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Wir schaffen Wissen – heute für morgen

Exploring ultrafast chemical and biological reaction dynamics using X-ray techniques

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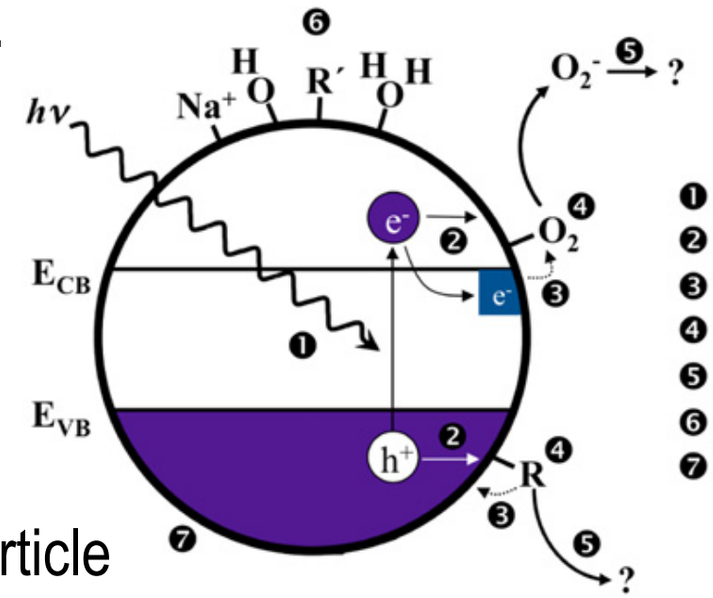
Photocatalysis and energy conversion

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

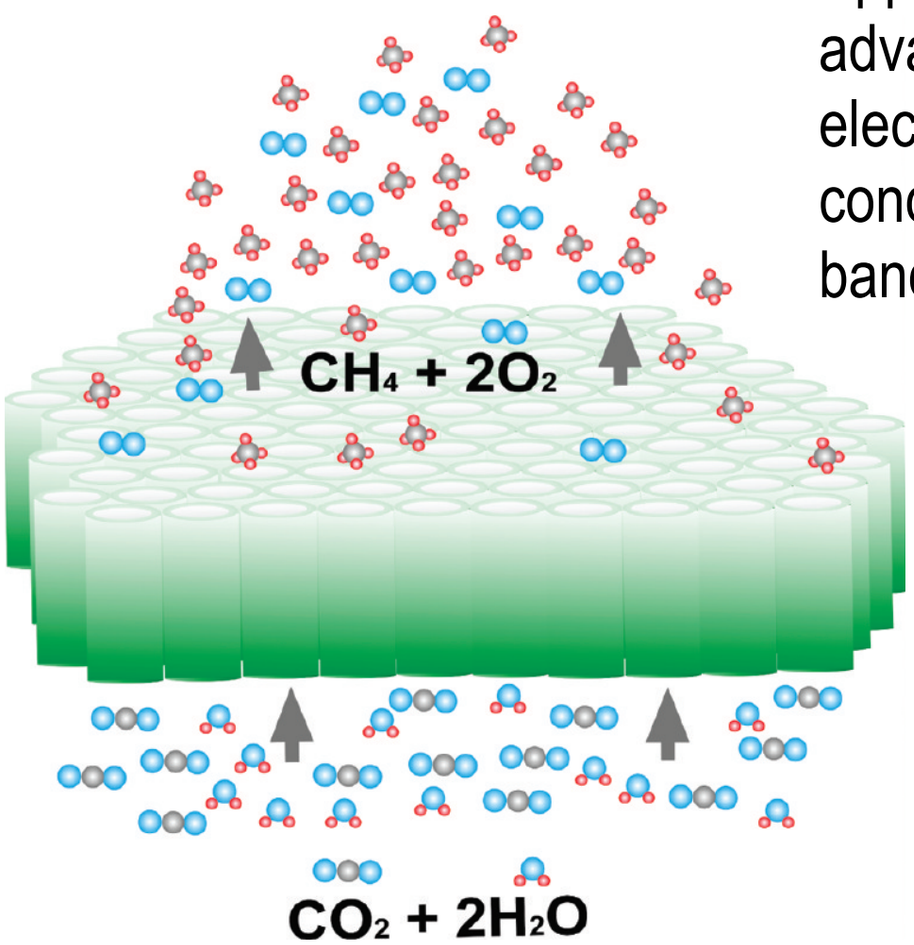


M. Henderson *Surf. Sci. Rep.* **66**, 185 (2011)

Important issues

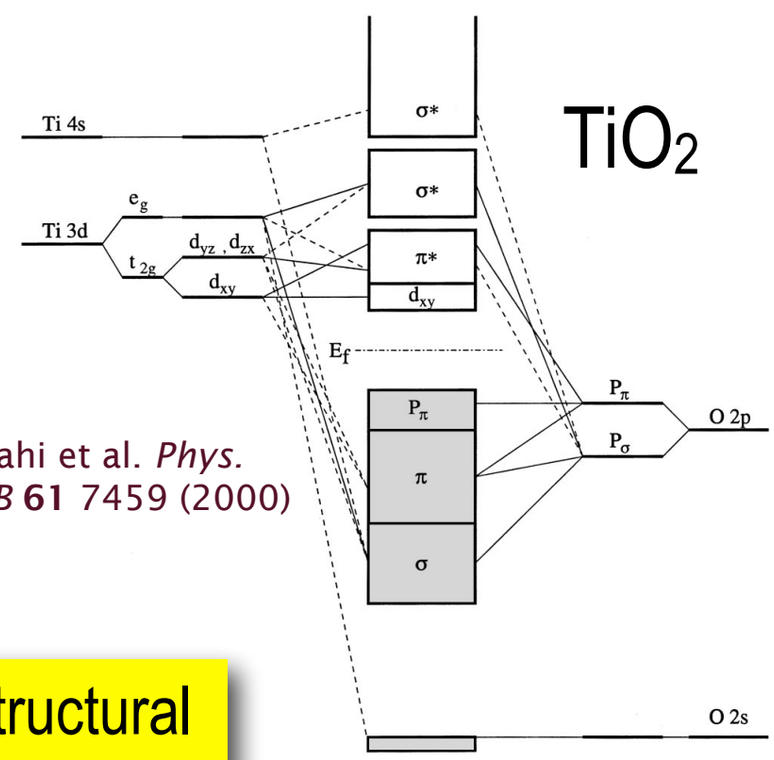
1. excitation
2. charge transport and trapping
3. charge transfer
4. molecular adsorption
5. reaction mechanisms
6. poisons and promoters
7. surface and material structure

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

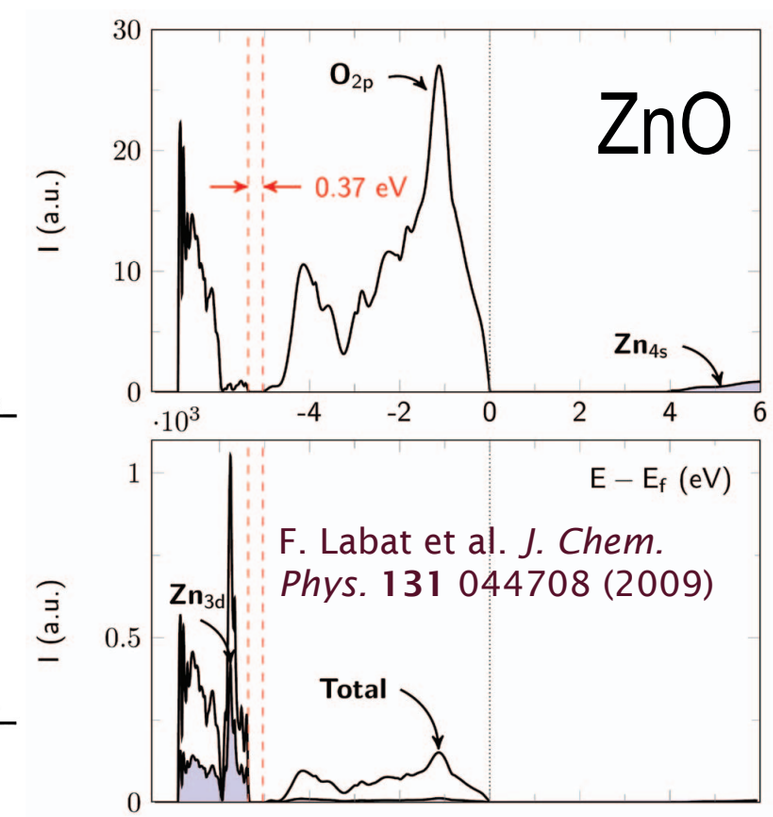


S.C. Roy et al. *ACS Nano* **4**, 1259 (2010)

Valence and conduction bands have distinct atomic character



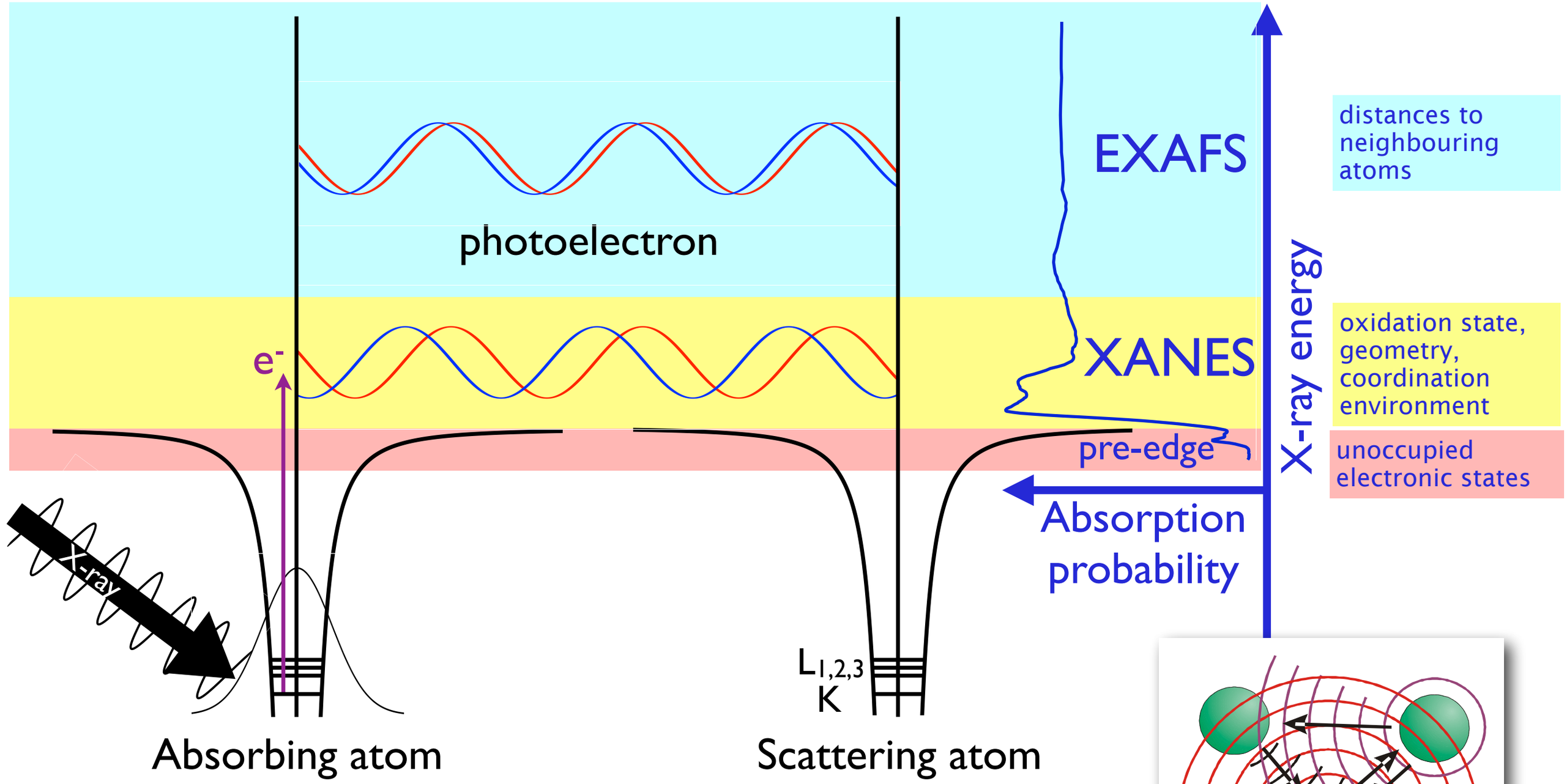
R. Asahi et al. *Phys. Rev. B* **61** 7459 (2000)



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

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

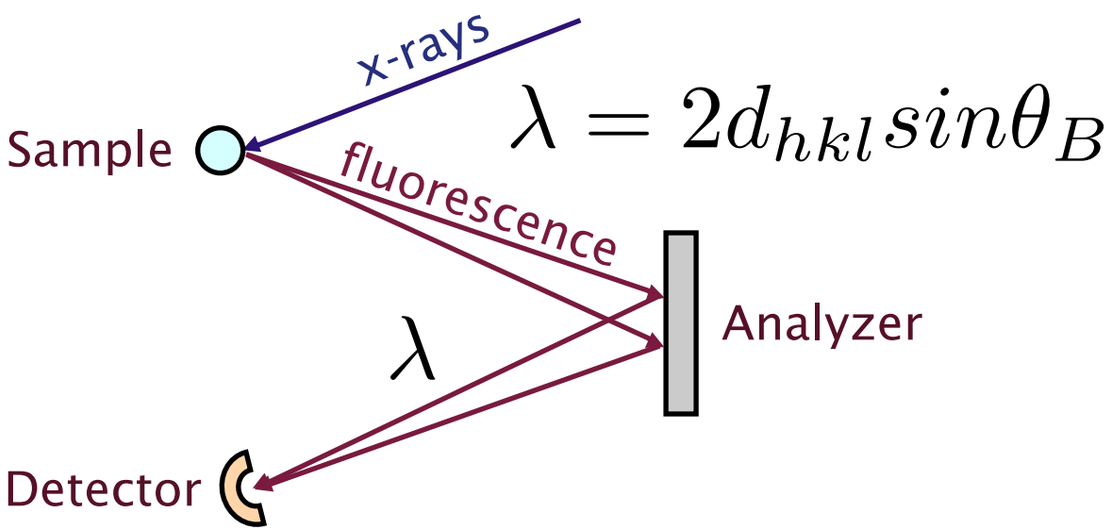
X-ray absorption: Retrieving local structure



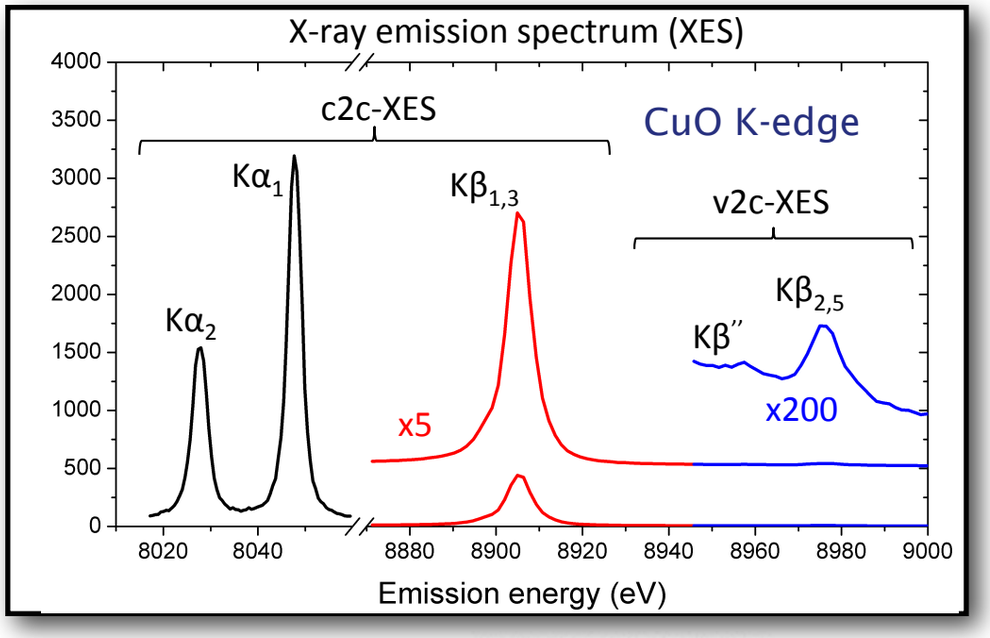
X-ray absorption gives information on the unoccupied electronic states and the local structure

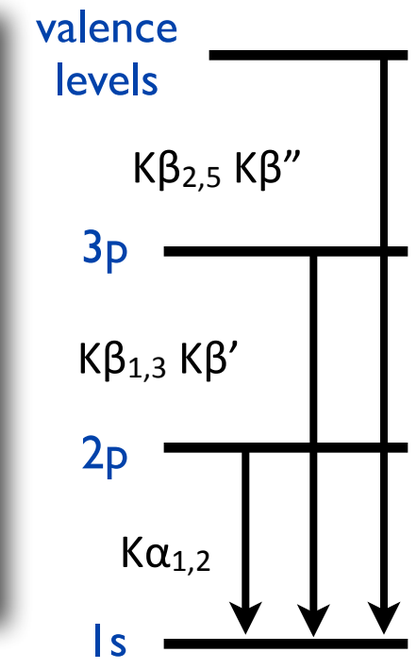
C.J. Milne et al. *Coord. Chem. Rev.* **277** 44 (2014)

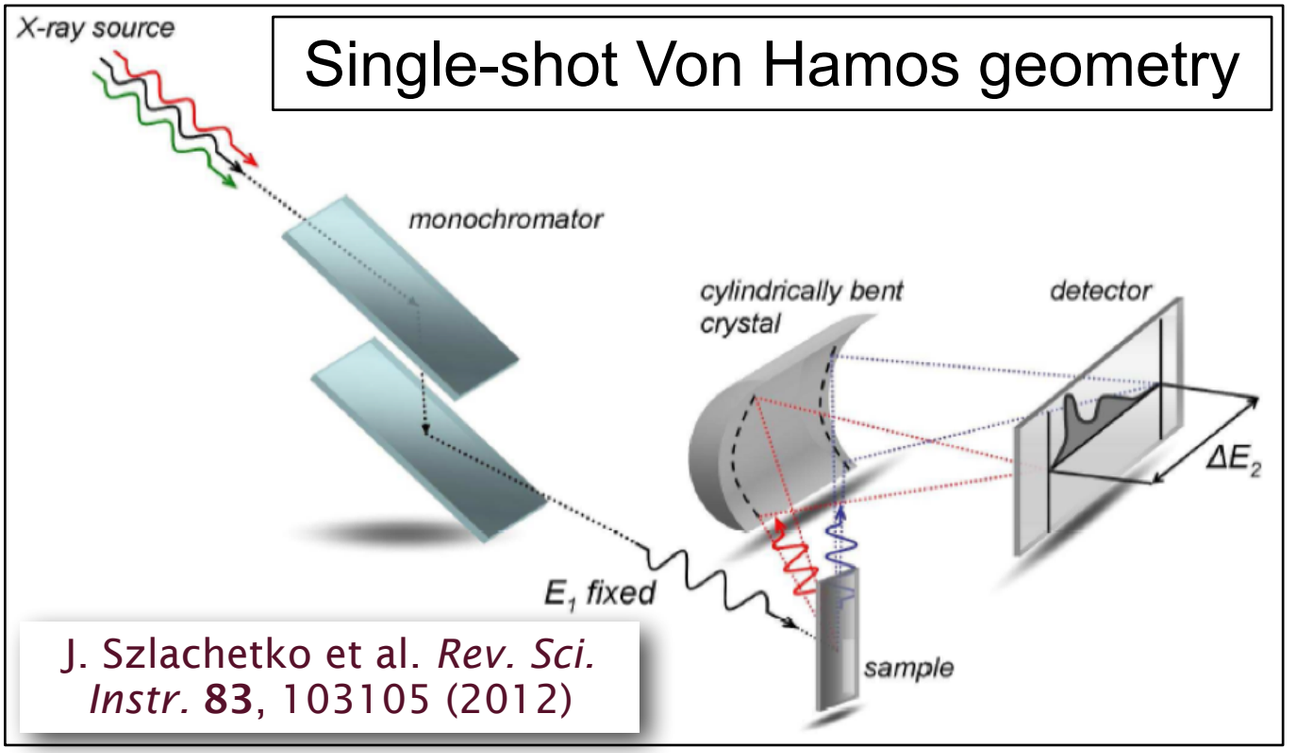
X-ray emission: Retrieving electronic information



