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Coupled electronic and nuclear dynamics at interfaces of artificial photosynthesis devices

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Chapter 8: Conclusions and Outlook

Conclusions of this work are summarized and **future perspectives** are discussed.

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8.1 Conclusions

At the photoanode of a dye-sensitized photoelectrochemical cell (DS-PEC), significant electron-hole recombination losses can occur due to the kinetic bottleneck associated with the slow oxygen evolution reaction. The development of efficient water oxidation catalysts (WOCs) continues to be an area of active research, where mechanistic insights into catalytic cycles are highly valuable.

Chapter 3 and 4 of this thesis focus on photocatalytic water oxidation in two model catalyst-dye systems applicable to DS-PECs.

In **Chapter 3**, the proton coupled electron transfer (PCET) steps that comprise the catalytic cycle were found to be characterized by an electronic reactant and product state that cross in the transition state region along the proton transfer reaction coordinate. Based on this finding, we propose a strategy to accelerate these catalytic steps by optically populating specific excited states that would drive the system towards the conical intersection.

In **Chapter 4**, we investigate a specific supramolecular complex comprising the Ru-bda²⁻ catalyst covalently bound to an NDI dye. Through means of hybrid DFT-based molecular dynamics (MD) simulations, we examined the equilibrium dynamics of the low-valent Ru^{III}-OH₂ intermediate. These simulations revealed that the complex maintains a pseudo-seven-coordinated environment, where the aqua ligand remains close to the ruthenium center. Enhanced sampling simulations of the high-valent Ru^V=O intermediate showed that oxygen-oxygen bond formation via the water nucleophilic attack (WNA) mechanism is associated with a free energy barrier of ~20.2 kcal mol⁻¹, indicating that this pathway is considerably slower than the interaction of two metal centers (I2M) pathway. Finally, the effects of including a fraction of Hartree-Fock exchange were investigated for several reaction steps in the catalytic mechanism. In agreement with the literature, the hybrid functional largely corrected the excessive delocalization of the hole observed when using a GGA functional. This improved description of the hole affected the relative energies of intermediates along the

catalytic cycle, slightly increased the barrier for the rate-determining O-O formation step and facilitated the release of the O₂ molecule at the end of the cycle.

Chapter 5 of the dissertation examines the photocatalytic proton reduction activity of a series of cobalt porphyrin complexes in various aqueous solutions with different acidity. Counterintuitively, we find that modification of the catalyst with electron withdrawing substituents leads to an increased photocatalytic activity in pH neutral conditions compared to acidic conditions. A combination of kinetic experiments, electrochemical experiments and extensive DFT modeling shows that this increased activity originates from a substituent-induced change from a metal-catalyzed to a ligand-catalyzed mechanism. These results provide an important guideline for the design of hydrogen evolution catalysts that are highly active at neutral conditions.

In addition to photoinduced water oxidation and proton reduction catalysis, charge transfer processes at the dye-semiconductor interface pose a challenging aspect of DS-PEC design. **Chapter 6** of this thesis presents combined quantum/classical dynamics and transient absorption spectroscopy (TA) study of the photoinduced charge transfer dynamics in a push-pull dye-NiO photocathode interface. Two surface species are identified in the TA measurements. The first species exhibits a photoinduced hole injection lifetime of ~0.5 ps and is assigned to dye molecules standing perpendicular to the surface. The second species injects on a much faster timescale compared to first species, and is assigned to dye molecules that are more strongly coupled to the surface, possibly through π -stacking interactions. Quantum/classical dynamics simulations on a model system with the dye standing perpendicular to the NiO surface yield a lifetime in close agreement with TA and show that dynamics of the hole wave packet are strongly correlated with thermal nuclear motion of the dye. This chapter provides critical insights into the photoinduced charge separation dynamics at the dye-NiO interface, which are important for the design of efficient DS-PEC's.

