PAUL SCHERRER INSTITUT

Wir schaffen Wissen – heute für morgen

Paul Scherrer Institut

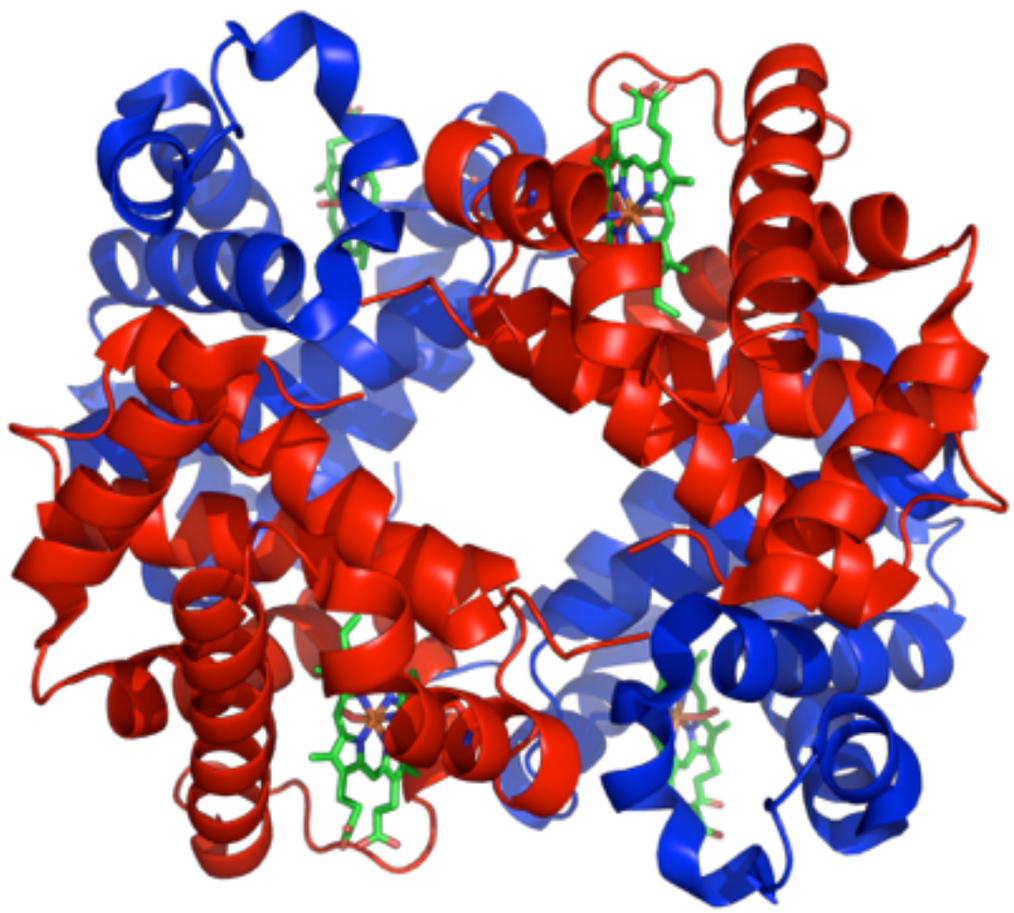
Chris Milne

XFEL techniques and instrumentation (time-resolved spectroscopy)

Is function structure or dynamics ?

Structure

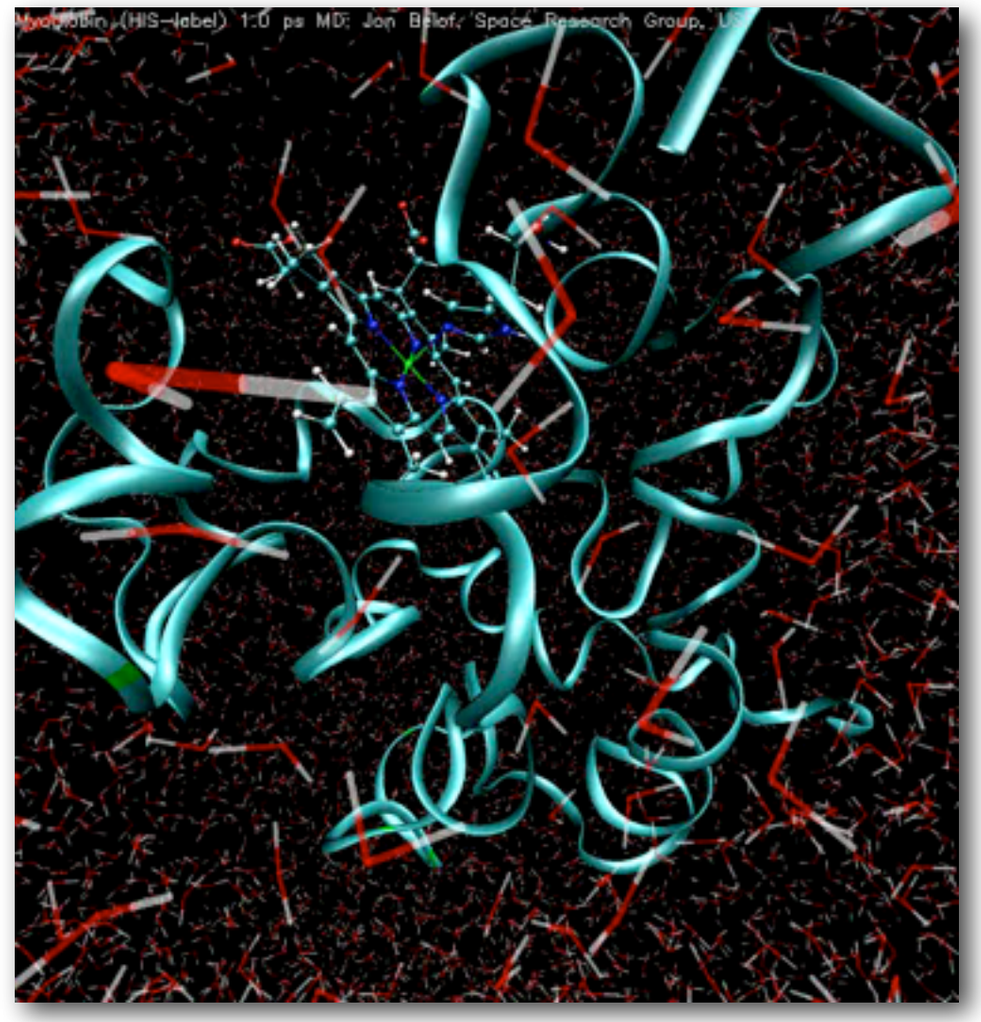
- X-ray crystallography
- electron microscopy
- atomic force microscopy
- electron diffraction
- X-ray absorption spectroscopy
- NMR



Protein structure of human hemoglobin in the T-state with oxygen bound at all 4 hemes (from PDB 1GZX Wikipedia)

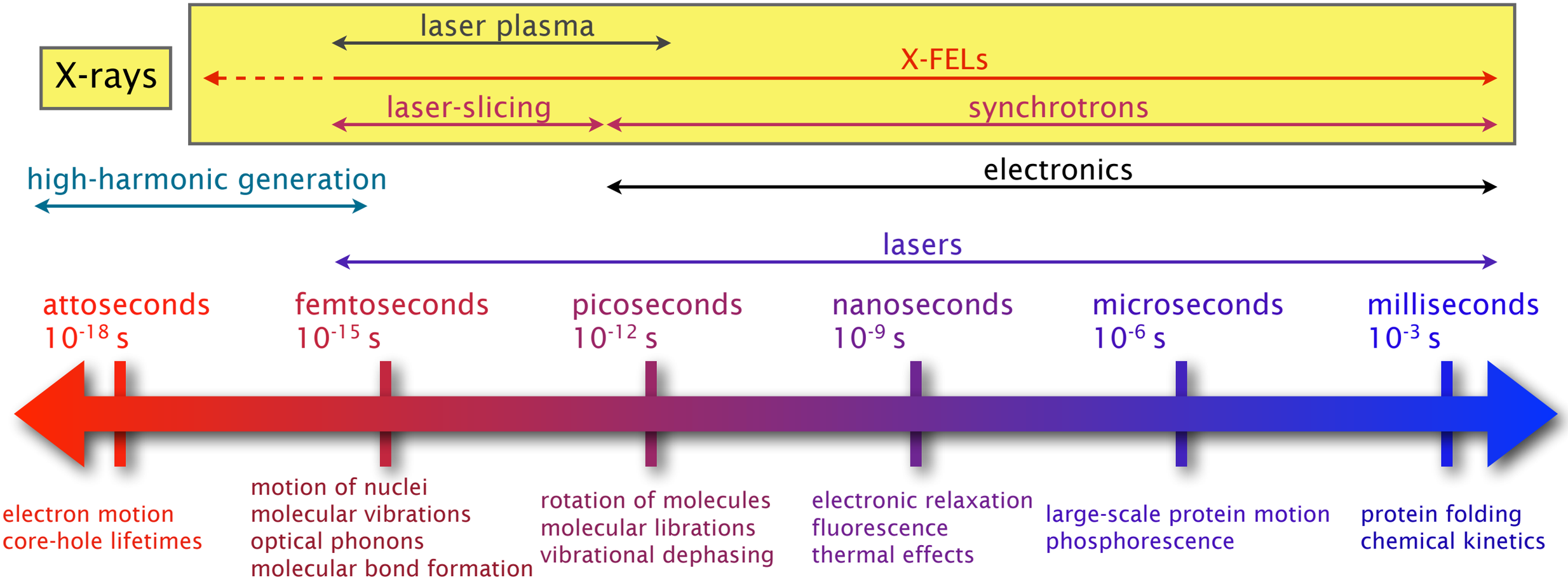
Dynamics

- Laser spectroscopy
- NMR
- time-resolved diffraction
- X-ray absorption spectroscopy



Rotating hydrated myoglobin molecule
http://uweb.cas.usf.edu/chemistry/faculty/space/
B. Space & J. Belof (University of South Florida)

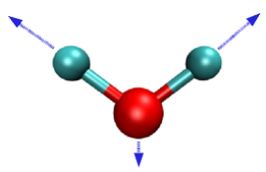
On what timescale do we want to measure structure ?

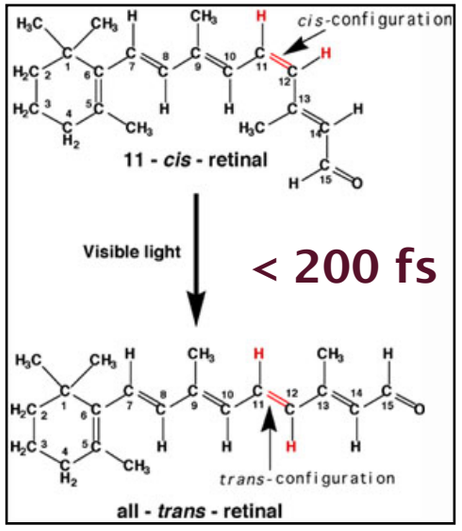


110 as delay between electron emission from conduction band and lower-lying states in Tungsten upon irradiation

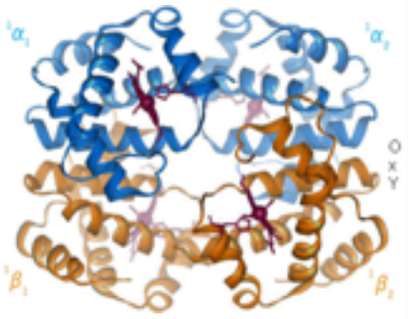
The Fe K-edge core-hole lifetime is **4 fs**

period of the symmetric stretch in H_2O is **10 fs**





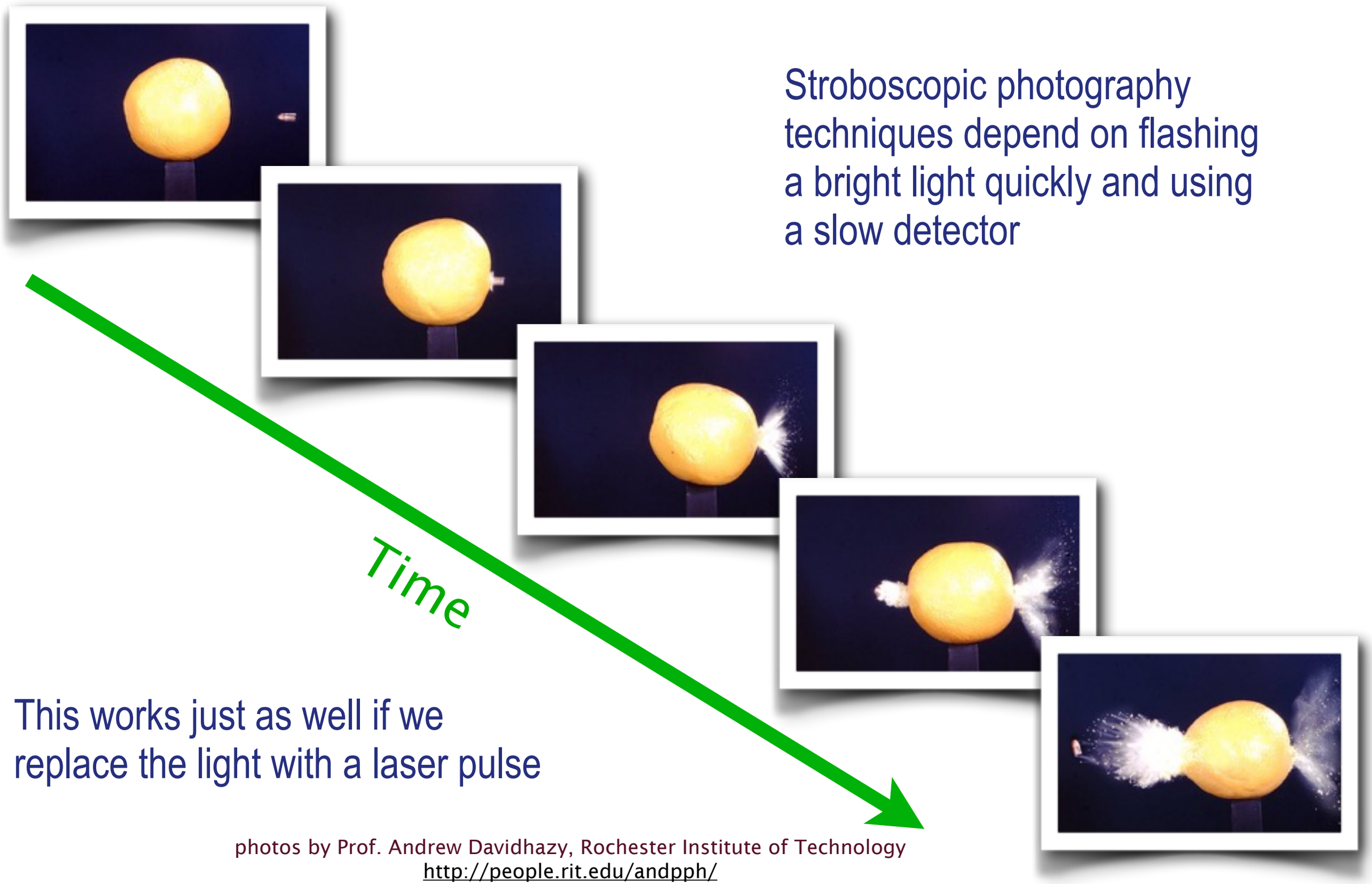
Hemoglobin R→T transition takes **microseconds**



Camera shutter speeds range from **ms** through to **seconds**

Hb animation from Wikipedia

How do we measure fast things ?



Stroboscopic photography techniques depend on flashing a bright light quickly and using a slow detector

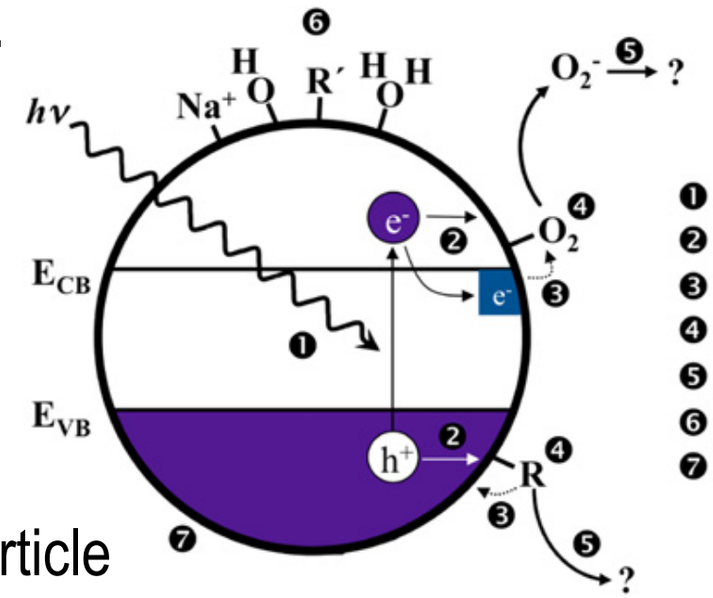
This works just as well if we replace the light with a laser pulse

photos by Prof. Andrew Davidhazy, Rochester Institute of Technology
http://people.rit.edu/andpph/

What are we interested in ?

Photocatalysis and energy conversion

Metal-oxide nanoparticles are commonly used in dye-sensitized solar cells (DSSCs) and as photocatalysts

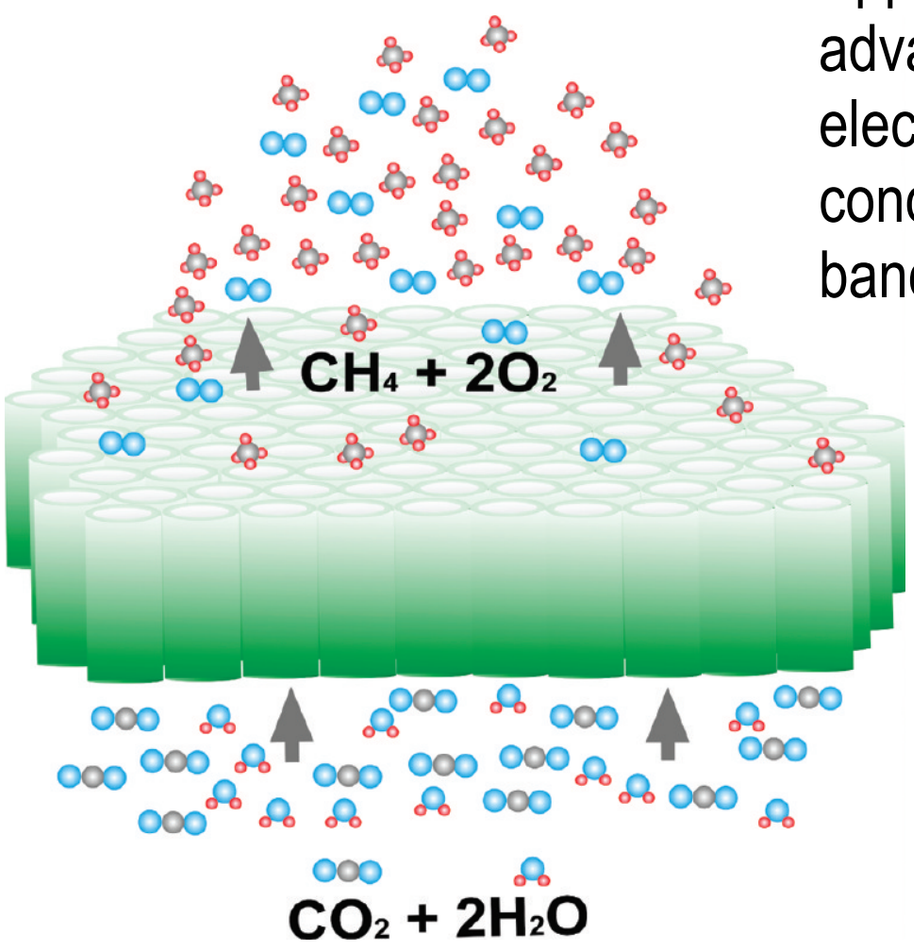


M. Henderson *Surf. Sci. Rep.* **66**, 185 (2011)

Important issues

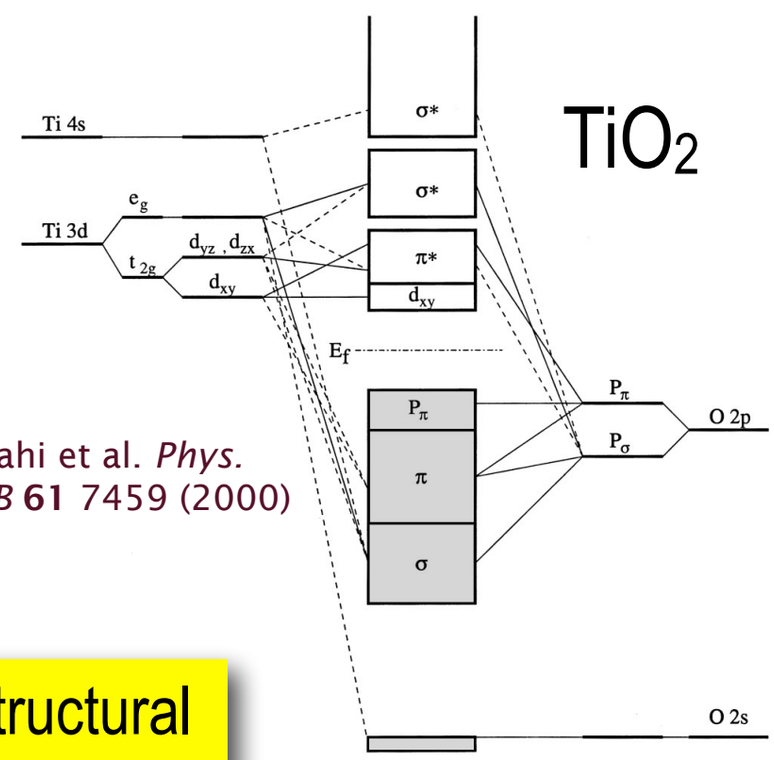
1. excitation
2. charge transport and trapping
3. charge transfer
4. molecular adsorption
5. reaction mechanisms
6. poisons and promoters
7. surface and material structure

Applications take advantage of an electron/hole in the conduction/valence band of the nanoparticle

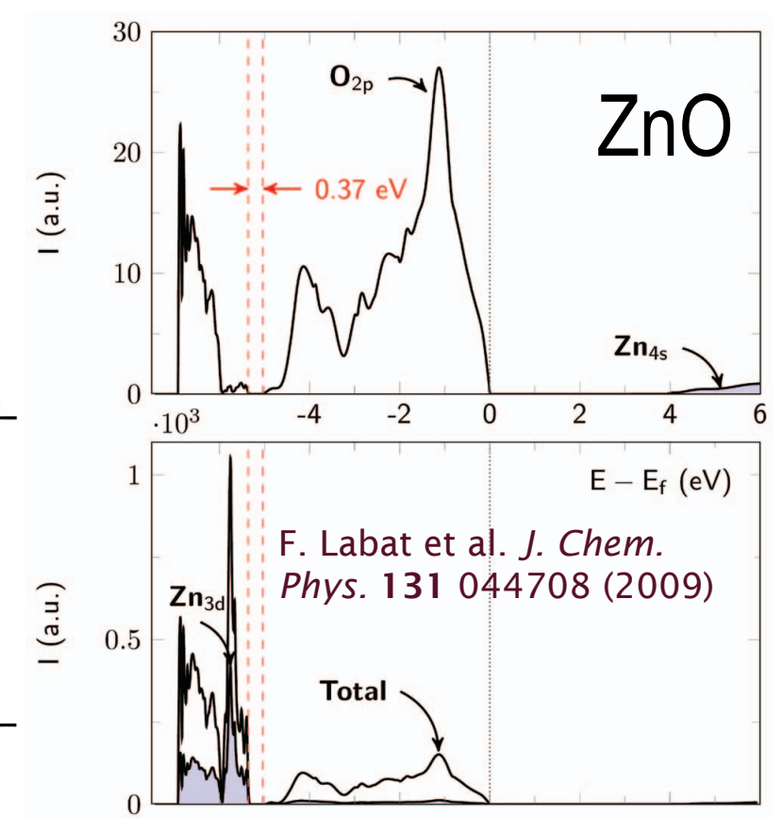


S.C. Roy et al. *ACS Nano* **4**, 1259 (2010)

Valence and conduction bands have distinct atomic character



R. Asahi et al. *Phys. Rev. B* **61** 7459 (2000)

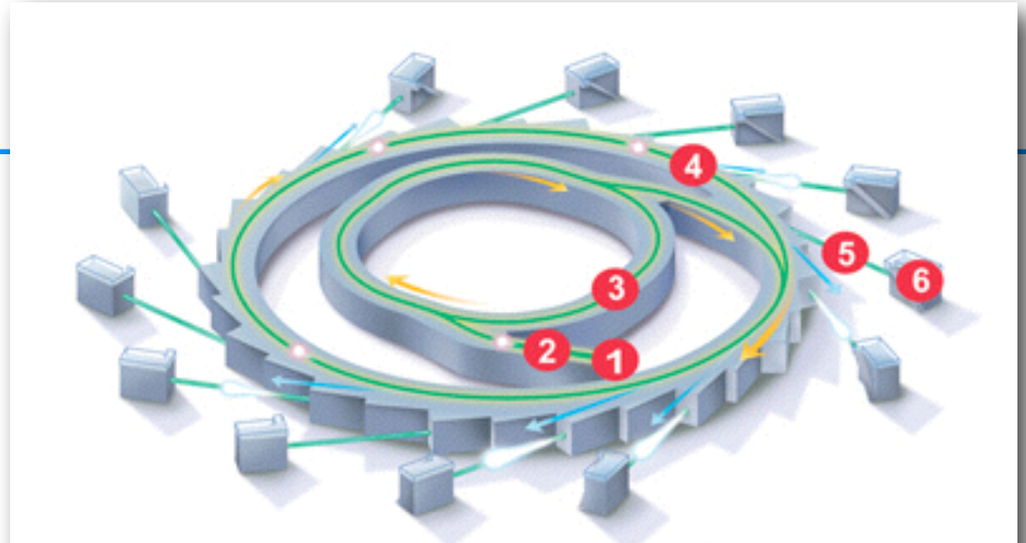


F. Labat et al. *J. Chem. Phys.* **131** 044708 (2009)

We want time-resolved electronic and structural information on these systems as they function

Introducing the X-ray techniques

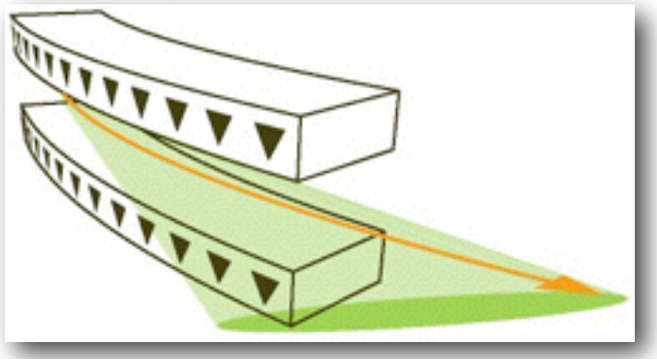
Swiss Light Source

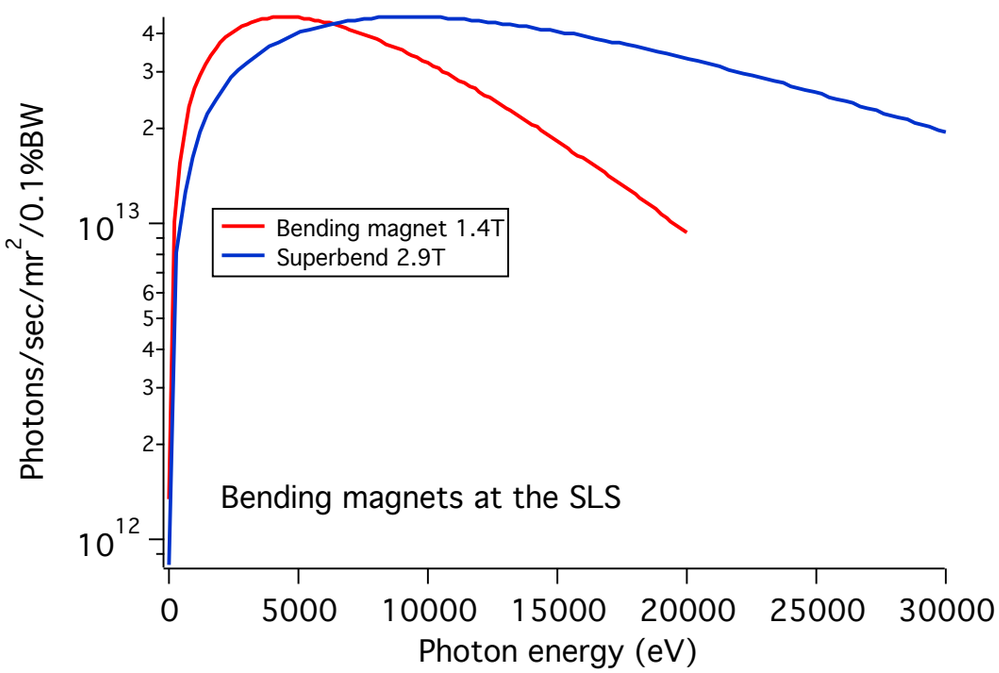


http://www.synchrotron.org.au/content.asp?Document_ID=97

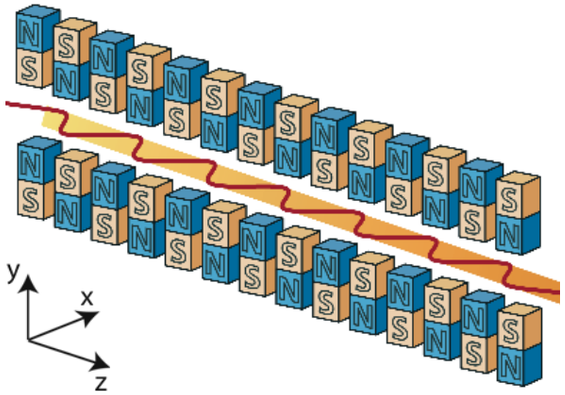
There are two methods of generating light at a 3rd-generation storage ring source (synchrotron)

