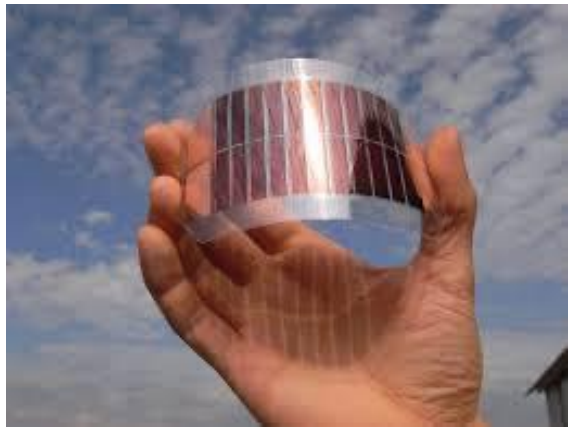
Capturing Chemical Motion in Solution: Insights from Femtosecond X-ray and Electron Scattering

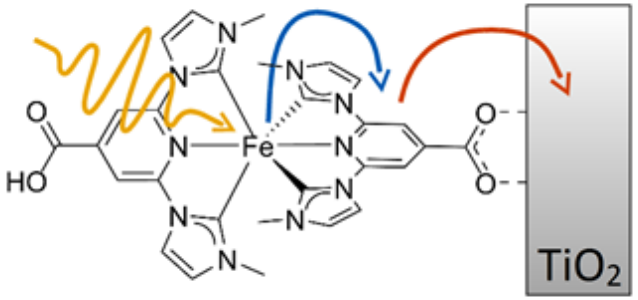
Elisa Biasin

Frontiers in Ultrafast Scattering of Electrons
Menlo Park, CA
August 27-29,2025

Efficient solar energy conversion

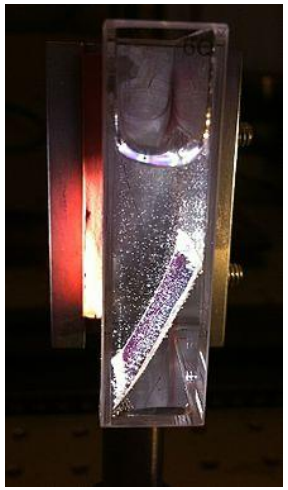
Light to electricity

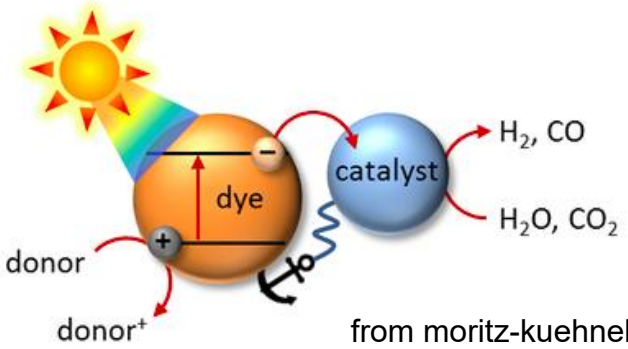




from T. Harlang *at al.*, *Nat. Chem.* 7 883 (2015)

Light to chemical fuels



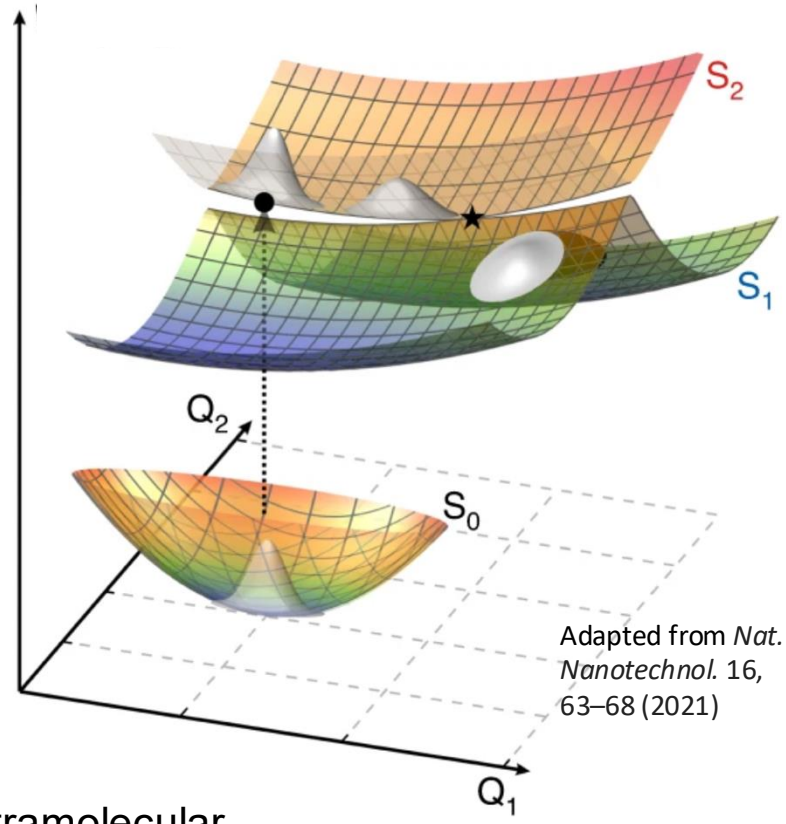


from moritz-kuehnel.com

Motivation:
Provide new design criteria for efficient solar energy conversion processes.

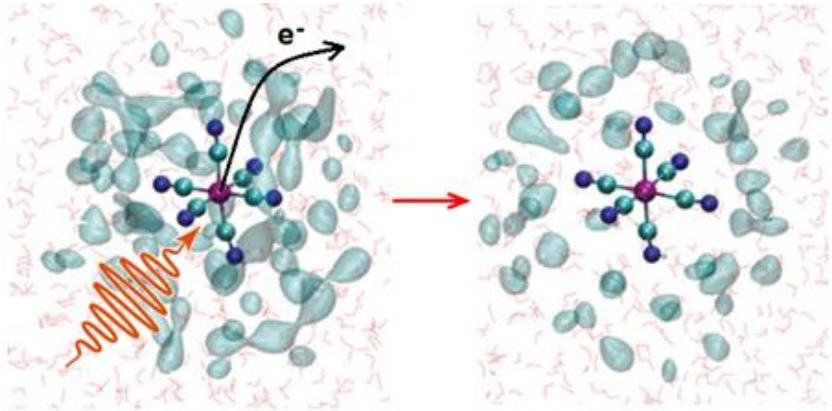
An atomistic view of charge and solvation dynamics

Scientific challenge: direct real-time visualization of the crucial electronic and nuclear degrees of freedom involved, **including the solvent**



Adapted from *Nat. Nanotechnol.* 16, 63–68 (2021)

Q_1 = intramolecular.
Q_2 = solvent. *A continuum picture hides the *molecularity* of the solvent.

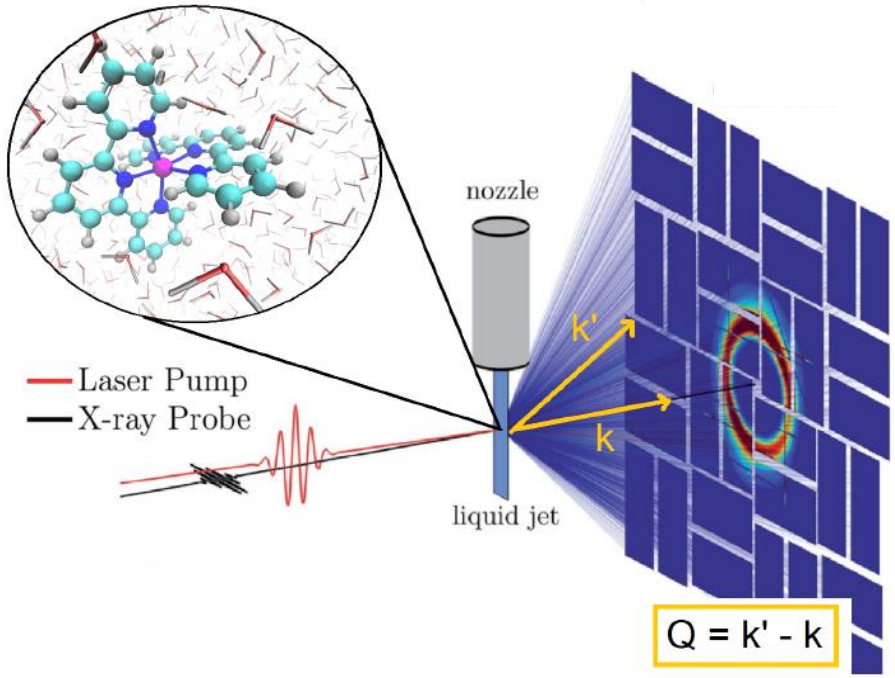


Adapted from: M. Ross *et al.*, J. Phys. Chem. B (2018), 122

- Local (element-specific) picture of charge distribution and chemical bonding
- Mechanistic and quantitative understanding of the role of the solvent, with sensitivity to the the first-solvation-shell solvent molecules

Approach: time-resolved X-ray scattering at XFELs

$$S(\mathbf{Q}, \Delta t) \propto \int dR\ \rho(\mathbf{R}, \Delta t)|F_{mol}(\mathbf{R}, \mathbf{Q})|^2$$



Ambient conditions
5-50 mM solutions
50 um liquid jet
~80 fs (FWHM)

- Femtosecond X-ray pulses available at X-ray Free Electron Lasers (XFELs) can probe electronic and nuclear dynamics at the atomic scales (~100 femtoseconds and Ångström)

