Novel perspectives for Chemistry and Biology with seeded FELs

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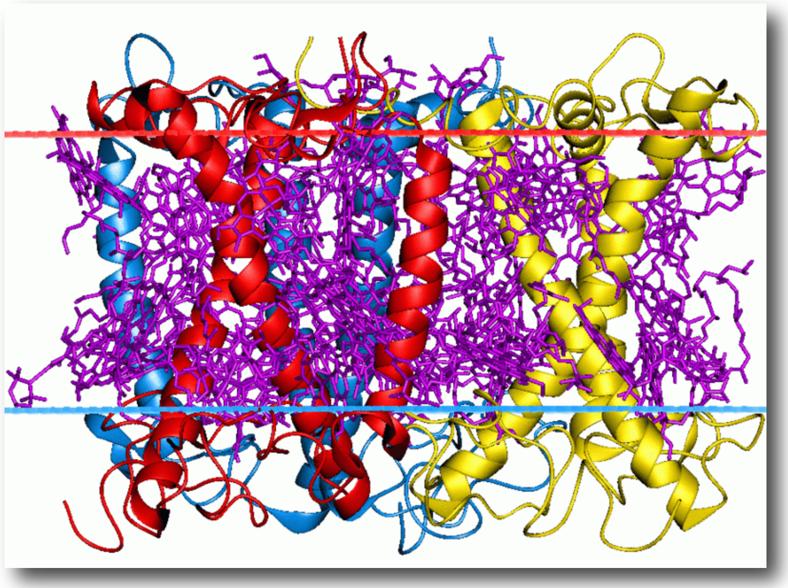
FUSEE Workshop, Trieste 2019

"If you want to understand function, study structure"
(Francis Crick)

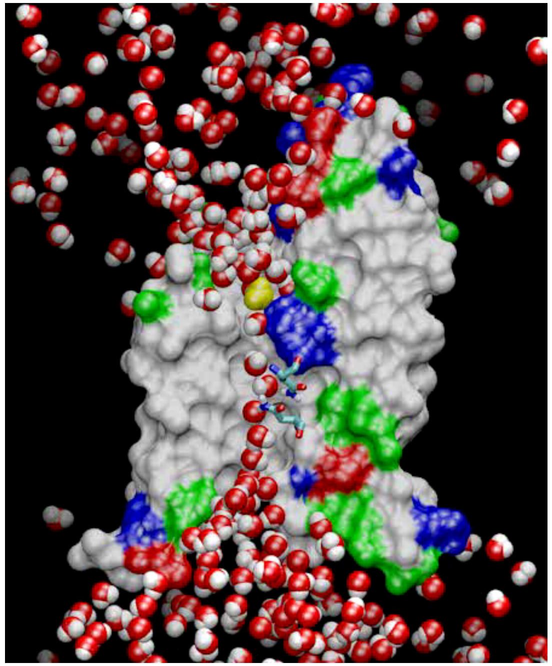
Structure

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



Side view of the light-harvesting complex II in chlorophyll (PDB)

Dynamics



Water transport through an aquaporin channel in a cell membrane
http://www.ks.uiuc.edu/Research/aquaporins/
Tajkhorshid et al. Science 296 (2002) 525-530

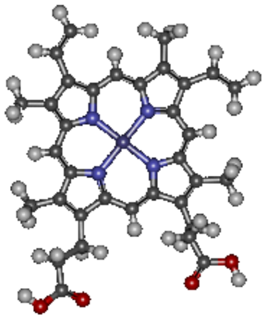
"If you want to understand function, study <u>time-dependent</u> *electronic and molecular* structure

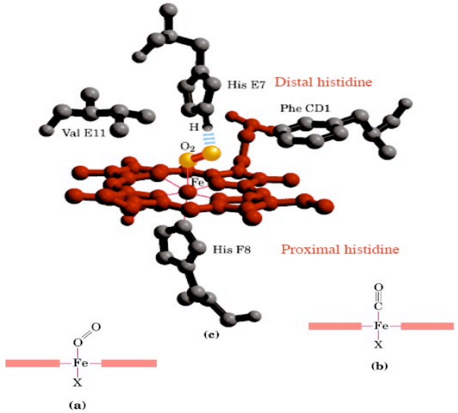
Wish list for chemical and biochemical dynamics

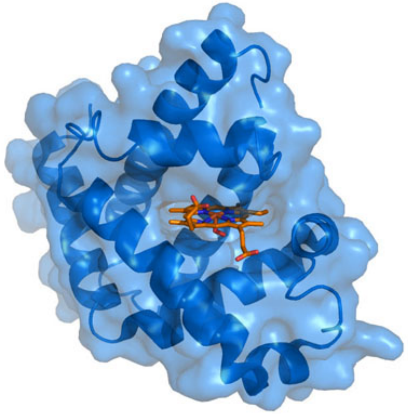
- Element-selectivity
- Molecular structure
- Electronic structure
- Spin structure
- Energy tunability
- Polarization
- Time scales: ≥ 20 fs to ms
- Condensed phase media (liquid, interfaces, amorphous, etc.)

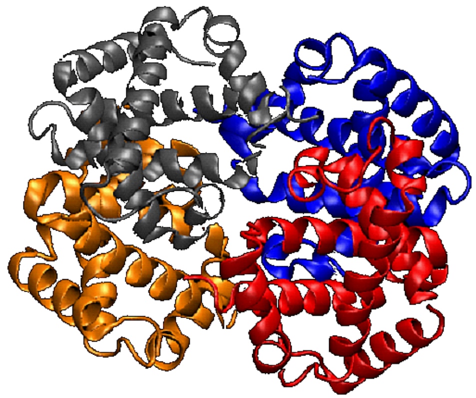
Protein Dynamics in Solution – From Local to Global

10 fs ... 10 ps | **1 ps ... 10 ps** | **10 ps … 100 ps** | **ps ... µs** | **> µs**









Spin dynamics (singlet to quintet)
- *intramolecular ET (ring to metal, metal to ring)*
- *Intramolecular vibrational redistribution (IVR)*
- *Electronic relaxation: internal conversion*

- *Structural dynamics*
- *Ligand dissociation*
- *Doming*
- *Cooling*

- *Dielectric response of amino-acid residues*
- *Cooling and heat transfer*
- *Helix motion*
- *Conformational changes*
- *Correlated motions*
- *Role of biological water*
- *intermolecular ET*

- *Cooperativity*
- *Allostery*
- *Signaling*
- *Respiration*

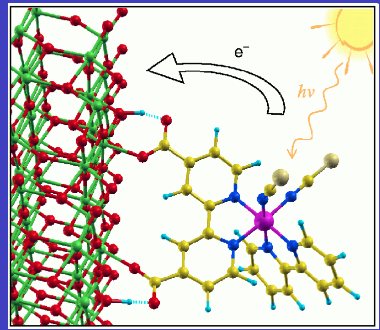
X-ray protein scattering

X-ray spectroscopy (XAS, XES)

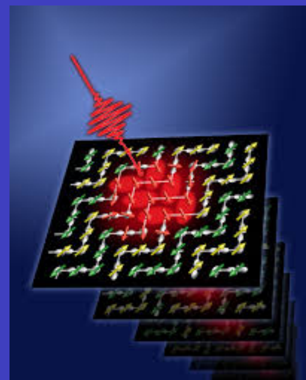
Deep-UV Circular Dichroism

Transition metals

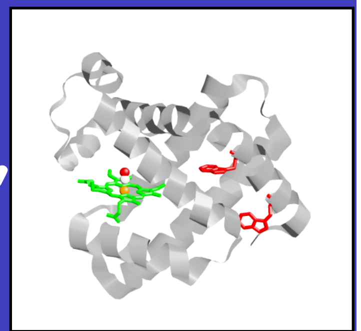
Transition metal complexes



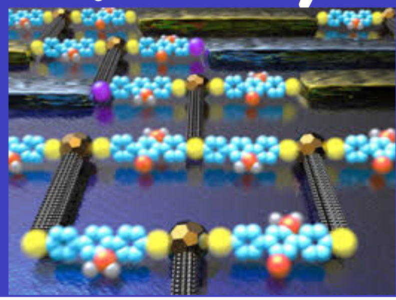
- Solar energy
- Photocatalysis
- Optical materials, OLED, etc.
- Optical writing/magnetic reading (OW/MR) materials



