

CHAPTER I

INTRODUCTION

1. Literature reviews

The details with respect to structure and dynamics of ions that are solvated in aqueous solutions has long been investigated, both by experimental and theoretical techniques, in order to understand the role and functionality of these ions in various chemical and biological processes (Frank, 1956; Clementi, 1976; Marcus, 2009 and Gutmann, 1978). It is known that when ions interact with water, the effect of ions causes modifications in the local structure and changes in the dynamic properties of the surrounding water molecules. The manners in which ions order the structure of their surrounding waters are strongly related to the strength of ion-water interactions. Basically, if the ion-water interactions are stronger than that of water-water interactions, such ions are classified as “structure-making” ions, *i.e.*, they can break H-bond structure of the surrounding waters and can order those water molecules to form specific ion-water complexes. In contrast, if the ion-water interactions are comparable or weaker than the water-water interactions, such ions can be classified as “structure-breaker”. In this respect, water molecules surrounding the ions prefer to form H-bond network with their neighboring water molecules, rather than to form specific hydration structure with the ions. On the other hand, these “structure breaking” ions are regarded as perturbation of the water’s H-bond structures (Hribar, Southall, Vlachy, and Dill, 2002).

In this study, the characteristics of phosphonium ion (PH_4^+) solvated in aqueous solution is of our interest. PH_4^+ is the smallest form of phosphonium cations (*i.e.*, the species with the chemical formula PR_4^+ , where R = H, alkyl, aryl, halide)

which is found in iodide salt (phosphonium iodide:PH₄I) (Sequeira, Hamilton, Walter 1967). In general, salts of the parent PH₄⁺ are rarely encountered, and this ion is usually used as an intermediate in the preparation of the industrially useful tetrakis(hydroxymethyl)phosphonium chloride (Moiseev and James, 2019). Consequently, the details with respect to the solvation structure and dynamics of PH₄⁺ ion in simple solvent, like water, could be expected to provide fundamental insights into the behaviors of such PH₄⁺ intermediate. It is worth noting that, in aqueous solution, the PH₄⁺ ion could be formed by adding a proton to PH₃. However, the pK_a value of PH₄⁺ is low, indicating that PH₄⁺ is a strong acid with a tendency to readily release a proton. On the other hand, the pK_a value of PH₃ is high, signifying that PH₃ is a weak base and does not readily donate protons, making it less acidic when compared to PH₄⁺. In this respect, the PH₃ molecule is more stable than PH₄⁺, *i.e.*, the formation of PH₄⁺ could be formed as an intermediate in aqueous solution.

Since the PH₄⁺ ion is rather unstable, experimental and theoretical studies of this ion in aqueous solution have not yet been reported in the literature. In this respect, the microscopic details of this specific system could be obtained by performing computer simulations. As compared to the case of ammonium ion (NH₄⁺), an important chemical species which has tetrahedral molecular geometry similar to PH₄⁺, the characteristics of NH₄⁺ in aqueous solution have been extensively studied (Intharathep, Tongraar and Sagarik, 2005; Bruge, Bernasconi, and Parrinello, 1991; Chang, and Dang, 2003; Pálincás, Radnai, Szász, and Heinzinger, 1981). According to the QM/MM MD simulation of NH₄⁺ in aqueous solution (Intharathep, Tongraar and Sagarik, 2005), it has been reported that NH₄⁺ rotates quite fast in the water environment, despite the relatively strong hydrogen bonding between the NH₄⁺ ion and its nearest-neighbor water molecules. Interestingly, it has been shown that the solvation structure of NH₄⁺ is rather flexible, in which many water molecules are cooperatively involved in the solvation shell of the ion. In addition, the QM/MM MD

results clearly demonstrate fast translation and rotation of NH_4^+ in water. These observed phenomena could be ascribed due to the multiple coordination, which drives the NH_4^+ to translate and rotate quite freely within its surrounding water molecules. In this study, it is of particular interest, therefore, to investigate the detailed knowledge with respect to the behaviors of PH_4^+ that solvated in water environment.

In terms of theoretical studies, computer simulations can be considered as an elegant tool for studying condensed-phase systems at molecular level. The advantage of computer simulations is apparent, especially for the treatment of systems where experimental observations are difficult or hardly feasible. With regard to computer simulation techniques, Monte Carlo (MC) and molecular dynamics (MD) are two well-known techniques. For the treatment of such condensed-phase system, the MD technique is more preferential than the MC framework since it can provide both structural and dynamical properties of the system under investigation.

