



Lawrence Berkeley National Laboratory



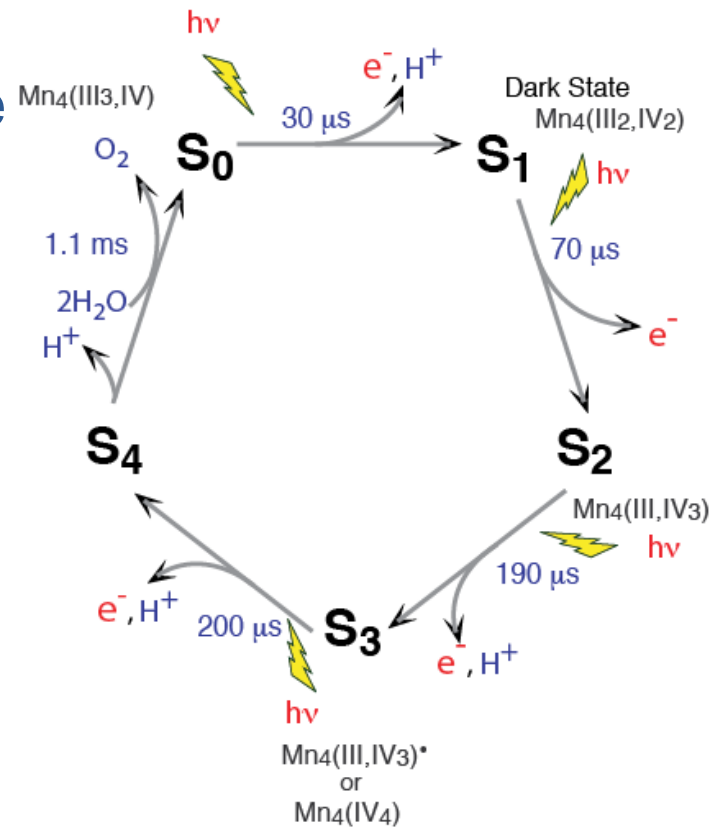
What can we learn with XFEL radiation?

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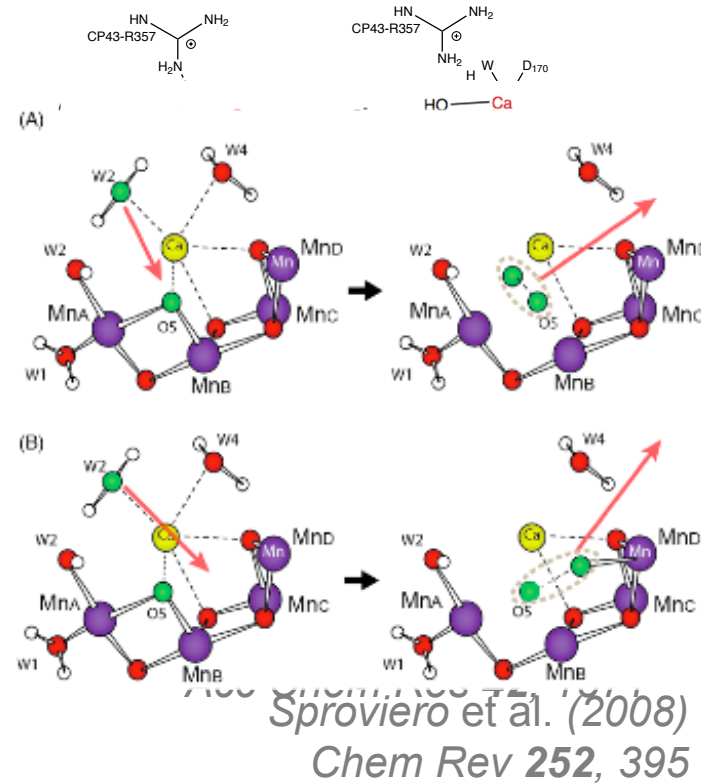
Unlocking the mysteries of photosynthesis: photosystem II (PS II)

- Critical for sustaining aerobic life
 - Found in green plants, algae, and cyanobacteria
- Powered by photons absorbed by Chl around an Mn-rich catalytic center
- Protein residues provide pathways for electrons, substrates, and products
- Artificial photosynthesis using earth-abundant elements?



