Introduction to Photon Science

Part III: Examples of Science at Synchrotrons & FELs

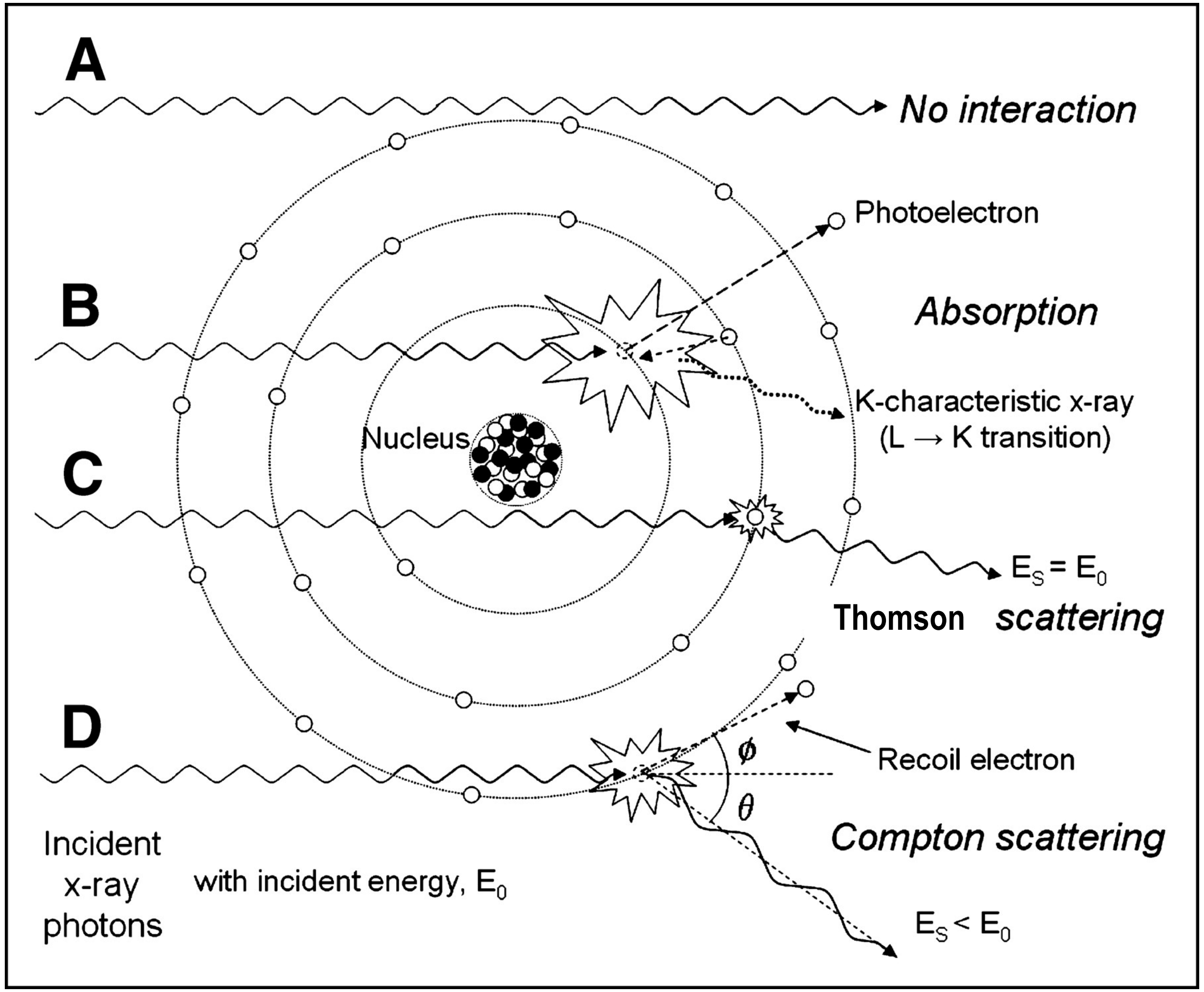
Summary

- 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)

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

X-ray – matter interaction



/ (or Auger electron)

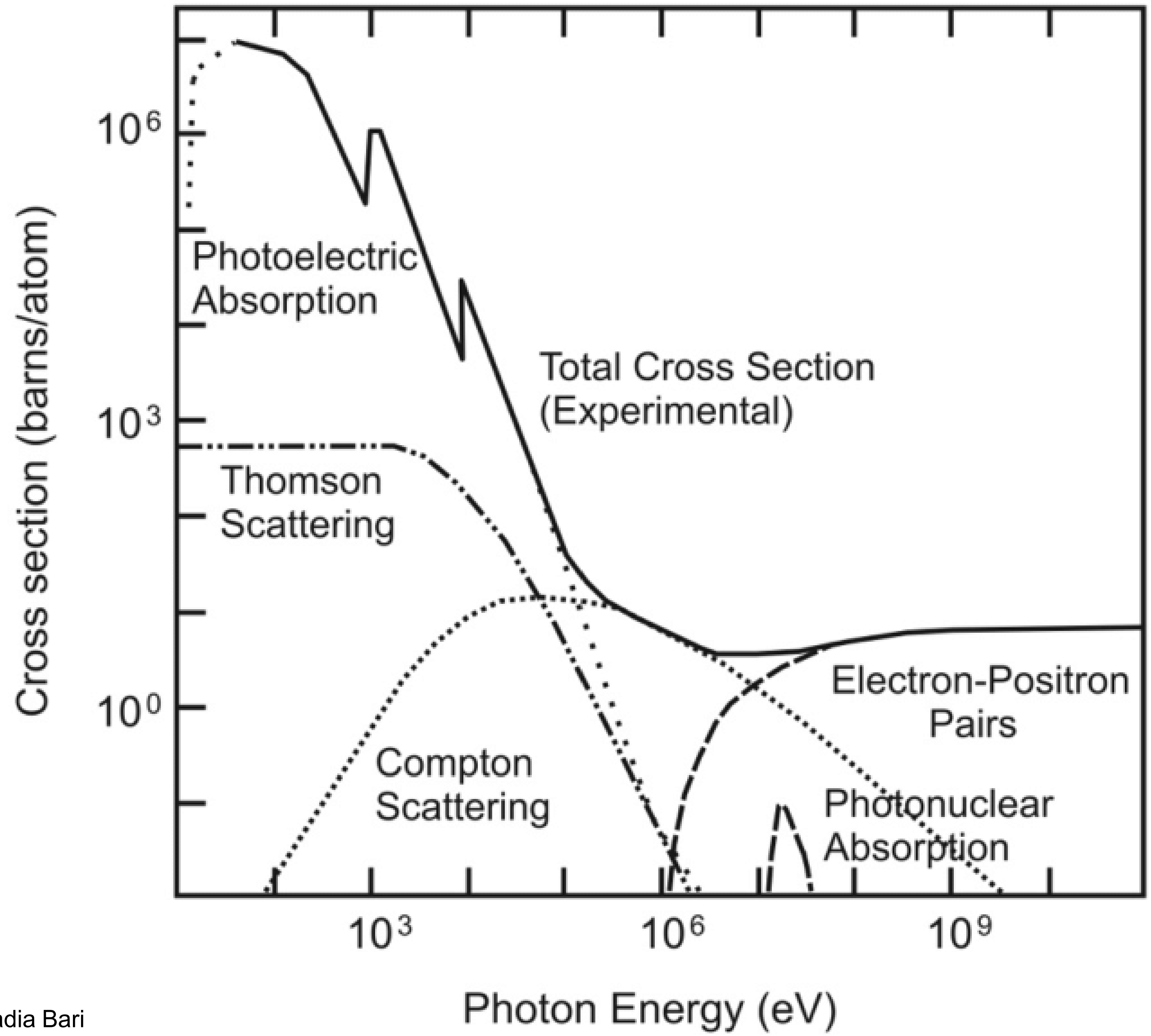
(Fluorescence)

(elastic)

(inelastic)

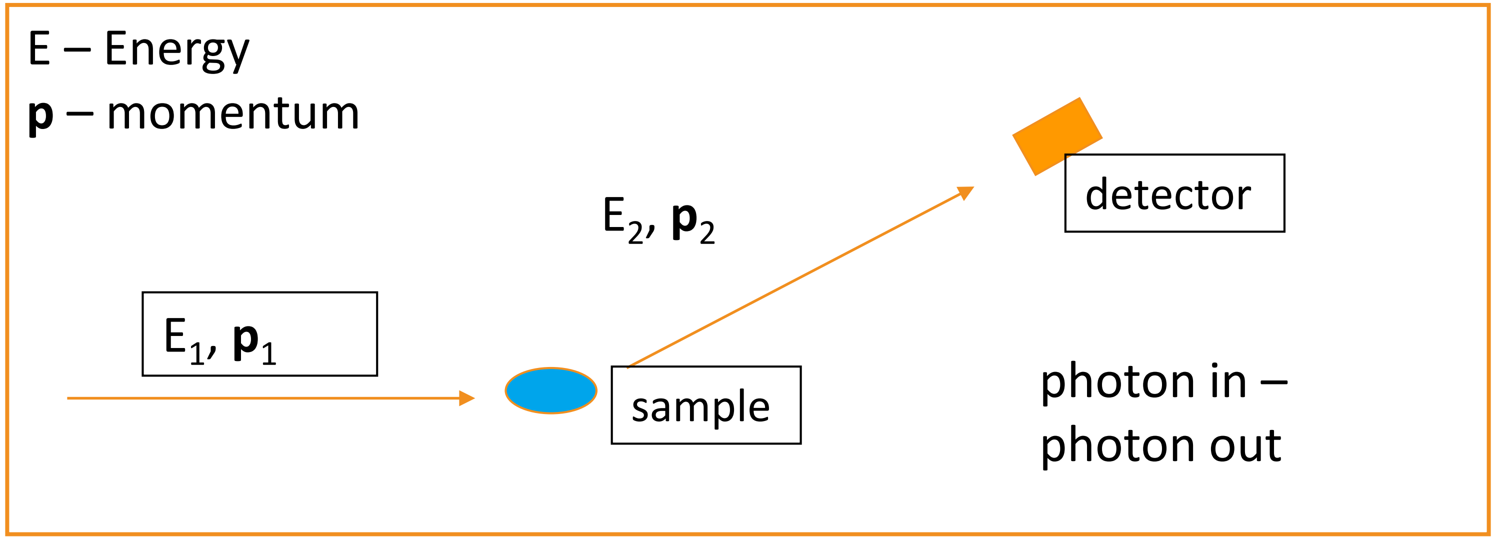
Illustrative summary of x-ray and γ-ray interactions. J. Anthony Seibert, and John M. Boone JNMT 2005;33:3-18

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 the photon facilities

Physics, Chemistry, Biology, Medicine

Scattering and diffraction

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

Imaging

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

Spectroscopy

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

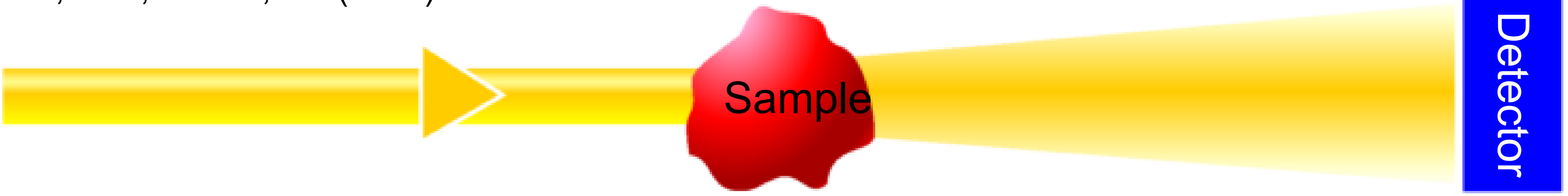
Weak signals
e.g. High collimation
e.g. Small samples
Tunable wavelength
Time structure

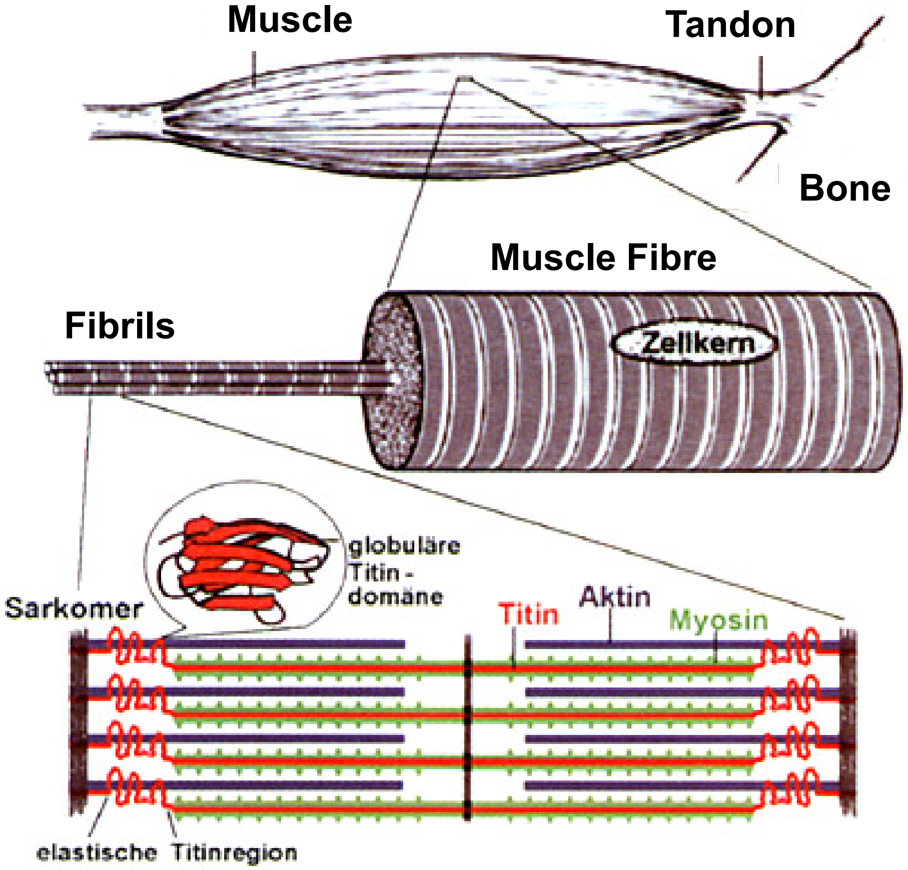
Experiments concentrate on experiments with small focus primary beams ($\mu m, nm$) and “photon hungry” experiments

First experiments using synchrotron radiation (1964 – 1975)

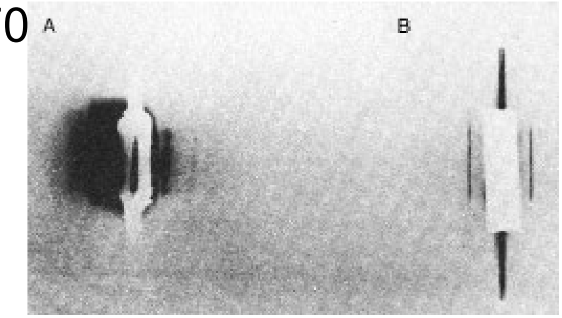
1970: Small angle X-ray scattering on muscle fibres

