

# 6. Science Opportunities in Chemical Sciences and Energy

Virtually any chemical reaction is accompanied by simultaneously occurring structural, electronic, and often spin-changes.

XFELs give unique and incisive access to these dynamics which are vital to scientific understanding and to myriad of real-world applications.

- 6.1 Fundamentals of reaction dynamics: Coupling between nuclear, electronic and spin degrees of freedom
- 6.2 Exploring complex energy landscapes through chemical activation
- 6.3 Energy materials and devices: Solar cells and batteries
- 6.4 Understanding catalysis
- 6.5 Chemistry and the environment: Aerosols, atmospheric, space chemistry, combustion, corrosion

## **Chemical Sciences team:**

*Andrew Burnett (Leeds), Sofia Diaz-Moreno (Diamond LS), Russell Minns (Southampton) – presenter for part 2, Tom Penfold (Newcastle), Julia Weinstein (Sheffield) – presenter for part 1 and C Milne, C Bressler, P Wernet, and all speakers at all w/shops*



## UK XFEL Science Case



**Project Lead:**  
Jon Marangos (UCL)  
**STFC Project Champion:**  
John Collier (CLF)

**SYNERGY WITH OTHER AREAS in the Science Case: (3.1-5; 4.1, 5.1, 5.2, 7.2, 8.2, 8.3)**

# 6. Science Opportunities in Chemical Sciences and Energy

## The Periodic Table of X-rays

																		18 VIIIA																	
1 IA																	2	18 VIIIA																	
1 <b>H</b> Hydrogen 1.008																	2 <b>He</b> Helium 4.002602																		
3 <b>Li</b> Lithium 6.94	4 <b>Be</b> Beryllium 9.0121831																	10 <b>Ne</b> Neon 18.998403263																	
11 <b>Na</b> Sodium 22.98976928	12 <b>Mg</b> Magnesium 24.305																	18 <b>Ar</b> Argon 39.948																	
		3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB							13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA													
19 <b>K</b> Potassium 39.0983	20 <b>Ca</b> Calcium 40.078	21 <b>Sc</b> Scandium 44.955908	22 <b>Ti</b> Titanium 47.867	23 <b>V</b> Vanadium 50.9415	24 <b>Cr</b> Chromium 51.9961	25 <b>Mn</b> Manganese 54.938044	26 <b>Fe</b> Iron 55.845	27 <b>Co</b> Cobalt 58.933194	28 <b>Ni</b> Nickel 58.6934	29 <b>Cu</b> Copper 63.546	30 <b>Zn</b> Zinc 65.38	31 <b>Ga</b> Gallium 69.723	32 <b>Ge</b> Germanium 72.630	33 <b>As</b> Arsenic 74.921595	34 <b>Se</b> Selenium 78.971	35 <b>Br</b> Bromine 79.904	36 <b>Kr</b> Krypton 83.798	5 <b>B</b> Boron 10.81	6 <b>C</b> Carbon 12.011	7 <b>N</b> Nitrogen 14.007	8 <b>O</b> Oxygen 15.999	9 <b>F</b> Fluorine 18.998403263													
37 <b>Rb</b> Rubidium 85.4678	38 <b>Sr</b> Strontium 87.62	39 <b>Y</b> Yttrium 88.90584	40 <b>Zr</b> Zirconium 91.224	41 <b>Nb</b> Niobium 92.90637	42 <b>Mo</b> Molybdenum 95.95	43 <b>Tc</b> Technetium (98)	44 <b>Ru</b> Ruthenium 101.07	45 <b>Rh</b> Rhodium 102.90550	46 <b>Pd</b> Palladium 106.42	47 <b>Ag</b> Silver 107.8682	48 <b>Cd</b> Cadmium 112.414	49 <b>In</b> Indium 114.818	50 <b>Sn</b> Tin 118.710	51 <b>Sb</b> Antimony 121.760	52 <b>Te</b> Tellurium 127.60	53 <b>I</b> Iodine 126.90447	54 <b>Xe</b> Xenon 131.293	13 <b>Al</b> Aluminium 26.9815385	14 <b>Si</b> Silicon 28.085	15 <b>P</b> Phosphorus 30.973761998	16 <b>S</b> Sulfur 32.06	17 <b>Cl</b> Chlorine 35.45													
55 <b>Cs</b> Caesium 132.90545196	56 <b>Ba</b> Barium 137.327	57 - 71 Lanthanoids	72 <b>Hf</b> Hafnium 178.49	73 <b>Ta</b> Tantalum 180.94788	74 <b>W</b> Tungsten 183.84	75 <b>Re</b> Rhenium 186.207	76 <b>Os</b> Osmium 190.23	77 <b>Ir</b> Iridium 192.227	78 <b>Pt</b> Platinum 195.084	79 <b>Au</b> Gold 196.966569	80 <b>Hg</b> Mercury 200.592	81 <b>Tl</b> Thallium 204.38	82 <b>Pb</b> Lead 207.2	83 <b>Bi</b> Bismuth 208.98040	84 <b>Po</b> Polonium (209)	85 <b>At</b> Astatine (210)	86 <b>Rn</b> Radon (222)	87 <b>Fr</b> Francium (223)	88 <b>Ra</b> Radium (226)	89 - 103 Actinoids	104 <b>Rf</b> Rutherfordium (261)	105 <b>Db</b> Dubnium (268)	106 <b>Sg</b> Seaborgium (269)	107 <b>Bh</b> Bohrium (270)	108 <b>Hs</b> Hassium (285)	109 <b>Mt</b> Meitnerium (278)	110 <b>Ds</b> Darmstadtium (281)	111 <b>Rg</b> Roentgenium (282)	112 <b>Cn</b> Copernicium (285)	113 <b>Nh</b> Nihonium (286)	114 <b>Fl</b> Flerovium (289)	115 <b>Mc</b> Moscovium (289)	116 <b>Lv</b> Livermorium (293)	117 <b>Ts</b> Tennessine (294)	118 <b>Og</b> Oganesson (294)

0.1-1 keV  
1-2 keV  
2-7.5 keV

## The time-resolution



57 <b>La</b> Lanthanum 138.90547	58 <b>Ce</b> Cerium 140.116	59 <b>Pr</b> Praseodymium 140.90766	60 <b>Nd</b> Neodymium 144.242	61 <b>Pm</b> Promethium (145)	62 <b>Sm</b> Samarium 150.36	63 <b>Eu</b> Europium 151.964	64 <b>Gd</b> Gadolinium 157.25	65 <b>Tb</b> Terbium 158.92535	66 <b>Dy</b> Dysprosium 162.500	67 <b>Ho</b> Holmium 164.93033	68 <b>Er</b> Erbium 167.259	69 <b>Tm</b> Thulium 168.93422	70 <b>Yb</b> Ytterbium 173.045	71 <b>Lu</b> Lutetium 174.9668
89 <b>Ac</b> Actinium (227)	90 <b>Th</b> Thorium 232.0377	91 <b>Pa</b> Protactinium 231.03688	92 <b>U</b> Uranium 238.02891	93 <b>Np</b> Neptunium (237)	94 <b>Pu</b> Plutonium (244)	95 <b>Am</b> Americium (243)	96 <b>Cm</b> Curium (247)	97 <b>Bk</b> Berkelium (247)	98 <b>Cf</b> Californium (251)	99 <b>Es</b> Einsteinium (252)	100 <b>Fm</b> Fermium (257)	101 <b>Md</b> Mendelevium (258)	102 <b>No</b> Nobelium (259)	103 <b>Lr</b> Lawrencium (260)