Linac Coherent Light Source

Approach: time-resolved X-ray scattering at XFELs

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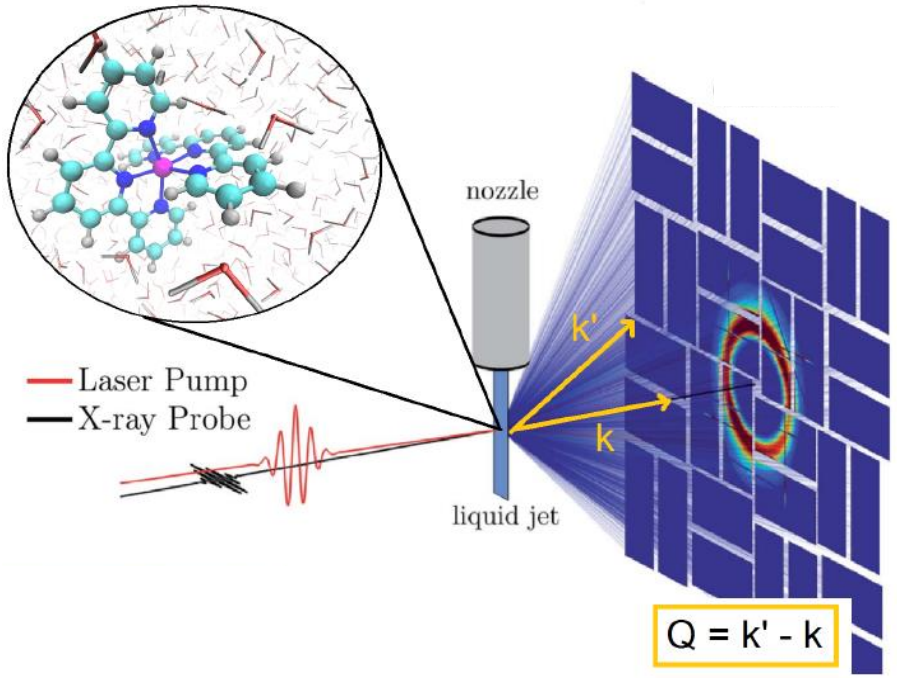

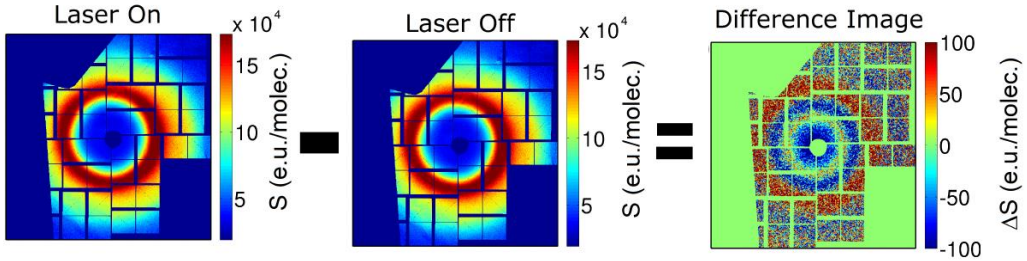

- Femtosecond X-ray pulses available at X-ray Free Electron Lasers (XFELs) can probe electronic and nuclear dynamics at the atomic scales (~100 femtoseconds and Ångström)
- After baseline subtraction (i.e. unchanging solvent contribution) even subtle modulations in nuclear positions—such as those arising from vibrational motions—manifest as measurable changes in the scattering curves.

Linac Coherent Light Source

Approach: time-resolved X-ray scattering at XFELs

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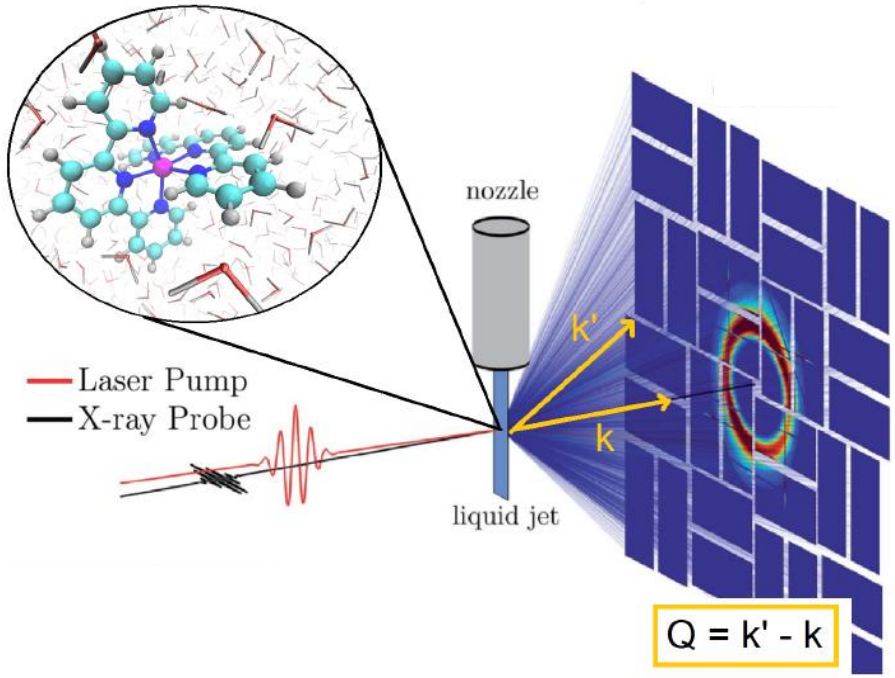
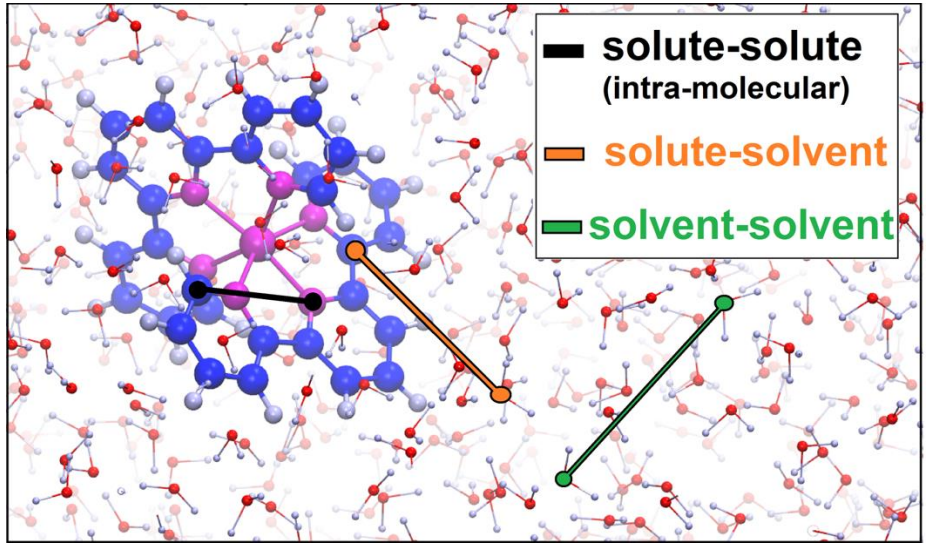


- The difference scattering signal can be directly compared to Molecular Dynamics Simulations



$$\Delta S(Q) = \Delta S_{solute}(Q) + \Delta S_{solute-solvent}(Q) + \Delta S_{solvent}(Q)$$

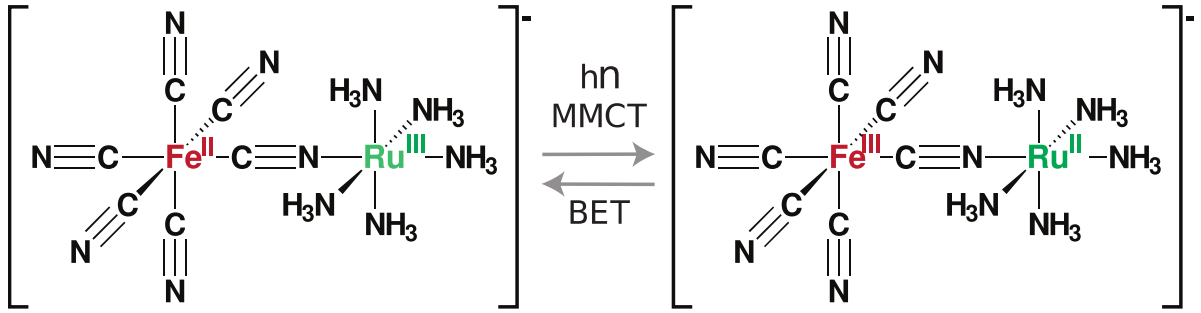
from DFT/MD

Heating, from separate experiments

Understanding the role of H-bonding interactions

Hydrogen bonding is one of the key ways the solvent actively shapes reactivity

- It stabilizes or destabilizes charge-separated states.
- It mediates proton-coupled electron transfer (PCET) reactions.
- It modulates barriers and pathways



FeRu: a mixed-valence system and a prototype for studying ultrafast electron transfer

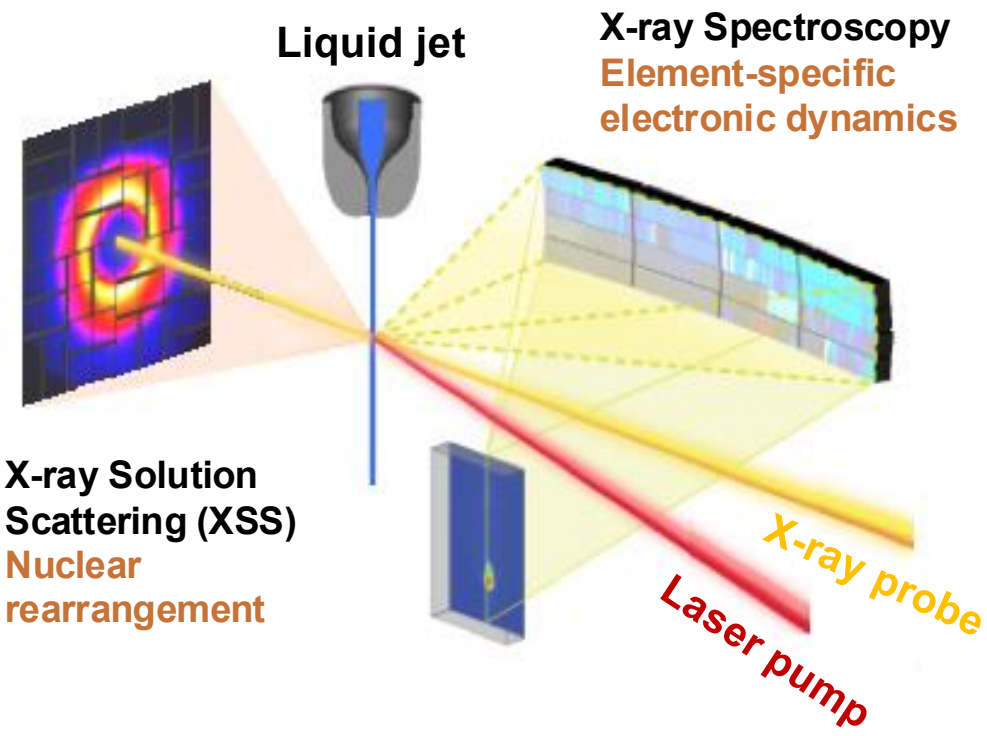
Previous optical studies: Electron Transfer (ET) in FeRu is solvent dependent!