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

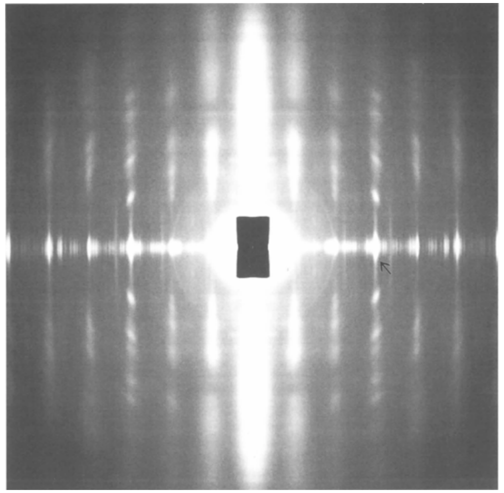




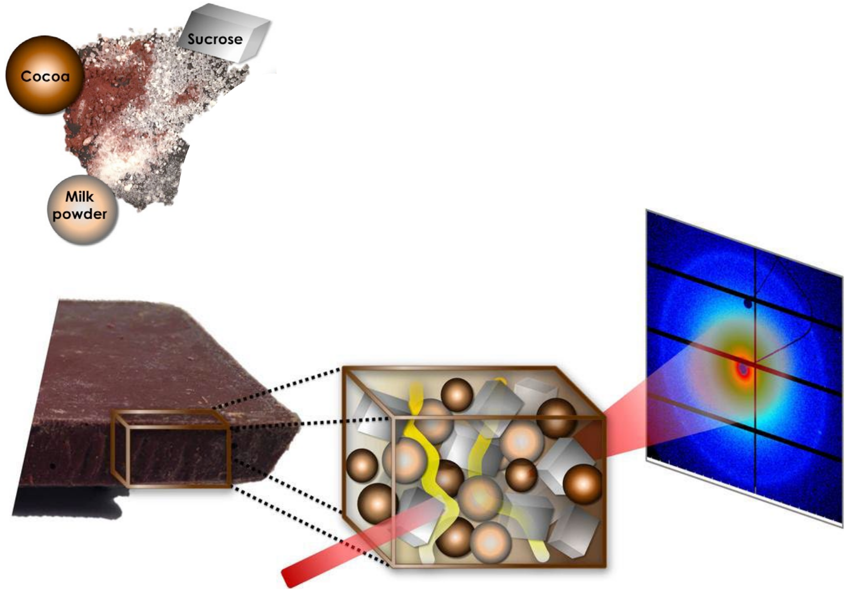
1970



1996

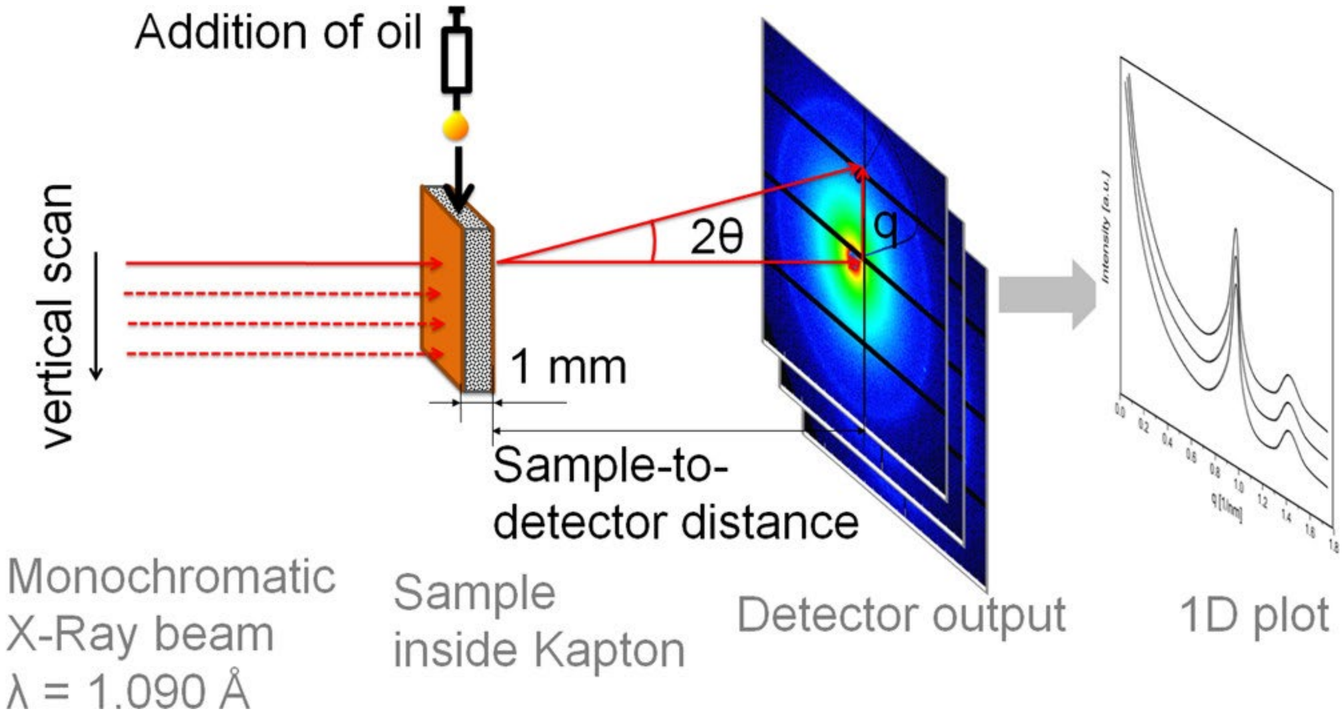


Study at PETRA III shows ways to reduce unwelcome fat bloom on chocolate



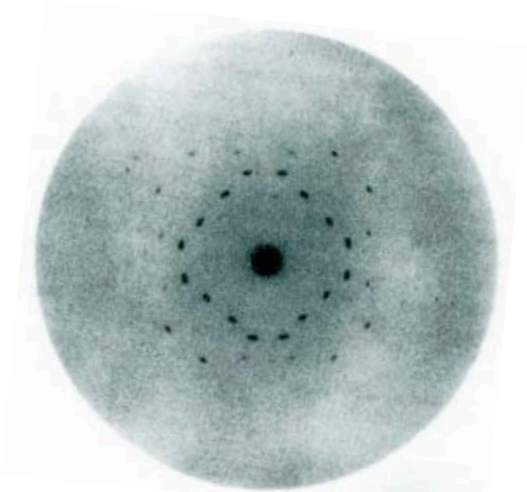
Credit: Svenja Reinke/TUHH

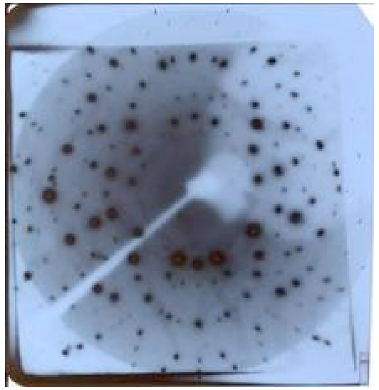
Small angle X-ray scattering



ACS Appl. Mater. Interfaces 2015, 7, 18, 9929-9936

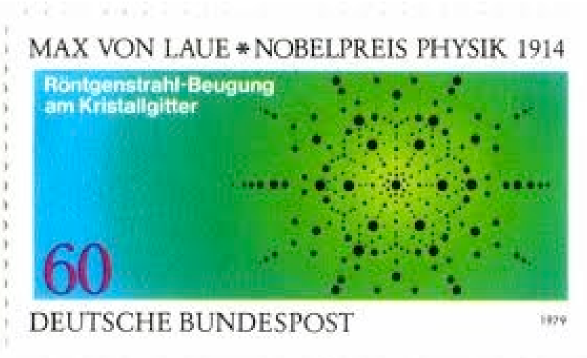
X-ray diffraction from crystalline structures

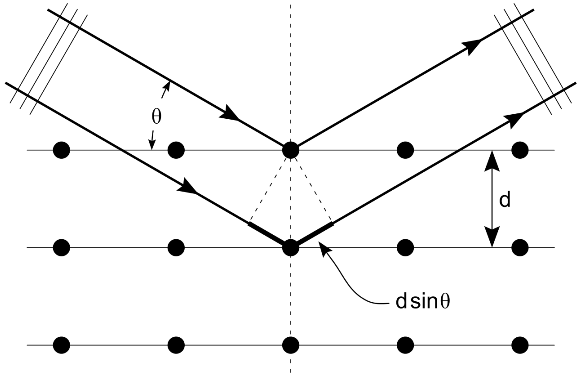




First diffraction patterns obtained by Max v. Laue in 1912 with X-ray tubes

Max von Laue
(1879 – 1960)

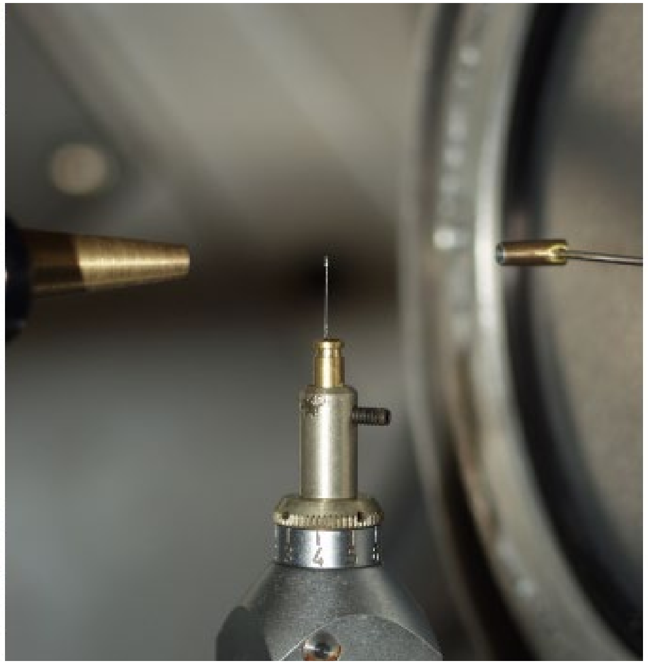




- Each scatterer re-radiate sperical waves
- Constructive interference if $n\lambda = 2d\,sin\,\theta$

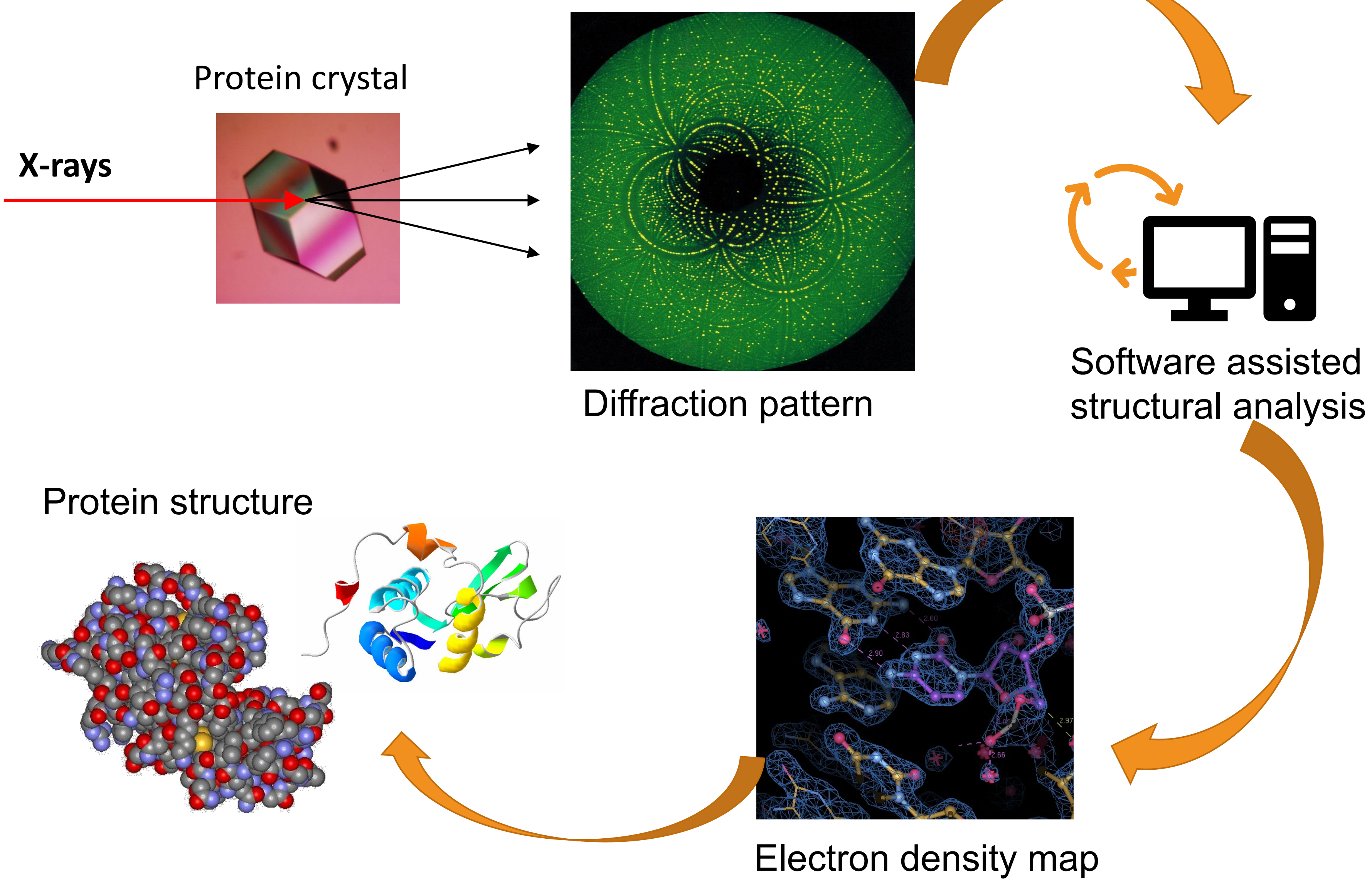
Protein crystallography

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

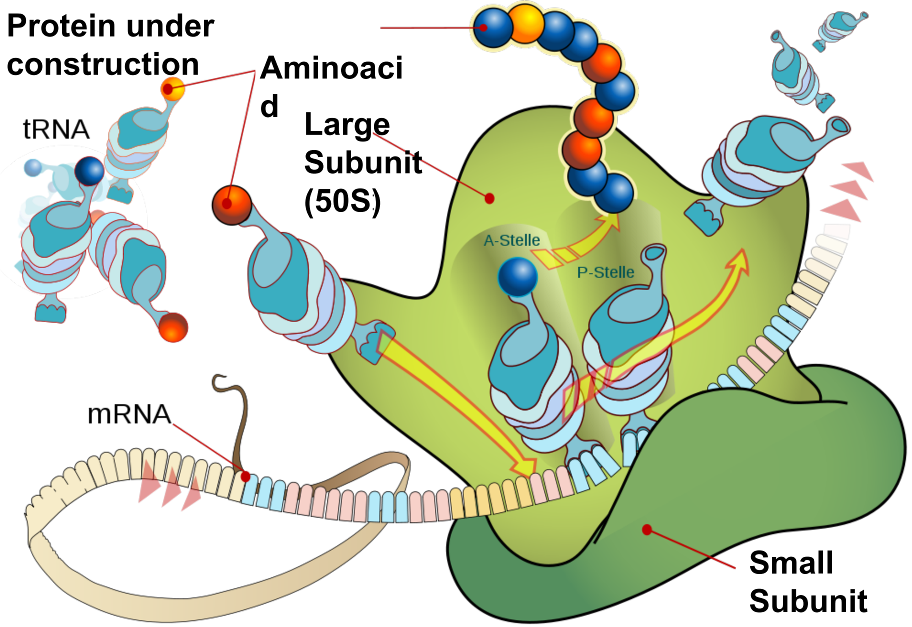


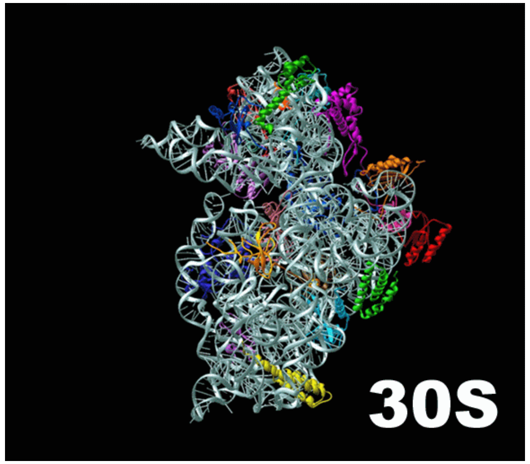
Structure determination of proteins

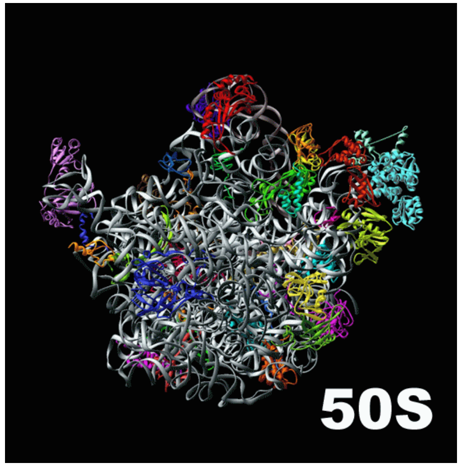
From diffraction pattern to 3D structure



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

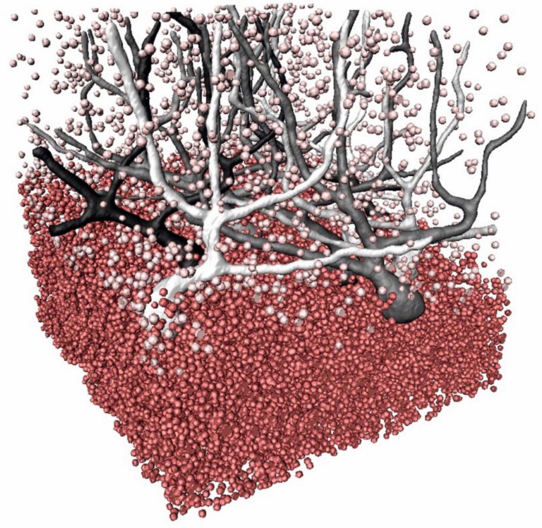
Corona research

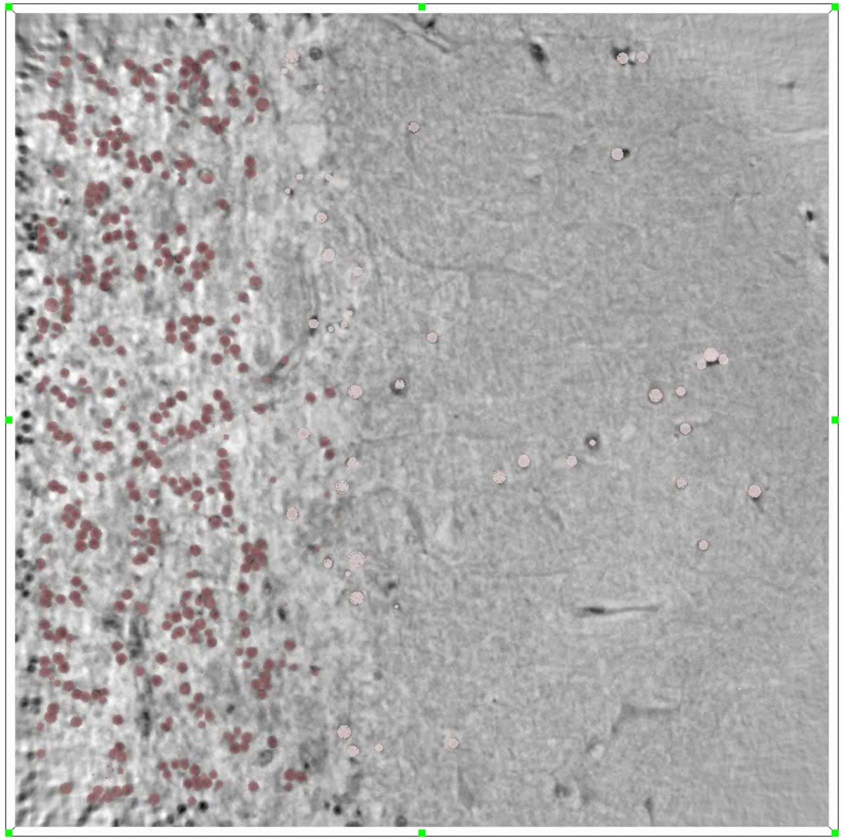
https://www.desy.de/news/corona_research/index_eng.html

