Closing information gaps in photochemical reaction dynamics with ps x-ray spectroscopy

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Guiding questions

- Why using a 1 ps SR instead of a fs lab source?

… for photochemical studies…

Guiding questions

- Why using a 1 ps SR instead of a 100 ps SR?

… for photochemical studies…

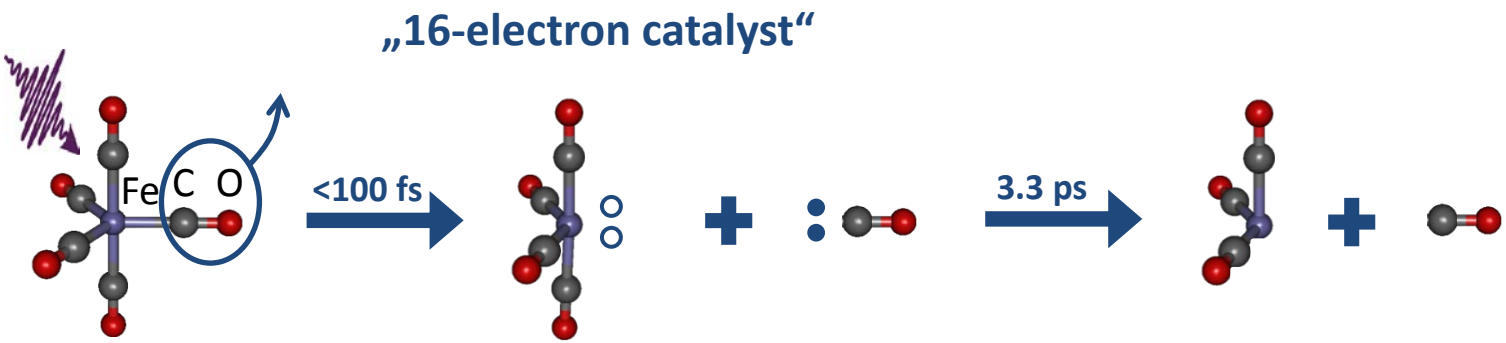
Guiding questions

- Why using a 1 ps SR instead of an XFEL?

