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Henrik Lemke :: SwissFEL :: Paul Scherrer Institut

Charge, spin and structural dynamics in Spin-Cross-Over materials

School on Synchrotron and Free-Electron-Laser Methods for Multidisciplinary Applications school, Trieste, 15. 5. 2018

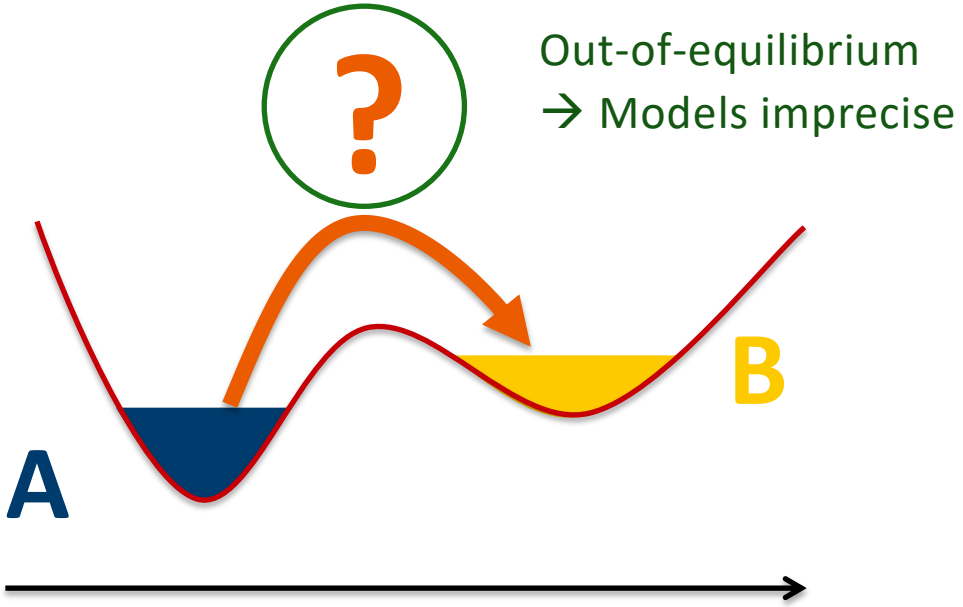
Outline

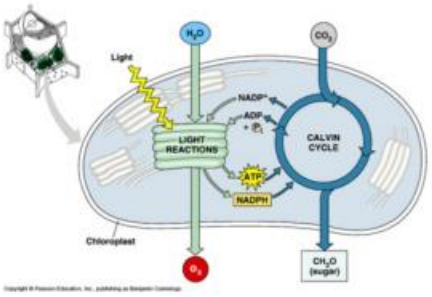
- Functions of materials and Free Electron Lasers
- The ultrafast FEL Toolset

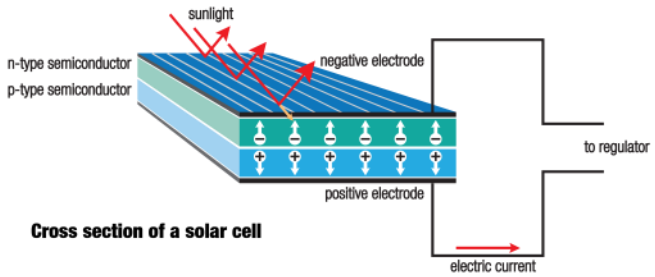
- Ultrafast charge/spin/structure in molecular transition metal complexes
  - The Problem
  - The Findings

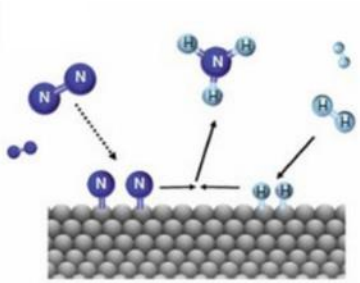
- Ultrafast phenomena in solid state
- The SwissFEL free electron laser

How do materials change their function?





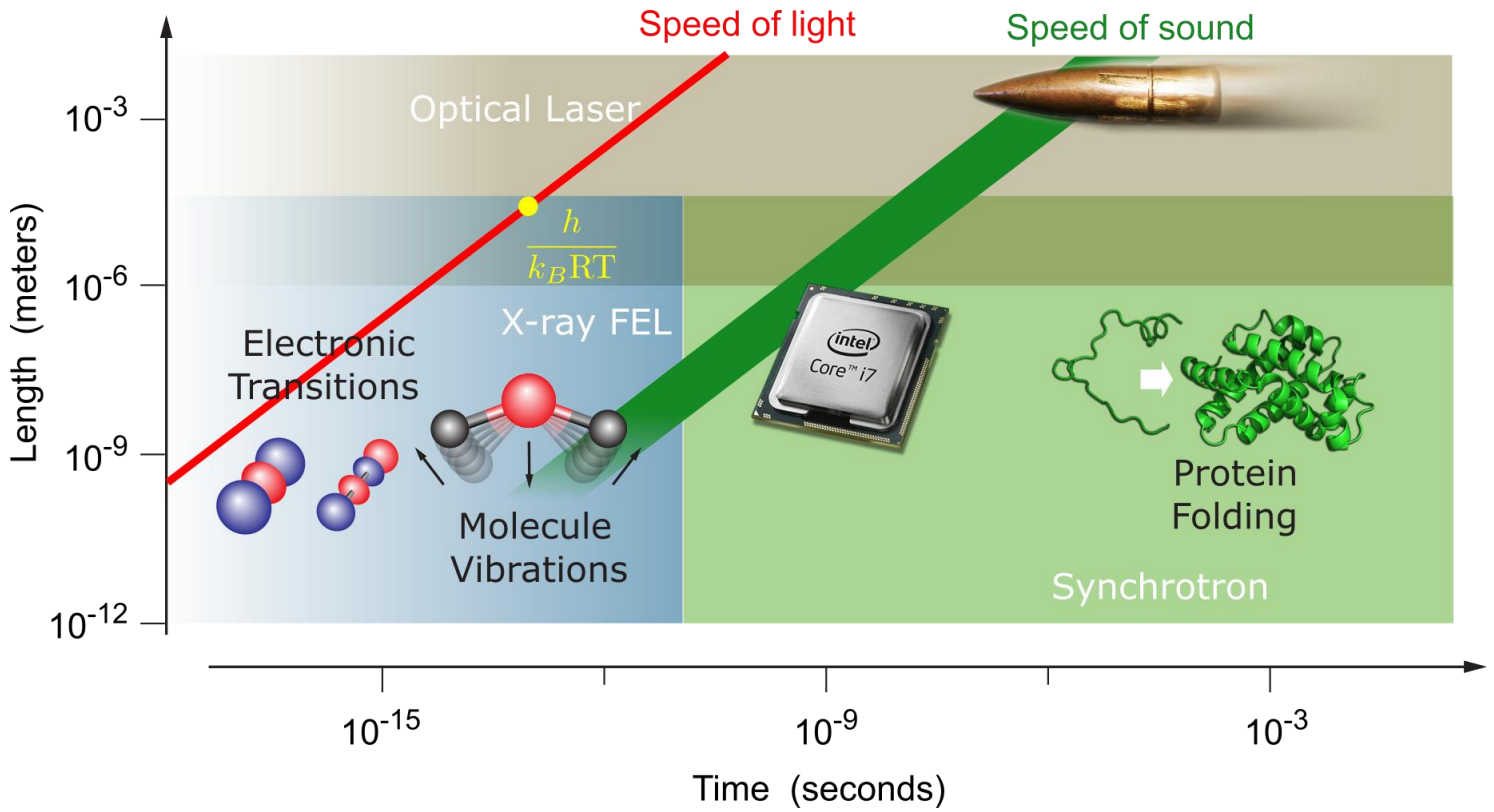




Contribution of Free Electron Lasers

Electronic and nuclear structure sensitivity

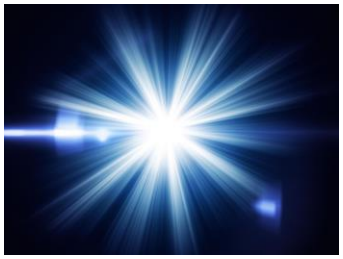
- at atomic length scale
- ***at the timescale of transitions***



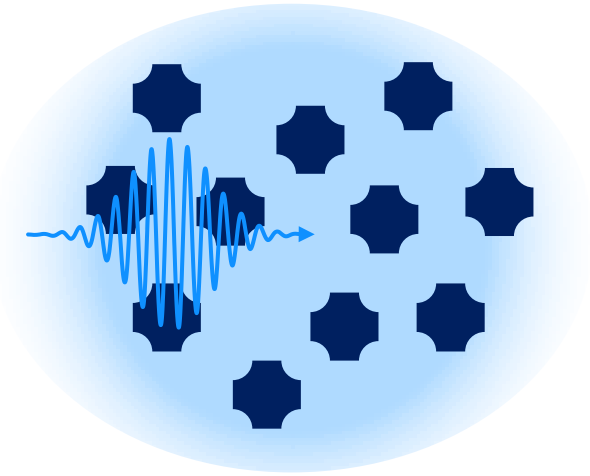
Bostedt (2016), Rev. Mod. Phys. 88, 15007.

The Toolset

How can we learn about functional transitions with FELs?



Pump/probe tracks ultrafast processes



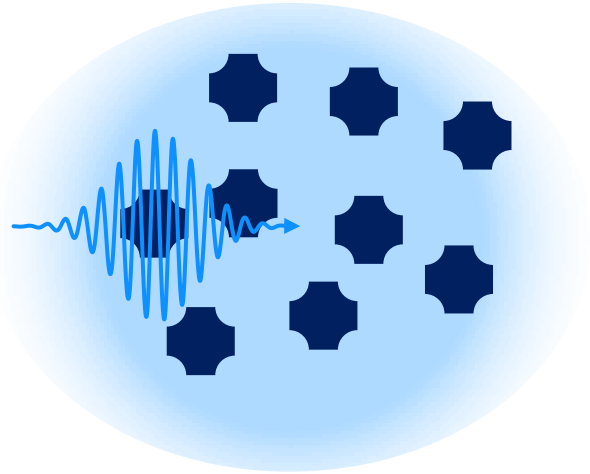
A

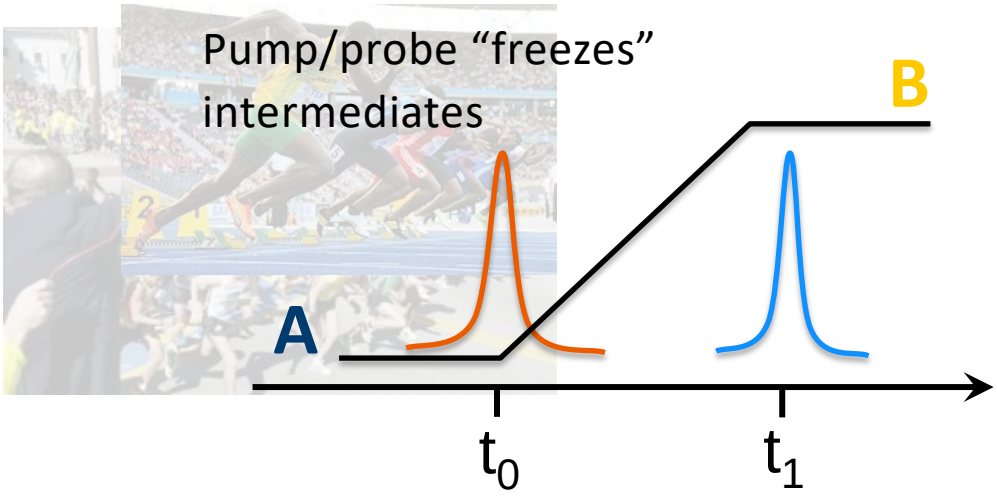
B

?

Transition states are

- ultrashort lived
- **ultra-dilute** at a given point in time

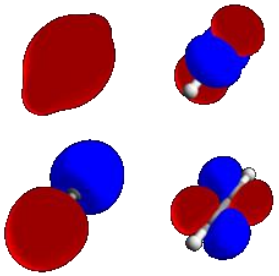


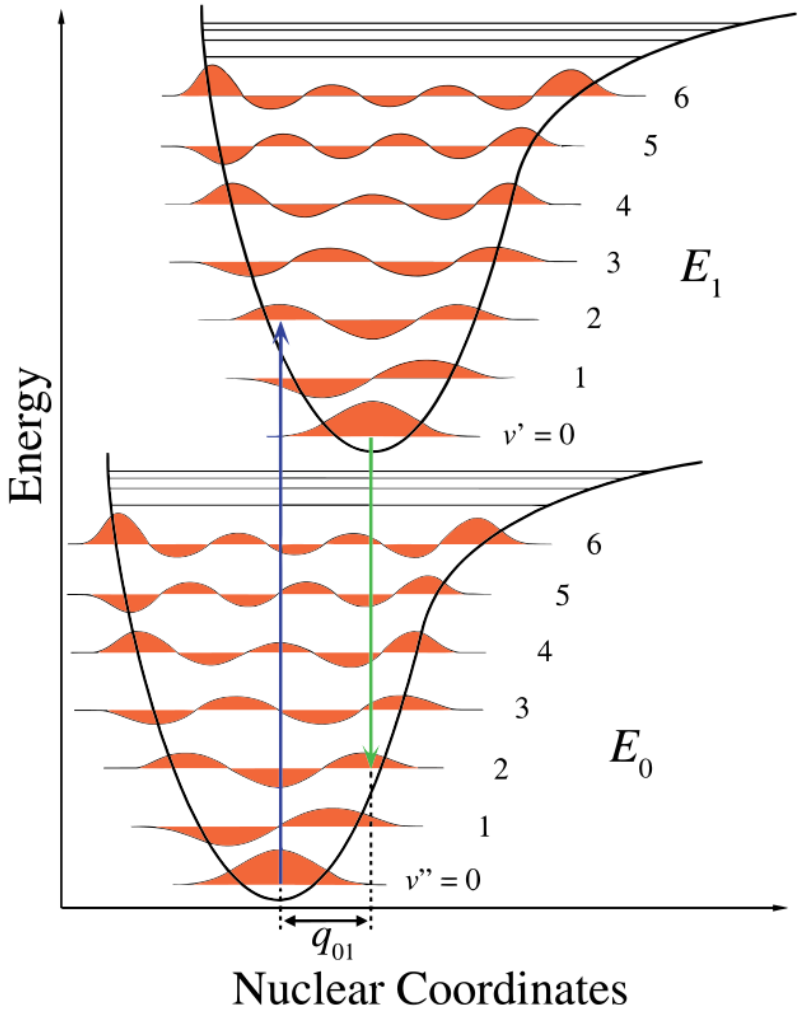


Excitation mechanisms - **pump**

Ultrafast femtosecond excitation by ultrafast laser light pulses

- **UV-Vis**: excitation of unoccupied electronic state (valence)
- **Infrared/THz**: vibrational states, phonons in solids

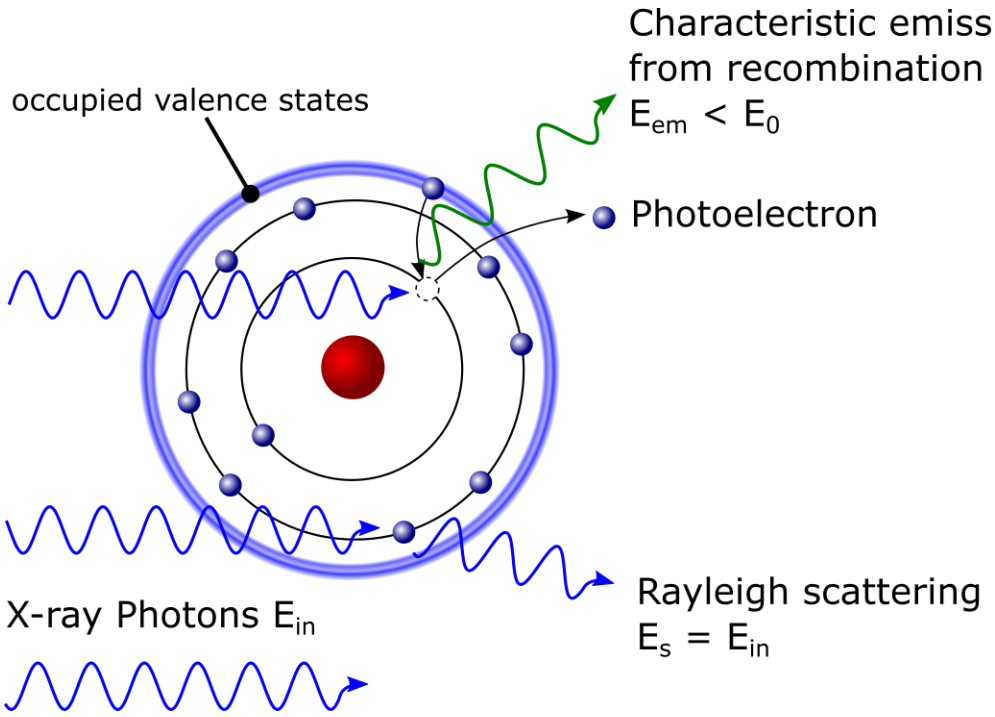




wikipedia.org

Measure mechanisms – X-ray **probe**

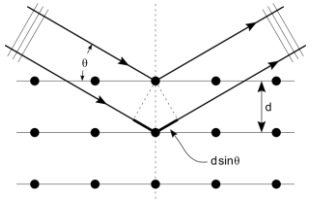
X-ray photons can interact with electrons,
also from core shell levels.

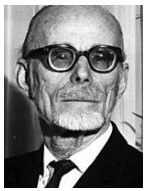


→ **electronic state**

→ **can interact with atom environment**

→ **can interfere**





…and they often pass by.

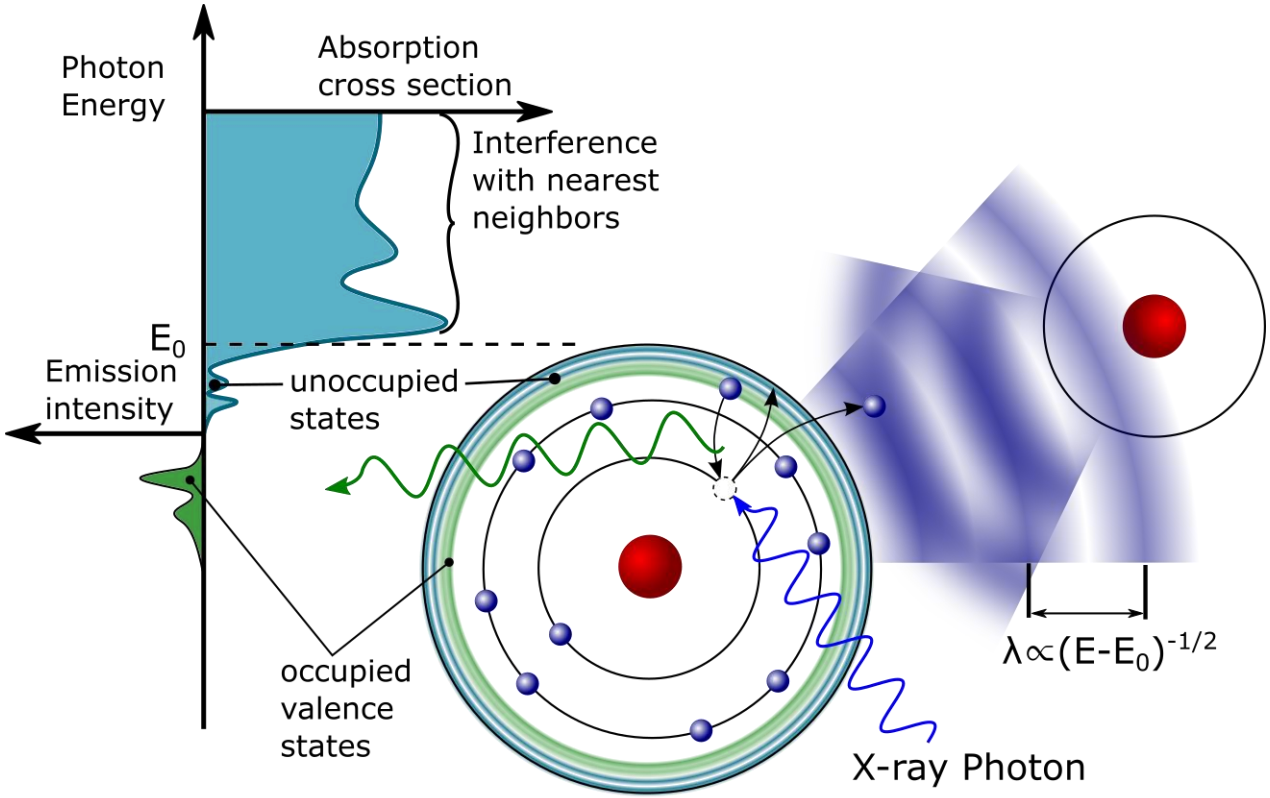
X-ray Spectroscopy

Emission spectrum

- Occupied valence states

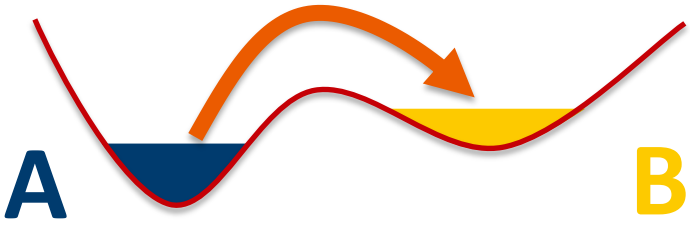
Absorption spectrum

- Chemical potential
- Unoccupied states



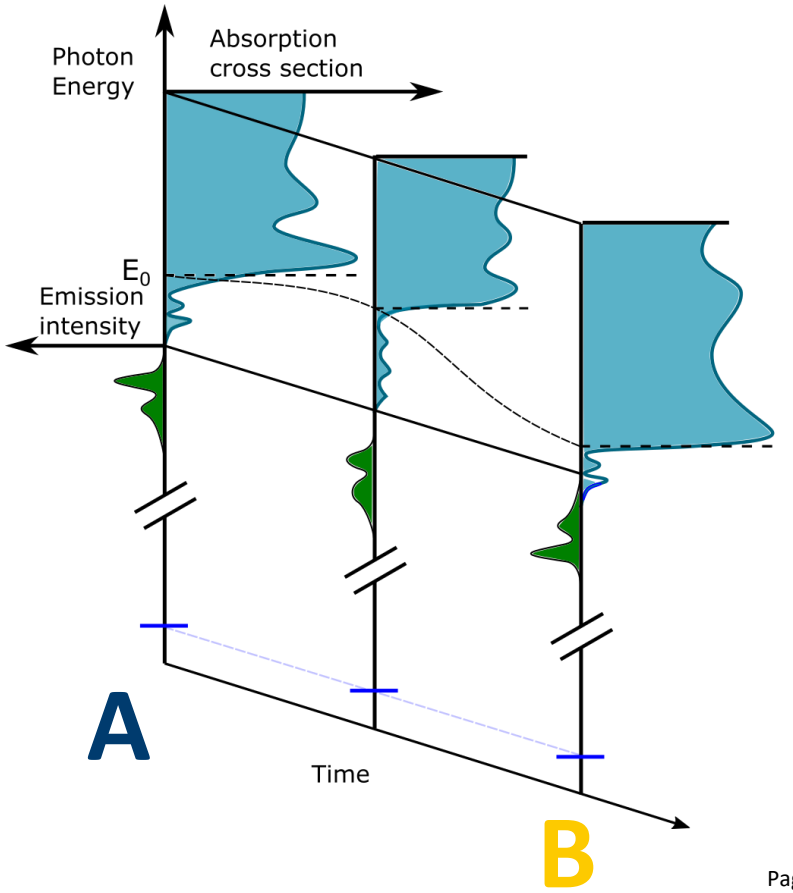
X-ray spectroscopy is element specific

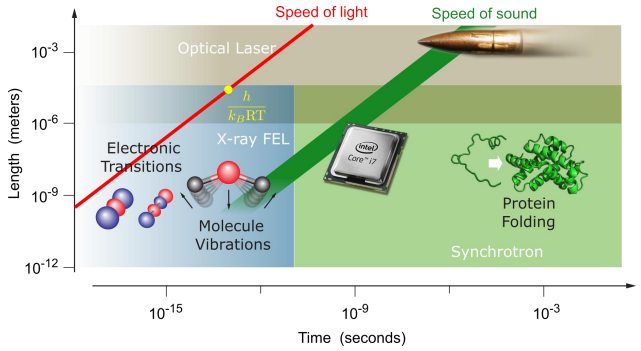
Ultrafast x-ray Spectroscopy



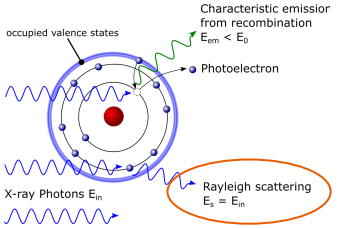
Ultrafast transitions

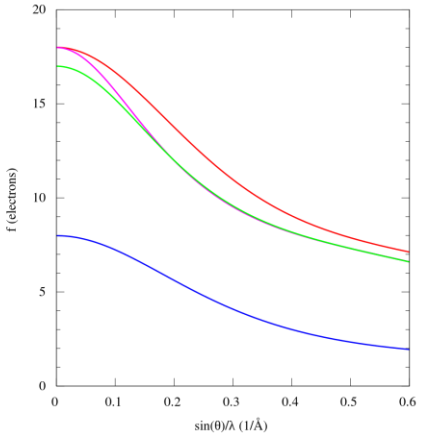
- High variations in “chemistry”
  - Chemical potential
  - Electronic states
  - Local environment
- Low variations in core electron levels

