Røntgenteknikker, Synchrotroner og XFELs

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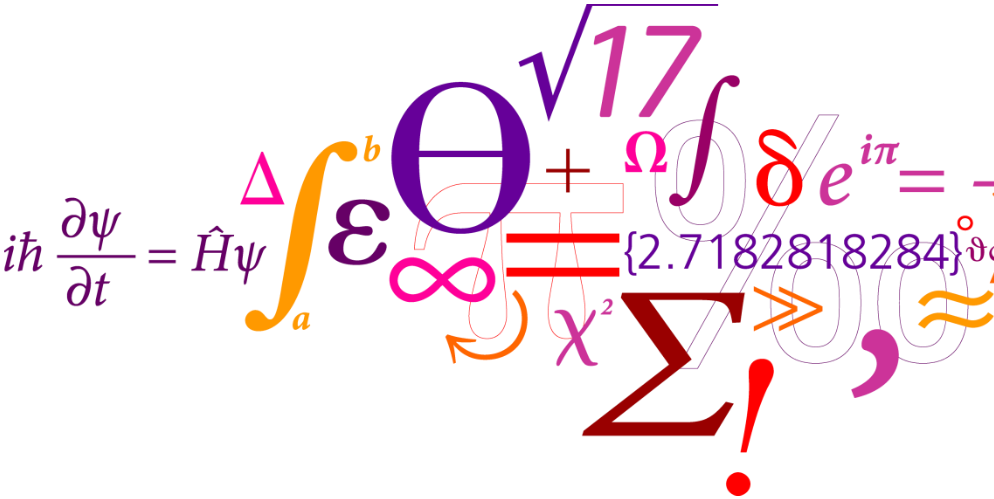
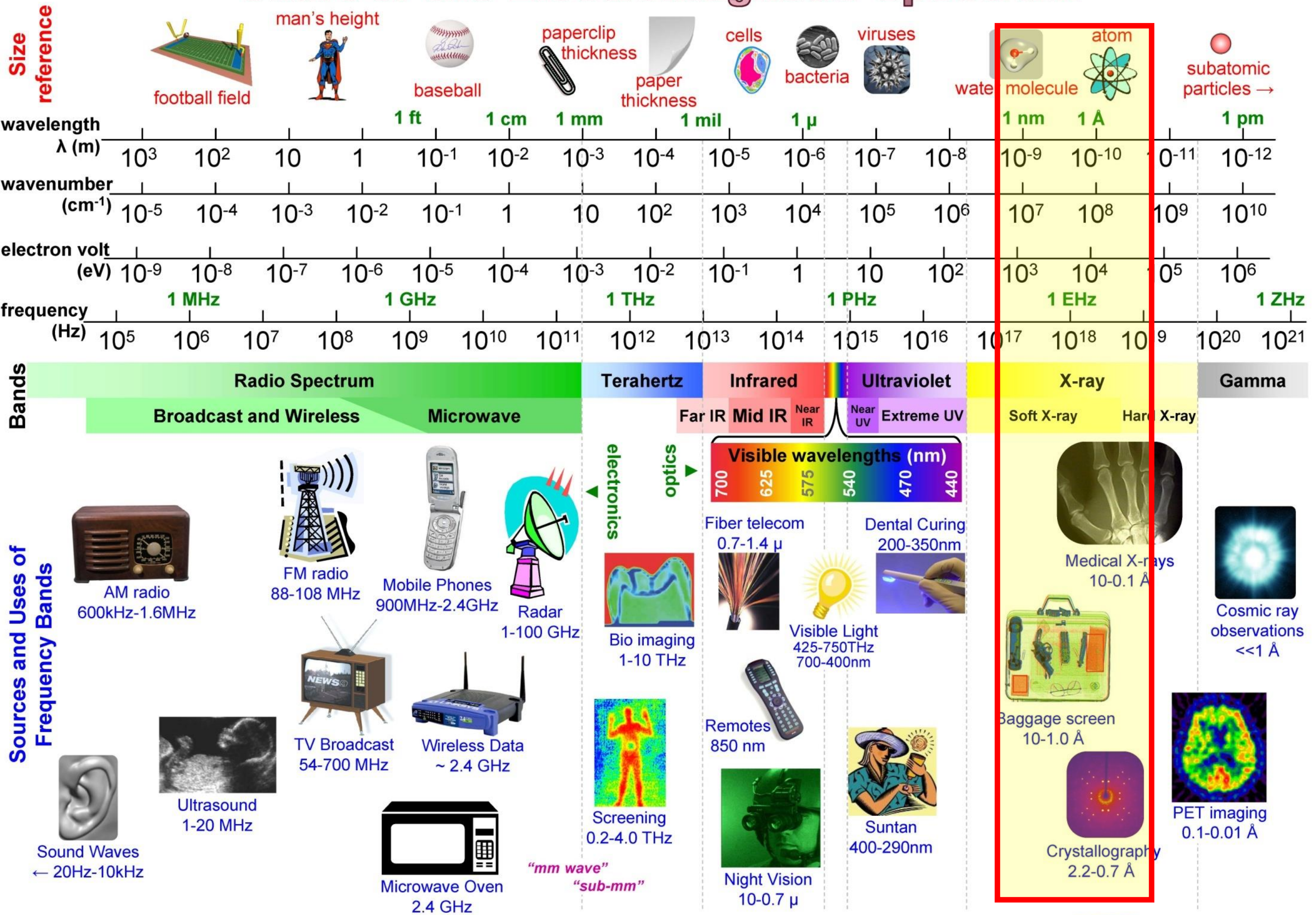


Chart of the Electromagnetic Spectrum

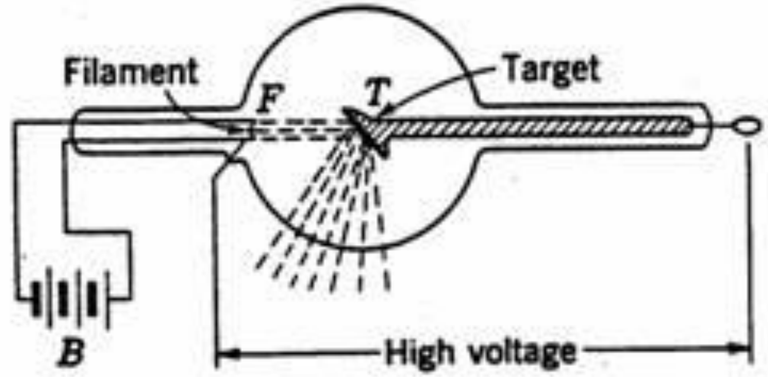


$\lambda = 3\times10^8/freq = 1/(wn*100) = 1.24\times10^{-6}/eV$

SURA Southeastern Universities Research Association ®

Hvordan dannes røntgenstråling?

Hurtig nedbremsning af energirige elektroner: katodestrålerøret

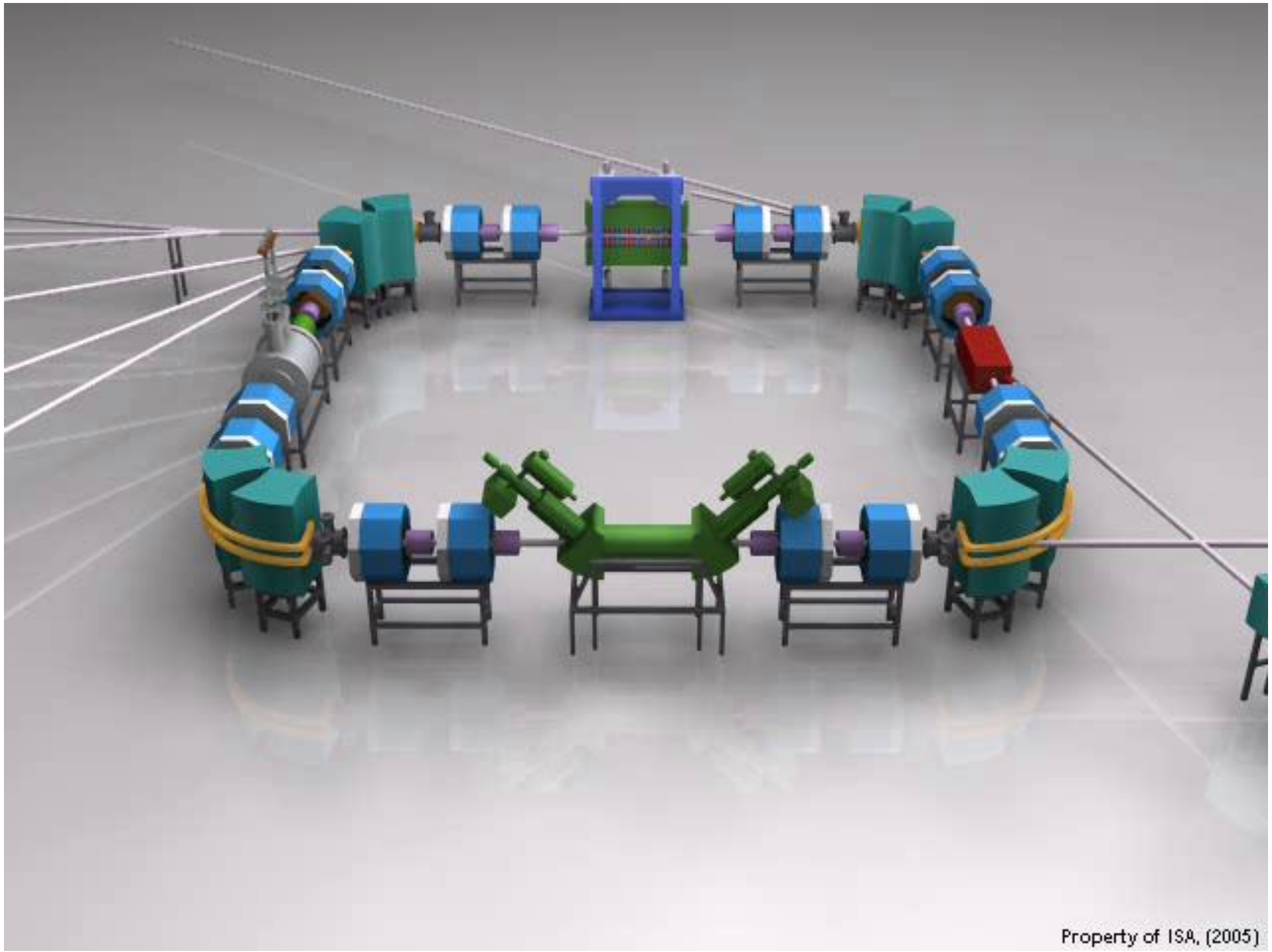


W.C. Röntgen i 1895:

*...if one **covers the tube** with a rather closely fitting envelope of thin black cardboard, one observes in the completely darkened room that a piece of paper painted with barium platinocyanide lying near the apparatus **glows brightly**.. fluorescence is still visible at a distance of 2 m*

