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... for a brighter future

U.S. Department of Energy

UChicago ▶ Argonne LLC

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Extreme Pair-Distribution-Function Measurements

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X-ray Science Division
Argonne National Laboratory

Talk Overview

(1) PDF Instrumentation (at the APS)

(2) Emerging scientific opportunities

- "Time Resolved" measurements

- Measurements requiring high sensitivity & applications in Hydrogen research

-Fossil Fuels

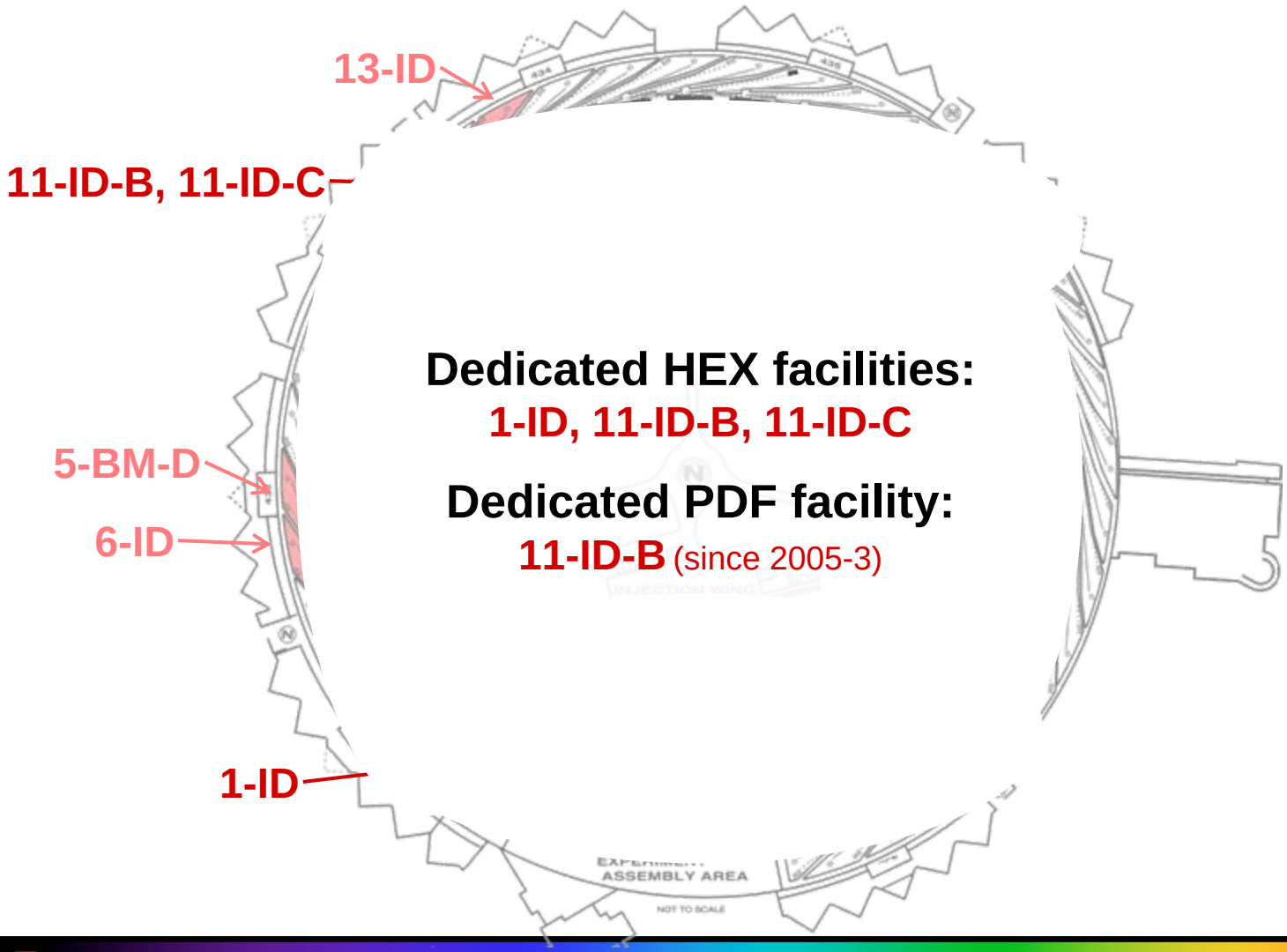
- PDF at High Pressures (DAC)

- Spatially resolved measurements

(3) Potential instrumental advances & future opportunities

-Where do we go from here?

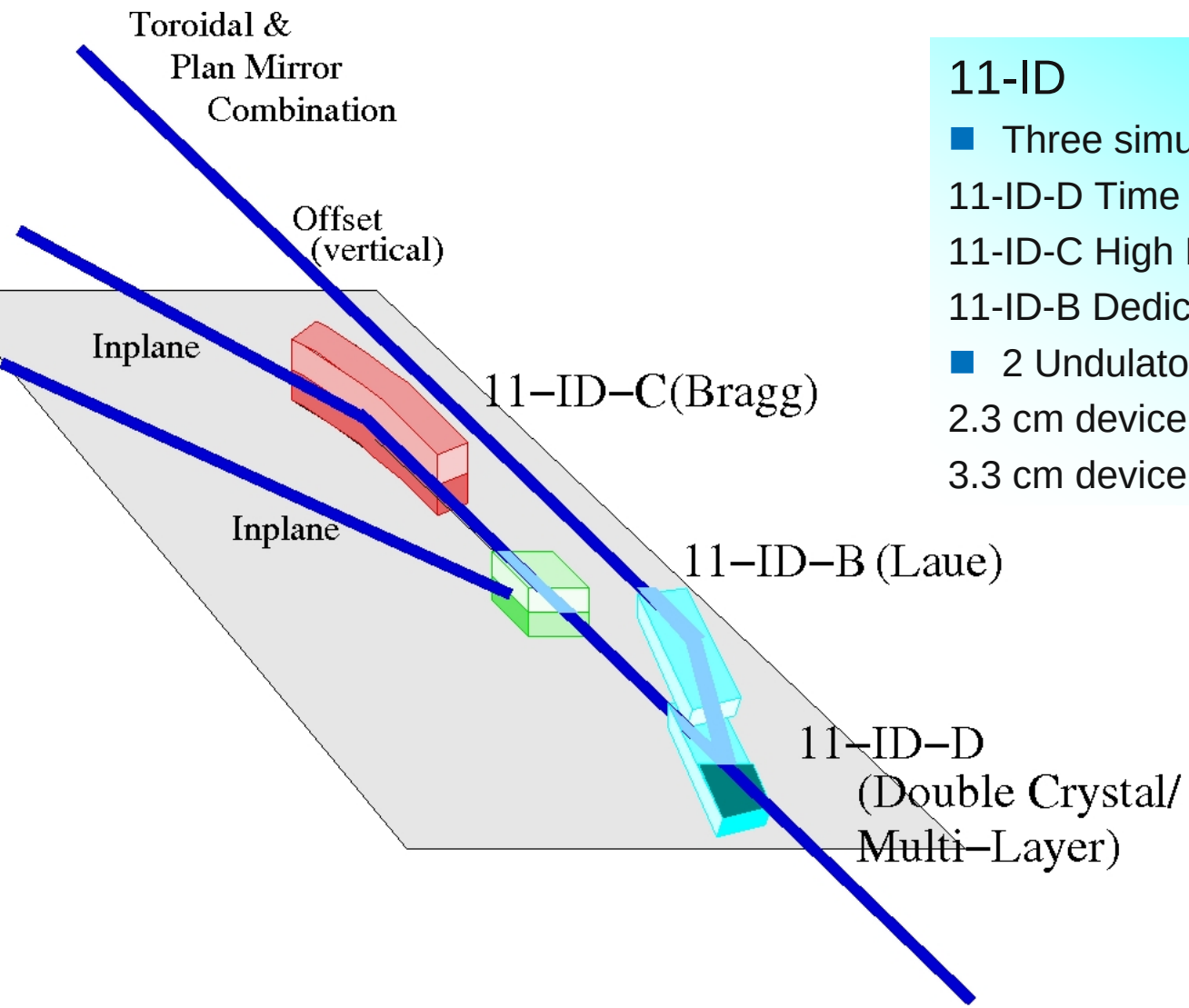
High Energy X-rays at the APS



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

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

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

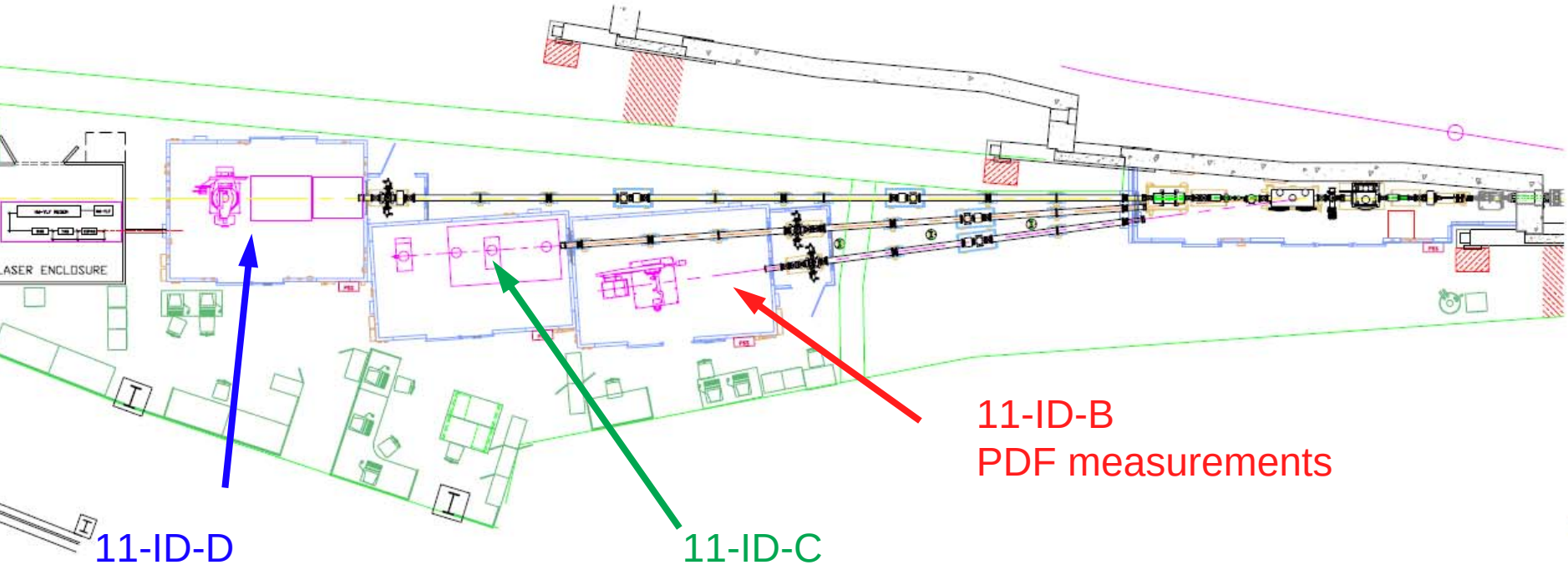
11-ID-B Dedicated PDF Beamline

- 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

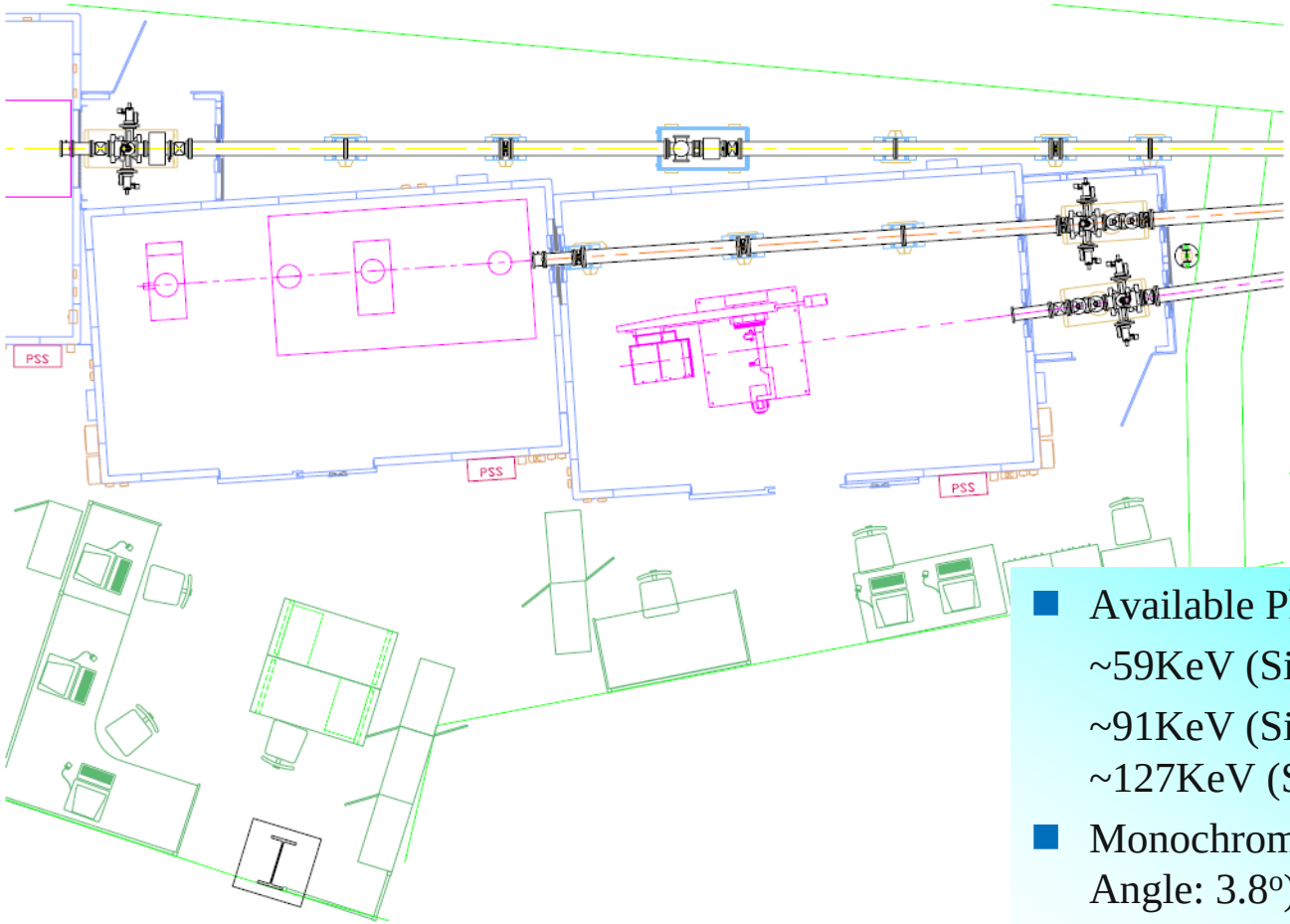


11-ID-B
PDF measurements

11-ID-D
Time-Dependent pump-probe
XAFS, SAXS, WAXS

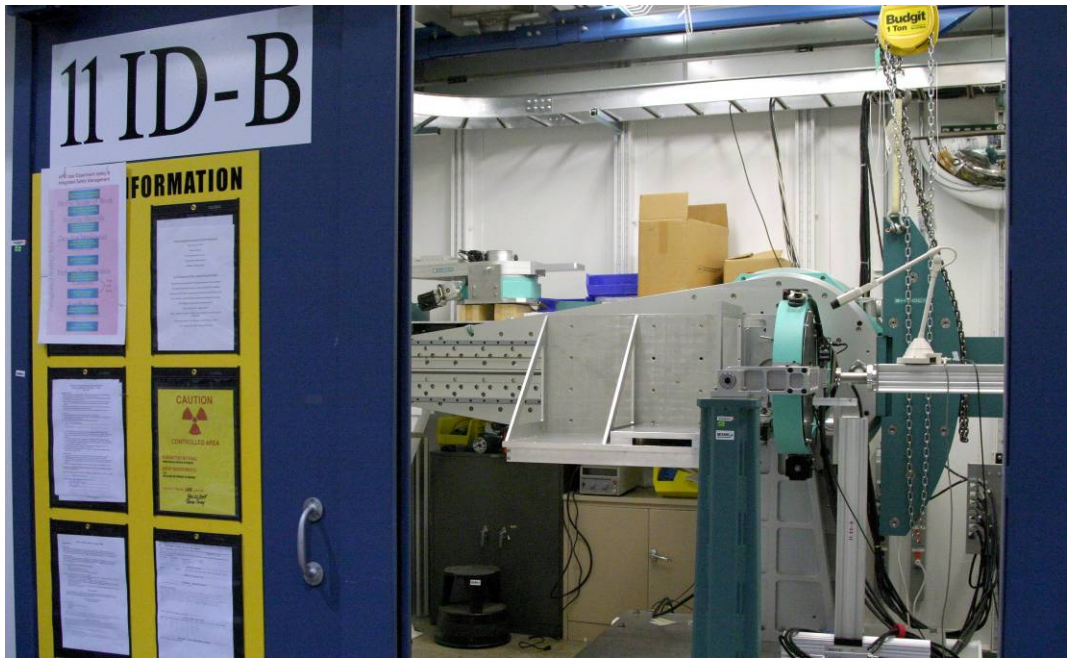
11-ID-C
High Energy Scattering

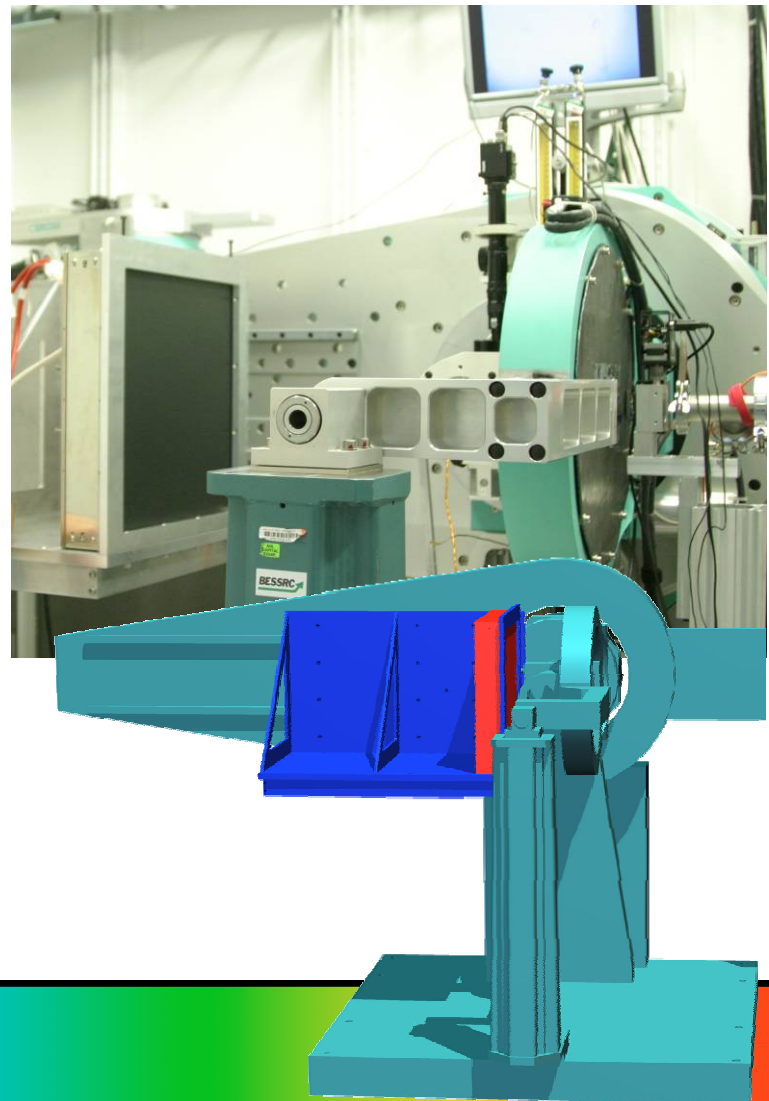
High Energy X-rays at the APS



- Available Photon Energies:
  ~59KeV (Si311)
  ~91KeV (Si 511),
  ~127KeV (Si 711),
- Monochromator: Laue crystal (Fixed Bragg Angle: 3.8^{o})
- Max beam size: 3 x 2 mm^{2}
- Flux: 10^{12} Photons/s

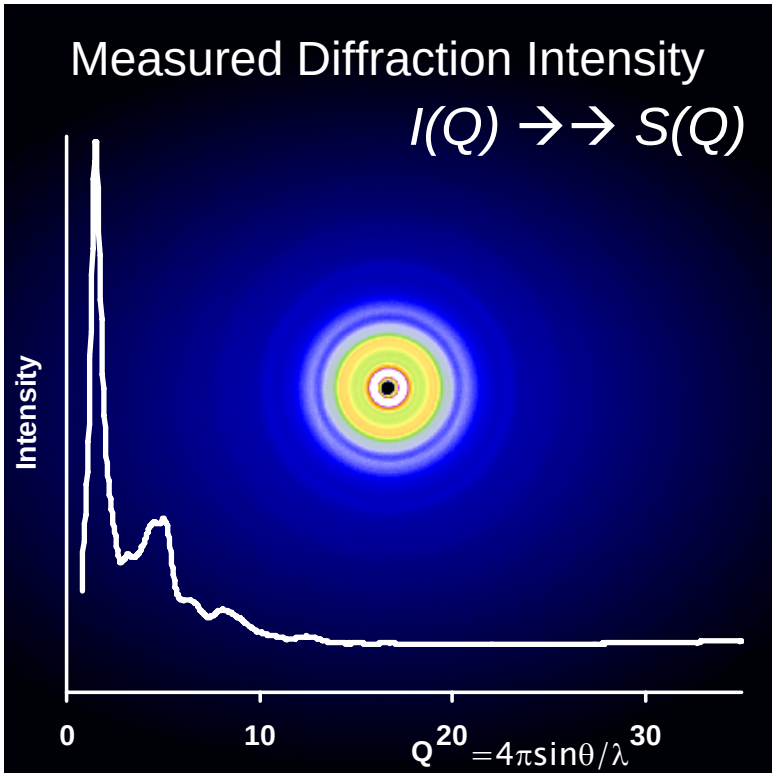
Dedicated PDF facility at the APS

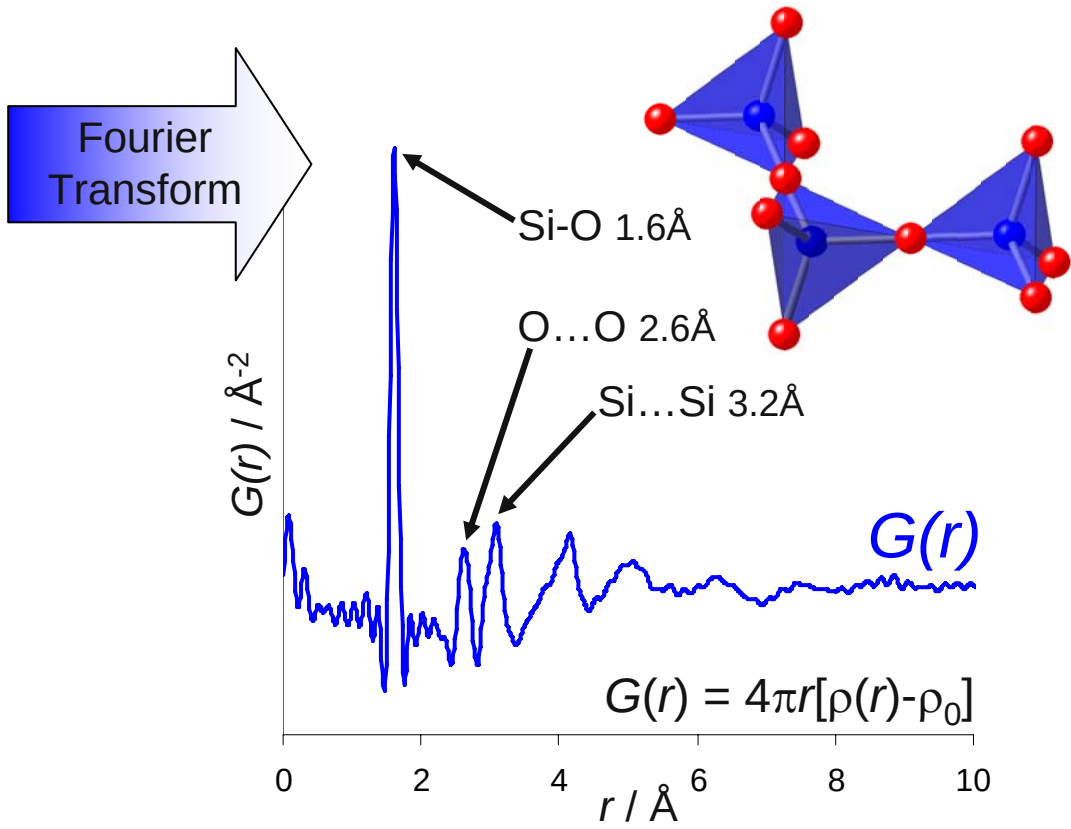




The Pair Distribution Function Method

- 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.

