Unraveling the interplay of ultrafast electronic, spin, nuclear, and solvent dynamics in a solvated iron complex using the SHARC method

VISTA Seminar

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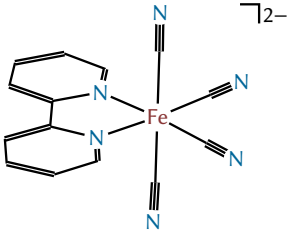
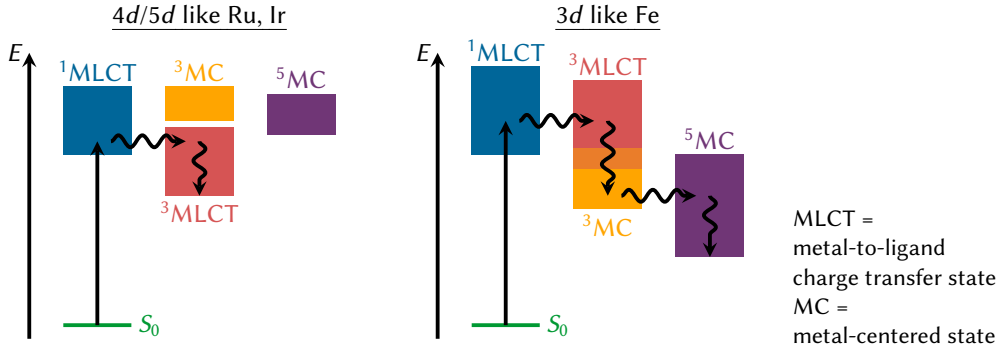


August 17th, 2022

Transition metal photosensitizers

Motivation?
Background?
Essential questions?

Transition metal photosensitizers

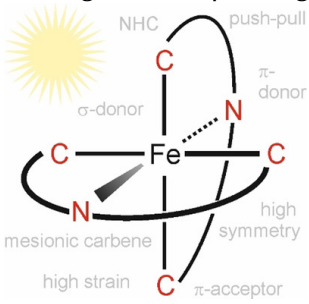


MLCT =
metal-to-ligand
charge transfer state
MC =
metal-centered state

- Desired: Formation of long-lived CT states after excitation
- Very efficient for $4d/5d$ metals
- $3d$ metals have low-lying MC states

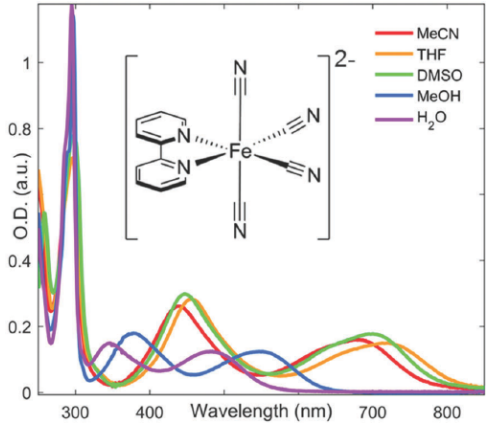
Transition metal photosensitizers with $3d$ elements

Much efforts to make viable photosensitizers with $3d$ metals, e.g., Fe with special ligands:



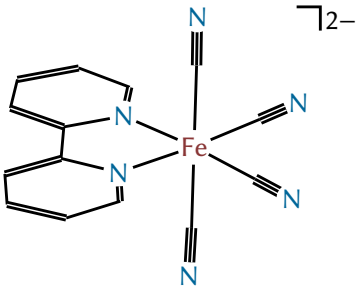
Chem. Eur. J **2019**, 25, 6043.

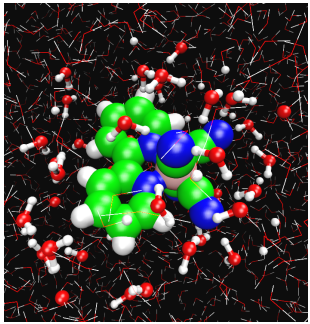
Another way to control the MLCT lifetimes:
Solvent effects!

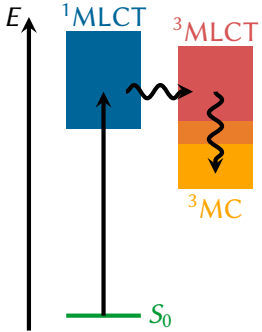


Kjær et al, PCCP **2018**, 20, 4238.

