

THE CHARACTERISTICS OF PHOSPHONIUM ION (PH₄⁺) IN WATER: AN ONIOM-XS MD STUDY

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Received: October 17, 2025; Revised: February 02, 2026; Accepted: February 05, 2026

Abstract

The characteristics of phosphonium ion (PH₄⁺) in aqueous solution were studied by an ONIOM-XS molecular dynamics (MD) simulation, which describes the interactions between PH₄⁺ and the surrounding waters based on the HF/def2-SVP model. Detailed analyses of the ONIOM-XS MD trajectories clearly show that the solvation structure of PH₄⁺ hydrate is less organized and asymmetric, consisting of between 3 and 11 neighboring water molecules. The hydrogen bonds between PH₄⁺ and the neighboring waters are rather weak, *i.e.*, compared to the case of NH₄⁺ in aqueous solution or compared to the hydrogen bonds in bulk water. These observations align with the classification of PH₄⁺ as a “structure-breaking” ion in water.

Keywords: Hydrogen Bonds; Hartree-Fock; ONIOM-XS MD; Structure-Breaking

Introduction

Insights into the structural aspect and associated dynamics of ion solvation in aqueous solutions have been extensively explored through experimental and theoretical approaches. The detailed knowledge gained from these studies is crucial for describing the function and reactivity of ions in chemical and biological systems (Barbara *et al.*, 2002; Sequeira and Hamilton, 1967; Moiseev and James, 2019). It is well known that, when dissolved in water, ions can significantly alter the local hydrogen-bond (HB) structure and affect the mobility of neighboring water molecules. In aqueous systems, “structure-making” ions are defined as ions that

reorganize the HB framework of the surrounding water molecules, promoting the formation of a more ordered ion-water structure. In contrast, the term “structure-breaker” refers to large, highly polarized ions whose interactions with neighboring waters are comparable to or weaker than the water-water HB interactions. As a result, water molecules around the ions tend to maintain their HB network with nearby waters, rather than forming stable complexes with the ions. Therefore, these “structure-breaking” ions act as perturbations, weakening or distorting the HBs in liquid water.

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This study focuses on the behavior of phosphonium ion (PH₄⁺) dissolved in the HB network of water. PH₄⁺ is the simplest form of the phosphonium ion family (PR₄⁺, where R = H, alkyl, aryl, or halide) and is most commonly found in the form of phosphonium iodide (PH₄I) (Sequeira and Hamilton, 1967). Due to their inherent instability, the PH₄⁺ salts are rarely isolated and are commonly used as intermediates in the synthesis of industrial compounds such as tetrakis (hydroxymethyl) phosphonium chloride (Moiseev and James, 2019). In particular, phosphonium-based ionic liquids (ILs) are increasingly favored in green chemistry as thermally stable, non-volatile alternatives to hazardous organic solvents, allowing for safer reaction environments and high recyclability (Fraser and MacFarlane, 2009). In extraction processes, these ions demonstrate exceptional selectivity for recovering precious metals and organic acids from complex industrial waste streams, often outperforming traditional nitrogen-based counterparts. Furthermore, their unique ability to form aqueous biphasic systems and facilitate efficient CO₂ capture highlights their critical role in developing sustainable, low-emission separation technologies (He *et al.*, 2019). Based on theoretical investigations, molecular dynamics (MD) techniques using quantum mechanics, such as ONIOM-XS MD (Kerdcharoen and Morokuma, 2002, 2003; Wanprakhon *et al.*, 2011; Thaomola *et al.*, 2012; Kabbalee *et al.*, 2015a, 2015b; Sripradite *et al.*, 2015; Chaiyasit *et al.*, 2017; Sripa *et al.*, 2013, 2015, 2016, 2017, 2020), represent a promising approach for studying condensed-phase systems, providing detailed information, especially where experimental access is limited. Therefore, the ONIOM-XS MD framework was employed to explore the structure and some relevant dynamic details of the PH₄⁺ hydrates in water.

