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Chapter 7

Proton-Coupled Electron Transfer

7.0.1 ABSTRACT

Proton-coupled electron transfer is a fundamental processes in nature, most noticeably in photosynthesis. Within the adiabatic molecular dynamics approach we present real-time evidence of proton-coupled electron transfer upon oxidation of a benzimidazole-phenol redox relay. The decoupling of spin and positive charge observed in this system may be an important motif to mediate between the fast charge separation and slower water oxidation catalysis in artificial photosynthesis.

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7.1 Introduction

Proton coupled electron transfer (PCET) is a fundamental process in many biochemical reactions and molecular electronic device functions [1-3]. Also in the oxygen evolving complex (OEC) of Photosystem II successive PCET reaction steps are crucially important to overcome the thermodynamically demanding water splitting reaction avoiding the accumulation of excess positive charge in the manganese cluster [4]. Moreover, in Photosystem II a tyrosine-histidine pair mediates the electron transfer between the OEC and the radical cation $P680^{\bullet+}$ and provides a kinetic intermediate between the slow catalytic water oxidation steps and the fast photoinduced charge transfer through an intermolecular PCET process (Figure 7.1) [5,6].

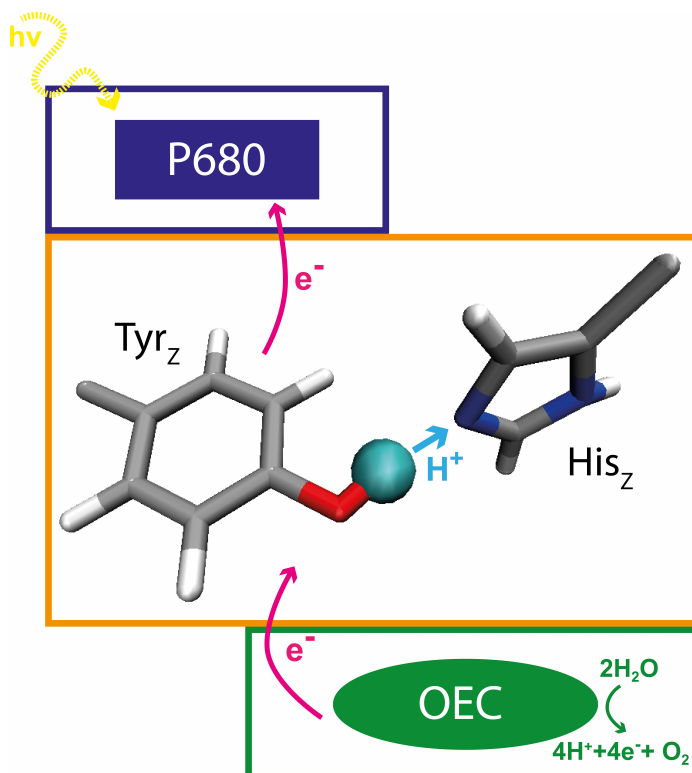


Figure 7.1: Redox mediation between the lightactive P680 pigments and the oxygen evolving complex (OEC): A proton is transferred from Tyrosine_Z to the imidazole ring of Histidine_Z upon oxidation of the tyrosine.

We present ab initio molecular dynamics simulations of the benzimidazole-phenol redox relay recently included in an artificial triad for efficient charge separation [6] and show real-time evidence of the PCET process induced by oxidation of the benzimidazole-phenol that leads to the formation of the stable phenoxyl radical.

7.2 Model and Methods

The real-time simulations of proton-coupled electron transfer were performed on a single adiabatic potential energy surface. The model we study is a benzimidazole-phenol (Figure 7.2) that mimics the tyrosine-histidine pair in Photosystem II [6]. In analogy with natural photosynthesis the PCET from the phenol to the benzimidazole can prevent charge recombination by stabilizing the photoinduced hole. To simulate the PCET process in real-time we use the Car-Parrinello method as implemented in the CPMD code [7,8]. The total time of the trajectories is 5 ps with a time step of 0.1 fs. A Nosé thermostat is used in all simulations to keep the temperature around an average of 300 K. At this temperature we expect that quantum effects on the proton dynamics are not dominant and that the classical description of the nuclear motion is appropriate.

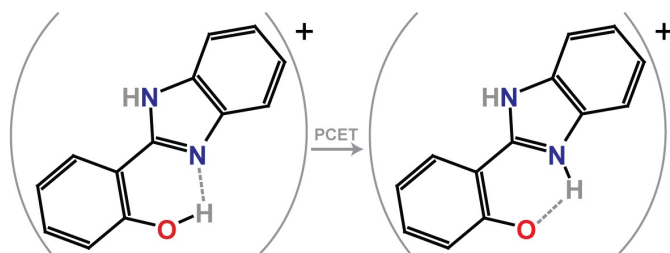


Figure 7.2: Proton-coupled electron transfer in benzimidazole-phenol upon (photoinduced) oxidation.

