



# Investigation of structural and dynamical properties of hafnium(IV) ion in liquid ammonia: An ab initio QM/MM molecular dynamics simulation



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## ABSTRACT

The structure and dynamics of  $\text{Hf}^{4+}$  ion in liquid ammonia have been investigated by an ab initio quantum mechanics molecular mechanics (QM/MM) molecular dynamics simulation. The structural data was obtained in terms of radial distribution, coordination number and angular distribution, and then the dynamics in mean ligand residence time. The  $\text{Hf}^{4+}$  ion is coordinated by five ammonia molecules in the first solvation shell showing a distorted square pyramidal structure with an average  $\text{Hf}^{4+}$ –N distance of 2.38 Å. No ammonia ligand was observed for exchange processes between the first and second shells.

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## 1. Introduction

Interest in studying complex formation of metal ions has grown rapidly. It is necessary to understand the interactions of metal ions with a ligand in biochemical, and chemical processes. Research on metal interactions with proteins has developed in the recent years [1–3]. The question that arises then how to understand the reactivity of these metals. In a solution system reactivity of metal ions is affected by the coordination shell of the metal ions [4]. In this context, the molecular dynamics simulation plays an important role to investigate the structure of solvation of the metal ion and its reactivity. Characteristics of solvated ions in water or liquid ammonia have been a topic of special interest since such detailed knowledge is essential for understanding the role of these ions in chemical and biological processes [5–7]. Liquid ammonia has the weakest hydrogen bonds in nature and its associated ions also play an essential role in the chemistry of fertilizers, biochemical processes of the liver, kidneys and intestines, and a variety of organic reactions [8–13]. Hafnium(Hf) from group 4 has been known as implant materials but its biocompatibility of little-known one [14]. The  $\text{Hf}^{4+}$  ion could be solvated in water and also in liquid ammonia. Indeed, the structure investigation of  $\text{Hf}^{4+}$  in aqueous solution has

been carried out by the spectroscopy as well as Quantum Mechanics Charge Field (QMCF) method whereas the structural and dynamical aspect for the  $\text{Hf}^{4+}$  ion in liquid ammonia has not been reported so far [15–21]. However, there is no many investigations of metal ions in liquid ammonia. Therefore, it is still interesting to investigate the solvation of  $\text{Hf}^{4+}$  in liquid ammonia.

The pentaammoniates of  $\text{MF}_4$ , namely  $\text{M}(\text{NH}_3)_4\text{F}_4\cdot\text{NH}_3$  (1,  $\text{M}=\text{Zr}$ ; 2,  $\text{M}=\text{Hf}$ ) are formed if  $\text{Ag}_3\text{M}_2\text{F}_{14}$  and liquid  $\text{NH}_3$  were prolonged in the storage. Compounds 1 and 2 are also formed in the reaction of the  $\text{MF}_4$  with liquid  $\text{NH}_3$  in weeks. The  $\text{Hf}^{4+}$ –N distance of 2.383 Å has been known by the X-ray diffraction method [22].

The hydration structure of some tetravalent ions as  $\text{U}^{4+}$ ,  $\text{Th}^{4+}$ ,  $\text{Hf}^{4+}$ , and  $\text{Zr}^{4+}$  has been extensively investigated by the diffraction, spectroscopy, and computer simulation methods [23–27]. Hybrid quantum mechanics/molecular mechanics molecular (QM/MM MD) dynamics simulation methods have successfully investigated structural and dynamical properties of metal ions in water as well as in liquid ammonia. The simulation method has thus become an alternative to experiments, in particular where the experiments reach their limitations [15–17]. Determinations of the structure and dynamics properties of solvation ions are very sensitive to the accuracy of the simulation methods. It is known that the investigations of the solvation of metal ions by QM/MM MD methods provide a high level of accuracy. Therefore, in the present work, we performed a QM/MM MD simulation for  $\text{Hf}^{4+}$  in liquid ammonia, in order to investigate the structure and dynamics of the solvated  $\text{Hf}^{4+}$  ion in liquid ammonia at 235.15 K.

