Opportunities at Liquid-Solid Images with the New MBA Lattice:*

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Contributions from:

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Sang Soo Lee (Ions on muscovite)
Ahmet Uysal (RTILs)

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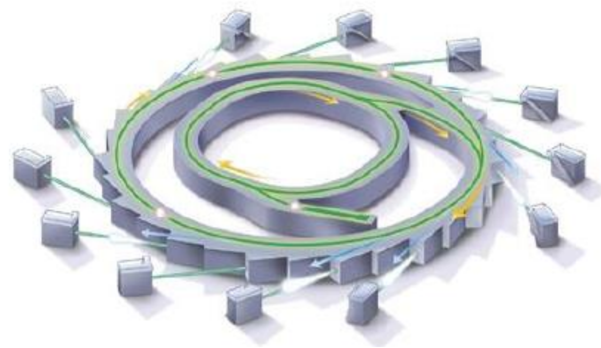
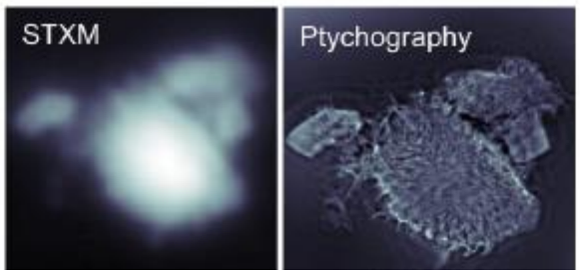
Outline:
- From XRIM2 to the "Ultimate XRIM"
  - opportunities and challenges
- Interfacial dynamics with speckle and XPCS
- Resonant Contrast

*Work is supported by the Department of Energy, Office of Basic Energy Sciences: (Geoscience Research Program, FIRST EFRC)

Grand Challenge Science on Diffraction-Limited Storage Rings



Microstructures in hydrating cement



Nanostructured electrodes in Lithium ion batteries

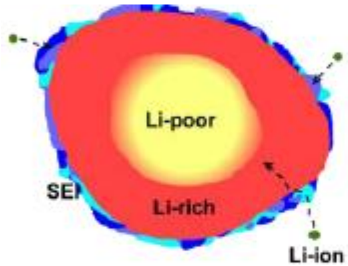
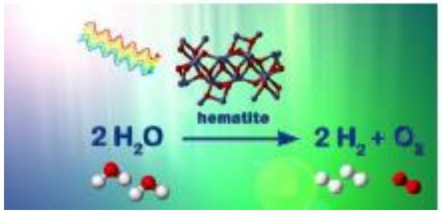


Photo-electrochemical water splitting



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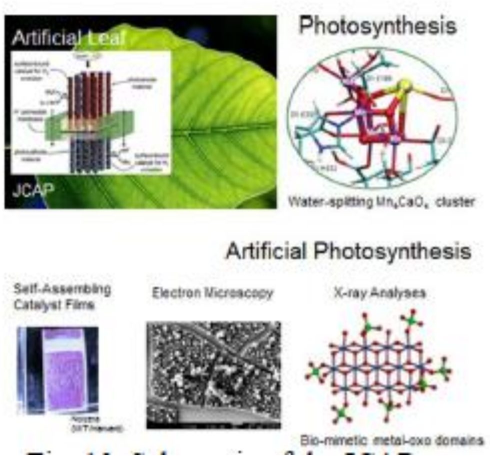

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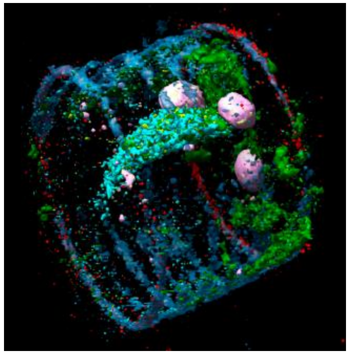

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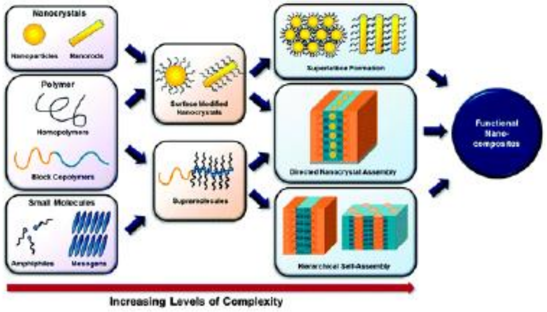
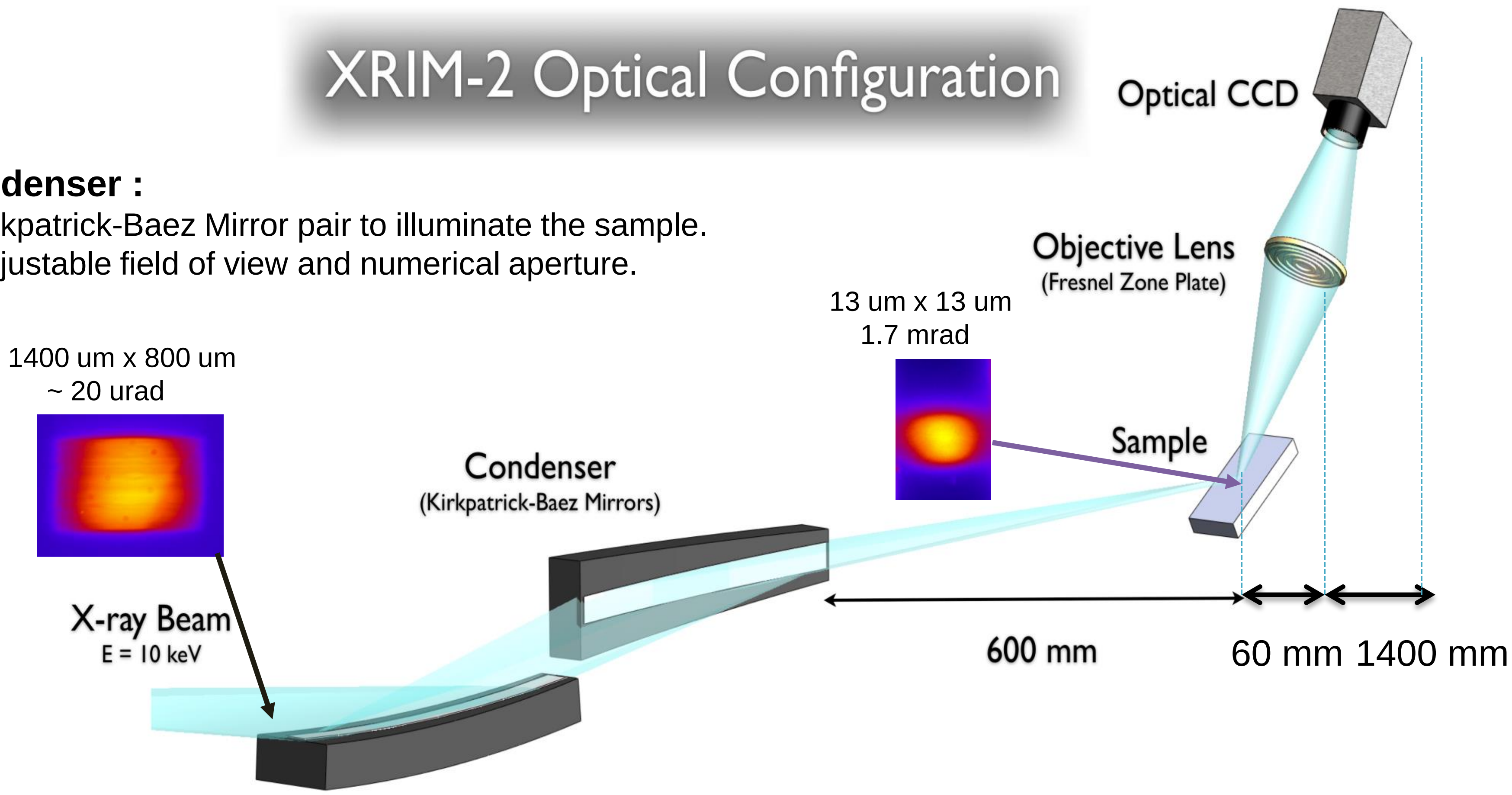


