Introduction to Photon Science

Part II: Experiments at synchrotrons and FELs

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DESY Ukraine Winter School 2023

Summary

- Basics of synchrotron radiation
- Wiggler/undulator
- Synchrotrons/FELs
- Self-amplified spontaneous emission – SASE

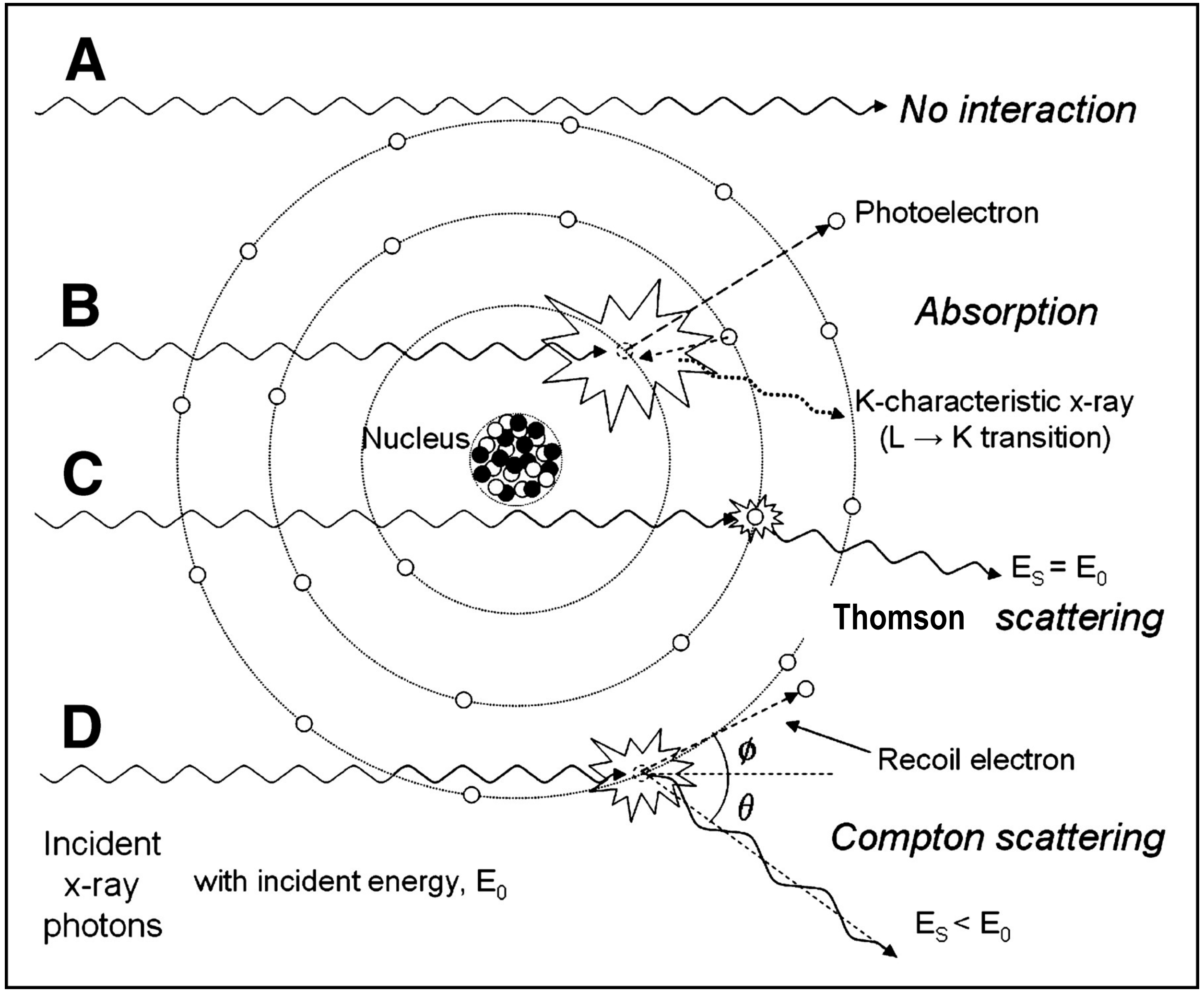
- Properties: high brilliance, wide energy range, small source size
  (for FELs: short pulses, full coherence)

Today: What can we investigate with the light sources?: some examples

Questions:

- What properties of the light must be considered in experiments?
- What are they important for, for example?
- What is so useful in using synchrotrons or FELs? Why X-rays?

X-ray – matter interaction



/ (or Auger electron)

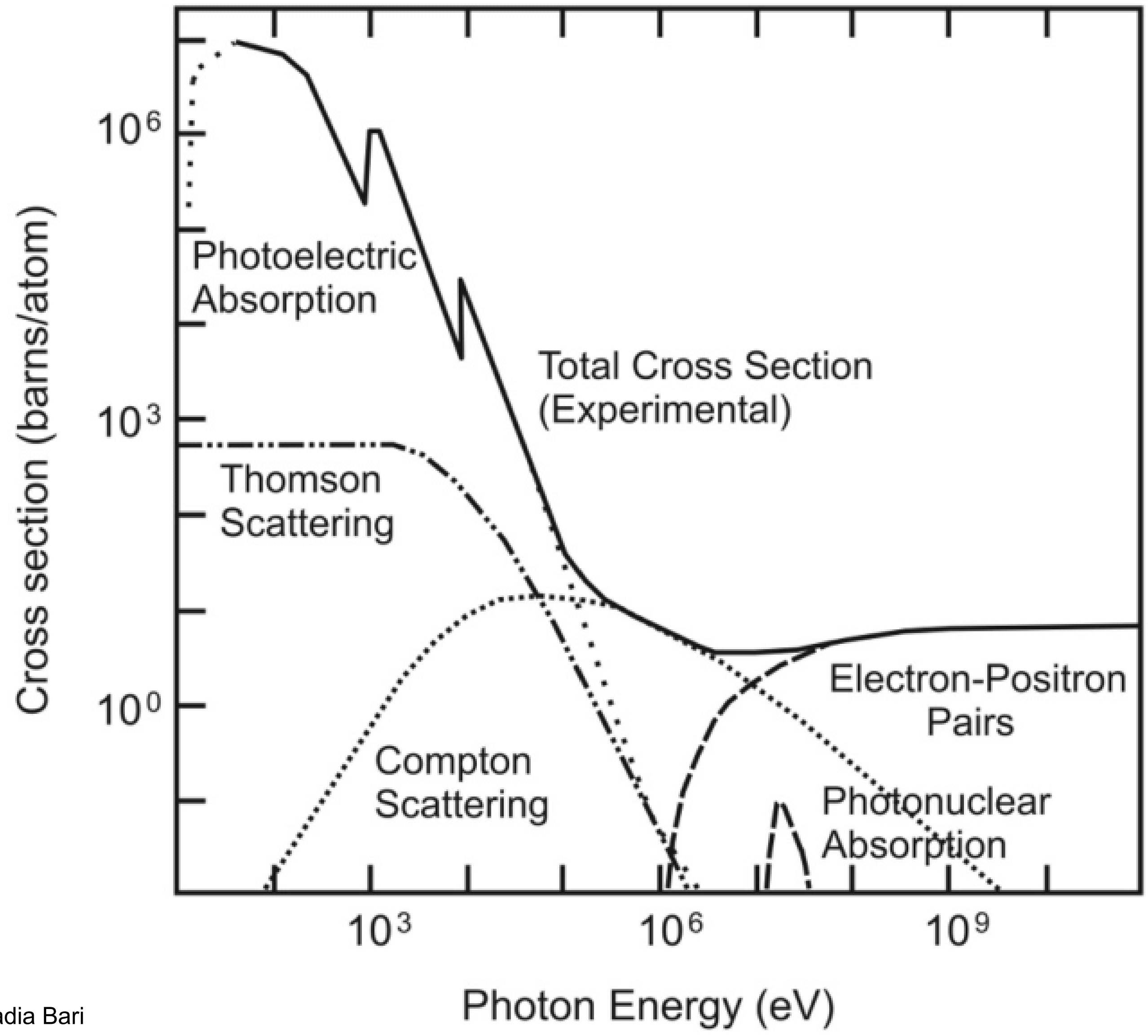
(Fluorescence)

(elastic)

(inelastic)

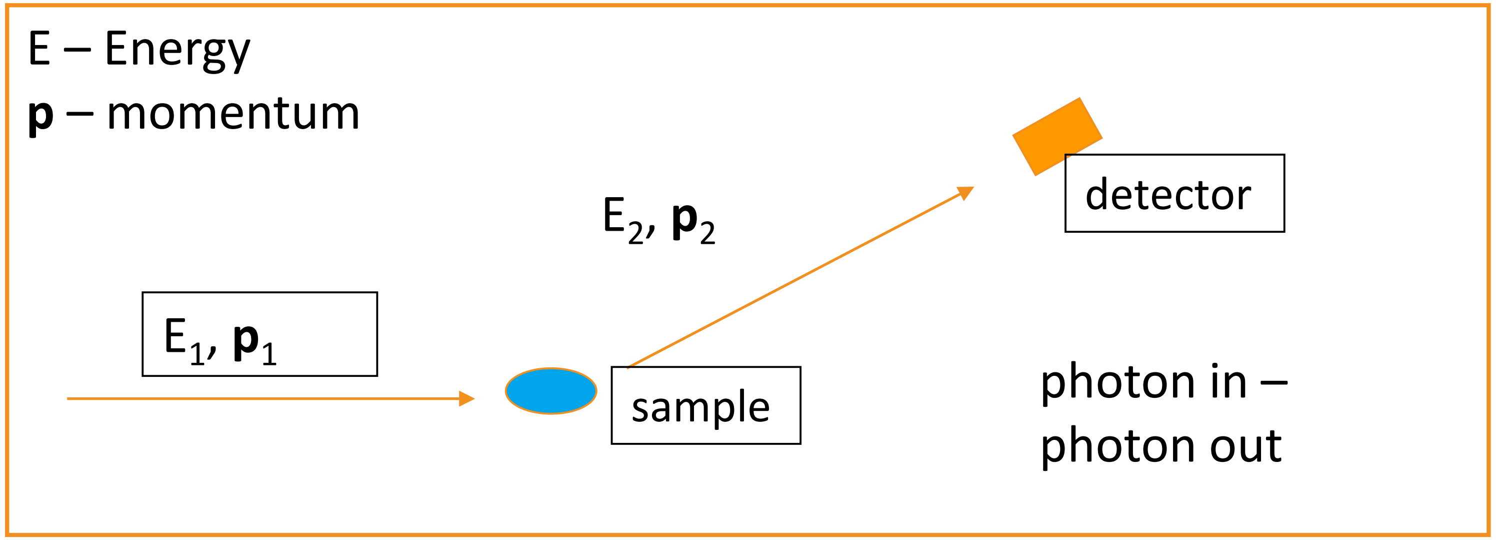
Illustrative summary of x-ray and γ-ray interactions. J. Anthony Seibert, and John M. Boone JNMT 2005;33:3-18

Photon energy dependent…



Probing structure and dynamics of matter

Reveal the structure and dynamics of matter by performing scattering experiments with photons



Analyze the distribution of scattered photons in reciprocal space → Diffraction

… in real space → Imaging

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

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

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** (General, powders, proteins, high pressure, surfaces)

Imaging

- **Microtomography**
- **X-Ray micro fluorescence**

Spectroscopy

- **XUV fluorescence spectroscopy**
- **X-ray absorption spectroscopy**
- **X-ray photoemission spectroscopy**

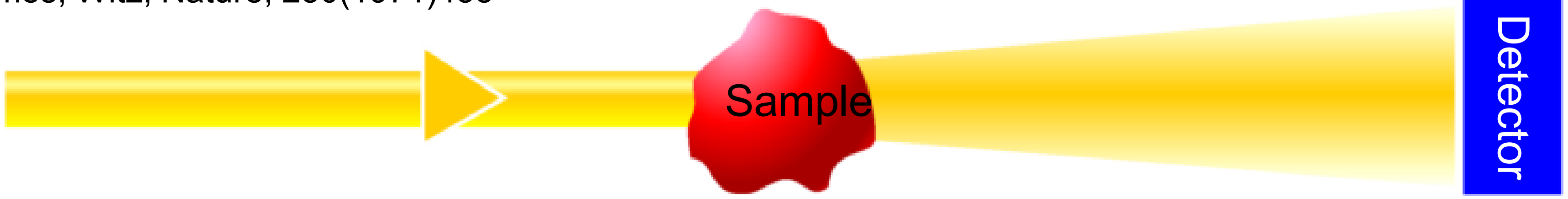
Weak signals
e.g. High collimation
e.g. Small samples
Tunable wavelength
Time structure

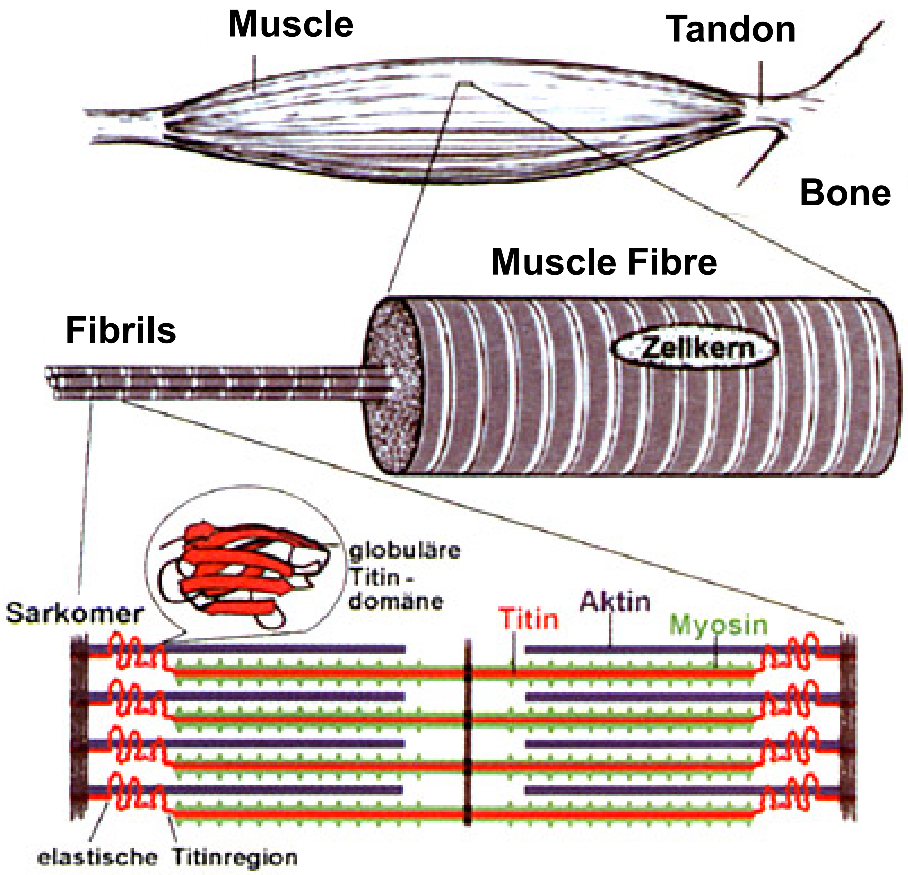
Experiments concentrate on experiments with small focus primary beams ($\mu m, nm$) and “photon hungry” experiments

First experiments using synchrotron radiation (1964 – 1975)

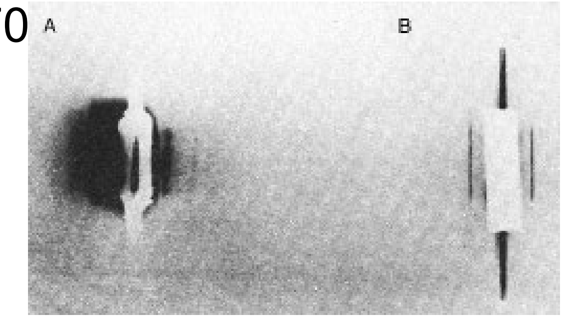
1970: Small angle X-ray scattering on muscle fibres

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

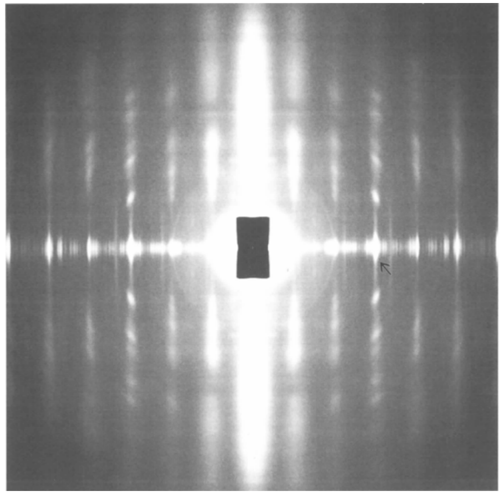




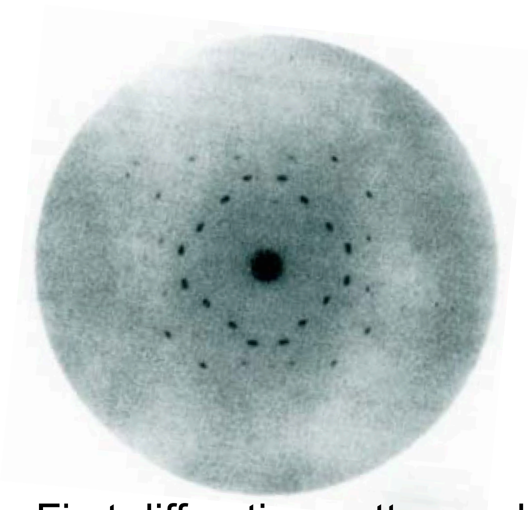
1970

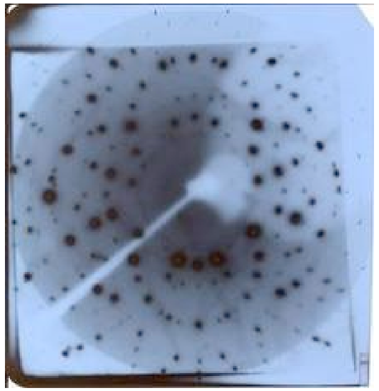


1996



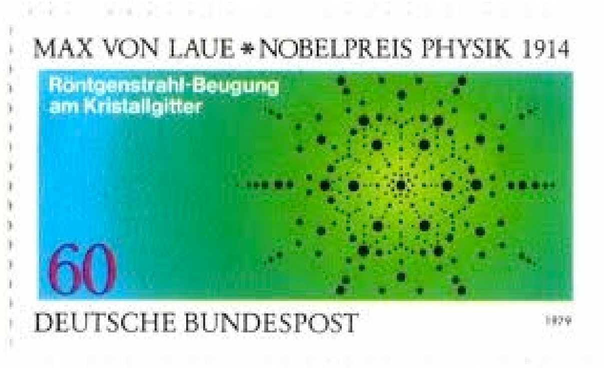
X-ray diffraction from crystalline structures

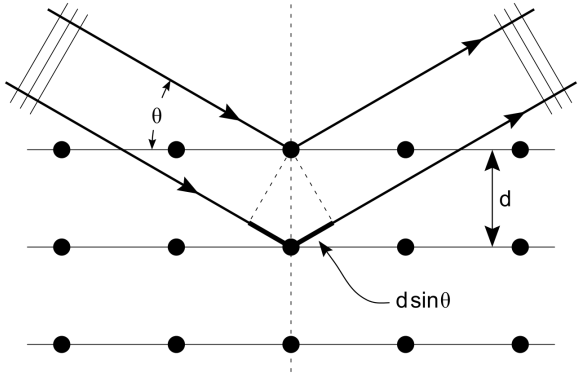




Max von Laue
(1879 – 1960)

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

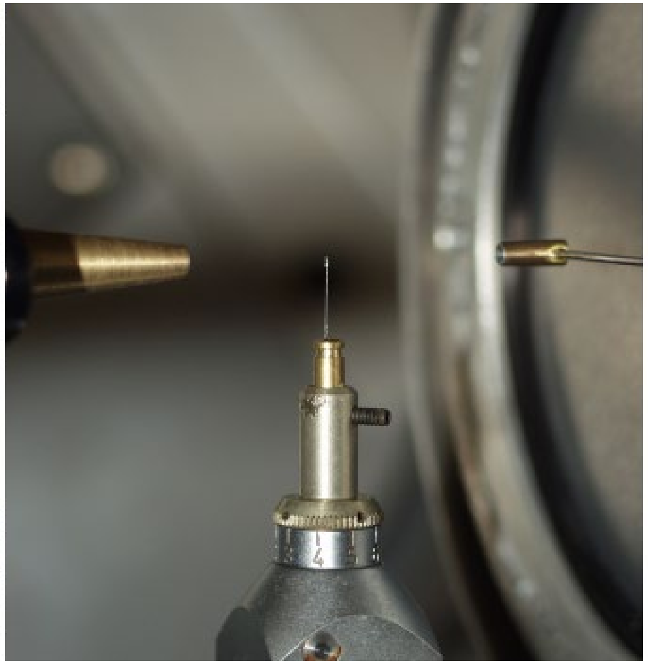




- Each scatterer re-radiate sperical waves
- Constructive interference if $n\lambda = 2d\,sin\,\theta$

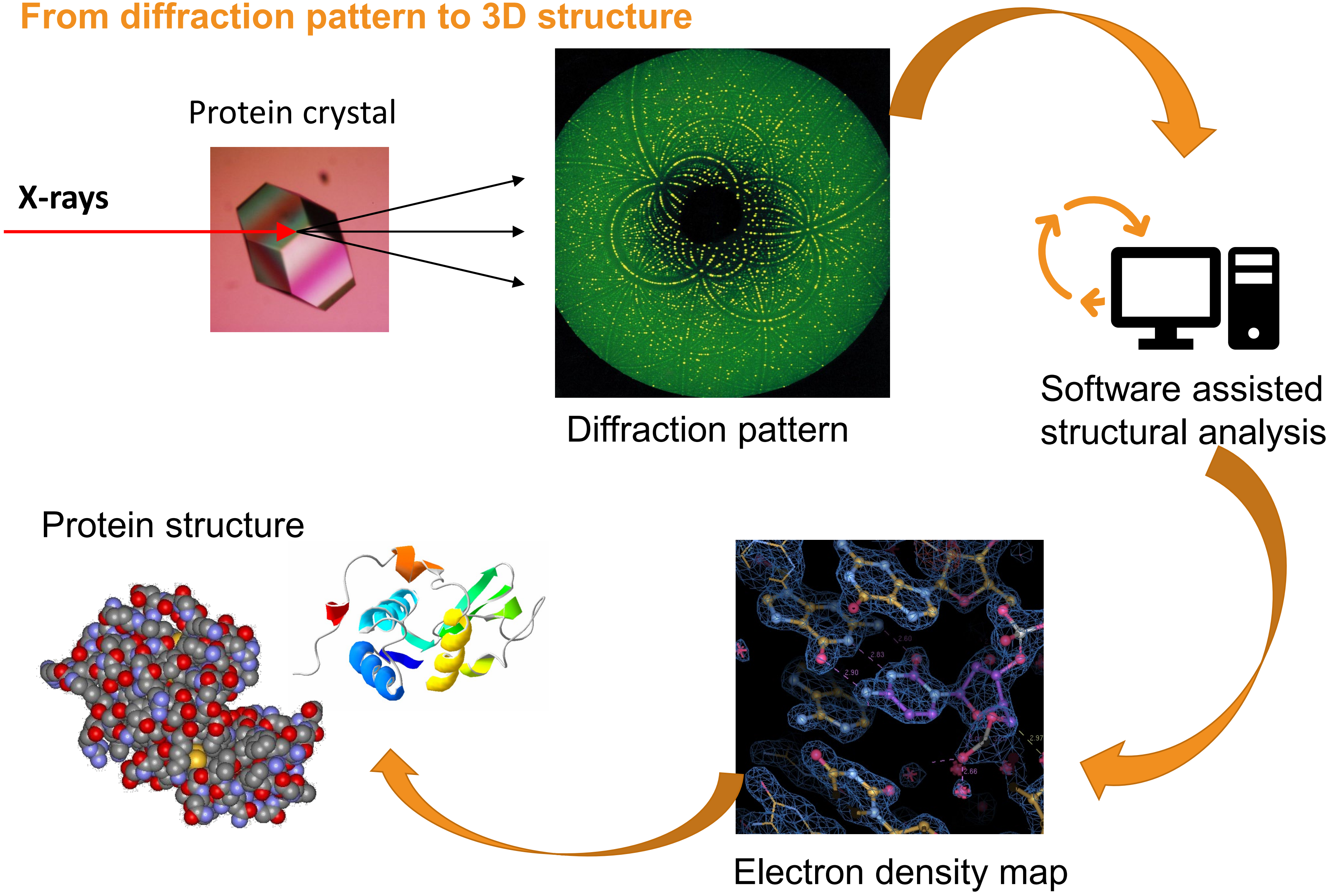
Protein crystallography

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

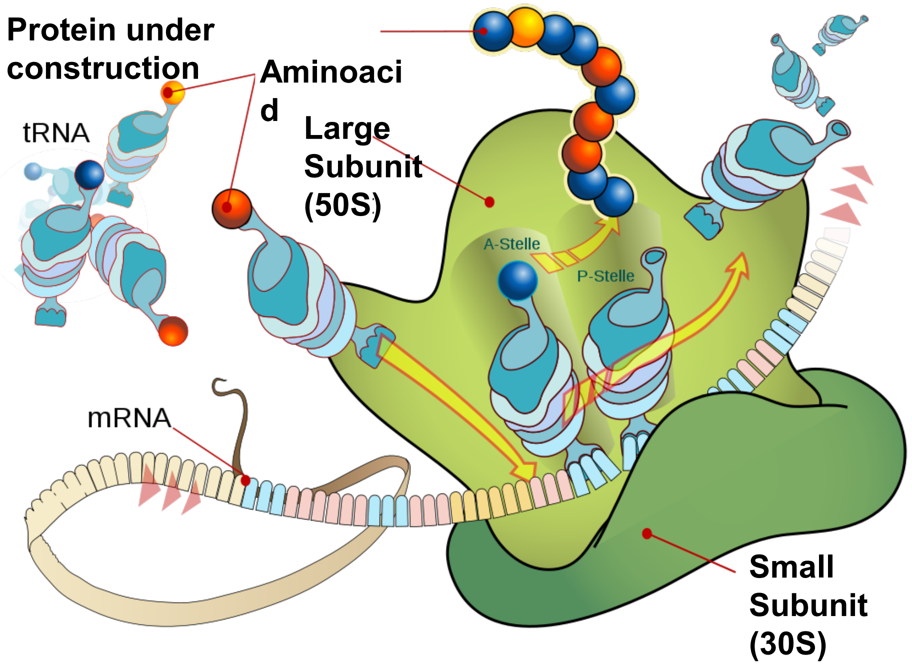


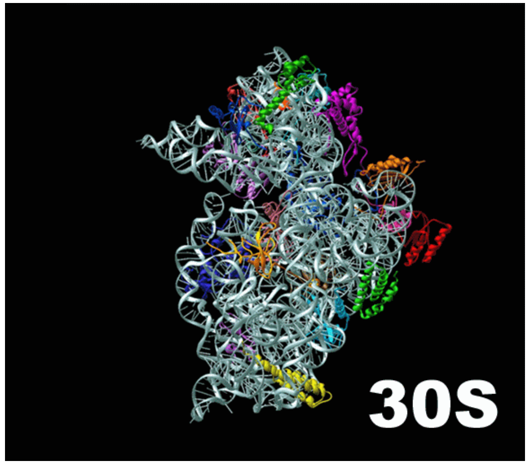
Structure determination of proteins

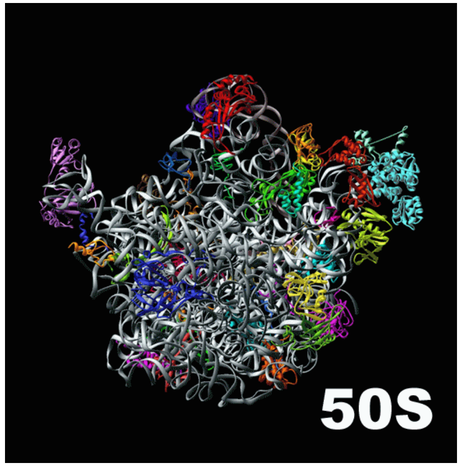
From diffraction pattern to 3D structure