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



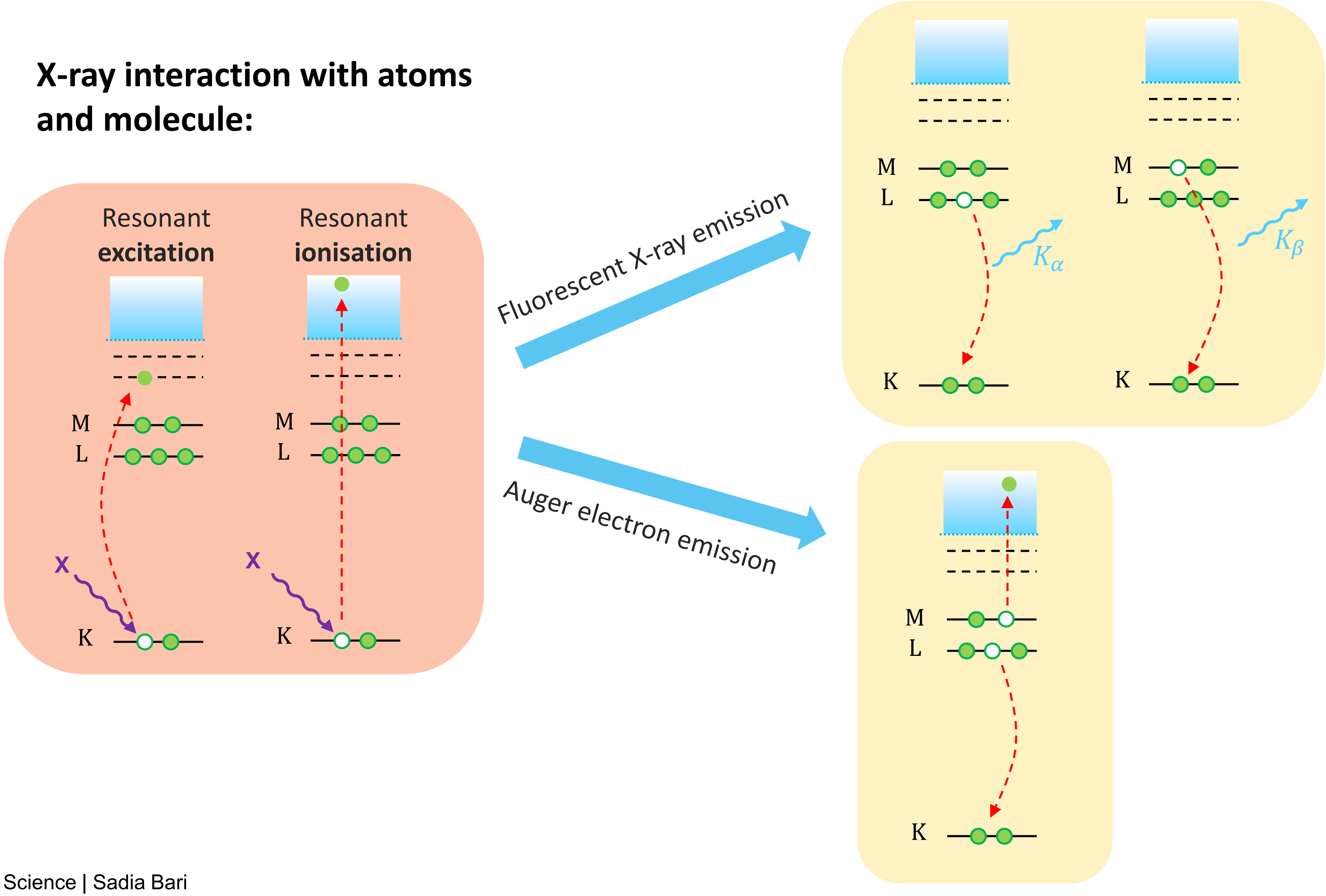


M. Töpperwien, F. van der Meer, C. Stadelmann, T. Salditt; „PNAS“, 2018

X-ray resonant core excitation spectroscopy

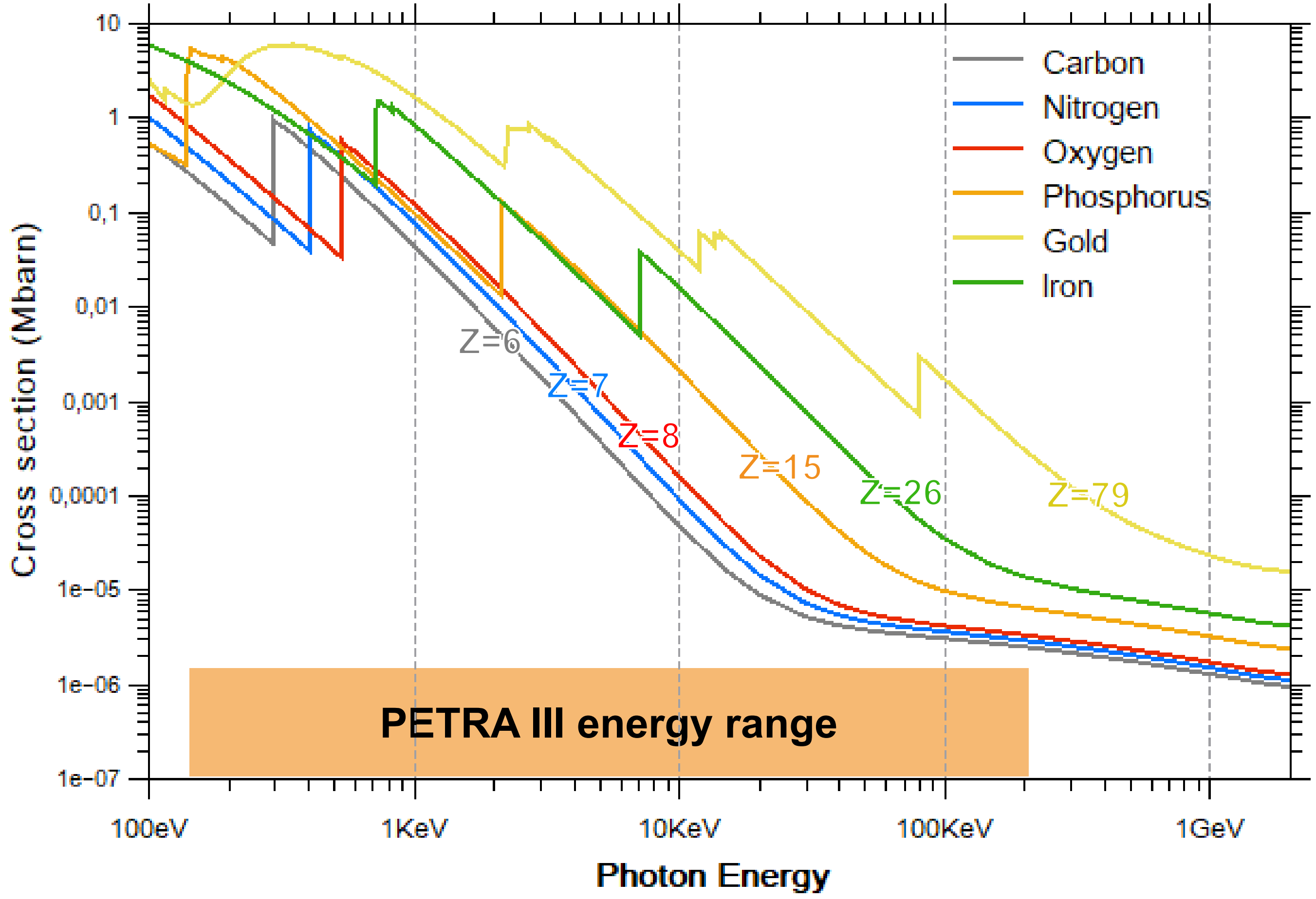
Probing the local environment with atomic resonances

X-ray interaction with atoms and molecule:



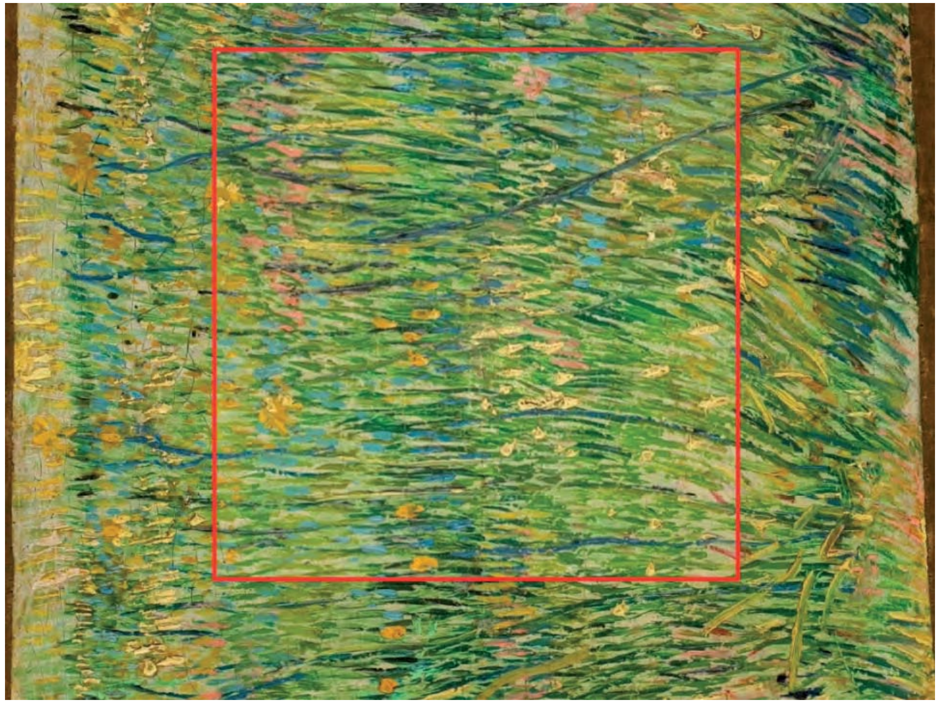
X-ray Absorption Spectroscopy

Atom specific



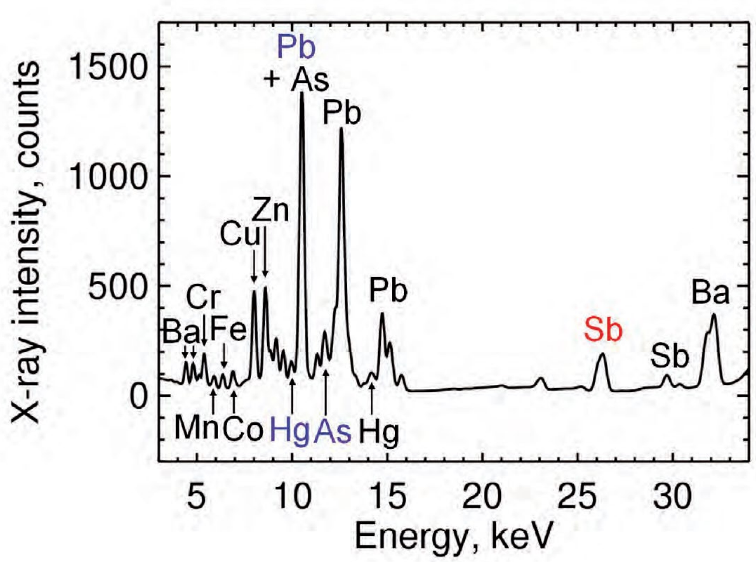
Raster scanning X-ray fluorescence

Vincent van Gogh: Meadow with flowers

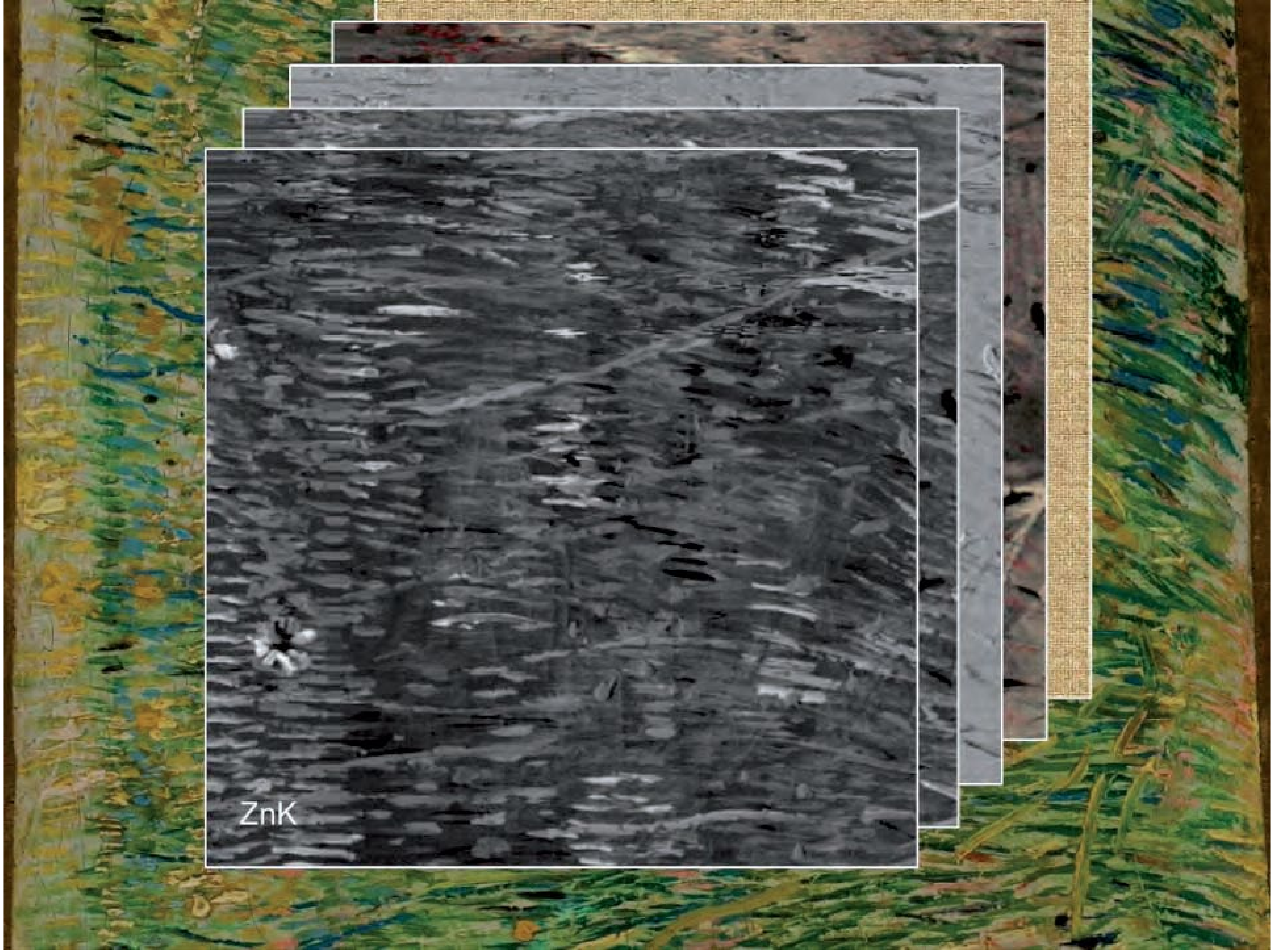


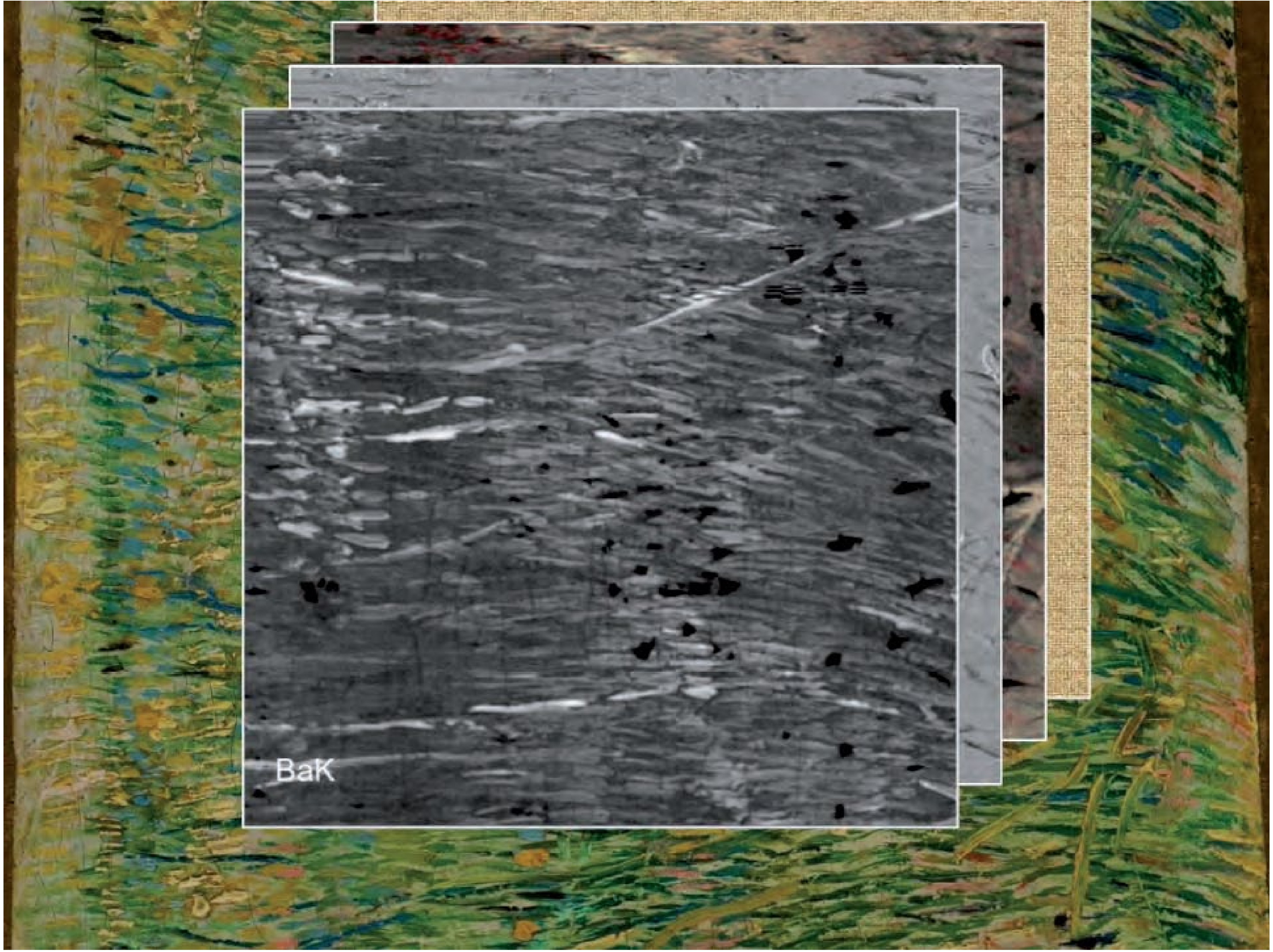
Raster scanning along 90000 pixels with 0.5 mm resolution