- Biology and biomimetic devices

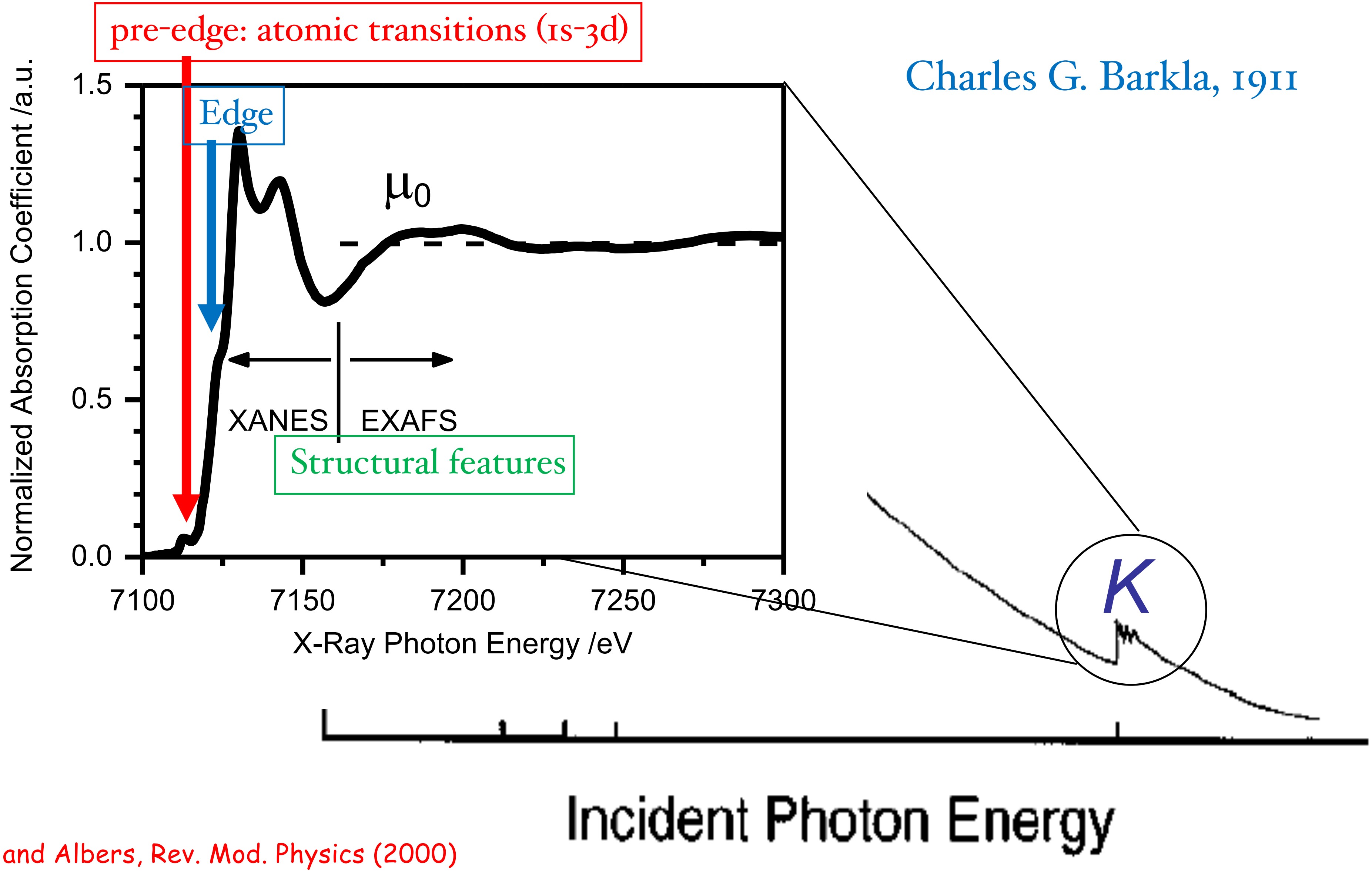


- Molecular electronics (molecular conductors, rectifiers, transistors, memories)



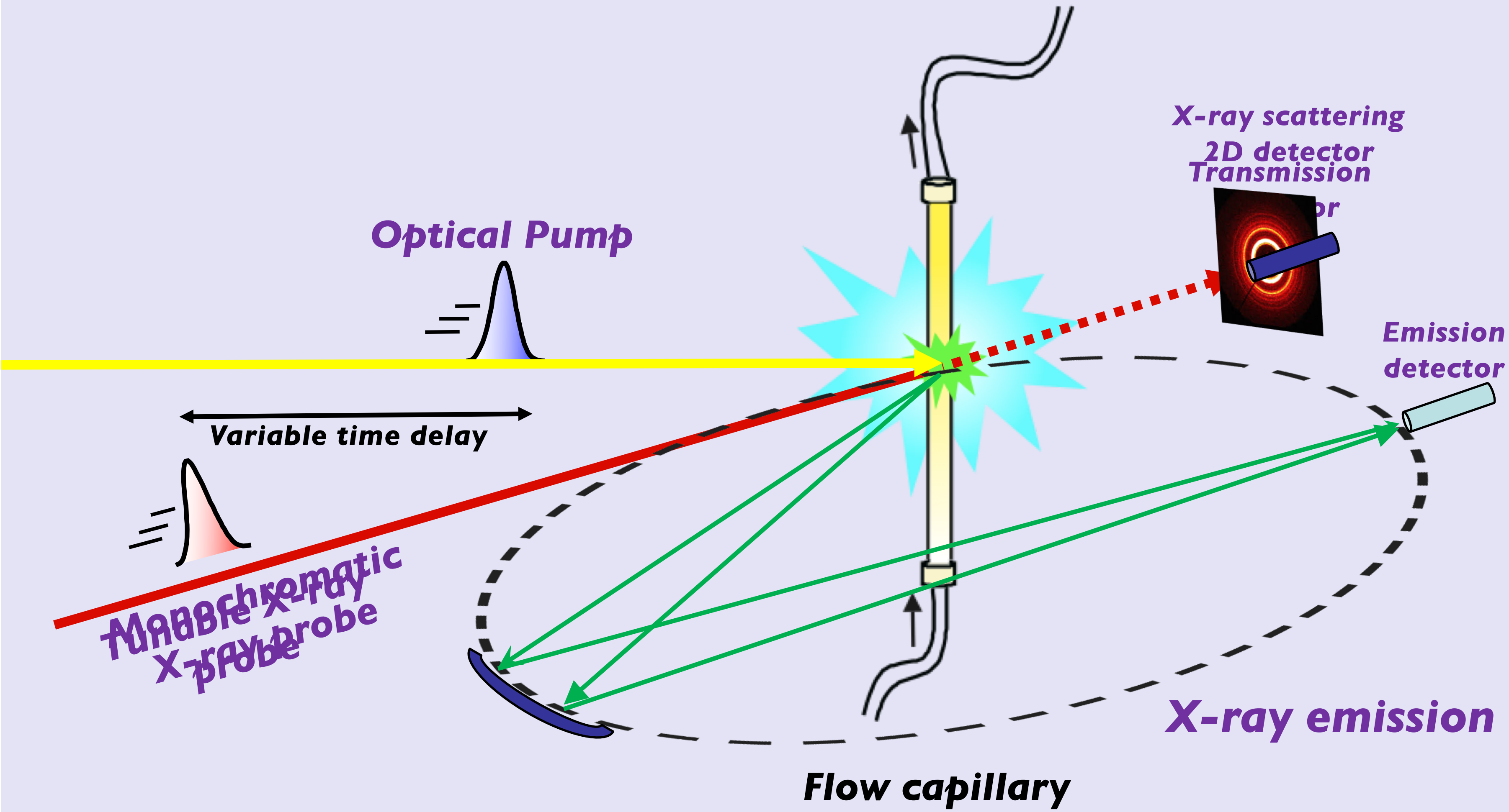
X-Ray Absorption Spectroscopy

Fe K-edge



Rehr and Albers, Rev. Mod. Physics (2000)

Optical pump/X-ray probe spectroscopy



Measured signal= pumped minus unpumped signals

Milne et al, Coord. Chem. Rev. 2014; Chergui and Collet, Chem. Rev. 2018

Energy Tunability

The 200-1000 eV region

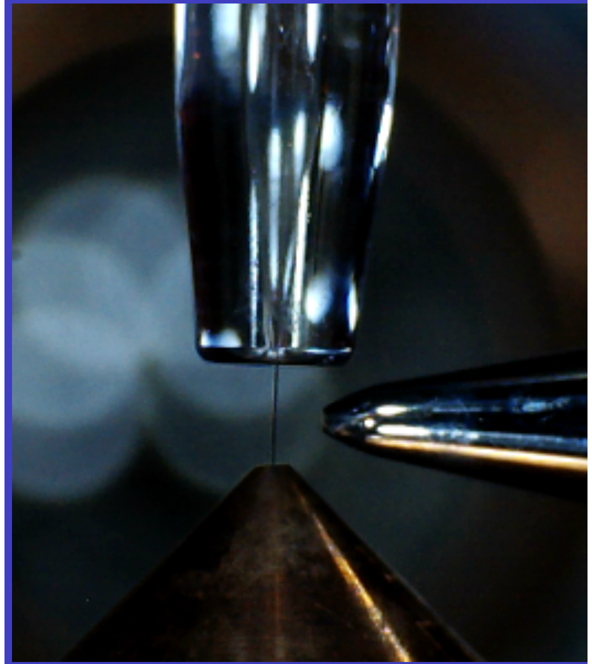
Group → / ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											Al	Si	P	S	Cl	Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

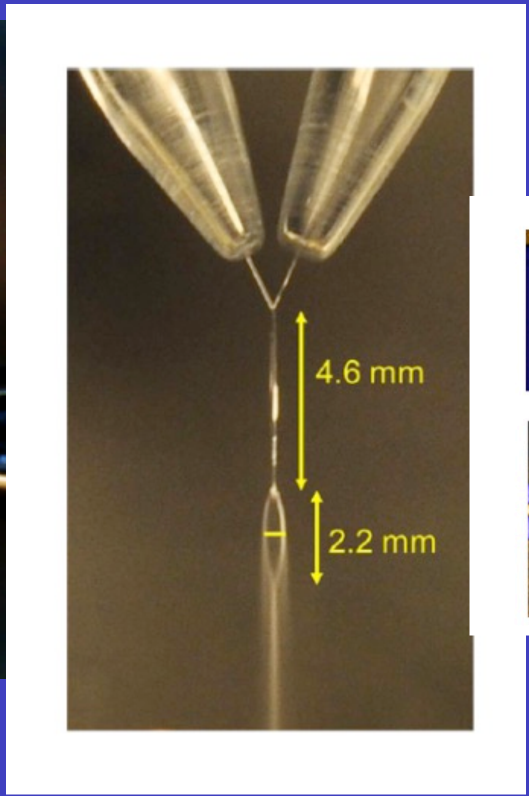
* Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
** Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

