

A QM/MM SIMULATION METHOD APPLIED TO THE SOLUTION OF Zr^{4+} IN LIQUID AMMONIA

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Abstract

The structural and dynamics properties of solution Zr (IV) in liquid ammonia has been investigated by the method of ab initio QM/MM molecular dynamics simulations at the Hartree-Fock level. In this method, region with a high interest in the ion solvation layer of Zr (IV) were investigated by ab initio quantum mechanical Born-Oppenheimer while the rest of the system is described as classical 2-body potential. Structural properties were indicated by the coordination number, radial distribution, and angle distribution, while the dynamic properties were characterized by the mean ligand residence time. The Solvation number of 5 was found through methods of QM/MM with the modified LANL2DZ ECP basis set for Zr(IV) ion and DZP for N and H, in contrast to 10 obtained through 2-body potential simulation. No ligand migration occurs between the first and second shell. The mean ligand residence time in the second solvation shell is 8.67 ps.

Key words: ab initio QM/MM MD method, 2-body potential, Zr (IV) ion, liquid ammonia, solvation

INTRODUCTION

The structure and dynamics of solvation of some metal ions has been investigated both experimentally and theoretically. This investigation is important because in the fact that the chemical processes occurring between substances in solution. Solvation structure of metal ions in solution can be determined by spectroscopic, scattering and simulation methods. Spectroscopic methods include Nuclear Magnetic Resonance spectroscopy (NMR), Extended X - ray Absorption Fine Structure Spectroscopy(EXAFS), Mössbauer, infrared (IR), and Raman scattering method include the X-ray, electron, and neutron diffraction. In addition to these two experimental methods, there are two methods of simulation that is often used is the Monte Carlo (MC) and Molecular Dynamics (MD) (Hofer et al . , 2006) .

Several studies of metal ion solvation in liquid ammonia has been done through MD and MC simulations. Examples of metal ions has been successfully investigated the Li^+ (Kerdcharoen et al . , 1996) , Co^{2+} , Cu^+ , and Cu^{2+} (Pranowo et al . , 1999) , Ag^+ , Au^+ , Co^{2+} (Armunanto , 2004) , and K^+ (Tongraar et al . , 1997) .

By reaction of the tetrafluorides MF_4 ($M = Zr, Hf$) with dry liquid ammonia at $-40^\circ C$, the pentaammoniates $[M(NH_3)_4F_4] \cdot NH_3$ (**1** , $M = Zr$; **2** , $M = Hf$) were obtained, and these compounds represent inorganic Zr and Hf compounds that simultaneously bear nitrogen and fluorine ligands. The Zr-N distance of 2.397 Å are known by X-ray diffraction method (Kraus, et.al., 2009).

Structure and dynamics of Zr^{4+} in water, liquid ammonia and ammonia solution is very

interesting to study experimentally and theoretically for the role of ions in the nuclear industry, solution chemistry, and biochemistry. The use of zirconium and zirconium compounds currently as an artificial joint material and support material production of antibodies. Zirconium is also used in nuclear reactors as a structural material and containers (Messner, et.al, 2011).

Metallic zirconium in the aspect of the nuclear industry is very important but its role in biological has not been known, and only a few experimental studies and theoretical study of the structure of solvation ions in a state of the monomer so that the investigation of structure and dynamics of solvation of ions Zr^{4+} interesting to do through QM/MM dynamic molecular simulation. Structure and especially the dynamics of solvated transition metal ions are highly sensitive to the accuracy of simulation techniques, and it has been shown in several cases that only ab initio QM/MM simulations reach a sufficient level of accuracy for these data. In the present work, we carried out a QM/MM MD simulation for Zr^{4+} in liquid ammonia.

2. METHOD

2.1 Construction of potential functions

The simulation of molecular dynamics was done through some steps. The first step is determining a proper basis sets and calculation method used at interest region. The basis set of DZP for N and H atom were selected as proofed sucessfully in a previous investigations. The LANL2DZ ECP of Zr was modified in order to compatible with Zr(IV). The Hartree-Fock method was choosen because it usually gives information about structural solvation well and indicates results of calculation were not different with MP2 method.