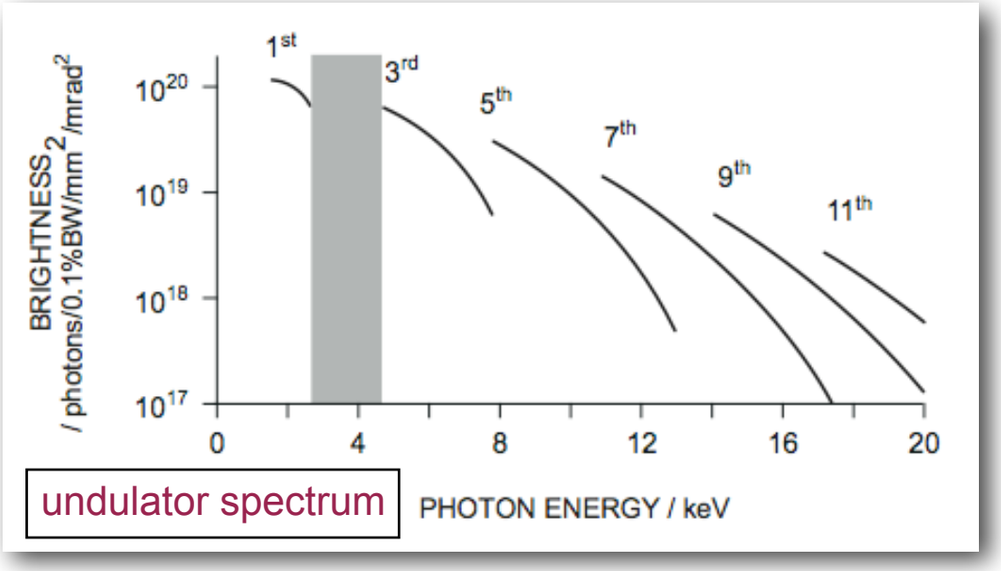
Bending magnet



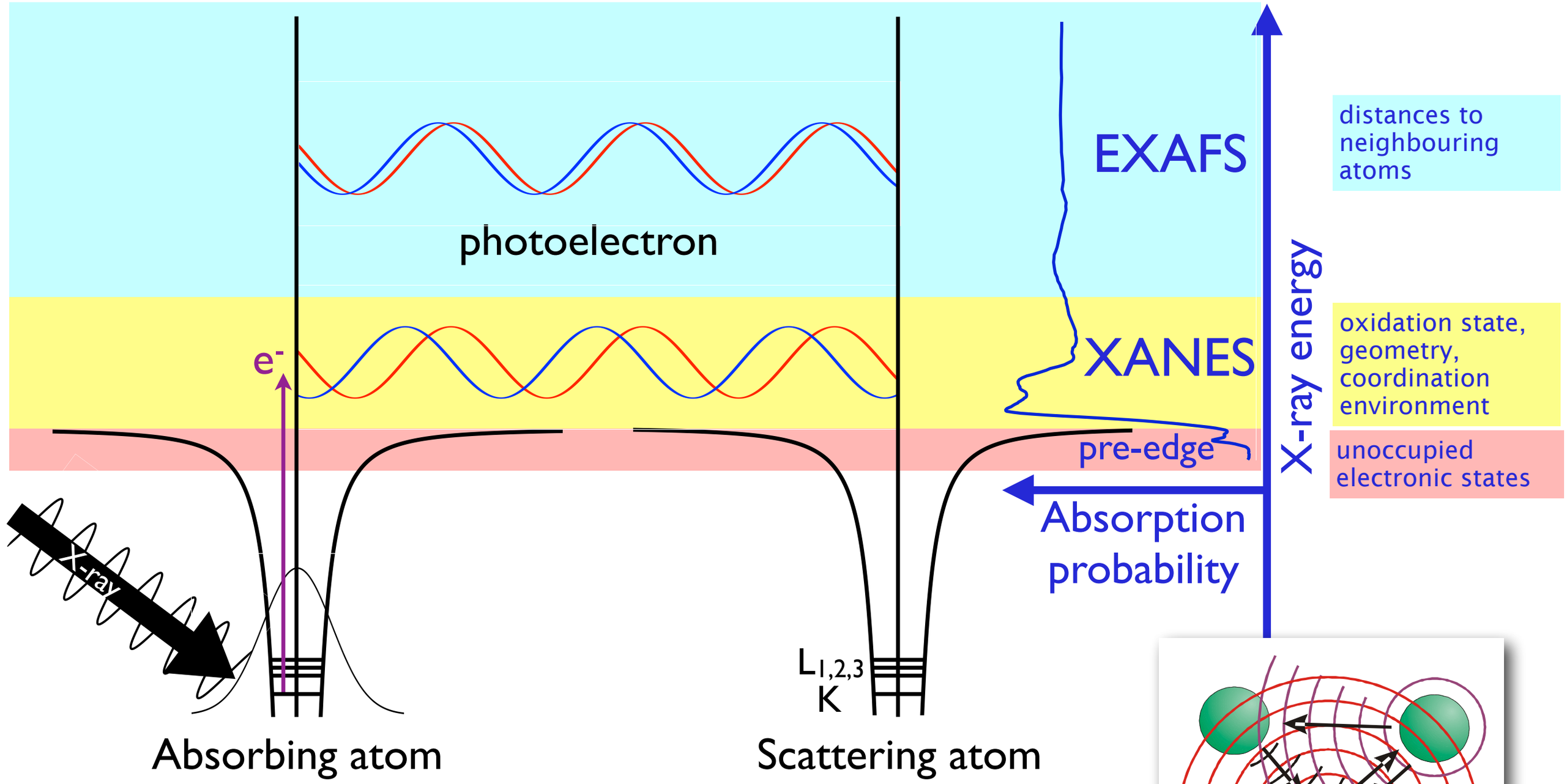


Wiggler/Undulator





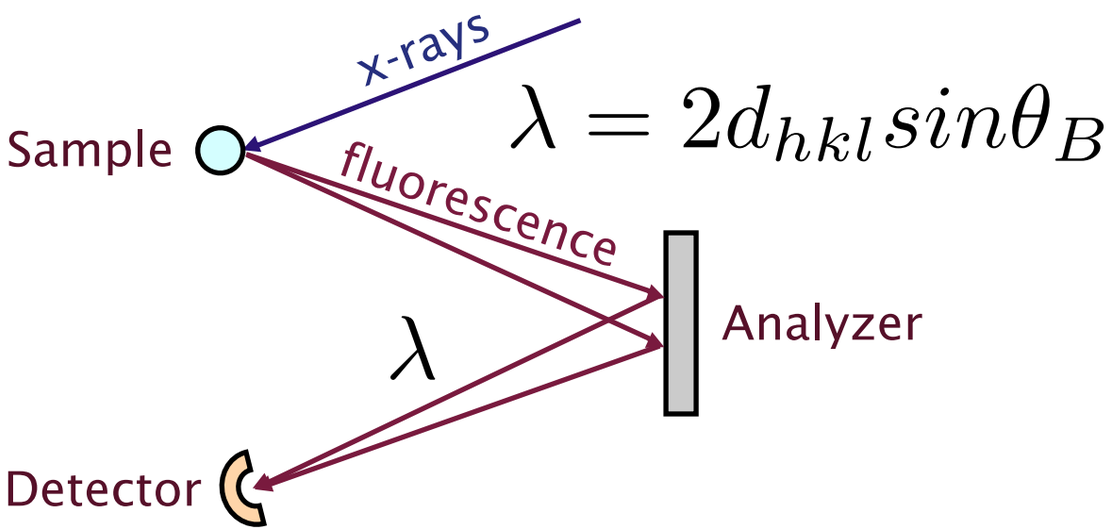
X-ray absorption: Retrieving local structure



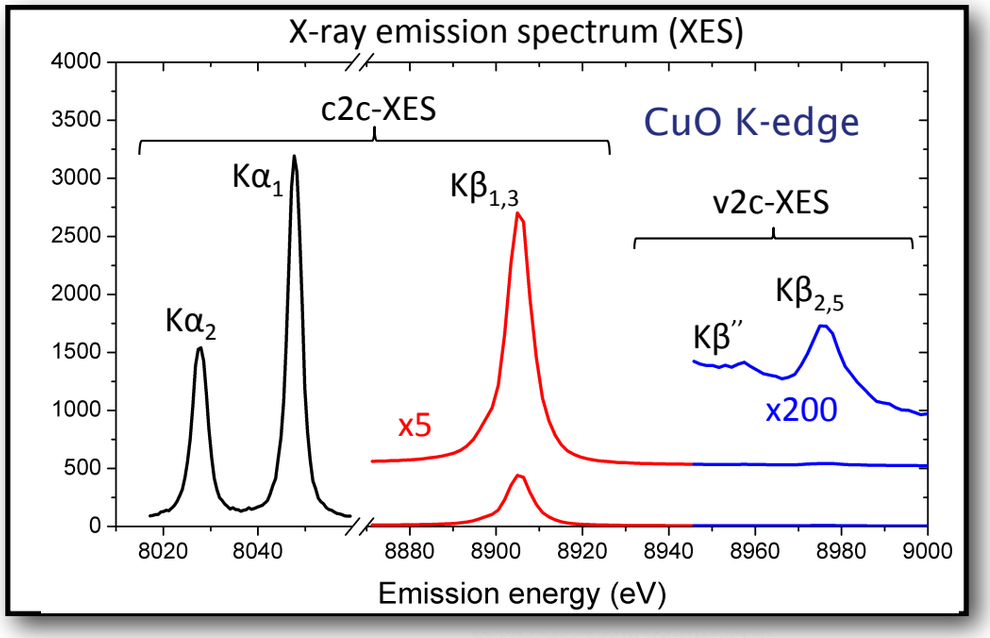
X-ray absorption gives information on the unoccupied electronic states and the local structure

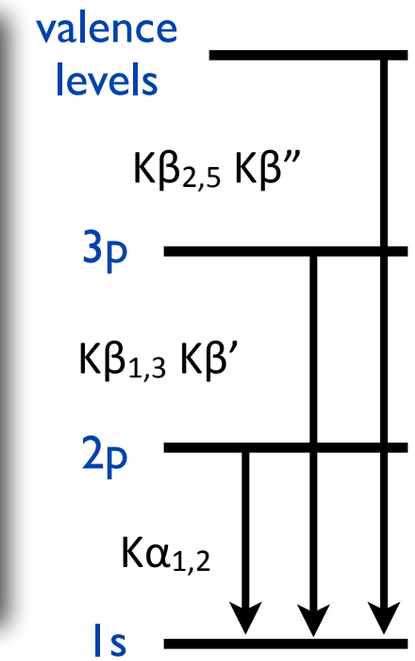
C.J. Milne, T.J. Penfold & M. Chergui *Coord. Chem. Rev.* **277**, 44 (2014)

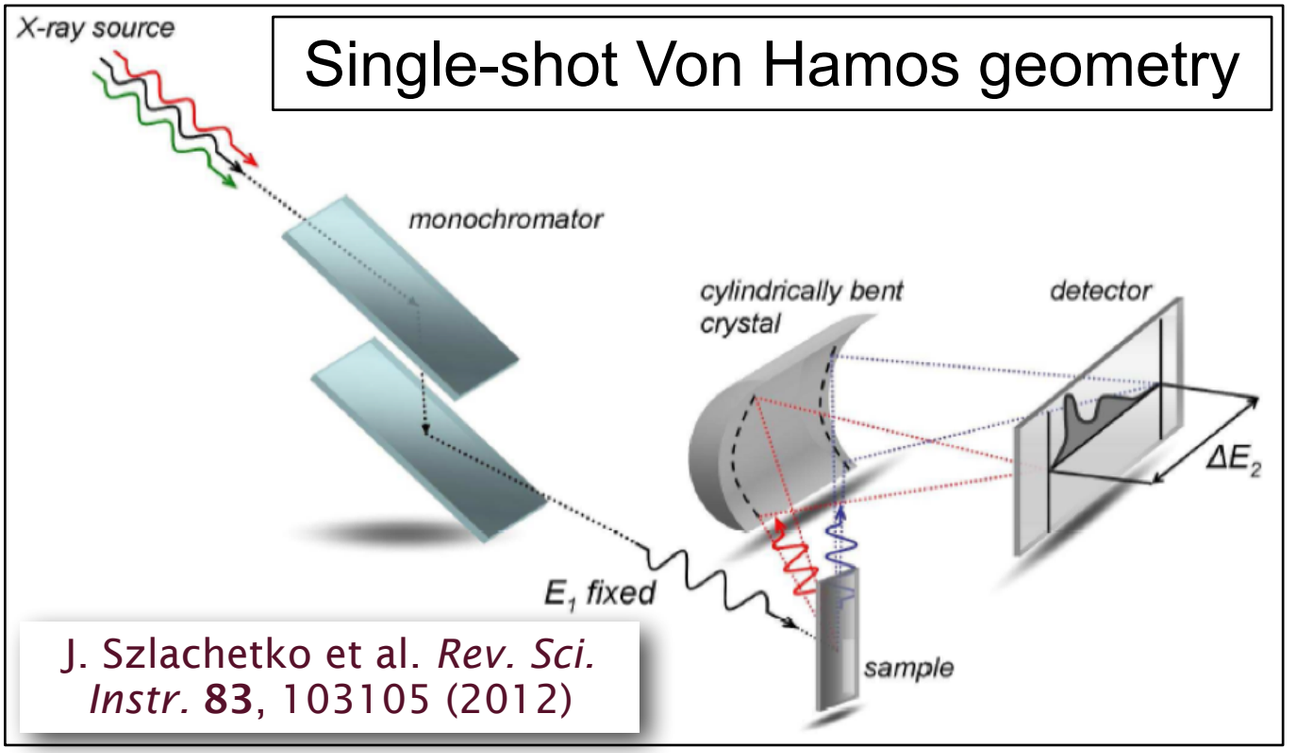
X-ray emission: Retrieving electronic information



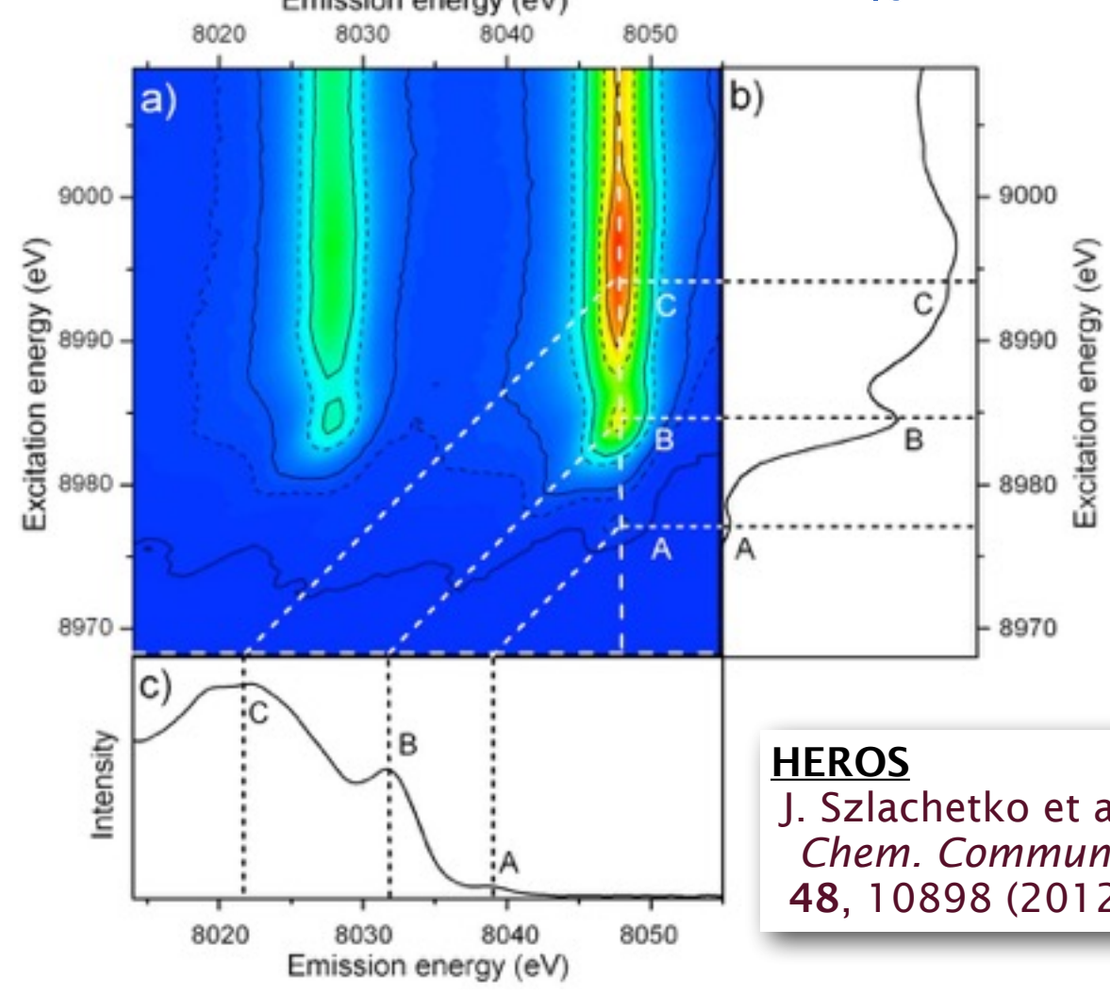
P. Glatzel et al. *Coord. Chem. Rev.* **249**, 65 (2005)
G. Vankó et al. *JPCB* **110**, 11647 (2006)







J. Szlachetko et al. *Rev. Sci. Instr.* **83**, 103105 (2012)



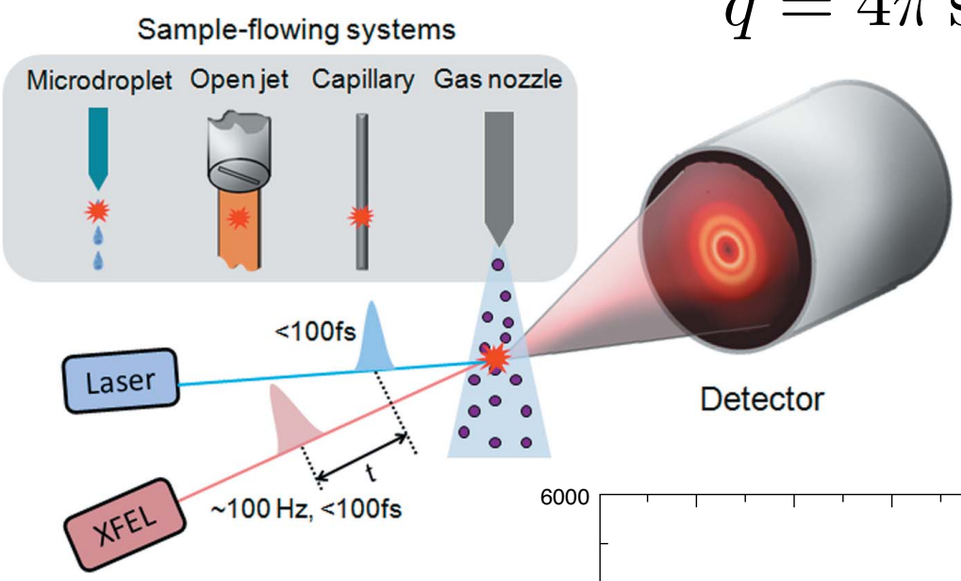
HEROS
J. Szlachetko et al. *Chem. Commun.* **48**, 10898 (2012)

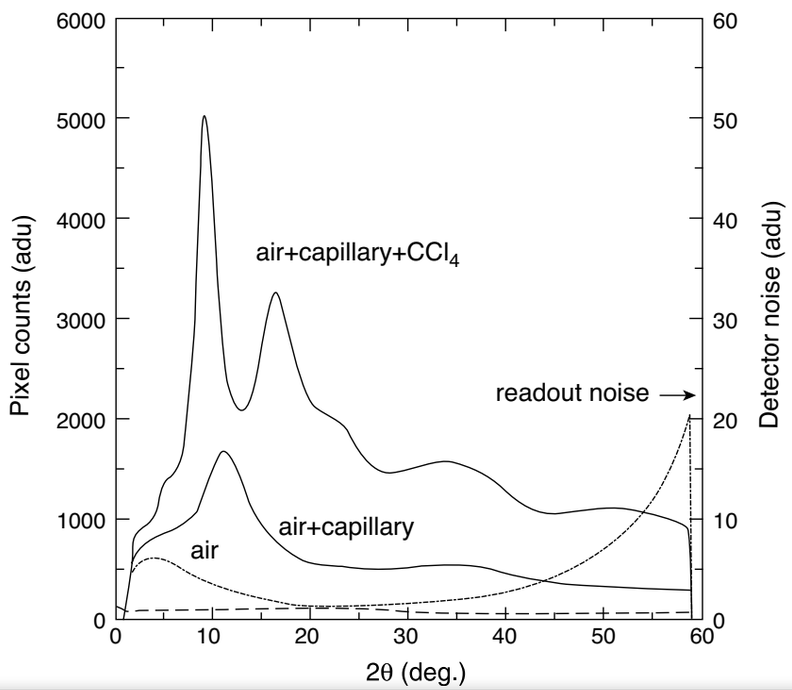
X-ray emission gives information on the occupied electronic states

X-ray scattering: Retrieving local and global structure

X-ray scattering is sensitive to all the atoms in the sample

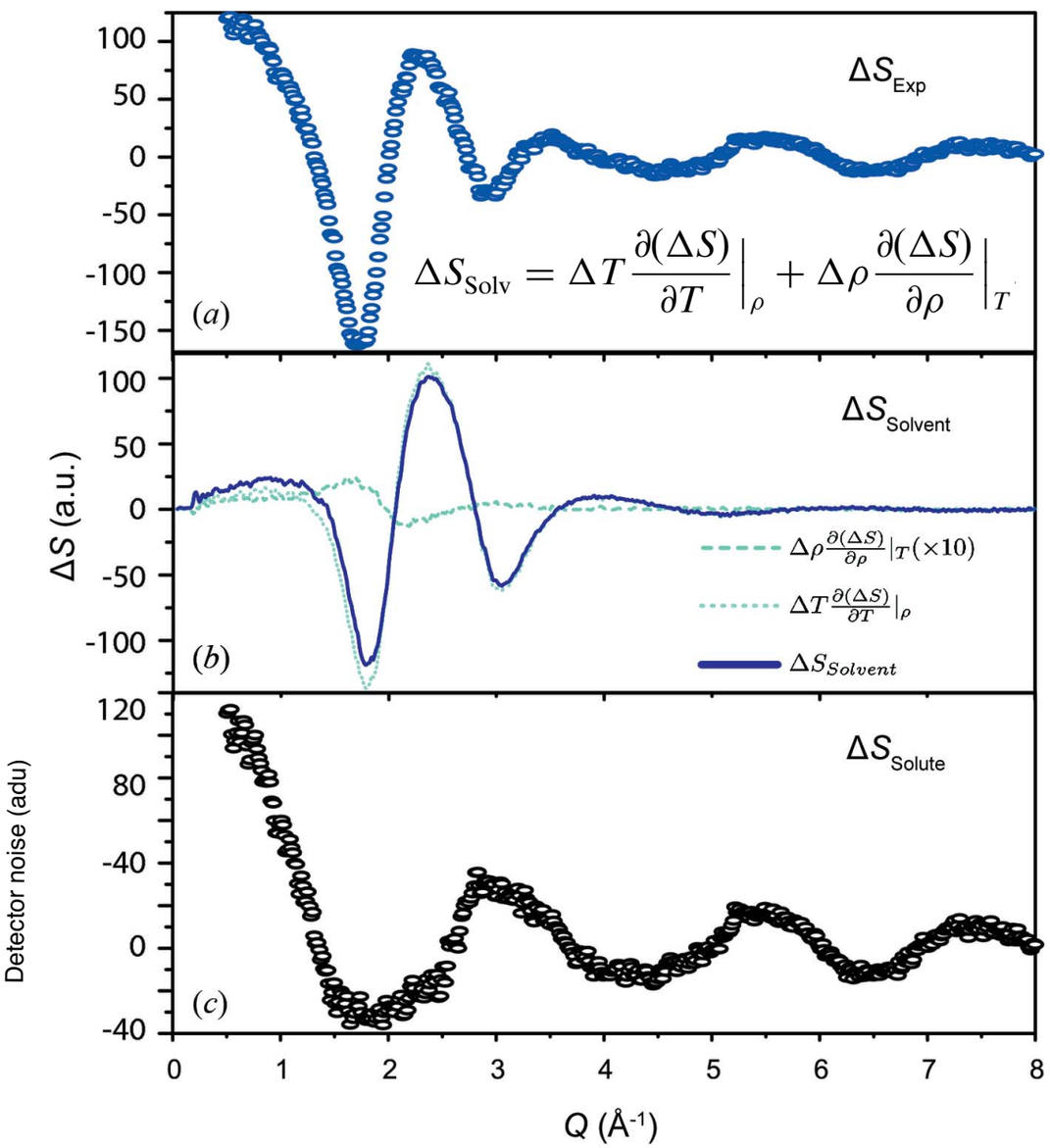
$$q = 4\pi \sin\theta/\lambda$$





- S. Bratos and M. Wulff *Adv. Chem. Phys.* **131**, 1 (2008)
- J. Kim et al. *Acta. Cryst. A* **66**, 270 (2010)

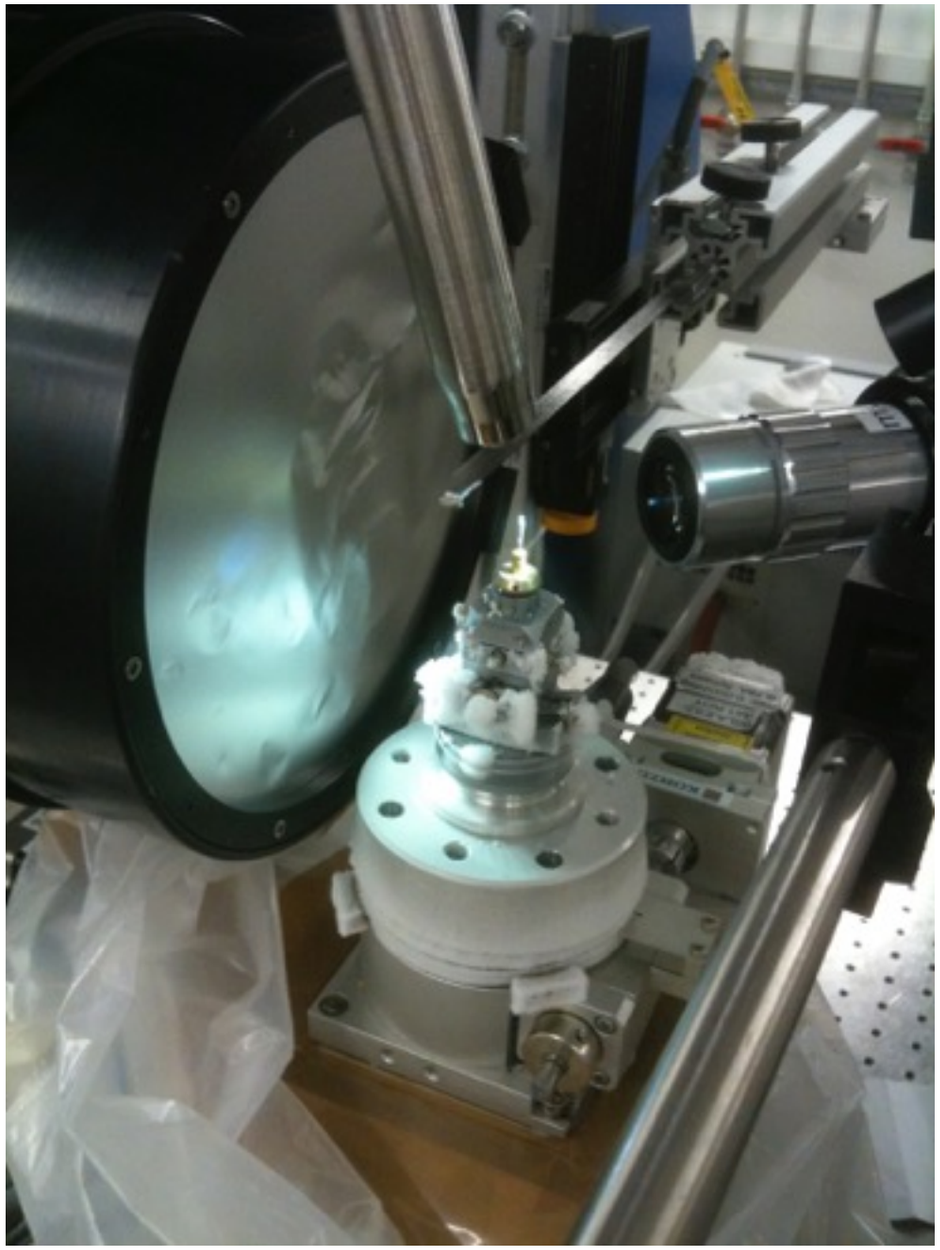
K. Haldrup et al. *Acta. Cryst.* **A66**, 261 (2010)

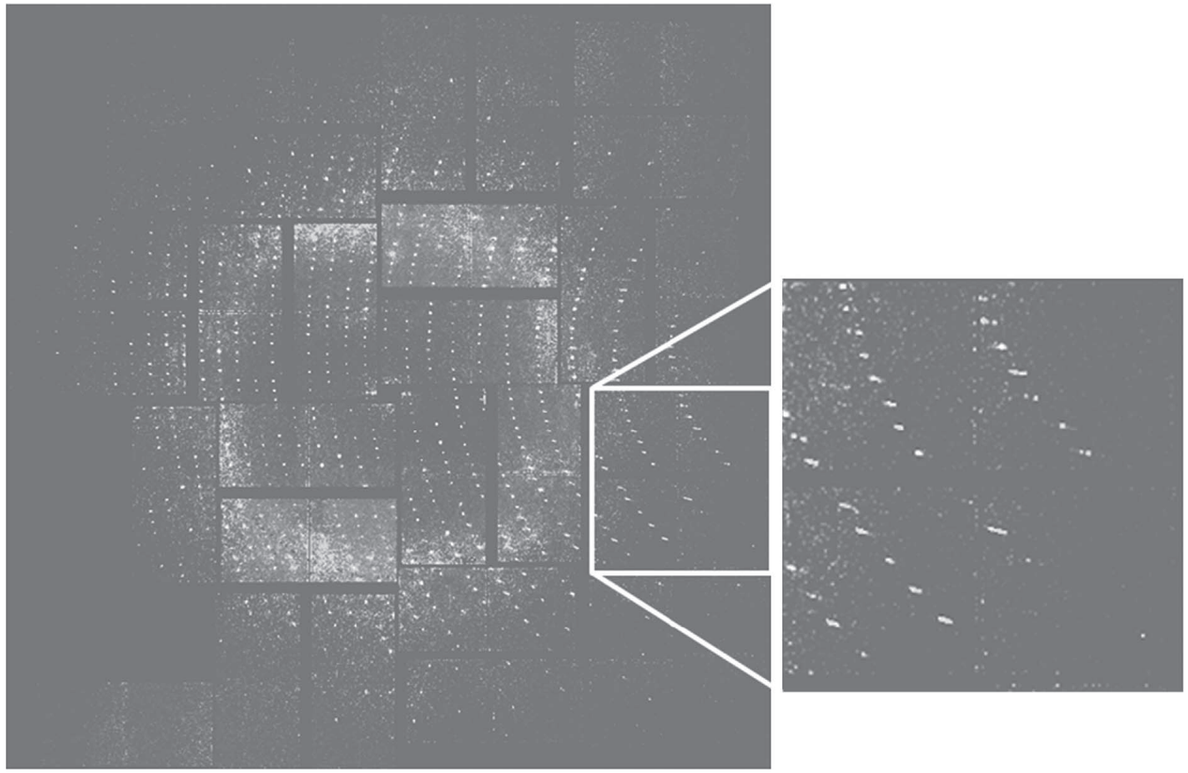


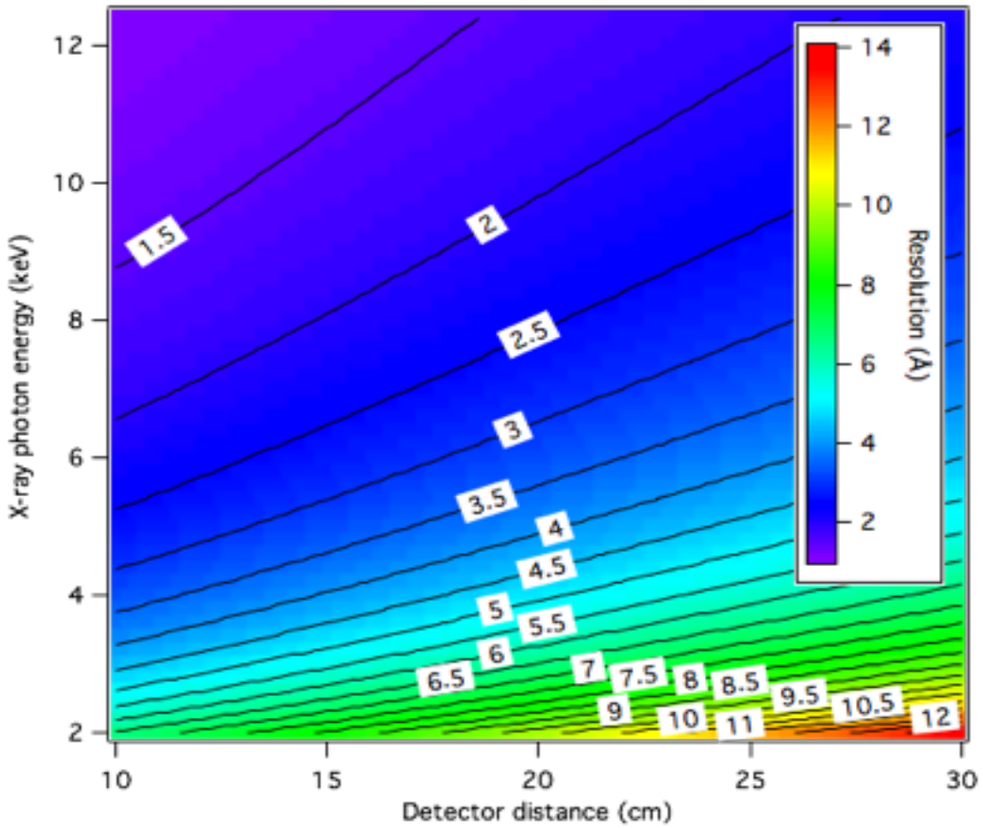
X-ray scattering gives information on relative atomic positions of all atoms in the sample

You can retrieve the pair distribution function, giving the distances between two atoms in the sample

X-ray diffraction: Retrieving atomic-scale structure



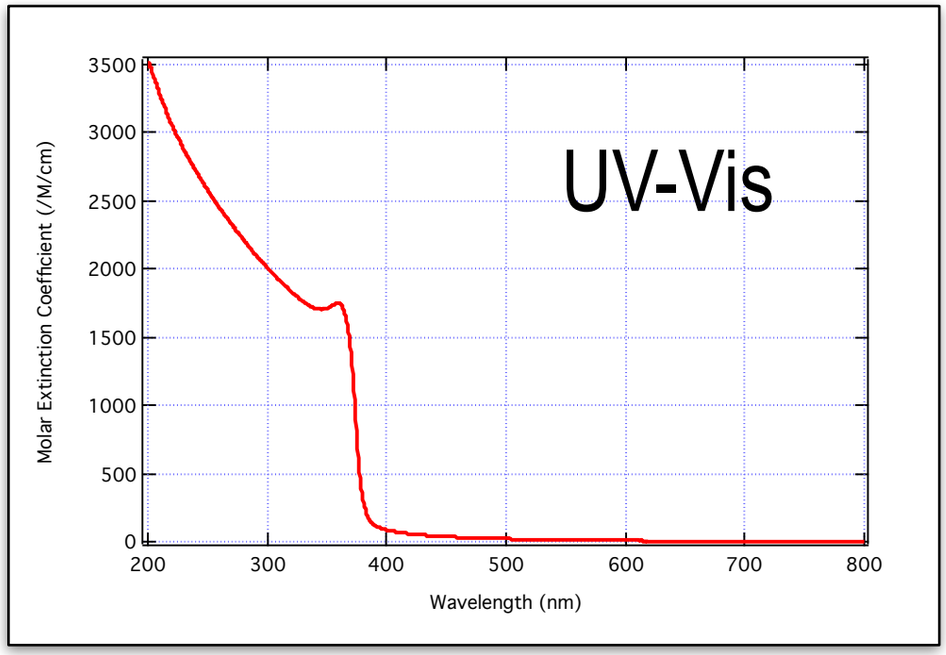




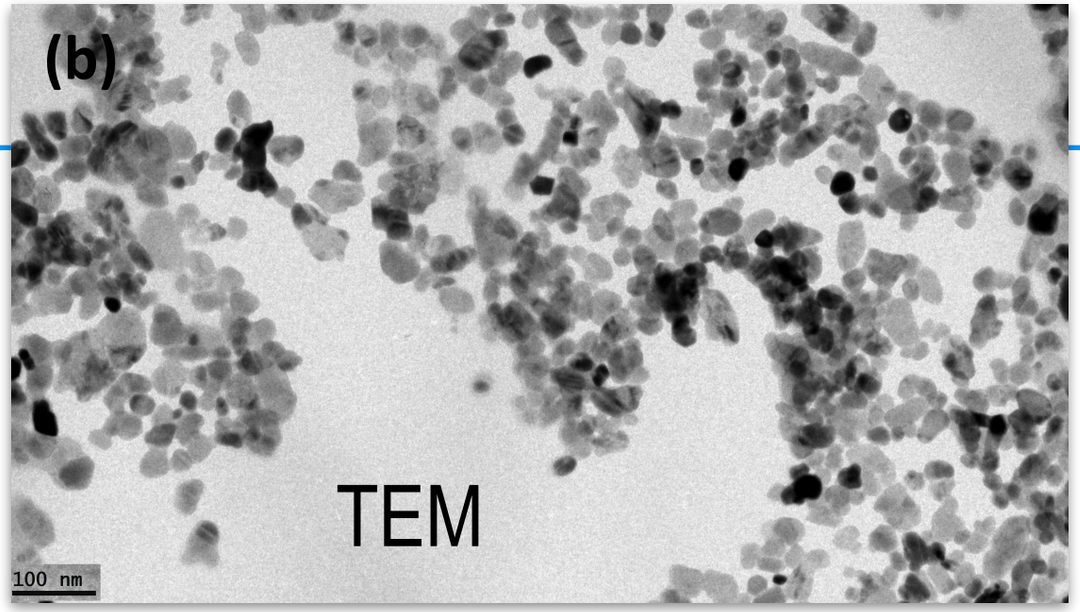
X-ray diffraction gives information on the atomic positions of all atoms in the crystal with Ångstrom accuracy

