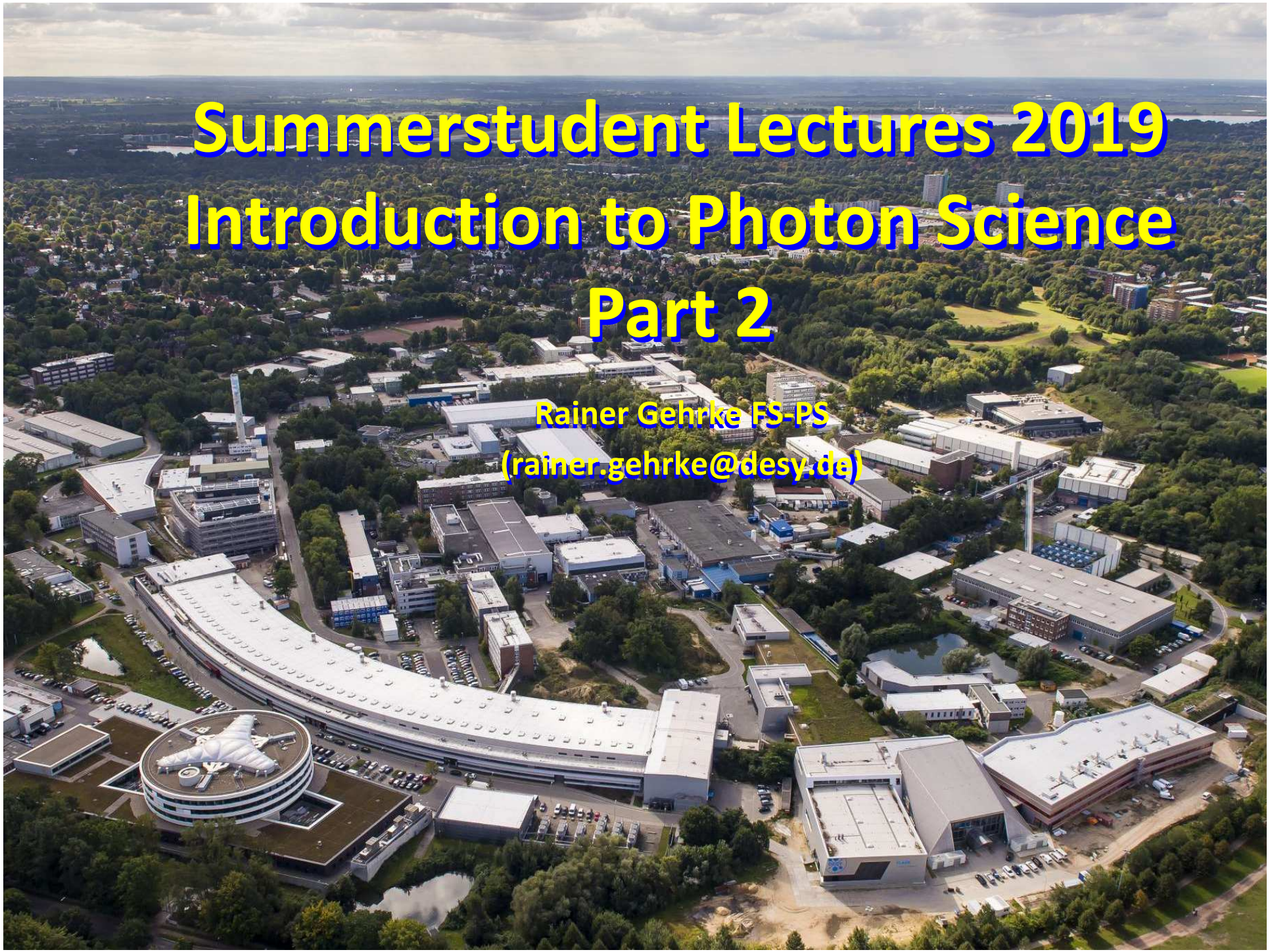


Summerstudent Lectures 2019
Introduction to Photon Science
Part 2

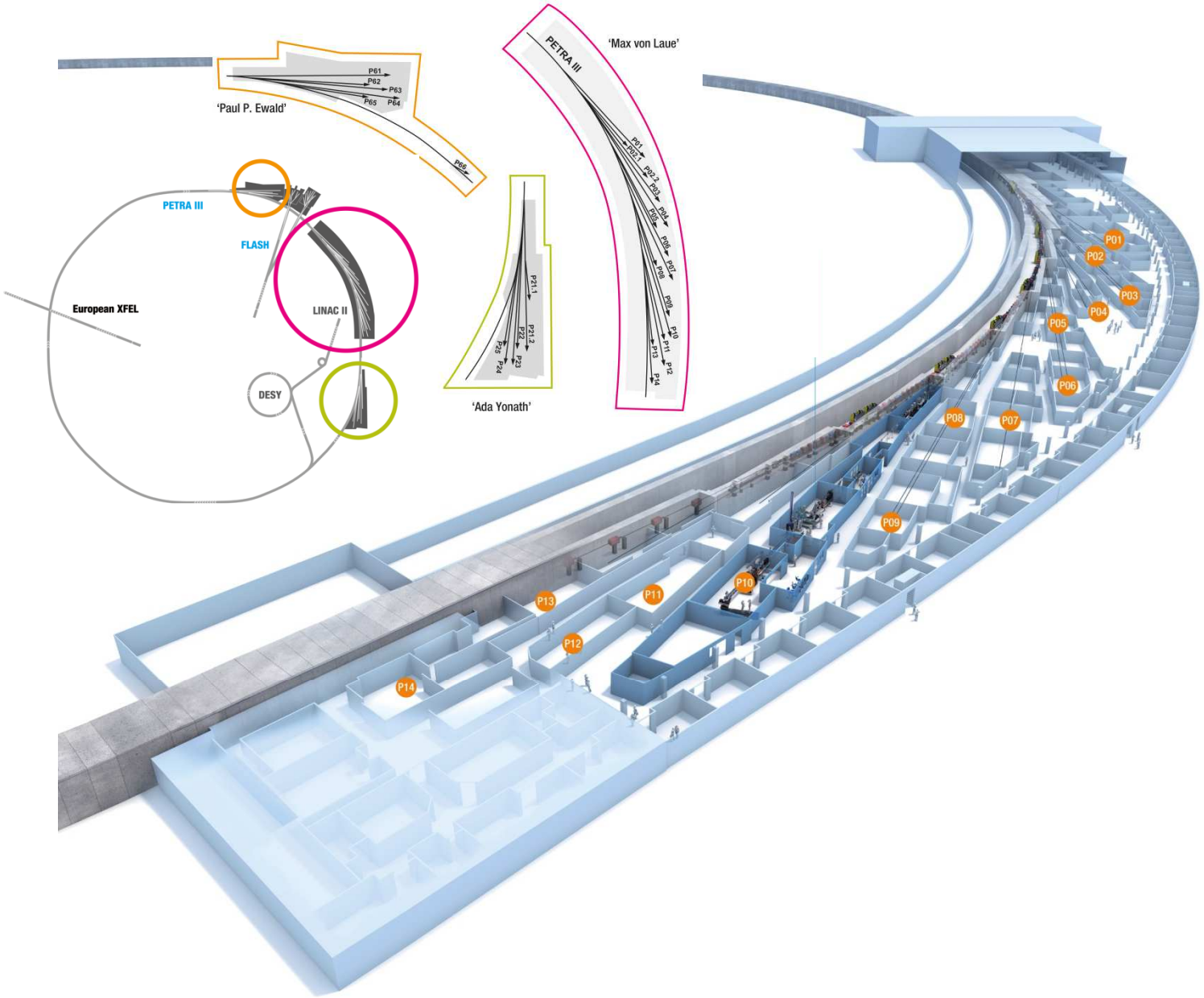
Rainer Gehrke FS-PS
(rainer.gehrke@desy.de)

Scientific Experiments

DESY Photon Science Annual Reports 2010 - 2018 (PDF)
http://photon-science.desy.de/research/scientific_media/desy_photon_science_annual_reports/

Hasylab Annual Reports 1998 - 2007 (Web Versions) and DESY Photon Science Annual Reports 2008 - 2009 (PDF)
http://photon-science.desy.de/research/scientific_media/desy_photon_science_annual_reports/archive/

PETRA III Facilities



Scientific Experiments with photons at PETRA III

24 Undulator Beamlines
About 2000 Scientists from about 400 Institutes
about 4000 hours of user beamtime per year

Physics, Chemistry, Biology, Medicine

Scattering and Diffraction

- **Small Angle X-Ray Scattering** **(SAXS, USAXS, GISAXS, ASAXS)**
- **Diffraction and Crystallography** **(General, Powders, Proteins, High Pressure, Surfaces)**

Spectroscopy

- **XUV Fluorescence Spectroscopy**
- **X-Ray Absorption Spectroscopy**
- **X-Ray Photoemission Spectroscopy**
- **Inelastic X-Ray Scattering** **(Nuclear Resonant Scattering)**

Imaging

- **Microtomography**
- **X-Ray Micro Fluorescence**

Weak Signals
e.g. High Collimation
e.g. Small Samples
Time resolved measurements
Tunable wavelength
Time Structure

Experiments concentrate on experiments with small focus primary beams ($\mu m, nm$)

PETRA III Facilities

P01: **Nuclear Resonant and inelastic scattering**
2.5 - 80 keV, Resolution 1 eV to 1 meV, sub-micron spatial resolution
P02.1: **High-Resolution Powder Diffraction**
60 keV, Resolution
P02.2: **Microdiffraction under Extreme Conditions**
25 - 60 keV, high pressure, high/low temperatures
P03: **X-ray scattering with micro-/nano-focus**
9 – 23 keV
P04: **Variable Polarization XUV-Beamline**
250 - 3000 eV High-Resolution Photoelectron Spectroscopy
P05: **Imaging Beamline**
5- 50 keV Micro- and Nanotomography
Phase- and Absorption Contrast imaging,
P06: **Hard X-ray Micro/Nanoprobe**
5 - 21 keV Visualization with micro- to nanometer resolution using X-ray Fluorescence, absorption spectroscopy, diffraction
Coherent diffraction imaging, Ptychography
P07: **High Energy Materials Science**
30 - 200 keV, Microfocus
P08: **High Resolution Diffraction, Small angle Scattering, Reflectivity**
5 - 29 keV, Microfocus
P09: **Resonant Scattering and Diffraction, XMCD**
2.7 - 50 keV
P10: **Coherence Applications Beamline**
5 - 25 keV Photon Correlation Spectroscopy, Coherent diffractive imaging of nanostructures, Rheo-SAXS
P11: **Bio-Imaging and diffraction**
5 - 30 keV, Micro/Nanobeam, Biological Samples and microcrystals
P12: **Small Angle Scattering at biological samples (proteins) in solution**
P13/P14: **Macromolecular CrystallographY**

Surface Science (P01, P03, P08, P10)
Thin films, Wetting phenomena, Phase transitions

Materials Science (P01, P02, P04, P07, P09,)
Catalysis, Magnetism, Superconductivity, Metallic Glasses, Batteries

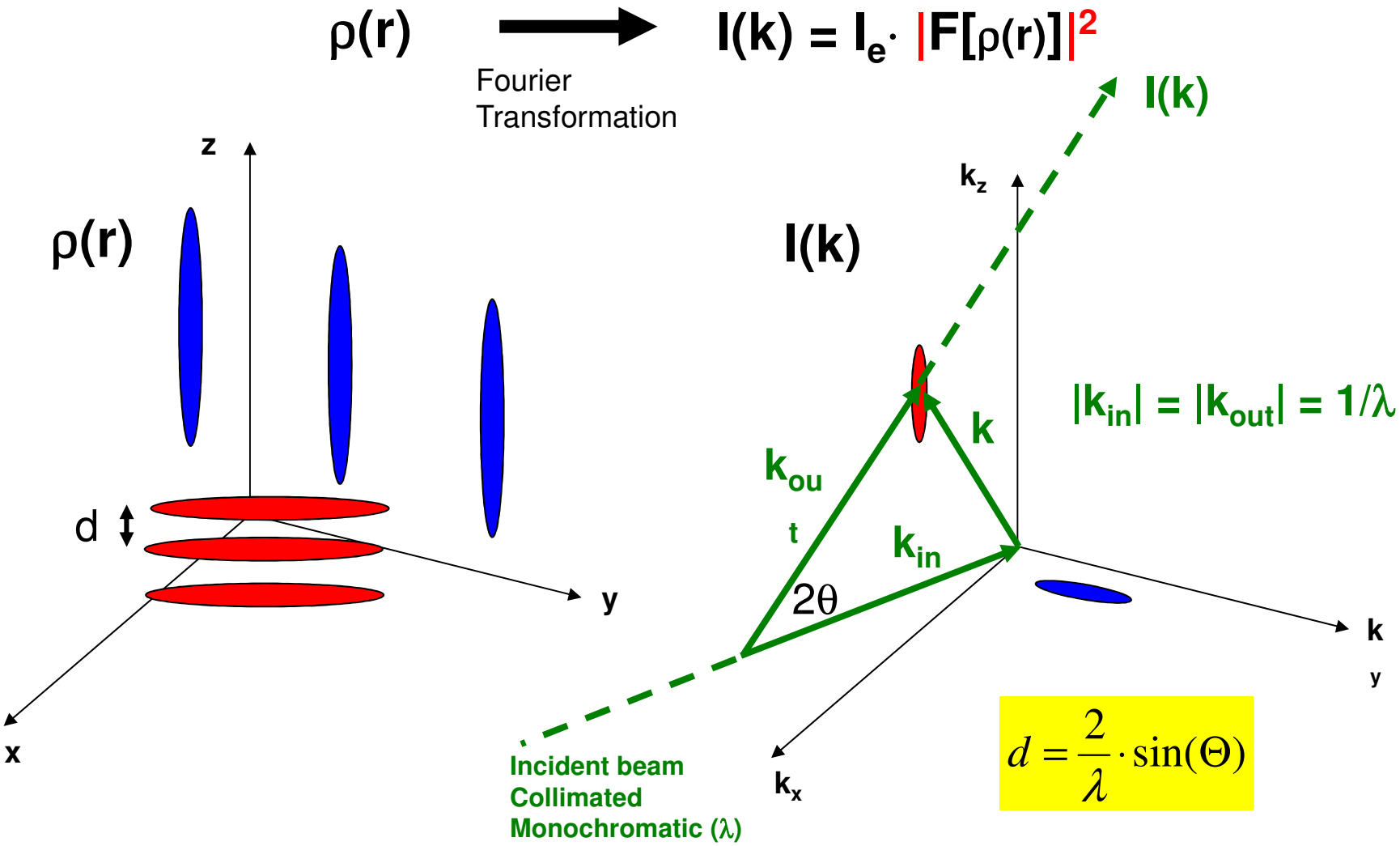
Soft Matter Research (P01, P03, P08, P09, P10)
Polymers, Colloids, Glass Transitions

Earth Science (P01, P02, P08, P09)
High Pressure Research, Geophysics, Mineralogy, Trace Element Analysis

Life Science (P11, P12, P13, P14)
Protein Structure, Drug Development

Scientific Experiments
Scattering & Diffraction

Basics of an Elastic Scattering Experiment



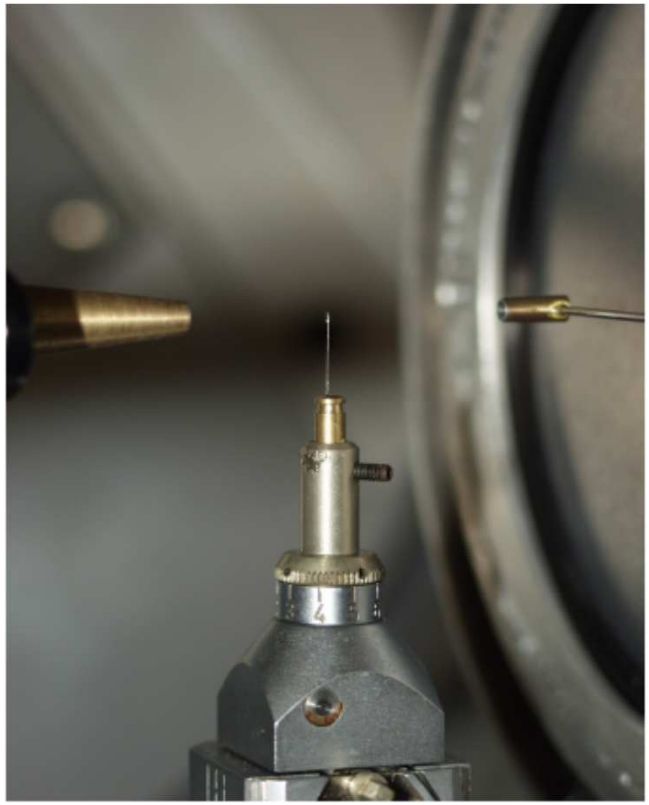
Real space

Reciprocal space

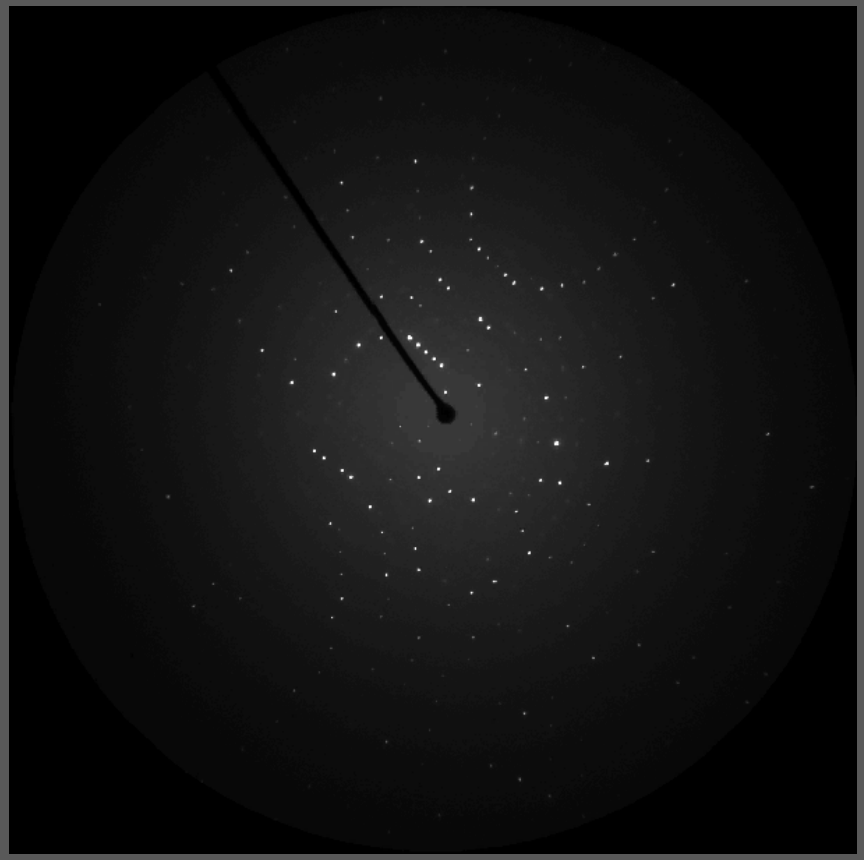
No direct back-transformation possible, because phase is lost!

Protein Crystallography (PX)

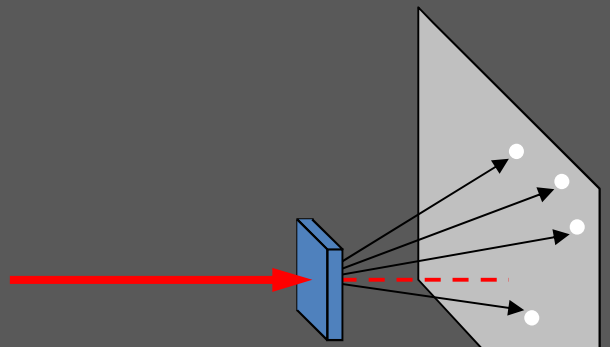
Tiny samples
Huge unit cells
Light elements
Sensitive to radiation damage → High brilliance required
High resolution necessary
- narrow energy band
- high degree of collimation

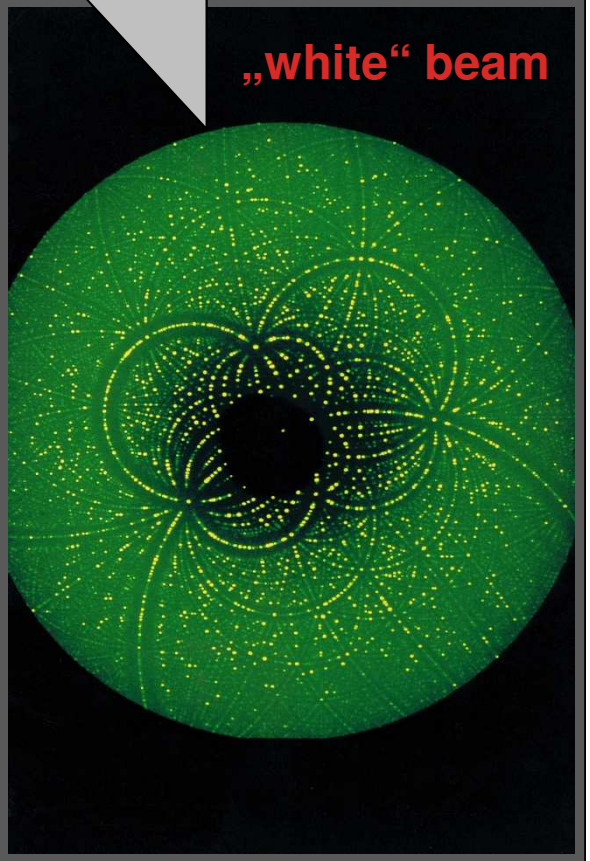


Protein Crystallography (PX)



Monochromatic beam



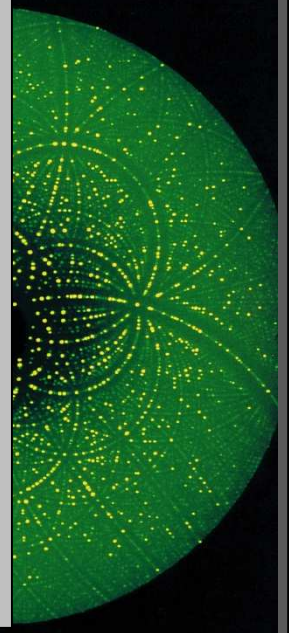


Protein crystal: Yeast Proteasome (50000 Atoms/unit cell)

Resolution 0.09 nm, mean position error 0.001 nm
Even Position of Hydrogene Atoms resolved!

