

CHAPTER III

RESULTS AND DISCUSSION

3.1 HF-based ONIOM-XS MD simulation

3.1.1 Structural properties

Structural properties of the solvated PH_4^+ are characterized through a series of P-O_w , P-H_w , $\text{H}_p\text{-O}_w$, and $\text{H}_p\text{-H}_w$ radial distribution functions (RDFs) and their corresponding integration numbers, as shown in Figure 3.1. In this context, the first atom in the RDFs refers to the atom of PH_4^+ , and the latter, with the subscript “W”, represents the atom of water molecules. According to Figure 3.1a, the HF-based ONIOM-XS MD simulation reveals a broad unsymmetrical first P-O_w peak with two maxima at 2.98 and 3.65 Å, respectively, which correspond to two possible geometrical arrangements of the PH_4^+ -water complexes, *i.e.*, a trifurcate configuration in which each water molecule is hydrogen-bonded to three hydrogen atoms of PH_4^+ (type 1) and another configuration where water molecules are directly hydrogen-bonded to each hydrogen atom of PH_4^+ (type 2). Note that, in gas-phase, the geometry optimizations of $\text{PH}_4^+(\text{H}_2\text{O})_4$ complexes with respect to type 1 and type 2 configurations, as obtained by the HF calculations using the def2-SVP basis sets (Zheng, Xu, and Truhlar, 2011), yield the P-O_w distances of 2.86 and 3.50 Å together with the stabilization energies of -58.31 and -48.96 kcal.mol⁻¹, respectively. In aqueous solution, however, it could be expected that some nearest-neighbor water molecules could also prefer to form bifurcated complex between two hydrogen atoms of PH_4^+ (type 3). The shape and height of the first P-O_w RDF, together with a considerable tailing up to around 5 Å, clearly suggests a high flexibility of the PH_4^+

solvates. In addition, the first P-O_W peak is not well separated from the bulk, indicating that water molecules surrounding the PH₄⁺ ion are highly labile, *i.e.*, they are weakly induced by the ion. According to Figure 3.1a, an integration up to the P-O_W distance of 5 Å (*i.e.*, a rough estimated first minimum of the P-O_W peak) yields about 16 water molecules. Regarding the broad and unsymmetrical first P-O_W peak, this observed large number of water molecules can certainly not be assigned as the first-shell coordination number of PH₄⁺. Instead, it could be demonstrated as a combination of nearest-neighbor water molecules those that are arranged according to the influence of PH₄⁺ and those that are arranged within the vicinity of the ion with respect to the HB interactions among the water molecules. In addition, according to Figure 3.1a, the smooth shape of the P-O_W RDF between 4.4 and 4.6 Å (*i.e.*, between the ONIOM-XS parameters r_0 and r_1) clearly implies that the interchange of water molecules between the QM and MM regions occurs smoothly. In this sense, it could be expected that the ion-water and water-water interactions beyond the QM region are well accounted for by the MM potentials.

The HB interactions between PH₄⁺ and its surrounding water molecules can be analyzed through the H_P-O_W and H_P-H_W RDFs, as depicted in Figure 3.1c and d, respectively. According to Figure 3.1c, the non-pronounced peak of the H_P-O_W RDFs between 1.8-2.0 Å clearly suggests that the HB interactions between PH₄⁺ and its nearest-neighbor water molecules are relatively weak, *i.e.* when compared to the case of NH₄⁺-water HBs in aqueous solution (Intharathep, Tongraar and Sagarik, 2005) as well as to the water-water HBs in the bulk (Thaomola, Tongraar and Kerdcharoen, 2012). The HF-based ONIOM-XS MD results clearly point out that the HB interactions between PH₄⁺ and its surrounding water molecules could be expected to occur at the H_P-O_W distances beyond 2.0 Å. Note that the gas-phase geometry optimizations of PH₄⁺-(H₂O)₄ complexes with respect to type 1 and type 2 configurations predict the H_P-O_W distances of 2.73 and 2.10 Å, respectively.