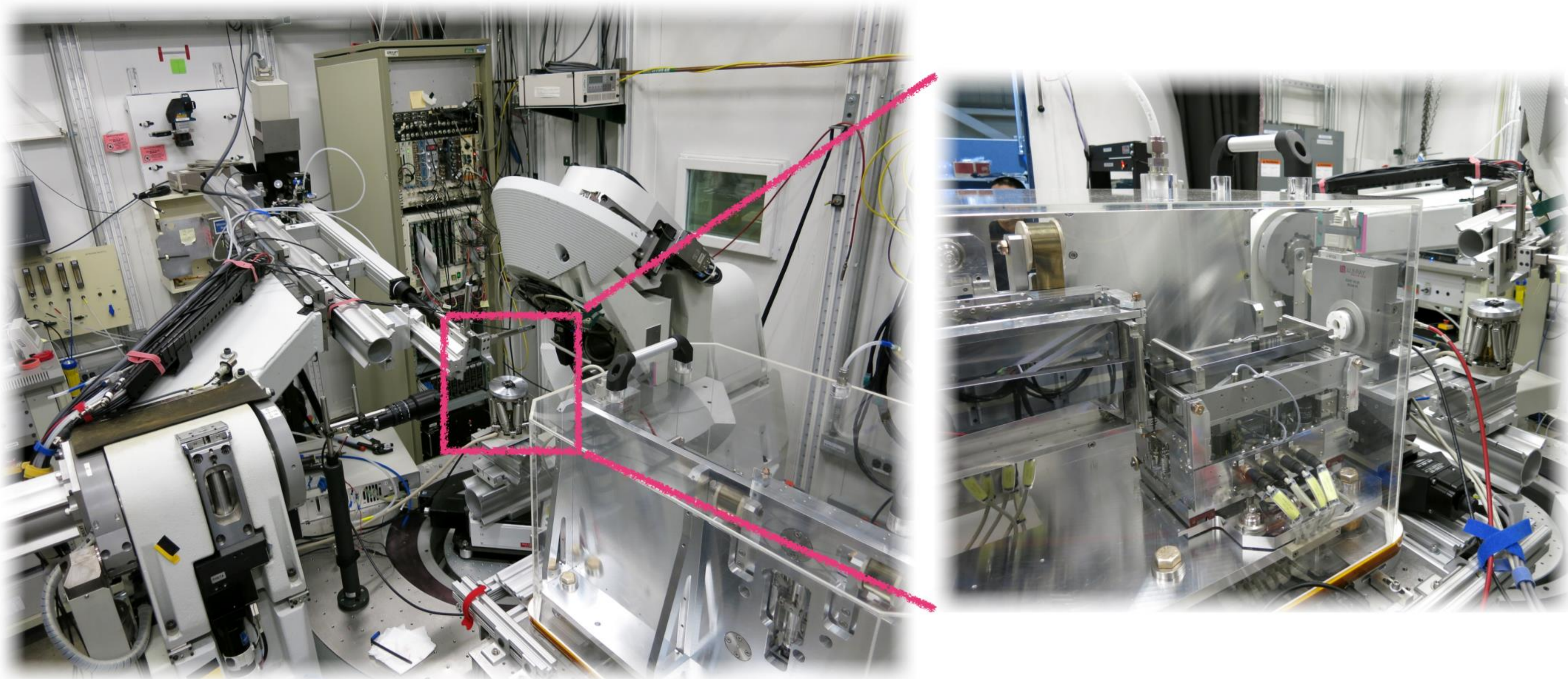
Current Status: XRIM2

Condenser :
- Kirkpatrick-Baez Mirror pair to illuminate the sample.
- Adjustable field of view and numerical aperture.



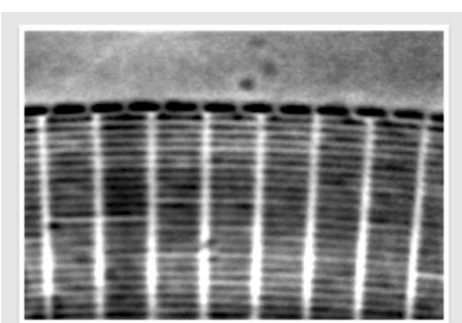
Specs :
- Illumination = 13 x 13 um^2 or larger.
- NA = 1.8 mrad or less.
- 6 x 10^{12} photons/sec, **>10x higher flux density than XRIM-1.**

Current Status: XRIM2

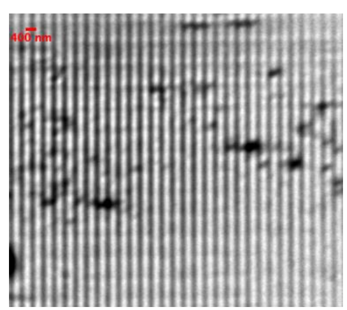


Test objects:

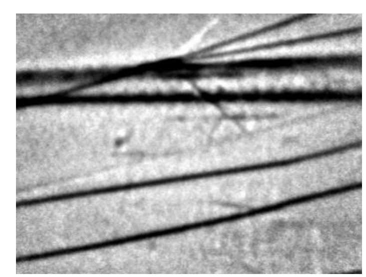
FZP, 60 nm zone width



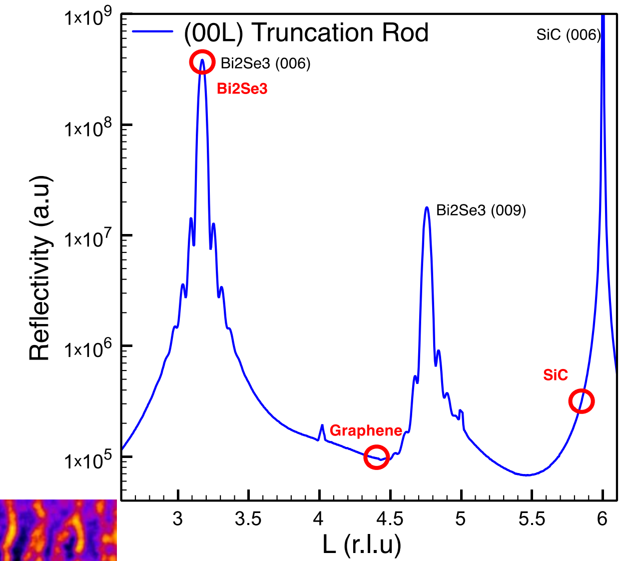
Gold Wires: 90 nm wide



Steps on Orthoclase (001)

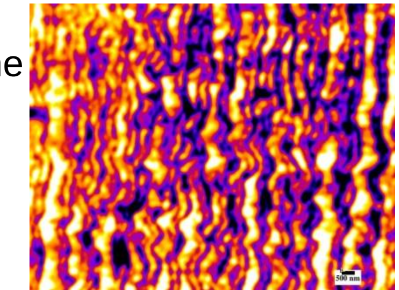


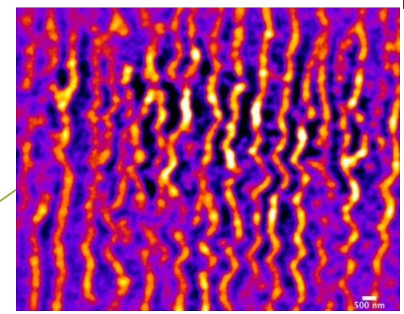
XRIM Example: Bi_2Se_3/Graphene/SiC(001):

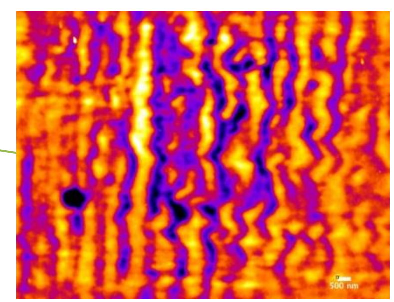


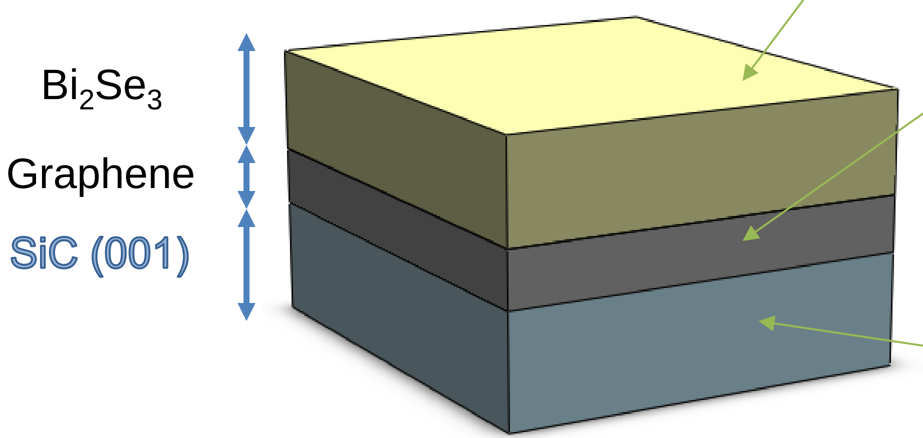
Thin film diffraction:

- ~30 nm thin film of Bi_2Se_3 MBE grown on epitaxial graphene/SiC(001).
- Q-dependent image contrast: changes sensitivity to the different components of the structure (e.g., Bi_2Se_3, SiC, graphene, etc).







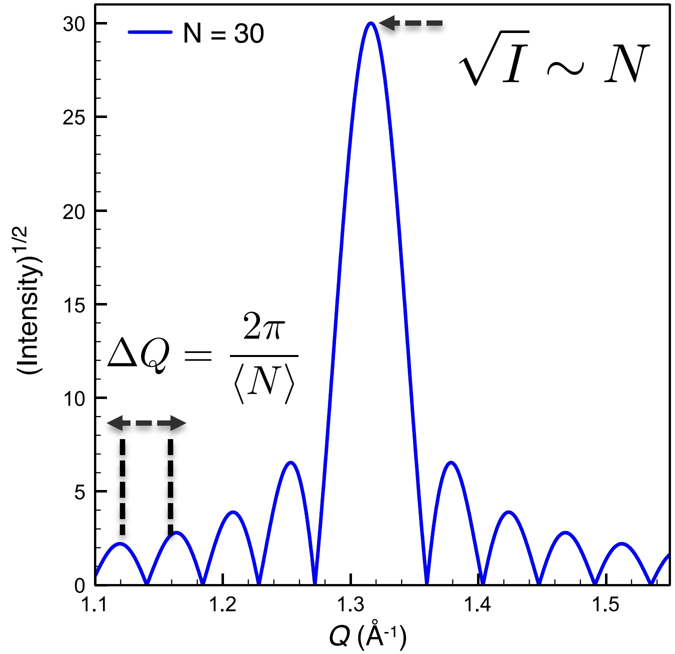


Laanait et al., Manuscript in preparation; in collaboration with J. Emery (CSE/ANL), L. Li (UW Milwaukee), K. Gaskill (Naval Research Labs)

