NSF's ChemMatCARS

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A Synchrotron X-ray National Facility for Chemistry and Materials Research

NSF's ChemMatCARS: A Synchrotron X-ray National Facility for Chemistry and Materials Research

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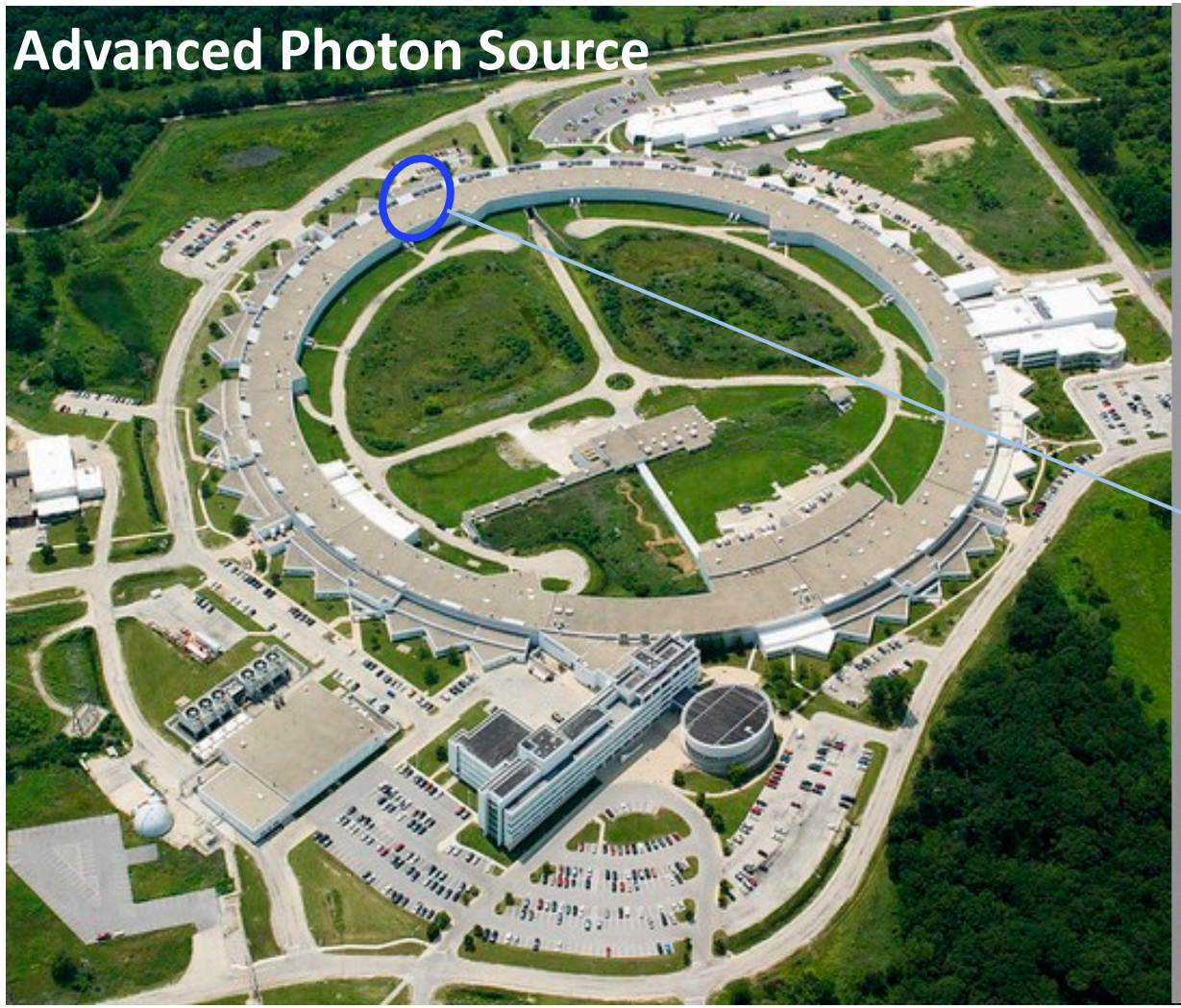
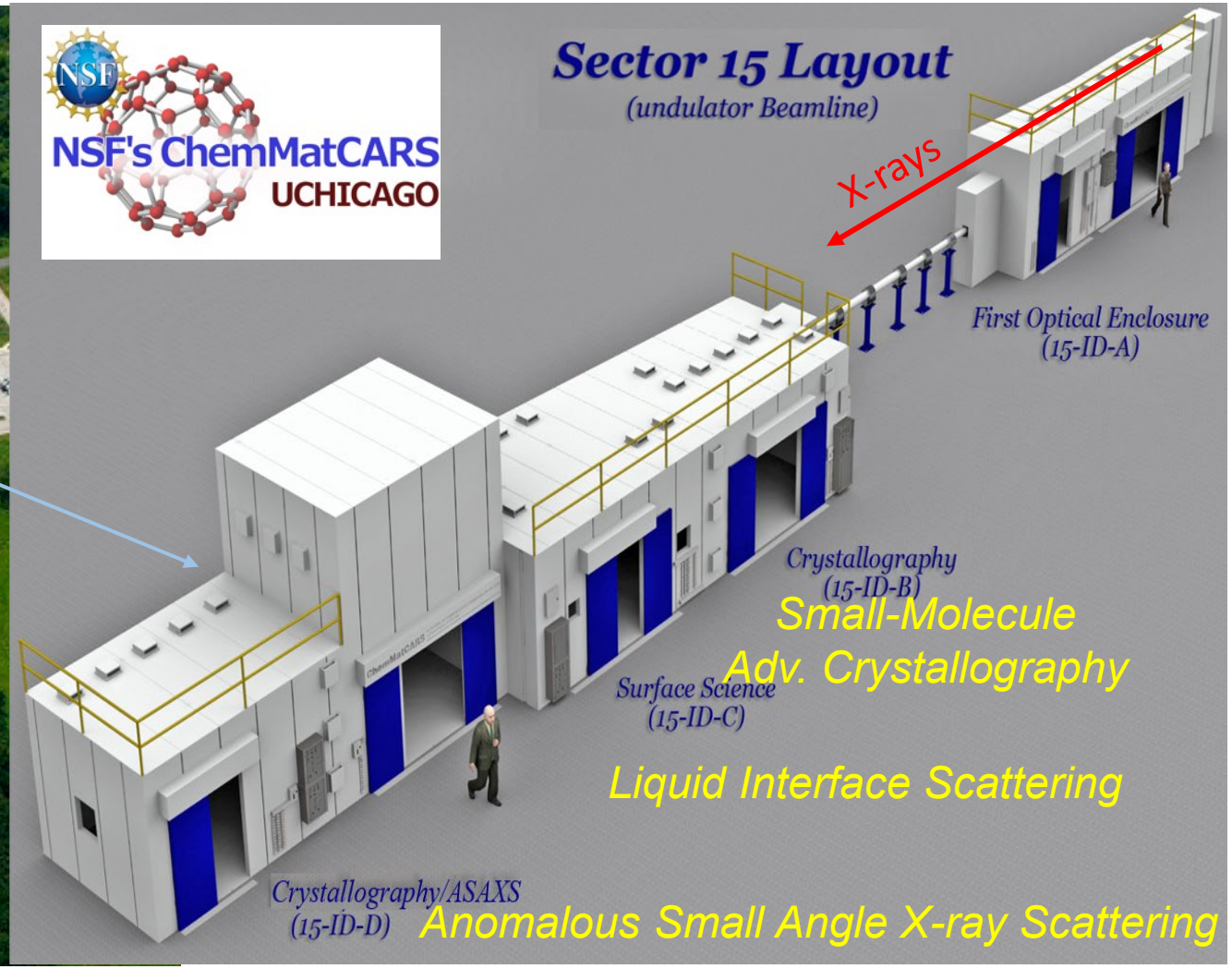
Introduction

Matthew Tirrell
PI and Director of NSF's ChemMatCARS, University of Chicago

NSF's ChemMatCARS, Sector 15 at the Advanced Photon Source

Funded by NSF, located at the Advanced Photon Source (APS), Argonne National Laboratory, Illinois





NSF's ChemMatCARS PI/co-PIs and Staff

https://chemmatcars.uchicago.edu/people/

Matthew Tirrell, PI and Director, U of Chicago

Jason Benedict, co-PI, U at Buffalo

Ted Betley, co-PI, Harvard U

Ka Yee C. Lee, co-PI, U of Chicago

Mark Schlossman, co-PI, U of Illinois at Chicago

Mrinal Bera, ASAXS

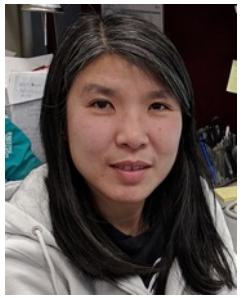
Yu-Sheng Chen, Adv. Crystallography, Operations Manager

