# Resonant Soft X-ray Scattering at the NIST beamlines of NSLS-II:

## RSoXS in the time of COVID

**ALBA II Colloquium Series – May 17, 2021**

National Institute of Standards and Technology
U.S. Department of Commerce

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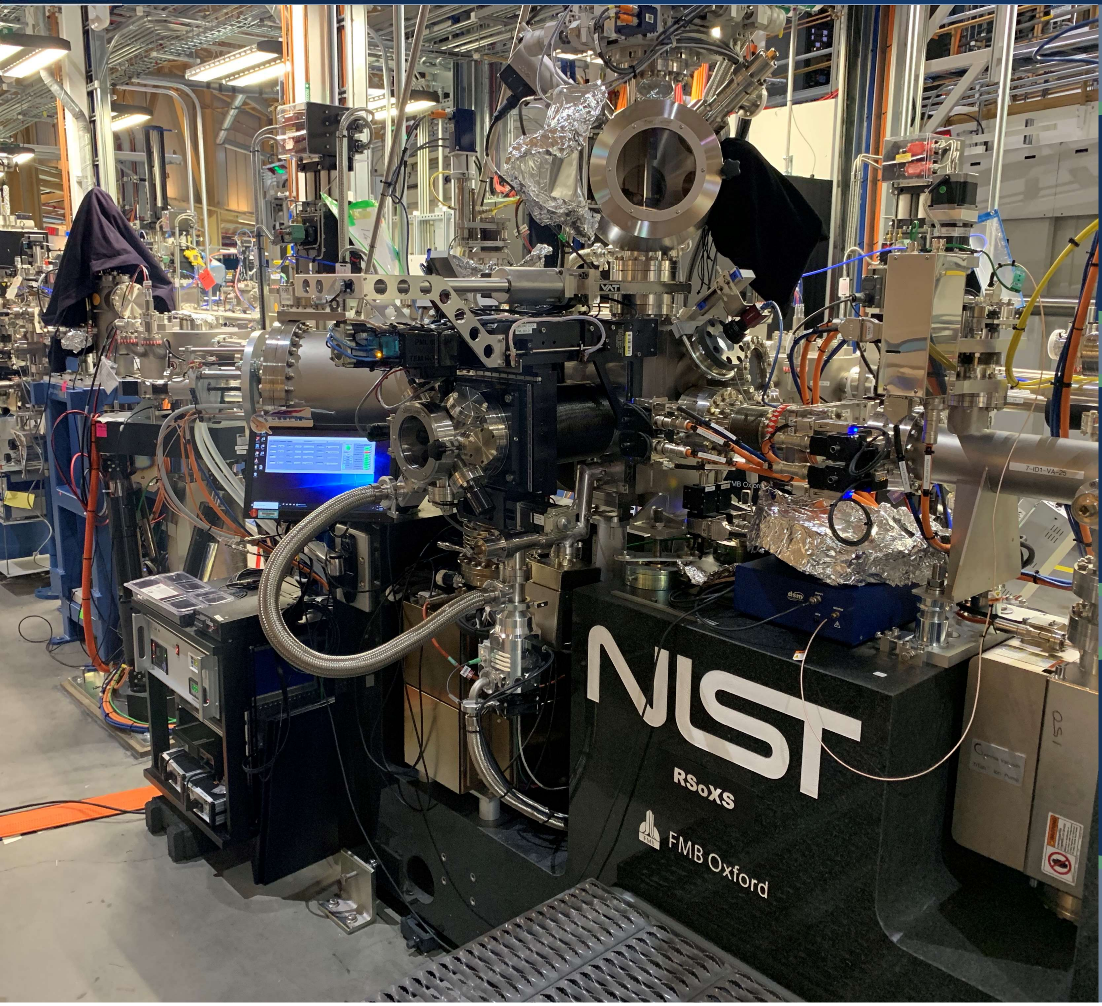
RSoXS station – SST-1 Beamline – NSLS-II

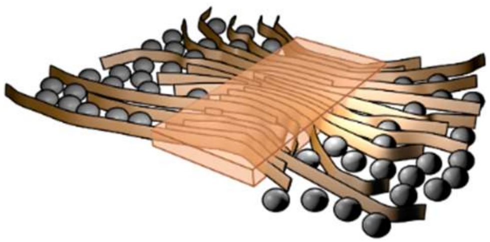
# Outline

NIST

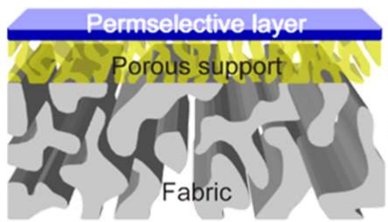


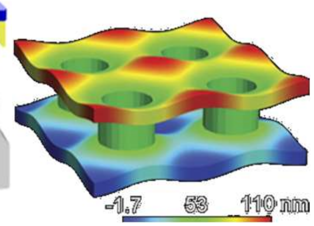

- RSoXS overview
- Review of expanding fields of RSoXS – recent results
- Station at NSLS-II design and operation developments in the time of Covid-19