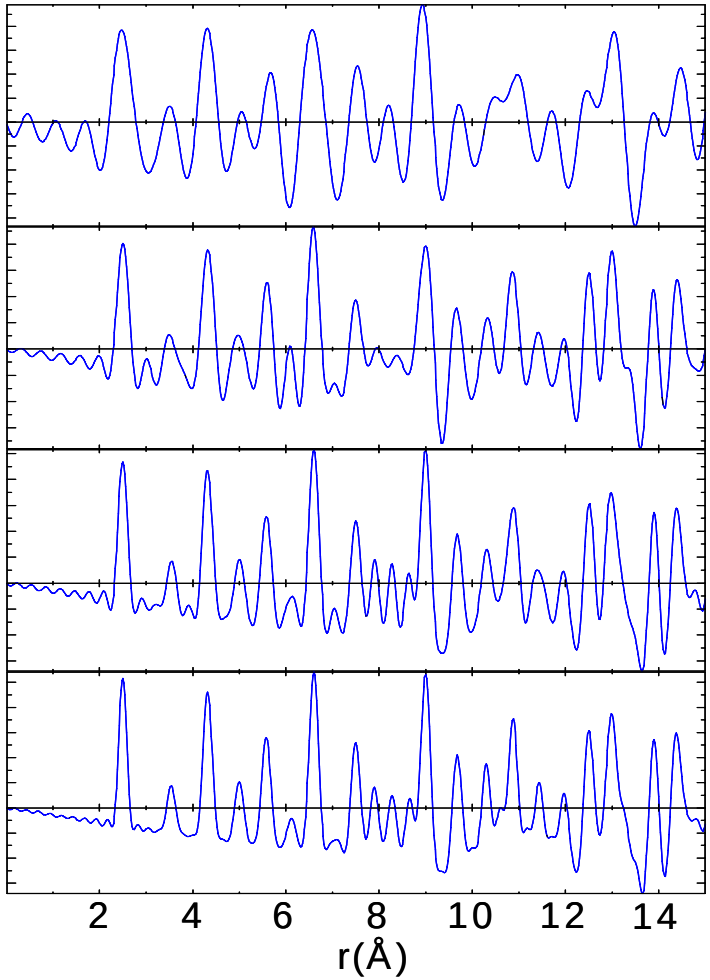
High Real Space Resolution PDFs: The Need for High Q Measurements

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

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



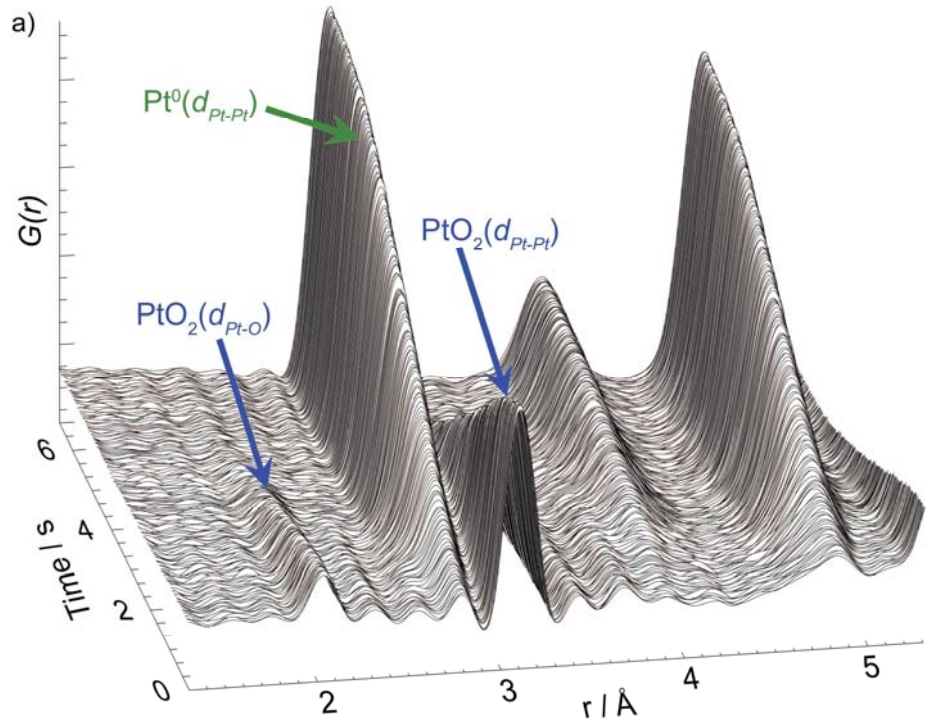
Q_{max} = 10 Å^{-1}

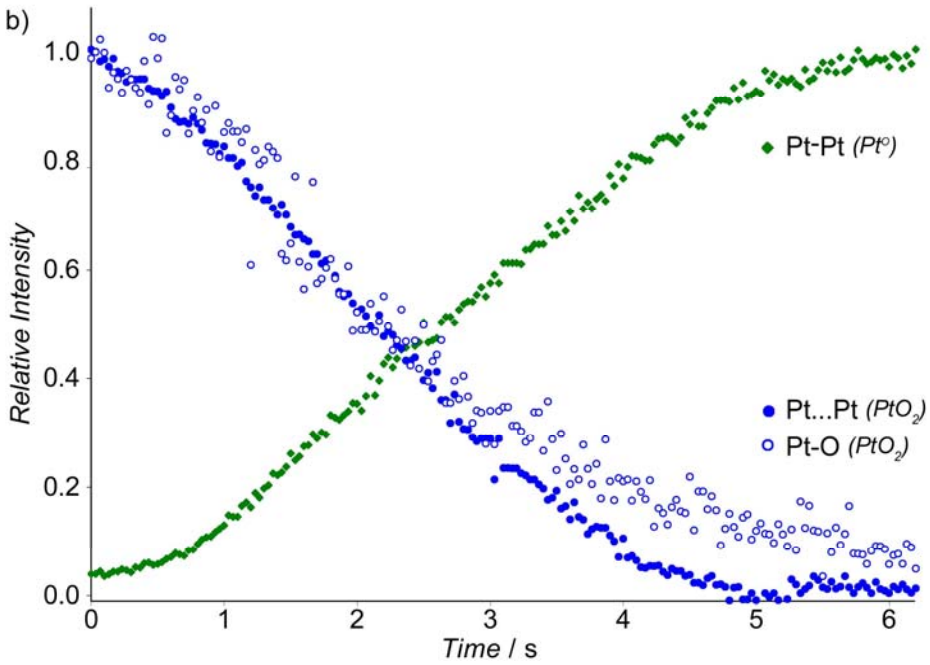
Q_{max} = 15 Å^{-1}

Q_{max} = 20 Å^{-1}

Q_{max} = 25 Å^{-1}

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

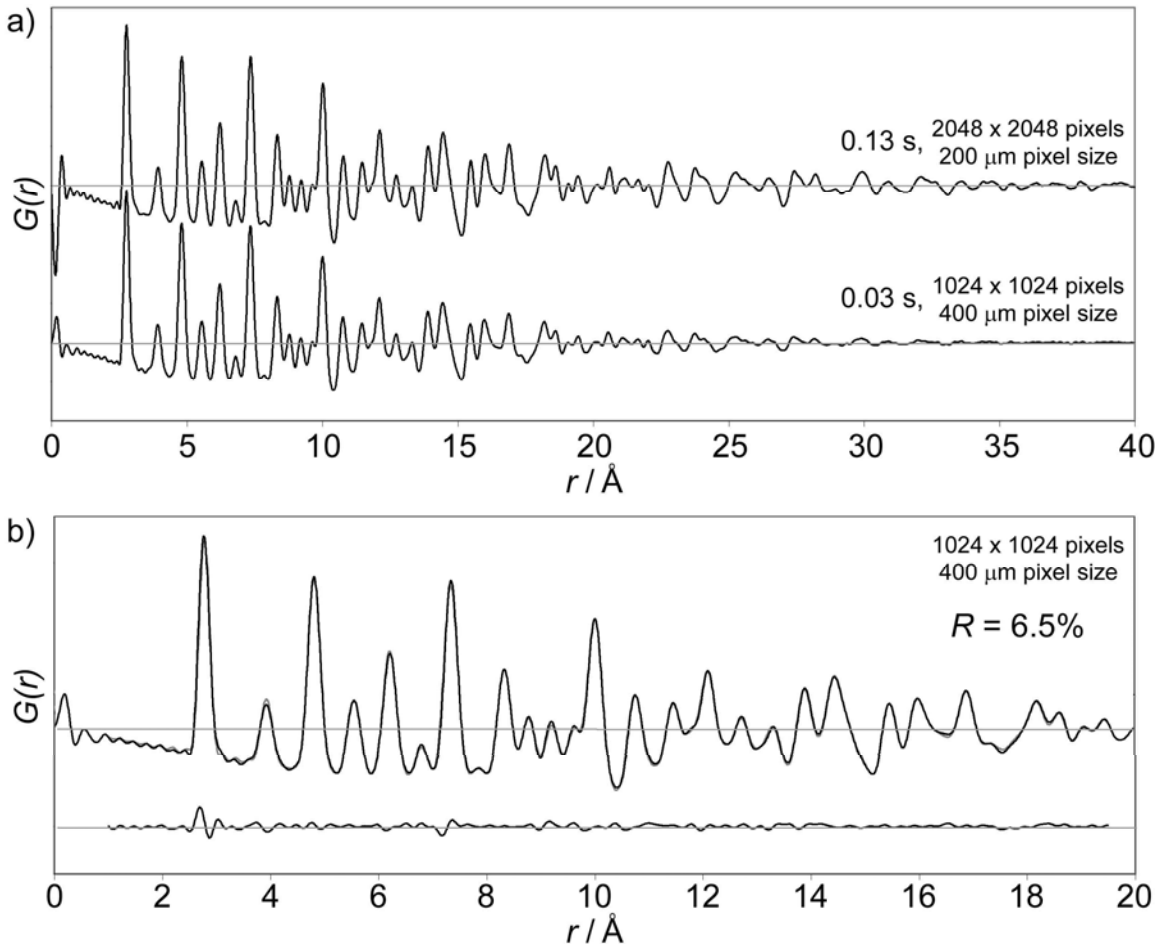




Data can be collected in only 30 ms

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

In-situ measurements: The reduction of PtO_2 to Pt

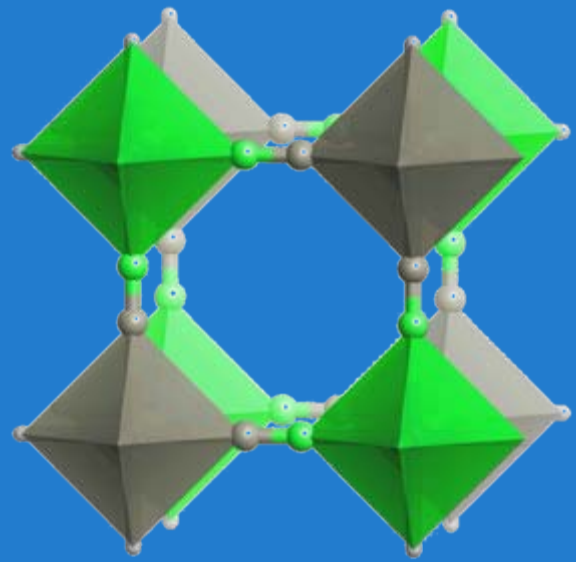


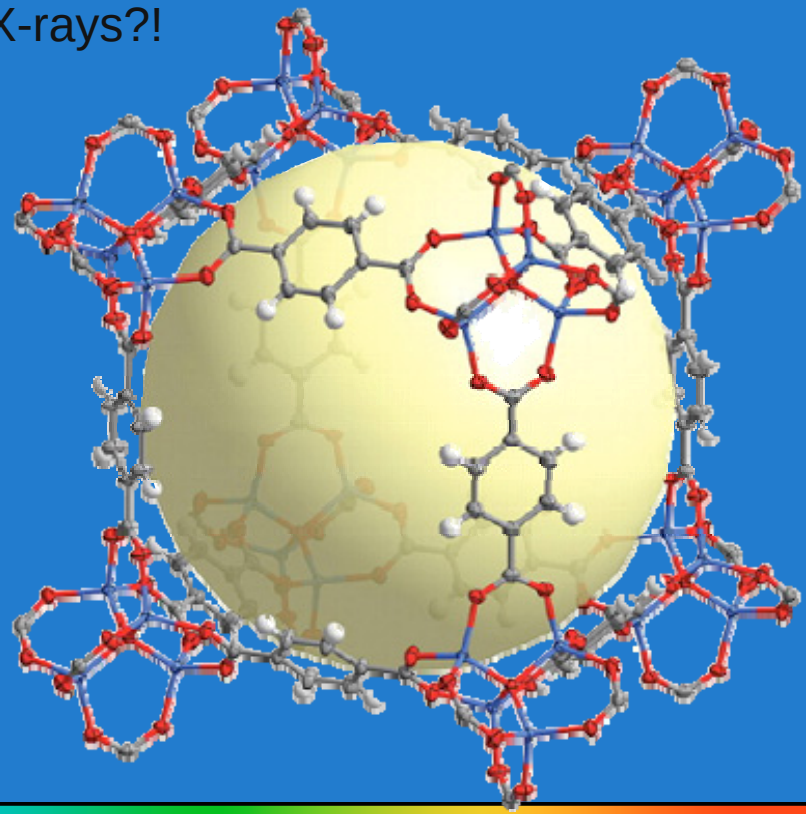
Hydrogen Storage in Porous Coordination Frameworks

Can we probe the structure of weakly bound guest molecules?

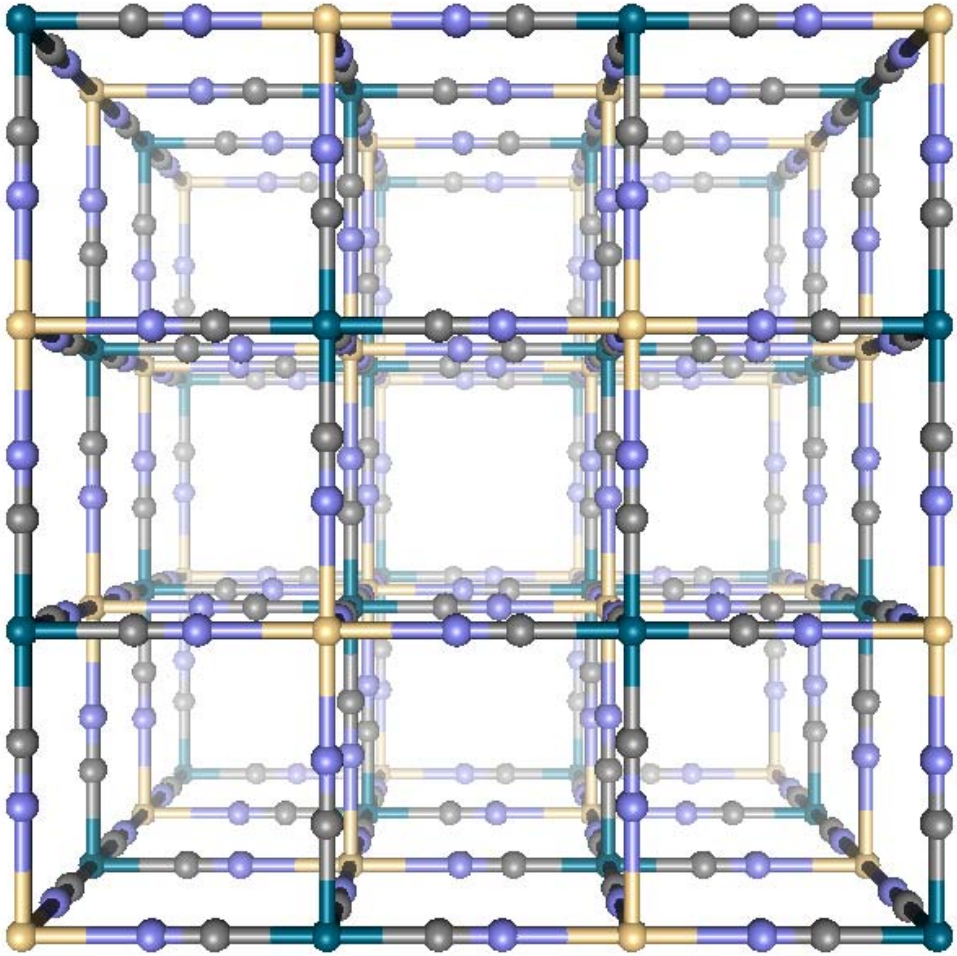
Are open metal sites important for binding H_2?

Seeing hydrogen with X-rays?!