In QM/MM dinamics molecular simulations, potential 2-body and 3-body must be composed accurate. In this case potential of Zr(IV)-NH₃ and NH₃-Zr(IV)-NH₃ interaction were based on 7632 point of ab initio energy calculated using TURBOMOLE at Hartree-Fock level. The Interaction Energy of Zr(IV)-NH₃ calculated as this formula:

$$\Delta E_{2bd} = E_{Zr(NH_3)^{4+}} - E_{Zr^{4+}} - E_{NH_3} \quad (1)$$

More than 7000 point energy are fitted by Levenberg-Marquardt algorithm to an analytical function of the following form (Durdagi, S., et. al, 2005) :

$$E_{fit}^{2bd} = \frac{q_{Zr(IV)} q_N}{r} + \frac{A_N}{r^5} + \frac{B_N}{r^9} + \frac{C_N}{r^{11}} + \frac{D_N}{r^{12}} + \sum_{i=1}^3 \left(\frac{q_{Zr(IV)} q_H}{r_i} + \frac{A_H}{r_i^4} + \frac{B_H}{r_i^5} + \frac{C_H}{r_i^6} + \frac{D_H}{r_i^{12}} \right) \quad (2)$$

The fitting parameters of A, B, C, and D were listed in Table 1, while $q_{Zr(IV)}$, q_N , and q_H are the charges of Zr(IV), N, and H, respectively. The r and r_i are distances of Zr(IV)-N and Zr(IV)-H, respectively. The lowest of interaction energy for Zr(IV)-NH₃ was found to be -148.0177 kcal mol⁻¹ at 2.3 Å, the root mean square deviation of the fitted function is 5. kcal mol⁻¹. The three-body ab initio energies were computed as follows:

$$\Delta E_{corr}^{3bd} = E_{L_1ML_2}^{ab} - (E_M^{ab} + E_{L_1}^{ab} + E_{L_2}^{ab}) - (E_{ML_1}^{2bd} + E_{ML_2}^{2bd} + E_{L_1L_2}^{2bd}) \quad (3)$$

where $E_{L_1ML_2}^{ab}$ is the SCF energy of the H₃N-Zr(IV)-NH₃ interaction, E_M^{ab} , $E_{L_1}^{ab}$, and $E_{L_2}^{ab}$ represent the ab initio energy of the Zr(IV) ion, ligand-NH₃(1) and ligand-NH₃(2). $E_{ML_1}^{2bd}$ and $E_{ML_2}^{2bd}$ account for the Zr-ligand-NH₃(1) and Zr-ligand-NH₃(2) interaction energies, respectively, obtained from the 2-body potential and $E_{L_1L_2}^{2bd}$ denotes the ligand-NH₃(1)-ligand-NH₃(2) interactions. (i.e., ammonia-ammonia interactions, calculated by the flexible four site ammonia model). The analytical three-body fitting function was set up as

$$E_{3bd} = A_1 e^{-A_2 r_{12}} e^{-A_2 r_{13}} e^{-A_3 r_{23}} (r_{cut} - r_{12})^2 (r_{cut} - r_{13})^2 \quad (4)$$

the ion-nitrogen distances for ammonia molecules are denoted by r_{12} and r_{13} , respectively whereas r_{23} is the nitrogen-nitrogen distances between two ammonia molecules. The r_{cut} is a cutoff limit set to 6.0 Å, where three-body terms become negligible.

