Argonne NATIONAL LABORATORY

... for a brighter future

U.S. Department of Energy

UChicago ▶ Argonne LLC

Office of Science U.S. DEPARTMENT OF ENERGY

A U.S. Department of Energy laboratory managed by UChicago Argonne, LLC

In-Situ Pair Distribution Function Measurements

Peter J. Chupas

Chemistry, Environmental, and Polymer Science Group
X-ray Science Division
Argonne National Laboratory

Talk Overview

(1) PDF Instrumentation (at the APS)

(2) ”Time Resolved” Measurements

(3) Measurements requiring high sensitivity
(e.g.. seeing hydrogen with X-rays)

(4) New applications

(5) Potential instrumental developments

A brief history of X-ray PDF analysis

1st PDF

Direct methods

Rietveld methods

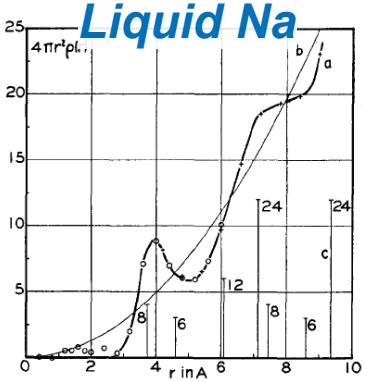
Computers

Synchrotrons & Spallation Sources

HEX+Area Detectors

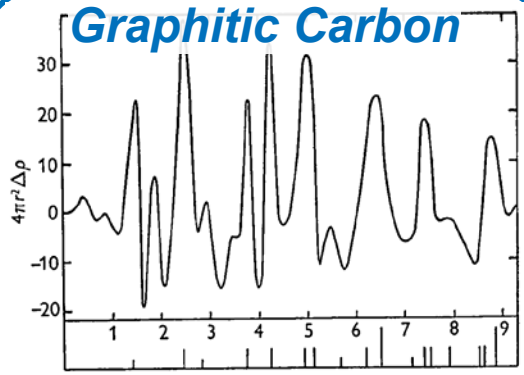
1930 1940 1950 1960 1970 1980 1990 2000

Liquid Na



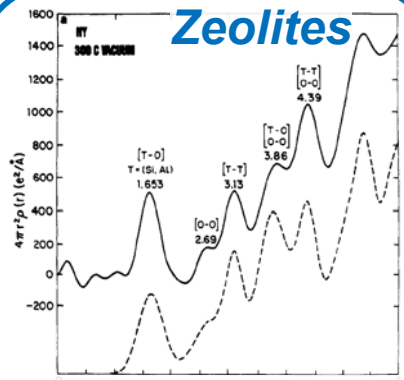
Tarasov & Warren *J.Chem.Phys.*(1936)

Graphitic Carbon



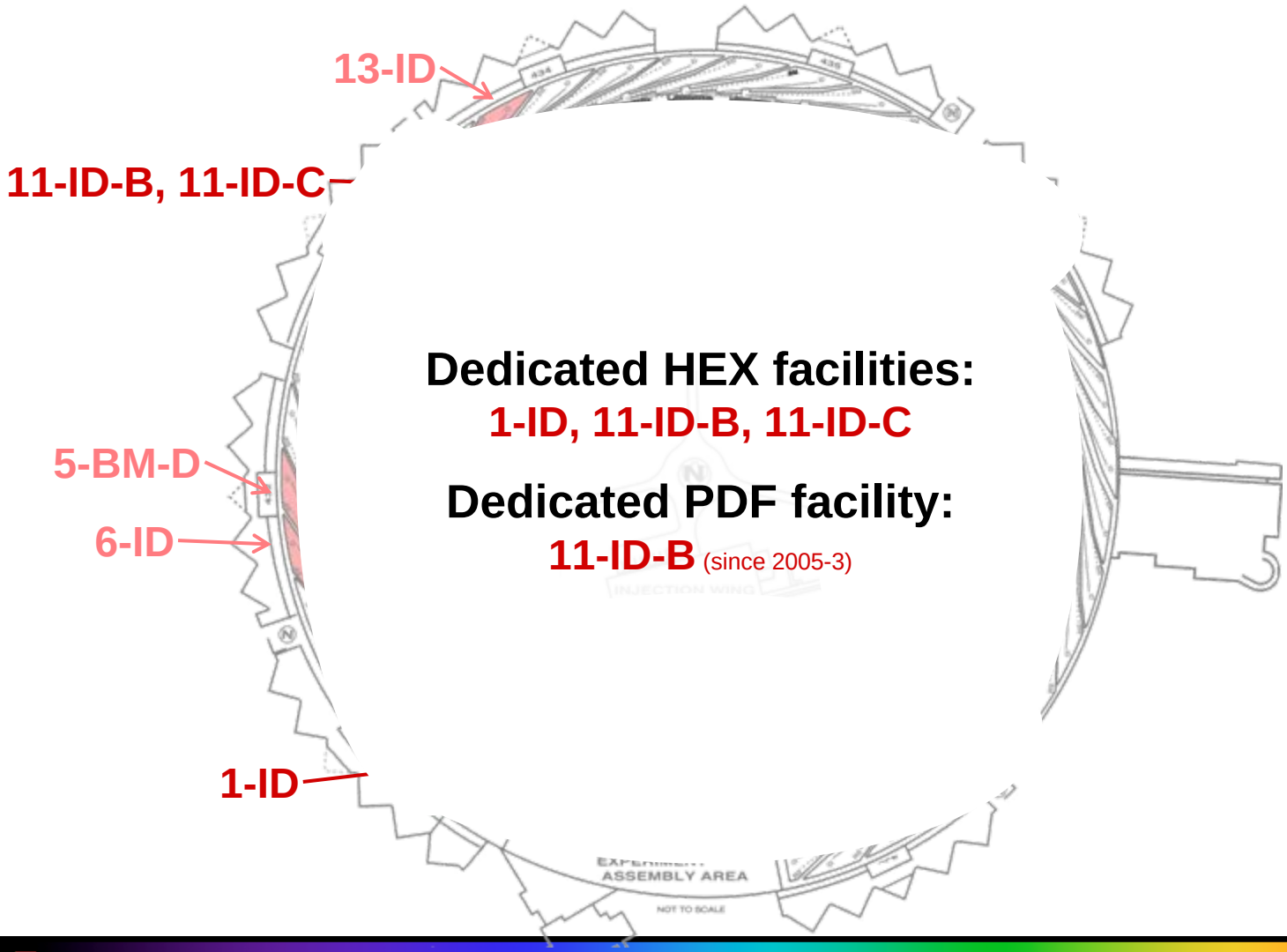
RE Franklin *Acta. Cryst.* (1950)

Zeolites



RD Shannon *J.Phys.Chem.*(1985)

High Energy X-rays at the APS

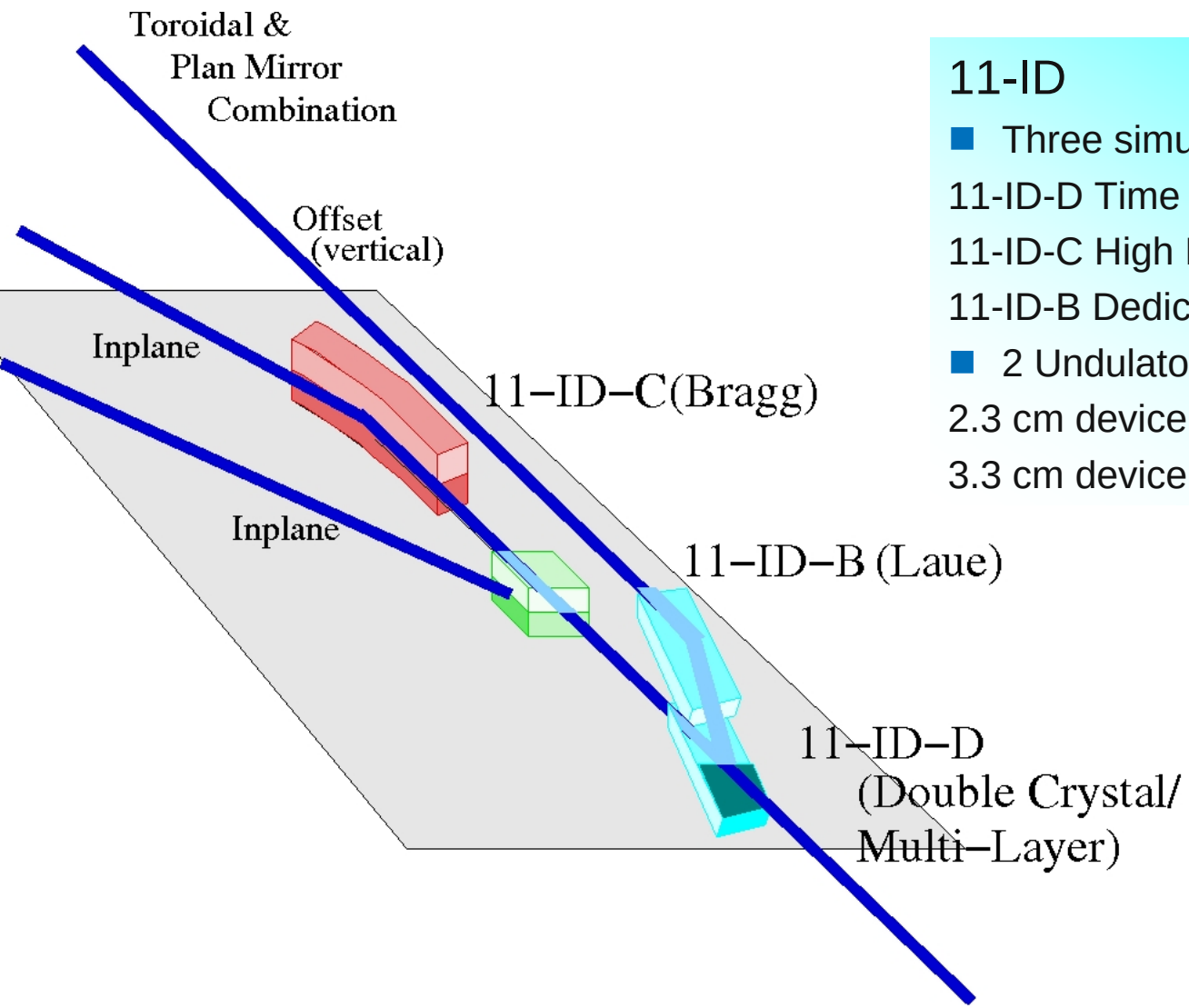


Dedicated HEX facilities:
1-ID, 11-ID-B, 11-ID-C

Dedicated PDF facility:
11-ID-B (since 2005-3)

The Advanced Photon Source - APS

High Energy X-Rays at beamline 11-ID at the APS



11-ID

- Three simultaneously operating stations;

11-ID-D Time Dependent

11-ID-C High Energy Scattering

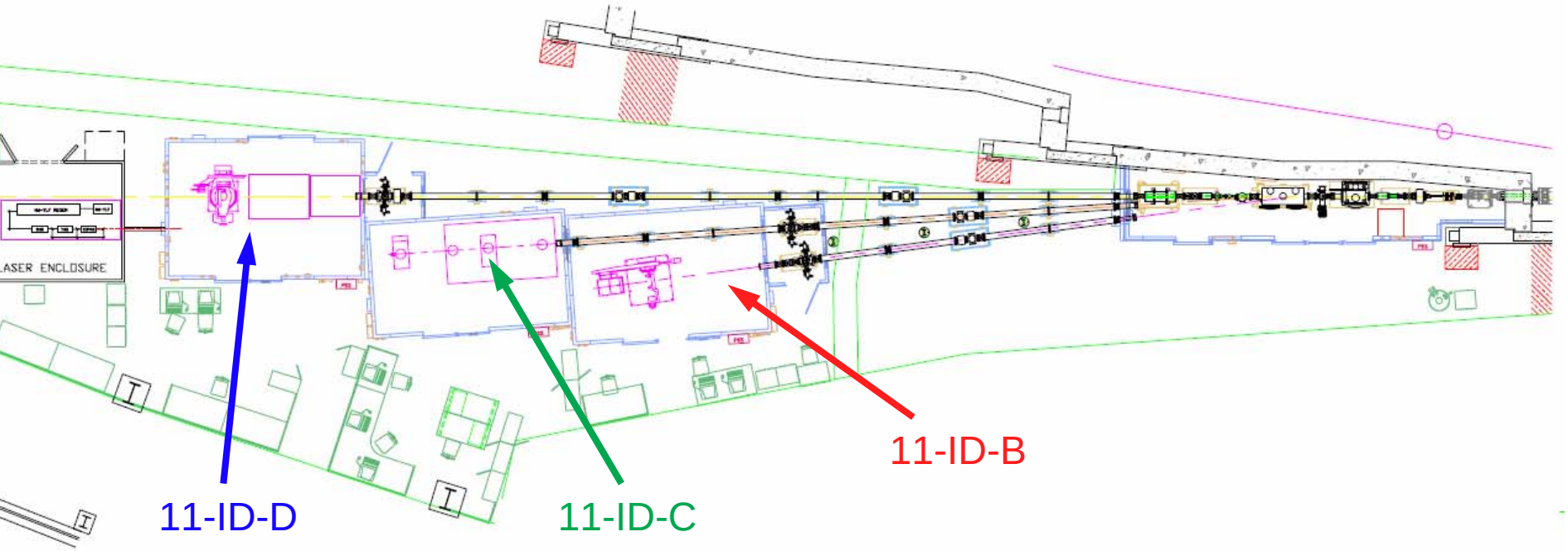
11-ID-B Dedicated PDF Beamline

- 2 Undulators

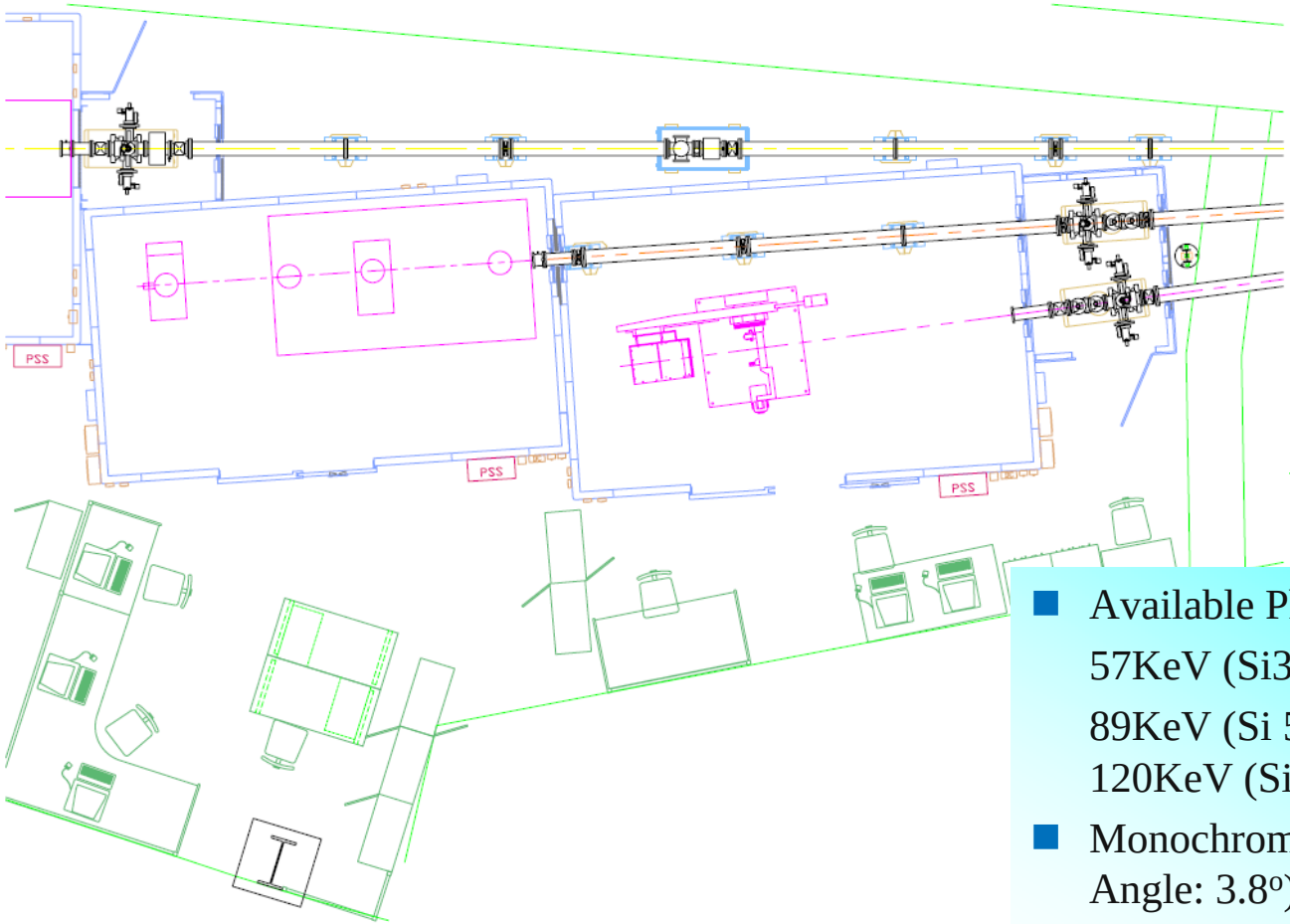
2.3 cm device used by 11-ID-B and -C

3.3 cm device utilized by 11-ID-D

Overview of 11-ID at the APS

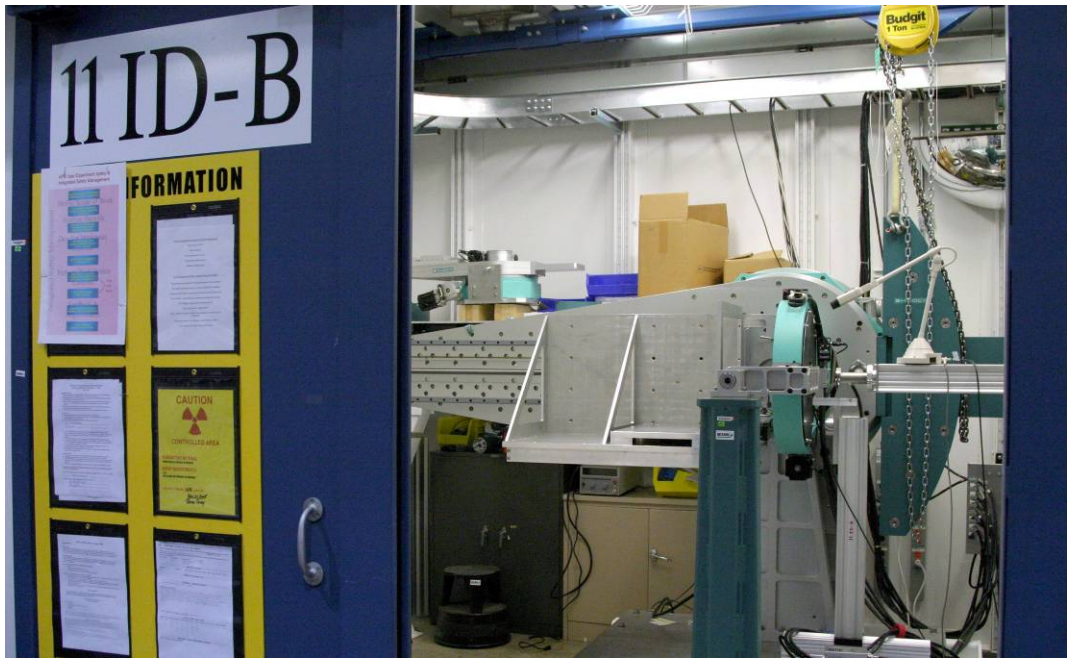


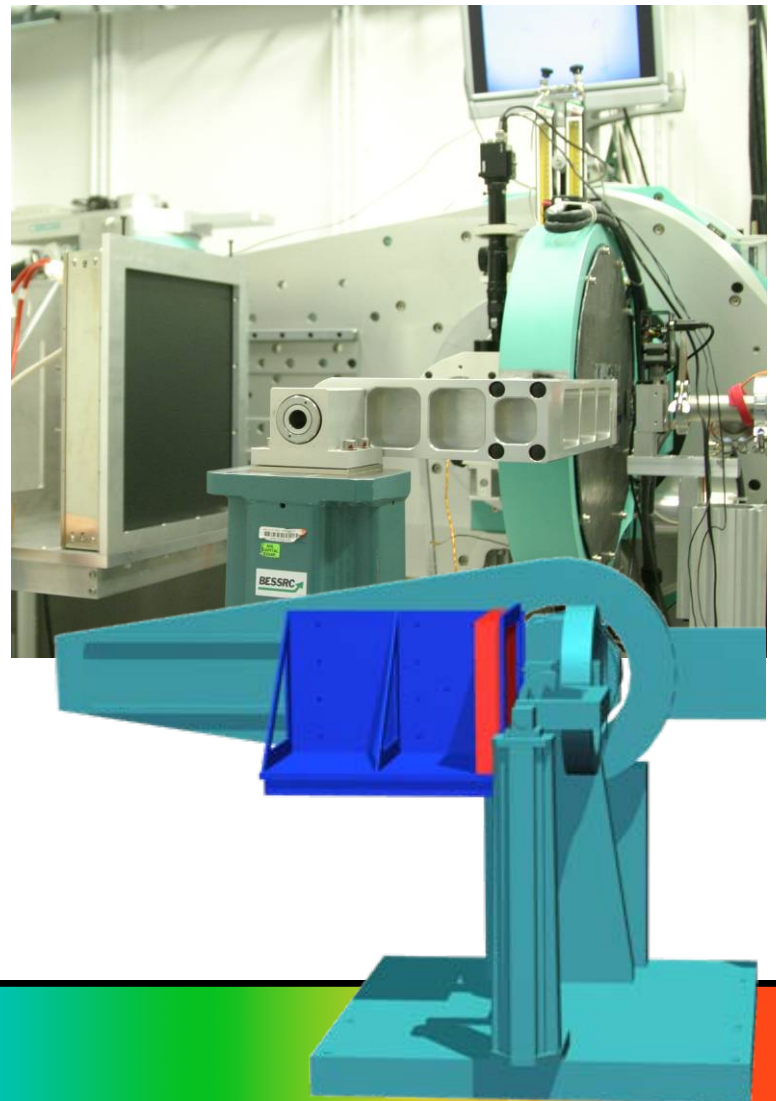
High Energy X-rays at the APS



- Available Photon Energies:
  57KeV (Si311)
  89KeV (Si 511),
  120KeV (Si 711),
- Monochromator: Laue crystal (Fixed Bragg Angle: 3.8^{o})
- Max beam size: 3 x 2 mm^2
- Flux: 10^{12} Photons/s