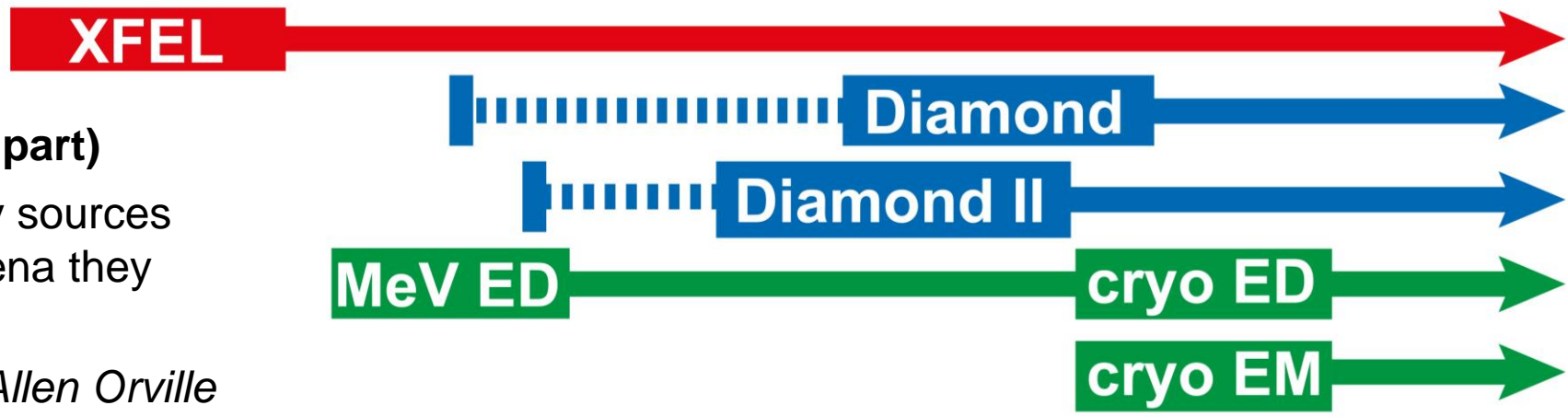
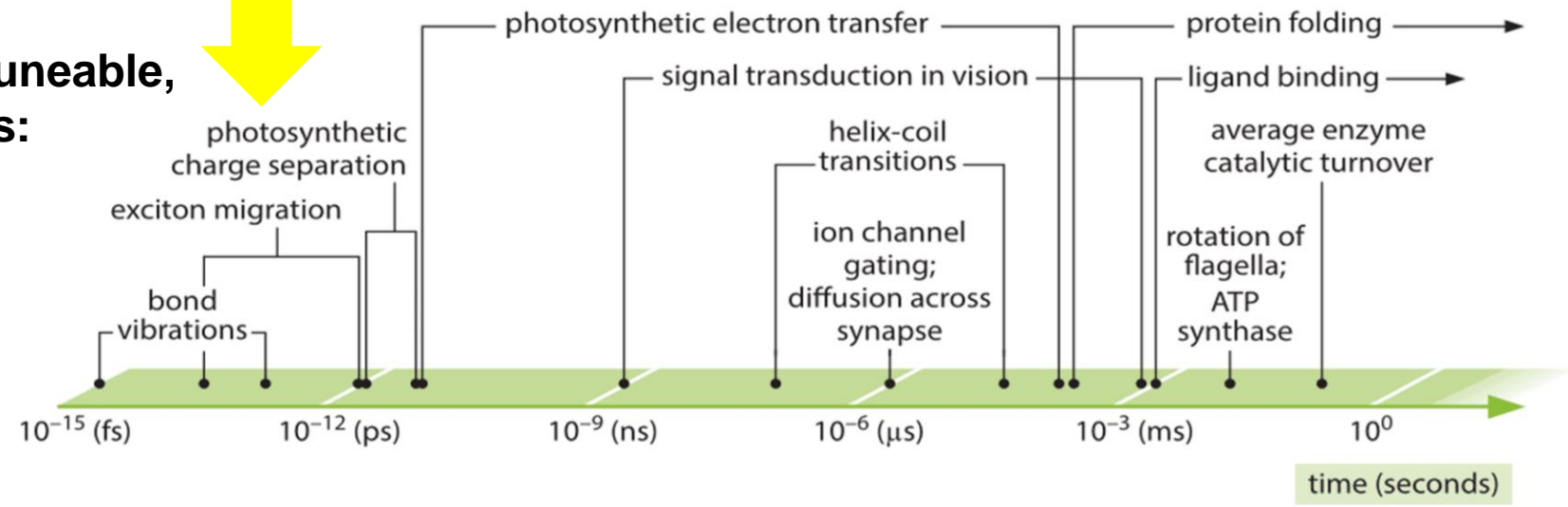
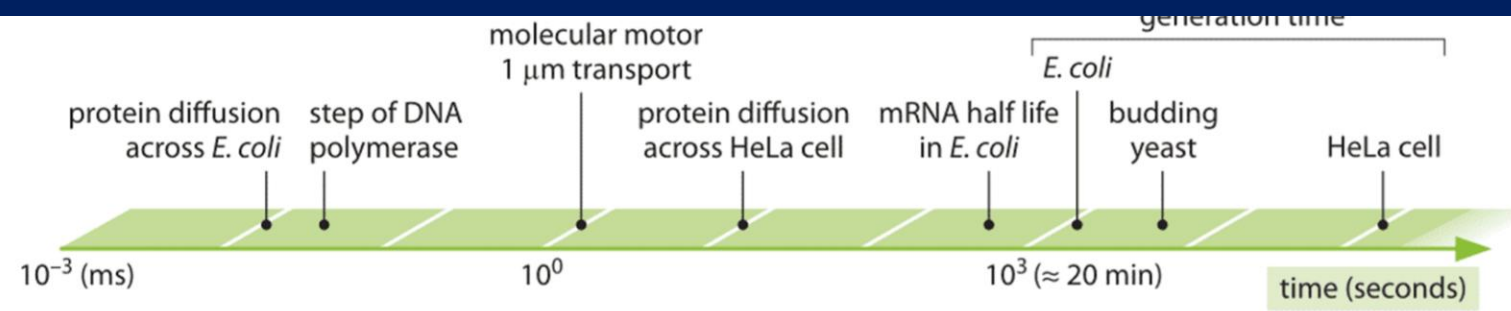
Chemistry, Physics, Biology, Materials, Applications

# 6. Science Opportunities in Chemical Sciences and Energy

**Chemical processes span decades of time, from femto- to giga-seconds**

**Ultrafast, powerful, tuneable, high rep-rate sources:**

“optical” lasers ✓  
 X-ray ?