Mati Meron, X-ray Optics

Wei Bu, Liquid Interfaces

Binhua Lin, Liquid Interfaces, Exec. Director

Charlie Smith, IT



Natalie Chen, User Coordinator

Guy Macha, Vacuum specialist and Tech support

SuYin Wang, Adv. Crystallography

Agenda

Overview and Access to NSF's ChemMatCARS	Binhua Lin, *NSF's ChemMatCARS*
Advanced Crystallography Science and Facility	Yu-Sheng Chen, *NSF's ChemMatCARS*
Liquid Interface Scattering Science and Facility	Wei Bu, *NSF's ChemMatCARS*
New Initiative, Anomalous Small Angle X-ray Scattering (ASAXS) Science and Facility	Mrinal Bera, *NSF's ChemMatCARS*
Science Highlights in Advanced Crystallography	Ted Betley, *co-PI of NSF's ChemMatCARS, Harvard University*
Science Highlights in Liquid Interface Scattering	Mark Schlossman, *co-PI of NSF's ChemMatCARS, University of Illinois at Chicago*
Science Highlights in ASAXS	Matthew Tirrell, *University of Chicago*

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Overview and Access

Binhua Lin
NSF's ChemMatCARS
lin@cars.uchicago.edu

NSF's ChemMatCARS – Current Beamline Layout (first experiments in 2002)

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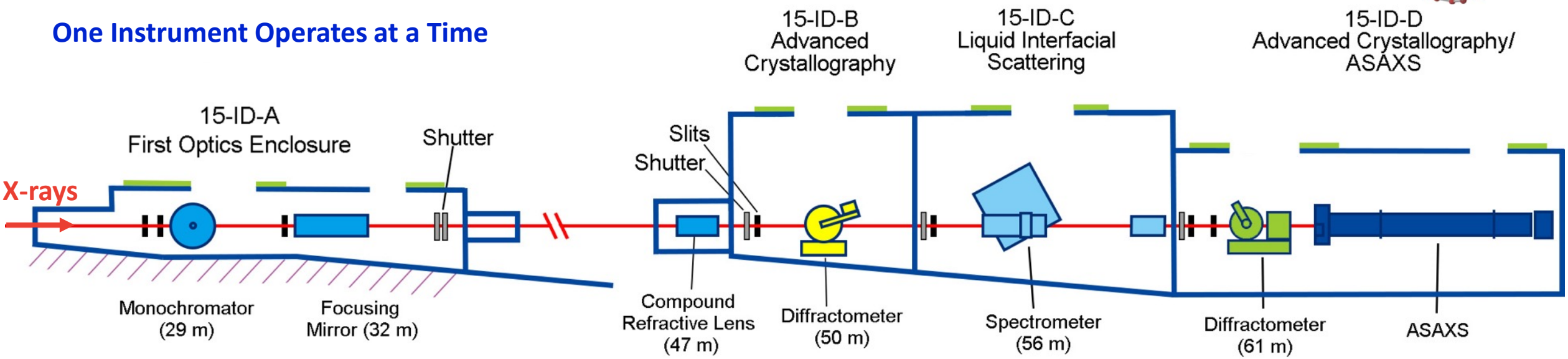
One Instrument Operates at a Time



Small-Molecule Adv. Crystallography:

- Charge Density
- Transient States – Photo-crystallography
- Resonant Diffraction
- Structural Dynamics
- Extreme Conditions (High *p*, Low *T*)
- Single Micro-Crystal Diffraction
- 3D Δ-Pair Distribution Function
  New Initiative

Liquid Interface Scattering:

- Reflectivity
- Grazing-Incidence Diffraction (GID)
- Diffuse Scattering
- Fluorescence near Total Reflection
- Temporal resolution:
  1-D Pinhole GID, GIXOS
- GISAXS
- Surface XAS *New Initiative*

Anomalous Small Angle X-ray Scattering (ASAXS):
New Initiative

Beamline Parameters

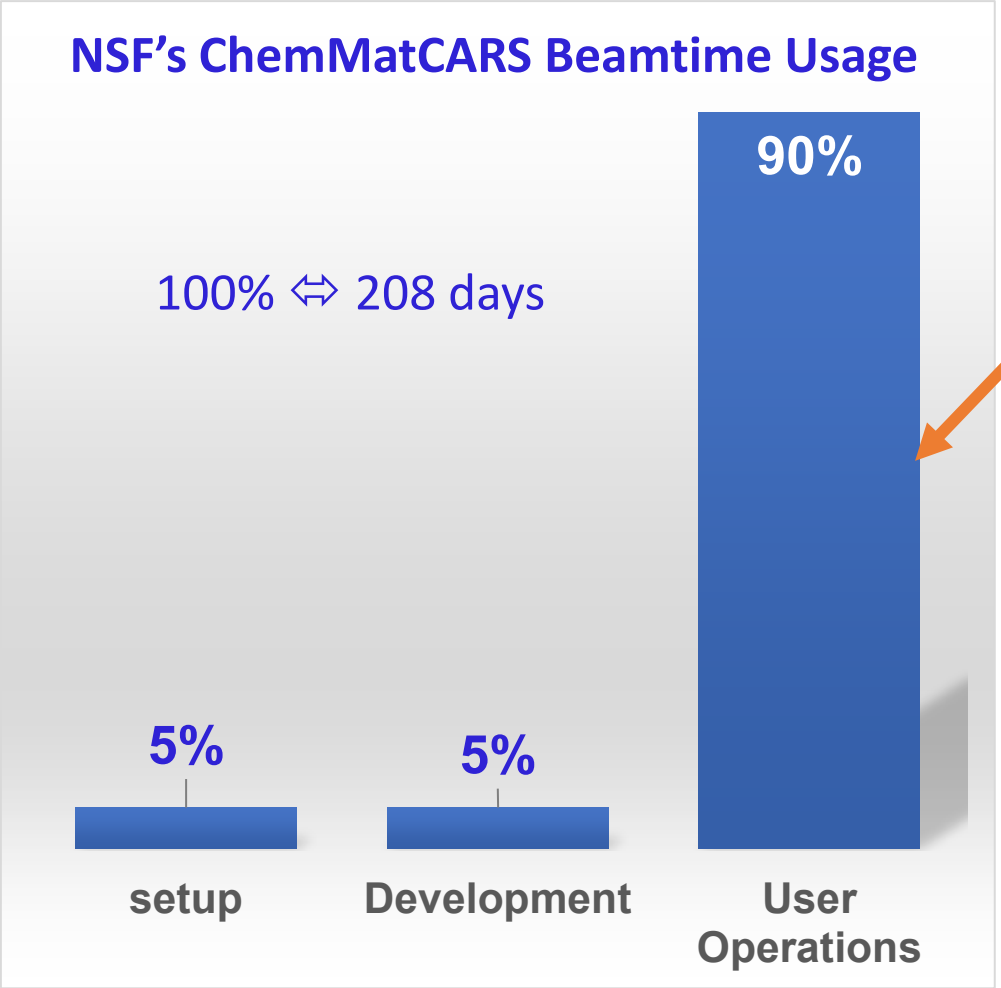
- Energy range: 5.5 keV to 70 keV
- X-ray Flux (phot/s/0.1%BW):
  ~4×10^{14} @ 10 keV;
  ~1×10^{14} @ 30 keV
- X-ray Energy Resolution: $\Delta E/E \sim 10^{-4}$

https://chemmatcars.uchicago.edu/experimental-facility/source-parameters/

Unusually broad range of techniques serves a wide range of scientific interests

NSF's ChemMatCARS User Access to Beamtime

X-ray beam on 208 days (5000 hours) per year



Open to the scientific community via **APS "General User Proposal" portal**

All beamtime proposals peer-reviewed and ranked by APS external review panels

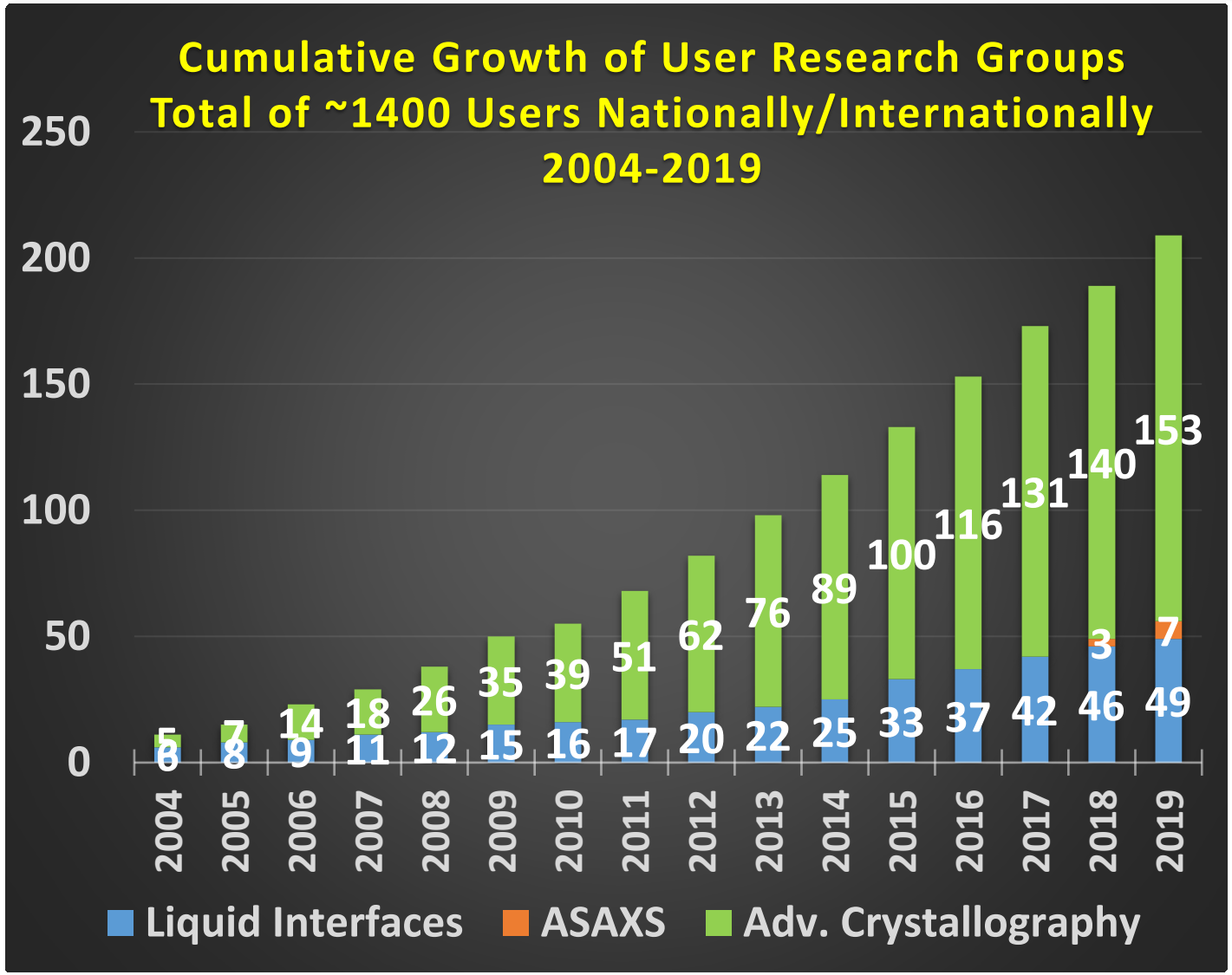
Scores determine the allocation of available beamtime

