Total scattering and PDFs using X-ray free-electron lasers: quality data in 30 femtoseconds

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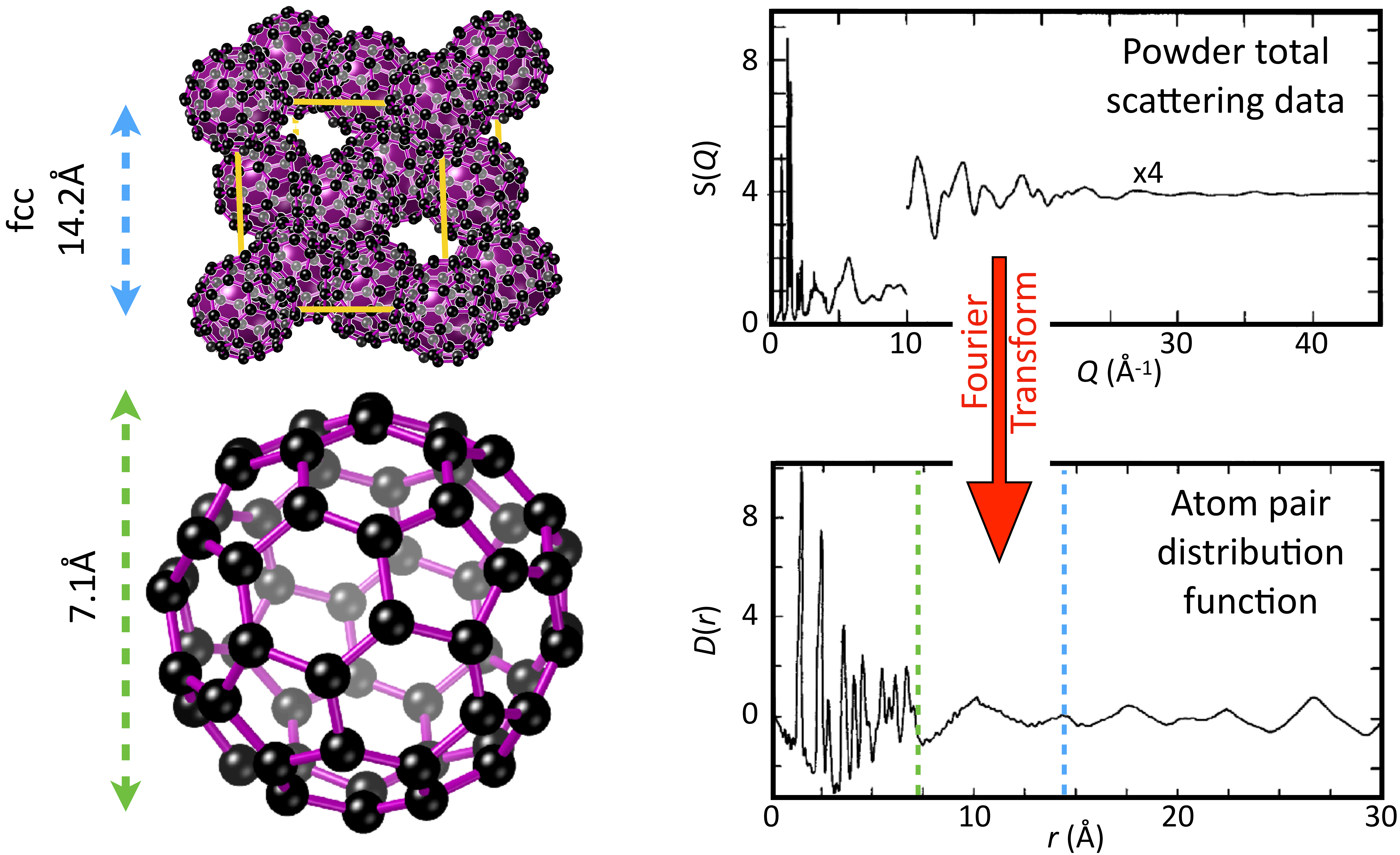
Science and Technology Facilities Council

ISIS Neutron and Muon Source

ADD2026, EPN Campus, Grenoble, 11th-16th January 2026

Neutron total scattering from C_{60} at room temperature



J R D Copley *et al*, *J. Phys. Chem. Sol.* **53** (1992) 1353

Timescales for processes in matter

<table>
<tr><th>Timescale</th><th></th><th></th><th></th></tr>
<tr><td>10^{-6} (μs)</td><td rowspan="3">Lattice dynamics; thermal effects; secondary structure dynamics in biomolecules; nanoparticle formation</td><td></td><td></td></tr>
<tr><td>10^{-9} (ns)</td><td></td><td></td></tr>
<tr><td>10^{-12} (ps)</td><td rowspan="2">Electron-phonon dynamics; Valence electron dynamics</td><td></td></tr>
<tr><td>10^{-15} (fs)</td><td></td><td rowspan="2">Inner shell electron dynamics</td></tr>
<tr><td>10^{-18} (as)</td><td></td><td></td></tr>
</table>

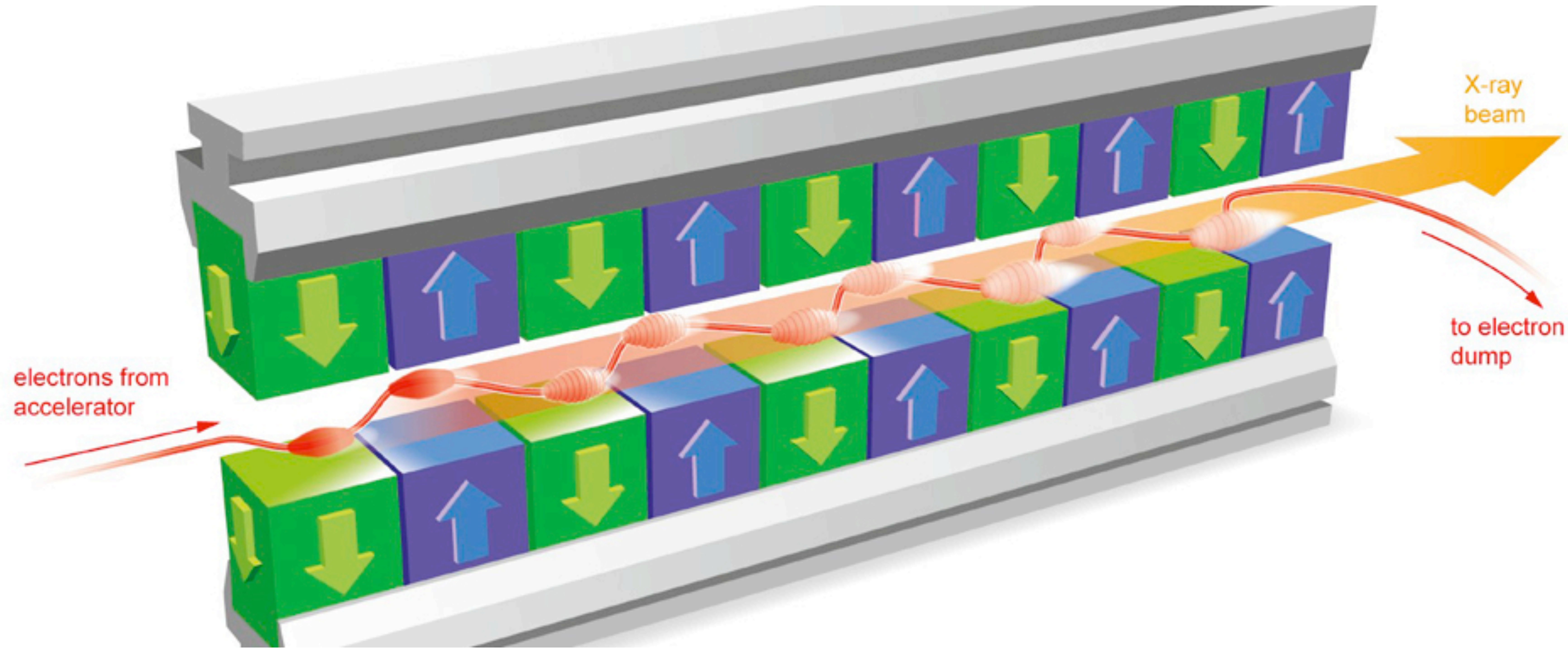
Can total scattering/PDF methods be used to usefully interrogate these processes, even if the data could be collected fast enough?

XFELs within the history of total scattering

Source	Q_{max} (Å^{-1}) (r-resolution$\sim\pi/Q_{max}$)	Timescale for measurement	Year method started
Cu/Mo X-ray	~ 16	~ days	1930s
Neutron	~ 40	~ hours	1990s
Synchrotron X-ray	~ 26	~ seconds	2000s
XFELs	~ 8	~ 100fs	2010s
XFELs (our work)	~ 20	~ 30fs	2023

Principles of X-ray free-electron lasers

- Bunches of electrons are formed using a 1.9km long superconducting accelerator
- Electrons pass through long (>100m) undulators where SASE of X-rays takes place
- The intense X-ray beam is pulsed, polarised and coherent
- The EuXFEL is 3.4km long and produces 27,000 X-ray pulses/s



www.xfel.eu/facility/overview/how_it_works/index_eng.html

The European XFEL

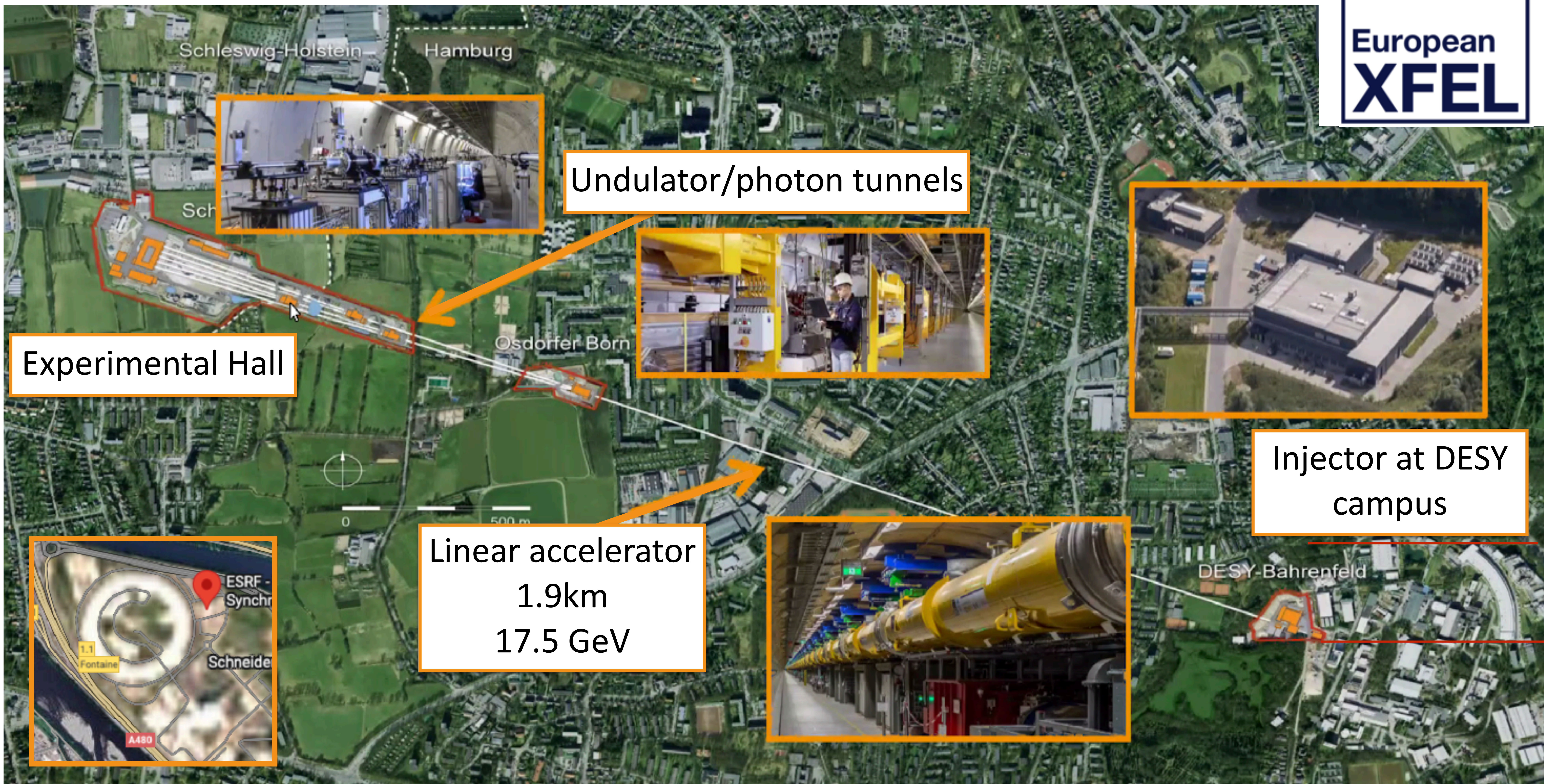
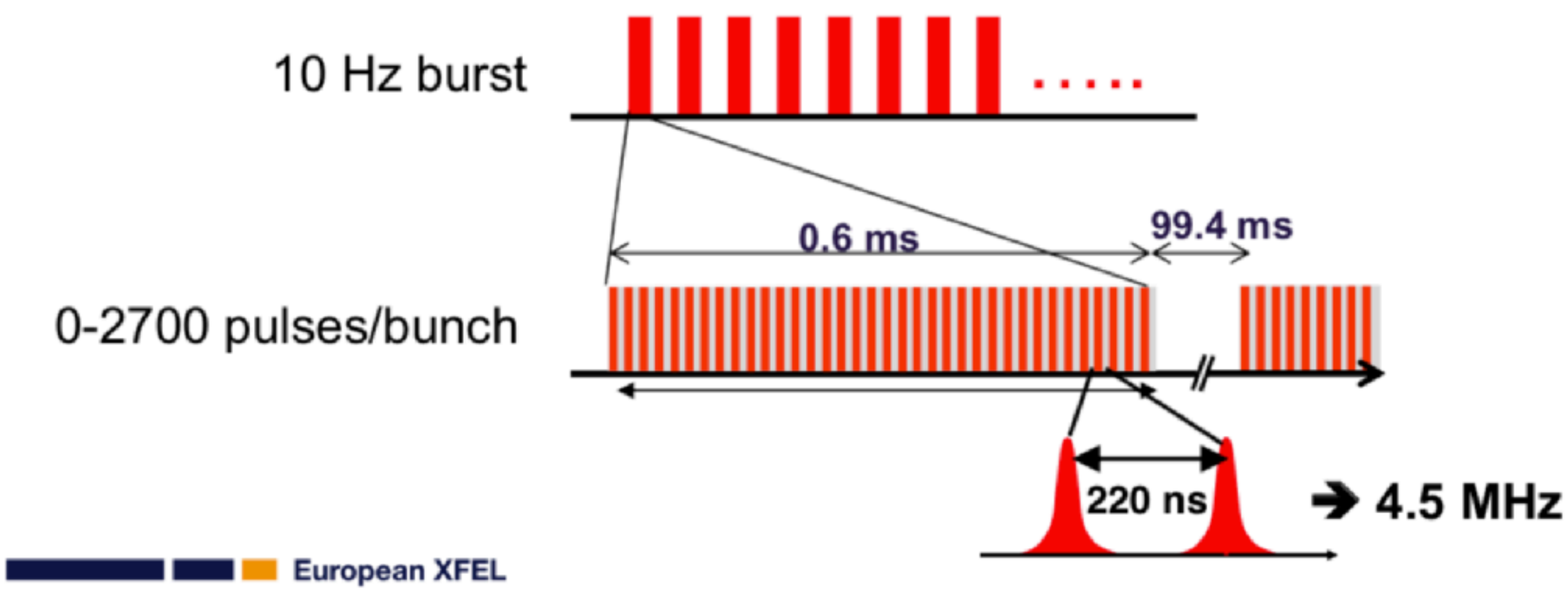


Image c/o Sakura Pascarelli (EuXFEL)

XFELs - useful characteristics for total scattering?

- X-ray intensity is very high, ~10^{10-11} photons/pulse
- Each X-ray pulse is very short, ~30 fs (30×10^{-15} s)
- XFEL X-ray energies are low, but are increasing
- Total scattering is a 'snap-shot' technique but it isn't quick
- At an XFEL you can measure PDF 'snap-shots' *very* quickly



ultra-fast total scattering/PDF
Any experiment where the local structure changes 'quickly' in response to external 'stimuli' *should be possible*

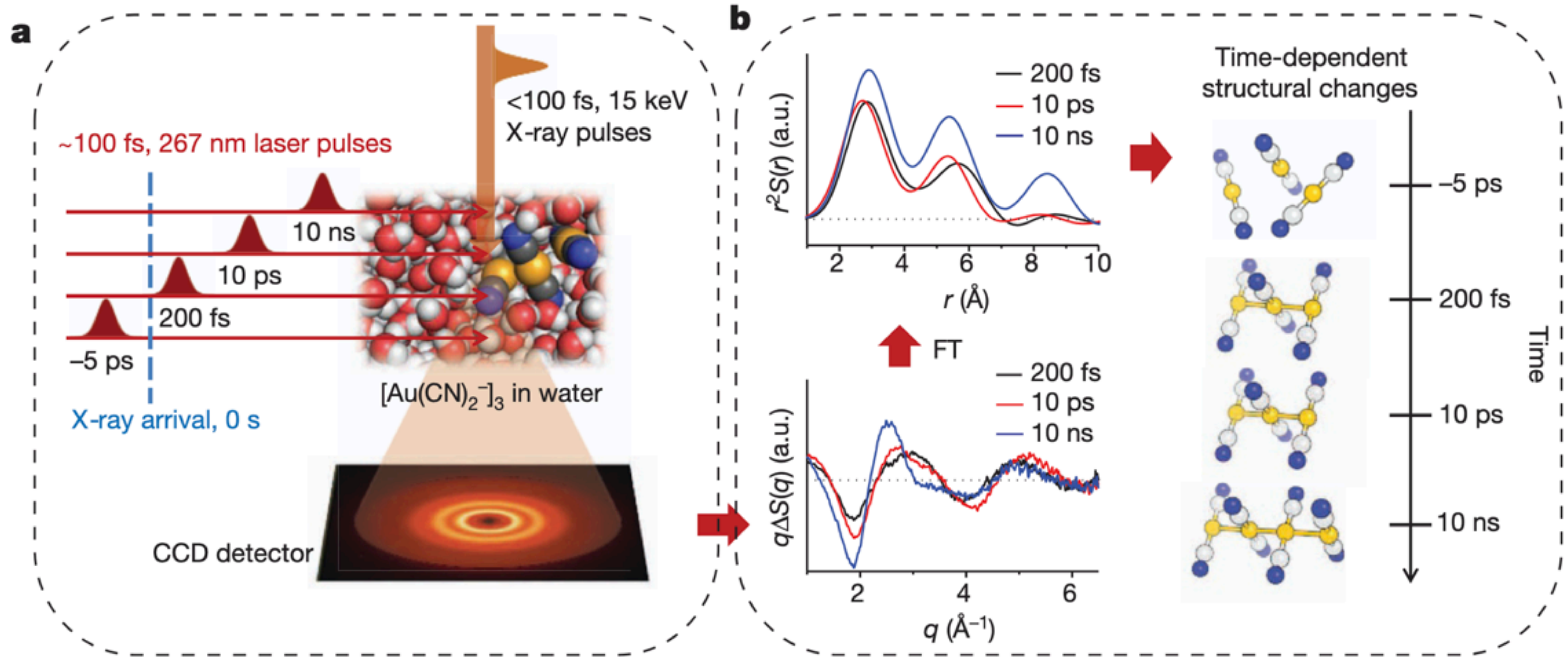
Opportunities for *uf*-TS/PDF at XFELs

Any transition with a structural component can be followed using *uf*-TS/PDF; the method is not dependent on the state of matter.

- High-pressure, high-temperature liquid structures (Planetary science, fundamentals of structure)
- Melting, recrystallisation, nanoparticle formation, supercooling
- Structural studies of solutions, gas phases and warm dense matter
- Phases transitioning, non-equilibrium transformative phenomena in materials.