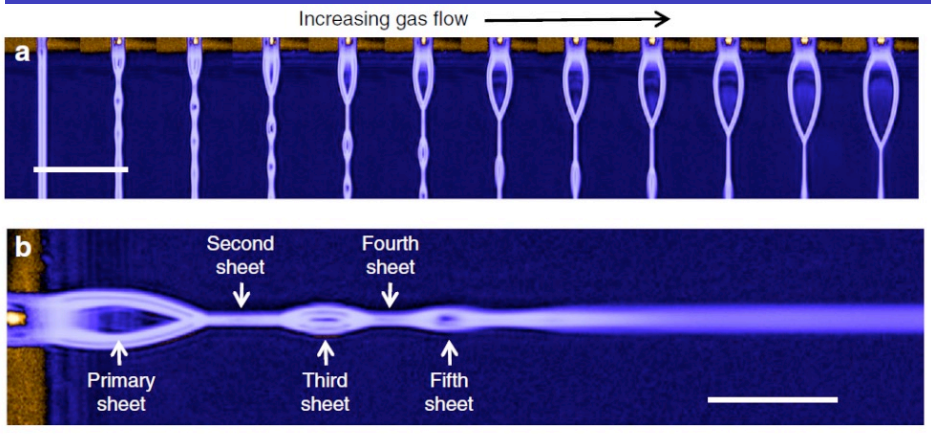
- *K-edges of low-Z elements : C, N, O, S, etc.*
- *$L_{2,3}$-edges of transition metals ($2p_{\frac{1}{2},3/2}$- nd), intense p-d transitions (as compared to s-p for K-edge). d-orbitals are the ligand orbitals.*
- *Sharp spectral features: Γ_L=0.5 eV=$\hbar$/ t = 6.58 10^{-16}/t. 3-5 times better energy resolution than corresponding K-edge*
- *Low-Z elements XAS requires high photon fluxes. $\alpha_{abs} \sim Z^4$.*
- *Observables: energies, line shapes and L3/L2 intensities*
- *Sensitive to molecular structure*
- *Spin and electronic information (Sawatzky, van der Laan, de Groot, etc..), s-d mixings, etc...*
- *Theory is well established (Ligand fields, multiplets code, ab-initio, etc.)*

Requires vacuum!