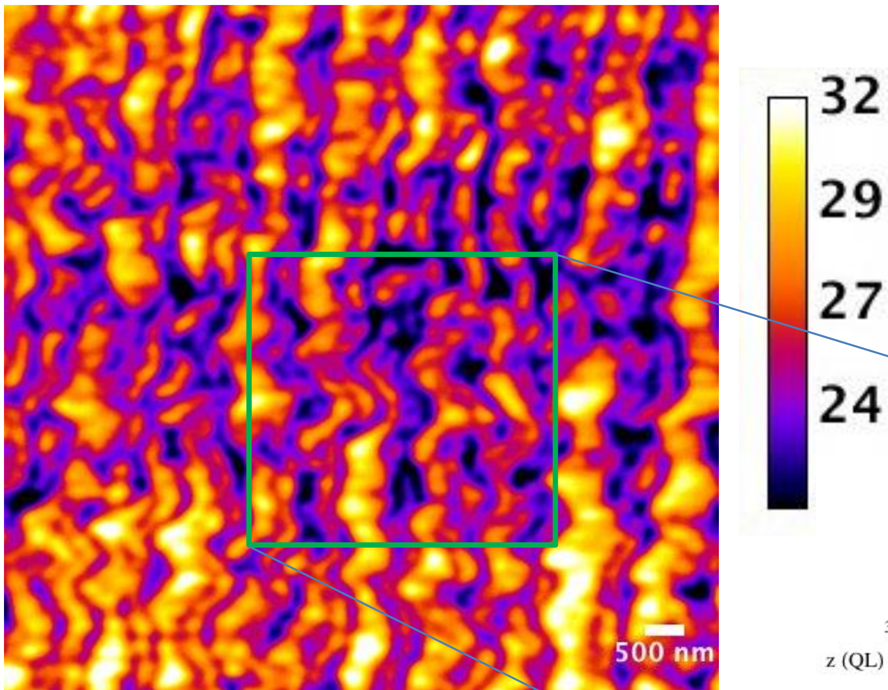
XRIM Example: Bi_2Se_3/Graphene/SiC(001):

Thickness distribution:
- Convert image intensity to spatially resolved measurement of Bi_2Se_3 film thickness.

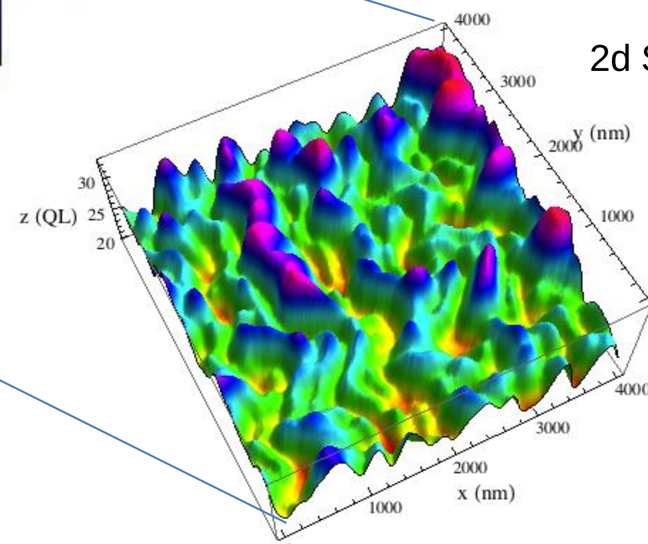
N-slit Diffraction



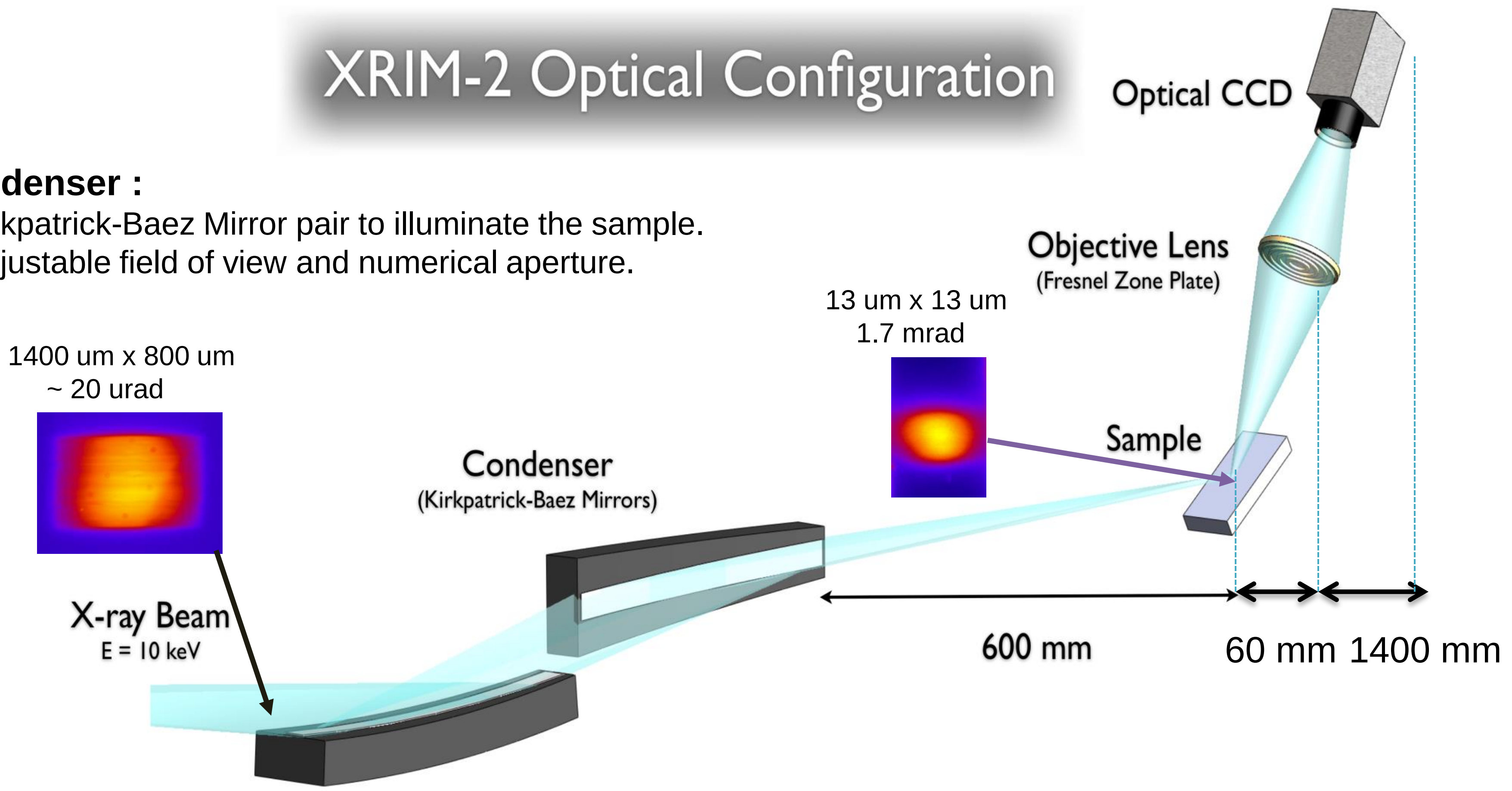
Bi2Se3 QL



2d Surface Plot



Needed Improvements: XRIM2



Condenser :

- Kirkpatrick-Baez Mirror pair to illuminate the sample.
- Adjustable field of view and numerical aperture.

→ Next generation objective lens (multilayer Fresnel zone plate)

- High (~50%) efficiency at ~10keV (less damaging)
- ~10% efficiency near 17keV (enables in-situ observations)
- Requires robust in-house synthesis capability

→ Robust mechanical stability (achieve high resolution for long exposure times)

Imaging Interfacial Heterogeneity with Combined XRIM/CDI/Ptychography

Opportunity:

Understanding the reactivity of spatially heterogeneous interfaces in complex environments remains a general challenge (e.g., catalysis, growth, geochemistry, etc.)

Challenge:

Directly observe changes of interfacial structure, topography, composition during reactions through observations with high-spatial resolution.

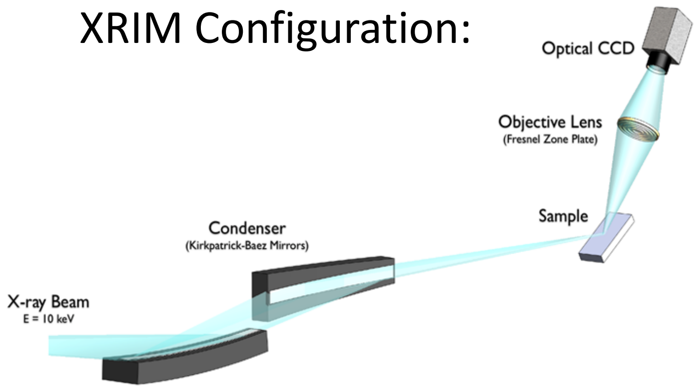
4GSR Strength:

- High coherent flux enables robust imaging of interfacial heterogeneity through complementary observations by (incoherent) XRIM and (coherent) CDI/Ptychography.

- XRIM provides real-time direct space images with a large (~10 μm ×10 μm) field of view.

- CDI/Ptychography provides higher spatial resolution imaging of individual features of interest from XRIM images (e.g., red highlighted region).