NSF's ChemMatCARS Oversubscription Factor is ~ 2

(Oversubscription Factor = Beam days requested over awarded)

NSF's ChemMatCARS Productivity and Broader Impacts

NSF's ChemMatCARS is one of the most productive beamlines at the Advanced Photon Source



Publications

https://chemmatcars.uchicago.edu/publications/

- 65 -70 Publications annually in peer reviewed journals
- Total Citations 33,772 (as of 9/10/2020)

  h-index 91

  i10-index 550

Broader Impacts

https://chemmatcars.uchicago.edu/education-and-outreach/

- Training the next generation of scientists:
  annually 60+% of 200+ users are students/postdocs
- 2 Diversity outreach programs for URM faculty and students
  - Faculty and Student Team Research Award at ChemMatCARS (FaSTRAC)
  - Graduate Student Research Award at ChemMatCARS (GSRAC)
- Workshops/schools with hands-on experiments and data analysis lectures
  3 per year with 40+ participants
- General Public Tours to NSF's ChemMatCARS
  ~12 per year with ~150 people

New Initiatives at NSF's ChemMatCARS

2-Beamline ChemMatCARS

New techniques at both beamlines – in Adv. Crystallography, Liquid Interfaces, Anomalous SAXS

More capacity to expand in Chemistry and Mat. Research, and extend to Chemical Eng. and Mol. Biosciences

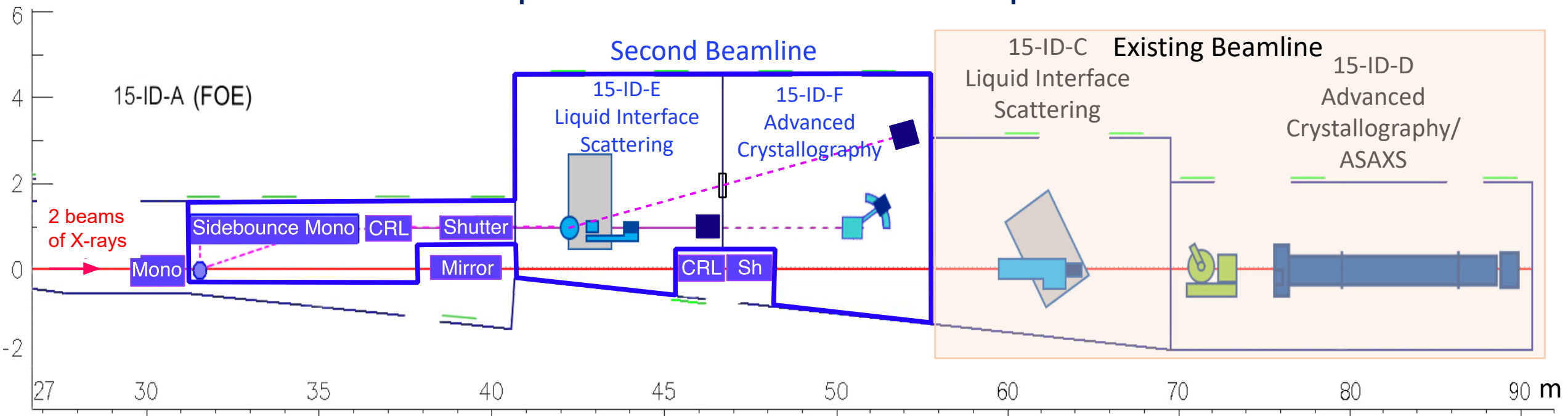
Modernize the **existing beamline** for APS-U (NSF CHE-1834750)

Construct **second beamline** optimized for APS-U (NSF CHE-1836674)

(Two workshops on new initiatives in adv. crystallography and liquid interfaces were held in Nov. 2019)

A Second, Independent Beamline on NSF's ChemMatCARS Sector

2 independent beams to serve 2 concurrent experiments



Apply for Beamtime at NSF's ChemMatCARS

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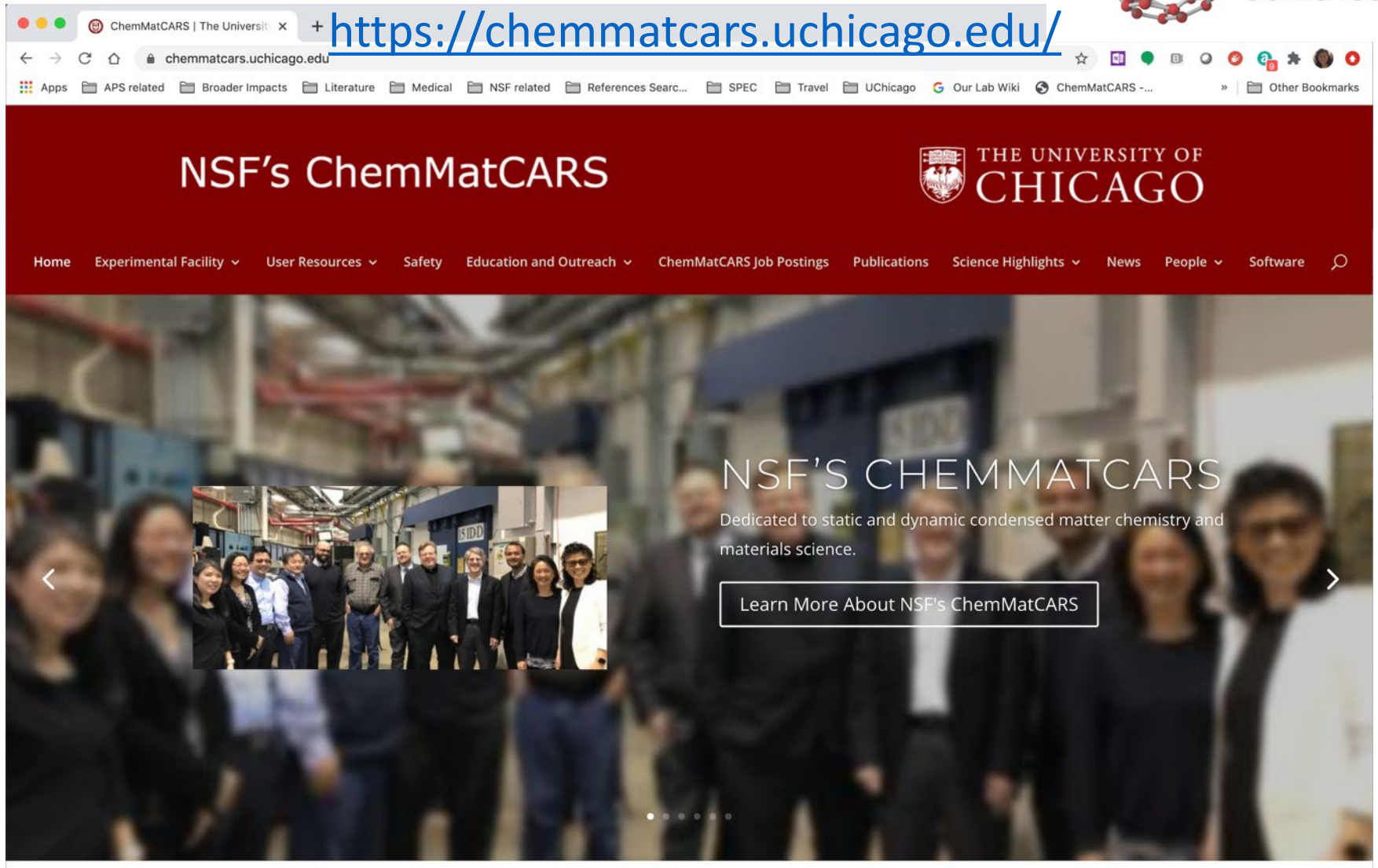
Resources:

- NSF's ChemMatCARS website
- User Coordinator, Natalie Chen, (nchen@cars.uchicago.edu)
- Lead Beamline Scientists:
  - Adv. Crystallography: Yu-Sheng Chen (yschen@cars.uchicago.edu)
  - Liquid Interfaces: Wei Bu (bu@cars.uchicago.edu)
  - ASAXS: Mrinal Bera (mrinalkb@cars.uchicago.edu)

https://chemmatcars.uchicago.edu/



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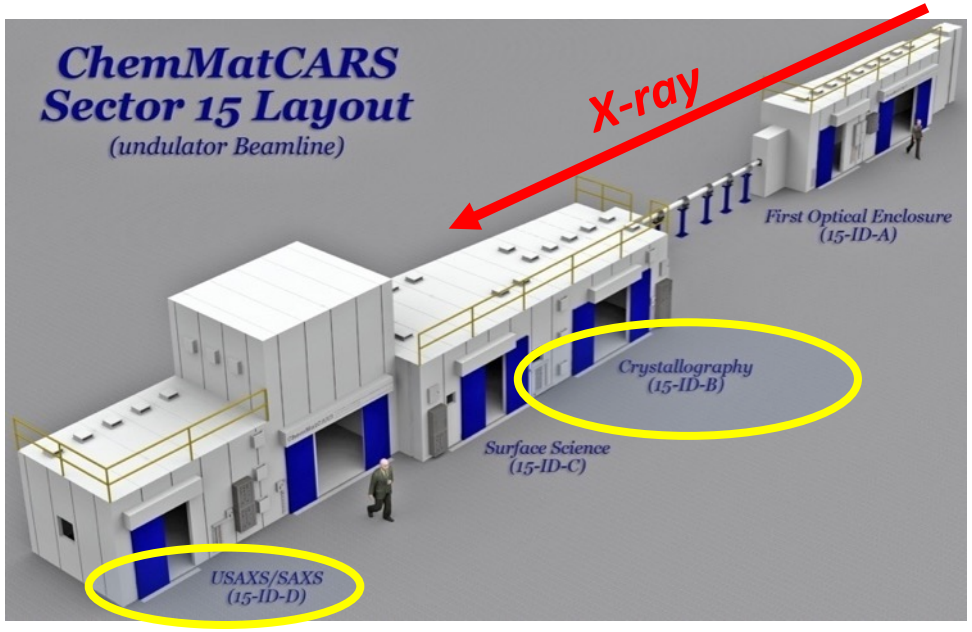
Advanced Crystallography Science and Facility



Yu-Sheng Chen
Advanced Crystallography
yschen@cars.uchicago.edu

Advanced Crystallography Science and Facility

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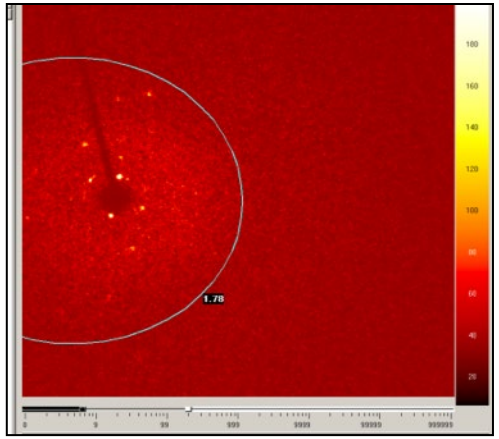
Why use Synchrotron Radiation for Chemical and Material Crystallography?

- Intense radiation
  - Small crystals < 2 μm
    - ✓ Reduces absorption
    - ✓ Increases signal to noise ratio
- Short wavelength
  - High resolution in reciprocal space
  - Reduces absorption, anomalous scattering
- Monochromatic
  - No $k_{\alpha 1}$, $k_{\alpha 2}$ splitting
    - Easy data integration
    - Better data quality
- Tunable energy(Resonant Diffraction)
  - Circumvents absorption problems
  - Element specific structural information
- Fast data collection
  - Study of highly air-sensitive samples

Lab Source



exposure time/120 s
d=1.78 Å

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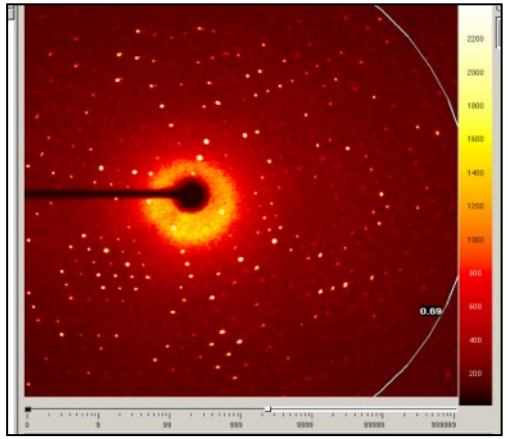

exposure time/0.2 s
d=0.69 Å

Synchrotron data:

- Much less exposure
- Strong data up to **1.78** Å region
- Significant intensity out to **0.69** Å

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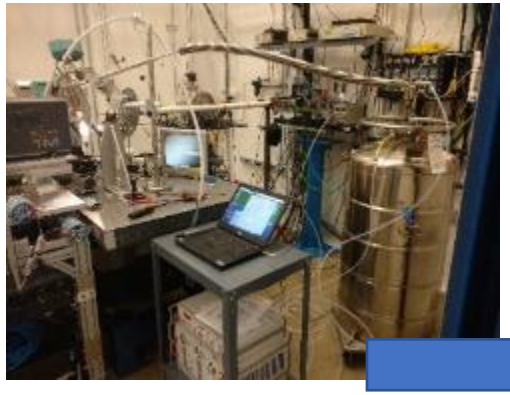
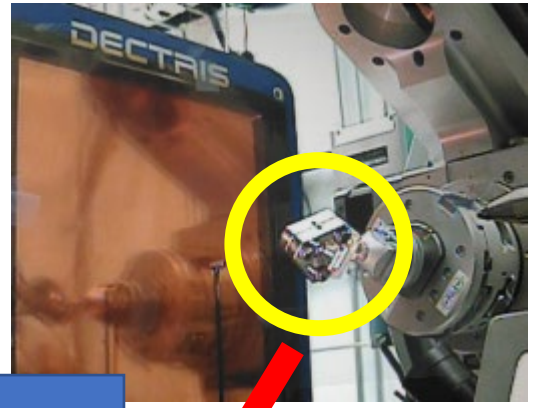
Crystal Structure under Extreme Conditions: Beyond Routine Service Crystallography!

•*Variable Temperature: 10K ~ 700K*



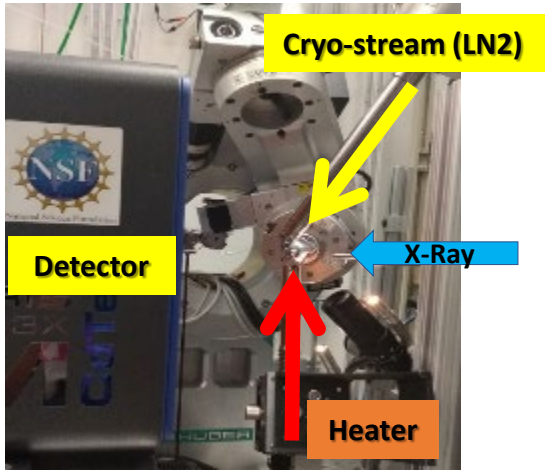
Sample Preparation Area

•*Variable Pressure: < 10 GPa*

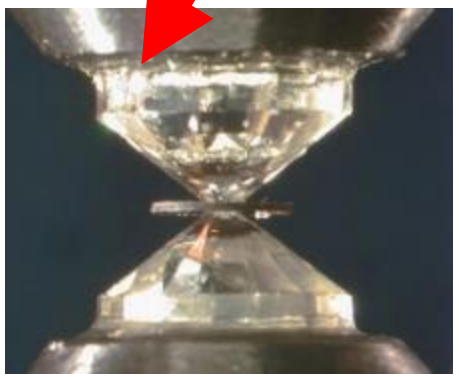


Thermal expansion

Compressibility



Phase diagram



Diamond Anvil Cell(DAC)

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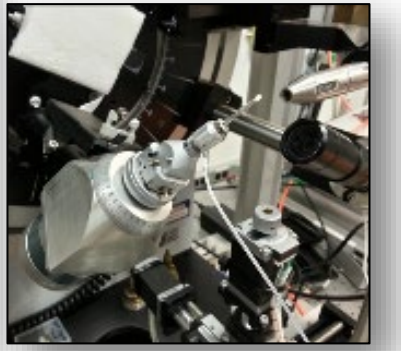
Structural Dynamics:

In-situ crystal diffraction

Environmental Control Cell (ECC)