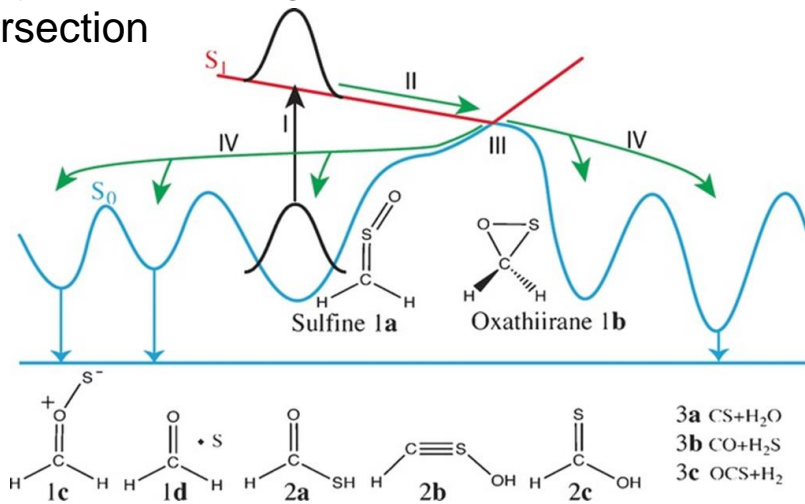


**Figure 7.2:**  
 (From Life Sciences part)  
 A comparison of X-ray sources and types of phenomena they are used to study.

@ Allen Orville

# 6. Challenges in Chemical Sciences and Energy: an overview

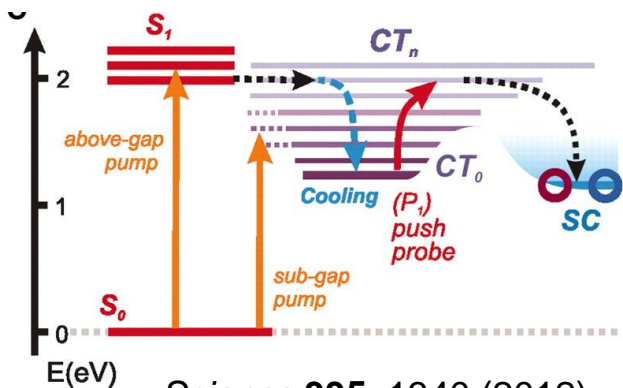
## Ground-State Chemistry Triggered by Dynamics through a Conical Intersection



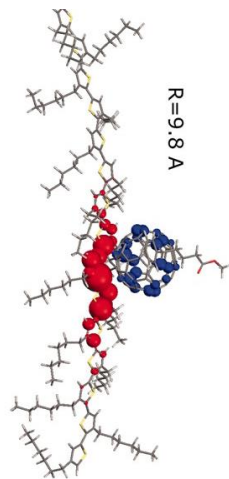
*Angew. Chem. Int. Ed.*, **55**, 14993 (2016)

## Charge- and energy transfer dynamics

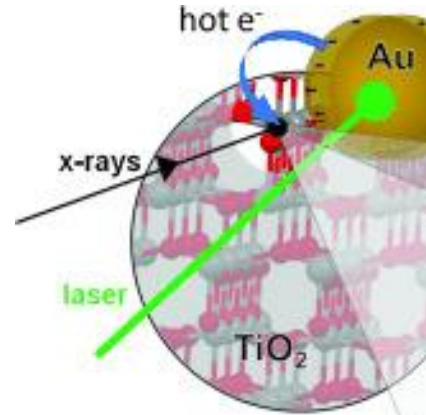
### Exciton Dynamics



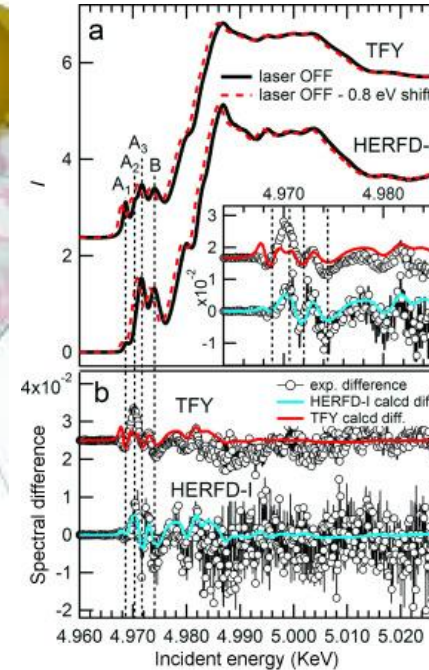
*Science* **335**, 1340 (2012)



## Plasmonic Photocatalysis

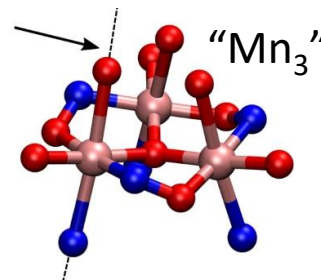


*Angew. Chem. Int. Ed.*  
**54**, 5413 (2015).



## Spin dynamics:

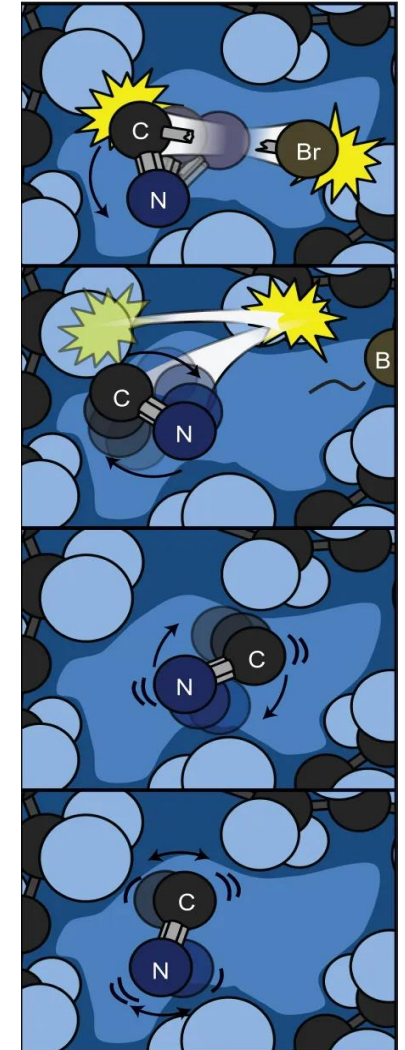
Vibrational coherence in single-molecule magnets



*Nature Chem.* 452 (2020)