Delivery of liquid samples into vacuum







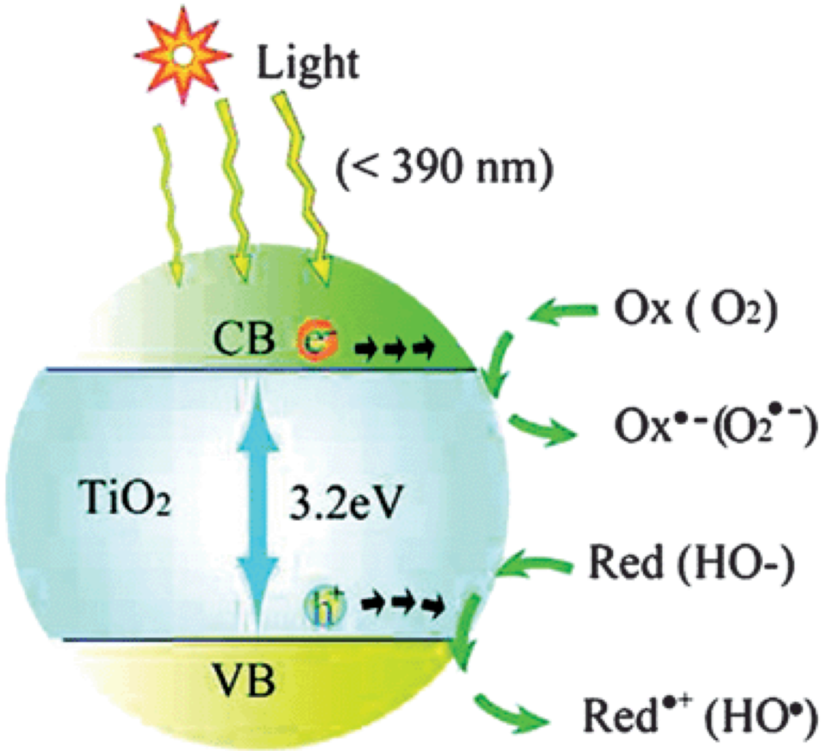
Koralek et al, Nature Comm. 2018

Winter and Faubel, Chem. Rev. 2006

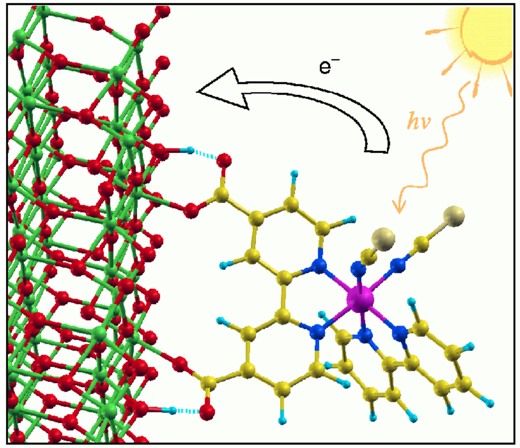
Ekimova et al, Struct. Dyn. 2015

Solar materials: Catalysis and energy conversion

Photocatalysis

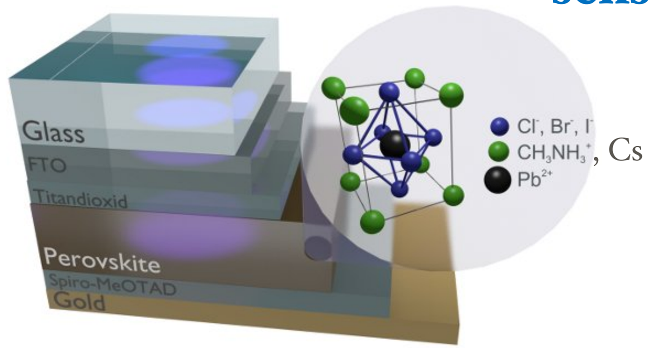


Solar energy



Dye-sensitization

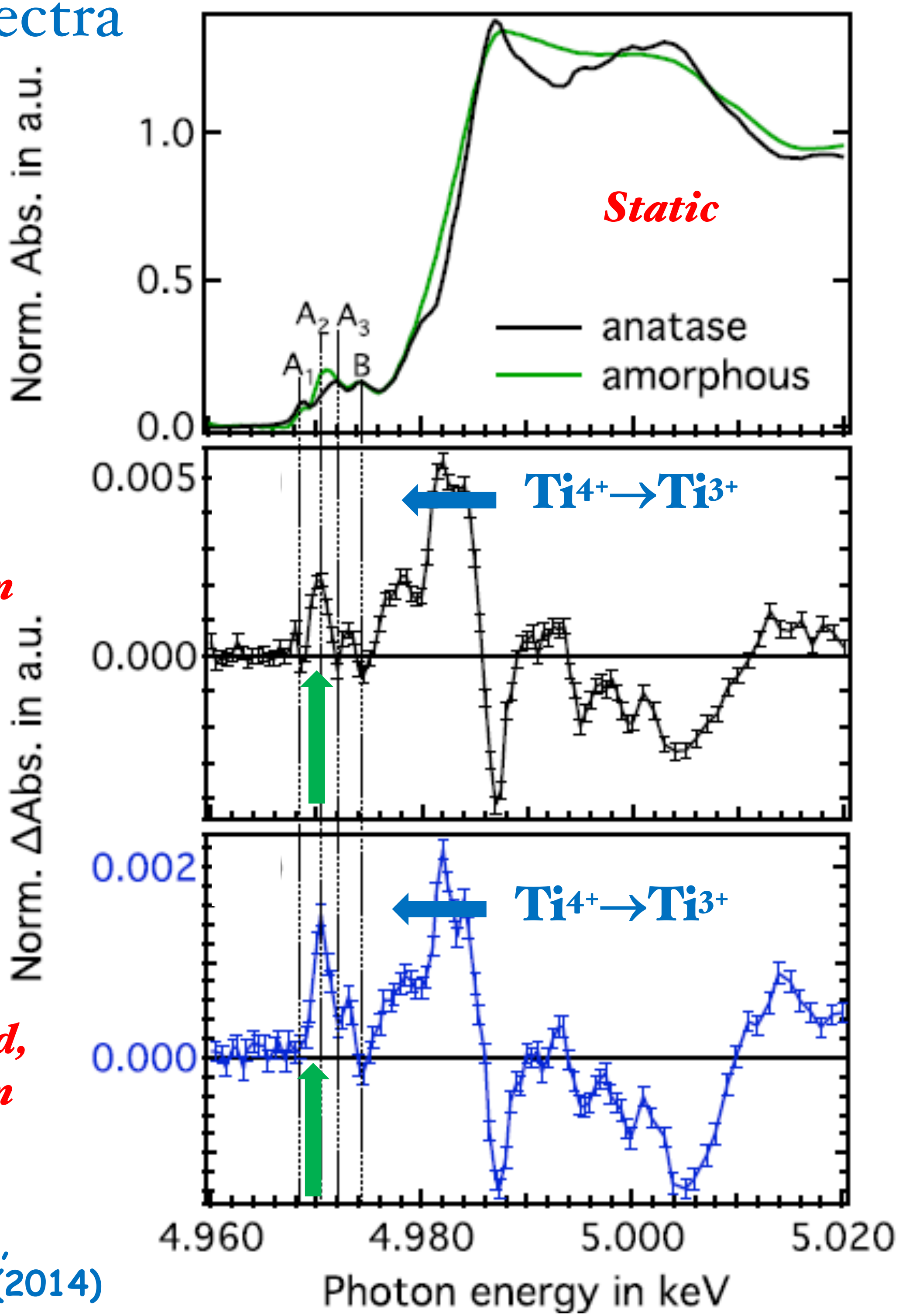
perovskite-sensitization

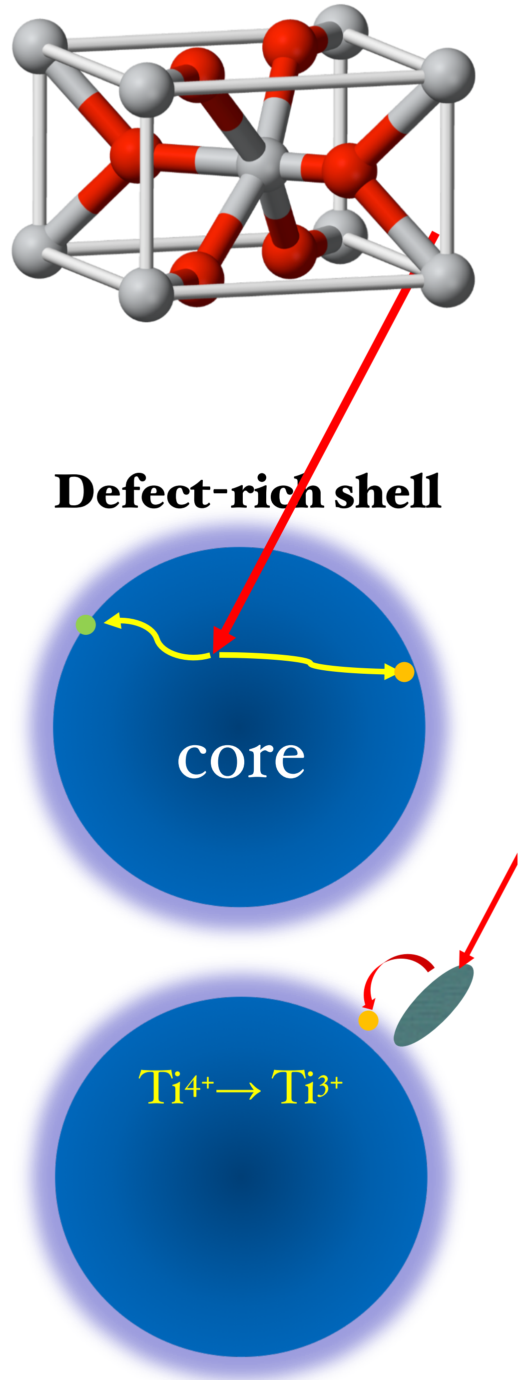


- Charges at surfaces
- Long time trapping

- Long range transport
- High mobility: no trapping

Ti K edge spectra



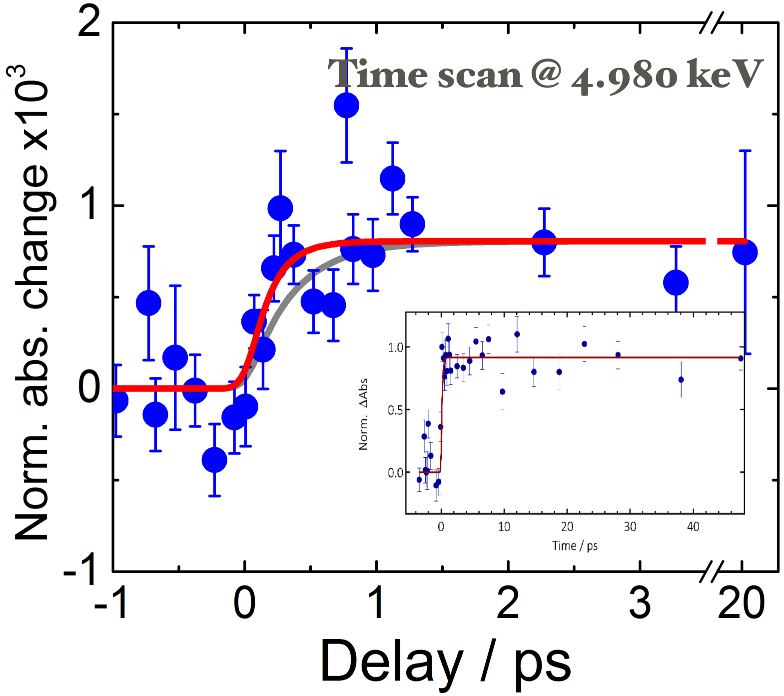


Bare,
100 ps, Exc. 355 nm

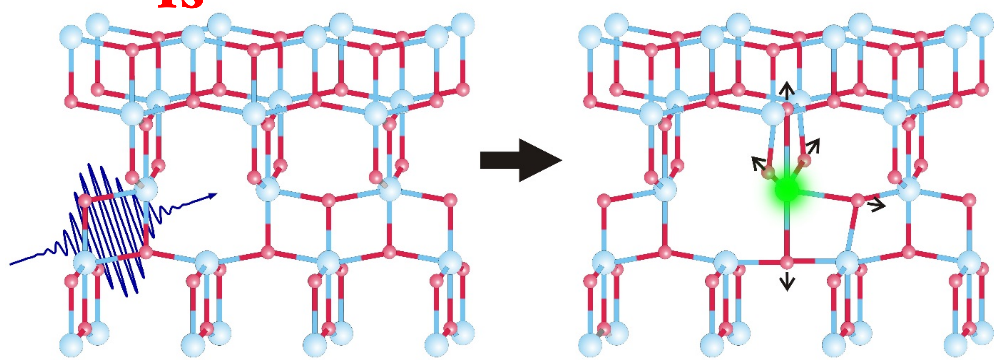
N719 dye-sensitized,
100 ps, Exc. 532 nm

Rittmann-Frank et al,
Ang. Chem. Int. Ed (2014)

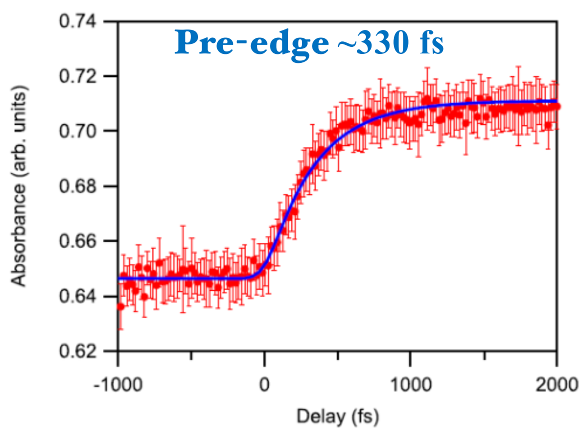
Femtosecond X-ray absorption experiment at the Ti K-edge

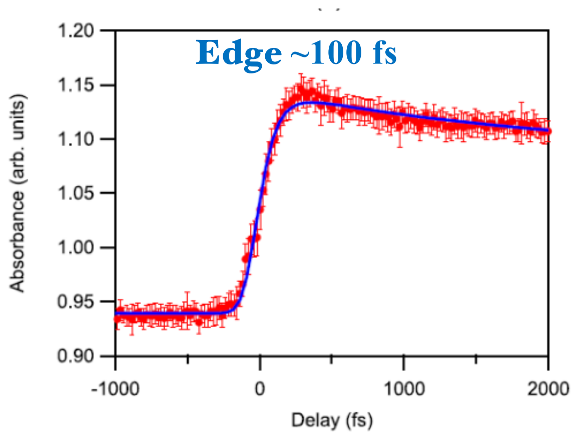


Electron trapping time <200 fs



Santomauro *et al*, Scient. Rep. (2015)