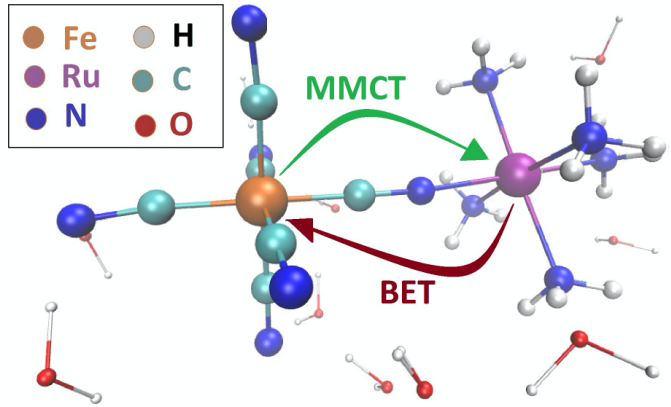
However, a direct correlations between solvent motions and ET could not be established.

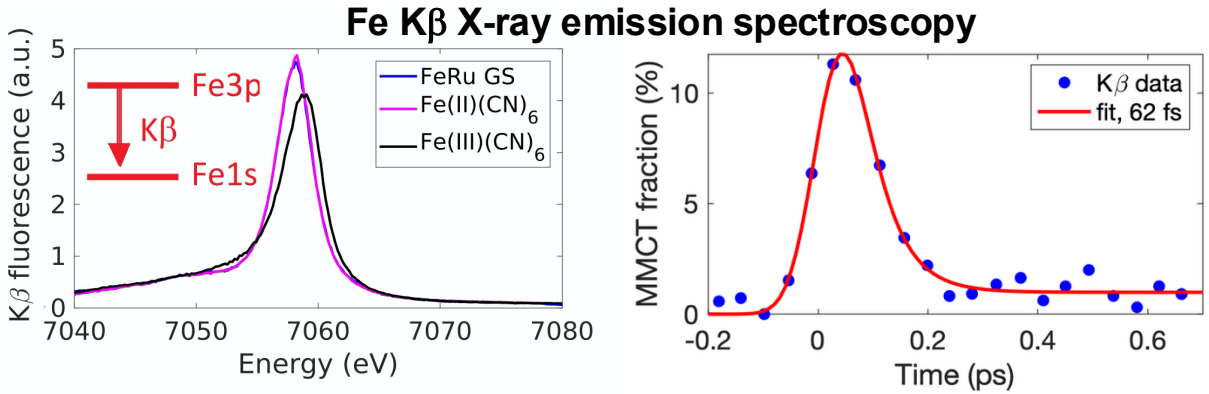
Objectives

- Directly capture H-bonding rearrangements in real time after photoexcitation
- Disentangle H-bonding effects from mean-field interactions

Ultrafast X-ray spectroscopy



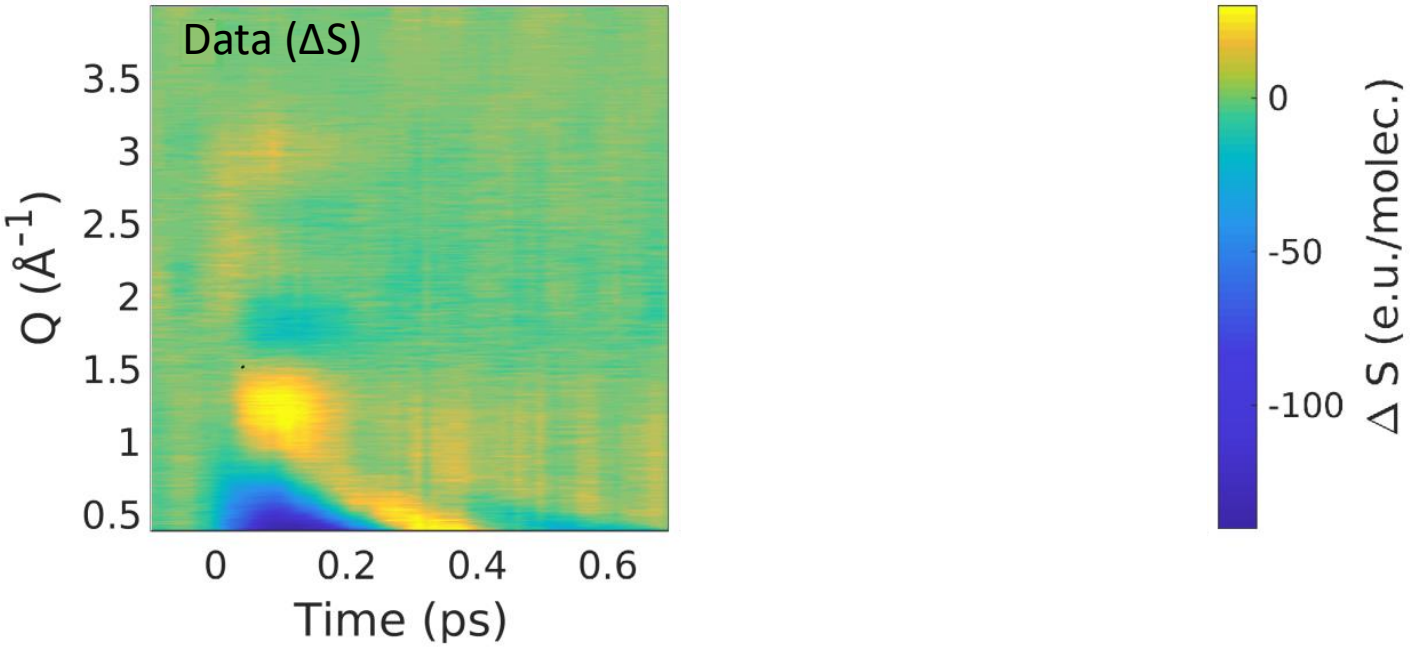


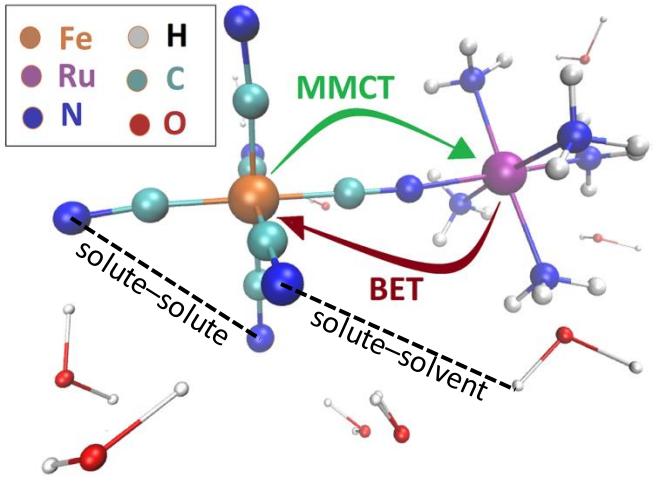


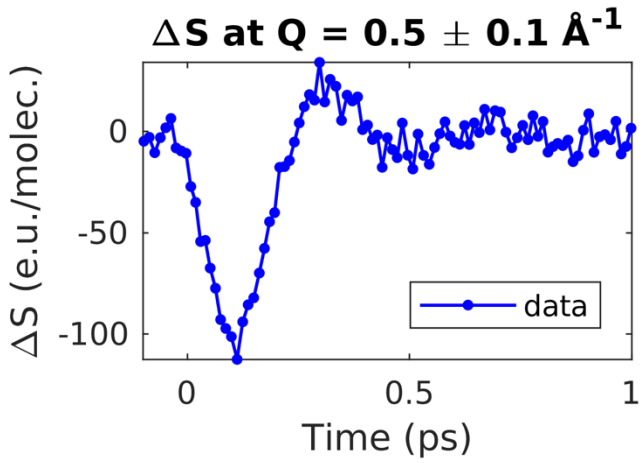
Fe Kβ is sensitive to the oxidation state of the Fe and reports on the BET time (65 fs)

E. Biasin et al., *Nature Chemistry* **13**, 343–349 (2021)

$$\Delta S = \cancel{\Delta S_{\text{solute-solute}}} + \Delta S_{\text{solute-solvent}}$$