- *Vacuum, gas, solution and humidity*

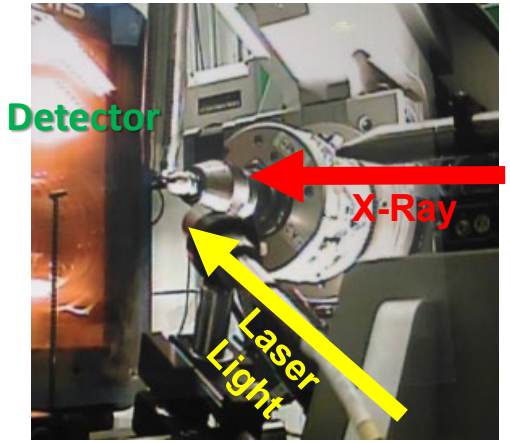
Study crystalline materials under 'real world' conditions



Benedict Group and NSF's ChemMatCARS
J. Appl. Cryst.(2015), 48, 578-581

Photo-Crystallography

- *Light-Induced Metastable State Crystal Structure*



Time-Resolved Crystallography

- ❑ Provide an adjustable time window
  - 190 ns and 20 µs in duration.
- ❑ Easy select single pulses, and longer temporal resolution by adjusting table height.
- ❑ Fully compatible with FPGA

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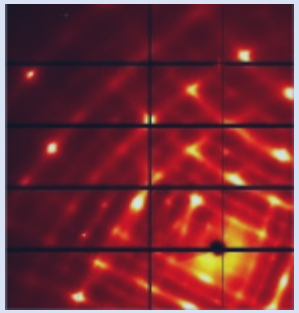
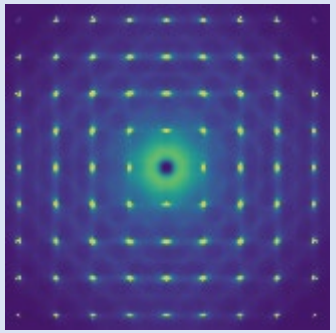
High energy Pilatus CdTe 1M detector; much better measurements!

3D Diffuse Scattering:

Raw Image(PbTe)

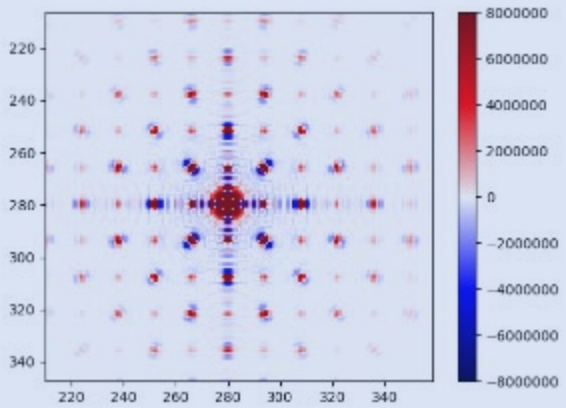


Reciprocal Space



3D-ΔPDF map shows

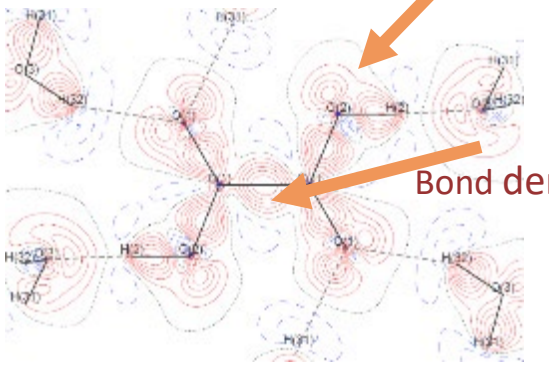
- ***Peaks appear at interatomic vectors***
- ***Negative-positive-negative profiles, shows correlated displacements***



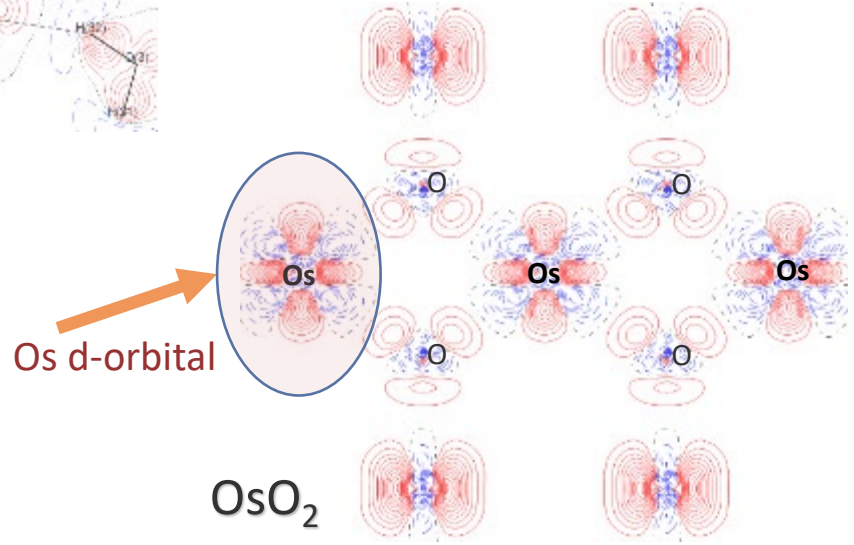
Charge Density:

- ***Calculate intermolecular interaction energy.***
- ***Calculate electrostatic potential of the molecule.***
- ***Provide bonding information (topological analysis and source function analysis).***
- ***Characterization of the H-BOND.***
- ***Determine the atomic charge using Atom in Molecular Theory(AIM).***
- ***Extract the "experimental wave function".***

Deformation Electron Density



Oxalic Acid



OsO_2

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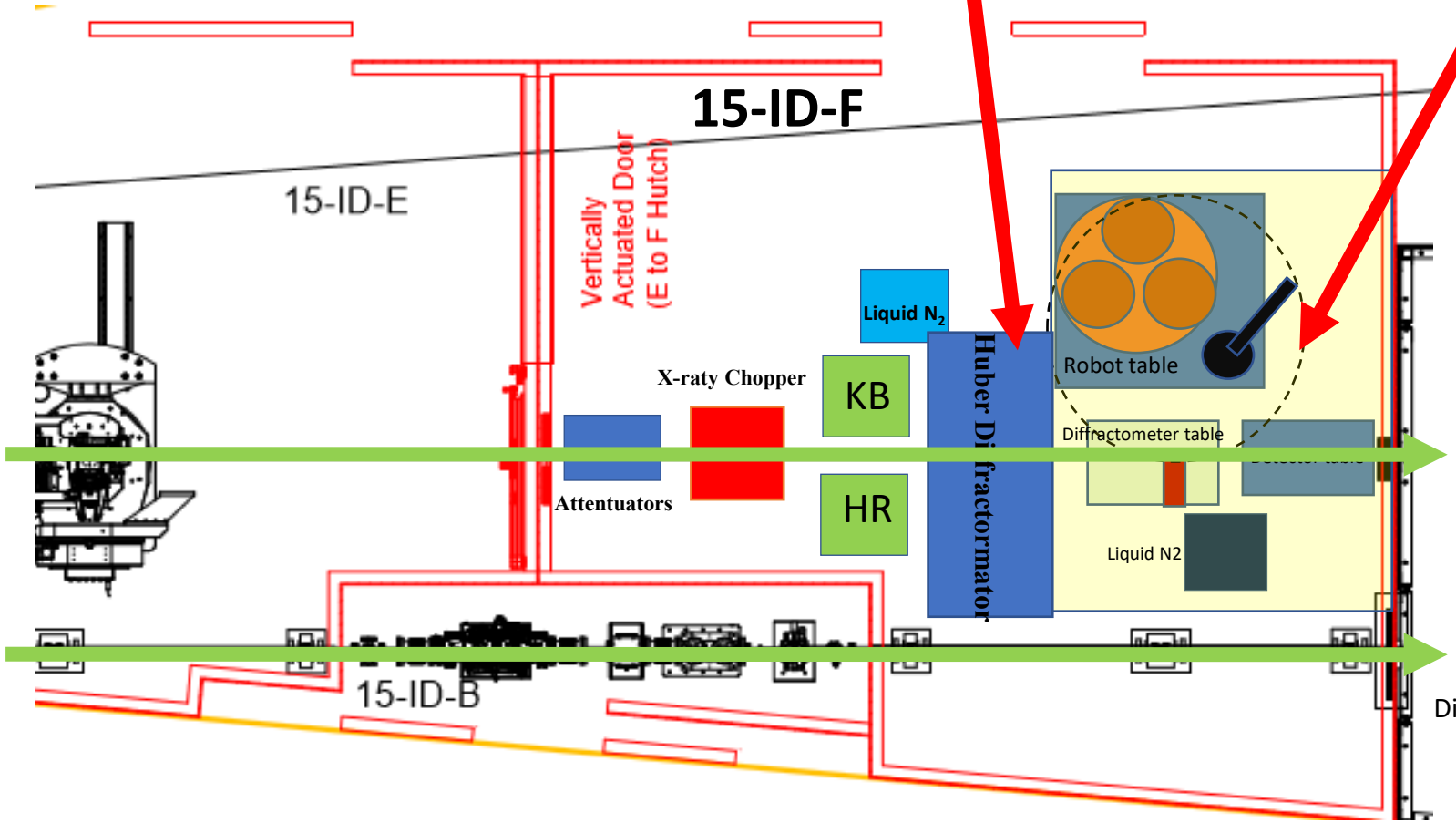
New initiative experiments