Revealing structure and dynamics of ribosome







Ada Yonath:

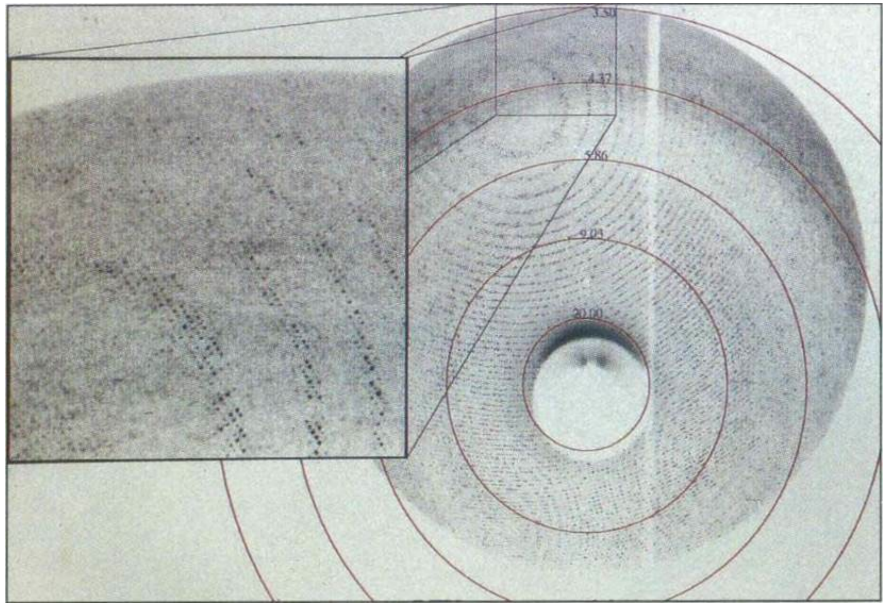
- Head of the MPG-work group „Structure of the Ribosome“ at DESY, 1986 – 2004
- Nobelprize Chemistry 2009 (with T. Steitz and V. Ramakrishna)

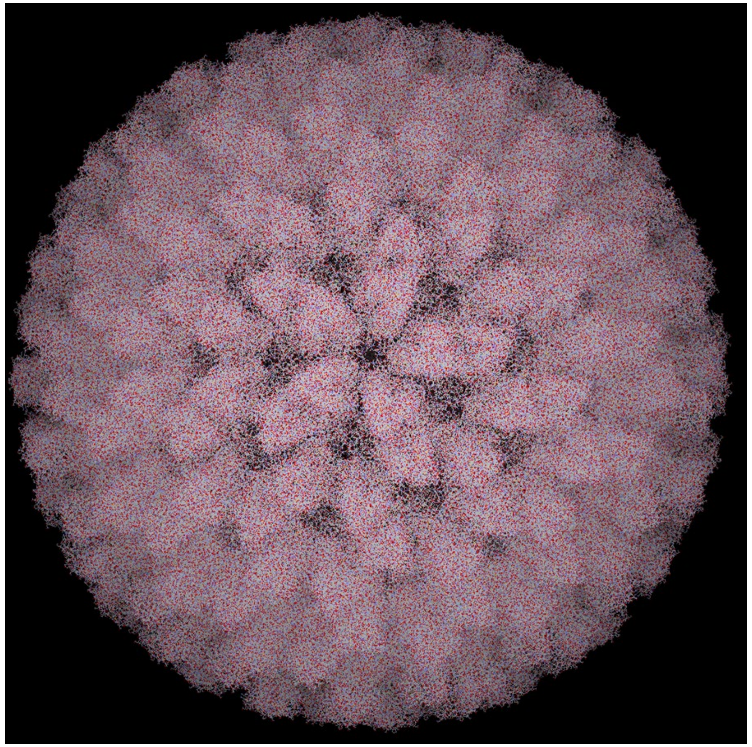
Schlünzen, ..., Yonath, Cell, 102(2000)615

Very large biomolecules

Nanometer-sized viruses

Example: Blue Tongue Virus
70 nm diameter!





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

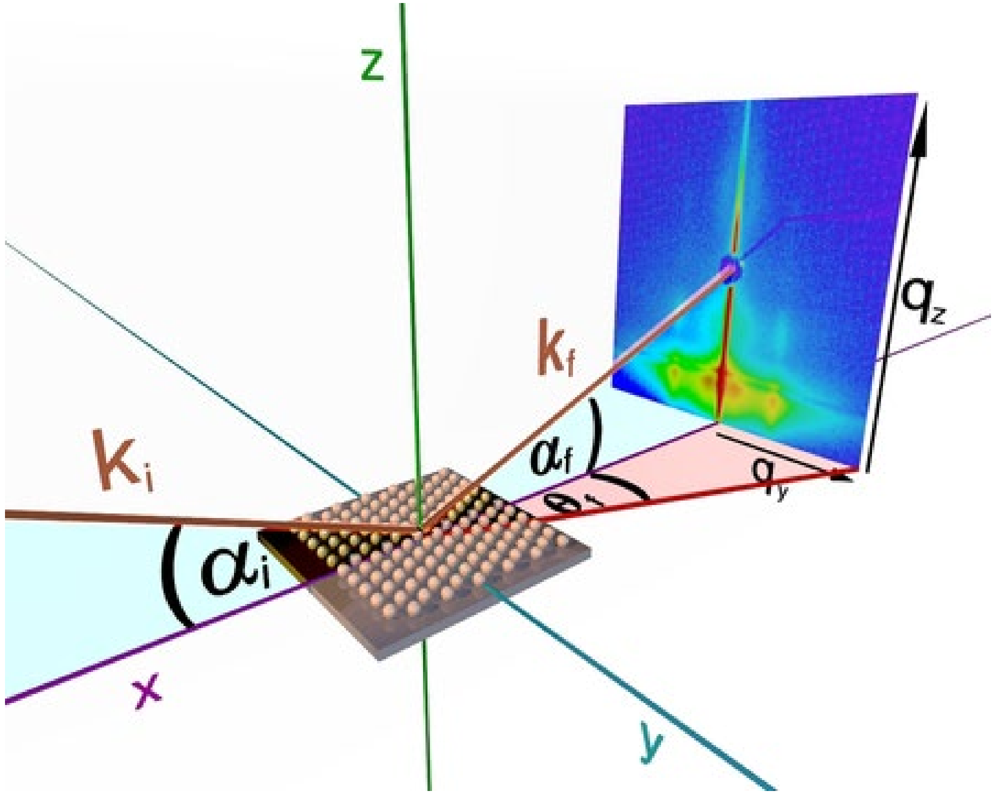
Corona research

https://photon-science.desy.de/research/research_on_sars_cov_2_at_desy_light_sources/index_eng.html

Grazing-incidence small-angle scattering

GISAXS for surface analysis

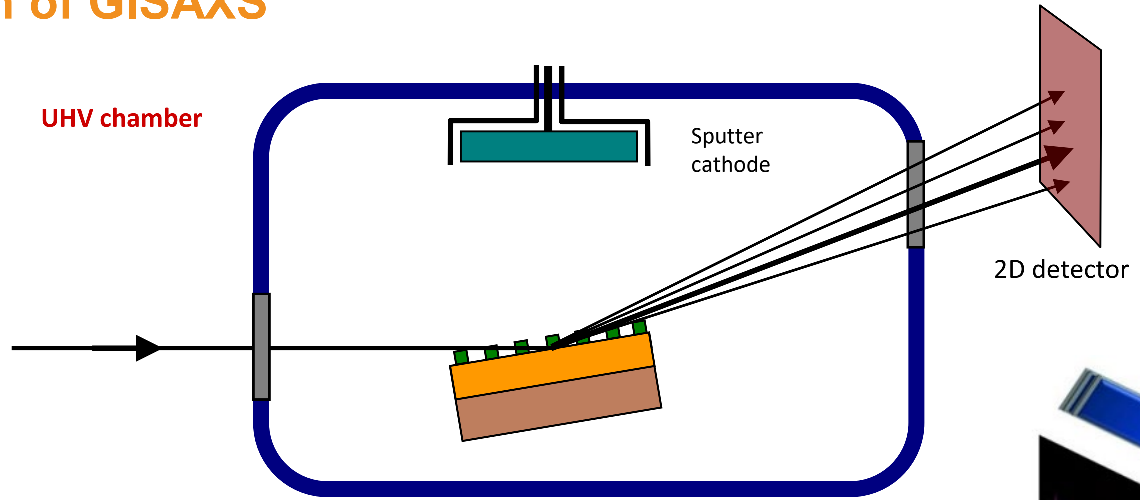
Image plate or
CCD detector

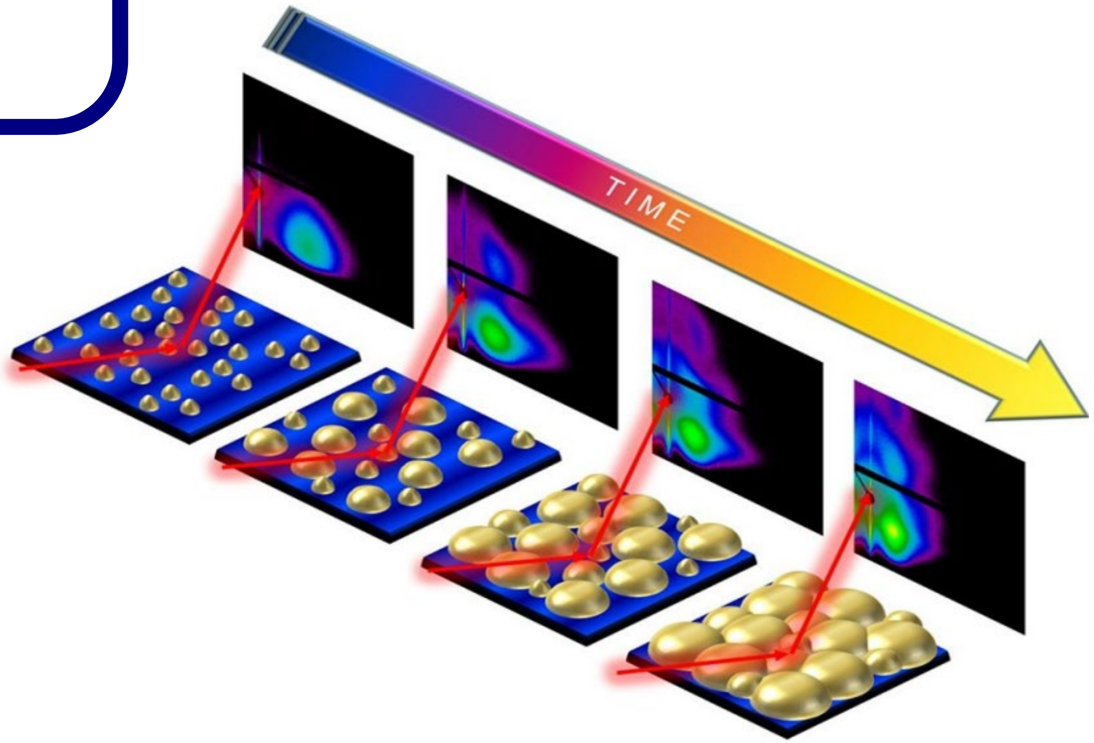


- Scattering by structures that are much larger than the wavelength of the radiation
- 2-D detector records the scattered intensity at small angles for the observation of lateral sizes ranging from a few up to hundreds of nanometers.
- The direct and the reflected specular beam are blocked by two small beamstops to prevent damage or saturation of the detector.

In-situ studies of nanostructure formation

Application of GISAXS

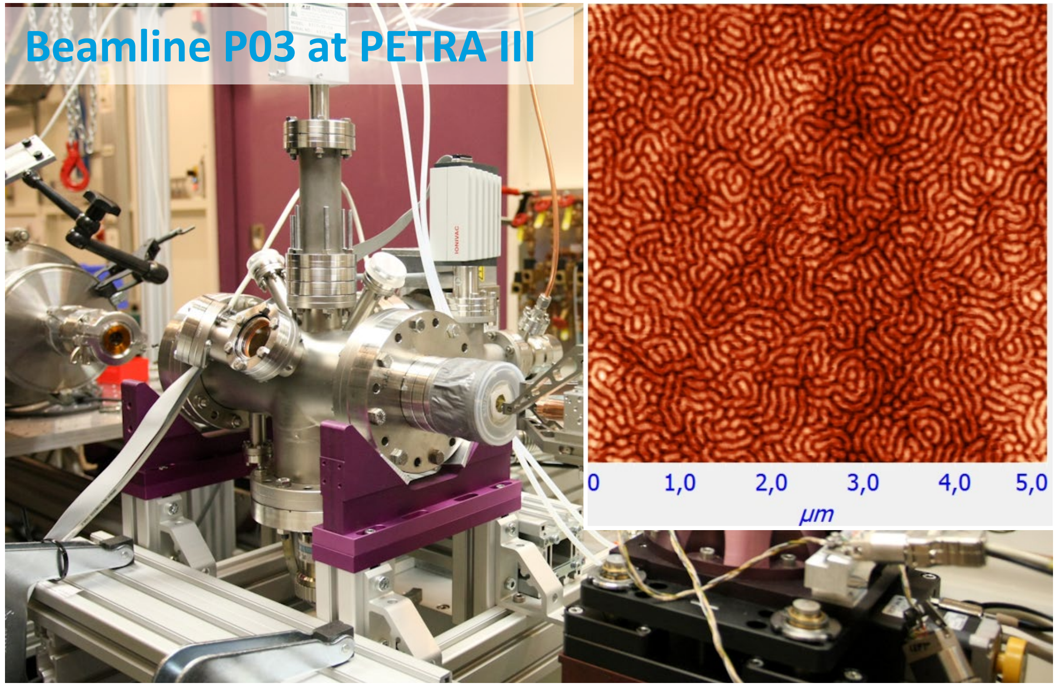




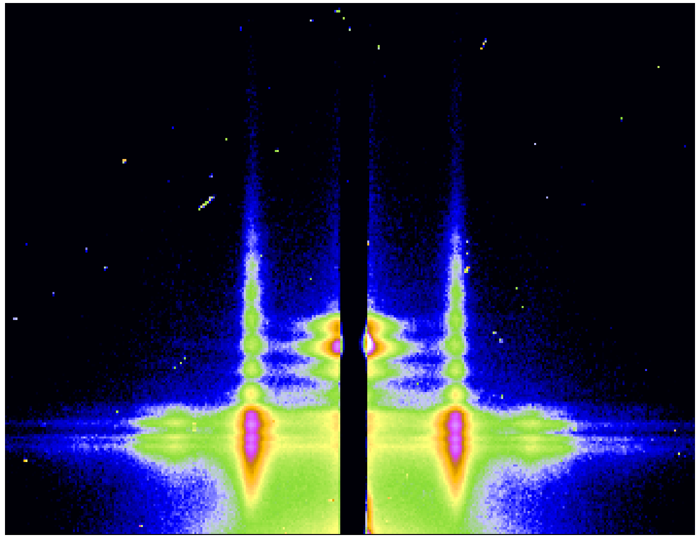
- Observation of growth process of thin films during deposition
- Formation and self-organization of nanoparticles on surfaces

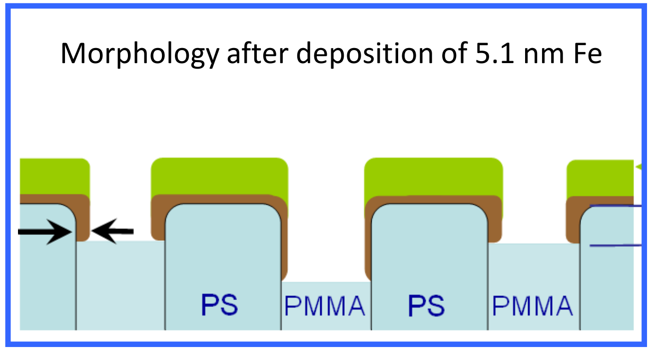
Directly observing magnetic nanostructures during growth via GISAXS

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



PILATUS 300k pixel detector





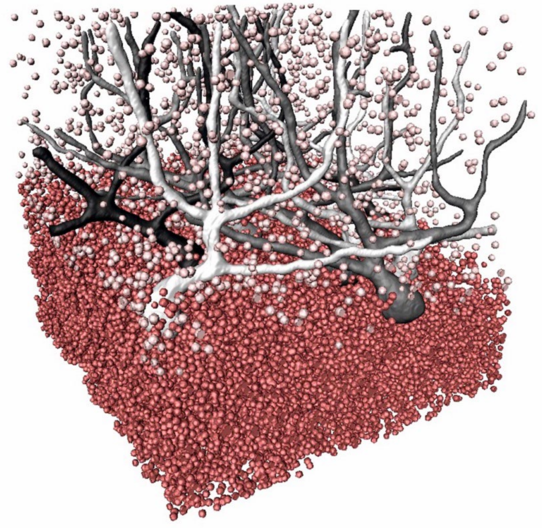
Results

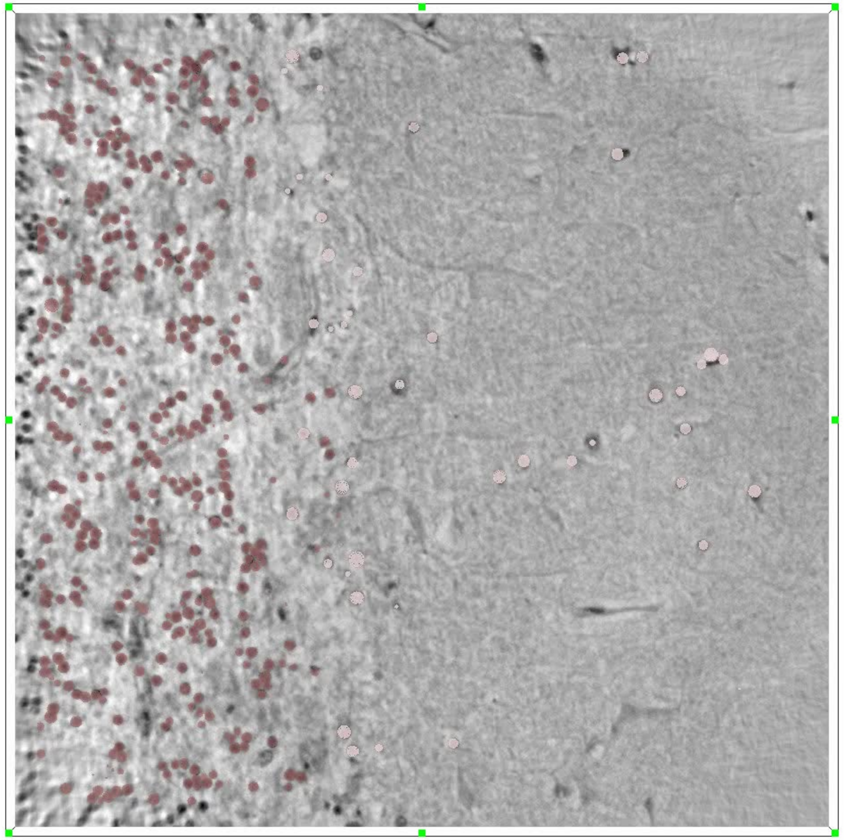
- Selective vertical growth of FePt on PS/PMMA
- Lateral structure defined by the polymer template

Phase contrast tomography of neurons in brain tissue

Measure phase shift (measured 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



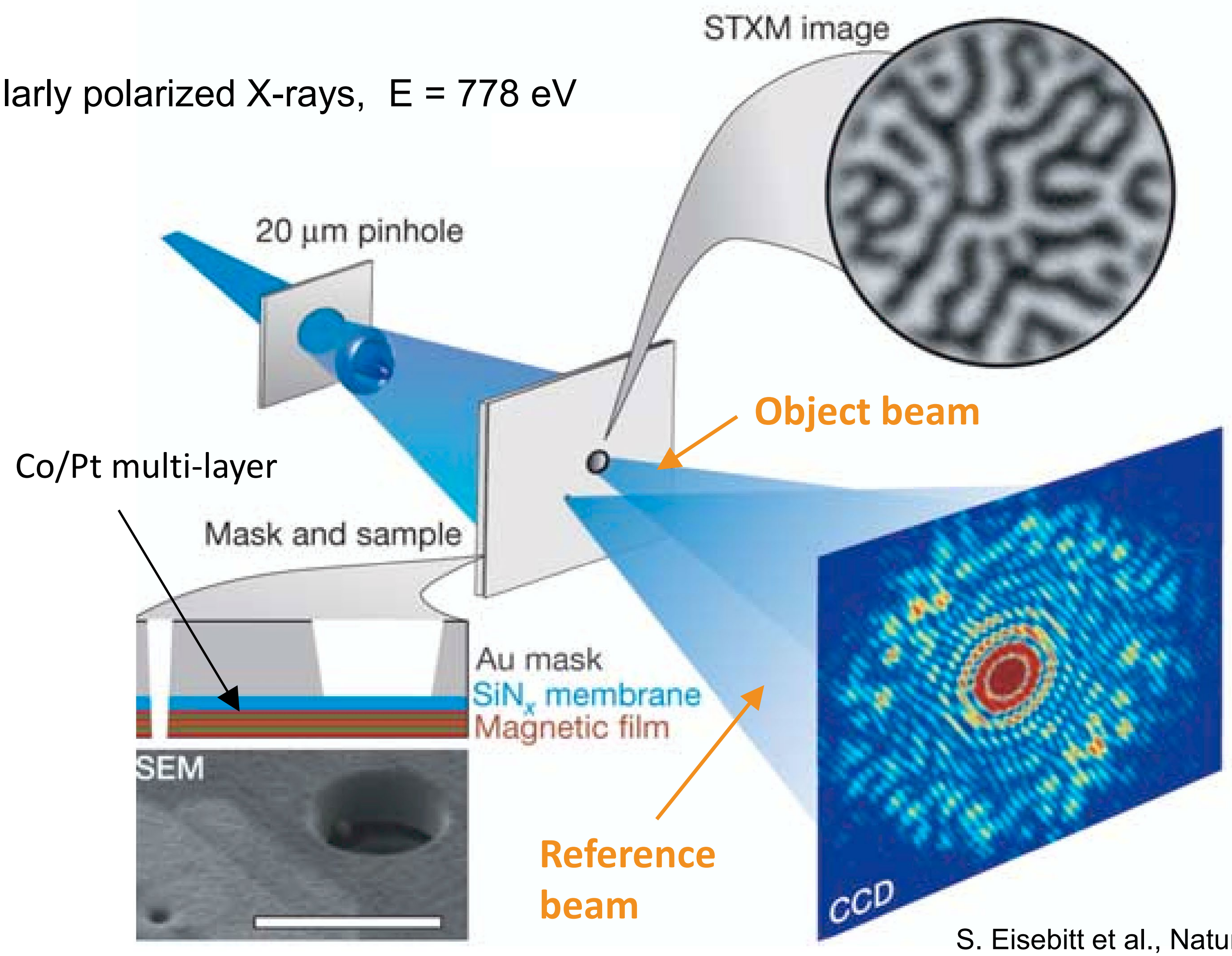


M. Töpperwien, F. van der Meer, C. Stadelmann, T. Salditt; „PNAS“, 2018

Exploiting the coherence of X-rays: static structure

Imaging of magnetic domains via x-ray holography

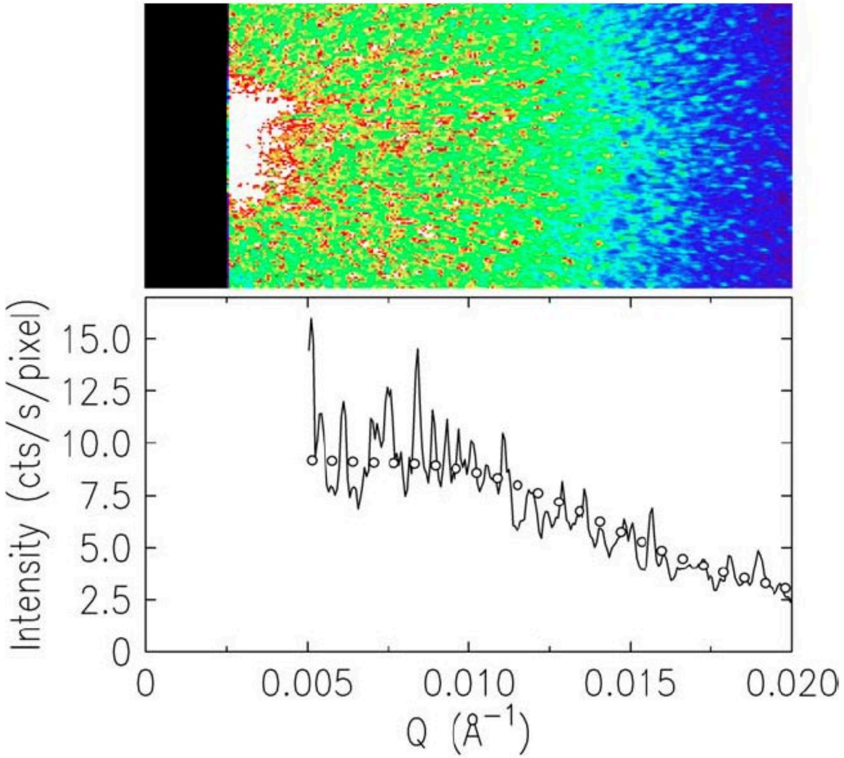
Circularly polarized X-rays, E = 778 eV



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

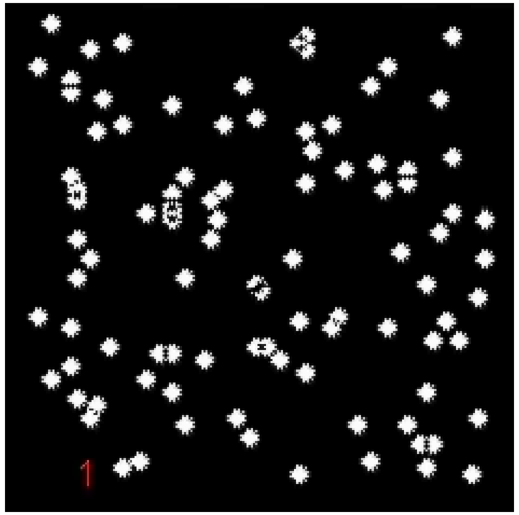
Exploiting the coherence of X-rays: dynamic structure