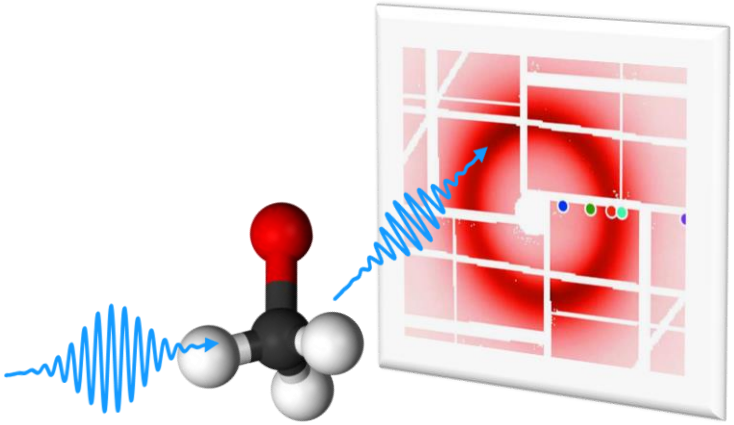




X-ray solution scattering

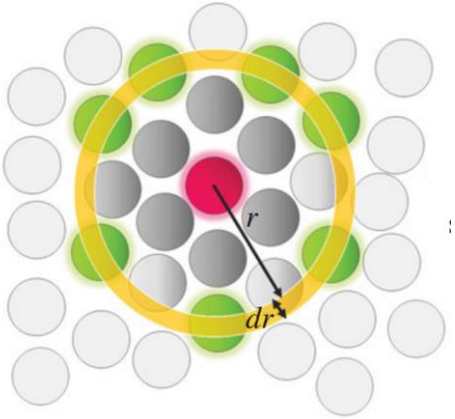






Elastic scattering interference from
all electrons in a sample

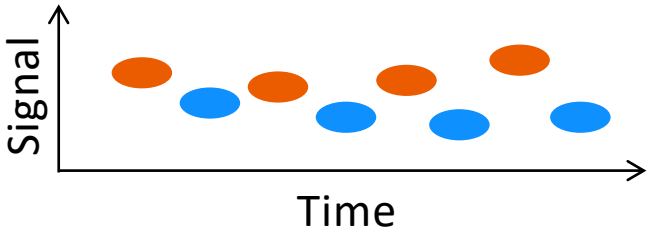
approximated by
atomic form factor and Debye scattering equation



$$I(q) = \sum_n \sum_m f_n(q) f_m(q) \frac{\sin(q r_{nm})}{q r_{nm}}$$

General concepts in pump probe methods

$$S_{\text{pumped}} = a\, S_{\text{excited}} + (1-a) S_{\text{static}}$$
$$S_{\text{unpumped}} = S_{\text{static}}$$



Reference measurements can correct drifts

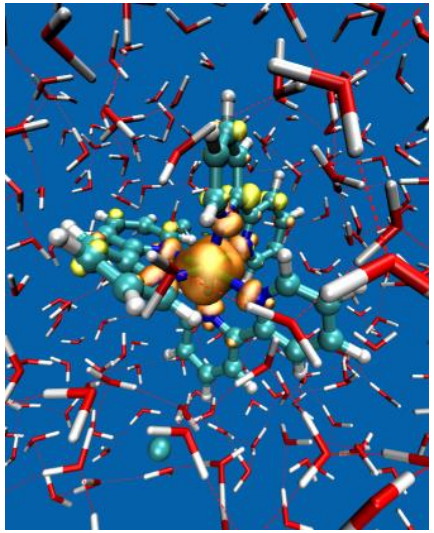
Slow drifting parasitic signal

$$S_{\text{pumped}} = a\, S_{\text{excited}} + (1-a) S_{\text{static}} + X_{\text{drift}}(t)$$
$$S_{\text{unpumped}} = S_{\text{static}} + X_{\text{drift}}(t)$$
$$\Delta S = S_{\text{pumped}} - S_{\text{unpumped}} = a\,[S_{excited} - S_{static}]$$

Slow drifting sensitivity

$$S_{\text{pumped}} = [a\, S_{\text{excited}} + (1-a) S_{\text{static}}] \times X_{\text{drift}}(t)$$
$$S_{\text{unpumped}} = S_{\text{static}} \times X_{\text{drift}}(t)$$
$$\frac{S_{\text{pumped}}}{S_{\text{unpumped}}} - 1 = a\left[\frac{S_{\text{excited}}}{S_{\text{static}}} - 1\right]$$

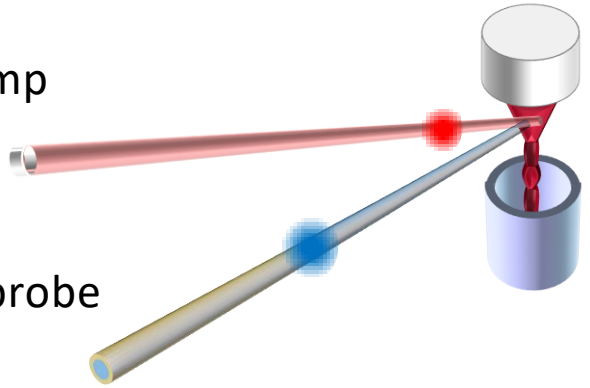
Pump/probe on liquids



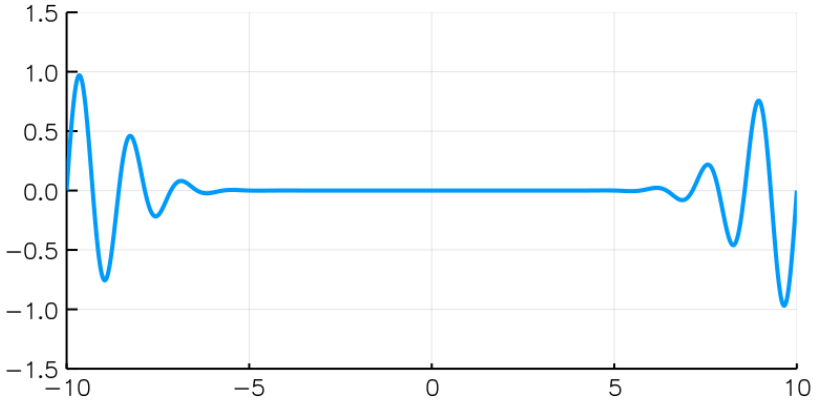
Circulating sample solution

Optical pump

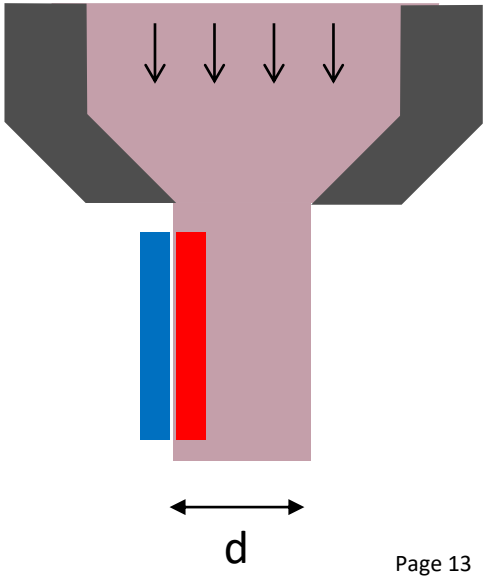
X-ray probe



Pump/probe group velocity mismatch scales with sample thickness

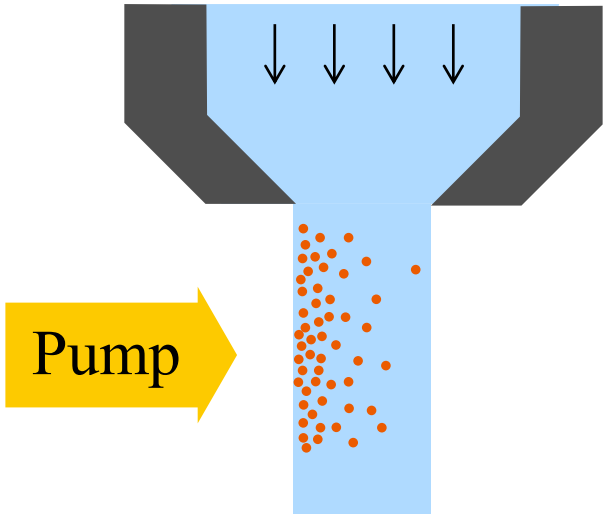


$t_L - t_X = d/c\,(n-1)$



Pump excitation

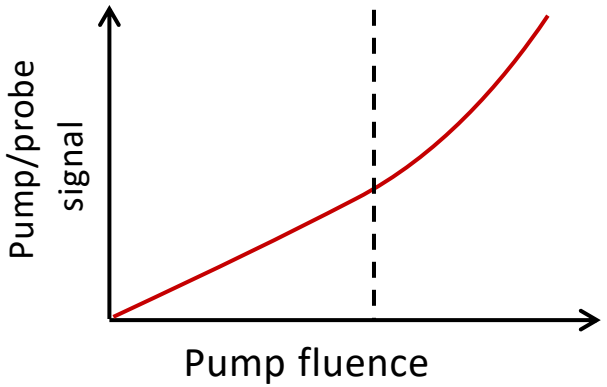
High concentration of excitations
→ high excitation fraction *a*



High pump fluence can lead to sequential excitation of already excited states.

- Difficult to interpret
- Usually not of interest

→ Search for linear signal regime



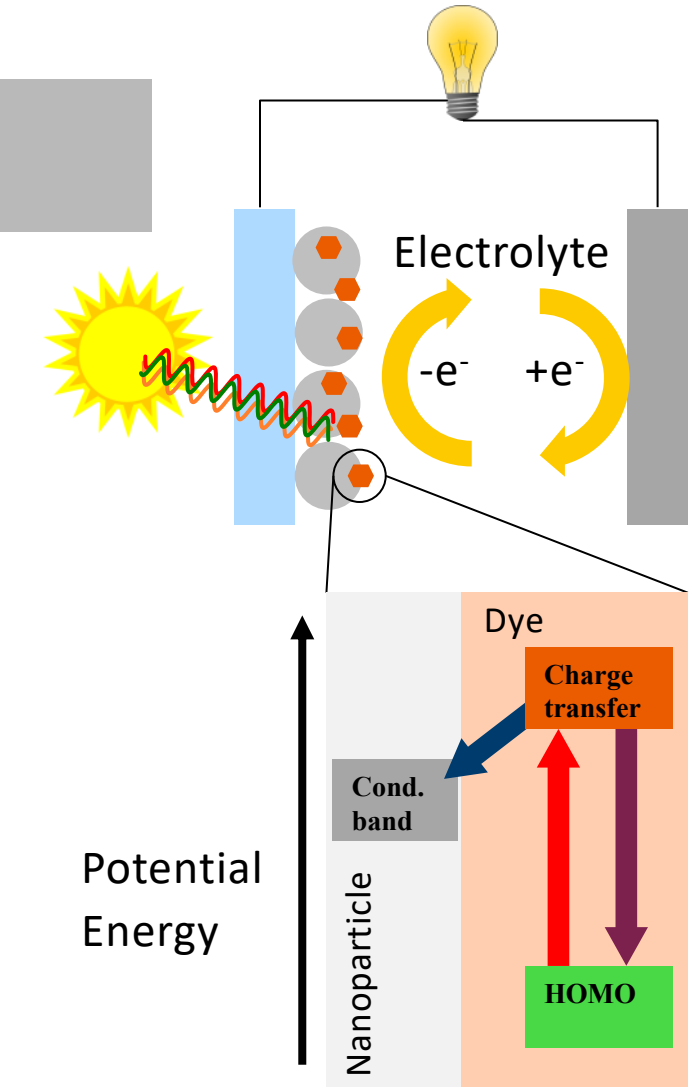
Summary FEL toolset

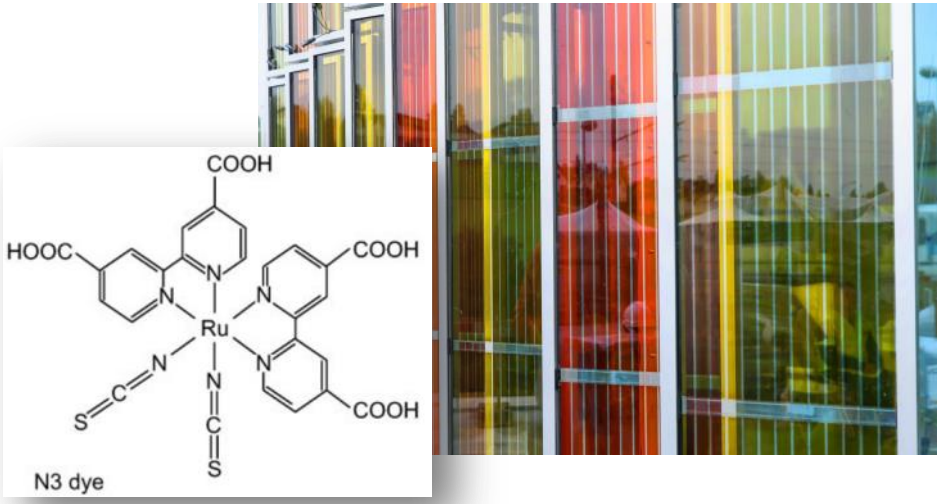
- Accumulation of non-equilibrium states by pump/probe
- Element specific electronic states, chem. potential local structure by X-ray spectroscopy
- Global structure by X-ray scattering

The Problem

Charge transfer and spin transitions in transition metal complexes

Charge transfer in dye sensitized solar cells



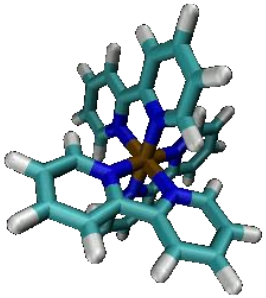


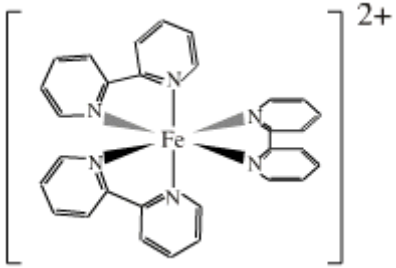
- **Competition (= Race) between charge separation and recombination**
- **Dye development**
  - **Absorption spectrum**
  - **Price**