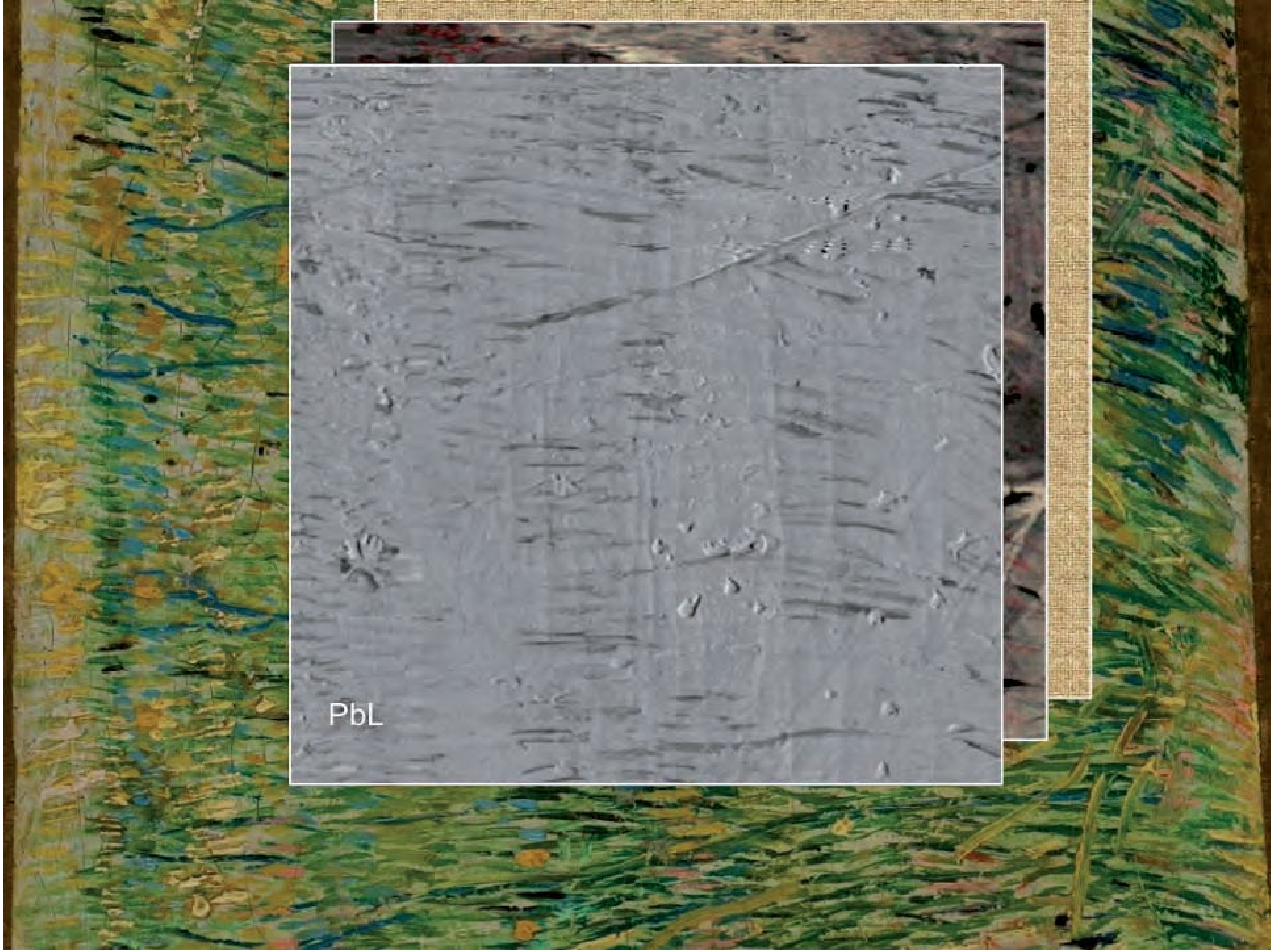
Typical fluorescence spectrum in a single pixel



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


ZnK


BaK


PbL


SbK + HgL

What else?

Journal of Radioanalytical and Nuclear Chemistry, Vol. 270, No.1 (2006) 167–171

Analysis of beers from Brazil with synchrotron radiation total reflection X-ray fluorescence

S. Moreira,[1]* A. E. S. Vives,[2] O. L. A. D. Zucchi,[3] E. F. O. de Jesus,[4] V. F. Nascimento Filho,[5] S. M. B. Brienza[2]

[1] *State University of Campinas, FEC/UNICAMP, P. O. Box 6021, 13083-852 Campinas, Brazil*
[2] *Methodist University of Piracicaba, FEAU/UNIMEP, Rodovia Sta.Bárbara/Iracemápolis km 1, 13450-000 Sta.Bárbara D'Oeste, Brazil*
[3] *University of São Paulo, FCFRP/USP, Avenida do Café s/n, 14040-903 Ribeirão Preto, Brazil*
[4] *Federal University of Rio de Janeiro, COPPE/UFRJ, P.O. Box 68501, 21945-970 Rio de Janeiro, Brazil*
[5] *University of São Paulo, CENA/USP, P.O. Box 96, 13400-970 Piracicaba, Brazil*

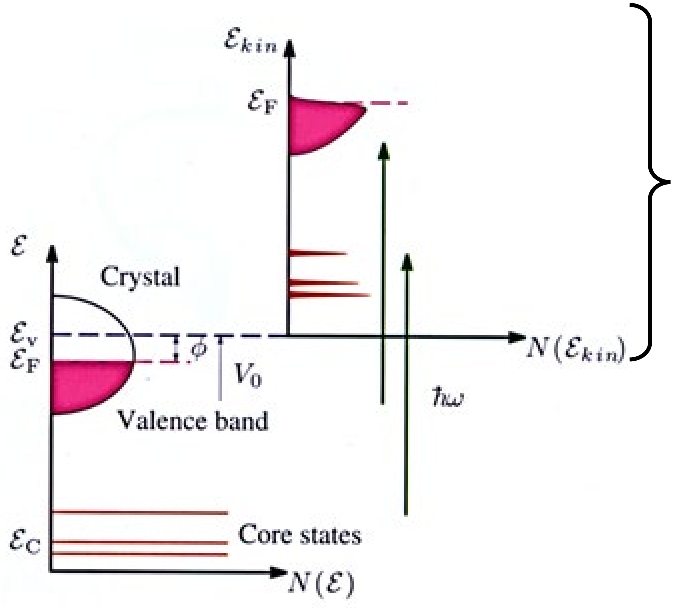
(Received April 6, 2006)

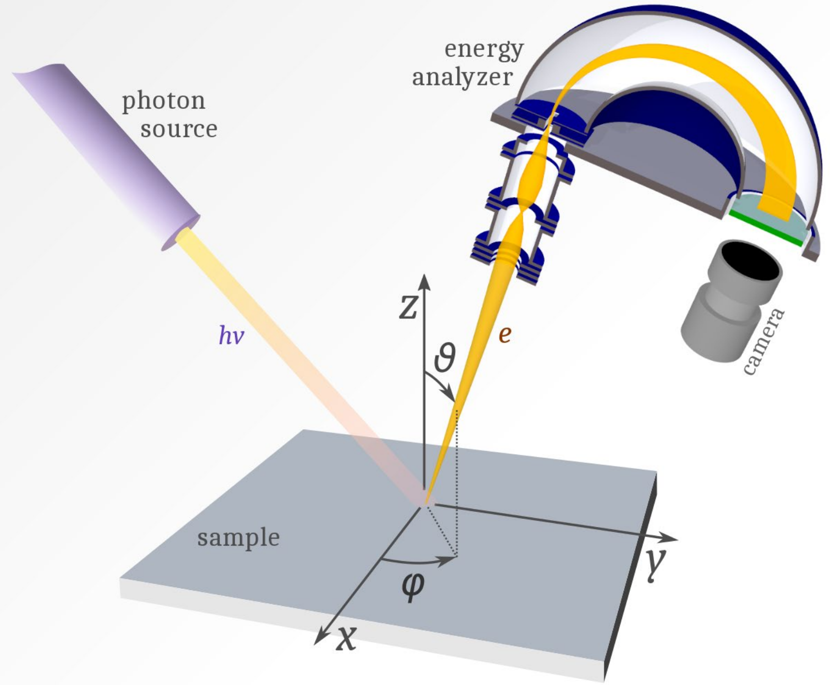
In this study the concentrations of P, S, Cl, K, Ca, Mn, Fe, Zn and Br in twenty-nine brands of national and international beers were determined by synchrotron radiation total reflection X-ray fluorescence analysis (SR-TXRF). The results were compared with the limits established by the

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

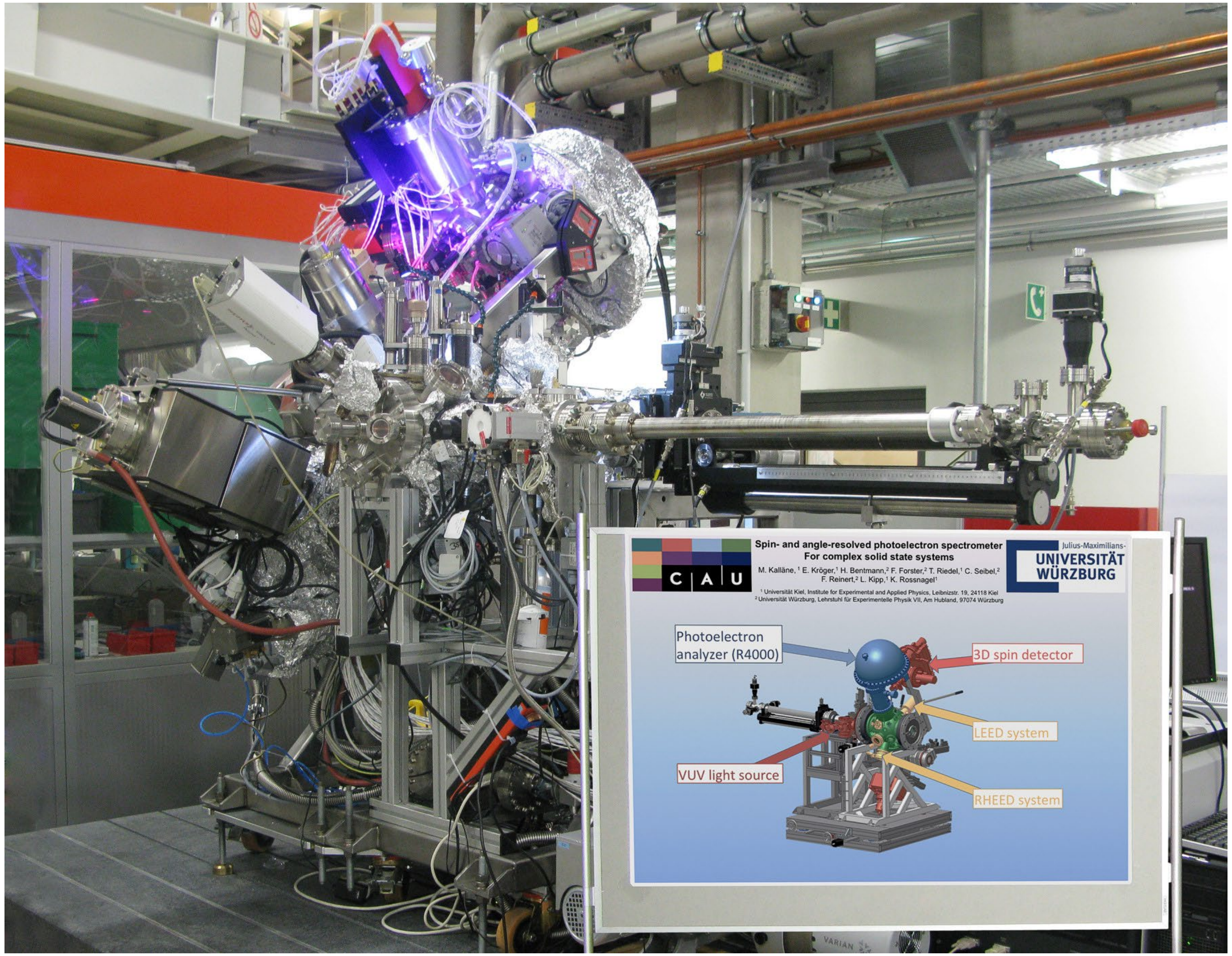




https://commons.wikimedia.org/w/index.php?curid=90955767

Photoelectron Spectroscopy

Angle-resolved photoemission spectroscopy (ARPES):



X-ray Photoelectron Spectroscopy

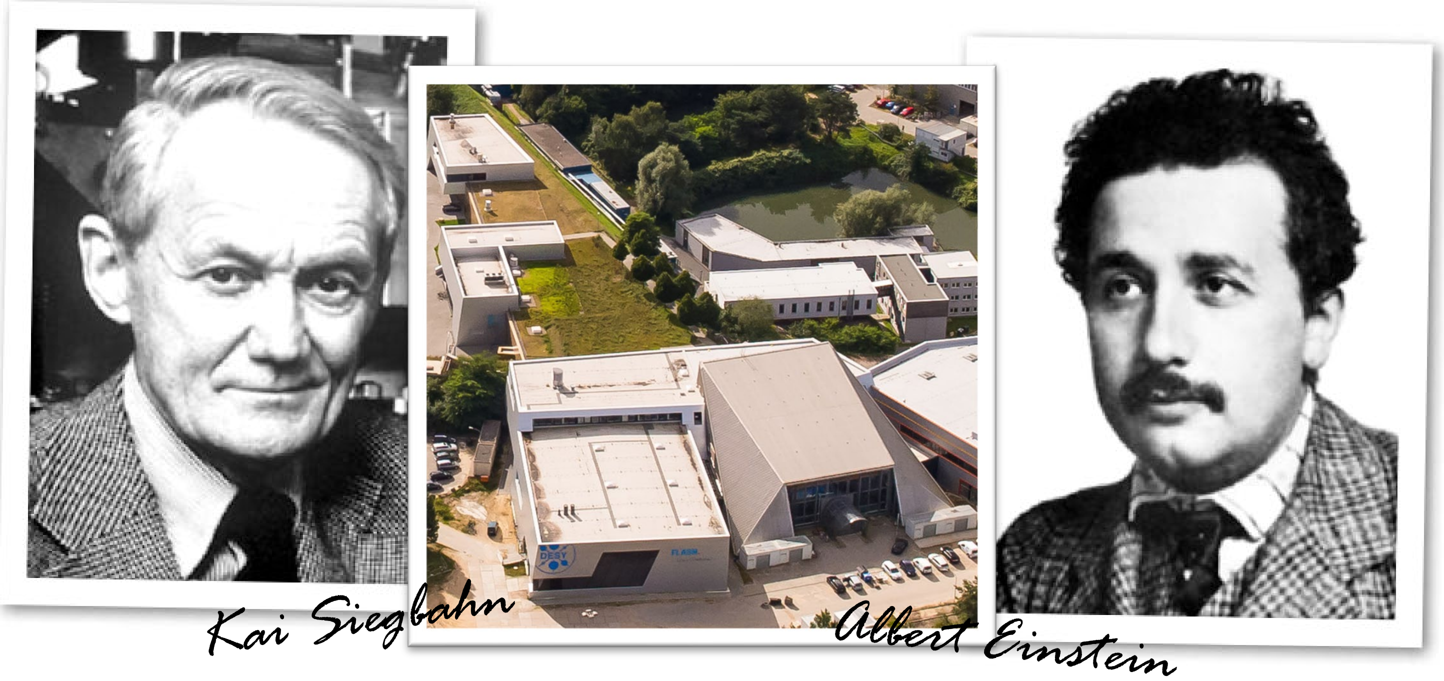
Angle-resolved photoemission spectroscopy (ARPES):