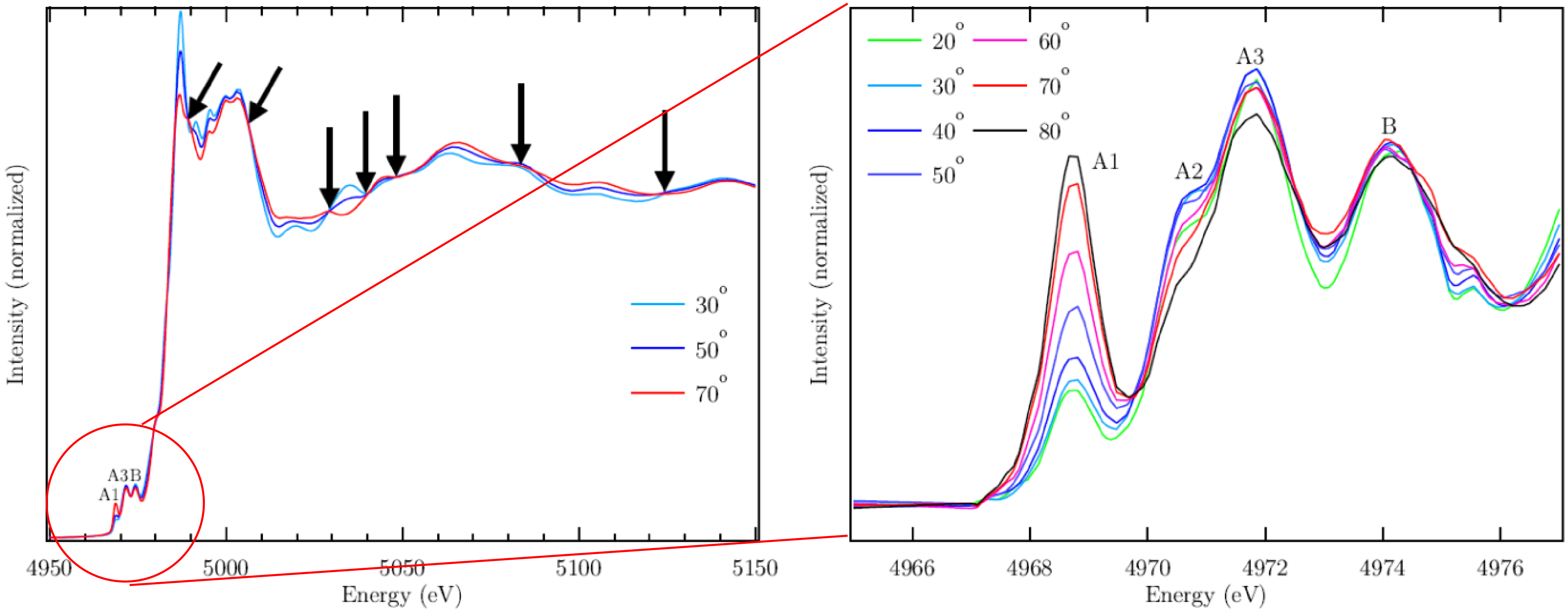




Ti reduction is instantaneous. Structural rearrangement is 3x slower

Obara et al, Struct. Dyn. (2017)

Linear dichroism of single crystals of TiO_2



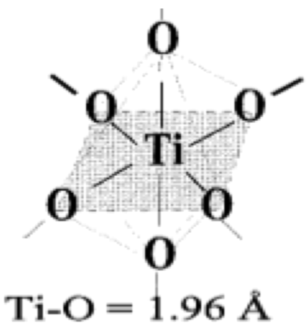
Transitions governed by final-state effects:

A1 :on-site 3d-4p hybridized transition

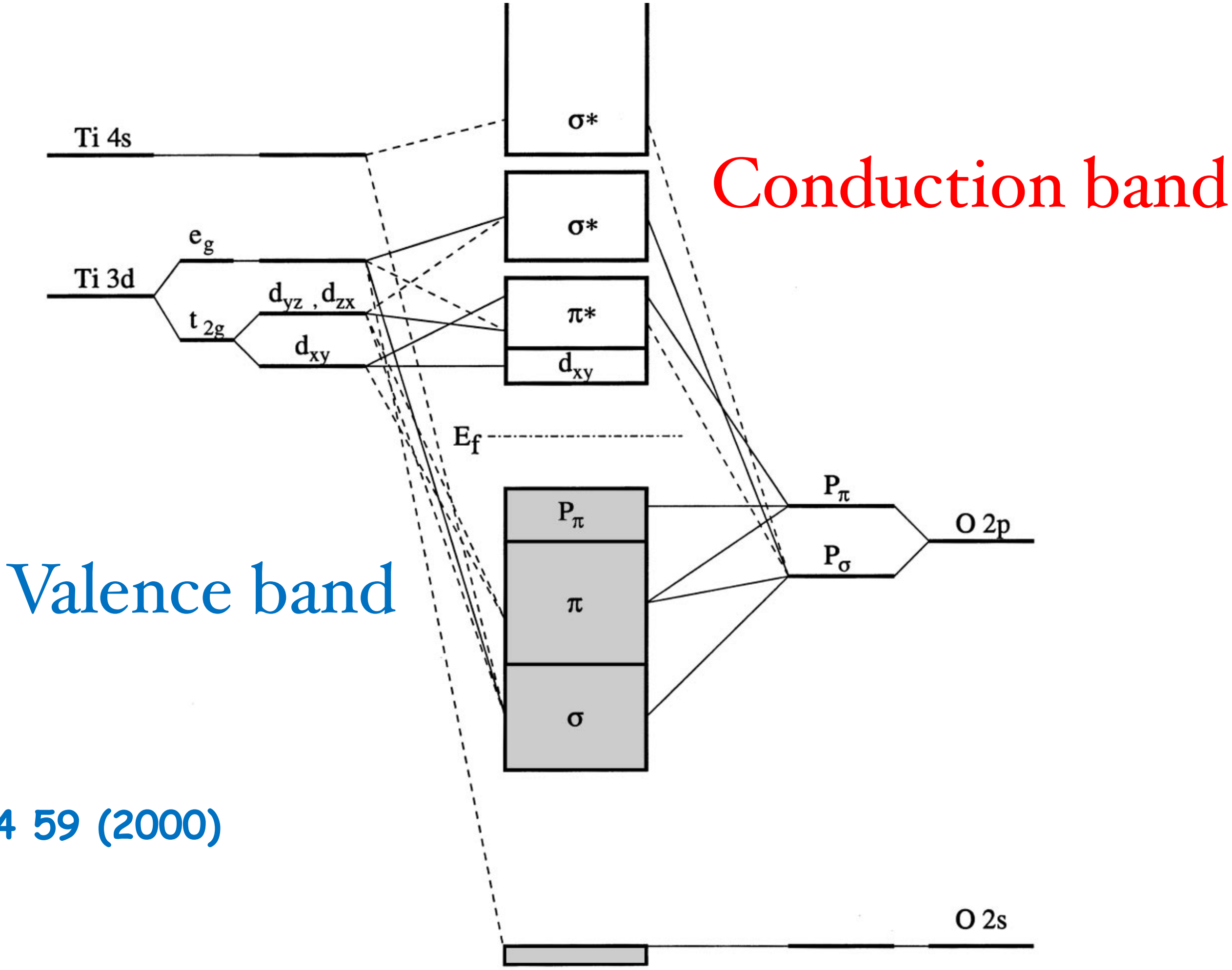
A2: quadrupolar character

A3: dipolar and 3d-4p intersite hybridization

B: intersite, dipolar



Rossi et al, Phys. Rev. B (in press); J. Synch. Rad. (under review)



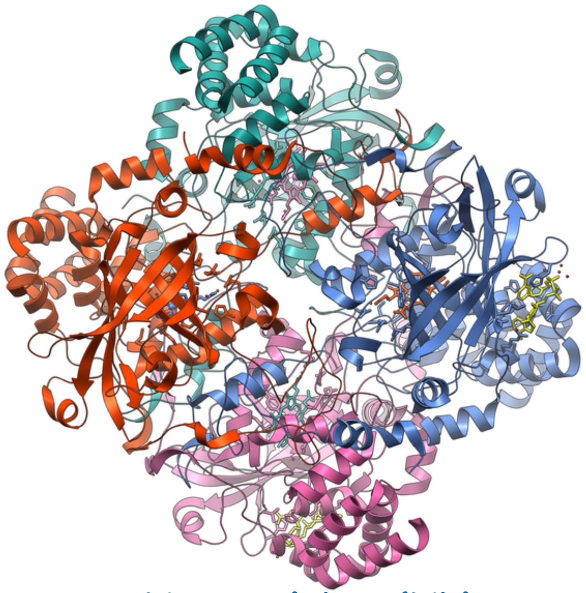
Asahi et al, PRB 61 74 59 (2000)

Time-resolved X-ray studies dominated by charge trapping but most photogenerated charges are free carriers

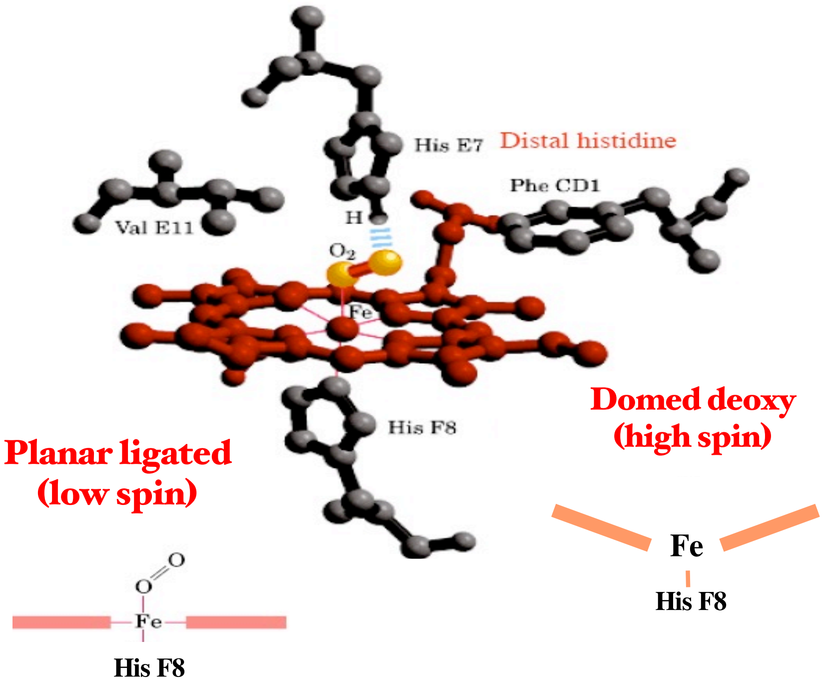
Optical domain spectroscopies: Drude response, no band specificity

