In situ & Operando Measurements
From Atoms to Applications

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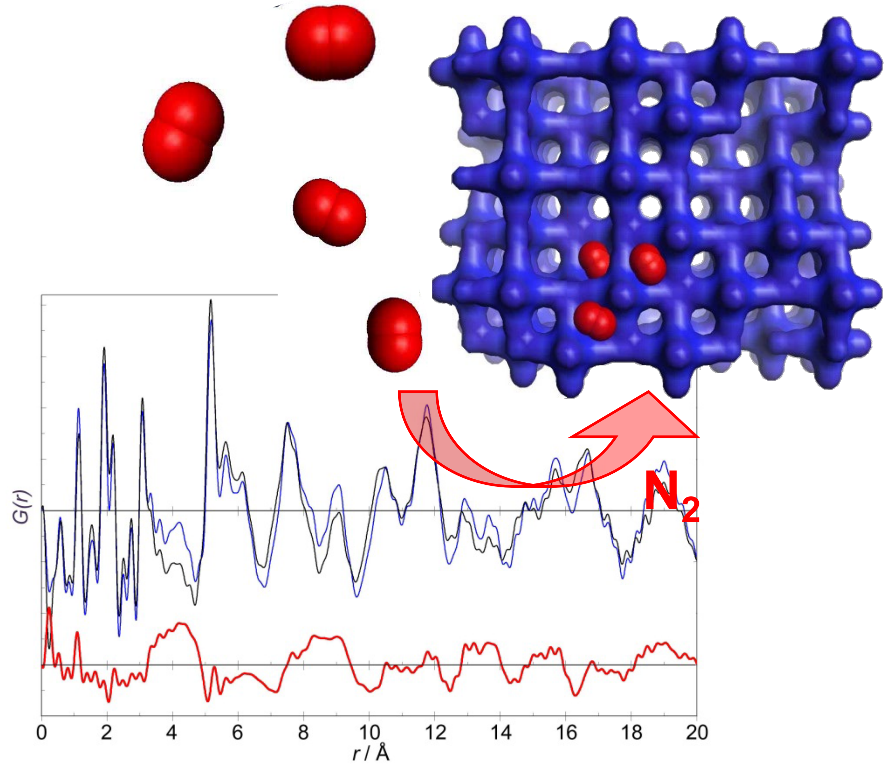


Stony Brook University

My Bio. My Bias

- Chemist
- Energy problem solver
- High energy X-ray scatterer
- PDF-fangirl
- In-situ/operando experimentalist
- Retired beamline scientist

- Contact me: karena.chapman@stonybrook.edu

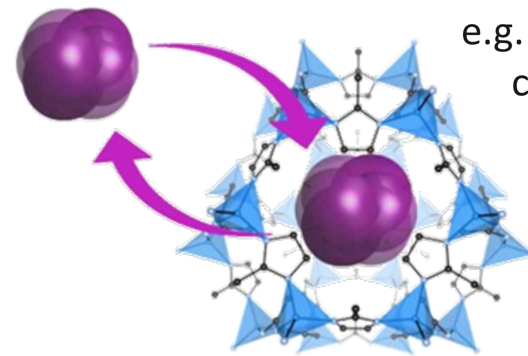
- Feedback form→

A focus on functional energy materials

Energy Storage

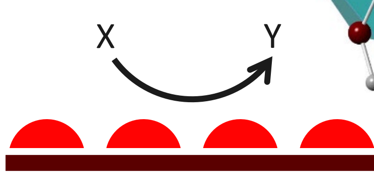
Optimize Function &
Mitigate Failure

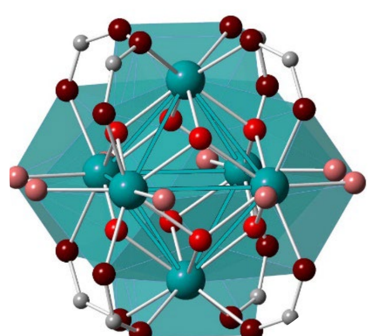
Sorption & Separations



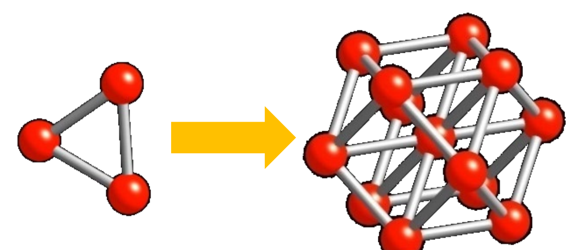
e.g. for nuclear waste
capture, carbon
sequestration

Designing
Catalysts



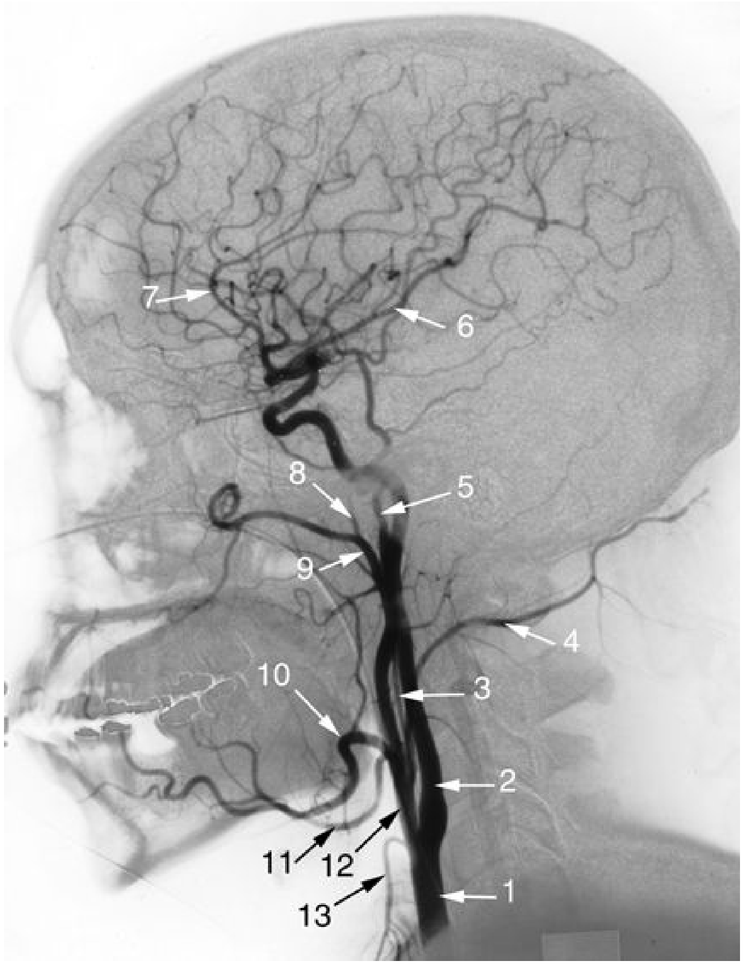


Materials Discovery,
Nucleation & Growth



Control structure
& chemistry

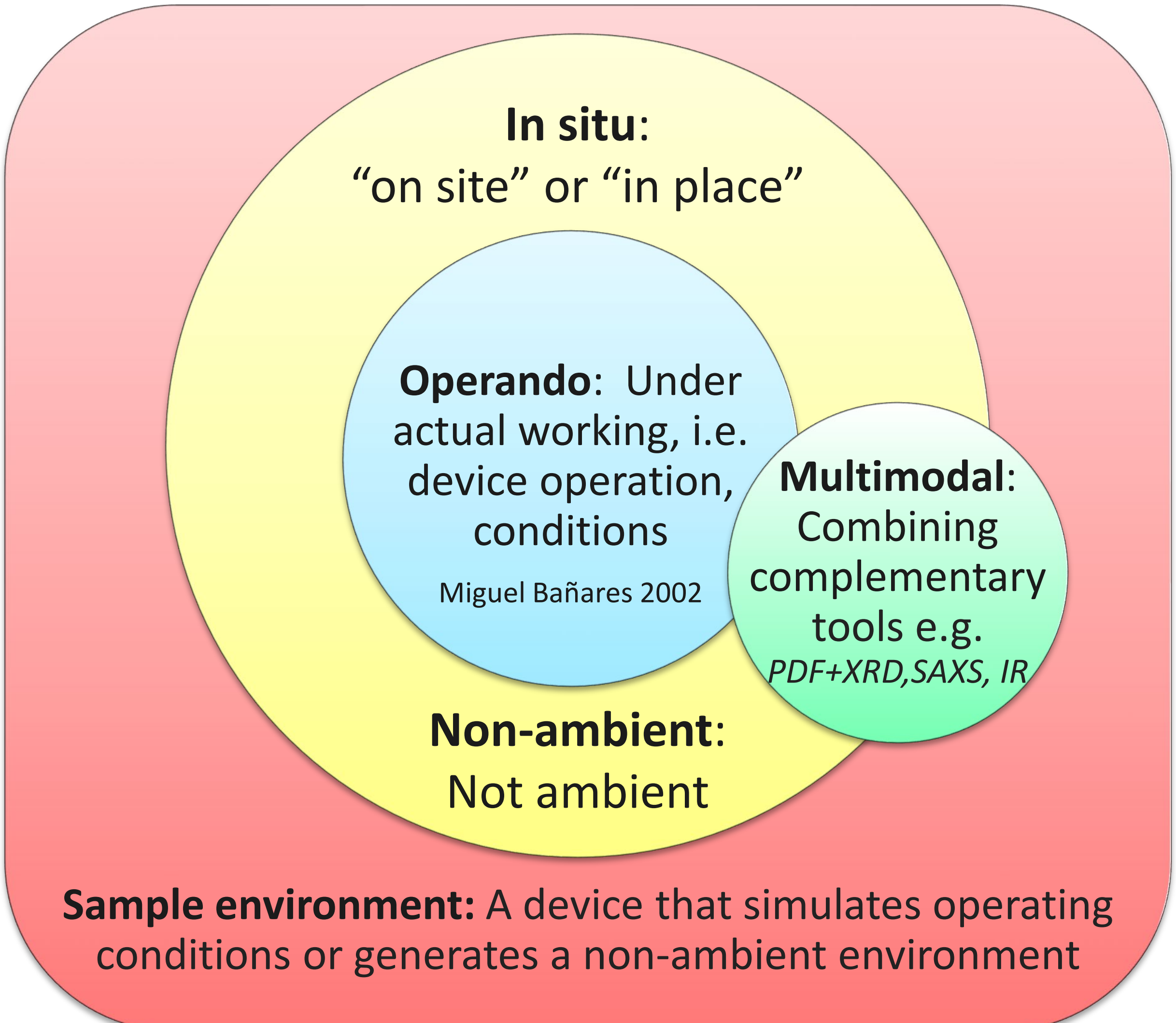
X-rays illuminate structure & function



X-rays can penetrate working systems without damage, to allow us to probe their function or understand failures

Illuminating structure & function

Some Definitions

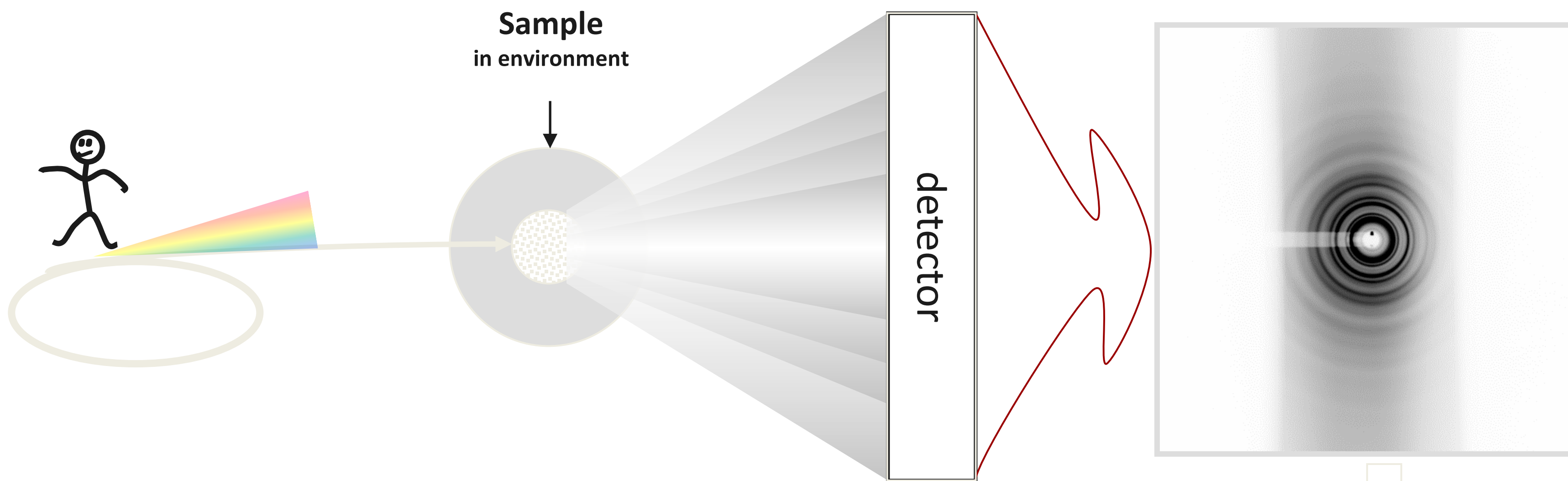


vs

ex situ:
"off site"
or recovered

IUPAC Project 2021-009-2-500 : to clarify Latin terms used to describe the characterization of materials made under non-ambient conditions, materials within systems, and of materials during change

Diverse possibilities



Environmental /In situ

ΔT,   ΔP

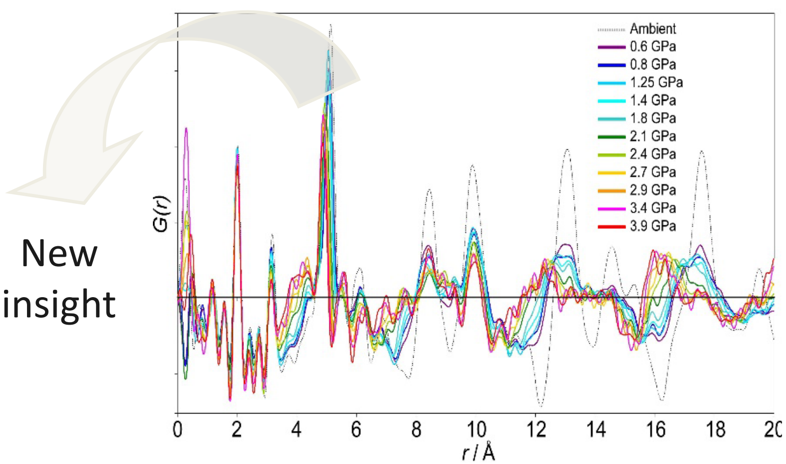
ΔB, ΔE

Δe⁻ echem

Δt reaction

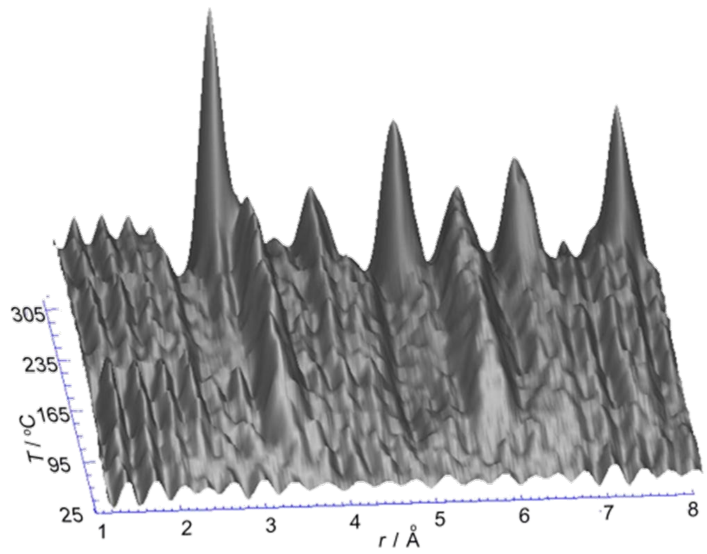
Δ ion/molecule, Δx/y

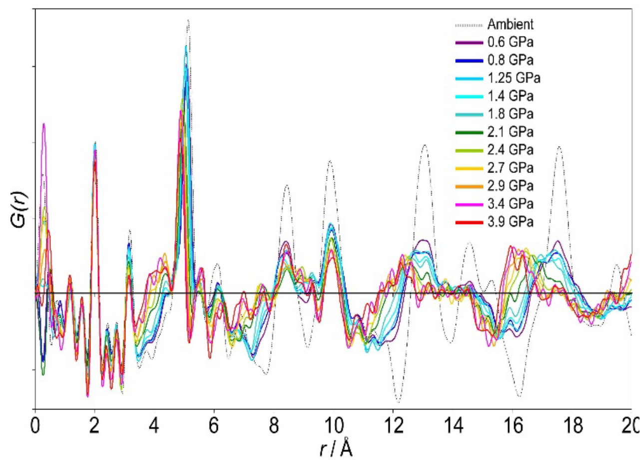
Functional /Operando

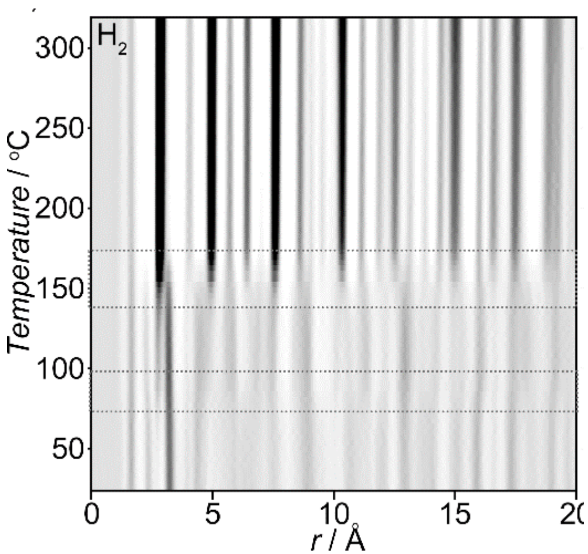


New insight

Visualizing in situ/operando data







Why in situ/operando studies?

Why in situ/operando?

States that only exist in situ

- State functions, Phase transitions
- Dynamic processes, reactions, kinetics, & mechanisms
- Transient, short-lived, & non equilibrium states

vs recovered

- More efficient data/sample
- Finer intervals
- More consistent = more sensitive

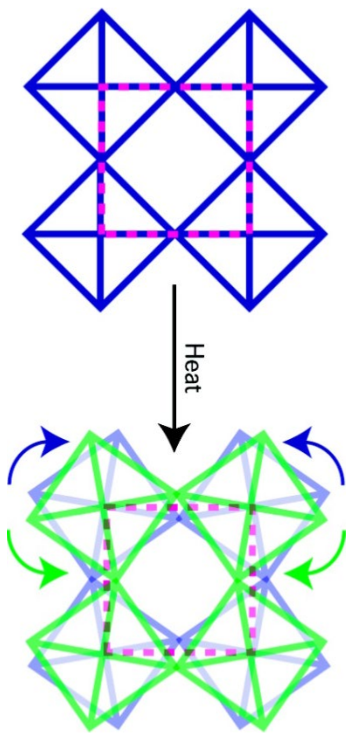
New analysis options

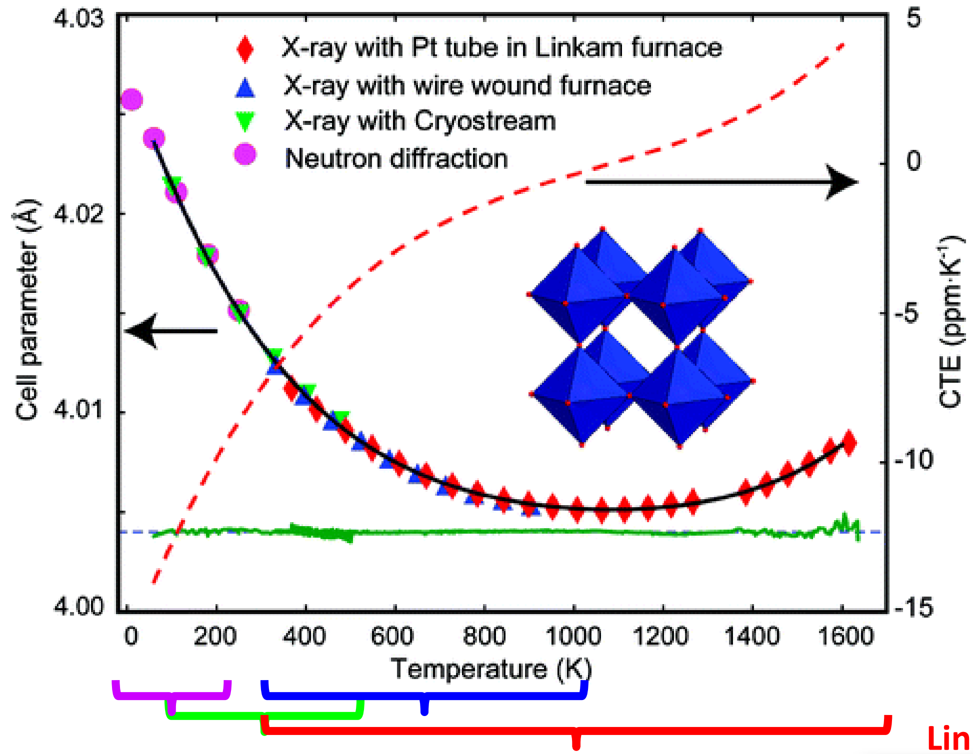
- Differential methods for chemical selectivity
- Analysis of selected features
- Model-free multivariate & correlation analyses

Example: Variable temperature

Pronounced Negative Thermal Expansion from a Simple Structure: Cubic ScF_3

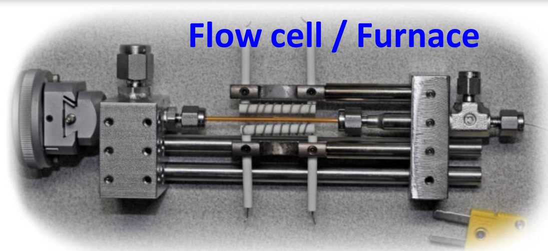
Angus Wilkinson *et al. J. Am. Chem. Soc.*, 2010, 132 (44), pp 15496–15498



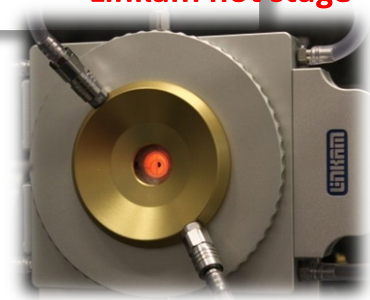


N_2 Cryostream:

Flow cell / Furnace

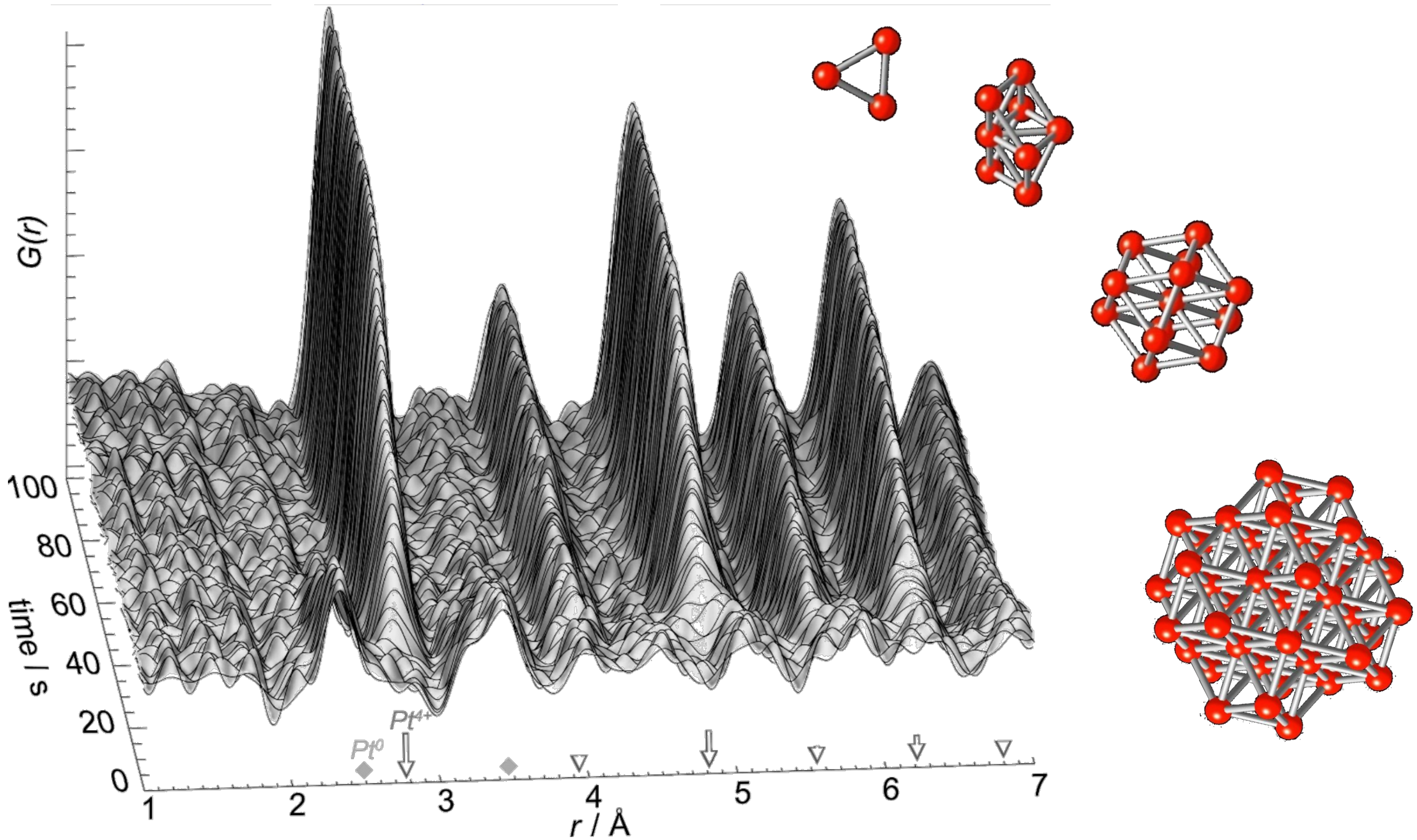


Linkam hot stage



Example: Reaction kinetics & mechanism

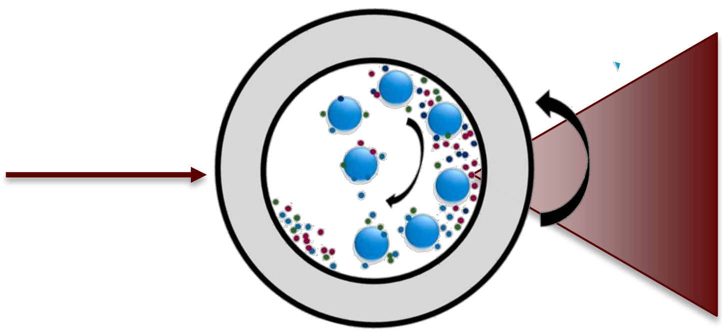
Watching Nanoparticles Grow: The Mechanism and Kinetics for the Formation of Supported Nanoparticles