Table 1. The final parameters of the analytical two-body potential functions and three-body correction function

2-body	A (kcal mol ⁻¹)	B (kcal mol ⁻¹)	C (kcal mol ⁻¹)	D (kcal mol ⁻¹)
Zr(IV)-N	-13416.0701810	627532.6722430	- 2997676.689089	2652060.1088025
Zr(IV)-H	-3237.0978587	10444.5473273	-7650.8783546	799.5098014
3-body	A ₁ (kcal mol ⁻¹ Å ⁻⁴)	A ₂ (Å ⁻¹)	A ₃ (Å ⁻¹)	
N-Zr(IV)-N	0.6430085	0.4313762	-0.2344404	

2.2. Protocol Simulation

The QM/MM MD simulation was performed in a canonical NVT ensemble, consisting of one Zr(IV) ion solvated by 215 ammonia molecules in a cubic box with a side length 20.826 Å was employed. The simulation temperature of 235.16 K was kept constant by the application of the Berendsen algorithm with a bath relaxation time of 0.1 ps. The density of the system was fixed to the density of pure ammonia at the simulation temperature (0.690 g/cm³). The reaction field method was employed as a correction of the cutoff of long-range electrostatic interactions. The Newtonian equations of motion were integrated by a predictor corrector algorithm, and a time step of 0.2 fs was applied, which allows for explicit movement of hydrogens. A cut-off 10.413 Å was set except for N-H and H-H non-Coulombic interactions for which it was set to 6.0 and 5.0 Å. The reaction field method was used to account for long range electrostatic interactions (Armunanto, R., et.al., 2004).

Starting from a random configuration a classical 2-body potential molecular dynamics simulation was performed for 102 ps. With this equilibrated system the simulation was continued adding the 3-body potential as correction of 2-body potential for a total simulation time of 102 ps. Then the combined QM/MM treatment was invoked, in which the ion and its full first solvation shell were included into the QM region. To ensure the full inclusion of the first shell into the QM zone the radius of the QM sphere was set to 3.8 Å in accordance with the Zr-N RDF obtained from the classical simulation. After 2 ps of reequilibration, QM/MM simulation was continued for 400000 steps in resulting trajectory of 80 ps. The whole of QM/MM MD simulations were worked in Austrian-Indonesian Center for Computational Chemistry Laboratory, FMIPA UGM. The total force acting on a particle is calculated according to the expression

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

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_{tot} is the total force acting on a particle. The $S(r)$ is a smoothing function that applied in a region of 0.2 Å to ensure smooth transitions of ammonia molecules between the MM and QM regions.

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

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

$$S(r) = 0, \text{ for } r > r_0$$
(6)

Free migration of ligands between QM and MM region is permitted in this approach (Hofer, T.S., et. Al., 2006)

2.3. Dynamical properties evaluation

The ammonia exchange between solvation shell is important for the reactivities of the ions. The rates of ammonia exchange was evaluated by mean residence time (MRT) analysis for the ammonia molecules in the second shell. The MRT of ammonia molecules in that shell was calculated by the direct method using a t^* value of 0.0 and 0.5 ps (Armunanto, R., et.al., 2004).

3. RESULT AND DISCUSSION

3.1 Structural properties

The RDFs of Zr-N and Zr-H and their integration number are displayed in Figure 1. The sharp peak located at 2.4 Å is observed for the first solvation shell, indicating a rigid structure of that shell. A coordination number of 5 is found in this shell, quite contrast to the flexible eight-coordinated hydrate complex, $\text{Zr}(\text{H}_2\text{O})_8^{4+}$. The higher coordination number in this complex indicated Zr^{4+} has the higher affinity to H_2O compared to NH_3 .