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

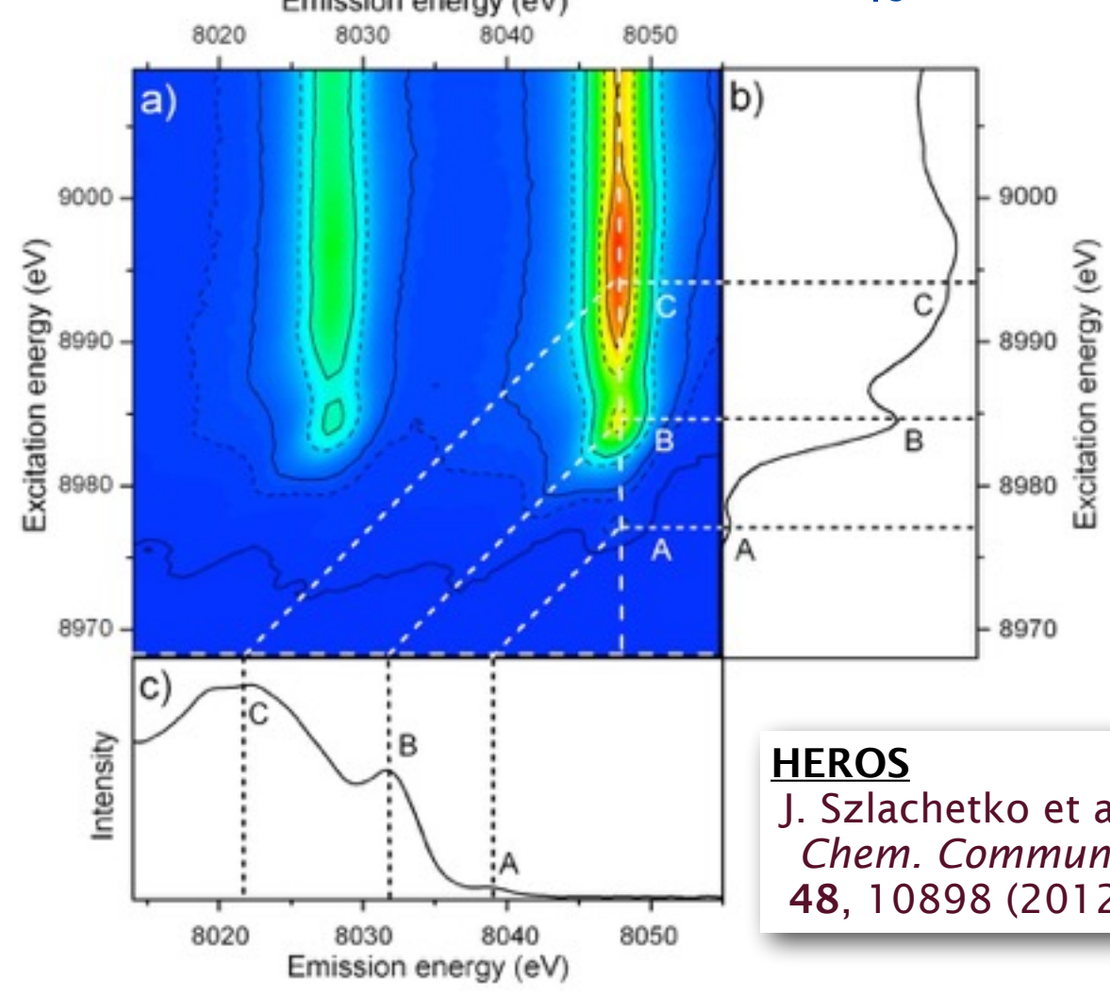






Single-shot Von Hamos geometry

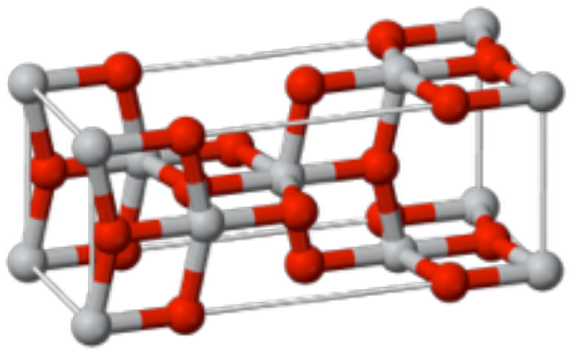
J. Szlachetko et al. *Rev. Sci. Instr.* **83**, 103105 (2012)

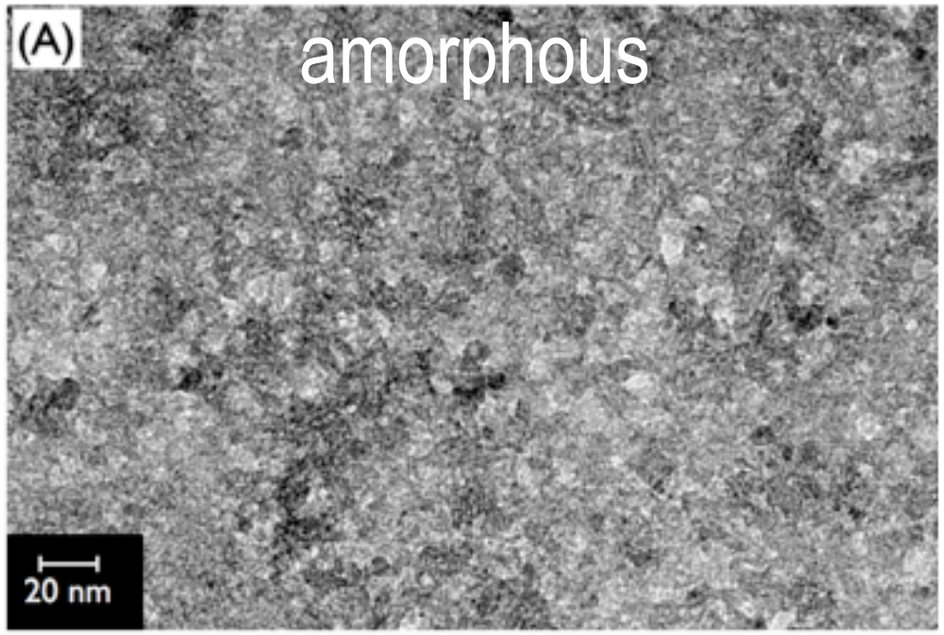


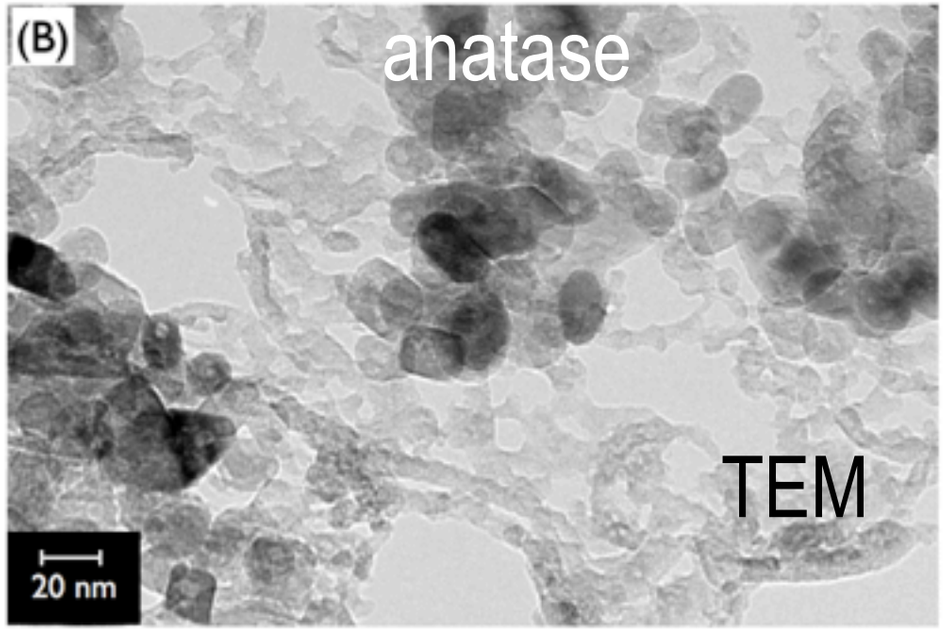
HEROS
J. Szlachetko et al. *Chem. Commun.* **48**, 10898 (2012)

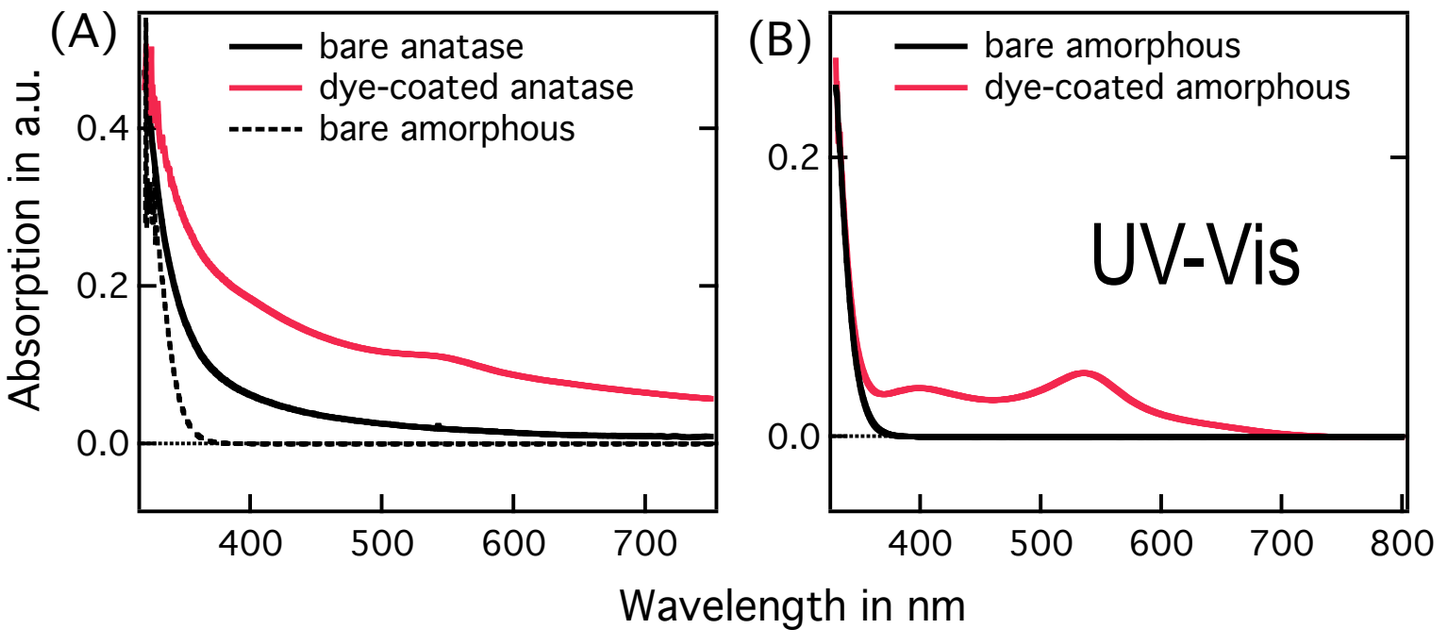
X-ray emission gives information on the occupied electronic states

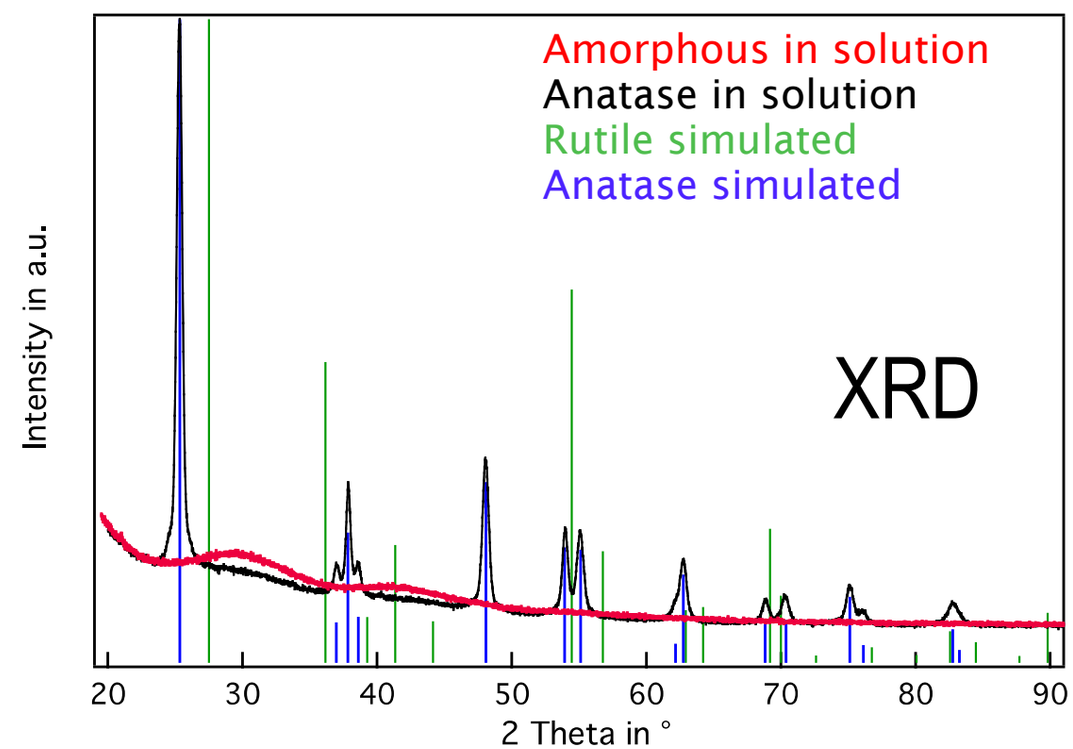
Colloidal TiO_2 sample details









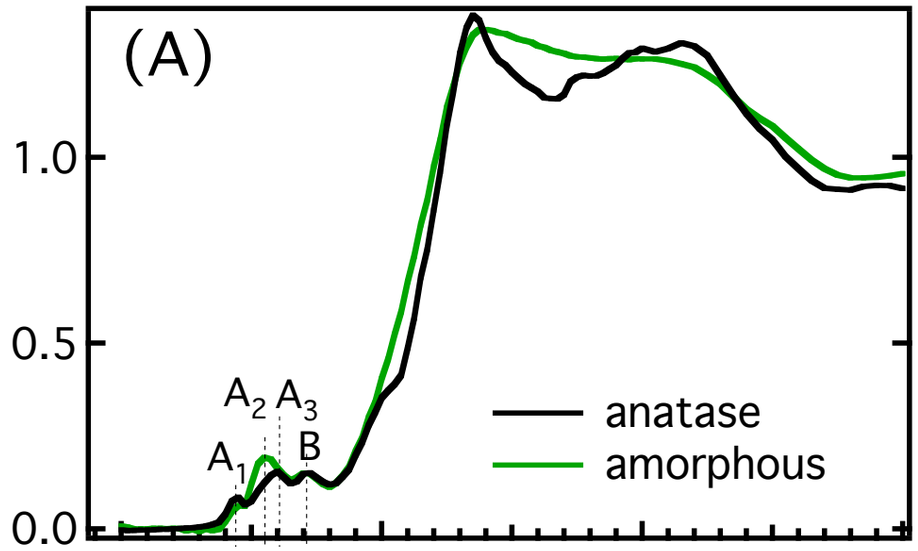


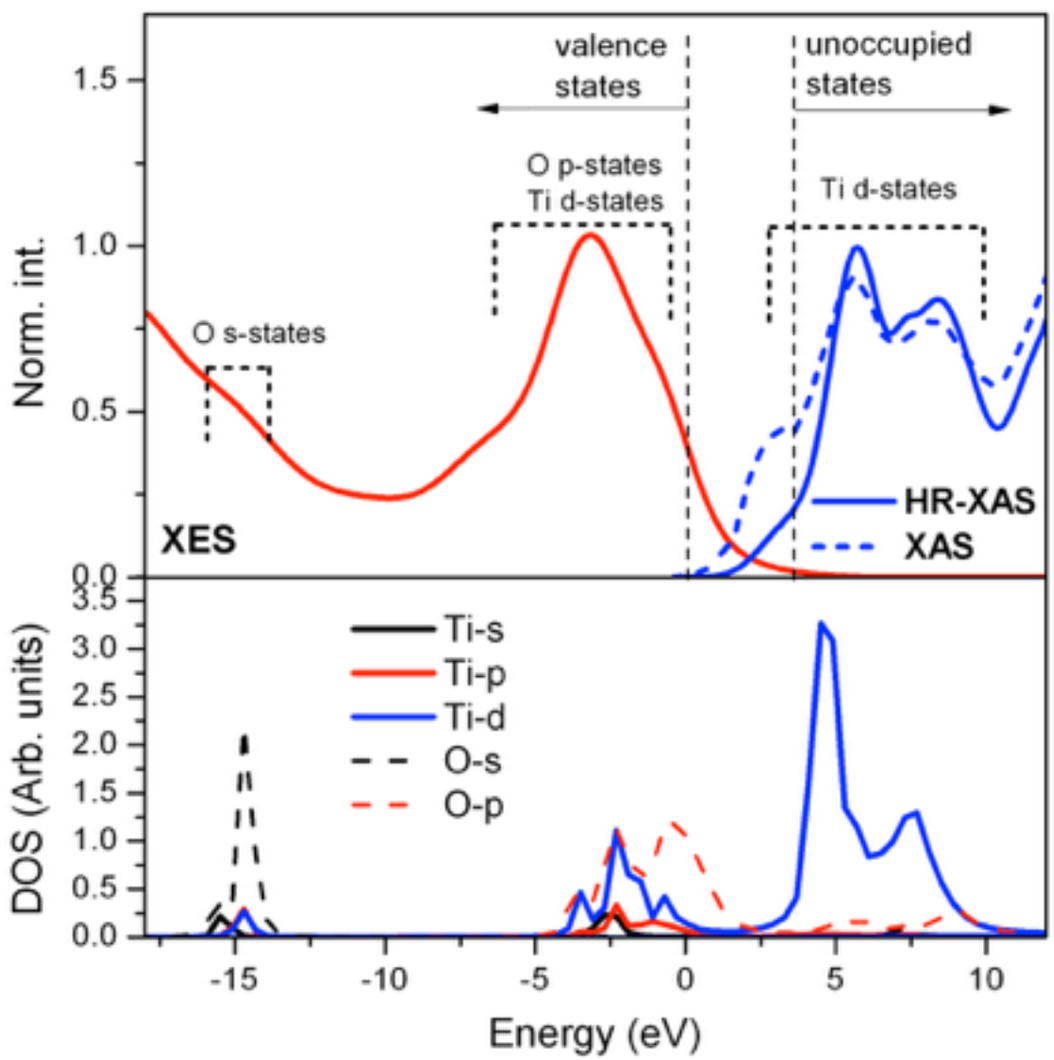
Samples synthesized using sol-gel method

TEM, DLS and XRD characterisation confirm **amorphous** 10 ± 5 nm diameter and disordered **anatase** 20 nm and crystalline with well-defined shape

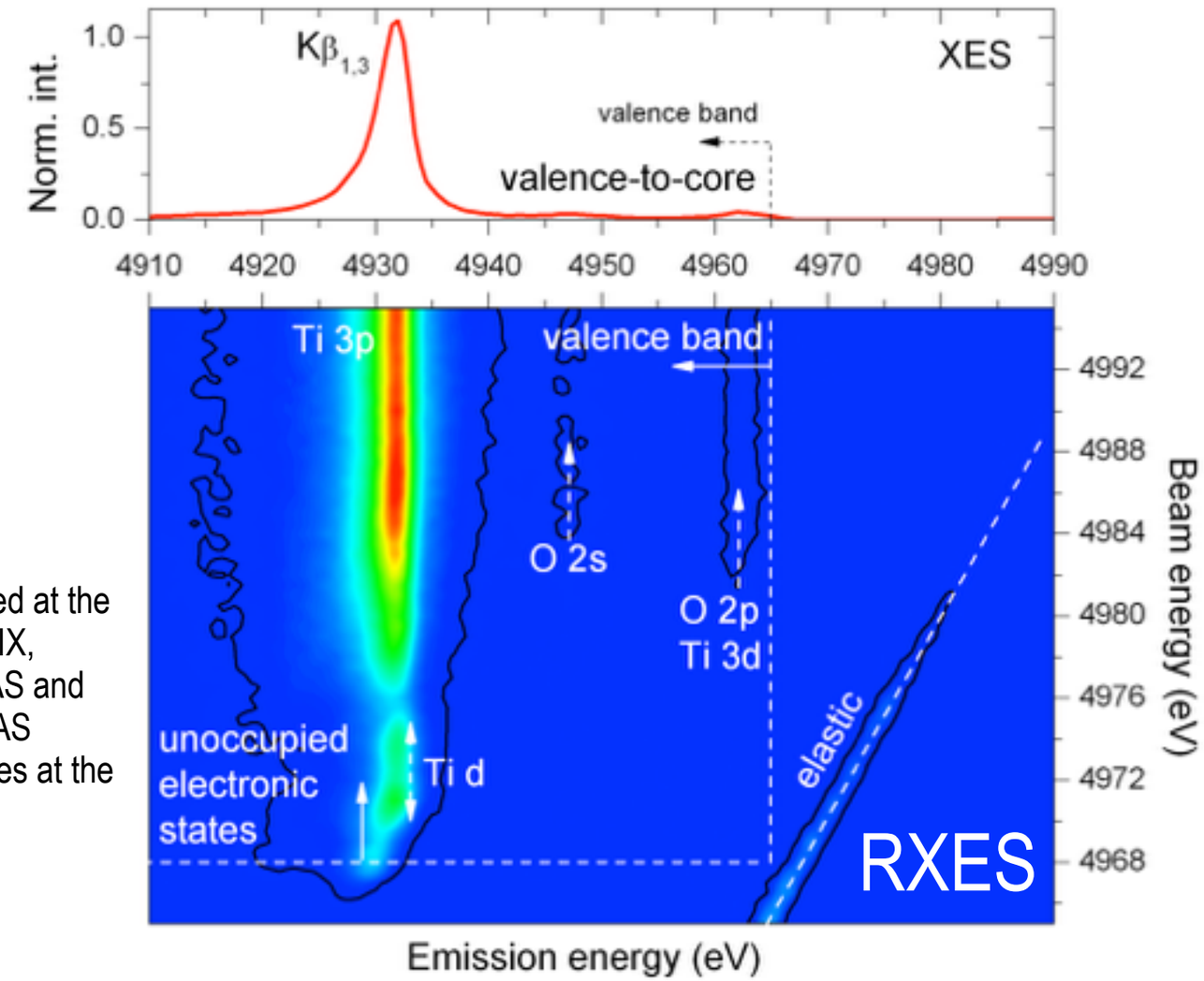
See M.H. Rittmann-Frank, C.J. Milne et al. *Angew. Chem. Int. Ed.* **53**, 5858 (2014) and SI for further details

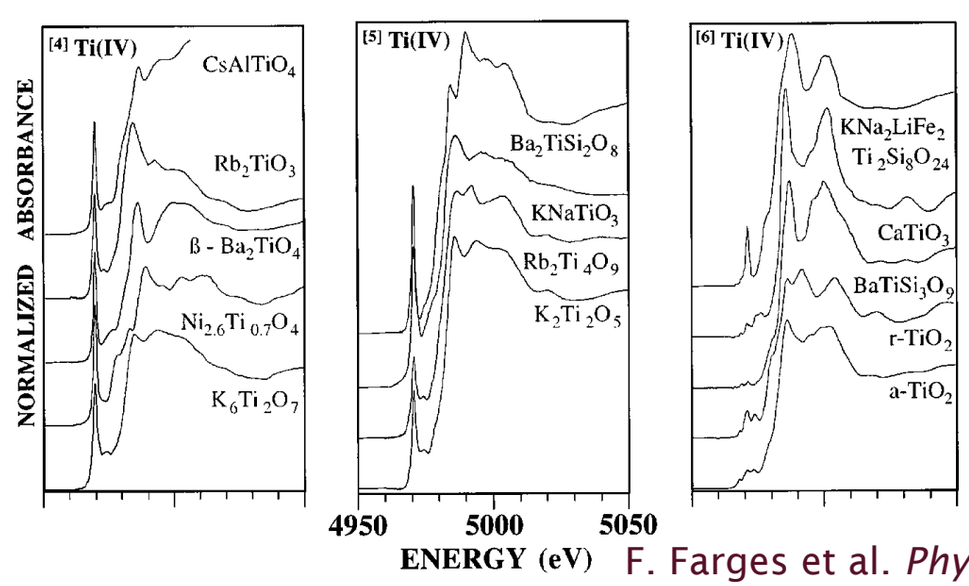
TiO_2 ground state measurements





measured at the PHOENIX, microXAS and SuperXAS beamlines at the SLS





Pre-edge peaks contain information on the band gap and the local Ti-coordination

F. Farges et al. *Phys. Rev. B* **56**, 1809 (1997)

High-repetition rate pump-probe XAS at the SLS

REVIEW OF SCIENTIFIC INSTRUMENTS **82**, 063111 (2011)