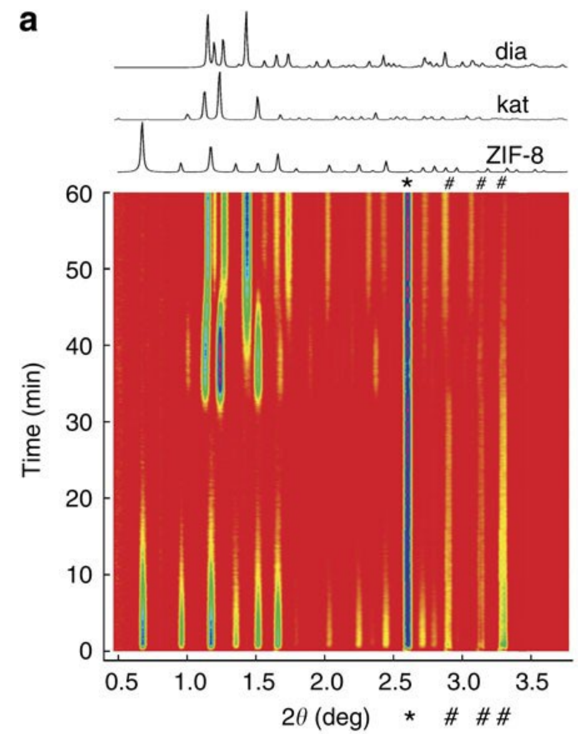


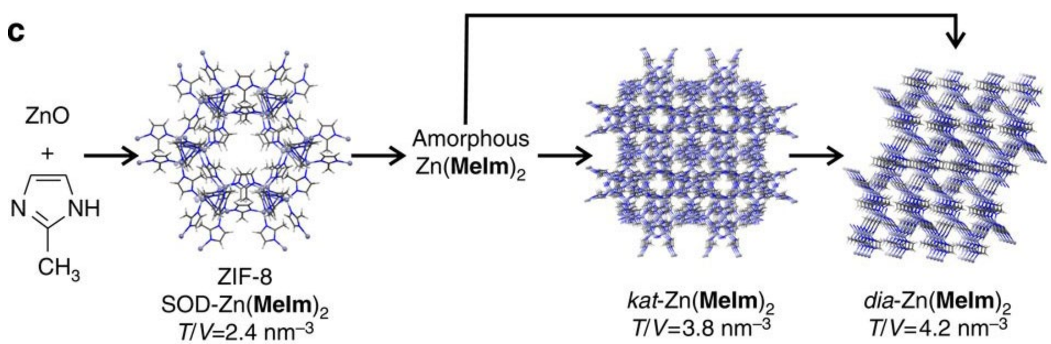
J. Am. Chem. Soc., **2007**, 13822-13824.

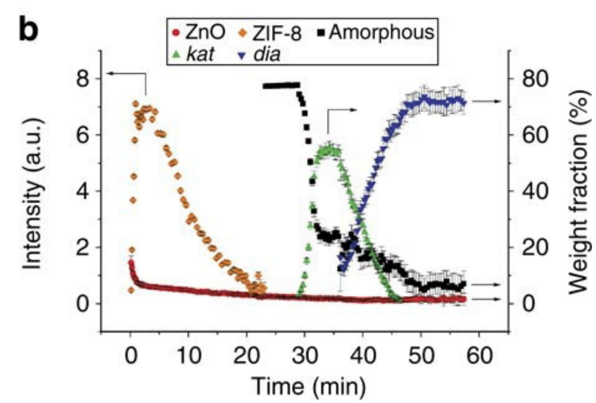
Mechanochemical Reaction

X-ray studies during mechanochemical milling allowed a new intermediate phase to be identified





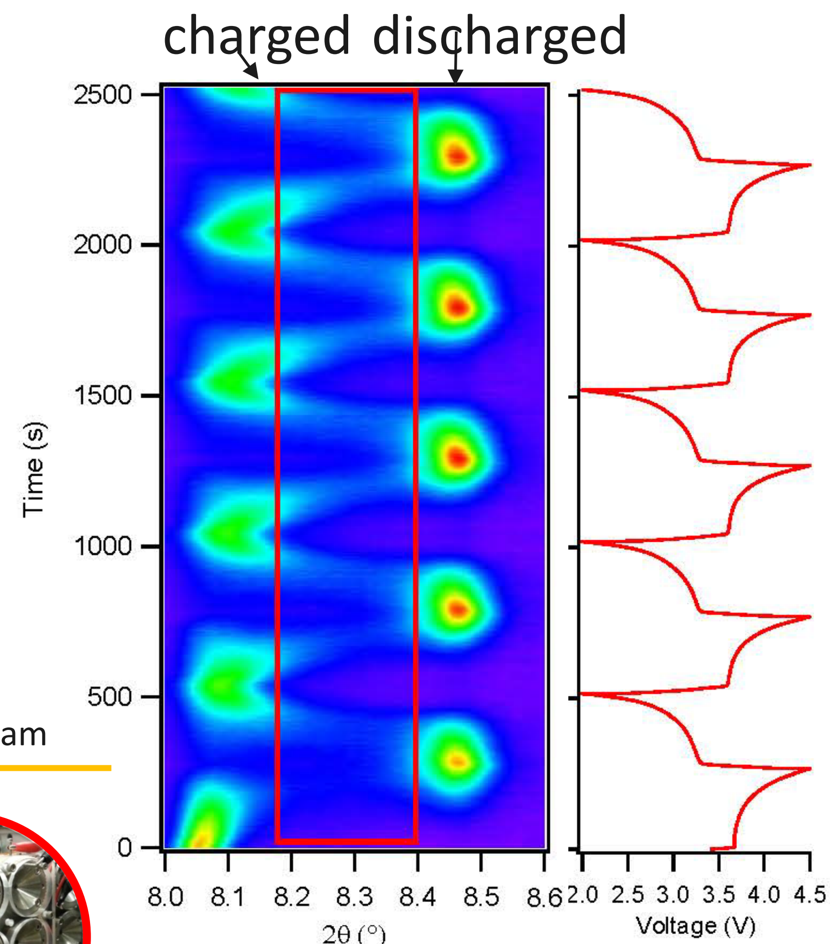


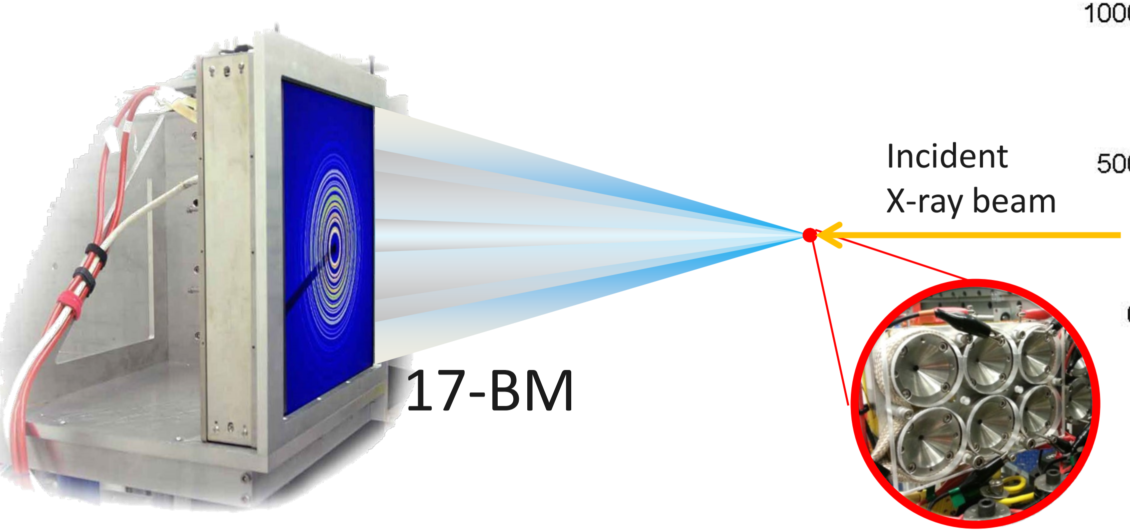


Nature Commun 6, 6662 (2015)

Example: Dynamic Non-equilibrium States

Evidence for metastable intermediate phase with variable lattice dimensions – a “solid solution”

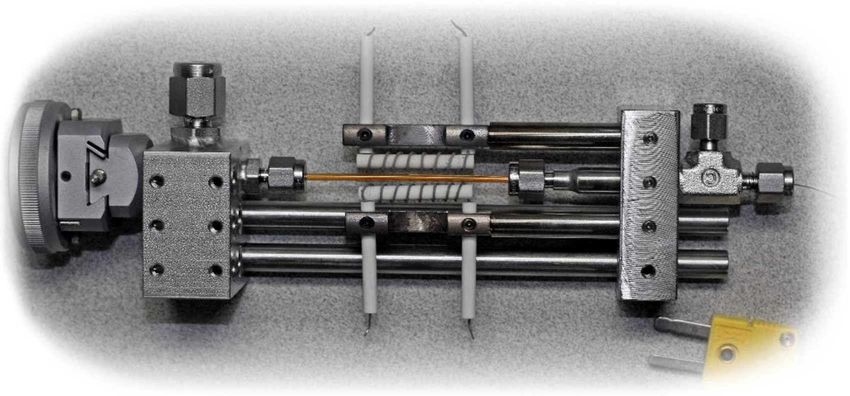




Science **2014**, *344*, 1252817

How to *in situ*?

Anything is possible. Not everything is easy

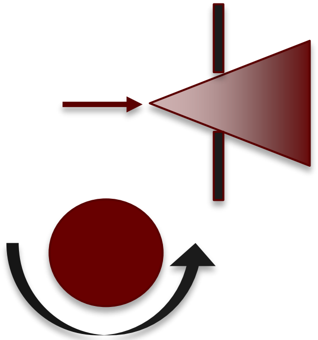


Making it work. The X-ray/neutron perspective

No compromises

The measurement still needs to be possible!

- Geometry (more difficult for scattering)
  - access of the incident and scattered/transmitted beams
  - sample motion (spinning, rotations/translations etc)
  - shadowing



- Sample signal
- Cell contributions
  - To signal. Measurement background. Ideally low, reproducibly, correctable
  - Absorption

- Note for neutron TOF/energy dispersive X-ray

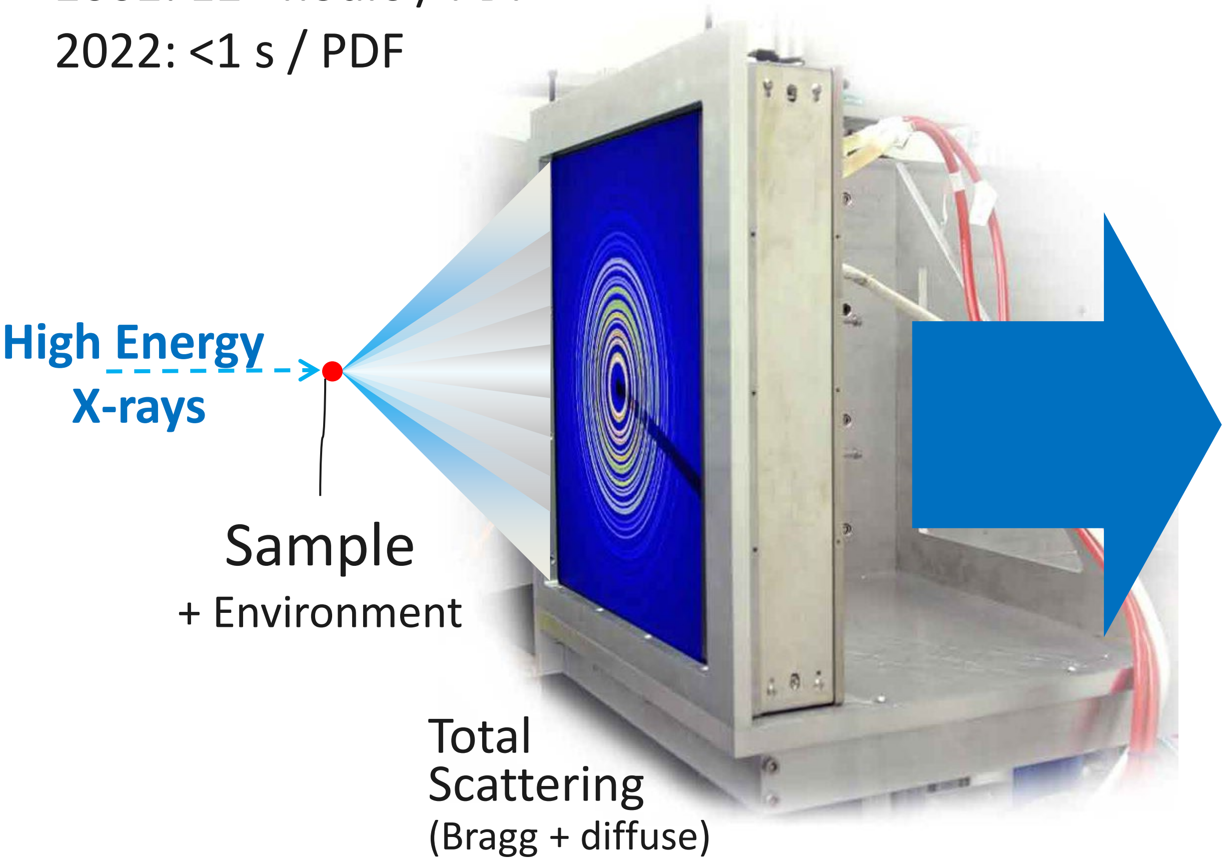
Modern X-ray Pair Distribution Function measurements

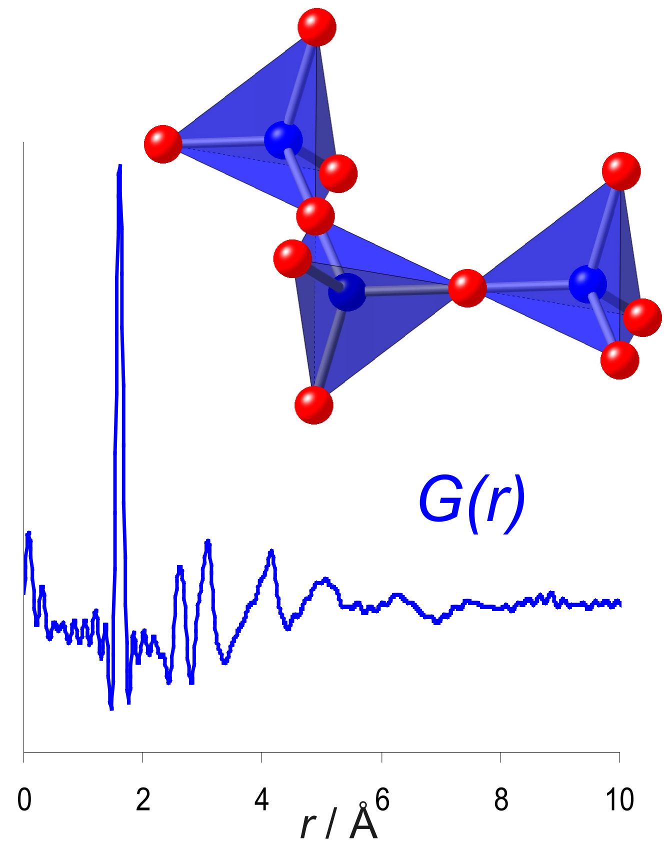
A specialized synchrotron powder diffraction experiment

Rapid acquisition PDF with area detectors + high energy X-rays

2002: 12+ hours / PDF

2022: <1 s / PDF





Peter J. Chupas, X. Qiu, J. C. Hanson, P. L. Lee, C. P. Grey & S. J. L. Billinge *J. Appl. Cryst.* **2003**. 1342-1347

Modern X-ray Pair Distribution Function measurements

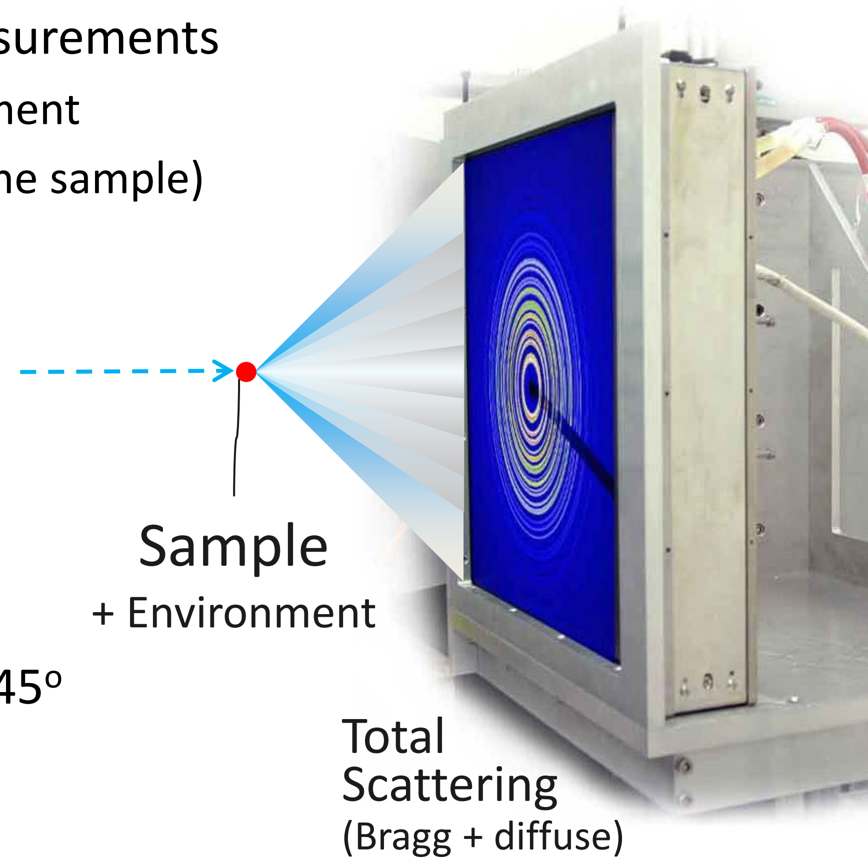
A specialized synchrotron powder diffraction experiment

Rapid acquisition PDF with area detectors + high energy X-rays

Total scattering => at least 2 separate measurements

1. Sample + background/sample environment
2. Background(s) (everything that is not the sample)

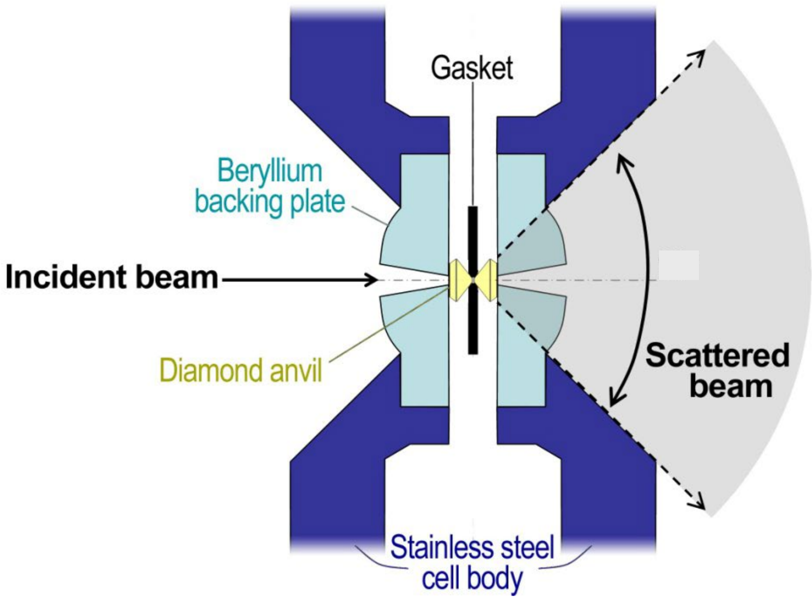
- Backgrounds *must* be reproducible.



