Introduction to Photon Science

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DESY Summer Student Lectures 2023

HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

DESY.

Content

- **PART I:**
  - History of X-ray Source
  - Principle of Synchrotrons
  - Principle of Free-Electron Lasers
- **PART II:**
  - Science at Synchrotron facilities
  - Science at FEL facilities

Introduction to Photon Science

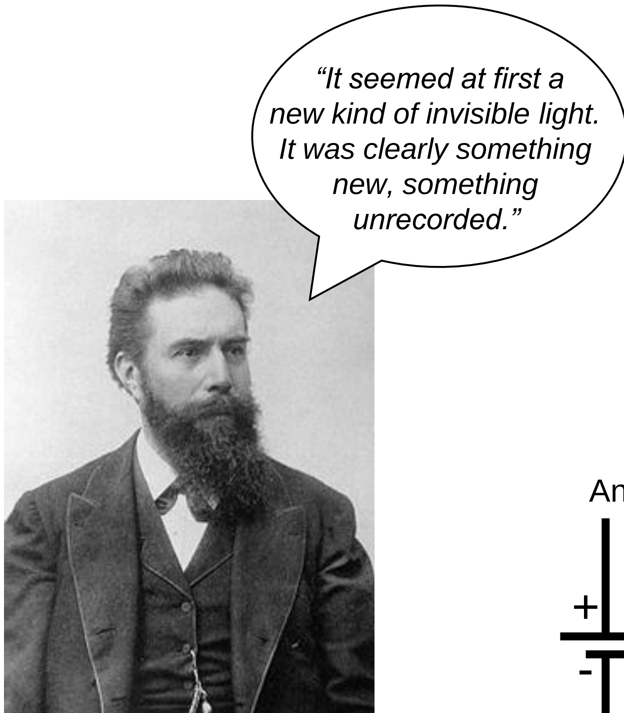
Part I: Basics of synchrotrons and free-electron lasers

A short history of X-ray sources

Generation of X-rays: X-ray tube

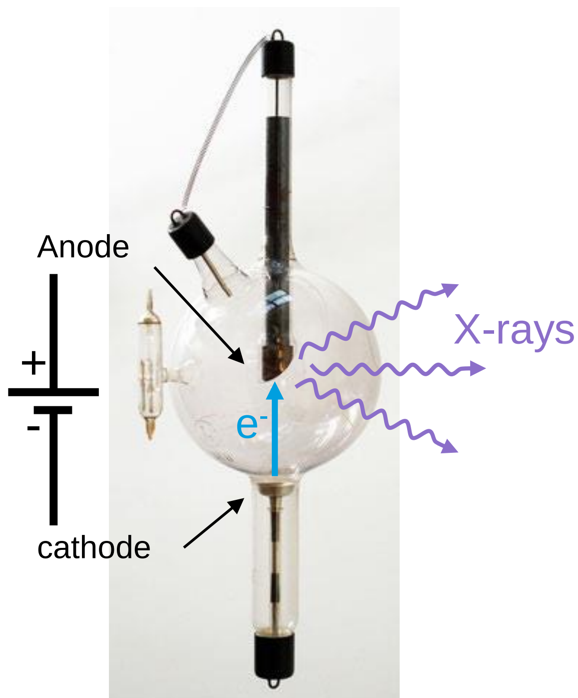
From discovery to first application

1895: Discovery of X-rays by Wilhelm Conrad Röntgen

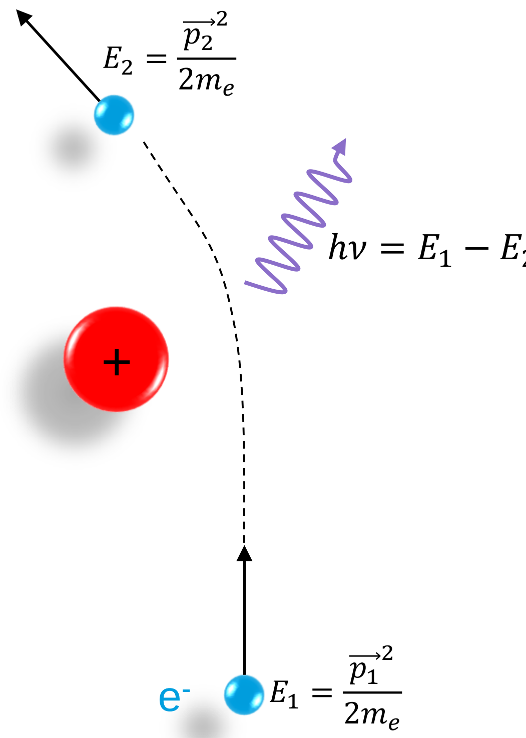


Wilhelm Conrad Röntgen
(1845 – 1923)
Nobel Prize 1901

Crookes tube



General principle for generation of X-rays: Bremsstrahlung

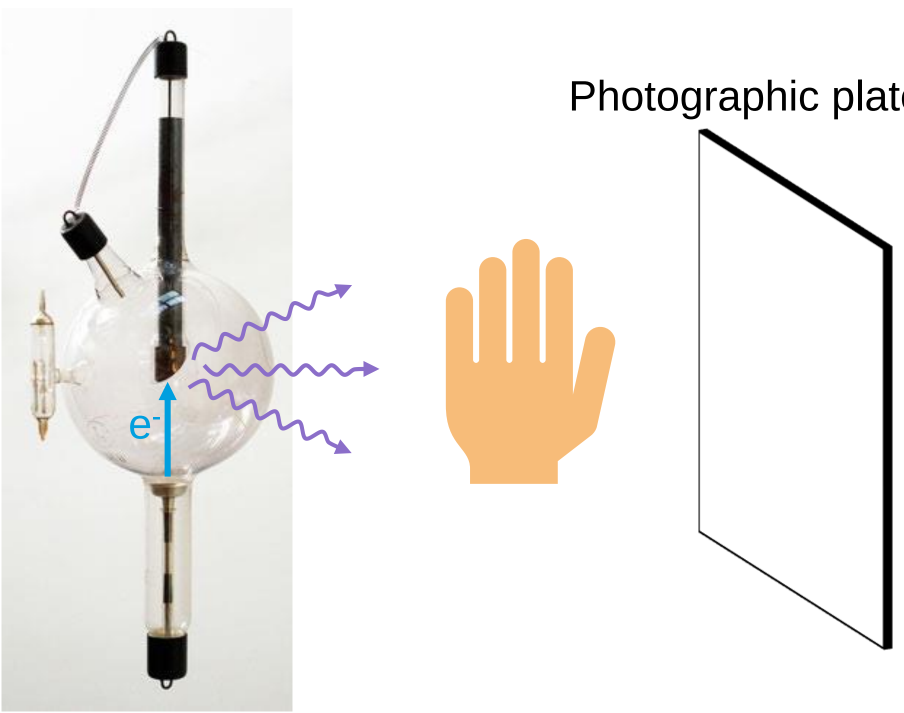


Generation of X-rays: X-ray tube

From discovery to first application

1 month later: first X-ray image

Photographic plate



30-150 kV → ~0.7 *c*

25 min exposure time

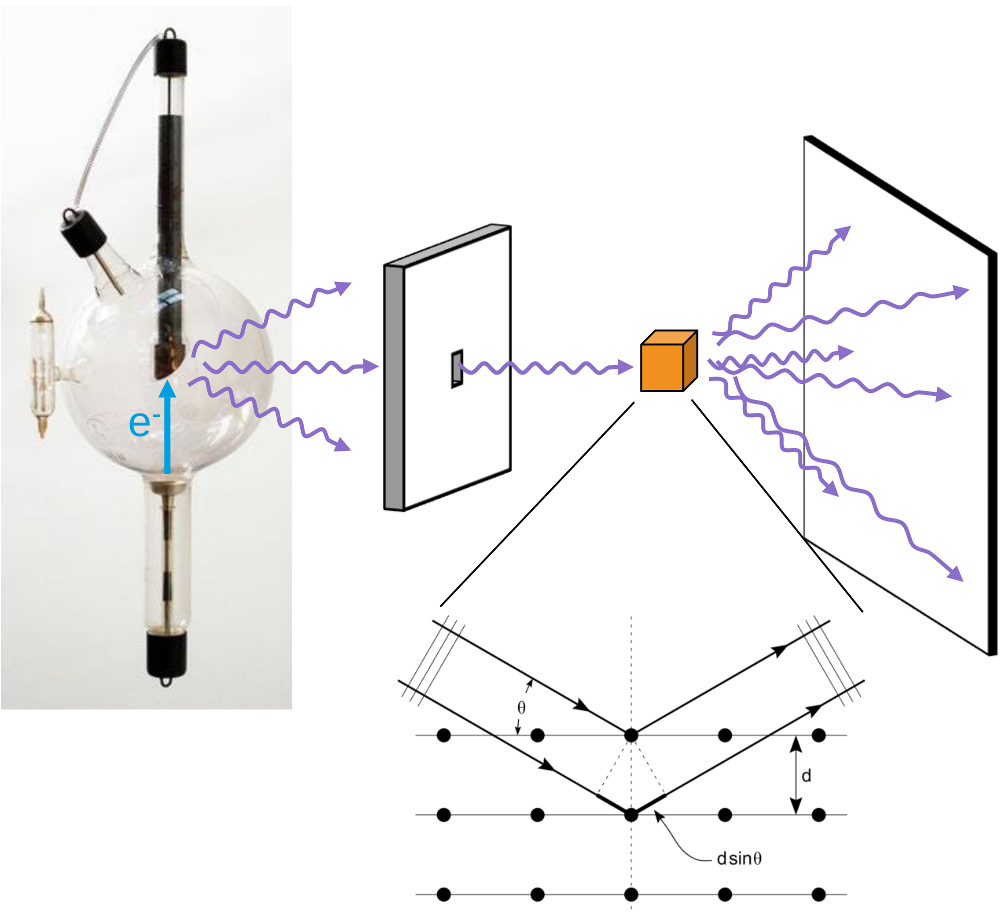
Röntgen’s wife hand

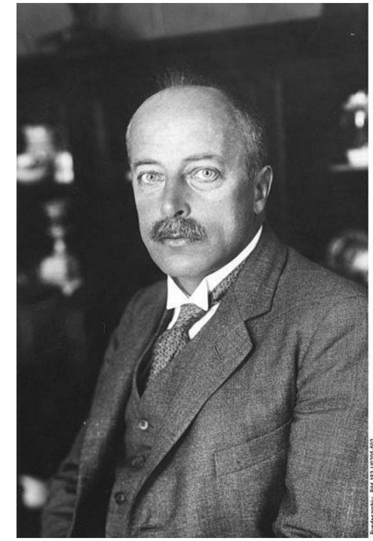
Generation of X-rays: X-ray tubes

X-ray diffraction from crystalline structures

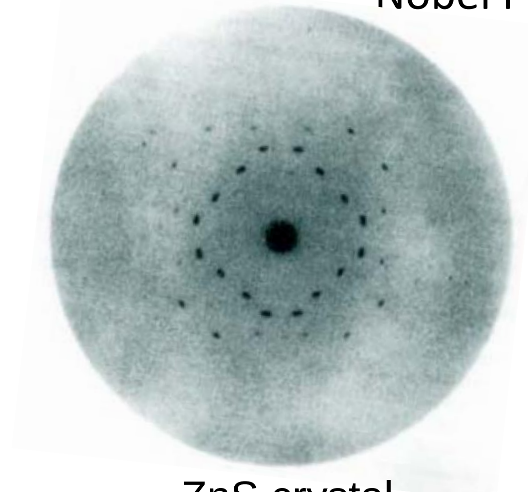
First diffraction patterns obtained by Max von Laue in 1912

W. Friedrich *et al*. *Annalen der Physik* **346**, 971–988 (1913)





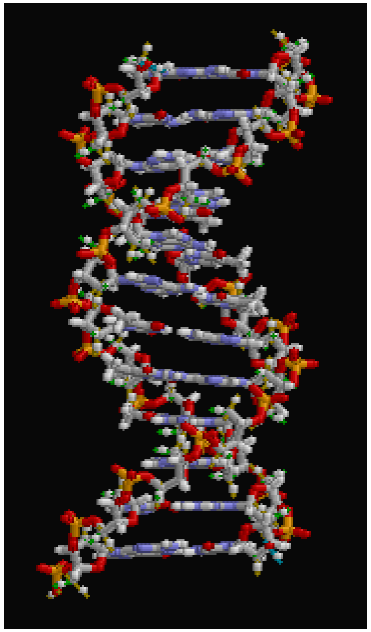
Max von Laue
(1879 – 1960)
Nobel Prize 1914

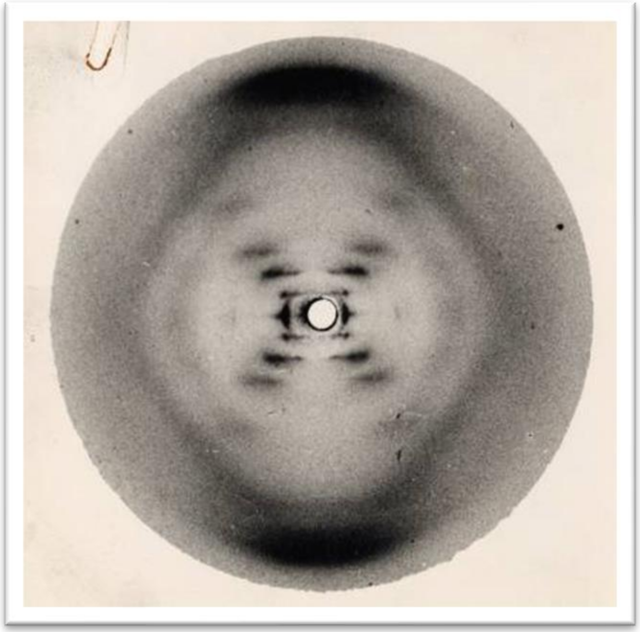


ZnS crystal

Generation of X-rays: X-ray tubes

X-ray diffraction from crystalline structures





1952: The first X-ray diffraction pattern of DNA
62 hours exposure time !

Rosalind Franklin
(1920 – 1958)
~~Nobel Prize 1962~~

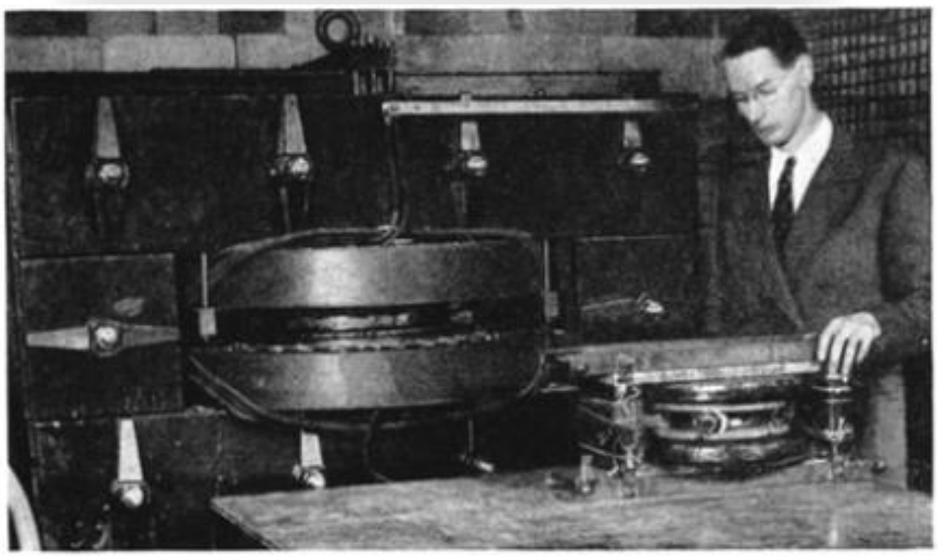
The **Nobel Prize in Physiology or Medicine 1962 was awarded** jointly to Francis Harry Compton Crick, James Dewey Watson and Maurice Hugh Frederick Wilkins **"for their discoveries concerning the molecular structure of nucleic acids and its significance for information transfer in living material"**

Generation of X-rays: Betatron

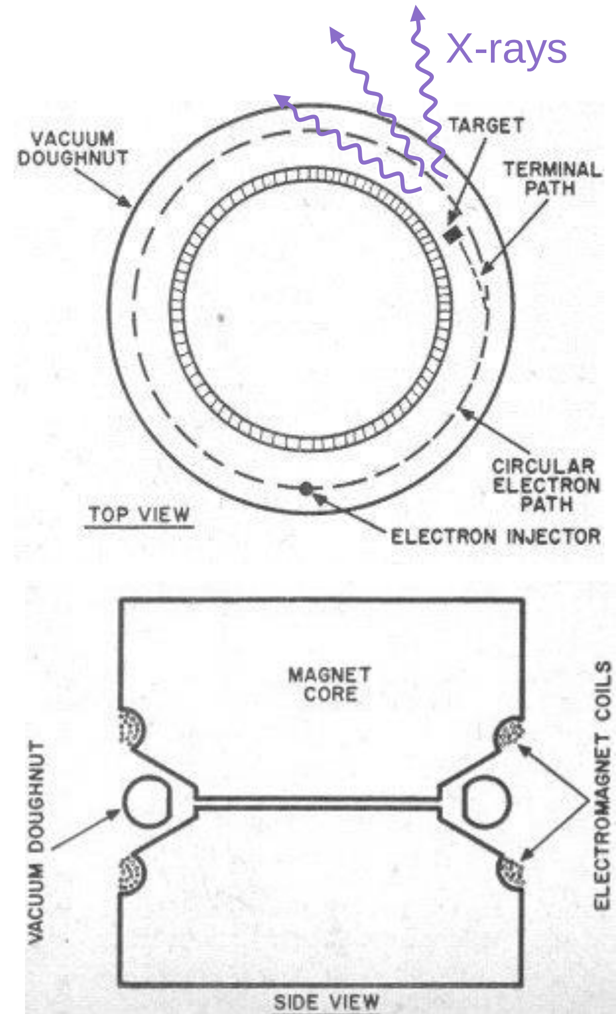
Acceleration in a magnetic field

The Betatron

World's Most Powerful X-Ray Machine Holds Vast Possibilities for Medicine, Industry, Research



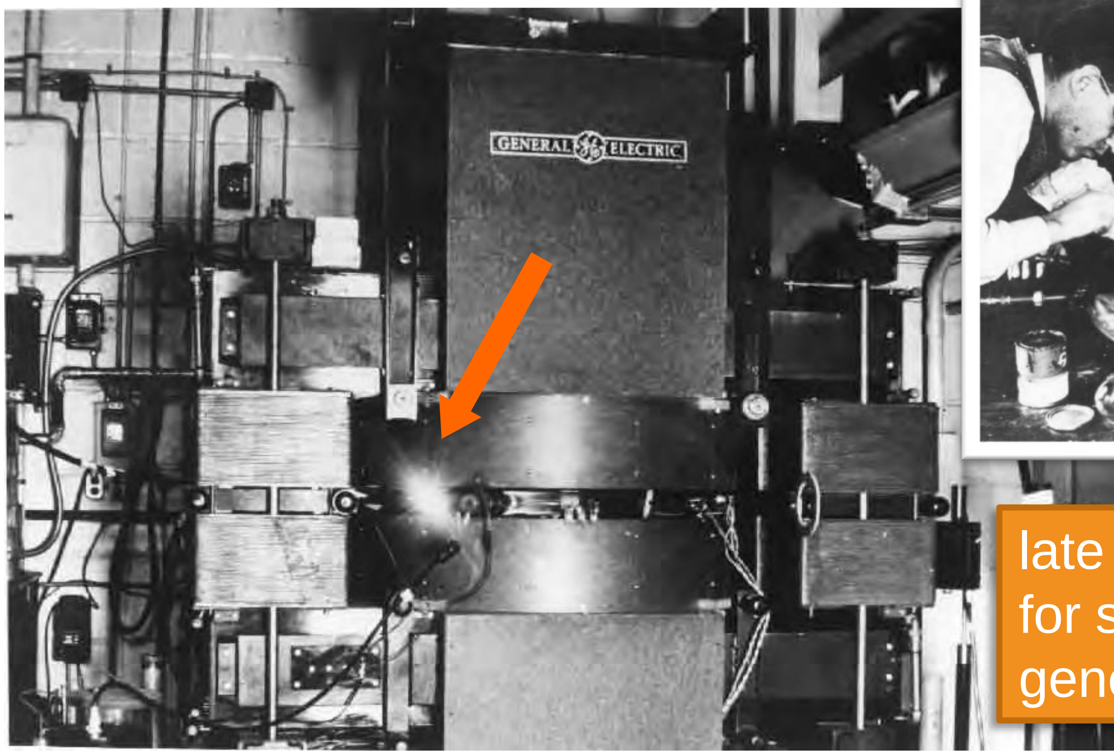
Professor Donald W. Kerst with the first betatron, having 2.3-million volts output energy, on the table and the 20-million-volt machine alongside. The circular vacuum tube of the large unit can be seen in place in the center of the betatron, between the pole faces of the 3½-ton magnet. The larger betatron is only three feet high



Scientific American, Vol. 168, No. 5 (MAY · 1943), pp. 207-209

Generation of X-rays : Synchrotron

First observation of synchrotron radiation



late 1970s → planning began for special accelerators to generate synchrotron radiation

April 24, 1947: First observation of SR at General Electric 70 MeV synchrotron (Langmuir, Elder, Gurewitch, Charlton, Pollock)

>10x *c* ! → relativistic speed

Generation of X-rays : and now?

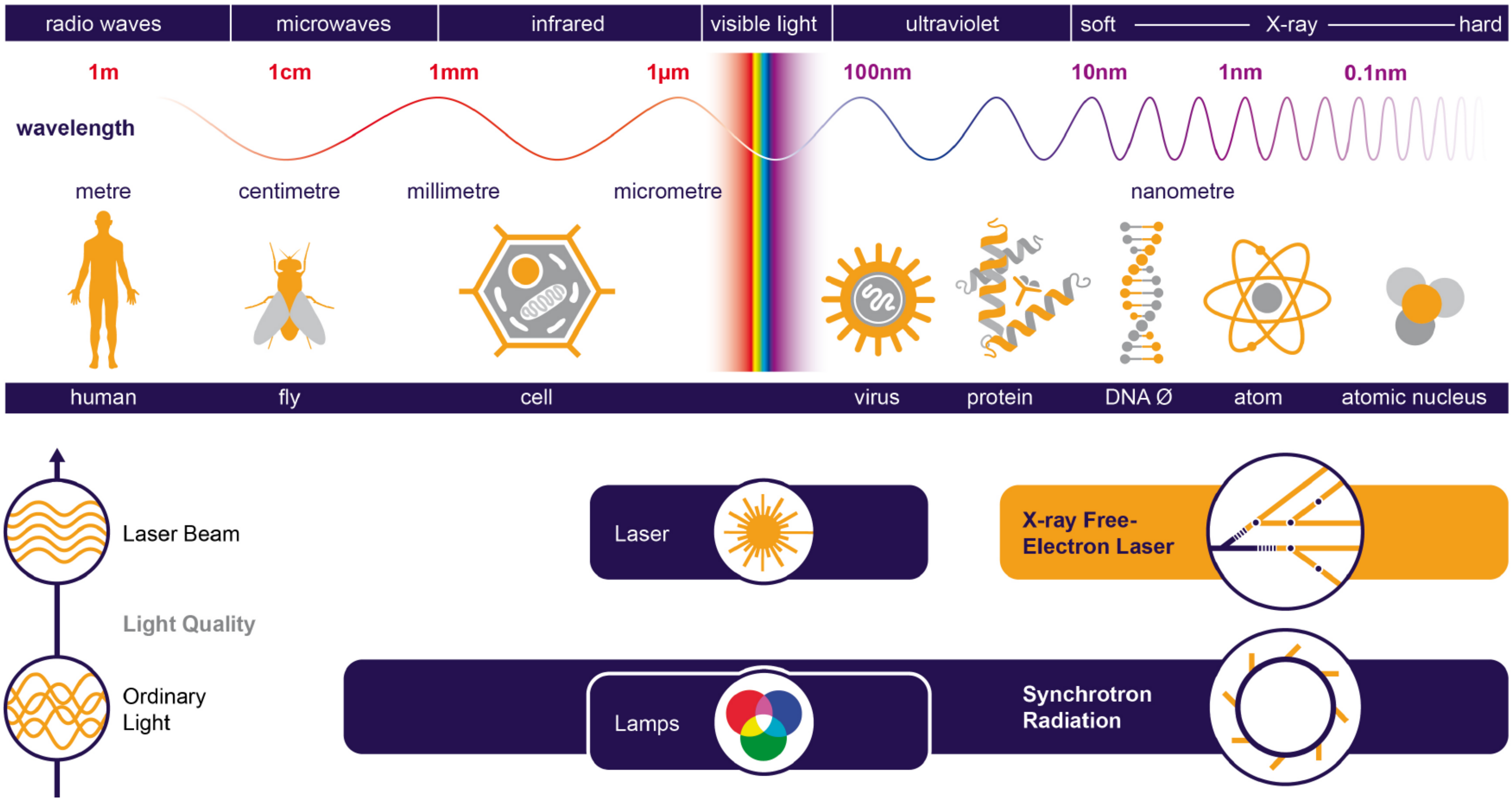
Linac and 3rd generation synchrotron

few MeV radiotherapy linac

ESRF (Grenoble, FR), 6 GeV synchrotron

Big facilities for studying tiny objects…

Reveal structure and dynamics of matter with highest spatial and temporal resolution



Courtesy European XFEL

Synchrotron radiation facilities worldwide

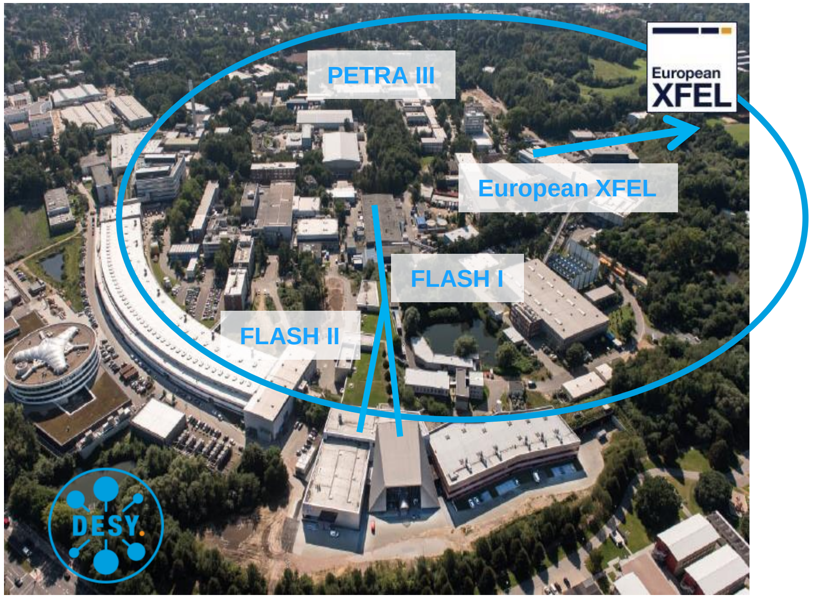
Today, more than 50 lights source in the world

HZB Helmholtz Zentrum Berlin
MAX IV
NSRRC
SPring-8
Photon Factory
Institute of Materials Structure Science
High Energy Accelerator Research Organization,KEK
PAL
POHANG ACCELERATOR LABORATORY
SYNCHROTRON THAILAND
Canadian Light Source
DESY.
Argonne NATIONAL LABORATORY
PAUL SCHERRER INSTITUT PSI
ALS ADVANCED LIGHT SOURCE
diamond
SOLEIL SYNCHROTRON
BROOKHAVEN NATIONAL LABORATORY
SLAC NATIONAL ACCELERATOR LABORATORY
ESRF The European Synchrotron

ALBA
Elettra Sincrotrone Trieste
SESAME
Australian Synchrotron
LNLS
CHESS CORNELL HIGH ENERGY SYNCHROTRON SOURCE

Synchrotron radiation facilities in Europe

DESY machine history



2400 Employees, 3000 International Guests
(100 apprentice, 100 undergraduate, 350 PhD, 300 Postdoc)
Annual budget: 232 M€ (2020)

DESY founded 1959 as an Electron Synchrotron Facility
for Elementary Particle Research

1964 DESY (Synchrotron) e- 7.4 GeV
1974 DORIS (Storage Ring) 300m e+/e- 3.5 GeV (later 5 GeV)

1980 HASYLAB@DORIS
1984 Upgrade with 7 Wiggler/Undulator Beamlines
1993 Dedicated SR Source at 4.5 GeV

1978 PETRA (Storage Ring) 2.3km e+/e- 19 GeV

1990 HERA (Storage Ring) 6.3km p+/e- 920 GeV / 27.5 GeV (using PETRA as Booster)

1997 FLASH (Free Electron Laser)
2005 Dedicated User Facility

2007 Shutdown of HERA and Reconstruction of PETRA → PETRA III

2009 PETRA III Dedicated SR Source at 6 GeV (one of the most brilliant SR sources worldwide)

2012 Shutdown of DORIS
2014 FLASH II (Extension of FLASH)

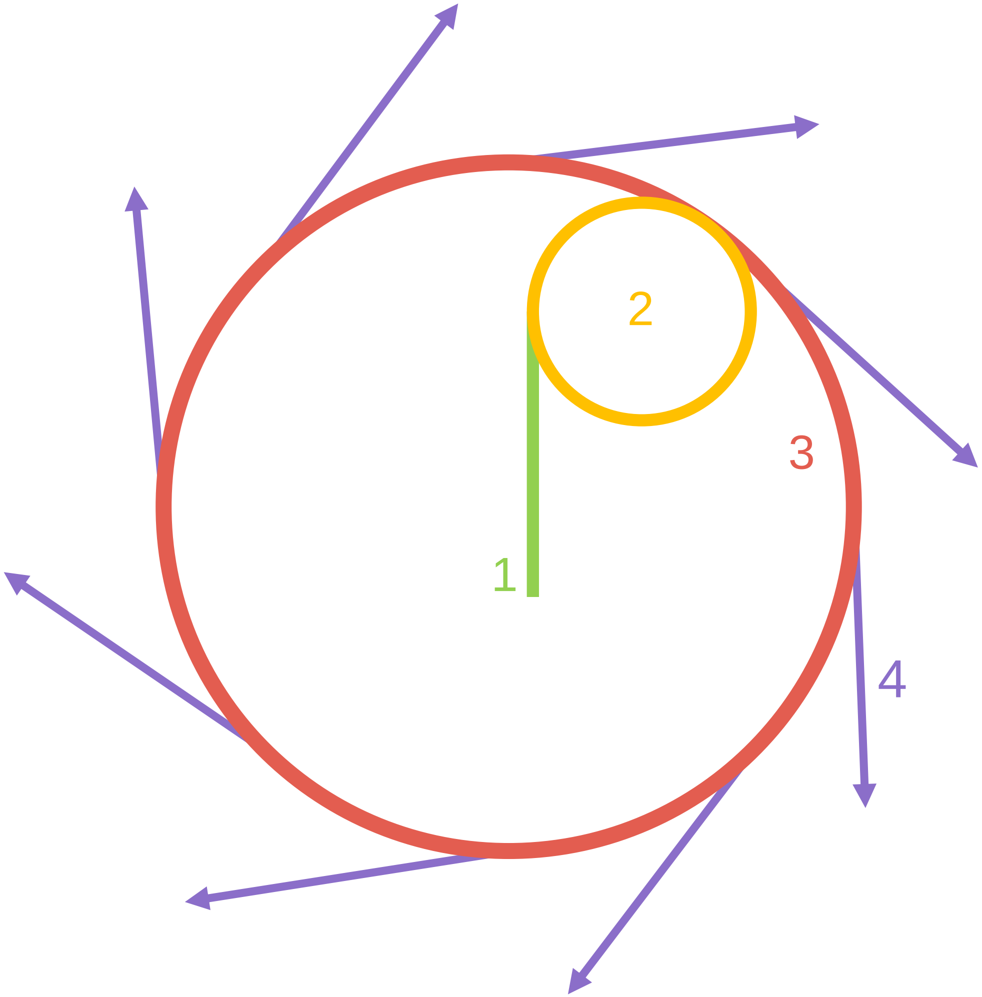
Participation in the European XFEL project (operation since 2017)
2032 PETRA IV

Principle of Synchrotrons

Synchrotron

Principal structures

1. e^- are produced and accelerated in a LINAC
2. e^- are accelerated to nominal energy (GeV) in the booster accelerator
3. e^- bunches travel in the storage ring in a wide circular path, emitting light as they change directions
4. X-ray light, emitted towards “beamlines”
→ experiments



Synchrotron Radiation (SR)

Radiation of relativistic particules

SR is electromagnetic radiation emitted when a relativistic particle is subject to an acceleration perpendicular to its velocity

Many features can be understood in terms of two processes:

- Lorentz contraction
- Doppler shift

γ is the relativistic **Lorentz factor**

$$\gamma = \frac{E}{E_0}$$

$$\beta = \frac{v}{c}$$

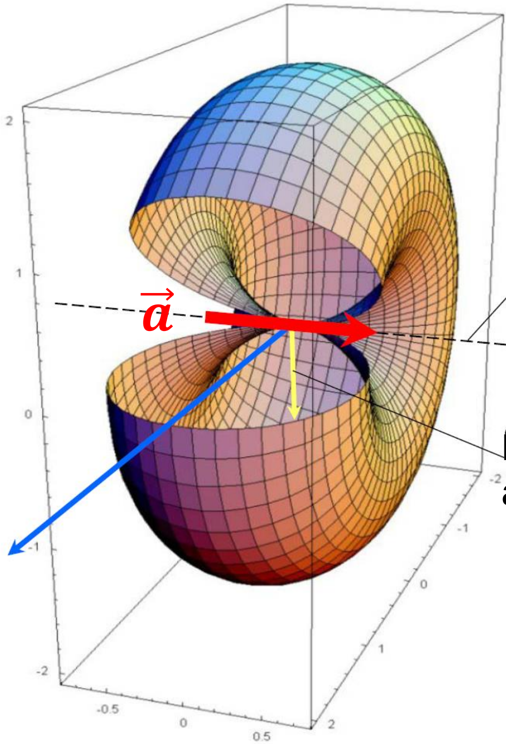
$$\beta = \sqrt{1 - \frac{1}{\gamma^2}}$$

c is the velocity of light in free space
v is the velocity of the electron
β is the relative velocity of the electron
E is the electron energy (6 GeV @ PETRA III)
E_0 is the electron rest energy (0.511 MeV)

This γ factor turns up again and again in SR !
(≈ 12 000 @ PETRA III)

Emission pattern for circular acceleration

Radiation emission in the rest frame

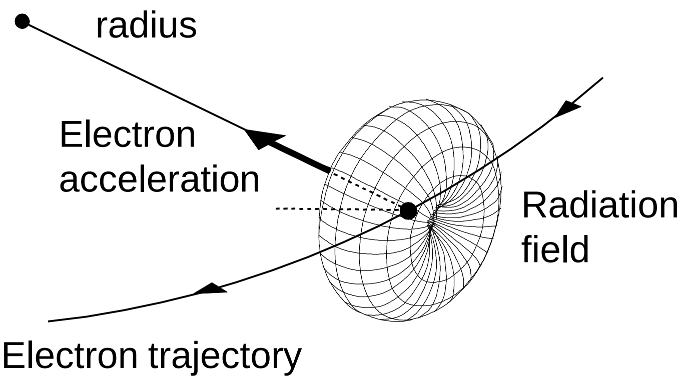


- Every accelerated charge radiates electromagnetic waves
- Oscillatory motion: No radiation in the forward-backward direction
- The maximum radiated power is observed perpendicular to the acceleration direction

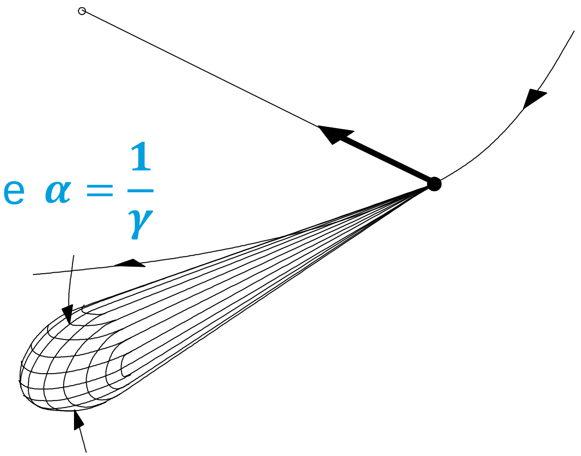
Emission pattern for circular acceleration

Laboratory frame → Forward cone emission

Rest frame — Lorentz transformation → Laboratory frame

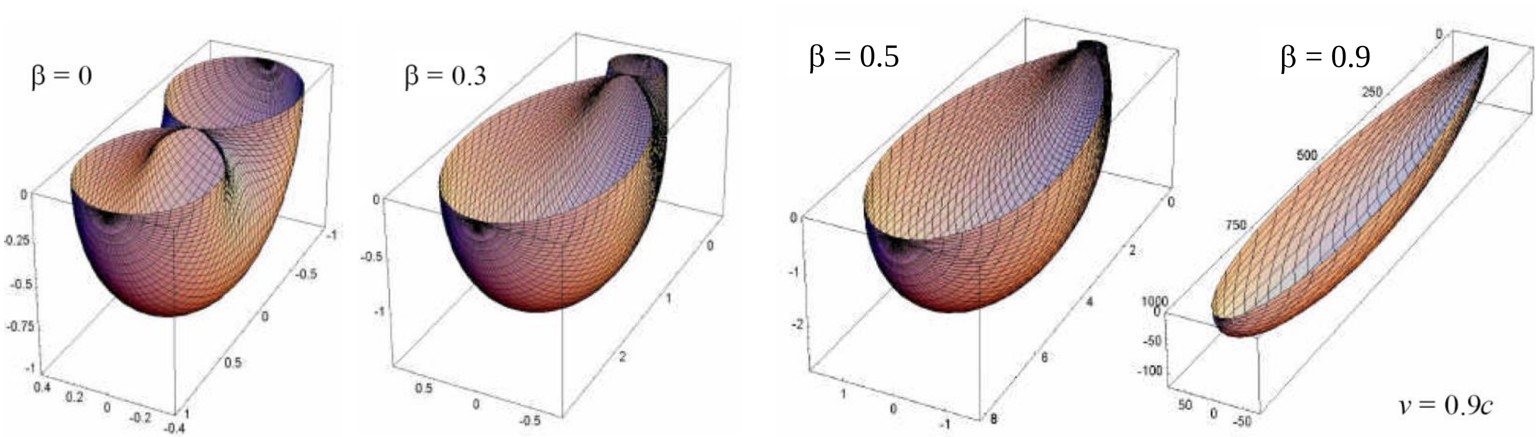


Opening angle $\alpha = \frac{1}{\gamma}$



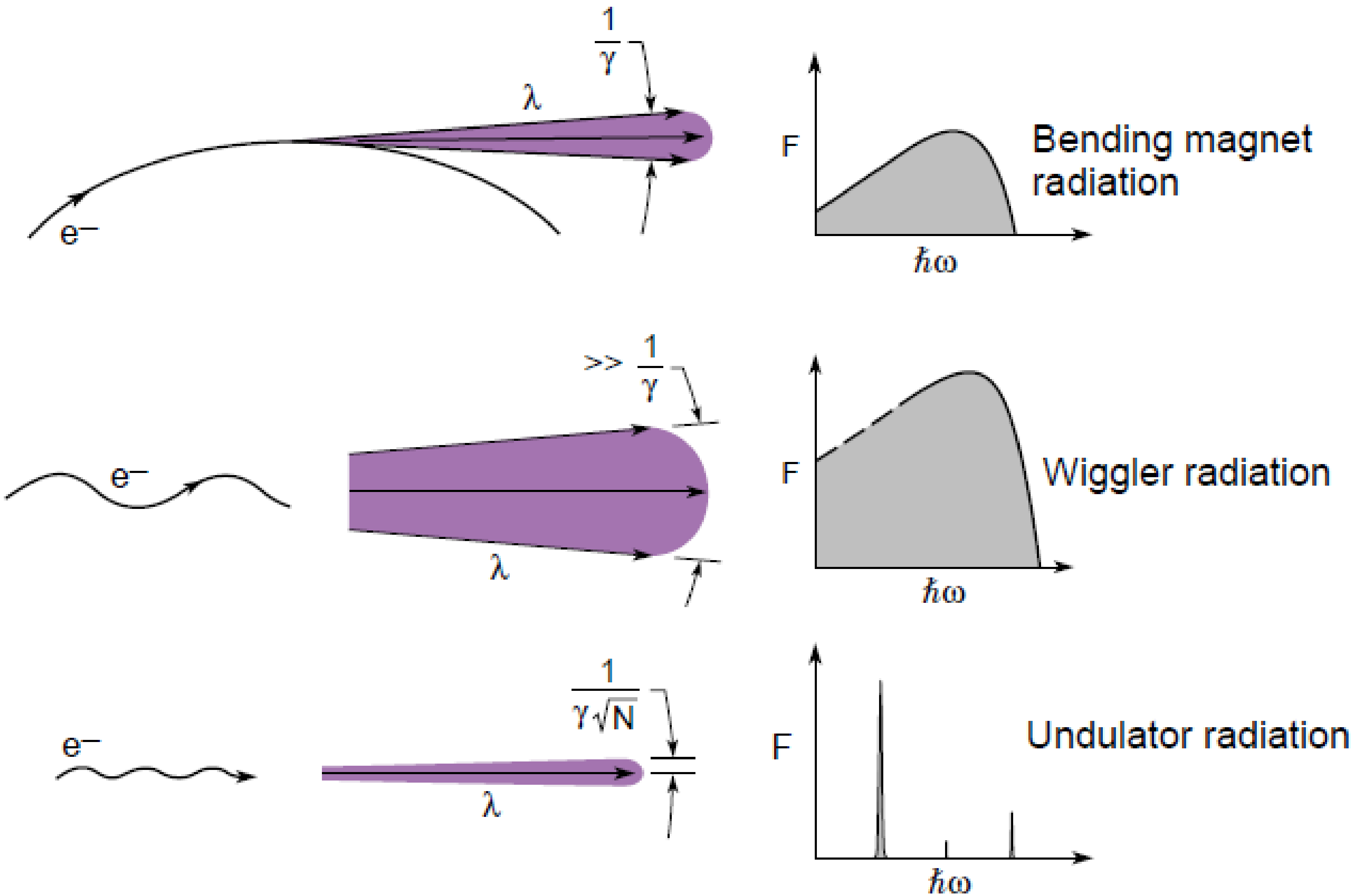
Lorentz factor: $\gamma = \frac{1}{\sqrt{1-\beta^2}} = \frac{E}{m_0 c^2}$

$\beta = \frac{v}{c}$



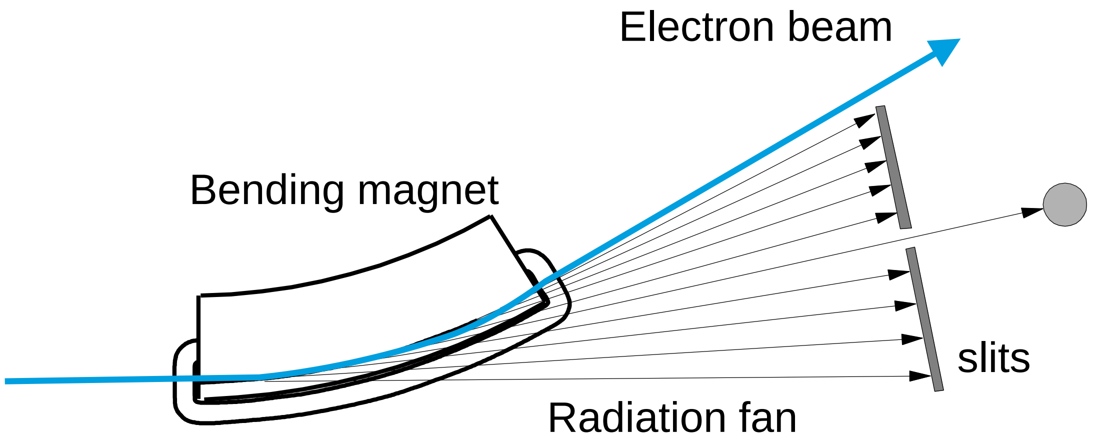
„Three types“ of radiation

Bending magnet, Wiggler, Undulator



Radiation from a bending magnet

Radiation spectrum and critical energy



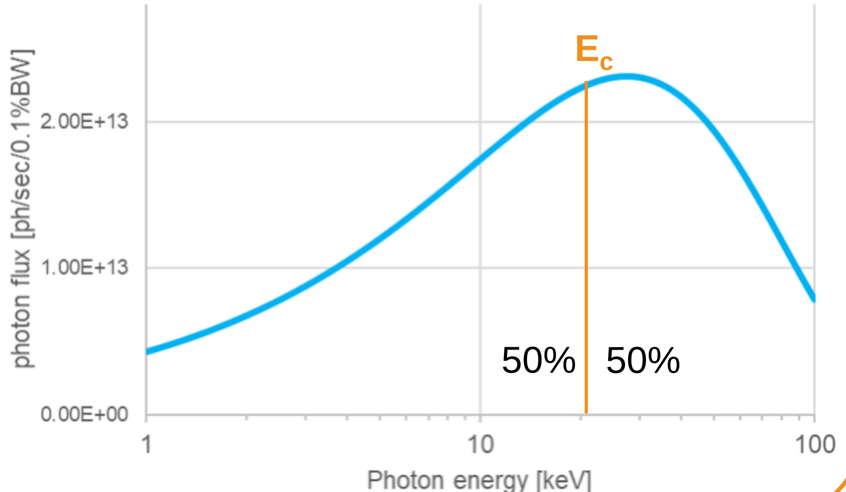
- The radiation is emitted in the plane of the orbiting particles
- The radiation is linearly polarized in the orbit plane

