PAUL SCHERRER INSTITUT

PSI

Pump-probe x-ray spectroscopy and scattering to study OLED materials and molecular catalysts

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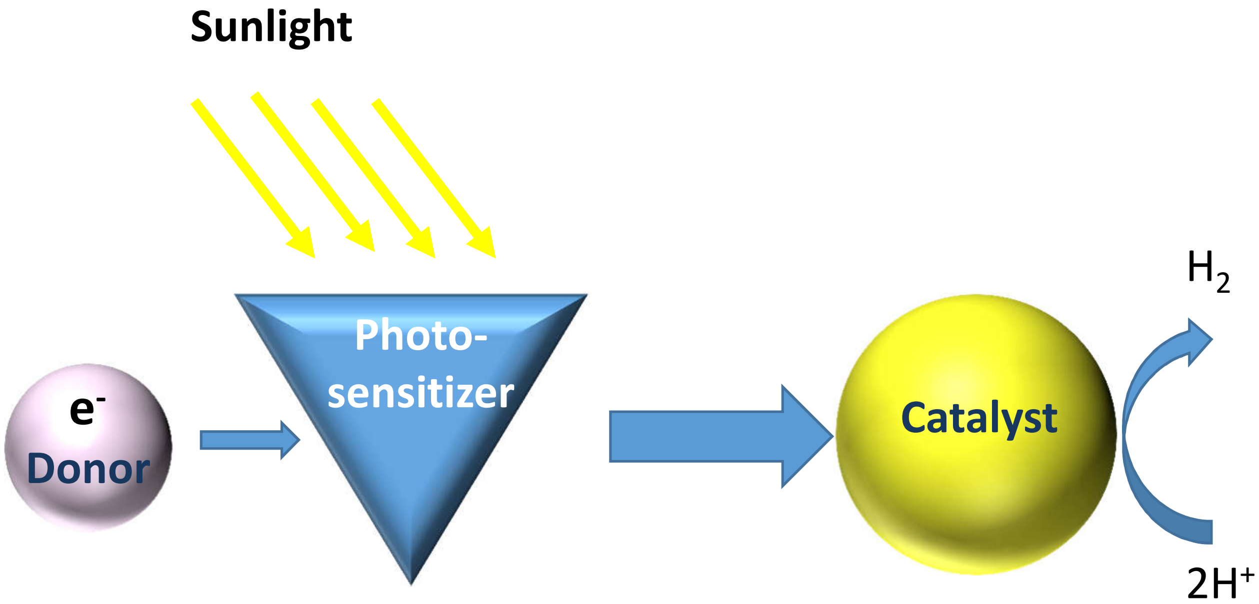
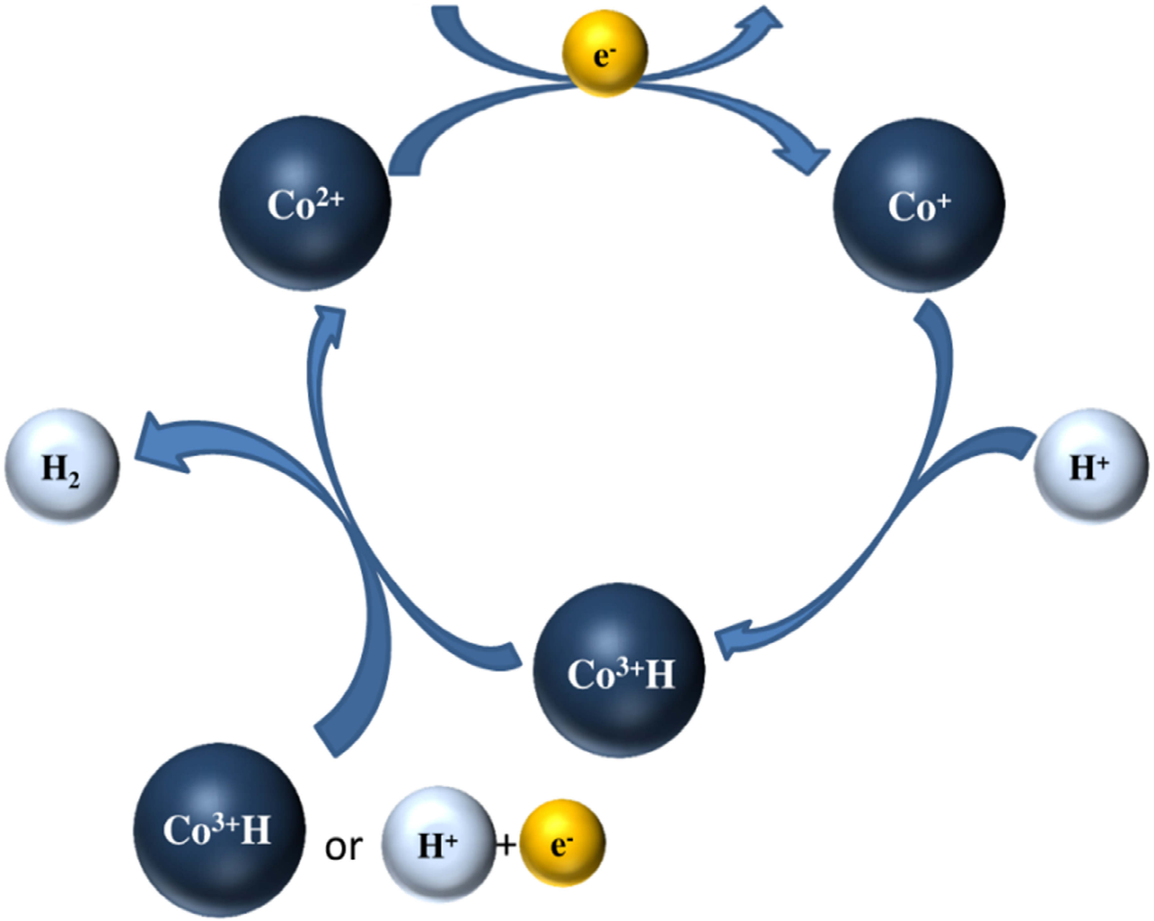
Main scientific area: investigation of the structure of intermediates during photocatalytic reactions

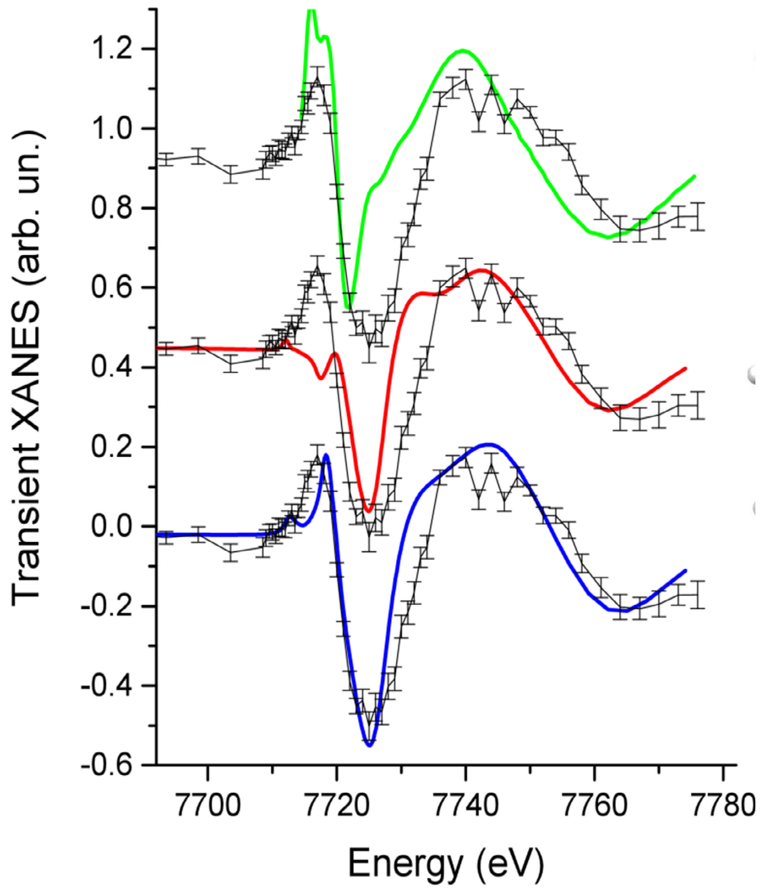


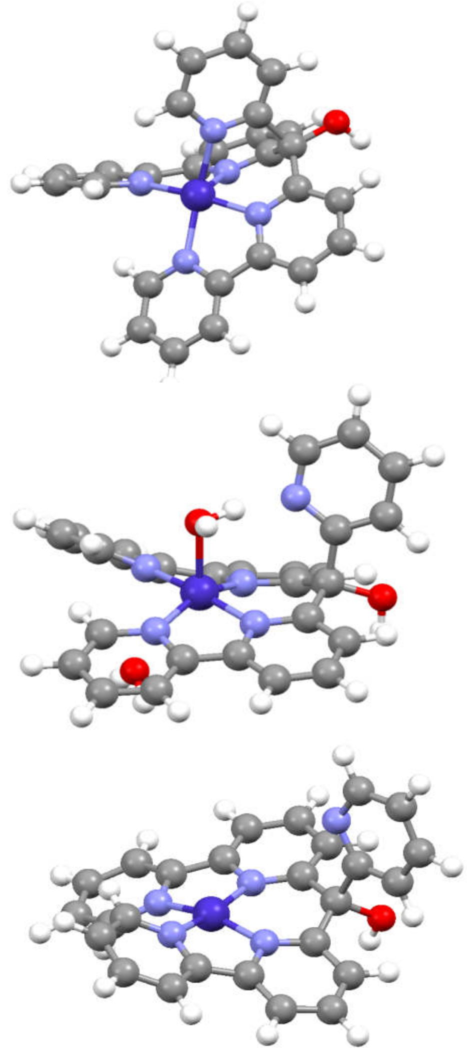
Smolentsev et. al. *Chem. Sus. Chem.* 11 (2018) 3087

Intermediates of photocatalytic reactions are formed in the microsecond time range

