XAFS spectroscopy at 4th generation synchrotron radiation sources

Opportunities and challenges

Edmund Welter

Hamburg/Melbourne, 16.06.2021

HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

DESY.

Agenda

01 Ultra low emittance storage rings

- The PETRA IV project as example
- Photon beam properties
- Brilliance / coherence / focusing

02 ”Classical” XAFS spectrocopy

- Which properties are important for (XAFS) spectroscopy?
- Detectors
- Beam homogeneity

03 Beyond classical XAFS spectroscopy

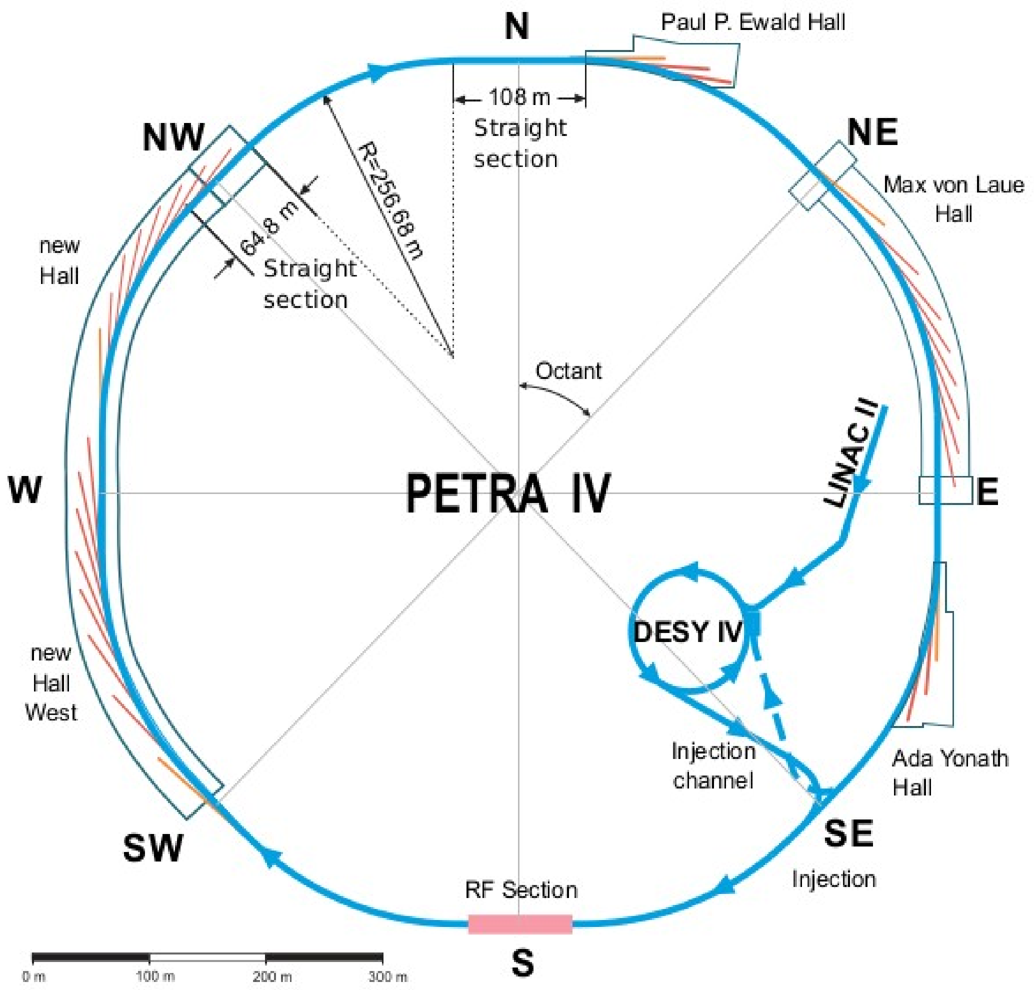
- High brilliance applications
  - µ-XAFS
  - XAFS tomography
- Coherence applications
  - XAFS-Ptychography

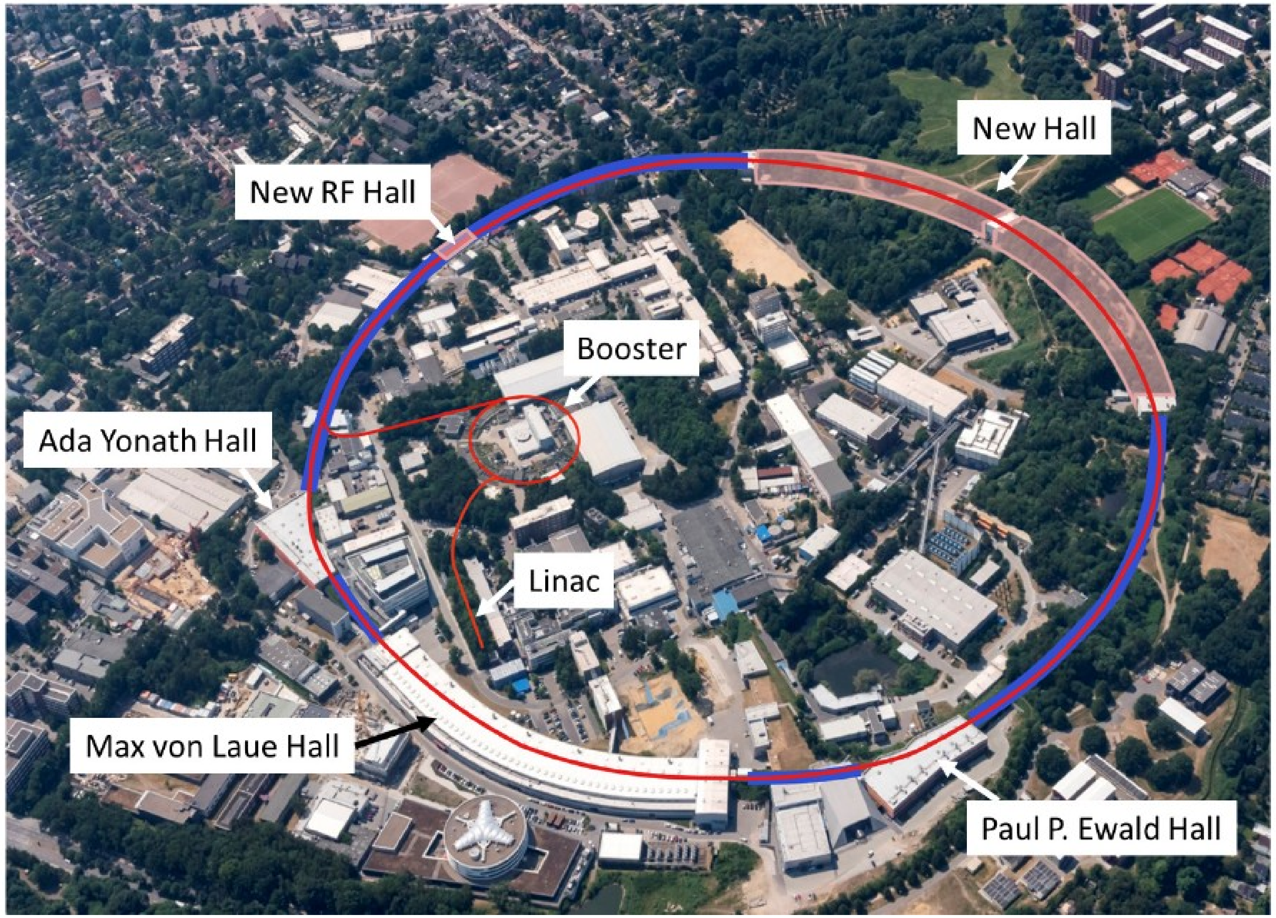
04 Summary

- Prospects for classical XAFS
- Prospects for high brilliance/coherence requiring methods

PETRA IV

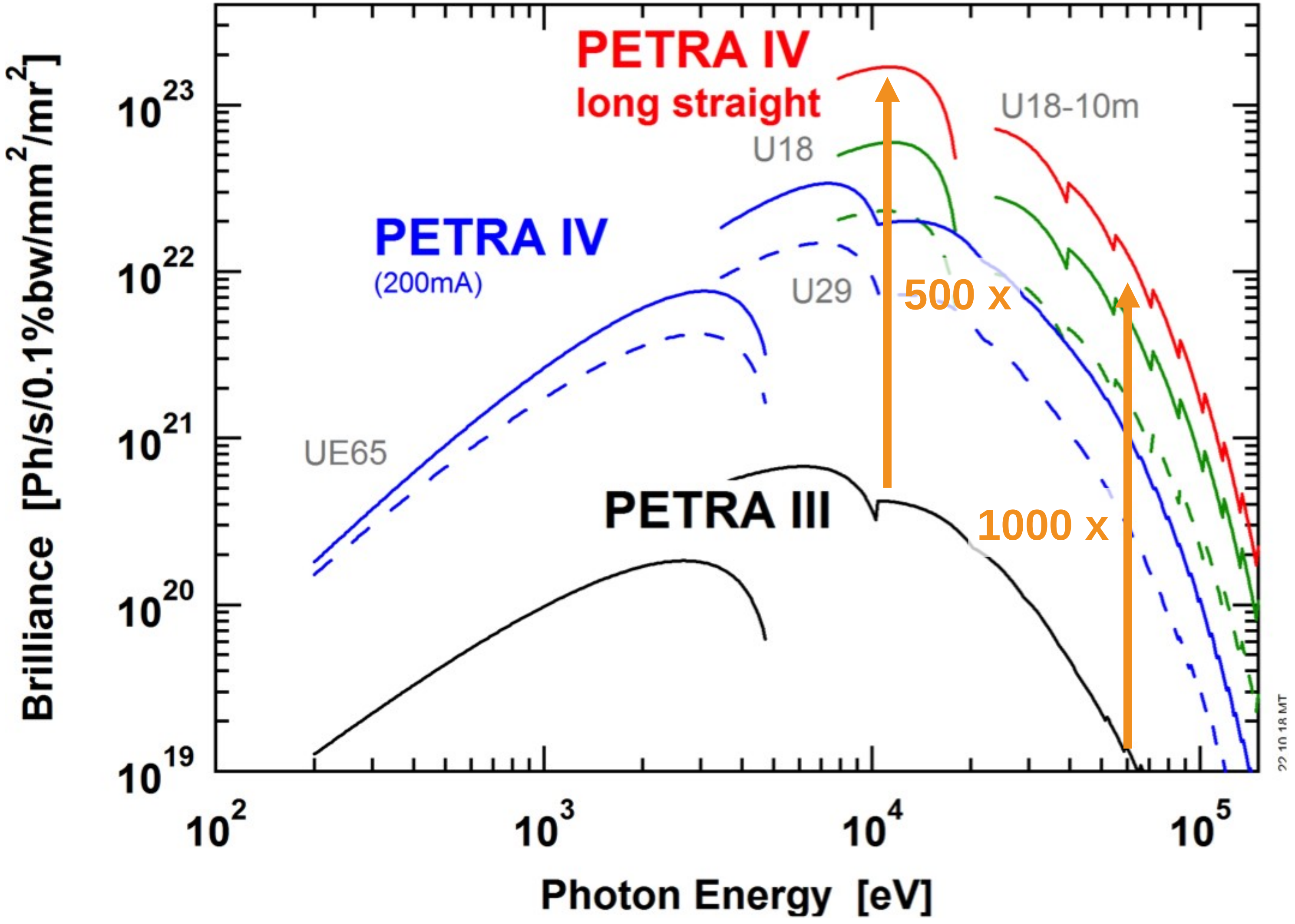
Conversion of PETRA into a diffraction limited storage ring





PETRA IV

Brilliance



Based on current reference lattice:

- emittance:
  - ➔ coherence mode: 20 x 2 pmrad²
  - ➔ timing mode: 50 x 5 pmrad²
- undulators: 5 m, 10 m
- optimised beta (in 10 m section): 2 x 2 m²
- ring current: 200 mA

Brilliance increase by

- ➔ 500 x (hard X-rays)
- ➔ 1000 x (high-energy X-rays)

PETRA IV brilliance at 100 keV
same as for 10 keV at PETRA III today!!

