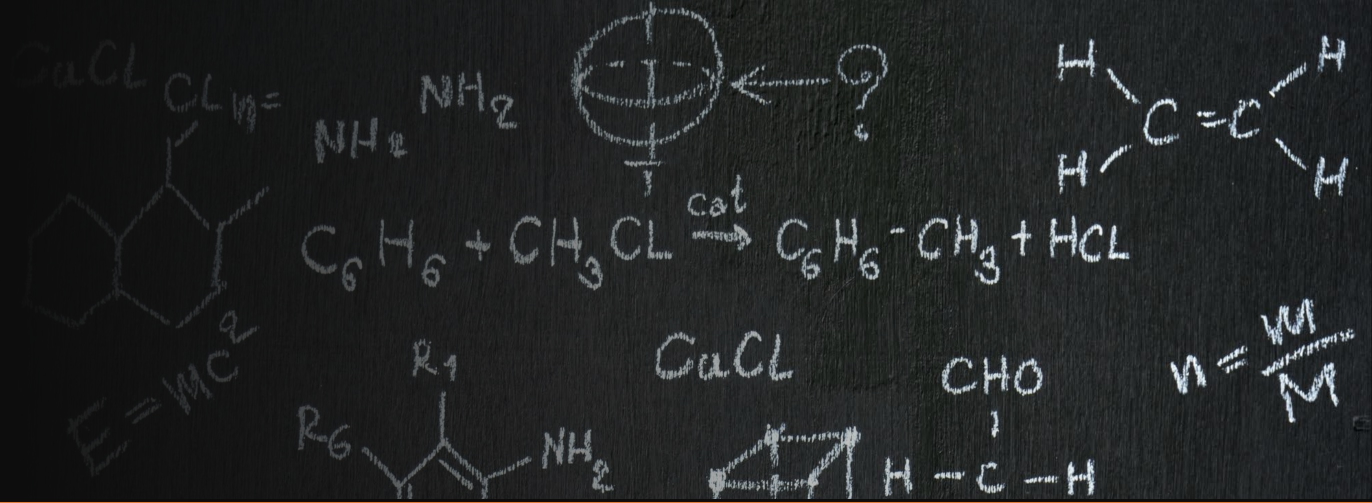
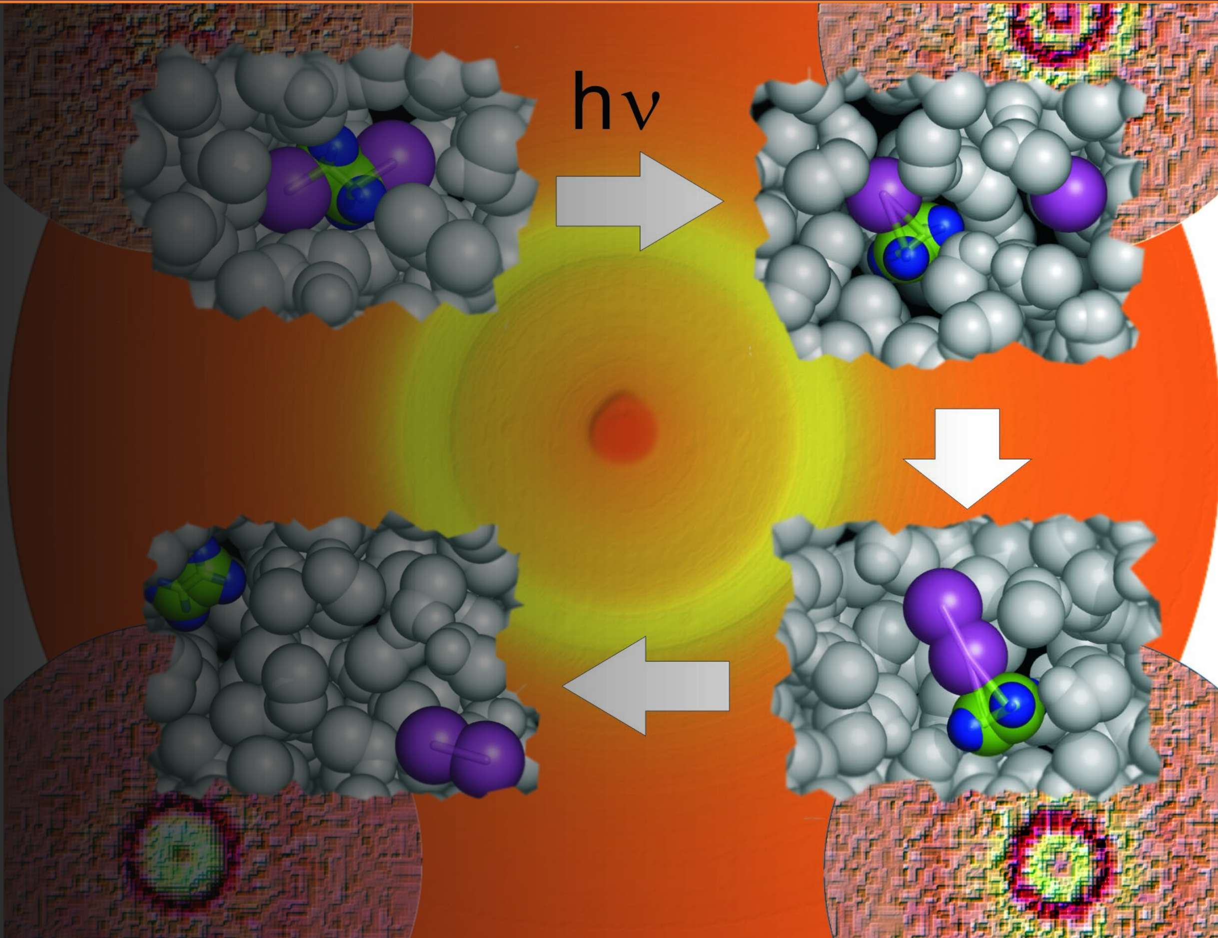


2023. 2. 9.

Jae Hyuk Lee

Reaction Dynamics Studied *via* femtosecond X-ray Liquidography at XFELs



Diffraction

Simple Object

Complex Object

Single

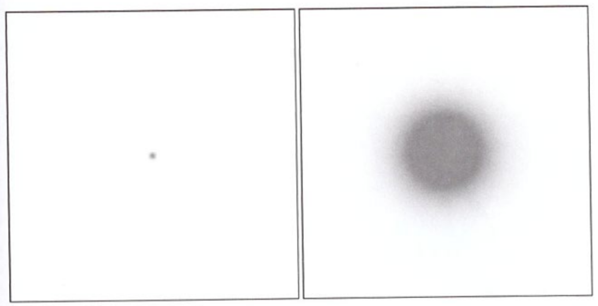


Figure 2.8 ▶ Sphere (cross-section, on left) and its diffraction pattern (right). Images for Figs. 2.8–2.11 were generously provided by Dr. Kevin Cowtan.

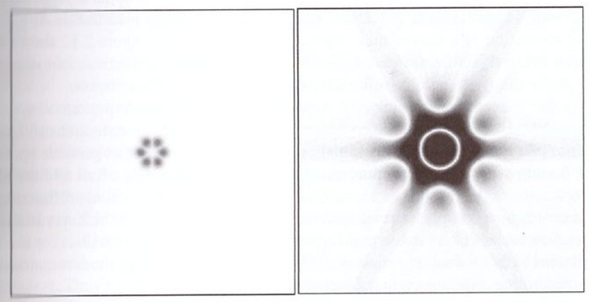


Figure 2.10 ▶ A planar hexagon of spheres (left) and its diffraction pattern (right).

Array

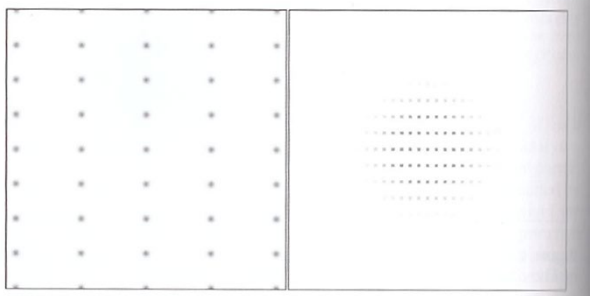


Figure 2.9 ▶ Lattice of spheres (left) and its diffraction pattern (right). If you look at the pattern and blur your eyes, you will see the diffraction pattern of a sphere. The pattern is that of the average sphere in the real lattice, but it is sampled at the reciprocal lattice points.

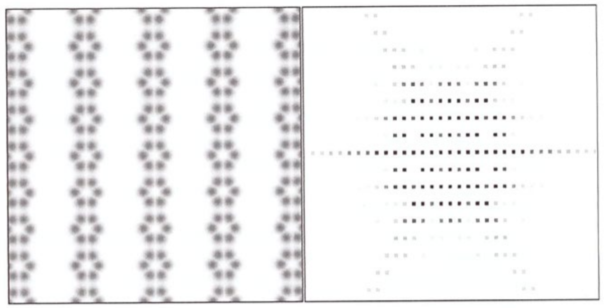


Figure 2.11 ▶ Lattice of hexagons (left) and its diffraction pattern (right). If you look at the pattern and blur your eyes, you will see the diffraction pattern of a hexagon. The pattern is that of the average hexagon in the real lattice, but it is sampled at the reciprocal lattice points.

From "crystallography made crystal clear", Elsevier

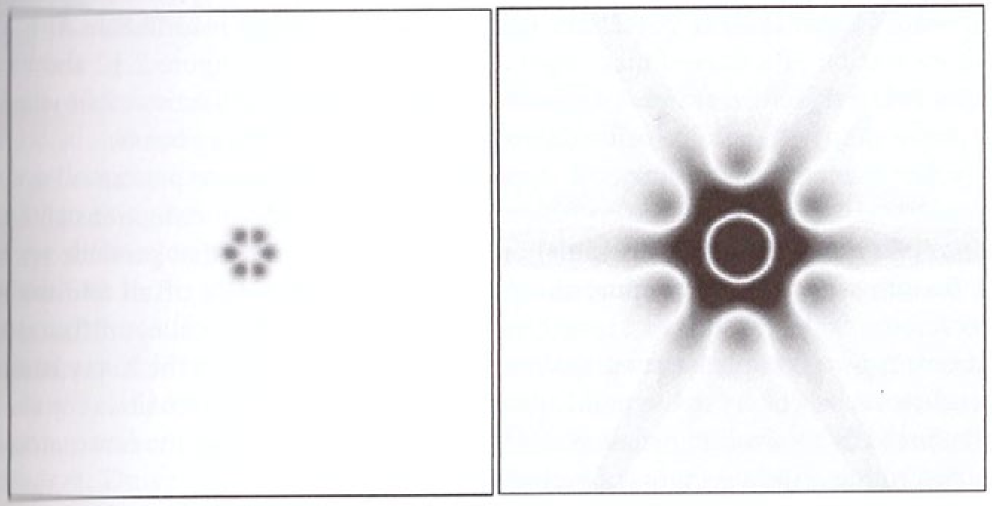


Figure 2.10 ▶ A planar hexagon of spheres (left) and its diffraction pattern (right).

