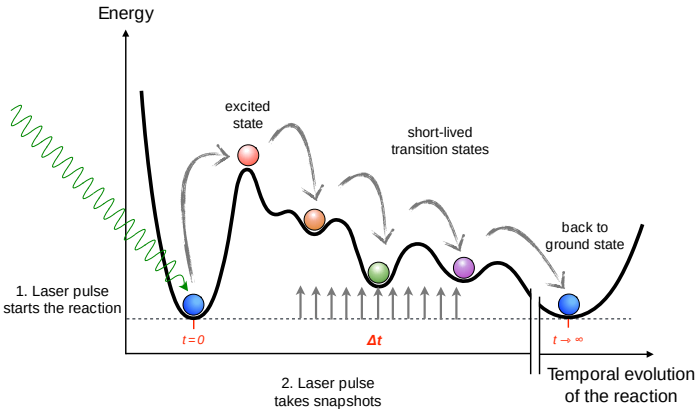
Ultrafast X-ray Spectroscopies at the European XFEL

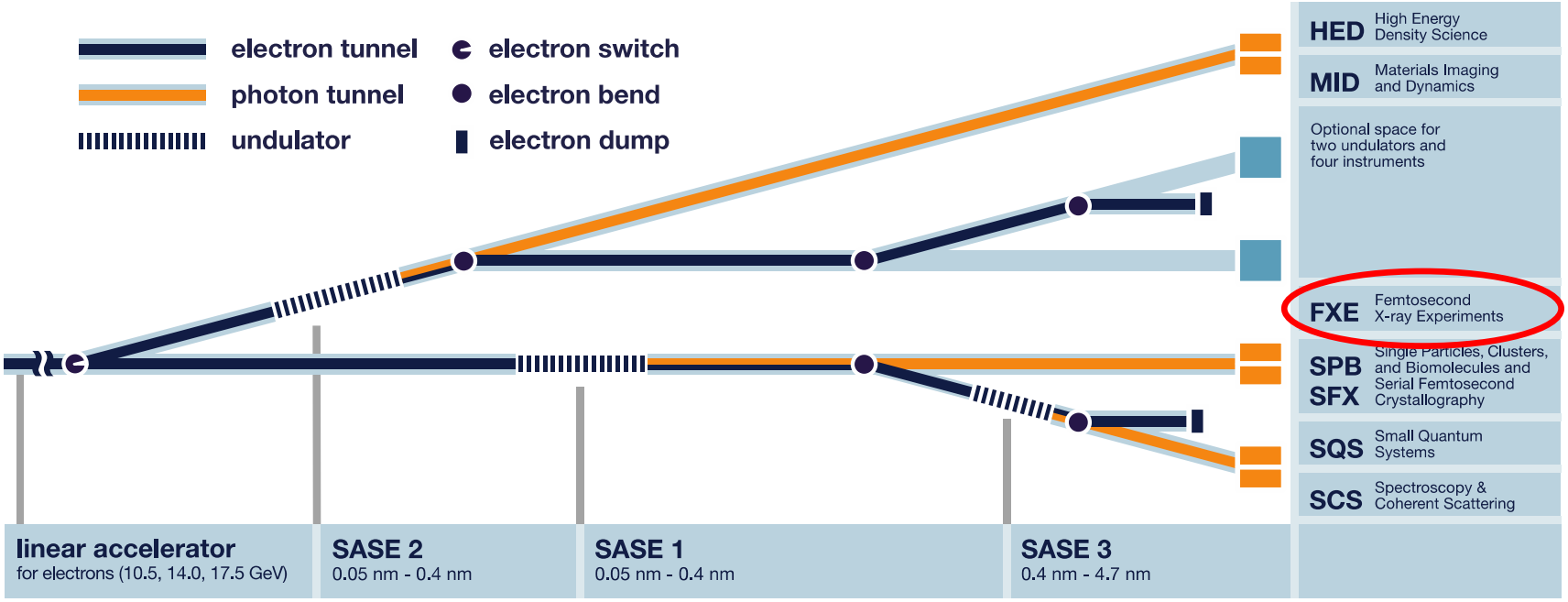
Frederico Alves Lima
European XFEL – FXE

Workshop on Chemical Dynamics and Energy, 11.12.2019



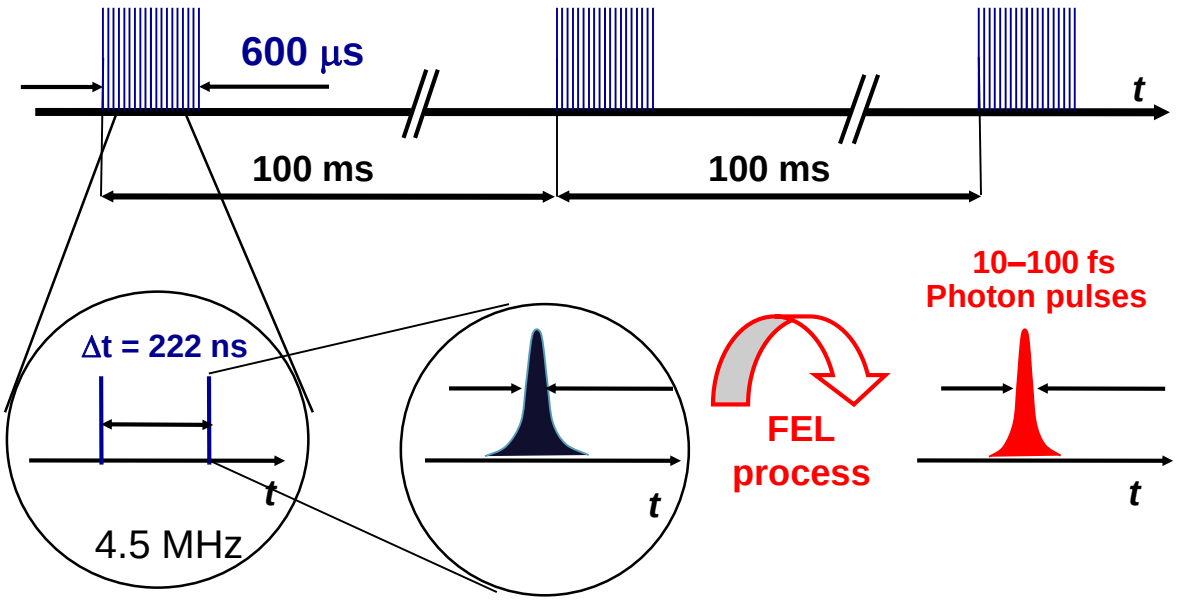
The European XFEL

The European XFEL



EuXFEL: radiation time structure

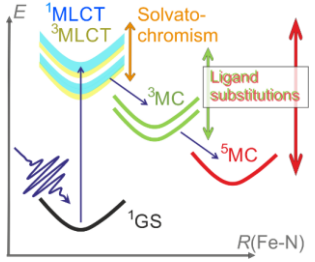
Electron bunch trains
(with up to 2700 bunches, 0.1–1 nC)



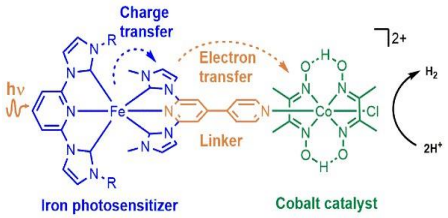
Up to 27 000 pulses/s

Scientific cases

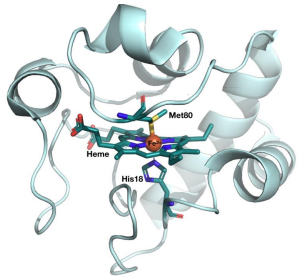
- Manipulating and mapping out the potential energy surface (PES) landscape in Fe(II)-based complexes