Ultrafast dynamics in $[Fe(CN)_4(bipy)]^{2-}$







- High charge:
  Strong solvent interactions
- Strong ligand field effects:
  Shifts of MLCT and MC states

Questions

- Processes after photo-excitation?
- Interrelation between solvent, vibrational, and electronic dynamics?

Background

universität wien

DTU

Collaboration with **Diana Bregenholt-Zederkof** and **Kristoffer Haldrup** from Technical University of Denmark (DTU).

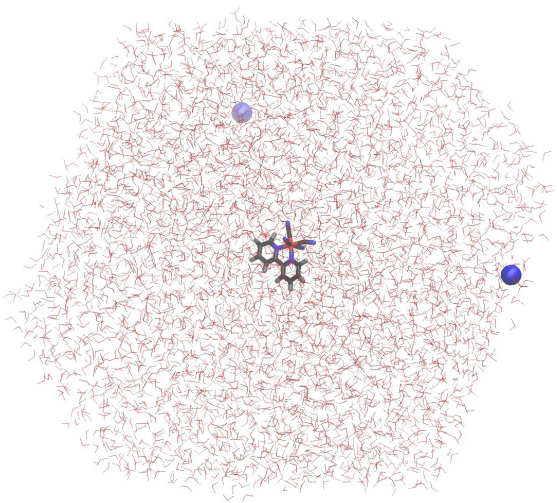
Combination of **nonadiabatic dynamics simulations** and **time-resolved X-ray scattering**

D. B. Zederkof, K. B. Møller, M. M. Nielsen, K. Haldrup, L. González, SM, *JACS* 144, 12861–12873 (2022).

Nonadiabatic dynamics simulations with SHARC and TDDFT/MM

System?
Methods?

System setup I



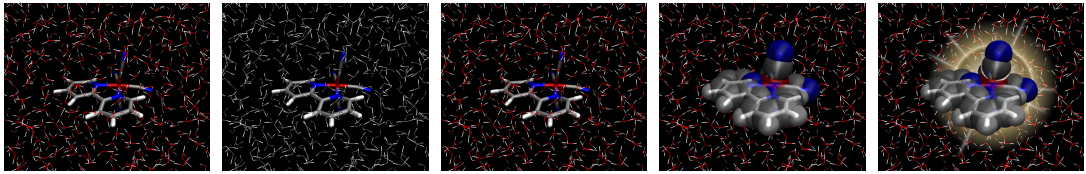
Simulation box:

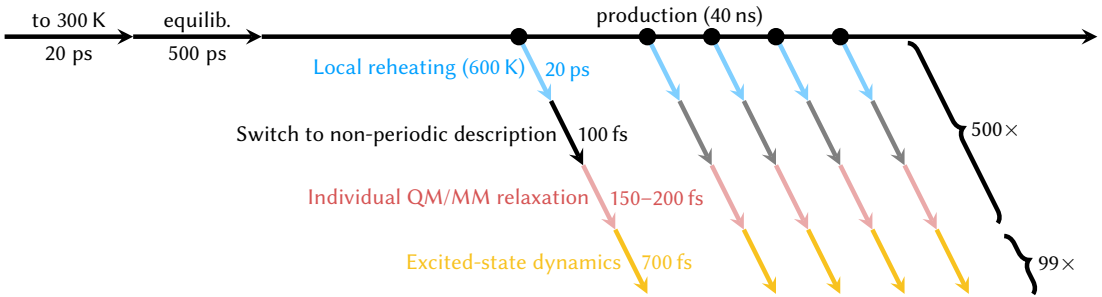
- $[Fe(CN)_4(bipy)]^{2-}$, 2 Na^+, 5412 waters
- QM/MM with TD-B3LYP*/mixed basis

Initial condition generation:

- Fully equilibrated solvent distribution:
  Needs cheap sampling
- Adequate ground state geometries:
  Needs QM/MM sampling
- Adequate internal energy of molecule:
  Classical mechanics is
  colder than zero-point energy

System setup II





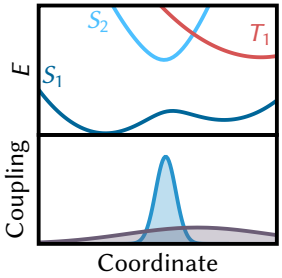
SM et al., *Front. Chem.* 6, 1 (**2018**).