C. G. Schroer, et al., JSR **25**, 1277 (2018).

Ultra Low Emittance Storage Rings

PETRA IV for example

source size
& divergence:
155 µm x 6 µm
7.7 x 3.8 µrad²

extended & divergent X-ray beam

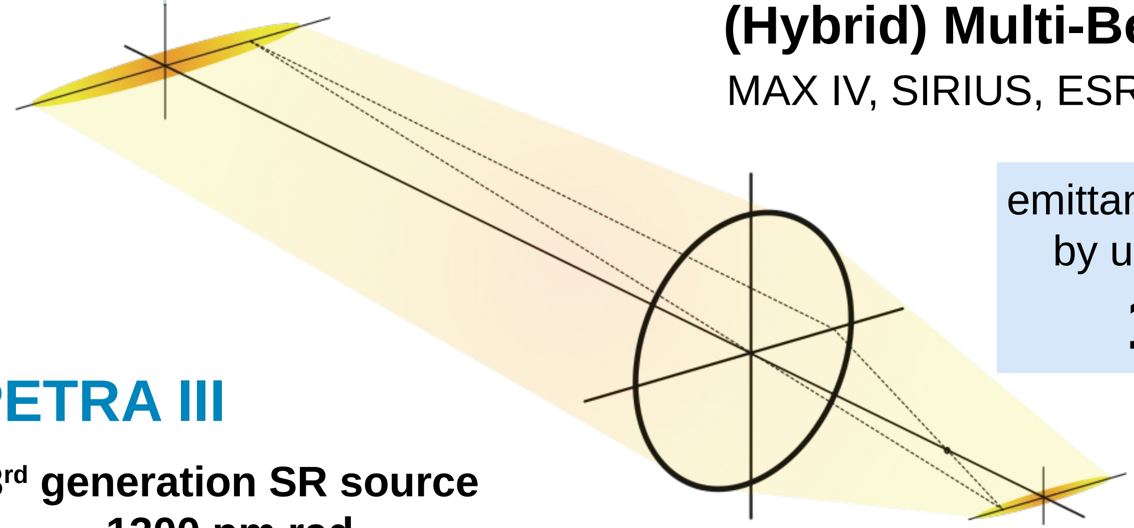
transformative technology:

(Hybrid) Multi-Bend-Achromat

MAX IV, SIRIUS, ESRF-EBS, APS-U, SPring-8-II

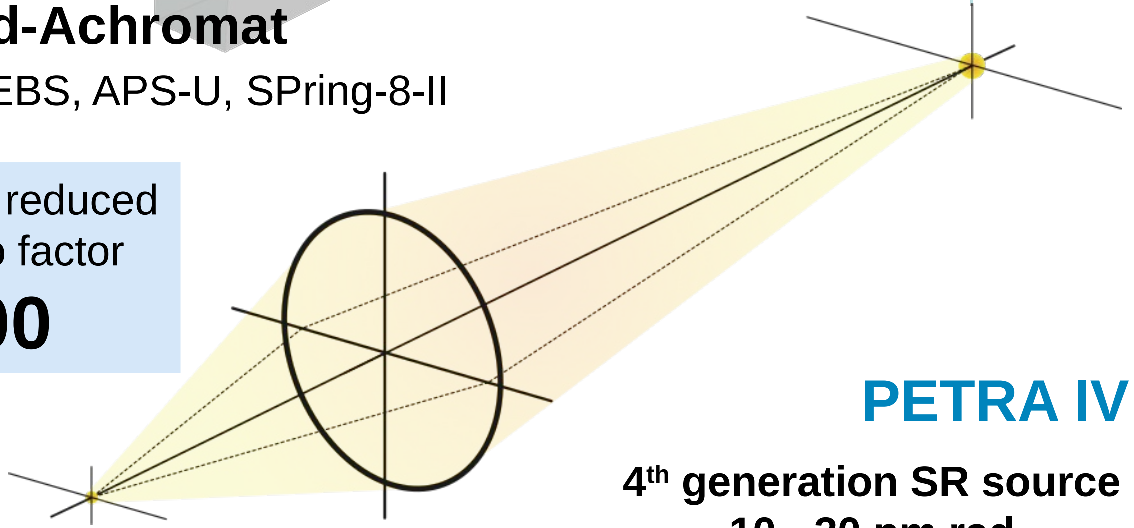
source size
& divergence:
11 µm x 3.2 µm
1.7 x 1.5 µrad²

small & collimated X-ray beam



emittance reduced by up to factor

100



efficient nanometer focusing

PETRA III

3rd generation SR source
1300 pm rad

Max. brightness: ~10^{21}
Coherence: ~0.1-1%

PETRA IV

4th generation SR source
10 - 30 pm rad

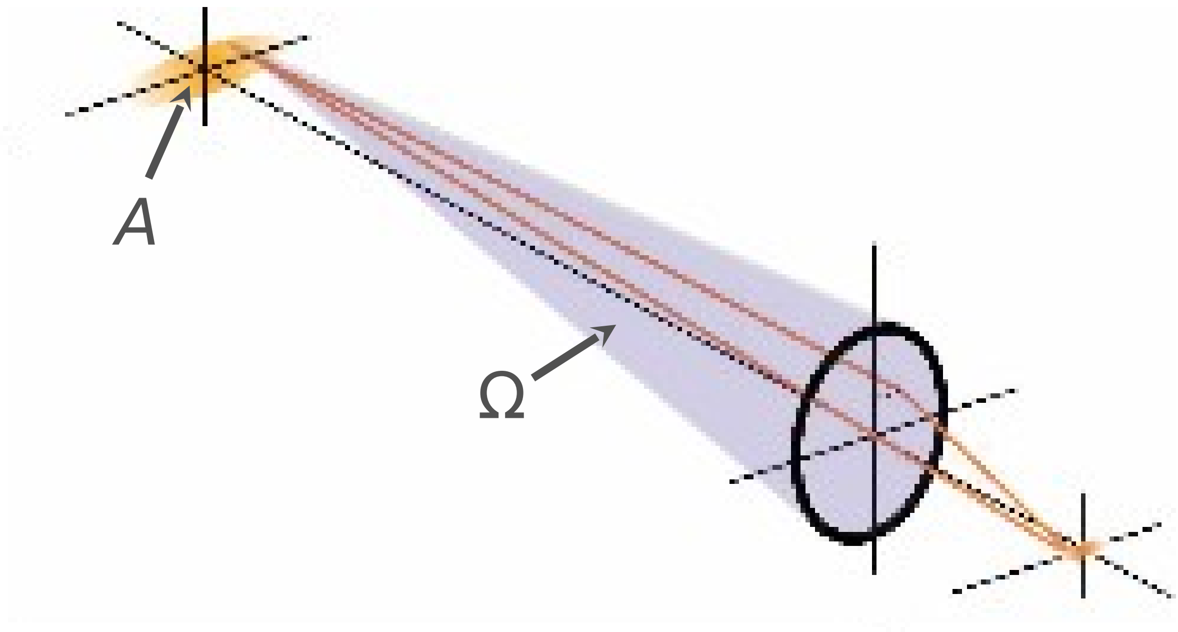
Max. brightness: ~10^{23}
Coherence: > 25%

Brilliance and coherent flux

Brilliance:

Flux per phase-space volume

$$B_{\mathrm{sp}} = \frac{F}{\Omega \cdot A \cdot \Delta E/E}$$



Coherent flux:

$$F_c \propto B_{\mathrm{sp}} \cdot \lambda^2 \cdot \frac{\Delta E}{E}$$

Improvements in Brilliance allow:

- faster measurements (time resolution)
- nano-imaging (spatial resolution)
- spectroscopy (energy resolution)

Coherent flux

Coherent flux for a given bandwidth:

$$F_c = F_0 \cdot \frac{l_{c_h}}{2\Sigma_h} \cdot \frac{l_{c_v}}{2\Sigma_v} \cdot = F_0 \cdot \frac{\lambda^2}{(4\pi)^2 \sigma_{T_h} \sigma'_{T_h} \sigma_{T_v} \sigma'_{T_v}} = Br \cdot \left(\frac{\lambda}{2}\right)^2$$

The total flux F_0 depends on storage ring energy and undulator

→ F_0 will not change with improved emittance as long as storage ring energy remains unchanged (improvements using better (longer) undulators)

→ Experiments that do not require focusing or coherence will not profit much!

Up to 10 keV:

> diffraction limited beam: whole beam can be focused (lateral coherence)

High-energy x-rays:

> diffraction limit can not be reached

> full gain in coherent (focused) flux (~ 100 x).

PETRA IV:

Ultimate 3D Microscope for Physical, Chemical and Biological Processes

Hard X-ray beam (nearly) diffraction limited:

➔ **Nanoprobes:** focus nearly full flux to nanobeam

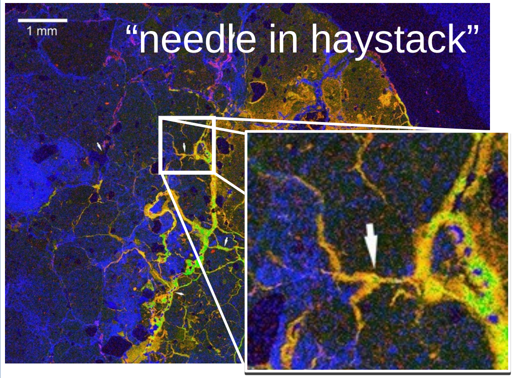
> up to **500 x faster** (movies rather than static images)

> up to **20 x better sensitivity** (signal-to-noise ratio)

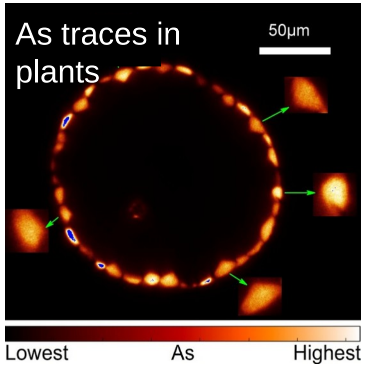
> up to **500 x larger field of view** or sample volumes (“needle in hay stack” problem)

➔ **Coherent imaging:**

> 4 to 5 orders of magnitude higher coherent flux density



CSIRO: gold deposit in clay



S. Mishra et al, J Exp Bot **67**, 4639 (2016).

New, unique properties:

➔ **Local quantitative measurements with all X-ray analytical techniques!**

➔ **Flux-hungry techniques go nano!**

> inelastic X-ray scattering,

> nuclear resonance scattering

> resonant magnetic hard X-ray scattering

➔ **High-energy X-ray techniques go nano!**

> Compton scattering

> Pair distribution function, …

➔ **Spatial resolution of coherent imaging:**
➔ **all spatial dimensions down to < 1 nm!**

> ptychographic imaging

1

PETRA IV:

Ultimate 3D Microscope for Physical, Chemical and Biological Processes

What about X-ray absorption spectroscopy?

Hard X-ray beam (nearly) diffraction limited:

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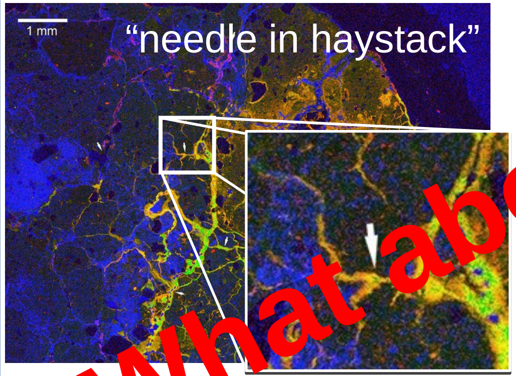

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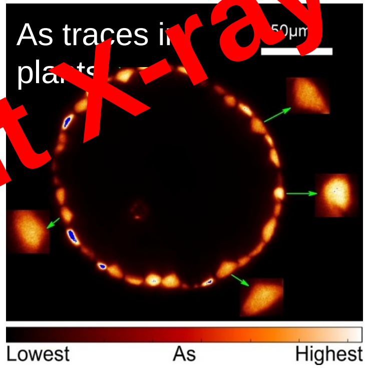

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> Pair distribution function, …