- Dynamics of light conversion in iron based photosensitizers

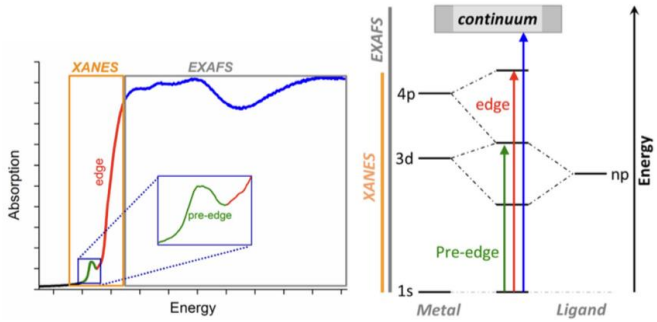


- Electron transfer and doming in ferric heme proteins

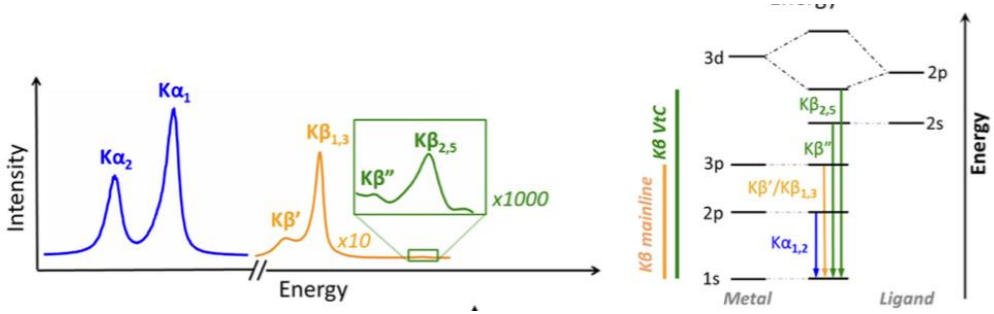


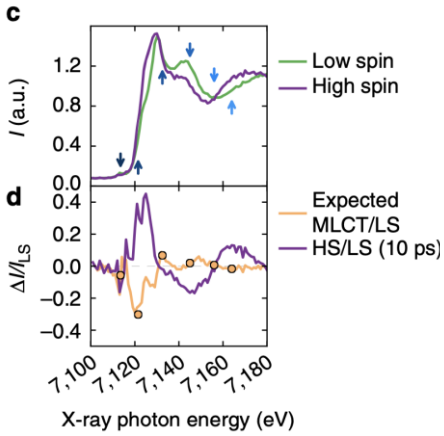
Tools and observables: time-resolved X-ray spectroscopy