SYNCHROTRONS

Synchrotronen



Making superintense x-radiation

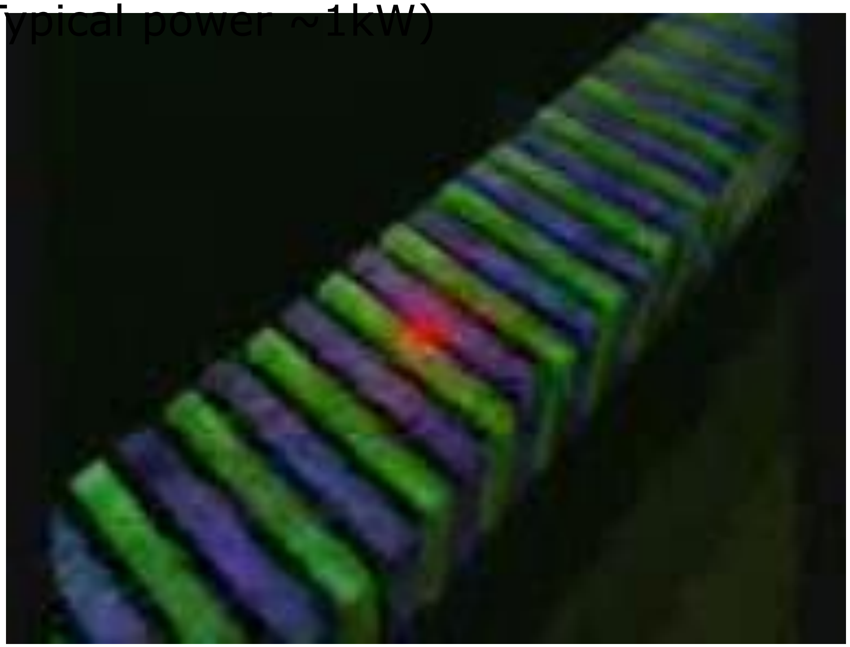
Classical electromagnetism + special relativity gives for a bending magnet:

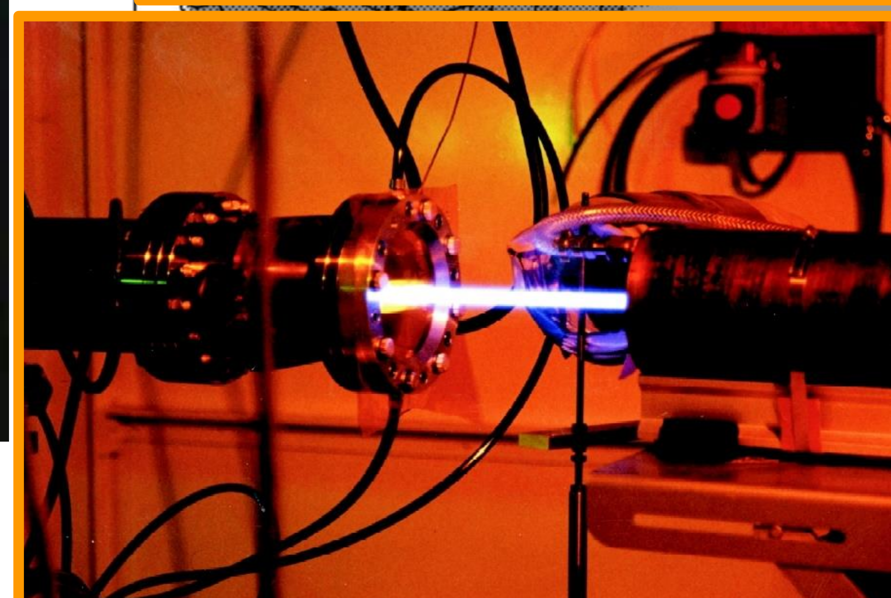
(Typical power for a modern BM ~10W)

If one magnet is good – many magnets are better

...insertion devices!

(Typical power ~1kW)





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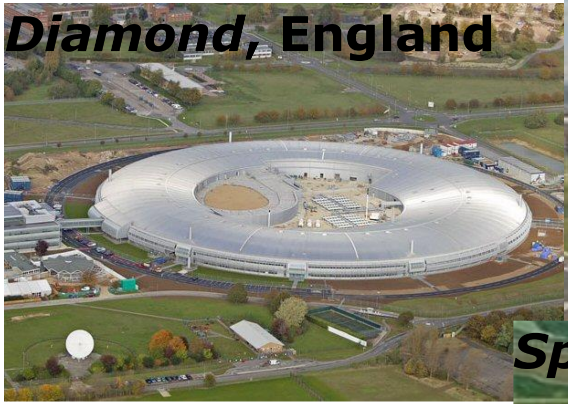
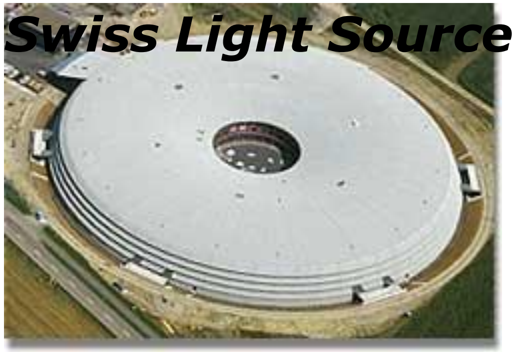
Synchrotron x-ray Sources





-and many other...

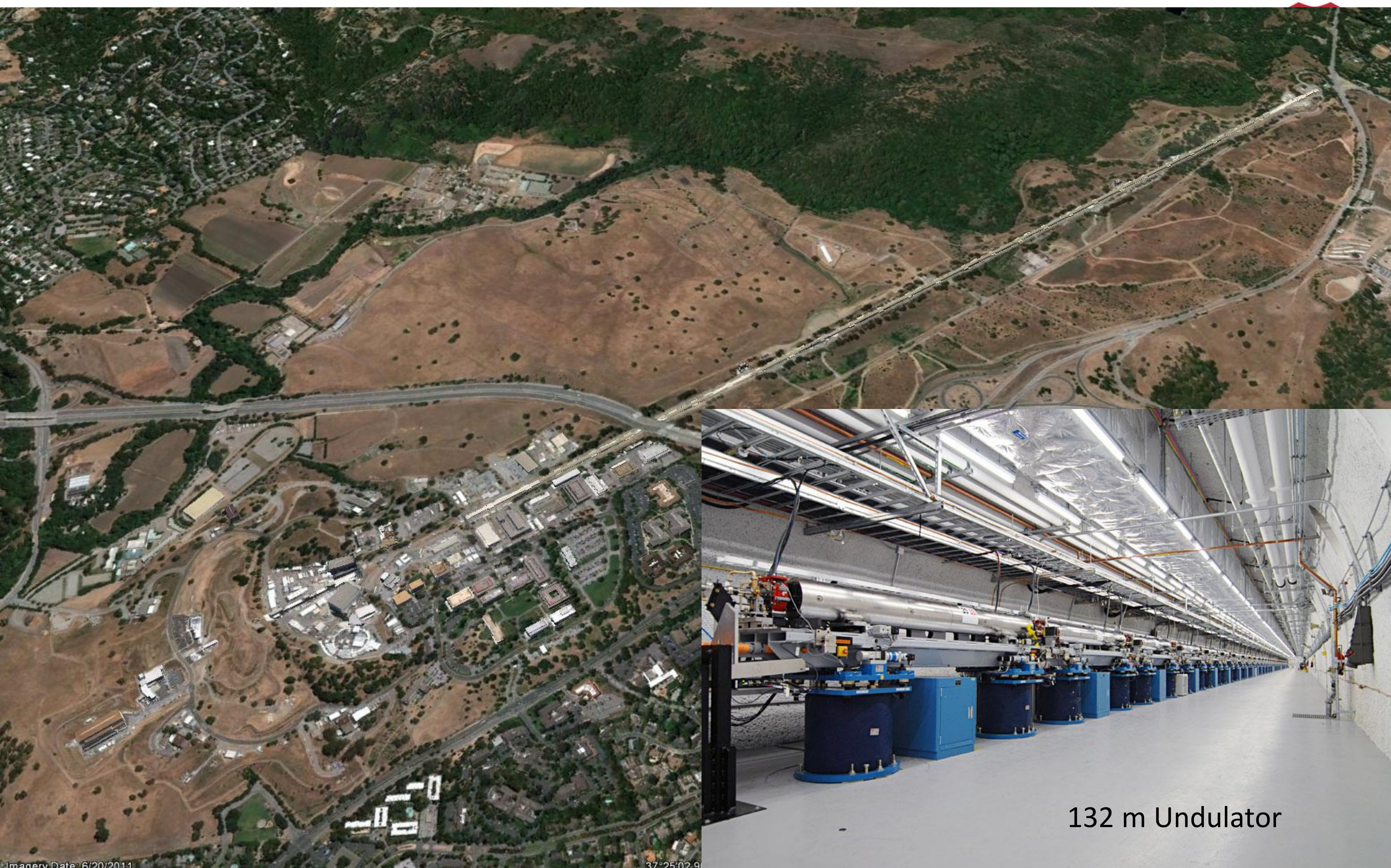
MAX IV in Lund

MAX IV synchrotron

- DANMAX, the Danish Beamline: Imaging and powder diffraction
- Responsible: Innokenti Kantor (NEXMAP)