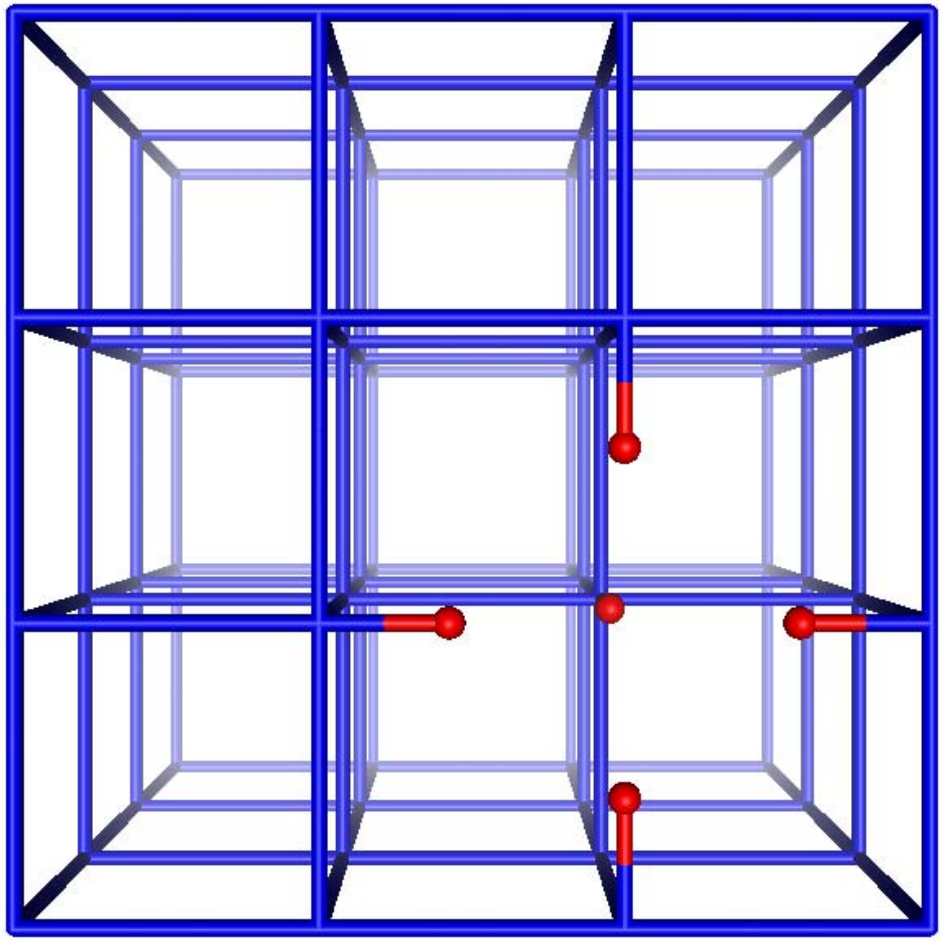


Open Metal Sites in Prussian Blue Analogues



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

Open Metal Sites in Prussian Blue Analogues



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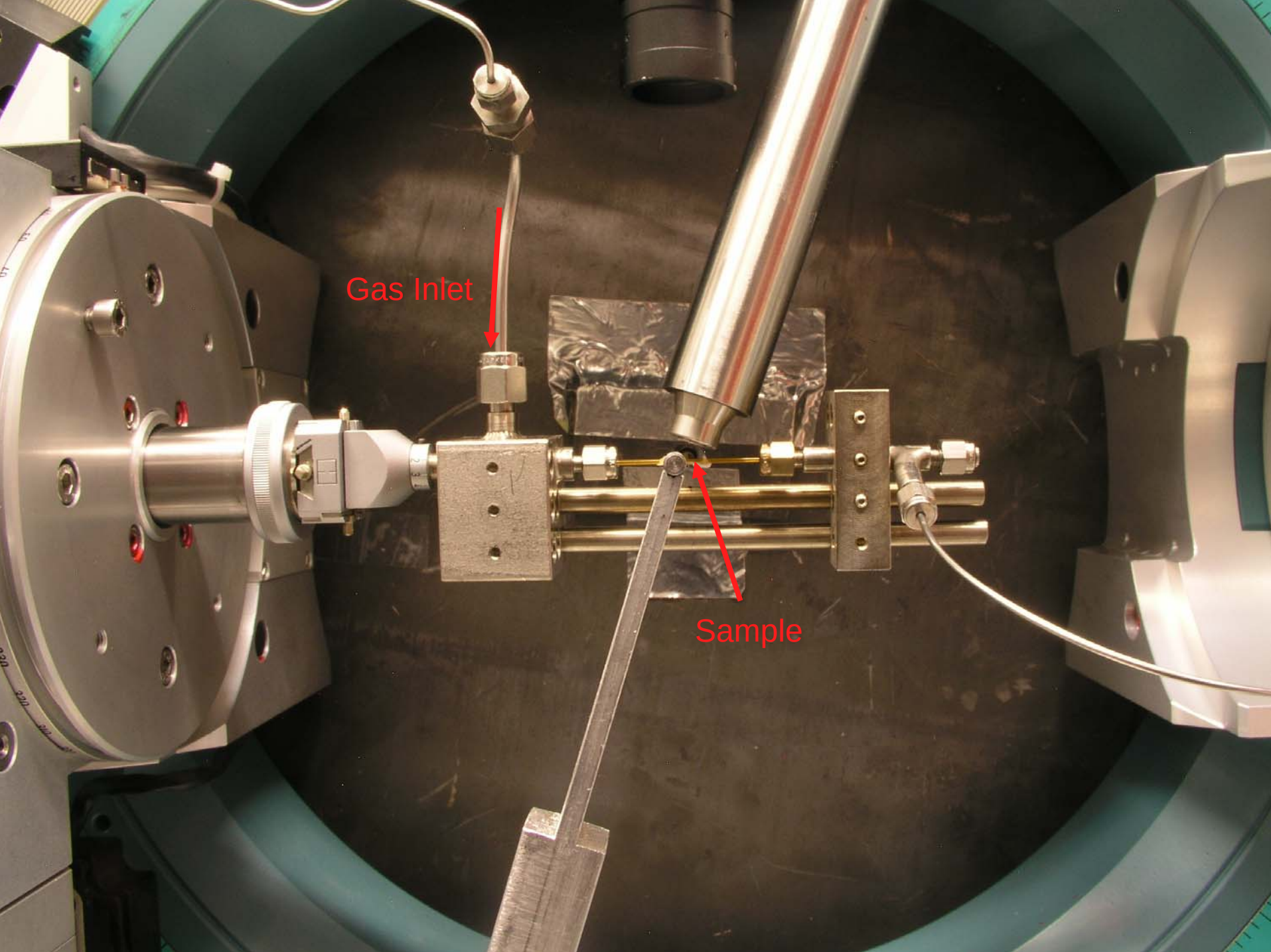
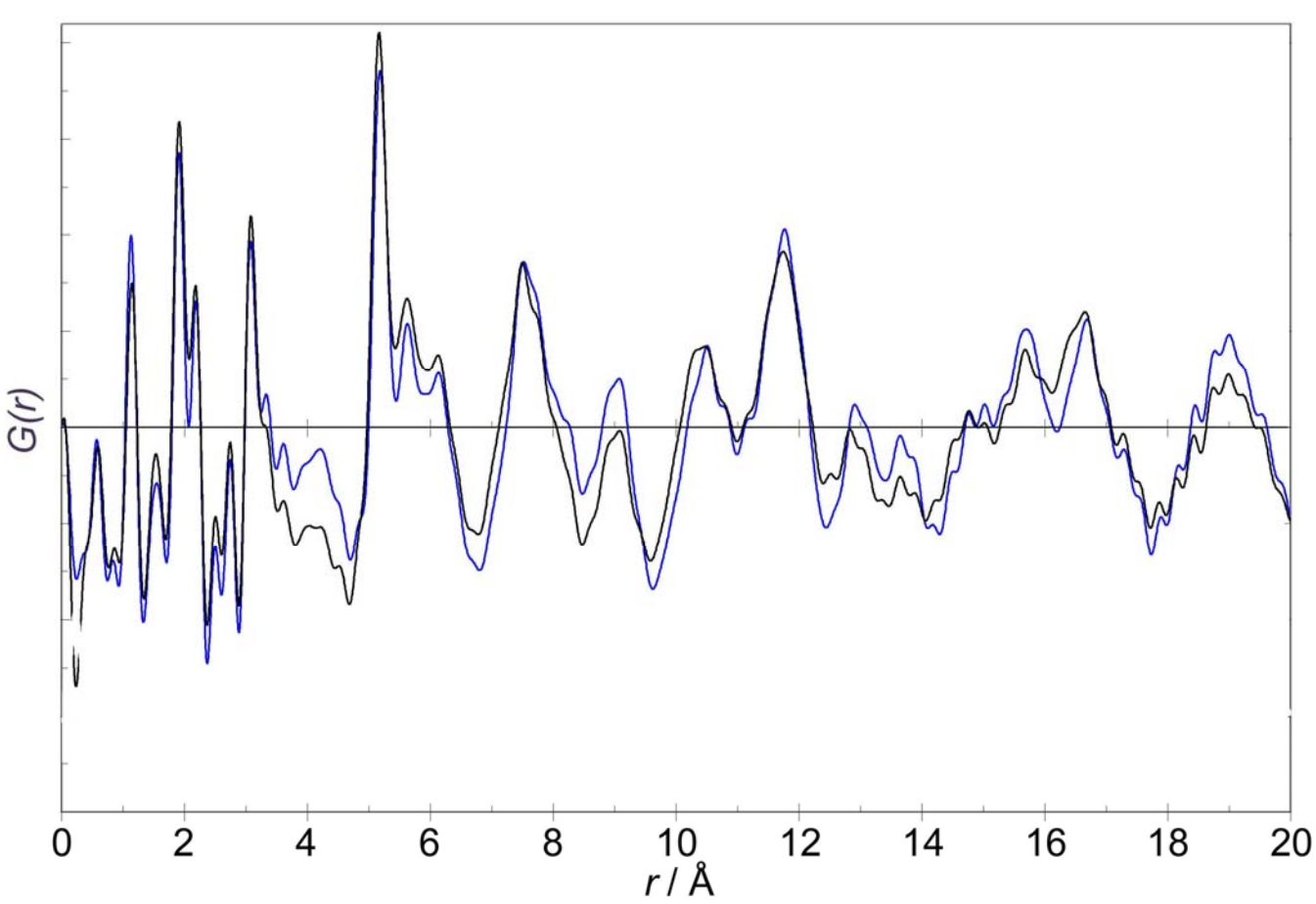
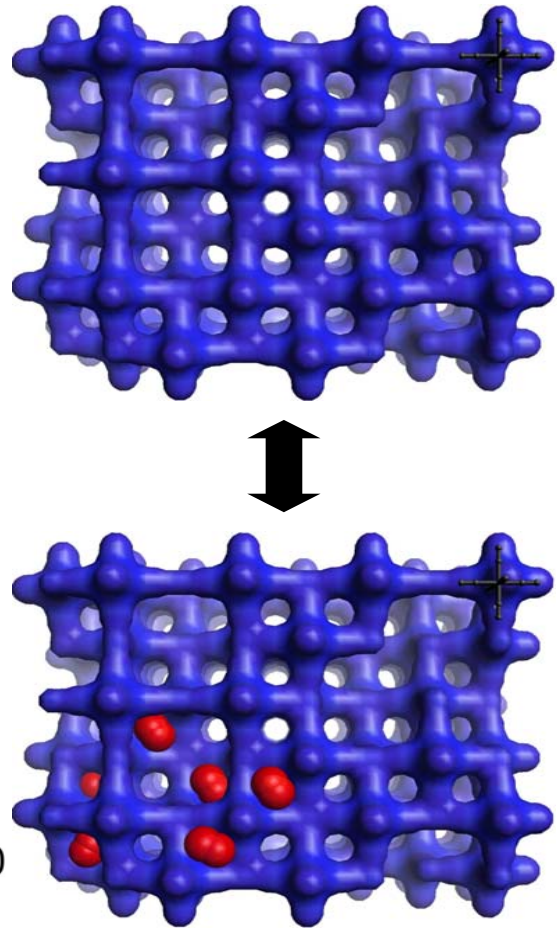
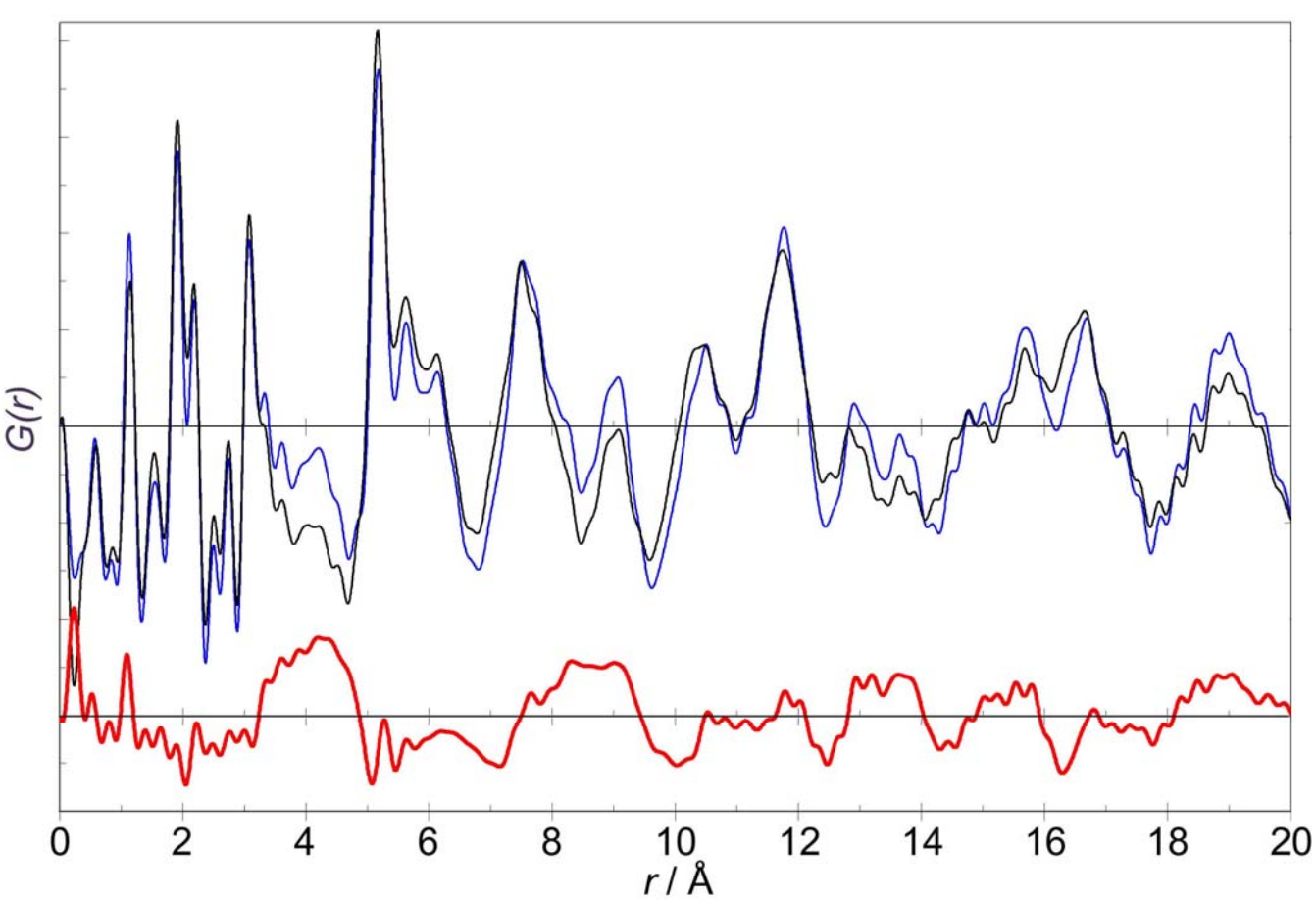

Gas Inlet
Sample

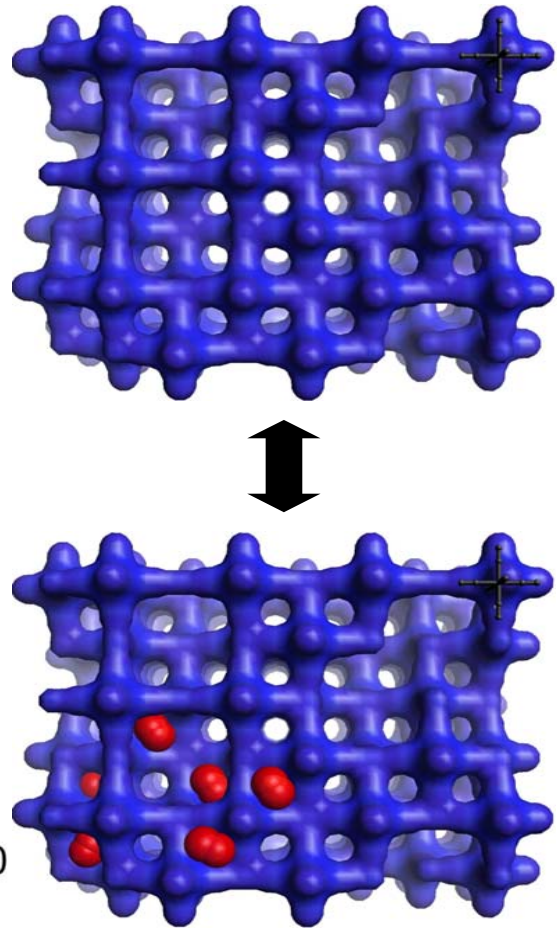
Differential PDF





Differential PDF





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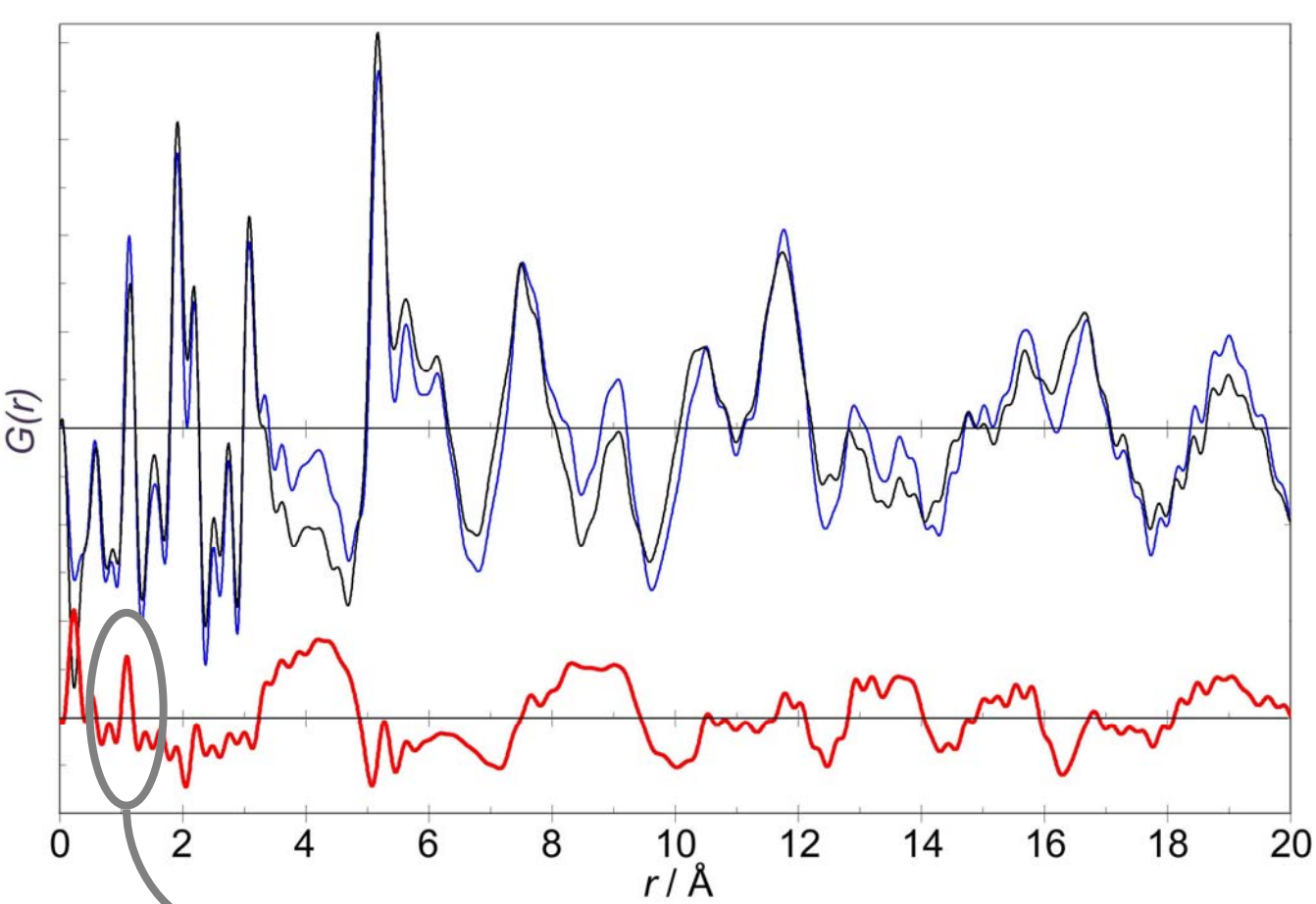
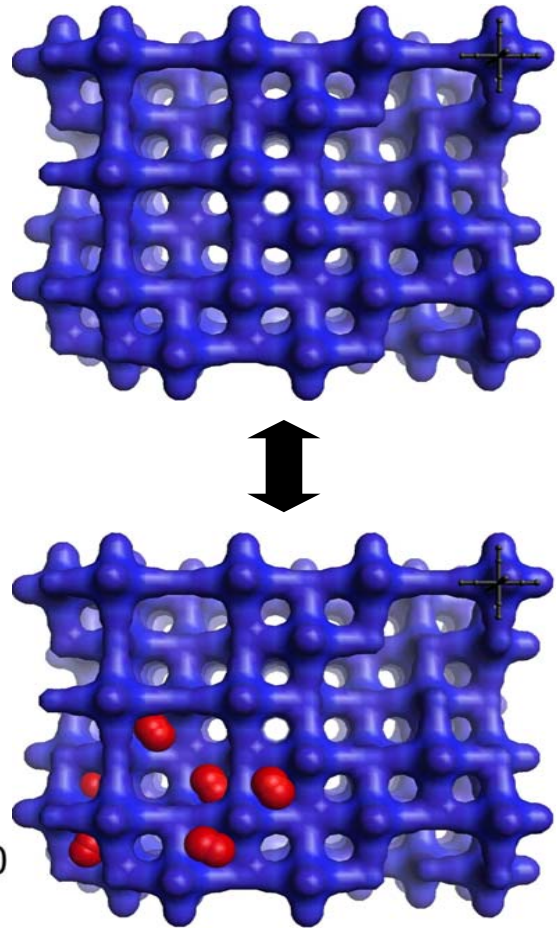
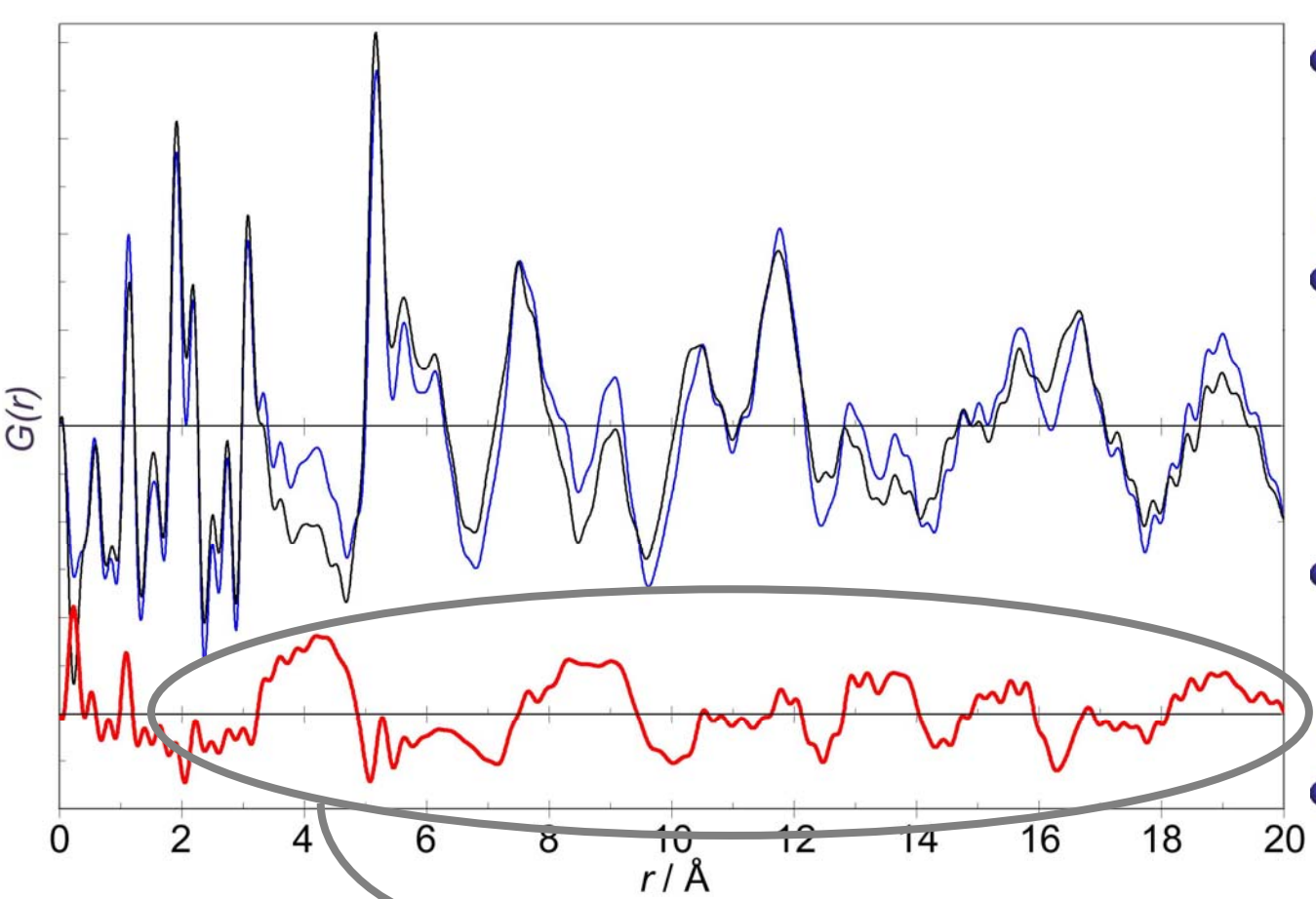
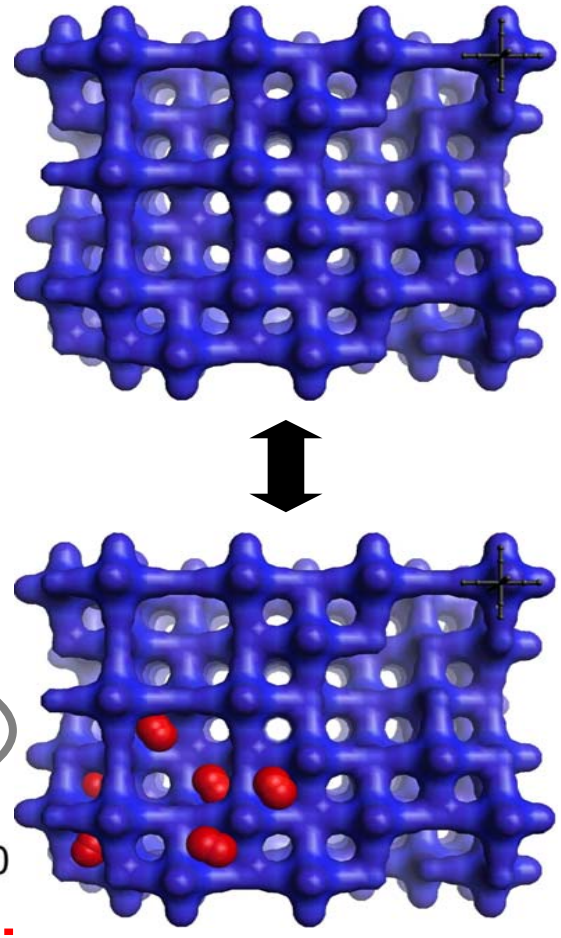