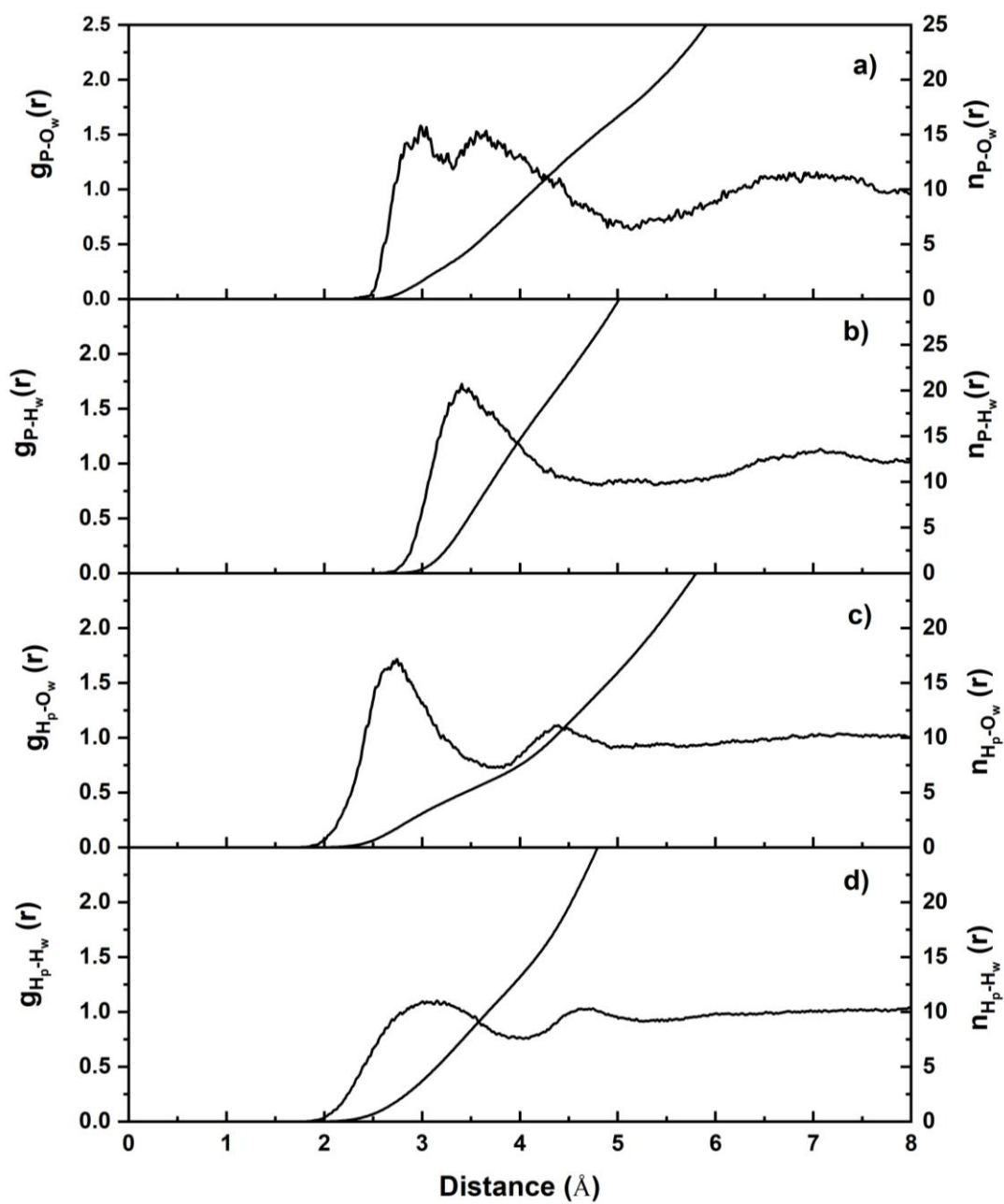


Figure 3.1 a) P-O_w, b) P-H_w c) H_p-O_w and d) H_p-H_w radial distribution functions and their corresponding integration numbers, as obtained by the HF-based ONIOM-XS MD simulation.

Figure 3.2 displays the probability distributions of the number of oxygen atoms of nearest-neighbor waters, calculated up to the P-O_w distances of 3.8, 4.0, 4.2, 4.4 and 5.0 Å, respectively. It is obvious that a small shift of the P-O_w distance will have significant impact on the number of water molecules. Since the HB interactions between PH₄⁺ and its surrounding water molecules are weak, the P-O_w distance of 3.8 Å is selected as rough estimate for the longest distance of nearest-neighbor water molecules that able to form HB to hydrogen atoms of PH₄⁺. According to Figure 3.2a, it is observed that various numbers of water molecules, ranging from 3 to 11, are cooperatively involved within the P-O_w distance of 3.8 Å. The observed broad distributions of oxygen atoms of nearest-neighbor waters, with the most frequent numbers of 7±1, provide clear evidence for the formation of a rather weak and unstructured solvation shell of PH₄⁺.

