parallel imaging system
  - helical orbits $r = mv_{perp}. /qB$
  - Nearly 100% Collection efficiency
    - » (high throughput)
- Large depth of field
  - i.e, Curved surfaces
- Orientation images
  - (via sample rotation)
- High pass grid energy analyzer
  - Rejected electrons return to sample (plays role in sample neutralization)
  - Depth selectivity 3D imaging
  - Spatial resolution optimization
- ~725 images per hour
  - 800X600 pixels

Benefits

- Sensitivity, sensitivity, sensitivity.
- Ease-of-use. Easy to get images.
- No column tuning.
- Robust. Insensitive to mechanical tolerances. Insensitive to stray fields.
- No high voltages (except detector).
- Very wide bandwidths with no loss of sensitivity.
- No neutralizer.
- Image resolution constant across field.
- The sample can be rotated normal to the x-ray beam if desired.
- Simple electronics.

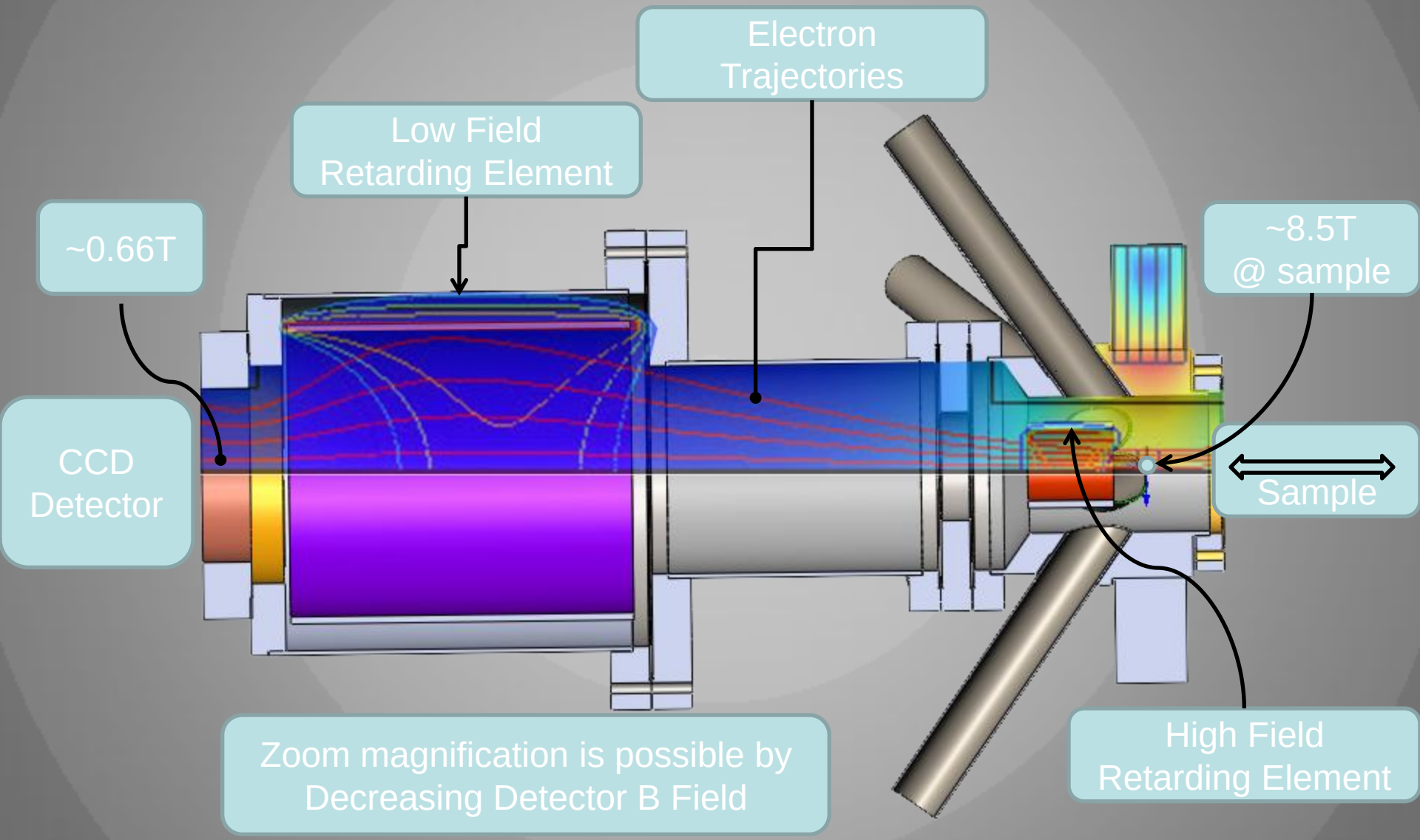
NIST SBIR Phase III Awarded to E. L. Principe & Assoc. (Imaging NEXAFS detector)
"LARIAT MKII Super Conducting NEXAFS Imaging Spectrometer"
ARRA Funding (NIST SB134109SU1067)



