New opportunities in liquid-phase science via picosecond soft X-ray spectroscopy

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at the University of Hamburg

CFEL Symposium

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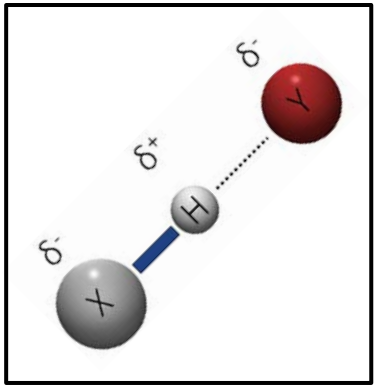
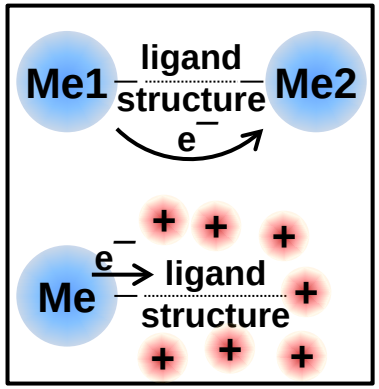
Courtesy: hammeskrause architekten

CFEL SCIENCE

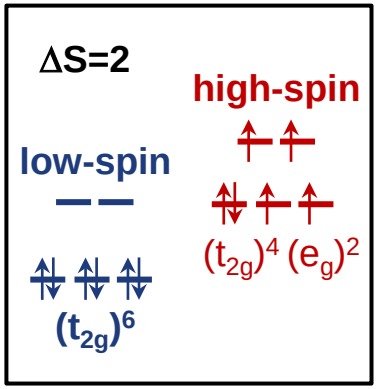
Research Interests



hydrogen bond & solvent dynamics in solutions



transition metal chemistry in organic materials and proteins



molecular magnetism and spin-dependent chemistry

Ultrafast Experimental Approaches

probing multiple length and time scales in matter

X-ray
(diffraction, absorption)

↓

bond distances, angles, coordination geometry, local electronic structure

↓

time-evolving structures

IR/optical/THz
(nonlinear, multidimensional)

↓

vibrational and electronic time-dependent couplings, coherent and incoherent dynamics

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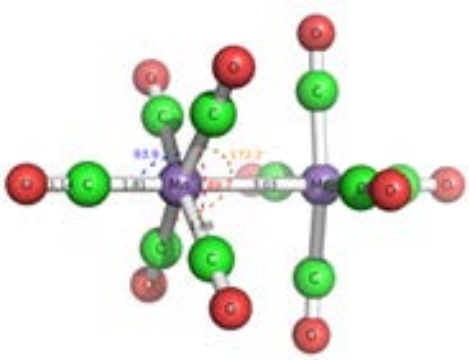
energy transfer pathways

Structural dynamics in Solvated Systems

Photodissociation:

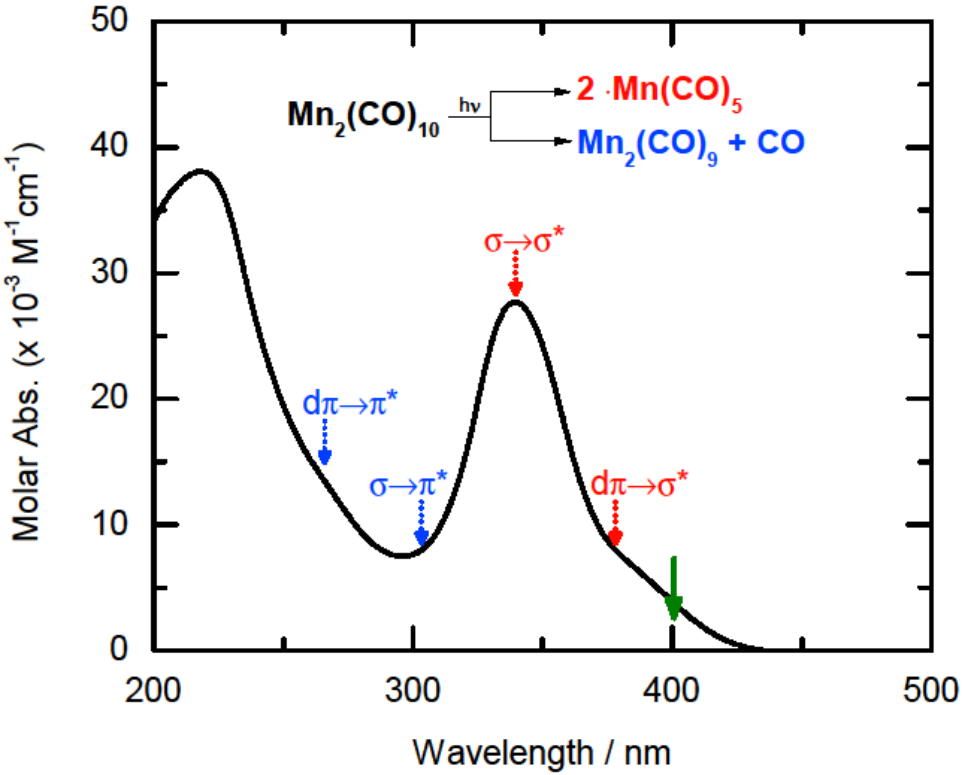
characterizing product states with X-rays