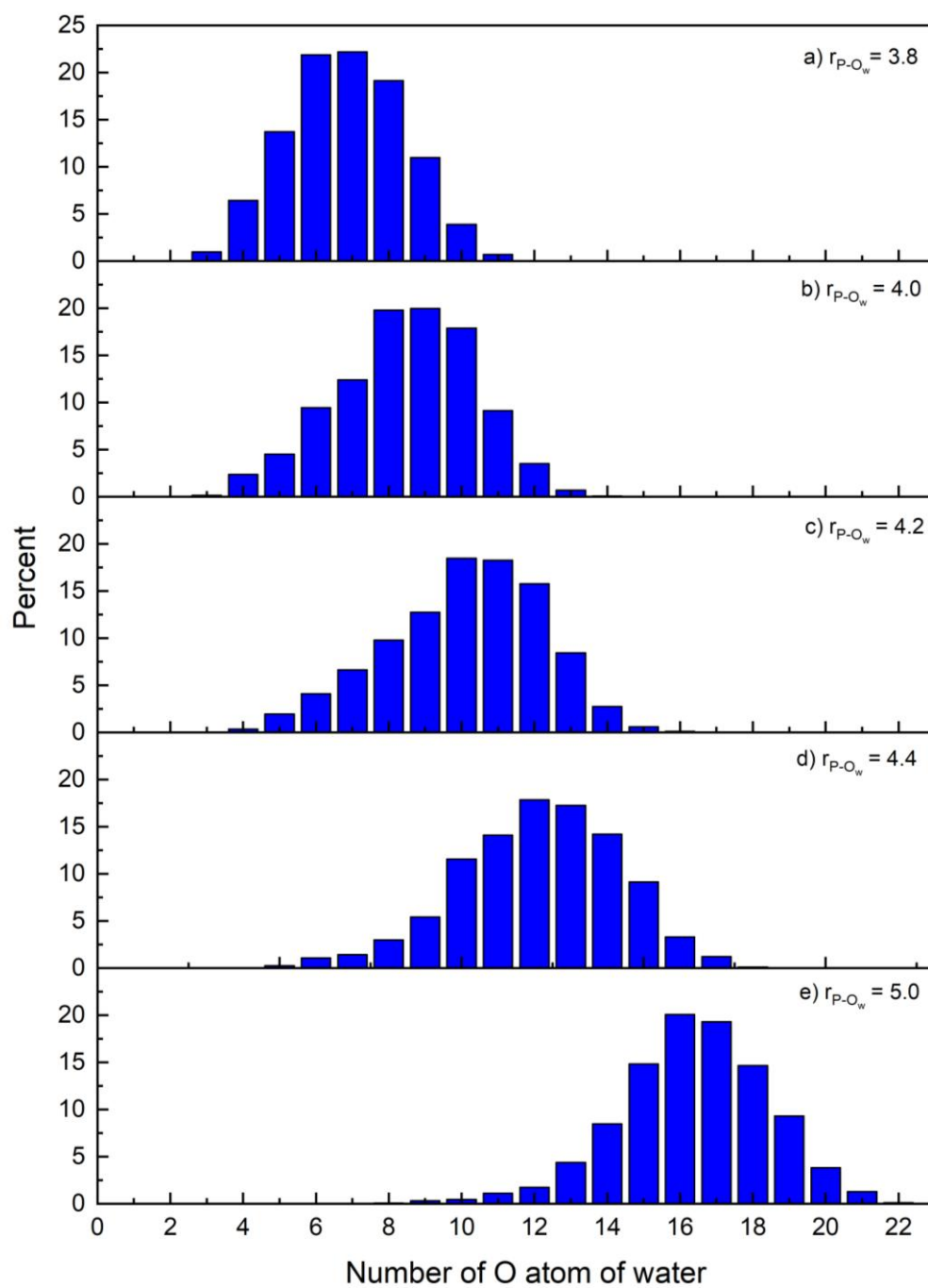


Figure 3.2 Probability distributions of water's oxygen atoms, calculated up to the P-O_w distances of 3.8, 4.0, 4.2, 4.4 and 5.0 Å, respectively, as obtained by the HF-based ONIOM-XS MD simulation.

Figure 3.3 displays the H_P-P-O_w angular distributions, calculated up to the $P-O_w$ distance of 3.8 Å. The geometrical arrangement of the PH_4^+ -water complexes with respect to type 1 configuration could be recognized from the two pronounced peaks between 60–80° and between 160–180°. In conjunction with type 1 configuration, the arrangement of the bifurcated structure (type 3) could also be recognizable from the two pronounced peaks between 60–80° and between 110–130°. In contrast, the probability of finding type 2 configuration becomes less visible, as can be seen from the less pronounced peaks between 0–20°. As can be seen in Figure 3.3, the observed broad distributions of the H_P-P-O_w angle clearly supplies information that water molecules surrounding the PH_4^+ ion are rather labile, *i.e.*, they are arranged with respect to small influence of the ion.

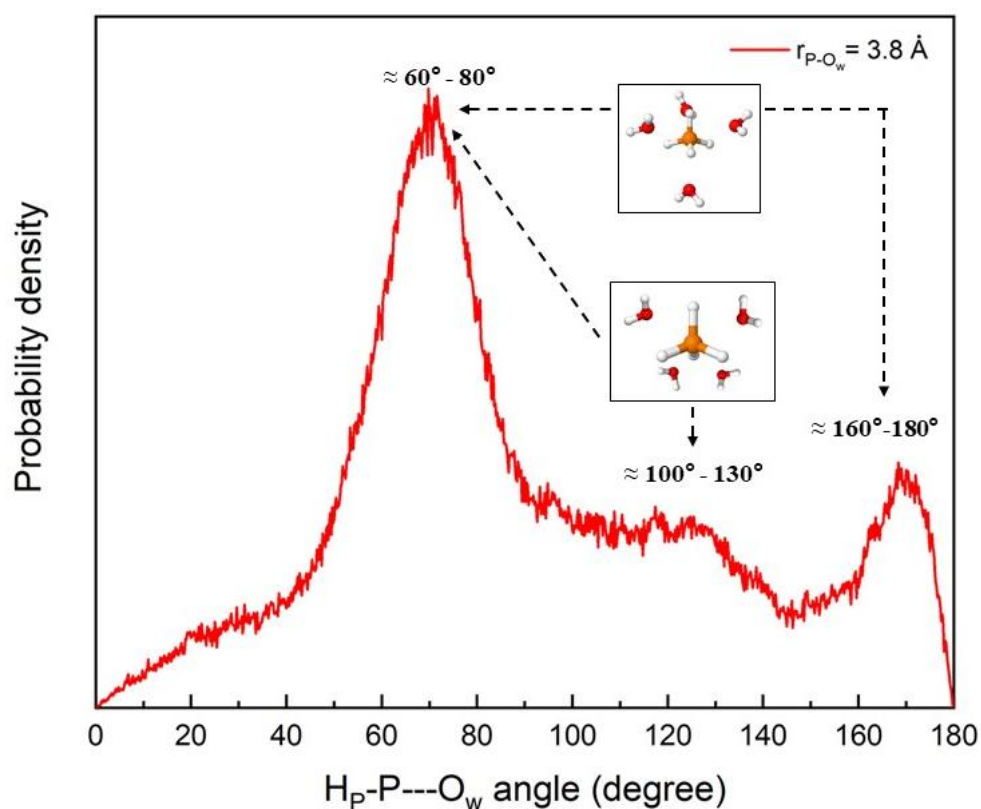


Figure 3.3 Angular distribution function (ADF) of $H_P-P---O_W$ angle, calculated up to the $P-O_W$ distance of 3.8 Å, as obtained by the HF-based ONIOM-XS MD simulation.

Figures 3.4 and 3.5 provide more detailed information on the arrangements of water molecules surrounding the ion. According to Figure 3.4, the pronounced peak of the $O_W---P---O_W$ ADF between 40-60° clearly indicates the appearance of HB interactions between the nearest-neighbor water molecules. In Figure 3.5, the pronounced peak of the $P-H_P---O_W$ ADF with maximum at about 80° clearly supports the arrangement of nearest-neighbor water molecules with respect to type 1 and 3 configurations.