Method

The concept and algorithm of the ONIOM-XS MD technique have been described in detail in literature (Kerdcharoen and Morokuma, 2002, 2003; Wanprakhon *et al.*, 2011; Thaomola *et al.*, 2012; Kabbalee *et al.*, 2015a, 2015b; Sripradite *et al.*, 2015; Chaiyasit *et al.*, 2017; Sripa *et al.*, 2013, 2015, 2016, 2017, 2020;). Briefly, this technique divides the entire system into two parts: the QM subsystem, *i.e.*, a sphere where the interactions between PH₄⁺ and the neighboring waters are described by means of quantum mechanics calculations, and the MM region, where all particle interactions within the MM region and

between the QM and MM regions are modeled using appropriate molecular mechanical force fields. In this study, the QM subsystem was set to have a radius of 4.6 Å, corresponding to the ONIOM-XS parameters: $r_0 = 4.4$ Å and $r_1 = 4.6$ Å, with a switching width of 0.2 Å. It is assumed that this QM size is large enough to allow a continuous and stable transition of forces between the QM and MM regions. During the ONIOM-XS MD simulation, a number of water molecules, ranging from 8 to 18, were found to be involved in this QM region. All interactions within the defined QM region were obtained from *ab initio* Hartree-Fock (HF) calculations using the def2-SVP basis set (Zheng *et al.*, 2011), with TURBOMOLE 7.3. Note that, the size of the QM, together with the chosen level of theory and basis set, represents a good compromise in terms of computational cost and simulation accuracy. In particular, the HF method has been proven to be a reliable choice in previous QM/MM and ONIOM-XS MD studies of various condensed-phase systems (Kerdcharoen and Morokuma, 2002, 2003; Kabbalee *et al.*, 2010, 2015; Wanprakhon *et al.*, 2011; Thaomola *et al.*, 2012; Sripa *et al.*, 2013; Sripradite *et al.*, 2015; Chaiyasit *et al.*, 2017; 2015, 2016, 2017, 2020). Interestingly, according to a comparative study of liquid water using the HF/MM B3LYP/MM and MP2/MM MD models, it has been shown that when the QM region is sufficiently large, the HF/MM MD yields results in consistent with the MP2/MM MD, while the B3LYP/MM MD tends to over-stabilize the HB structure of water (Xenides *et al.*, 2005). The interactions of water molecules within the MM region and between the QM and MM regions were described by flexible BJH-CF2 potentials, which include both intra - and intermolecular terms (Stillinger and Rahman, 1976; Bopp *et al.*, 1983). Classical pair potential functions for describing the interactions between PH₄⁺ and water were newly developed using 20, 347 HF/def2-SVP-energy points calculated from diverse PH₄⁺-H₂O configurations, and fitted to the analytical expression of

$$\Delta E_{PH_4^+-H_2O} = \sum_{i=1}^5 \sum_{j=1}^3 \left(\frac{A_{ij}}{r_{ij}^4} + \frac{B_{ij}}{r_{ij}^6} + C_{ij} \exp(-D_{ij}r_{ij}) + \frac{q_i q_j}{r_{ij}} \right), \quad (1)$$

With regard to the reproduction of reference HF interaction energies, various PH₄⁺-H₂O configurations employed in the HF calculations were generated by varying the distance (r) and relative orientations (angles θ , ϕ) between a single PH₄⁺ ion and one H₂O molecule, with emphasis on minimum energy and repulsive barriers (short