- Critical energy of bending magnet:

$$\boldsymbol{E_c} = \frac{3}{2} \cdot \frac{\hbar c}{E_0^3} \cdot \frac{E^3}{r} = \frac{3}{2} \cdot \frac{\hbar c^2}{E_0^3} . B . E^2$$

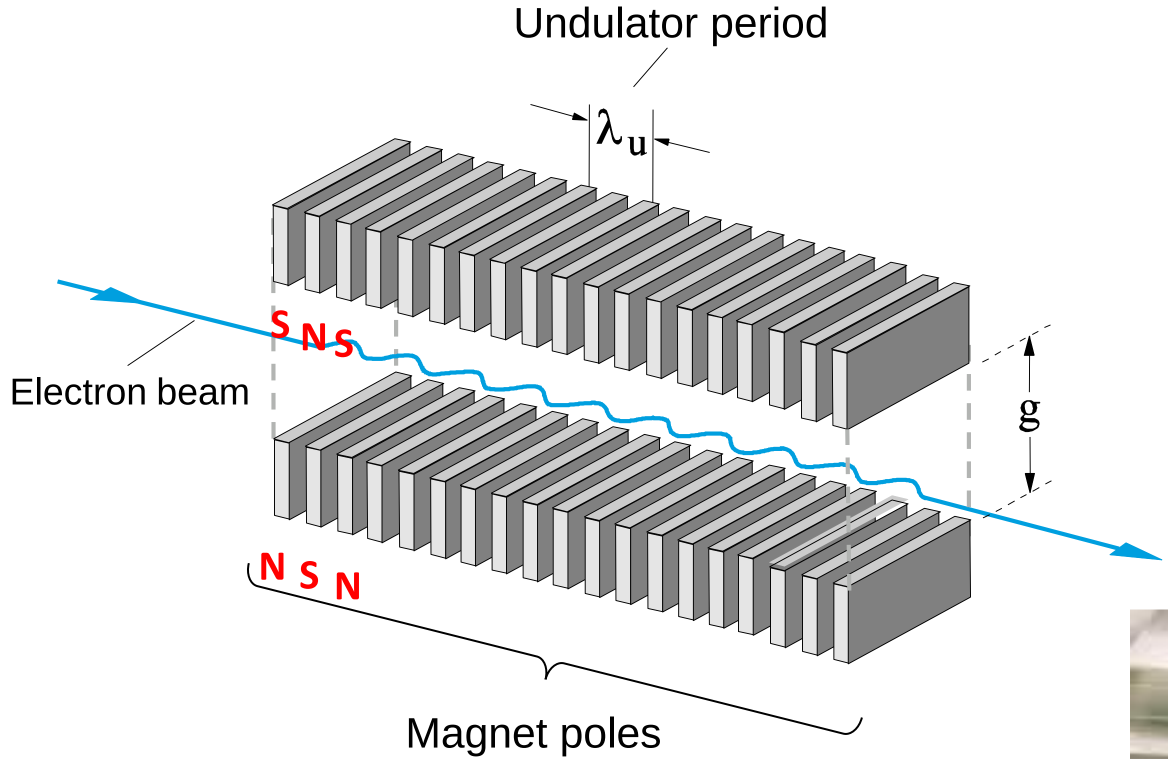
$$\boldsymbol{E_c}[eV] = 665.0255 \times B[T] \times E[GeV]^2$$

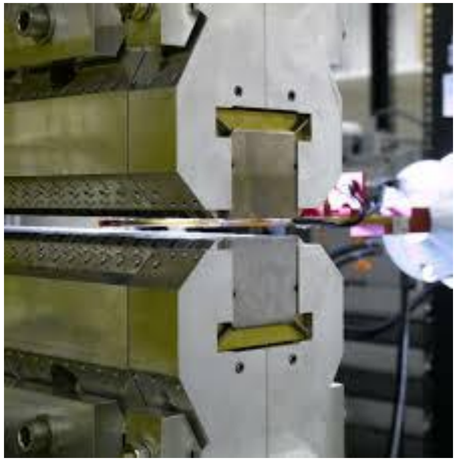
Example PETRA III bending magnet:
E = 6 GeV, B = 0.87 T (r = 22.9 m)
→ **E_c = 20.9 keV**



Insertion devices: Wigglers and Undulators

Undulation motion





- Multiplication of the radiation intensity by periodically repeated magnet structures

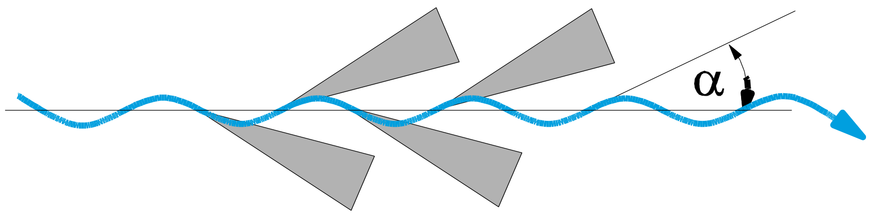
Undulator strengh parameter $K = \dfrac{eB\lambda_u}{2\pi m_e c}$

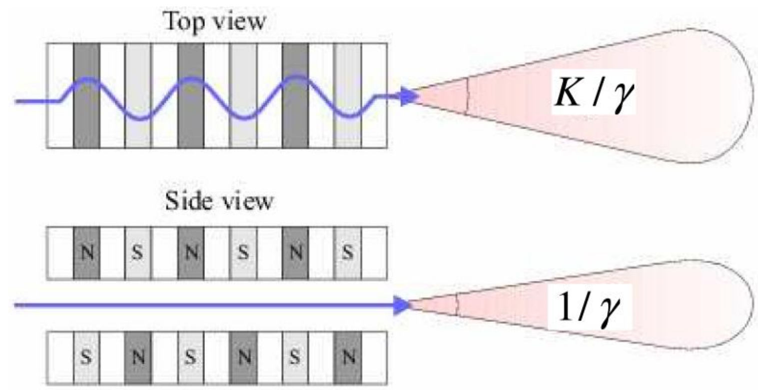
Insertion devices: Wigglers and Undulators

Energy and direction of radiation emission

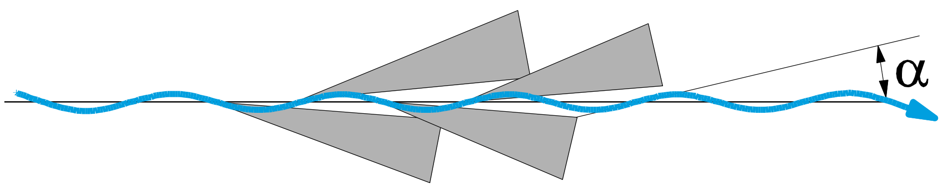
$K \gg 1$ ➔ Wiggler regime: $\alpha > 1/\gamma$

broad photon energy range



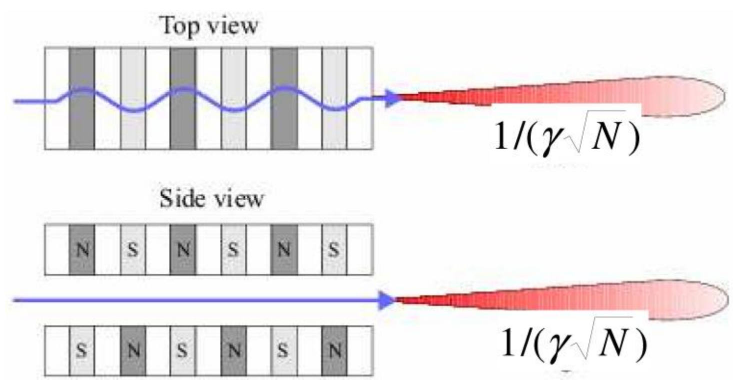


$K \ll 1$ ➔ Undulator regime: $\alpha < 1/\gamma$



$$\lambda \approx \frac{\lambda_u}{2\gamma^2}\left(1 + \frac{K^2}{2}\right)$$

and $\frac{\Delta\lambda}{\lambda} \approx \frac{1}{N}$ with N= # periods of undu



- In the undulator regime the radiation cones overlap and the wave trains can interfere constructively → increase of intensity

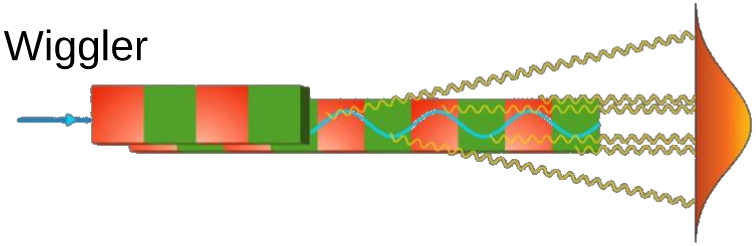
Insertion devices: Wigglers and Undulators

intensity of the emitted radiation

N_p = Number of magnet poles

N_e = Number of electrons/bunch

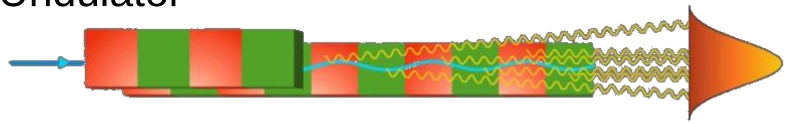
Wiggler



Incoherent superposition

$$I \sim N_e\, N_p$$

Undulator



Partially coherent superposition

$$I \sim N_e\, N_p^{\,2}$$

Quantities to describe photon intensity

Total Flux *F*
number of photons
per time and energy interval

$$[F_{tot}] = \frac{Number of\ photons}{s}$$

Spectral Flux
number of photons
per time, and energy bandwidth (BW)

$$[F] = \frac{Number\ of\ photons}{s \cdot 0.1\% BW}$$

Brilliance *B*
number of photons
per time, source area, solid angle
and energy bandwidth (BW)

$$[B] = \frac{Number\ of\ photons}{s \cdot mm^2 \cdot mrad^2 \cdot 0.1\% BW}$$

Emittance = size × divergence

$$\textbf{Brilliance} = \frac{\textbf{Flux}}{\textbf{Emittance}}$$

Peak brilliance B^{peak}
brilliance scaled to pulse duration τ

$$B^{peak} = \frac{B}{\tau \times f}$$

Degree (fraction) of lateral **coherence**

$$\frac{4\lambda^2}{Emittance} \leq 1 \Rightarrow$$

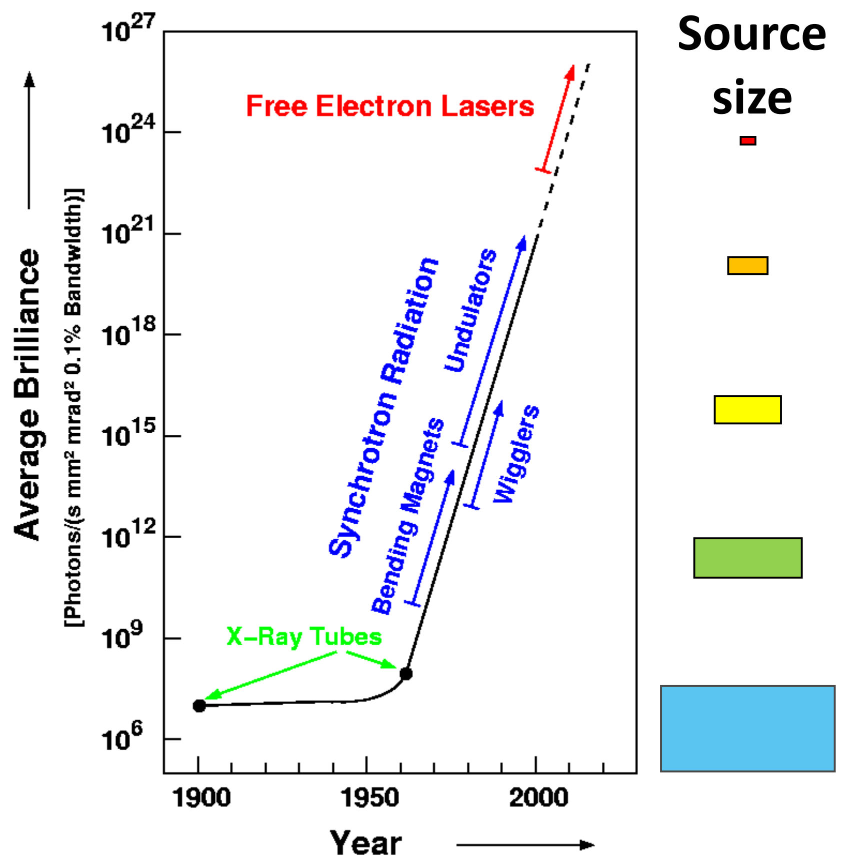
Emittance has a lower (diffraction) limit, at which the source becomes fully lateral coherent

Evolution of synchrotron radiation sources

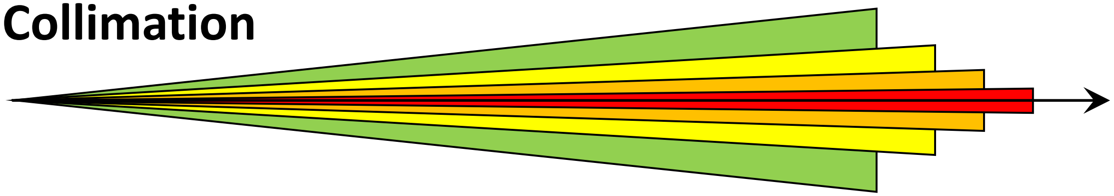
Bigger, brighter!

$$\text{brilliance} = \frac{Photon\ flux}{\sigma_x \sigma_y \sigma'_x \sigma'_y\ BW}$$

Photon flux	= photons/s
σ_x, σ_y	= transverse area from which SR is emitted
σ'_x, σ'_y	= solid angle into which the SR is emitted
BW	= bandwidth of the monochromator

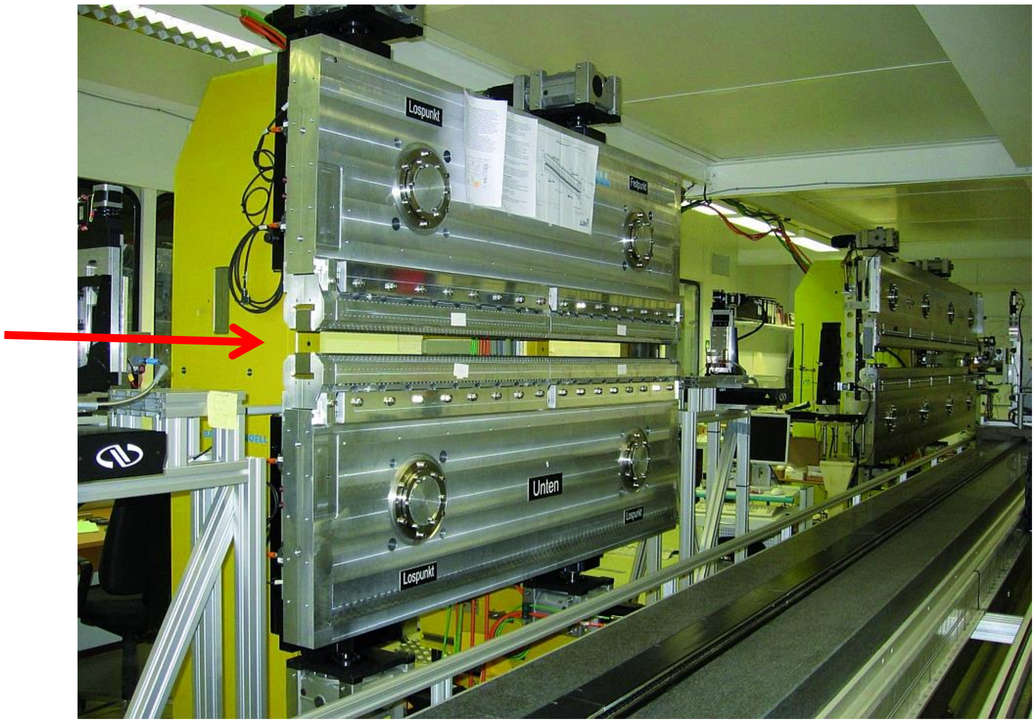


Collimation



PETRA III @ DESY

Characteristic parameters



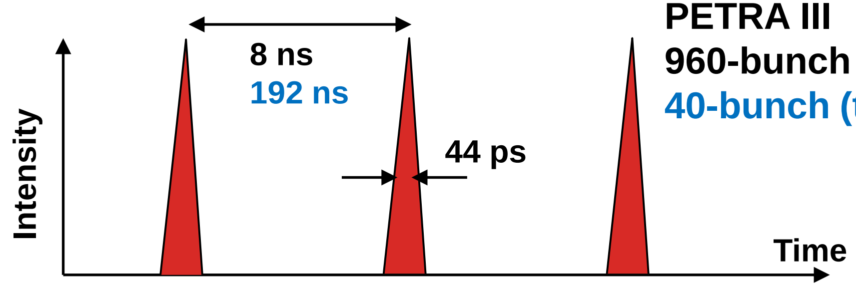
PETRA III machine parameters

Electron energy: **6 GeV**
Circumference: 2304 m
Revolution time: 7.685 µs
Number of bunches: 960, 480, 40
Bunch separation: 8, 16, 192 ns
Bunch length: 13.2 mm, **44 ps**
Total beam current: **100 mA** (top-up mode)

Horizontal emittance: **1.2 nm rad**
Vertical emittance: **0.012 nm rad**

Bending magnet field: 0.873 T
Bending magnet radius: 22.92 m
Critical photon energy: **20.9 keV**

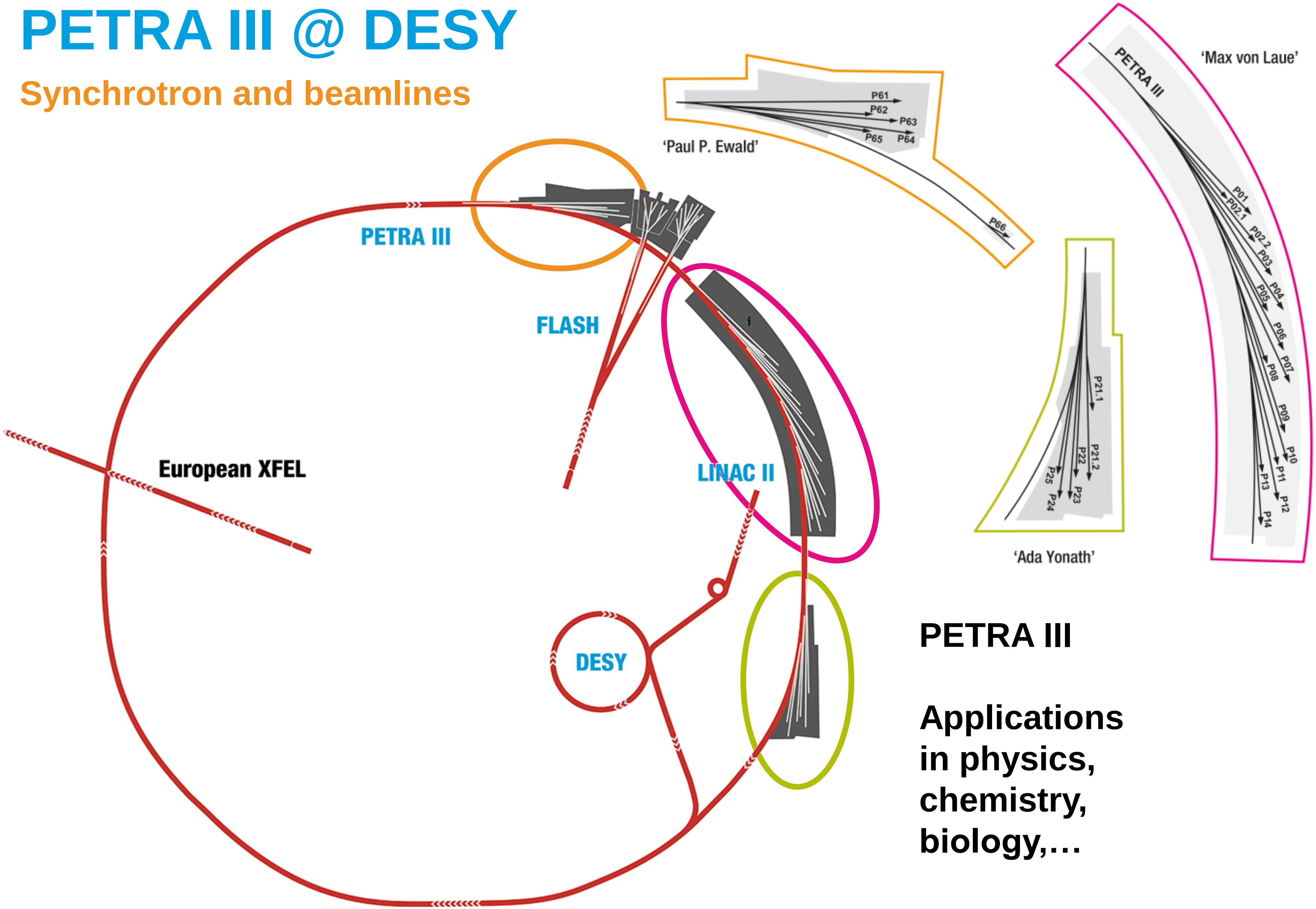
Vertical aperture of vacuum chamber: 7 mm



PETRA III
960-bunch mode
40-bunch (timing) mode

PETRA III @ DESY

Synchrotron and beamlines



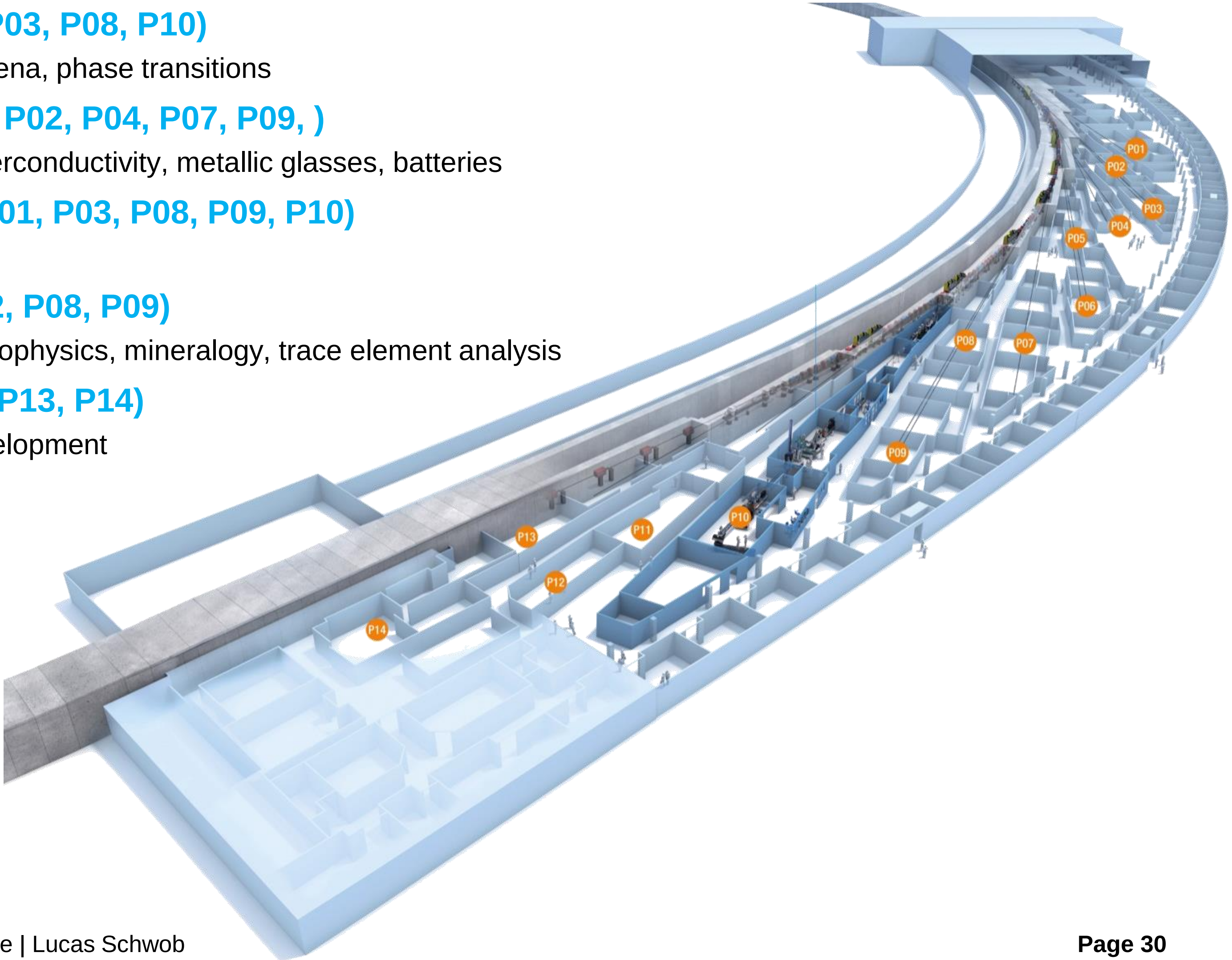
PETRA III

Applications in physics, chemistry, biology,…

PETRA III Facilities

Max von Laue hall

- **Atomic and molecular science (P04)**
- **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)**
  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



PETRA III Facilities

Max von Laue hall

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 ion and photoelectron spectroscopy

P05: **Imaging beamline**
5- 50 keV, Phase- and absorption contrast imaging, tomography

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

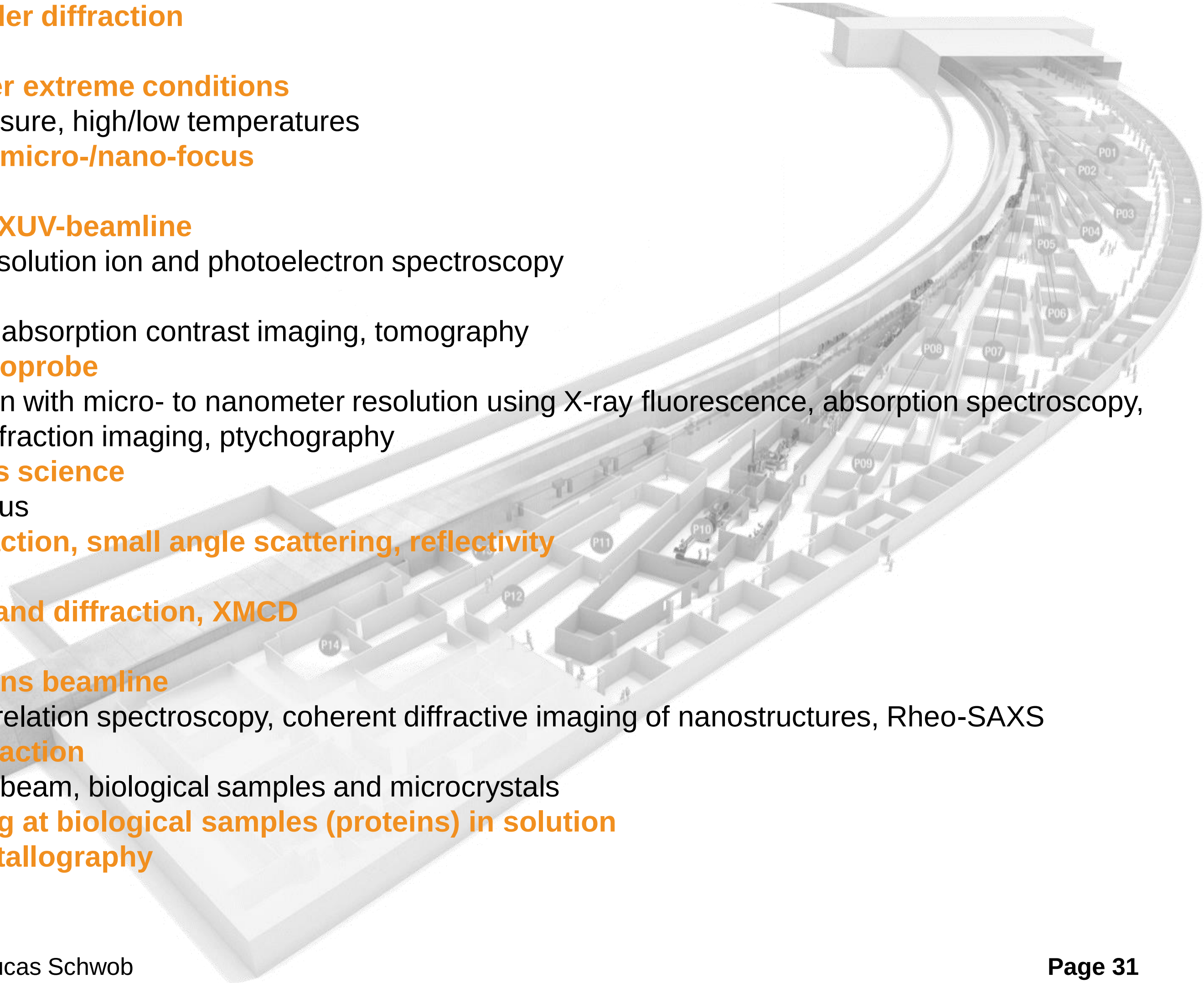
P09: **Resonant scattering and diffraction, XMCD**
2.7 - 50 keV

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**

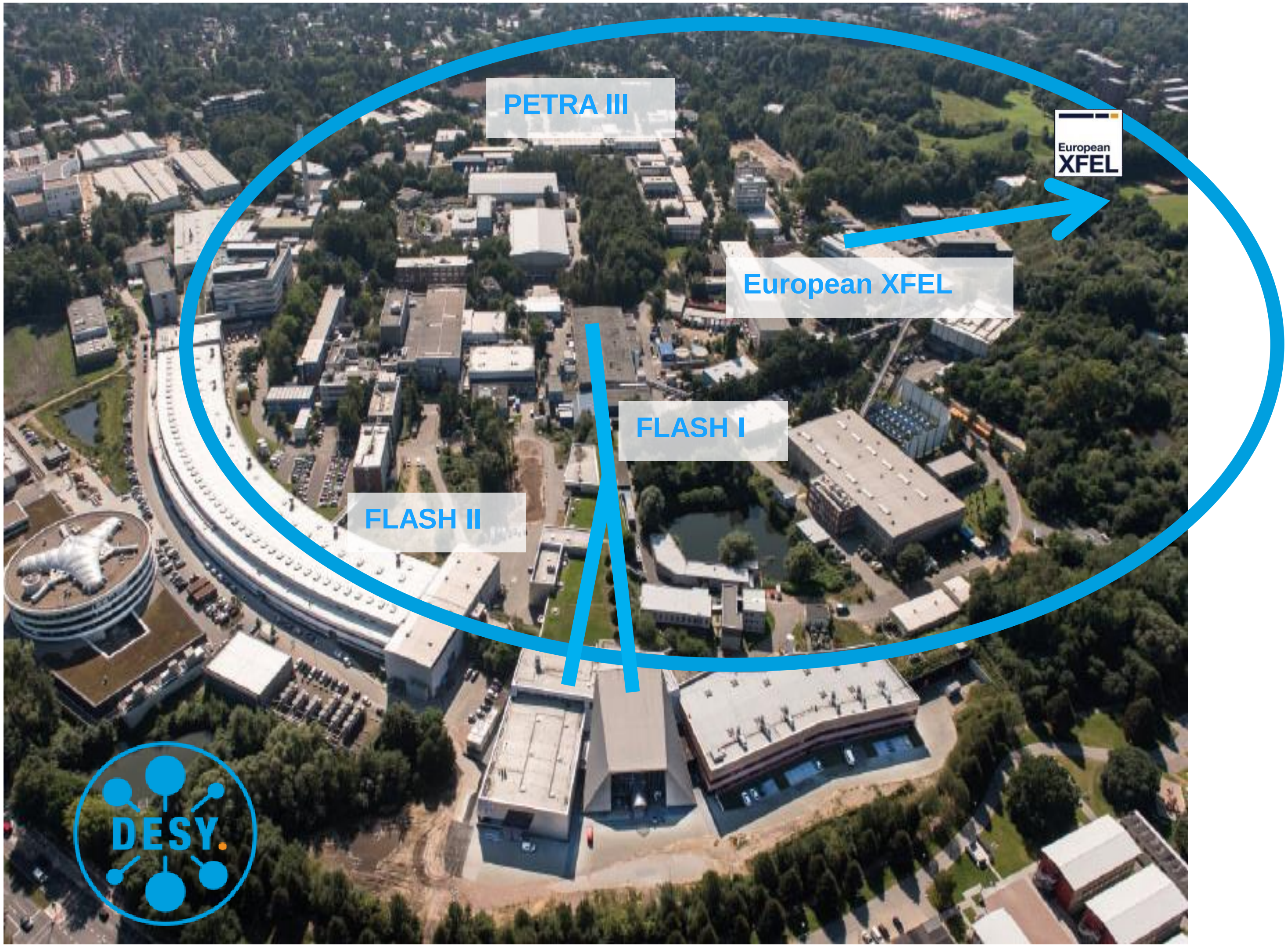
P13/P14: **Macromolecular crystallography**



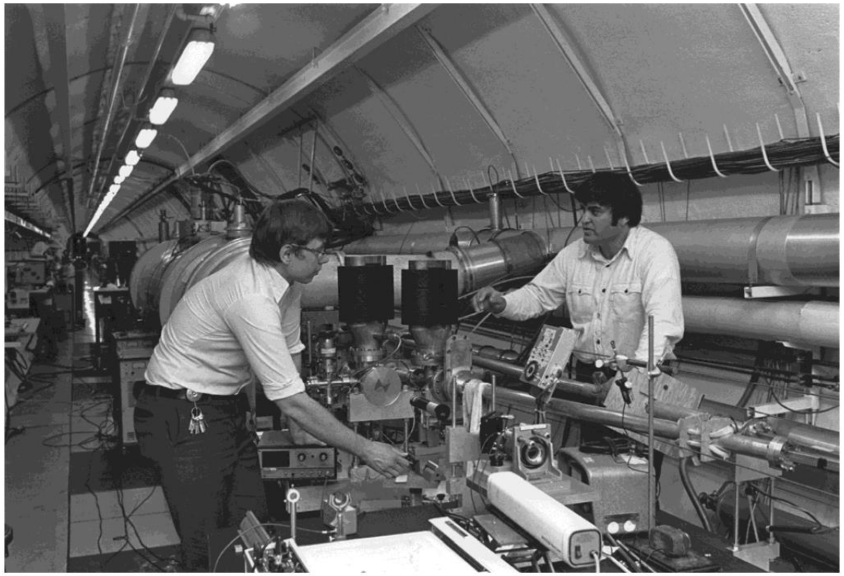
Principle of Free-electron Lasers

FELs at DESY

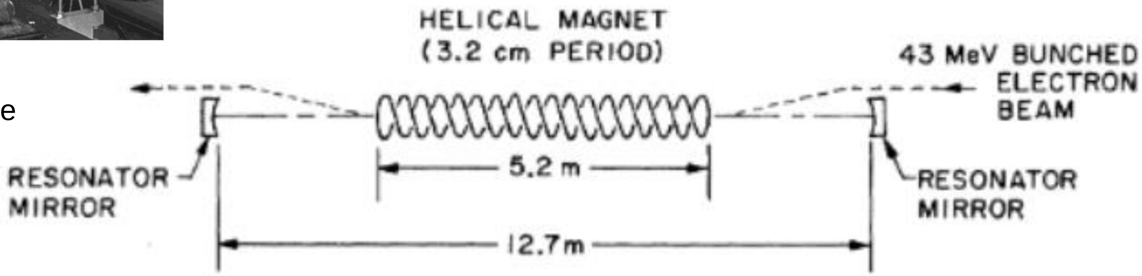
FLASH and euXFEL



Invention of free-electron laser



John Madey and Luis Elias working inside the Superconducting Acceleration (SCA) tunnel with the FEL equipment, Stanford University, 1995



FEL was theorized by John Madey in his Ph.D. thesis, Stanford 1970:
J.M.J. Madey, J. Appl. Phys. 42, 1906 (1971)

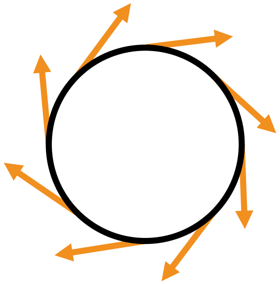
First realization: Stanford, Electron energy: 43.5 MeV, FEL radiation: 3.4 µm
D.A.G. Deacon, L.R. Elias, J.M.J. Madey, G.J. Ramian, H.A. Schwettman, T.I. Smith; Phys. Rev. Lett. 38, 892 (1977)

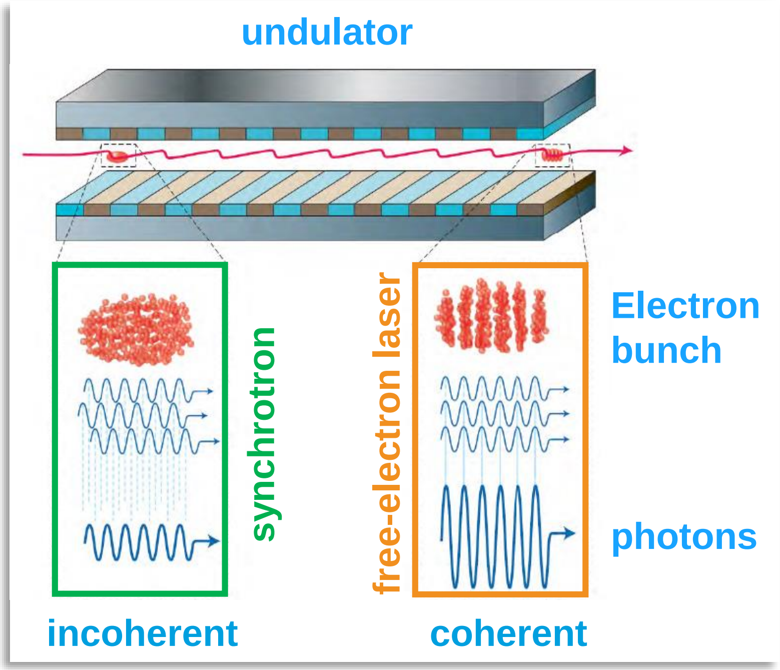
Free-electron lasers (FELs)

Differences with a synchrotron?

Synchrotrons

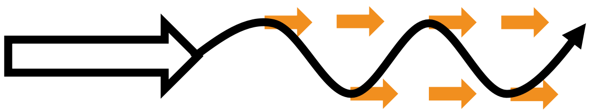
- Electrons traveling in a wide circular path, emitting light as they change directions
- Light is UV or X-ray, but not (fully) coherent
- Multiple users





Free-electron lasers

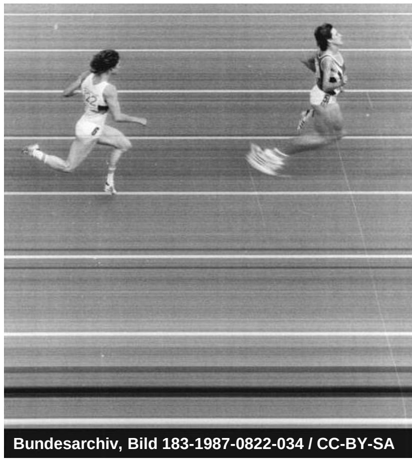
- Electrons accelerated in a straight line and manipulated to generate light
- **Light is coherent and intensely bright in very <u>short pulses</u>**
- Single user



Courtesy European XFEL

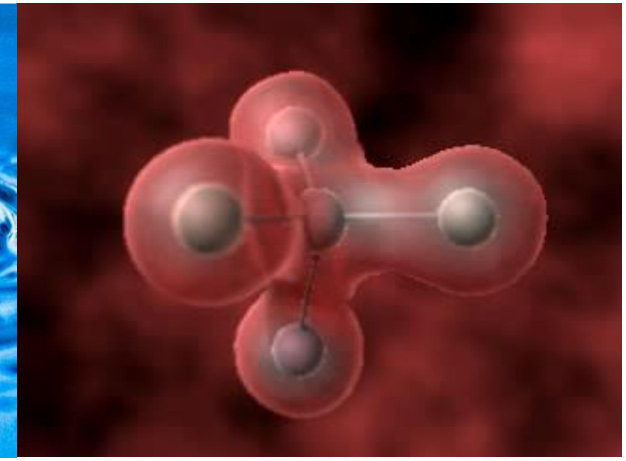
…high photon flux at very short times…

How to image faster and smaller processes?