N-N distance in N_2 molecule

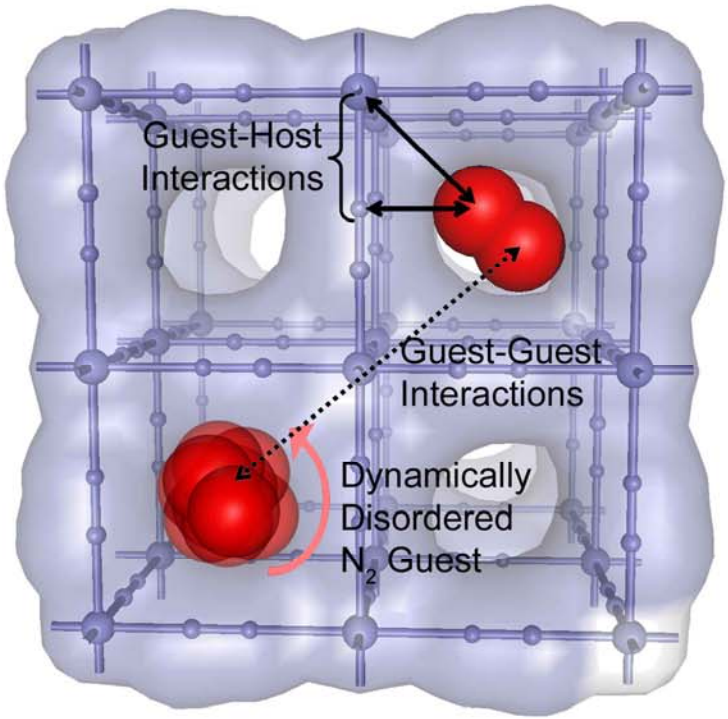
Differential PDF

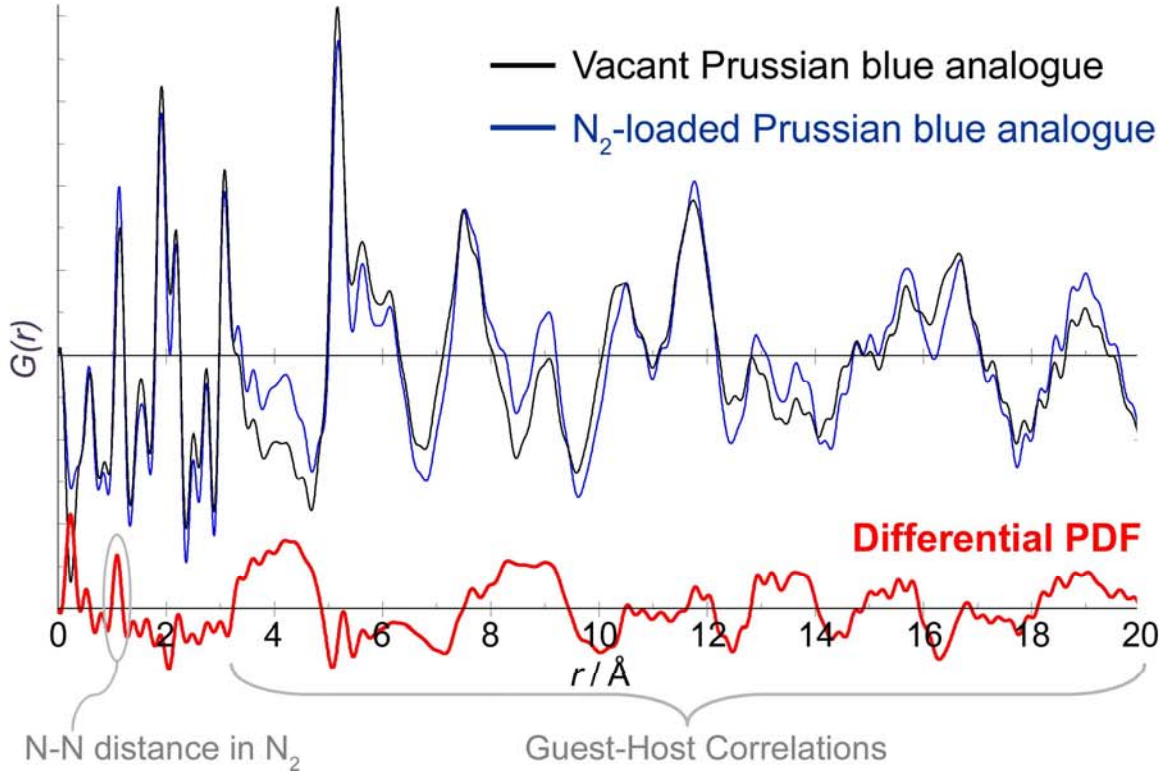




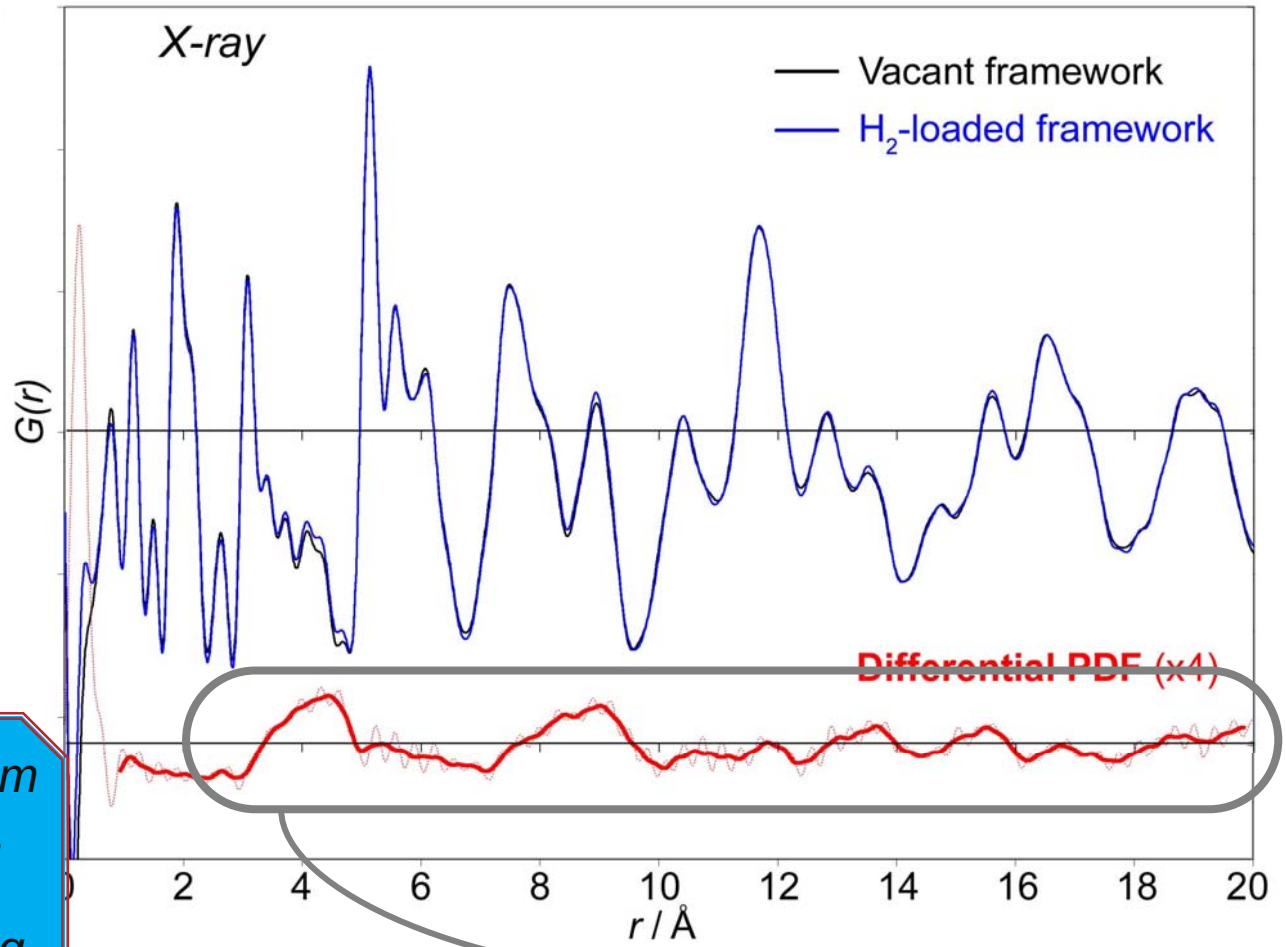
N-framework & N-N interactions

Differential PDF





Hydrogen Differential PDF

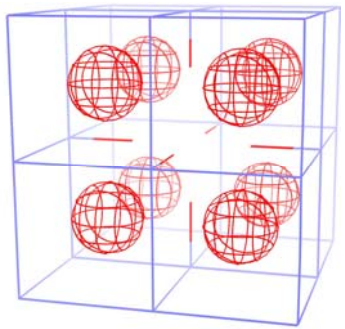


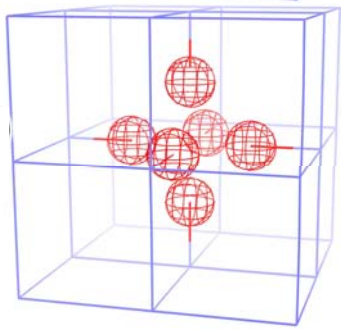
*Contribution from disordered H_2 evident from **X-ray** scattering*

H_2-framework interactions

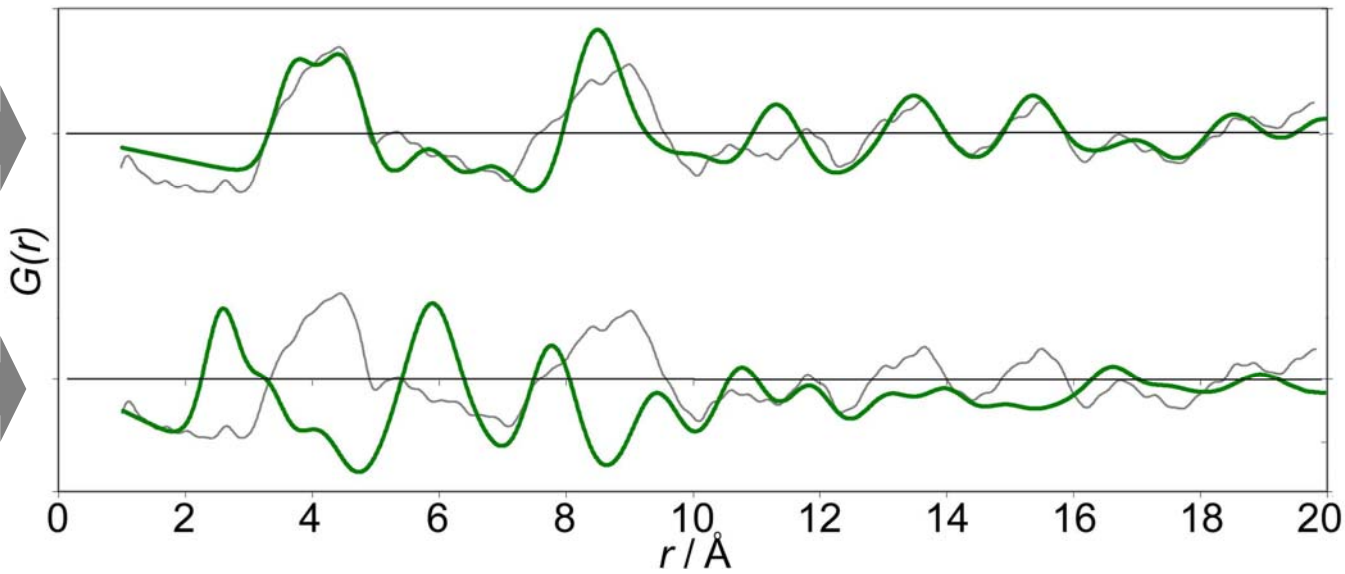
Structural Models

van der Waals interactions only



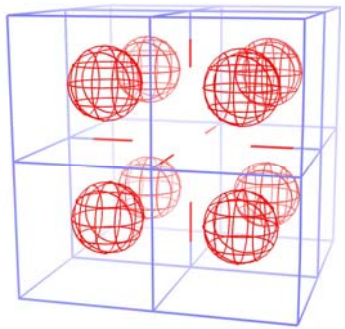


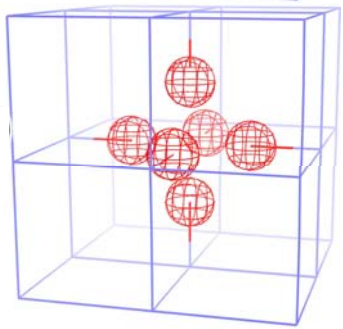
Binding at open metal sites



Structural Models

van der Waals interactions only





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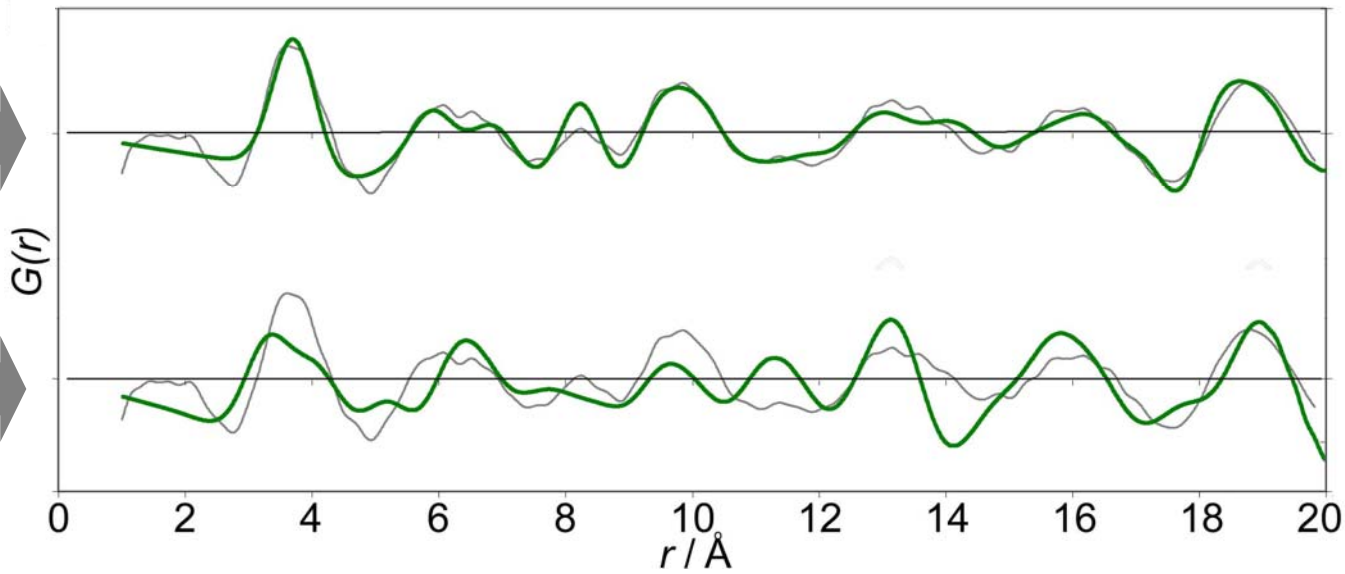
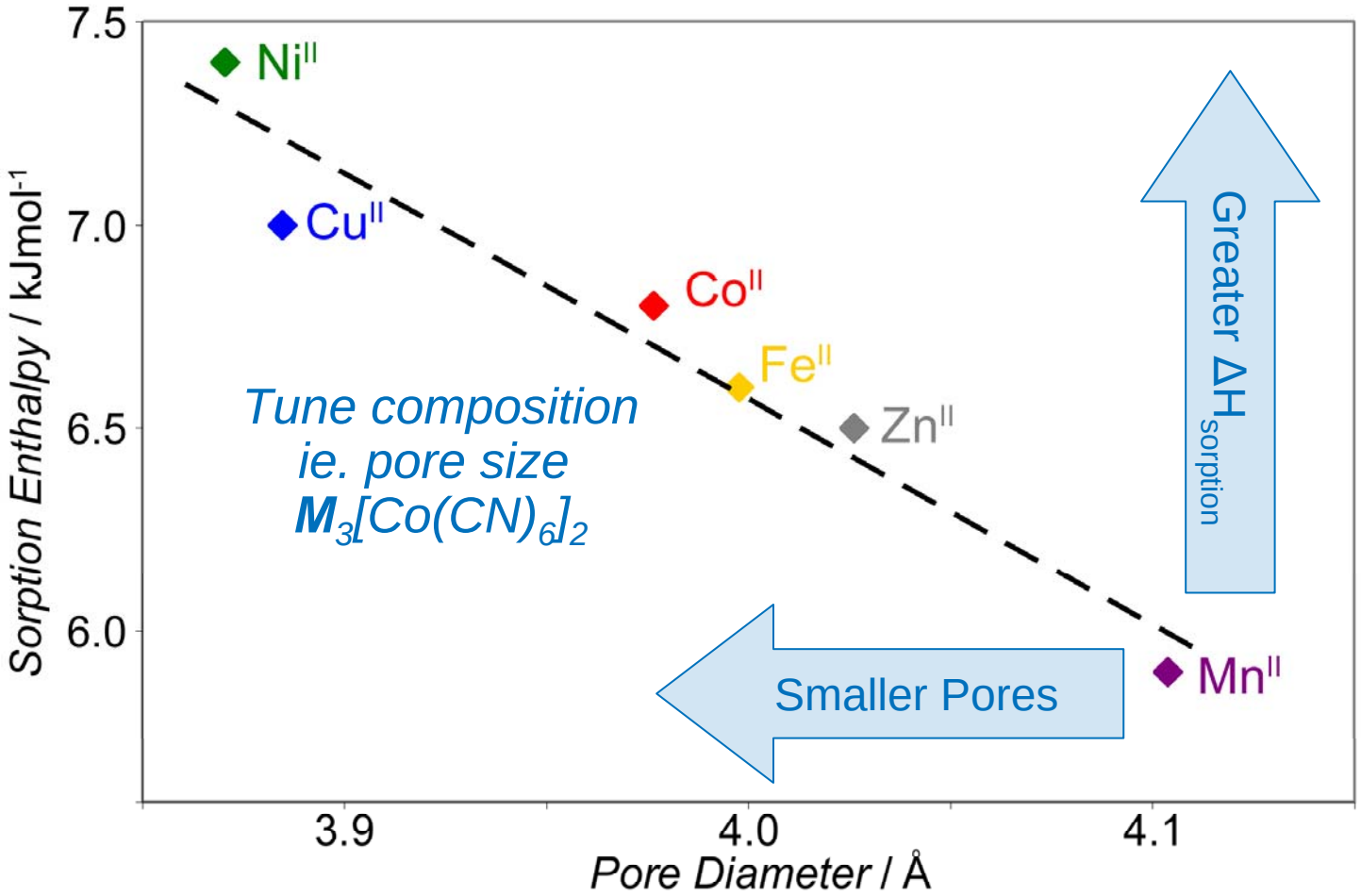