distances). The binding energy for each $\text{PH}_4^+ \text{-H}_2\text{O}$ configuration can be calculated using the supermolecular approach (e.g., $E_{\text{inter}} = E_{\text{complex}} - (E_{\text{ion}} + E_{\text{water}})$). According to equation (1), the atomic charges used for each species were defined prior to the fitting procedure. The charge values for the P and H atoms of PH_4^+ were set to +0.3166 and +0.1708, respectively. For H_2O , the charge values of -0.6598 and +0.3299 for the O and H atoms, respectively, were adopted from the BJH-CF2 model (Stillinger and Rahman, 1976). In expression (1), A - D are fitted parameters (Table 1), r_{ij} denotes interatomic distances between the PH_4^+ ion and the i -th atom of water, while q_i and q_j denote the corresponding atomic charges. Note that, following the nonlinear least squares algorithm, the goal is to minimize the residual sum of squares (RSS), which measures the discrepancy between the HF energies and the energies predicted by the analytical formula in equation (1). Since the $\text{PH}_4^+ \text{-H}_2\text{O}$ interaction involves strong ion-dipole forces, i.e., the total interaction energies are much larger than those of neutral molecules, the root mean square (RMS) error is set to be less than 0.2 kcal.mol⁻¹, together with a relative error of less than 5% of the total binding energy at the minimum. In practice, once the fitted parameters are obtained, the fitted potential functions must be validated, i.e., by plotting the fitted potential curve against the HF data points to check for “ghost” minima or poor tuning in the repulsing wall, or by performing a test MD simulation of one PH_4^+ ion in a box of water molecules to ensure that the fitted potential functions are “transferable” and physically reasonable.

The ONIOM-XS MD simulation was carried out in the NVT ensemble at 298 K, with periodic boundary conditions. The cubic box contained one PH_4^+ and 199 H_2O molecules (18.19 Å per side). The Berendsen algorithm (Berendsen *et al.*, 1984) was used for controlling the system's temperature. The particle motions were integrated using a generalized predictor-corrector algorithm ($\Delta t = 0.2$ fs). The cutoff values for Coulombic and non-Coulombic interactions are constrained by the minimum image convention, which is 9.095 Å (e.g., half the length of the simulation box). The reaction-field procedure (Adams *et al.*, 1979) was applied to maintain long-range interactions. After 20,000 steps of equilibration, trajectories were collected every 10th step over 300,000 production steps.

Results and discussion

The radial distribution functions (RDFs) for the P-O_w, P-H_w, H_p-O_w, and H_p-H_w atom pairs, along

with their associated integration numbers, were analyzed to investigate the solvation structure of PH_4^+ in water, as shown in Figure 1. Here, the initial atom represents a site within the PH_4^+ ion, while the latter atom with subscript “w” denotes the water atoms. In Figure 1a, the P-O_w RDF displays a broad and asymmetric peak, with two recognizable maxima at 2.98 and 3.65 Å. The feature of the P-O_w RDF is explainable since geometry optimizations of $\text{PH}_4^+ \text{-(H}_2\text{O)}_4$ complexes in the gas phase, as obtained from the HF/def2-SVP calculations, reveal two possible conformations, namely (type 1) a trifurcate structure where each water molecule forms HBs with three hydrogen atoms of PH_4^+ , and (type 2) a conformation in which each water molecule has a direct HB to each hydrogen atom of PH_4^+ . These type 1 and type 2 geometries correspond to the P-O_w distances of 2.86 and 3.50 Å, with associated stabilization energies of -58.31 and -48.96 kcal.mol⁻¹, respectively. In aqueous solution, however, some water molecules nearby the PH_4^+ ion could be expected to form also a bifurcated structure by simultaneously interacting with two hydrogen atoms of PH_4^+ (type 3), resulting in several possible $\text{PH}_4^+ \text{-water}$ conformations. The broad shape and extended tail of the P-O_w RDF, which can be up to approximately 5 Å long, clearly reveal a high conformational flexibility of the PH_4^+ solvation. Furthermore, the P-O_w peak lacks a clear separation from the bulk region, implying that water molecules around the PH_4^+ ion are highly labile and are only weakly perturbed by the ion. According to Figure 1a, the integration of the P-O_w RDF up to 5 Å (approximately the first estimated minimum) results in approximately 16 water molecules. Apparently, the observed large number of neighboring waters should not be taken as the coordination number of PH_4^+ , since the P-O_w peak is rather broad and asymmetric. This number is likely due to the mixing of neighboring waters, which are directly influenced by the PH_4^+ ion together with neighboring waters positioned nearby via the HB interactions between the water molecules. Moreover, according to Figure 1a, the P-O_w RDF shows a continuous variation between 4.4 and 4.6 Å (i.e., the ONIOM-XS parameters r_0 and r_1), suggesting a smooth exchange of water molecules across the QM-MM boundary. This clearly indicates that the MM potentials employed can reliably describe the ion-water and water-water interactions over the QM boundary.