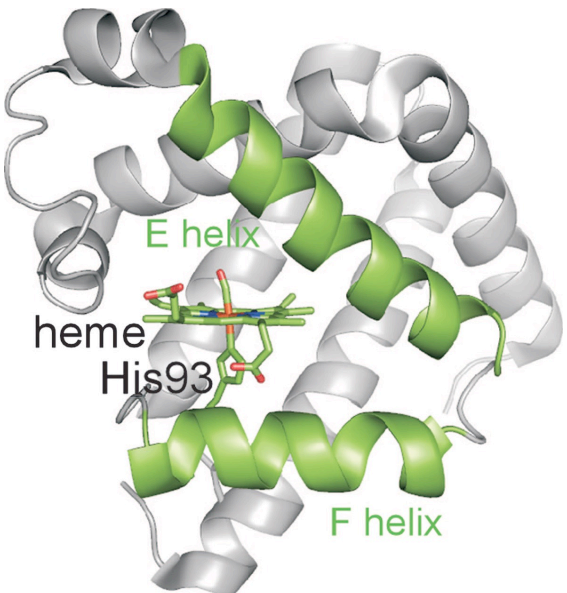
At seeded XFELs: XUV Transient Grating studies tuning to the p-d transitions

Haem proteins: respiration, neurotransmission, electron transfer, etc.



Haemoglobin (Hb)





Myoglobin (Mb)

The " transition state" of the respiratory function

CO, O_2 ***Fe^{2+}, $3d^6$*** ***S=0***	***Fe^{2+}, $3d^6$*** ***S=2***
NO ***Fe^{2+}, $3d^6$*** ***S= ½***	

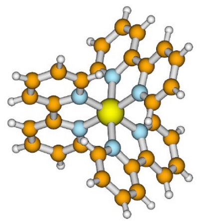
$\longrightarrow$

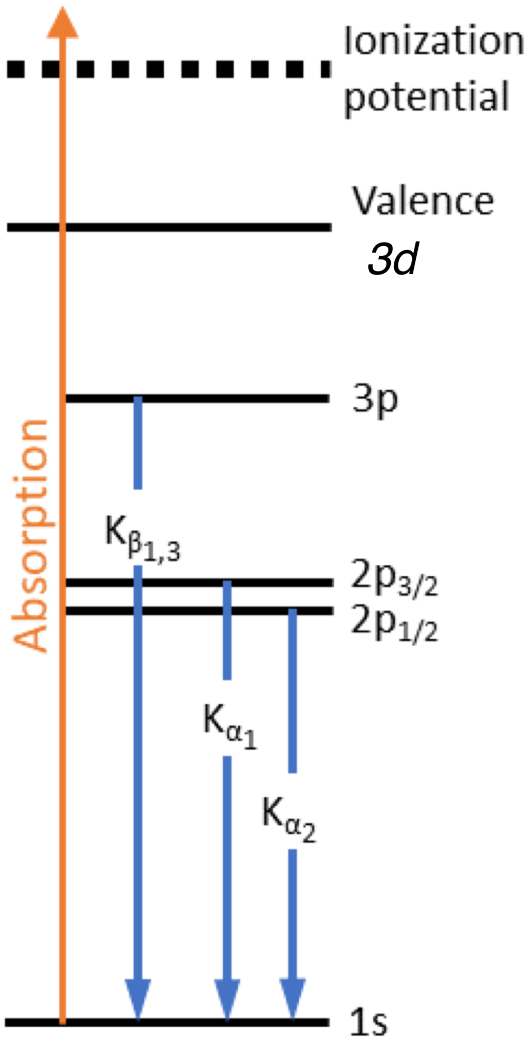
Tense-to-Relaxed state

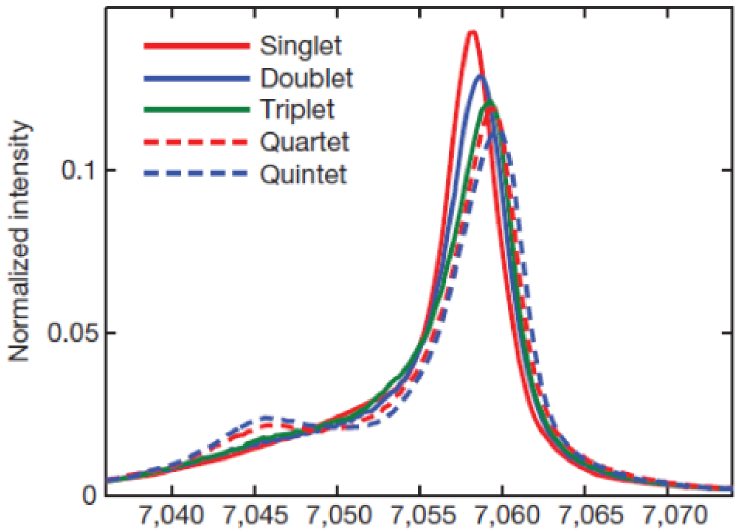
Perutz et al, Annu. Rev. Biophys. Biomol. Struct. 1998