# What is RSoXS: Soft Matter Nanostructure

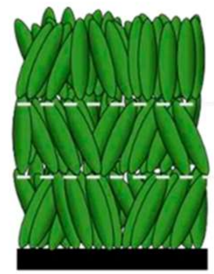


Organic Electronics



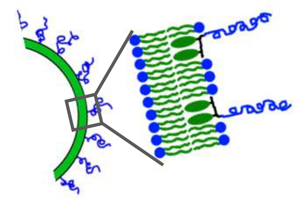




membranes

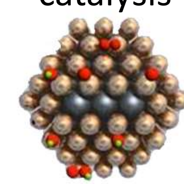


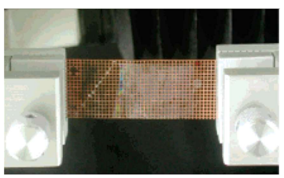
Liquid crystals

Polyelectrolyte
Solutions & Gels



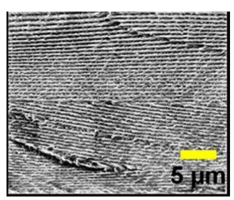
Low Z
catalysis

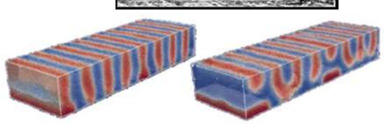




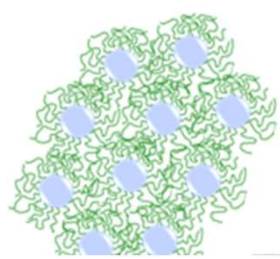
Structural Polymers

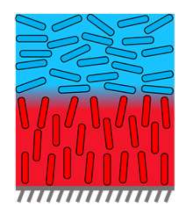
Self directed assembly



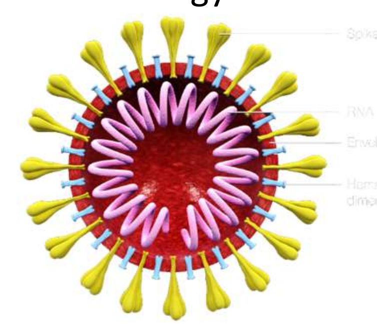
nanocomposites



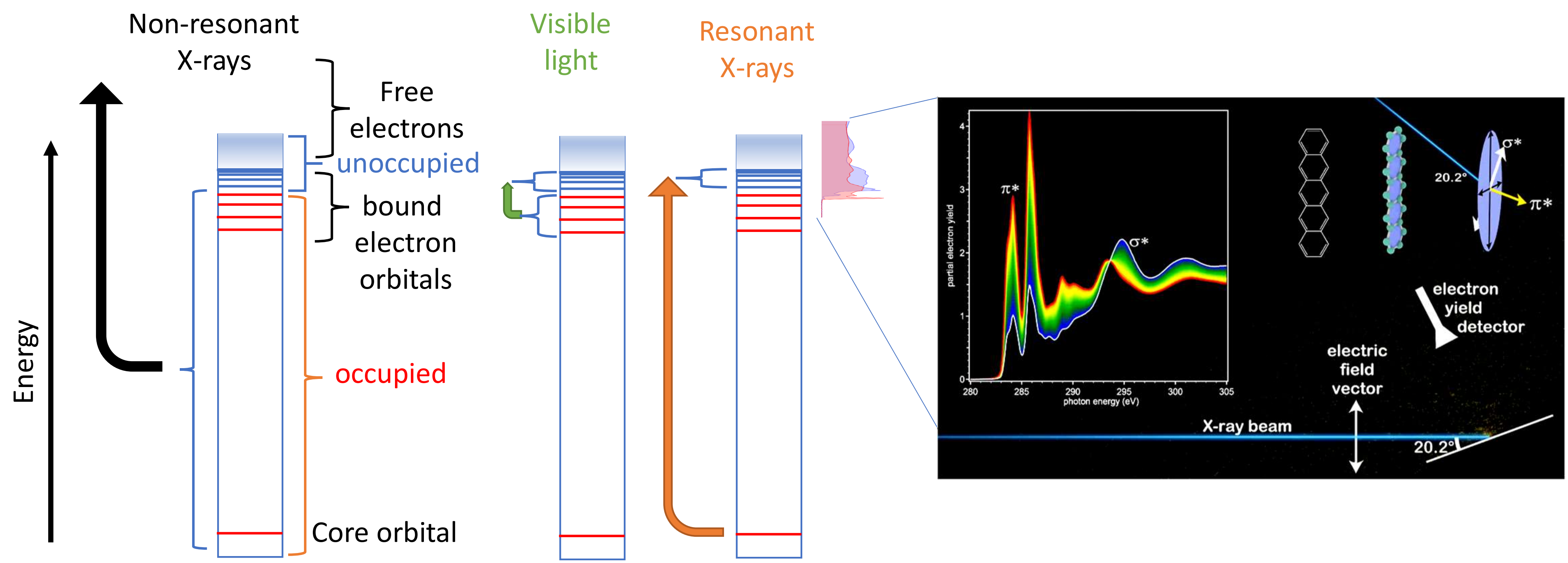


Interfacial structures

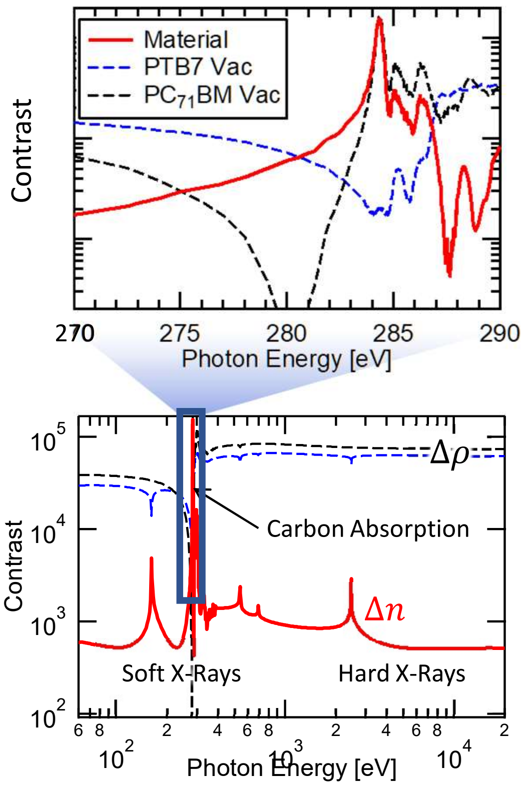
Biology

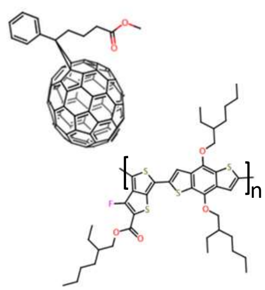


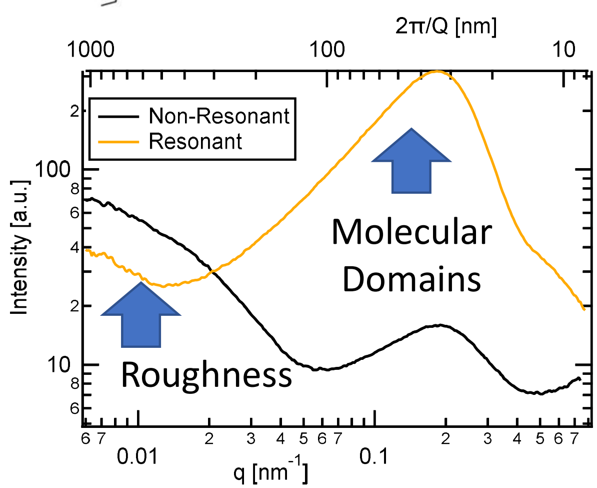
# Resonant Soft X-ray spectroscopy



# Spectroscopy -> Scattering Contrast



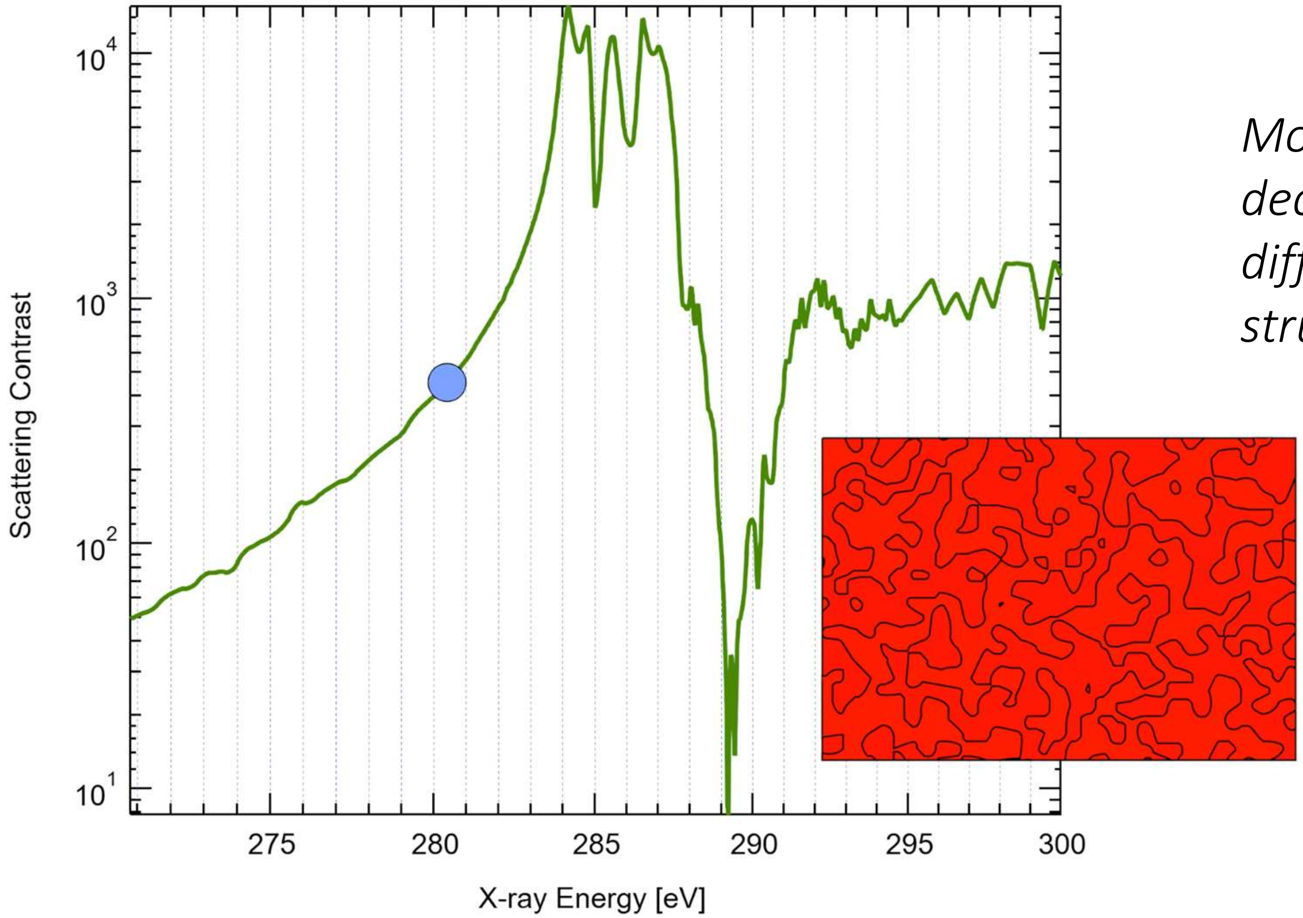




Non-resonant scattering has difficulty distinguishing organic materials. They all have very similar electron densities.

In the most basic/common usage RSoXS can increase the contrast between these materials orders of magnitude.

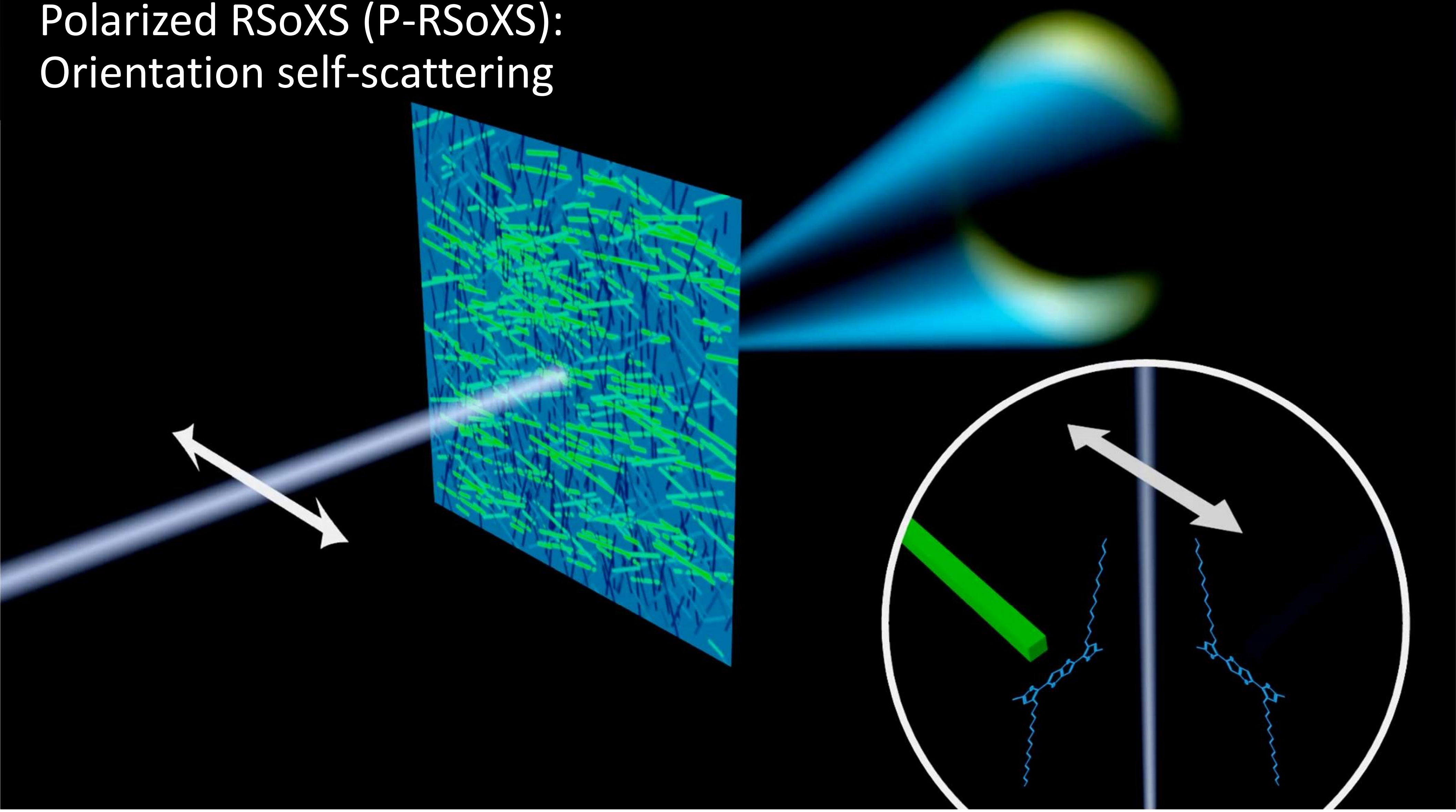
**Absolute Measurement of Domain Composition and Nanoscale Size Distribution Explains Performance in PTB7:$PC_{71}$BM Solar Cells** Brian A. Collins Zhe Li John R. Tumbleston, Eliot Gann, Christopher R. McNeill, Harald Ade Advanced Materials 2013

# Label-Free, Chemistry-Based Contrast Variation

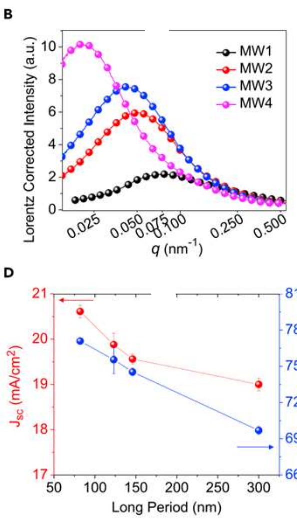


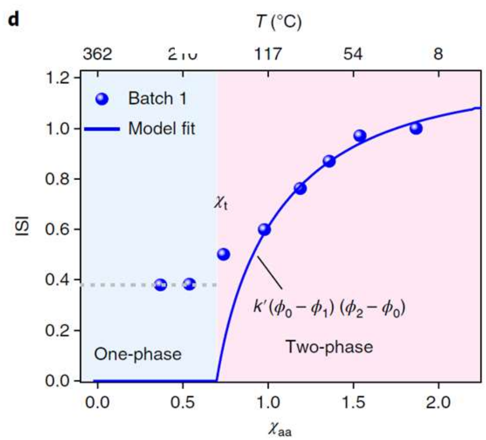

*More advanced contrast variation decomposition can quantify different film components and structure by their chemistry*

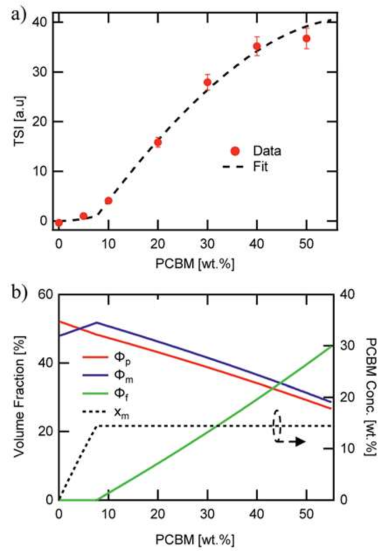
# Polarized RSoXS (P-RSoXS): Orientation self-scattering

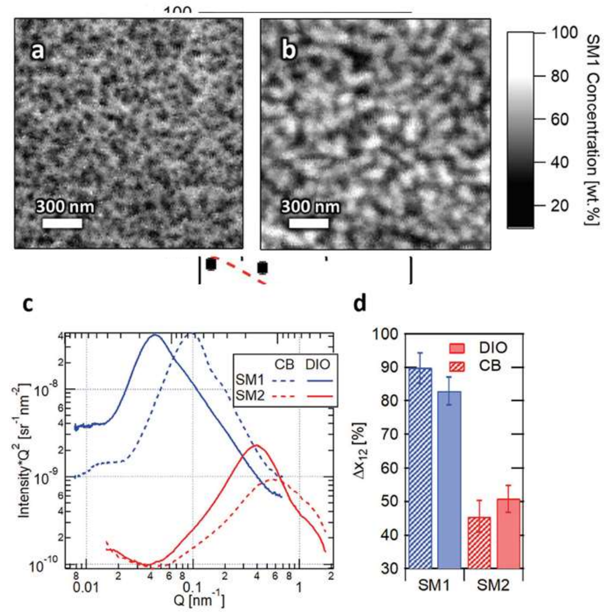


# RSoXS Applied – Organic Electronics




## Original application of RSoXS

- Domain size
- Quantifying domain purity

Yi, Ade; Nat Mater (2018)

Arunagiri, Ade; Joule (2019)

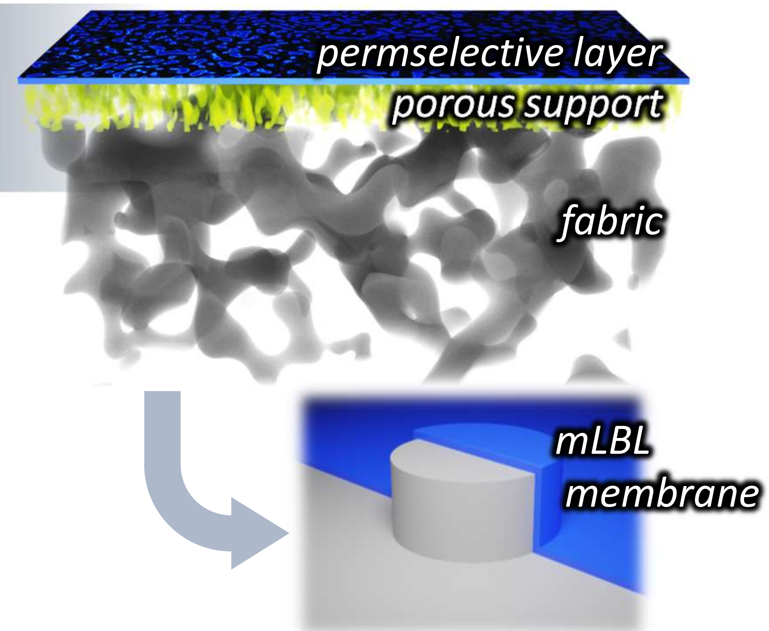
Ferron; J Mat Chem C (2019)