Protein Crystallography (PX)

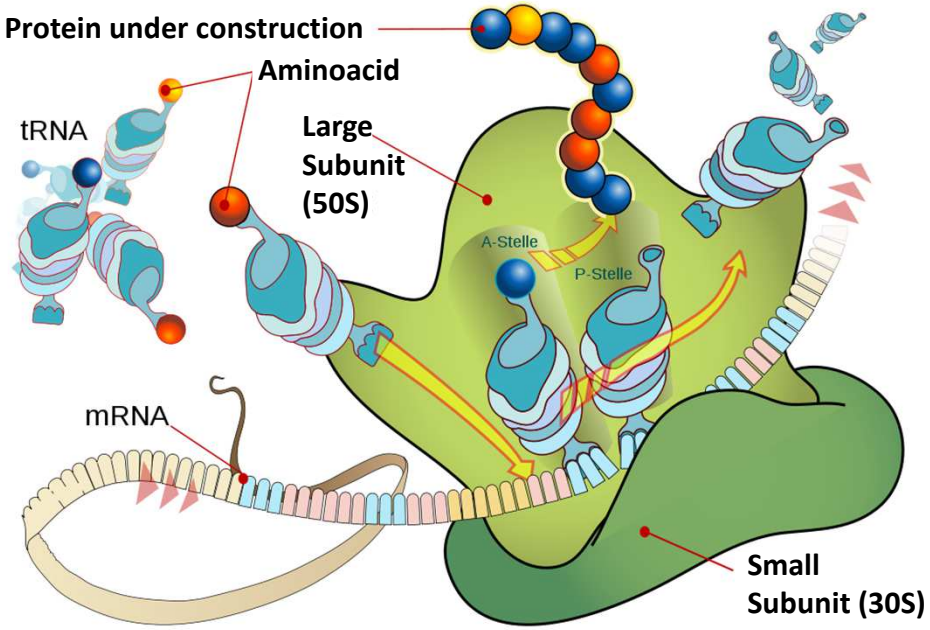
hite“ beam

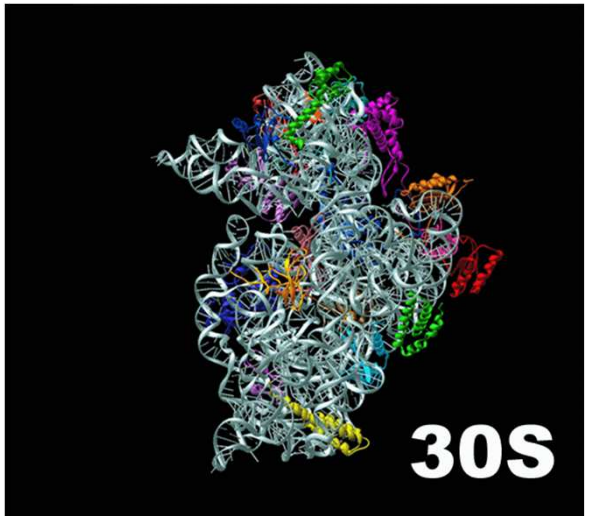


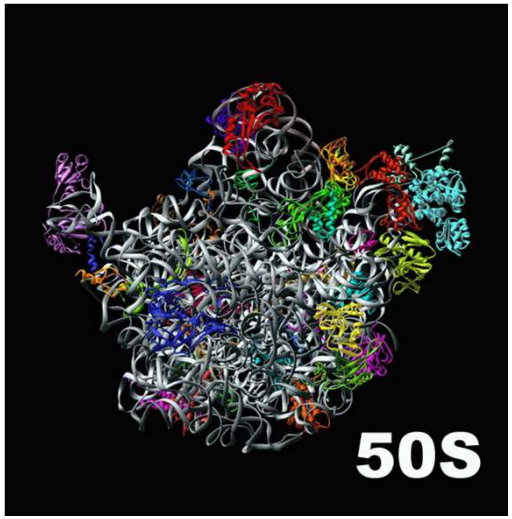
Protein

Resolution 0.09 nm, mean position error 0.001 nm
Even Position of Hydrogene Atoms resolved!

Revealing Structure and Dynamics of Ribosome







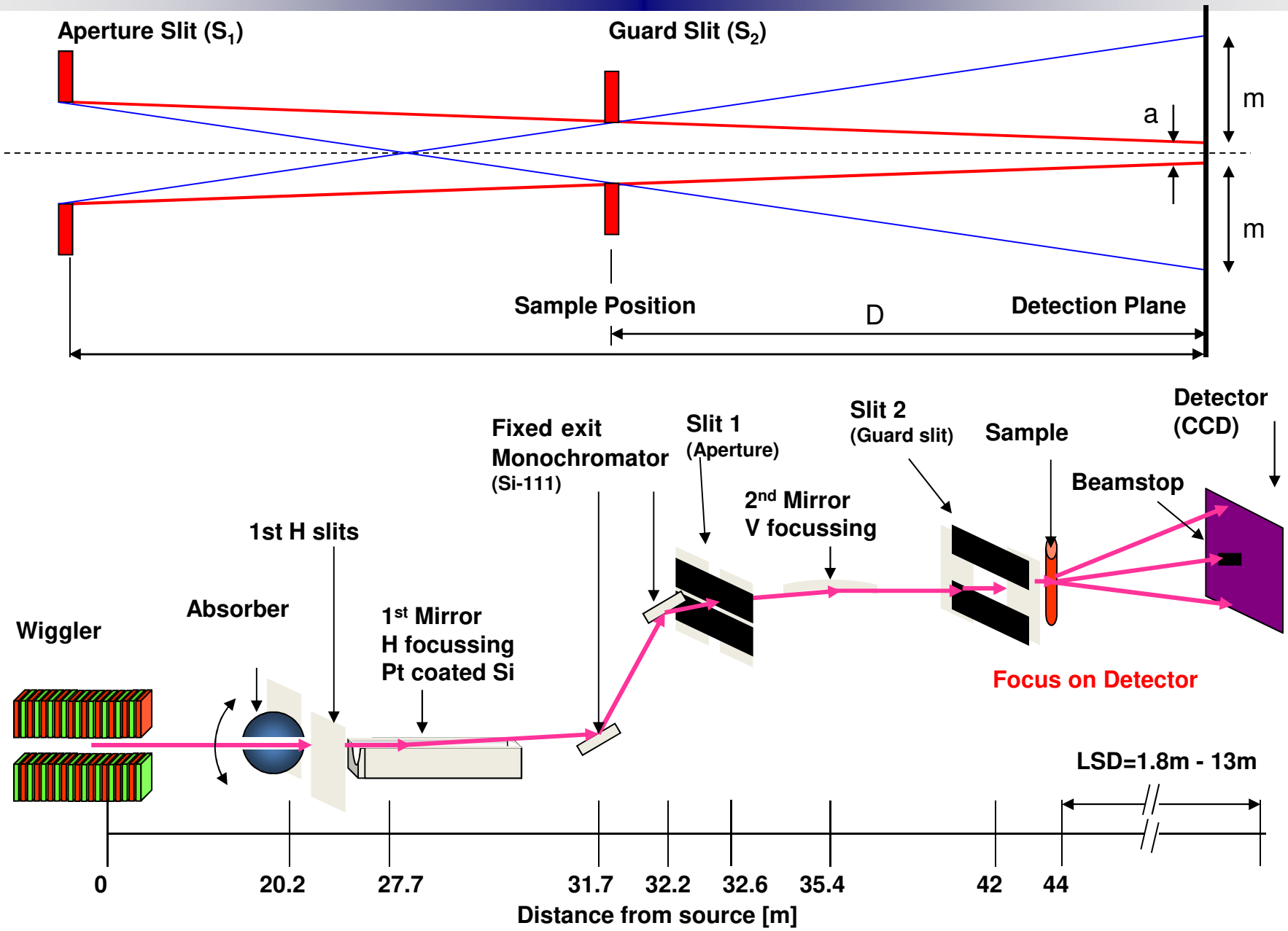
Ada Yonath:

- **Head of the MPG-work group „Structure of the Ribosome“ at DESY, 1986 - 2004**
- **Nobelprize Chemistry 2009**

With T. Steitz and V. Ramakrishna

Schlünzen, ..., Yonath, Cell, 102(2000)615

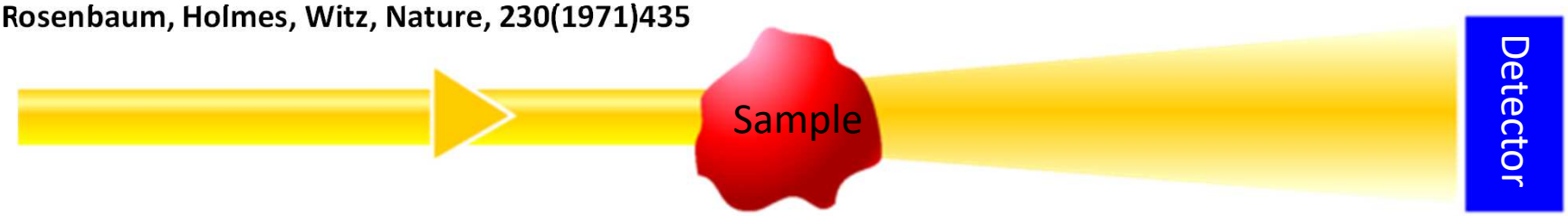
Layout of a SAXS Instrument

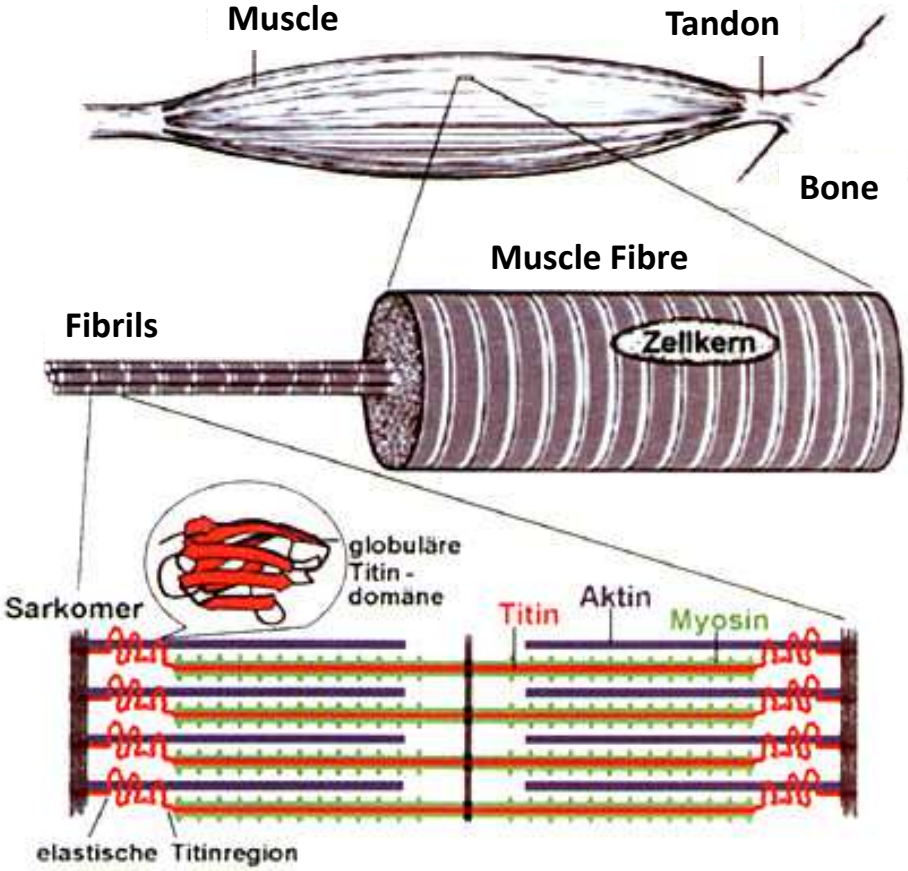


First Experiments Using Synchrotron Radiation (1964 – 1975)

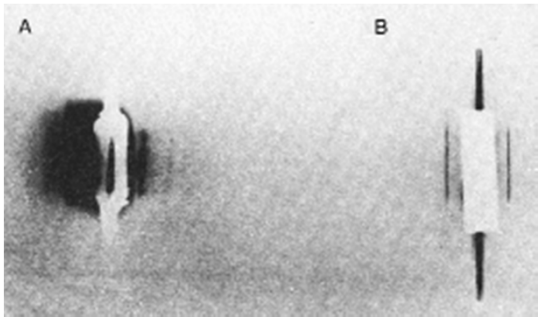
- **1970: Small angle X-ray scattering on muscle fibres**

Rosenbaum, Holmes, Witz, Nature, 230(1971)435

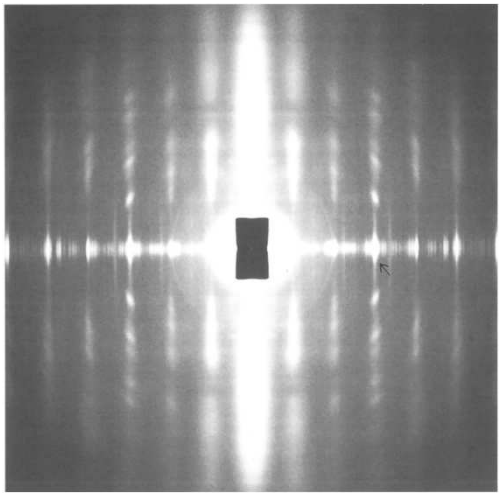




1970

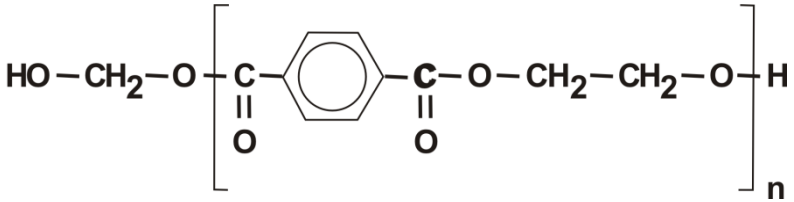


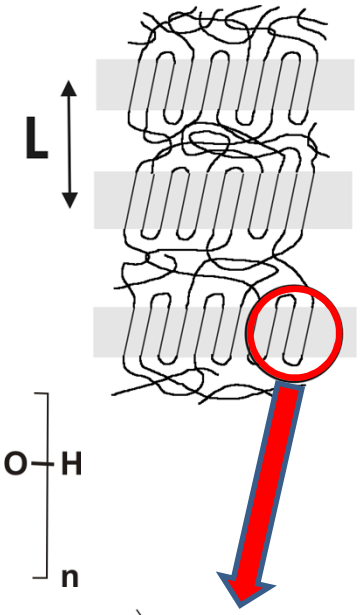
1996



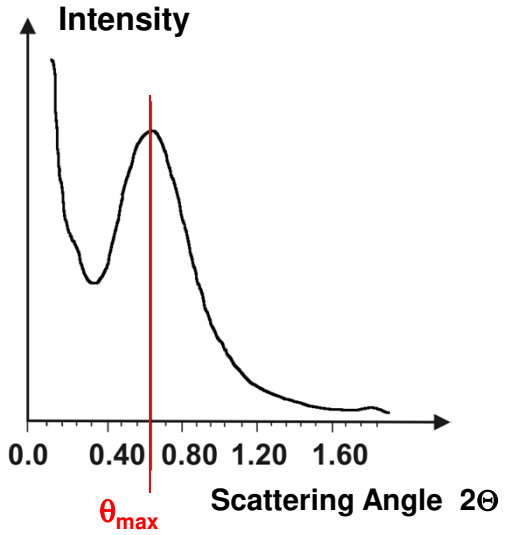
SAXS/WAXS at lamellar polymer systems

Example: Polyethylenterephtalate (PET)

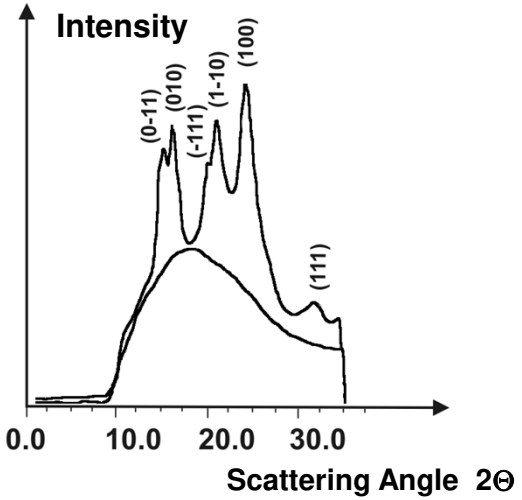




SAXS



WAXS



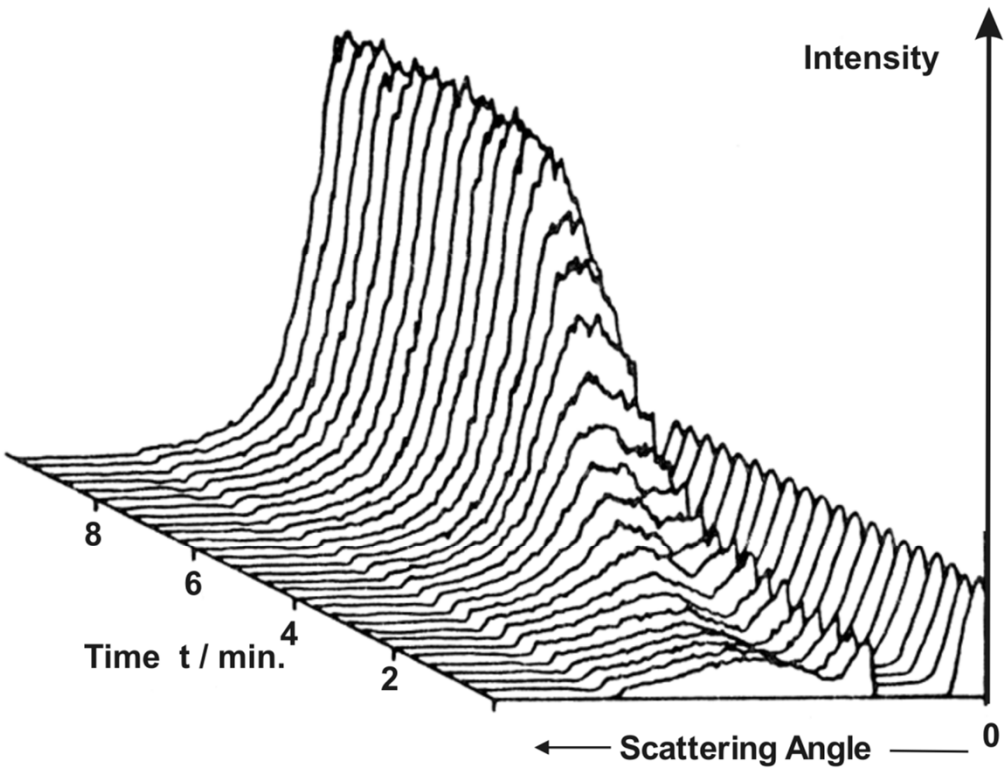
$$q_{\max} = \frac{4\pi}{\lambda} \cdot \sin(\theta_{\max}) \approx \frac{4\pi}{\lambda} \cdot \theta_{\max}$$

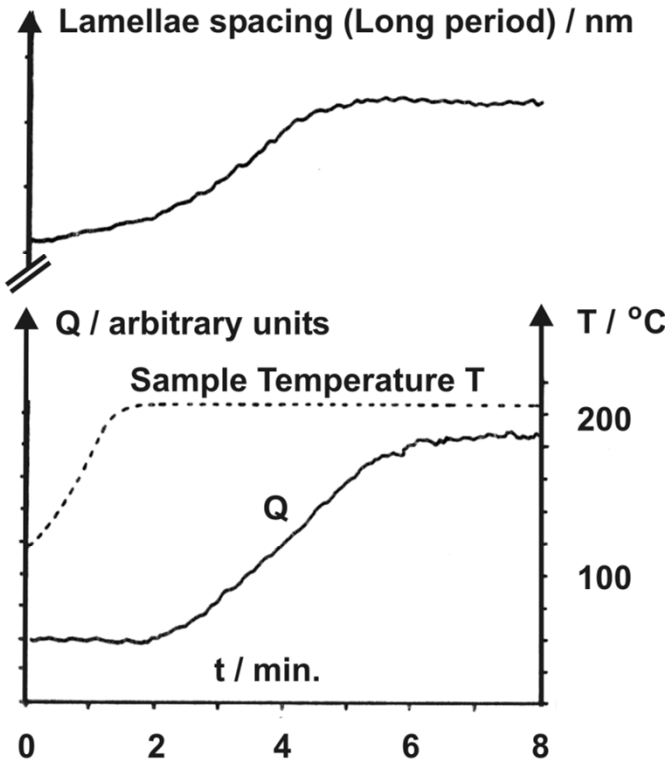
Long Period

$$L = \frac{2\pi}{q_{\max}}$$

$$Q = \int I(q) q^2 dq = 2\pi^2 \cdot \Phi \cdot (1 - \Phi) \cdot (\Delta\rho)^2$$

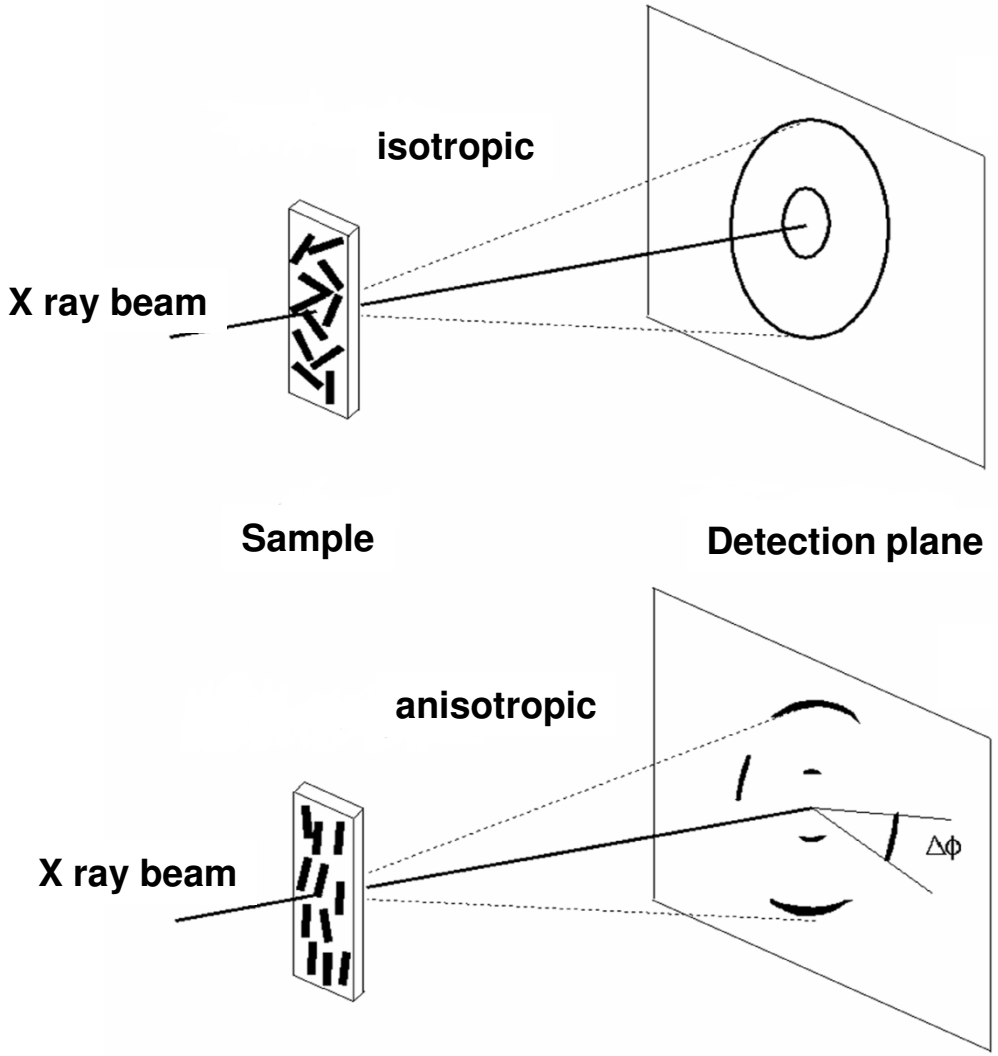
Time resolved in-situ SAXS: Recrystallisation of PET