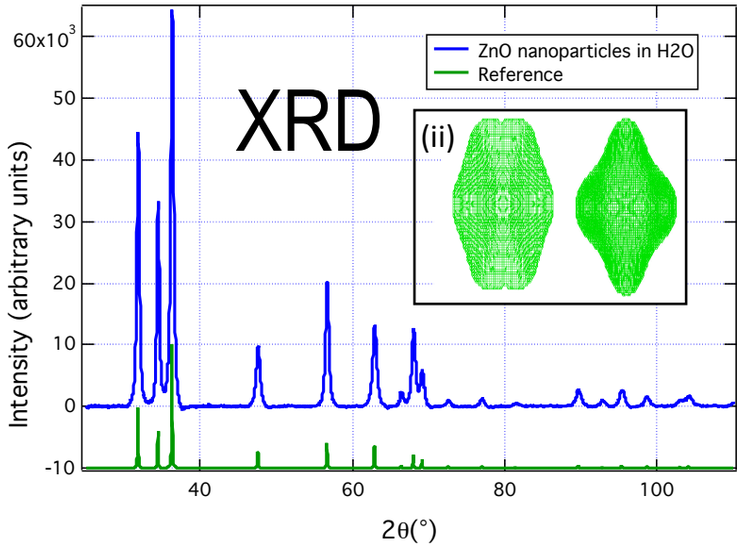
Application to a photoactive material

Colloidal ZnO sample details



Commercial sample of ~35 nm ZnO nanoparticles suspended in water



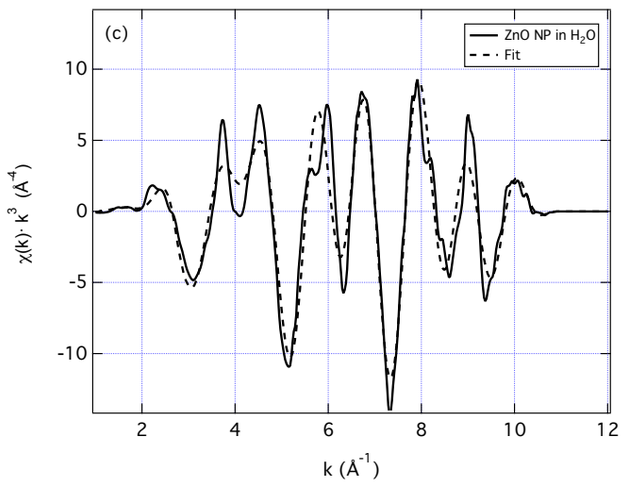


	ZnO NP in H_2O
Radius (nm)	16(2)
a	3.2500(1)
c	5.2087(1)
$\Delta(z)$	0.3816(4)
$N(O)/N(Zn)$	0.990(1)
R-factor	1.29

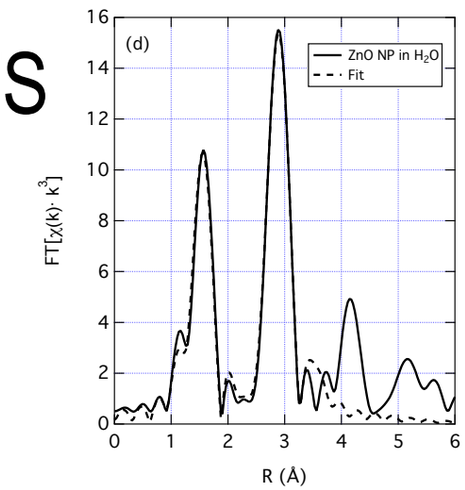
T. Rossi et al. *JPC C* **118** 19422 (2014)

Results

- 32 nm diameter
- presence of both O and Zn vacancies



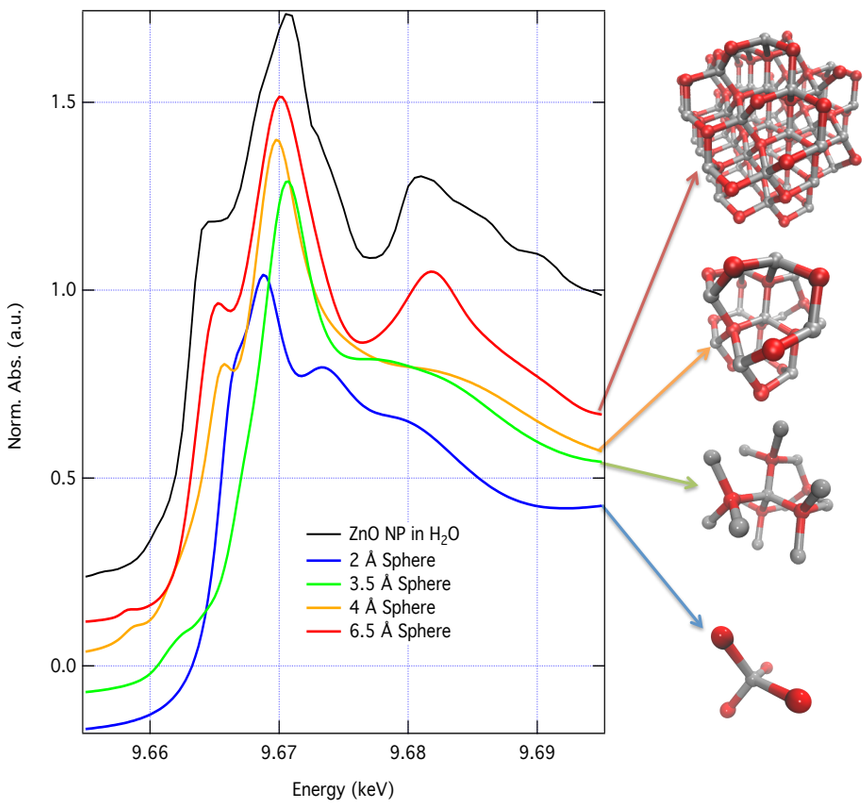
EXAFS

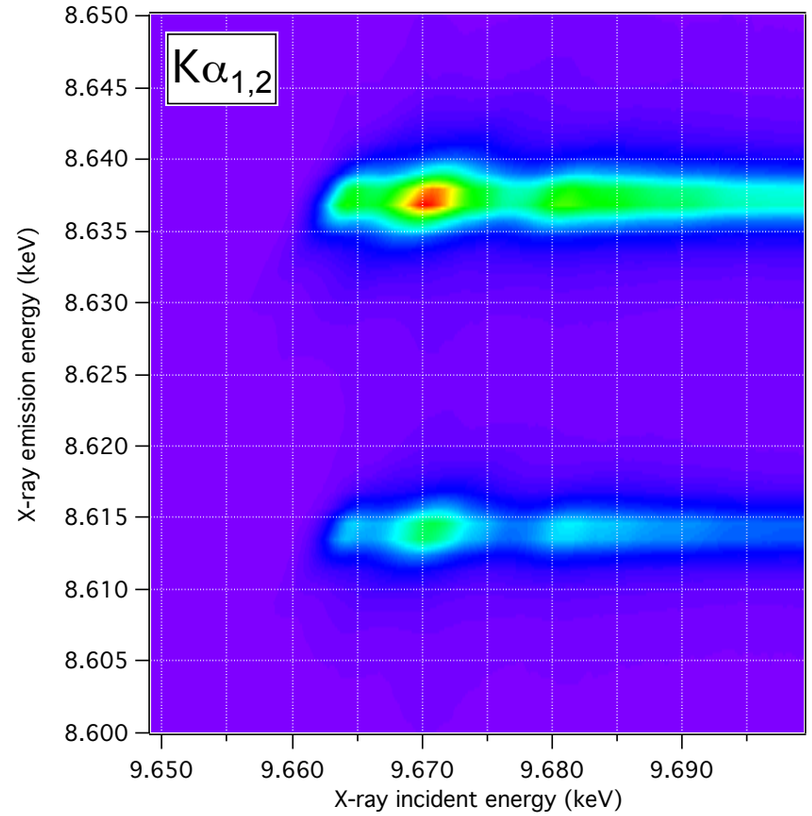


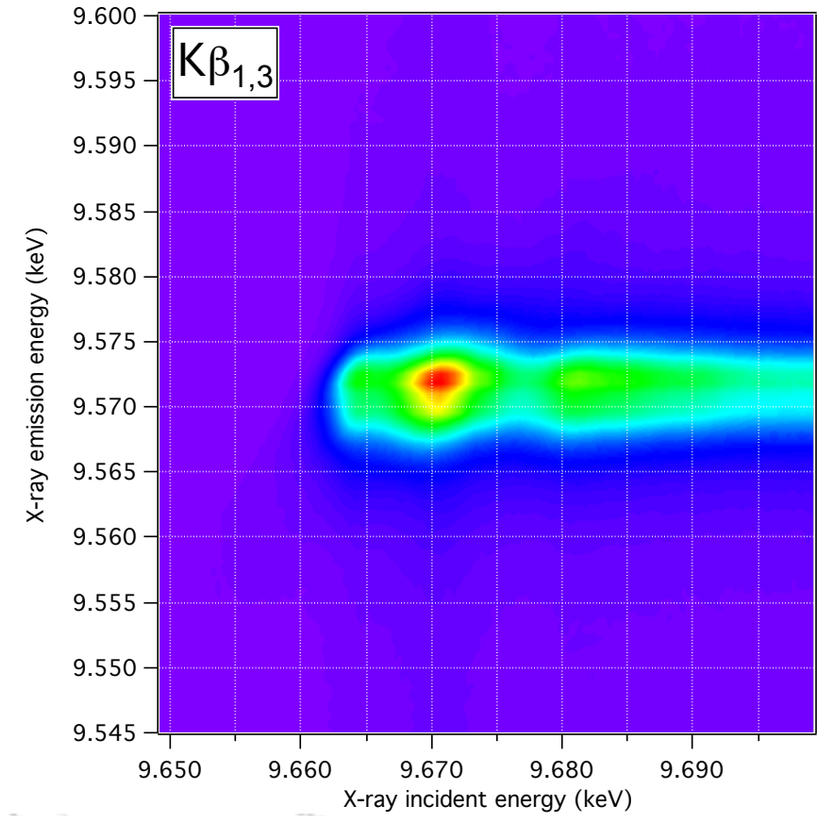
	N_γ	**ZnO NPs in H_2O**	Hatch *et al.* J. App. Phys. **114**, 153517 (2013)
S_0^2	-	0.756±0.036	
E_0	-	4.366±0.452	
R_{Zn-O_1}	4	1.961±0.005	1.9526
R_{Zn-Zn_1}	6	3.178±0.008	3.2090
R_{Zn-O_2}	1	3.216±0.005	
R_{Zn-Zn_2}	6	3.290±0.013	3.2496
σ_{Zn-O}	-	0.003±0.001	0.0040
σ_{Zn-Zn}	-	0.004±0.002	0.0020
σ_{Zn-O}	-	0.003±0.001	
σ_{Zn-Zn}	-	0.004±0.002	0.0020

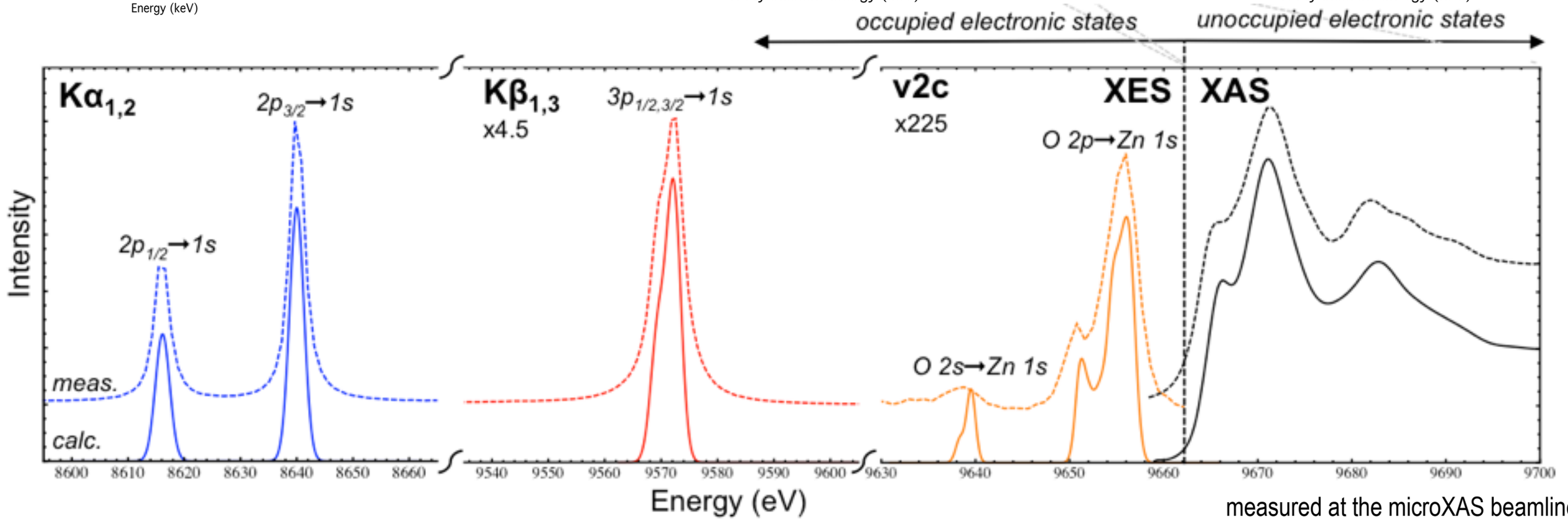
measured at the microXAS beamline at the SLS

ZnO ground state measurements





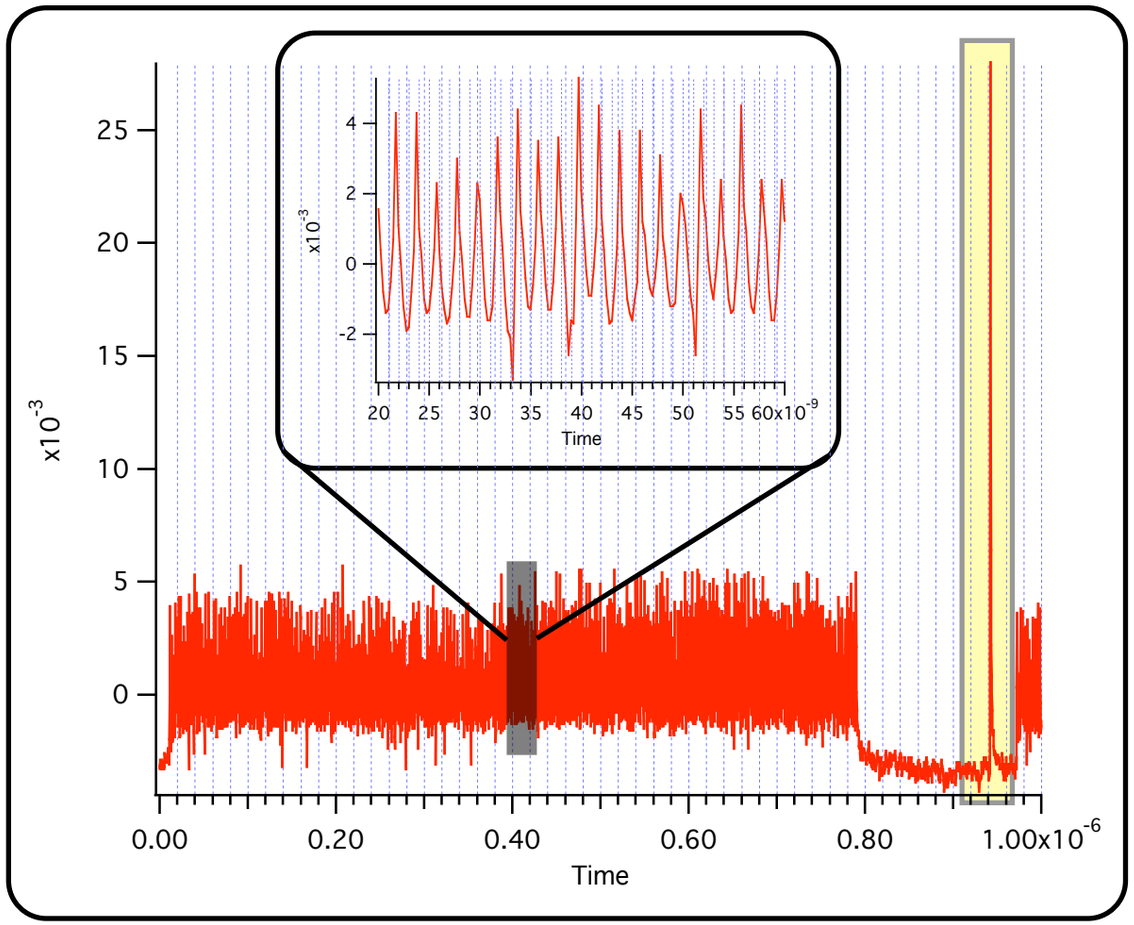




measured at the microXAS beamline at the SLS and Sector 7 ID-D of the APS

How do we extend this to time-resolved experiments ?

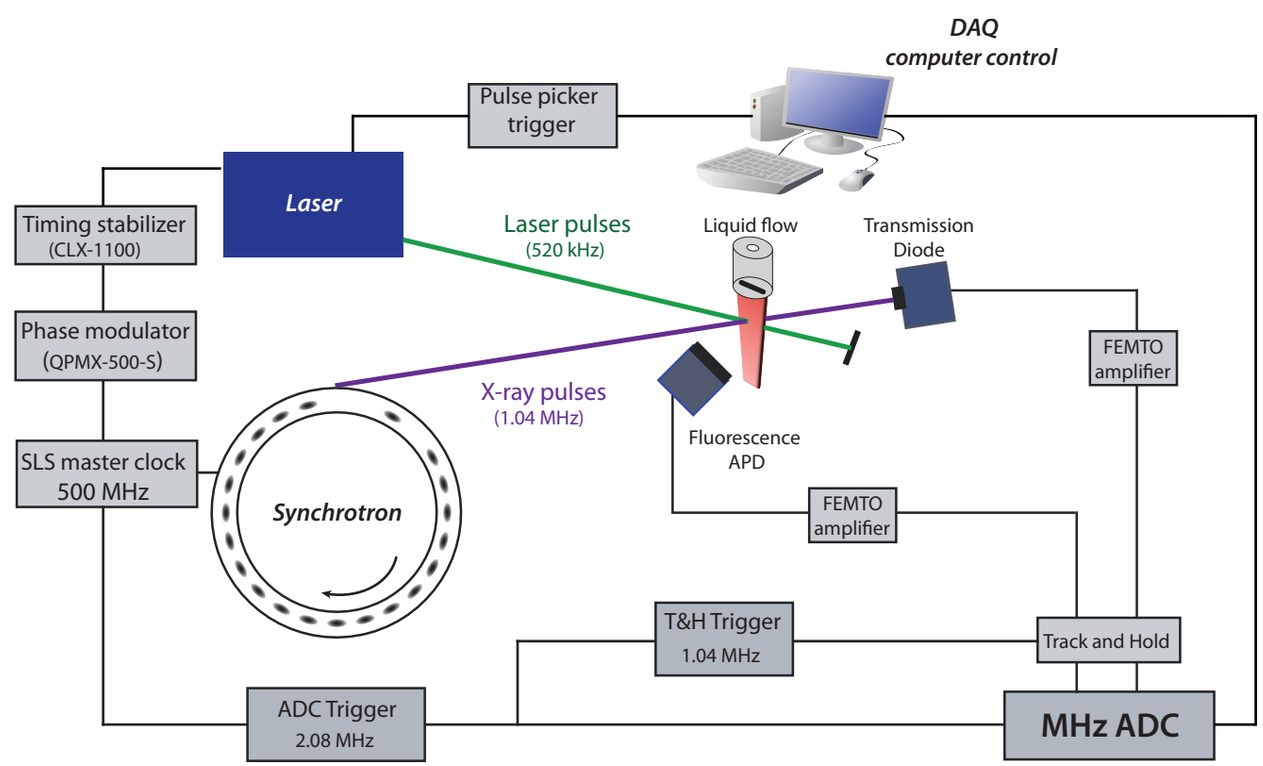
High-repetition rate pump-probe X-ray experiments



microXAS beamline
- tuneable hard x-ray in-vacuum undulator (4-20 keV)
- Si (111), Ge(111) & Si(311) monochromator crystals
- micro-focus capability (< 1μm^2)
- 10^{12} photons/second

PHOENIX beamline
- tuneable 'tender' x-ray in-vacuum undulator (0.8-8 keV)
- Si (111), KTP, Be, InSb monochromator crystals
- micro-focus capability (< 1μm^2)
- 10^{11}-10^{12} photons/second

Using fast avalanche photodiodes and either boxcar integrators or track-and-hold circuits we can selectively measure using only the camshaft pulse giving us **100 ps** time resolution



F.A. Lima, C.J. Milne et al. *Rev. Sci. Instr.* **82**, 063111 (2011)

High-repetition rep rate RXES at the APS

REVIEW OF SCIENTIFIC INSTRUMENTS **82**, 073110 (2011)

Development of high-repetition-rate laser pump/x-ray probe methodologies for synchrotron facilities

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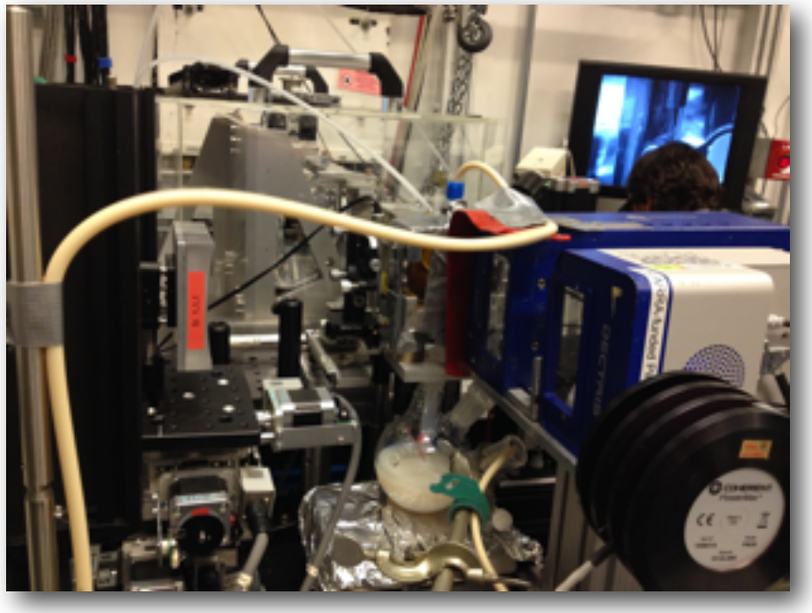
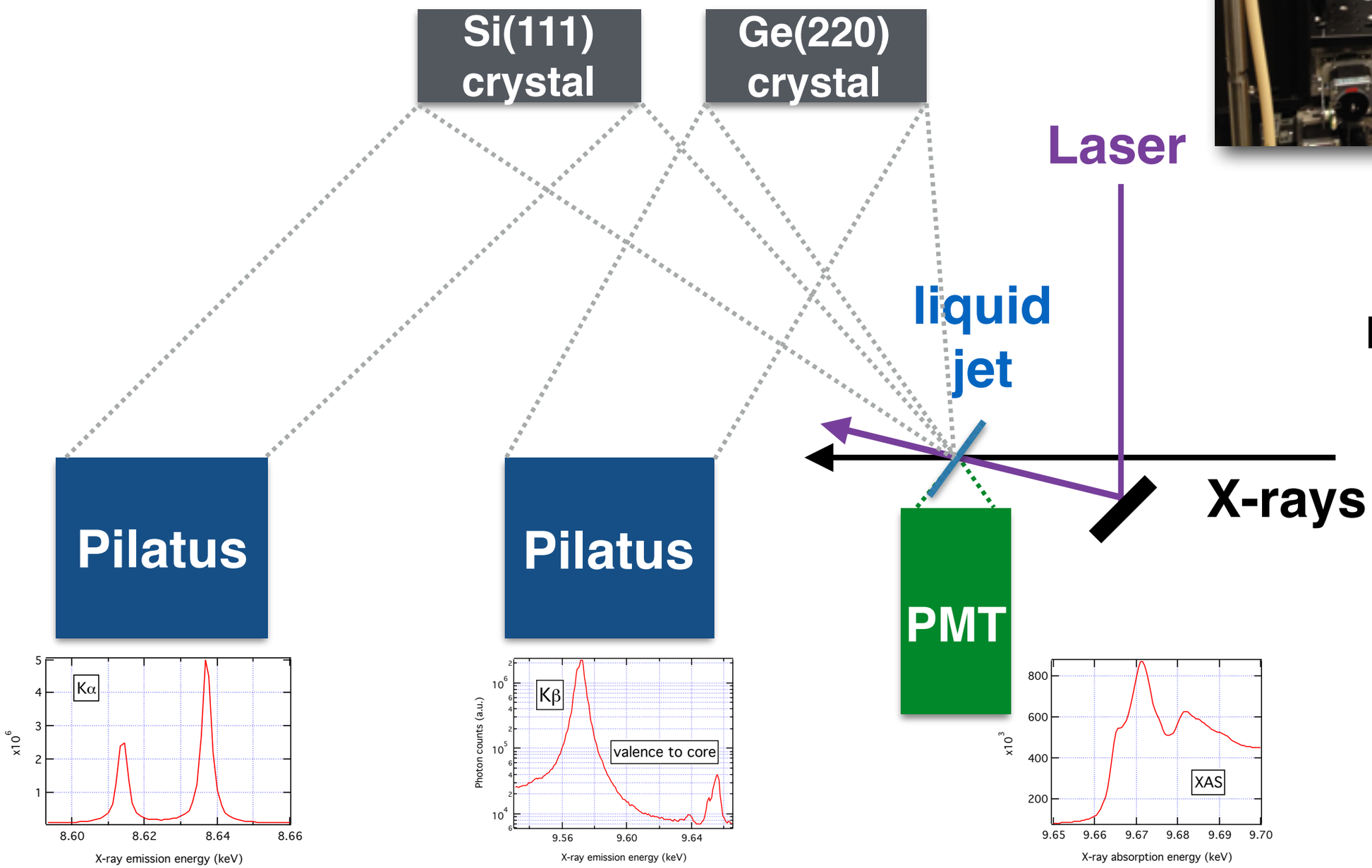
Bertold Krässig,[1] Stephen H. Southworth,[1] Klaus Attenkofer,[1] Charles A. Kurtz,[1]
Lin X. Chen,[2,3] and Linda Young[1]
[1]*X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, Illinois 60439, USA*
[2]*Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, Illinois 60439, USA*
[3]*Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, USA*

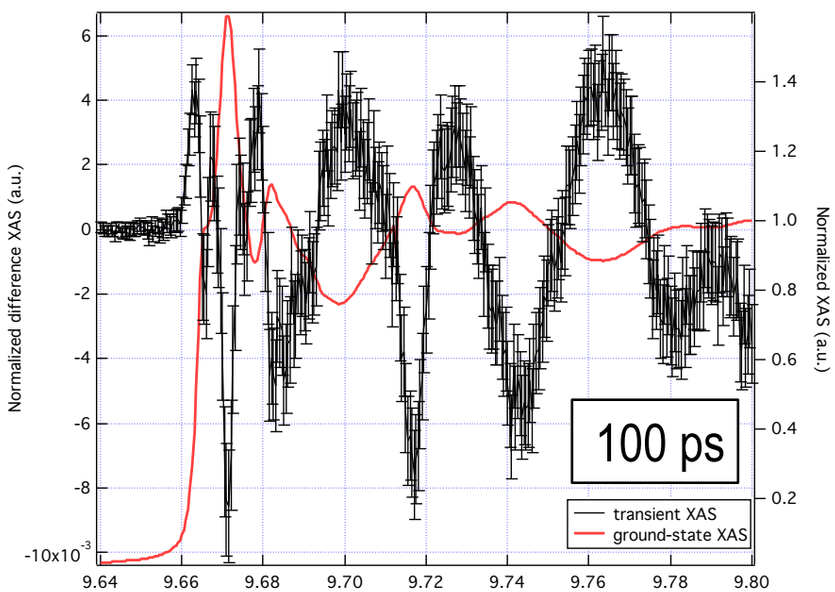


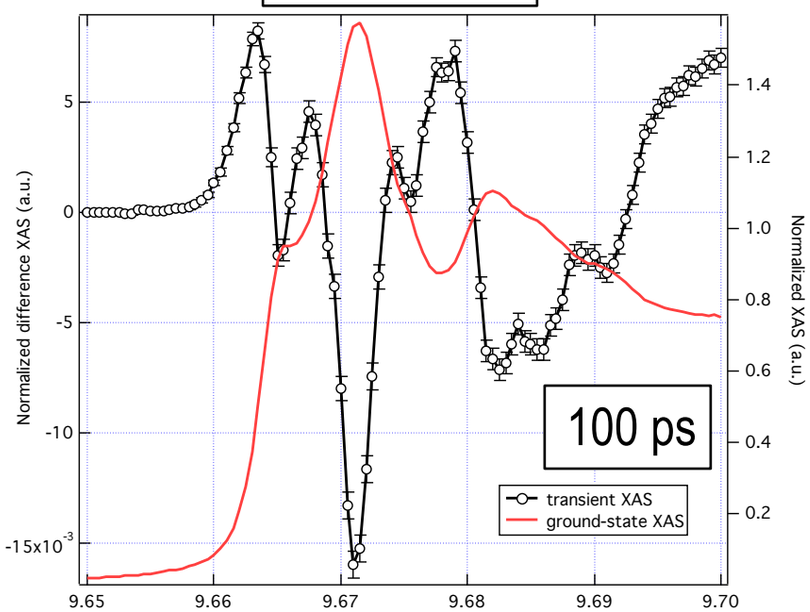


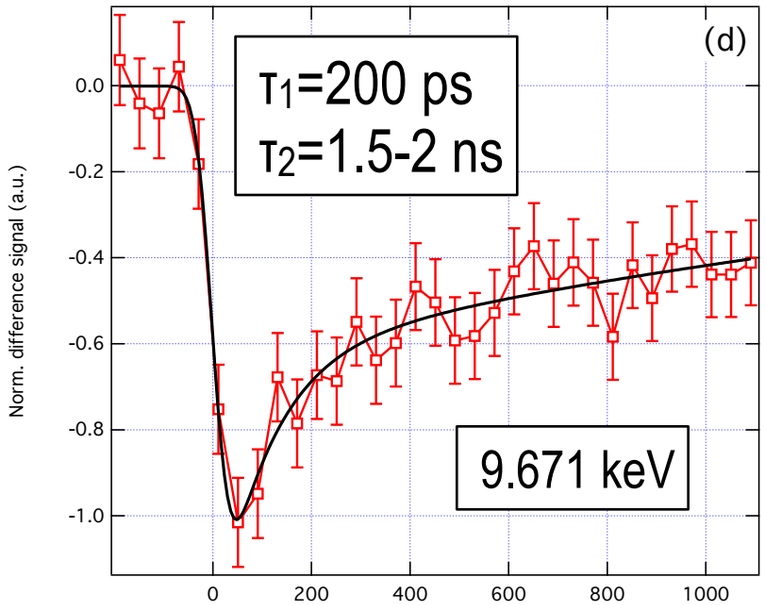
Details

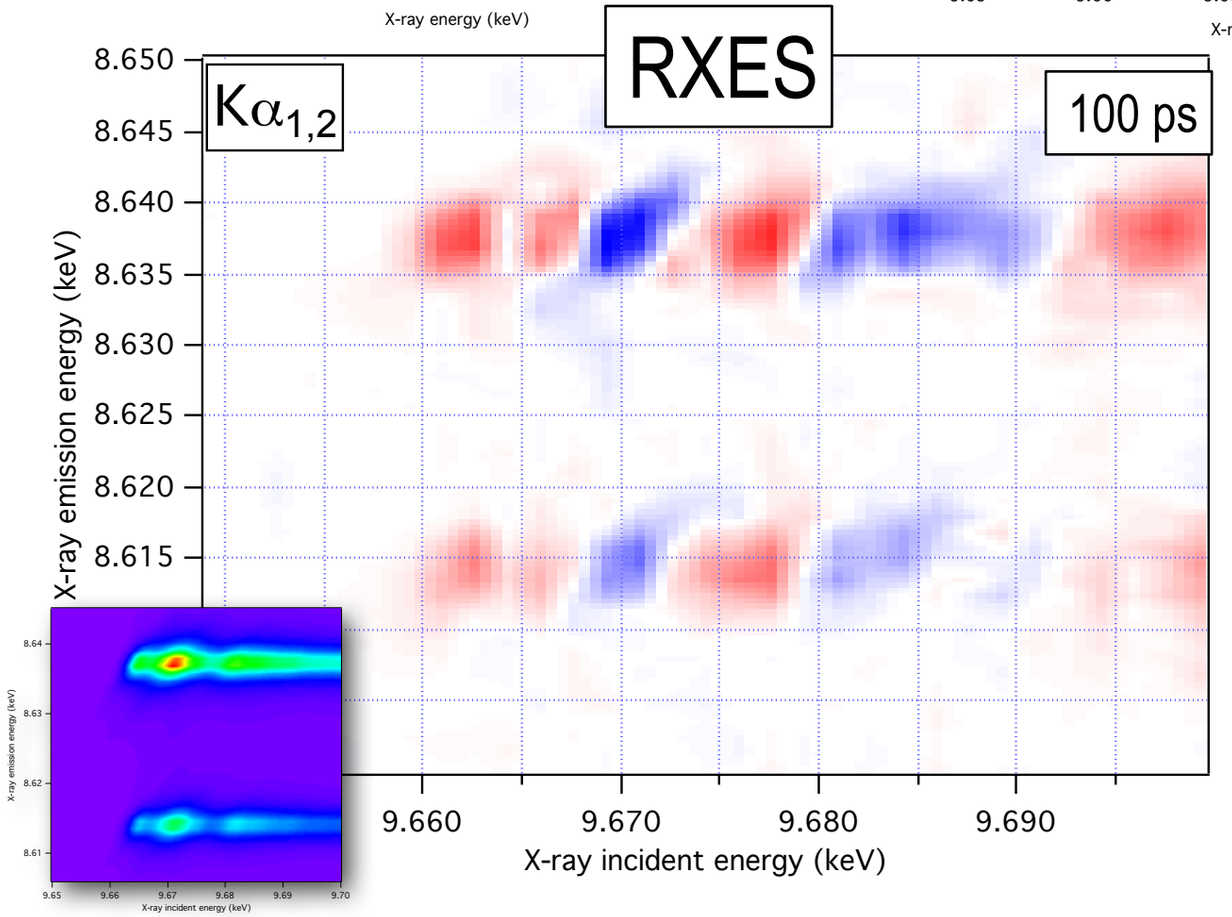
- Sector 7 @ APS
- Zn K-edge (9 keV)
- 355 nm excitation
- 80 mJ/cm^2
- 100 µm liquid jet
- Diamond(111) mono
- $\Delta E/E=5.4\times10^{-5}$
- 10^{12}-10^{13} photons/s
- 100 ps X-ray pulse
- 10 ps laser pulse