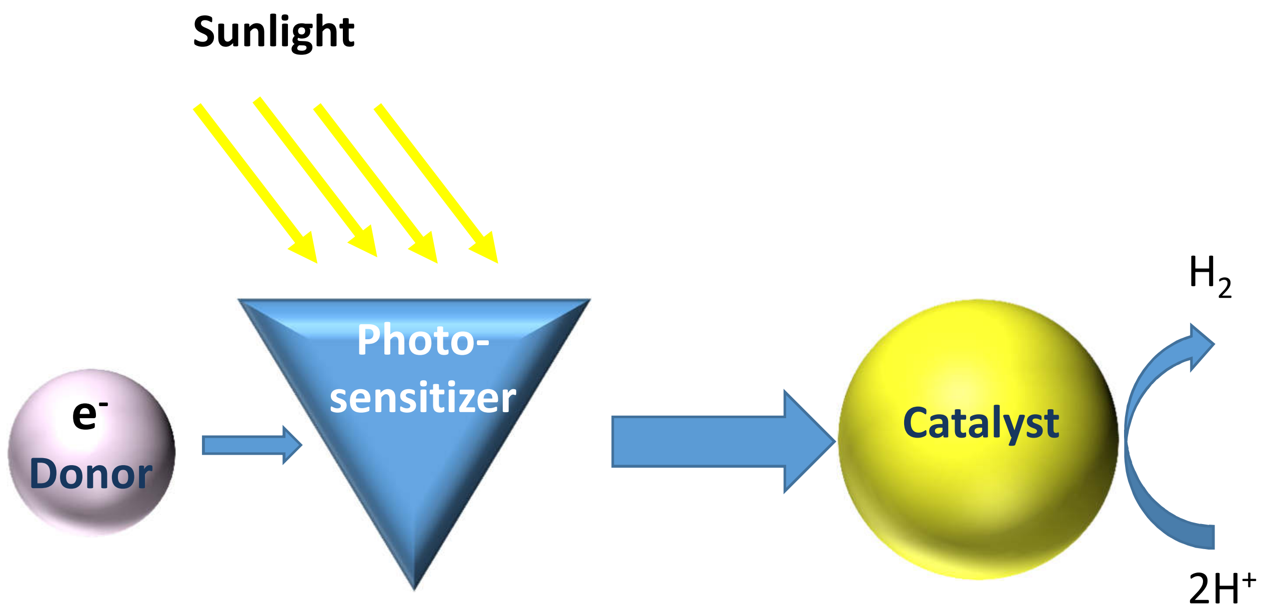


Co(I) intermediate has been observed with transient XANES. 4-coordinated structure with dissociated pyridine agrees with the experiment





How to make the bridge between chemistry and European XFEL



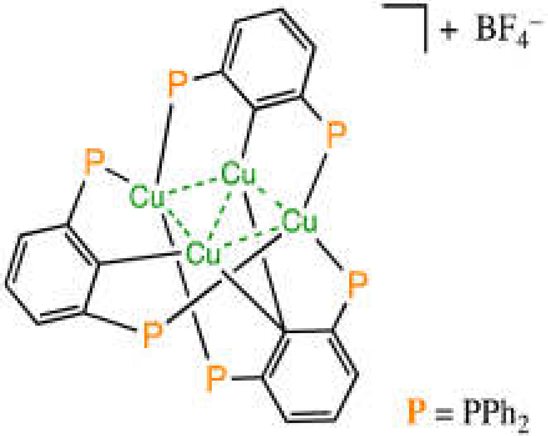
Photophysics of photosensitizers?

Use burst mode to probe catalyst with photon-hungry techniques?

Complementarity of 4 large-scale facilities has been used:

SuperXAS of **SLS**:
Pump-probe XAS (Cu K- edge)
-10µs time range

ID09 of **ESRF**:
Pump-probe WAXS
100 ps - 2µs



Alvra of **SwissFEL**
Pump-probe XES (P Kα lines)

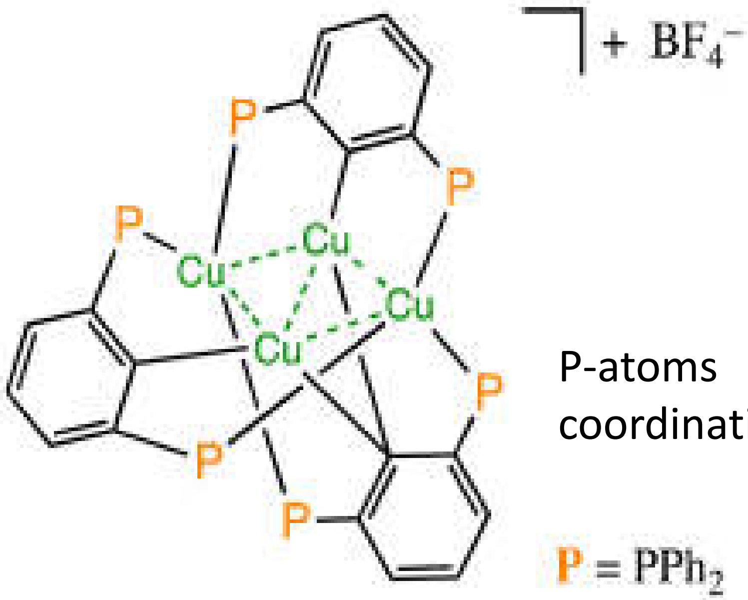
FXE of **European XFEL**
Pump-probe WAXS and
Cu K-beta XES

Acknowledgements

- C Milne, J. Szlachetko and team of ALVRA at SwissFEL
- K. Haldrup and team from DTU (WAXS at European XFEL and ID09)
- M. Sander, V. Kabanova, M. Levantino (support of ID09 experiment)
- W. Gawelda, D. Khakhulin (and FXE team at European XFEL)
- N. Azzaroli (SuperXAS of SLS)
- S. Ketkov, A. Guda and team from SFedU (calculations),
- A. Cannizzo (optical pump-probe)
- M. Olaru, M. Vogt (synthesis of samples, Bremen Uni.)

Two types of Cu atoms with CuC_2 and CuP_3 coordination are present in CuPCP

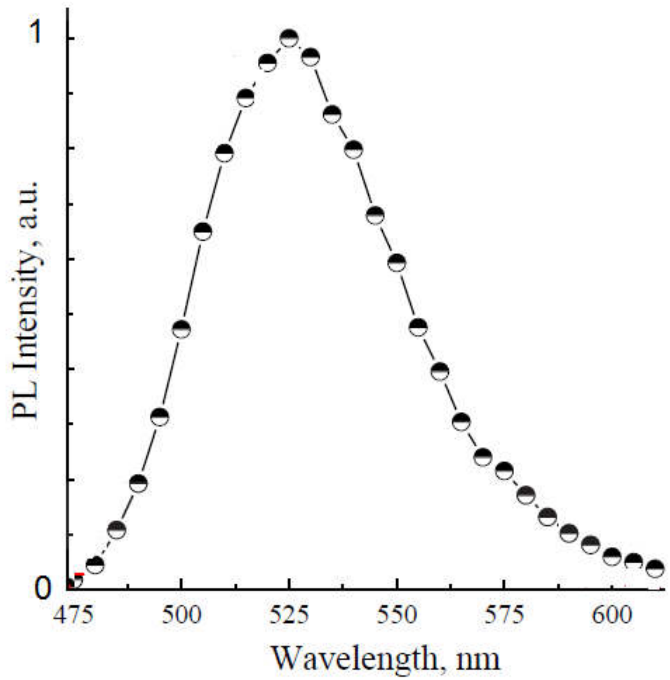
phenyl rings coordinating Cu

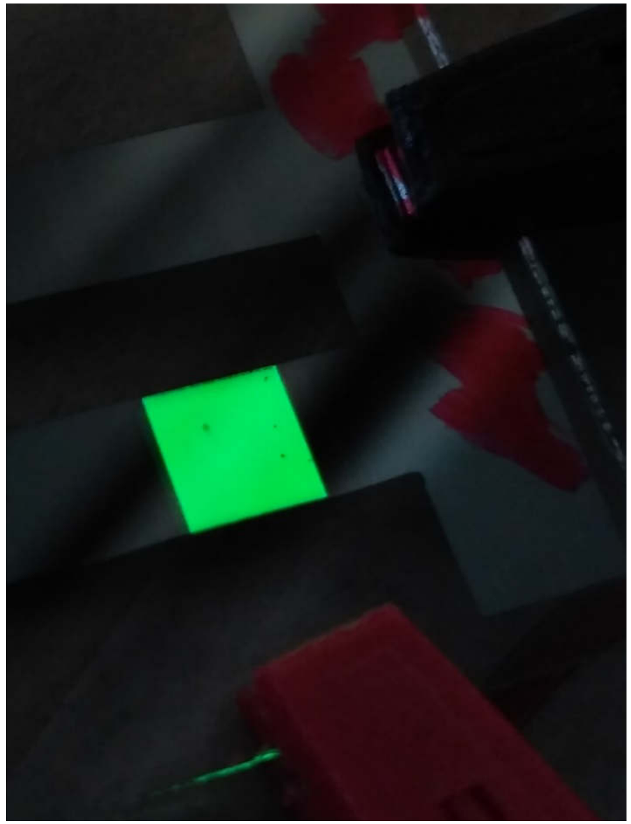


P-atoms coordinating Cu

CuPCP is promising material for OLED applications due to strong photo- and electroluminescence