A high-repetition rate scheme for synchrotron-based picosecond laser pump/x-ray probe experiments on chemical and biological systems in solution

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[1]*Laboratoire de Spectroscopie Ultrarapide, Ecole Polytechnique Fédérale de Lausanne, ISIC, FSB, 1015 Lausanne, Switzerland*
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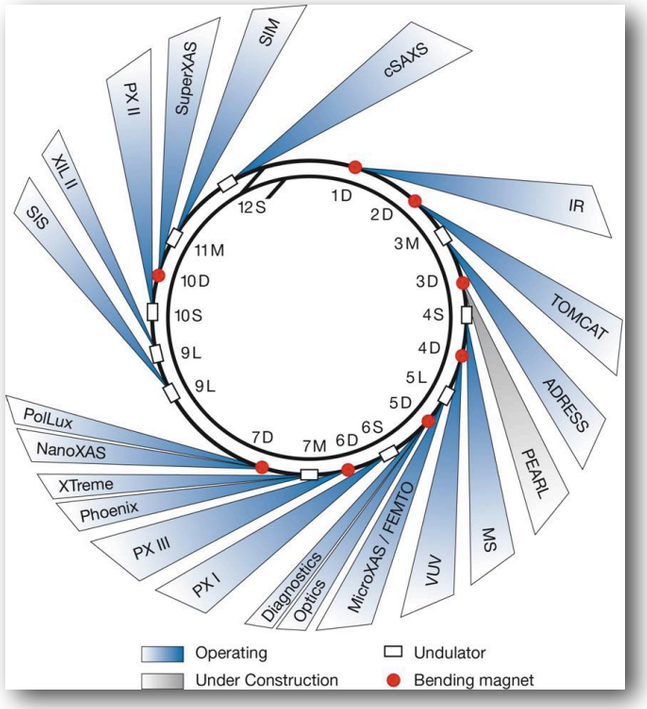
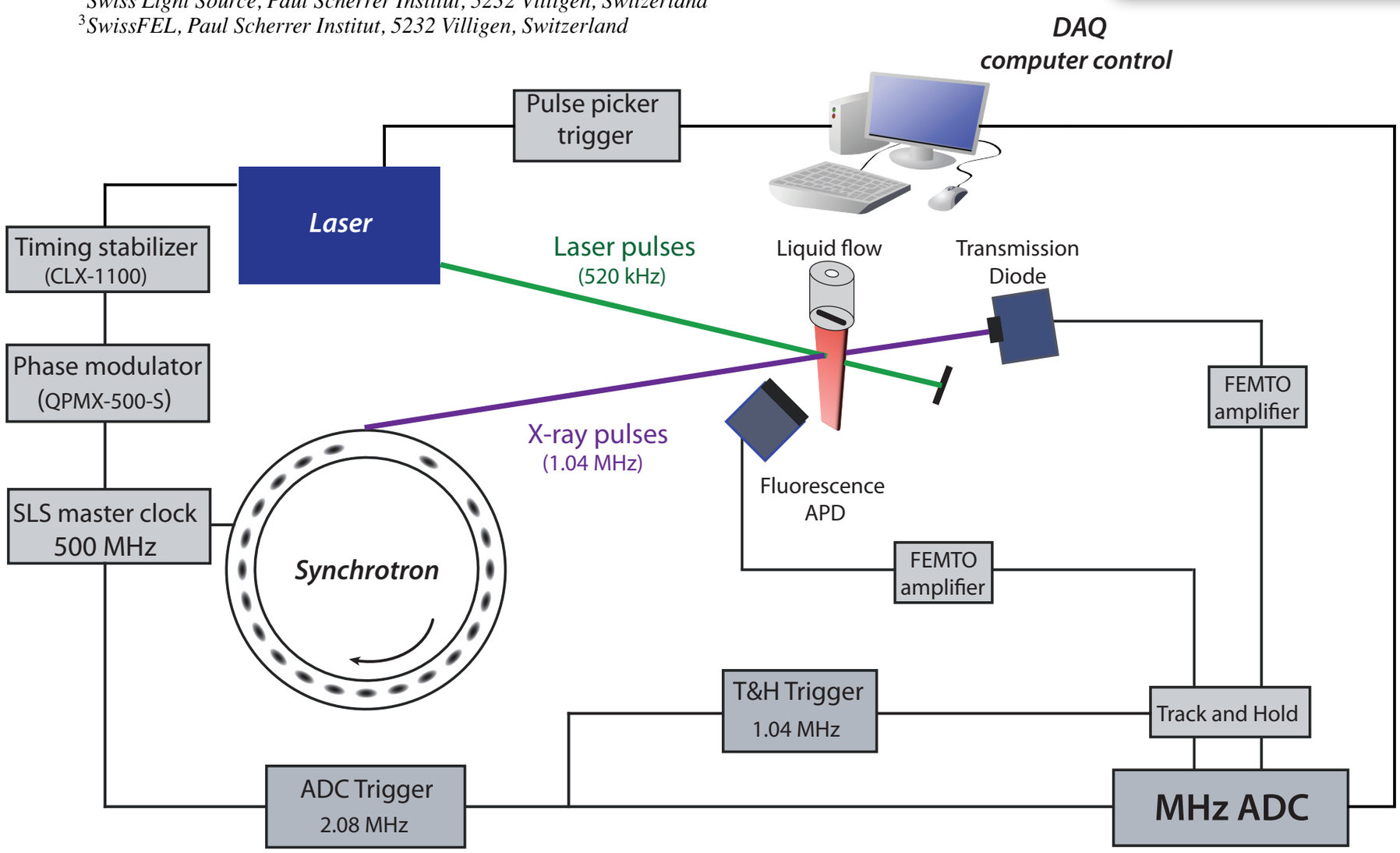
Portable TBWP Duetto
- 10 ps pulse duration
- 8.3 MHz to 50 kHz
- 2-200 μJ at 1 μm
- 5-40 μJ at 532 nm
- 2-29 μJ at 355 nm
- 1-5 μJ at 266 nm



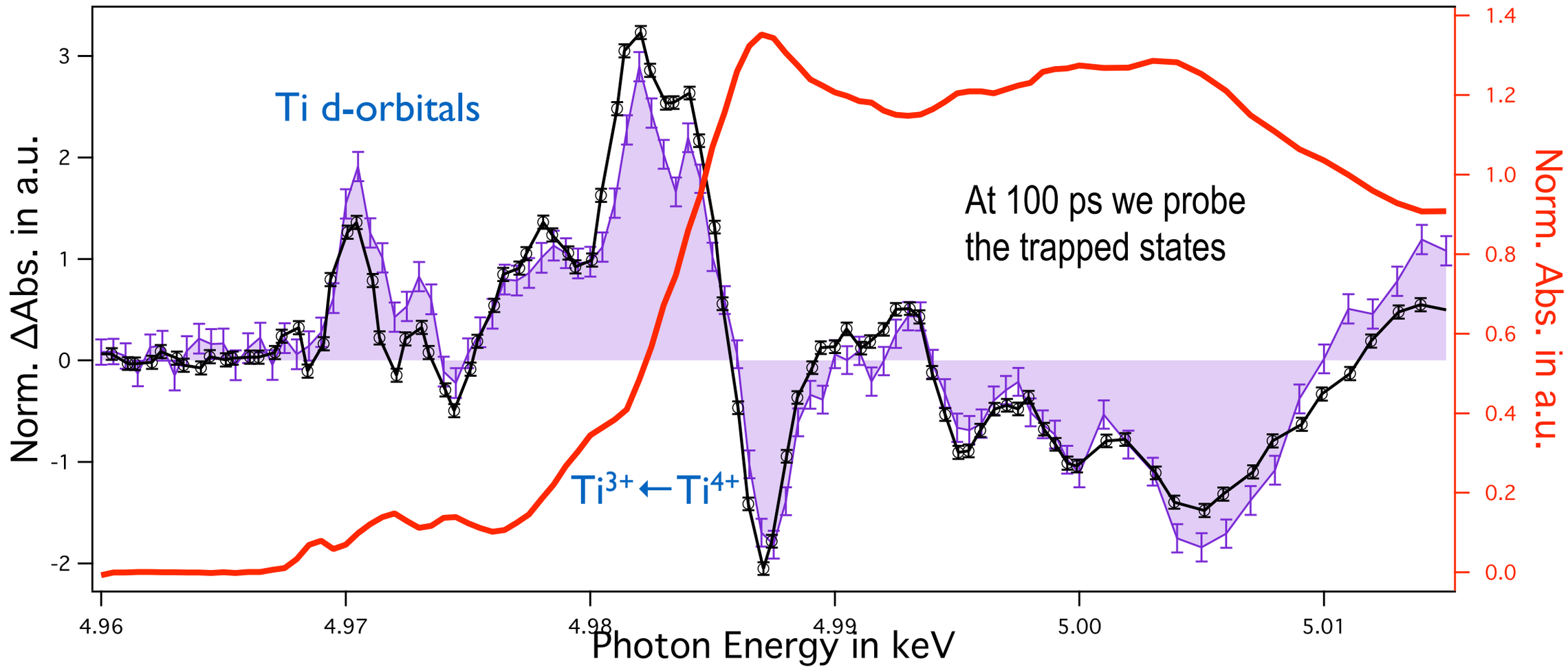


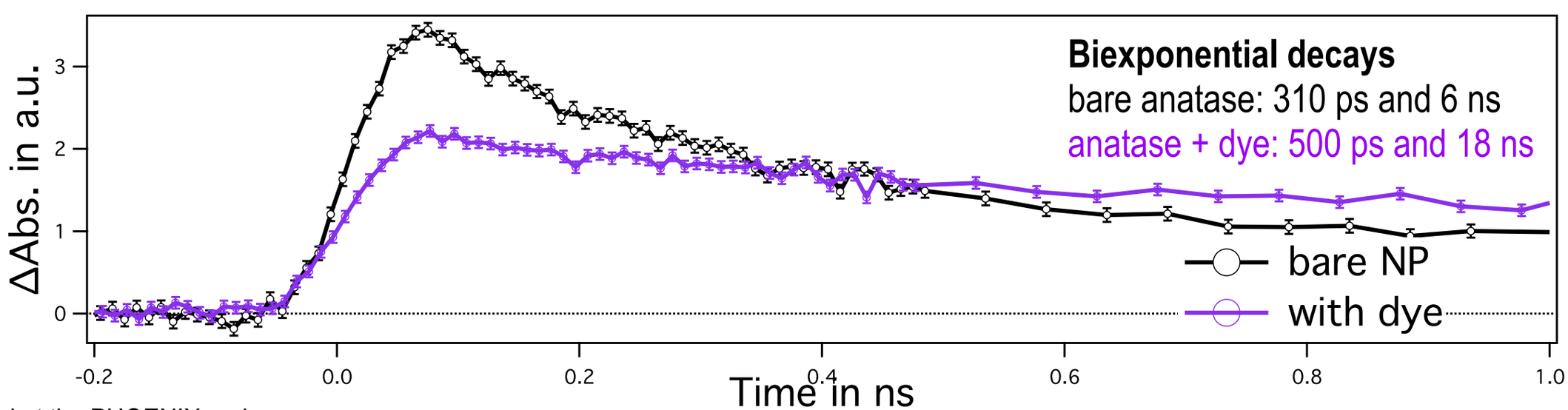
SuperXAS
- SuperBend from 4.5 to 35 keV
- Si(111), Si(311) mono crystals
- X-ray emission spectrometers
- 10^{11}-10^{12} photons/second

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

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

Electronic and structural dynamics in TiO_2

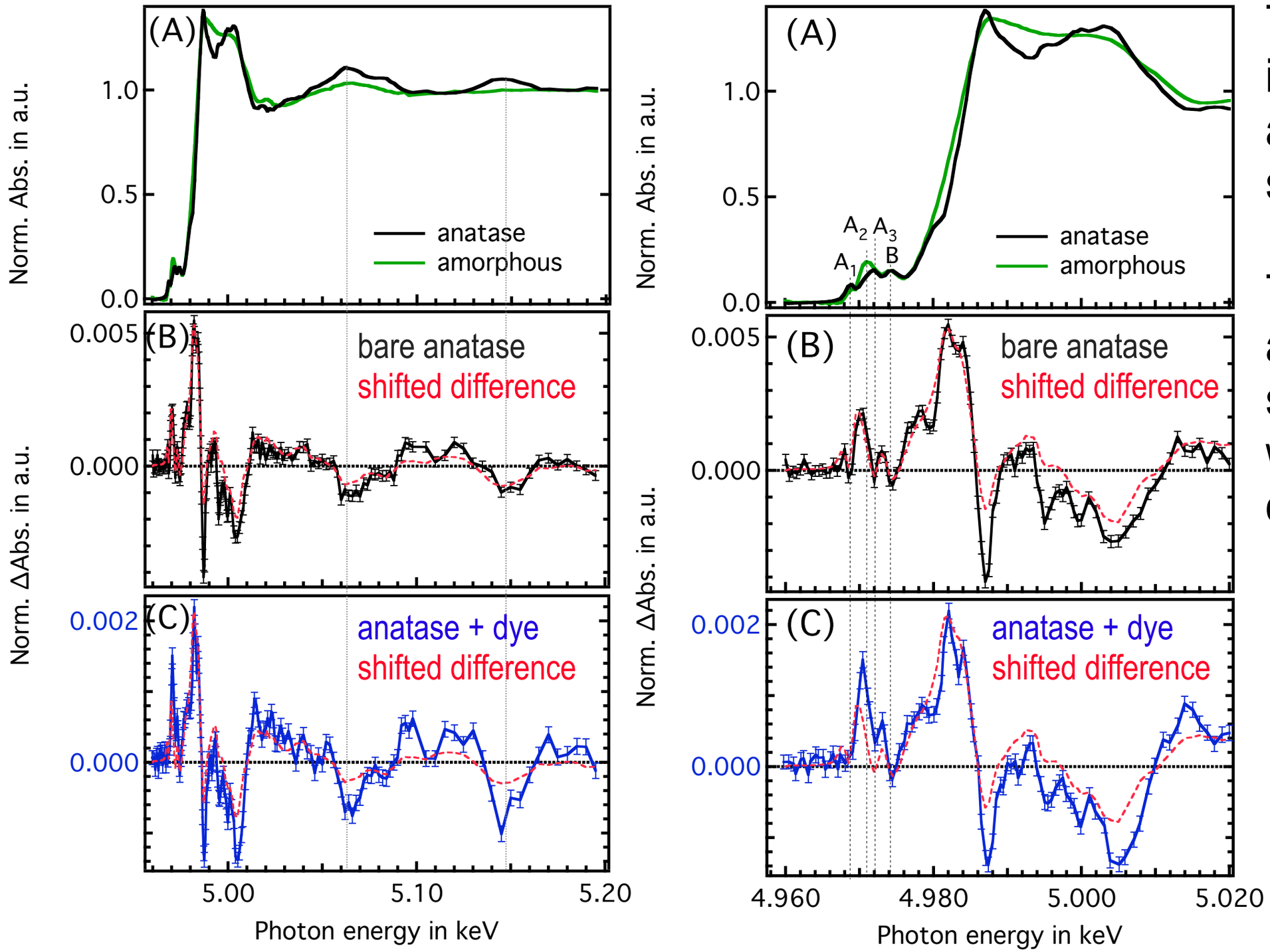




measured at the PHOENIX and microXAS beamlines at the SLS

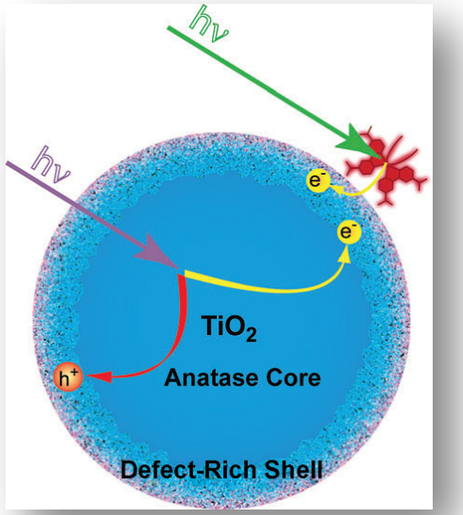
M.H. Rittmann-Frank, C.J. Milne et al. *Angew. Chem. Int. Ed.* **53**, 5858 (2014)

Trap sites in TiO_2 are amorphous-like Ti centres



The excited state XAS is consistent with the amorphous XAS red-shifted by 1 eV

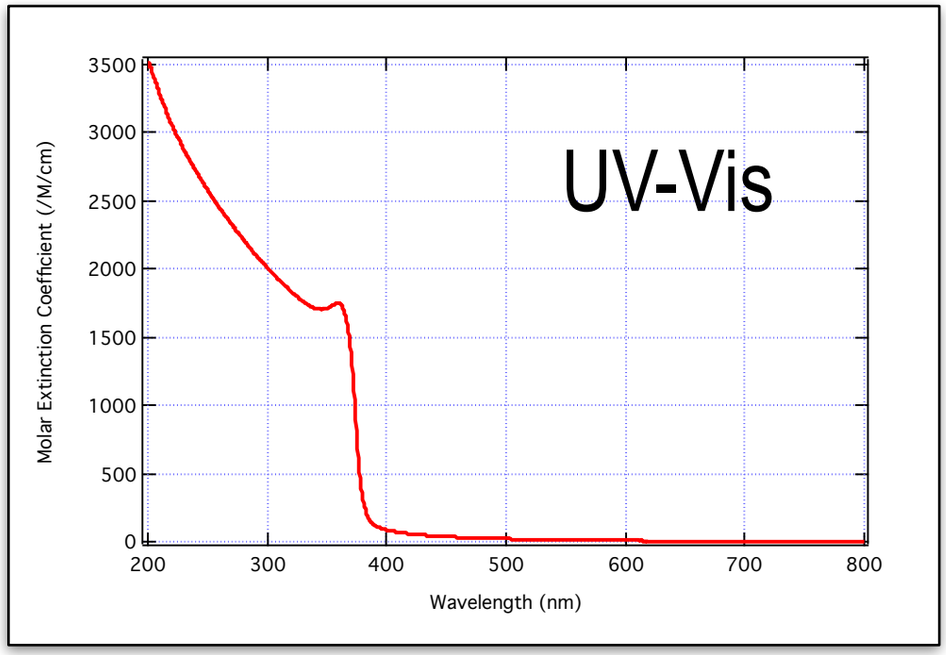
The electron is trapped at amorphous-like Ti sites in the lattice whether directly excited or injected from the dye



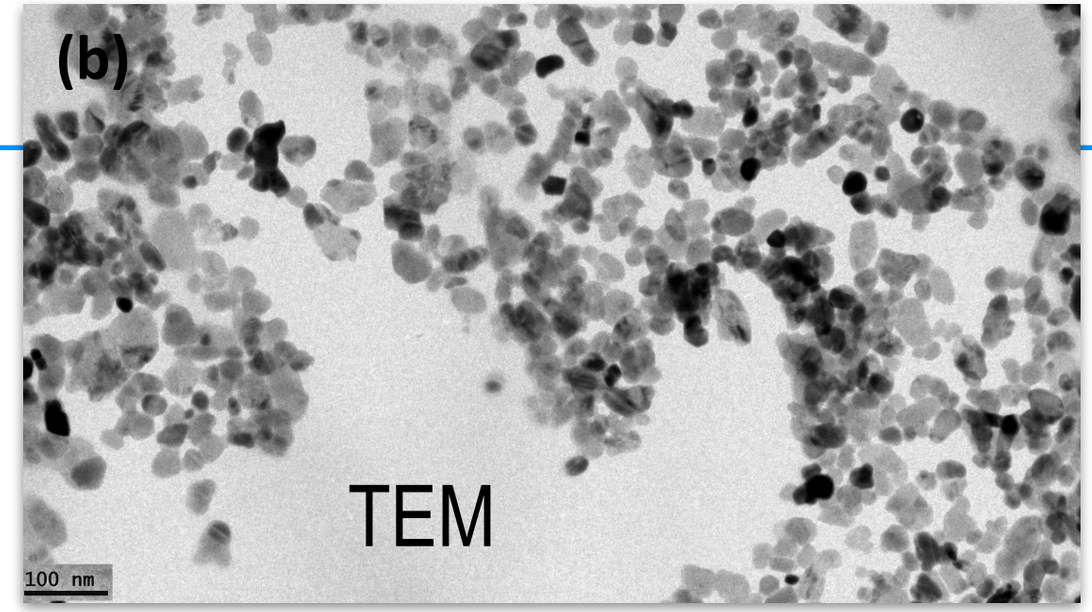
M.H. Rittmann-Frank, C.J. Milne et al. *Angew. Chem. Int. Ed.* **53**, 5858 (2014)

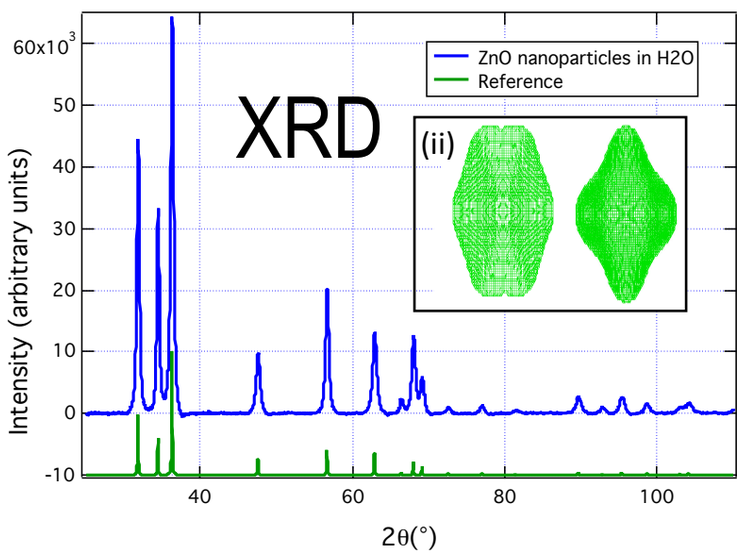
Is this a general property of metal oxide semi-conductor nanoparticles ?