… for photochemical studies…

Time scales in $Fe(CO)_5$ dissociation

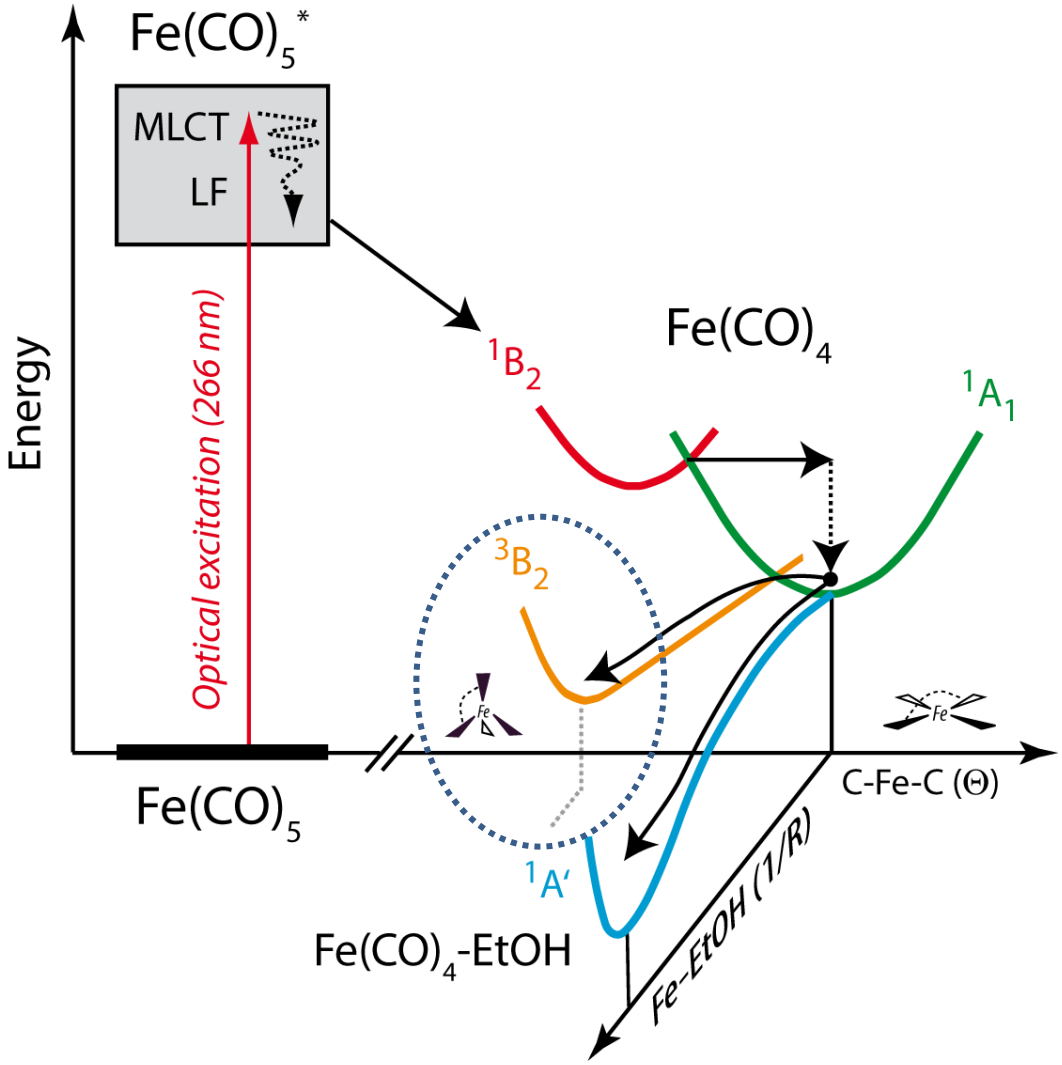
$Fe(CO)_5$



MLCT excitation

- Dissipation of excess energy
- Learn how to make use of it

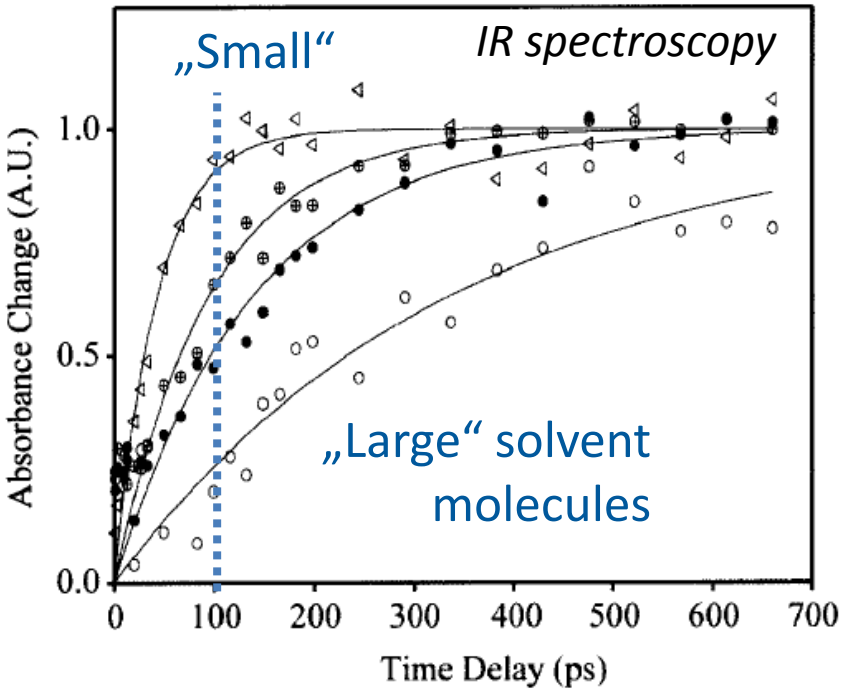
The first picosecond in solution – Beyond?



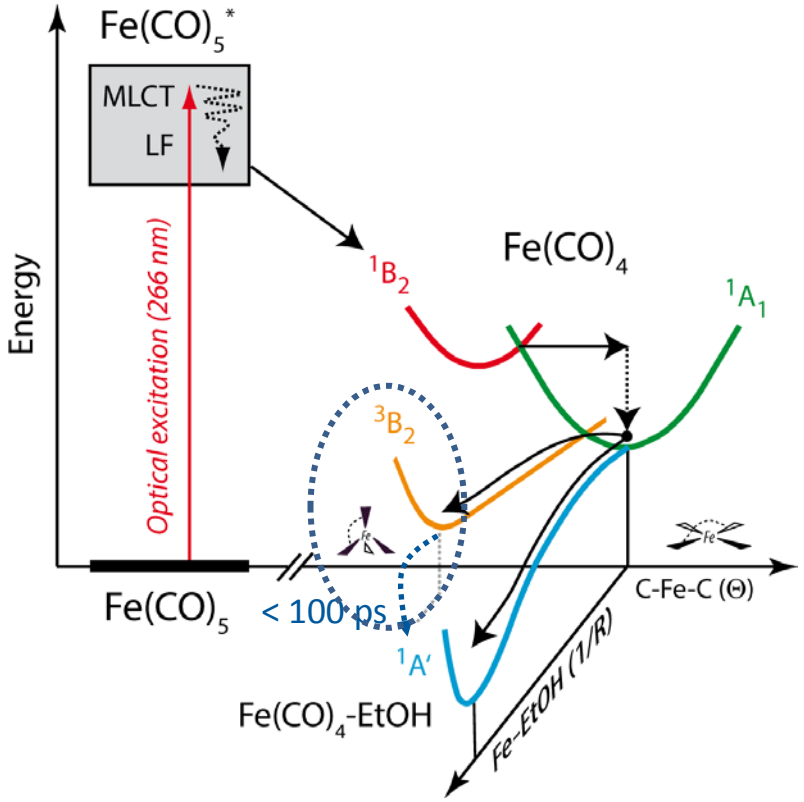
Kunnus et al., Struc. Dyn. **3**, 043204 (2016)
Wernet et al., Nature **520**, 78 (2015)