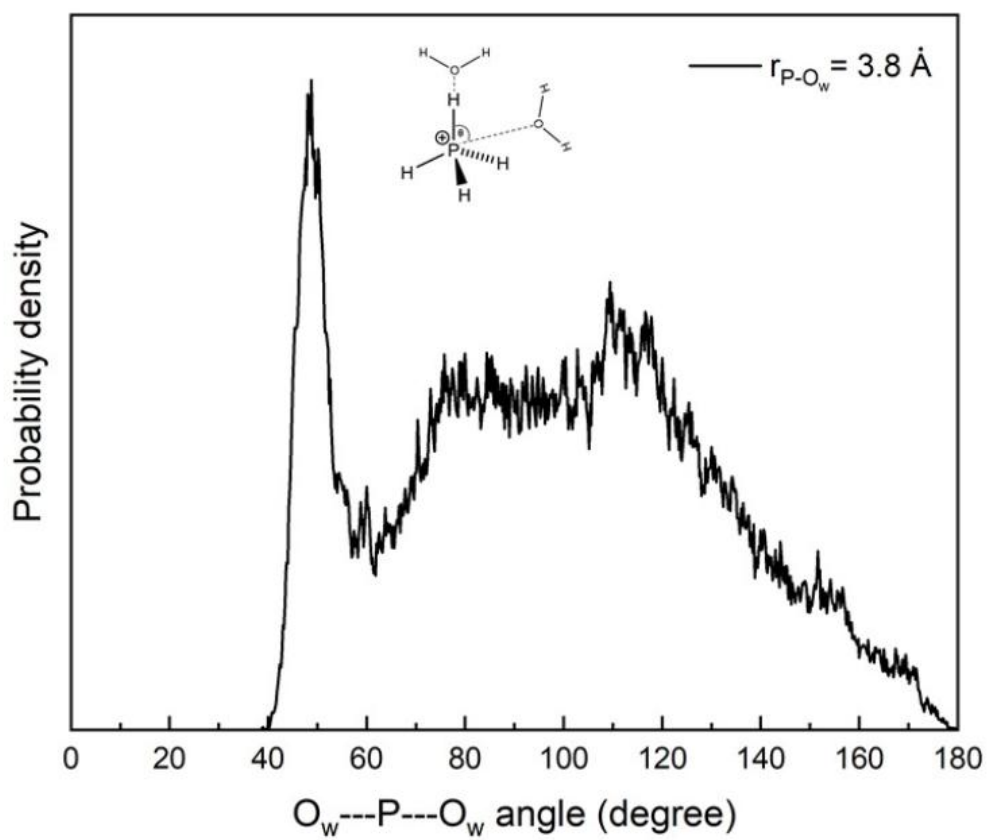


Figure 3.4 Angular distribution function (ADF) of $O_w \cdots P \cdots O_w$ angle, calculated up to the $P-O_w$ distance of $3.8 \text{ \AA}$, as obtained by the HF-based ONIOM-XS MD simulation.

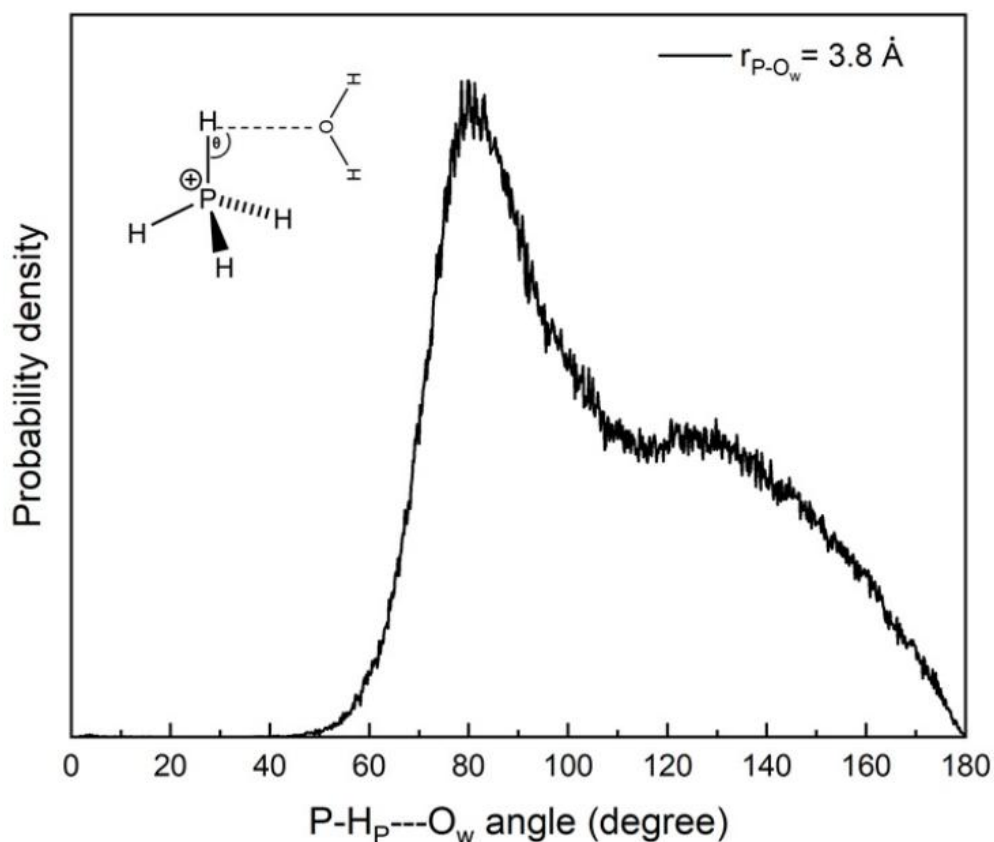


Figure 3.5 Angular distribution function (ADF) of P-H_p---O_w angle, calculated up to the P-O_w distance of 3.8 Å, as obtained by the HF-based ONIOM-XS MD simulation.