Annealing of PET, previously crystallised at T_1=130°C,
recrystallisation at T_2=230°C

Scattering of Anisotropically Oriented materials

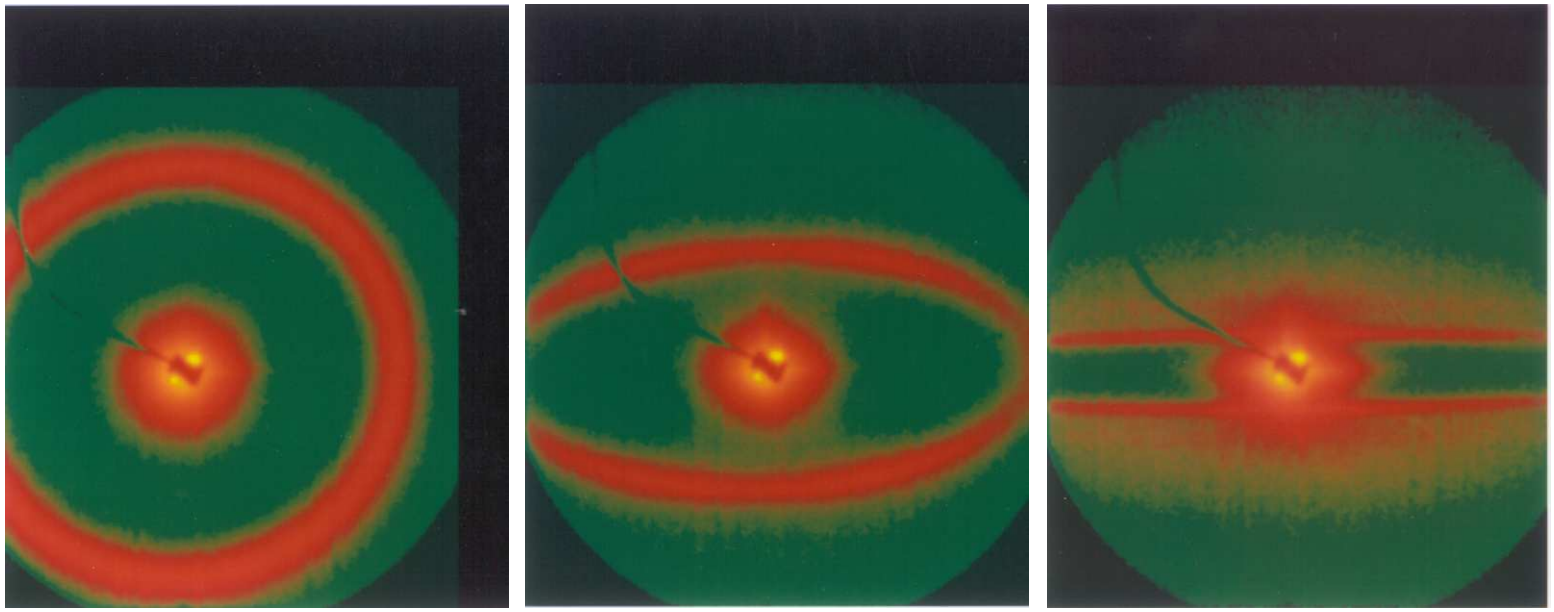


Deformation of an SBS-Triblock Copolymer (Thermoplastic Elastomer)

$$\lambda \equiv \frac{L_{final}}{L_{initial}} = 1$$

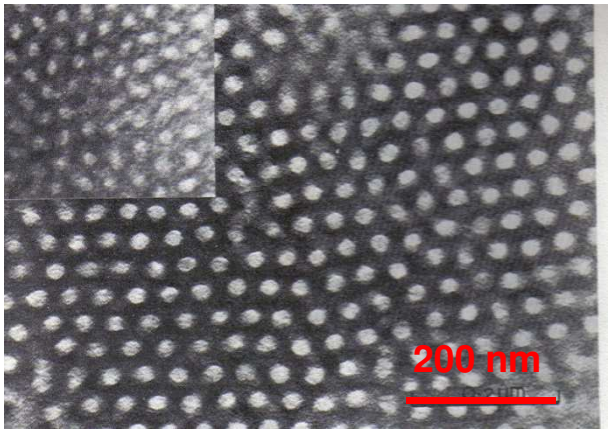
$\lambda = 2$

$\lambda = 6$



PS PB PS

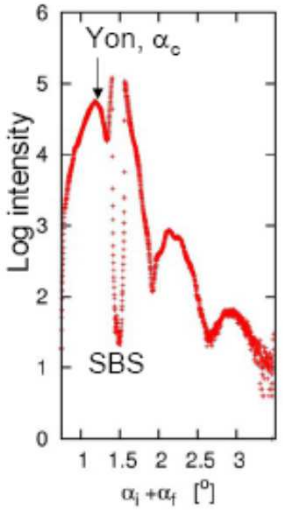
80% Polystyrene
20% Polybutadiene
→ PS cylinders in PB-Matrix

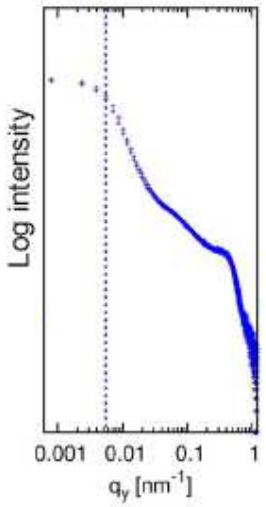


Electron micrograph

Grazing Incidence Small Angle Scattering (GISAXS)

q_z-dependence (in-plane) → height H





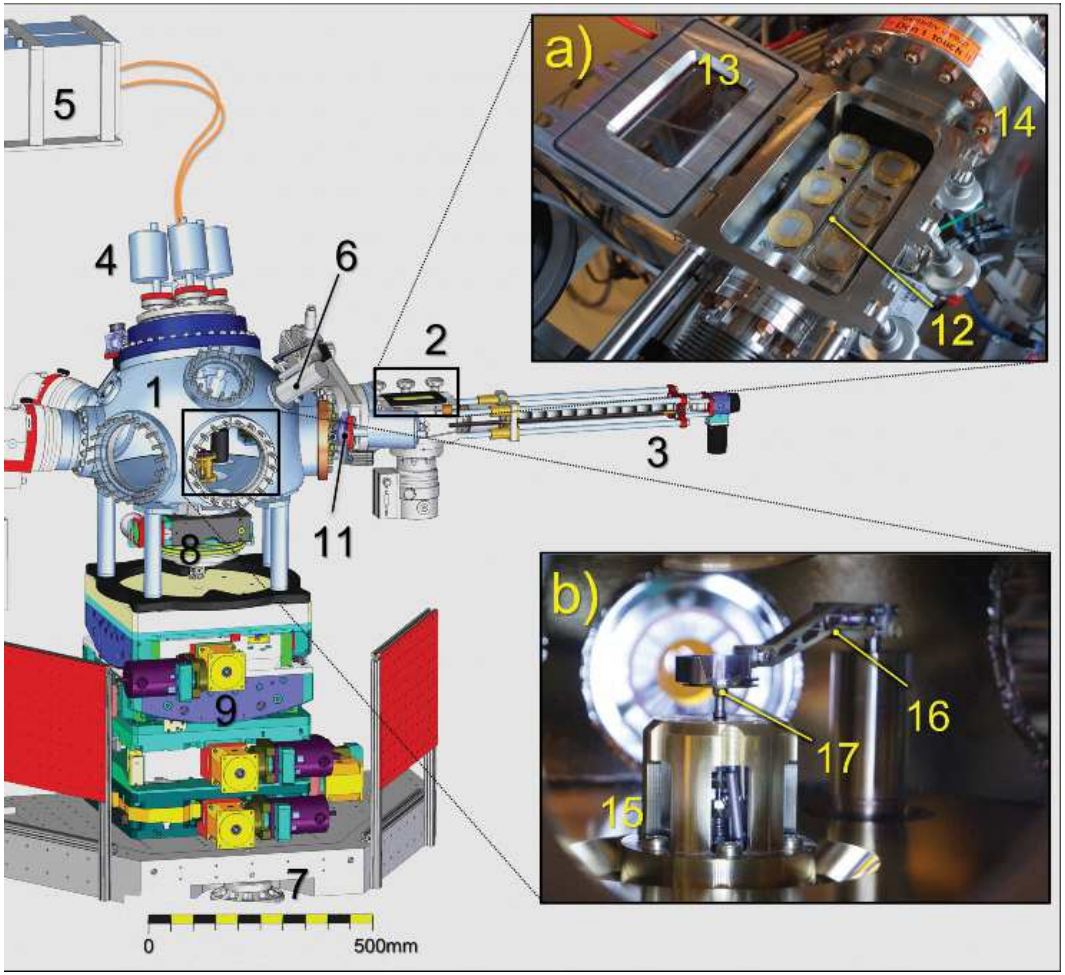
q_y-dependence (out-of-plane) → lateral distance D, lateral size R

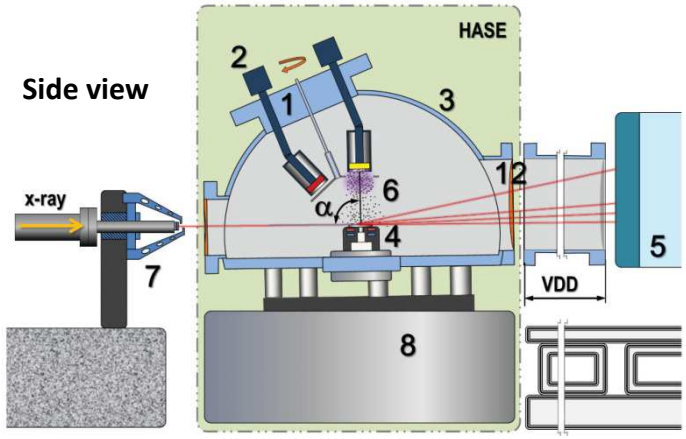
$q_z = 2\pi/\lambda \sin(\alpha_i+\alpha_f)$

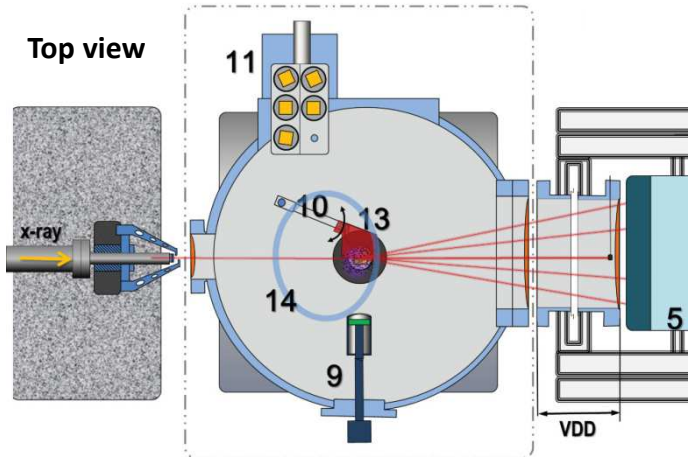
$q_y = 2\pi/\lambda \sin(2\theta)\cos(\alpha_f)$

Method only probes thin layer on surface

In-Situ Sputtering Equipment at PETRA III (P03)

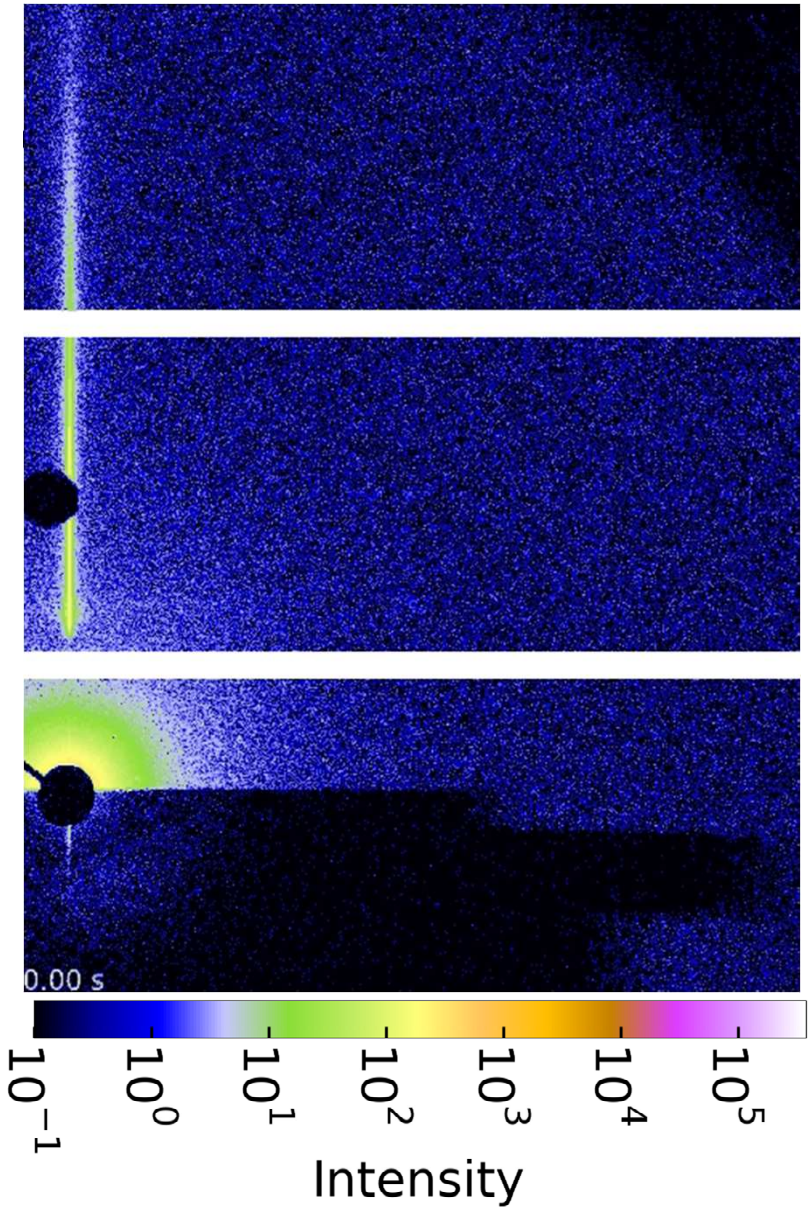




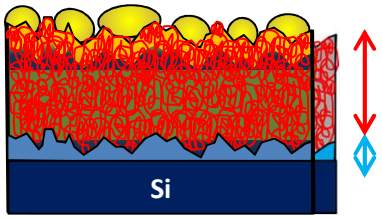


In-Situ Real-Time GISAXS Experiment

In-Situ Au sputtering on PS



The System:



δ(Au) ≈ (8 ± 1) nm

δ(PS) ≈ (91 ± 2) nm

δ(SiOx) ≈ (6 ± 2) nm

spin casted polystyrene thin film (M_w = 270 kDa) on acid cleaned silicon with correlated roughness

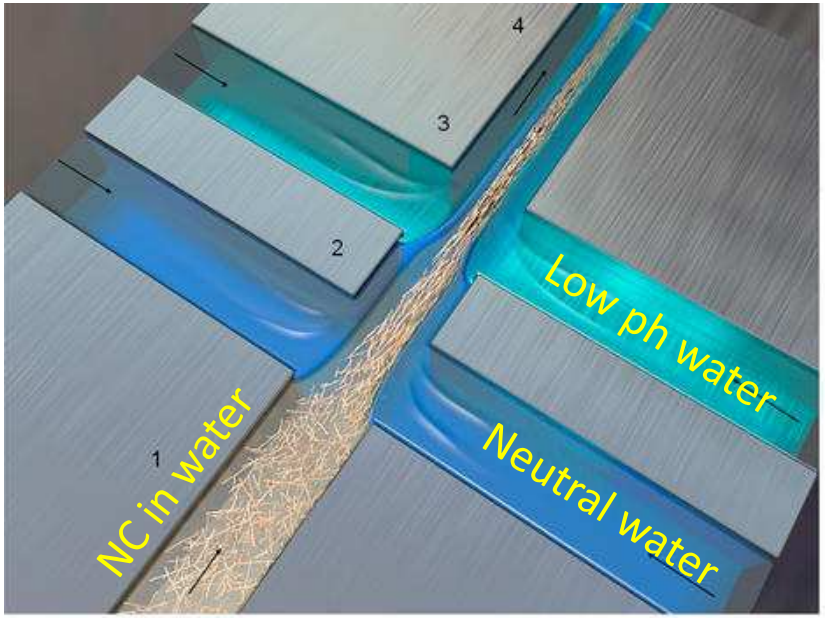
Nanostructural evolution *during* fabrication observed with subpicometer resolution

- wavelength = 0.1 nm
- D_{SD} = 1.8 m
- PILATUS 300K: Frame rate = 10 fps
- Deposition time: 1013 s
- Deposition rate: 0.0082 nm/s

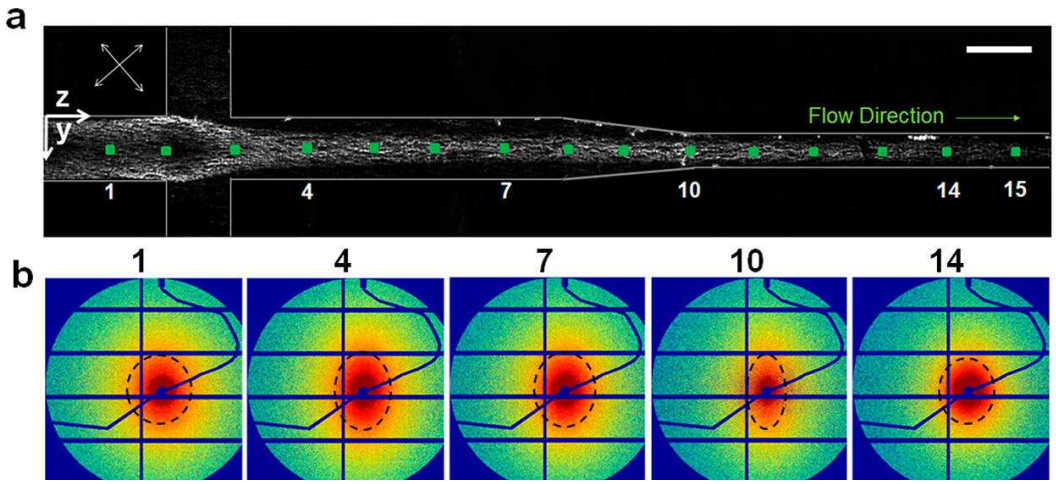
Schwartzkopf et al., ACS Appl. Mater. Interfaces 7, 13547 (2015).

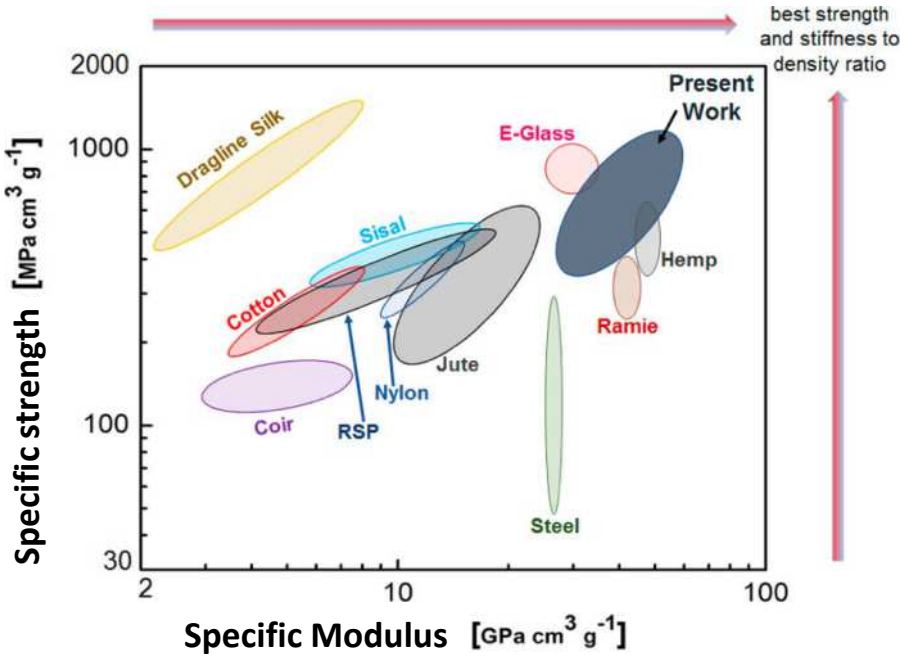
Microfluidics: Flow Assisted Assembly of Nanocellulose

Orientation of cellulose nano-fibrils by means of hydrodynamic focusing and pH reduction