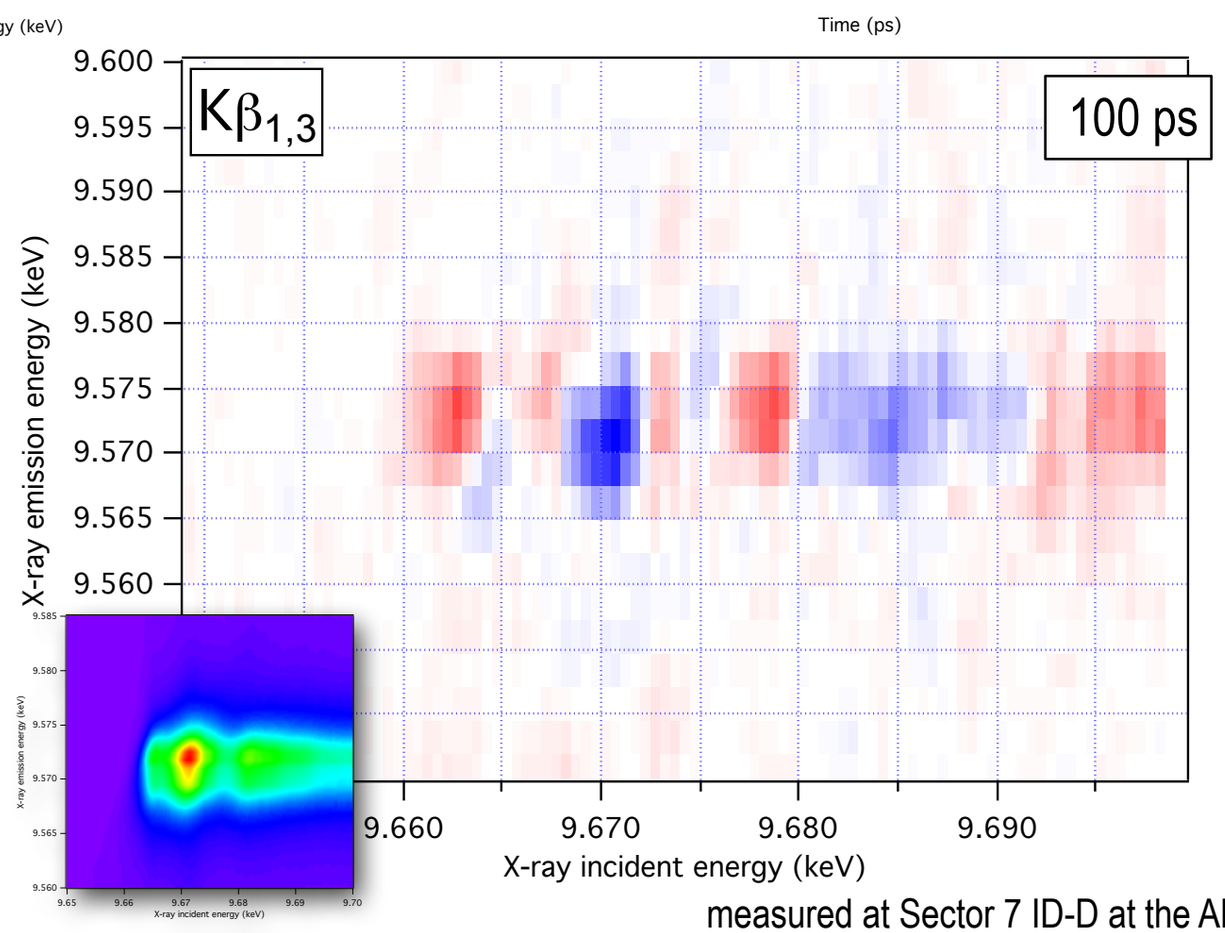
ZnO pump-probe X-ray spectroscopy at the APS







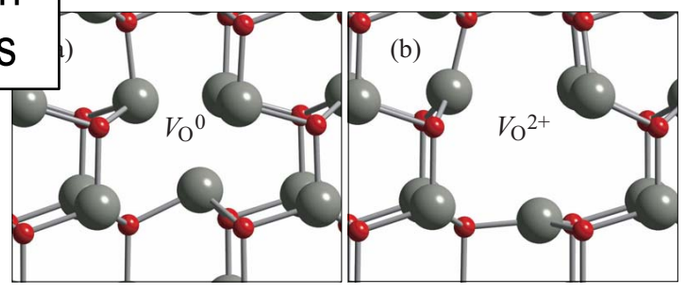


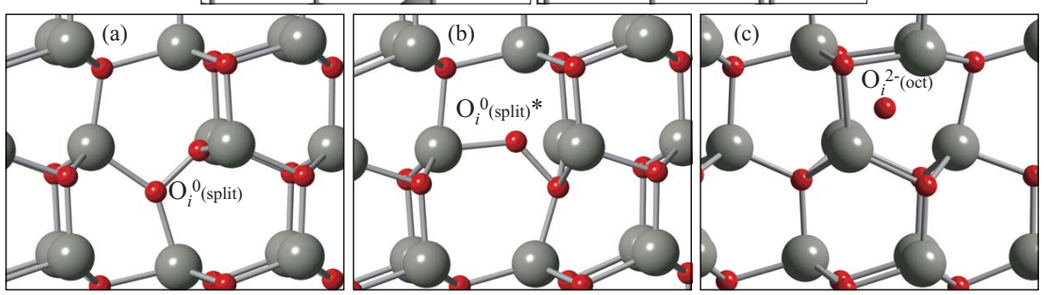


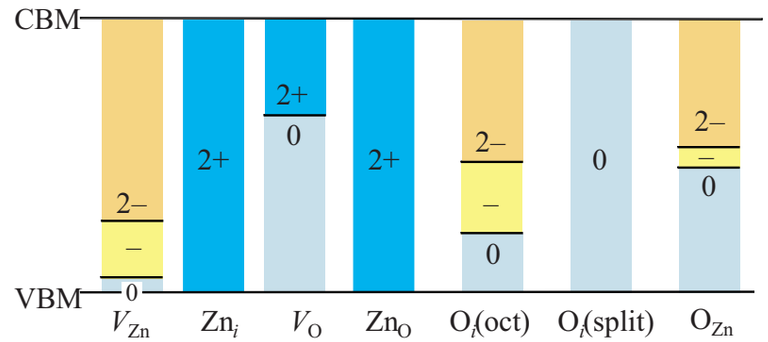
measured at Sector 7 ID-D at the APS

Many different forms of lattice defects in ZnO

Oxygen defects

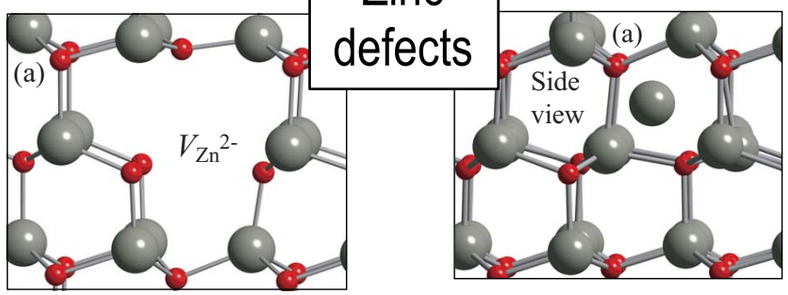


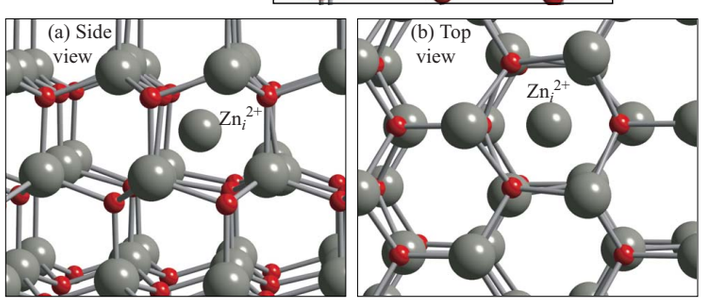


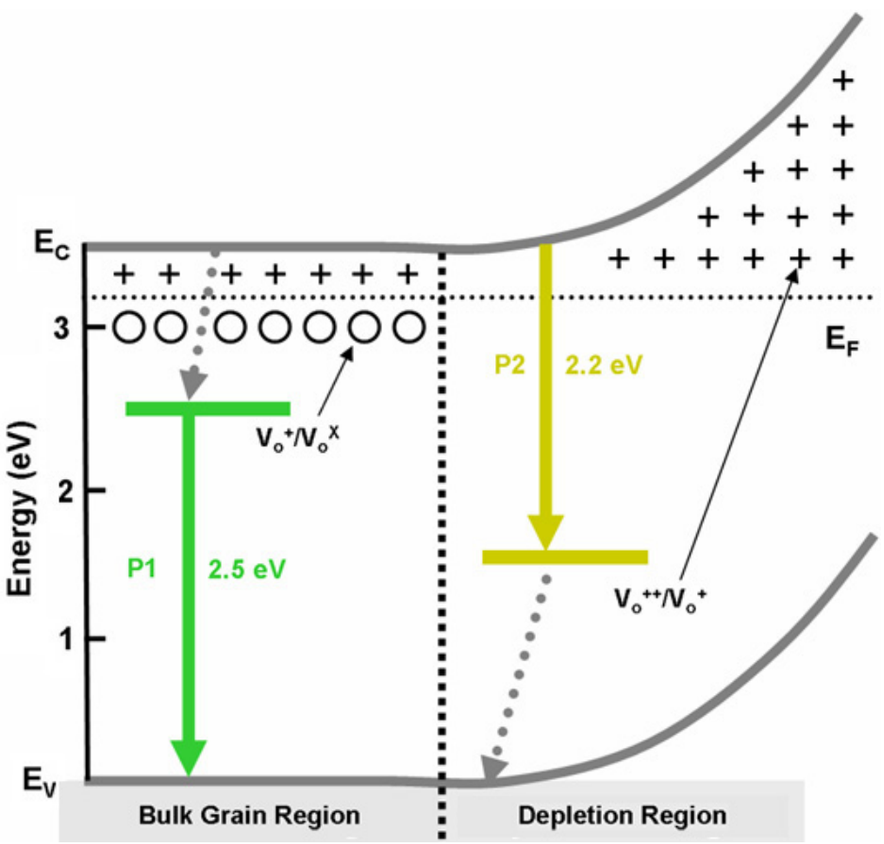


A. Janotti et al. *Phys. Rev. B* **76** 165202 (2007)

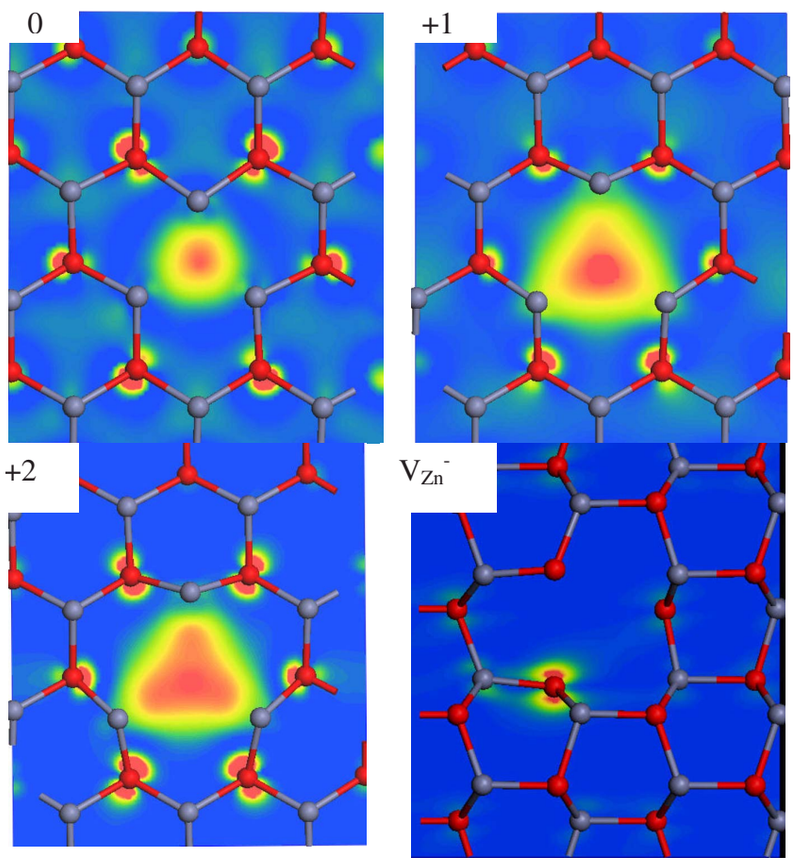
Zinc defects





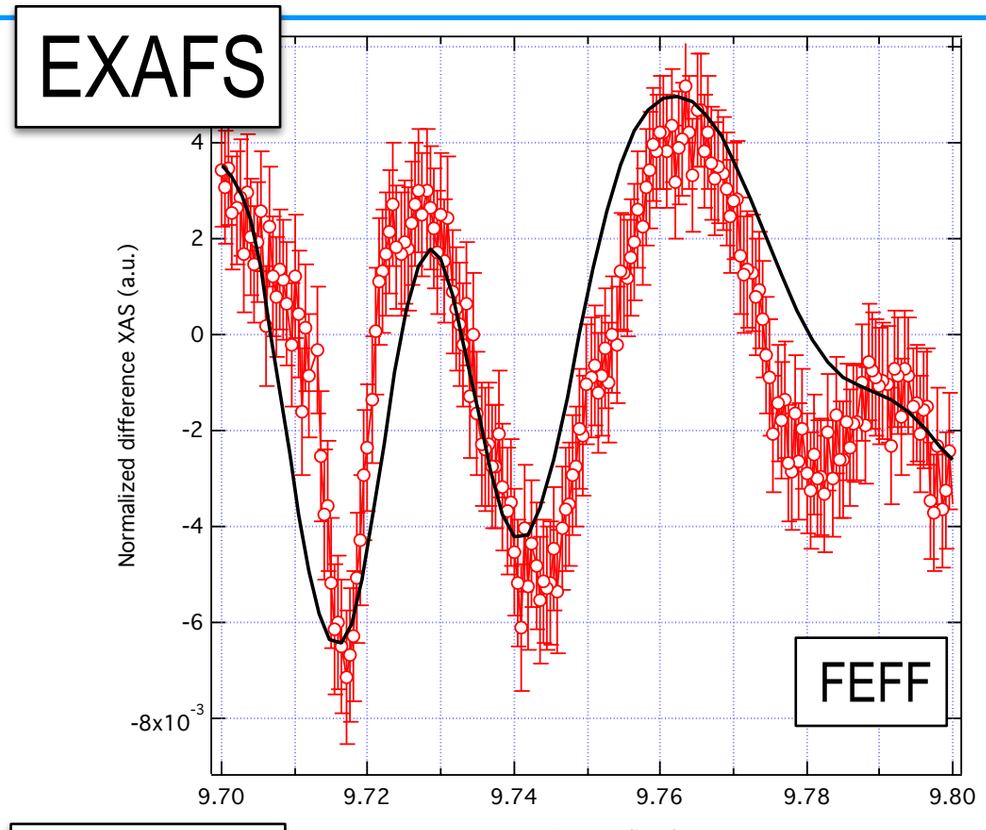


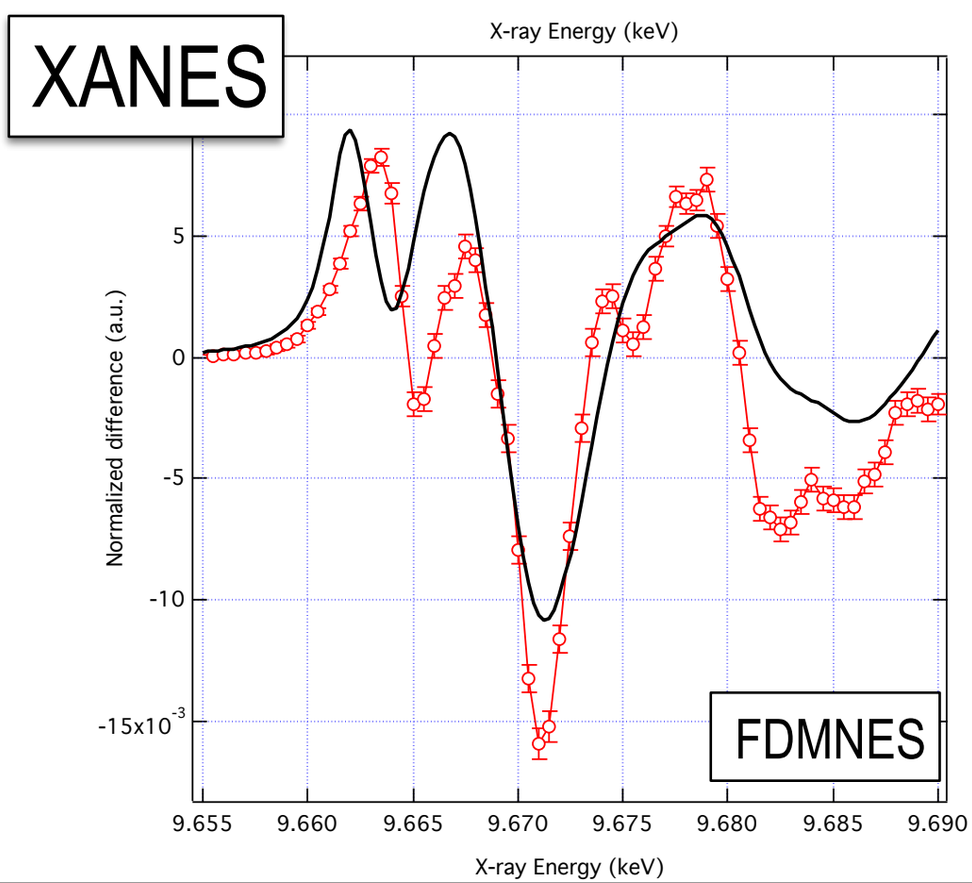
M. Ghosh et al. *Nanotechnology* **19** 445704 (2008)

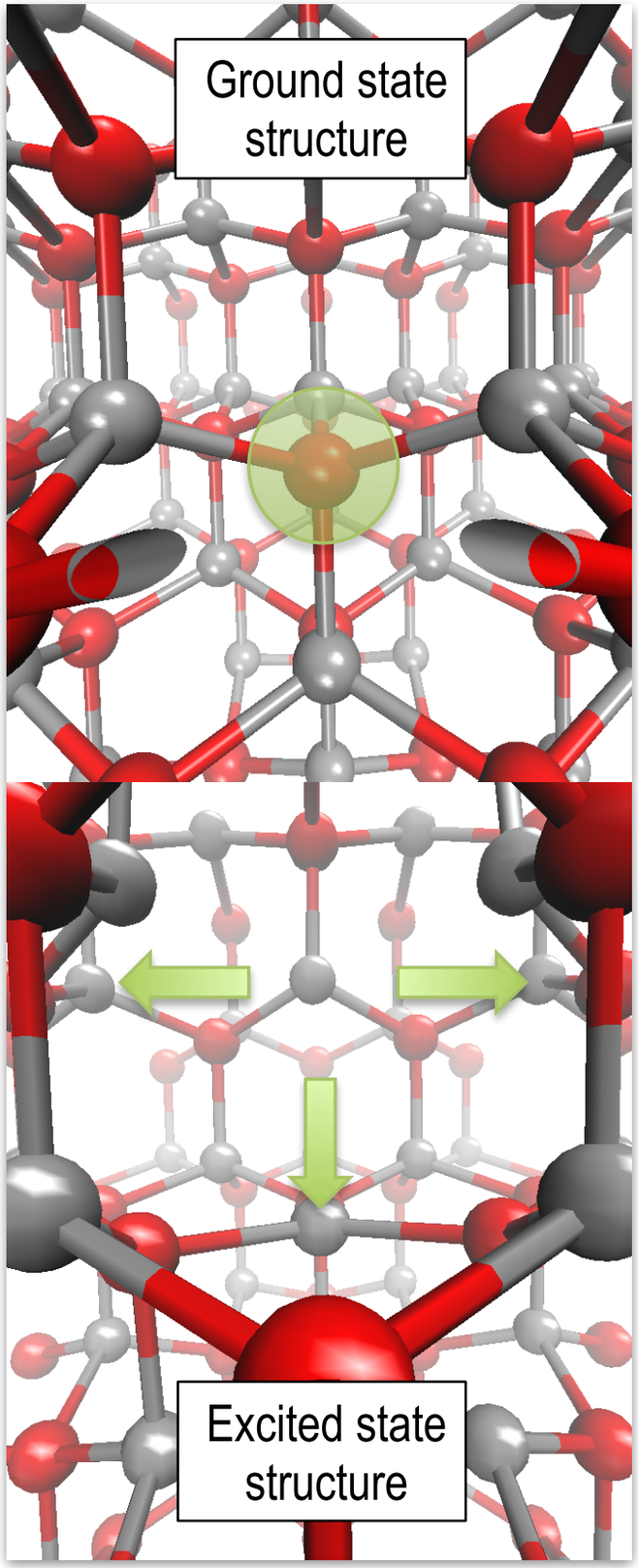


S.J. Clark et al. *Phys. Rev. B* **81** 115311 (2010)

ZnO analysis & simulation: Structural dynamics







Simulation shows the hole trapping sites are consistent with native oxygen defects within the lattice

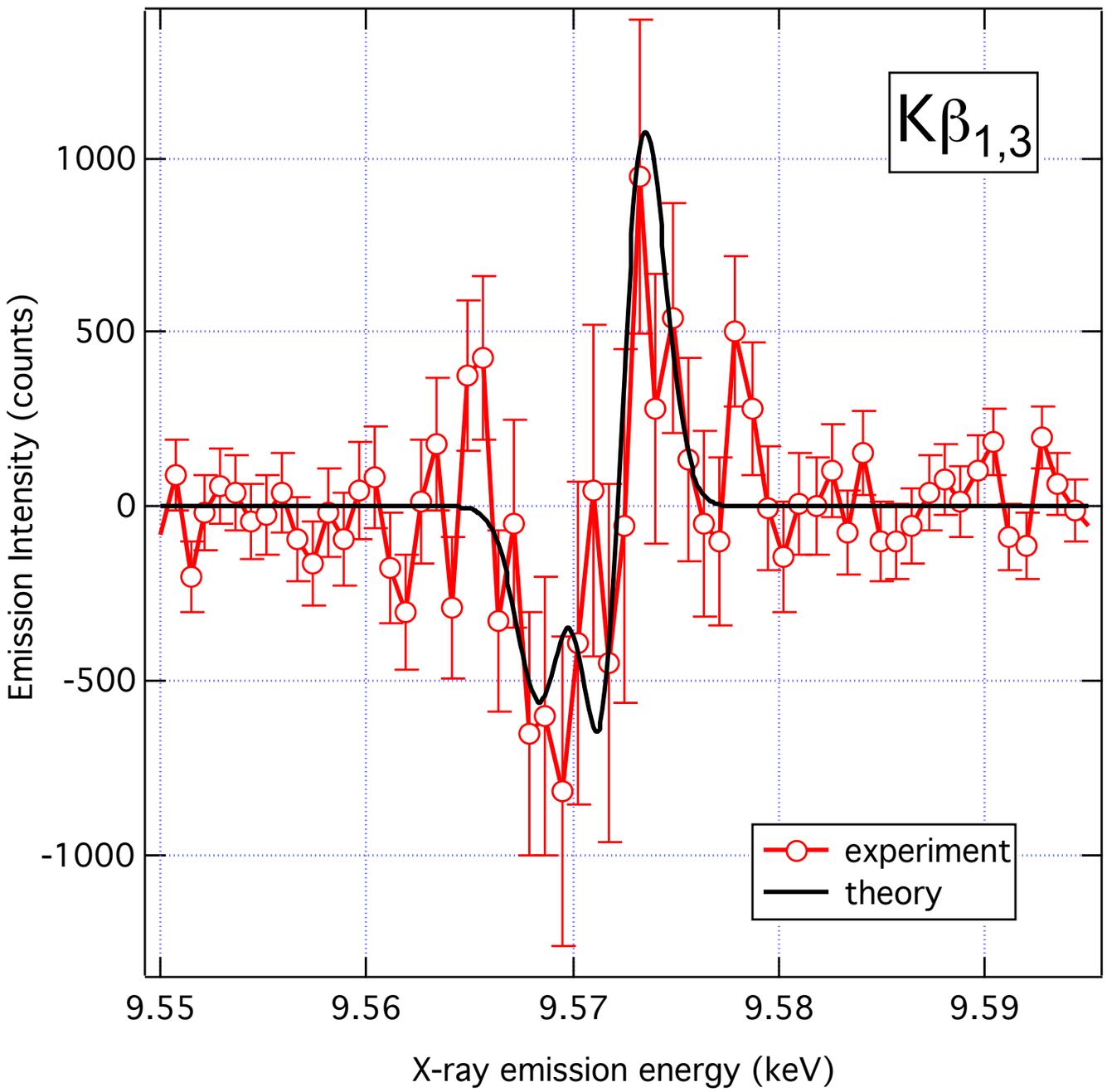
$V_O^{+} + h^{+} \rightarrow V_O^{++}$

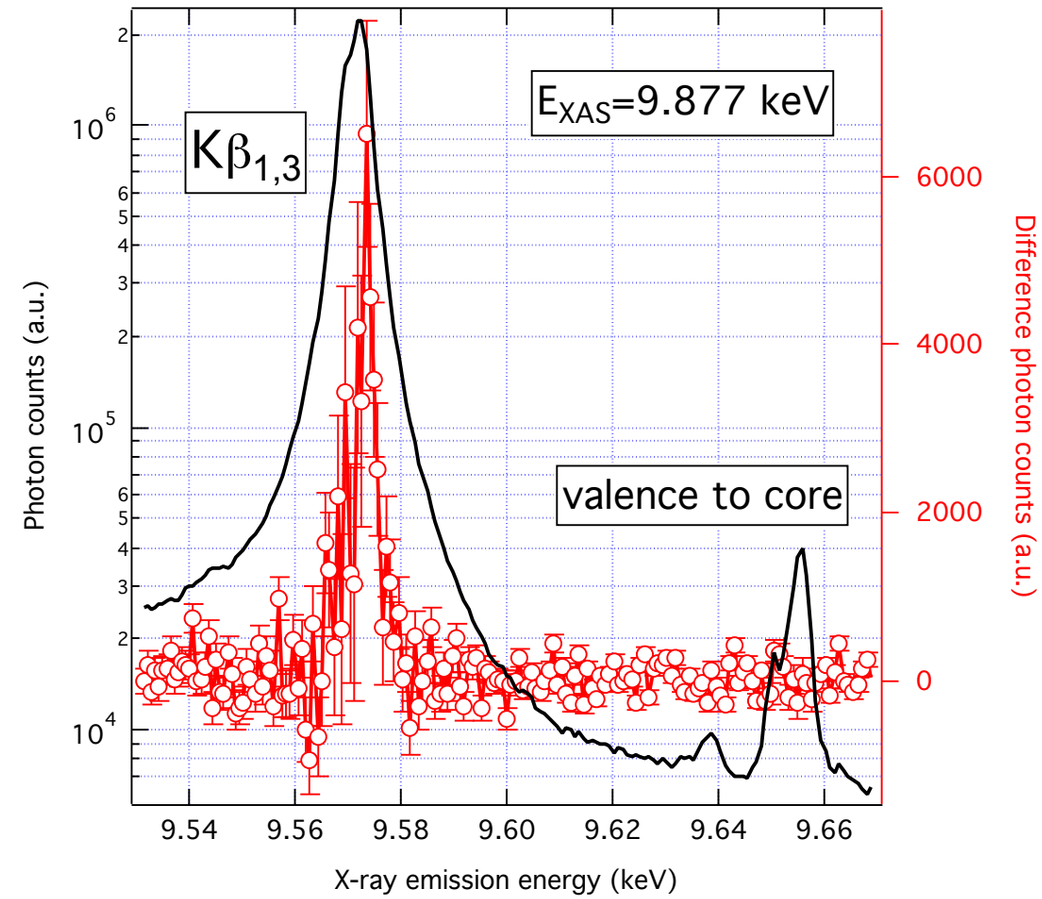
Which causes an expansion of the neighbouring Zn atoms by ~20%

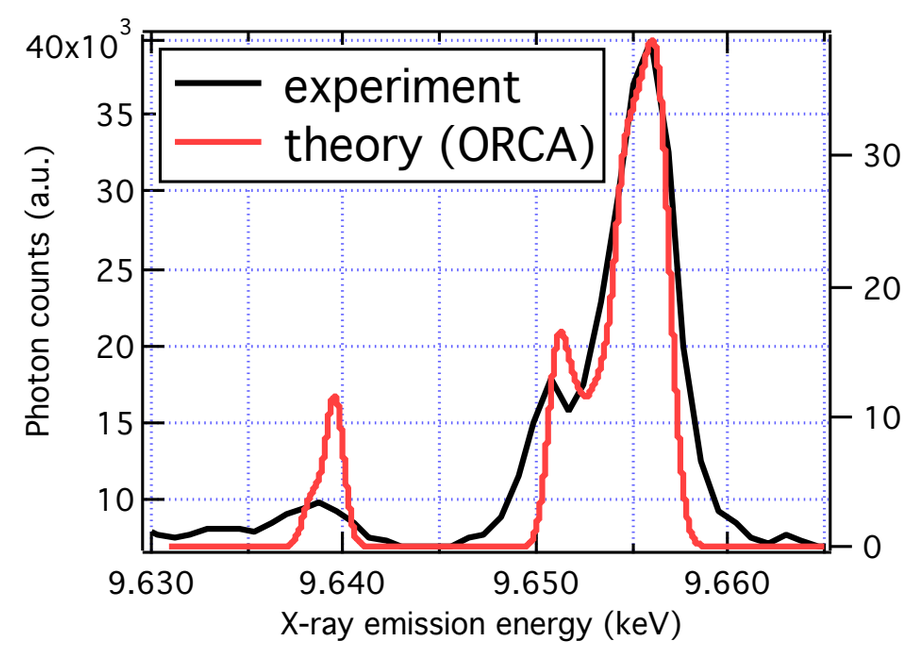
The majority of the changes we see are structural in nature, but not all …