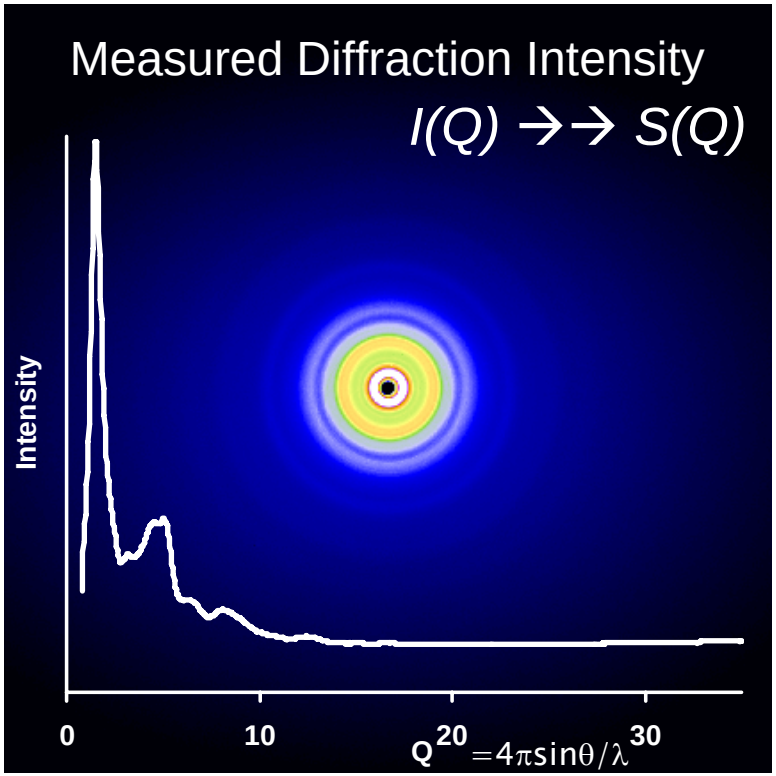
Dedicated PDF facility at the APS

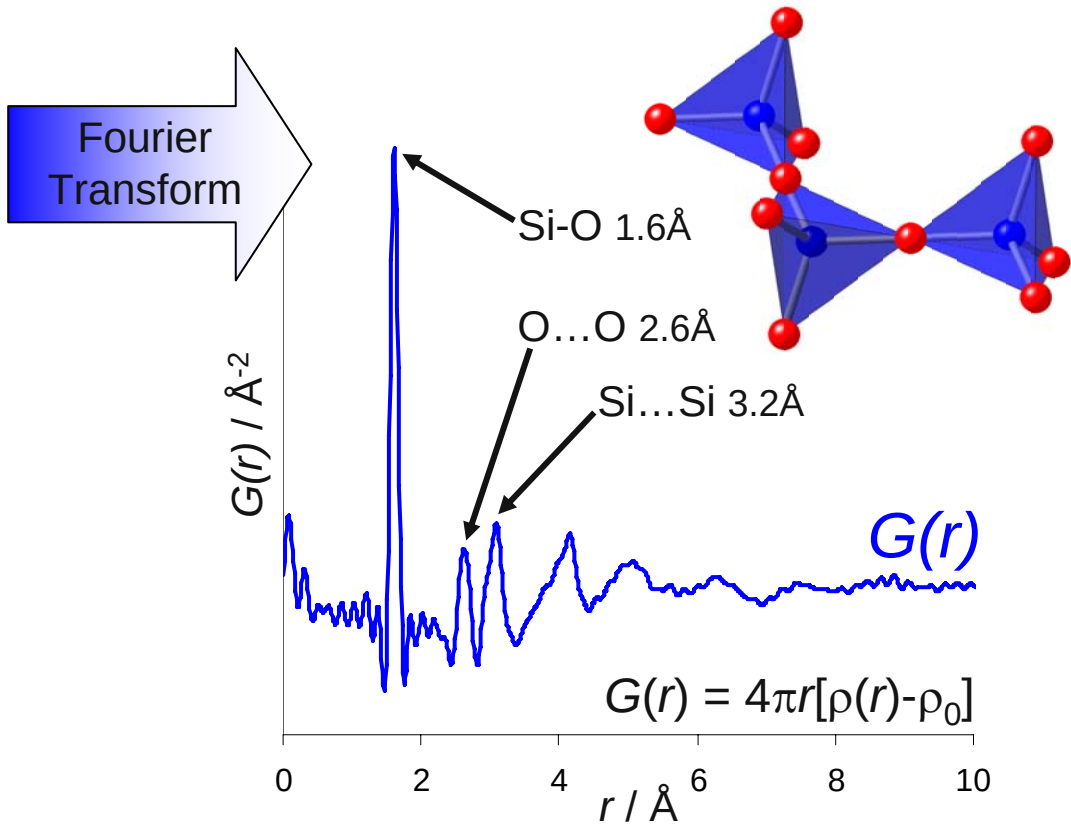




The Pair Distribution Function Method

- The structure factor S(Q) can be measured as a function of diffraction angle using monochromatic X-rays
- Application of area detector to yield more rapid measurements by collecting all data simultaneously





P.J. Chupas, X. Qiu, J.C. Hanson, P.L. Lee, C.P. Grey, S. Billinge, *J. Applied Cryst.*, **2003**, 36, 1342-1347.

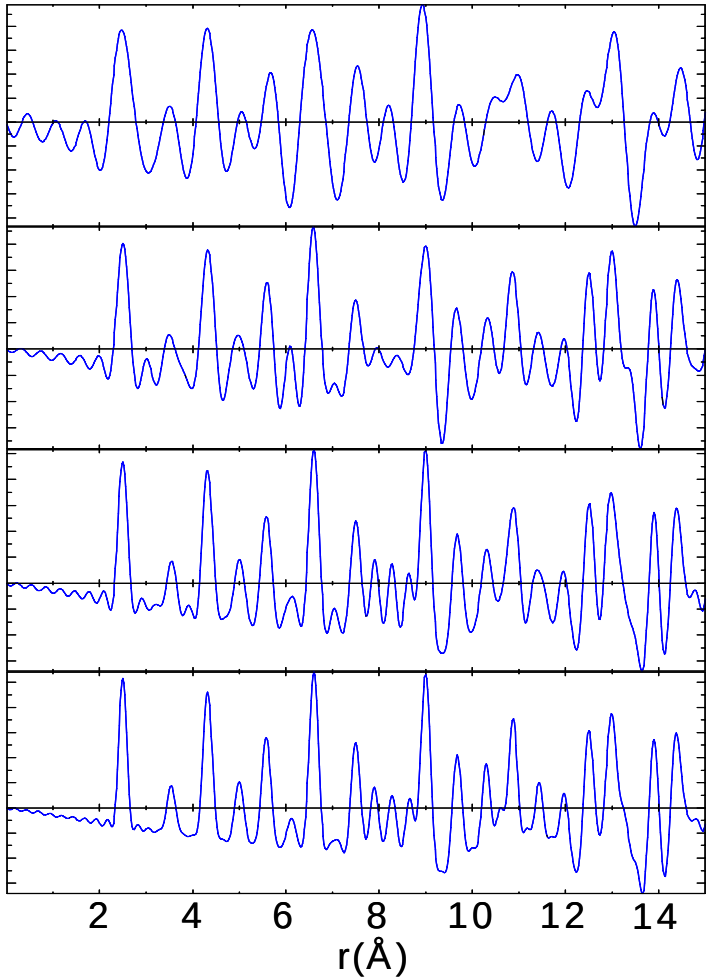
High Real Space Resolution PDFs: The Need for High Q Measurements

$$Q_{max} = 4\pi\sin\theta/\lambda$$

for Cu Kα, λ=1.54Å, 2θ=180°

$$Q_{max} = 4\pi\sin 90/1.54 = 8\ \text{Å}^{-1}$$

We typically use wavelengths between 0.20 and 0.08 Å



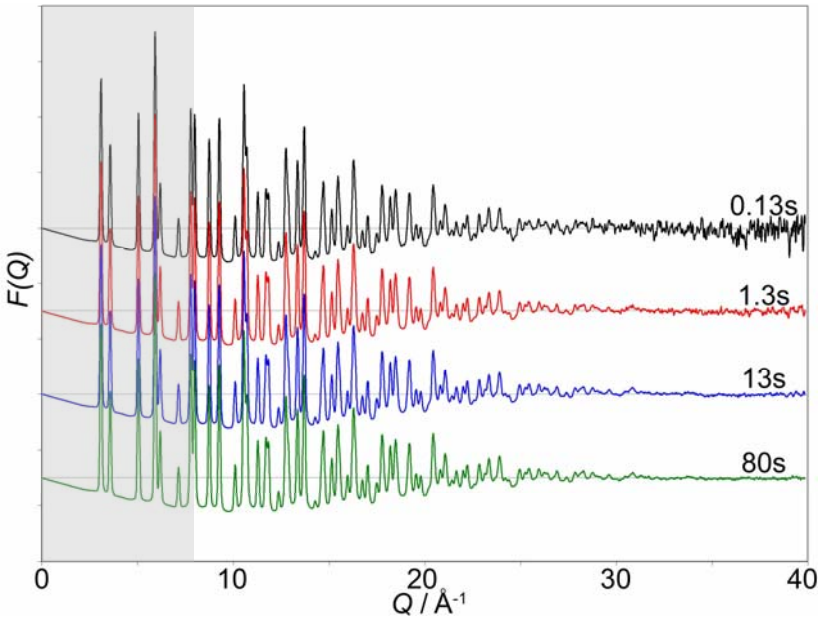
Q_{max} = 10 Å^{-1}

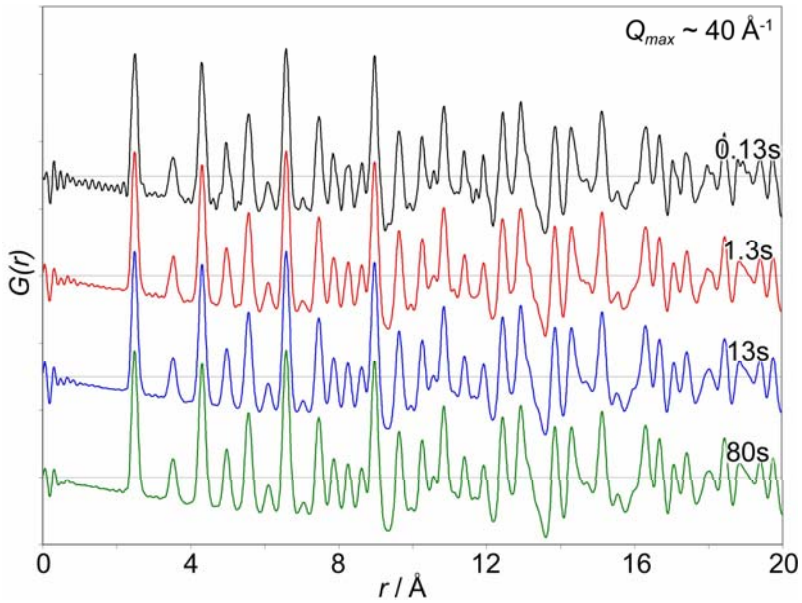
Q_{max} = 15 Å^{-1}

Q_{max} = 20 Å^{-1}

Q_{max} = 25 Å^{-1}

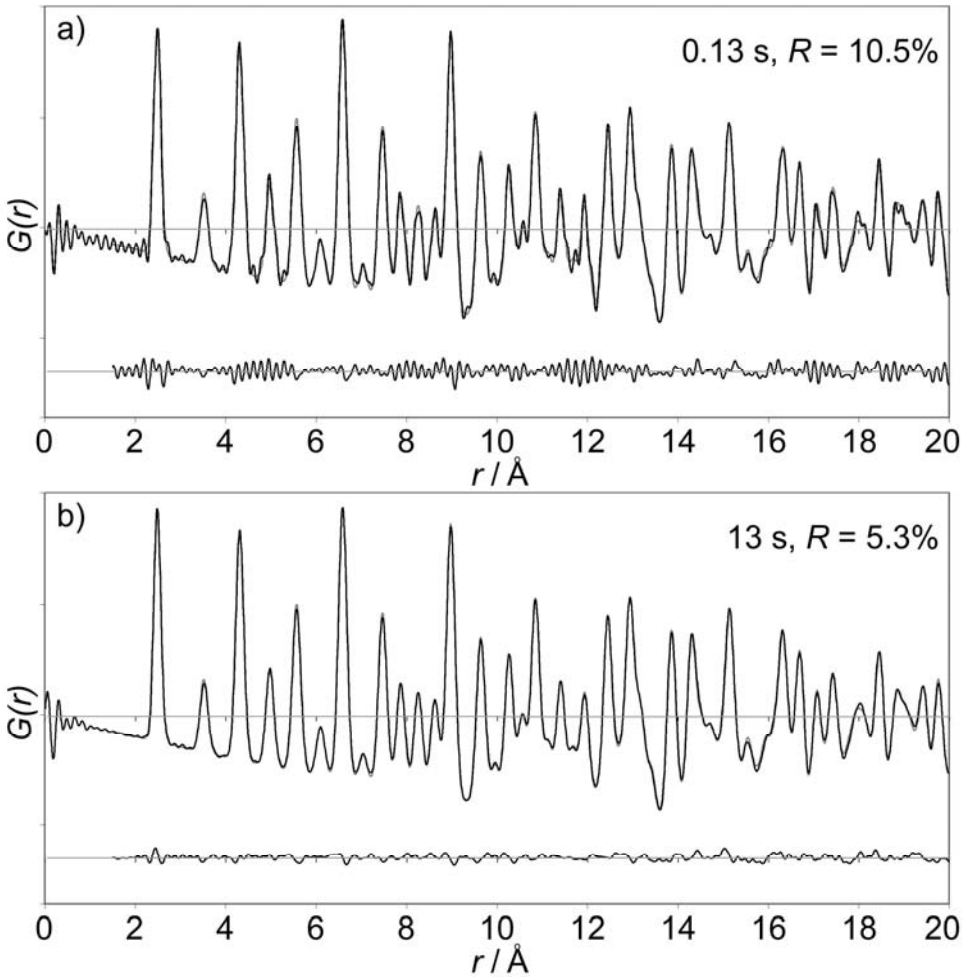
Accessibility to high resolution measurements



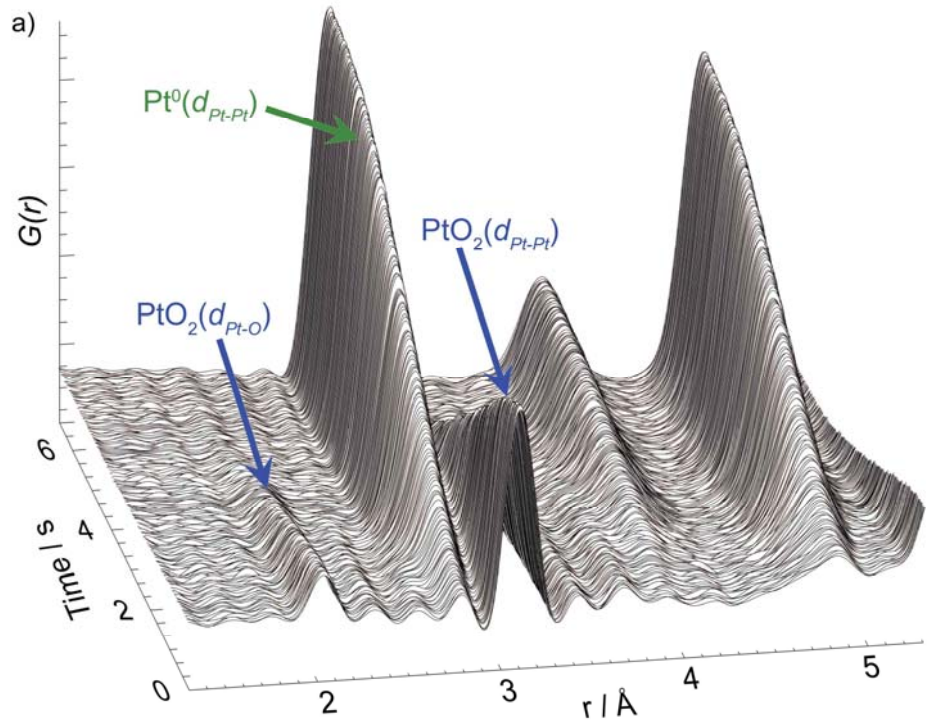


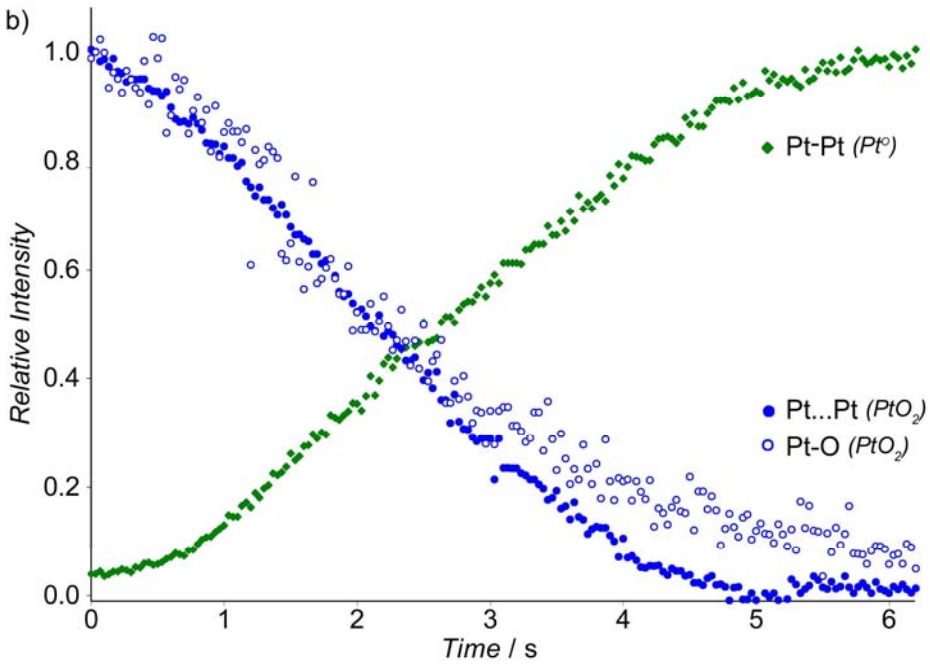
- Sample volume ~ 0.08 mm^3
- Detector specific corrections are VERY import
  - Energy sensitivity and Compton Scattering
  - "Oblique Incidence"