Schematic illustration of the microfluidic setup

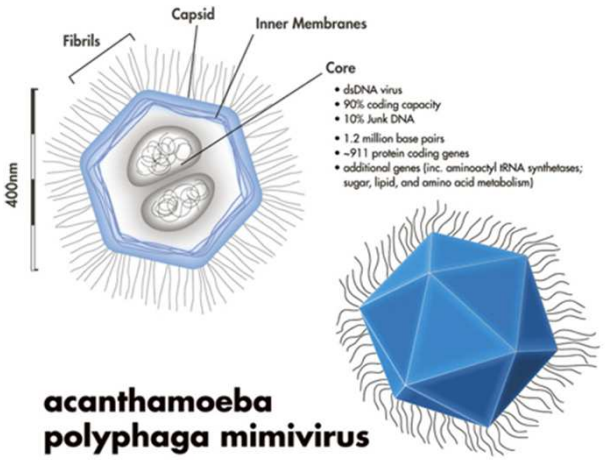


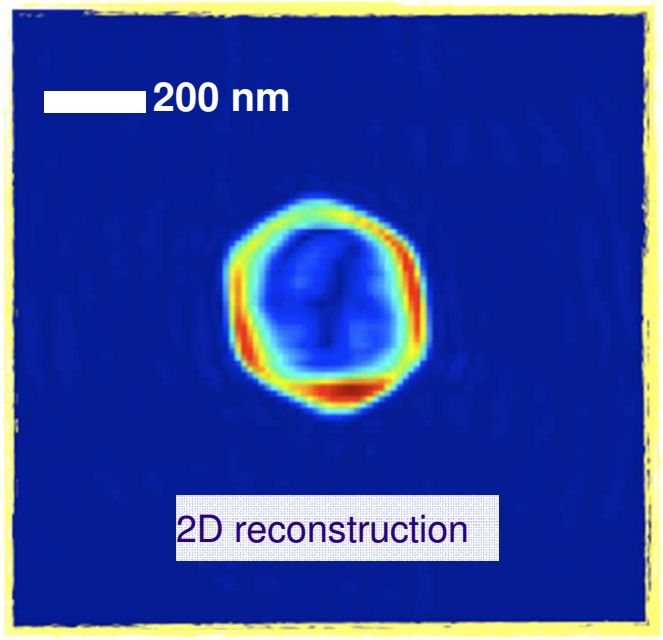


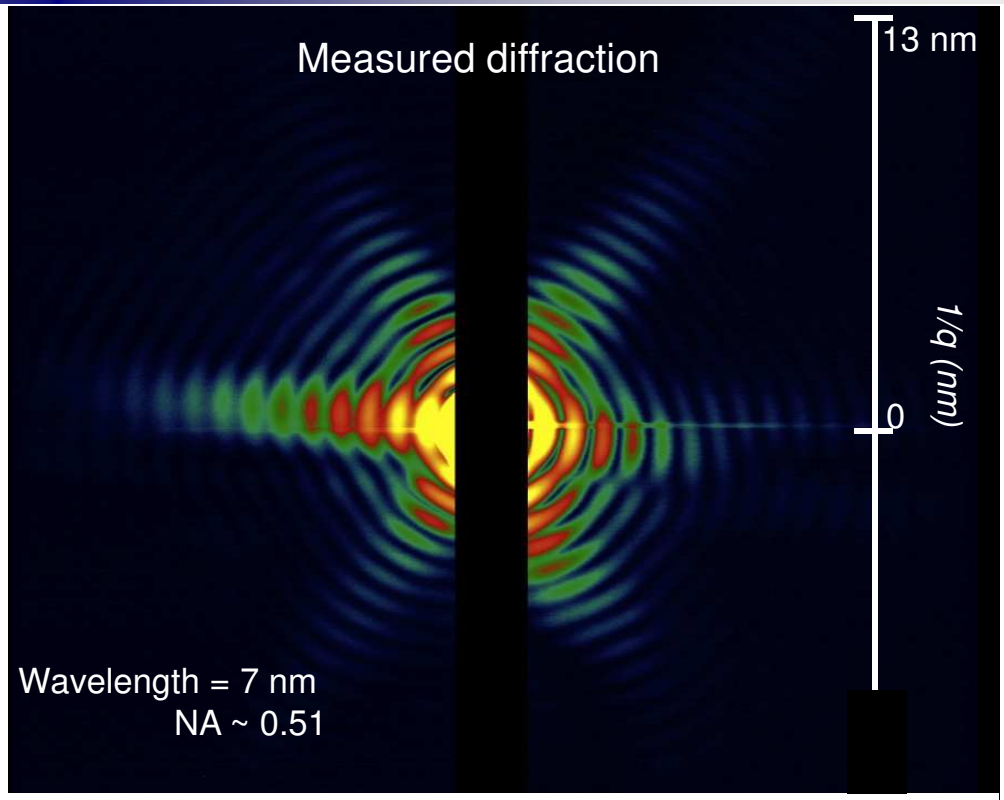
Nanocellulose (NC):
rods of crystalline cellulose,
length= 100 – 1000 nm, width= 3 – 10 nm

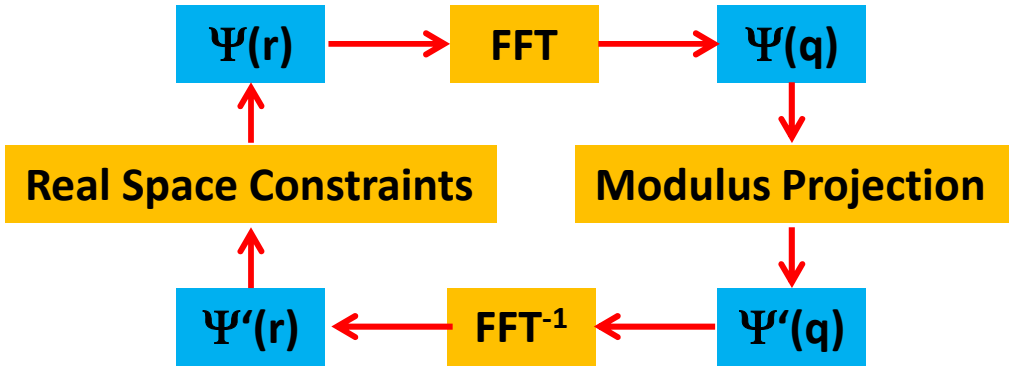
N. Mittal et. al., ACS Nano (2018)

Coherent Diffraction Imaging of a Mimivirus





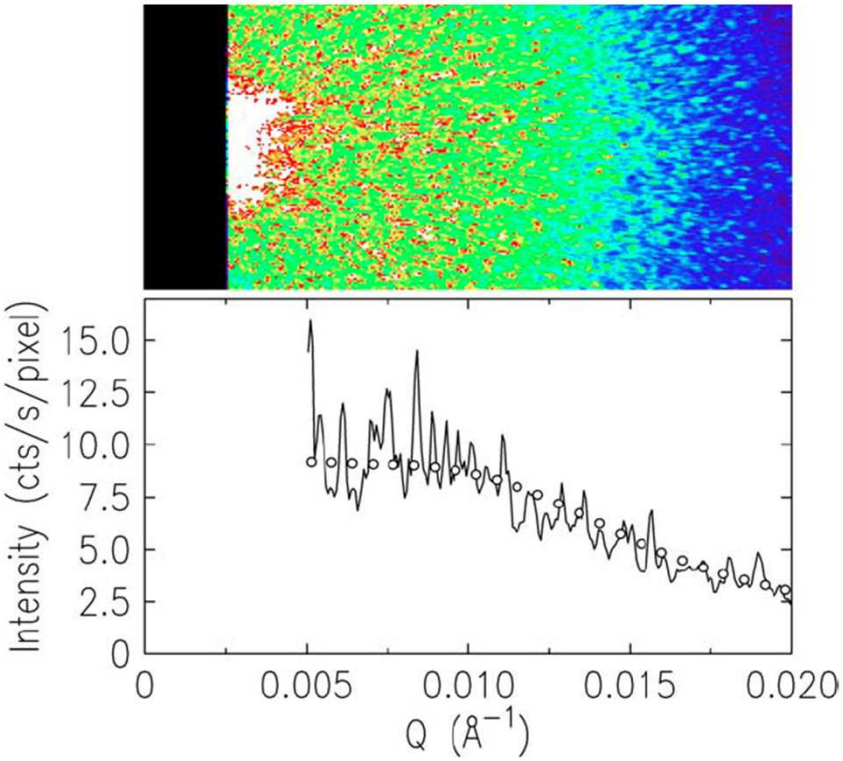




Samples: Uppsala University and CNRS, Aix-Marseille Université
FEL experiments: CFEL @ DESY, Uppsala, SLAC, MPMI

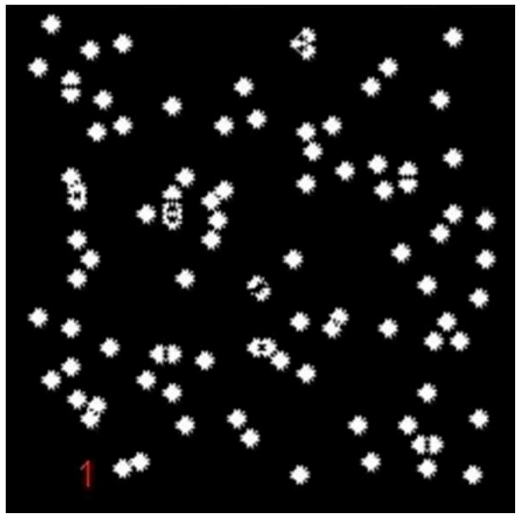
Chapman, Hajdu et al.

X-ray photon correlation spectroscopy (XPCS)

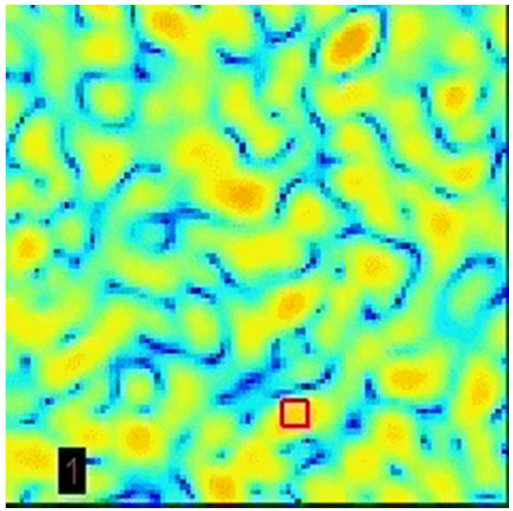


Diffraction of coherent light from a disordered sample leads to a ‘grainy’ diffraction pattern (speckles)

Simulation of Brownian motion



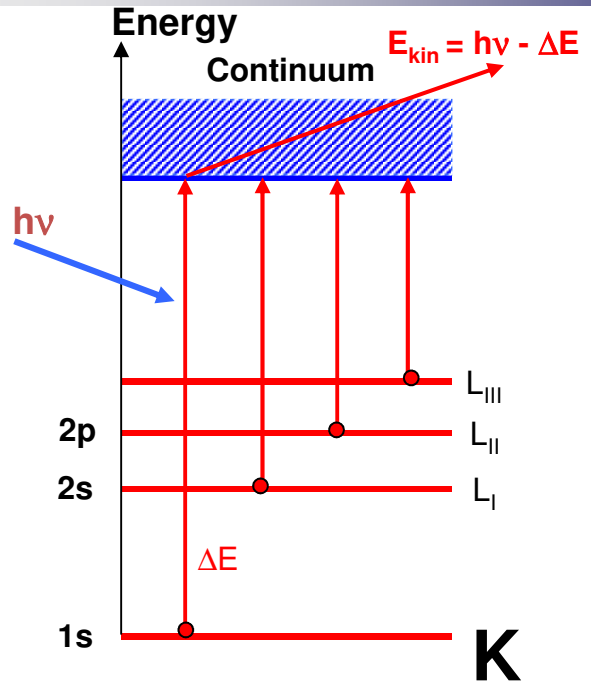
Real space

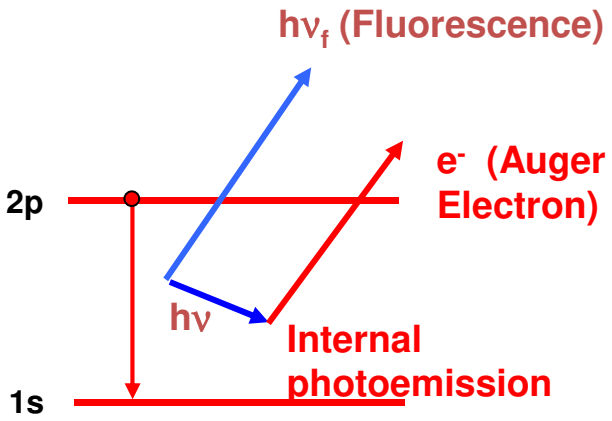


Diffraction pattern

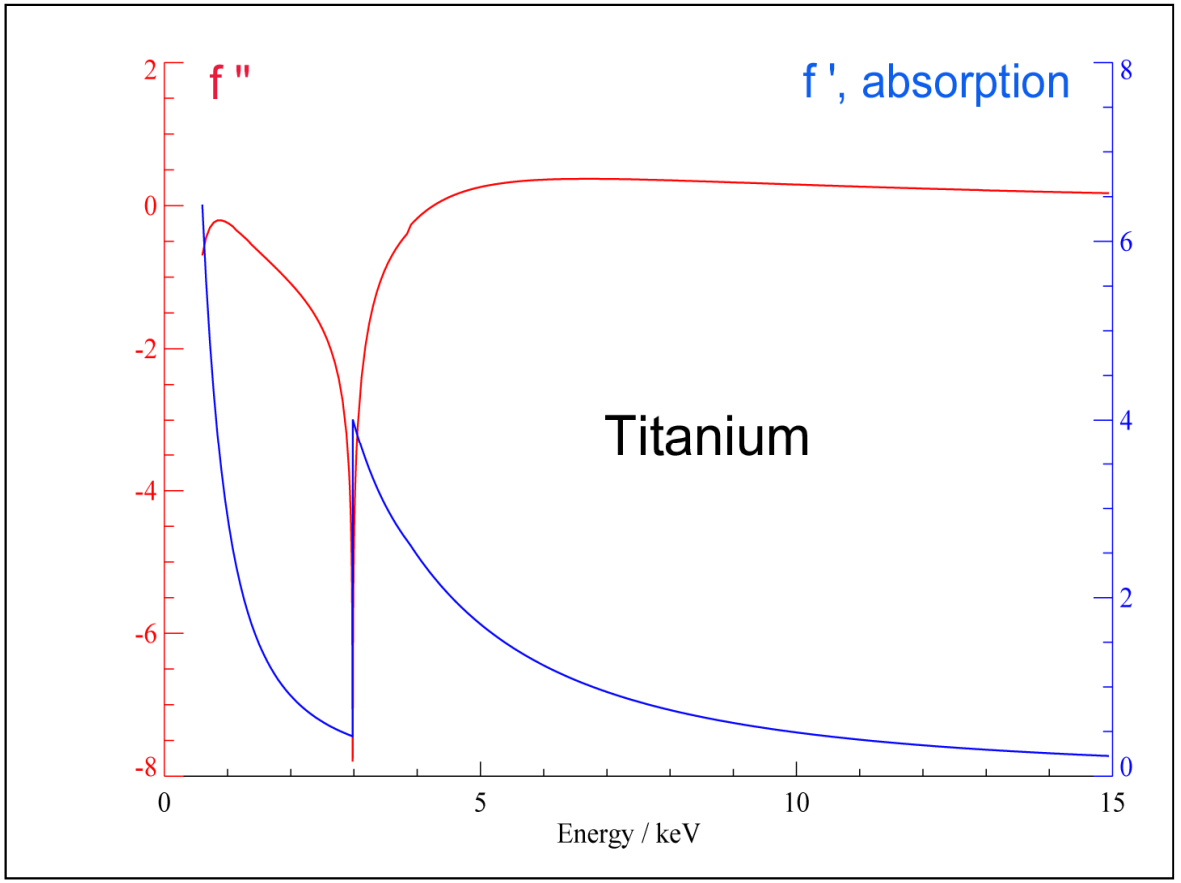
Scientific Experiments
Spectroscopy

Basics of X-ray Spectroscopy





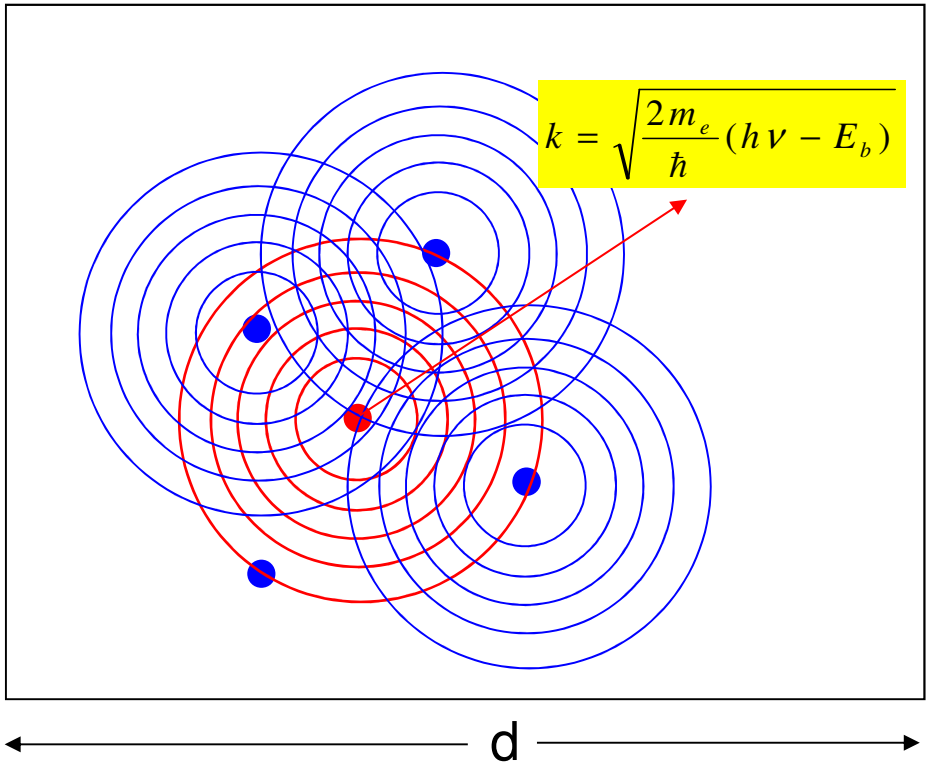
X-Ray Absorption Edges (example Titanium K-Edge)



$$f(s,E) = f_0 + f'(E) + i\,f''(E)$$

Atomic scattering Amplitude

X-Ray Absorption Spectroscopy (XAS)



Linear absorption coefficient μ

$$I = I_0 \cdot e^{-\mu d}$$

Detected Signal: Absorption or Fluorescence as function of energy of incident radiation

Photoionisation of a K-electron in the „red“ ad-atom →

Free electron: $E_{kin} = h\nu - E_{binding}$
→ Electron Wave with wavevector

$$k = \sqrt{\frac{2m_e}{\hbar}E_{kin}}$$

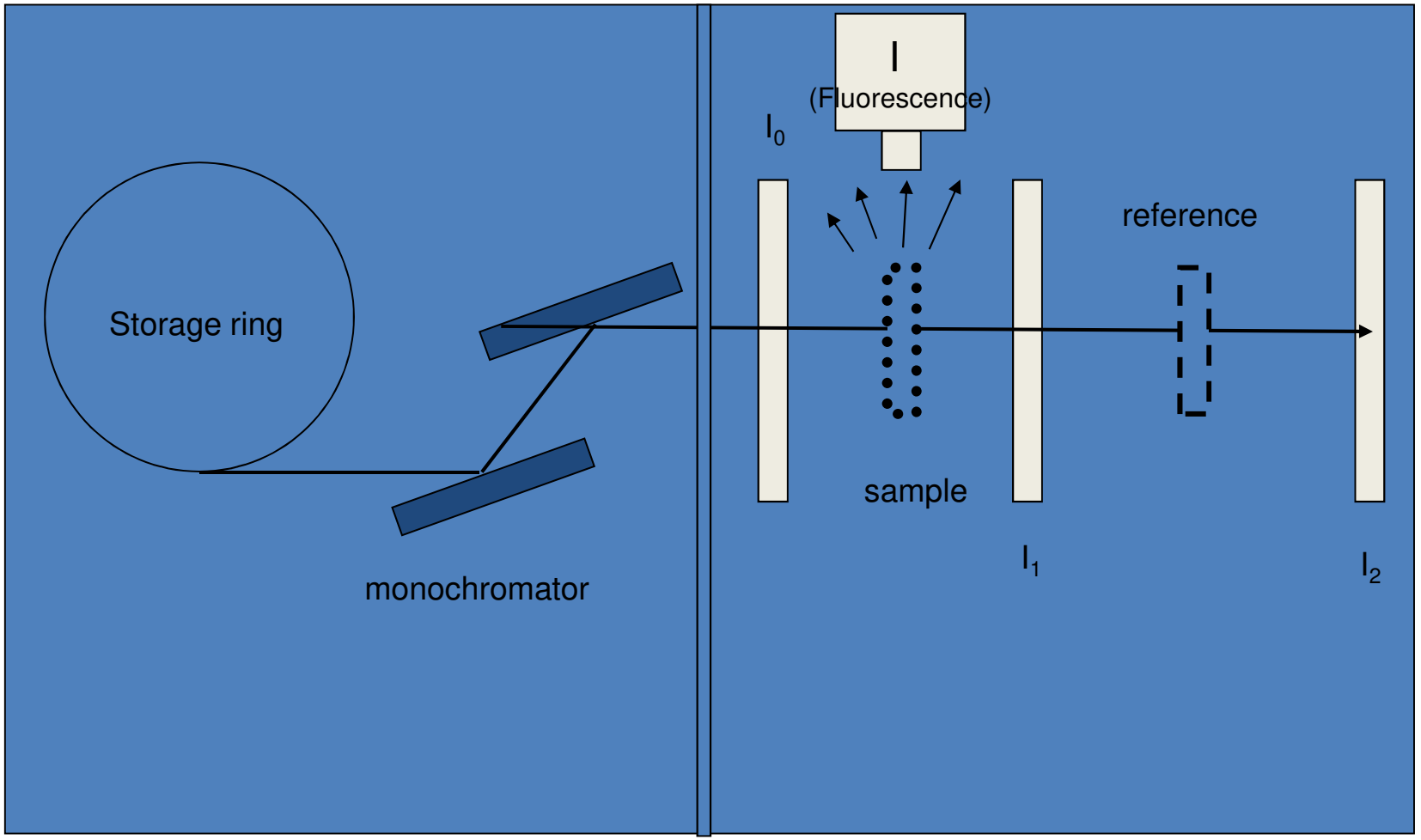
Fermis „Golden Rule“

$$\mu \propto |\langle\Phi_f| H |\Phi_i\rangle|^2 \cdot \delta(E_f - E_i - \hbar\omega)$$

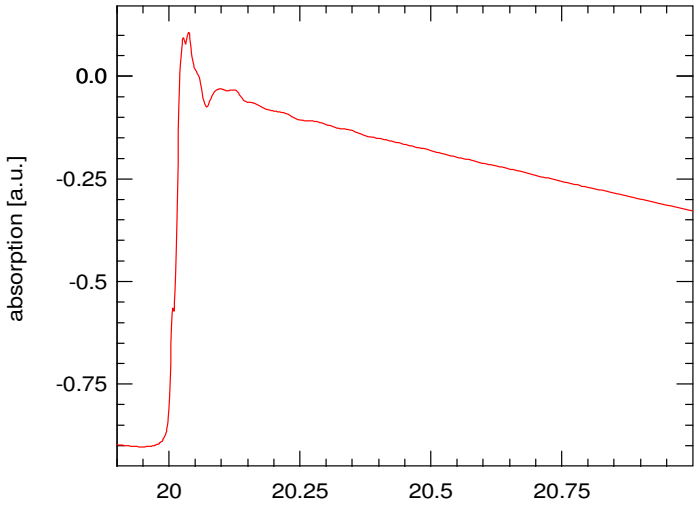
Initial state

final state $\Phi_f = \Phi_{outgoing} + \Phi_{backscattered}$

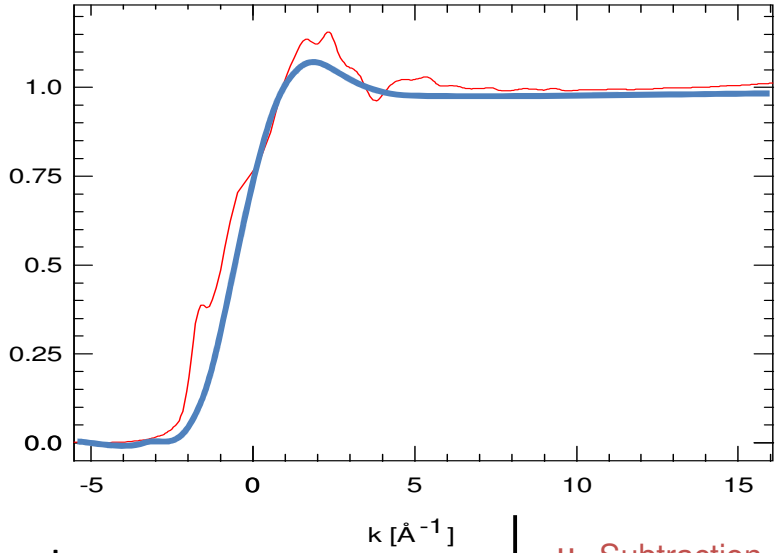
X-Ray Absorption Spectroscopy Experiment Setup