K_β X-ray emission spectroscopy as a marker of spin

Spin cross-over dynamics in $[Fe(bpy)_3]^{2+}$



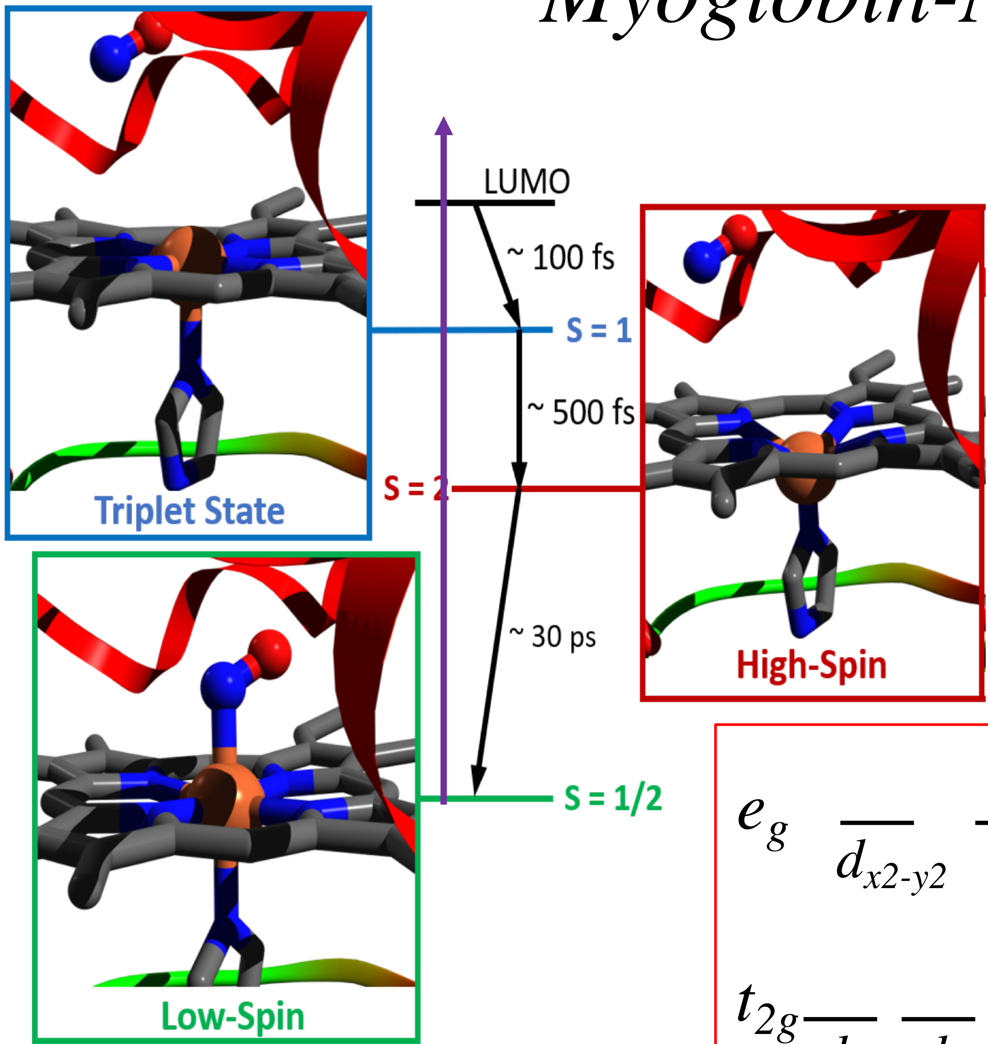




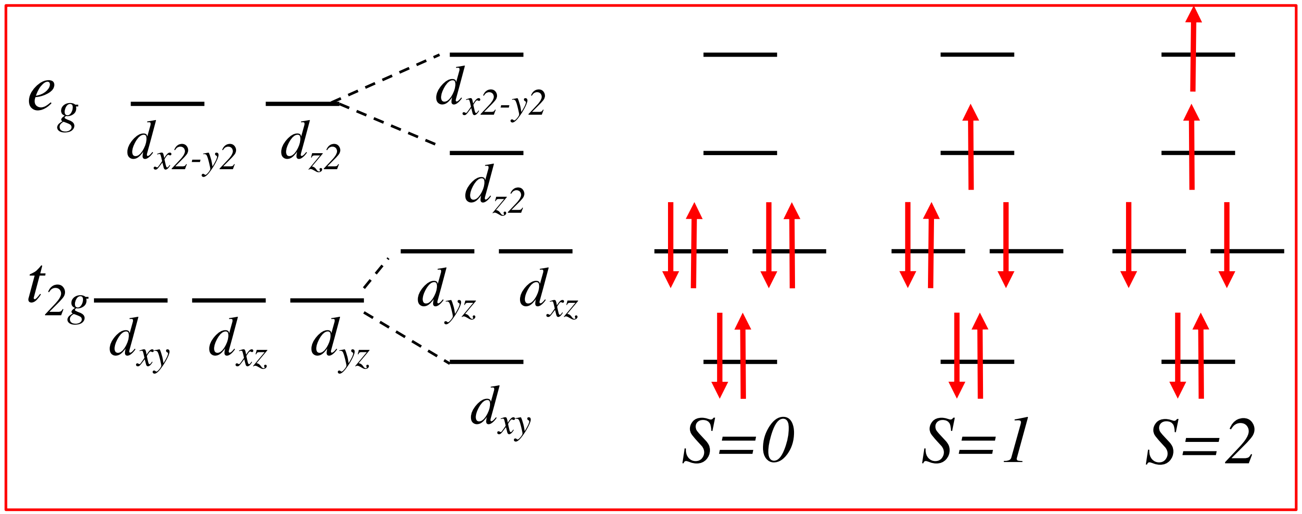
Glatzel and Bergmann, Coord. Chem. Rev. 2006

Zhang et al, Nature 2014

Femtosecond K_β and K_α emission on Myoglobin-NO at SACLA



Do away with the use of reference spectra:
Direct $L_{2,3}$ (2p-3d) spectroscopy

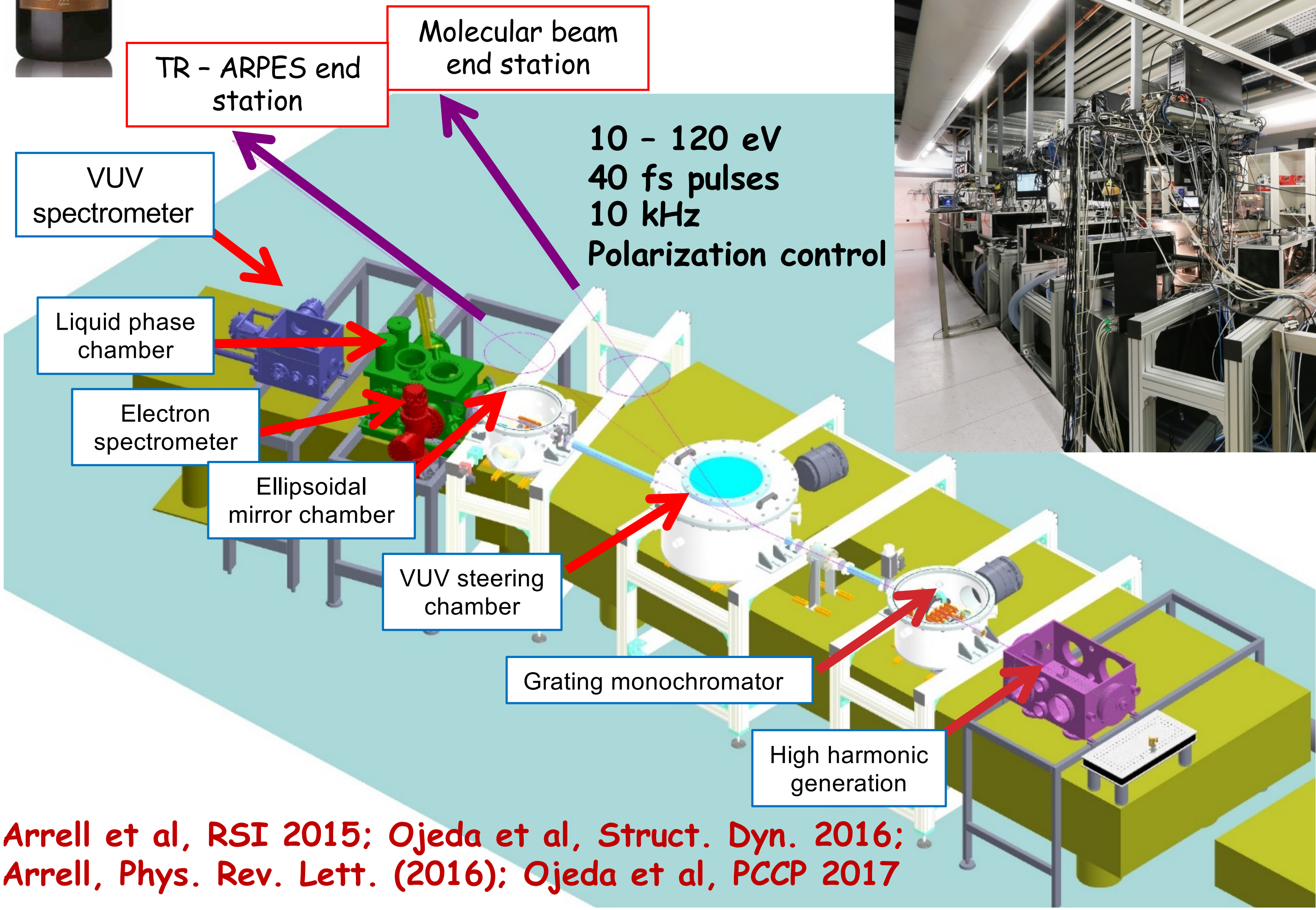


Kinschel et al, Nature (under review)

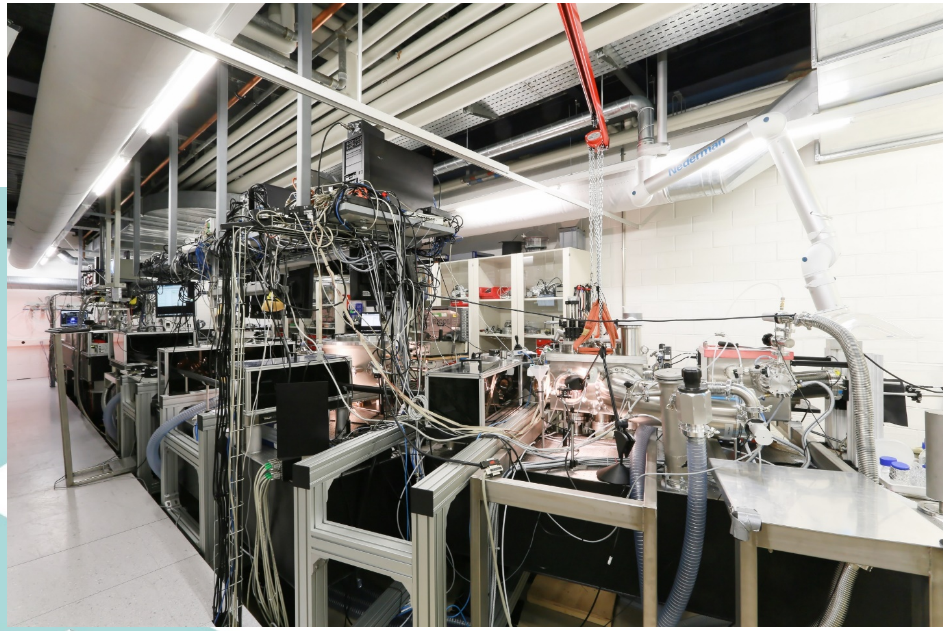
Studies on Cytochrome c at swissFEL: Bacellar et al, Draft

Harmonium @

Extreme-UV femtosecond source:
Facility for photoelectron spectroscopy (ESCA) of liquid, gas and solid phases.
Complementary to X-ray studies at the SLS and XFELs



10 – 120 eV
40 fs pulses
10 kHz
Polarization control



Funding:

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erc European Research Council

Arrell et al, RSI 2015; Ojeda et al, Struct. Dyn. 2016;
Arrell, Phys. Rev. Lett. (2016); Ojeda et al, PCCP 2017

Harmonium @ LACUS

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Arrell et al PRL **117,** 143001 (2016)

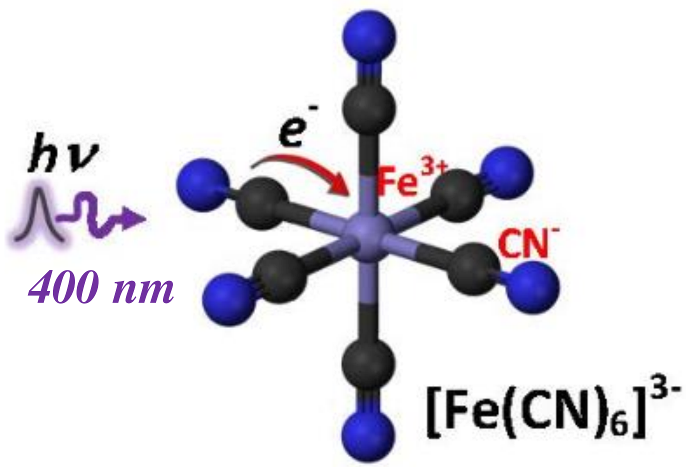
Charge-transfer and impulsive electronic-to-vibrational energy conversion in ferricyanide: ultrafast photoelectron and transient infrared studies† *Ojeda et al* *Phys. Chem. Chem. Phys.*, 2017, 19, 17052