Photocatalyst



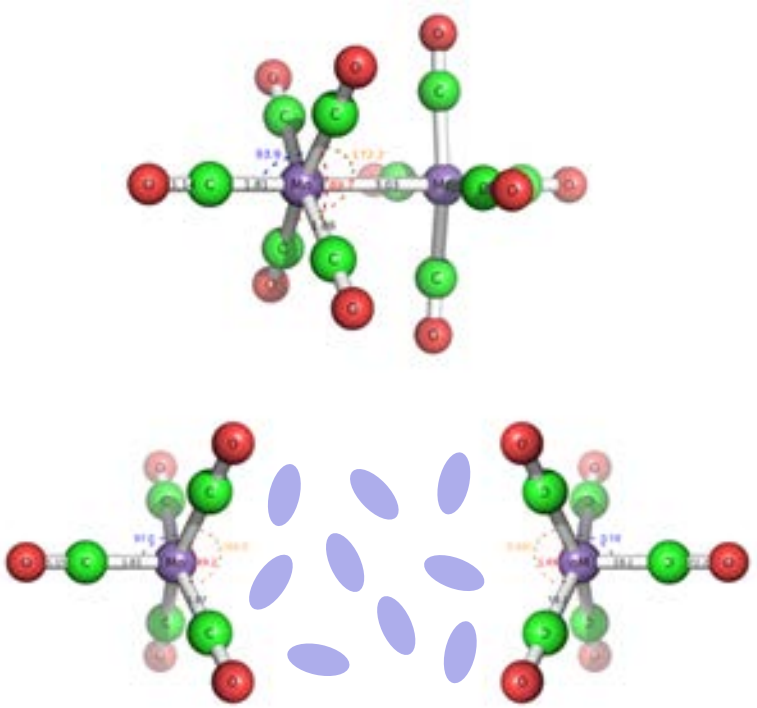
hv

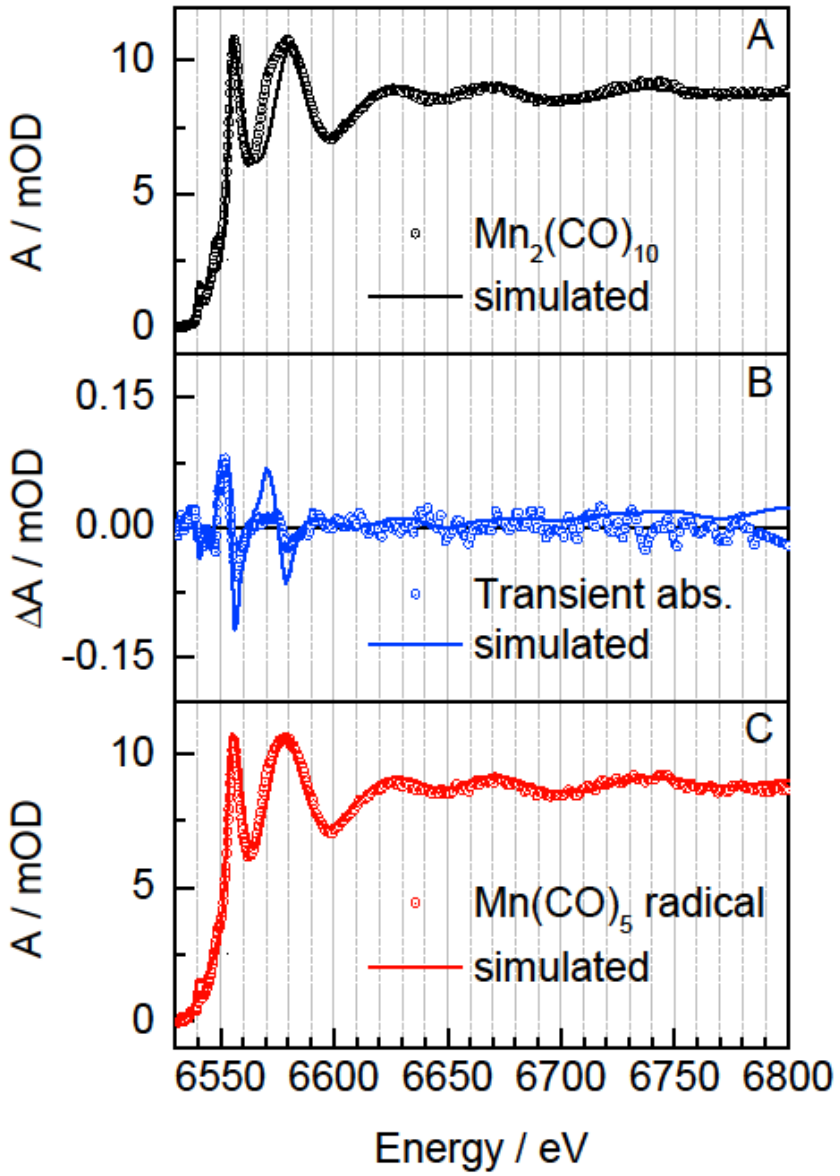
?



- Effective photocatalyst for organic synthesis
- Two known reaction pathways, catalytic one not well understood