3.1.2 Dynamical properties

The dynamical properties of the weakly bound PH₄⁺ solvation could be analyzed through the self-diffusion coefficients (D). The D value for water molecules that are arranged within the P-O_w distance of 3.8 Å was calculated from the center-of-mass velocity autocorrelation functions (VACFs) using the Green-Kubo relation (MaQuarrie, 1976),

$$D = \frac{1}{3} \lim_{t \rightarrow \infty} \int_0^t C_v(t) dt. \quad (3.1)$$

The D values for nearest-neighbor water molecules, calculated within the P-O_w distance of 3.8 Å, together with the corresponding value for pure water, as

derived by the analogous HF-based ONIOM-XS MD scheme (Thaomola, Tongraar and Kerdcharoen, 2021), are summarized in Table 3.1. Based on the HF-based ONIOM-XS MD simulation, the D value for the nearest-neighbor water molecules is estimated to be $3.22 \times 10^{-5} \text{ cm}^2.\text{s}^{-1}$. As compared to the value of $2.73 \times 10^{-5} \text{ cm}^2.\text{s}^{-1}$ for pure water (Thaomola, Tongraar and Kerdcharoen, 2021), it is apparent that the HB interactions between PH_4^+ and its surrounding water molecules are weak and are comparable to that of water-water HBs in the bulk. In this respect, the influence of the PH_4^+ ion can be considered as causing perturbation to the water's HB networks.

Table 3.1 D values of water molecules in the bulk and in the defined hydration sphere of PH_4^+ , as obtained by the HF-based ONIOM-XS MD simulation.

Phase	$D \text{ (cm}^2.\text{s}^{-1}\text{)}$
Hydration sphere of PH_4^+	3.22×10^{-5}
Pure water ^a	2.73×10^{-5}

^a (Thaomola, Tongraar and Kerdcharoen, 2012)

Figure 3.6 shows the time dependence of the number of nearest-neighbor waters, *i.e.*, the number of water molecules having oxygen atom's positions located within the P-O_w distance of $3.8 \text{ \AA}$, together with some selected geometrical arrangements of the PH_4^+ -water configurations showing the HB formations between the ion and its nearest-neighbor water molecules, *i.e.*, the dash lines highlighted in “red” representing the HB formations among PH_4^+ and it's nearest-neighbor water and the dash lines highlighted in “blue” representing the HB formations among the nearest-neighbor waters. Note that, according to the selected PH_4^+ -water complexes in Figure 3.6, the dash lines representing the HB interactions are highlighted only for those within the HB distance of $2.5 \text{ \AA}$. Figure 3.7 provides the extension of the

selected PH_4^+ -water conformations, as depicted in Figure 3.6, which includes some water molecules located beyond the P-O_w distance of $3.8 \text{ \AA}$ (labeled in “green”) that can mutually form HBs with the nearest-neighbor waters. The ONIOM-XS MD results clearly confirm that the solvation shell of PH_4^+ in aqueous solution is rather unstructured and diffuse, and that water molecules surrounding the ion are arranged with respect to the delicate balance between the influence of the ion and the forces exerted by the neighboring water molecules in the same shell and/or the bulk.

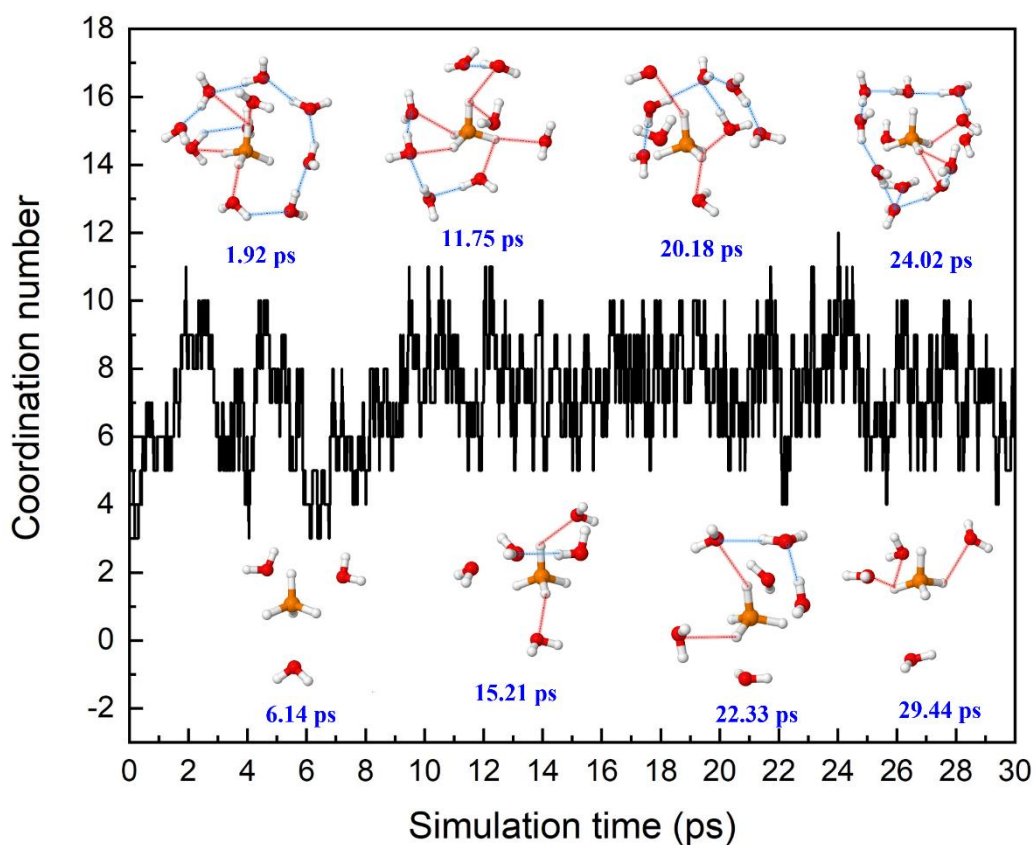


Figure 3.6 Time dependences of the number of water molecules located within the P-O_w distance of $3.8 \text{ \AA}$, together with some geometrical arrangements of the PH_4^+ -water complexes showing the HB interactions between PH_4^+ and its nearest-neighbor waters (*i.e.*, the dash lines highlighted in “red”), as well as the HB interactions between the nearest-neighbor waters (*i.e.*, the dash lines highlighted in “blue”), selected only for the first 30 ps of the HF-based ONIOM-XS MD data collection.