Beyond the first picosecond

Solvation of triplet $Fe(CO)_4$

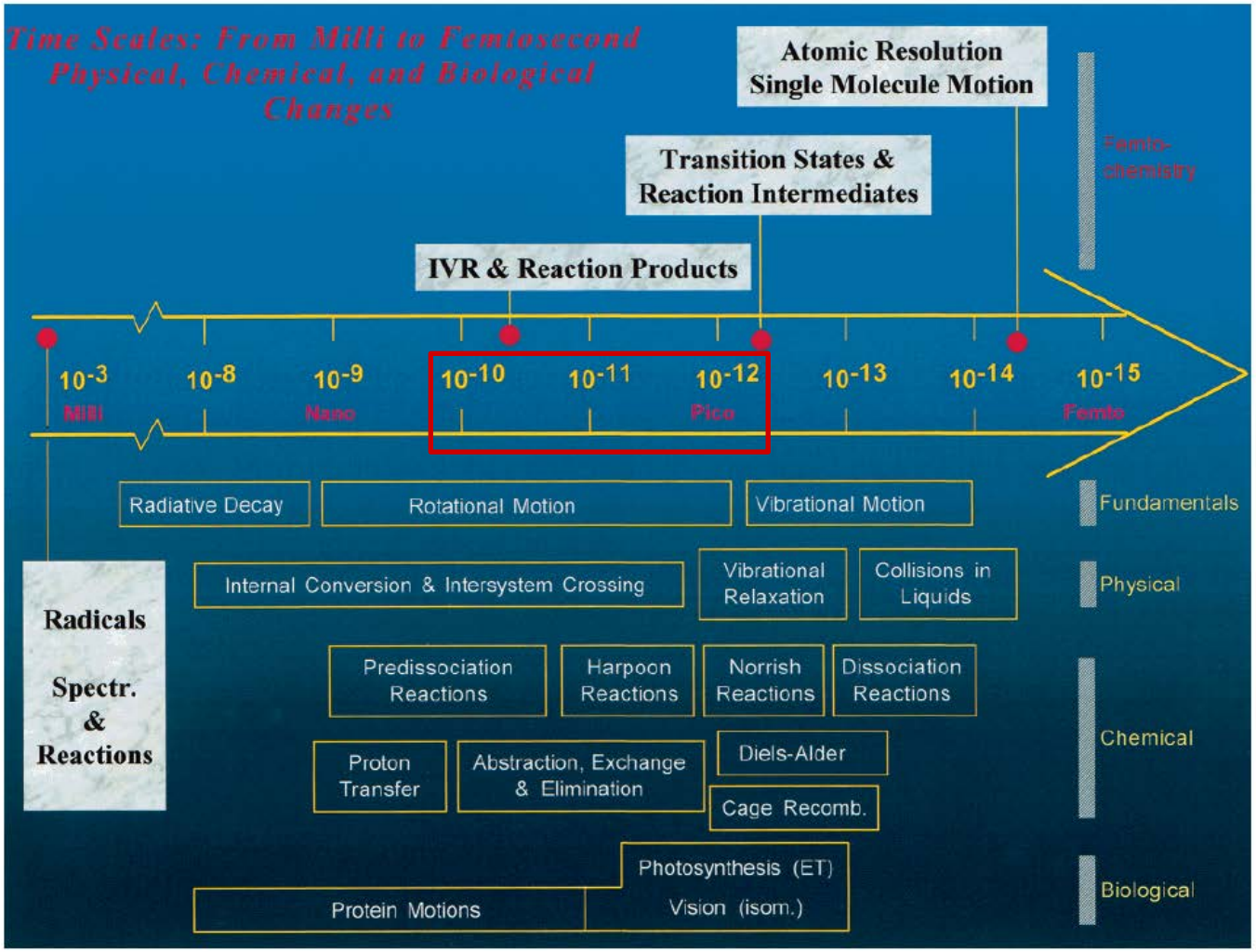


Snee, Harris, et al., *J. Am. Chem. Soc.* **123**, 6909 (2001)



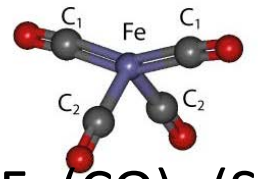
- Solute-solvent interactions
- H-bond dynamics
- Diffusion

Beyond the first picosecond



Zewail, J. Phys. Chem. A **104**, 5660 (2000).

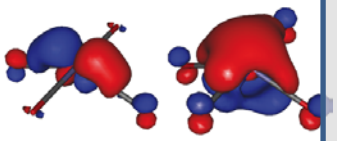
UV/Vis absorption spectroscopy

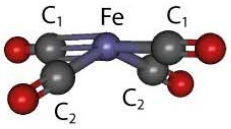


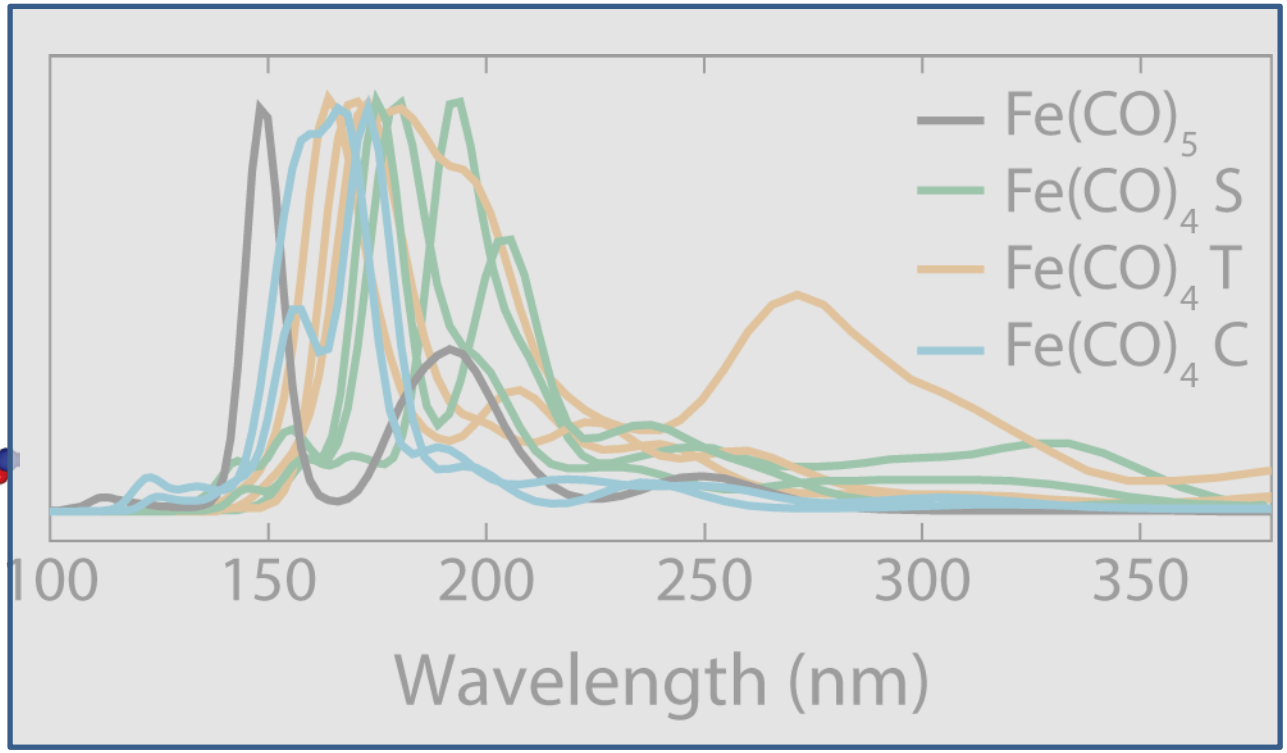
$Fe(CO)_4$ (S)