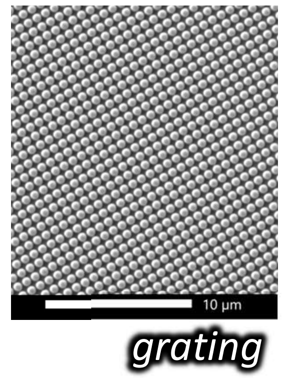
Alqahtani; AEM (2018)

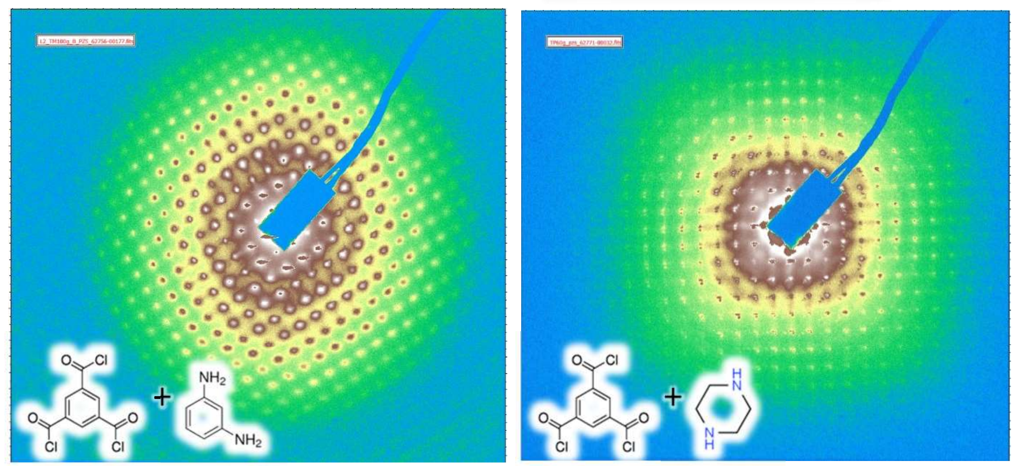
# RSoXS Applied – Membranes

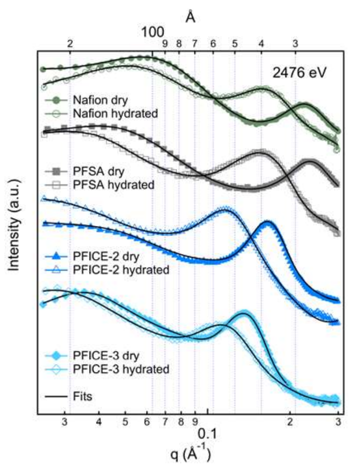
In state-of-the-art industrial films a complex interplay of chemistry, structure, processing, orientation determines performance.

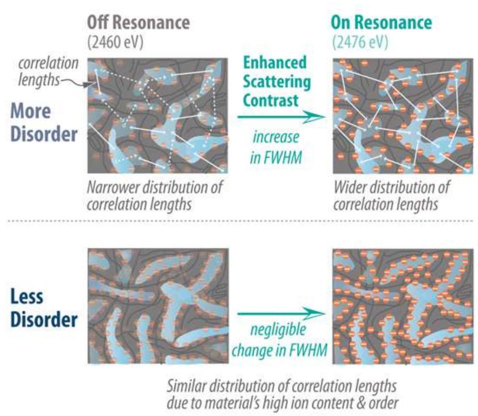
- Artificial structure with a grating allows fitting far below wavelength limit
- Orientation varies with monomer chemistry, a new engineering axis for industrial materials.
- Expansion of uses at higher energy “tender” edges available with joint proposals



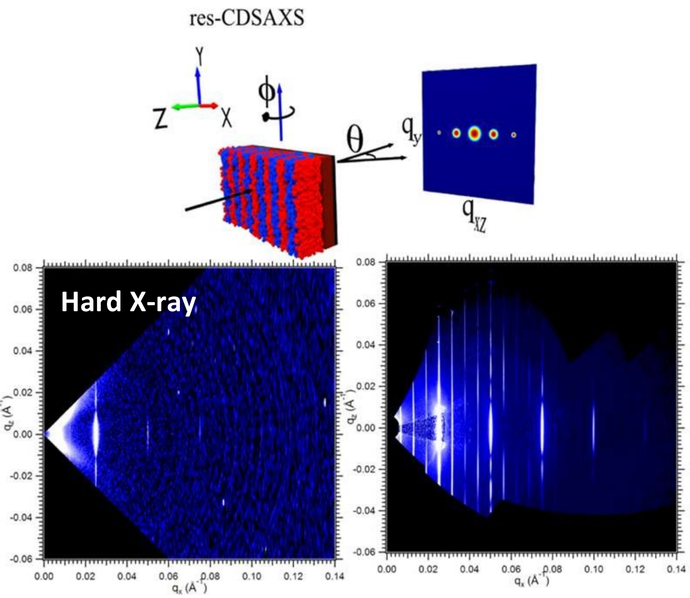



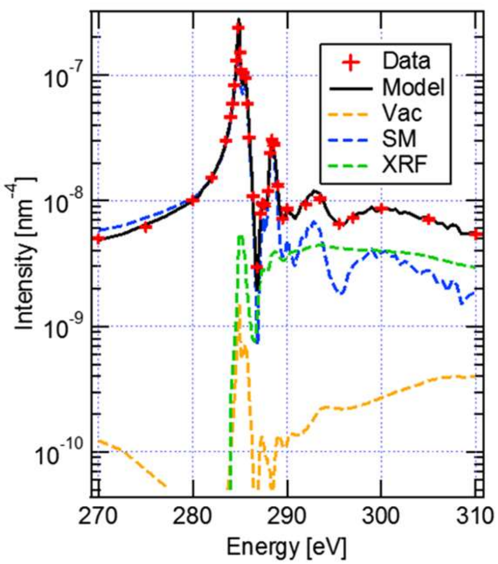

Su, JACS 2019

# RSoXS Applied – Self Assembly

NIST

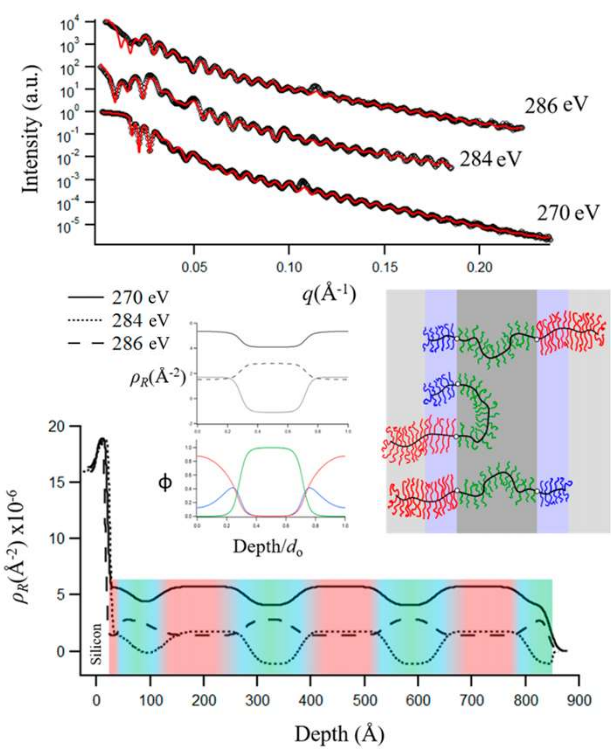



Resonant critical dimension SAXS developed at NIST solves for grating structure, using resonance allows structure determination before etching




Ferron; PRL 2017

Quantitative contrast variation allows precise microstructural fitting, including interfaces

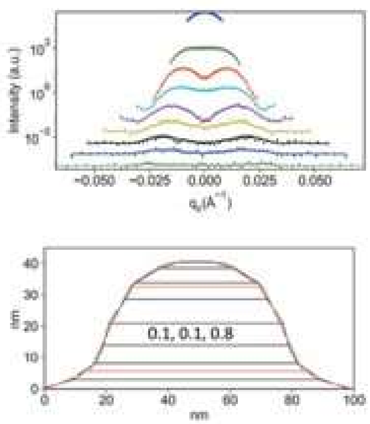



Sunday, Soles; Macromol 2018

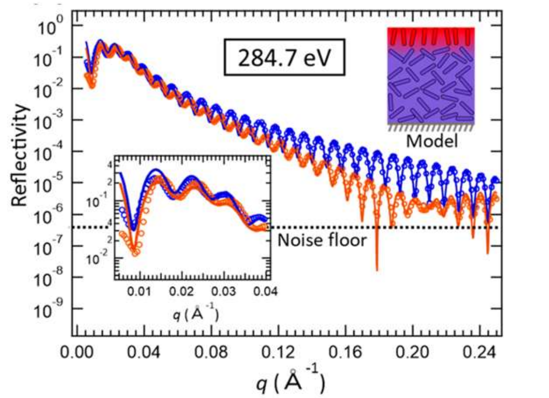
RSoXS has enhanced material contrast and measures the right size scales for Block Copolymer assemblies.

Utilizing reflectivity to get chemical species vs depth

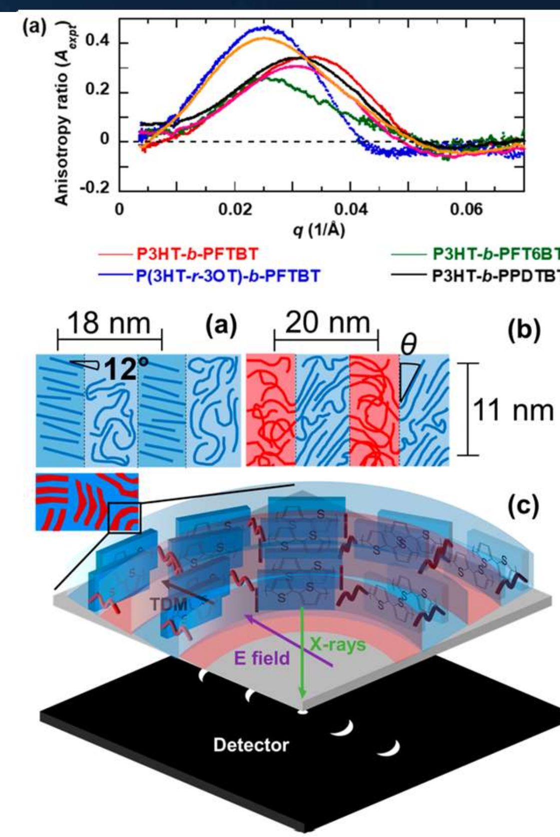
# RSoXS Applied – Polarization




Liman, Kline; J App Crst; 2017




Thelen; Chem Mat; 2020




Litofsky, Gomez; Macromol; 2019

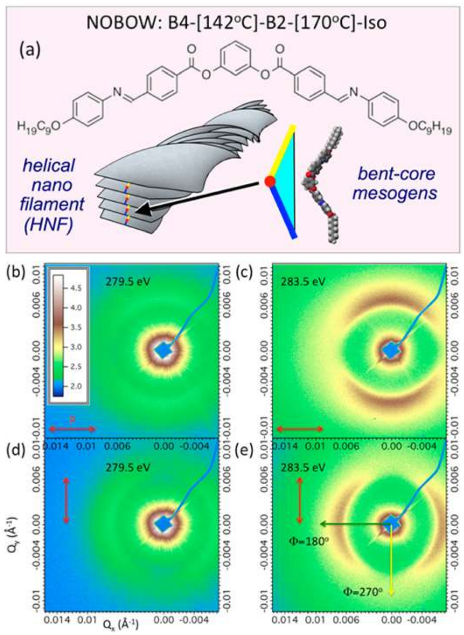
Simulations show possibility of measuring molecular alignment within a self organized lithographic grating

Demonstration of depth profiling orientation within a chemically homogenous non crystalline film

Molecular orientation in block copolymer structures

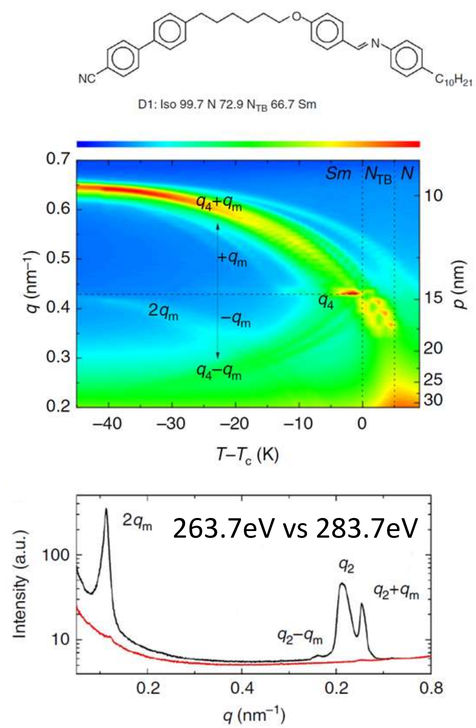
Polarization is slowly being added as an extra knob, allowing the orientational distribution within nanostructures to be solved