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> ptychographic imaging

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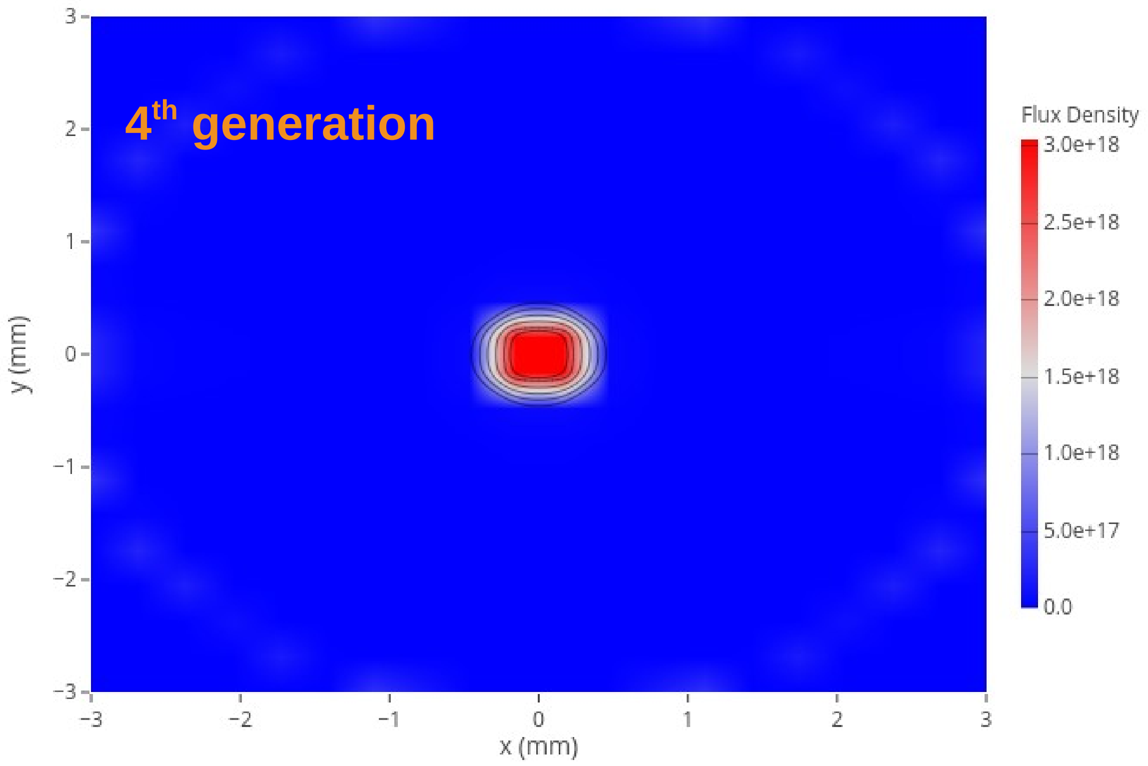
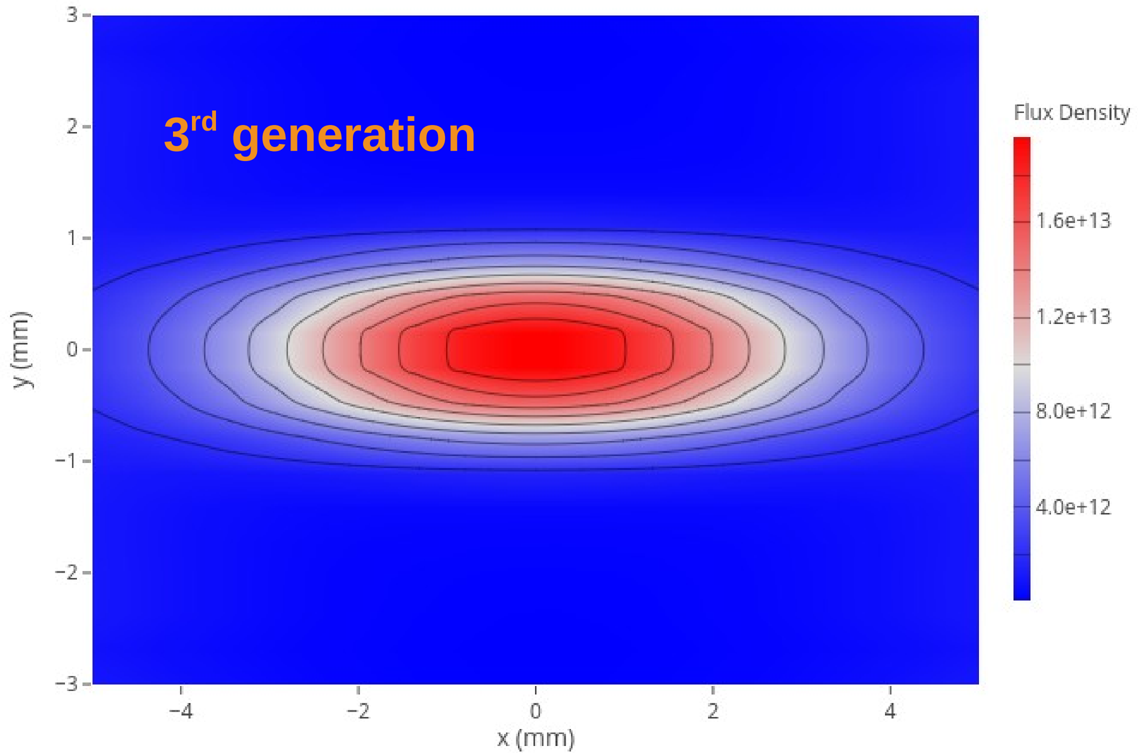
Beam properties at the sample

Flux density

80 m from a 5 m long undulator





Undulator: U33, 150 periods, 3^{rd} harmonic
Storage ring: PETRA IV, 200 mA, 1600 bunches

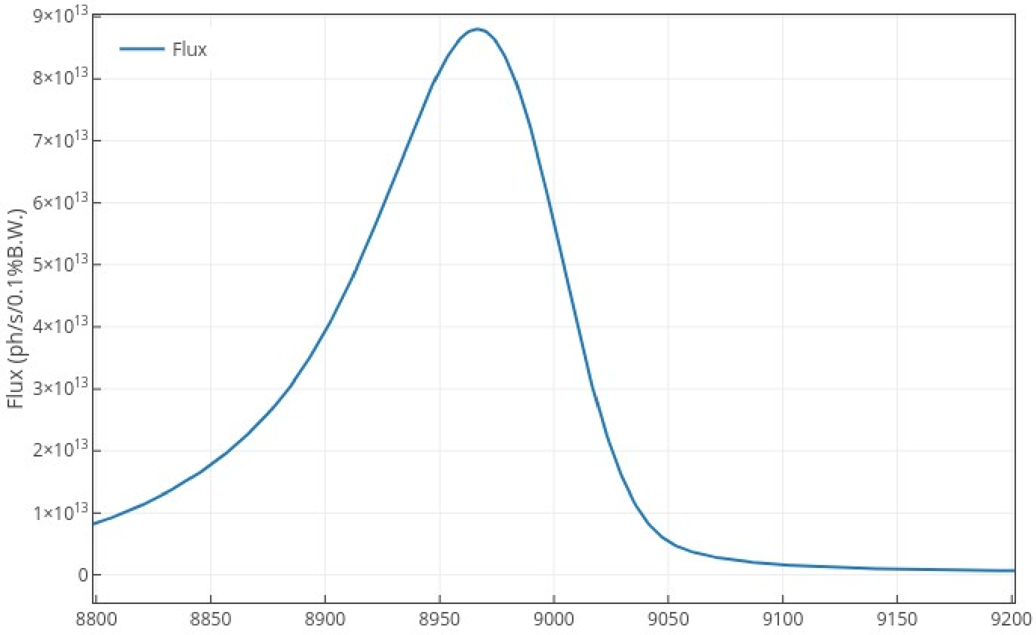
Undulator: U33, 59 periods, 3^{rd} harmonic
Storage ring: PETRA III, 100 mA, 480 bunches

Calculations done using SPECTRA 11, Tanaka T and Kitamura H 2001 J. Synchrotron Rad.8 1221

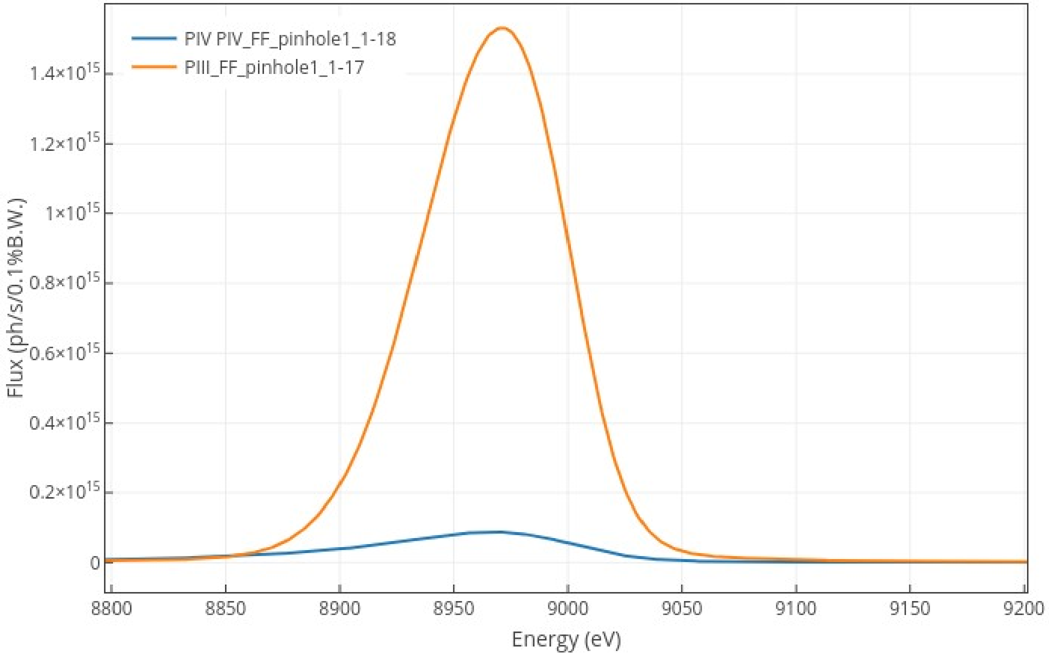
Flux through pinhole

80 m from source

PETRA III
- 5 m U33
- Nat. emittance: 1.01 **n**mrad, 1 % coupling
- Ring current: 100 mA, 480 bunches
- 6 GeV
- 3rd harmonic



PETRA IV
- 2 m U33
- Nat. emittance: 12 **p**mrad, 20 % coupling
- ring current: 200 mA, 1600 bunches
- 6 GeV
- 3rd harmonic



Ray tracing through a moderatly focused beamline

P64 as an example

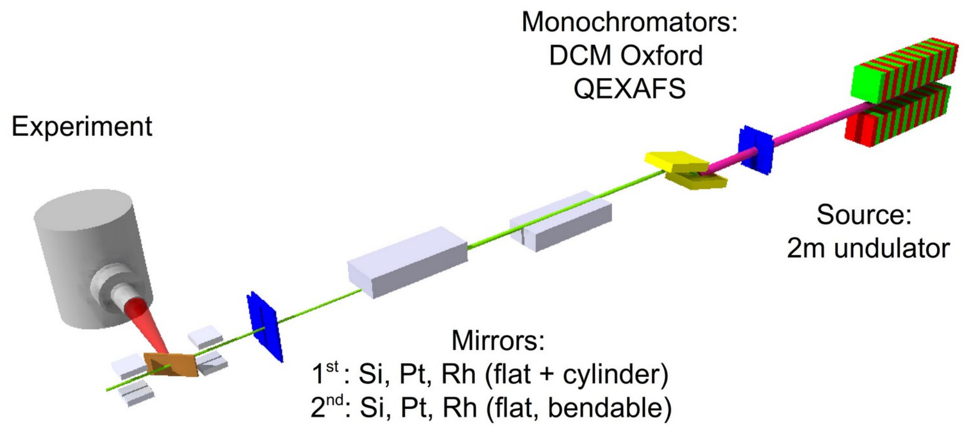
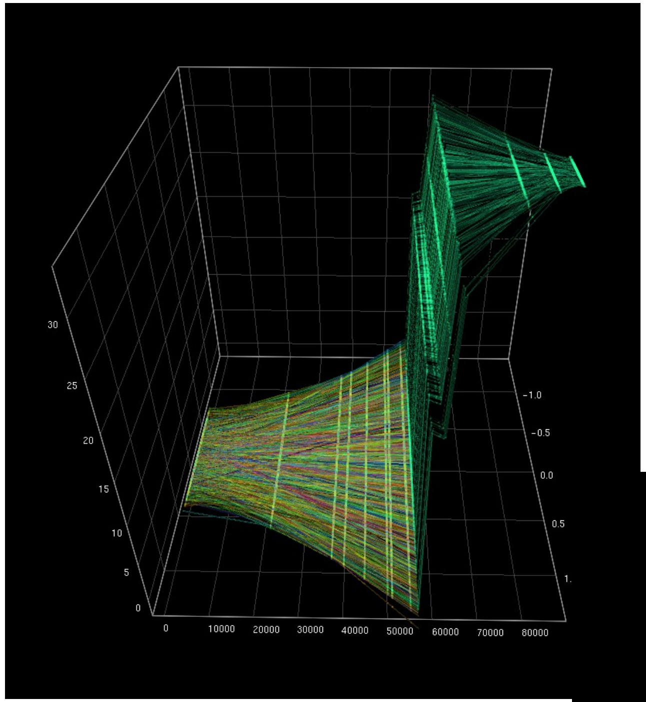


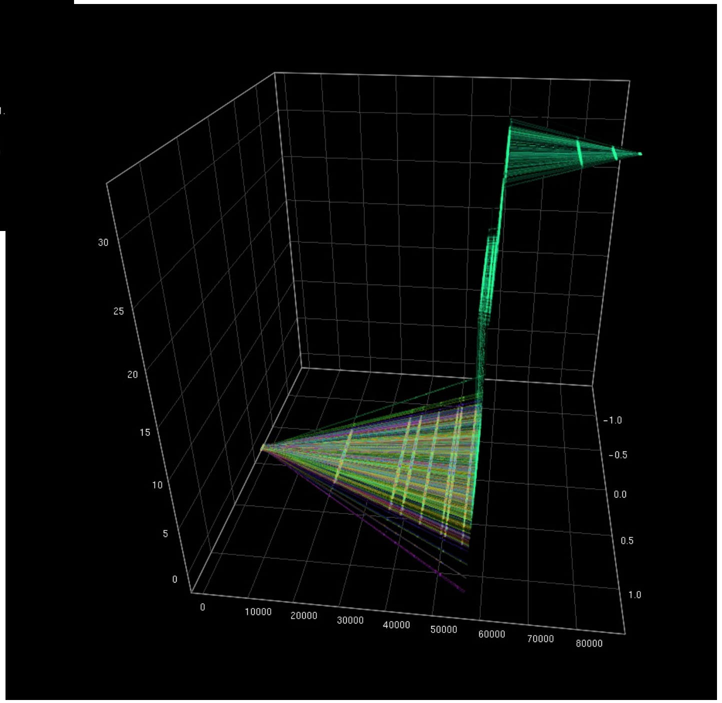
TABLE 1. Distances of optical components from the source (middle of undulator).