Nowadays, as a consequence of the rapid development in computer capacity and performance, more sophisticated quantum-mechanics-based MD simulations, in which the force on each particle in the system can be computed directly from the first principle calculations, have been well demonstrated. Among the QM-based MD techniques, *ab initio* (AI) MD technique and combined quantum mechanics/molecular mechanics (QM/MM) approach have been widely used for studying various condensed-phase systems (Lyubartsev, Laasonen, and Laaksonen, 2001; Ramaniah, Bernasconi, and Parrinello, 1999; Field, Bash, and Karplus, 1990; Stanton, Hartsough, and Merz, 1995; Gao, 1996; Bernardi, Olivucci, and Robb, 1992; Åqvist and Warshel, 1993; Cummins and Gready, 1997). In general, the main advantage of the AI-MD technique is that the whole system is treated by quantum mechanics, most of which are based on density functional theory (DFT) (Lyubartsev,

Laasonen, and Laaksonen, 2001; Ramaniah, Bernasconi, and Parrinello, 1999). Regarding the AI-MD technique, however, some limitations still exist. Especially for the treatment of aqueous ionic solutions, it has been well demonstrated that the use of relatively small system size may lead to problems of ion-ion interactions (Lyubartsev, Laasonen, and Laaksonen, 2001). In addition, it has been reported that the use of simple DFT functionals may result in too strong ion-H₂O interactions, leading to more rigidity of the structure of ion-H₂O complexes (Schwenk, Loeffler, and Rode, 2001; Vande Vondel, Mohamed, Krack, Hutter, Sprik, and Parrinello, 2005).

Based on the QM/MM MD technique, the most recent approach is to apply a so-called QM/MM MD technique based on the ONIOM-XS method (which will be abbreviated throughout this work as “ONIOM-XS MD”). (Kerdcharoen and Morokuma, 2002; Kerdcharoen and Morokuma, 2003). This technique has been successfully applied for studying various condensed phase systems (Kabbalee, Sripa, Tongraar and Kerdcharoen, 2015; Kabbalee, Tongraar and Kerdcharoen, 2015; Kerdcharoen and Morokuma, 2003, 2002; Sripa, Tongraar and Kerdcharoen, 2016, 2013, 2015, 2017, 2019; Sripradite, Tongraar and Kerdcharoen, 2015; Thaomola, Tongraar and Kerdcharoen, 2012; Wanprakhon, Tongraar and Kerdcharoen, 2011; Chaiyasit, Tongraar and Kerdcharoen, 2017). Of particular interest, in the case of liquid water, the results obtained by the ONIOM-XS MD simulation (Thaomola, Tongraar and Kerdcharoen, 2012) have provided more insights into the multiple HB species among water molecules which correspond to the experimental XAS data for the arrangement of one strong and one weak (for both donor and acceptor), rather than the equivalent two donors and two acceptors tetrahedral structure. In addition, the ONIOM-XS MD technique has been successfully applied for characterizing the “structure-making” and “structure-breaking” abilities of many essential ions in water (Sripa, Tongraar and Kerdcharoen, 2016, 2013, 2015, 2017, 2019; Wanprakhon, Tongraar and Kerdcharoen, 2011). In the present study, therefore, the high-level

ONIOM-XS MD technique will be applied for studying the behaviors of PH_4^+ in aqueous solution. The results obtained by the ONIOM-XS MD simulations are expected to provide fundamental insights into the solvation structure and dynamics of the hydrated PH_4^+ ion.

1.2 Research objectives

1. To apply the high-level ONIOM-XS MD technique for obtaining the detailed knowledge with respect to the behaviors of PH_4^+ in aqueous solution.
2. To test the validity of the HF and B3LYP methods for describing the structural and dynamical properties of PH_4^+ in aqueous solution.

1.3 Scope and limitation of the study

In this work, the high-level ONIOM-XS MD technique will be employed to investigate the structural and dynamical properties of PH_4^+ in aqueous solution. By the ONIOM-XS MD technique, the system is comprised of a “high-level” QM region, *i.e.*, a sphere which contains the PH_4^+ ion and its surrounding water molecules, and the remaining “low-level” MM bulk waters. Since the QM region is regarded as the most interesting part, the selection of QM methods as well as the QM size and basis set are crucial for obtaining reliable results. In practice, these parameters must be optimized, compromising between the quality of the simulation results and the requirement of the CPU time. Particularly, it should be noted that the use of correlated QM calculations, even at the simple MP2-level of accuracy, is still too time-consuming, *i.e.*, beyond our computational feasibility. In this study, two ONIOM-XS MD simulations will be separately performed, in which all interactions within the QM-treated region are evaluated through *ab initio* calculations at the Hartree-Fock (HF) and Becke-3-parameter-Lee-Yang-Parr (B3LYP) levels of accuracy, respectively, using a moderate df2-SVP basis set (Zheng, Xu, and Truhlar, 2011). For the QM size, a

QM radius of 4.4 Å and a switching width of 0.2 Å were chosen, corresponding to the ONIOM-XS parameters r_0 and r_1 of 4.4 and 4.6 Å, respectively. During the ONIOM-XS MD simulations, it was observed that there were about 10-11 water molecules involved within the QM-treated region. The structural properties of the hydrated PH_4^+ will be analyzed in terms of a set of radial distribution functions (RDFs) and their corresponding integration numbers, together with the angular distribution functions (ADFs) and the orientations of water molecules surrounding the ion. The dynamical properties will be characterized through the mean residence times (MRTs) of nearest-neighbor water molecules and the water exchange processes at the ion.

1.4 References

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