- **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

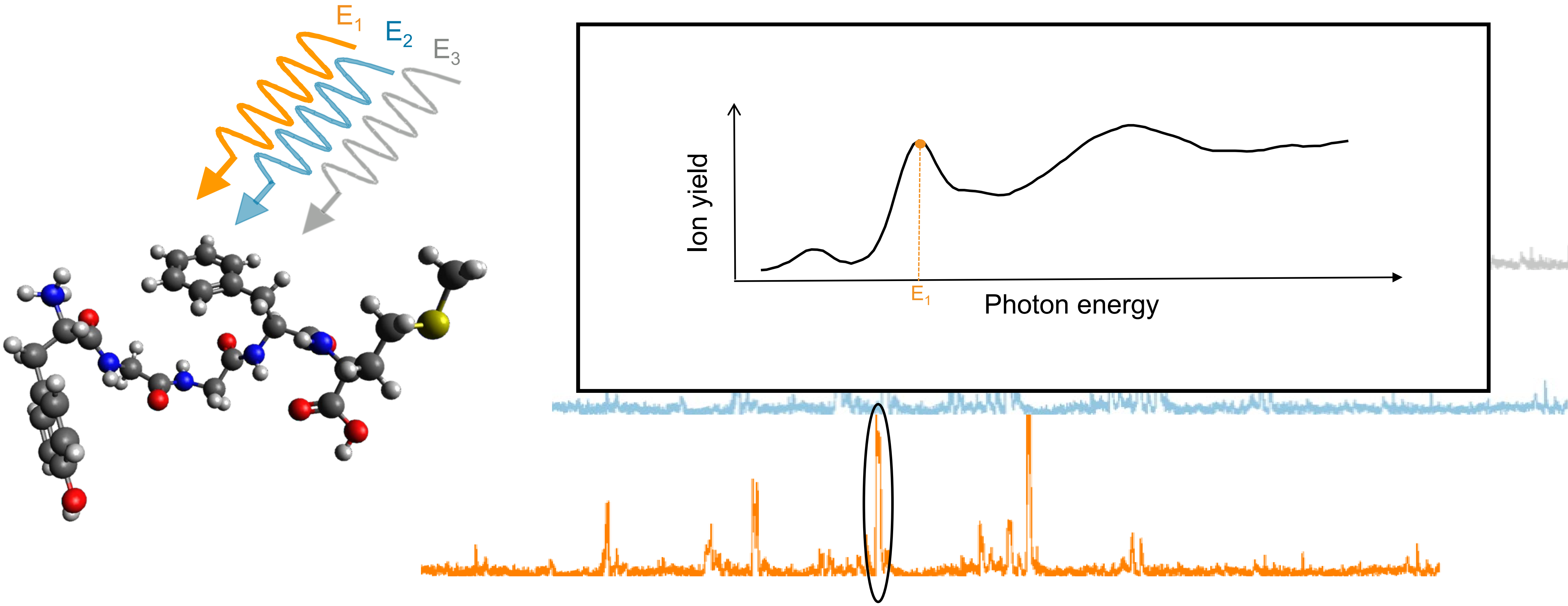
When photons or electrons cannot be measured

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

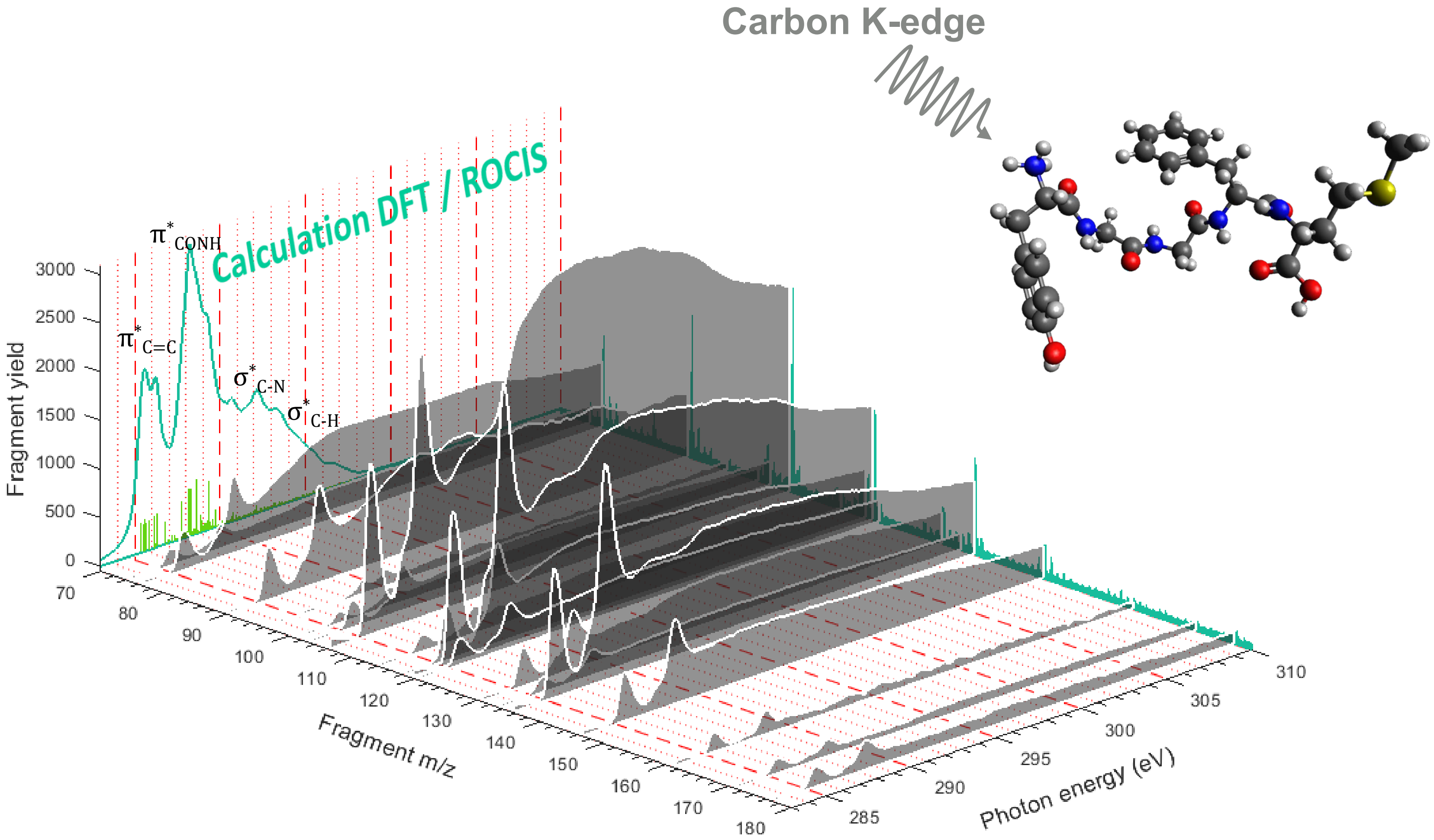
Photo-ionization → Ions can be manipulate in electric fields

Action spectroscopy



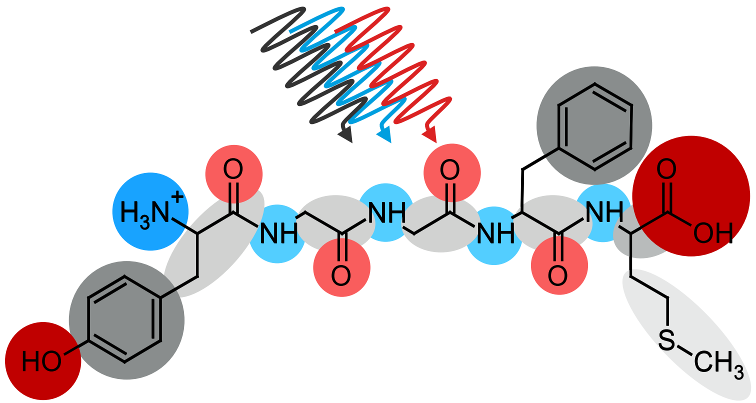
X-ray Action Spectroscopy

Near Edge X-ray Absorption Mass Spectrometry (NEXAMS)

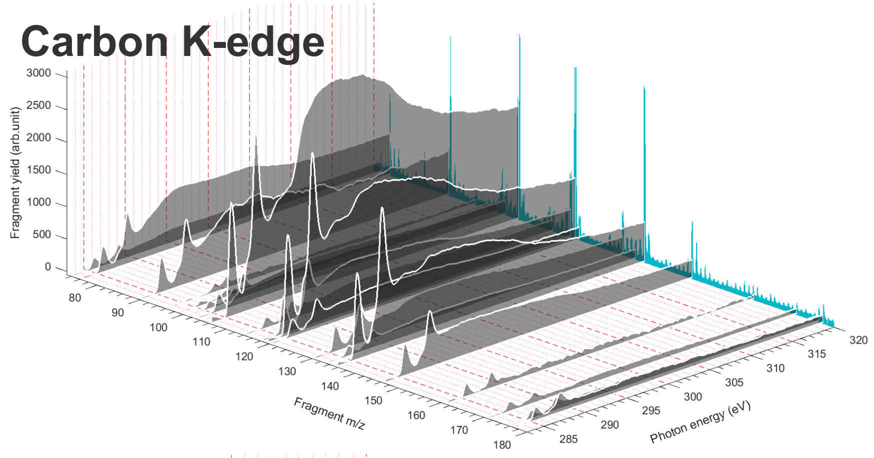


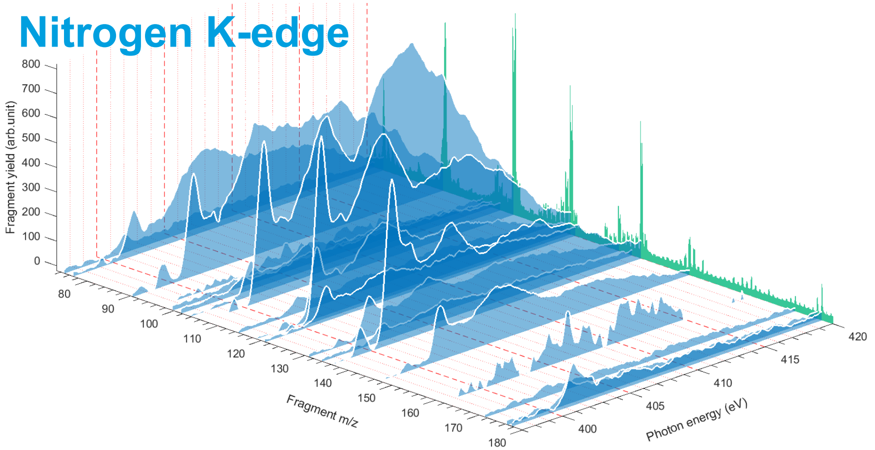
NEXAMS

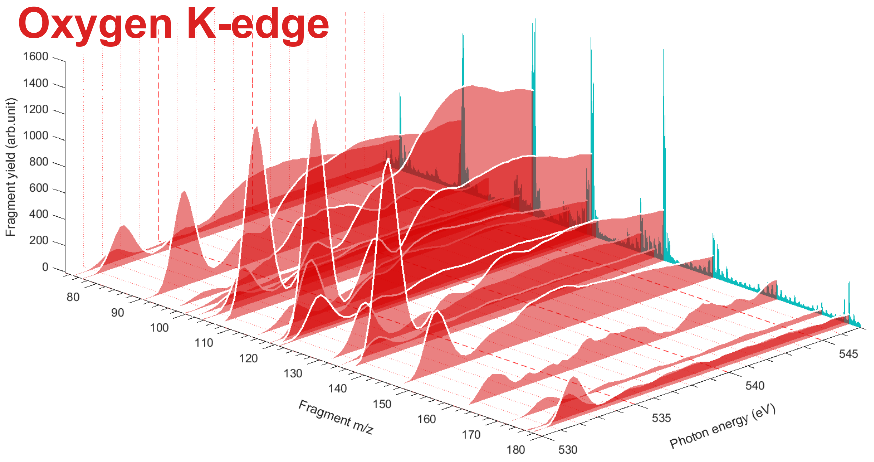
at the C, N, and O K edges



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







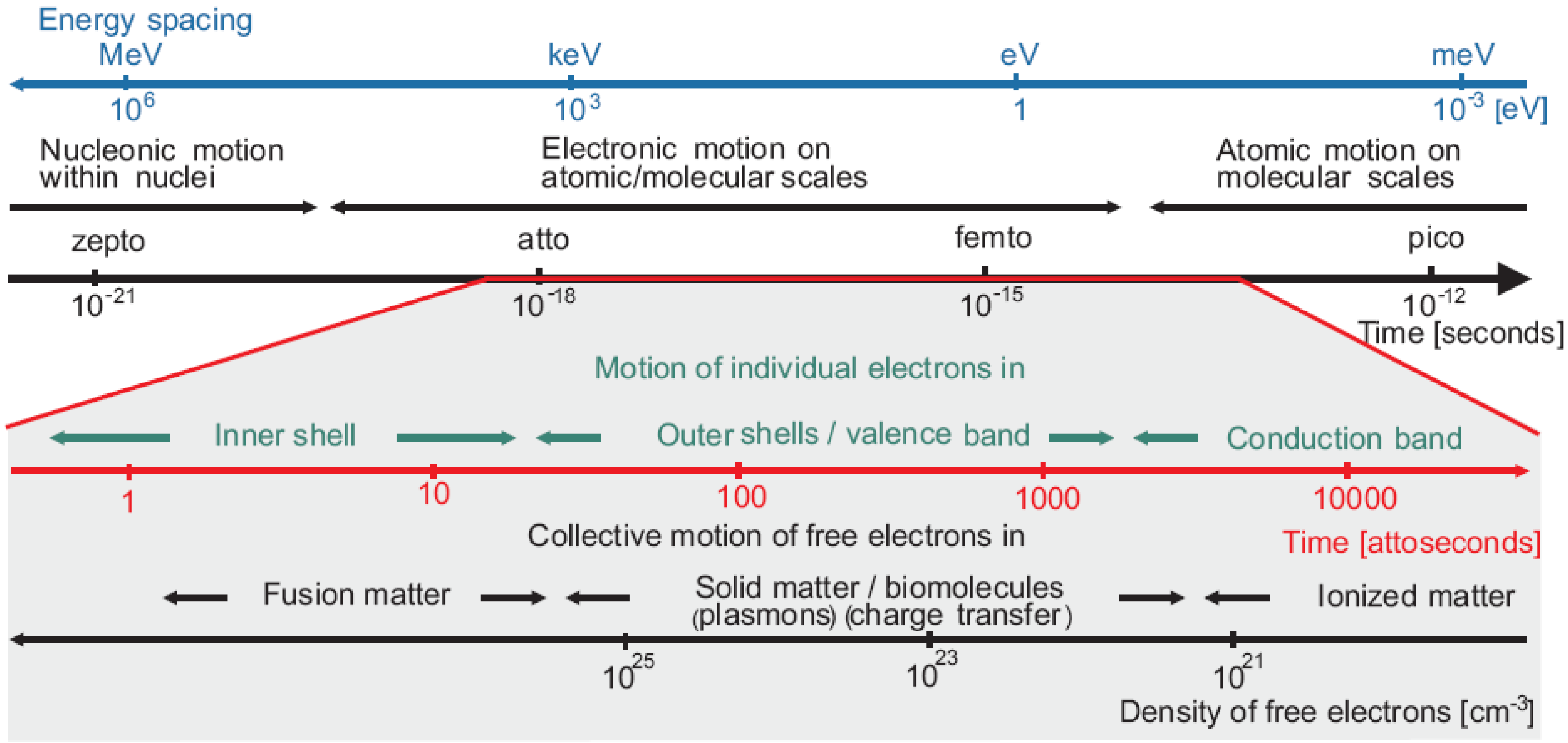
S. Dörner *et* al., J. *Am. Soc. Mass Spectrom.* **32**, 670 (2021).