Component	Slit I (v)	Slit II (vxh)	Filter	Shutter	Q-Mono	DCM	Mirror I	Mirror II	Slit III (vxh)	Sample
Distance/m	37.1	44.8	45.6	48.9	52.4	56.6	58.7	60.5	87	87.2

From W.A. Caliebe, AIP Conference Proceedings 2054, 060031 (2019);
https://doi.org/10.1063/1.5084662

PETRA III





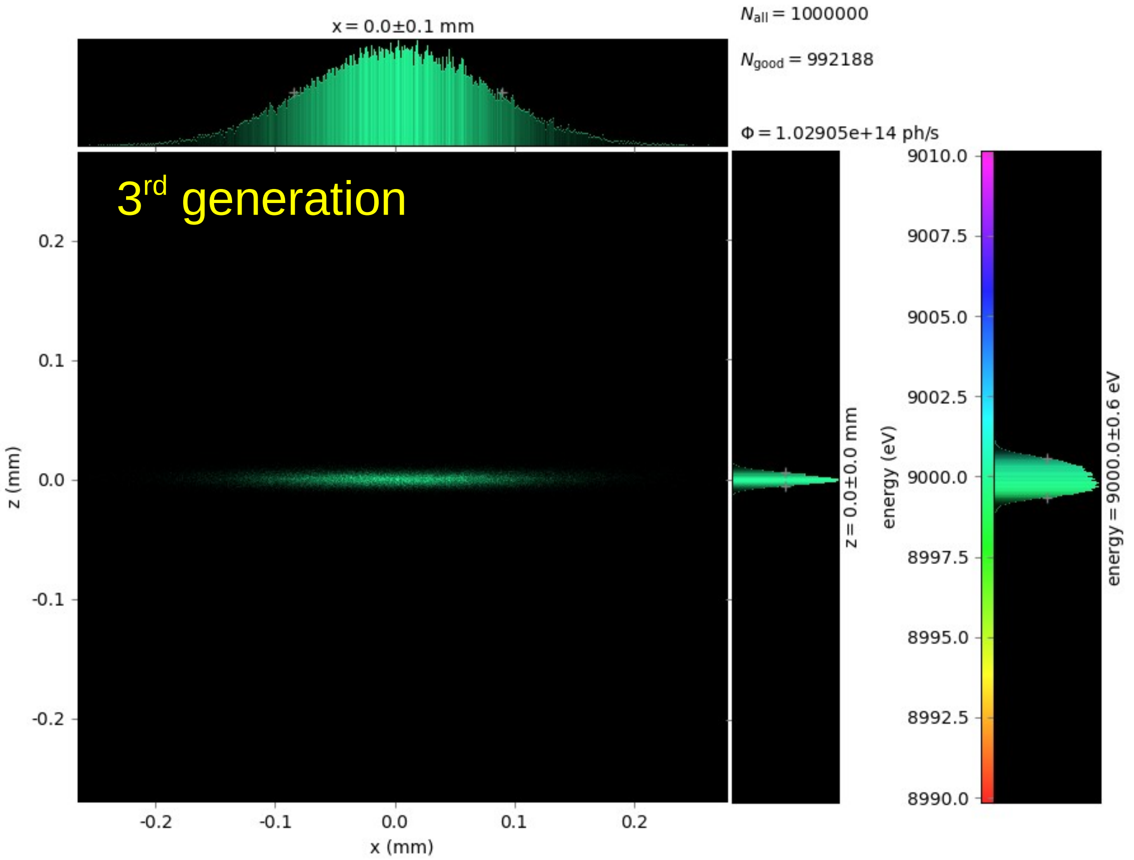
PETRA IV

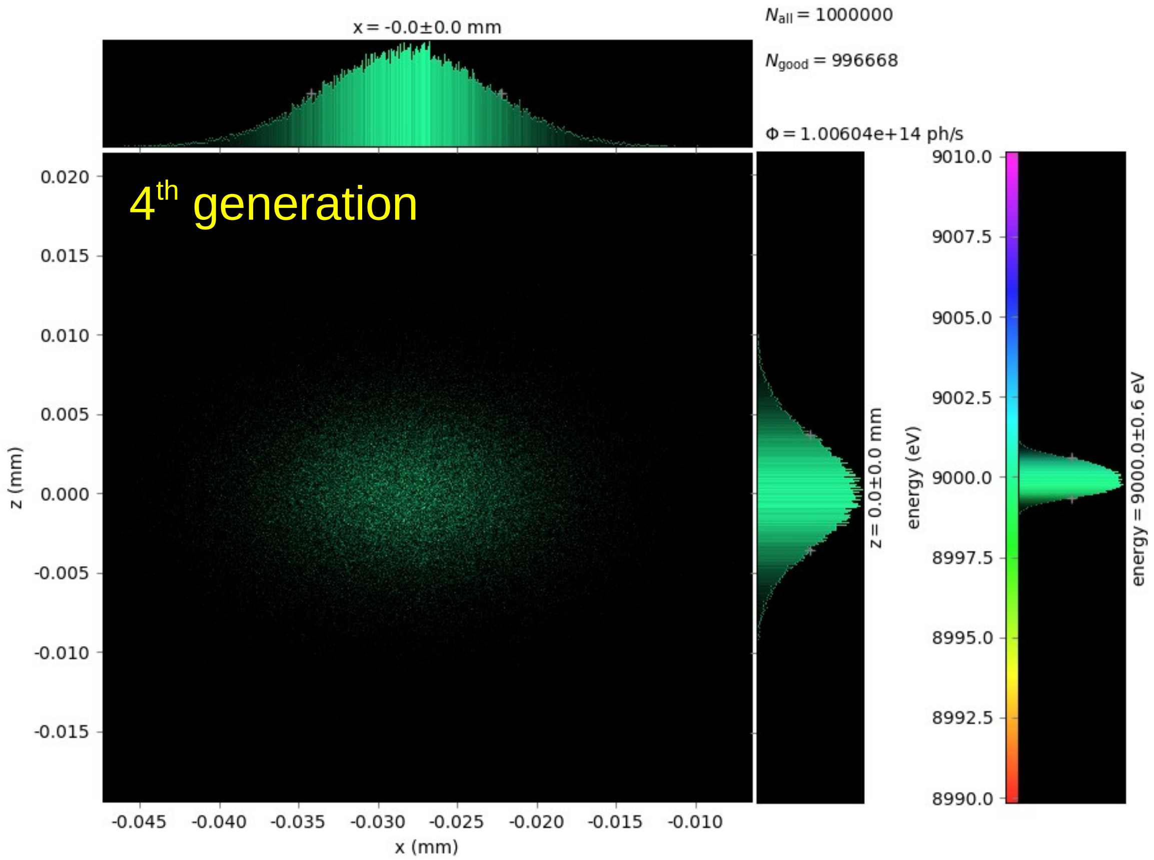
Ray tracing done with xrt 1.3.5

K. Klementiev and R. Chernikov, "Powerful scriptable ray tracing package xrt", Proc. SPIE 9209, Advances in Computational Methods for X-Ray Optics III, 92090A; doi:10.1117/12.2061400

Footprint 80 m from source

Focused beam 80 m from source





Observe the different scaling!

Classical XAFS spectroscopy

“Classical” X-ray absorption spectroscopy

The Swiss knife in catalysis...

Requires:

- mm^2 sized beam
- Homogeneous and incoherent beam
- Monochromatic flux: > 10^9 s^{-1}

=> Ideal source: Bending magnet or short wiggler

Methods:

- XANES, EXAFS (Q-EXAFS)

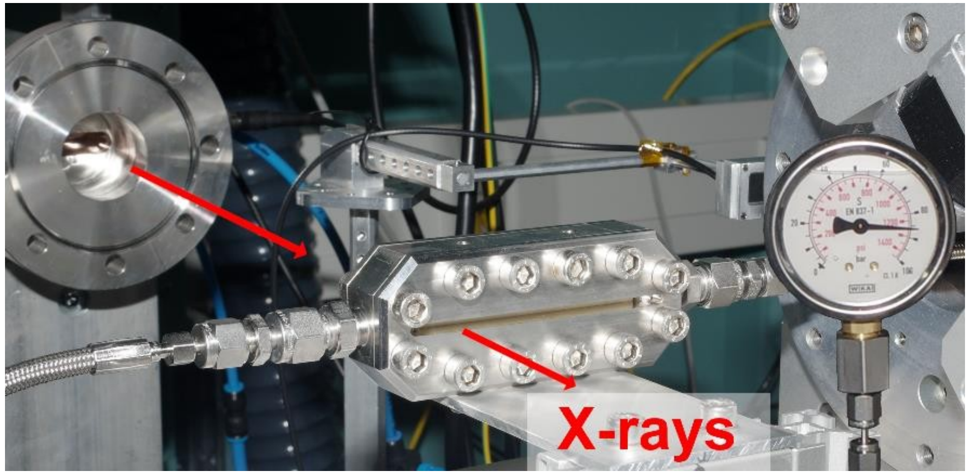
Applications:

- In-situ experiments

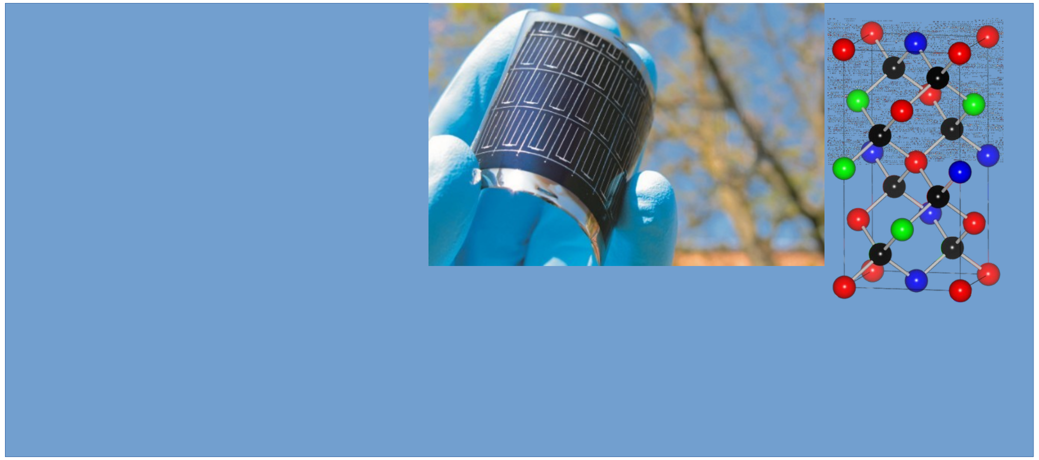
    Catalysis, Batteries…

- ex-situ

    Geochemistry, material science, solid state physics...



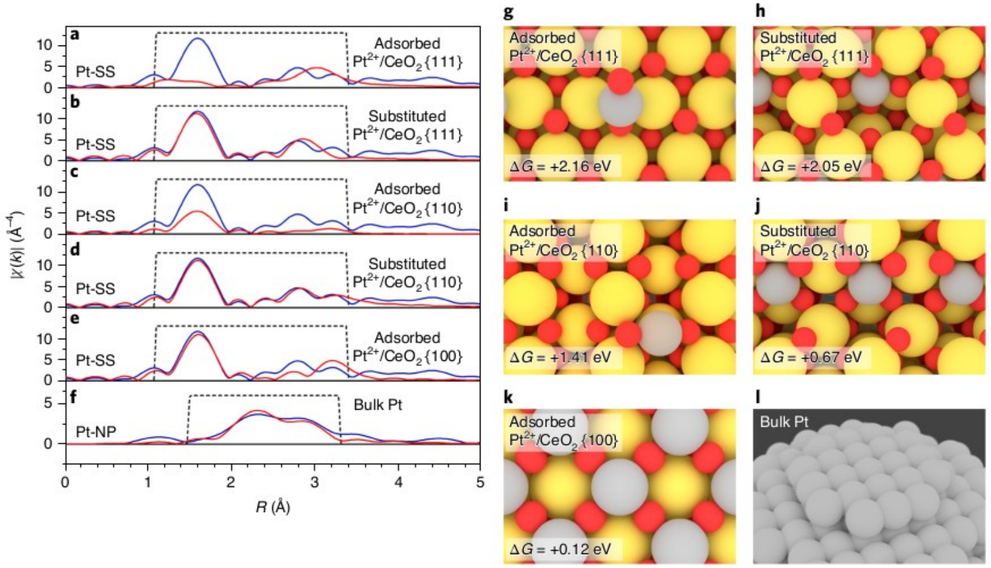
In situ reactor cell for operando XAS studies of direct synthesis of hydrogen peroxide at high pressure.



A “typical” XAFS experiment

Bulk XAFS with mm sized beam

- Use XANES and mainly EXAFS as analytical method
- In-situ/operando experiment
- XAFS as part of a suite of analytical methods
- XAFS results often decisive for the understanding of the structure of the system
- In high demand (High overbooking)



Fits of EXAFS spectra (left) of different structures found by DFT calculations (right) to the experimental spectrum of the active catalyst.