X-Ray Absorption Spectroscopy (EXAFS)

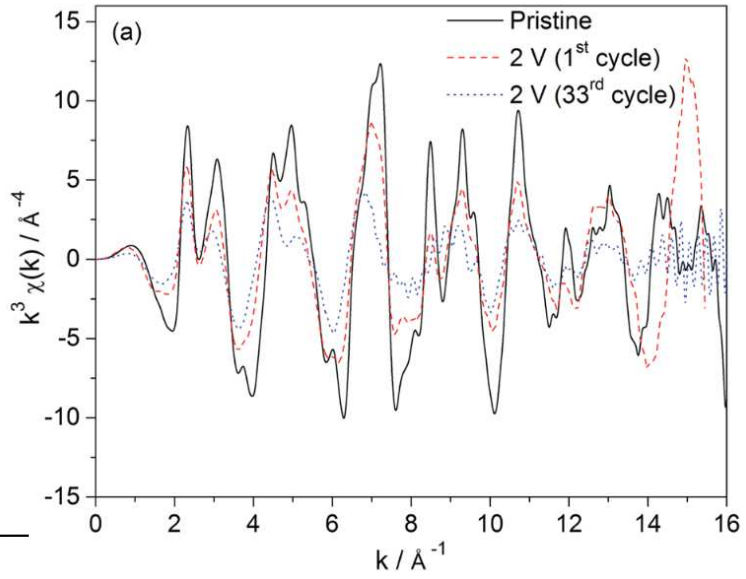


Energy calibration
Background subtraction
Normalization
E to k conversion



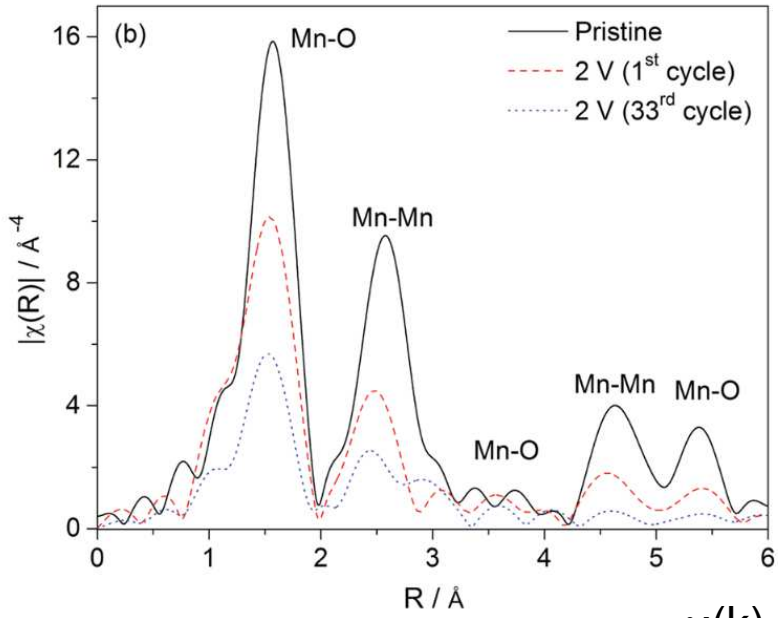
μ_0 Subtraction

Li_2MnO_3 in a battery



Fourier-Transformation

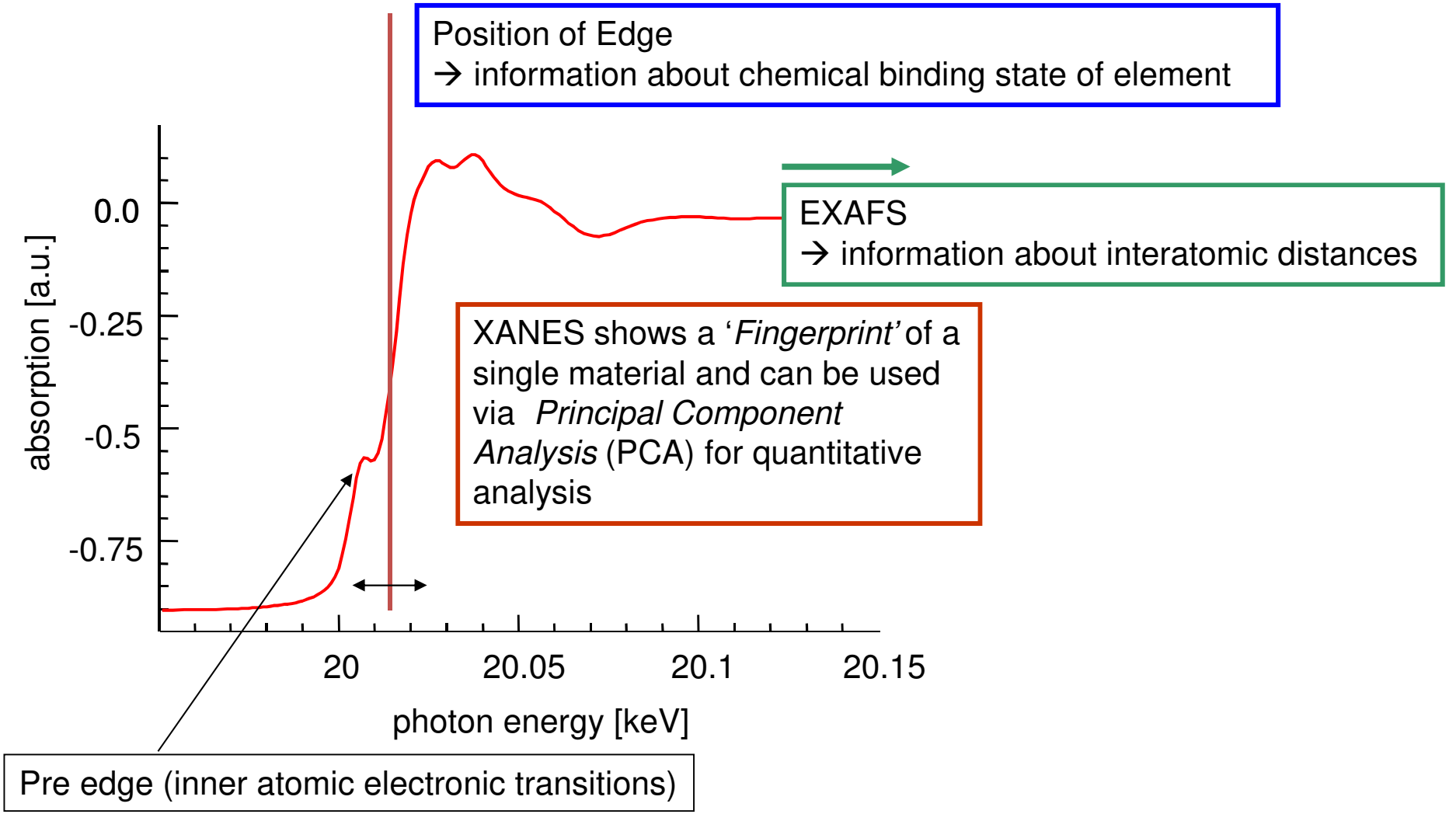
$\chi(k)$



$$\chi(k) = \frac{\mu(k) - \mu_0(k)}{\mu_0(k)}$$

Rana et. al., Adv. Energy Mat., 2014

Near Edge X-Ray Absorption Spectroscopy (XANES)

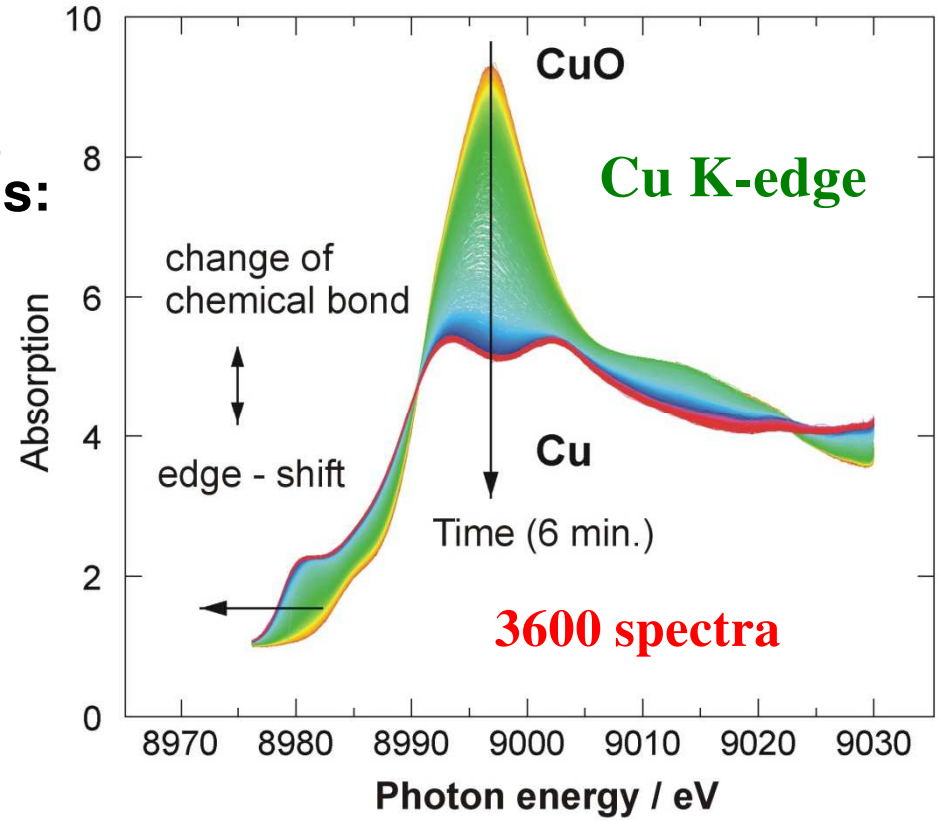


XAS: In-Situ Time Resolved Experiment

Instrumental development: QEXAFS (piezo scanning)
Study of solid state transformations in catalysis

Activation of a $CuO/ZnO/Al_2O_3$ catalyst for methanol synthesis:

- **In-situ reduction in H_2 gas flow at elevated temperatures**
- **50 ms time resolution**
- **Detailed analysis of transient chemistry (here Cu_2O)**
- **Experiment done at BW1**



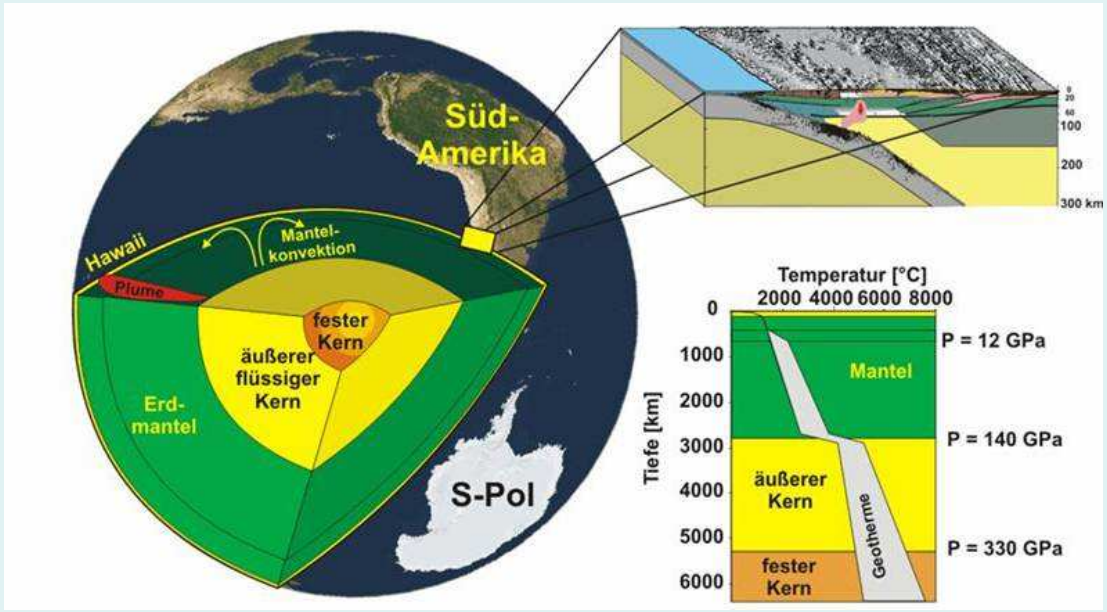
J.-D. Grunwaldt et al., J. Phys. Chem. B **105**, 5161 (2001)

Geo Science Experiments (High p, High T)

Large volume press of GFZ (Geo Research Center Potsdam) at DESY

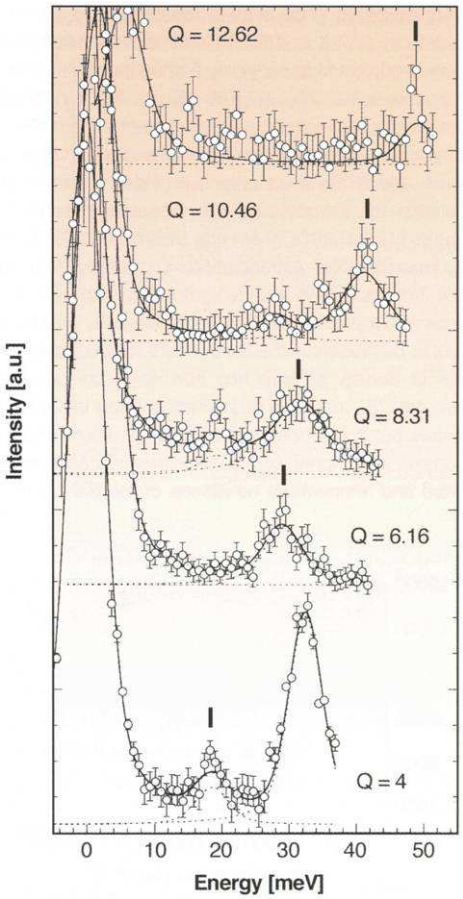
1750t press for in situ studies of large sample volumes.
Maximum pressure: ~ 25 GPa
Temperature: > 2000 K

Study of material under the conditions of the earths lower mantle.

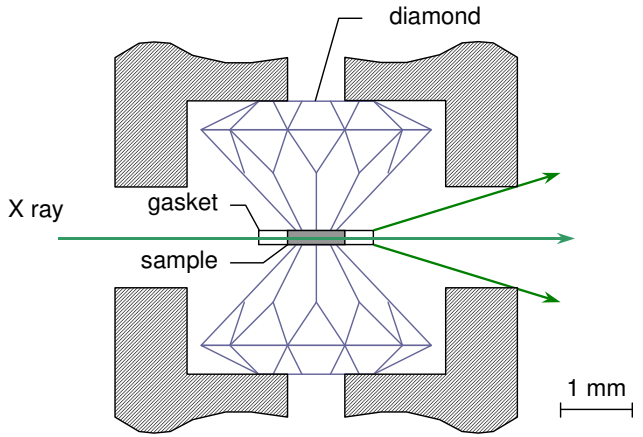


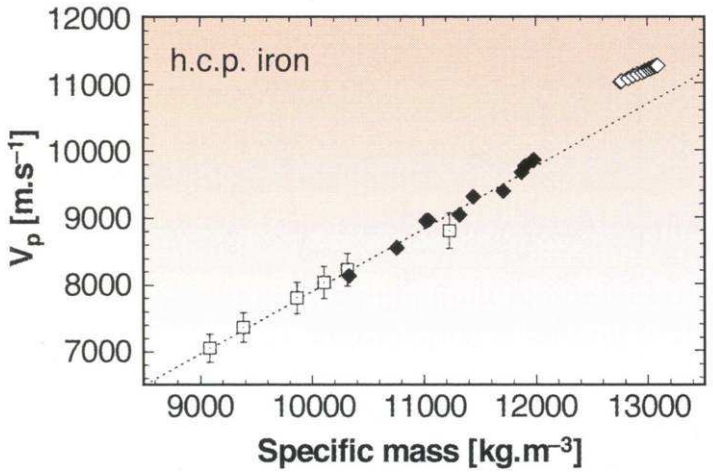
Inelastic X-ray scattering under High Pressure

Speed of sound of Fe under pressure (19 to 110 GPa)



P=28GPa

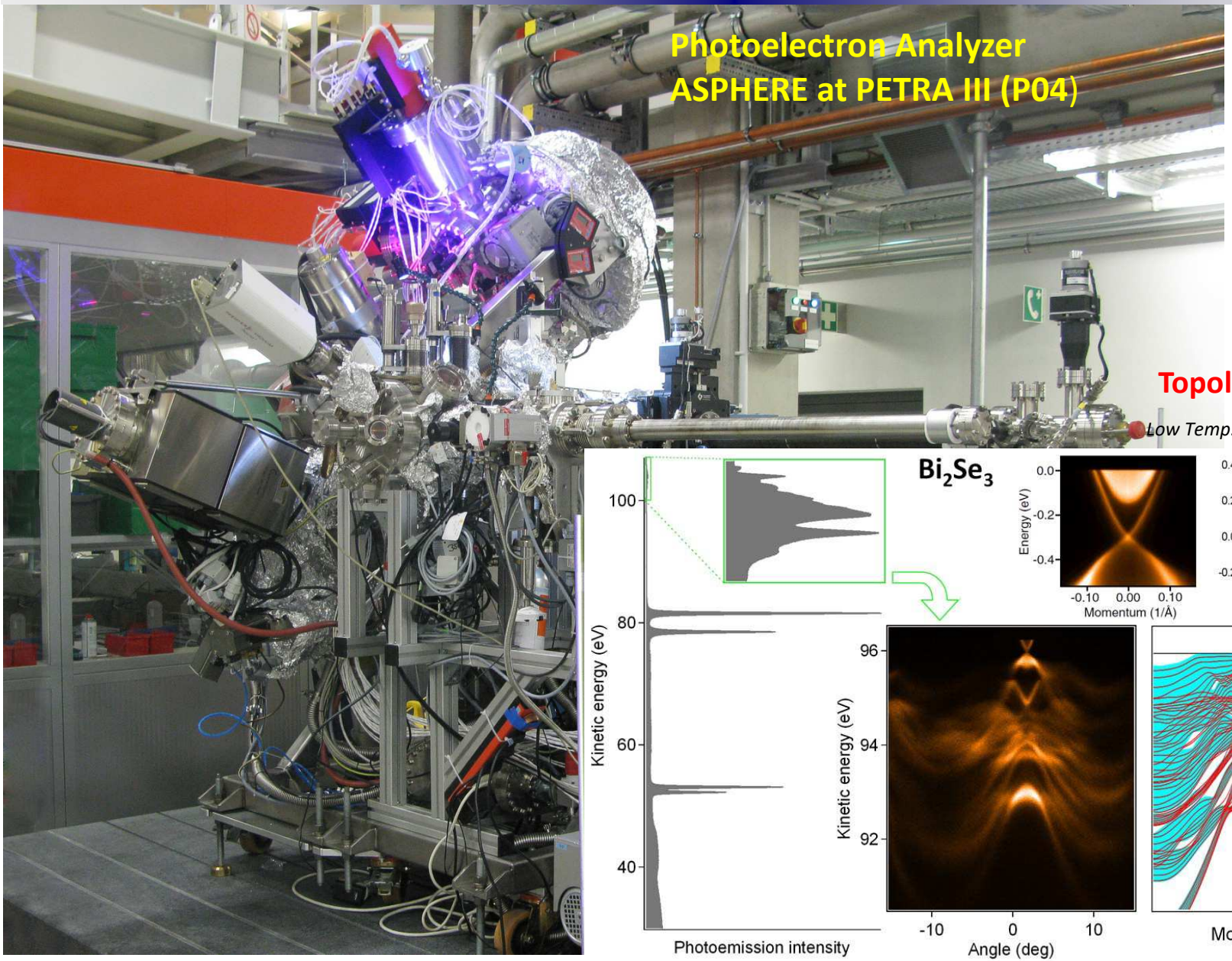




Determining the acoustic phonon dispersion E(Q) at a given pressure by means of inelastic X-ray scattering

G. Fiquet et al., Science (2000)

Angular Resolved Photoelectron Spectroscopy (ARPES)



Topological Insulator

Low Temp. Phys. **40**, 286-296 (2014)

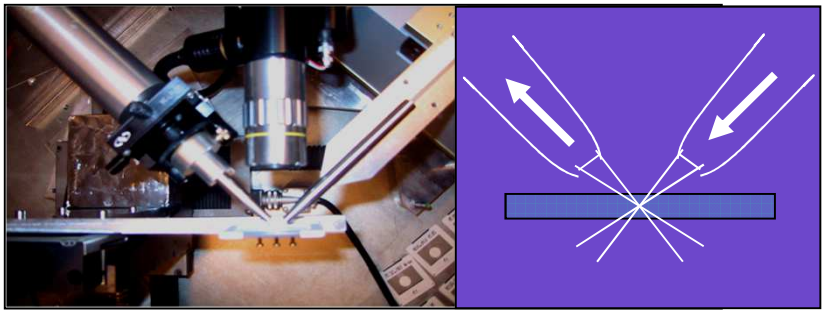
Scientific Experiments
Imaging

3D imaging with confocal X-ray Microfluorescence

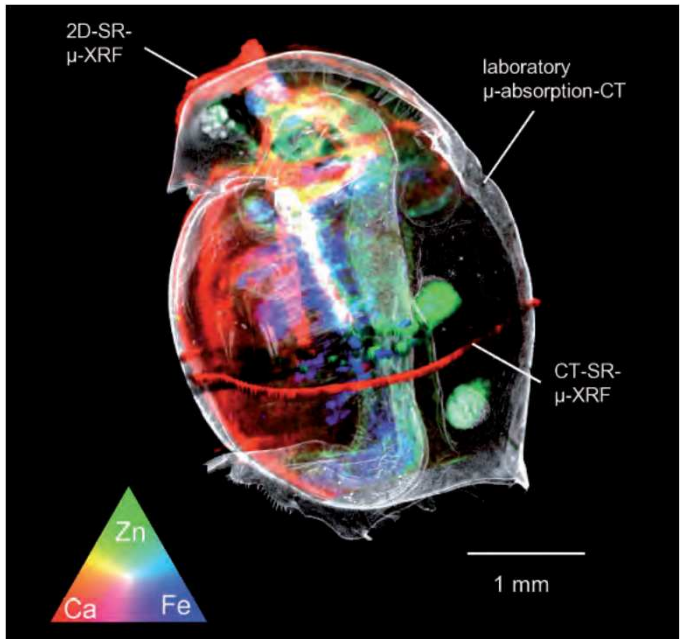
Micro X-ray Fluorescence on Daphnia Magna (water flea)