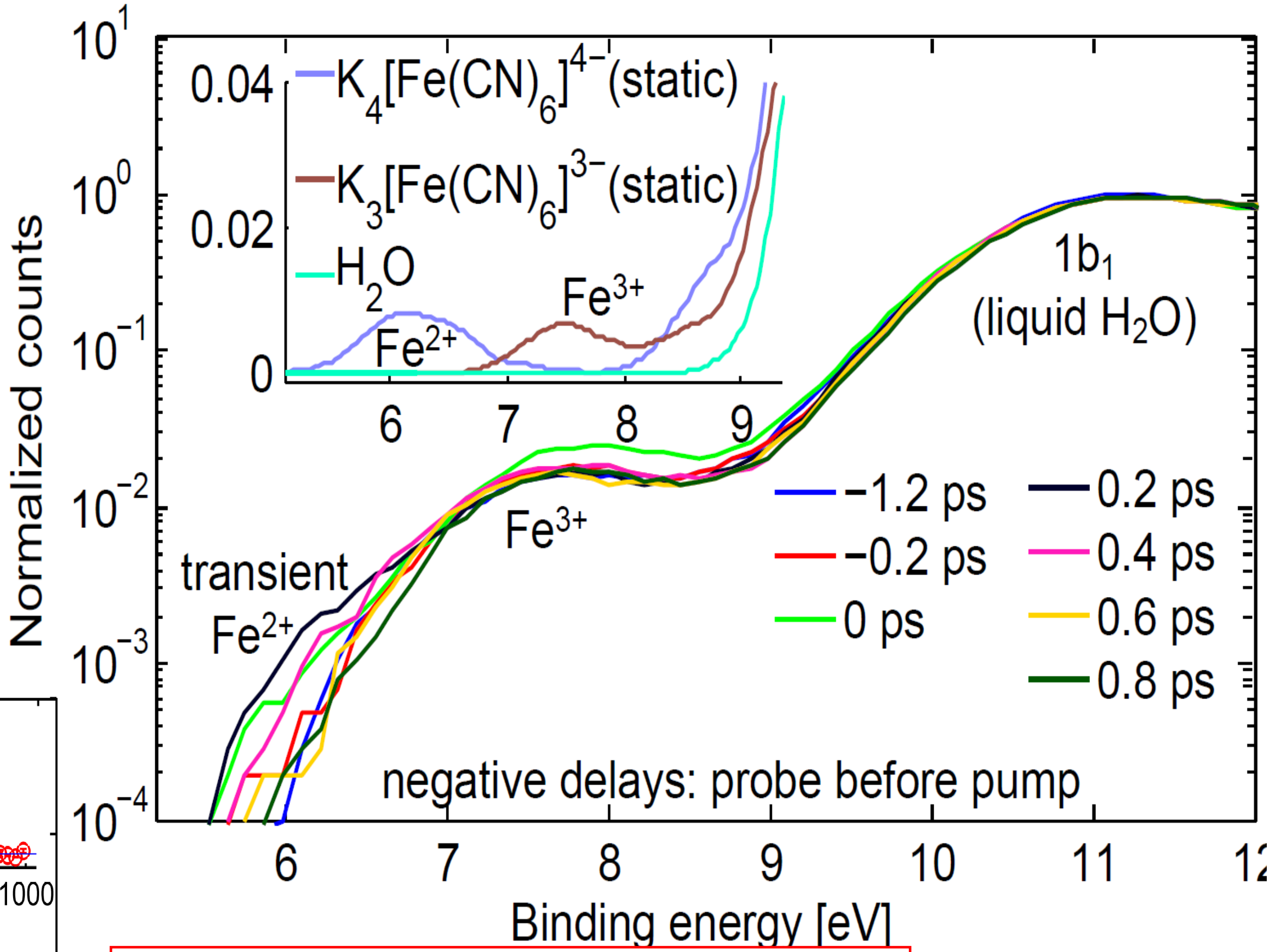
Photocarrier-induced band-gap renormalization and ultrafast charge dynamics in black phosphorus *Roth et al* *2D Mater.* **6** (2019) 031001

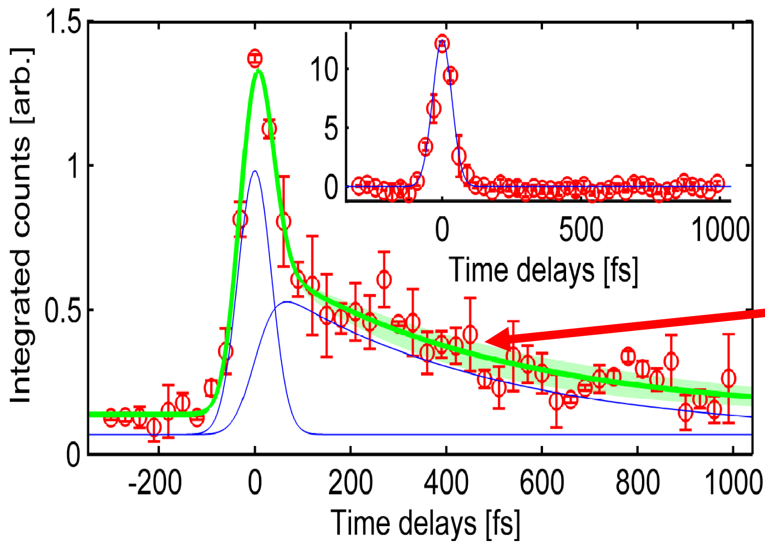
Evidence of large polarons in photoemission band mapping of the perovskite semiconductor $CsPbBr_3$ *Puppin et al, PRL (under review)*

Light-induced renormalization of the Dirac quasiparticle in the nodal line semimetal ZrSiSe
Gatti et al, PRL (submitted)

Transient photoelectron spectroscopy of Ferric hexacyanide (probe energy=39 eV)







Decay of the reduced Fe in ~500 fs

Ojeda et al, Phys. Chem. Chem. Phys. (2017)

Perspectives at seeded XFEL's

- High flux/high energy allows for better liquid phase PES studies (Winter et al, Bozek et al)
- Limited tunability can be used for X-ray absorption studies with helically or circularly polarized light (J. Rouxel, B. Rösner et al, to be published. Theory by S. Mukamel and co-workers)
- 4-wave mixing experiments on materials, nanoparticles and molecules with selective excitation of specific orbitals.

Grand Technical Challenge: Tunability at seeded XFEL!

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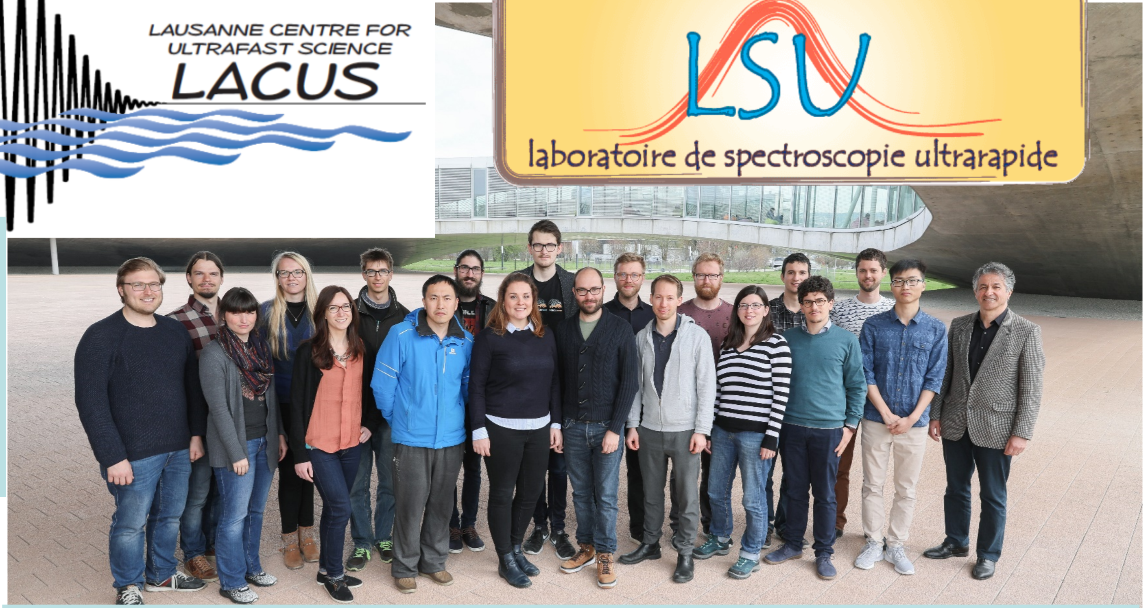

E. Baldini, C. Bacelar, Th. Barillot, B. Bauer, J. Budarz, O. Cannelli, R. Ingle, D. Kinschel, L. Longetti, G. Mancini, H. Marroux, N. Nagornova, M. Oppermann, T. Palmieri, S. Polishchuk, M. Puppin, Th. Rossi, B. Sorokin, L. Wang. LES: A. Crepaldi, M. Grioni, S. Roth

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must Molecular Ultrafast Science and Technology National Center of Competence in Research

70 NRP Energy Turnaround National Research Programme