Bundesarchiv, Bild 183-1987-0822-034 / CC-BY-SA

Shan Sheehan/CC-BY-2.0

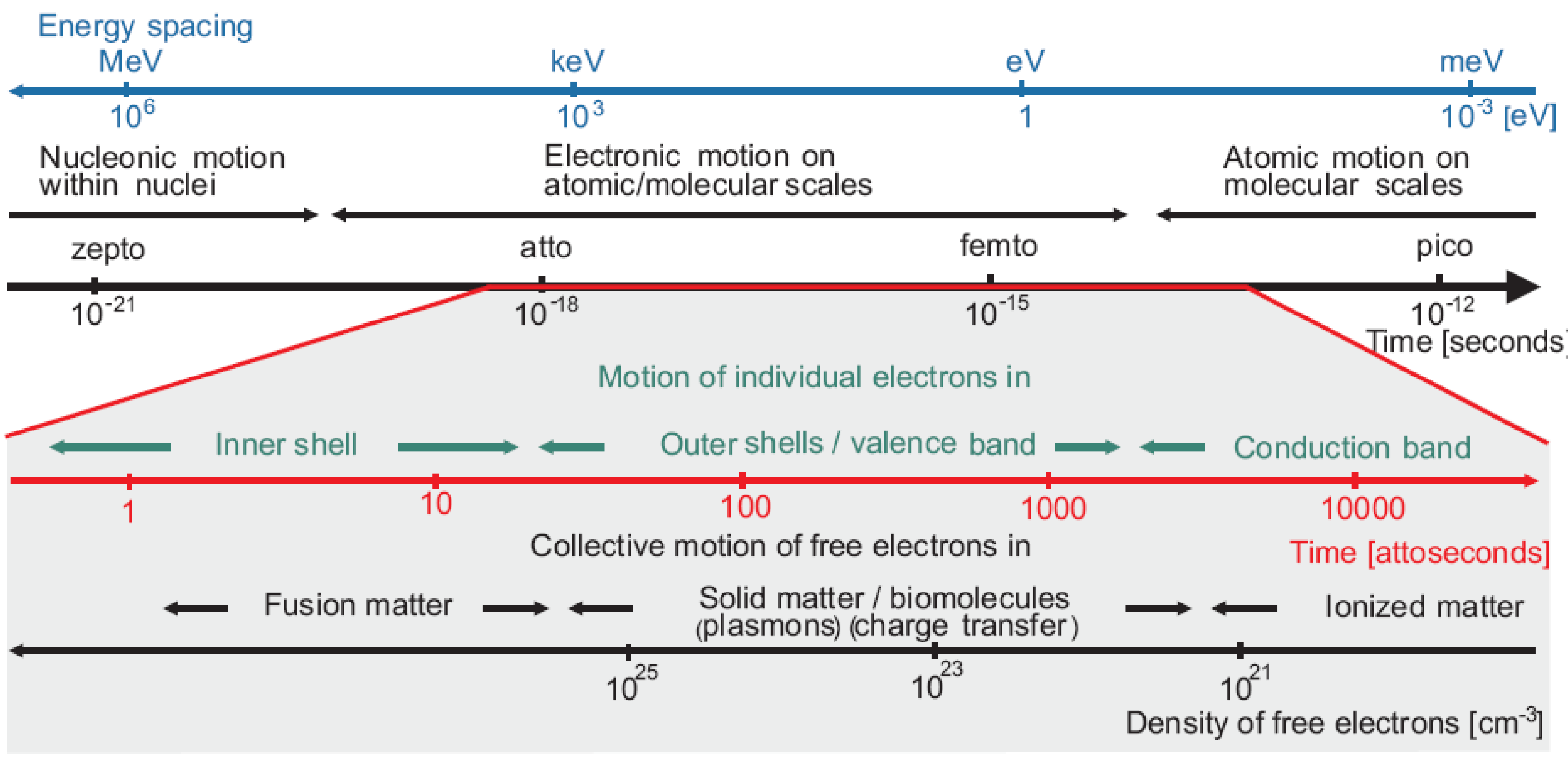


Speed of subject	10 m/s	1000 m/s	1000 m/s (rattling speed of atoms)
Picture resolution	10 mm	1 mm	1/10 000 000 mm
Time resolution	1/1000 s = 1 ms	1/1 000 000 s = 1 µs	1/10 000 000 000 000 s = 100 fs

Courtesy European XFEL

The science of electrons in motion

Time scales

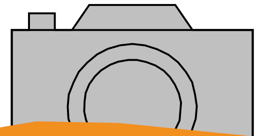


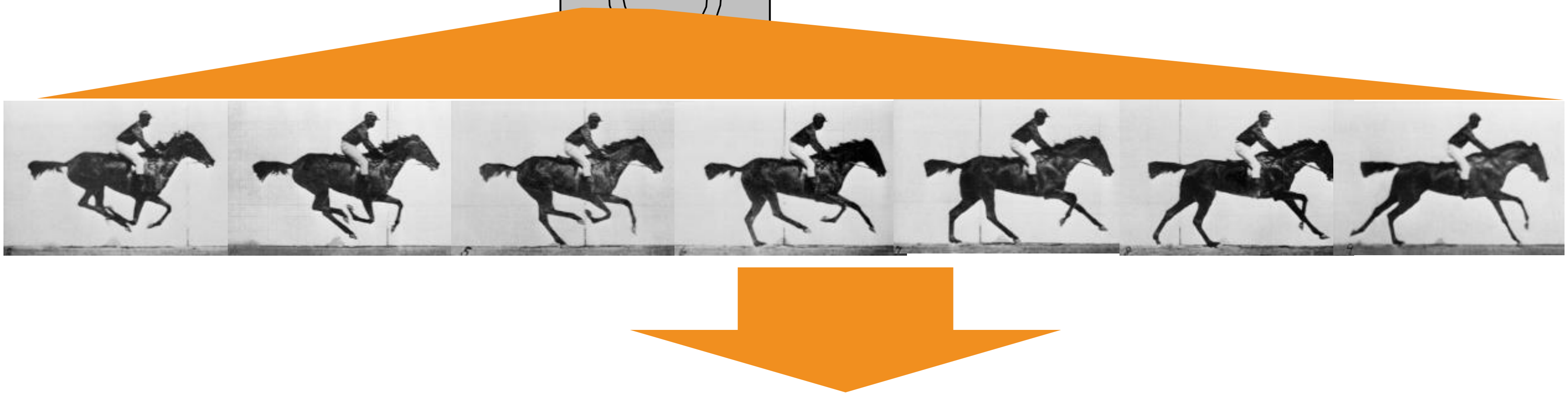
F. Krausz, M. Ivanov
Review of Modern Physics **81**, 163 (2009)

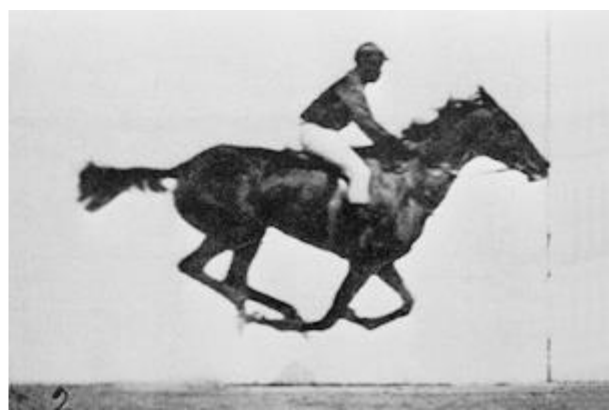
The science of electrons in motion

Making molecular movies

Eadweard Muybridge
1880‘s





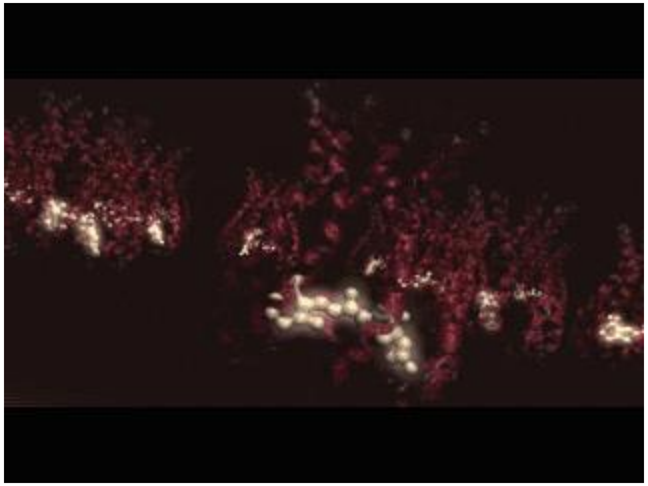


Courtesy European XFEL

The science of electrons in motion

Making molecular movies

European XFEL



Courtesy European XFEL

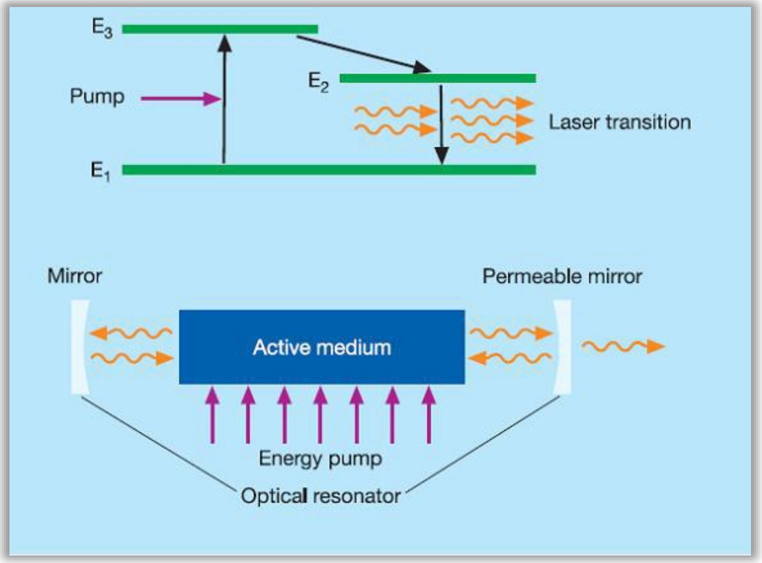
Free-electron laser vs. conventional laser

- **Laser:**
  amplification due to stimulated emission of electrons bound to atoms (crystal, liquid dye, gas)

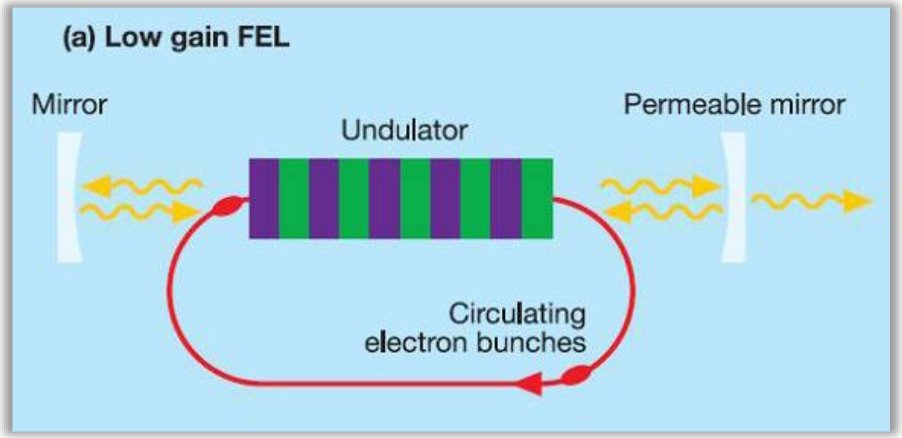
- **FEL:**
  amplification / gain medium = „free“ (unbound) electrons, stripped from atoms in an electron gun, accelerated to relativistic velocities and travelling through an undulator (= periodic magnetic multipole structure) to produce intense radiation

Free-electron laser vs. conventional laser

- **Laser:**
  - Quantized energy levels
  - Pump energy initiates population inversion
  - Stimulated emission
  - Optical resonator (cavity)



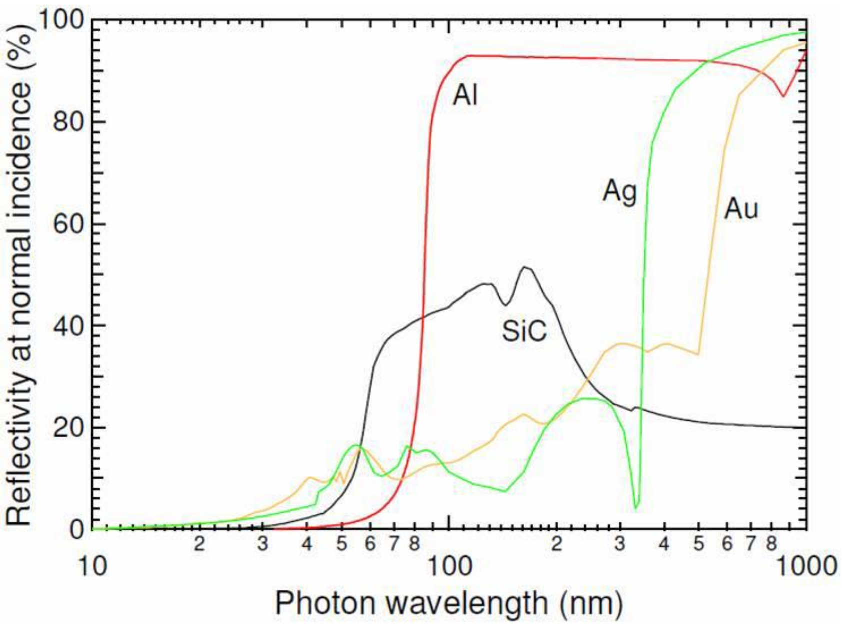
- **FEL:**
  - Electron energy is not quantized
  - ”Pump energy” is the kinetic energy of the electrons
  - Stimulated emission
  - Optical cavity or single pass SASE (Self-Amplified Spontaneous Emission)



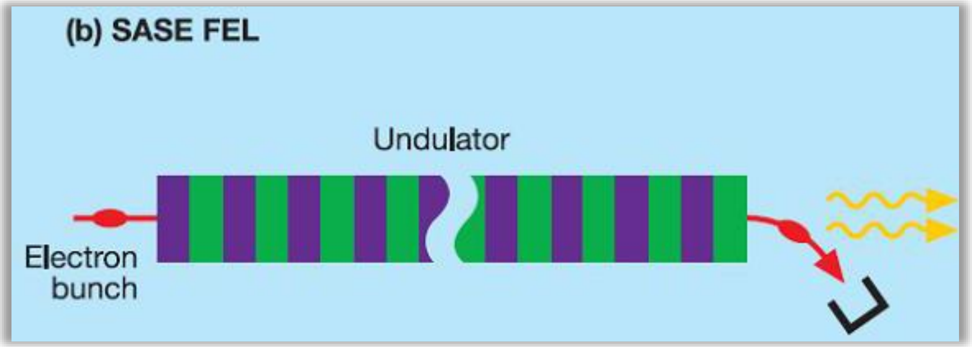
Free-electron laser at short wavelength

Optical cavity or single pass SASE

- Optical cavity does not work for wavelength λ < 100nm
  (low reflectivity, radiation damage)

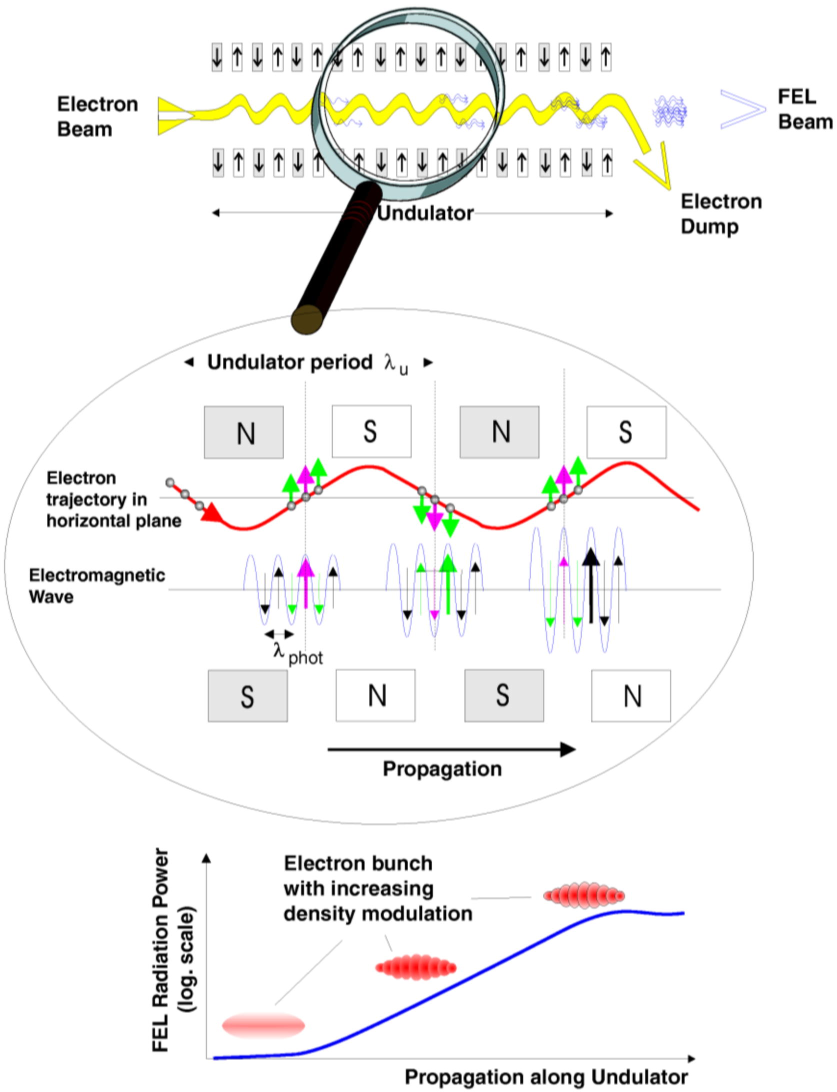


- → single pass SASE FEL
  - Undulator radiation produced in 1st section,
    amplified in later section



Self-amplified spontaneous emission – SASE

Electron micro-bunching



- Slippage between electrons and photons is λ_{photon} per undulator period
- Electrons in phase with e.m.-wave are retarded ("emit photons"), electrons with opposite phase gain energy ("absorb photons")
- Different trajectories in the undulator (see Lorentz force)
- Longitudinal charge density modulation ("micro-bunching") with periodicity equal to λ_{photon}
- Self-amplification of spontaneous emission due to increasingly coherent emission from micro-bunches

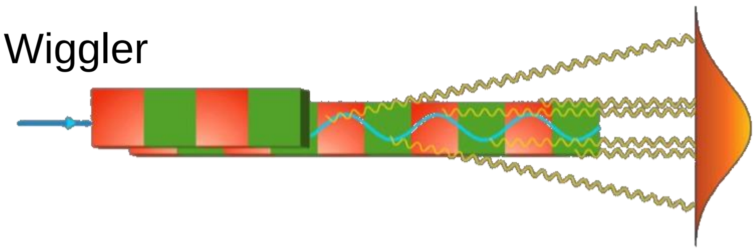
Insertion devices: Wigglers and Undulators

intensity of the emitted radiation

N_p = Number of magnet poles

N_e = Number of electrons/bunch

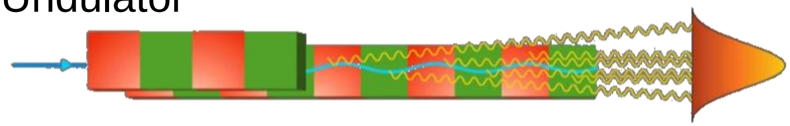
Wiggler



Incoherent superposition

$$I \sim N_e\, N_p$$

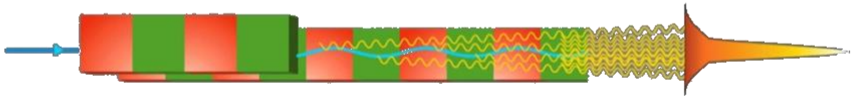
Undulator



Partially coherent superposition

$$I \sim N_e\, N_p^{2}$$

Free-Electron Laser



Fully coherent superposition

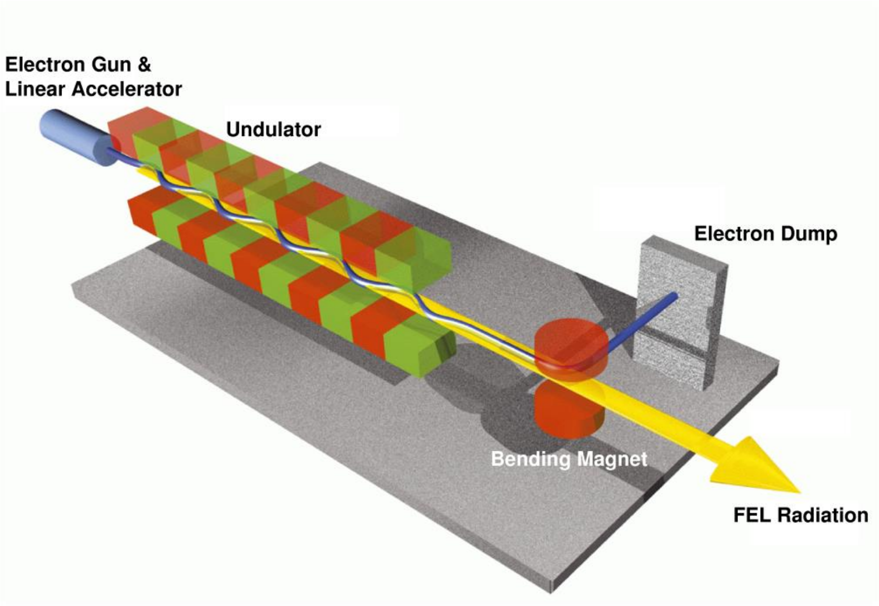
$$I \sim N_e^{2}\, N_p^{2}$$

Self-Amplified Spontaneous Emission (SASE)

Self-amplified spontaneous emission – SASE

Requirement for SASE

- Good electron beam quality and sufficient overlap between electron-beam and radiation pulse along the undulator:
  - **low emittance, low energy spread of electron beam**
  - **extremely high charge density (kA peak currents)**
  - **precise magnetic field of undulator**
  - **accurate beam steering through undulator (few µm precision)**



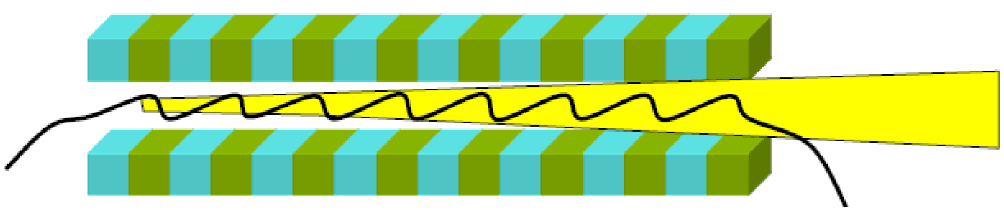
Self-amplified spontaneous emission – SASE

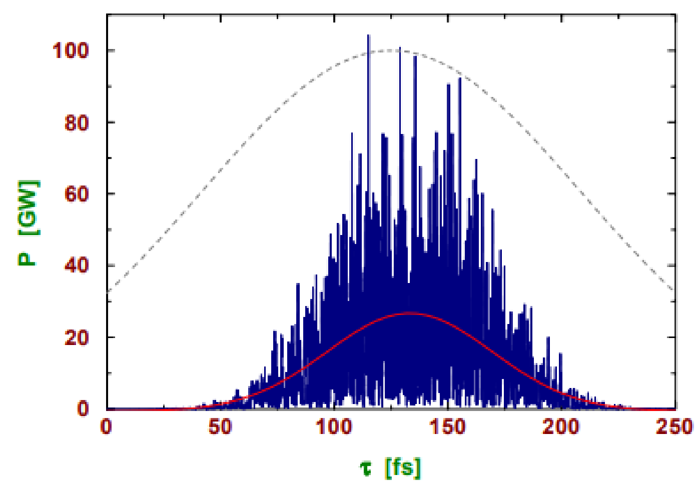
Emitted light, temporal distribution

- For a given wavelength there is only one resonant electron energy (continuous energy transfer)

$$\lambda_l = \frac{\lambda_u}{2\gamma^2}\left(1 + \frac{K^2}{2}\right)$$

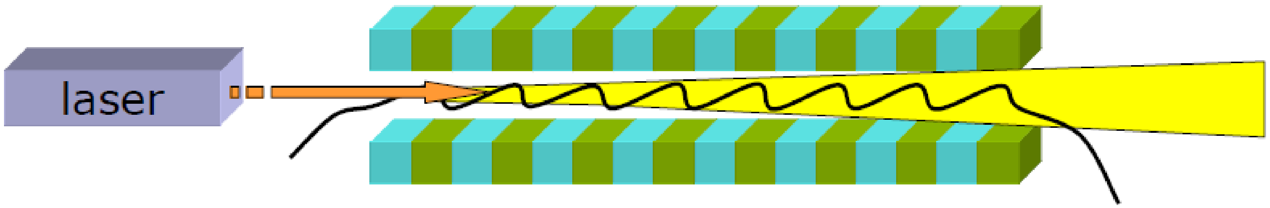
- Wavelength change by changing the electron energy or magnetic field strength
- FEL process starts from noise: randomly distributed electron bunch and spontaneous undulator radiation
- Radiation pulse is “spiky” in time (and frequency) domain



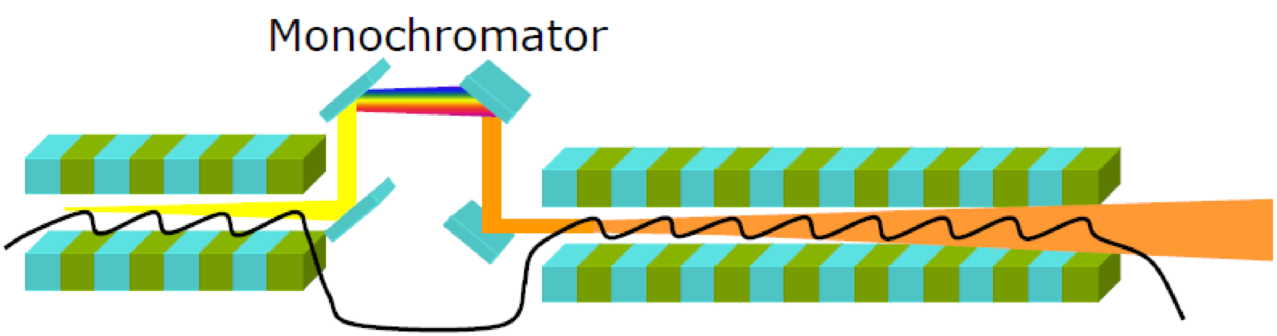


Seeding an FEL

Overcoming temporal incoherence



- External laser seeding



- Self-seeding

SASE FEL properties

summary

- high intensity (GW peak power)
- coherence (laser-like radiation)
- femtosecond pulses
- narrow bandwidth
- full wavelength tunability
- down to X-rays

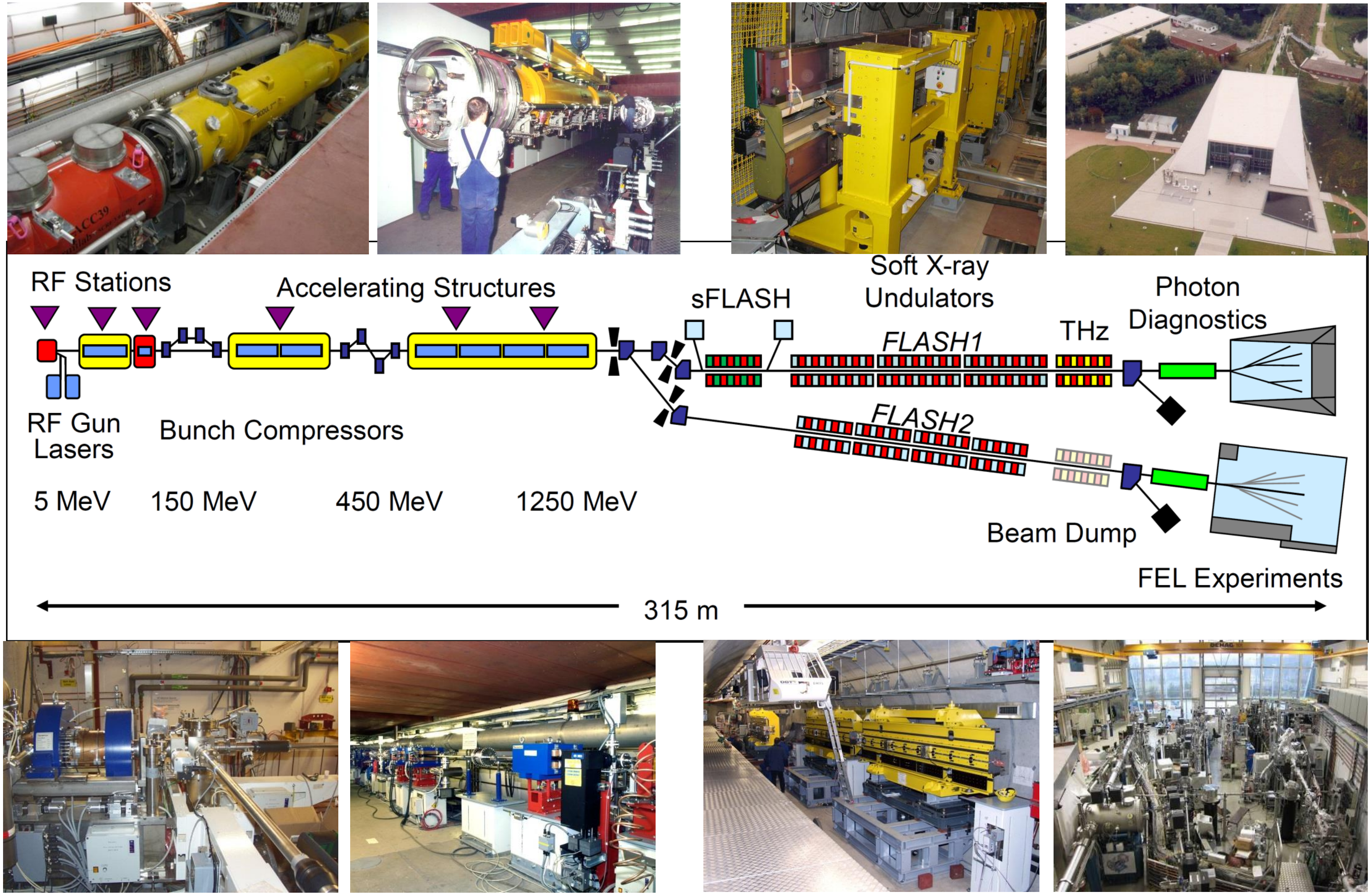
- but: shot-to-shot fluctuations (without seeding)

  → very good photon diagnostics are mandatory!

X-ray free-electron lasers worldwide

Courtesy European XFEL

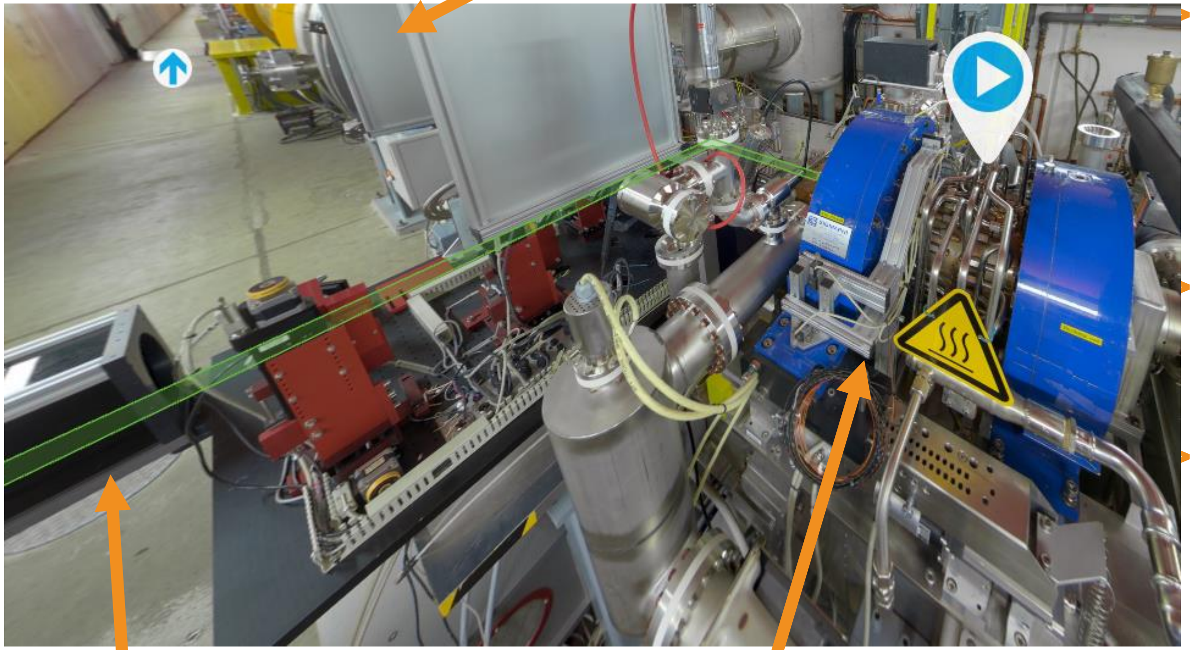
The FLASH facility



Injector: creating bunches of electrons

Laser-driven photocathode RF gun

To acceleration modules



Optical laser

RF gun cavity

- Optical laser strikes Cs_2Te photocathode, releasing a cloud of electrons (1-3% quantum efficiency)
- RF field accelerate bunch to 5-6 MeV into the main electron accelerator
- Electrons move into a magnetic field, 1 1/2-cell resonator, shaping into a bunch with almost parallel trajectories

Injector: creating bunches of electrons

Laser-driven photocathode RF gun

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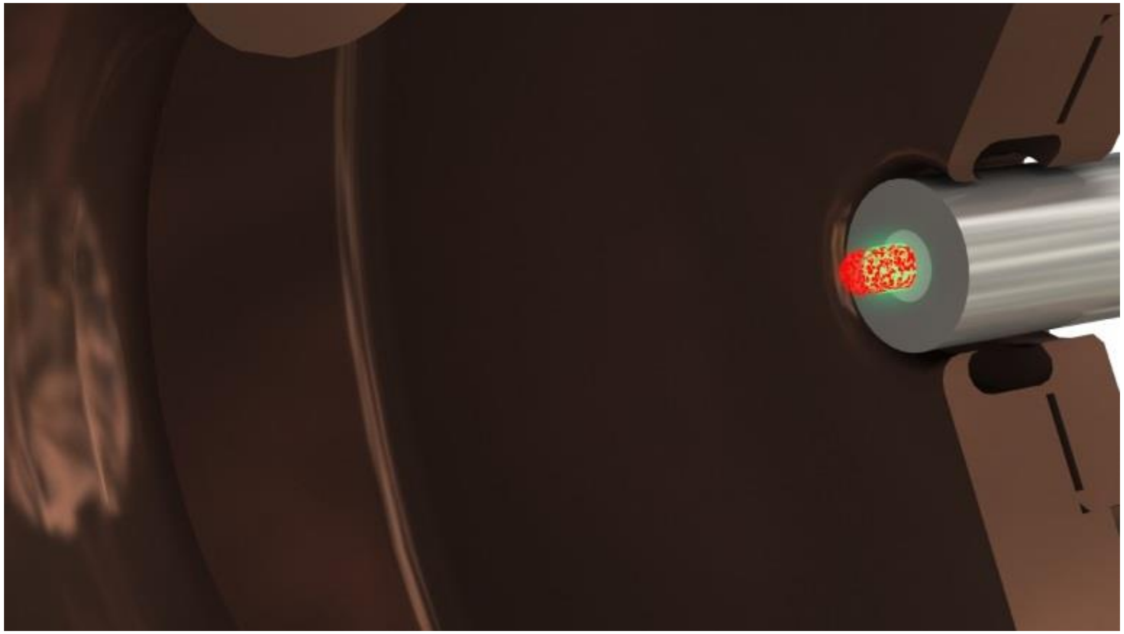
Injector: creating bunches of electrons

Laser-driven photocathode RF gun



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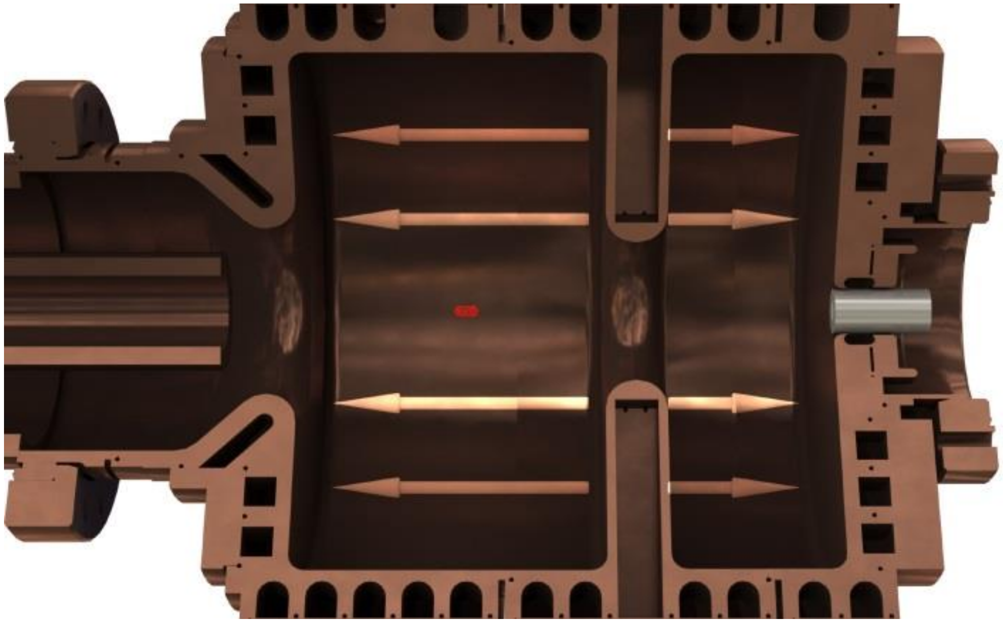

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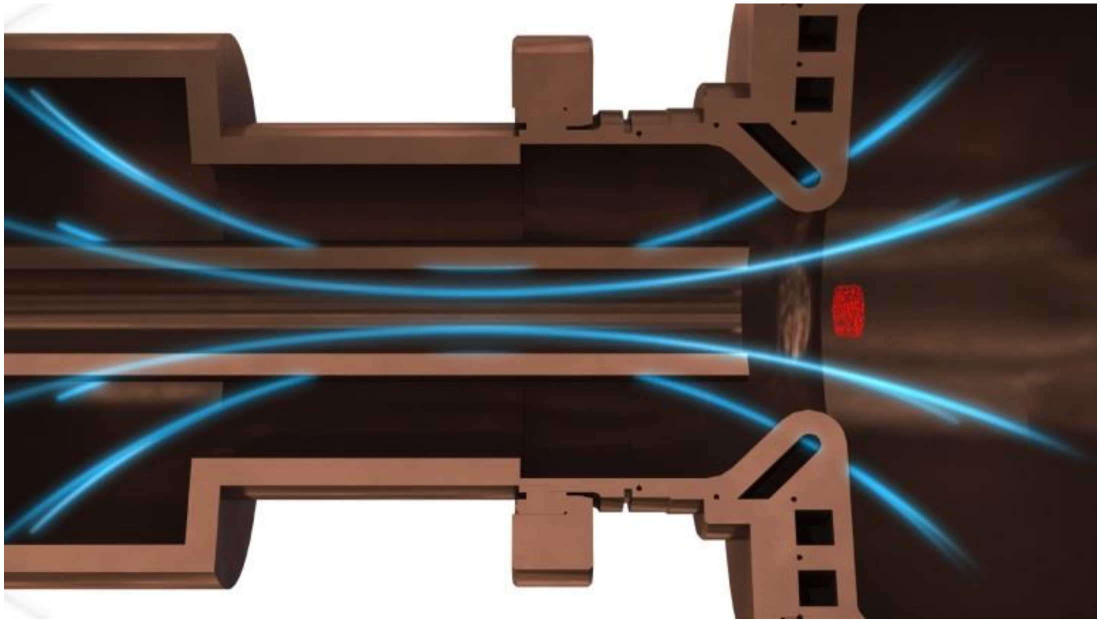

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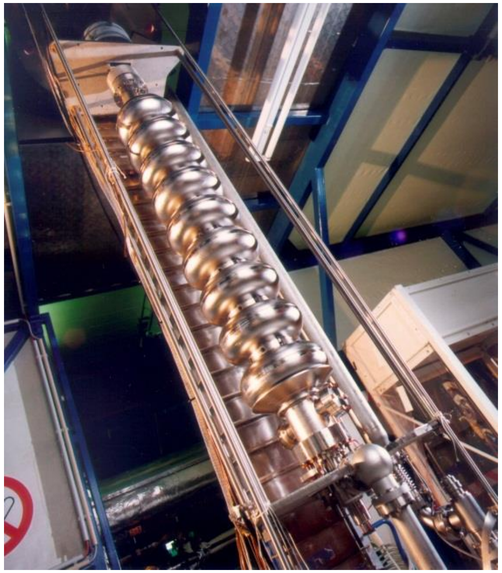
Superconducting accelerator module

LINAC RF module

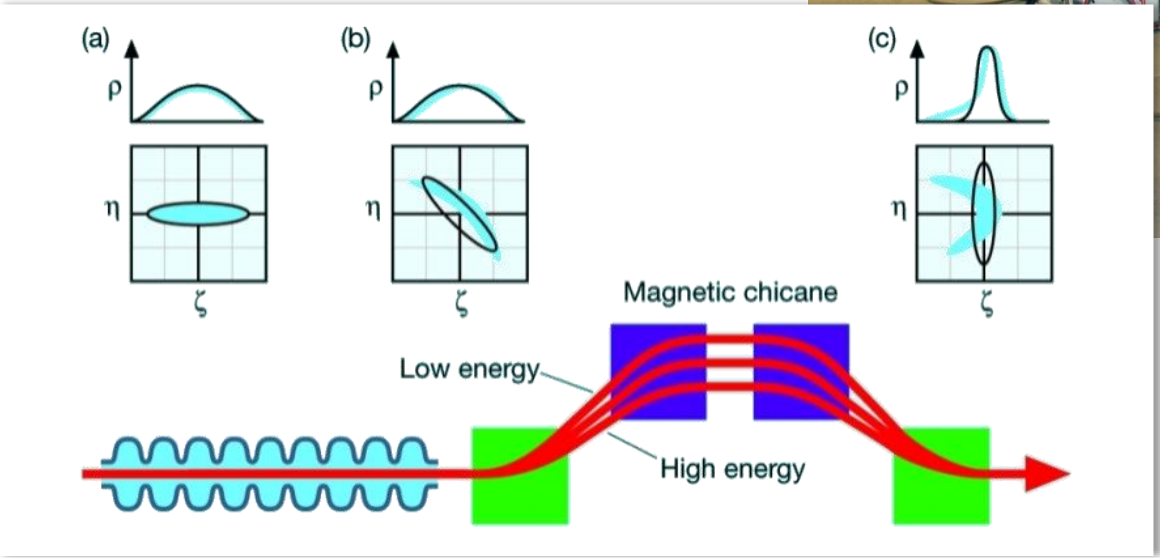


- 7 Accelerator RF modules with superconducting niobium cavities
- Up to 1.25 GeV
- Length: 12 m
- Weight: about 10 tons

Electron bunch compression

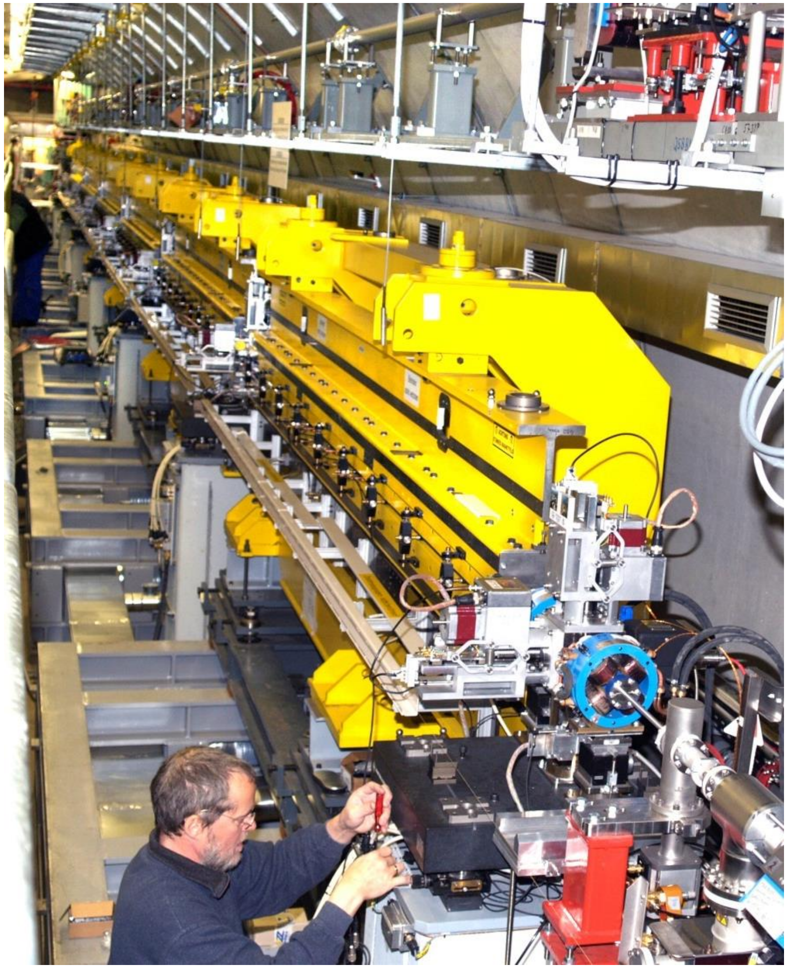
Increase of electron peak current

- electromagnetic chicane (4 dipole magnets)
- longitudinal compression of electron bunches
- ~1-2 mm → 0.1 mm
  70 A to >1 kA peak current



Undulators

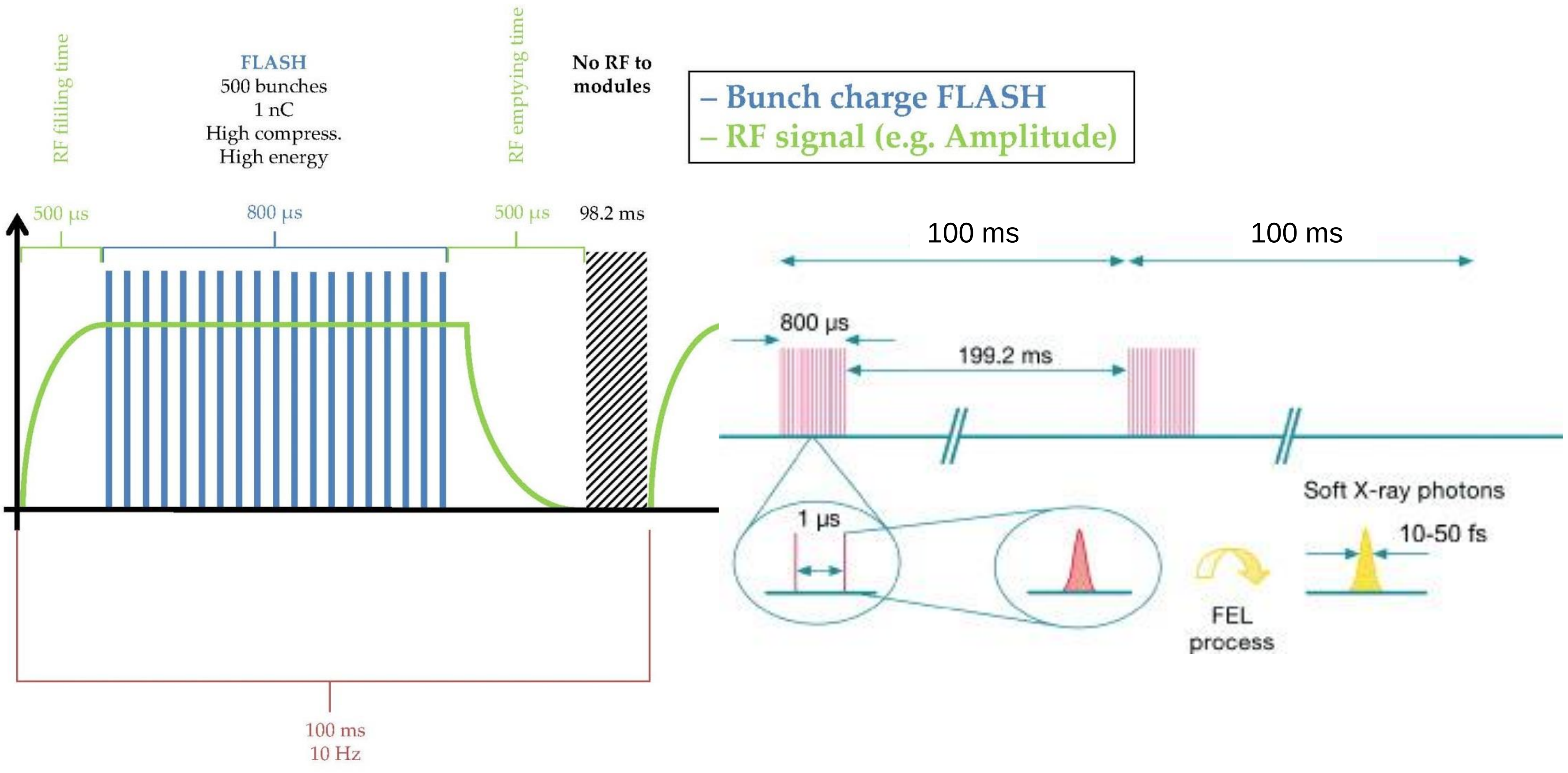
FEL = long undulator



- 6 x 4.5 m undulators → 27m !
- 12 mm fixed gap → tuning with accelerator
- $\lambda_u = 27.3\ mm$ → $4 < \lambda_{ph} < 120\ nm$
- Intersections with quadrupole doublets for focusing electron beam, electron beam diagnostics and steerer coils