X-ray photon correlation spectroscopy (XPCS)

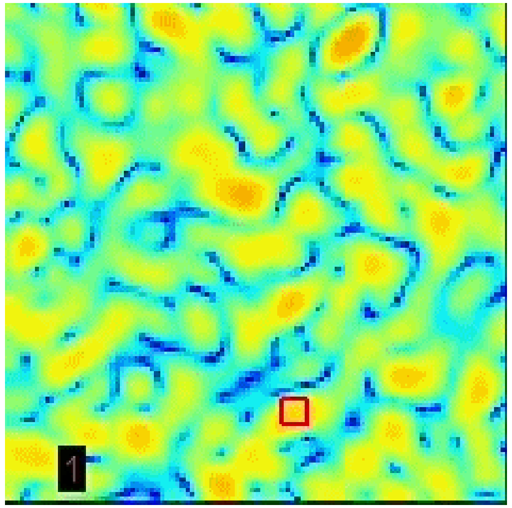


Diffraction of coherent light from a disordered sample leads to a 'grainy' diffraction pattern (speckles)

Simulation of Brownian motion



Real space



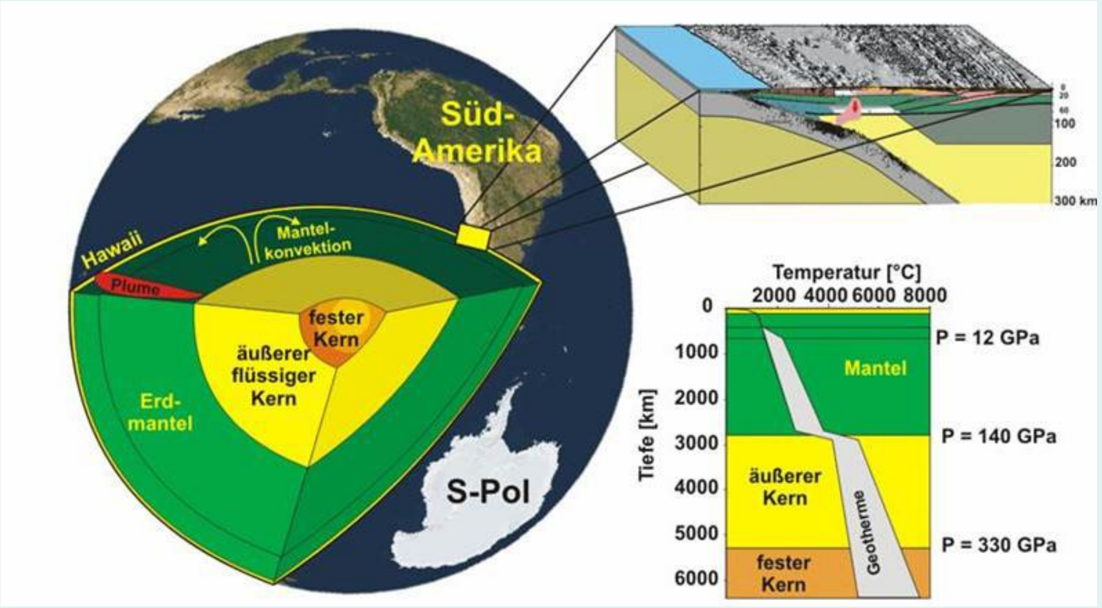
Diffraction pattern

Geo science experiments (high p, high T)

Large volume press 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

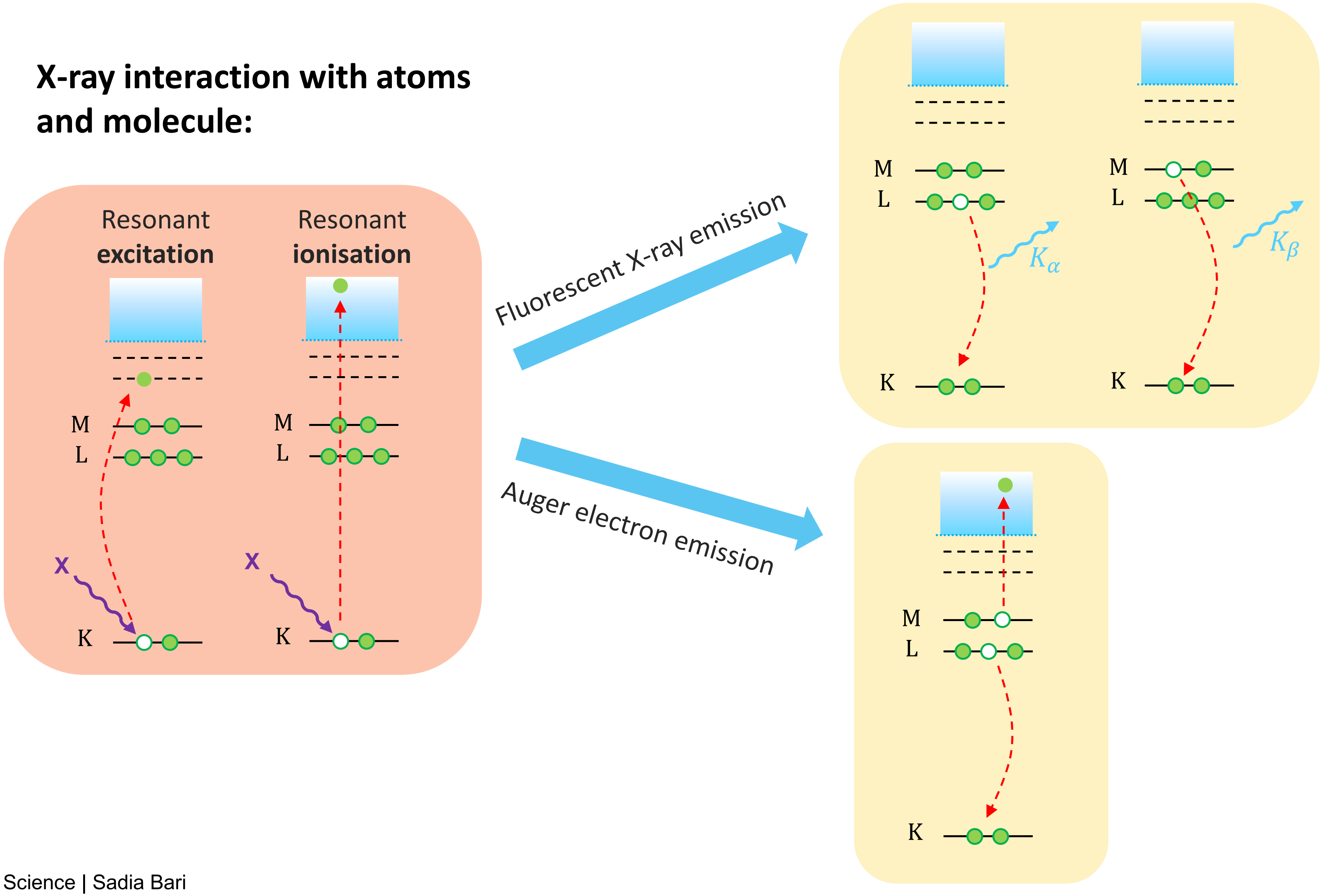
Study of material under the conditions of the earths lower mantle.



X-ray resonant core excitation spectroscopy

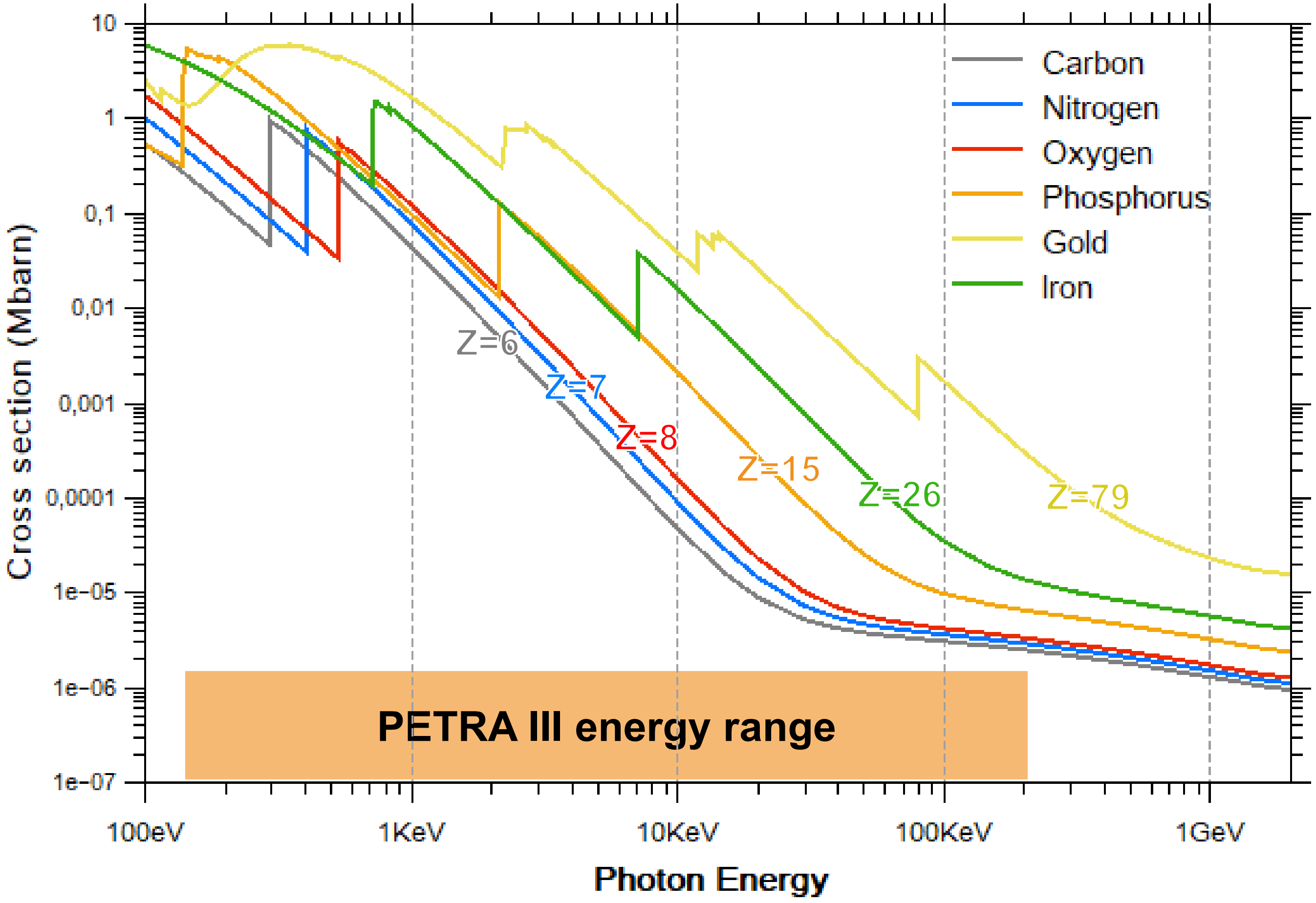
Probing the local environment with atomic resonances

X-ray interaction with atoms and molecule:



X-ray Absorption Spectroscopy

Atom specific



X-ray Absorption Spectroscopy

The three energy regions

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

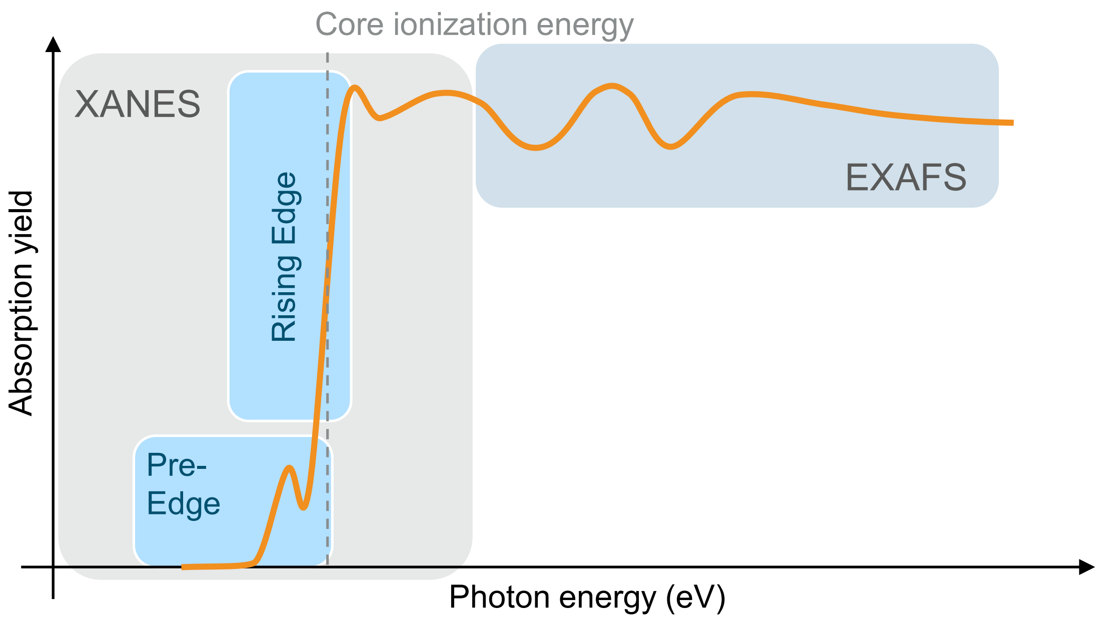
   Electronic structure information (oxidation state, unoccupied molecular levels, and charge transfer)

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

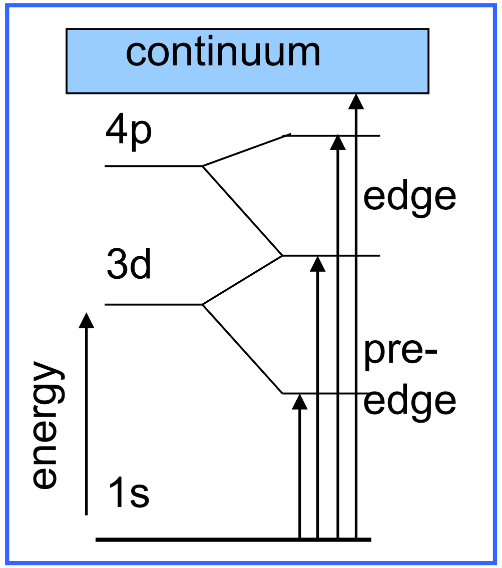
   Dominated by single photoelectron scattering events (interatomic distances)

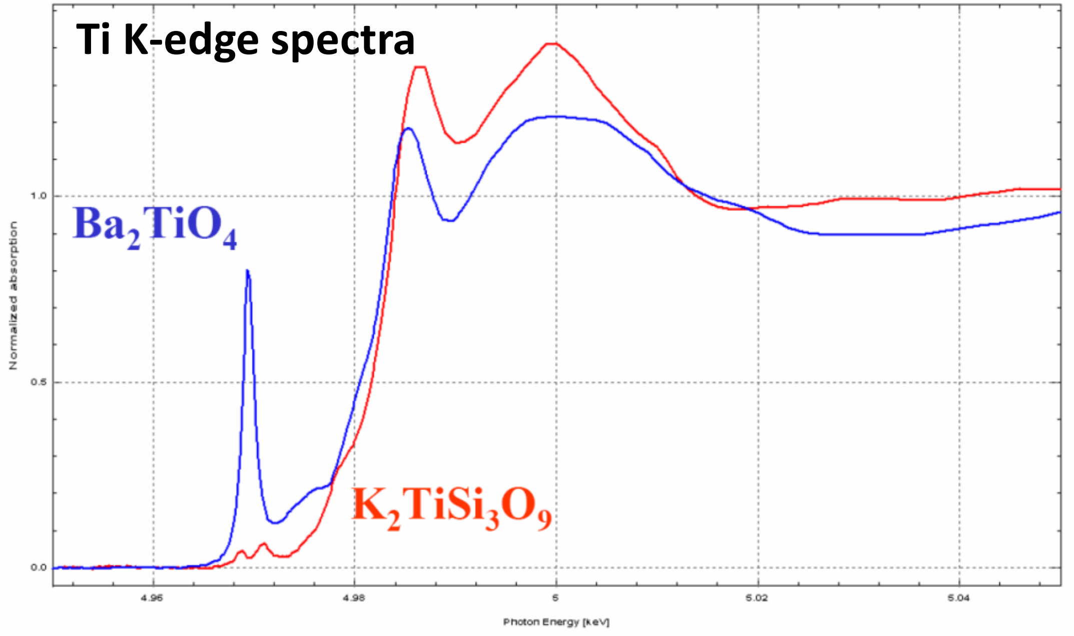


X-ray Absorption Near Edge Structure XANES

Probing the local environment with atomic resonances

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

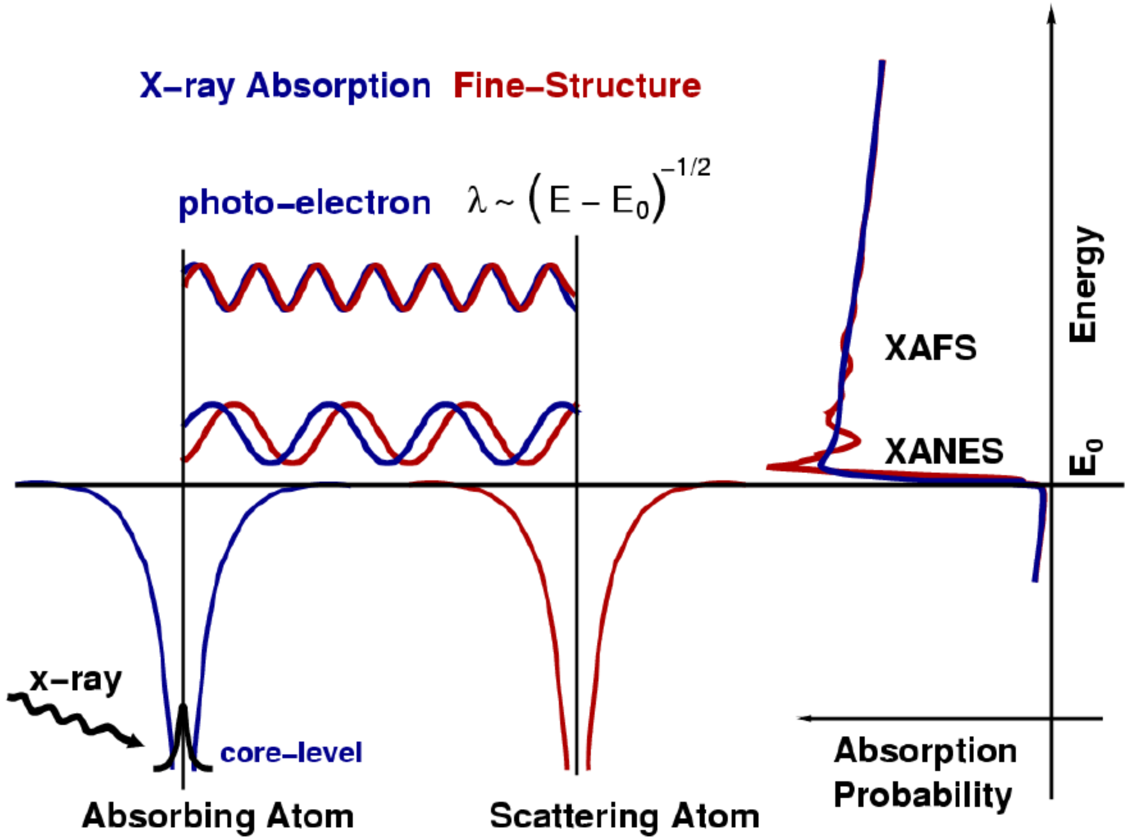




- dependence on local coordination chemistry
- provides electronic structure information (oxidation state, occupancy of valence orbitals, and charge transfer)

X-ray Absorption Fine Structure XAFS

Probing the local environment of the absorbing atom



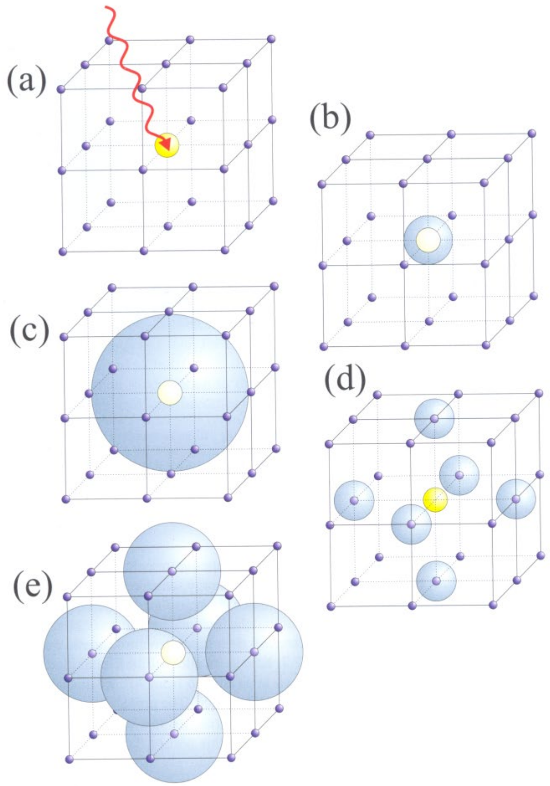
Origin of XAFS: photoelectron (PE) can scatter from neighboring atom

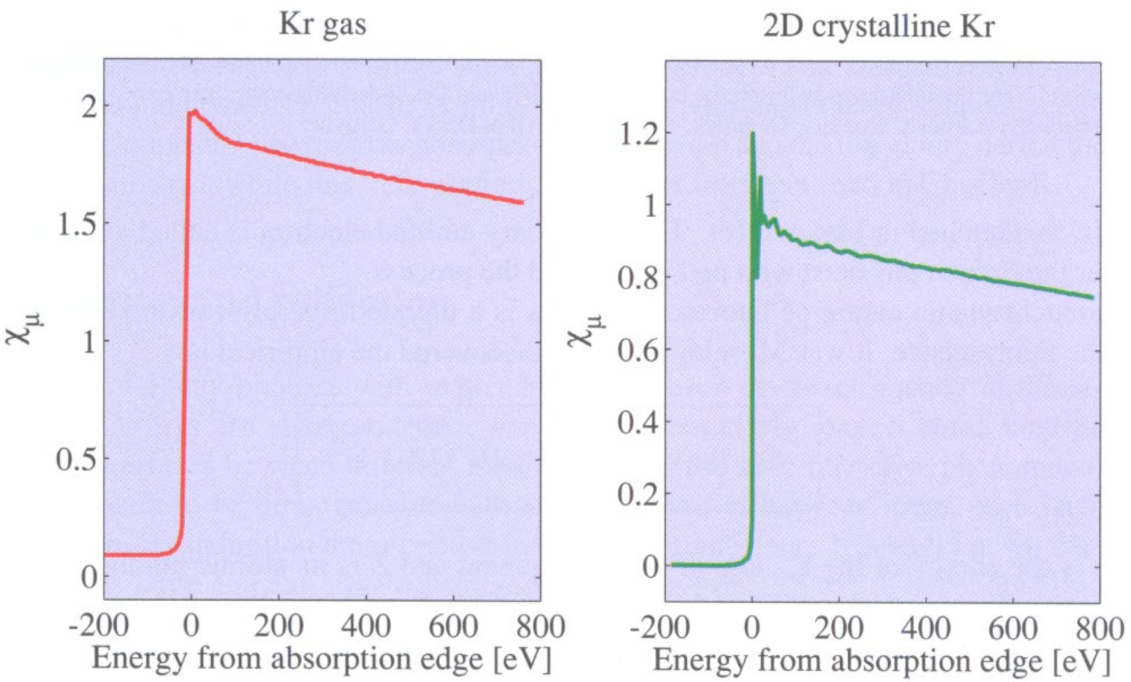
→ Scattered PE can return to the absorbing atom, modulating the PE wave function