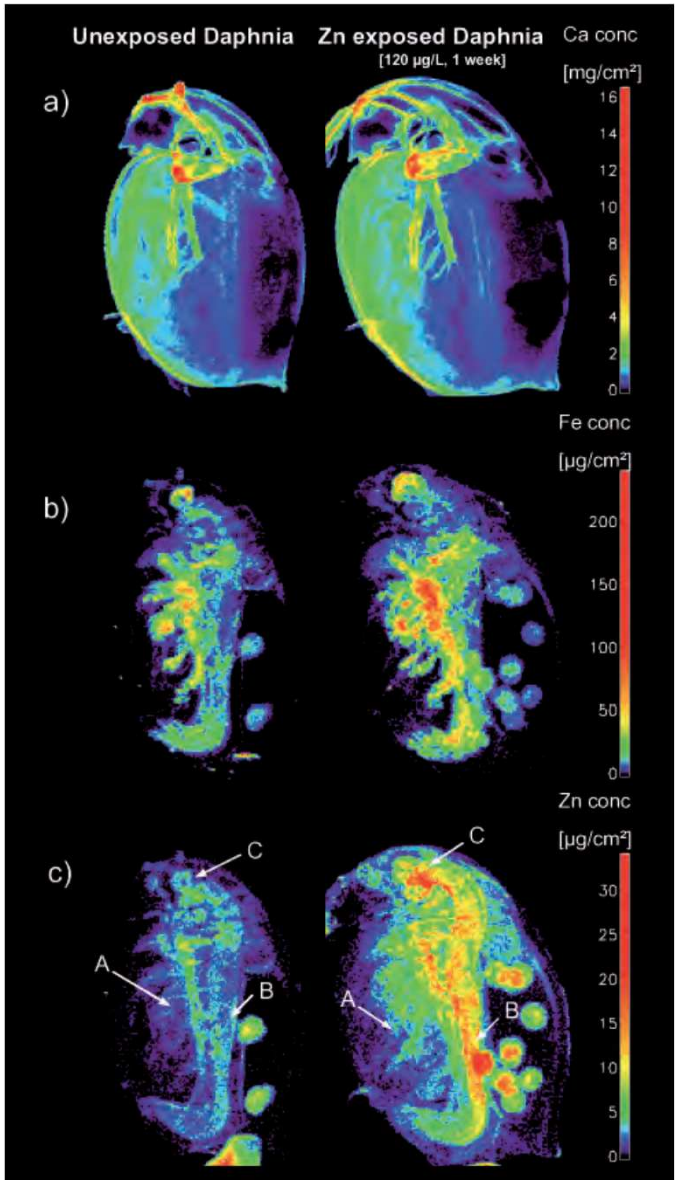
Principle

DORIS III beamline L



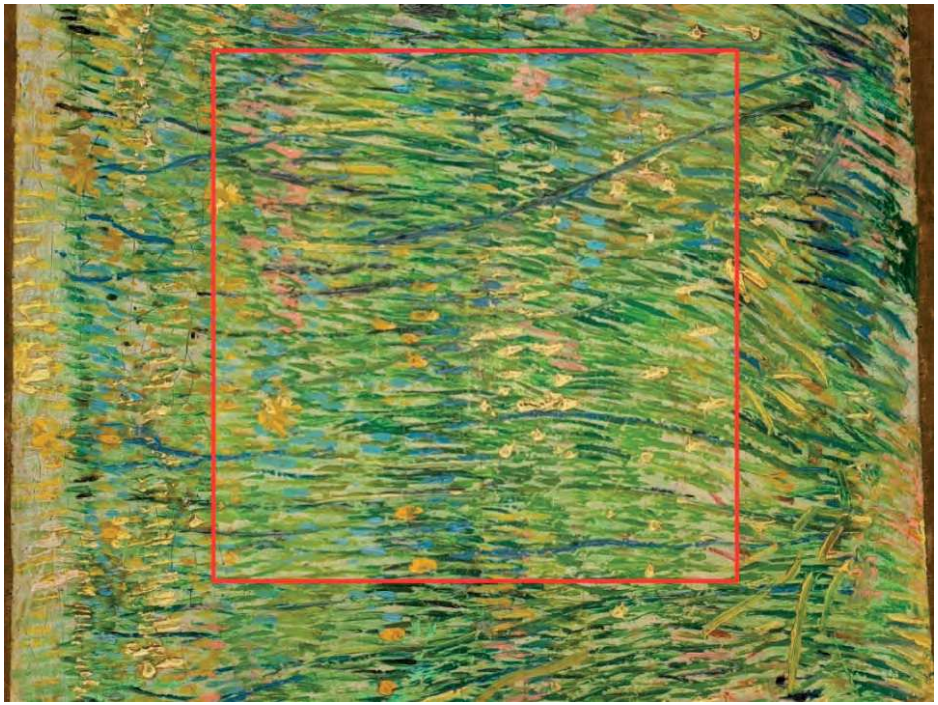
Focus 10 µm



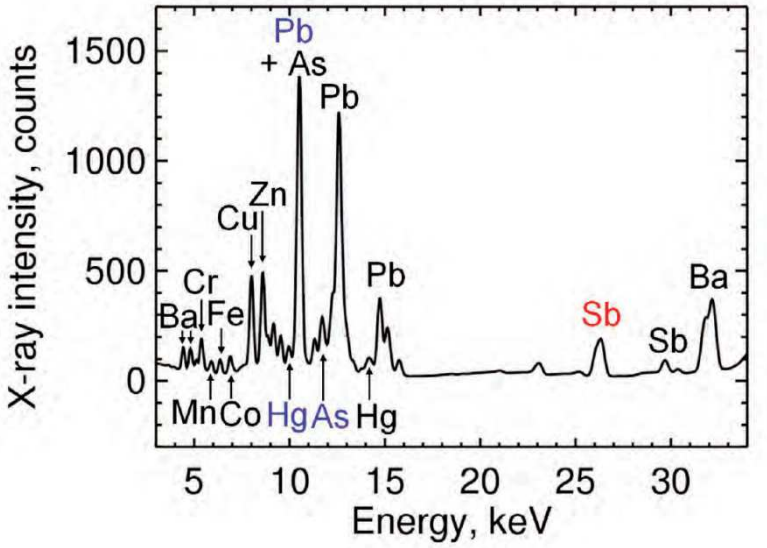


Raster Scanning X-ray Fluorescence

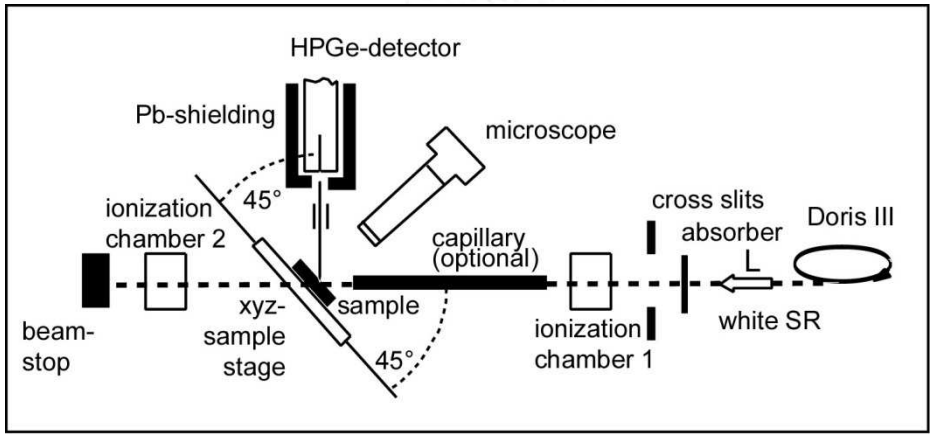
Vincent van Gogh: Meadow with flowers

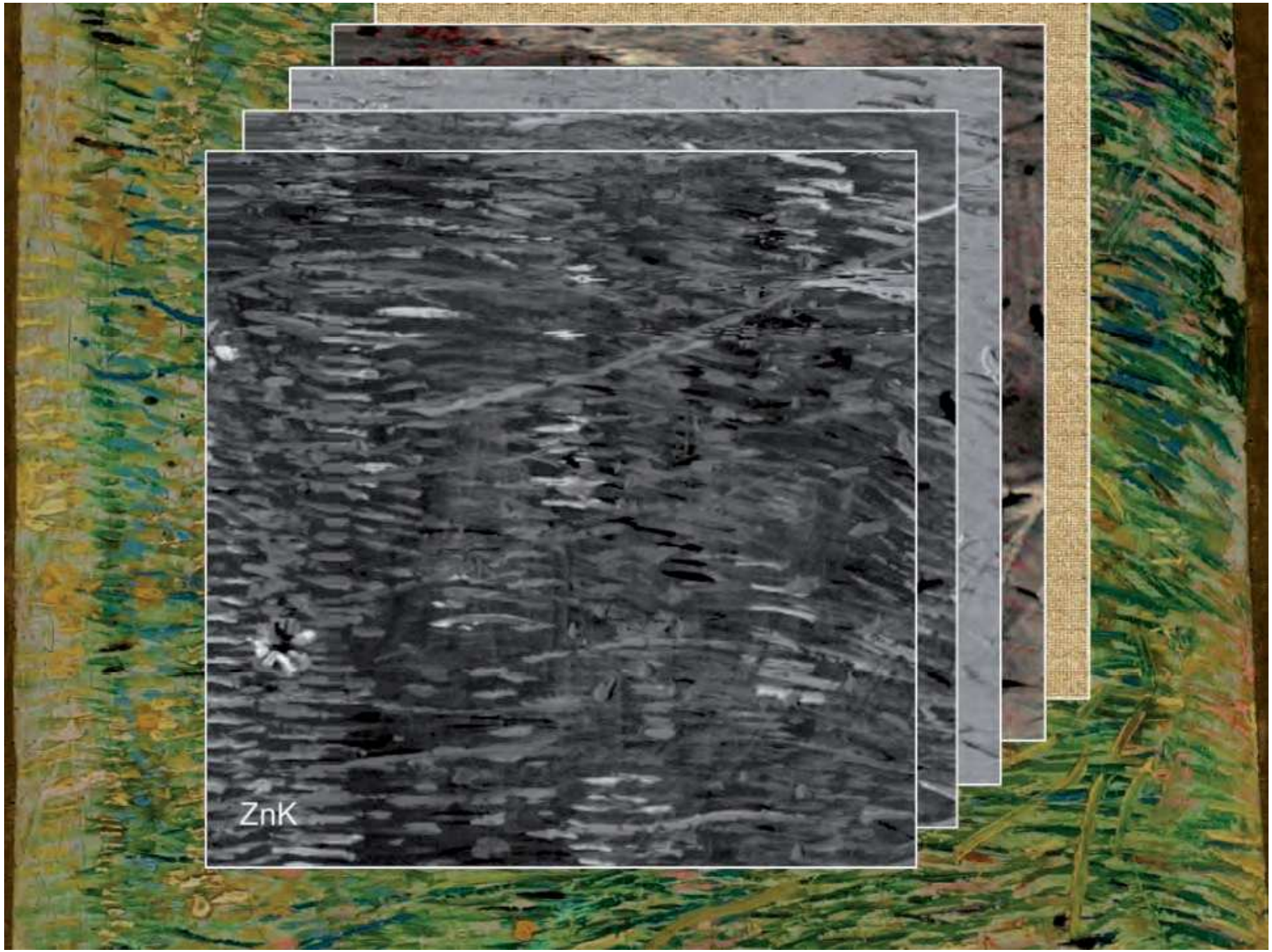


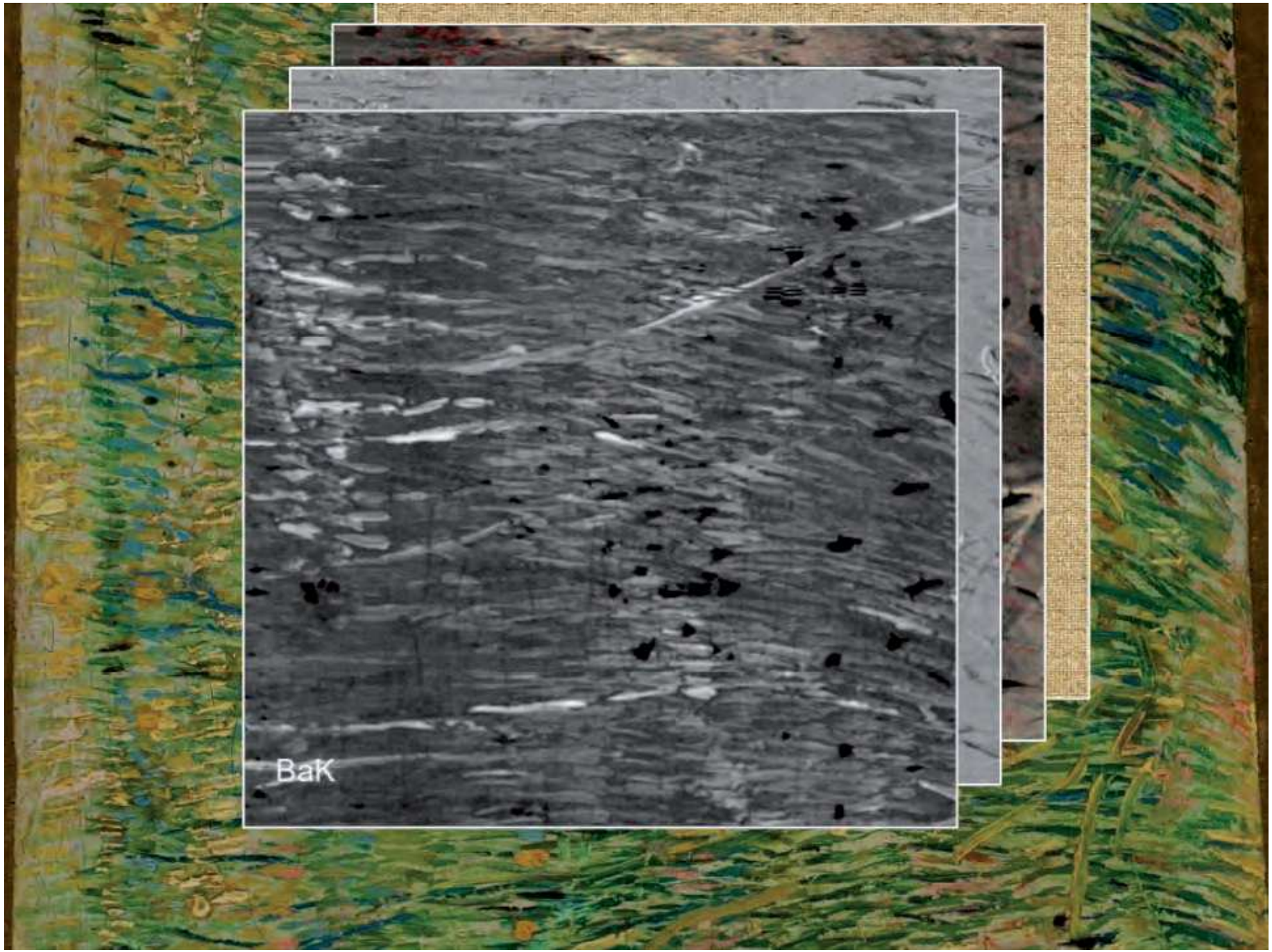
Typical fluorescence spectrum in a single pixel

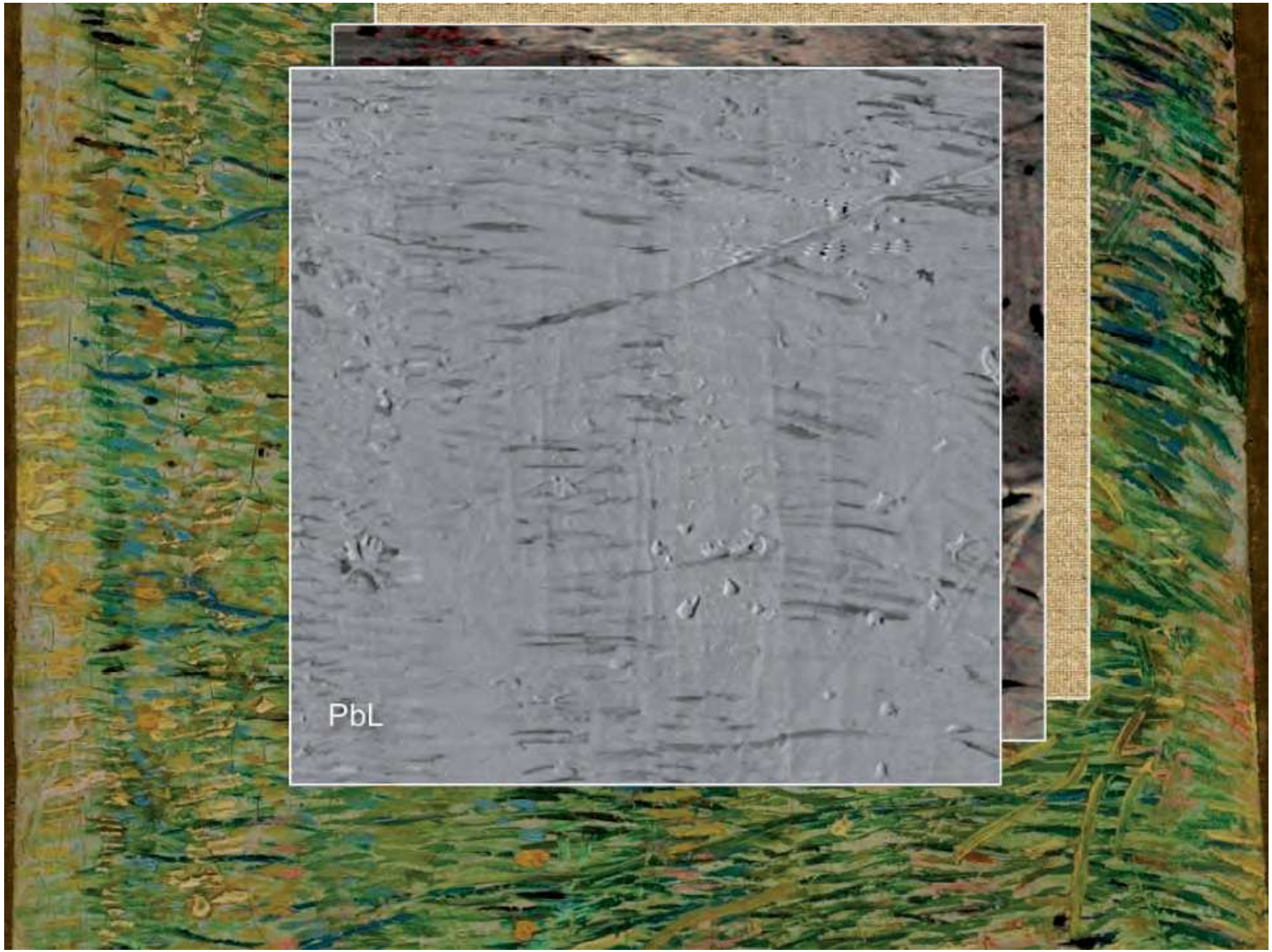


Raster scanning along 90000 pixels with 0.5 mm resolution



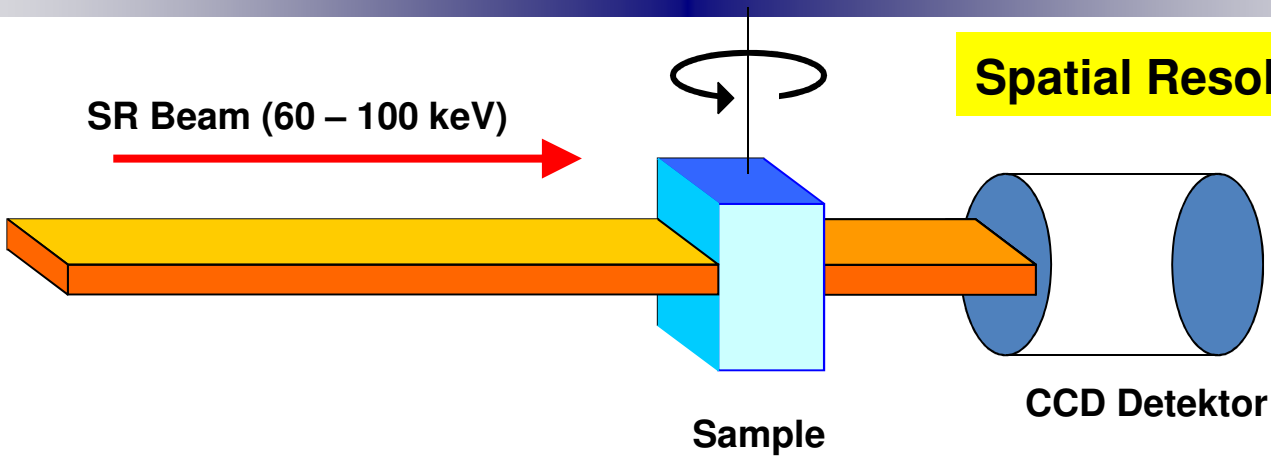

ZnK


BaK

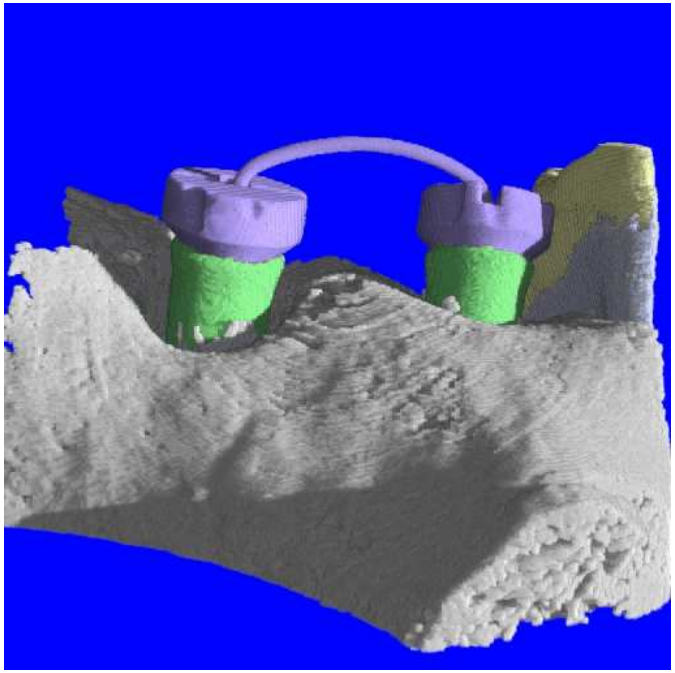

PbL


SbK + HgL

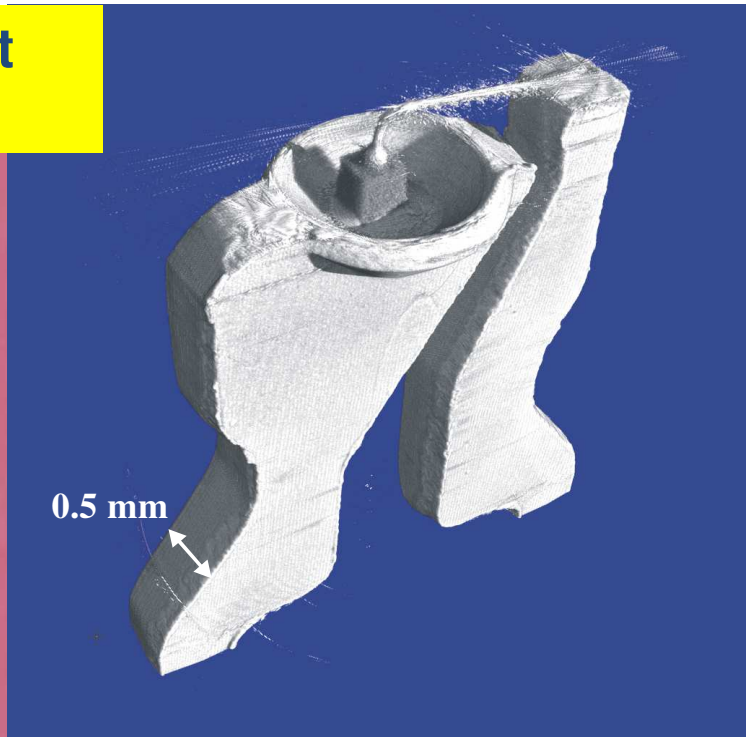
Parallel Beam X-Ray Tomography



Spatial Resolution: 10 µm

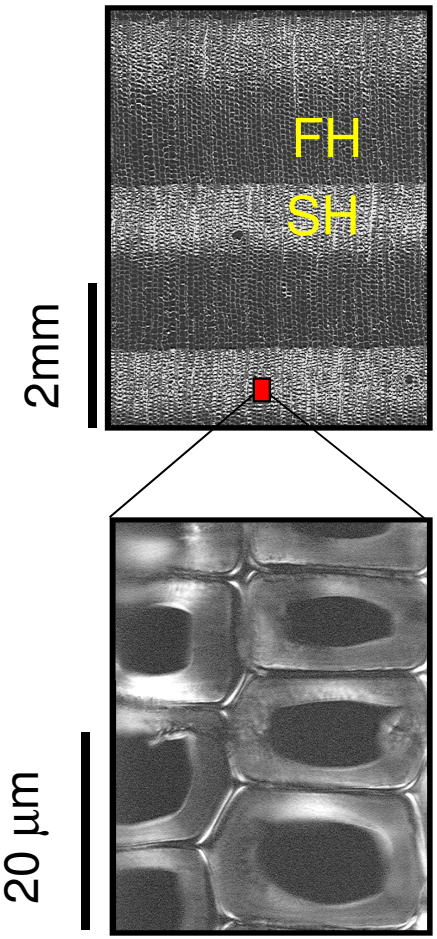


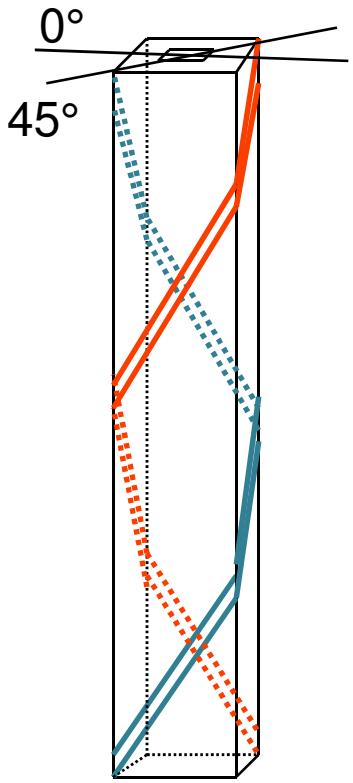
Sample: LED at 60 keV



Wood - Determination of the microfibril angle (Microfocus SAXS and WAXS)

