Exploring photoinduced structural relaxation and solvation dynamics with multiscale simulations

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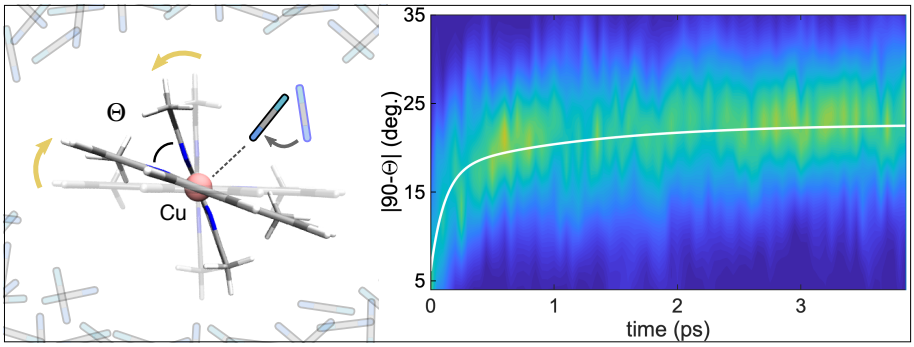
Efficiently harvesting solar energy using photoactive molecules requires a deep understanding of the transient structural changes after light excitation in solution. The excited-state relaxation can be influenced by many factors, most importantly the accompanying dynamical response of the solvent. Despite recent advances in ultrafast techniques, extracting a detailed picture of the instantaneous nuclear dynamics from time-resolved measurements in solution remains impossible without the support of atomistic simulations.
To address this challenge we have developed and implemented a multiscale quantum mechanics/molecular mechanics (QM/MM) Born-Oppenheimer Molecular Dynamics (BOMD) method [1] using a grid-based implementation of density functional theory (DFT) with a fast and robust description of excited states [2]. The methodology has been used to uncover highly elusive mechanisms of the ultrafast excited-state dynamics of photocatalytic transition metal complexes. We will show examples of these applications, ranging from predicting the vibrational relaxation and site-specific solvation dynamics following photoinduced bond formation in prominent bimetallic complexes for the interpretation of time-resolved X-ray scattering data [3,4], to resolving controversies regarding the solvent influence on the excited-state flattening of an archetype Cu photosensitizer [5].



QM/MM BOMD simulations of a prototype Cu(I) bis-phenanthroline complex reveal the coupling between the excited-state flattening dynamics, which controls the efficiency of photosensitization, and the intercalation of acetonitrile molecules between the ligands [5].

References

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