The H_p-O_w and H_p-H_w RDFs (Figures 1c and 1d) were used to analyze the HB interactions between PH_4^+ and the neighboring waters. From Figure 1c, the invisible peak of the H_p-O_w RDF between 1.8-2.0 Å clearly indicates that the HB interactions between PH_4^+ and the neighboring

waters are rather weak, especially compared to the NH₄⁺-water HBs in aqueous solution (Intharathep *et al.*, 2005) and the water-water HBs in bulk water (Thaomola *et al.*, 2012). Note that, according to the QM/MM MD study of NH₄⁺ in aqueous solution, the type 2 conformation, which corresponds to a tetrahedral structure of hydrated NH₄⁺, is well characterized by a pronounced first H_N-O_W peak at 1.84 Å, along with a distinct peak in the N-H---O_W angular distribution between 150°-180°.

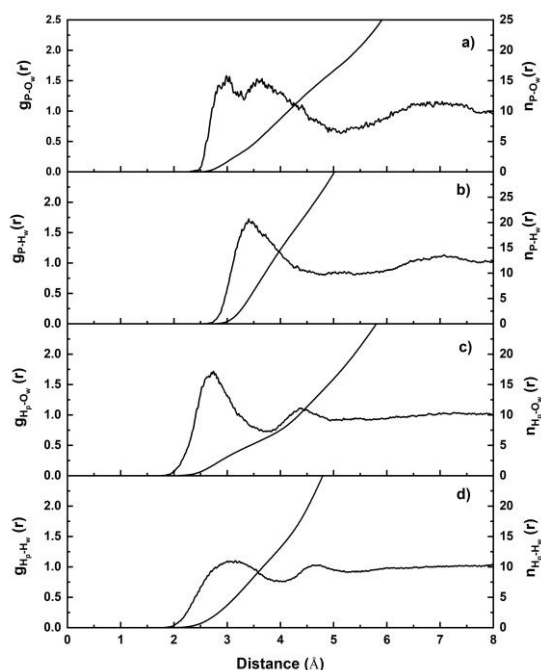


Figure 1. a) P-Ow, b) P-Hw, c) Hp-Ow and d) Hp-Hw RDFs, together with their associated integration numbers.

The probability distributions of the oxygen atoms of neighboring waters, calculated up to the P-O_W distance of 3.8 Å, are plotted in Figure 2. Note that the P-O_W distance of 3.8 Å was chosen as a rough estimate for the longest distance of the neighboring water molecules that can form HBs with the hydrogen atoms of PH₄⁺, due to the weak HB interactions between PH₄⁺ and the surrounding water molecules. The selection of 3.8 Å as the cutoff distance for solvation and HB analysis is appropriate, encompassing all possible type 1, type 2 and type 3 structures. Note that, according to the optimized structures of the PH₄⁺-(H₂O)₄ complexes in the gaseous state, the type 2 conformation (which corresponds to the formation of a linear P-H_P---O_W HB, *i.e.*, the furthest P-H_P---O_W distance) exhibits an optimal P-O_W distance of 3.50 Å. Furthermore, this cutoff value is justified when compared to the