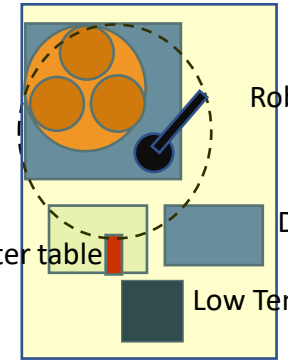
- *Resonant Diffraction Experiment below 5KeV*
- *Serial Crystallography for Small Molecule Crystallography*

Mail-in Service(remote data collection)



Pilatus3X (Si) 2M

ALIO Diffractometer



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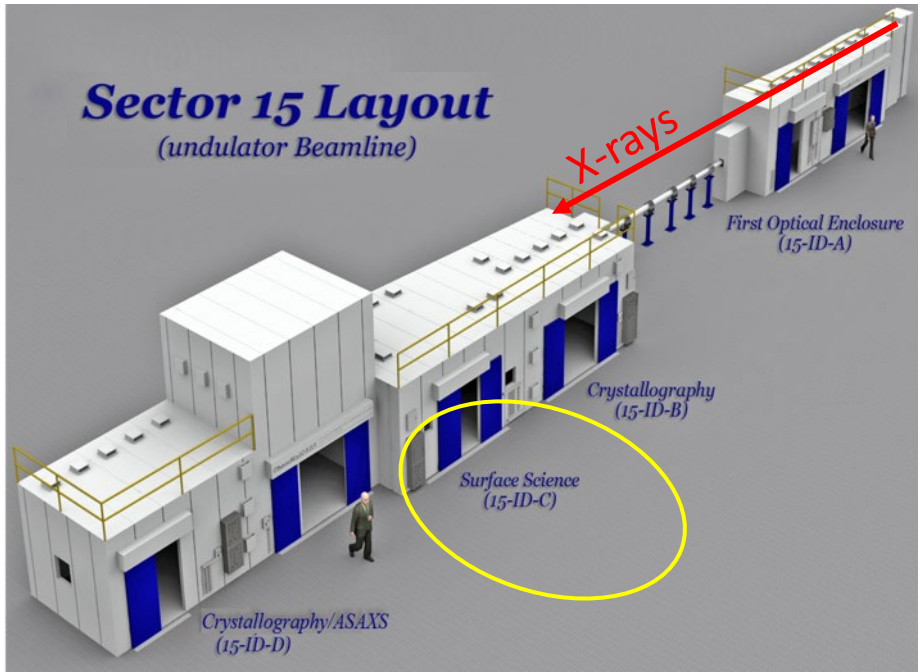
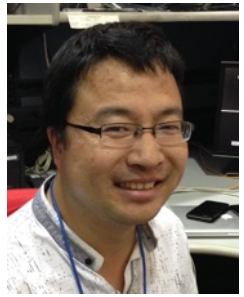
Liquid Interface Scattering Science and Facility





Wei Bu
NSF's ChemMatCARS
bu@cars.uchicago.edu

Experimental Hutch

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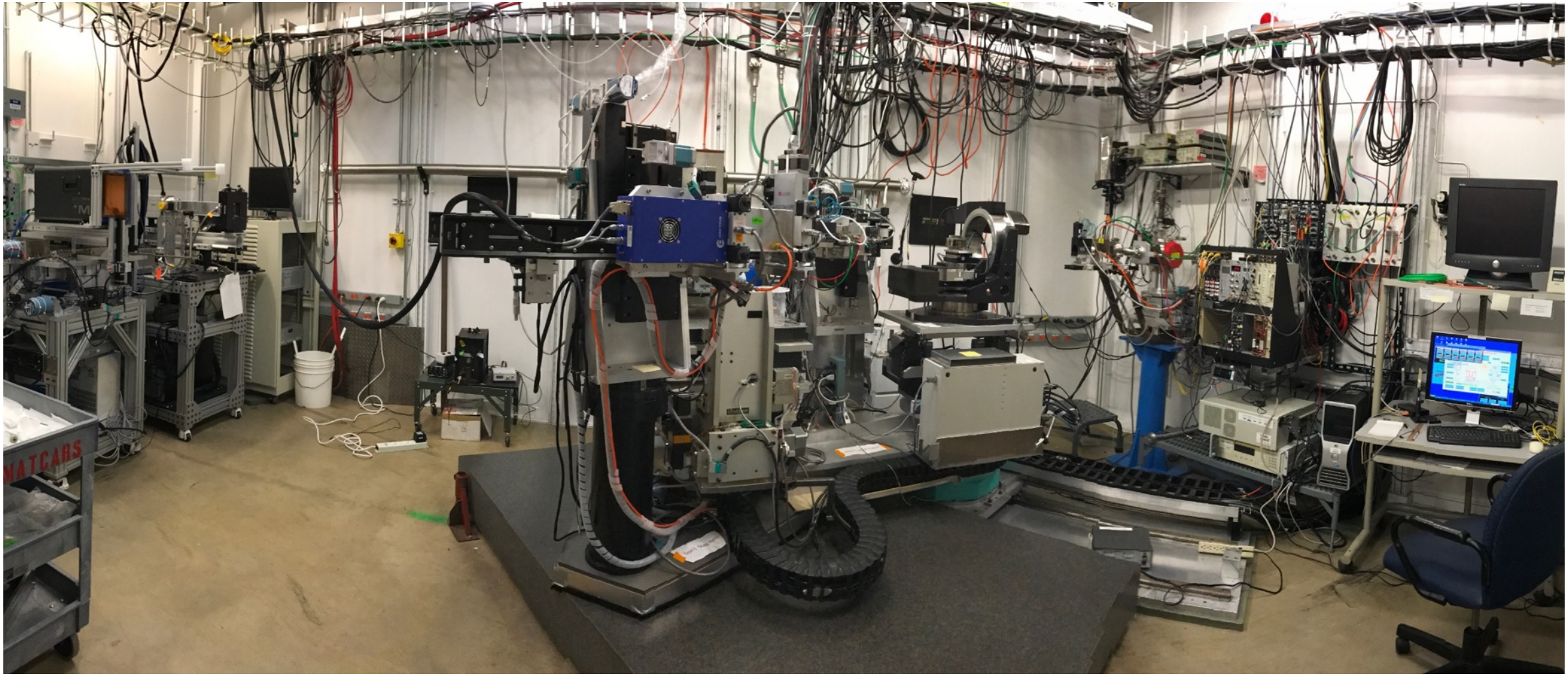


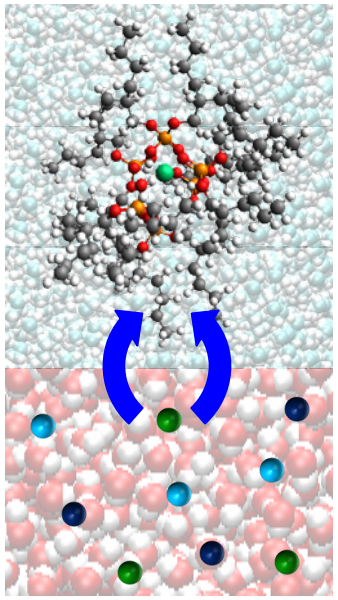
Scientific Focus

Probe the assembly of molecules, ions, and nanoparticles at liquid interfaces to understand their interfacial distribution, ordering, transport, reactions, and the underlying chemical and physical interactions.

Environmental Chemistry at Liquid Interfaces

- Separations science (ion extraction) at liquid/liquid interfaces
- Ion distributions near the interface
- Surfactant organization for oil recovery and cleanup

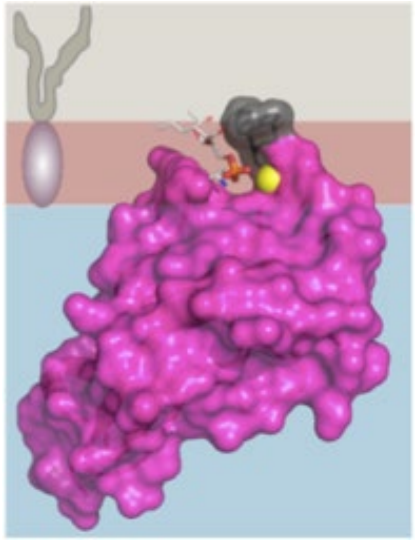
(PNAS, 116, 18227, 2019)



Chemistry of Life Processes at Liquid Interfaces

- Biomolecular recognition
- Lipid-protein binding
- Peptide ordering and interactions
- Interfacial properties of polymers

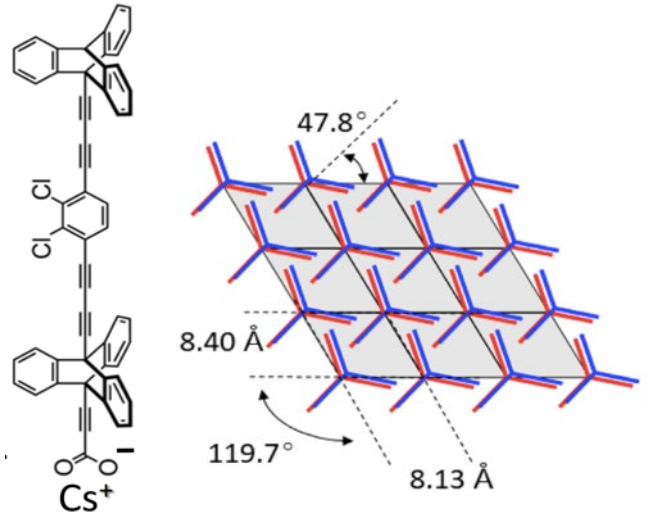
(PNAS, 111, E1463, 2014)
(Biophysical J., 113, 1505, 2017)



Directed Assembly for Tailored Functionality

- Functional materials
- Interfacial complexation for emulsions, films, and coatings
- Synthesis/ordering of nanoparticles
- Optical sensor for biomolecule detection
- Voltage control of interfacial assembly

(PNAS, 115, 9373, 2018)



Why Use X-ray Scattering?