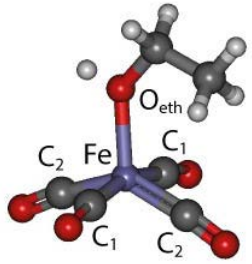
HOMO $d_\pi(b_2)$

LUMO $d_\sigma^*(a_1)$









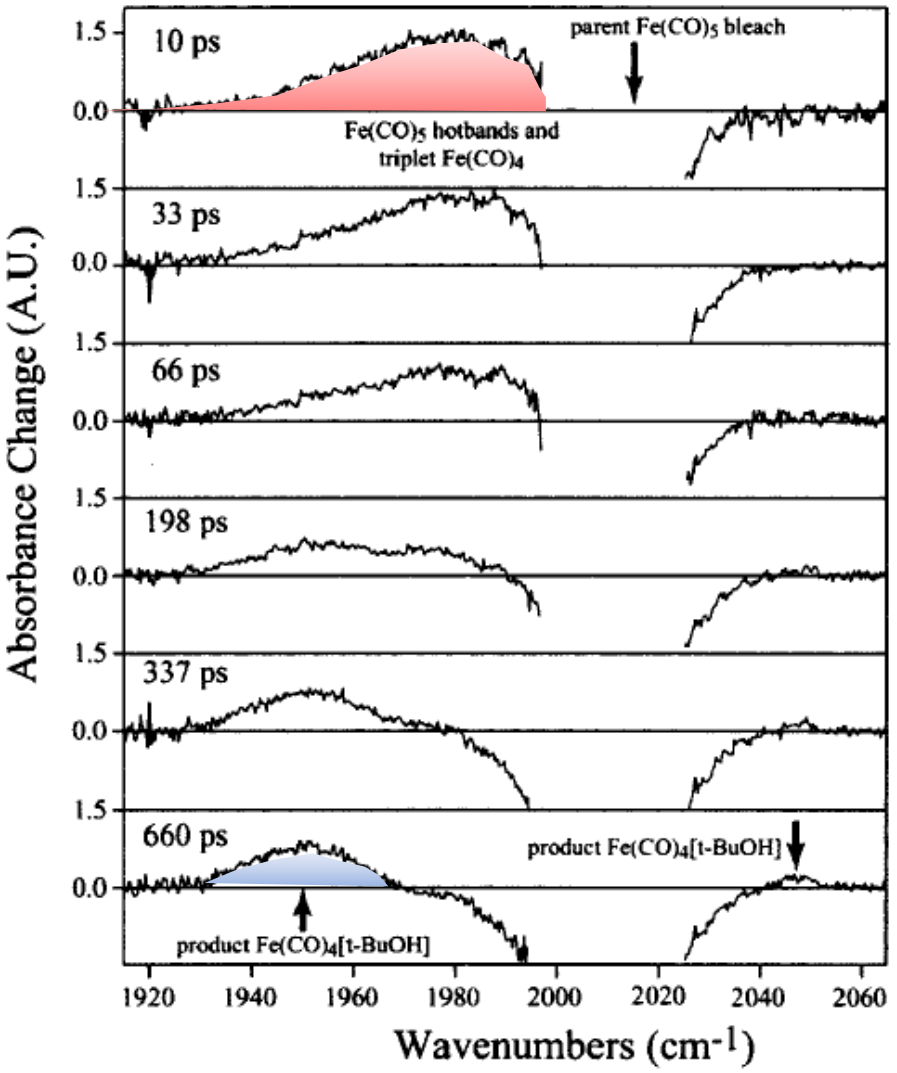
IR absorption spectroscopy

10 ps

$Fe(CO)_5$ hot bands and T $Fe(CO)_4$

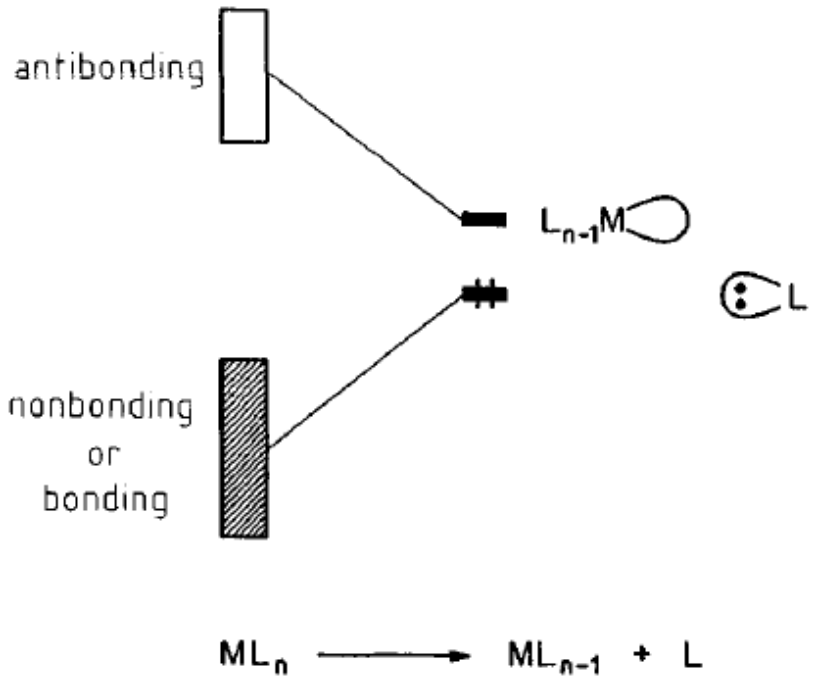
660 ps

$Fe(CO)_4$ - Alcohol complex



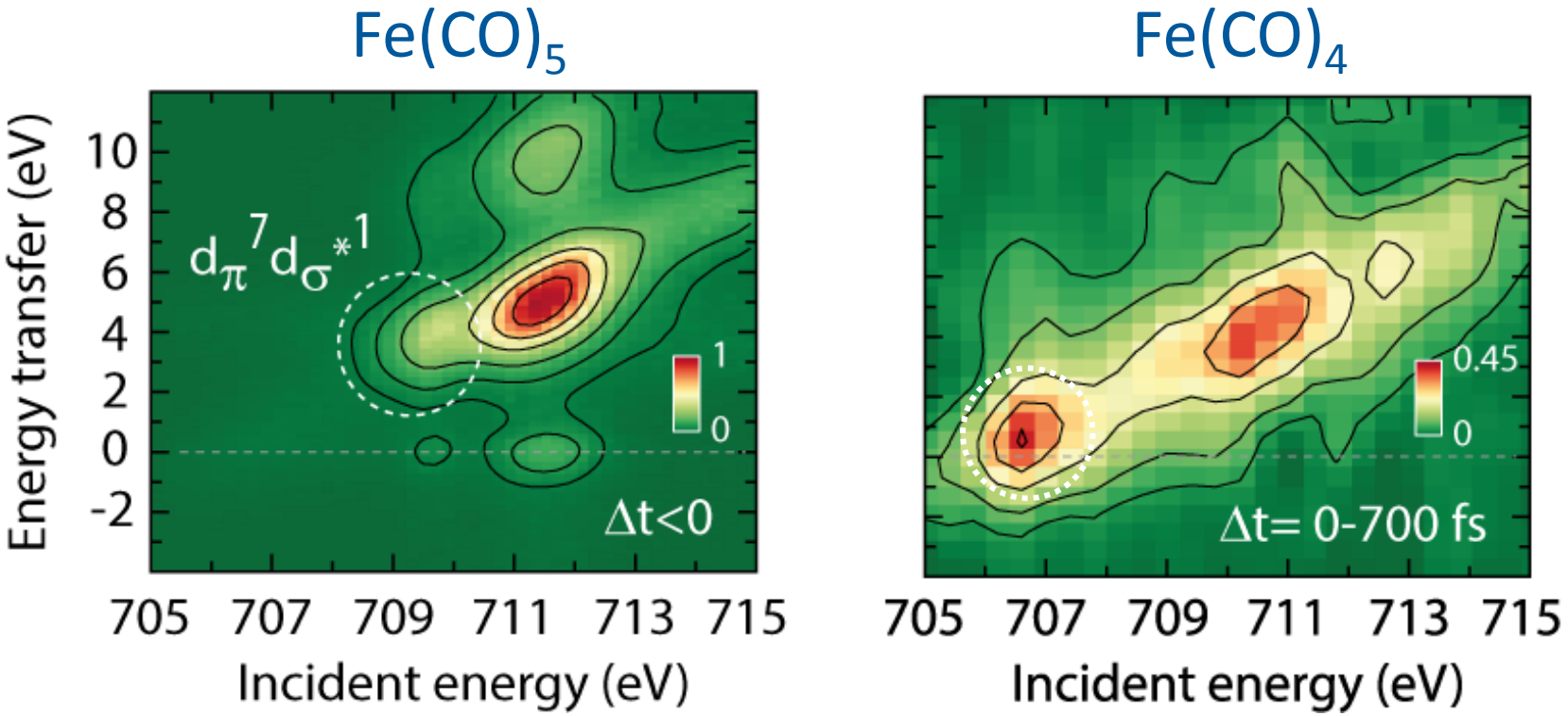
Snee, Payne, Mebane, Kotz, Harris, JACS **123**, 6909 (2001)

