New opportunities for chemical sciences at current and future x-ray free-electron lasers

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My guiding questions

- Why chemical sciences?
- Why XFELs?
- Why x-rays?

An outline

- “Experiments”
- Obvious but still important arguments (1)
- “More experiments”
- Less obvious and hopefully still important arguments (2)
- Some thoughts about a facility

“The Weinstein experiment”

Design of the experiment

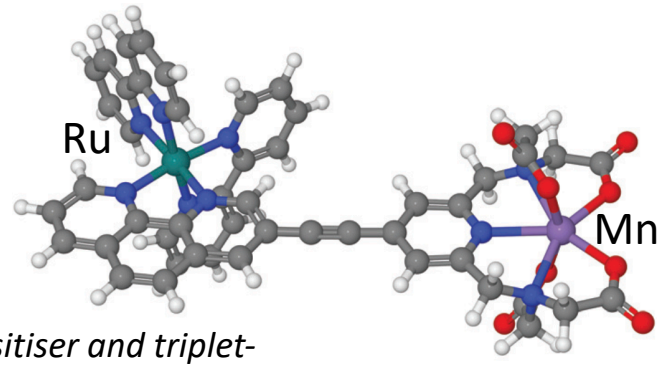
- I arbitrarily choose Julia Weinstein
- I take from her web pages the latest publication
- I check it for the driving questions
- Then I ask myself:
- **Can XFEL research answer these questions, and maybe better than the employed methods?**

- This is not to show that Julia Weinstein should replace her lab-based methods
- But to show that they could be complemented with XFEL methods
- And that some of the critical questions may be best answered with XFEL research

“The Weinstein experiment”

Heteronuclear metal complexes

- MR imaging (contrast agents)
- Cell imaging (Ru luminescence)
- Photophysical properties



Photosensitiser and triplet-state Ru phosphorescence

Unpaired 3d electrons (water relaxivity and electron transfer)

Why does Mn quench Ru phosphorescence?
How does this depend on structure?

$^1Ru^{II} \xrightarrow{h\nu} {}^3Ru^{III}$ (MLCT) $\xrightarrow{\text{Phosphorescence}} {}^1Ru^{II}$

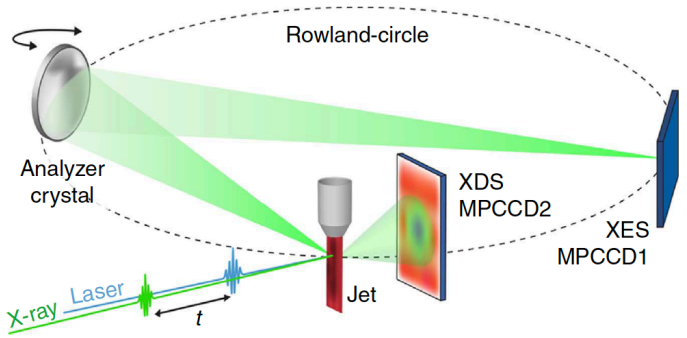
Quenching could be due to transfer of

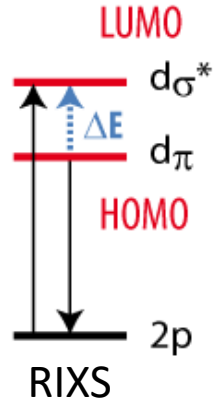
1) Electron $Ru^{III} – Mn^{II} \rightarrow Ru^{II} – Mn^{III}$
2) Energy $^3Ru^{III} – {}^1Mn^{II} \rightarrow {}^1Ru^{II} – {}^3Mn^{II}*$

TR-UV/Vis + calculations: 1), planar geometry.

fs x-ray spectroscopy and scattering at XFELs

Ru and Mn oxidation and spin states, geometry (Å), Ru and Mn d-d excitations, all as function of fs time





Crowston et al., Dalton Trans. **48**, 6132 (2019)

Canton et al., Nat. Com. **6**, 6359 (2015), Wernet et al. Nature **520**, 78 (2015)

What matters in the UK fits to XFEL capabilities

*"A key element will be an assessment of the level of interest within the UK Scientific Community."**

Yet another experiment to extend this argument to the chemical sciences community in the UK

- Tom Penfold helped me compiling an incomplete list of groups in photochemistry in the UK
- Tom didn't know about the experiment
- Purpose not to have a complete list
- Go to their web pages and copy-paste keywords (systems and phenomena, no methods)
- This shows the breath of topics in the chemical sciences in the UK
- It automatically renders (part of) the scientific case for a UK-XFEL
- There is an almost 1:1 correspondence of questions and XFEL properties and capabilities
- The "Weinstein experiment" could have worked for each of these groups!