Enhancing Sorption

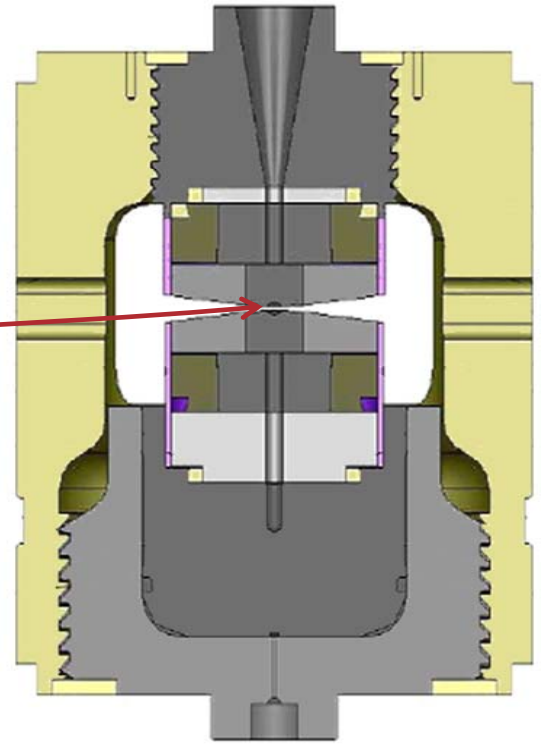


Energy Related Issues from Fossil Fuels

-CO_2 management

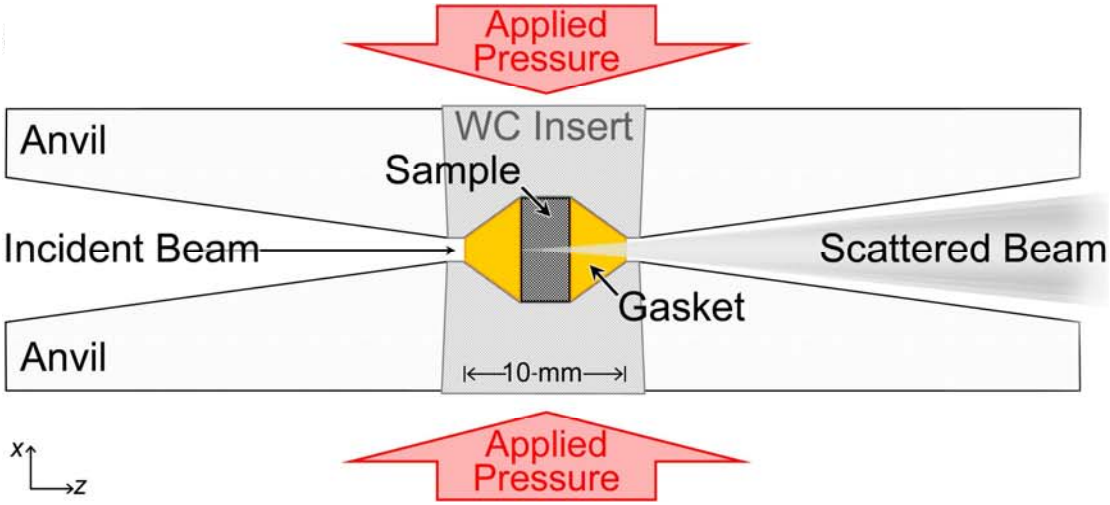
-Energy security

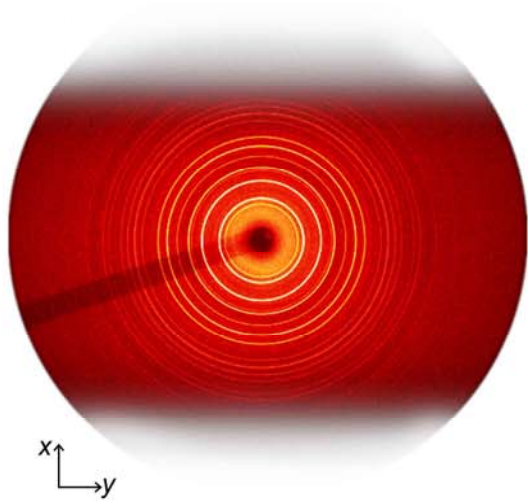
High-pressure experiments: The Paris-Edinburgh press

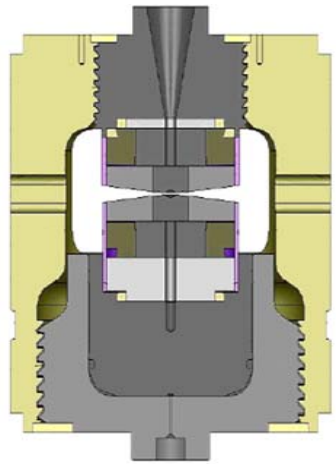


- Large sample volume: 3.5 mm diameter
- Retain microstructure – core sample
- No fluid pressure media

High-pressure experiments: The Paris-Edinburgh press







- Large sample volume: 3.5 mm diameter
- Retain microstructure – core sample
- No fluid pressure media

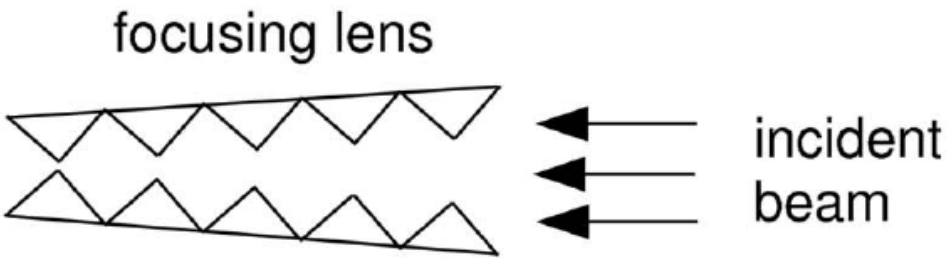
Applications of Micro-focused High-Energy X-rays (currently available at 1-ID at the APS)

-High pressure Studies from Diamond Anvil Cells

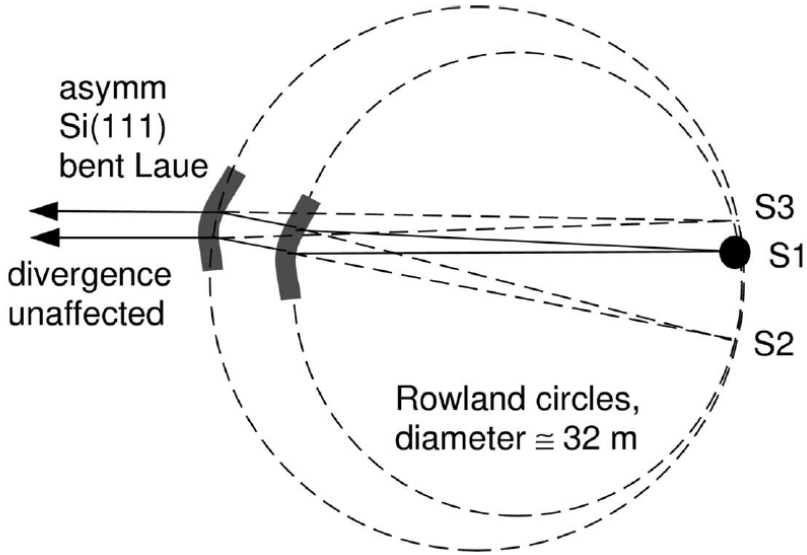
-Spatially Resolved Measurements

Focusing High-Energy X-Rays at 1-ID

Focusing Lens
(Si saw-tooth type*)

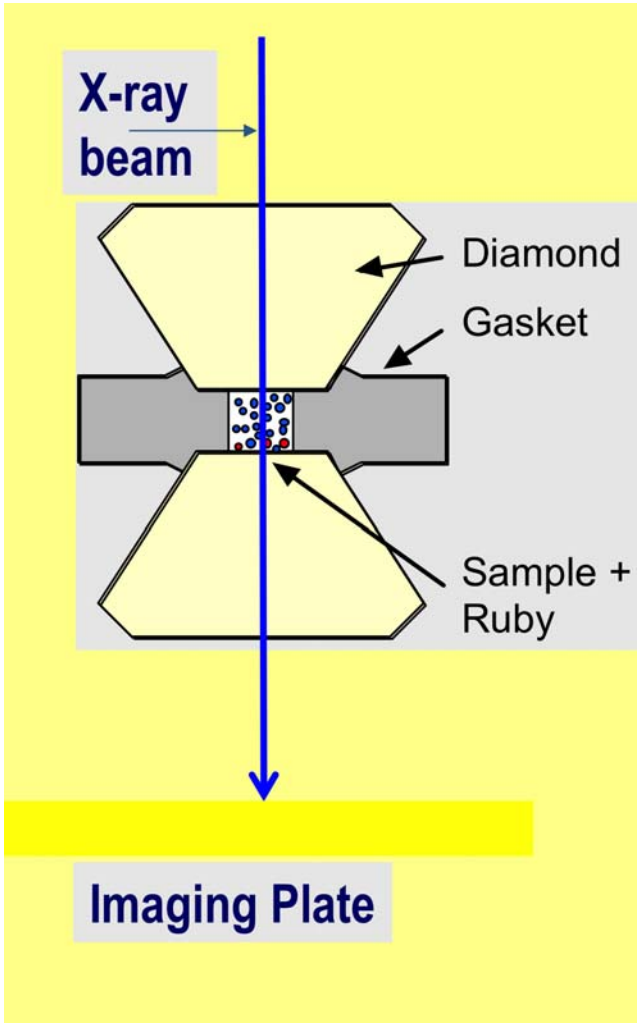


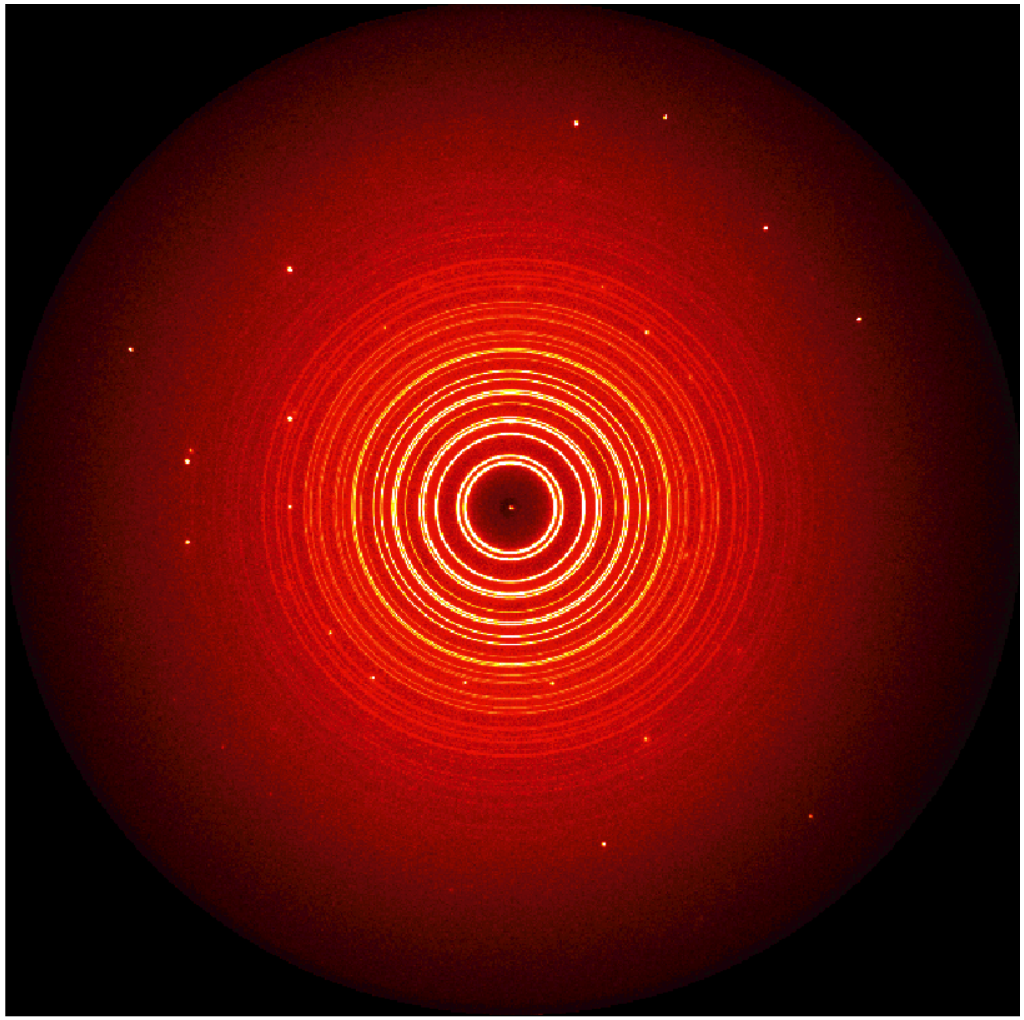
Bent Laue
Monochromator



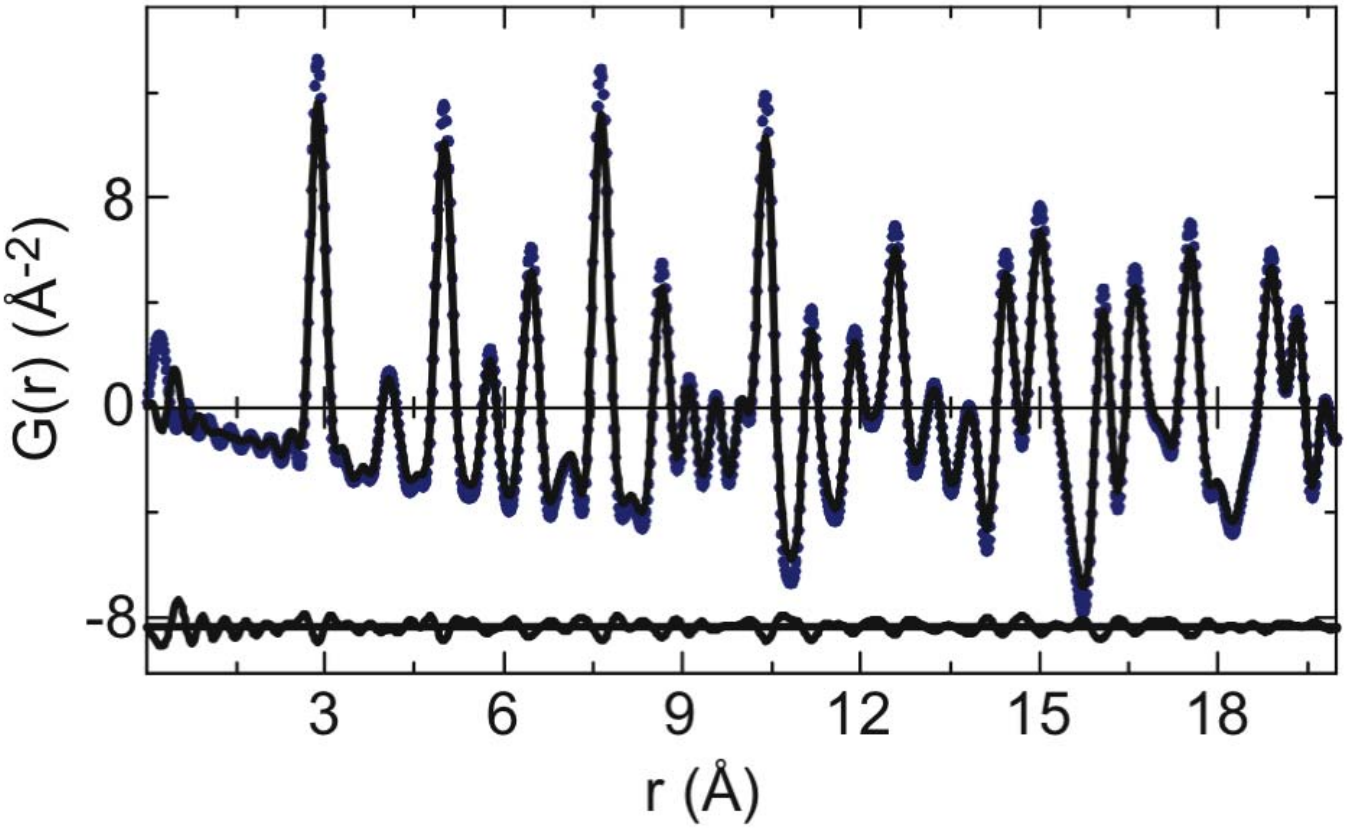
*S. D. Shastri et al., *J. Synchrotron Rad.*, **14**, 204 (2007)

PDF at High Pressures



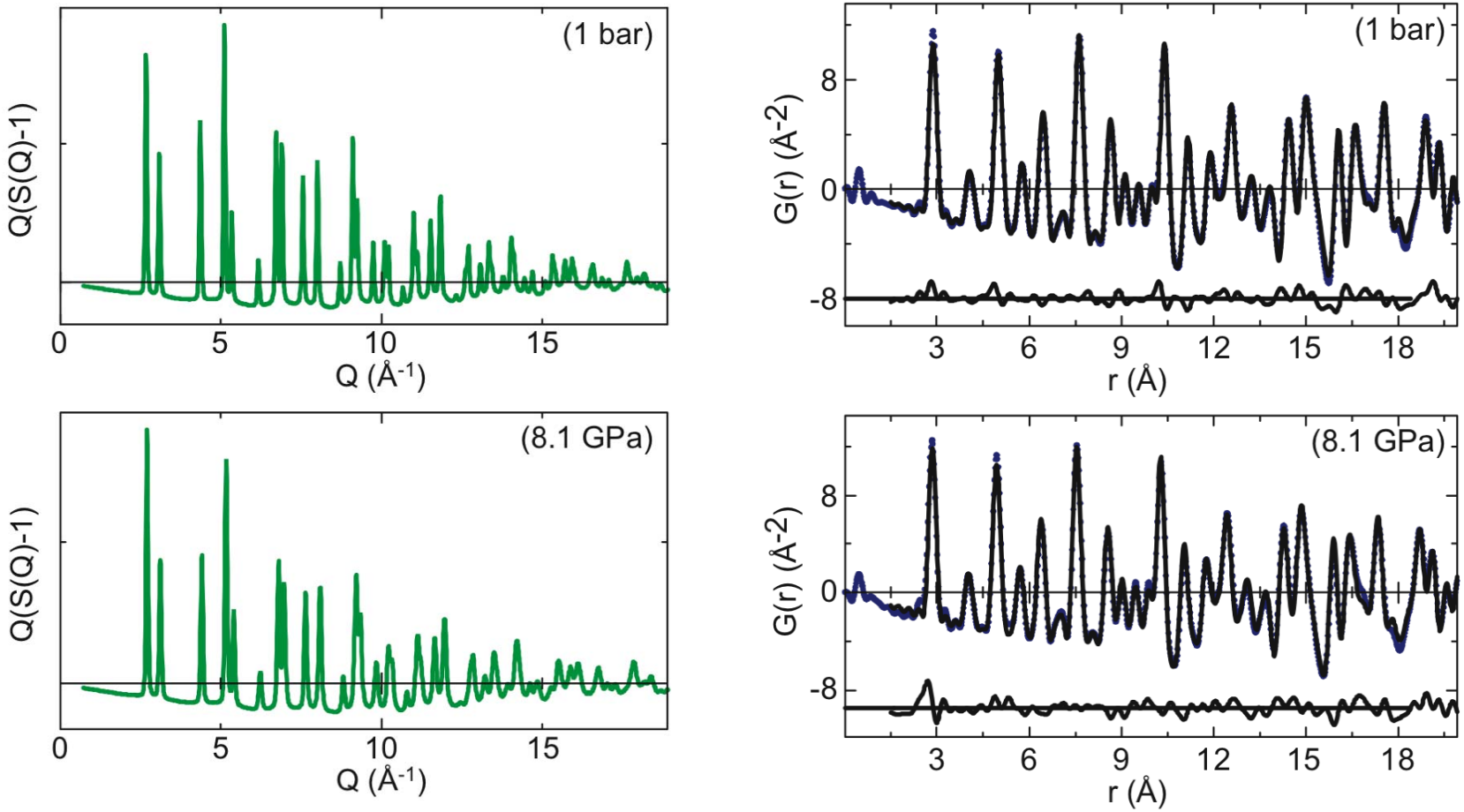


PDF of Gold in the DAC and Measured ex-situ

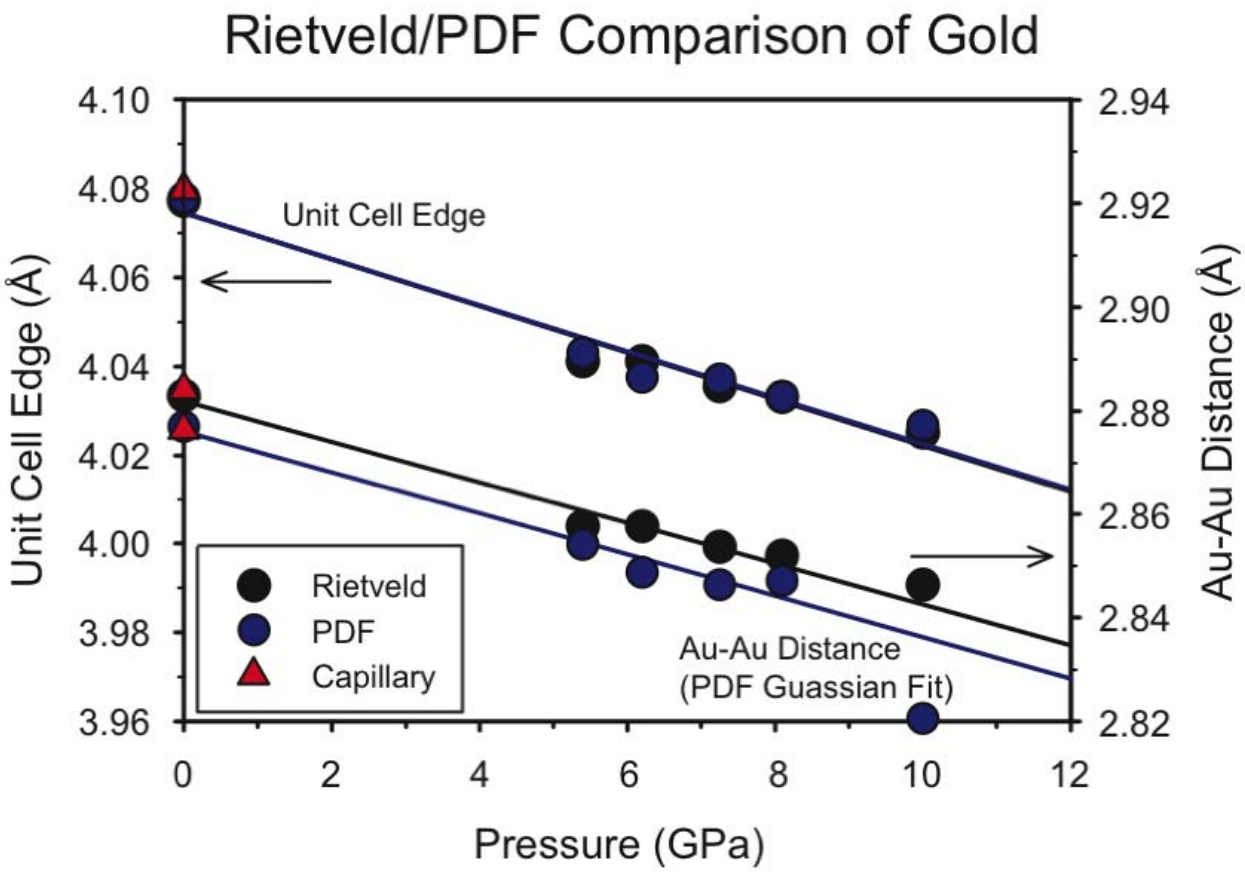


Martin, Antao, Chupas, Lee, Shastri, Parise *Applied Physics Letters* 86 (2005) 061910.