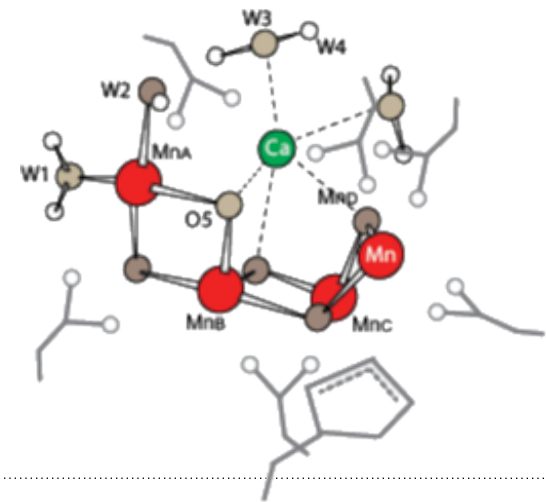
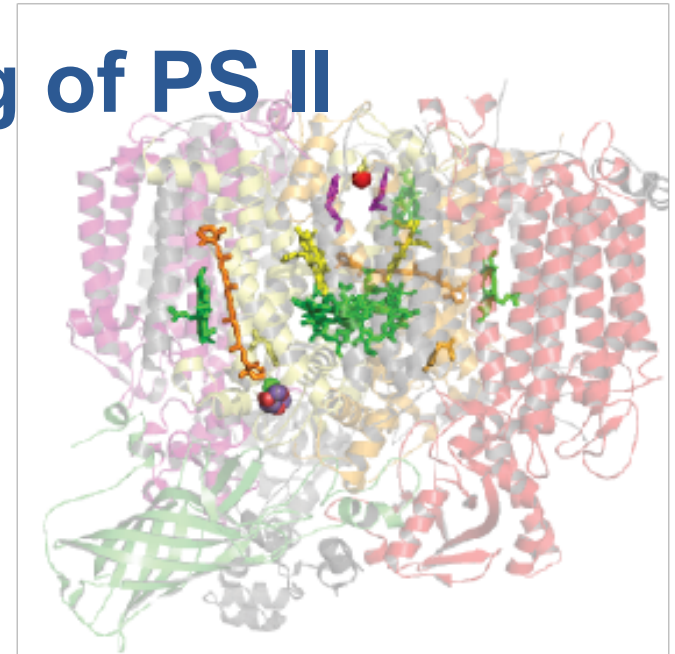
Kok et al. (1970) *Photochem Photobiol* **11**, 457–475

How does water oxidation work?