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Synchrotron X-ray Scattering is the leading technique for the study of structure at liquid surfaces with high spatial resolution

Molecular organization at the interface

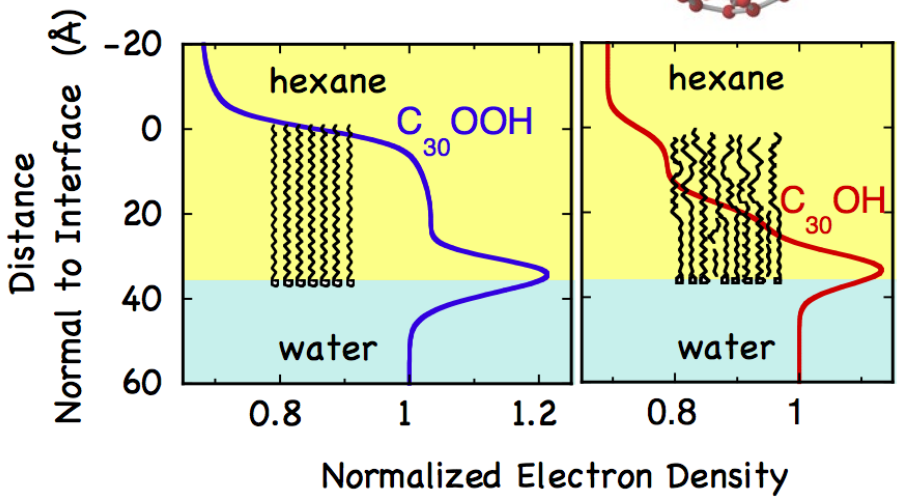
- Molecular ordering and configuration on the sub-nanometer scale
- Structural response to perturbations
  pH, electric field, temperature, chemical reactions

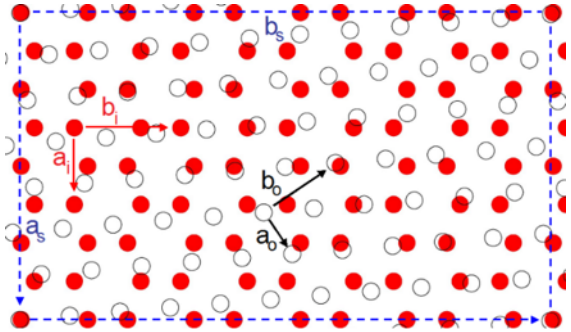
Order and disorder within the interface

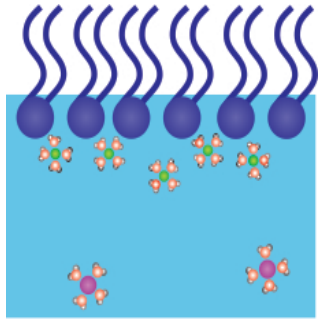
- In-plane structure of ions, lipids, macromolecules and nanoparticles

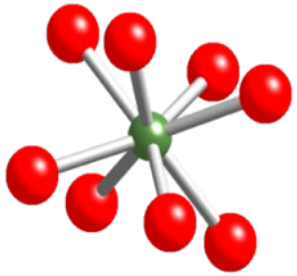
Element-specific probes

- Identify elements in complex interfaces
- Monitor variations in interfacial composition
- Local chemical environment at interfaces









New Beamline Initiatives in Liquid Interfaces

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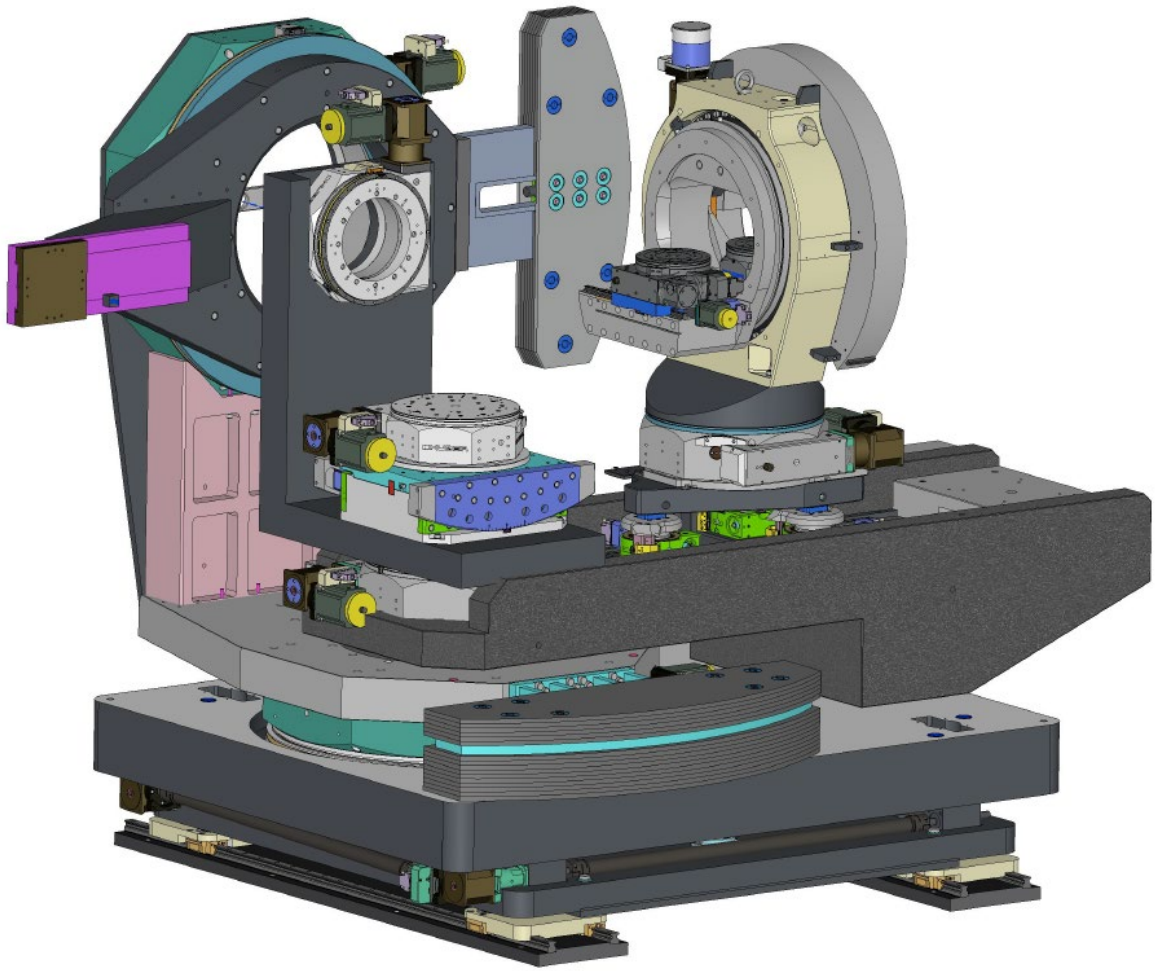
Hybrid interface scattering instrument

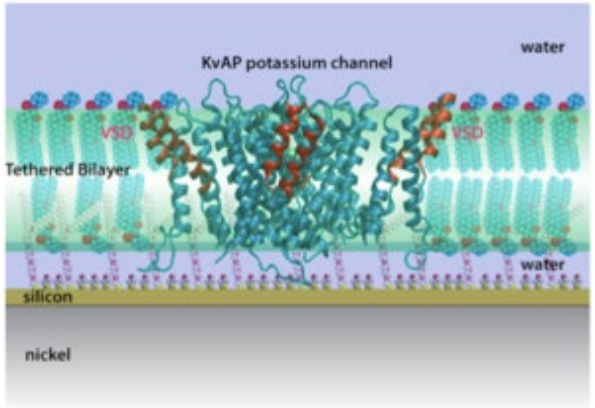


https://chemmatcars.uchicago.edu/experimental-facility/experimental-techniques/liquid-surface-x-ray-scattering/

New initiatives

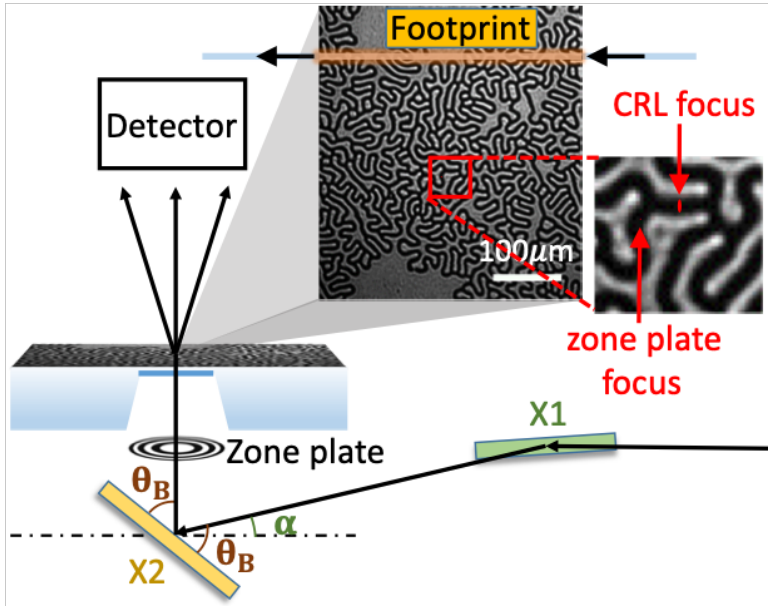
Liquid-solid interfaces

(Langmuir 30, 4784, 2014)