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**Table 1**

Hafnium(IV)–ammonia distances ( $r$ ), binding energies per ammonia ligand obtained by quantum mechanical calculations of  $\text{Hf}^{4+}$ –ammonia complex at HF, MP2, CCSD, and B3LYP levels.

Method	$r$ (Å)	Binding energy (kcal/mol)
HF	2.24	–152.06
MP2	2.25	–160.75
CCSD	2.25	–158.95
B3LYP	2.21	–167.51

## 2. Methods

### 2.1. Construction of potential function

There are two steps that must be done prior to QM/MM simulation could be run, that is selecting the proper basis sets for  $\text{Hf}^{4+}$ , N and H atoms and calculation method applied in the quantum mechanics zone. According to the literature, DZP basis sets for H and N atoms could be applied successfully and have been selected, therefore, also in this investigation [15,28]. The LANL2DZ ECP basis sets of Hf with a minor modification (s and p basis functions with the smallest exponent have been removed to make the basis sets more compatible with the  $\text{Hf}^{4+}$  ion rather than the hafnium atom) was selected for  $\text{Hf}^{4+}$ , including the relativistically in order to be compatible with hafnium(IV) ion [29]. The levels of theory for QM region namely, Hartree–Fock (HF), MP2, CCSD, and B3LYP were applied in energy calculation using GAUSSIAN09 program, optimizing the geometry of  $\text{Hf}^{4+}$ – $\text{NH}_3$  complex. The result shows that HF calculated energy closes to the most correlated CCSD as seen in Table 1. In recent investigations of alike ionic systems, results of HF calculations were in good agreement with experimental data, whereas electron correlation methods such as MP2 and CCSD seemed to have more expensive and consuming time, and even the current hybrid B3LYP functional sometimes provide a poor result or at best result take a long computation time [28]. Therefore, Hartree–Fock method was chosen to describe the QM part in the simulation.

The two-body energies,  $\Delta E_{2bd}$ , between ammonia and  $\text{Hf}^{4+}$  ion were evaluated by subtracting the ab initio energies of the isolated species  $E_{\text{Hf}^{4+}}$  and  $E_{\text{NH}_3}$  from those of the monosolvates [30]  $E_{\text{Hf}(\text{NH}_3)^{4+}}$

$$\Delta E_{2bd} = E_{\text{Hf}(\text{NH}_3)^{4+}} - E_{\text{Hf}^{4+}} - E_{\text{NH}_3} \quad (1)$$

The new pair potential of  $\text{Hf}^{4+}$ – $\text{NH}_3$  system was constructed. More than 7600 ab initio energy points were generated at Hartree–Fock level with the modified LANL2DZ ECP basis sets for  $\text{Hf}^{4+}$  and DZP basis sets for N and H atoms using TURBOMOLE program [31–33]. The following pair potential function was constructed and

used in the simulation,

$$E_{\text{fit}}^{2bd} = \frac{q_{\text{Hf}^{4+}}q_{\text{N}}}{r} + \frac{A_{\text{N}}}{r^5} + \frac{B_{\text{N}}}{r^9} + \frac{C_{\text{N}}}{r^{11}} + \frac{D_{\text{N}}}{r^{12}} + \sum_{i=1}^3 \left( \frac{q_{\text{Hf}^{4+}}q_{\text{H}}}{r_i} + \frac{A_{\text{H}}}{r_i^4} + \frac{B_{\text{H}}}{r_i^5} + \frac{C_{\text{H}}}{r_i^6} + \frac{D_{\text{H}}}{r_i^{12}} \right) \quad (2)$$