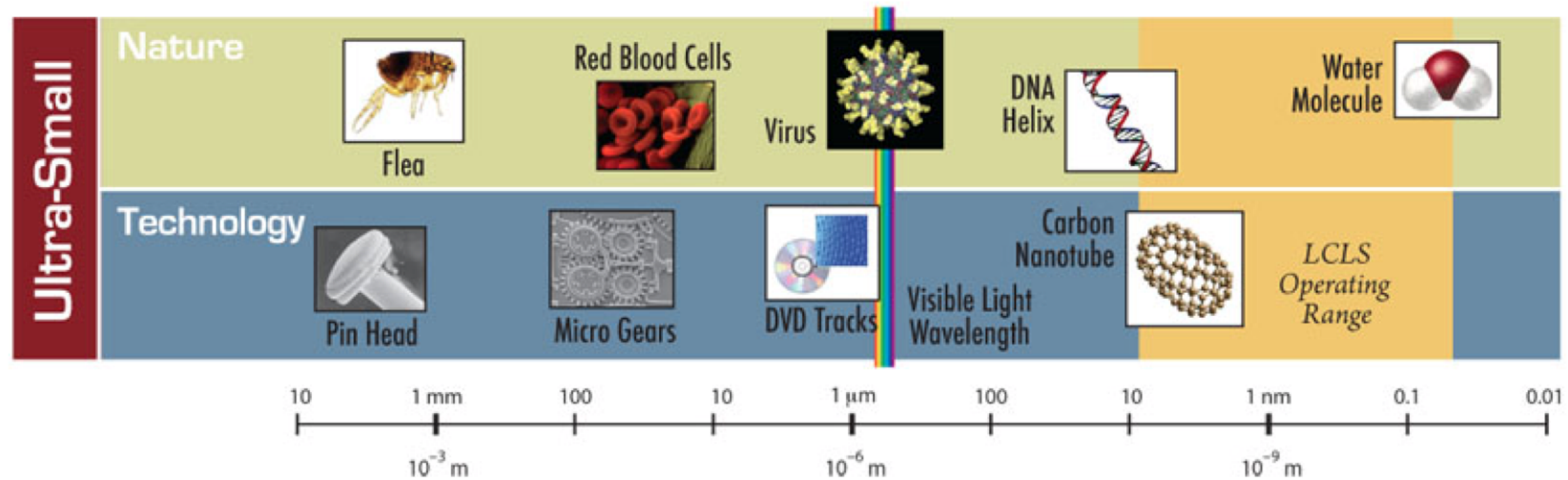


Towards an understanding of PS II

- Structural dynamics
 - Protein side-chain motions
 - Quinone sites
 - Geometry of the Mn_4CaO_5 cluster
- Chemistry at the Mn_4CaO_5 site
 - Charge density changes of Mn
 - Ligand environment changes
- Time-resolved coupling between atomic motion and electronic structure

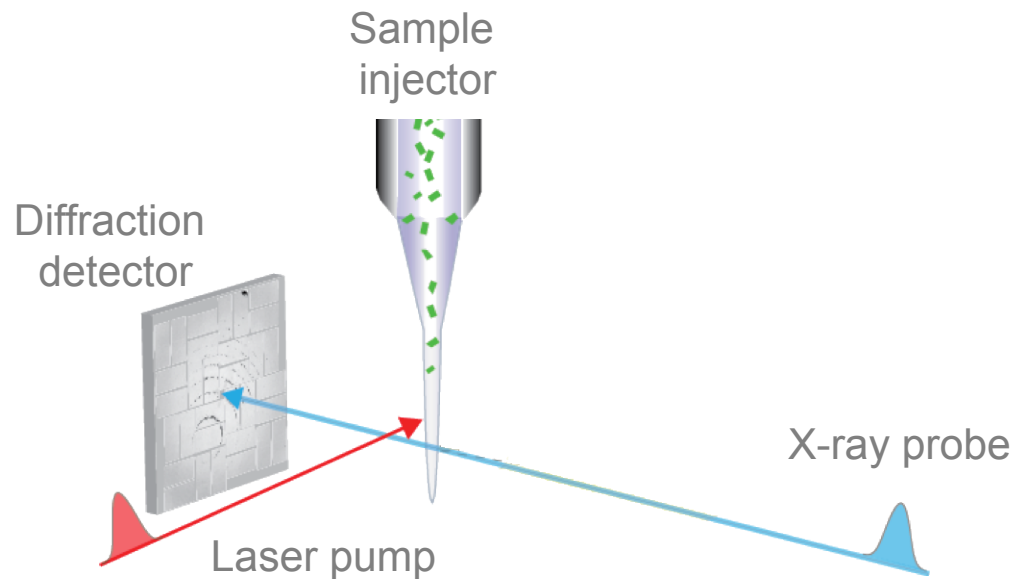


X-ray diffraction



- Radiation damage
 - Measurement problem of PS II:
OEC collapses due to radiation damage
- Dehydrated or cryo-cooled sample does not turn over
- S₄ is kinetically unstable and cannot be cryo-trapped
- *Interesting biology is dynamic*