MAX IV Free Electron Laser

LCLS: The first hard X-ray FEL



XFEL experiments

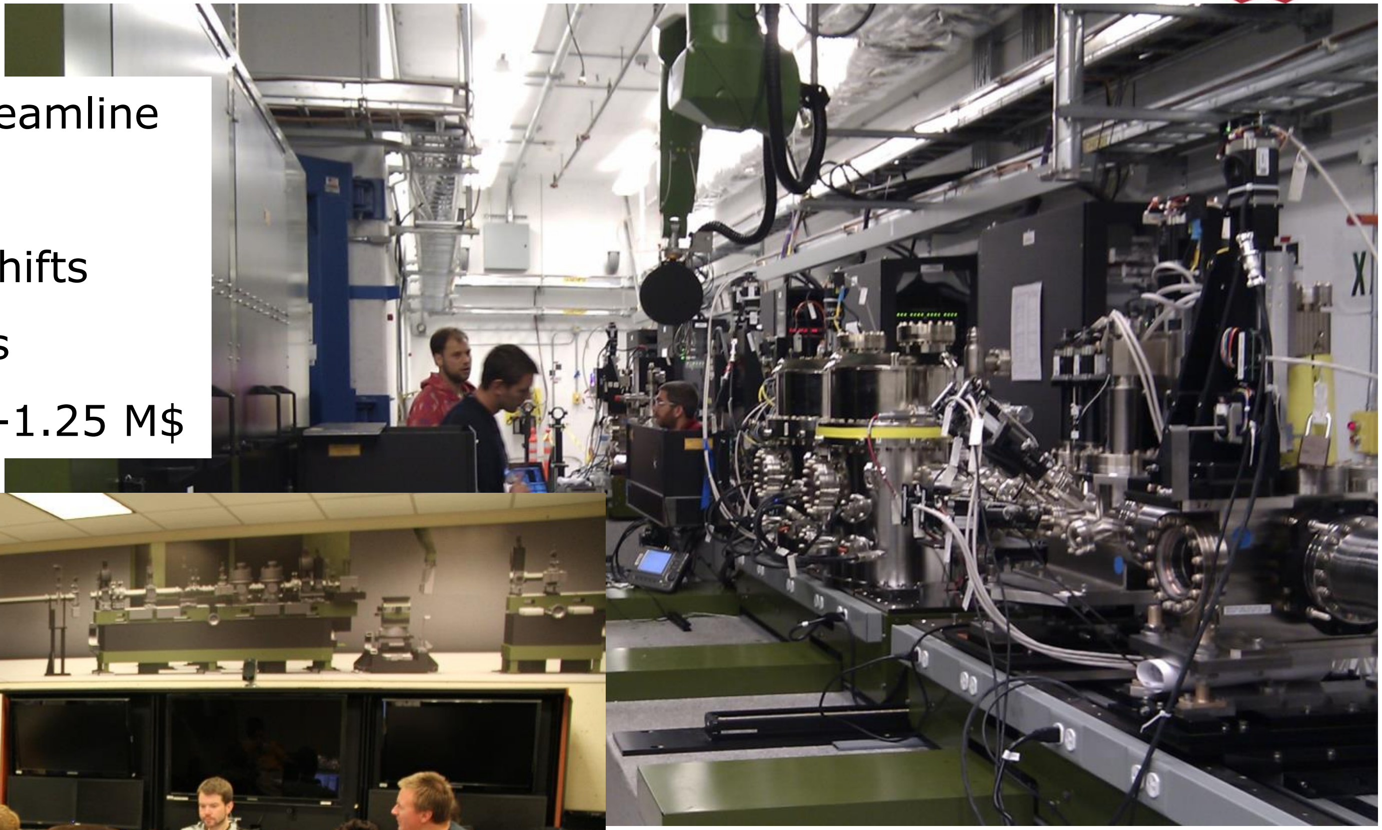
10-20 people at the beamline

Operation~100 M$/yr

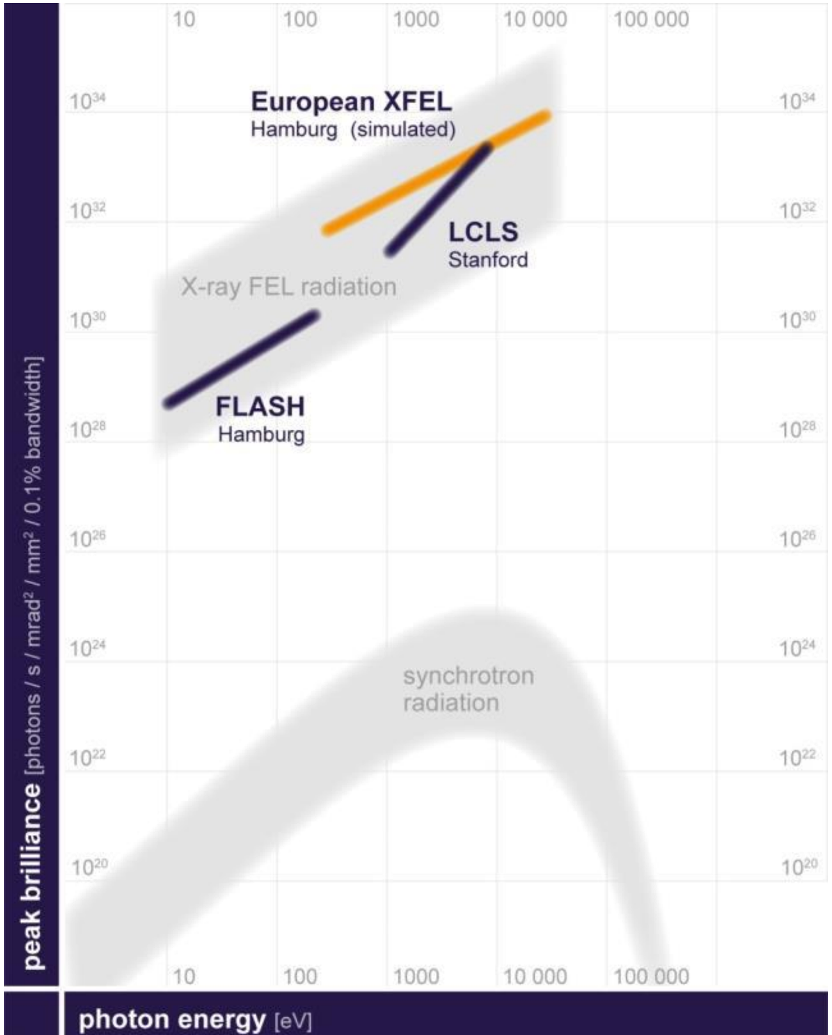
200 beam-days @ 2 shifts

Beamtime ~ 3-5 shifts

Beamtime cost ~0.75-1.25 M$

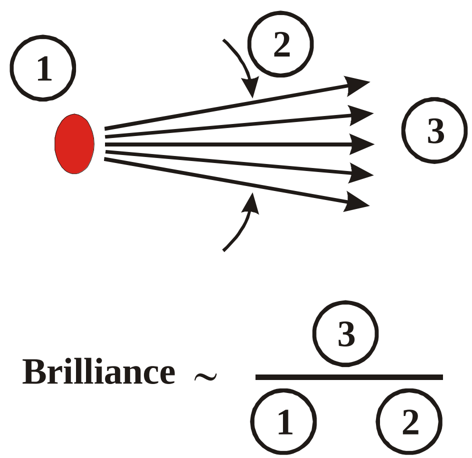


XFEL radiation - properties



The peak brilliance of X-ray free-electron lasers exceeds that of the most modern synchrotron radiation sources by several orders of magnitude.

The European XFEL will be capable of generating more pulses per second and more intense X-rays than any other X-ray free-electron laser in the world.



Later XFELs

- SACLA
  - Spring-8, Harima, Japan
- PAL XFEL
  - Pohang Accelerator Lab., Corea
- SwissFEL
  - PSI, Switzerland

Molecular Movies

DTU

European XFEL

Online 2016
~100 times more flux than existing XFELS

- Denmark ~1%, 100 MDKR
- France
- Germany ~55%
- Hungary
- Italy
- Poland
- Russia ~25%
- Slovak Republic
- Spain
- Sweden
- Switzerland

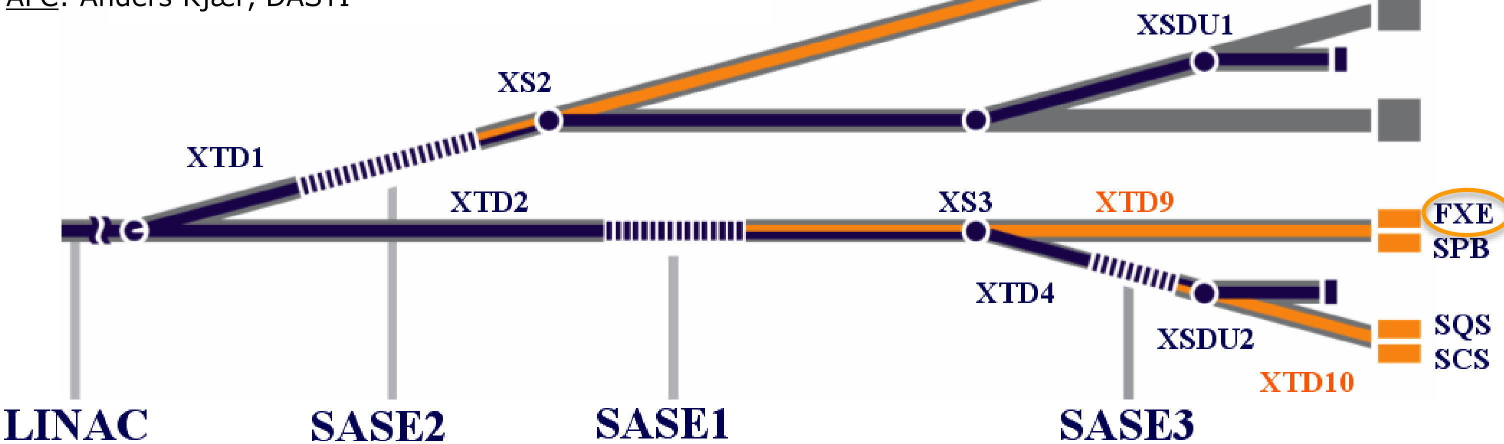
Danish members of

Council: Robert Feidenhans'l, KU; Anders Kjær, DASTI; Martin Meedom Nielsen (chair), DTU

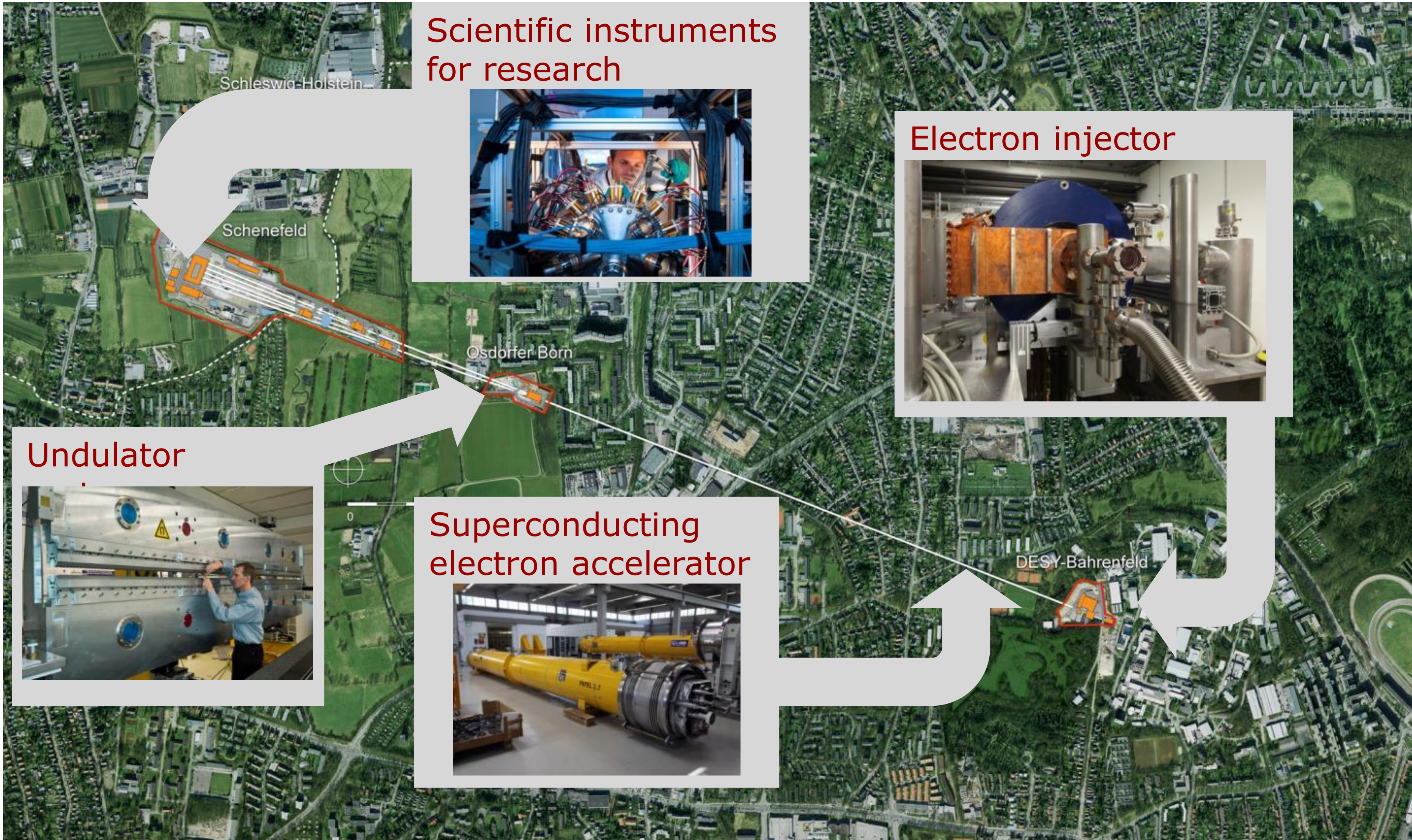
SAC: Sine Larsen, KU (until 2015)