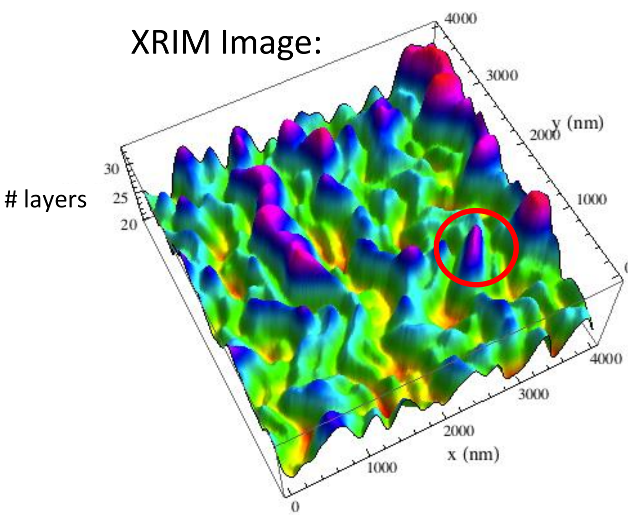
XRIM Configuration:



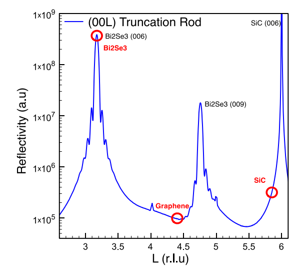
Bi_2Se_3 Quantum Layers: Film Thickness Map

(films grown on Graphene/SiC(001))

XRIM Image:

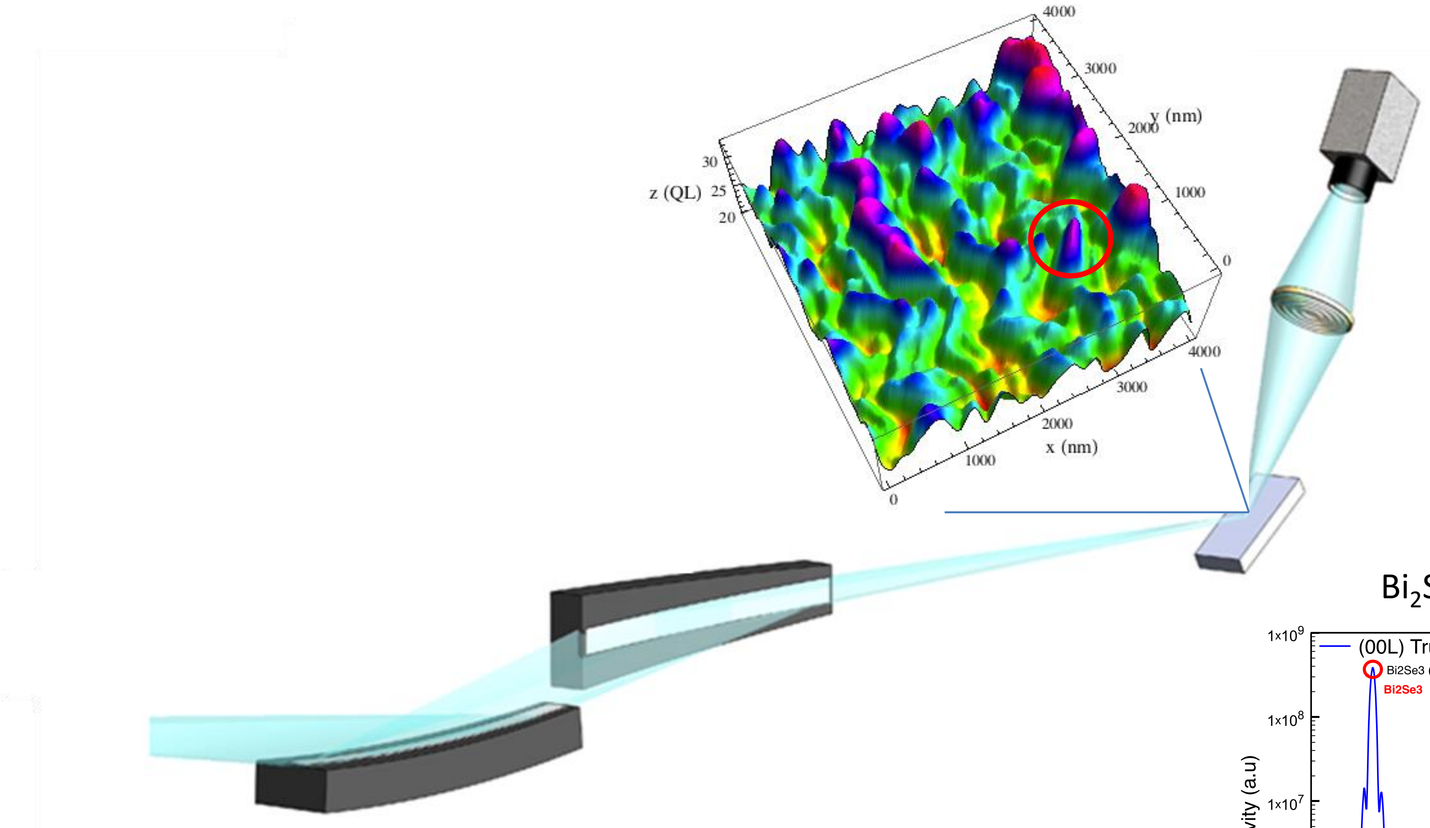


Bi_2Se_3 Film CTR:

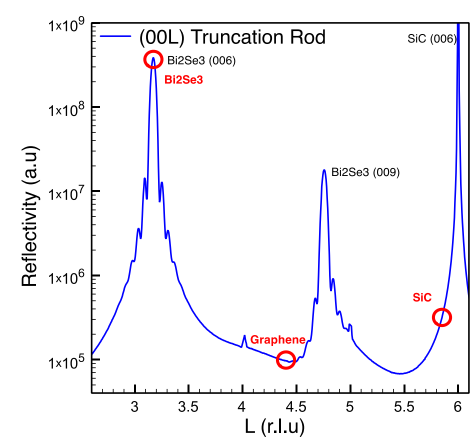


Imaging Interfacial Heterogeneity with Combined XRIM/CDI/Ptychography

XRIM Configuration:



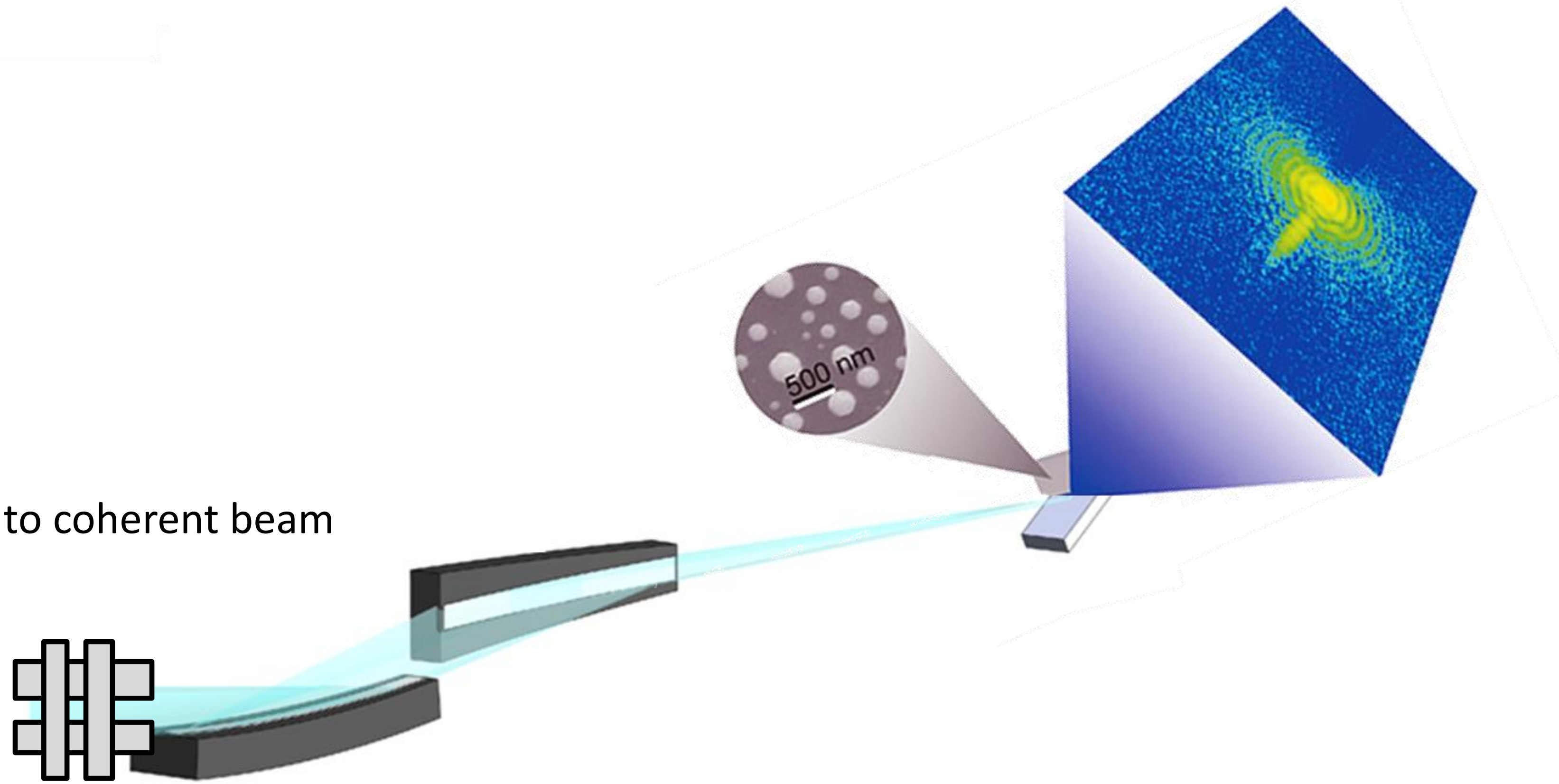
Bi_2Se_3 Film CTR:



Imaging Interfacial Heterogeneity with Combined XRIM/CDI/Ptychography

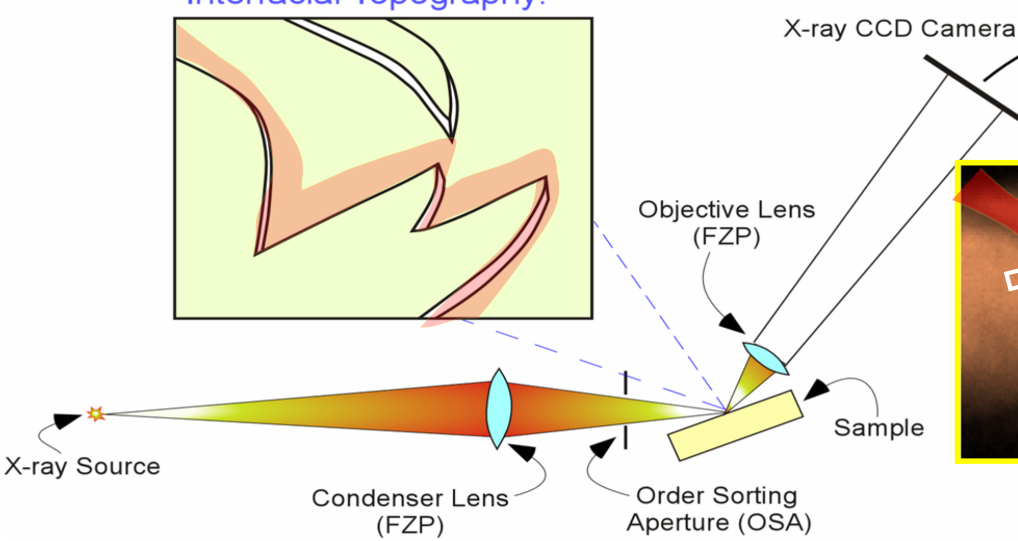
CDI/Ptychography Configuration:

Slit down to coherent beam

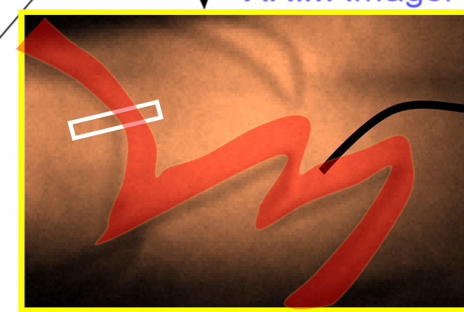


CDI schematic from: Pfeifer et al., *Nature* **442**, 63-66 (2006)

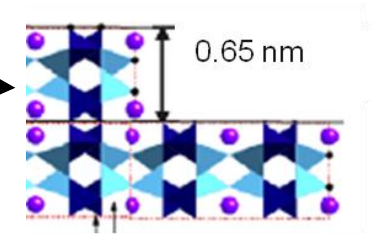
Elemental Contrast in X-ray Reflection Interface Microscopy:



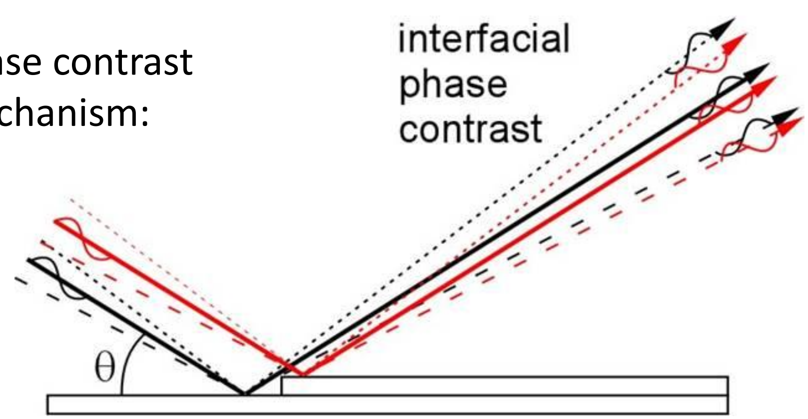
XRIM Image:



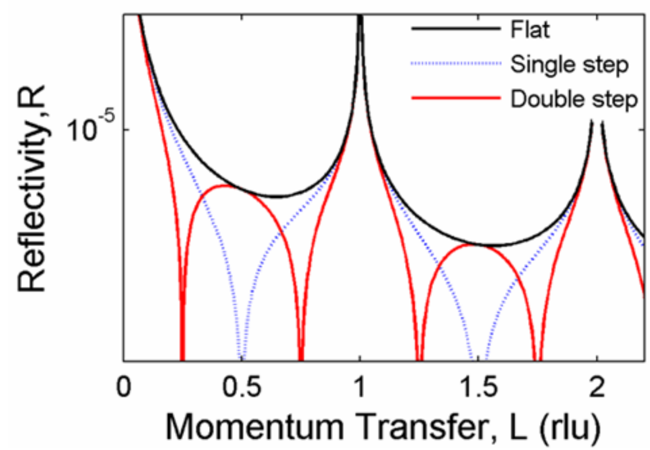
Elementary Step:



Phase contrast mechanism:



Intensity contrast at a step:

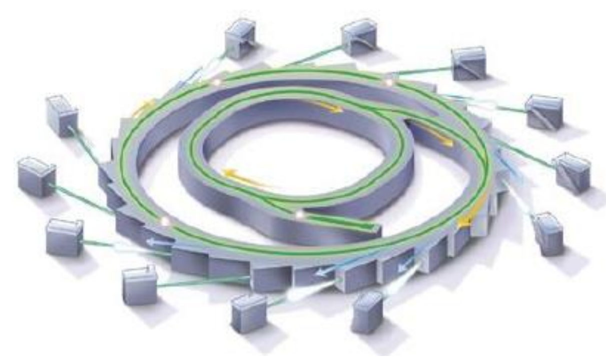


Resonant scattering provides an elemental contrast mechanism

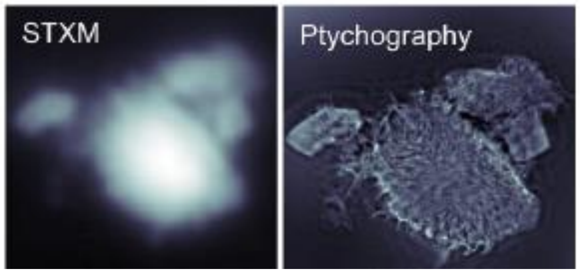
- Enables the ability to spatially resolve elemental/chemical heterogeneity
- Orbital ordering and domain structures can be visualized with polarization contrast

*Fenter et al., *Nature Physics* **2**(10) 700-704 (2006)

Grand Challenge Science on Diffraction-Limited Storage Rings



Microstructures in hydrating cement



Nanostructured electrodes in Lithium ion batteries

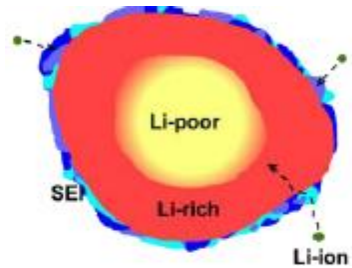
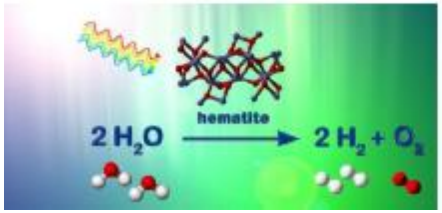


Photo-electrochemical water splitting



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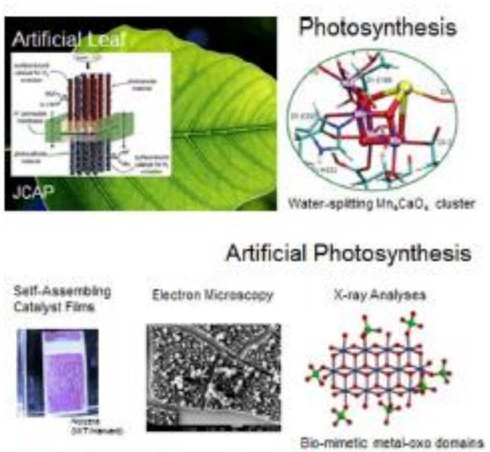

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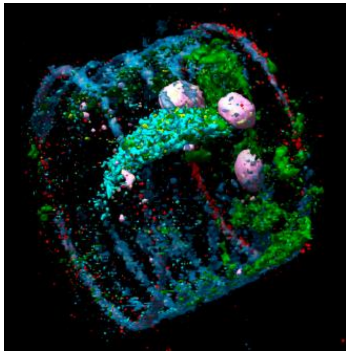

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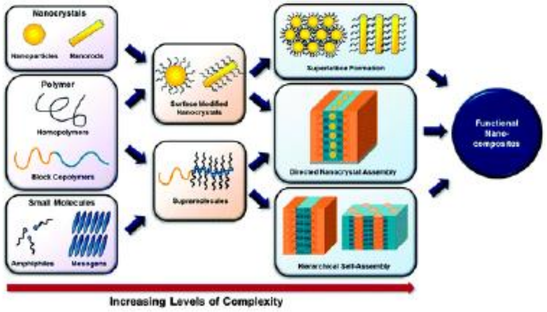

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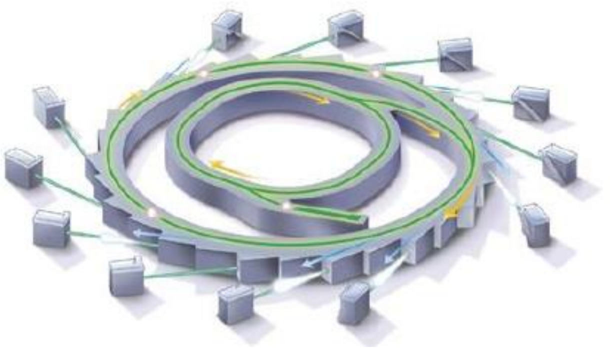


General Characteristics:

1) High degree of spatial heterogeneity
2) In-situ (water, solvents, etc.)
3) Beam-sensitive components (organics)