** UK XFEL Science Case project 2019-2020 web pages (https://www.clf.stfc.ac.uk/Pages/UK-XFEL-science-case.aspx)*

What matters in the UK fits to XFEL capabilities

*"A key element will be an assessment of the level of interest within the UK Scientific Community."**

Julia Weinstein (University of Sheffield)
Russell Minns (University of Southampton)
Tom Penfold (Newcastle)
Mike Ashfold (Bristol)
Andrew Orr-Ewing (Bristol)
Thomas Oliver (Bristol)
Mike Towrie (CLF, Rutherford Appleton Lab)
James Durrant (Imperial College London)
Helen Fielding (University College London)
Vas Stavros (Warwick)
Steve Meech (University of East Anglia)
Olof Johansson (University of Edinburgh)
Klaas Wynne (University of Glasgow)
Akshay Rao (Uiversity of Cambridge)
Philipp Kukura (University of Oxford)
Jenny Clark (University of Sheffield)
…
…

Light-induced electron transfer in chemical and biological systems, solar energy conversion, ultrafast excited state dynamics, motions of atoms and electrons in molecules that underlie chemical change, how hydrogen bonding affects photochemical processes, how do we most efficiently design and exploit the excited state properties of molecules and materials?, UV photophysics and photochemistry of molecules and biomolecules in the gas phase, chemical reaction dynamics in liquids, chemical reactivity in the gas phase, atmospheric chemistry, aerosol science, photo-protection pathways in DNA, excitation transport mechanisms in photo-voltaic materials, delocalised energy transport in bacterial reaction centres, nanoscale design principles of natural and artificial light harvesting systems, ultrafast lab methods applied to structural chemical molecular biology and energy materials, new chemical approaches to solar energy conversion, new functional device, harnessing solar energy for electricity or molecular fuels, light driven electron and energy transfer reactions, electronic structure and dynamics of excited state of molecules and ions in the gas-phase, in solution and on surfaces, photoactive protein chromophores, molecular motors, clusters and nanoparticles, photoprotection in biologically important molecules such as DNA bases and chemical filters, ultrafast liquid state dynamics, fast photochemical reactions and photoactive proteins, ultrafast spectroscopy of molecular materials, molecular magnetism, thin films, photoinitiated electron dynamics in carbon nanomaterials, fundamental chemical physics of liquids, proteins, and soft matter, phase transitions, liquid-liquid transitions, nucleation of new phases such as crystals, solar energy harvesting in photovoltaics and artificial photosynthetic complexes, molecular spintronics, charge delocalisation, spin and vibrational coherence, (bio)molecular structure and dynamics, visualise and quantify energetics and kinetics of biomolecular interactions at the single molecule level, photophysics of carbon-based materials such as biological materials, organic semiconductors and graphene

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What matters in the UK fits to XFEL capabilities

*"A key element will be an assessment of the level of interest within the UK Scientific Community."**

Develop the chemical X-RAY science community and the chemical XFEL science community will follow

** UK XFEL Science Case project 2019-2020 web pages (https://www.clf.stfc.ac.uk/Pages/UK-XFEL-science-case.aspx)*

Chemical sciences with XFELs (1)

*Jon: "*It will deliver science for the 2030's, 40's & 50's*"*

- Photochemistry – Predict photochemical processes
  - Mechanistic understanding of excited-state dynamics, derive simple rules and develop concepts to control dynamics
  - XFEL methods are the decisive tool (with chemical synthesis + theory)
  - New groups routinely use XFELs and care about details (of the XFEL methods)

- Photocatalysis – Explain photocatalytic function
  - Use fundamental knowledge to engineer chemical bonds
  - XFEL methods are important in a range of other (including lab-based) methods
  - New groups use XFELs but don't care about details (of the XFEL methods)

XFEL methods (1)

To predict photochemical processes and explain photocatalytic function

- X-ray scattering/diffraction – Structure
  - Nuclear structures on Å/fs scales (molecular movies – See Adam Kirrander)
  - Determine the key reaction coordinates and modes
  - Can also be done with hard x-ray spectroscopy (XANES, EXAFS) and UED
- X-ray spectroscopy – Electronic structure
  - Detect species (use the elemental specificity)
  - Extract charge + spin densities (use the site specificity)
  - Relate Bonding and reactivity
  - Use soft and hard x-ray methods, complement lab-based methods

XFEL methods (1)