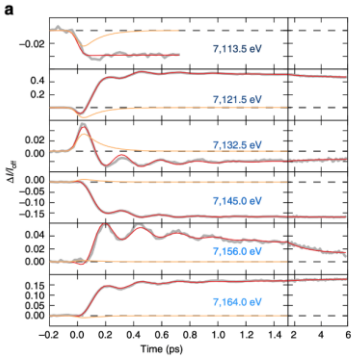
XAS

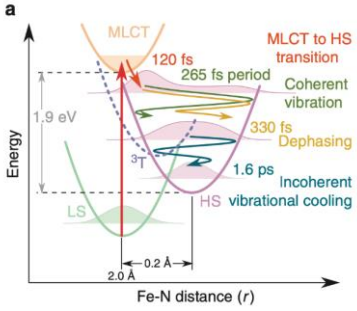


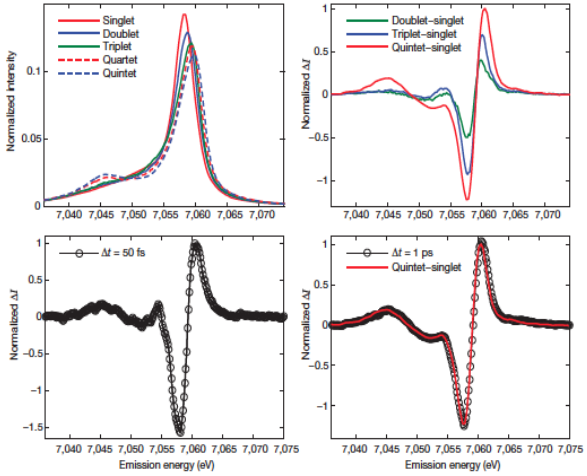
XES







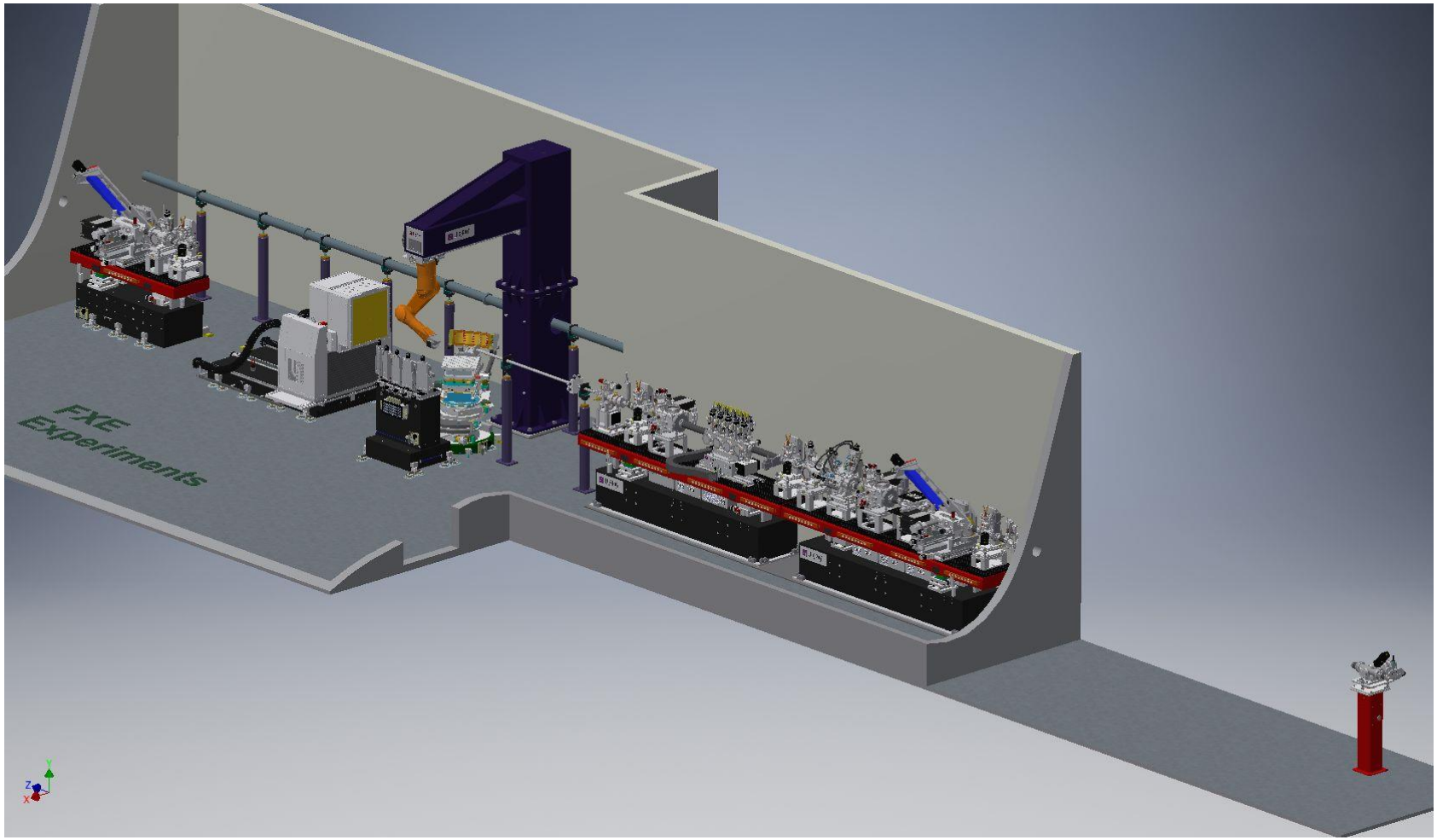




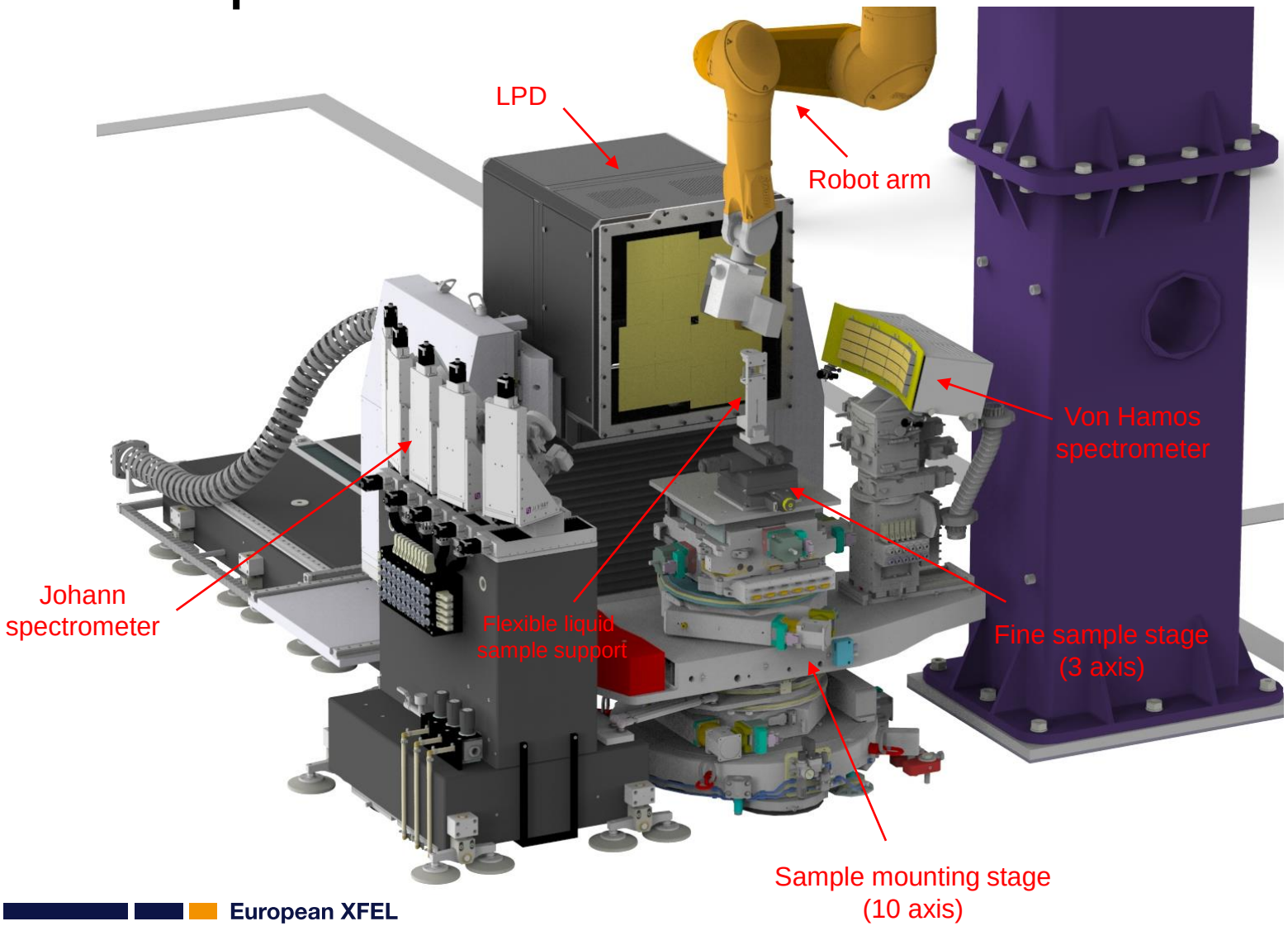
Spin crossover dynamics of $[Fe(bpy)_3]^{2+}$

Kowalska, J. K., Lima, F. A., *et al.*, Isr. J. Chem., **56**, 9-10 (2016) 803
W. Zhang *et al.*, Nature, **509** (2014) 345
H. Lemke *et al.*, Nature Comm., **8**, (2017) 15342