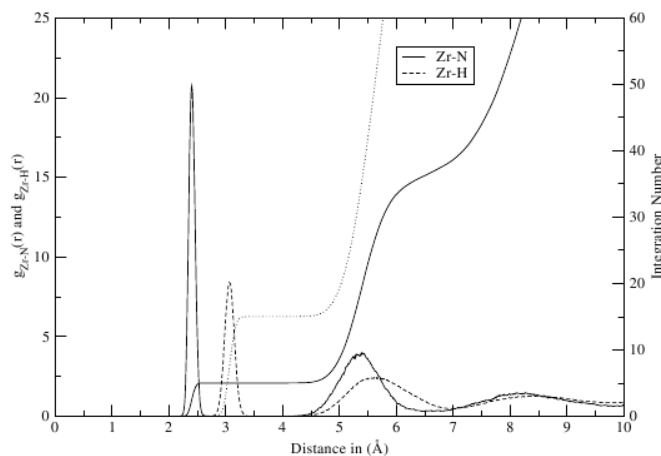


Figure 1. The Radial Distribution Functions of Zr-N and Zr-H and their corresponding running integration numbers.

The broad second peak is centered at 5.3 Å and extends from 4.3 to 6.5 Å indicating a much more flexible second coordination shell. The Zr-N distance of 2.4 Å is in good agreement with experimental investigation that resulted a Zr^{4+} -N distance is 2.397 Å (Kraus, F., et. al, 2009).

To clarify the number of ammonia molecules surrounding the Zr^{4+} ion, the Coordination number (CN) distributions for the first and second solvation shells obtained from the dynamics molecular simulation are depicted in Figure 3. A five-coordinated Zr^{4+} complex (100% occurrence) is observed for the first shell. In the second solvation shell, a large variation of the coordination number ranging from 9 to 21 is observed, with the highest occurrence percentage of 15. In the second shell, it was observed about 15 ammonia ligand that indicated

almost all hydrogen in the first shell bind to nitrogens in the second shell form hydrogen bonds. In this respect, the presence of 5-coordinated complexes in liquid ammonia and also angle distribution (see Figure 4) supplies information that the first solvation shell of Zr^{4+} is trigonal bipyramidal $[Zr(NH_3)_5]^{4+}$ arrangement (see Figure 2.).

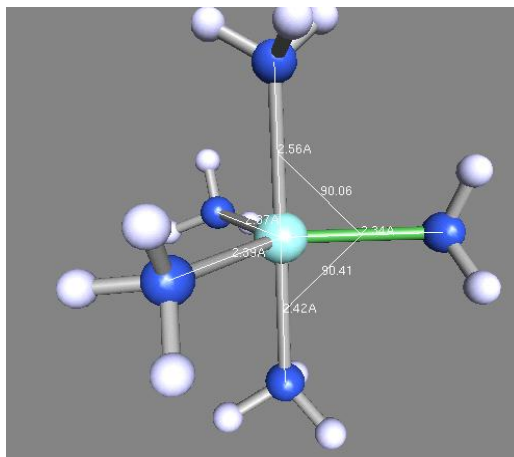


Figure. 2. Solvation structure of Zr^{4+} in liquid ammonia. Molecules form a trigonal bipyramidal arrangement.

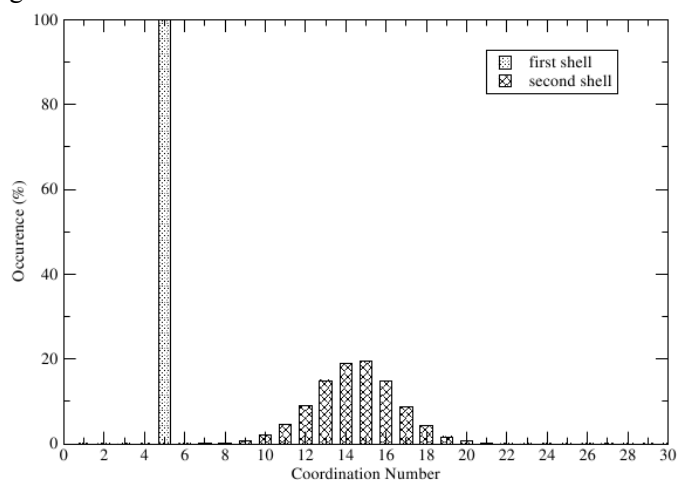


Figure. 3. Coordination number distributions of the first and second solvation shell of Zr(IV) in liquid ammonia obtained from a QM/MM MD simulation.