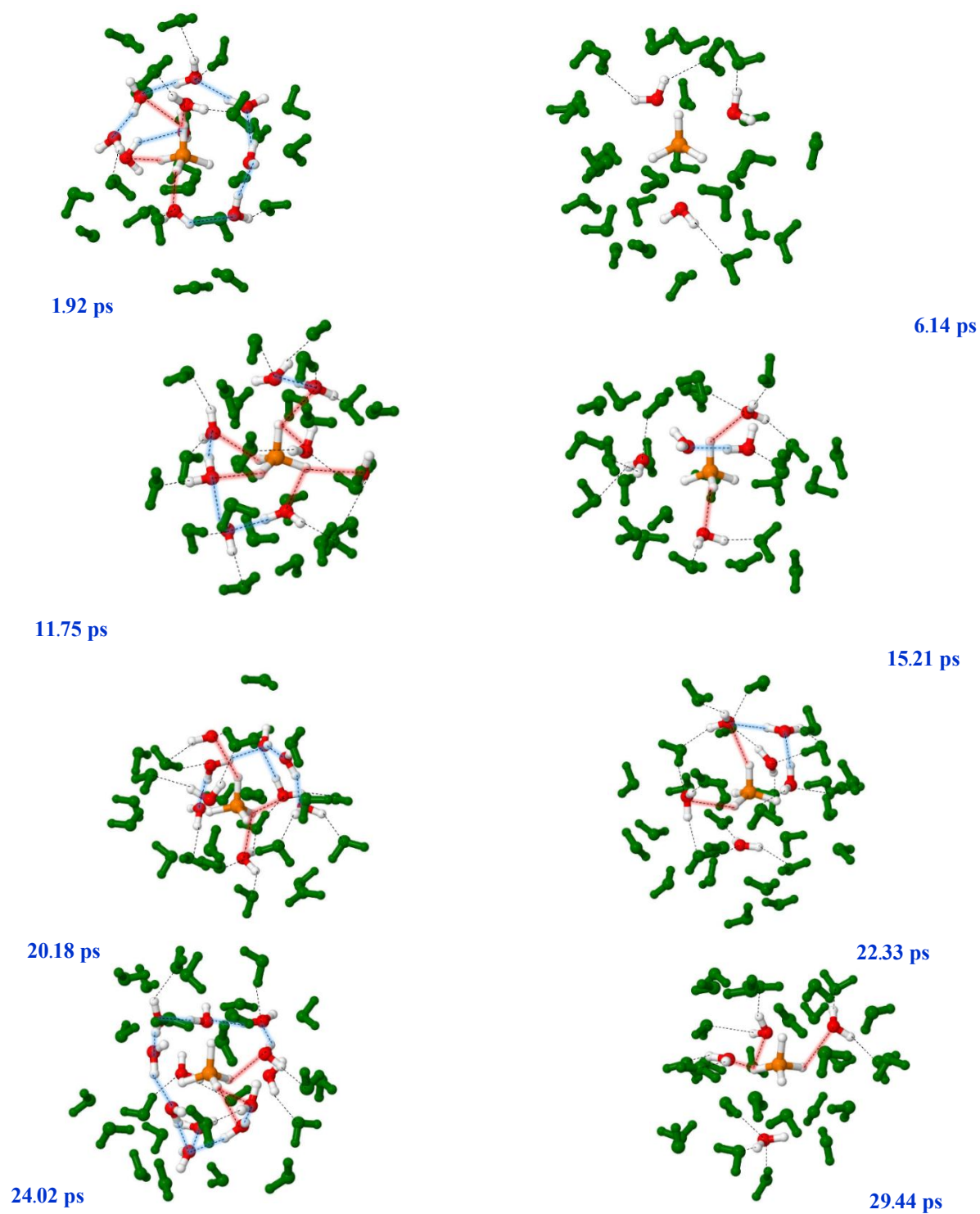


Figure 3.7 Selected geometrical arrangements of the PH_4^+ -water complexes in Figure 3.6, which include some water molecules in the outer region (labeled in “green”). The dash lines (without highlight) refer to the HB interactions between water

molecules located within the P-O_w distance of 3.8 Å and other water molecules in the outer region.

The lability of water molecules surrounding the ion was further analyzed through the mean residence times (MRT) using the direct method (Hofer, Tran, Schwenk and Rode, 2004), being the product of the average number of nearest-neighbor water molecule locate within the defined solvation shell with the duration of the ONIOM-XS MD simulation, divided by the observed number of exchange events lasting a given time interval t^* ,

$$MRT(\tau) = \frac{CN \times t_{sim}}{N_{ex}}. \quad (3.2)$$

According to the diffuse character of the PH₄⁺ solvation, the P-O_w distance of 3.8 Å was selected, assuming to be rough estimate of the first solvation shell and a limit for significant ion-water interactions. All the calculated MRT values are summarized in Table 3.2, together with the corresponding values for pure water (Thaomola, Tongraar, and Kerdcharoen, 2012). Based on the HF-based ONIOM-XS MD simulation, the MRT data of water molecules involved in the PH₄⁺-water HBs are estimated to be 0.19 and 2.03 ps for the time parameters t^* of 0.0 and 0.5 ps, respectively. Note that, according to the direct method, the t^* value of 0.0 ps was proposed as a suitable choice for the estimation of HB lifetime, while the t^* value of 0.5 ps was used as a good measure for water exchange processes. As compared to the corresponding MRT values of 0.23 and 2.17 ps for pure water (Thaomola, Tongraar, and Kerdcharoen, 2012), it is apparent that the ability of PH₄⁺ to order its surrounding water molecules is small. Hence, the nearest-neighbor waters favor to arrange according to the forces exerted by the neighboring water molecules in the same shell and/or the bulk, rather than by the influence of the ion.