Translational,  
 rotational  
 and vibrational  
 relaxation dynamics

## Solvent-Solute interactions



*Nature Chem.* **8**, 242 (2016)

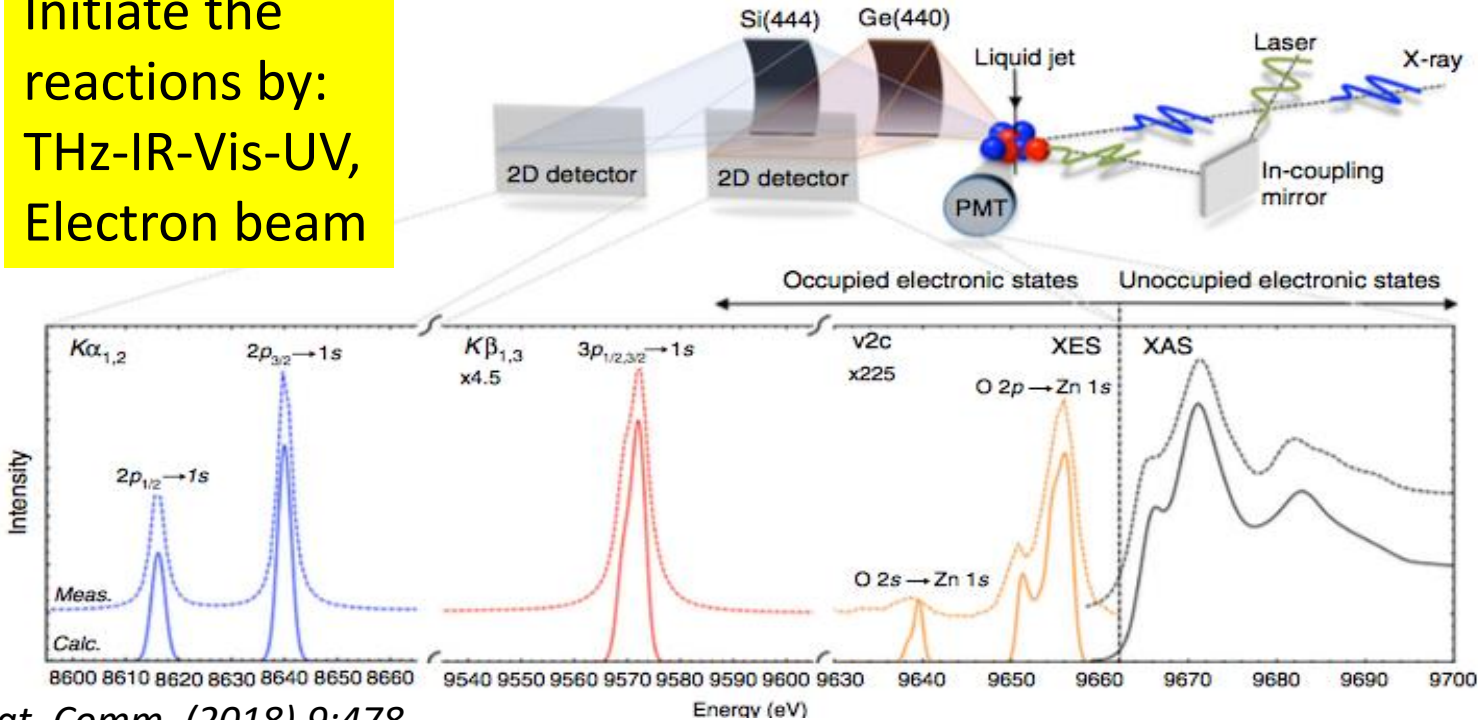
# 6. Opportunities in Chemical Sciences: Tools and Goals

G  
O  
A  
L  
S

- Predict photochemical processes
- Relate reactivity and quantum-chemical concepts
- Learn fundamental chemistry in proteins, metalloproteins, photoresponsive proteins
- Explain and control photocatalytic function
- Develop new efficient materials for solar applications, information, and security

**PROBE: Many of these techniques can be used simultaneously**

Initiate the reactions by:  
THz-IR-Vis-UV,  
Electron beam



## X-ray Spectroscopy:

- *X-ray absorption*: Probe Structure and Unoccupied Electronic Density of states.
- *X-ray emission*: Probed Occupied Density of States. **SPIN!**
- *Resonant X-ray Emission*: High resolution experiments.
- *X-ray Raman*: Probe edges of light elements using harder X-rays.

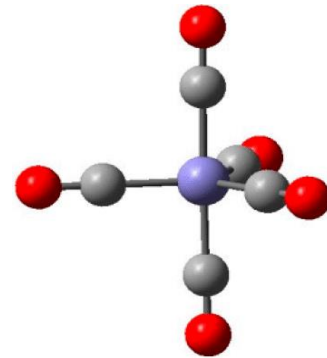
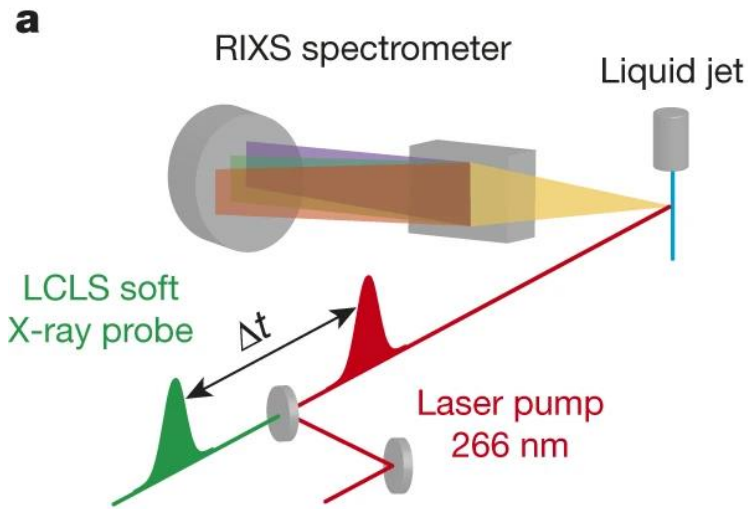
## X-ray scattering:

Time evolution and structural dynamics of global structure.