Excited-state dynamics simulations with SHARC

Choice of electronic basis is essential:

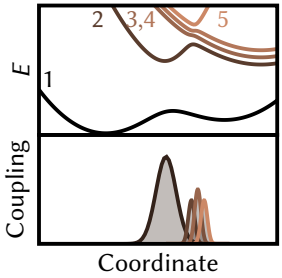
MCH representation

Eigenstates of $\hat{H}^{\mathrm{MCH}}$



Diagonal representation

Eigenstates of $\hat{H}^{\mathrm{full}}$

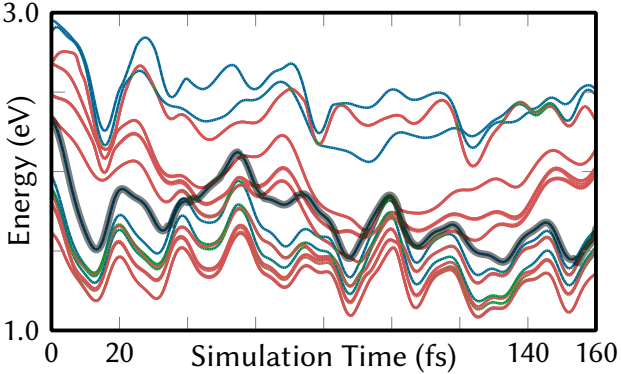


For SH the **diagonal representation** is best:

+ Energies include spin–orbit effects
+ Multiplets treated correctly
+ All couplings localized

Excited-state dynamics simulations with SHARC

Choice of electronic basis is essential:

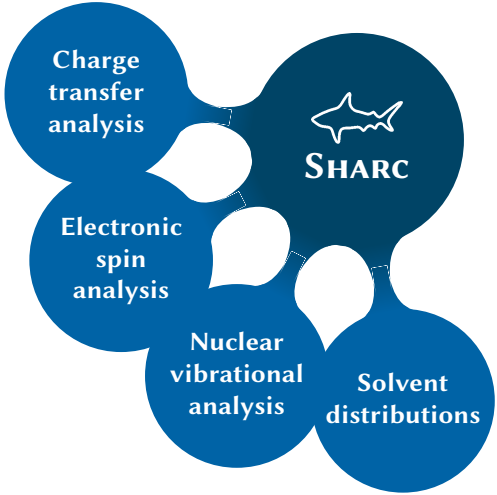


For SH the **diagonal representation** is best:

- \+ Energies include spin–orbit effects
- \+ Multiplets treated correctly
- \+ All couplings localized

Nonadiabatic dynamics analyses

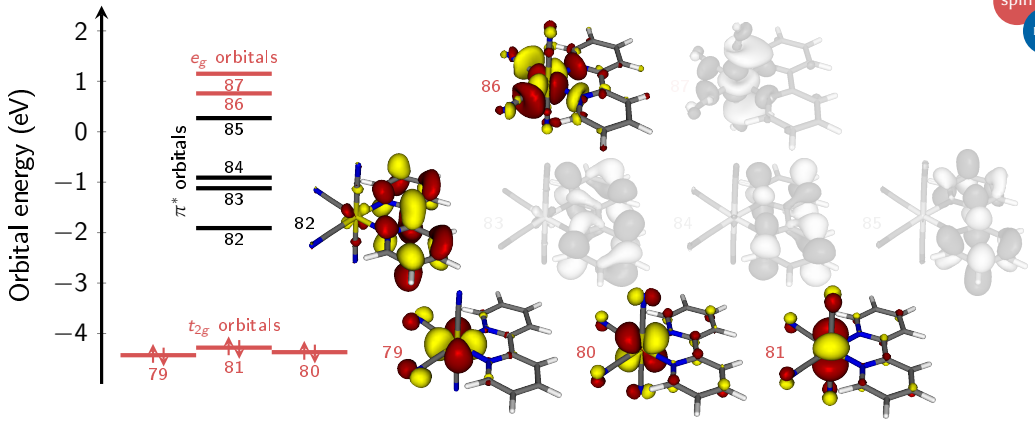
We analyzed all relevant **molecular degrees of freedom**:



Effects of photo-excitation on $[Fe(CN)_4(bpy)]^{2-}$

Ultrafast processes?
Unexpected findings?