Filling in the UV/Vis gap



M. Dartiguenave, Y. Dartiguenave, H. B. Gray, Bull. Soc. Chim. Fr. **12**, 4223 (1969).
R. Hoffmann, Angew. Chem. Int. Ed. Engl. **21**, 711-724 (1982).

Filling in the UV/Vis gap



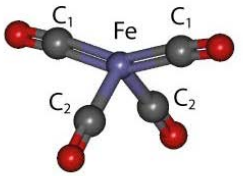
- *fs RIXS at the Fe L_3-absoprtion edge (LCLS XFEL, Stanford, USA)*
- *Ab initio calculations of x-ray spectra (M. Odelius, Stockholm)*

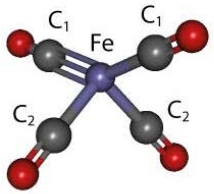
Probing frontier orbital interactions locally at the metal

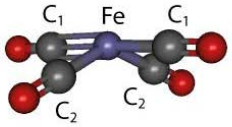
Wernet, Kunnus, Josefsson, Rajkovic, Quevedo, Beye, Schreck, Grübel, Scholz, Nordlund, Zhang, Hartsock, Schlotter, Turner, Kennedy, Hennies, de Groot, Gaffney, Techert, Odelius, Föhlisch, Nature **520**, 78-81 (2015).