# RSoXS Applied – Liquid Crystals



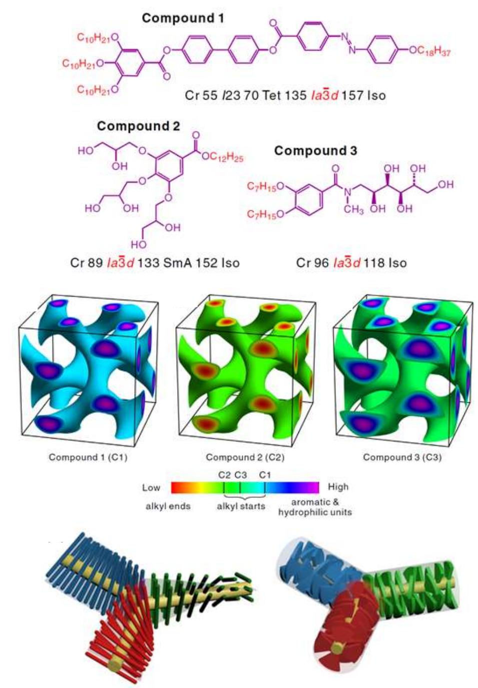

Zhu, Hexemer; Nano Lett. 2015

RSoXS determines pitch on non-labeled chiral LCs




Salamonczyk, Gorecka; Nat Comm 2019

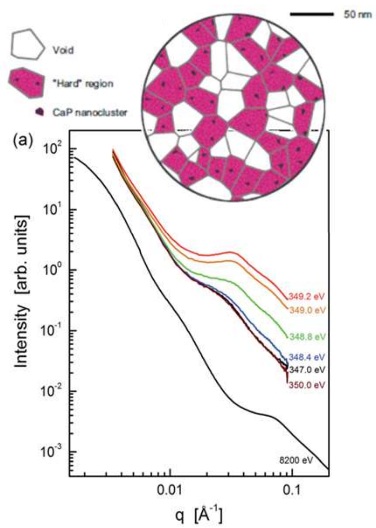
Monitoring LC helical pitch and phase transitions




Cao, Zhu; PRL; 2020

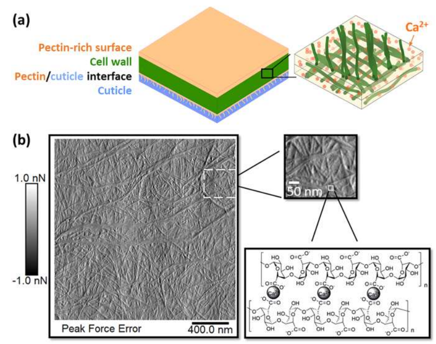
determining orientational structure in gyroid LCs

# RSoXS Applied – Bio/Liquid



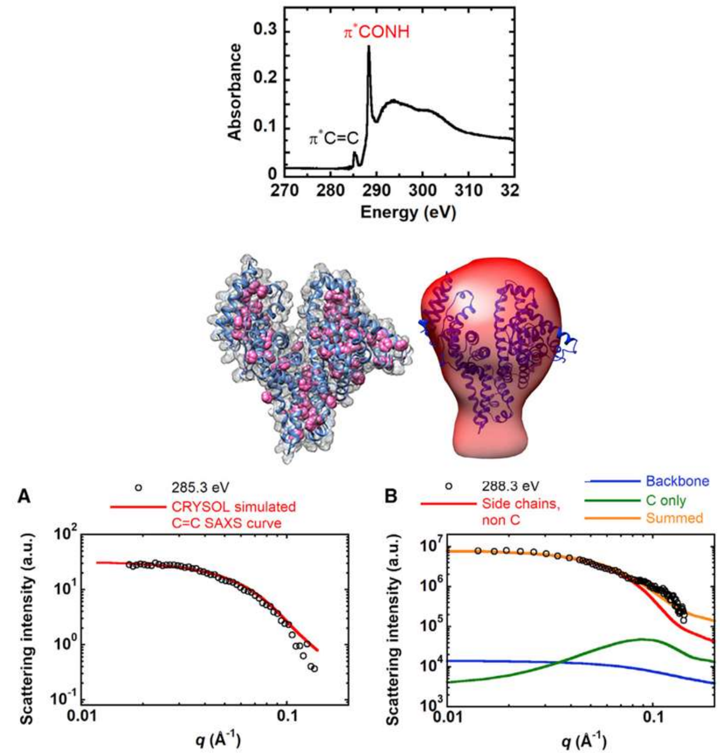

Ingham, Soft Matter (2015)

Locating Calcium within milk microstructure casein micelles




Gomez Group, Penn State

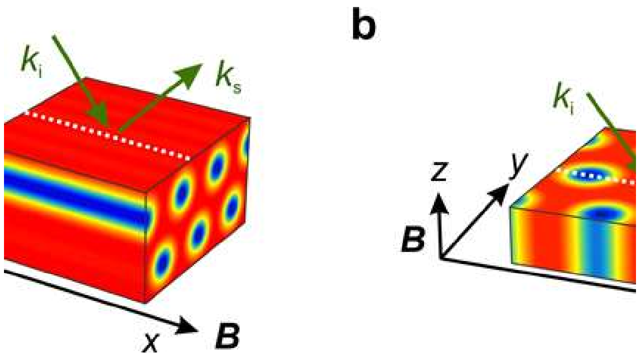
Calcium structure within cell wall relative to celuouse fibers

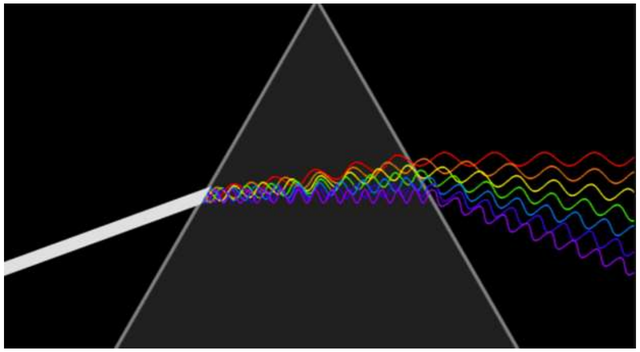



Ye, Gomez; Structure (2018)

Non staining contrast variation demonstrated in Protein scattering from bovine serum albumin

# Comparison to other scattering techniques



### Resonant Elastic/Anomalous X-ray Scattering

Soft matter entails less crystallinity

Material-centric view rather than atomic/unit-cell centric

Index of Refraction / optical constants rather than scattering factors

magnetic effects are negligible

### Neutron Scattering

Similar material view

Neutron contrast variation is through deuteration (making a different physical sample)

samples are ~ 10^8 times smaller

magnetic effects are negligible

### Light scattering

Similar material view

Index of refraction is considerably smaller

Spectroscopy is sensitive to mainly at unoccupied states

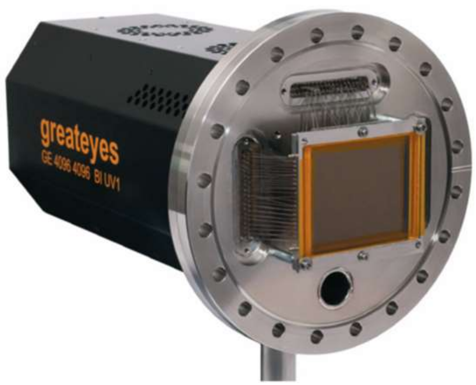
Wavelength (and resolution) ~200x smaller

# Defining Feature of RSoXS – Beam Damage

NIST

Soft Matter focus as leads to very different design from normal resonant scattering facilities.

Focus on making the most of every photon incident on material




4096 x 4096 imaging array
15 x 15 µm pixels
61.4 x 61.7 mm area
***vacuum-incompatible*** body

Most sensitive detectors

- sacrificing speed for now
- Back illuminated thinned (soft X-ray sensitive) CCD
- Cooled to -80C to remove noise
- As large as feasible angular range of scattering collected

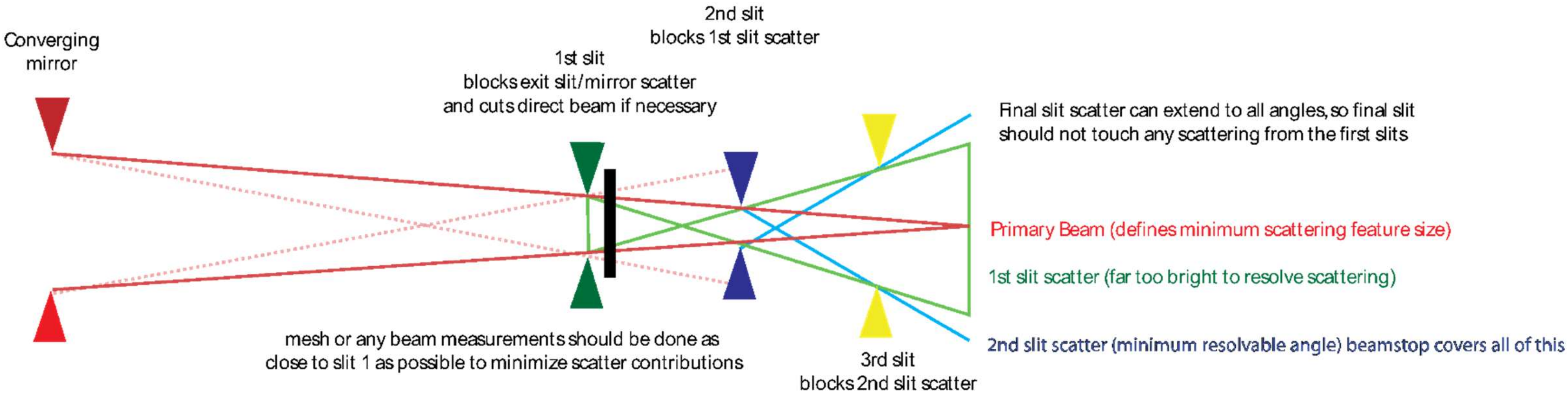
Lower flux density

- Same flux (or more) in a bigger beam size
- Sacrifices coherent scattering, highest possible resolution
- Resolution matches Soft Matter needs – low crystallinity
- Appropriate for scattering (ensemble measurement) make measurement more statistically useful/ less local
- Need large (300 um) area clear on samples

* Any mention of commercial products within NIST slides is for information only; it does not imply recommendation or endorsement by NIST.

# Classical scattering focusing arrangement

NIST

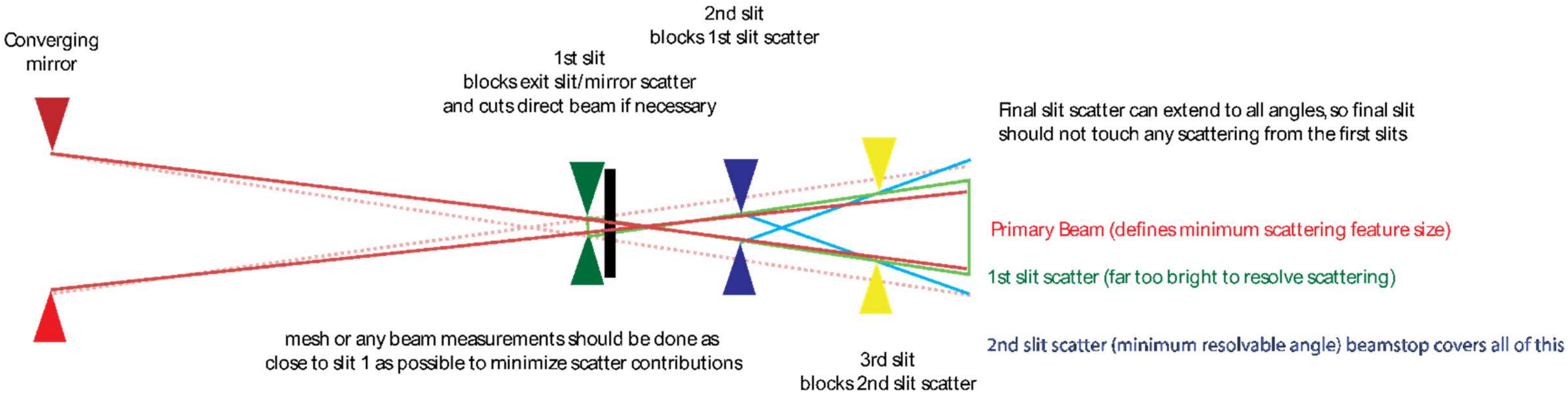



Normal Scattering beamlines focus the beam on the detector (near sample) for ultimate resolution, resulting in high flux density but high resolution

Slit scattering is far more of a problem with Soft X-rays.