case of NH₄⁺ in aqueous solution (Intharathep *et al.*, 2005), which uses an N-O cutoff value of 3.5 Å. From Figure 2, it is observed that different numbers of water molecules, ranging from 3 to 11, can participate in the arrangement of the PH₄⁺ hydrates. The broad distributions of the oxygen atoms of the neighboring waters, most frequently occurring at 7±1, provide clear evidence of a weak and highly flexible arrangement of the PH₄⁺ solvation. Figure 3 illustrates the H_P-P-O_W angular distributions, calculated up to the P-O_W range of 3.8 Å. The type 1 configuration of the PH₄⁺-water complexes is recognizable, by two prominent angular peaks observed in the ranges of 60-80° and 160-180°. In addition, the bifurcated configuration (type 3) can be identified by the angular peaks at 60-80° and 110-130°. In comparison, the type 2 configuration is less visible, as reflected by the relatively weak angular peaks in the range of 0-20°. From Figure 3, the broad angular distributions of the H_P-P---O_W angles clearly supply information that the solvation structure of the PH₄⁺ hydrates is highly flexible and that the water molecules in the vicinity of PH₄⁺ are highly labile and are only slightly affected by the presence of PH₄⁺.

The mobility of the water molecules in the loosely bound PH₄⁺ solvation was evaluated through the calculation of self-diffusion coefficients (*D*). Specifically, the diffusion coefficient for water molecules located within the 3.8 Å radius of the PH₄⁺ ion was derived using the velocity autocorrelation function (VACF) of their center of mass, following the Green-Kubo formalism (McQuarrie 1976),

$$D = \frac{1}{3} \lim_{t \rightarrow \infty} \int_0^t C_v(t) dt. \quad (2)$$

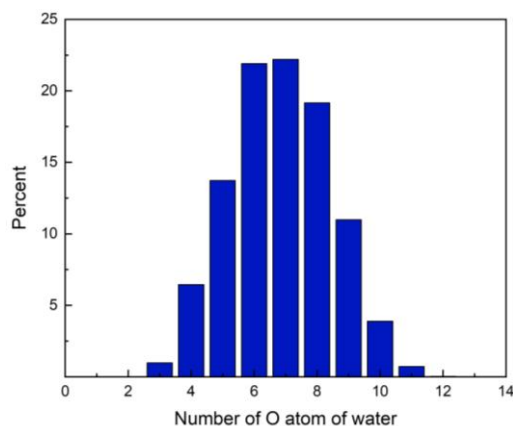


Figure 2. Probability distributions of oxygen atoms from water molecules found within the P---O_W distance of 3.8 Å, expressed in terms of probability percentage.

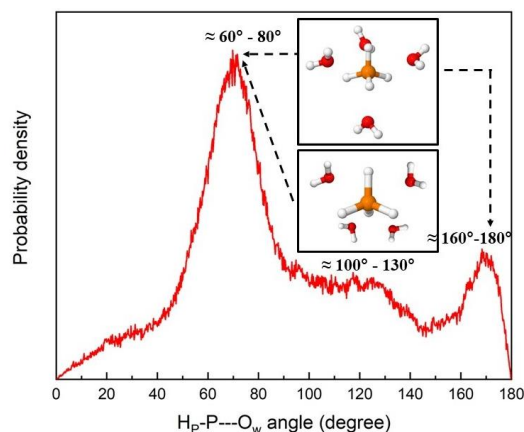


Figure 3. Angular distribution profiles of $H_P-P---O_w$ angles, calculated within the 3.8 Å $P-O_w$ range.