Photocatalyst

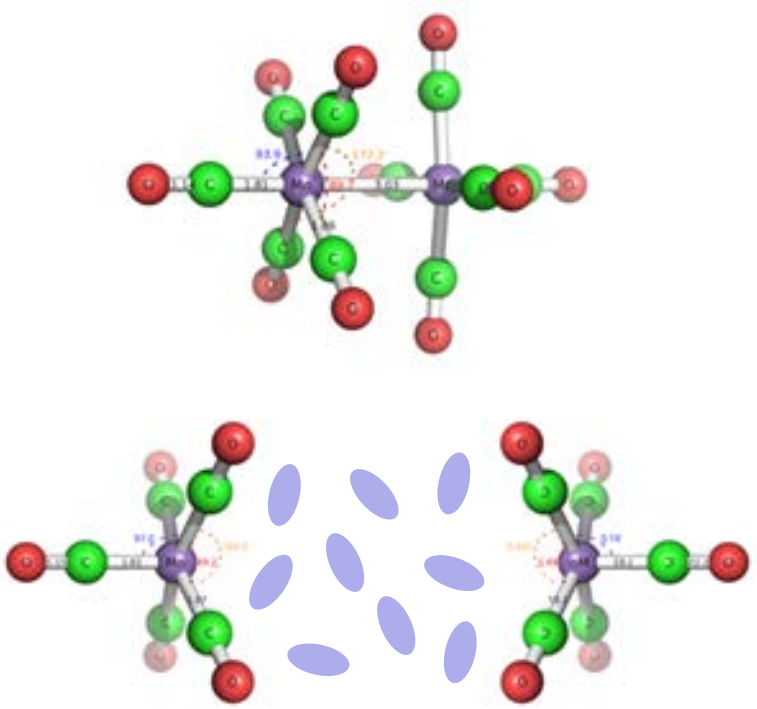




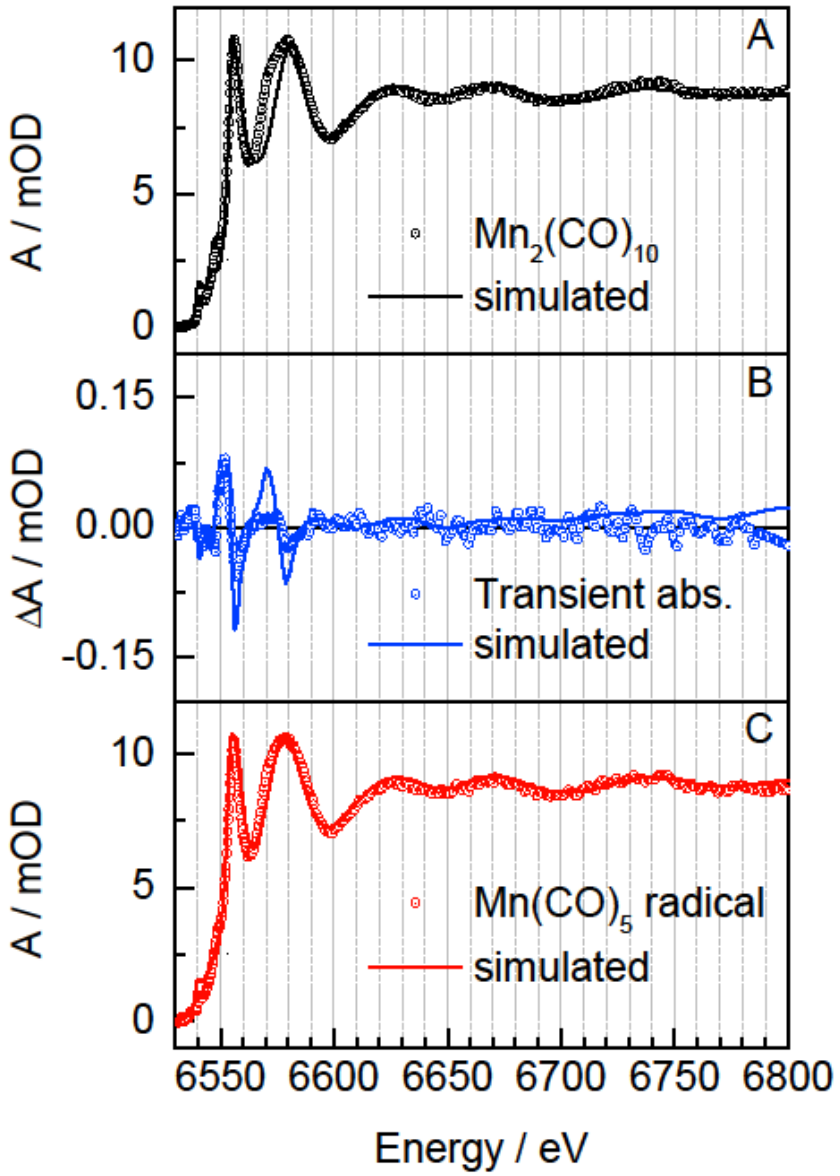
- Almost no change in geometry:
  (<3pm, <5°)
- High quantum yield at 400nm excitation
  (little-to-no geminate recombination)

Hana Cho et al., in preparation

Photocatalyst



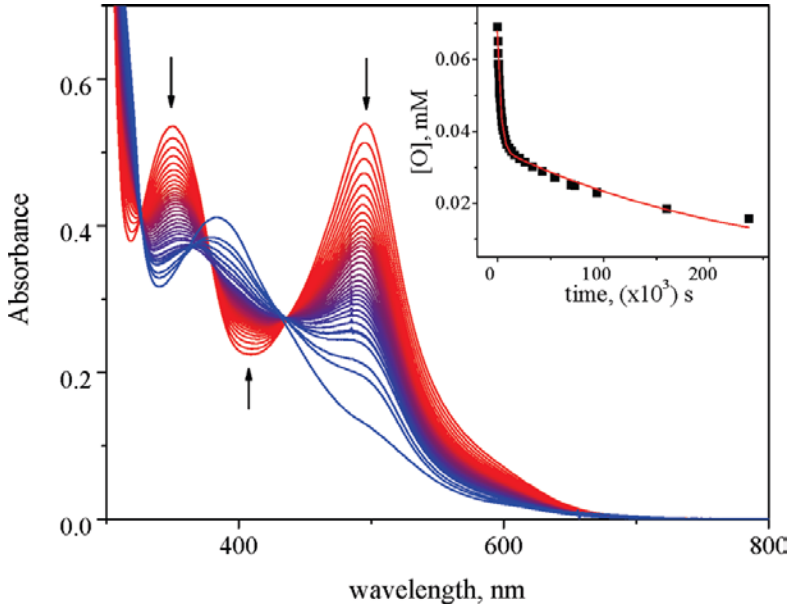
- Recombination dynamics in other systems may be too fast for ‘ordinary’ synchrotrons
- Need for picosecond time resolution to capture dissociated products

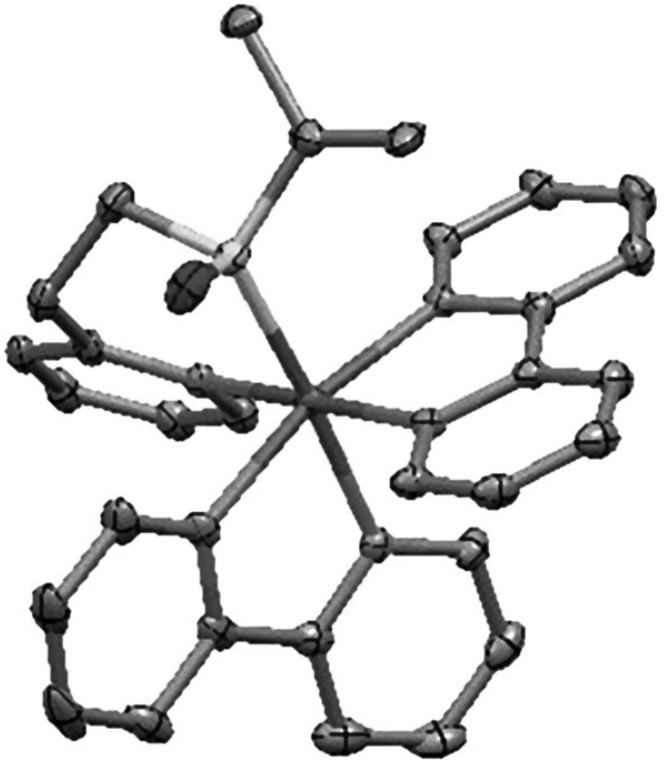


Photochromic Switches:

characterizing intermediate states with unique detail

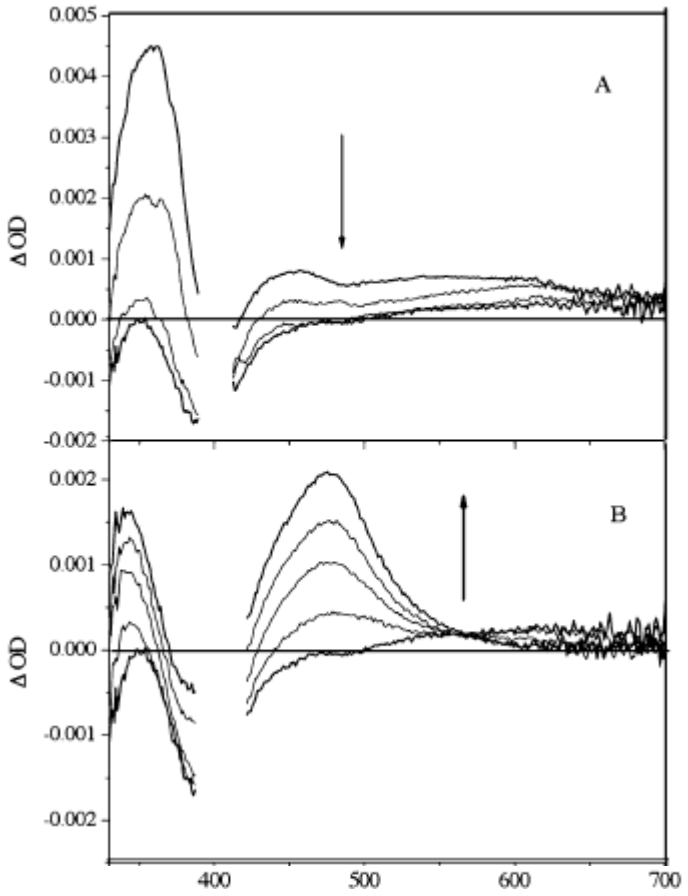
Characterization of Transient States





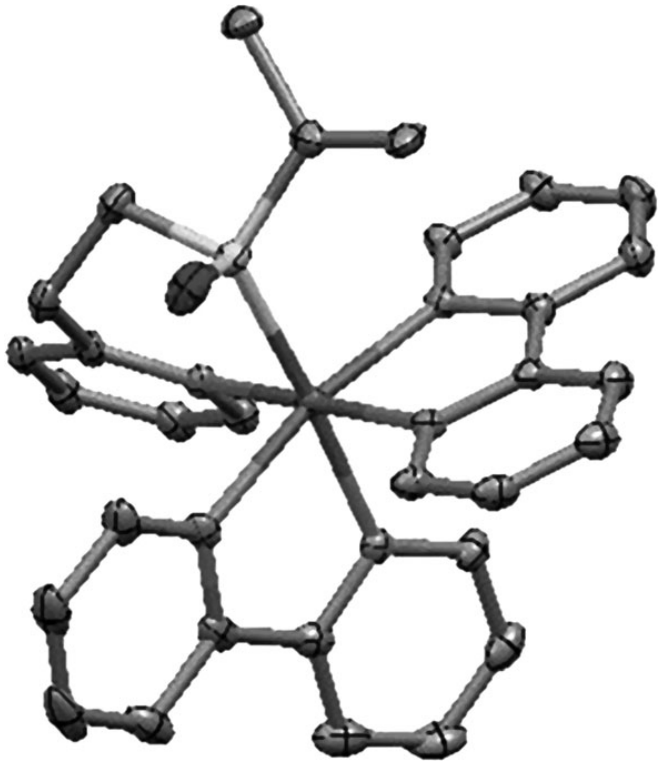
- Photoswitch, controlling visible absorption
- High quantum yield at 400nm excitation (little-to-no geminate recombination)