Results I: Electronic structure



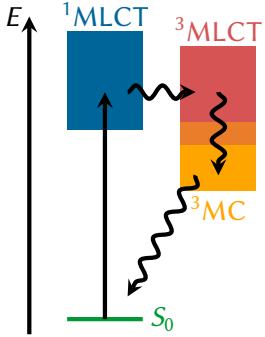
Relevant orbitals:

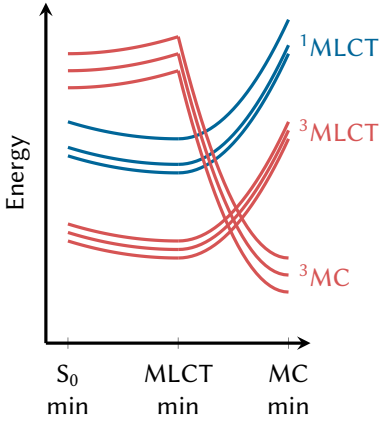
- Metal d orbitals
- Bipyridine π^* orbitals

Relevant electronic states:

- 3 singlet + 3 triplet MLCT states
- 3 triplet MC states

Results I: Electronic structure





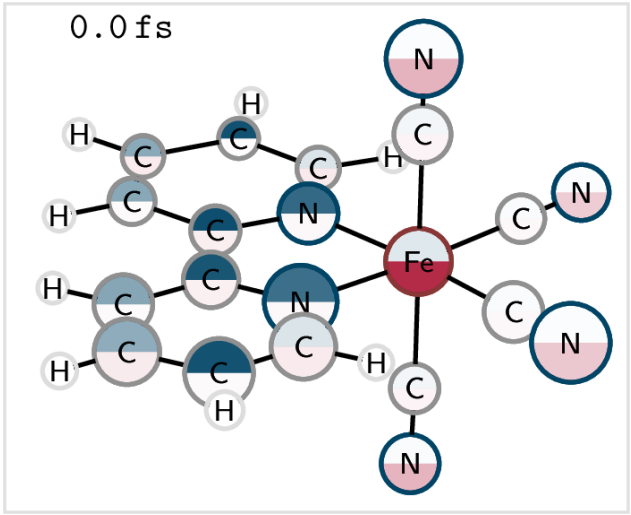
Expectations:

- Start in ^{1}MLCT
- ISC to ^{3}MLCT
- CT from ^{3}MLCT to ^{3}MC via Fe–N and Fe–C stretch modes

Nuclear motion **affects** CT character.

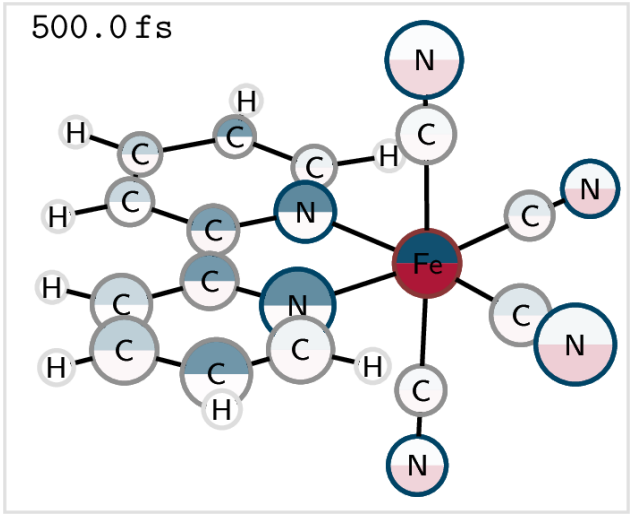
Nuclear motion **affects** ISC dynamics.

Results II: Charge transfer dynamics



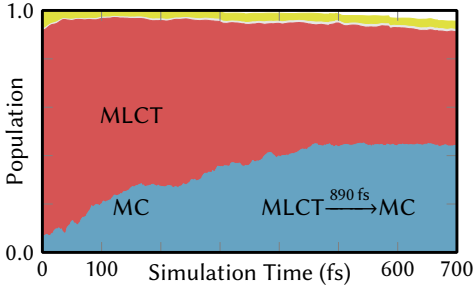
- Excitation hole mostly on Fe, contributions on CN^-
- Excited electron slowly migrates from bpy to Fe

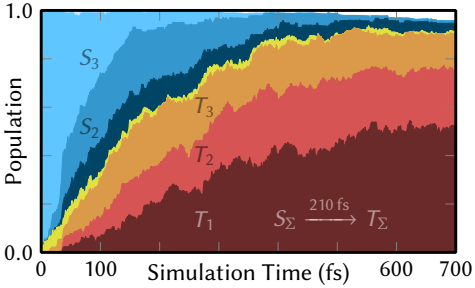
Results II: Charge transfer dynamics

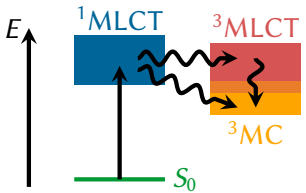


- Excitation hole mostly on Fe, contributions on CN^-
- Excited electron slowly migrates from bpy to Fe