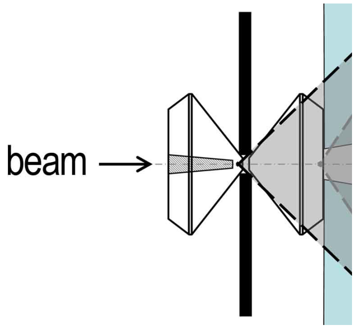
To high *Q* => Wide angular access

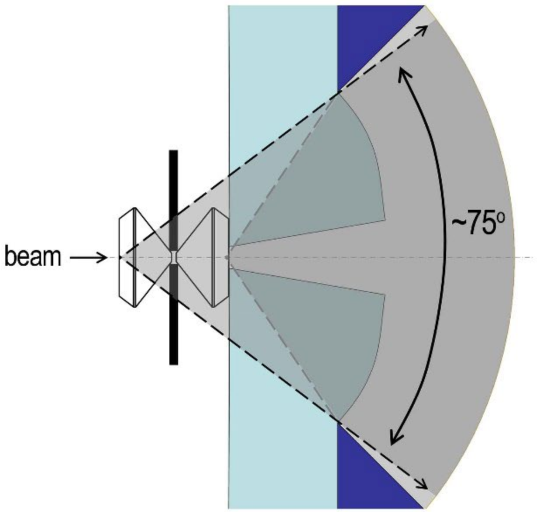
- At ~60keV, Q_{max}~20 A^{-1}
  requires that data are collected to ~40-45^{o}

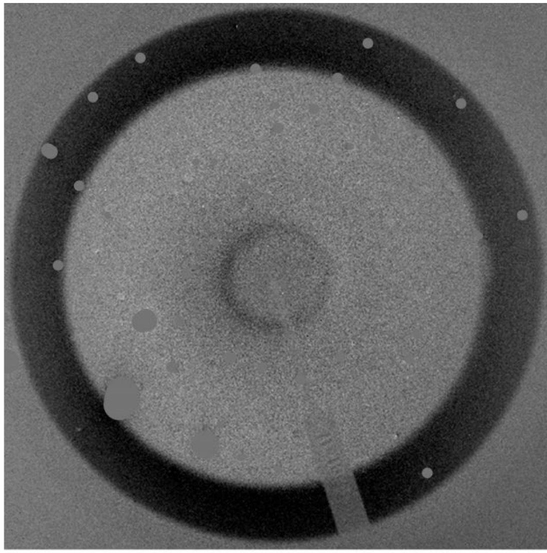
Example: Diamond anvil cell for High Pressure



- Limited scattering aperture
- Small sample volume
- Thick "windows"
- Distortion of cell, changes the cell contribution
- Mitigate with perforated anvil

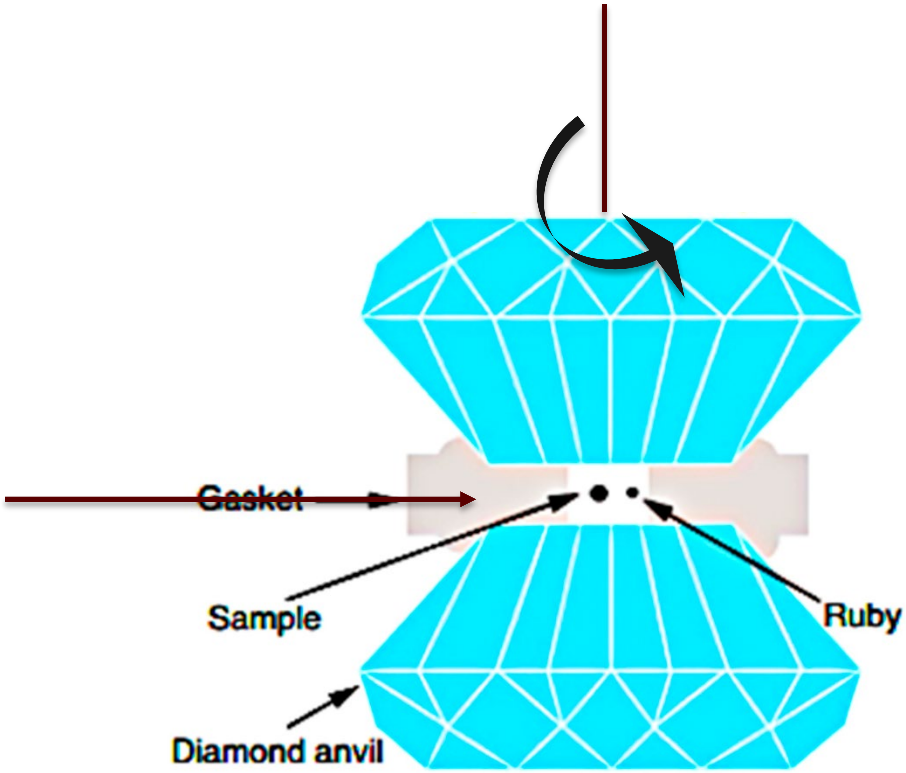




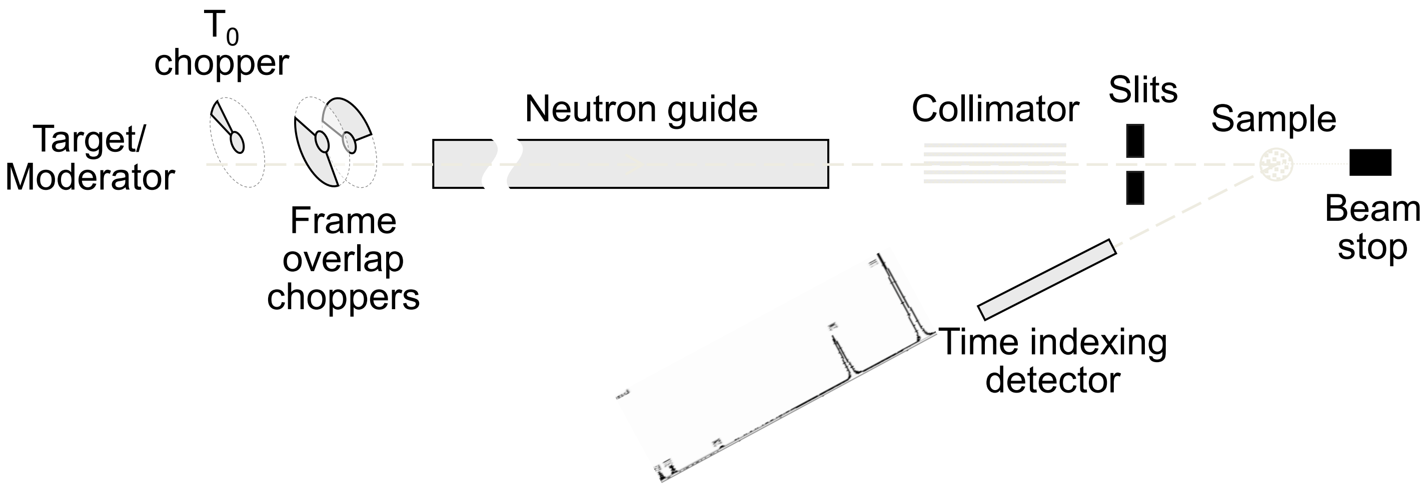


Example: HP tomography requires rotation

- Direct beam through “transparent” gasket

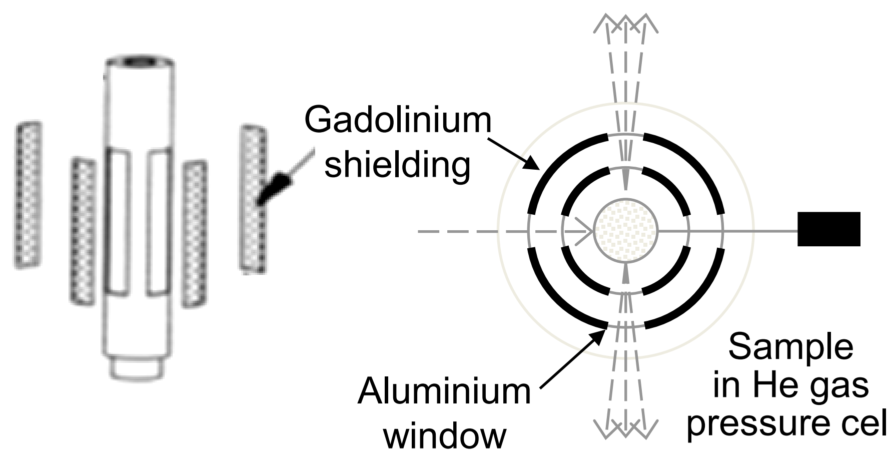


Example: High Pressure with TOF neutrons



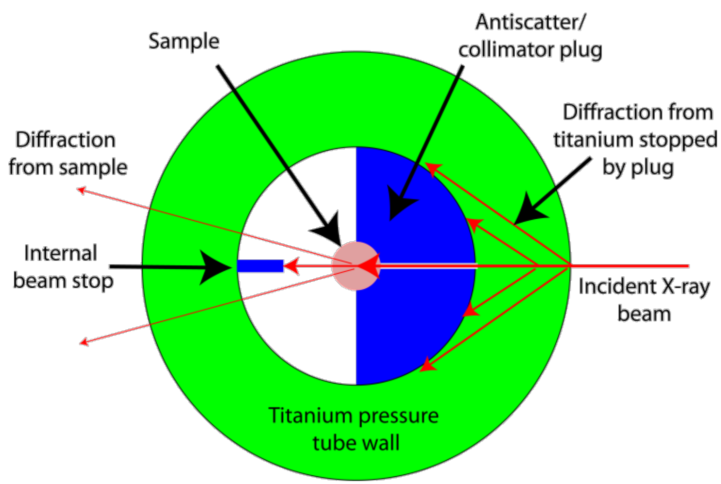
TOF neutrons or energy dispersive X-ray scattering, collect a full diffraction pattern at every position.

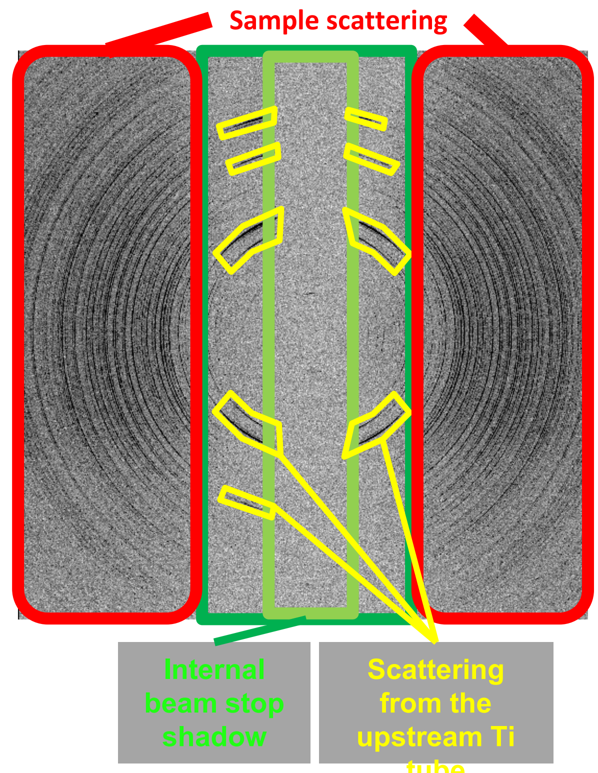
Only a small angle is needed



Example: Reducing background from HP cells

Fluid pressure cell + BRIM (Background Reducing Internal Mask)





- Fluid pressure offers extreme precision
- Large contribution from sample environment
- Reduces scattering from sample environment
- Use highly penetrating nature of high energy X-rays

J. Appl. Cryst. (2011). 44, 1047-1053

Making it work. The environment perspective

No compromises

The functional environment HAS to work!

- Stability/fidelity of the environment
- Heterogeneity/uniformity
- Beware the potential for beam induced effects

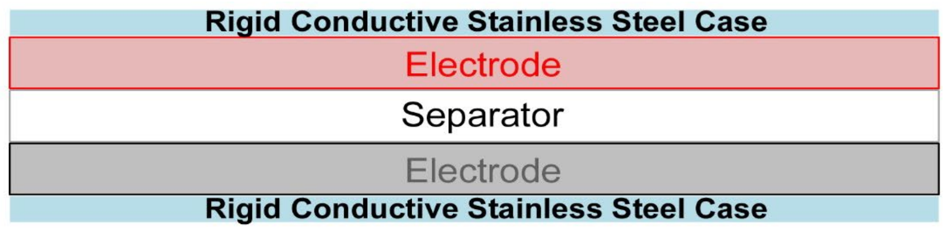
- Characterize your sample environment with a known, model system, before using the environment to characterize your sample!

Example: Enabling operando echem measurements

X-ray enable a battery coin cell by adding an X-ray window

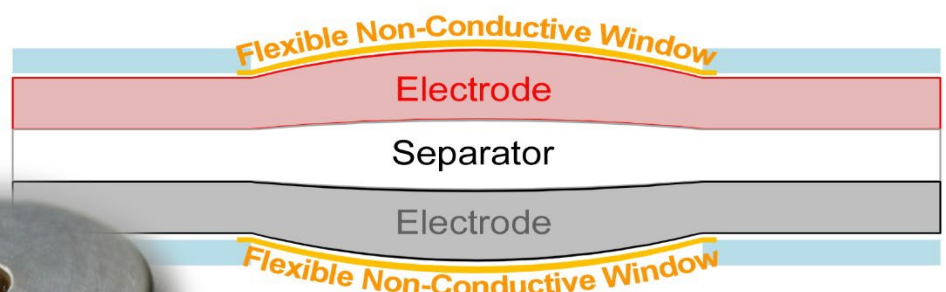
Standard coin cell

Uniform pressure & conductivity

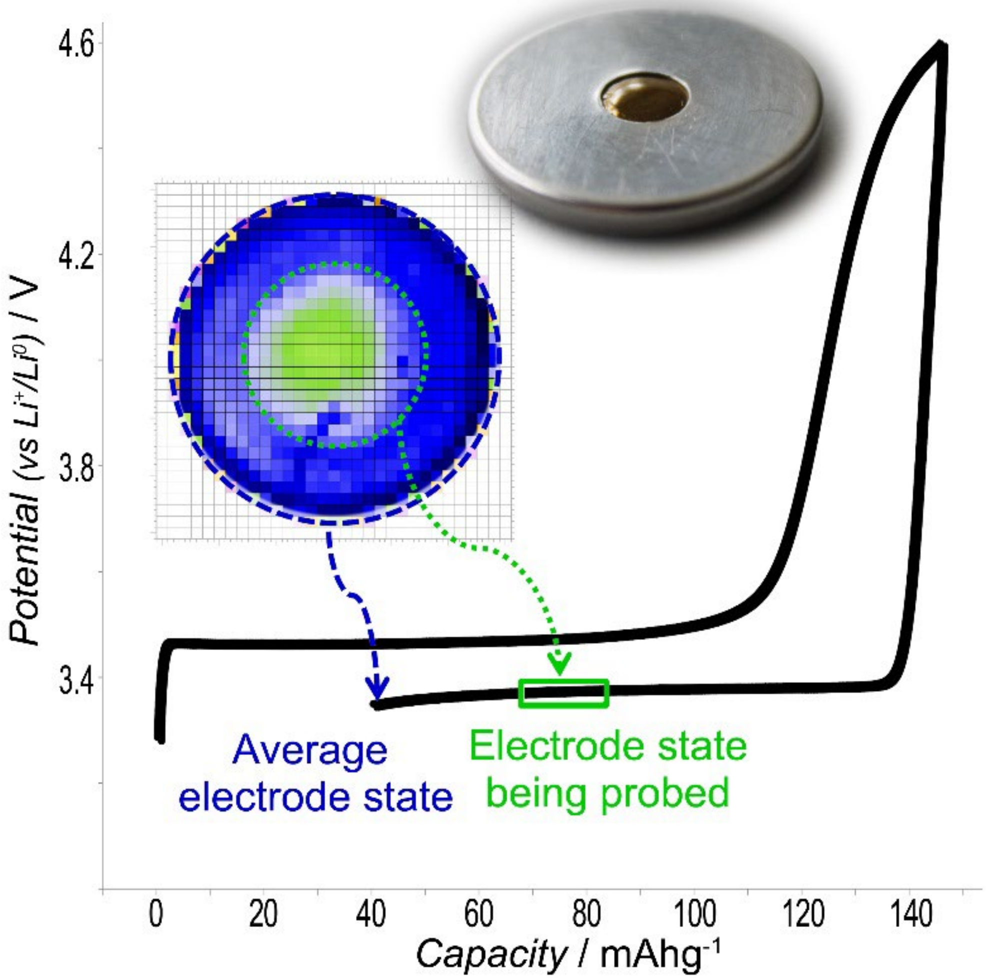


Modified coin cell

Non-uniform pressure & conductivity



The reaction may be delayed



<u>On average</u>
the cell electrochemistry may be only ~1% off

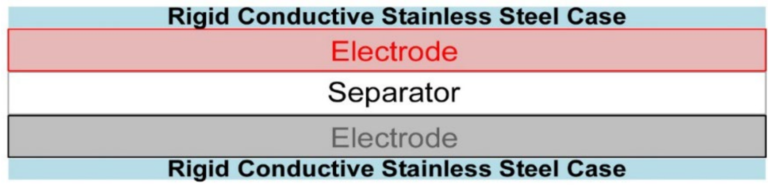
BUT

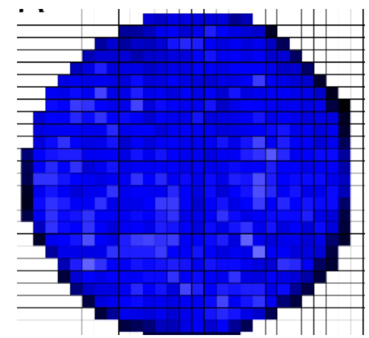
<u>Locally</u> the electrochemistry of the probe volume is 20% off

Enabling operando echem measurements

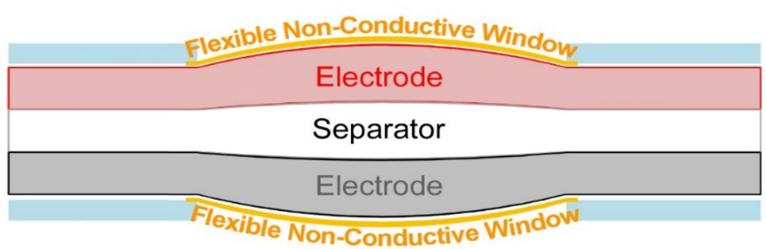
J. Phys. Chem. Lett. 2015 2081
J. Appl. Cryst., **2012**, 1261

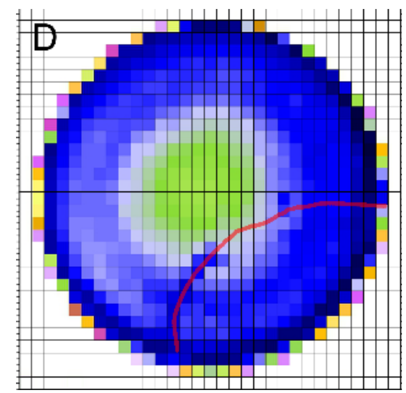
Coin Cell



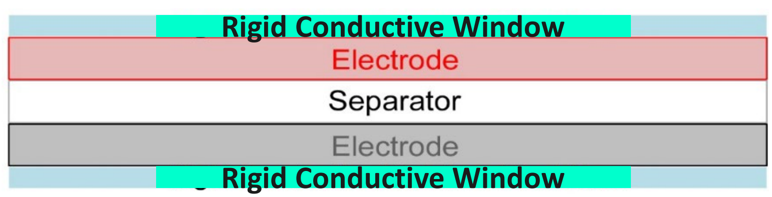


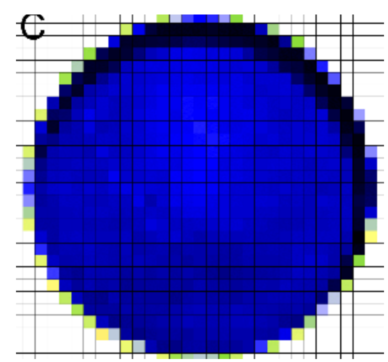
Modified coin cell





AMPIX



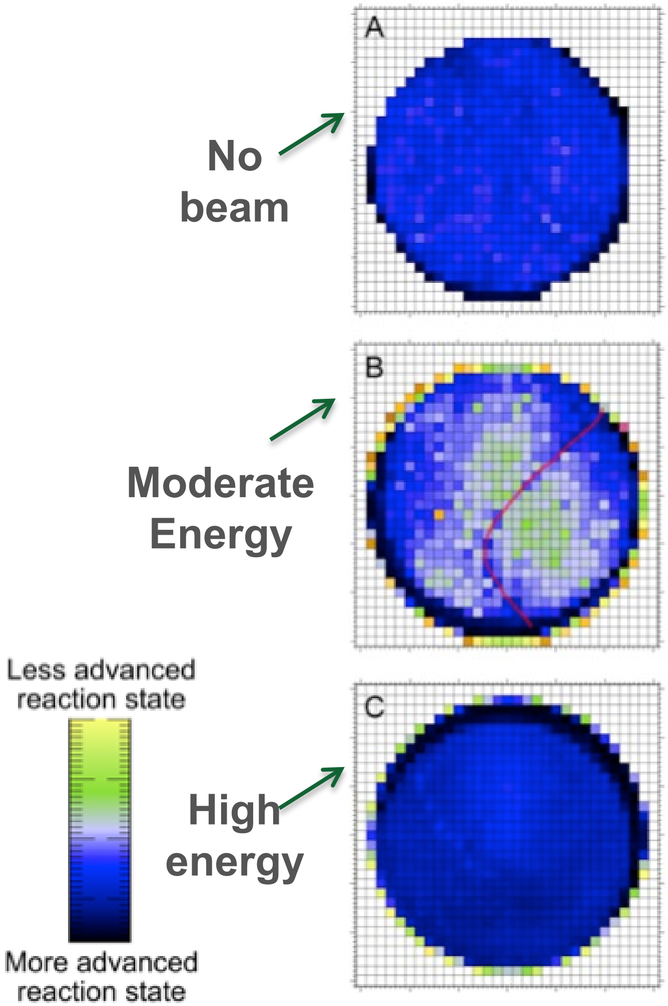


The Operando Challenge

Like a cat-in-a-box*, experiments that observe a reaction can change the state of that reaction*

J. Phys. Chem. Lett., **2015**, 2081–2085

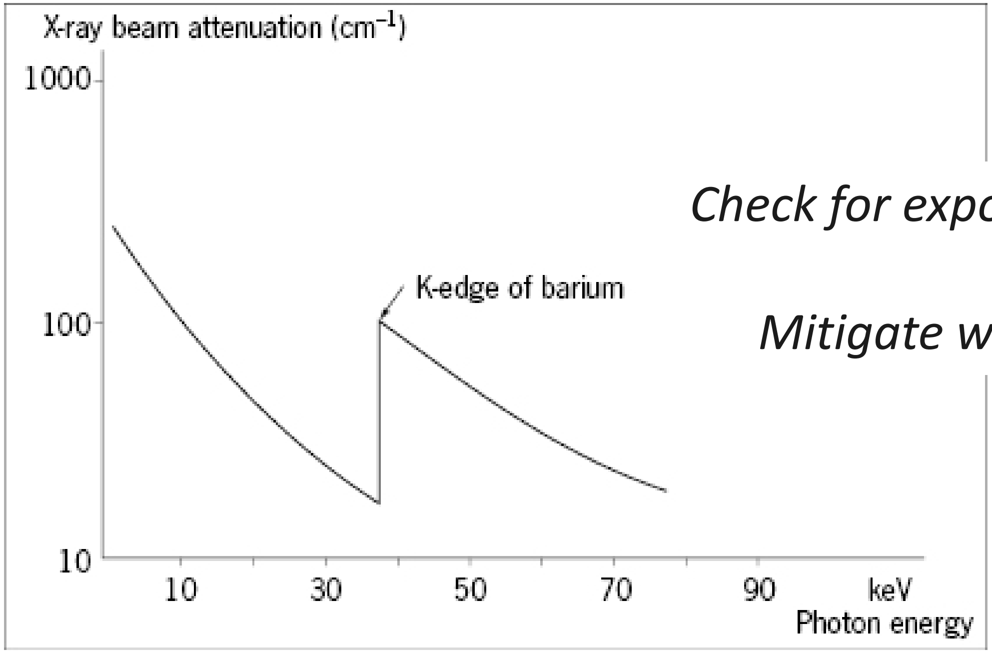
Beam interactions: X-ray energy matters



- X-ray beam interactions (and damage) scale with absorption
- X-ray absorption is minimized at high energies BUT attains a maximum close to an absorption edge
- Beam interactions can impact operando studies using:
  - soft X-rays
  - X-ray absorption spectroscopies (i.e. EXAFS and XANES)

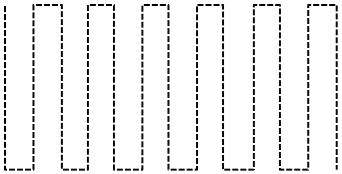
Special cases: Beam effects

- Beam effects/damage scale with absorption
- Absorption is maximized at low energy and just above edge.
- Soft X-ray/XANES/EXAFS measurements can be highly sensitive
- This depends on sample composition



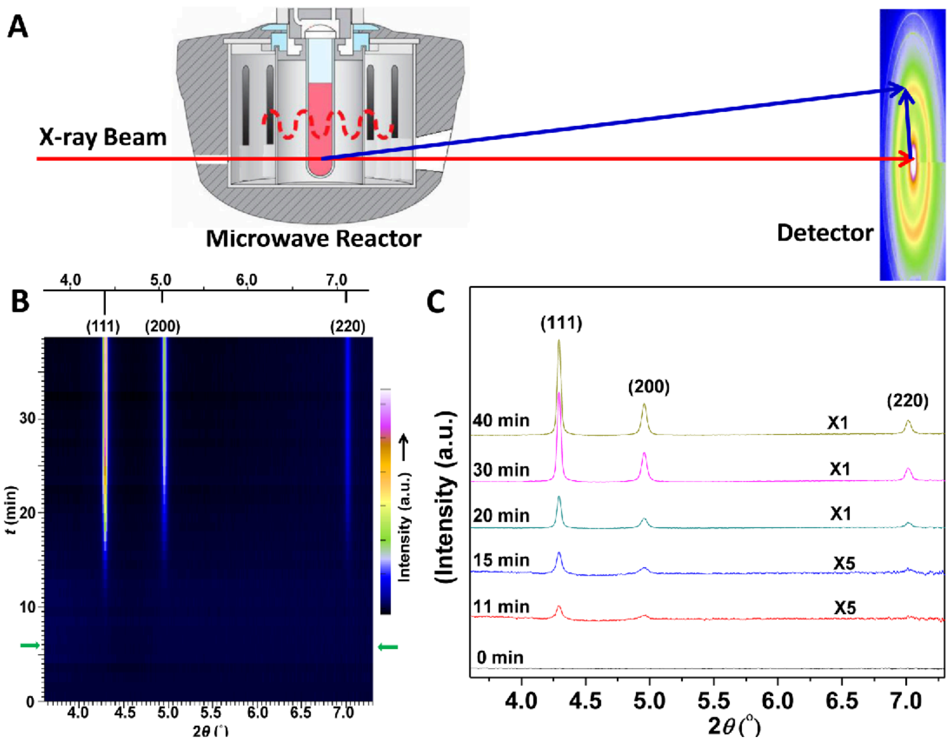
Check for exposure dependent effects

Mitigate with sample rastering



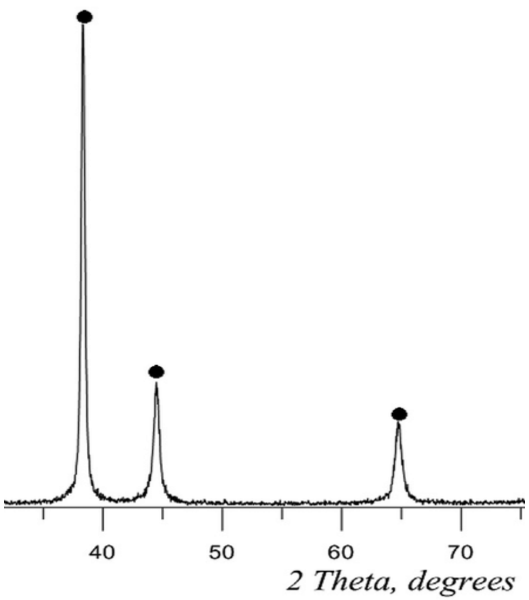
Special cases: High Energy X-rays

- High energy X-rays are highly penetrating. I.e. absorption is low. I.e. Beam effects/damage is minimized
- Scattering is compressed in the forward direction. A smaller scattering aperture is needed to access the same d-spacing/Q-range