Refinement Against Crystalline Models



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

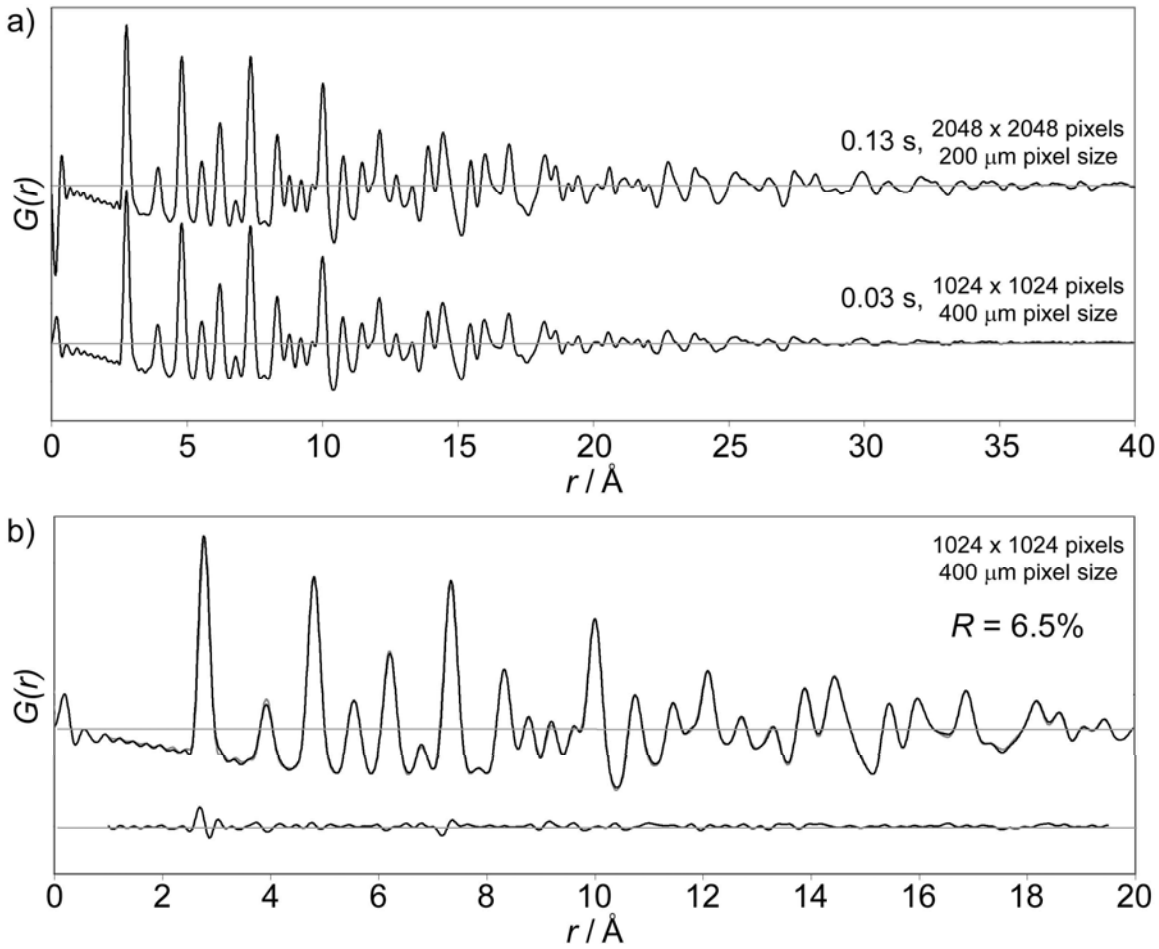




Data can be collected in only 30 ms

Chupas, Chapman, Lee *J. Appl. Crystallogr.*, 2007, 40, 463-470

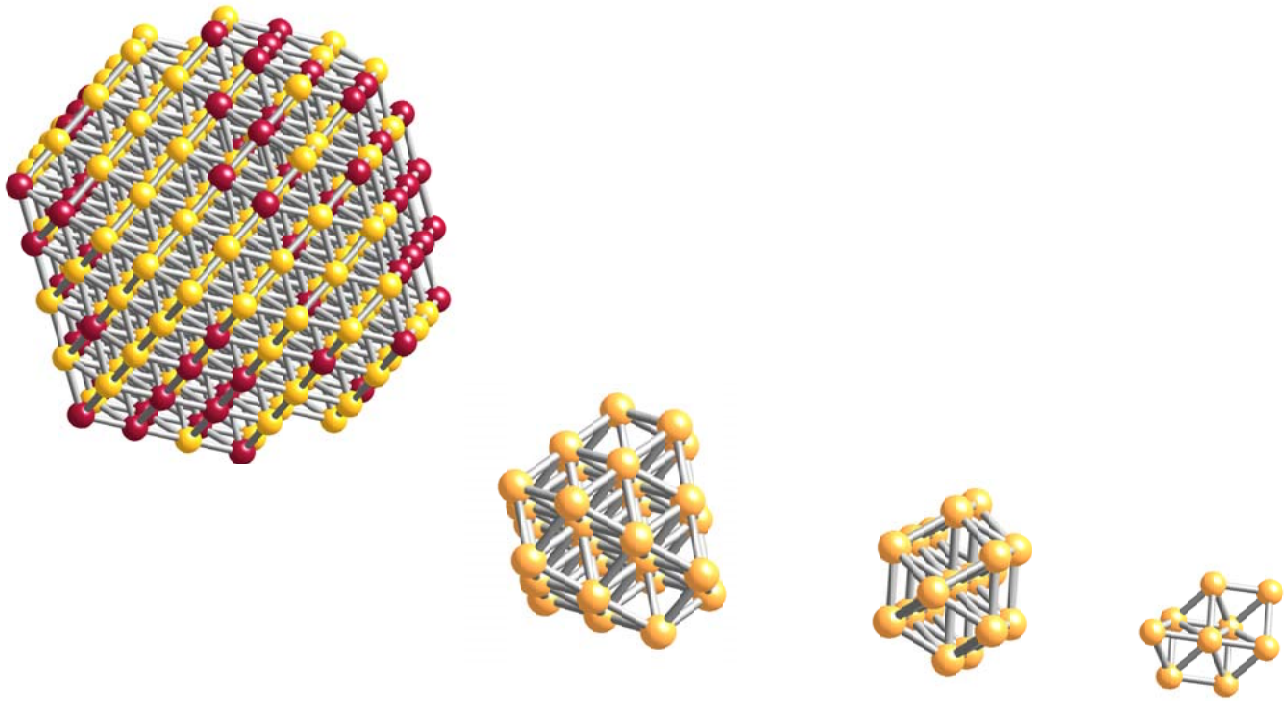
In-situ measurements: The reduction of PtO_2 to Pt



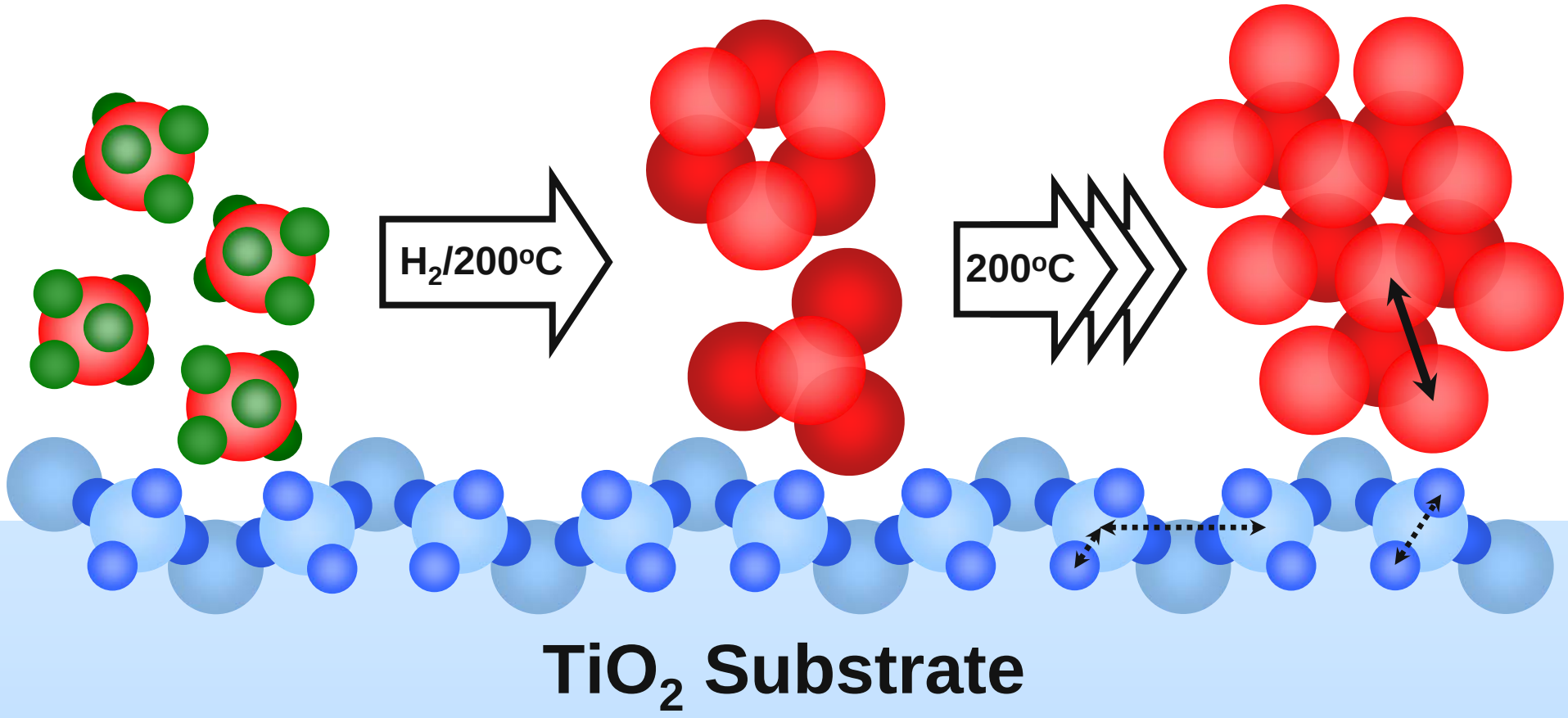
Application of Time Resolved Studies:

Supported Metal Catalysts

Following the kinetics formation of catalytic particles



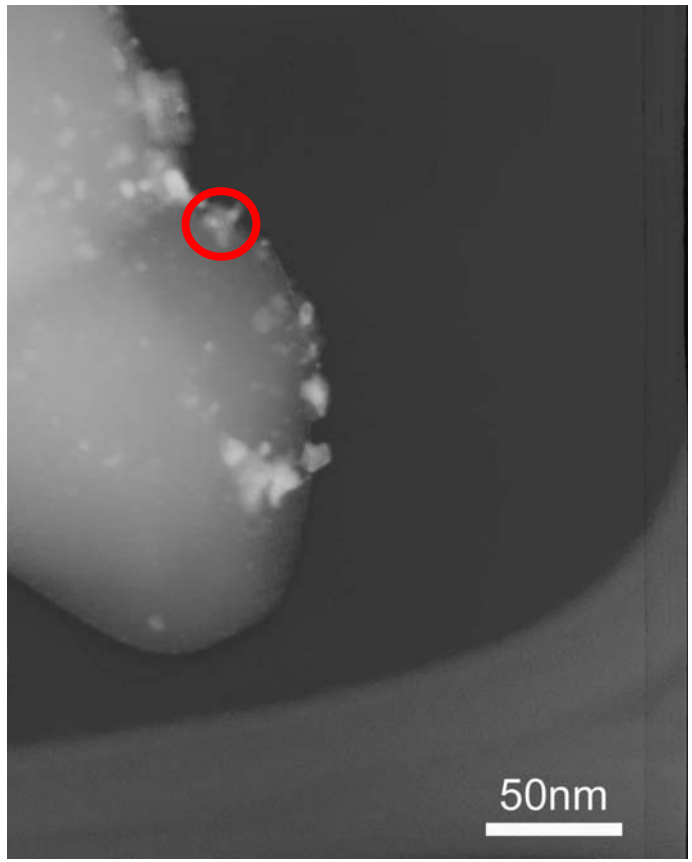
Forming Supported Nanoparticles

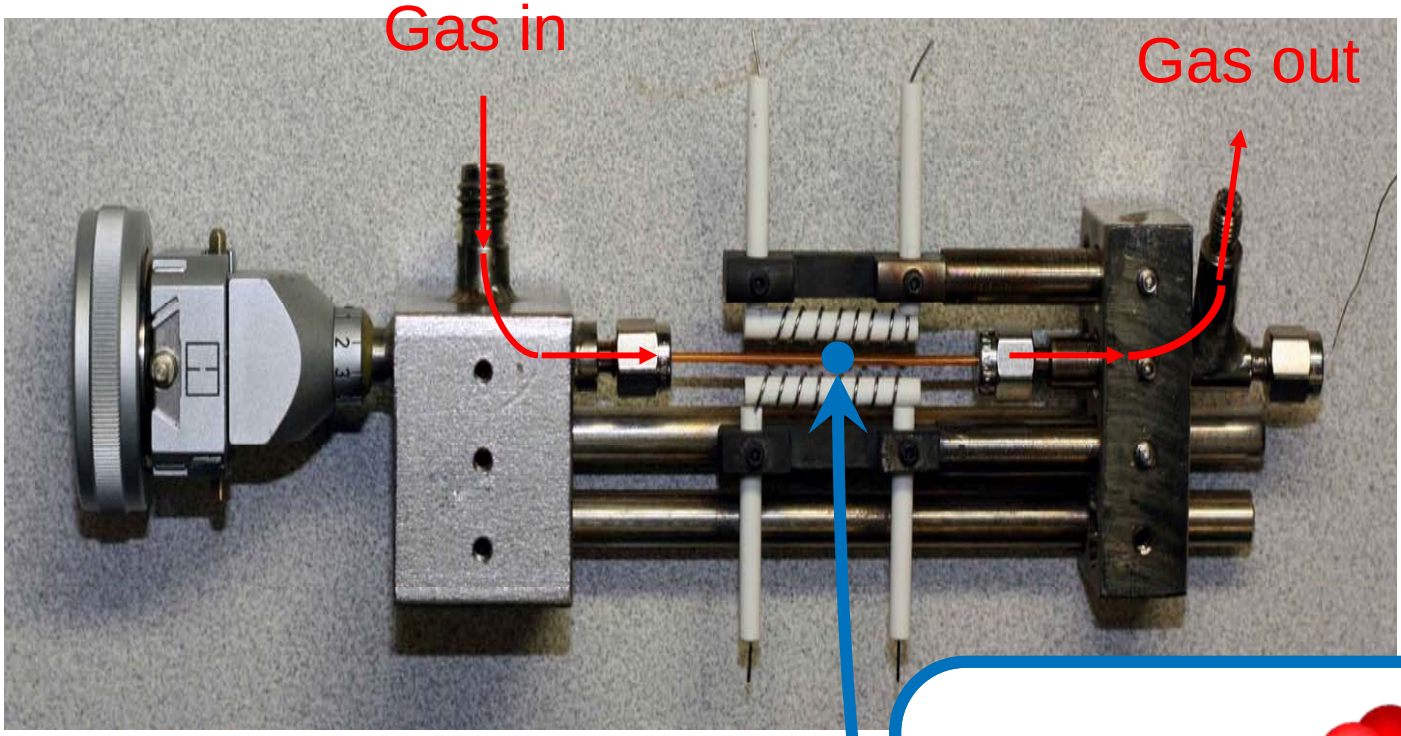


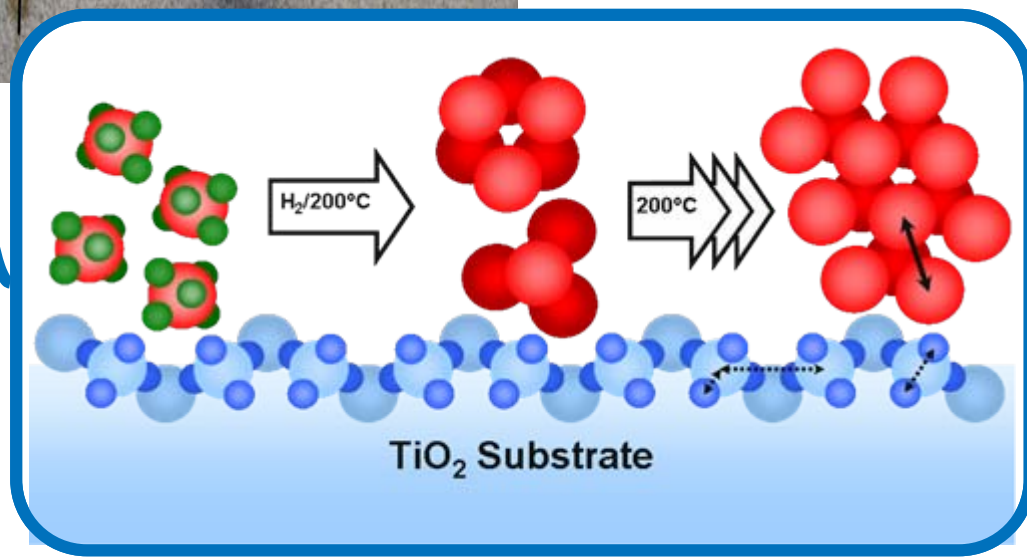
Forming Supported Nanoparticles

$$Pt^{4+} + 4\ e^- \rightarrow Pt^0$$

$$H_2 \rightarrow 2H^+ + 2e^-$$

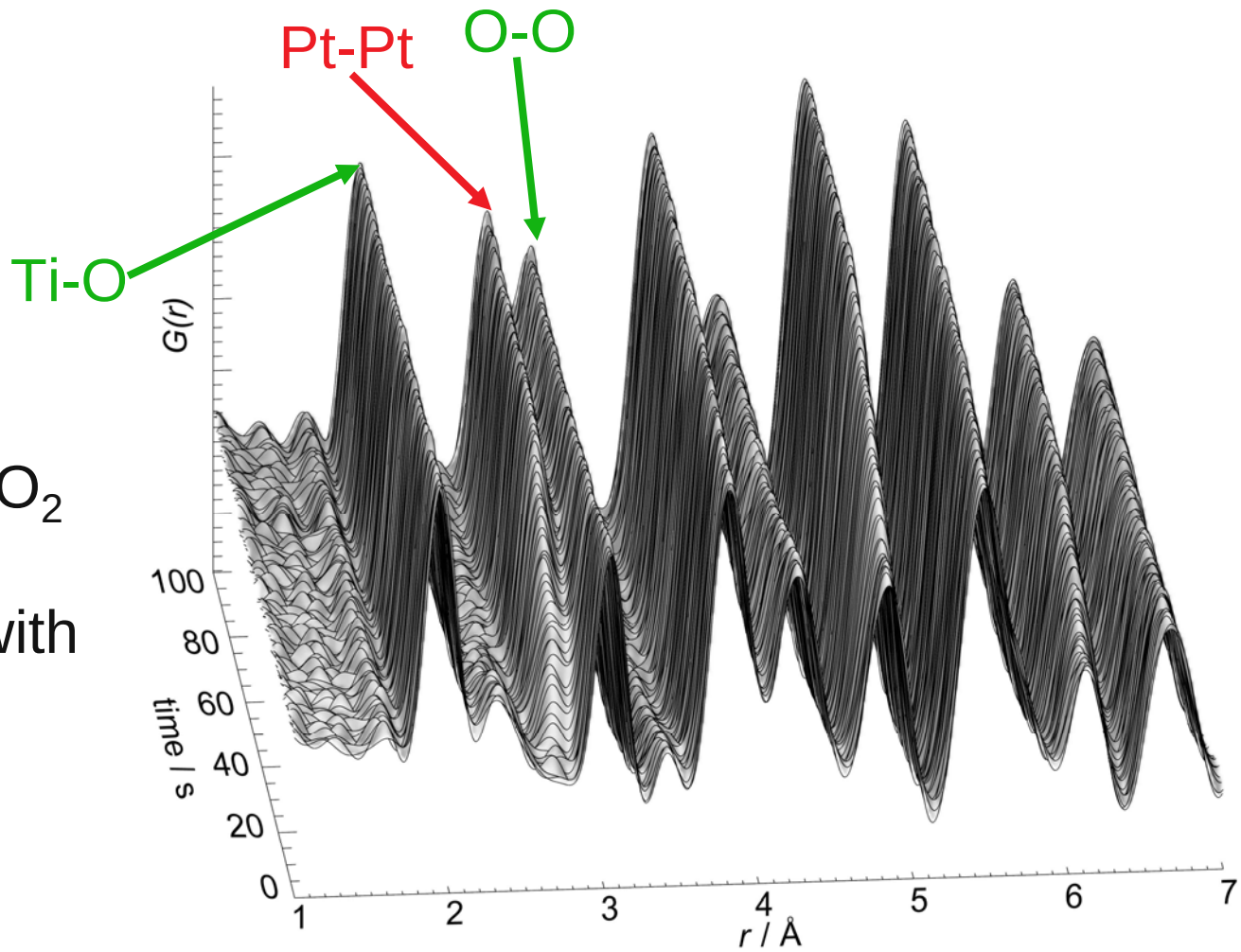



Gas in
Gas out


H2/200°C
200°C
TiO2 Substrate

Reduction of 5% Pt^{4+} on TiO_2 Under H_2

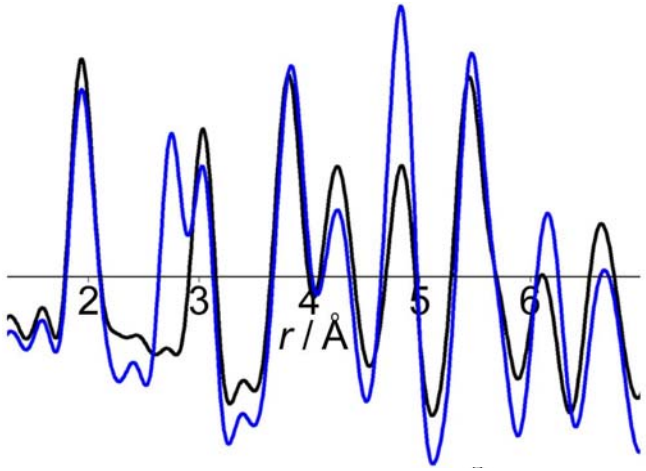
- Reduction at constant temperature, 200 ˚C



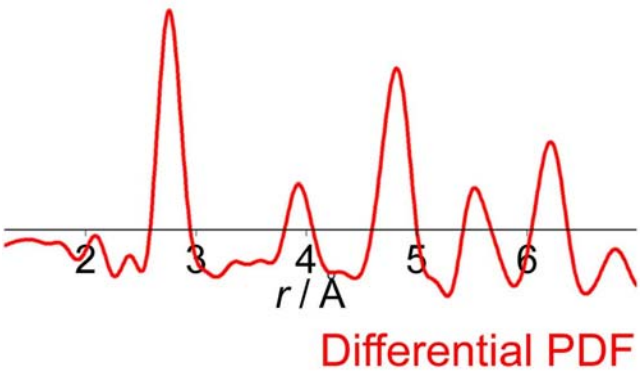
5wt % Pt on TiO_2 (via aqueous impregnation with H_2PtCl_6)