This method would sacrifice low Q and flux density could be too high

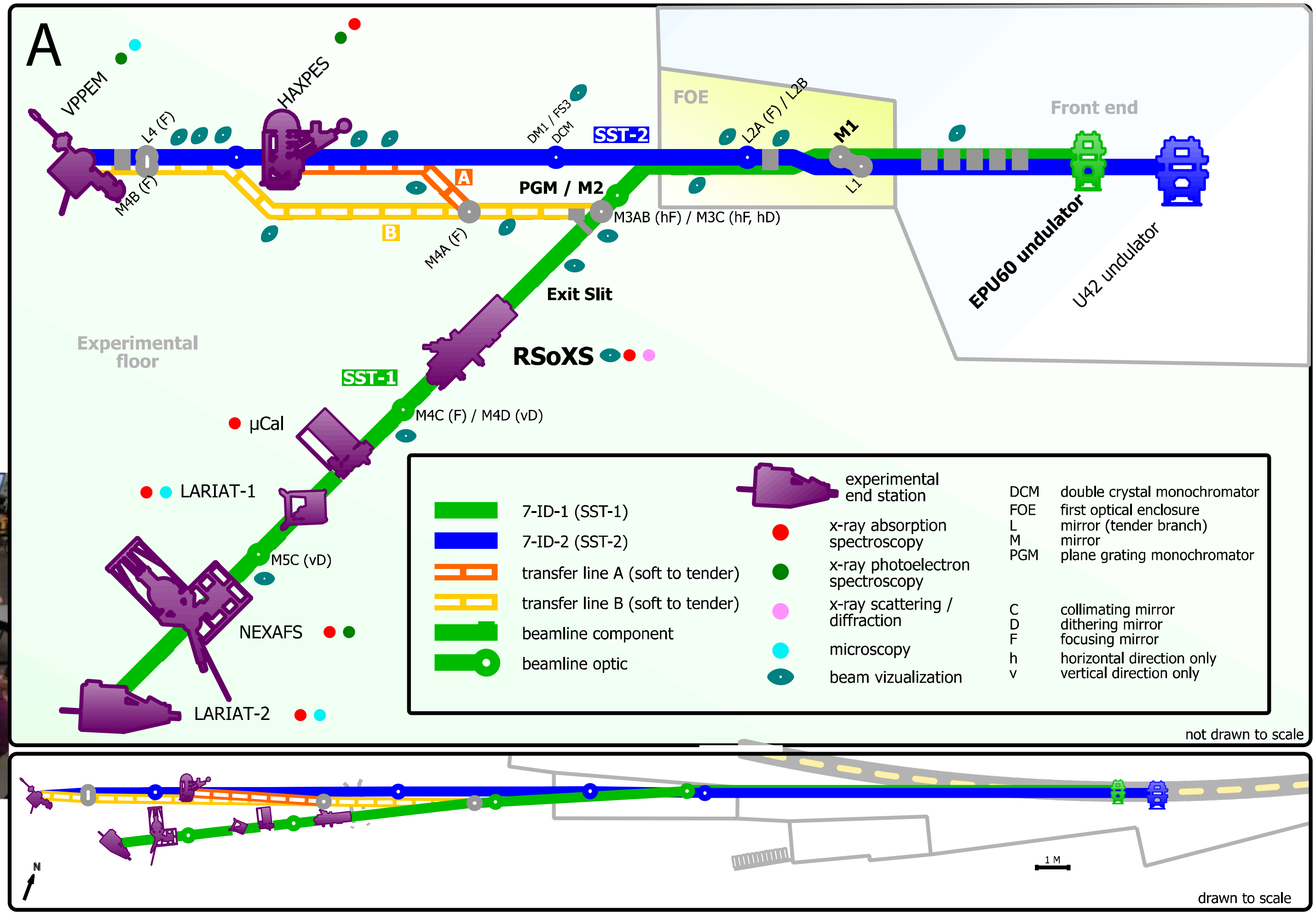
# Optimized for Low Q, minimized damage



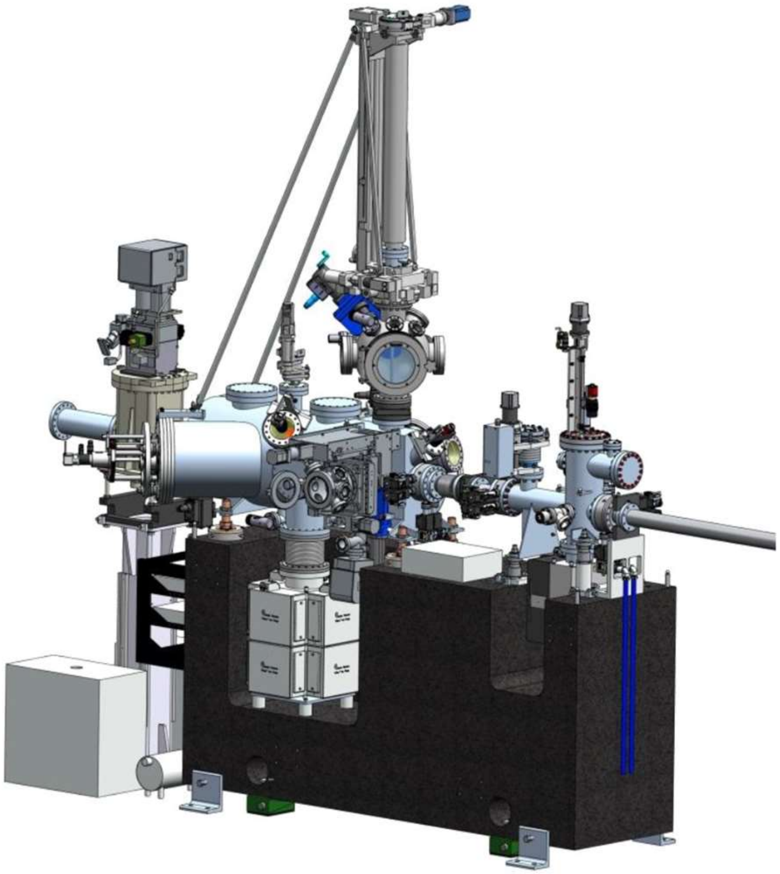

The NSLS-II RSoXS station is designed with a diverging beam, optimizing slit scatter, reducing ultimate resolution, but also the flux density on the sample

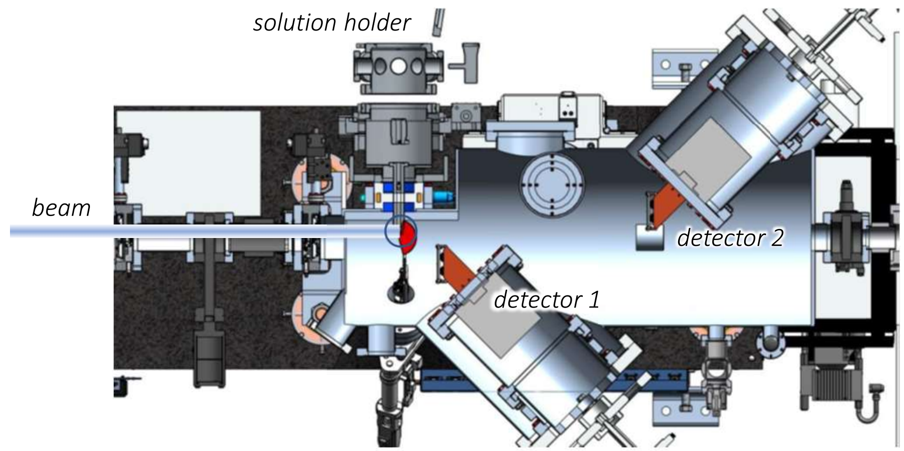
# NIST beamlines at NSLS-II


NIST beamlines
During commissioning



# NIST RSoXS Measurement Station



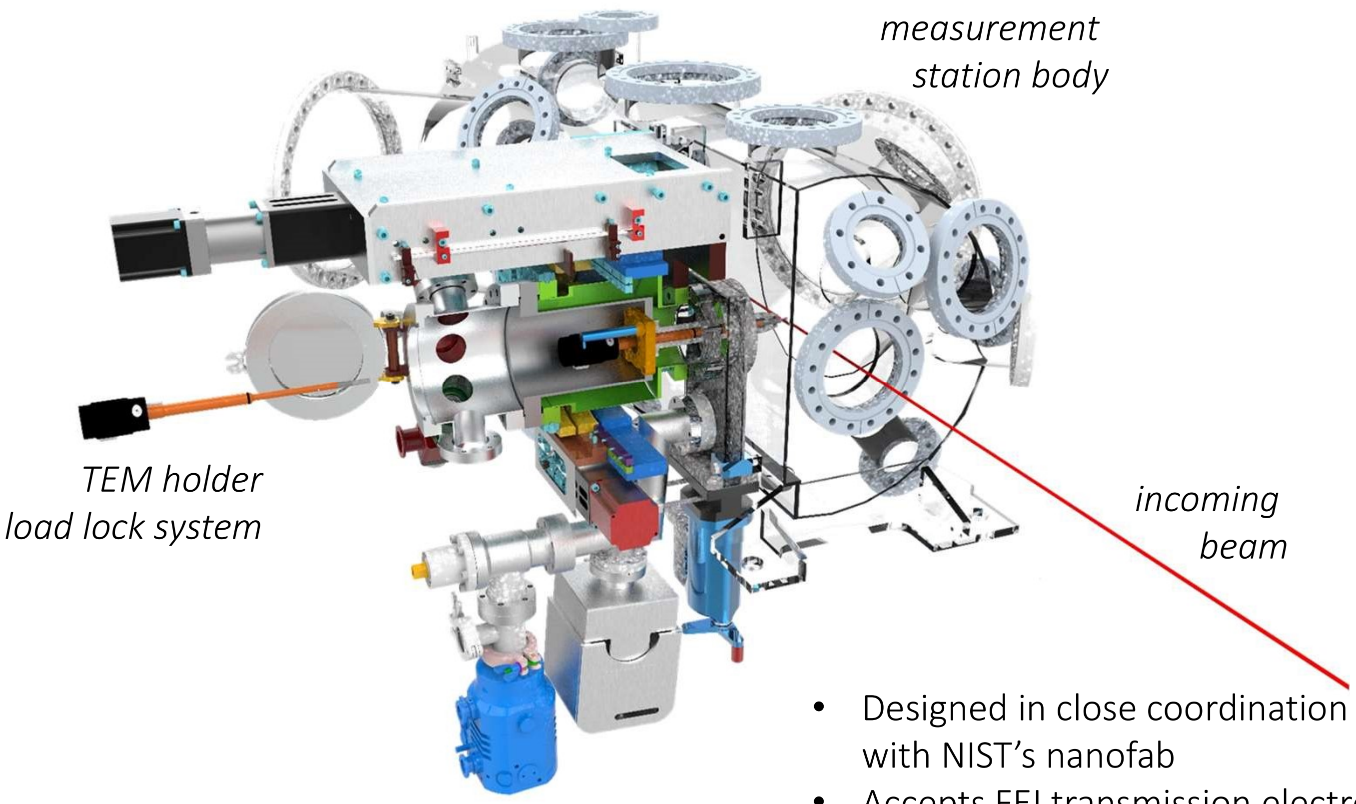


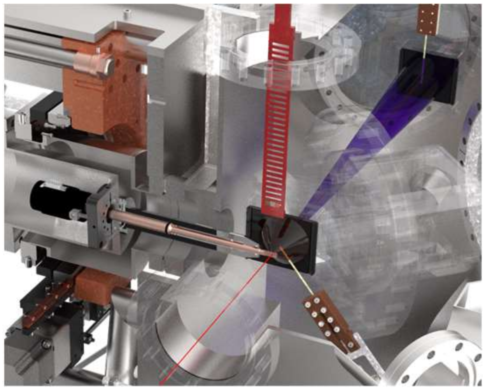

*top-down cutaway view*

*NIST design team:*
*Gann, DeLongchamp, Fischer, Holland*

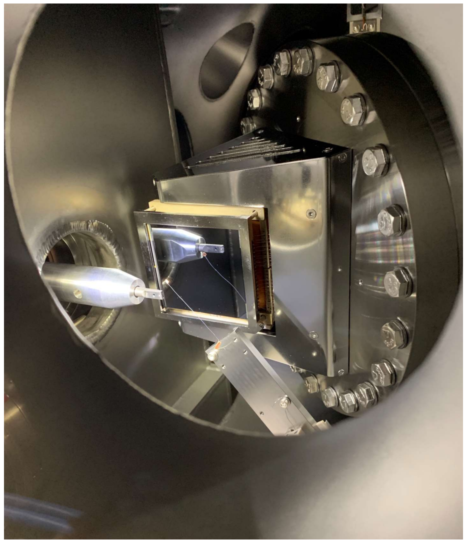
A NIST facility for resonant soft x-ray scattering measuring nano-scale soft matter structure at NSLS-II
E Gann, T Crofts, G Holland, P Beaucage, T McAfee… - Journal of Physics: Condensed Matter, 2021