F. Maurer et al., ***Nature cat.***, 3, 824-833 (2020)

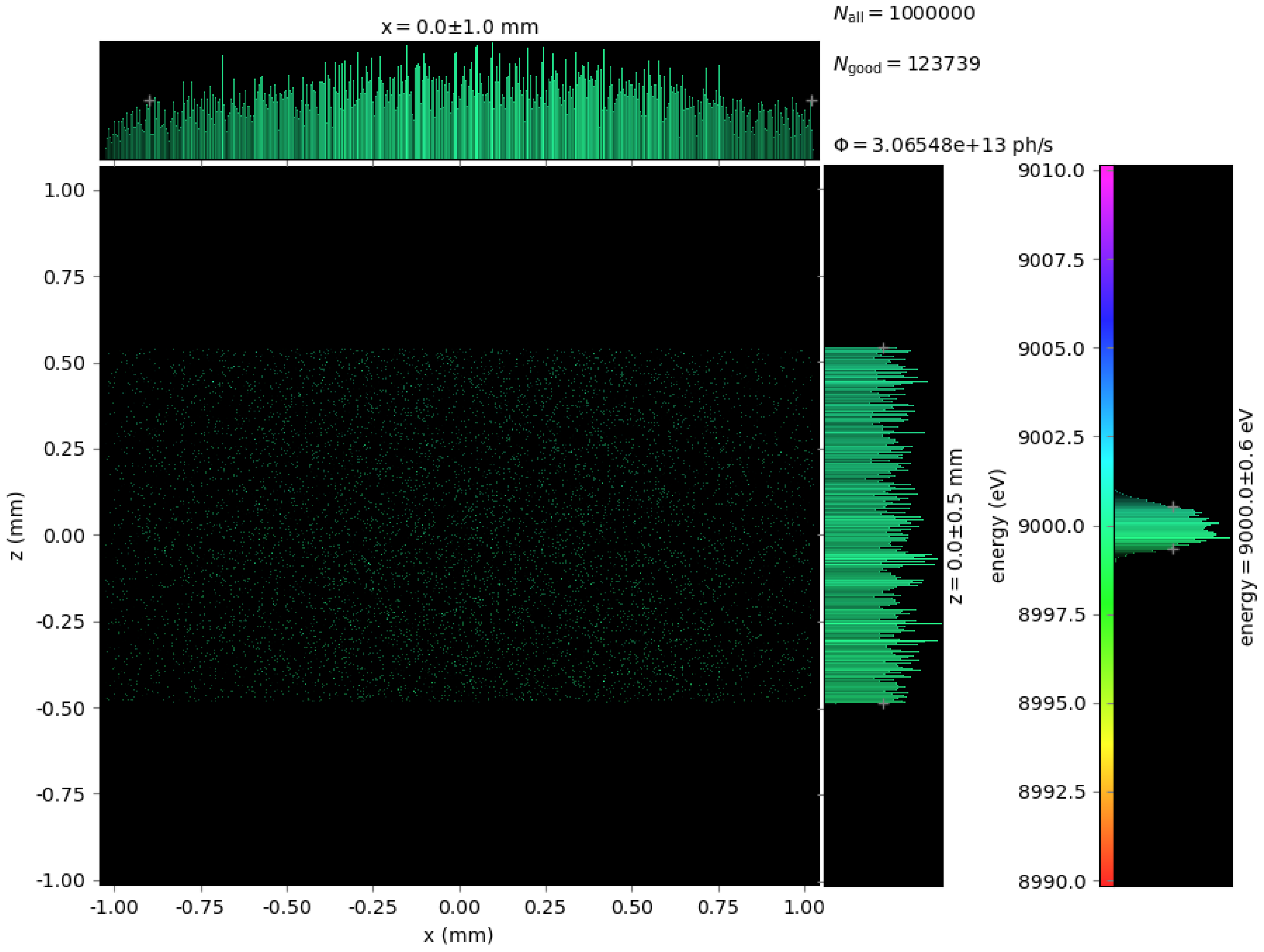
An undulator beamline for bulk XAFS

Ray tracing parameter:

- 15 period U33
- Sample 80 m from source
- 2 plane mirrors for higher harmonic rejection
- Si 111 (and 311) DCM
- Final slit 0.5*1 mm² (v*h)
- Tuned to 9000 eV

Today (P65):

- 11 period U33
- Beamsize 0.5*1.5 mm² (v*h)
- Monochromatic flux ~10^{12} s^{-1}



=> Comparable beamsize, x10 increased flux (density)

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- 15 period U33
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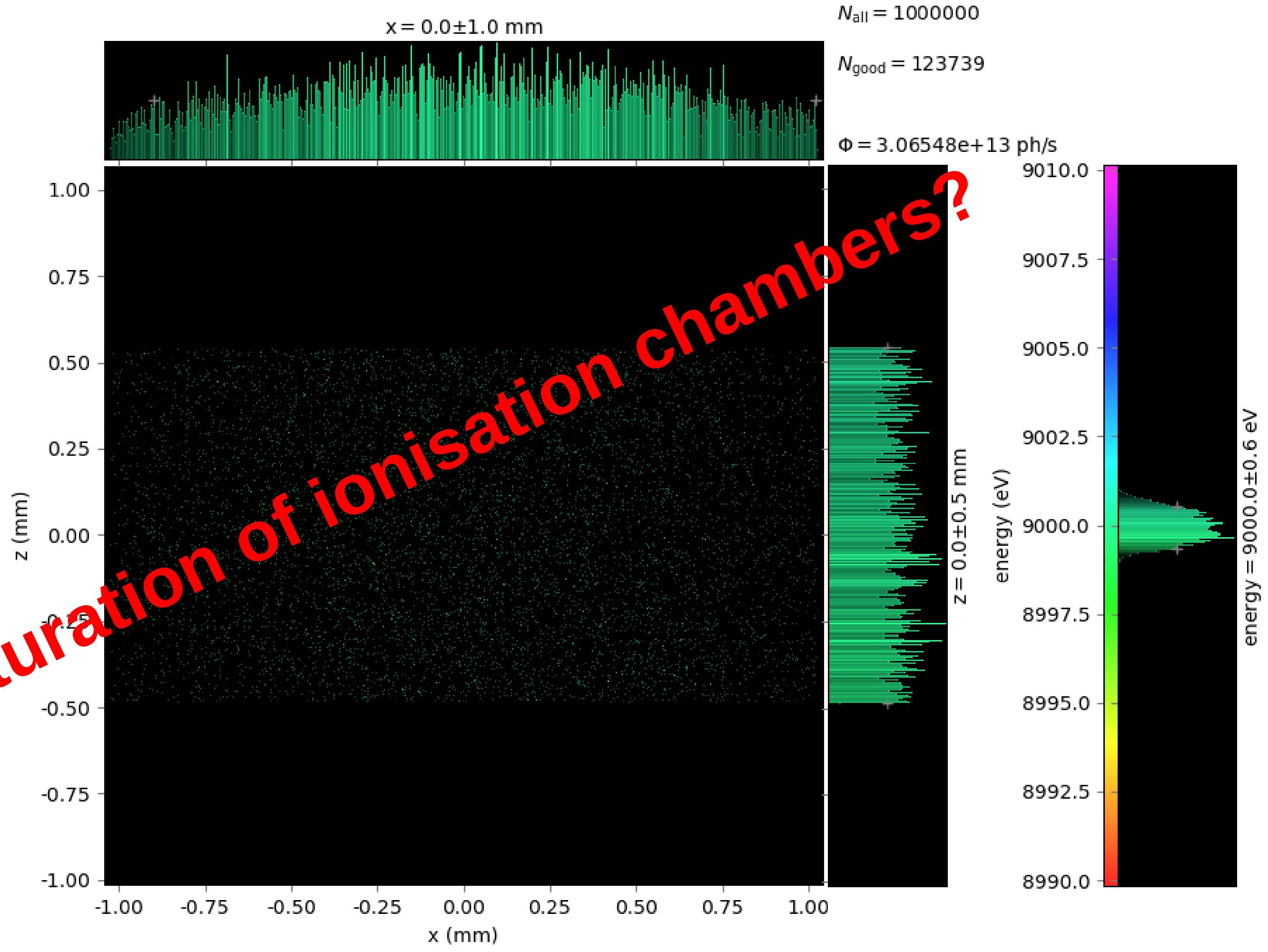
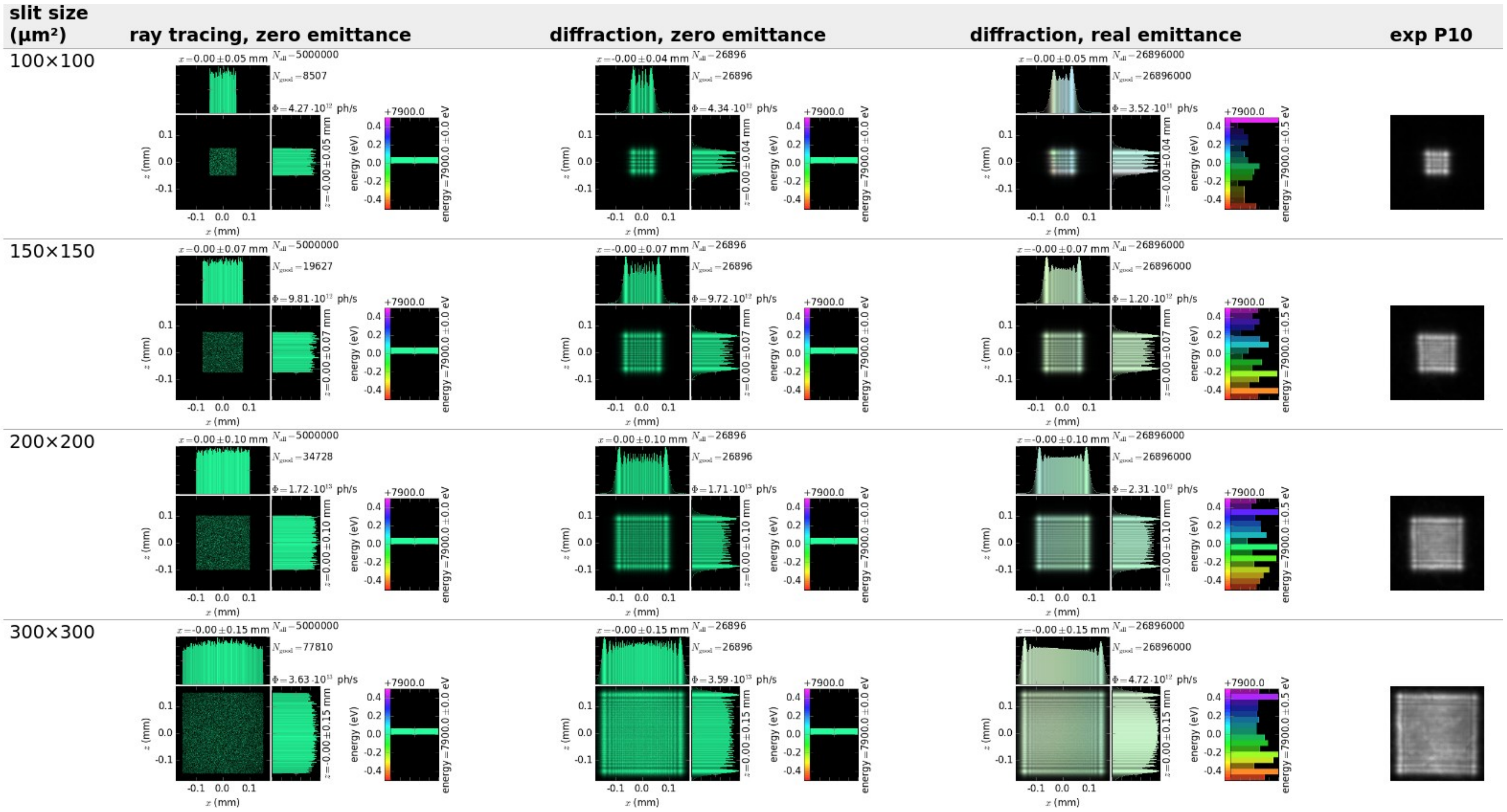


Radiation damage, saturation of ionisation chambers?

Diffraction by slits

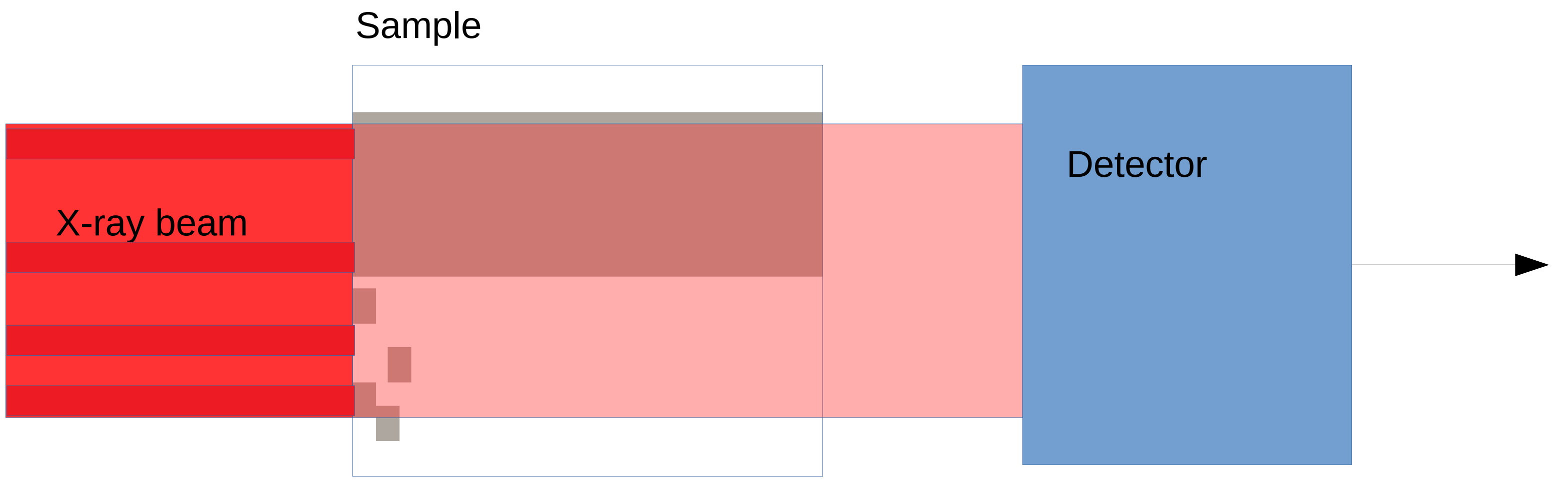


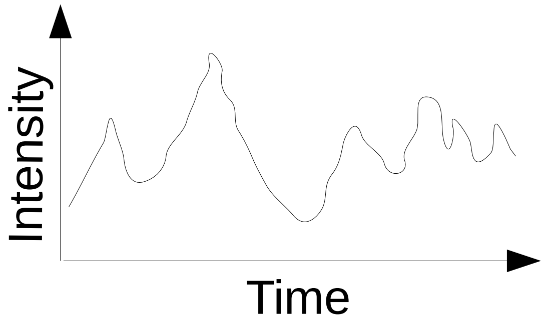
Xrt calculations of undulator beam diffraction at rectangular slits by K. Klementiev and R. Chernikov.