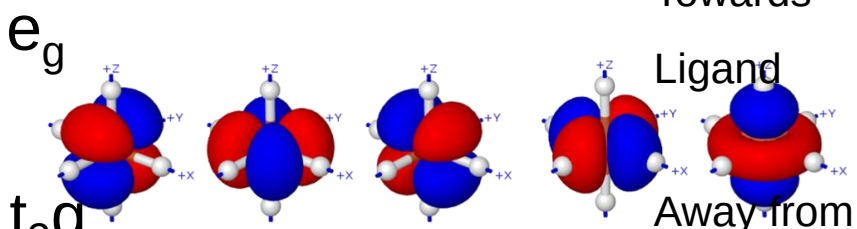
Spin transition molecular system

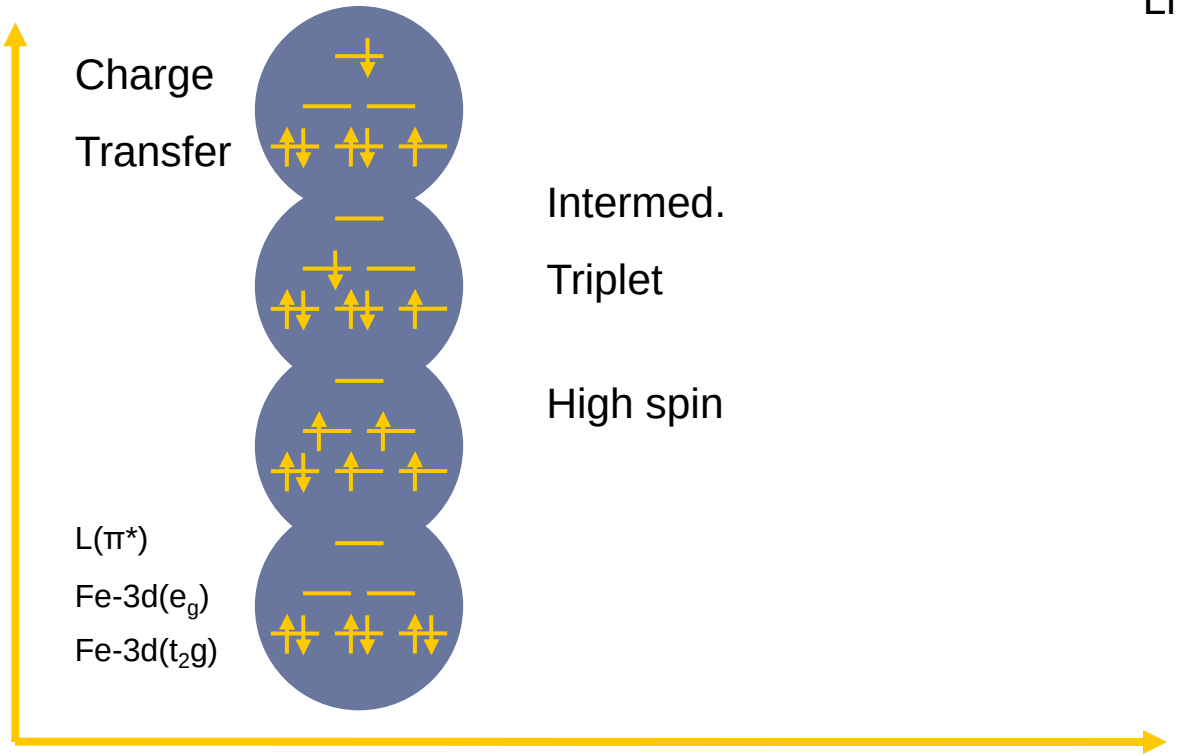
$Fe(bipy)_3$

Transition metal complex in octahedral symmetry

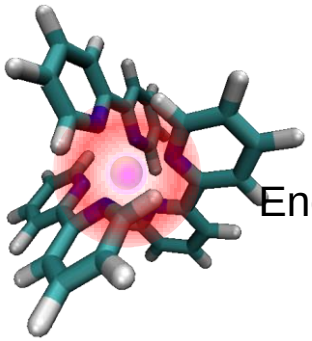


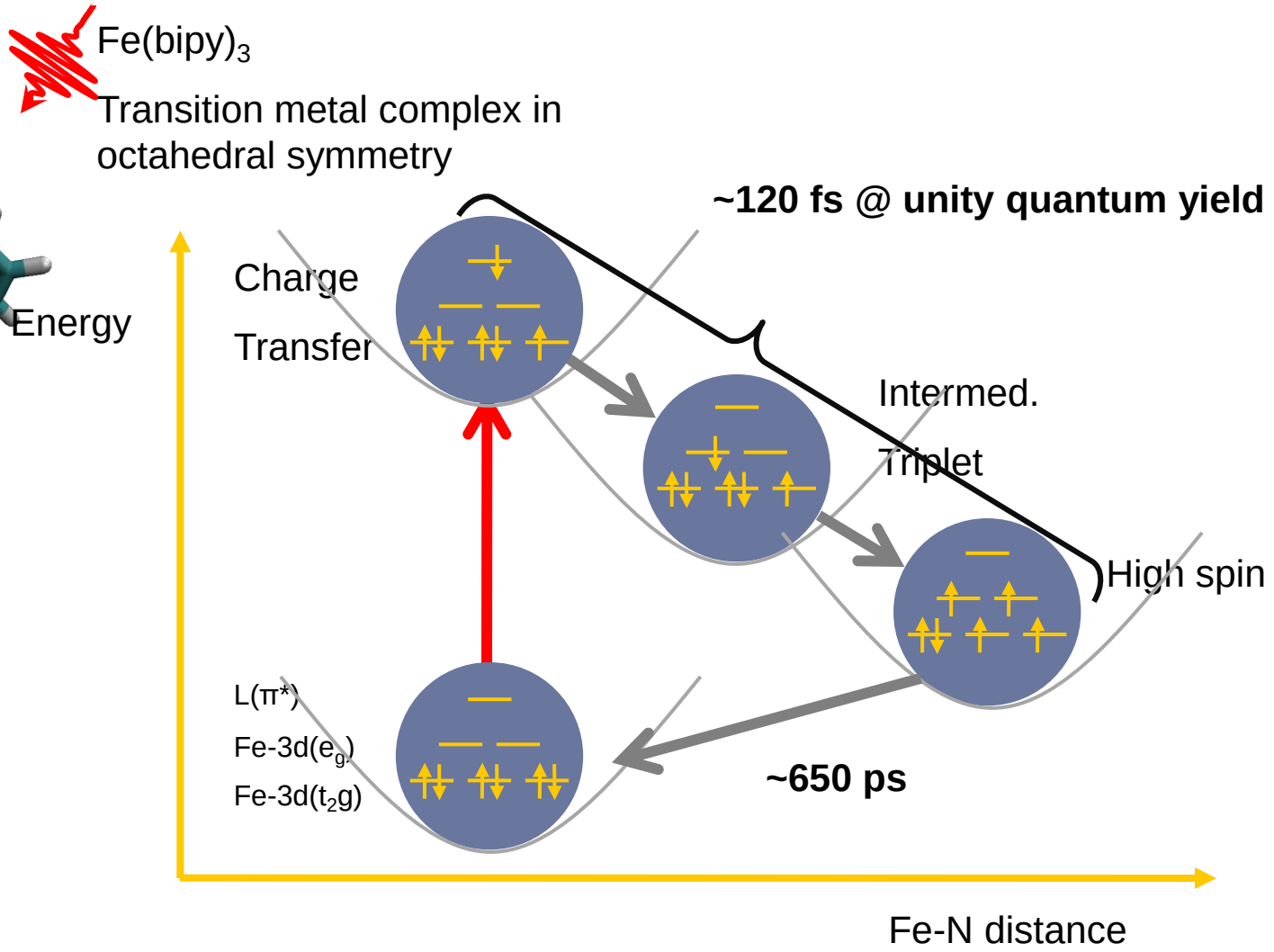




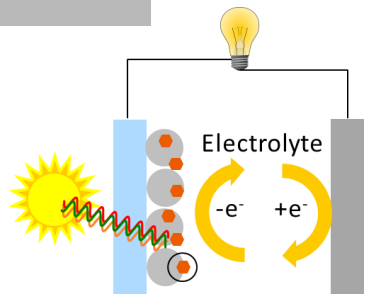


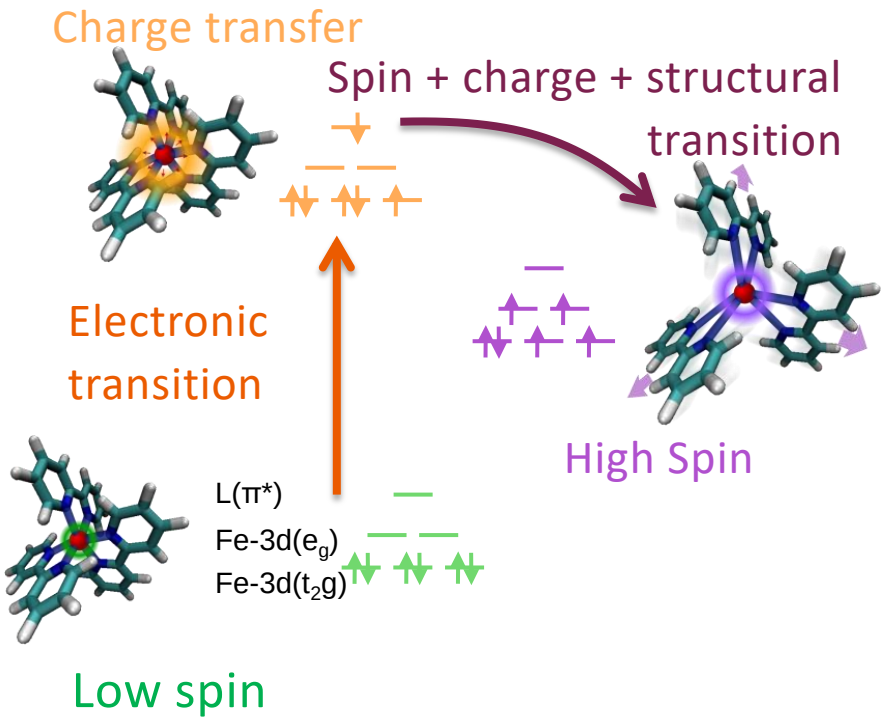
Spin transition molecular system

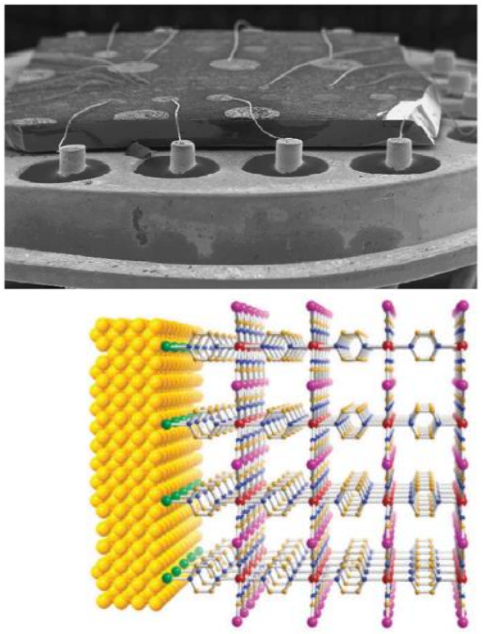




Summary "The Problem"







Bousseksou et al., Chem. Soc. Rev. 40, 3313, (2011).

- **Model system for**
  - **Fe-based solar cell materials**
  - **Molecular switches**
- **Transitions interact on femtosecond time scale**

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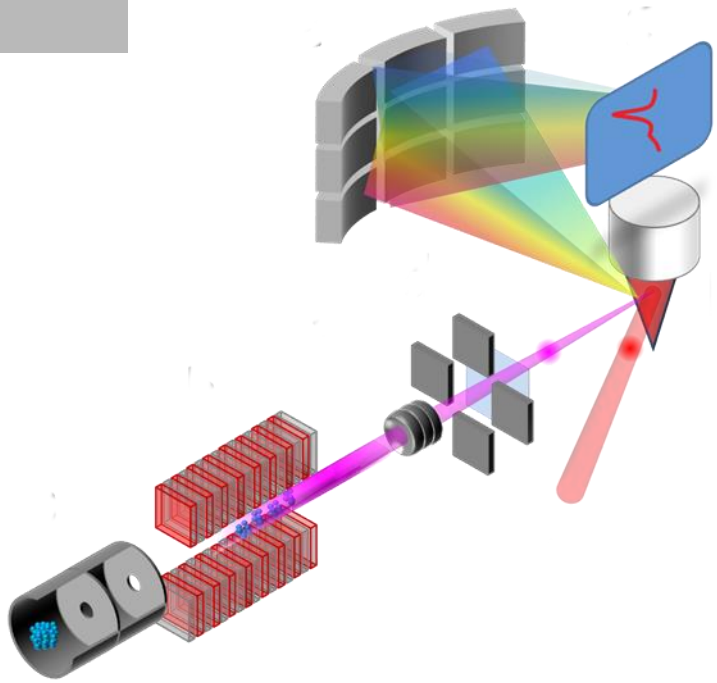
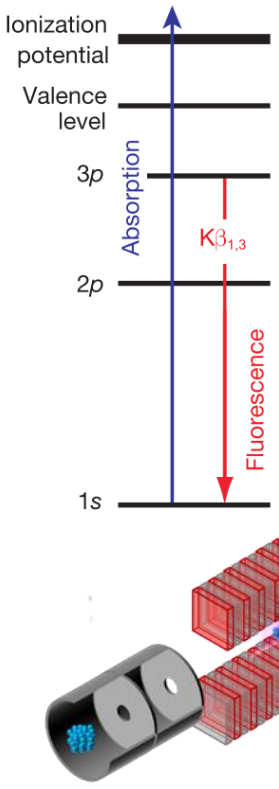
The Findings

Ultrafast Xray Emission Spectroscopy

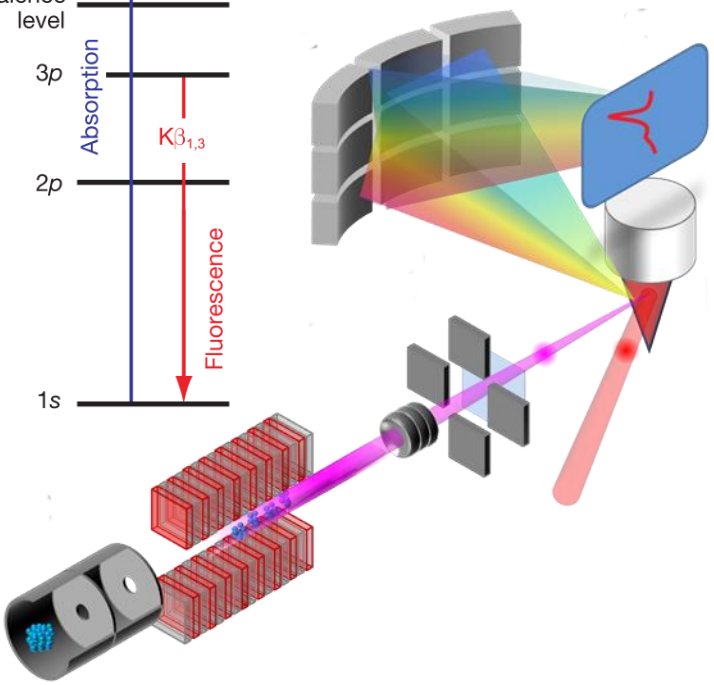
Dispersive spectrometer

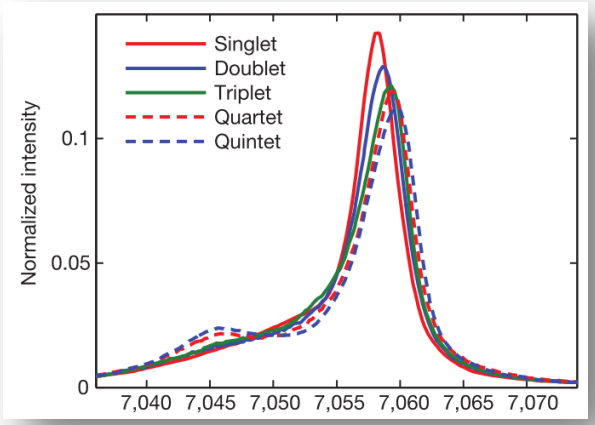


Transient species Fingerprinting



Dispersive spectrometer

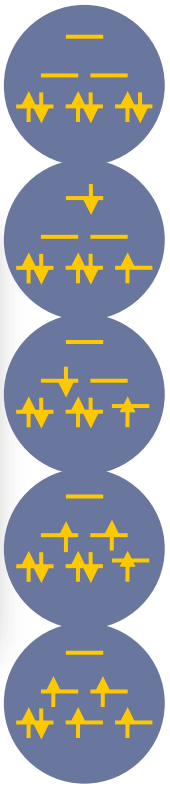


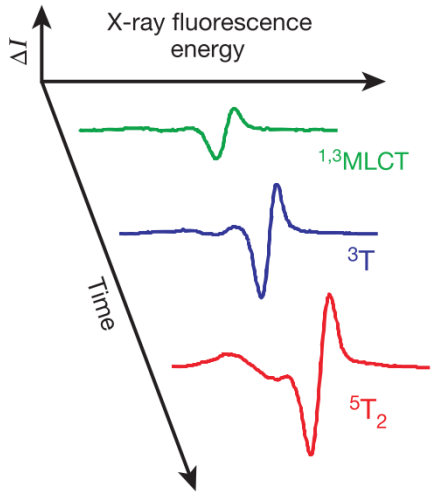


L(π*)

Fe-3d(e_g)

Fe-3d(t_2g)





= Doublet - Singlet

= Triplet - Singlet

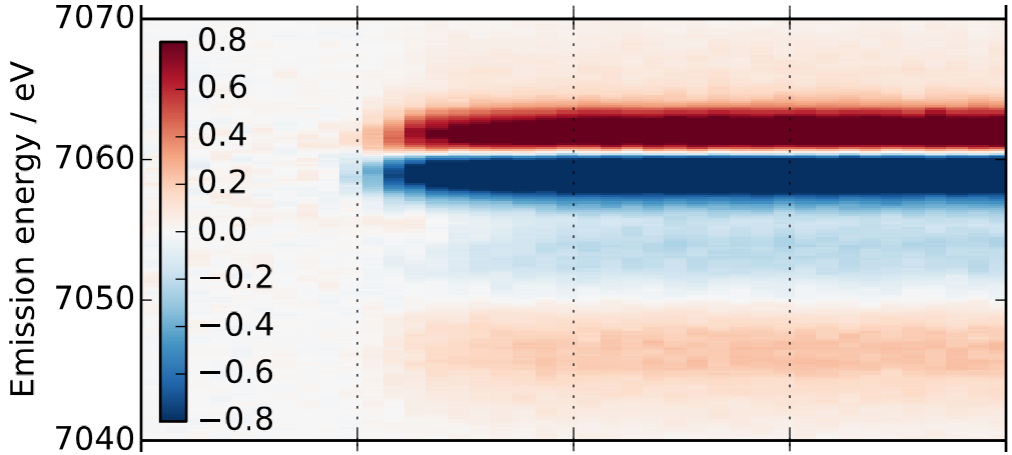
= Quintet - Singlet

Interpretation through Emission spectra from reference samples

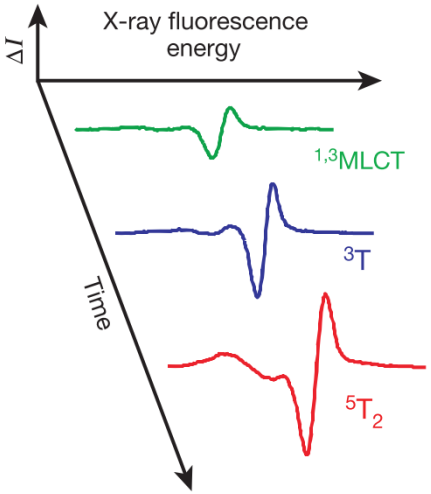
Zhang et al., Nature 509, 345–348 (2014)

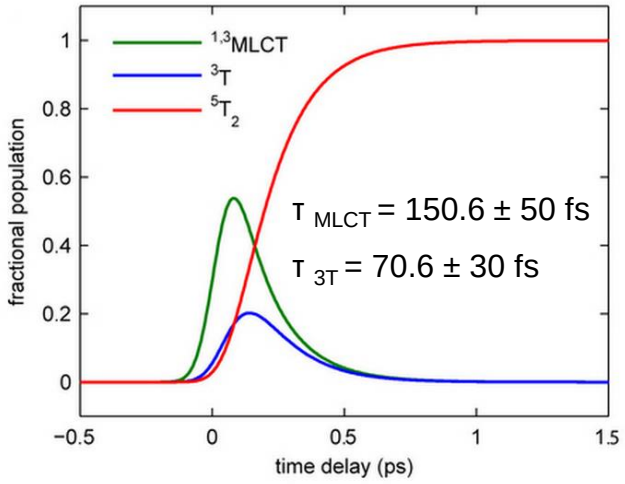
Global kinetic electronic state model

Reconstruction of Diff. signal by linear combination of reference differences in a kinetic model.



$$\Delta S(t) = a_{MLCT}(t)\,\Delta S_{MLCT} + a_{3T}(t)\,\Delta S_{3T} + (1 - a_{MLCT} - a_T)\,\Delta S_{5T2}$$



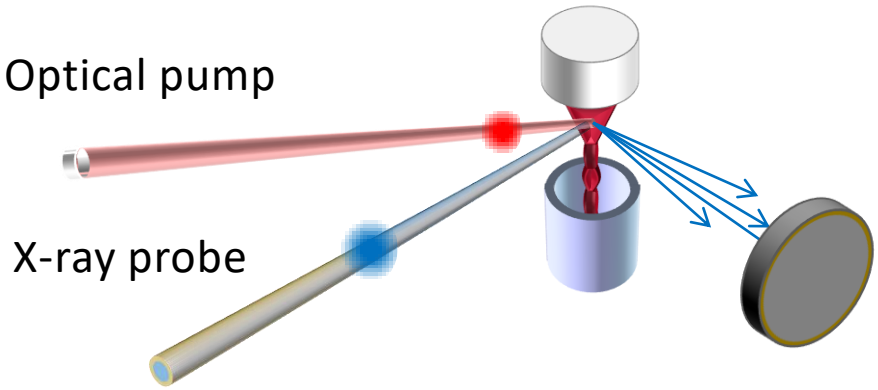


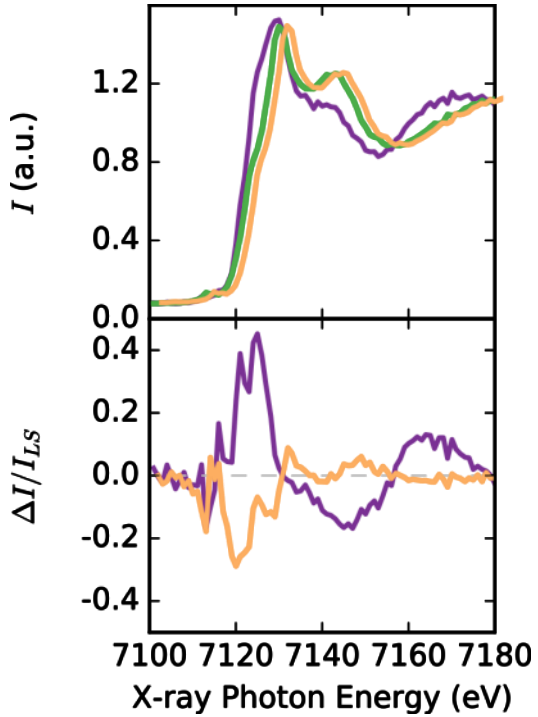
- **Triplet state can be observed**
- **Triplet state is relatively short lived**
  → small population

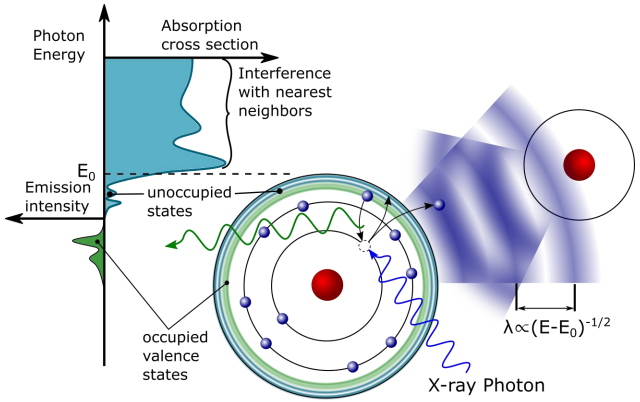
Zhang et al., Nature 509, 345–348 (2014)

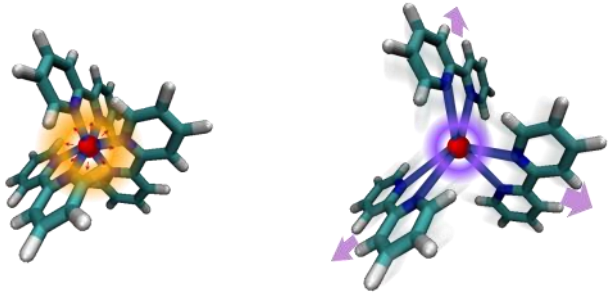
Ultrafast Xray Absorption Near-edge Structure

Absorption spectroscopy
in dilute Sample by total Emission









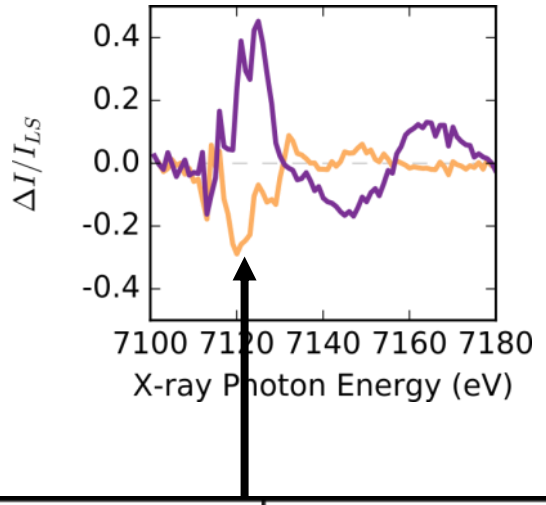
Charge transfer
= “3+” Ox. state

High Spin
= larger distance

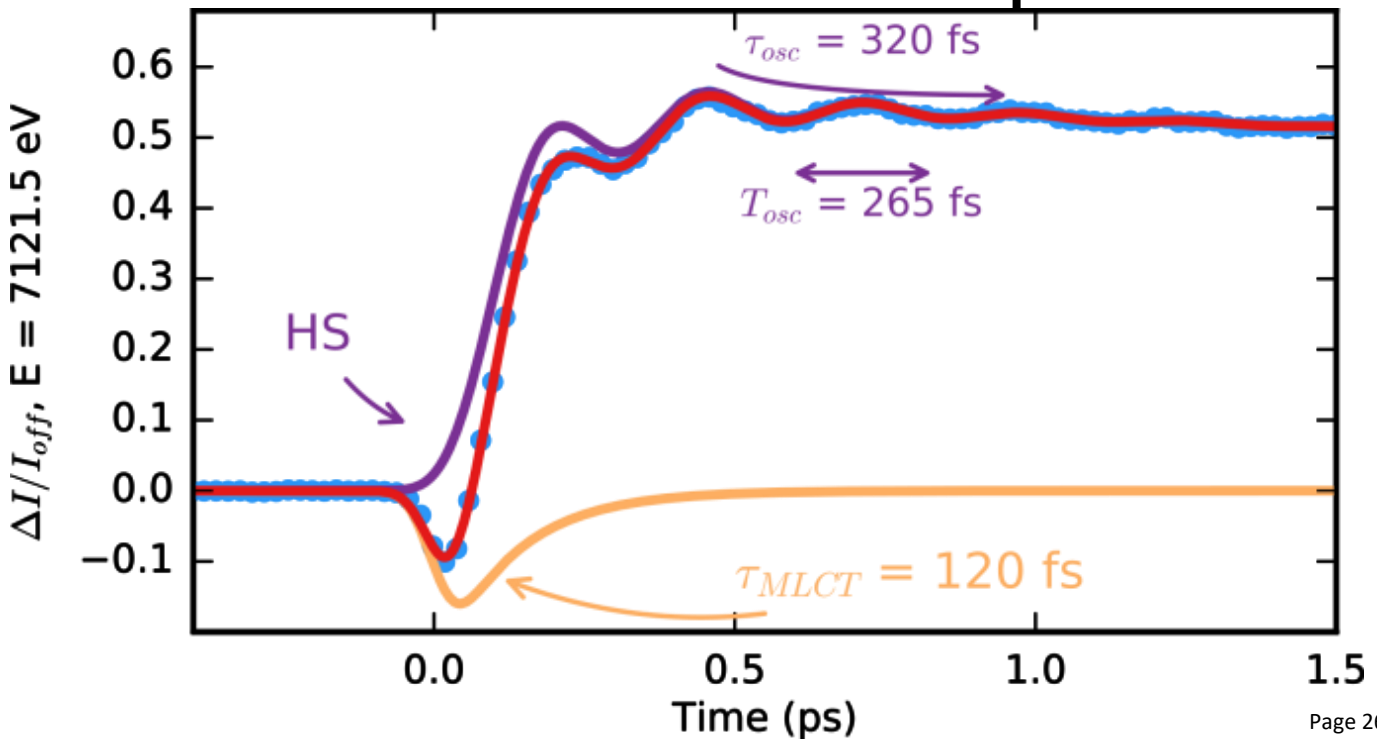
Time resolved XANES

Time resolved measurement at Absorption edge

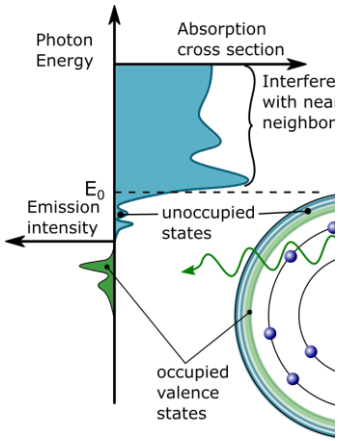
- Strong modulation in MLCT and HS state
- Opposite sign of both contributions