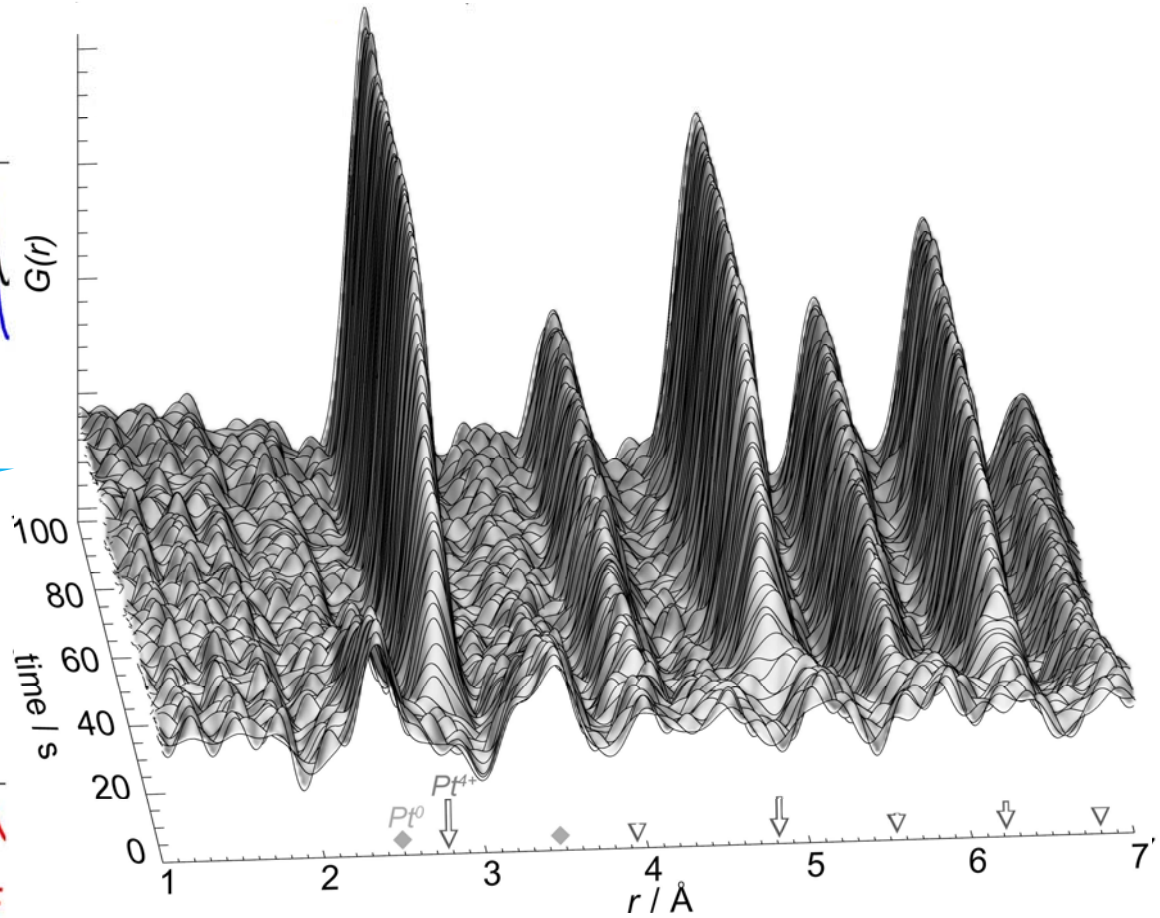
In situ *reduction:* Pt^{4+} *on* $TiO_2 \rightarrow Pt^0$

H_2

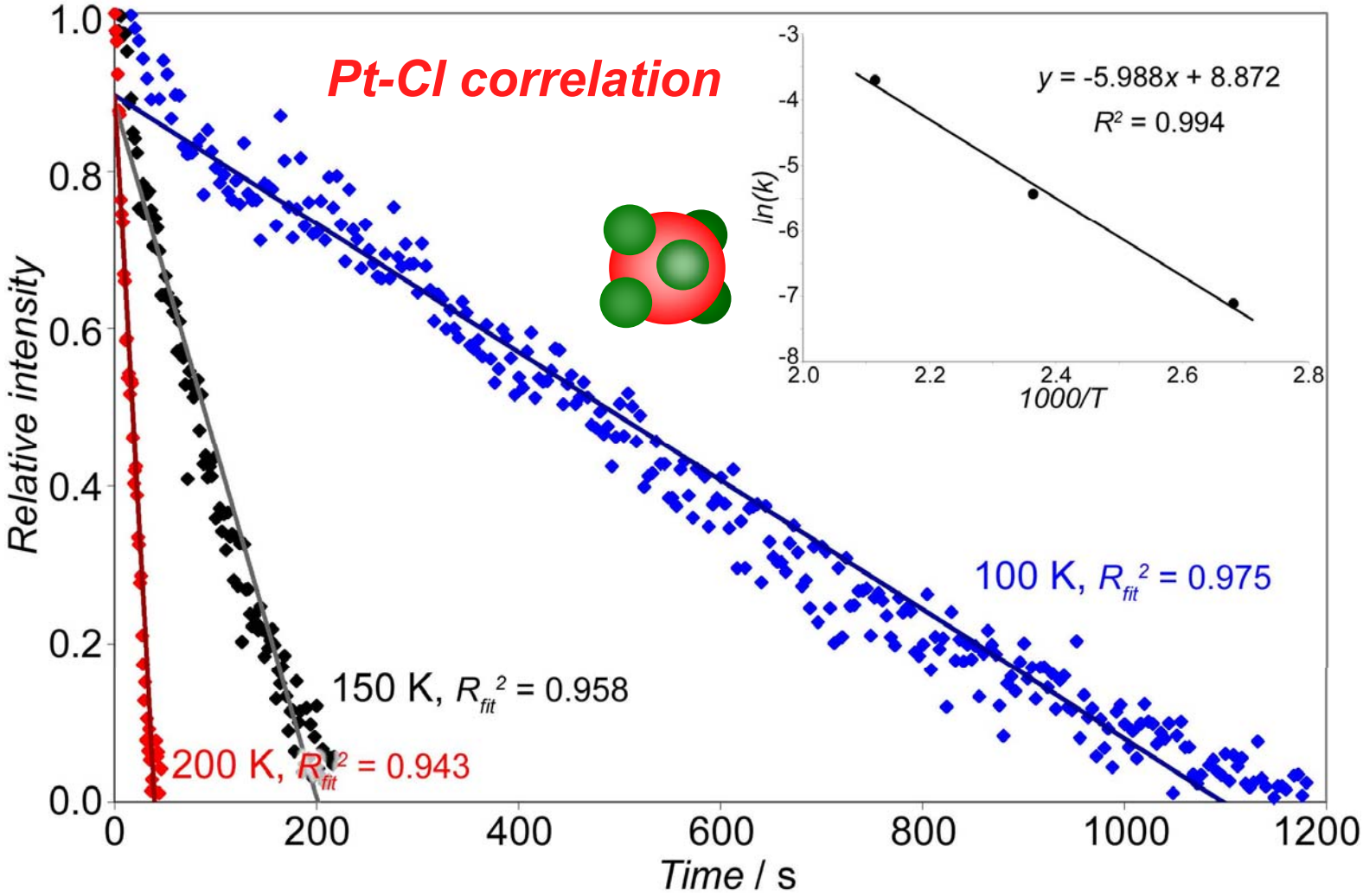


$G(r)_{Pt/TiO_2} - G(r)_{TiO_2}$

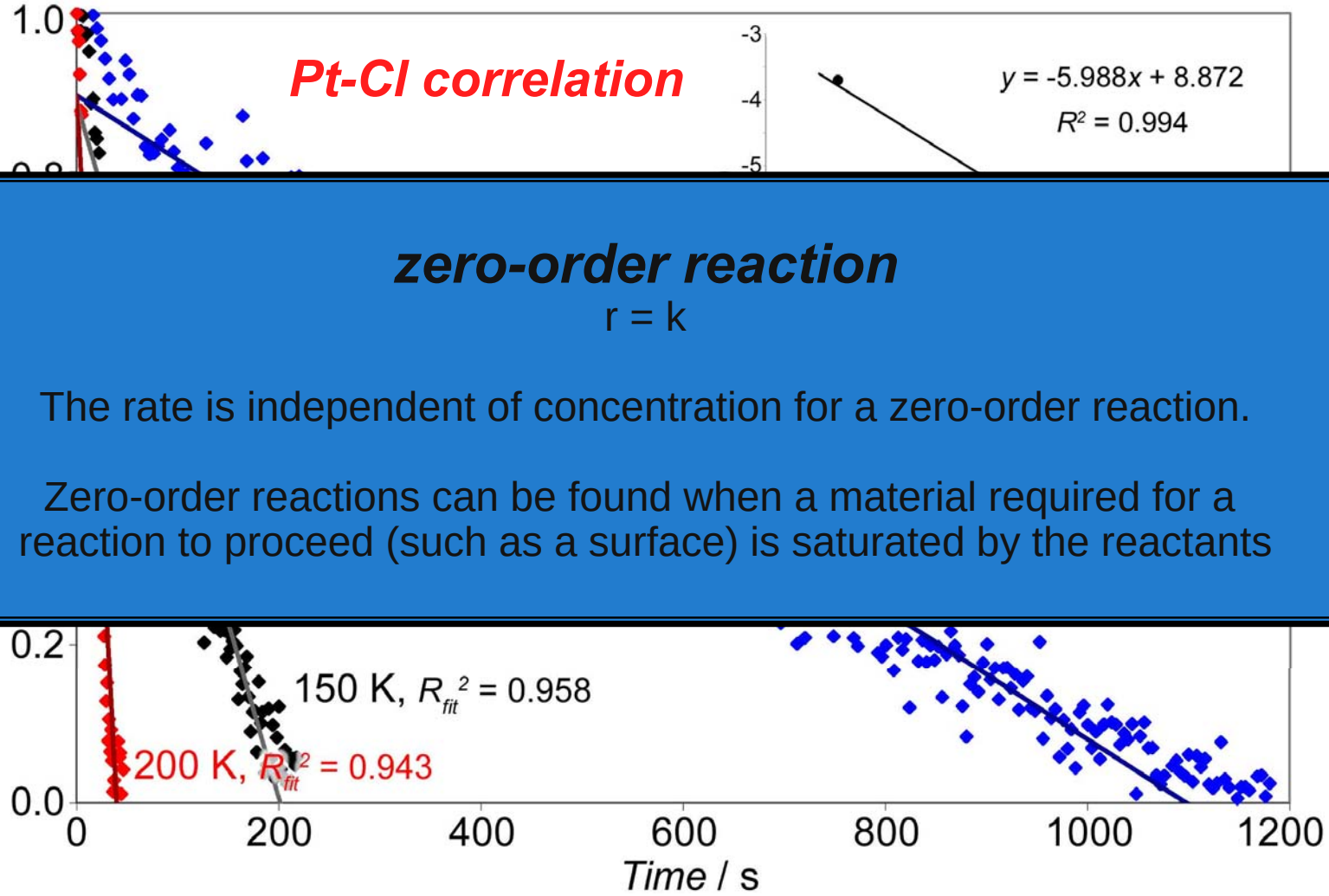




Tracking the Kinetics of Particle Formation



Tracking the Kinetics of Particle Formation



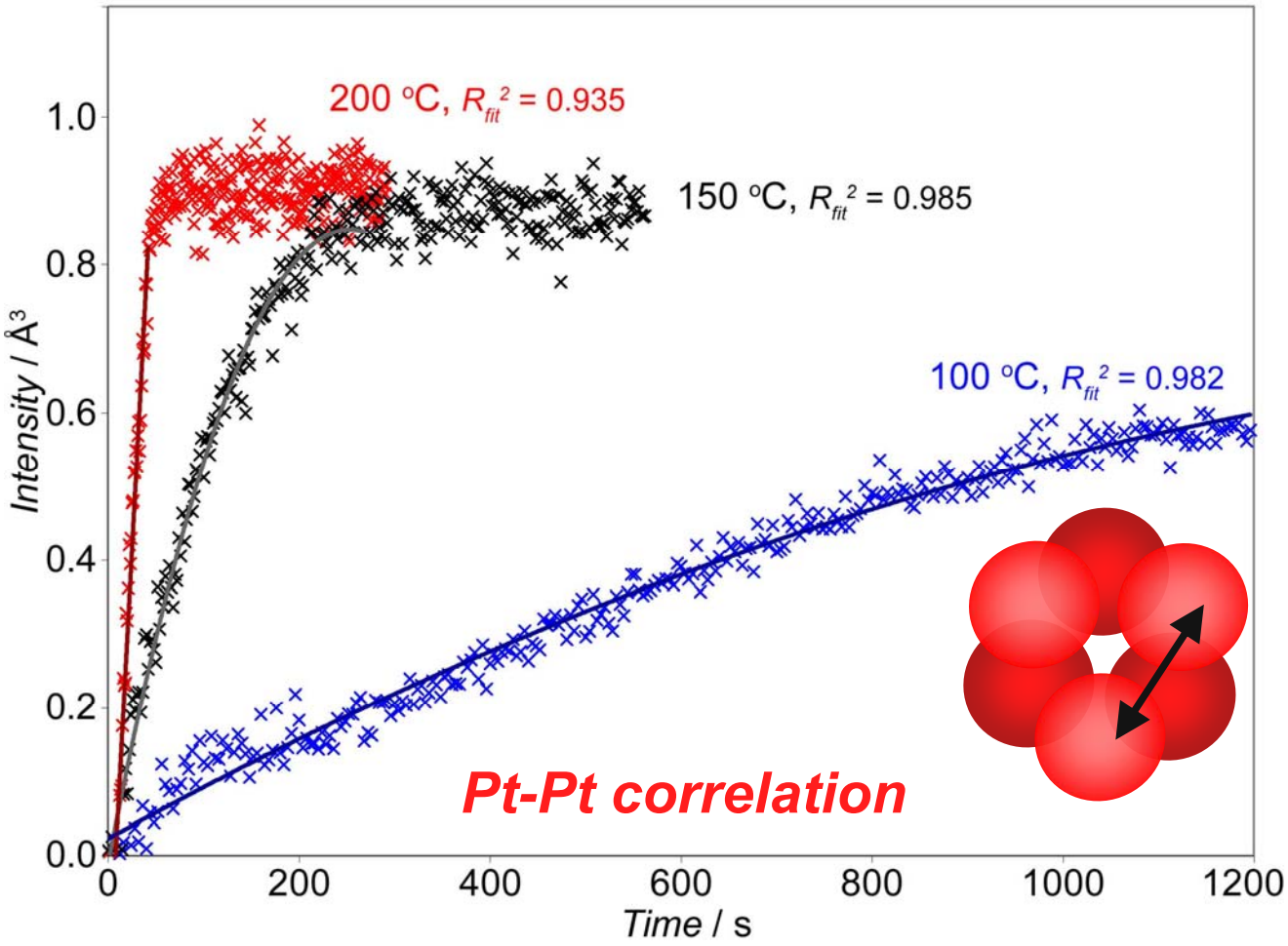
zero-order reaction

r = k

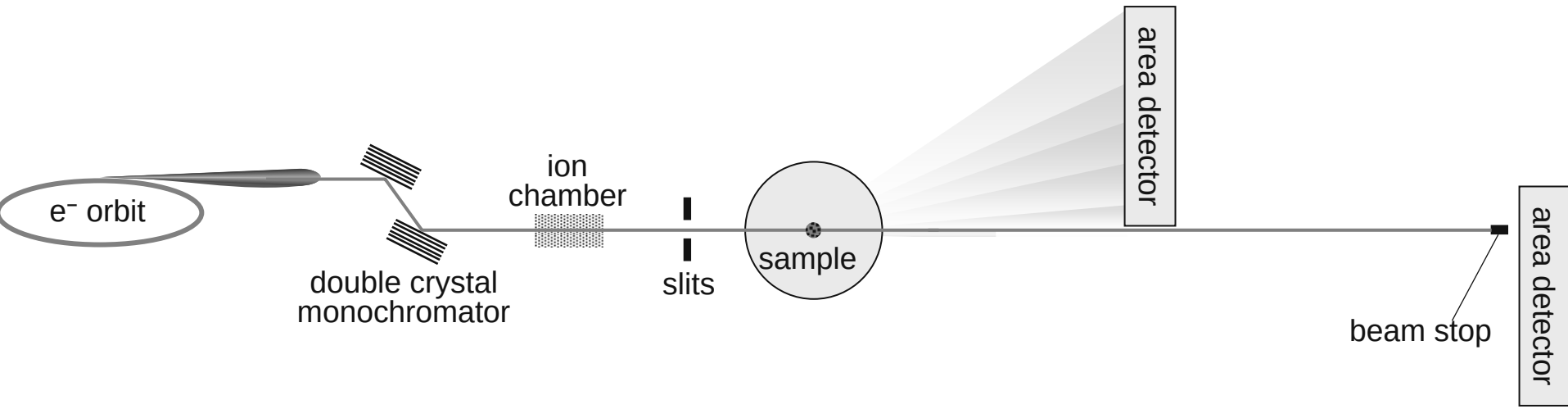
The rate is independent of concentration for a zero-order reaction.

Zero-order reactions can be found when a material required for a reaction to proceed (such as a surface) is saturated by the reactants

Nest Step: Particle Growth



Combined PDF and SAXS measurements



Overview

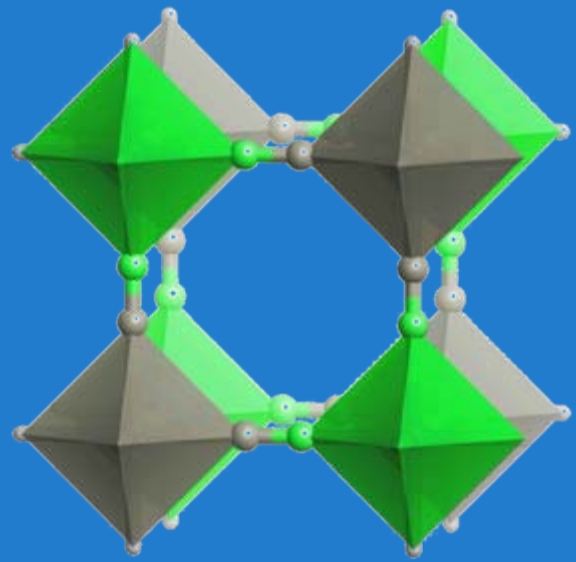
- Differential PDF selectively probes supported nanoparticles
  - Fast time resolution possible
  - Follow reaction
- Probes reaction mechanism & kinetics
  - Reagent consumption (bonds breaking)
  - Bond formation
  - Particle growth/annealing

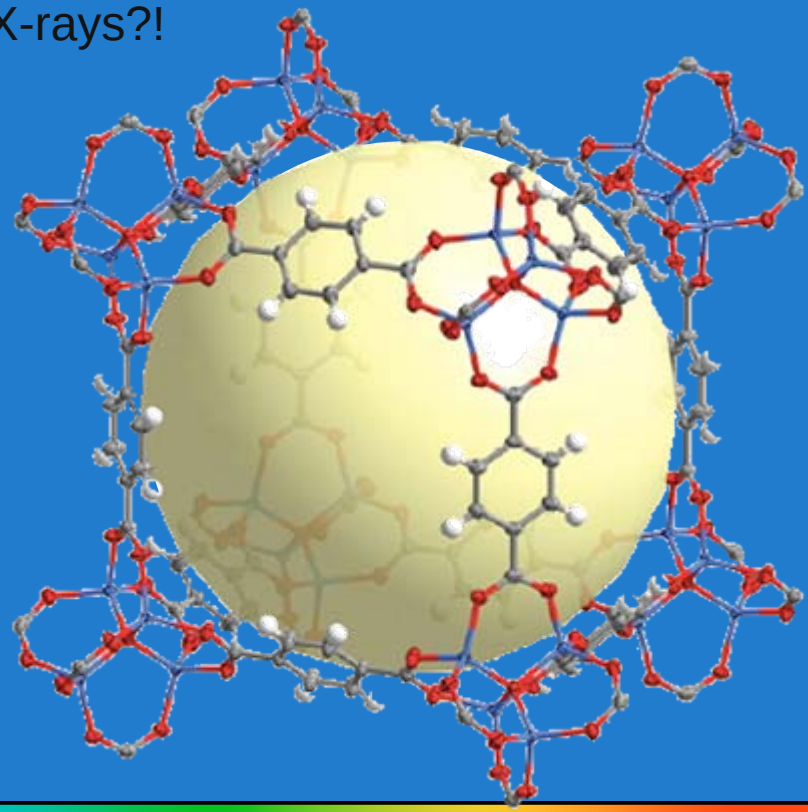
Porous Coordination Frameworks

Can we probe the structure of weakly bound guest molecules?

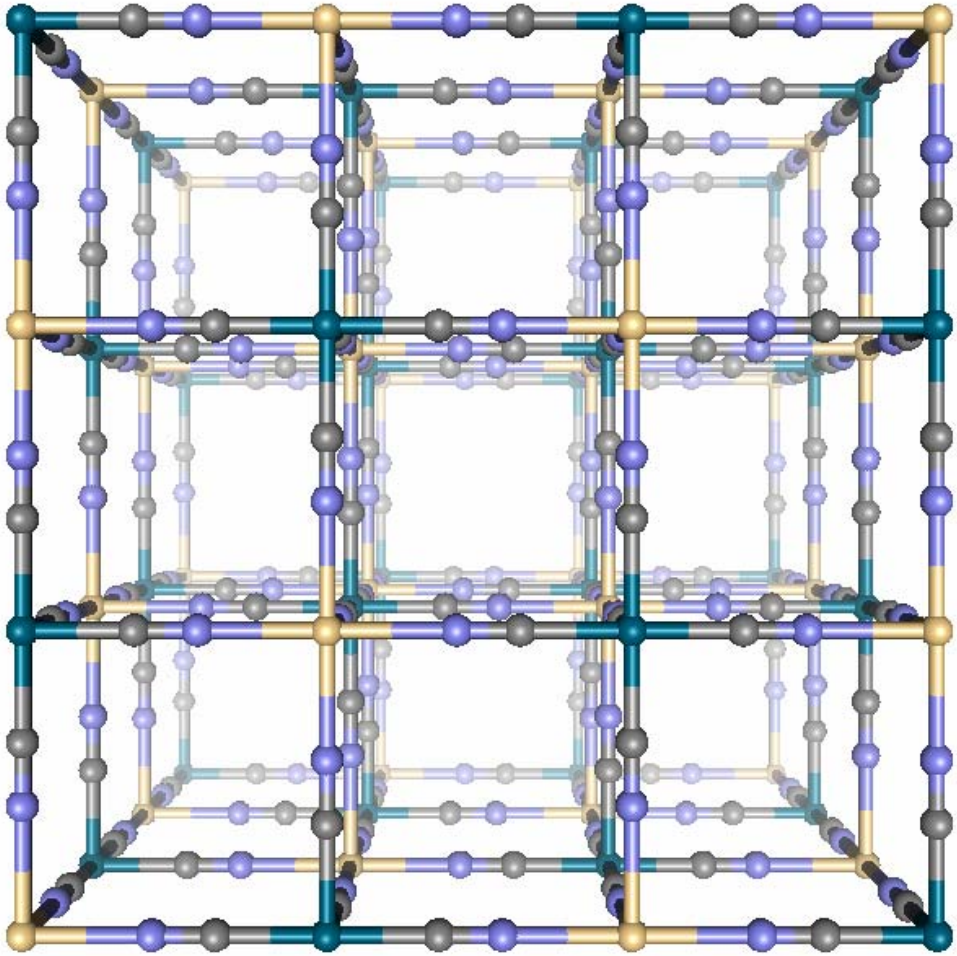
Are open metal sites important for binding H_2?