# Nanofluidic environment



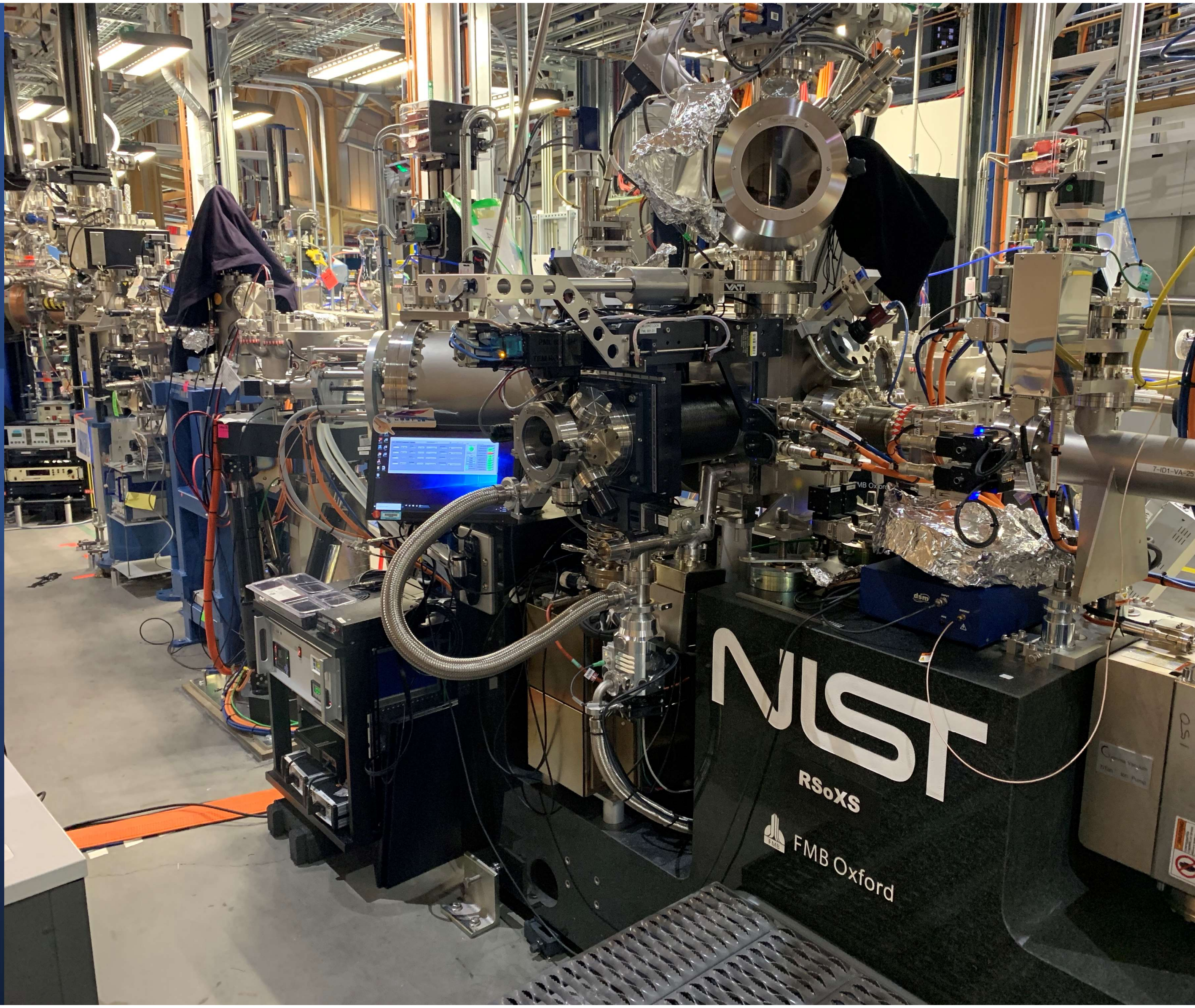
Sample location



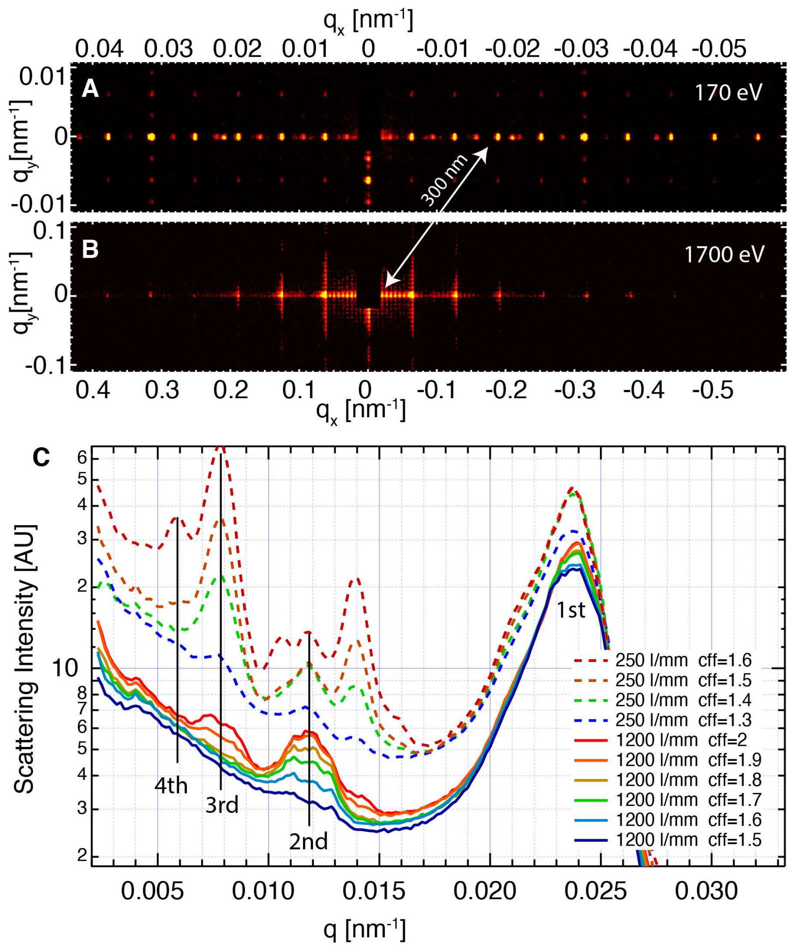
- Designed in close coordination with NIST's nanofab
- Accepts FEI transmission electron microscopy (TEM) sample holders

A NIST facility for resonant soft x-ray scattering measuring nano-scale soft matter structure at NSLS-II
E Gann, T Crofts, G Holland, P Beaucage, T McAfee… - Journal of Physics: Condensed Matter, 2021

# Current Station

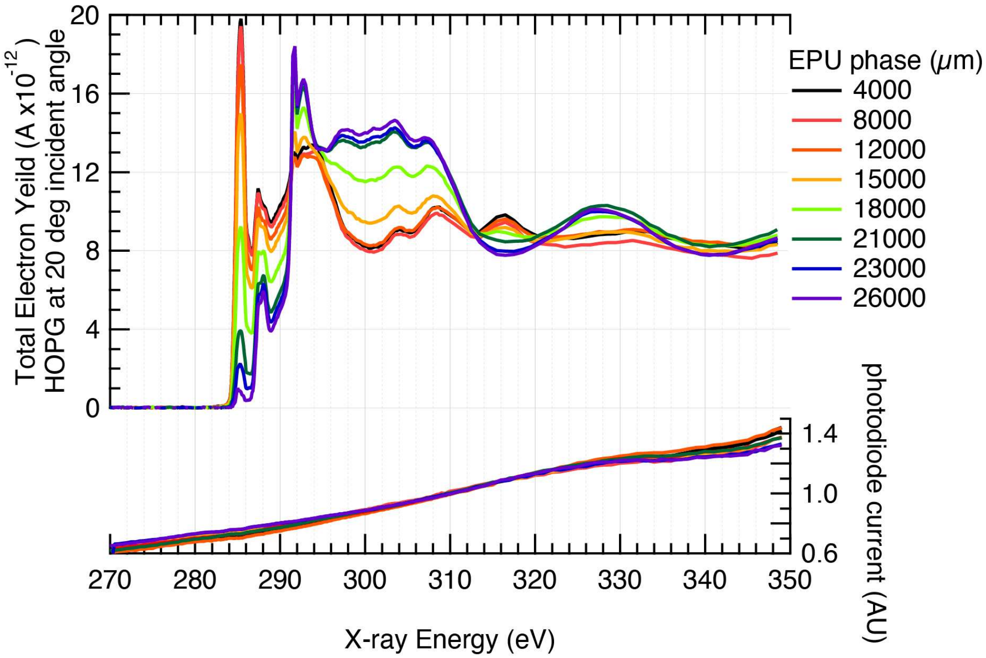


# RSoXS at NSLS-II Performance



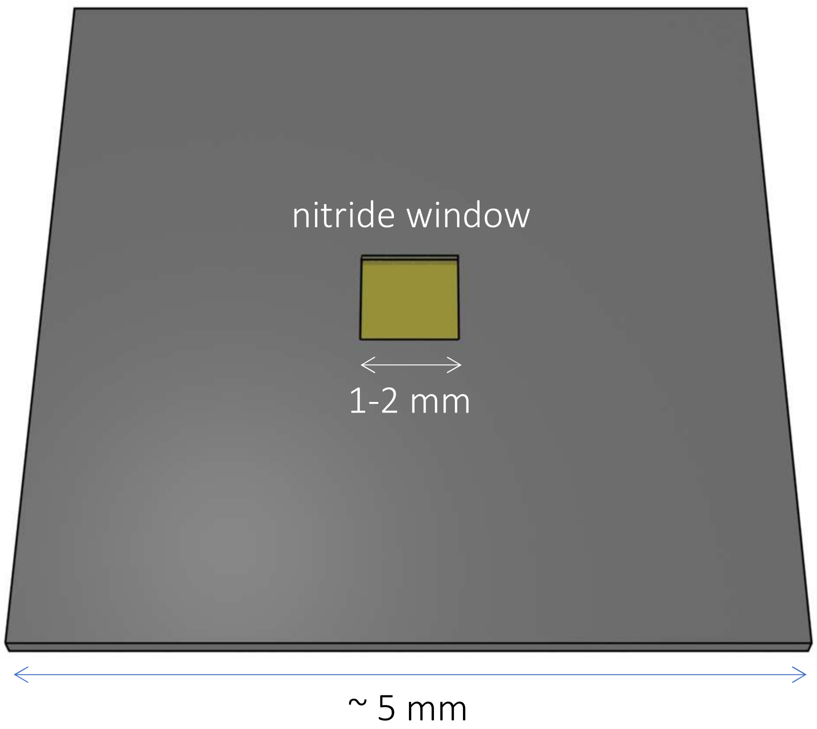

- **Energy 100 eV – 2 keV**
- **Angular range 0.1 – 70 deg**
- **Higher order contamination mitigated by choice of grating and constant of fixed focus (cff)**
  - Allows for high flux spectroscopy mode and high purity scattering mode

# RSoXS and NSLS-II Performance



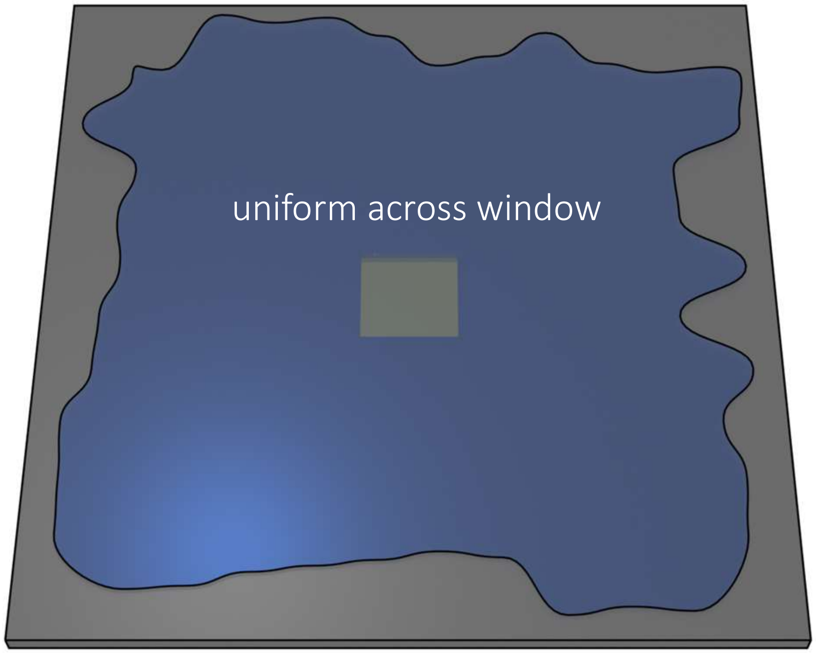

- **Polarization control**
  - Full linear control
  - Circular, elliptical
- **Carbon dip removed**
  - Oxygen on all optics
  - RSoXS immediately after exit slits, so all optics have pink/zero order light