To predict photochemical processes and explain photocatalytic function

New aspect of x-ray spectroscopy at XFELs:

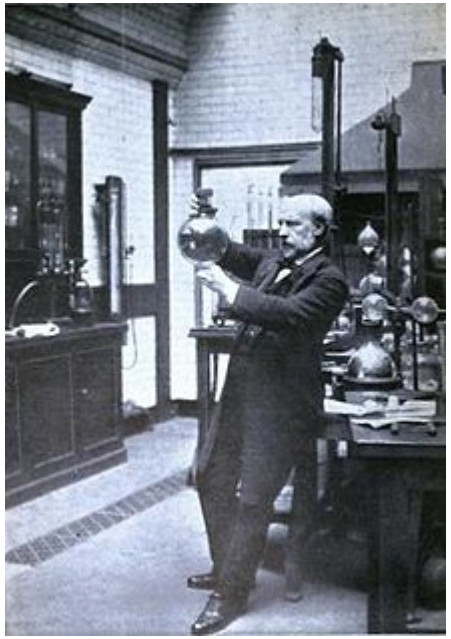
Dissect orbital interactions (use the orbital specificity)

Richard Henderson*: "…cryo-EM is seeing the chemistry…"

"…x-ray spectroscopy is seeing the QUANTUM chemistry…"

*BBC, The Life Scientific by Jim Al-Khalili

An example for this: From Dewar to XFELs…With $Fe(CO)_5$



Sir James Dewar (1842-1923)

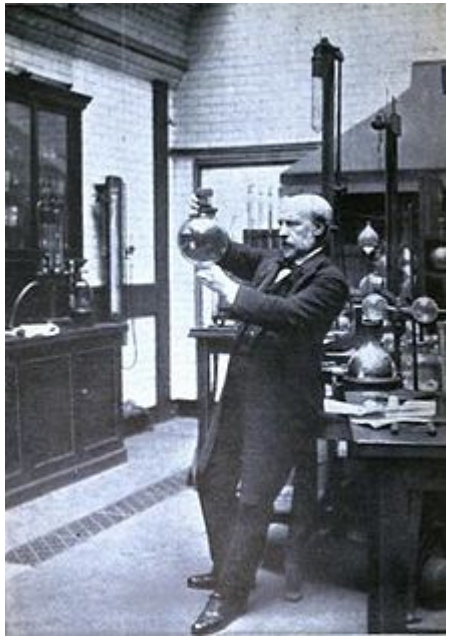
The Royal Institution and University of Cambridge

"… in the laboratory on bright days in February the decomposition was extremely slow, but on the same days in direct sunlight the decomposition was rapid…"

Dewar and Jones, *The physical and chemical properties of iron carbonyl*, Proc. R. Soc. London A **76**, 558-577 (1905).

Wernet, Phil. Trans. R. Soc. A **377**, 20170464 (2019)

From Dewar to XFELs…With $Fe(CO)_5$



Sir James Dewar (1842-1923)

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- Where are the Nuclei?
- Charges?
- Spins?
- During this reaction

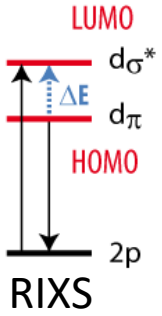
The initial action of light on iron carbonyl might be represented by the equation

$$Fe(CO)_5 = Fe(CO)_4 + CO,$$

Wernet, Phil. Trans. R. Soc. A **377**, 20170464 (2019)

New observables – New concepts

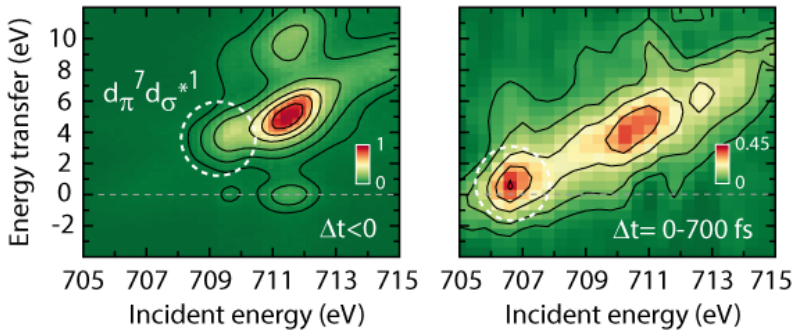
From probing frontier orbitals at the active site