Analytical Modeling

Numerical Methods Modeling

LARIAT MK II Configuration: Axial Introduction



Analytical Modeling of LARIAT MK II

Cyclotron Radius distribution at sample

Sq root of energy matrix

$$CR0_{i,j} := \frac{3.38}{B0} \cdot sqrEE_{i,j} \cdot cosTT_{i,j}$$

Sample B Field

Angular Distribution Matrix

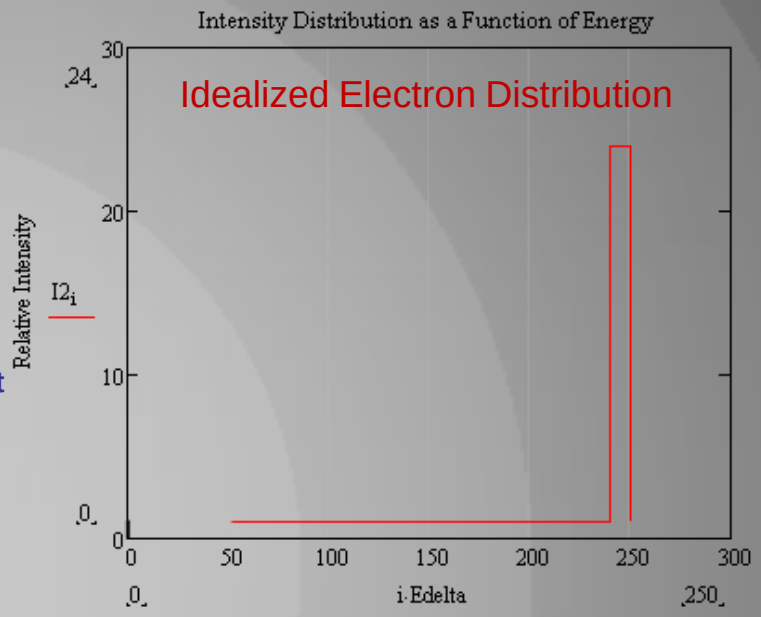
Total Intensity

Angular Intensity Distribution

1st Retarding Element

$$II2TT_{i,j} := II2_{i,j} \cdot \sin\left(TT_{i,j}\right) \cdot TMT0_{i,j} \cdot TMT1_{i,j}$$