Results II: Spin and charge transfer dynamics



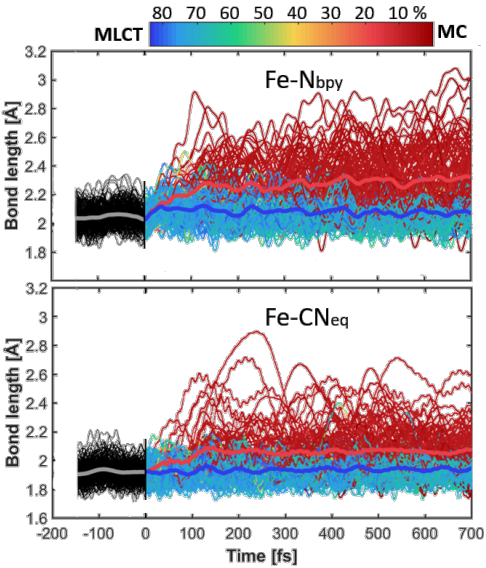




ISC dynamics **affects** charge transfer.

Charge transfer will **affect** solvent dynamics.

Results III: Bond lengths

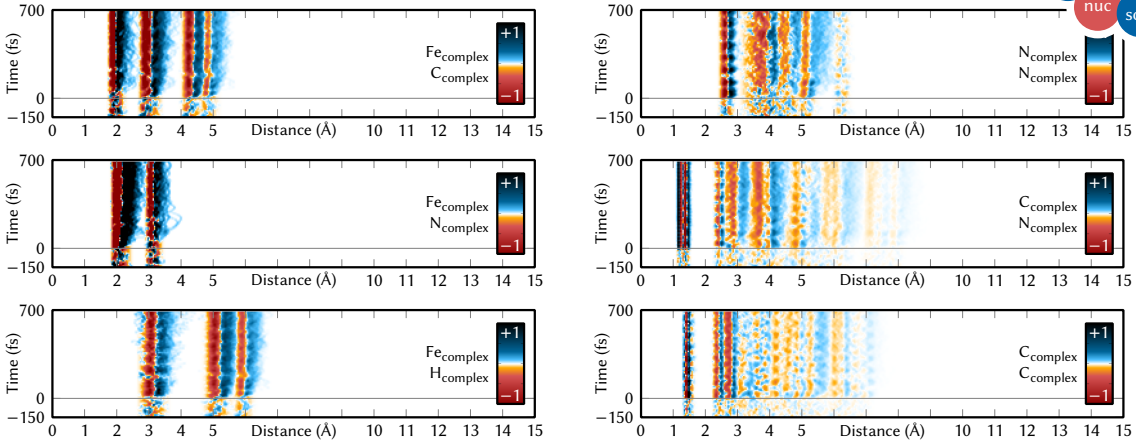


- Fe–X bonds short in ground state
- Extend strongly for ^{3}MC states

Charge transfer **affects** nuclear dynamics.

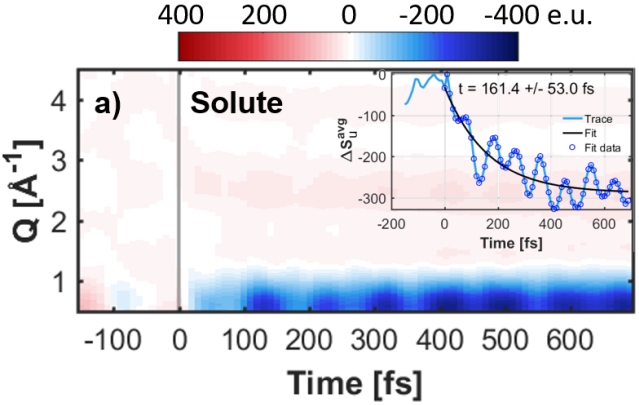
ISC dynamics **affects** nuclear dynamics.