→ 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





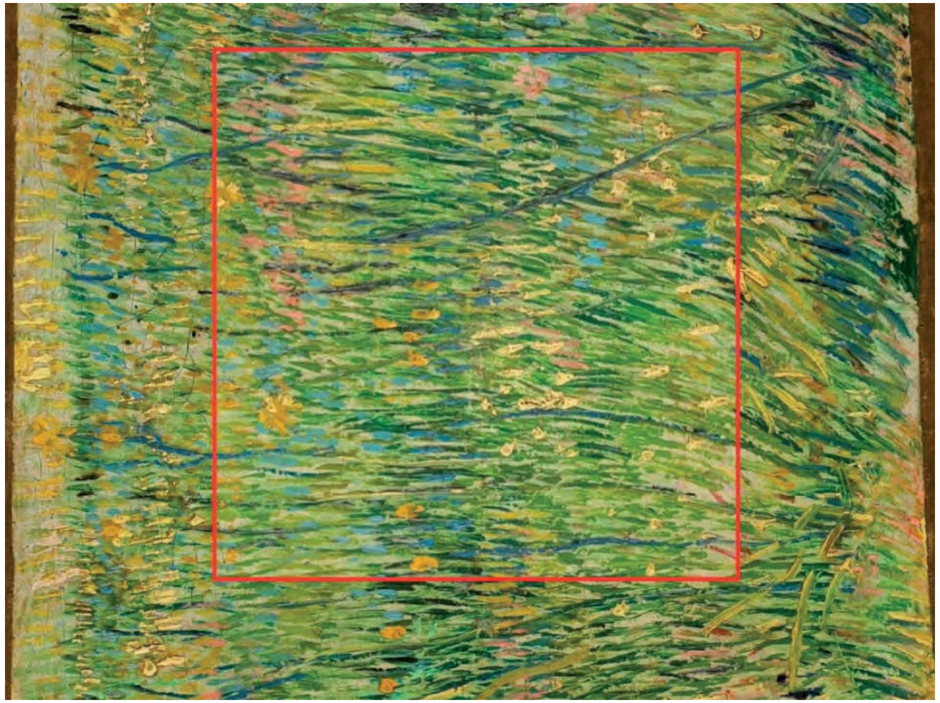
Origin of XAFS: photoelectron (PE) can scatter from neighboring atom

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

→ Modulation of the absorption probability

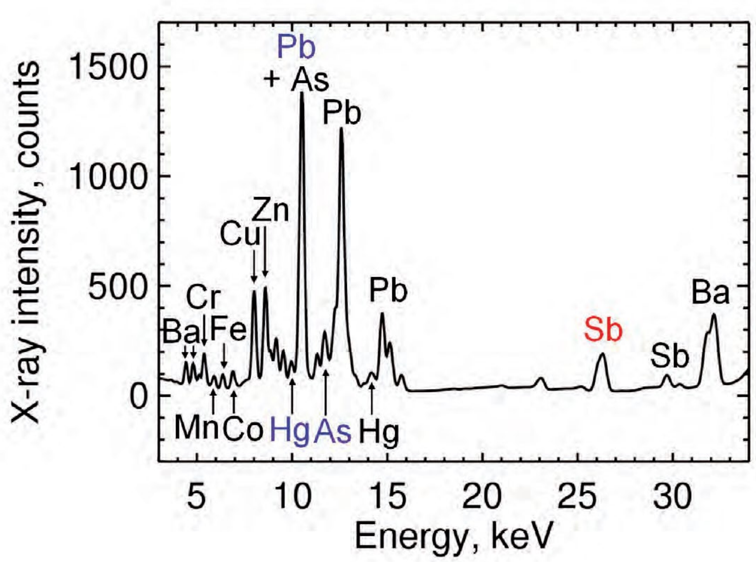
Raster scanning X-ray fluorescence

Vincent van Gogh: Meadow with flowers

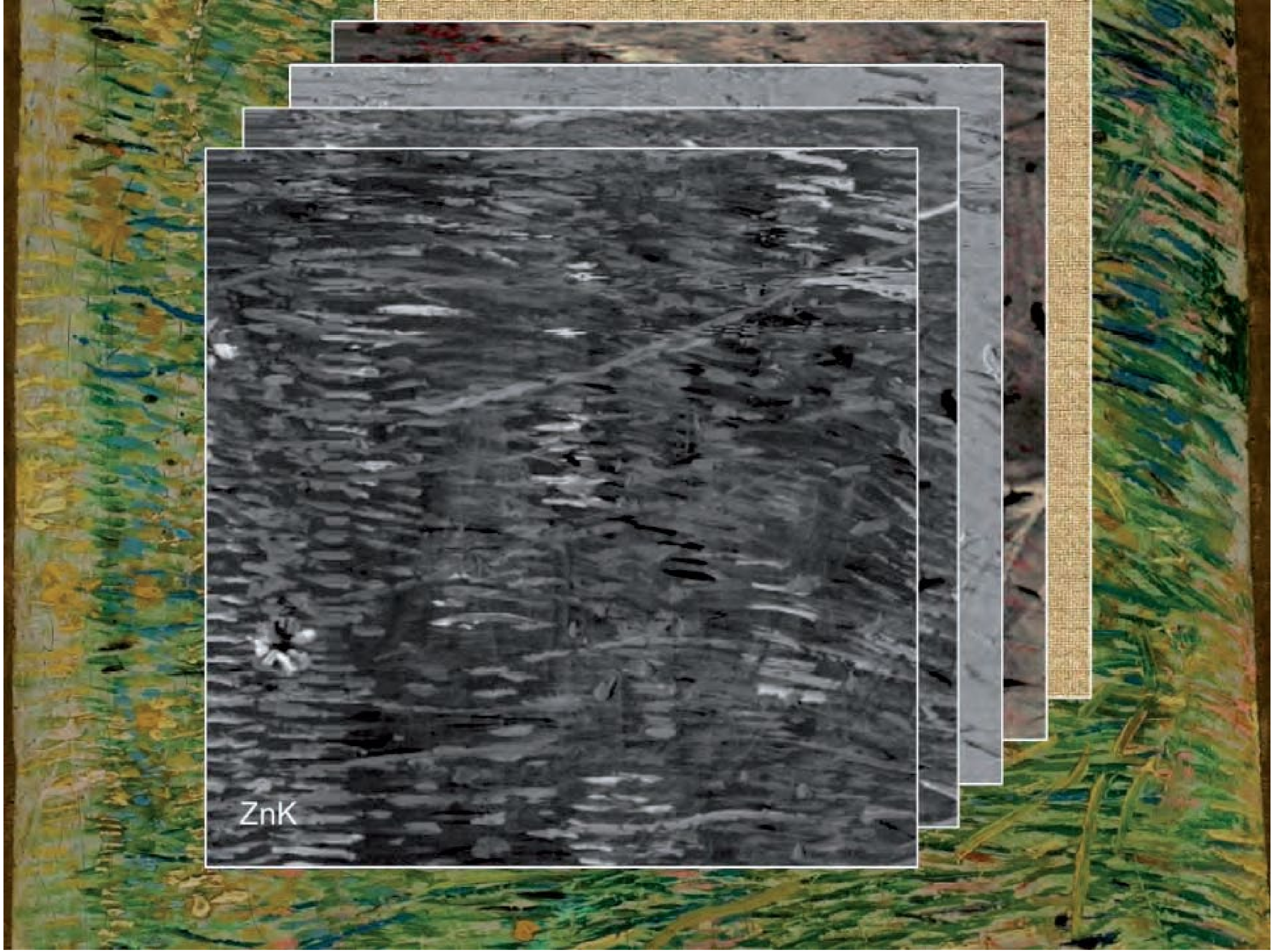


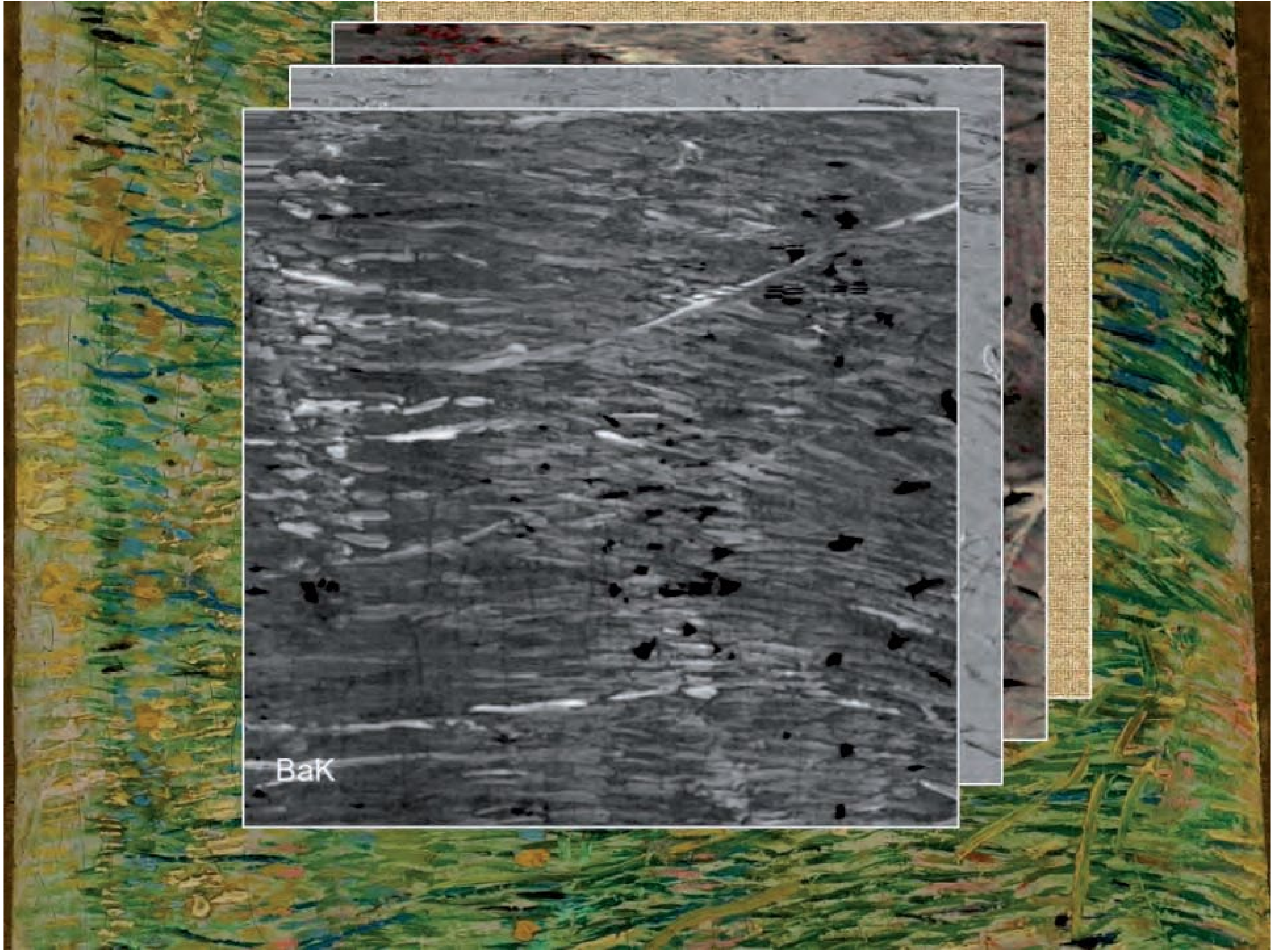
Raster scanning along 90000 pixels with 0.5 mm resolution

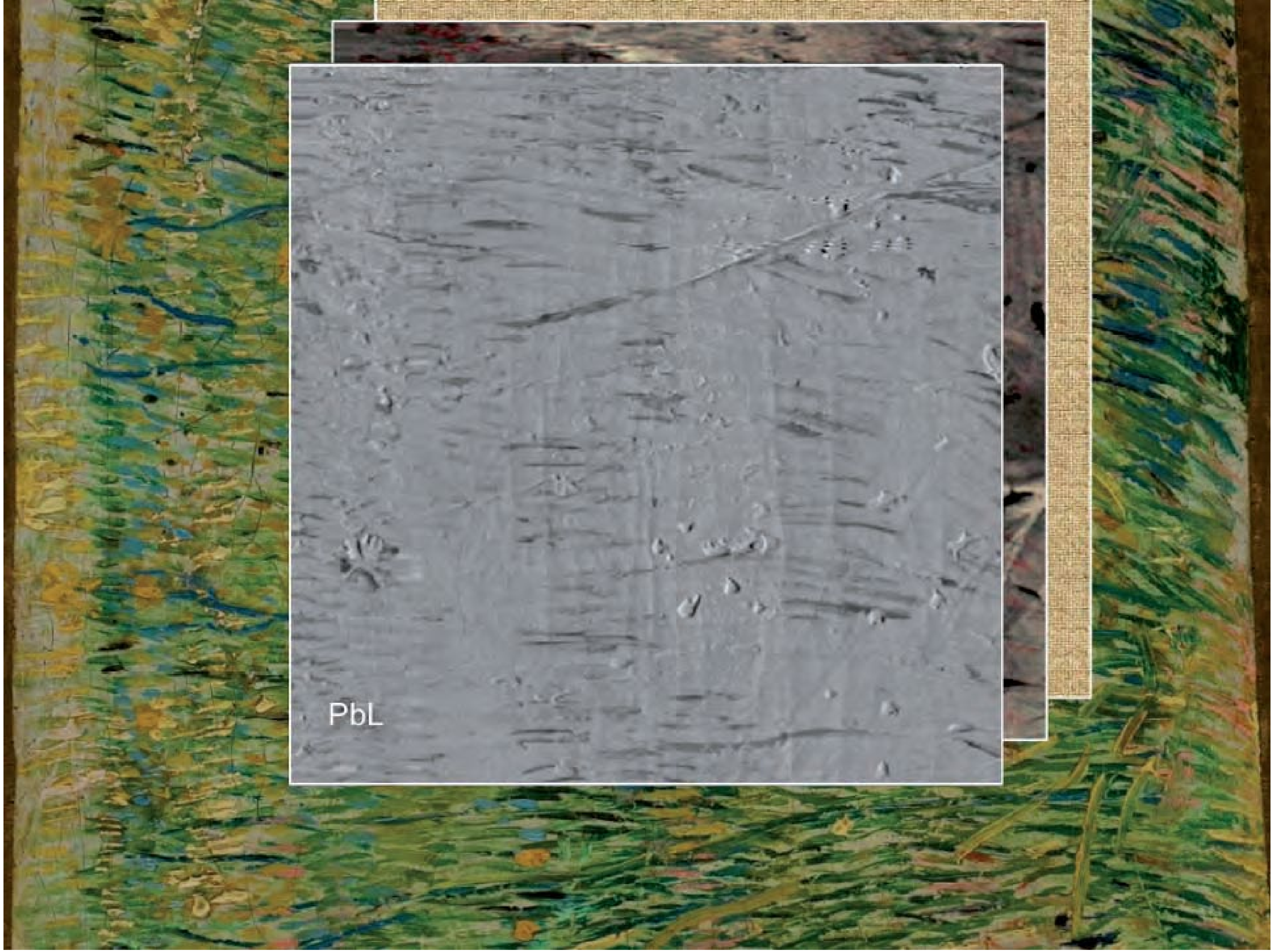
Typical fluorescence spectrum in a single pixel



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


ZnK


BaK

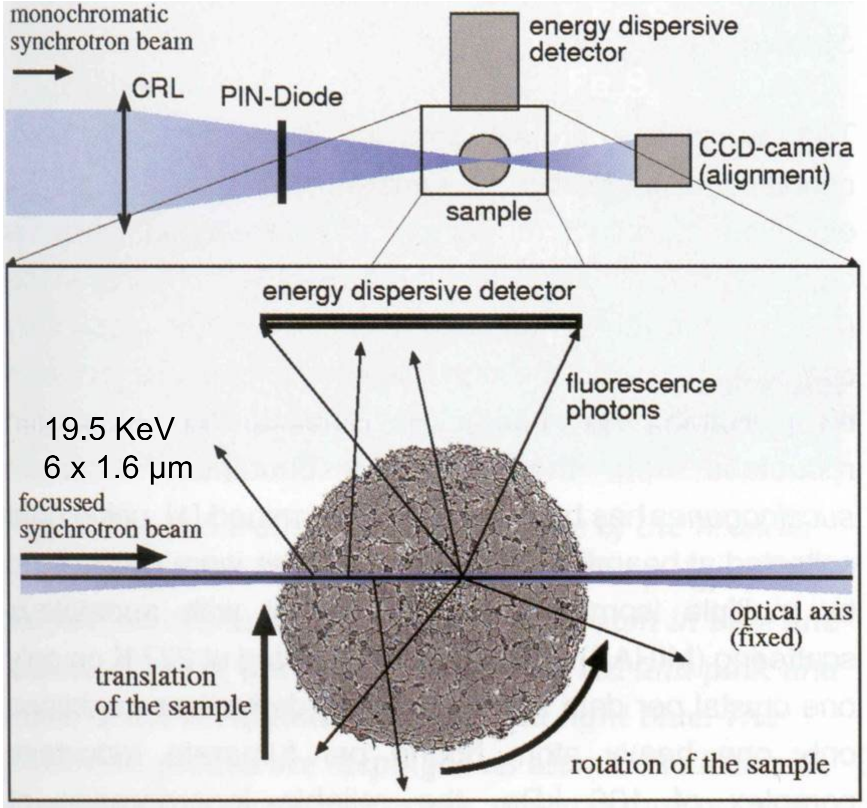

PbL

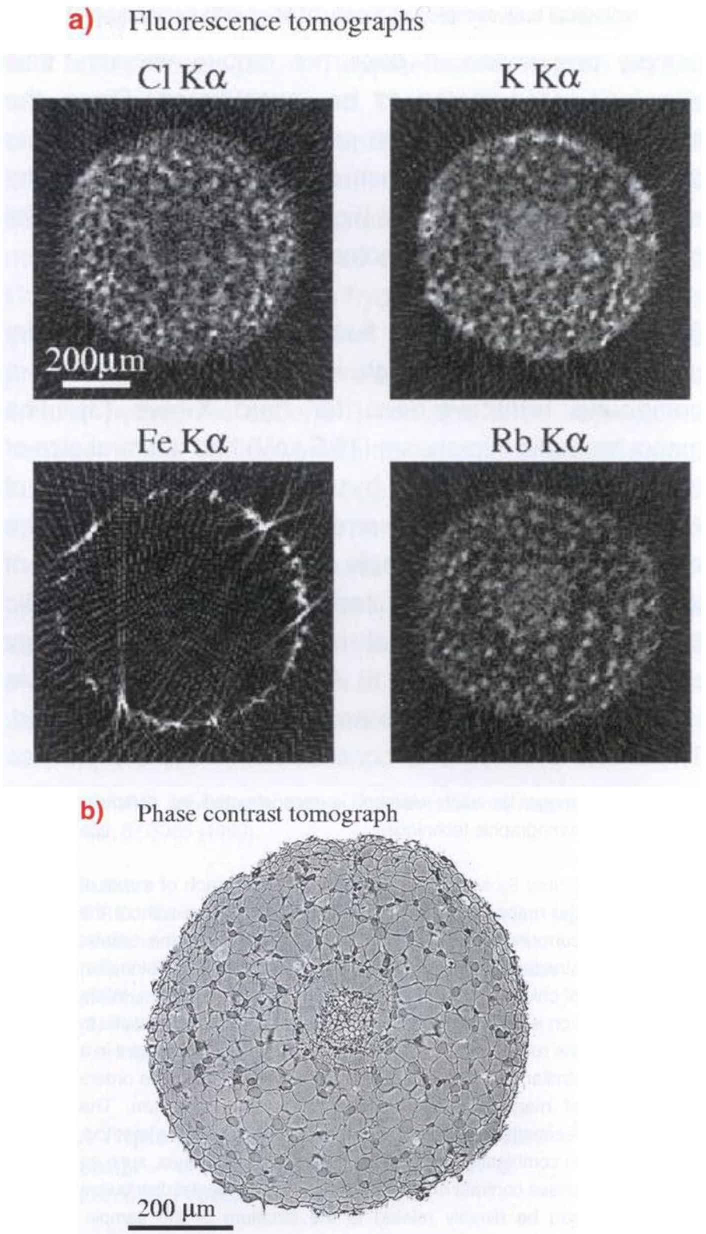

SbK + HgL

Micro fluorescence tomography

Analysis of elemental distributions

Example: Root of a mahagoni tree

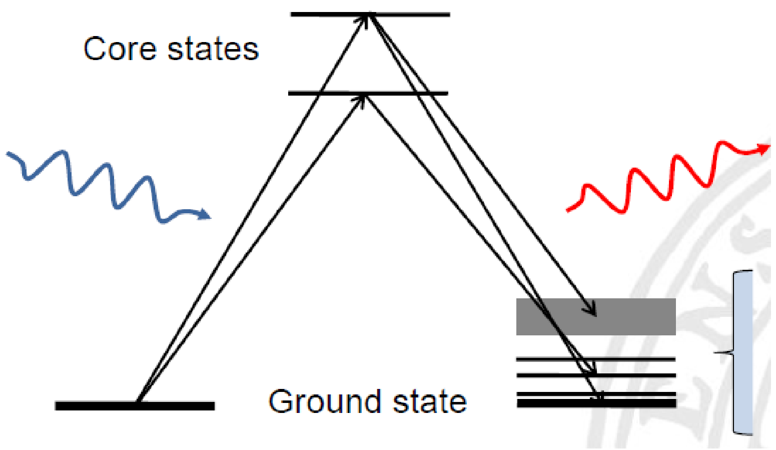




B. Lengeler et al. JSR. 6, 1153-1167 (1999)

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

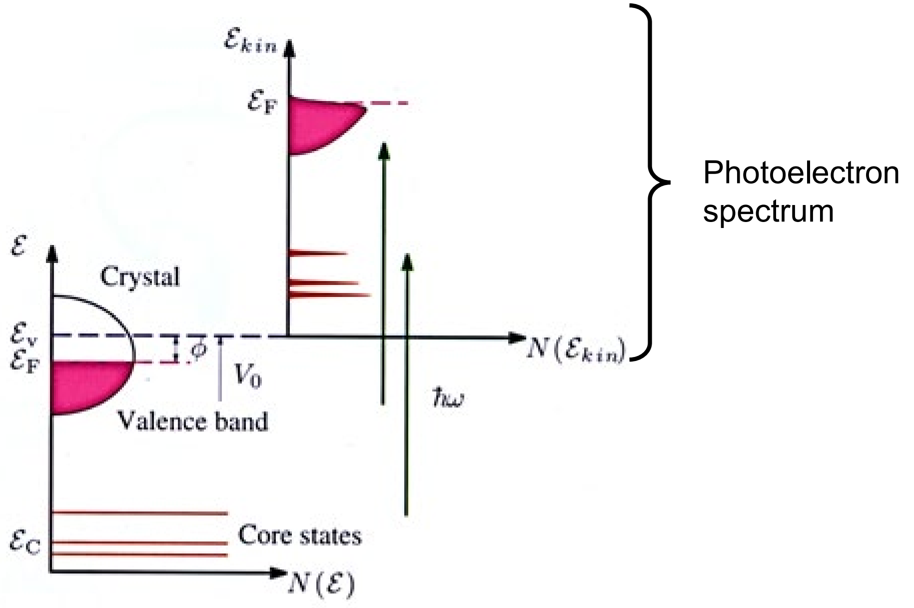
- site, element, orbital selectivity
- polarization dependent (symmetry selectivity)
- probing of low-energy excitations
- access ultrafast dynamics
- sensitive to bulk (large penetration depth)

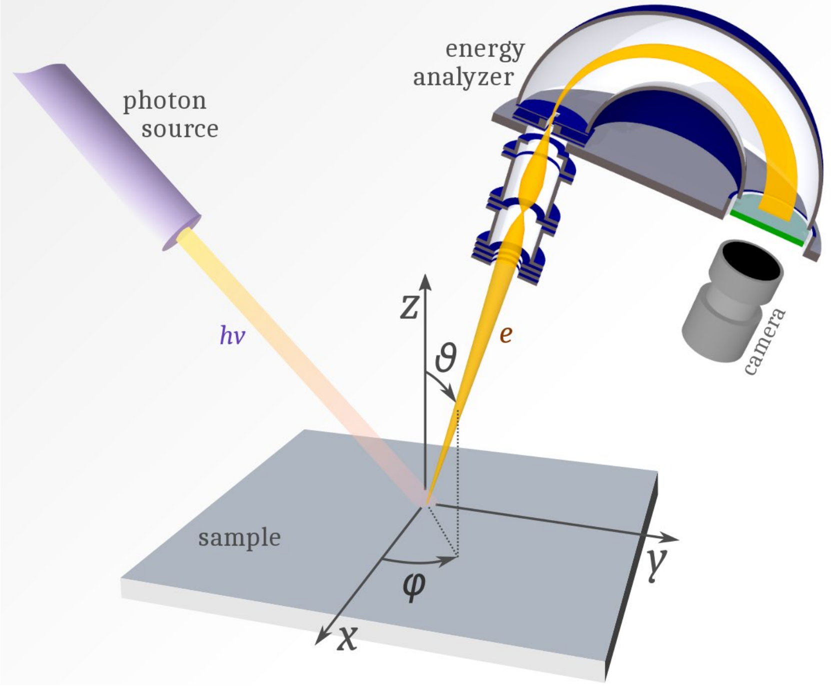
Courtesy: J. Nordgren et al.
Dept. of Physics and Astronomy, Uppsala University, Sweden