2nd Retarding Element



CRavg = 1.37

E0 = 250

B0 = 8

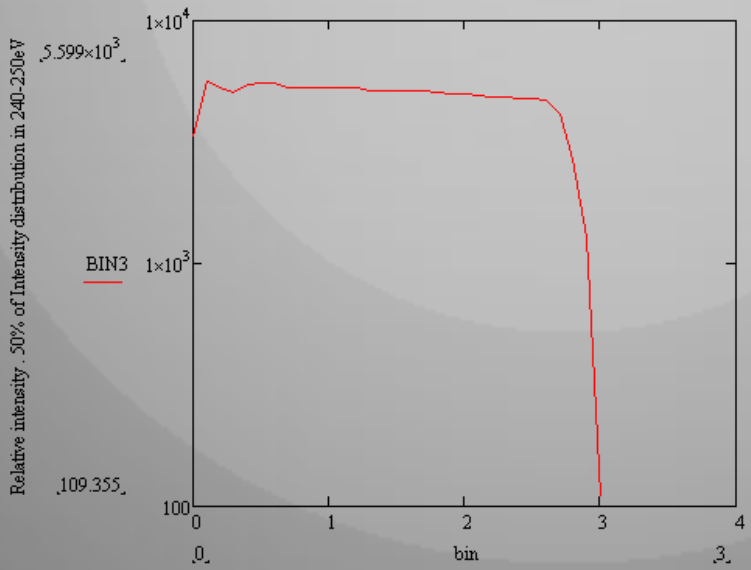
Vg0 = 200

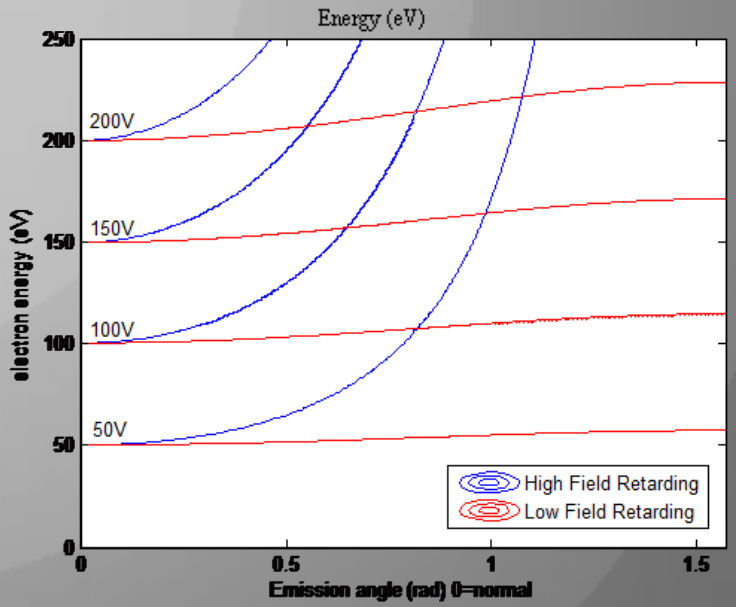
Bg1 = 1

Vg1 = 0

max(CR0) = 6.68

max(CR3) = 8.42





Parallel process NEXAFS imaging of Soft Matter (13 mm x 18 mm areas)

SAM gradients, DNA / protein chips, Catalyst libraries, Patterned surfaces

Creating Orientation Images of SAM gradients

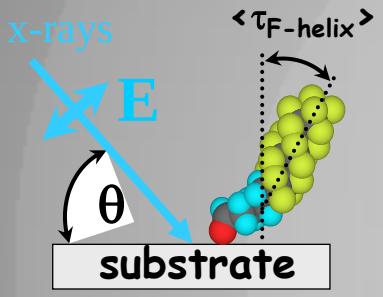
Dichroic Ratio of C-F NEXAFS peaks derived from

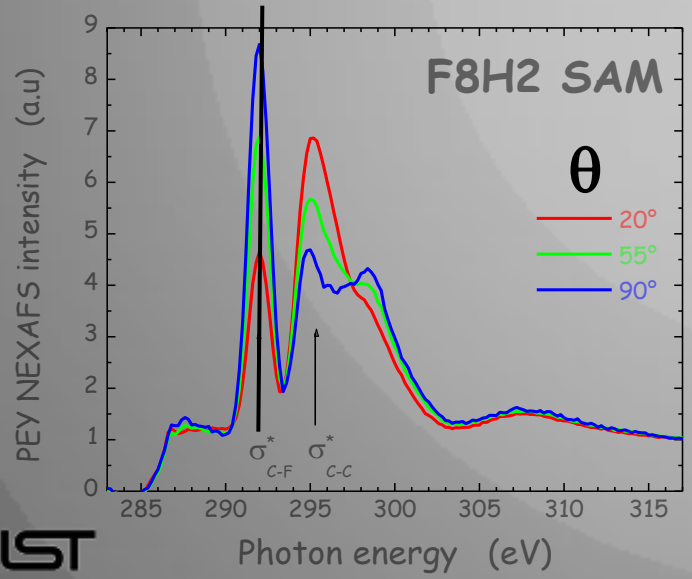
20°, 55°, and 90° θ incidence NEXAFS image stacks

300 + 300 +300 = 900 images!