$$\rho(\boldsymbol{x}) = \int A(\boldsymbol{q}) \mathrm{e}^{i\mathbf{q}\cdot\boldsymbol{x}}\, \mathrm{d}v_{\boldsymbol{q}}$$

$$A(\boldsymbol{q}) = \int \rho(\boldsymbol{x}) \mathrm{e}^{-i\boldsymbol{q}\cdot\boldsymbol{x}}\, \mathrm{d}v_{\boldsymbol{x}}$$

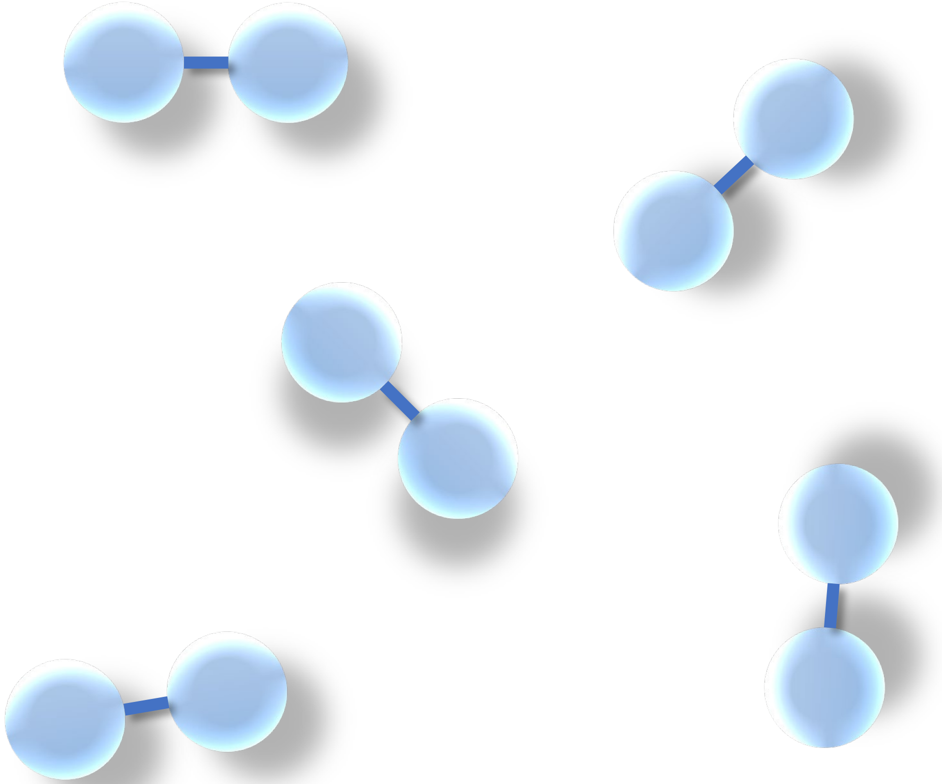
$$A(\boldsymbol{q}) = \sum_{1}^{N} f_n \mathrm{e}^{-i\mathbf{q}\cdot\boldsymbol{x}_n}$$

$$S(\boldsymbol{q}) = |A(\boldsymbol{q})|^2 = \sum_1^N {f_n}^2 + \sum_{n\neq n'} \sum f_n f_{\mathrm{n}'} \cos(\boldsymbol{q}\cdot\boldsymbol{x}_{nn'})$$

$$S(\boldsymbol{q}) = |A(\boldsymbol{q})|^2 = \iint \rho(\boldsymbol{u})\rho(\boldsymbol{u}+\boldsymbol{x})\mathrm{e}^{-i\boldsymbol{q}\cdot\boldsymbol{x}}\, \mathrm{d}v_{\boldsymbol{x}}\, \mathrm{d}v_{\boldsymbol{u}} = \int \mathrm{P}(\boldsymbol{x})\mathrm{e}^{-i\boldsymbol{q}\cdot\boldsymbol{x}}\, \mathrm{d}v_{\boldsymbol{x}}$$

where $\mathrm{P}(\boldsymbol{x}) = \int \rho(\boldsymbol{u})\rho(\boldsymbol{u}+\boldsymbol{x})\, \mathrm{d}v_{\boldsymbol{u}}$

Diffraction by randomly oriented object

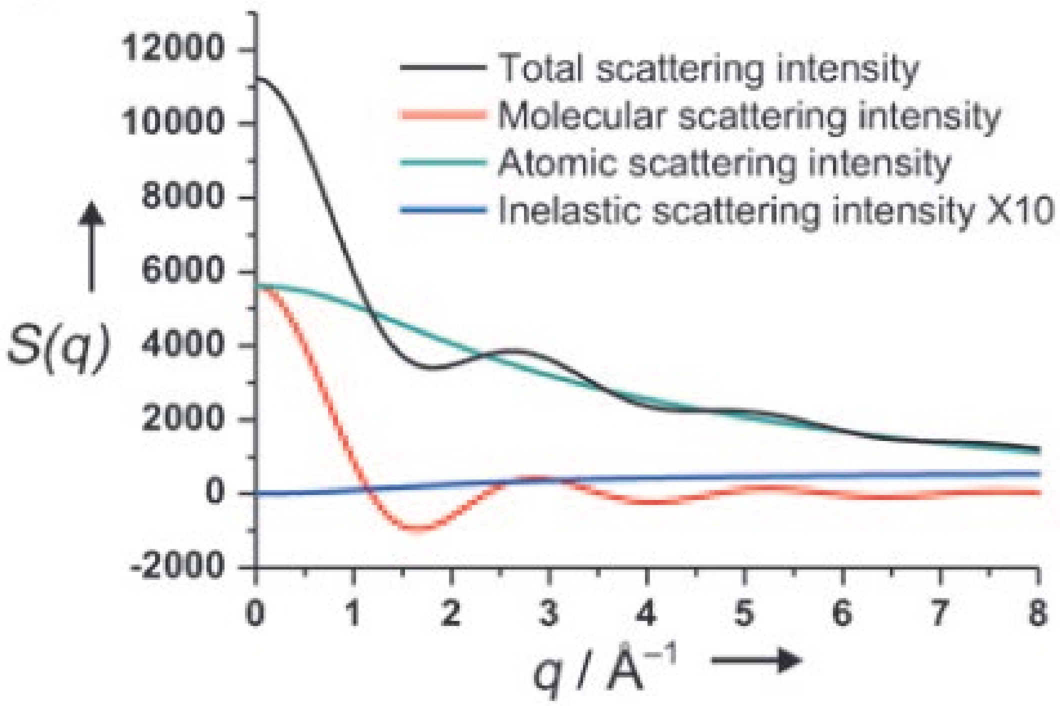


$$S^{elastic}(q) = \left\langle \sum_n \sum_m f_n(q) f_m(q) \exp(-i\mathbf{q} \cdot (\mathbf{r}_n - \mathbf{r}_m)) \right\rangle_\Omega$$

$$= \sum_n \sum_m f_n(q) f_m(q) (1/4\pi) \int_0^\pi \exp(-iqr_{nm} \cos\alpha) 2\pi \sin\alpha \, d\alpha$$

$$= \sum_n \sum_m f_n(q) f_m(q) \frac{\sin qr_{nm}}{qr_{nm}}$$

$$= \sum_n f_n^2(q) + \sum_n \sum_{m \neq n} f_n(q) f_m(q) \frac{\sin qr_{nm}}{qr_{nm}}$$

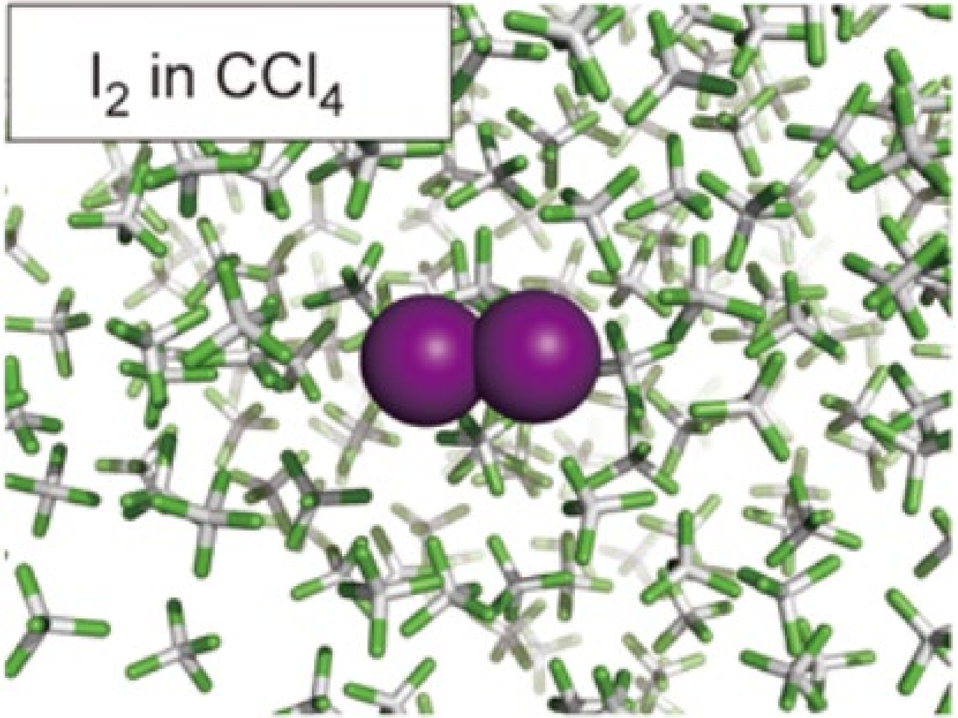


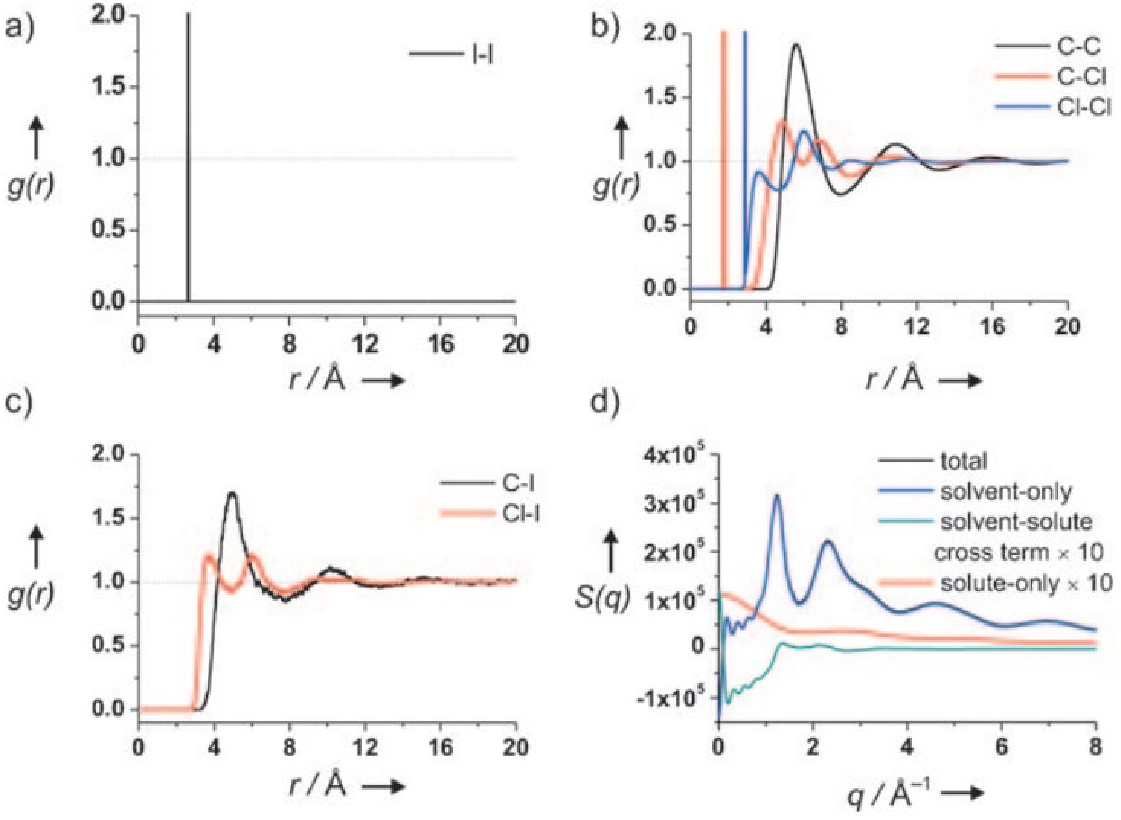
T.K. Kim, *et al.*, *ChemPhysChem* 2009, 10, 1958 – 1980