T.J. Penfold, J. Szlachetko et al. in preparation (2015)

ZnO analysis & simulation: Electronic dynamics



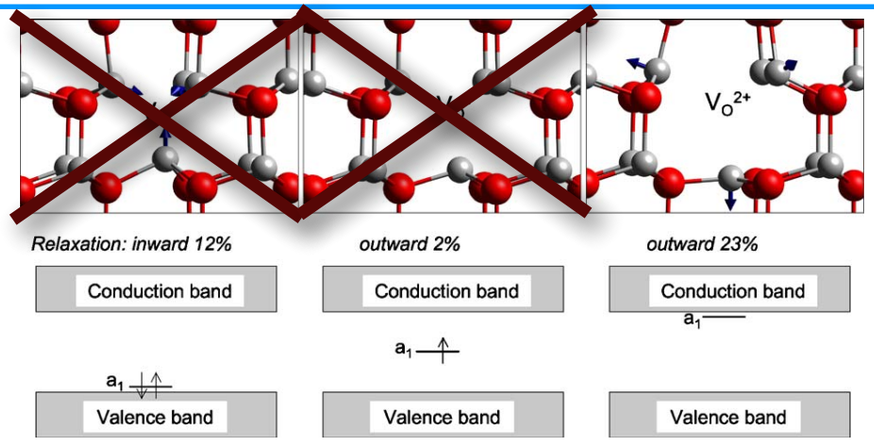




Correcting for change in X-ray absorption cross-section reveals small change in local electronic density around Zn which matches well with theory

Nanoparticle conclusions & the future

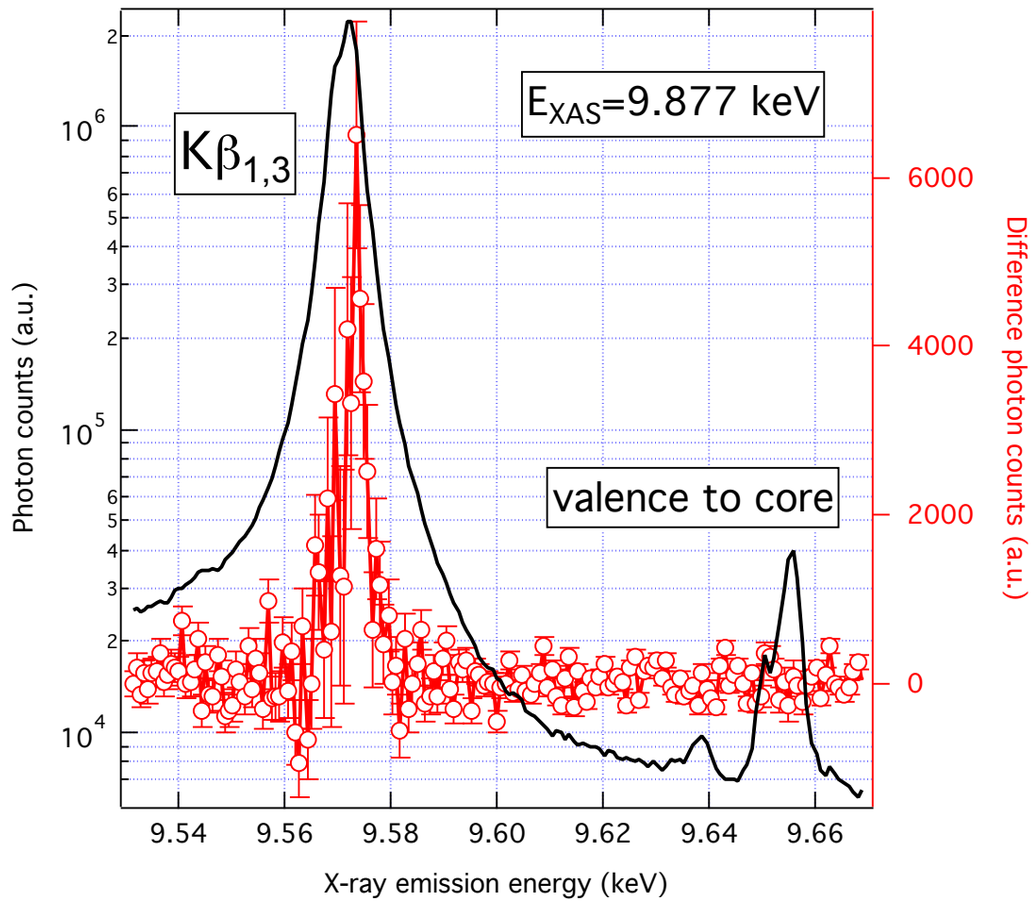
- We've identified the long-lived electron traps in ZnO as oxygen-defect sites in the lattice
- The structure of this site is consistent with a charge density shift from the predominantly oxygen valence band to the zinc conduction band
- This is confirmed by a slight change in charge density in the XES signals



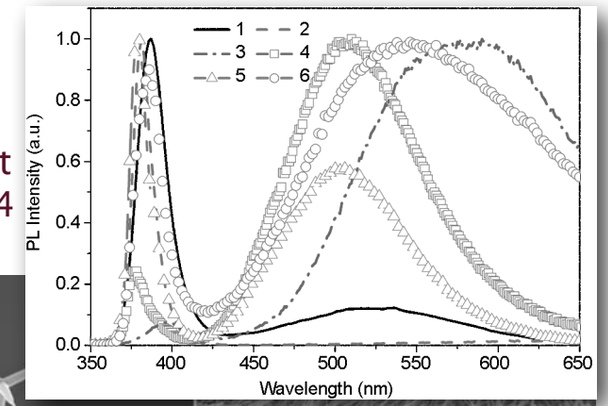
Janotti et al. *App. Phys. Lett.* **87** 122102 (2005)

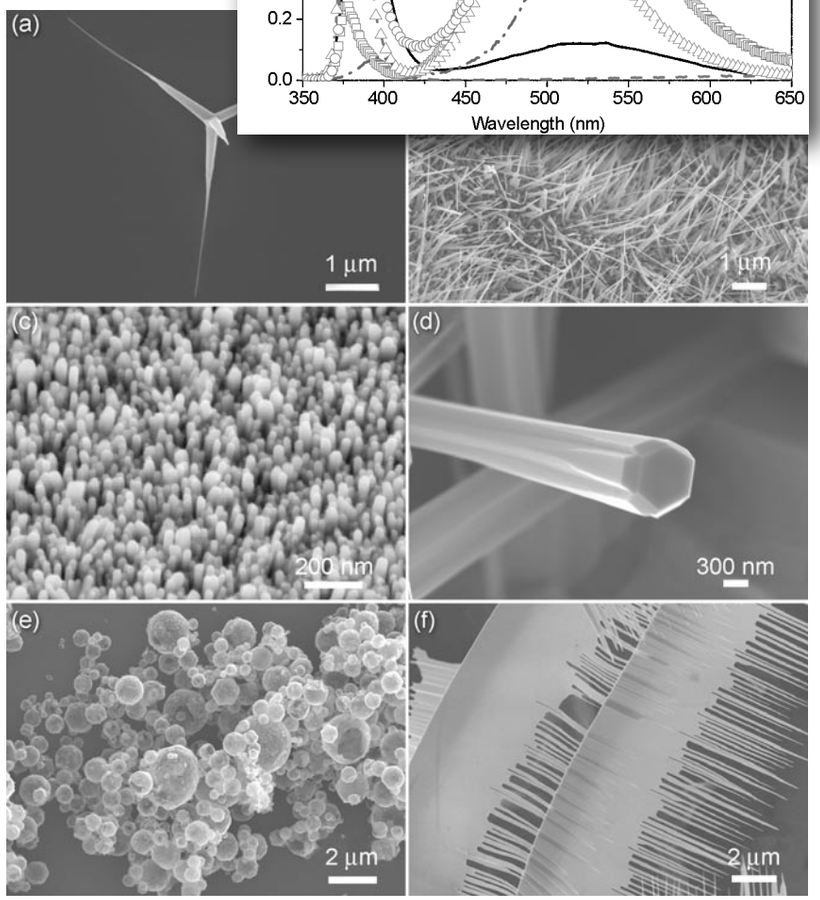
What's next ?

Valence-to-core XES can provide details on the valence band character but this requires better signal-to-noise (more photons)



A.B. Djurišić et al. *Small* **2** 944 (2006)



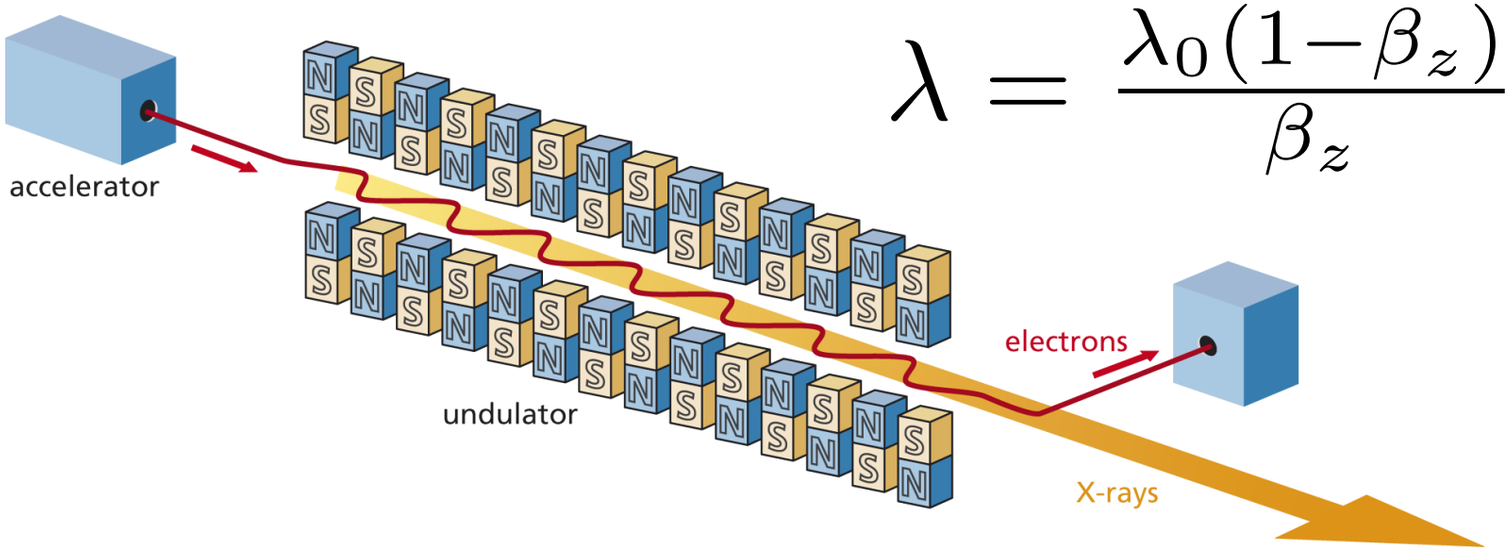


Size and shape dependence will influence trap geometry, energy and concentration

Better time resolution will allow us to observe initial electronic relaxation processes in the conduction band, as well as perhaps observe coupling to lattice phonons on the 100-300 fs timescale

How are we going to get better time-resolution ?

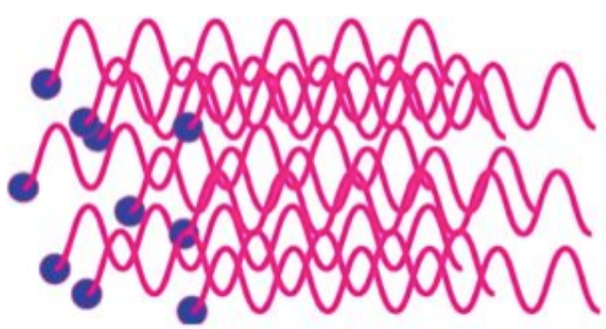
Free electron lasers



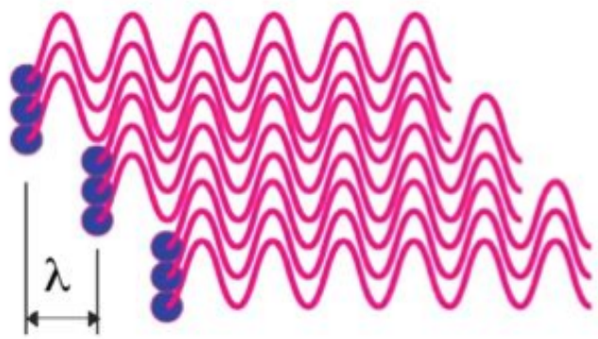
$$\lambda = \frac{\lambda_0(1-\beta_z)}{\beta_z}$$

If the electrons and light are resonant they can exchange energy as they propagate through the undulators

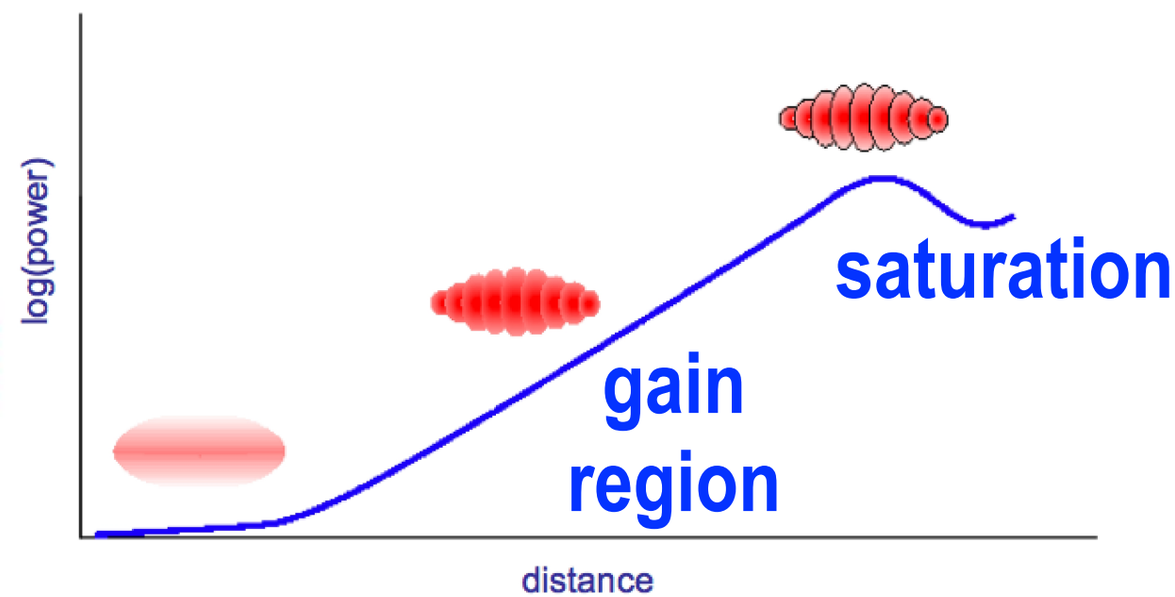
$$I \propto N_e$$



$$I \propto N_e^2$$



Which leads to microbunching and the electrons emit light in phase



which leads to exponential gain than saturation

So we have a single-pass, noise-seeded free electron laser

C. Pellegrini and S. Reiche, in *Digital Encyclopedia of Applied Physics*, Wiley (2003).

Moving FELs into the X-ray regime

Table 1 | Design and typical measured parameters for both hard (8.3 keV) and soft (0.8–2.0 keV) X-rays. The 'design' and 'hard' values are shown only at 8.3 keV. Stability levels are measured over a few minutes.

Parameter	Design	Hard	Soft	Unit
Electrons				
Charge per bunch	1	0.25	0.25	nC
Single bunch repetition rate	120	30	30	Hz
Final linac e^- energy	13.6	13.6	3.5–6.7	GeV
Slice† emittance (injected)	1.2	0.4	0.4	μm
Final projected† emittance	1.5	0.5–1.2	0.5–1.6	μm
Final peak current	3.4	2.5–3.5	0.5–3.5	kA
Timing stability (r.m.s.)	120	50	50	fs
Peak current stability (r.m.s.)	12	8–12	5–10	%
X-rays				
FEL gain length	4.4	3.5	~1.5	m
Radiation wavelength	1.5	1.5	6–22	Å
Photons per pulse	2.0	1.0–2.3	10–20	10^{12}
Energy in X-ray pulse	1.5	1.5–3.0	1–2.5	mJ
Peak X-ray power	10	15–40	3–35	GW
Pulse length (FWHM)	200	70–100	70–500	fs
Bandwidth (FWHM)	0.1	0.2–0.5	0.2–1.0	%
Peak brightness (estimated)	8	20	0.3	10^{32} *
Wavelength stability (r.m.s.)	0.2	0.1	0.2	%
Power stability (r.m.s.)	20	5–12	3–10	%

*Brightness is photons per phase space volume, or photons s^{-1} mm^{-2} $mrad^{-2}$ per 0.1% spectral bandwidth.
†'Slice' refers to femtosecond-scale time slices and 'projected' to the full time-projected (that is, integrated) emittance of the bunch.

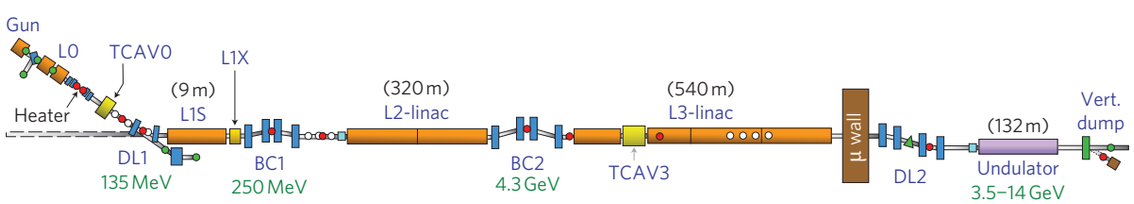
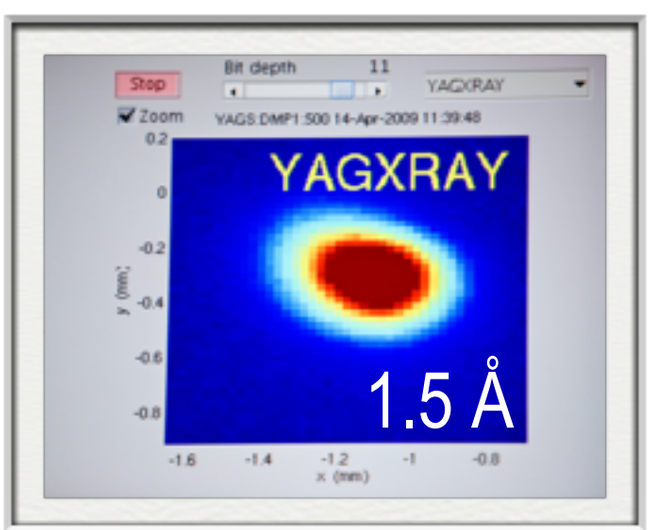


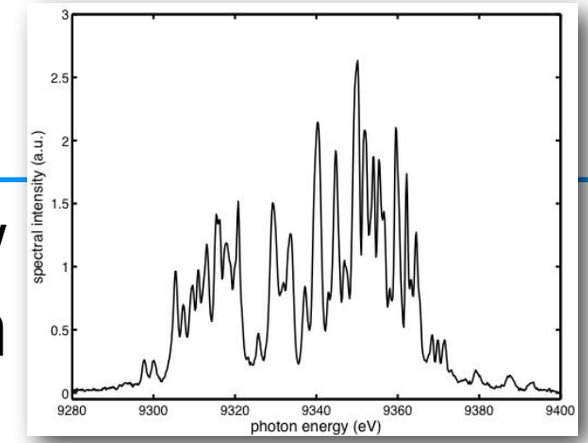
Figure 1 | LCLS machine layout. Layout from the electron gun to the main dump, with two bunch compressors, BC1 and BC2, and a 132-m-long undulator.

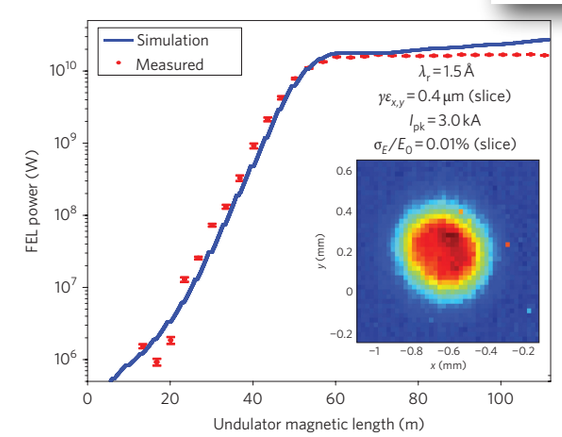


2009: LCLS first achieved lasing at hard X-ray wavelengths

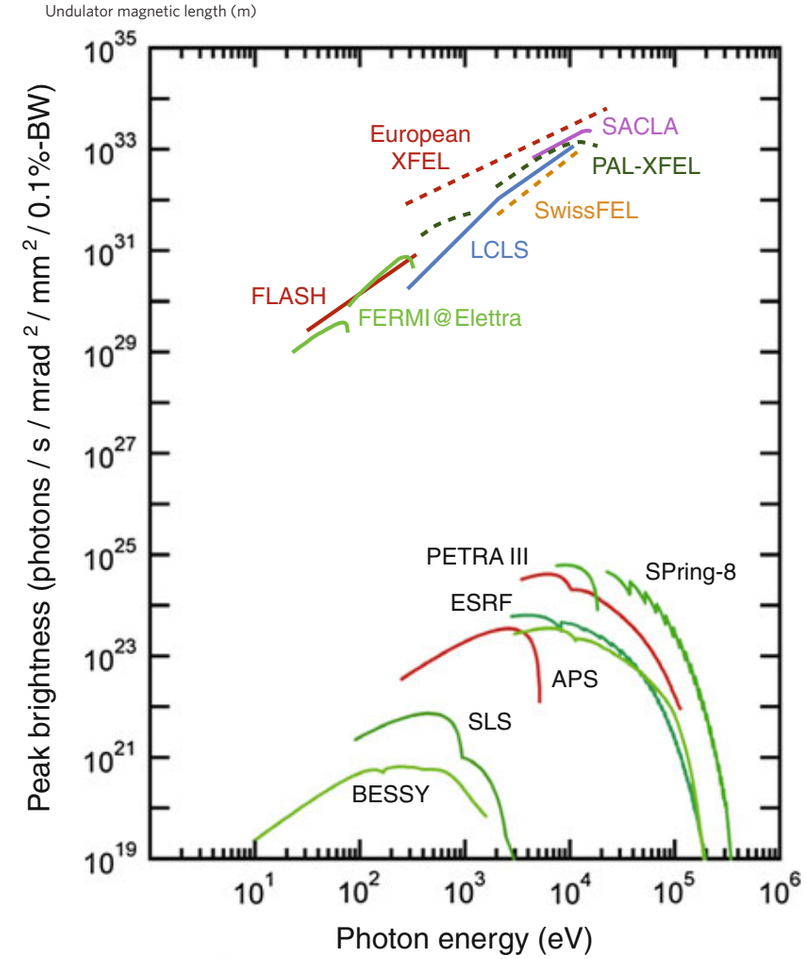
P. Emma et al., *Nat. Phot.* **4**, 641 (2010)

spiky X-ray spectrum



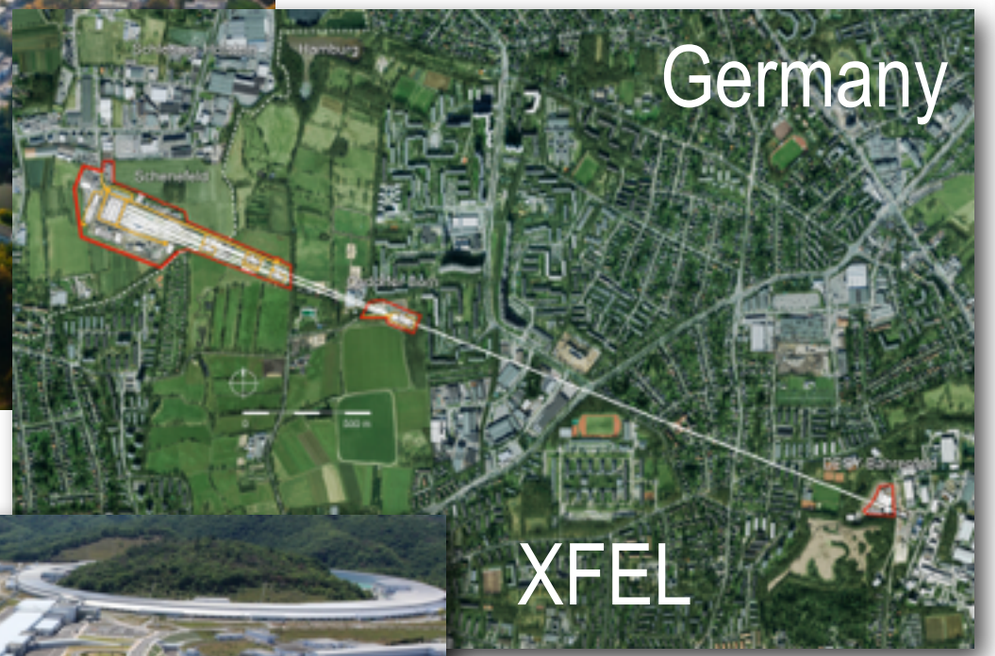


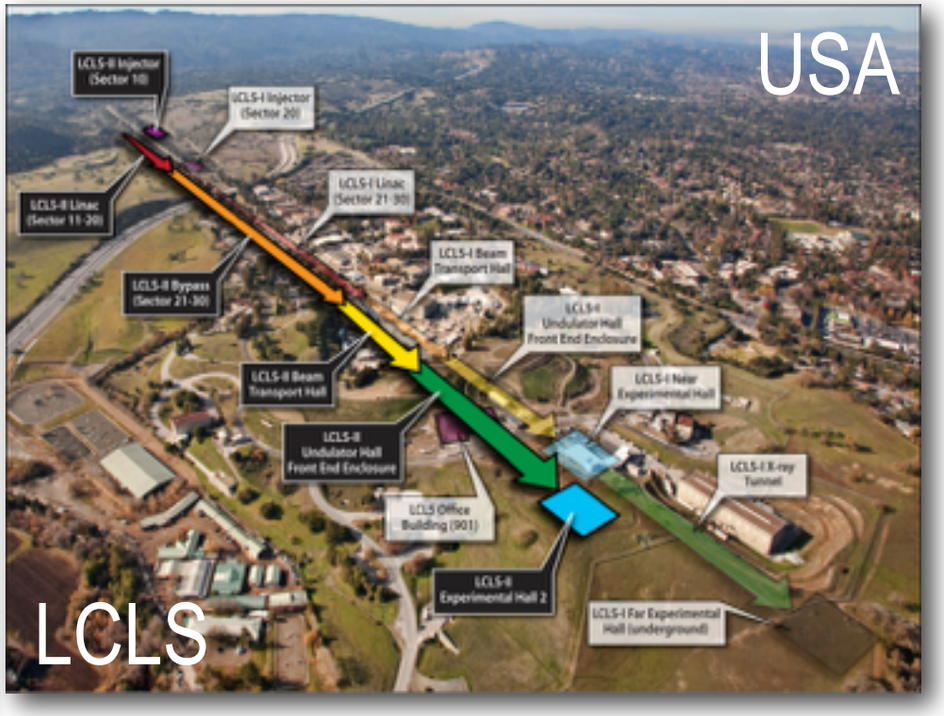
shows power saturation profile



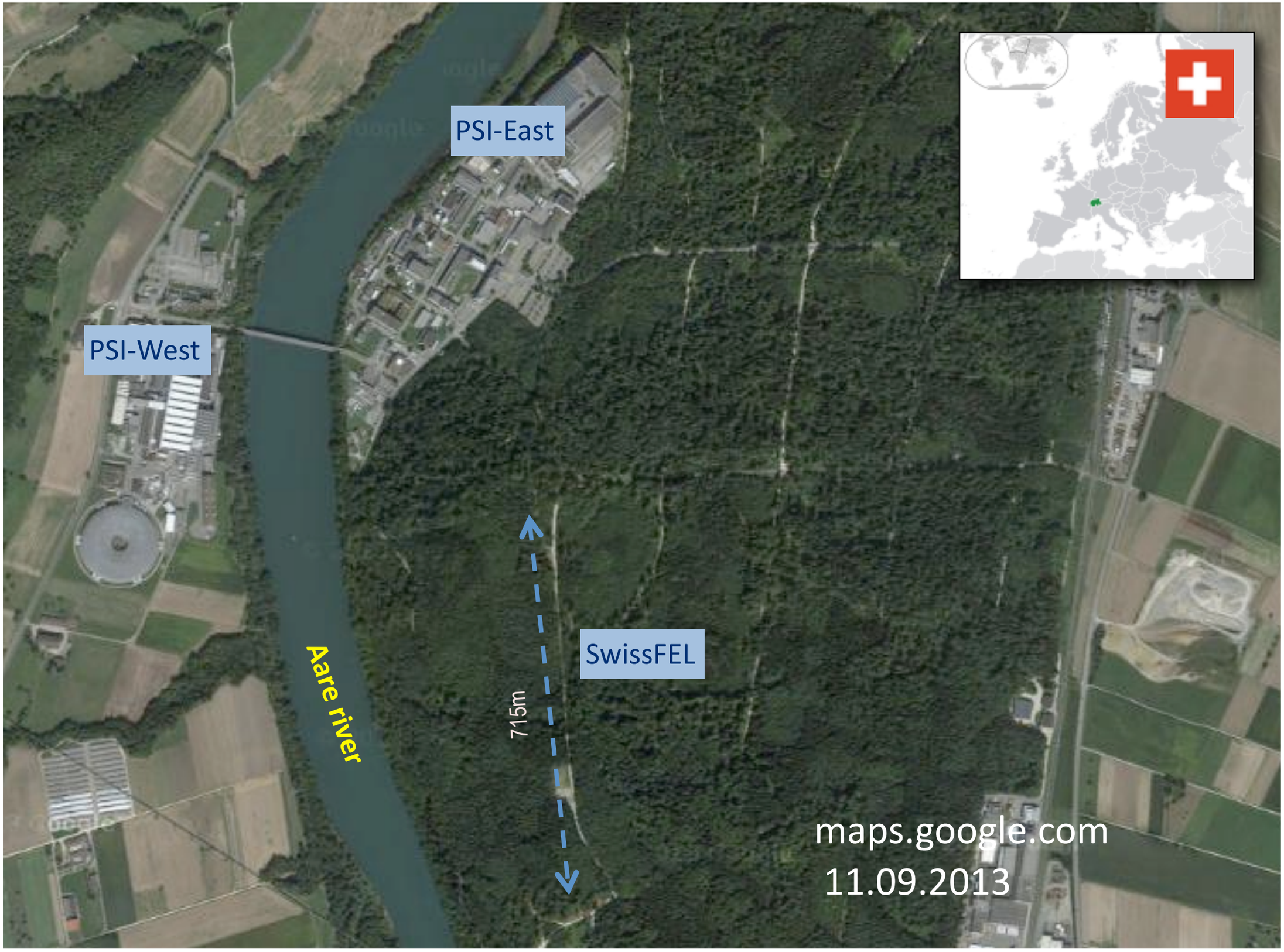
P. Schmüser et al., *Free-Electron Lasers in the Ultraviolet and X-ray Regime*, Springer Tracts in Modern Physics **258** (2014)

Now there are XFEL projects everywhere…



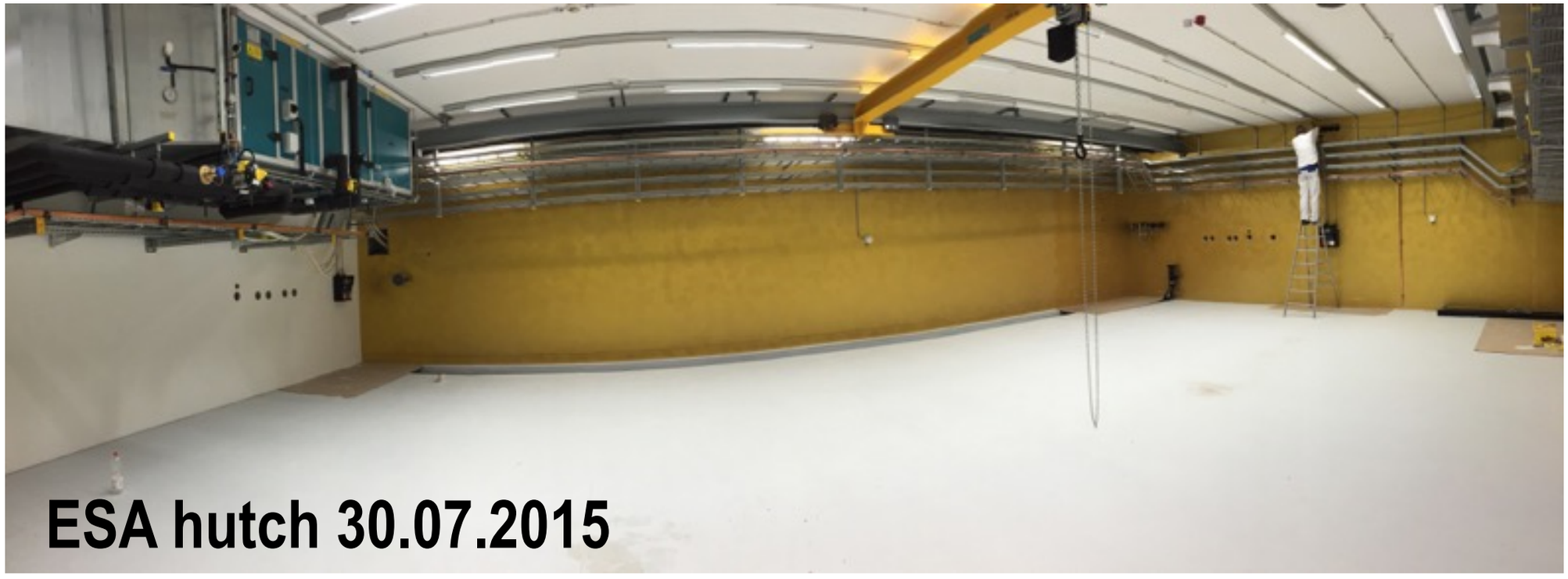


…including at PSI, introducing SwissFEL

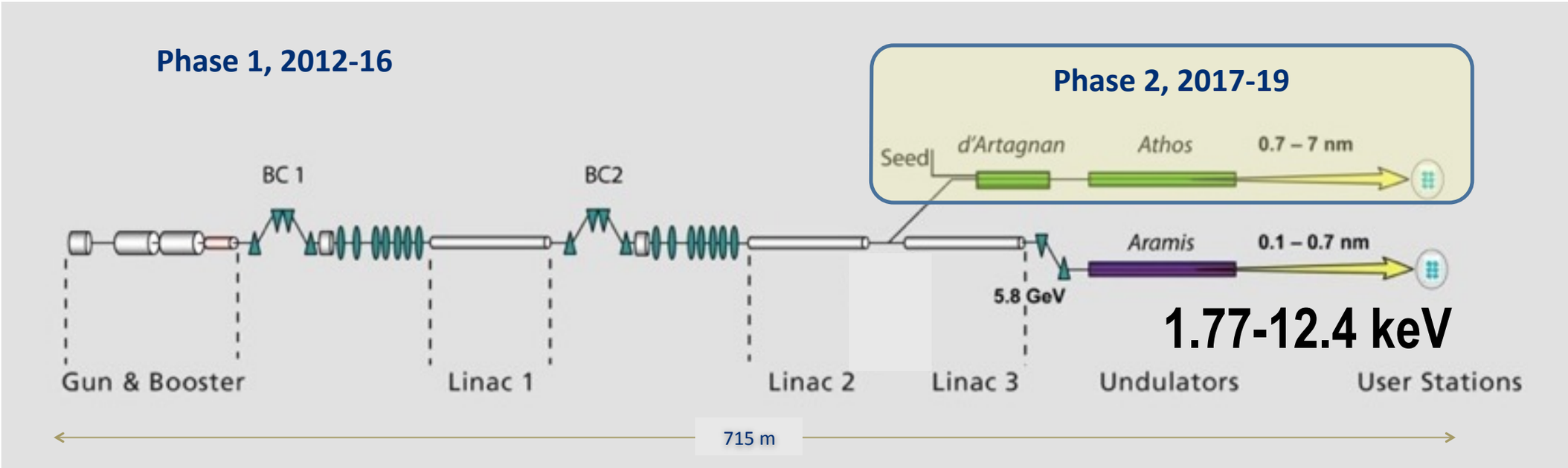


SwissFEL: June 27, 2013

SwissFEL under construction



What are we going to put into this building ?