IKC: Søren Schmidt, DTU

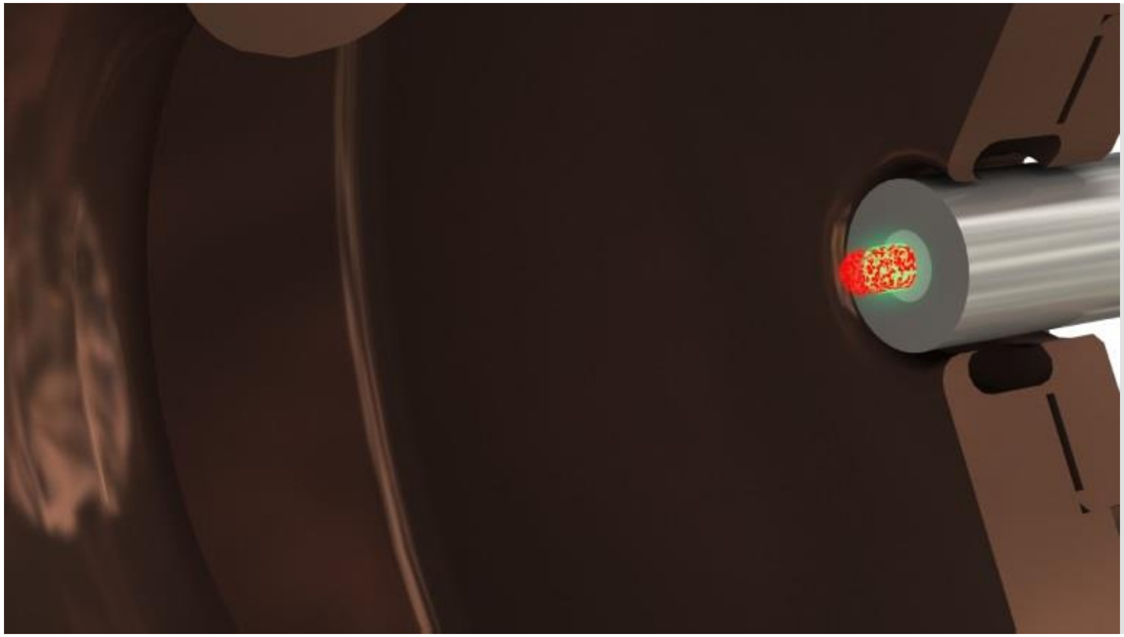
AFC: Anders Kjær, DASTI



A closer look at the XFEL.EU



Injector: creating bunches of electrons



- Optical laser strikes Cs_2Te surface, releasing a cloud of electrons
- Electrons move into a magnetic field, shaping into a bunch
- Small accelerator module "fires" bunch into the main electron

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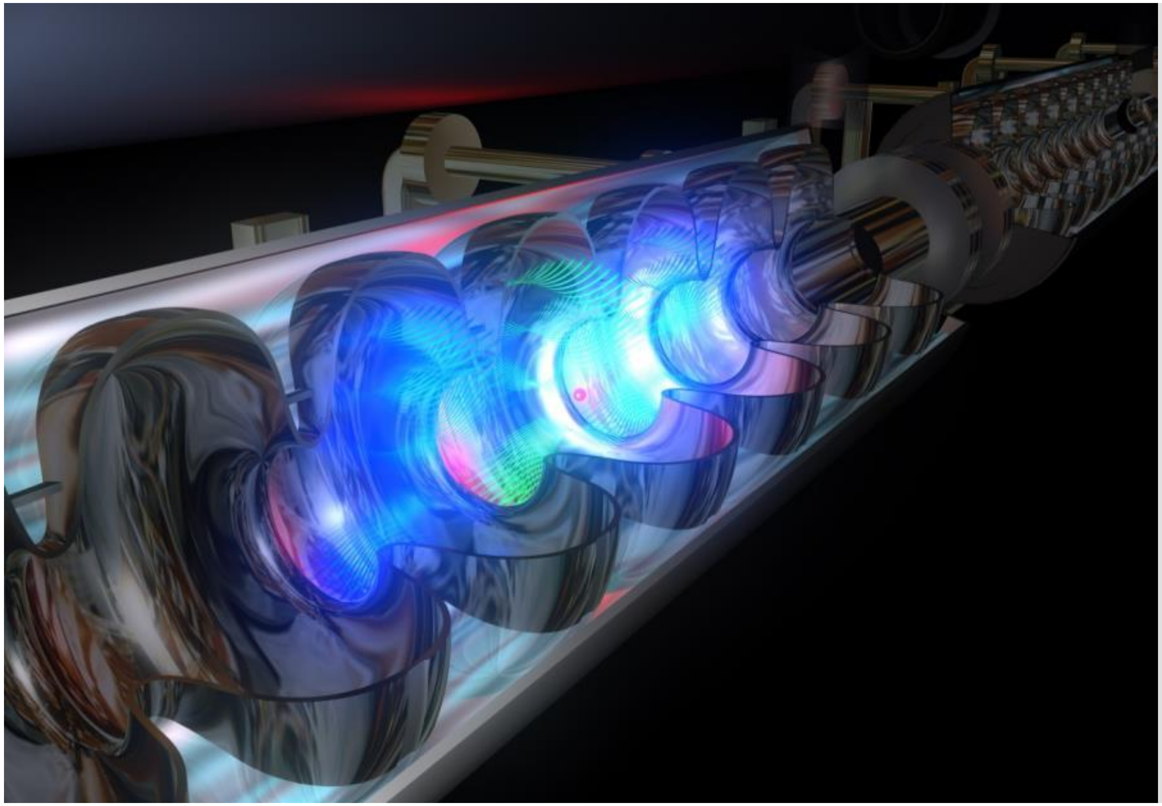
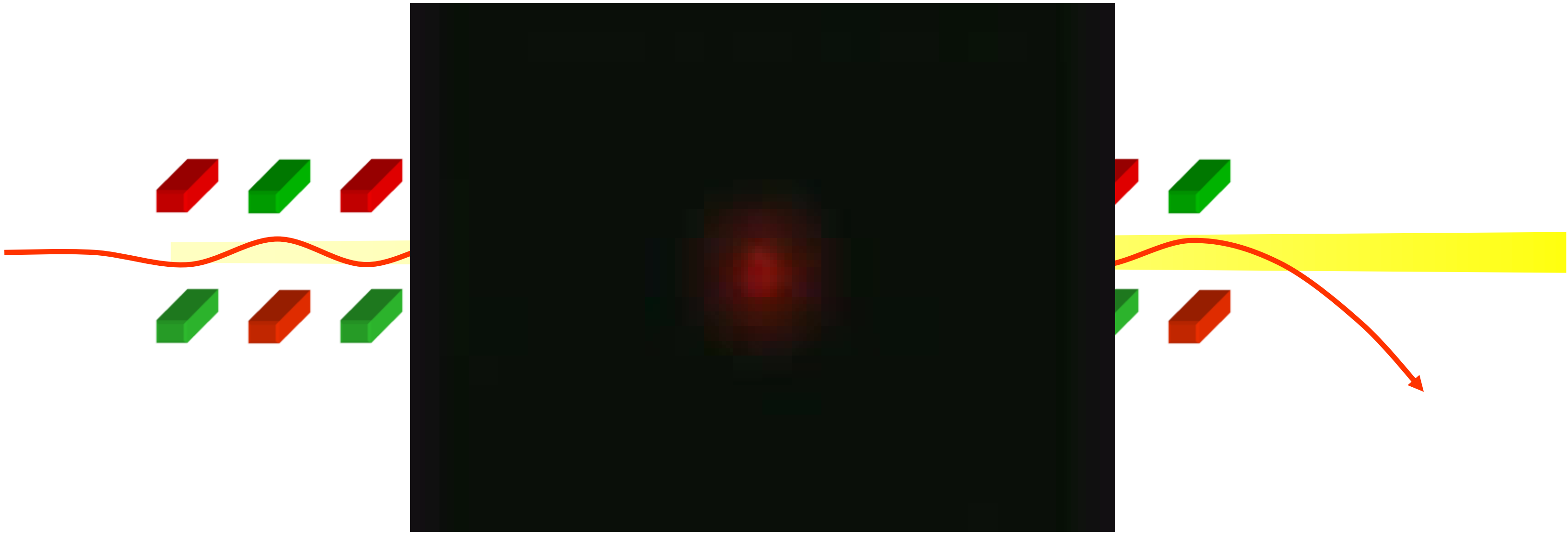
Accelerator: electrons at close to light speed



- 100 accelerator modules over 2 km bring the electron bunch to near light speed and high energies
- Superconducting niobium cavities powered by intense radio frequency accelerate electrons

XFEL radiation – SASE production

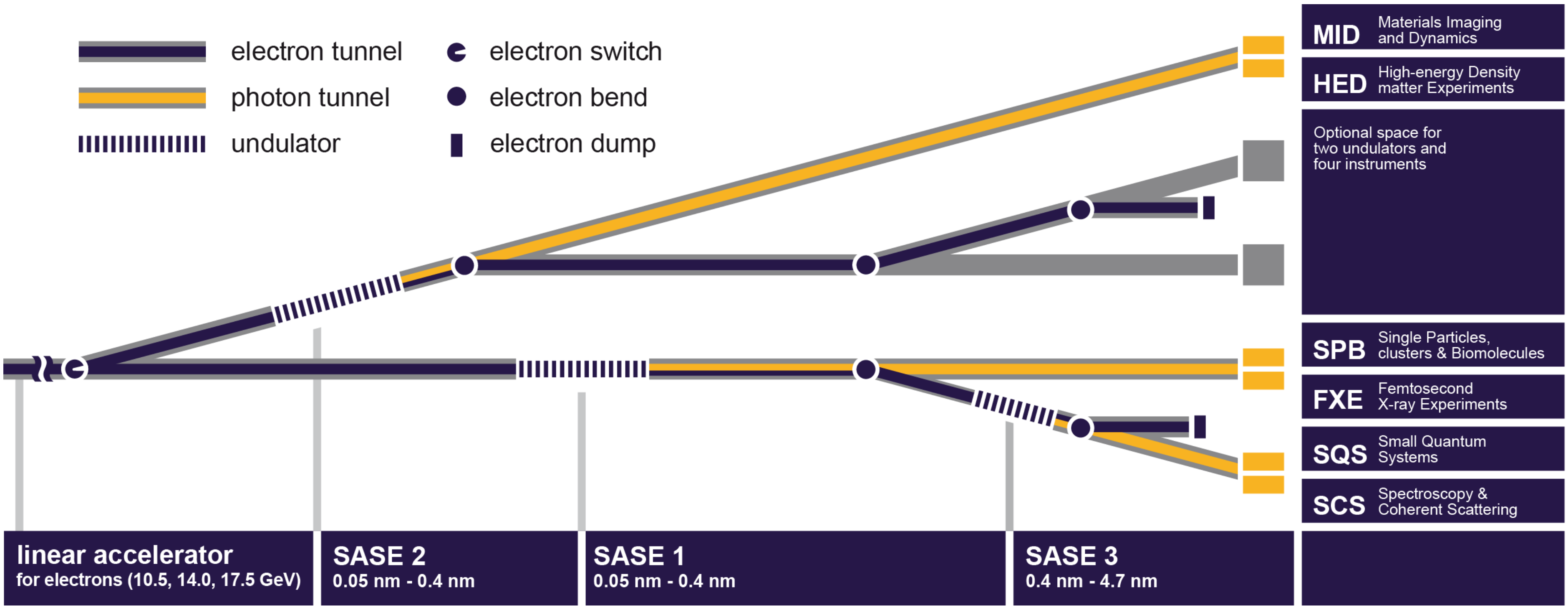


- Synchrotron radiation
  - low emittance electron beam
  - relativistic electron energy
  - periodic acceleration of electron in magnetic field of an undulator
  - collimated radiation
  - tunable by electron energy & magn. field