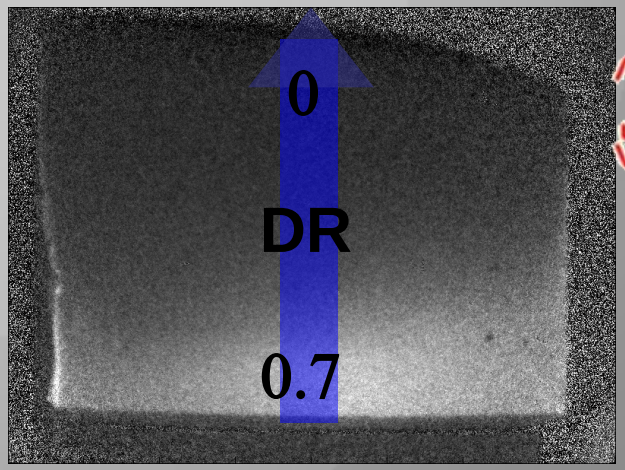
~500,000 NEXAFS spectra / stack

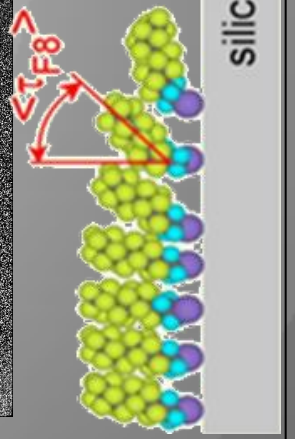
C-F Dichroic Ratio = $(I_{90} - I_0) / (I_{90} + I_0)$





55° degree incidence (magic)
C-F NEXAFS peak image





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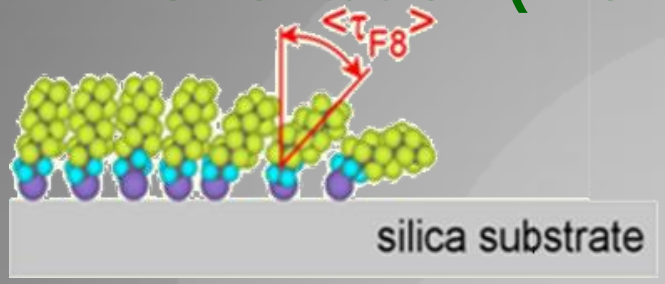
Parallel process NEXAFS imaging of Soft Matter (13 mm x 18 mm areas)

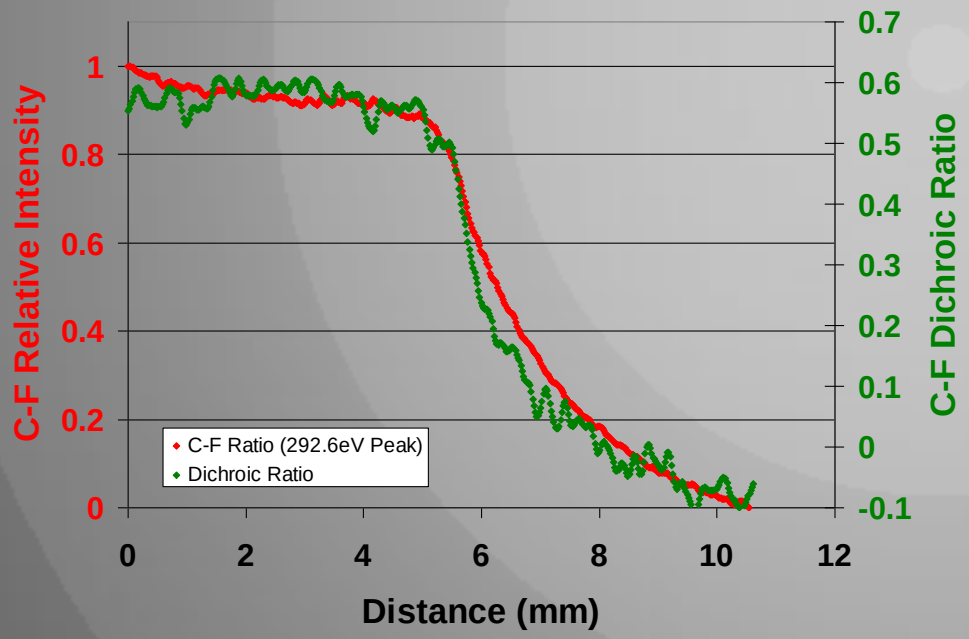
SAM gradients, DNA / protein chips, Catalyst libraries, Patterned surfaces