Colloidal ZnO sample details



Commercial sample of ~35 nm ZnO nanoparticles suspended in water



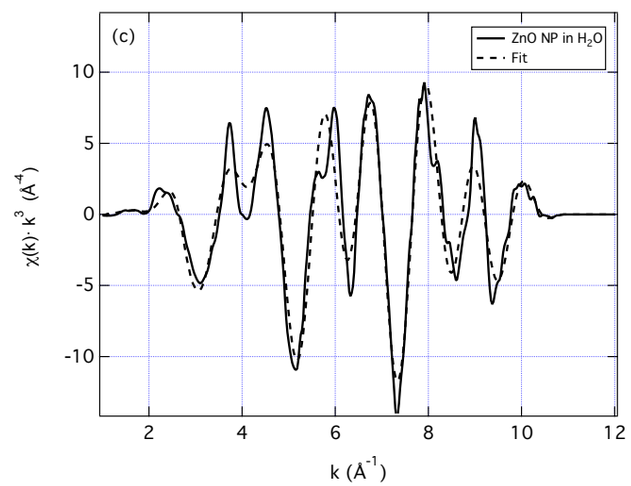


	ZnO NP in H_2O
Radius (nm)	16(2)
a	3.2500(1)
c	5.2087(1)
$\Delta(z)$	0.3816(4)
$N(O)/N(Zn)$	0.990(1)
R-factor	1.29

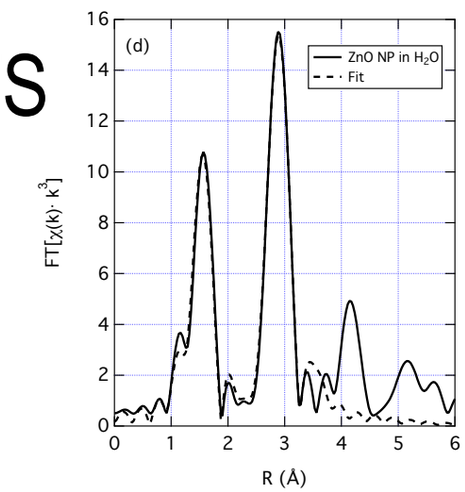
T. Rossi et al. *JPC C* **118** 19422 (2014)

Results

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



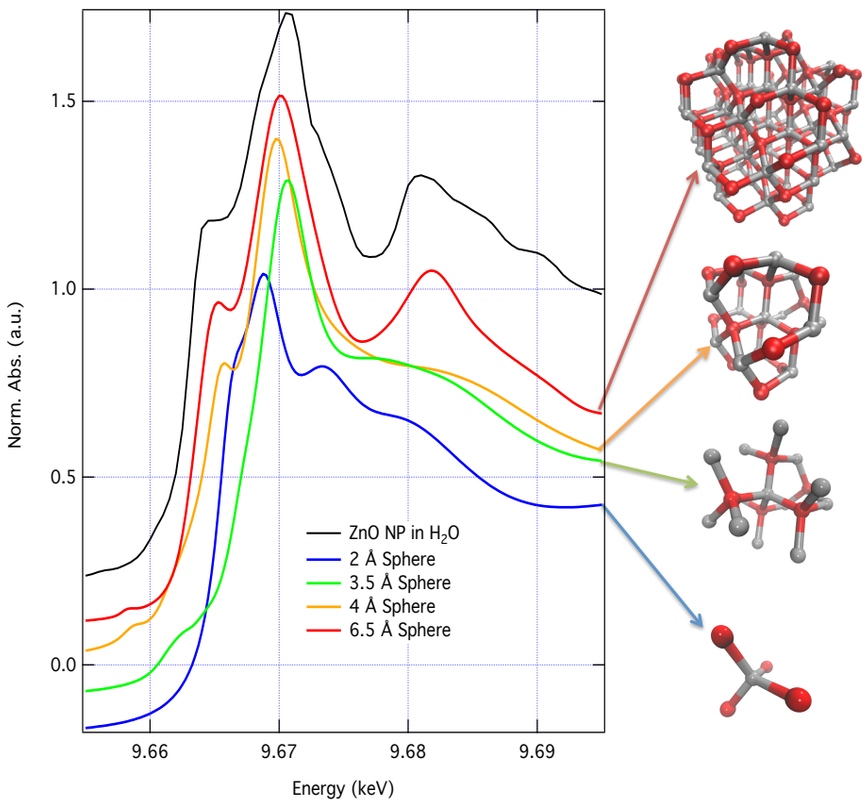
EXAFS

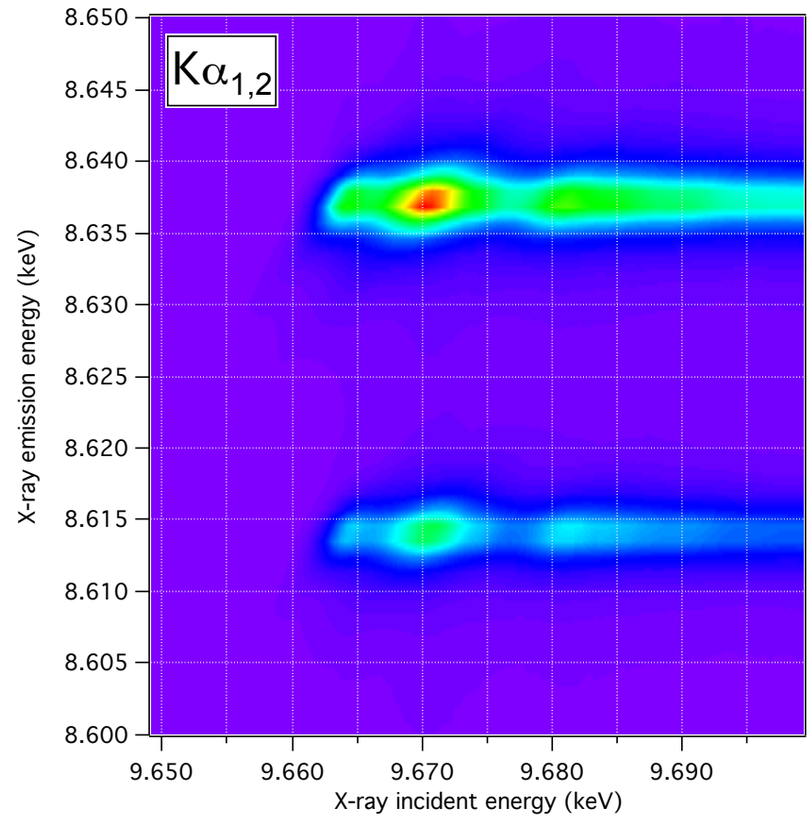


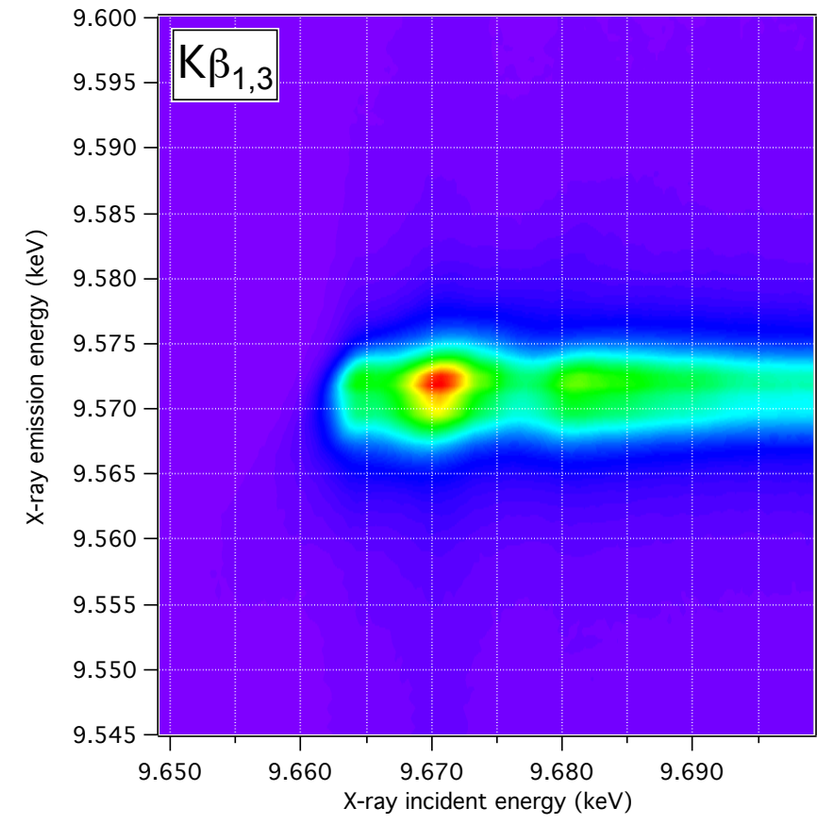
	N_γ	**ZnO NPs in H_2O**	Hatch *et al.* J. App. Phys. **114**, 153517 (2013)
S_0^2	-	0.756±0.036	
E_0	-	4.366±0.452	
R_{Zn-O_1}	4	1.961±0.005	1.9526
R_{Zn-Zn_1}	6	3.178±0.008	3.2090
R_{Zn-O_2}	1	3.216±0.005	
R_{Zn-Zn_2}	6	3.290±0.013	3.2496
σ_{Zn-O}	-	0.003±0.001	0.0040
σ_{Zn-Zn}	-	0.004±0.002	0.0020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

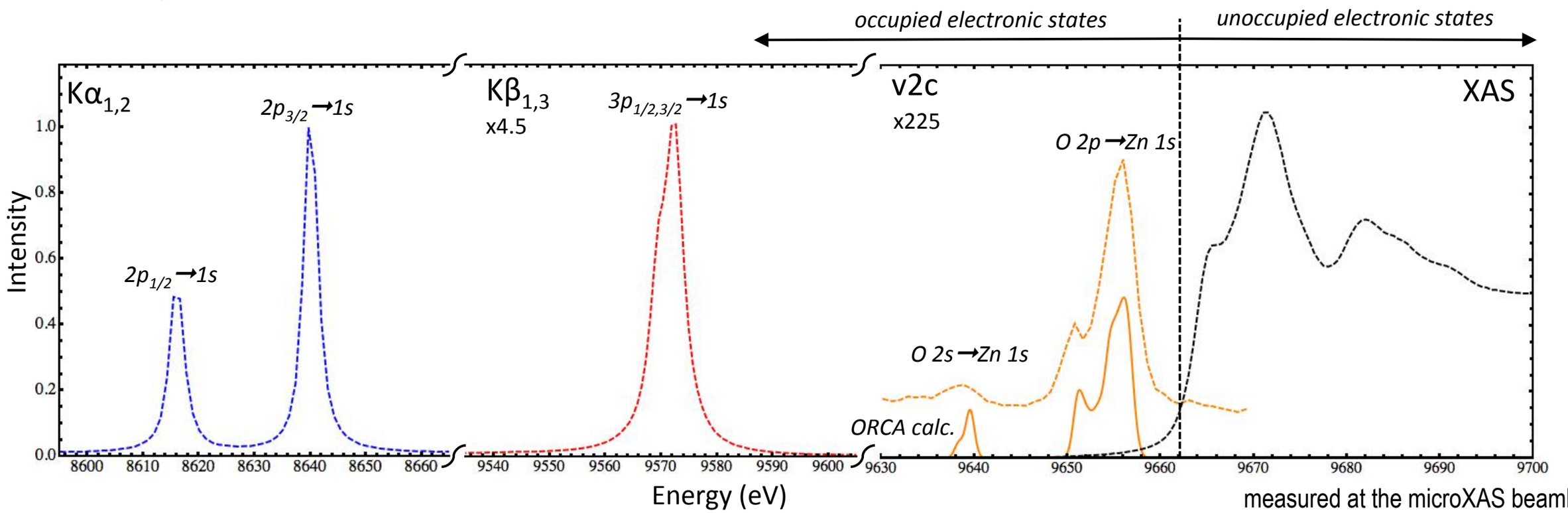
measured at the microXAS beamline at the SLS

ZnO ground state measurements









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

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]
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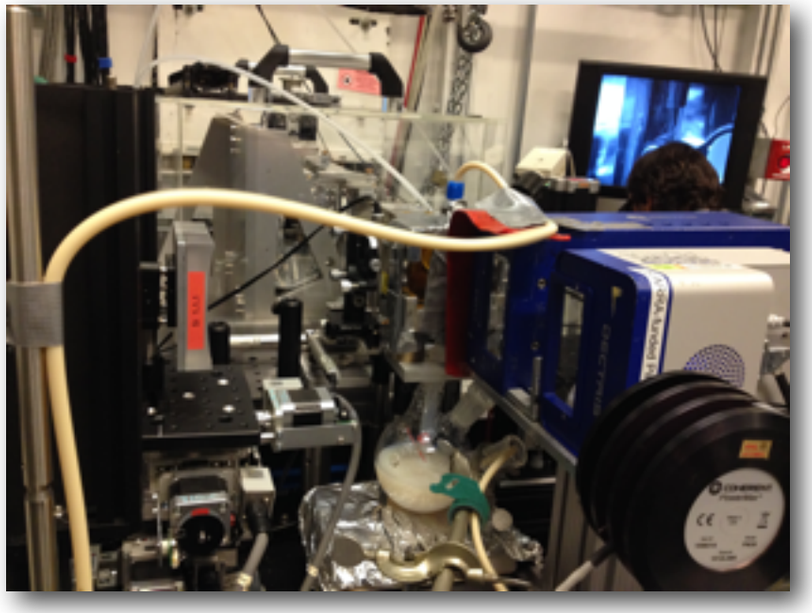
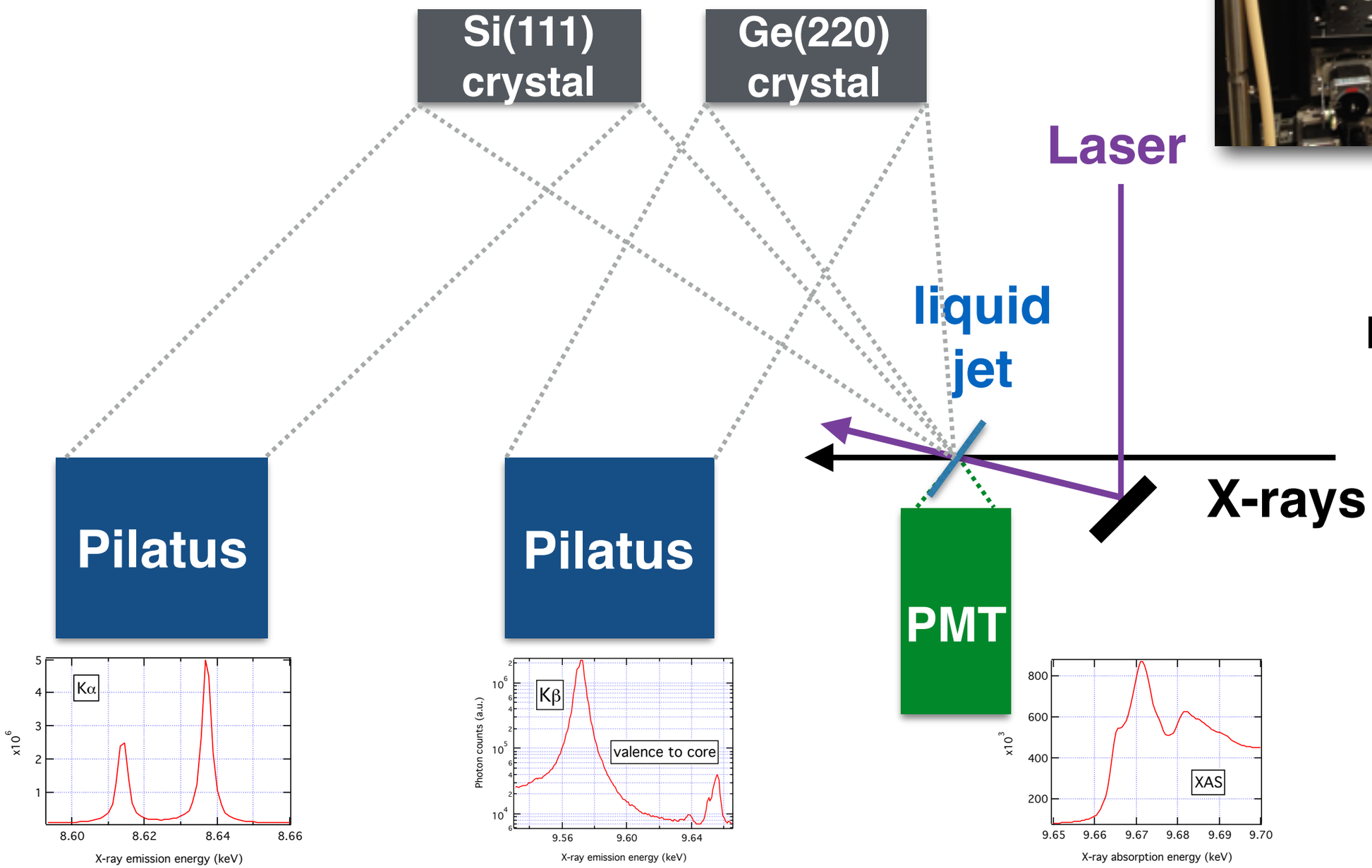
[3]*Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, USA*