Experiments with FELs

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

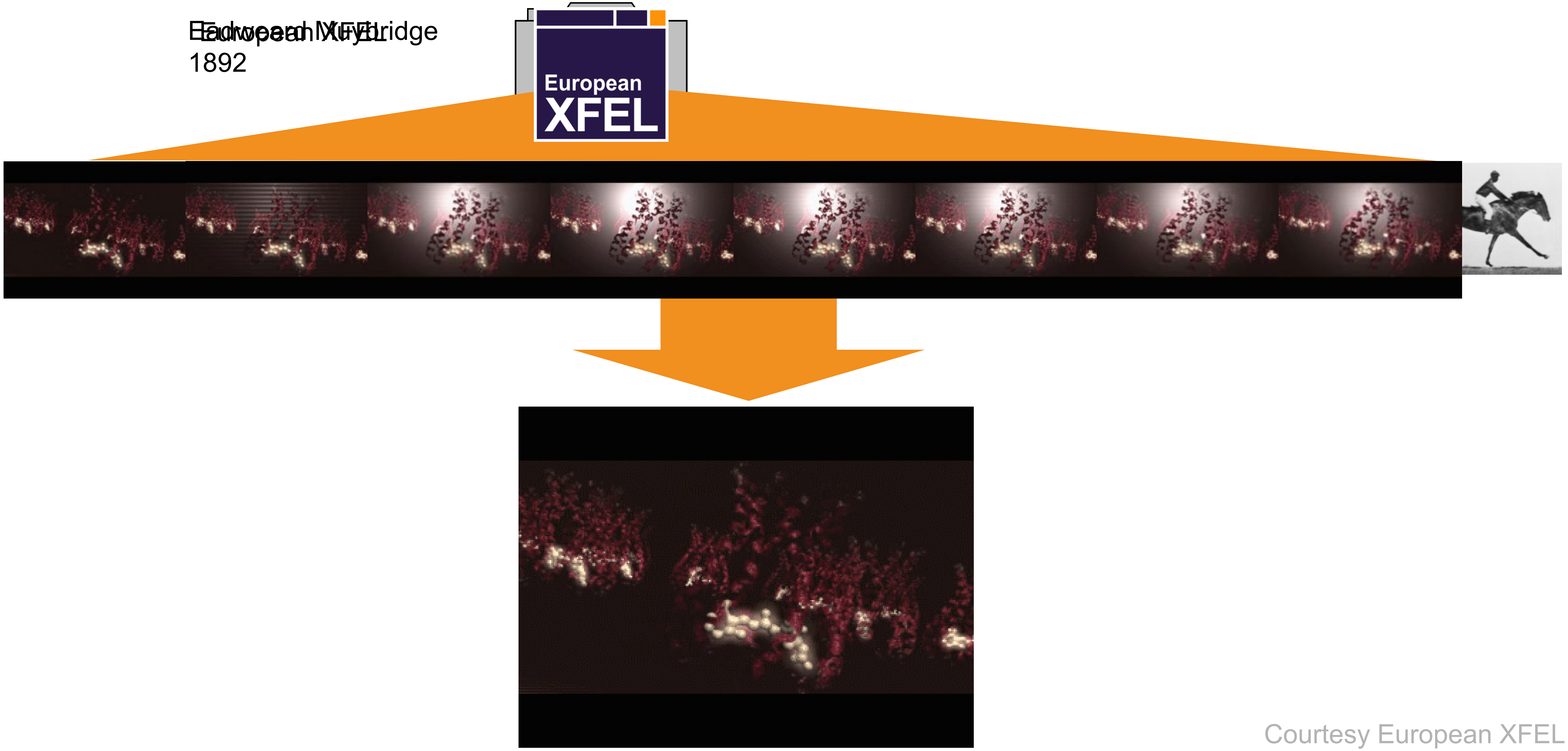
Time scales



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

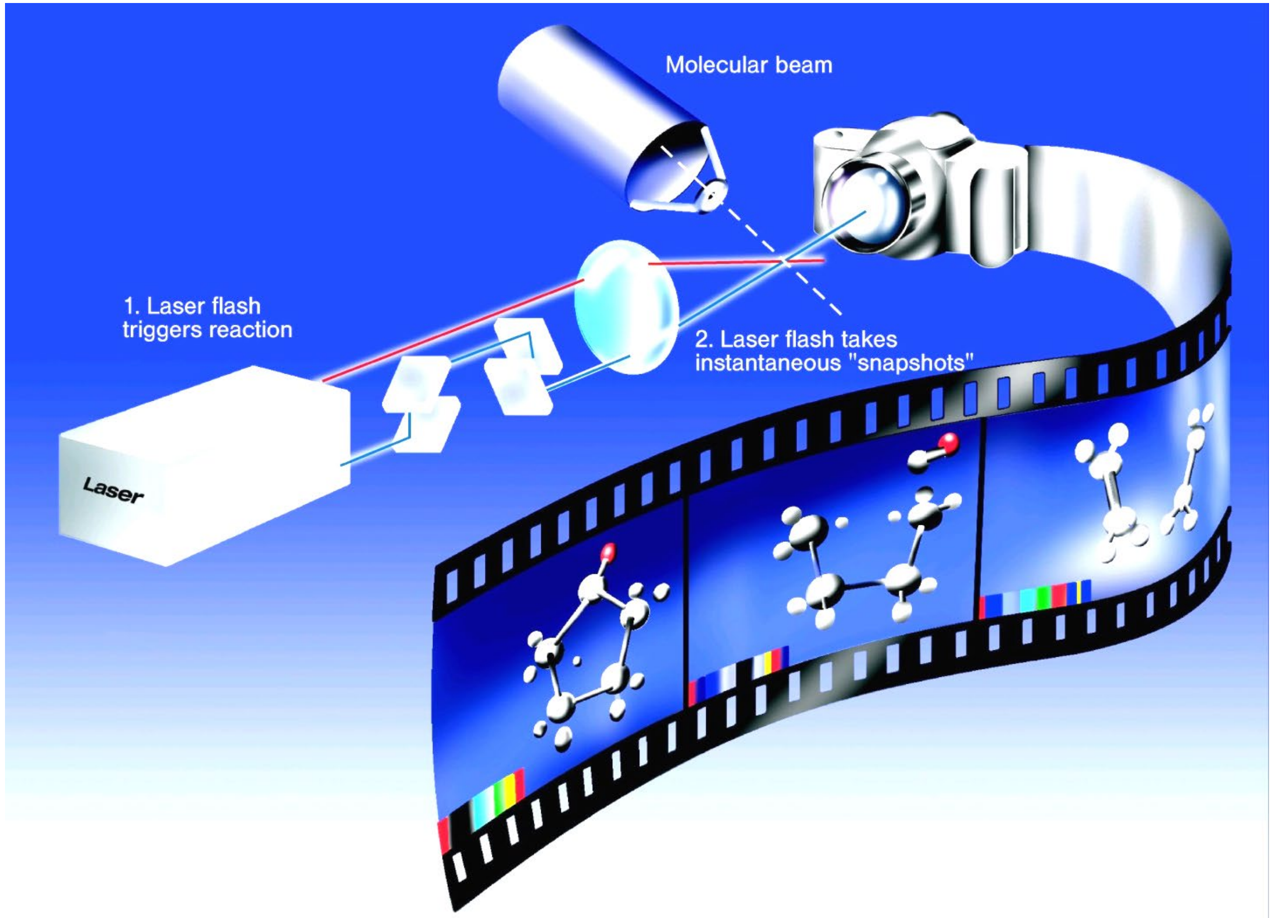
Making molecular movies

Eadweard Muybridge
European XFEL
1892



Courtesy European XFEL

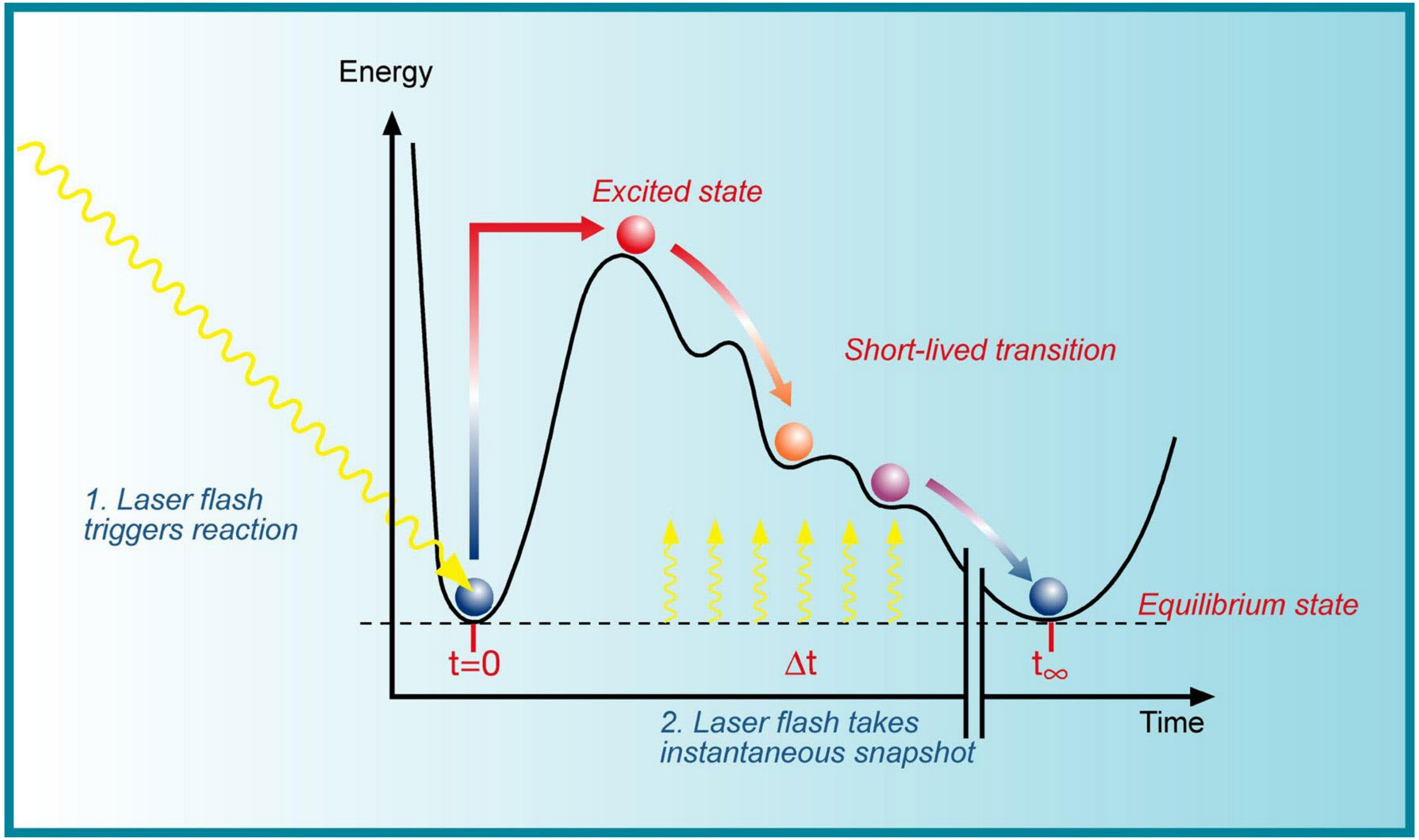
The ultimate goal: recording the “molecular movie”



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

→ “motion picture” of the reaction

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

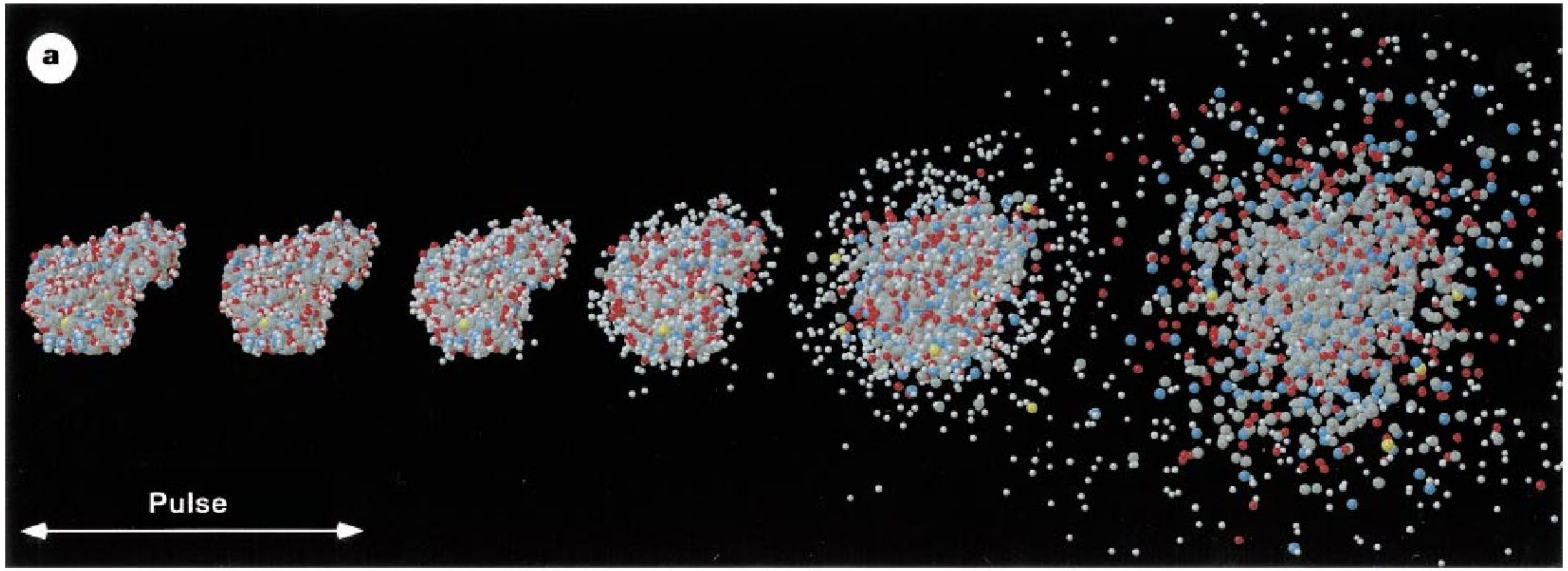
Richard Neutze*, Remco Wouts*, David van der Spoel*, Edgar Weckert†‡ & Janos Hajdu*

* *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)

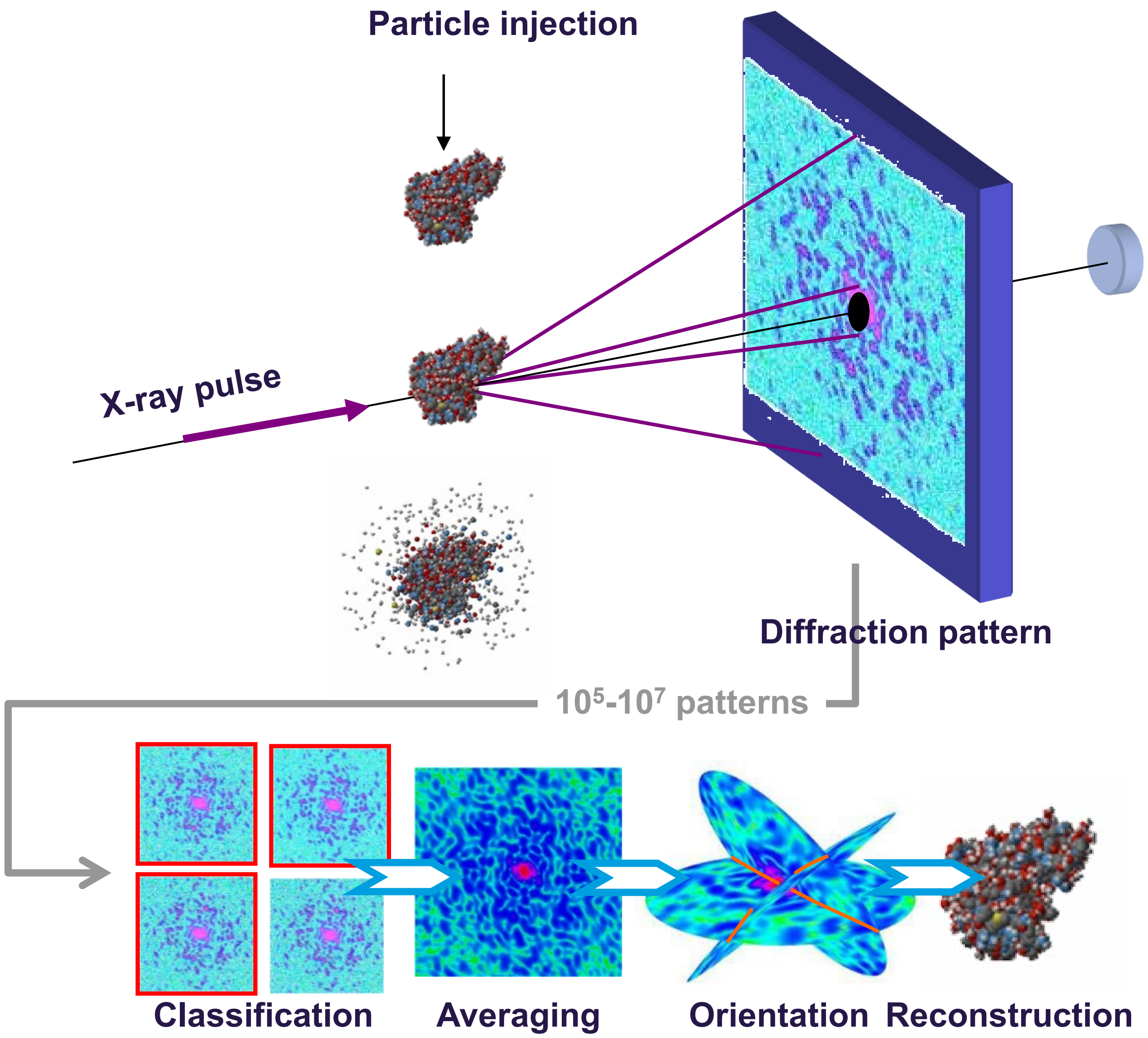
‘diffract before destroy’
(it works !)

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



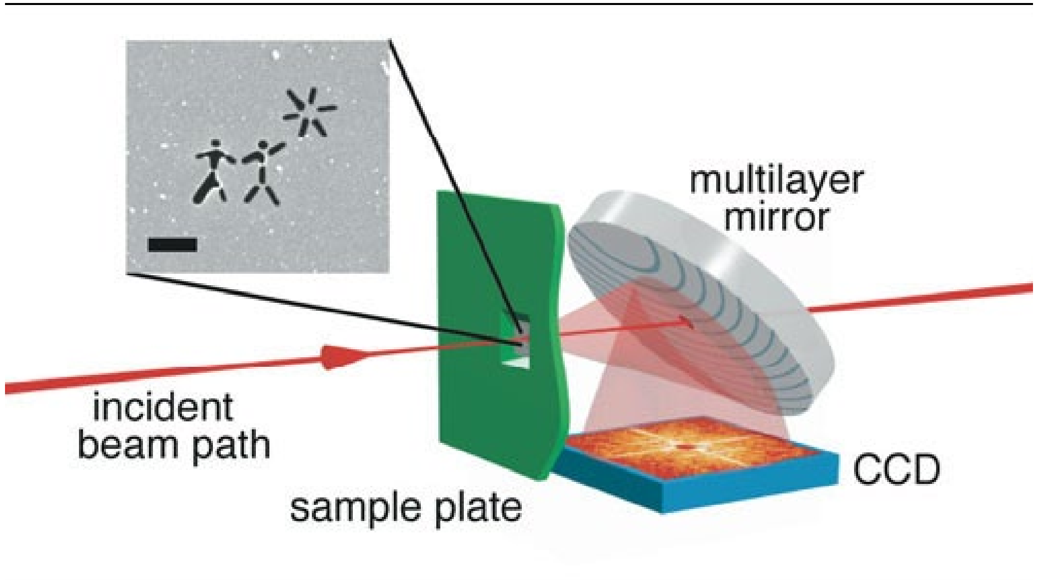
t=–2fs *t*=2fs *t*=5fs *t*=10fs *t*=–20fs *t*=50fs