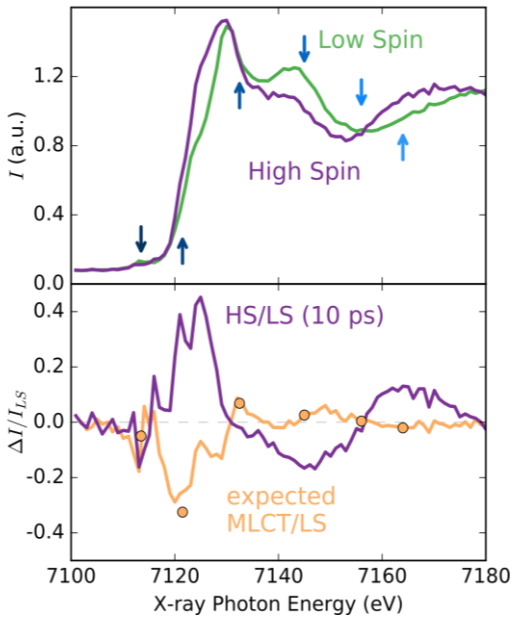


Time resolution
~ 25 fs RMS



XANES with improved sample jet

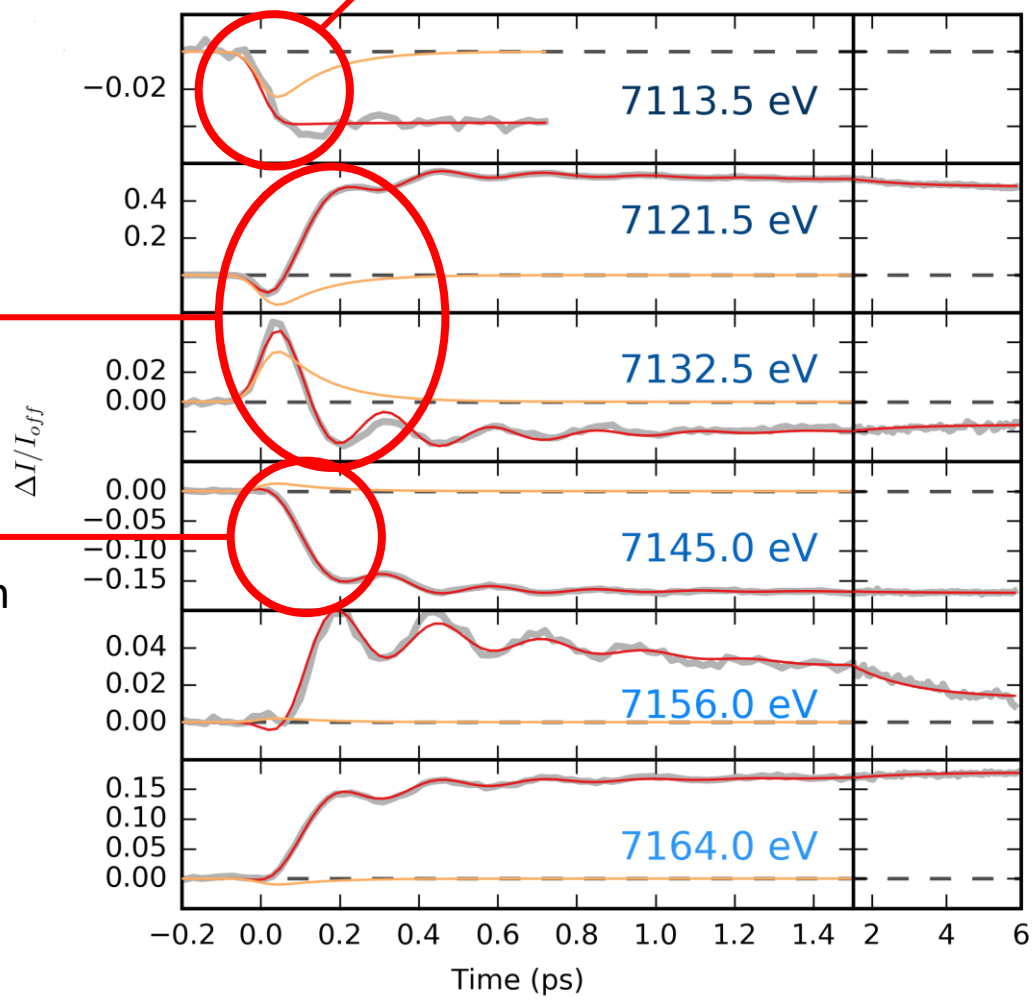




Fast pre-edge rise (~25 fs RMS)

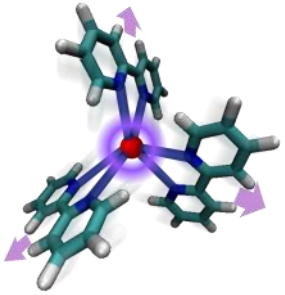
Mixed signals

Delayed Oscillation

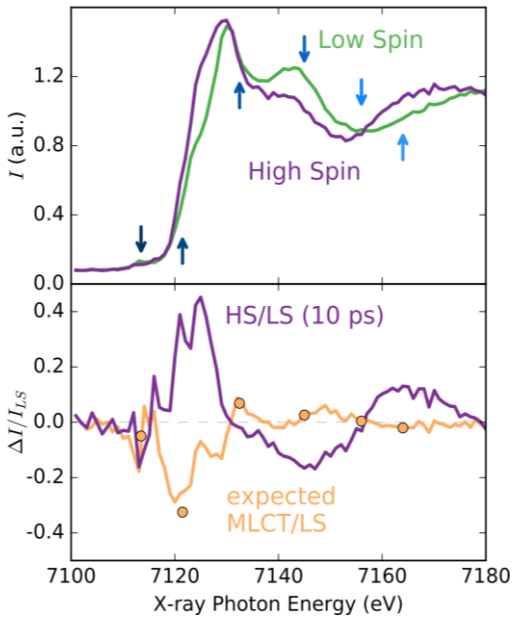


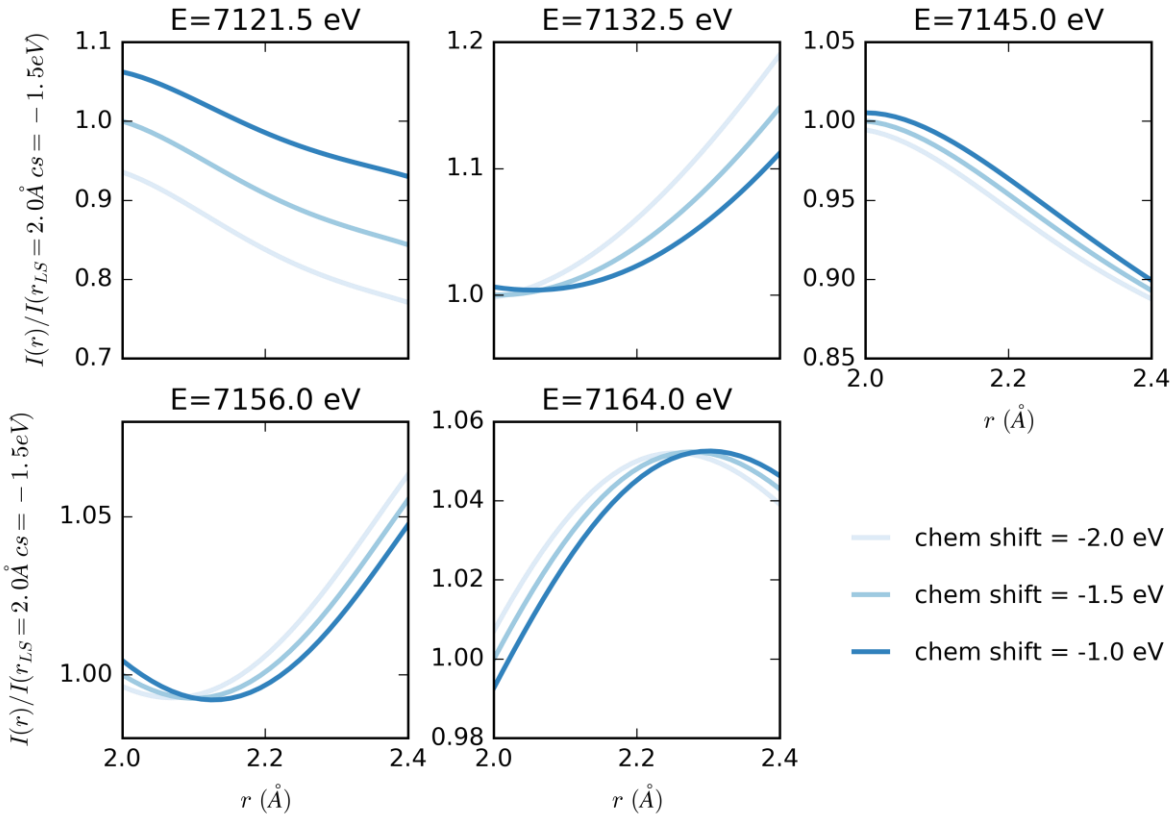
Lemke et al. **Nat. Comm**. 8, 15342 (2017)

Structural signal analysis



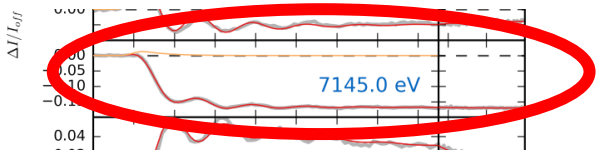
Simulation of Structural signal as fuction of Fe-N distance



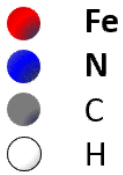


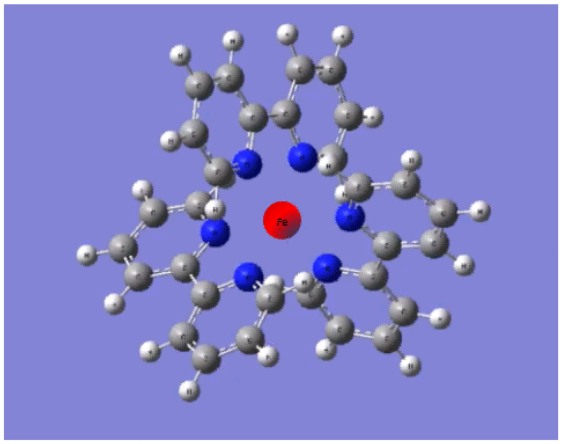
MXAN: Benfatto *et al.* J. Synchrotron Radiat. 10, 51–57 (2002).

Linear structure/XANES signal dependence



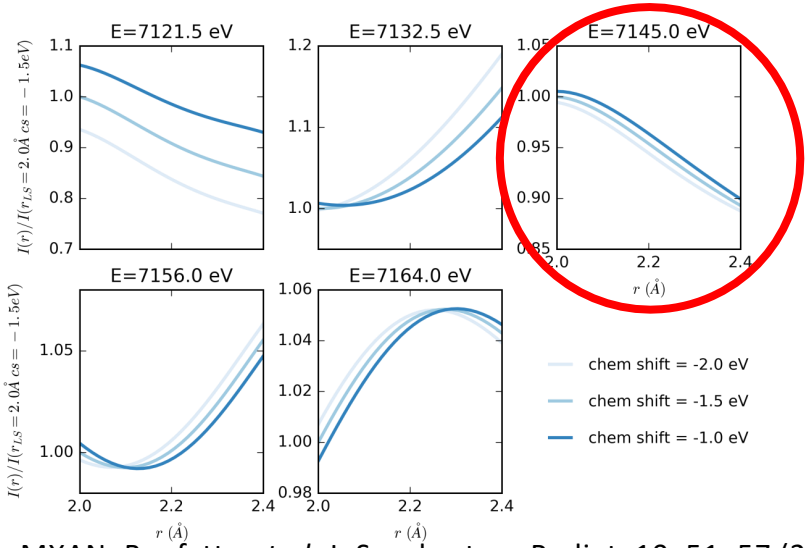
Breathing mode of $Fe(bpy)_3^{2+}$ at 124 cm^{-1}:
in-phase stretching of the 6 Fe-N bonds, with almost rigid bpy ligands





Direct average structural information at linear signal dependence

Structural signal as fuction of Fe-N distance



MXAN: Benfatto *et al.* J. Synchrotron Radiat. 10, 51–57 (2002).

Molecular vibration frequencies calculations were carried out with Gaussian09

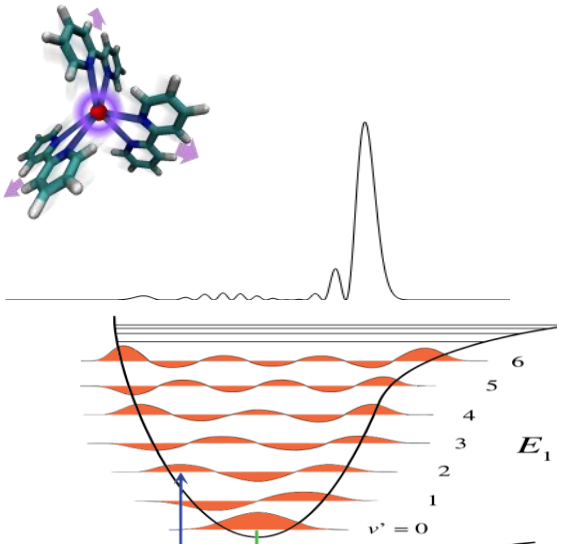
Oscillation: 126(3) cm^{-1}

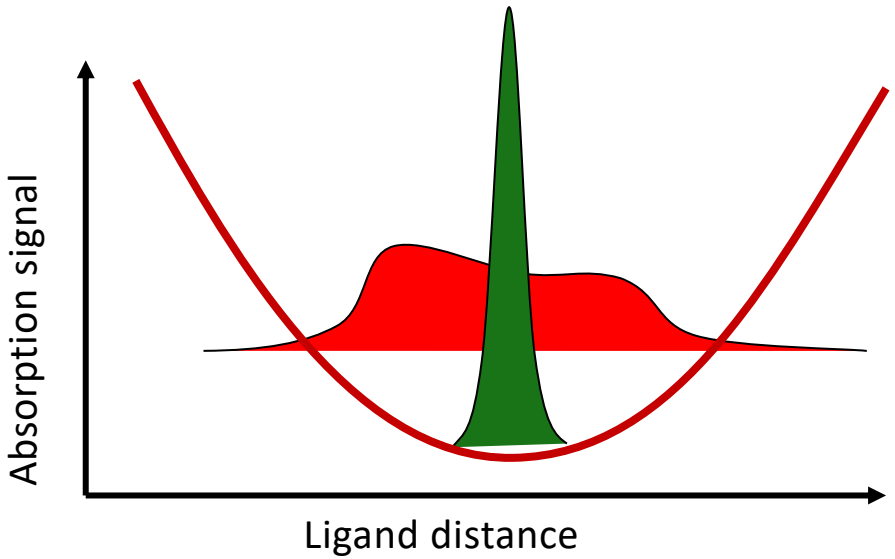
Breathing mode, from DFT calculations

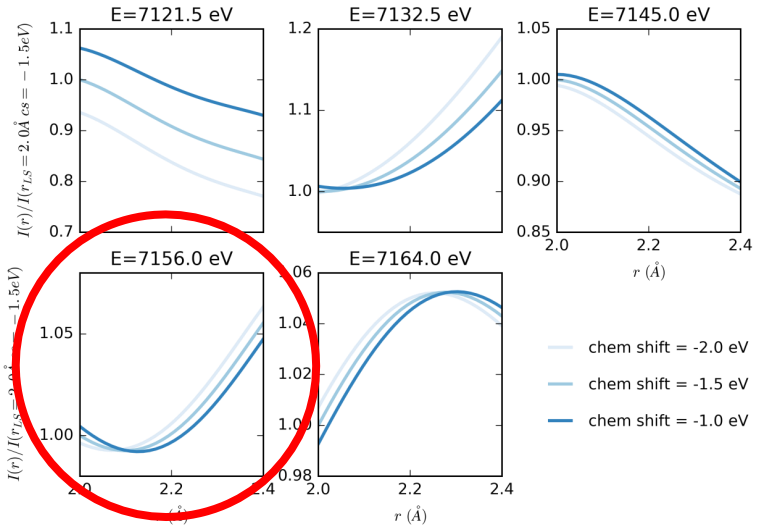
124.4 cm^{-1} / 121.4 cm^{-1}

Sousa *et al.* Chem. - A Eur. J. 19, 17541–17551 (2013).

Nonlinear structure/XANES signal dep.



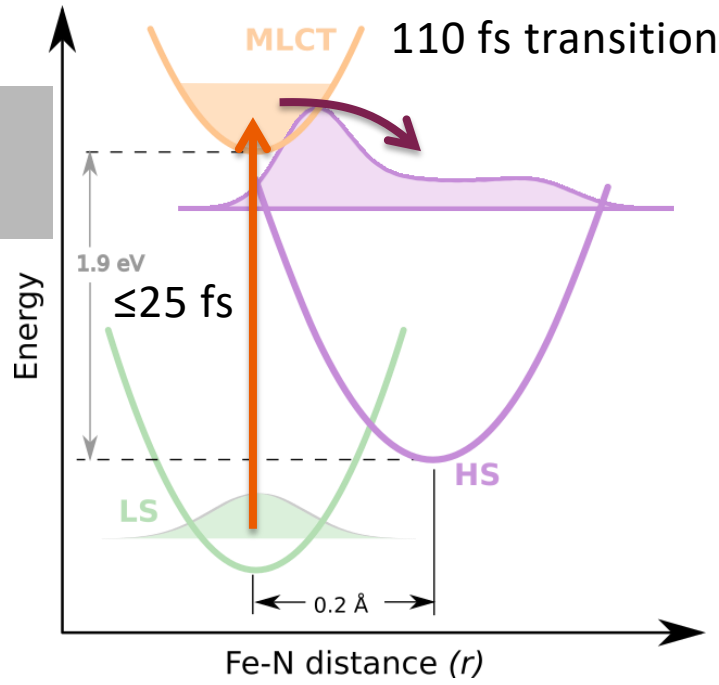


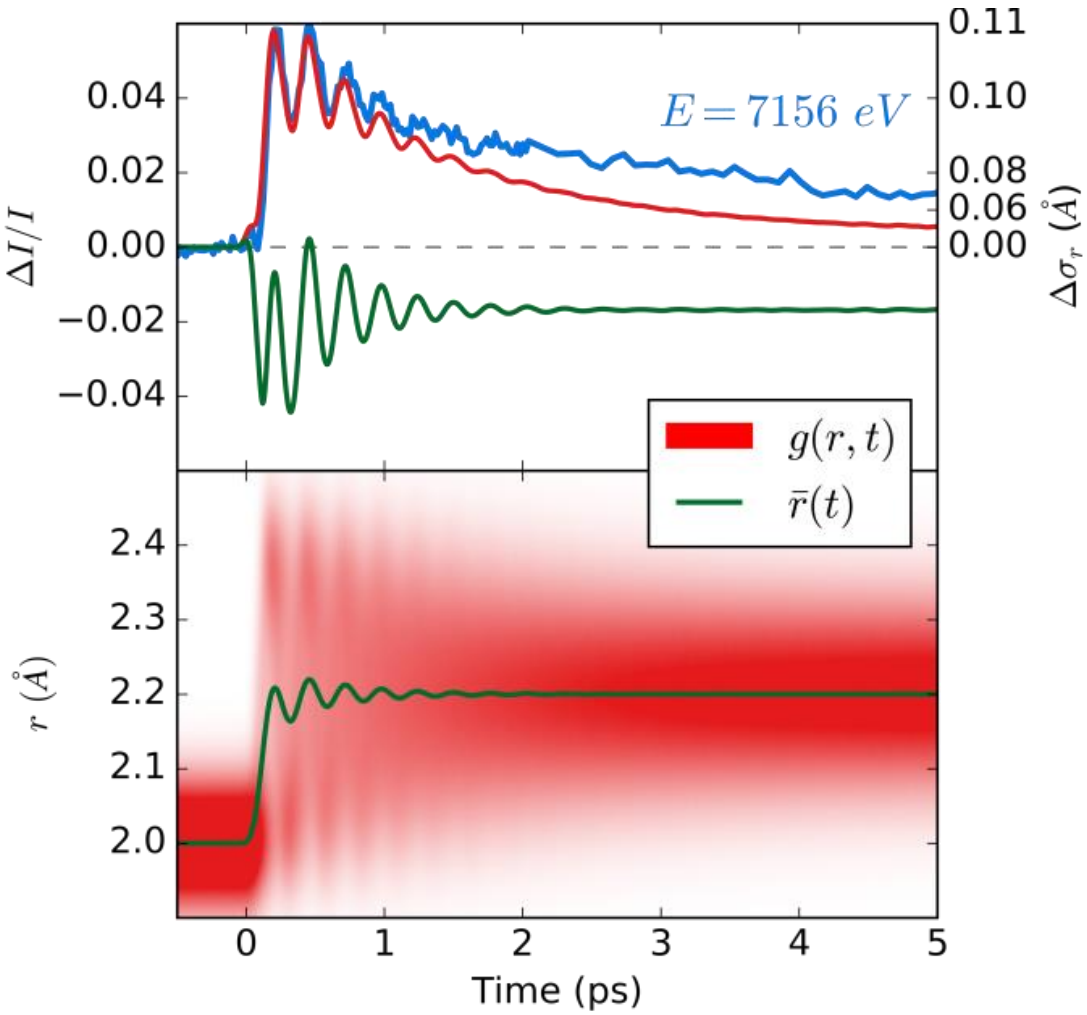


Non-linear signal dependence

Sensitivity to ensemble distribution

Dispersion of coherent wave packet



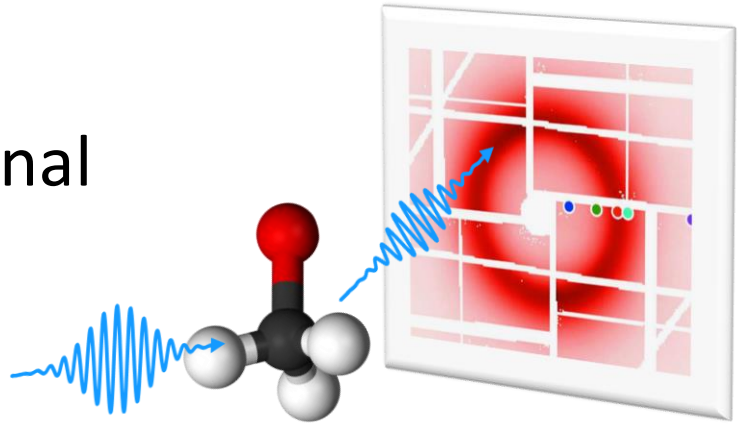


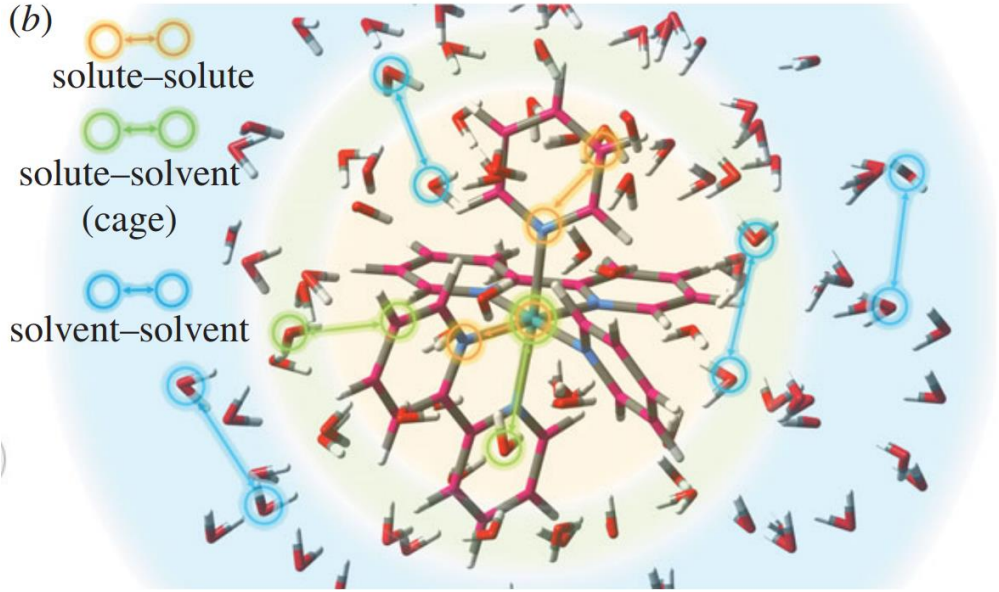
- **Transient measurement of ensemble distribution width**
- **Dispersion of coherence faster (~320 fs) than narrowing of distribution (1.6 ps) due to vibrational cooling**