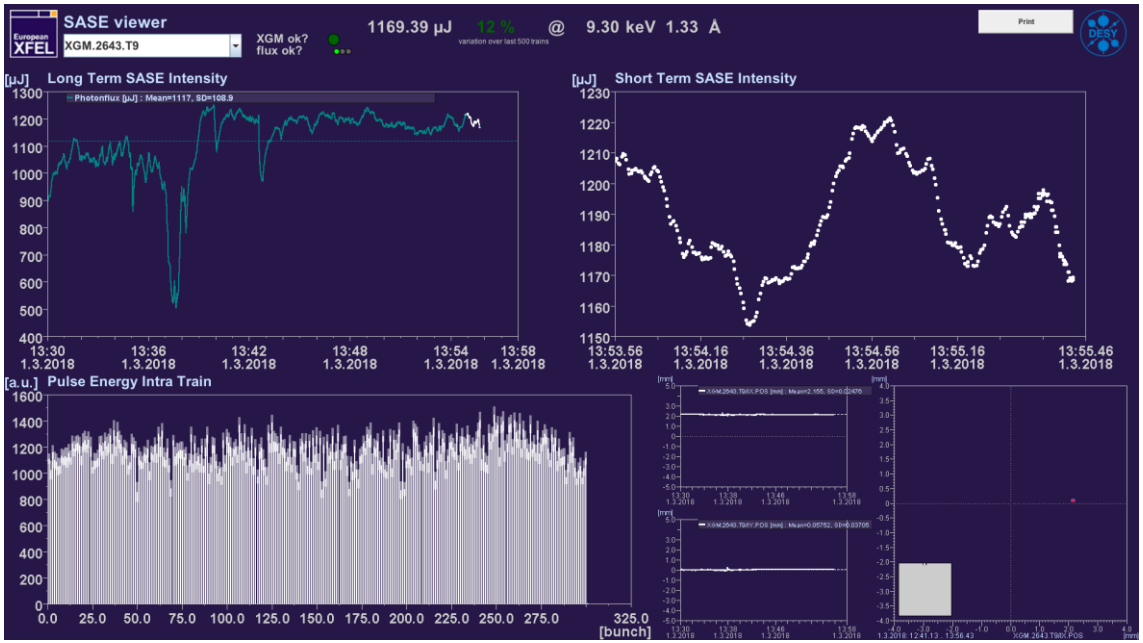
FXE Instrument Overview

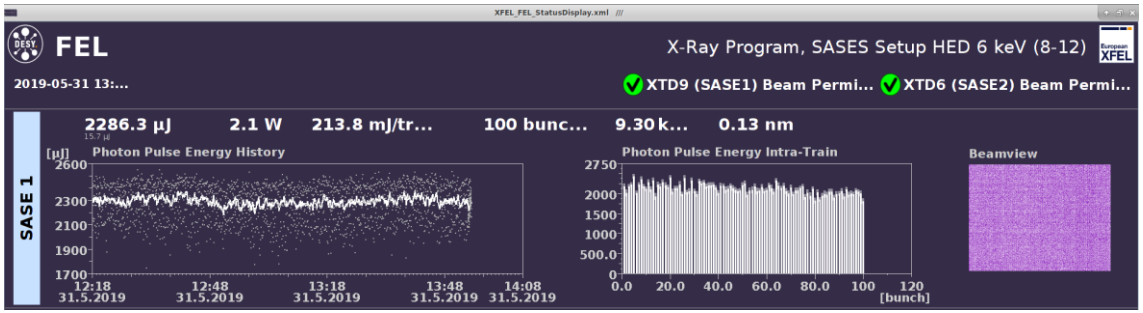


FXE: Sample interaction area

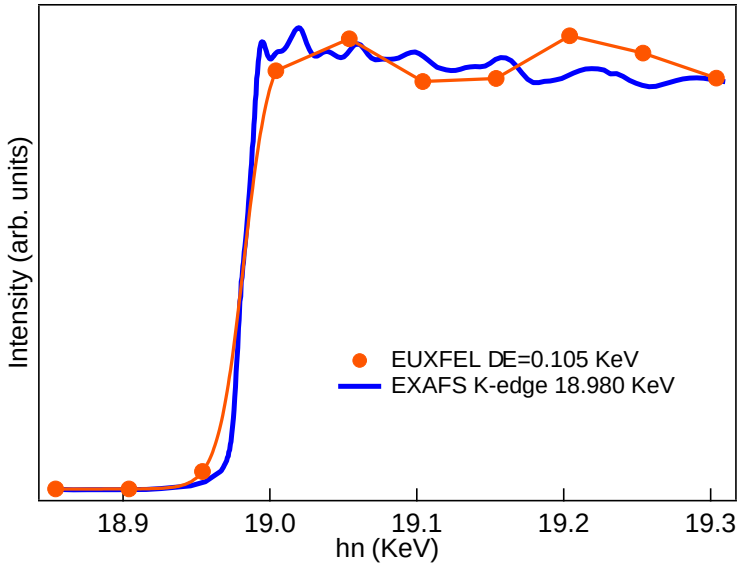


Milestones: 300 pulses in a train at 1 MHz & >2mJ/pulse

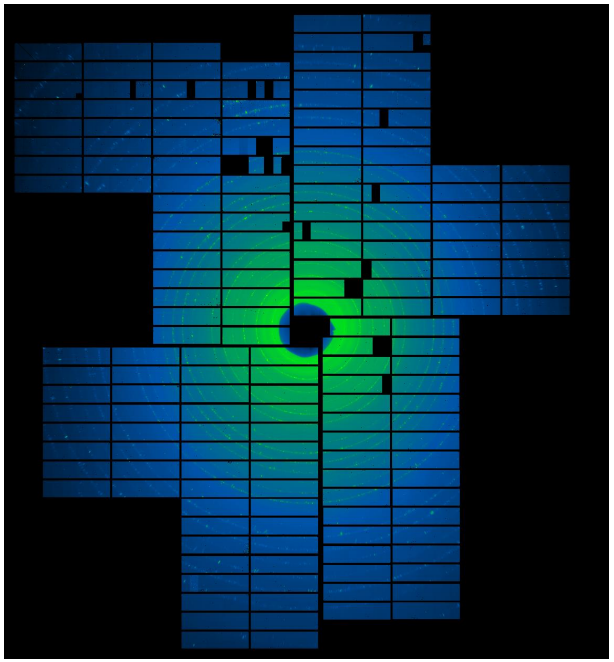




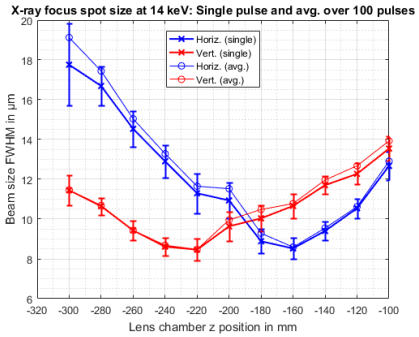
Milestones: high photon energies



Nb K-edge ~19 keV



LaB_6 diffraction collected with LPD @ 14 keV

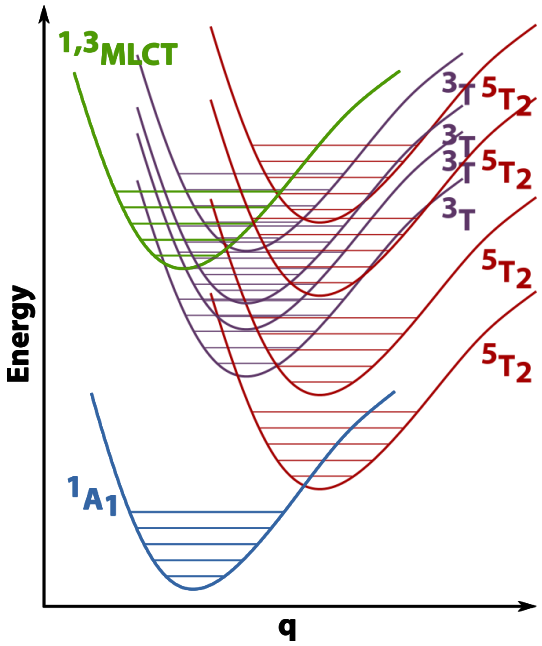


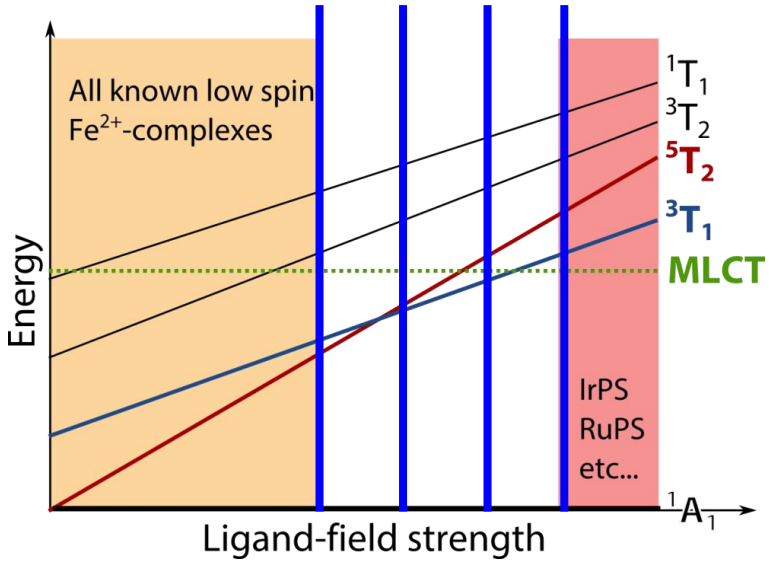
Beam size at sample: ~10 µm

Unique opportunities at high X-ray energies!

Long-lived charge-separated excited states in Fe^{II} complexes

Using solvent and DFT-optimized ligand substitution the PES landscape (in particular conical intersections) can be controlled and intramolecular relaxation rates can thus be modified.

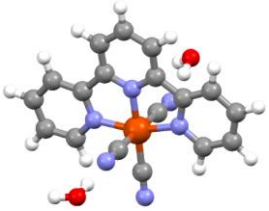




Perspective: Fe(II)-based photosensitizers in photovoltaics or molecular photocatalysis (*i.e.* H_2O splitting)

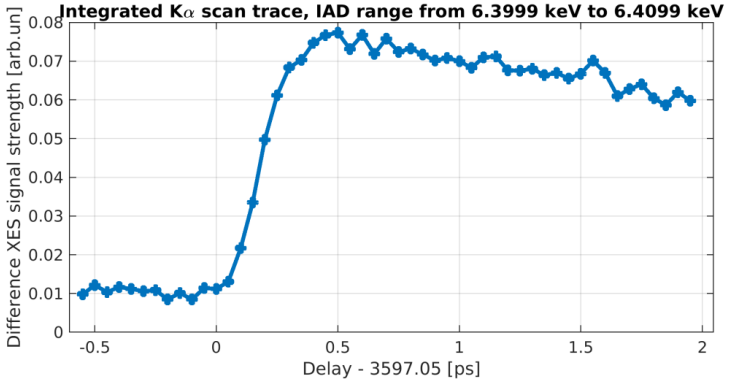
T. Harlang *et al.,* Nature Chemistry (2015), Y. Liu *et al.,* Chem. Eur. J. (2015)
L. Jamula *et al.*, Inorg. Chem. (2014), D. Bowman et al., Inorg. Chem. (2015)

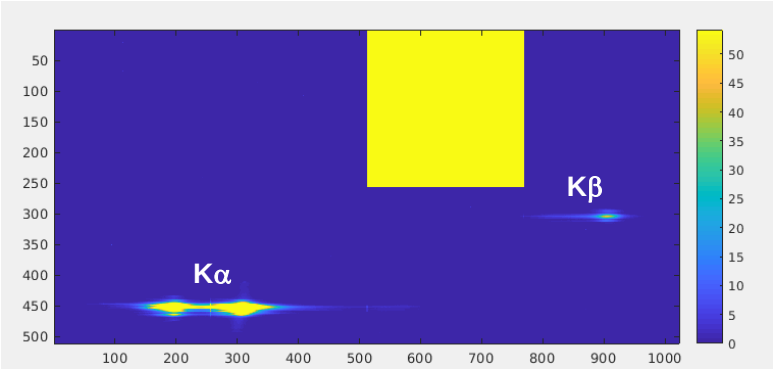
Femtosecond XES on $[Fe(tpy)(CN)_3]^-$ solutions