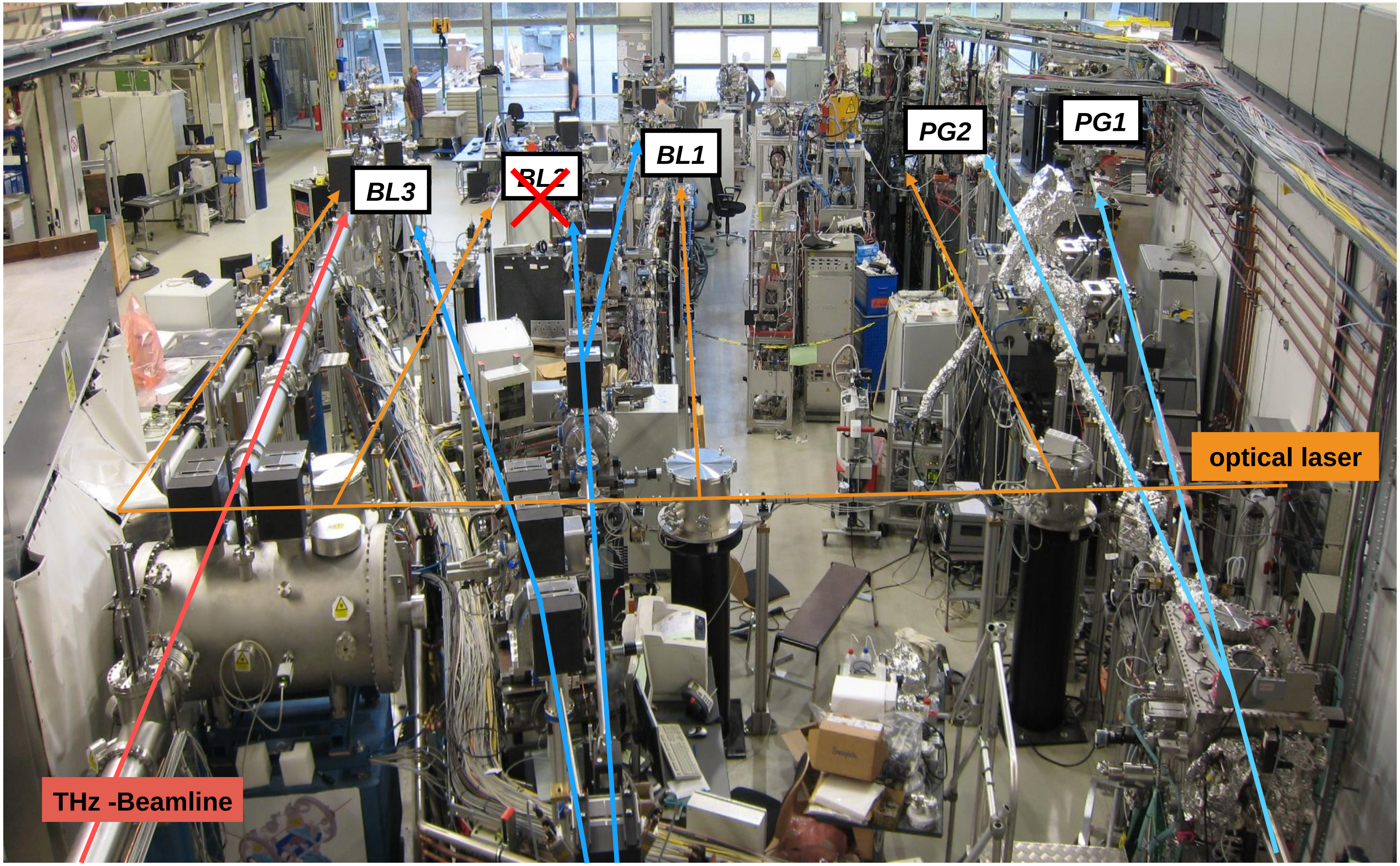
Superconducting accelerator module

bunch structure

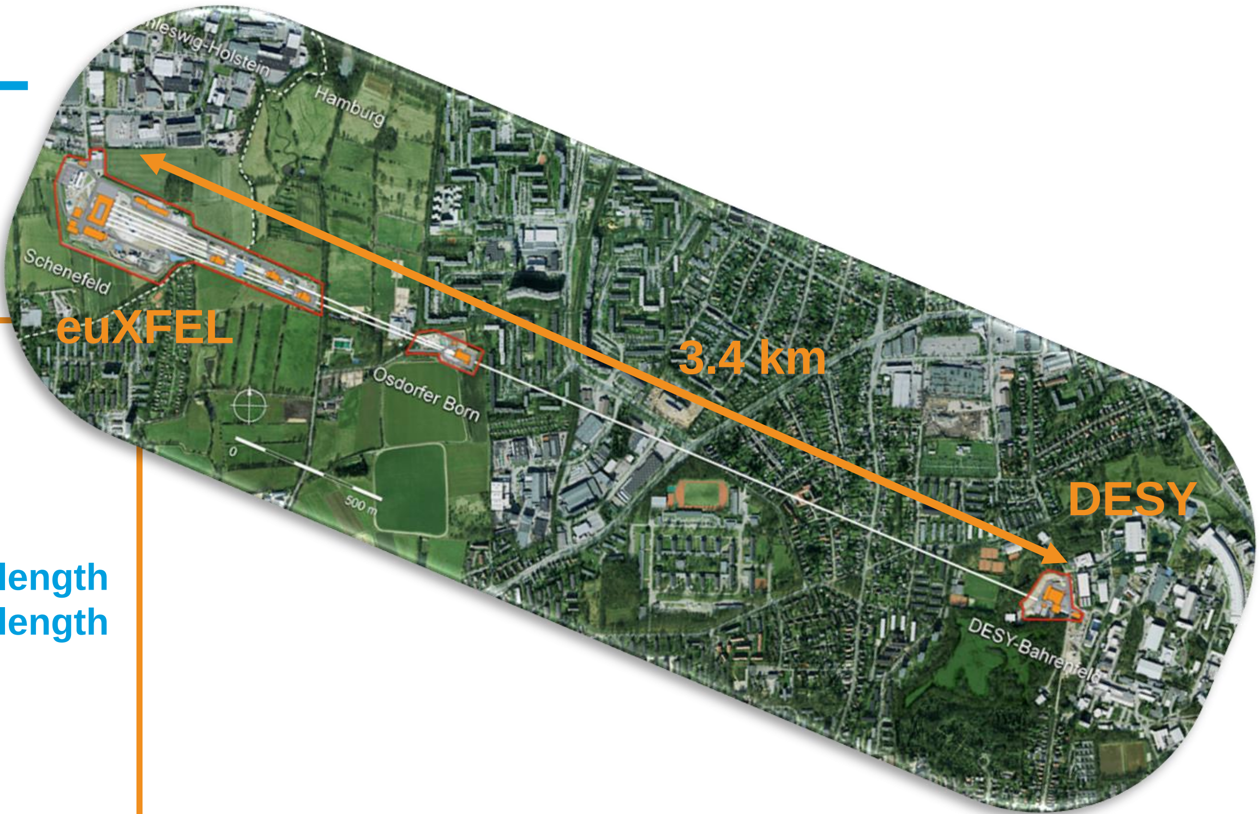


FLASH1 experimental hall

Albert-Einstein hall



European XFEL



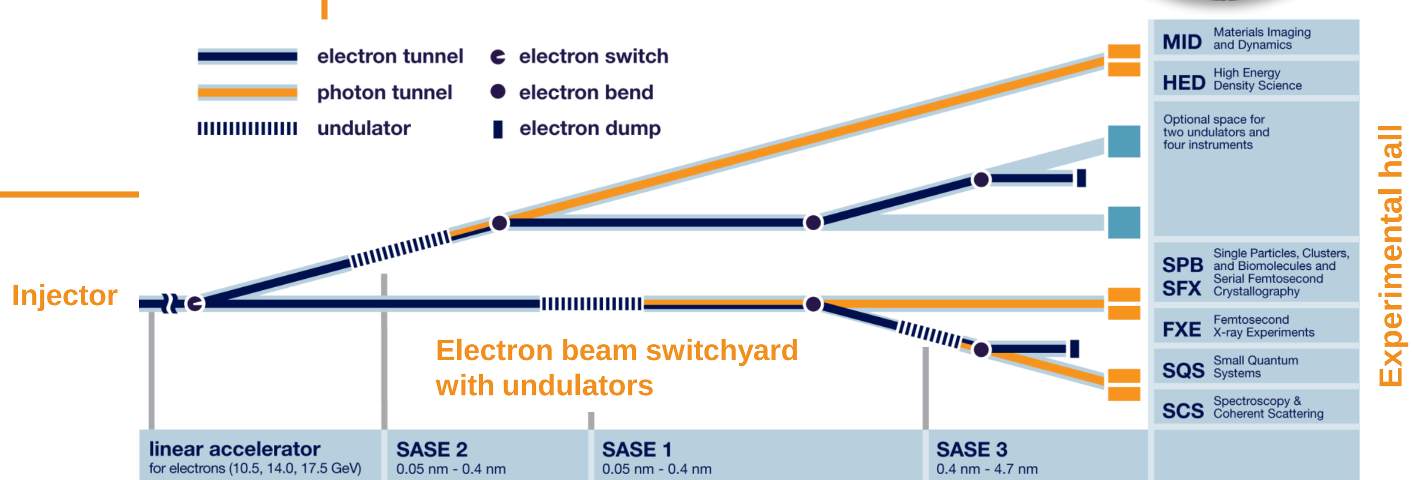
Supercond. Linac: up to 17.5 GeV
768 Niobium Cavities
total length 1.7 km

Undulators:
SASE1/2: 34 modules, 212 m total length
SASE 3 : 20 modules, 125 m total length

Photon energies: 0.2 – 3 – 26 keV
Average brilliance: ~10^{25}
1/(s·mm^2·mrad^2·0.1%BW)

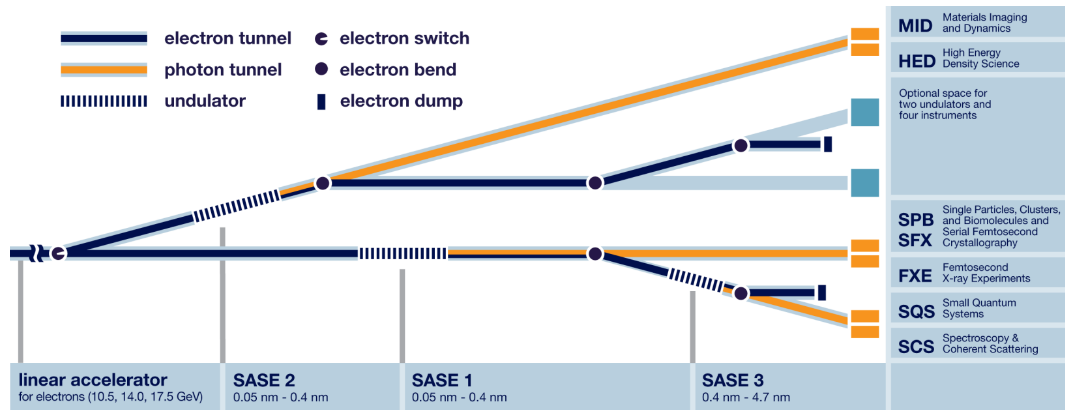
Peak brilliance: ~10^{33}

Pulse length: <100 fs



European XFEL

Science at the beamlines



3100-24800 eV (MID, HED, SPB/SFX, FXE)

260-3100 eV (SQS, SCS)

Endstation	Science
MID	**Materials imaging & dynamics:** structure determination of nanodevices and dynamics at the nanoscale
HED	**High energy density science:** investigation of matter under extreme conditions using hard X-ray FEL radiation, e.g. probing dense plasmas
SPB/SFX	**Ultrafast coherent diffraction imaging of single particles, clusters and biomolecules**: structure determination of single particles (atomic clusters, biomolecules, virus particles, cells), serial femtosecond crystallography
FXE	**Femtosecond X-ray experiments**: time-resolved investigations of the dynamics of solids, liquids, gases
SQS	**Small quantum systems:** investigation of atoms, ions, molecules and clusters in intense fields and non-linear phenomena
SCS	**Spectroscopy & coherent scattering**: Electronic and atomic structure and dynamics of nanosystems and of non-reproducible biological objects using soft X-rays

Introduction to Photon Science

Part II: Experiments at synchrotrons and FELs

What can we investigate with the light sources?

some examples

Scientific experiments at PETRA III

Physics, Chemistry, Biology, Medicine

24 Undulator beamlines
About 2000 scientists from about 400 institutes
About 4000 hours of user beamtime per year

Scattering and diffraction

- **Small angle X-ray scattering**
- **Diffraction and crystallography** **(powders, proteins, high pressure, surfaces)**

Imaging

- **Microtomography**
- **X-ray micro fluorescence**

Spectroscopy

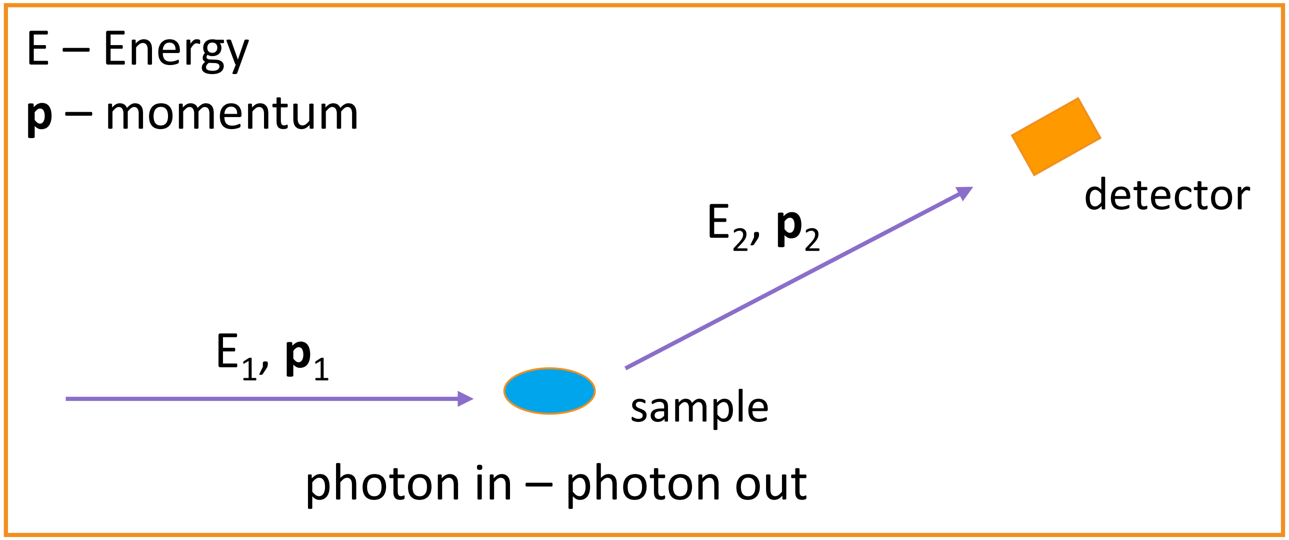
- **X-ray fluorescence spectroscopy**
- **X-ray absorption spectroscopy**
- **X-ray photoelectron spectroscopy**
- **Inelastic X-ray scattering**

Weak signals
e.g. High collimation
e.g. Small samples
Tunable wavelength
Time structure

Experiments concentrate on experiments with small focus incident photon beams ($\mu m, nm$) and "photon hungry" experiments

Probing structure and dynamics of matter

Experiments using light-matter interaction



Analyse…

the distribution of scattered photons in reciprocal space → Diffraction

… in real space → Imaging

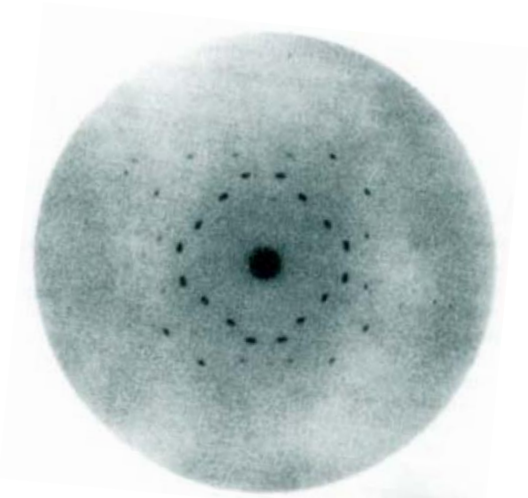
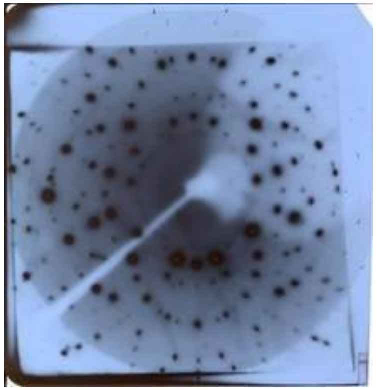
the energy spectrum of scattered (or absorbed) photons or electrons and ions → Spectroscopy

the temporal evolution of the scattering/absorption process → Time-domain methods

X-ray Scattering: Biology and Material Science

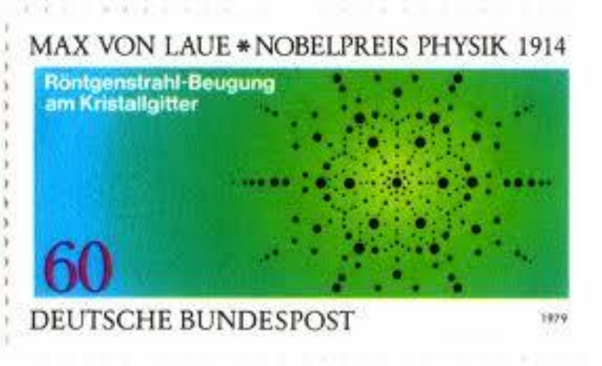
X-ray diffraction from crystalline structures

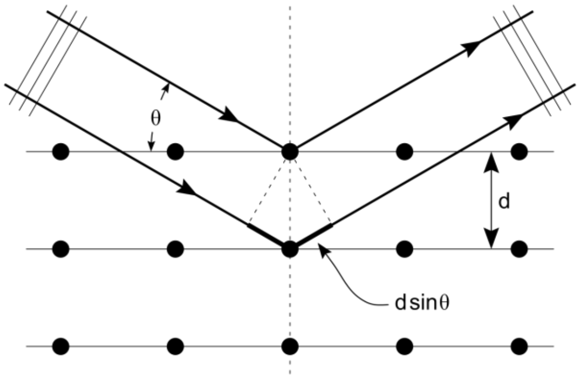
X-rays are preferentially scattered in particular directions


Max von Laue
(1879 – 1960)

First diffraction patterns obtained by Max v. Laue in 1912 with X-ray tubes



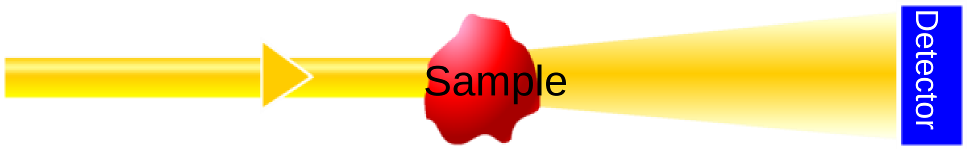


- Each scatterer re-radiate spherical waves
- Constructive interference if $n\lambda = 2d \sin\theta$

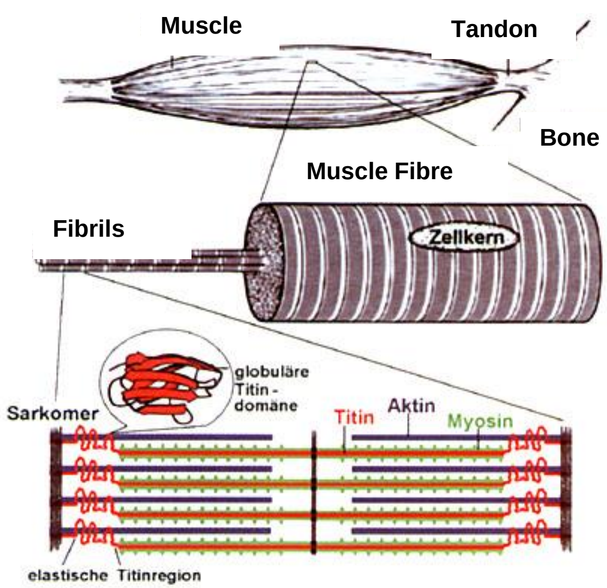
First experiments using synchrotron radiation

1970: Small angle X-ray scattering (SAXS) on muscle fibres

Rosenbaum, G., Holmes, K. C., and Witz, J. (**1971**) Nature, 230, 434-137.



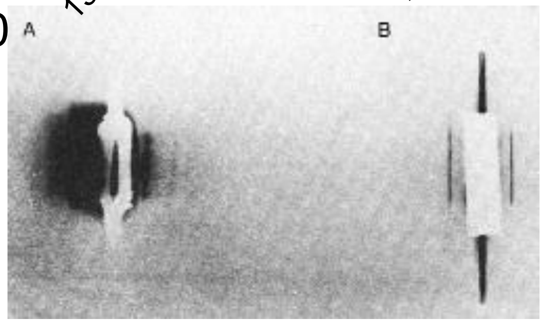
Equatorial reflexions from dorsolongitudinal flight muscle of *Lethocerus maximus*



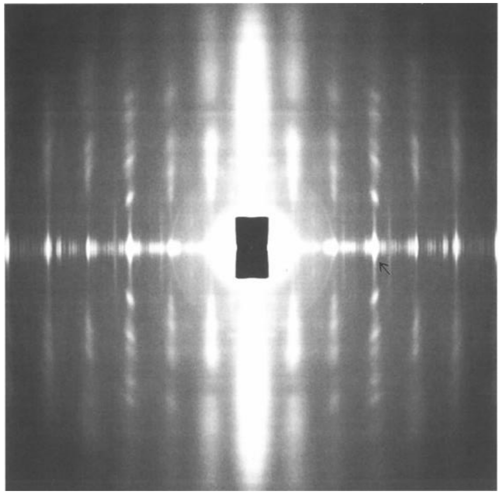
Synchrotron @5GeV 15min irradiation

X-ray tube @40kV 1h irradiation

1970



1996

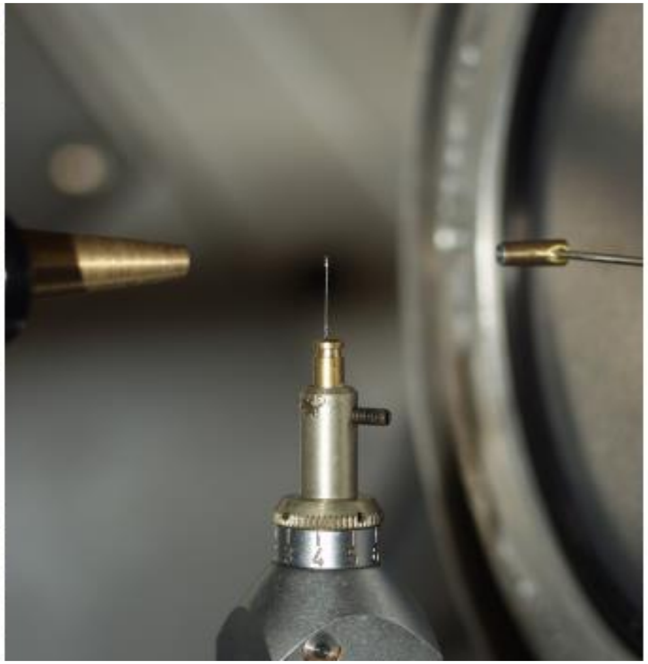


Protein crystallography

State-of-the-art protein's structure characterization

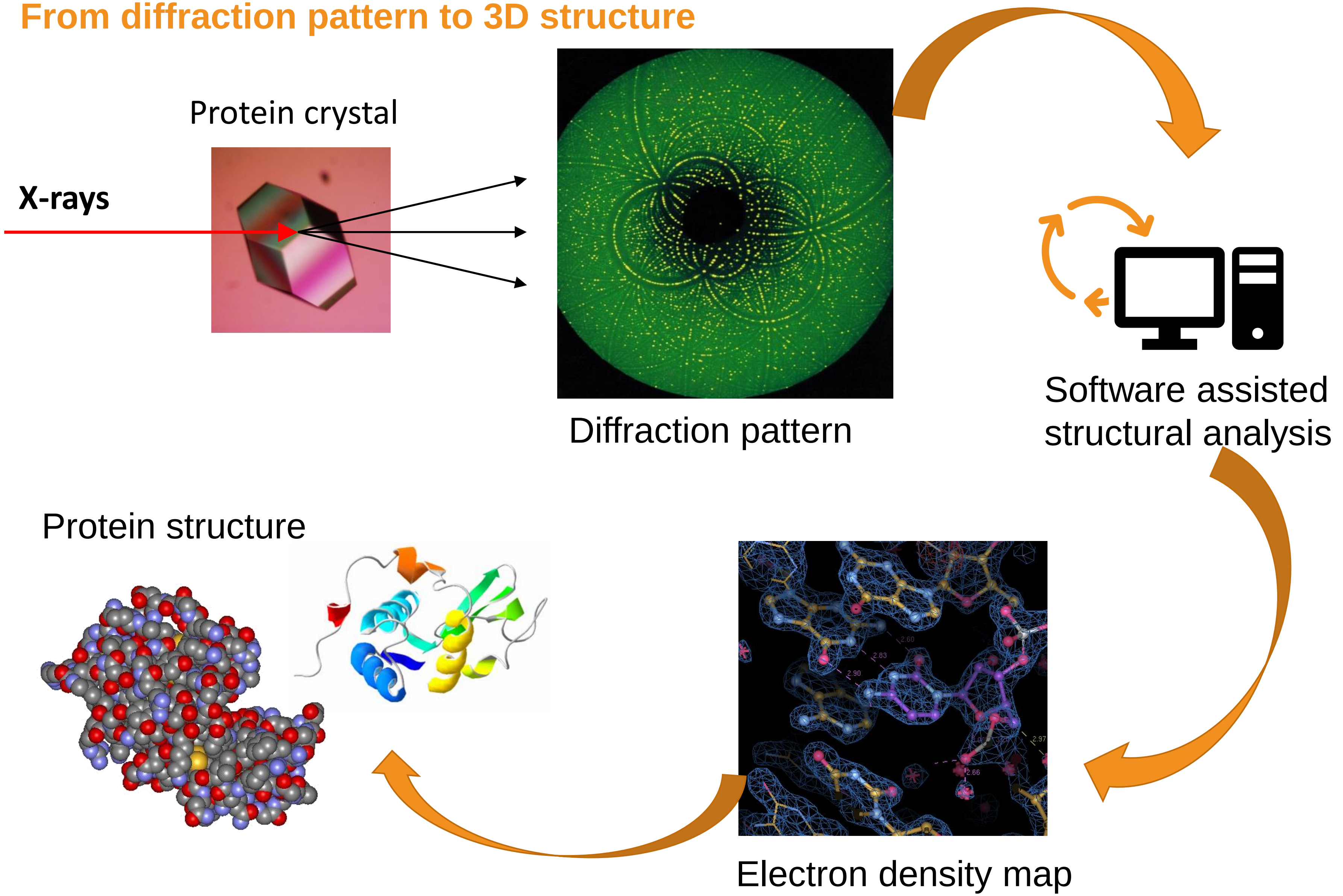
Proteins crystals are tiny sample (few tenth of µm)
Proteins = „huge“ unit cells
Light elements (mostly H, C, N, O)
Sensitive to radiation damage
High resolution necessary
- narrow energy band
- high degree of collimation

→ High brilliance required



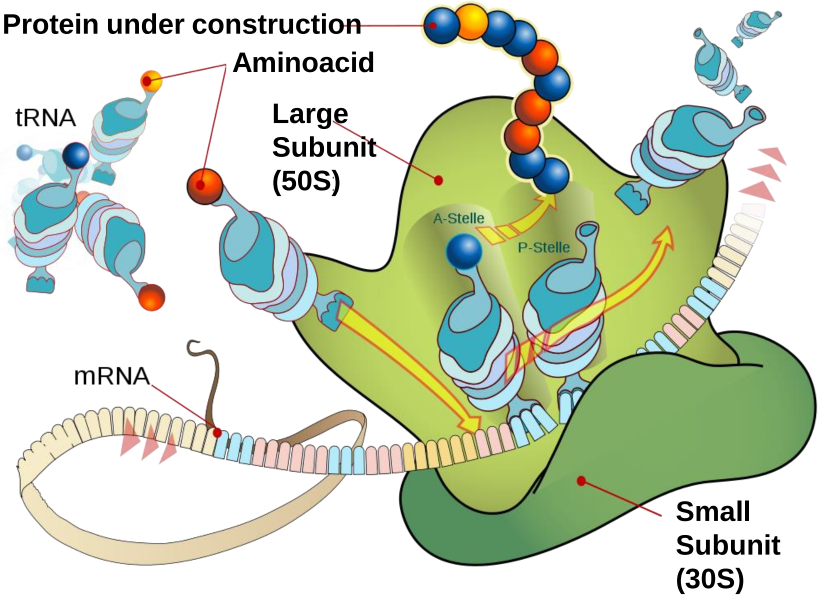
Structure determination of proteins

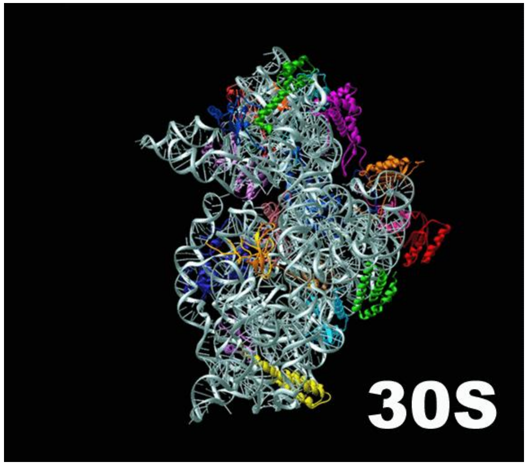
From diffraction pattern to 3D structure



Revealing structure and dynamics of ribosome

The protein factory





Ada Yonath

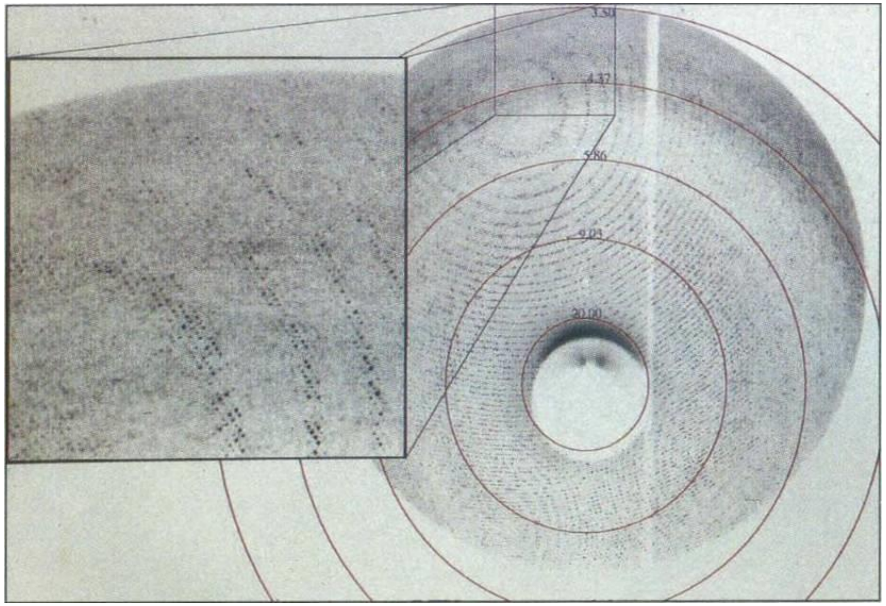
- Head of the MPG-work group „Structure of the Ribosome“ at DESY, 1986 – 2004
- Nobelprize Chemistry 2009 (with T. Steitz and V. Ramakrishna)

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

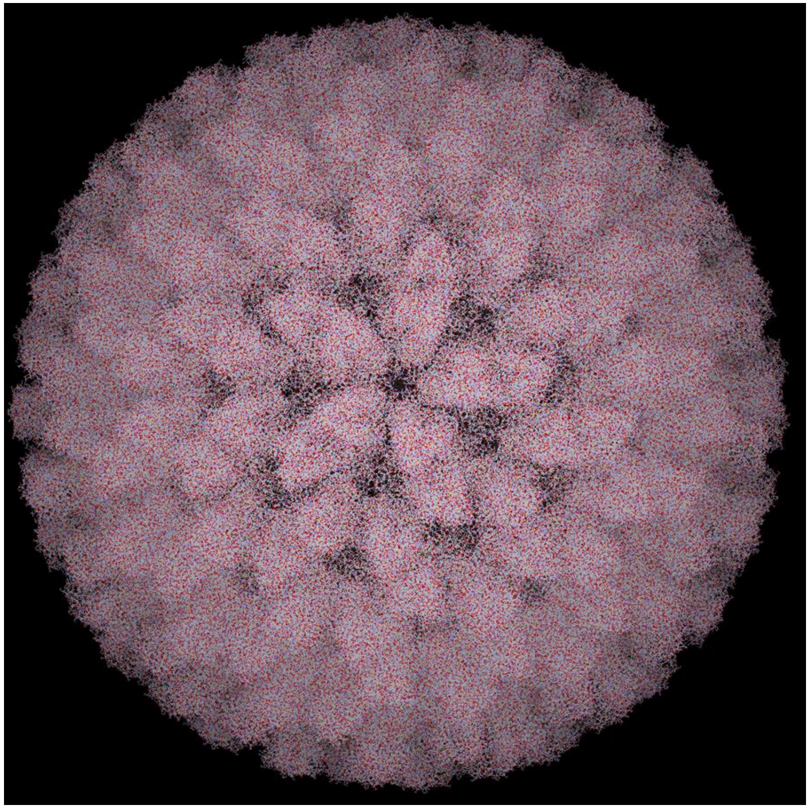
Very large biomolecules

Nanometer-sized viruses

Example: Blue Tongue Virus
70 nm diameter!
Resolution 3.5 Å



Diffraction pattern



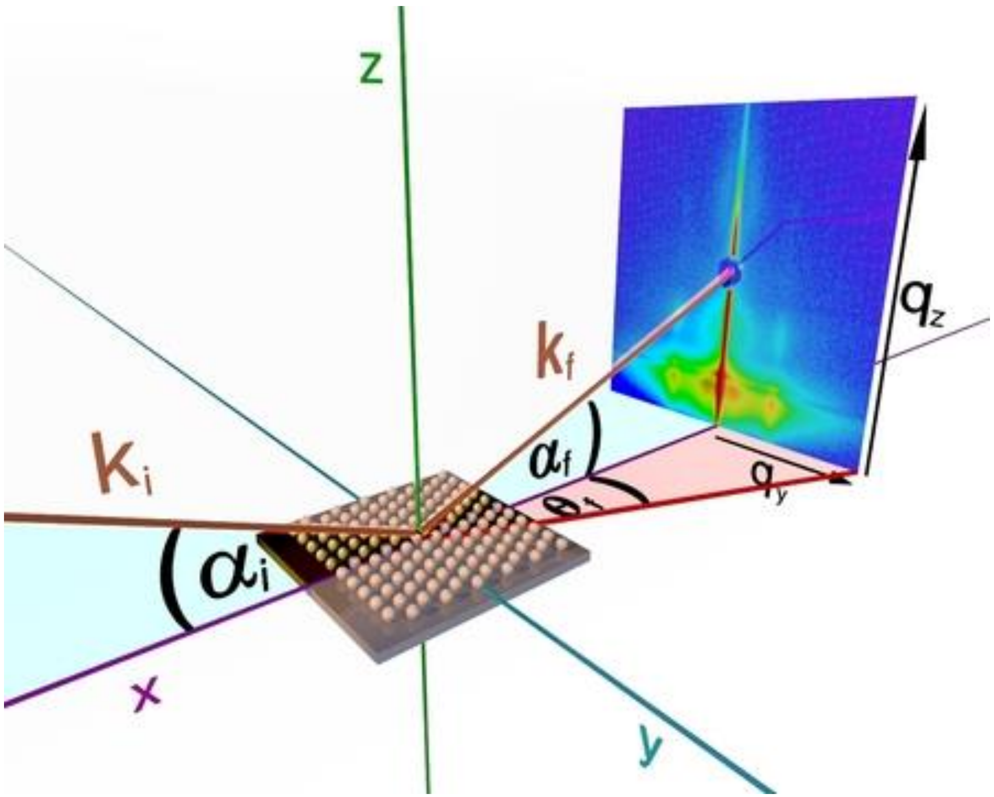
Molecular structure

J.M. Grimes et al., Nature 395, 470-478 (1998)

Grazing-incidence small-angle scattering

GISAXS for surface analysis

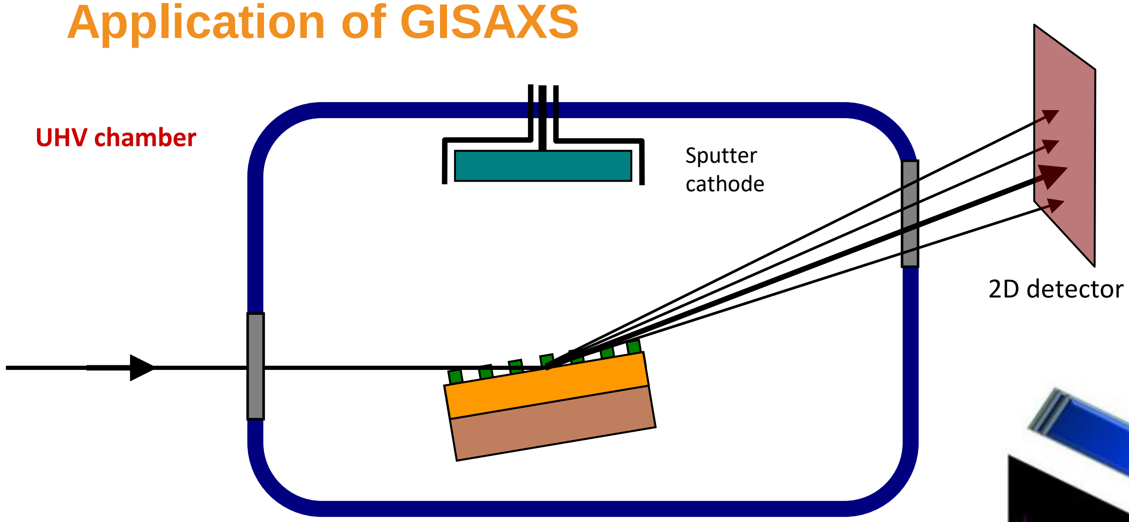
Image plate or CCD detector

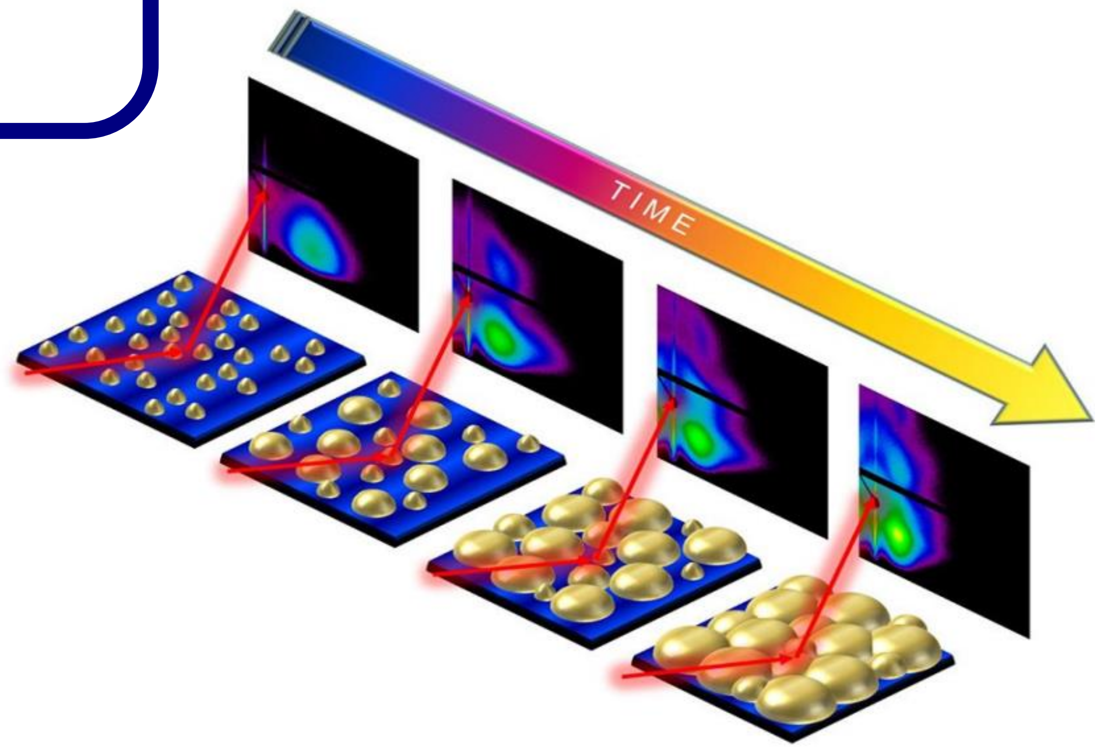


- Scattering by structures that are much larger than the wavelength of the radiation
- 2-D detector records the scattered intensity at small angles (0.1-10°) for the observation of lateral dimensions and arrangement ranging from a few up to hundreds of nanometers.
- Determine the size, shape, and distribution of nanostructures, such as nanoparticles, nanocrystals, or thin film domains.