Seeing hydrogen with X-rays?!



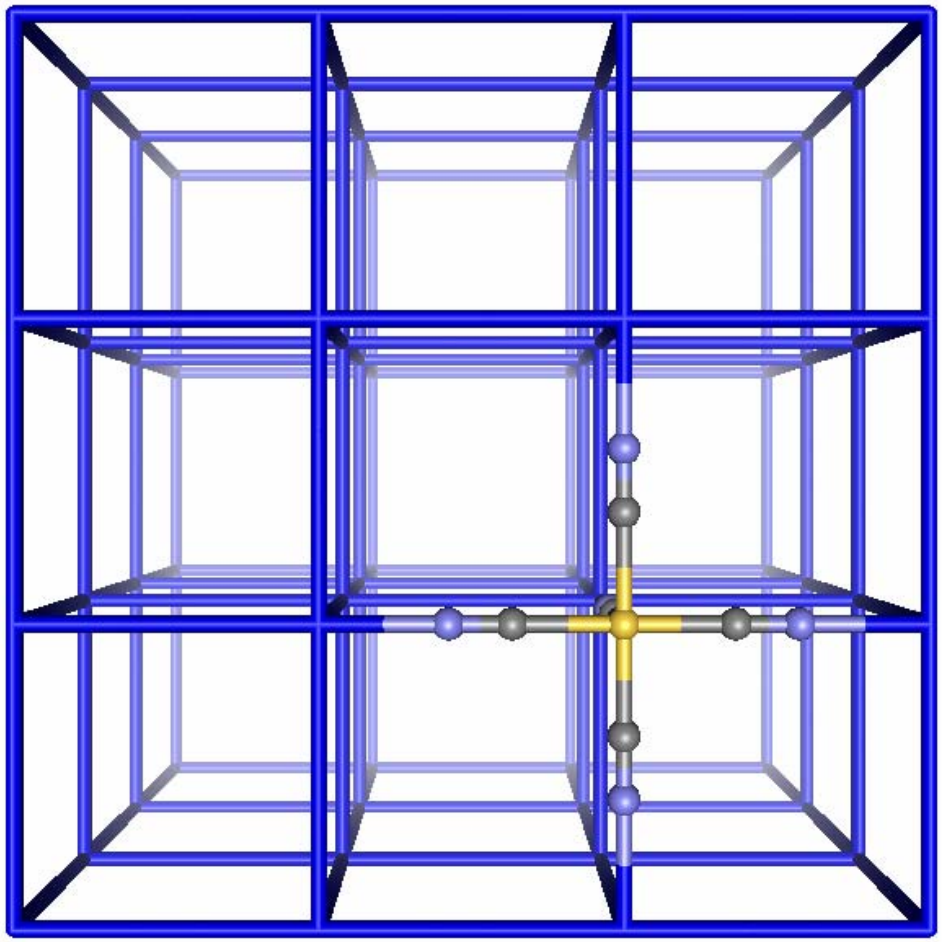


Open Metal Sites in Prussian Blue Analogues



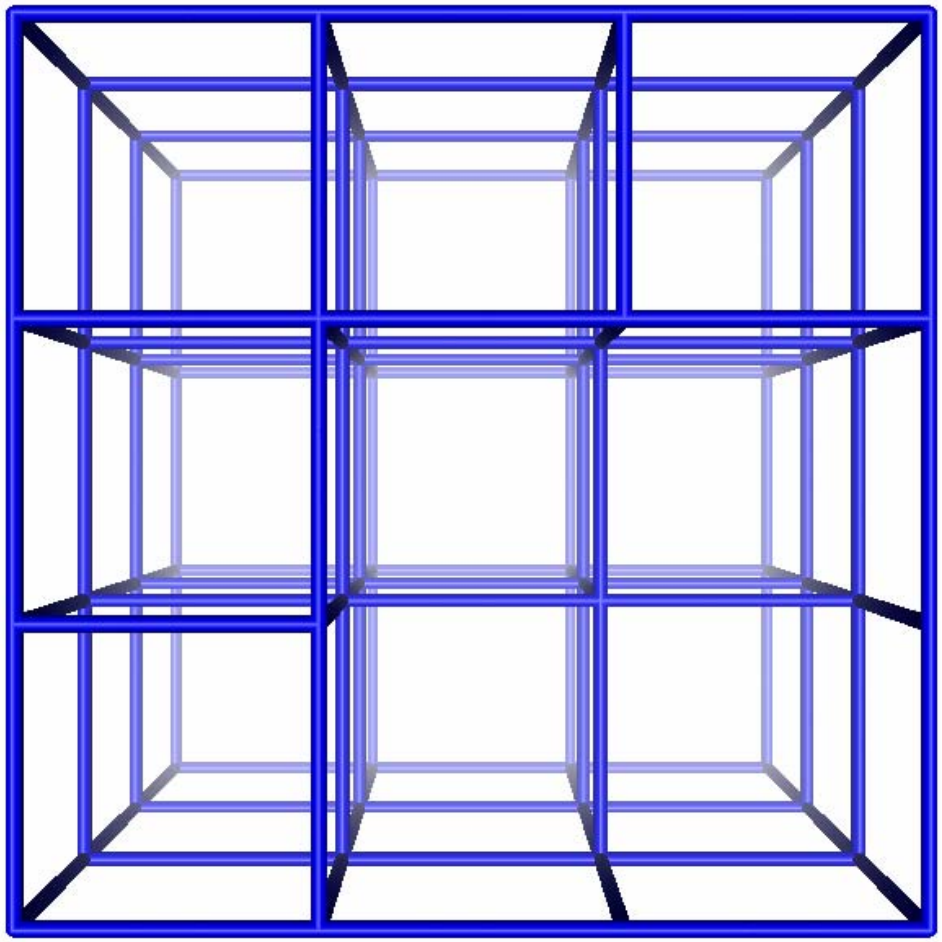
e.g.
$Mn^{II}_3[Co^{III}(CN)_6]_2$

Open Metal Sites in Prussian Blue Analogues



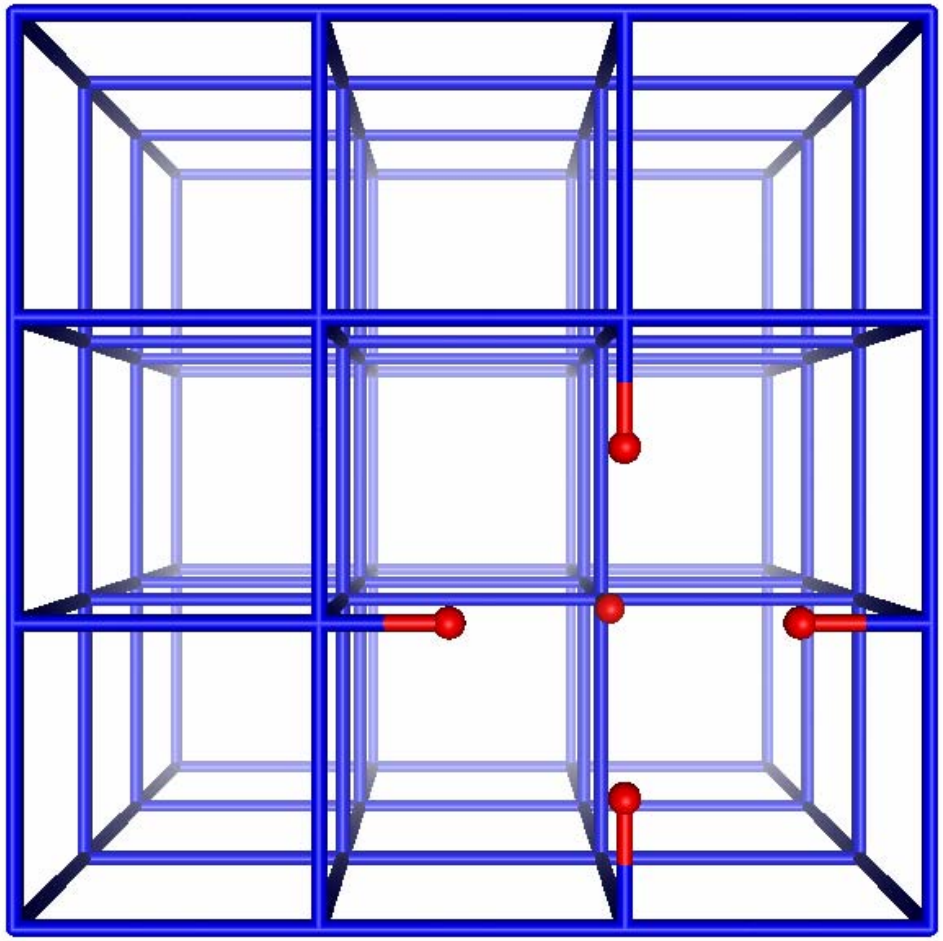
e.g.
$Mn^{II}_3[Co^{III}(CN)_6]_2$

Open Metal Sites in Prussian Blue Analogues



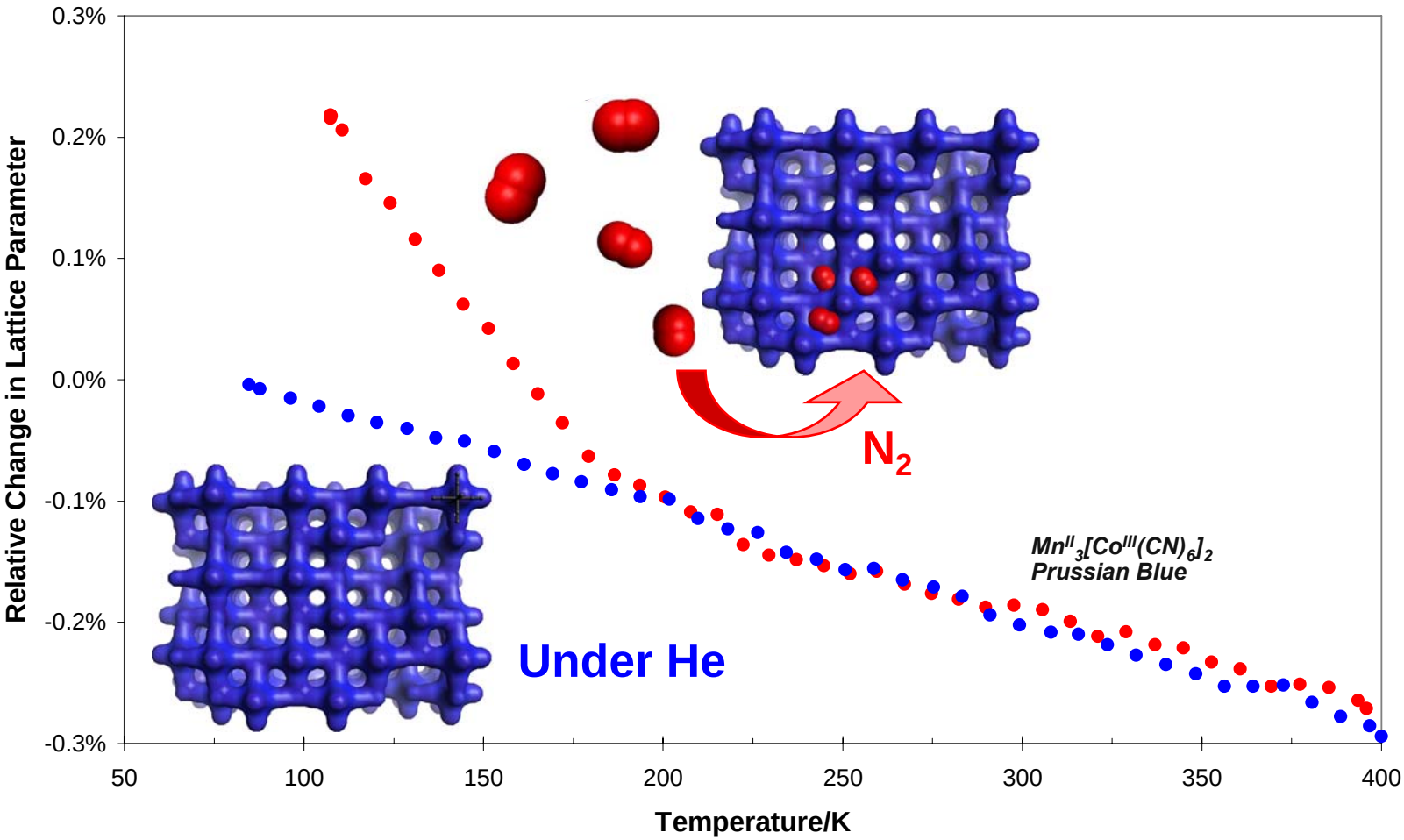
e.g.
$Mn^{II}_3[Co^{III}(CN)_6]_2$

Open Metal Sites in Prussian Blue Analogues

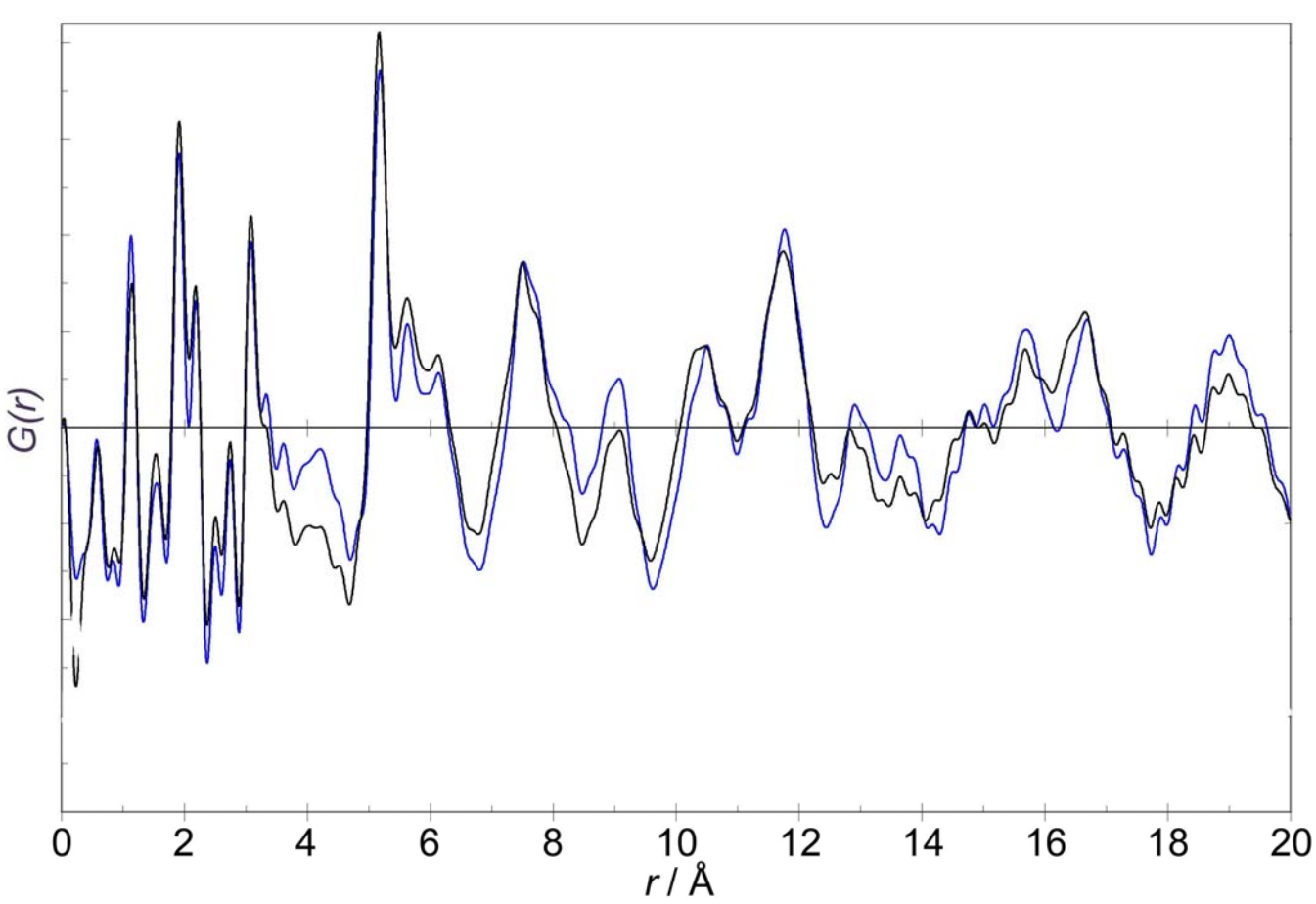


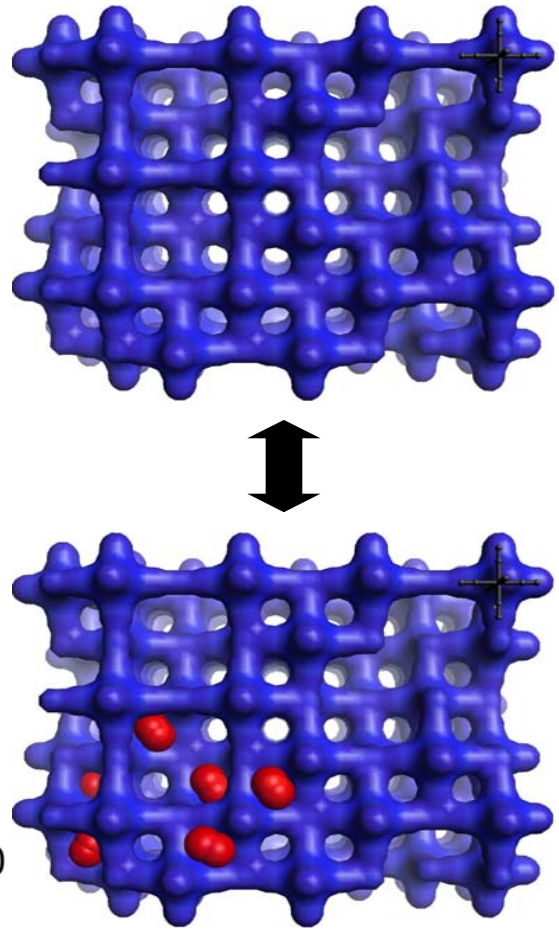
e.g.
$Mn^{II}_3[Co^{III}(CN)_6]_2$

N_2 Sorption

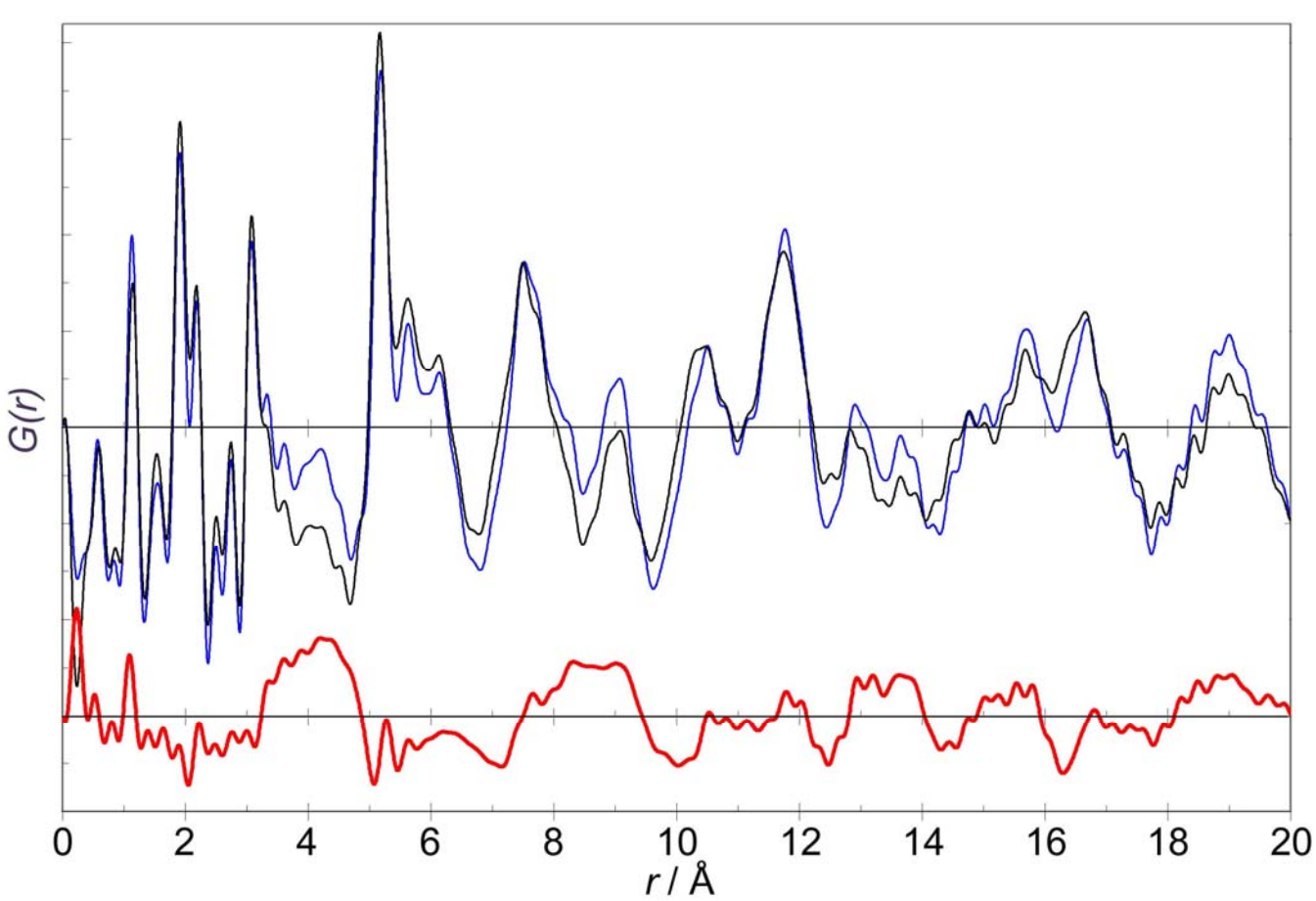

0.3%
0.2%
0.1%
0.0%
-0.1%
-0.2%
-0.3%
Relative Change in Lattice Parameter
50
100
150
200
250
300
350
400
Temperature/K
N2
Under He
Mn^II_3[Co^III(CN)6]2
Prussian Blue

