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

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

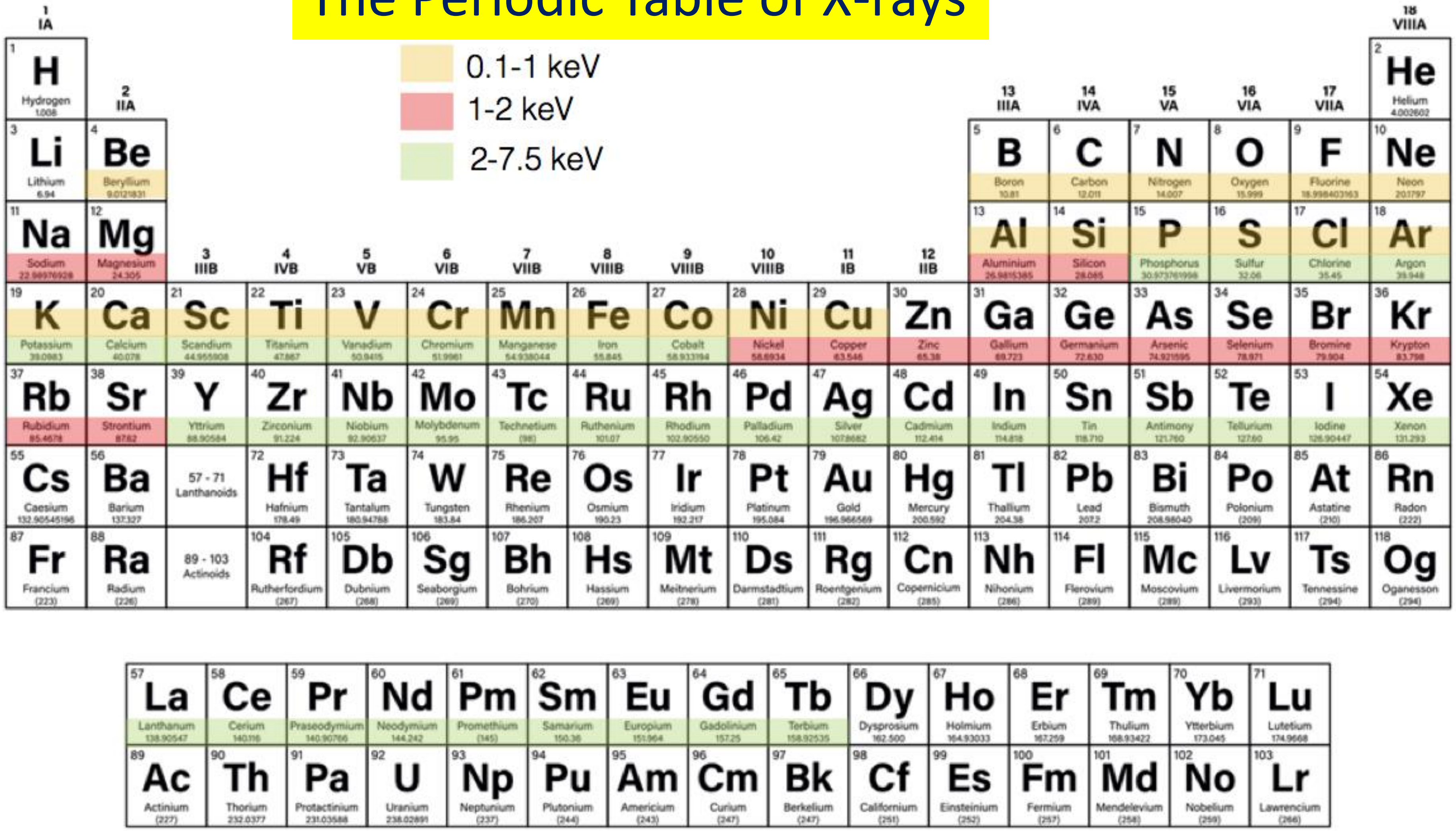
Chemical Sciences team:

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

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



The time-resolution

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 V

X-ray ?

