X-ray Scattering From Molecular Dynamics Simulations of Photoactivated Molecules in Aqueous Solution

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This poster presents a method for modelling solution scattering signals from (Pair) Radial Distribution Functions (RDFs) using Molecular Dynamics (MD) simulations. If set up with care, computational models can bring great insight into a plethora of properties, for example the interaction between a solute and solvent. The photoaquation reaction of ironhexacyanide displays remarkable solvation dynamics as it undergoes ligand substitution after photoexcitation in aqueous solution (figure 1). Here, a cyanide ligand is dissociated, with a water molecule subsequently binding to the vacant ligand site. This reaction has been investigated thoroughly previously.[1-3] Still, the exact kinetics and mechanism are very intricate and occur on an ultrafast timescale. Thus, to deepen the fundamental understanding of aqueous solvation dynamics, time-resolved X-ray solution scattering (TR-XSS) experiments and MD simulations are utilized. Since water is one of the most prevalent solvents in chemistry and biology, such a study is of high relevance. In addition, transition metal-centered complexes have many interesting properties of their own, making them apt candidates for use in light-harvesting materials, catalysis and photovoltaics, and more.[4,5]

In our group, the ironhexacyanide photoaquation has been studied at high-energy light sources, enabling intra- and intermolecular changes to be observed on a sub-picosecond timecale. To characterize the structural changes following photoexcitation, TR-XSS has been used, as the X-ray probe enables high temporal and spatial resolution. To decipher the convoluted signal and unravel the details hidden deep within experimental data, MD simulations and *ab initio* Quantum Mechanical (QM) calculations has been employed. With previously developed methods,[6] MD simulations can be used to compute RDFs then used for calculating the scattering signal. With explicit solvent models, the solute-solvent interactions can be examined efficiently in bulk solutions. This procedure is highlighted in this poster presentation.

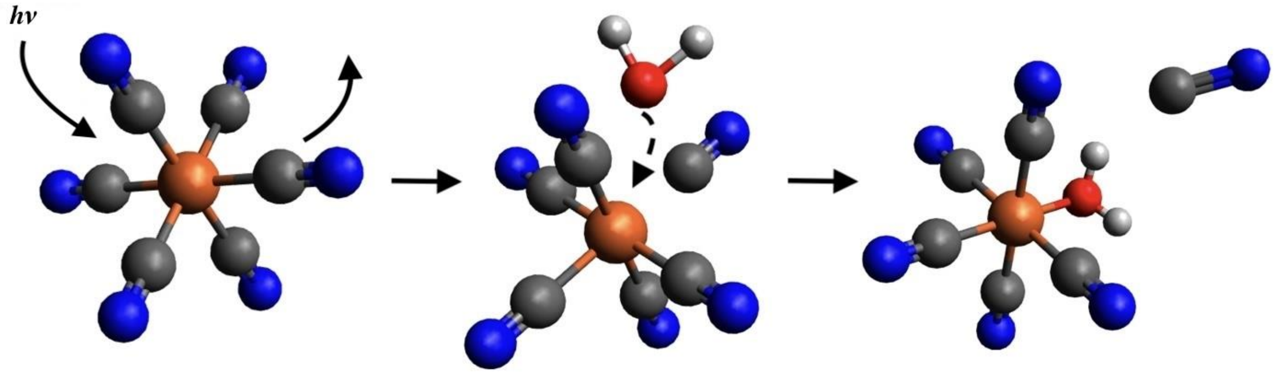

Figure 1: Overview of the Ironhexacyanide photoaquation reaction. The cyanide ligand dissociates after the complex is excited, followed by a water molecule attacking the penta-coordinated complex.

References
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