Aurophillic bond formation in aqueous solution of $Au(CN)_2$

Kim *et al Nature* **518** (2015) 385



Charge ordering at the metal-insulator transition in $CuIr_2S_4$ spinel

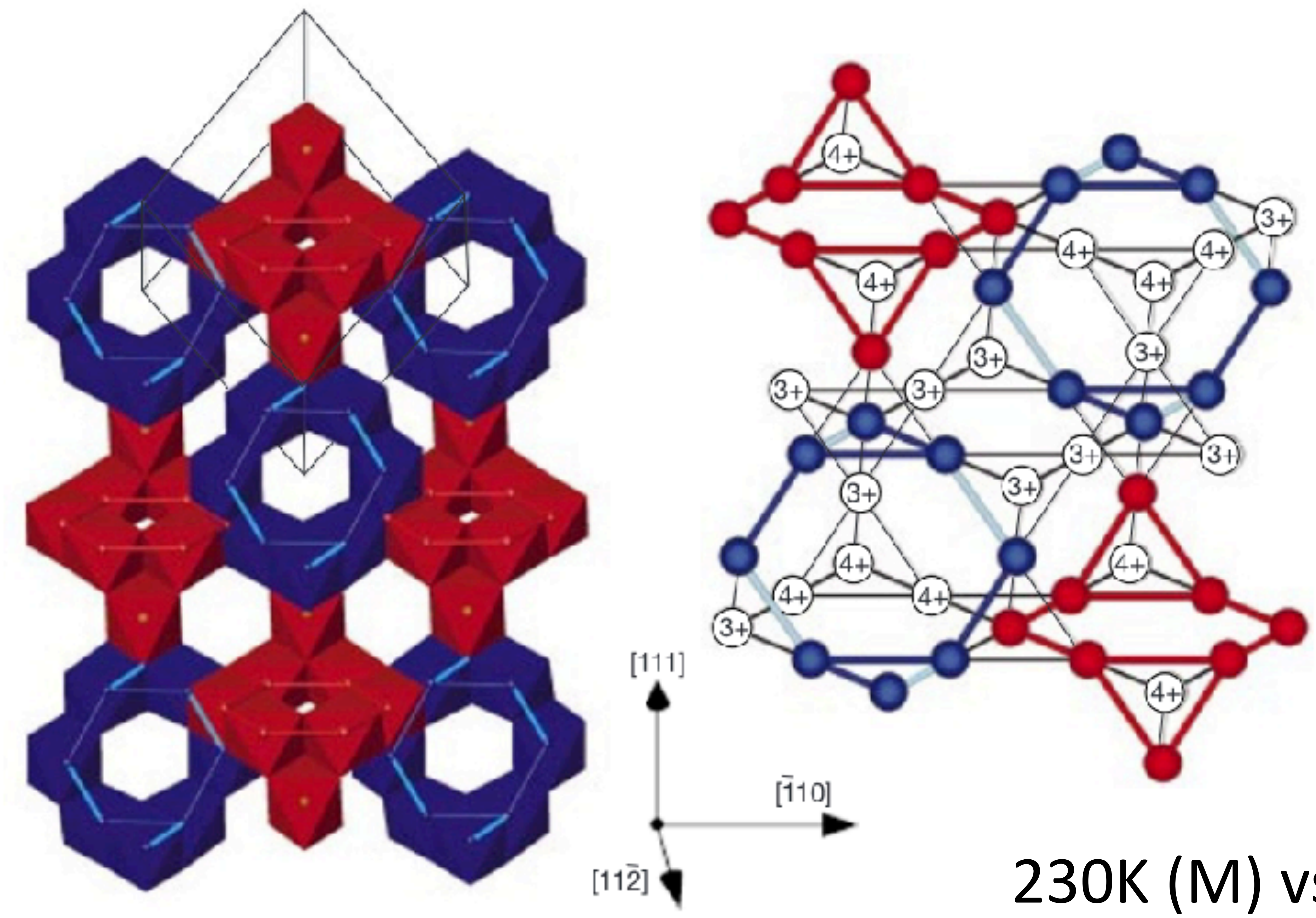
A <u>*difference*</u> *ultra-fast* PDF XFEL study

letters to nature

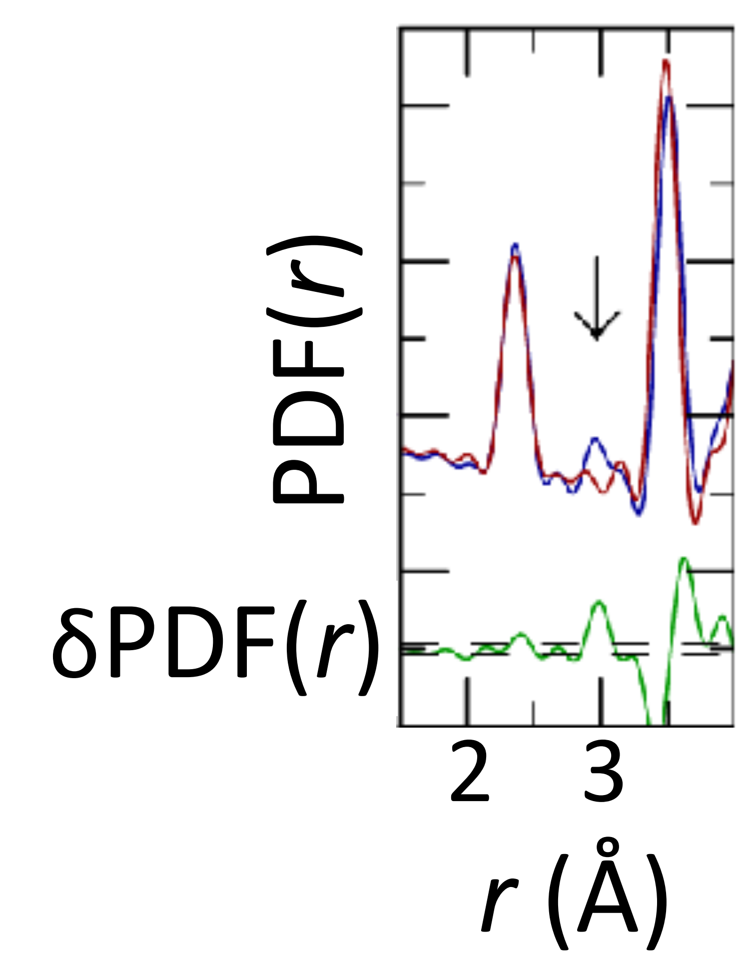
Formation of isomorphic Ir^{3+} and Ir^{4+} octamers and spin dimerization in the spinel $CuIr_2S_4$

Paolo G. Radaelli*, Y. Horibe†‡§, Matthias J. Gutmann*, Hiroki Ishibashi§‖, C. H. Chen†, Richard M. Ibberson*, Y. Koyama‡, Yew-San Hor§, Valery Kiryukhin§ & Sang-Wook Cheong§

NATURE | VOL 416 | 14 MARCH 2002 | www.nature.com



230K (M) vs 220K (I)



PRL **106**, 045501 (2011) PHYSICAL REVIEW LETTERS week ending 28 JANUARY 2011

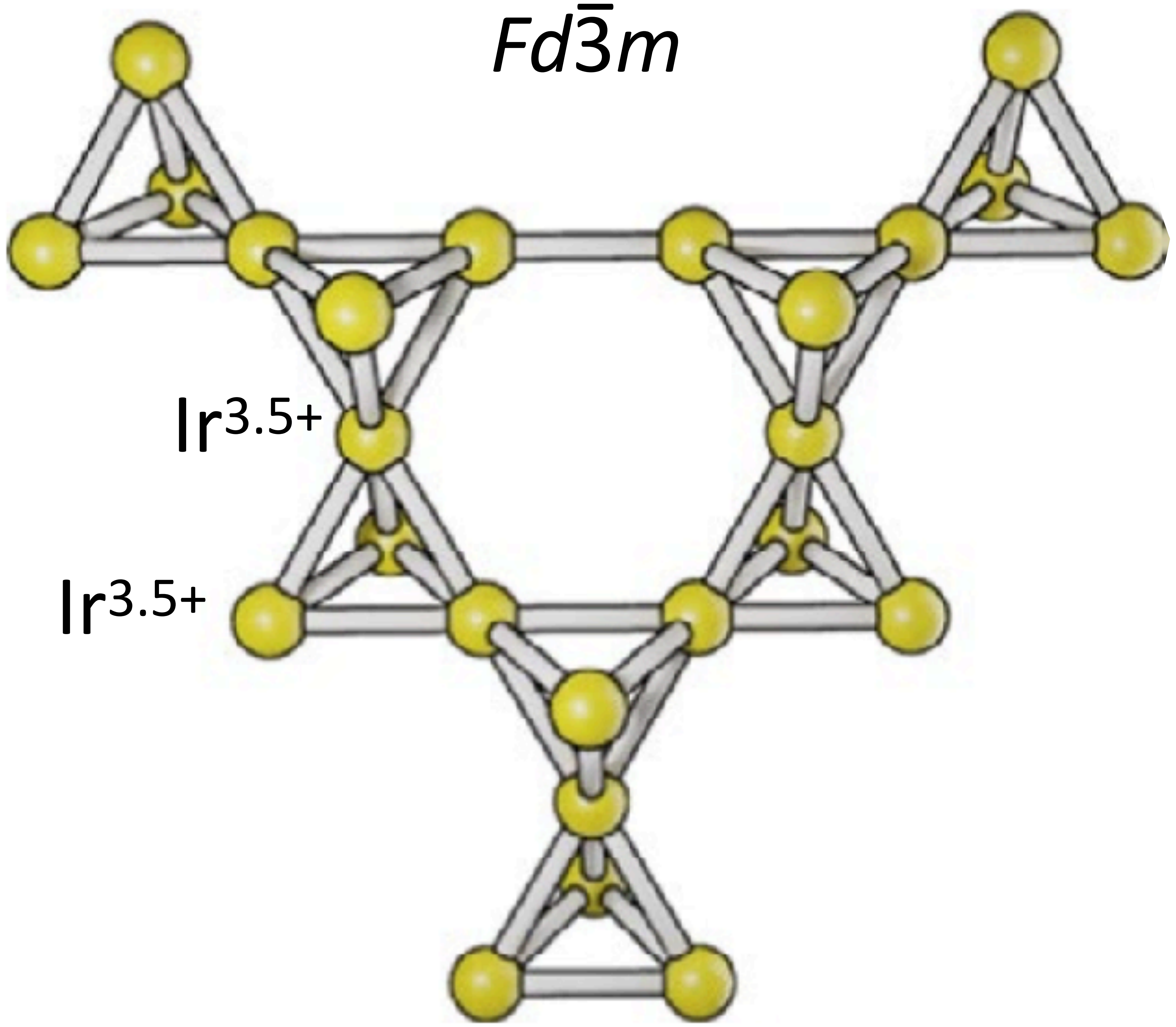
Detailed Mapping of the Local Ir^{4+} Dimers through the Metal-Insulator Transitions of $CuIr_2S_4$ Thiospinel by X-Ray Atomic Pair Distribution Function Measurements