In-situ studies of nanostructure formation

Application of GISAXS



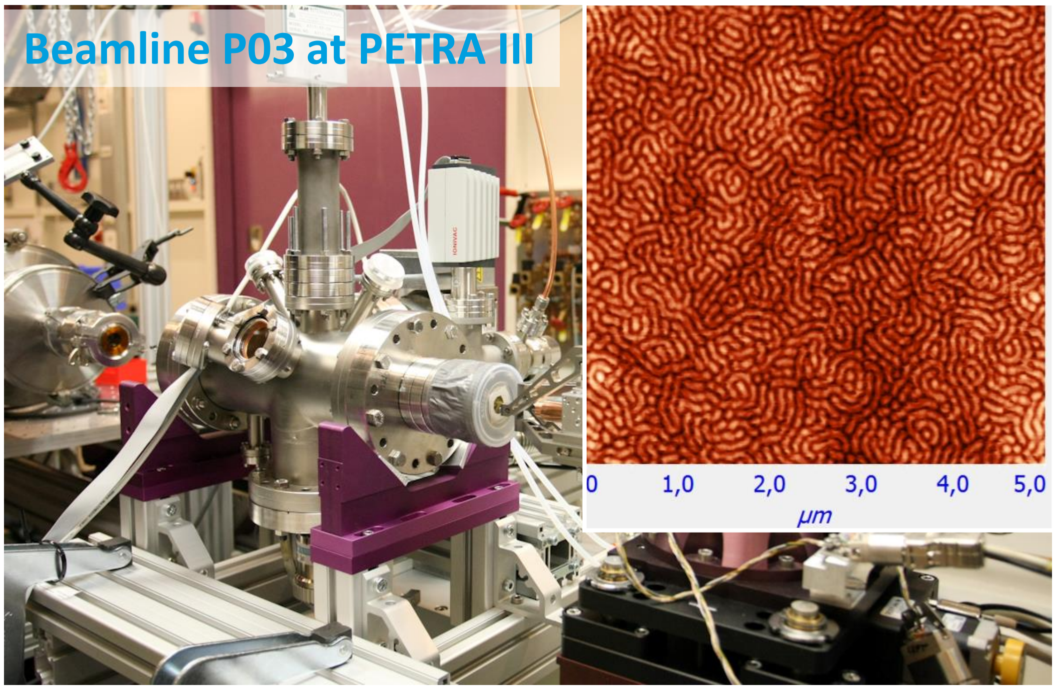


Observation of growth process of thin films during deposition

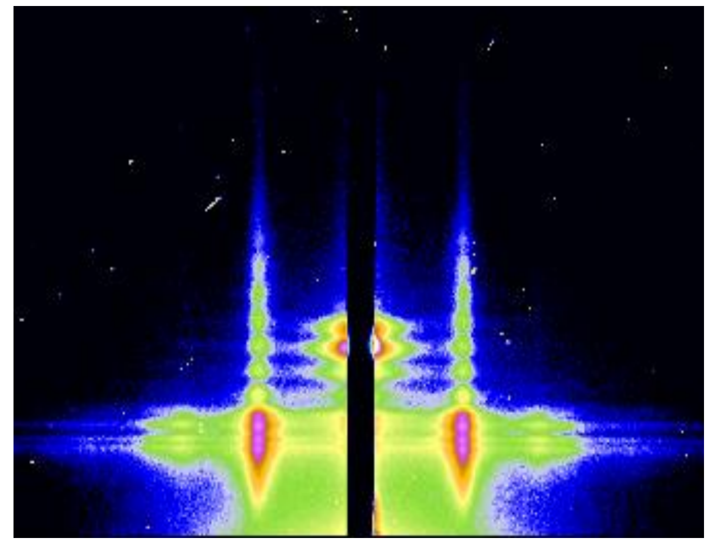
Formation and self-organization of nanoparticles on surfaces

Directly observing magnetic nanostructures during growth via GISAXS

Deposition of 10 nm FePt onto flat PS-b-PMMA



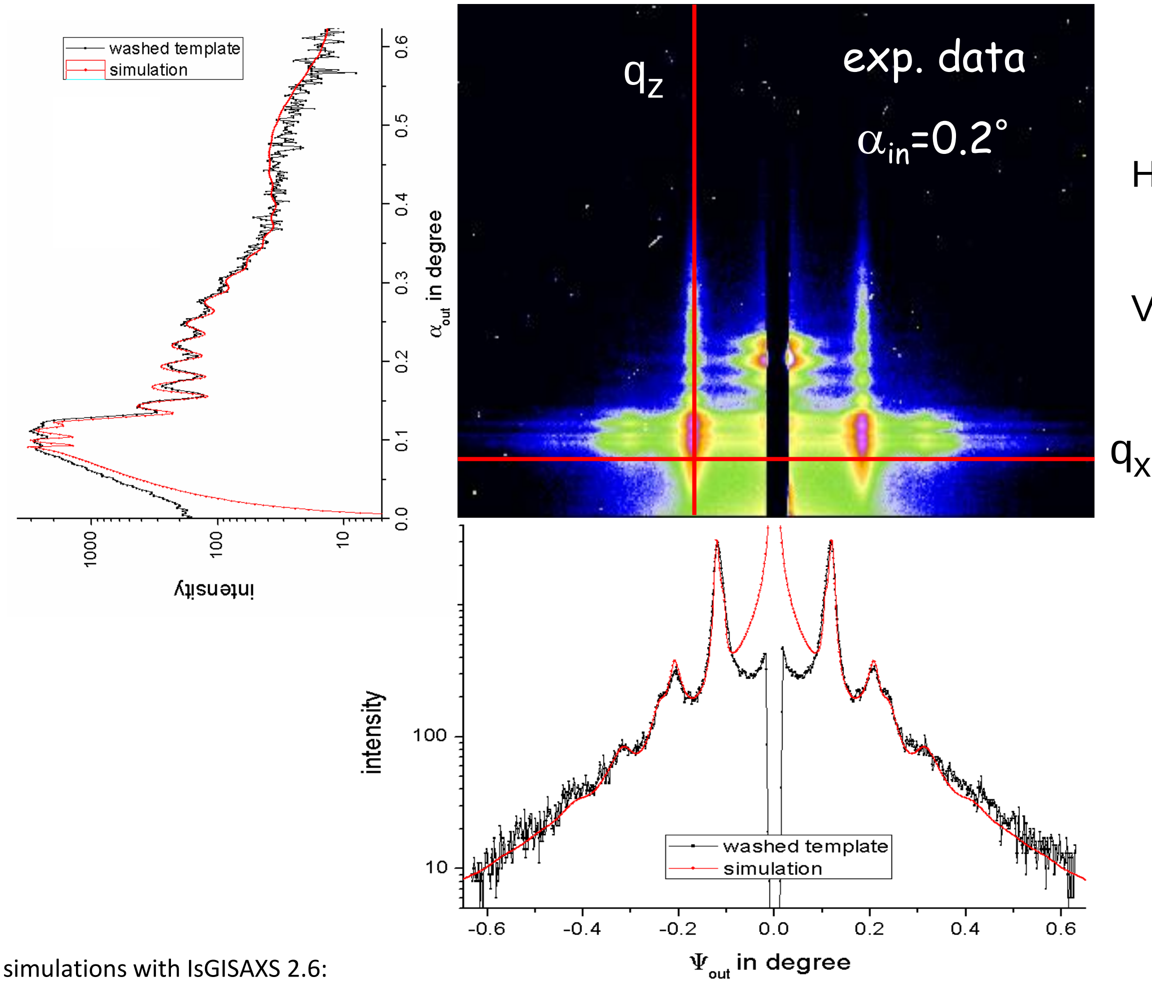
PILATUS 300k pixel detector



Results

- Selective vertical growth of FePt on PS/PMMA
- Lateral structure defined by the polymer template

Directly observing magnetic nanostructures during growth via GISAXS



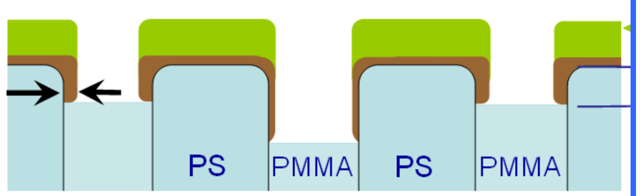
Horizontal stripes

= layers parallel to substrate

Vertical stripes

= a rod-like shape normal to substrate

Morphology after deposition of 5.1 nm Fe



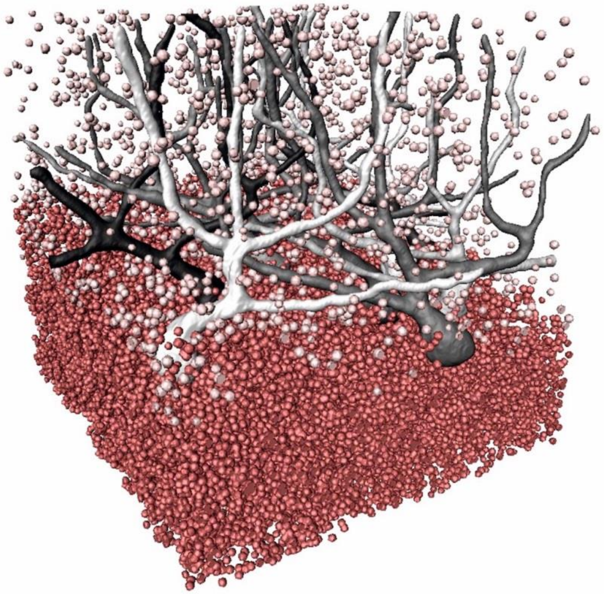
simulations with IsGISAXS 2.6:

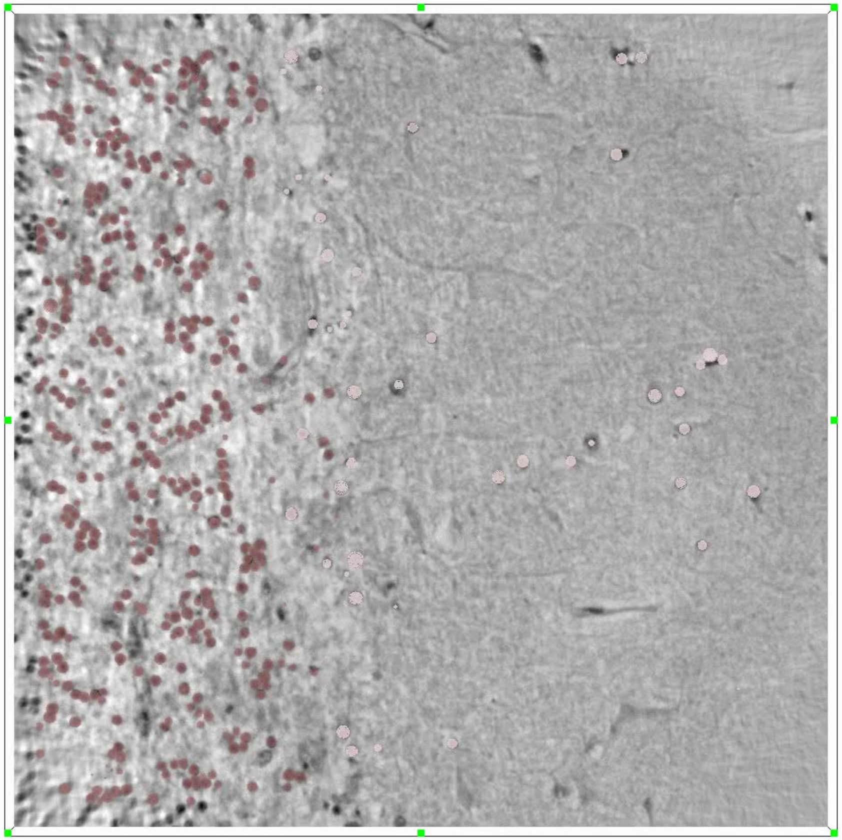
R. Lazzari, Appl. Cryst. **35**, 406 (2002)

Phase contrast tomography of neurons in brain tissue

Measure phase shifts (measure as intensity variation) caused by the sample. Application for low Z materials (e.g. soft tissue).

3D virtual histology at beamline P10
Photon energy 8 keV
Automatic cell segmentation
Rendering of $1.8 \cdot 10^6$ neurons

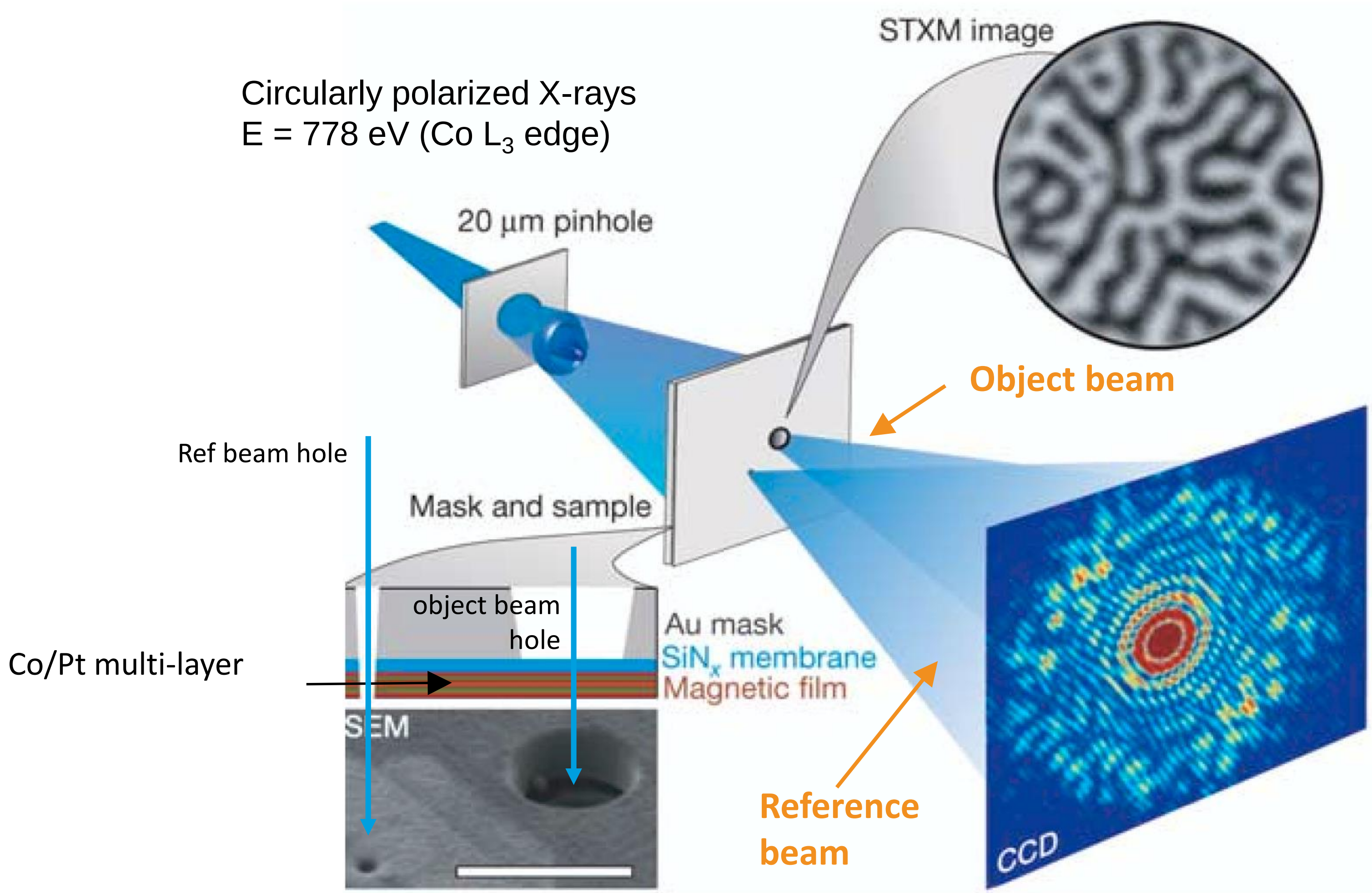




M. Töpperwien, F. van der Meer, C. Stadelmann, T. Salditt; „PNAS“, 2018

Exploiting the coherence of X-rays: static structure

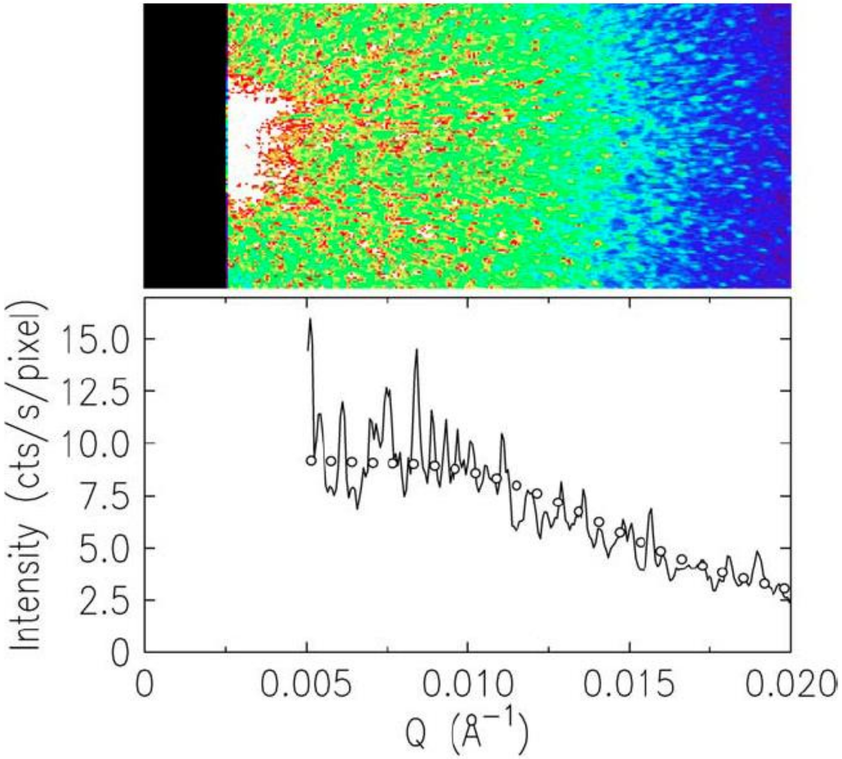
Imaging of magnetic domains via X-ray holography



S. Eisebitt et al., Nature 432, 885 (2004)

Exploiting the coherence of X-rays: dynamic structure

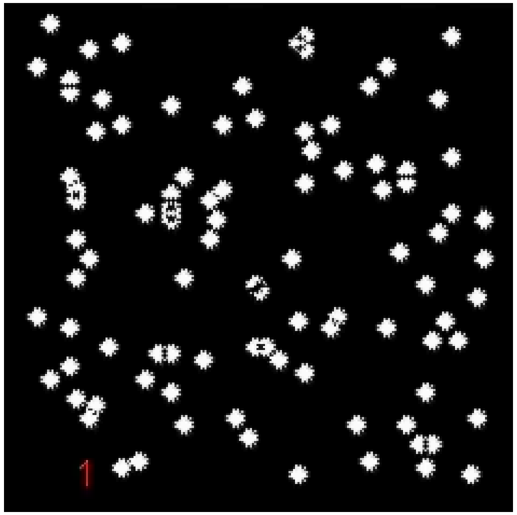
X-ray photon correlation spectroscopy (XPCS)



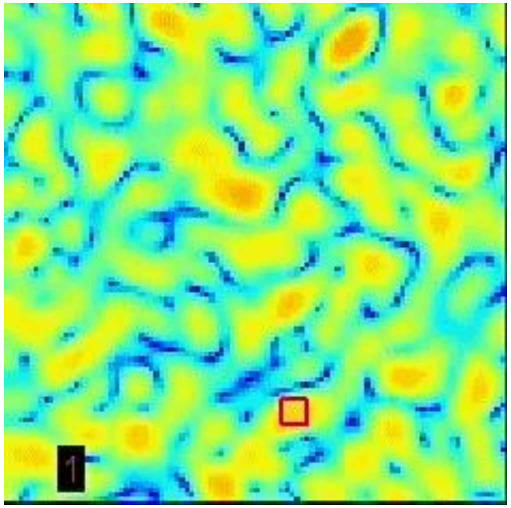
Diffraction of coherent light from a disordered sample leads to a ‘grainy’ diffraction pattern (speckles)

Simulation of Brownian motion

Real space



Diffraction pattern

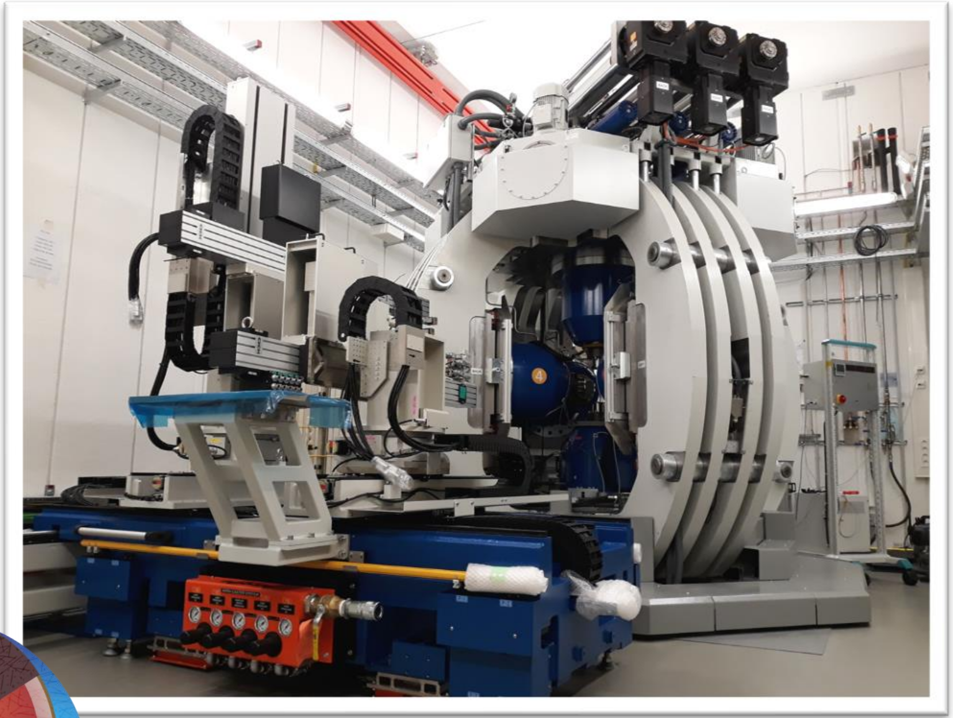


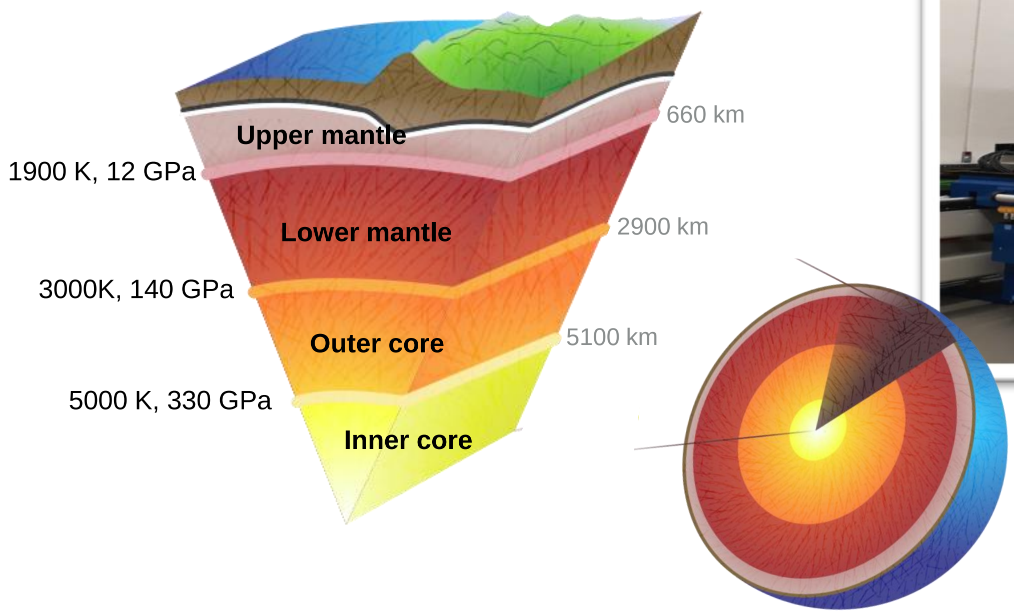
Geo science experiments (high P, high T)

Large Volume Press at DESY

30 - 160 keV, diffraction and radiography imaging technique

1750t press for in situ studies of large sample volumes.
Maximum pressure: ~ 24 GPa
Temperature: up to 2400 K
Study of material under the conditions of the earths lower mantle.



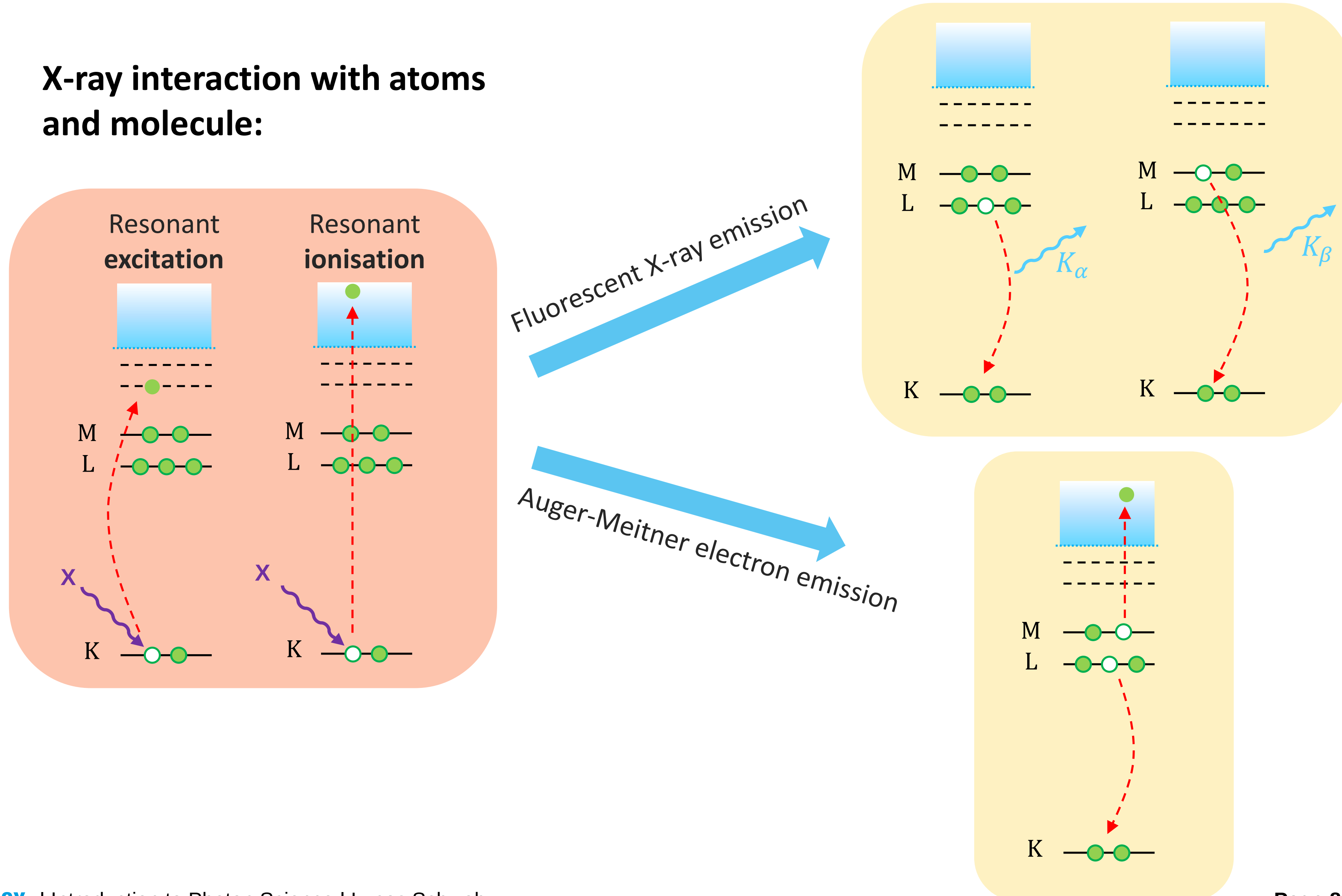


X-ray absorption-based methods: Atomic, Molecular and Material Science

X-ray resonant core excitation spectroscopy

Probing the local environment with atomic resonances

X-ray interaction with atoms and molecule:



X-ray Absorption Spectroscopy

The three energy regions

1. Edge Region: ± 10 eV across the edge:

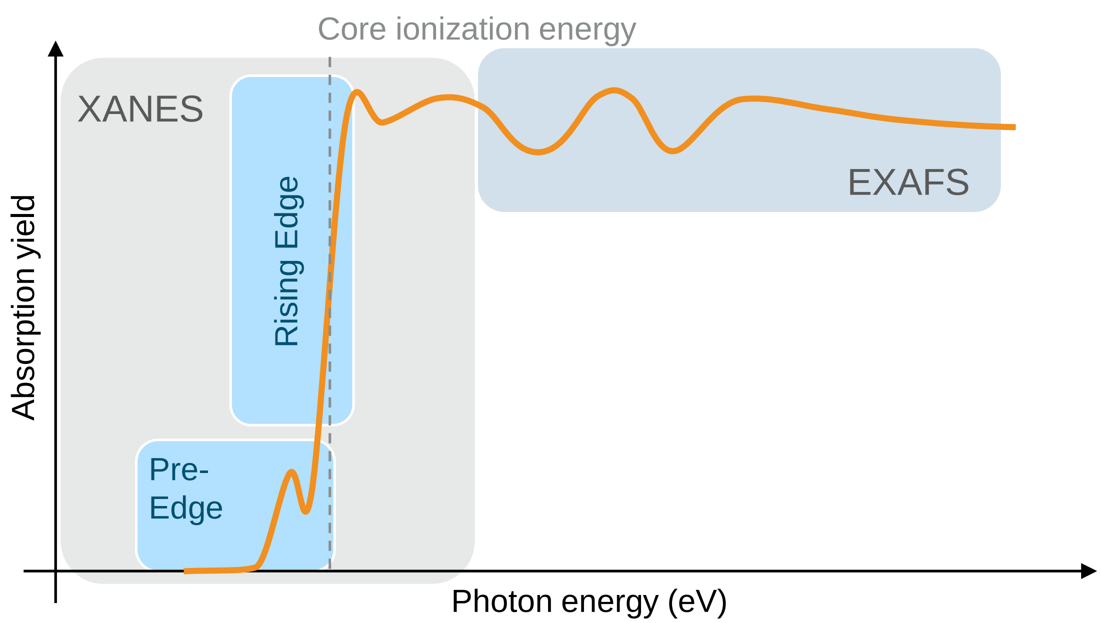
   Electronic structure information (oxidation state, unoccupied molecular levels, and charge transfer)

2. X-ray Absorption Near Edge Structure **(XANES, or NEXAFS):** 5-150 eV across the edge

   Local geometric structure (3D atomic geometry, coordination from multiple scattering analysis)

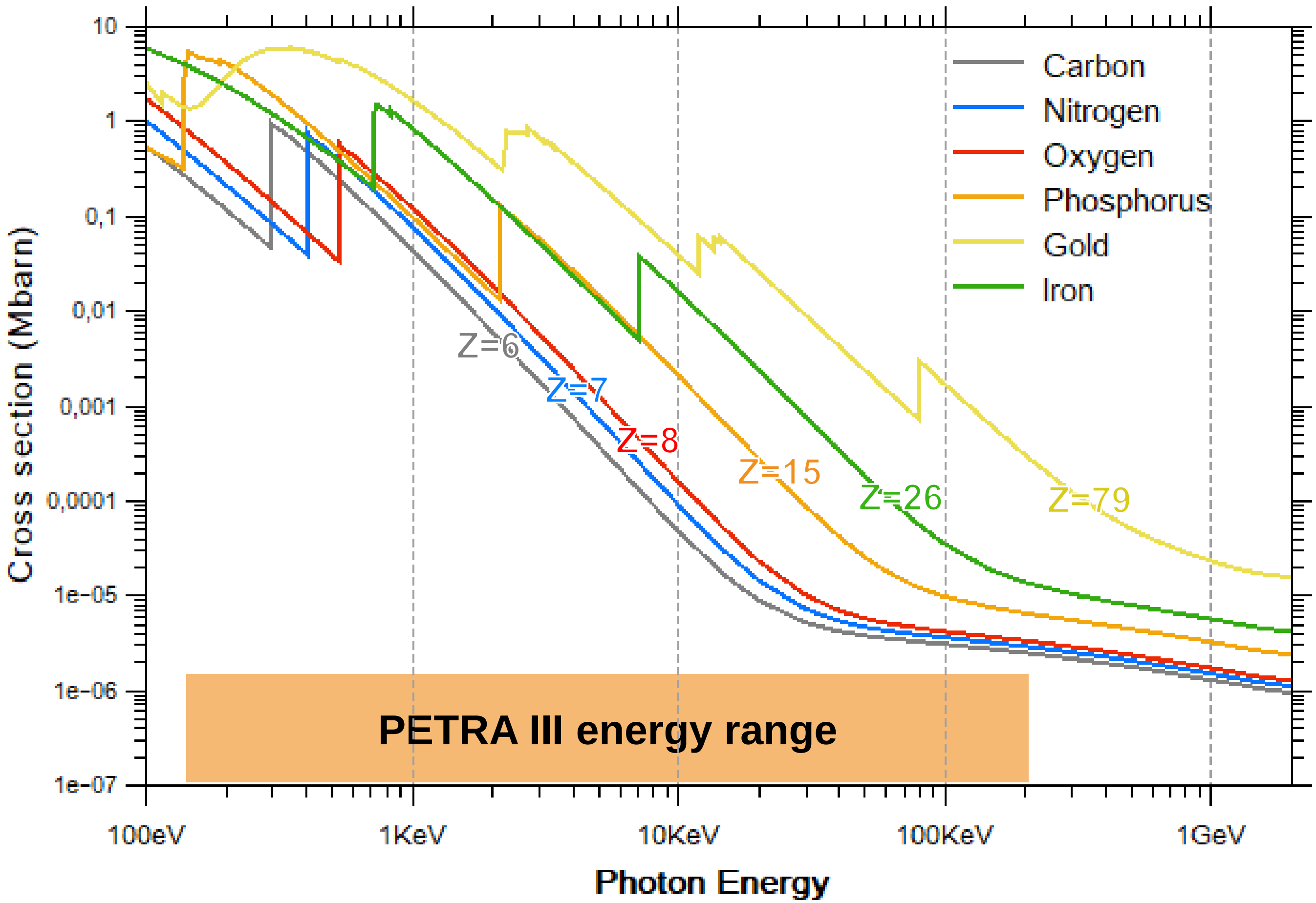
3. Extended X-ray Absorption Fine Structure **(EXAFS):** >150 eV above the edge

   Dominated by single photoelectron scattering events (interatomic distances)



X-ray Absorption Spectroscopy

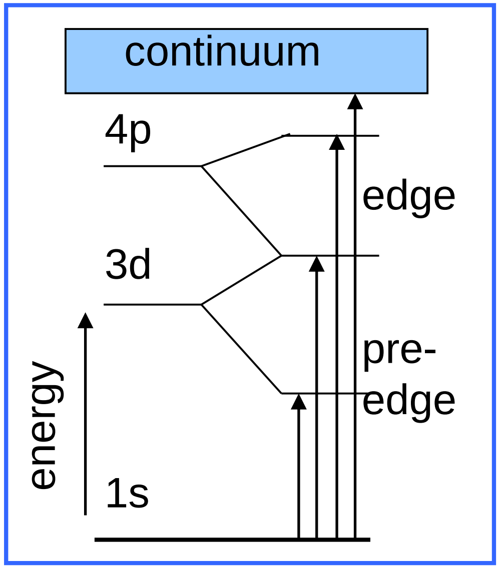
Atom specific

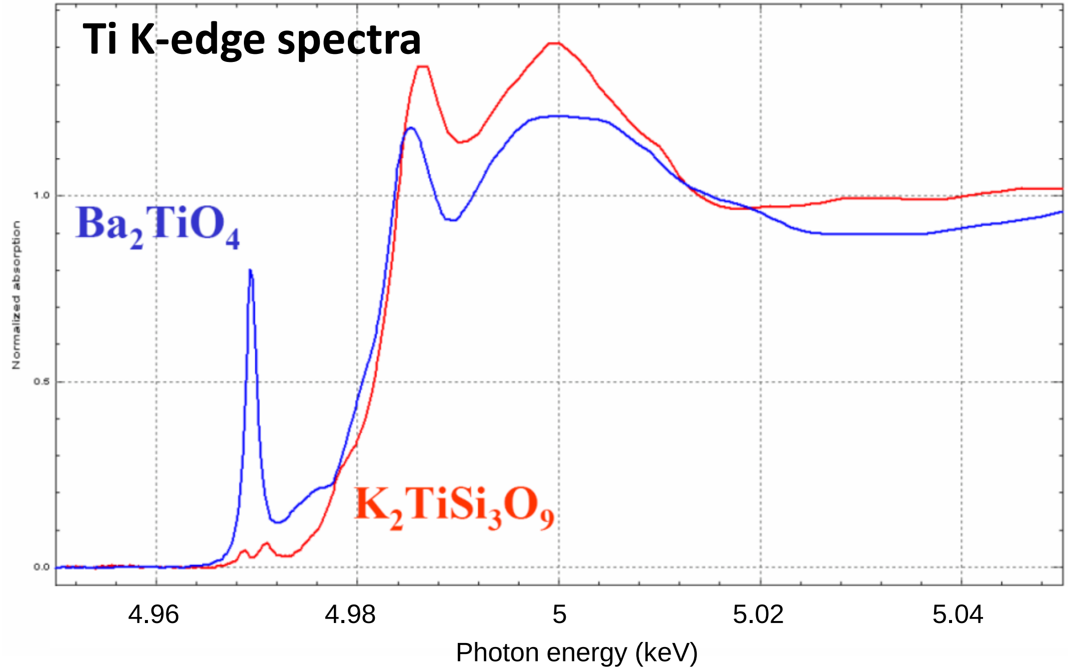


X-ray Absorption Near Edge Structure XANES

Probing the local environment with atomic resonances

Pre-edge and edge structures are caused by transition to empty bound states

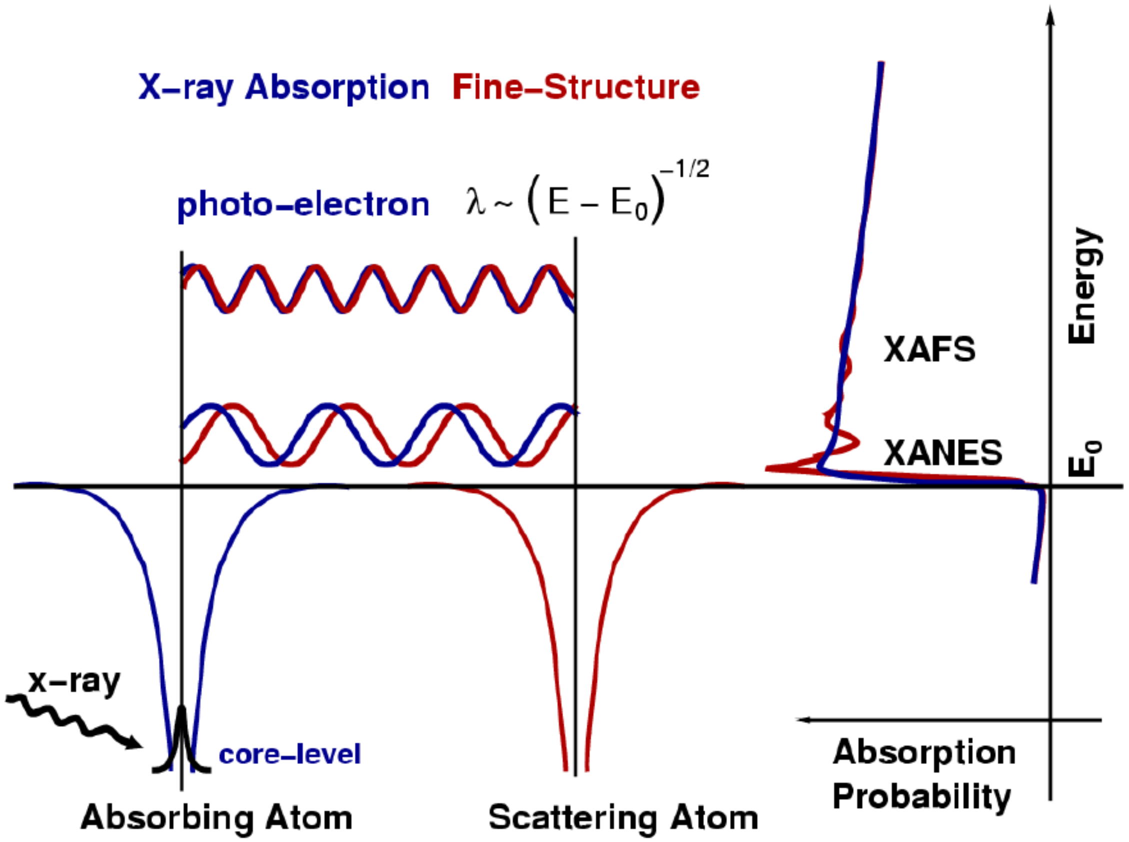




- dependence on local coordination chemistry
- provides electronic structure information (oxidation state, occupancy of valence orbitals, and charge transfer)

X-ray Absorption Fine Structure XAFS

Probing the local environment of the absorbing atom



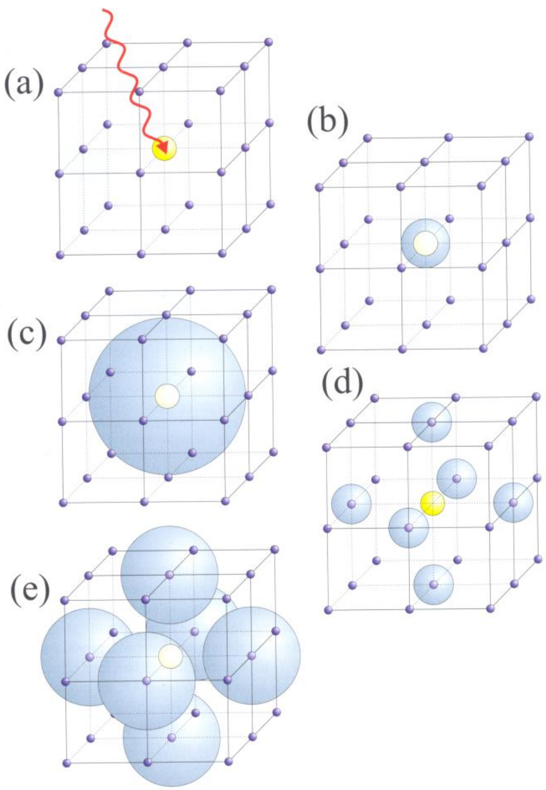
Origin of XAFS: photoelectron (PE) can scatter from neighboring atom

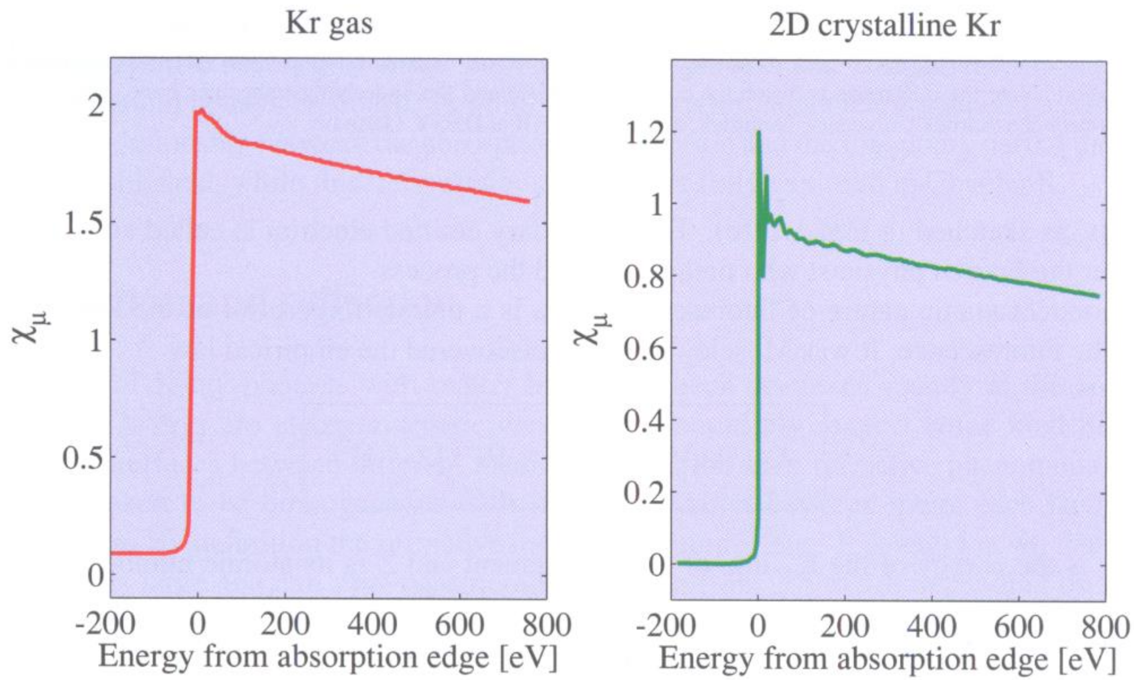
→ Scattered PE can return to the absorbing atom, modulating the PE wave function

→ Interference at the absorbing atom creates oscillation of the absorption probability

X-ray Absorption Fine Structure (XAFS)