Based on the ONIOM-XS MD approach, the D value for the water molecules surrounding the PH_4^+ ion is found to be $3.22 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$. Comparing to the corresponding D value for pure water ($2.73 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$) (Thaomola *et al.*, 2012), it is apparent that the HBs between PH_4^+ and its surrounding waters are relatively weak, with strength comparable to that observed in bulk water. In this sense, the PH_4^+ ion can be interpreted as a perturbing agent that disrupts the HB network of the surrounding waters. Figure 4 shows how the number of neighboring waters with oxygen atoms within the $P-O_w$ distance of 3.8 Å changes over time. The figure also includes some selected configurations of the PH_4^+ -water complexes, highlighting the HB formations between the PH_4^+ ion and its surrounding waters. It is important to note that in Figure 4, the dashed lines indicating the HB interactions are emphasized only for those within the HB distance of 2.5 Å. Figure 5 provides an enlarged view of the selected PH_4^+ -water configurations as shown in Figure 4, incorporating some water molecules beyond the $P-O_w$ distance of 3.8 Å (marked in “green”) that can make HBs with first solvation layer waters. The ONIOM-XS MD results clearly indicate that the solvation shell structure of the PH_4^+ ion is poorly organized, with a highly diffuse character. In this regard, the arrangement of water molecules around the PH_4^+ ion is expected to occur based on the subtle influence between the ion’s effects and the forces from surrounding waters in the same shell and/or the bulk.

The lability of the water molecules around the PH_4^+ ion was further analyzed through the mean residence time (MRT) using the so-called direct

method (Hofer *et al.*, 2004). This method involves multiplying the average number of water ligands within a given solvation layer by the simulation time, and then dividing by the amount of exchange events observed over a specific time period t^* ,

$$MRT(\tau) = \frac{CN \times t_{sim}}{N_{ex}} \quad (3)$$

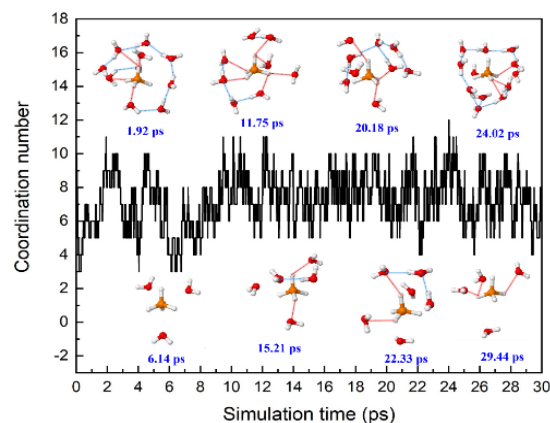


Figure 4. Time evolution of the number of water molecules within the $P-O_w$ cutoff distance of 3.8 Å, accompanied by some selected snapshots of the PH_4^+ -water complexes showing the HB interactions between PH_4^+ and nearest neighboring waters (*i.e.*, the dash lines highlighted in “red”) and between the nearest neighboring waters (*i.e.*, the dash lines highlighted in “blue”), captured from the first 30 ps of the ONIOM-XS MD trajectories

The calculated MRT values for the water molecules in the vicinity of PH_4^+ , *i.e.*, within the 3.8 Å $P-O_w$ range, and the relevant data for pure water (Thaomola *et al.*, 2012), are given in Table 2. Note that, according to the direct method, the t^* value of 0.0 ps was suggested as a suitable criterion for estimating the HB lifetime, whereas the t^* value of 0.5 ps was proposed as an appropriate indicator for studying the water exchange processes. Based on the ONIOM-XS MD simulation, the MRT values for water molecules participating in the PH_4^+ -water HBs were estimated to be 0.19 and 2.03 ps for the time parameters t^* of 0.0 and 0.5 ps, respectively. Compared to the corresponding MRT values of 0.23 and 2.17 ps for pure water (Thaomola *et al.*, 2012), it is evident that PH_4^+ has a limited ability to organize its surrounding water molecules.