Diffraction by randomly oriented object

$$S(q) = \sum_i N_i f_i^2(q) + \sum_i \sum_{i \neq j} N_i N_j f_i(q) f_j(q) \int_v 4\pi r^2 \rho_0 (g_{ij}(r) - 1) \frac{\sin qr}{qr} dr$$

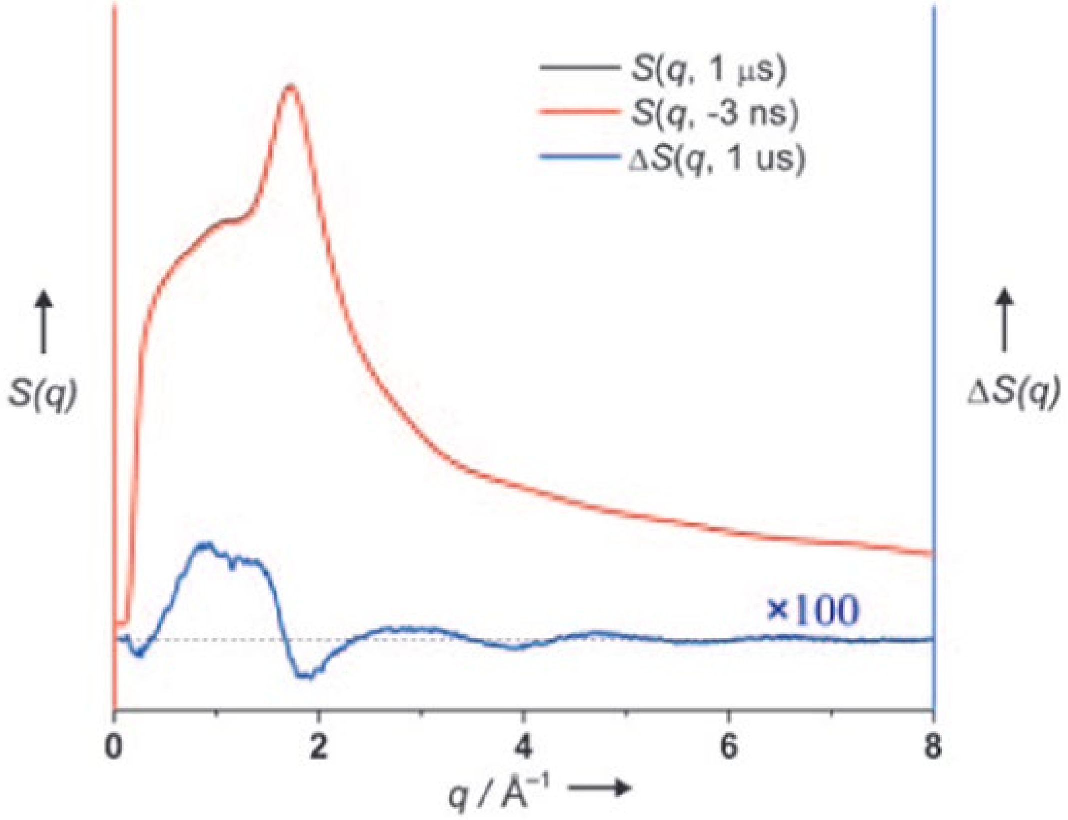
$$\Delta S(q,t) = S^{on}(q,t) - S^{off}(q) = \Delta S_{solute} + \Delta S_{cage} + \Delta S_{solvent} = \Delta S_{sol\text{-}rel} + \Delta S_{solvent}$$

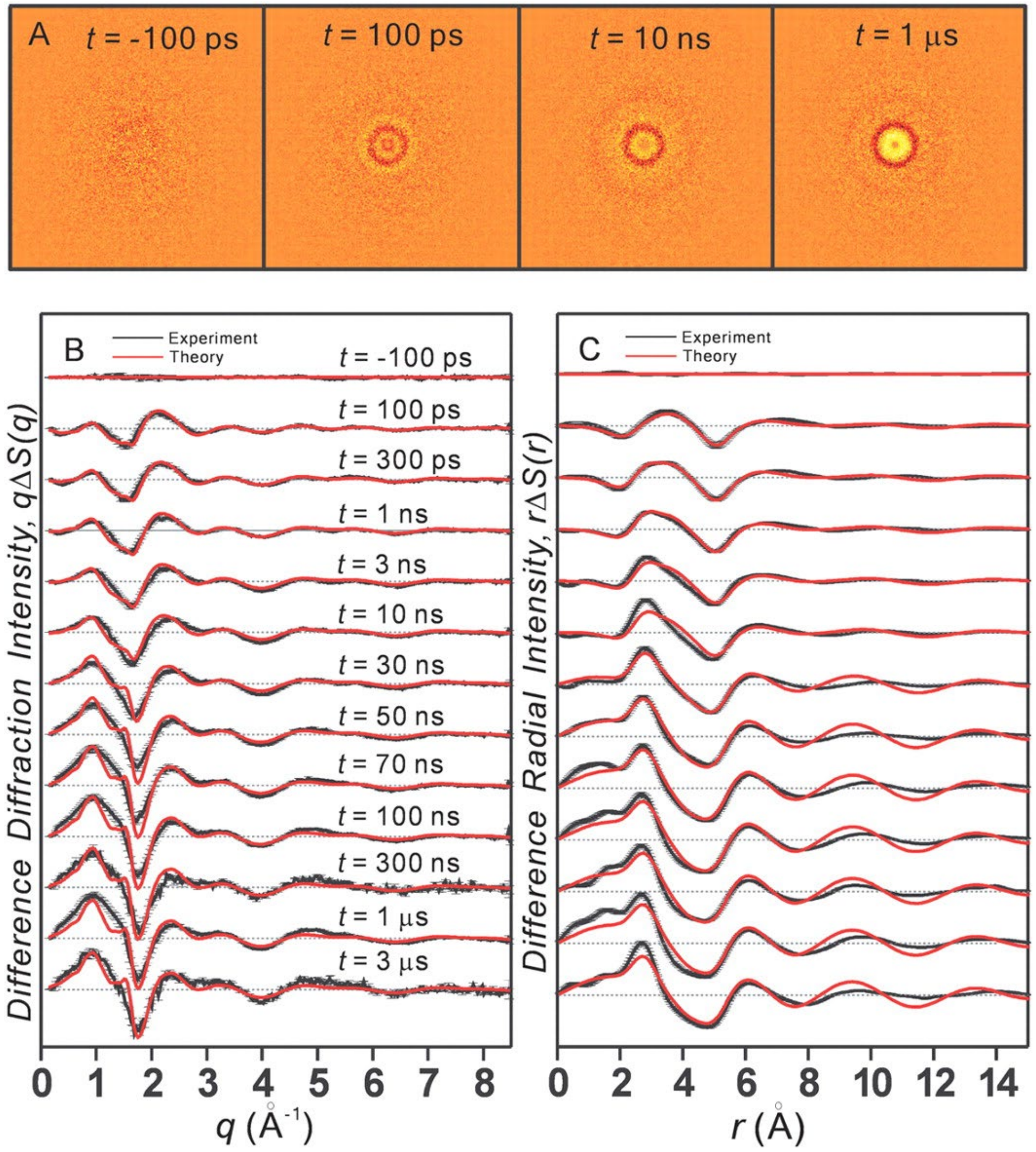




T.K. Kim, *et al.*, *ChemPhysChem* 2009, 10, 1958 – 1980

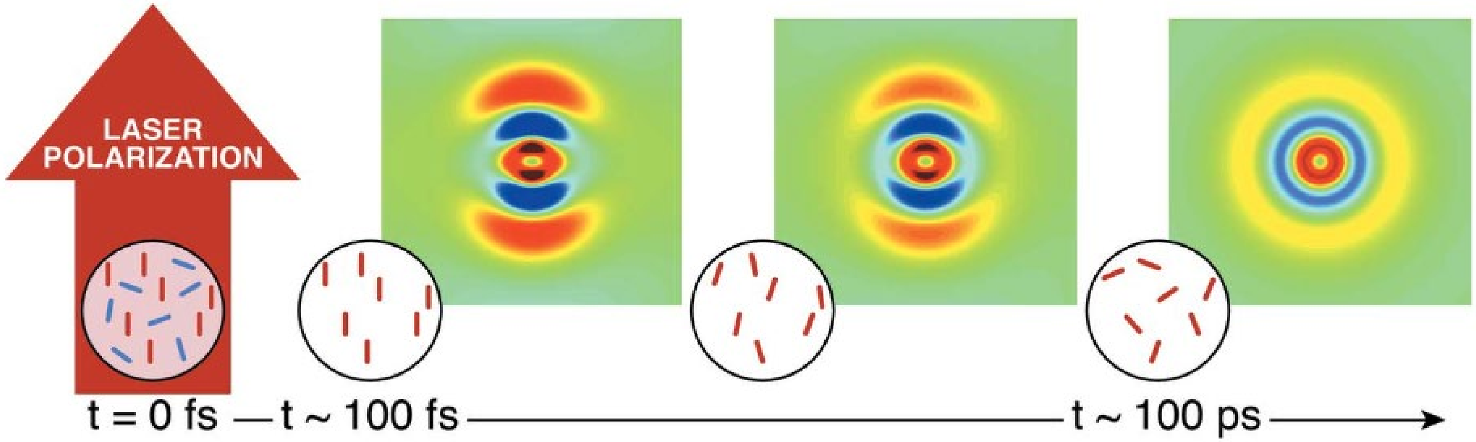
Static vs transient Scattering intensity from liquid





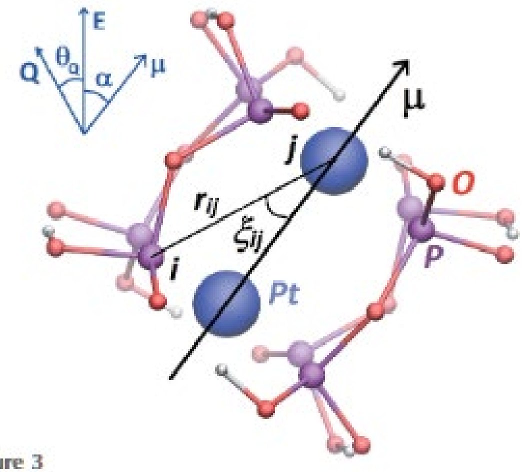
T.K. Kim, *et al.*, *ChemPhysChem* 2009, 10, 1958 – 1980
H. Ihee, *et al.*, *Science* 2005, 309, 1223-1227