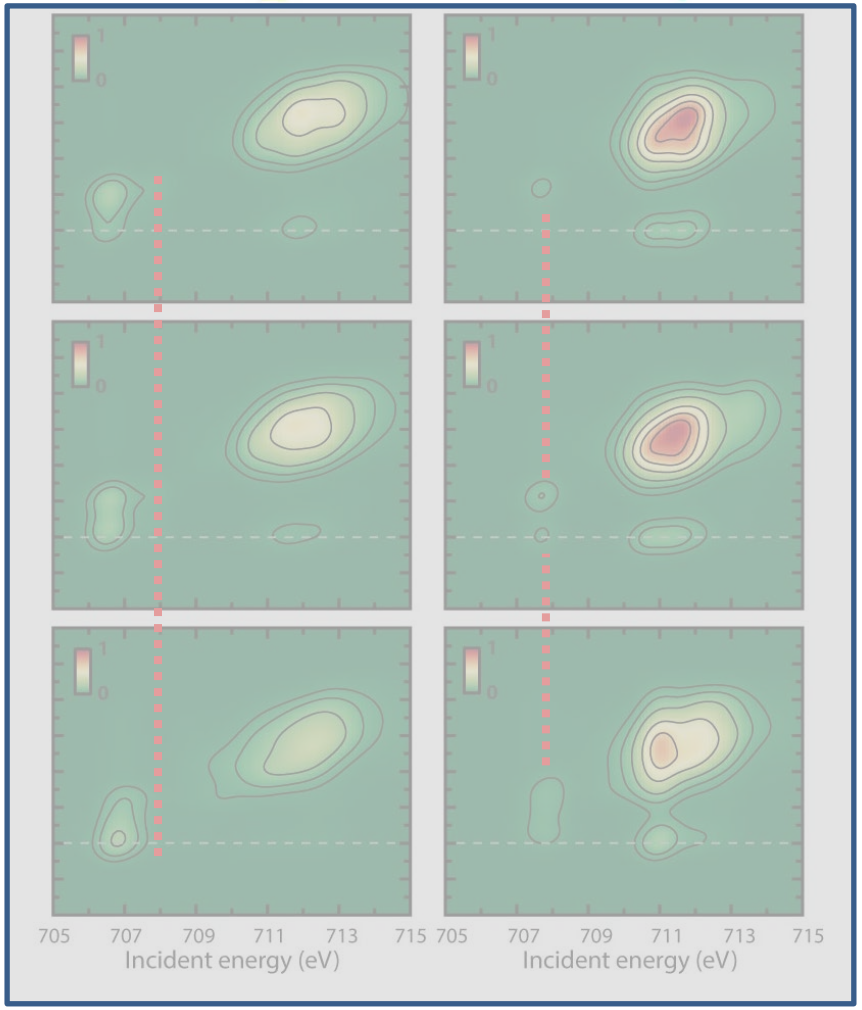
Filling in the IR gap

Triplet *Singlet*







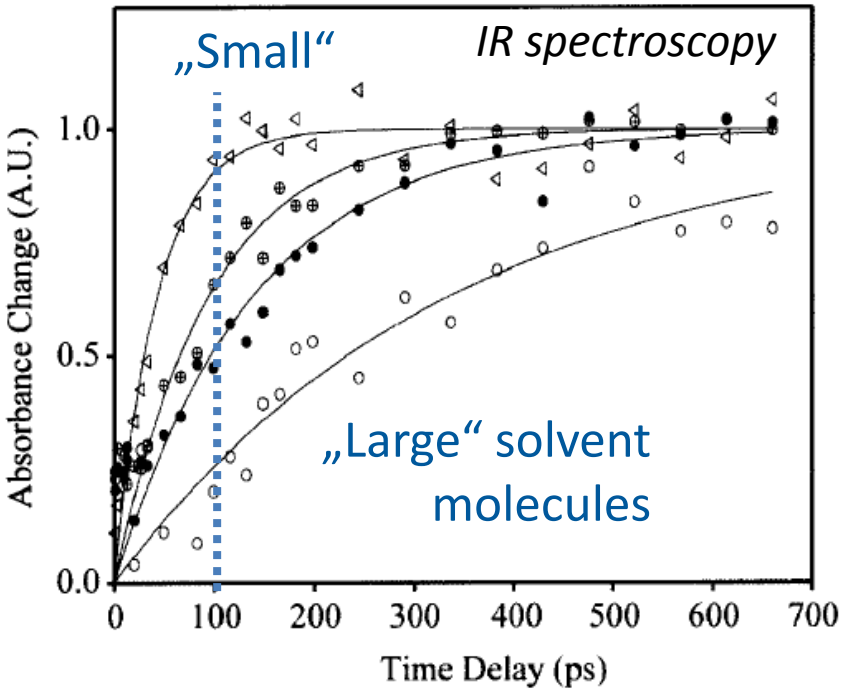


RAS calculations: I. Josefsson, K. Kunnus

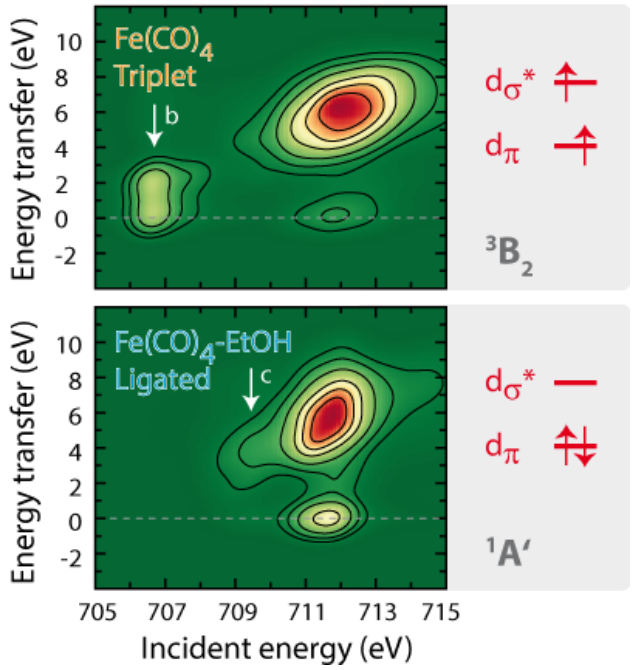
Beyond the first picosecond

Ligand substitution with 3d transition-metal systems

Solvation of triplet $Fe(CO)_4$



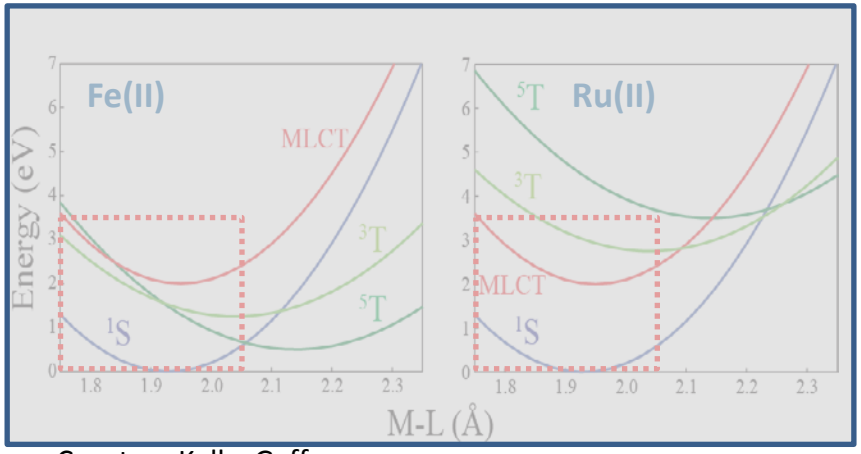
Snee, Harris, et al., *J. Am. Chem. Soc.* **123**, 6909 (2001)



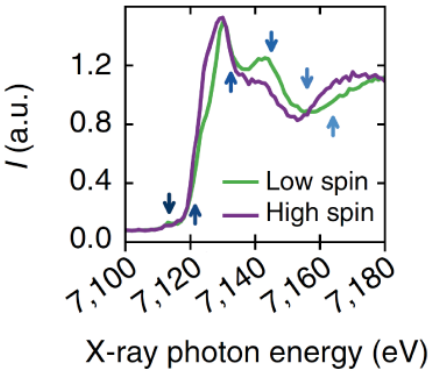
- Solute-solvent interactions
- H-bond dynamics
- Diffusion

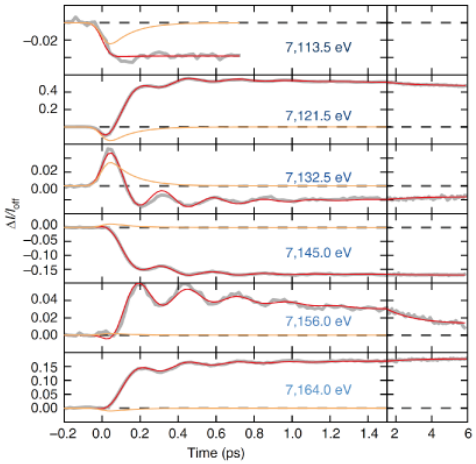
Beyond the first picosecond

Charge transfer excited states in transition-metal systems

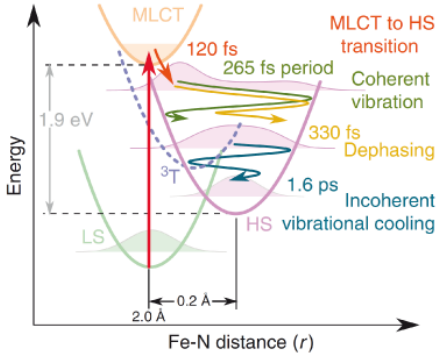


Courtesy Kelly Gaffney





- Mixed ligand complexes
- $[Fe(bpy)_N(CN)6\text{-}2N]^{2N\text{-}4}$, N=1-3
- Control symmetry, ligand field, covalency
- Suppress spin cross over
- Extend charge-transfer excited-state lifetime