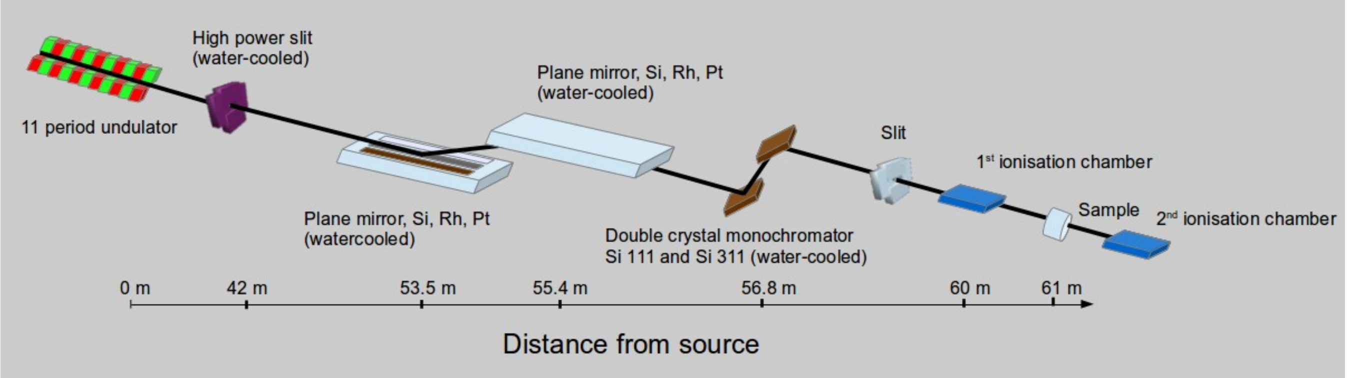
https://xrt.readthedocs.io/gallery3.html

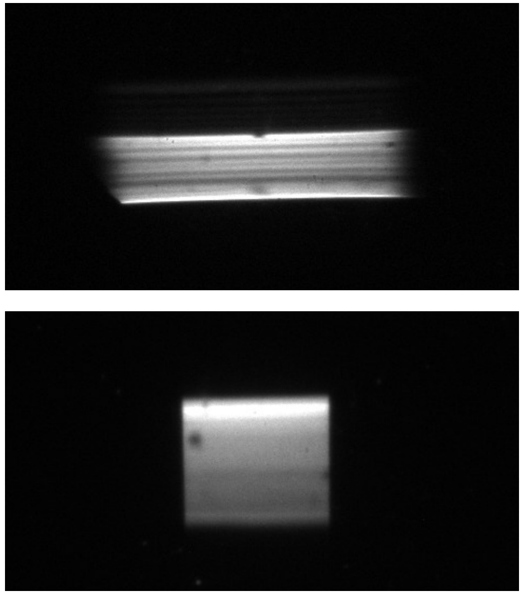
Calculated and measured diffraction by rectangular slits, exp. from PETRA III beamline P10 (A. Zozulya and M. Sprung, 2010, unpublished)

Inhomogeneous beam hits inhomogeneous sample









Beam at sample positon (P65)

Long distances => Small movements of beam position unavoidable…
=> NOISE!

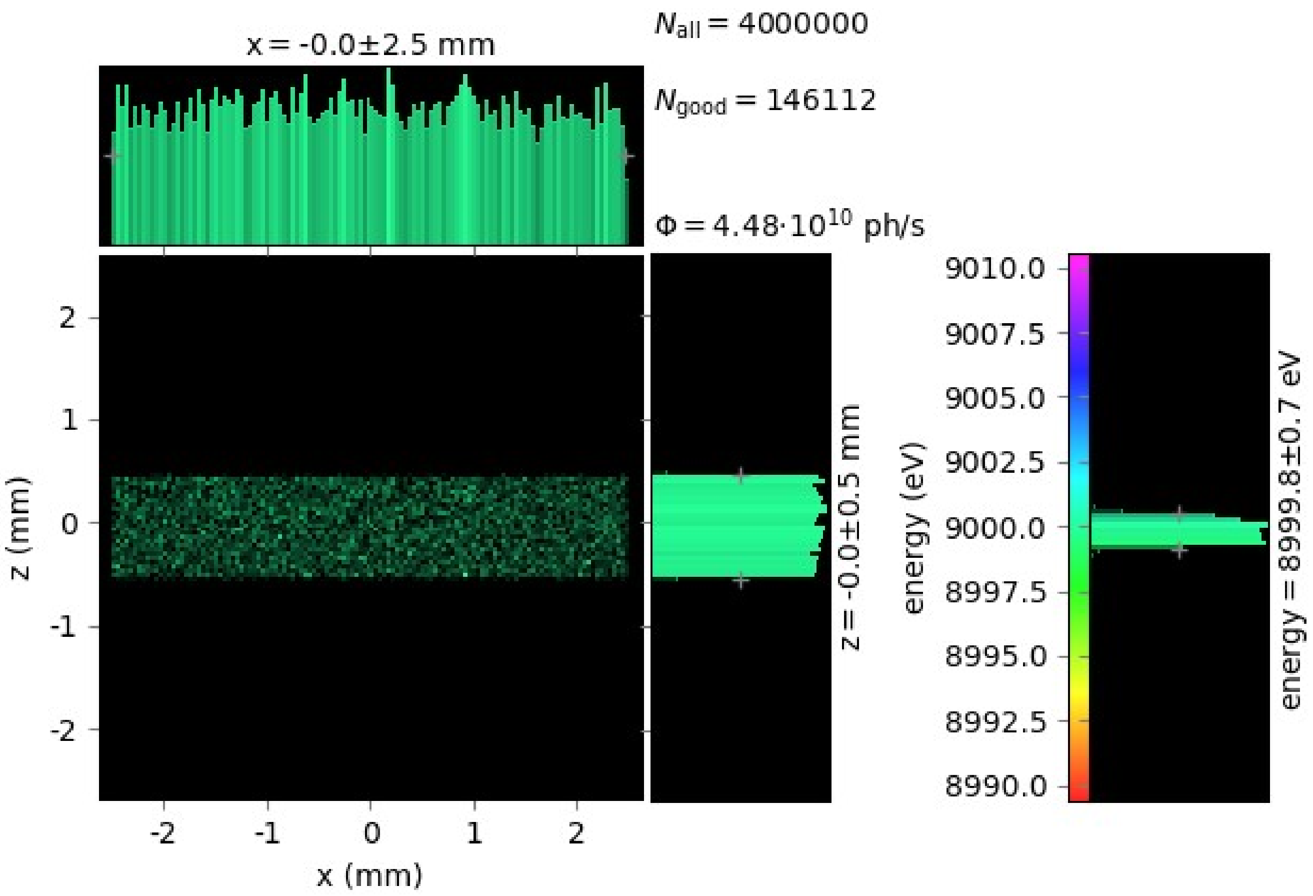
A bending magnet beamline for bulk XAFS

Ray tracing parameter:

- Bending magnet 1.2 Tesla
- Sample 60 m from source
- Collimating mirror (toroid) at 37 m collects 2 cm of horizontal divergence
- Si 111 DCM at 38.5 m
- Final slit 1*5 mm² (v*h)
- Tuned to 9000 eV

Today (P65):

- 11 period U33
- Beamsize 0.5*1.5 mm² (v*h)
- Monochromatic flux ~10^{12} s^{-1}



PETRA specific problem: Large radius => large distance of first optical element (Collimating mirror)

Quick scanning XAFS

EXAFS with 100 Hz

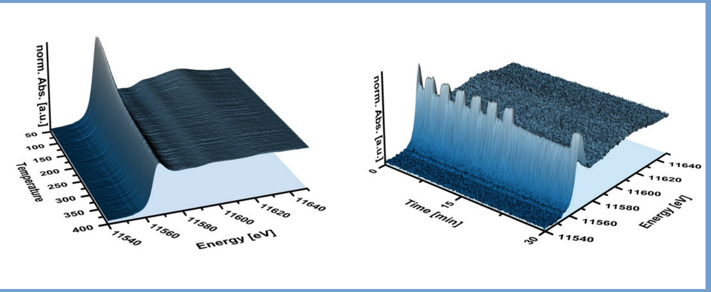
Needs:

- Homogeneous beam

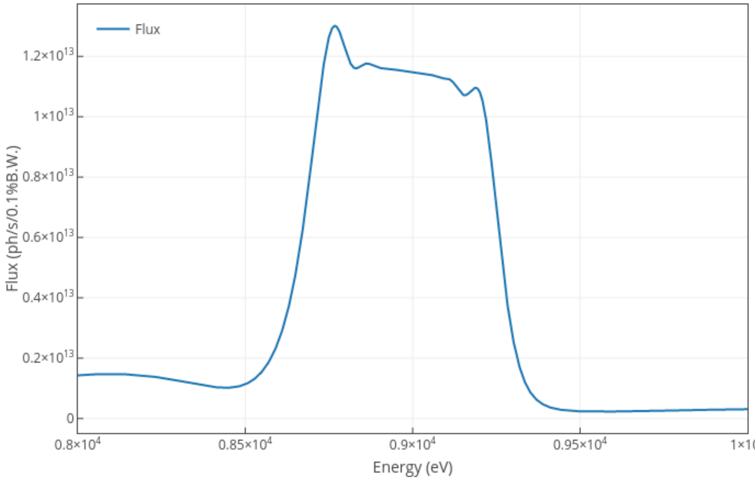
- Now spatial intensity fluctuations with energy

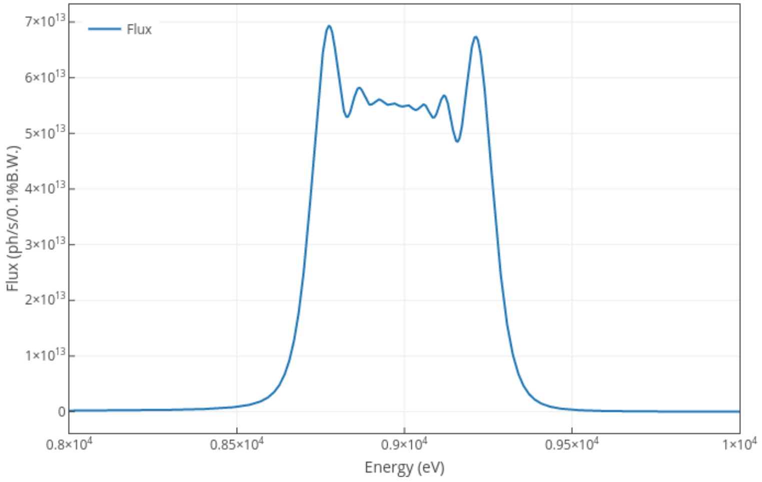
- High photon flux on the sample surface > 10^{12} s^{-1}

- Fast scanning monochromator



Pt-L3 edge XANESduring a temperature programmed reduction (left) and reducing/oxidizing cycles (right) of a Pt based catalyst.
Data courtesy by Andreas Gänzler (KIT).