The fitting parameters of A, B, C and D are listed in Table 2. The  $q_{\text{Hf}^{4+}}$ ,  $q_{\text{N}}$  and  $q_{\text{H}}$  are the charge of hafnium, nitrogen, and hydrogen, respectively, and  $r$  and  $r_i$  are the  $\text{Hf}^{4+}$ –N and  $\text{Hf}^{4+}$ –H distances, respectively. The net charges of nitrogen and hydrogen were set to –0.8022 and 0.2674, respectively. The geometry of ammonia was kept constant throughout the whole calculation at its experimental gas phase values (N–H = 1.0124 Å, H–N–H = 106.68°) [15,16]. The corrected 3-body energy ( $\Delta E_{\text{corr}}^{3bd}$ ) was calculated as the following formula:

$$\Delta E_{\text{corr}}^{3bd} = (E_{\text{AMA}}^{ab} - E_{\text{M}}^{ab} - 2E_{\text{A}}^{ab}) - \Delta E_{\text{MA}}^{2bd}(r_1) - \Delta E_{\text{MA}}^{2bd}(r_2) - \Delta E_{\text{AA}}^{2bd}(r_3) \quad (3)$$

where  $ab$ ,  $2bd$  denote ab initio and pair energy; MA and AA indicated ion–ammonia and ammonia–ammonia interactions;  $r_1$ ,  $r_2$ , and  $r_3$  are according to the distance of ion–ammonia(1), ion–ammonia(2), and ammonia(1)–ammonia(2), respectively. The corrected 3-body energy was generated at Restricted Hartree–Fock (RHF). The obtained three-body correction function was

$$\Delta E_{\text{Fit}}^{3bd} = 0.684e^{0.447(r_1+r_2)}e^{-0.233r_3}(CL - r_1)^2(CL - r_2)^2 \quad (4)$$

where  $r_1$  and  $r_2$  are the distances  $\text{Hf}^{4+}$ –N1 and  $\text{Hf}^{4+}$ –N2, respectively, and  $r_3$  is the distance between N1 and N2. The CL is a cutoff limit set to 6.0 Å, after which three-body terms become negligible. The QM/MM simulation system is divided into two parts, a region that includes the ion and the first solvation shell (QM) are treated by quantum mechanics and remaining area (MM) by molecular mechanics. The system force is described by the following formula

$$F_{\text{tot}} = F_{\text{MM}}^{\text{sys}} + (F_{\text{QM}}^{\text{QM}} - F_{\text{QM}}^{\text{MM}})S(r) \quad (5)$$

where  $F_{\text{MM}}^{\text{sys}}$  is the MM force of the whole system and  $F_{\text{QM}}^{\text{QM}}$  and  $F_{\text{QM}}^{\text{MM}}$  are QM and MM forces in the QM region while  $F_{\text{tot}}$  is the total force acting on a particle. To ensure a continuous change of forces, a smoothing function  $S(r)$  is applied between the radii  $r_0$  and  $r_1$ :

$$S(r) = 1, \quad \text{for } r \leq r_1$$

$$S(r) = \frac{(r_0^2 - r^2)^2(r_0^2 + 2r^2 - 3r_1^2)}{(r_0^2 - r_1^2)^3}, \quad \text{for } r_1 < r \leq r_0 \quad (6)$$

$$S(r) = 0, \quad \text{for } r > r_0$$

Free migration of ligands between QM and MM region is permitted in this approach [15–17].

**Table 2**

The optimized parameters of the analytical 2-body potential function for  $\text{Hf}^{4+}$ –ammonia interaction.

2-Body	$A_{\text{N}}$ (kcal/mol A <sup>5</sup> )	$B_{\text{N}}$ (kcal/mol A <sup>9</sup> )	$C_{\text{N}}$ (kcal/mol A <sup>11</sup> )	$D_{\text{N}}$ (kcal/mol A <sup>12</sup> )
$\text{Hf}^{4+}$ –N	–13579.1072059	618783.1566433	–2950364.7296899	2609462.3322842
2-Body	$A_{\text{H}}$ (kcal/mol A <sup>4</sup> )	$B_{\text{H}}$ (kcal/mol A <sup>5</sup> )	$C_{\text{H}}$ (kcal/mol A <sup>6</sup> )	$D_{\text{H}}$ (kcal/mol A <sup>12</sup> )
$\text{Hf}^{4+}$ –H	–3122.0580214	10116.2899080	–7446.7423029	804.5610333

**Table 3**

The structure parameters of the solvated  $\text{Hf}^{4+}$  in liquid ammonia determined by the classical and QM/MM MD simulations.