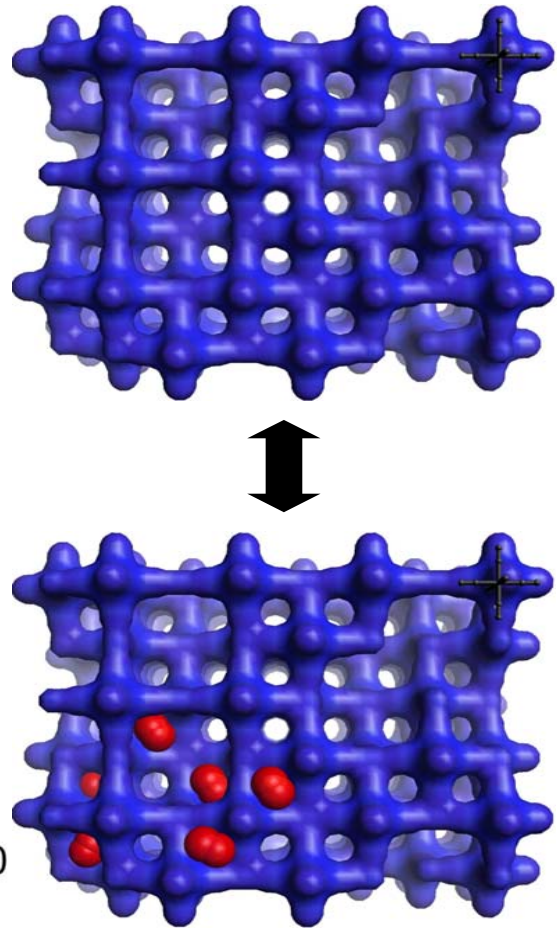
Differential PDF



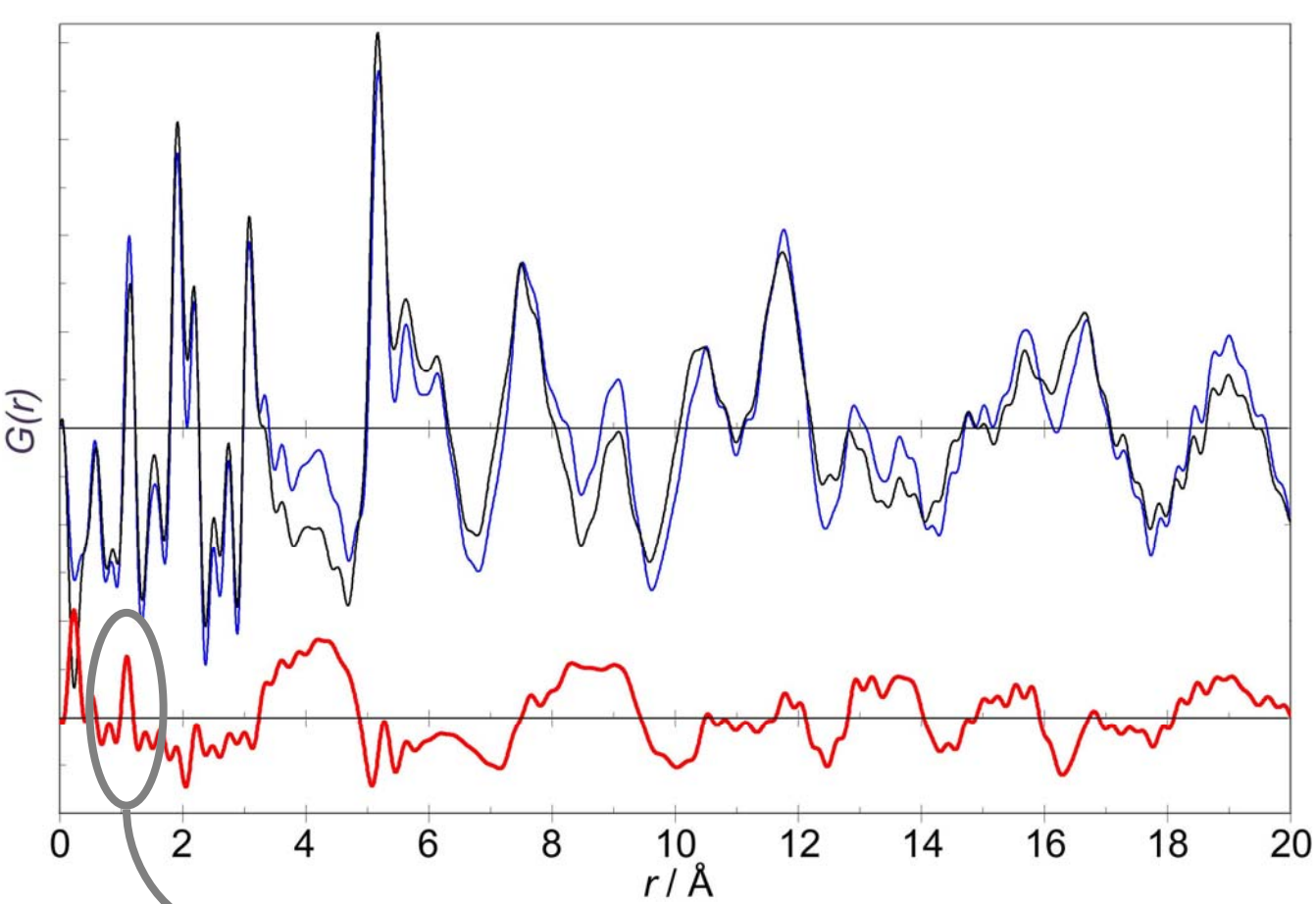


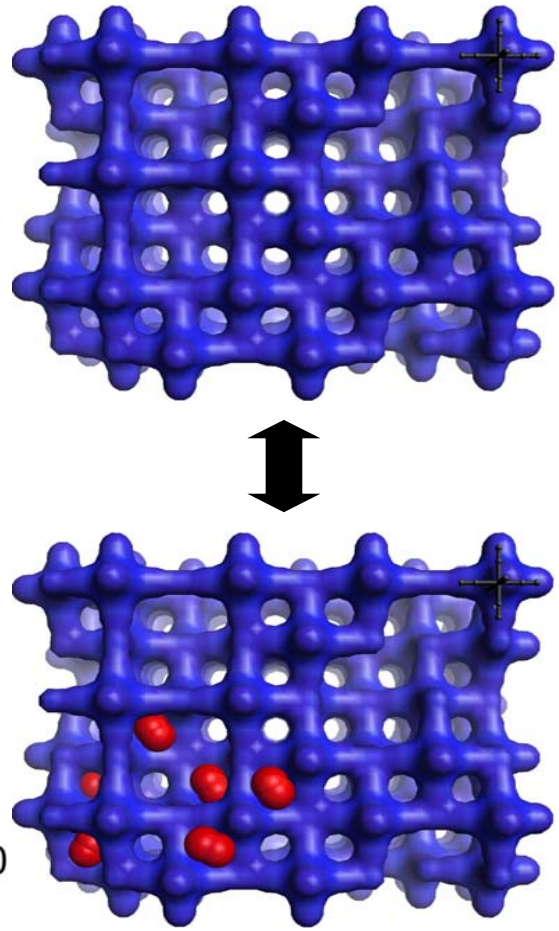
Differential PDF





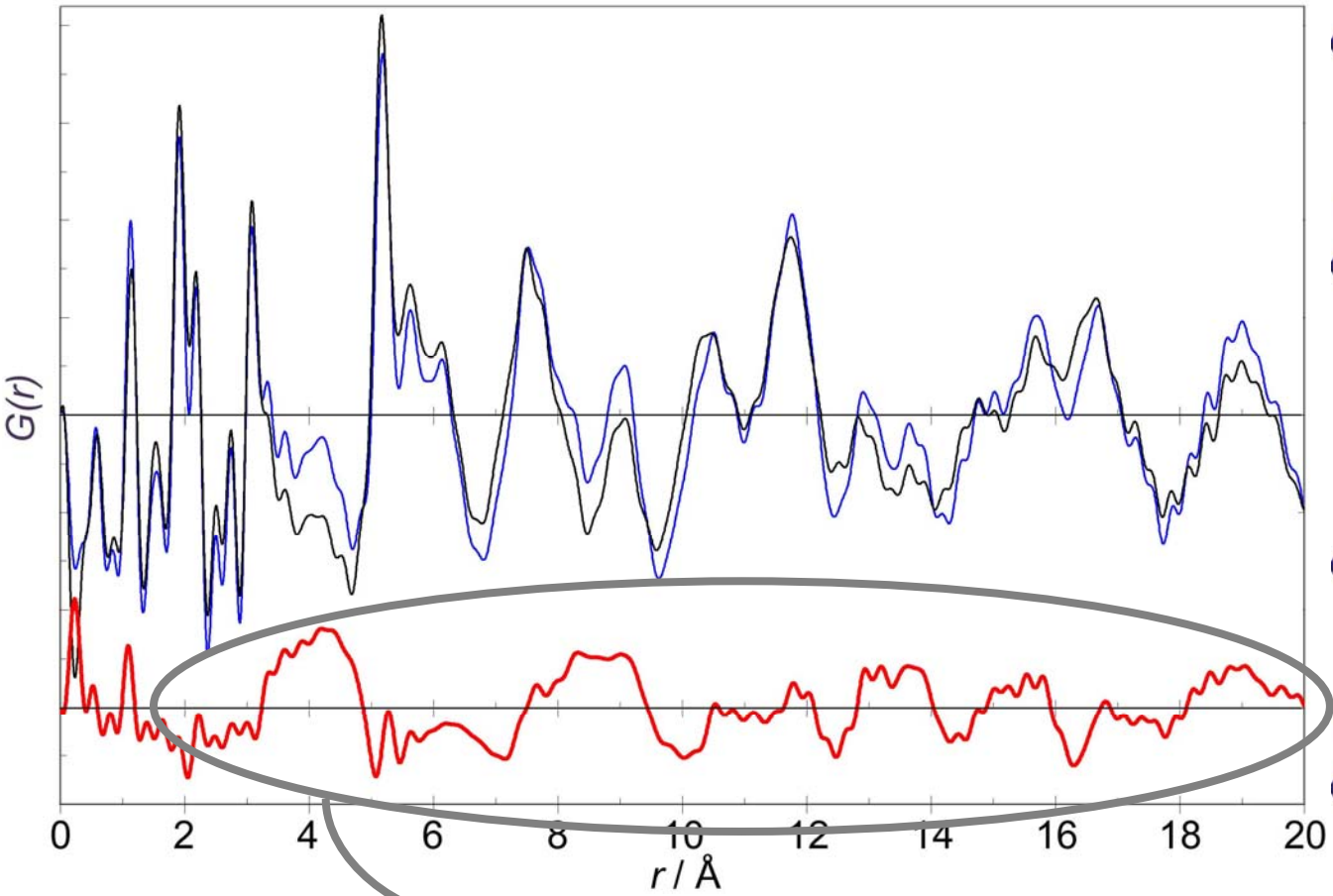
Differential PDF

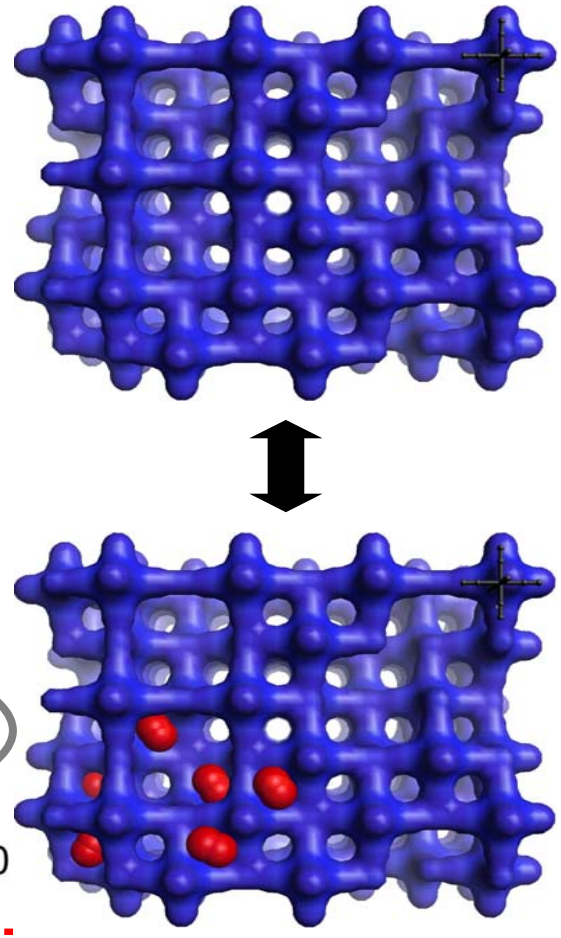




N-N distance in N_2 molecule

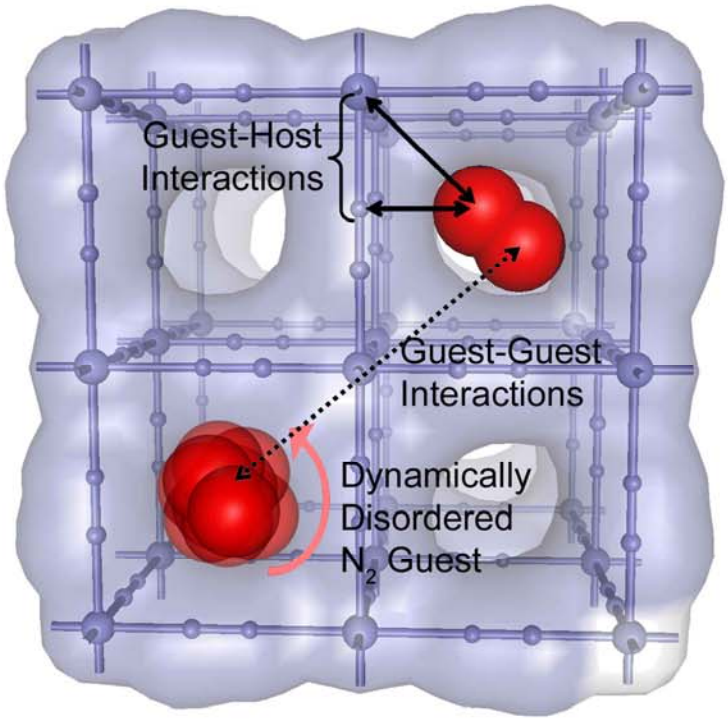
Differential PDF

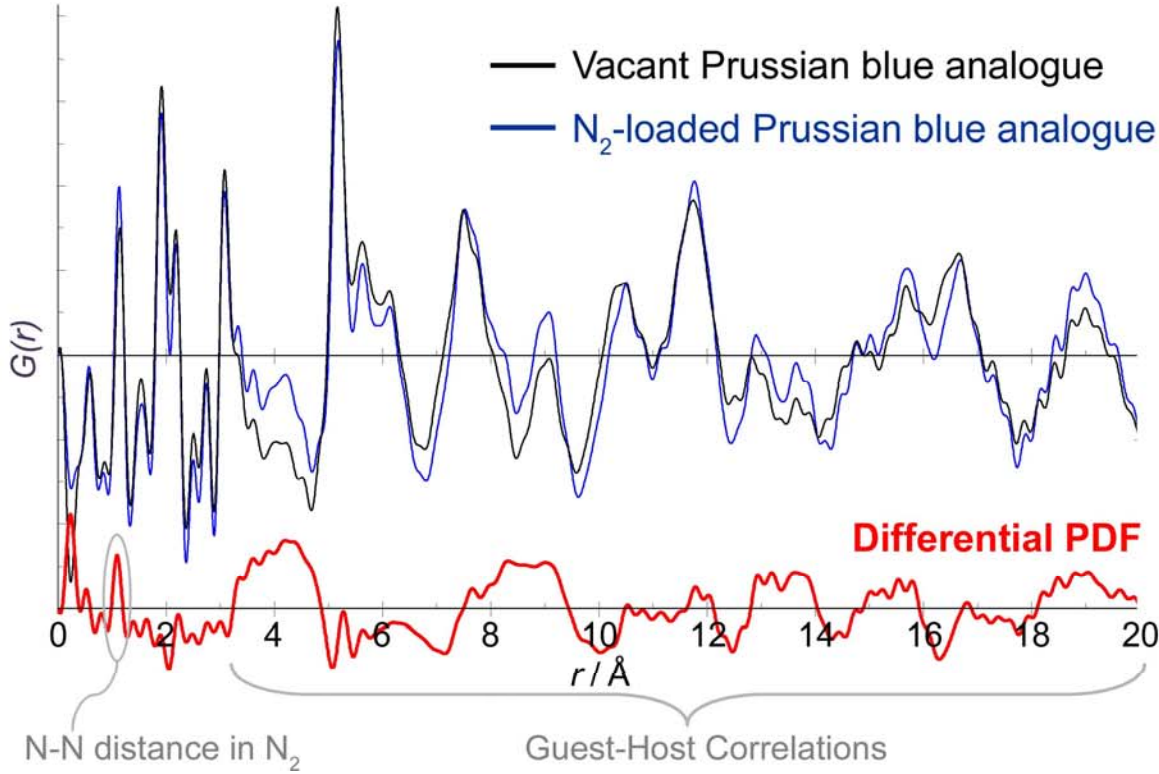




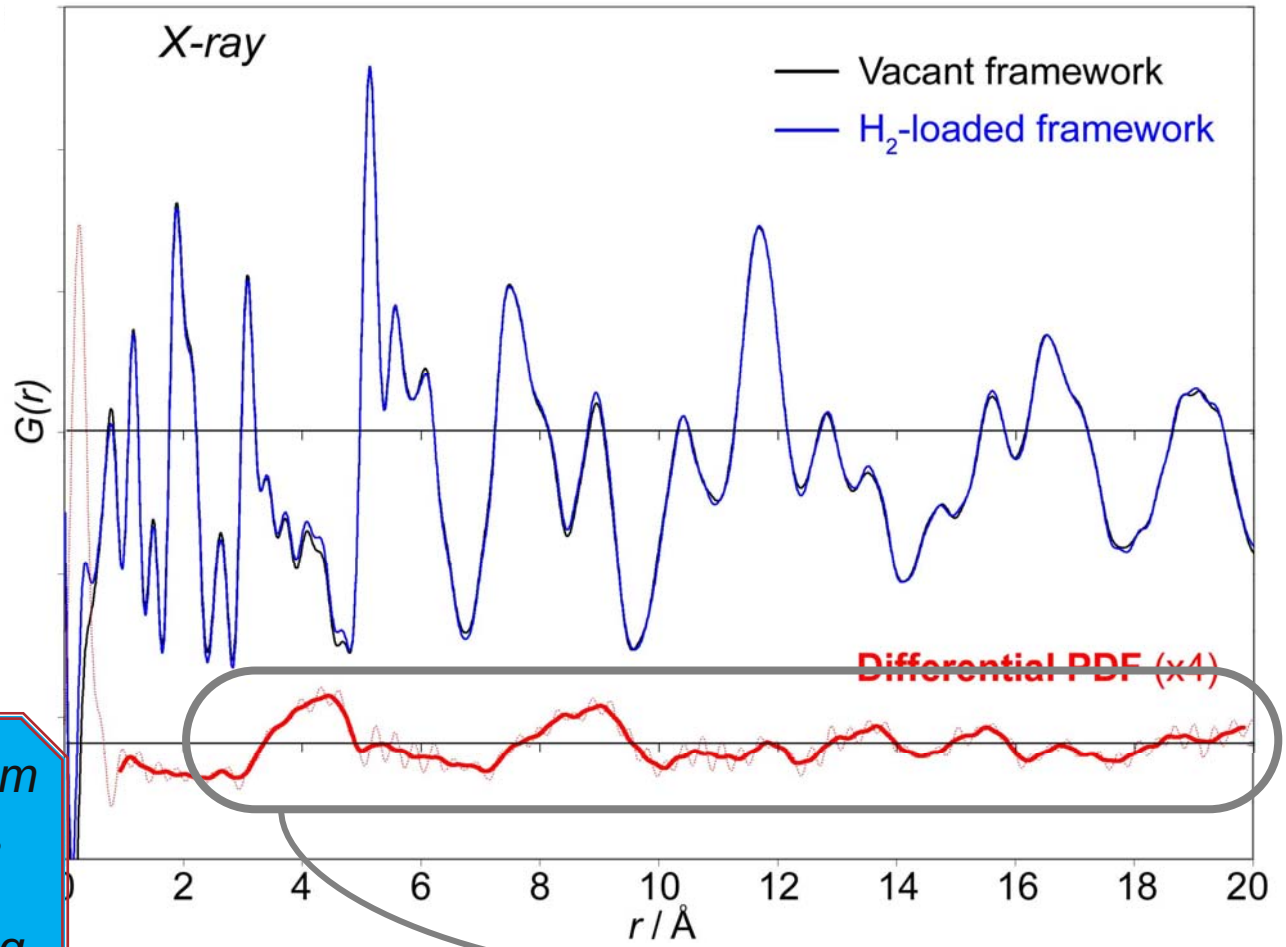
N-framework & N-N interactions

Differential PDF





Hydrogen Differential PDF

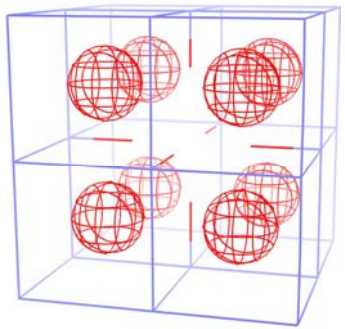


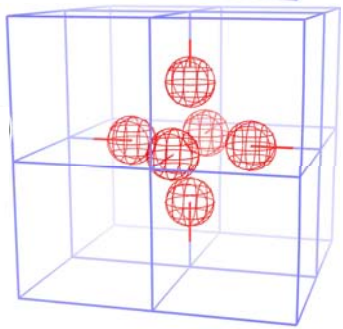
*Contribution from disordered H_2 evident from **X-ray** scattering*