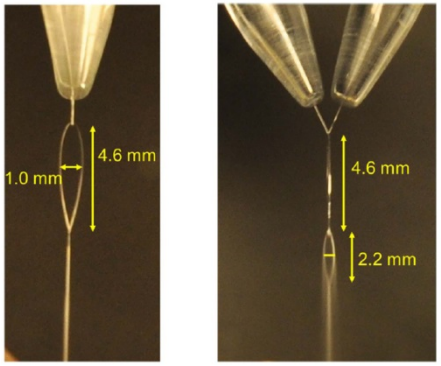


Lemke at al., Nat. Commun. **8**, 15342 (2017)

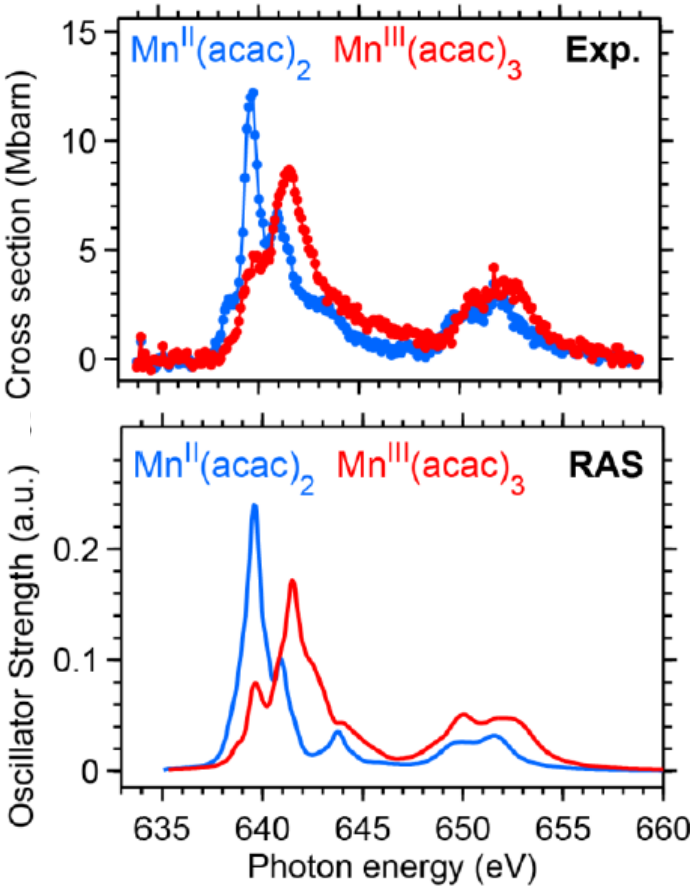
Zhang, Gaffney, et al., Chem. Sci. **8**, 515 (2017)
Kjaer, Gaffney et al., Struc. Dyn. **4**, 044030 (2017)
Zhang, Gaffney, Acc. Chem. Res. **48,** 1140 (2015)

Method aspects

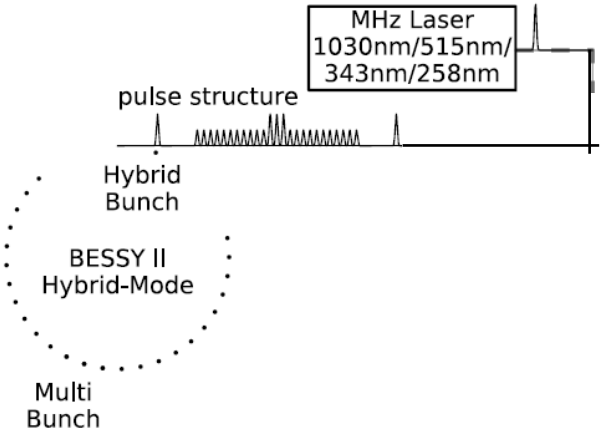
Flat jet



Ekimova, Quevedo, Faubel, Wernet, Nibbering, Structural Dynamics **2**, 054301 (2015)



Pump-probe transmission

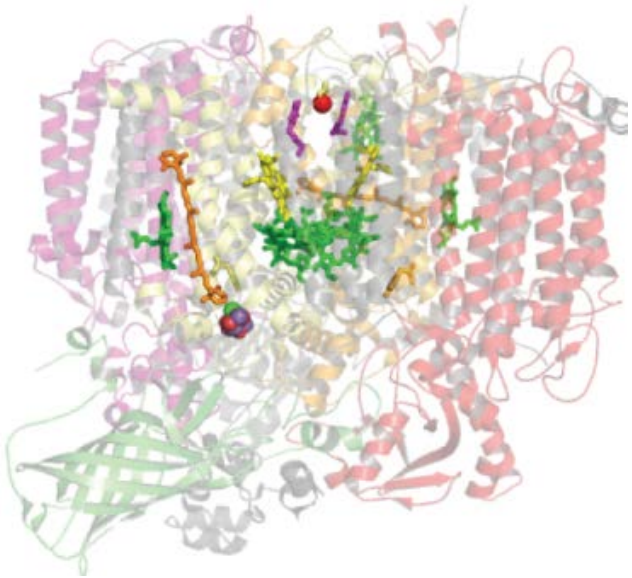


Fondell et al., Struc. Dyn. **4**, 054902 (2017)