Anisotropic scattering intensity



$$S_k(q,t) = 2(2\pi)^2 \sigma_T \sum_n P_n(\cos\theta_q) s_n(q,t)$$

$$s_n(q,t) = (-1)^{n/2} k_n(t) \sum_{i,j} f_i(q) f_j(q) P_n(\cos\theta_{ij}) j_n(q r_{ij})$$



ure 3

$$s_0(q,t) = \sum_{i,j} f_i(q) f_j(q) \frac{\sin(q r_{ij})}{q r_{ij}}$$

$$s_2(q,t) = -k_2(t) \sum_{i,j} f_i(q) f_j(q) P_2(\cos\theta_{ij}) j_2(q r_{ij})$$

$$\Delta S(Q,\theta_Q,t) \propto \Delta S_0(Q,t) + P_2(\cos\theta_Q)\Delta S_2(Q,t)$$

E. Biasin, *et al.*, *J. Synchrotron Radiation* 2018, 25, 306-315

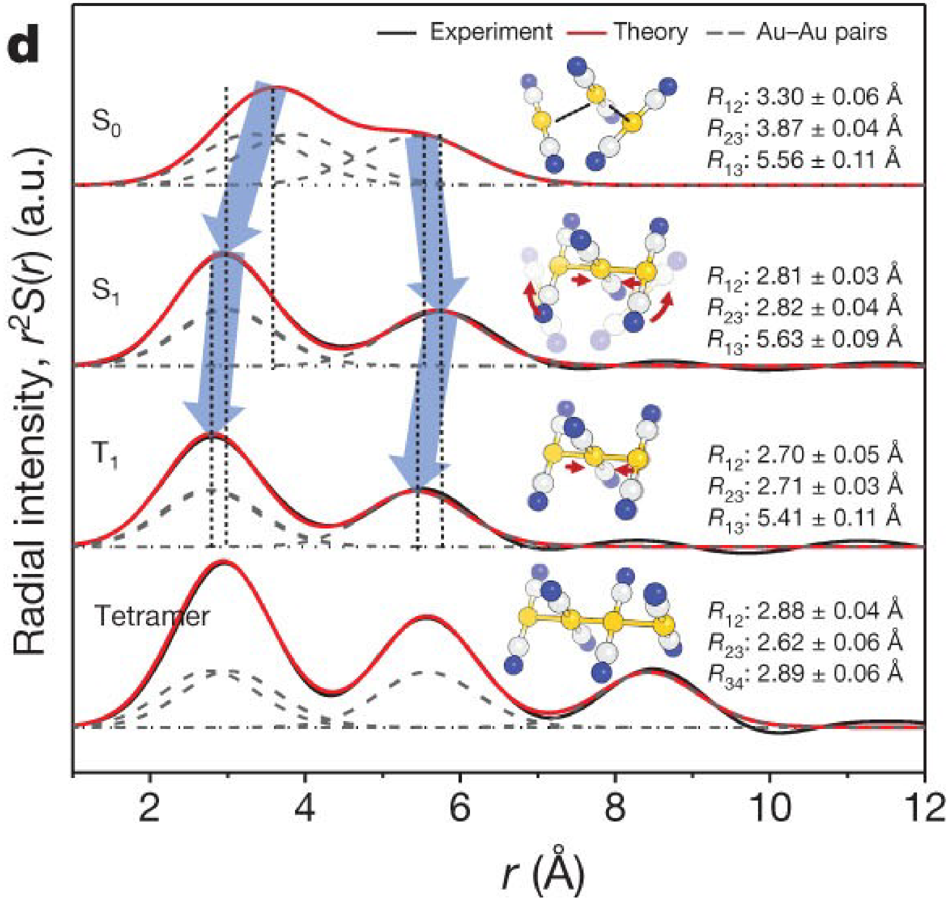
Reaction Dynamics via FXL at XFELS

- Bond cleavage/formation
- Charge distribution and electron transfer
- Orientational dynamics
- Solvation dynamics
- Coherent nuclear wavepacket dynamics
- Protein structural dynamics

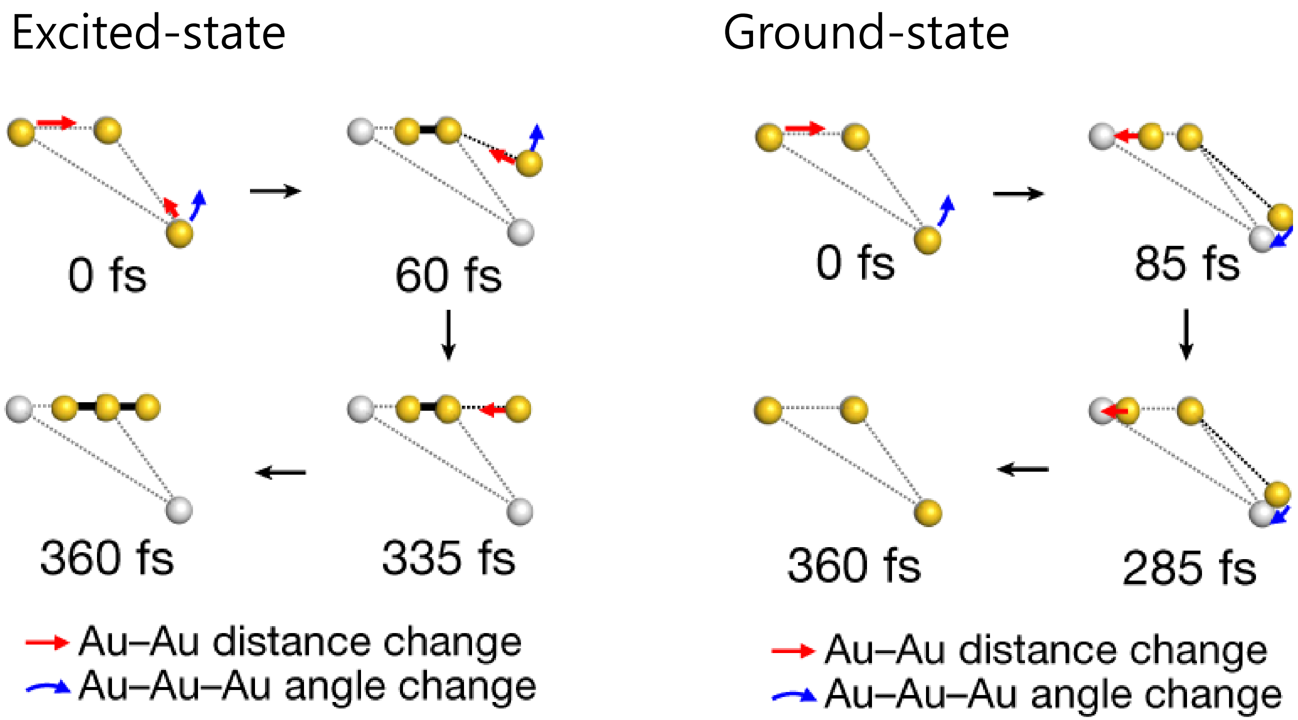
Bond cleavage/formation

- $[Au(CN)_2^-]_3$ in water

SACLA



PAL-XFEL



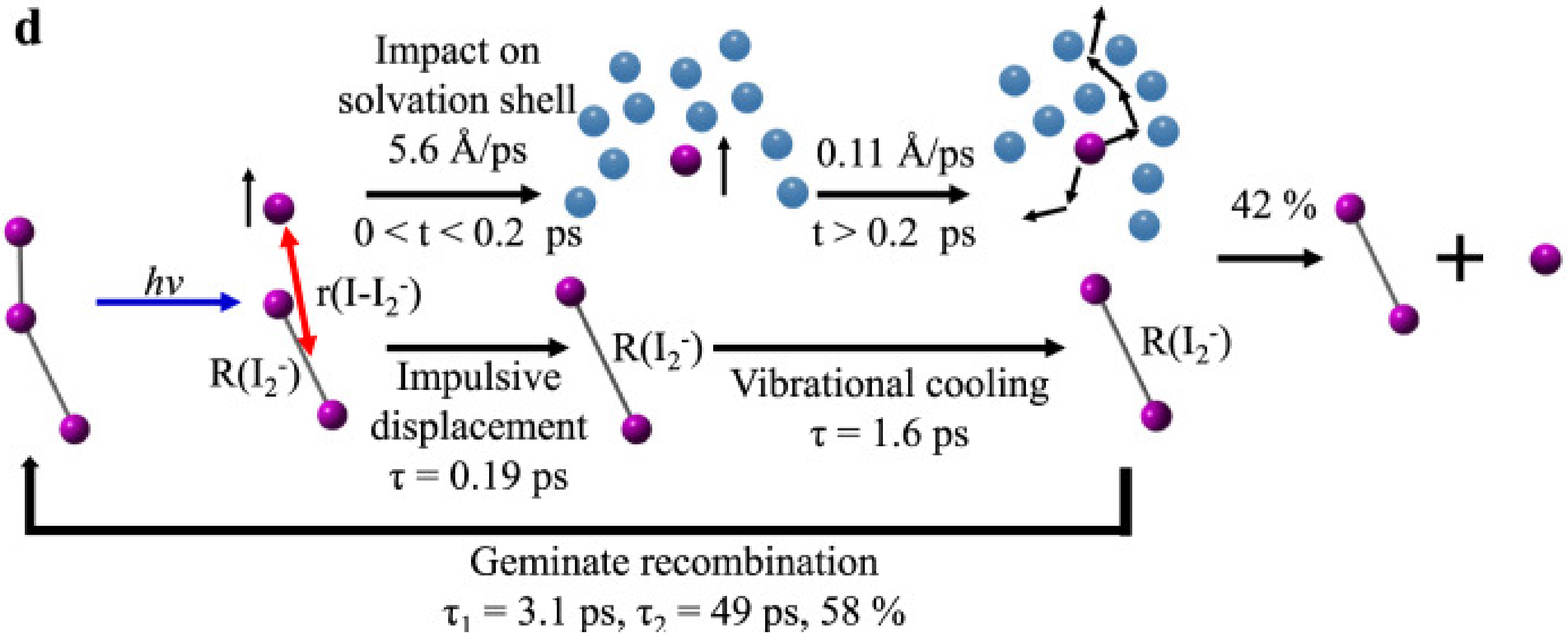
K. H. Kim, *et al.*, *Nature* 2015, 518, 385-389