1 ct/pulse $(CO)_4$ – Fe – CO

0.01 ct/pulse $(CO)_4$ – Fe ··· CO

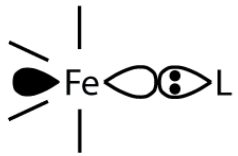
10^{12} photons/s (5 µJ/pulse, 60 Hz, LCLS) on 1M sample



1. Ligand takes away 2 electrons
2. Dissociation creates 16-e^- catalyst
3. Reactivity due to e^- deficiency at Fe

Make coordinatively unsaturated species

Reactive



Singlet

Ligand-Fe σ donation

Unreactive

Singlet, triplet

No ligand-Fe σ donation

1. Charge density at Fe does not change*
2. Dissociation creates empty σ orbital**
3. Reactivity due ability of L-M donation

Make localized empty σ orbitals

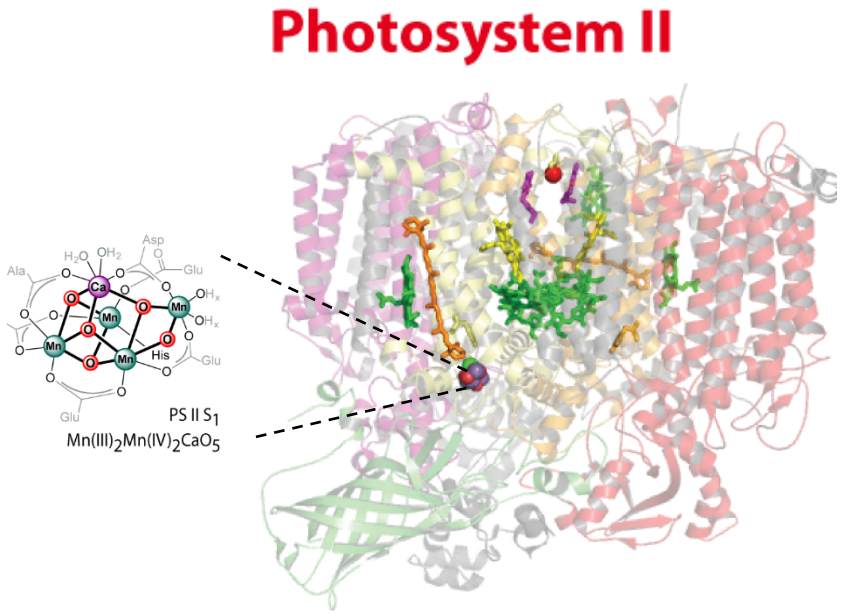
** R. Hoffmann, Angew. Chem. Int. Ed. Engl. **21**, 711-724 (1982)

* Minor charge density changes by 0-0.5 electrons, depending on method (M. Odelius with RAS, DFT, Mulliken, LoProp)

Wernet, Phil. Trans. R. Soc. A **377**, 20170464 (2019), Wernet et al., Nature **520**, 78-81 (2015).

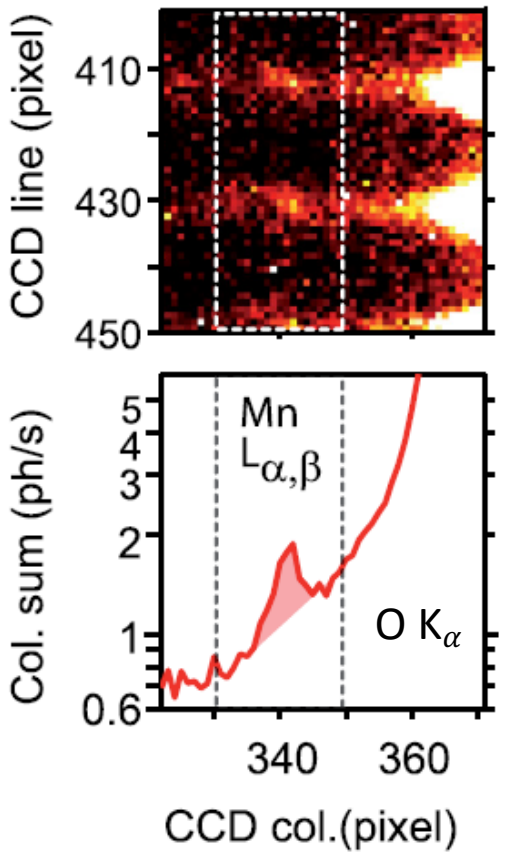
The local chemistry of metalloproteins at *in operando* conditions

Probe-before-destroy x-ray spectroscopy of high-valent species enabled by femtosecond x-ray pulses
With Junko Yano, Jan Kern, Vittal Yachandra and Marcus Lundberg



- Physiological (in operando) conditions
- Mn 0.8 10^{-3} mol/l (Mn:O = 1:64000)
- 1 ml/12 h shift (μl/min)

0.04 ct/pulse, 5 cts/s



First counts from Mn in PSII under physiological conditions for Mn L-edge soft x-ray spectroscopy (LCLS)

10^{12} photons/s (5 µJ/pulse, 120 Hz LCLS) on 1mM sample

Kubin et al., Structural Dynamics **4**, 054307 (2017).