E. S. Božin,[1,*] A. S. Masadeh,[2,3] Y. S. Hor,[4,†] J. F. Mitchell,[4] and S. J. L. Billinge[1,5]

Iridium pyrochlore substructure of $CuIr_2S_4$

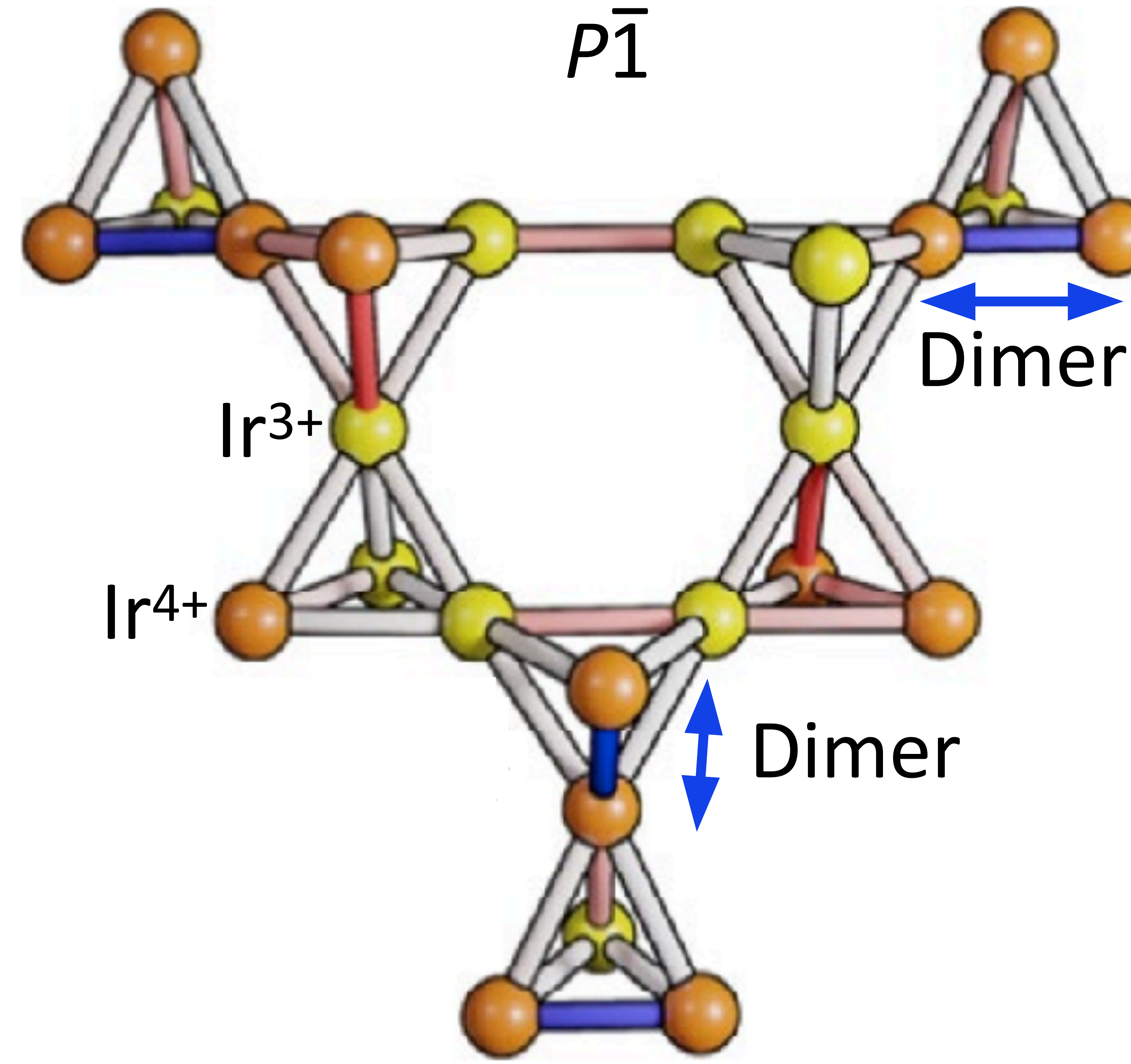
Cubic 300K Structure

$Fd\bar{3}m$



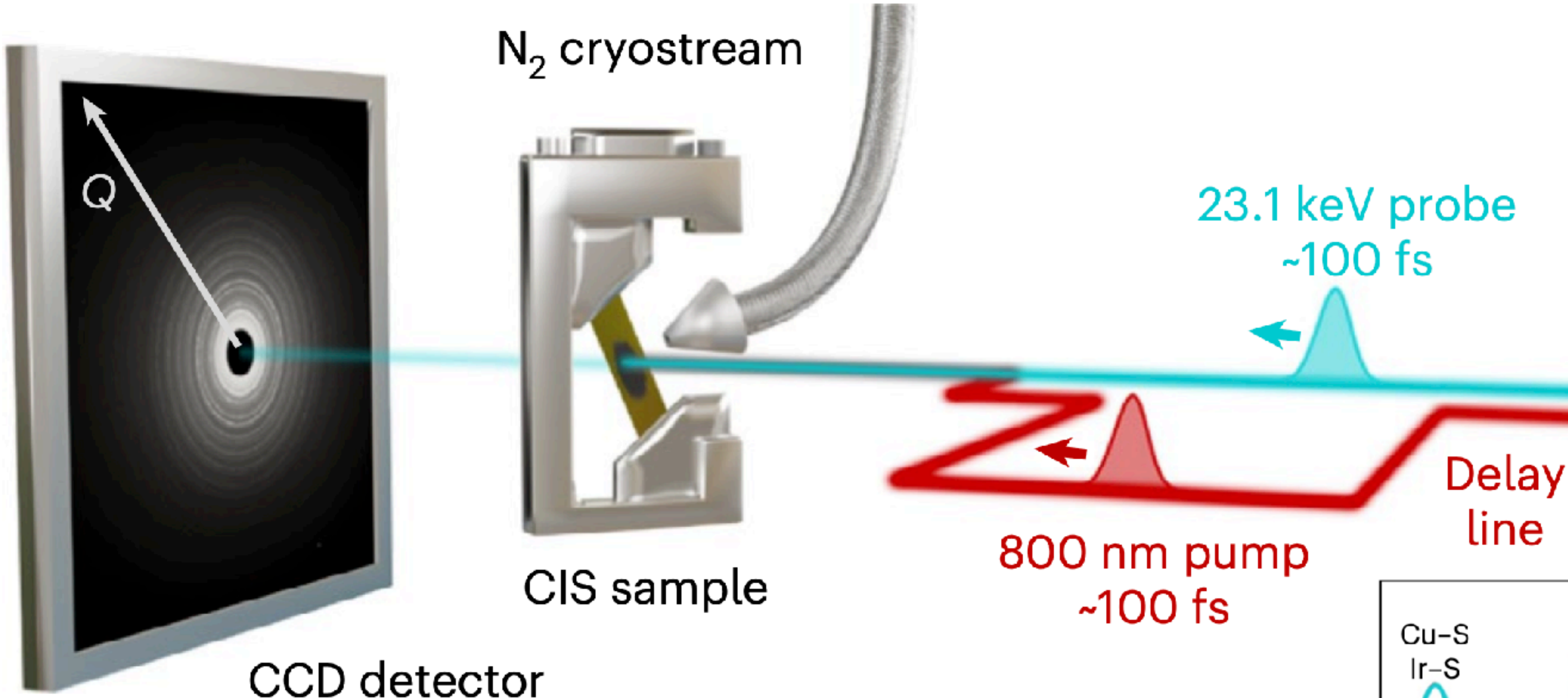
Triclinic 150K Structure

$P\bar{1}$

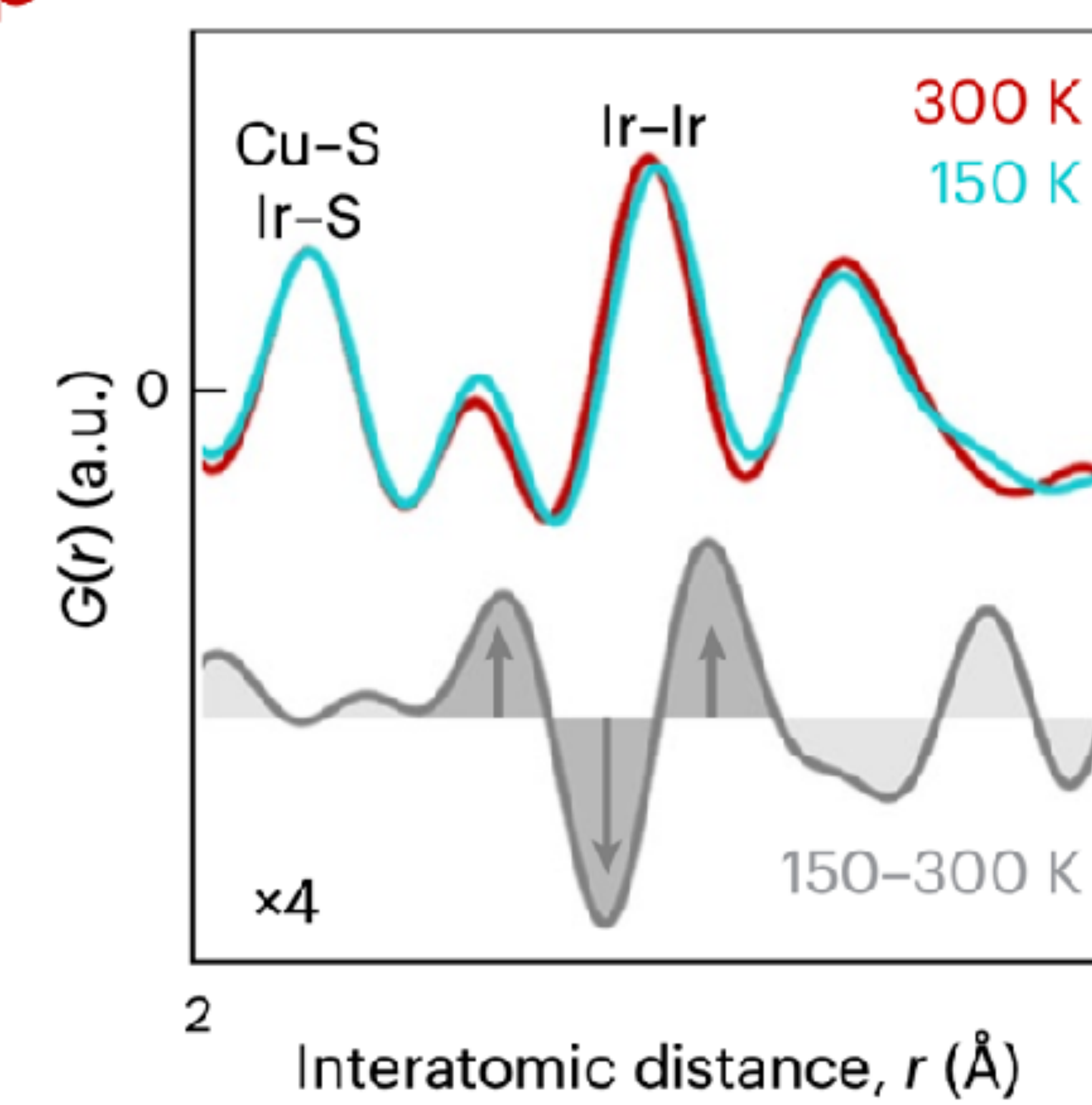


Griffiths *et al*, *Nature Mater.* (2024) doi.org/10.1038/s41563-024-01927-8

LCLS XFEL MFX pump-probe experiment



~70 mm from sample
$2\theta_{max}$~60°; Q_{max}~12.5Å^{-1}



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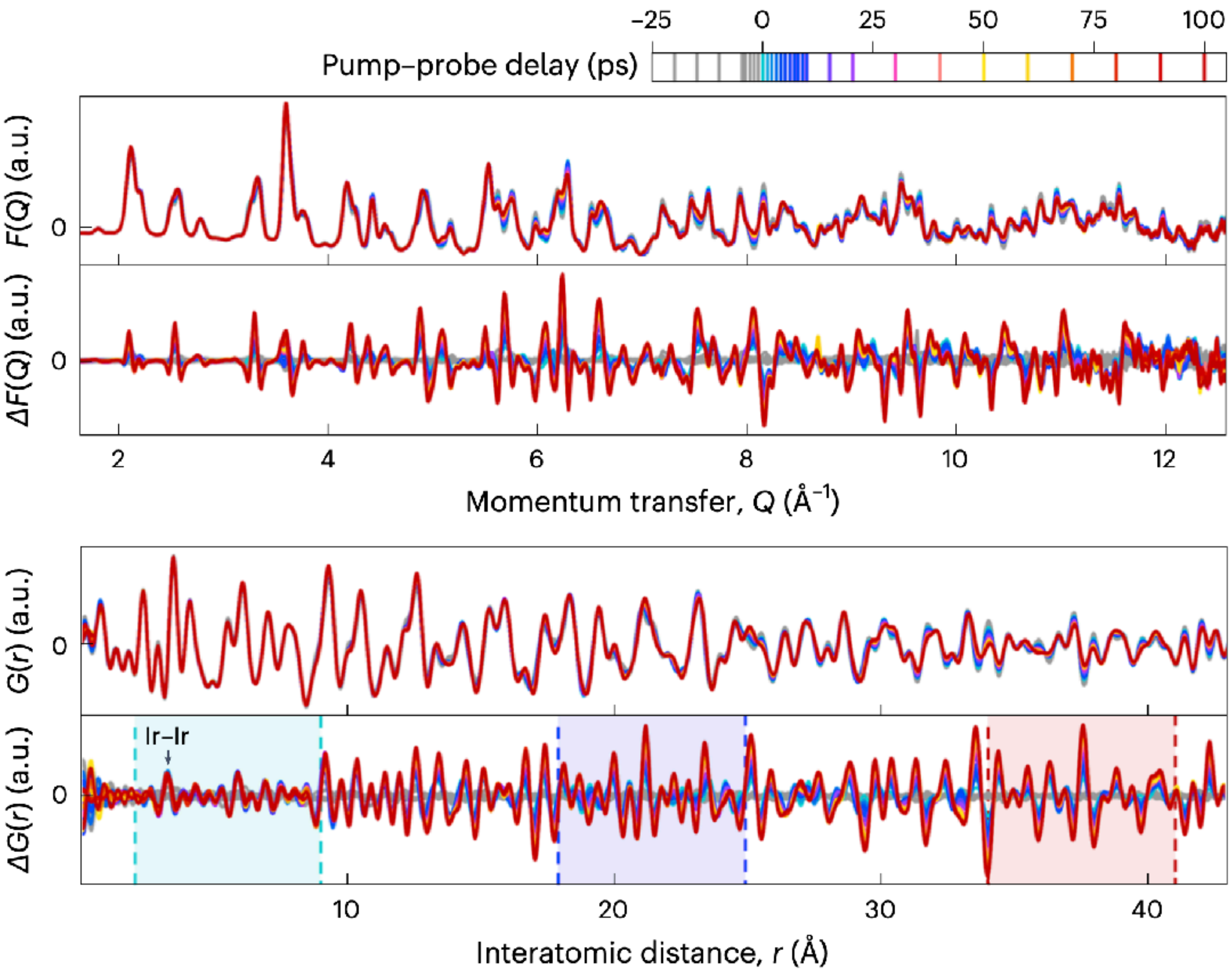
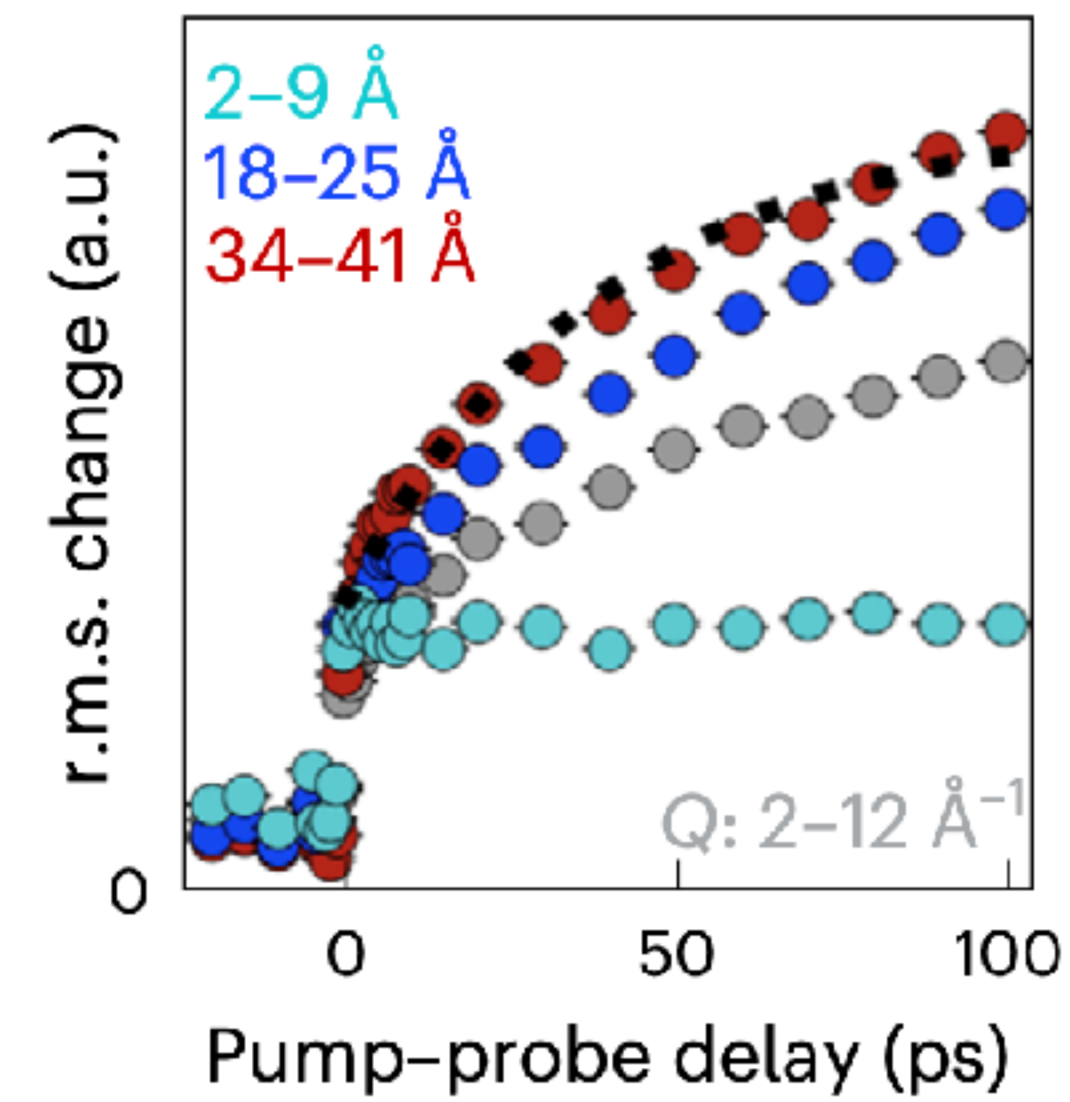
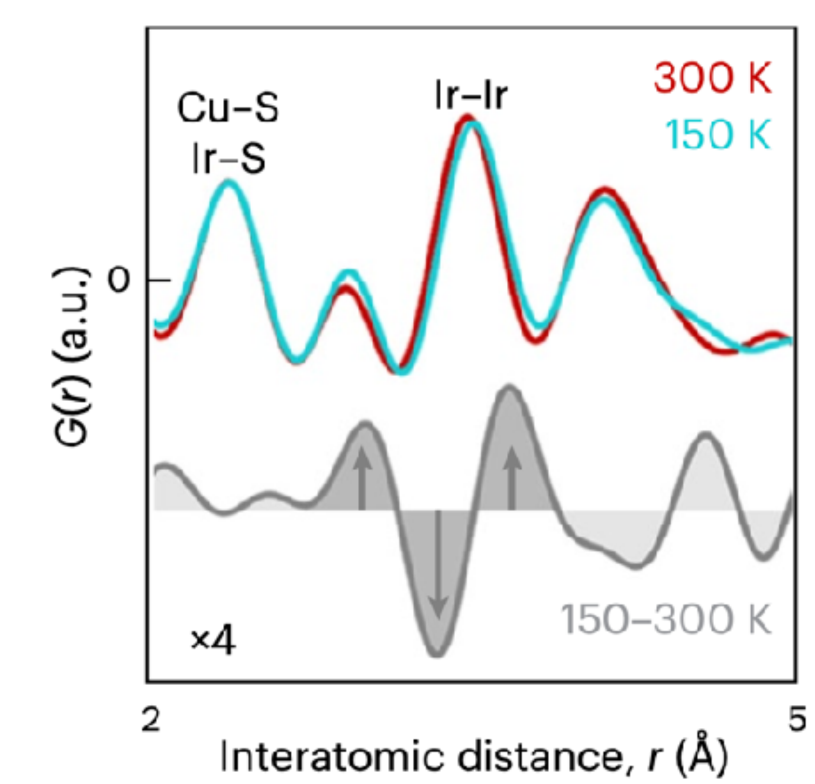
Structural response of $CuIr_2S_4$ to laser pumping



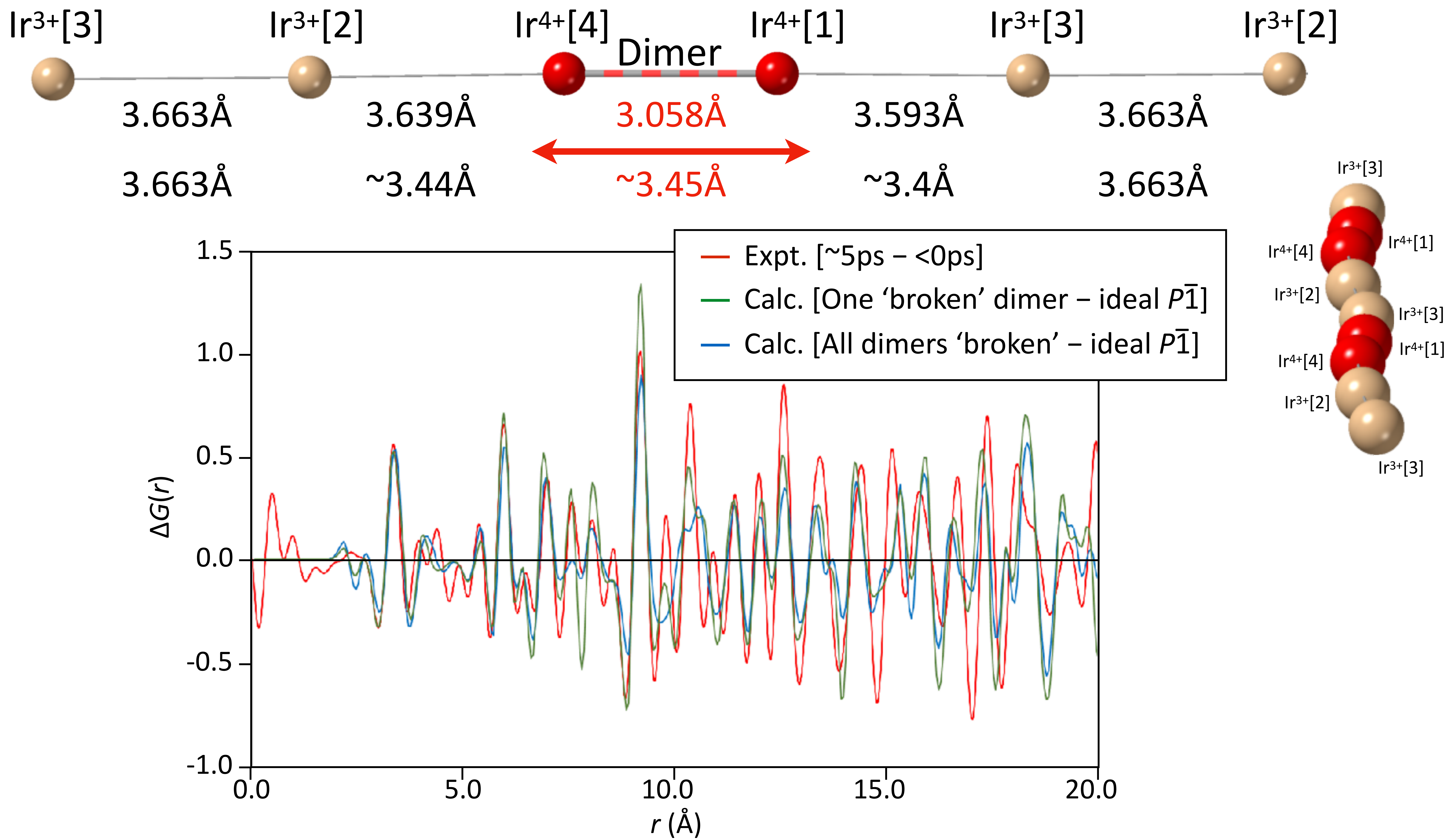


150K (M) – 300K (I)



Griffiths *et al*, *Nature Mater.* (2024) doi.org/10.1038/s41563-024-01927-8

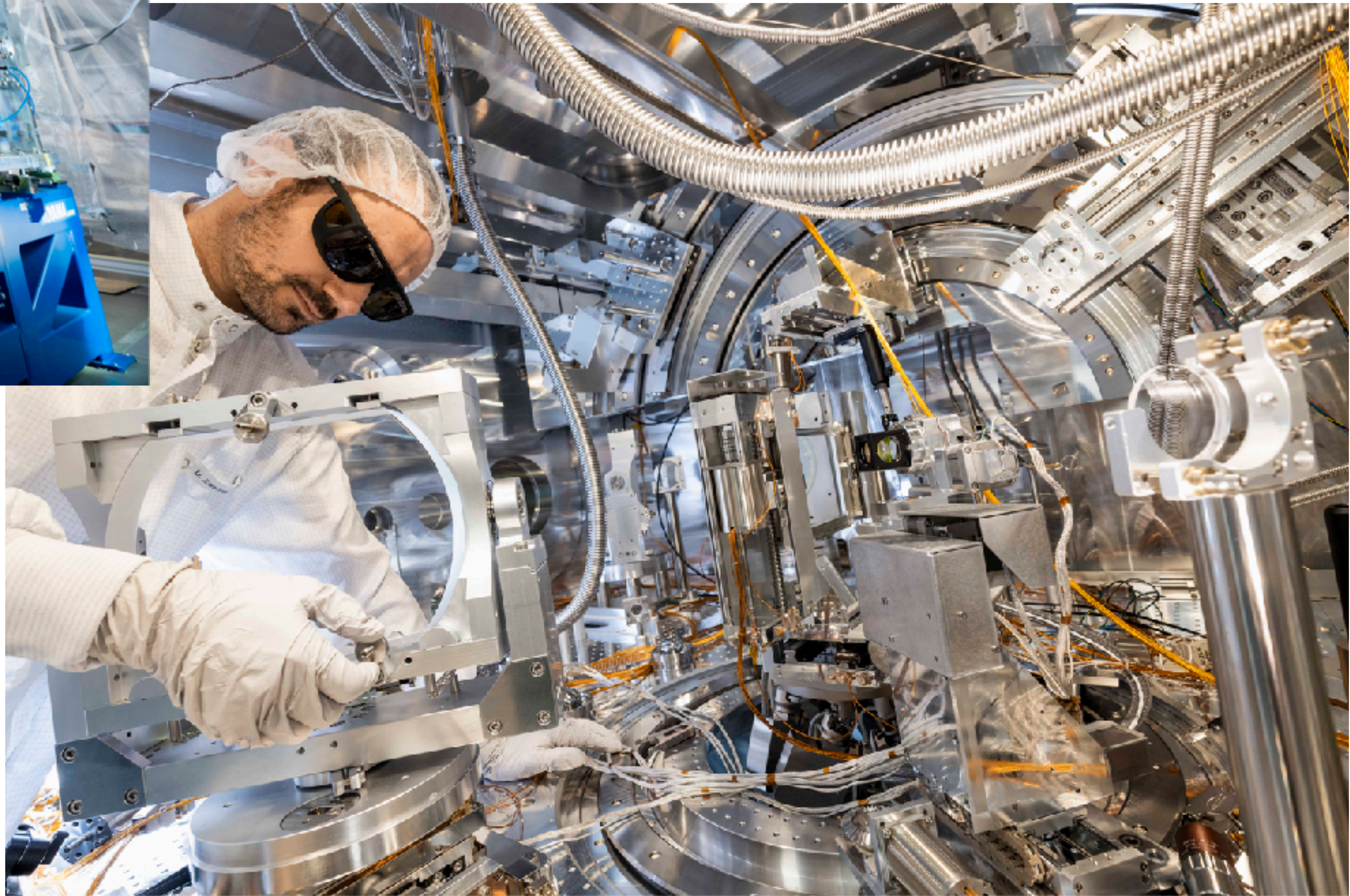
Simple modelling of ΔPDF data from $CuIr_2S_4$