- Bio-membrane processes
- Biological cell-surface interactions

Scanning interfacial X-ray probe for heterogeneities at soft interfaces



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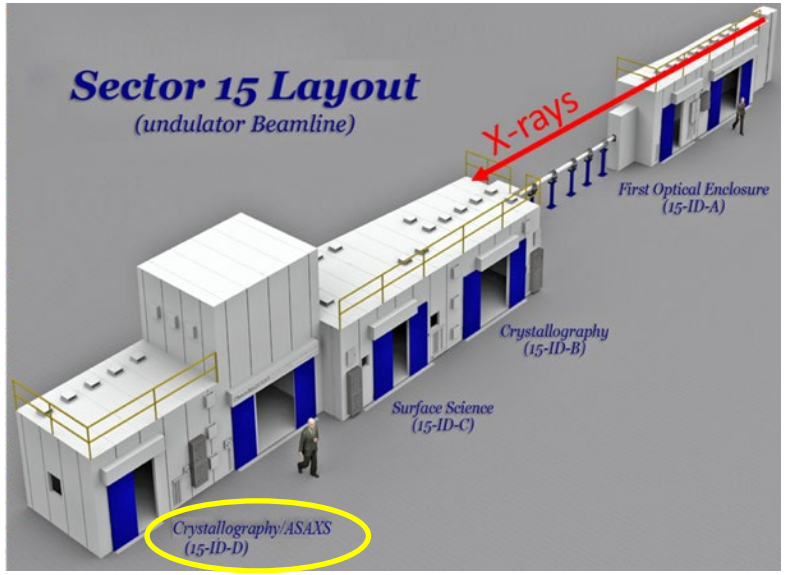
New Initiative,
Anomalous Small Angle X-ray Scattering (ASAXS)
Science and Facility



Mrinal Bera
mrinalkb@cars.uchicago.edu

Scientific Scope

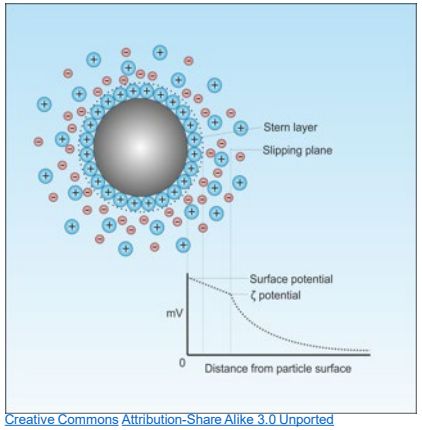
ASAXS: Anomalous Small Angle X-ray Scattering

SAXS done at the energy edges of element of interest

Provides quantitative *element-specific* non-destructive structural characterization in nanometer length scales (1-1000 nm)

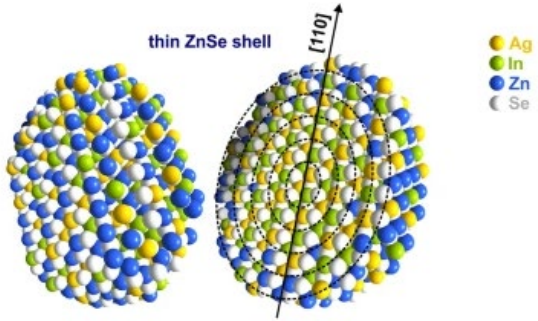
How are elements and ions distributed?

Charged Colloids & Macro-ions



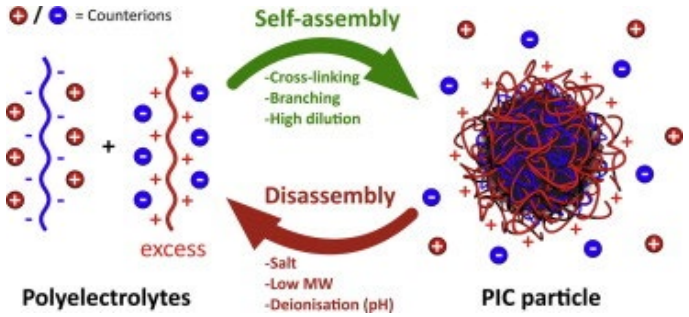
Ballauf et al, *Annu. Rev. Biophys.*, **40**, 225 (2011)

Nanomaterials



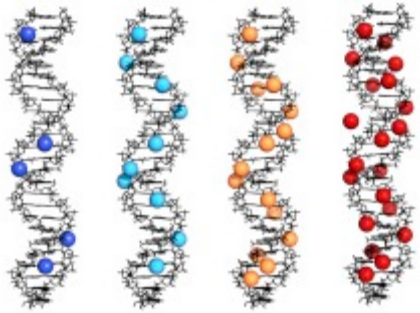
Yarema et al, *Sci. Rep.*, **7**, 1178 (2017)

Polyelectrolytes



Insua et al, *Euro. Polymer J.*, **81**, 198 (2016)

DNA, RNA, & Proteins



Pabit et al, *JACS*, **132**, 16334 (2010)

Expert only technique: No easy to use data reduction and analysis tool

ASAXS Facility @ NSF's ChemMatCARS started in 2017

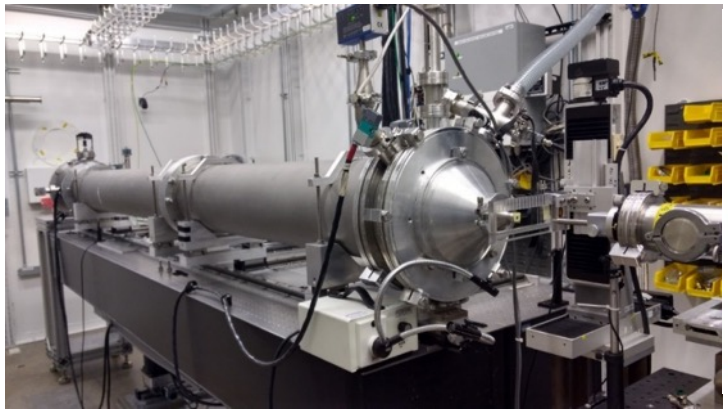
To develop and bring ASAXS to all users, experts and non-experts alike, in providing them with simple but quantitative element-specific structural characterization tool

ASAXS Facility at NSF's ChemMatCARS

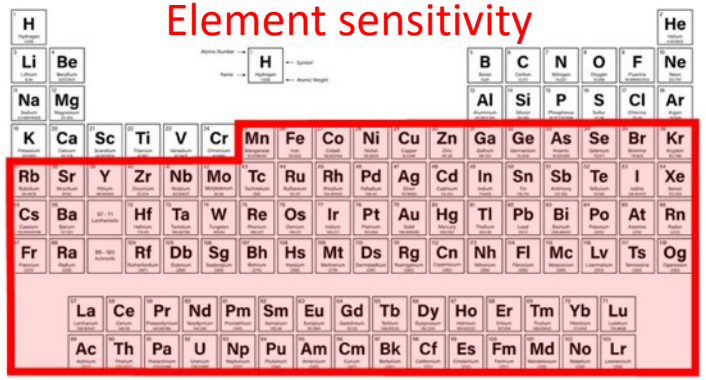
NSF's ChemMatCARS UCHICAGO

Important features

- Energy Tunable X-rays (5.5-70 keV)
- High X-ray flux ~ 10^{14} at 10keV (ph/sec/0.1%BW)
- Element sensitivity for Z>25



Element sensitivity



- Software for automated data collection, reduction and ASAXS data modeling

ASAXS Experiments: Energy dependent SAXS patterns

BRIDGING The GAP

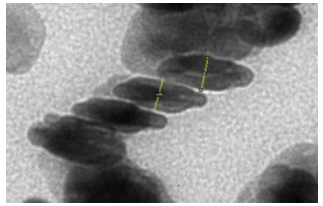
ASAXS Data Reduction and Modeling

- Sample shape, size (1-200nm) and size distribution
- Quantitative spatial distribution of elements (Z>25) of choice

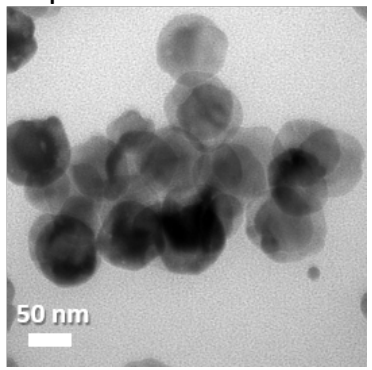
Tirrell's group (UChicago)

Multilayered Yb-doped nanoparticles

side-view



Top-view



ASAXS Measurement

@NSF's ChemMatCARS