	Classical MD	QM/MM MD	Experiment <sup>c</sup>
$r_{1\text{Hf}^{4+}-\text{N}}^{\text{a}}$	2.51	2.38	2.383
$r_{2\text{Hf}^{4+}-\text{N}}^{\text{a}}$	5.27	5.31	–
$\text{CN}^{\text{1stb}}$	5.00	5.00	5.00
$\text{CN}^{\text{2ndb}}$	~34.70	~30.00	–
$\text{N-Hf}^{4+}-\text{N}$ angle ( $^\circ$ )	73.90/146.70	90.00/173.00	–

<sup>a</sup> First and second peak maximum of  $\text{Hf}^{4+}-\text{N}$  RDF in Å.

<sup>b</sup> Coordination numbers of the first and second solvation shell.

<sup>c</sup> Based on X-ray diffraction measurement of the crystal of  $\text{Hf}(\text{NH}_3)_4\text{F}_4 \cdot \text{NH}_3$ .

## 2.2. Details of QM/MM-MD simulation

The simulation was carried out in the canonical NVT ensemble, consisting of one  $\text{Hf}^{4+}$  ion and 215  $\text{NH}_3$  molecules in a cubic box of 20.8 Å side length, corresponding to the density of the system 0.690 g/cm<sup>3</sup>. The simulation temperature was kept constant at 235.15 K using the Berendsen algorithm. The flexible ammonia model including intra- and inter-molecular potential was used. Consequently, the time step of the simulation was set to 0.2 fs, which allows for explicit movement of the hydrogen. A cutoff of 10.40 Å was set except for N–H and H–H non-Coulombic interactions where it was set to 6.0 and 5.0 Å. The reaction field method was used to account for long-range electrostatic interactions.

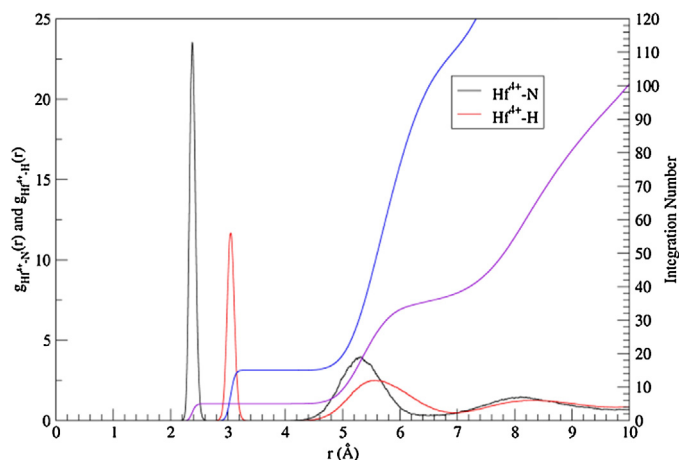
The classical 2-body potential molecular dynamics simulation has been performed first for 100 ps and continued with 2-body + 3-body potential for 100 ps. Then, a 90 ps of the QM/MM simulation was carried out from the equilibrium configuration of the classical simulation. To ensure the full inclusion of the first shell into the QM zone the radius of the QM sphere was set to 3.9 Å in accordance with the  $\text{Hf}^{4+}-\text{N}$  RDF obtained from the classical simulation. The work of the MD simulations were performed in Austrian–Indonesian Center (AIC) for Computational Chemistry, Gadjah Mada University, Yogyakarta, Indonesia.