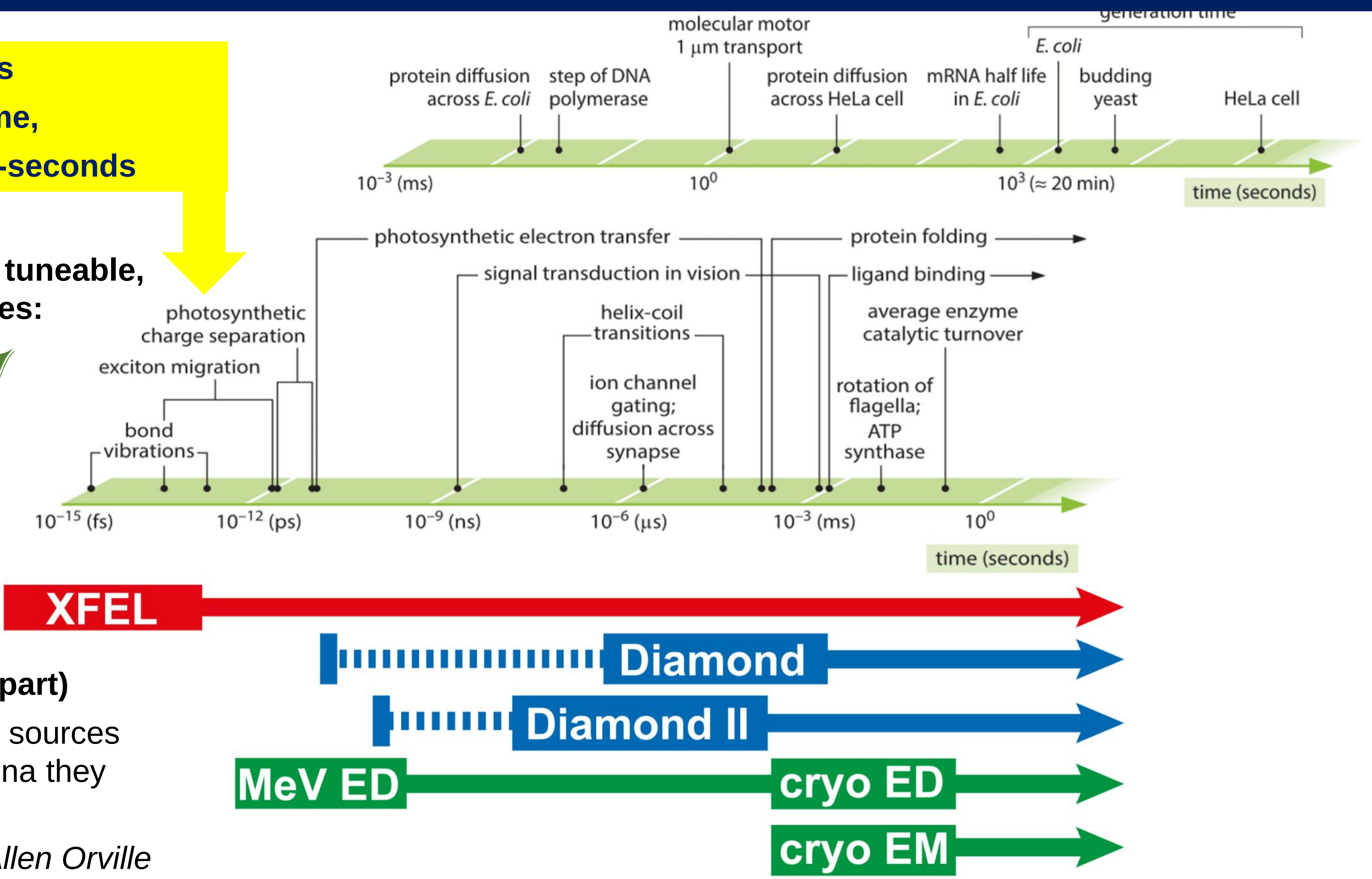


Figure 7.2:

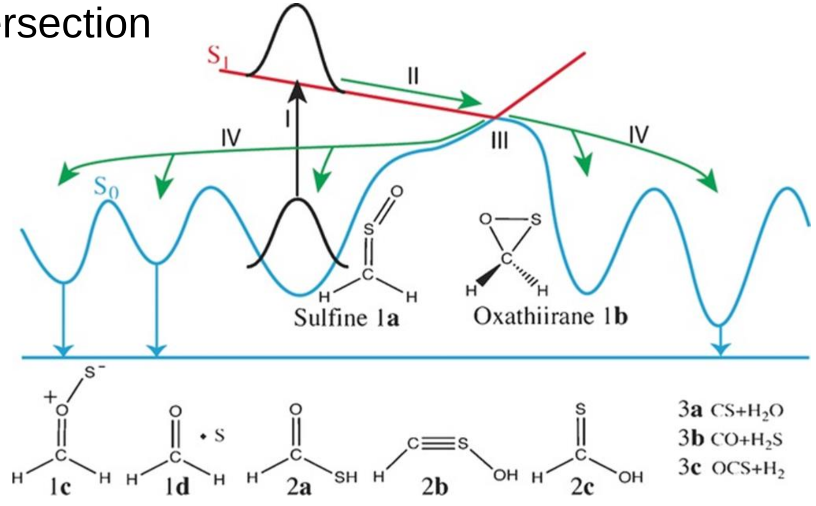
(From Life Sciences part)

A comparison of X-ray sources *and* types of phenomena they are used to study.

@ Allen Orville

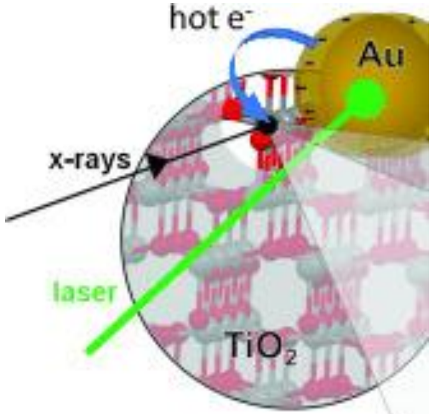
6. Challenges in Chemical Sciences and Energy: an overview

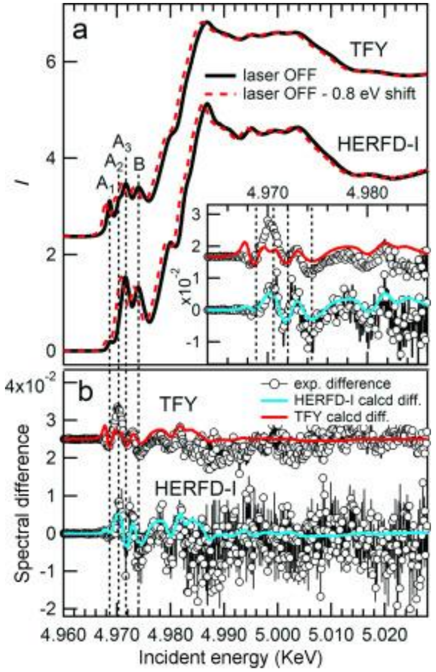
Ground-State Chemistry Triggered by Dynamics through a Conical Intersection



