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Summary

Coupled Electronic and Nuclear Dynamics at Interfaces of Artificial Photosynthesis Devices

Reducing greenhouse gas emissions is one of the most pressing challenges that humanity faces in the coming decades. As a platform for generating solar fuels, dye-sensitized photoelectrochemical cells (DS-PECs) offer a promising solution. DS-PECs effectively address the intermittency issues inherent to solar and wind energy by storing solar energy in chemical bonds to generate sustainable fuels. However, the design of efficient DS-PECs remains challenging due to sluggish catalytic turnovers and low charge separation efficiencies. Addressing these limitations requires a deeper understanding of the physical mechanisms that govern these processes. With this goal in mind, this dissertation aims to elucidate at an atomistic level the mechanisms that drive photo-induced charge separation and catalysis in various components of DS-PEC devices. A strong emphasis is placed on the coupled motion of nuclear and electronic degrees of freedom, which I demonstrate to be crucial for many of the investigated systems.

Chapter 1 and 2 provide an introduction into DS-PEC devices and into the computational methodologies relevant to this work. Subsequently, I focus on photocatalytic water oxidation in dye sensitized photoanodes. Slow catalytic turnovers often present a kinetic bottleneck for these systems, making it highly relevant to come up with innovative approaches to accelerate individual catalytic steps. **Chapter 3** explores the excited state potential energy landscape of two dye-catalyst complexes which could be employed in a DS-PEC photoanode. The most intriguing result is that the proton-coupled electron transfer steps that govern the photocatalytic water oxidation cycle are characterized by an electronic reactant and product state which cross along the proton transfer reaction coordinate. This result leads to novel strategies to accelerate these photocatalytic steps. **Chapter 4** examines the dynamic properties of a [Ru-bda]-NDI complex through simulations

that include explicitly the water environment. These simulations provide critical insights on the equilibrium dynamics of the low-valent Ru^{III}-OH_2 intermediate, clarifying EPR observations reported in literature. Detailed analysis of the rate limiting O-O bond forming step following the water nucleophilic attack mechanism (WNA) reveals that this process is viable, though with a slow turnover frequency and minimal driving force. This highlights the need for alternative catalysts optimized for the WNA mechanism in immobilized systems.

The discourse of the dissertation than shifts to DS-PEC photocathode design. A critical challenge in these systems is maintaining a pH gradient to facilitate proton diffusion from photoanode to photocathode. While high-turnover hydrogen evolution catalysts (HECs) exist for neutral pH conditions, they predominantly rely on precious metals. Therefore, identifying first-row transition metal catalysts that operate efficiently in pH neutral conditions is crucial for advancing DS-PEC technologies. In **Chapter 5**, a series of cobalt porphyrin complexes was investigated for their photocatalytic hydrogen evolution activity in a range of different pH conditions. The catalysts were functionalized by either electron withdrawing or electron donating groups, thereby tuning the charge density on the cobalt center. Strikingly, the electron poor catalysts outperformed the electron rich catalysts in neutral conditions. This observation is explained by extensive DFT modeling, which demonstrates that the electron withdrawing substituents promote a ligand-based mechanism, while the electron rich catalysts operate via a metal-based mechanism. These results open a promising new avenue for the design of porphyrin-based HECs that operate with high turnover frequencies in neutral conditions.

Besides catalyst performance, photoinduced charge separation at the dye-semiconductor interface impacts photon-to-product efficiency in photocathodes. While many studies have investigated energetic properties of such systems, the structural effects and the impact of thermal nuclear motion on the interfacial electron and hole-transfer dynamics has remained relatively unexplored. In **Chapter 6**, the photoinduced charge separation dynamics at the dye-NiO photocathode interface have been studied using a combination of quantum/classical dynamics simulations and transient absorption (TA) spectroscopy. The performed simulations provide an atomistic level interpretation for species observed in TA. It was found that the absorption mode of the dye on the surface dramatically impacts the photoinduced injection rate, and that thermal nuclear motion plays an important role in driving the process, particularly on timescales longer than 100 fs. These findings enhance our understanding of charge-transfer dynamics at dye-semiconductor interfaces and provide guidance for DS-PEC design.

The final section of this dissertation focuses on another system where the nuclear-electronic coupling is critical. Recently, it was shown that hexagonal boron nitride can serve as a host matrix for single-molecule fluorescence studies of organic dye molecules. When certain molecules adsorb onto these matrices, they display distinctive spectral features, including weak vibronic intensities and redshifted 0-0 zero phonon lines (ZPL). The potential applications of these highly sensitive spectra in molecular sensing and quantum technologies renders a physical understanding of the underlying mechanism behind these observations highly desirable. In **Chapter 7**, I employ extensive quantum chemical modeling to investigate these mechanisms. It was found that the ultra-weak vibronic coupling and redshift of the 0-0 ZPL can be explained by adsorption of the molecule on specific charge donating defect sites. These insights establish design principles for material-molecule interfaces capable of emitting highly resolved single photons with minimal vibrational coupling.