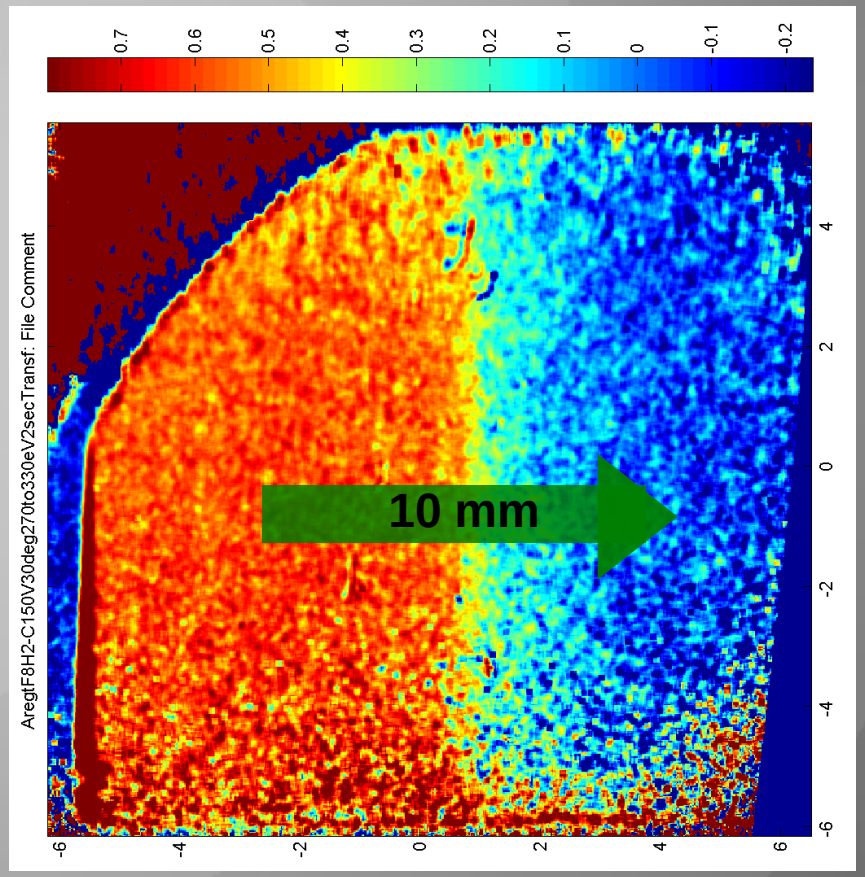
Synchrotron Methods and Measurements

Orientation (Dichroic) Image of SAM gradient



Orientation tracks Coverage





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SUMMARY
LARIAT Imaging NEXAFS Spectrometer

SUMMARY:

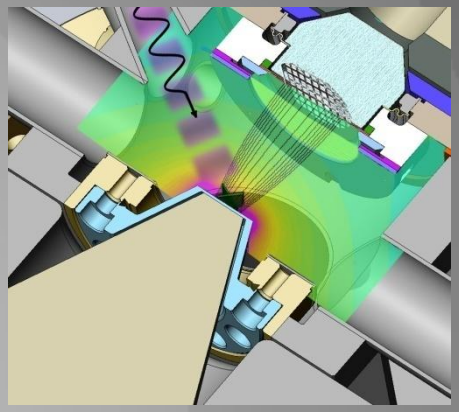
LARIAT - Large Area Rapid Imaging Analytical Tool
E.L. Principe & Associates, NIST SBIR Funded

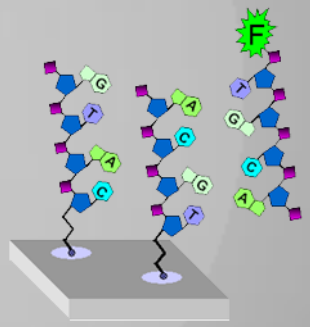
- **Bond Concentration and Orientation Images**
  NEXAFS partial electron yield images

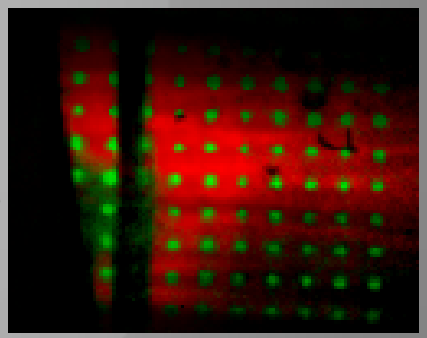
- High throughput, rapid full field imaging
  Large area 13 mm x 18 mm