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

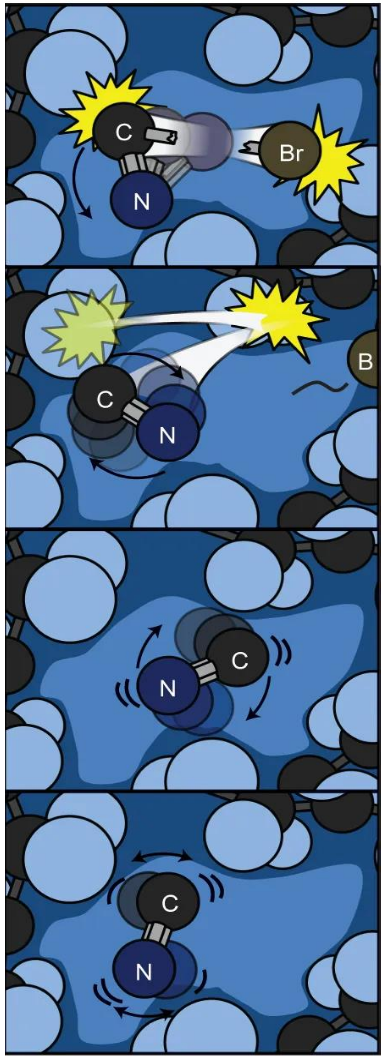
Plasmonic Photocatalysis





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

Solvent-Solute interactions

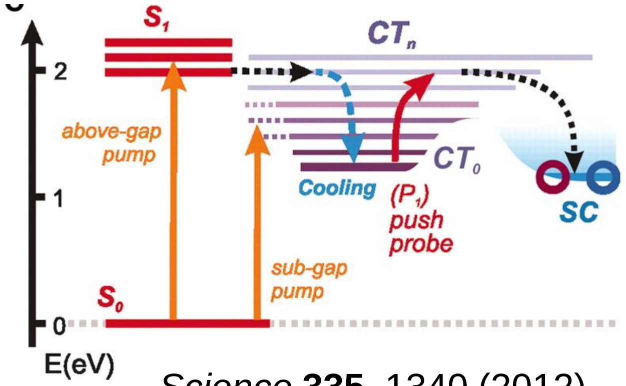


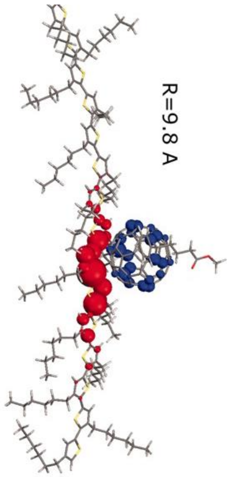
Translational, rotational and vibrational relaxation dynamics

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

Charge- and energy transfer dynamics

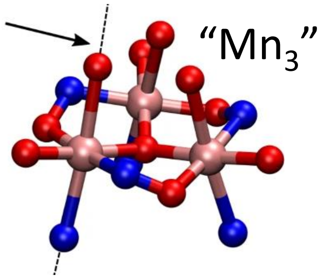
Exciton Dynamics





Science **335**, 1340 (2012)

Spin dynamics: Vibrational coherence in single-molecule magnets



Nature Chem. 452 (2020)

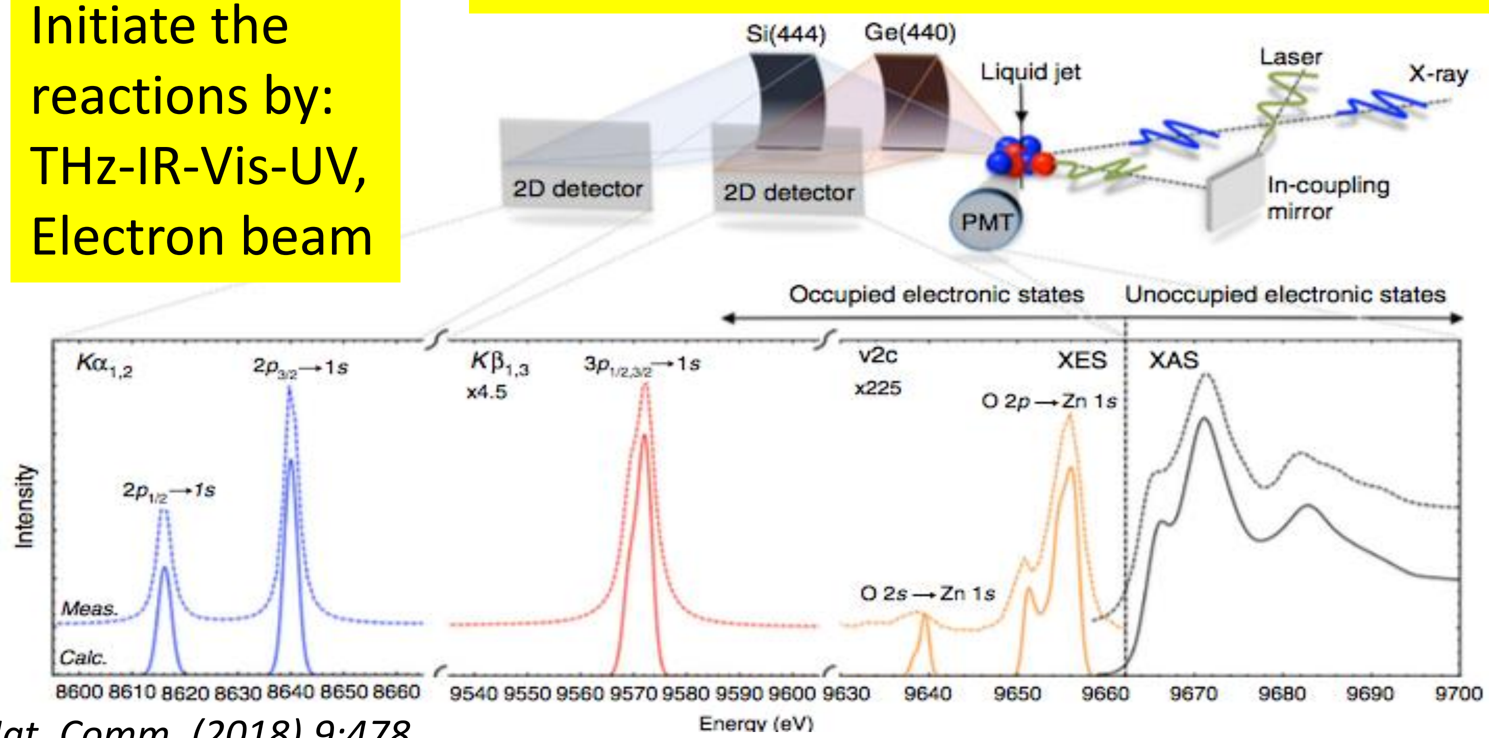
6. Opportunities in Chemical Sciences: Tools and Goals