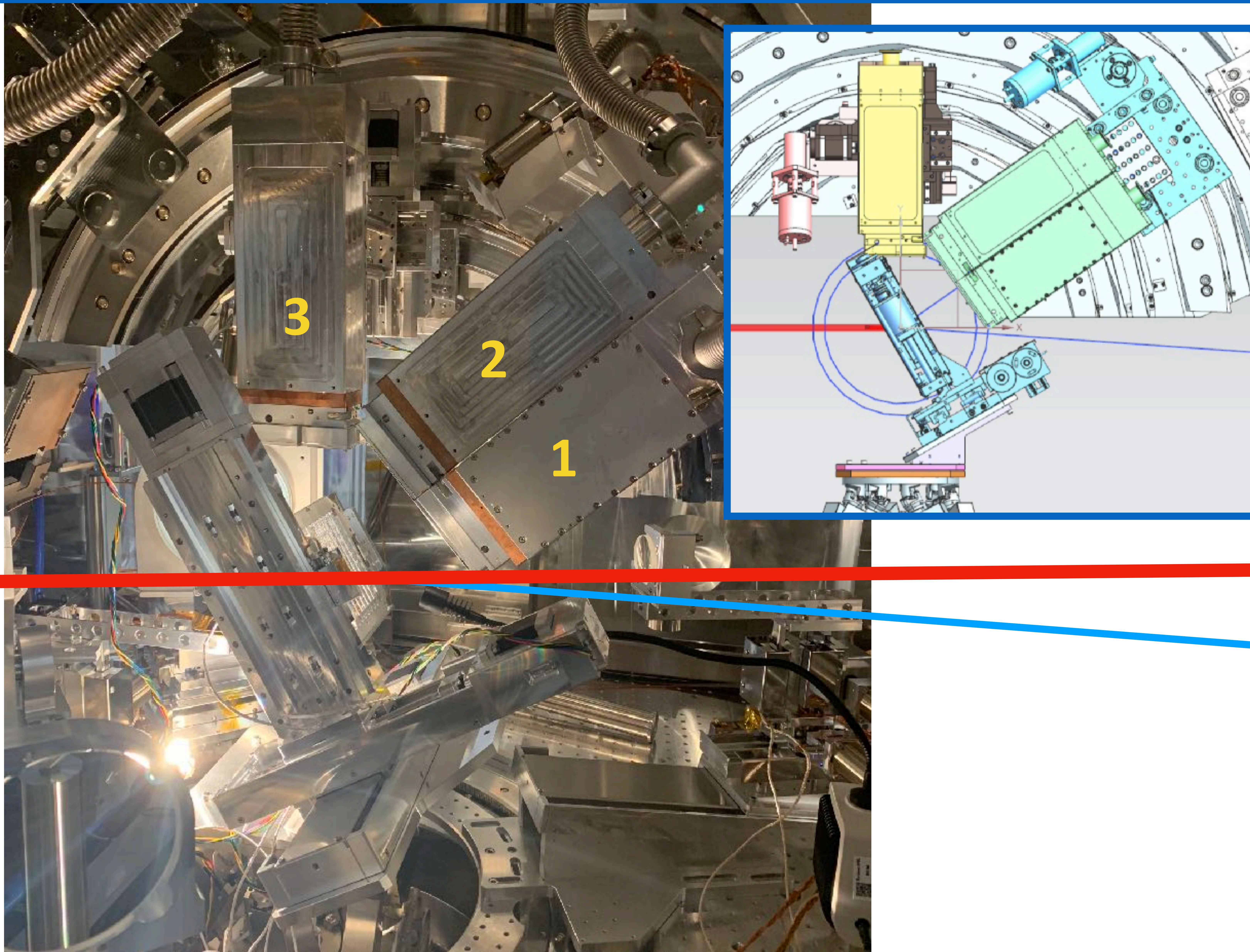
EuXFEL HED interaction chamber 1 (IC1)

Karen Appel

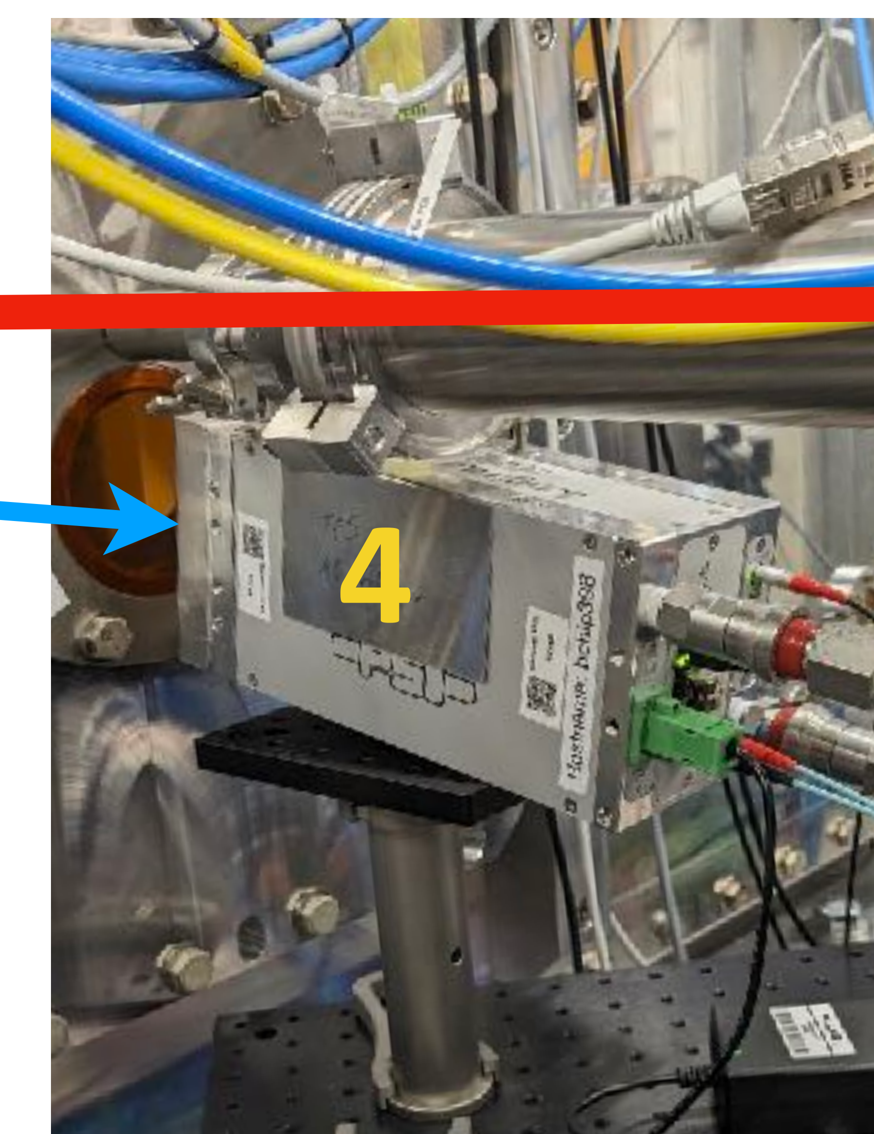
Ulf Zastrau



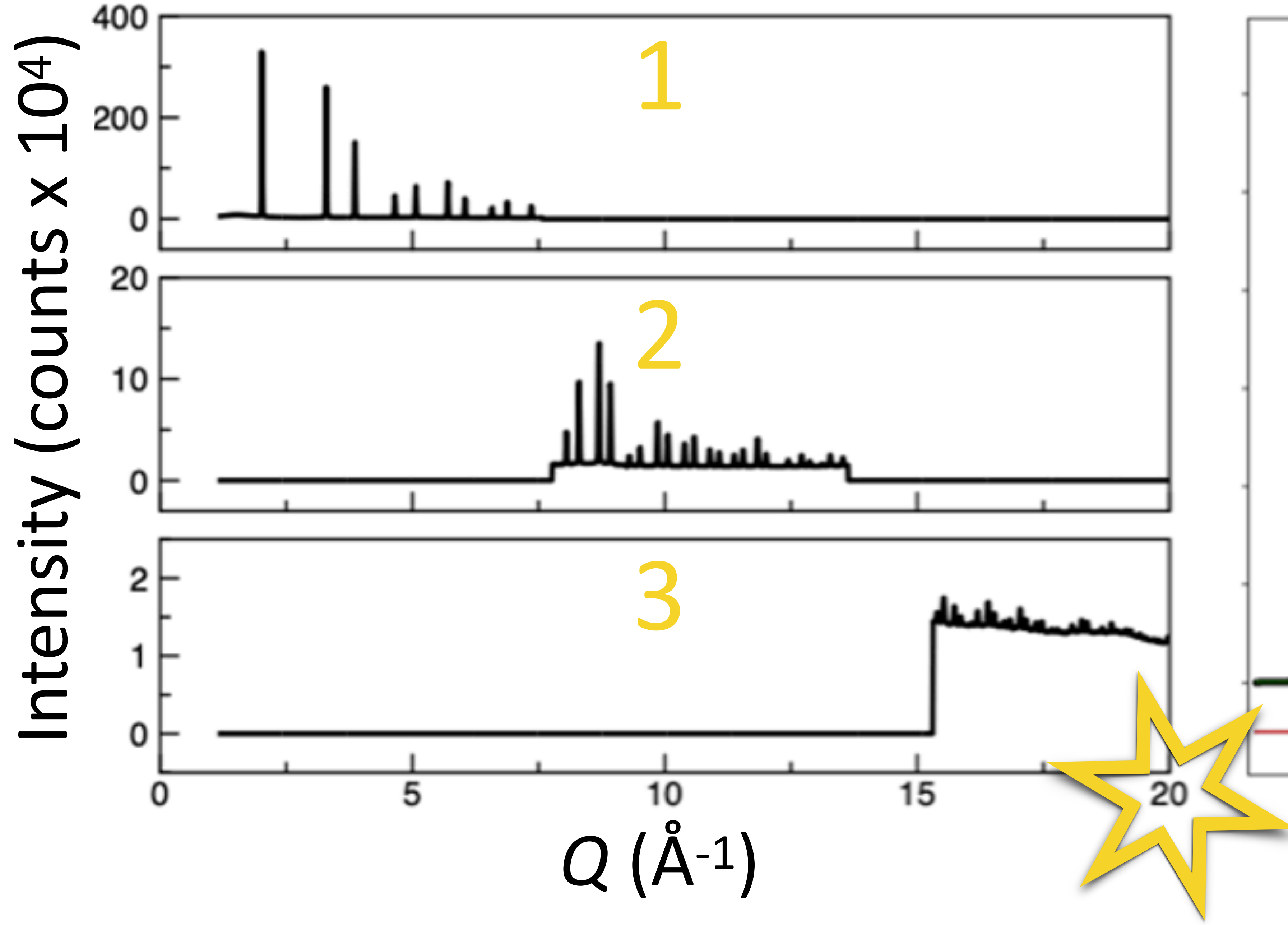
EuXFEL HED interaction chamber 1 set-up #1