The distribution of the N–Zr–N angle within the first solvation shell was depicted in Figure 4. The ADF peaks at about 90, 120 and 170° was observed. The structural arrangement of the ammonia molecules within the first shell may be thought as a trigonal bipyramidal arrangement.

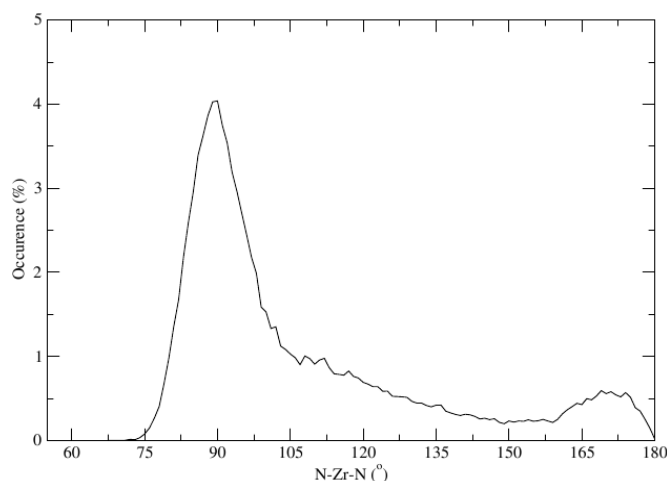


Figure. 4. Angular distribution function of the N–Zr–N angle in the first solvation shell of the Zr–NH₃ geometry obtained from a QM/MM MD simulation.

The ligand exchange of NH₃ can indicate reactivity of Zr⁴⁺ ion. In the case no migration ligand between the first solvation shell and second shell, however the exchange process occurred between the second shell and bulk as indicated in Figure 5. Because of that Zr⁴⁺ in liquid ammonia has the low reactivity.

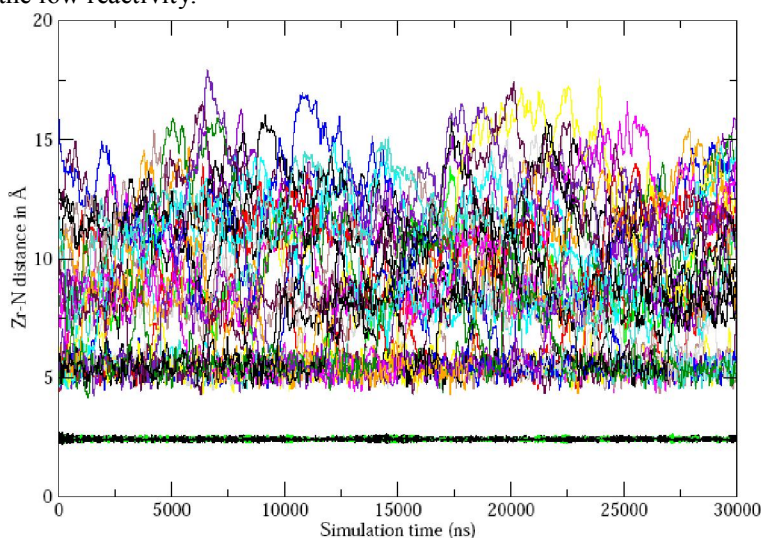


Figure. 5 The ligand exchanges of NH₃ between the second solvation shell and bulk. No ligand migration between the first and second shell.

The mean residence time of a ligand is defined as the average lifetime of a ammonia molecule in a given coordination shell. The mean residence times of ammonia molecules (τ) in solvation shells have been calculated according to Impey using $t^* = 0.5$ and 0.0 ps. For the QM/MM simulation, the mean residence time in the second solvation shell 8.67 ps ($t^*=0.5$) and 0.0437 ps ($t^*=0.0$ ps) for 30 ps simulations. The high MRT indicated the high stability of solvation structure in the first shell.