**Towards femtosecond-,  $< 0.01\text{\AA}$ - molecular movies**

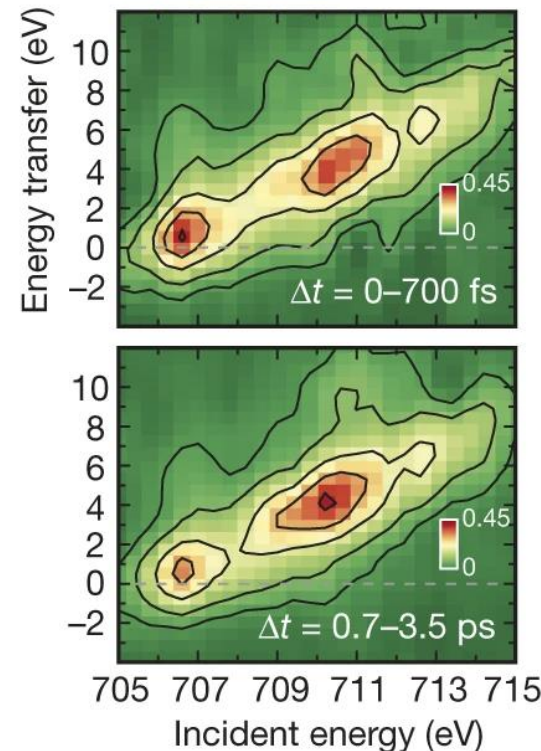
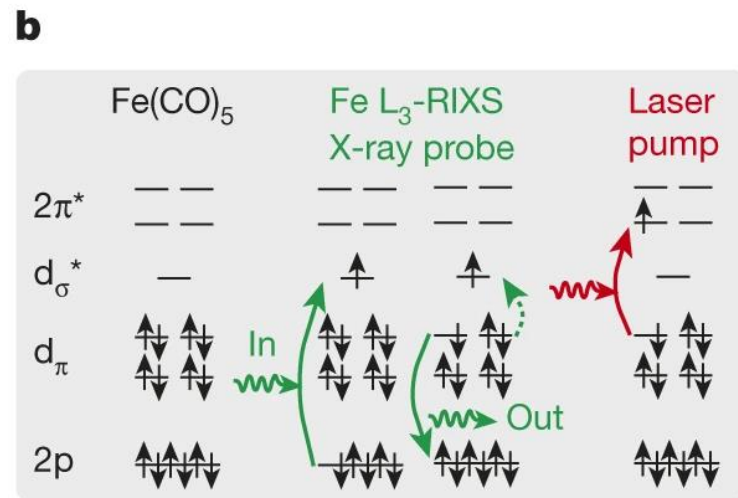
# 6.1. Fundamentals of reaction dynamics

## X-ray SPECTROSCOPY: Element- and site-specific probing



**RIXS** = Time-resolved resonant inelastic X-ray scattering, the X-ray analogue of resonance Raman scattering.

Probing HOMO-LUMO frontier-orbital interactions upon ligand dissociation (CO) from  $\text{Fe}(\text{CO})_5$  by time-resolved RIXS at the  $\text{Fe } L_3$  edge.



### The “movie” part:

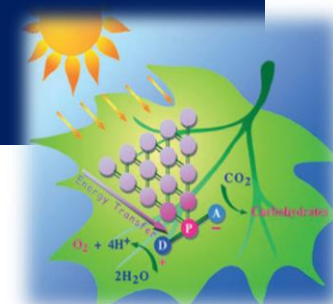
- Ligand dissociation
- Primary step in catalysis

### The applications part:

- Spin-change
- Magnetic materials
- Fundamentals of chemical reactivity

Fig. 6.12, from Wernet et al. "Orbital-specific mapping of the ligand exchange dynamics of  $\text{Fe}(\text{CO})_5$  in solution" *Nature* 520, 78 (2015)

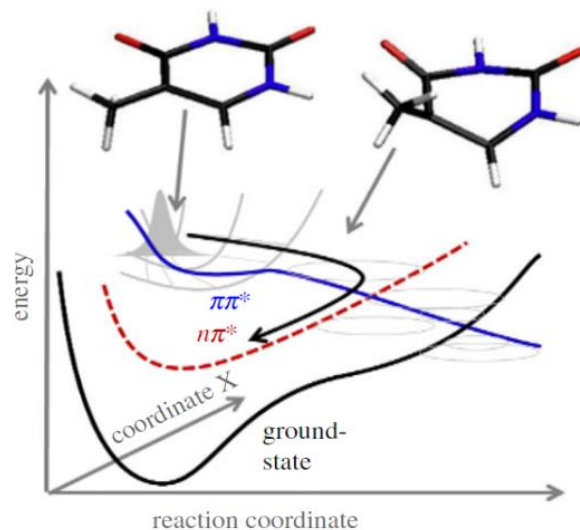
# 6.1 Fundamentals of reaction dynamics: Coupling between nuclear, electronic and spin degrees of freedom



## Element- and site-specific probing

**Soft X-ray:**  
organic molecules - C, N, O edges

### Photochemistry of DNA

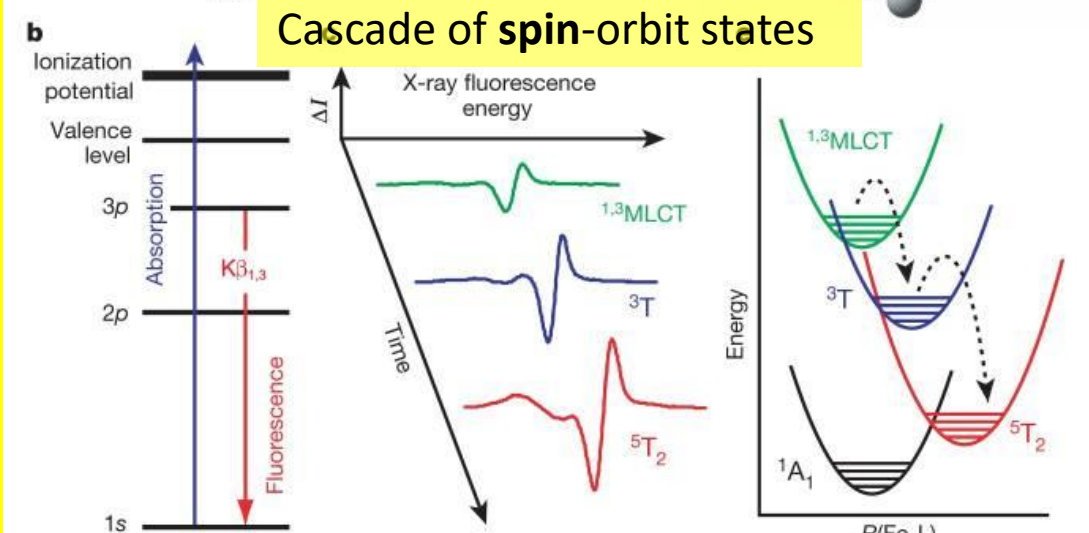
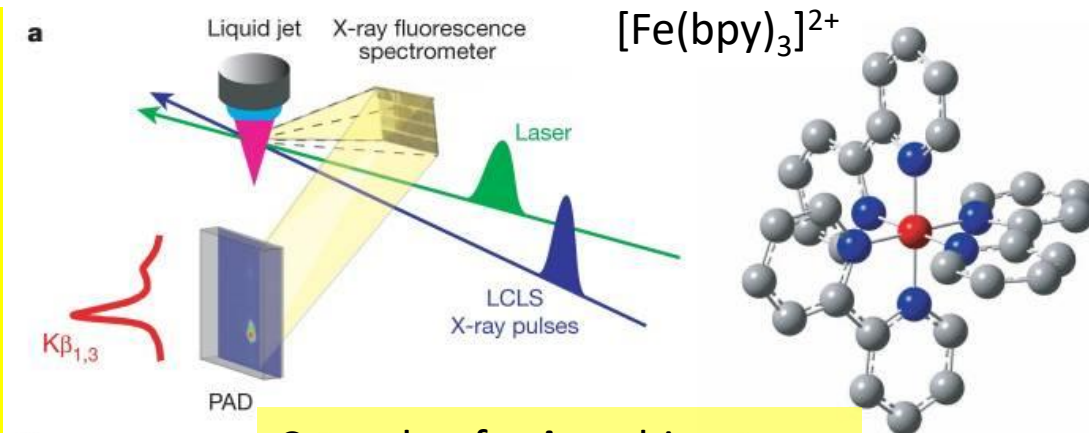


