

## CHAPTER IV

### CONCLUSION

In this work, the high-level ONIOM-XS MD technique has been applied for studying the behaviors of  $\text{PH}_4^+$  intermediate in aqueous solution. Two ONIOM-XS MD simulations using different QM methods for the treatment of QM region, namely HF and B3LYP, have been separately performed. According to the first ONIOM-XS MD simulation, where all interactions within the QM region were treated at the HF level of accuracy using the def2-SVP basis set, the simulation results clearly reveal a flexible  $\text{PH}_4^+$  solvation, consisting of various numbers of nearest-neighbor water molecules, ranging from 3 to 11. In this respect, water molecules surrounding the ion are rather labile, and are weakly hydrogen-bonded (HB) to the ion, *i.e.*, when compared to the water-water HBs in the bulk. This phenomenon corresponds to the “structure-breaking” ability of  $\text{PH}_4^+$  in aqueous solution. For the second ONIOM-XS MD simulation, in which all interactions within the QM region were described by means of B3LYP calculations using the def2-SVP basis set, it was observed that one proton of  $\text{PH}_4^+$  has transferred to solvent, leading to the formation of  $\text{PH}_3$  and  $\text{H}_3\text{O}^+$  species. Regarding the detailed analyses on the ONIOM-XS MD trajectories, it could be demonstrated that the B3LYP method is not applicable for describing the behaviors of  $\text{PH}_4^+$  intermediate in aqueous solution.