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



Nat. Comm. (2018) 9:478

X-ray Spectroscopy:

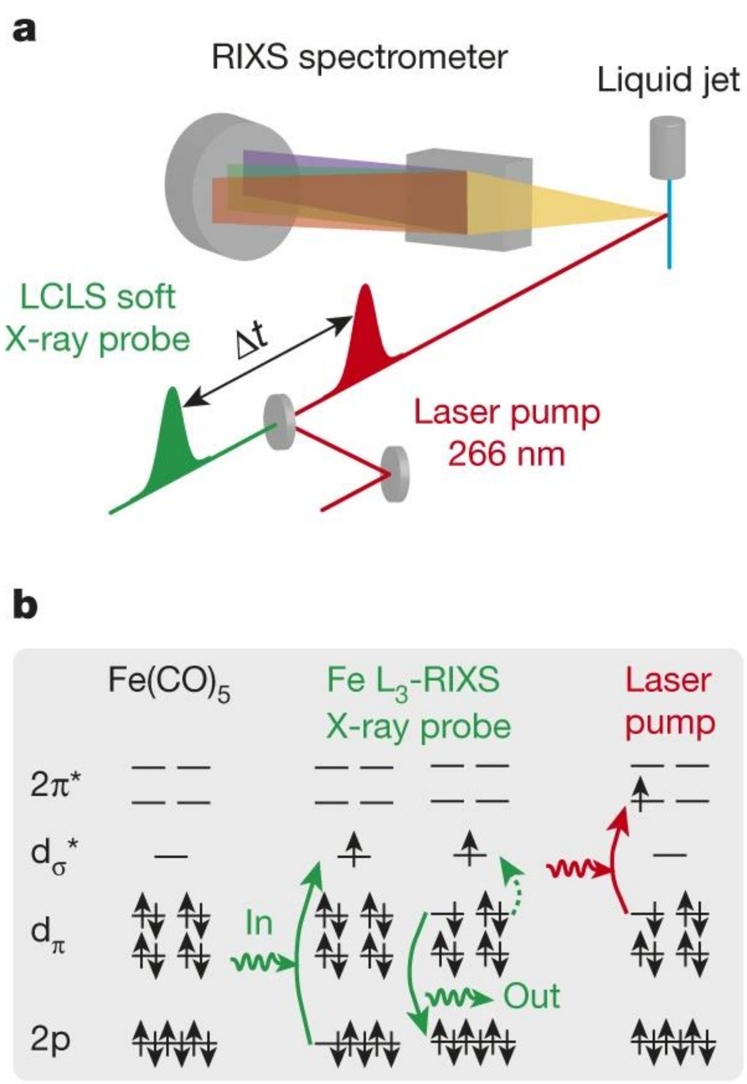
- *X-ray absorption*: Probe Structure and Unoccupied Electronic Density of states.
- *X-ray emission*: Probed Occupied Density of States. **SPIN!**
- *Resonant X-ray Emission*: High resolution experiments.
- *X-ray Raman*: Probe edges of light elements using harder X-rays.

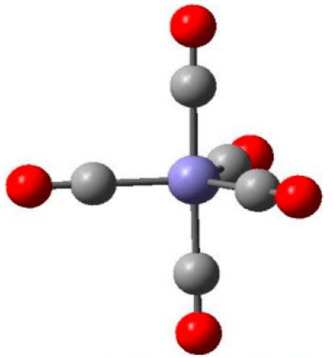
X-ray scattering:

Time evolution and structural dynamics of global structure.