Results III: Solute RDFs



- All Fe–X distances increase significantly (MC weakens Fe bonds)
- Coherent beating of bpy ligand (bpy is reduced in MLCT states)

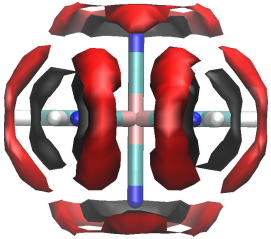
Results III: Predicted X-ray scattering

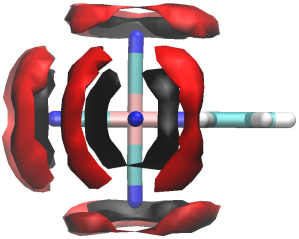


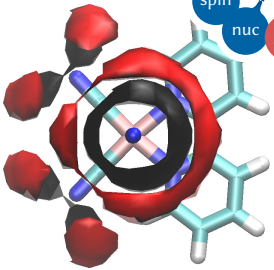
- Very strong negative feature at $Q \approx 1\,\text{Å}^{-1}$: **Fe–X bond stretch** (160 fs)
- Beating around $Q \approx 1\,\text{Å}^{-1}$: **Bpy beating** (90 fs period)

Results IV: Solvent interactions

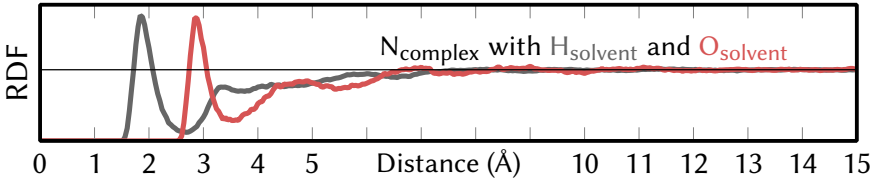
Solvent hydrogen
Solvent oxygen



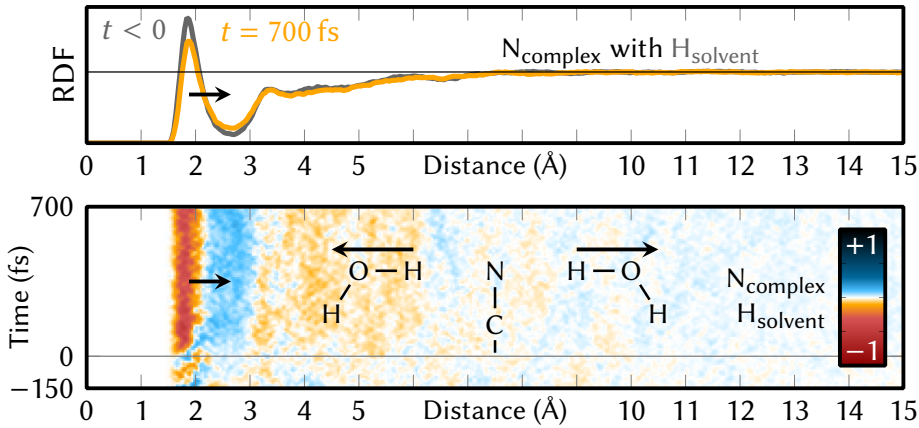




Represented via RDFs:



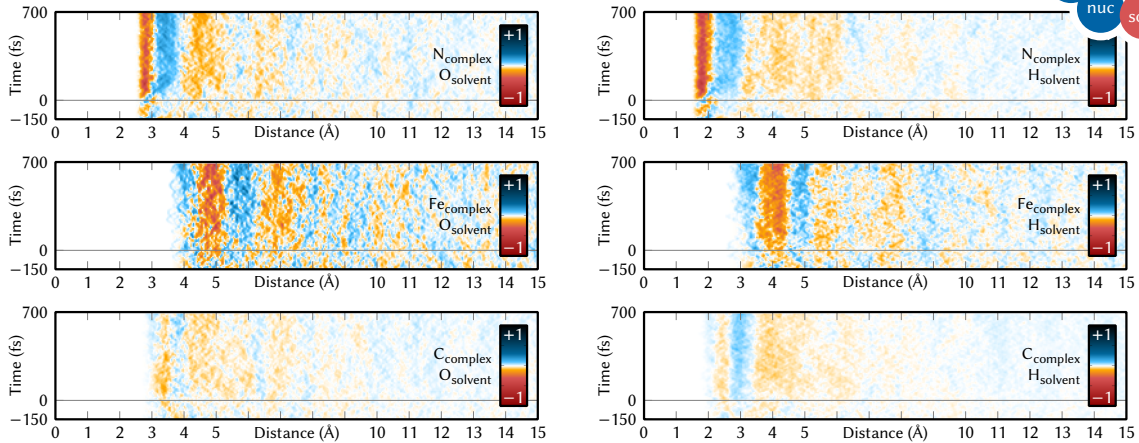
Results V: Solvent distribution dynamics