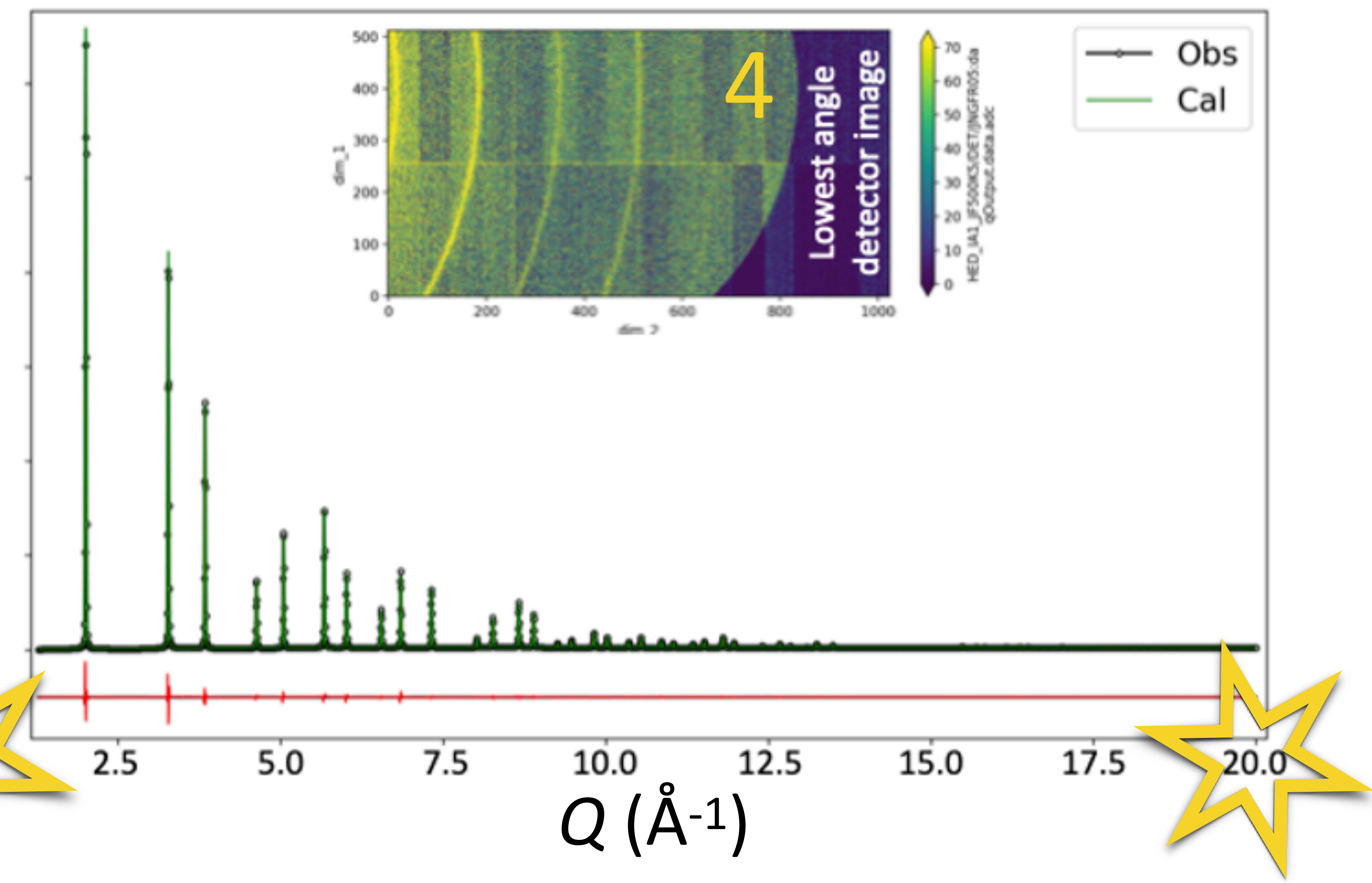


4 Jungfrau detectors
77 x 38 mm² (75 µm pixels)
Sample to detector >140 mm
Δ2θ > 90°
24 keV X-ray beam

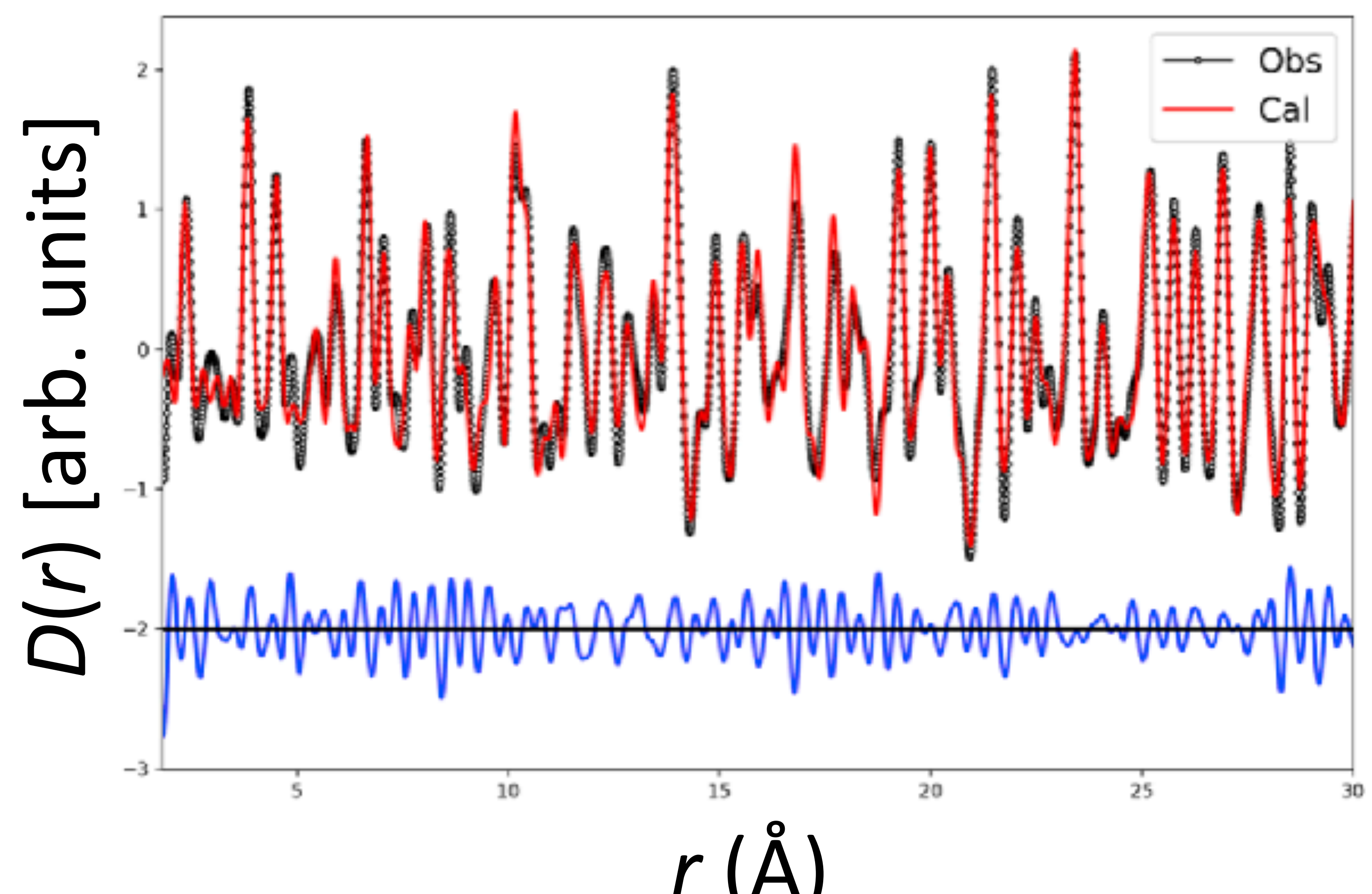


High-resolution EuXFEL data from NIST silicon

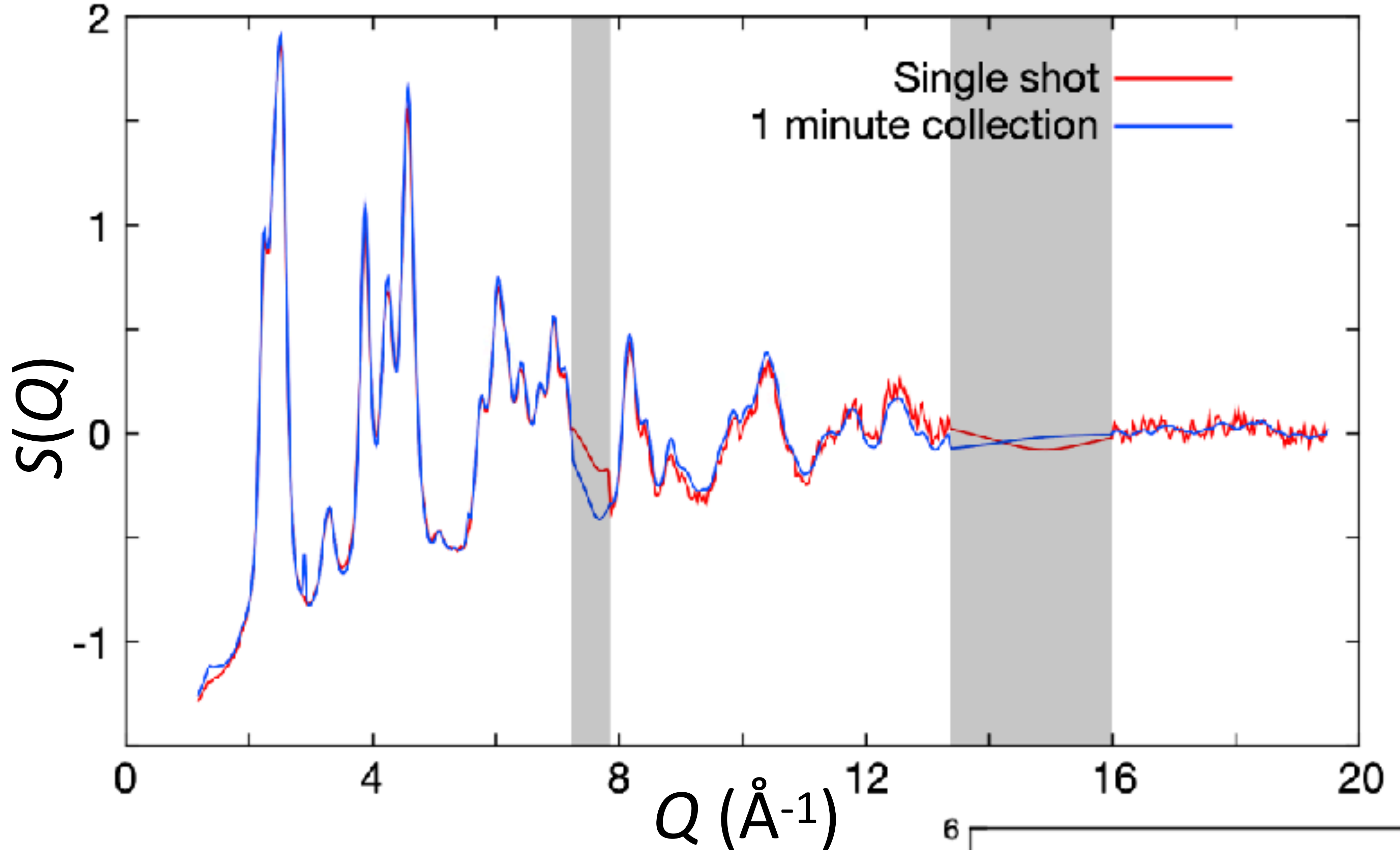


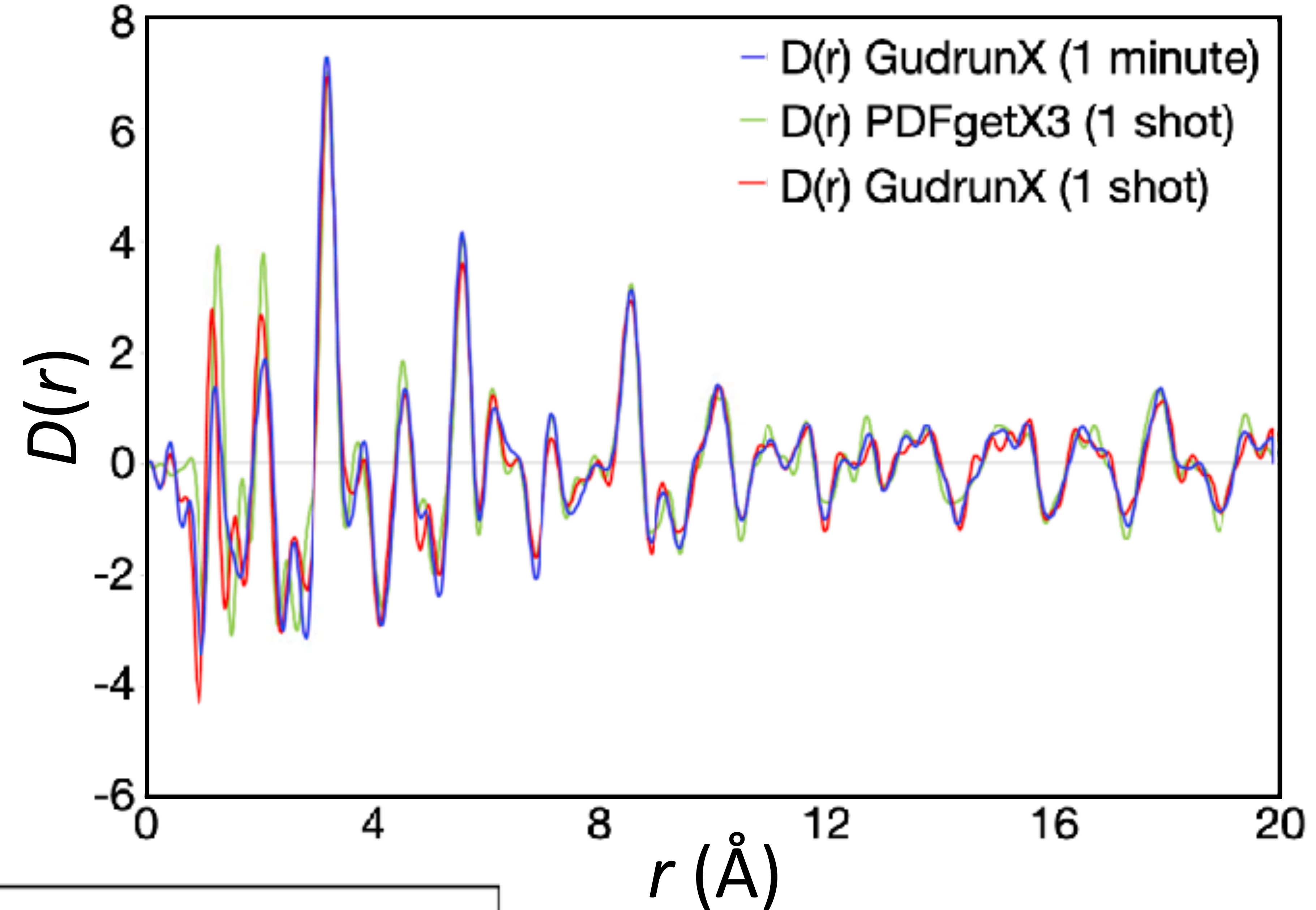


PDFFit to Silicon structure

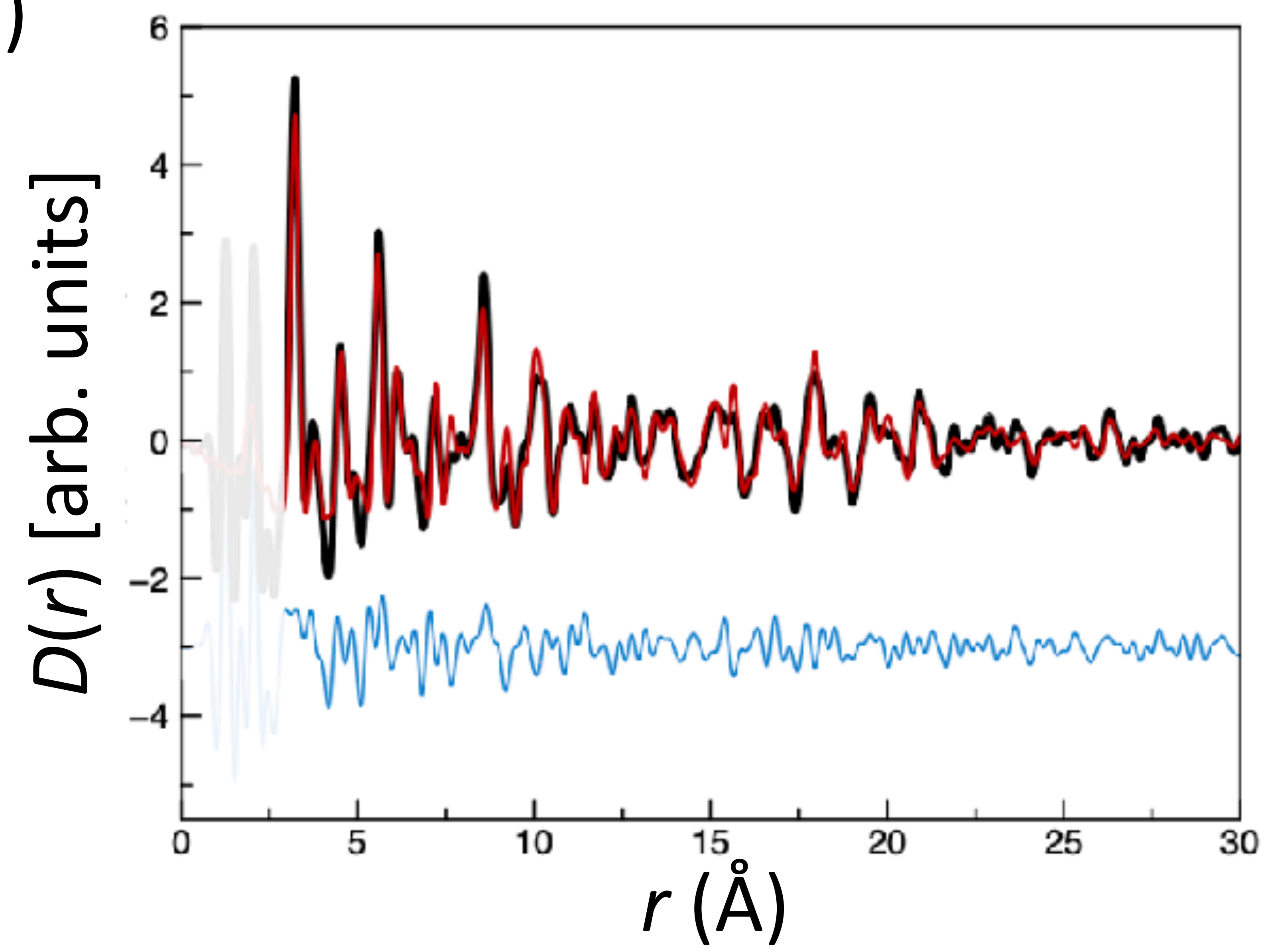


High-resolution EuXFEL data from ZnO nanoparticles

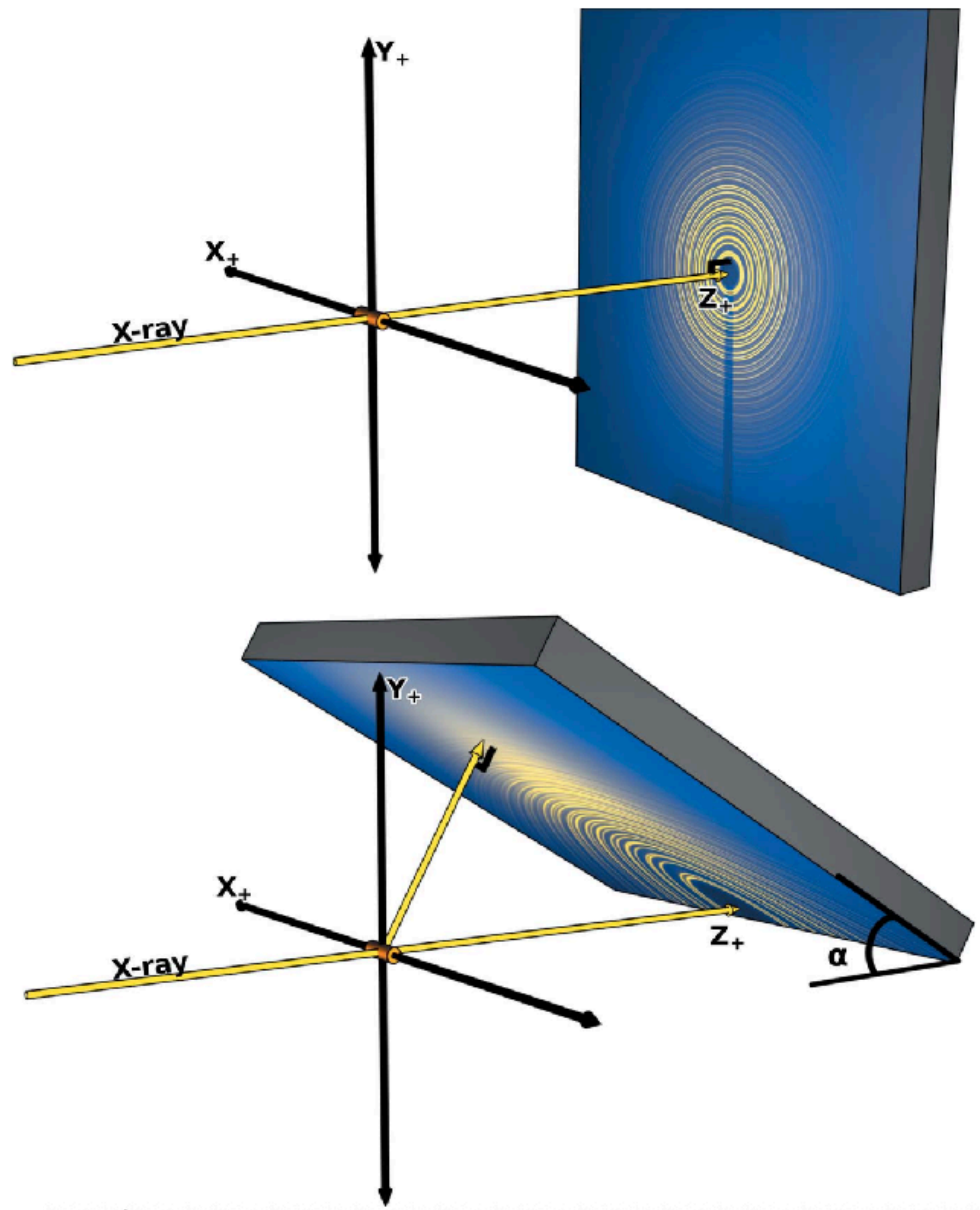


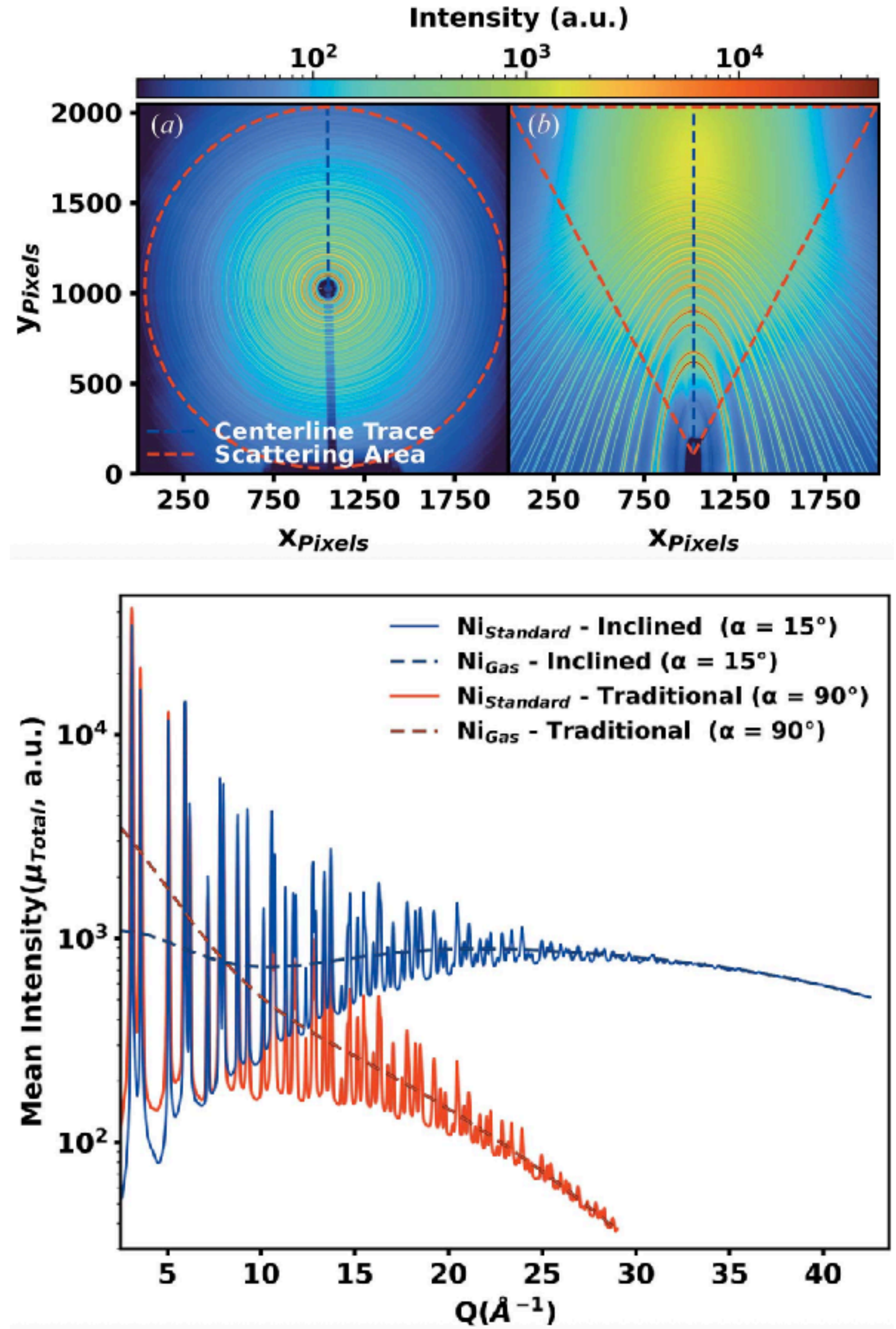


Discus fit using ZnO nanoparticle model



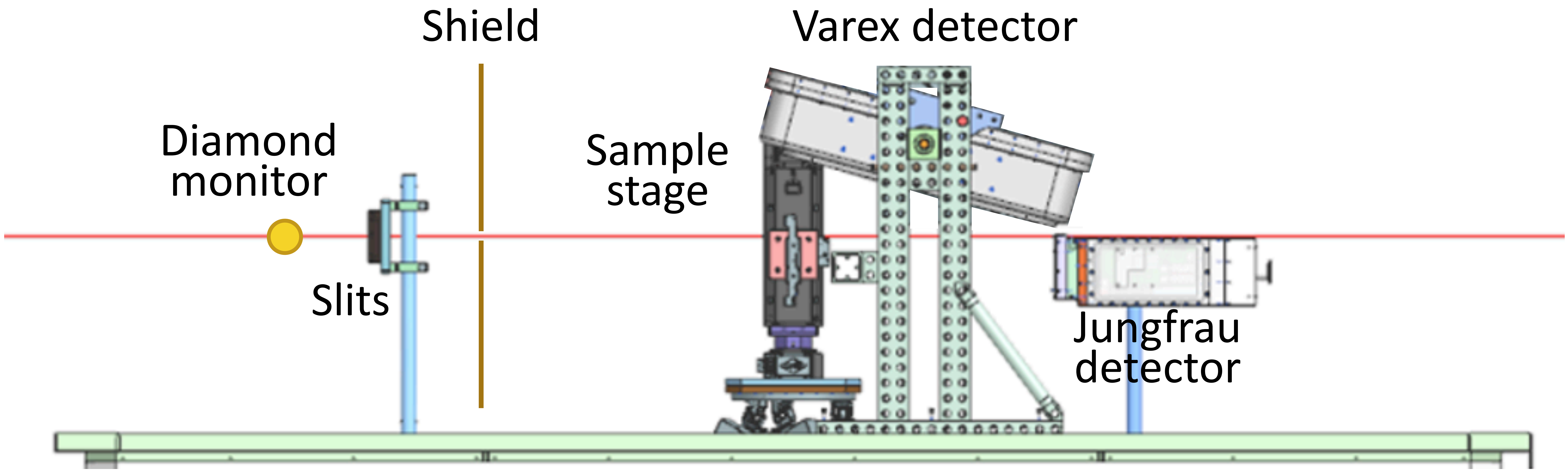
Using an inclined area detector for total scattering