Following Isomerization

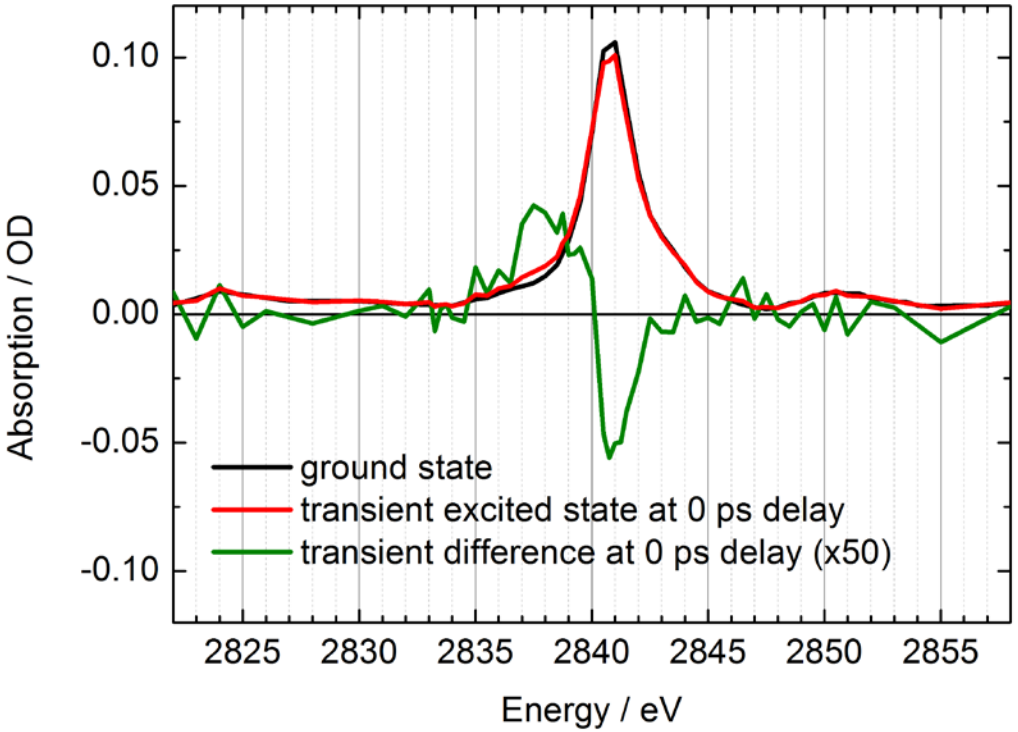


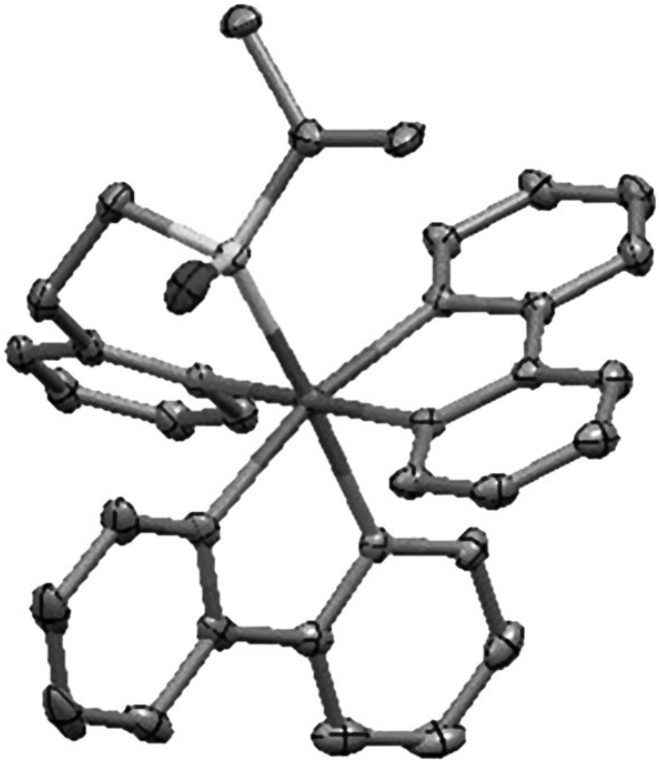
- What are the characteristics of the intermediate state?

- Characteristic reduced bipyridine absorption (few ps)
- Final state evolution (1ns)



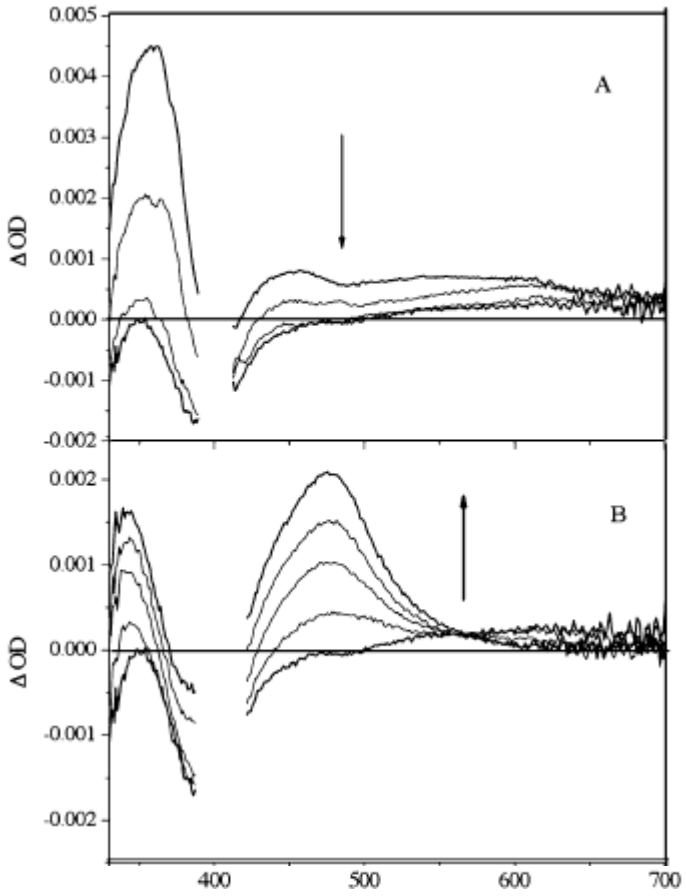
Following Isomerization





- Ru(II) oxidation state with increased charge
- Precursor state with elongated bond lengths?