J. G. Kim, *et al.*, *Nature* 2020, 582, 520-524

Bond cleavage/formation

- I_3^- in methanol
- Solvent dependent asymmetric bent structure

PAL-XFEL

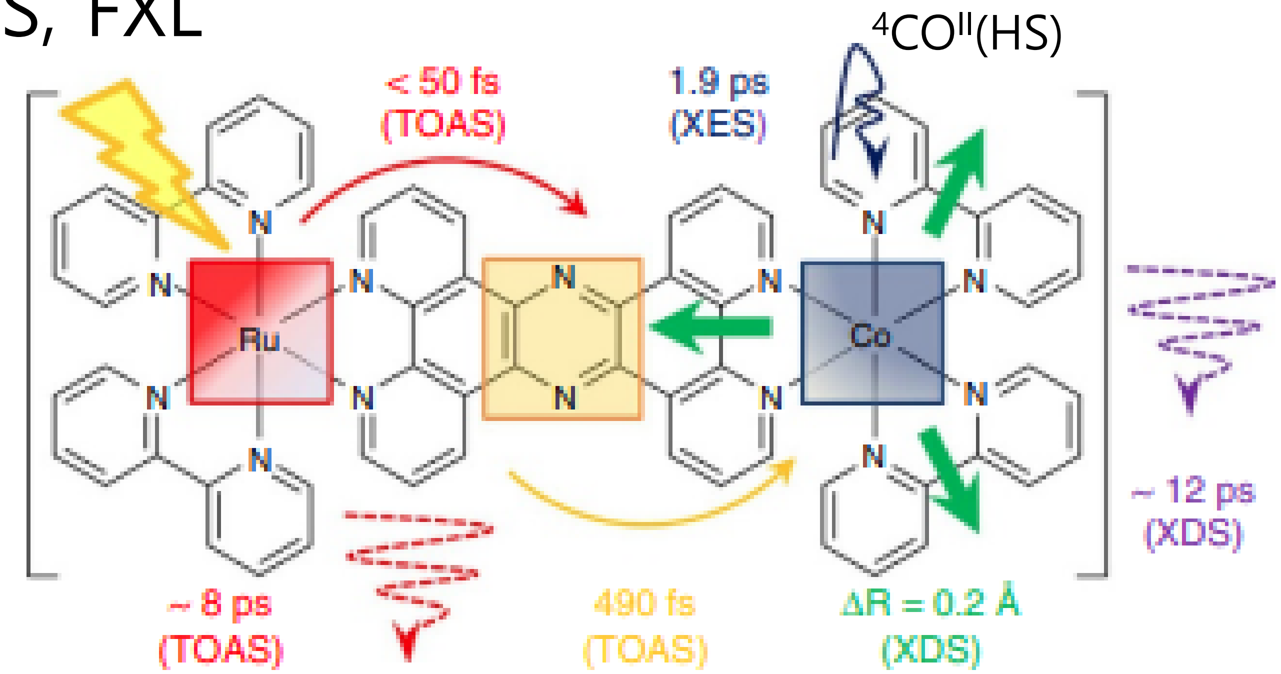


J. Heo, *et al.*, *Nature Communications* 2022, 13, 522

Charge distribution and electron transfer

- $[(bpy)_2{}^1Ru^{II}(tpphz){}^1CO^{III}(bpy)_2]^{5+}$ in acetonitrile
- TOAS, TR-XES, FXL

SACLA



Ru-Chromophore Co-electron acceptor, optically dark

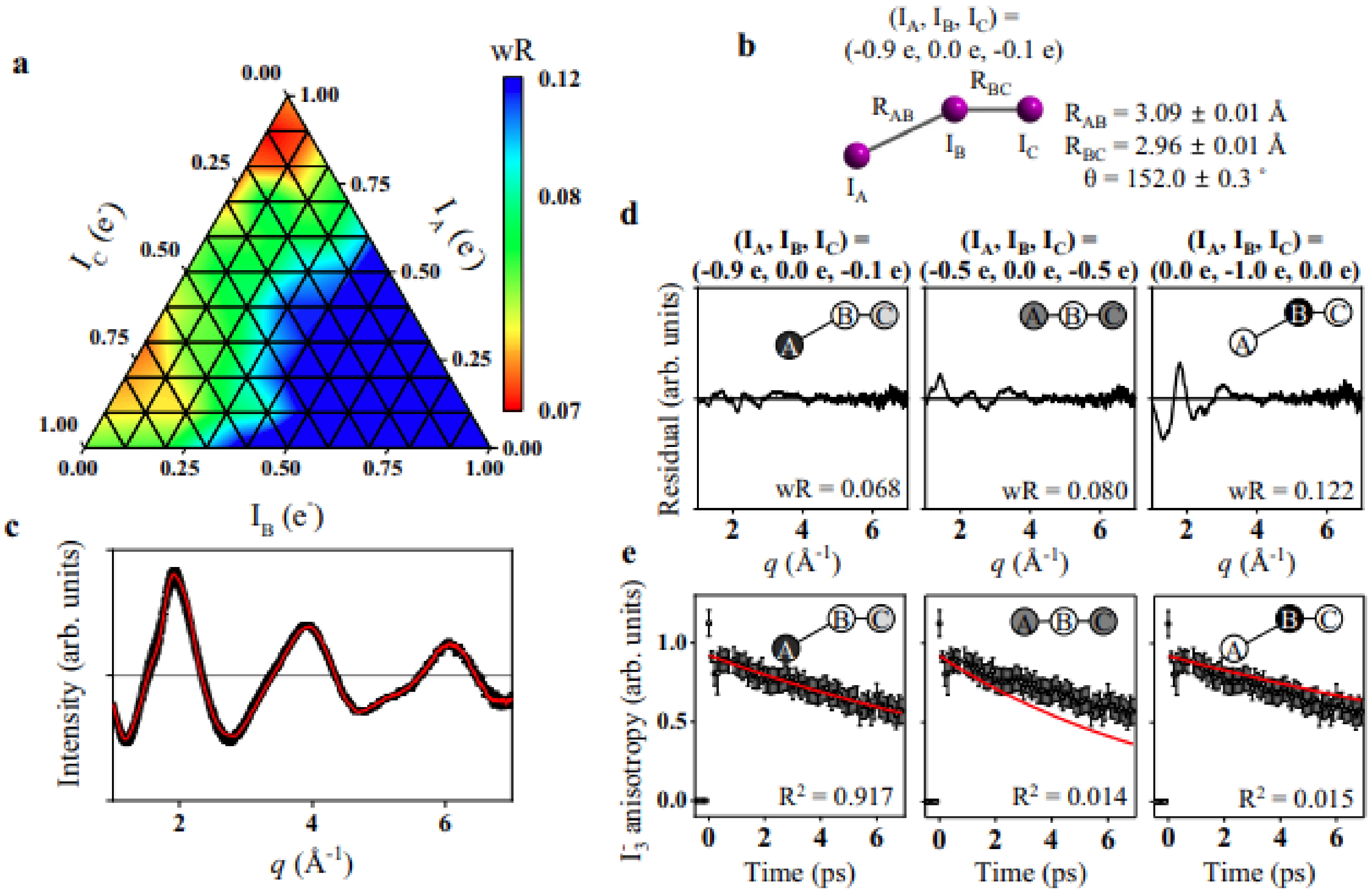
$[{}^1Ru^{II}={}^1Co^{III}(LS)]$ + hv (<50 fs) → $[{}^2Ru^{III}(=^{\cdot})Co^{III}(LS)]$ (490 fs by optical TA) → $[{}^2Ru^{III}={}^2Co^{II}(LS)]$ (1.9 ps by XES)
→$[{}^2Ru^{III}={}^4Co^{II}(HS)]$

S. E. Canton, *et al.*, *Nature Communications* 2015, 6, 6359

Charge distribution and electron transfer

- I_3^- in methanol

PAL-XFEL

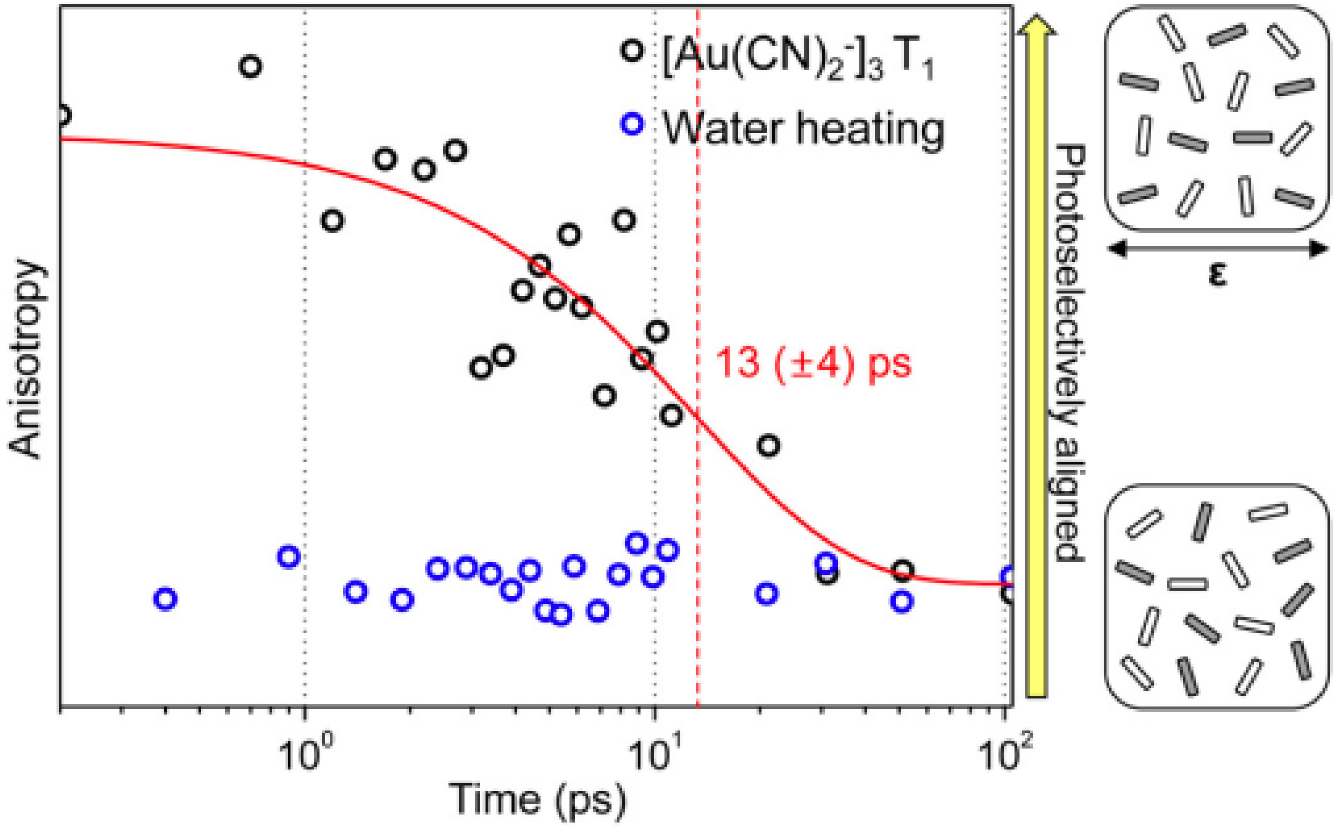


J. Heo, *et al.*, *Nature Communications* 2022, 13, 522

Orientational dynamics

- $[Au(CN)_2^-]_3$ in water vs heating dye in water
- Isotropic/anisotropic signal analysis