# Anatomy of an RSOXS sample: support




- Normal use is 5x5 mm nitride membranes on a Si frame
- Larger than typical TEM nitride grids.
- Typical silicon wafer thickness ~400 um
- Typical silicon nitride thickness 50 nm to 100 nm
- Silicon nitride *will* attenuate beam, especially at nitrogen edge
- Several vendors for these supports including Silson & Norcada,* or make them yourself

# Anatomy of an RSOXS sample: sample film



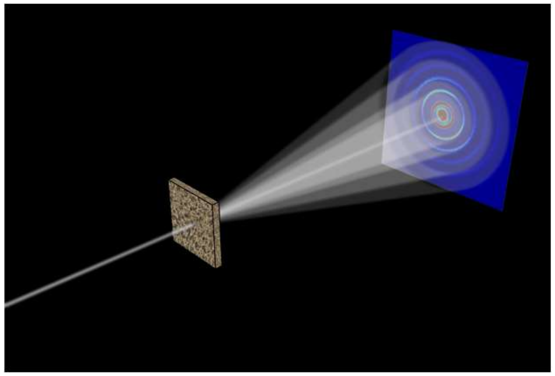

- typical organic film thickness: 100 nm to 200 nm
- typical beam is ~50 um to 200 um;
  must be uniform
- asperities (comets, dust) cause significant artifacts that can't be easily subtracted

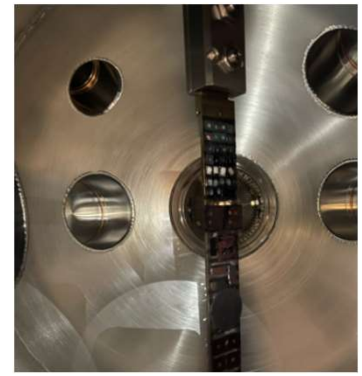
How to get the film on the support:

- Normally: Float off a substrate in water, catch on a nitride window
  - Water can cause problems
  - Cracks and folds are common
- If possible: Process directly atop window
  - silicon nitride may break
  - vacuum for spin-coating is especially bad
  - blade coating sometimes works; hard to make such a small sample
- Future: Process it directly with silicon backing before window is formed, then etch window

# Challenges with RSoXS

NIST





### Collecting good data

Always a time-consuming process, generally at least 50% of beamtime is hunting for a clean spot by hand

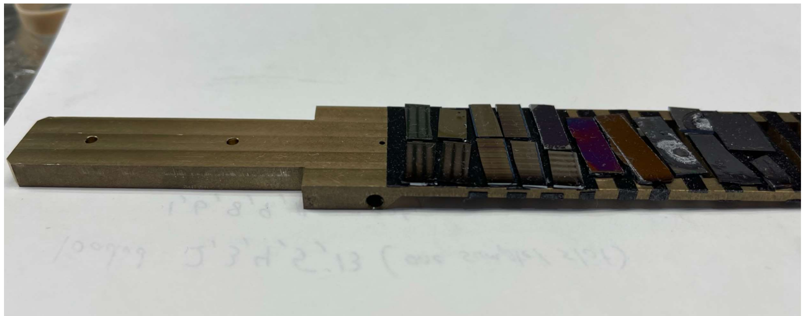
### Experimental Efficiency

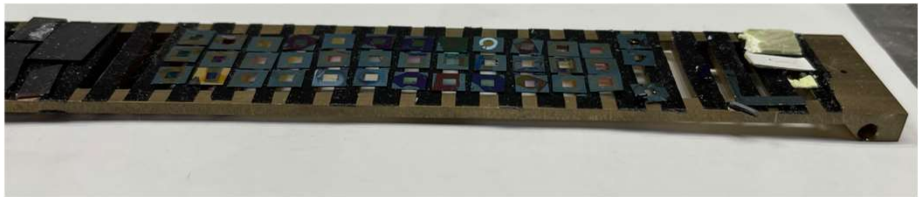
A limited number of samples can be loaded up at once, and pump down takes at least an hour

### Keeping track of data

An experiment is generally ~100 samples, each with many energies, polarizations, incident angles, exposure times, and two area detectors, lots of 1D measurements

# Solution 1 – Sample Management



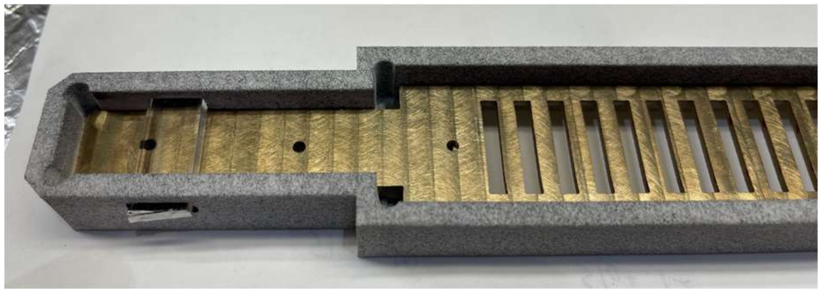


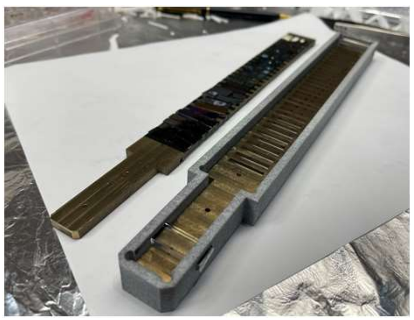
New Sample Bar design

- Maximized real estate for samples, front and rear available for grazing incidence (surface measurement) samples. ~120 standard transmission samples.
- Four fiducials for sample location/bar geometry corrections

# ✉ Sample Management - Shipping

NIST



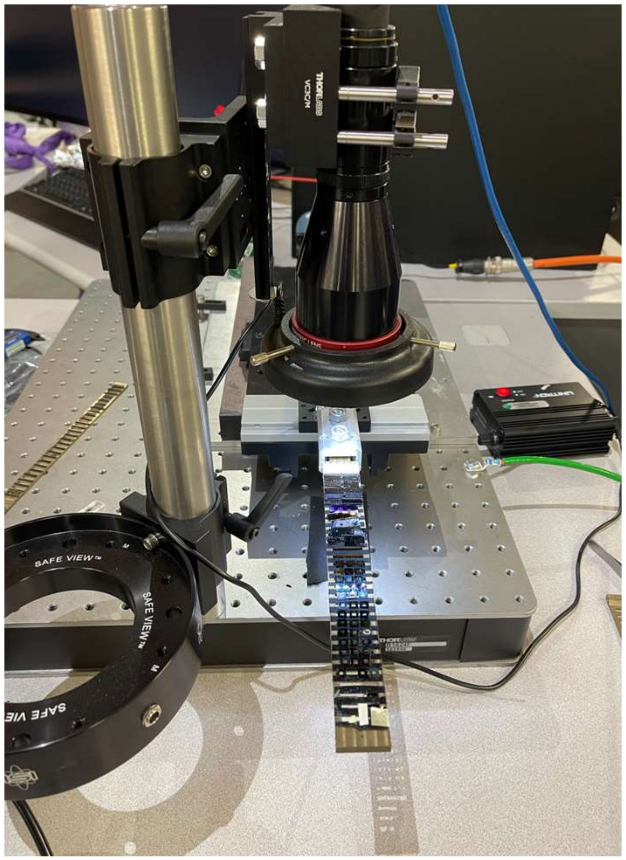


Pelican case and standard box size eliminate need for waste packaging

New shipping widget and standard case / box to eliminate packing waste and inconsistencies

- Widget offsets the bar so samples can be loaded on the front and back while it is installed, because it can be held by hand, it makes UHV prep significantly easier.
- Saves the beamline scientist significant headaches mounting and keeping track of samples!

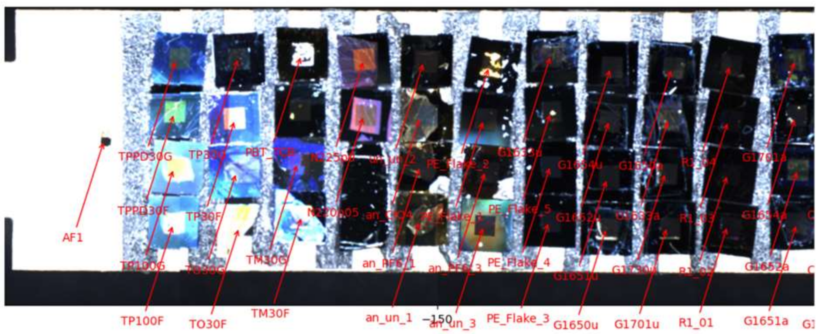
# Solution 2 – Sample positioning

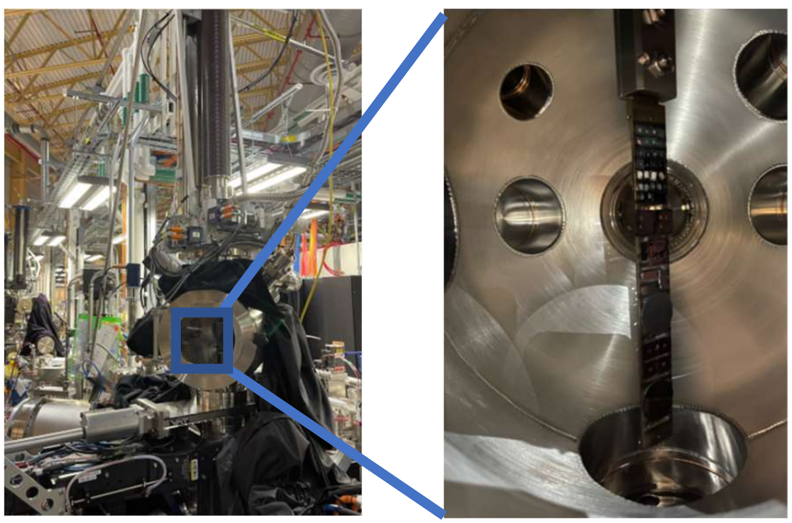



Simple linear stage and microscope allow for accurate high-resolution imaging of sample

- Done before beamtime, so no experimental time is wasted
- Different exposure times, lighting conditions, automatic image-image offsets are all planned to be added soon, but system as it is works very well.

# Interactive Sample positioning



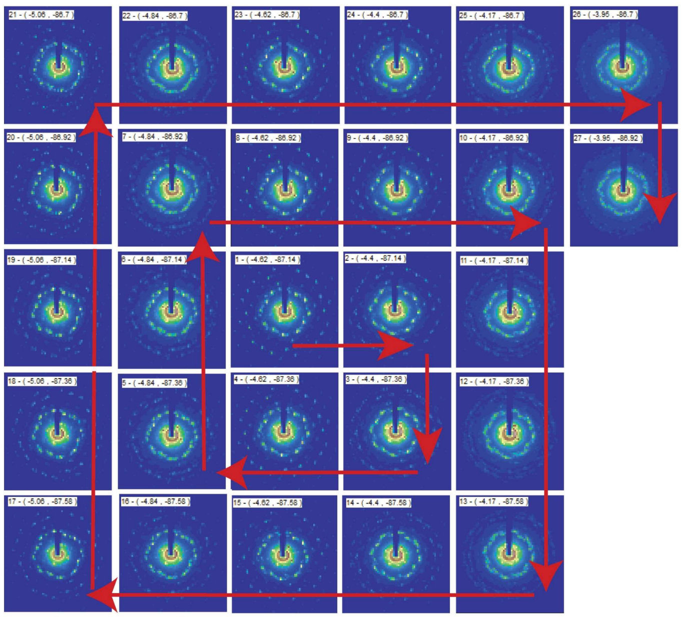



- The X-rays are used to find the fiducials, limiting the beamtime necessary to align sample from ~10 minutes/sample to ~10 minutes total.
- 3D position, based on what type of sample, the height, which the user hopefully entered, combined with the visual and X-ray location of fiducials is corrected for, so location well within the beamsize ~100 µm and arbitrary incident angles are accommodated.

