CHAPTER 4

SUMMARY

In this chapter, we summarize the ESInterPT reactions in the systems of 7AI with water ($7AI(W)_{n=1-5}$), ammonia ($7AI(A)_{n=1-3}$) and mixed water-ammonia($7AI(AW)_{n=2-3}$) clusters for study the microsolvation effects and PT time evoluation based on quantum dynamics simulations at RI-ADC(2)/SVP-SV(P) level.

First, the optimized ground-state structures of all clusters at RI-ADC(2)/SVP-SV(P) level in the gas phase were performed. Second, all these optimized structures were used to investigate the ESPT reactions using excited-state dynamics simulations. From this study, the ESInterPT reactions for all clusters exhibit ESPT reactions confirmed by no crossing between $\pi\pi^*$ and $\pi\sigma^*$ states. Moreover, the probability of tautomerization is anti-correlated with the maximum free energy barrier of proton transfer in the excited state.

For 7AI with water clusters ($7AI(W)_{n=1-5}$), PT take place preferentially through the first shell of solvent (two molecules) and an increasing number of water molecules tends to reduce the free energy barrier. Nevertheless, taking solvent effect only five water molecules as microsolvation in this work, the results might not mimic the real system in solution. If we study 7AI with more water molecules, the results may be more accurate because more complete solvent effect is taken into account. Furthermore, for 7AI with three water molecules, the proton transfer occurs mostly in the original ground state conformation that the complex has at the time of photoexcitation. We found, however, qualitative evidence of sub-picosecond photoinduced hydrogen bond reorganization of $7AI(W)_3$ from the bridged-planar to cyclic-nonplanar isomer prior the proton transfer. In the cases of $7AI(AW)_3$, the hydrogen-bond rearrangement from the bridged-planar leads to either bicyclic-nonplanar or cyclic-nonplanar(2+1) isomers may occur before the occurrence of ESTPT reaction.

For $7AI(A)_{n=1-3}$, ESIPT reactions occur in 7AI(A) more efficient than $7AI(A)_{2-3}$ clusters. When comparing the results with our previous work of $7AI(M)_{n=1-3}$ [36] and

7AI(WM)$_{n=2-3}$ [37], the proton transfer tends to be concerted process with at least one ammonia present in the clusters, but synchronous without ammonia. In addition, when an ammonia is placed near N-H of 7AI, the ESPT probability is found to be higher than the other isomers because of the decrease of free barrier energy. Furthermore, this study has revealed that the assistance of the second shell solvent play an important role in excited-state dynamics. Thus, all these clusters can be used as a good prototype for the excited-state intermolecular PT process and the information detailed obtained from this study will be useful for future studies on more complicated ESPT systems.