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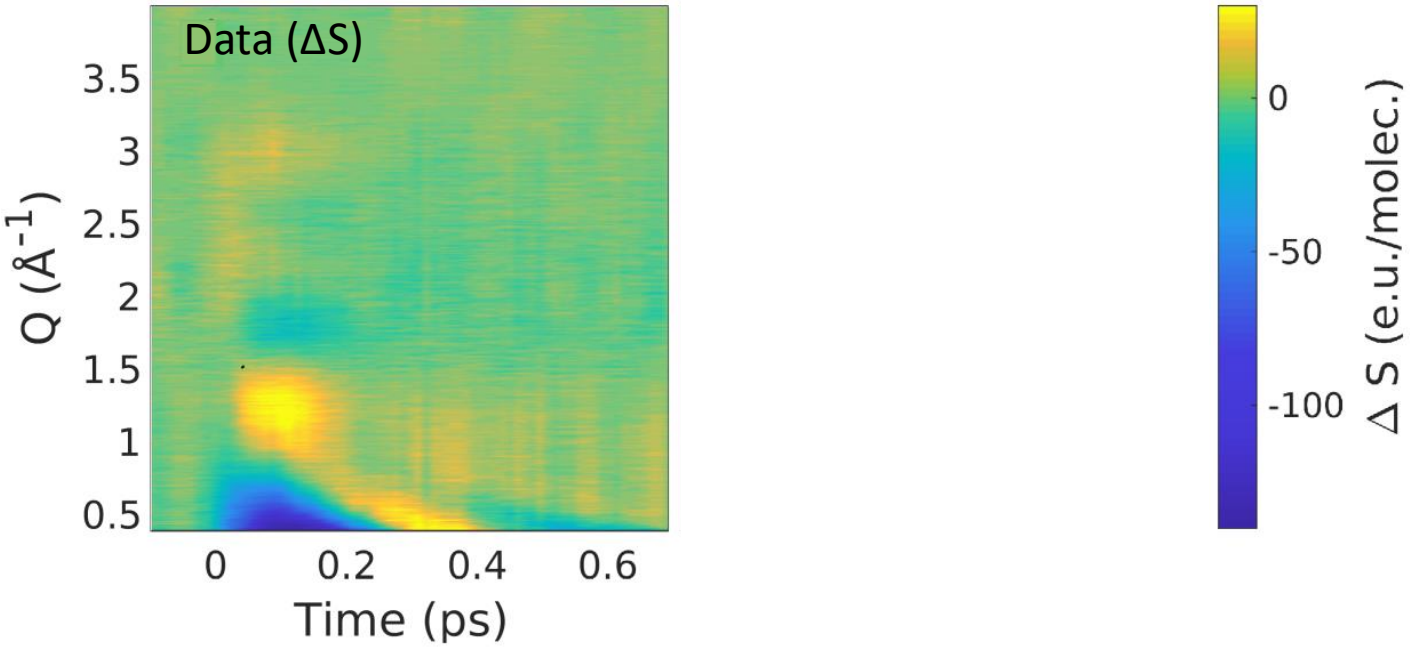
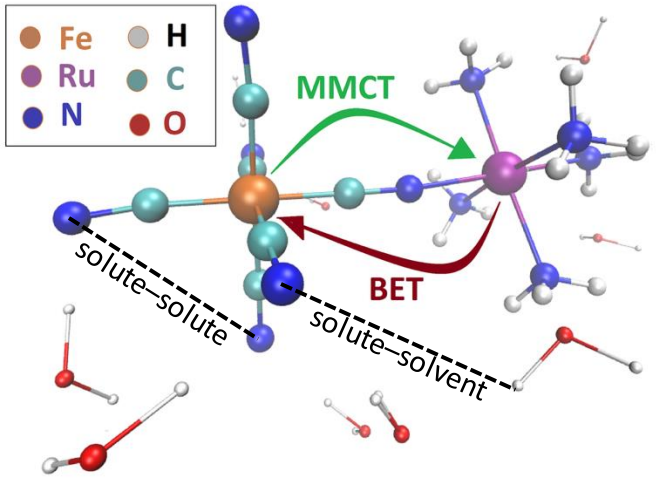
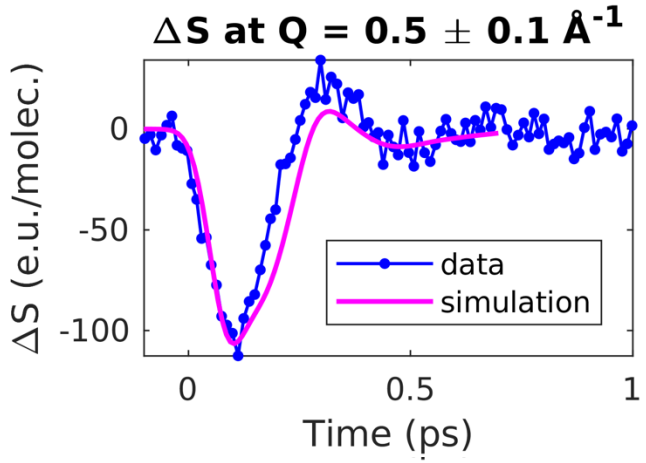


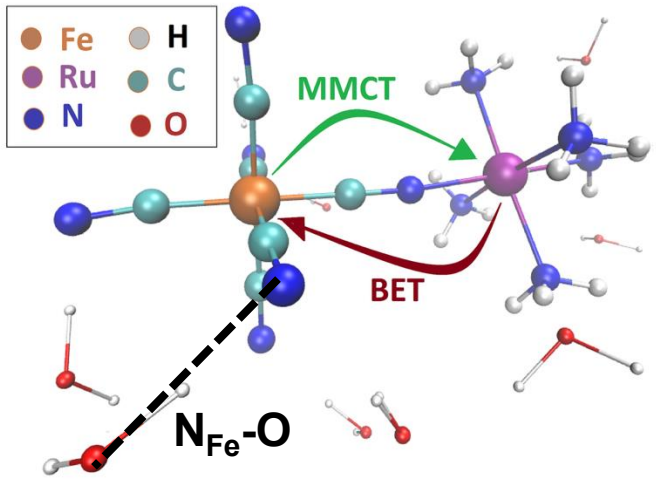
Non-equilibriums MD simulations:

- Trajectories are started from the GS equilibrium
- At t=0 the partial charges are switched to the MMCT values
- A t=BET the partial charges are switched back to the GS values

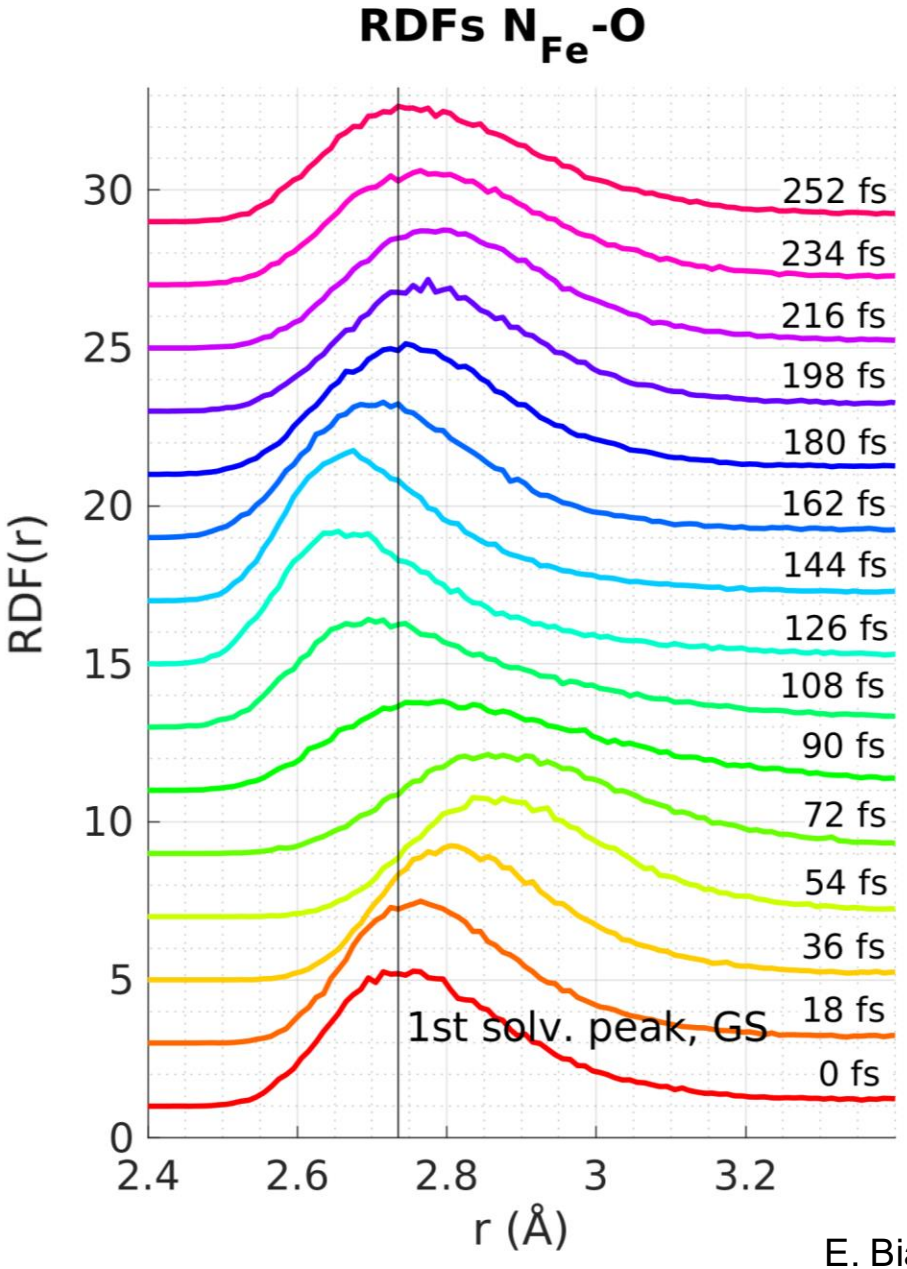


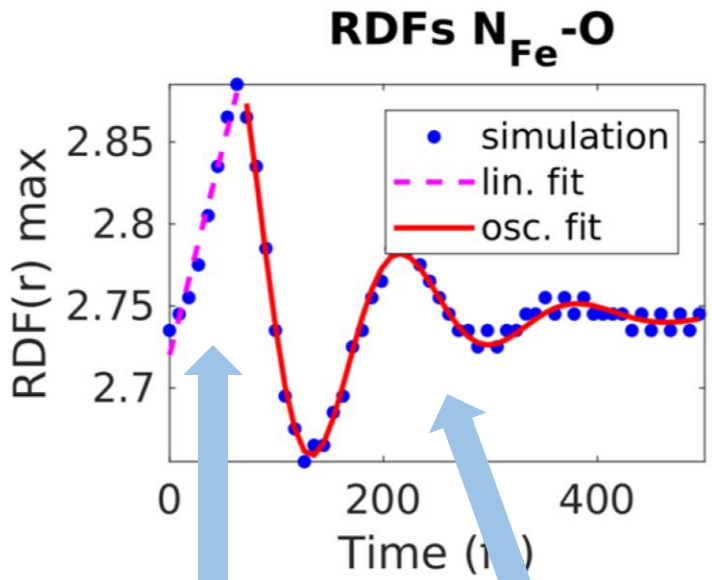


E. Biasin et al., *Nature Chemistry* **13**, 343–349 (2021)



- MD simulations explain nuclear motion giving rise to transient scattering signal.
- On both side of the molecules, water-shell respond to weakening/strengthening of H-bonding upon ET/BET