High Pressure PDF



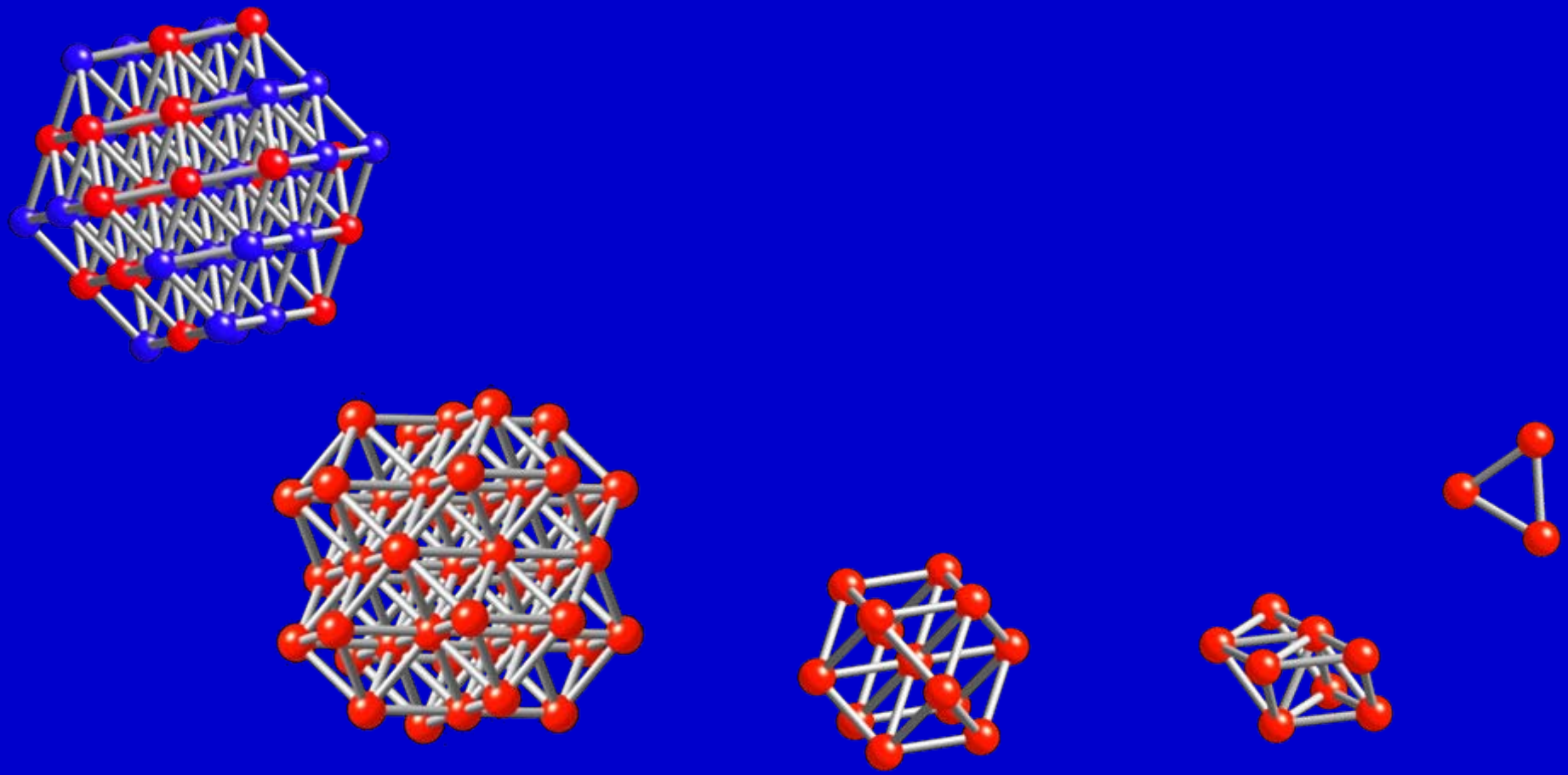
Gold at High Pressures



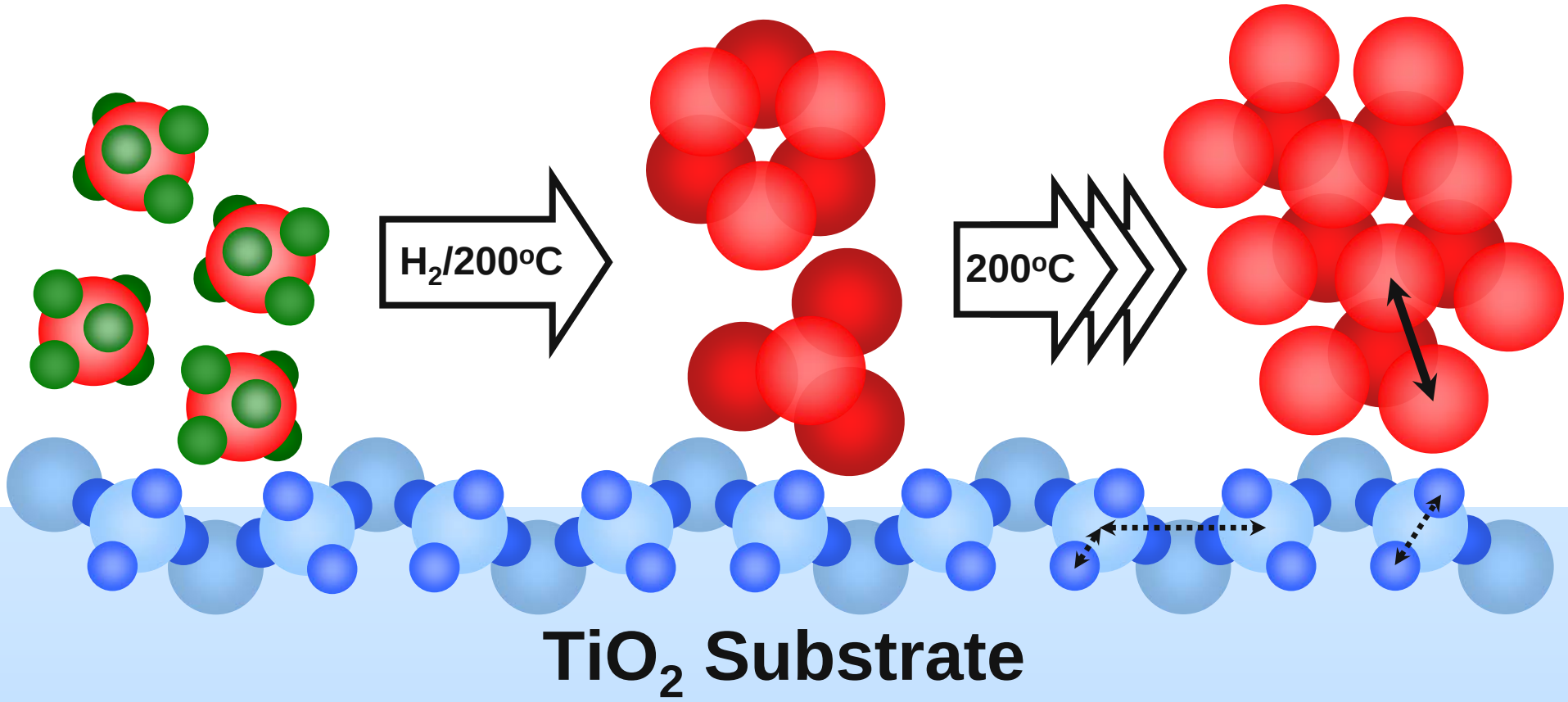
Time Resolved Studies:

Supported Metal Catalysts

Following the kinetics formation of catalytic particles



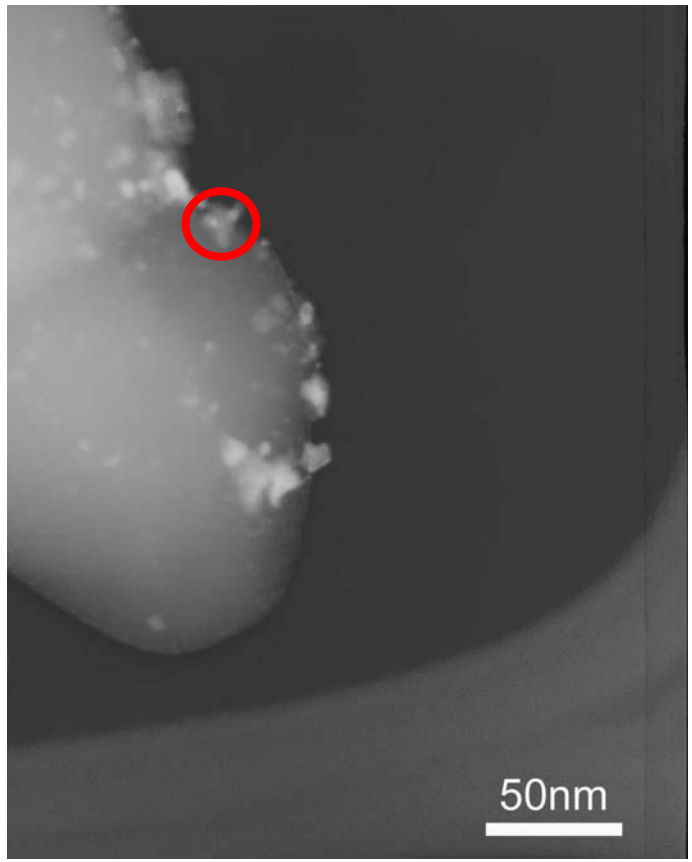
Forming Supported Nanoparticles

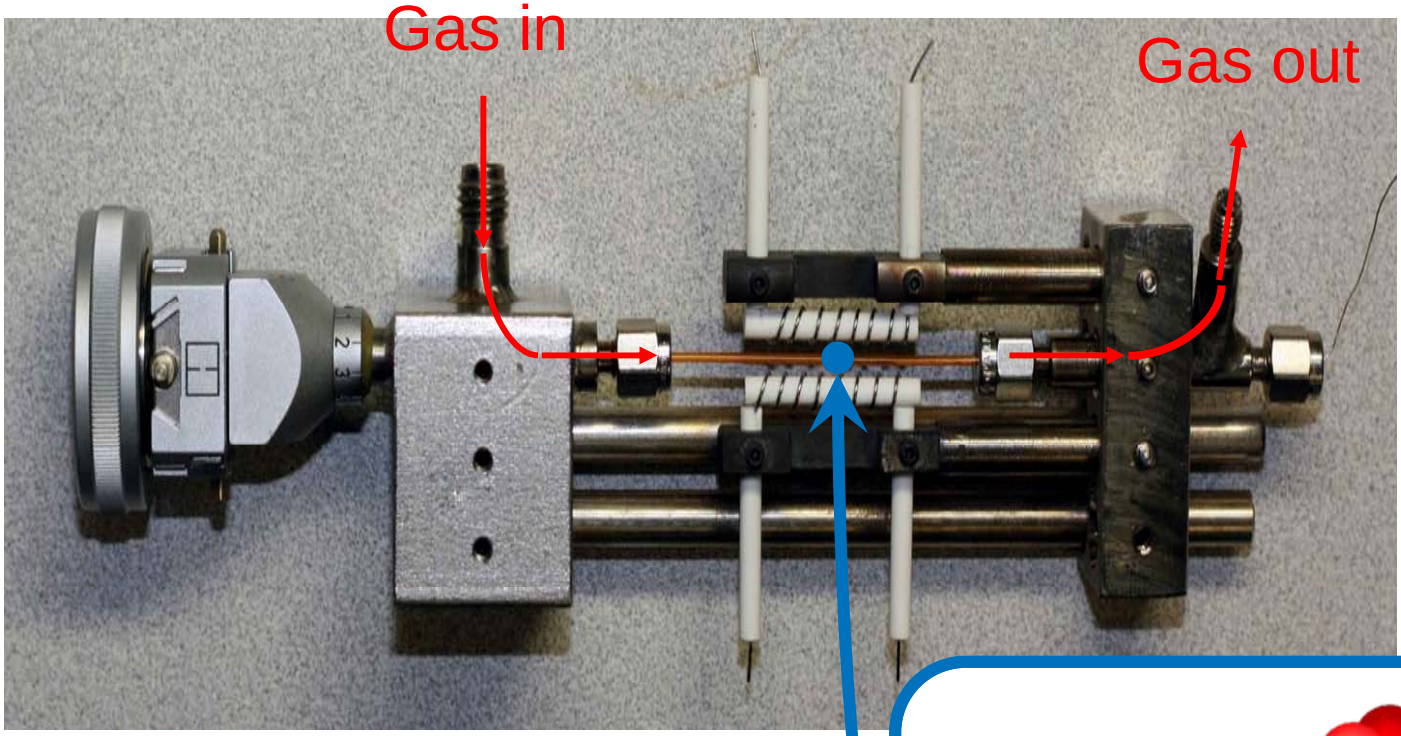


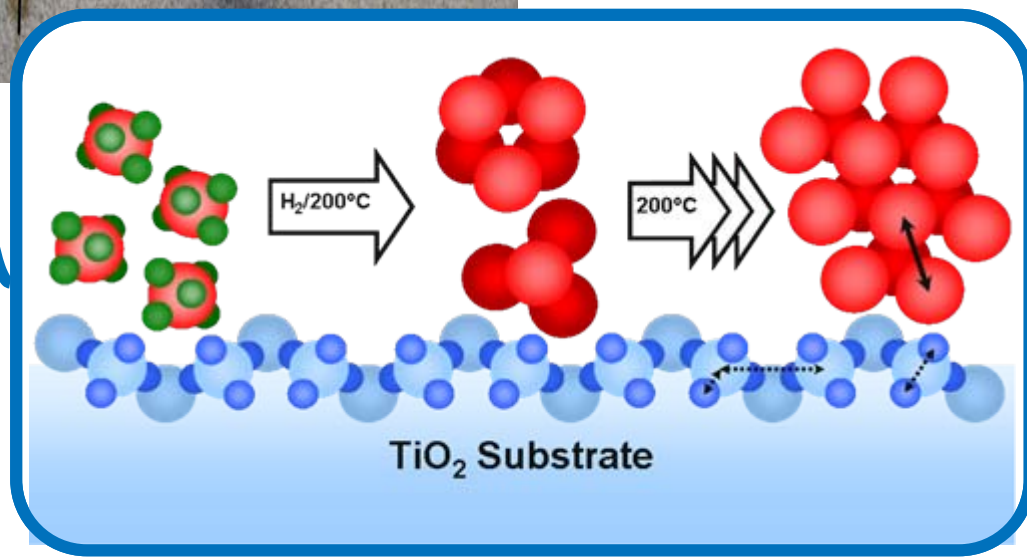
Forming Supported Nanoparticles

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

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

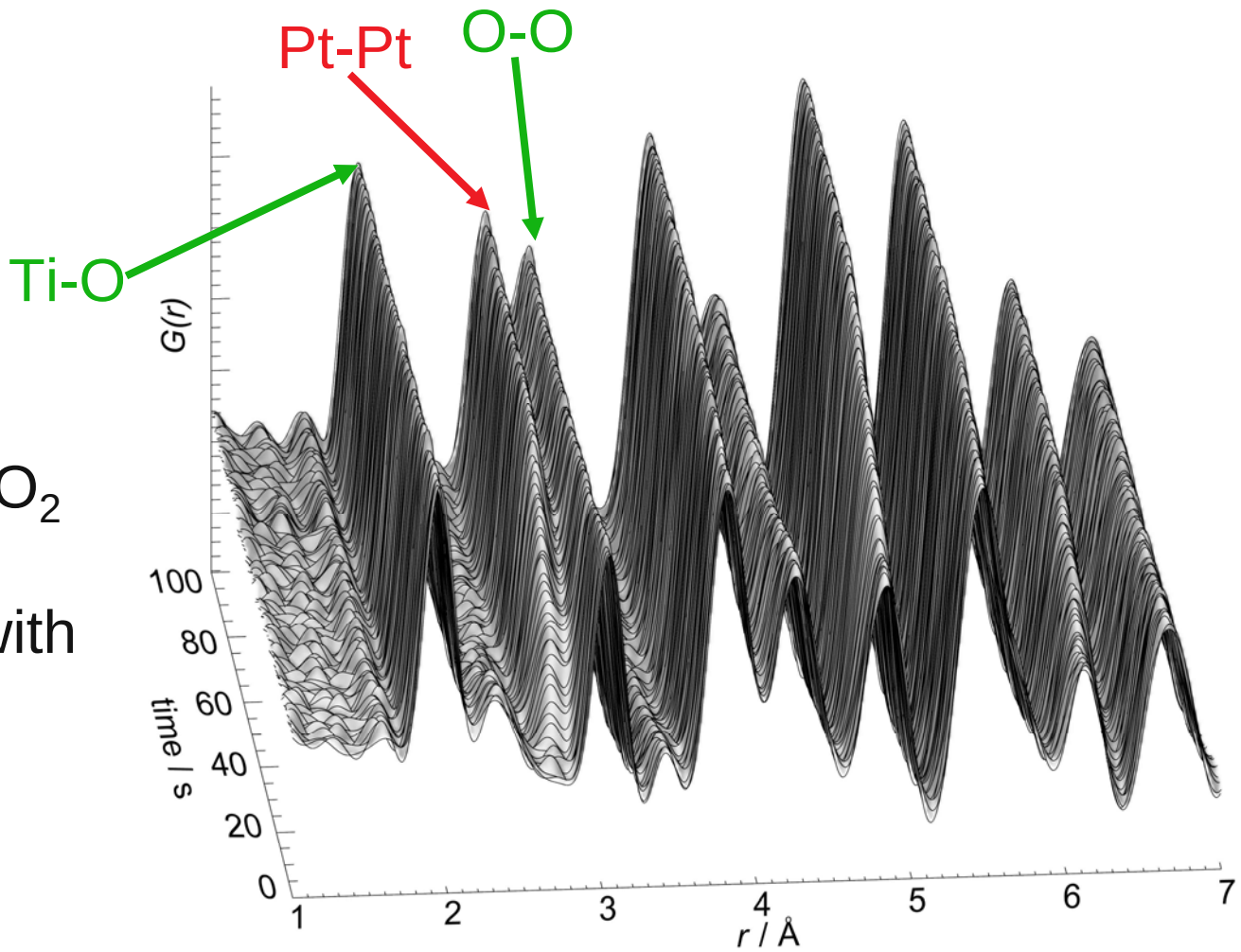



Gas in
Gas out


H2/200°C
200°C
TiO2 Substrate

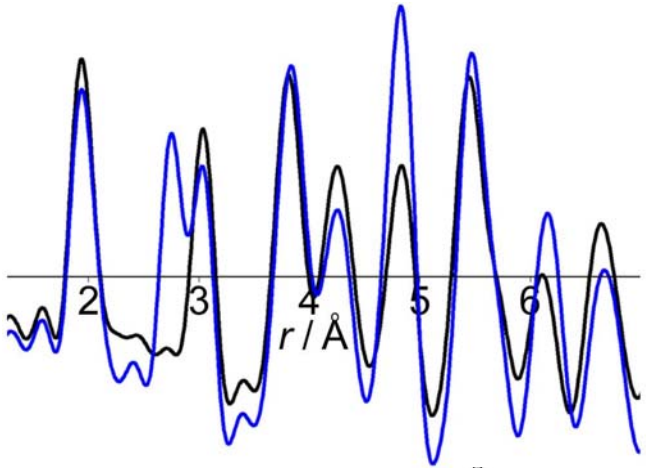
Reduction of 5% Pt^{4+} on TiO_2 Under H_2