Table 3.2 Mean residence times (MRTs) of water molecules in the bulk and in the vicinity of PH_4^+ , as obtained by the HF-based ONIOM-XS MD simulation.

Ion/solute	CN	t_{sim}	$t^* = 0.0 \text{ ps}$		$t^* = 0.5 \text{ ps}$	
			$N_{ex}^{0.0}$	$\tau_{\text{H}_2\text{O}}^{0.0}$	$N_{ex}^{0.5}$	$\tau_{\text{H}_2\text{O}}^{0.5}$
PH_4^+	6.8	60.0	2142	0.19	202	2.03
H_2O^a	4.7	30.0	607	0.23	65	2.17

^a (Thaomola, Tongraar and Kerdcharoen, 2012)

Additional information on the dynamical properties of water molecules surrounding the ion can be gained by computing the velocity autocorrelation functions (VACFs) and their corresponding Fourier Transformations. According to the normal-coordinate analysis developed by Bopp (Bopp, 1986), the three quantities, namely Q_2 , Q_1 and Q_3 , which are defined for describing bending vibration, symmetric and asymmetric vibrations of water molecules, respectively, are summarized in Table 3.3. Since the HF calculations usually produce vibrational frequencies that are too high, all frequencies were multiplied by a scaling factor of 0.905 (Scott and Radom 1996). According to the data in Table 3.3, it is obvious that the vibrational frequencies of water molecules surrounding the ion are not much different to that of water molecules in the bulk (Thaomola, Tongraar, and Kerdcharoen, 2012), confirming the small influence of PH_4^+ in ordering its surrounding water molecules. Overall, the ONIOM-XS MD results clearly reveal a high flexibility of the loosely bound PH_4^+ solvation, and thus supporting the “structure-breaking” ability of PH_4^+ in water.

On the basis of the HF-based ONIOM-XS MD simulation, since the electron correlation and the charge transfer effects are not typically well-described by the HF theory, it is worth noting that the interactions of particles within the defined QM region could be somewhat underestimated. However, according to a series of QM/MM MD simulations, namely HF/MM, B3LYP/MM and MP2/MM, which have been performed for studying the properties of liquid water (Xenides, Randolph and Rode, 2005), it has been shown that the use of the HF method with sufficiently large QM size can provide simulation results in good accord with those obtained by the correlated MP2 calculations. In addition, the HF method has been successfully employed for numerous QM/MM and ONIOM-XS MD studies of 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). In this work, therefore, the results obtained by the HF-based ONIOM-XS MD simulation are expected to provide reliable detailed knowledge with respect to the behaviors of PH_4^+ in aqueous solution. Consequently, the HF-based ONIOM-XS MD technique could be seen as an elegant simulation technique for the future work, especially for the study of more complicated phosphonium ions, such as methylphosphonium ion (CH_3PH_3^+), in aqueous solution.

Table 3.3 Power spectra of the vibrational motions of water molecules in the bulk and in the defined hydration sphere of PH_4^+ .

Ion/solute	Frequency (cm^{-1})		
	Q_1	Q_2	Q_3
PH_4^+	4030	1673	3731
H_2O^a	3606	1660	3720

^a (Thaomola, Tongraar and Kerdcharoen, 2012)

3.2 B3LYP-based ONIOM-XS MD simulation

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, the system was initially equilibrated by using the starting configuration obtained from the HF-based ONIOM-XS MD simulation. The P-O_w , P-H_w , $\text{H}_p\text{-O}_w$, and $\text{H}_p\text{-H}_w$ RDFs and their corresponding integration numbers, as obtained from the 4 ps of the re-equilibration step, are depicted in Figure 3.8. As can be seen in Figure 3.8c, a small pronounced peak at the $\text{H}_p\text{-O}_w$ distance of about 1 Å clearly indicates the formation of $\text{H}_p\text{-O}_w$ covalent bond. With regard to the population analysis on the charges of P and H atoms of PH_4^+ , it was observed that, during the equilibration process, one proton of PH_4^+ has transferred to one of nearest-neighbor waters, leading to the formations of PH_3 and H_3O^+ species (cf. See Figure 3.9). This implies that the B3LYP method is not applicable for describing the behaviors of PH_4^+ in aqueous solution. On the other hand, it could be demonstrated that the life span of the PH_4^+ intermediate according to the B3LYP calculations is too short to investigate the behaviors of such intermediate in aqueous solution. The failure of the B3LYP method has been well demonstrated in the literature. For example, according to the previous

B3LYP/MM MD simulation of liquid water (Xenides, Randolf and Rode, 2005), it has been shown that the B3LYP method predicted a too rigid water structure as well as too slow exchange rates.