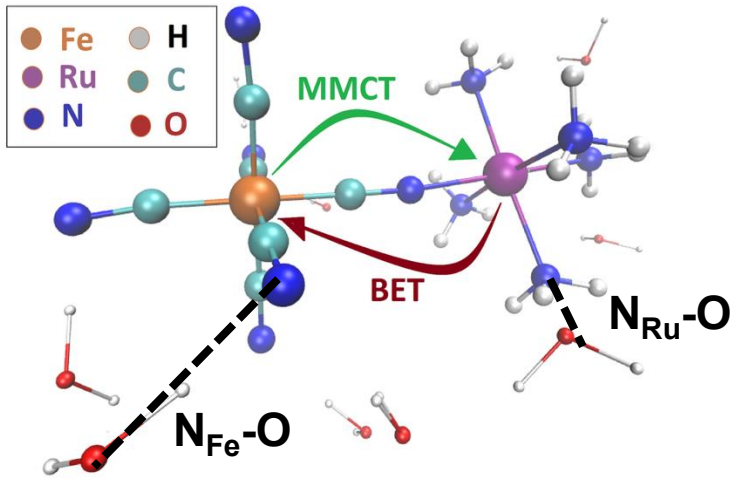




First solvation shell expansion: 2.5 Å/ps

Coherent motions:
180 fs period
100 fs dampening

E. Biasin et al., *Nature Chemistry* **13**, 343–349 (2021)



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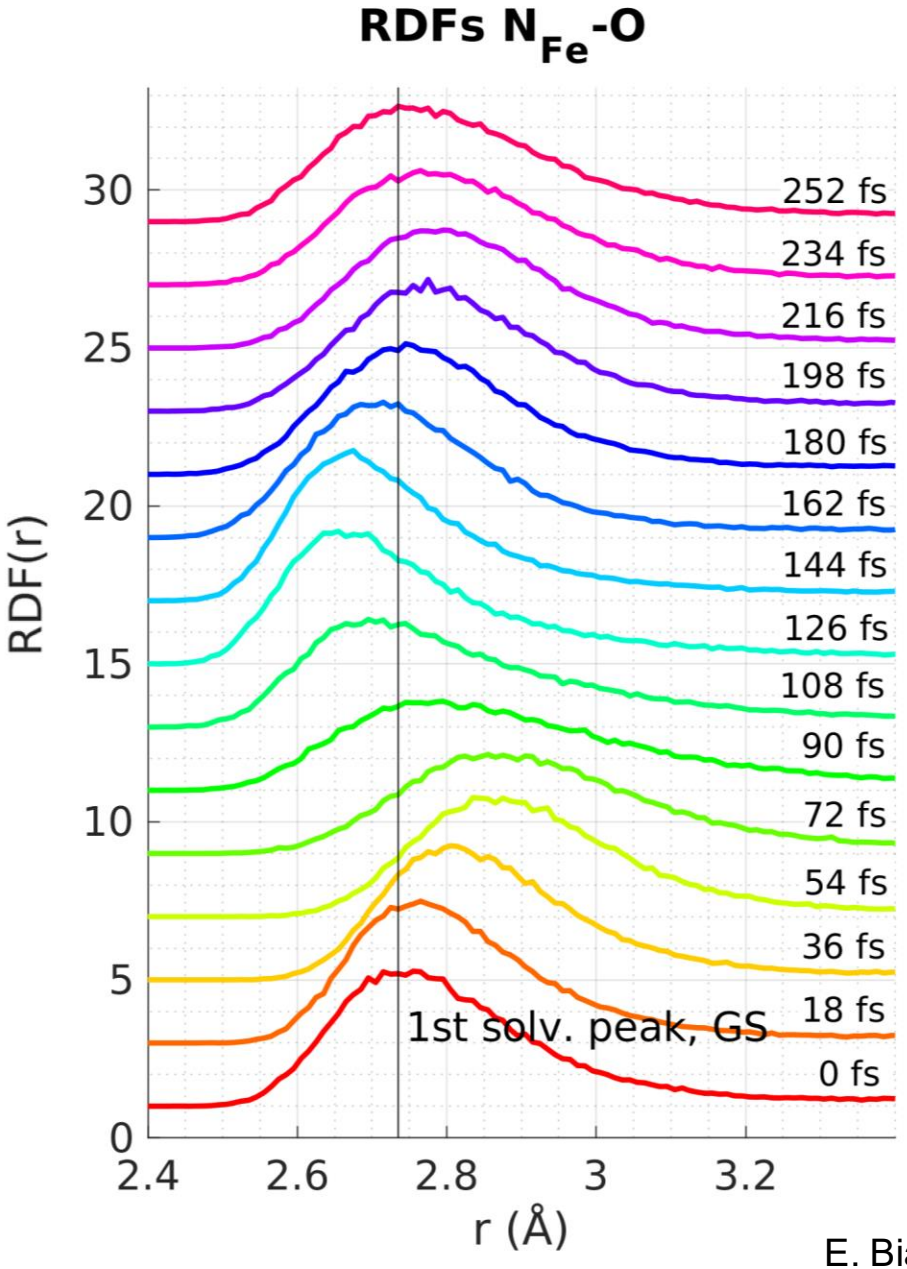
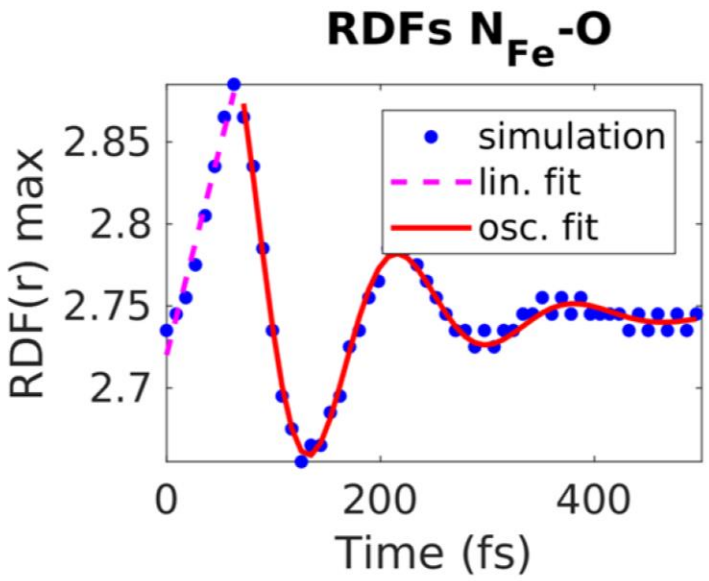
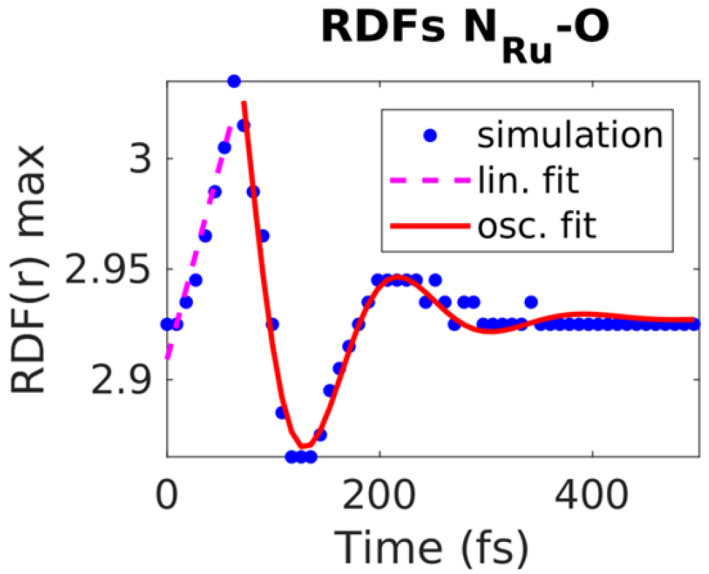
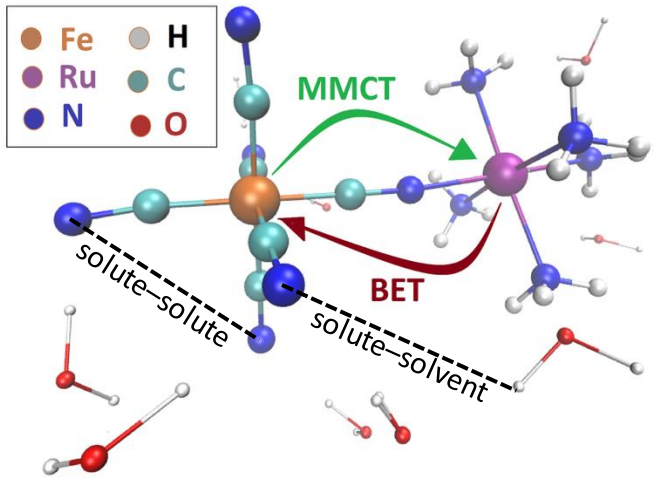