- Reduction at constant temperature, 200 ˚C

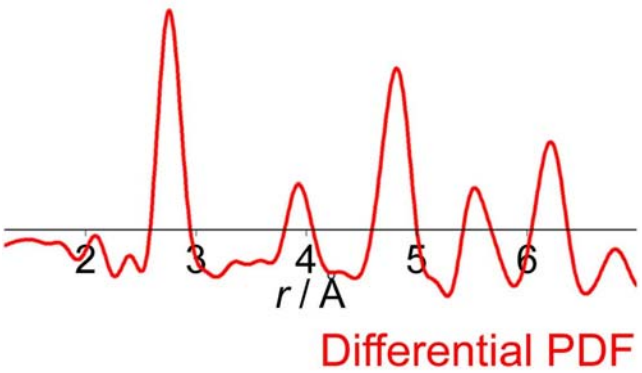


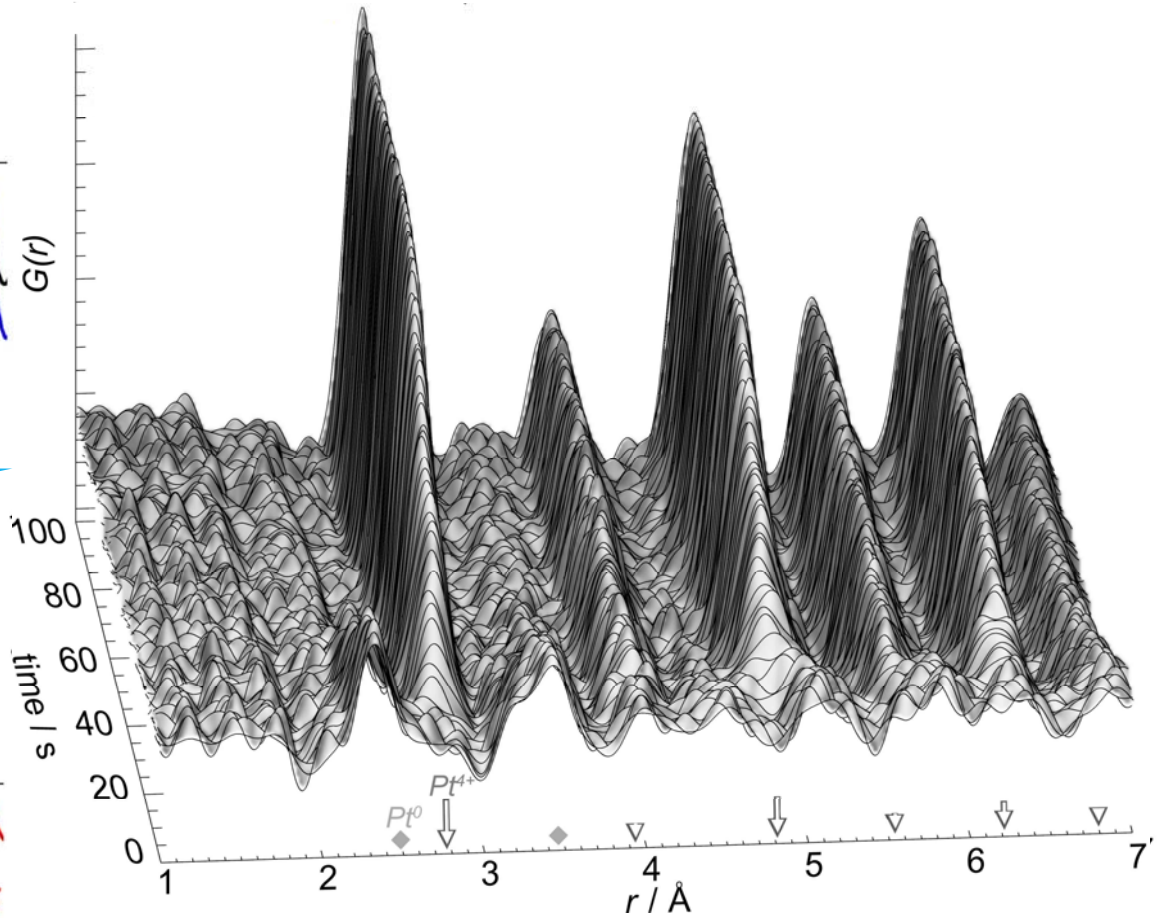
5wt % Pt on TiO_2 (via aqueous impregnation with H_2PtCl_6)

In situ *reduction: Pt^{4+} on TiO_2 → Pt^0*



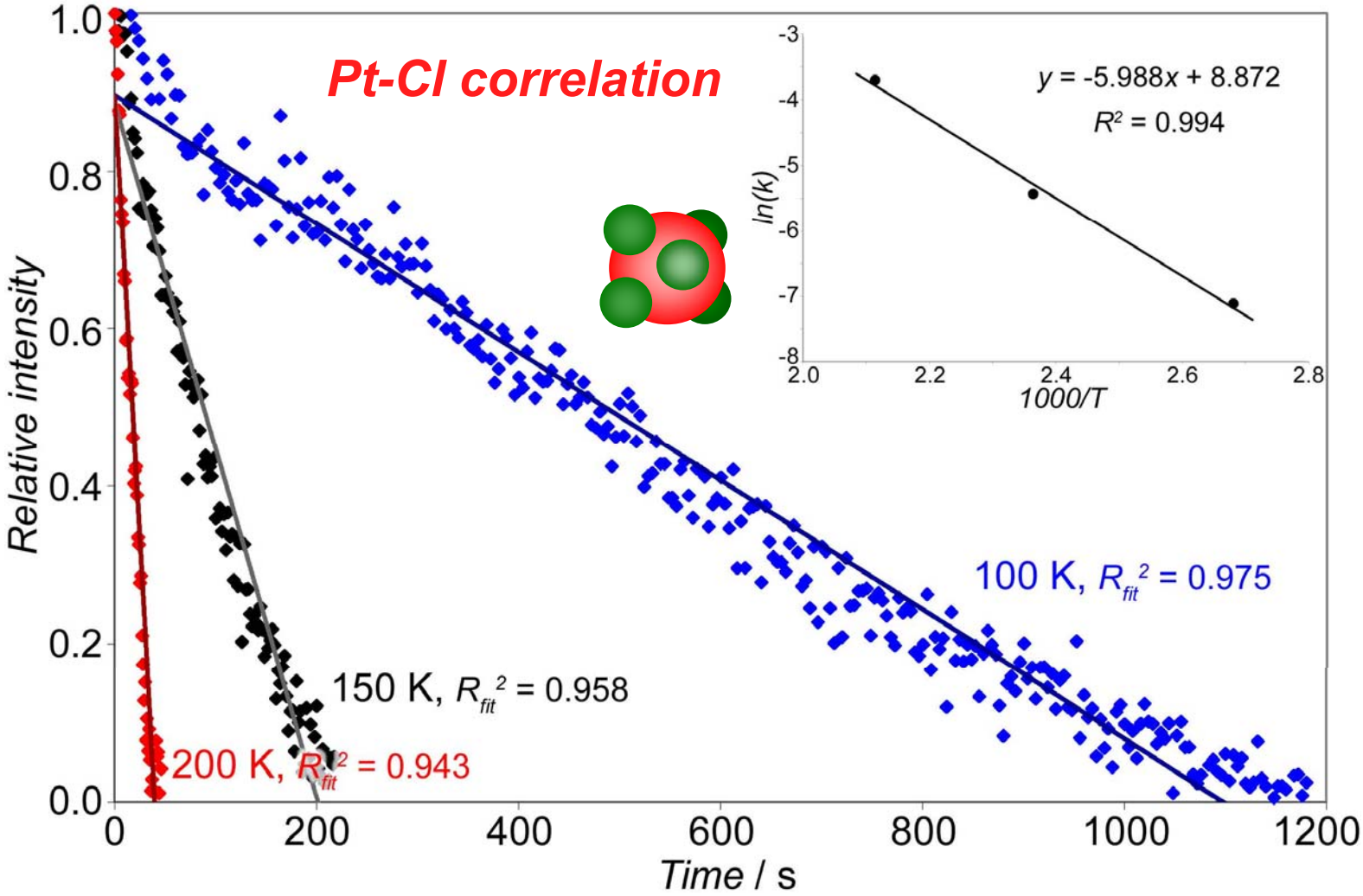
$G(r)_{Pt/TiO_2} - G(r)_{TiO_2}$



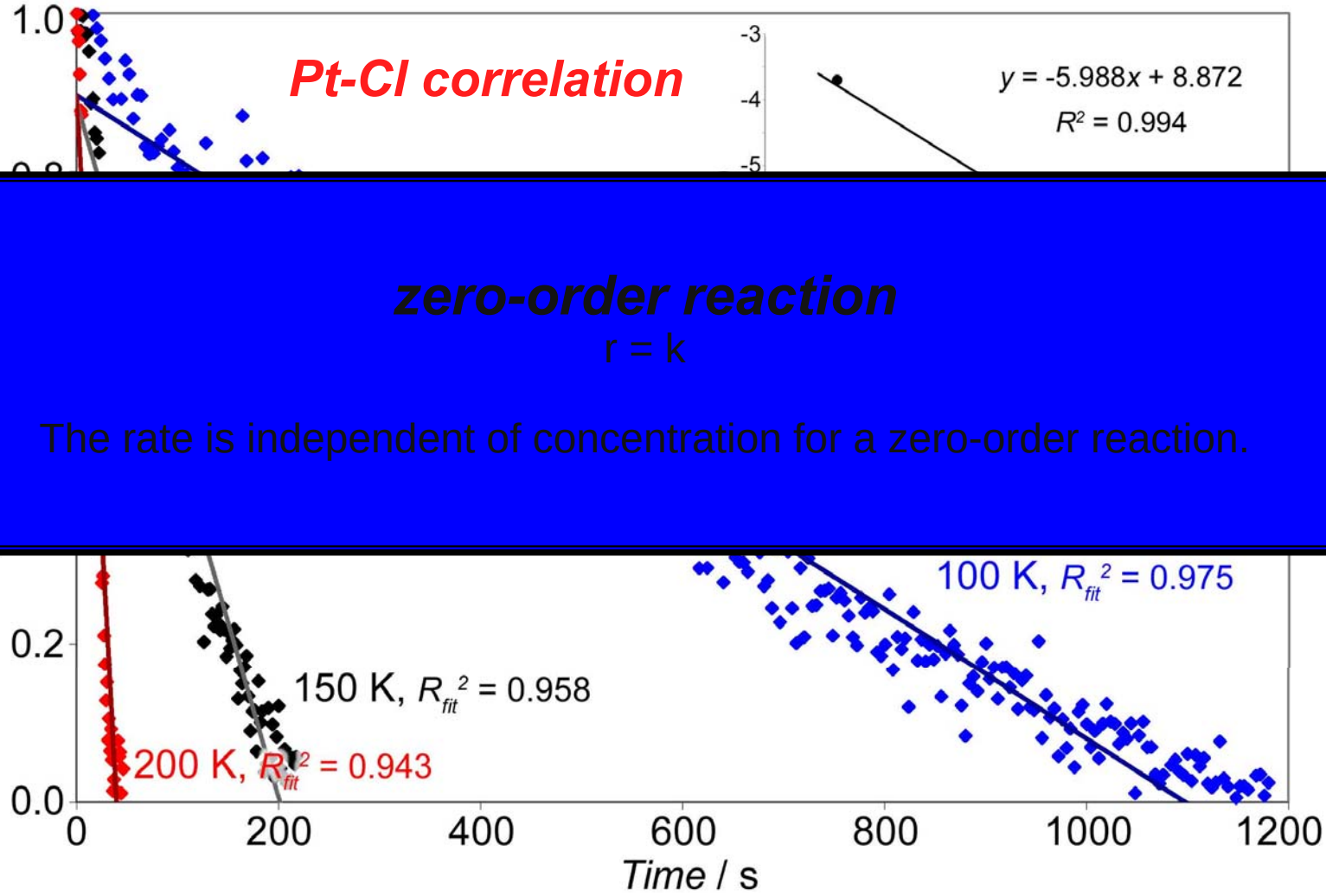


Chupas, Chapman, Jennings, Lee, Grey
J. Am. Chem. Soc., 2007, *129*, 13822-13824.

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.

High Temperature Measurements

Ceria as a Support/Catalyst

Ceria is a major component of Three Way Catalysts: Which Simultaneously treat the reducing pollutants CO and C_xH_y, and the oxidizing pollutant NO_x

Oxidation: $2\ CO + O_2 \rightarrow CO_2$

$C_xH_y + O_2 \rightarrow CO_2 + H_2O$

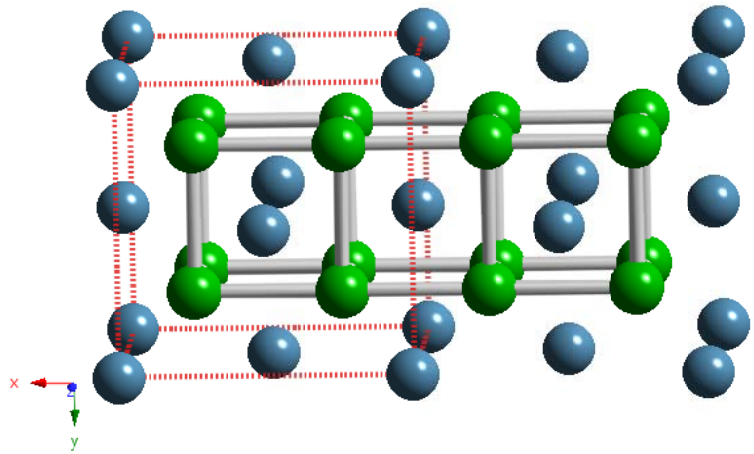
Reduction $2\ CO + 2\ NO \rightarrow 2CO_2 + N_2$

$C_xH_y + NO \rightarrow CO_2 + H_2O + N_2$

Ceria acts as an oxygen reservoir to stabilize the air/fuel ratio

Fluorite structure with variable composition

CeO_x $1.75<x<2.0$



In-situ Reduction of Ceria

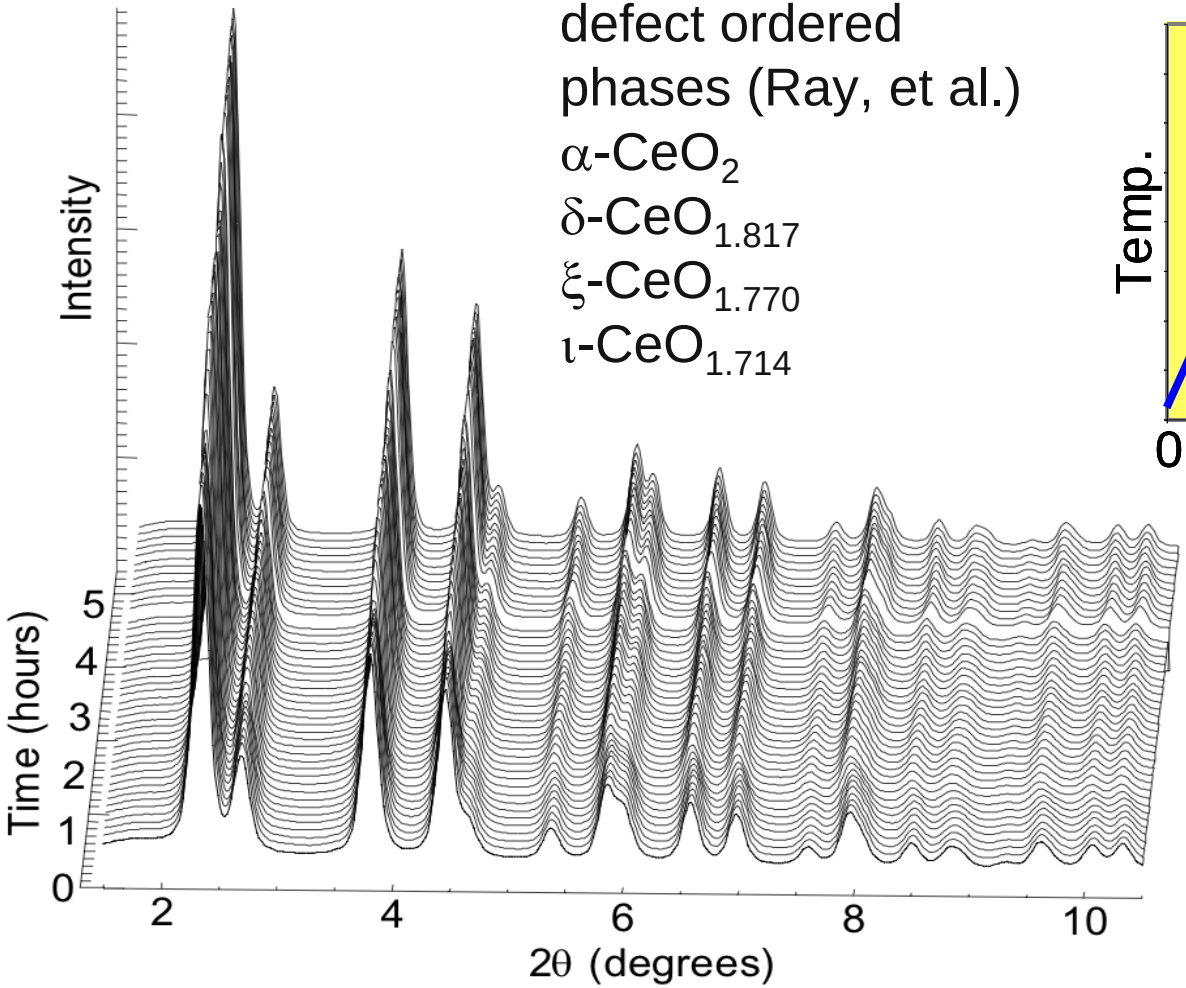
Previously identified defect ordered phases (Ray, et al.)

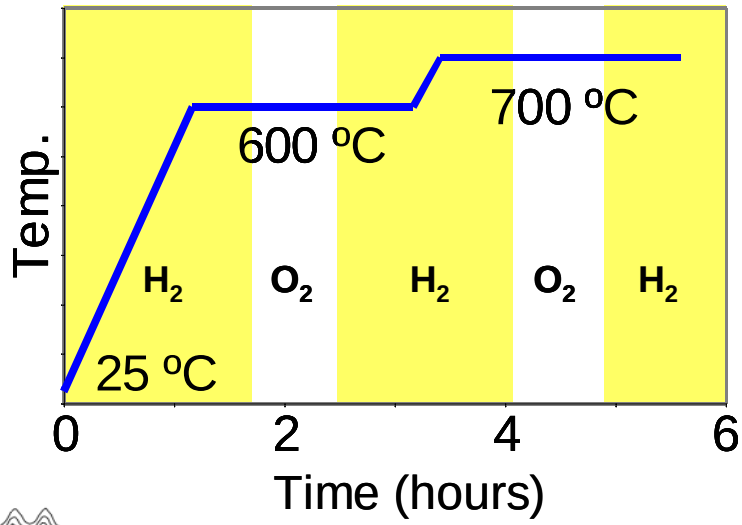
α-CeO_2

δ-$CeO_{1.817}$

ξ-$CeO_{1.770}$

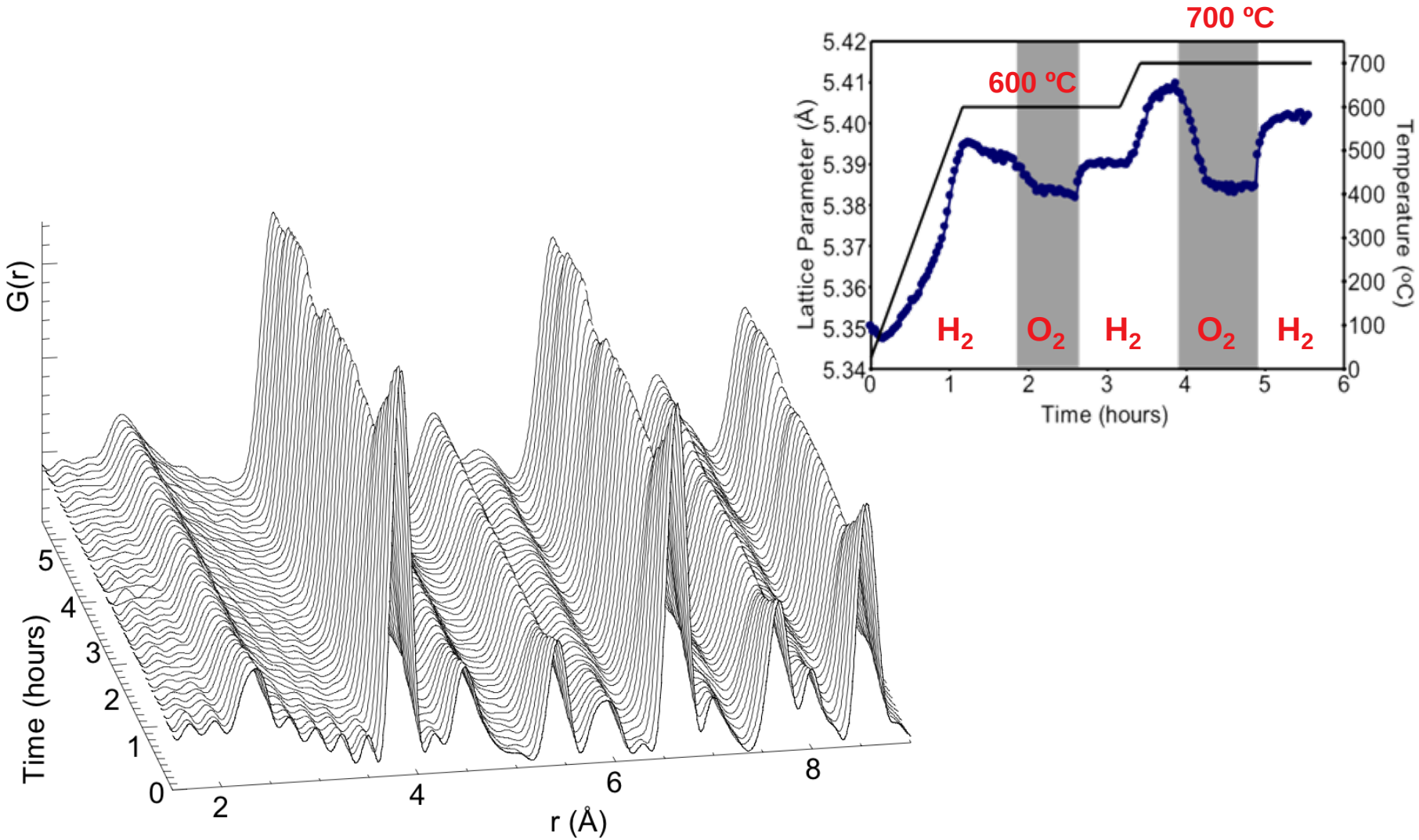
ι-$CeO_{1.714}$



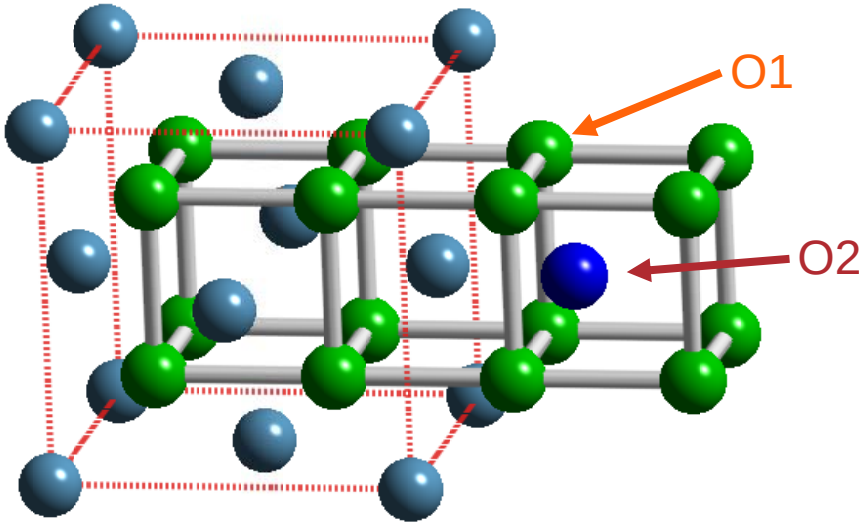


S.P. Ray, A.S. Nowick, D.E. Cox. *J. Solid State Chem.*, 15, 344-351, (1975)