The BLYP functional [9,10] is used for the exchange-correlation energy. The Kohn-Sham orbitals are expanded in a plane-wave basis set with an energy cutoff of 70 Ry. We employ dispersion-corrected atom-centered (DCACP) pseudopotentials [11,12]. Starting from a partially optimized structure with the proton on the phenol (Figure 7.3), we follow the dynamics of the proton and the unpaired electron in real-time. The unpaired electron is tracked

along the trajectories by monitoring the hole spin density (HSD):

$$HSD(r) = \rho^\beta(r) - \rho^\alpha(r) \quad (7.1)$$

where ρ represents the density, and α, β the respective spin species. The total integral over space of the HSD equals 1. By integrating the HSD over different partitions of the simulation box we quantify the localization of the unpaired electron. We perform CPMD simulations both in vacuum and in the presence of an explicit water solvent.

7.3 Results and Discussion

In many natural processes and most noticeably in photosynthesis electron transfer is often accompanied by a concerted proton motion that reduces the probability of charge recombination. Moreover the tyrosine-histidine redox mediator in Photosystem II becomes an extremely long lived neutral radical after removing the hole from the special pair. As such it facilitates the kinetically demanding water oxidation in the oxygen evolving complex [5]. To simulate the proton-coupled electron transfer in the benzimidazole-phenol mimic of this redox mediator, we perform ab initio molecular dynamics simulations in the state after electron injection to an acceptor. In this configuration the proton is still attached to the phenol oxygen. After 180 fs of dynamical evolution we observe a first attempt of a proton transfer to the imidazole nitrogen (Figure 7.3, upper left panel, 0.2 ps). This unsuccessful approach is at the end of the first characteristic fluctuation of the hydrogen bond. After another full period of this oscillation the proton is transferred to the imidazole nitrogen (~ 0.5 ps). The proton remains stable in this configuration during the entire simulation (5 ps) even though we still observe hydrogen bond dynamics that moves the proton close (1.3 Å) to the phenoxyl oxygen radical (see upper left panel ~ 0.8 ps). Initially the hole spin density is delocalized over the entire complex (Figure 7.3, lower left). After the proton transfer (0.6 ps) the spin density localizes on the phenol with a modified nodal structure forming a phenoxyl neutral radical (Figure 7.3, upper right). The integrated spin density on the phenol ring in the lower right panel of Figure 7.3 quantifies the spin transfer along the dynamics. Clearly, the spin density rearranges in a concerted fashion with the proton dynamics (Figure 7.3 upper left) and approaches unity as the proton is transferred to the imidazole nitrogen.