→ Requires high brilliance photon beam for spatially-resolved studies (e.g., highly focused beam, coherent flux, or both)

→ Increased sensitivity to perturbations from radiation chemistry (i.e., “beam damage”)

Flux Densities for Current and Expected Experiments:

Unfocused undulator beam: $\sim 10^{12}\ \gamma/(1000\ \mu m)^2/sec$ $= 10^6\ \gamma/\mu m^2 sec$

Bragg CDI (Sector 34): $\sim 10^9\ \gamma/0.5\ \mu m^2/sec$ $= 2\times10^9\ \gamma/\mu m^2 sec$
(soon $\sim 10^{10}\ \gamma/\mu m^2 sec$)

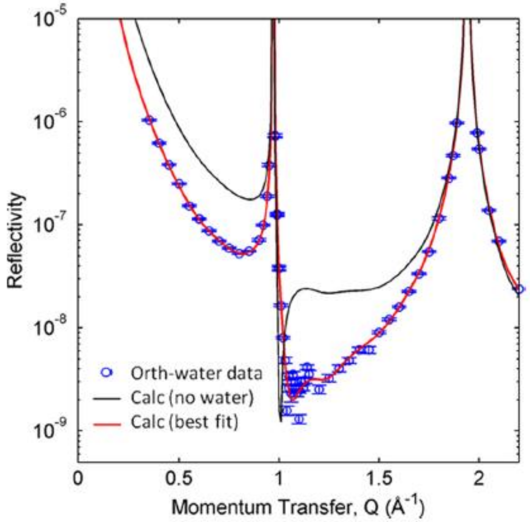
XRIM1 (focused incoherent beam): $\sim 10^{11}\ \gamma/(13\ \mu m)^2/sec$ $= 10^9\ \gamma/\mu m^2 sec$
XRIM2 (focused incoherent beam): $\sim 6\times10^{12}\ \gamma/(13\ \mu m)^2/sec$ $= 4\times10^{10}\ \gamma/\mu m^2 sec$

NanoProbe (focused coherent beam): $\sim 10^9\ \gamma/(35\ nm)^2/sec$ $= 8\times10^{11}\ \gamma/\mu m^2 sec$

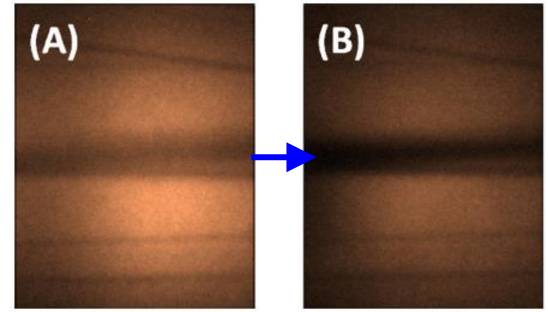
MBA Lattice (focused coherent beam): ~ 100*nanoprobe $= 8\times10^{13}\ \gamma/\mu m^2 sec$

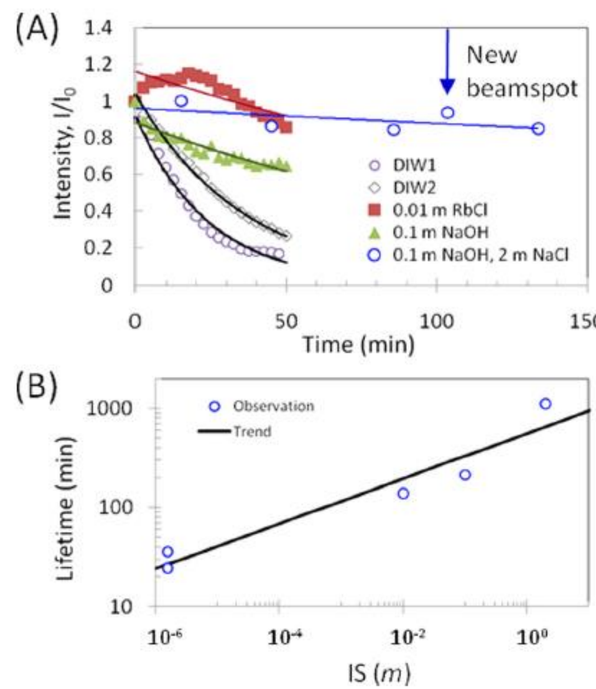
XRIM1 of Orthoclase in Water:

Orthoclase CTR:

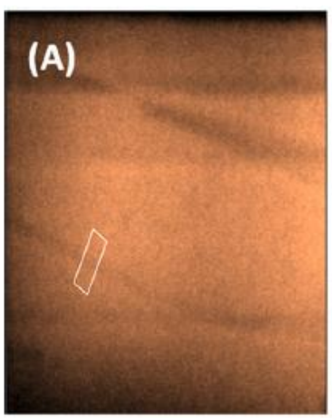


Damage due to XRIM Beam Exposure:





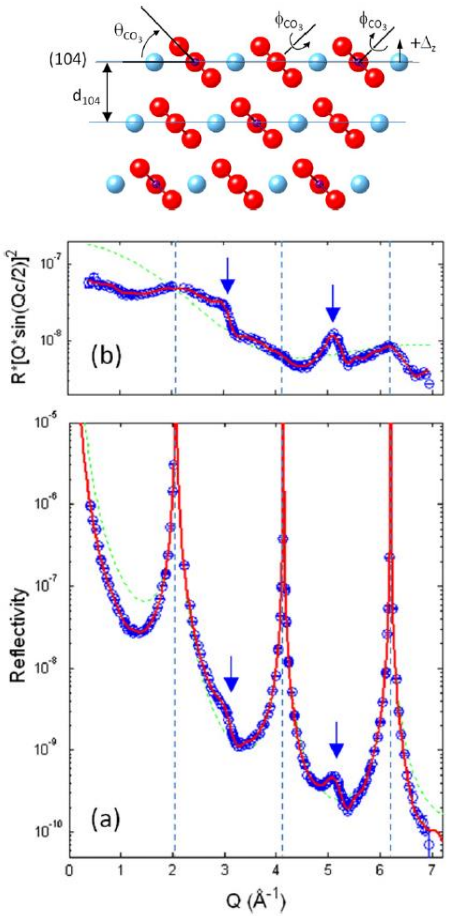
Elementary Steps on Orthoclase

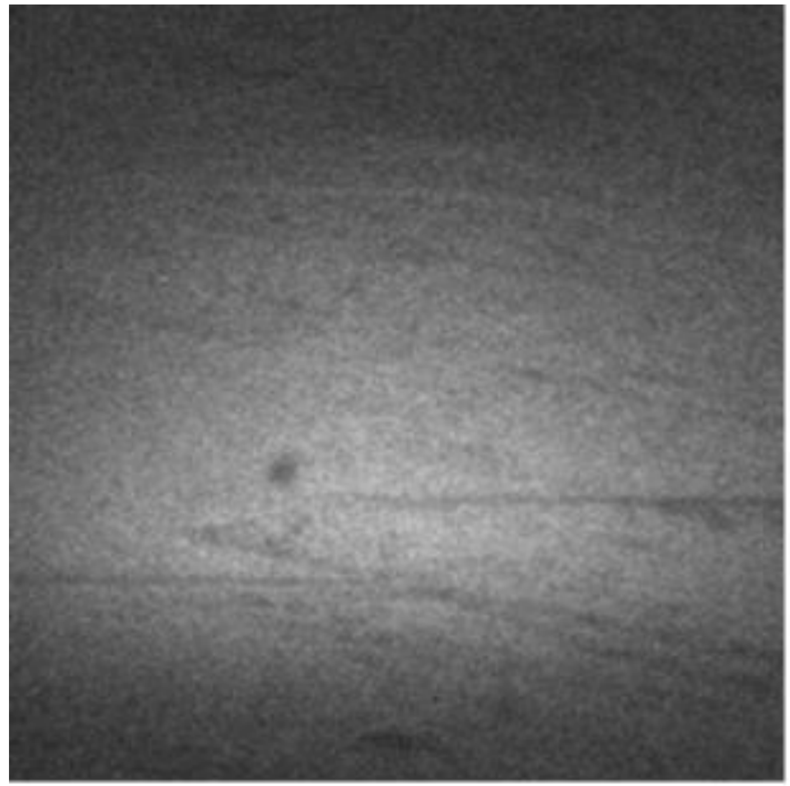


→ Orthoclase is highly radiation resistant in an unfocused undulator beam but "dies" in the XRIM1 beam

Fenter et al., *Journal of Applied Physics*, 2011

XRIM2 of Calcite in Water:



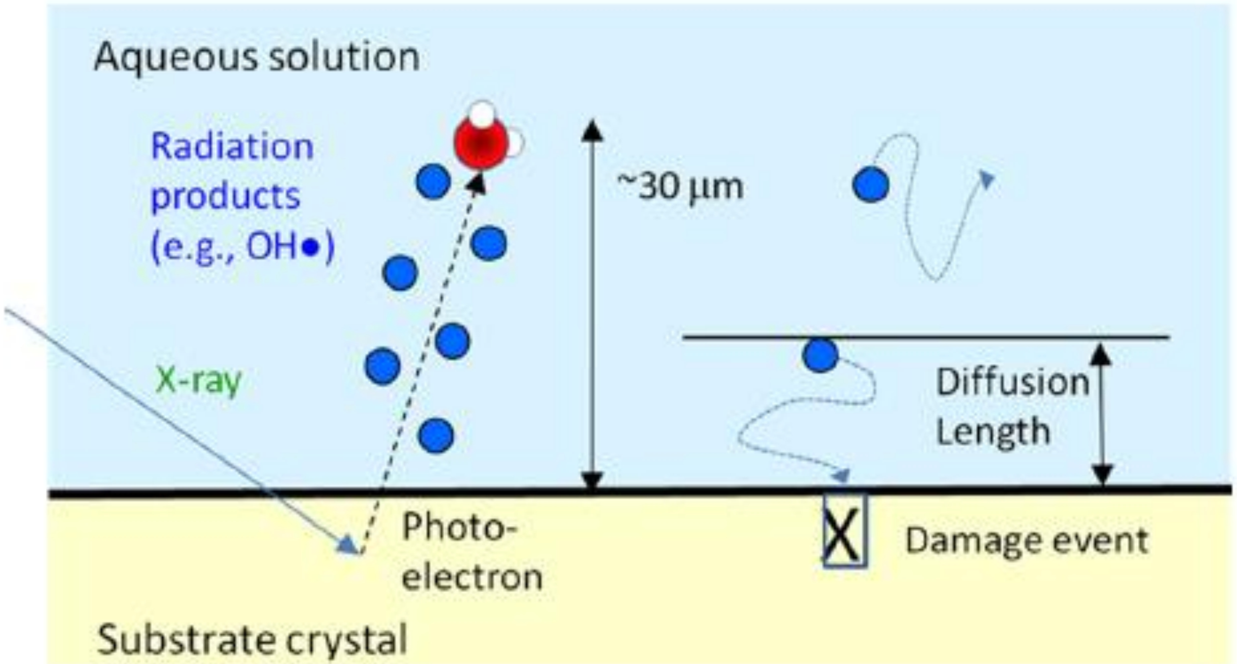


- In-situ XRIM imaging of a $CaCO_3$(104) single crystal in calcite-saturated water solution.
- Changes are caused by reaction with X-ray induced radiolysis products (e.g., OH radical and hydrated electron) generated by photoelectrons from the calcite.

(Each image is a 1 sec exposure, 0.5 sec sleep time, shown at 24 fps).

XRIM Movie: Laanait et al., in preparation: Calcite CTR data from Fenter et al., *Geochim. Cosmochim. Acta*, 2012

Mechanism of Radiation Damage at Solid-Liquid Interfaces:



Beam parameters (at 10 keV):

Adsorbed dose:

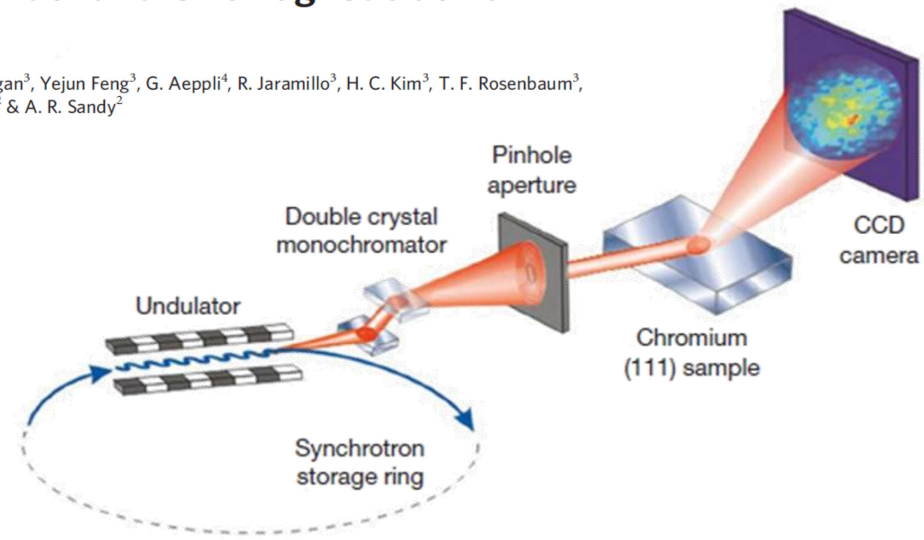
XRIM1:	XRIM2:	MBA Focused Beam:
~10^6 Grey/sec	~6×10^7 Grey/sec	~10^{11} Grey/sec

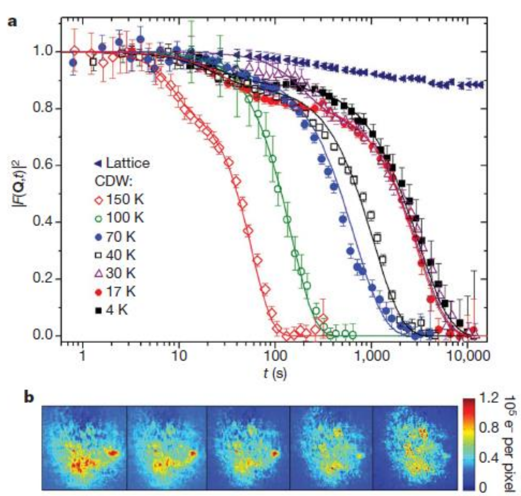
→ Radiation chemistry is the "high heat load problem" of the APS upgrade

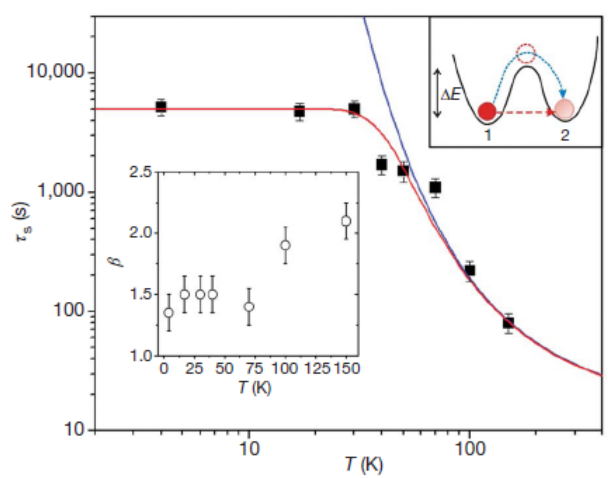
Opportunities with Coherent X-rays: Interfacial XPCS

Direct measurement of antiferromagnetic domain fluctuations

O. G. Shpyrko[1], E. D. Isaacs[1,3], J. M. Logan[3], Yejun Feng[3], G. Aeppli[4], R. Jaramillo[3], H. C. Kim[3], T. F. Rosenbaum[3], P. Zschack[2], M. Sprung[2], S. Narayanan[2] & A. R. Sandy[2]







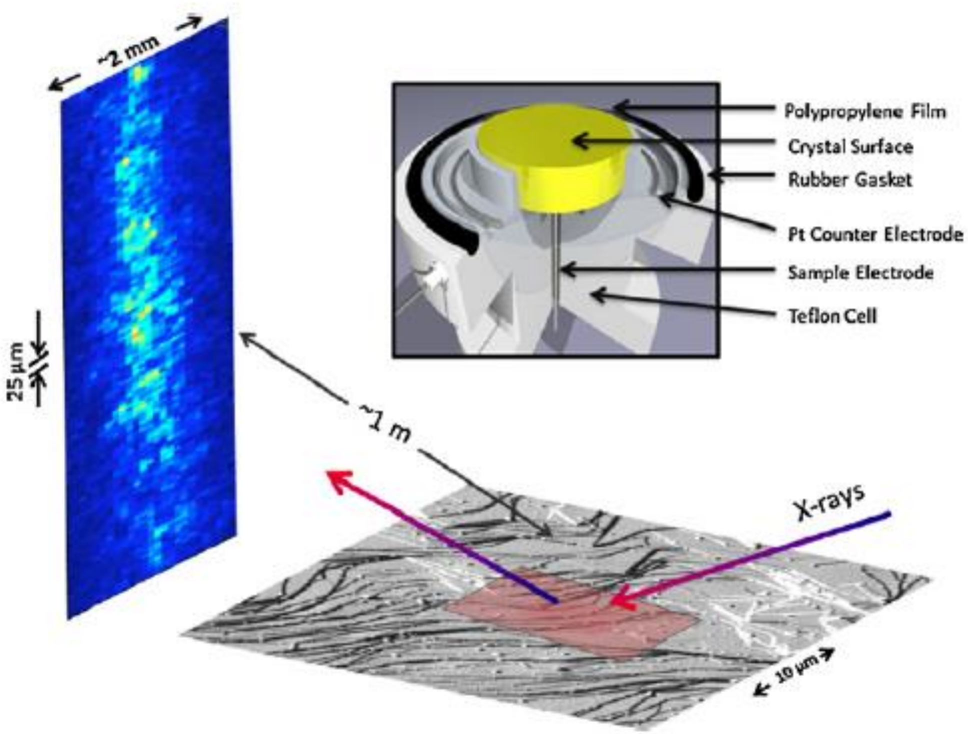
Contents lists available at SciVerse ScienceDirect

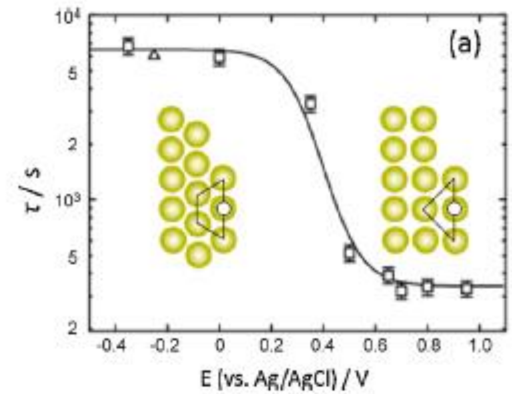
Electrochimica Acta

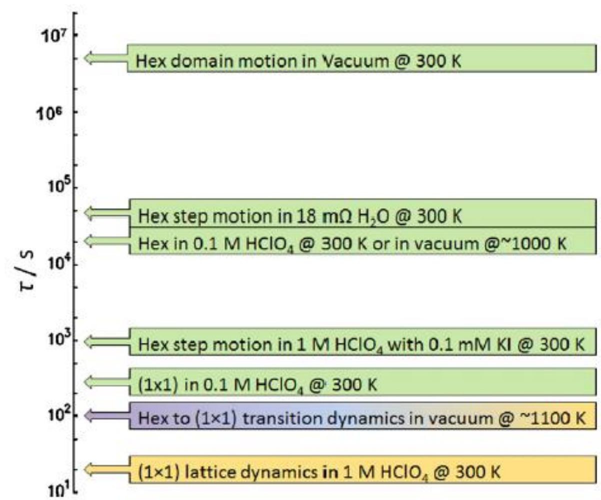
journal homepage: www.elsevier.com/locate/electacta