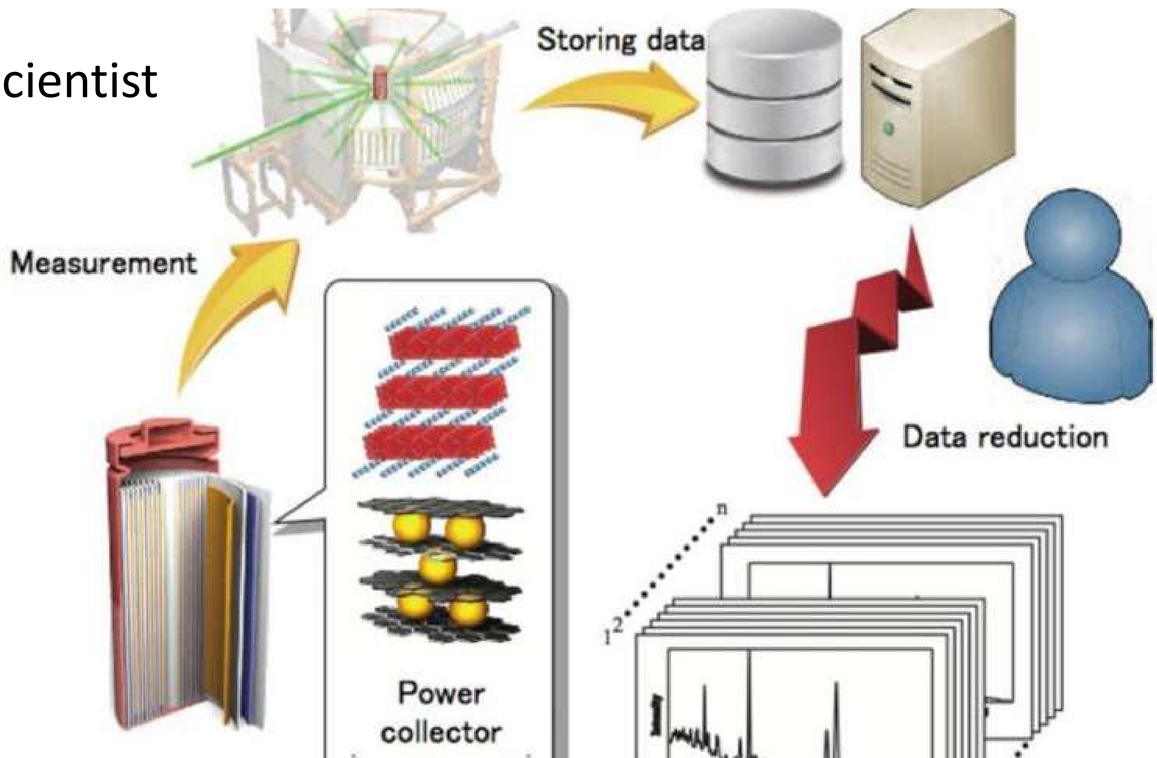
Nano Lett. 2016, 16, 1, 715–720

E = 117 keV vs 8 keV



Special cases: Neutrons

- Highly penetrating neutrons can probe real devices
- Larger samples - > greater safety hazards.
- More facility oversight on samples environments
- Talk to your beamline scientist



Time resolution & time span

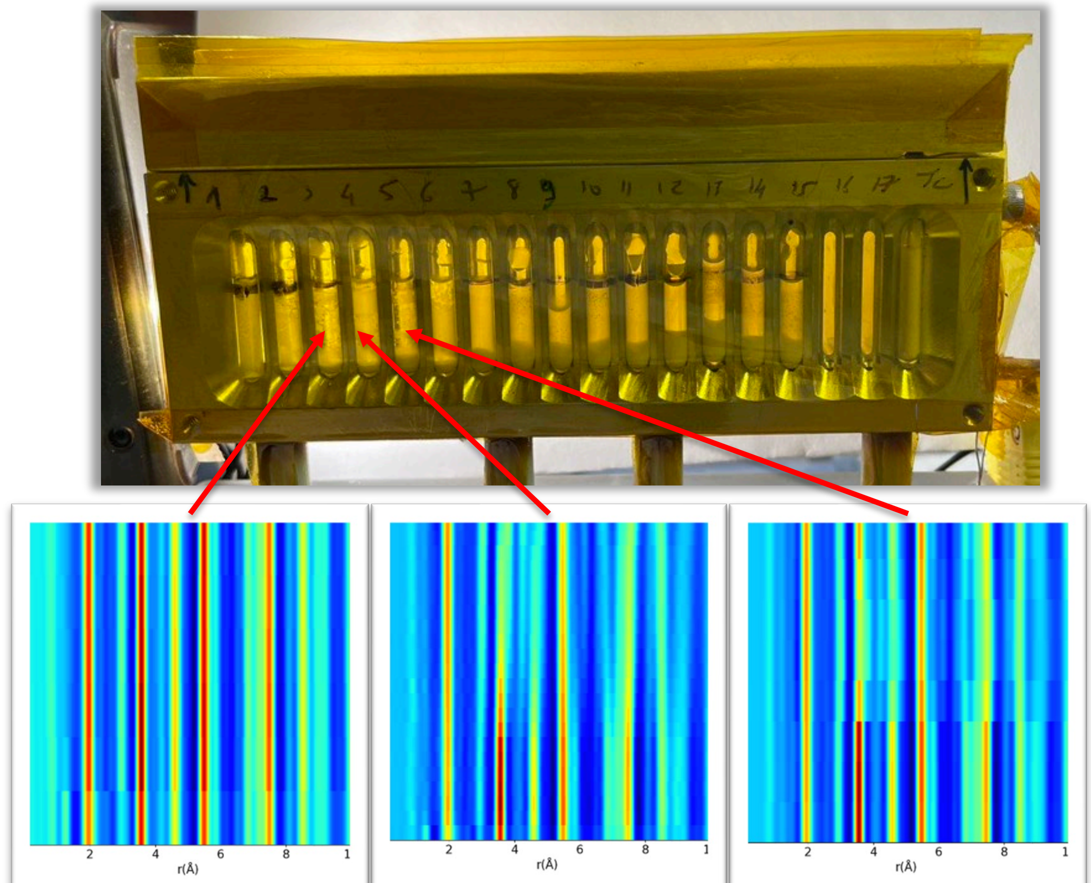
Long duration, multiplexing, time-resolved

Multiplexing: Fast measurements of slow processes

Some processes (electrochemical cycling or chemical reactions) are slow (hours) relative to the measurement time (min).

Multiple cells can be arranged in an array and studied in parallel e.g. for composition/concentration dependence

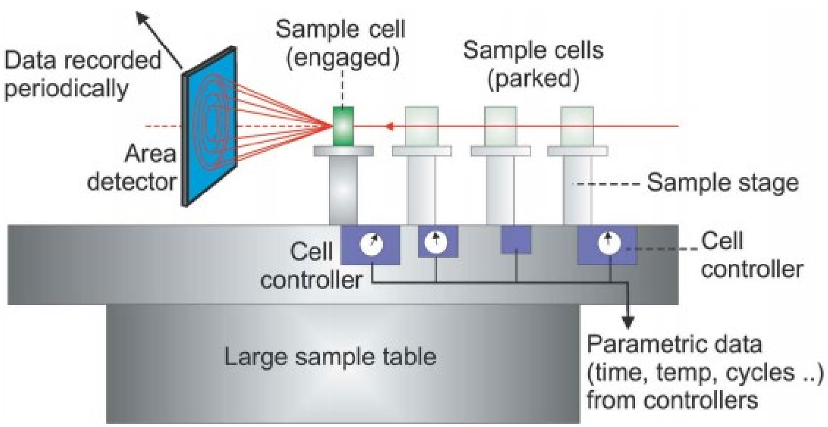
J. Appl. Cryst., **2012**, 1261
J. Appl. Cryst. **2016,** 1665



Possibility for Long-Duration Experiments

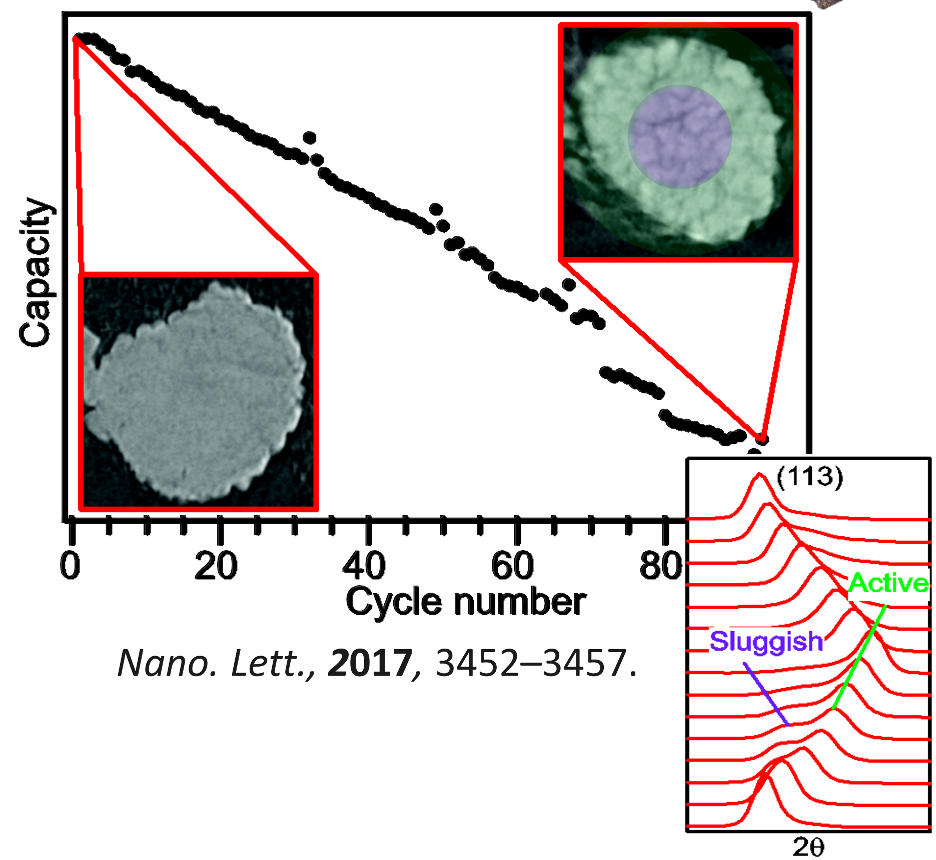
For very slow processes. E.g. Ice formation, battery degradation, corrosion

Samples probed at regular intervals over months



e.g. For XRD I11, Diamond Light Source
J. Appl. Cryst. **2017** 50, 172–183

Identify intergranular fracture as the origin of capacity loss in batteries

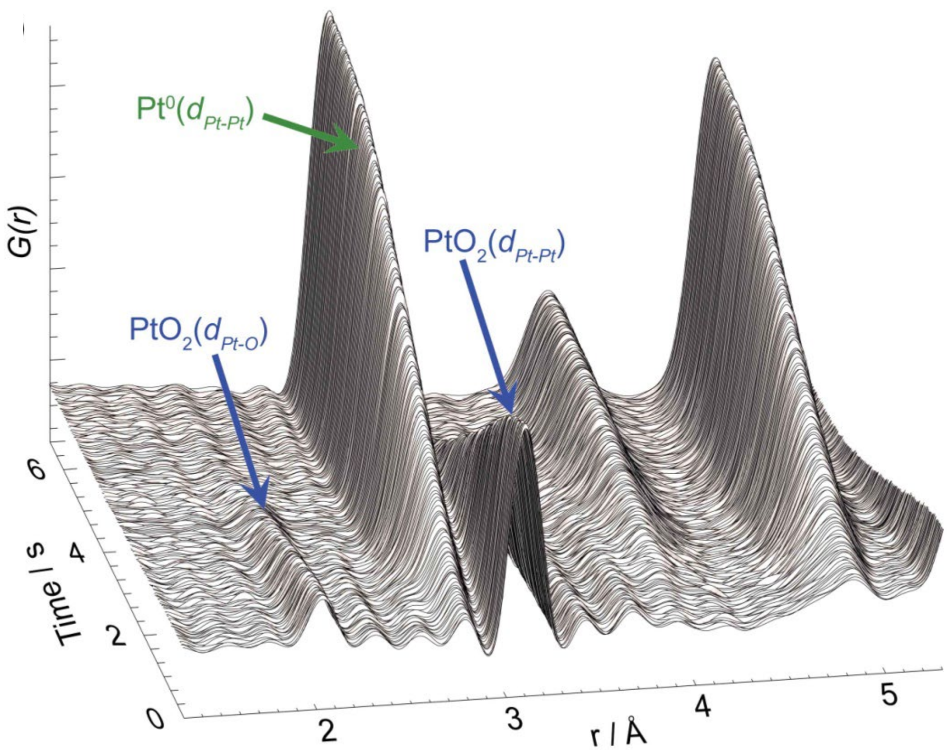


Nano. Lett., **2017**, 3452–3457.

Following fast kinetics

Time-resolution is limited by the detector read-out rate (0.03-0.1 s) and the signal-to-noise (i.e. sample scattering + X-ray intensity)

The time-resolution is well matched to the rate of gas-solid reactions

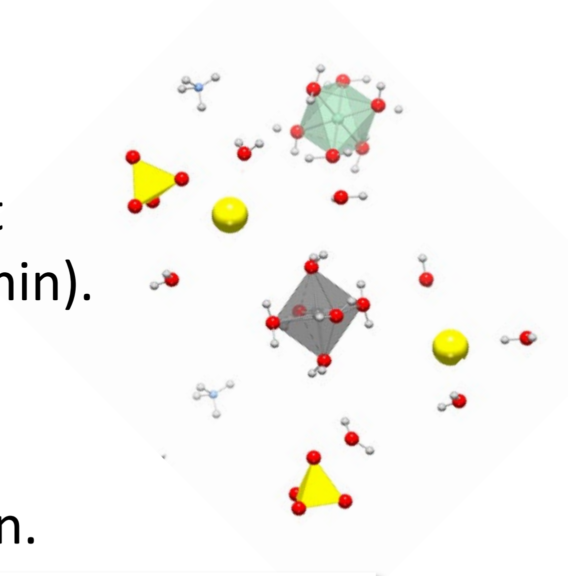


In situ reduction:
$Pt^{IV}O_2 \rightarrow Pt^0$

200 PDFs in 6 s
30 Hz/30ms per point

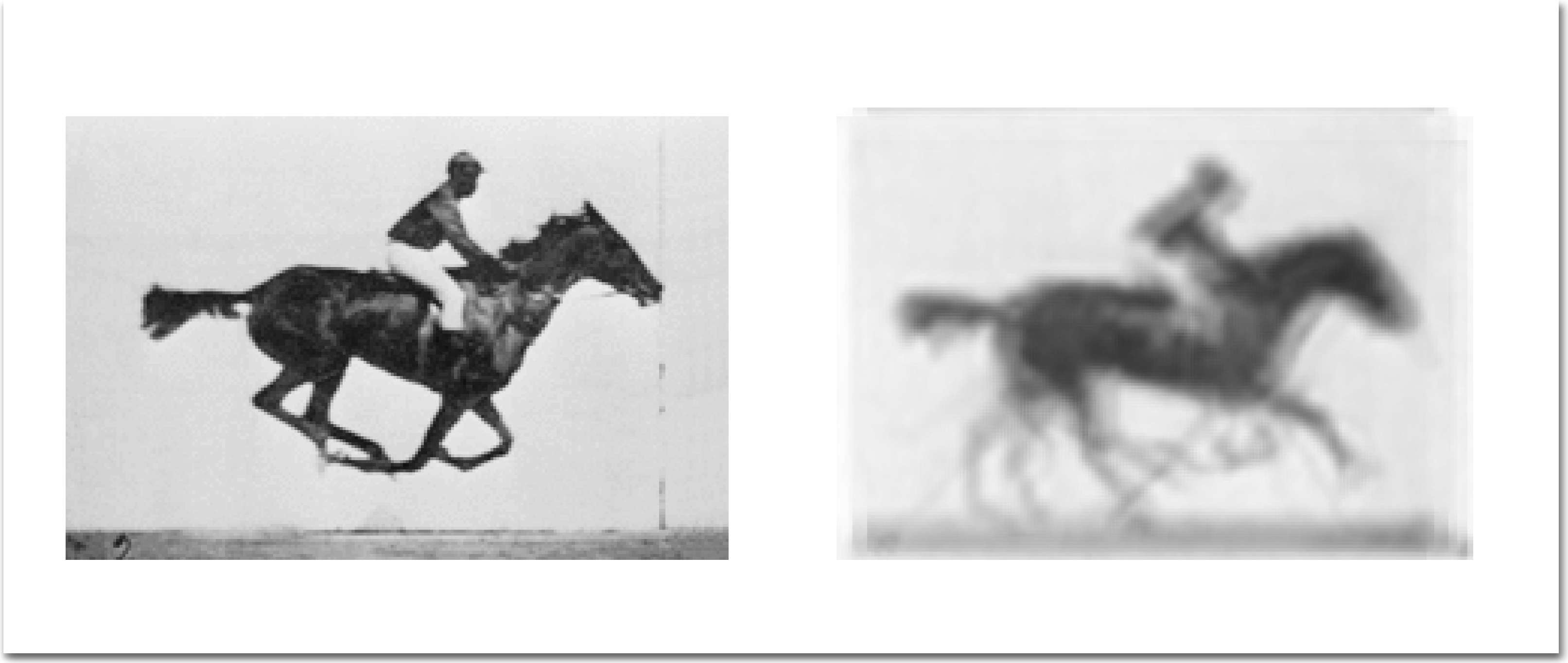
J. Appl. Crystallogr., **2007**, 40, 463-470

What if the system evolves faster than data rate?



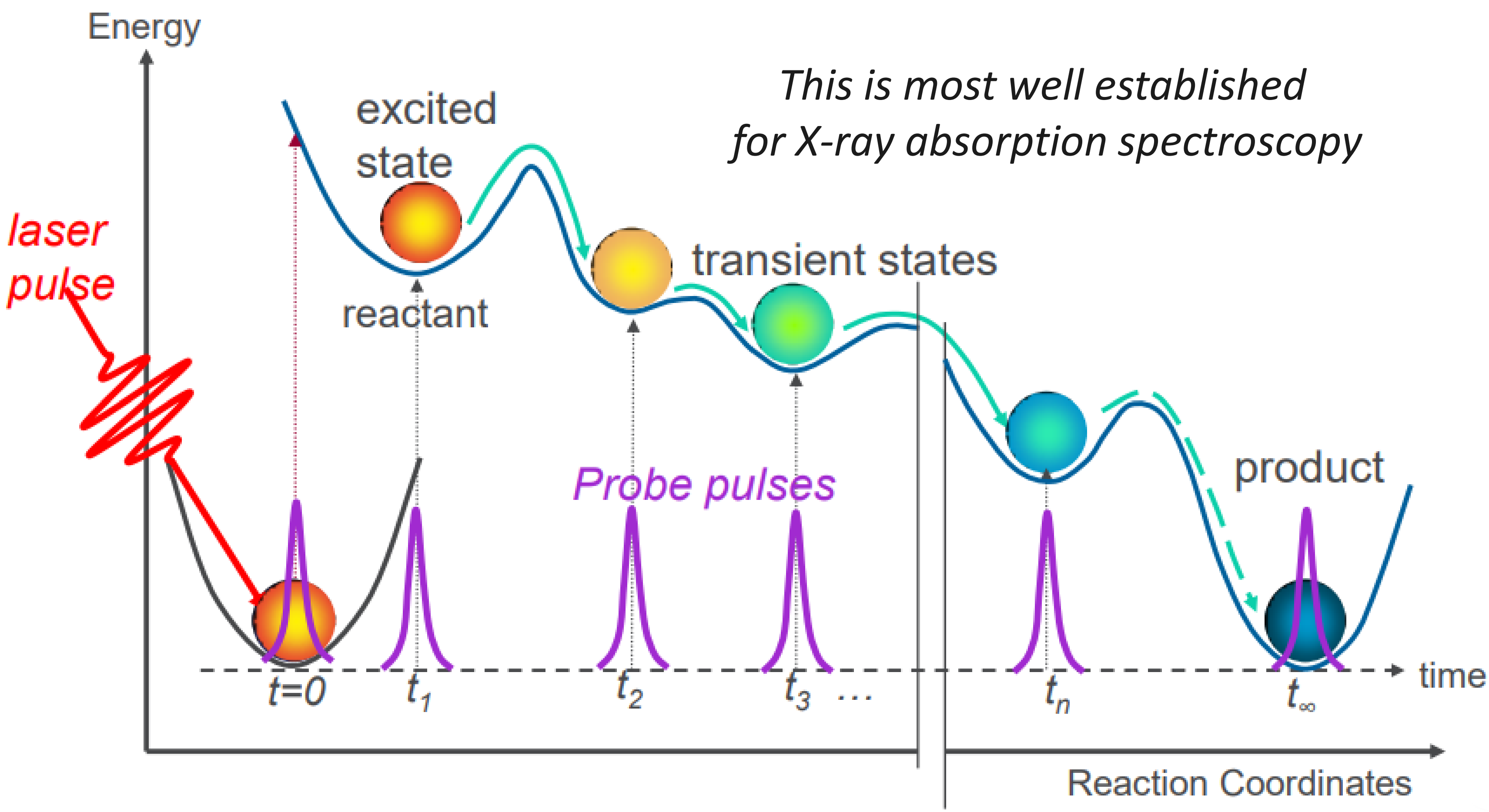
E.g. Reactions in solutions are fast(s), but
measurements are signal limited and slow (min).

Short-lived states cannot be resolved as
the data are a time-averaged superposition.



Ultra Fast-processes: Need Pump-probe strategies

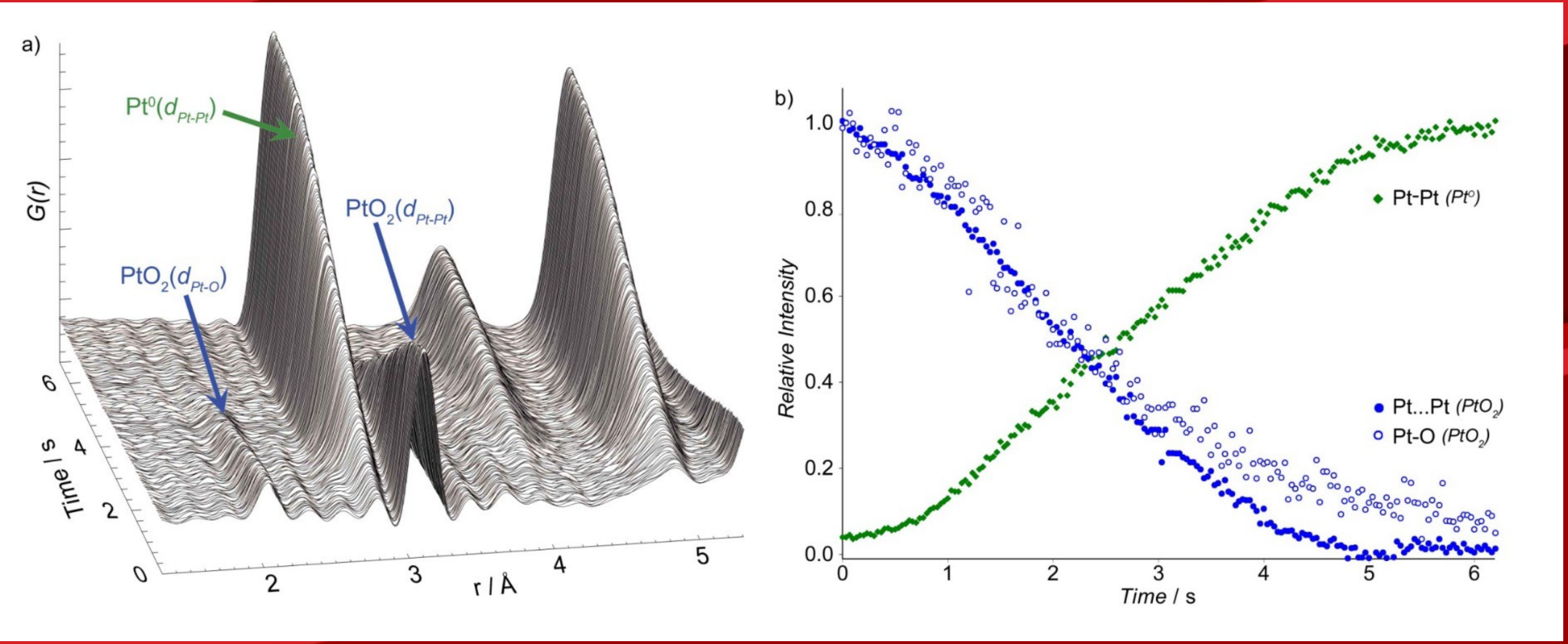
Use a pulsed source *(e.g. synchrotron with timing modes, XFELs)* to probe system at defined intervals after a reaction is initiated.