**Fig. 6. 4.** TR-AES and TR-NEXAFS reveals possible relaxation paths a  $\pi\pi^*$  state of thymine populated by UV-pulse, to the dark  $n\pi^*$  state and to the ground state via conical intersections. [Nat. Comm. 8, 29, (2017)]

### Areas:

- Fundamental photochemistry
- Reaction mechanisms
- Photoprotection
- DNA damage
- Free radicals in biology & medicine
- Photovoltaics
- Photocatalysis
- ...your science

**Hard X-ray: metals**



[Nature 509: 345–348 (2014)]

# 6.1 Fundamentals of reaction dynamics: spin, charge, structure

## Correlated spin and structural dynamics

the dissociation/recombination of NO to Fe-centre in **Myoglobin**.

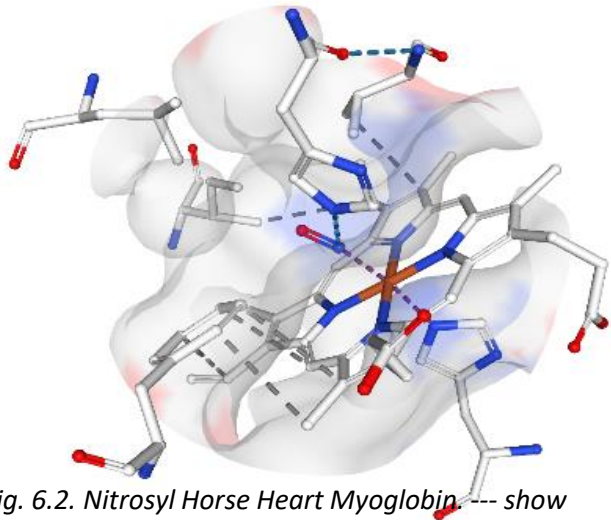
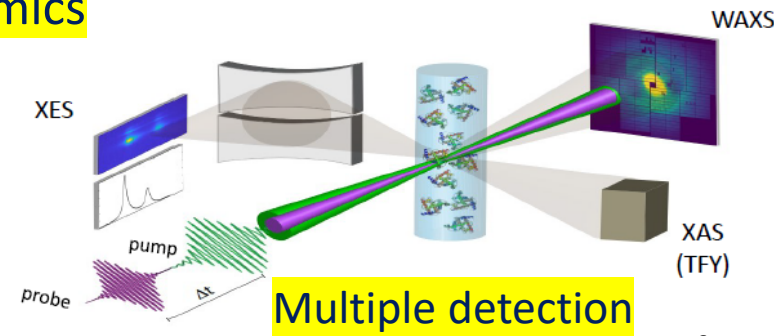


Fig. 6.2. Nitrosyl Horse Heart Myoglobin ---- show bonds which reversibly form and break. PDB 2FRJ.

- Structures of the short-lived intermediates by XAS and WAXS;
- Spin information from XES monitoring high /low-spin transition.

Kinschel et al, 2020,  
<https://arxiv.org/ftp/arxiv/papers/2005/2005.05598.pdf>



Multiple detection

Figure: Courtesy of C Bressler

### The “movie”:

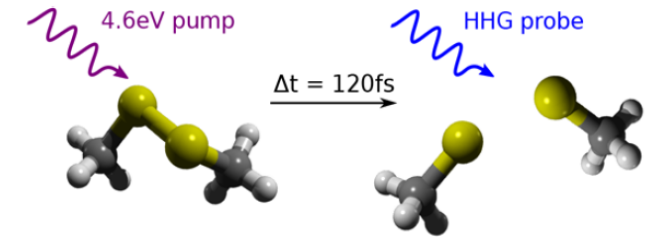
- Ligand dissociation
- Primary steps in protein dynamics

### The applications:

- Enzyme catalysis
- Photoprotection
- Drug-target
- ...your science

## -S-S- bonding in proteins

The fs-TRXAS...shows that gas-phase  $\text{CH}_3\text{-S-S-CH}_3$ ...undergoes fast direct dissociation into  $2 \text{H}_3\text{C-S}\bullet$ .



*J. Phys. Chem. Lett.* **10**, 1382 (2019)

### Next:

to follow the formation and breaking of H-bonds, the changes of electron density of the protein ligands.

### Need:

- higher sensitivity,
- high repetition rate,
- multiple detection, correlative XAS and XES methods, and RIXS, e.g.

Towards detailed molecular movie in chemistry and biochemistry



# Mechanisms of light-driven therapies (PDT), antimicrobial resistance, real-time imaging of intracellular small molecule-biomolecule interaction

Recent huge advances in transition metal complexes as PDT drugs, antimicrobial agents, singlet oxygen sensitisers – Pt, Re, Ru, Ir, Co, Cu, Fe.....

Questions that could be tackled ONLY by femtosecond-millisecond structural methods:

- Dynamics of drug-organelle interaction;
- Dynamics of DNA damage by  $^1\text{O}_2$ ;
- What are *structural* changes in the drug itself;
- What are cooperative effects;
- 1<sup>st</sup> step in PDT...

Directly linked to:

- Radiation damage of DNA
- Protein dynamics, signalling pathways
- Therapies

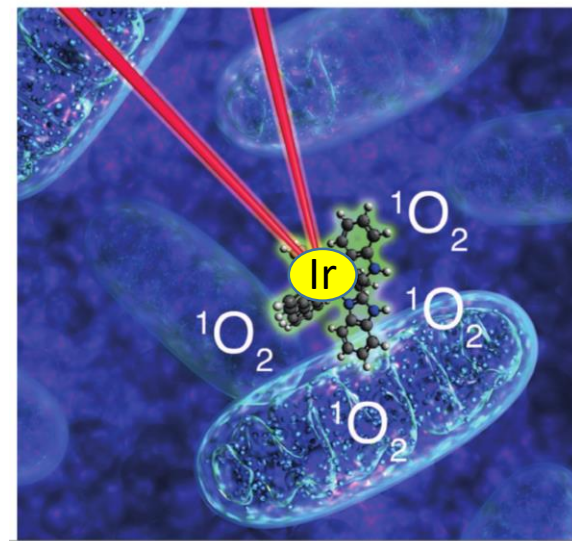
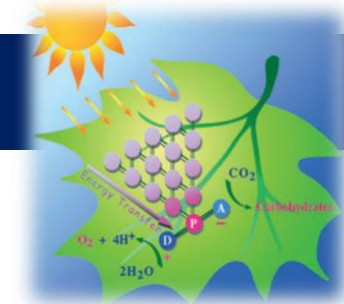


Fig. 6. 6. McKenzie et al, Chem Eur J, 2017

Important: sample delivery, energies, rep rates, precious samples, sensitivity. complementary to emission lifetime imaging, TEM, CLEM – is there potential for 4D imaging? SciFi....