## 3. Results and discussion

### 3.1. Structure

The structure of solvation of  $\text{Hf}^{4+}$  in liquid ammonia has been obtained by QM/MM simulation at the HF level. The structural properties are confirmed on several parameters such as Radial Distribution Function (RDF), Coordination Number Distribution (CND), Angle Distribution Function (ADF). Their parameter values obtained from the classical as well as QM/MM simulation are presented in Table 3. The  $\text{Hf}^{4+}-\text{N}$  and  $\text{Hf}^{4+}-\text{H}$  RDFs are depicted in Figure 1 that obtained by the QM/MM simulation at Hartree–Fock level. The maximum peak of  $\text{Hf}^{4+}-\text{N}$  RDF is located at 2.38 Å in the first shell while the first maximum peak in classical 2-body + 3-body potential simulations is observed at 2.51 Å. The  $\text{Hf}^{4+}-\text{N}$  distance of 2.38 Å is consistent with experimental data 2.383 Å obtained by Kraus et al. [22]. The probabilities  $g_{\text{Hf}^{4+}-\text{N}}(r)$  between the first and second shell equal to zero that indicate no ligand exchange to occur between the two shells during simulation. A broad peak located between 4.2 and 6.4 Å with a maximum at 5.31 Å indicated for high flexibility of ammonia molecules within this shell.

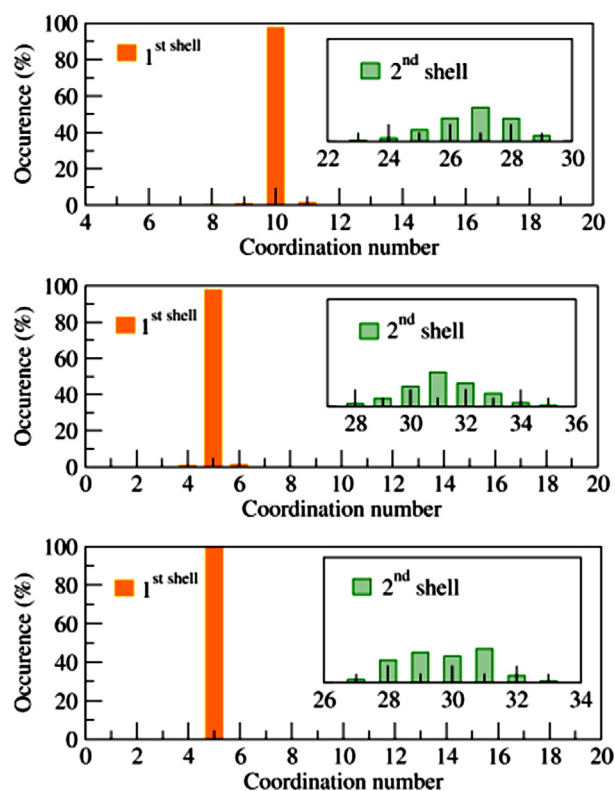
Coordination number distribution for solvated  $\text{Hf}^{4+}$  in liquid ammonia derived from the classical and QM/MM simulations were displayed in Figure 2. According to the QM/MM simulation, coordination number of 5 observed in the first solvation shell with a 100% occurrence is in agreement with the experimental data while the coordination number of 10 is obtained from the classical 2-body potential simulations. Giving correction 3-body effect to the 2-body potential showed a decrease to the coordination number 5