This is most well established for X-ray absorption spectroscopy

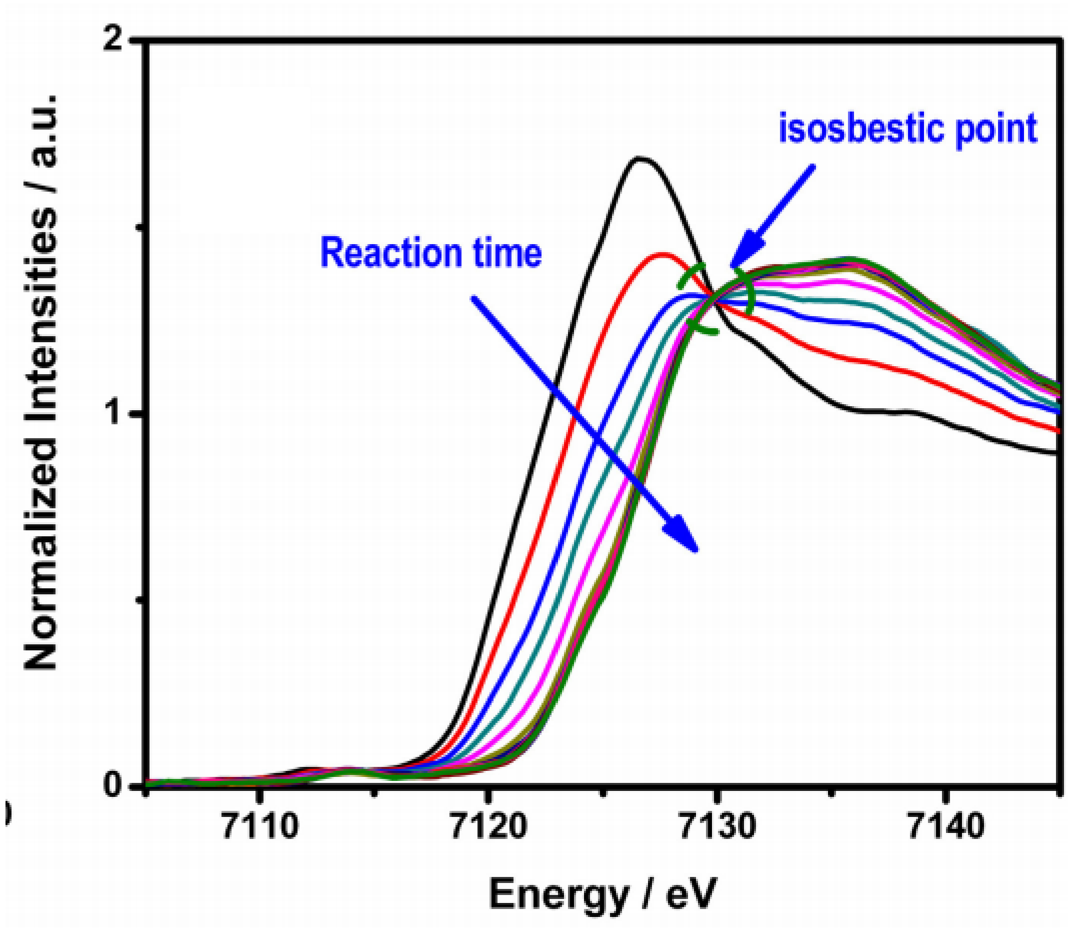
Expanded analysis opportunities

Correlation to variables, Parametric refinement, Multivariate analysis



Isosbestic points

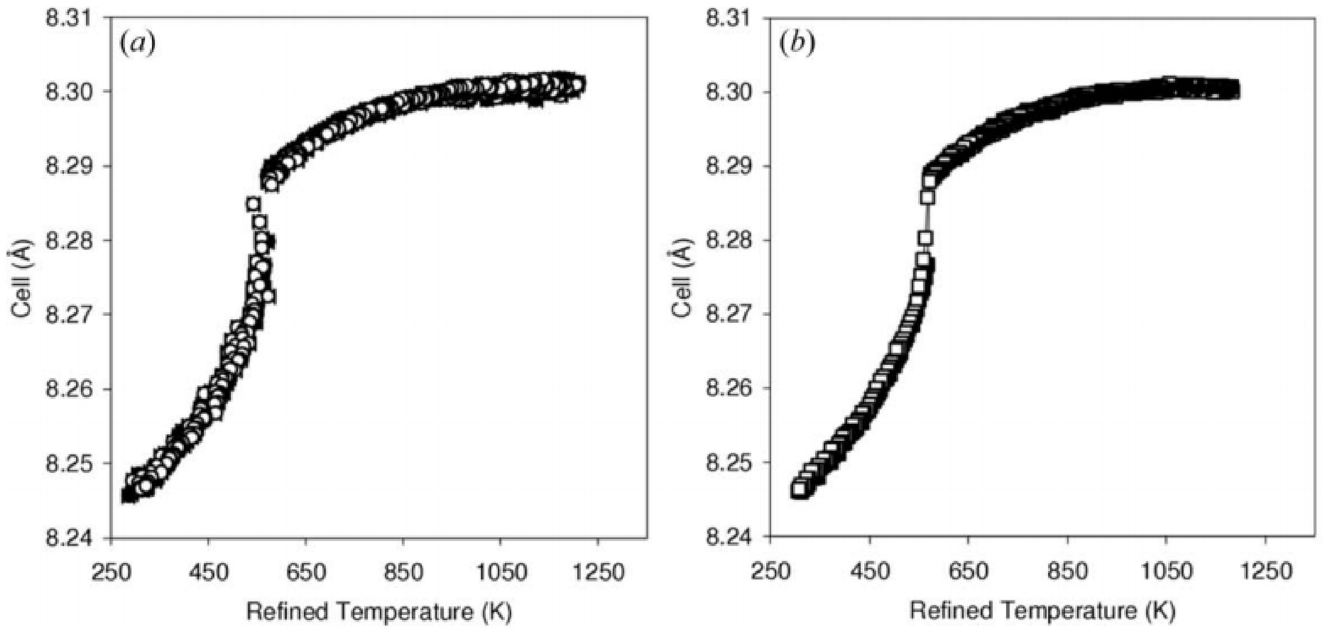
Suggests transformation from 1 component to another. “2 phase”



J. Appl. Cryst. (2007). 40, 87-95

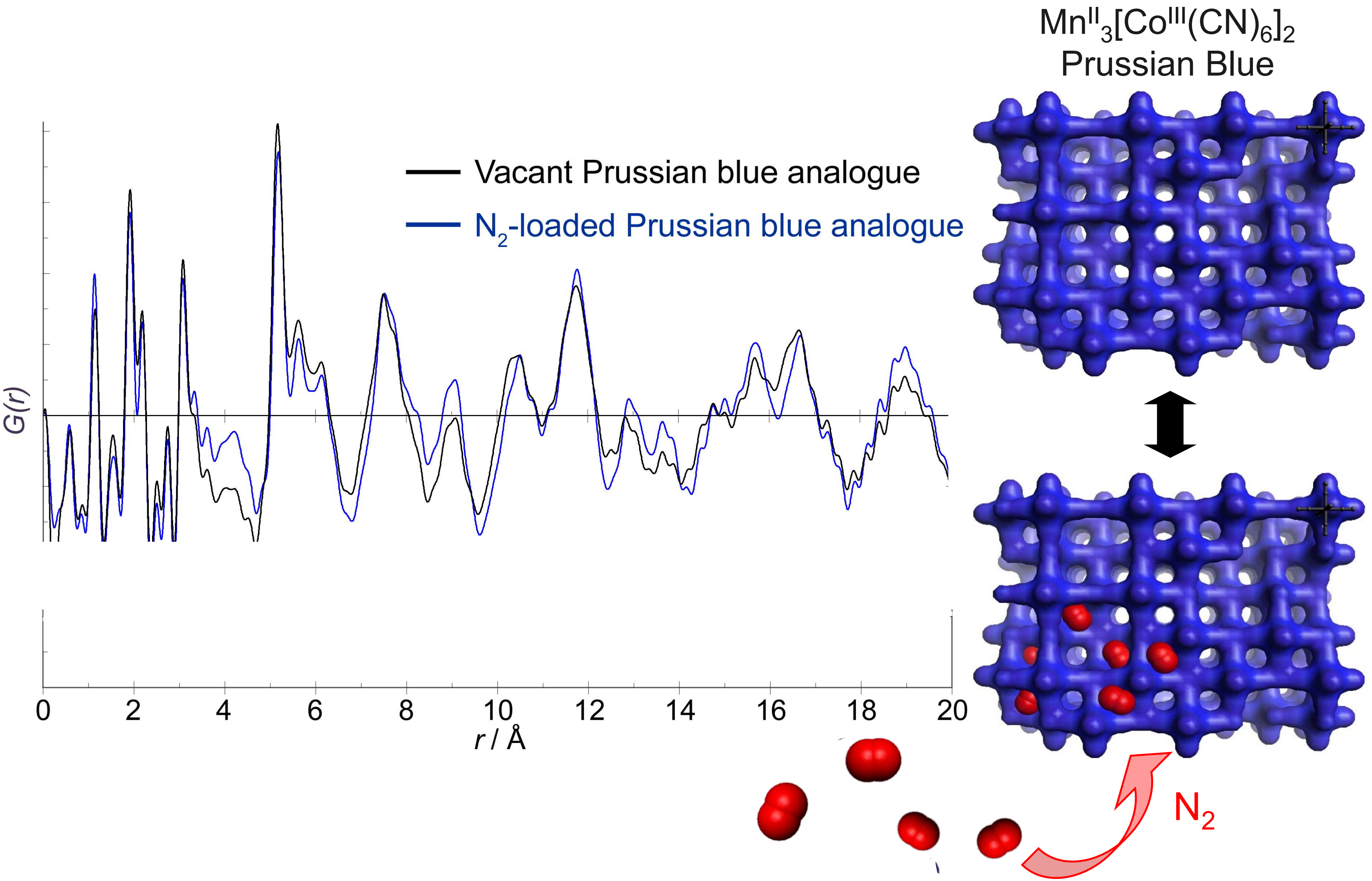
Parametric refinement

- “Surface” refinement using correlated parameters
- E.g. The value of the lattice parameter at T1 is related to that at T2 based on the thermal expansion of the material



J. Am. Chem. Soc. **2005** 11232-11233.

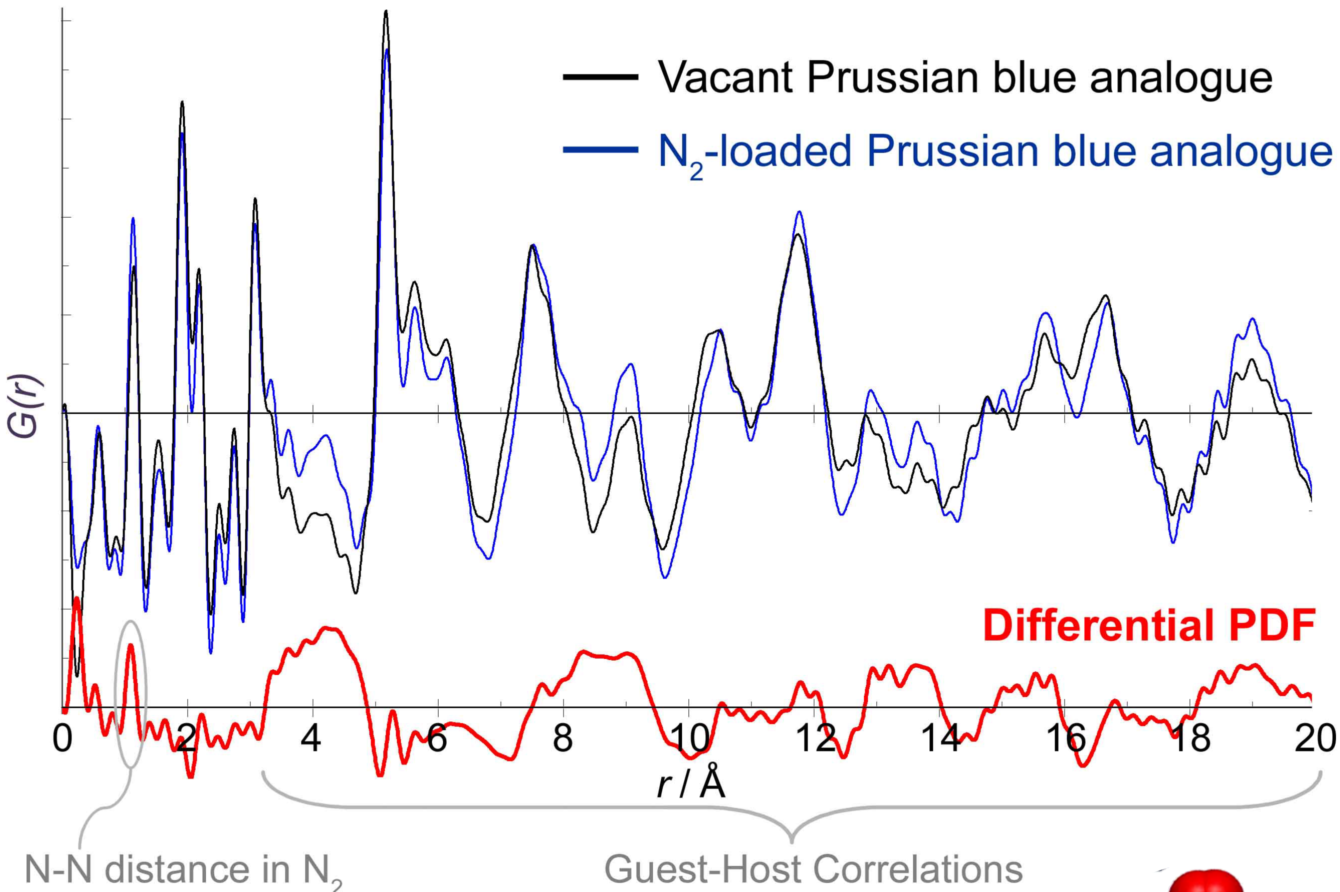
Differential PDF to recover chemical sensitivity

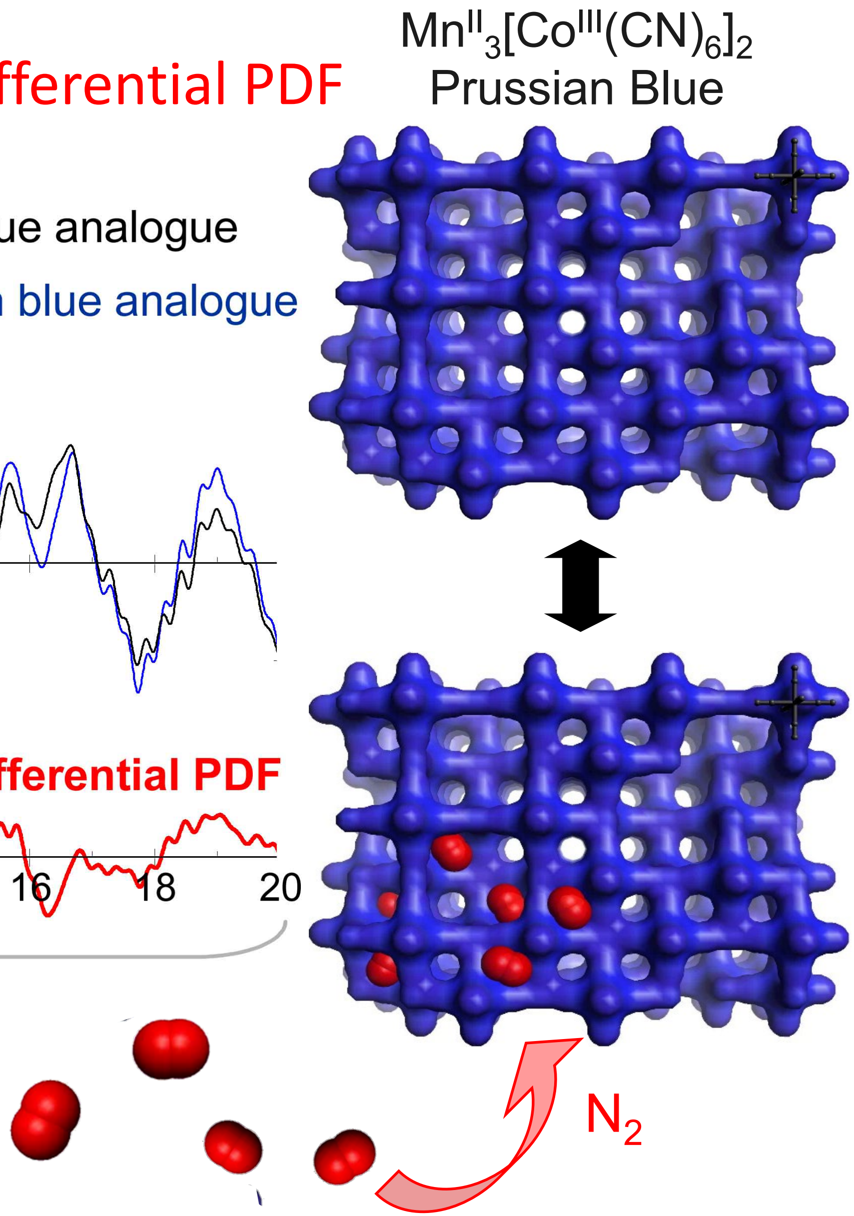


J. Am. Chem. Soc. **2005** 11232-11233.

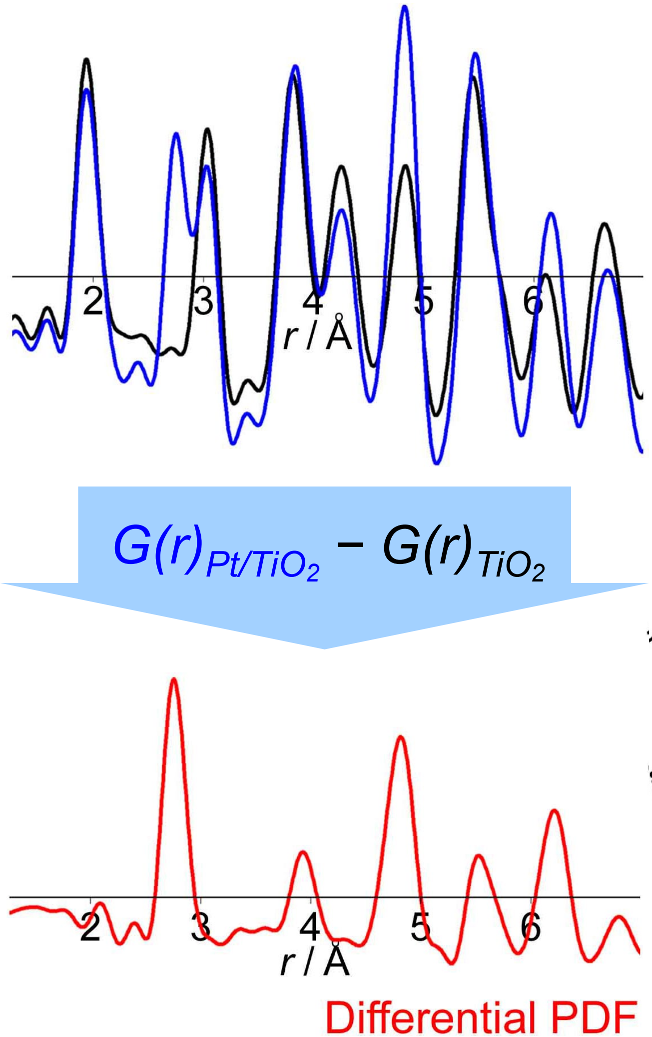
Differential PDF to recover chemical sensitivity

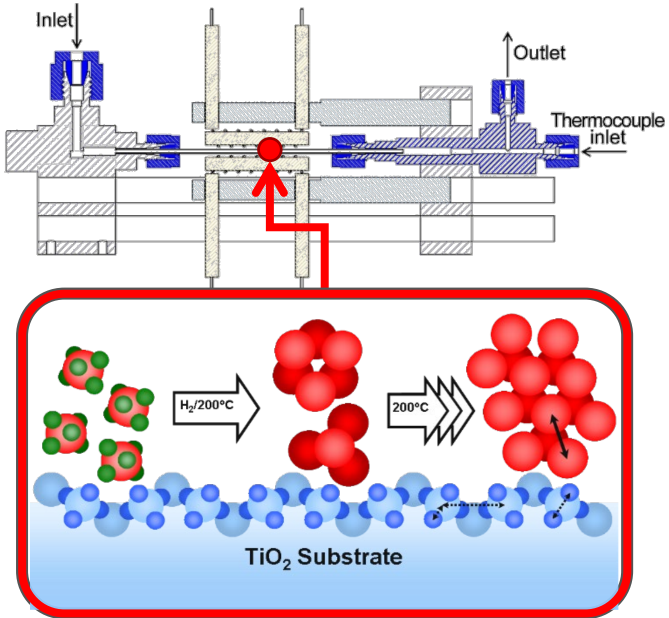
$G(r)_{\text{Prussian Blue}} - G(r)_{\text{Prussian Blue+N2}}$ = Differential PDF