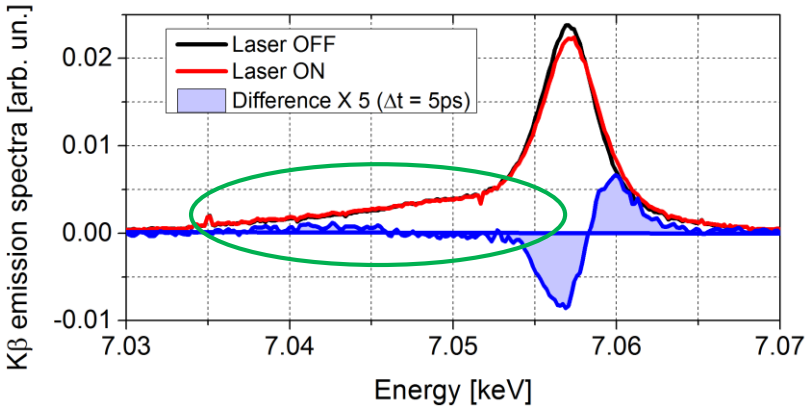


Substituting weak ligand field (LF) polypyridyl ligands, *e.g.* bipyridines or terpyridines, with electron-donating ligands, *i.e.* cyano groups, modifies the relative energies of MLCT and MC states and consequently extends the lifetime of the CT states (charge-separated states)

- Simultaneous detection of both iron Kα and Kβ emission
- Excellent temporal resolution
- High quality XES → lineshape analysis

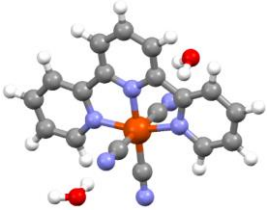




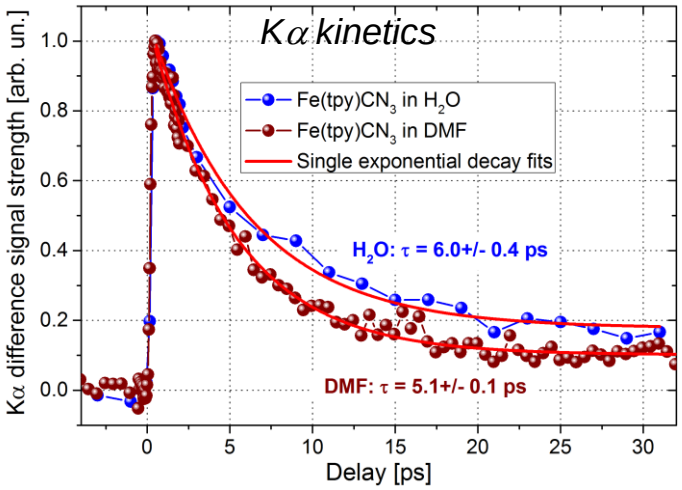


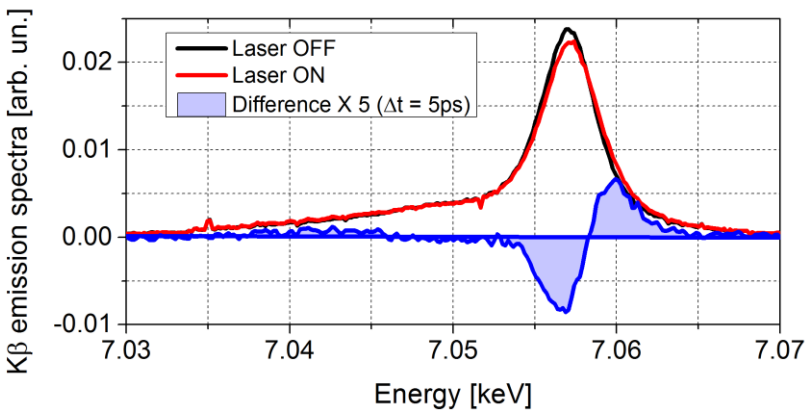
We are on our way!

Femtosecond XES on $[Fe(tpy)(CN)_3]^-$ solutions

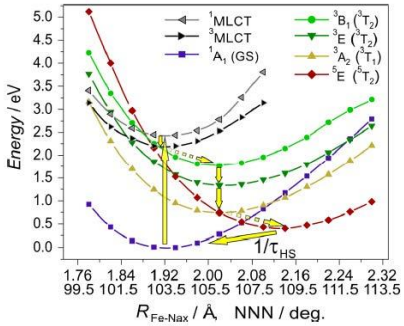


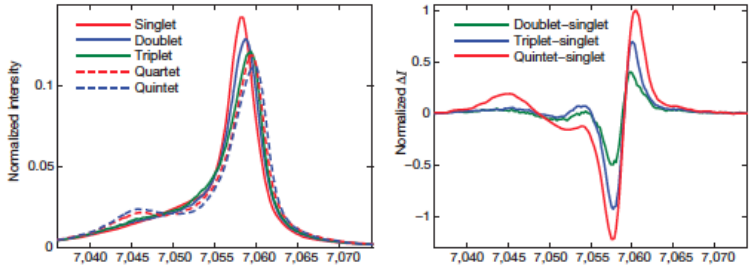
XES kinetics agrees with intermediate spin state lifetime via (TD-)DFT and femtosecond optical spectroscopy.





Mixture of triplet and quintet states, but <u>mostly</u> triplet

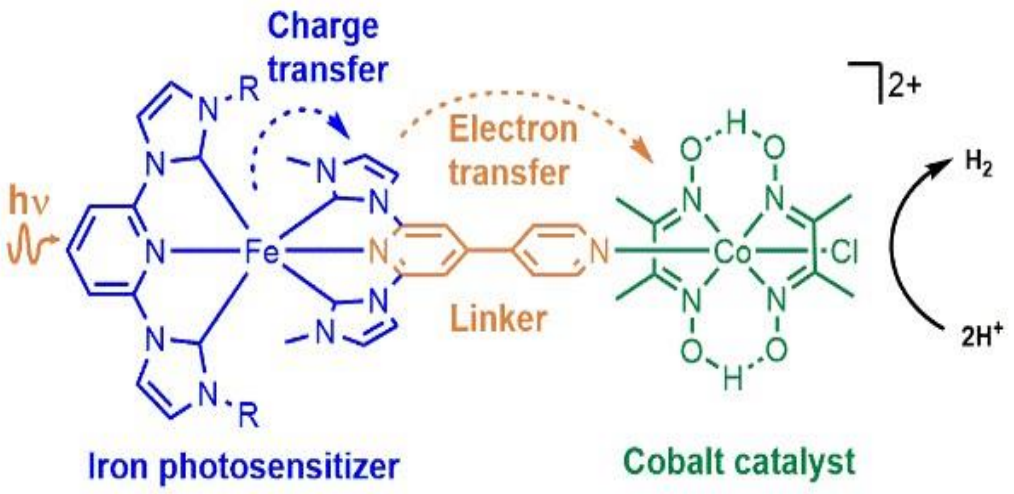


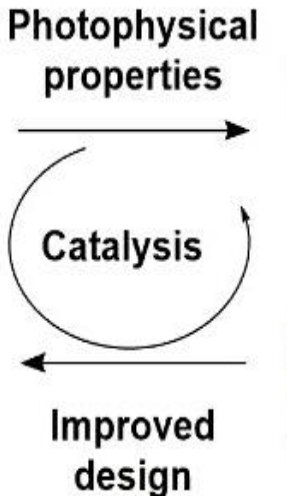


W. Zhang *et al.*, Nature, **509** (2014) 345
G. Vankó, et al; J. Phys. Chem. C, (2015)

Dynamics of light conversion in iron based photosensitizers

Iron-based photosensitizers present a drawback compared to Ru or Ir analogous due to short-lived MLCT states, which rapidly relax into long-lived MC states affecting efficient catalysis.