N Burns *et al*, *J Appl Cryst* **56** (2023) 510

EuXFEL HED IC1 set-up #2

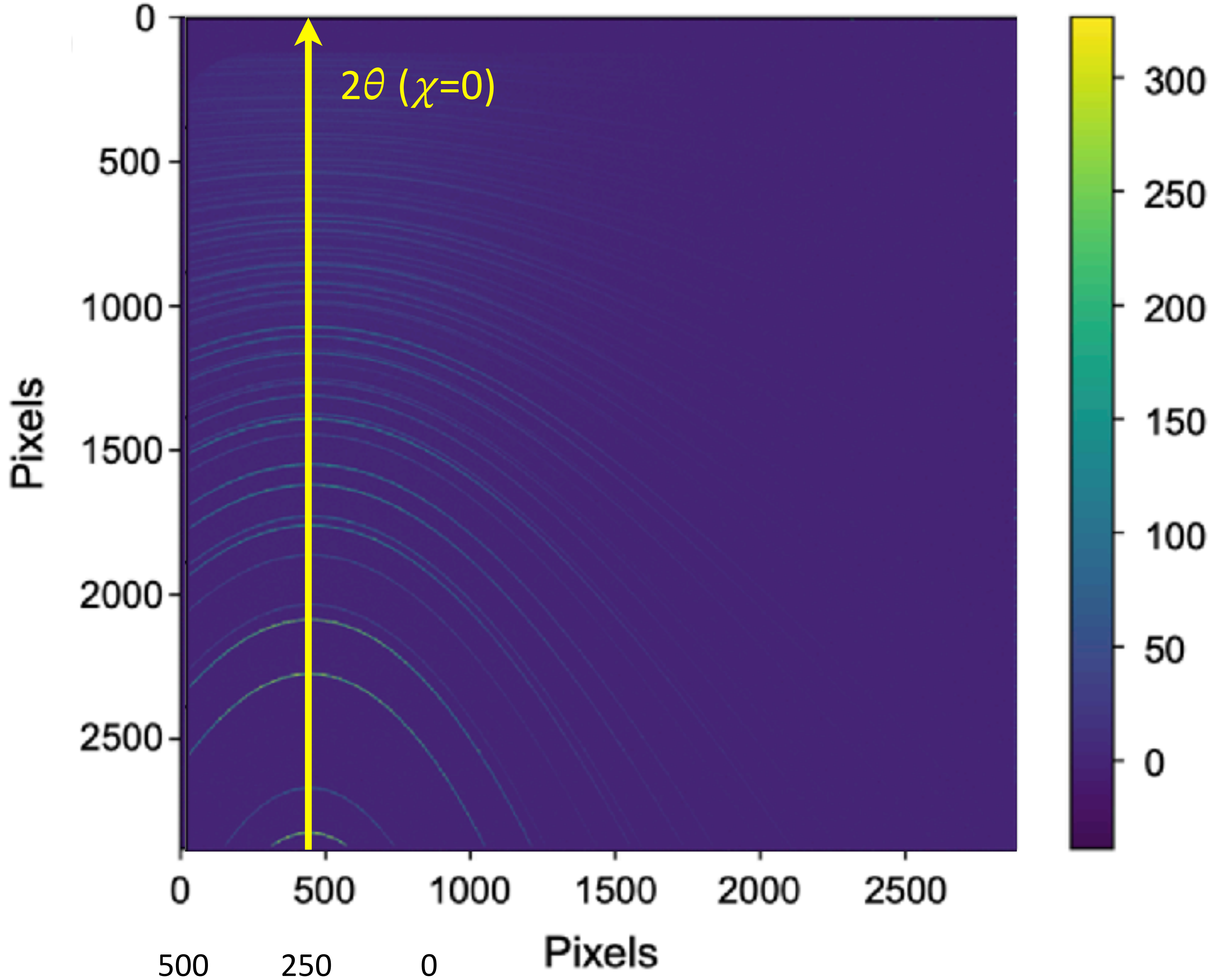


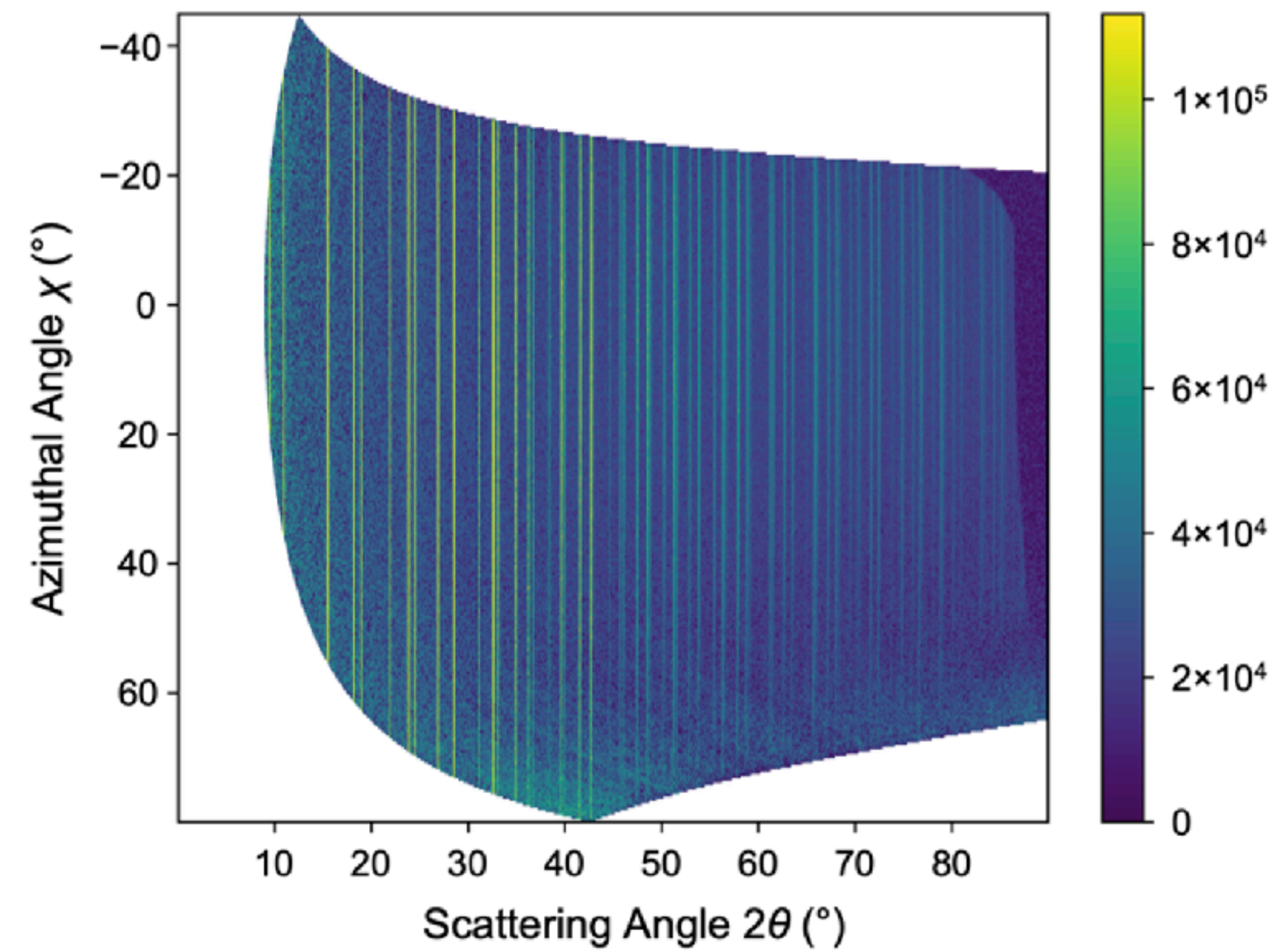
Varex detector coverage: ~9° < 2θ < ~89° : PONI = 171mm at 2θ ~ 75°

Jungfrau detector coverage: ~1° < 2θ < ~14.5° : PONI = 407mm at 2θ = 0°

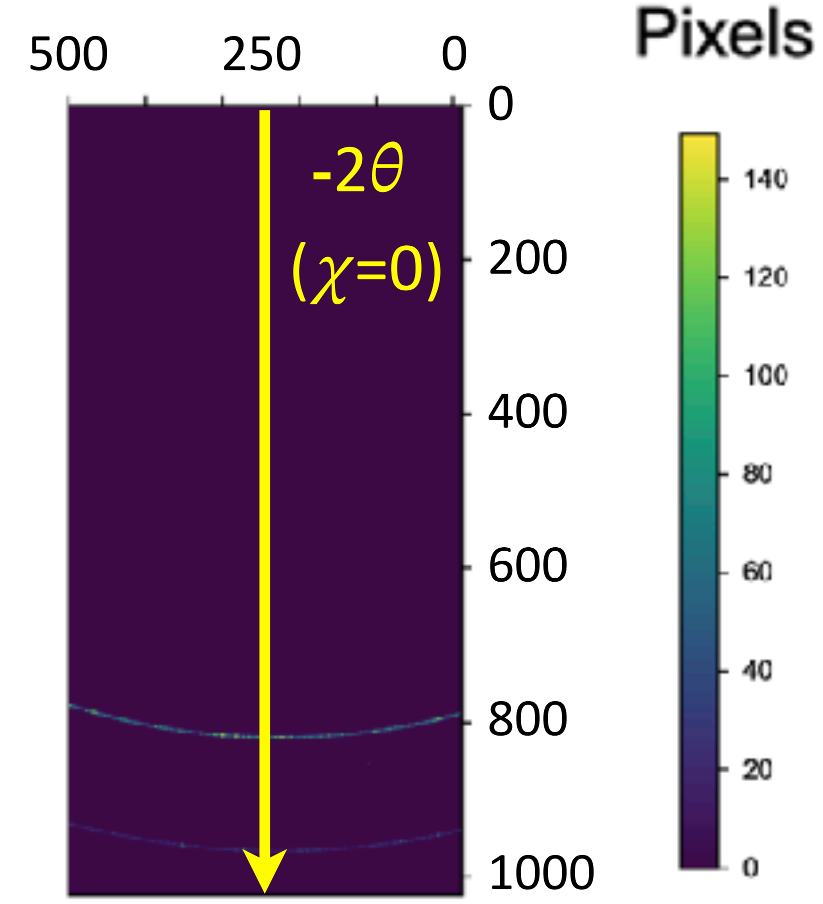
Detector coverage (CeO_2 powder)

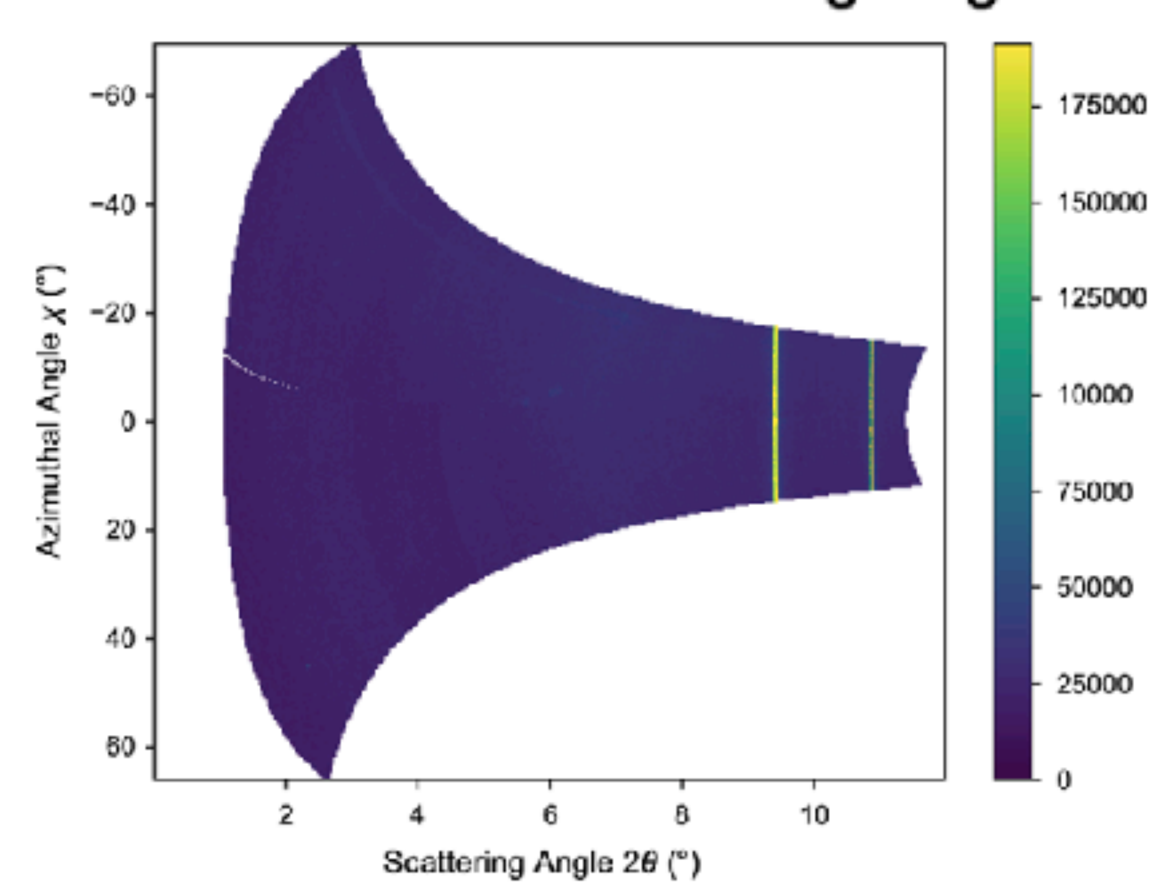
Varex



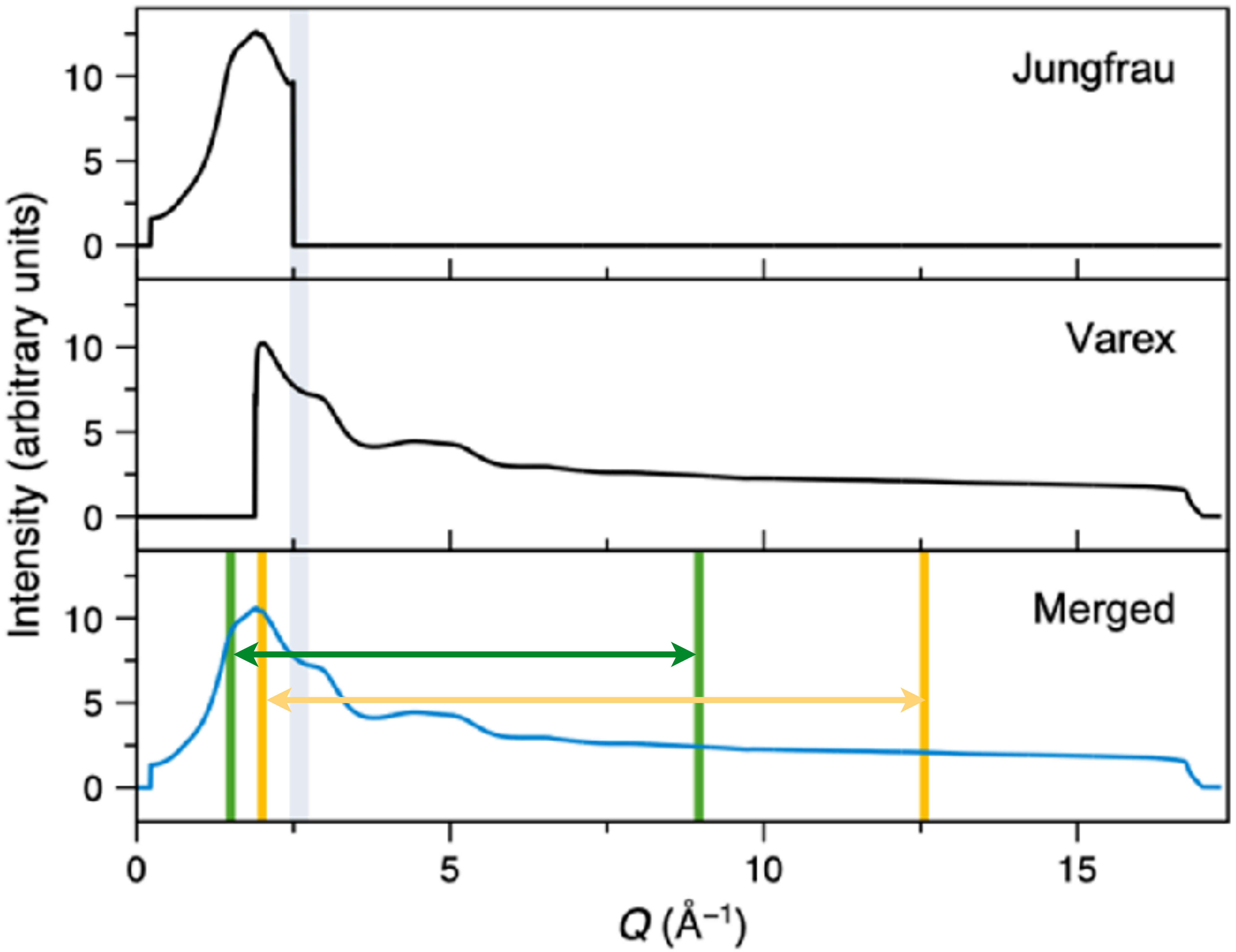


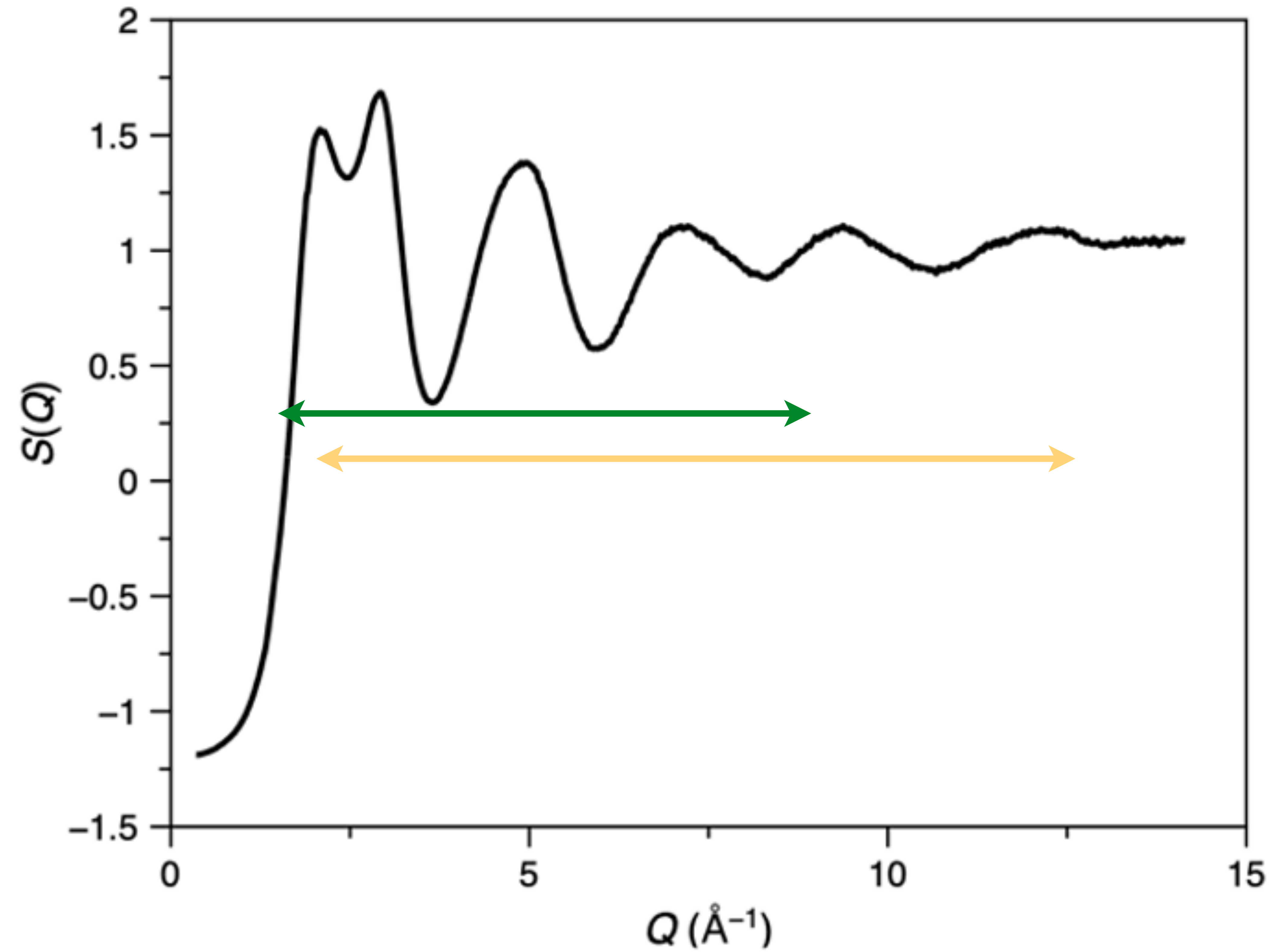
Jungfrau





Detector coverage (water in silica capillary)