... but for X-ray wavelength

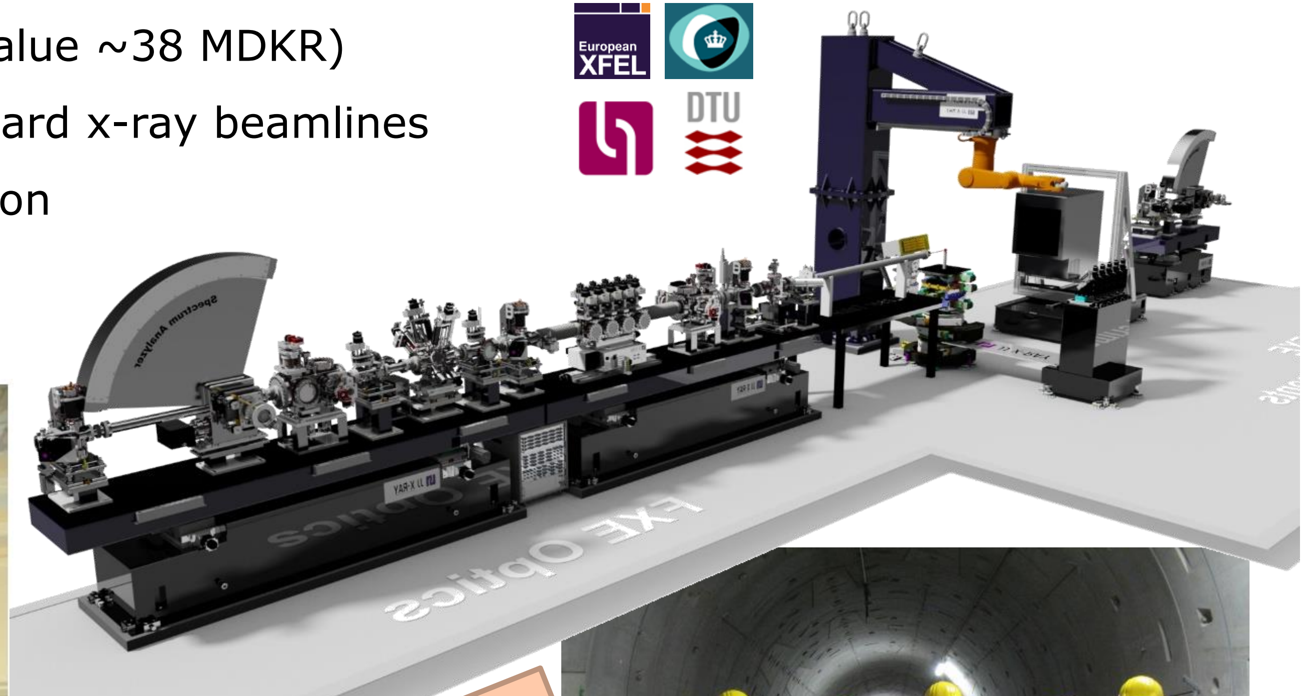
- no efficient reflectors exist
- lasing in a ‚single-pass'
- amplified spontaneous emission

Beamline layout & experiment stations



DK in-kind project at XFEL.EU

- 2 In kind Contracts (value ~38 MDKR)
  - Components for hard x-ray beamlines
  - FXE instrumentation



1^{st} call for beamtime expected by late 2016!

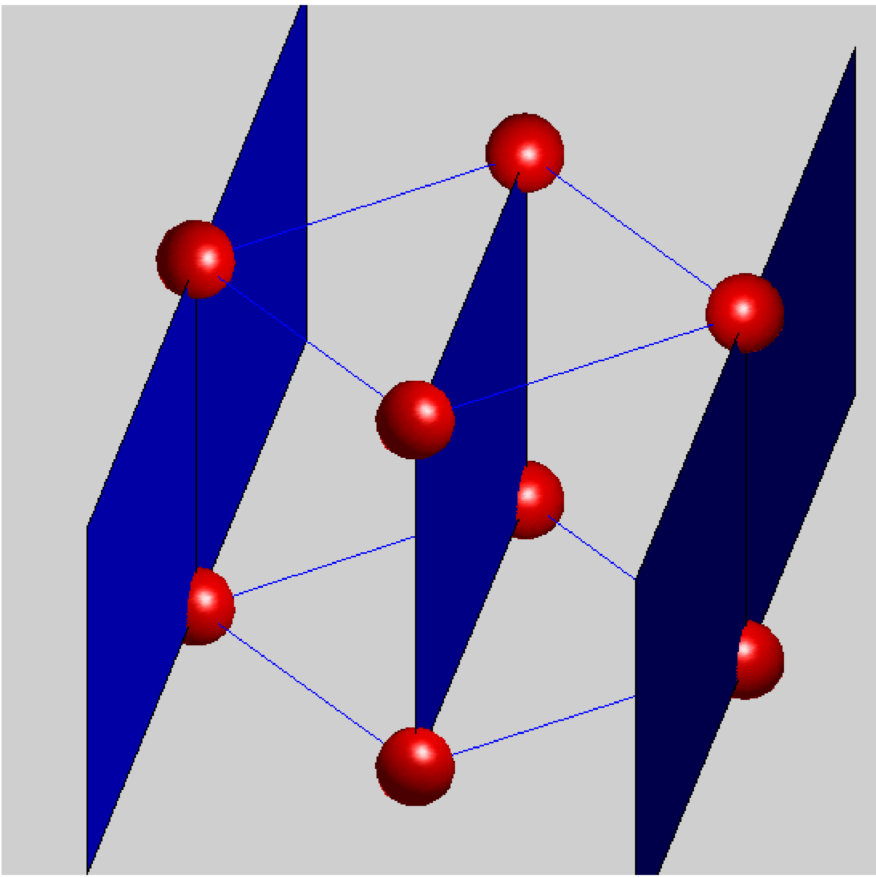
XFEL.EU, DTU, JJ X-ray A/S

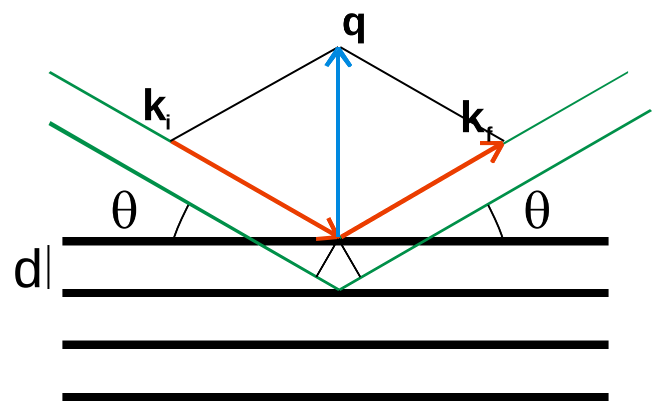
X-RAY INTERACTION WITH MATTER

X-ray interaction with matter (1):
Absorption

—Cartoon from *Life*, February, 1896. The New Roentgen Photography.
" Look Pleasant, Please."

X-ray interaction with matter (2): Braggs law





$$n\lambda = 2d \sin\theta$$

$$k = 2\pi / \lambda$$

$$q = 2k \sin(\theta)$$

$$\mathbf{d} \bullet (\mathbf{k}_i - \mathbf{k}_f) = 2\pi n$$

$$\Downarrow$$

$$\mathbf{d} \bullet \mathbf{q} = 2\pi n$$

Phase difference

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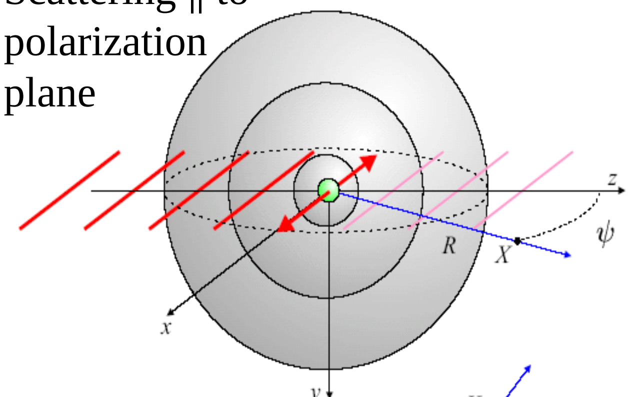
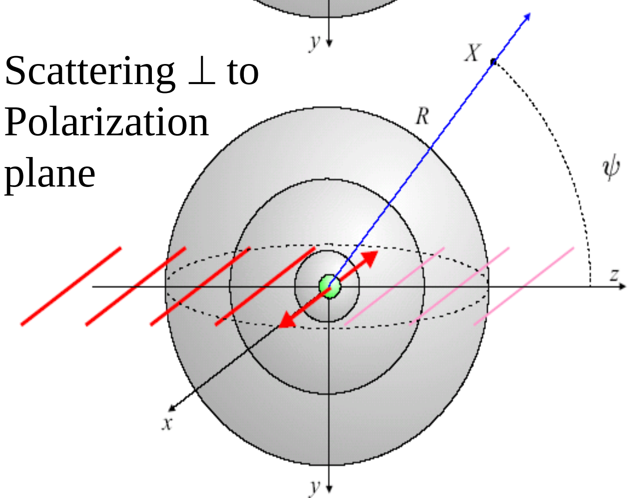
X-ray Interaction with matter (3): One Electron

Scattering || to polarization plane



Scattering ⊥ to Polarization plane



Thomson Scattering:

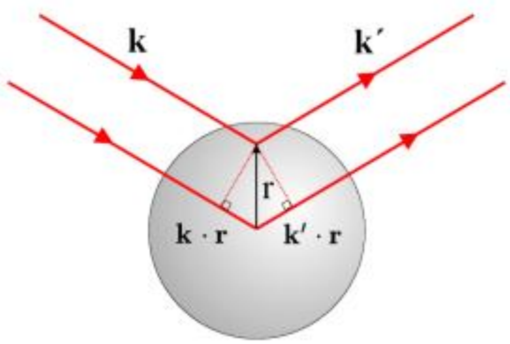
$$\left(\frac{d\sigma}{d\Omega}\right) = r_0^2 P$$

$$r_0 = \frac{e^2}{4\pi\varepsilon_0 mc^2} = 2.82\times10^{-5}\ \text{Å} \qquad \text{(Thomson radius)}$$

$$P = \begin{cases} 1 & \text{synchrotron: vertical scattering plane} \\ \cos^2\psi & \text{synchrotron: horizontal scattering plane} \\ \frac{1}{2}\left(1+\cos^2\psi\right) & \text{unpolarized source} \end{cases}$$

X-ray Interaction with matter (4): Scattering from...