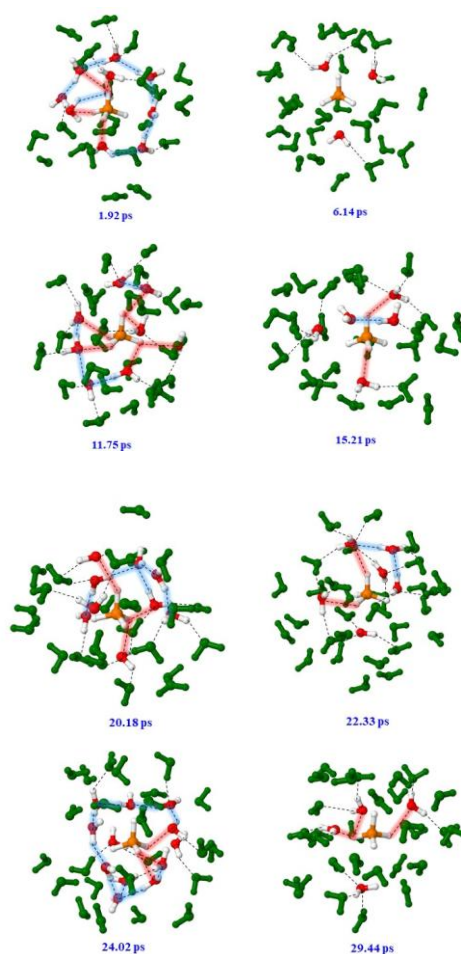


Figure 5. The selected snapshots of the PH_4^+ -water complexes as shown in Figure 4, which include some water molecules in the outer region (labeled as “green”). The dash lines (not highlighted) represent the HB interactions between water molecules within the P- O_w distance of 3.8 Å and other water molecules in the outer region

Hence, the neighboring waters tend to self-organize based on interactions with adjacent waters in the same solvation layer and/or in the bulk, rather than being ordered by the PH_4^+ ion. Overall, the results obtained from the ONIOM-XS MD study clearly demonstrate the high asymmetry and flexibility of the weakly bound PH_4^+ solvation, thus supporting the “structure-breaking” behavior of PH_4^+ in water. Notably, although this ONIOM-XS MD study provides a molecular-level understanding of PH_4^+ solvation, the results are limited to a single ion under very dilute conditions. In this respect, further studies under a wide range of concentrations or in mixed ion environments may be necessary in order to correctly understand the “structure-breaking” ability of PH_4^+ in aqueous environments.

Table 2. Angular distribution profiles of $\text{H}_\text{P}-\text{P}---\text{O}_w$ angles, calculated within the 3.8 Å P- O_w range.

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

^{*}(Thaomola *et al.*, 2012)

Conclusions

The characteristics of the PH_4^+ hydrates in aqueous solution were studied by performing an ONIOM-XS MD simulation, in which the interactions between the PH_4^+ ion and the adjacent water

molecules were described by means of the HF/def2-SVP model. From the analyses of the ONIOM-XS MD trajectories, it was shown that the HB interactions between the PH_4^+ ion and its neighboring water molecules are weak, resulting in loosely bound and asymmetric PH_4^+ hydrates. The observed high asymmetry and flexibility of the weakly bound PH_4^+ solvation supports the role of PH_4^+ as a “structure-breaking” species in aqueous solution.

Funding

The authors received no specific financial support for the research, authorship, and/or publication of this article.

Author Contributions

Conceptualization: A.T., N.I.; Methodology: A.T., N.I., P.S.; Investigation: N.I.; Data Curation: N.I., P.S.; Writing – Original Draft: N.I., P.S.; Writing – Review & Editing: A.T., N.I.; Supervision: A.T. All authors have read and agreed to the published version of the manuscript.

Ethics Statement

Ethical approval was not required for this study because it did not involve human participants, animals, identifiable personal data, or materials requiring institutional ethical review.

Declaration of Generative AI Use

During the preparation of this manuscript, the authors used ChatGPT (OpenAI) to assist with English language editing and grammar correction. All AI-assisted outputs were critically reviewed, verified, and revised by the authors, who accept full responsibility for the content of this manuscript.

Conflict of Interest

The authors declare that they have no conflicts of interest related to this work.

Data Availability Statement

No new data were generated or analyzed in support of this research.

Acknowledgement

The authors gratefully acknowledge generous support from Suranaree University of Technology (SUT). Computational resources were provided by the National e-Science Infrastructure Consortium through its high-performance computing facilities.

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