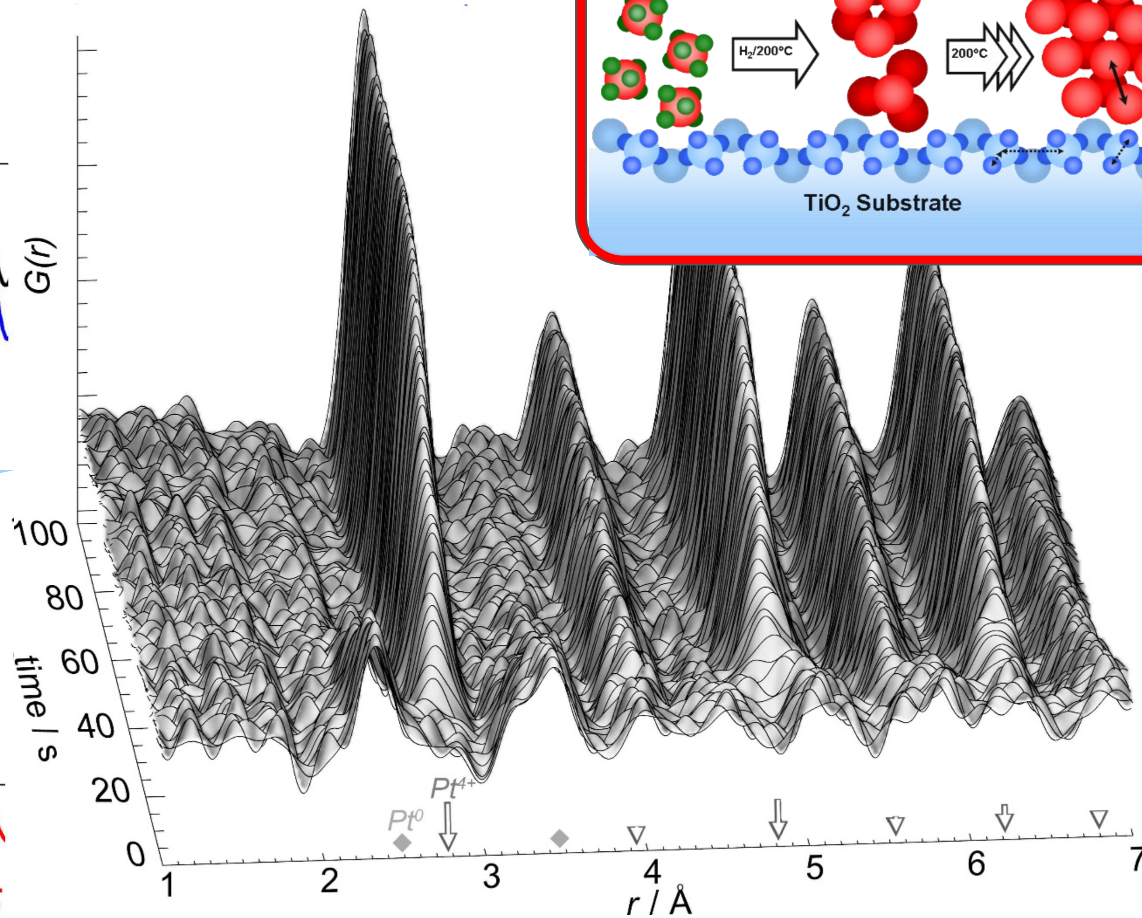




Correlating individual features

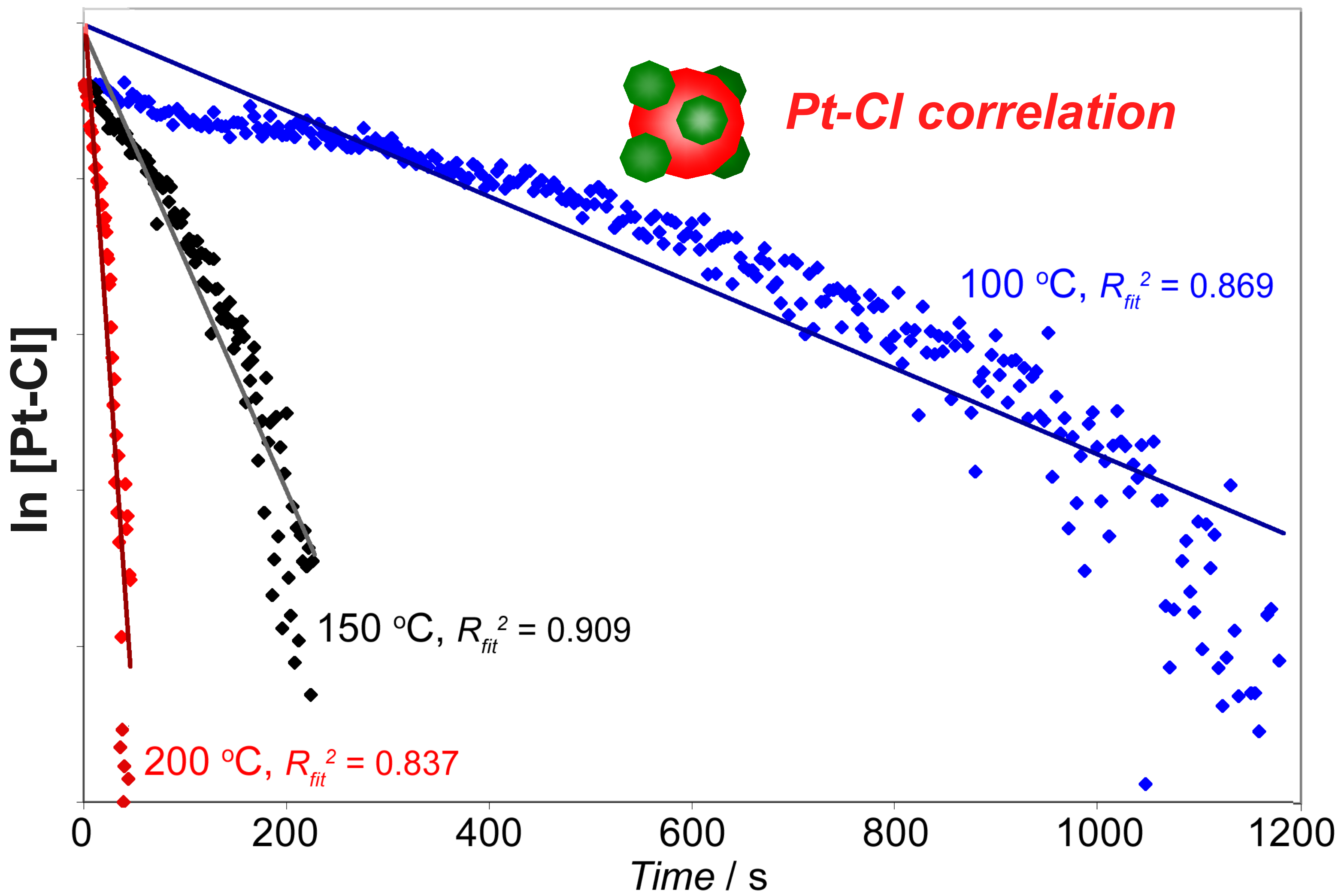




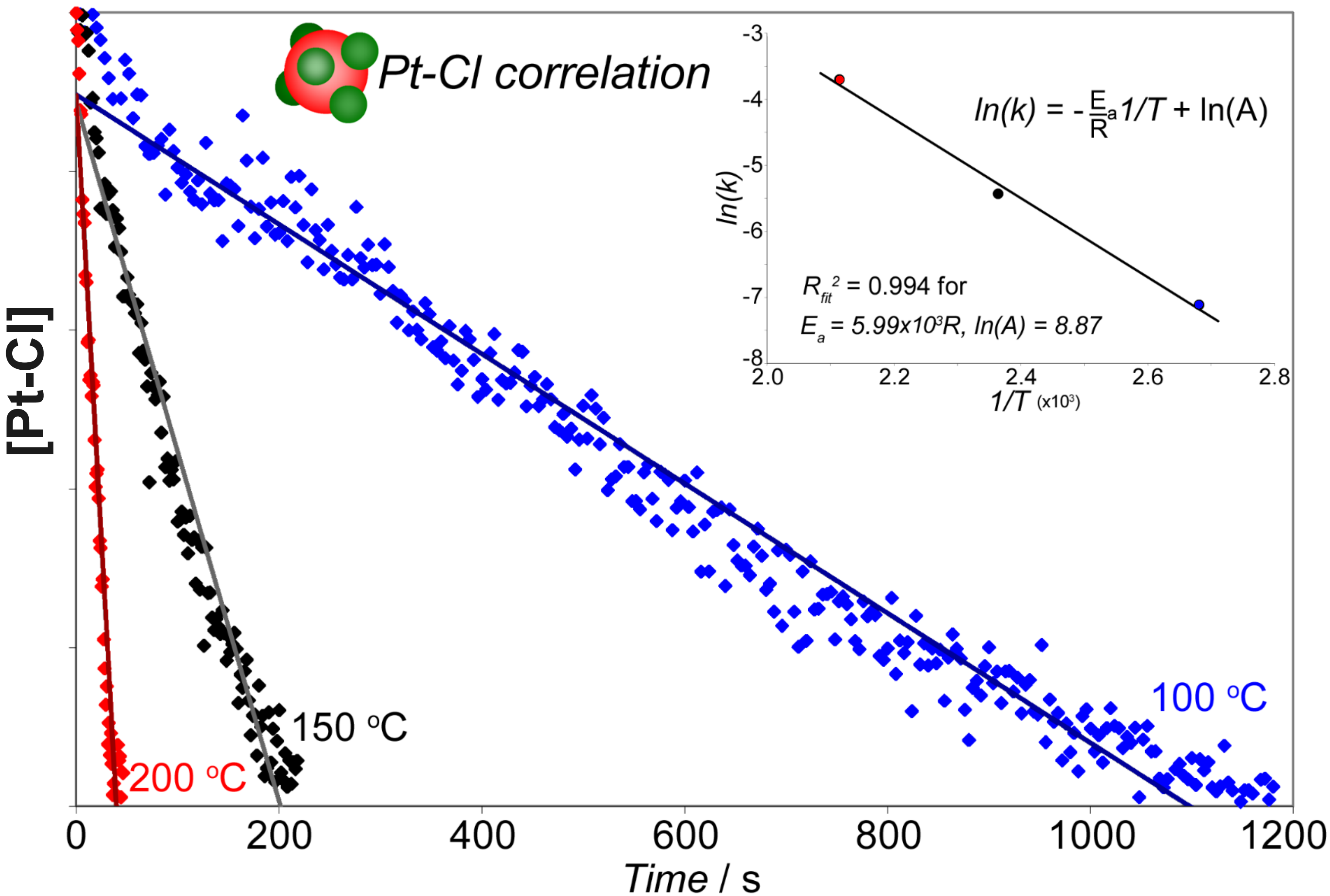


In situ reduction: Pt^{4+} on $TiO_2 \xrightarrow{H_2} Pt^0$

Reaction order: 1st order reduction kinetics ??

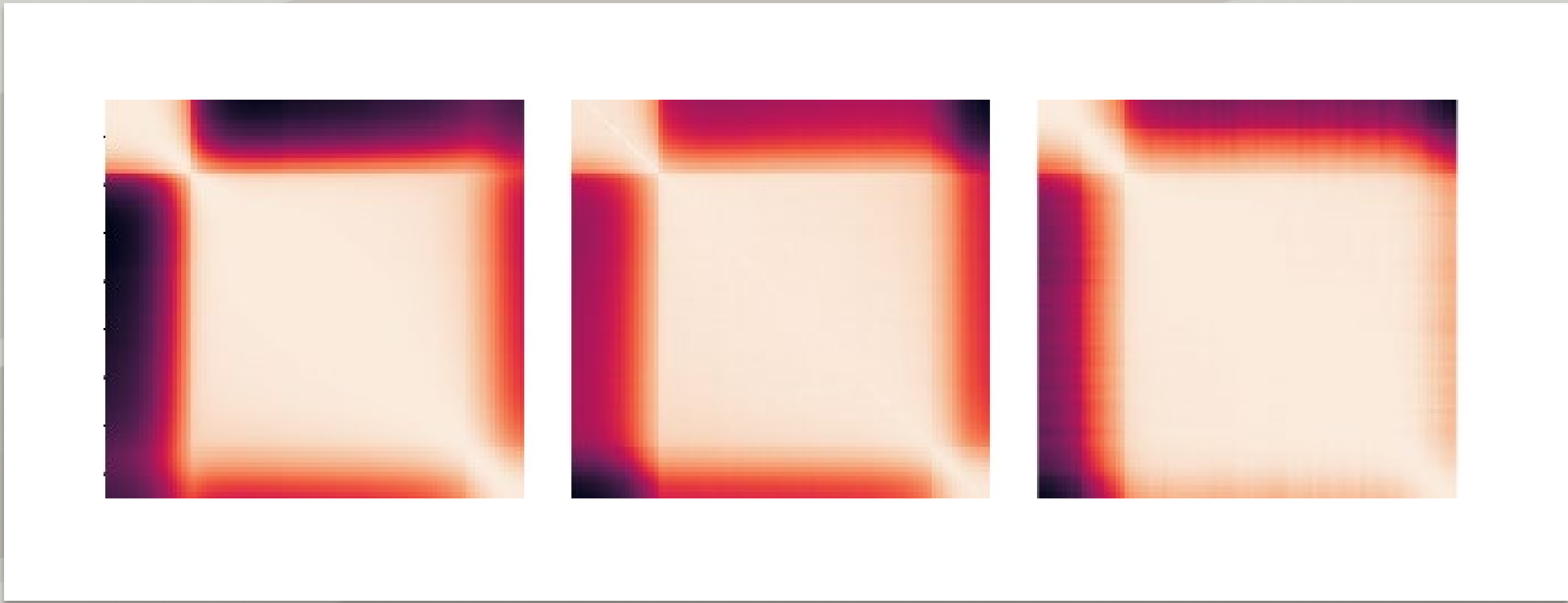


Reaction order: 0^{th} order reduction kinetics



Data Science Tools

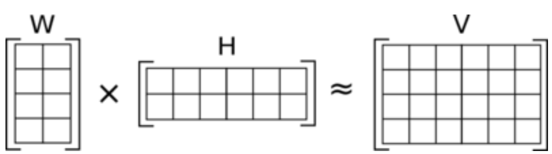
Model & data-type agnostic analysis using blind signal separation, dimensional reduction strategies (NMF,PCA), correlation analyses



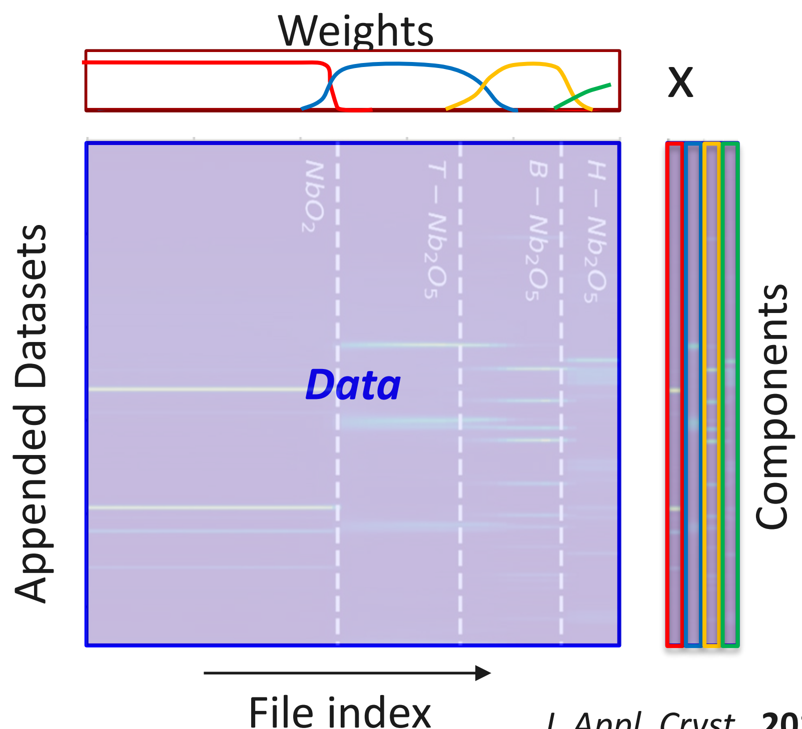
Multivariate analysis for blind signal separation

Dimensional reduction algorithms such as Principal Component Analysis (PCA) & Non-Negative Matrix Factorization (NMF) cluster features that change together *(e.g.)*

This provides model-free, data agnostic approach to separate and quantify distinct "states" or phases of the system.



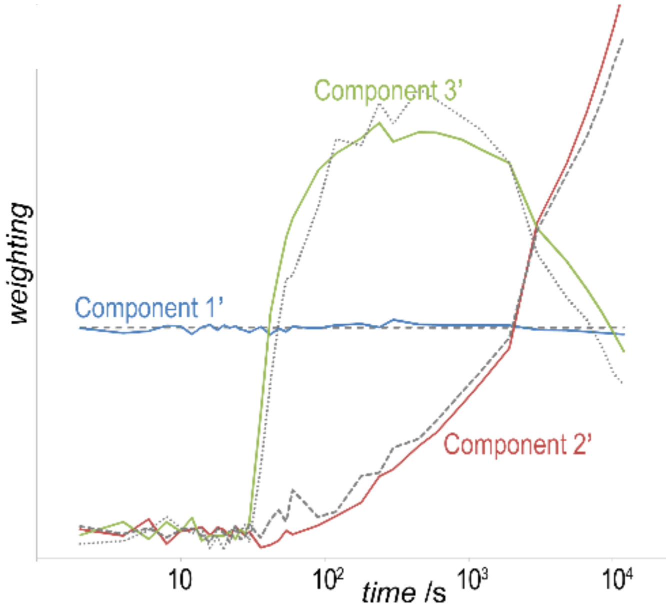
- Visualizes large complex data series in terms of a smaller number of variables
- Expresses data as a linear combination of components



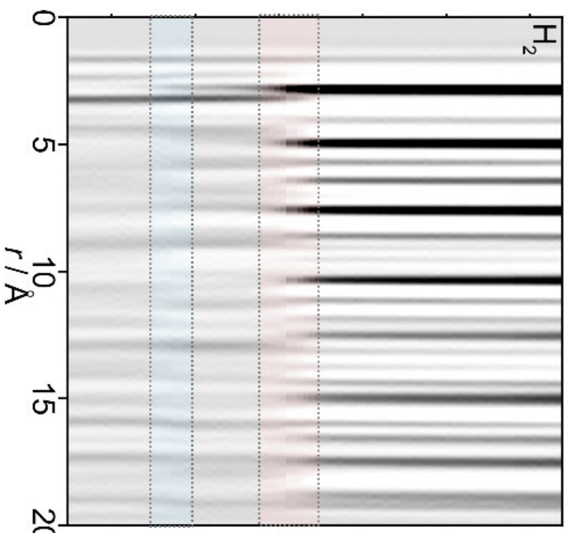
J. Appl. Cryst, **2015**, 1619-1626
J. Appl. Cryst. **2020** 662-670

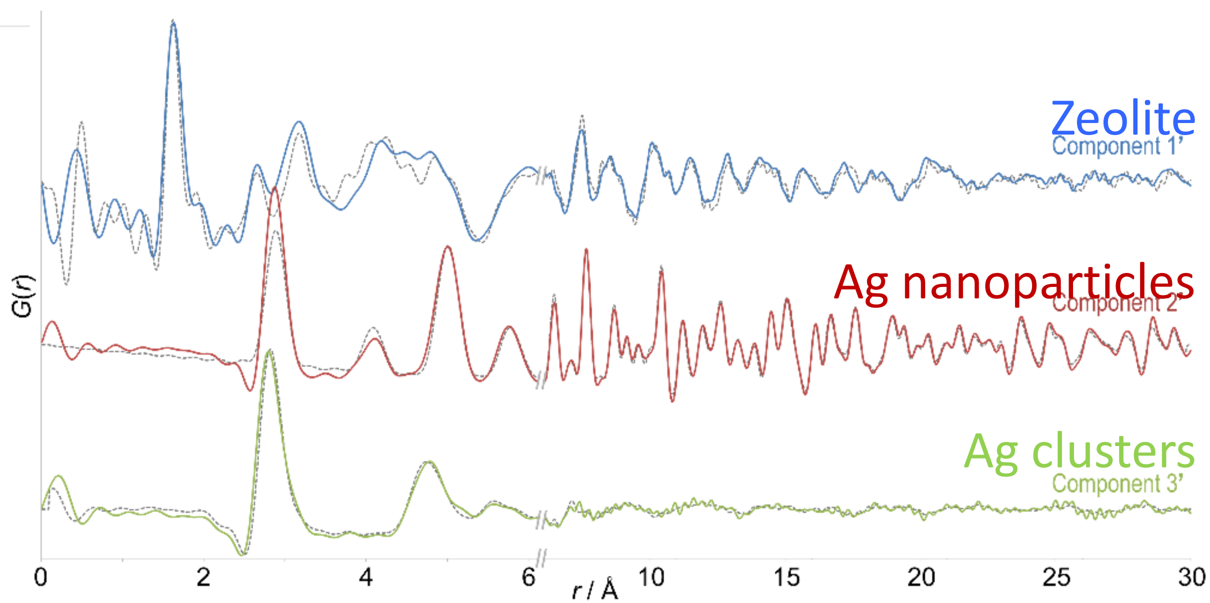
J. Appl. Crystallogr., **2015**, 1619-1626

Multivariate analysis gives recognizable components

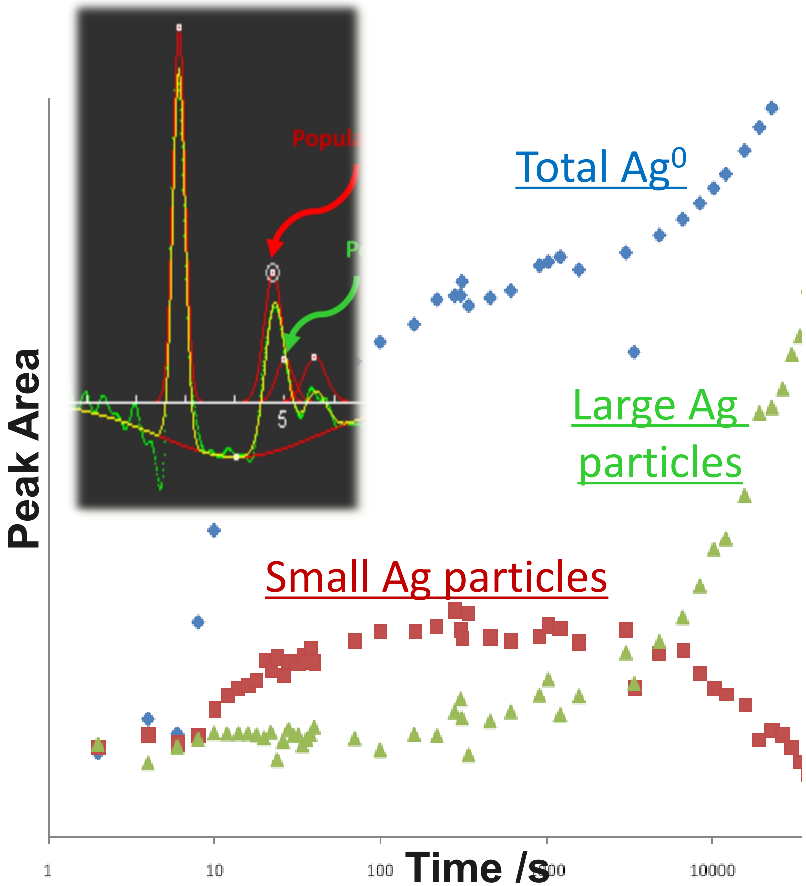


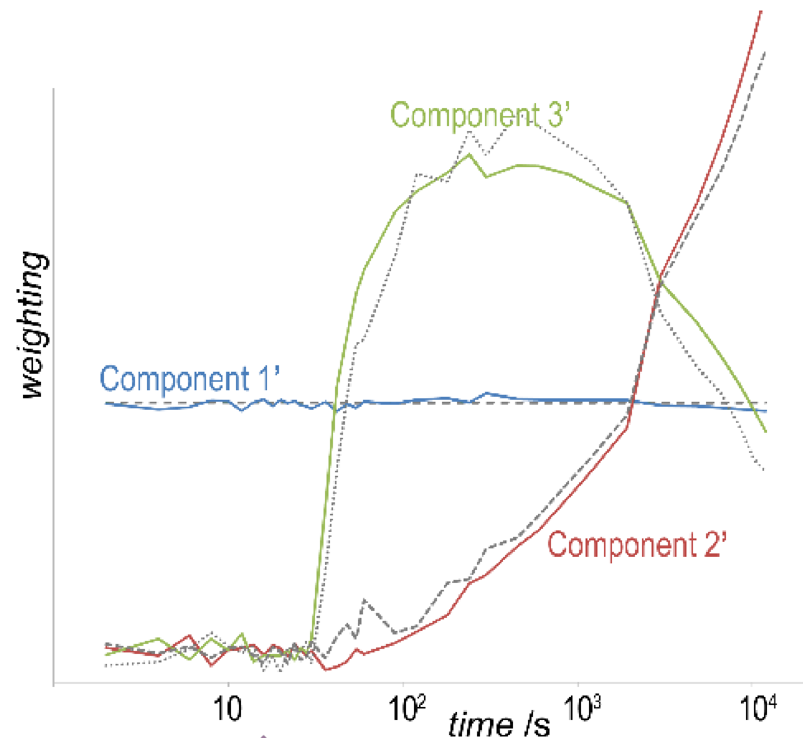
Reconstructed components reproduce PDFs for phases and quantitative phase abundances determined through conventional analysis

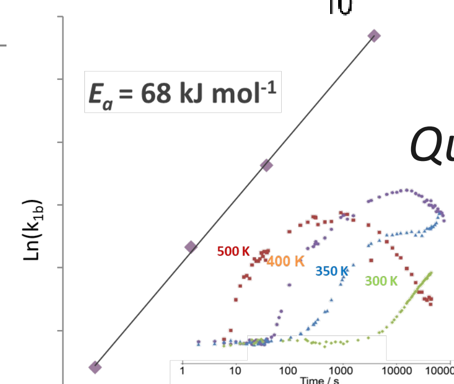




Reaction profiles match conventional analyses







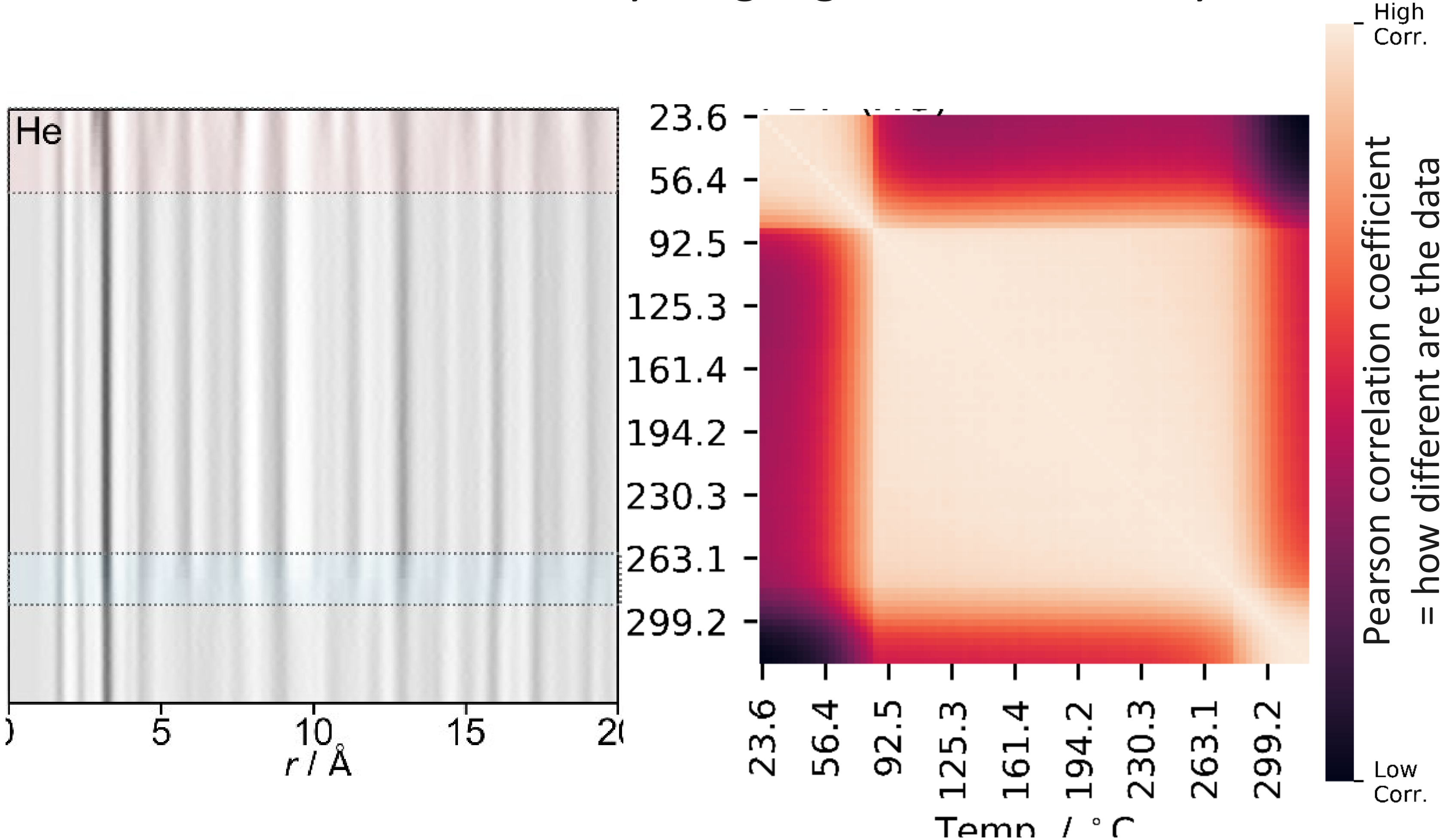
Quantify kinetic parameters
e.g. activation energy