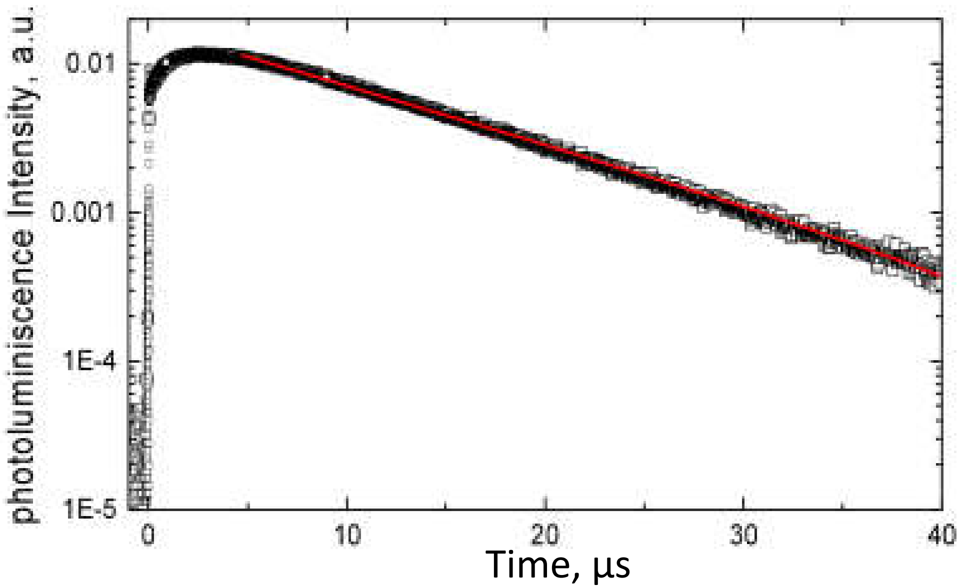
Strong green photoluminescence





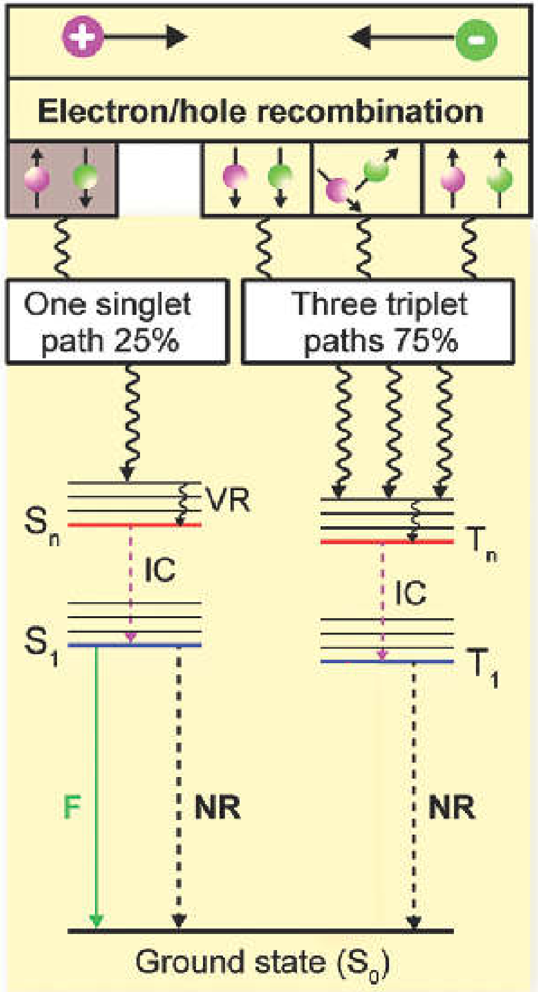
Hypothesis: long-lived emission is due to temperature-activated delayed fluorescence

Long lived excited state



Electroluminescence of Organic Light Emitting Diodes (OLEDs)

Classical organic materials

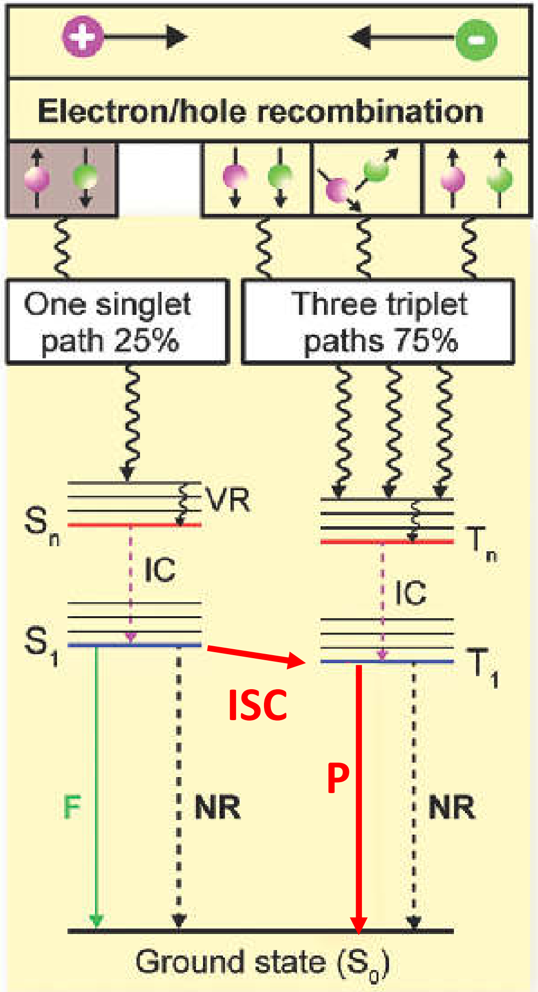


Emission only from singlet

Goal:
make bright and efficient OLEDs

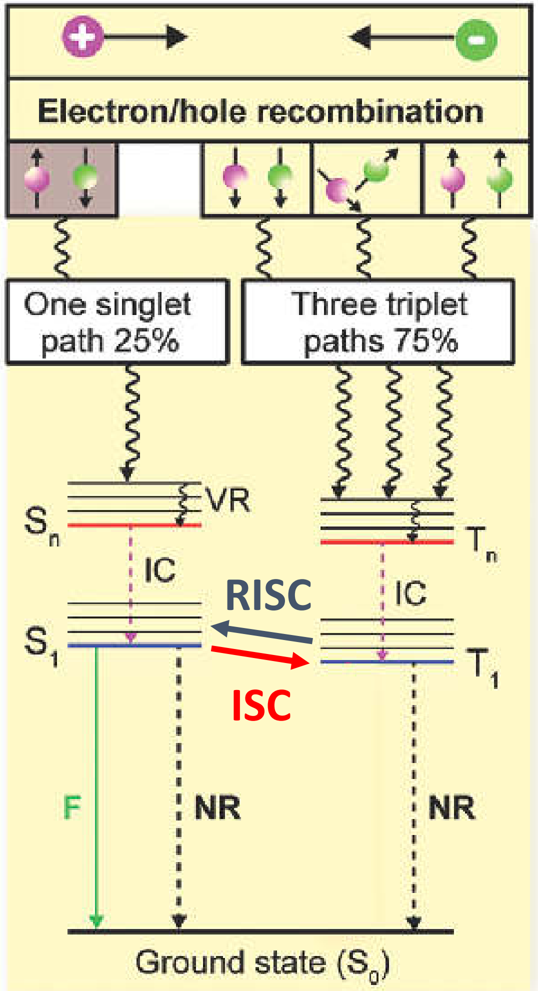
Theoretical limit for efficiency – 25%

Doping with heavy elements enables emission from triplet



- Theoretical efficiency limit 100%
- High price
- Limited availability

Temperature activated delayed fluorescence allows to increase the efficiency using cheap chemical elements



Emission from singlet

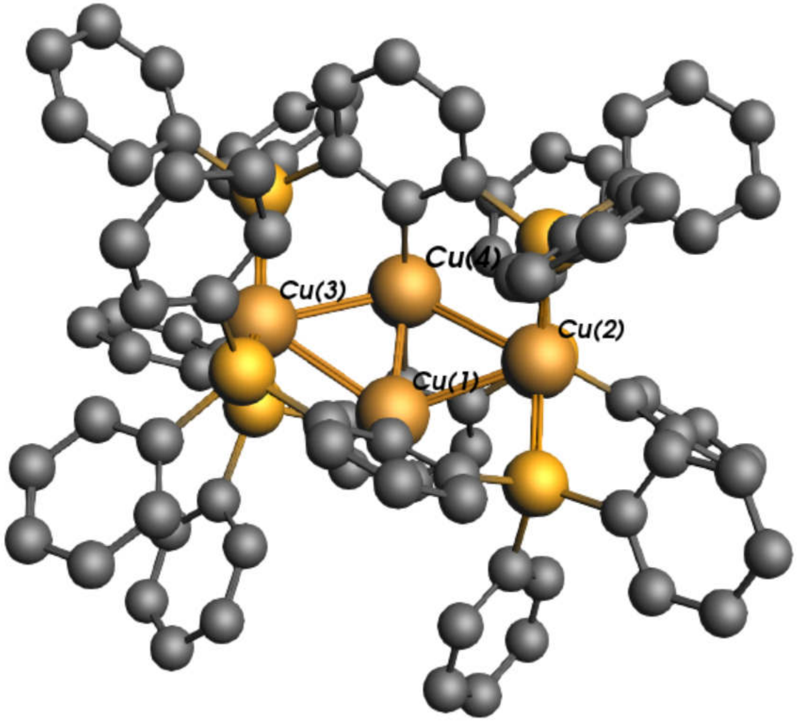
Theoretical limit 100%

Reverse ISC activated by temperature

Key questions: how is the charge density and local structure in the excited state different from the ground state

Which Cu atoms are involved in the charge transfer?

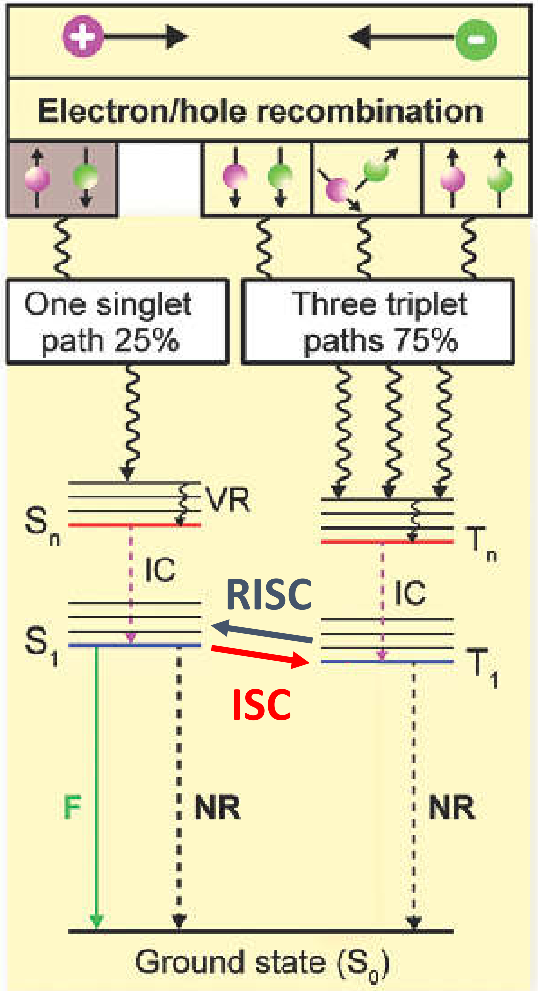
What is the role of P atoms:? Do they keep structural integrity only or participate in the charge transfer?