After loading the excel sheet and stitched sample image, an interactive prompt asks the user to click on locations for different samples in a matplotlib window

A new spreadsheet / sample list is produced with all the chosen positions entered in the location entry.

# Sample positioning



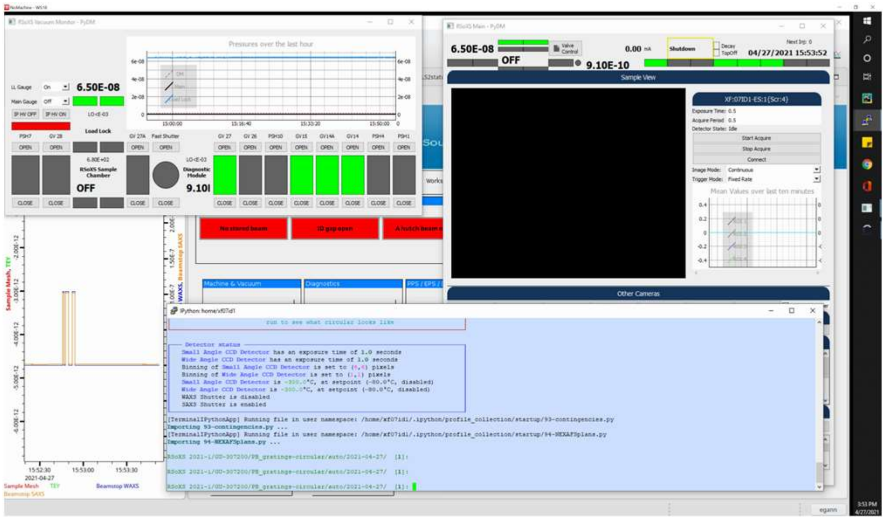
Typically, ~2-5 minutes per sample

## Further refinement through optional spiral scan

- Visually the best area often can't be precise enough, so a high-resolution quick spiral scan at a fixed energy of interest is often queued up first

- User can stop scan when a "good" position is found, or just let all of the spirals run automatically and go back later. "good" positions are corrected in the excel sheet and reloaded into bluesky.

# Acquisition interface

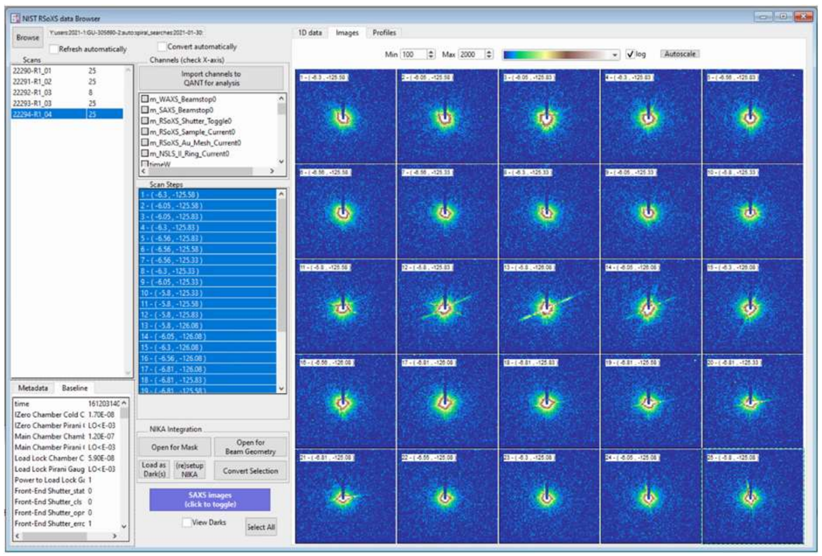



Windows interface computer – locally three monitors, reduced to a single remote monitor, showing PYDM, CSS, and bluesky

Excel files are usually edited locally on which ever computer the user is on for a better experience, and synced through onedrive

PYDM serves as a more compact customizable pythonic single-view CSS screen – used to monitor, not to be adjusted by users

# Live analysis interface




Analysis is currently done through a second beamline windows computer and Igor Pro data analysis

- data is opened automatically by Igor pro, and 1D datasets, 2D images, reduced 1D data waterfalls, and metadata are all shown.

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- Future analysis will be done in a jupyterhub website accessible by users remotely

# Covid Beamtime results breakdown

NIST

- 2021-1 cycle had 10 user groups with 40 projects – 87 shifts requested
- 30 shifts available
- Accepted and measured all projects
- Combined and mounted all samples onto 4 sample bars
- 1 full sample bar of ~100 transmission samples
- Users interact over video chat with me during alignment and creation of queue, finding optimal sample locations, and live analysis during acquisition
- Beamline updates status via slack (and email when there is a problem)

Day 1 (before beamtime)

- mount, create sample sheet, image and locate all samples visually, begin pump down

Day 2 (beamtime)

- within 20 minutes of having beam, fiducials are found, sample locations corrected
- 5 hours of spiral scans finding optimal measurement locations

Days 2 – 4/5 (3-4 days of beamtime)

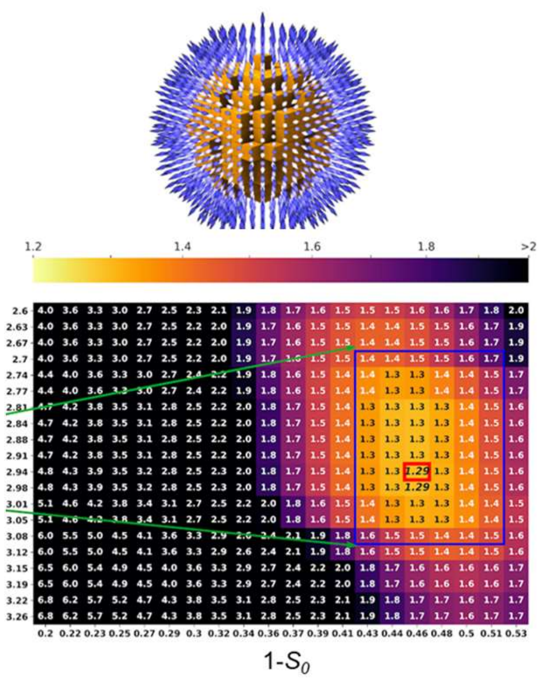
- Automated collection and attended analysis refining queued sample scans as data is collected

Additional a single TEM holder heating experiment completed

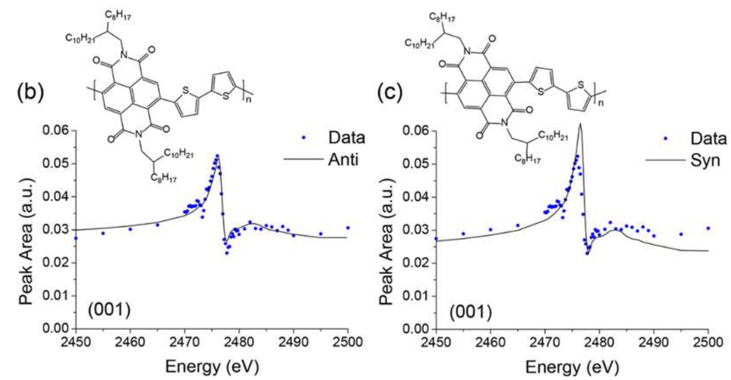
In future, daytime will be filled with in-situ samples and ex-situ samples will be queued for overnight

# Future of RSoXS – HPC and new environments

Numerical forward simulations to fit polarized RSoXS

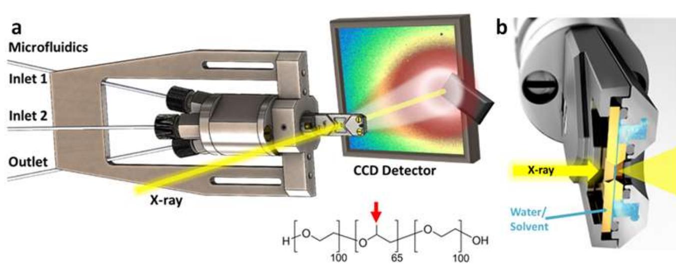


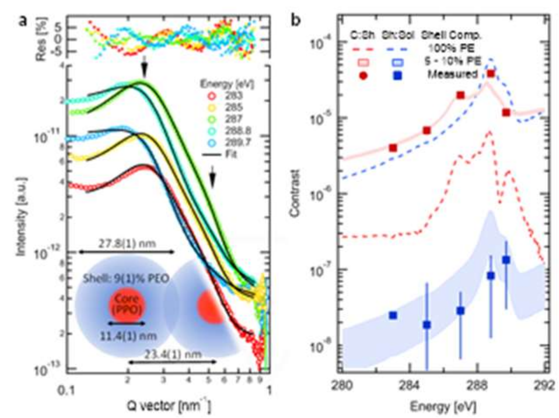

New analytic solutions for quantitative spatiochemical analysis




Freychet; JACS (2021)

New environments to expand beyond vacuum environments:



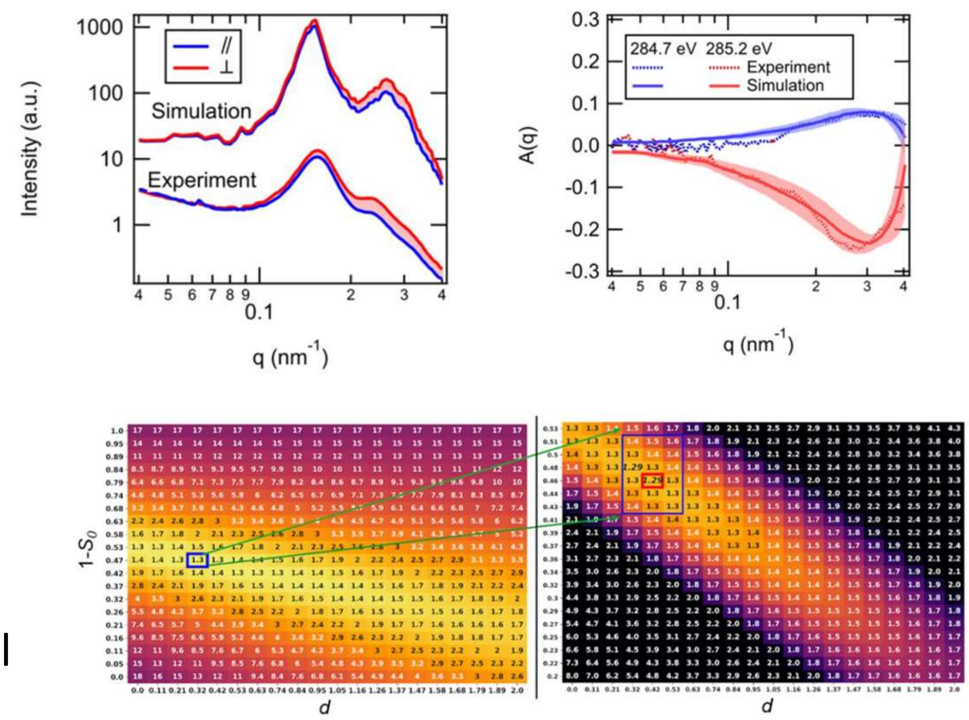




McAfee; Nat Comm; 2021

# Near Future RSoXS

RSoXS simulation codebase (initially developed in my grad work) needed massive speedup and an accessible platform to become useful for the user community

- NIST collaborated with Iowa State university partner Ganapthysubramanian to refactor the Igor code
    - C++ with NVIDIA CUDA
    - Massive speed-up, roughly 400x.  From weekend scale simulations to coffee break scale
    - Enables quantitative fitting of polarized RSoXS
- Current status: Late Beta
    - Great results two results in publication/under review
    - Currently working on making this a Beamline tool available for users to interpret (after beamtime), and predict (ahead of beamtime) RSoXS data




Fitting results

# Summary / Outlook for RSoXS

- RSoXS is an emerging soft matter characterization tool
- Hyperspectral diffuse scattering data is undeniably complex and needs continued development of new tools to lower barrier to entry into field
- Historic connection with organic electronics is strong but many additional fields are opening up
  - Idea in the nano characterization field that RSoXS is only a tool for OPV is diminishing
- 2021-1 cycle was intense, but ultimately manageable with just the beamline scientist running everything.
  - User-oriented results were a success
  - User control not extensively tested – new system for 2021-2 is very easy (simple website)
  - Automation made it possible without extraordinary toll on beamline scientist
  - RSoXS station shares time with other endstations, making it considerably more manageable
- Streamlining the sample shipping / mounting / metadata entry continues to make everything better
- Pre-alignment and automatic transit scans is a game changer for data quality
- Getting users their data continues to be a challenge, although it is improving in the 2021-2 cycle
- Hopefully 2021-1 is only the start of a continually improving RSoXS experience at NSLS-II

THANKS