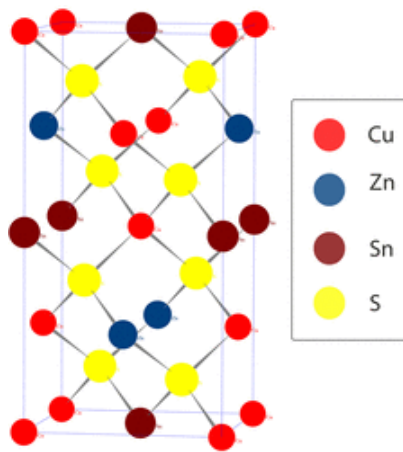
# 6.4. Understanding Catalysis with XFELs



Molecular Photocatalysis, Heterogeneous Photocatalysis, Light-Absorbing Semiconductors

Applications: CO<sub>2</sub> reduction; Water oxidation; Solar fuel; Artificial Photosynthesis

## Solar-harvesting materials



Kesterite

Applied Physics A **124**,  
Art. N: 225 (2018)

### Cu<sub>2</sub>ZnSnS<sub>4</sub> nanoparticles:

Earth abundant solar cell material, which has complex dynamics.

Ability to probe **each absorption edge** would give unique complementary insight into excited state processes.

## Simultaneous detection

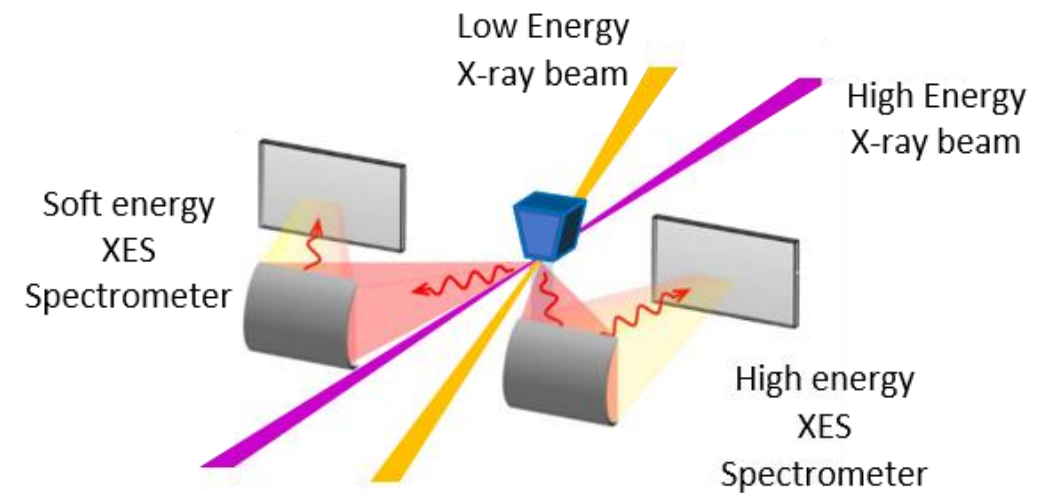
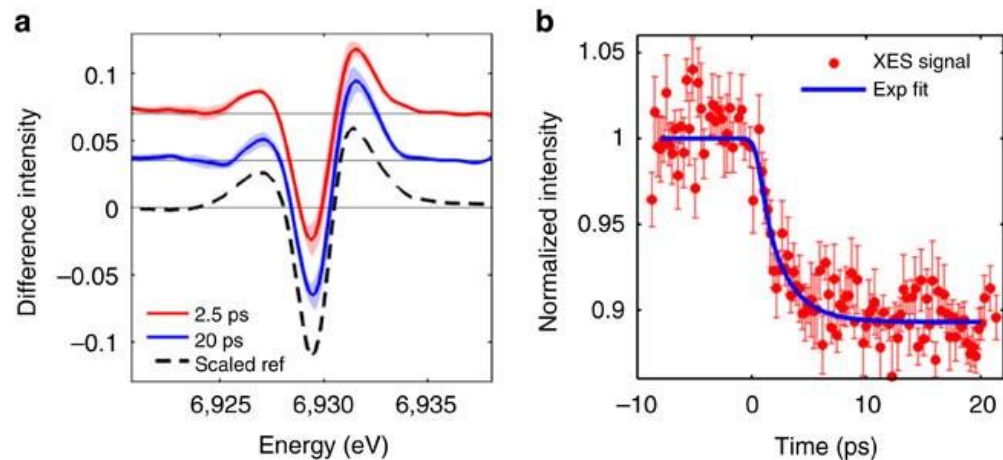
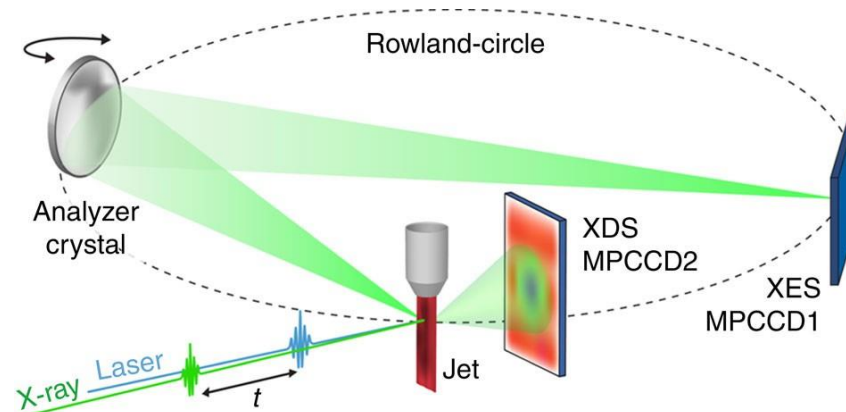
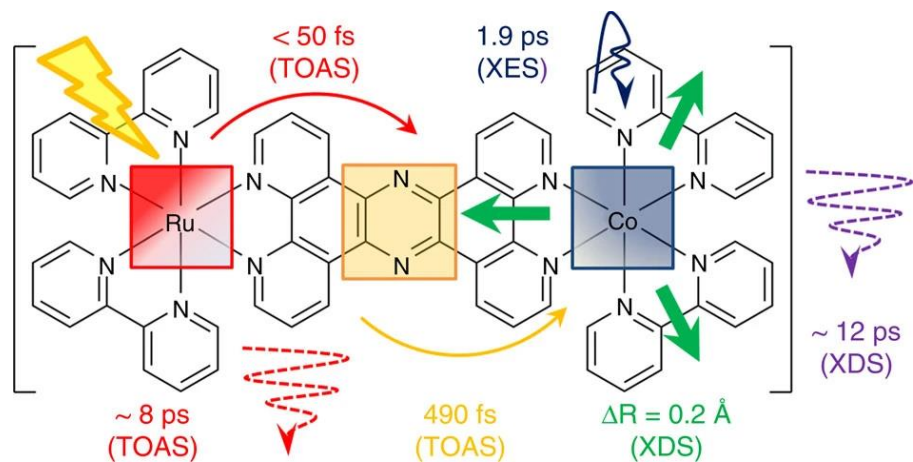