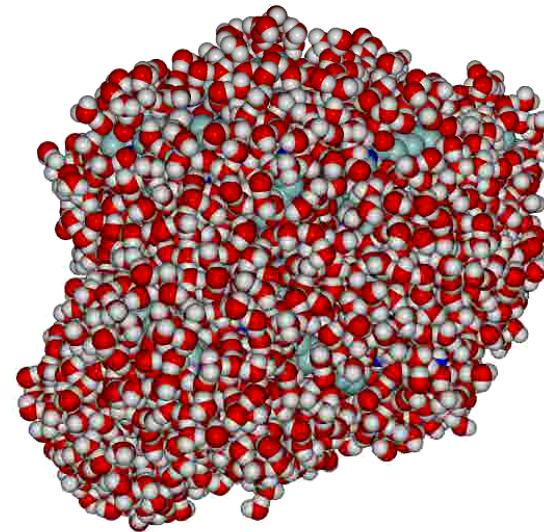
SFX—serial femtosecond crystallography



- Experiment run at room temperature
- Radiation damage does not accumulate
- No time for dehydration
- *Can follow reaction dynamics!*

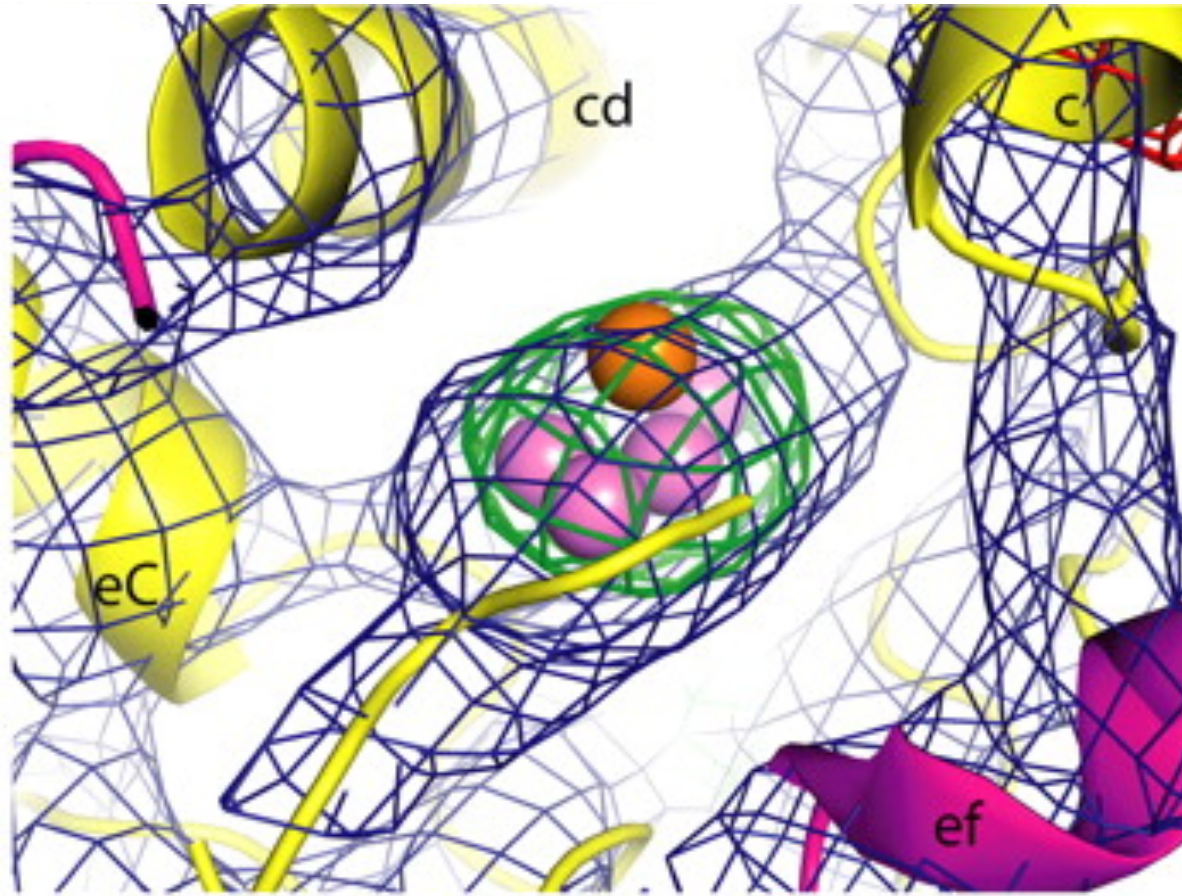
SFX: *collect-before-destroy*

- Hydrolase from *Coccidioides immitis*
 - Globular shape
 - 392 aa in one chain
 - 0.3 nm water layer
- Total pulse
 - Flux 10^{12} X-ray photons
 - FWHM 20 fs