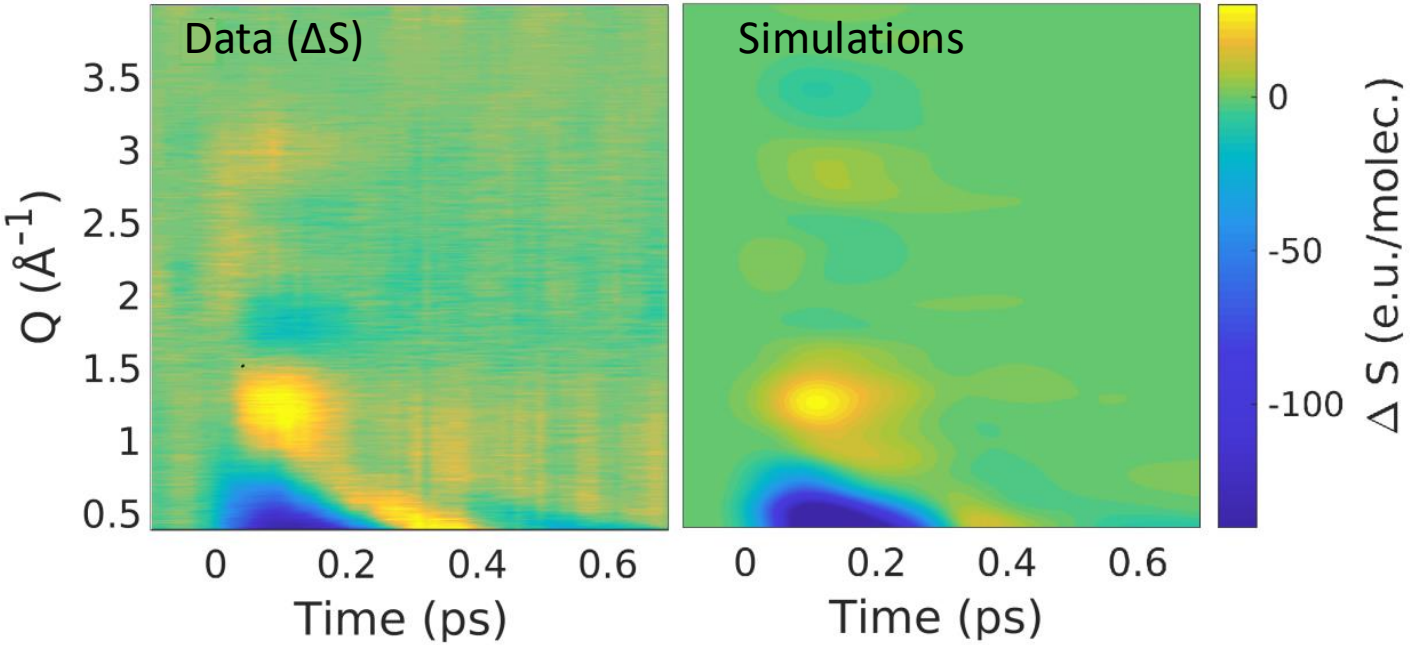




E. Biasin et al., *Nature Chemistry* **13**, 343–349 (2021)

FeRu: conclusions





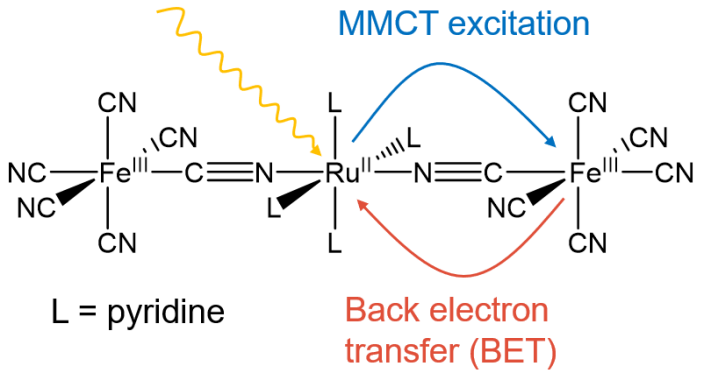
We have directly observed femtosecond coherent translational motions of the first-solvation-shell water molecules.

- These motions arise from the from strong modification of the solute-solvent hydrogen bonding upon electron transfer;
- and contribute to the solvent reorganizational energy of the electron transfer process.

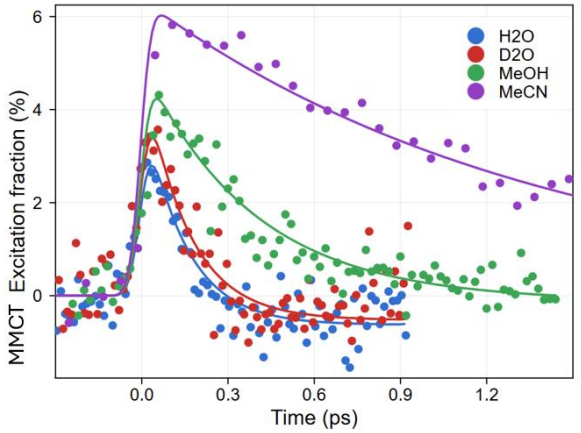
E. Biasin et al., Nature Chemistry **13**, 343-349 (2021)

A systematic investigation of H-bonding

FeRuFe



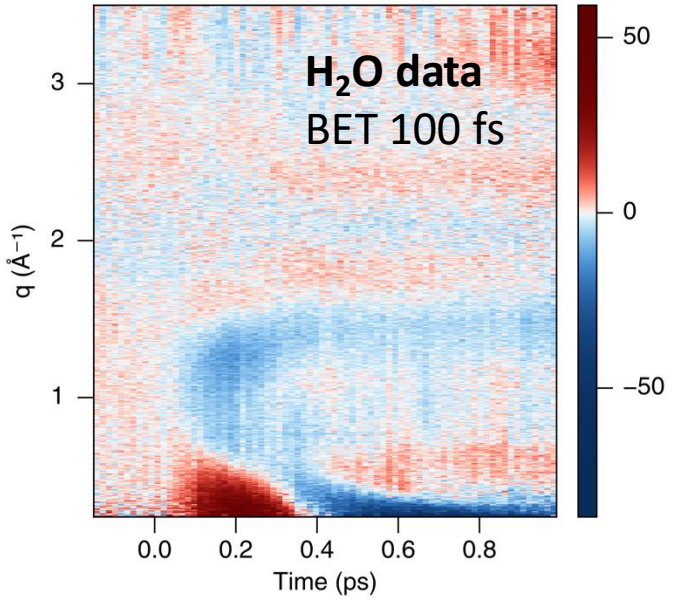
Ultrafast Fe Kβ measure BET time

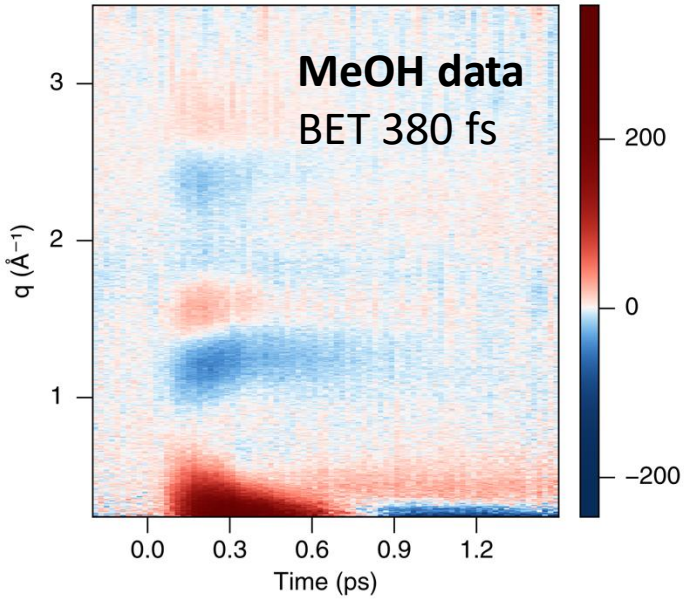


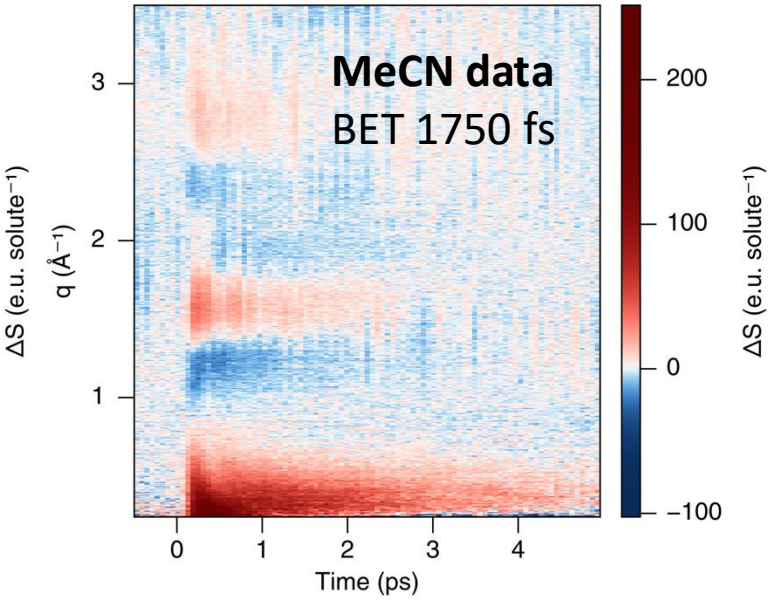
H2O = 100 +/- 40 fs
MeOH = 380 + 120 fs
MeCN = 1750 + 600 fa

