Structural Dynamics:
Small Molecule Serial Crystallography

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Structural Dynamics

Quantifying time-dependent phenomena in crystalline materials

Guest Exchange

Photochemical reactions

Catalysis

Flexible crystals

Charge transport

Nature 495, 80–84 (07 March 2013)


X-ray Diffraction – The Basics
Quantifying time-dependent phenomena in crystalline materials

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In-situ crystal diffraction

Environmental Control Cell (ECC)

• Vacuum, gas, solution and humidity

Environmental control cells (ECCs)
Study crystalline nanoporous materials under ‘real world’ conditions

Benedict Group and ChemMatCARS
Structural Dynamics

Gases and liquids as chemical stimuli

Approaching ‘real time’ structural information about guest and framework – solving single crystal structures!
How do water molecules leave?
- Stepwise?
- Simultaneous?

What is the relationship between compression of $a$-axis and dehydration?

Dynamic in situ X-ray Diffraction experiments should address both questions!

Trihydrate (one coordinated water and two 'free' water molecules)

Space group $P2_1/c$
- $a = 12.4381$ Å
- $b = 7.6827$ Å
- $c = 15.8704$ Å
- $\beta = 106.1466^\circ$

Anhydrous

Space group $P2_1/c$
- $a = 11.078$ Å
- $b = 7.761$ Å
- $c = 15.945$ Å
- $\beta = 106.829^\circ$
Carefully controlled flow rates of dry nitrogen gas trigger the dehydration.

- Note the large change in $\beta$ and $a$!

- ‘Slice up’ the data to yield single crystal structures

- Faster data collection = shorter time to collect complete data set
Structural Dynamics

Jump to the conclusion....

“trihydrate”

P2₁/c
a = 12.607 Å
b = 7.685 Å
c = 15.926 Å
β = 106.527°
V = 1479 Å³

Twist and compress
(Rapid loss of single water)

“dihydrate”

P2₁/c
a = 11.165 Å
b = 7.766 Å
c = 15.784 Å
β = 103.19°
V = 1332 Å³

Un-twist
(slow simultaneous loss of remaining two waters)

“anhydrous”

P2₁/c
a = 11.326 Å
b = 7.694 Å
c = 15.83 Å
β = 106.49°
V = 1323 Å³

• More complex motion than predicted by ex situ measurements
• 2-step activation process
• Room temperature activation
What is it?
- Technique developed by structural biologists
- Datasets consist of single images collected from tens or hundreds of thousands of single crystals
- New sample delivery methods
- New data analysis methods

Why would you do this?
- Only method capable of obtaining time-resolved data on:
  - Irreversible processes
  - Applies to process and damage
  - Sub-micron crystals

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Many of these data analysis tools – built for macromolecular crystals – will not work on crystals with small- to medium-sized unit cells.

New computational tools required!

Tens of thousands to hundreds of thousands to millions of frames of data each from a crystal of unknown size and orientation must be turned into a single data set of indexed intensities.
So what does NSF ChemMatCARS need from you?

What are your Structural Dynamics Dreams?

What are your systems of interest?

What are your physical processes of interest?

What crystalline thing would you want to watch?

What would you need to make your Structural Dynamics Dreams come true?
X-ray Chopper
Profs. Philip Coppens and Jason Benedict
U. Buffalo

Isolating single X-ray pulses is critical for time-resolved studies.

The width of the X-ray pulse limits the temporal resolution of the experiment.

Time-resolved Crystallography

- Timing FPGA (field-programmable gate array)

Commissioning in 2017-3

Select single pulses
- Some operational modes requires disk change plus extensive realignment (several hours)
- For experiments that do not require single X-ray pulses, the chopper must be completely removed from beam path

Soon to-be–obsolete
- Code to operate not compatible with the APS-U time structure
- May not be possible to integrate into FPGA

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