- Significant effect after excitation to MLCT
- Rather small differences: use difference plots for time dependence

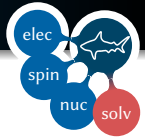
CT character **affects** solvent structure

Results IV: Solvent distribution dynamics

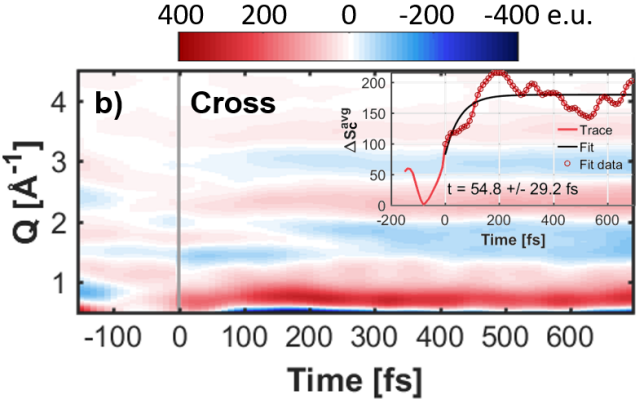


- Significant weakening of hydrogen bonds around cyanides (N atoms)
- Weaker effect around bipy (C atoms)

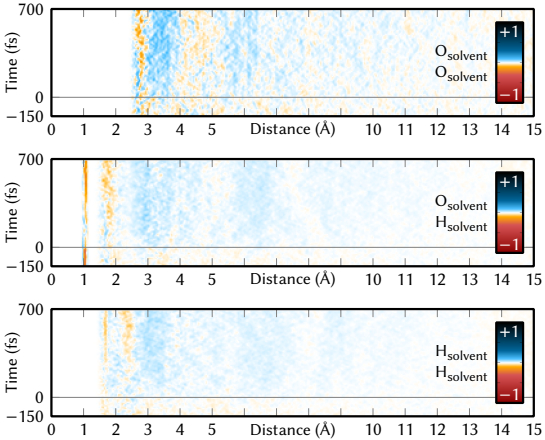
Results IV: Predicted X-ray scattering



- Strong positive feature at $Q \approx 1\,\text{Å}^{-1}$: **break of hydrogen bonds** (50 fs)
- Negative-positive-negative feature at $Q \approx 2.5\,\text{Å}^{-1}$: **Solvent heating** (few 100 fs)

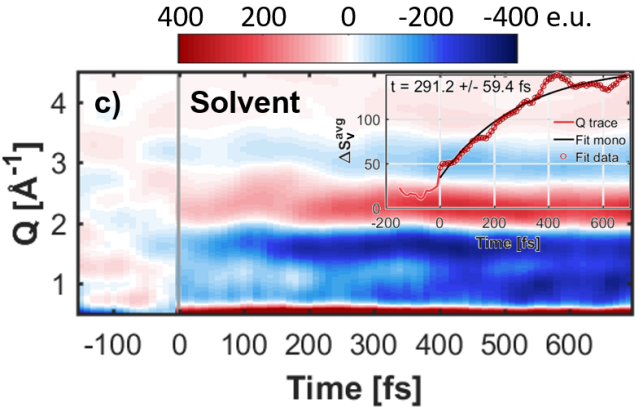


Results V: Solvent–solvent dynamics



- Shortening of O–H bond lengths, decrease in water–water hydrogen bonding
- Slight heating of solvent

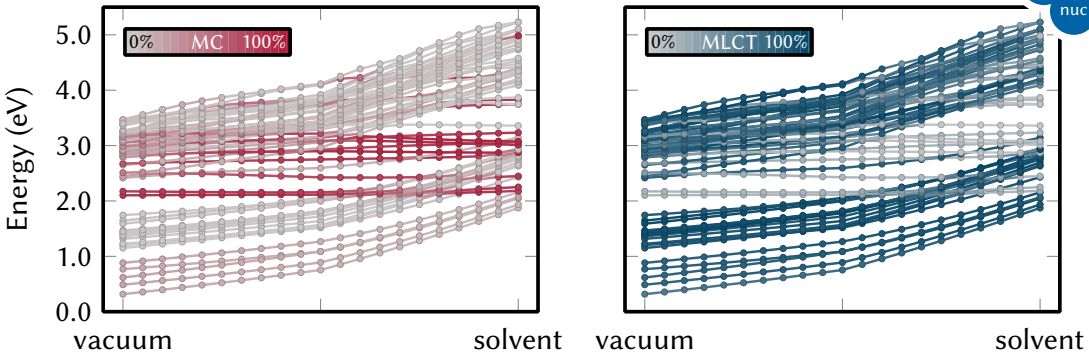
Results V: Predicted X-ray scattering



- Negative-positive-negative feature at $Q \approx 2.5\,\text{Å}^{-1}$: **Solvent heating** (few 100 fs)