Hydrogen bond ability

BET times

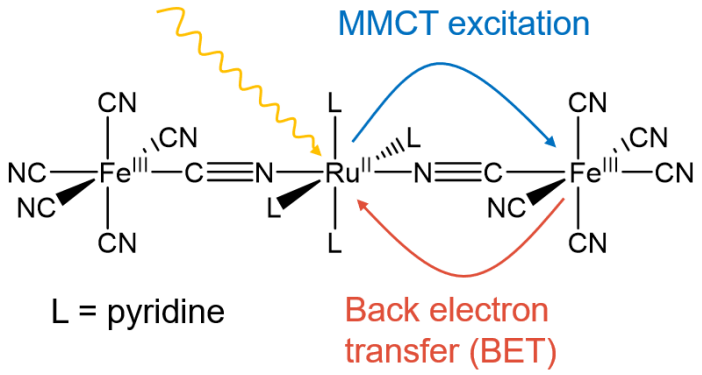






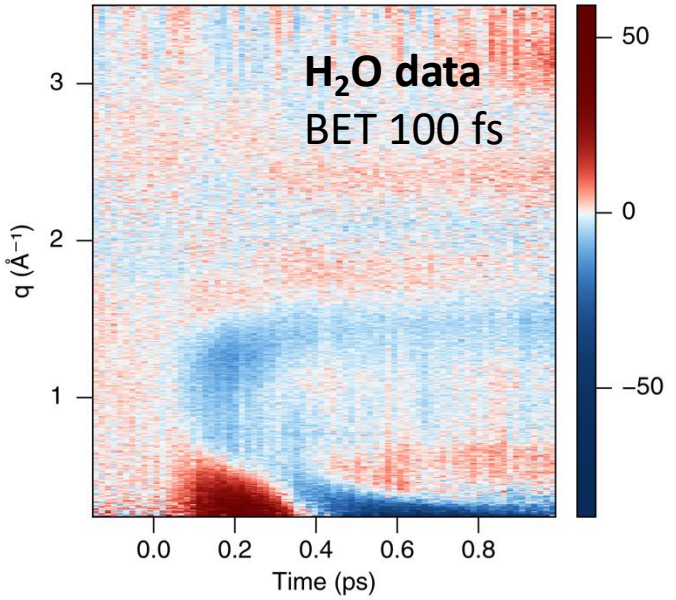
A systematic investigation of H-bonding

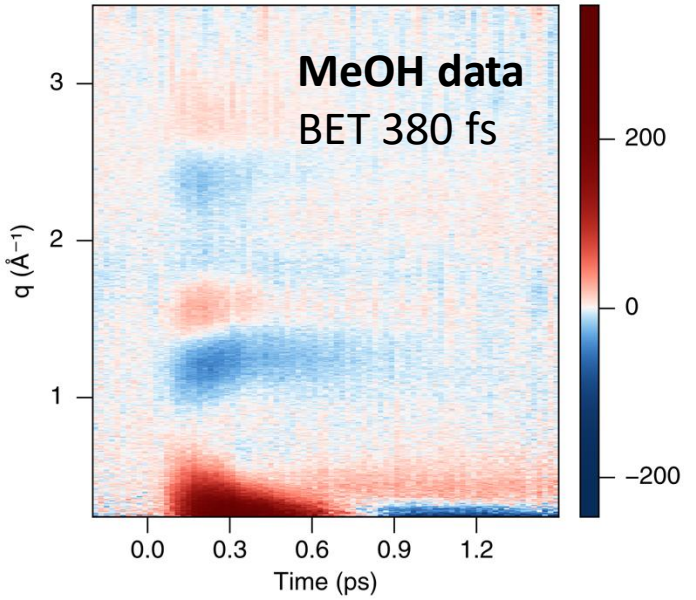
FeRuFe

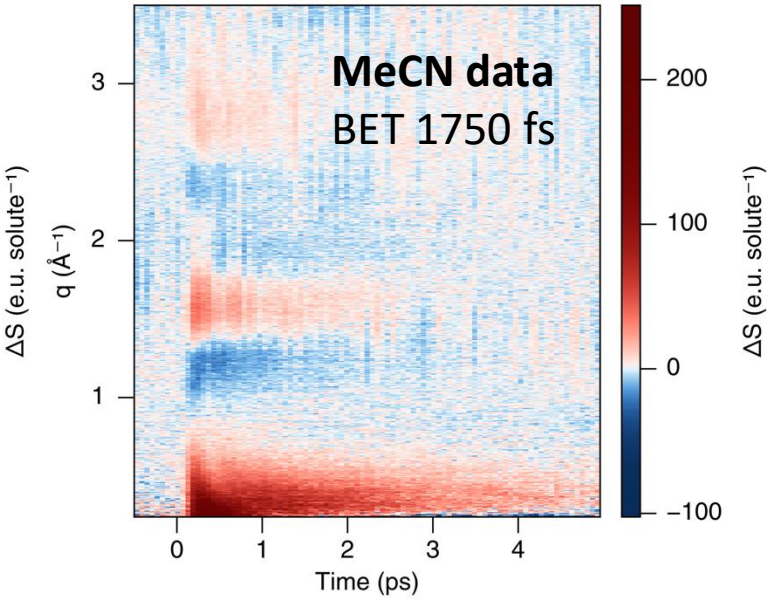


See talk by Micheal Sachs

SLAC User Meeting 2025
Condensed Phase Chemistry at LCLS-II-HE
(September Monday 22nd)







Conclusions

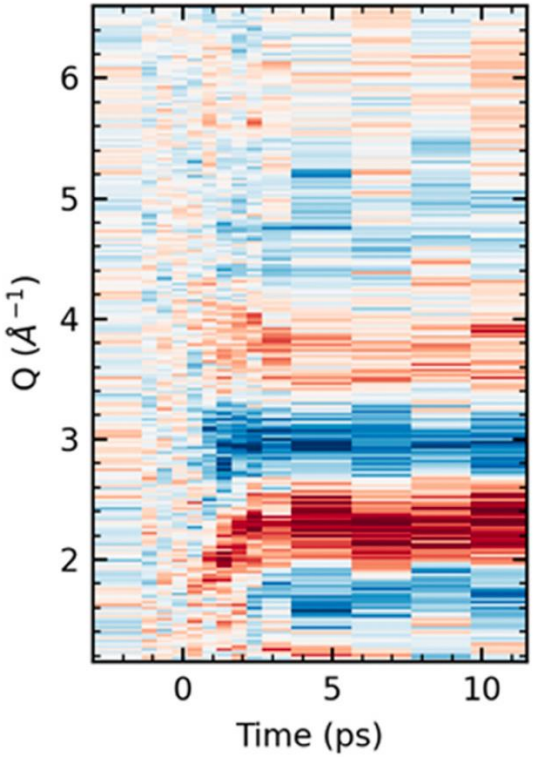
- Time-resolved X-ray Solution Scattering – in combination with X-ray Spectroscopy and Molecular Dynamics Simulations - have been used to visualize:
  - Coherent translational motions of first-solvation-shell molecules due to modulation of solute-solvent hydrogen bonding interactions upon electron transfer
  - Solvent reorganization coupled to excited state proton transfer (not shown in this version)

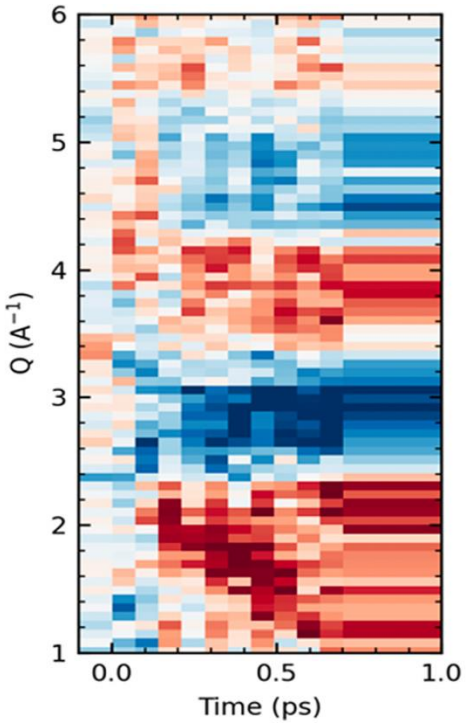
- This work will shed new necessary fundamental insight on designing microenvironment that control excited state reactivity and directly inform molecular design principles for artificial photosynthetic systems

- This work will help benchmark theoretical tools to model and reliably predict excited state structural and electronic dynamics with explicit inclusion of the solvent

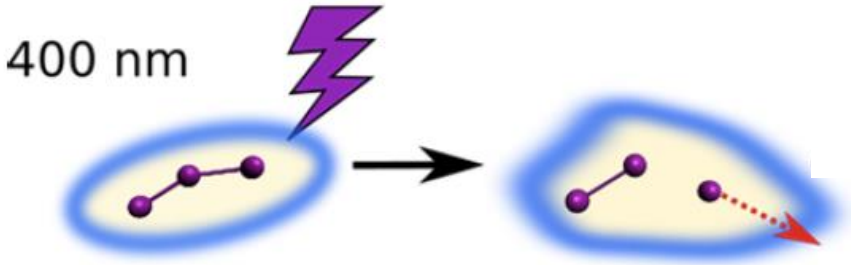
LUED to probe photochemical reactivity

750 fs	Time resolution (FWHM)	**180 fs**
High	Electron bunch charge mode	**Low**





130 mM / 100 nm jet
~150 mJ cm^{-2}



- Two body dissociation ($I_3^- \rightarrow I_2 + I^-$)
- T recombination = 0.6 ± 0.3 ps
- P escape = 0.26 ± 0.1
- Average dissociation speed 5.8 ± 0.3 Å/ps

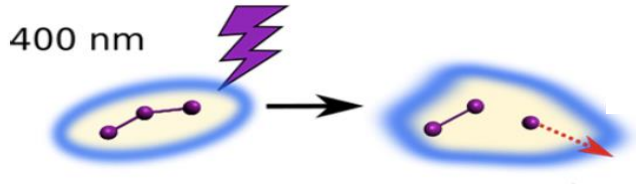
K. Ledbetter *et al.*, Struct. Dyn. 7, 064901 (2020)