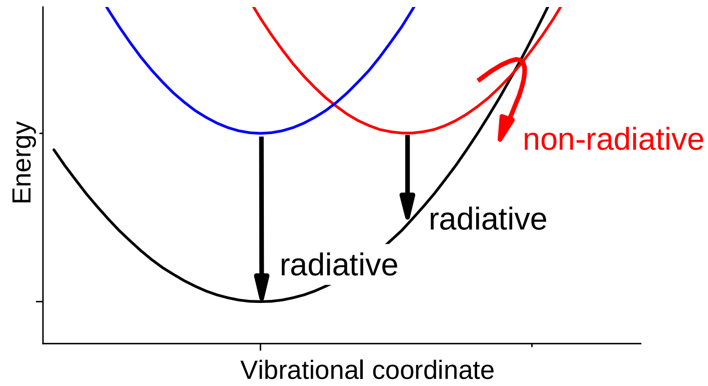


How big are the structural changes in the singlet and triplet states

Experimental verification of DFT predictions is required

Minimization of non-radiative losses is important to create efficient OLED materials

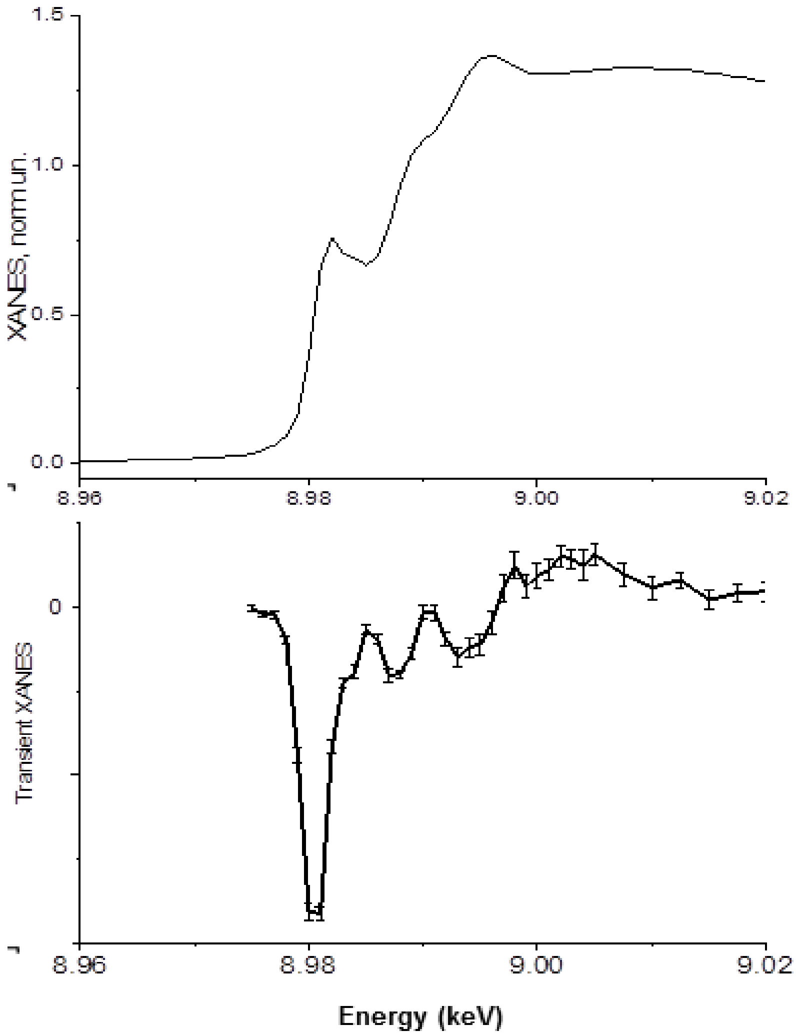


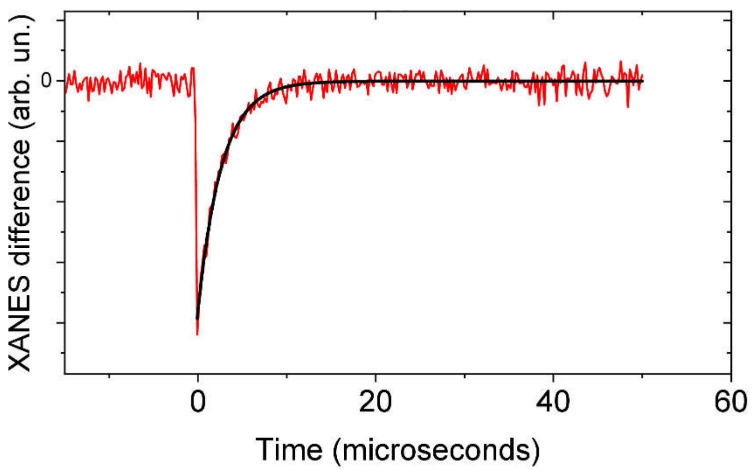


Experimental verification of DFT predictions is required

Pump-probe XANES provides information about changes of Cu oxidation state

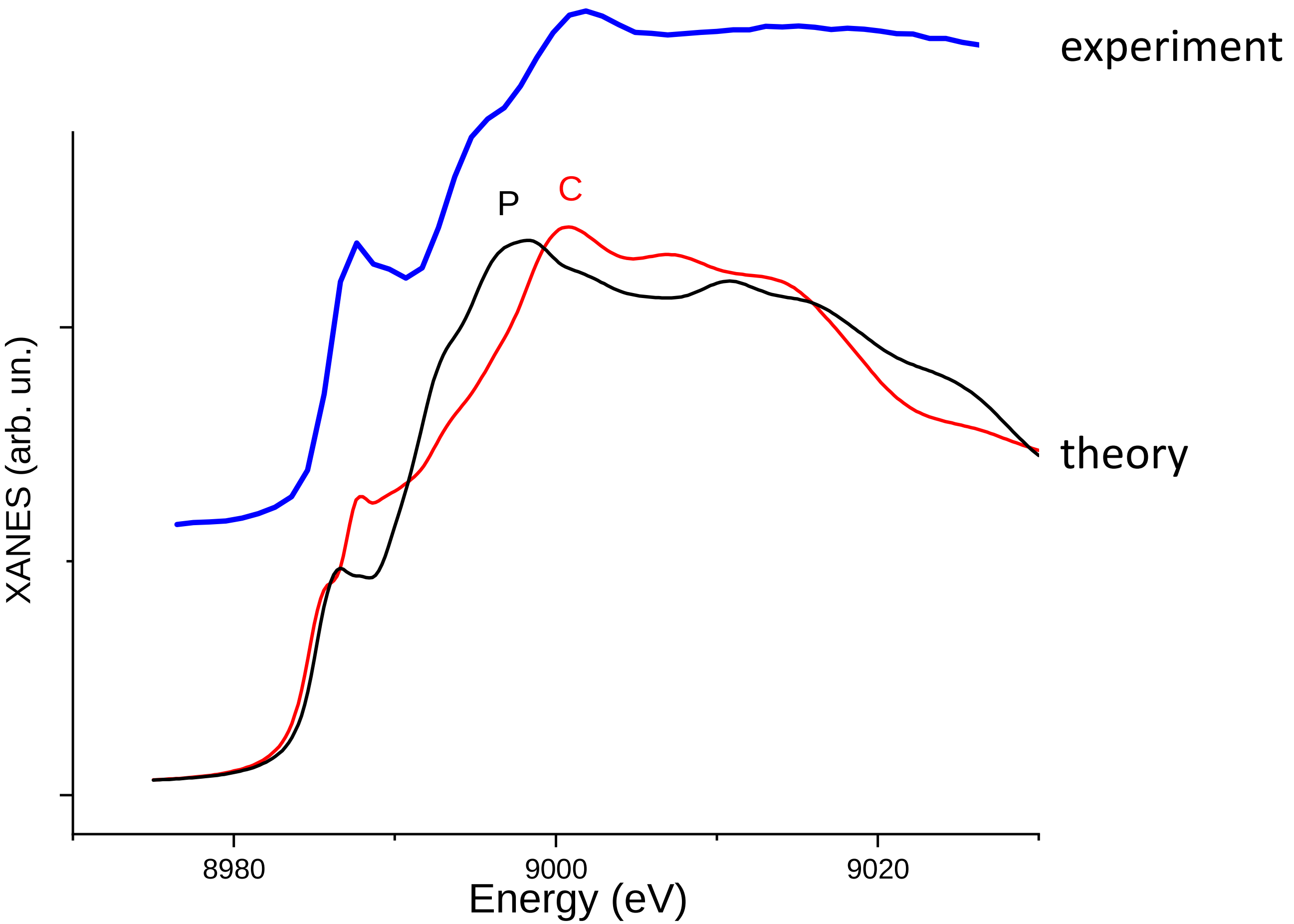
SLS (SuperXAS)