2012-2017

Aramis: 1-7 Å (2-12.4 keV) hard X-ray SASE FEL,
In-vacuum , planar undulators with variable gap.
User operation from mid 2017

after 2017

Athos : (2nd phase) 7-70 Å soft X-ray FEL for SASE & Seeded operation .
APPLE II undulators with variable gap and full polarization control.
To be implemented after 2017

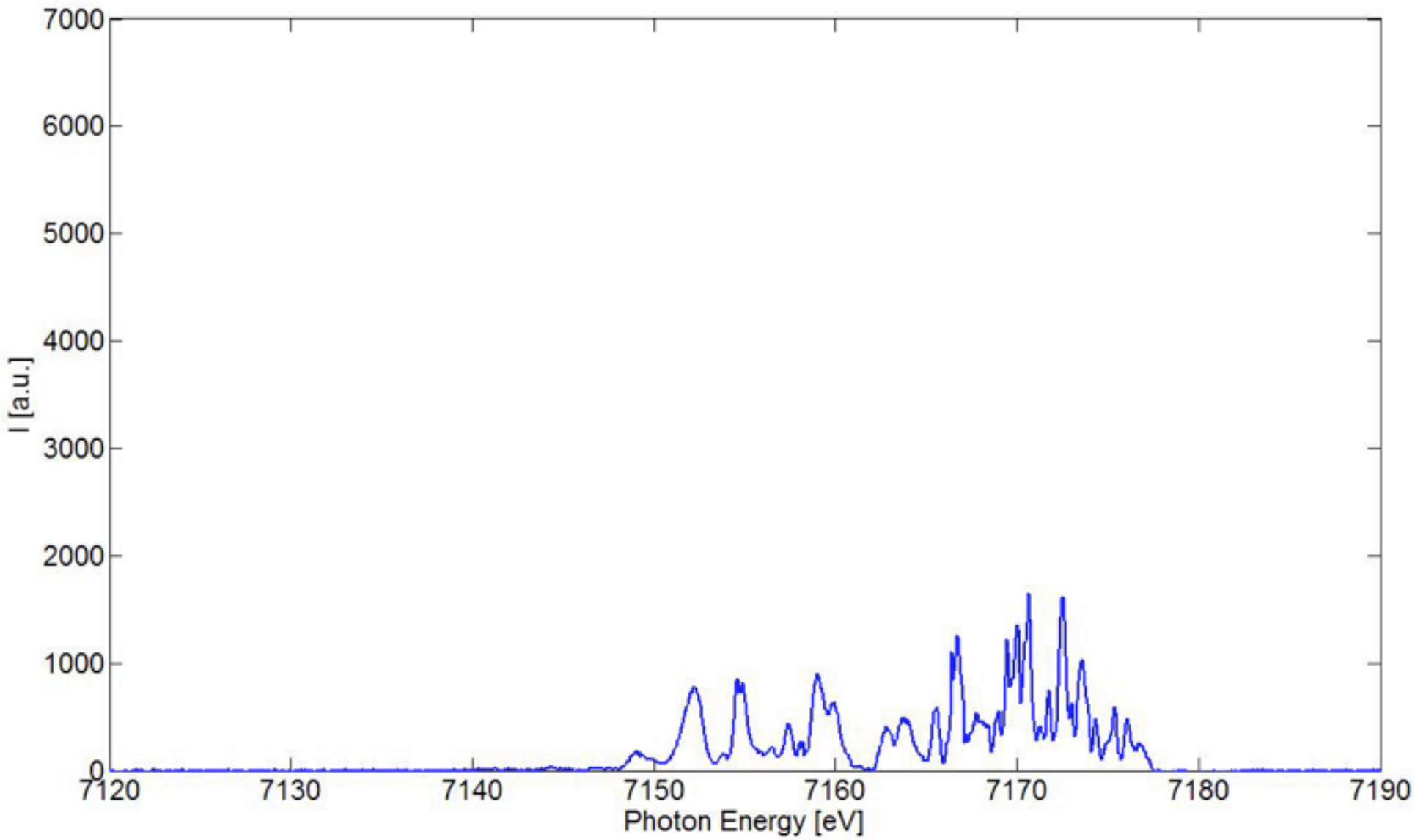
SwissFEL parameters

Wavelength from	1 Å - 70 Å
Photon energy	0.2-12 keV
Photon / pulse (1Å)	7.3E+10
Pulse duration	1 fs - 20 fs
Energy bandwidth	0.05-0.16%
e^- Energy	5.8 GeV
e^- Bunch charge	10-200 pC
Repetition rate	100 Hz

What are the properties of the X-rays from an XFEL ?

XFEL spectral properties

The photon spectrum of an XFEL varies enormously from shot-to-shot



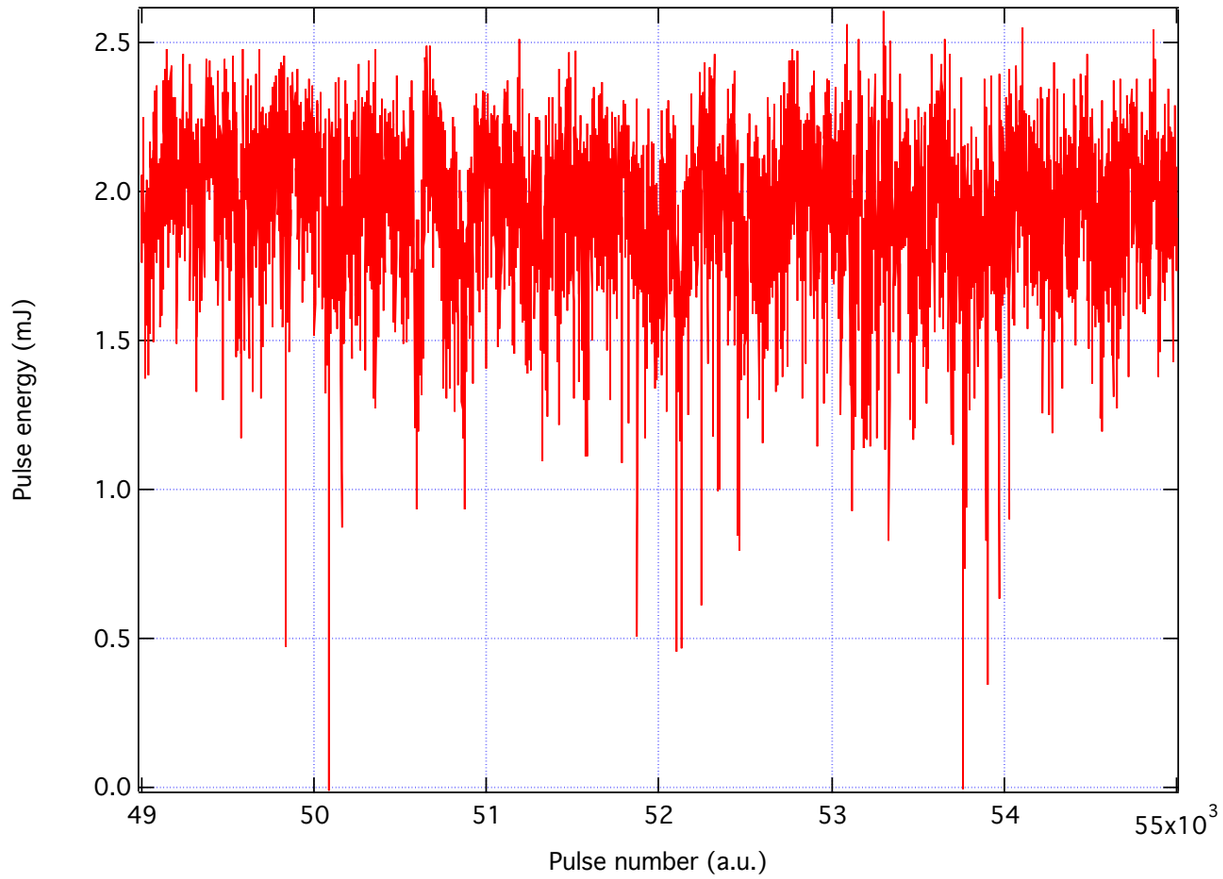
Measured at LCLS

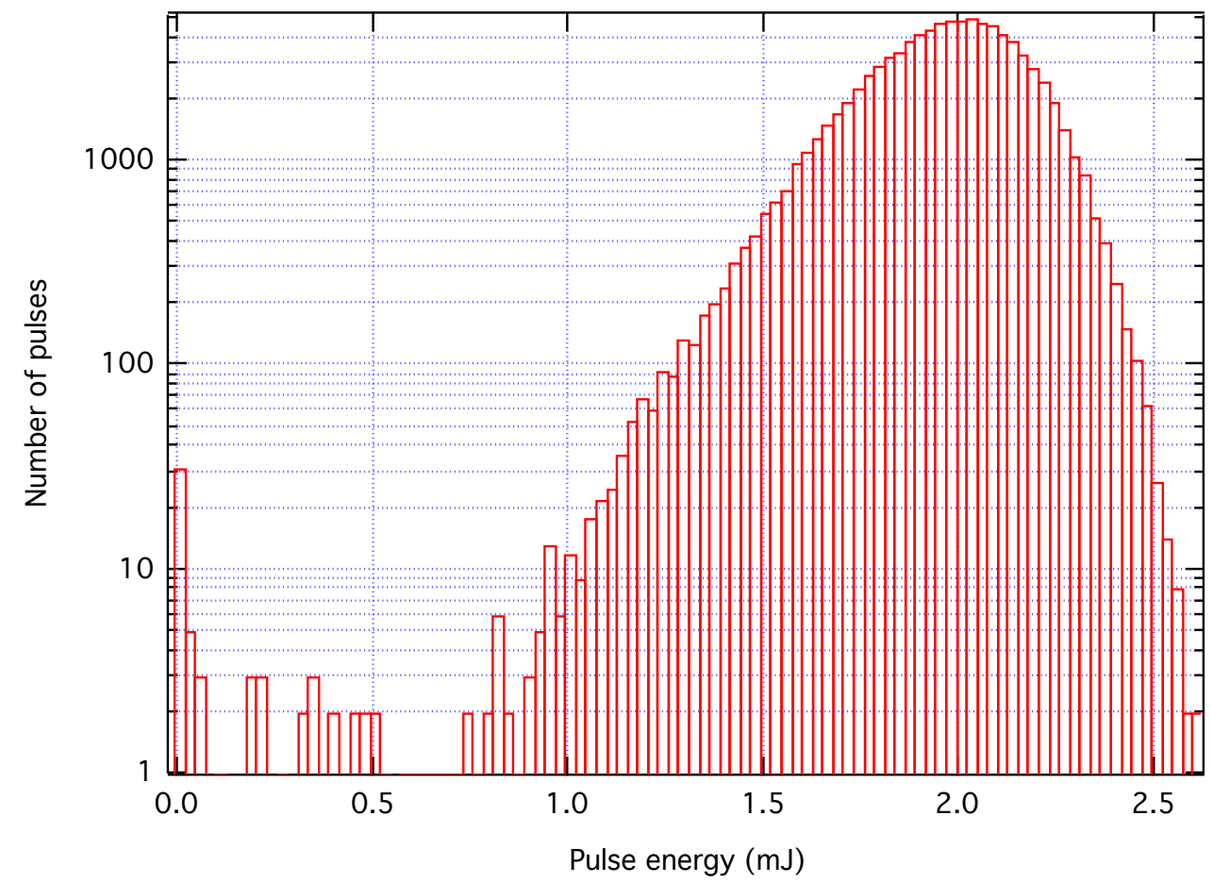
P. Karvinen et al., *Opt. Lett.* **37**, 5073 (2012)

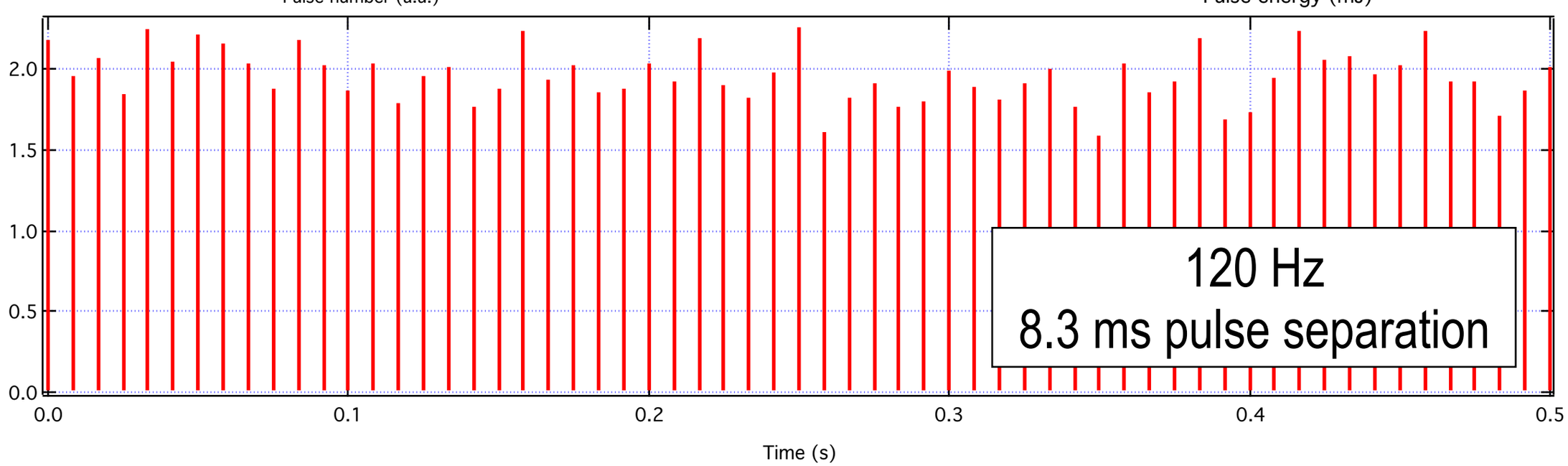
Courtesy of Dr. Mikako Makita

XFEL pulse energy properties

The number of photons per XFEL pulse also varies a lot from shot-to-shot

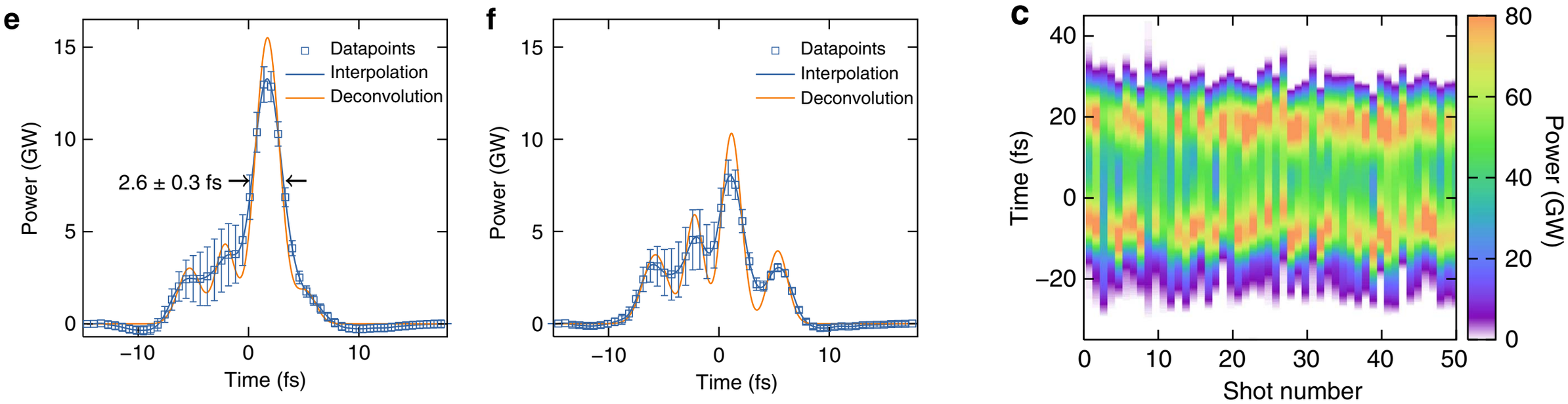




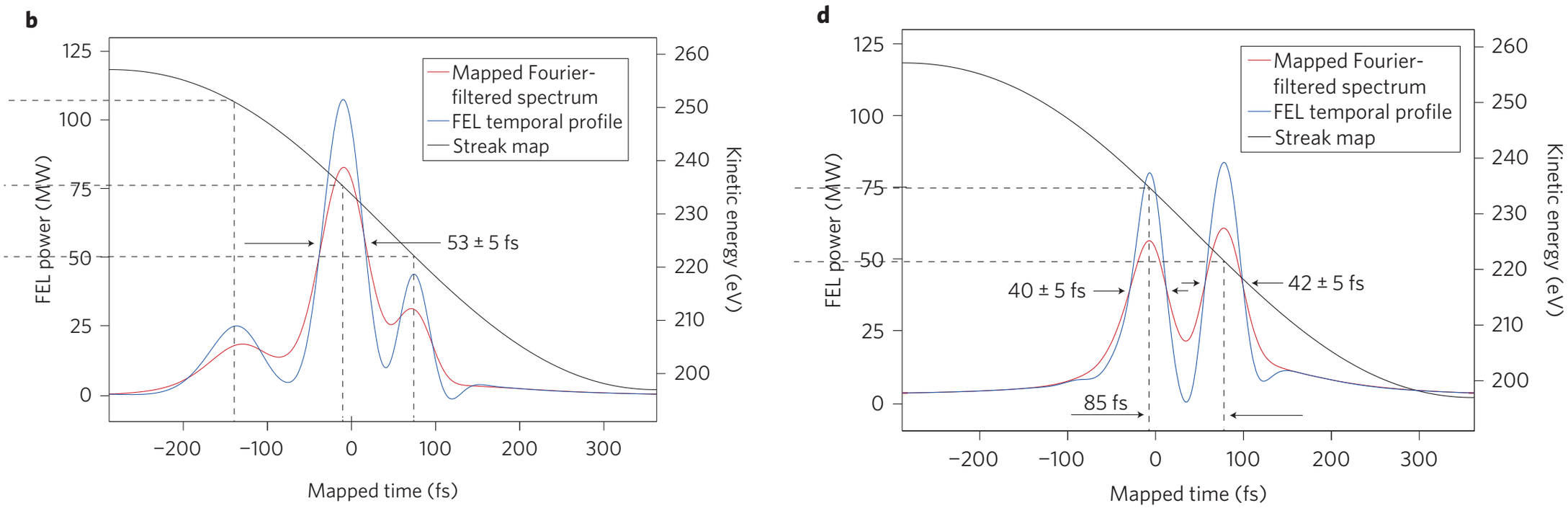


XFEL pulse duration properties

The pulse shape and duration in time also varies from shot to shot

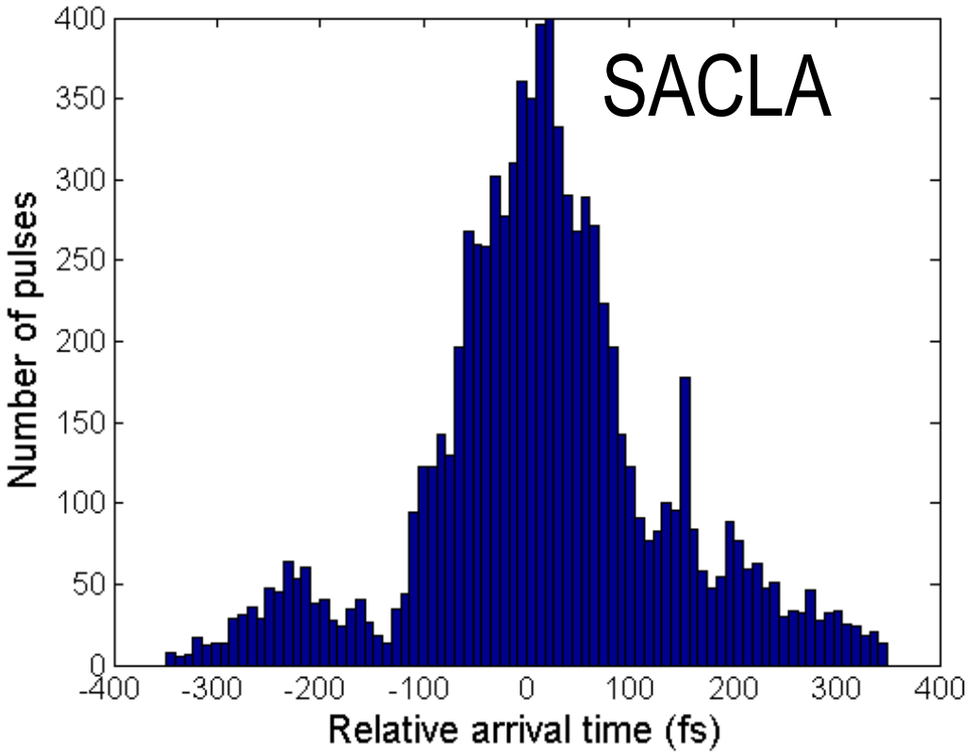


C. Behrens et al., *Nat. Comm.* **5**, 3762 (2014)



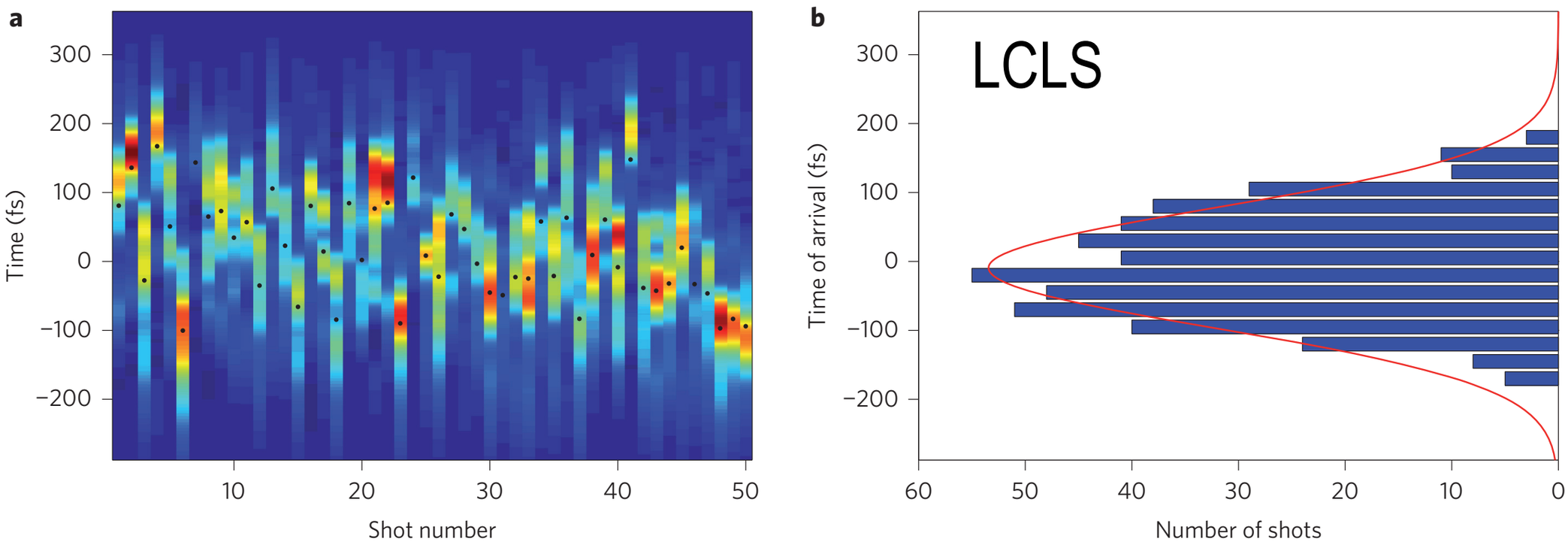
I. Grguraš et al., *Nat. Phot.* **6**, 852 (2012)

XFEL pulse arrival jitter



P. Juranić et al., *Opt. Exp.* **22**, 30006 (2014)

Because the ~1 ps electron bunch can lase at any longitudinal position the X-ray pulse has an arrival time jitter

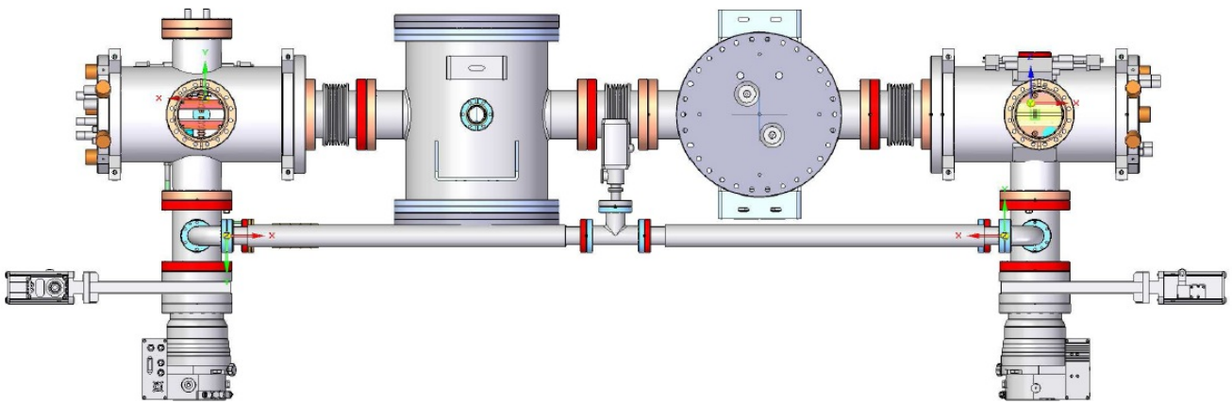


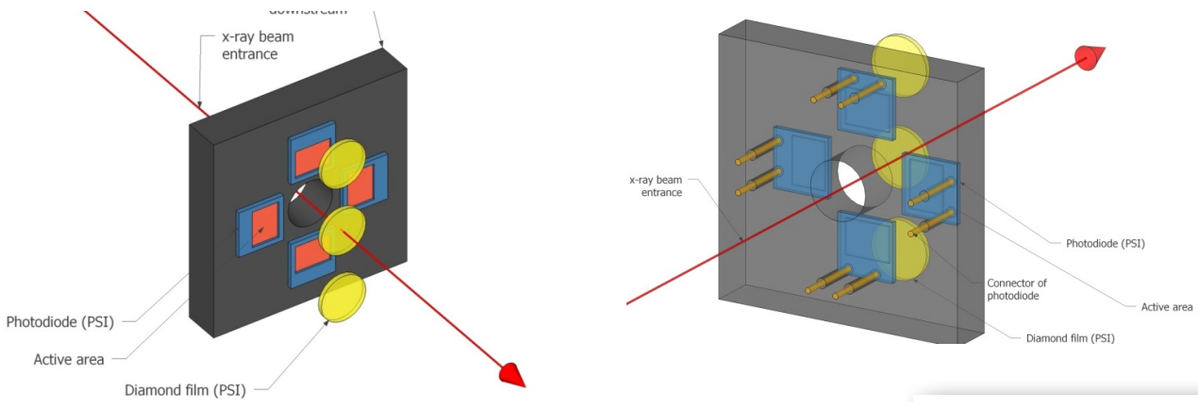
I. Grguraš et al., *Nat. Phot.* **6**, 852 (2012)

So we need to measure as much information as possible for every single X-ray pulse

X-ray Photon Diagnostics

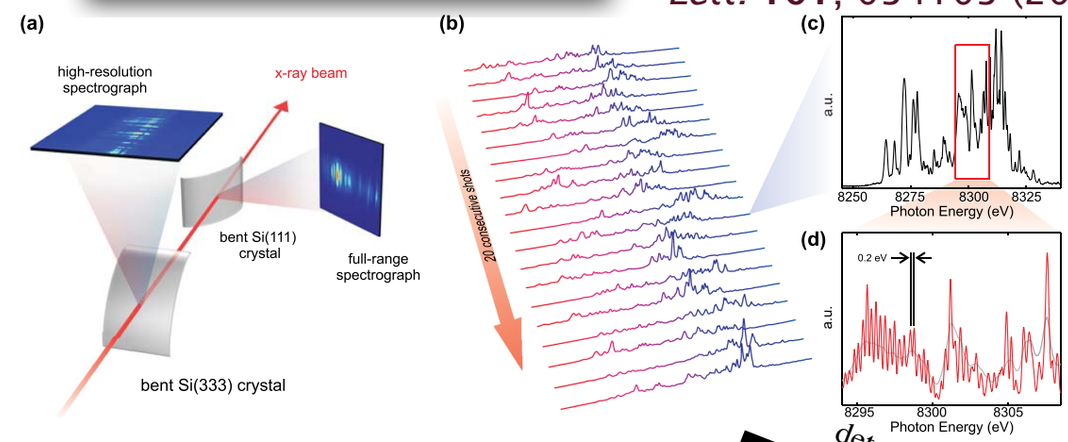
Position and Intensity Monitors

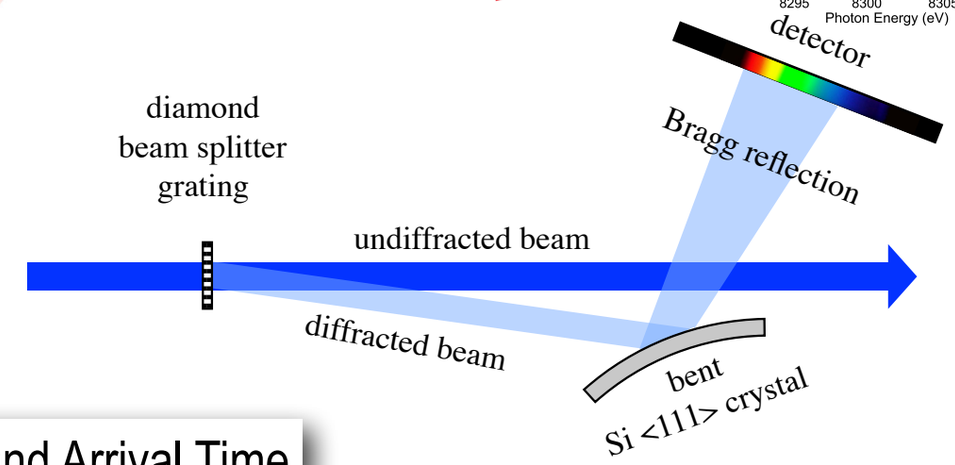




Incident X-ray Spectrum

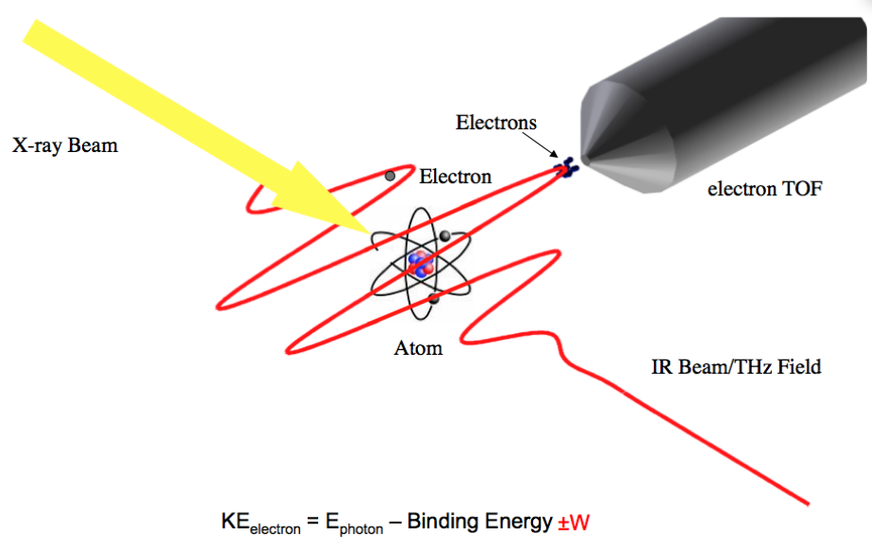
D. Zhu et al. *App. Phys. Lett.* **101**, 034103 (2012)



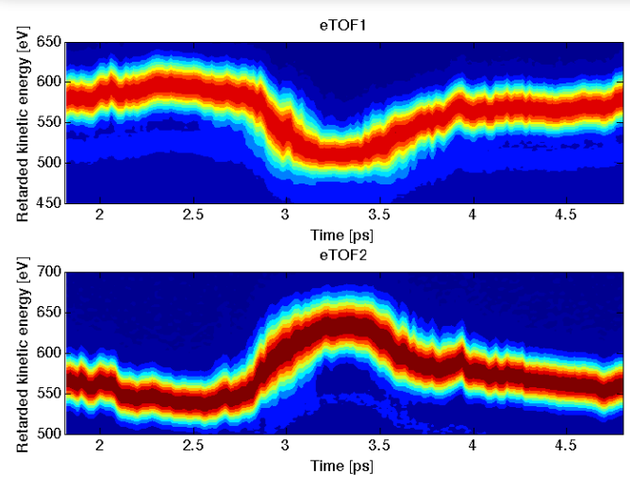


X-ray Pulse Duration and Arrival Time

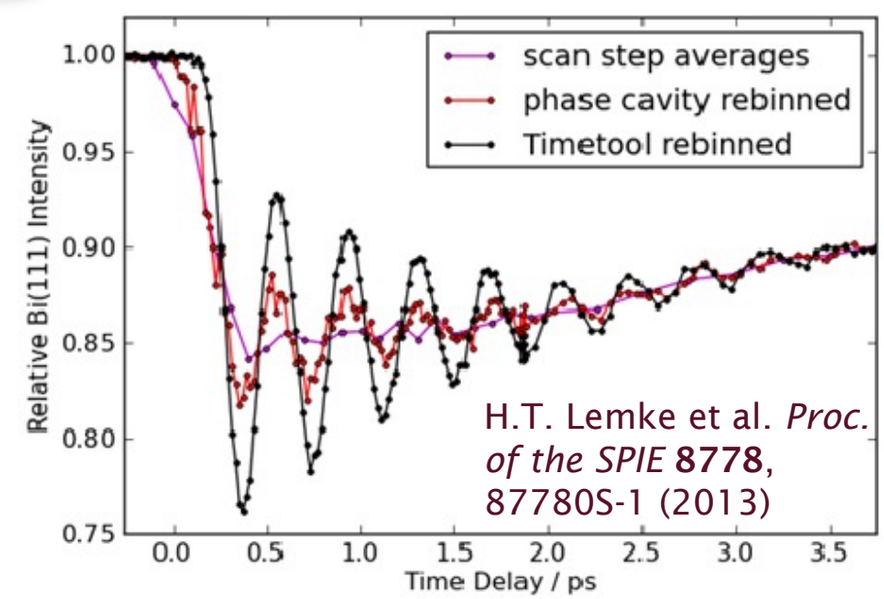
- Use a THz streak camera concept to measure the arrival time and length of the photon pulse.