Flux through a pinhole (1*1 mm²), 80 m distance from source, tapered U33 undulator, 150 periods. PIII left, PIV right. FwhM ~ 500 eV

Calculations done with Spectra 11 (J. Synchrotron Radiation 8, 1221 (2001))

Beyond classical XAFS spectroscopy

High brilliance / Small focus

Spatial resolution and high flux density

Beam properties:

- Focused beam

- Monochromatic flux: > 10^{12} s^{-1}

- Ideal source: Undulator

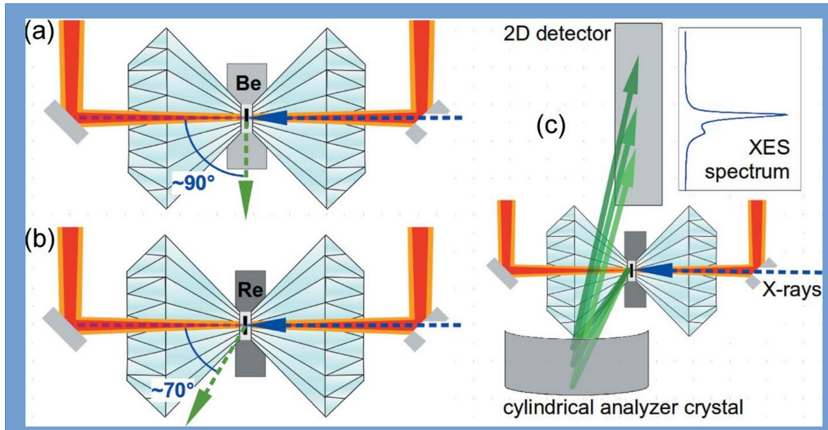
Methods:

- µ-XAFS

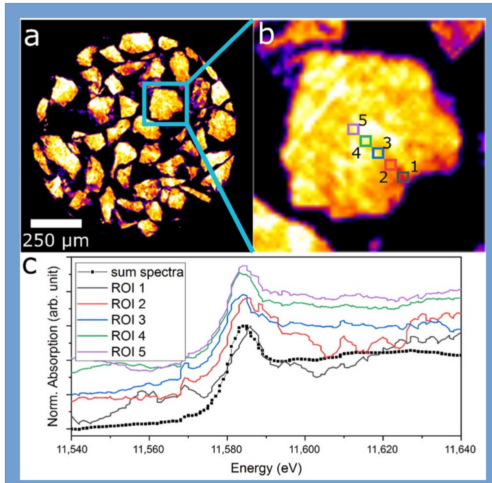
- XAFS-tomography

Applications:

Catalysis, highly diluted samples, extreme conditions, grazing incidence XAFS



Laser heated Diamond Anvil Cellc & Spectroscopy
spectroscopy (and diffraction) on laser-heated melts, heated spot 20 µm, rapid measurements or pulsed heating & measurement
G. Spiekermann et al., J. Synchr. Rad. **27** (2020)



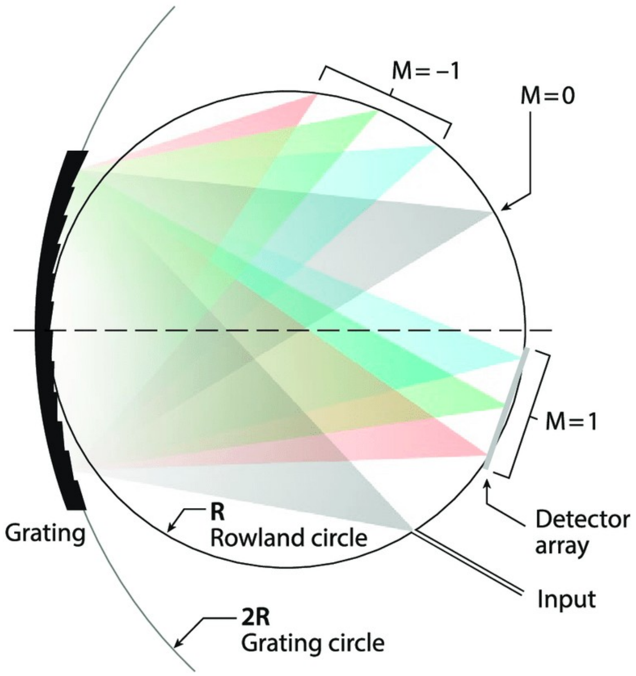
Catalyst sample in capillary measured at 553 K; (a) reconstructed slice, color-coding depicting the absorption intensity at 11,585 eV; (b) extracted single particle of the same slice with marked regions of interest; (c) XANES spectra extracted from each region of interest

J. Becher at al., *Catalysts*, **11**, 459 (2021)
https://doi.org/10.3390/catal11040459

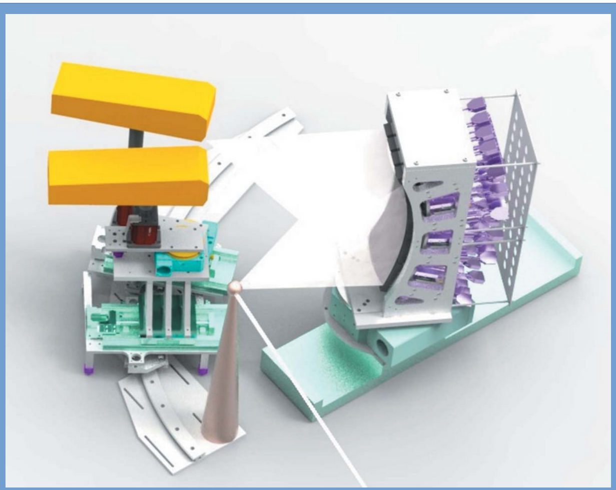
Spectrometers on the Rowland circle

High resolution emission spectroscopy and Co.

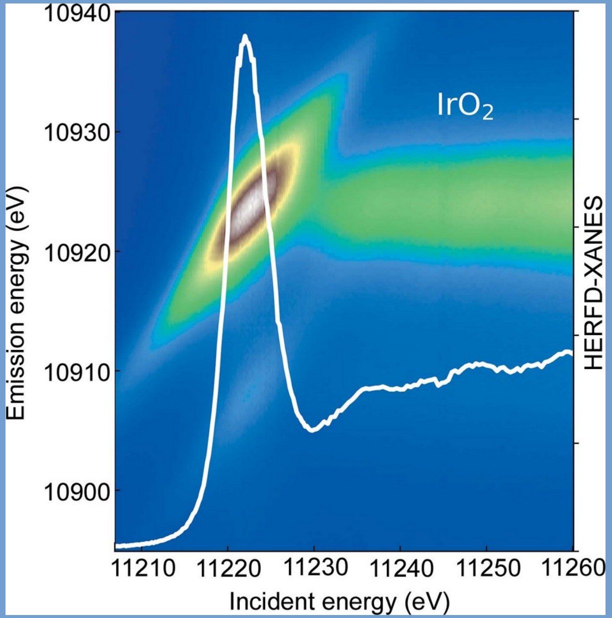
- Beamsize limits energy resolution
- Photon hungry
- Applications profit from higher brilliance



From: Cataldo, Giuseppe (Thesis, 2015). *Development of ultracompact, high-sensitivity, space-based instrumentation for far-infrared and submillimeter astronomy.*



Mechanical drawing of the von Hamos spectrometer at P64 equipped with two detectors.



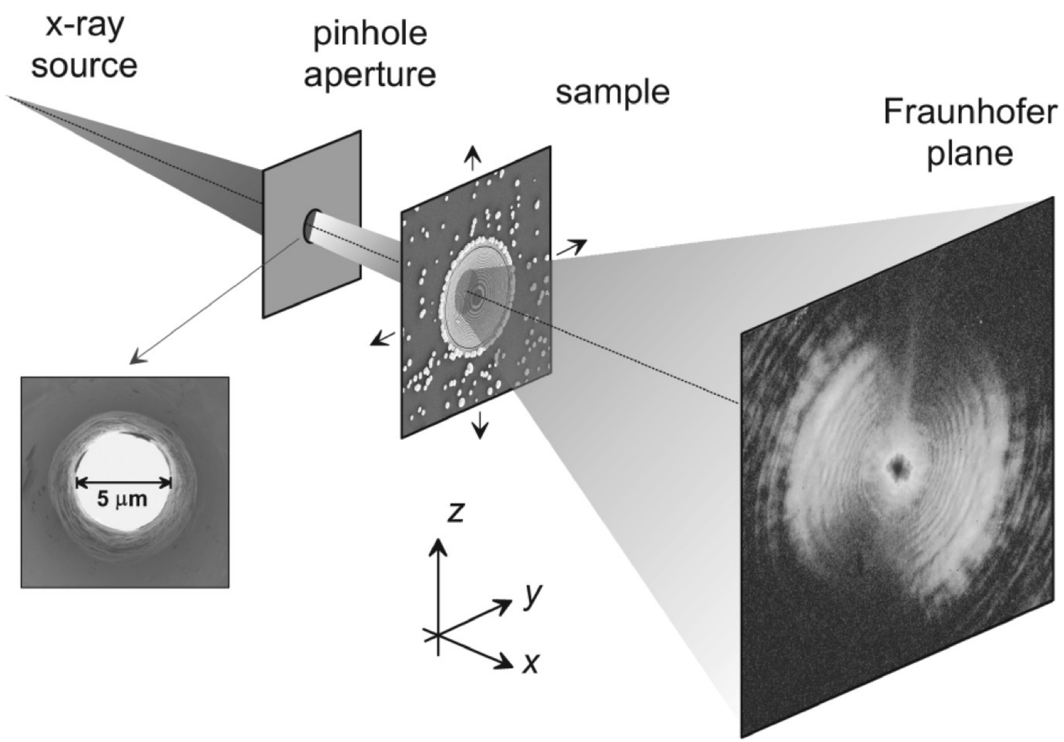
Ir L 3 -edge RXES plane and HERFD-XANES spectrum constructed from the plane by a cut at the maximum of the L 1 emission line.

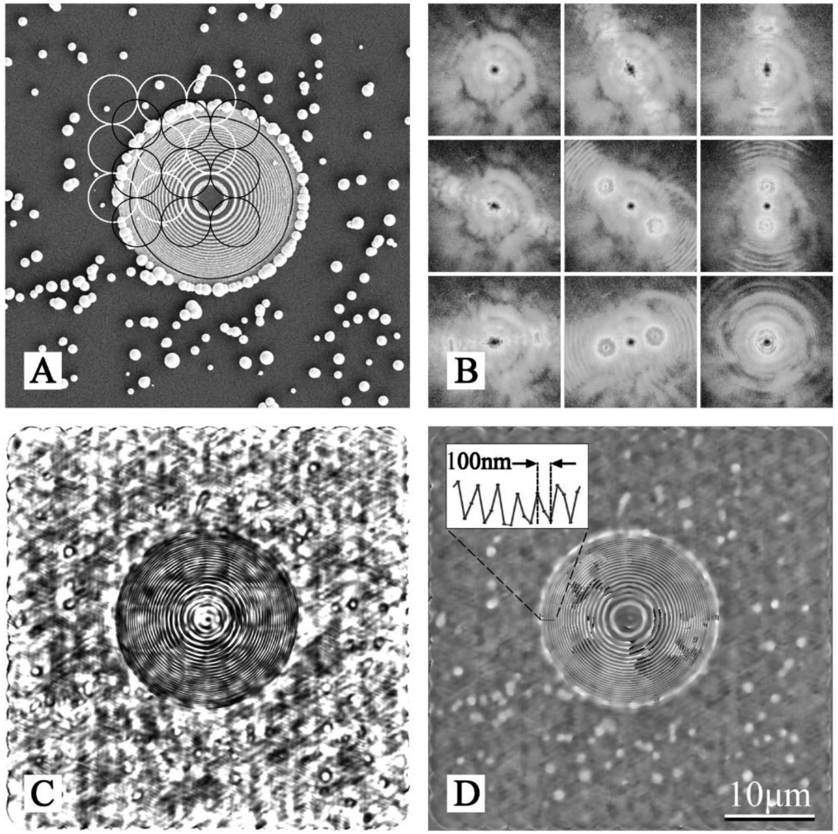
A. Kalinko et al. J. Synchrotron Rad. **27**, 31–36 (2020)

And finally coherence!

Ptychography

Hard-X-Ray Lensless Imaging of Extended Objects



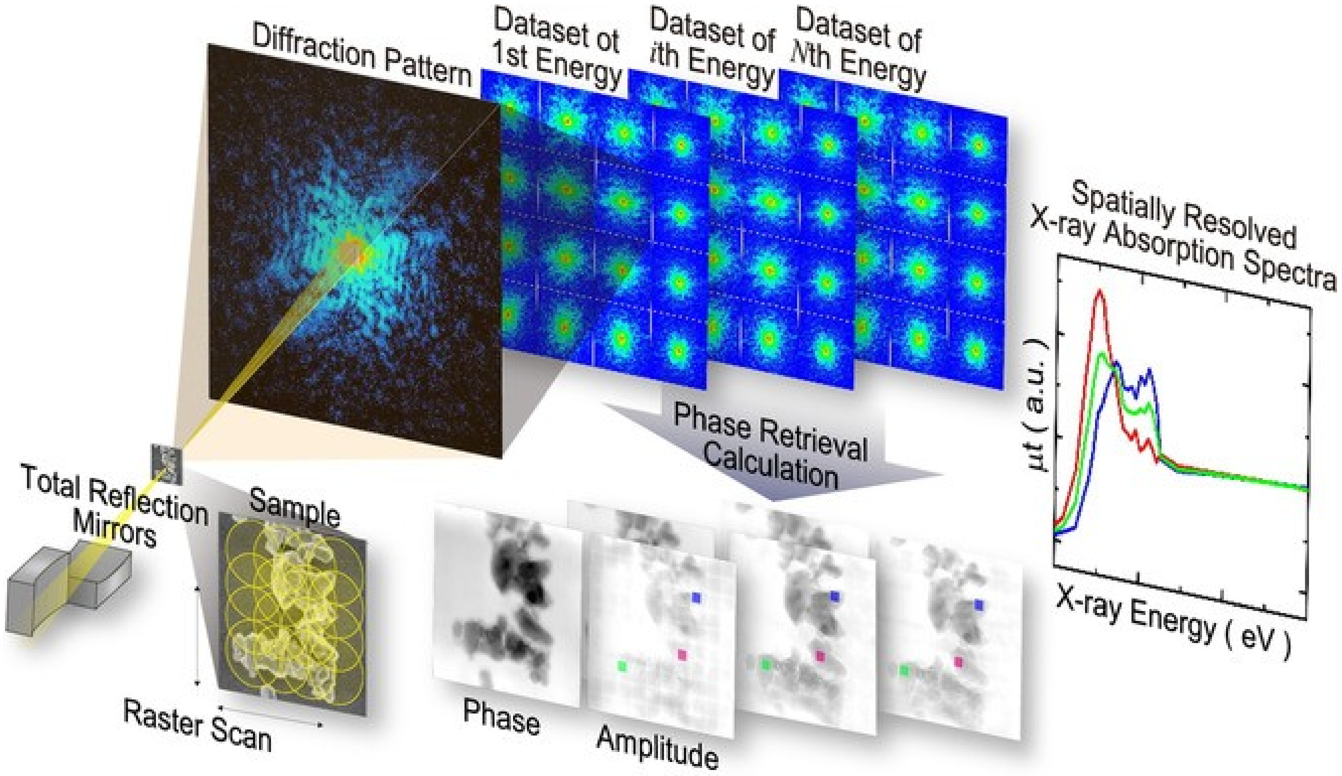


Schematic of the experimental setup for a shifting specimen coherent x-ray diffraction microscopy.