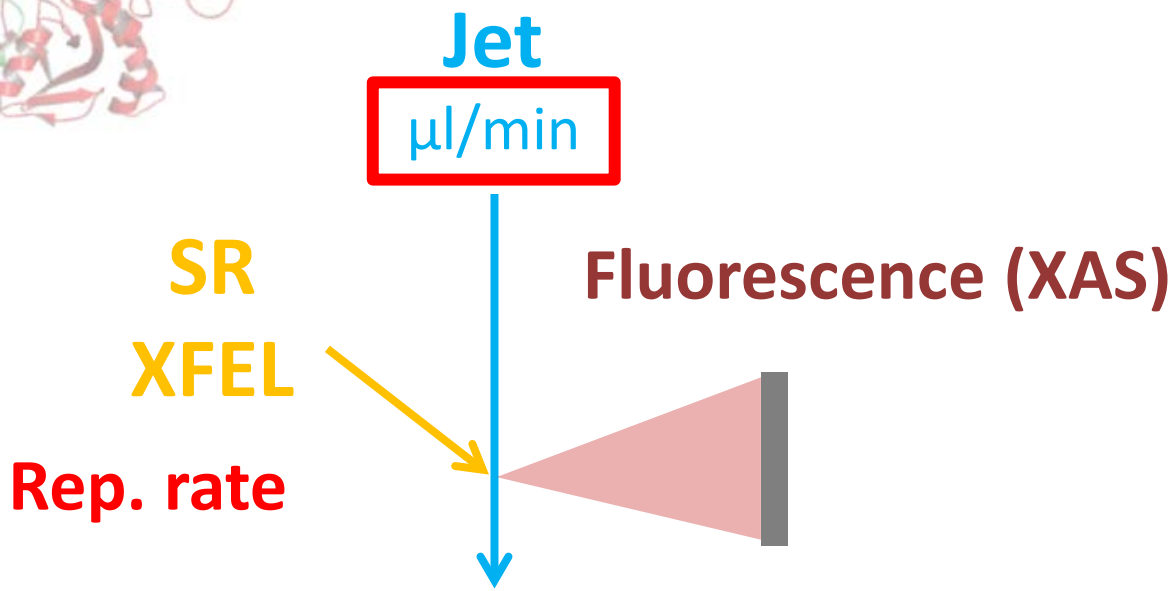
Kubin, Guo, Ekimova, Baker, Kroll, Källman, Kern, Yachandra, Yano, Nibbering, Lundberg, Wernet, Inorg. Chem. **57**, 5449 (2018)
Kubin, Guo, Ekimova, Källman, Kern, Yachandra, Yano, Nibbering, Lundberg, Wernet, Chem. Sci. **9**, 6813 (2018)
Kubin, Guo, Ekimova, Källman, Kern, Yachandra, Yano, Nibbering, Lundberg, Wernet, J. Phys. Chem. B **122**, 7375 (2018)

„Probe before destroy“ spectroscopy

With J. Yano, V. Yachandra and others



Photosystem II



Kubin, Kern, …, Borovik, Agapie, Messinger, Erko, Föhlisch, Bergmann, Mitzner, Yachandra, Yano, Wernet, Struc. Dyn. **4**, 054307 (2017).

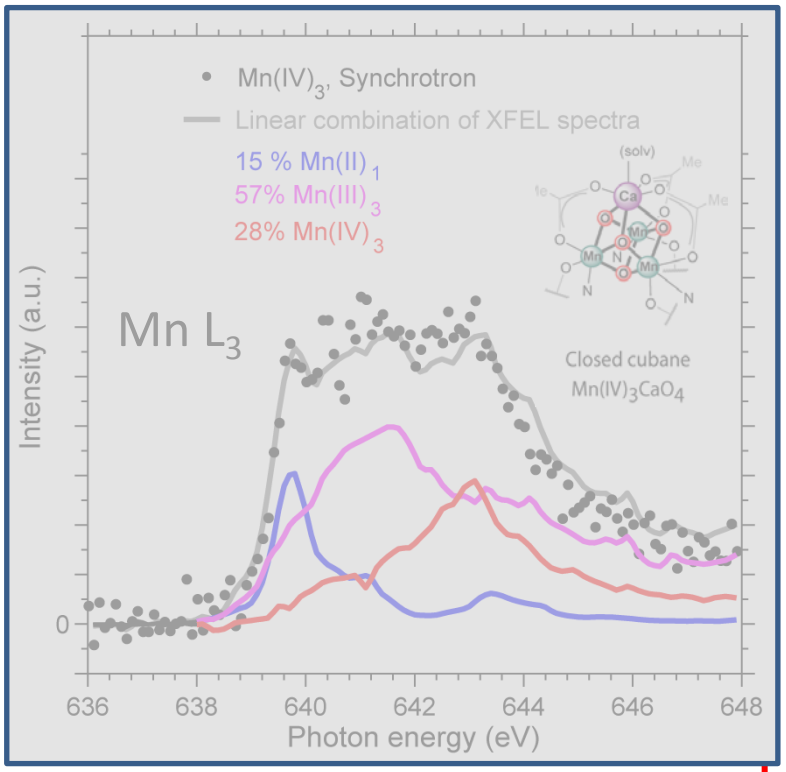
Beyond the first picosecond

Mechanisms and effects of ionizing radiation

$5 \cdot 10^{12}$ photons/s

Synchrotron

- Hit vol. 10^6
- 50 ps pulses
- 0.5 MGy*
- 6 h acquisition



XFEL

- Hit vol. 1
- 100 fs pulses
- 5 MGy*
- 0.5 h acquisition

„probe before destroy“

* Skin dose = Energy in spot · attn. Length
Critical dose in cryo crystallography at synchrotrons = 30 MGy

Ludwig, Kubin, Agapie, Kern, Yano, Yachandra, Wernet et al., unpublished.
Kubin, Kern, Guo, Källman, Mitzner, Yachandra, Lundberg, Yano, Wernet, Phys. Chem. Chem. Phys. **20**, 16817 (2018).

Representative cases

- Ligand substitution with 3d transition-metal systems
- Charge transfer excited states in transition-metal systems
- Mechanisms and effects of ionizing radiation
- Proton-transfer kinetics in acid-base reactions
- Fundamental processes in organic systems

Where (soft) x-ray spectroscopy gives access to structures and bonding

Systematics and small effects!

Guiding questions

… for photochemical studies…

- Why using a 1 ps SR instead of a fs lab source?
  - Use x-ray methods: Fill information gap of TR UV/Vis and TR IR
  - Add essential information on geometric and electronic structure
- Why using a 1 ps SR instead of a 100 ps SR?
  - Probe transition from dynamics to kinetics: Fill information gap in TR IR investigations between 0 and 10 ps
  - Add essential information on reaction intermediates
- Why using a 1 ps SR instead of an XFEL?
  - Systematic studies on the few ps time scale: Fill information gap in TR x-ray spectroscopy studies between fs (XFEL) and ns (SR)
  - Add electronic-structure information on transition from (coherent wavepacket) dynamics to (population) kinetics to connect excited-state dynamics and reaction rates

Some conclusions

Learn the Fundamental Chemistry

- In weird bonding configurations
- In metalloproteins

Soft x-ray spectroscopy of 3d TM systems with short pulses

Attract the (photo)chemistry and biology communities to (soft) x-ray methods

Thank you

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LBNL, Berkeley

Athina Zouni
HU Berlin

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Uppsala University

Helmholtz Virtual Institute

Dynamic Pathways in Multidimensional Landscapes