Study of electrode surface dynamics using coherent surface X-ray scattering

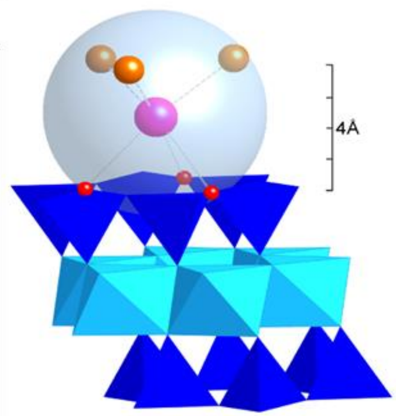
Hoydoo You[a,*], Michael Pierce[a,b], Vladimir Komanicky[a,c], Andi Barbour[a], Chenhui Zhu[a]

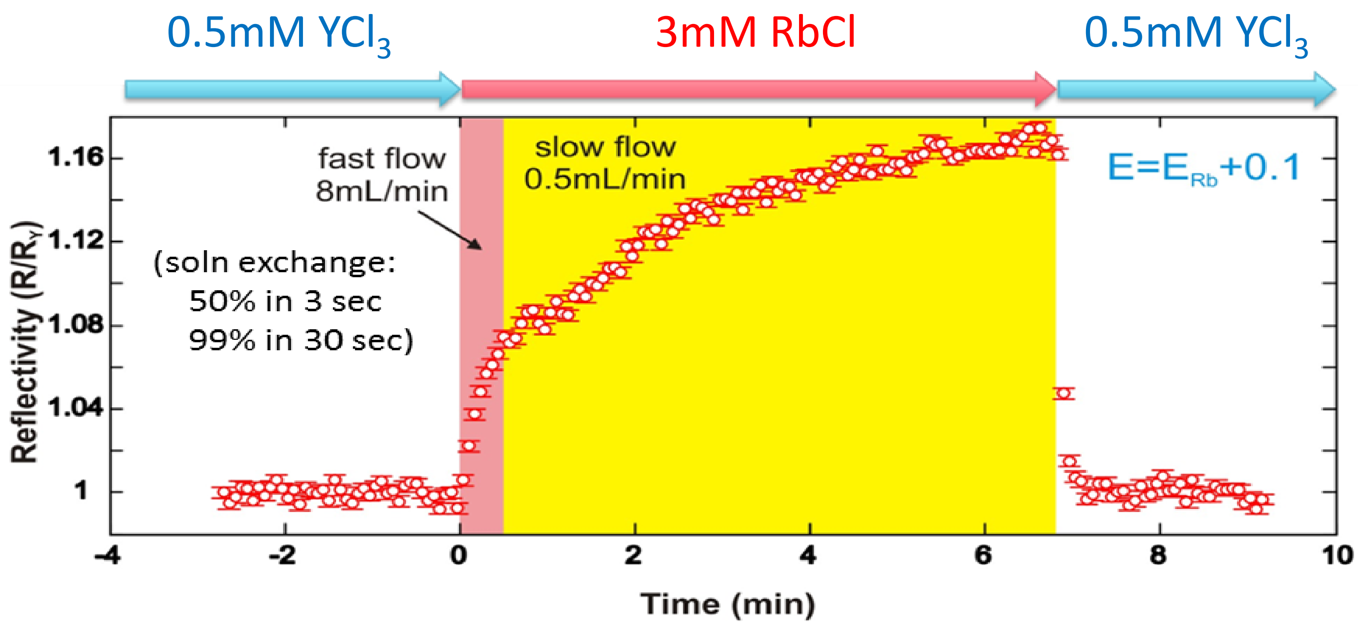


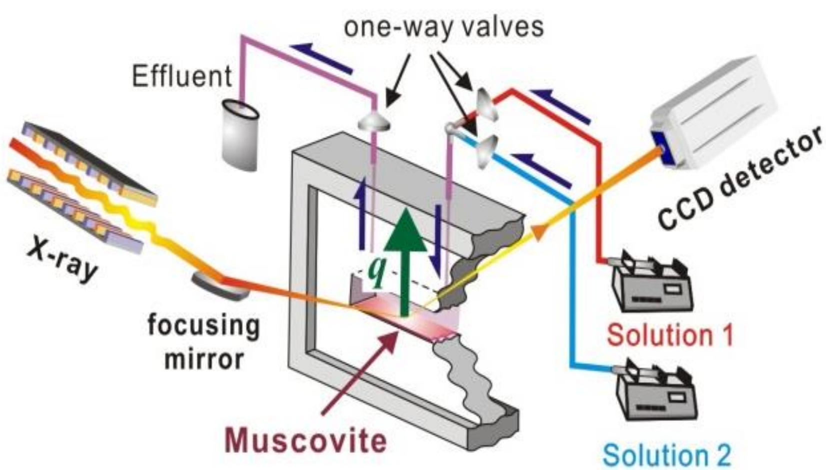




Real-Time Studies of Adsorption Kinetics At the Muscovite-Water Interface







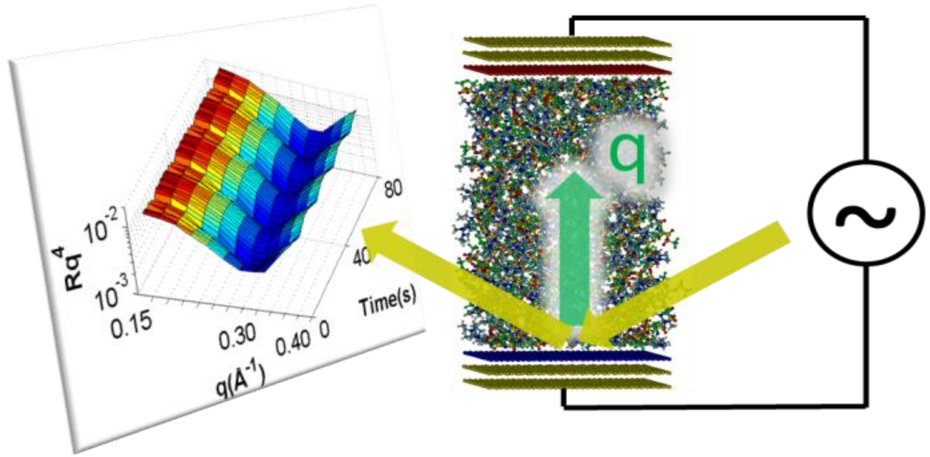
- Intrinsically slow ion exchange kinetics even though elementary process is most likely intrinsically fast (~nano-sec).

→ Due to collective behavior?

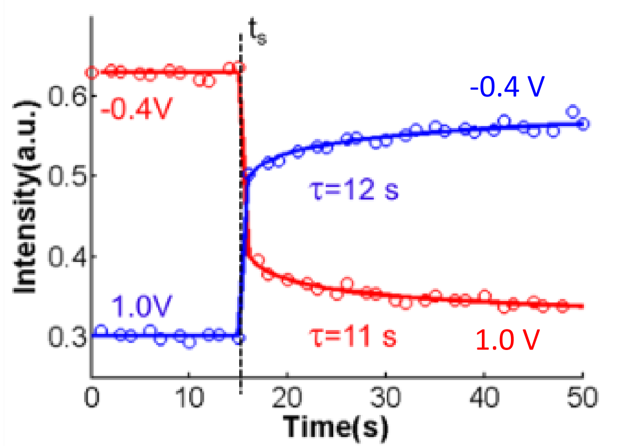
→ May be amenable to XPCS studies at steady state

Lee, *J. Synch. Rad.* (2012).

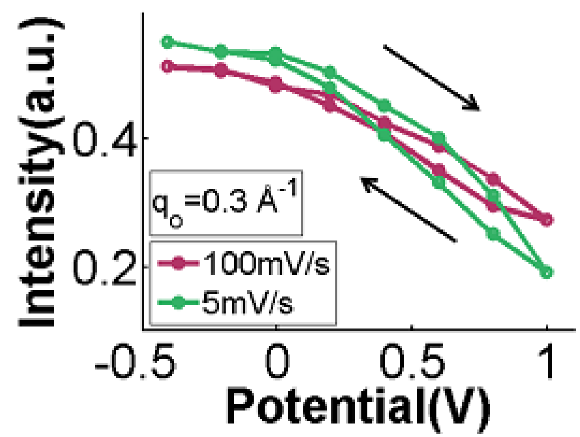
Real-Time Studies of RTIL Switching at Graphene Surfaces



Slow Switching:



Structural hysteresis:



Unexpectedly slow kinetics of RTIL evolution in time
→ Interesting for XPCS measurements??

Uysal et al., *in review* (2013).

Substantial Opportunities:

- Real-time XRIM
    - multilayer monochromators, $\Delta E/E = 10^{-3}$
    - higher efficiency optics
    - Resonant contrast in XRIM

- Combined XRIM/CDI/Ptychography
- Interfacial XPCS

Challenges:

There are numerous critical needs to enable this capability:

→ To make state of the art optics (objective lens) to minimize beam perturbations and to enable higher energy imaging (for in-situ studies).

→ To achieve a high degree of mechanical stability (dedicated instrument).

→ Create a concerted research program to understand, and control, radiation chemistry in order to enable in-situ imaging with <100 nm spatial resolution in non-trivial environments.