Lemke et al. **Nat. Comm**. 8, 15342 (2017)

Solution X-ray Diffuse Scattering

Separation of scattering signal



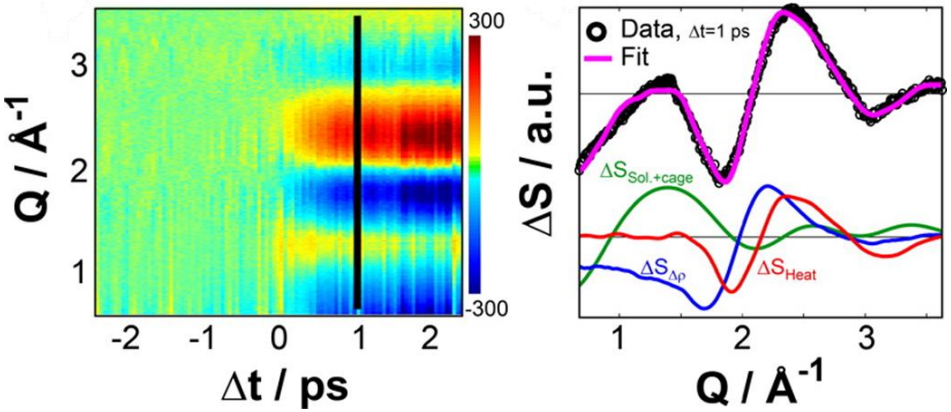


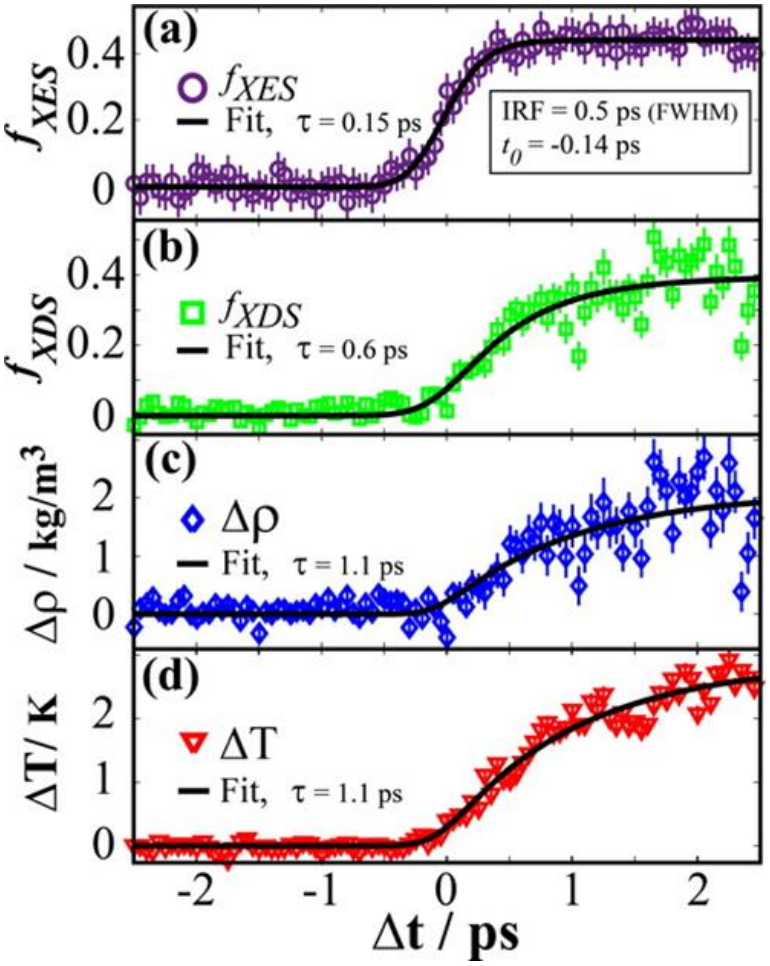
$$\Delta I(q,t) = \Delta I_{\text{solute}}(q,t) + \Delta I_{\text{cage}}(q,t) + \Delta I_{\text{solvent}}(q,t)$$

$$\Delta I_{solvent}(q,t) = \left(\frac{\partial I}{\partial T}\right)_{\rho} \Delta T(t) + \left(\frac{\partial I}{\partial \rho}\right)_{T} \Delta\rho(t)$$

Energy transfer to Solvent

$$\Delta I_{solvent}(q,t) = \left(\frac{\partial I}{\partial T}\right)_{\rho} \Delta T(t) + \left(\frac{\partial I}{\partial \rho}\right)_{T} \Delta\rho(t)$$

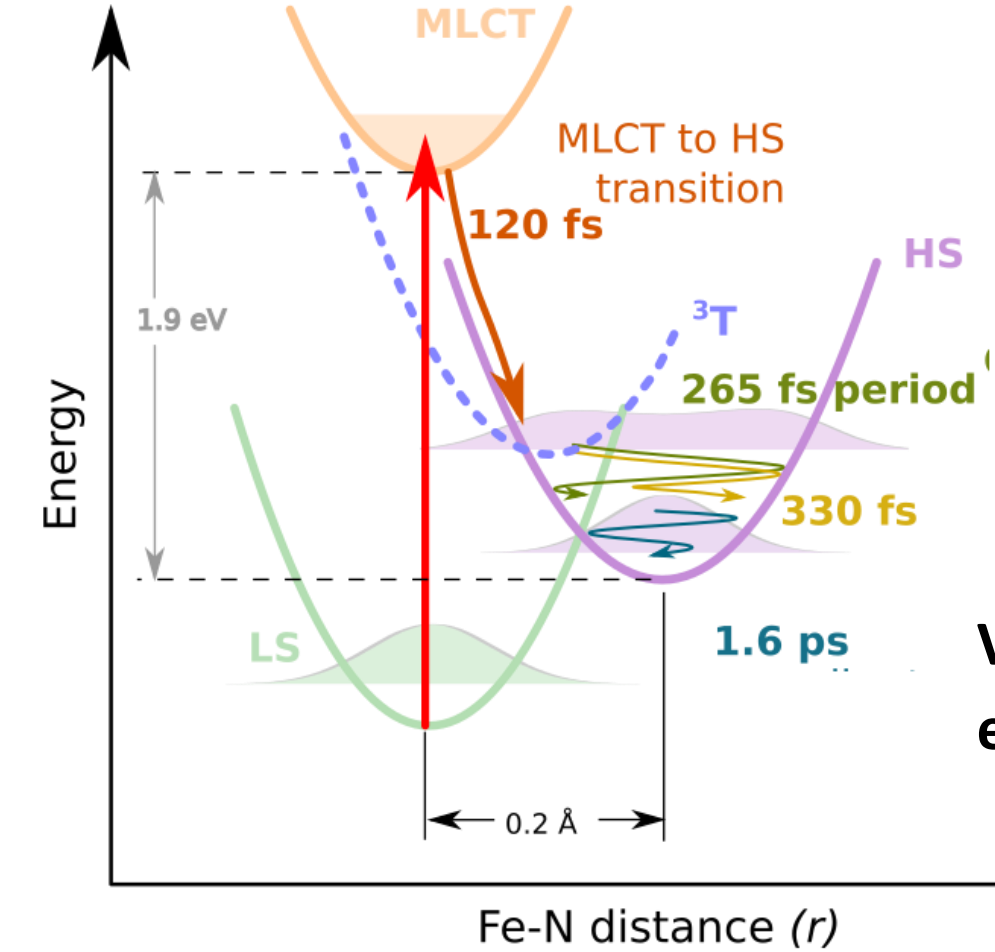




Timescale of solvent heating fits vibrational cooling time constant

Haldrup et al. 2016, J. Phys. Chem. B

Summary molecular spin-transition



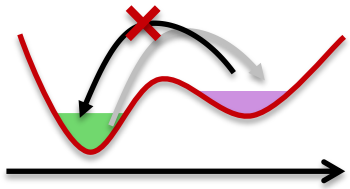
Lifetime MLCT state

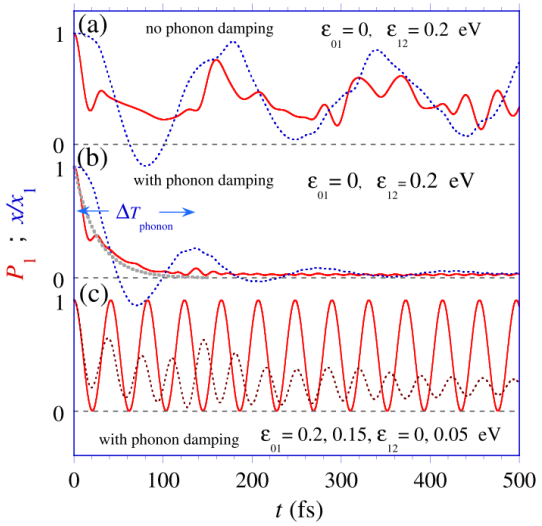
Short population of Triple state

Dephasing, intramolecular coupling

Vibrational cooling with environment

Quantum efficiency





High quantum efficiency can be explained
by strong coupling to intramolecular vibrations

van Veenendaal *et al.* PRL 104, 67401 (2010).

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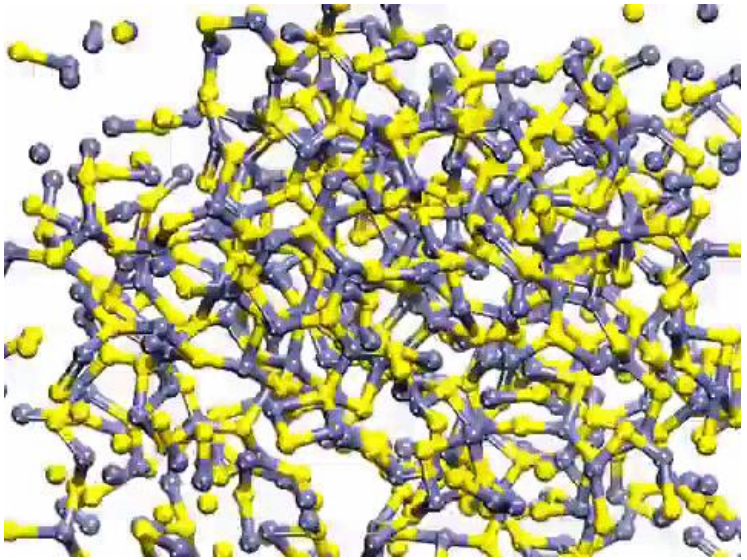
Solid state transitions

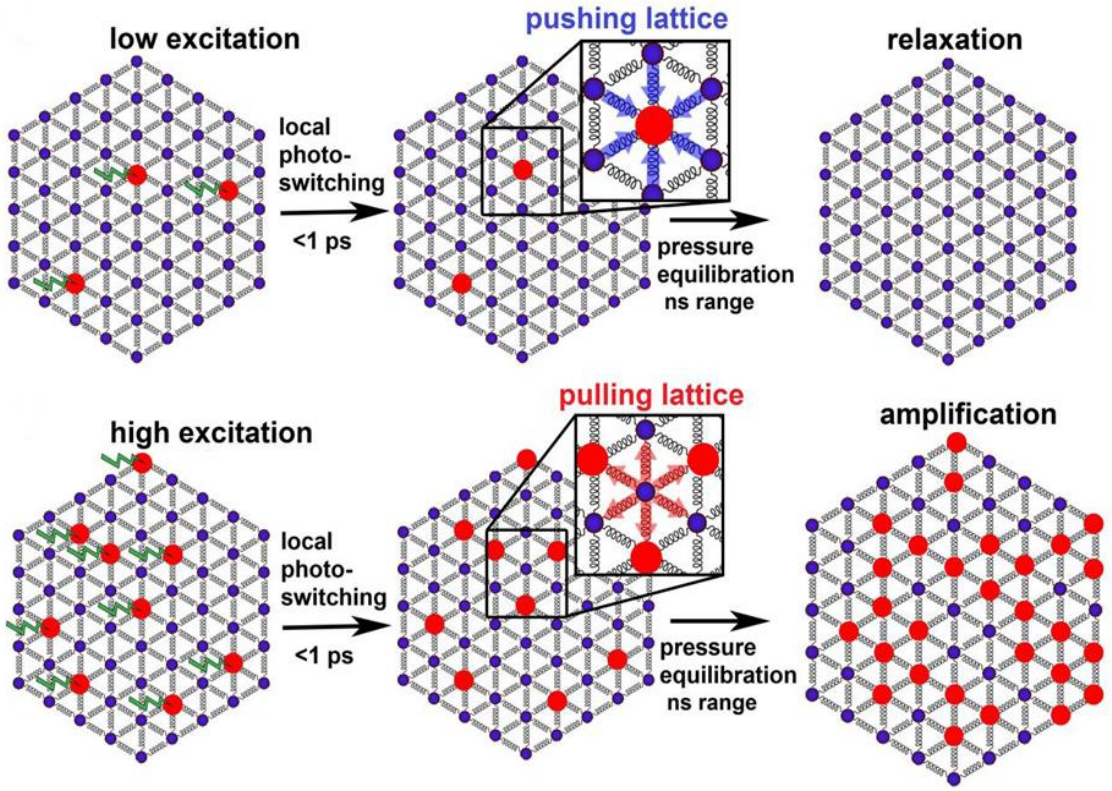


Spin transition in solid states

In solids, neighbor excitations can efficiently excert

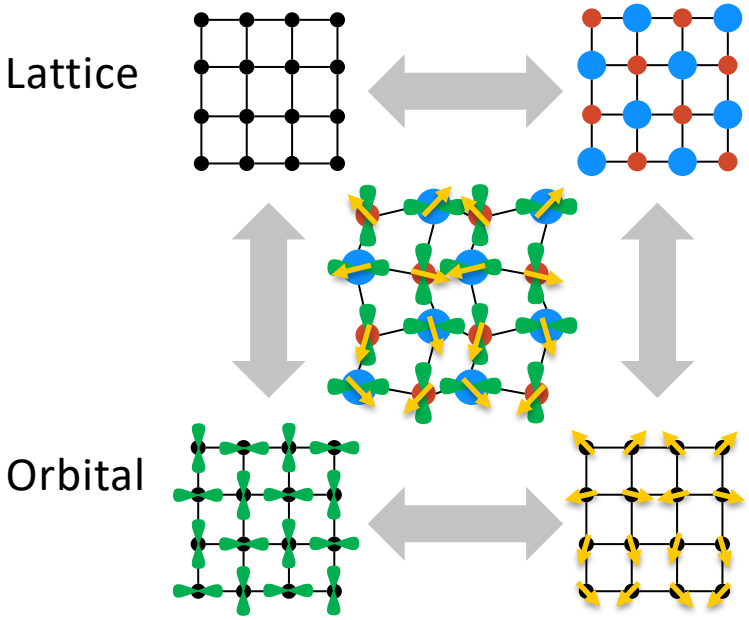
- Pressure/stress
- Electric field/polarisation
- Magnetic moment/spin

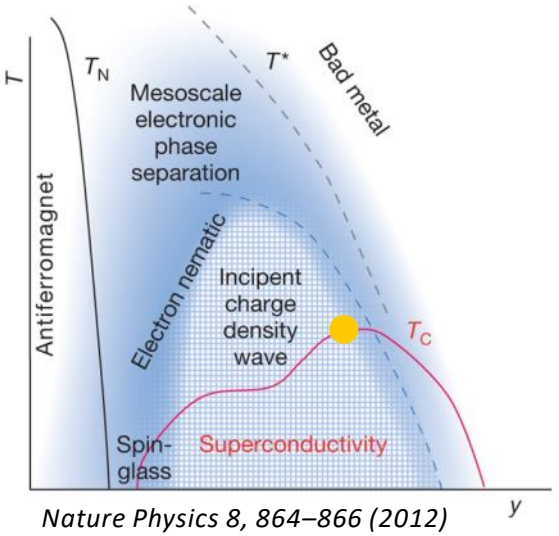
Higher switching efficiency by collaborative effect



R. Bertoni et al, Nature Materials 15, 606 (2016)

Ultrafast information in correlated systems

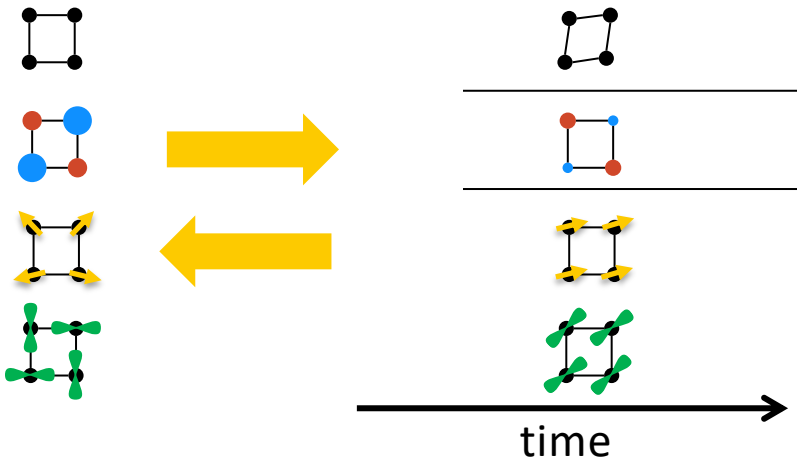




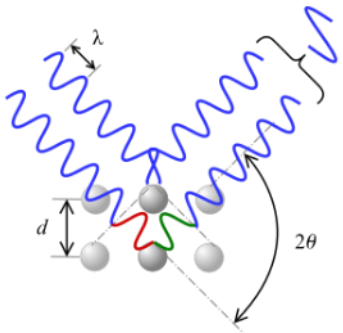
Nature Physics 8, 864–866 (2012)

Temporal separation

→ Causality between degrees of freedom



Selective probe
Bragg diffraction
Resonant diffraction
+ Polarisation transfer



Resonant X-ray Diffraction

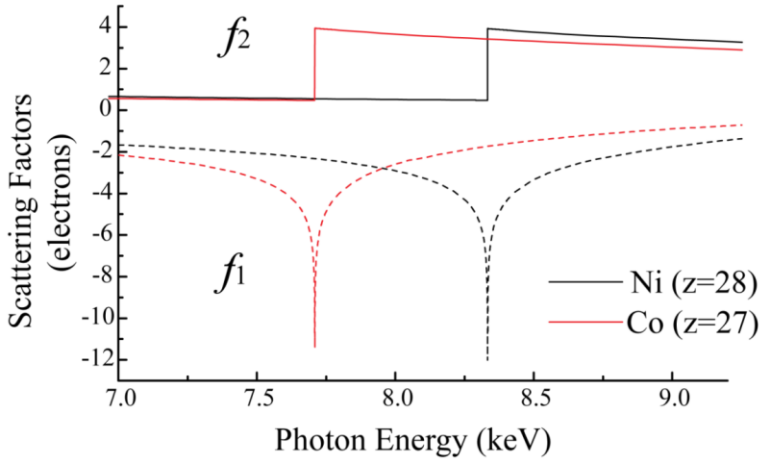
- Orbital and magnetic contrast by Polarisation transfer