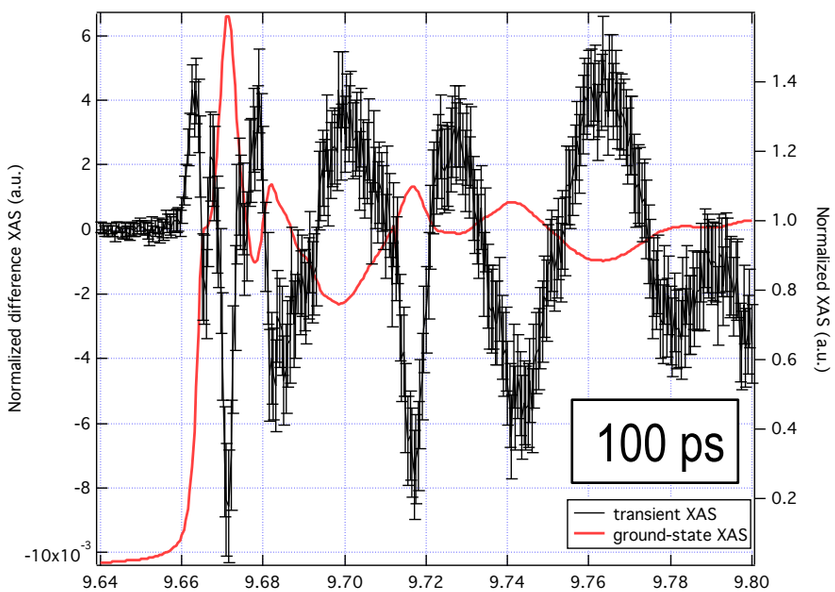


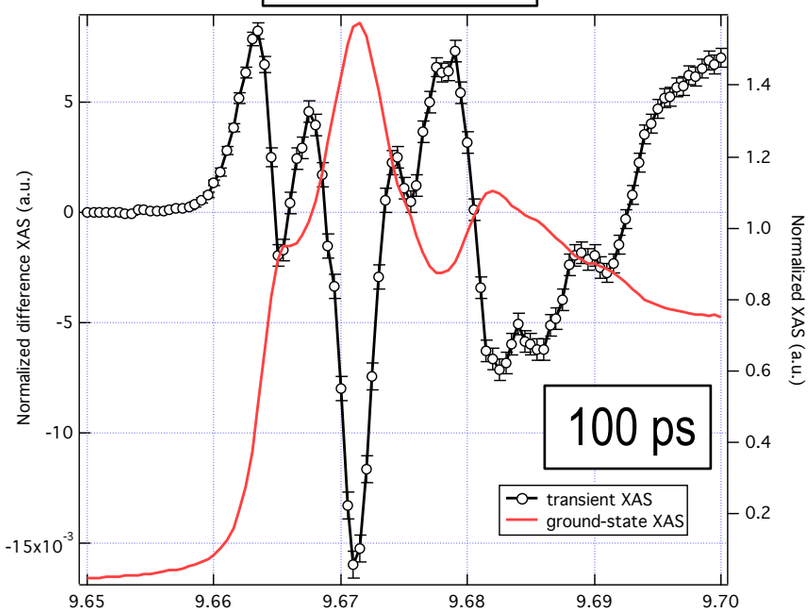


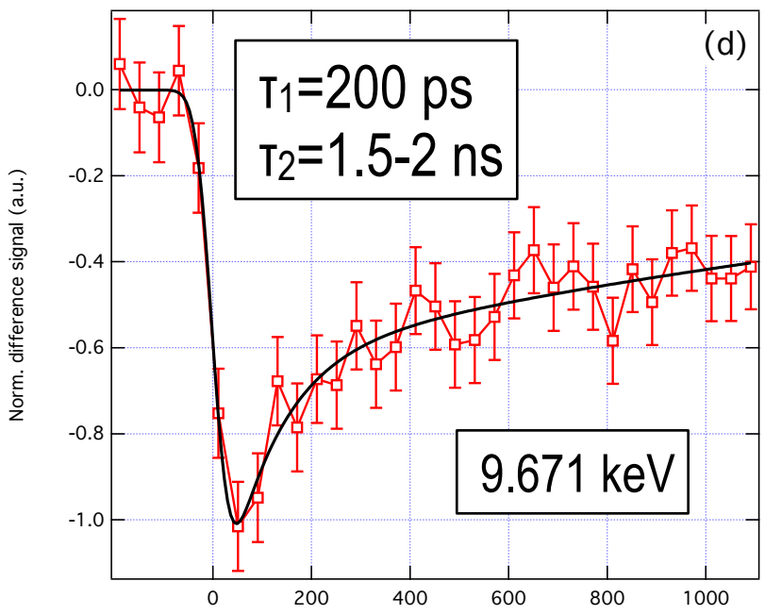
Details

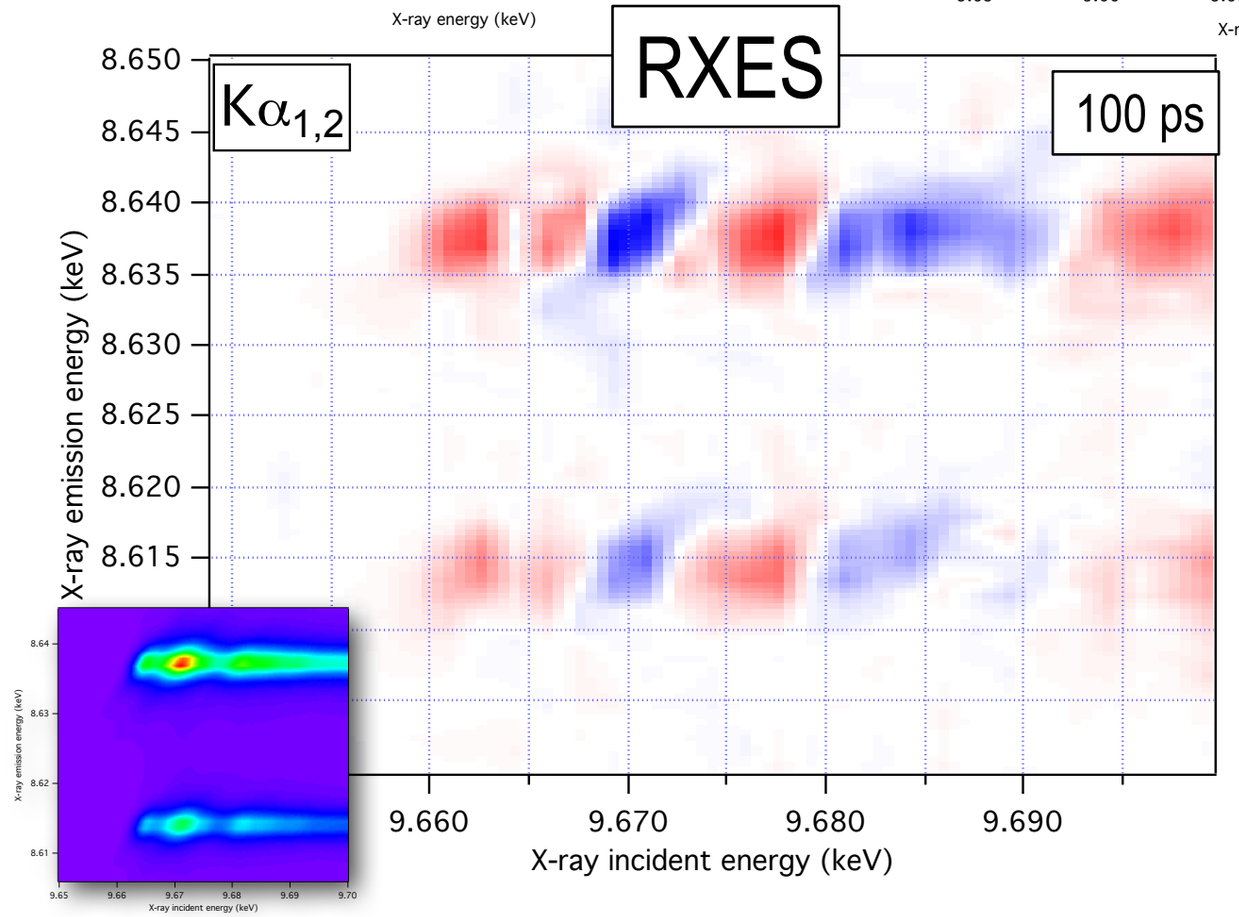
- Sector 7 @ APS
- Zn K-edge (9 keV)
- 355 nm excitation
- 80 mJ/cm^2
- 100 µm liquid jet
- Diamond(111) mono
- $\Delta E/E=5.4\times10^{-5}$
- 10^{12}-10^{13} photons/s
- 100 ps X-ray pulse
- 10 ps laser pulse

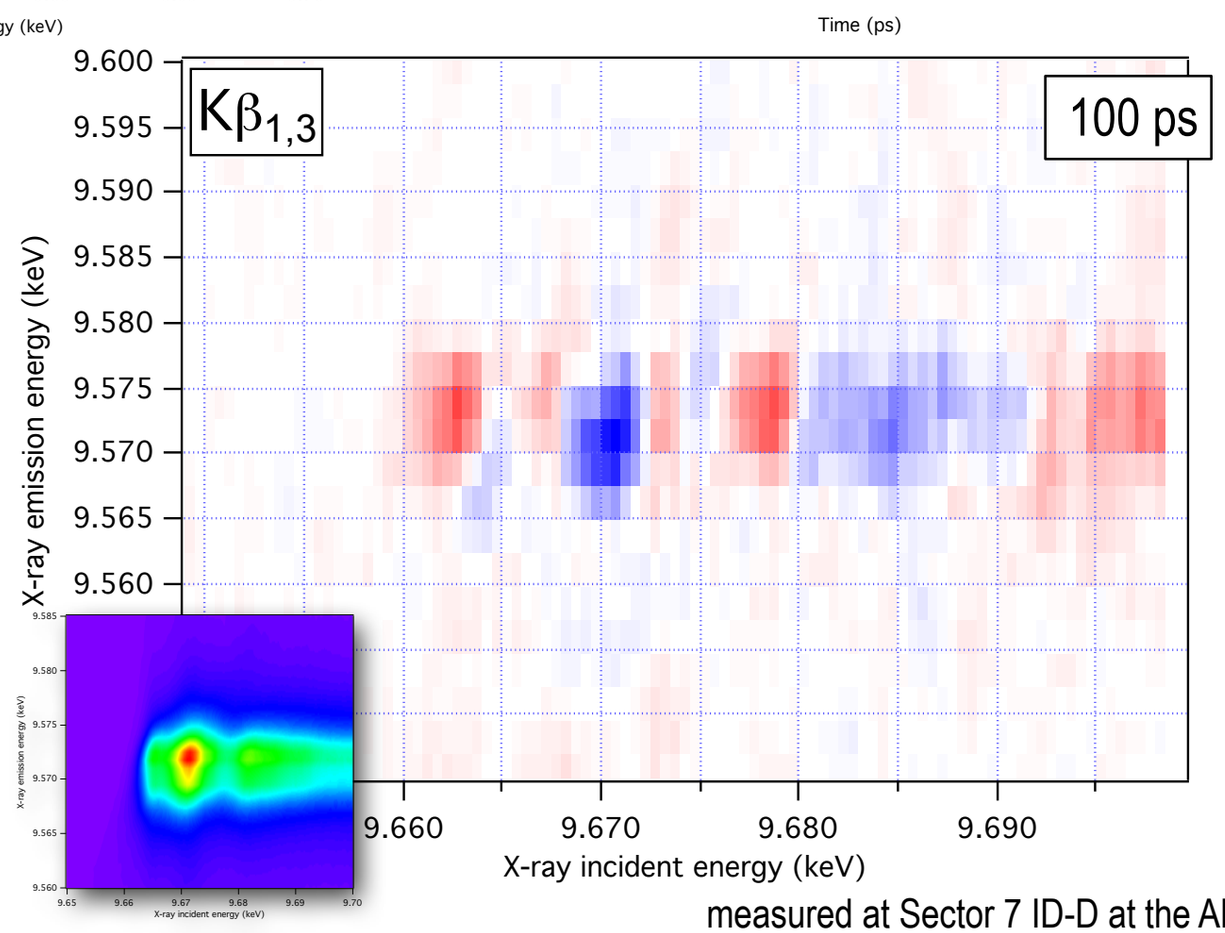
ZnO pump-probe X-ray spectroscopy







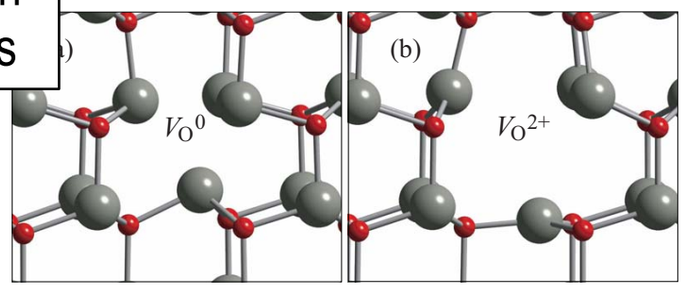


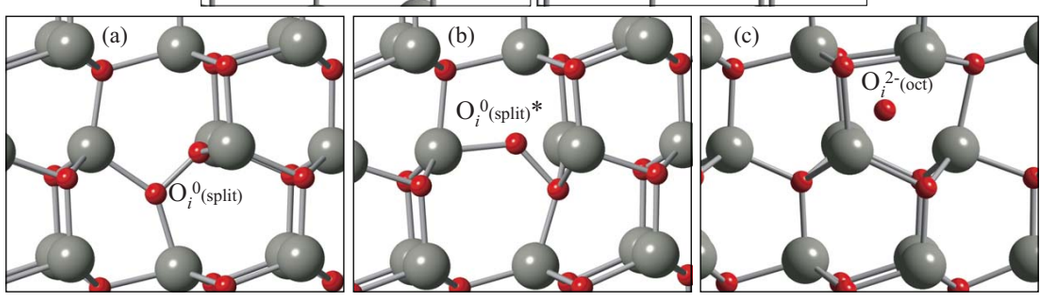


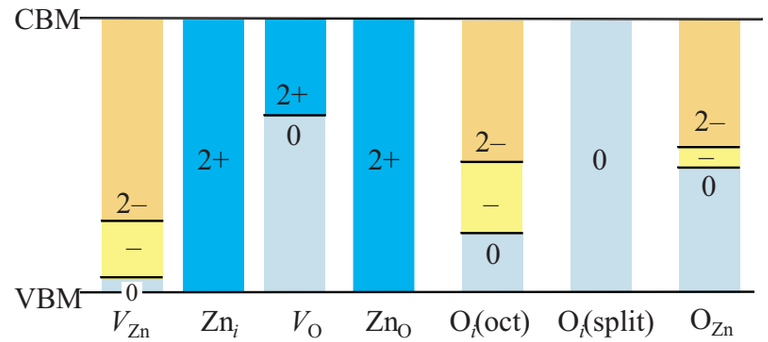
measured at Sector 7 ID-D at the APS

Many different forms of lattice defects in ZnO

Oxygen defects

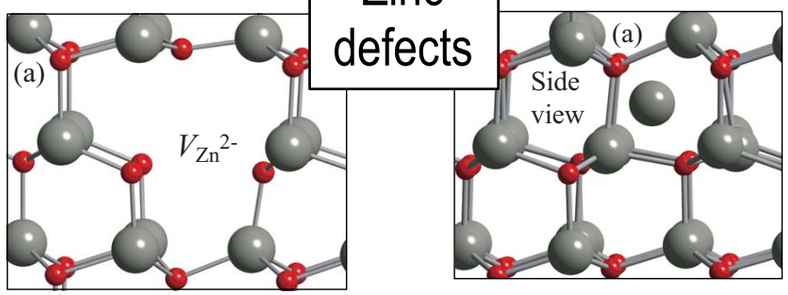


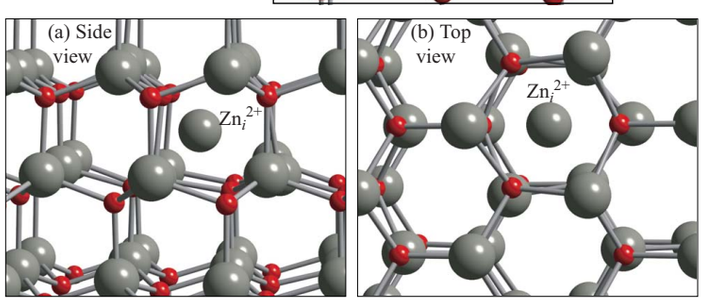


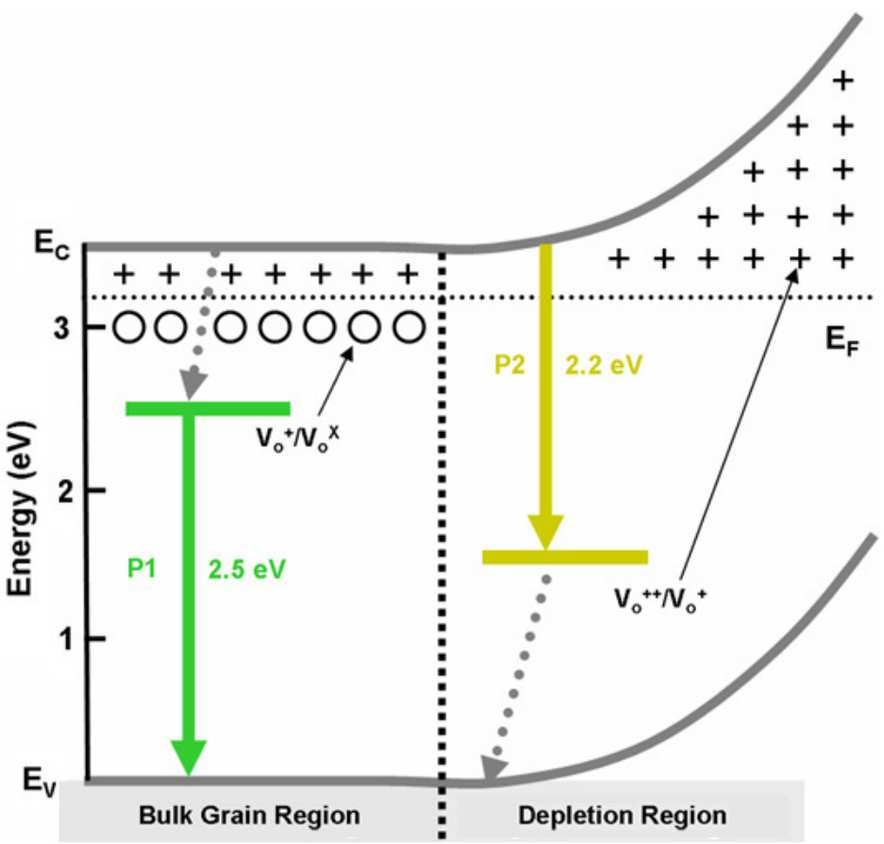


A. Janotti et al. *Phys. Rev. B* **76** 165202 (2007)

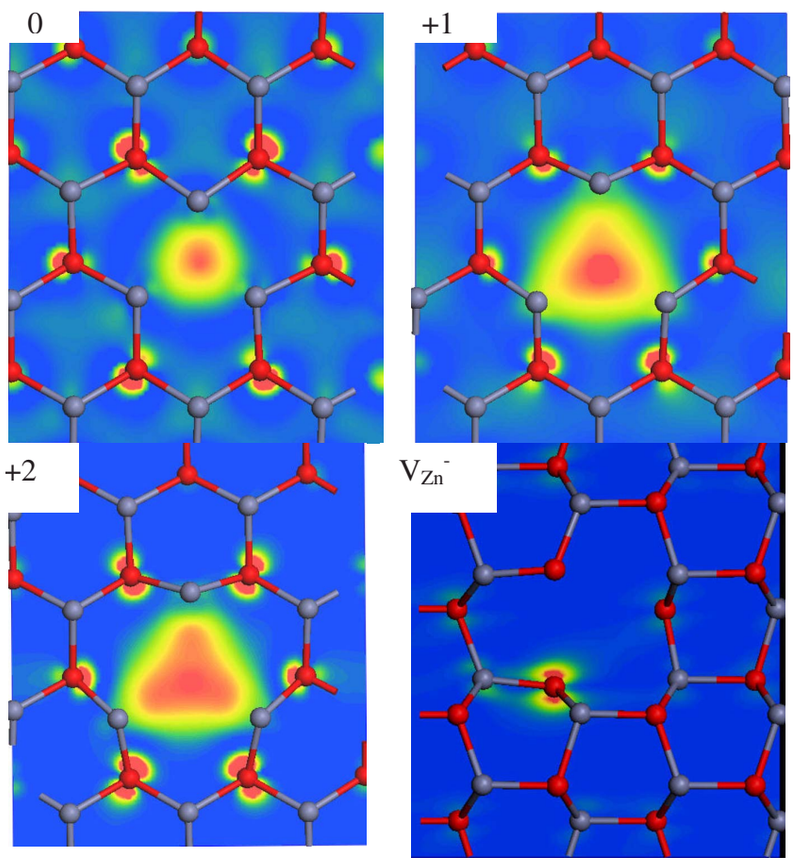
Zinc defects





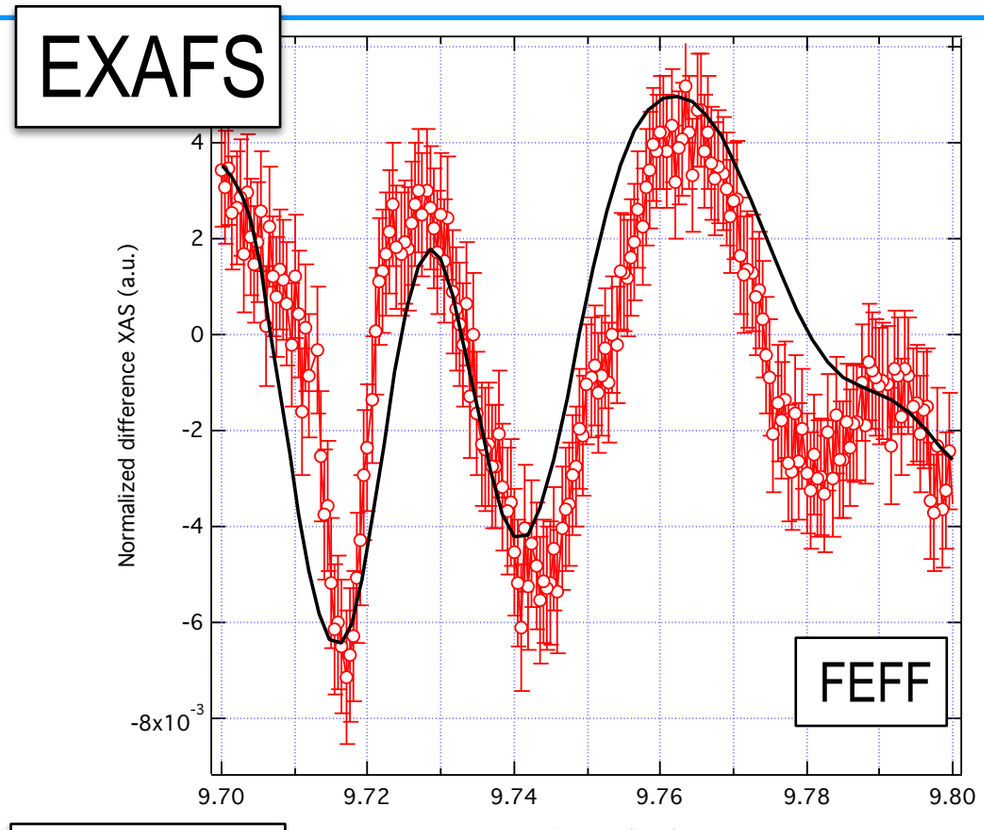


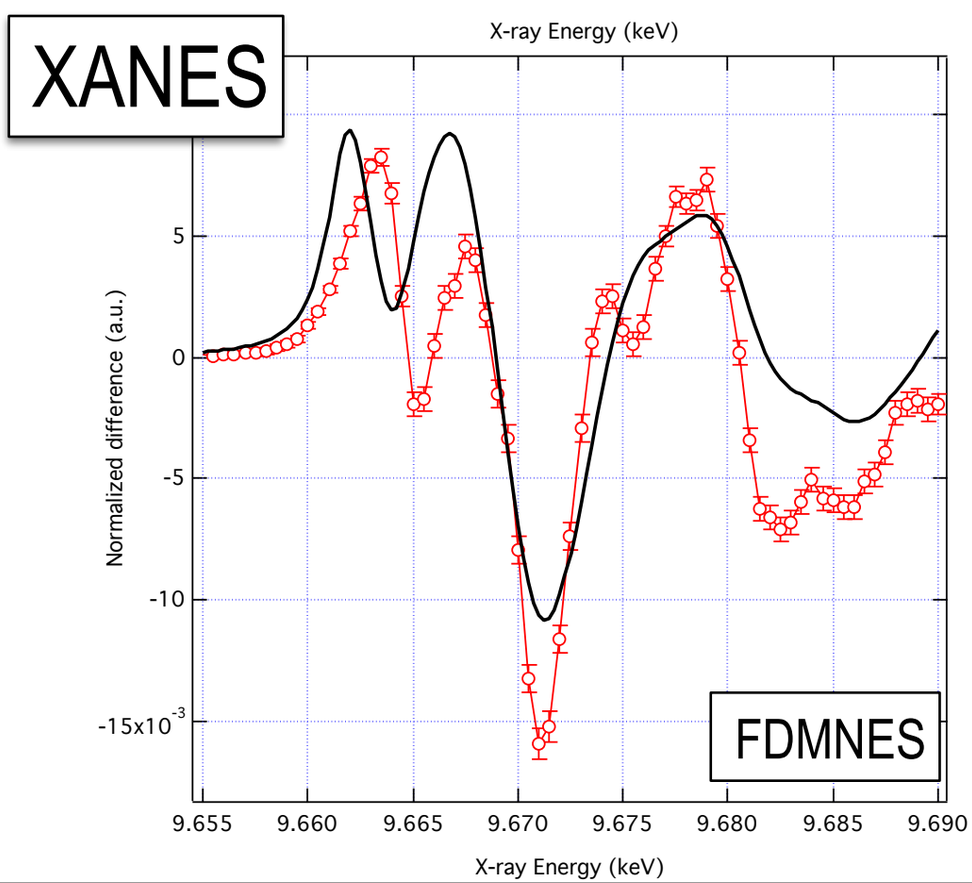
M. Ghosh et al. *Nanotechnology* **19** 445704 (2008)