Towards femtosecond-, < 0.01Å- molecular movies

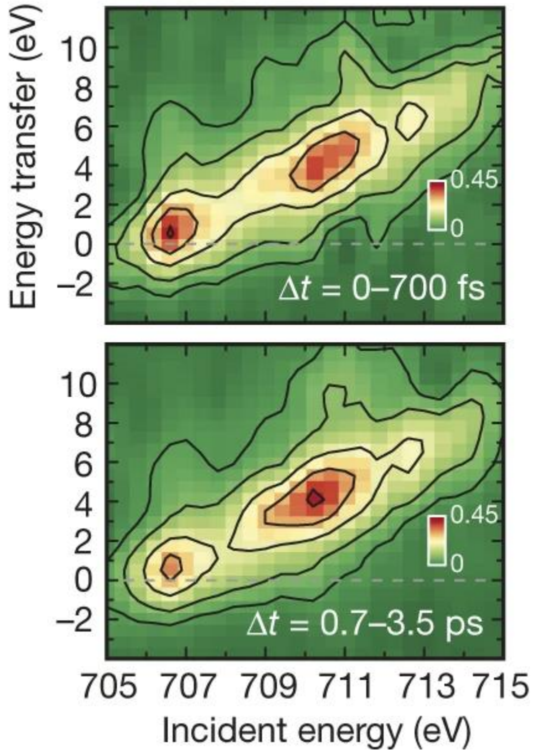
X-ray SPECTROSCOPY: Element- and site-specific probing





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 $Fe(CO)_5$ by time-resolved RIXS *at the Fe L_3 edge.*



The "movie" part:

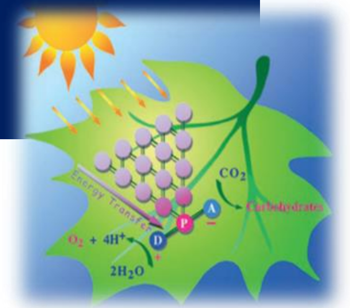
- Ligand dissociation
- Primary step in catalysis

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 $Fe(CO)_5$ 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

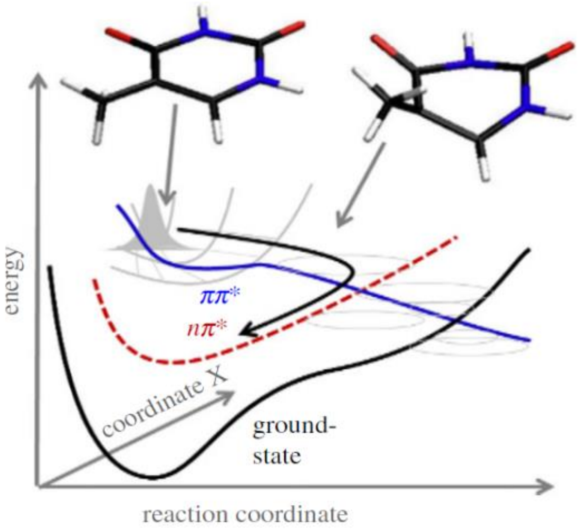
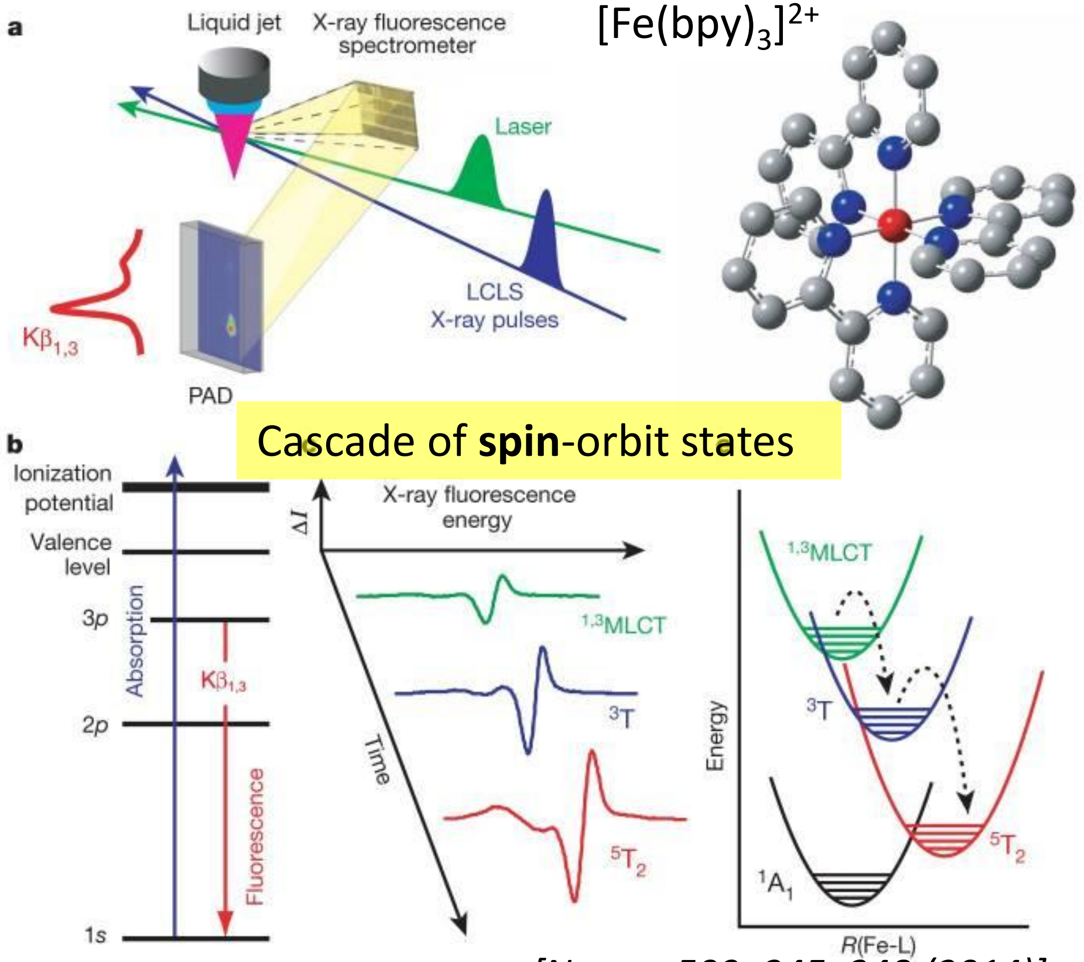