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

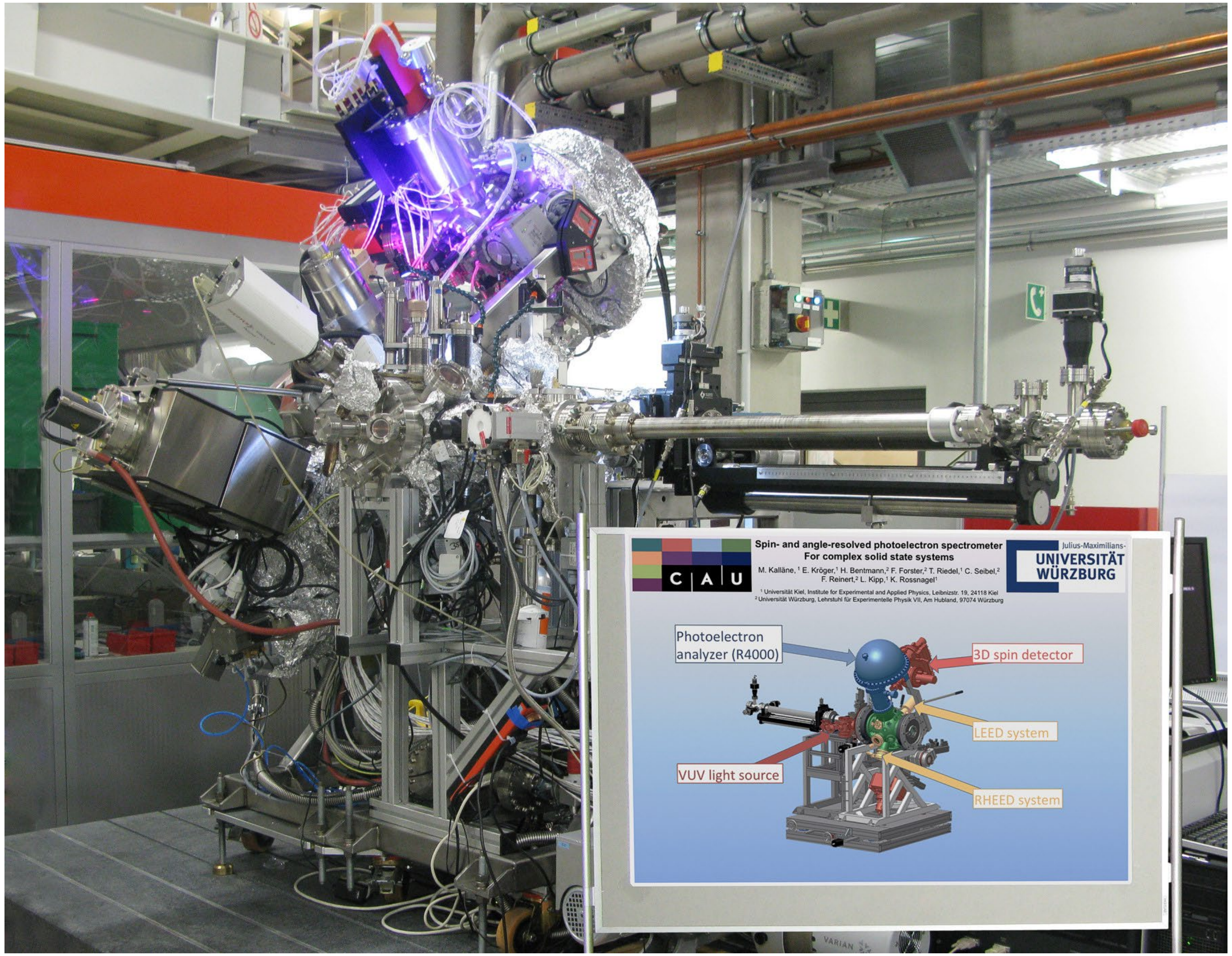




https://commons.wikimedia.org/w/index.php?curid=90955767

Photoelectron Spectroscopy

Angle-resolved photoemission spectroscopy (ARPES):



X-ray Photoelectron Spectroscopy

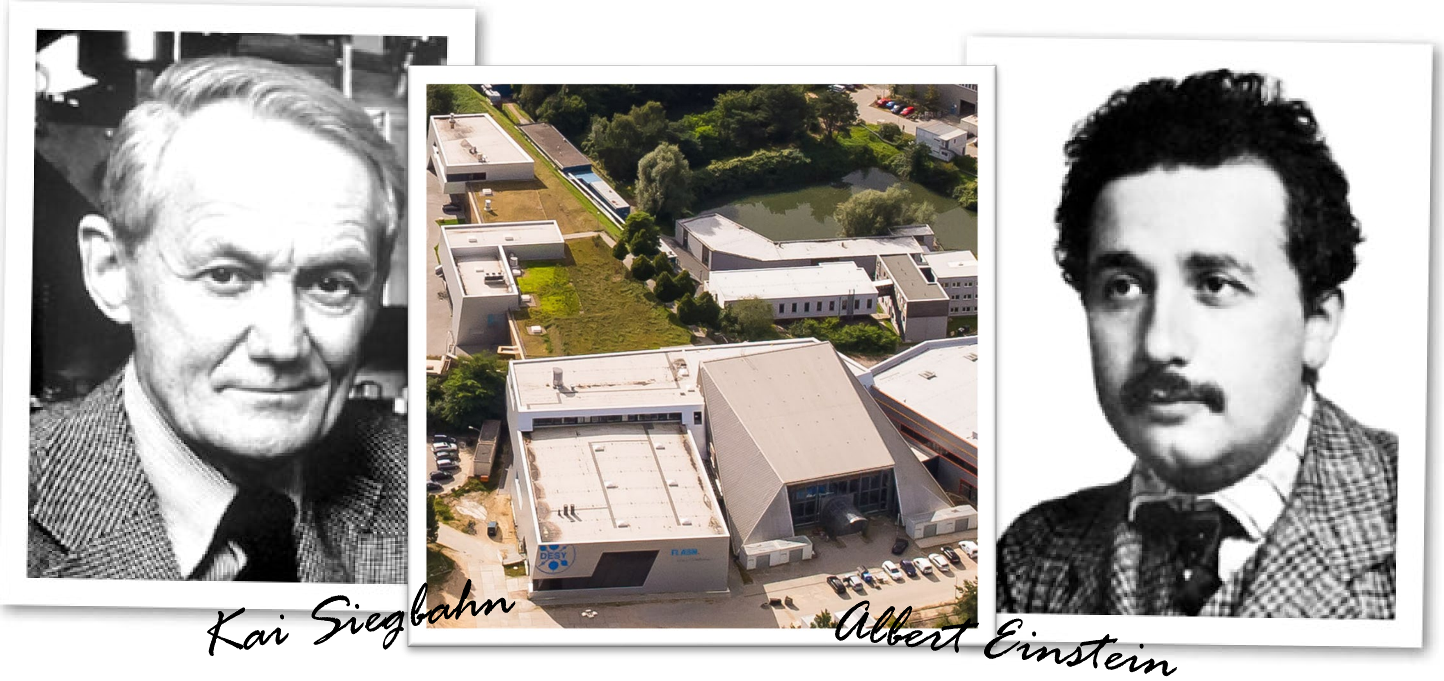
Angle-resolved photoemission spectroscopy (ARPES):

- **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)**



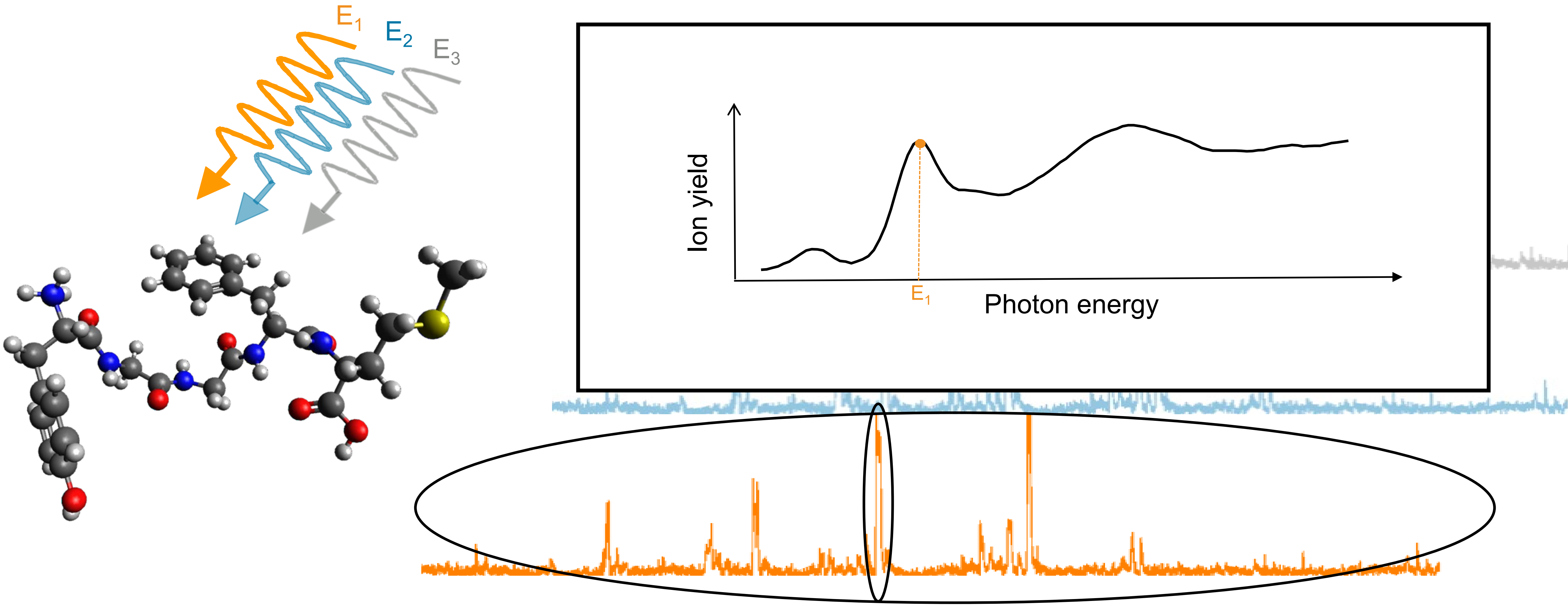
Action spectroscopy

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.

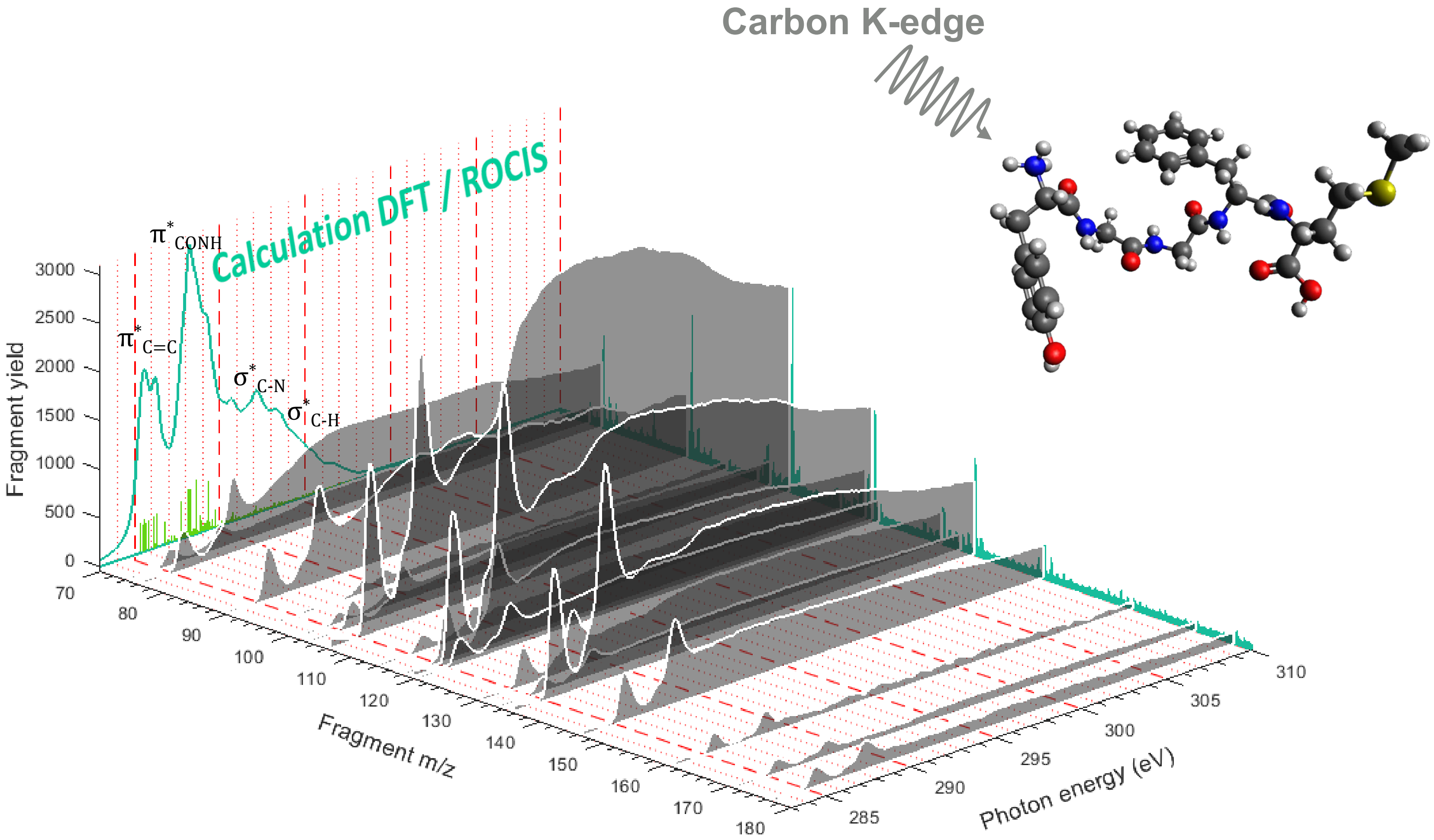
Instead: measure the action of the light on the molecule = fragmentation
Photo-ionization → Ions can be manipulate in electric fields

Action spectroscopy



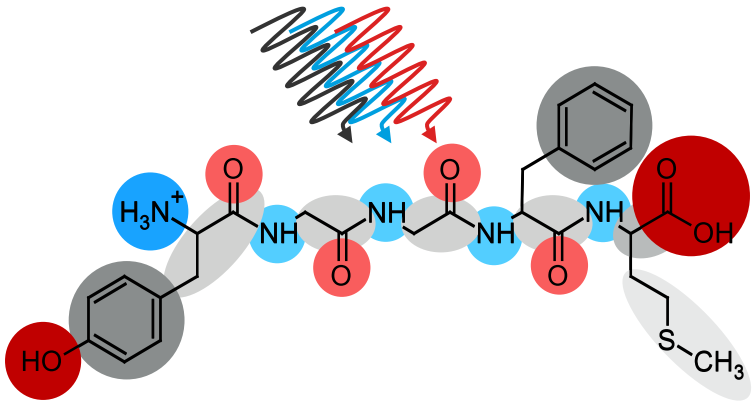
X-ray Action Spectroscopy

Near Edge X-ray Absorption Mass Spectrometry (NEXAMS)

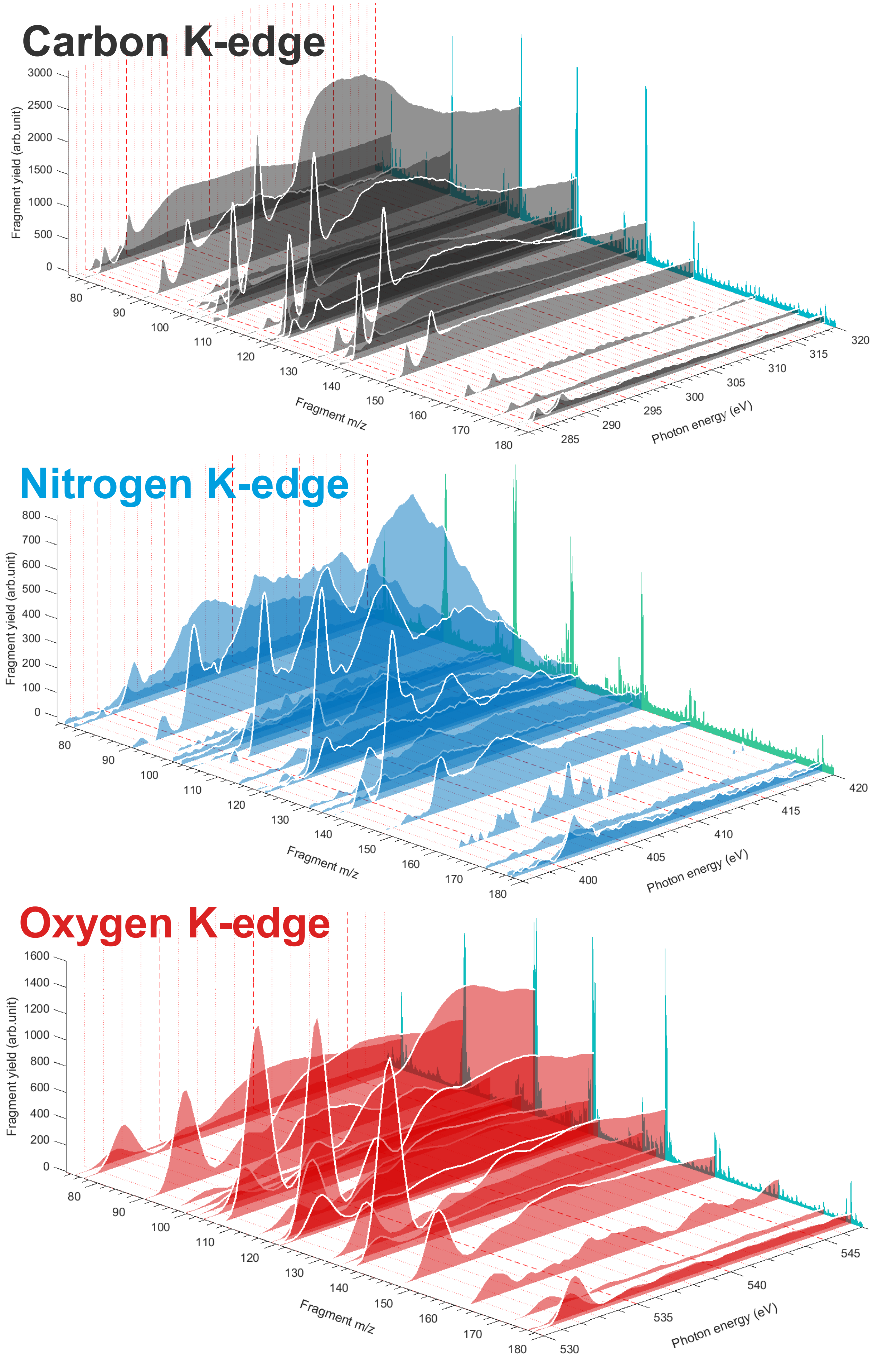


NEXAMS

at the C, N, and O K edges



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

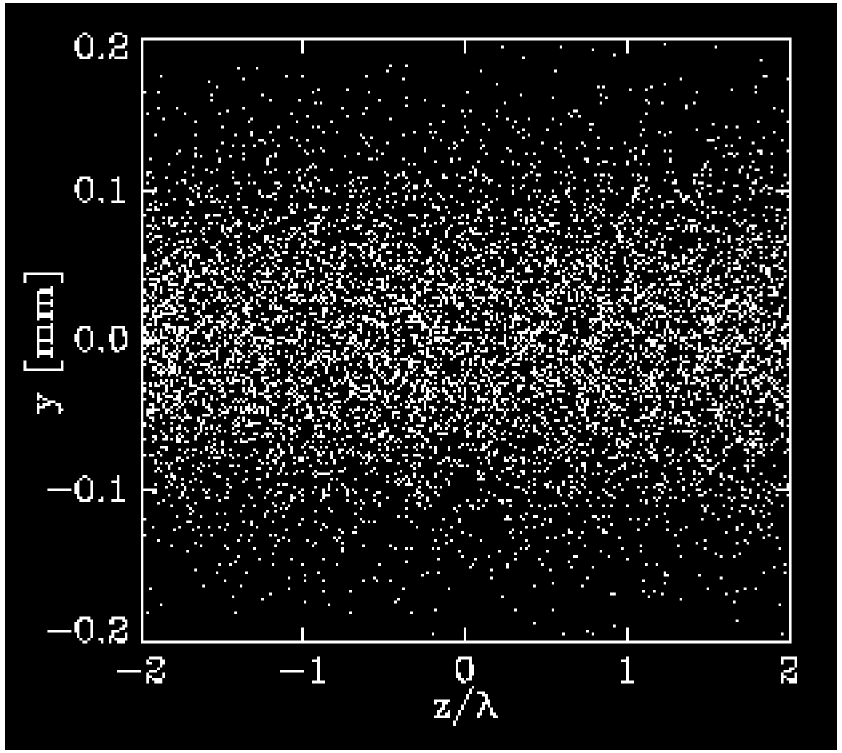


S. Dörner *et* al., J. *Am. Soc. Mass Spectrom.* **32**, 670 (2021).

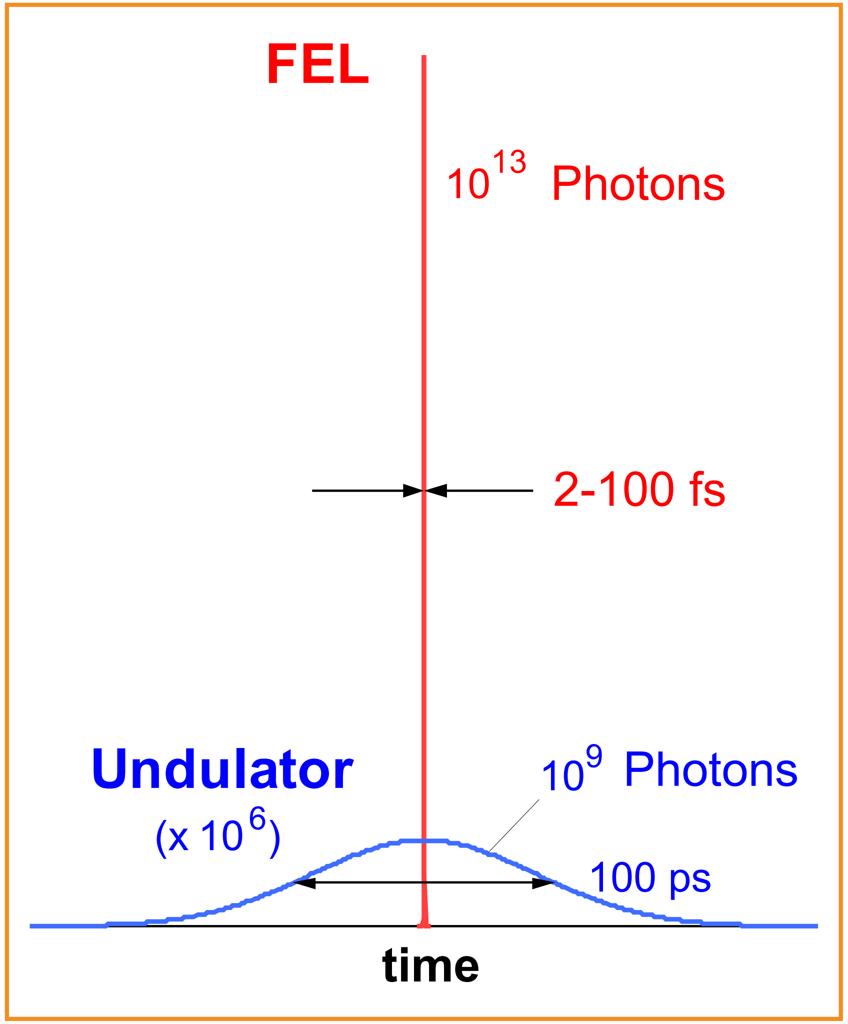
Experiments with FELs

Comparison undulator radiation – X-ray FEL radiation

Microbunching in the SASE process



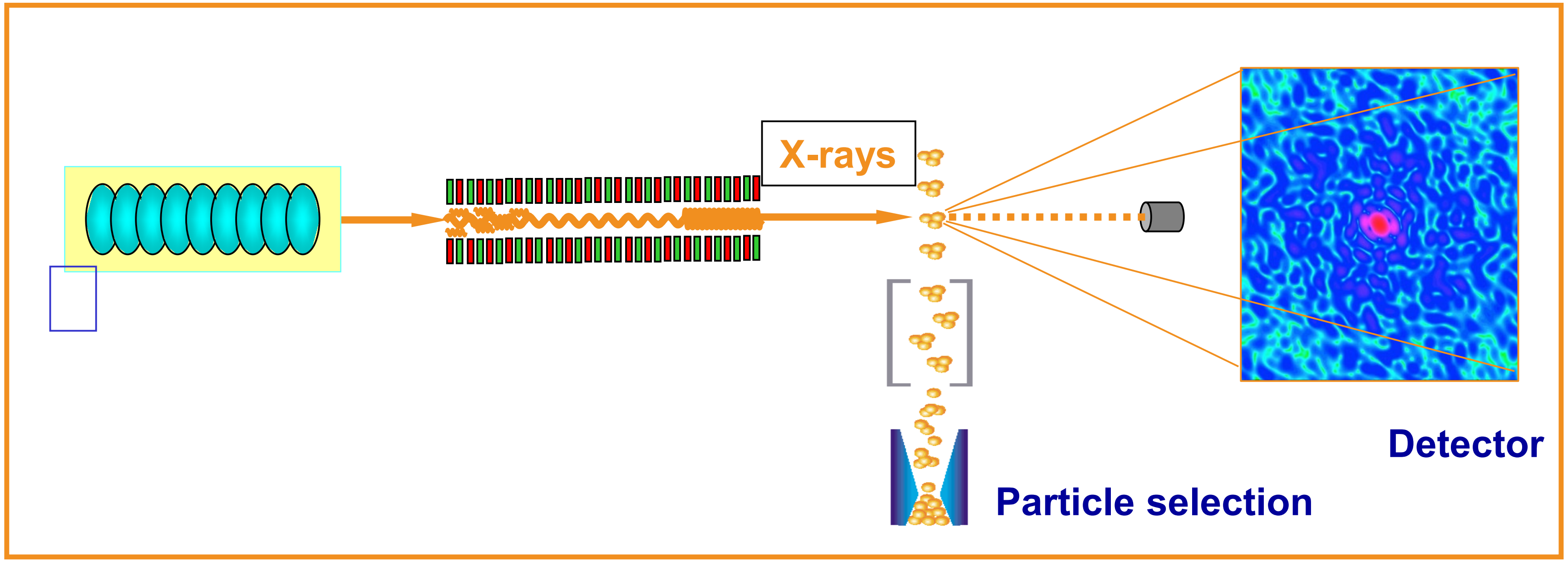
(simulation by Sven Reiche)