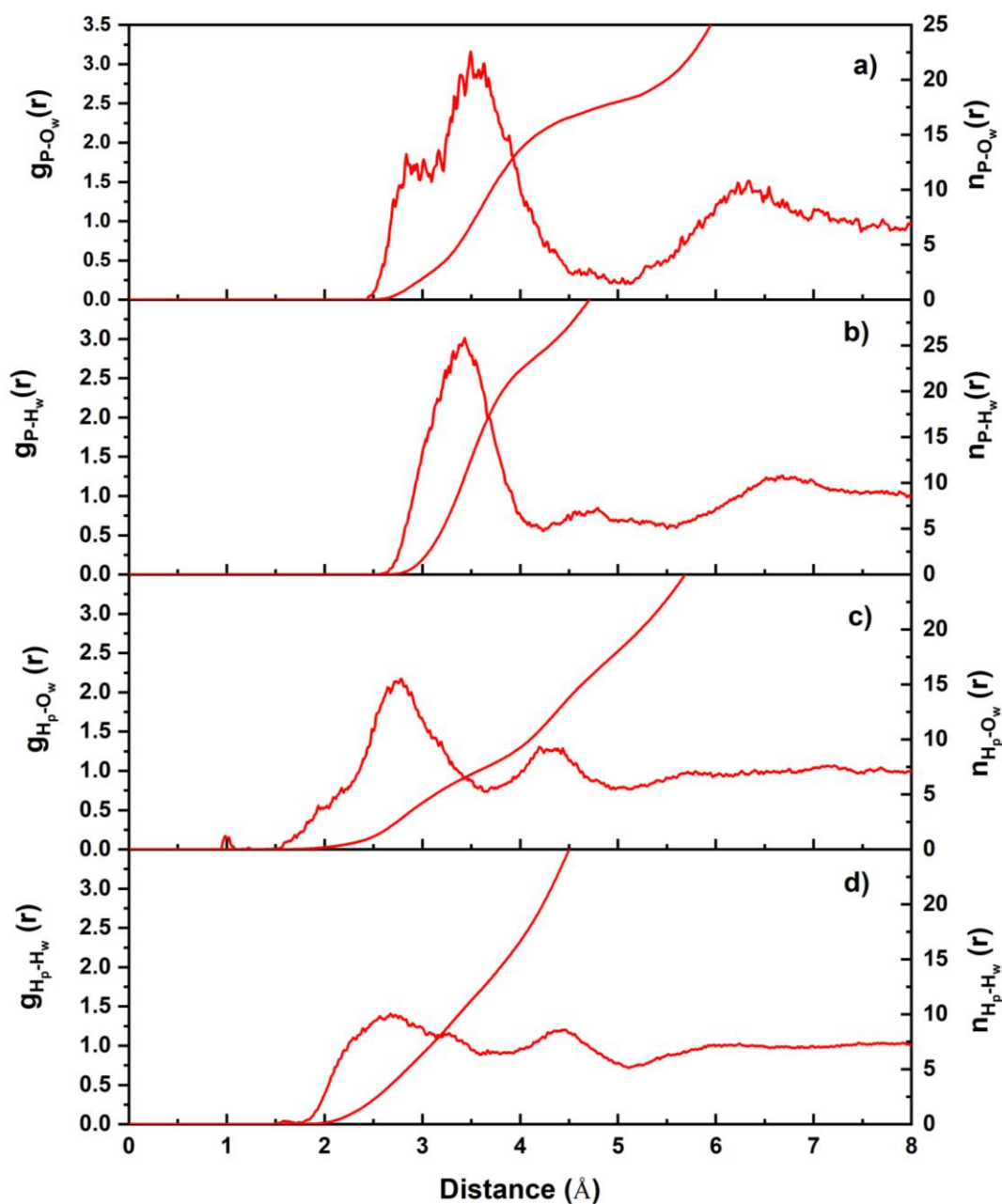


Figure 3.8 a) P-O_W, b) P-H_W, c) H_P-O_W and d) H_P-H_W radial distribution functions and their corresponding integration numbers, as obtained by the B3LYP-based ONIOM-XS MD simulation.

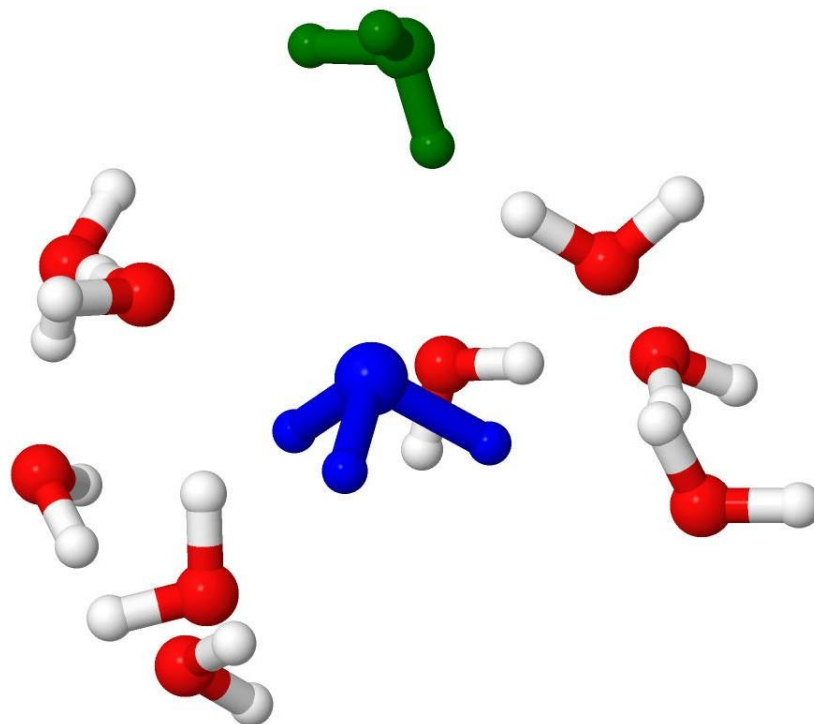


Figure 3.9 A snapshot of the B3LYP-based ONIOM-XS MD trajectories, showing the formations of PH_3 and H_3O^+ species.

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