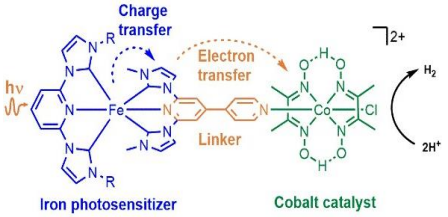




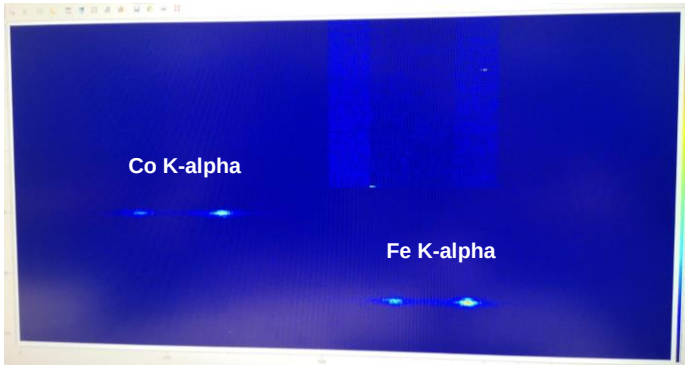
Perspective: Circumvent diffusion-controlled, hence inefficient charge transfer during charge injection in semiconductors or direct electron transfer in bimetallic dyads for photocatalytic proton reduction.

Dynamics of light conversion in iron based photosensitizers

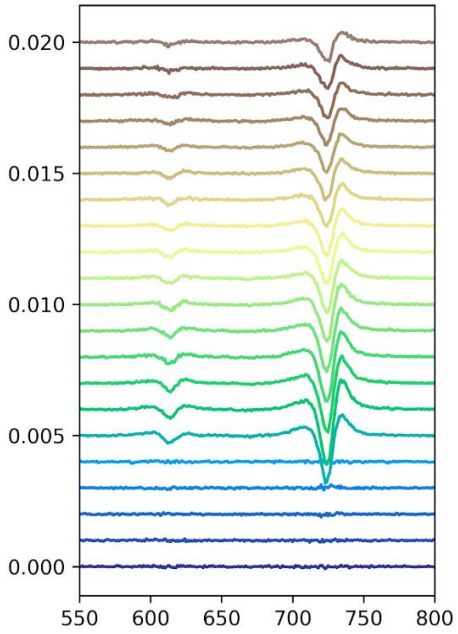
Does a long(er) MLCT lifetime implies on a more efficient charge transfer?



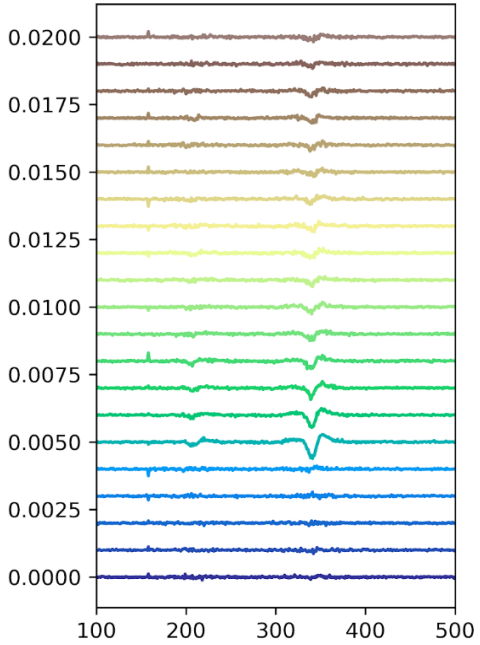
- Simultaneous detection of both iron Kα and iron Kα emission
- No uncertainty about t_0

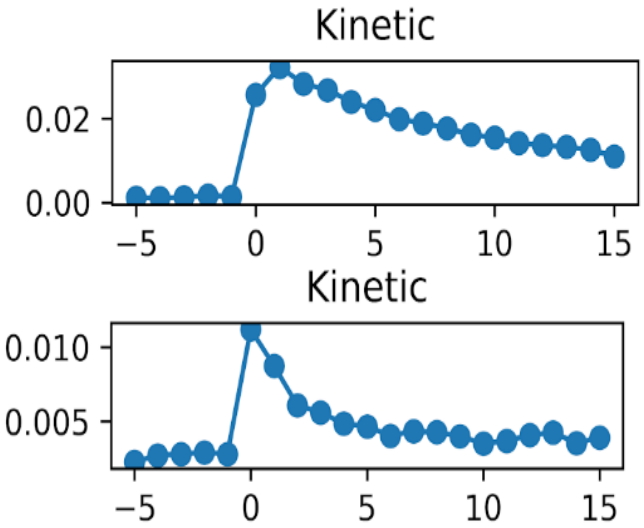


Fe Kα



Co Kα




Kinetic
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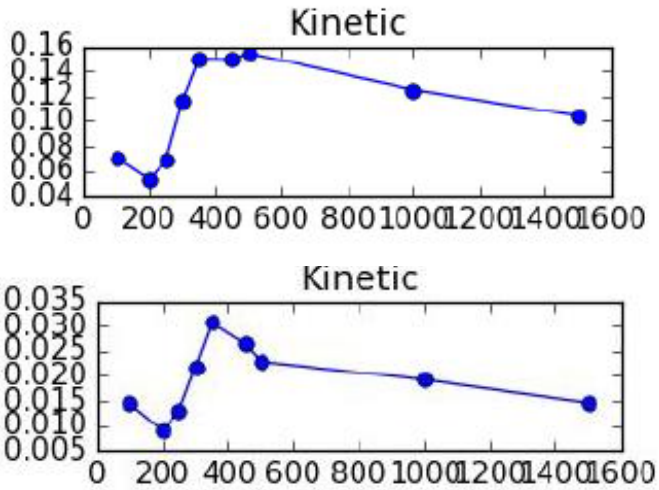
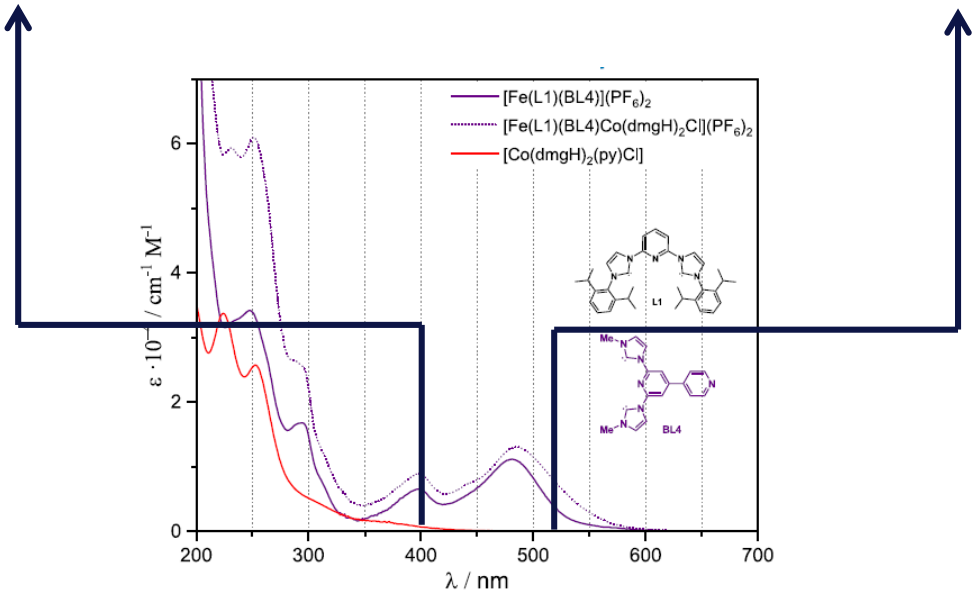
0.00
−5
0
5
10
15
Kinetic
0.010
0.005
−5
0
5
10
15


Kinetic
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0
200
400
600
800
1000
1200
1400
1600
Kinetic
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0
200
400
600
800
1000
1200
1400
1600