Fig. 6.13. Schematic of a XES experiment performed in the soft and the hard X-ray regime simultaneously [Y. Kayser et al. "Core-level nonlinear spectroscopy triggered by stochastic X-ray pulses". Nat. Commun. 10, 1, (2019)]

Simultaneous Detection of Different edges, Different Components (organic / metal); of spin- and structural dynamics in a photocatalytic system, **in real conditions**

# 6.4. Understanding Catalysis with XFELs

## Multinuclear molecular catalysts; intermolecular electron- and energy transfer



(a) Co K $\alpha$ 1  $\Delta$ SXES( $t$ ) at 2.5 (red) and 20 ps (blue) pump-probe delay.  $^1\text{Co}^{\text{III}}(\text{LS}) \rightarrow ^4\text{Co}^{\text{II}}(\text{HS})$  (b) Kinetic trace at 6.93 keV.

This optical pump-X-ray probe detection scheme combining XES and XDS on photoexcited species in solution was implemented at the SACLA XFEL facility.

Canton et al. *Nat. Comm.* 6, Art. N. 6359, (2015)

**Simultaneous Detection of Different edges, Different Components (organic / metal); of spin- and structural dynamics in a photocatalytic system, in real conditions**

# 6. 4. Understanding Catalysis with XFELs

## Molecular Photocatalysis

Example: Cu(I) photosensitisers

XAS:  
STRUCTURAL  
dynamics

Pseudo Jahn-Teller distortion,  
damping time 540 fs.  
[Katayama *et al. Nat. Comm.*  
10, 1, (2019)]

Next step:  
XES, SPIN dynamics  
timescale??

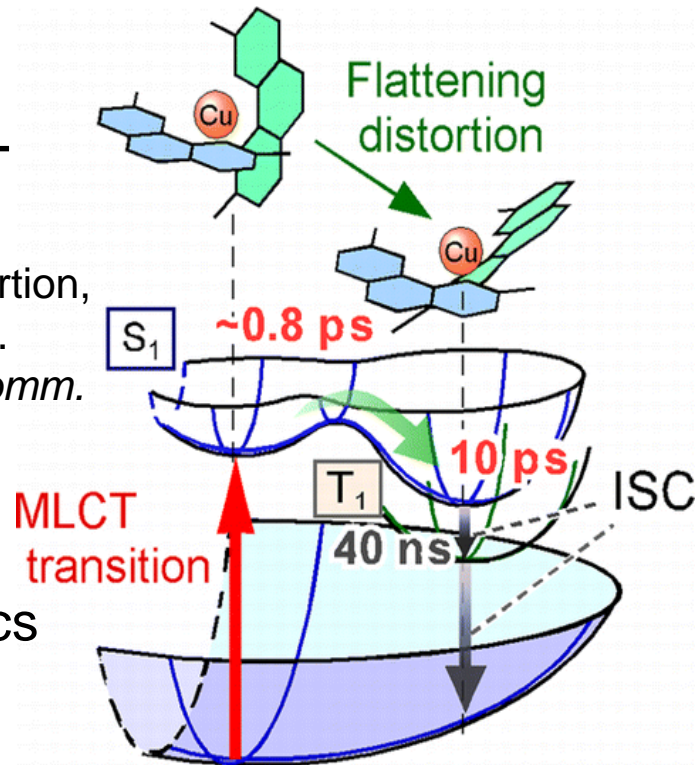
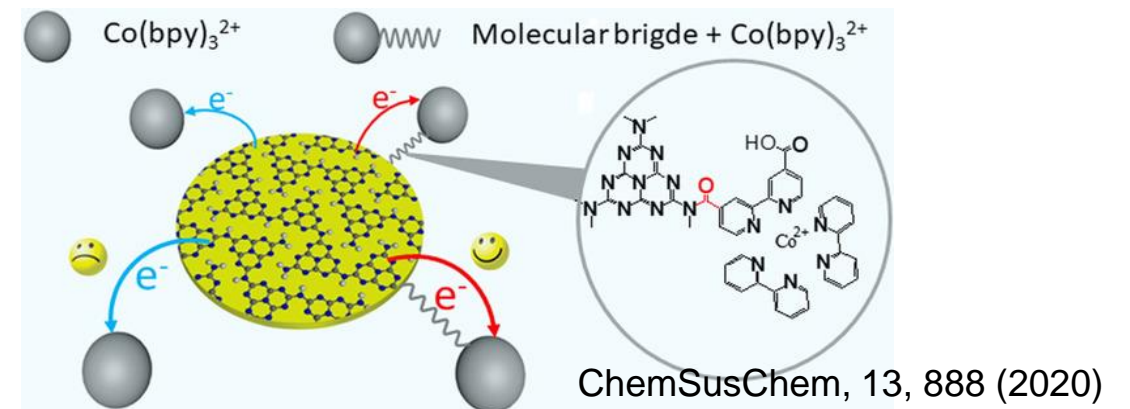


Fig. 6.5 Light-triggered distortion in a Cu-complex. Iwamura *et al. JACS*, 133, 7728 (2011)

## Materials, surfaces and interfaces:

- Charge flow inside semiconducting structure;
- The nature of losses in materials – perovskite solar cells, silicon
- Dynamics of electron transfer from the SC to the catalyst – structural dynamics on surfaces
- Exciton diffusion

Example: A photocatalytic system for  $H_2$  generation and  $CO_2$  reduction



a molecular catalyst  $Co(bpy)_3^{2+}$ ,  
with light-harvesting polymeric **carbon nitride** nanosheets.

spin, electron- and structural dynamics; solution, solid, interface

# End of Part 1 on Scientific Opportunities in Chemical Sciences and Energy –

Part 1 presented:

6.0. Introduction and Overview of Scientific Opportunities in Chemical Sciences in Energy from XFELs;

6.1 Fundamentals of reaction dynamics: Coupling between nuclear, electronic and spin degrees of freedom

6.4 Understanding catalysis

**Over to Russell Minns (U. Southampton), who will talk about**

6.2 Exploring complex energy landscapes through chemical activation

6.3 Energy materials and devices: Solar cells and batteries

6.5 Chemistry and the environment: Aerosols, atmospheric, space chemistry, combustion, corrosion