Following Isomerization



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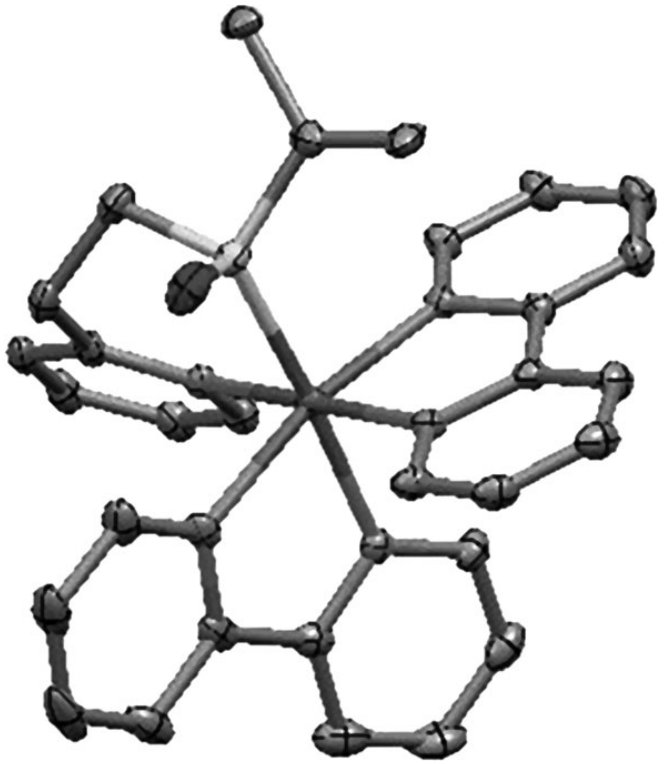
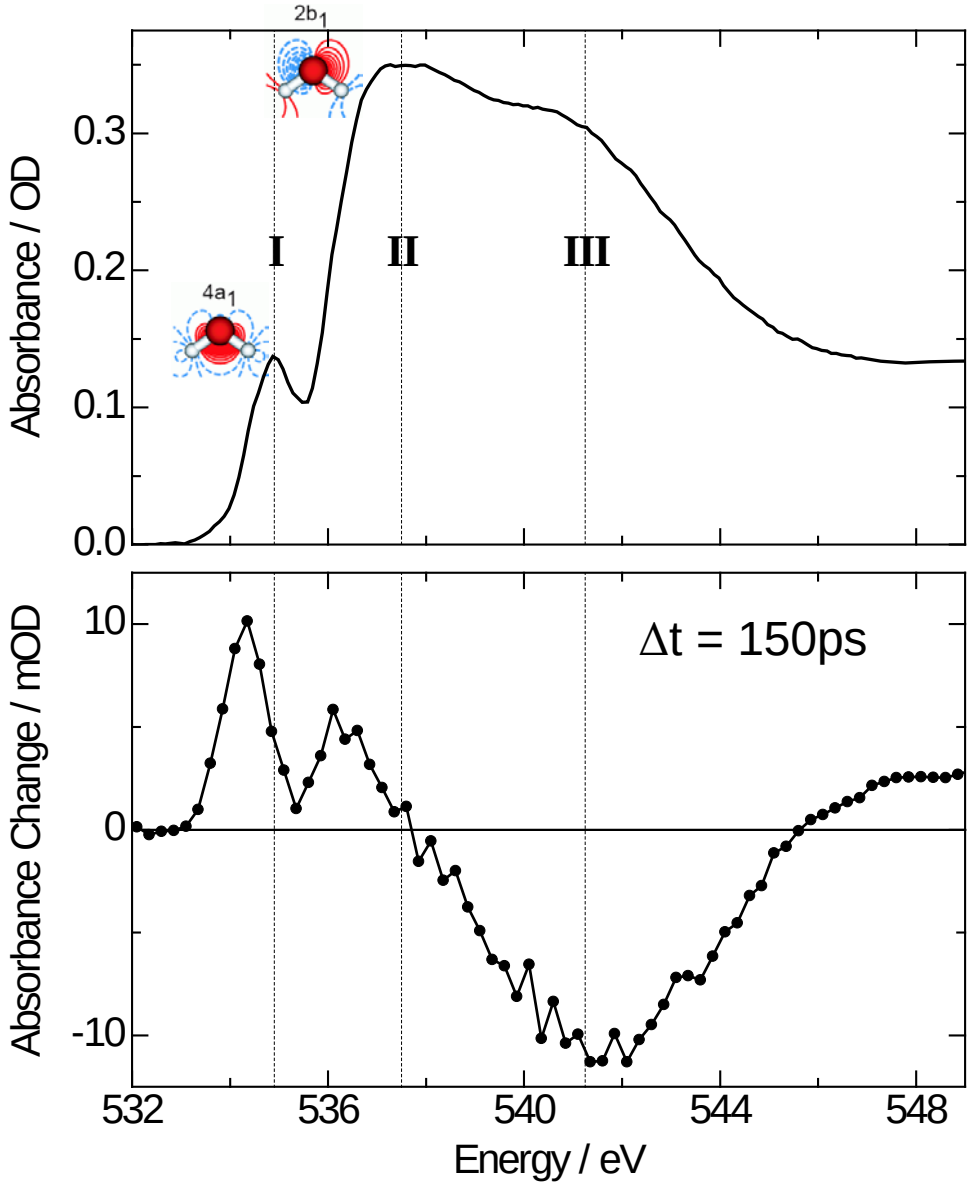


- Picosecond spectroscopy would allow characterizing the initially excited state.

Heat Jumps:

beyond UV-vis photo-excitations in solutions

Picosecond Soft X-ray Spectroscopy on H_2O



- **Distinct absorption increase at leading edges of pre- & main peak**

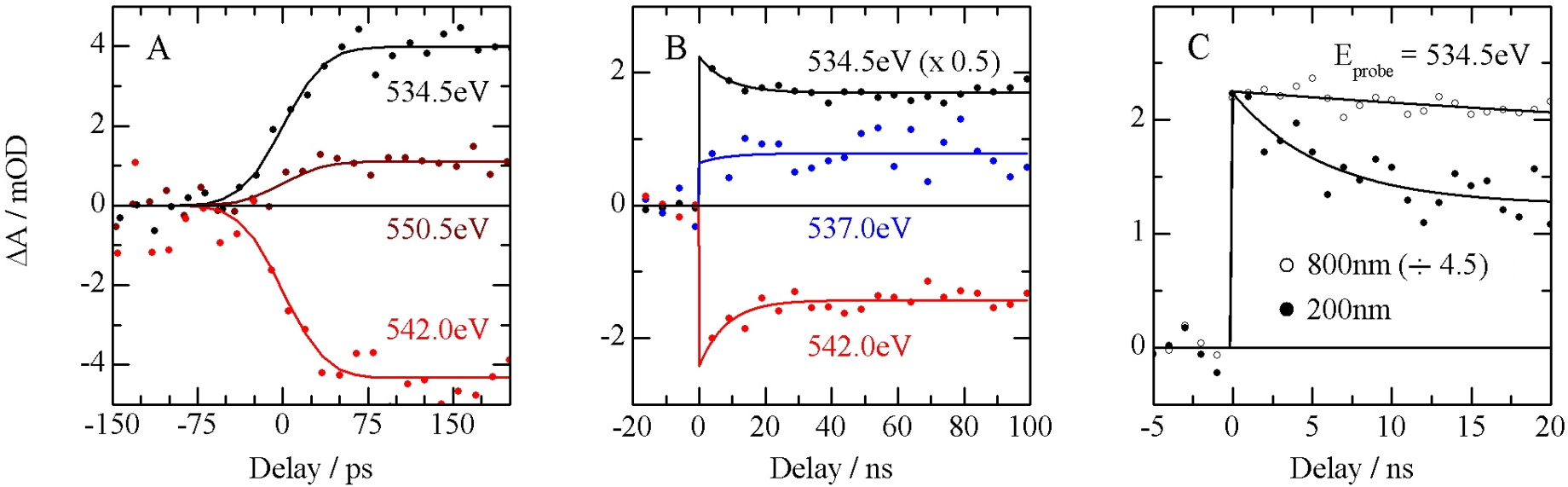
  → HB strength decreases

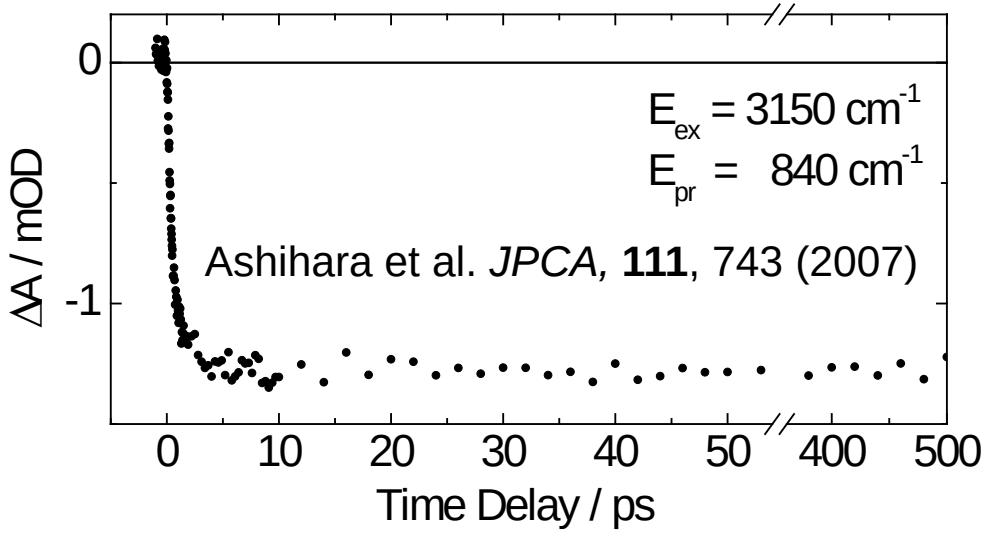
- **Broad loss of absorption at post-edge**

  → HB distance decreases, disorder increases

- **Proper calibration should allow for HB length measure**

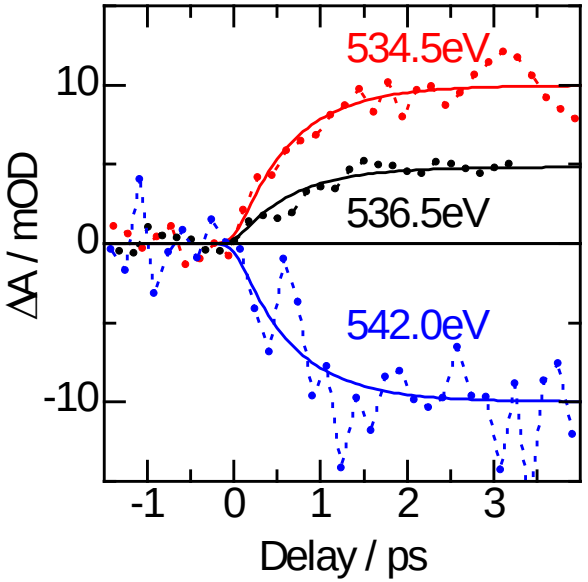
Picosecond Soft X-ray Spectroscopy on H_2O

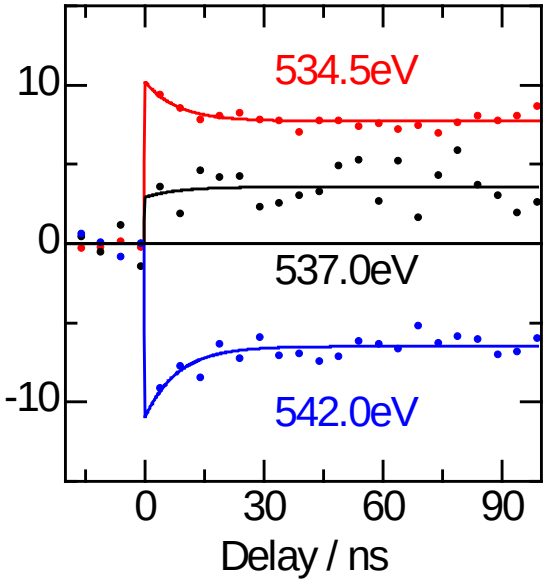


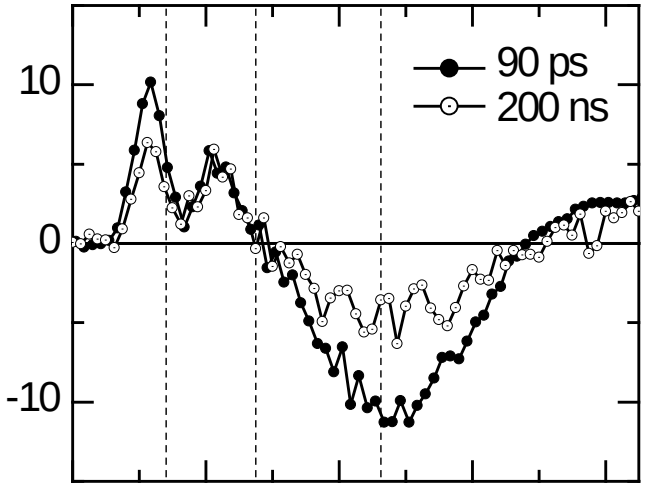


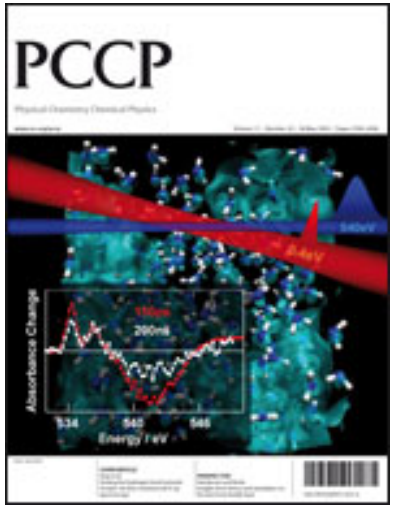
Vibrational excitations in pure water thermalize with a (sub-)picosecond time constant