Neutze et al. (2000) *Nature*
406, 752–757

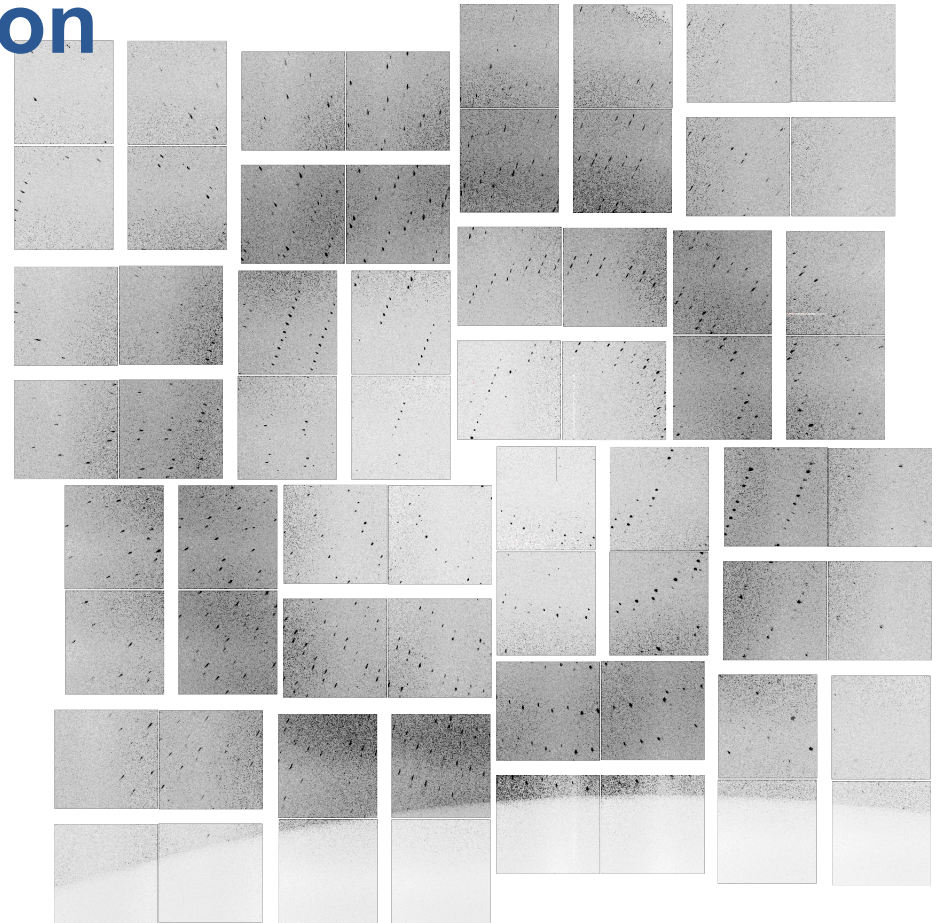
Crystallography results



Kern et al. (2012)
PNAS 109, 9721–9726

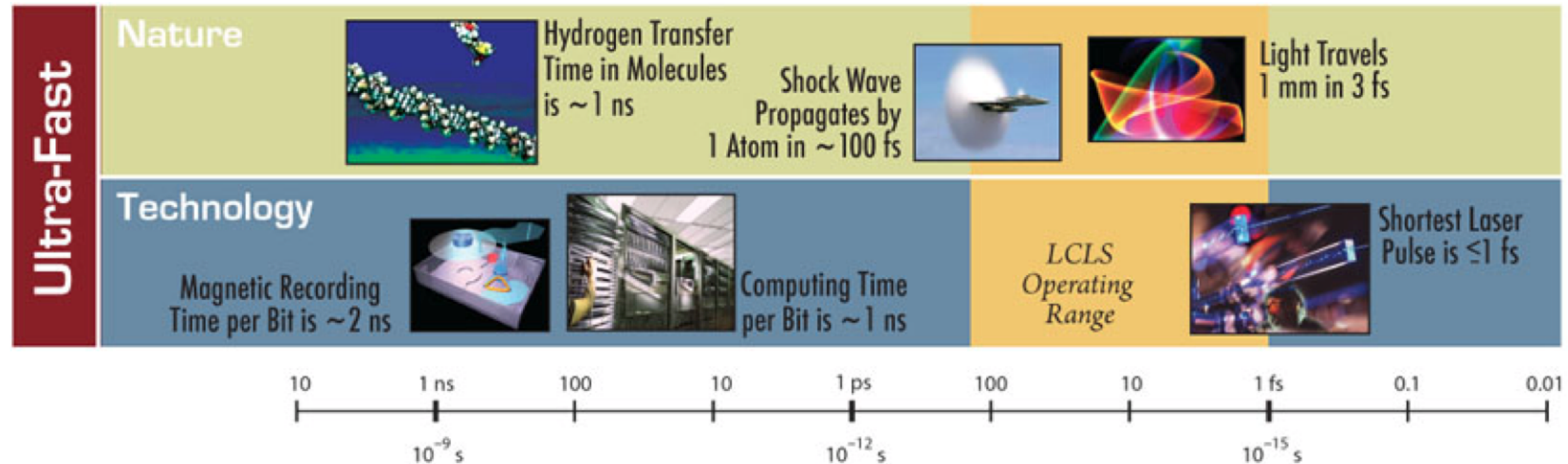
SFX: atomic resolution