Probing the local environment of the absorbing atom





Origin of XAFS: photoelectron (PE) can scatter from neighboring atom

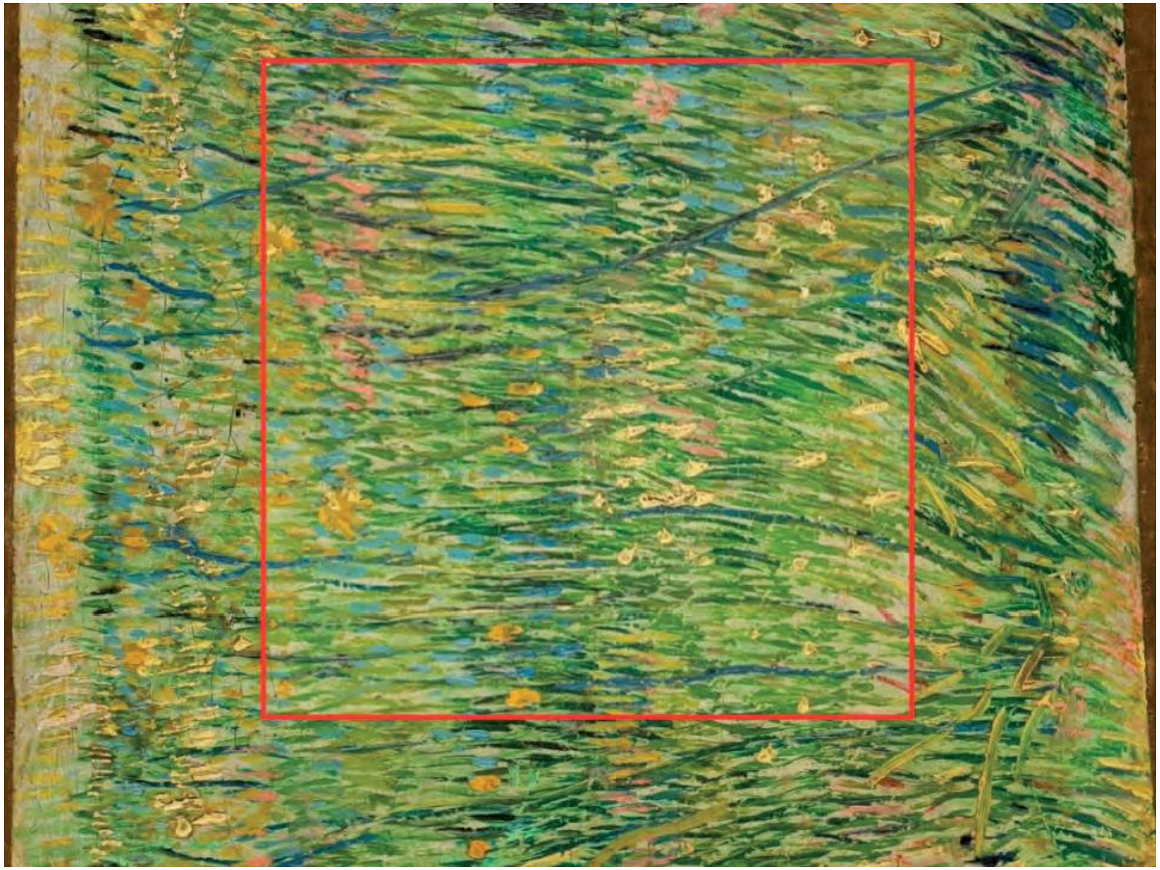
→ Scattered PE can return to the absorbing atom, modulating the PE wave function

→ Modulation of the absorption probability

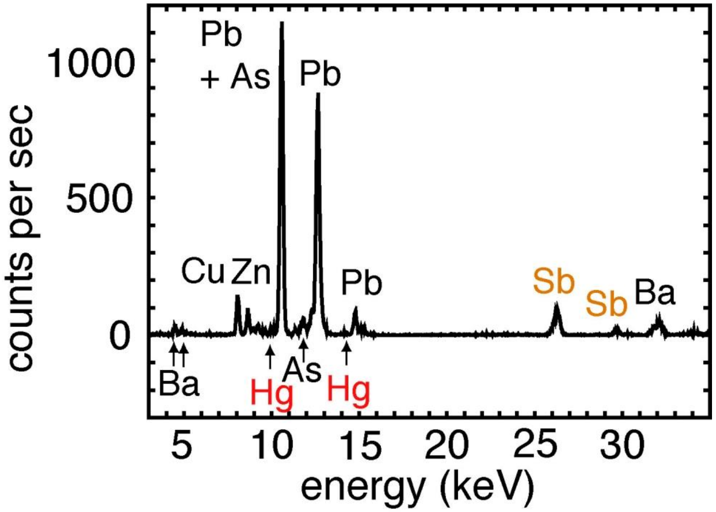
X-ray Fluorescence Mapping

Visualisation of a lost painting

Vincent van Gogh: Meadow with flowers



Raster (zig-zag) scanning along
90000 pixels with 0.5 mm resolution



Typical fluorescence spectrum in a single pixel

J. Dik, et al. *Analytical Chemistry* **2008** *80* (16), 6436-6442

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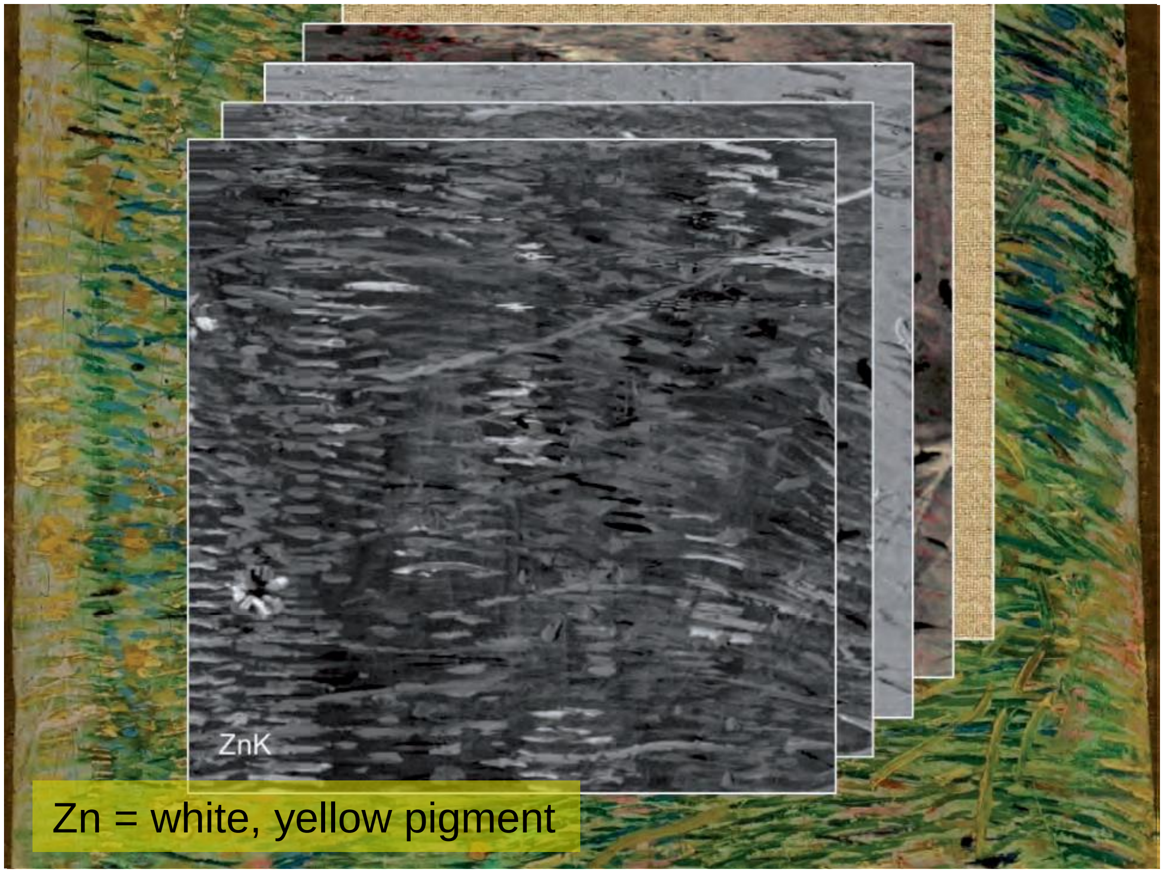

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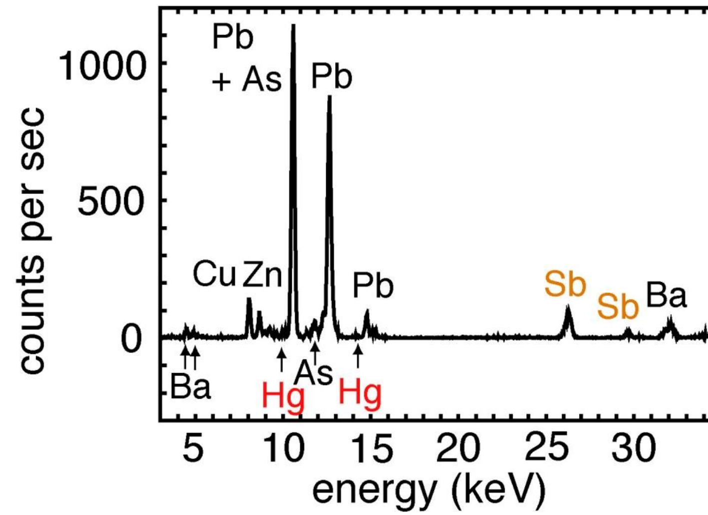

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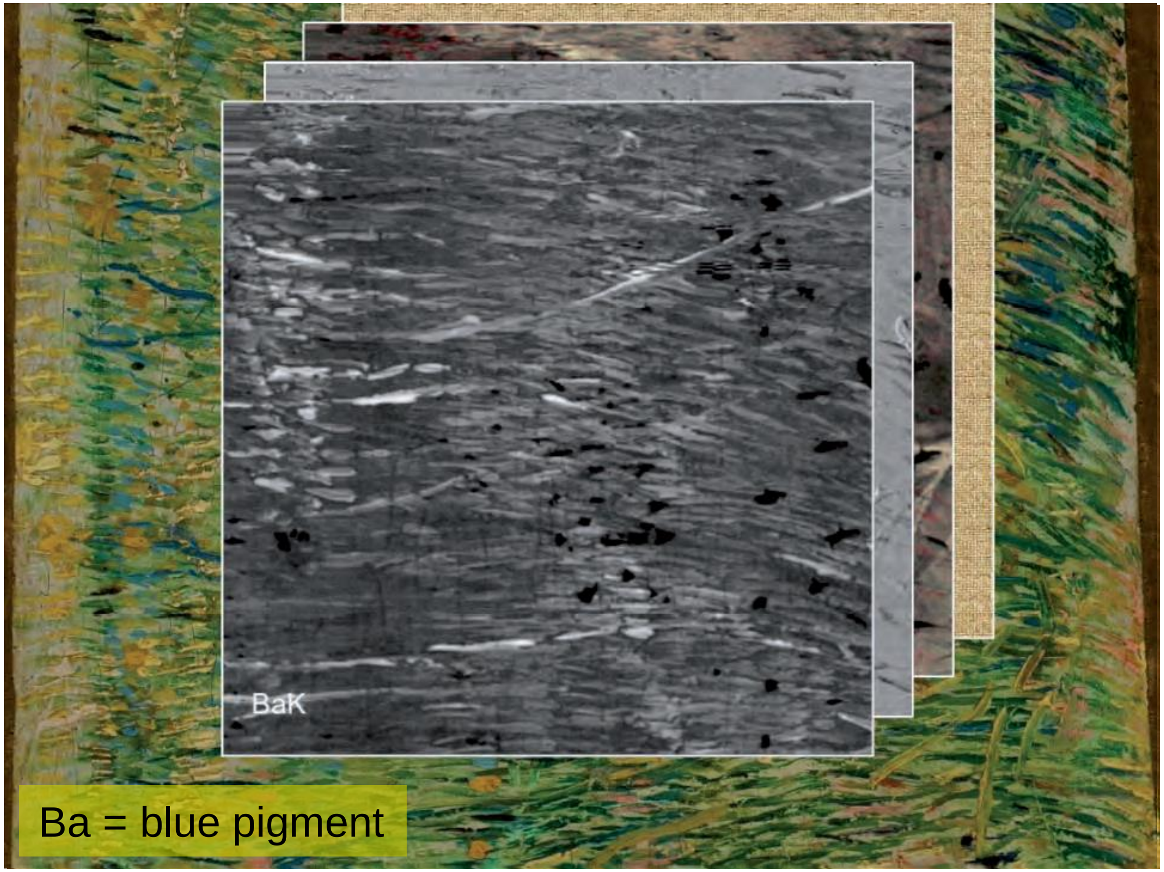

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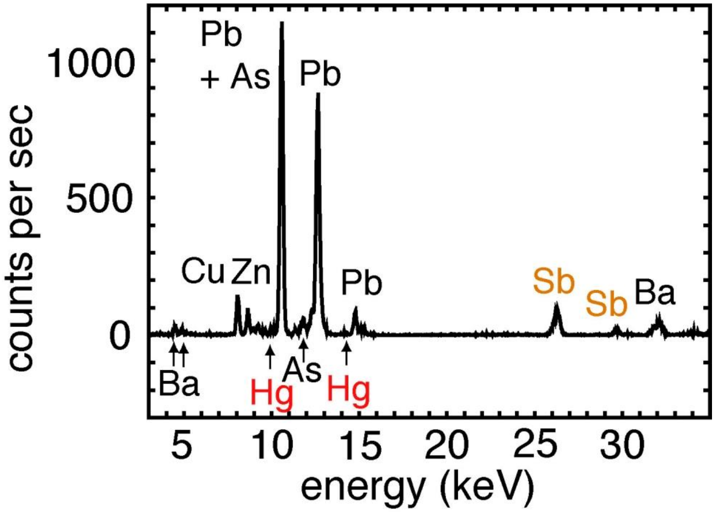

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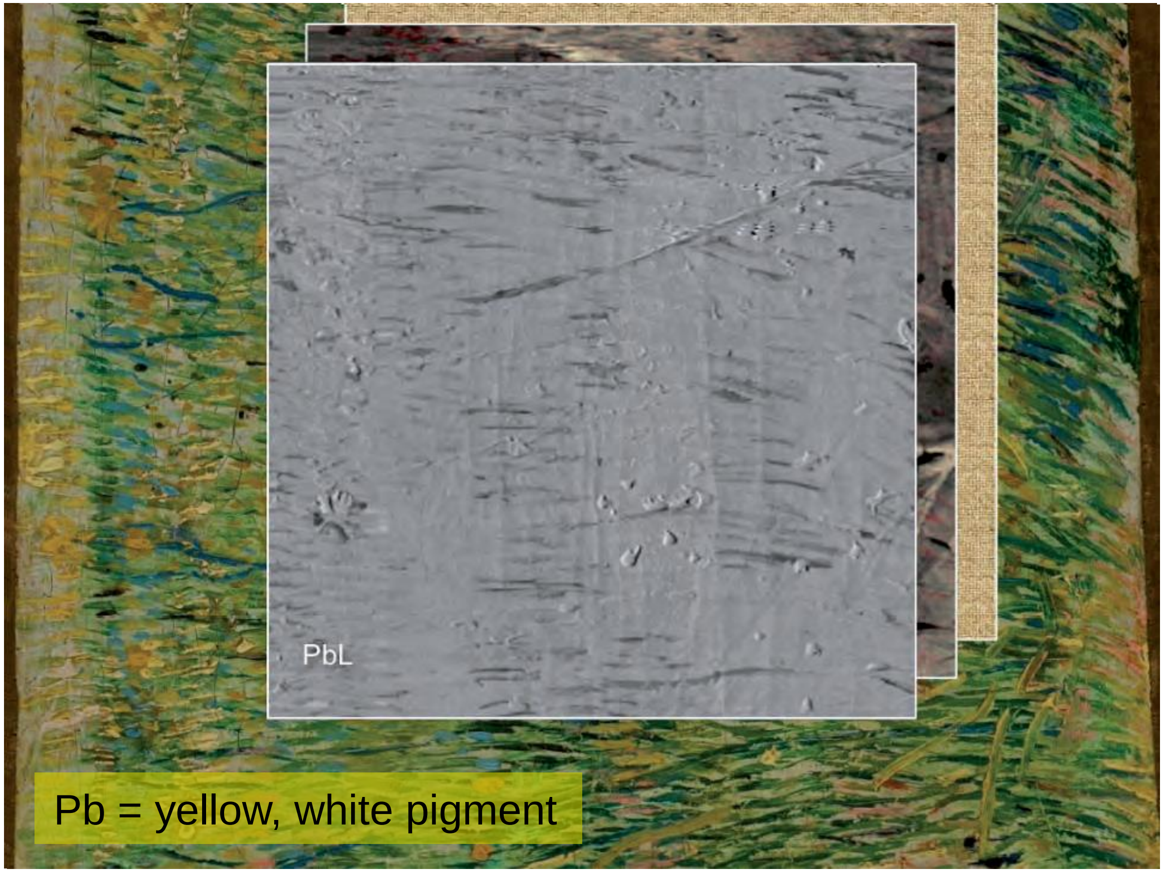
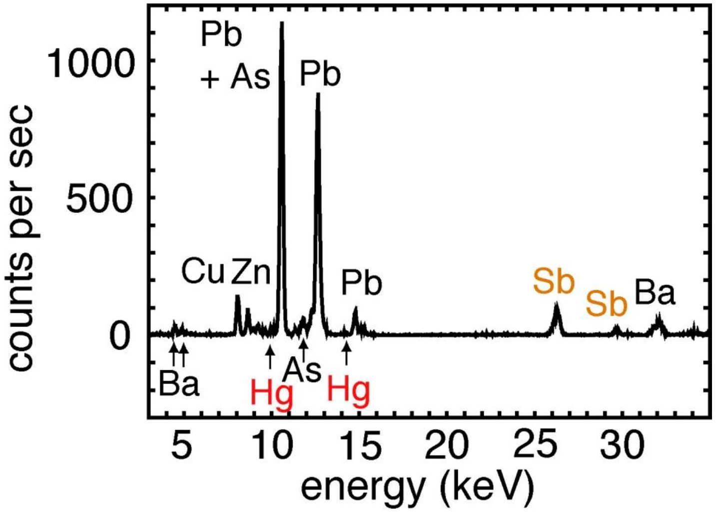


Raster (zig-zag) scanning along
90000 pixels with 0.5 mm resolution



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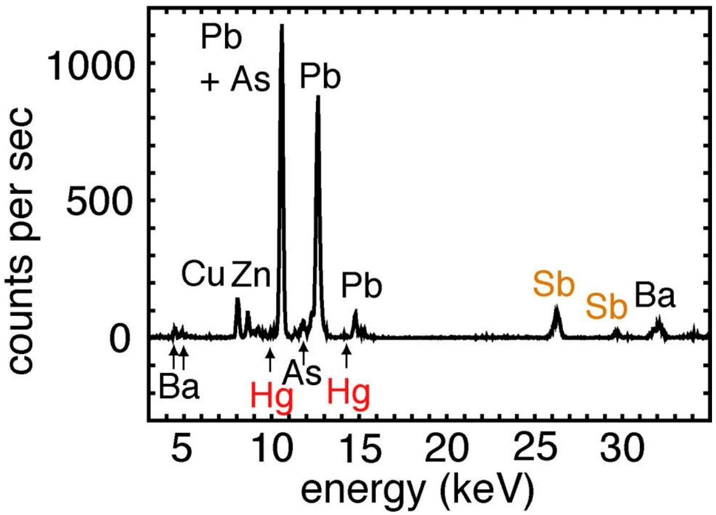


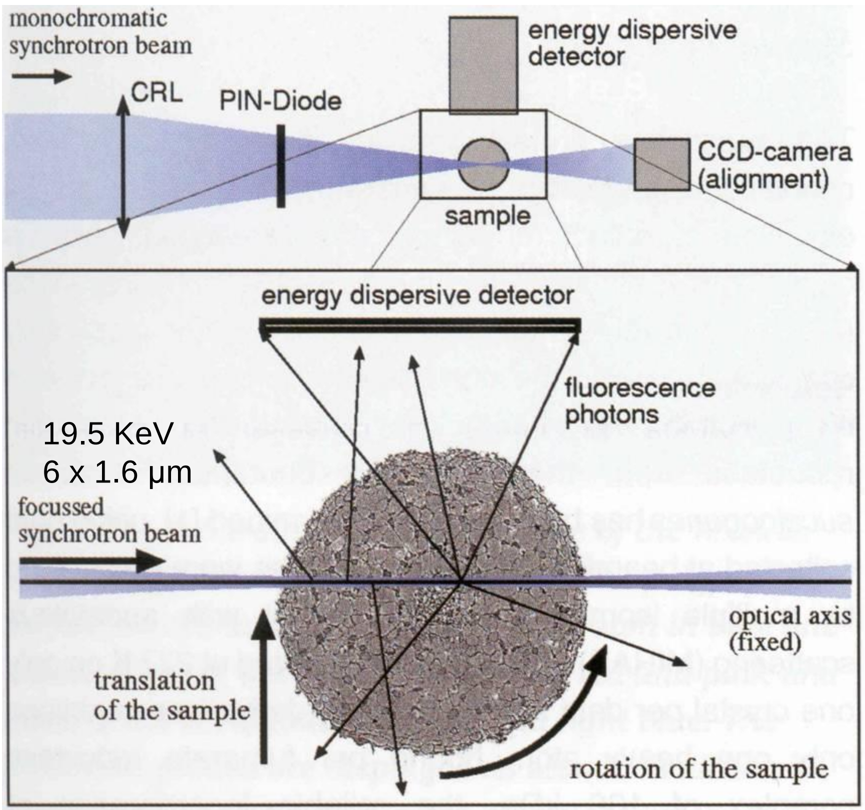
Typical fluorescence spectrum
in a single pixel

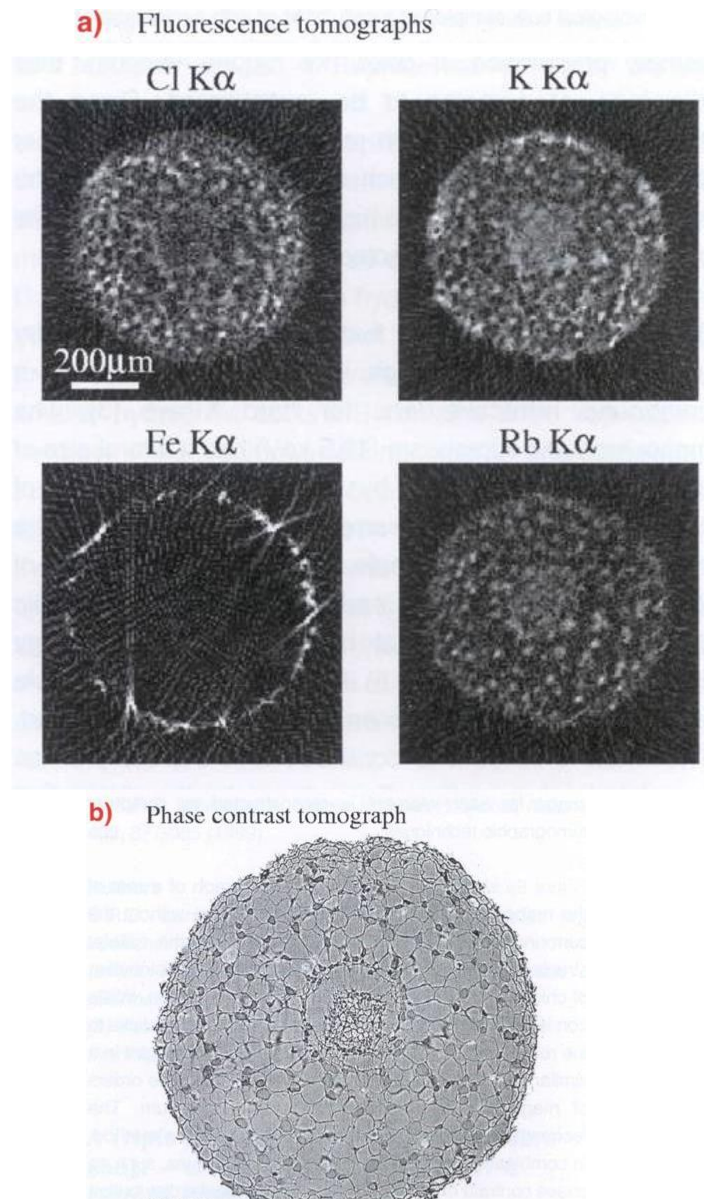
J. Dik, et al. *Analytical Chemistry* **2008** *80* (16), 6436-6442

Micro fluorescence tomography

Analysis of elemental distributions

Example: Root of a mahagoni tree

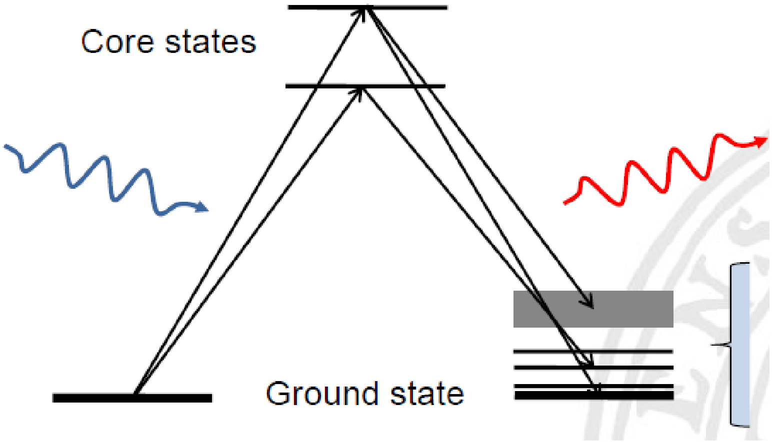




B. Lengeler et al. JSR. 6, 1153-1167 (1999)

Resonant inelastic X-ray scattering (RIXS)

Resonant excitation and photon emission



→ measures energy, momentum, and polarization change of the scattered photon

→ changes of the photon are transferred to intrinsic excitations of the material

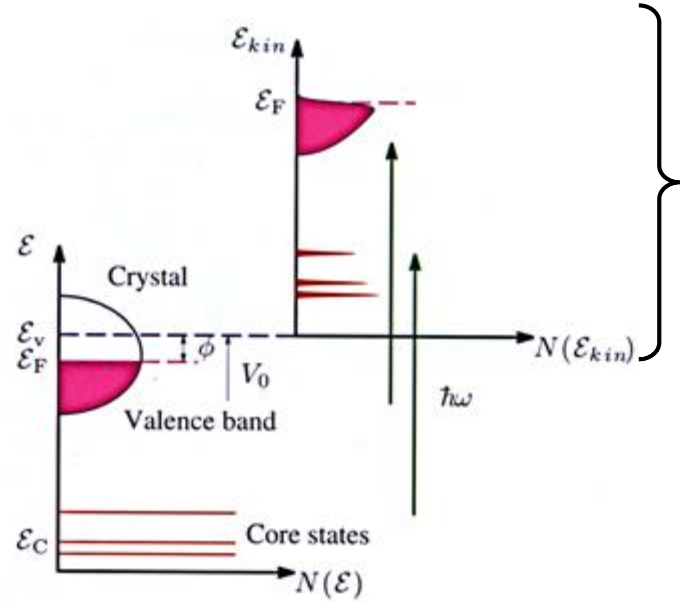
→ provides information about those excitations

- site, element, orbital selectivity
- polarization dependent (symmetry selectivity)
- probing of low-energy excitations
- access ultrafast dynamics
- sensitive to bulk (large penetration depth)

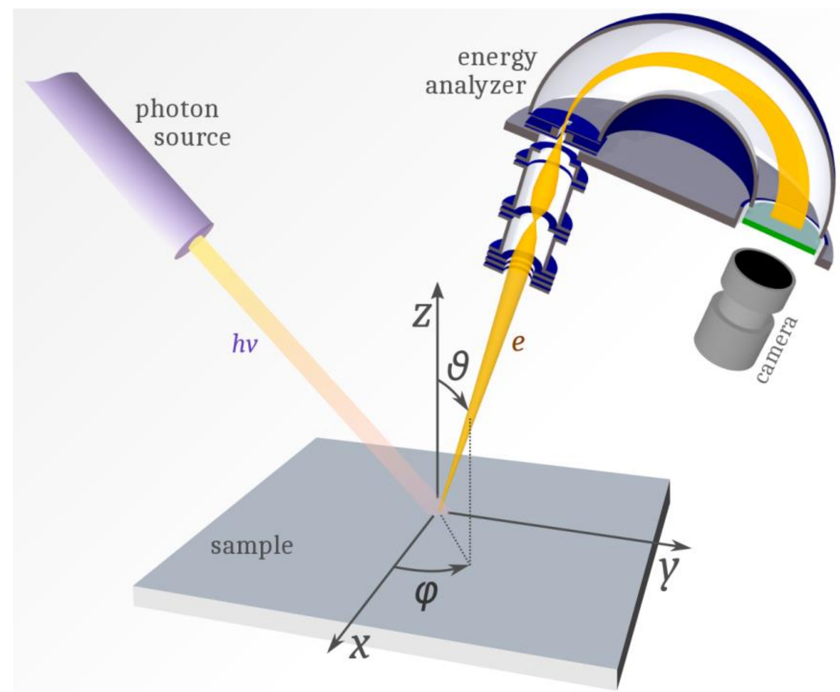
X-ray Photoelectron Spectroscopy

Angle-resolved photoemission spectroscopy (ARPES):

- **General idea**: physical properties of materials can be understood and classified according to how electrons propagate within it. Use of higher energy photon to probe deeper layer of sample.
- **Electron band theory**: electron motion in crystals is described by the dispersion relation $\mathcal{E}_B(\vec{q})$
  → gives the electronic binding energy as a function of the wave vector of the electron
- **Working principle:** $\mathcal{E}_B(\vec{q})$ is deduced by measuring energy and momentum of “free” photoelectrons and applying the energy and momentum conservation law
- **Energy:** $$\mathcal{E}_{kin} = \frac{\hbar^2 {q_v}^2}{2m} = \hbar\omega - \phi - \boldsymbol{\mathcal{E}_B}$$
  ϕ the work function of the material



Photoelectron spectrum



https://commons.wikimedia.org/w/index.php?curid=90955767

X-ray Photoelectron Spectroscopy

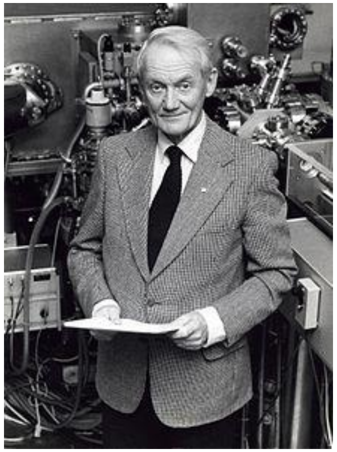
Angle-resolved photoemission spectroscopy (ARPES):

- **Localized core states:** determination of $\mathcal{E}_B$ by measuring $\mathcal{E}_{kin}$ (knowing $\hbar\omega$ and ϕ)

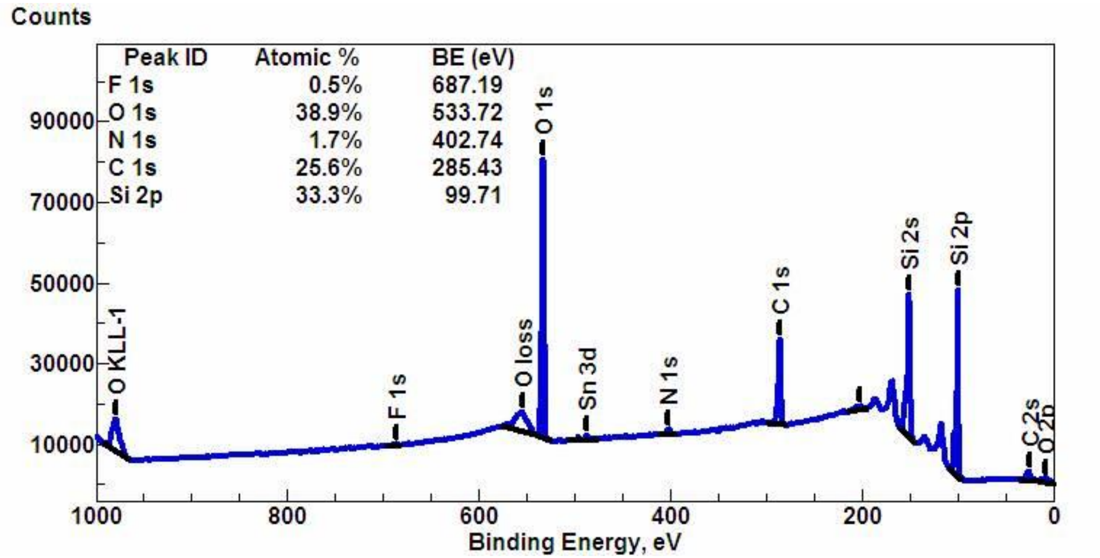
→ provides fingerprint of chemical composition of the near-surface region

→ basis for UV and X-ray photoelectron spectroscopy (UPS and XPS) in surface science

→ **electron spectroscopy for chemical analysis (ESCA)**



Kai Siegbahn
1981 Nobel Prize in Physics



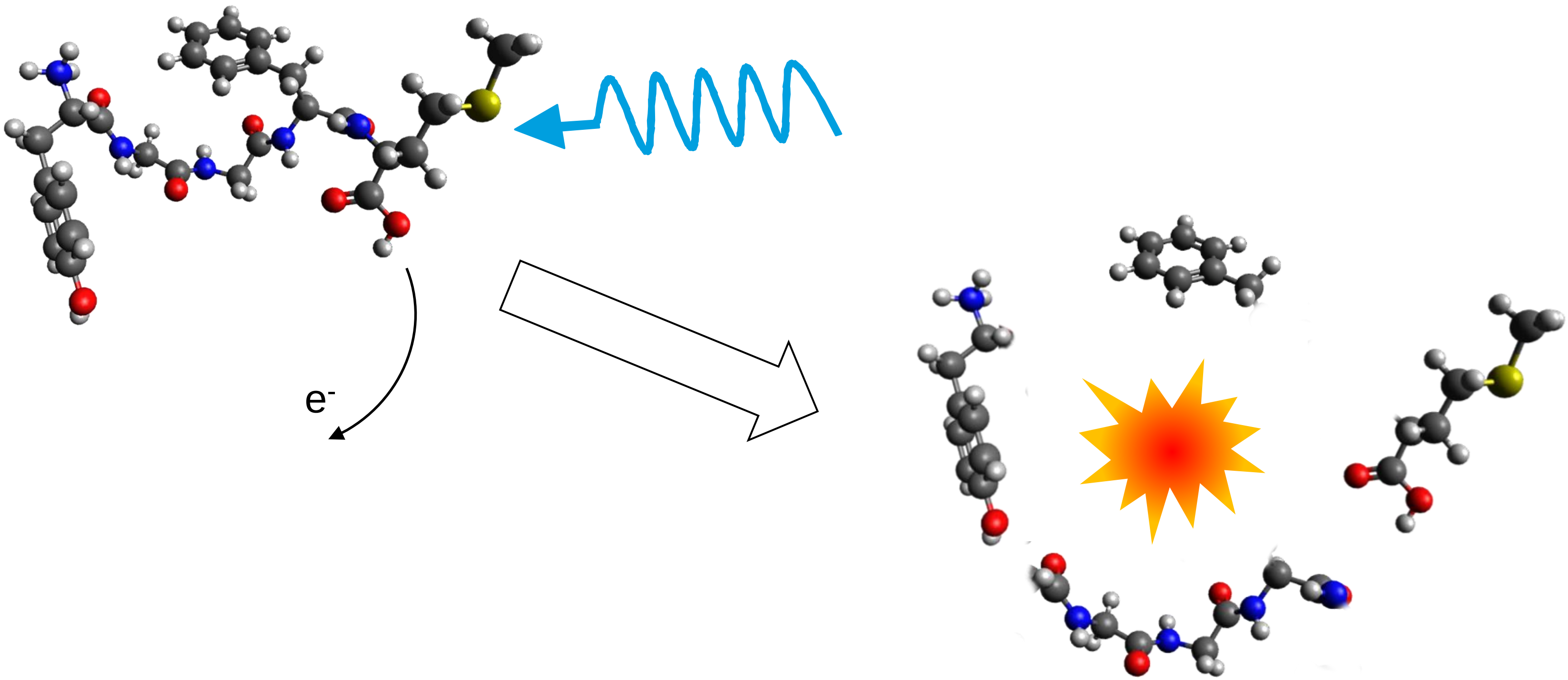
https://commons.wikimedia.org/w/index.php?curid=17267639

Action spectroscopy

When photon or electron cannot be measured

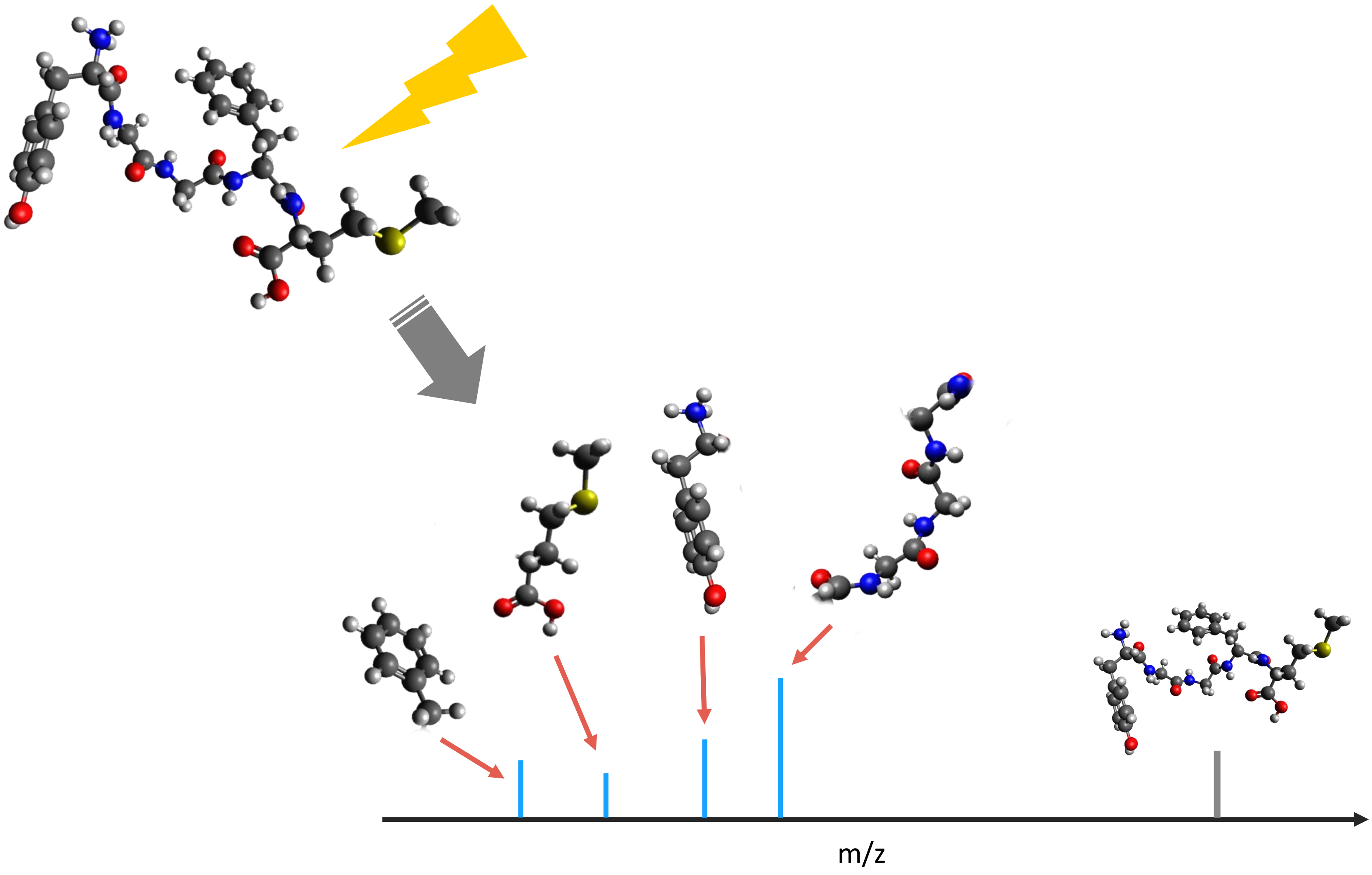
In some cases (low target density, confined experimental geometry etc..), measuring the absorption or scattering of light is impossible.