P. Juranić et al., *Opt. Exp.* **22**, 30006 (2014)



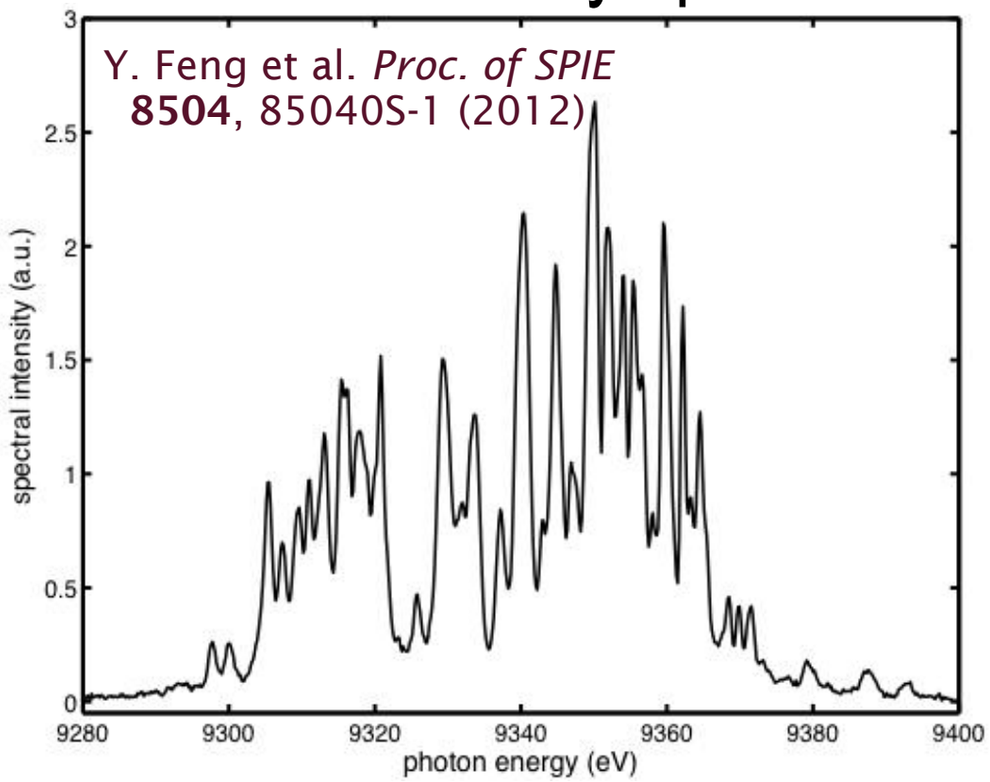
Streak scan for the Xe $2p_{3/2}$ electrons at a photon energy of 10 keV



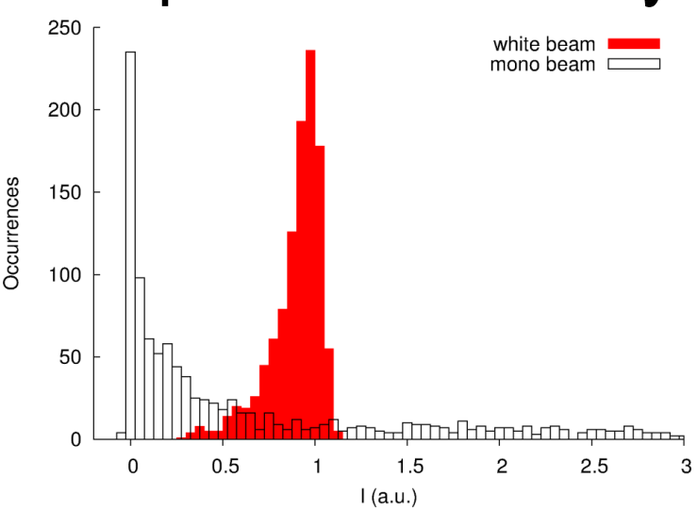
H.T. Lemke et al. *Proc. of the SPIE* **8778**, 87780S-1 (2013)

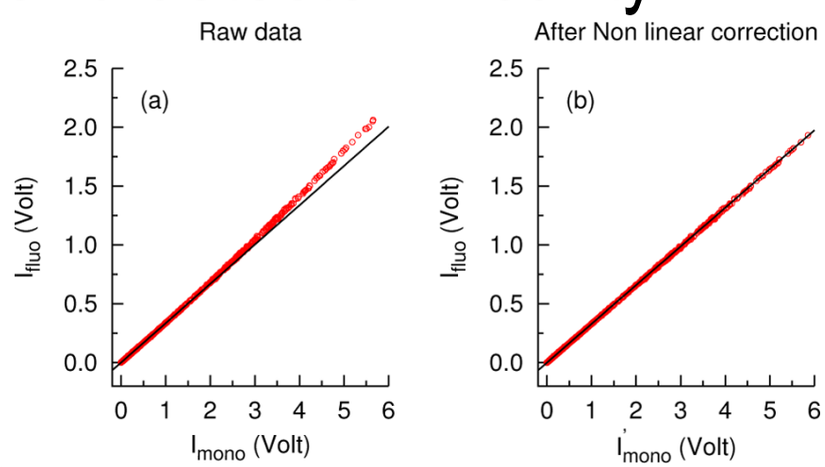
X-ray spectroscopy experiments at XFELs

Stochastic X-ray spectrum



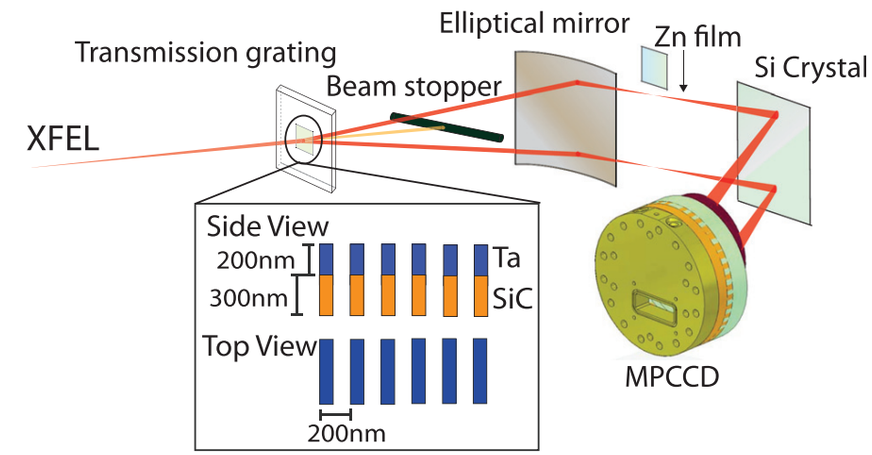
Spectral instability and detector linearity

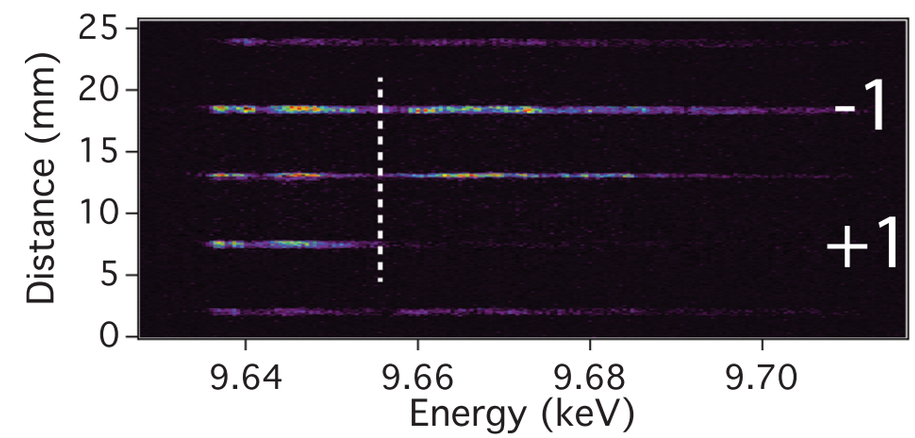


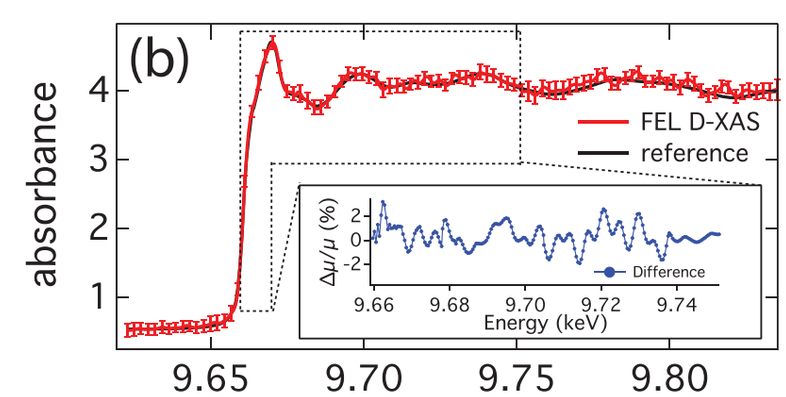


H.T. Lemke et al. *JPCA* **117**, 735 (2013)

Single-shot XAS



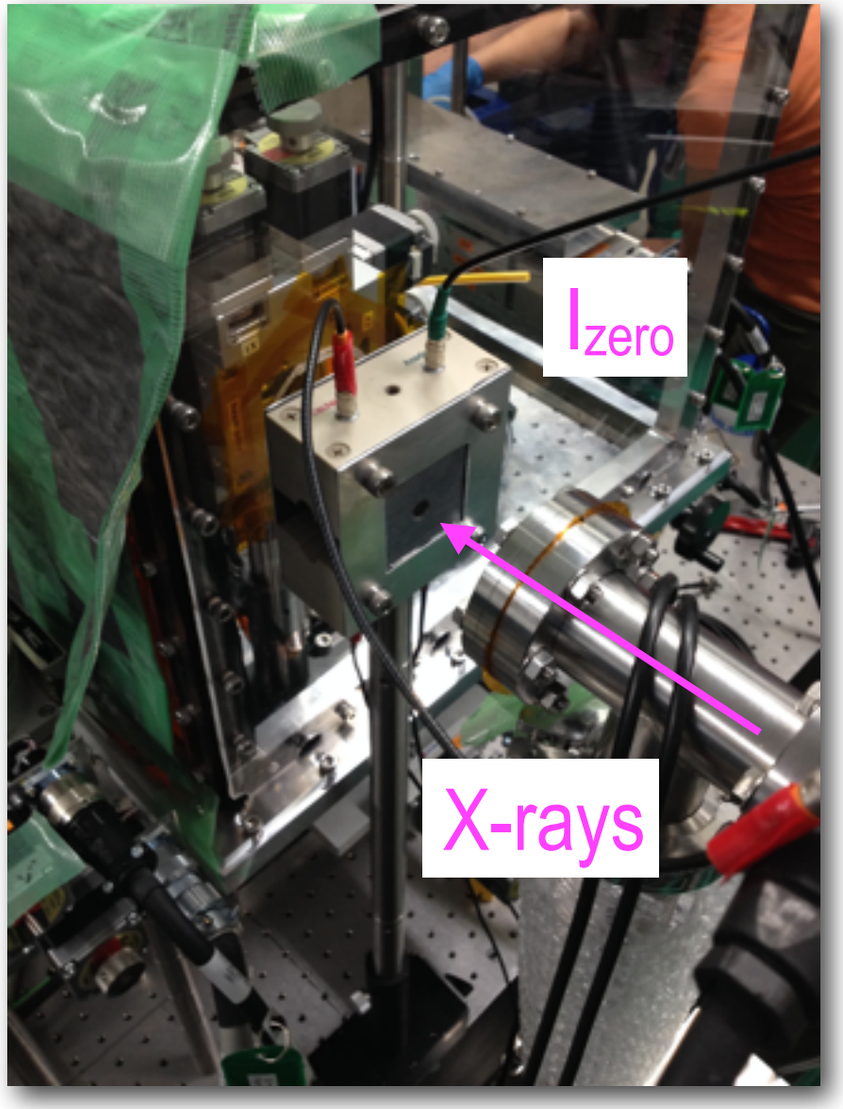


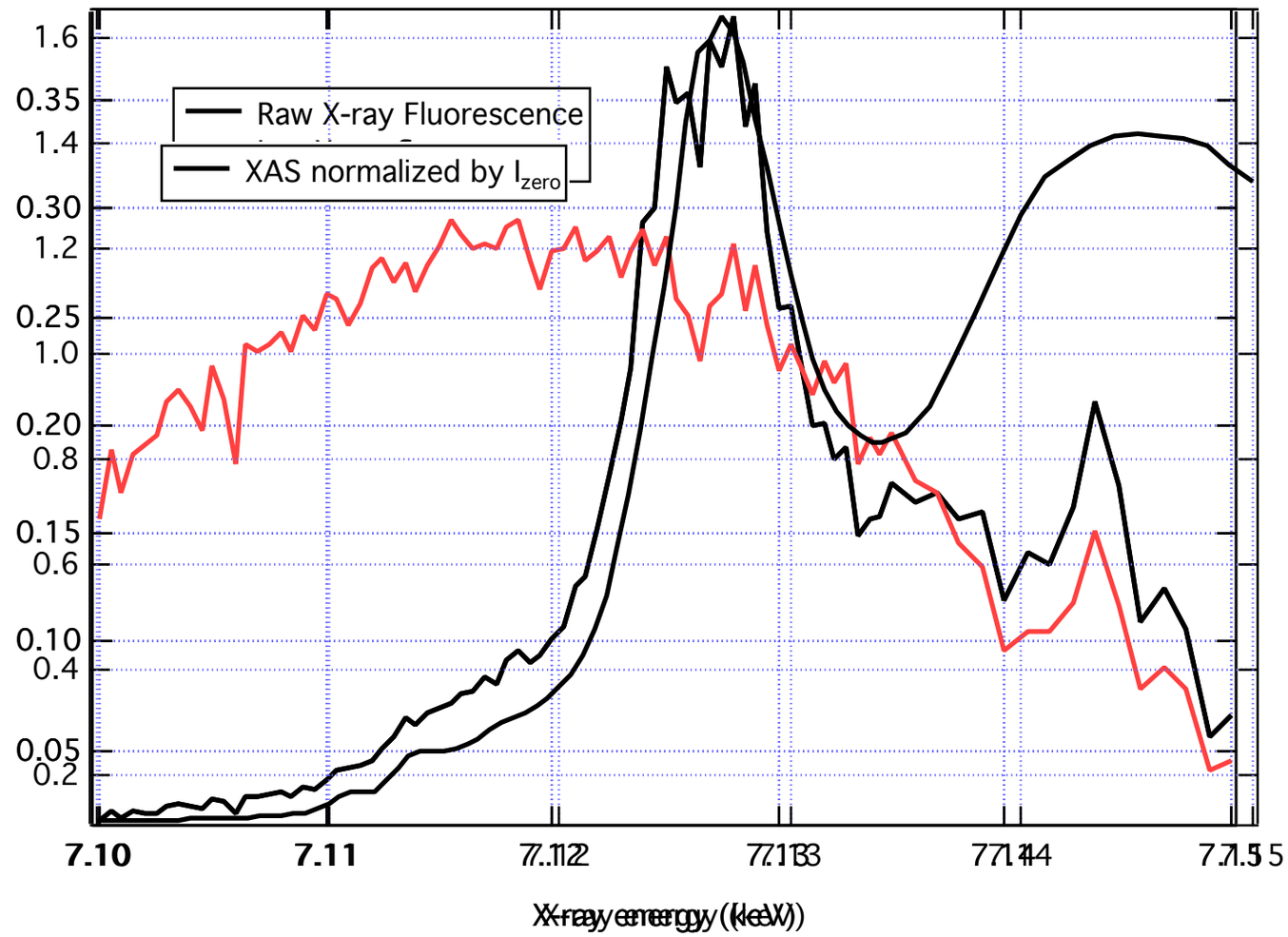


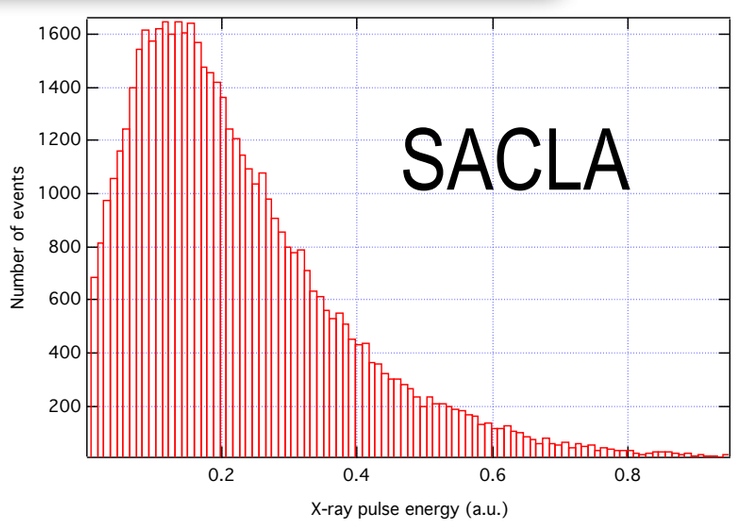
T. Katayama et al. *App. Phys. Lett.* **103**, 131105 (2013)

Shot-by-shot diagnostics and techniques have significant advantages at XFELs

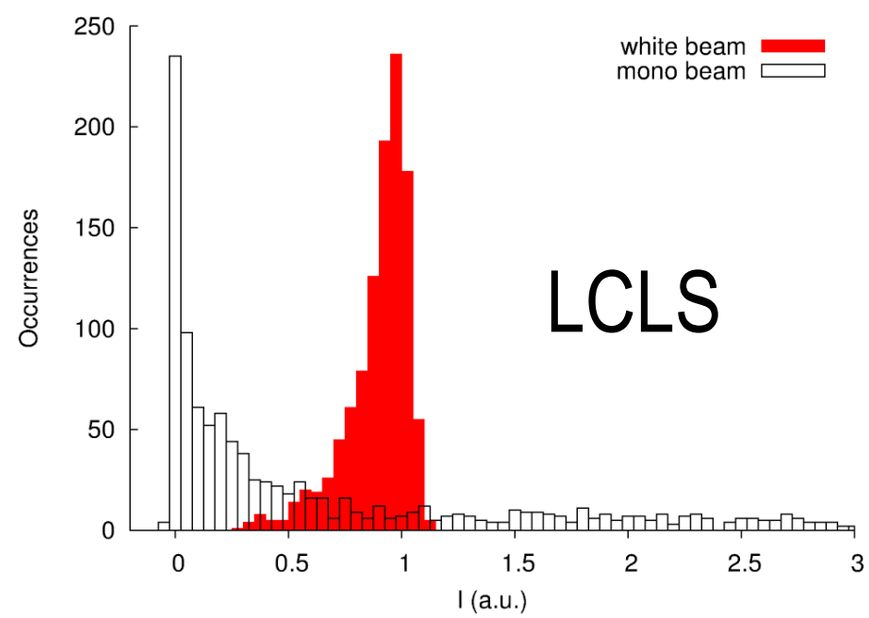
X-ray intensity normalization for scans



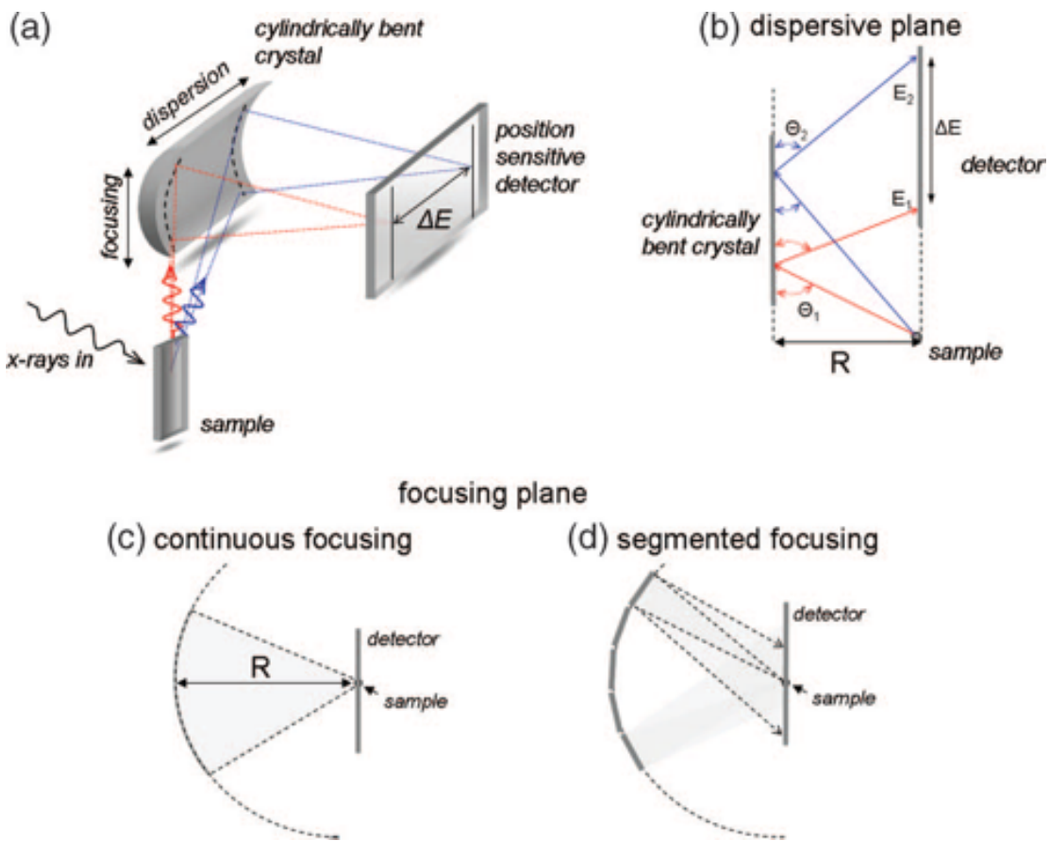


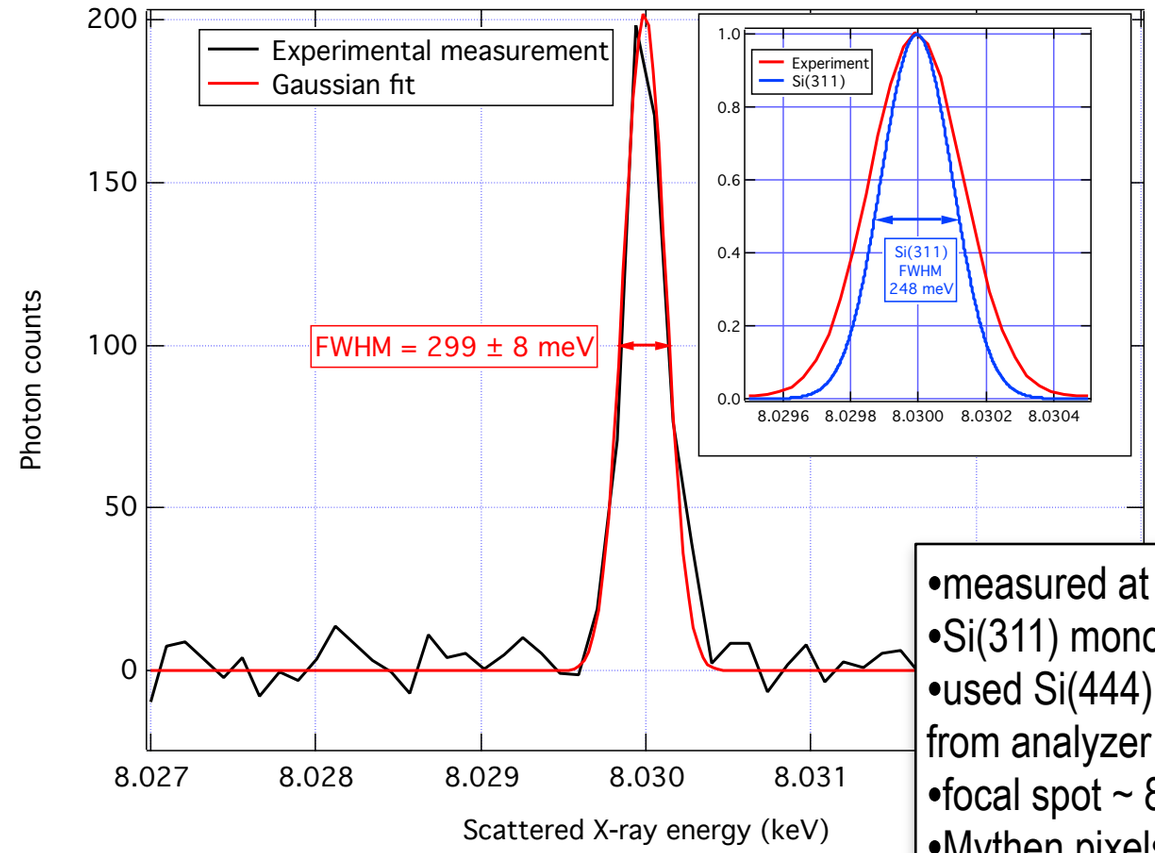


Vs



Introduction to von Hamos X-ray spectrometers





- measured at SuperXAS
- Si(311) mono
- used Si(444) diffraction from analyzer
- focal spot ~ 80 μm
- Mythen pixels 50 μm
- Resolution: 100 meV

von Hamos geometry

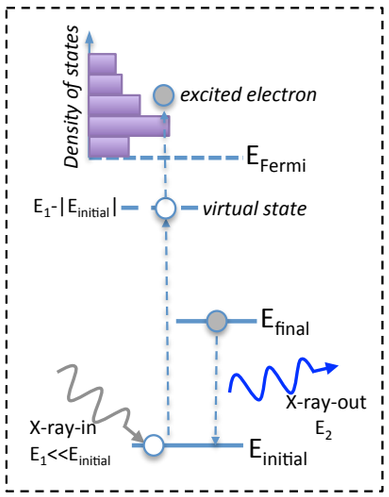
- Dispersive so you get a complete energy range per XFEL pulse
- 25 cm radius of curvature crystals means compact setup
- Scan-free setup means no moving parts
- Development of segmented crystals provides excellent energy resolution
- Scales easily with additional crystal+detector pairs to cover other energies

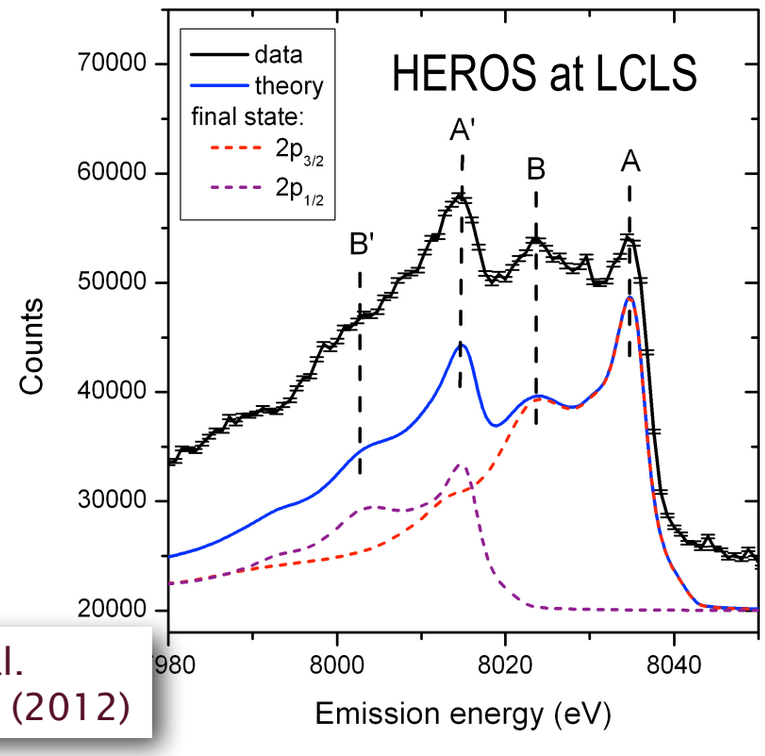
HoXS: Holochromatic X-ray Spectroscopy

Goal: The ability to obtain a holistic picture of the sample

High energy resolution off-resonant spectroscopy (HEROS)