...an atom



Each volume element, $d\mathbf{r}$ at $\mathbf{r}$ contributes:

$$-r_0 \rho_{el}(\mathbf{r})\, d\mathbf{r}$$

Phase difference from origin to $\mathbf{r}$:

$$(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r} \quad = \mathbf{Q}\cdot\mathbf{r}$$

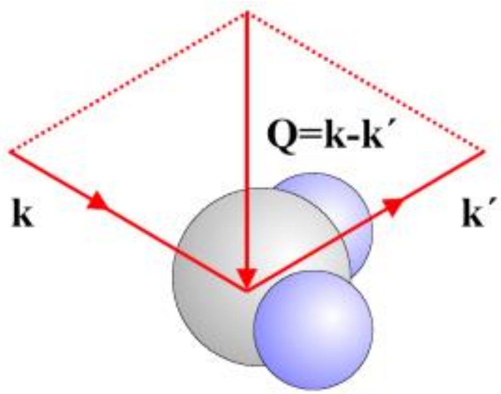
Scattering vector

Total scattering length of the atom is:

$$-r_0 \int \rho_{el}(\mathbf{r})\, e^{i\mathbf{Q}\cdot\mathbf{r}} d\mathbf{r} \quad = -r_0 f_0(\mathbf{Q})$$

Atomic form factor

...a molecule



Total scattering length of the molecule is:

$$F^{mol}(\mathbf{Q}) = \sum_{\mathbf{r}_j} f_j(\mathbf{Q})\, e^{i\mathbf{Q}\cdot\mathbf{r}_j}$$

Molecular form factor

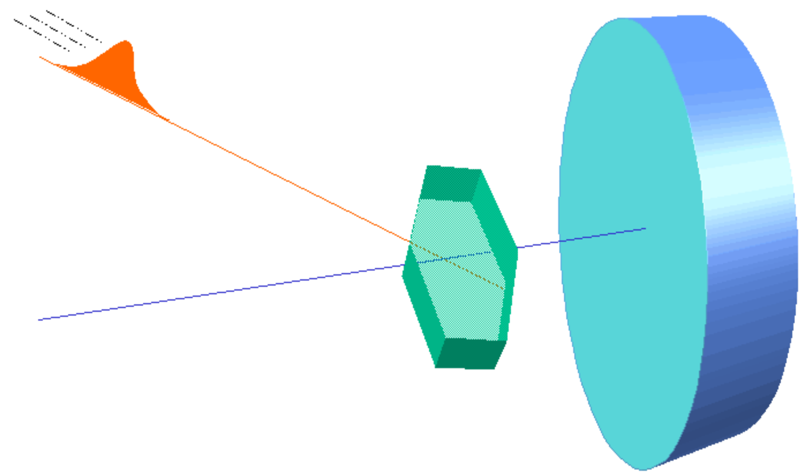
Total scattered intensity:

$$I(\mathbf{Q}) = \left|F^{mol}(\mathbf{Q})\right|^2$$

Time resolved scattering

Timeresolved experiments offer opportunities for investigating dynamics

– something occuring out of equilibrium



Separate measurements at different time intervals are combined into a ‘movie’

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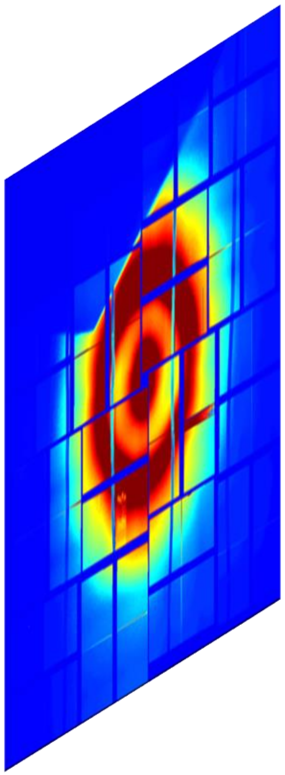
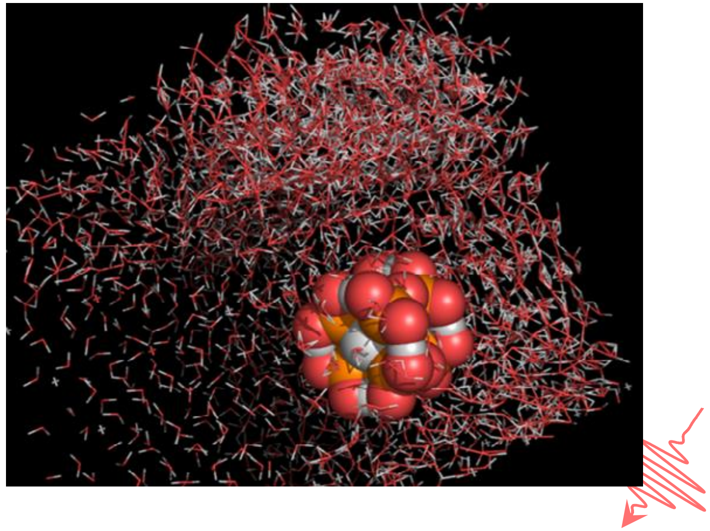
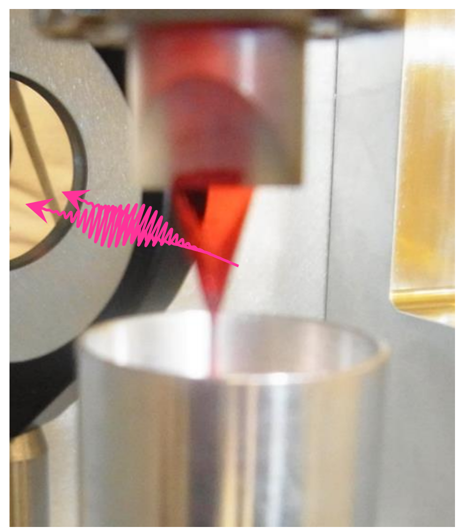
Time resolved scattering from Molecules in solution



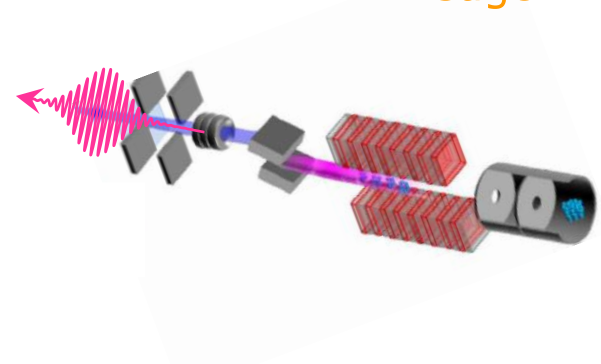




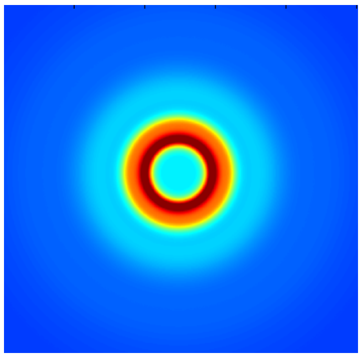
Scattering ”sees everything”:

- Solute
- Solvent
- Solvation cage

$$\Delta S_{XDS} = \Delta S_{Solute} + \Delta S_{Solvent} + \Delta S_{Cage}$$



Making molecular movies



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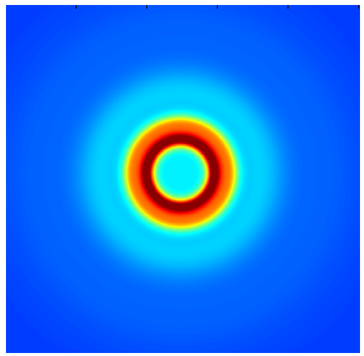

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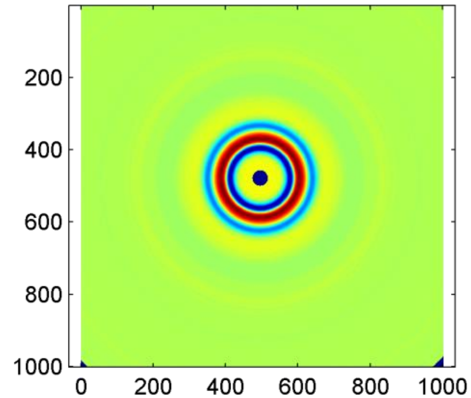
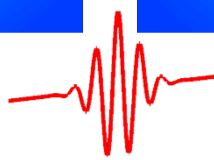


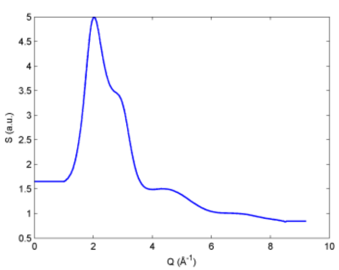
After



Before

Difference

$\Delta S_{XDS} = \Delta S_{Solute} + \Delta S_{Solvent} + \Delta S_{Cage}$



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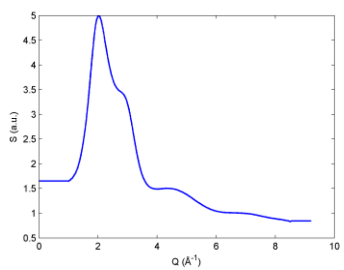

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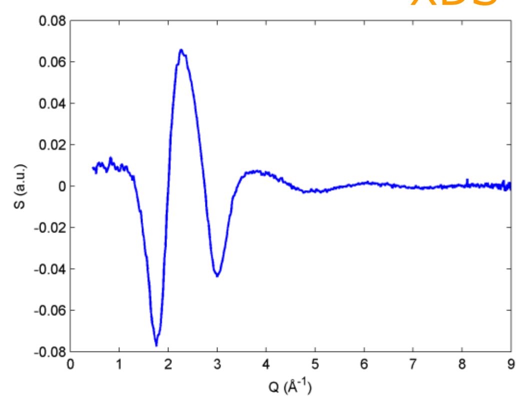


$$Q = \frac{4pi \cdot sin(\frac{2\theta}{2})}{\lambda}$$

Ru=Co dynamics @ SACLA

Worlds 2nd X-ray Free Electron Laser
1h from Osaka, 4h from Tokyo
500fs time resolution
Up to 20 KeV