Fig. 6. 4. *TR-AES and TR-NEXAFS reveals possible relaxation paths a ππ* state of thymine populated by UV-pulse, to the dark nπ* state and to the ground state via conical intersections. [Nat. Comm. 8, 29, (2017)]*

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.**

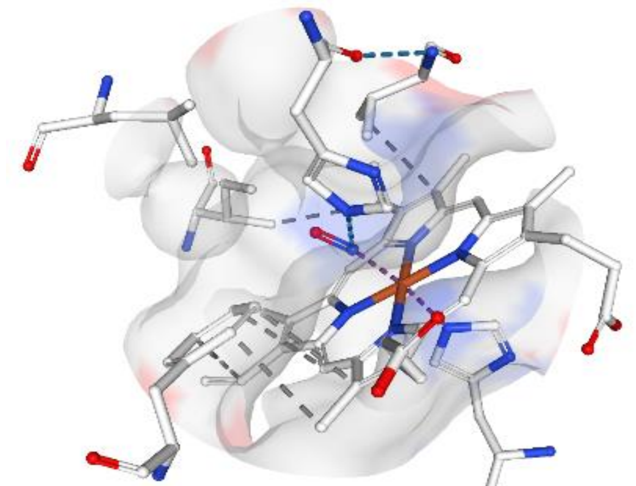
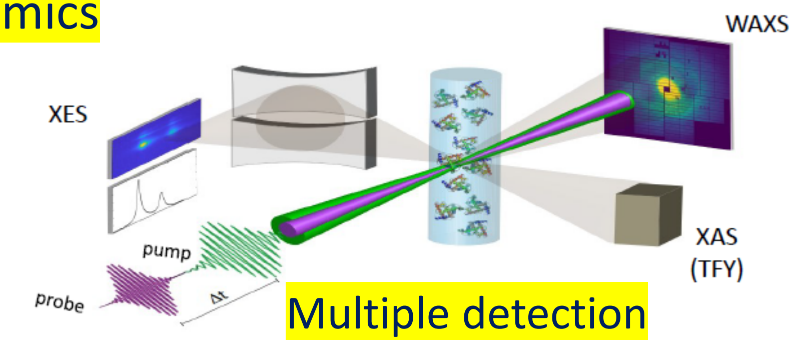


Fig. 6.2. Nitrosyl Horse Heart Myoglobin. --- show bonds which reversibly form and break. PDB 2FRJ.

- 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

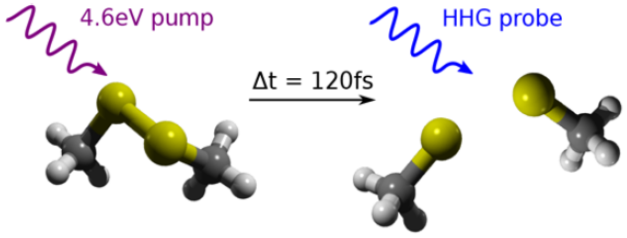
Figure: *Courtesy of C Bressler*

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 CH_3-S-S-CH_3…undergoes fast direct dissociation into 2 H_3C-S•.



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 $^1O_2$;
- What are *structural* changes in the drug itself;
- What are cooperative effects;
- 1st step in PDT…

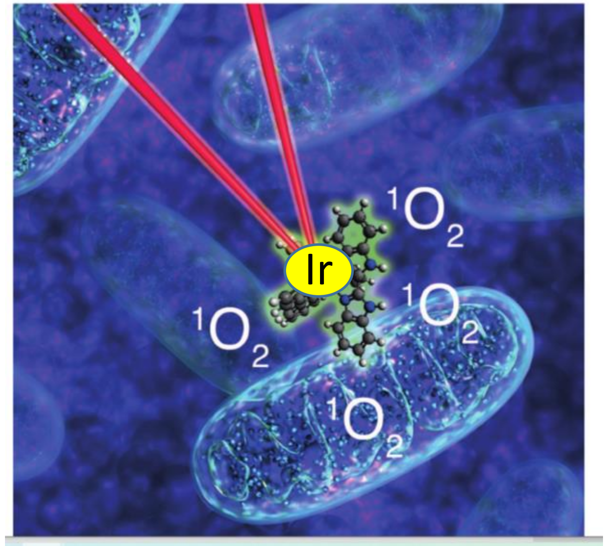


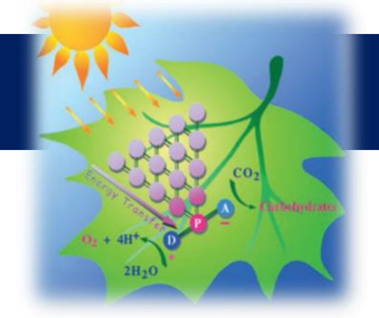
Fig. 6. 6. McKenzie et al, Chem Eur J, 2017