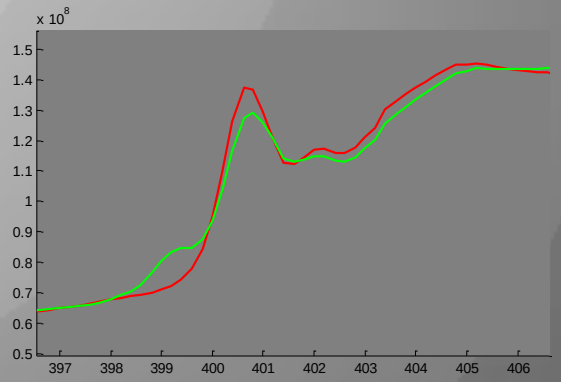
- 50 micron spatial resolution, **5 micron coming**

- Depth selectivity over a 10nm range
  Possible 3D imaging









EXAMPLES

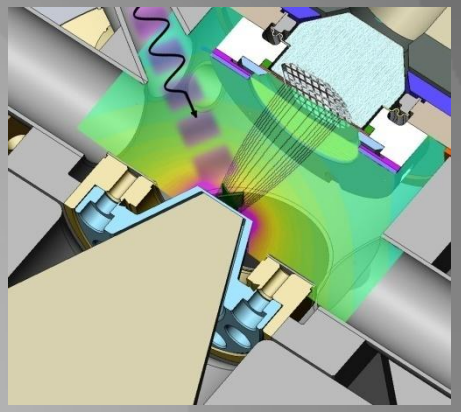
1. Semi-fluorinated SAM gradients
2. Single-strand DNA micro array sensors
   - ***AXSIA multivariate analysis (Sandia)***
3. Organic electronic combinatorial device arrays

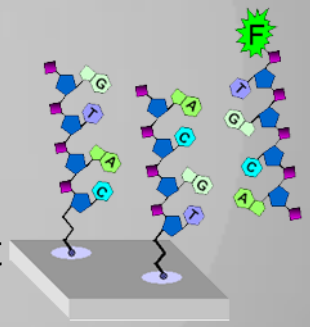
SUMMARY
LARIAT Imaging NEXAFS Spectrometer

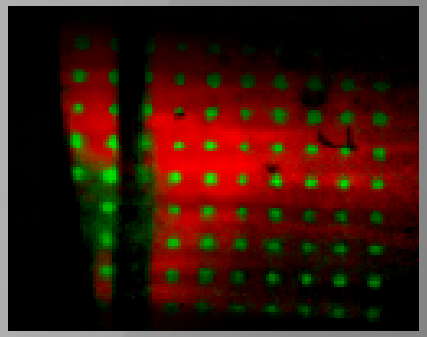
Synchrotron Methods and Measurements

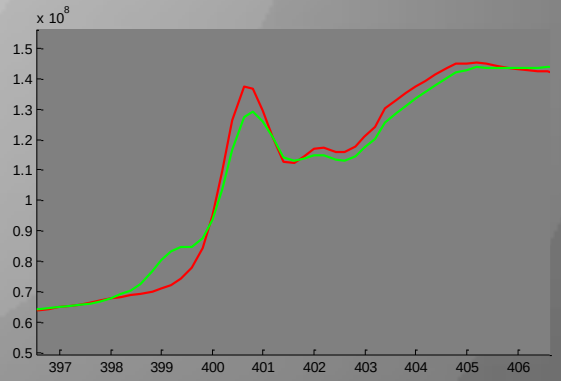
Some of our users since July 2008:

- Dean - organic electronics - photo voltaic -> device array, PV blends x3
- Jan Genzer - SAM gradients-> 1 and 2 dimensional gradients, different condition lots of samples
- Castner group - single strand DNA arrays, SAM arrays (mosaic x2), protein arrays
- Carpick (U Penn) - arrays of small spheres subjected to triboligical wear
- Sandia - SAMs subjected to various troblogical treatments - some Tony test samples, twenty dollar bill - arrays of sputtered dots on an oxide sample
- BNL Battery group - array of Li ion batteries (2-3 mm) at various stages of charge and discharge - these are really neat!
- BNL Diamond Group. diamond sample subjected to laser abolation, an array of different laser power densities and times all laser spots in the array subjected to repeated UV ozone cleaning to remove graphite to clean the ablated laser spots.









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As well as users who gave permission to use their data!