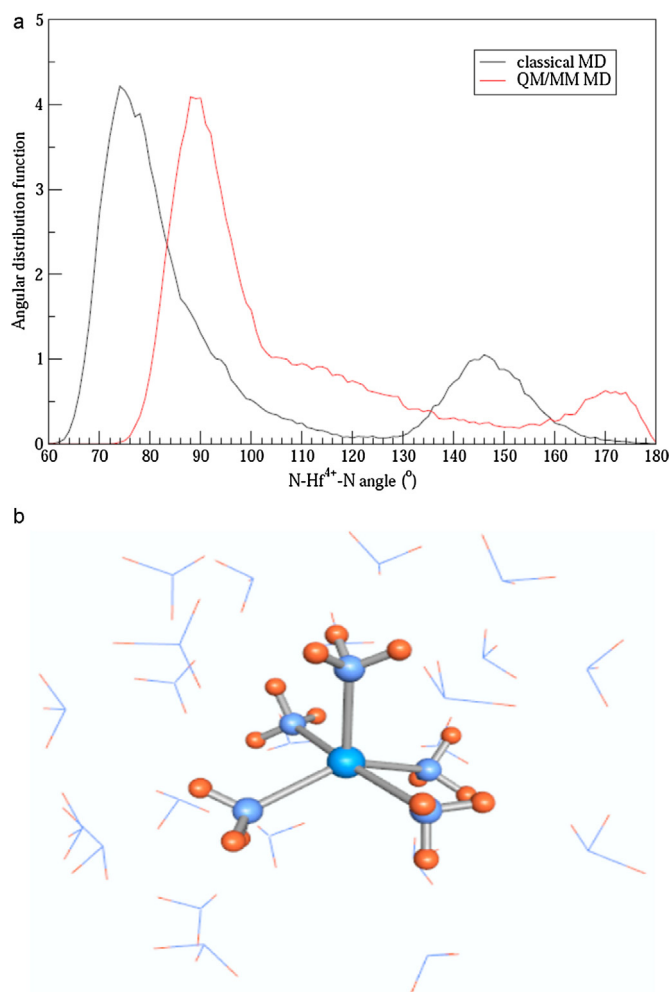
**Figure 1.** The radial distribution functions of  $\text{Hf}^{4+}-\text{N}$  and  $\text{Hf}^{4+}-\text{H}$  and their running integration numbers obtained by QM/MM-MD simulation.

with a nearly 100% occurrence. The coordination number in second shell ranged from 28 to 34 for the classical 2-body + 3-body potential and 27–33 for QM/MM-MD simulations (average: 30.2) while if only using 2-body potential the broad coordination number distribution with a high occurrence of about 27 was obtained. As comparison, the second solvation shell contains about 30 ammonia molecules in the case of solvation  $\text{Li}^+$  in liquid ammonia [34].

The solvation structure could be characterized on the basis of angular distribution function. Angular distribution of  $\text{N-Hf}^{4+}-\text{N}$  angles in the first solvation shell was depicted in Figure 3a. In the distribution plots of the  $\text{N-Hf}^{4+}-\text{N}$  angles, the obtained two peaks by the classical simulation are located at 73.90° and 146.70°. The changes of the  $\text{N-Hf}^{4+}-\text{N}$  angles are found after the many-body

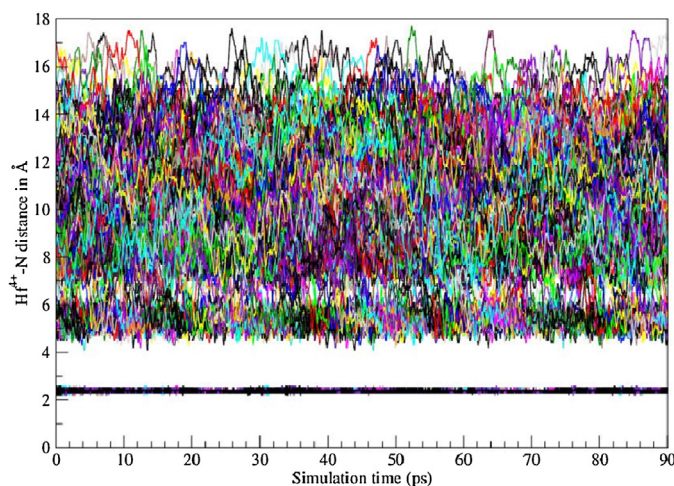


**Figure 2.** The coordination number distribution of the first and second shell of  $\text{Hf}^{4+}$  in liquid ammonia obtained by the classic (top: 2-body), middle (2-body + 3-body) and QM/MM-MD (down) simulation.