M. Rodenburg, A. C. Hurst, A. G. Cullis, B. R. Dobson, F. Pfeiffer, O. Bunk, C. David, K. Jefimovs, and I. Johnson, PRL 98, 034801 (2007)

XAFS-Ptychography

Adding a further “dimension”



X-ray spectro-ptychography
or **ptychographic-XAFS**).

- Scanning of a focuseded coherent X-ray beam across the specimen at multiple X-ray energies.

- Phase and amplitude images are reconstructed from diffraction patterns by phase retrieval calculation.

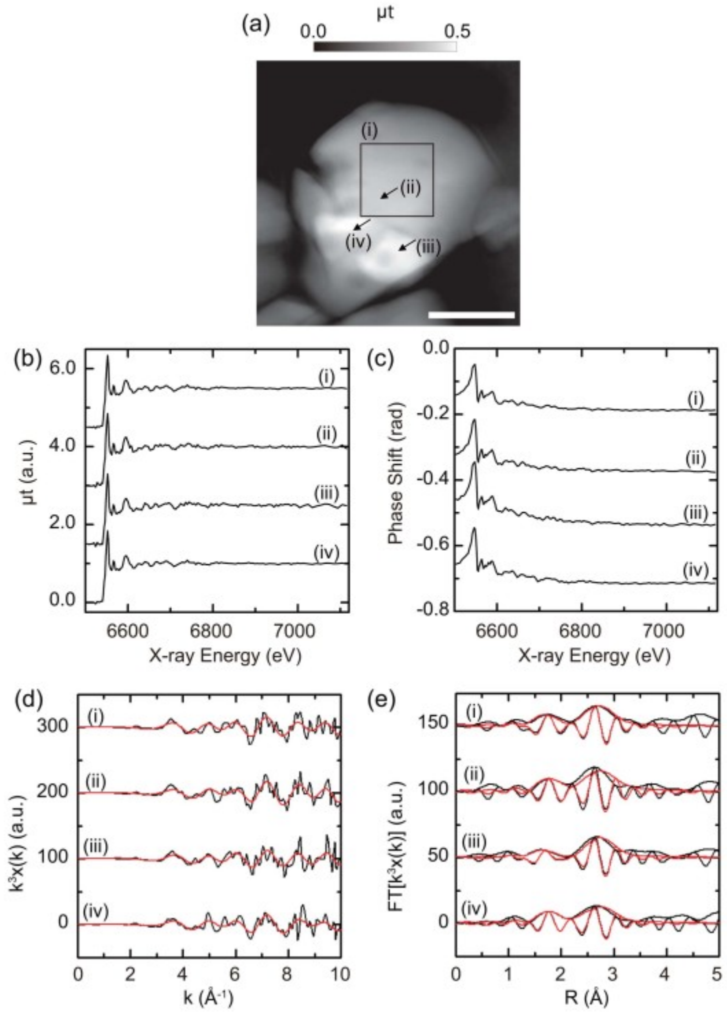
- By analysing the energy dependence of the reconstructed images, spatially resolved X-ray absorption spectra are derived.

M. Hirose, N. Ishiguro, K. Shimomura, N. Burdet, H. Matsui, M. Tada and Y. Takahashi, Angew. Chem. Int. Ed., **57(6)**, 1474-1479, (2017)
DOI: (10.1002/anie.201710798)

XAFS ptychography

Current limits

"Currently, the available flux of incident X-rays for the ptychography-XAFS method is **limited for the present synchrotron light source** since X-ray ptychography experiments **require highly coherent X-rays**. In **near-future synchrotron facilities**, the coherent X-ray flux will be **increased by a few orders of magnitude**, which will open up the possibility of visualization of spatio temporal chemical reactions and structural heterogeneities at an unprecedented high spatial resolution."



Hirose et al., J. Synchrotron Rad. (2020). 27, 455–461 https://doi.org/10.1107/S1600577519017004

XAFS ptychography

Future perspectives

Mode	Undulator	Photon energy (keV)	Brilliance (ph/s/mm^2/mrad^2/0.1%bw) (Gauss) using Spectra	Brilliance (ph/s/mm^2/mrad^2/0.1%bw) (Wigner) using spectra	RMS photon source size (µm) (h x v)	RMS photon source divergence (µrad) (h x v)	FWHM beam size @ 100 m (µm) (h x v)	Coherence length @ 100 m (µm) (h x v) (GSM model)	Coherent fraction (GSM model) (%) (h x v)	Total Flux (ph/s) after DCM 38.5 m Si(111)	Coherent Flux (ph/s) after DCM 38.5 m Si(111)	Gain in coherent flux after DCM 38.5 m Si(111) comp. PIII	Total coherent fraction (GSM model) (%)
PETRA III high beta	**U33 / 2m**	**2.4 (1st**	6.72E+19		160.64 x 9.06	14.33 x 12.11	4791 x 2760	85 x 1588	2.10 x 56.1	1.22E+13	1.46E+11	0.00	1.20
		6 (1st)	1.12E+20		160.54 x 7.14	10.99 x 7.87	4416 x 1767	42 x 635	1.12 x 39.0	2.81E+13	1.12E+11	0.00	0.40
		8 (1st)	8.56E+19		160.52 x 6.77	10.33 x 6.91	4493 x 1449	34 x 448	0.90 x 34.2	2.07E+13	6.42E+10	0.00	0.31
PETRA IV Brightness mode	**U33 / 5m**	**2.4 (1st**	1.15E+22	1.38E+22	14.54 x 11.71	8.21 x 8.16	1789 x 1845	992 x 1775	54.7 x 74.4	6.49E+13	2.63E+13	179.98	40.60
		6 (1st)	3.16E+22	3.69E+22	11.52 x 7.62	5.29 x 5.22	1153 x 1208	452 x 983	41.9 x 69.2	1.47E+14	4.25E+13	377.96	28.90
		8 (1st)	2.87E+22	3.32E+22	10.93 x 6.71	4.63 x 4.55	1022 x 1022	342 x 787	36.7 x 67.2	1.08E+14	2.67E+13	415.71	24.70
PETRA IV Timing mode	**U33 / 5m**	**2.4 (1st**	2.82E+21	3.69E+21	16.28 x 11.79	7.41 x 7.32	2059 x 2059	884 x 1846	45.1 x 72.6	2.60E+13	8.50E+12	58.07	32.70
		6 (1st)	7.11E+21	8.69E+21	13.74 x 7.91	6.05 x 5.94	1344 x 1344	302 x 956	25.6 x 64.2	5.87E+13	9.63E+12	85.65	16.40
		8 (1st)	6.28E+21	7.53E+21	13.24 x 7.02	5.31 x 5.19	1131 x 1188	204 x 693	20.8 x 56.6	4.36E+13	5.14E+12	80.17	11.80

XAFS ptychography

Future perspectives

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		6 (1st)	1.12E+20		160.54 x 7.14	10.99 x 7.87	4416 x 1767	42 x 635	1.12 x 39.0	2.81E+13	1.12E+11	0.00	0.40
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Summary

Summary

Challenges

- Classical XAFS spectroscopy does not gain from brilliance and/or coherence of 4th generation storgae rings

- Beam inhomogenieties caused by diffraction will be amplified in more coherent beam

- The large flux density will increase problems with radiation damage and saturation of detectors (ionisation chambers)

- Superbends / short wigglers can be an attractive alternative at rings with smaller circumference and lower e^- energy than PETRA IV

Summary

Gains

- Methods that need high brilliance will gain from 4^{th} generation sources

- This methods include µ-XAFs and XAFS-tomography

- Ptychographic XAFS is a very intersting method which will profit (be enabled) by the large fraction of coherent photons in the beam

- It will provide a 3-dimensional chemical mapping with high spatial resolution

Thank you

XAFS Journal Club Europe and Asia organised by Kiyotaka Asakura and Hitoshi Abe

Proposed talk by Prof. Takahashi about ptychographic-XAFS

Registration via:
https://docs.google.com/forms/d/e/1FAIpQLScyZVGEpGgFaAnMMk_ztaoasFrSx4nZ9fl1Ym_v8uVKiQZIlQ/viewform

Contact

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Planning new beamlines

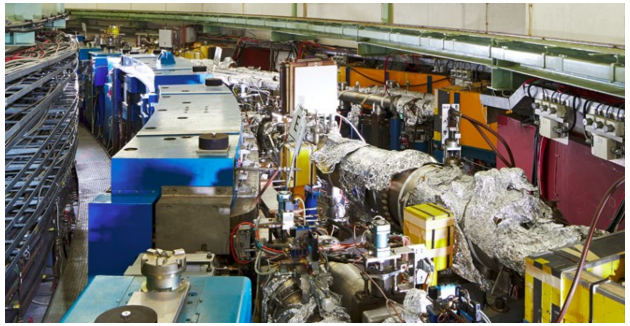
Ask users what they want to do in 5 – 10 years...

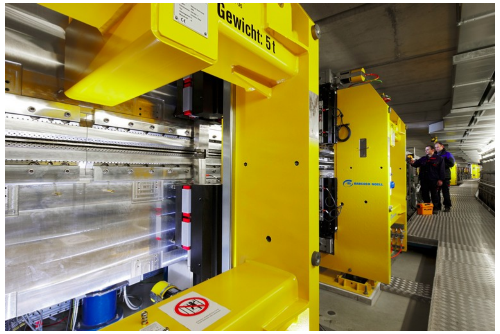
- Standard EXAFS (“large” beam, 1 min per scan, moderate flux density)
- Fast scanning XAFS (variable beamsize, 10 – 100 scans s^{-1})
- High precision EXAFS ($k > 20$ $Å^{-1}$) (Usually “large” beam, highest possible spatial beam stability and homogeneity, moderate flux density)
- XAFS imaging with high spatial resolution (XAFS-tomography, µm² sized beam, high intensity/flux density)
- µ-XAFS << 10 µm (µm² sized beam, high intensity/flux density)
-

Home lab to synchrotron

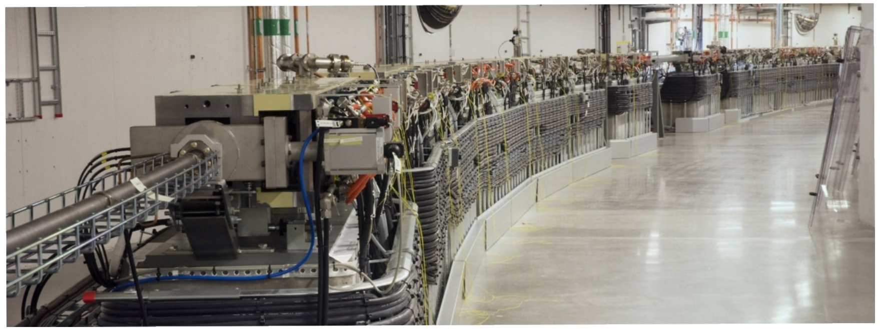
The gap is getting larger

DORIS III bending magnets



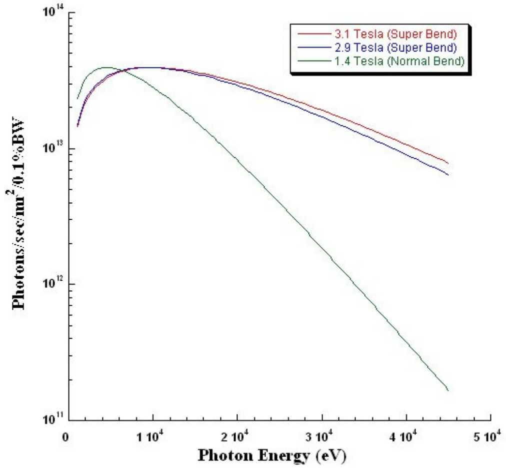


PETRA III undulators



MAX IV, the first operating 4th generation 3 GeV storage ring
Balder beamline, In vacuum wiggler (K=9), 38 periods, L = 50 mm

X-ray tube based bench-top XAFS devices



SuperBend at SLS (3 GeV, 3rd)
SuperXAS beamline