4. CONCLUSION AND SUGGESTION

The structure and dynamics of Zr^{4+} in liquid ammonia were investigated in much detail. The coordination number and Zr-N bond length was resulted in this simulation similar with experimental XRD data. The coordination number of 5 observed for the first solvation shell similar to an trigonal bipyramidal $Zr(NH_3)_5^{4+}$ complex. No first shell ligand-exchange processes occurred during the simulation time of 30 ps. In contrast, the mean residence time of ligands in the second coordination shell is large enough, indicating a high stability of the second solvation shell in the case of ammonia. The extended QM treatment in this simulations may improve the accuracy of the results or using a new method, that is QMCF method.

5. REFERENCES

- Armunanto, R., Schwenk, C.F., Randolph, B.R., dan Rode, B.M., 2004, Structure and dynamics of Co^{2+} in liquid ammonia: ab initio QM/MM molecular dynamics simulation. *Chemical Physics* 305, 135-140
- Armunanto, R., Schwenk, C.F., dan Rode, B.M., 2004, Gold(I) in Liquid Ammonia: Ab Initio QM/MM Molecular Dynamics Simulation, *J. AM. CHEM. SOC.*, 126, 9934-9935
- Armunanto, R., Schwenk, C. F., Randolph, B.R., and Rode, B.M., 2004, Ag(I) ion in liquid ammonia, *hemical Physics Letters*, 388, 395-399.
- Durdagi, S., Hofer, T.S., Randolph, B.R., Rode, B.M., 2005, Structural and dynamical properties of Bi^{3+} in water, *Chemical Physics Letters*, 406, 20–23
- Hofer, T.S., Rode, B.M., dan Randolph, B.R., 2005, Structure and dynamics of solvated Ba(II) in dilute aqueous solution – an ab initio QM/MM MD approach, *Chemical Physics*, 312, 81–88.
- Hofer, T. S., Scharnagl, H., Randolph, B. R., dan Rode, B. M., 2006, Structure and dynamics of La(III) in aqueous solution–An ab initio QM/MM MD approach, *Chemical physics*, 327, 31–42.
- Kraus, F., Baer, S.A, and Fichtl, M.B., (2009), The Reactions of Silver, Zirconium, and Hafnium Fluorides with Liquid Ammonia: Syntheses and Crystal Structures of $Ag(NH_3)_2F \cdot 2NH_3$, $[M(NH_3)_4F_4] \cdot NH_3$ (M = Zr, Hf), and $(N_2H_7)F$. *Eur. J. Inorg. Chem.* 2009, 441–447
- Kerdcharoen, T., Liedl, K. R., dan Rode, B. M., 1996, A QM/MM simulation method applied to the solution of Li^+ in liquid ammonia, *Chemical physics*, 211, 313–323.
- Messner, C.B., Hofer, T.S., Randolph, B.R., dan Rode, B.M., 2011, Structure and dynamics of the Zr^{4+} ion in water, *Phys. Chem. Chem. Phys.*, 13, 224–229
- Pranowo, H.D., Mudasir, Kusumawardani, C., dan Purtadi, S., 2006, The structure of Co^{2+} in liquid ammonia: Monte Carlo simulation including three-body correction, *Chemical Physics*, 324, 573–578
- Pranowo, H.D., dan Bernd M. Rode, 1999, Solvation of Cu^{2+} in Liquid Ammonia: Monte Carlo Simulation Including Three-Body Corrections, *J. Phys. Chem. A*, 103, 4298-4302
- Pranowo, H.D., A. H. Bambang Setiaji, dan Bernd M. Rode, 1999, Cu^+ in Liquid Ammonia and in Water: Intermolecular Potential Function and Monte Carlo Simulation, *J. Phys. Chem. A*, 103, 11115-11120
- Tongraar, A., Hannongbua, S., Rode, B.M., 1997, Molecular dynamics simulations of a potassium ion and an iodide ion in liquid ammonia, *Chemical Physics*, 219, 279-290
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