Coupled proton-electron transfer in excited states of X-MnOH$_2$:

A nonadiabatic electron wavepacket study

(X-MnOH$_2$ -   )

1 Introduction

An early process of photosynthesis, that is, photodecomposition of water to give protons and electrons, is now widely studied not only to understand itself, but also to find a guiding principle of a solar buttery and a photocatalyst. Crystal structure of photosystem II (PSII) at a resolution 1.9 Å [1] is known to be a breakthrough. Nevertheless, the mechanism of the early process of photosynthesis is still a matter of controversy. As for theoretical aspect, this problem has been tackled in terms of energetics with stationary state quantum chemistry. However, the mechanism should involve electron dynamics in excited states related to the water decomposition. Thus the study with nonadiabatic electron dynamics is inevitable for direct description of the mechanism.

Here we perform nonadiabatic electron wavepacket dynamics of X-MnOH$_2$. The target is taken from the Mn cluster of PSII, where the water decomposition occurs in nature. In this context, this work is regarded as the first step to establish the mechanism of early process of photosynthesis.

2 Theory

We calculate nonadiabatic electron wavepacket dynamics with the theory based on the path-branching representation (PBR) [2]. In this theory, electron wavepackets propagate along branching nuclear
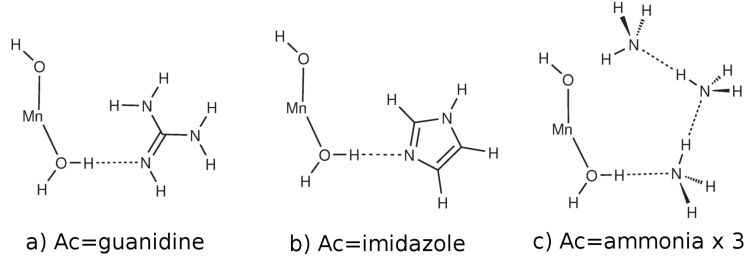
Figure 1: The chemical structures of the targets. $Mn(OH)OH_2$ is common and Ac is different from each other.

paths. The path-branching is invoked by so-called force matrix $\mathcal{F}_{IJ}^k$.

$$\mathcal{F}_{IJ}^k = \langle \Phi_I | \frac{\partial \hat{H}^{(el)}}{\partial R_k} | \Phi_J \rangle. \tag{1}$$

An electron wavepacket $\Psi(\mathbf{R}, \mathbf{r}, t)$ on each path is expanded in the form

$$\Psi(\mathbf{R}, \mathbf{r}, t) = \sum_I C_I(t) \Phi_I(\mathbf{r}; \mathbf{R}(t)). \tag{2}$$

The equations of motion for electrons have the following form

$$i\hbar \dot{C}_I = \sum_J \left(H_{IJ}^{(el)} - i\hbar \sum_k \dot{R}_k X_{IJ}^k - \frac{\hbar^2}{4} \sum_k (Y_{IJ} + Y_{JI}^*) \right) C_J. \tag{3}$$

Exact PBR dynamics needs calculations of infinite number of branching paths, which is technically impossible. Instead of it, we somehow extract representative paths. The simplest way would be averaging the force matrix to give the equivalent force to the semiclassical Ehrenfest theory to the first order.

$$F_k = \sum_{IJ} C_I^* \mathcal{F}_{IJ}^k C_J \tag{4}$$

3 Application

We investigate the coupled proton-electron transfer in excited states of $X\text{-MnOH}_2 \cdots Ac$, where Ac is a hydrogen-bonded proton-electron accepter. Here we demonstrate the case of X=OH and Ac=guanidine. A similar mechanism can also be found when another Ac such as imidazole and ammonia cluster is used. See Fig. 1 for their chemical structures.

First we examine the static property as a function of position of the transferred H atom. In this

analysis, the H atom moves linearly between O and Ac, and all the other atoms are fixed to the optimized geometry. Adiabatic potential curves in this coordinate are shown in Fig. 2. From the static property, we can expect the following photo-chemical reaction.

$$X\text{-MnOH}_2 + h\nu \rightarrow X\text{-MnOH} + H^{m+} + me^-,$$
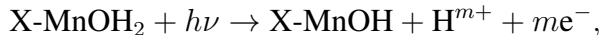
where $0 < m < 1$. The expected mechanism is summarized as follows:

1. Electronically excited states (3.0 - 3.5 eV) are generated by UV-visible light.

2. H^{m+} ($m \approx 0.6$, not a radical) passes by near a conical intersection to be transferred to the accepter, which involves nonadiabatic transitions.

3. me^- are transferred at the same time, but they take different pathways from H^{m+} to reach Rydberg-like states on the accepter.

They are common in all accepters shown in Fig. 1.