LUED vs XSS: Selected Comparisons

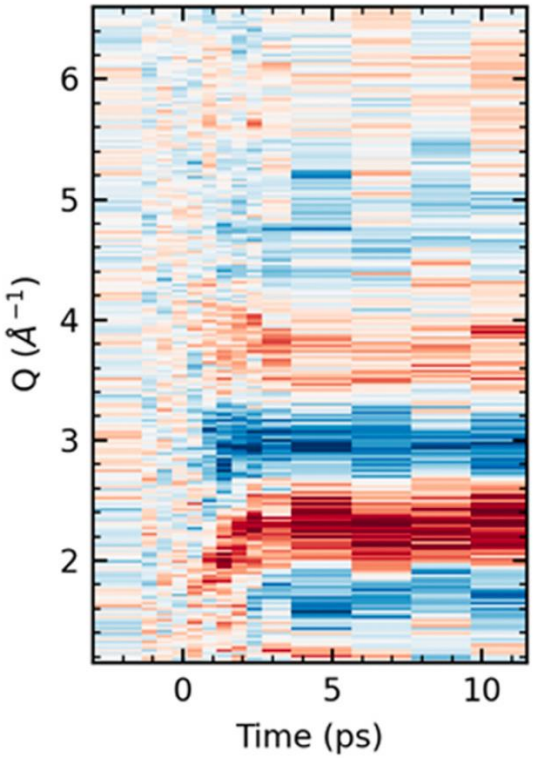
	LCLS I (120 Hz)	**SLAC MeV-UED (360 Hz)**
Form factor	Electron density	Electrostatic potential
Scattering power	1	10^9 (more sensitive to light elements wrt X-rays)
Sample environment	Ambient	Vacuum
Jet thickness	50 um	100 nm
Time-resolution	80 fs (FWHM)	< 200 fs (FWHM)
Relative signal-to-noise*	1	0.4

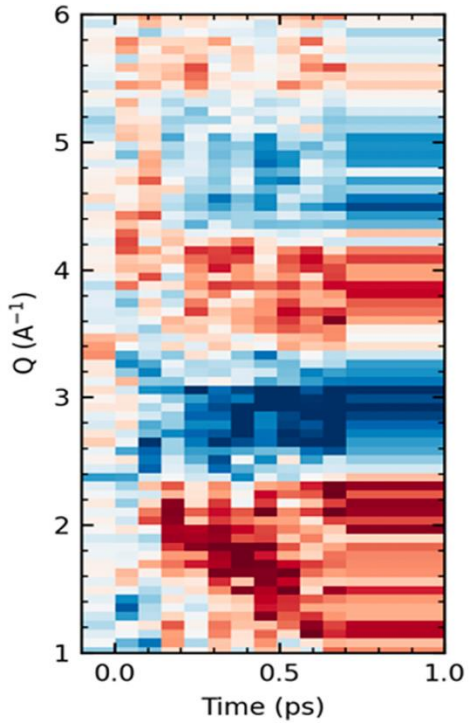
*Y. Lee, K. Y. Oang, D. Kim, H. Ihee, *Struct. Dyn. 11*, 031301 (2024)

LUED vs XSS: Selected Comparisons



SACLA (360 Hz) – 4 to 8 hours

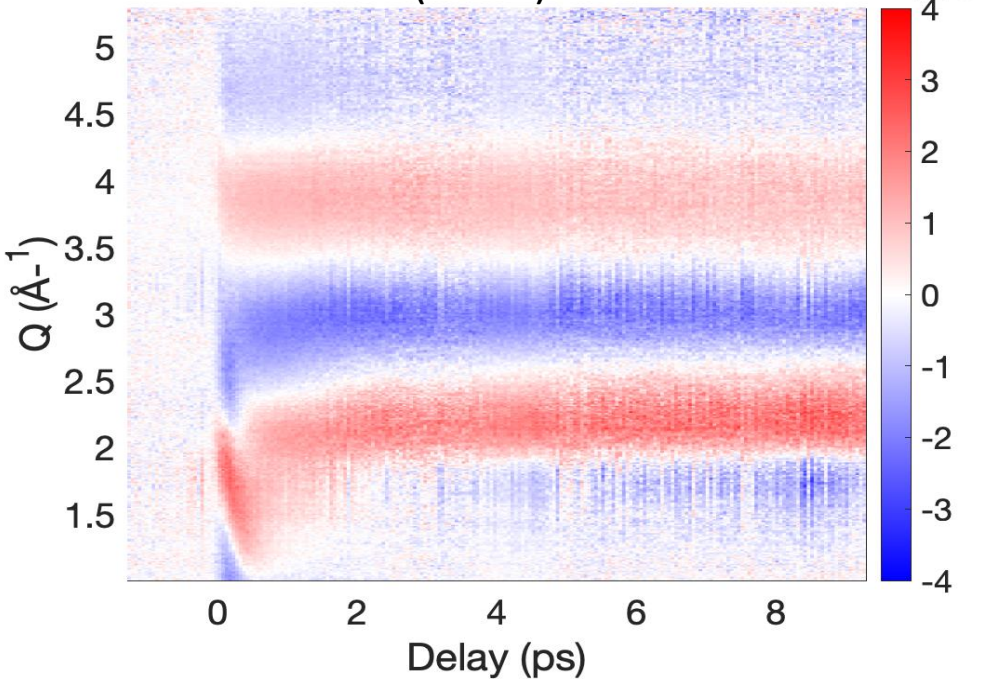




130 mM
~150 mJ/cm^2

K. Ledbetter *et al.*, *Struct. Dyn.* **7**, 064901 (2020)

SACLA (30 Hz) – 2 to 3 hours



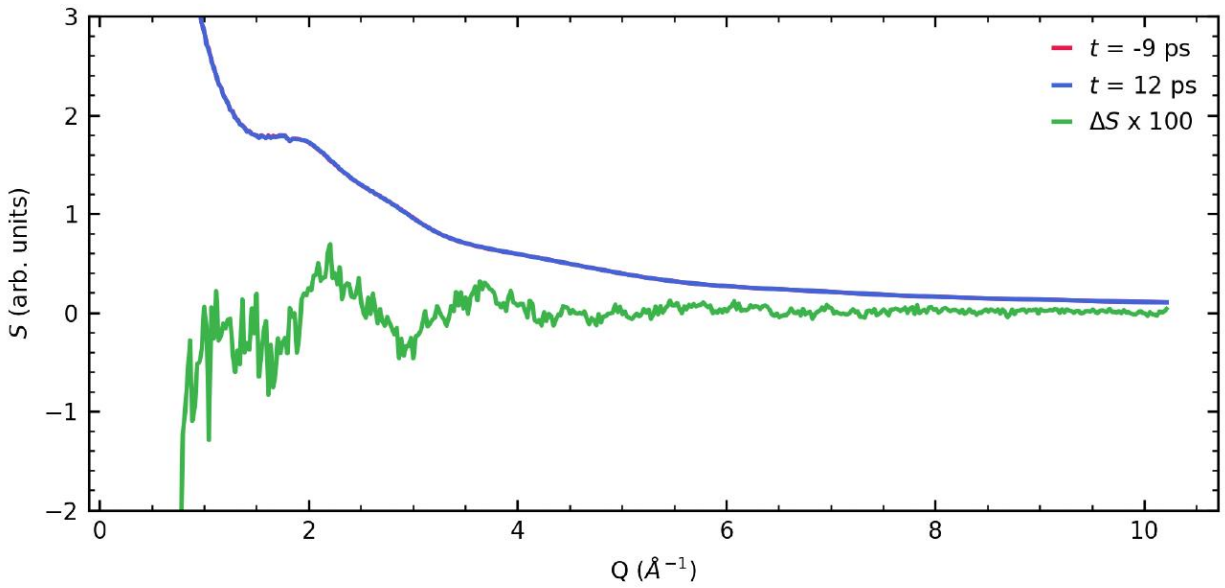
10 mM
230 mJ/cm^2

A. Nimmrich et al., *J. Am. Chem. Soc.* 2023, 145, 15754−15765

LUED vs XSS: Selected Comparisons

Maximum difference signal magnitude relative to the liquid peak

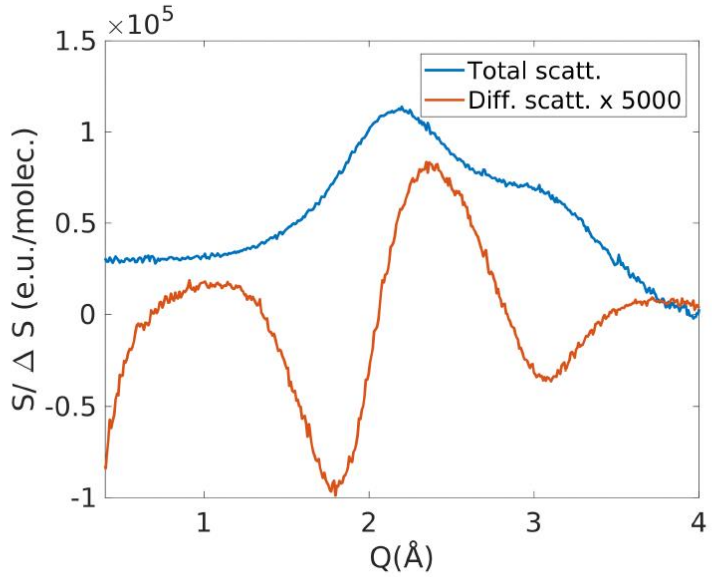
SLAC MEV UED = **0.4%**



I_3^- photodissociation

K. Ledbetter et al., *Struct. Dyn*. 7, 064901 (2020)

SLAC LCLS I = **0.02 %**



FeRu experiment

E. Biasin et al., *Nat. Chem.* **13**, 343–349 (2021)

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