Instead: measure the action of the light on the molecule = ionization / fragmentation
Photo-ionization → Ions can be manipulated in electric fields



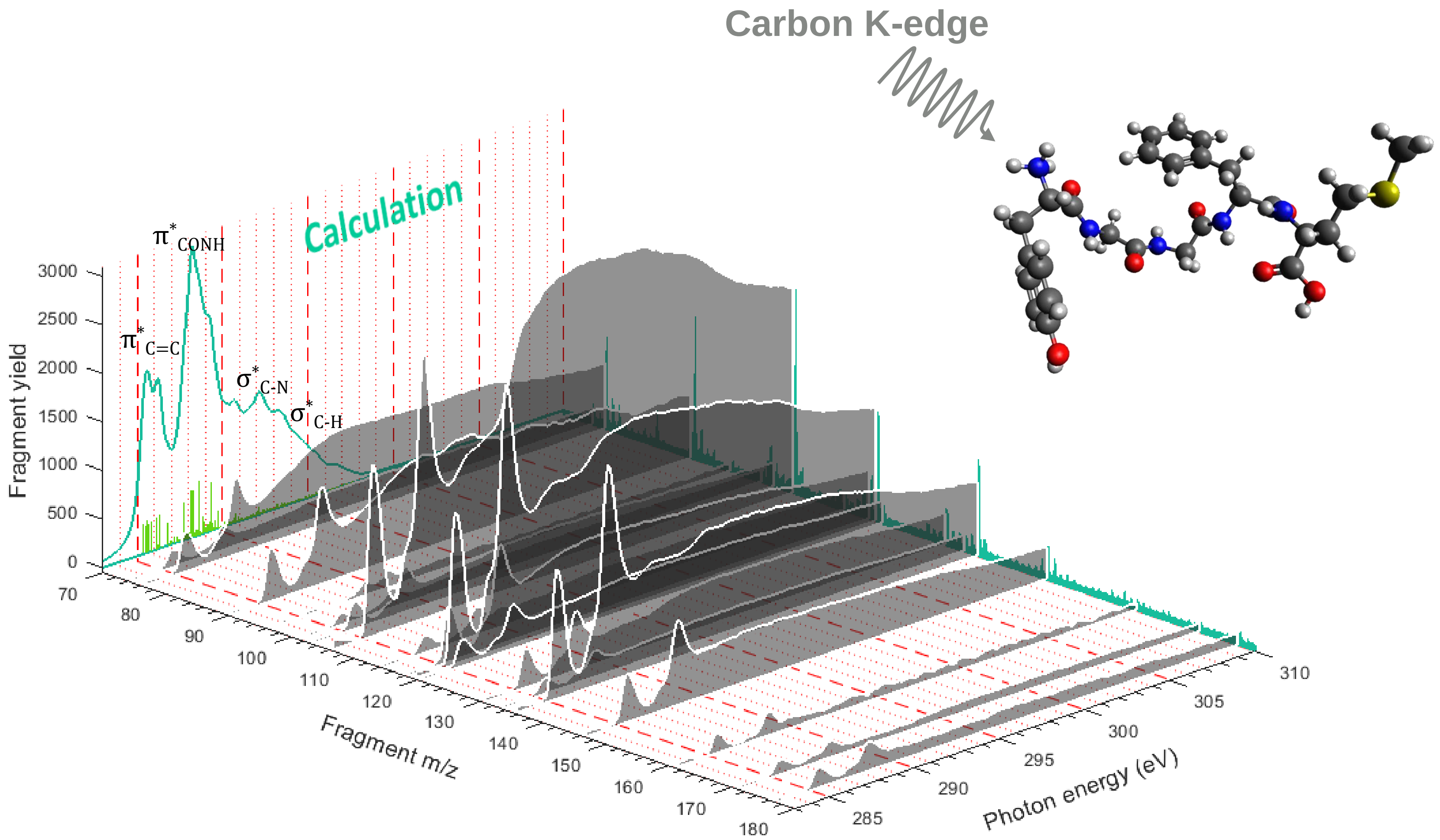
Action spectroscopy

Measuring charged fragments with mass spectrometry



X-ray Action Spectroscopy

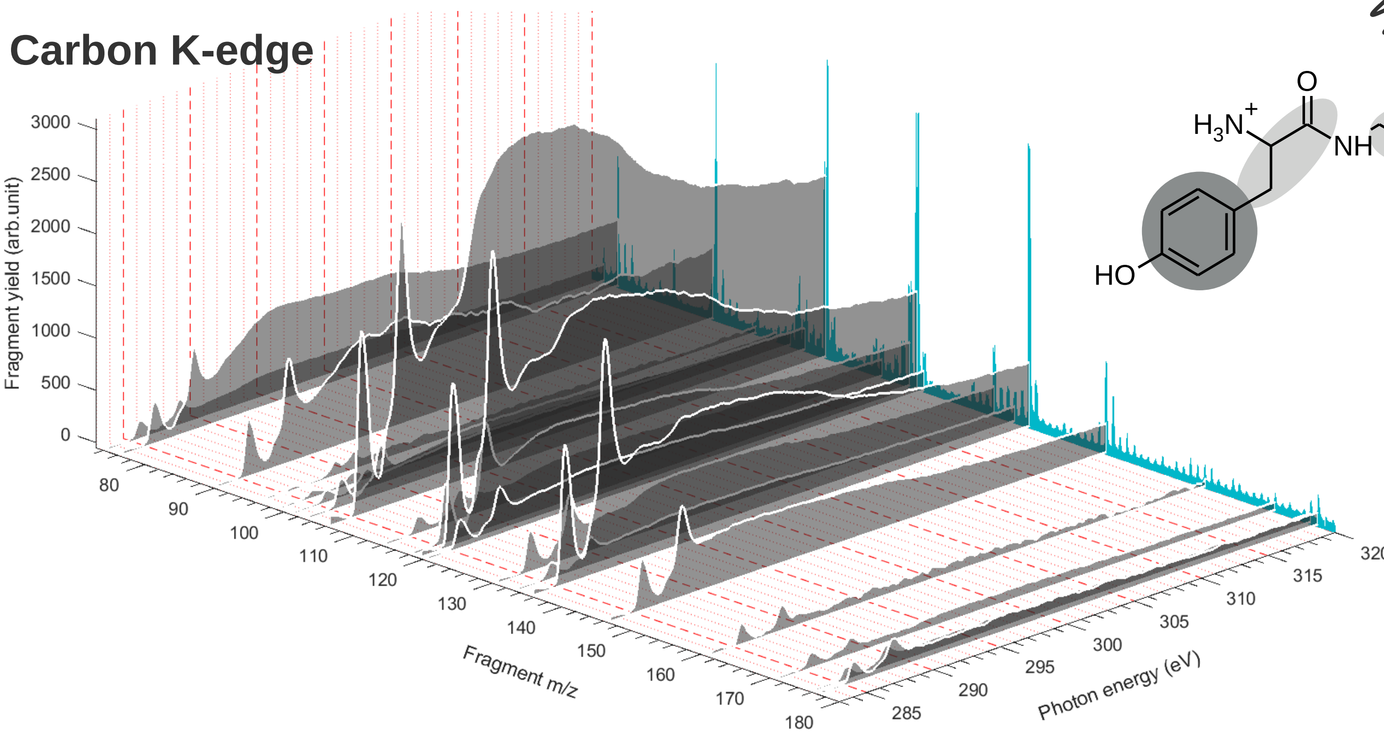
Near-Edge X-ray Absorption Mass Spectrometry (NEXAMS)

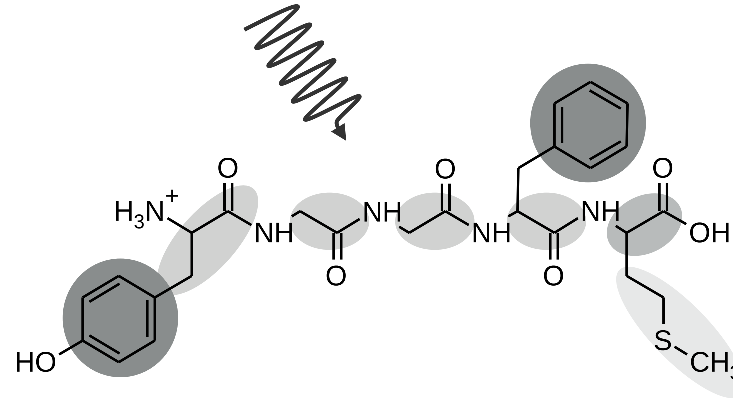


NEXAMS

at the C, N, and O K edges

Carbon K-edge





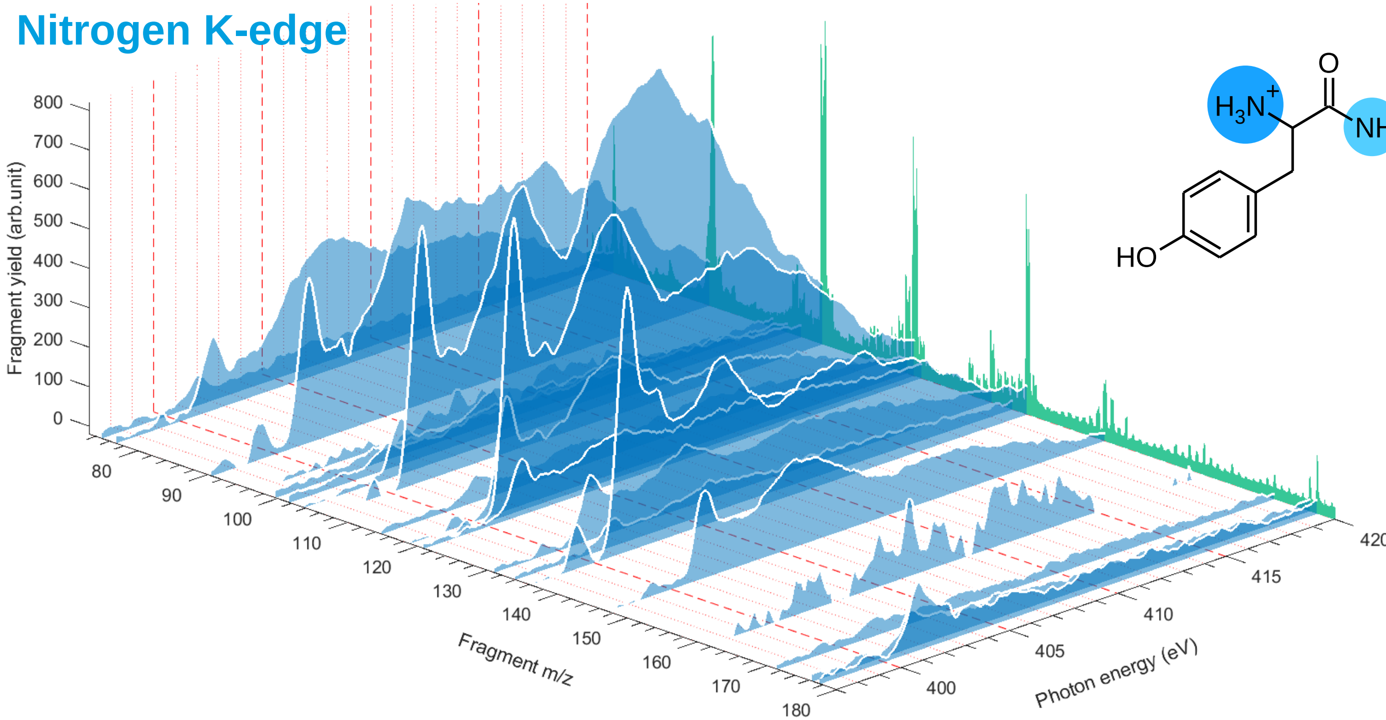
- Resonant excitation to molecular orbitals
- Probe of the local structure and conformation
- Probe of the protonation site

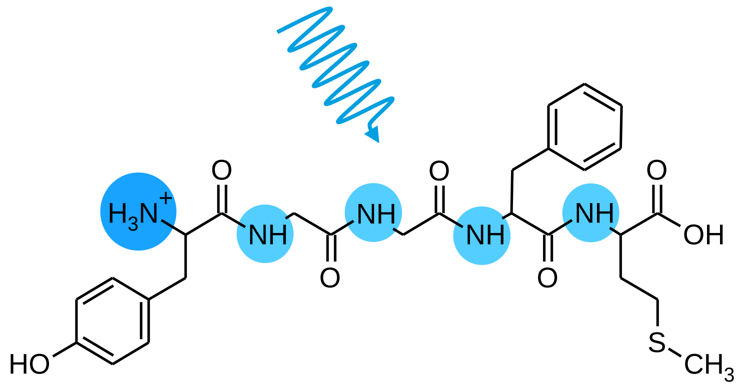
S. Dörner *et* al., J. *Am. Soc. Mass Spectrom.* **32**, 670 (2021).

NEXAMS

at the C, N, and O K edges

Nitrogen K-edge





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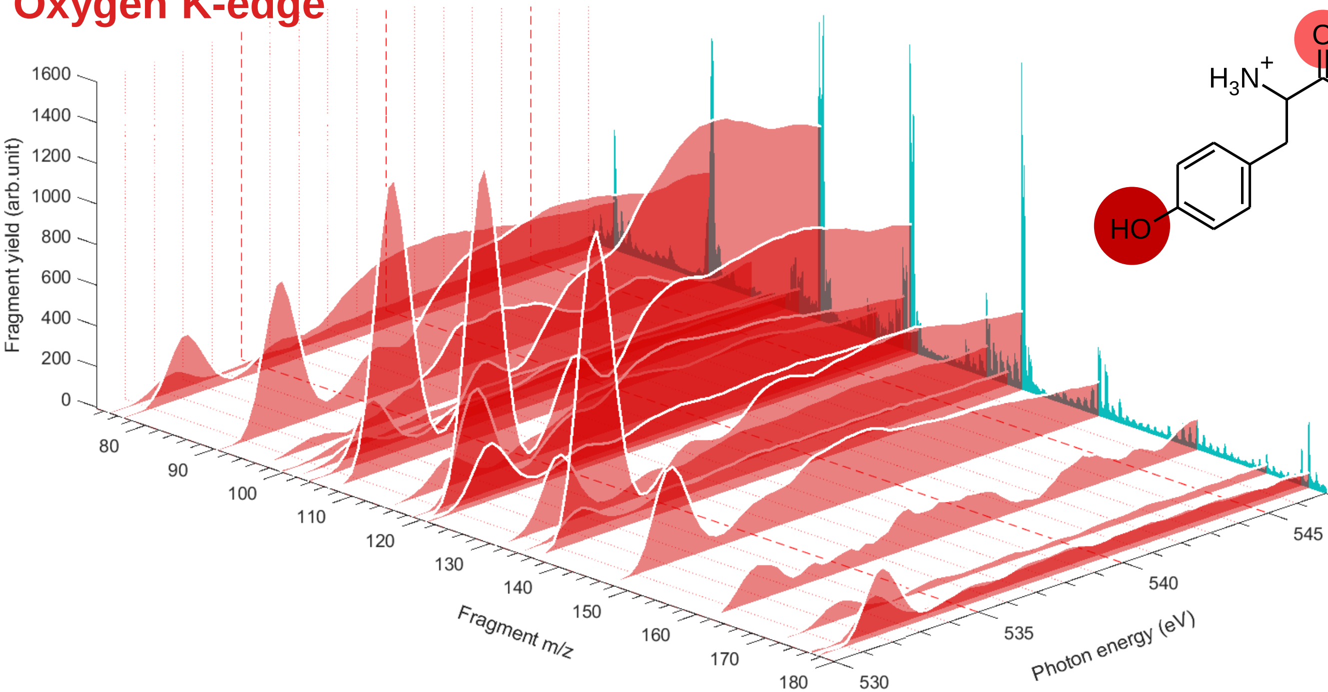
- Probe of the protonation site

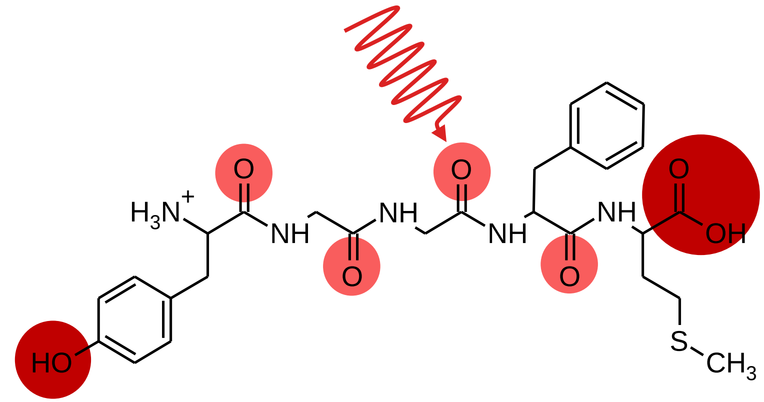
S. Dörner *et* al., J. *Am. Soc. Mass Spectrom.* **32**, 670 (2021).

NEXAMS

at the C, N, and O K edges

Oxygen K-edge





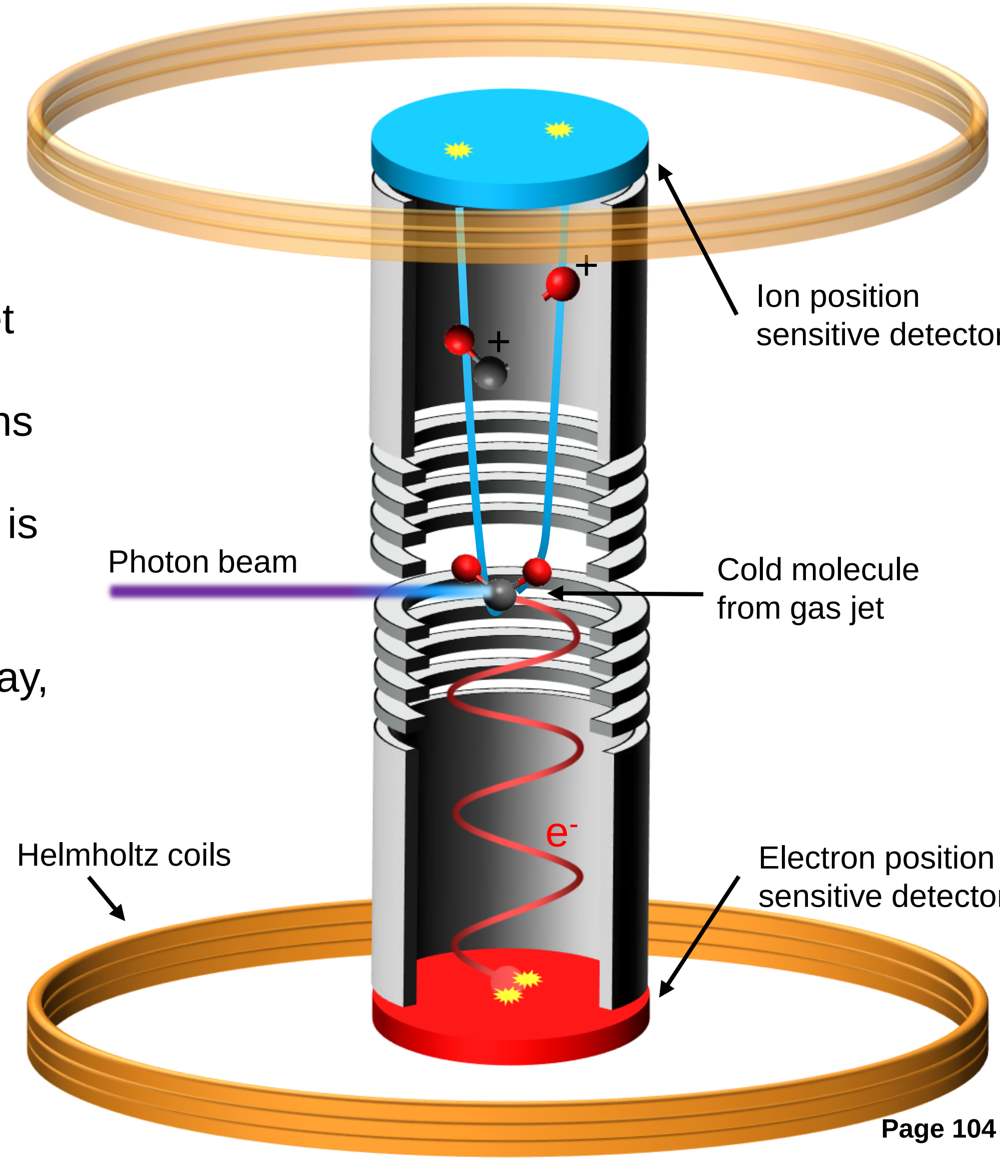
- Resonant excitation to molecular orbitals
- Probe of the local structure and conformation
- Probe of the protonation site

S. Dörner *et* al., J. *Am. Soc. Mass Spectrom.* **32**, 670 (2021).

Photo-electron photo-ions coincidence

Cold Target Recoil Ion Momentum Spectroscopy (COLTRIMS)

- Cold molecule from supersonic gas jet
- Coincident collection of all particles involved in the fragmentation: electrons and charged fragments
- Three dimensional momentum vector is obtained
- Study of fragmentation processes, circular dichroism, Auger-Meitner decay, inter-coulombic decay, FEL-induced multi ionization…

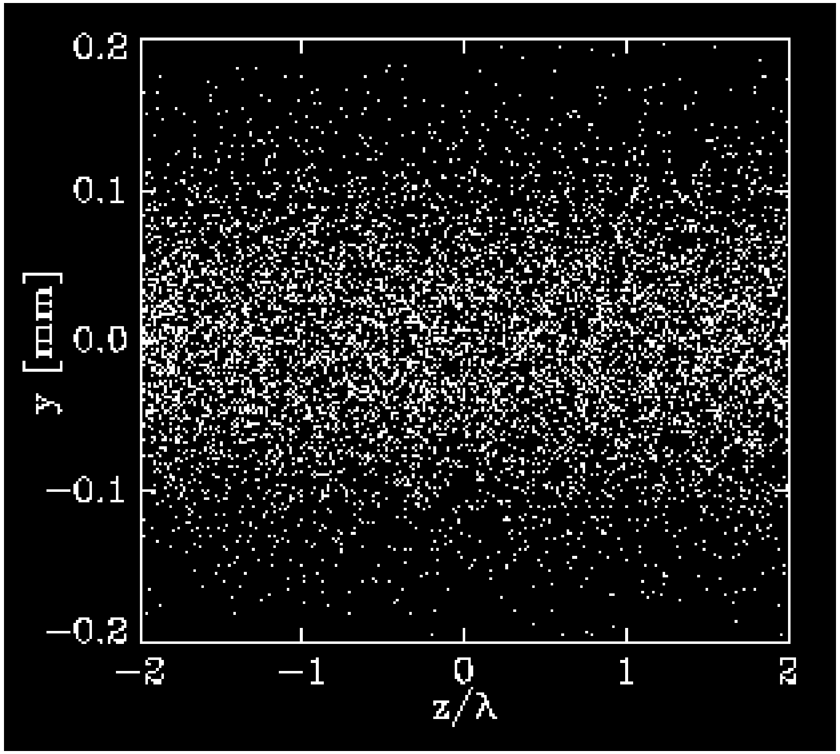


Experiments with FELs

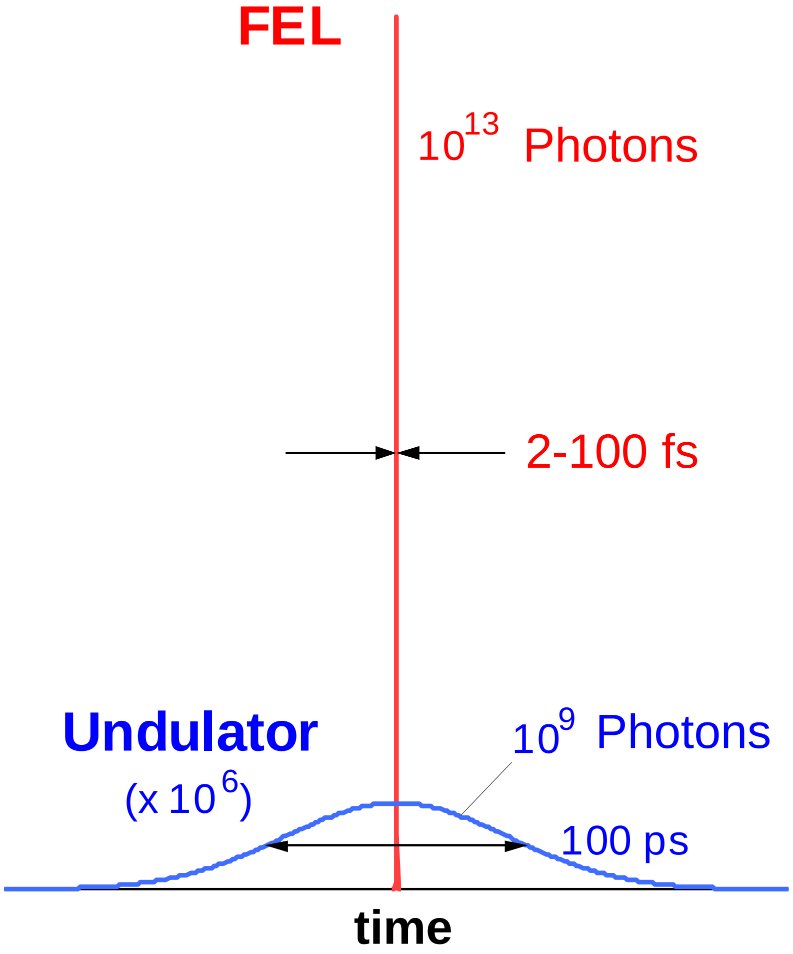
Undulator radiation – X-ray FEL radiation

Ultra bright, ultra short, pulses

Microbunching in the SASE process



(simulation by Sven Reiche)



Why use an FEL for structure studies?

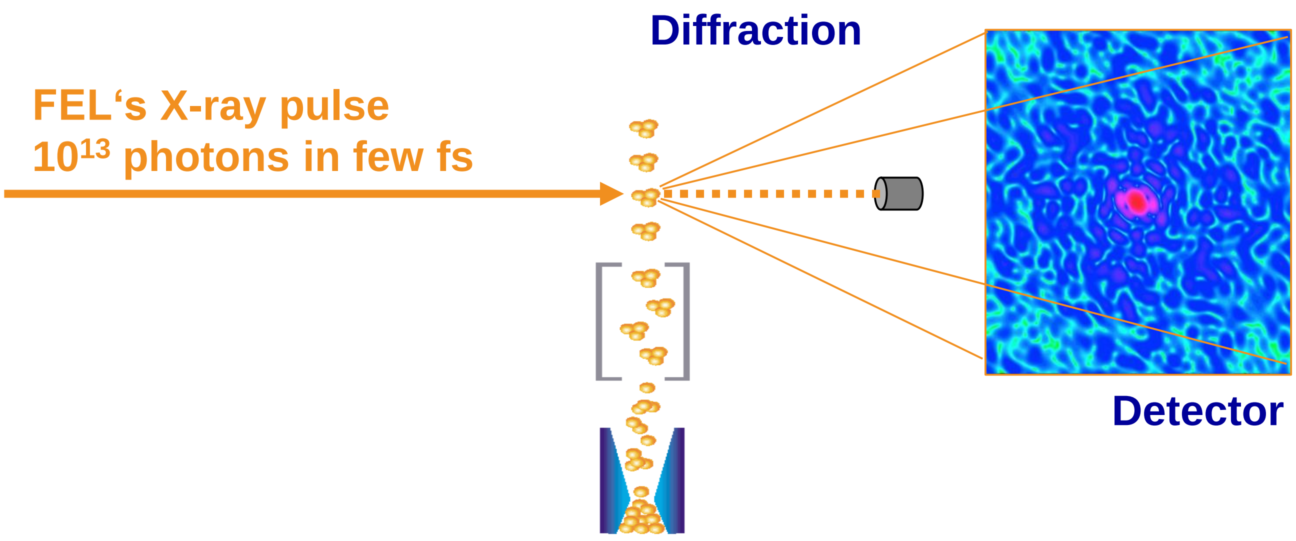
SPI , Ultrafast processes, extreme conditions

- **Structure determination of non-crystalline objects and very small (nano-) crystals**
  - Dream: bio-molecules in 3D that do not form crystals and single particle imaging
  - Understanding the structure of biomolecules with atomic (~0.1 nm) resolution enables to reveal & understand their function
  - Understanding function allows to develop treatments, medication, drugs
- **Ultrafast changes of structure**
  - from atoms to solids, including changes of the associated electronic structure
  - "femtochemistry": see how atoms in a molecule move during a chemical reaction
- **Extreme conditions**
  - Study matter under extreme conditions of temperature and pressure (planets)
  - Extreme electric and magnetic field

Single-molecule diffractive imaging

The ultimate goal

Imaging of non-crystalline biological samples.



Diffract before … destroy ?

Beware of the Coulomb repulsion…

Diffract before destroy ?

Theoretical prediction

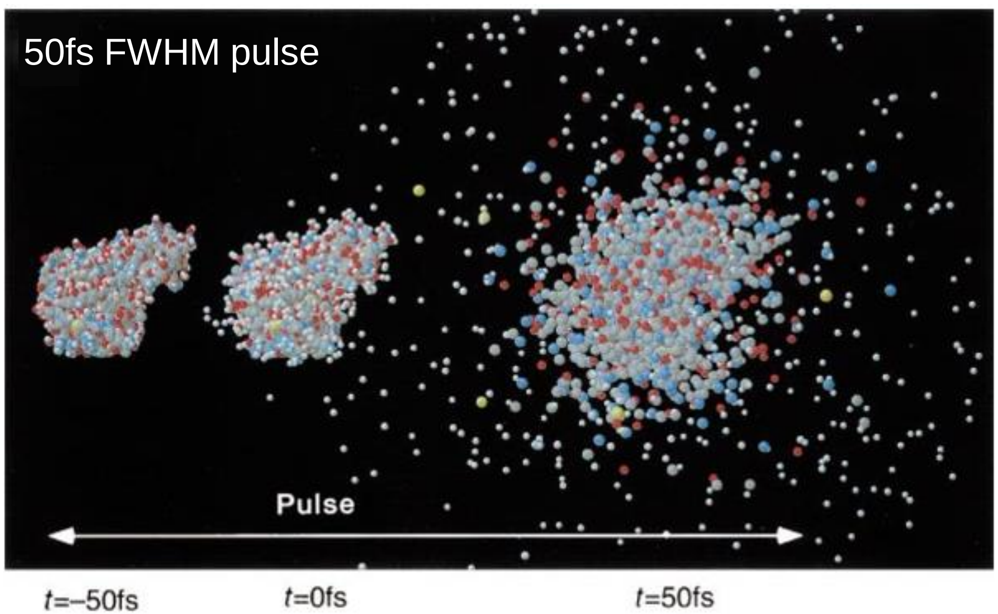
Potential for biomolecular imaging with femtosecond X-ray pulses

Richard Neutze*, Remco Wouts*, David van der Spoel*, Edgar Weckert†‡ & Janos Hajdu*

** Department of Biochemistry, Biomedical Centre, Box 576, Uppsala University, S-75123 Uppsala, Sweden*
† Institut für Kristallographie, Universität Karlsruhe, Kaiserstrasse 12, D-76128, Germany

Nature 406, 752 (2000)

Explosion of a biomolecule (T4 lysozyme) after exposure to a XFEL pulse (E = 12 keV)
~2000 primary ionization events on one protein!



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Nature 406, 752 (2000)

it works !

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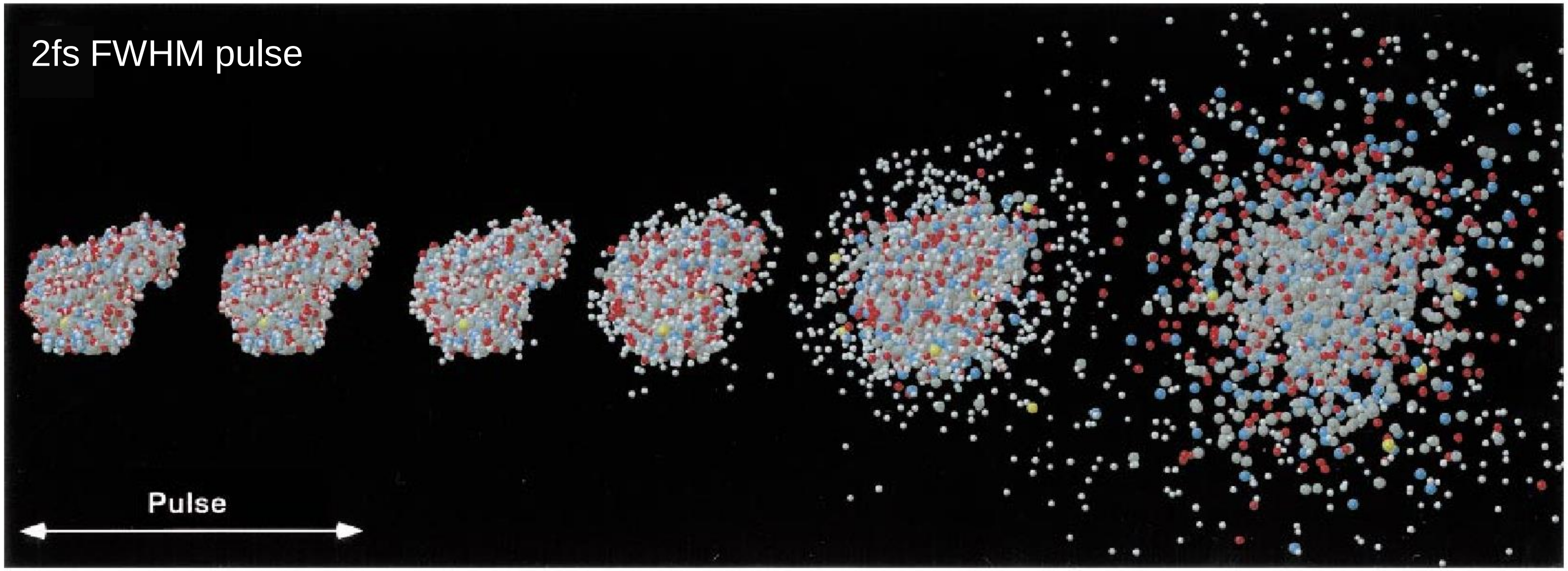
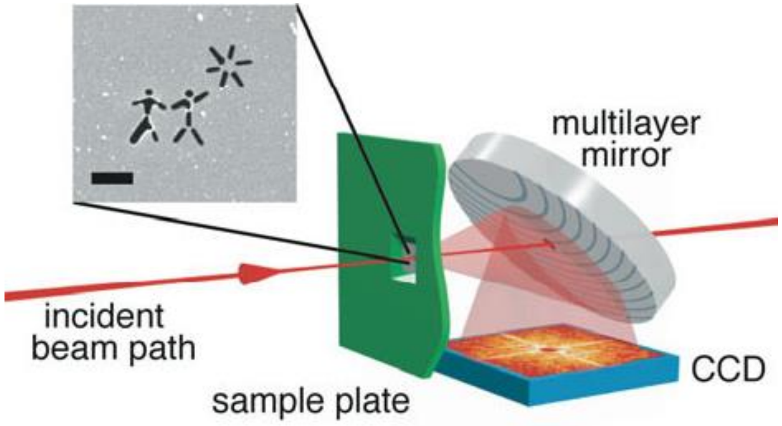


t=–2fs *t*=2fs *t*=5fs *t*=10fs *t*=–20fs *t*=50fs

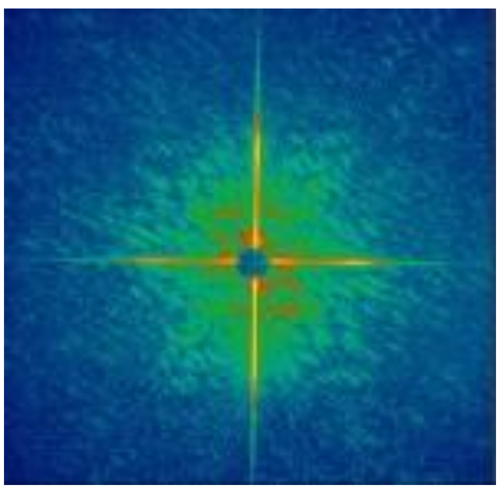
Ultrafast coherent X-ray diffraction

First demonstration at FLASH

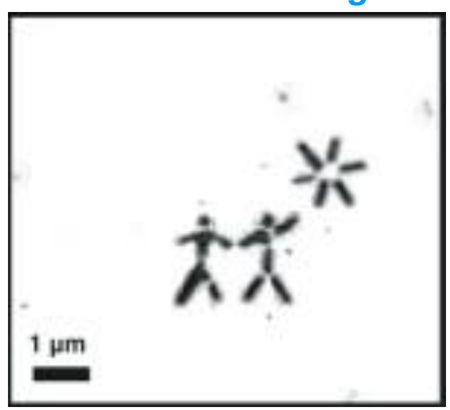
Incident FEL pulse:
25 fs, 32 nm,
10^{12} photon
20 µm focus



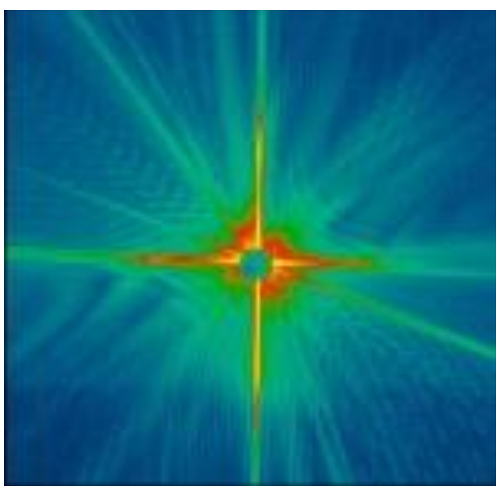
Pulse #1: Diffraction pattern



Reconstructed image



20s later: Pulse #2 sees structure destroyed by pulse #1

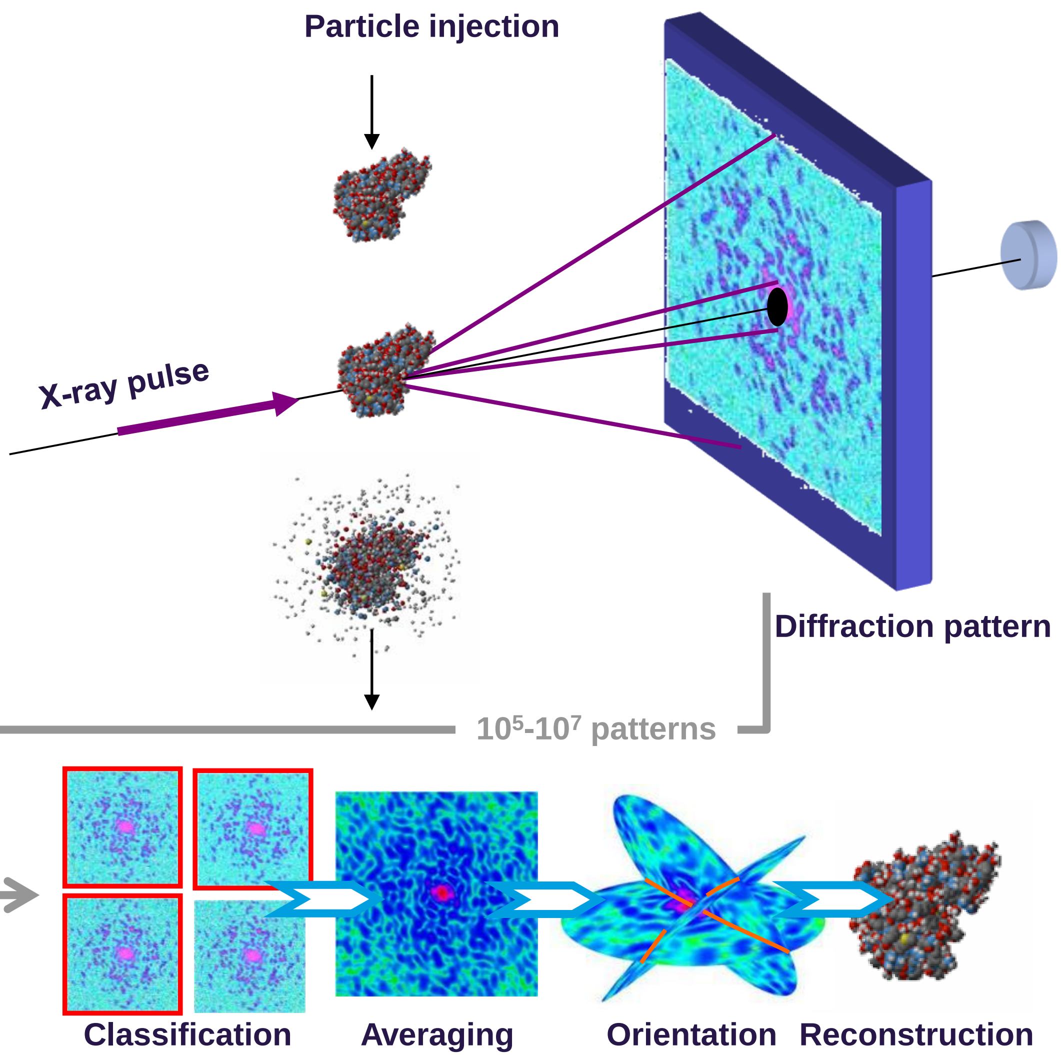


H. Chapman et al. Nature Physics 2, 839-843 (2006)

Conclusion: diffraction takes place before the sample is destroyed !

Determine the structure of bio-particles

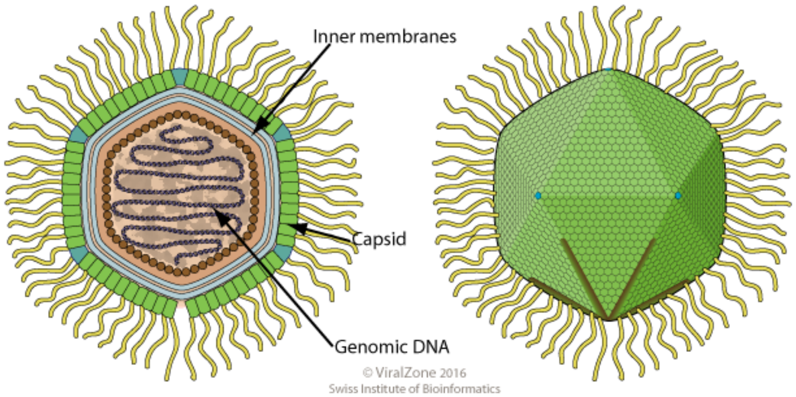
Diffraction, orientation, reconstruction



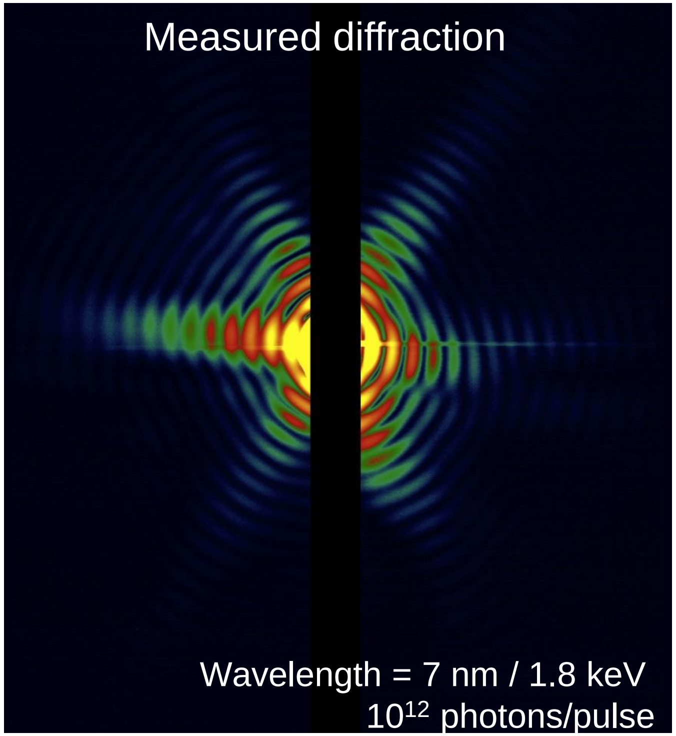
Henry Chapman, CFEL. Science, 2007, 316, 1444-48

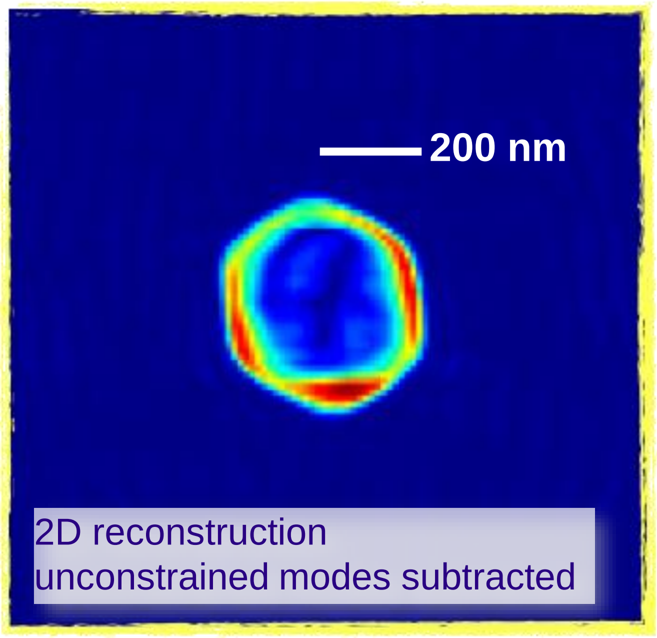
Diffraction from a mimivirus

One of the largest known viruses



Data collection: 103 min
Heat ~100 000 K
1.7e^{6} photons/image

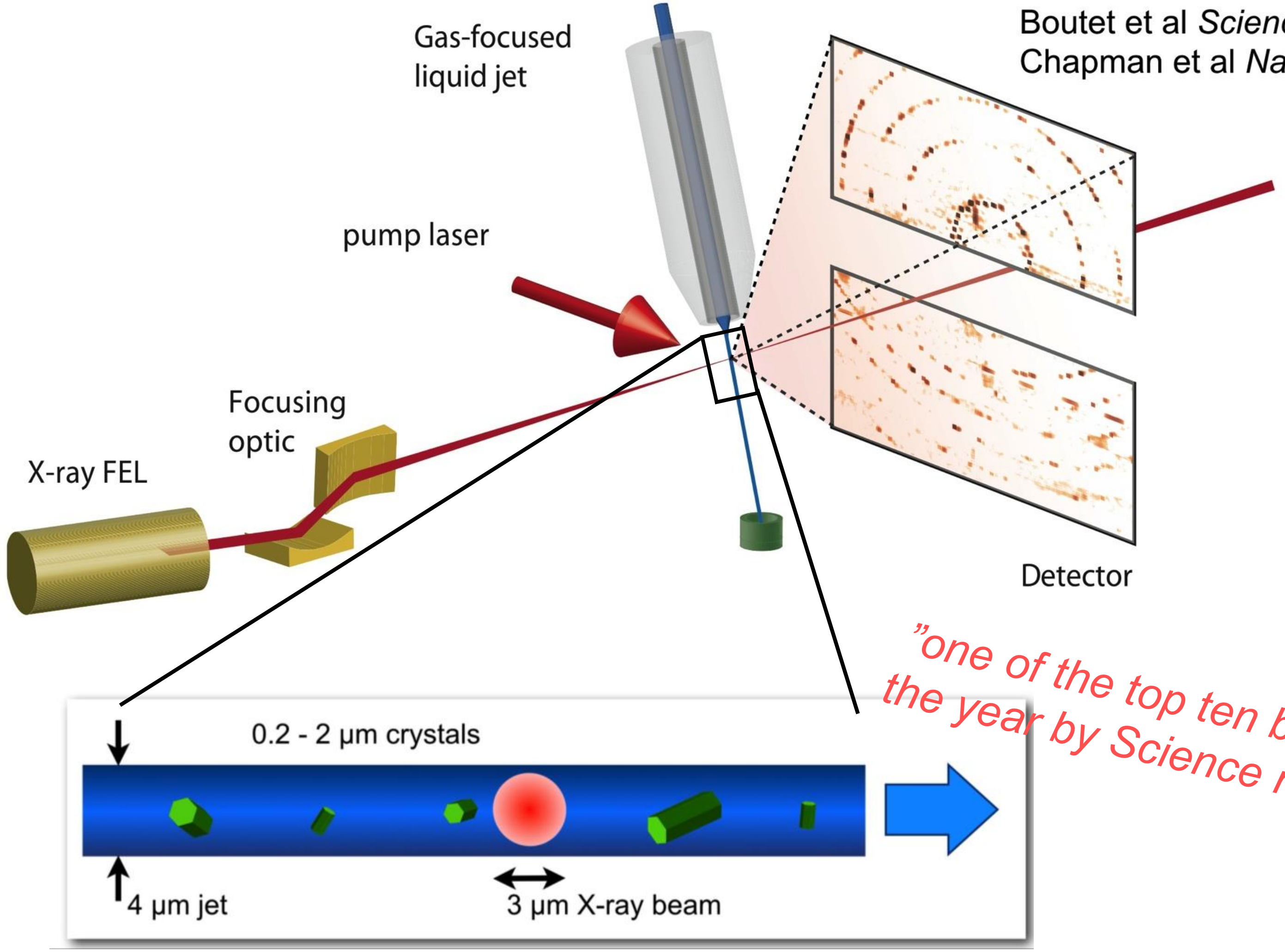




Seibert, …, Chapman, Hajdu, *Nature* 470, 78–81 (2011)

Serial femtosecond X-ray crystallography

Tiny crystals in liquid jet



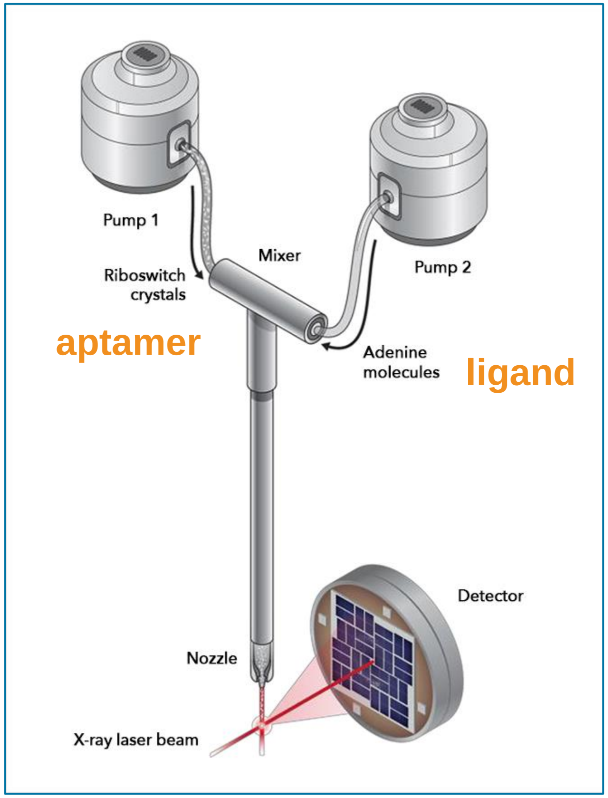
Boutet et al *Science* (2012)
Chapman et al *Nature* (2011)