In a recent article, Smit and coworkers reported the localized emission of single terrylene molecules on hexagonal boron nitride (hBN).^[1] A fraction of molecules

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displayed considerable redshifts in their 0-0 zero phonon line, along with exceptionally weak vibronic intensities across all vibrational modes. This latter observation is particularly interesting, as it demonstrates that hBN serves as a compelling host matrix for single-molecule emitters with very sharp spectral lines and potential applications in quantum technologies.^[2] In **Chapter 7** of this thesis, the observed ultra-weak vibronic coupling is further examined through extensive quantum chemical modeling. We show that terrylene adsorbs strongly to specific charge donating defect sites in hBN. This charge donation from the defect to terrylene narrows the dye's HOMO-LUMO gap and considerably reduces the change in its geometry upon electronic excitation. Calculations of terrylene adsorbed on these defect sites show that the vibronic couplings of all modes in the fluorescence spectrum are affected simultaneously, in line with the experimental observations. This chapter provides detailed insights into the physical mechanisms that govern vibronic coupling in dye adsorbate interfaces.

8.2 Outlook

8.2.1 Non-adiabatic surface hopping simulations of photo-activated proton transfer in a supramolecular water oxidation catalyst-dye complex

Chapters 3 and 4 provide detailed insights into the reaction dynamics of supramolecular catalyst-dye complexes for photocatalytic water oxidation. Simulations in chapter 4 show that proton transfer steps are coupled to electron transfer during the catalytic cycle. However, these simulations were carried out within the Born-Oppenheimer (BO) framework, where the electronic system is strictly quenched to the ground state. Chapter 3 suggests that this assumption may break down along the reaction path when the reactant and product electronic states move through a degeneracy in the region of the proton transfer transition state (see Chapter 3, Figure 3.5). These observations are interesting as they suggest that the PCET reaction can be accelerated by populating the electronic product state.

To explore this idea in detail, we have carried out non-adiabatic surface hopping simulations of the supramolecular complex with several explicit water molecules. The excited state surface hopping simulations were carried out with the SHARC version 2.1 molecular dynamics program interfaced with ADF2022.101^[3-6] The WFOverlap program was employed to evolve wavefunction coefficients between consecutive timesteps.^[7-10] Excited state calculations were performed with SF-TDDFT, employing the long-range corrected CAM-B3LYP exchange correlation functional and a double- ζ (DZ) basis set.^[11] Grimme's third generation of dispersion corrections were added to account for van der Waals forces.^[12-14] We note that we employed an in-house version of the ADF-SHARC interface, compatible with the post 2020 environment of the AMS program and with simulations based on spin-flip excitations.

The equilibrated BO molecular dynamics (BOMD) trajectory of the ¹(NDI-[Ru(IV)-OH])⁺ intermediate was taken from chapter 4 of this dissertation and further propagated at the GGA-PBE level for 7.5 ps at 300 K using the CP2K software package.^[15] During this simulation, a stable hydrogen bonding network emerged around the hydroxo ligand, as was also indicated in Chapter 4 (see Figure 4A.4.2). The seven water molecules in closest proximity to the hydroxo ligand are displayed in the Figure 8.1a with a thick ball and stick representation. Initial positions and velocities for a surface-hopping molecular dynamics (SHMD) simulation were taken from the BOMD trajectory. To save computational resources, only the 7 water molecules that actively participated in the hydrogen bonding network around the hydroxo ligand were included. In this proof-of-concept simulation, the lowest three electronic states were considered during the simulations, excluding the spin-flip reference state.

Two assumptions are made regarding the electronic structure of the catalyst-dye complex. First, electron injection from the excited dye into the TiO₂ semiconductor is simulated by removing an electron from the system, effectively oxidizing the dye instantaneously. We have shown in previous work that this injection process is fast on a picosecond timescale, validating this approach.^[16,17]

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Second, it is assumed that photoexcitation of the dye-catalyst complex to the electronic product state occurs immediately after photo-oxidation. We thus followed the time evolution of the complex as it is excited directly into the electronic product state (indicated in green in Figure 3.5, Chapter 3), but starting from the nuclear initial conditions corresponding to the complex in the unoxidized state. Figure 8.1b presents the energies associated with the two lowest electronic doublet states in the system along the SHMD simulation time, while Figure 8.1c shows the dissociating and forming O-H bond lengths (see enlarged detail in Figure 8.1a for the atomic labeling).