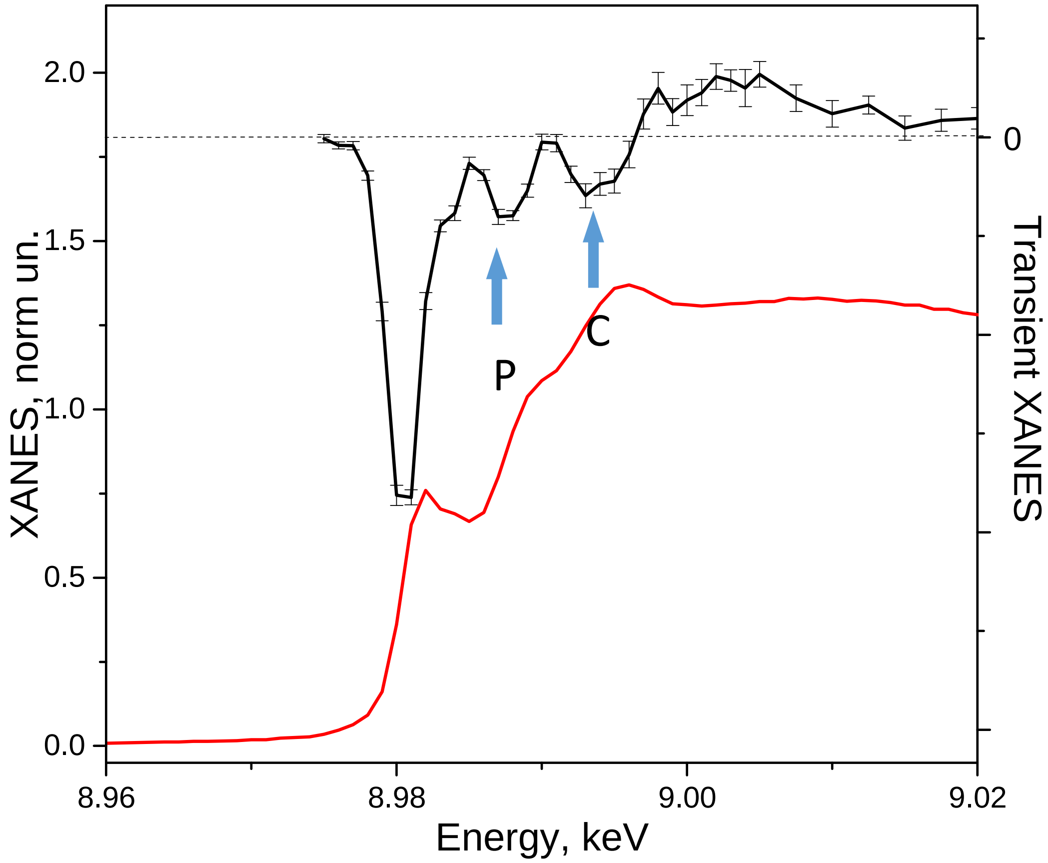


Lifetime: 2.7 μs

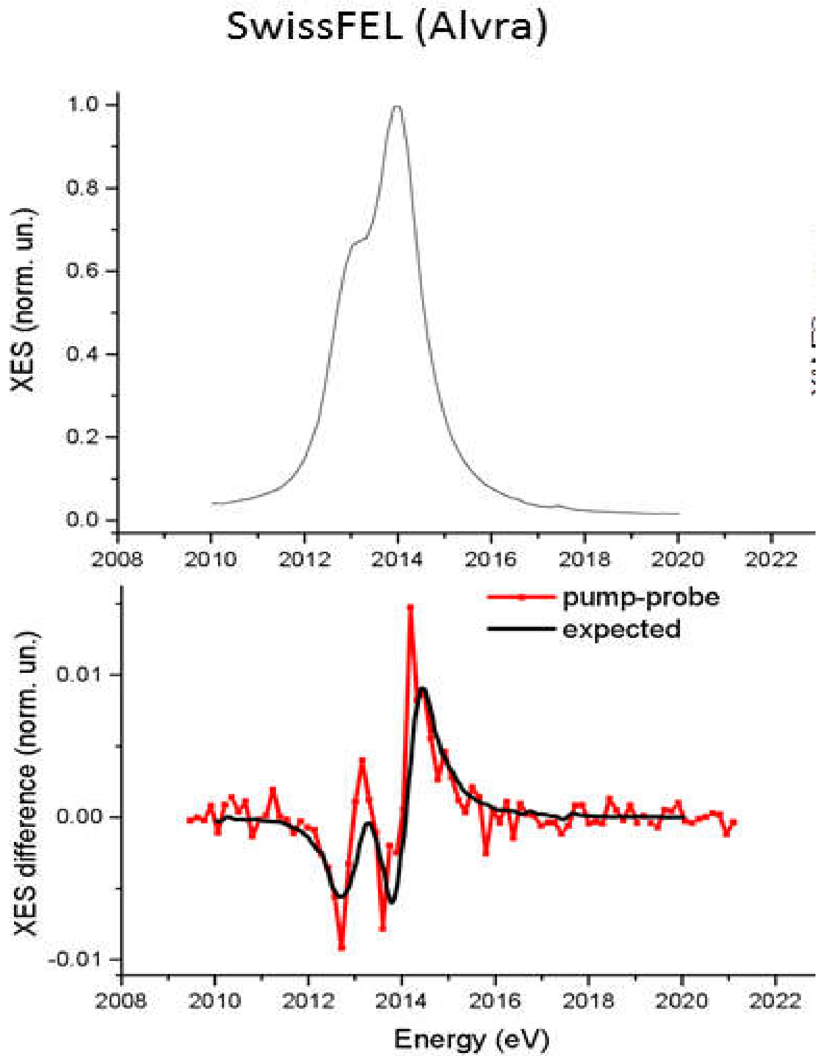
Contributions of Cu sites with different coordination are shifted in energy



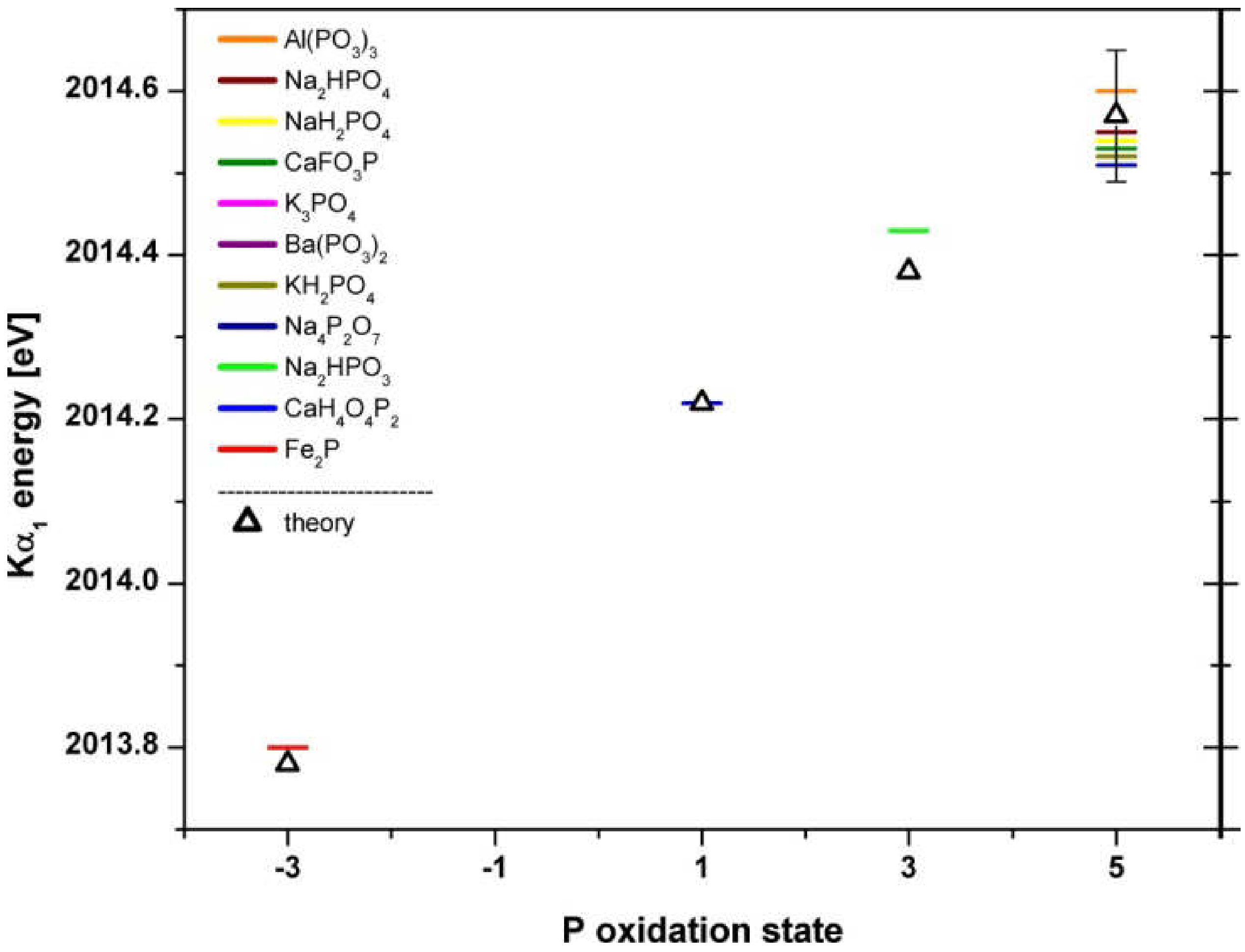
Two small peaks of the transient indicate that
both types of Cu atoms are involved in the charge transfer



Pump-probe XES around P Kα gives indicates that P is involved in the charge transfer



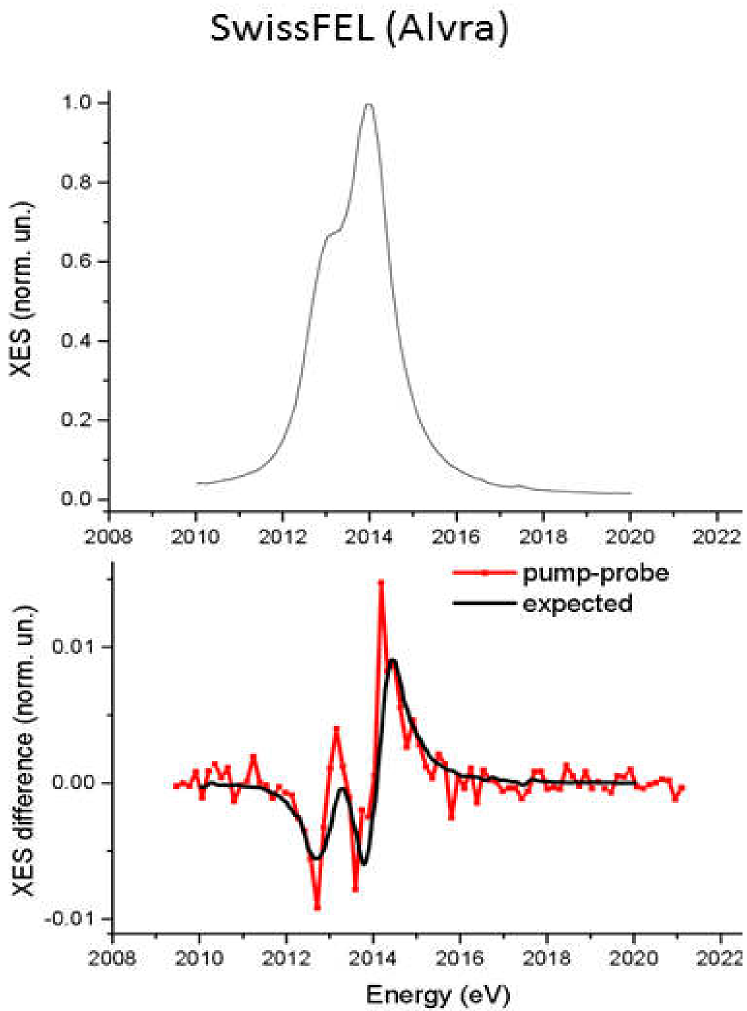
Position of P Kα lines and oxidation state of P (formal charge) correlate