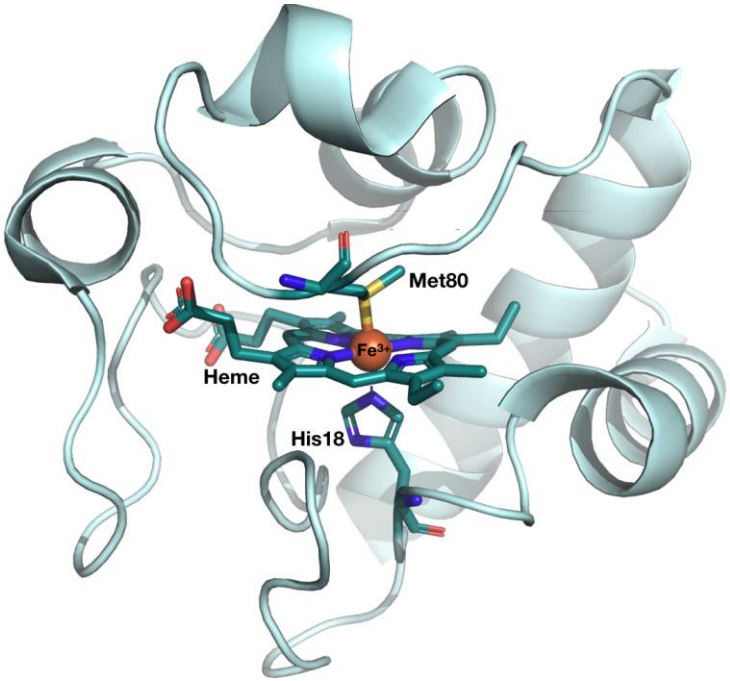
Fe Kα

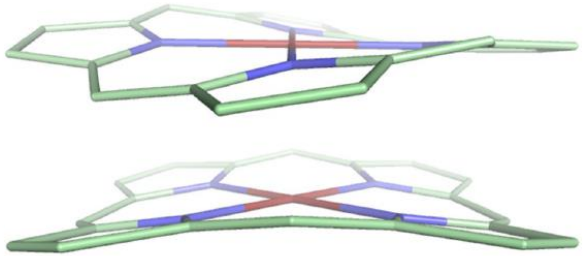
Co Kα


[Fe(L1)(BL4)](PF6)2
[Fe(L1)(BL4)Co(dmgH)2Cl](PF6)2
[Co(dmgH)2(py)Cl]
ε ·10⁻⁴ / cm⁻¹ M⁻¹
λ / nm
200
300
400
500
600
700
0
2
4
6
L1
BL4

Electron transfer and doming in ferric heme proteins

Heme structure ruffling ⟺ ability to tune the redox potential ⟺ relevant electron transfer properties in humans.

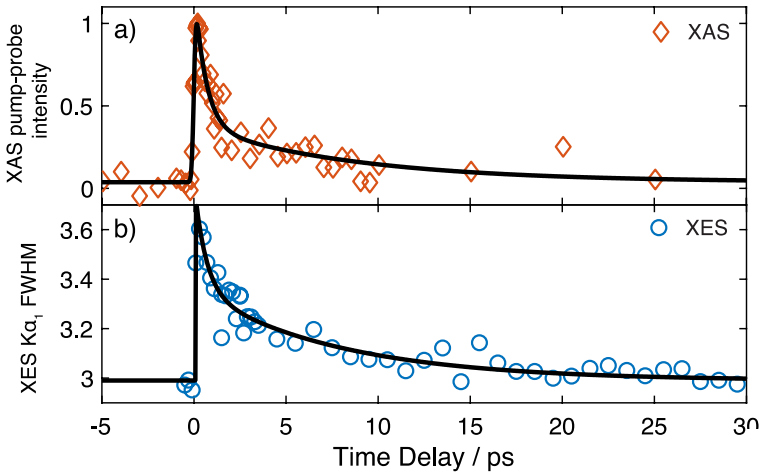


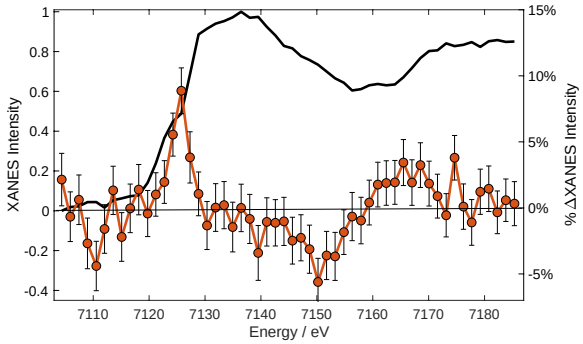


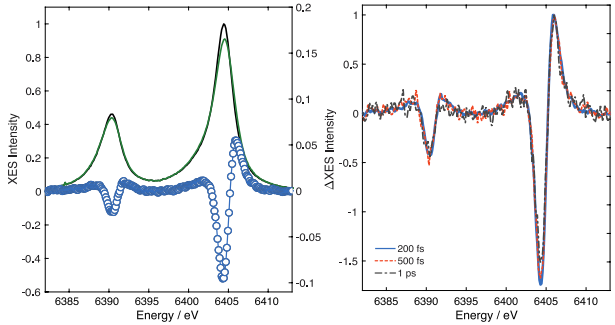
Perspective: Better understanding of the structure deformations (ruffling *vs.* doming) in the high-spin state and its connections with the protein electron transfer properties.

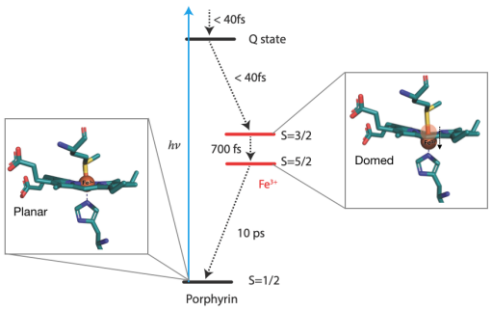
Electron transfer and doming in ferric heme proteins

- What are the structure and electronics of the exited-state(s)?
- Does a ligand detachment occur upon photoexcitation?
- Combined XAS (SwissFEL) and XES (Eu-XFEL)









Acknowledgements

European XFEL

Universität Hamburg
DER FORSCHUNG | DER LEHRE | DER BILDUNG

EUCALL

DESY.

JJ X-RAY
Danish Science Design

SFB
SFB 925: Light induced dynamics and control of strongly correlated quantum systems