Determine the structure of bio-particles

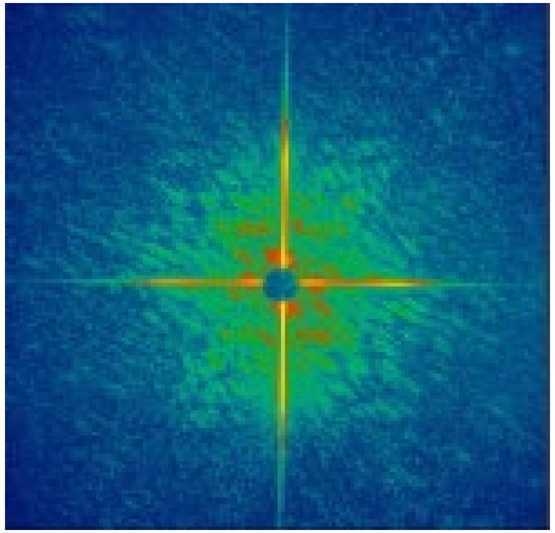


First demonstration of ultrafast coherent X-ray diffraction at FLASH

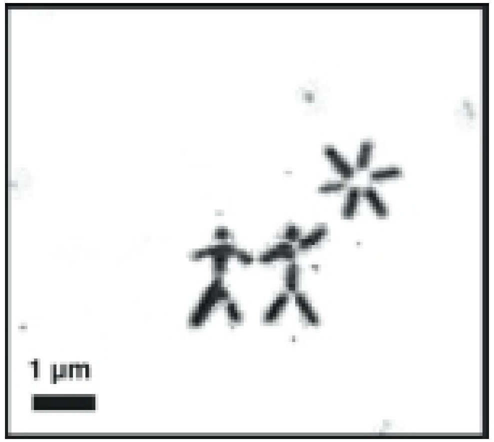
Incident FEL pulse:
30 fs, 32 nm,
3 x 10^{13} W cm^{-2}



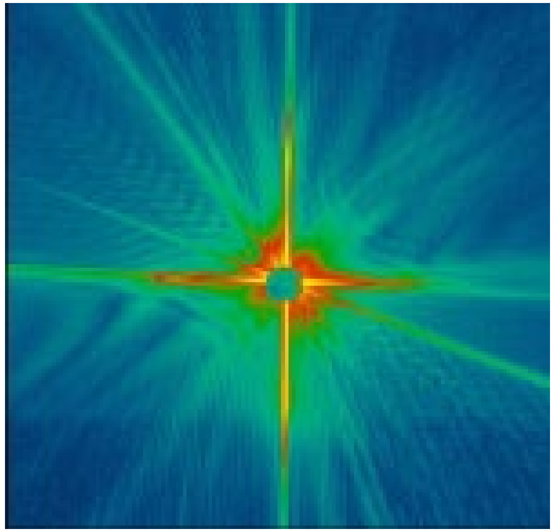
Pulse #1: Diffraction pattern



Reconstructed image



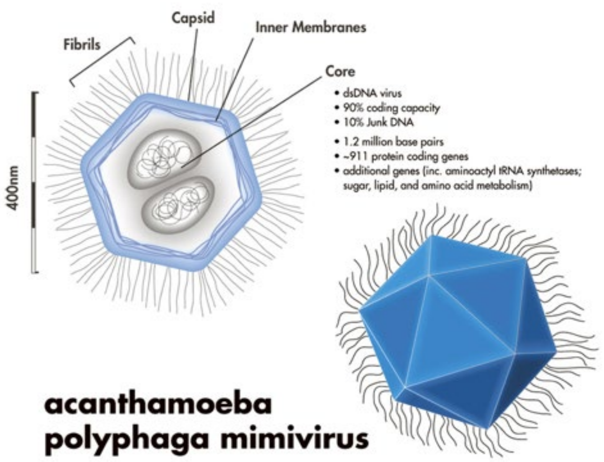
Pulse #2 sees structure destroyed by pulse #1



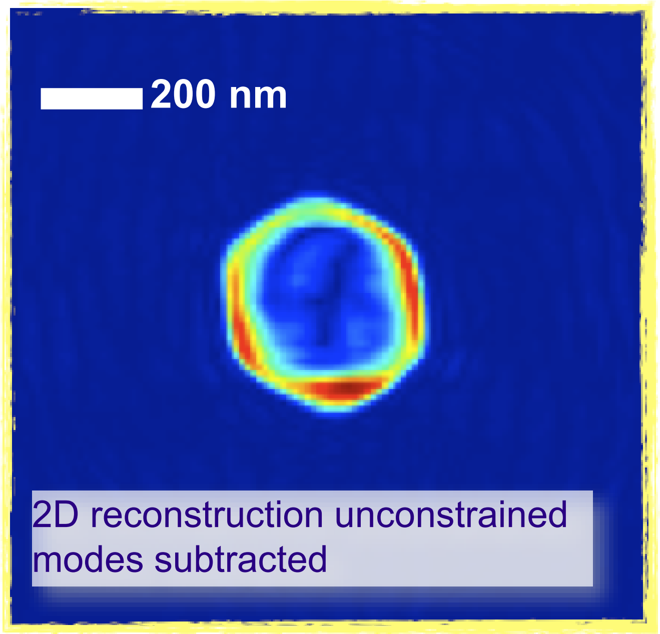
H. Chapman et al. Nature Physics 2, 839 (2006)

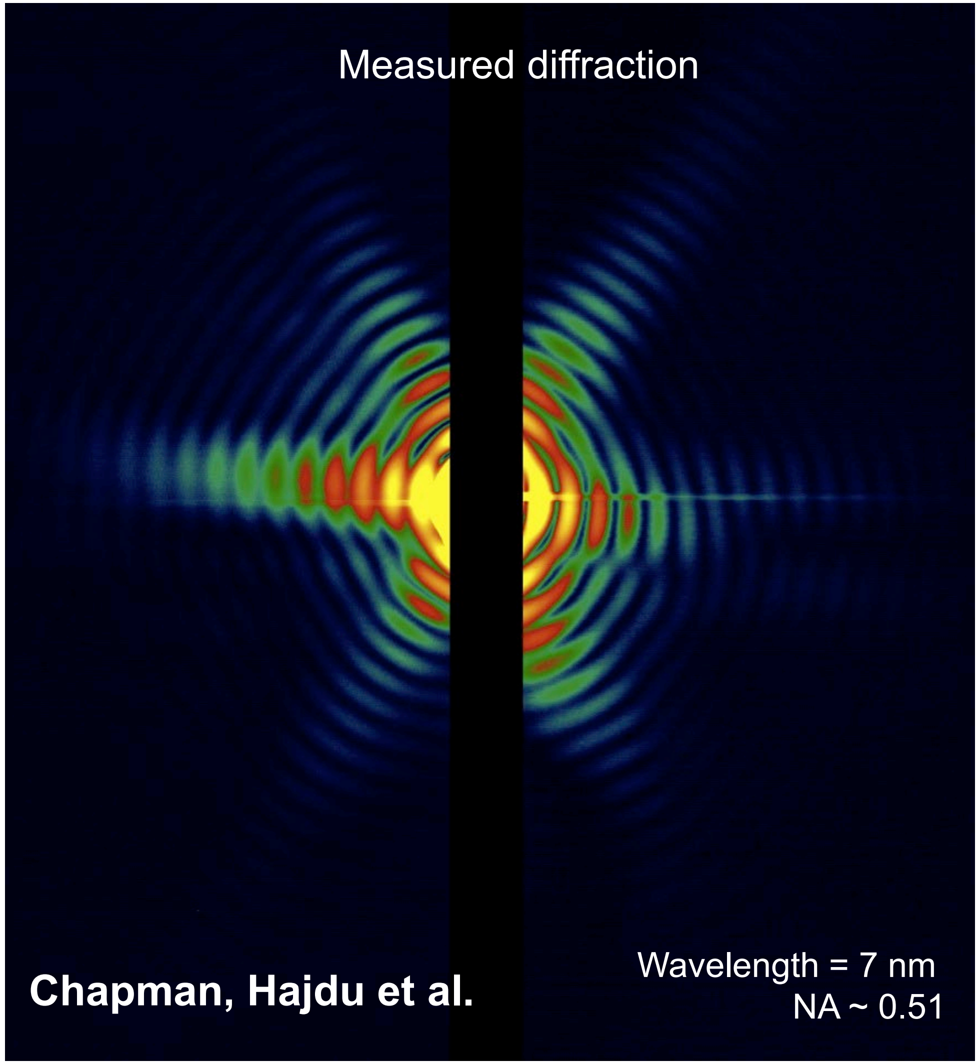
Conclusion: diffraction takes place before the sample is destroyed !

Diffraction from a mimivirus



Graphic: wikipedia.org

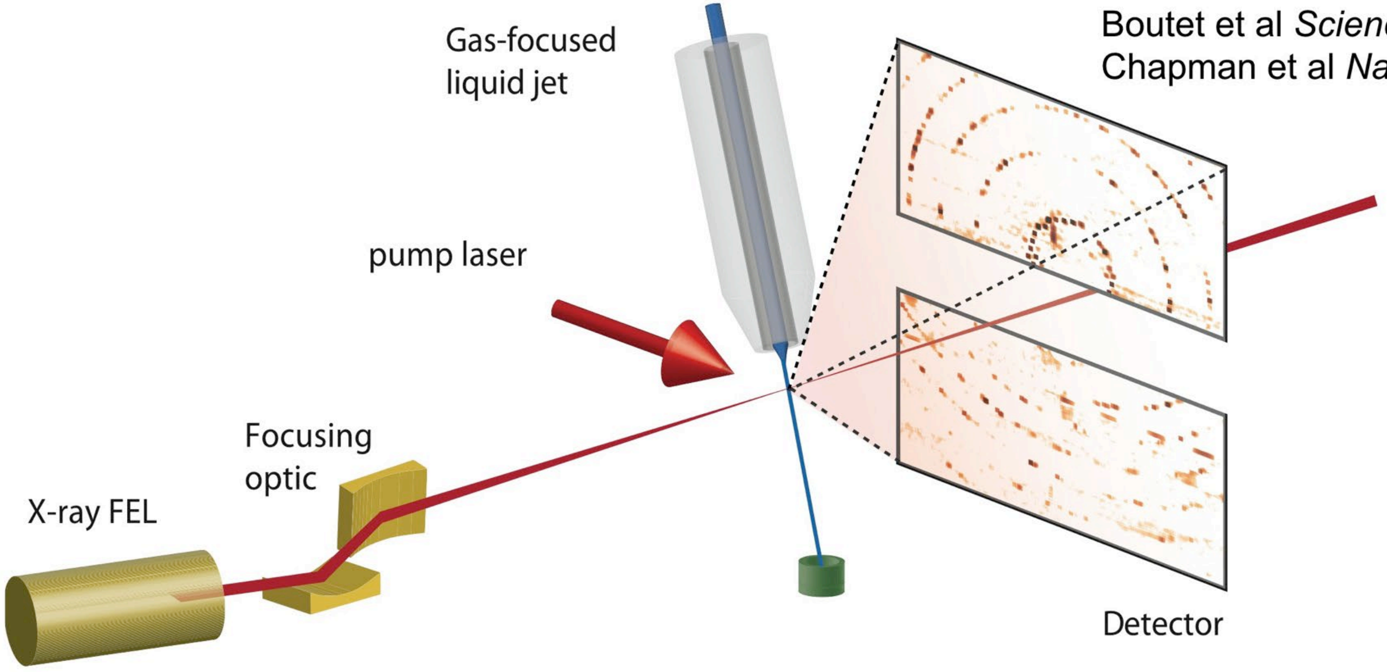


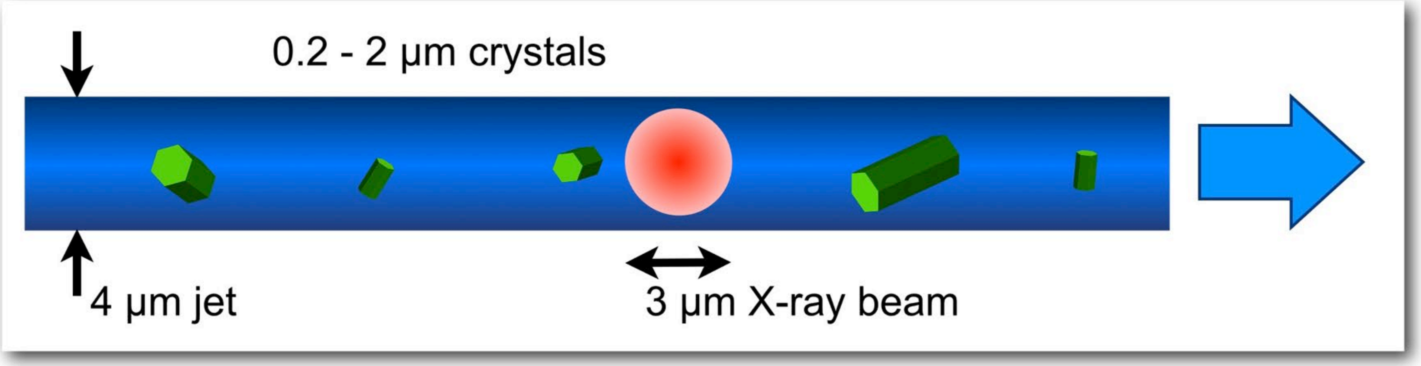


Samples: Uppsala University and CNRS, Aix-Marseille Université
FEL experiments: MPI , CFEL @ DESY, Uppsala, SLAC

Serial femtosecond X-ray crystallography (SFX)

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

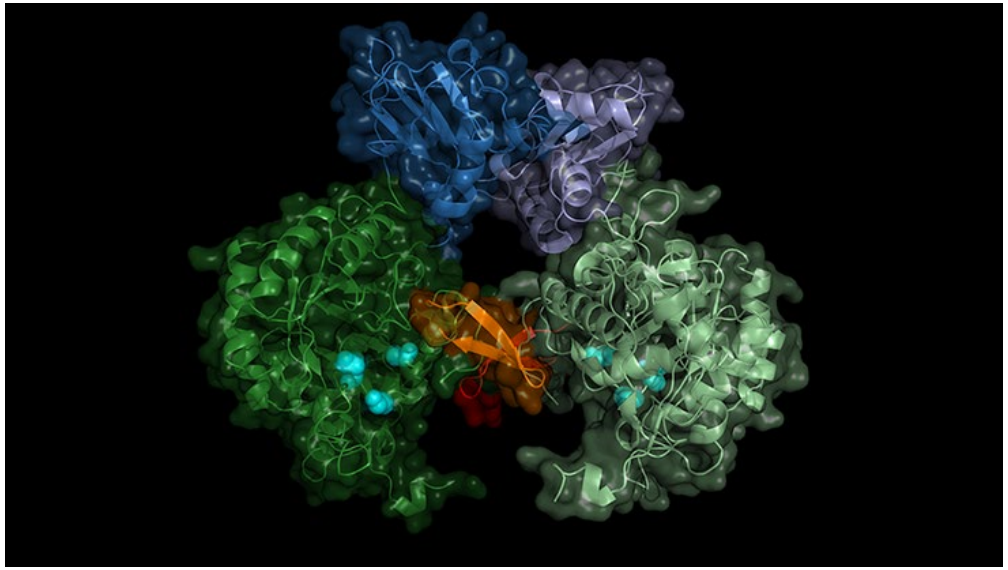




Possible new approach for sleeping sickness drugs

Serial femtosecond X-ray crystallography (SFX)

University of Lübeck/DESY, Lars Redecke



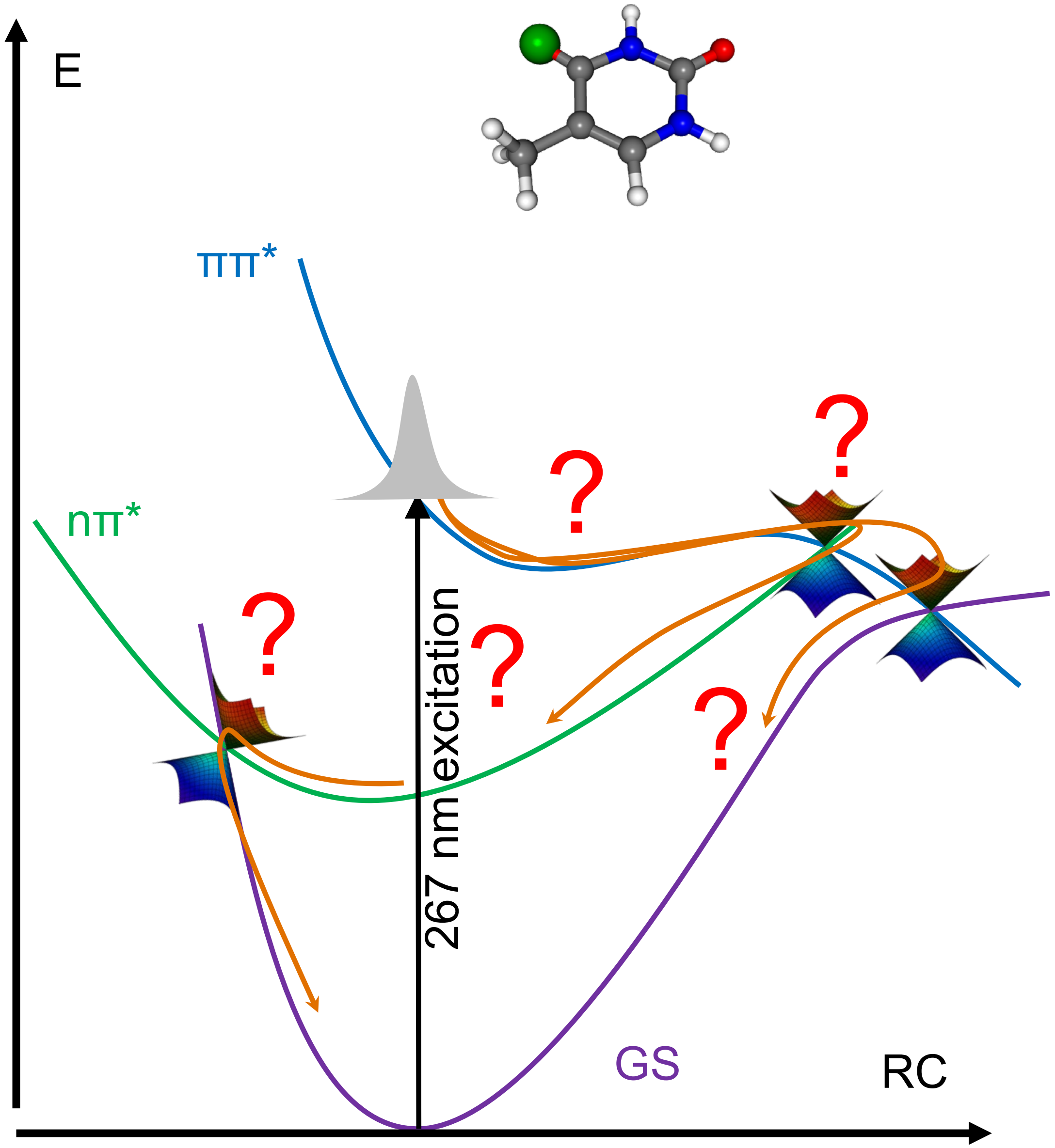
Structure of the parasite's IMP dehydrogenase. The active enzyme forms pairs (dimers), the “switch” region is shown in shades of blue.