X-ray solvent scattering observes **nuclear** and **solvent** dynamics, and indirectly **electronic** and **spin** dynamics.

Results VI: Solvent effect on electronic states



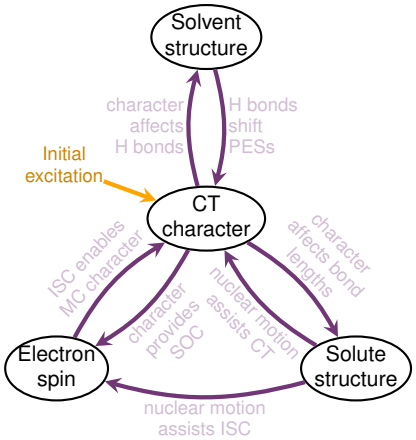
- Energies of MC states solvent-independent
- Energies of MLCT states increase strongly in solution

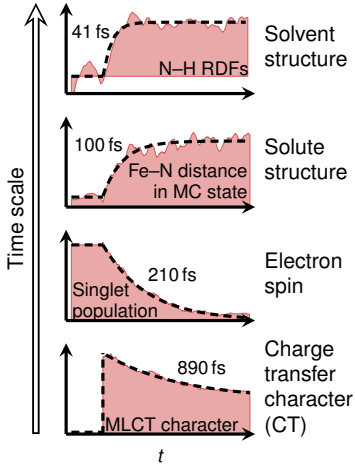
Solvent structure **affects** CT character

Interrelation of different degrees of freedom

What have we learned about $[Fe(CN)_4(bpy)]^{2-}$?

Processes and time scales in the nonadiabatic dynamics



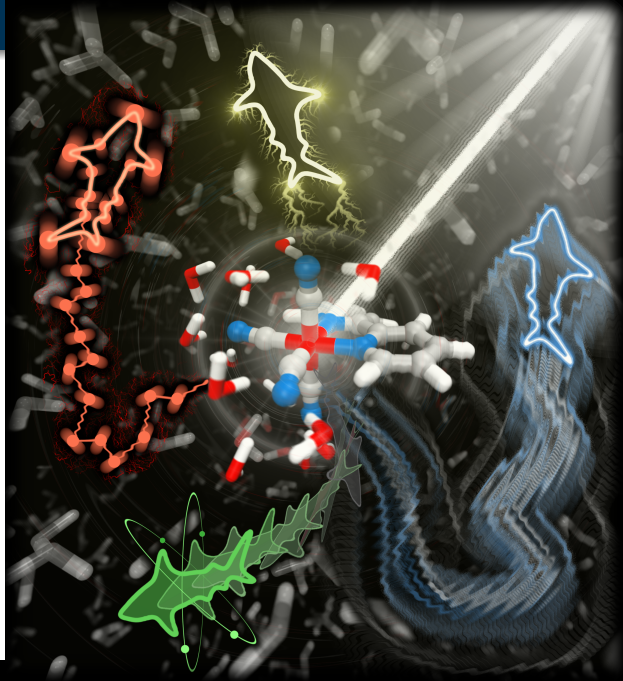


Counter-intuitive time scales:
solvent reorganization < nuclear relaxation < intersystem crossing < charge transfer

Summary

Ultrafast dynamics in $[Fe(CN)_4(bipy)]^{2-}$

- Initial excitation to ^{1}MLCT
- Cyanide ligands show very strong hydrogen bonding
- Hydrogen bonding is quickly weakened after excitation
- Fe–ligand bonds stretch quickly in MC states
- Sub-ps intersystem crossing and charge transfer
- **Time scales of processes are counter-intuitive**



Further thanks to:

- Diana Bregenholt-Zederkof
- DTU physics and chemistry

universität wien

VSC VIENNA SCIENTIFIC CLUSTER

FWF

DTU

Thank you for your attention!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