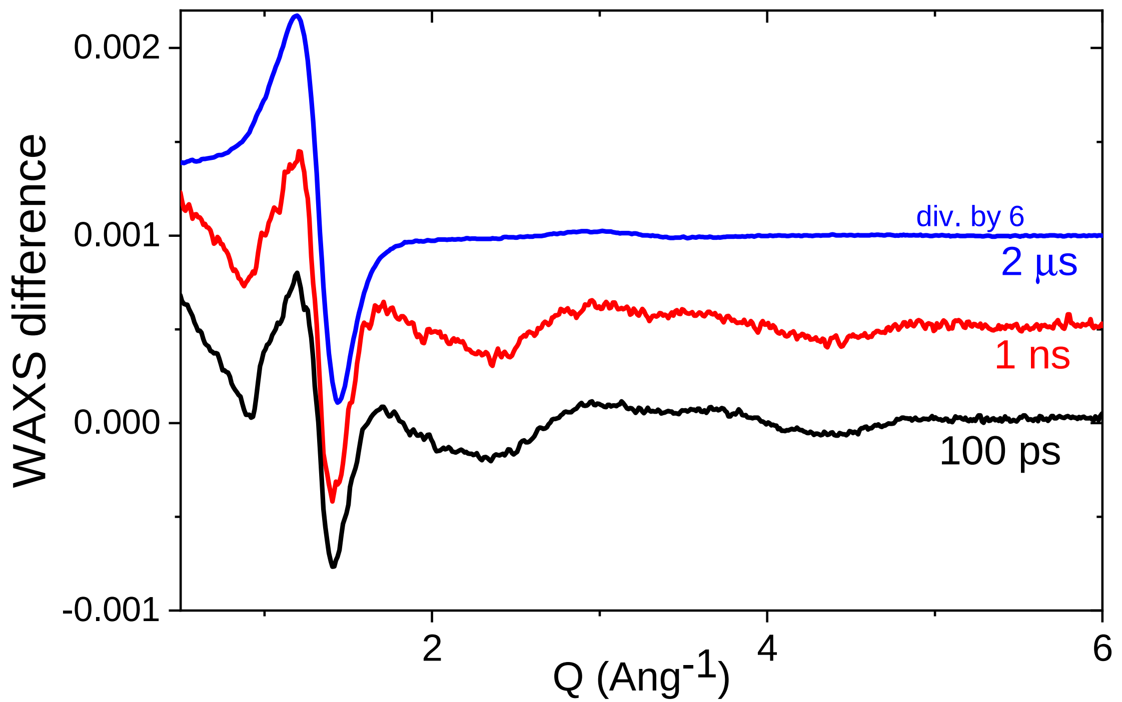
Petric et al Anal. Chem., 2015, 87 (11), p 5632

0.1 eV shift/electron

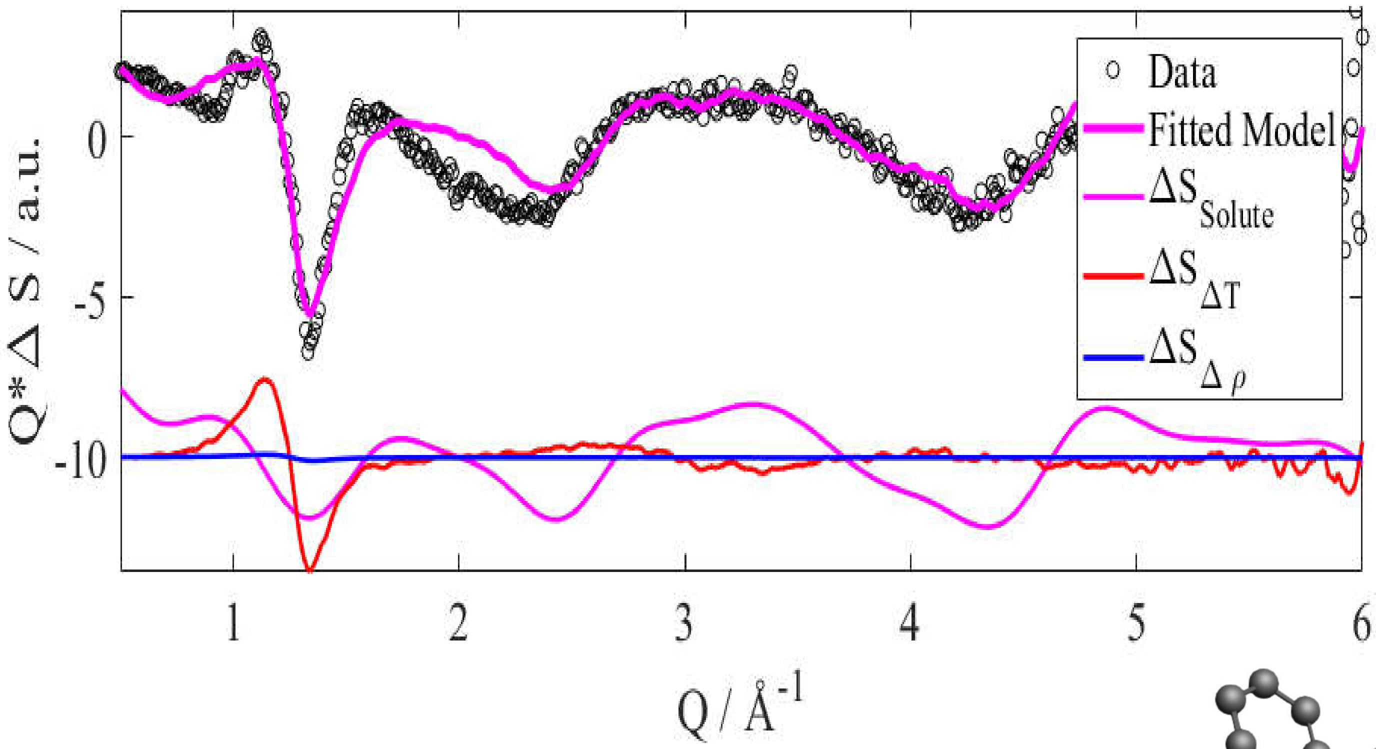
Electron density moves from P atoms.
Average change of P formal charge is more than 0.09

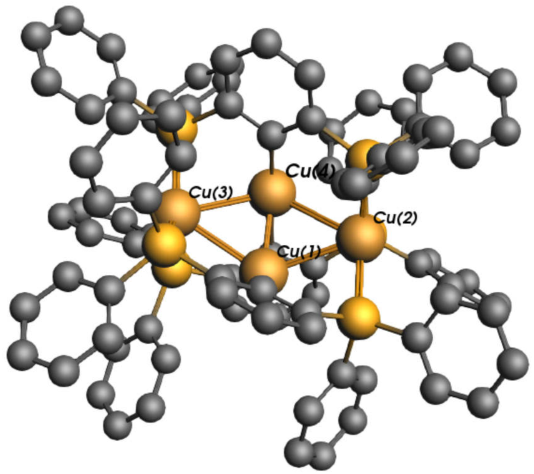


Pump-probe X-ray scattering data from ID09 provide information about local structure changes in the triplet state