7.3. RESULTS AND DISCUSSION

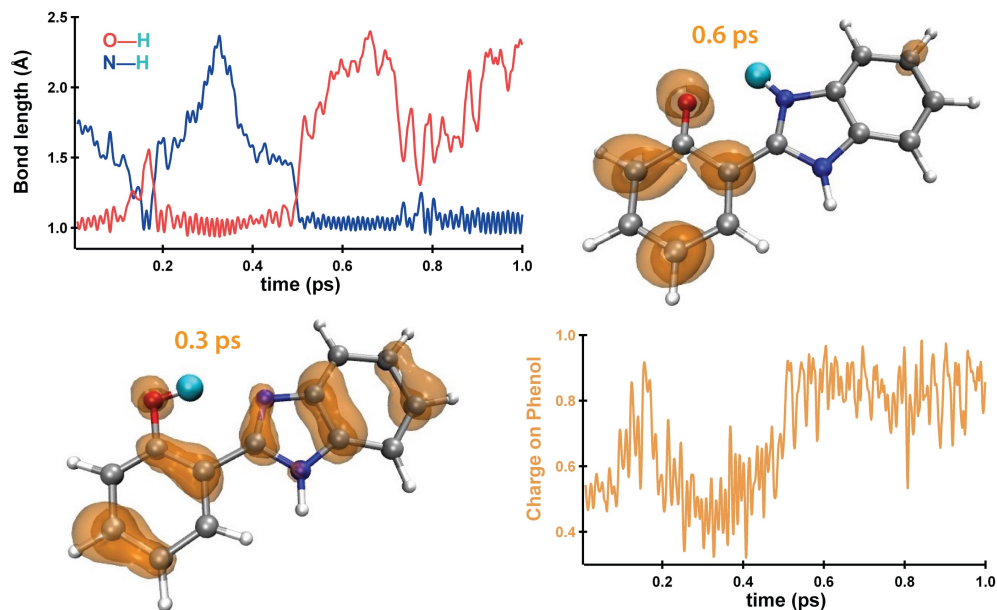


Figure 7.3: Real-time simulation of proton-coupled electron transfer in a mimic of the tyrosine-histidine pair in PSII (See Movie 7.1 in Appendix I). We start the ab initio molecular dynamics in the configuration of the benzimidazole-phenol immediately after oxidation. The upper left panel tracks the distance of the proton with respect to the phenol (O) and imidazole (N). We observe the proton transfer after ~ 0.5 ps. The hole spin density (orange) almost entirely localizes on the phenol as the proton is transferred under formation of a phenoxyl neutral radical (upper right panel). The symmetry of the unpaired electron changes with a modified nodal structure (compare lower left and upper right panels). When integrating the spin (*errata: NOT charge as on y-axes*) on the phenol as the simulation proceeds (lower right panel) the spin density on the phenol follows the proton motion and approximates unity after the proton transfer.

To investigate the possibility of a solvent mediated proton transfer in benzimidazole-phenol we perform ab initio molecular dynamics with an explicit water solvation shell and periodic boundary conditions. We start from the same initial conditions of the redox mediator as in the vacuum simulations and evolve the system starting with the proton attached to the phenolic oxygen. The proton transfer occurs on a significantly longer time scale with the inclusion of an explicit solvent (see Figure 7.4). Moreover the thermal fluctuations of the intramolecular hydrogen bond are damped by the formation of hydrogen bonds with the solvent. As we established in

the simulation for the isolated system, the fluctuations of the intermolecular hydrogen bond are crucial in facilitating the proton transfer. The reduced amplitude of these fluctuations in the presence of the solvent decreases the probability for the proton to be transferred to the imidazole. Water-assisted proton transfer through the temporary formation of a hydronium ion is not observed. In terms of hole spin density the symmetry before and after proton transfer changes in the same fashion as in vacuum. The nodal structure is modified and the localization is now almost entirely on the phenol that becomes a neutral phenoxyl radical (Figure 7.4, bottom panels).

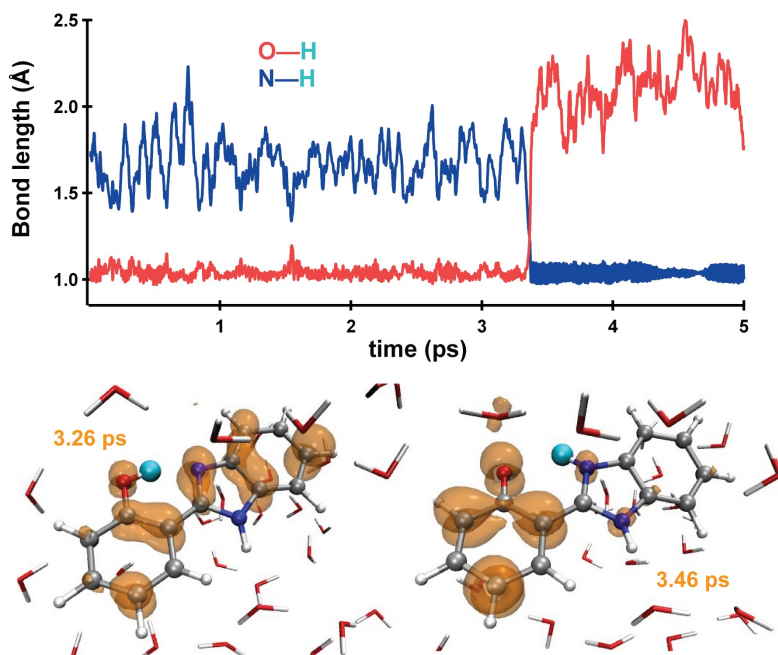


Figure 7.4: Proton-coupled electron transfer simulation with explicit water solvent. We find almost an order of magnitude slower proton transfer with respect to the simulations in vacuum (upper panel), which we attribute to hydrogen bonding between the proton and the solvent. The delocalized hole spin density before proton transfer (lower left panel) localizes on the phenol after proton transfer (lower right panel) and a phenoxyl neutral radical is formed.

Small fractions of spin density are also observed on water molecules further indicating the hydrogen bonding interaction with the solvent. We observe that the out-of-plane motion between the imidazole and phenol moieties is limited to a range of a few degrees ($+5$, -5) due to the presence of an

intramolecular hydrogen bond, consistently with experimental findings. [6] We find that the fluctuations in this dihedral angle are coupled to the proton transfer since they are associated with fluctuations in the distance between the proton donor and proton acceptor.