Green lines: previous best $S(Q)$ Q-range

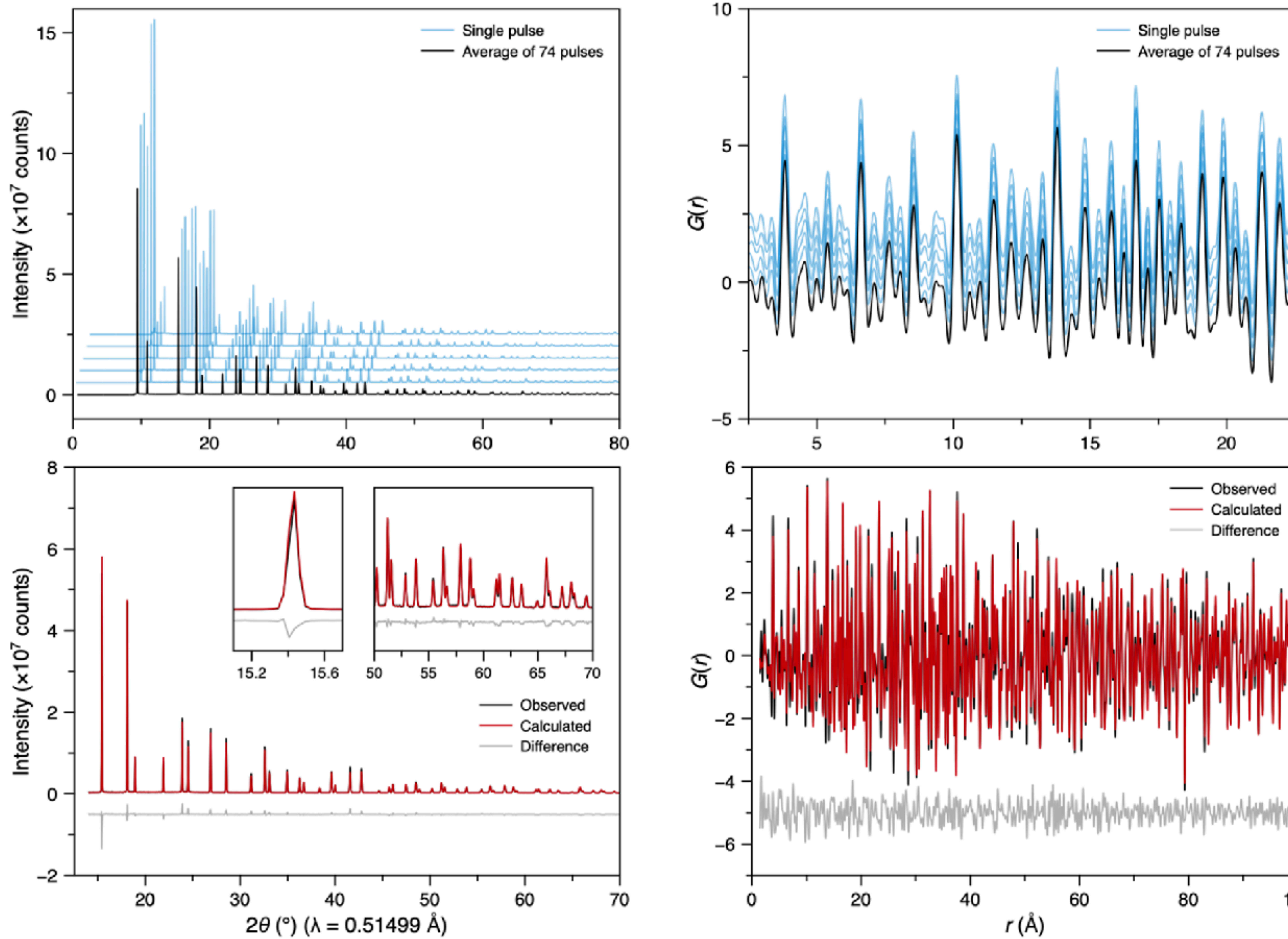
Yellow lines: previous best $\Delta S(Q)$ Q-range