Directly linked to:

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

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

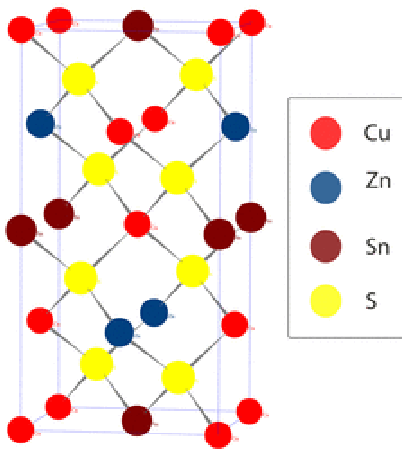
6.4. Understanding Catalysis with XFELs



Molecular Photocatalysis, Heterogeneous Photocatalysis, Light-Absorbing Semiconductors

Applications: CO_2 reduction; Water oxidation; Solar fuel; Artificial Photosynthesis

Solar-harvesting materials



Kesterite

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

Cu_2ZnSnS_4 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

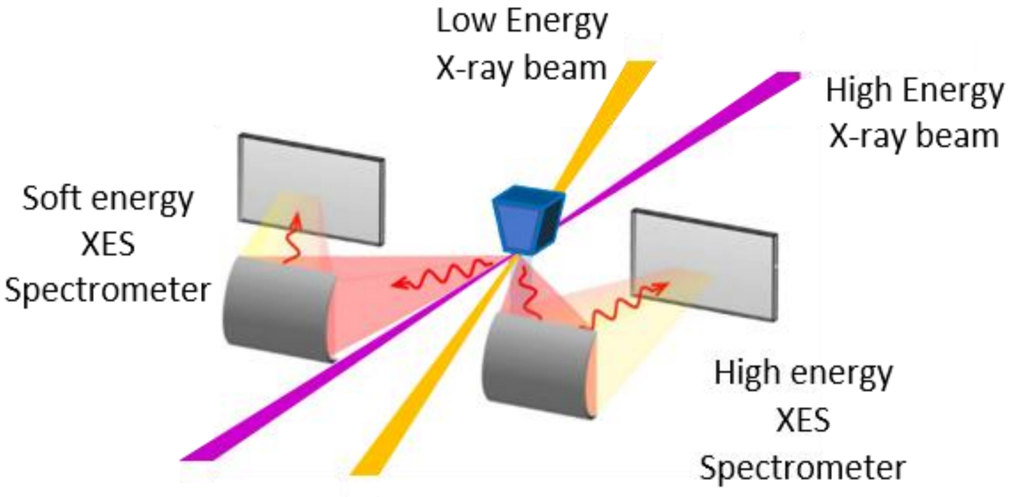
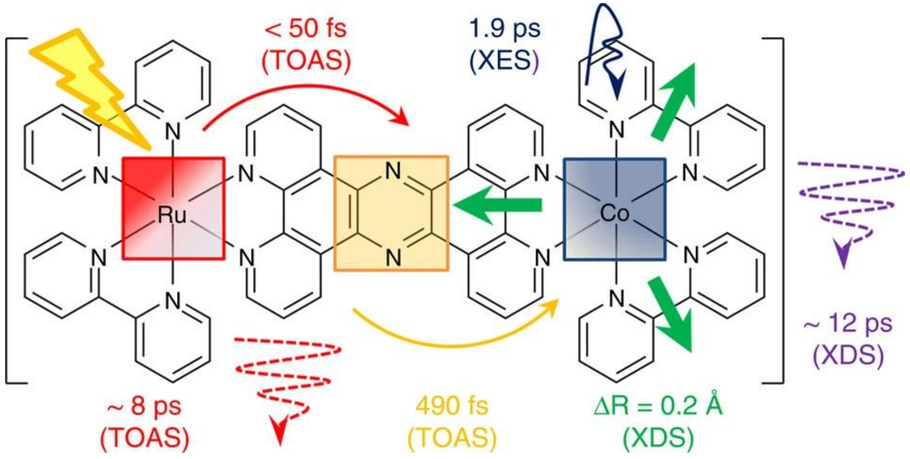


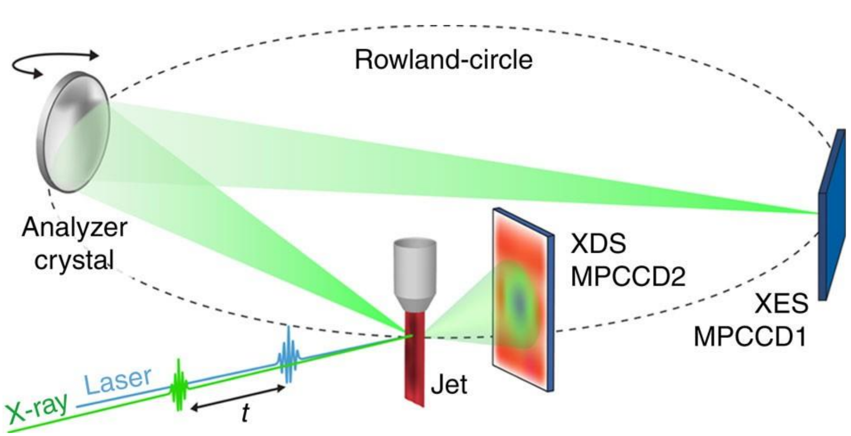
Fig. 6.13. Schematic of a XES experiment performed in the soft and the hard X-ray regime simultaneously [Y. Kayser et al. "Core-level nonlinear spectroscopy triggered by stochastic X-ray pulses". Nat. Commun. 10, 1, (2019)