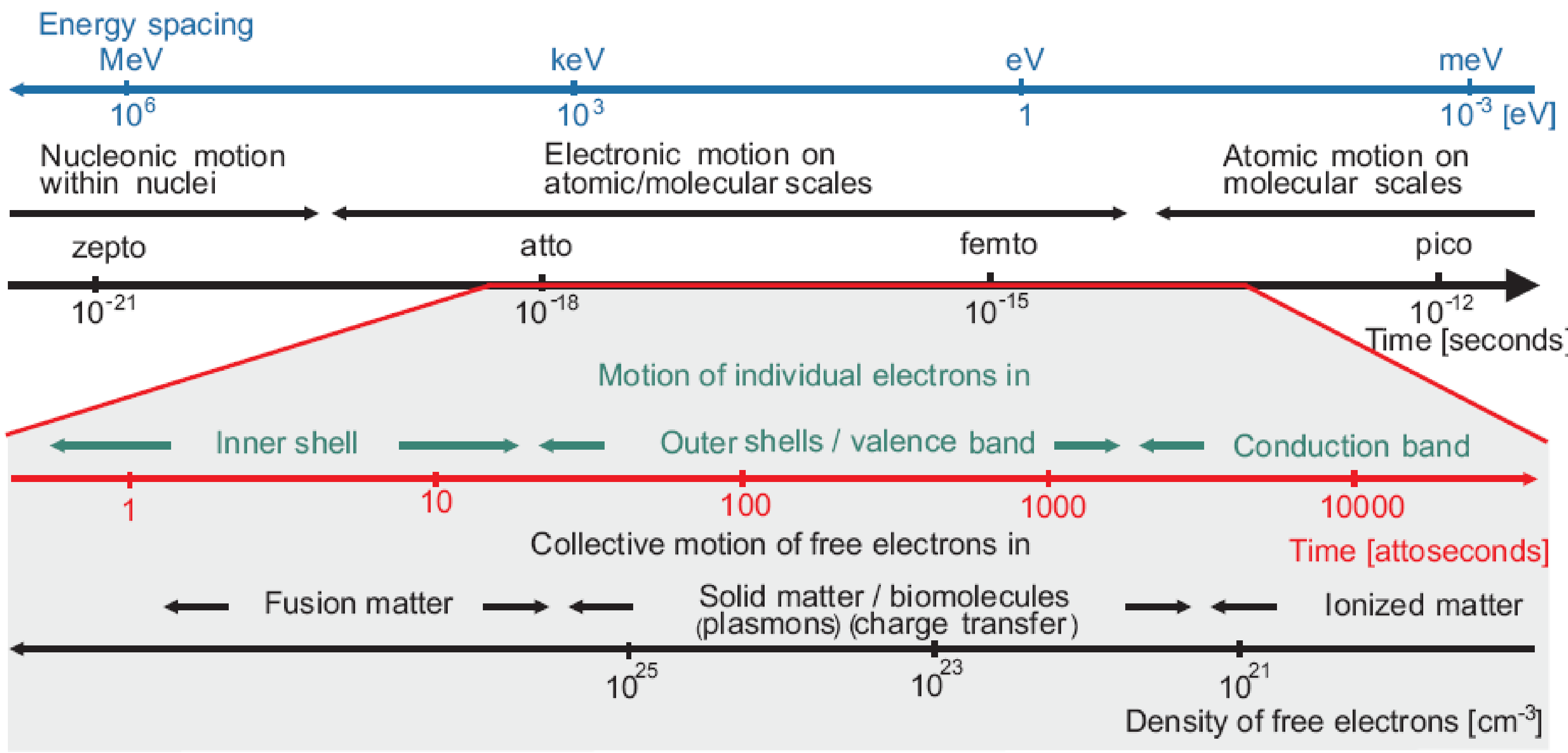
Why use an FEL for structure studies?

- **Ultrafast changes of structure**
  - from atoms to solids, including changes of the associated electronic structure
  - “femtochemistry”
- **Structure determination of non-crystalline objects and very small (nano-) crystals**
  - Dream: biomolecules in 3D that do not form crystals
  - 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

The ultimate goal: single-molecule diffraction



Time scales

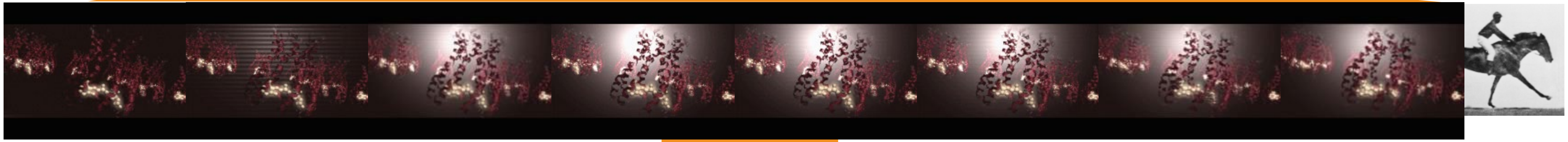


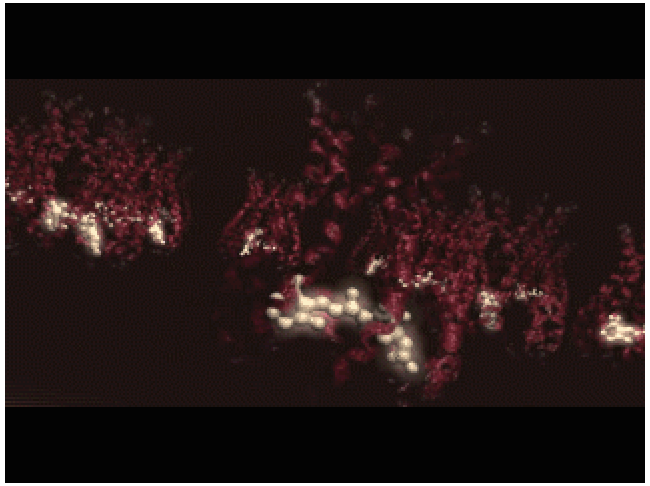
F. Krausz, M. Ivanov
Review of Modern Physics **81**, 163 (2009)

Making molecular movies

Eadweard Muybridge
1892

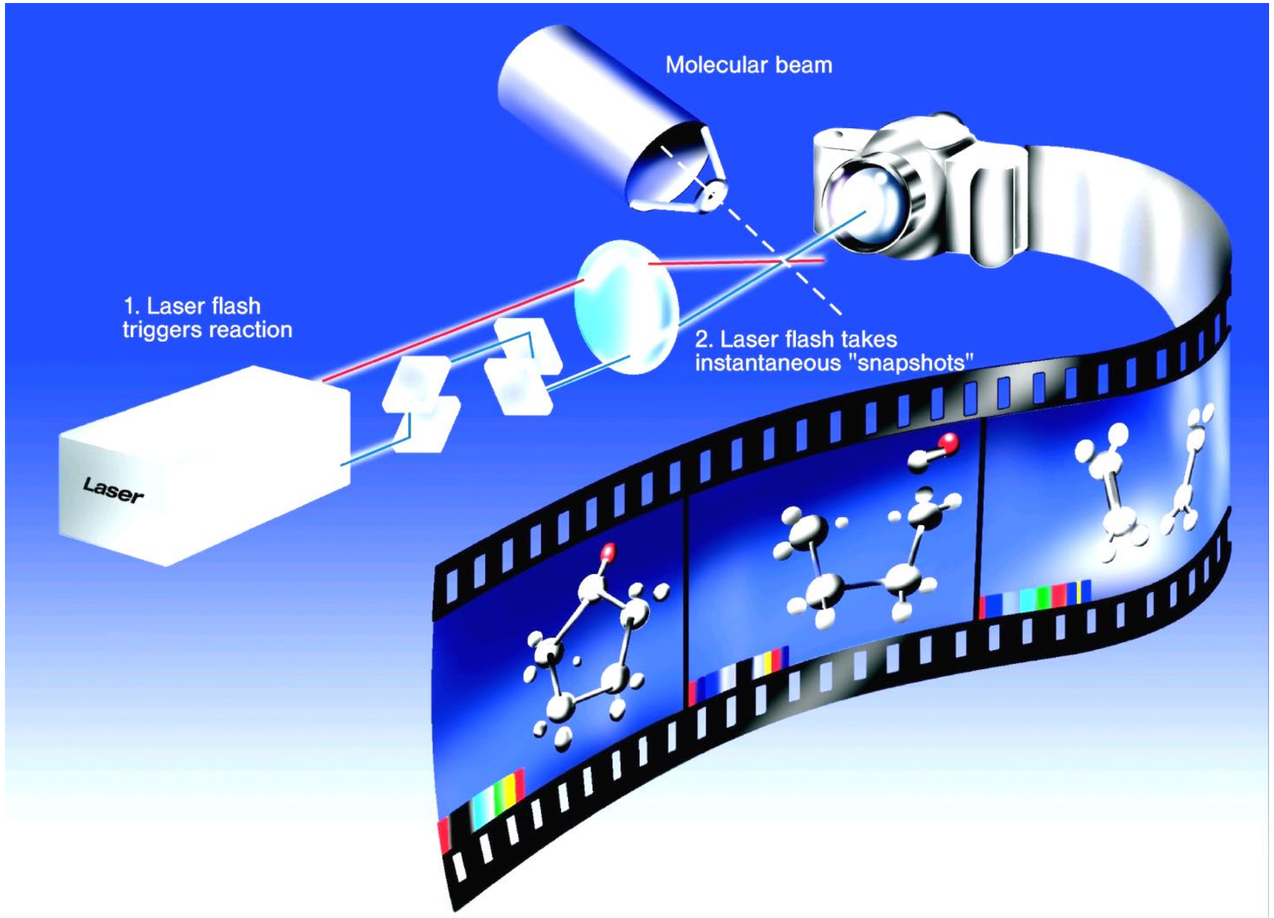
European XFEL





Courtesy European XFEL

The ultimate goal: recording the “molecular movie”



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

→ “motion picture” of the reaction

Coulomb repulsion…

http://www.magnificentrevolution.org/2009/07/mag-rev-on-bbc/

Theoretical Prediction

Potential for biomolecular imaging with femtosecond X-ray pulses

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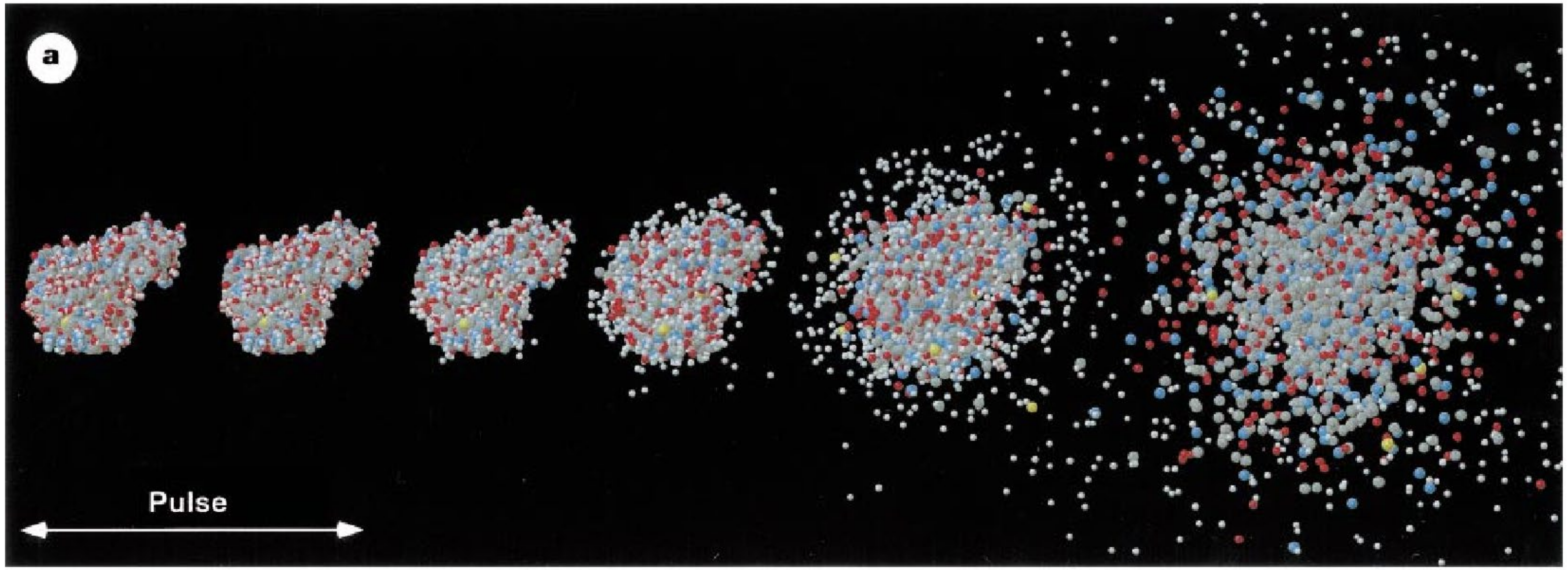
** Department of Biochemistry, Biomedical Centre, Box 576, Uppsala University, S-75123 Uppsala, Sweden*
† Institut für Kristallographie, Universität Karlsruhe, Kaiserstrasse 12, D-76128, Germany

Nature 406, 752 (2000)

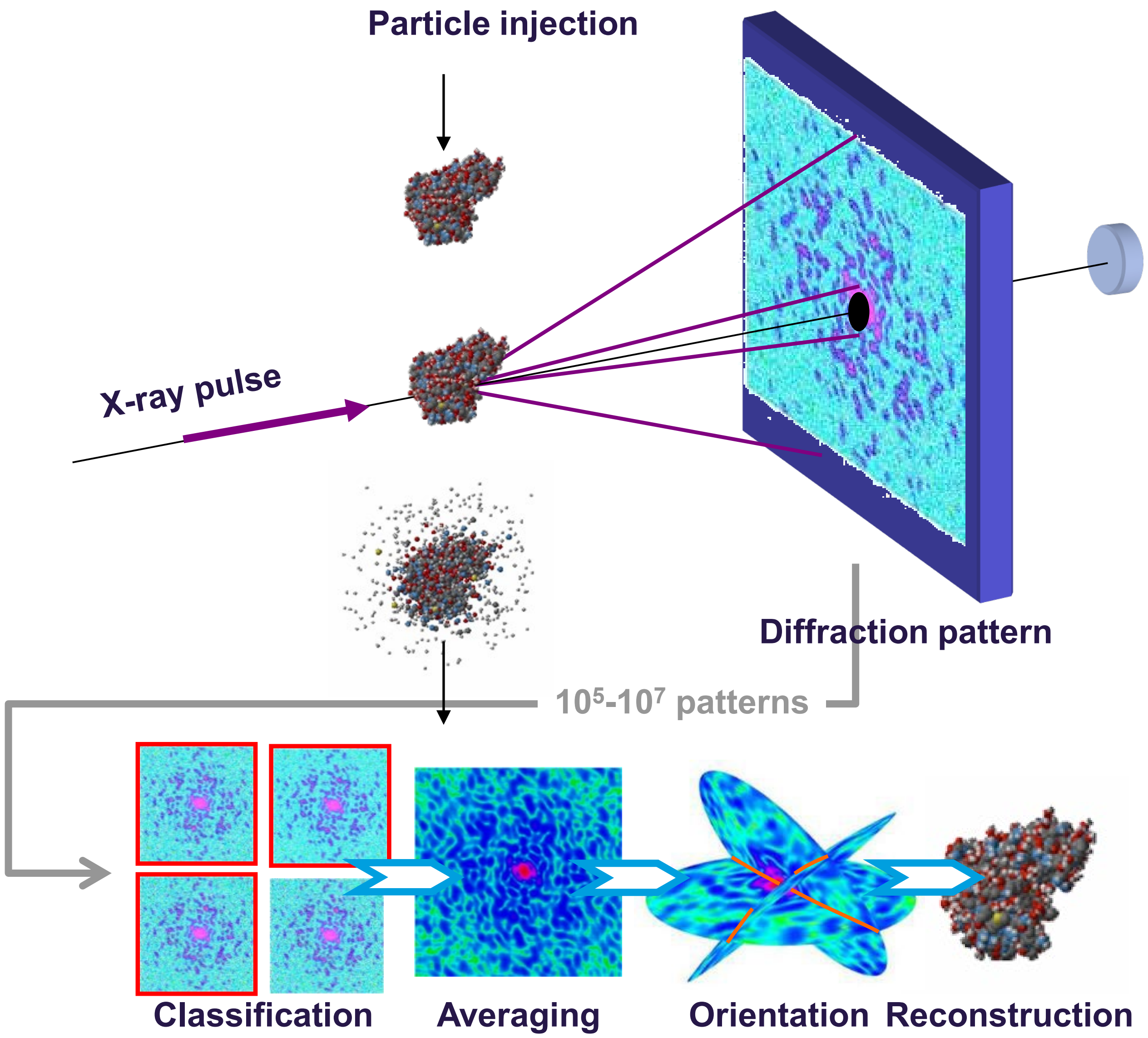
‘diffract before destroy’
(it works !)

Explosion of a biomolecule (T4 lysozyme) after exposure to a 2-fs XFEL pulse (E = 12 keV)

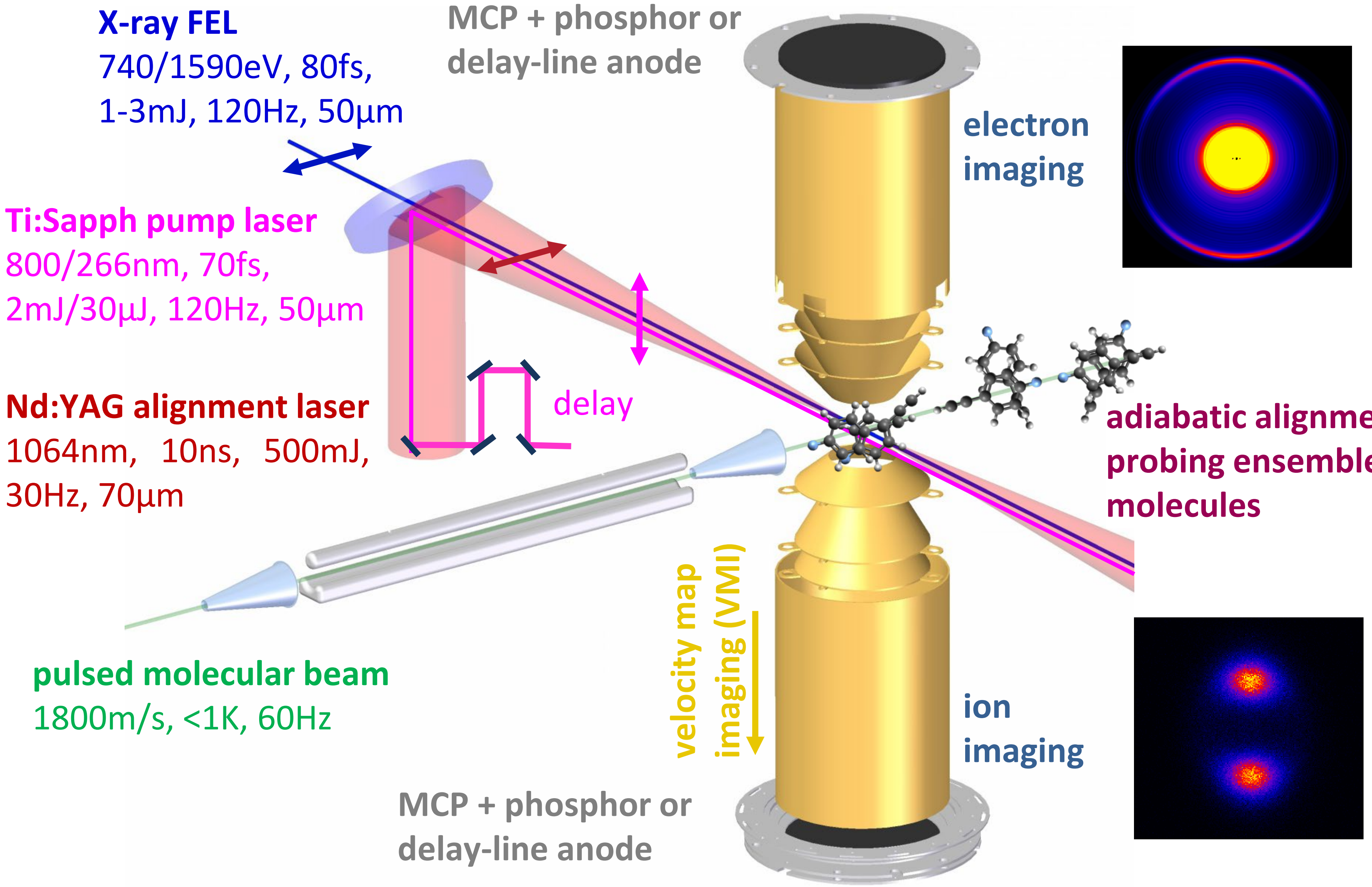


t=–2fs *t*=2fs *t*=5fs *t*=10fs *t*=–20fs *t*=50fs

Determine the structure of bio-particles



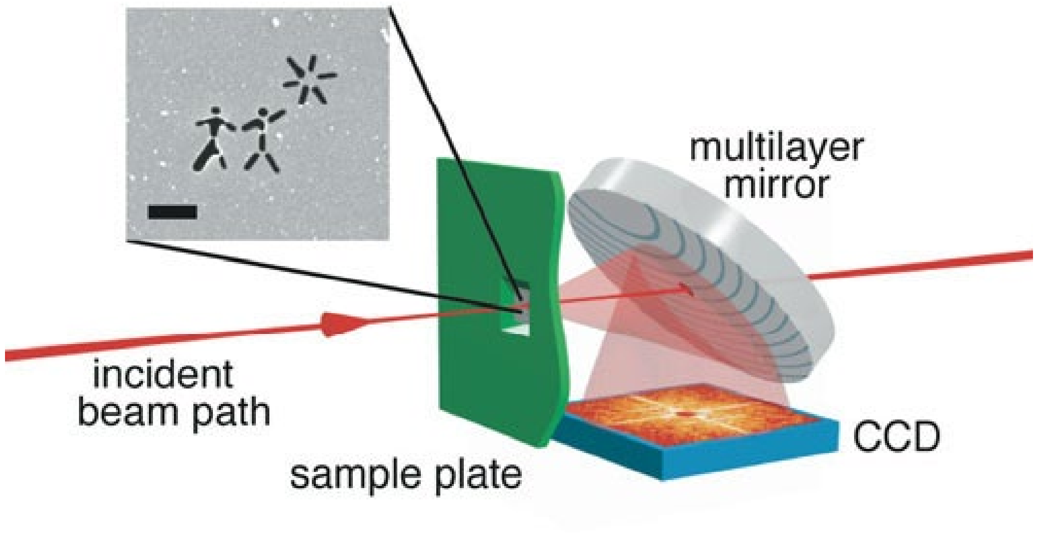
Double-sided velocity map imaging in CAMP at FLASH



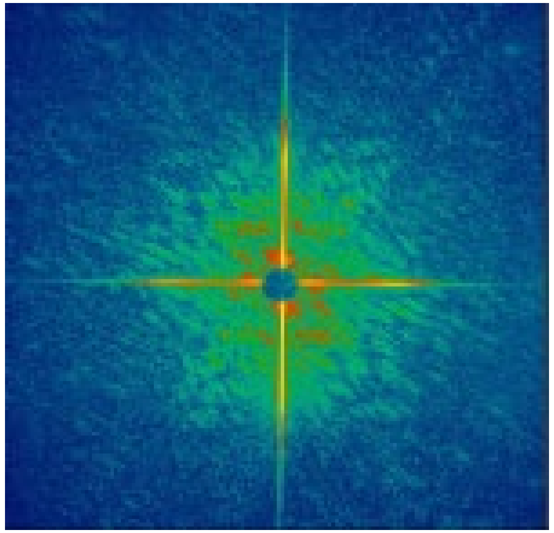
D. Rolles, R. Boll et al., J. Phys. B 47, 124035 (2014)
L. Strüder et al., Nucl. Instrum. Meth. A 614, 483 (2010)