- Boutet *et al.* (2012):
lysozyme diffracting to
1.9 Å resolution
- *Unpublished:*
thermolysin diffracting to
1.4 Å resolution



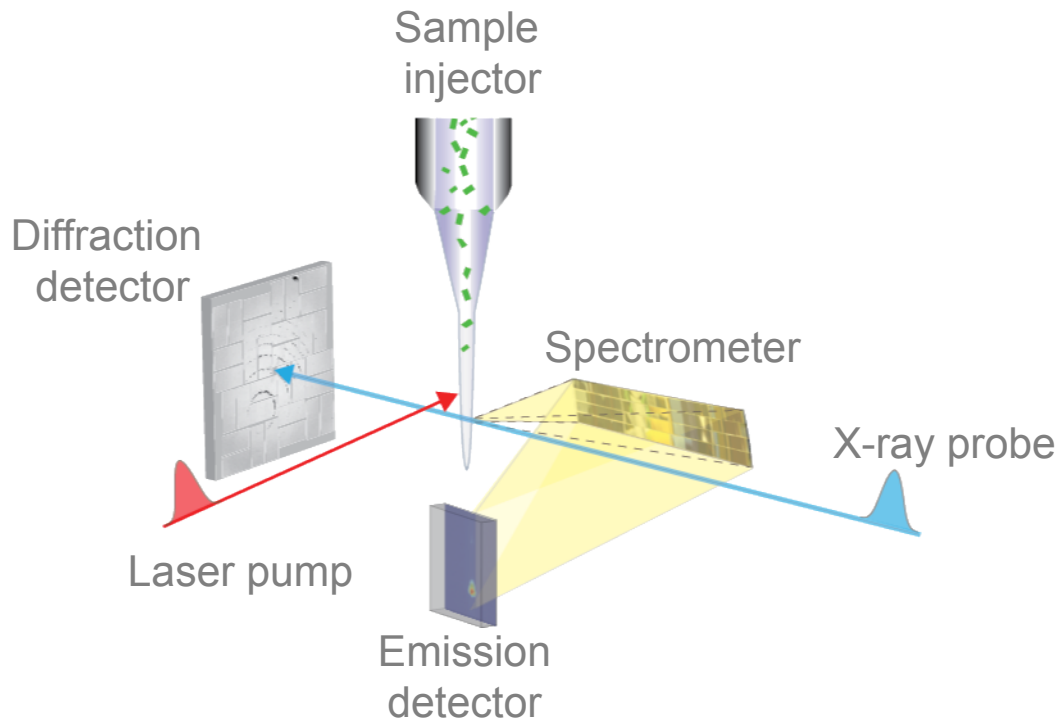
*Lysozyme (1.9 Å): Boutet et al.
(2012) Science 337, 362–364*