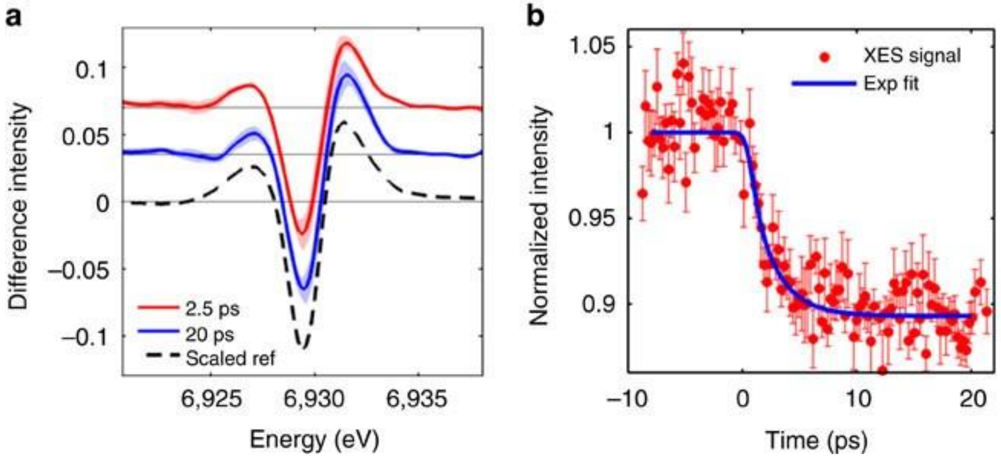
Simultaneous Detection of Different edges, Different Components (organic / metal); of spin- and structural dynamics in a photocatalytic system, **in real conditions**

6.4. Understanding Catalysis with XFELs

Multinuclear molecular catalysts; intermolecular electron- and energy transfer







(a) Co Kα1 ΔSXES(t) at 2.5 (red) and 20 ps (blue) pump-probe delay. $^{1}Co^{III}(LS) \rightarrow ^{4}Co^{II}(HS)$ (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??

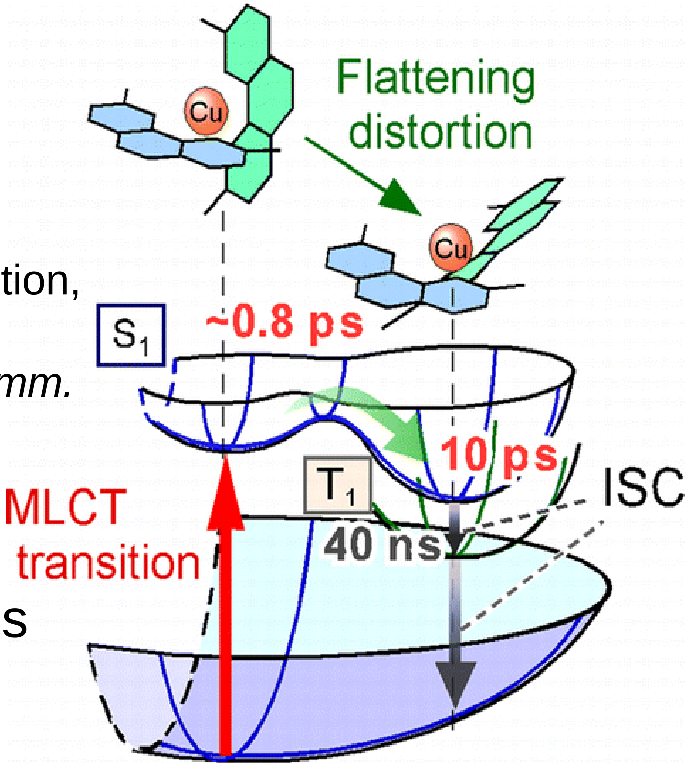
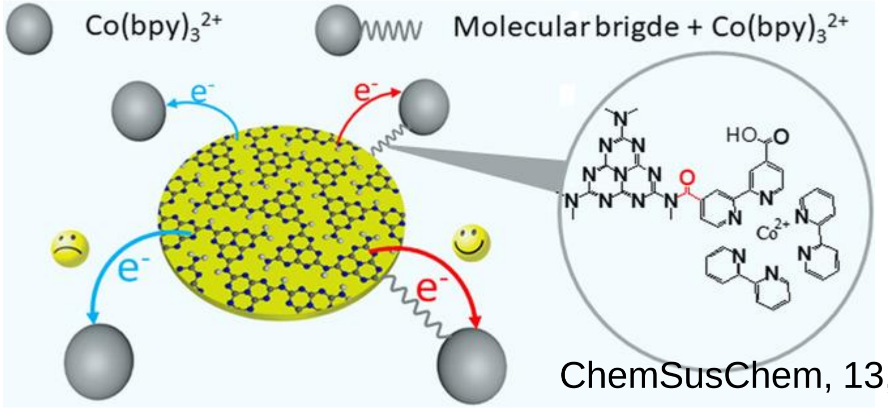


Fig. 6.5 Light-triggered distortion in a Cu-complex. Iwamura *et al.* JACS, 133, 7728 (2011)

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



ChemSusChem, 13, 888 (2020)

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