The Experiment Team

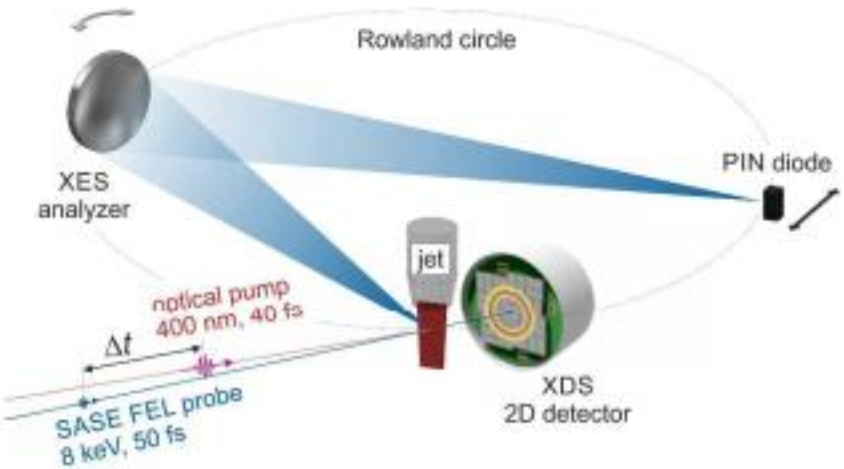
- PF-AR
- Budapest
- Lund Uni.
- DTU

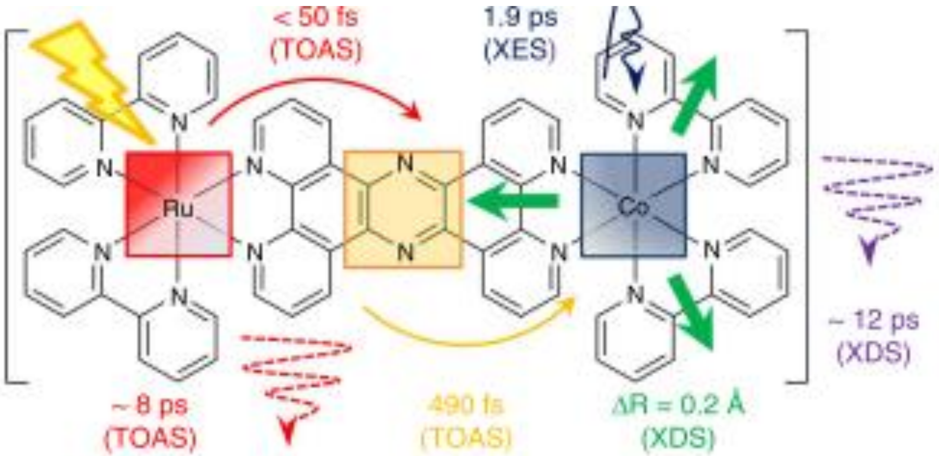
Solute dynamics, background:
Ru=Co dynamics following photo-excitation

$[(bpy)_2Ru^{II}(tpphz)^1Co^{III}(bpy)_2](PF_6)_5$

Prototypical molecule for intramolecular (pre-)catalysts

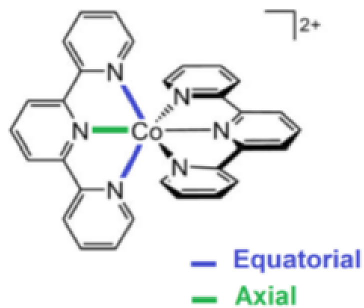
Challenge: Co centre is ”optically dark”, rendering full characterization difficult

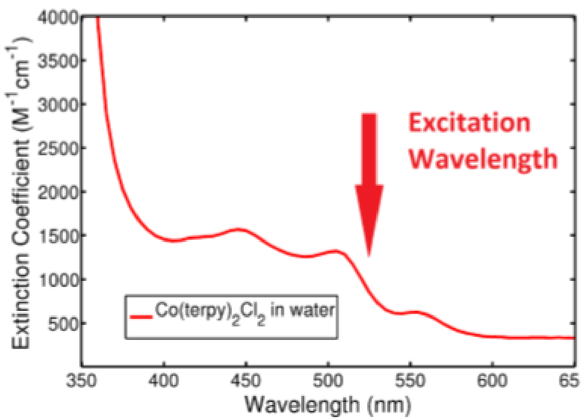


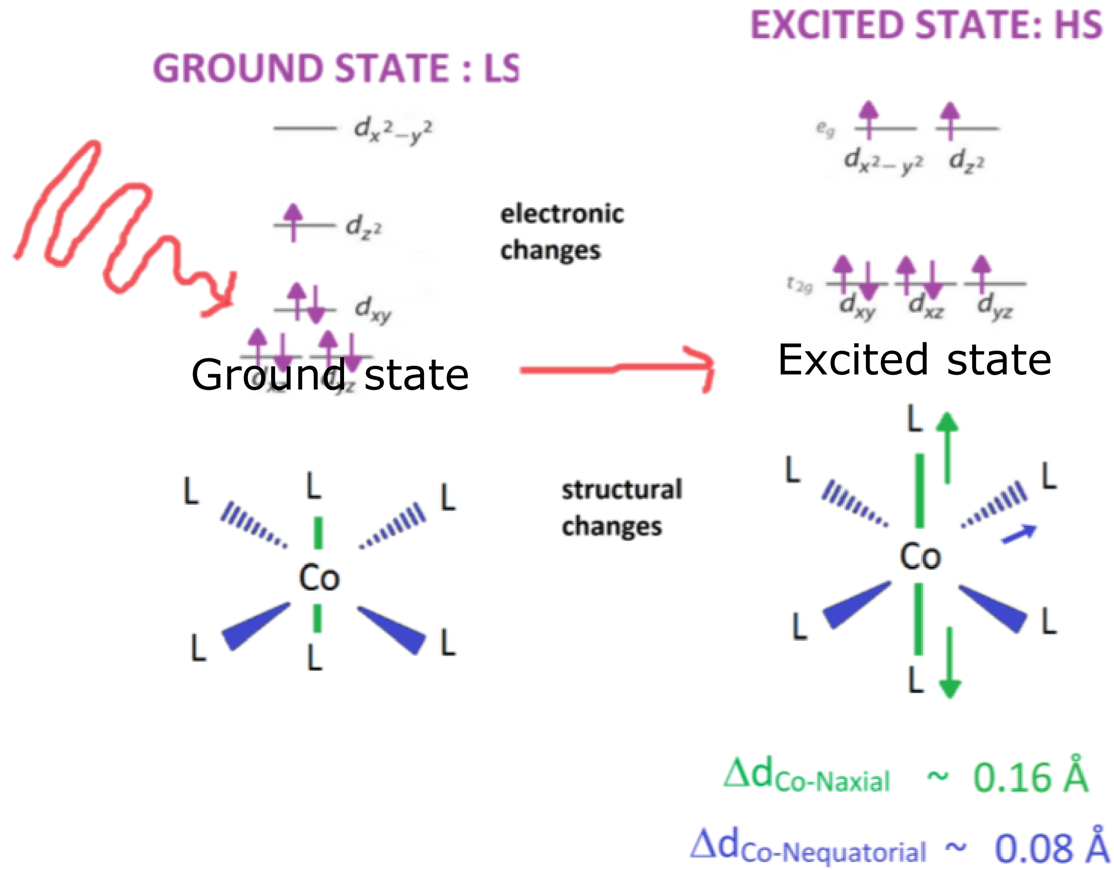


Canton, Kjær *et al* Nature Comm. 2015

Solute dynamics: A closer look at the structure of Cobalt-terpy at LCLS





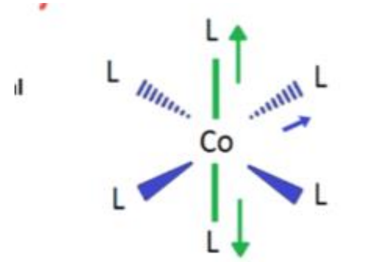


	LS	HS
$d_{\text{Co-Naxial}}$ (Å)	1.902	2.058
$d_{\text{Co-Nequatorial}}$ (Å)	2.08	2.16
η	0.91	0.95

DFT model of LS and HS structure as basis for solute structure model

Slide: E. Biasin

Results

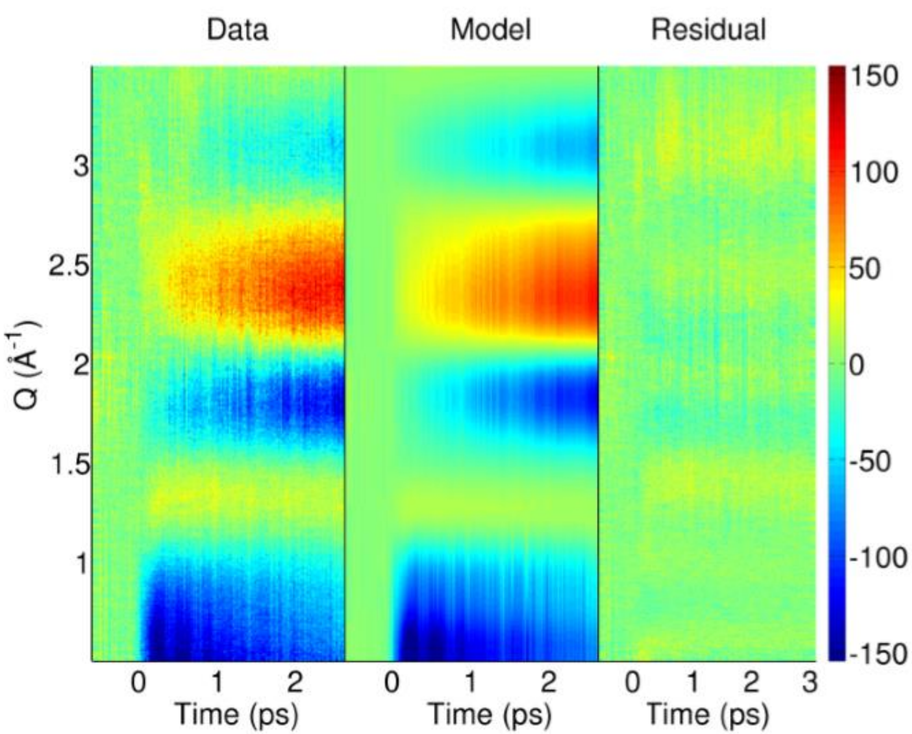


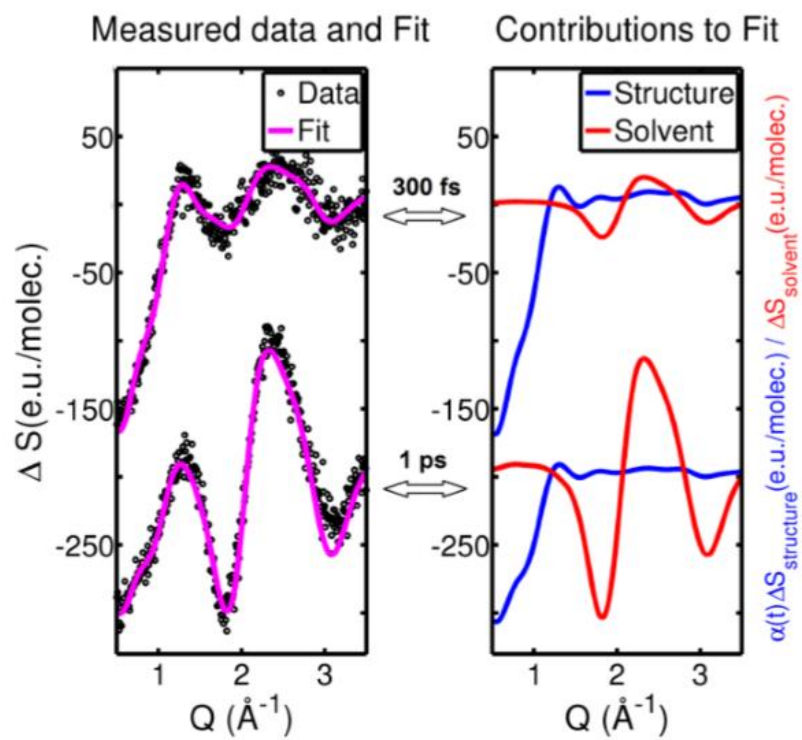
$\Delta d_{Co\text{-}Naxial} \sim 0.16$ Å

