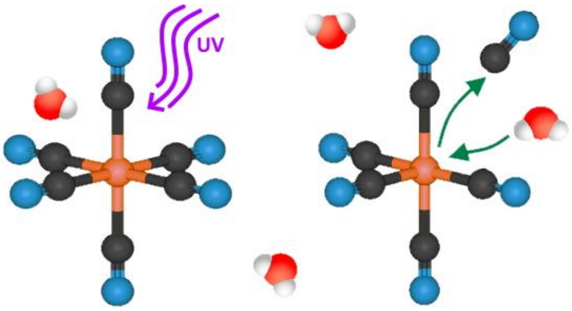
Light-induced bond-dissociation and aquation dynamics

Verena Markmann[1,*], Oliver Ohlson[1], Asmus O. Dohn[1], Kristoffer Haldrup[1]

[1]*Physics Deptartment, Technical University of Denmark*
**vmark@dtu.dk*

In liquid phase chemistry, the solvent environment often affects the geometry of the soluted molecules or the dynamic of a solutes' reaction pathway.[1-3] Within the context of the work presented here, we are studying the physical effects of the solvent cage on photochemical reactions, such as the aquation reation of $Fe(CN)_6^{4-}$ after bond-dissociation induced by a laser (Scheme 1). This class of solvated transition metal complexes have been investigated as model systems which allow investigations of the mechanistic details which govern molecular functionality for applications such as energy harvesting, molecular switches for memory storage or in biochemistry for photodynamic therapy.[3] However, a mechanistic understanding of the chemical reactions is challenging to obtain, as it involves molecular as well as electronic dynamics on ultrafast time scales.

This contribution will present very recent experimental results from time-resolved X-ray Solution Scattering experiments and highlight the sub-angstrom resolution for structural dynamics on the femtosecond time scale obtainable with this technique. The sensitivity of the method towards light-induced structural changes allows us to elucidate the long-debated issue of how square pyramidal or trigonal bipyramidal pentacoordinated geometries are involved in the aquation reaction of $Fe(CN)_5^{3-}$ following the photo-dissociation of a cyanide group. Furthermore, we can directly identify the X-ray scattering signal which arises from the formation of an aquated state within 20 ps after photo-excitation.



Scheme 1: Light-induced dissociation of $Fe(CN)_6^{4-}$ in water. In a subsequent aquation reation the penta-coordinatied of $Fe(CN)_5^{3-}$ adapts a watermolecule from the surrounding solvent.

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References

[1] M. Reinhard et al., Nat. Commun., 14 (2023): 2443.
[2] M. Reinhard et al., JACS, 139 (2017): 7335-7347.
[3] A. M. March et al., J. Chem. Phys., 151 (2019): 144306.