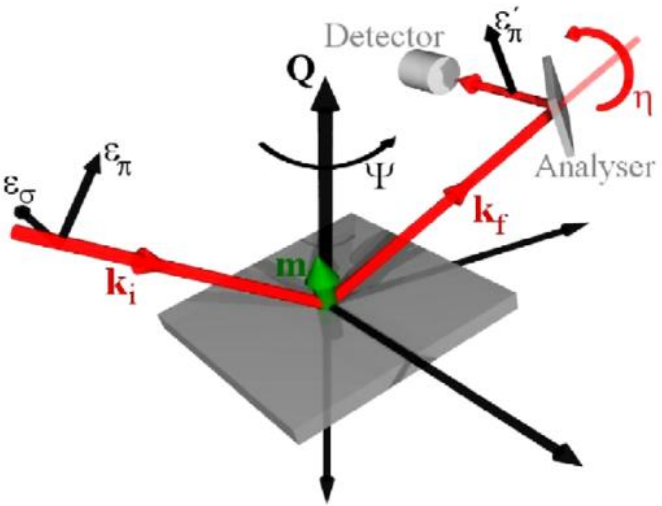
$$I(E) \propto |F_{hkl}|^2 \Rightarrow F_{hkl} = \sum_i x_i f_i(Q,E) \cdot e^{2\pi i(hx+ky+lz)}$$

element selectivity

Bragg (h,k,l) site selectivity

$$f = f_o(\bar{Q}) + f_1(E) + if_2(E)$$

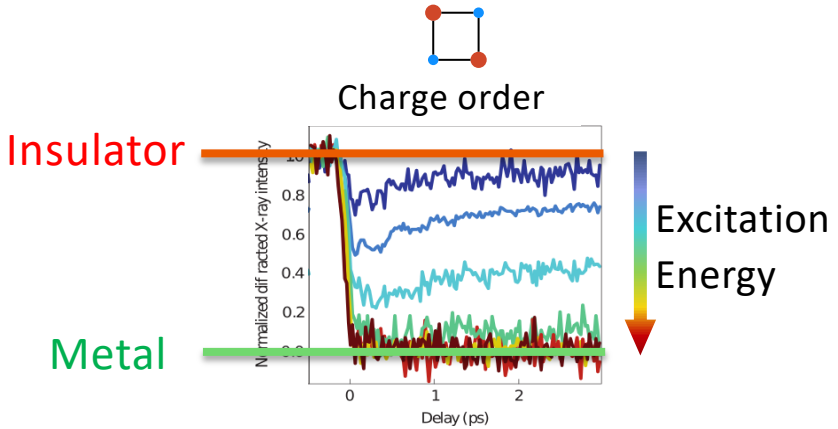




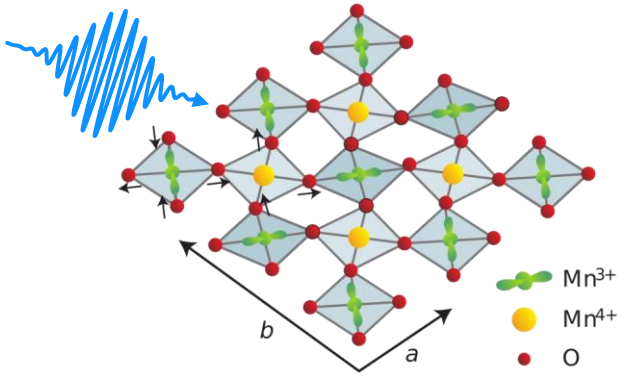
Selective ultrafast probe of degrees of freedom

Insulator to metal transition in manganite

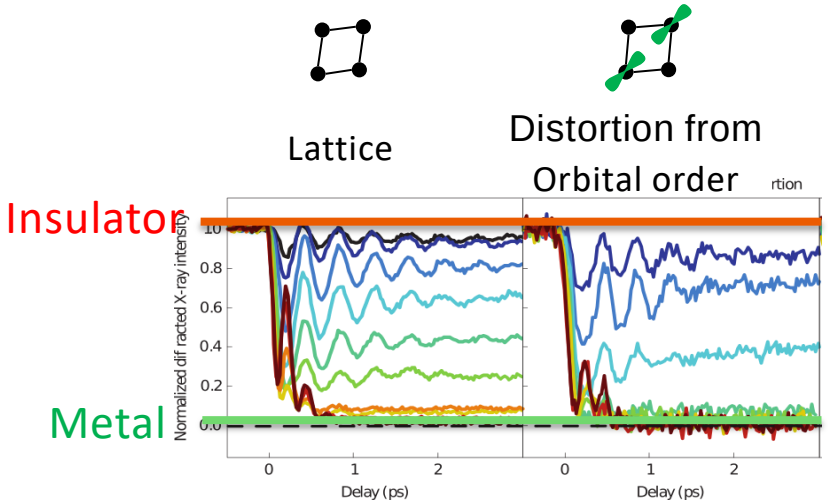
- Separation of charge from lattice order by resonant diffraction
- Destruction of order → Metal
- Lattice motion *follows* destruction of charge order



Excitation

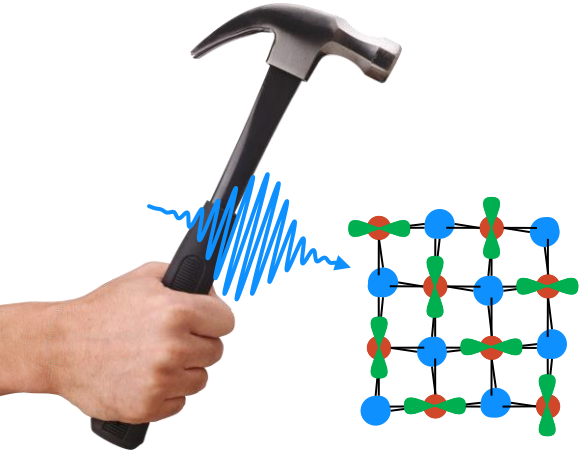


$Pr_{0.5}Ca_{0.5}MnO_3$



Beaud et al. Nat. Mater. 13, 923–927 (2014).

Selective excitation

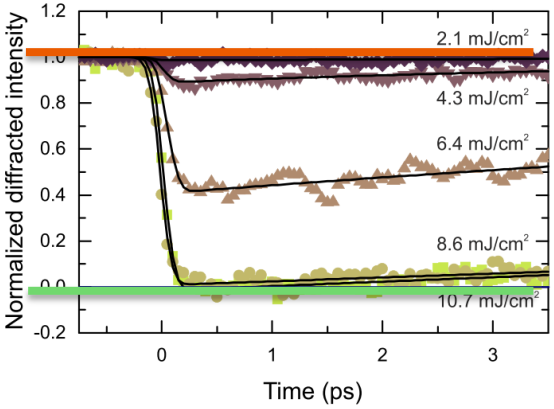


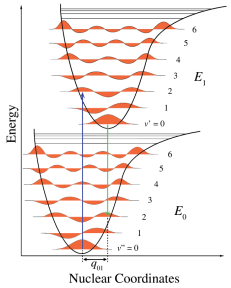
Resonant excitation of lattice (IR-active phonons)

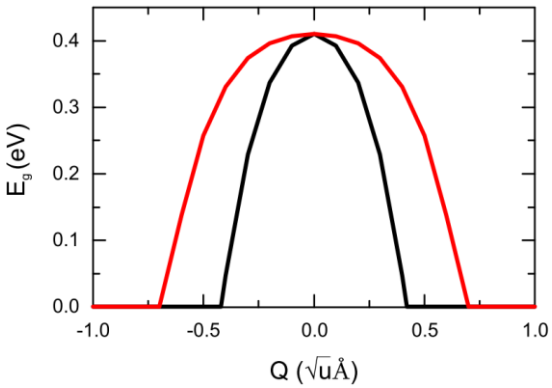
- Charge order destruction *follows lattice motion*
- Material band gap can be closed Phonons.

Insulator

Metal







Esposito et al. Phys. Rev. Lett. (2017)

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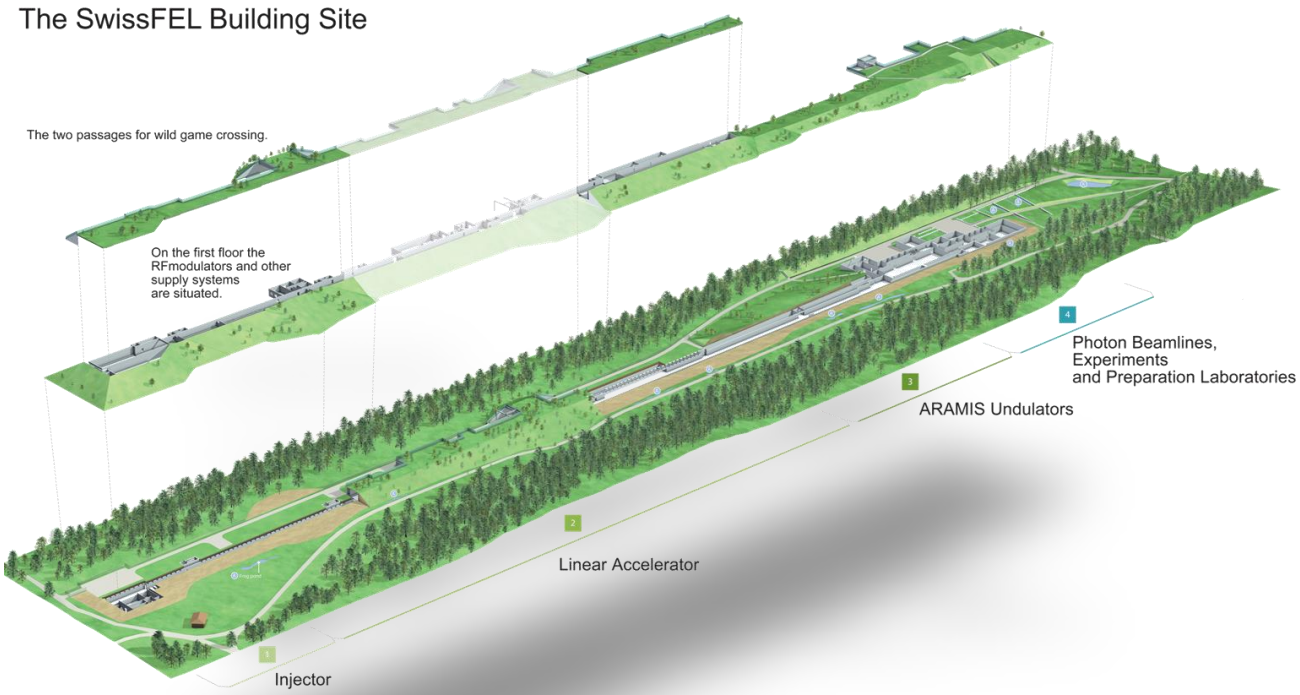
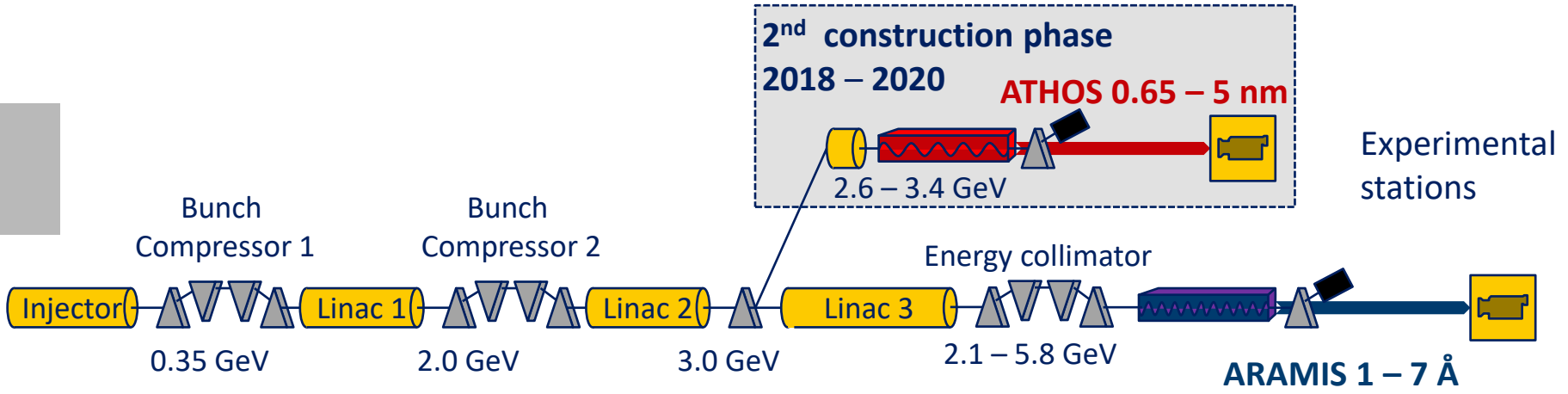
SwissFEL



SwissFEL entrance

SwissFEL machine



Main parameters	
Wavelength:	**1 Å – 5 nm**
Photon energy:	**0.24 – 12.4 keV**
Pulse energy:	**1 mJ**
Pulse duration:	**1 – 20 fs**
e^- Energy	5.8 GeV
e^- Bunch charge	10 – 200 pC
Repetition rate	**100 Hz**

ARAMIS

- Hard x-ray FEL, **λ = 1 – 7 Å (1.8 – 12.4 keV)**
- Special modes thanks to Energy collimator
  - Attosecond mode, 100 as FWHM (no pedestal), few ten uJ
  - pulse chirp with sign control
  - new two color tune (range -20 – 20 fs)
- Linear polarization, variable gap undulators
  - High k → "hot" @ 4 – 8 keV

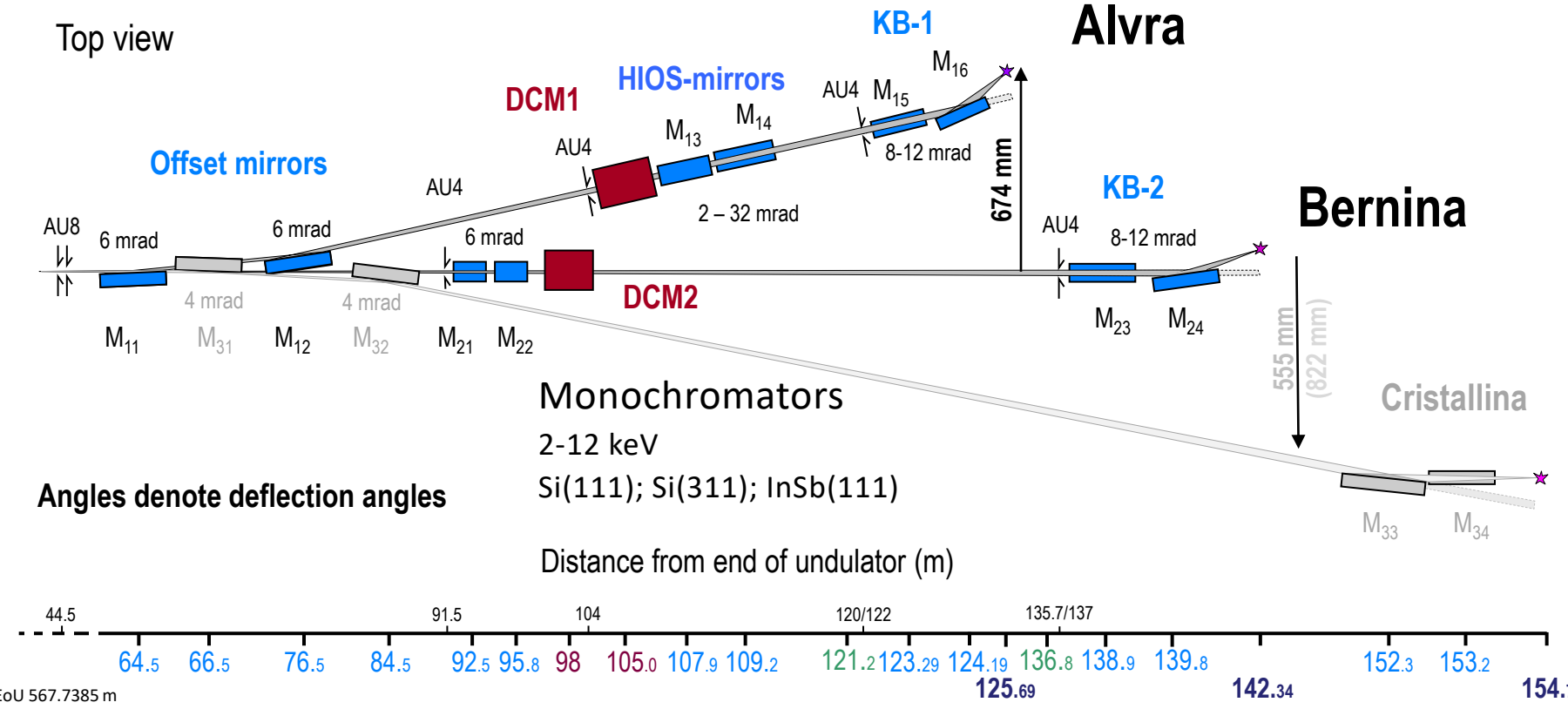
ATHOS

- Soft x-ray FEL, λ = 0.65 – 5 nm (240 – 1'930 eV)
- Variable polarization Apple X undulators
- Operation modes: SASE (CHIC)
  10x smaller BW, L_{sat} 80%

X-ray optics layout Aramis

R. Follath, U. Flechsig, U. Wagner

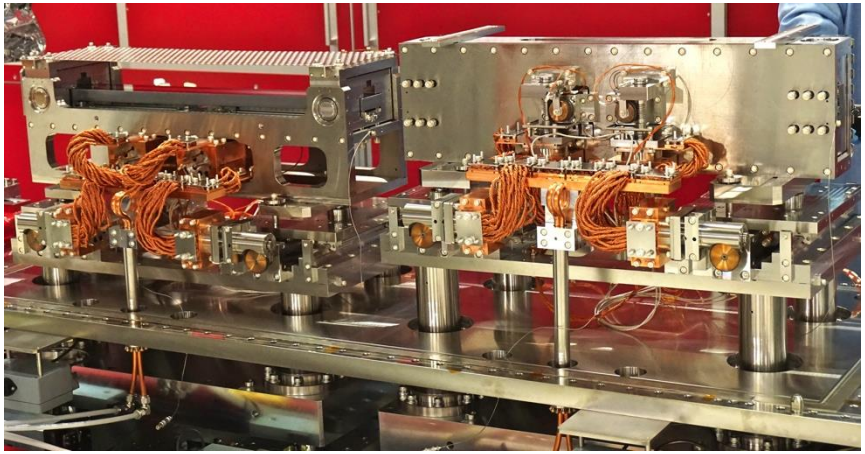
- Photon “switchyard” fanout to different instruments
- Steering/offset mirrors and Monochromators in optics hutch
- KB mirror focusing in experimental hutches



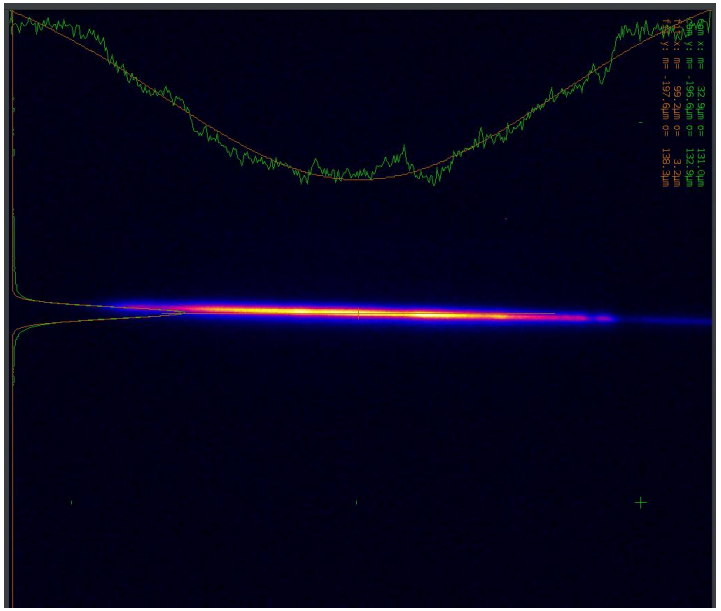
Commissioning: X-ray focusing optics

Focus on sample position of Bernina

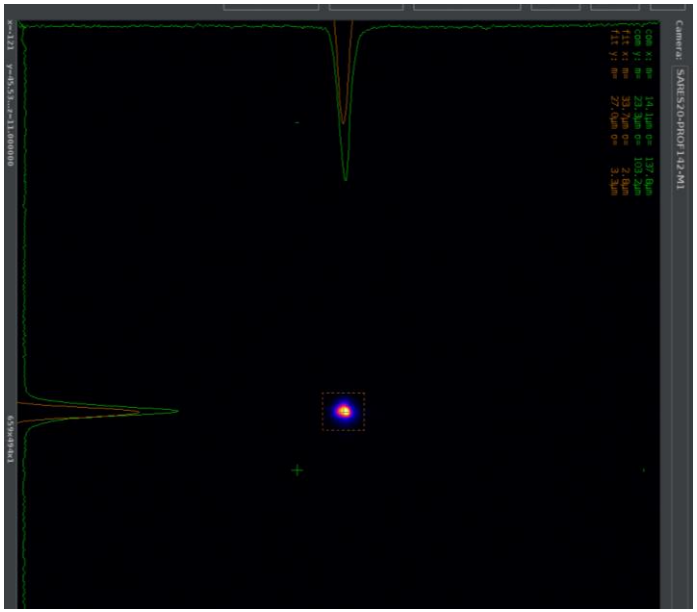
- KB from Toyama with JTEC mirrors
- Taken with X-ray eye
- Focal distance 2.5 m
- Pink beam 2200 eV



Line focus
140 x 3 µm^2 rms (hor x vert)

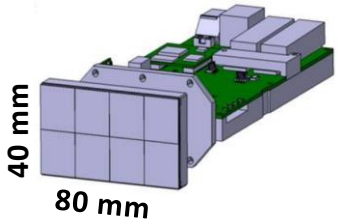


Point focus
3 x 3 µm^2 rms (hor x vert)