$\Delta d_{Co\text{-}Nequatorial} \sim 0.08$ Å

Solvent cage effects calculated by MD and included in the structural model of the solute

$$\Delta S_{model}(Q,t) = \alpha(t)\Delta S_{Structure}(Q, d_{Co-N}(t)) + \Delta T(t)\left.\frac{\partial S(Q)}{\partial T}\right|_{\rho}$$





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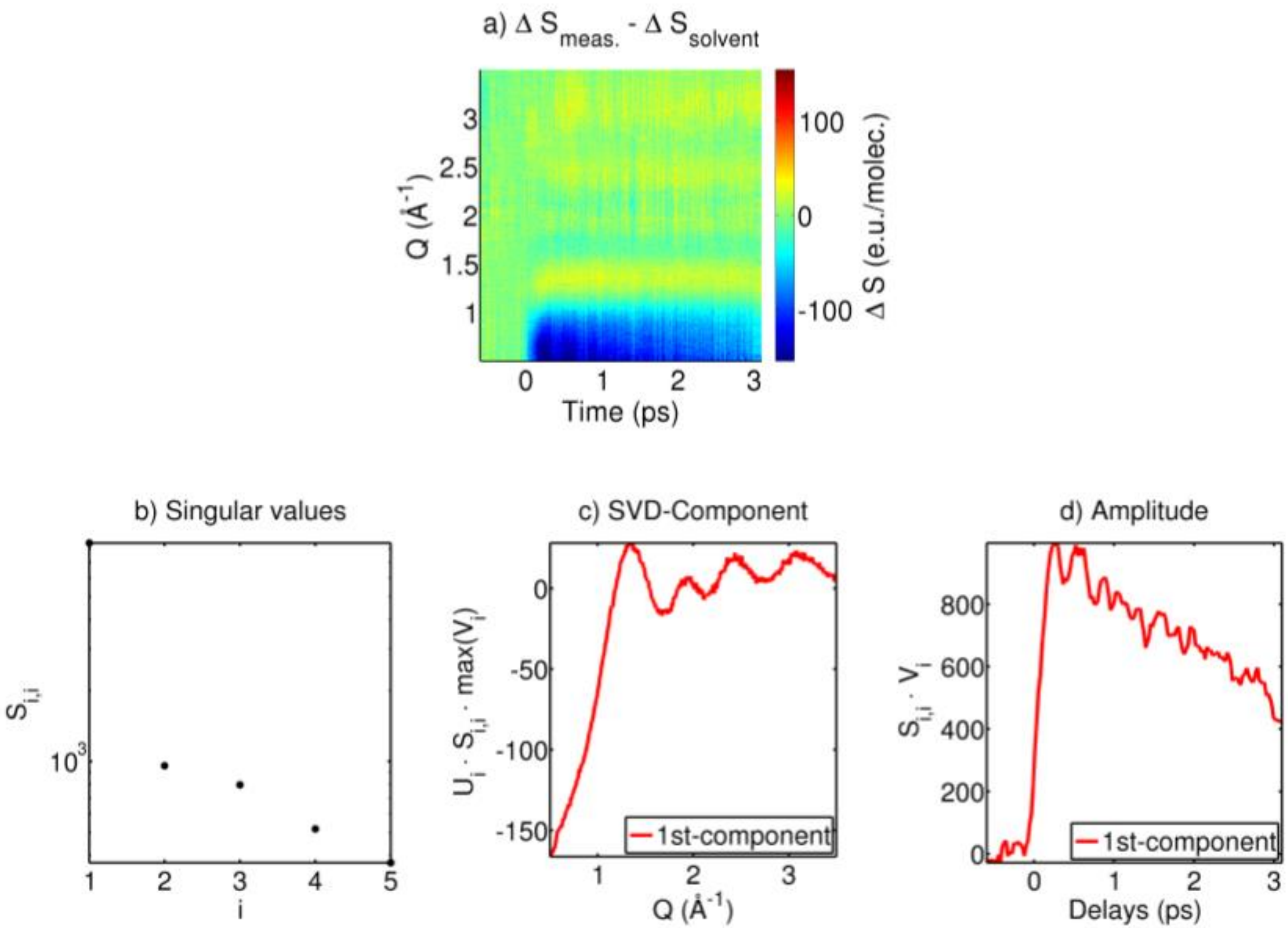
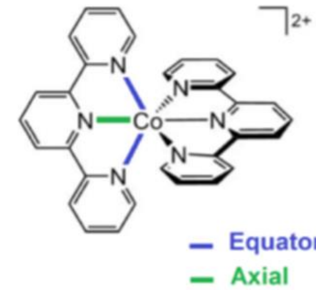
Slide: E. Biasin

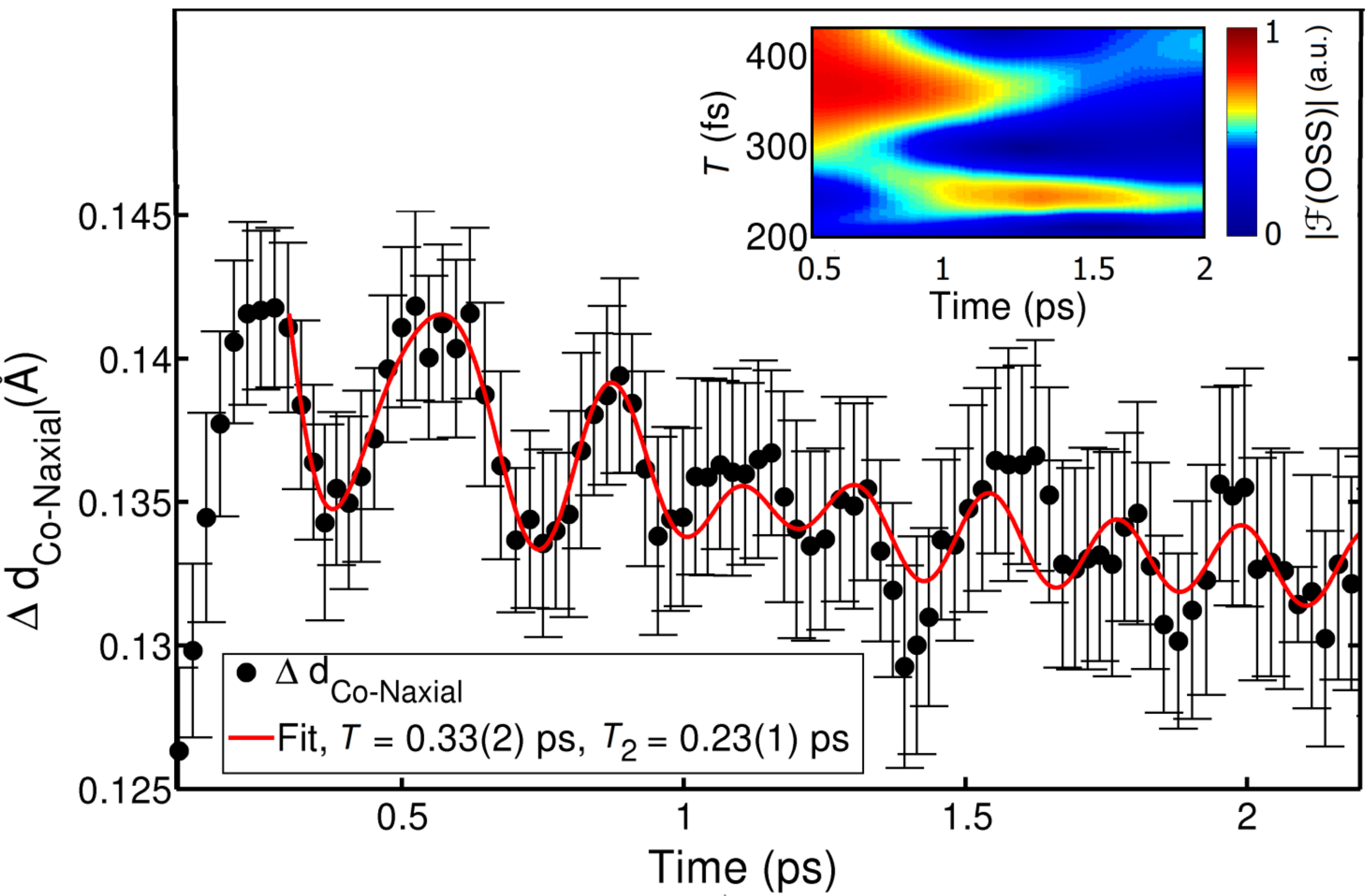
Subtracting the solvent 'background' – leaves the structural signal from the solute



Structural Dynamics

$$\Delta S_{model}(Q,t) = \alpha(t)\Delta S_{Structure}(Q, d_{Co-N}(t)) + \Delta T(t)\left.\frac{\partial S(Q)}{\partial T}\right|_{\rho}$$





excitation fraction: ~34%

elongation of the Co-N bonds:

0.13 Å axial

0.07 Å equatorial

coherently excited symmetric Co-N stretch mode

Period1: 0.33 ± 0.02 ps

Period1: 0.23 ± 0.01 ps

Damping time: ~0.6 ps

E. Biasin, PRL **117** (2016)

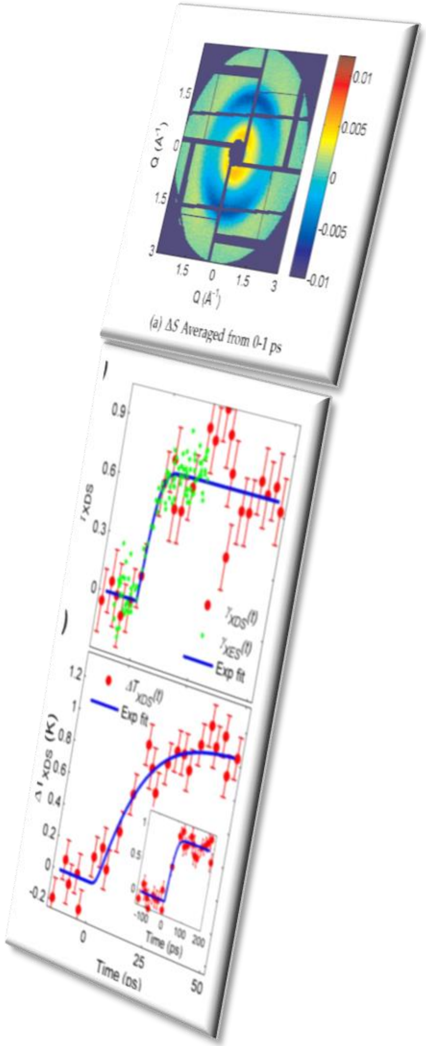
Summary and some thoughts

- New facilities
- Timeresolved experiments offer opportunities for investigating dynamics – something occuring out of equilibrium
  - ➢ track the structural evolution of molecules and 'see inside the reaction arrow'
  - ➢ Track effects of spin changes
  - ➢ Track charge transfer processes
  - ➢ Track the structural signatures of energy transfer from solute to solvent

➢ New Possibilities at XFEL.EU towards inverting XDS data

- ➢ Higher X-ray energies -> larger q-range -> discerning models
- ➢ High reprate -> thinner or more dilute samples -> use X-ray species?

➢ Need a faster route from *measurements* to *results*



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Zoltan Nemeth

Pulse, SLAC

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Klaus Møller

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Gialuca Levi

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Thank you for your attention