EPFL

HUNGARIAN ACADEMY OF SCIENCES

PADERBORN UNIVERSITY

CUI
THE HAMBURG CENTRE FOR ULTRAFAST IMAGING

PAUL SCHERRER INSTITUT
PSI

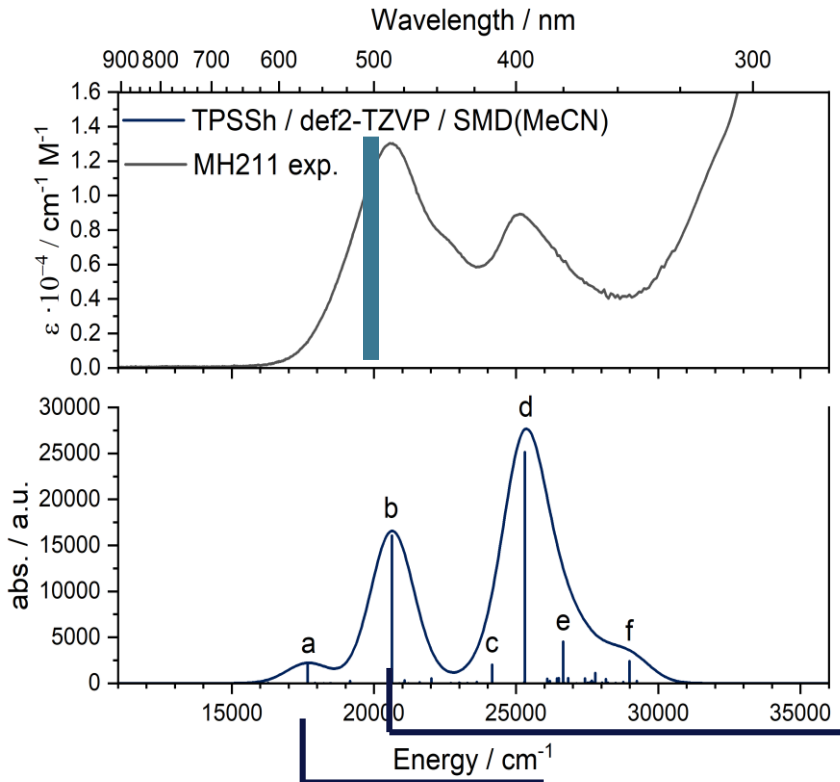
SACLA

IMPRS UFAST

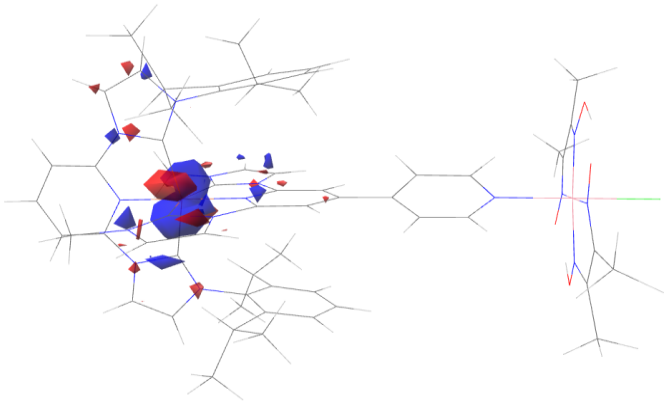
Thank You for Your Attention

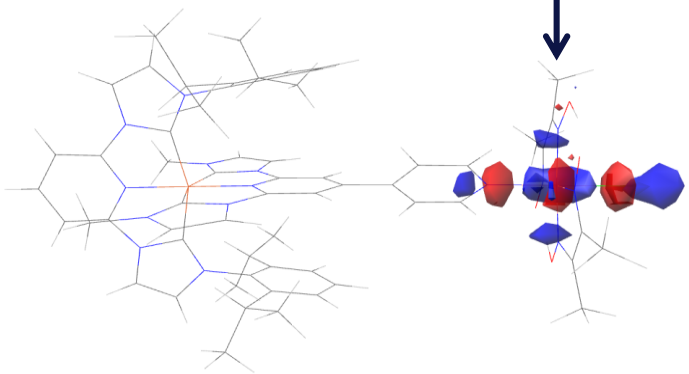
EXTRAS

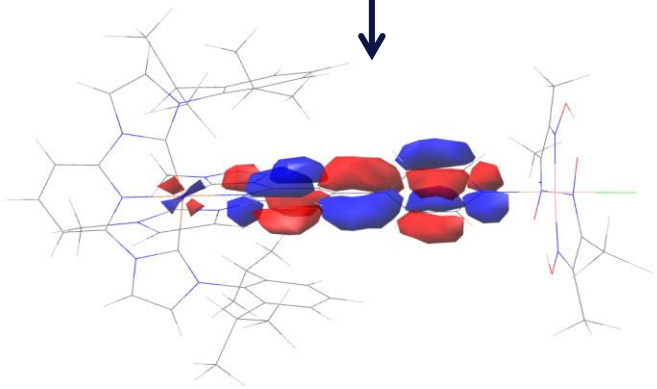
Sample chamber for liquid experiments



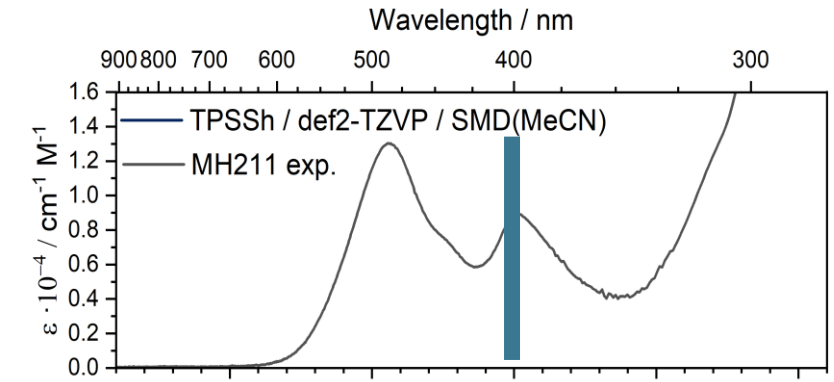
TPSSh, def2-TZVP, SMD (Acetonitrile)

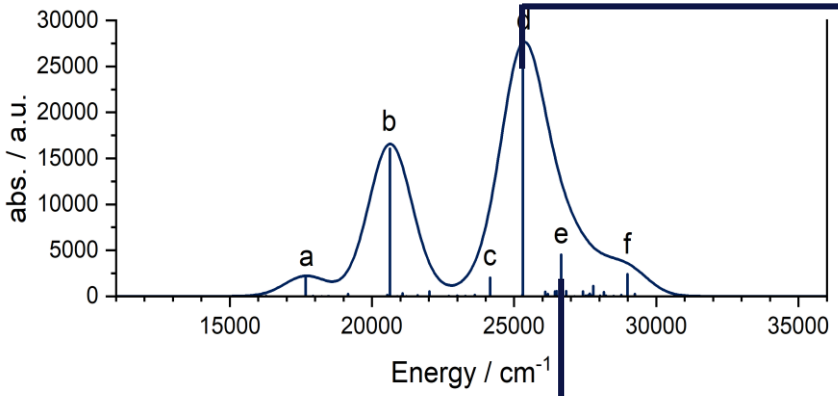


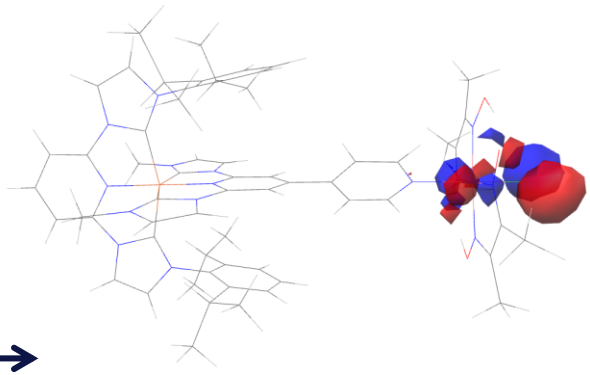


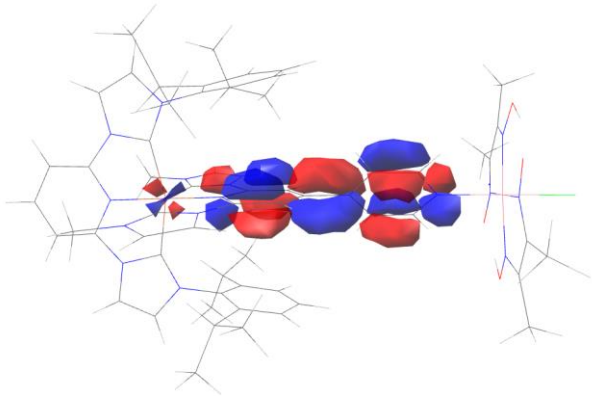


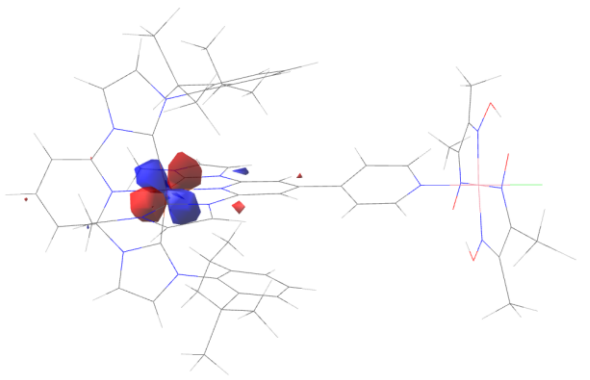
TPSSh, def2-TZVP, SMD (Acetonitrile)

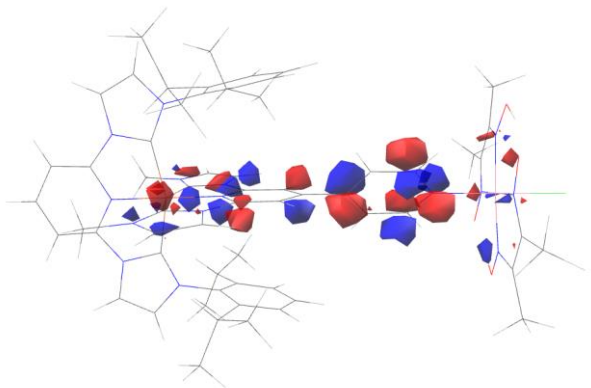












TPSSh, def2-TZVP, SMD (Acetonitrile)