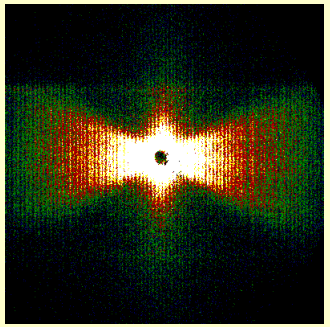
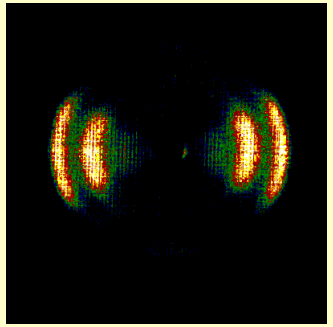
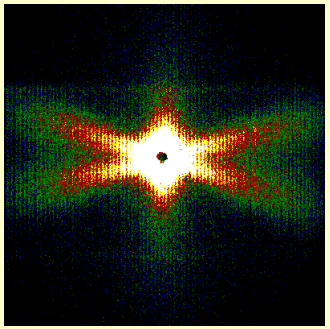
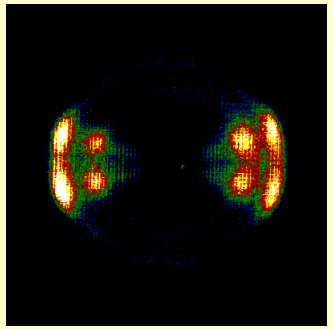
Picea abies (spruce)





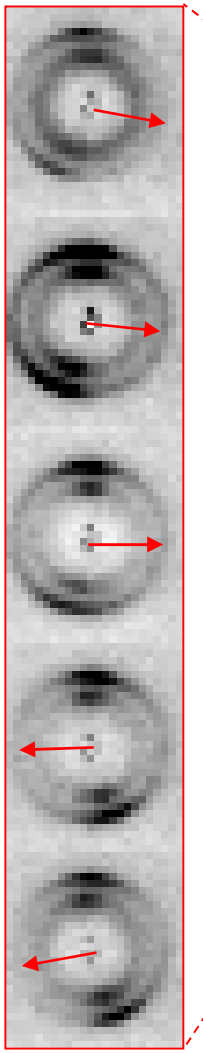
Focus 2x2µm²

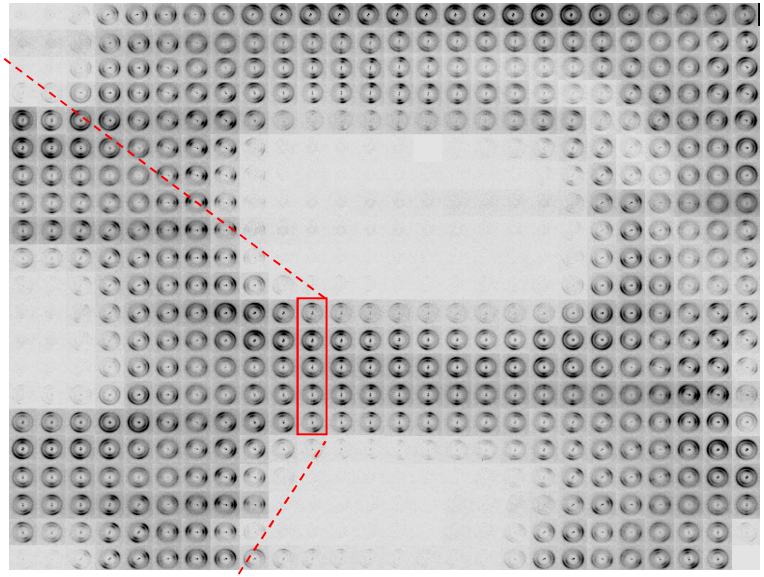
Fiber geometry

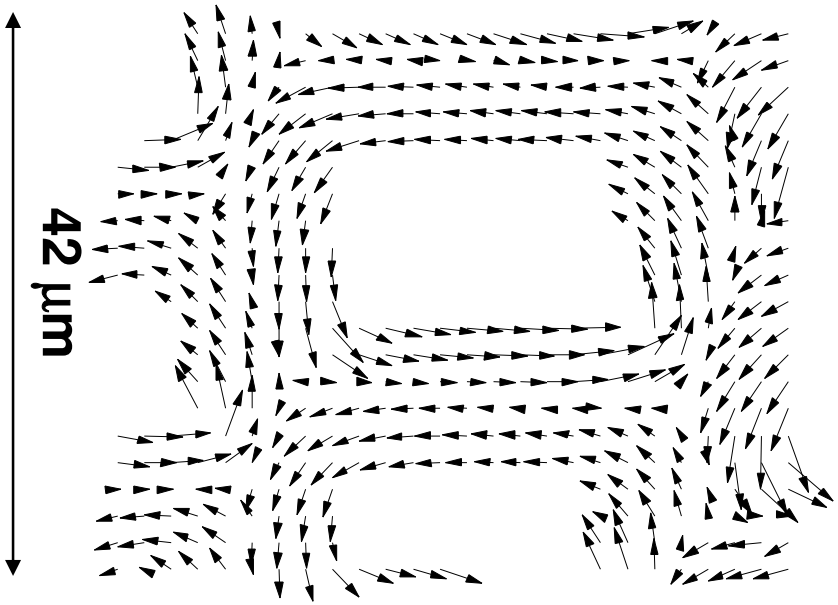
	SAXS	WAXS
ω = 0°		
ω = 45°		
	µ = 20.4°(±0.6°)	µ = 20.0°(±0.6°)

Lichtenegger et al. *J. Struct. Biol.* (1999)

Helical arrangement of cellulose fibers in the wood cell wall (Scanning Microfocus SAXS)







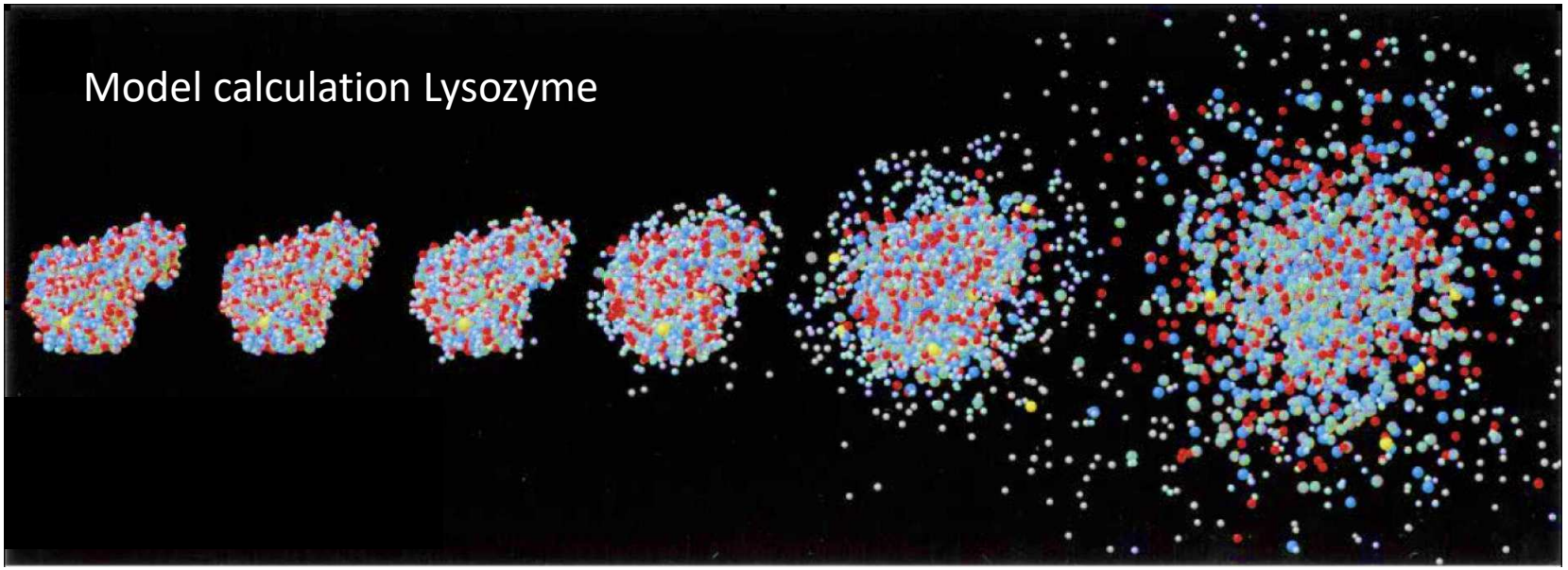
Z-Helix

Focus 2x2µm²

Lichtenegger, Müller, Paris, Riekel & Fratzl
J. Appl. Cryst. (1999)

Experiments at FELs

Coulomb Explosion

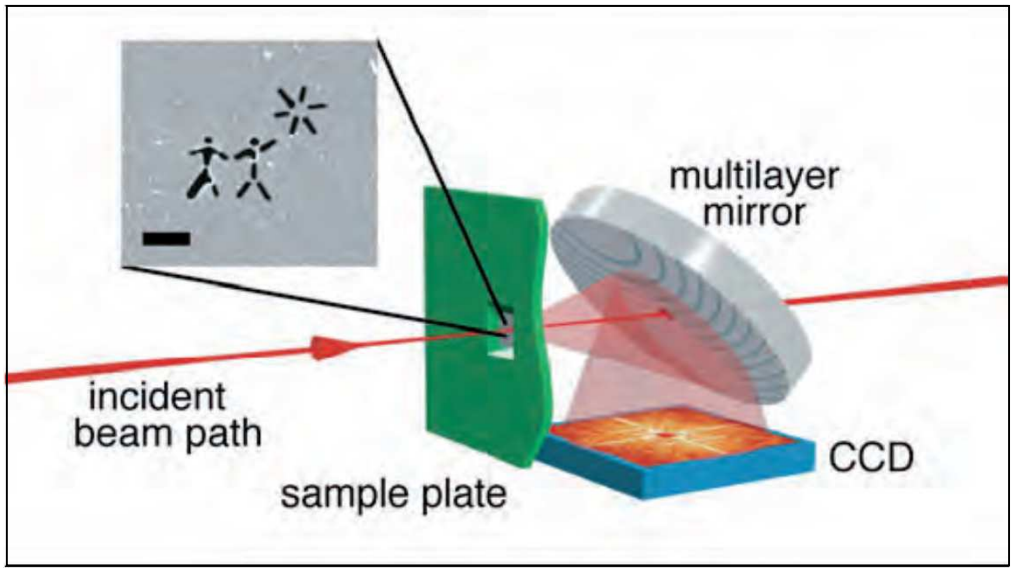


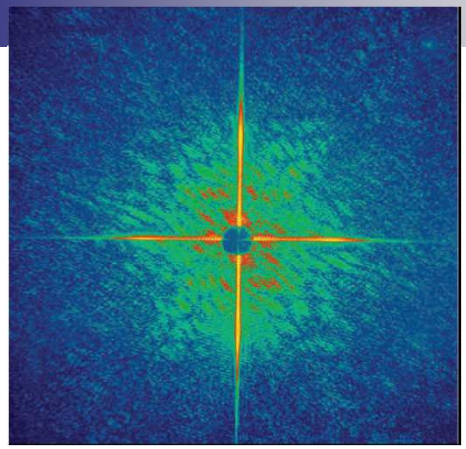
Time = 0 2 5 10 20 50 femtoseconds

„Coulomb Explosion“ of a molecule in the strong electric field of an FEL X-ray pulse

Ultrafast Coherent Diffractive Imaging at FLASH

Resolution 50 nm





1st shot

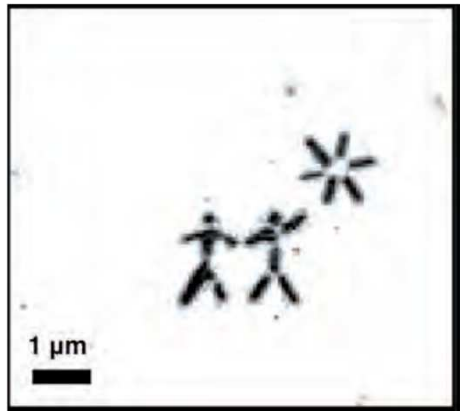
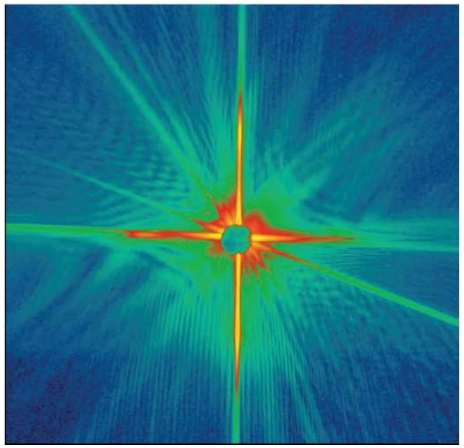


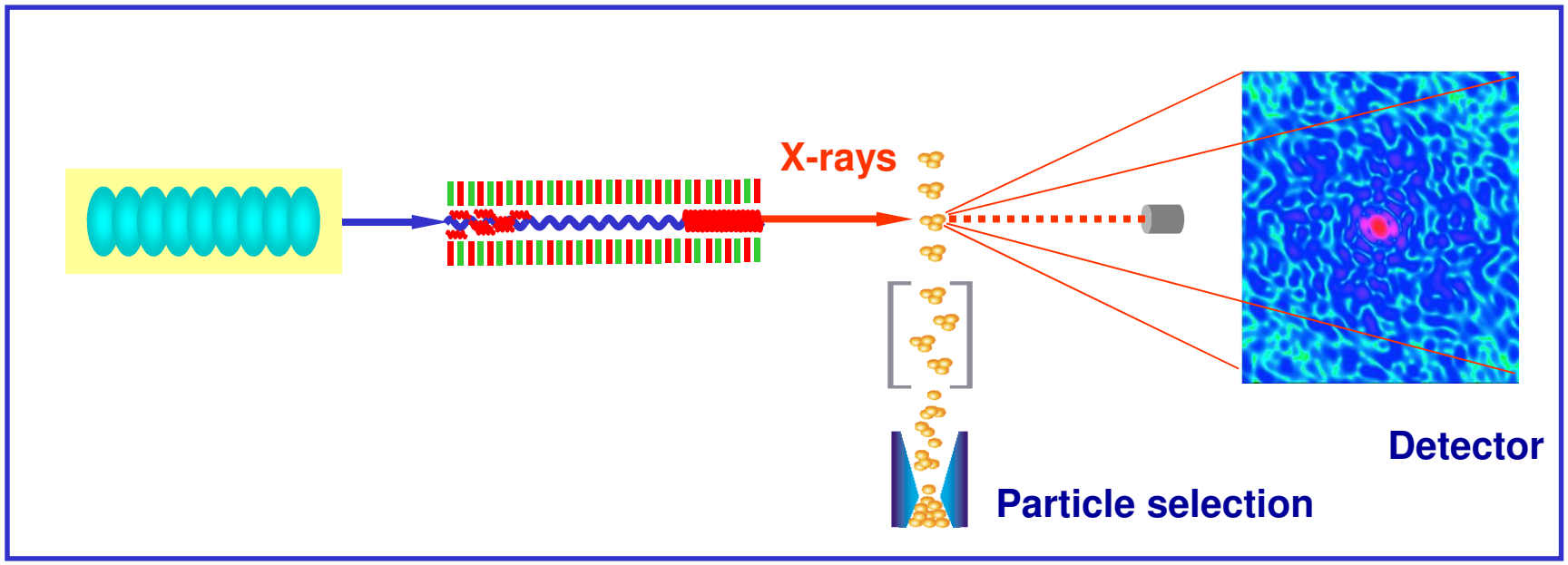
Image
Reconstructed
From
1st shot



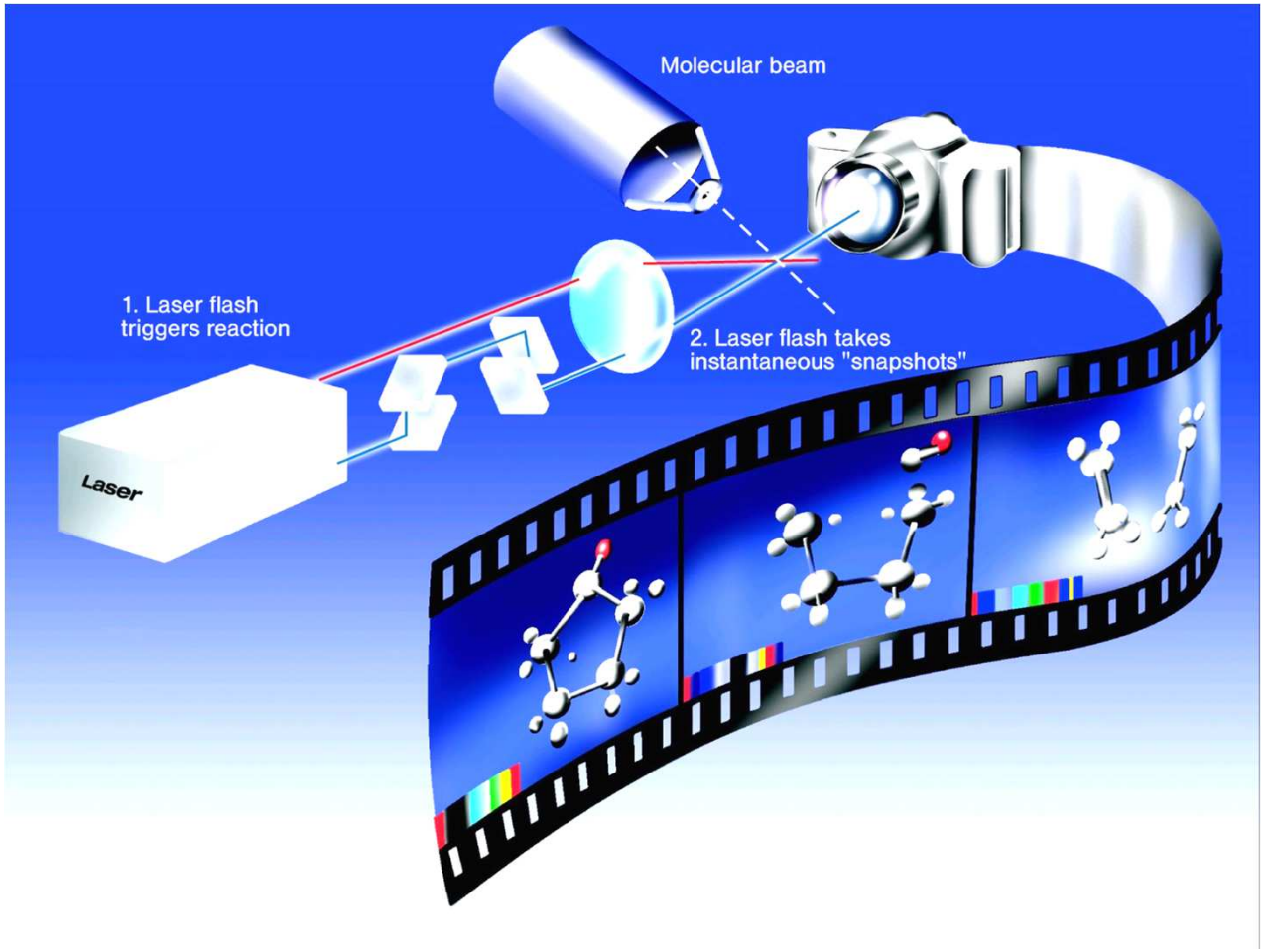
2nd shot
(target destroyed)

H. Chapman et. al., Nature Physics 2, 839 (2006)

The Ultimate Goal: Single-Molecule Diffraction



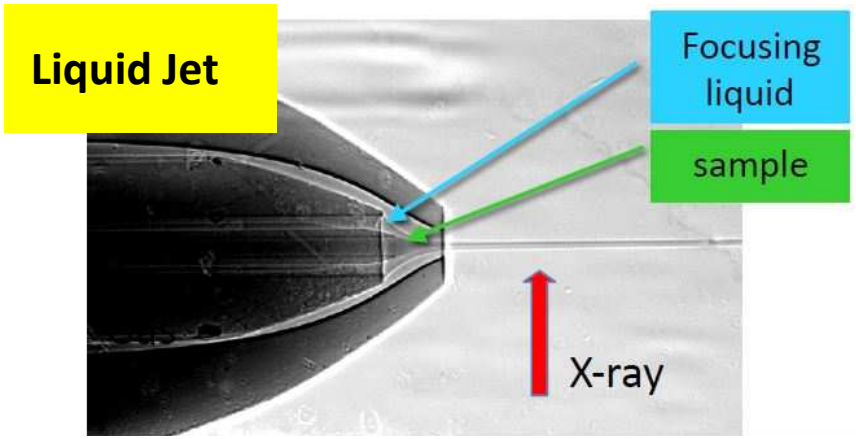
The Ultimate Goal: Recording the “Molecular Movie”



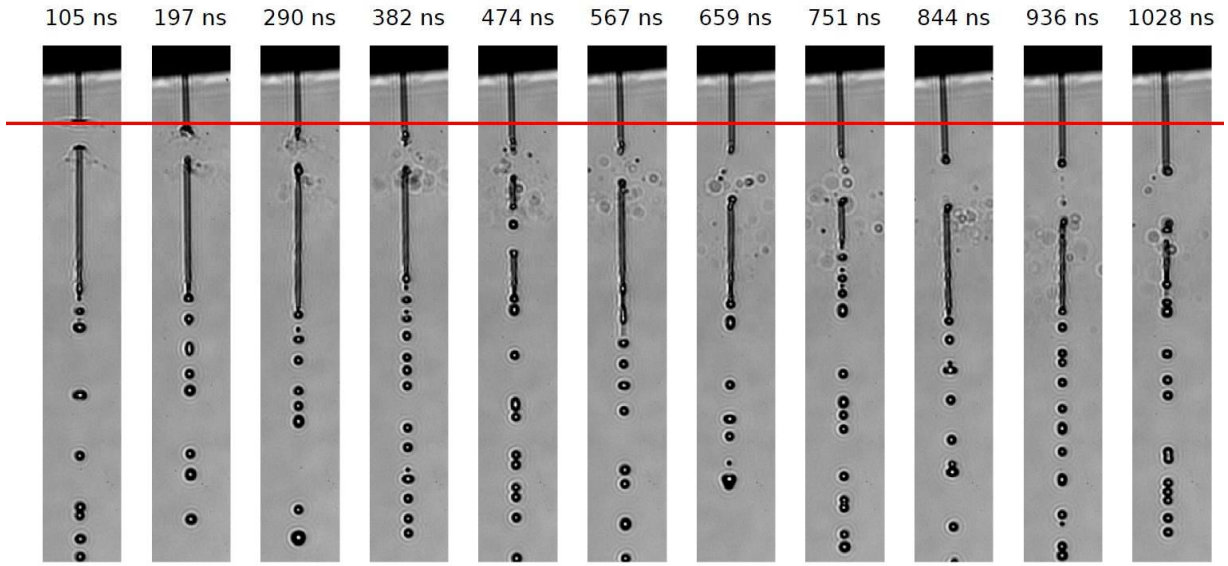
Snapshots for different times after excitation (pump-probe spectroscopy)

→ “motion picture” of the reaction dynamics (in contrast to reaction kinetics).