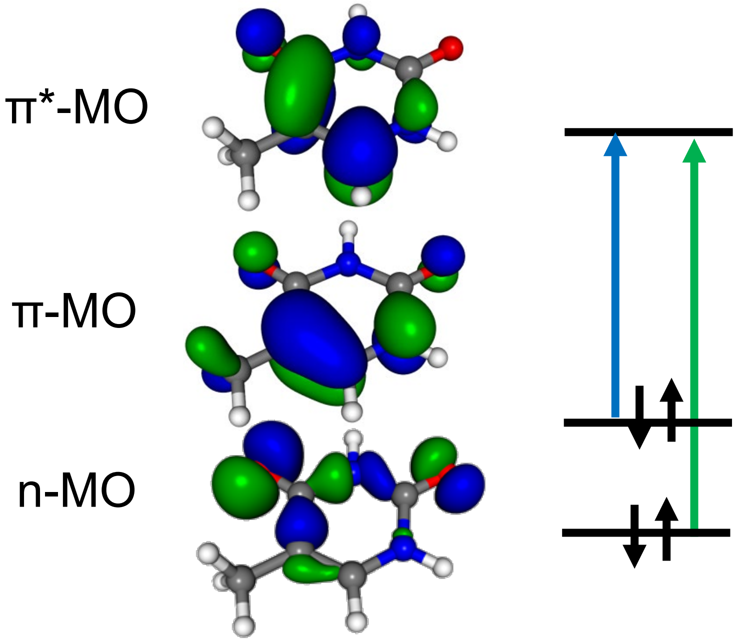
- Certain insect cells to crystallise biomolecules within them
- Tracked down a potential target for new drugs against sleeping sickness: By decoding the detailed spatial structure of a vital enzyme of the pathogen, the parasite Trypanosoma brucei. The result provides a possible blueprint for a drug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

Localized structural evolution:

Time-resolved Auger electron spectroscopy

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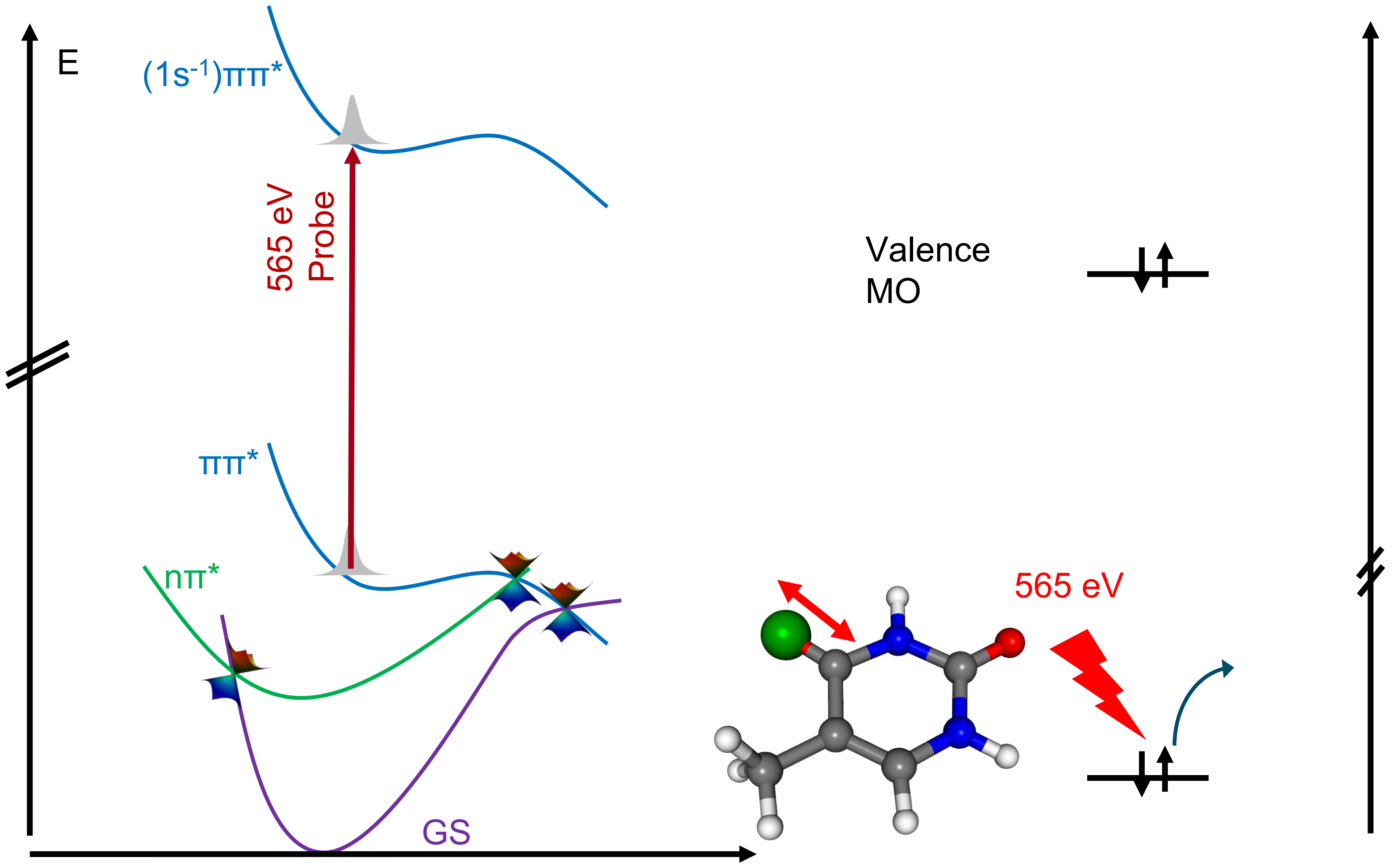

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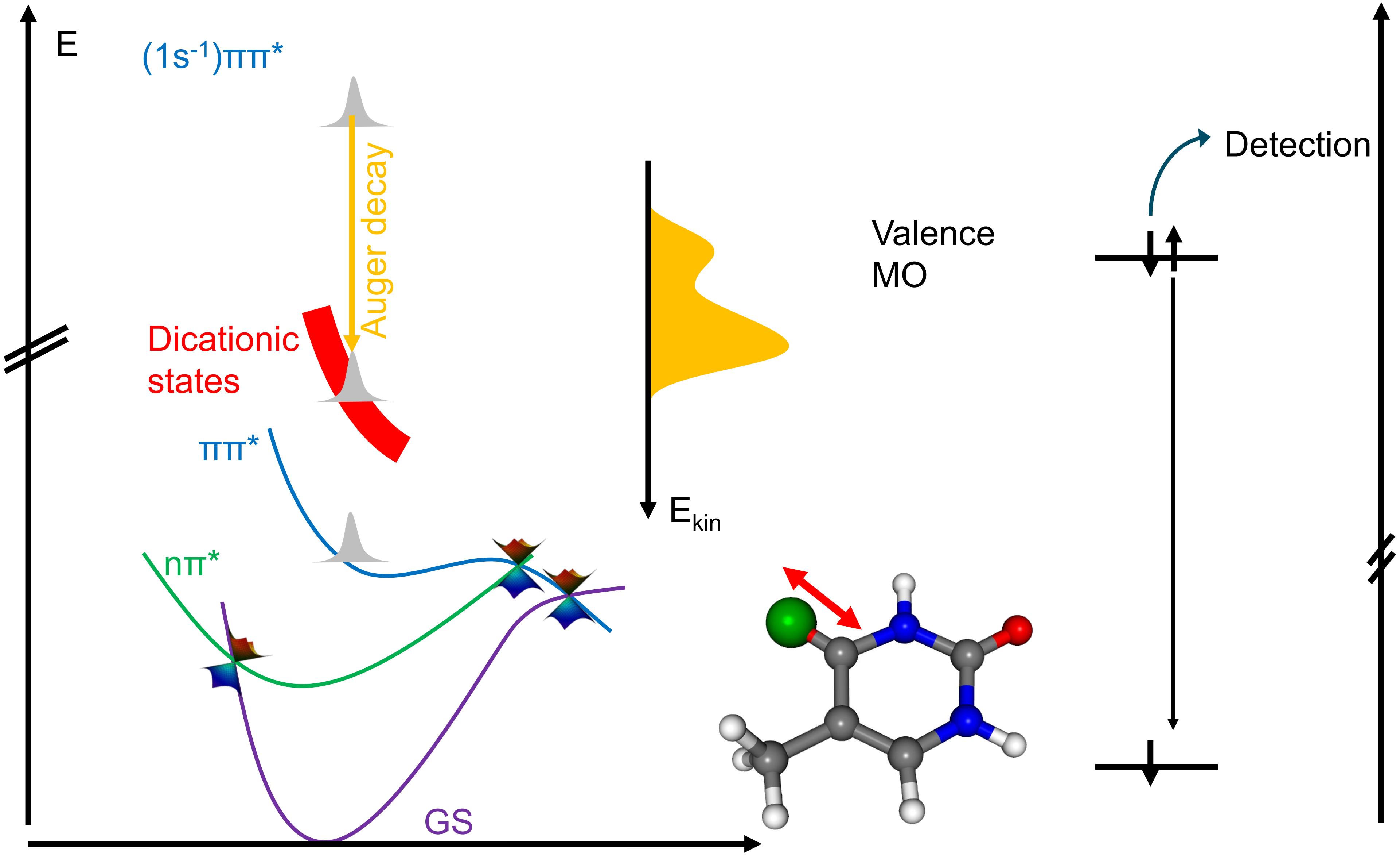
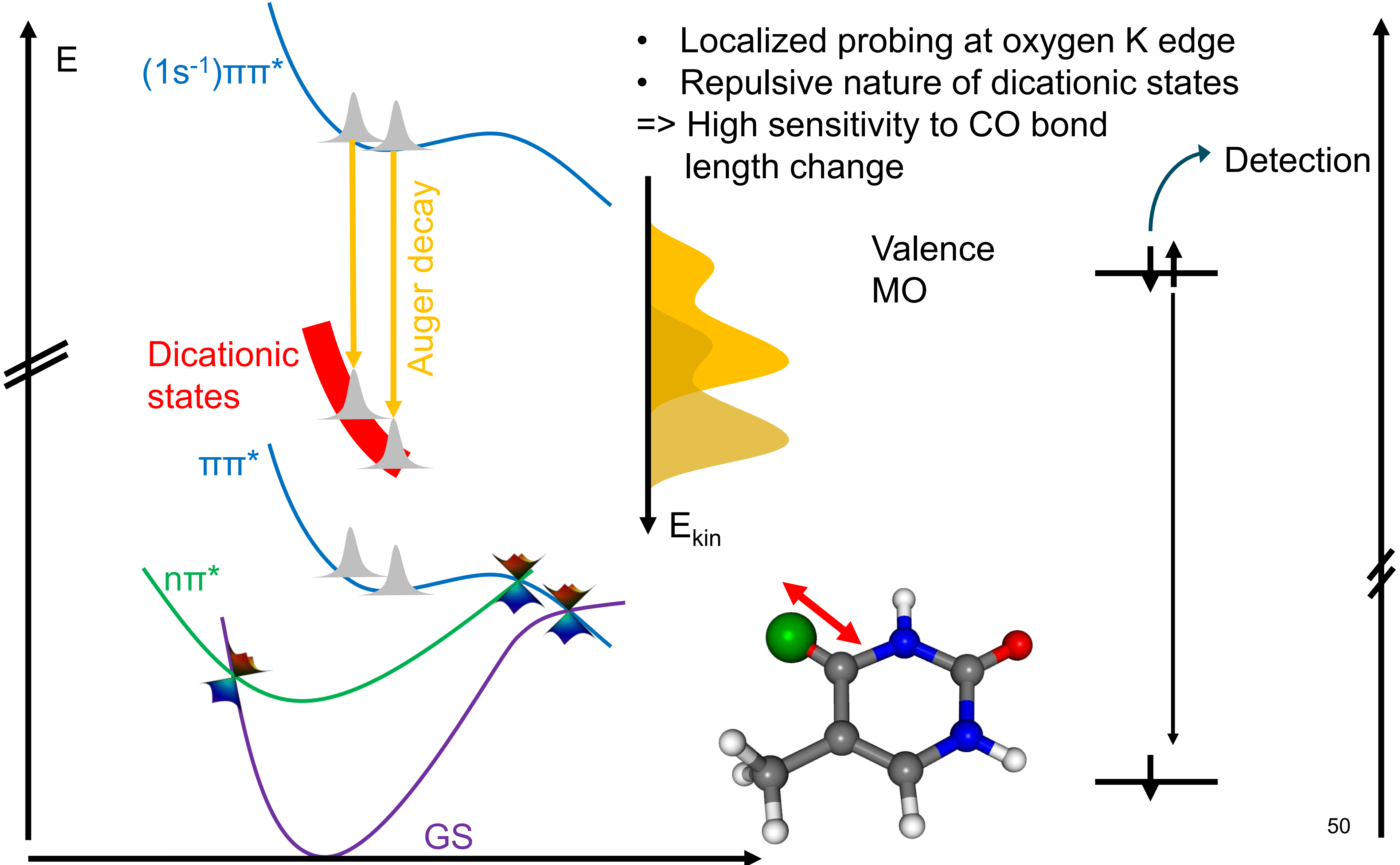


Localized structural evolution:

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

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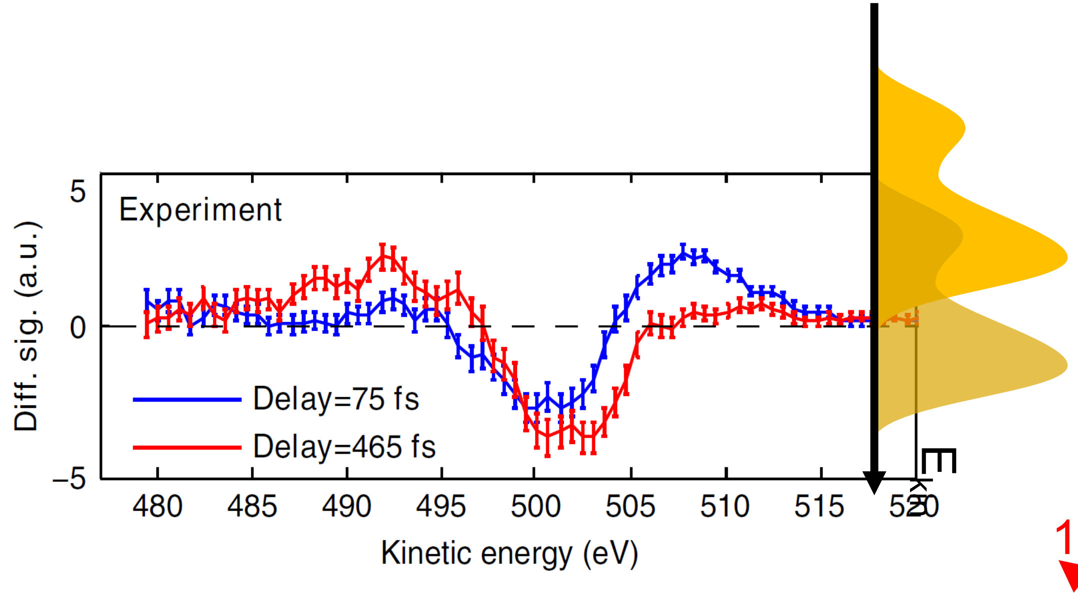
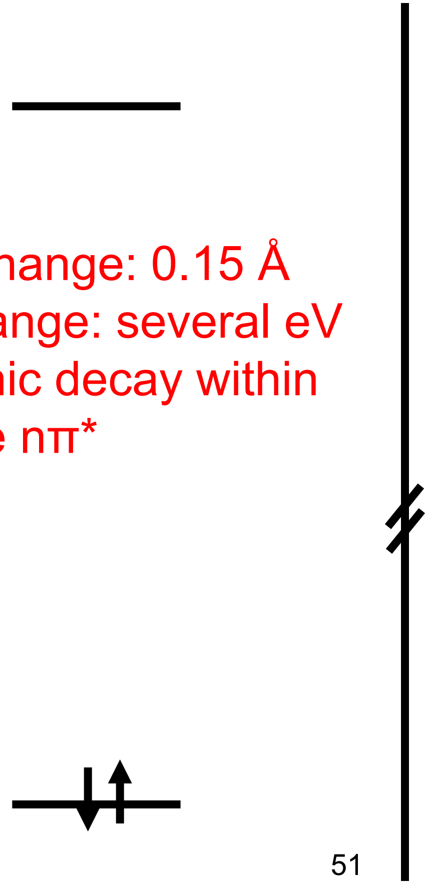
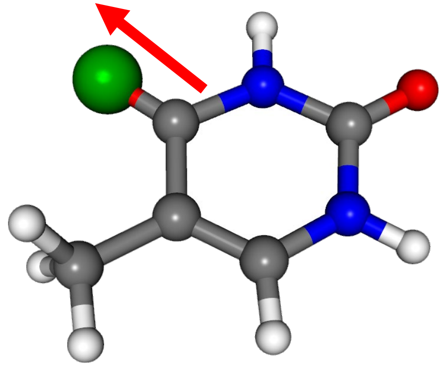


Valence MO



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?

X-ray interactions with matter: https://henke.lbl.gov/optical_constants/

Thank you!
Have fun with the further lectures!

And enjoy your projects@DESY!