X-ray scattering signal calculated for DFT models agrees with the experiment

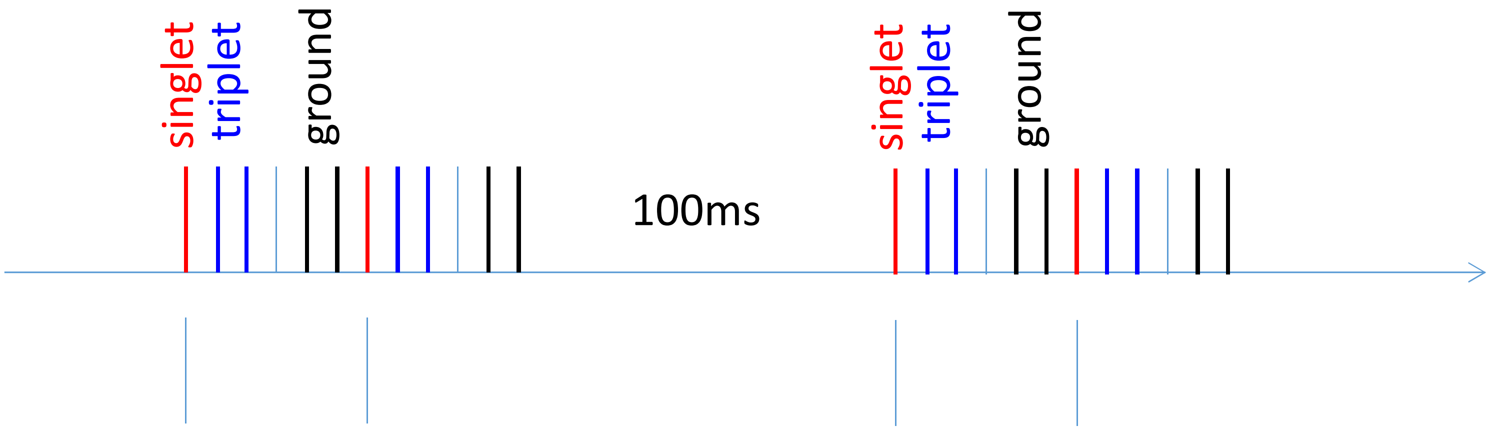




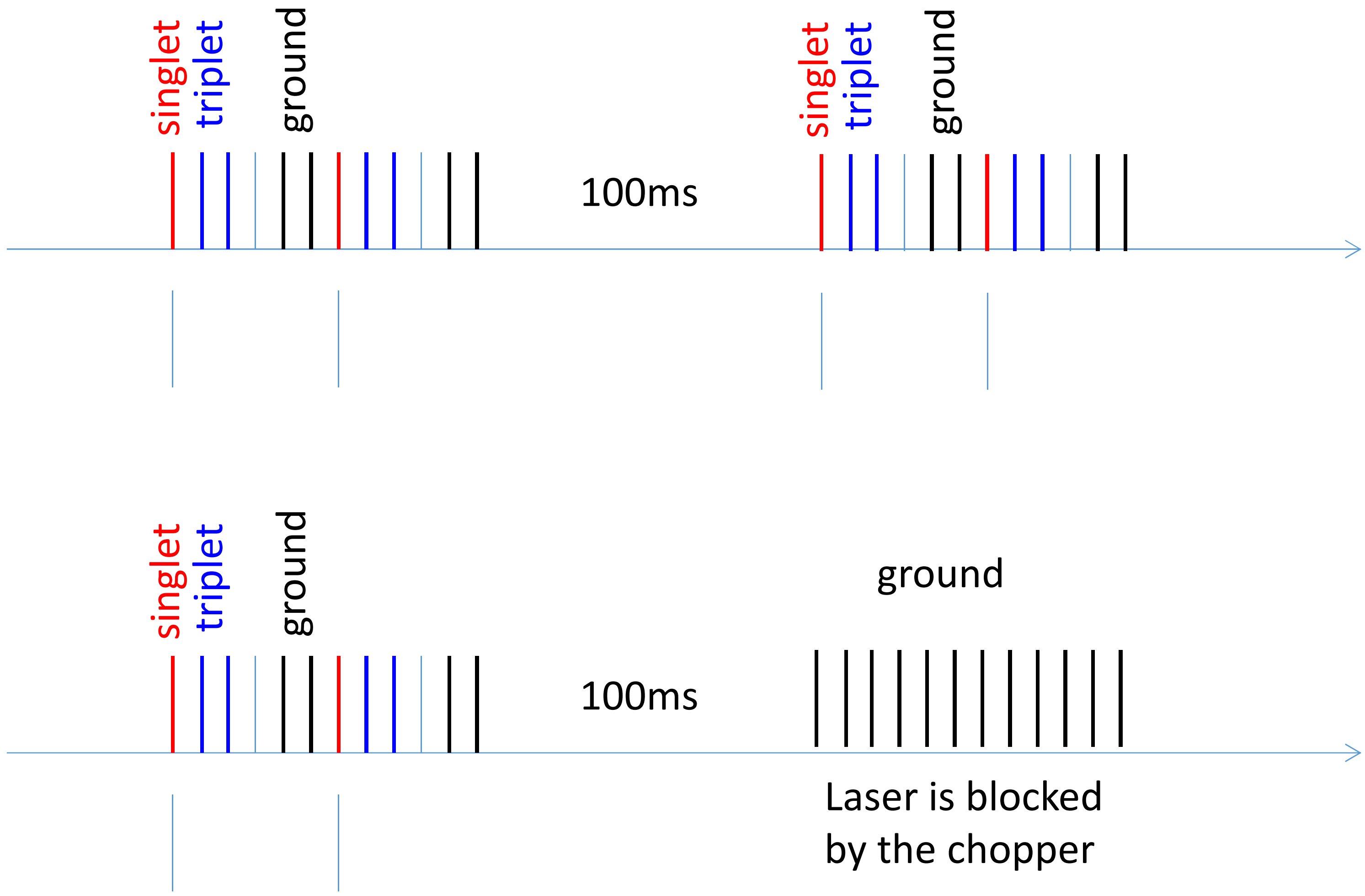
Cu_c-Cu_c increases by 0.05 Å

Cu_P-Cu_P decreases by 0.12 Å.

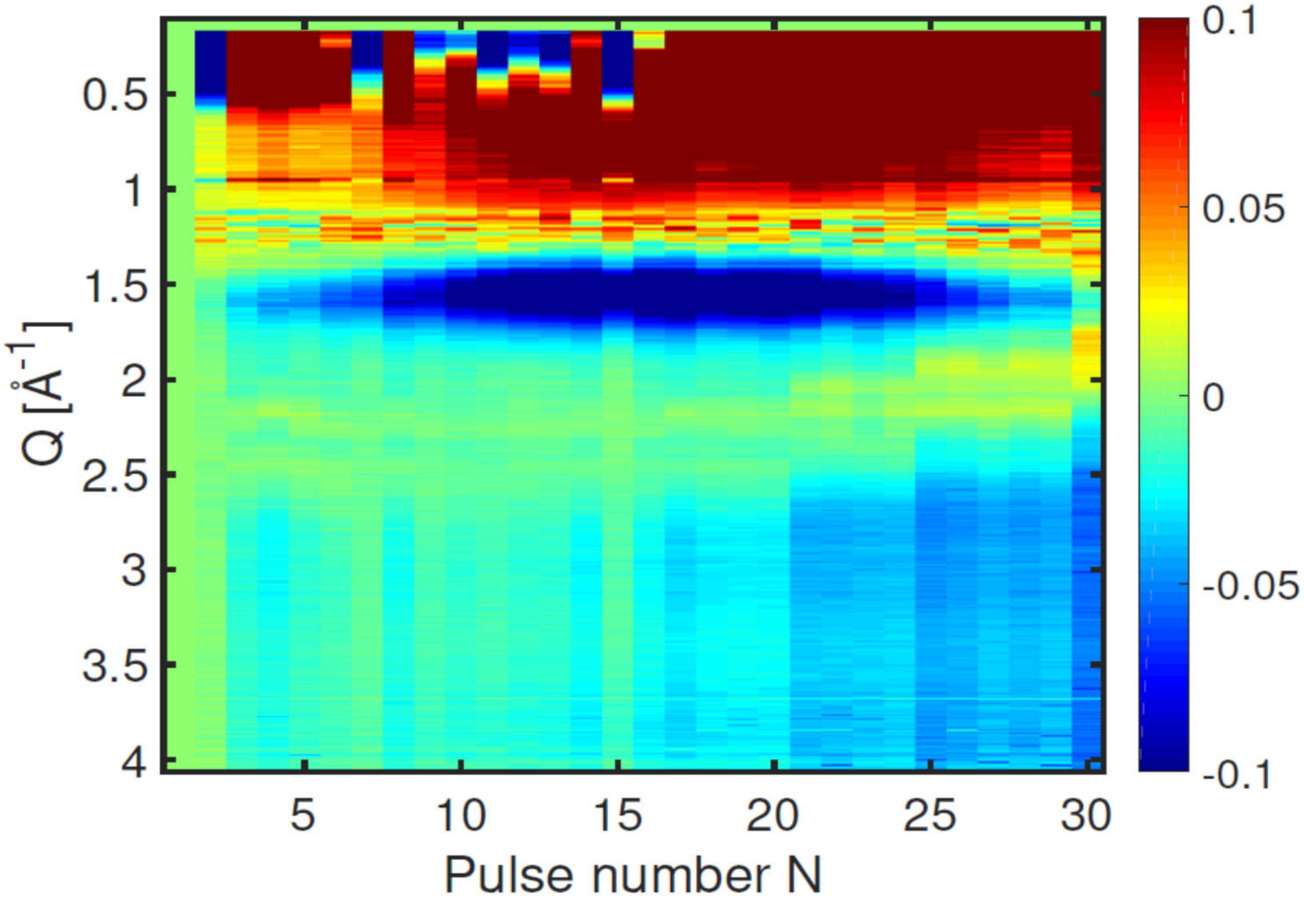
Strategies to use burst mode of European XFEL



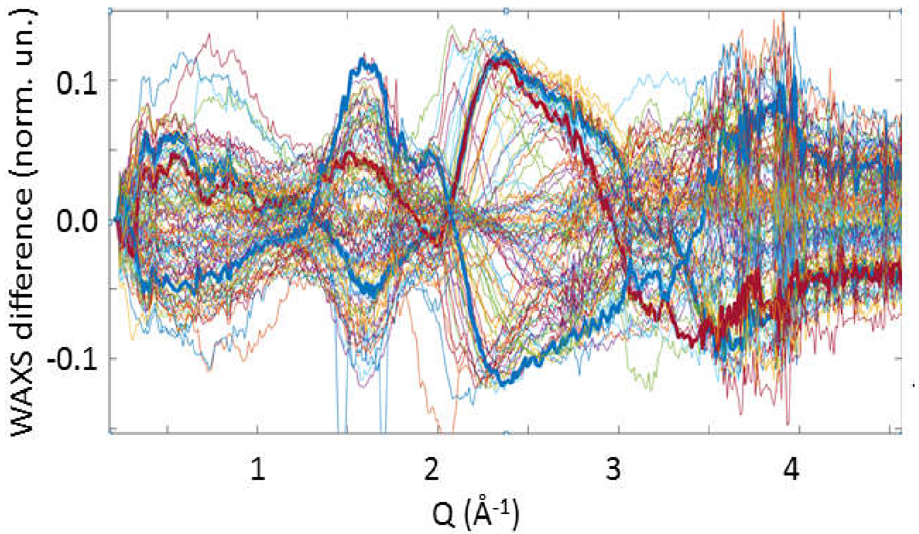
Strategies to use burst mode of European XFEL

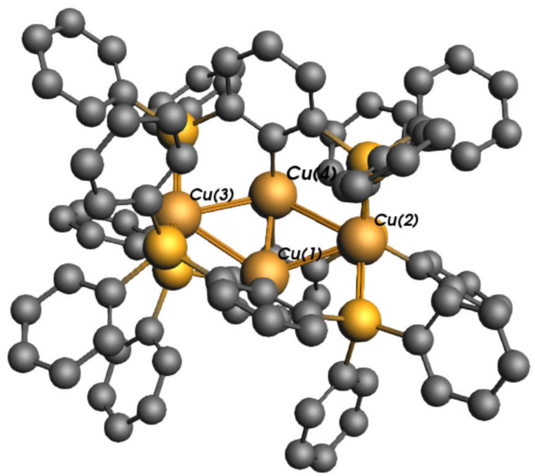


We observed X-ray induced changes within burst even at lower repletion rate of X-ray pulses