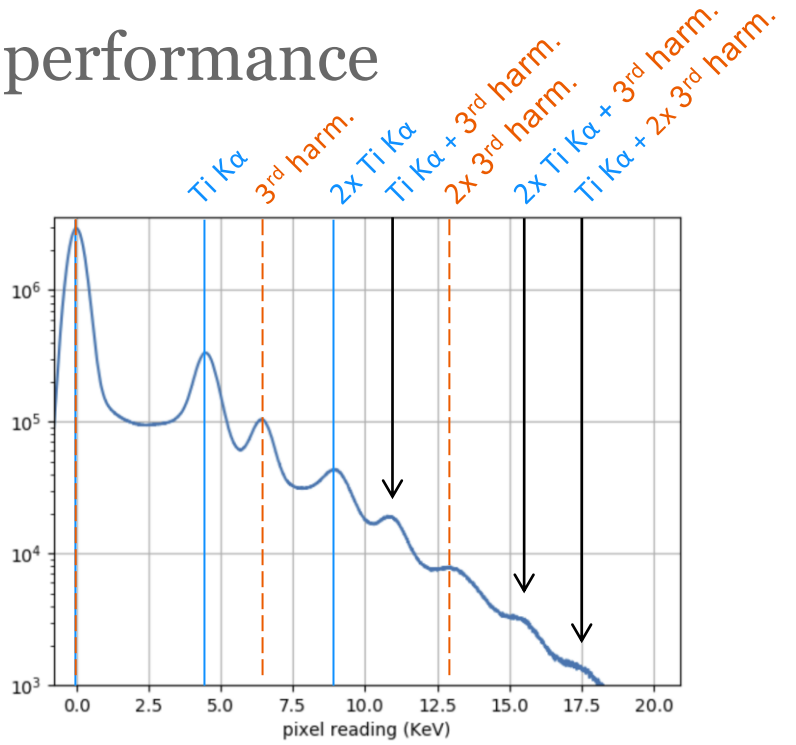


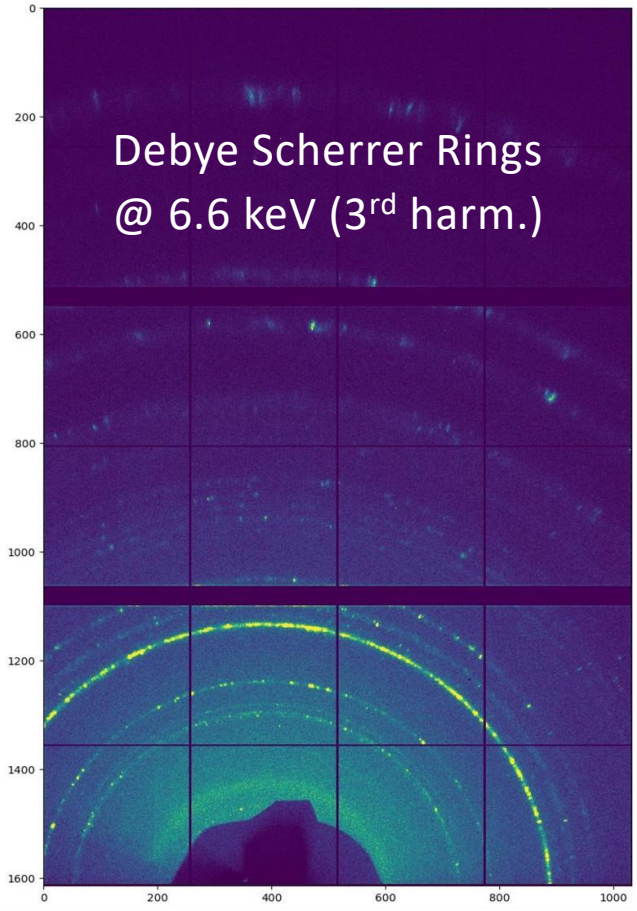
Roman

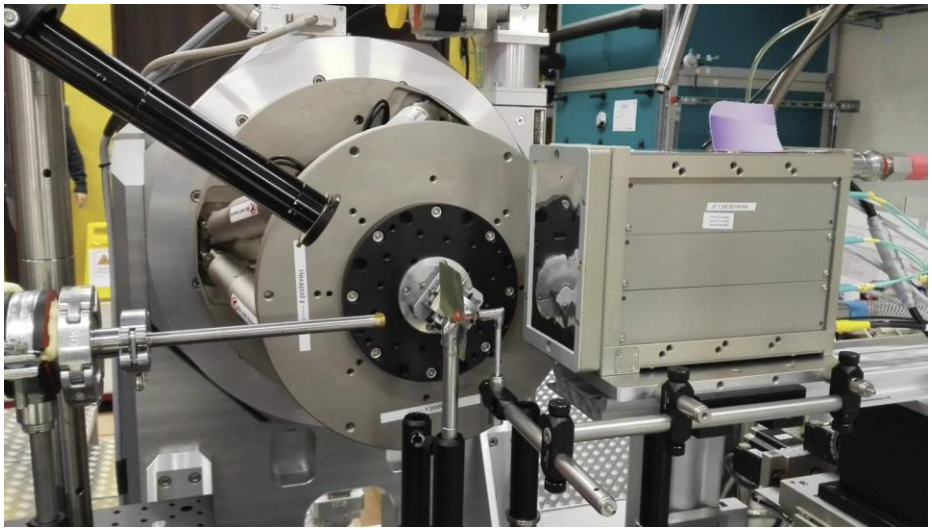
Jungfrau area detector performance



- 10^4 12 keV phot. dyn. range (gain switching)
- 75 µm pixel size
- Up to 2.4 kHz readout



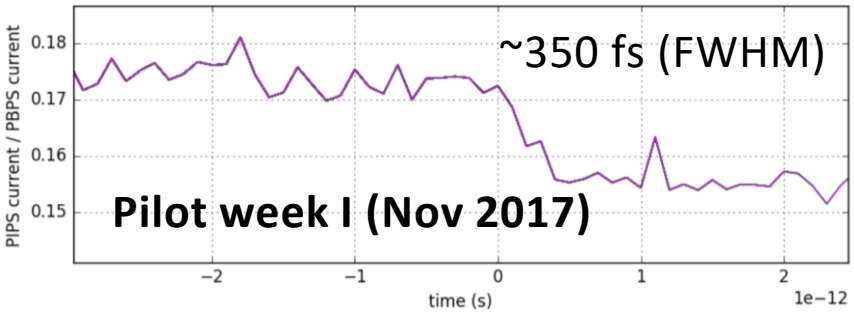


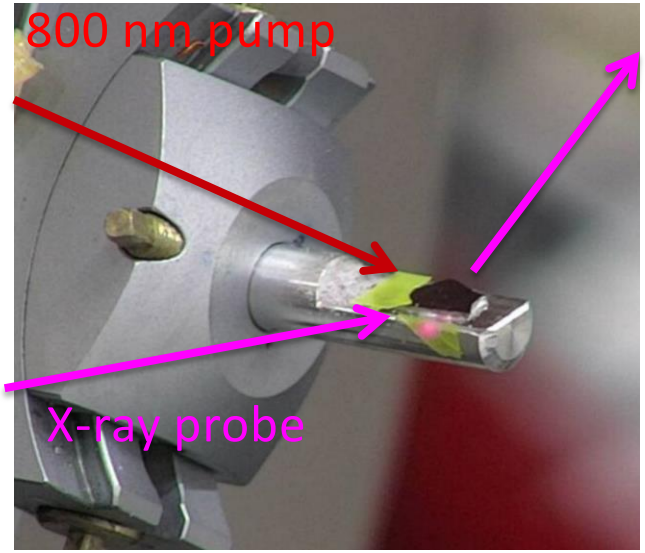


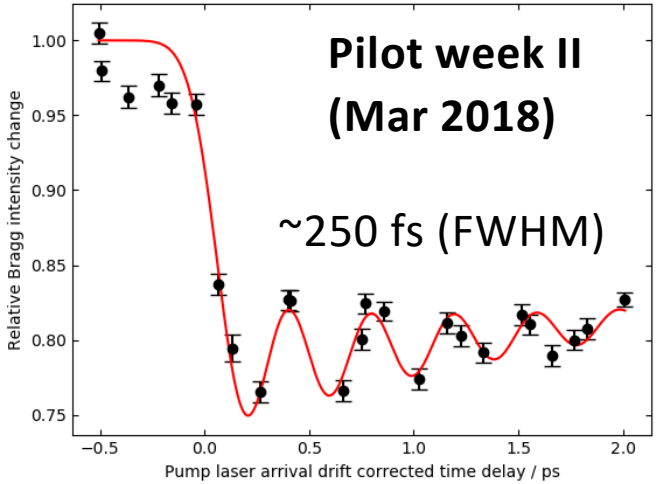
Average pump/probe time resolution

Static time resolution (no timetool) constantly improving

Displacive excitation in Bi(111)







Experimental station Alvra

G. Knopp, C. Cirelli, P. Radi,
C. Milne, J. Schneider

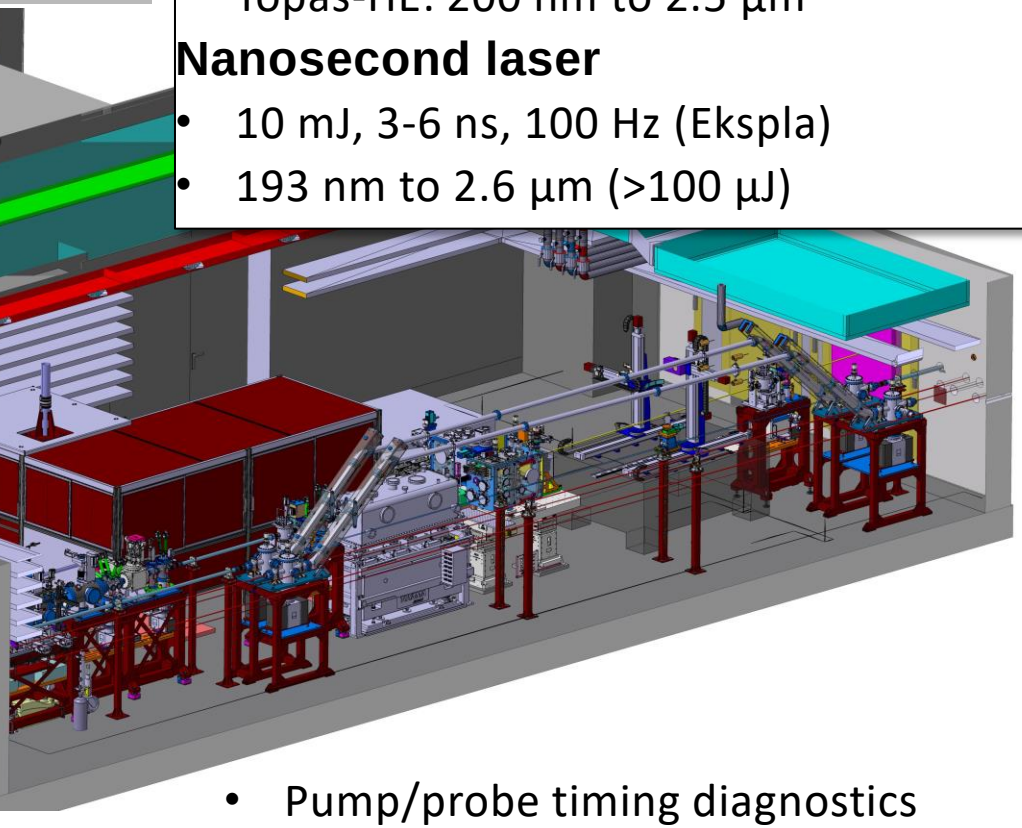
Ultrafast photochemistry and photobiology

Femtosecond laser

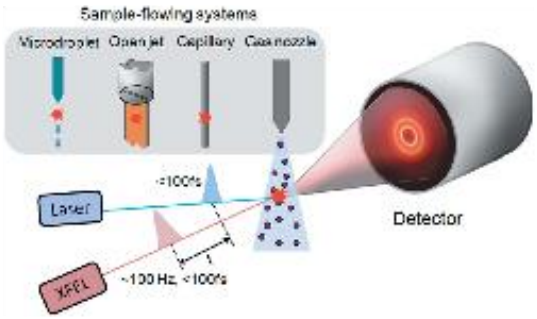
- 20 mJ, 35 fs, 100 Hz, 800 nm (Coherent)
- Topas-HE: 200 nm to 2.5 µm

Nanosecond laser

- 10 mJ, 3-6 ns, 100 Hz (Ekspla)
- 193 nm to 2.6 µm (>100 µJ)



- Pump/probe timing diagnostics
- X-ray intensity/pointing
- X-ray focusing



Endstations

Prime

- (Tender) X-ray Emission spectrometer
- X-ray scattering/diffraction

Flex

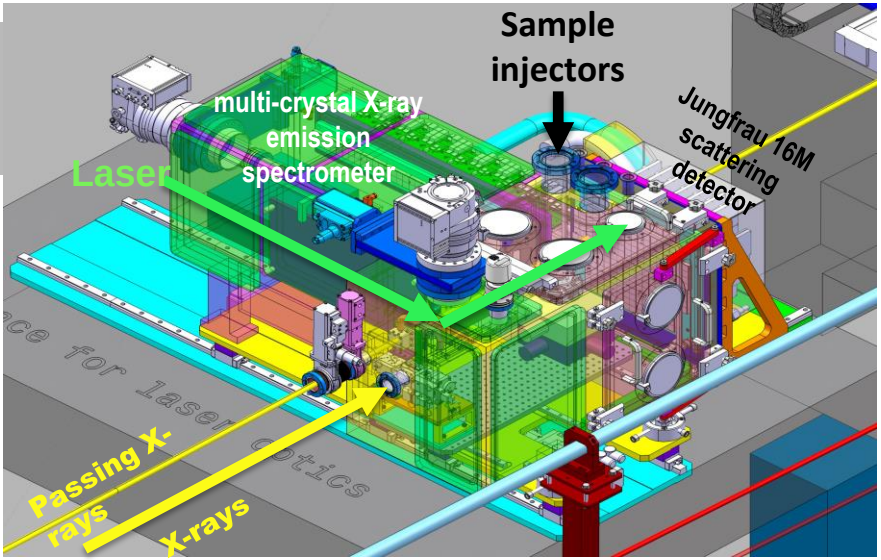
- Flexible emission spectrometer
- General purpose table

www.psi.ch/alvra

Experimental station Alvra

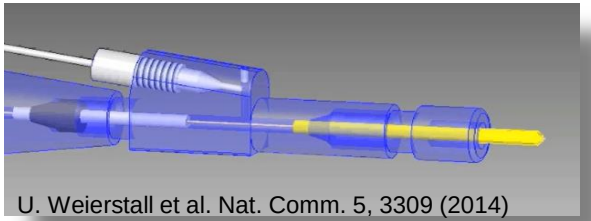
Alvra Prime: SFX & Spectroscopy

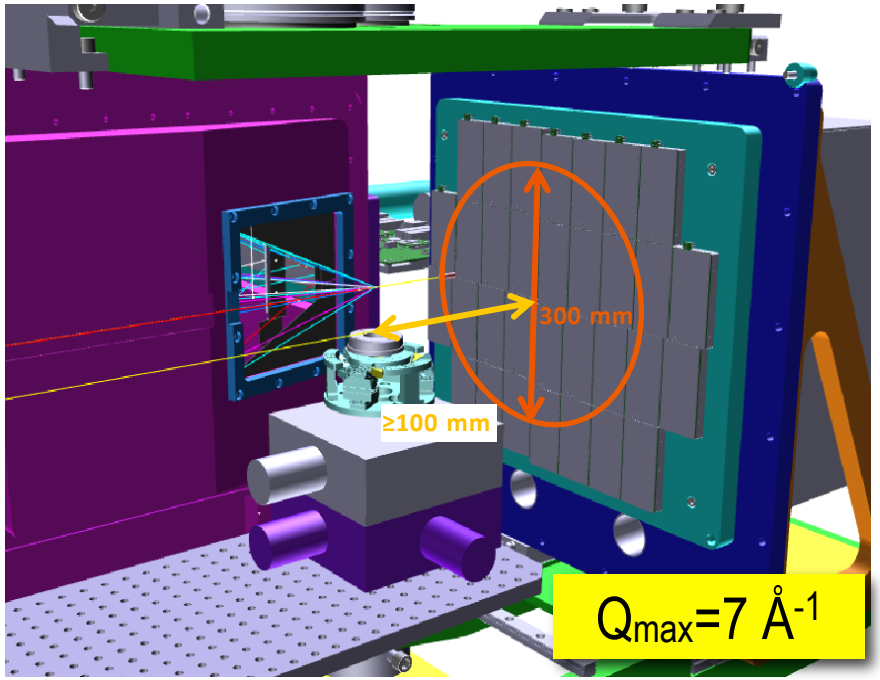
D. Hauenstein, A. Schwarb, J. Szlachetko, C. Milne



Injectors

- Flexible port
- Flat and round jets for femtochemistry
- GVD & LCP jets





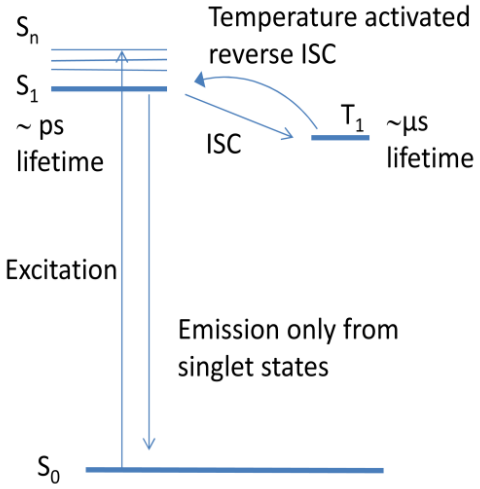
Design

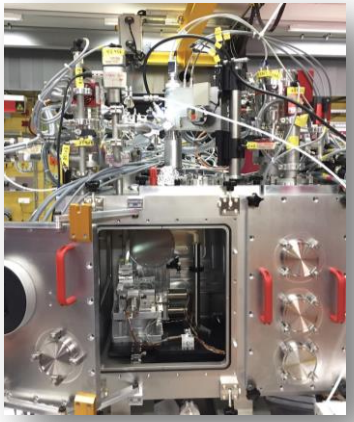
- Simultaneous use of spectrometer and Jungfrau 16M
- Two horizontal chamber positions for different experimental priorities (scattering/diffraction Vs spectroscopy)
- Time resolved pump/probe measurements
- 1.5 um focus (KB mirrors for achromatic focussing)

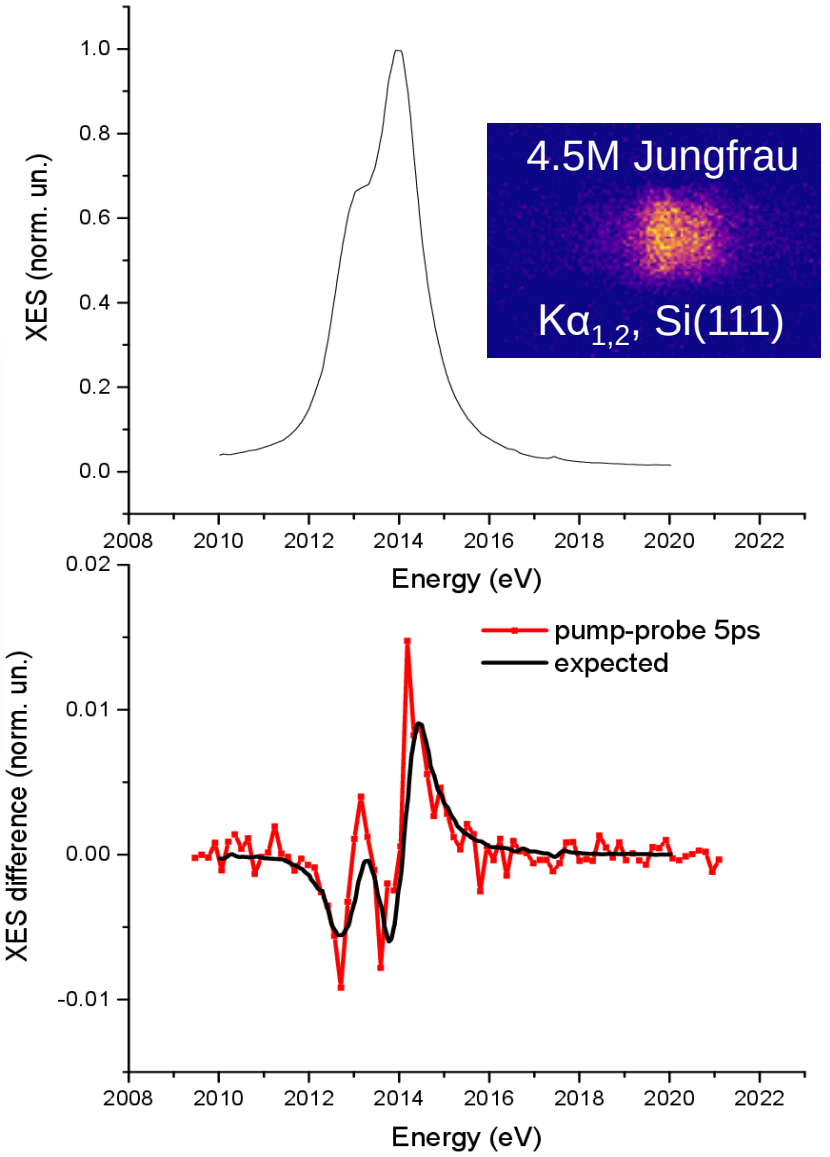
Novel OLED materials

Collaboration M. Vogt
(University of Bremen)

Cu-based OLED materials with temperature-activated delayed fluorescence







Experimental parameters

- Liquid jet (20-30 µm)
- Visible excitation (454 nm)
- XES measured at P $K\beta_{1,3}$ (2014 eV)

www.psi.ch/swissfel/alvra-pilot-experiment

Experimental station Bernina

G. Ingold, A. Oggenfuss, P. Beaud, H. Lemke

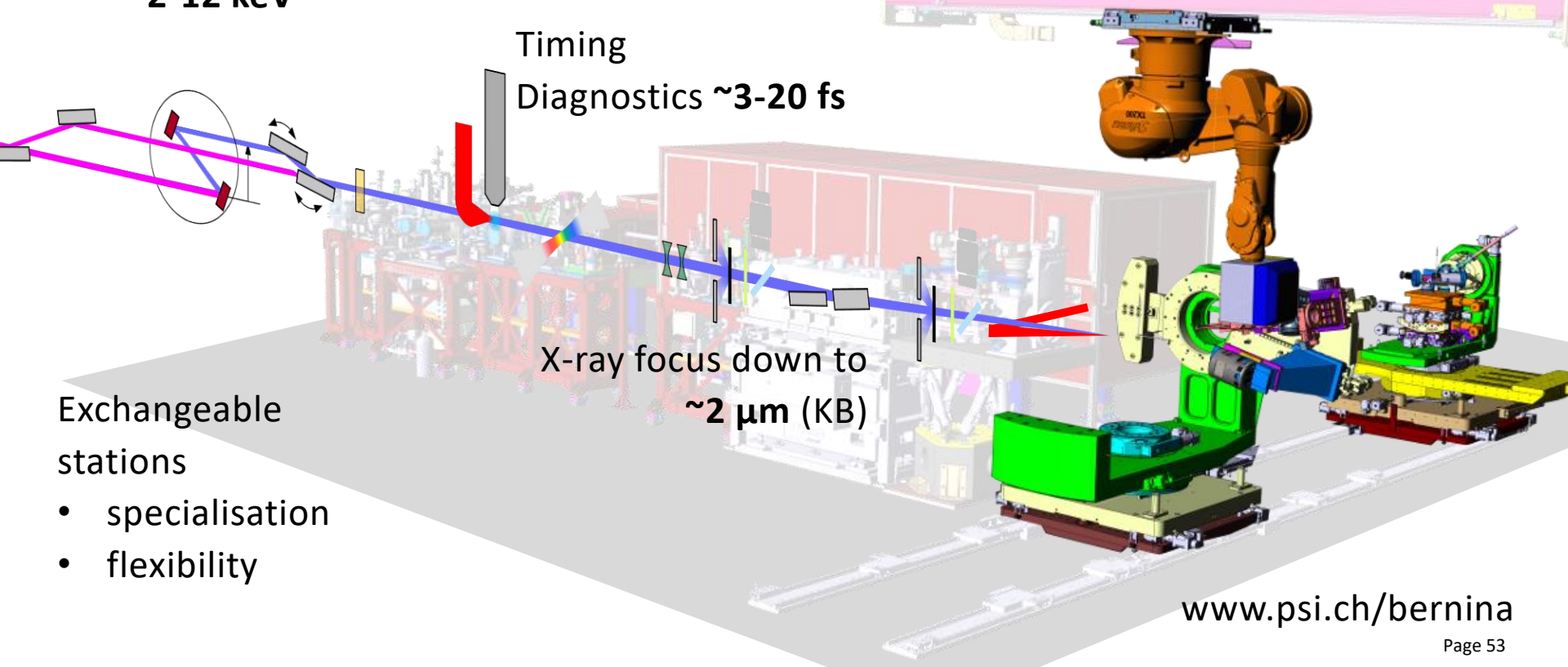
Ultrafast Material Science

Femtosecond laser

- 20 mJ, 35 fs, 100 Hz, 800 nm (Coherent)
- Topas-HE: 200 nm to 20 µm
- Phase stable extension
- 1 – 10 THz (30-300 µm) single cycle
- Shurt pulse < 10 fs @ 800 nm ca. 500 µJ