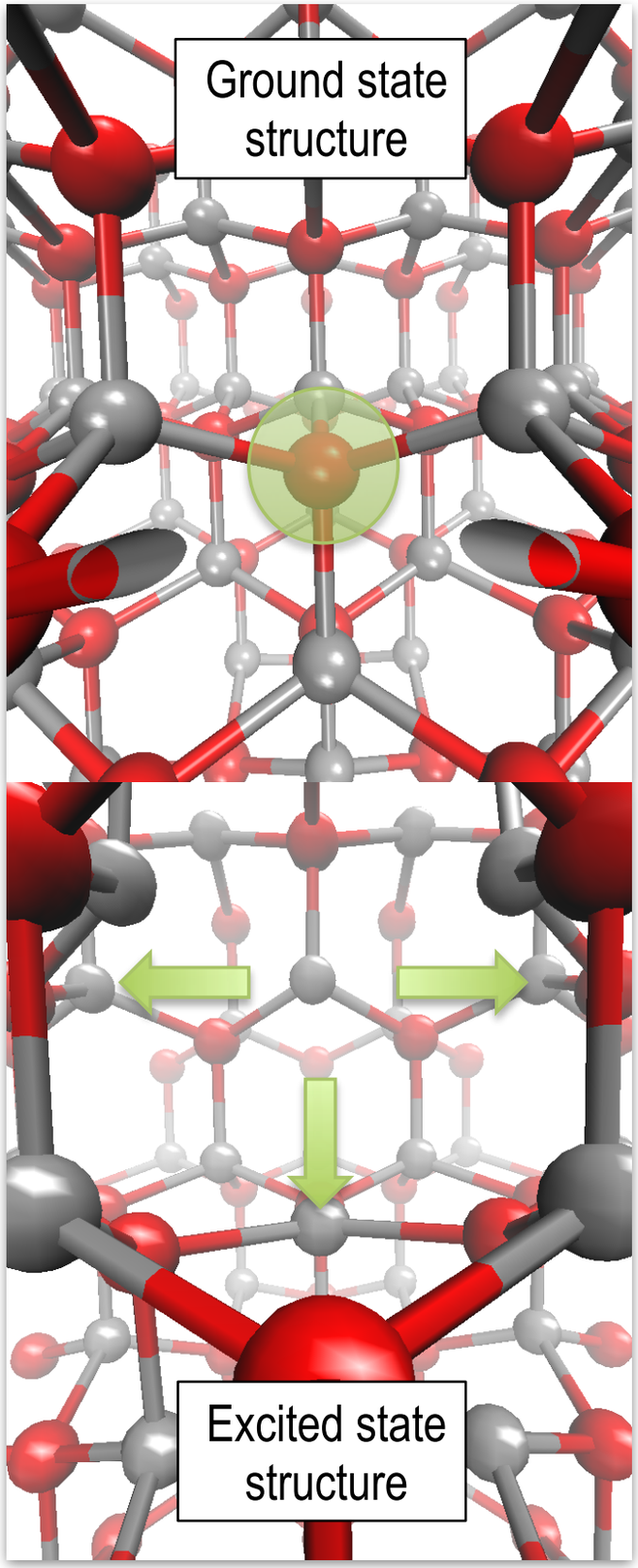


S.J. Clark et al. *Phys. Rev. B* **81** 115311 (2010)

ZnO analysis & simulation: Structural dynamics







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

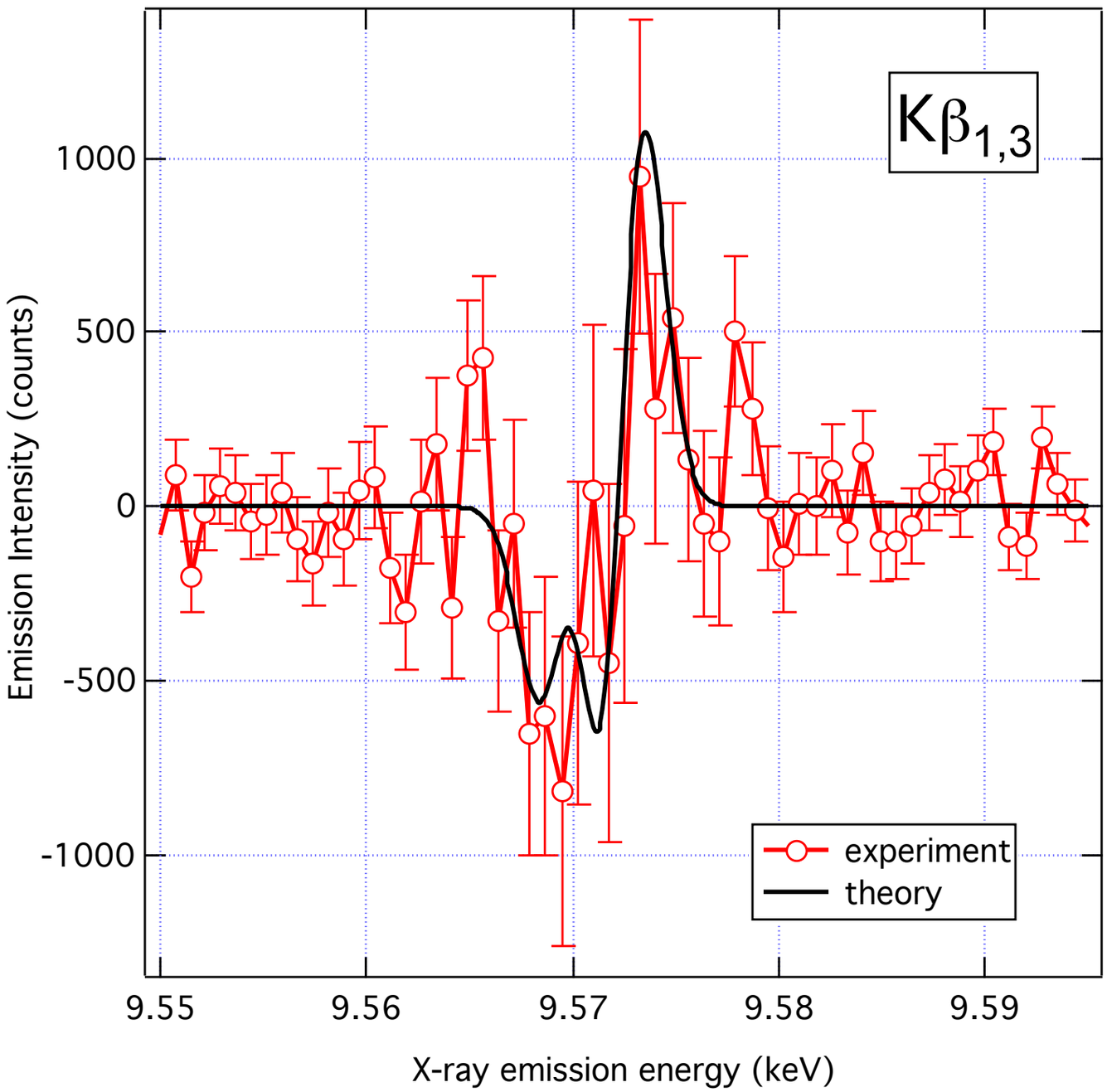
$V_O^{+} + h^{+} \rightarrow V_O^{++}$

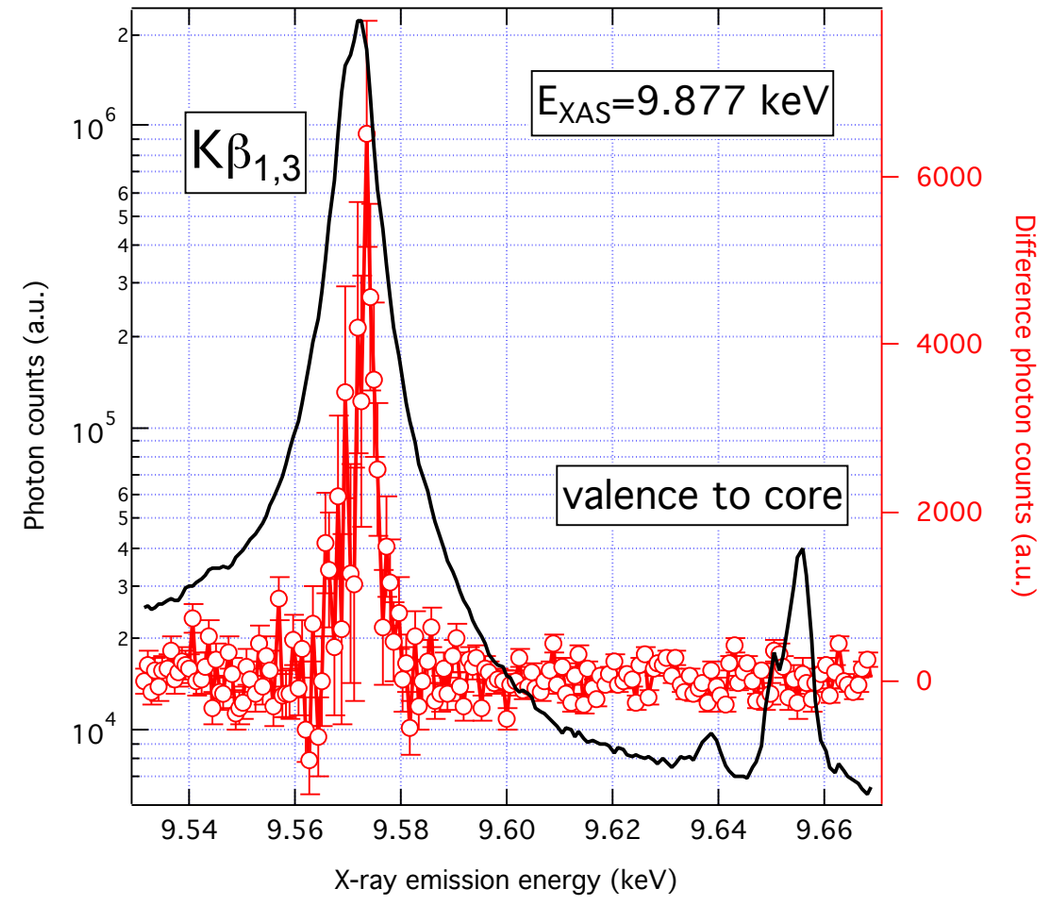
Which causes an expansion of the neighbouring Zn atoms by ~20%

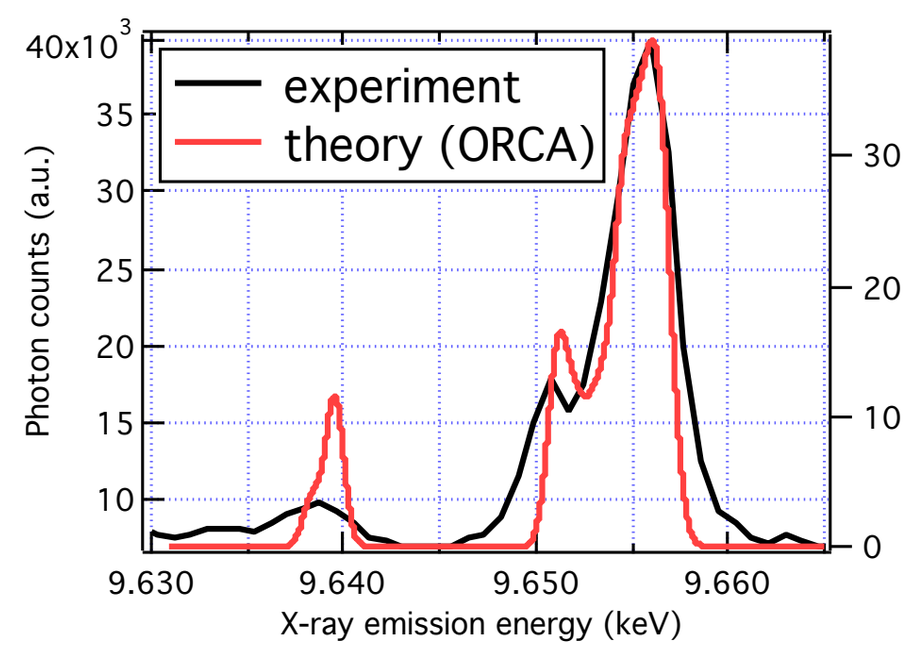
The majority of the changes we see are structural in nature, but not all …

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

ZnO analysis & simulation: Electronic dynamics



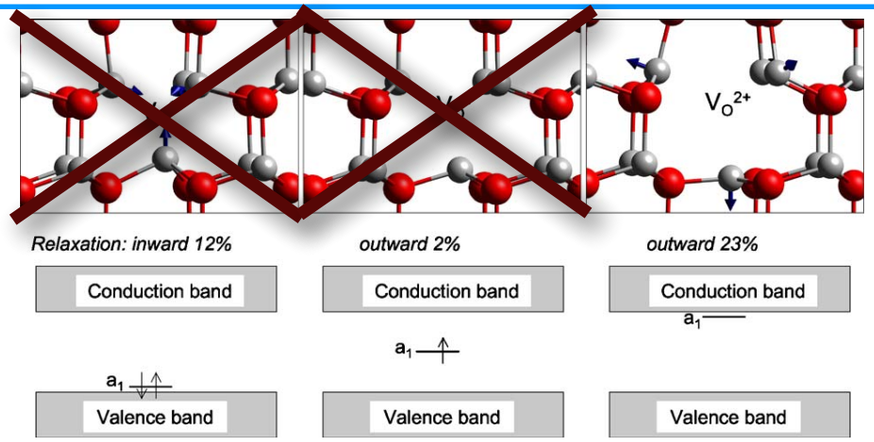




Correcting for change in X-ray absorption cross-section reveals small change in local electronic density around Zn which matches well with theory

Nanoparticle conclusions & the future

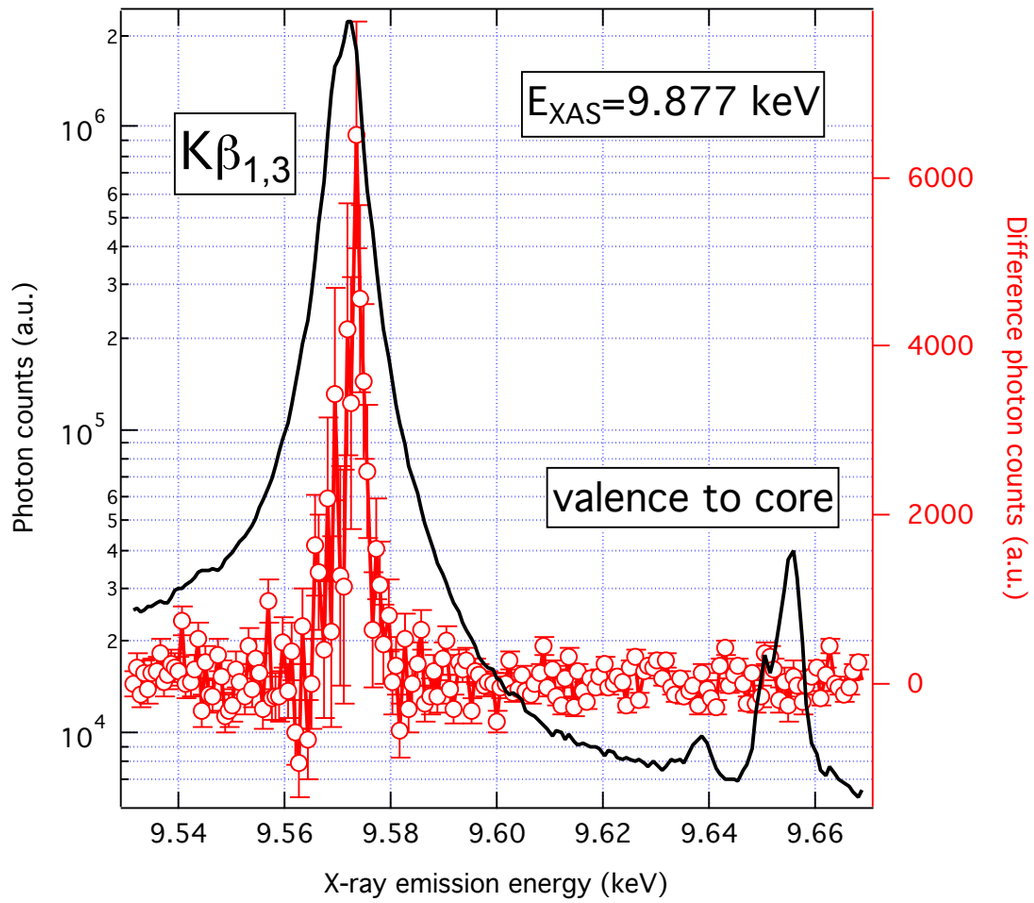
- We've identified the long-lived electron traps in ZnO as oxygen-defect sites in the lattice
- The structure of this site is consistent with a charge density shift from the predominantly oxygen valence band to the zinc conduction band
- Our measurements are primarily based on the XAS signal



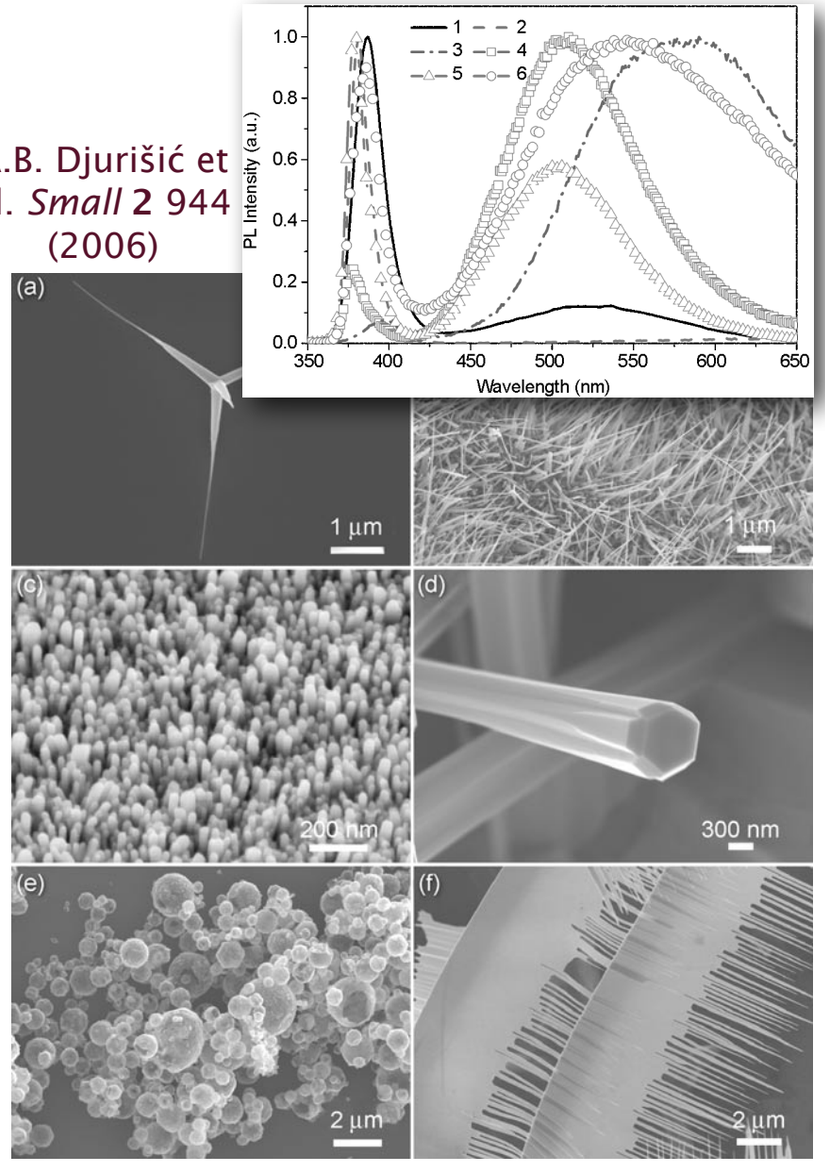
Janotti et al. *App. Phys. Lett.* **87** 122102 (2005)

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)



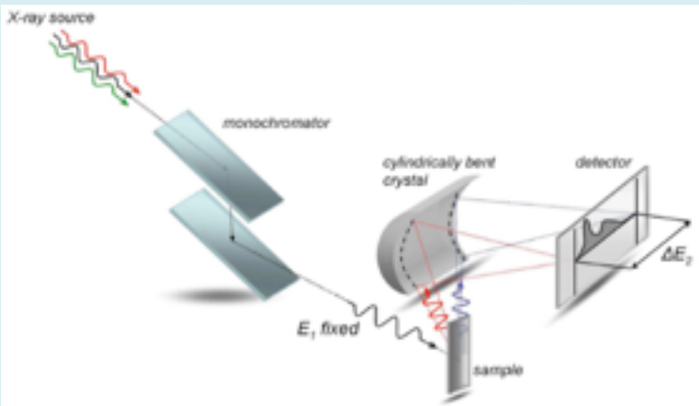
Size and shape dependence will influence trap geometry, energy and concentration

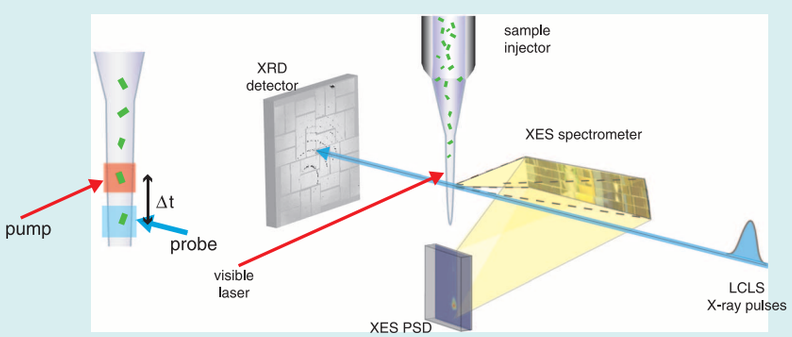
Better time resolution will allow us to observe initial electronic relaxation processes in the conduction band, as well as perhaps observe coupling to lattice phonons on the 100-300 fs timescale