Studying Local Structure During Chemical Reactions



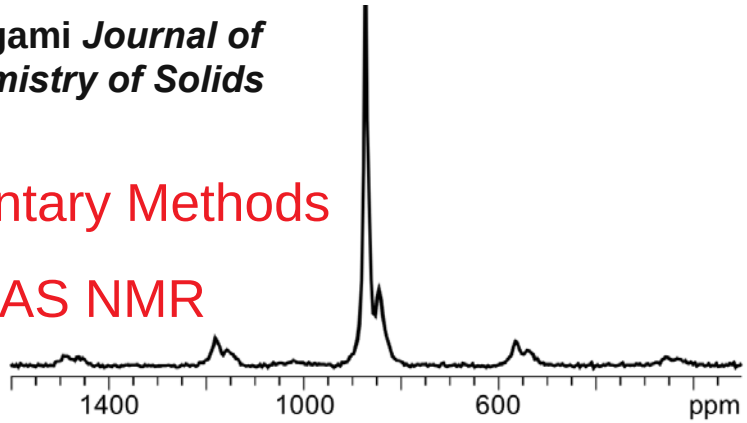
Frenkel Defects in nano-CeO_2

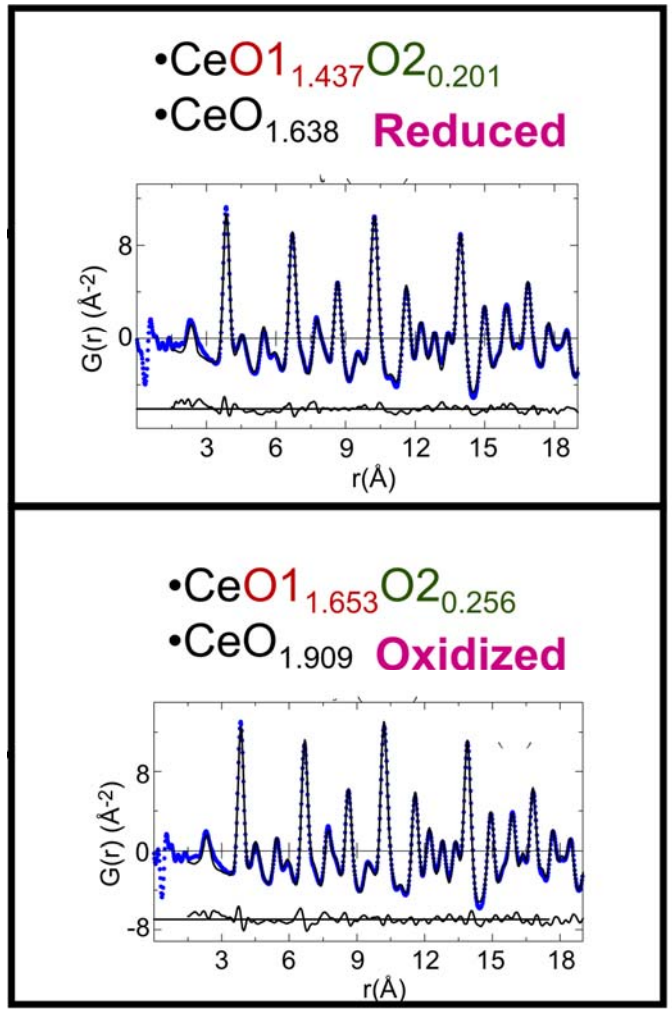


Mamontov and Egami *Journal of Physics and Chemistry of Solids* 61 (2000) 1345.

Complementary Methods

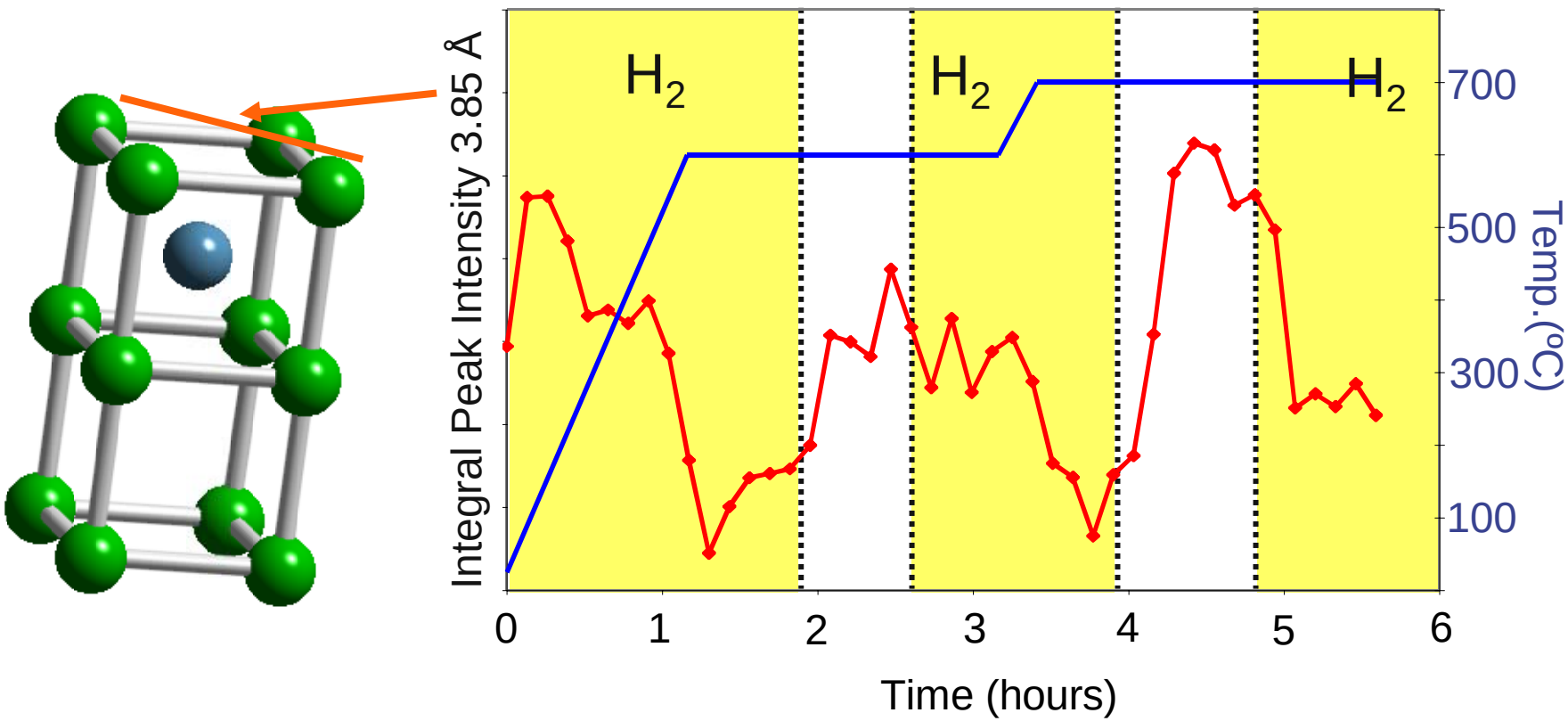
^{17}O MAS NMR





Nano-CeO_2: Changing Oxygen Content

Oxygen is removed from the 01 site in nano-Ceria on Reduction



What are the opportunities…

(1) Simultaneous measurements

-combine PDF, SAXS, *(maybe even EXAFS ???)*

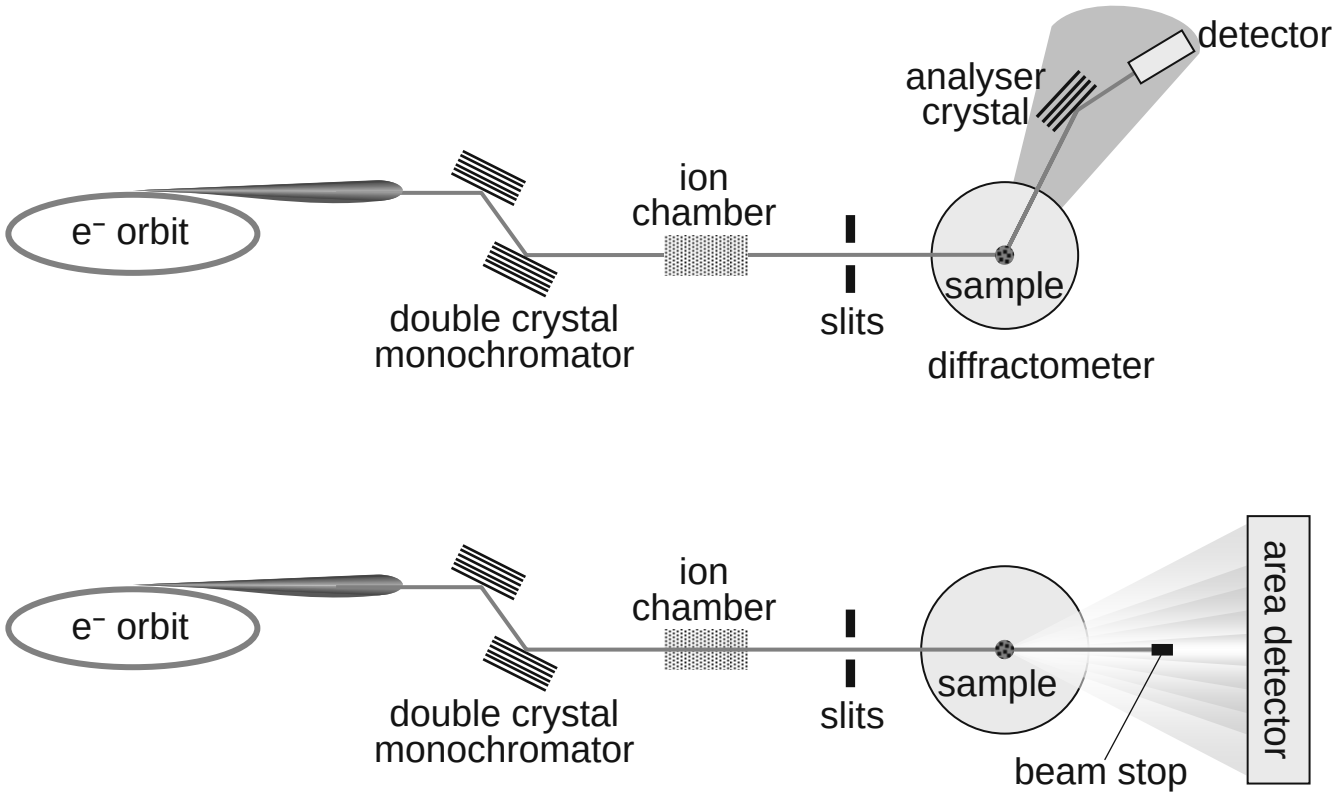
(2) Chemically Resolved Measurements

-resonant scattering

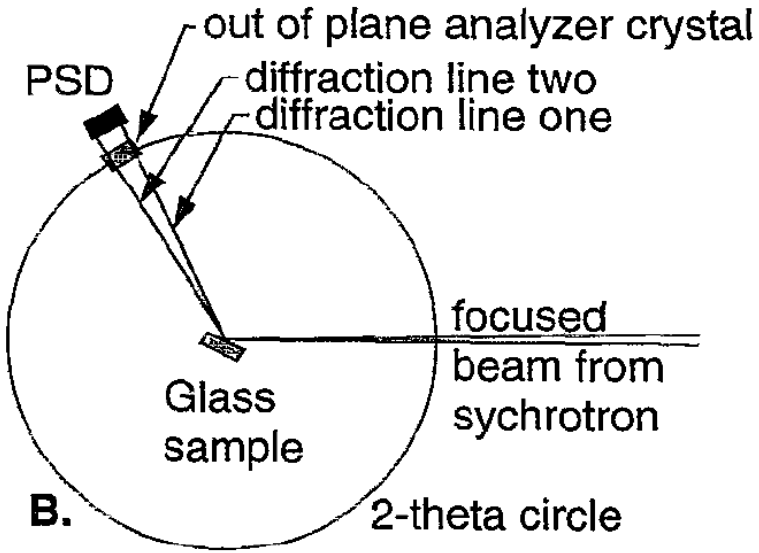
(3) Energy Resolved Measurements

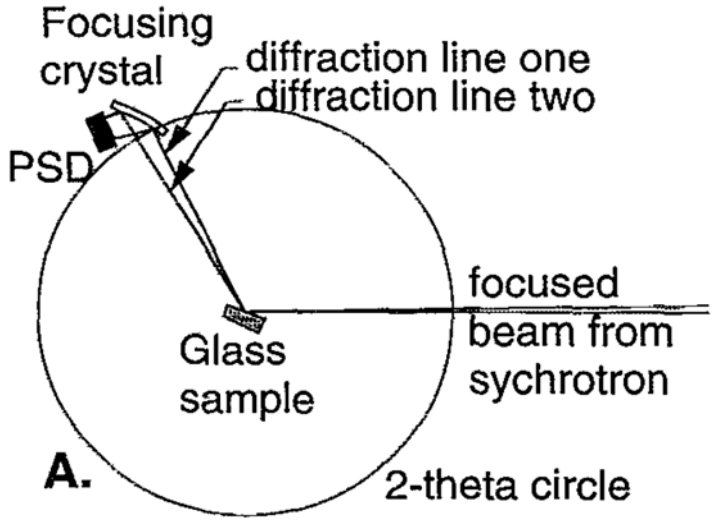
-Discriminating Compton Scattering

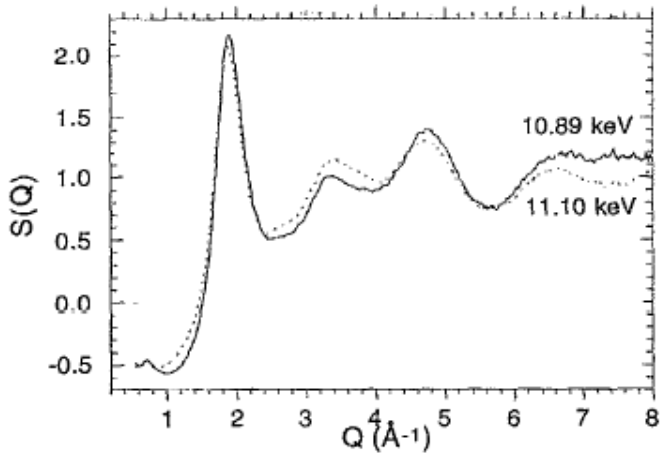
Common Instrumentation Configurations



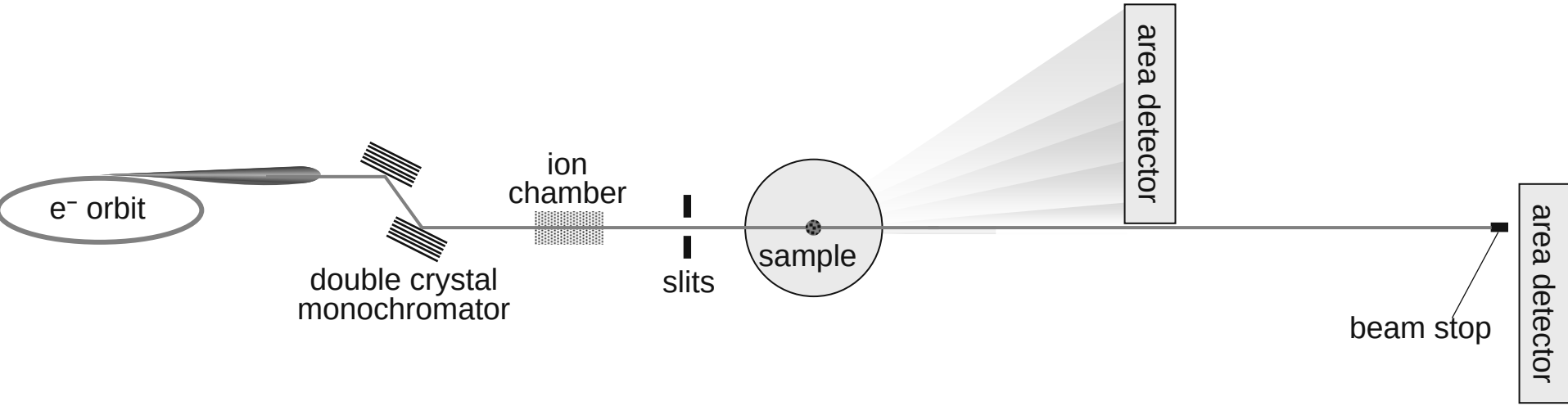
Rapid Energy Resolved Measurements?

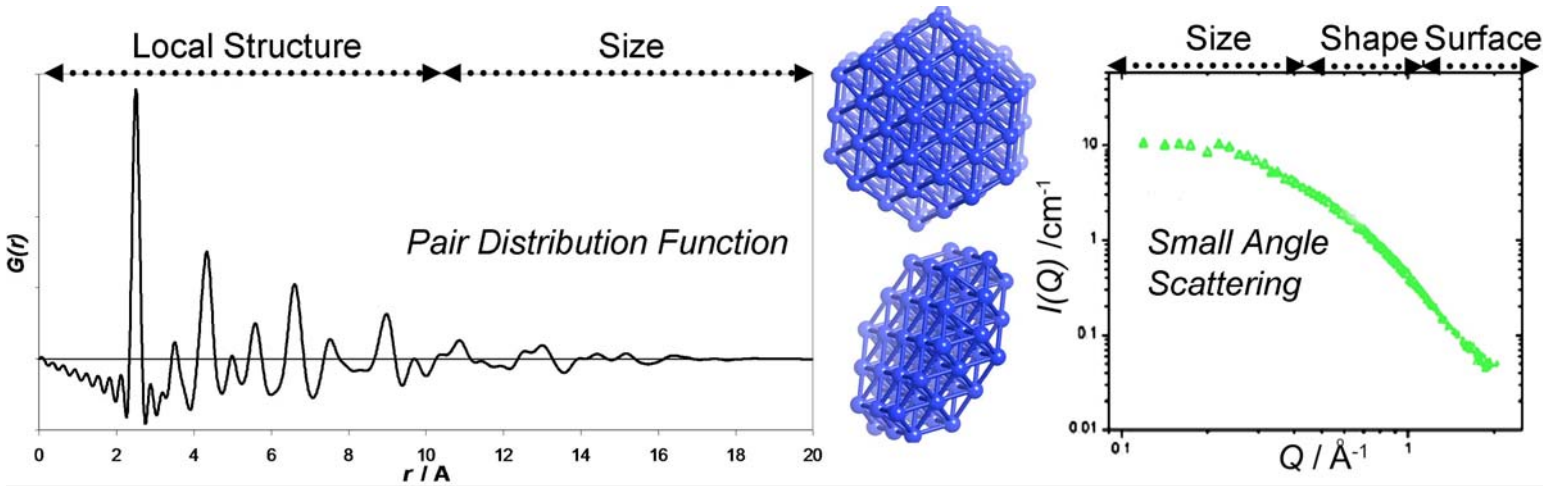






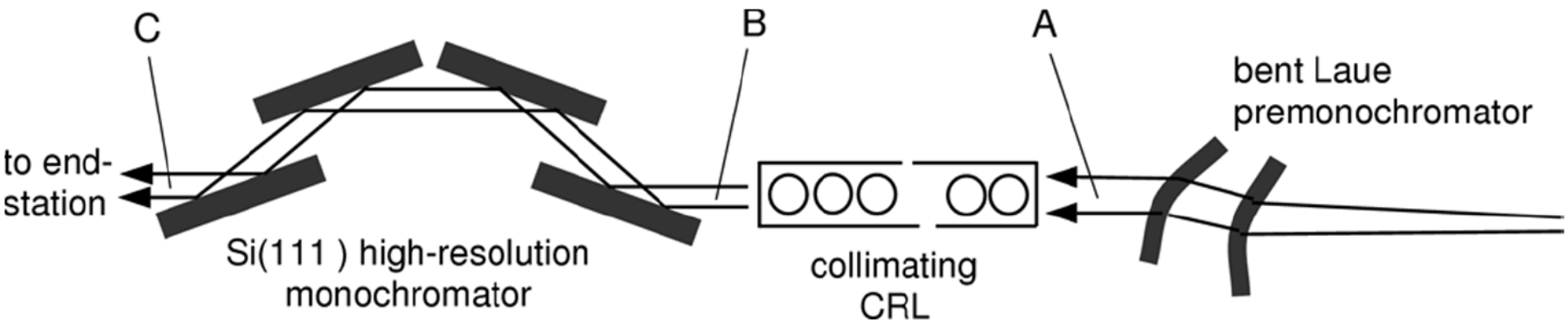
Combined PDF and SAXS measurements





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

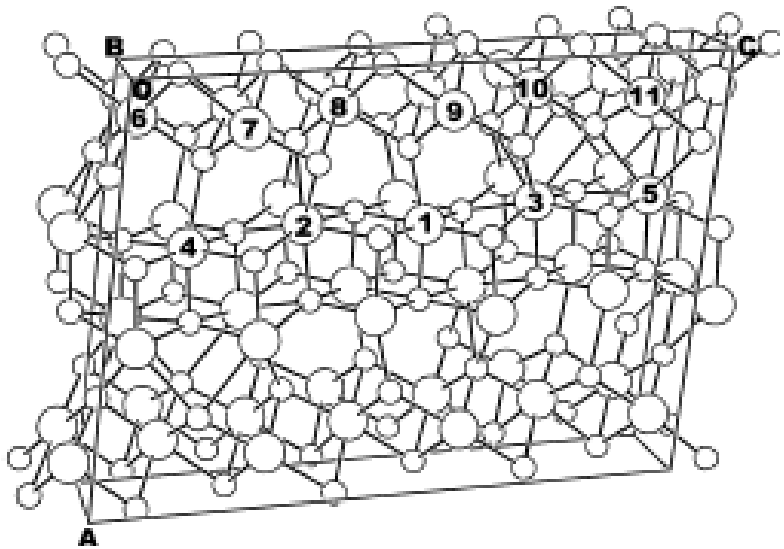
S. D. Shastri, *J. Synchrotron Rad*., **11**, 150 (2004)



Example of High-Energy Resonant Scattering

- Distribution of Pb and Bi 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)



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