H_2-framework interactions

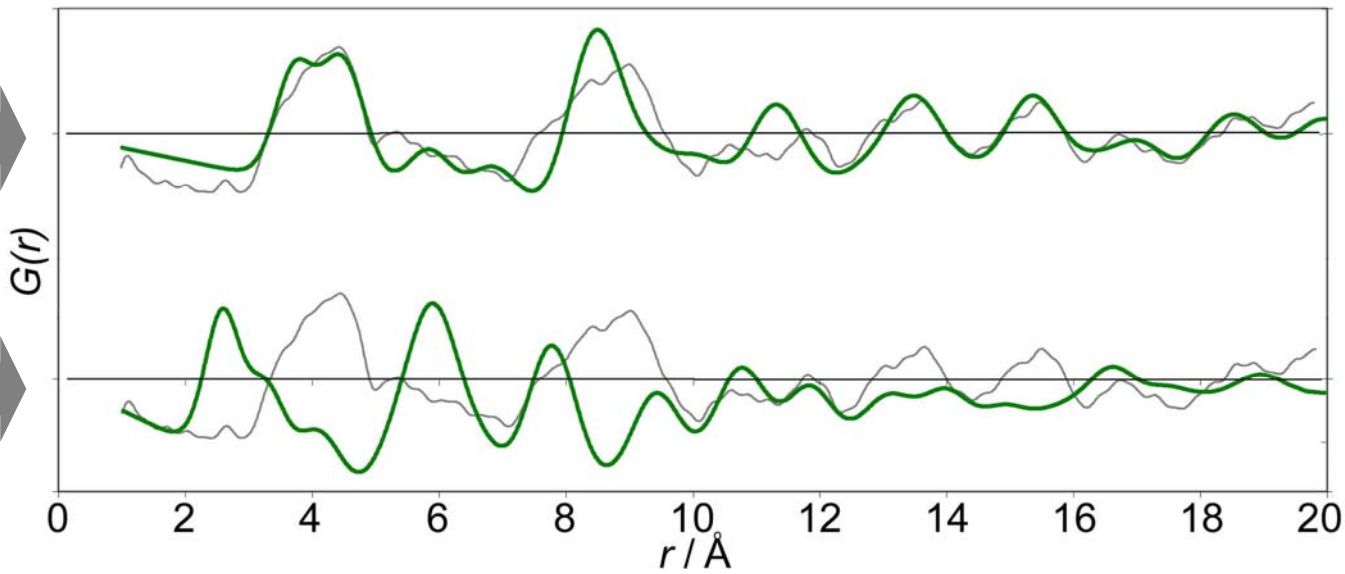
Structural Models

van der Waals interactions only



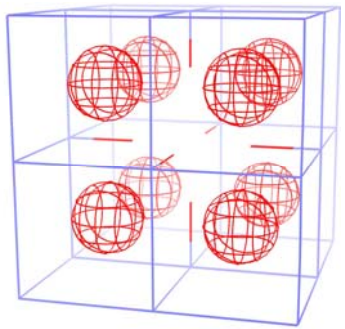


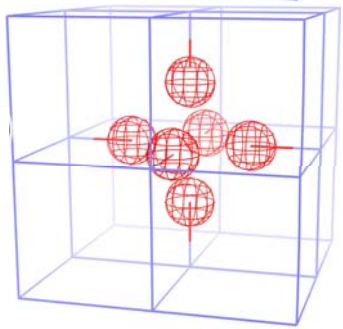
Binding at open metal sites



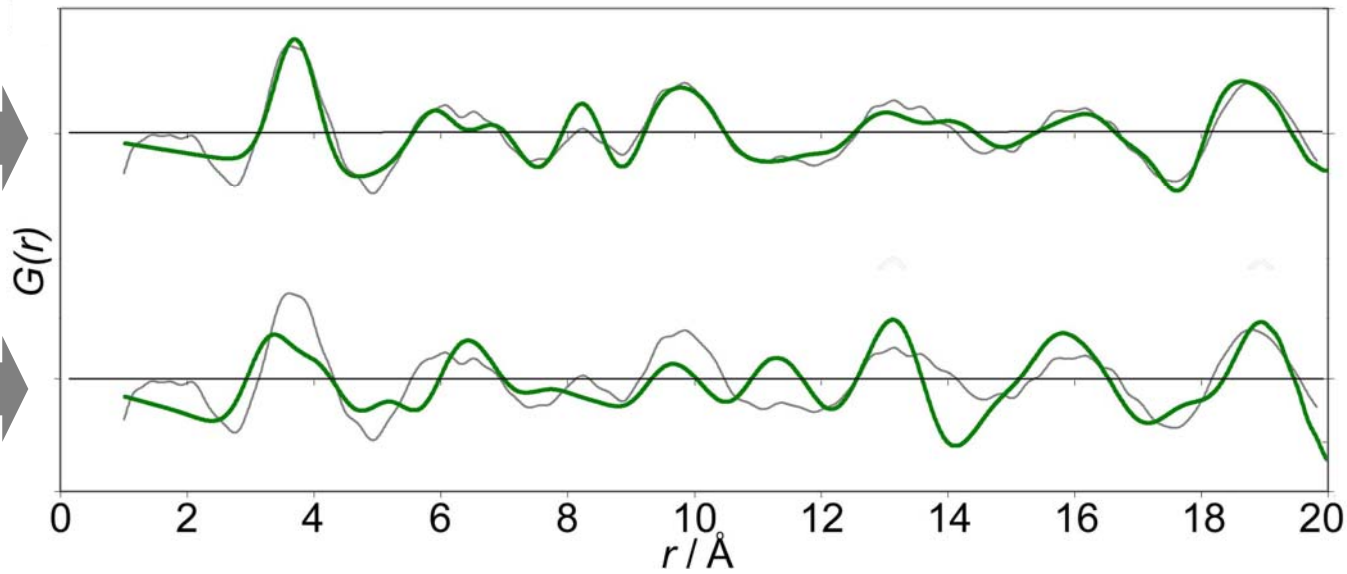
Structural Models

van der Waals interactions only

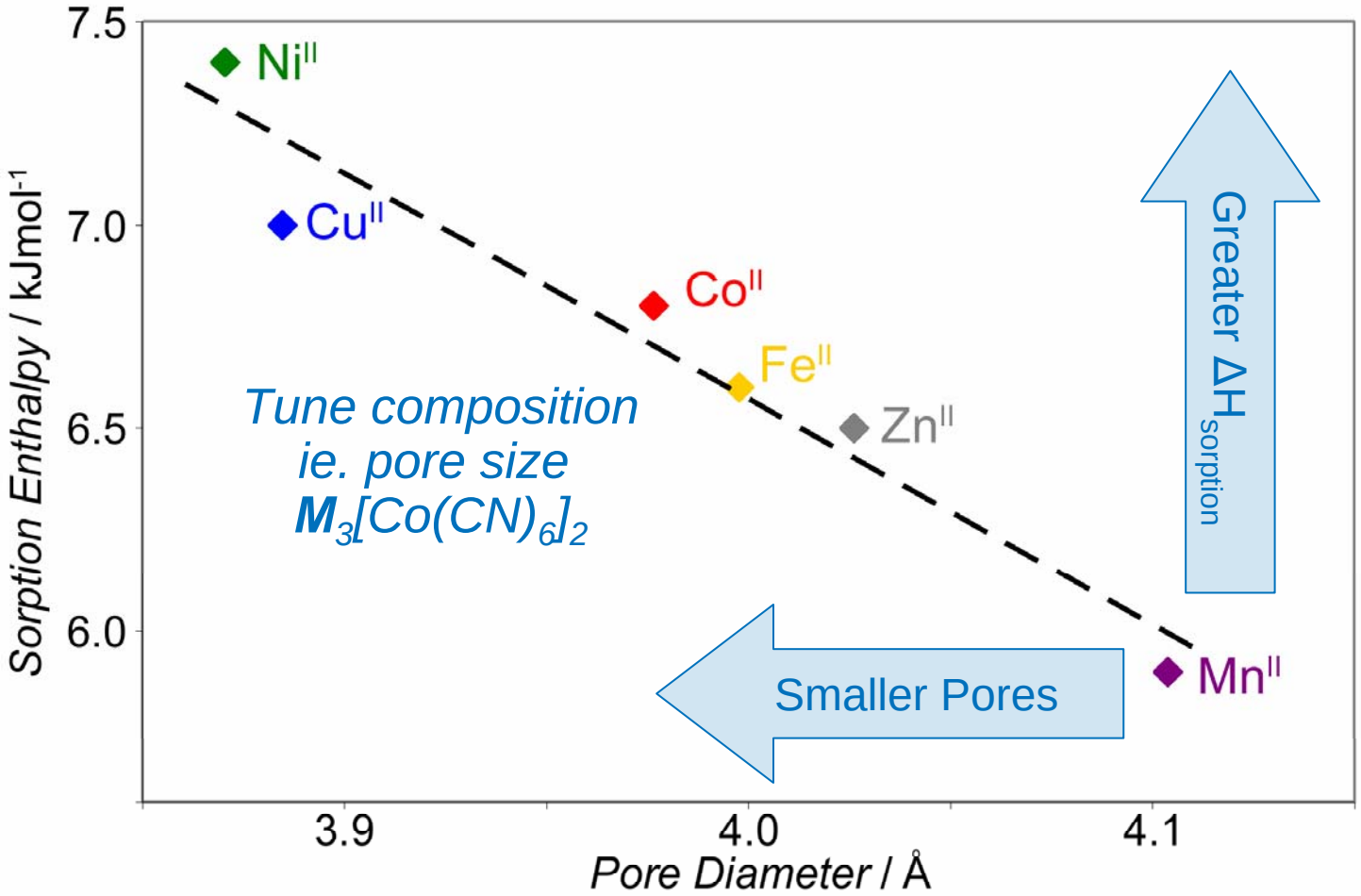




Binding at open metal sites



Enhancing Sorption



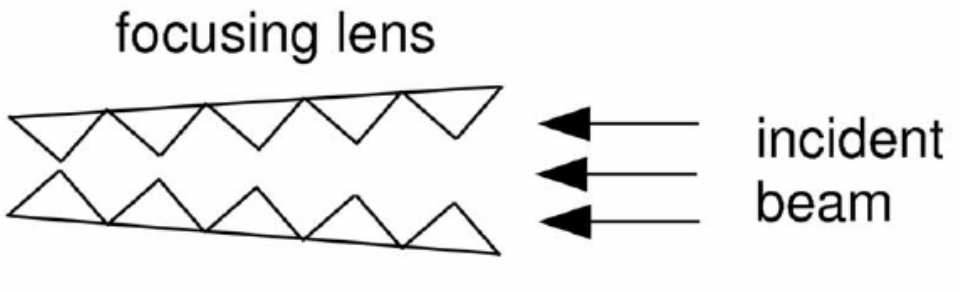
Applications of Micro-focused High-Energy X-rays (available at 1-ID at the APS)

-High pressure Studies from Diamond Anvil Cells

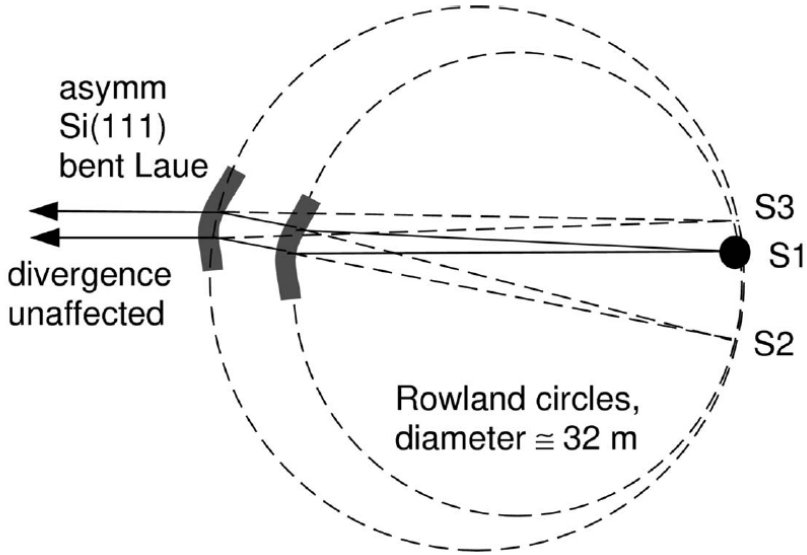
-Spatially Resolved Measurements

Focusing High-Energy X-Rays at 1-ID

Focusing Lens
(Si saw-tooth type*)

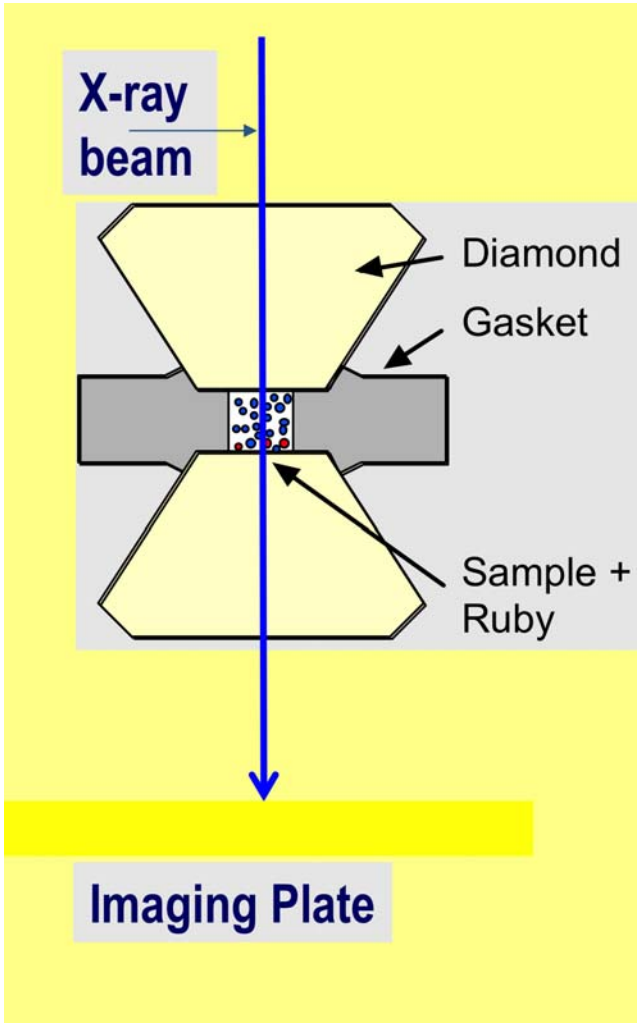


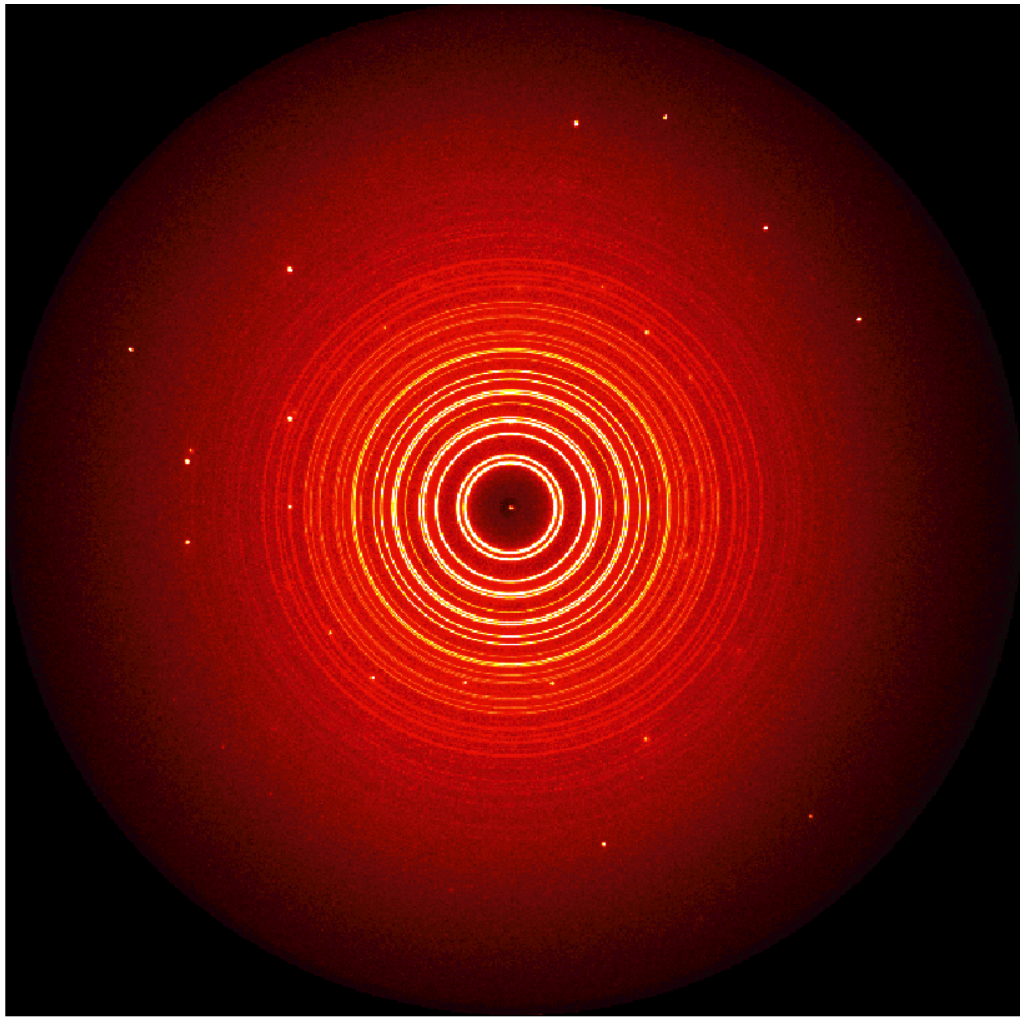
Bent Laue
Monochromator



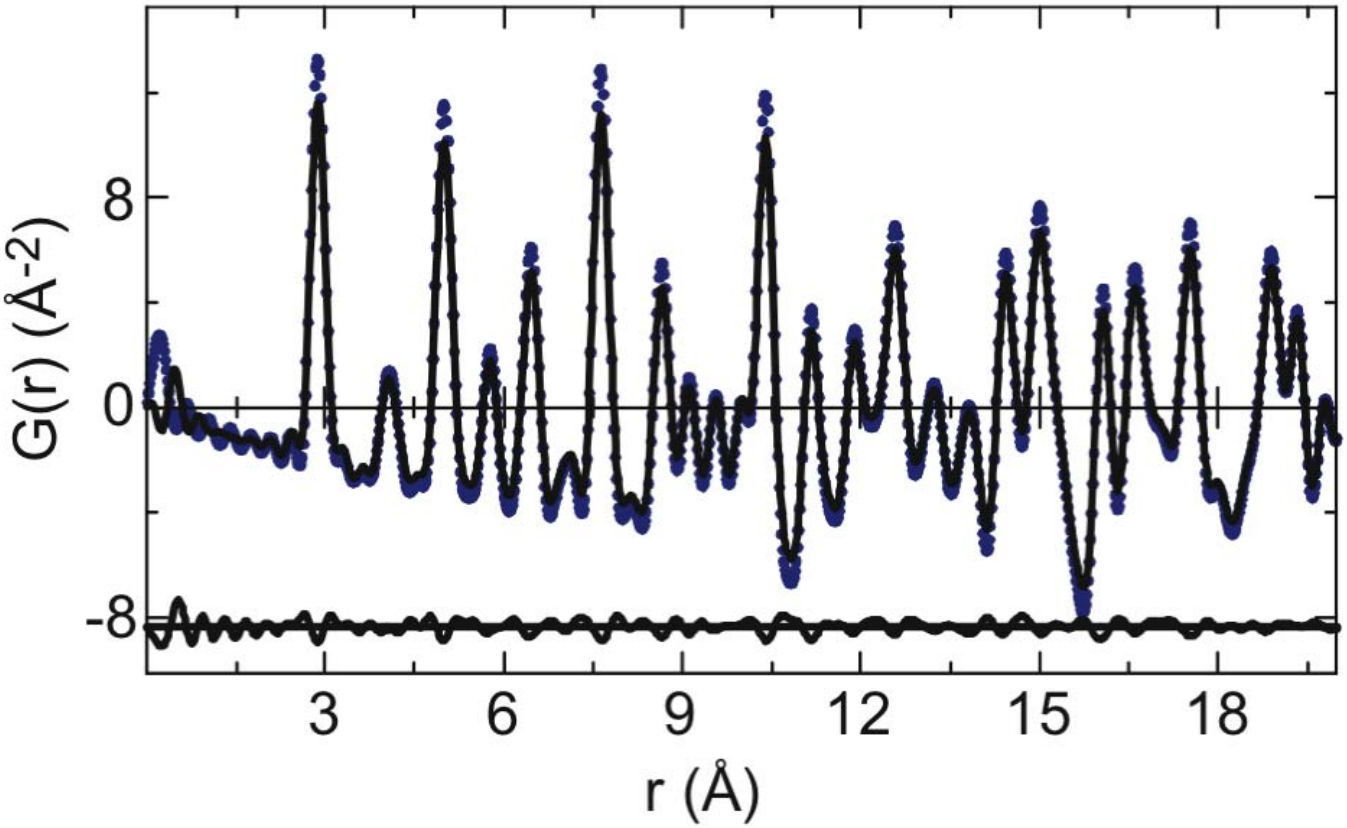
*S. D. Shastri et al., *J. Synchrotron Rad.*, **14**, 204 (2007)