SACLA

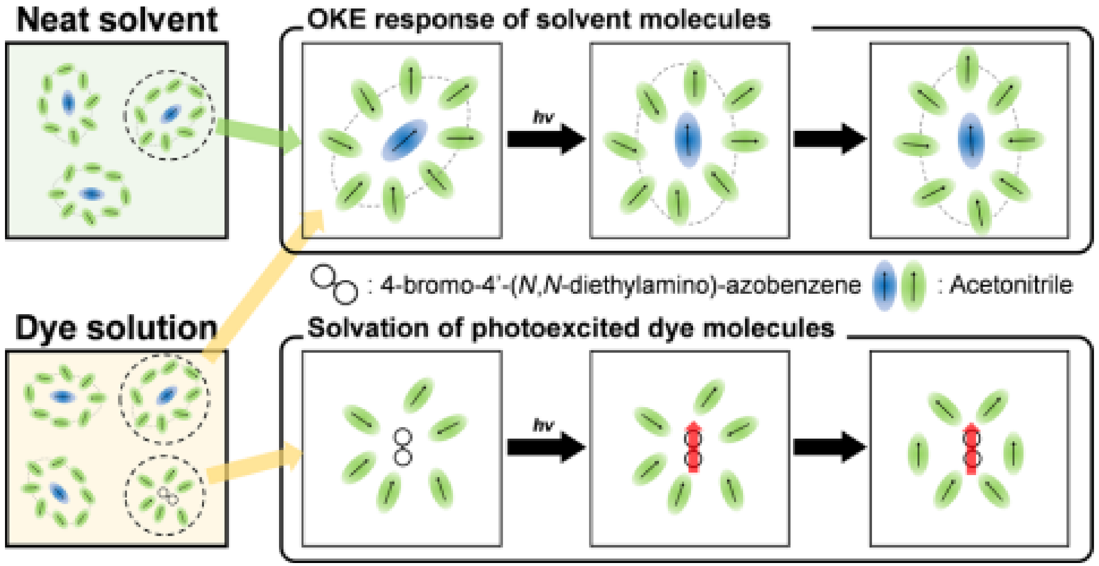


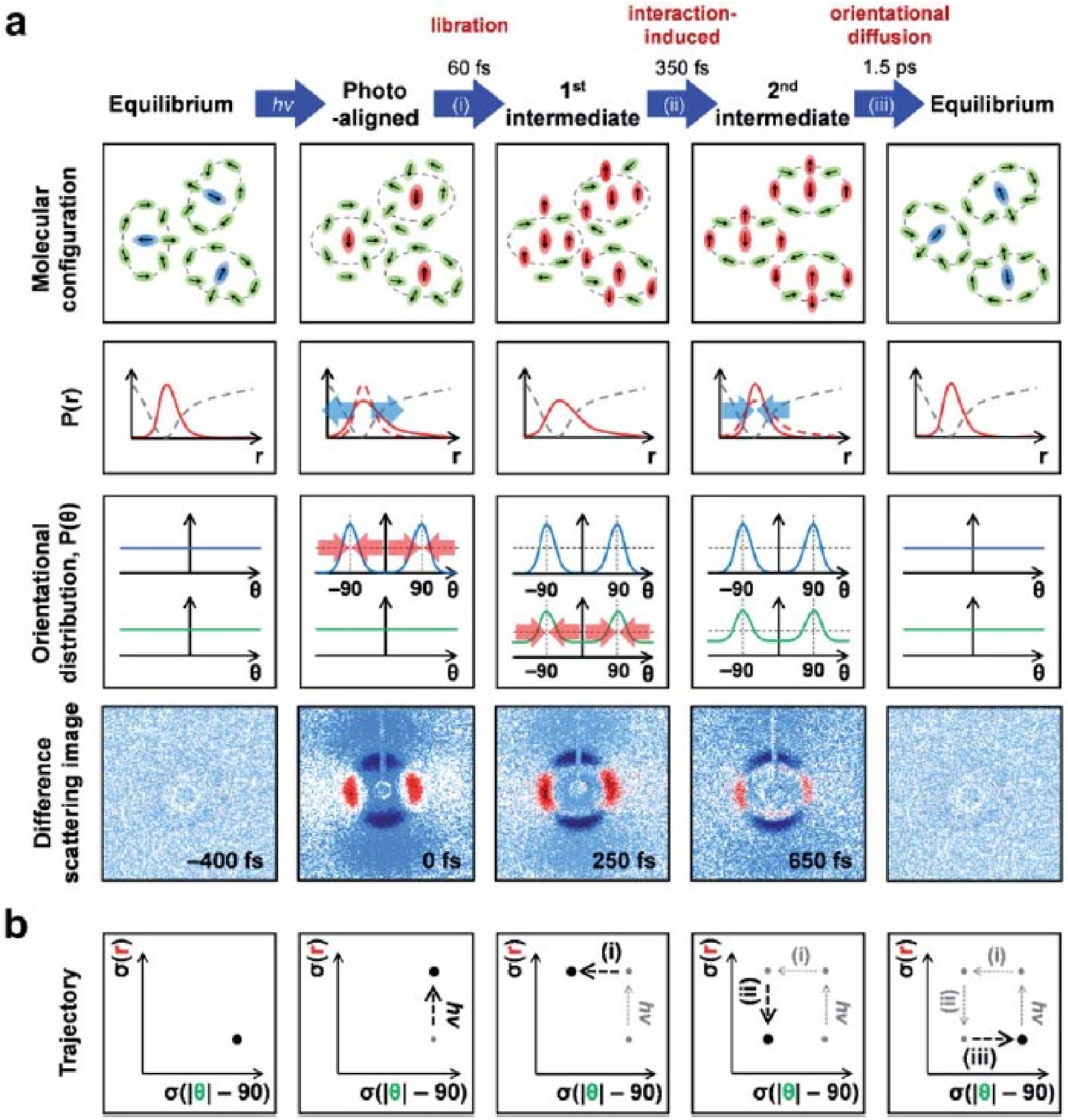
J. G. Kim, *et al.*, *J. Phys. B: At., Mol. Opt. Phys.*, 2015, 48, 244005

Orientational dynamics

- Optical Kerr effect

PAL-XFEL



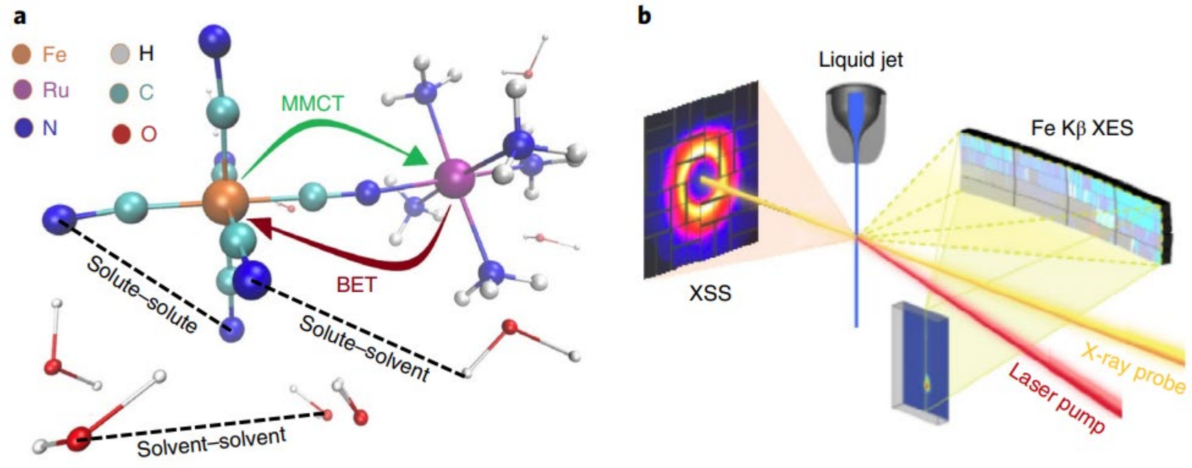


H. Ki, *et al.*, *J. Am. Chem. Soc.*, 2021, 143, 14261–14273

Solvation dynamics

- $[NCFe(CN)_5(NH_3)_5Ru]^-$ in water

LCLS



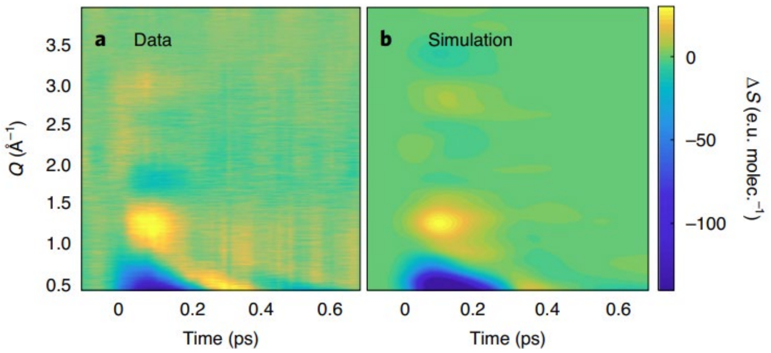
$Fe^{II}Ru^{III} \rightarrow Fe^{III}Ru^{II}$

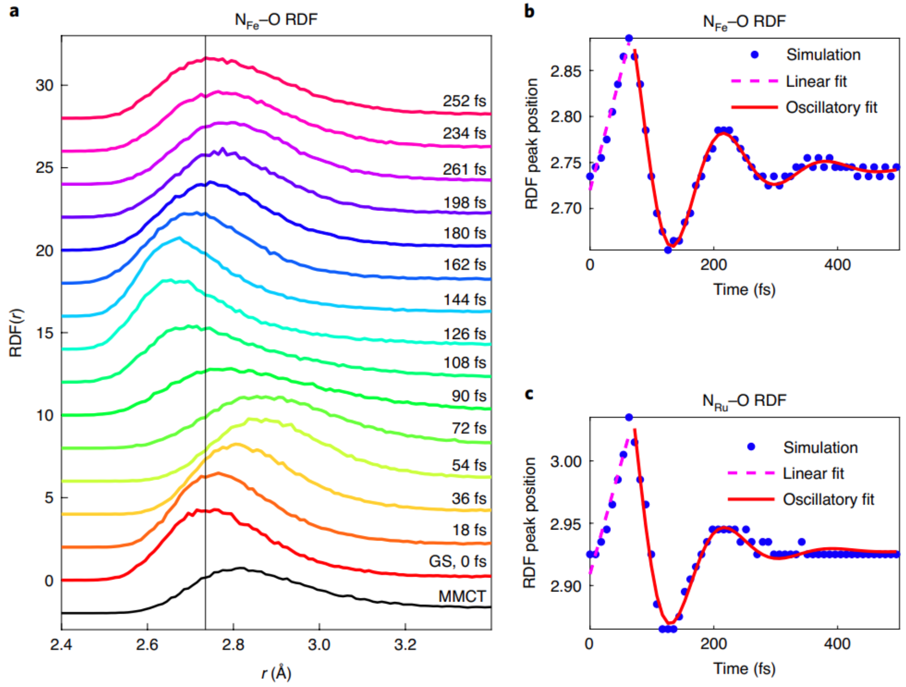
Fe Kβ XES ➔ Fe oxidation state/spin state