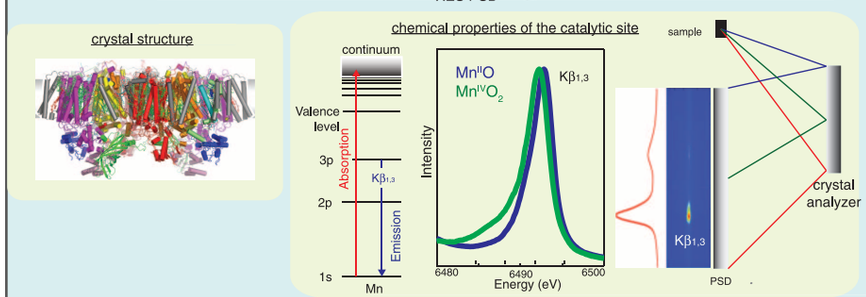
SwissFEL Experimental Stations

Bruce Patterson
and co-workers

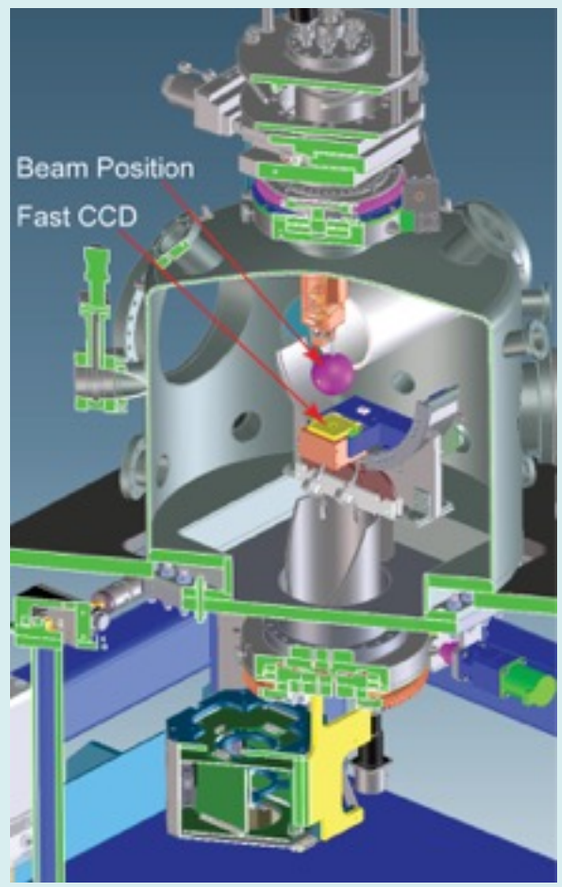
ESA:
Ultrafast photochemistry and photobiology







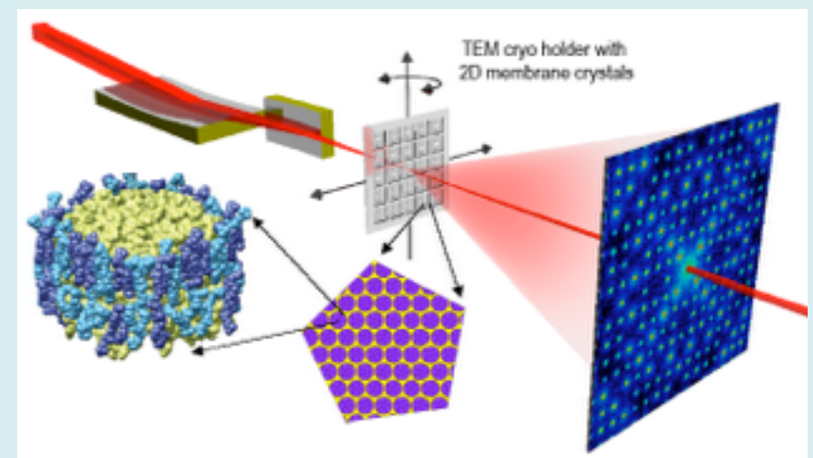
ESB:
Pump-probe crystallography



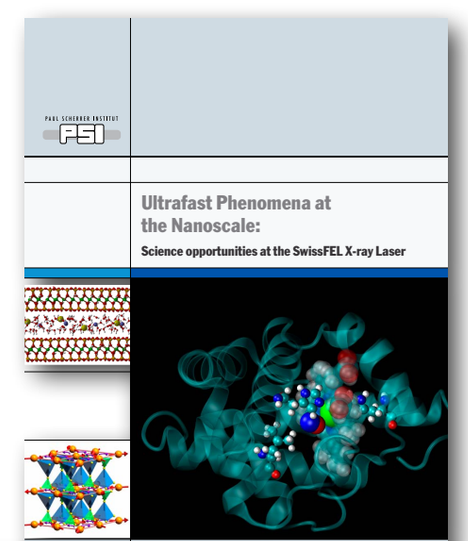
Phase I:
Ready by 2017

Phase II: >2017

ESC:
Materials science and nanocrystallography

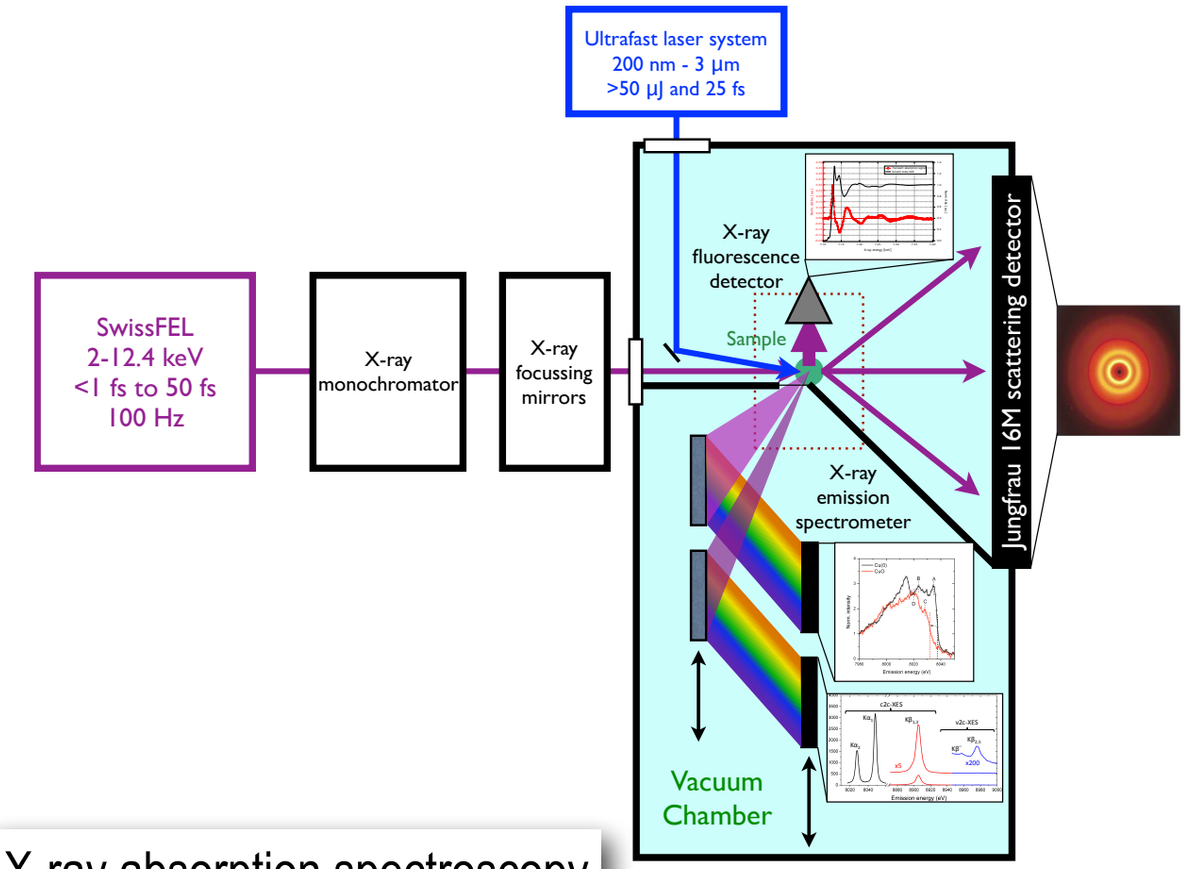


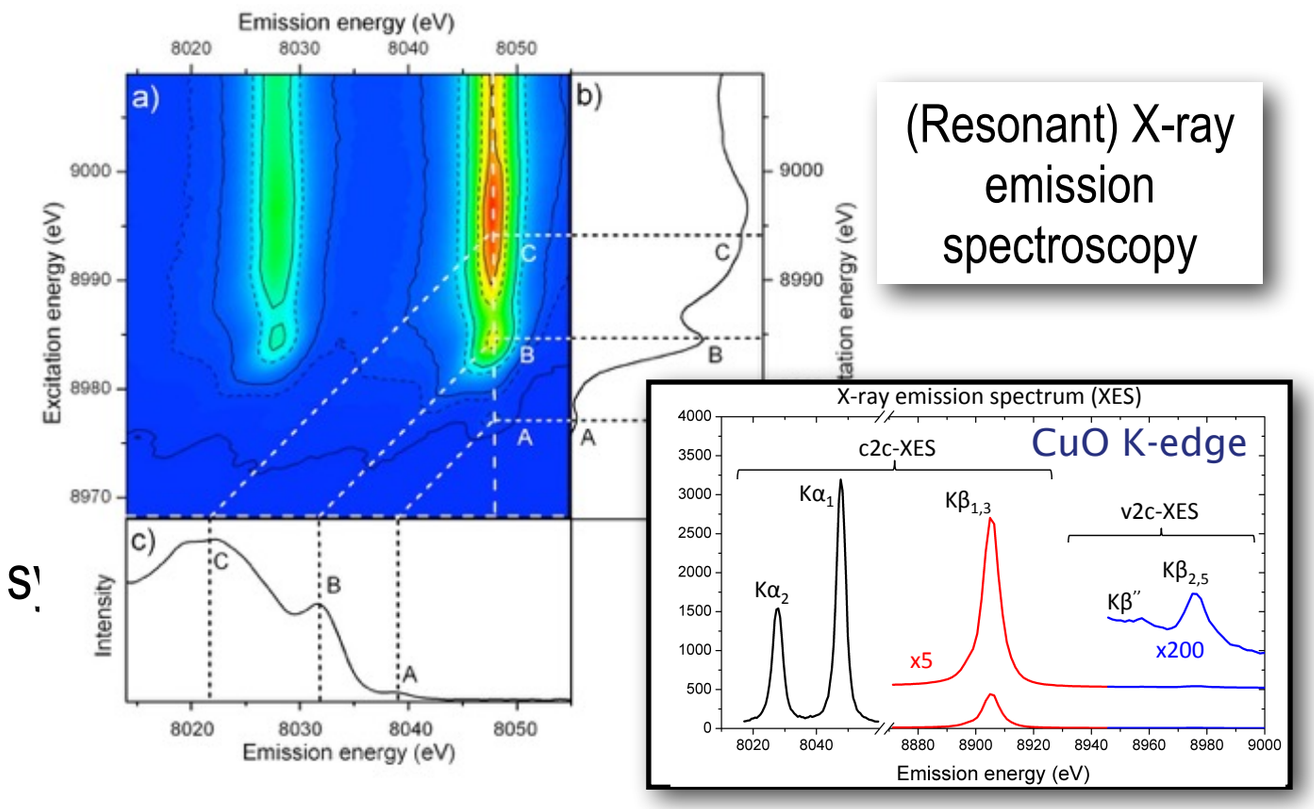
Scientific Case
B. Patterson
editor

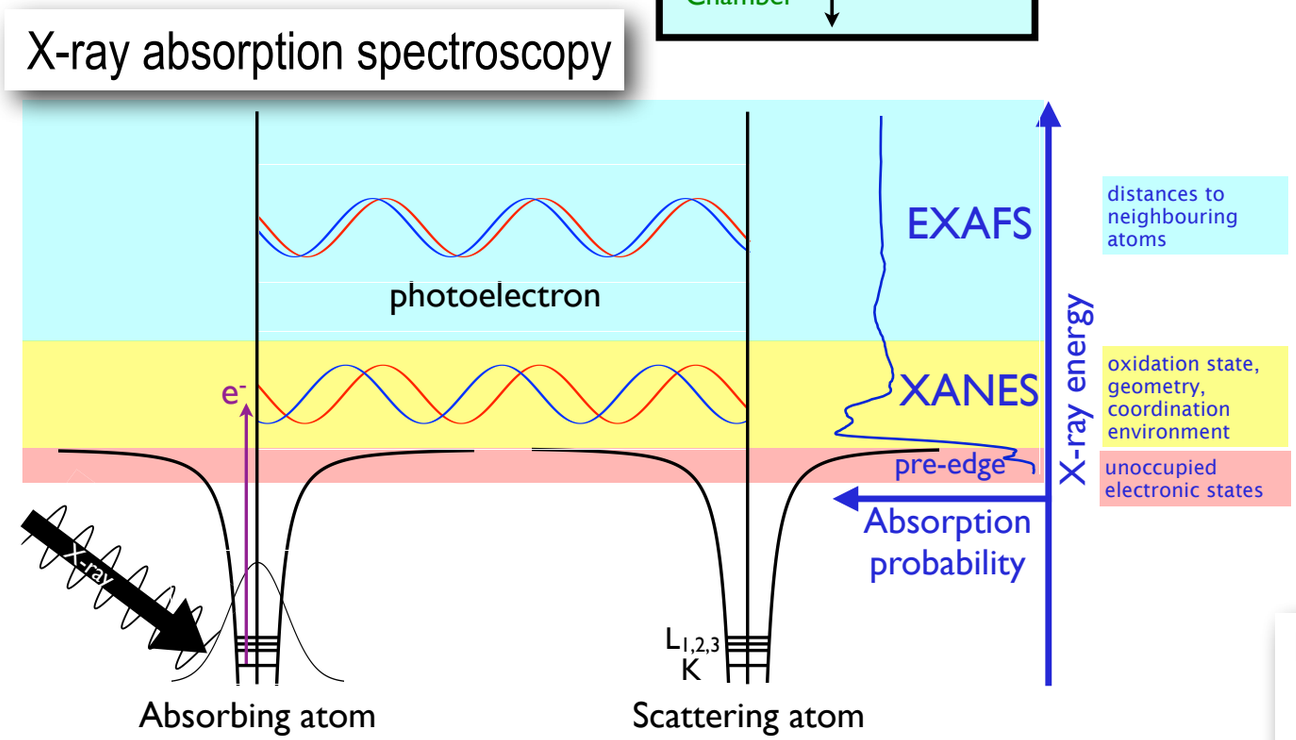


http://www.psi.ch/swissfel/

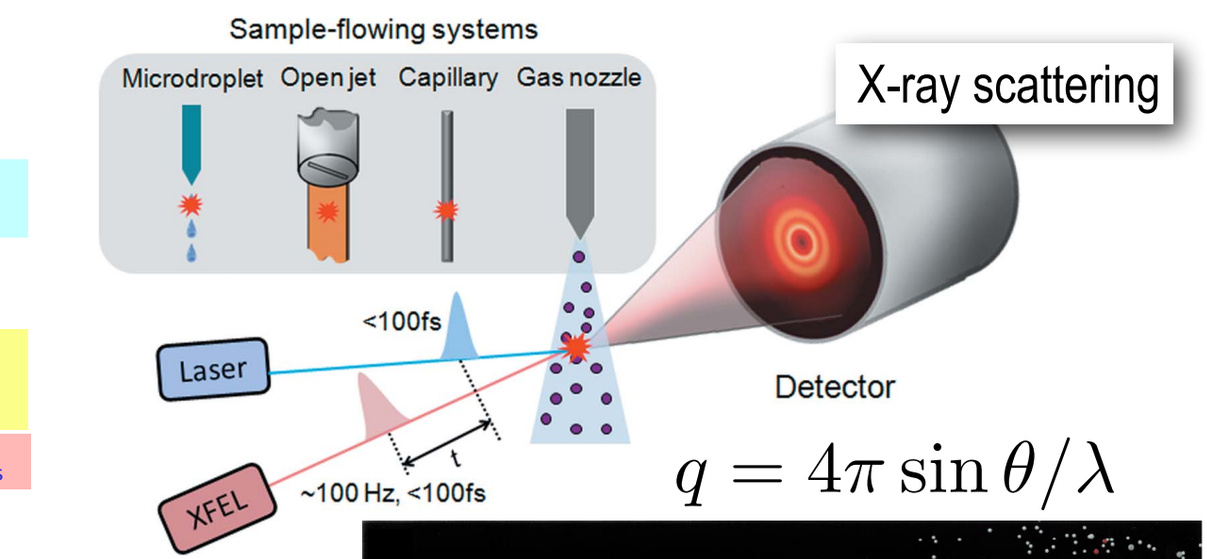
ESA: The X-ray probe techniques





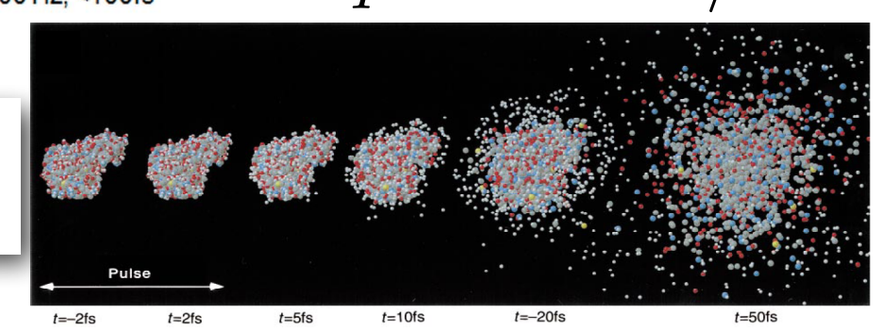


C.J. Milne et al. *Coord. Chem. Rev.* **277** 44 (2014)



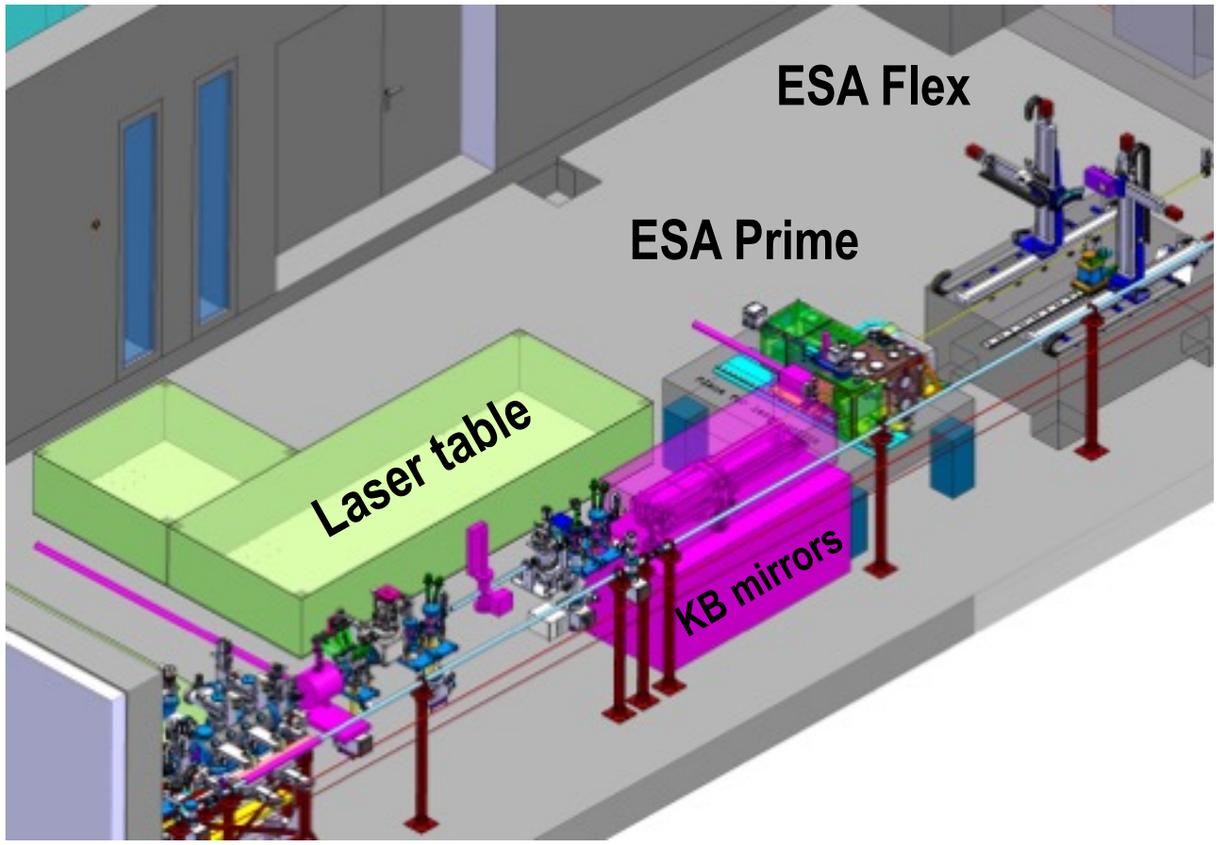
$$q = 4\pi \sin\theta/\lambda$$

R. Neutze et al. *Nature.* **406** 752 (2000)



The ESA Instruments: Prime and Flex

C. Milne,
J. Szlachetko
and G. Knopp



ESA Prime

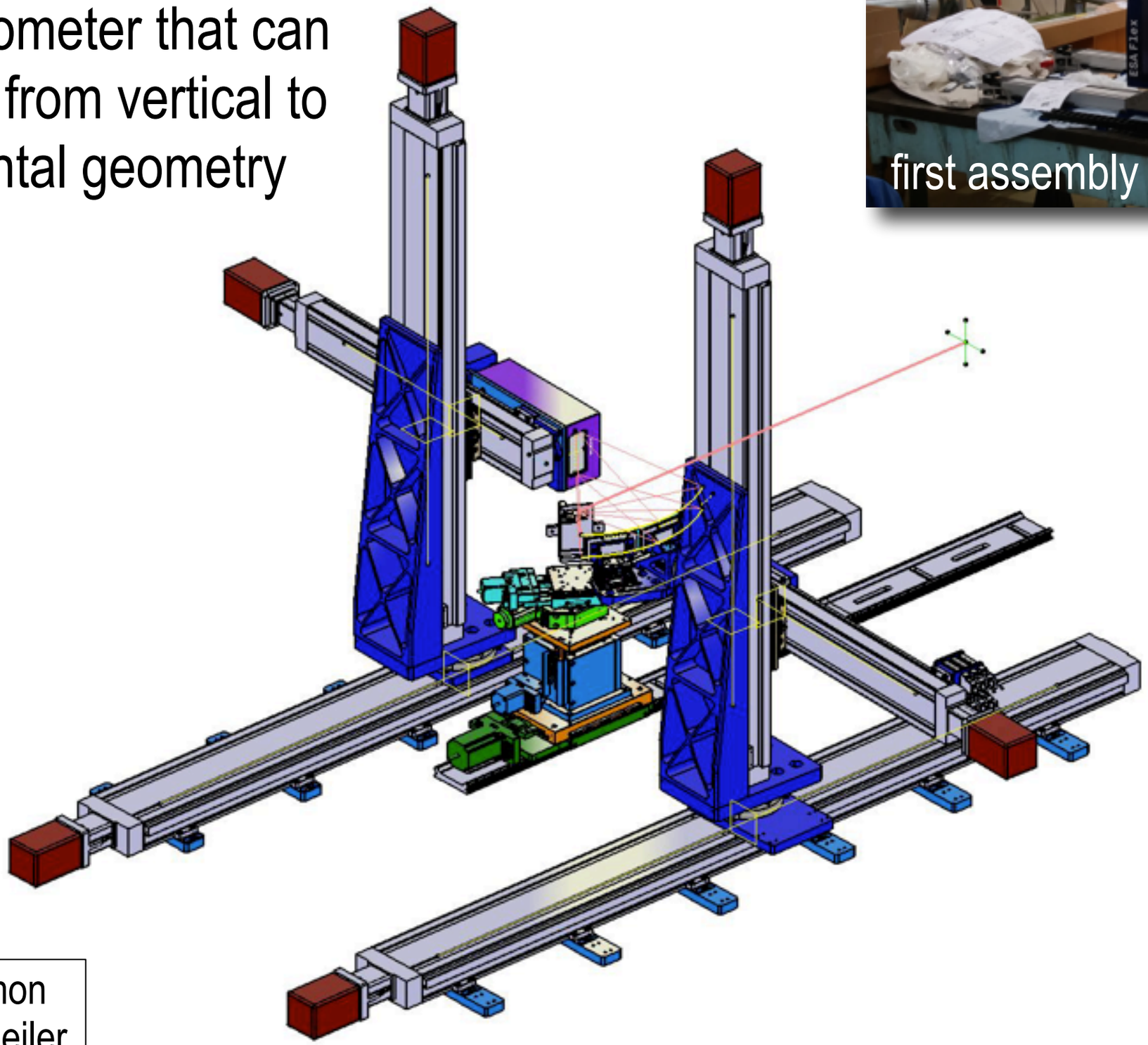
- works under He or vacuum to use the 2-5 keV range
- located at the 1 µm achromatic X-ray focus (KB mirrors)
- emphasis is on **combined scattering and spectroscopy measurements**

ESA Flex

- **flexible station** to accommodate user chambers and constrained geometries
- ability to easily change the spectrometer position will provide the highest energy resolution and the ability to change the scattering geometry

ESA Flex: In Action !