First demonstration of ultrafast coherent X-ray diffraction at FLASH

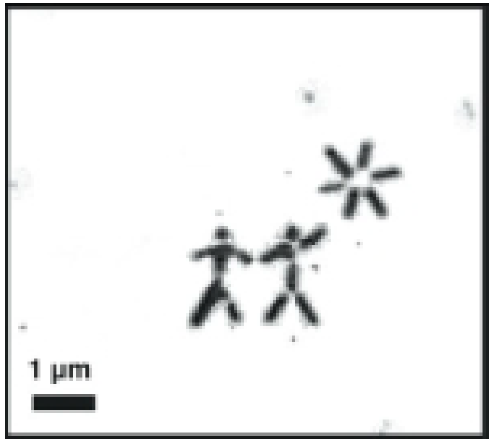
Incident FEL pulse:
30 fs, 32 nm,
3 x 10^{13} W cm^{-2}



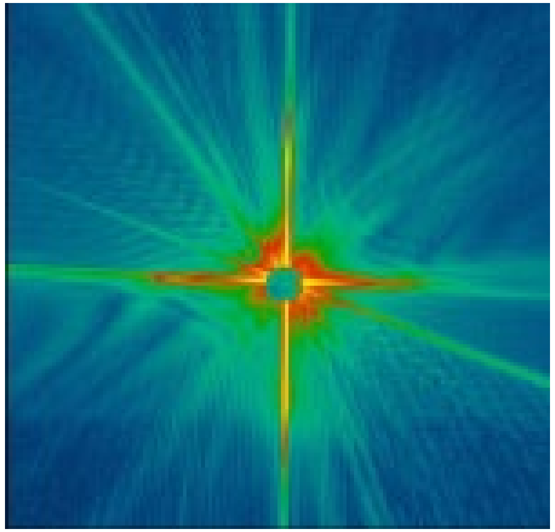
Pulse #1: Diffraction pattern



Reconstructed image



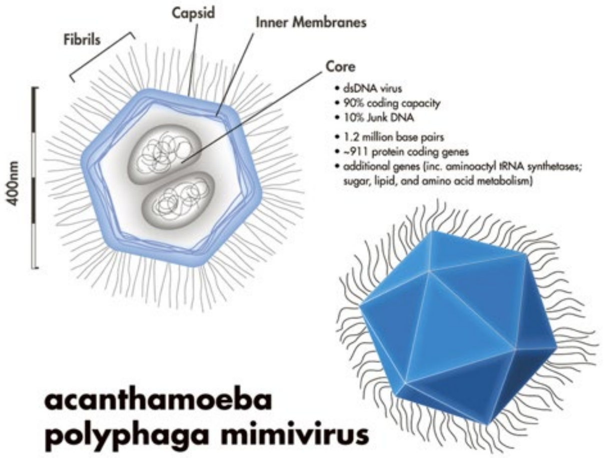
Pulse #2 sees structure destroyed by pulse #1



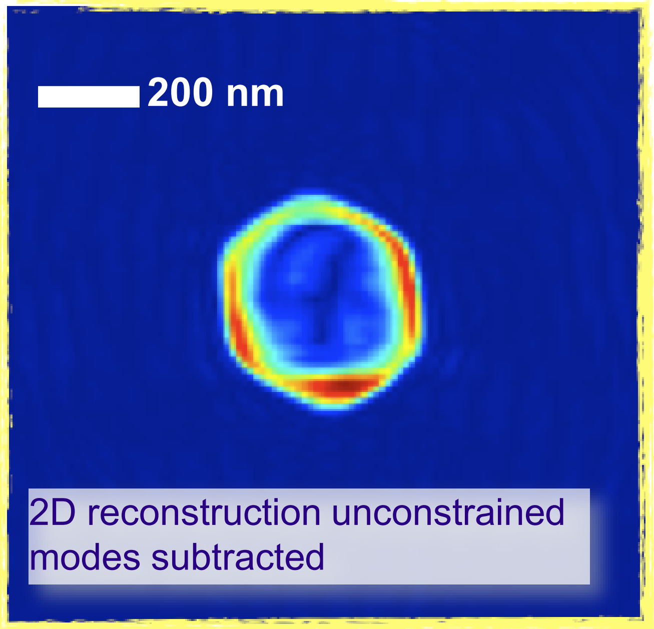
H. Chapman et al. Nature Physics 2, 839 (2006)

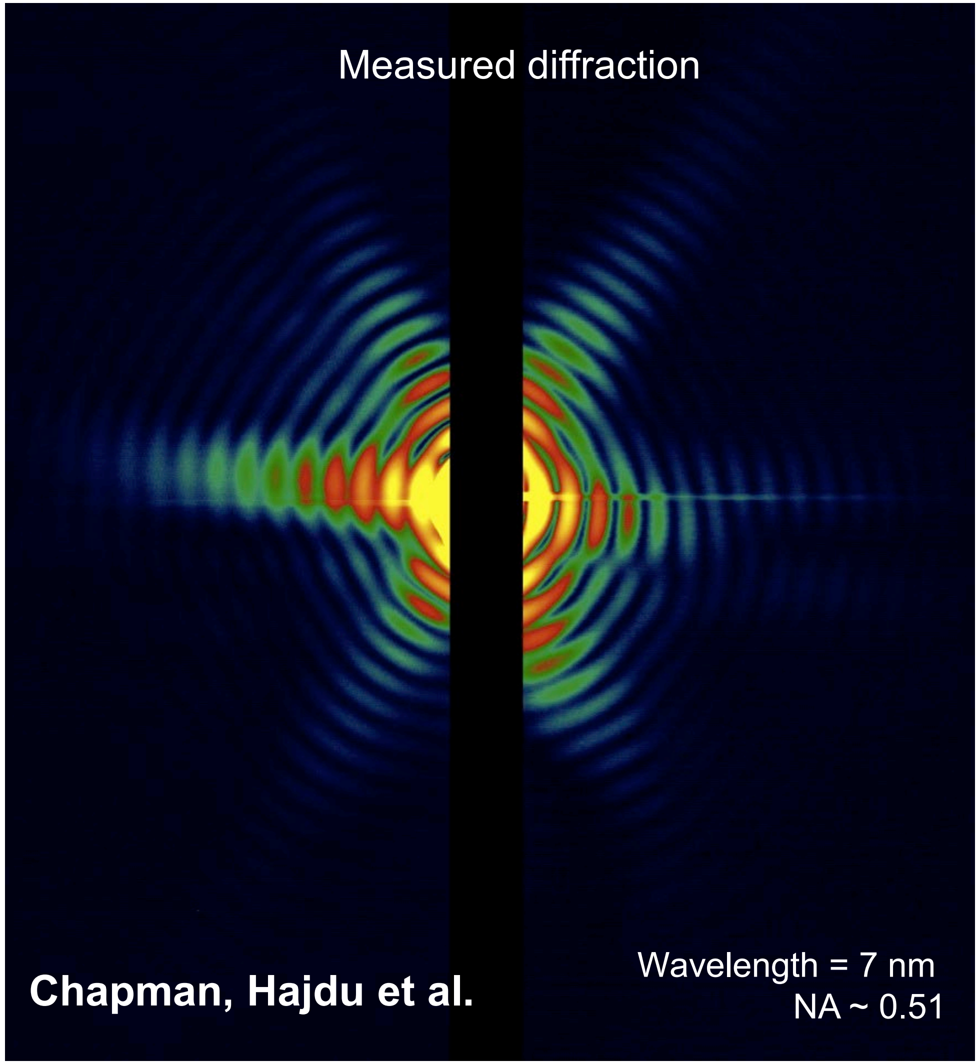
Conclusion: diffraction takes place before the sample is destroyed !

Diffraction from a mimivirus



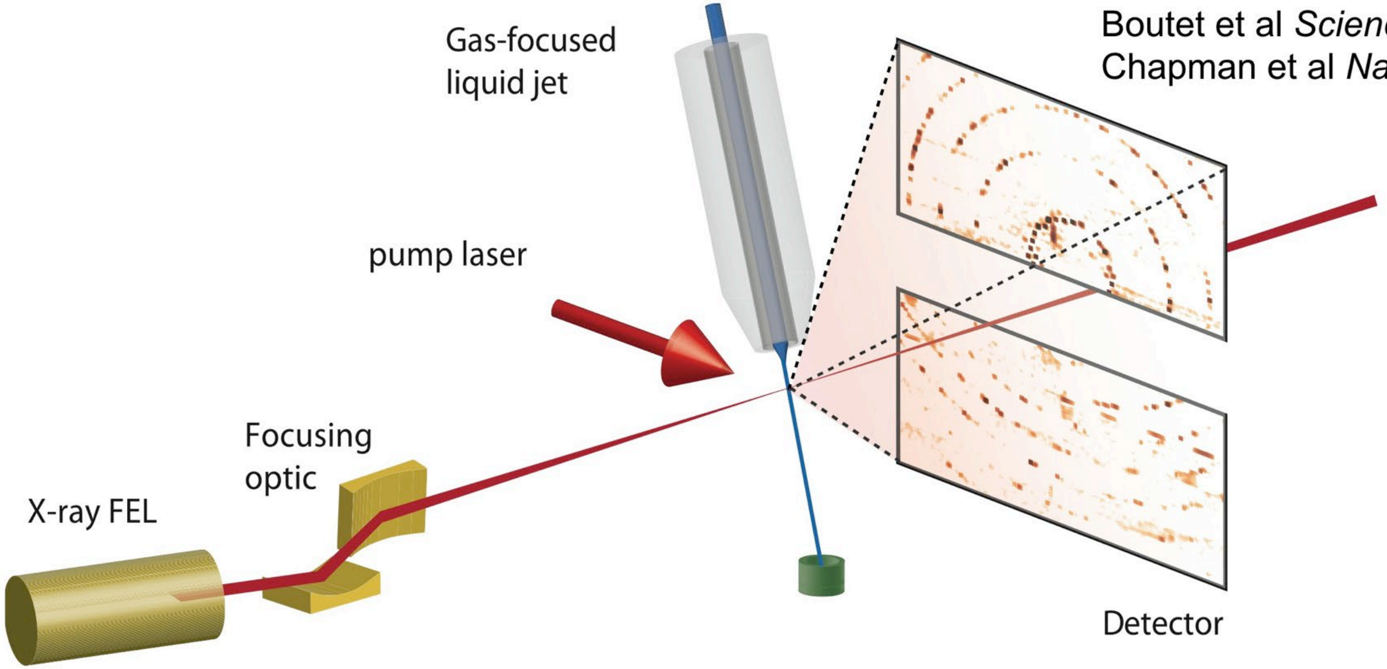
Graphic: wikipedia.org



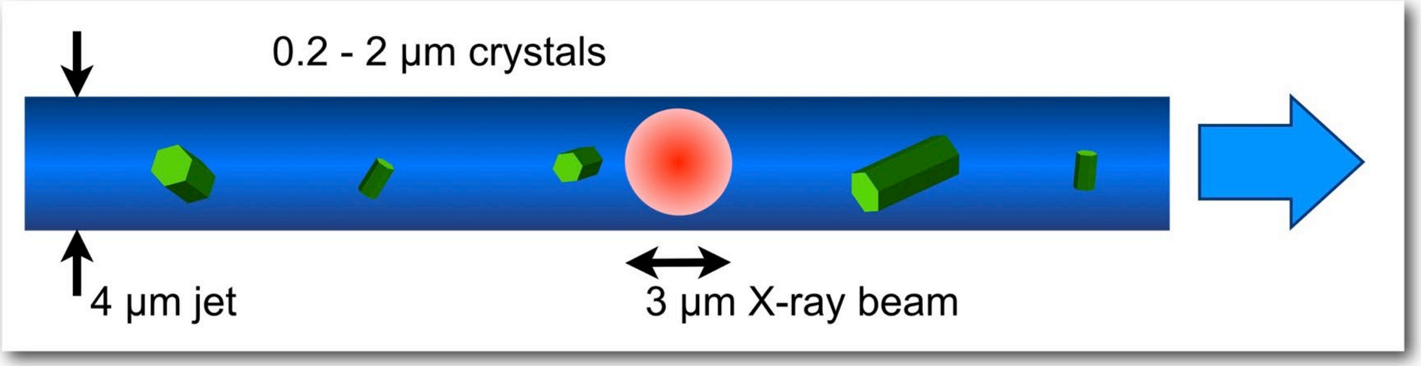


Samples: Uppsala University and CNRS, Aix-Marseille Université
FEL experiments: MPI , CFEL @ DESY, Uppsala, SLAC

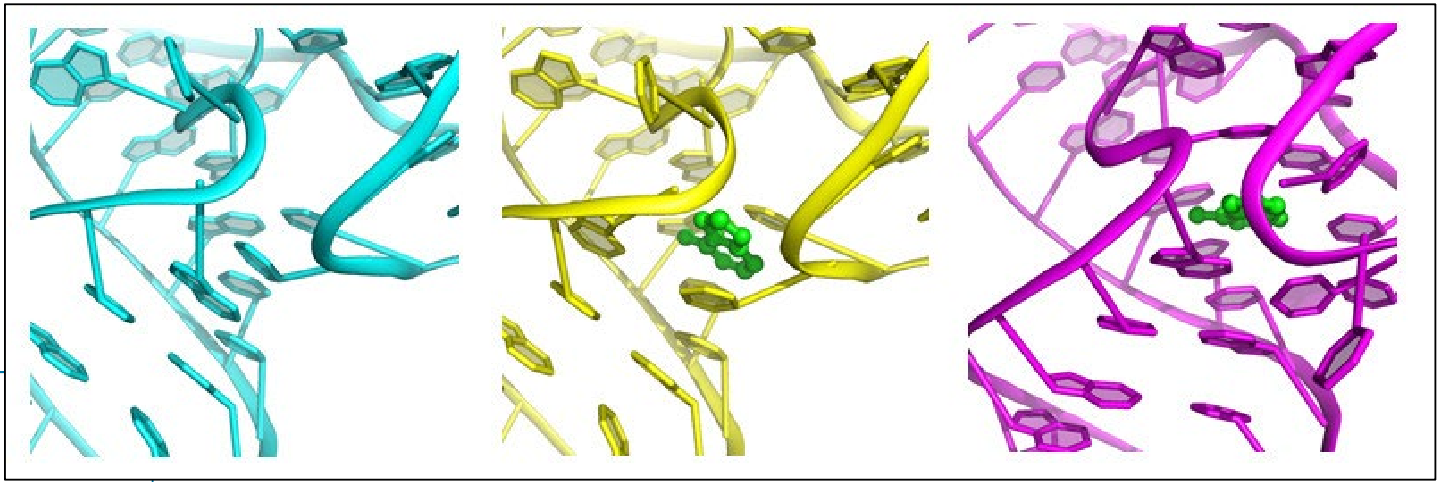
Serial femtosecond X-ray crystallography (SFX)



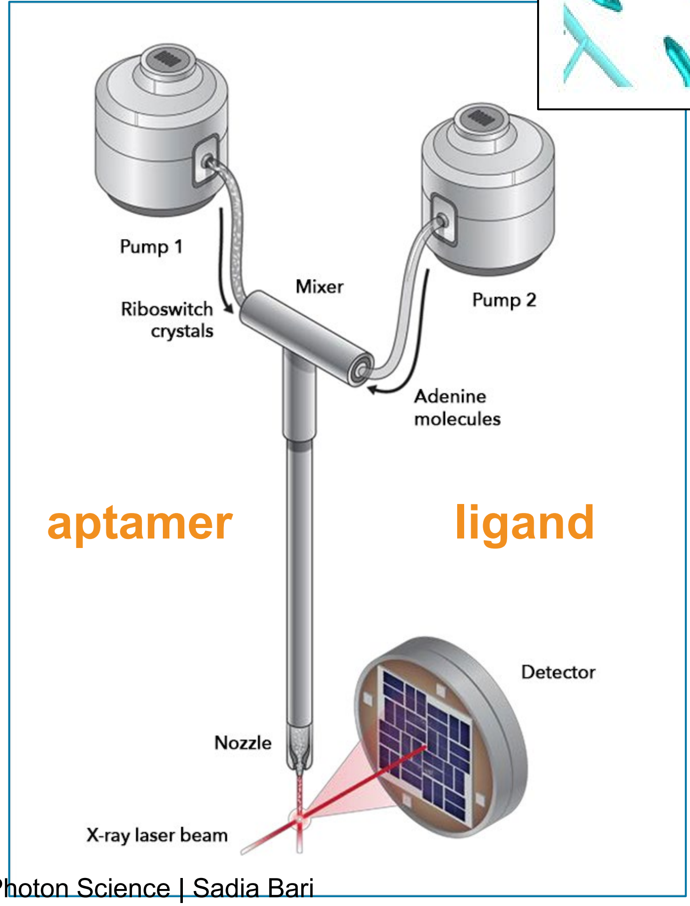
Boutet et al *Science* (2012)
Chapman et al *Nature* (2011)



A riboswitch at work



Mix and inject concept



Riboswitch from the bacterium **Vibrio vulnificus**
(a close relative of the cholera germ)
Active centre is aptamer = sequence of nucleic acids (easy to synthesize into nanocrystals

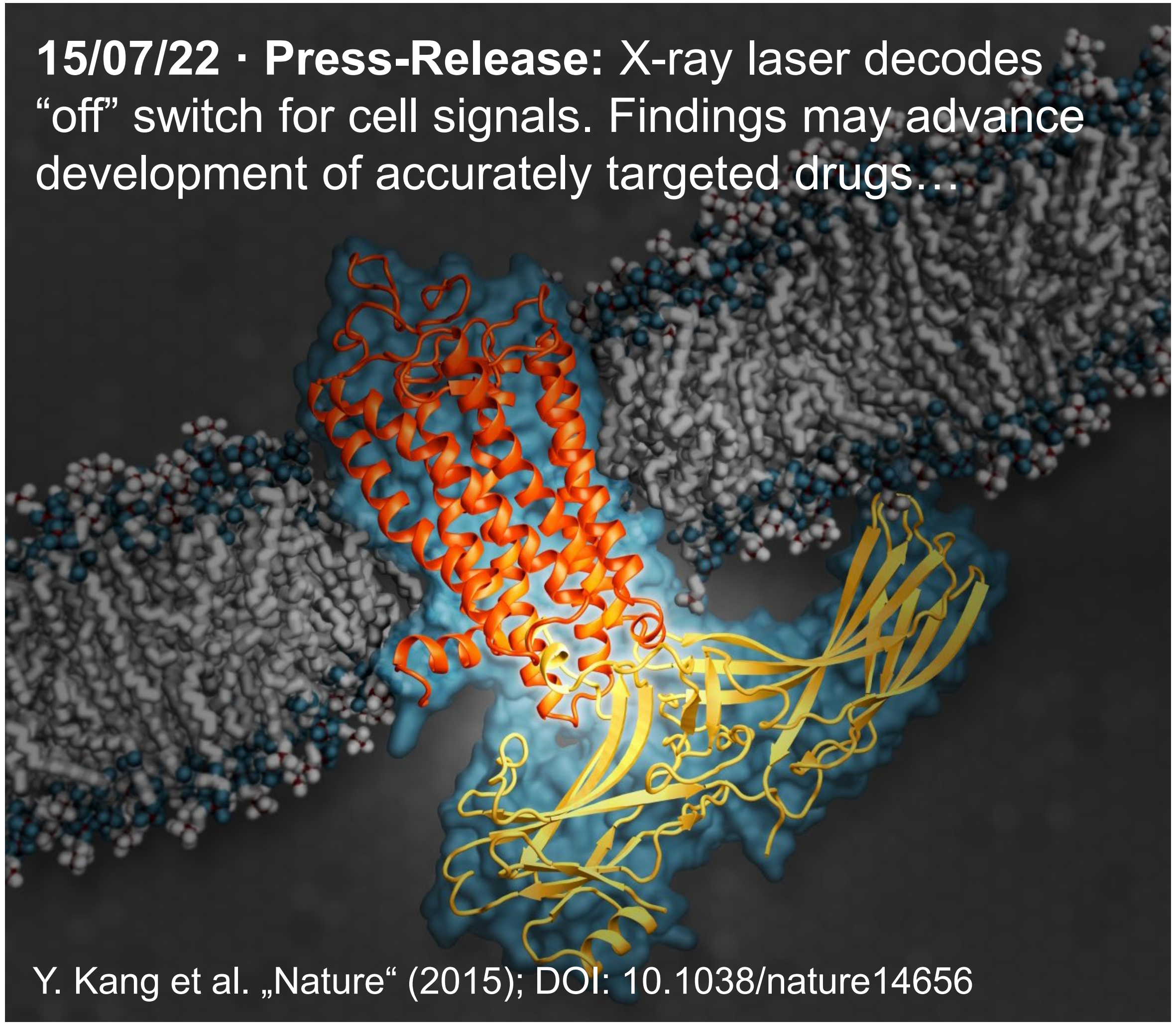
Activated by signal molecule (ligand) Adenine (in green)

After activation the gene related to the switch in not read out anymore

- 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)

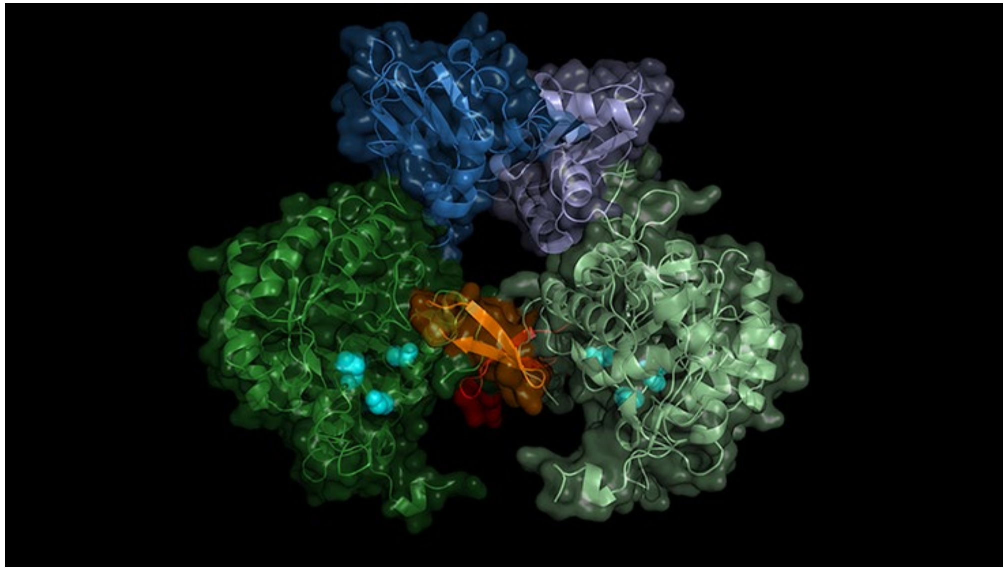
Serial femtosecond X-ray crystallography (SFX)



Possible new approach for sleeping sickness drugs

Serial femtosecond X-ray crystallography (SFX)

University of Lübeck/DESY, Lars Redecke



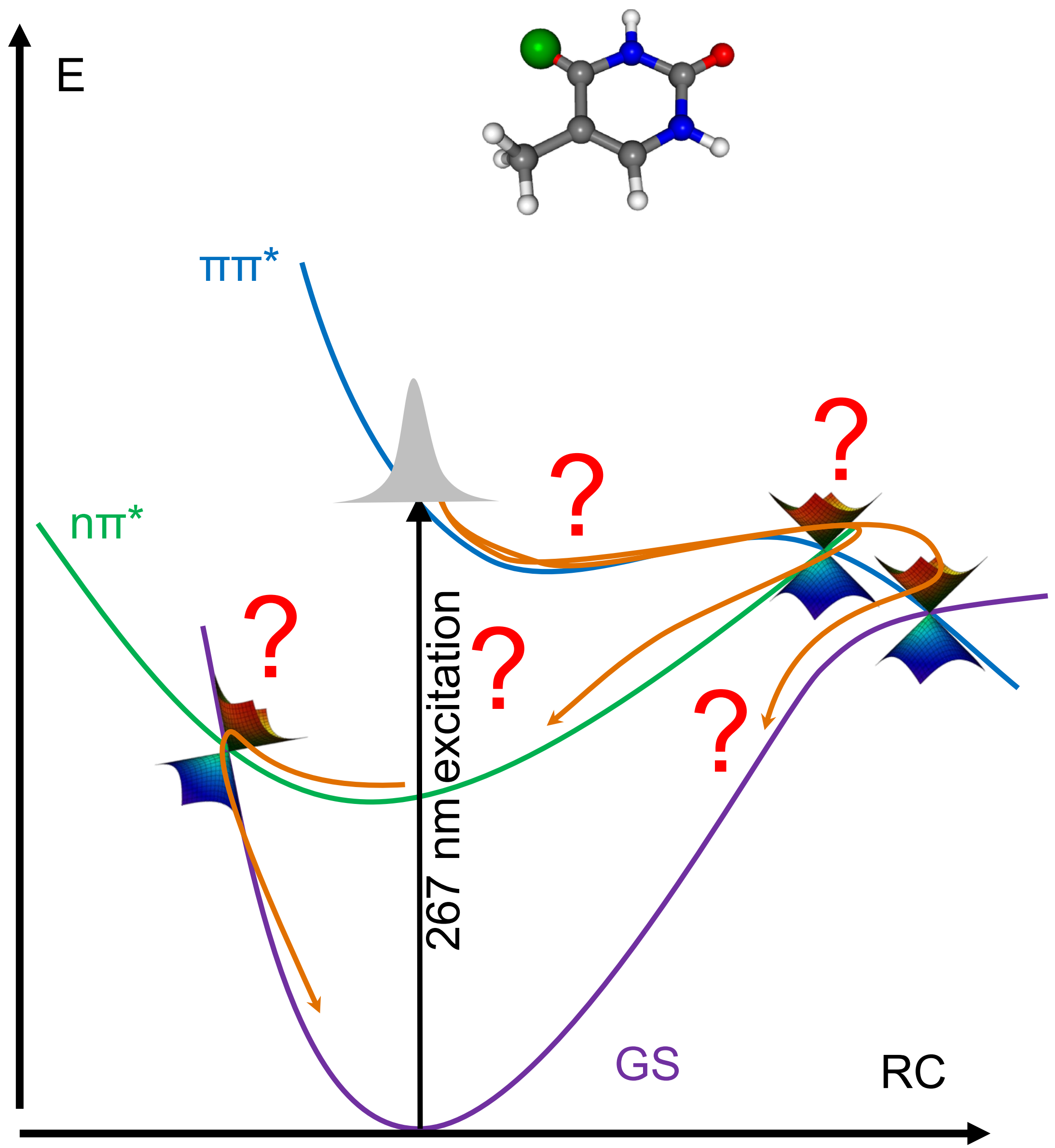
Structure of the parasite's IMP dehydrogenase. The active enzyme forms pairs (dimers), the “switch” region is shown in shades of blue.