➔ MMCT lifetime **62 fs**

E. Biasin, *et al.*, *Nature Chemistry*, 2021, 1038

Non-equilibrium MD simulation





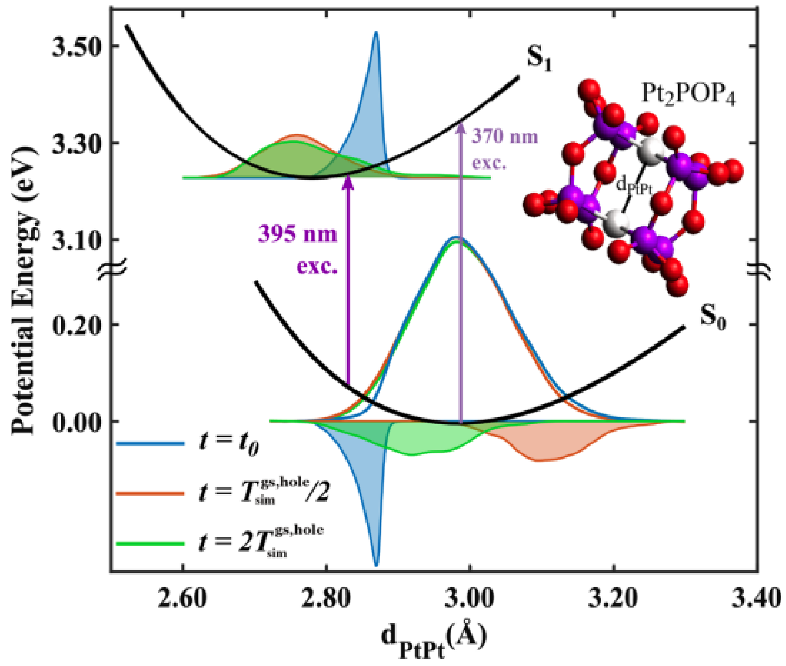
- 0.1 Å solvent shell expansion (2 Å/ps)
- Coherent (180 fs) translational motion

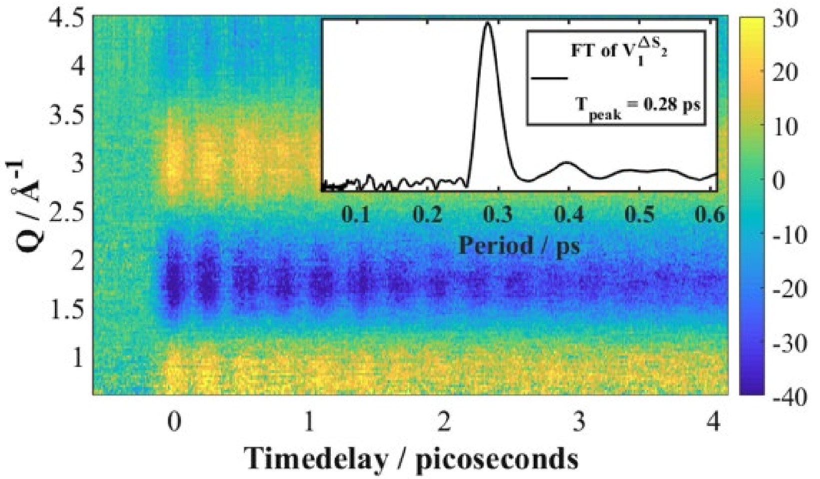
➔ MMCT weakened H-bond interaction (recovery upon BET)

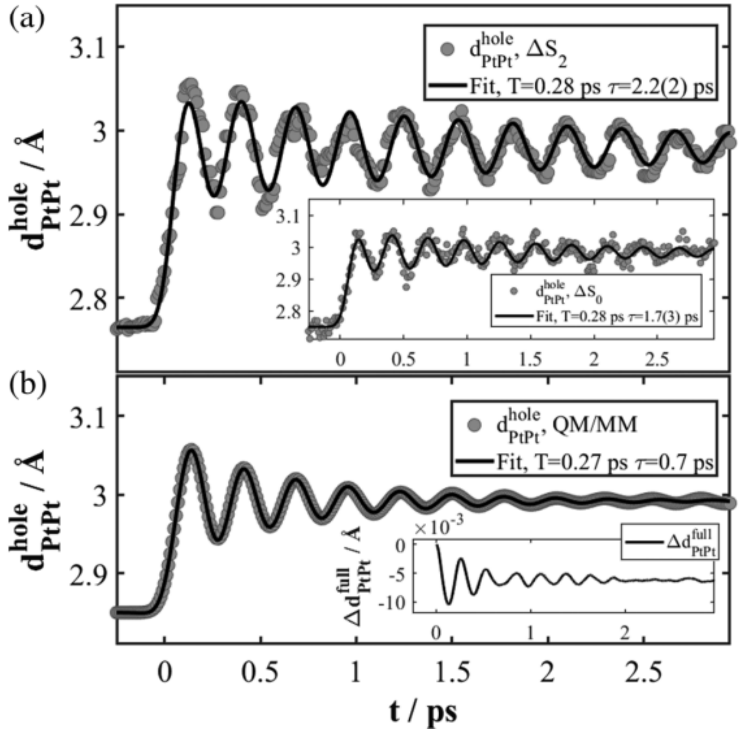
Coherent nuclear wavepacket dynamics

- $[Pt_2(P_2O_5H_2)_4]^{4-}$ in water

LCLS





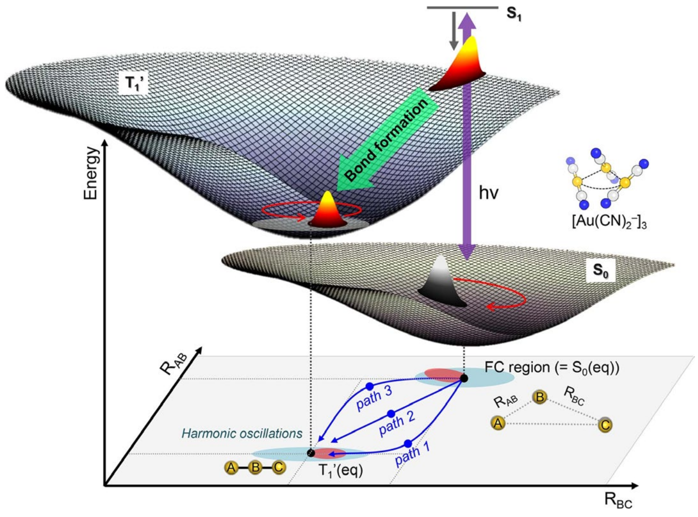


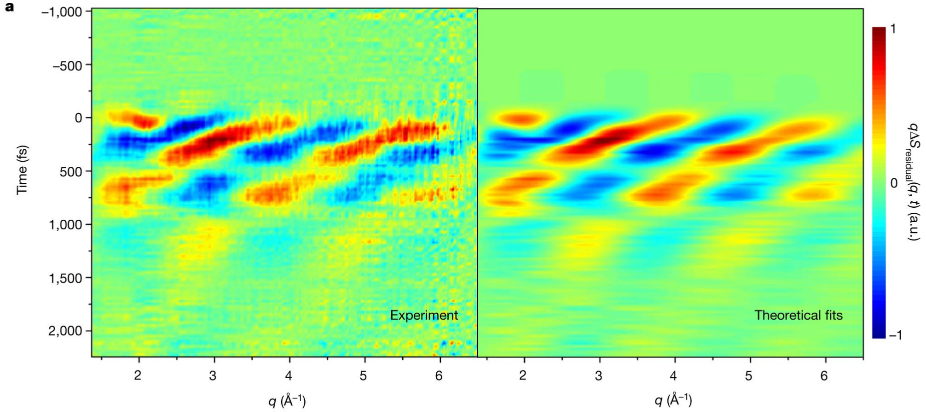
K. Haldrup, *et al.*, *PRL,* 2019, 122, 063001