Grey region: Q-region where data were merged

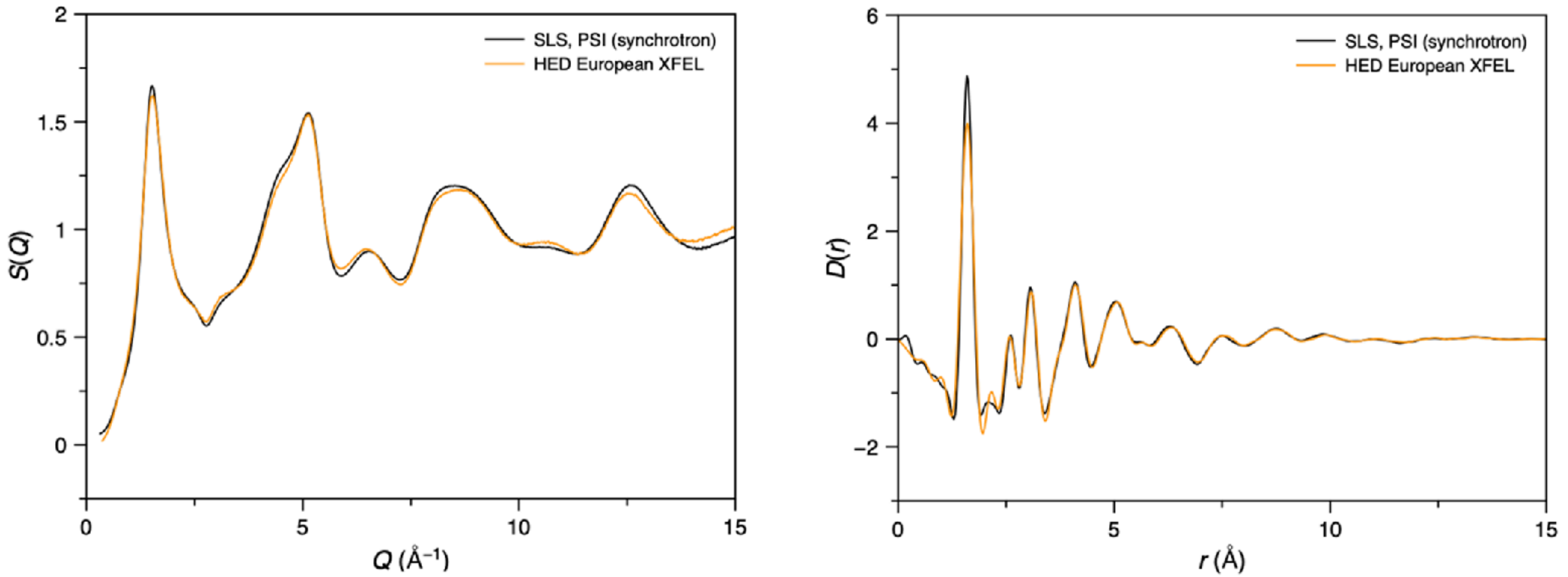
Results: NIST CeO_2 674 SRM

Average vs. single pulse data

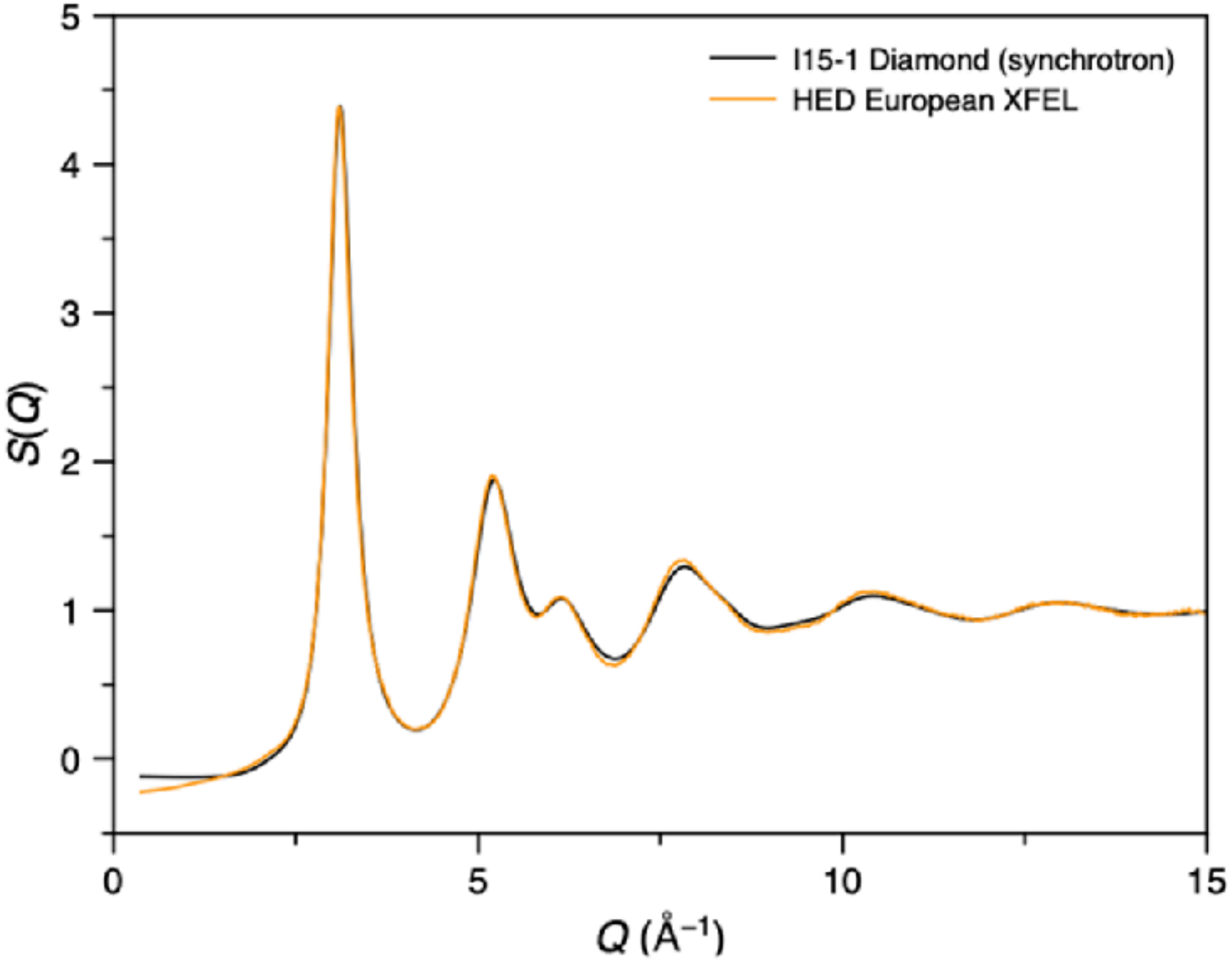
Refinement of average data using Topas

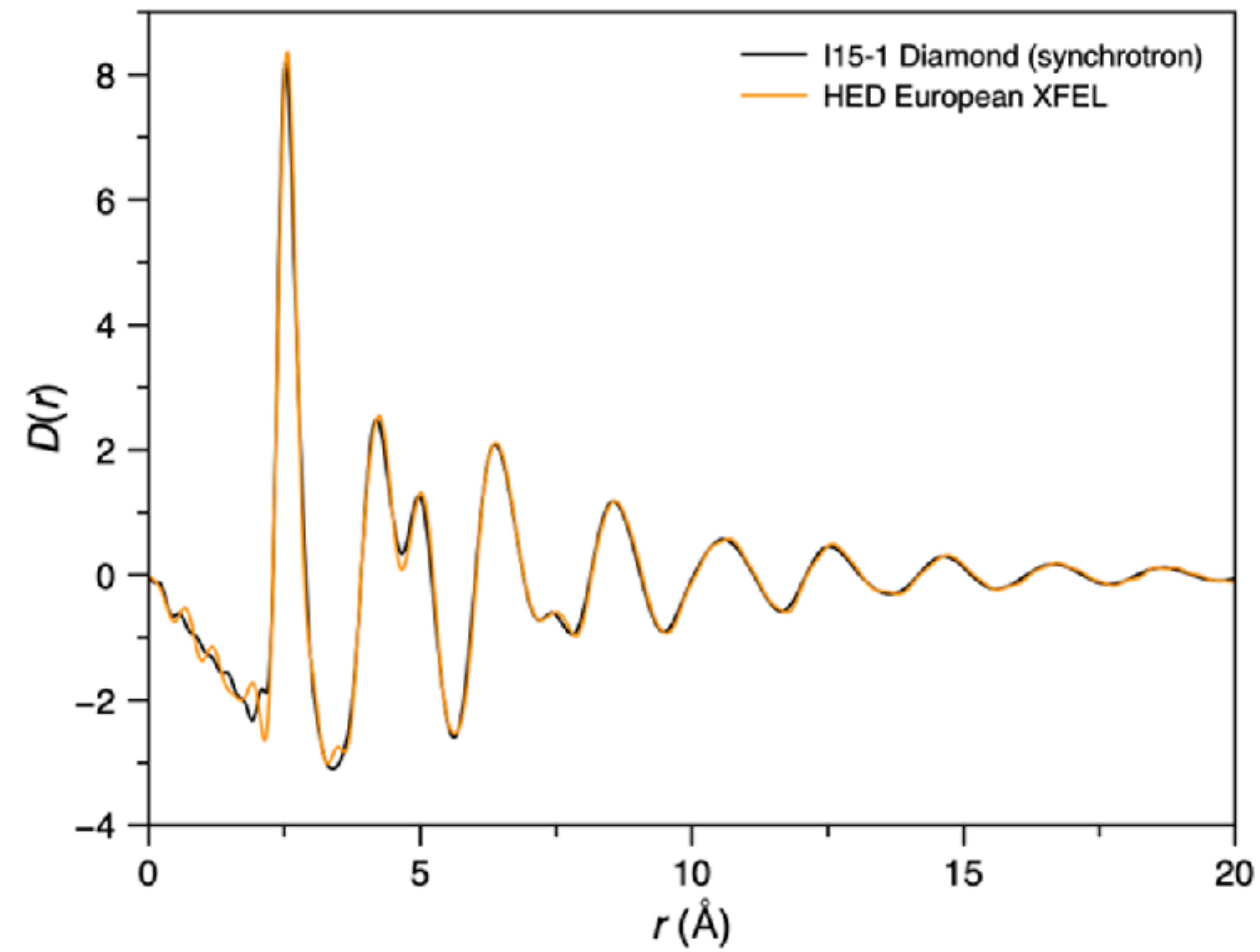


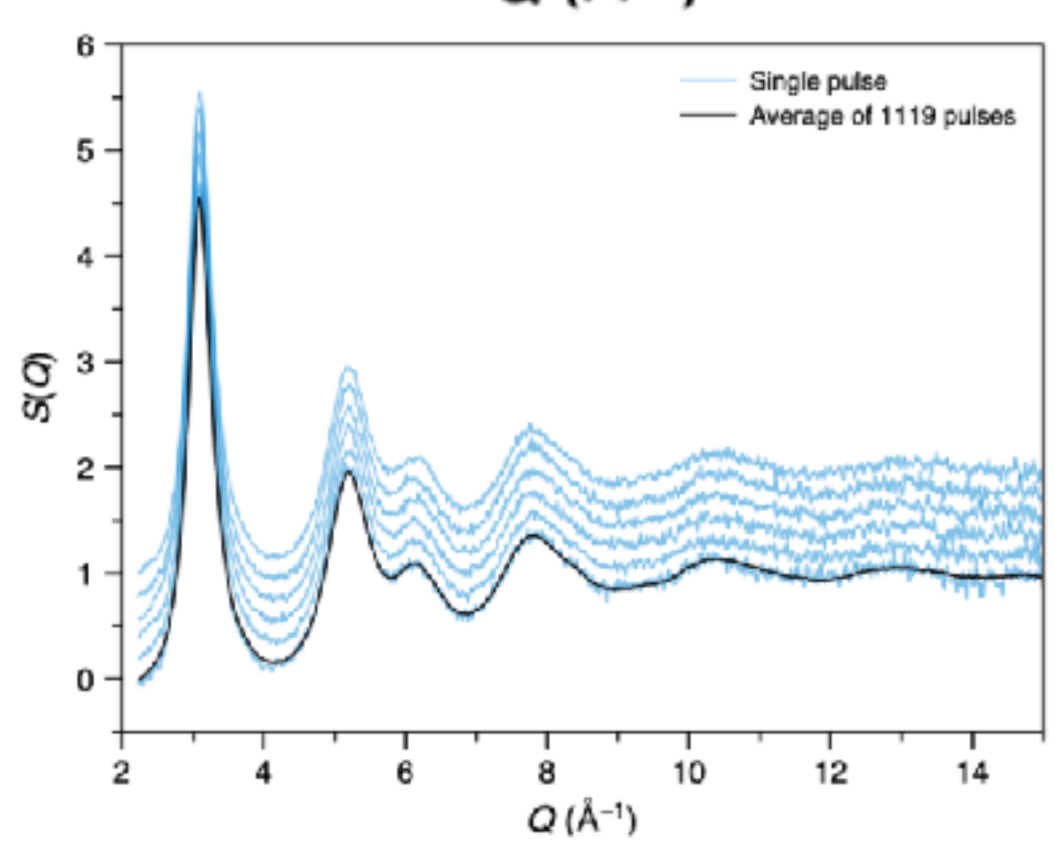
Results: silica glass

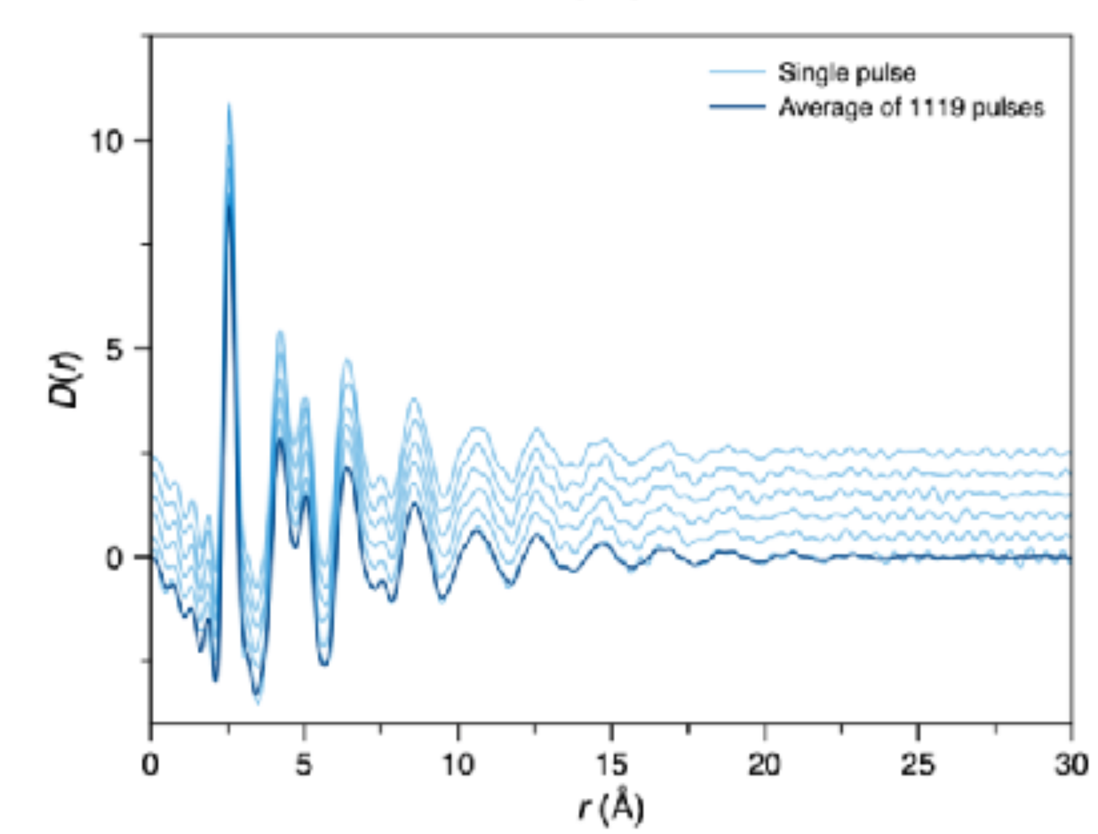


Results: metallic glass ‘standard’ $Fe_{78}B_{13}Si_9$

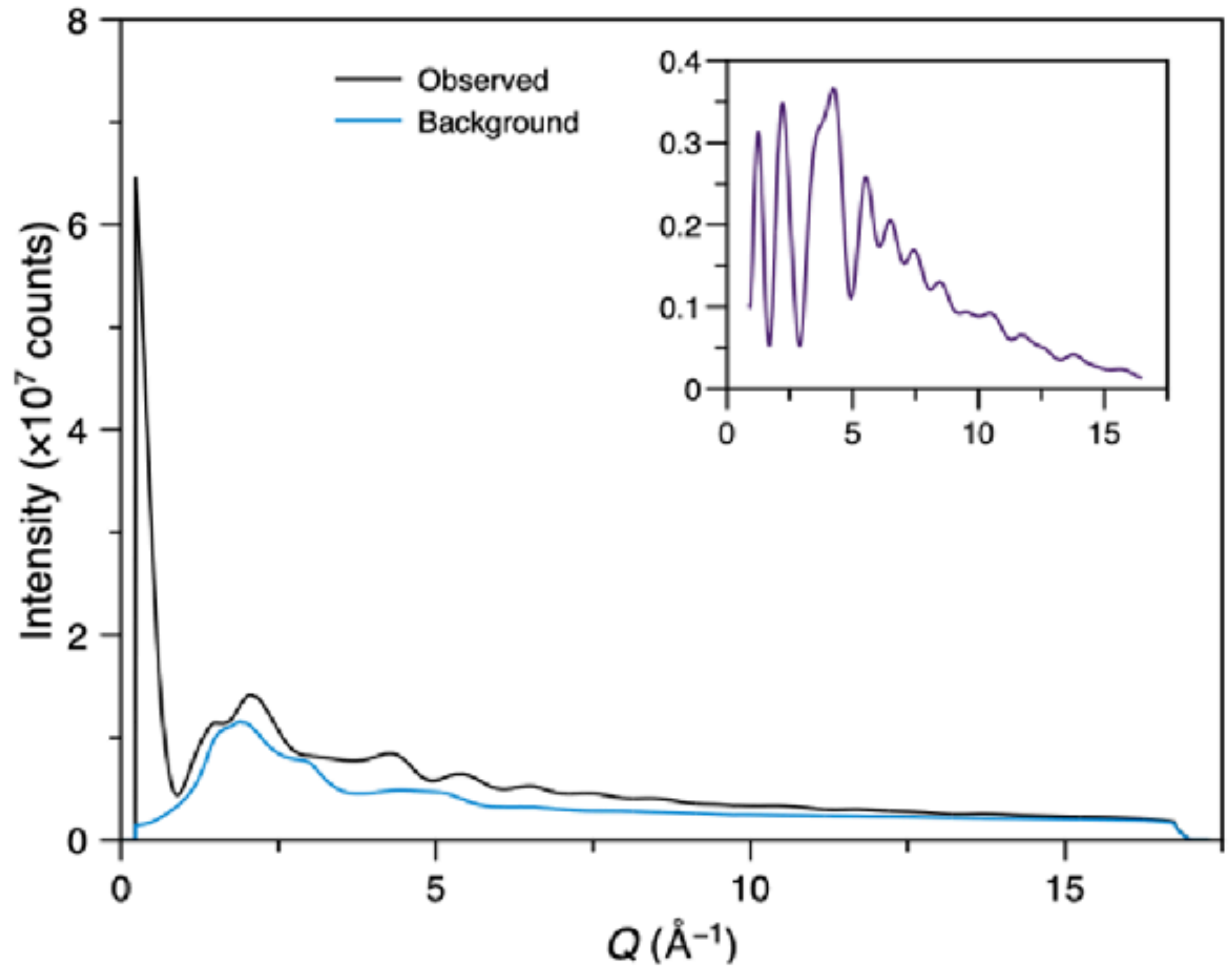


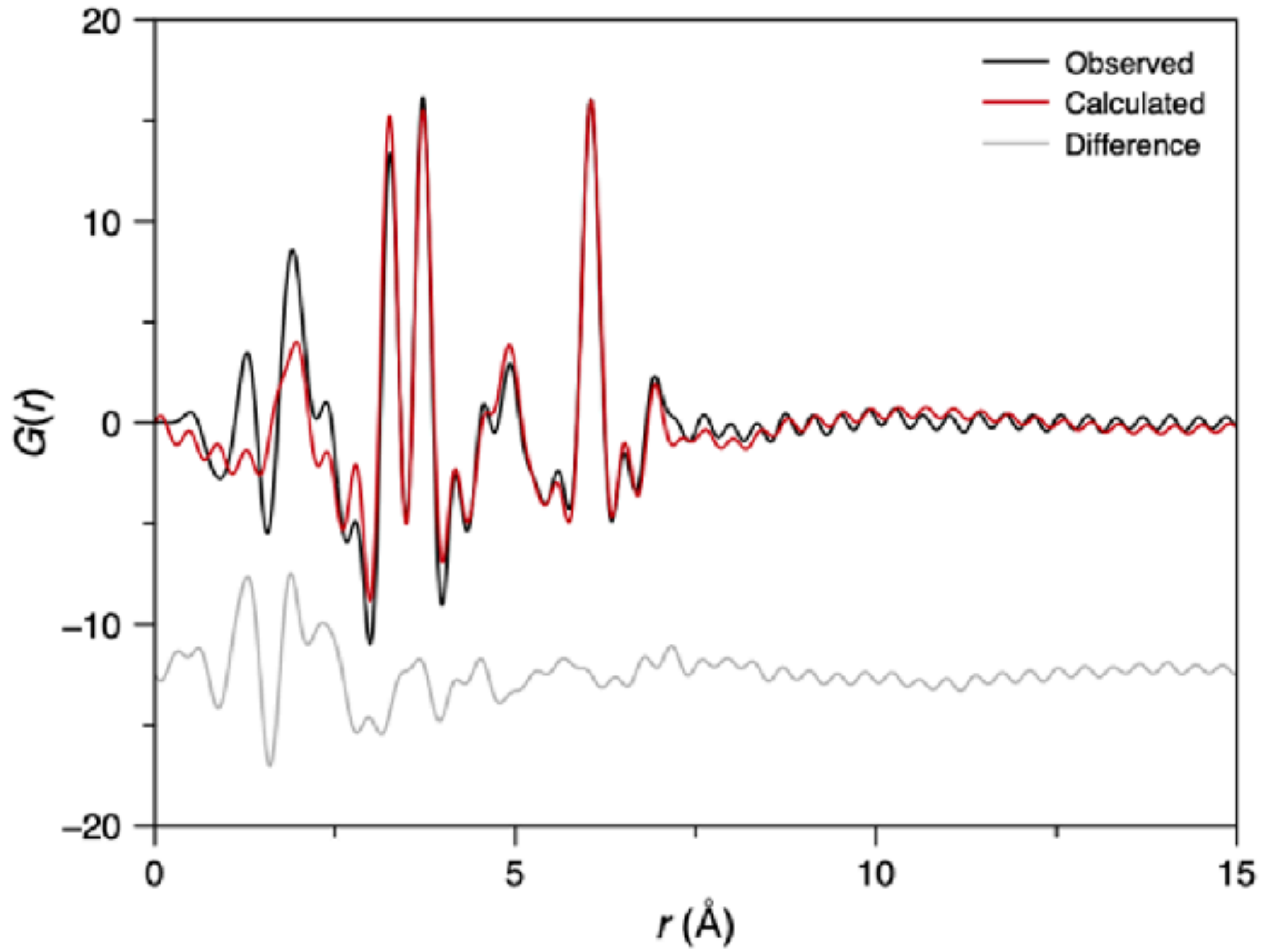


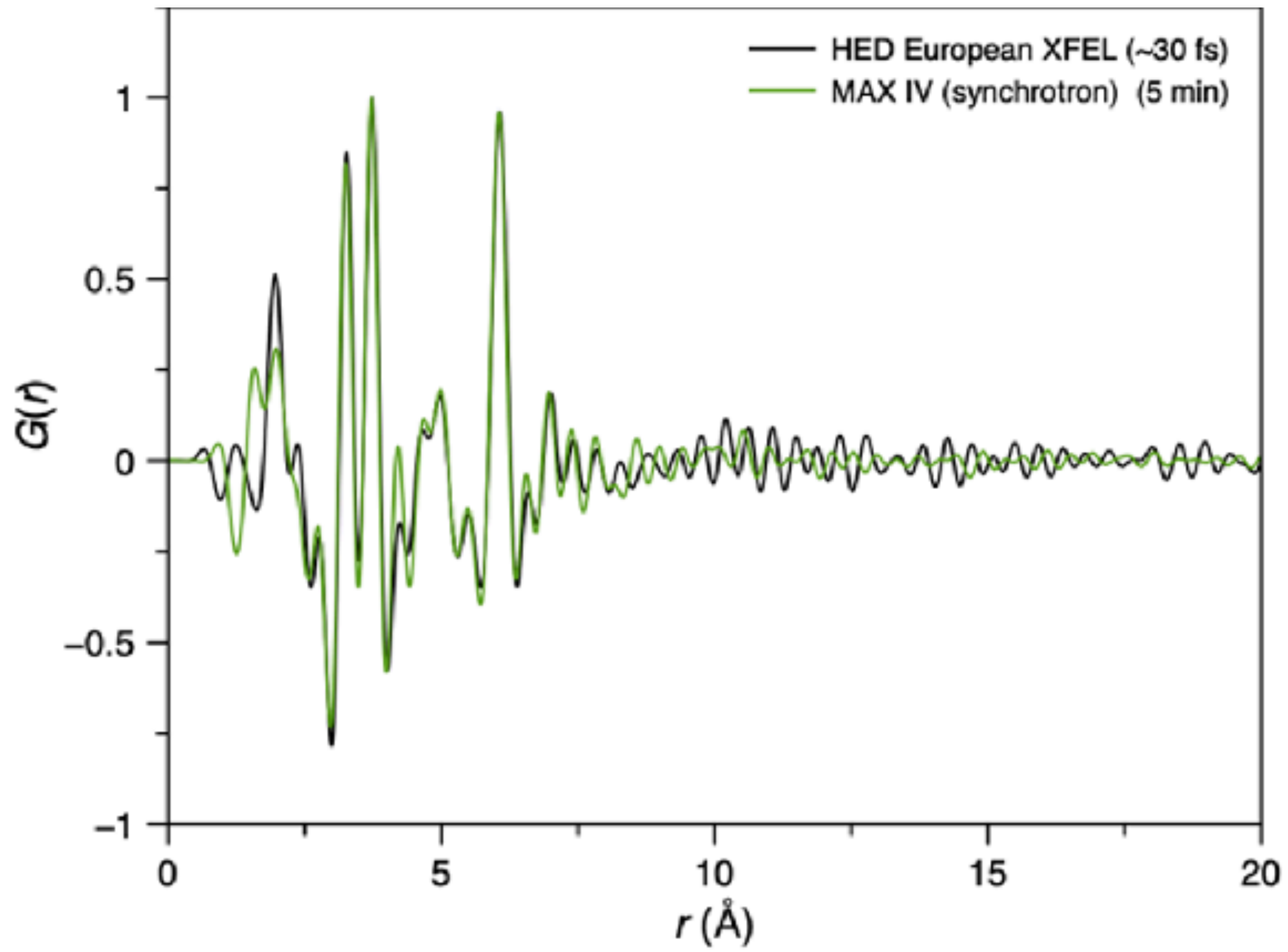


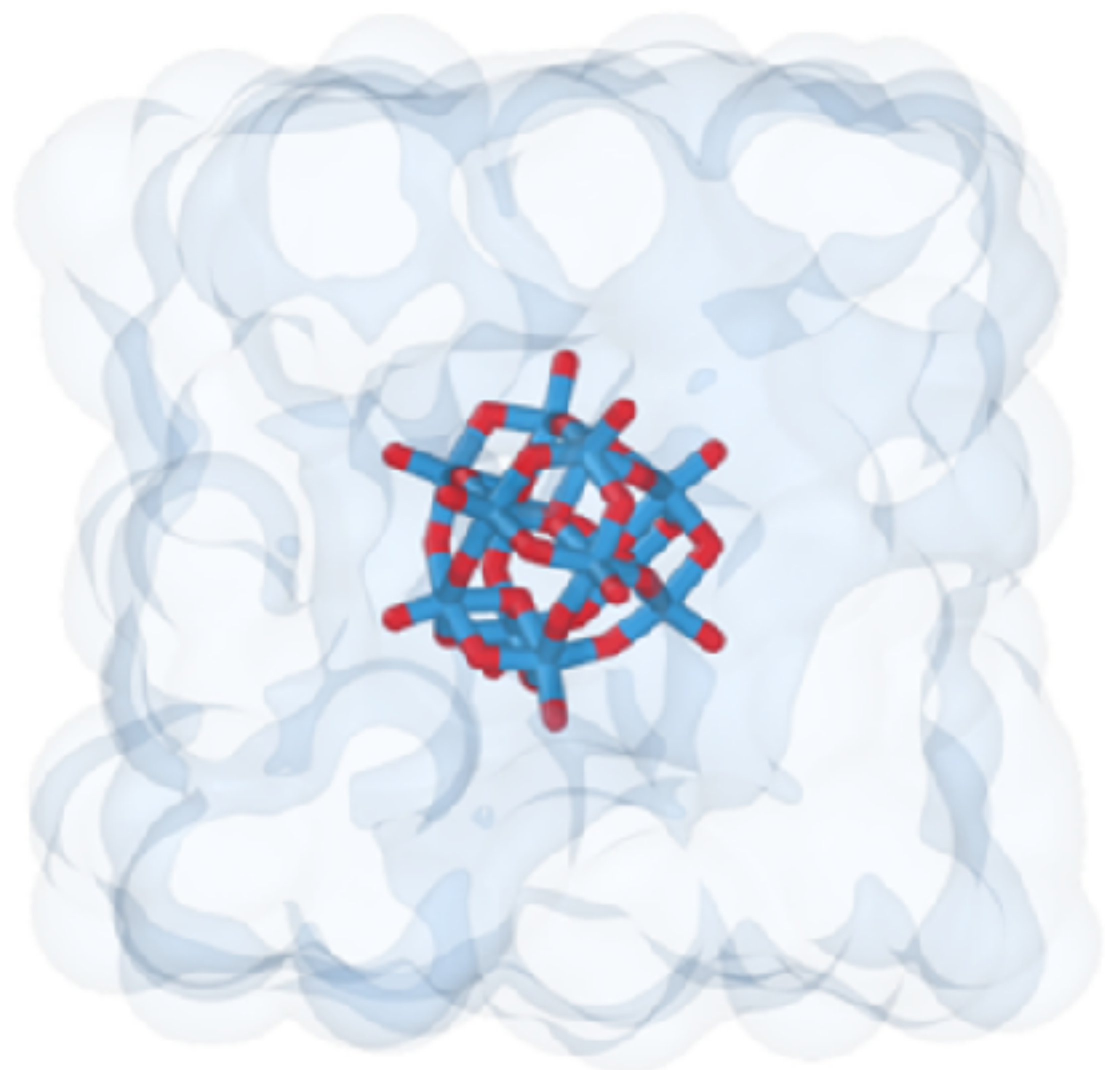


Results: 1M tungsten Keggin cluster $[W_{12}O_{40}]^{6-}$









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High-quality ultra-fast total scattering and pair distribution function data using an X-ray free-electron laser

Adam F. Sapnik,[a*] Philip A. Chater,[b] Dean S. Keeble,[b] John S. O. Evans,[c] Federica Bertolotti,[d] Antonietta Guagliardi,[e] Lise J. Støckler,[f] Elodie A. Harbourne,[g] Anders B. Borup,[f] Rebecca S. Silberg,[a] Adrien Descamps,[h] Clemens Prescher,[i] Benjamin D. Klee,[j] Axel Phelipeau,[k] Imran Ullah,[l] Kárel G. Medina,[l] Tobias A. Bird,[b] Viktoria Kaznelson,[f] William Lynn,[h] Andrew L. Goodwin,[g] Bo B. Iversen,[f] Celine Crepisson,[m] Emil S. Bozin,[n] Kirsten M. Ø. Jensen,[a] Emma E. McBride,[h] Reinhard B. Neder,[l] Ian Robinson,[o] Justin S. Wark,[m] Michał Andrzejewski,[p] Ulrike Boesenberg,[p] Erik Brambrink,[p] Carolina Camarda,[p] Valerio Cerantola,[p,q] Sebastian Goede,[p] Hauke Höppner,[r] Oliver S. Humphries,[p] Zuzana Konopkova,[p] Naresh Kujala,[p] Thomas Michelat,[p] Motoaki Nakatsutsumi,[p] Alexander Pelka,[r] Thomas R. Preston,[p] Lisa Randolph,[p] Michael Roeper,[k] Andreas Schmidt,[p] Cornelius Strohm,[k] Minxue Tang,[p] Peter Talkovski,[k] Ulf Zastrau,[p] Karen Appel[p] and David A. Keen[s*]

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Supporting information: this article has supporting information at www.iucrj.org

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Summary and Outlook

- We have shown that high-quality, *quantitative* total scattering data and pair distributions functions are measurable using an XFEL.
- The data are far higher quality than measured on any XFEL to date, covering $0.35 < Q < 16.6$ Å^{-1}, simultaneously to lower and higher Q than elsewhere.
- The data have an unprecedented time-resolution.
- There are still challenges when the technique is combined with pump-probe techniques and more complex sample environment, but none are insurmountable.
- Our next experiment will measure total scattering from high pressure high temperature liquids from shocked samples.
- Total scattering/PDF methods will undoubtably benefit from even higher energy XFEL beams - which are under development.
- The EuXFEL total scattering/PDF facilities are available for others to use.

Acknowledgements

Adam F. Sapnik,[a] Philip A. Chater,[b] Dean S. Keeble,[b] John S. O. Evans,[c] Federica Bertolotti,[d] Antonietta Guagliardi,[e] Lise J. Støckler,[f] Elodie A. Harbourne,[g] Anders B. Borup,[f] Rebecca S. Silberg,[a] Adrien Descamps,[h] Clemens Prescher,[i] Benjamin D. Klee,[j] Axel Phelipeau,[k] Imran Ullah,[l] Kárel G. Medina,[l] Tobias A. Bird,[b] Viktoria Kaznelson,[f] William Lynn,[h] Andrew L. Goodwin,[g] Bo B. Iversen,[f] Celine Crepisson,[m] Emil S. Bozin,[n] Kirsten M. Ø. Jensen,[a] Emma E. McBride,[h] Reinhard B. Neder,[l] Ian Robinson,[o] Justin Wark,[m] Michal Andrzejewski,[p] Ulrike Boesenberg,[p] Erik Brambrink,[p] Carolina Camarda,[p] Valerio Cerantola,[p,q] Sebastian Goede,[p] Hauke Höppner,[r] Oliver S. Humphries,[p] Zuzana Konopkova,[p] Naresh Kujala,[p] Thomas Michelat,[p] Motoaki Nakatsutsumi,[p] Alexander Pelka,[r] Thomas R. Preston,[p] Lisa Randolph,[p] Michael Roeper,[k] Andreas Schmidt,[p] Cornelius Strohm,[k] Minxue Tang,[p] Peter Talkovski,[k] Ulf Zastrau,[p] Karen Appel,[p] and David A. Keen[s] *plus no doubt others!*

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h: School of Mathematics and Physics, Queen's University Belfast, UK.
i: Institute of Earth and Environmental Sciences, University of Freiburg, Germany.
j: HUN-REN Wigner Research Centre for Physics, Budapest, Hungary.
k: Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany.
l: Friedrich-Alexander Universität Erlangen–Nürnberg, Germany.
m: Department of Physics, University of Oxford, UK.
n: Center for Solid State Physics and New Materials, Institute of Physics Belgrade, University of Belgrade, Serbia.
o: London Centre for Nanotechnology, University College London, UK.
p: European XFEL, Schenefeld, Germany.
q: University of Milano-Bicocca, Italy.
r: Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Dresden, Germany.
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