J. Phys. Chem. Lett. **2011**, 2742–2746

Chem. Sci., **2021**, 12, 13836-1384

Correlation analysis

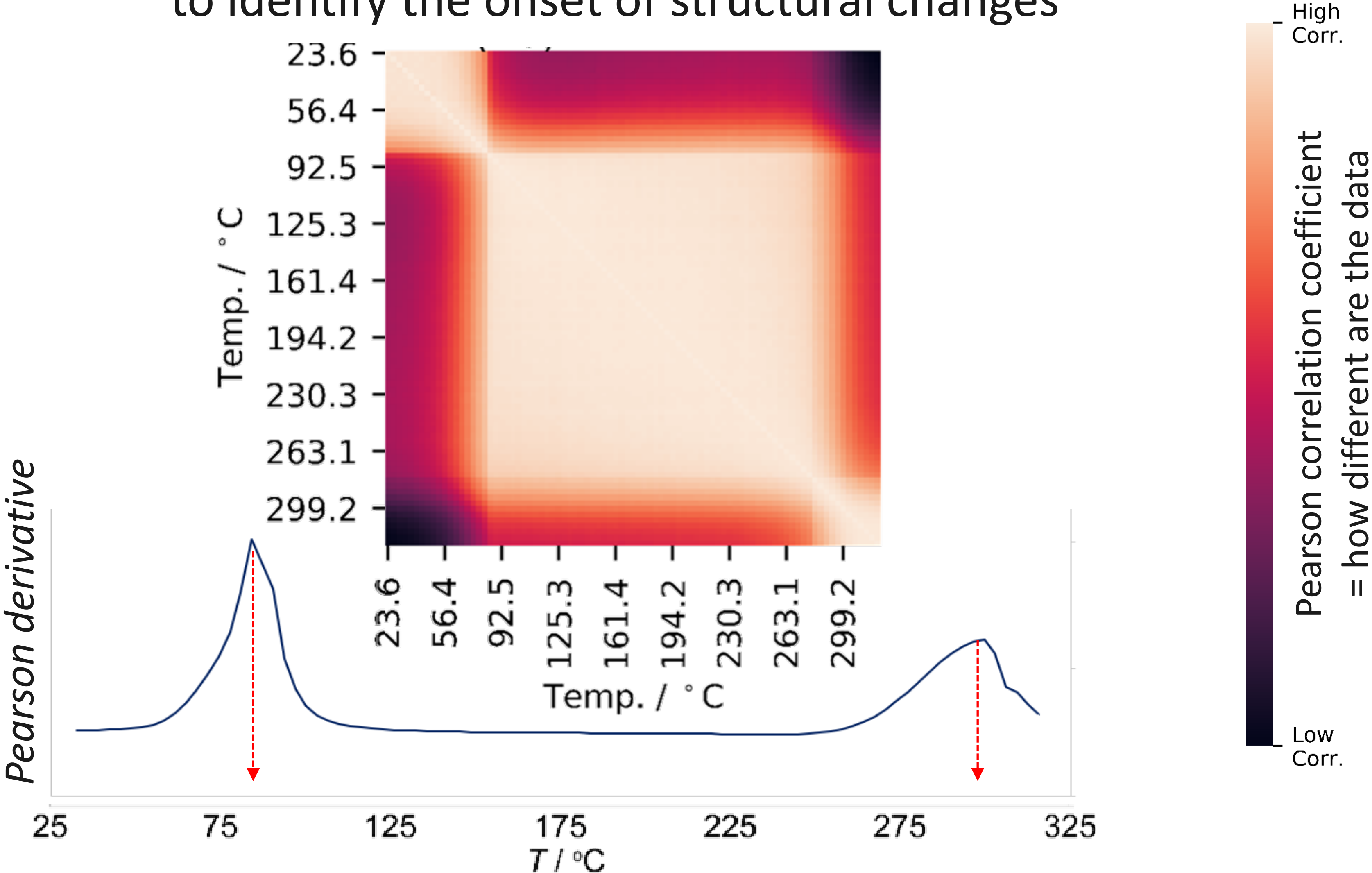
Pearson correlation analyses gauges data similarity



Chem. Sci., **2021**, 12, 13836-1384

Correlation analysis

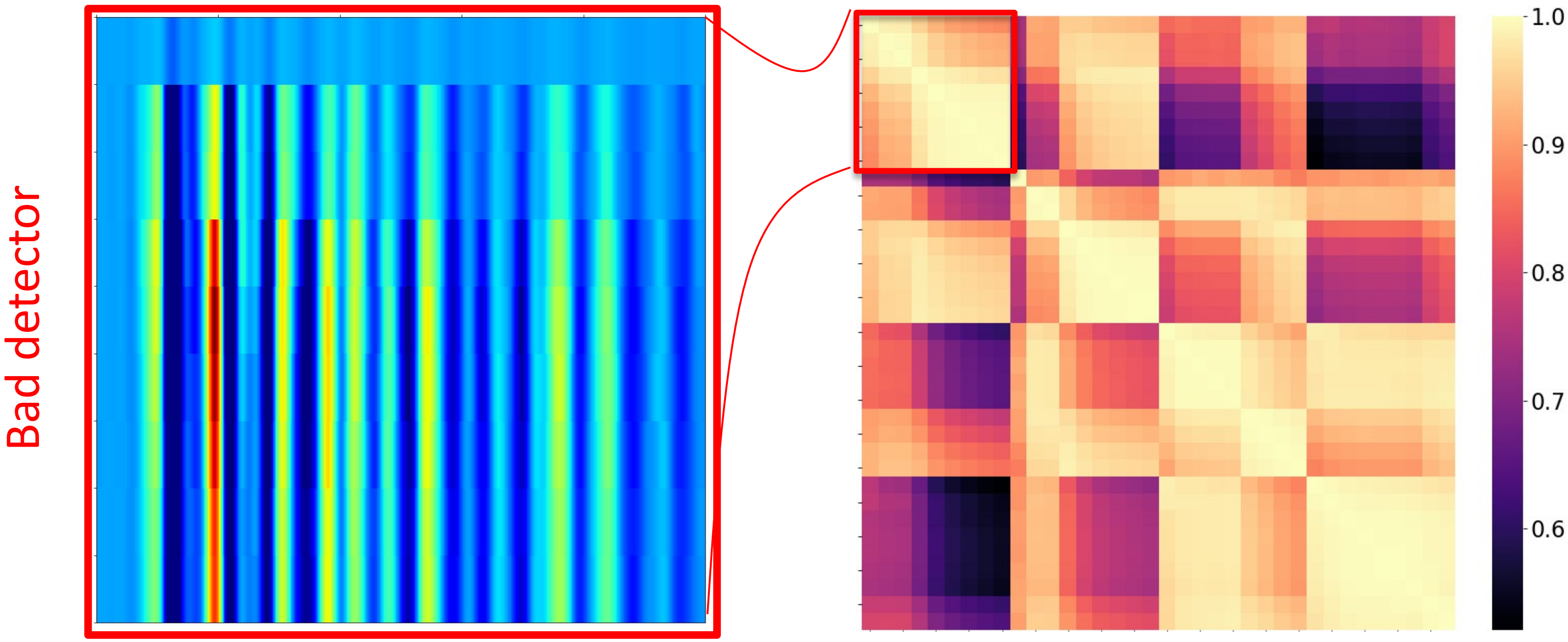
Pearson derivative with respect to experimental variable to identify the onset of structural changes



Life support for imperfect data

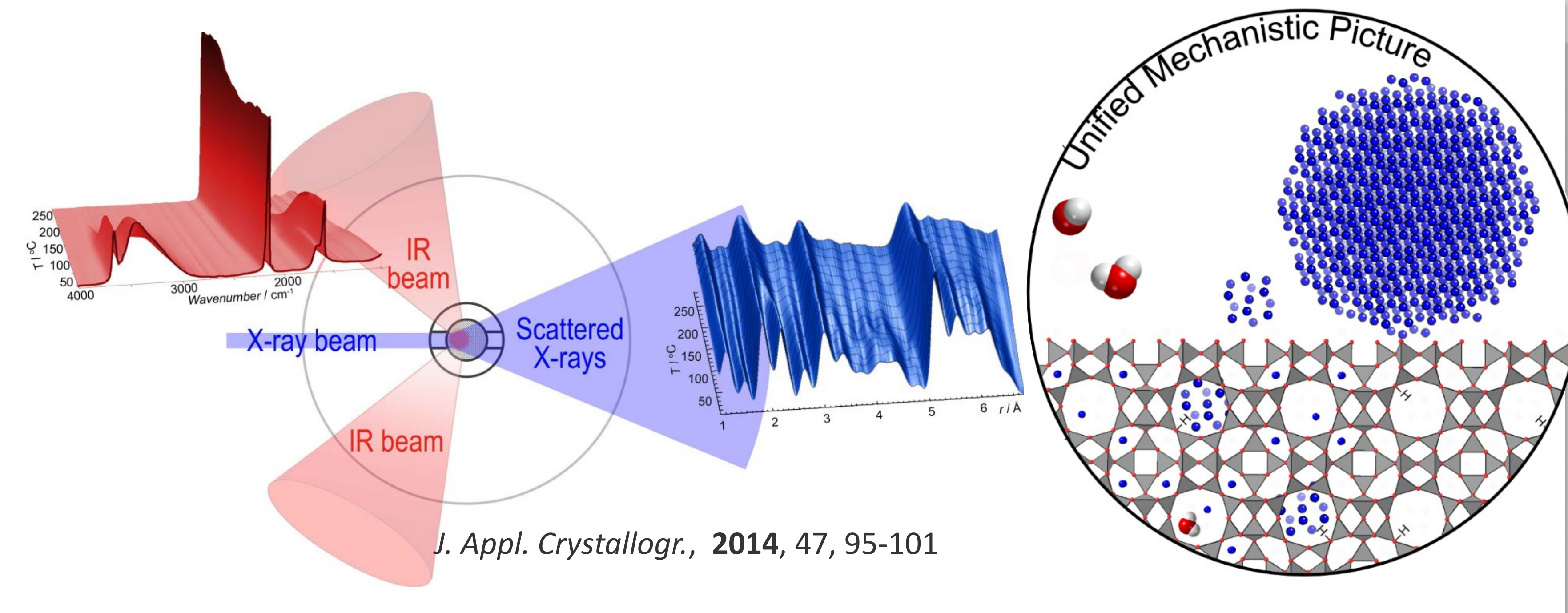
Can always using Pearson analysis to gain insights into
the evolution of an in situ/operando experiment
even if there are problems with the background corrections etc.

But without the constraints of a model,
its up to you to interpret the output appropriately



Multimodal measurements

Complementary insights into different aspects of the system:
The X-ray signal is dominated by high Z species
infra-red spectroscopy is sensitive surface species (H_2O/OH)

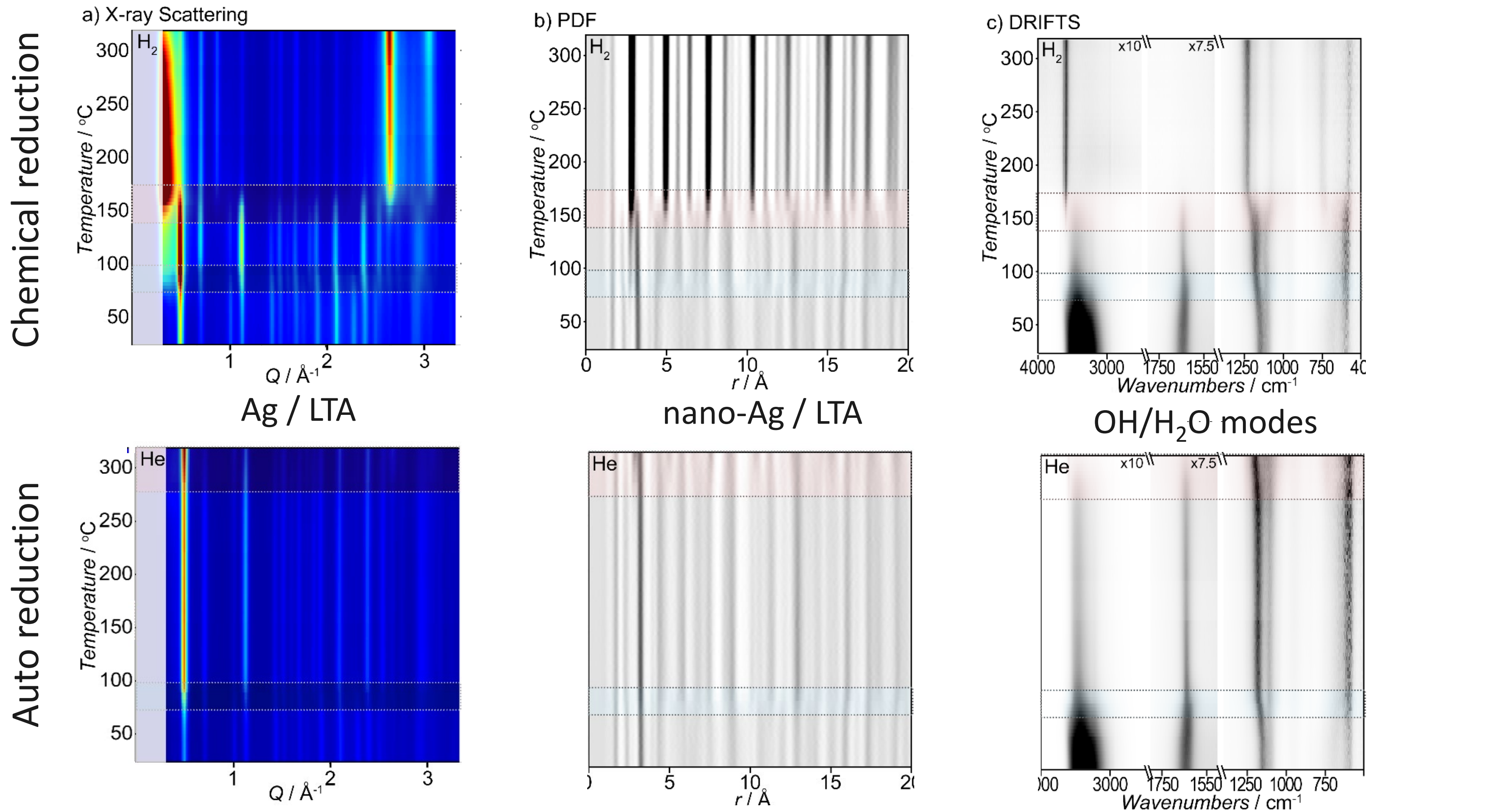


J. Appl. Crystallogr., **2014**, 47, 95-101

Chem. Sci., **2021**, 12, 13836-1384

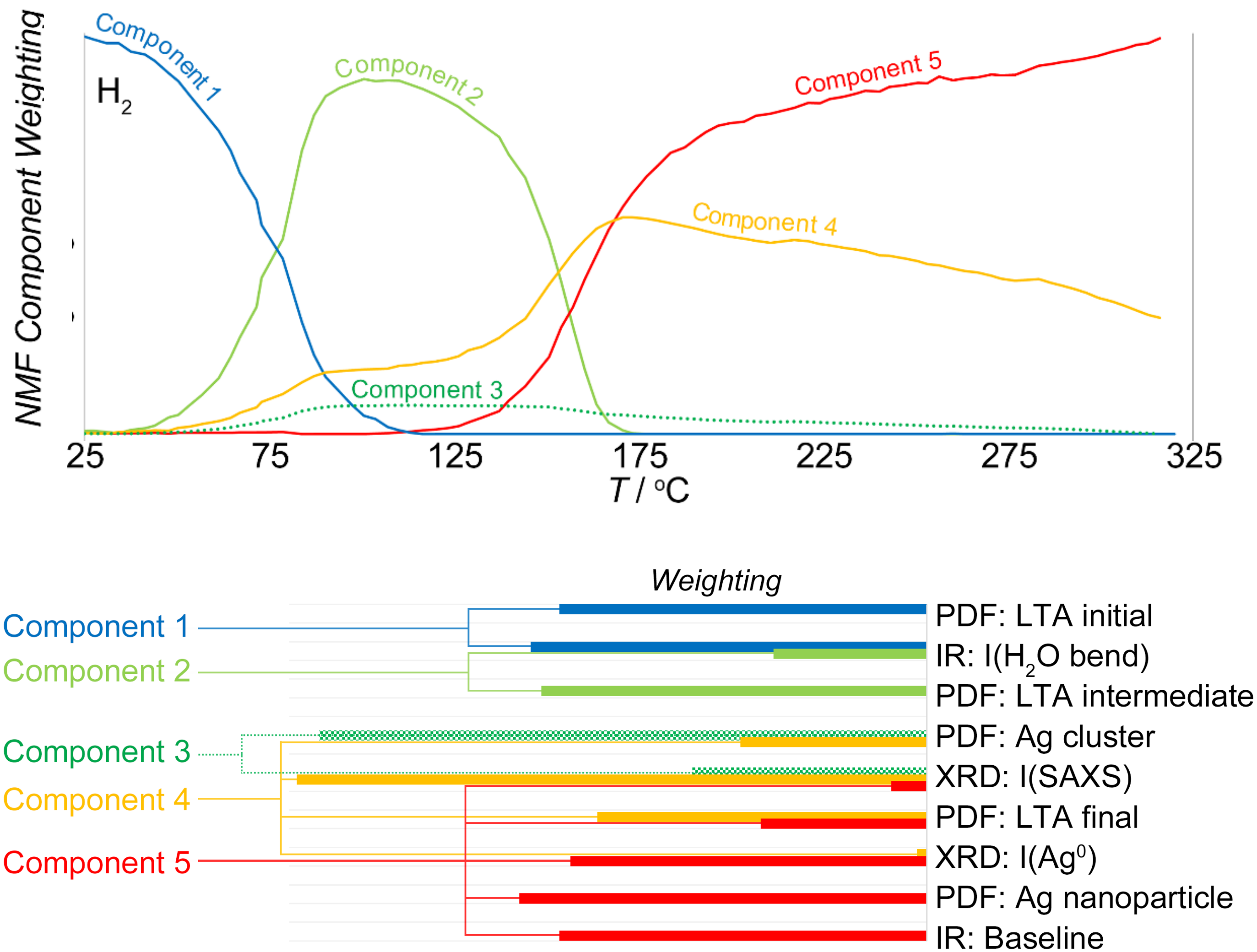
Multimodal measurements = data overload

All the information is collected, but the
volume & variety of data can be challenging to interpret



Chem. Sci., **2021**, 12, 13836-1384

Use NMF to describe 5 reaction states

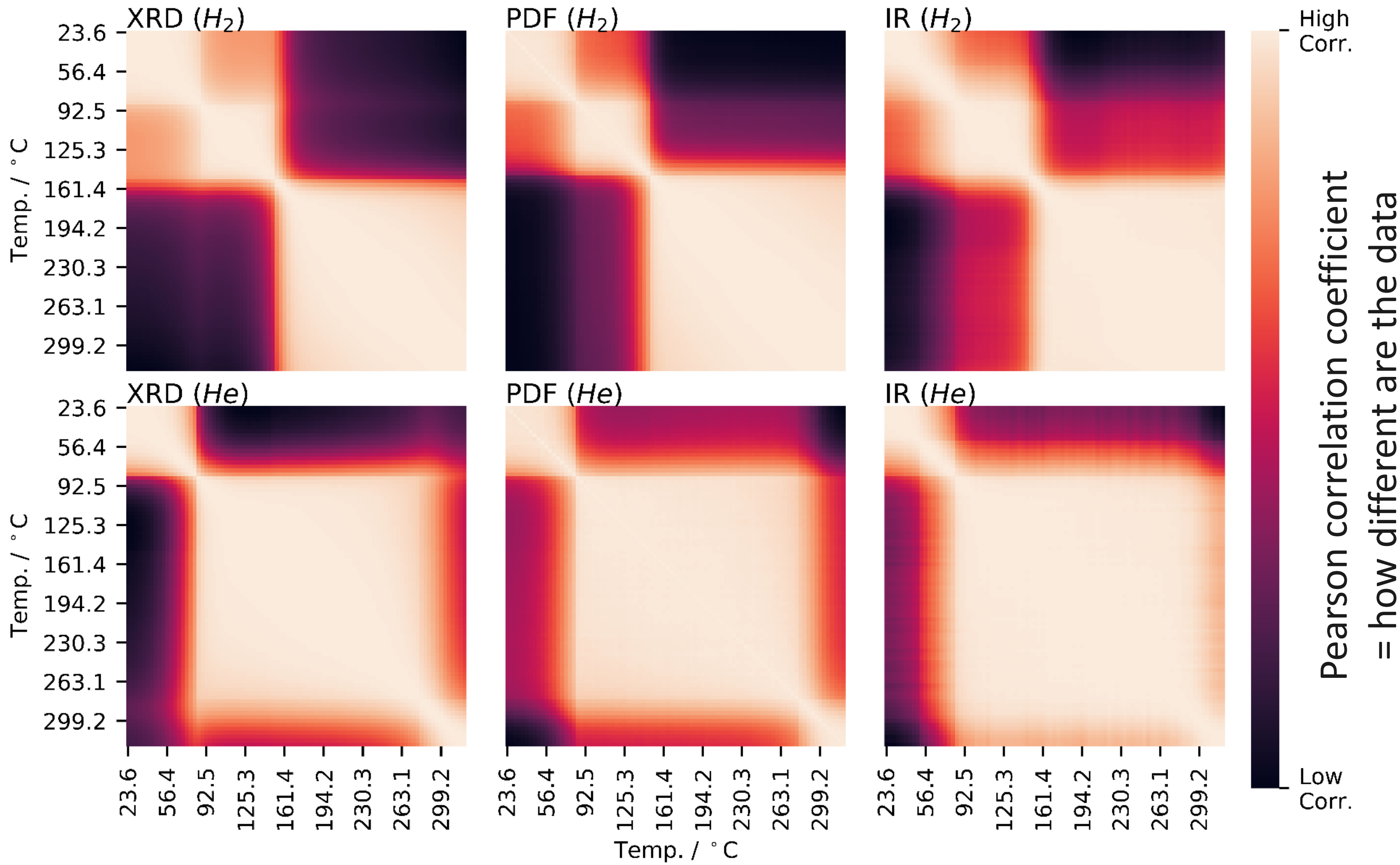


Chem. Sci., **2021**, 12, 13836-1384

Pearson Correlation analysis is data agnostic

The first transition is independent of atmosphere. Dehydration

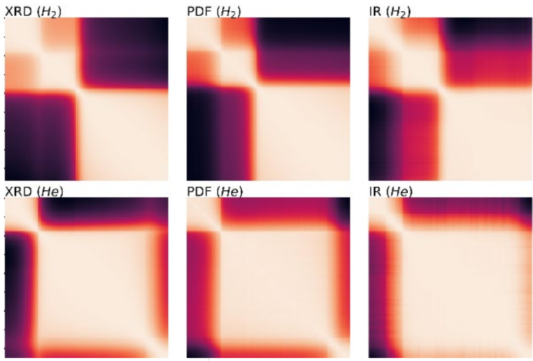
The second transition is shifted to higher T under He