**Figure 3.** (a) The angular distribution of N–Hf<sup>4+</sup>–N angles up to the first minimum of the Hf<sup>4+</sup>–N RDFs, (b) distorted square pyramidal structure of the solvation of Hf<sup>4+</sup> in liquid ammonia (snapshot taken by Tmolex).

corrections have been included. A sharp peak was observed at 90° while the broad peak appeared at 173° and a minimum occurring at 150°. The existence of the first peak at 90° with a high probability and the second peak at 173° (almost 180°) indicated the structure of



**Figure 4.** No ammonia ligands migration between first and second solvation shell are observed. The ammonia ligand exchanges are observed between second solvation shell and bulk.

**Table 4**

Mean ligand residence times (MRT),  $\tau$  in ps, number of accounted exchange events ( $N_{\text{ex}}$ ) obtained by direct method as a function of  $t^*$ , and sustainability coefficient ( $S_{\text{ex}}$ ).

	$t_{\text{sim}}$ ps	$t^* = 0$ ps		$t^* = 0.5$ ps		$S_{\text{ex}}$	$1/S_{\text{ex}}$
		$N_{\text{ex}}^0$	$\tau$	$N_{\text{ex}}^{0.5}$	$\tau$		
Second shell	90	1398	1.943	533	5.096	0.381	2.625

Hf(NH<sub>3</sub>)<sub>5</sub><sup>4+</sup> complex tends to a square pyramidal structure with the Hf<sup>4+</sup> ion lifted above the average nitrogen plane (Figure 3b) whereas for an ideal square pyramidal structure has 90° and 180°. As comparison, structure of solid copper(II) complex with ammonia has been reported, including coordination of four (square planar) and five (square pyramidal) nitrogens and six (distorted square bipyramidal) nitrogens [2,35] while for Na(NH<sub>3</sub>)<sub>5</sub><sup>+</sup> could be assigned to two main structures, namely a trigonal bipyramidal and a square pyramidal [36].

### 3.2. Dynamics

Ligand exchange of ammonia between the first and second shell is not observed for 90 ps simulation as displayed in Figure 4, while the ligand exchanges are occurred between ligands in the second solvation shell and bulk. Ultrafast ligand exchange is important to indicate the reactivity of Hf<sup>4+</sup> ion. It is possible to measure the number of exchange events leading to a longer-lasting change in the solvation structure by comparing the number of accounted exchange events with  $t^* = 0.5$  ps ( $N_{\text{ex}}^{0.5}$ ) and  $t^* = 0$  ps ( $N_{\text{ex}}^0$ ), defining a sustainability coefficient:

$$S_{\text{ex}} = \frac{N_{\text{ex}}^{0.5}}{N_{\text{ex}}^0} \quad (7)$$

Its inverse ( $1/S_{\text{ex}}$ ) accounts how many border-crossing attempts are needed to produce one longer-lasting change in the solvation structure of an individual ion [21,37]. Some dynamic properties such as the number of ligand exchange, mean ligand residence time (MRT), and the sustainability of the migration process are listed in Table 4. The mean ligand residence time in the second solvation shell of Hf<sup>4+</sup> was 5.096 ps. In contrast, the MRT in the second shell is significantly smaller than in water ( $\tau^{0.5 \text{ ps}} = 15.5$  ps) [19], indicating for an increased liability of the second shell in the case of ammonia. On the other hand, the sustainability coefficient  $S_{\text{ex}}$  of ligand migration has a value of 0.381, the corresponding  $1/S_{\text{ex}}$  is 2.625, which means that less than three attempts to leave or enter the second solvation shell are needed, to achieve one exchange process, which lasts at least 0.5 ps.

### 4. Conclusion

The simulation Hf<sup>4+</sup> ion in liquid ammonia has been performed successfully by the QM/MM method. The QM/MM simulation results indicated that the structure of the first solvation shell consists of five ammonia molecules tends to form a square pyramidal structure. The Hf<sup>4+</sup>–N distance of 2.38 Å is in accordance with the experimental X-ray diffraction data. There is no ligand exchange between the second shell and the first shell during the simulation of 90 ps. The residence time of the ligand in the second solvation shell is 5.096 ps. This value is smaller than in water, indicating a high flexibility of the second shell in the case of ammonia.

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