Monochromator
2-12 keV

Timing
Diagnostics **~3-20 fs**



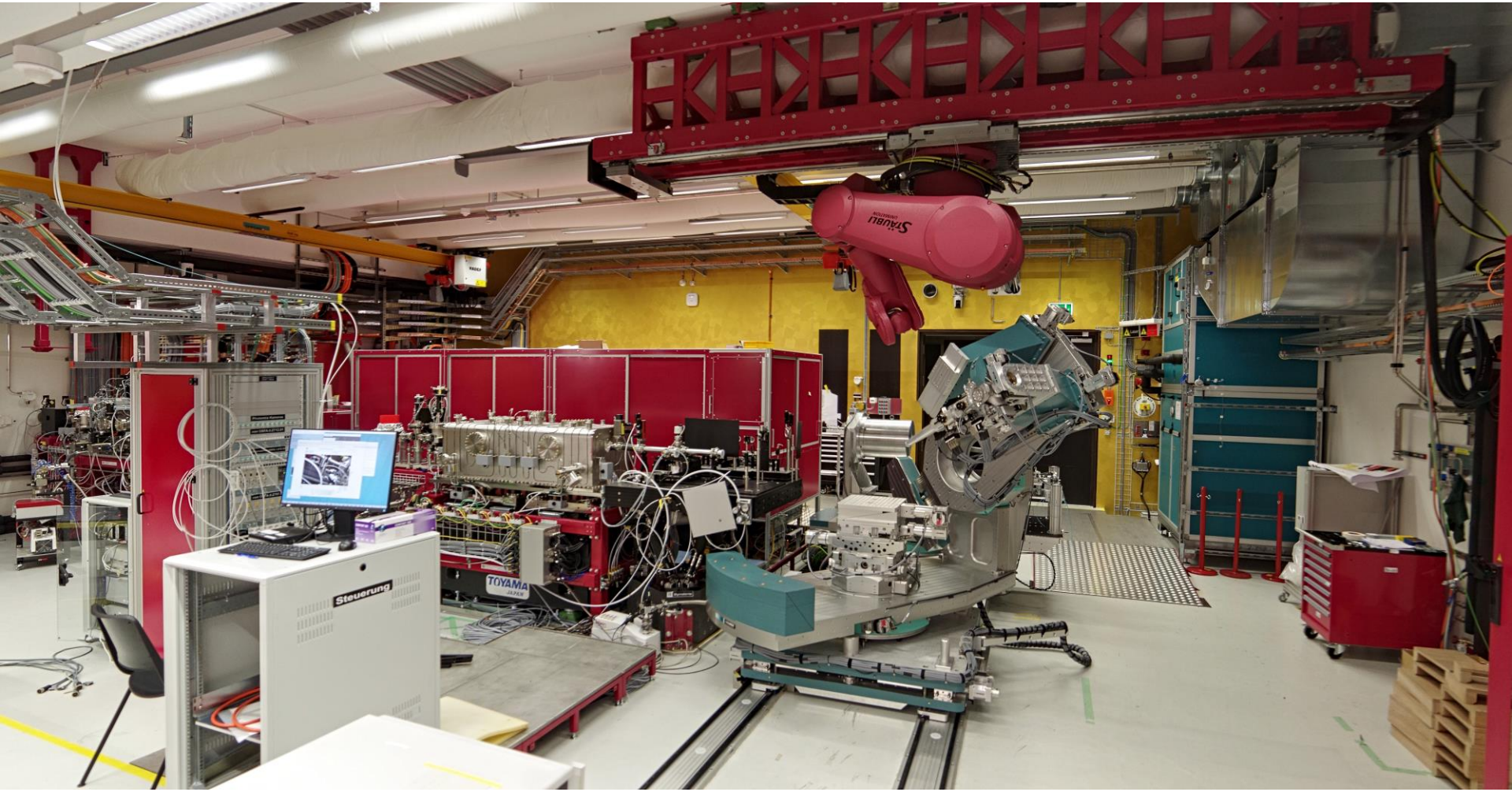
X-ray focus down to
~2 µm (KB)

Exchangeable stations

- specialisation
- flexibility

www.psi.ch/bernina

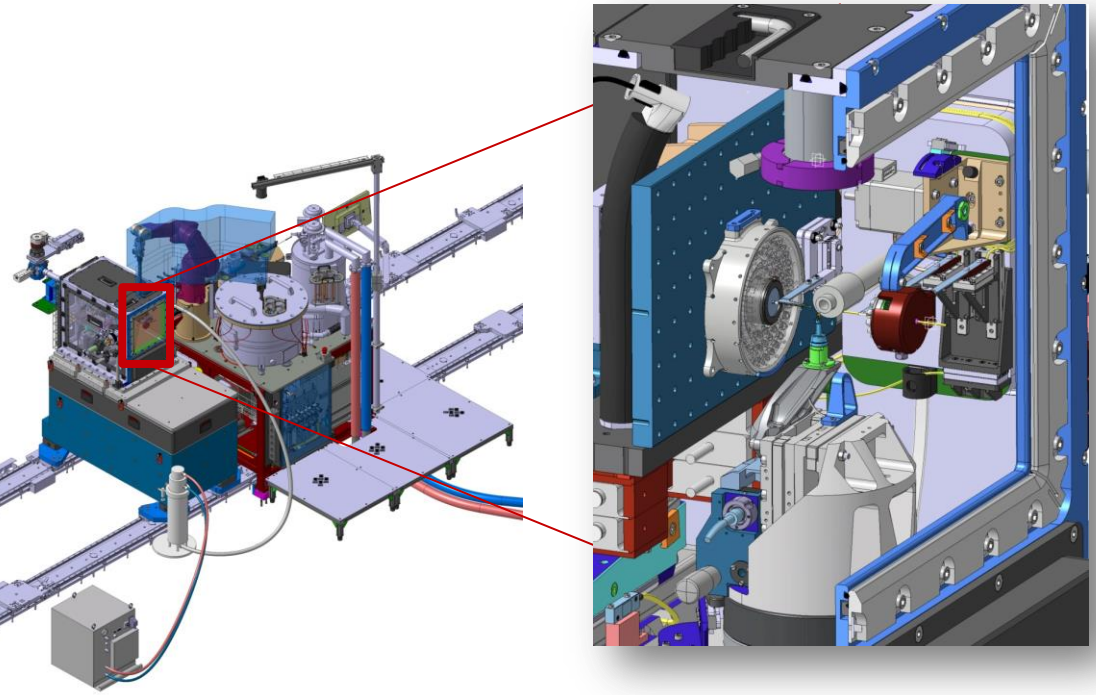
Experimental station Bernina



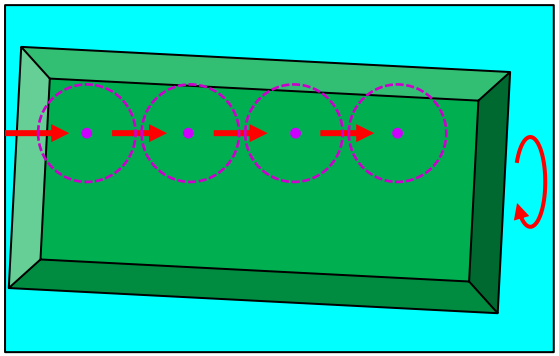
SwissMX - Fixed target endstation @ Bernina

- Sample changer / Fixed target
- Ambient pressure He chamber
- Pump/probe foreseen

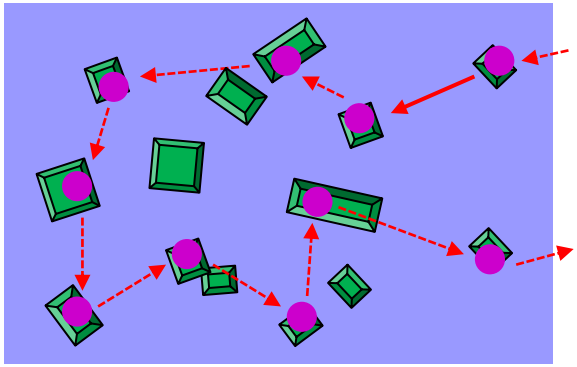
- Commissioning in Fall 2018



Fresh sample rotation scanning (>5um)



100 Hz Micro-Xtal mapping (>1um)



B. Pedrini, I. Martiel, C. Pradervand, M. Wang, E. Panepucci

PAUL SCHERRER INSTITUT

First Pilot …

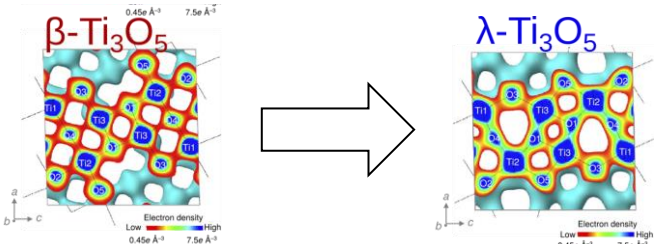
Phase Transition in Ti_3O_5

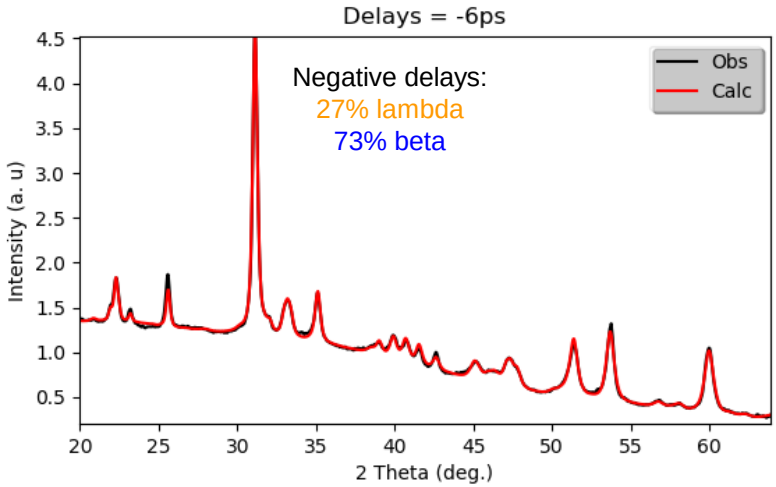
Collaboration M. Cammarata
(University of Rennes)

Reversible phase transition in nanoparticles

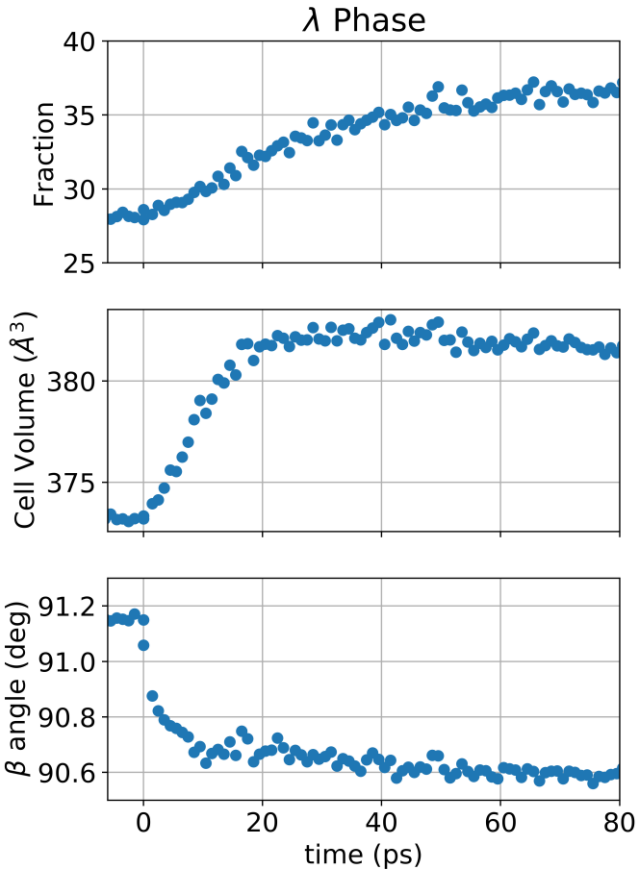
Semiconductor

Metal





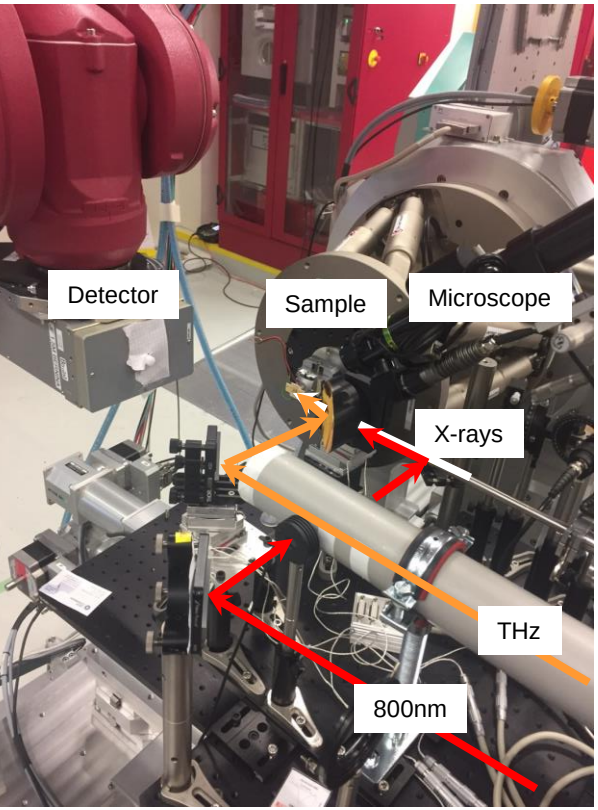
Rietveld refinement results

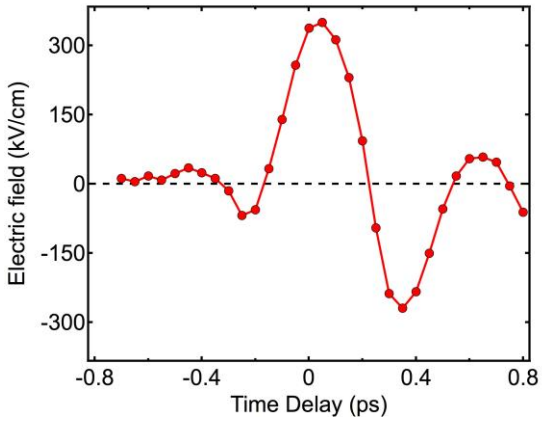


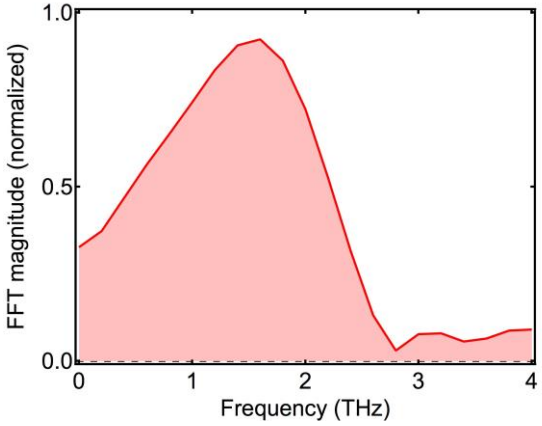
www.psi.ch/swissfel/first-pilot-experiment

THz switching of ferroelectric polarisation

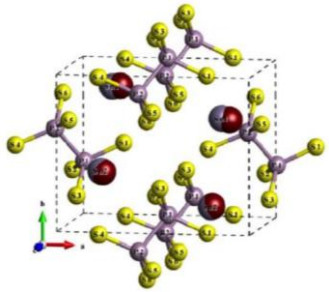
Organic crystal based THz pulse generation (OH1)
350 kV/cm

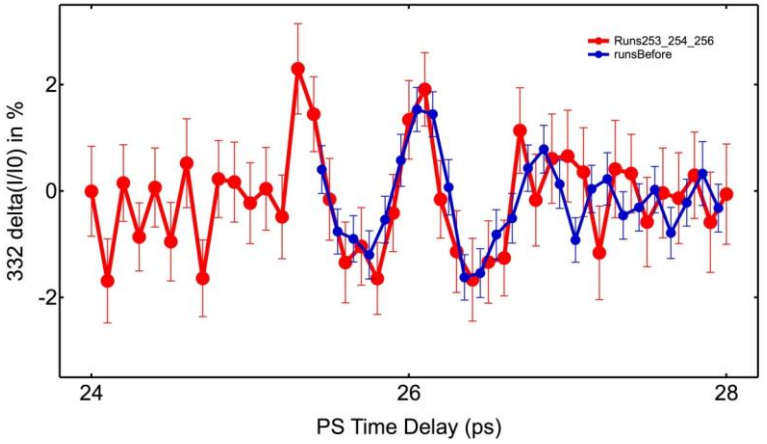






Partial switching of ferroelectric polarisation in $Sn_2P_2S_6$



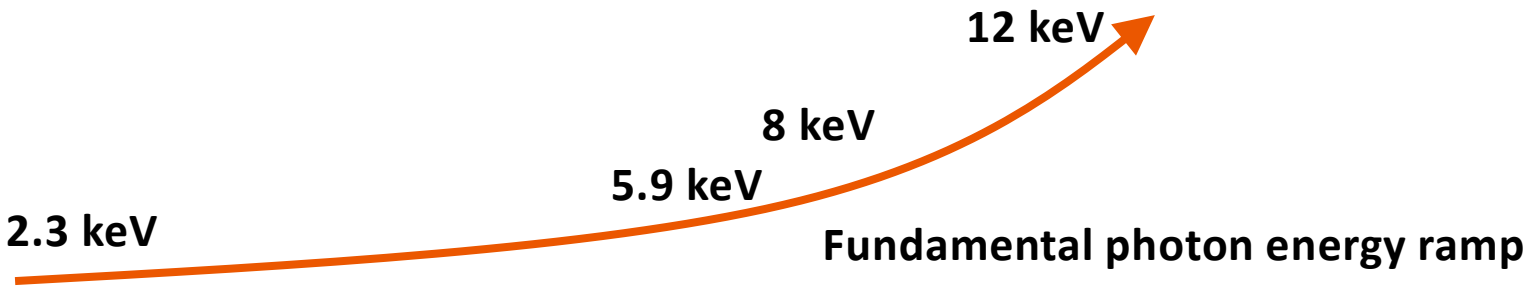


M. Savoini, S. Johnson et al.

Commissioning and Pilot Schedule

- Interleaved Commissioning and Pilot Experiments in 2018
- User operation from 2019 (**Call deadline September 2018**)

	Pilot I						Pilot II				Pilot III				User I		
Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar
2017			2018												2019		

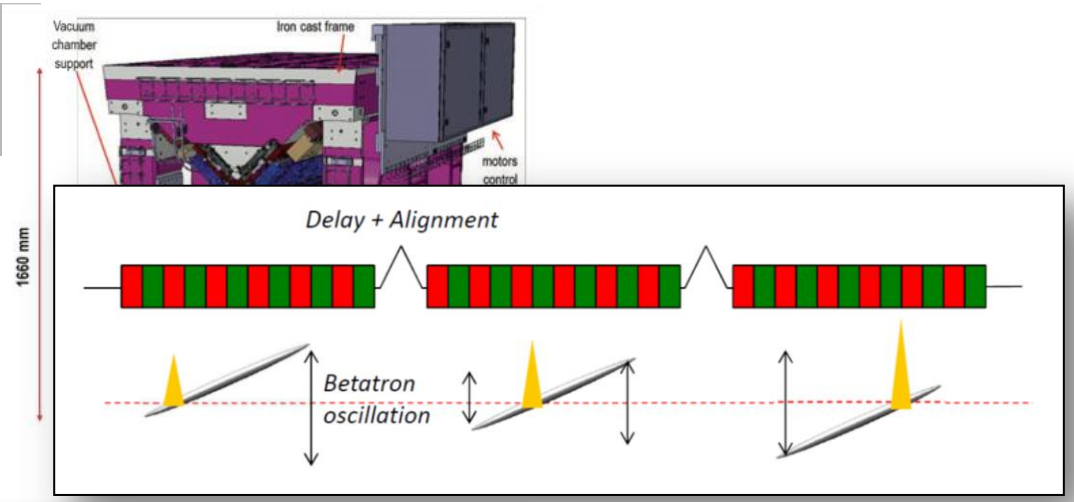


For joining the action, please contact

- Alvra → chris.milne
- Bernina → henrik.lemke
- SwissMX → bill.pedrini @psi.ch

SwissFEL Athos

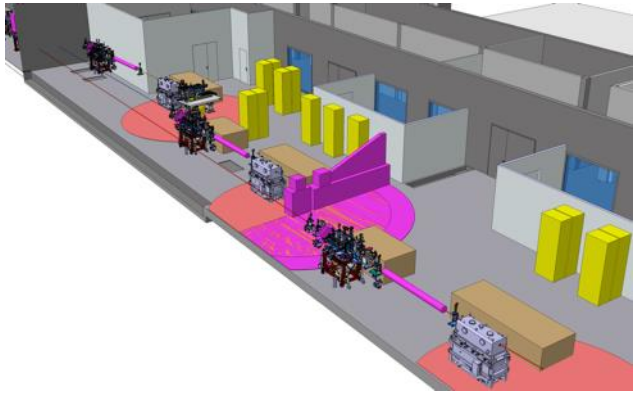
Undulator



- Soft x-ray: 250 – 1'930 eV
- Variable polarization Apple X U38 undulators
- Operation modes: SASE (CHIC) & self-seeded

➢ *In production*
➢ *Installation in 2019*

End-station



- AMO end-station: FEL X-ray combined with attosecond XUV and IR interferometer (EHTZ-PSI)
- Condensed matter and quantum materials end-station: tr-RIXS

➢ *First experiment in 2021*

Summary SwissFEL

- Tender x-ray range, high time resolution; ~~high rep rate~~
- Specialized exp. Setups & flexible platforms
- State of the art x-ray optics & area detectors
- SFX: Emphasis on hit rate; LCP jet and solid target, time-resolved
- Pilot and Commissioning in 2018 Open proposal call mid 2018 (for 2019)
- www.psi.ch/swissfel

Acknowledgments

SwissFEL team

PSI support groups

PSI intern and external helpers and consultants

Selected SwissFEL contacts @psi.ch

Beam dynamics	sven.reiche
Machine Commissioning	thomas.schietinger
Pump laser	steve.johnson
X-ray diagnostics	pavle.juranic
X-ray optics	rolf.follath
Data infrastructure	simon.ebner
Data processing	leonardo.sala
ATHOS	luc.patthey
Alvra	chris.milne
Bernina	henrik.lemke
SwissMX	bill.pedrini