Ultrafast Soft X-ray Spectroscopy on H_2O

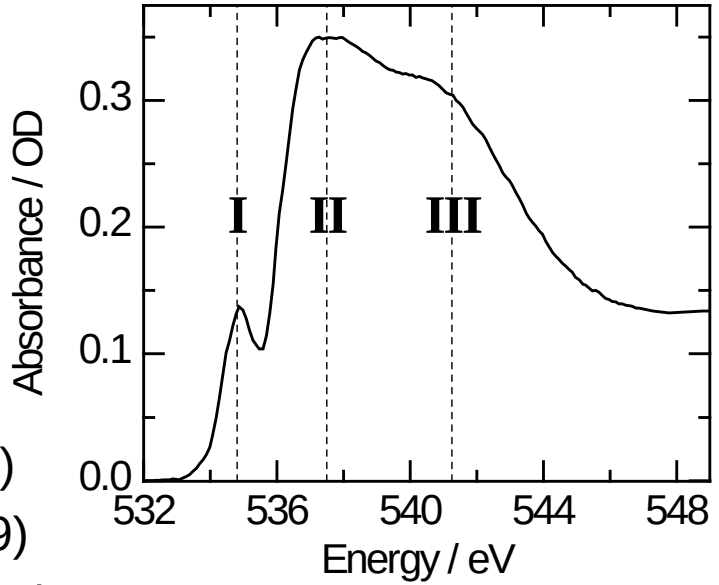








- **Thermalization**
  → Isochoric Heating
- **Less HBs & Order**
- **Adiabatic Expansion?**



Wernet et al., *APA* **92**, 511 (‘08)

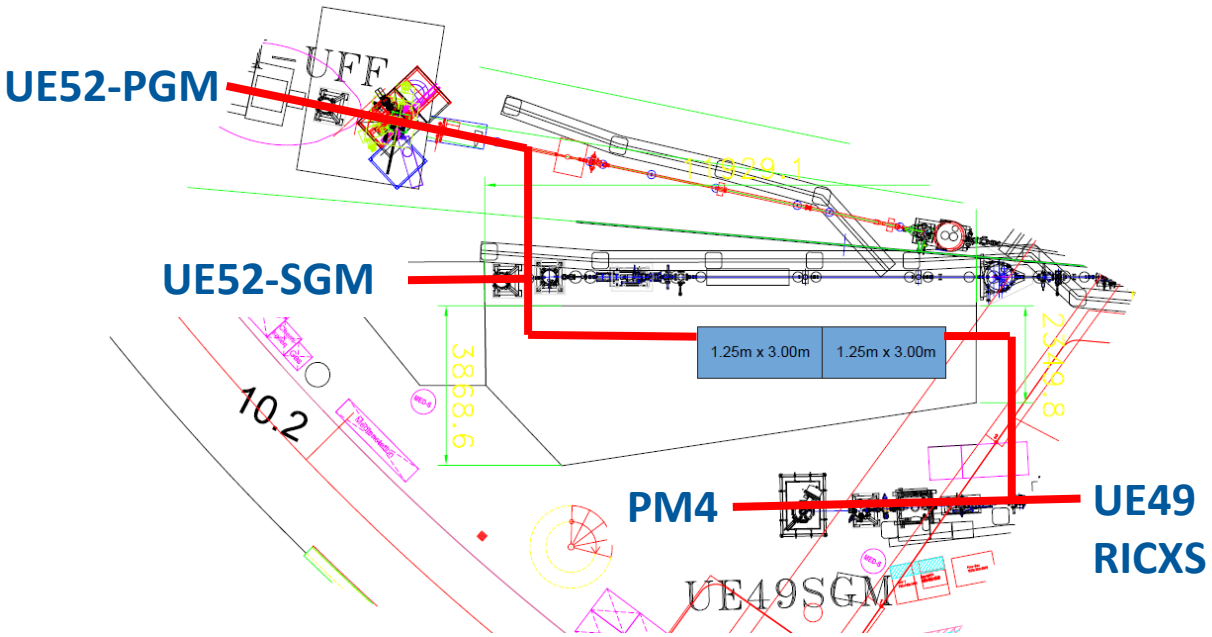
Huse et al. *PCCP* **11**, 3951 (‘09)

Wen et al. *JCP* **131**, 234505 (‘09)

Adjusting to storage rings:

MHz repetition rate experiments

MHz spectroscopy at HZB



XAS, PES, (RIXS)

↓

ps Dynamics in

- *Materials science*
- *Condensed matter*
- *Magnetism*
- *Surface science*
- *Catalysis*
- *Chemical systems*
- *Gas phase, clusters*
- *Bio molecules*

Considerations

- ~10^4 ph / camshaft at sample
- 10^{10} ph / s & MHz sampling
- 10^8 ph / s in short pulse mode
- Will transient RIXS work?
- PES in pseudo single-bunch mode?

Conclusions

- Plenty of new opportunities to investigate solution-phase chemistry with various X-ray spectroscopic methods in the soft X-ray range
- Laser technology has matured to the point that *widely tunable* MHz sources with 10mJ/cm² fluence are essentially on the market
- Primary challenges:

  sample handling, sample amounts, single bunch/MHz-chopper, continuous MHz-DAQ performance (especially for pixel detectors)
- What do I wish for: ***1ps @ 10^{11}ph/s***

Many Thanks

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