In-air flexible X-ray spectrometer that can switch from vertical to horizontal geometry

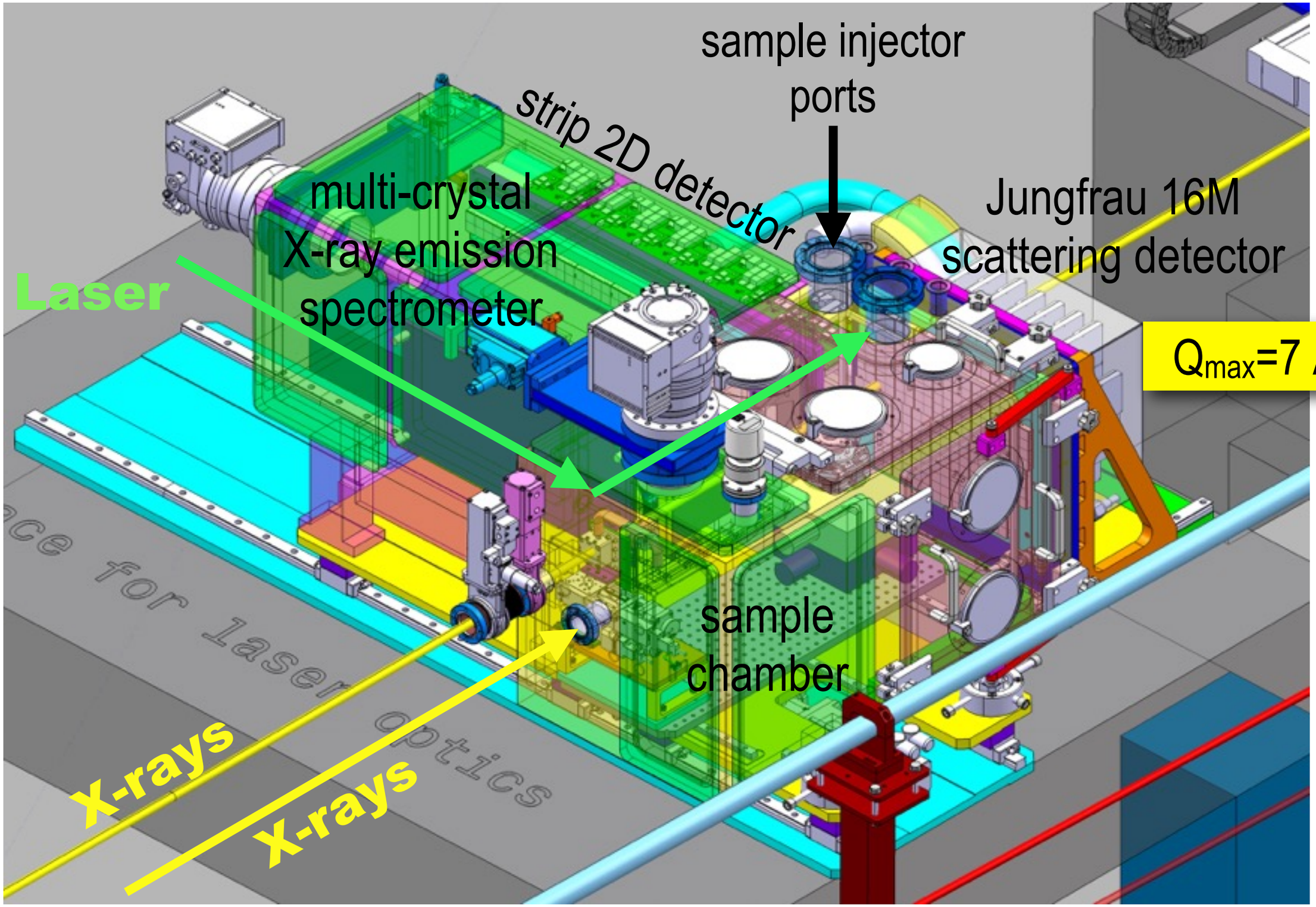


A. Ammon and C. Seiler

SLS commissioning May 5-12

ESA Prime: Pre-final design

Markus Vitins and
Jérome Stettler



ESA Prime status: design completion goal May 2015

Lipidic-cubic phase jets for SFX

J. Standfuss, P. Nogly,
G. Schertler (BIO)

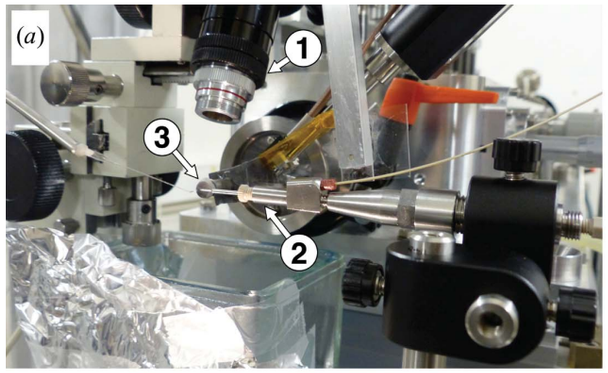
Tested LCP jet at ESRF microfocus beamline and under pump-probe conditions at LCLS (CXI)

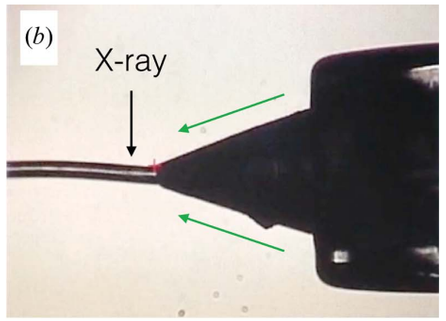
IUCrJ
ISSN 2052-2525
BIOLOGY | MEDICINE

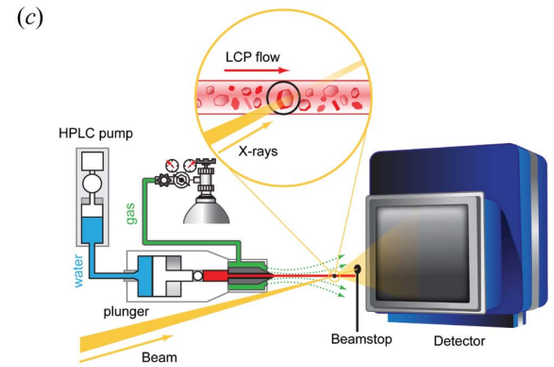
Lipidic cubic phase serial millisecond crystallography using synchrotron radiation

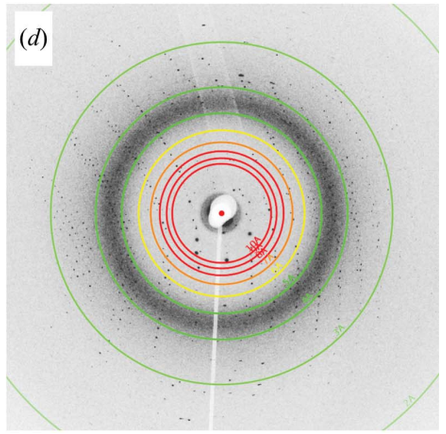
Przemyslaw Nogly,[a] Daniel James,[b] Dingjie Wang,[b] Thomas A. White,[c] Nadia Zatsepin,[b] Anastasya Shilova,[d] Garrett Nelson,[b] Haiguang Liu,[b] Linda Johansson,[e] Michael Heymann,[c] Kathrin Jaeger,[a] Markus Metz,[c,f] Cecilia Wickstrand,[g] Wenting Wu,[a] Petra Båth,[g] Peter Berntsen,[g] Dominik Oberthuer,[c,f] Valerie Panneels,[a] Vadim Cherezov,[e] Henry Chapman,[c,h] Gebhard Schertler,[a,i] Richard Neutze,[g] John Spence,[b] Isabel Moraes,[j,k,l] Manfred Burghammer,[d,m]* Joerg Standfuss[a]* and Uwe Weierstall[b]*

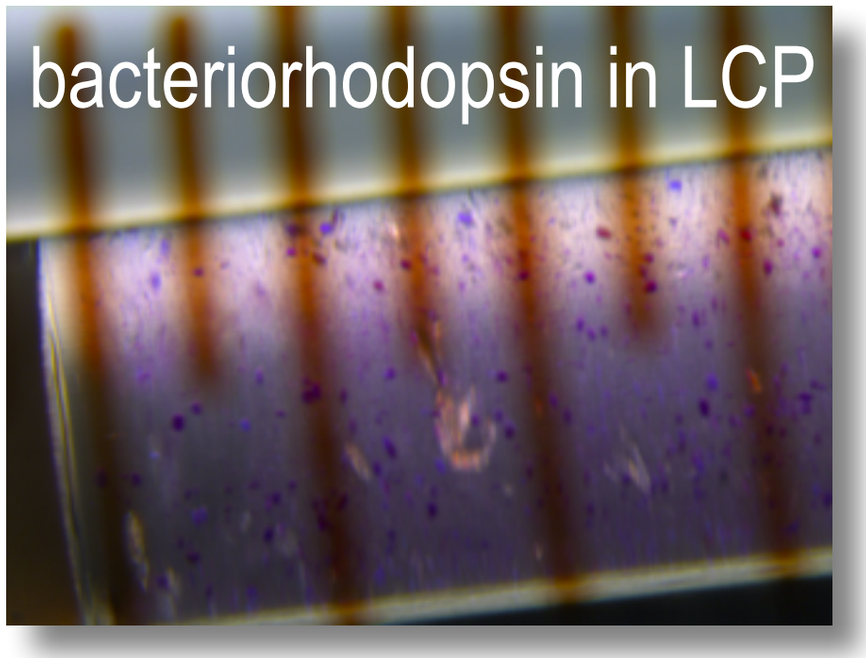
Received 16 October 2014
Accepted 1 December 2014





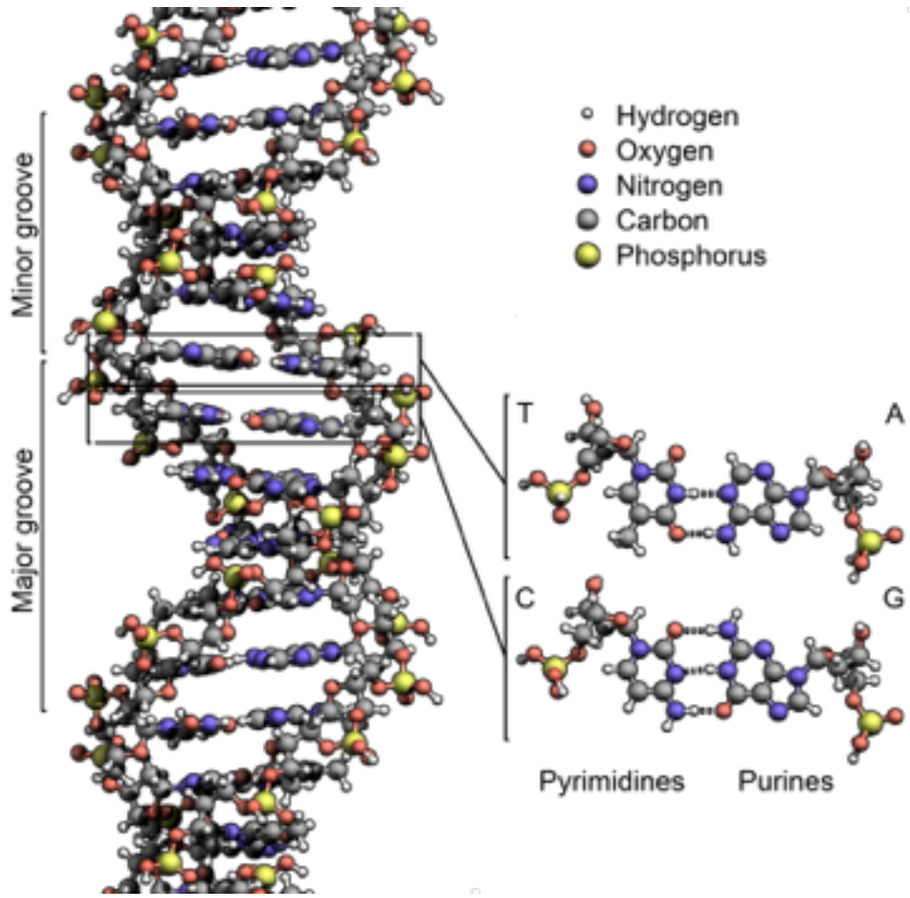


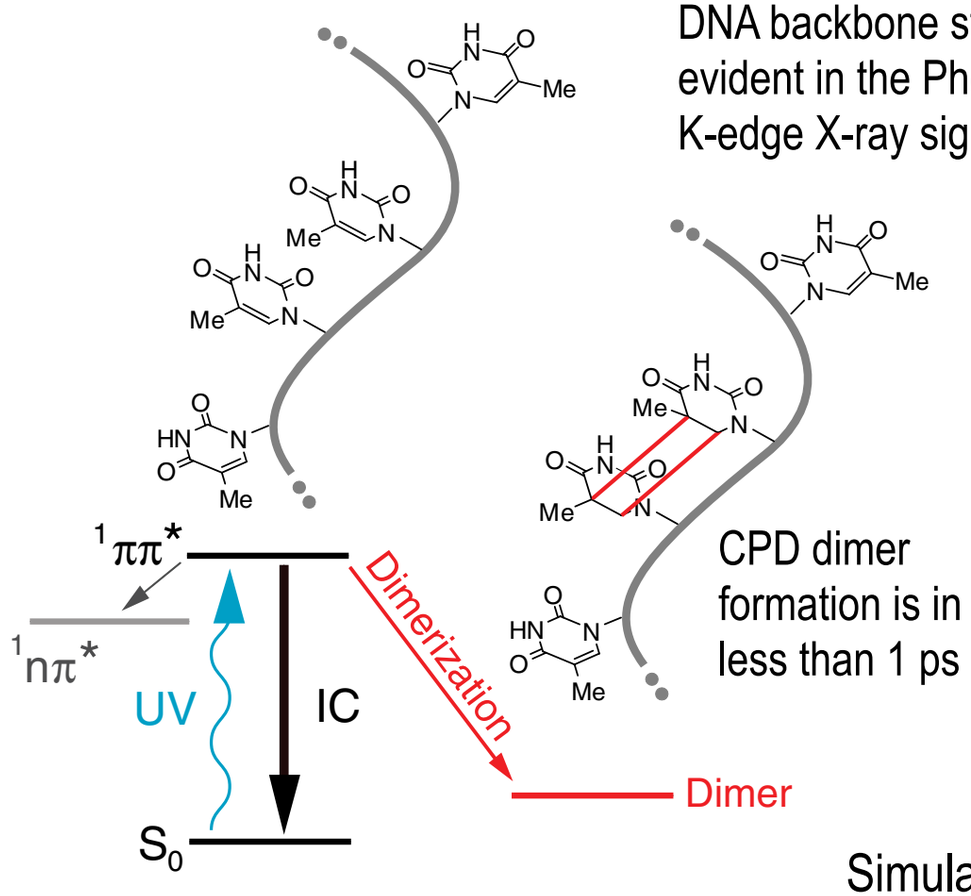




media courtesy of Przemek Nogly

Photo-damage and repair mechanisms in DNA



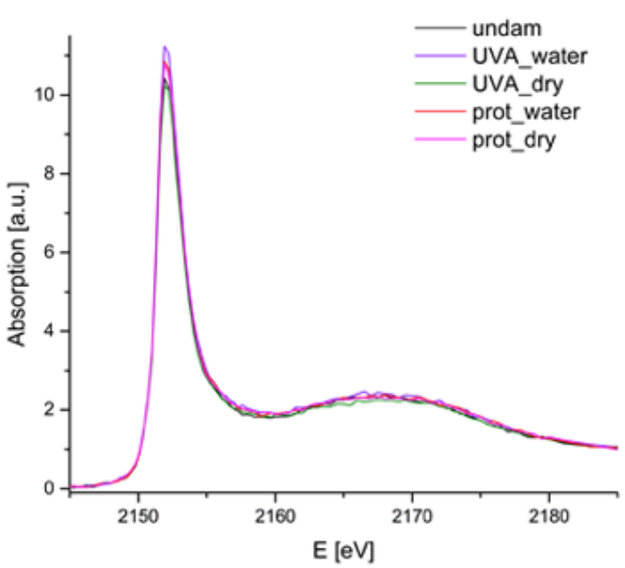


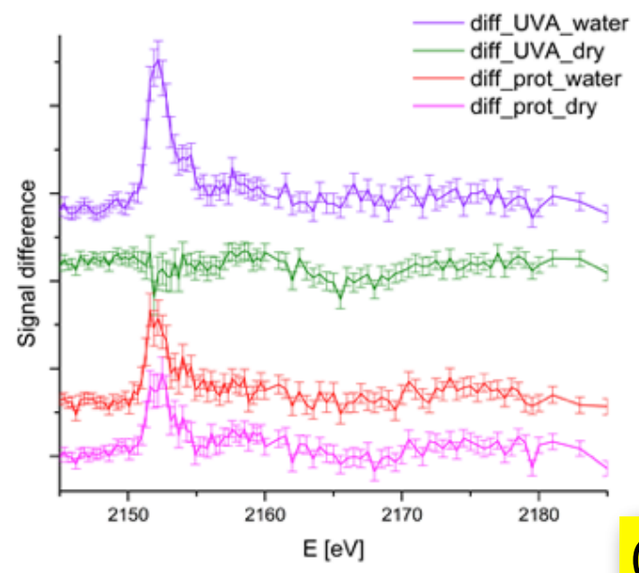
DNA backbone strain will be evident in the Phosphorus K-edge X-ray signals

W.J. Schreier et al. *Science* **315**, 625 (2007)

W. Zinth et al. *EPJ Web of Conferences* **41**, 07005 (2013)

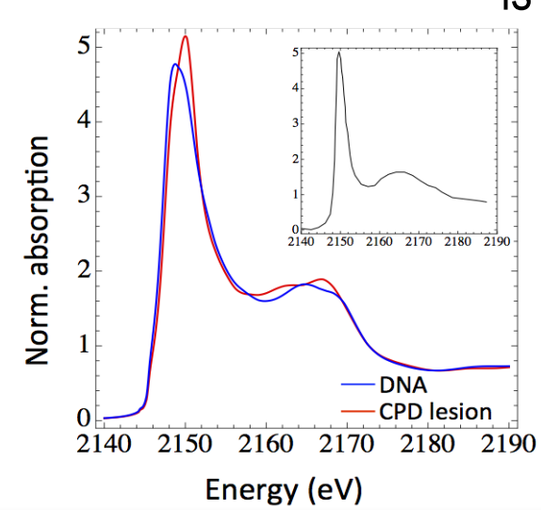
CPD dimer formation is in less than 1 ps

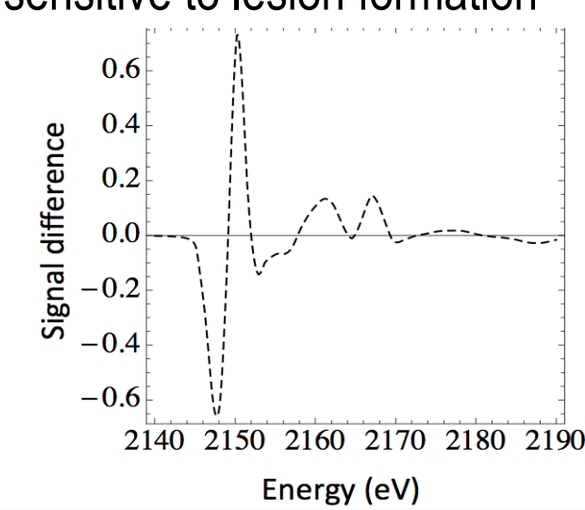




DNA XAS measured in solution (J. Czapla-Maszatafiak et al.)

Simulations indicate P K-edge XAS is sensitive to lesion formation





Can we follow the ultrafast electronic and structural damage formation ?

Acknowledgements

SwissFEL project:	R. Abela, P. Juranić, L. Sala, T.J. Penfold, J. Rittmann, G. Knopp, J. Czapla-Masztafiak
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BIO Department	J. Standfuss, P. Nogly, G. Schertler, V. Panneels
LCLS:	S. Boutet, G. Williams, M. Messerschmidt, M. Sikorski, A. Robert
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