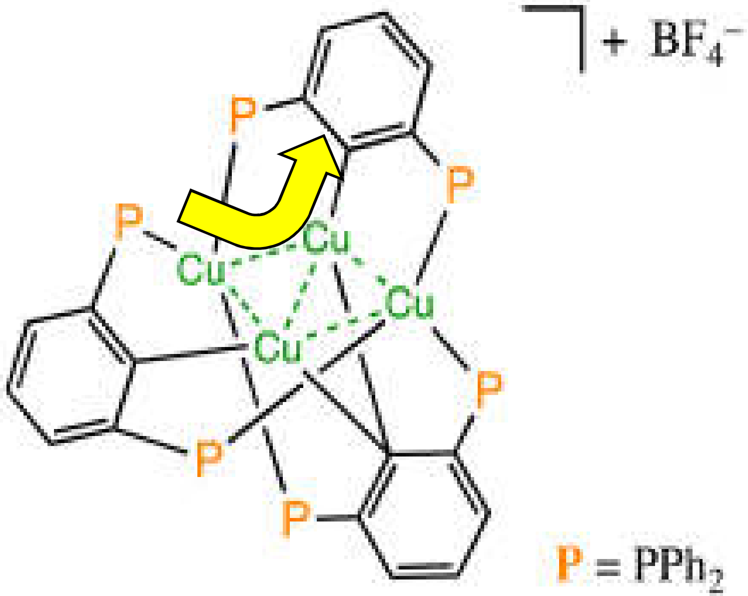


Analysis of a few ps data to determine the singlet structure is in progress





Conclusion



SuperXAS of SLS, ID09 of ESRF,
FXE of Eur. XFEL and Alvra of SiwssFEL
provides complementary information

Photoexcitation leads to the charge movement from both types of Cu and P atoms to phenyl groups

DFT predictions about structural changes in the triplet state has been verified using X-ray scattering

Thinking about SASE 4/5 options

Pump-probe spectroscopy (XAS XES RIXS with ultra hard x-rays (Pt K-edge (78 keV))

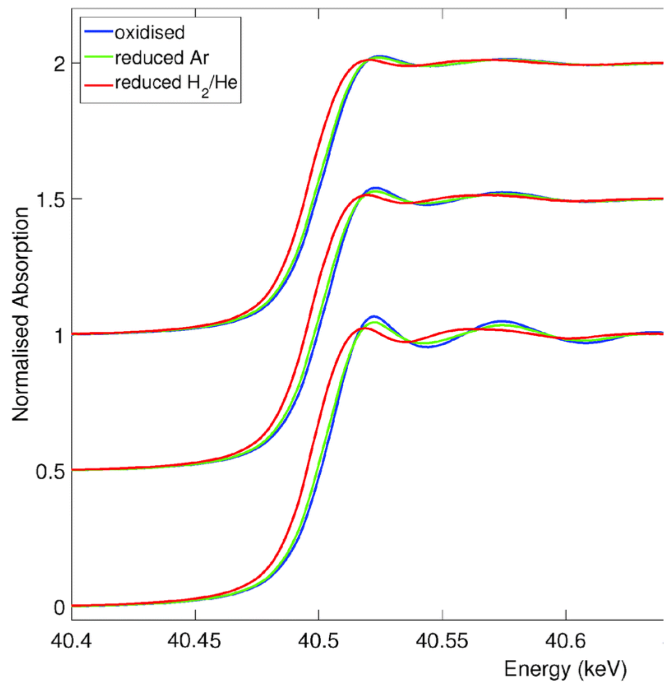
Normal XAS and XES not informative(large core hole energy width)

RIXS and (HERFD) are not explored (require high resolution (~1 eV) transmission type XES spectrometers and monochromators)

Hard X-ray are good for in situ/in operando (inside real reactors),

but mismatch of depth for ultrafast pump and probe

Ce K-edge (40.5 keV)



Pump-probe X-ray scattering with ultra hard X-ray

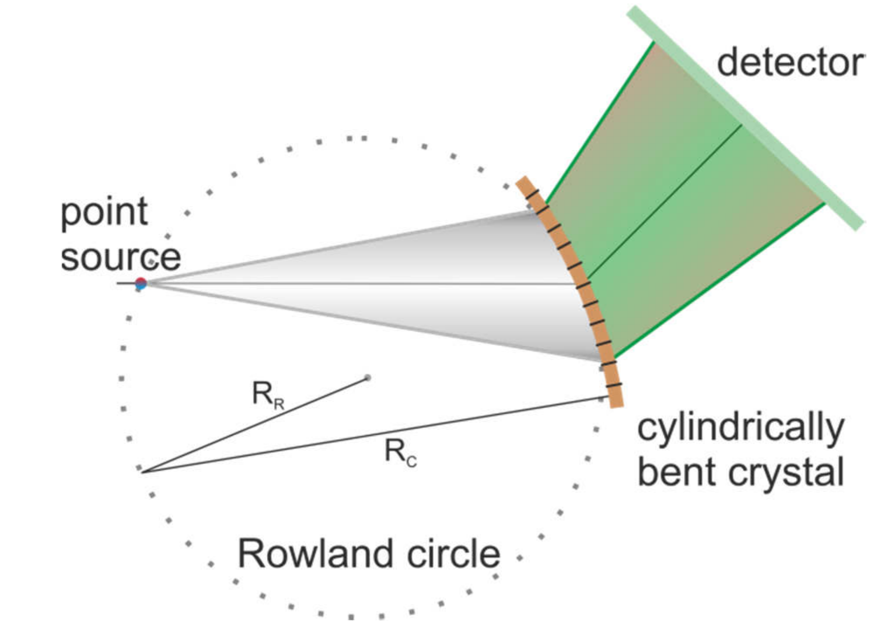
Clear benefits:

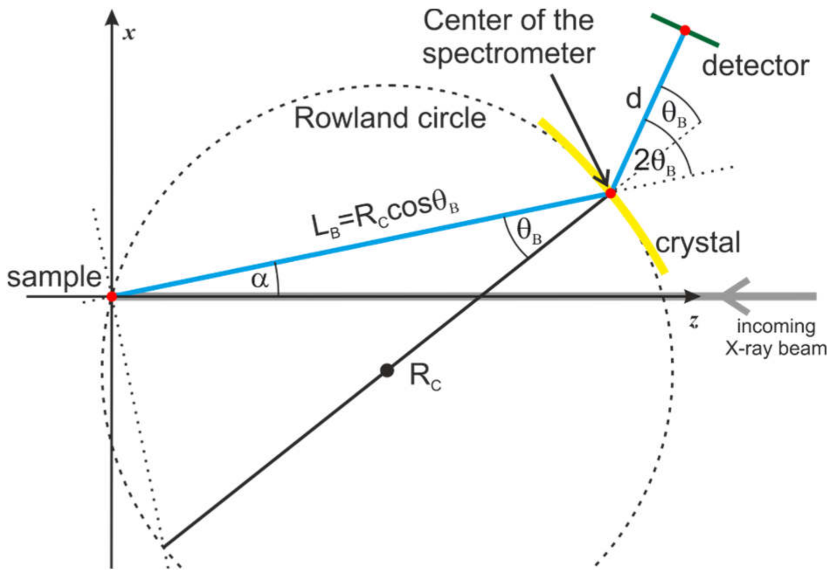
Extension of Q range (~30 $Å^{-1}$)

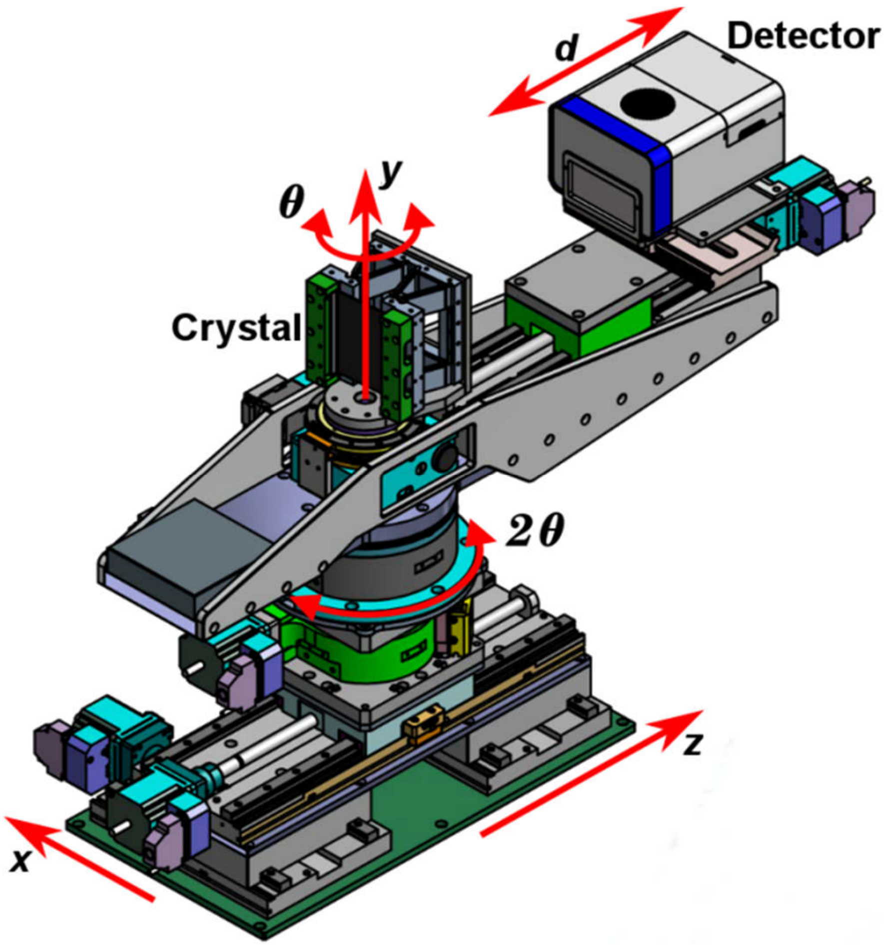
Going from verification or refinement of models (in the limited Q range) to

pair distribution function type of analysis

Requires attention:
Lower cross-section for hard X-rays
(sensitivity to movements of low Z elements lower)


detector
point
source
R_R
R_C
cylindrically
bent crystal
Rowland circle


x
Center of the
spectrometer
detector
d
θ_B
$2\theta_B$
Rowland circle
$L_B=R_C\cos\theta_B$
θ_B
crystal
sample
α
z
incoming
X-ray beam
R_C


d
Detector
θ
y
Crystal
2θ
z
x