Chemical sciences with XFELs (2)

*Jon: "*It will deliver science for the 2030's, 40's & 50's*"*

- QUANTUM chemistry – Relate reactivity and el. structure
  - New observables → New explanations, translate into new language, new concepts for inorganic (photo)catalysis
  - XFEL methods are decisive (synthesis, characterization, theory)
  - New groups routinely use XFELs and care about details

- Metalloproteins – Learn fundamental QUANTUM chemistry
  - Combine studies of metalloproteins, model systems and artificial catalysts
  - XFEL spectroscopy methods are unique
  - New groups use XFELs routinely and care about details

These are (completely) new fields and communities.

Some thoughts about a facility

First Second Third **Critical for chemical sciences (high rep. rate)**

country	name	electron energy (GeV)	photon energy (keV)	X-ray pulse energy[a] (mJ)	X-ray pulse length[b] (fs)	rep rate (Hz)	start of operation
Japan	SACLA BL2,3	6–8	4–20	0.1–1	2–10	60	2011
	SACLA BL1	0.8	0.04–0.15	0.1	60	60	2015
Italy	FERMI-FEL-1	0.9–1.5	0.01–0.06	0.08–0.2	40–90	10 (50)	2010
	FERMI-FEL-2	0.9–1.5	0.06–0.3	0.01–0.1	20–50	10 (50)	2012
Germany	FLASH1	0.4–1.25	0.02–0.3	0.01–0.5	30–200	(1–800) $\times 10^{9}$	2005
	FLASH2	0.5–1.25	0.01–0.3	0.01–1	10–200	(1–800) $\times$ 10	2016
Korea	PAL-XFEL	4–11	2.5–15	0.8–1.5	5–50	60	2016
		3	0.25–1.2	0.2	5–50	60	2016
Switzerland	SwissFEL	2–5.8	1.8–12.4	1	10–70	100	2017
		3	0.2–2	1	10–70	100	2021
Europe	XFEL-SASE1,2	8.5–17.5	3–25	2	10–100	2700×10^{d}	2017
	XFEL-SASE3	8.5–17.5	0.2–3	2	10–100	2700 $\times$ 10	2017
USA	LCLS	3–15	0.3–12	2–4	2–500	120	2009
	LCLS-II	3–15	1–25	2–4	10–100	120	2021
	LCLS-II	4	0.2–5	0.02–1	10–200	10^{6}	2021
	LCLS-II-HE	4–8	0.2–13	0.02–1	10–200	10^{6}	2026[e]

Schoenlein, Elsaesser, Holldack, Huang, Kapteyn, Murnane, Woerner, Phil. Trans. R. Soc. A **377**, 20180384 (2019)

Some thoughts about a facility

Jon: "…not to be obsolete at first light…", and if it was a soft x-ray machine…

- High repetition rate for high average brilliance (100 kHz)
- Seeded for ultimate sensitivity (flux, stability, 1 μJ)
- Attosecond pulses and multicolor schemes
  - Beyond NLXO and AMO (beyond electronic, local valence-exc. state wavepackets)
  - NL x-ray spectroscopy for chemical sciences
    - Better select species/states/orbital excitations
    - Enhance fluorescence (<0.1% FY)
    - "Direct" stimulated emission
    - (Beat 100 fs x-ray beam damage)
    - (XES: Few fs proton transfer)

Chemical sciences with a UK XFEL

*Jon: "*It will deliver science for the 2030's, 40's & 50's*"*

- Predict photochemical processes
- Relate reactivity and quantum chemical concepts
- Learn fundamental chemistry in metalloproteins
- Explain and control photocatalytic function

“…in the laboratory on a bright day…”

- Make available and accessible more XFELs
- Open up new science areas in chemical science

Thank you

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Vittal Yachandra
LBNL, Berkeley

Kelly Gaffney, Uwe Bergmann
SLAC, Stanford

Bill Schlotter, Josh Turner, Georgi Dakovski, Stefan Möller (SLAC), Tommaso Mazza, Michael Meyer (European XFEL), Stefan Düsterer, Simone Techert (DESY)