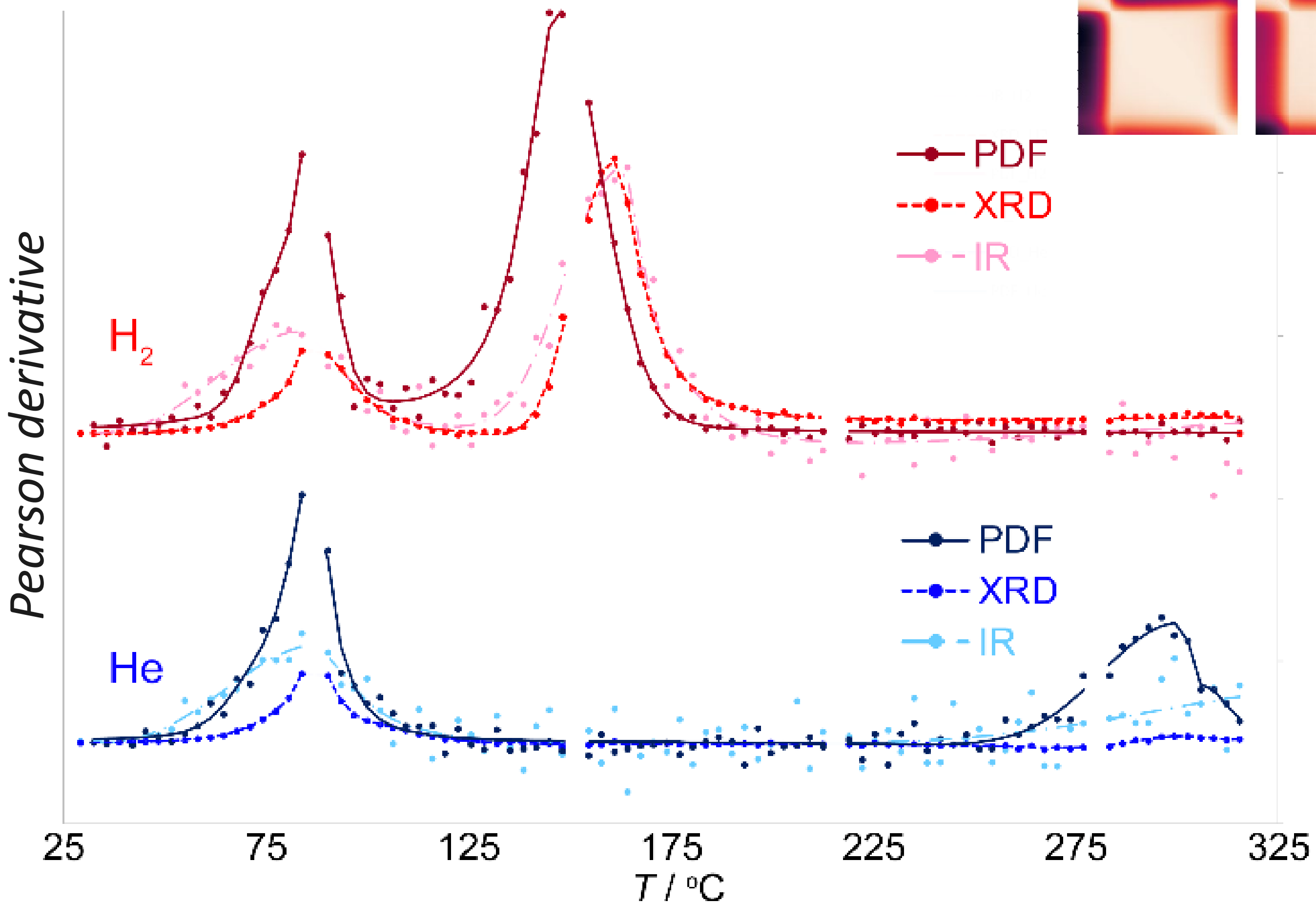


Chem. Sci., **2021**, 12, 13836-1384

Pearson derivative shows which changes drive process

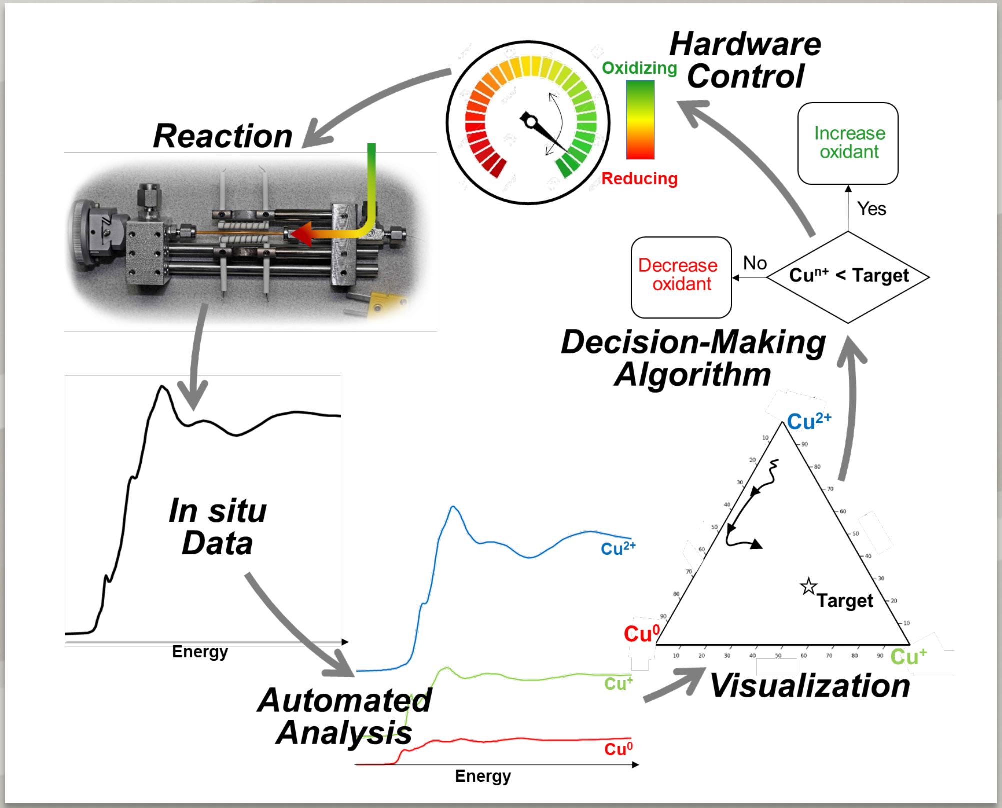
IR changes precede, local changes precede, long range crystallographic changes





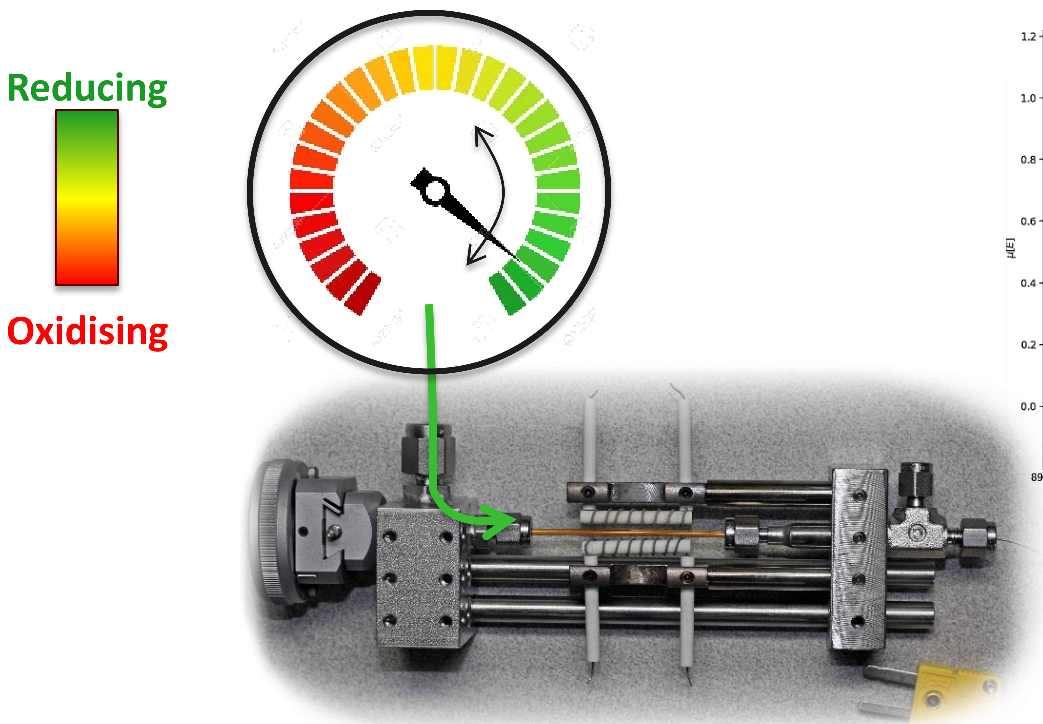
Active Experiment Control

Autonomously control sample state based on real-time feedback from in situ measurement

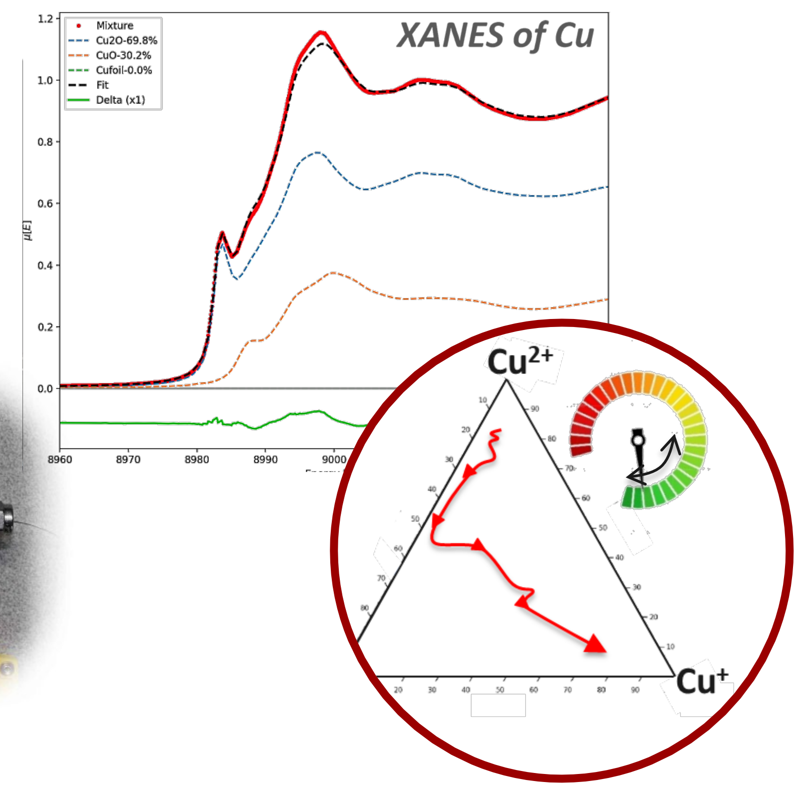


Steering reactions in real-time

We can target a specific oxidation state (and defect concentration) by evaluating the oxidation state distribution *during the reaction* and then changing the oxidising/reducing gas mix



For Cu-supported on γ-Al_2O_3 targeting Cu^{1+}

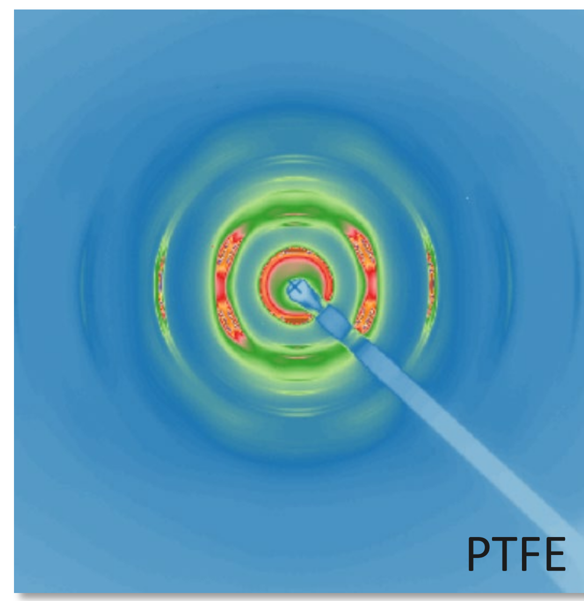


Where do I start?

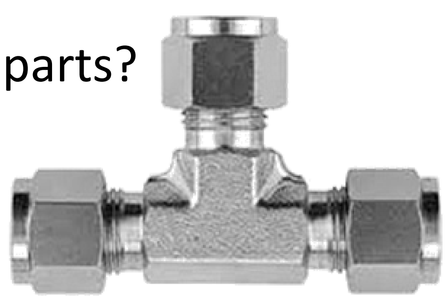
Materials? Machining?

Materials considerations

- X-ray windows/sample holder
  - **Good:** Kapton, sigradur (glassy carbon), glass
  - **Maybe:** Diamond
  - **Avoid:** PTFE, metal foils, sapphire, Si crystal
  - Consider: Rigidity, uniformity, thickness

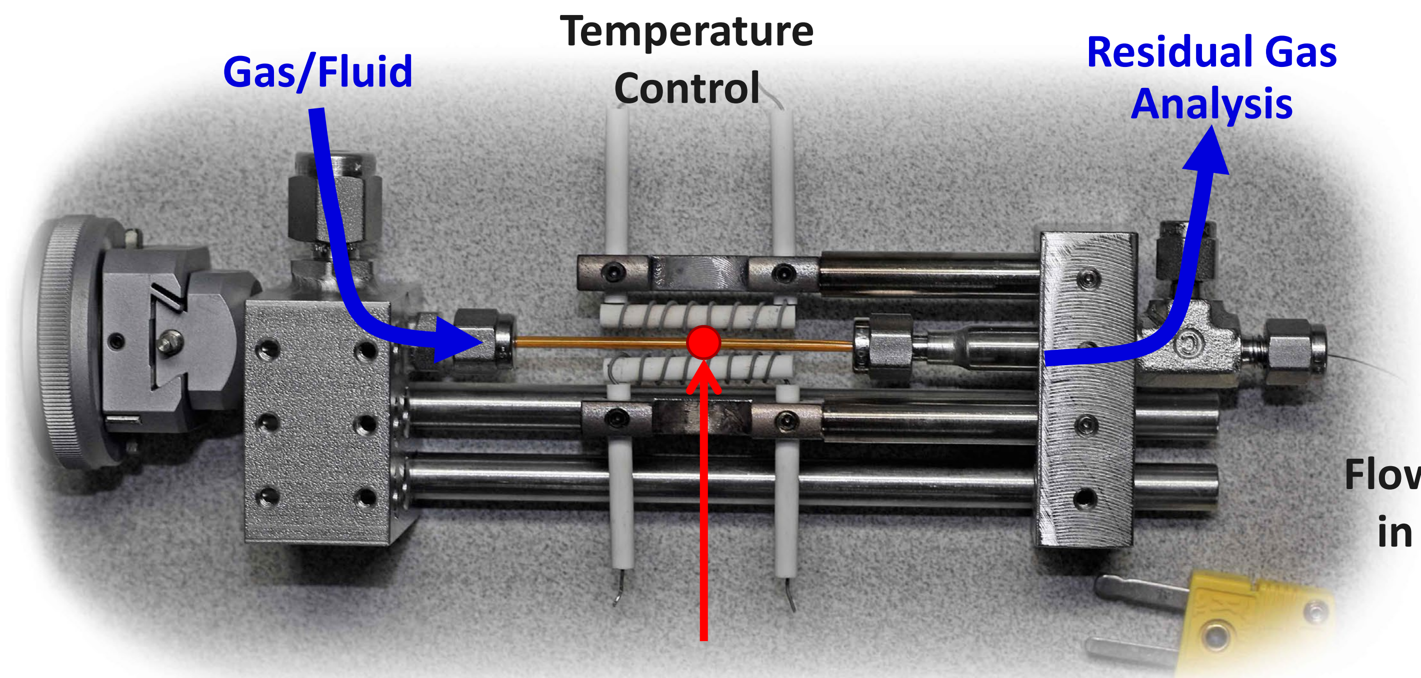


- Chemical compatibility
  - Teflon, 316 series stainless steel,
- Thermal conductivity/stability: Al, SS, Cu?
- Electrical conductivity: Sigradur (glassy carbon)
- Can you adapt commercial parts?

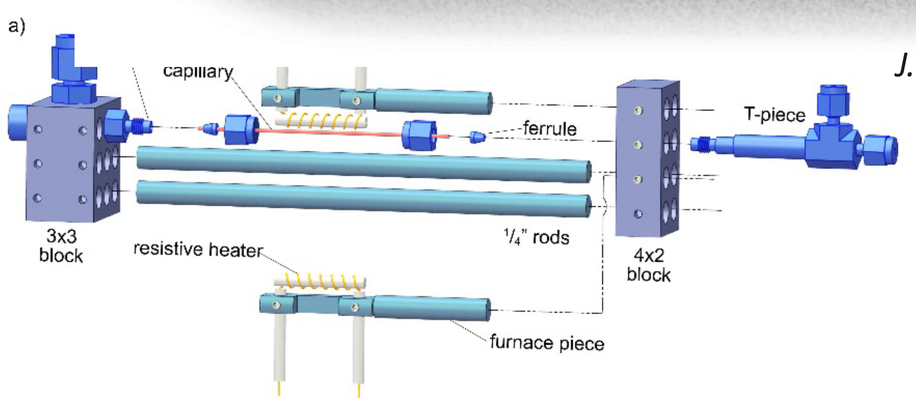


Example: The flow-cell/furnace

A versatile sample environment to control chemistry and temperature

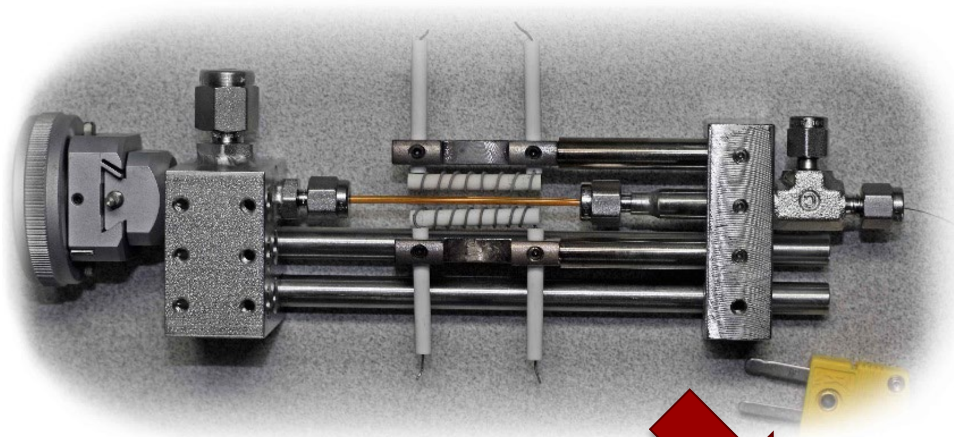


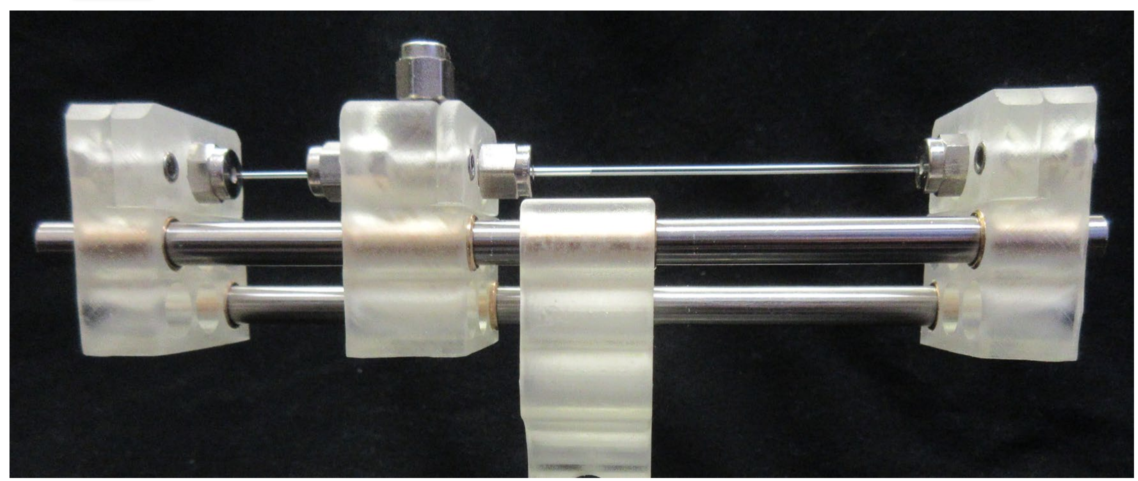
Flow cell/Furnace
in situ Reactor



J. Appl. Crystallogr. **2008** 822

3D printing to adapt commercial parts

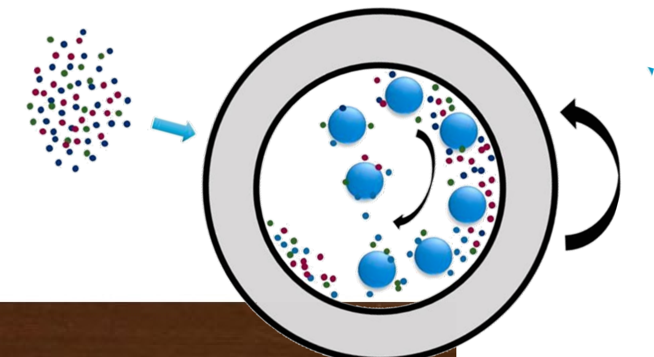




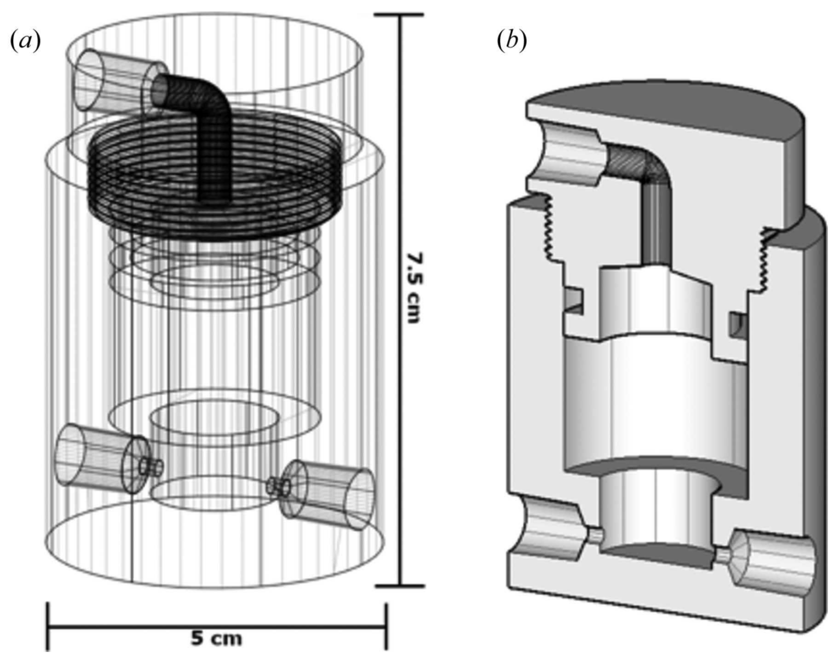
3D printing solutions

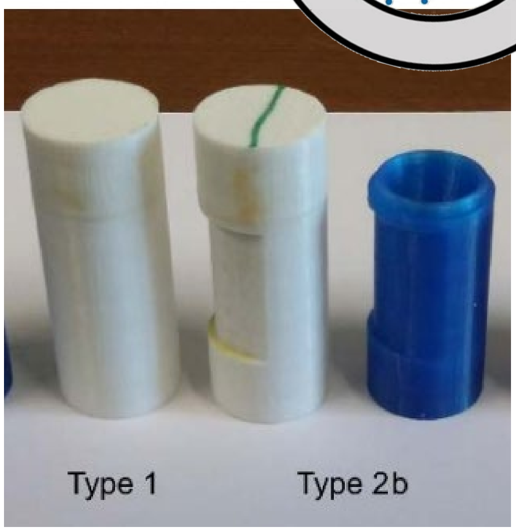
- Customized complex shapes
- Inexpensive fabrication
- Cheap aka Disposable

Ball milling



Solution Mixers





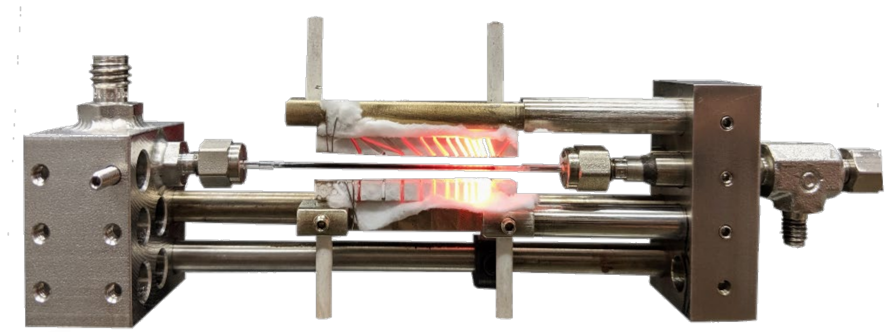
Acta Cryst. **2019**. A75, 758-765

J. Appl. Cryst. **2017**. 50, 994-999

3D printed ceramic for high/gradient temperature

We 3D print a high temperature ceramic template to reproducibly generate a continuously varying wire density

By controlling the winding density of the heater wire, we can control the spatial distribution of temperature across the sample.

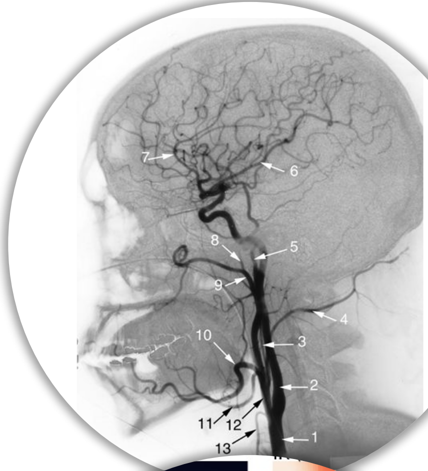


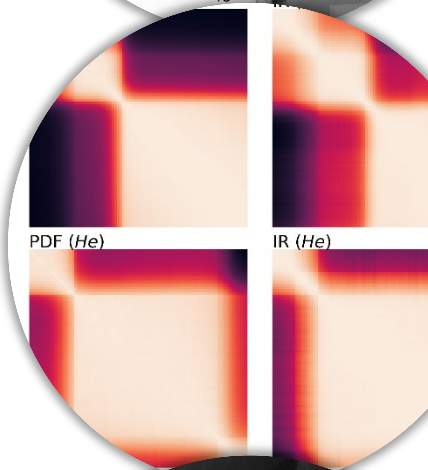
Accelerates variable temperature studies

J. Appl. Cryst. **2020**. 53, 662-670

Summary

- In situ and operando measurements allow us to understand the relationship between structure and function/reactivity
- New opportunities for extracting insight from in situ data
- Anything is possible. Not everything is easy.
- Characterize your characterization tool with a known system BEFORE you use it to study your samples
- Need help? Ask your friendly beamline scientist or reach out: karena.chapman@stonybrook.edu





Questions? Resources

- Contact me: karena.chapman@stonybrook.edu

- Methodology journals *e.g. Journal of Applied Crystallography., J Synchrotron Radiation*

- Ask your friendly beamline scientist