X-ray spectroscopy



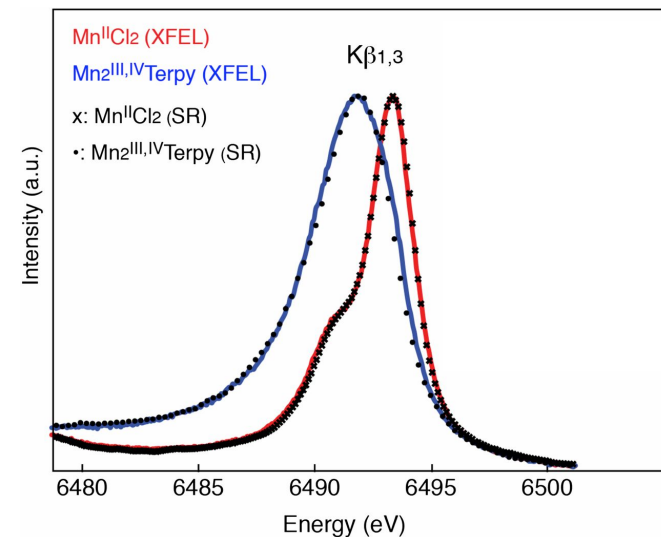
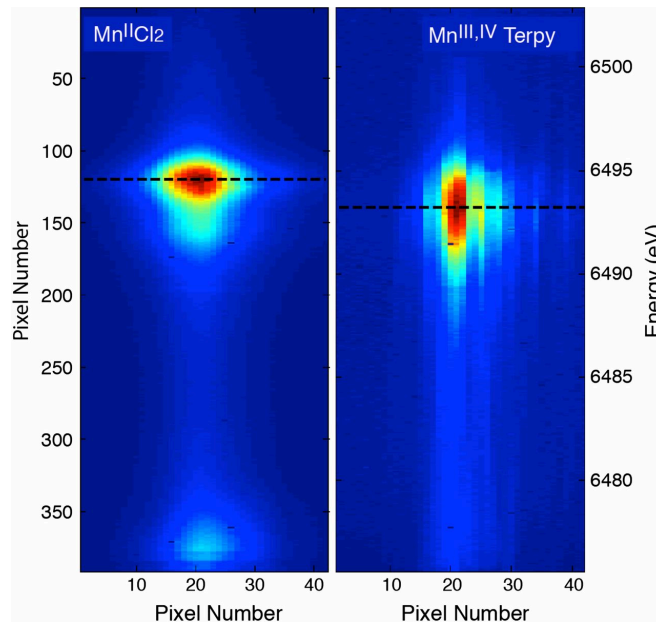
- Study electronic structure of Mn-cluster
 - Follow reaction dynamics with pump-probe
- X-ray absorption
 - Study O–O bond formation
- X-ray emission
 - Can be done simultaneously with X-ray diffraction

Simultaneous XRD and XES



- Spectrometer focuses emission signal on PSD
- Simultaneous collection of X-ray diffraction and X-ray emission
 - Record atomic and electronic structure from the same sample

XES of Mn model compounds



- Intact electronic structure of redox-active transition metal compounds in different oxidation states
 - Paves the way for studying PS II oxygen-evolving complex *Alonso-Mori et al. (2012) PNAS 109, 19103–19107*

Simultaneous XRD and XES

- XRD and XES provide complementary information
 - XRD gives geometric structure of overall protein
 - XES gives local chemistry of active metal sites
- Complementary information is useful for data processing
 - Crystal hits determined from XRD
 - Can infer atomic distances from XES, even when diffracting resolution too low

What do we still have to learn with XFEL radiation?

- Stable sample delivery
 - Undamaged, single crystals
 - High hit rate
- Big data > small data
 - Metadata-intensive operations become prohibitively expensive
 - Expect 1.1 GB/s in the near future (SATA rev. 3: 0.6 GB/s)
- How to write distributed file systems that work
 - Open-source development model inefficient
 - Small academic user-base not commercially attractive
- How to make hardware that works
 - Robust RAID controllers, network adaptors, *etc.*

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