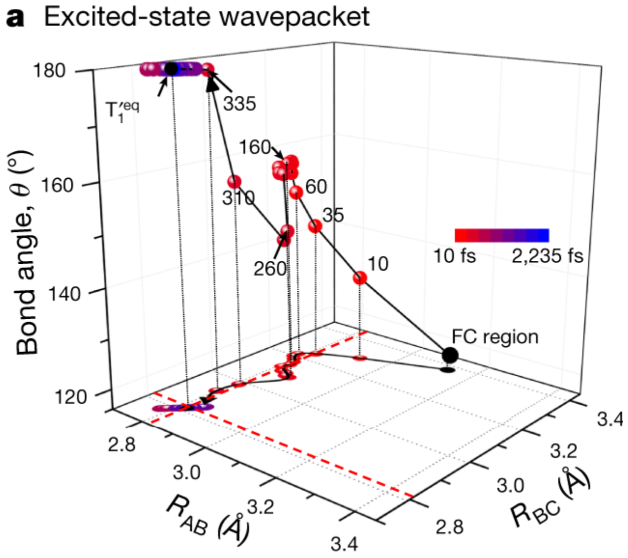
Coherent nuclear wavepacket dynamics

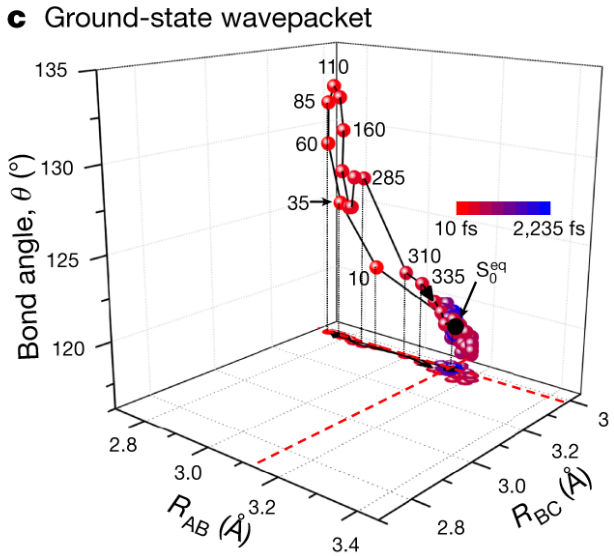
- $[Au(CN)_2^-]_3$ in water

PAL-XFEL







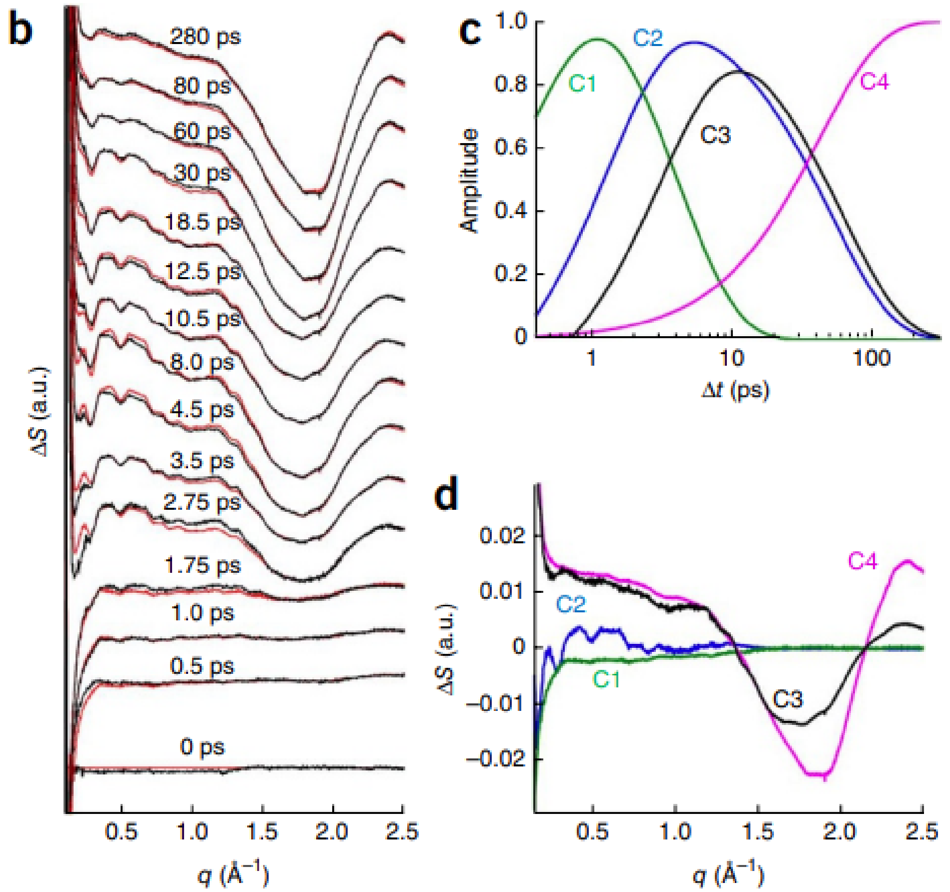


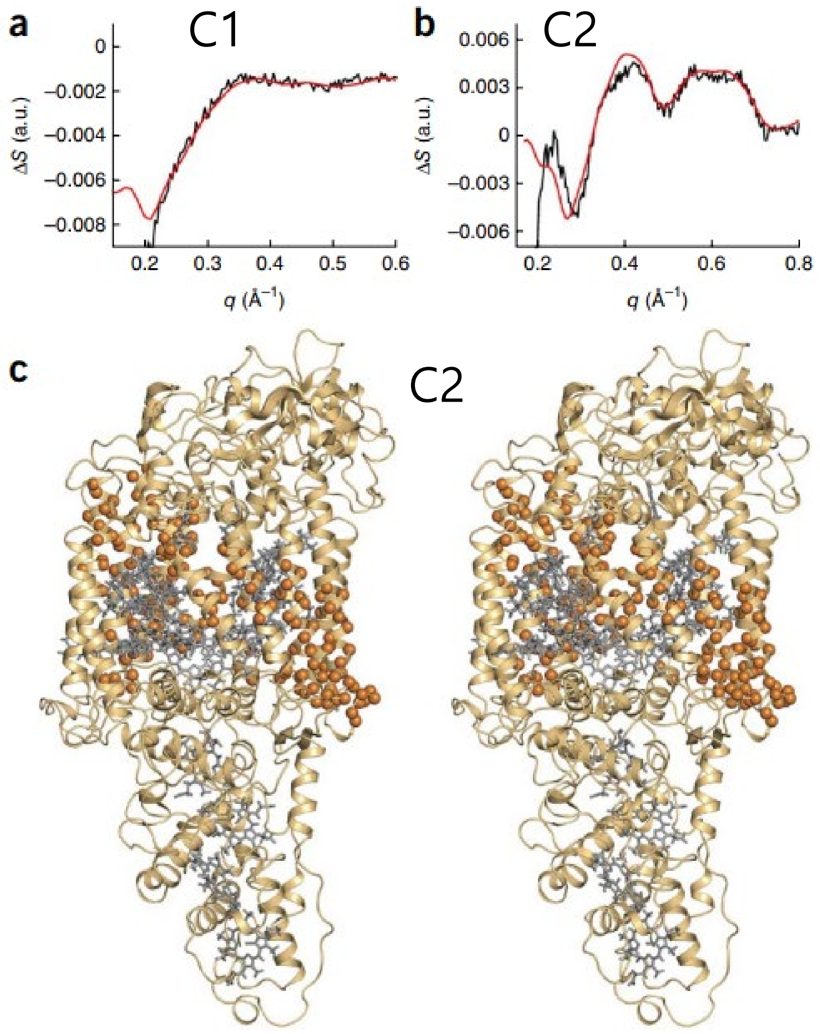
J. G. Kim, *et al.*, *Nature* 2020, 582, 520-524

Protein structural dynamics

- Photosynthetic reaction center

LCLS



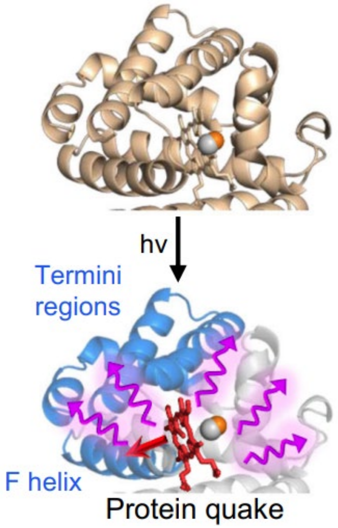


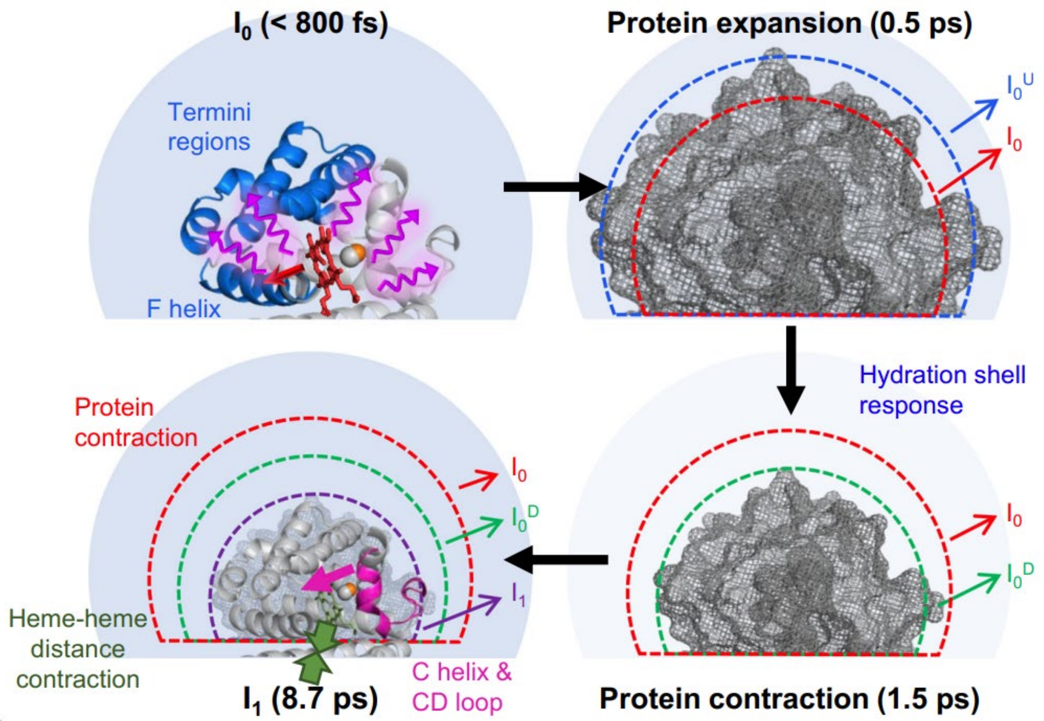
D. Arnlund, *et al.*, *Nature Methods* 2014, 11 923-927

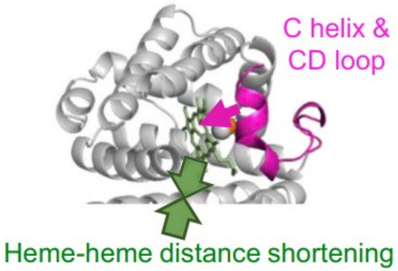
Protein structural dynamics

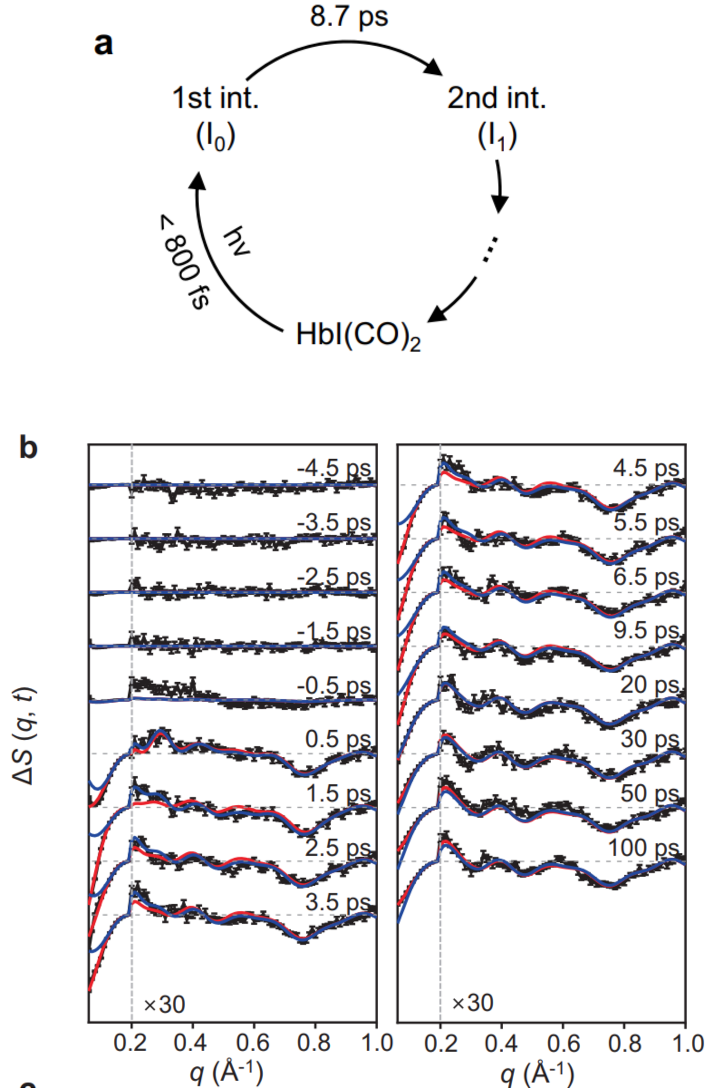
- Homodimeric hemoglobin (HbI)

LCLS









Y. Lee, *et al.*, *Nature Communications* 2021, 12 3677

Summary and Outlook

- fs-TRXL (fs-time-resolved x-ray liquidography)
  - Sub-angstrom structural sensitivity
  - Femtosecond time resolution
  - Reaction dynamics: structure changes in non-equilibrium state
- Challenges
  - Anisotropic responses of solvent cages
  - Data analysis based on the independent atomic models
  - Extend the research area to wider target system
    - Photo-caging, T-jump, *insitu/operando* experiment
    - Improvement sample injection
  - System containing no/less heavy atoms
    - MHz operation for enough S/N ratio
    - Expend max. q (using high energy X-ray)

Impressions

- Improvement in temporal resolution, stability of sample jet: Observing coherent vibration
- Expand sample environment: SAXS/WAXS for protein in water
- Multiplexing measurement
  - FXL + TR-XES
  - FXL / TR-XAS/XES / optical-TA