Now we show that the dynamics follows the expected mechanism. The zero-point oscillating molecule in S_0 is vertically excited to S_4. Let it propagate with Eqs. 3 and 4. The coupled proton-electron transfer is finished in as long as 10 fs. Large nonadiabatic transition between S_4 and S_3 (Fig. 3(a)) means that the molecule indeed passes by near the conical intersection. According to atomic charge (Fig. 3(b)) and atomic unpaired electron density (Fig. 3(c)) on the transferred H atom, it is indeed H^{m+} ($m \approx 0.6$) and not a radial. The snapshots of spatial distribution of unpaired electron density (Fig. 4) clearly show that the electrons take different pathways form H nucleus. They reach the Rydberg-like states of the accepter to invoke charge separation.
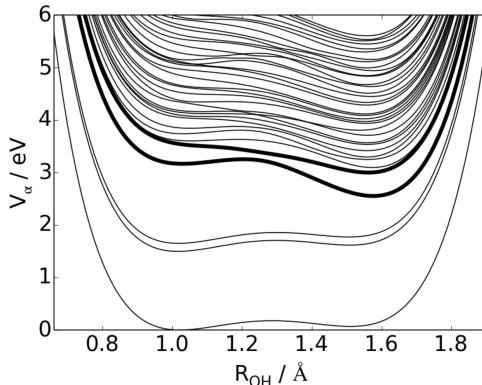

Figure 2: Adiabatic potential curves as functions of position of the transferred H atom. Thick lines are the states that electrons mainly populate in excited states.

4 Conclusion

Through the nonadiabatic electron dynamics of X-MnOH$_2$, we have shown that 3.0 - 3.5 eV photo excitation results in coupled proton-electron transfer to invoke charge separation. This mechanism
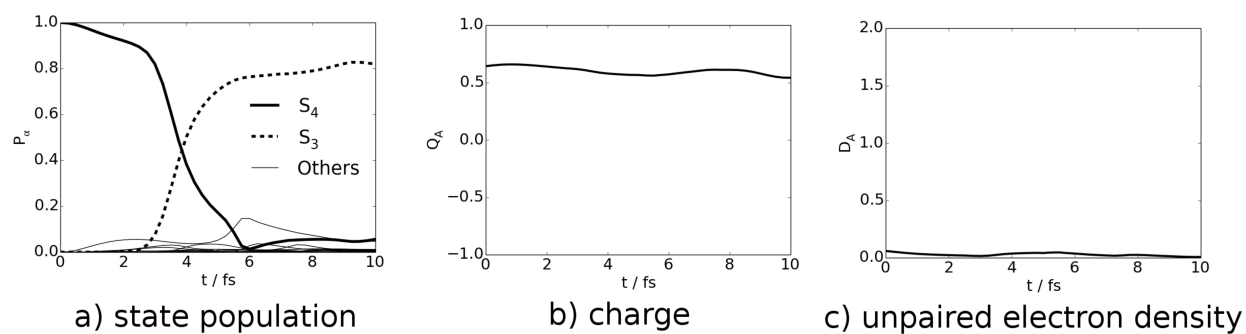
Figure 3: Property change along the path: (a) adiabatic state population, (b) atomic charge on the transferred H atom, (c) atomic unpaired electron density on the transferred H atom.

is similar to that of phenol-ammonia cluster established before [3], which needs excitation energy as much as 6 eV. The proposed mechanism can be a candidate of that in PSII in nature.

References

[1] Y. Umena, K. Kawakami, J-. R. Shen and N. Kamiya, Nature **473**, 55 (2011).

[2] T. Yonehara, K. Hanasaki and K. Takatsuka, Chem. Rev. **112**, 499 (2012).

[3] K. Nagashima and K. Takatsuka, J. Phys. Chem. A **116**, 11167 (2012).
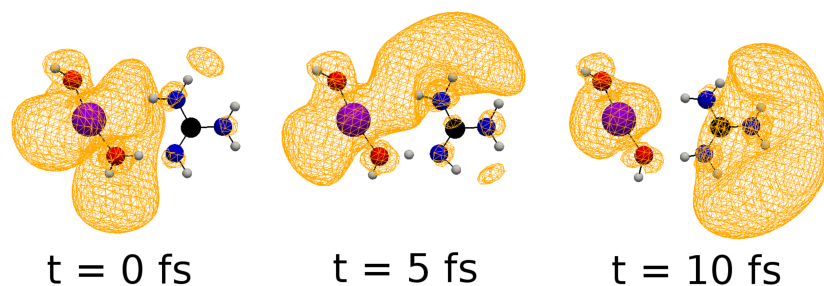
Figure 4: Snapshots of spatial distribution of unpaired electrons along the path.