PDF at High Pressures



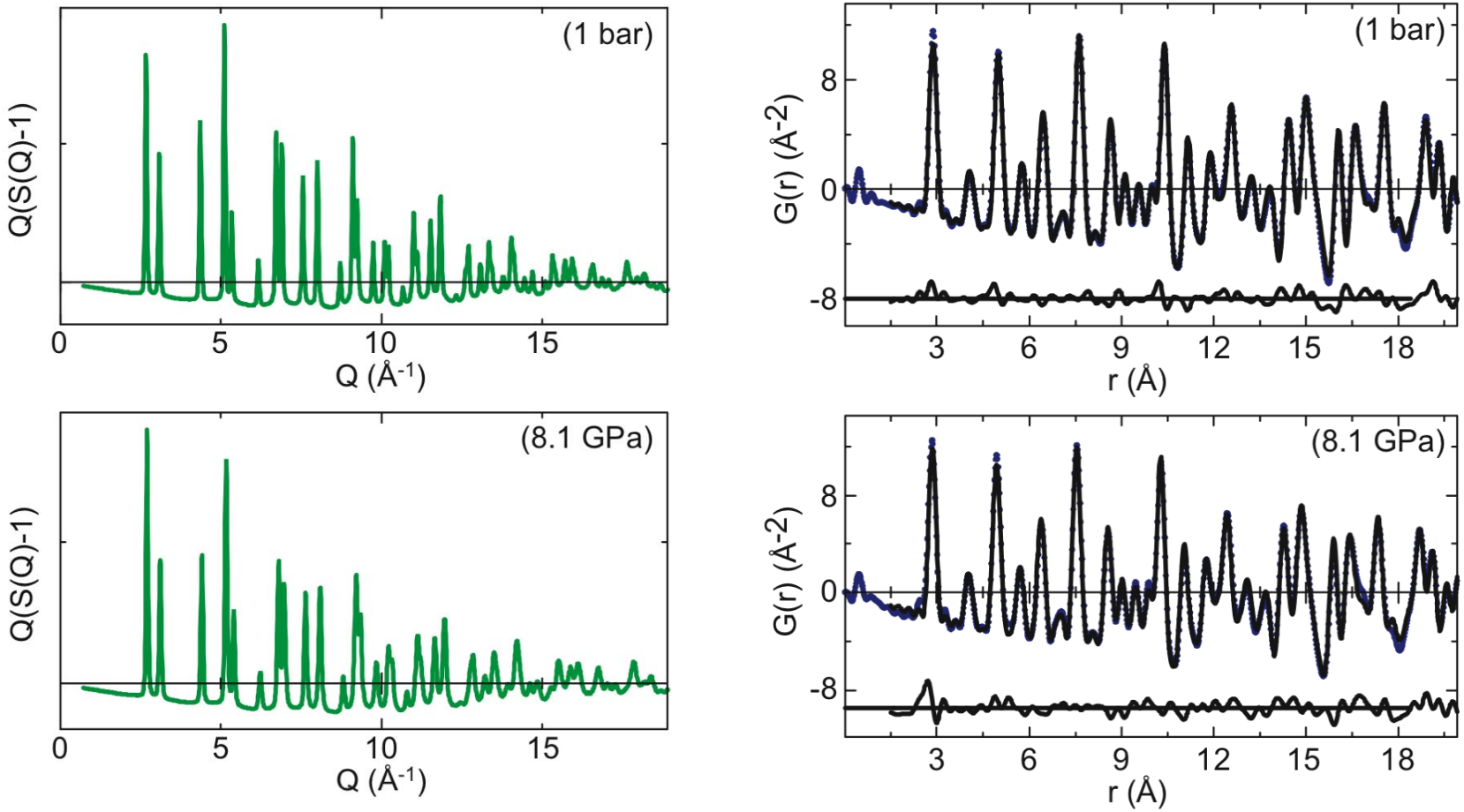


PDF of Gold in the DAC and Measured ex-situ

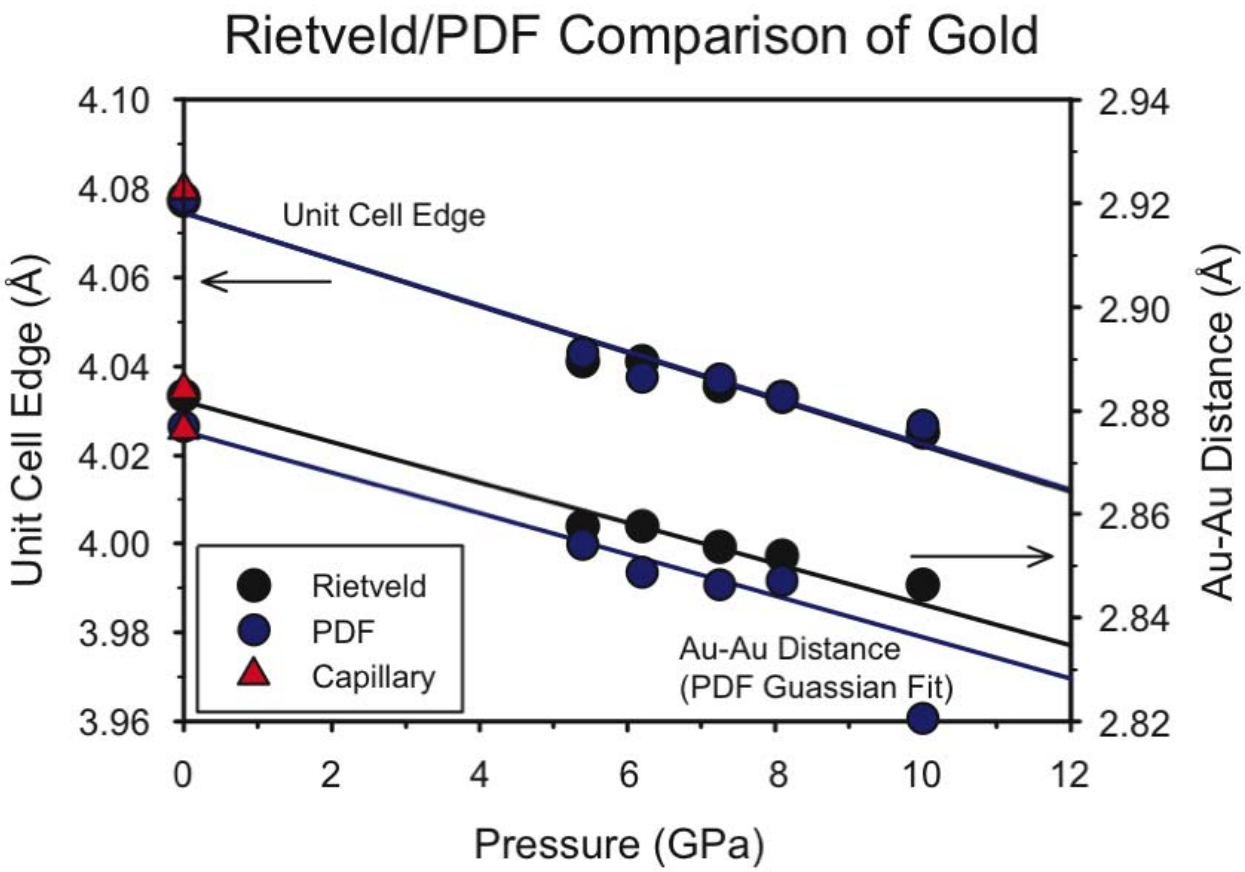


Martin, Antao, Chupas, Lee, Shastri, Parise *Applied Physics Letters* 86 (2005) 061910.

High Pressure PDF



Gold at High Pressures



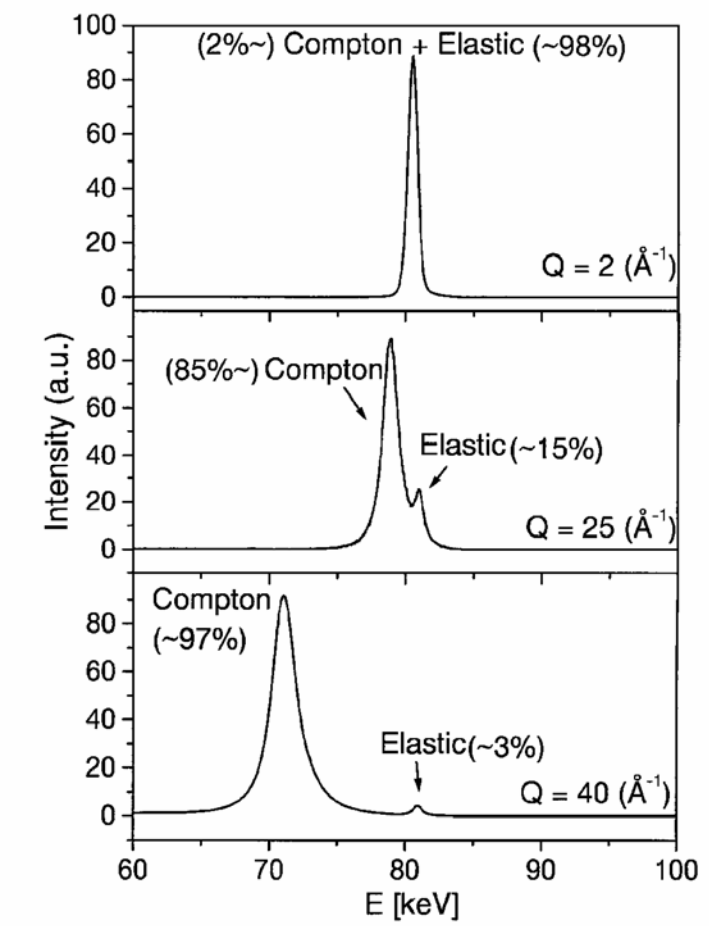
Looking Ahead:
The Potential for Future Instrumentation Developments

-Rapid Energy Resolved Measurements

-Simultaneous Measurements (e.g. combining PDF with SAXS)

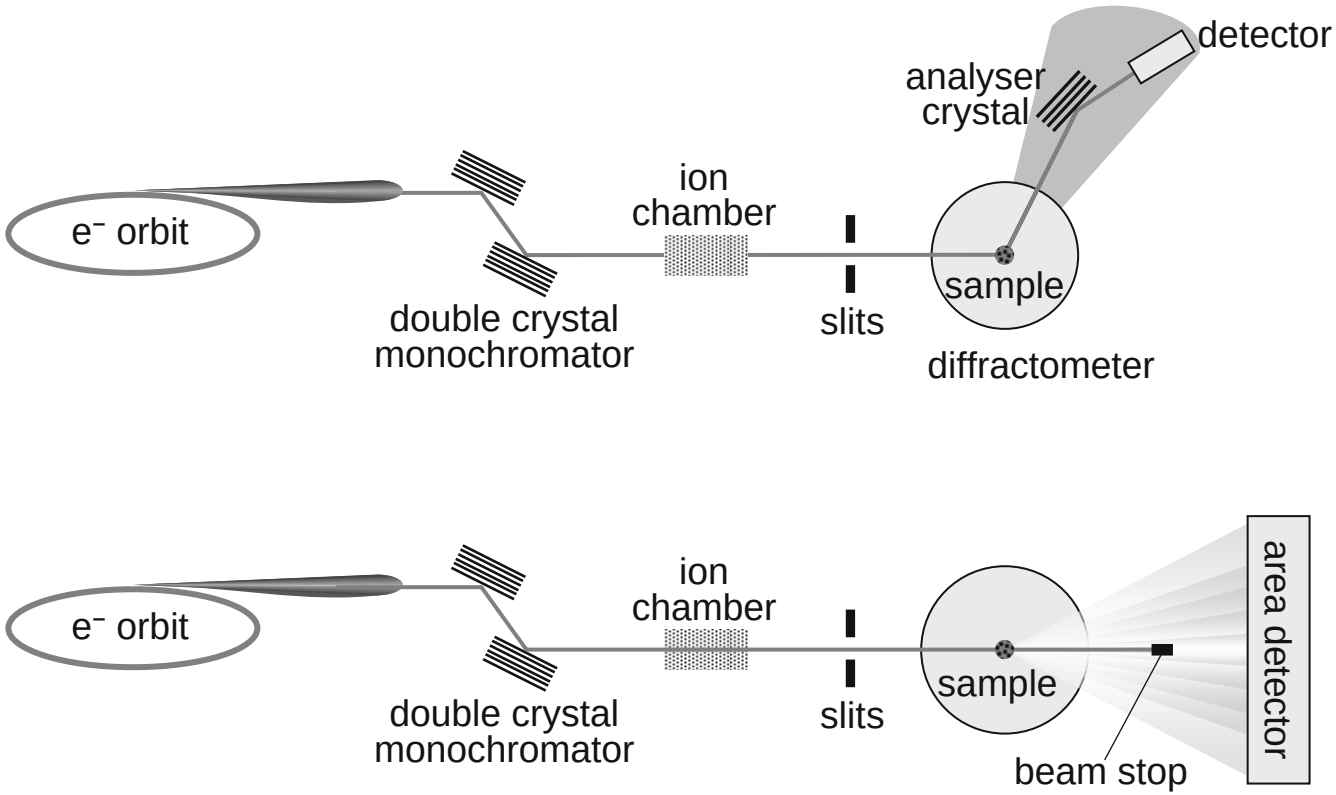
-Anomalous

Compton Scattering

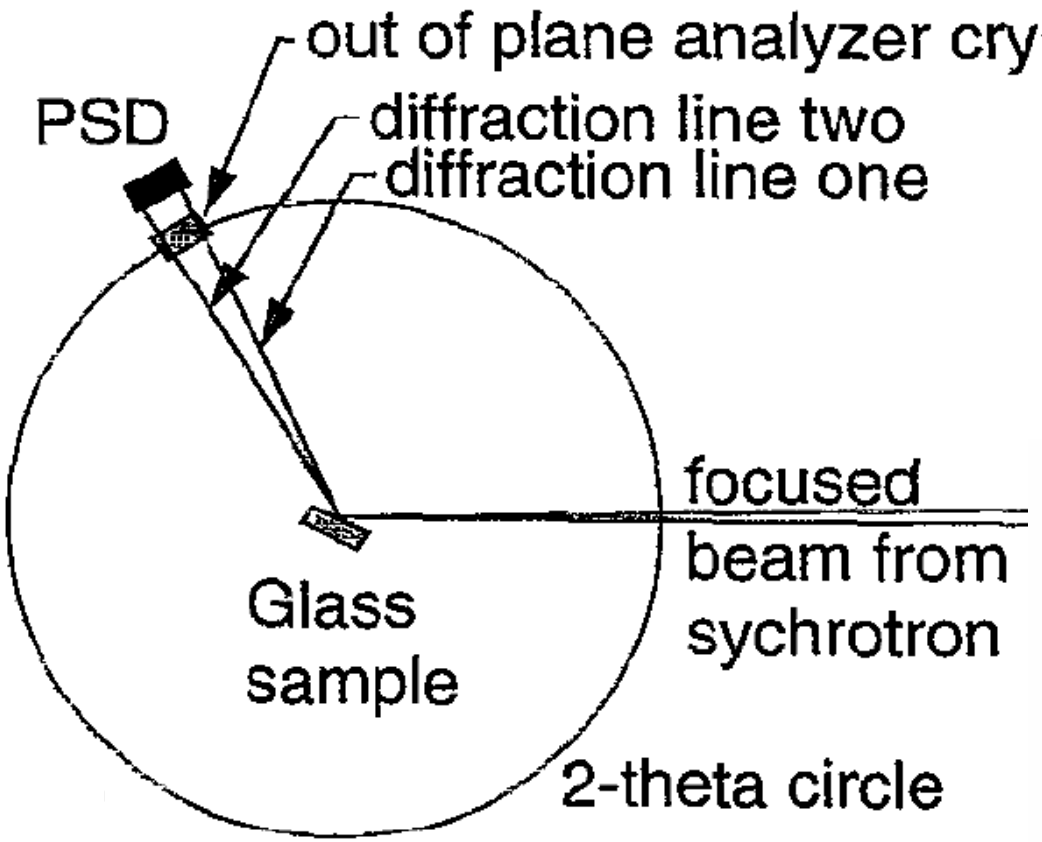


Petkov, Billinge, Shastri, Himmel, *Phys Rev. Lett.* **85**, 3436 (2000)

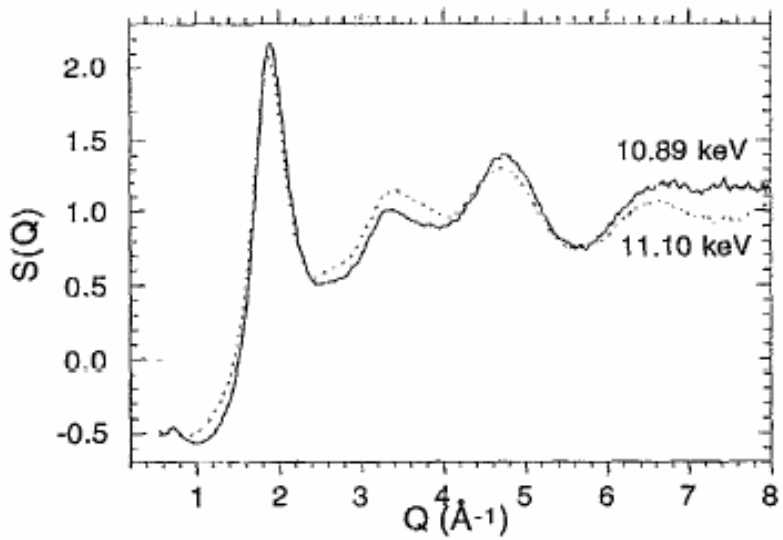
Common Instrumentation Configurations



Rapid Energy Resolved Measurements?



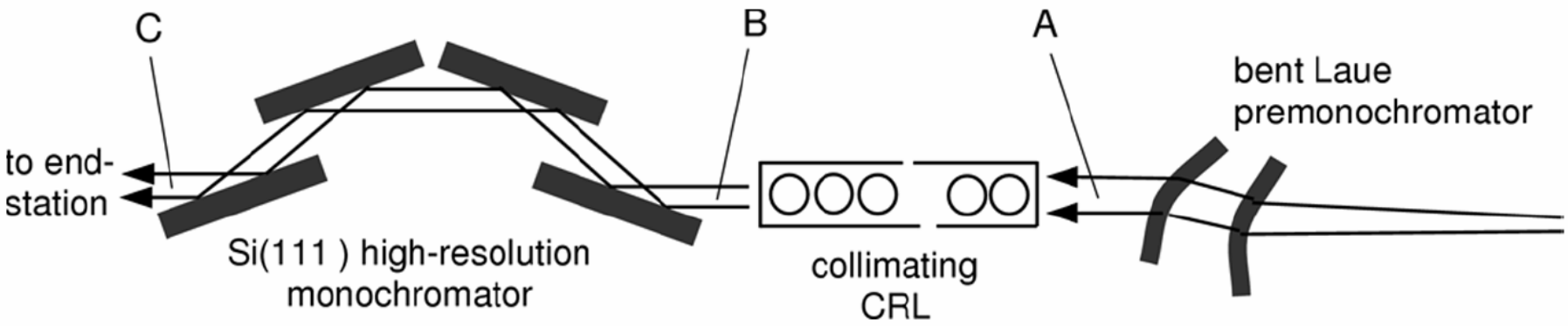
$Cs_2Ge_4O_9$



Beno and Knapp *Review of Scientific Instruments* (1995) 60, 1308-1310.

High Energy Resolution Optics for High-Energy X-rays:
Potential for Anomalous PDF Measurements

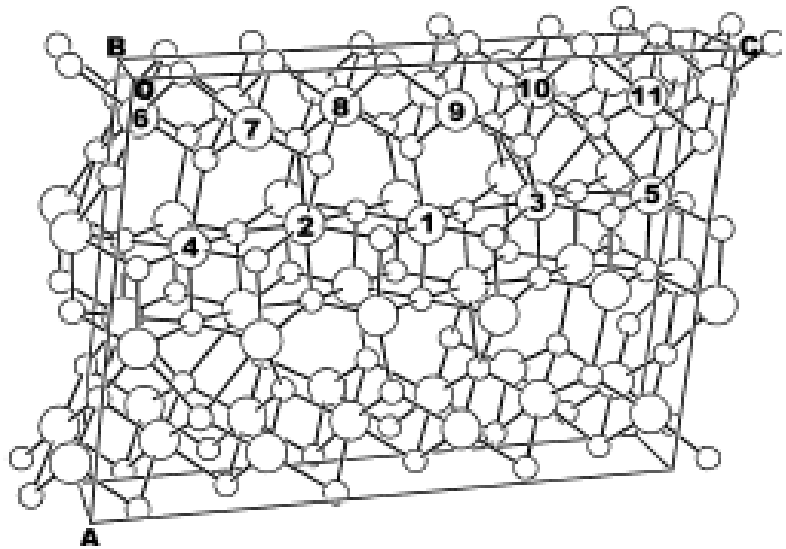
S. D. Shastri, *J. Synchrotron Rad*., **11**, 150 (2004)



Example of High-Energy Resonant Scattering

- Ion Distribution in $Pb_5Bi_6Se_{14}$
- Bi and Pb distributed over 11 crystallographically unique sites

Zhang, Wilkinson, Lee, Shastri, Shu, Chung, Kanatzidis, *J. Applied Crystall.*, **38**, 433 (2005)



Acknowledgements

Karena W. Chapman (XSD, ANL)
Evan R. Maxey (XSD, ANL)
James Richardson (IPNS, ANL)
Peter L. Lee (XSD, ANL)
Guy Jennings (XSD, ANL)
Mark Beno (XSD, ANL)
Sarvjit Shastri (XSD-ANL)
Clare P. Grey (Stony Brook)
John B. Parise (Stony Brook)
C. David Martin (XSD, ANL)
Gabrielle Long (XSD, ANL)
John W. Cahn (NIST)
Leo Bendersky (NIST)
Simon Billinge (MSU)
Xiangyun Qiu (MSU)

Work performed at the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.