Serial Femtosecond Crystallography SFX



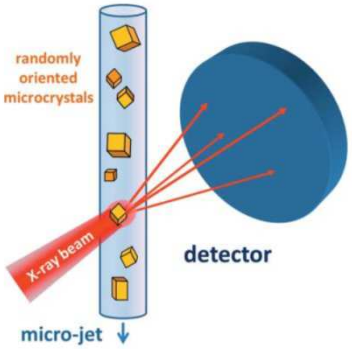
Fast liquid jet for sample delivery

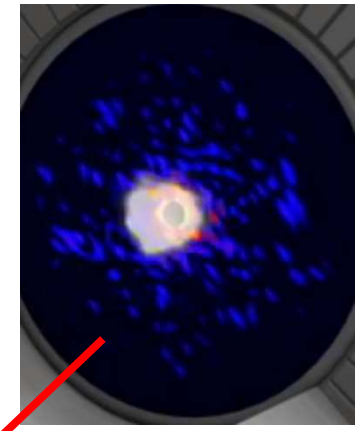


FLASH

Serial Femtosecond Crystallography SFX

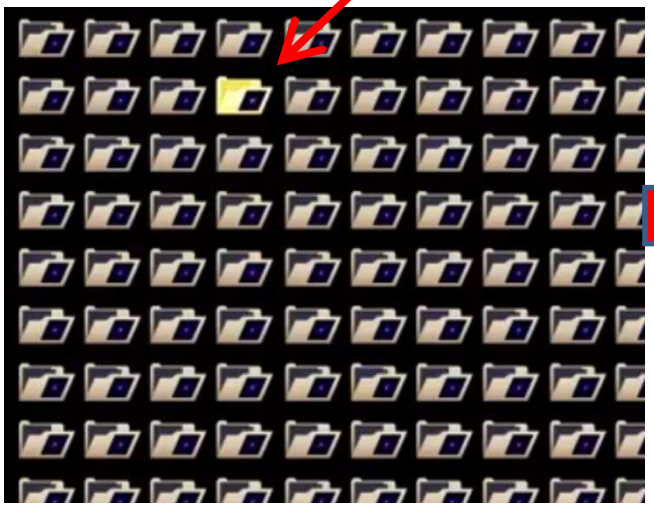
„Diffraction before Destruction“



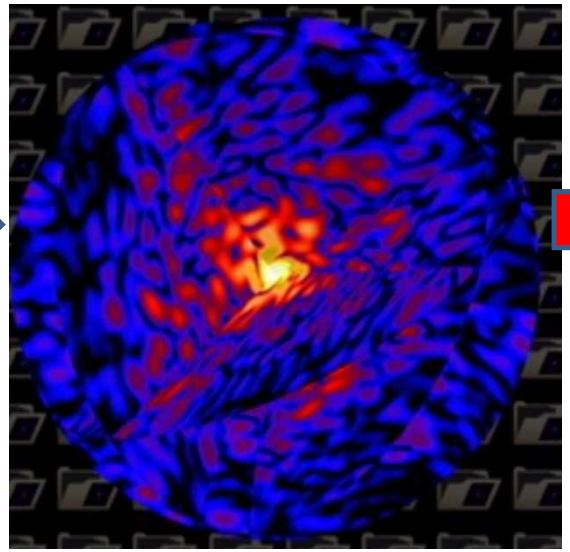


Single pattern

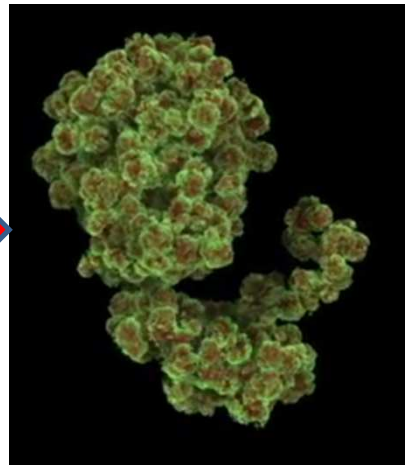
1. **Acquisition of scattering patterns**
2. **Classification and accumulation**
3. **Distribution in 3D reciprocal space**
4. **Reconstruction of structure in real space**



(accumulated) orientation classes



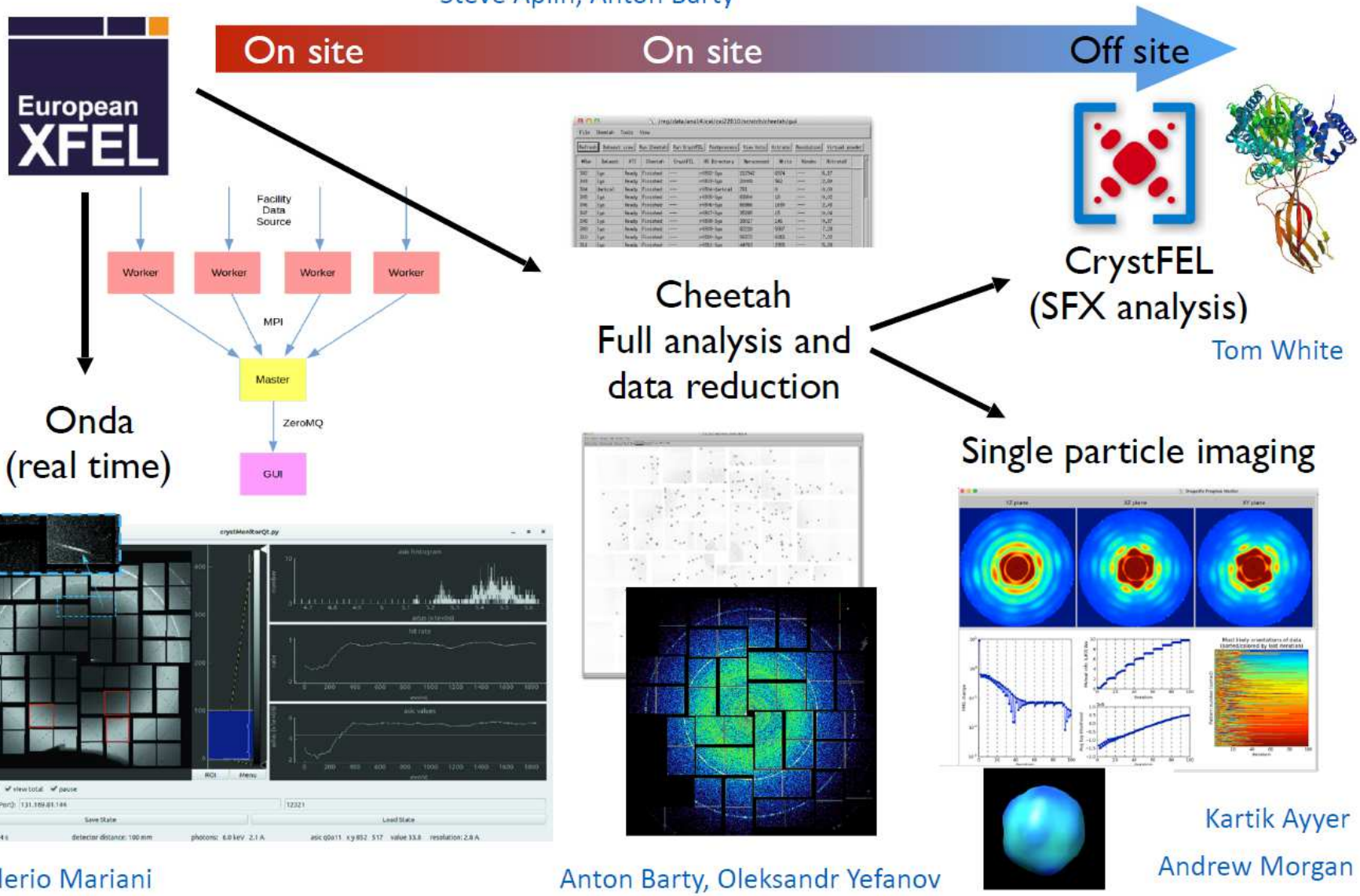
Intensity in reciprocal space



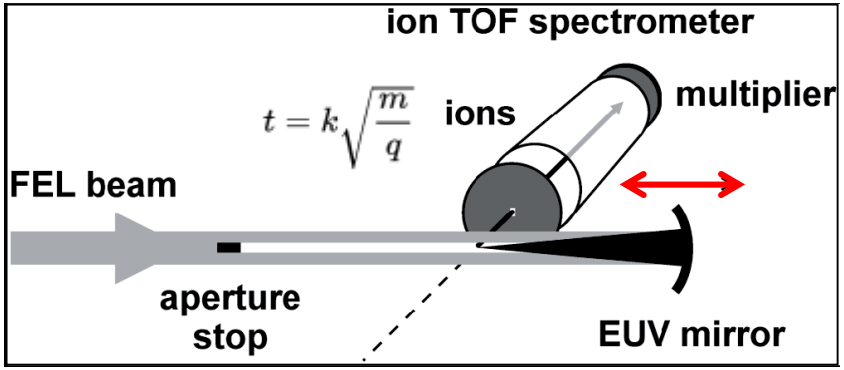
Electron density in real space

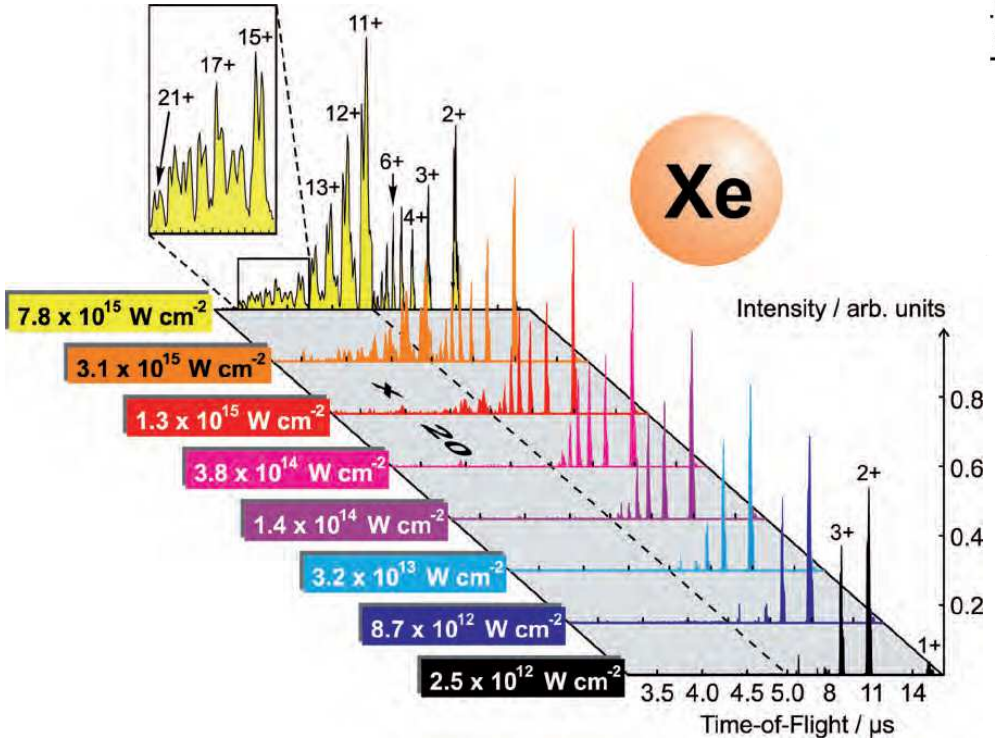
SFX Data Processing Stages

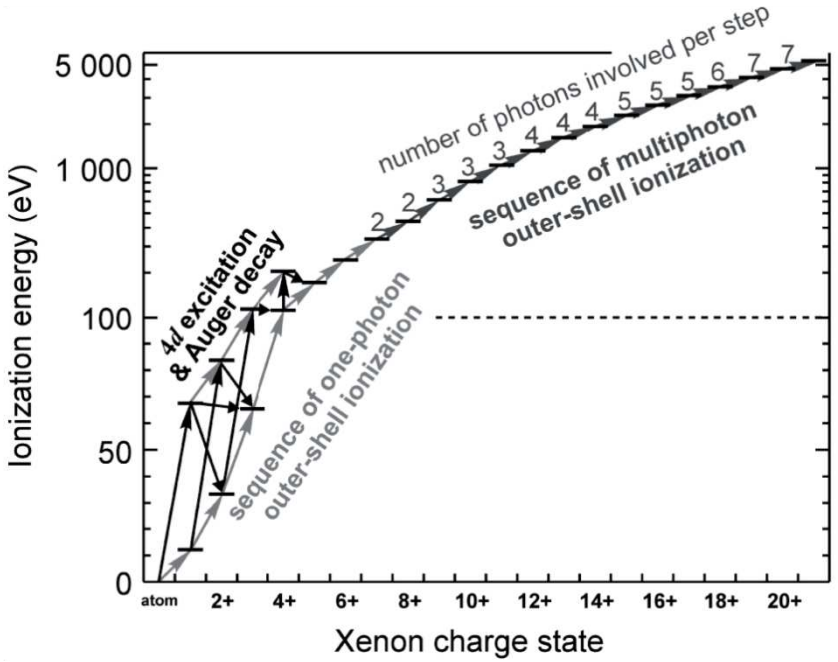
Steve Aplin, Anton Barty



Photoelectric Effect at Ultrahigh Intensities (FLASH, 13.5 nm]







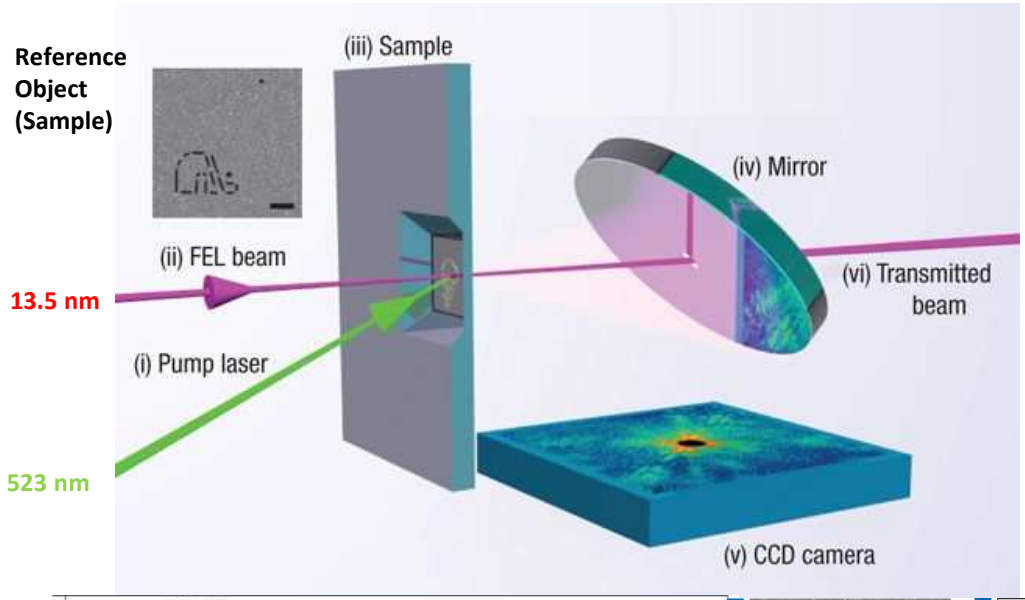
13.5 nm ≡ 91.8 eV

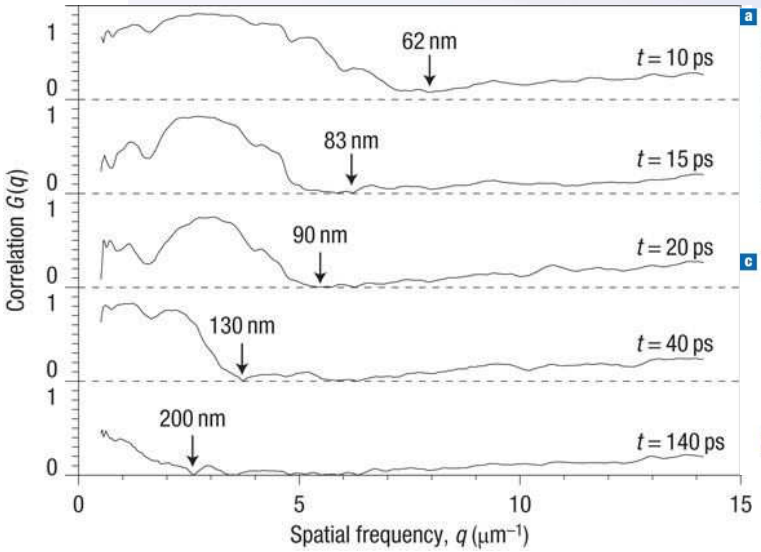
Dramatic changes in the ion charge state at high power densities

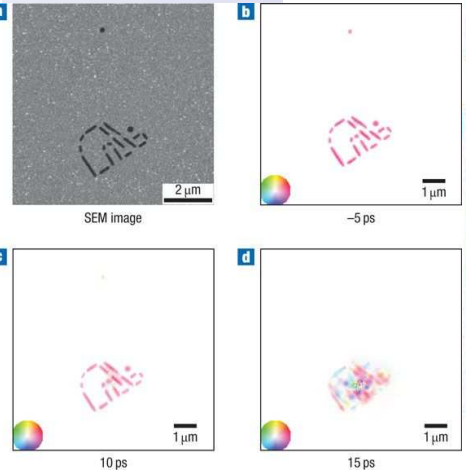
One atom has to absorb more then 50 photons!

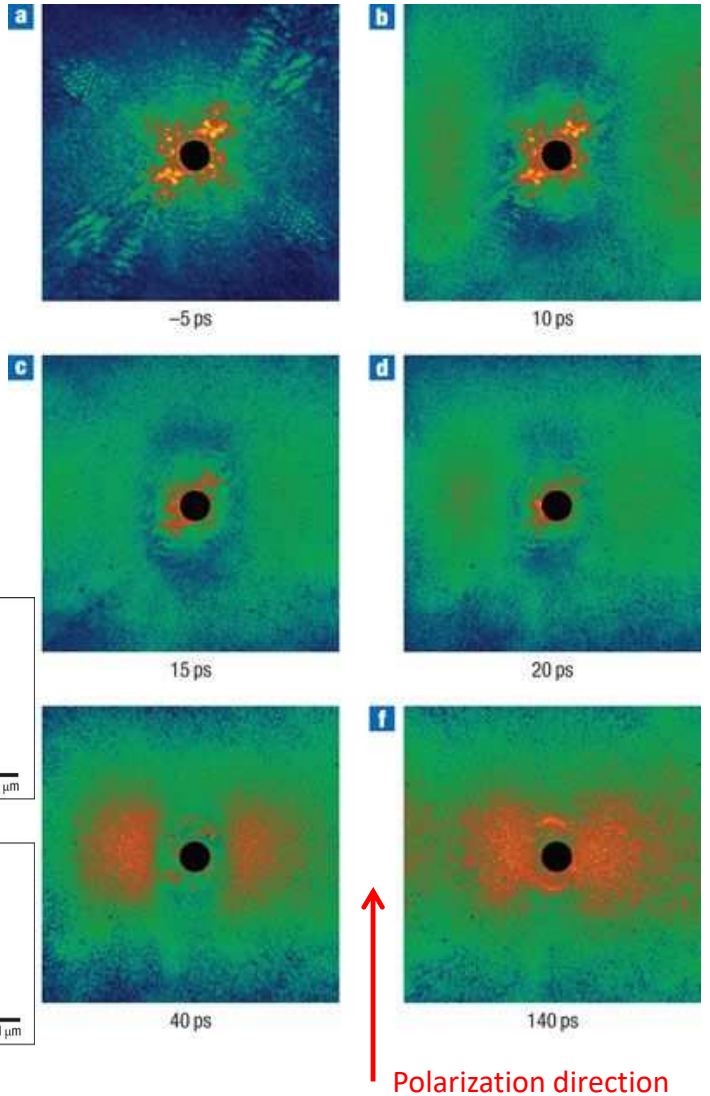
Phys. Rev. Let. 99, 213002 (2007)

Pump Probe Experiment









Reconstructed images (phase retrieval)

Correlation between actual and initial pattern quantifies progressive loss of mesoscale order (explosion speed about 5000 m·s^{-1})

A. Barty et. al., Nature Photonics **volume 2**, pages 415–419 (2008)

Photon Science Facilities on DESY Campus

CXNS = Center for X-Ray and Nano Science
CFEL = Center for Free Electron Laser Science (DESY, MPI, UniHH)
CHyN = Center for Hybrid Nanostructures

CSSB = Centre for Structural Systems Biology
MPSD = Max-Planck Inst. For Structure and Dynamics of Matter