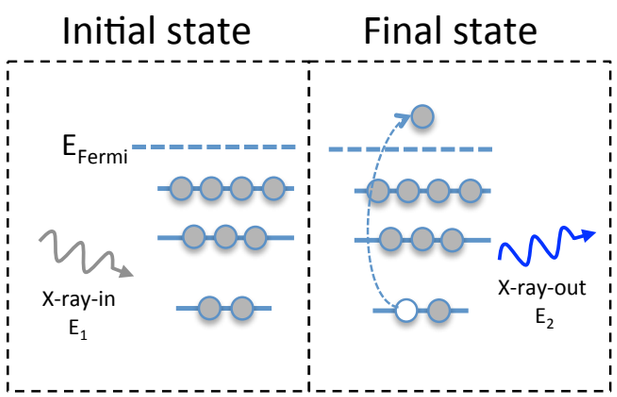
Energy diagram level

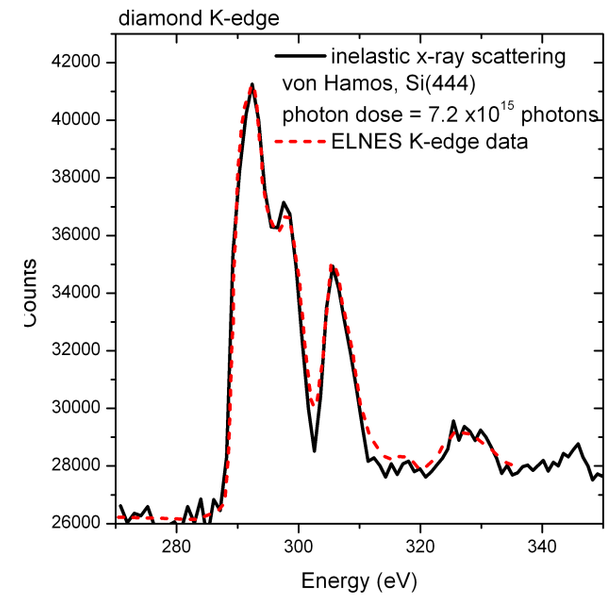




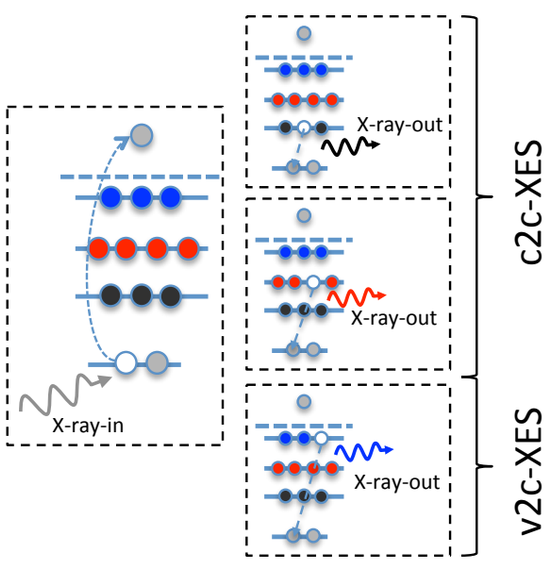
HEROS: J. Szlachetko et al. *Chem. Comm.* **48**, 10898 (2012)

Inelastic x-ray scattering (IXS)

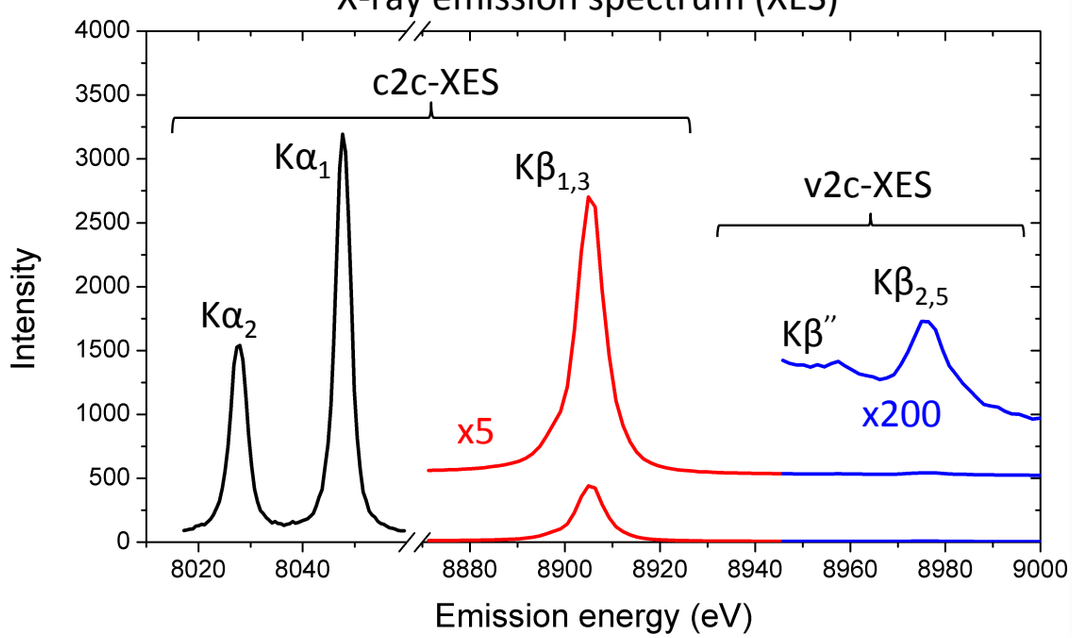




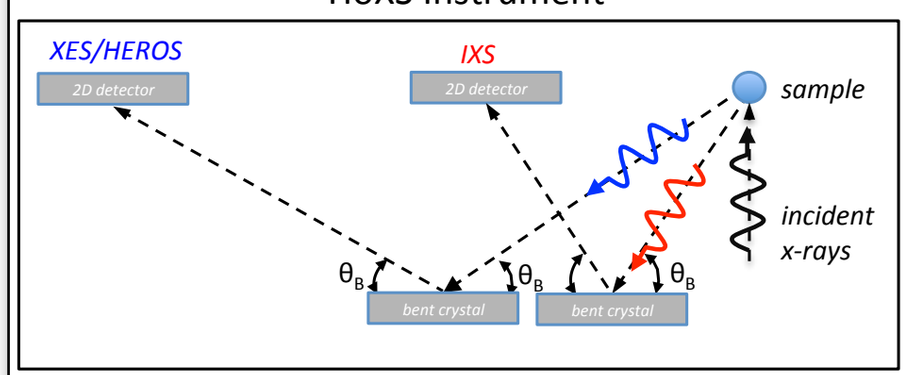
Initial state Final state

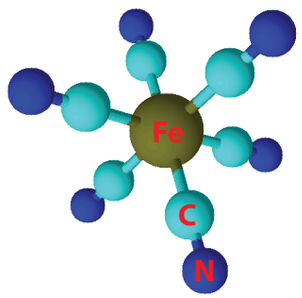


X-ray emission spectrum (XES)



HoXS Instrument





For example Fe Kβ XES and C or N K-edge IXS measured simultaneously

What types of experiments are XFELs good at ?

XFELS are defined by lots of photons in a very short pulse but the average flux isn't that different from a 3rd-generation synchrotron

Only ***three**** types of experiments benefit from the high peak flux from an XFEL:

1. **Single-shot experiments** that need lots of photons in a short pulse
2. **Pump-probe measurements** where the short pulse allows measurement of fast dynamics
3. **Nonlinear X-ray experiments** that depend nonlinearly on the number of incident X-ray photons

Not all experiments are going to automatically be better at an XFEL

*I'm ignoring the transverse coherence properties

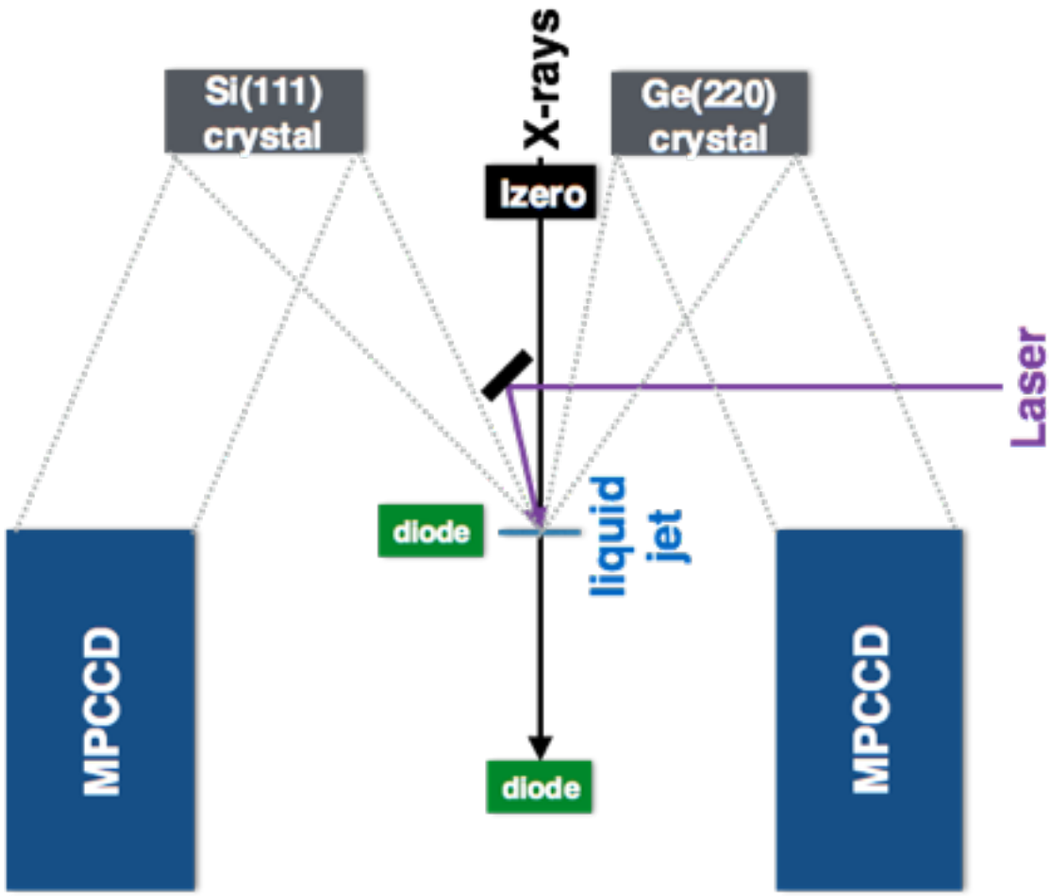
Applying what we've learned to an experiment at an XFEL

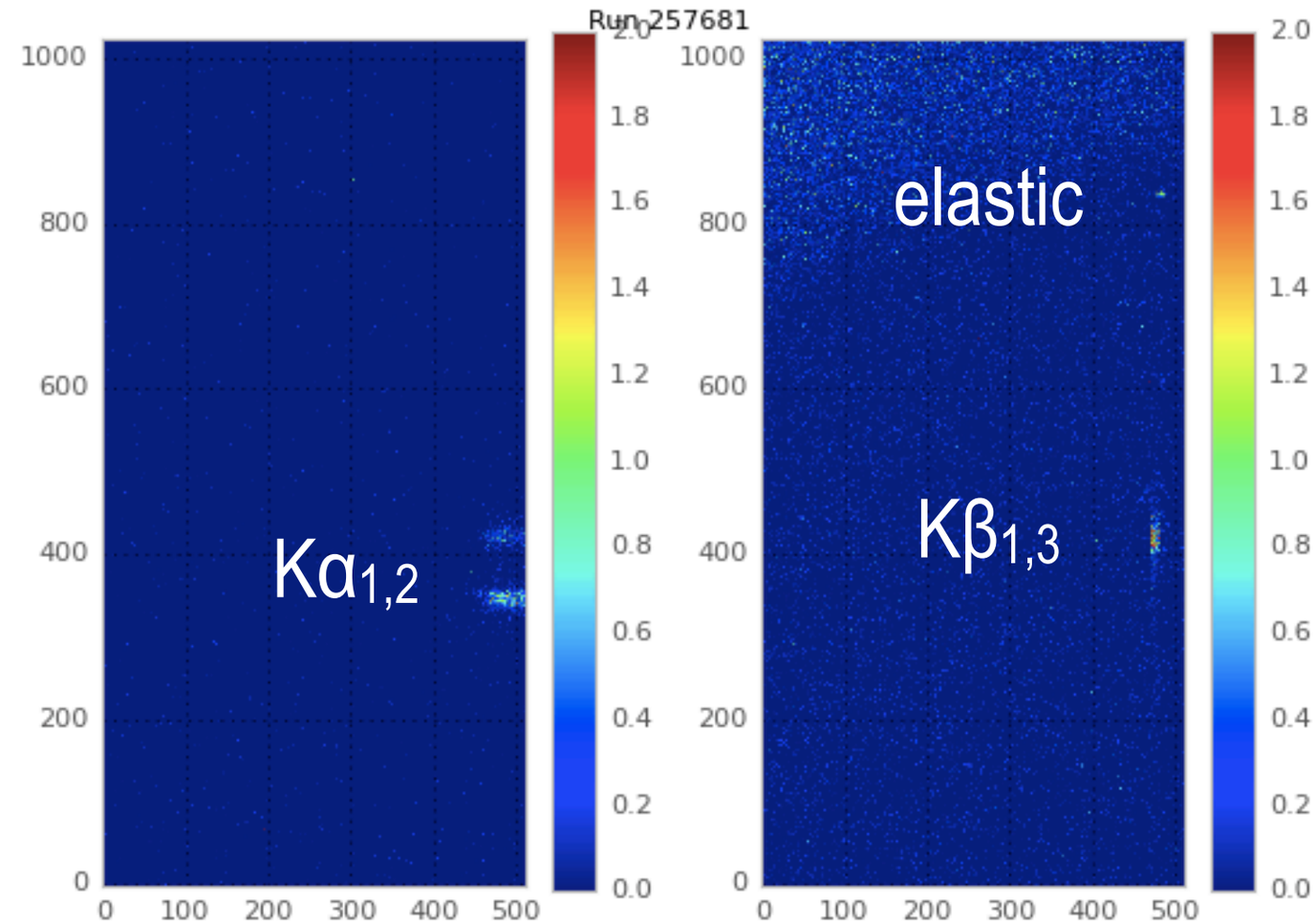
ZnO at SACLA: fs X-ray spectroscopy

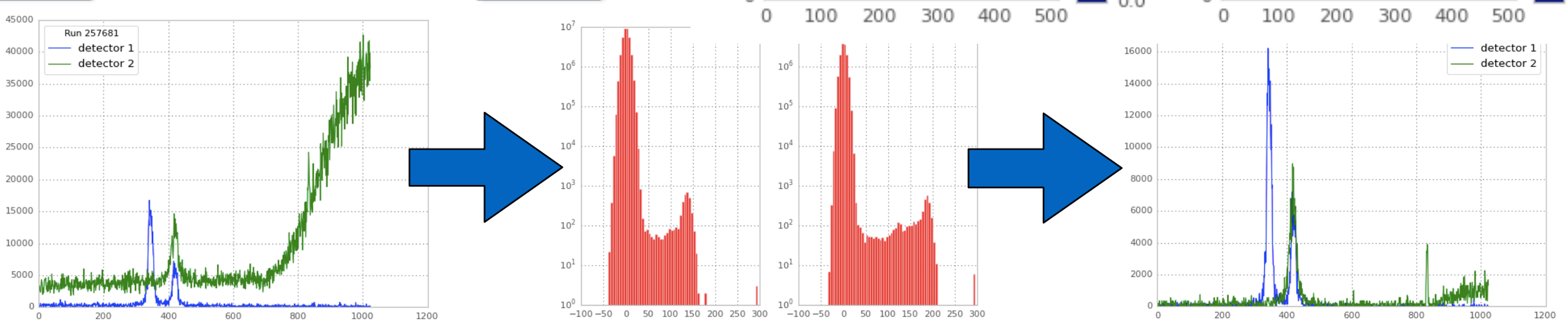
Collaboration with Argonne, EPFL, XFEL, SACLA, DTU, and Tohoku

T.J. Penfold[1], J. Szlachetko[1,10], W. Gawelda[2], F.G. Santomauro[3], A. Britz[2], T.B. van Driel[4], L. Sala[1], S. Ebner[1], S.H. Southworth[5], G. Doumy[5], A.M. March[5], C.S. Lehmann[5], T. Katayama[6], M. Mucke[9], D. Iablonskyi[8], Y. Kumagai[8], G. Knopp[1], K. Motomura[8], T. Togashi[6], S. Owada[7], M. Yabashi[7], J. Rittmann[3], M.M. Nielsen[4], M. Pajek[10], K. Ueda[8], M. Chergui[3], R. Abela[1], and C.J. Milne*[1]

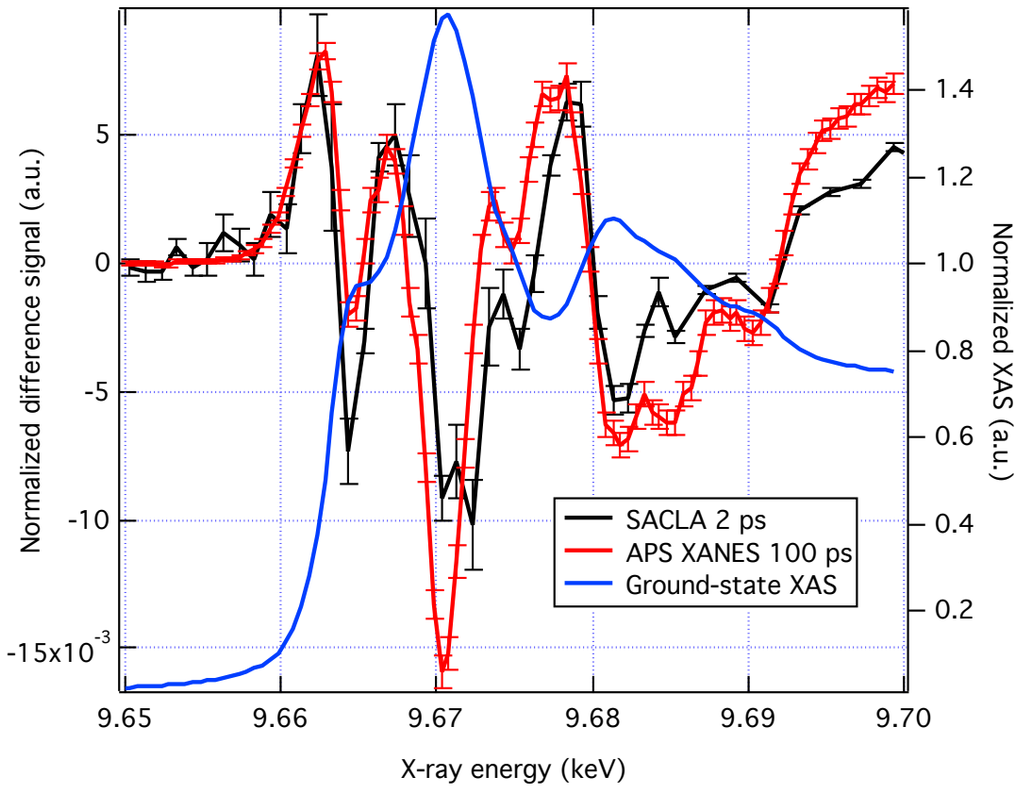
[1]Paul Scherrer Institute, Villigen-PSI, Switzerland, [2]European XFEL GmbH, Hamburg, Germany, [3]EPFL, Lausanne, Switzerland, [4]Technical University Of Denmark, Denmark, [5]APS, Argonne, USA, [6]JASRI, Spring-8, Japan, [7]RIKEN, Spring-8, Japan, [8]Tohoku University, Sendai, Japan, [9]Uppsala University, Uppsala, Sweden, [10]Jan Kochanowski University, Kielce, Poland

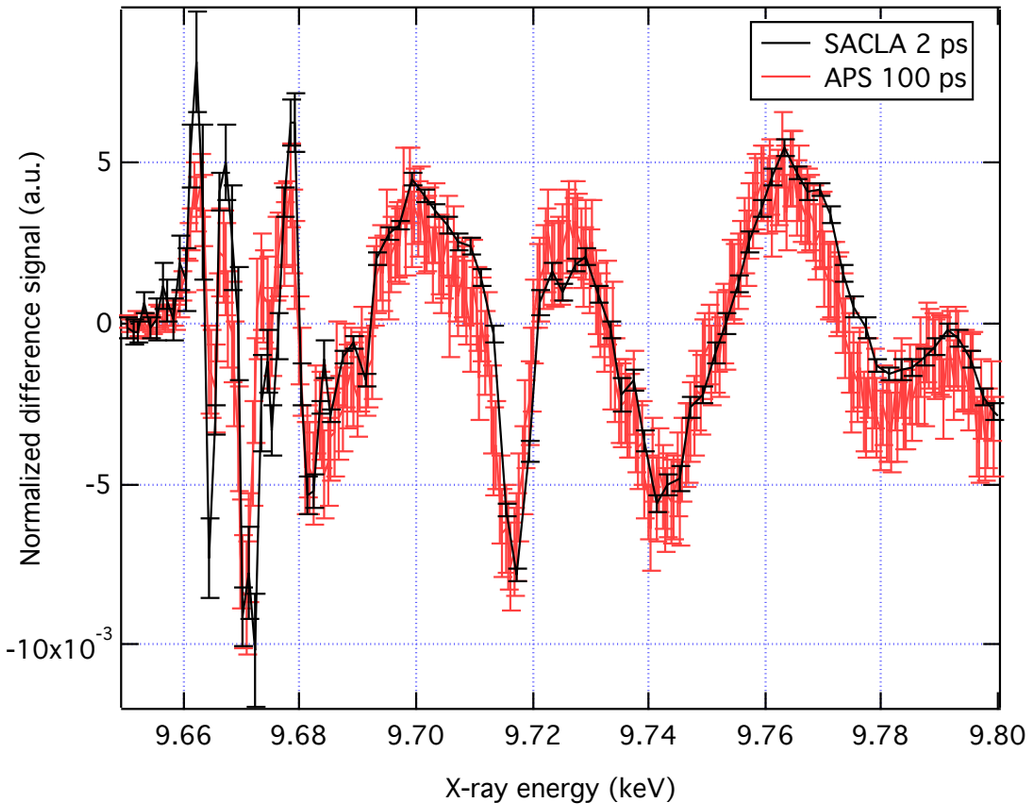


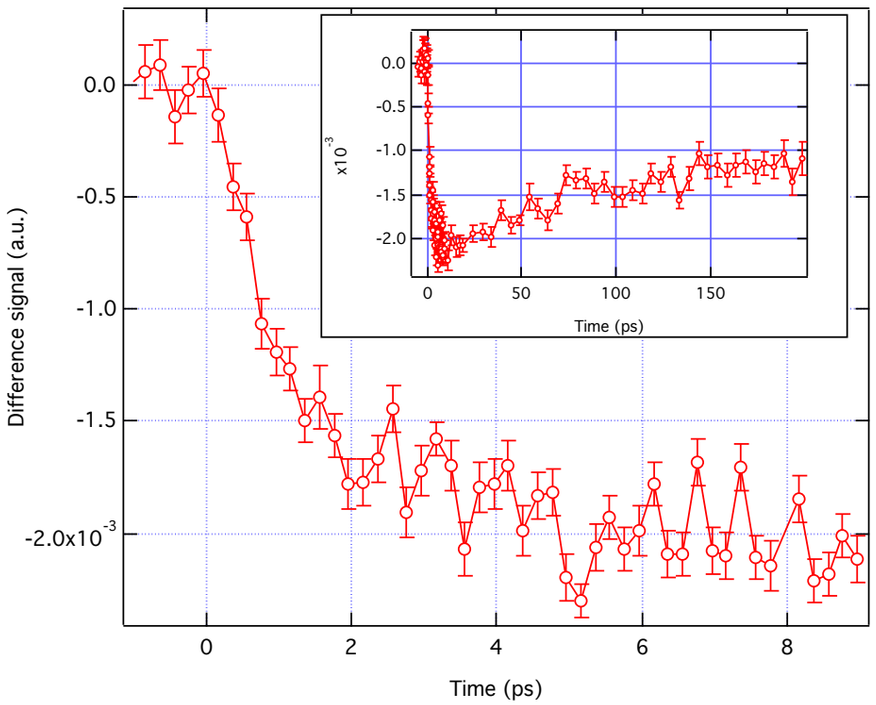


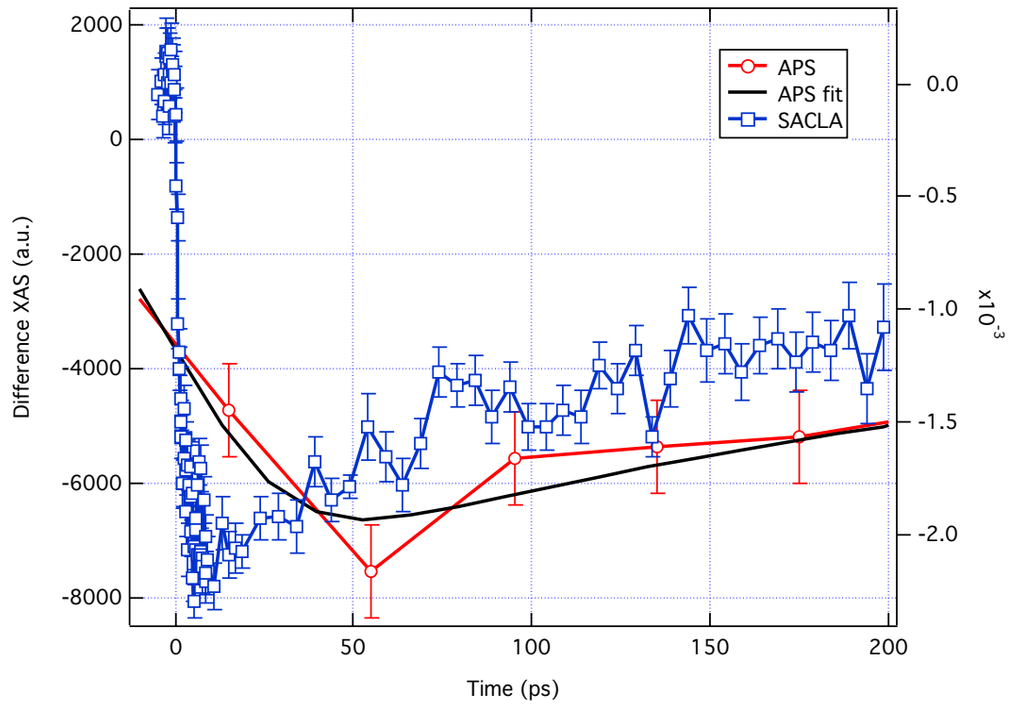


ZnO at SACLA: fs X-ray spectroscopy









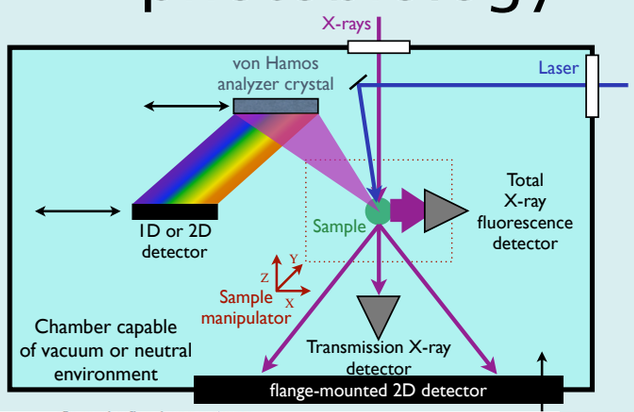
Preliminary analysis of XAS indicates we populate the oxygen vacancies within 1 ps

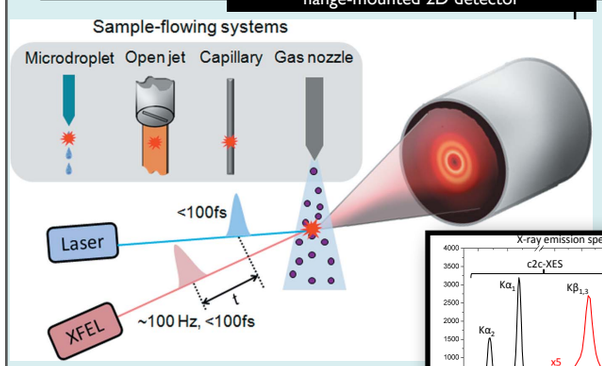
The future

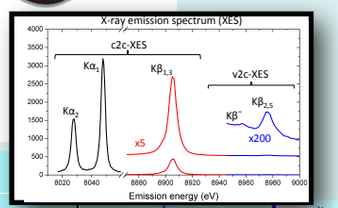
The Future: SwissFEL Experimental Stations

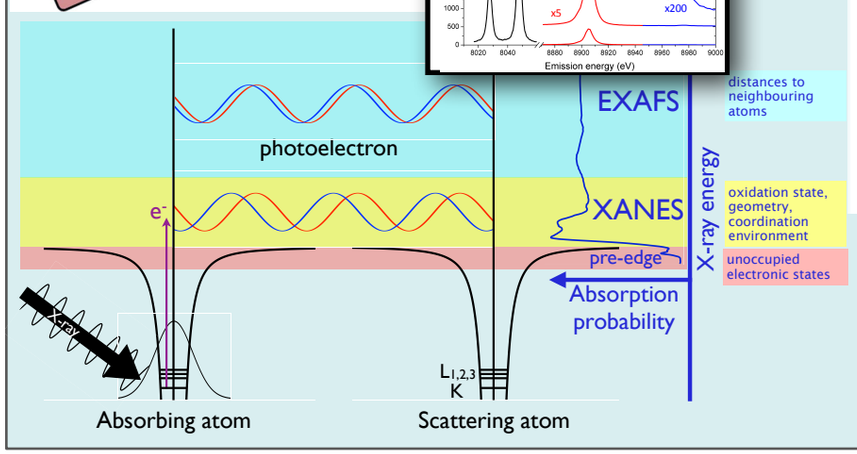
Bruce Patterson
and co-workers

ESA:
Ultrafast photochemistry and photobiology

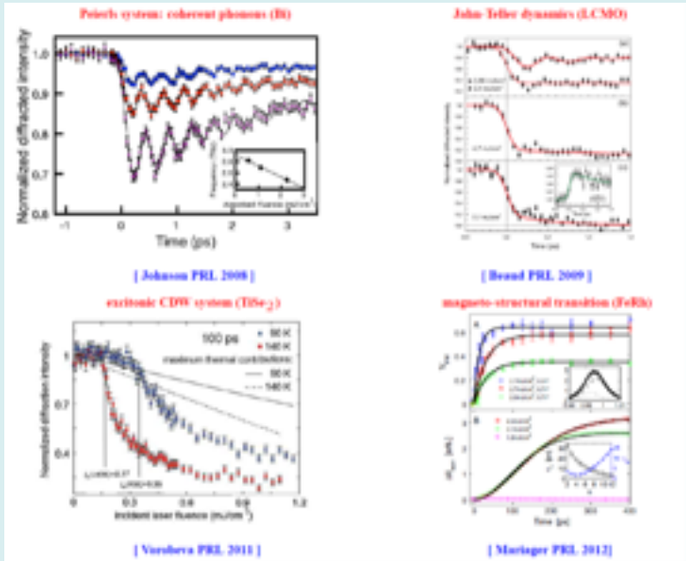


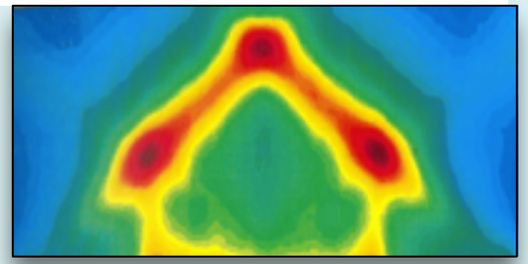


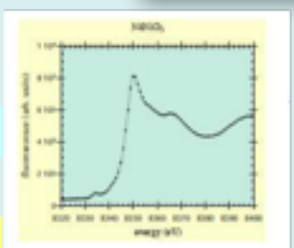


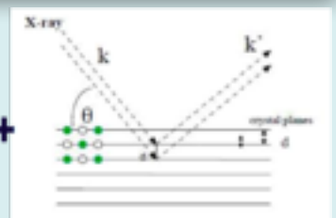


ESB:
Pump-probe crystallography





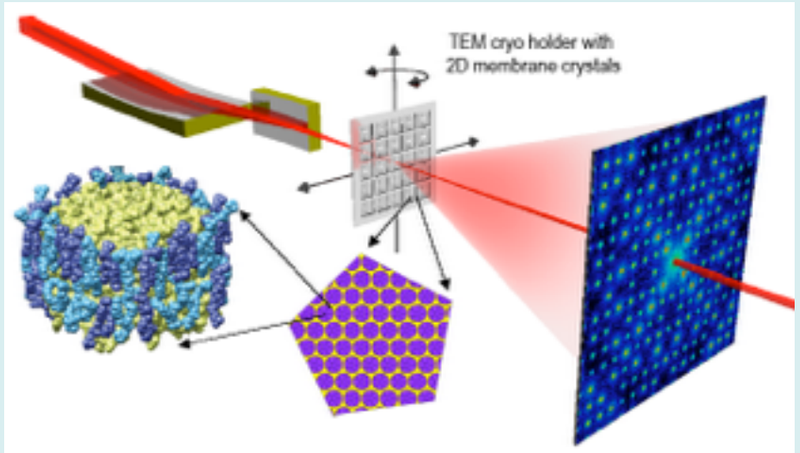




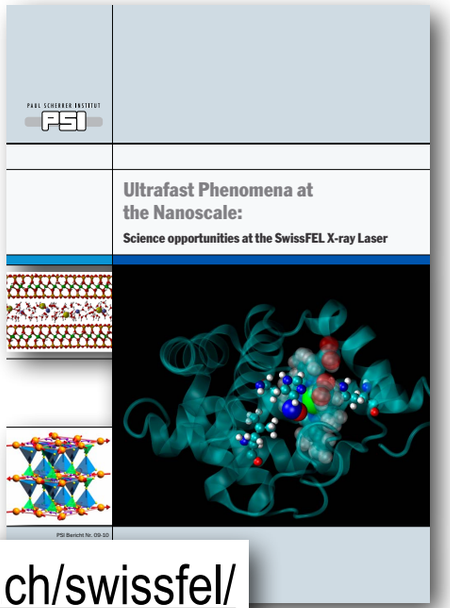
Phase I:
Ready by 2017

Phase II: >2017

ESC:
Materials science and nanocrystallography



Scientific Case
B. Patterson
editor



http://www.psi.ch/swissfel/