”one of the top ten breakthroughs of the year by Science magazine in 2013”

Serial femtosecond X-ray crystallography

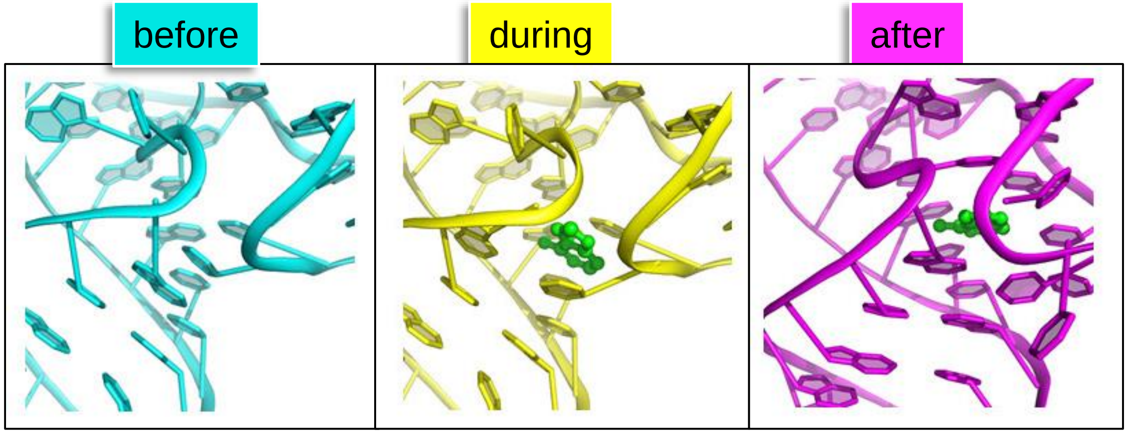
A riboswitch at work

Mix and inject concept



– Riboswitch: Gene regulator, present in bacteria and fungi
– After activation, the gene related to the switch is not read out anymore
– Activated by signal molecule (ligand) Adenine
– Active centre is aptamer = sequence of nucleic acids (easy to synthesize into nanocrystals

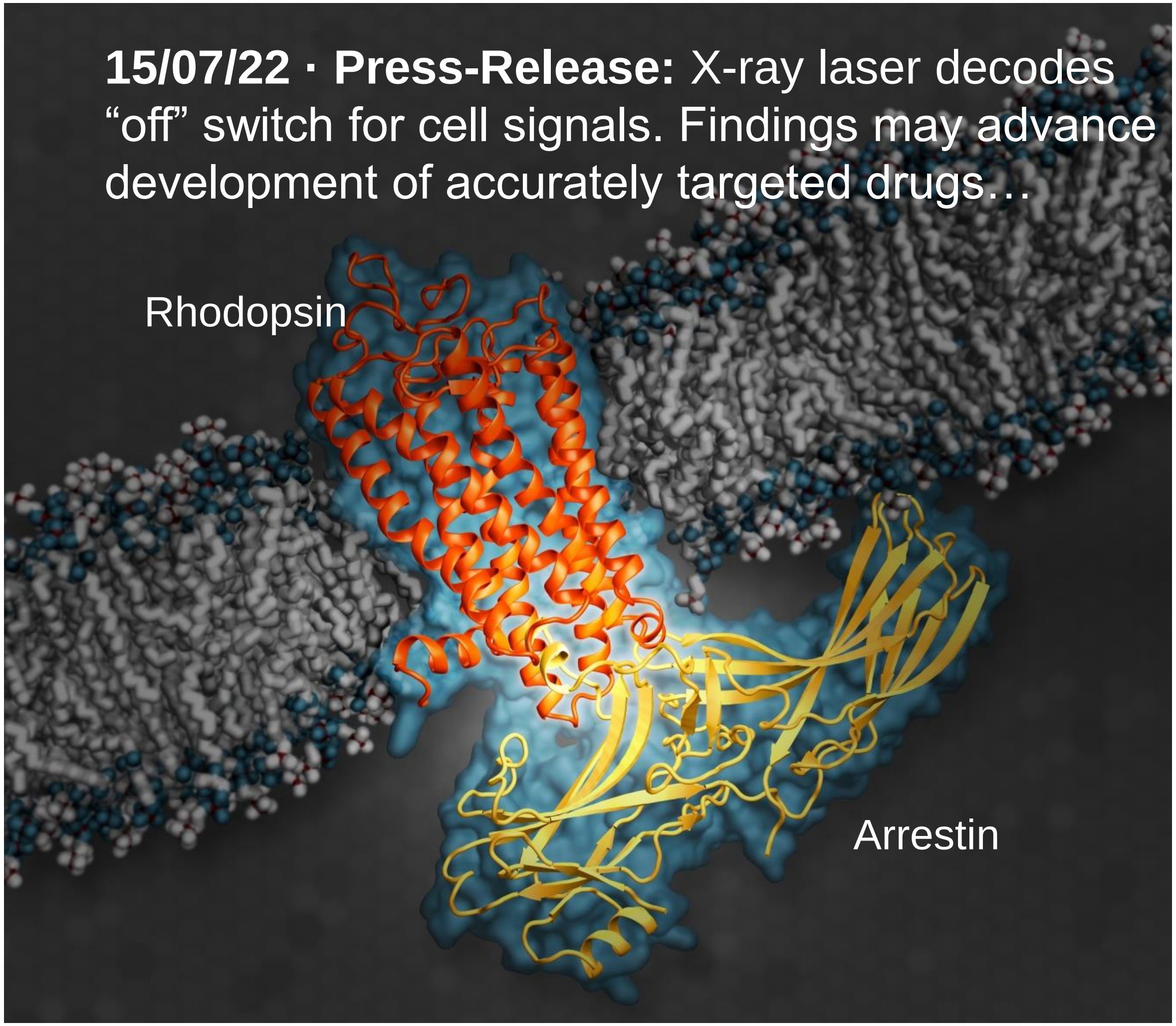
- Delay adjustment allows to follow intermediate states of reaction
- Tiny crystals are required, larger crystals would decompose upon the involved conformational changes and ligand diffusion would be too slow and uneven



Yun-Xing Wang, Nature (2014)

Serial femtosecond X-ray crystallography

Membrane protein complex



Rhodopsin: "G-protein-coupled receptors"; light sensitive pigment in the retina of the eye; present in cell's membrane

→ transmit signal via coupling with other proteins

Arrestin: "switch off" the receptors

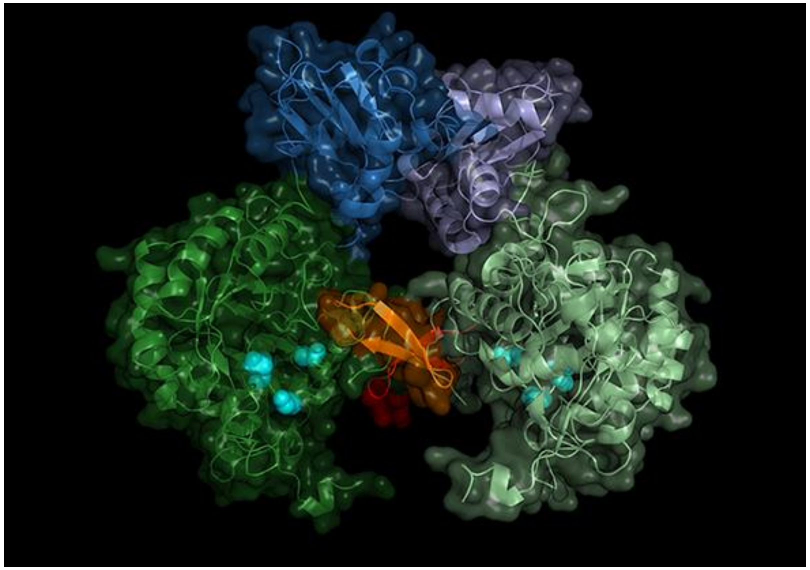
12h data acquisition
>5 million images
~19000 good diffraction patterns

Y. Kang et al. *Nature* (2015)

Serial femtosecond X-ray crystallography

Possible new approach for sleeping sickness drugs

University of Lübeck/DESY, Lars Redecke



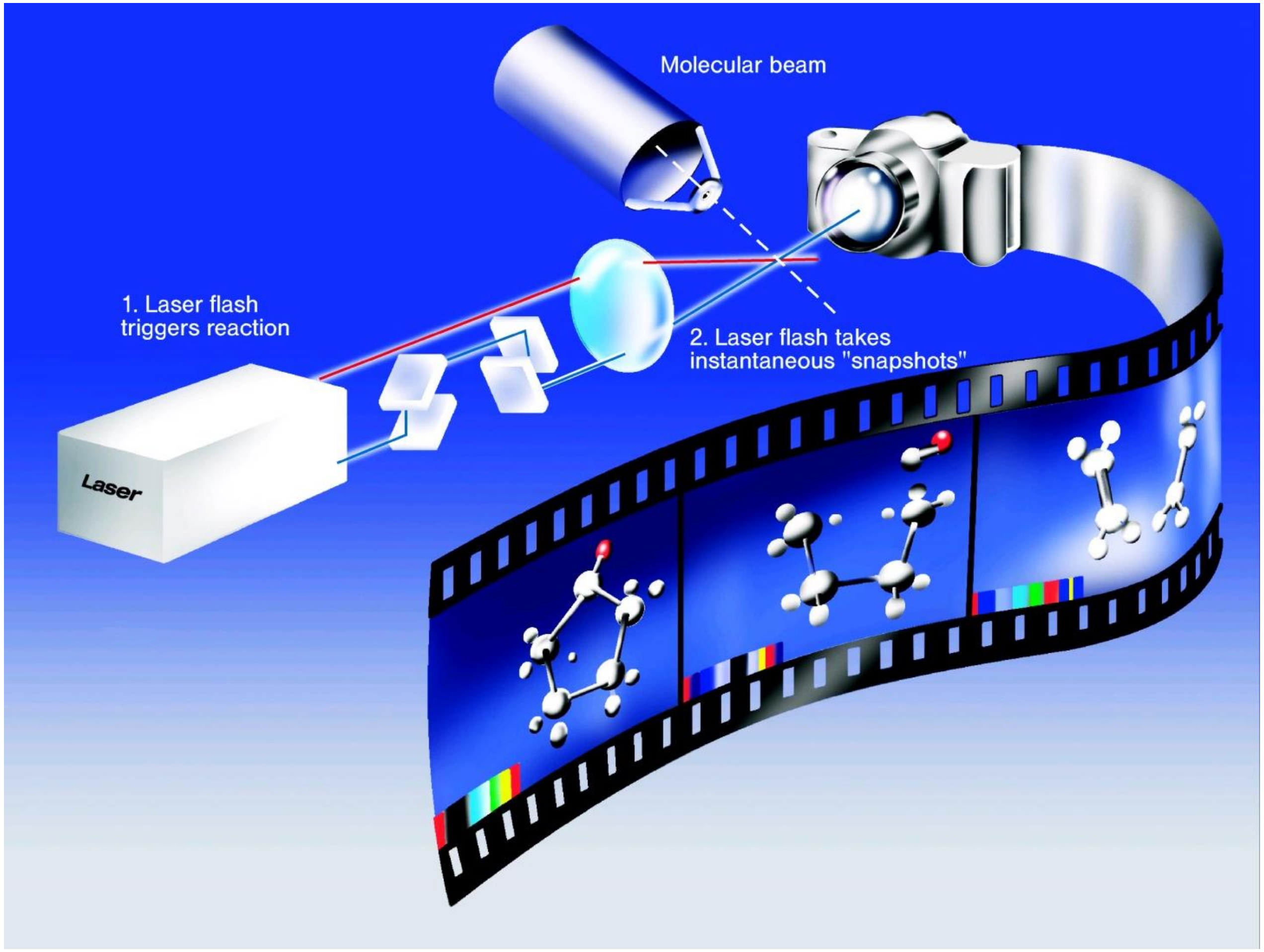
Structure of the parasite's IMP dehydrogenase. The active enzyme forms pairs (dimers), the "switch" region is shown in shades of blue.

- Sleeping sickness: tropical disease, caused by parasite transmitted by the Tsetse flies
- Decoding the detailed spatial structure of a vital enzyme of the pathogen (IMPDH), the parasite Trypanosoma brucei.
- **Idea**: switch off the enzyme of the parasite
- The result provides a possible blueprint for a drug that specifically blocks this enzyme and thus kills the parasite

K. Nass *et al.*, *Nature Commun.* **11**, 620 (2020)

Recording the “molecular movie”

The other ultimate goal

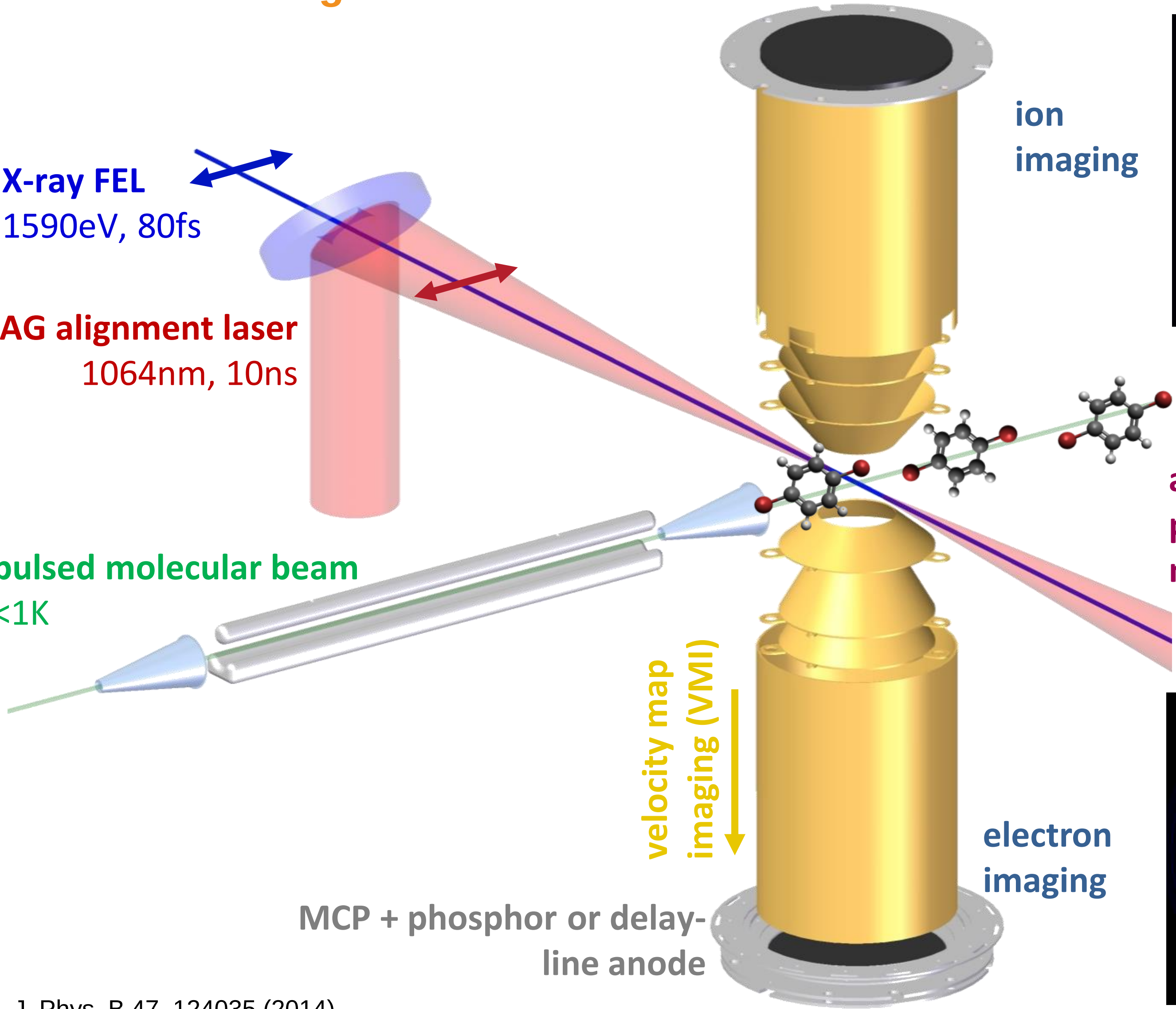


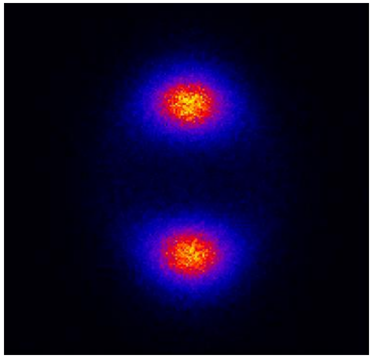
Snapshots for different times after excitation (pump-probe spectroscopy)

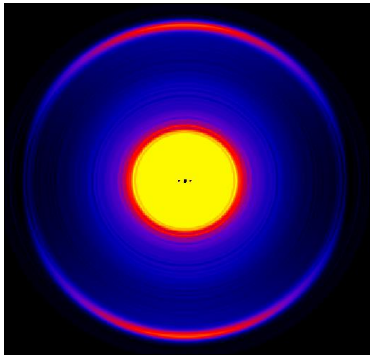
→ “motion picture” of the reaction

Double velocity map imaging in CAMP, FLASH

Multi-ionization of aligned molecules







D. Rolles, et al., J. Phys. B 47, 124035 (2014)

Double velocity map imaging in CAMP, FLASH

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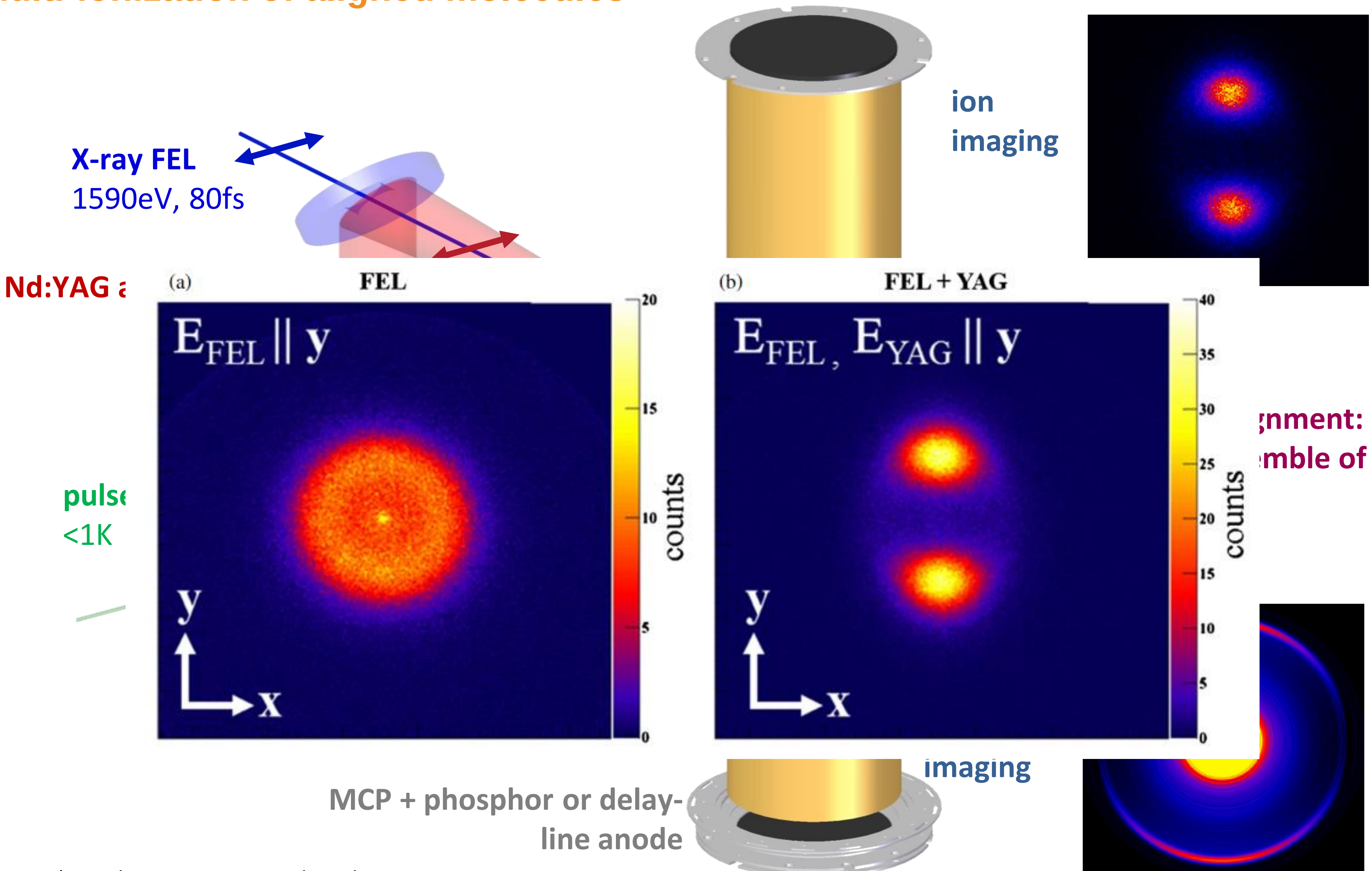
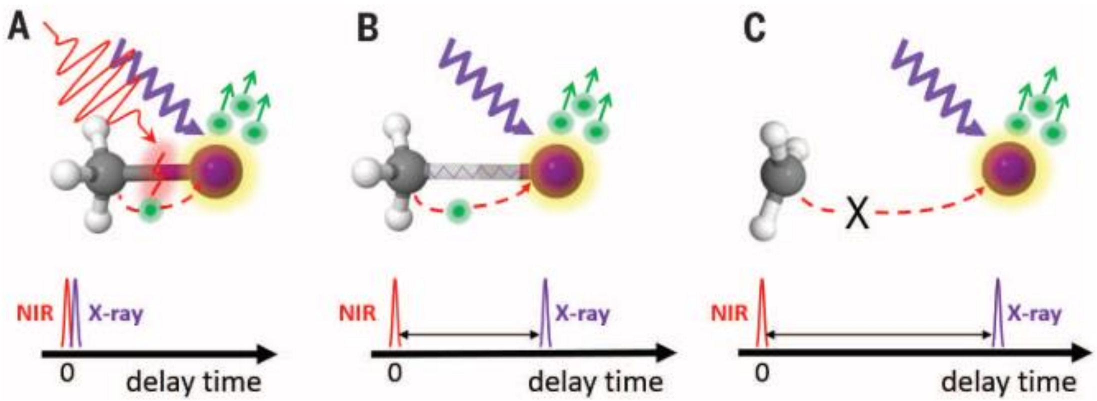


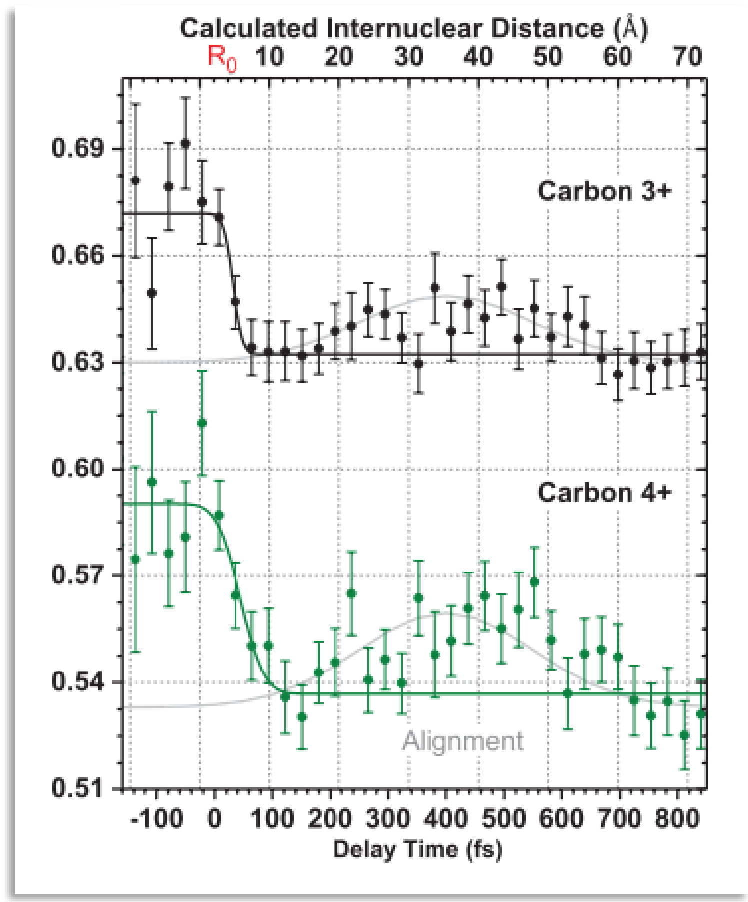
D. Rolles, et al., J. Phys. B 47, 124035 (2014)

Imaging charge transfer in iodomethane

IR-pump, XUV-probe



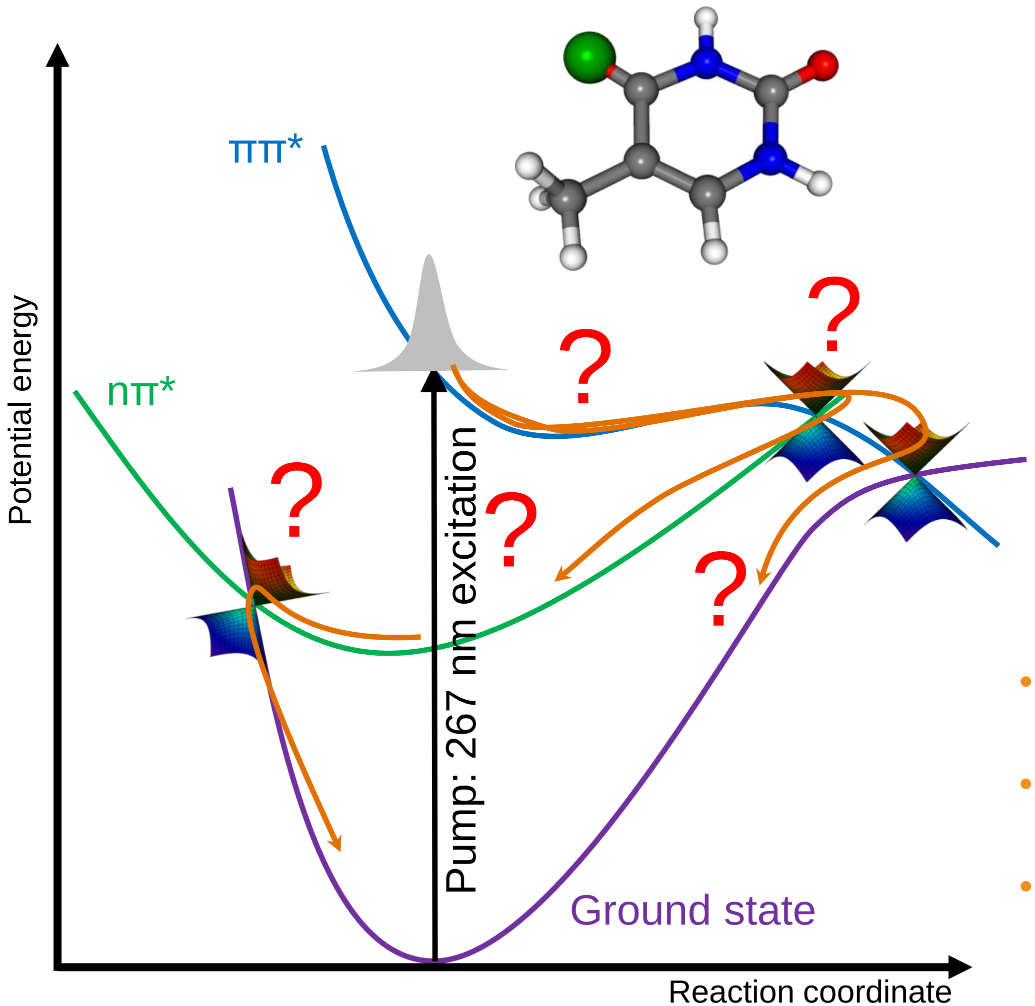
- IR-pump (800nm): dissociate the C-I bond
- XUV-probe (1500 eV): Core (M shell) ionization of iodine atom
- **Idea**: charge transfer from CH_3 to I depends on interatomic distance

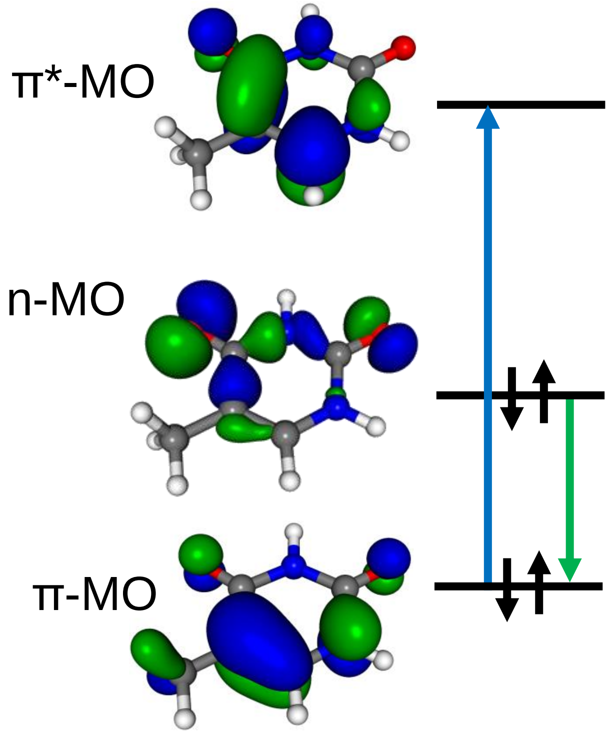


B. Erk, et al., Nature, 345, 6194 (2014)

What happens to thymine after photoexcitation

Deexcitation dynamic in a nucleobase





- Overall timescale?
- Which electronic states are populated?
- How does the geometry change?

McFarland et al. *Nature Commun.* **2014**, *5*, 4235
courtesy of T. Wolf

Photon energies to probe the dynamics

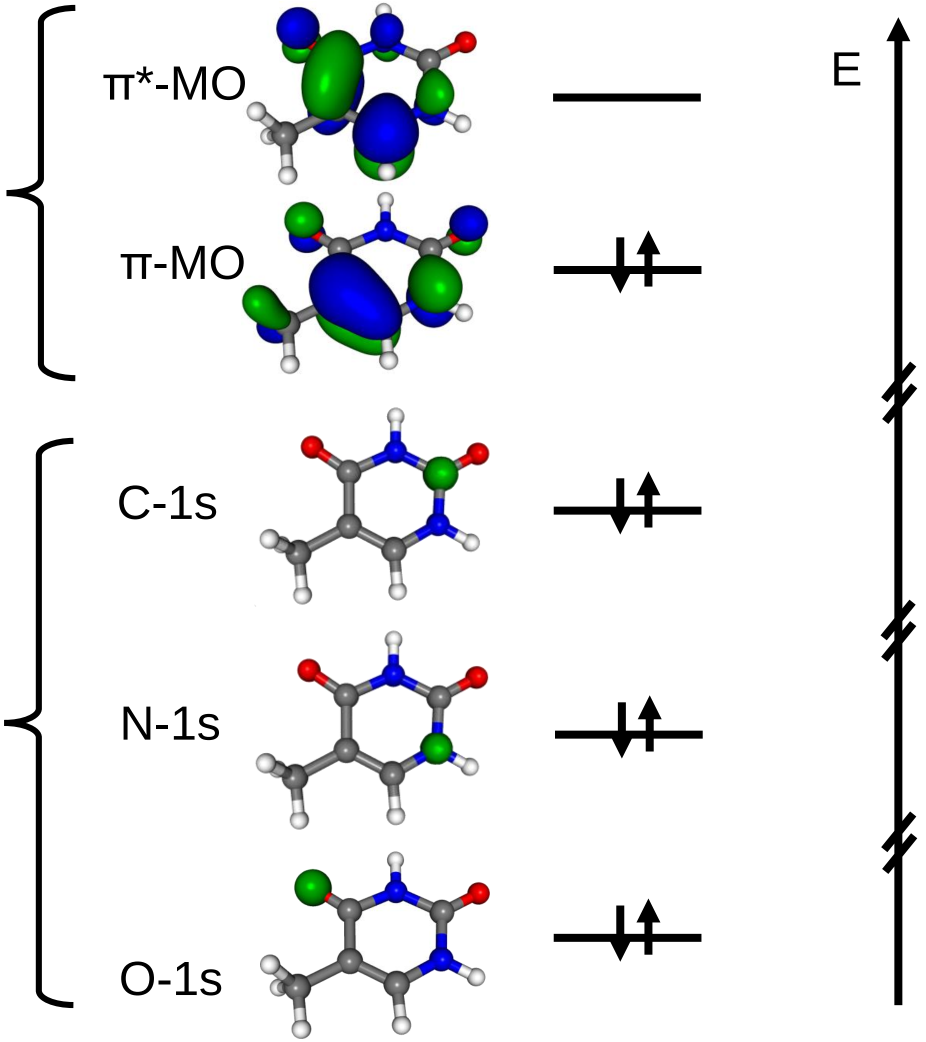
Probing valence electrons or core electrons

Valence electrons:

- Delocalized
- Overall time scales
- XUV, high harmonic generation

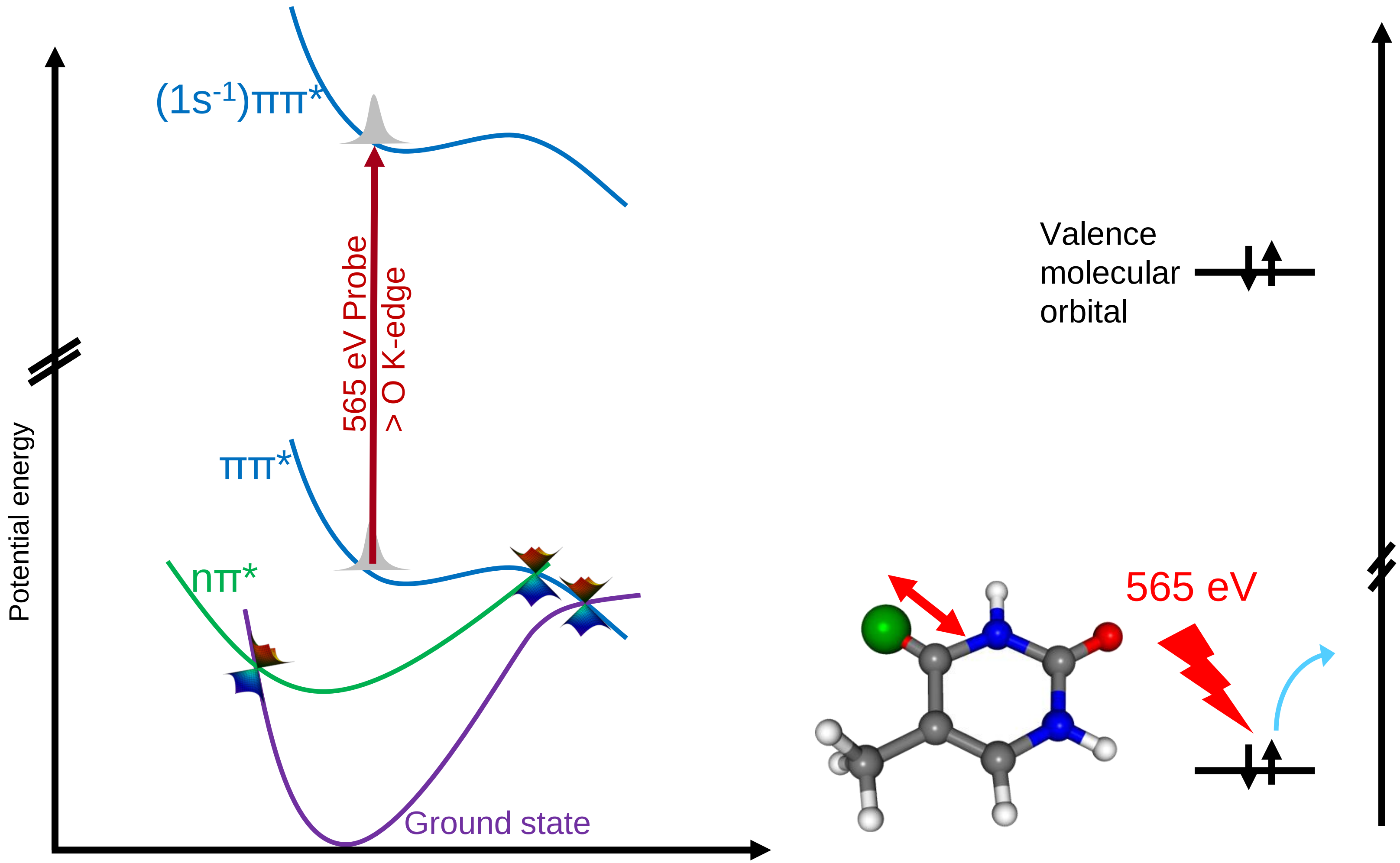
Core electrons:

- Localized
- site-specific geometry evolution
- excited state characters
- X-ray FEL



Localized structural evolution:

Time-resolved Auger electron spectroscopy



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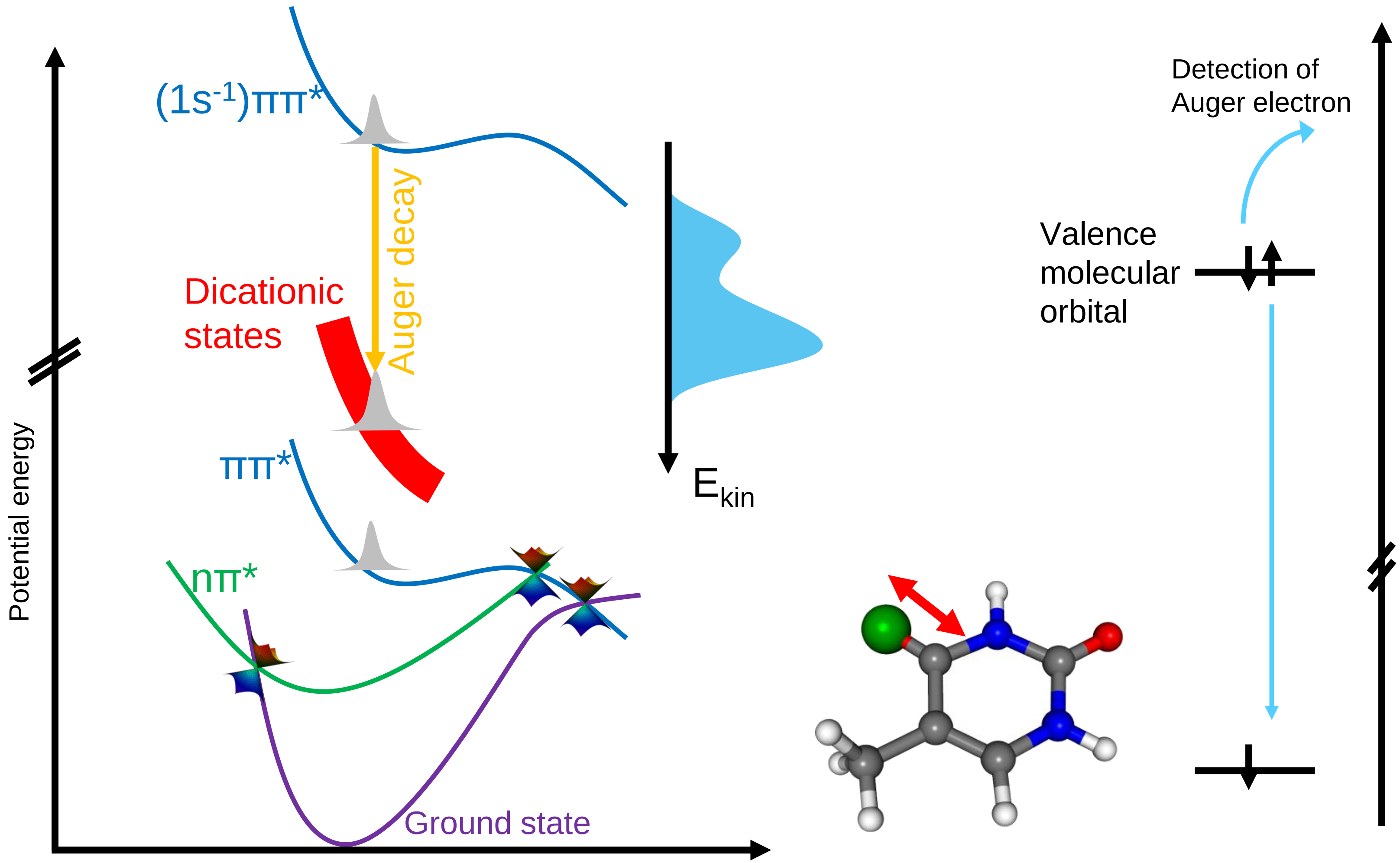
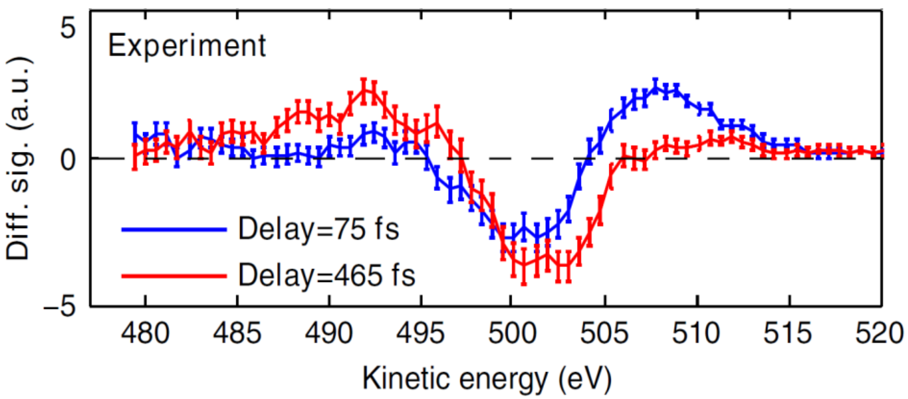
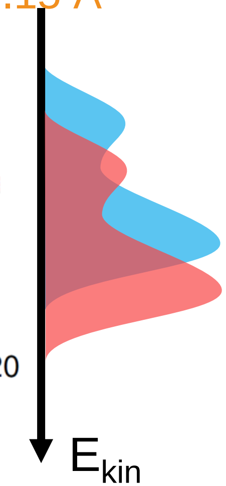


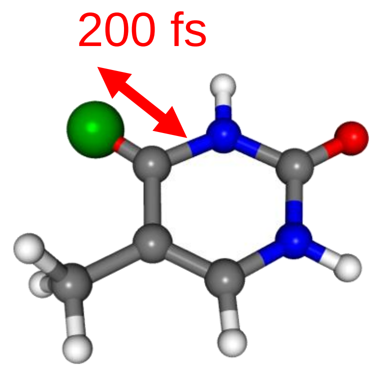
Localized structural evolution:

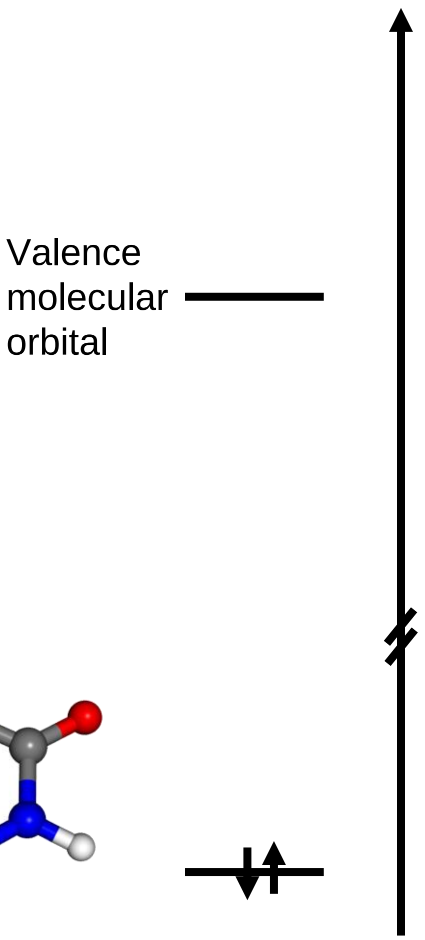
Time-resolved Auger electron spectroscopy

Spectral change: higher E_{kin} induced by UV excitation
Geometry change: C-O bond lengthening 0.15 Å









- Localized probing at oxygen K edge
- Repulsive nature of dicationic states

→ High sensitivity to CO bond length change

Thank you!
And have fun with the further lectures!