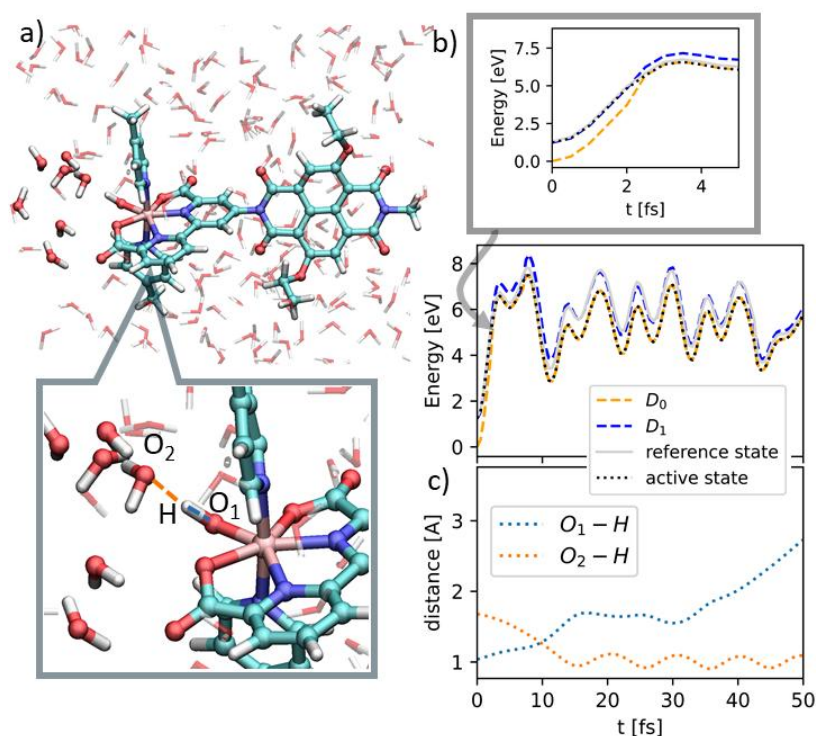


Figure 8.1. a) Snapshot of the Born-Oppenheimer MD simulation from which initial conditions for the surface hopping simulation were taken. The inset shows the relevant atomic labels and $O_1 - H$ and $O_2 - H$ bond distances. The time-evolution of the lowest two doublet state energies is provided in b). c) shows the evolution of the $O_1 - H$ and $O_2 - H$ bond distances.

Figure 8.1b) shows a swift increase in energy of ~ 5 eV in the first 0 to 10 fs of the trajectory, which is slightly larger than the typical fluctuations that are observed after the first 10 fs. We interpret this increase in potential energy to be a consequence of the initial velocity distribution that was extracted from the ground state dynamics of the unoxidized complex in explicit solvation. Overall, the trajectory decays from D_1 to the electronic ground state D_0 within the first ~ 5 fs of the trajectory (see enlarged detail in Figure 8.1b). Figure 8.1c shows that the proton transfer proceeds on a similar timescale, although it is completed only after the electron transfer. The $O_2 - H$ distance decreases immediately after initialization of the reaction and appears to stabilize around ~ 1 Å after less than 20 fs. Simultaneously, the $O_1 - H$ distance is elongated, first to ~ 2 Å, and then to larger distances, indicating that the bond has fully dissociated. Overall, the simulation shows that upon electronic excitation into the electronic product state, ultrafast proton transfer occurs for this complex. However, additional simulations should be performed to assess the influence of the initial starting conditions on this result. Furthermore, simulations should preferably include more electronic states to properly consider other decay pathways that might be missed when accounting only for the lowest two excited states. Nevertheless, this simulation presents an encouraging result that should be studied in further research.

8.3 References

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