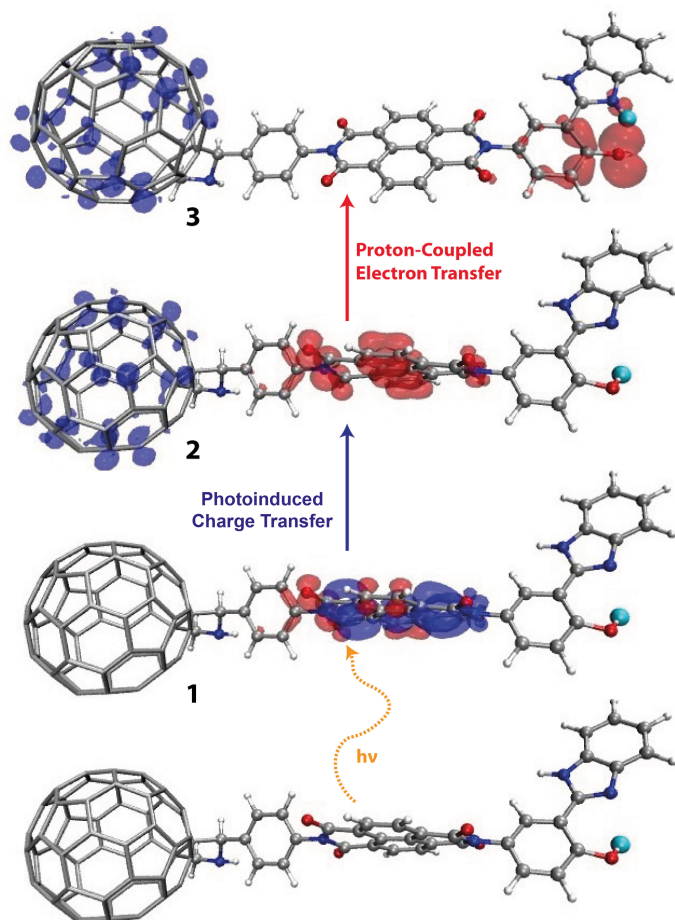


Figure 7.5: Artificial photosynthetic assembly consisting of a fullerene acceptor, a naphthalene diimide antenna and a benzimidazole-phenol electron donor. The latter will prevent charge recombination by filling the hole on the antenna that is formed after photoinduced charge transfer to the acceptor. Once oxidized, the donor will transfer a proton from the phenolic moiety to the imidazole through a proton-coupled electron transfer step. Depicted are the photoinduced spin densities (blue=electron, red=hole) after short TDDFT trajectories in the excitonic state (1), the intermediate charge transfer state (2) and the fully charge separated state (3) where the proton has been transferred to the imidazole.

7.3.1 Artificial Reaction Center

The concept and realization of an artificial reaction center for stable photoinduced charge separation based on properly chosen molecular building blocks has been developed for many years [13]. It is generally accepted that such supramolecular complexes should comprise at least three components (triad) with a light sensitive antenna molecule coupled to a donor and an acceptor to reach a charge separated state that lives long enough to support the kinetically demanding redox catalytic steps. One of the most studied triads in the literature is the carotenoid-porphyrin-fullerene complex [14] where ultrafast charge transfer dynamics have been observed with femtosecond spectroscopy [15]. Following a similar strategy as in Reference [13], we explore a triad including a fullerene acceptor, a naphthalene diimide (NDI) antenna and the benzimidazole-phenol (BiP) moiety discussed in the previous section as electron donor (see Figure 7.5). The NDI antenna is very versatile since it can be functionalized with different groups to adjust its optical and electronic properties [16,17]. This allows to control the molecular absorption range and to adapt the molecular redox properties to specific interface requirements. The BiP relay module is included in the triad to stabilize the charge separated state through the formation of the phenoxyl radical. We have verified that this radical state is accessible in the triad upon charge separation (see Figure 7.5, top). We are planning to perform long real time Ehrenfest dynamics simulations of the triad starting from the excitonic state to follow the full electron/hole transfer and the PCET step. These simulations should allow also to establish whether coherent motion might play a role in this supramolecular complex similarly to what has been observed in the carotenoid-porphyrin-C60 complex [15] and in Chapter 5 of this thesis [18].

7.4 Conclusions

We have presented ab-initio molecular dynamics simulations describing in real-time the proton-coupled electron transfer process in benzimidazole-phenol. The dynamics in this mimic of the tyrosine-histidine pair in PSII shows the proton transfer from the phenolic oxygen to the imidazole nitrogen upon oxidation. The proton dynamics is strongly coupled to the hole spin density that localizes on the phenol leading to the formation of the stable phenoxyl radical. Incorporating the decoupling of spin and charge in an artificial device has the potential to bridge the timescales between the fast photoinduced processes and catalysis.

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