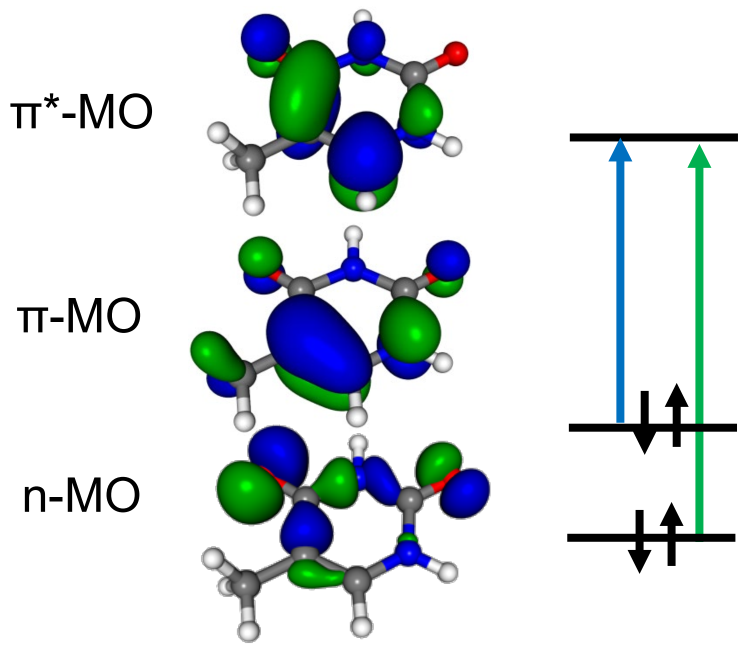
- Certain insect cells to crystallise biomolecules within them
- Tracked down a potential target for new drugs against sleeping sickness: By decoding the detailed spatial structure of a vital enzyme of the pathogen, the parasite Trypanosoma brucei. The result provides a possible blueprint for a drug that specifically blocks this enzyme and thus kills the parasite

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

One last example: spectroscopy at an FEL

What happens to thymine after photoexcitation?





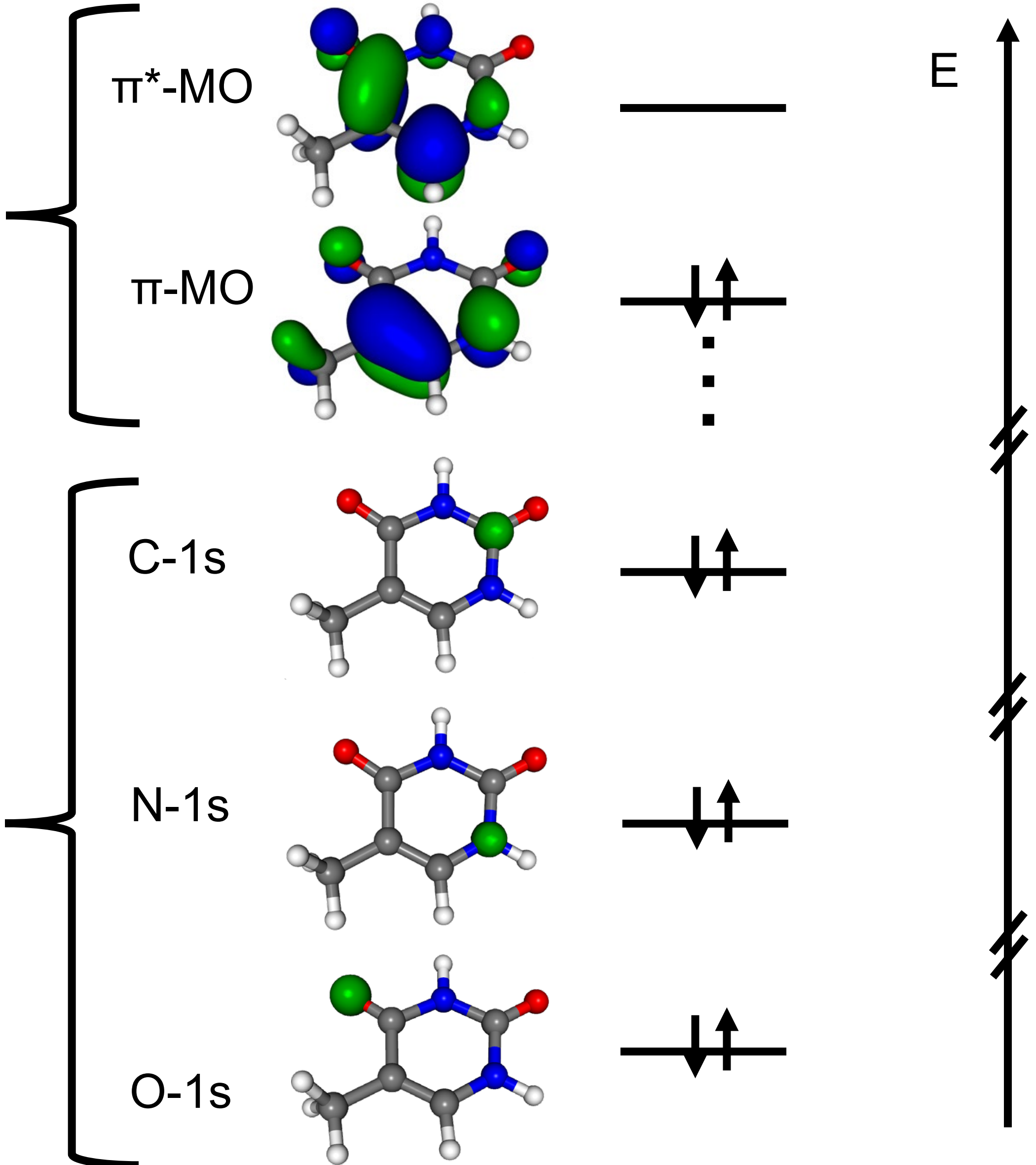
- Overall timescale?
- Which electronic states are populated?
- How does the geometry change?

Courtesy of T. Wolf (SLAC)

Photon energies to probe the dynamics

Valence electrons:
Delocalized,
Overall time scales,
XUV, high harmonic generation

Core electrons:
Localized,
site-specific geometry evolution,
excited state characters
X-ray FEL

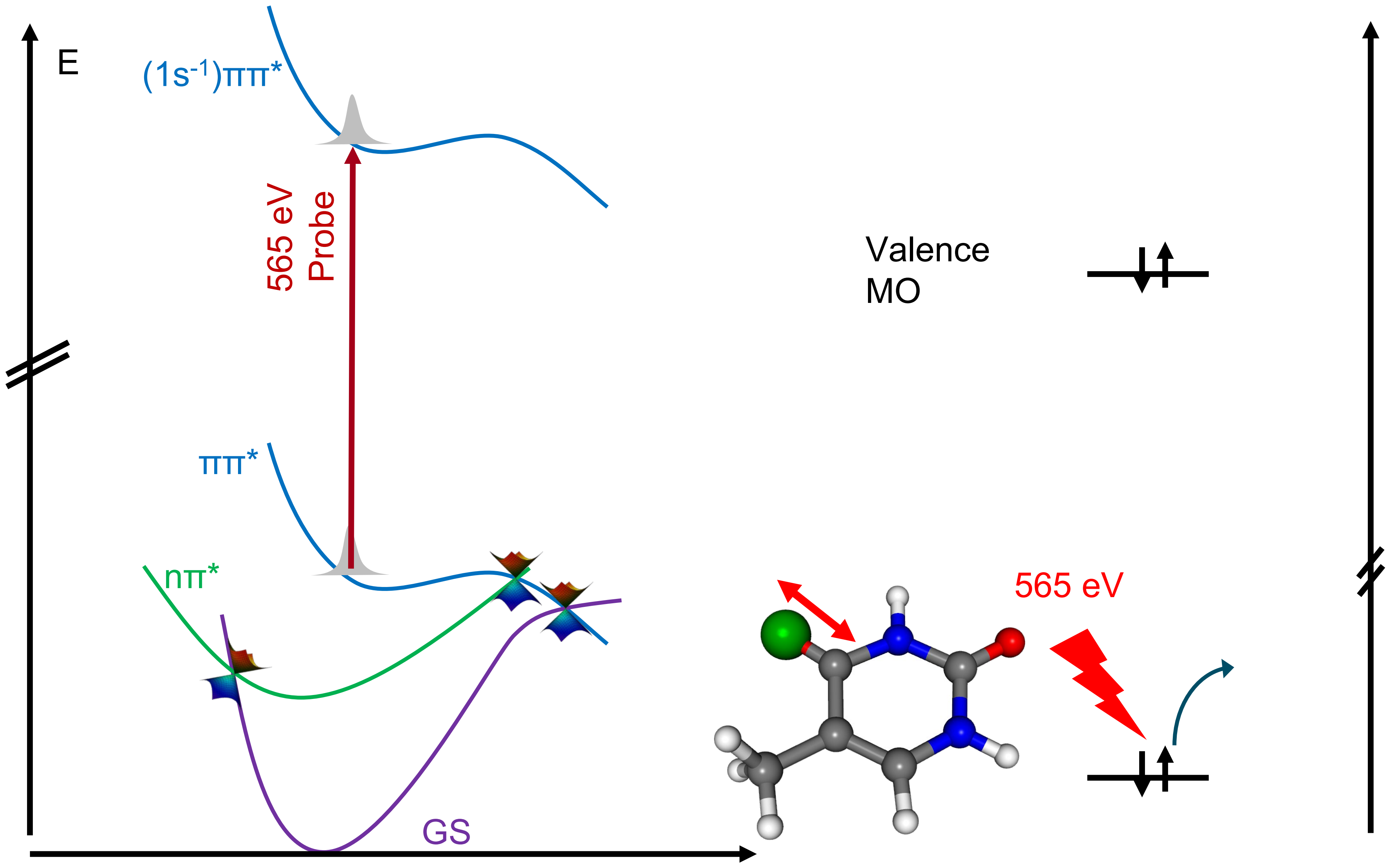


Courtesy of T. Wolf (SLAC)

Localized structural evolution:

Time-resolved Auger electron spectroscopy

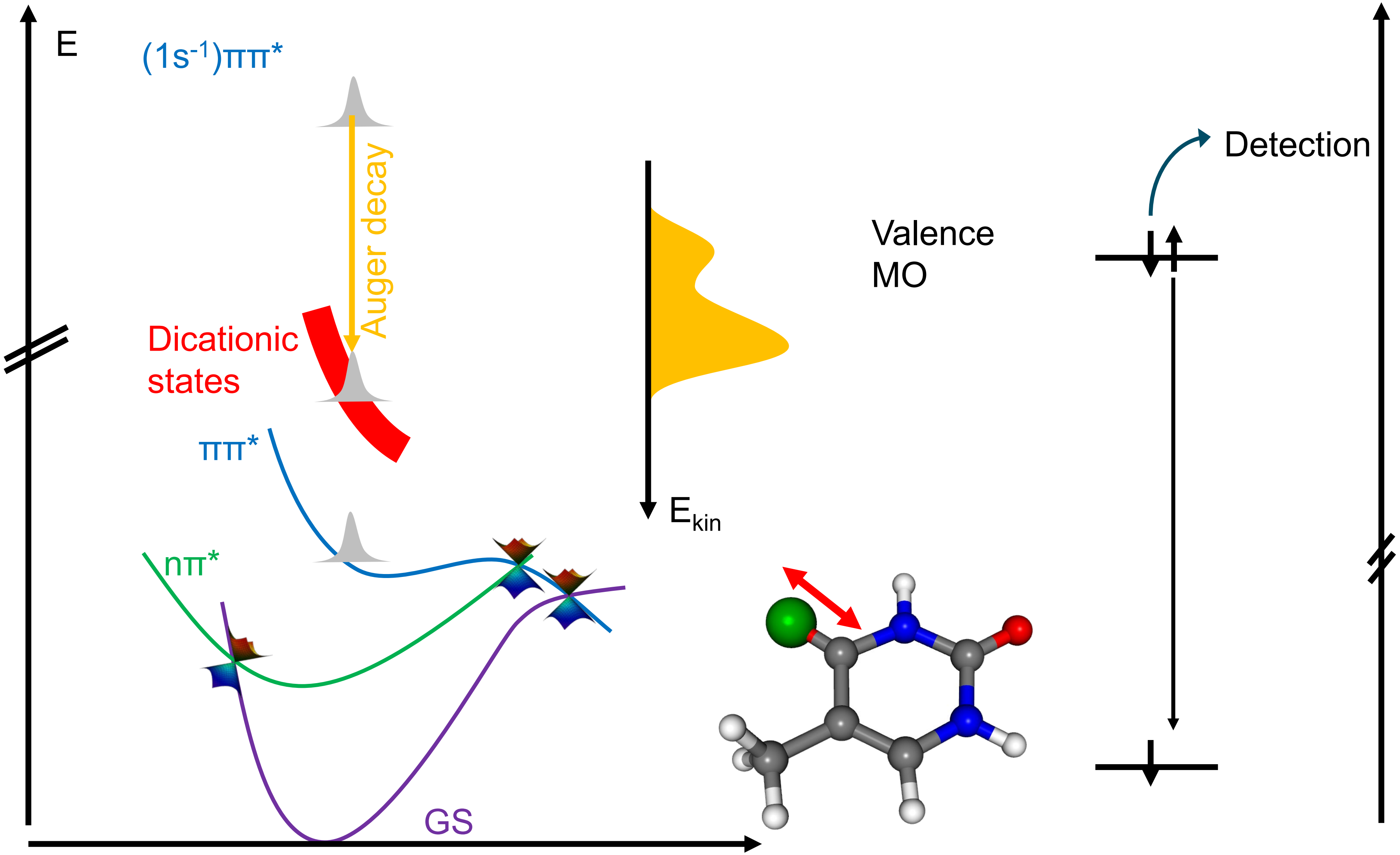
Courtesy of T. Wolf (SLAC)



Localized structural evolution:

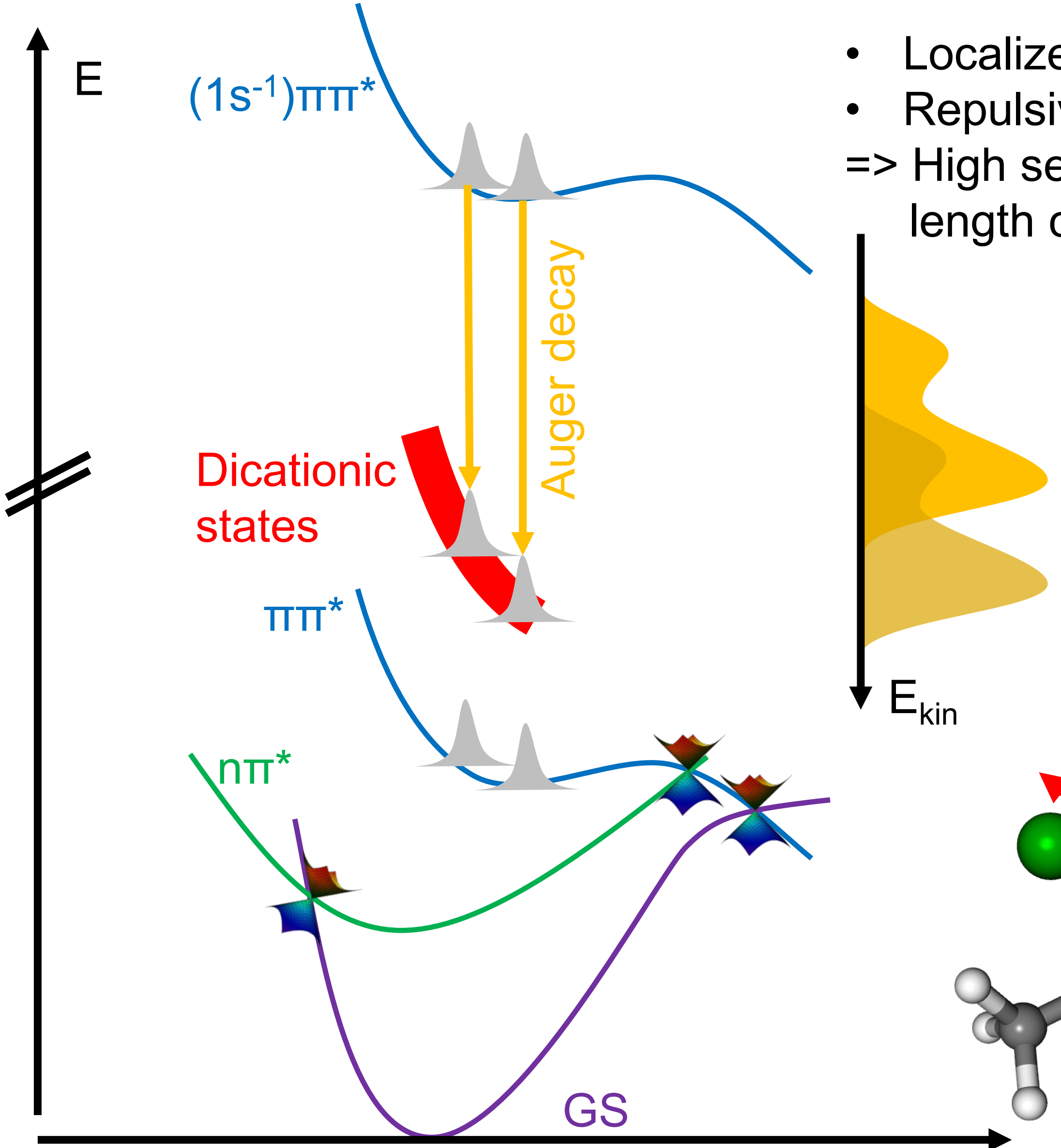
Time-resolved Auger electron spectroscopy

Courtesy of T. Wolf (SLAC)



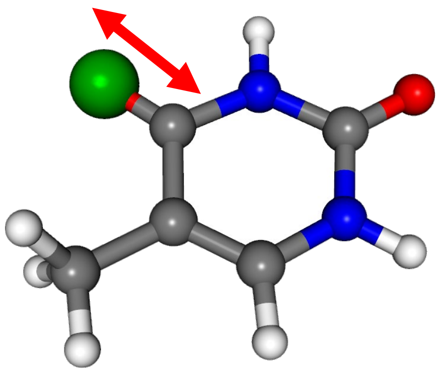
Localized structural evolution:

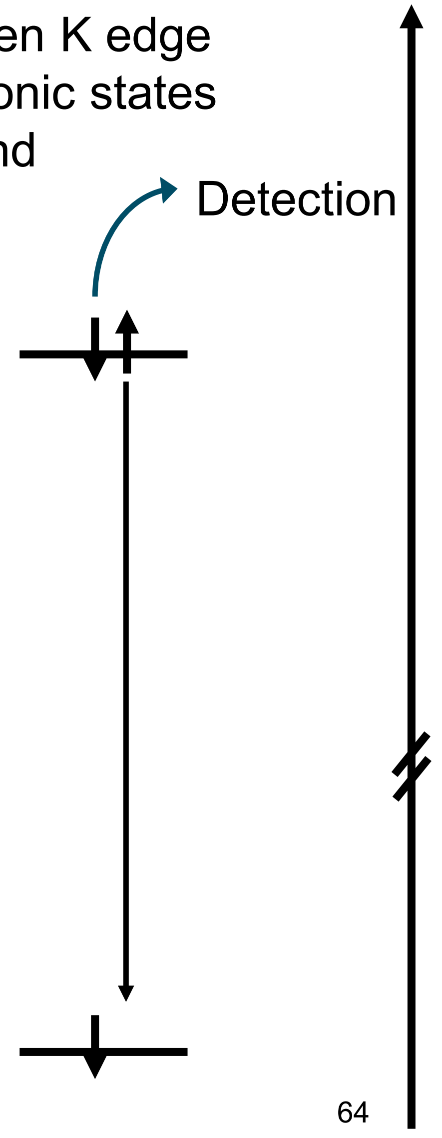
Courtesy of T. Wolf (SLAC)



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

=> High sensitivity to CO bond length change





Localized structural evolution: Time-resolved Auger electron spectroscopy

Courtesy of T. Wolf (SLAC)

- Localized probing at oxygen K edge
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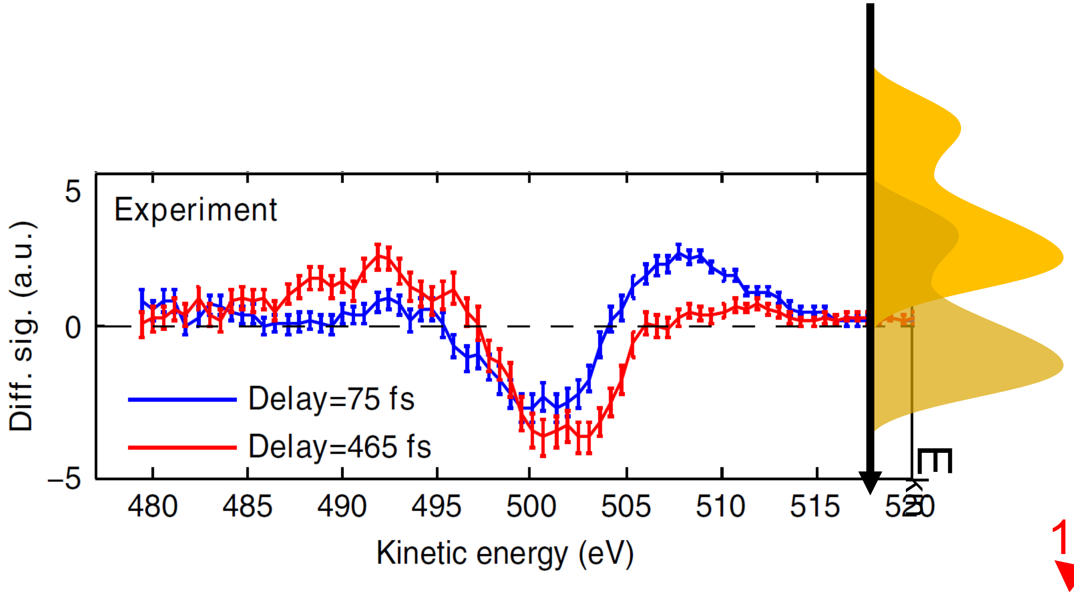
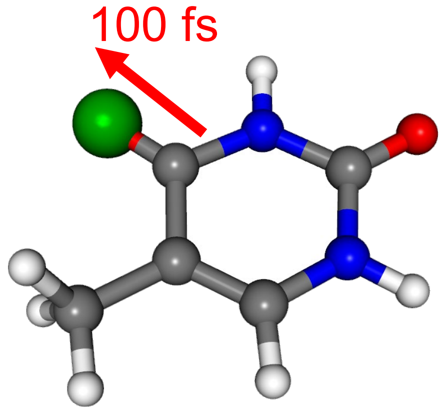
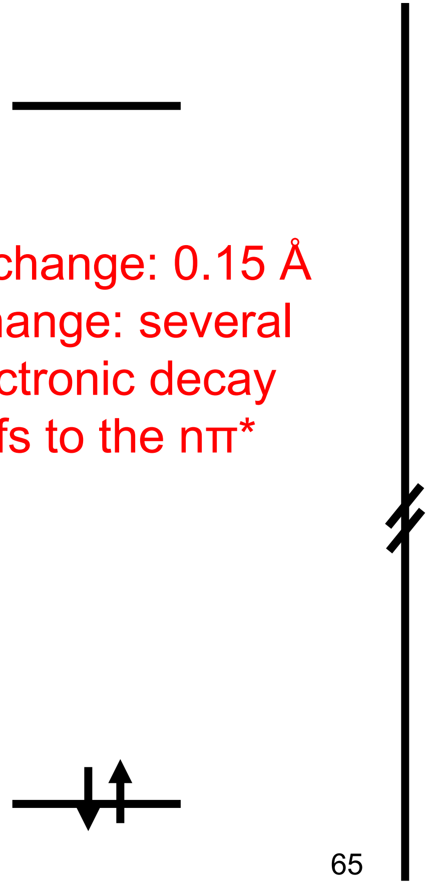


Valence MO

Geometry change: 0.15 Å
Spectral change: several eV and electronic decay within 200 fs to the nπ*





McFarland et al. *Nature Commun.* **2014**, *5*, 4235

Questions?

Rudek, B., Son, SK., Foucar, L. *et al.* Ultra-efficient ionization of heavy atoms by intense X-ray free-electron laser pulses. *Nature Photon* **6**, 858–865 (2012). https://doi.org/10.1038/nphoton.2012.261

Thank you!
Have fun with the further lectures!

And enjoy your projects@DESY!