

## Comprehensive Study on The Solvation of Sr(II) Ion

Ika N. Fitriani<sup>1,a</sup>, Wiji Utami<sup>1</sup>, Niko Prasetyo<sup>1</sup> and Ria Armunanto<sup>1,2</sup>

<sup>1</sup>Austria-Indonesia Centre (AIC) for Computational Chemistry, Gadjah Mada University, Indonesia

<sup>2</sup>Department of Chemistry, Gadjah Mada University, Indonesia

**Abstract.** Solvation of Sr<sup>2+</sup> ion in liquid ammonia has been studied using the HF, DFT (B3LYP), second-order Møller-Plesset (MP2) and CCSD theory. Single valence basis sets were applied. Total and sequential binding energies are evaluated for all strontium-ammonia clusters containing 1-6 ammonia molecules. Total binding energies and distance calculated using the high level G09 calculations. For each addition of an ammonia molecules, the change of the Sr-N distance in metal-ammonia clusters is the highest at the HF level. HF is the best compromise between computational effort and accuracy.

### 1 Introduction

Strontium is interest in the field of dentistry. Strontium is also known to inhibit caries formation in teeth and promote apatite formation. In addition, Sr is used as an additive in toothpastes in the form of strontium chloride and strontium acetate to reduce tooth sensitivity. Hence, the incorporation of Sr into bioactive glasses that are currently used as remineralising additives in toothpaste is an attractive proposition [1]. Low doses of strontium are reported to have beneficial effect on bone formation in osteoporotic patients and, in some studies, strontium has been given as a salt [2]. The solvation of strontium is carried over into the solid state with the production of ammoniates mixed with solid ammonia [3].

When dealing with biological processes, ions constitute an essential foundation of numerous vital processes. As most chemical and virtually all biochemical processes occur in liquid state, solvation of the reaction partners is one of the most prominent topics for the determination of chemical reactivity and reaction mechanisms and for the control of reaction conditions and resulting materials. Besides an exhaustive investigation by various experimental methods [4, 5] theoretical approaches have gained an increasing importance in the treatment of solvation effects [6]. These processes have become more and more the domain of computational simulations and a critical evaluation of the accuracy of simulation methods covering experimentally inaccessible systems is of most importance [7].

Solvation of Sr<sup>2+</sup> ion has stimulated considerable theoretical interest. Computational chemistry provides information on the arrangements of solvent molecules around metal ions, binding energy, and the vibrational frequencies of the complexes that are often useful for experimentalists. Interplay between theory and

experiment is crucial to obtain a molecular level understanding of ion solvation, which will aid to attain correct mechanistic conclusions about biological control of ion movements.

Hybrid *ab initio* Hartree-Fock (HF) simulations proved to achieve the necessary accuracy, although at enormous costs in terms of computational effort. On the other hand, the use of simple density functionals as in the RIDFT method or in Car-Parrinello simulations can lead to first-shell coordination numbers that are lower than almost all experimental and other theoretical data. The more sophisticated B3LYP-DFT formalism leads to a similar degree of accuracy as the *ab initio* Hartree-Fock method, but without saving computer time [8].

Many tests have finally shown that *ab initio* Hartree-Fock (HF) level is required to produce sufficiently accurate results. Correlated *ab initio* methods, even Møller-Plesset second order perturbation theory (MP2), would lead to an unaffordable computational effort, but they can be used to estimate the accuracy of HF level by calculations of small solute-solvent clusters at different levels of theory. Unfortunately also DFT level does not appear a suitable solution. QM/MM simulations employing the B3LYP functional, which are almost equally time consuming as *ab initio* HF calculations, have shown that hydrogen bonds as well as solvation structures are too rigid and thus give a wrong picture of structure and dynamics of solvents and solutions. At this point some misleading nomenclature in publications of simulations has to be clarified. This is indeed not correct as all available density functionals are of a more or less semiempirical nature of the B3LYP functional. Only by *ab-initio* is also enabled to perform a method inherent control of accuracy and deficiencies by increasing the level of theory from a one determinant also a multi-determinantal method [9].

<sup>a</sup> Corresponding author: ika.nur.f@mail.ugm.ac.id

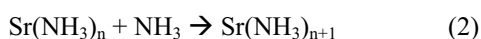
The use of simple density functionals for example, the most commonly used Becke-Lee-Yang-Parr (BLYP) includes further error sources. These functions imply all simplifications of the general gradient approximation formalism and, besides that, the other problems, common to virtually all contemporary density functional theory (DFT) methods, namely, the wrong treatment of kinetic energy, the semiempirical parameterization of some of the terms, and the attempt to compensate errors by empirical formulae, make the interpretation of the results to a certain extent ambiguous [10].

In the present study, ammonia molecules are added to  $\text{Sr}^{2+}$  ion and the solvated metal ion complexes  $[\text{Sr}(\text{NH}_3)_n]^{2+}$ ;  $n = 1-6$  is explored using ab initio and density functional theory methods. This study is not only provides insight into the nature of solvation of metal ions but also establishes the method and basis set dependency of this solvation. Because the solvation of metal ions is a topic of great interest, it is necessary to identify theoretical methods that can satisfactorily reproduce experimental results at the lowest computational cost.

## 2 Method

This method performed cluster calculation for  $[\text{Sr}(\text{NH}_3)_{1-6}]^{2+}$  with different methods including HF, MP2, B3LYP, and CCSD. We have chosen the SV(P) basis set [11] for  $\text{Sr}^{2+}$  ion and DZP for ammonia molecules [12]. Initially, all strontium-ammonia complexes considered in the present study  $[\text{Sr}(\text{NH}_3)_n]$ ;  $n = 1-6$  were explored on their respective potential energy surfaces. Among the various possible conformers, the lowest energy structure were considered for further geometry optimizations at the HF, B3LYP, MP2, and CCSD levels. Besides this, single point calculations were performed at the HF, MP2, B3LYP, and CCSD levels using the geometries optimized at the each levels. Calculations were also performed by the Gaussian-09 (G9) method [13] that employs a sequence of ab initio molecular orbital calculations to estimate the total energy of a given molecular system at a level where it cannot be calculated directly [14].

To calculate the basis set superposition error (BSSE), we have used the counterpoise correction of Boys and Bernardi. BSSE values obtained at the HF, MP2, B3LYP, and CCSD levels are used for BSSE corrections, respectively. The HF, MP2, B3LYP, and CCSD wave function methods with genecp basis set were used to obtain the distance and binding energy. The distance and binding energy were calculated. Total and sequential binding energies were calculated using the following equation:



## 3 Result and discussion

Tables 1 and 2 list the binding energy as well as the Sr-N distance obtained for geometry optimizations of  $[\text{Sr}(\text{H}_2\text{O})_n]^{2+}$  ( $n = 1-6$ ) clusters at various levels of theory employing the above-mentioned basis sets.

**Table 1.** Average Binding Energy in kcal/mol for  $\text{Sr}(\text{II})-(\text{NH}_3)_n$  Cluster of Different Size Obtained from HF, MP2, CCSD, and B3LYP calculations

HF	MP2	CCSD	B3LYP
-52.24	-57.82	-54.17	-55.89
-48.81	-54.07	-30.73	-54.91
-48.59	-51.74	-35.57	-52.25
-43.94	-28.54	-36.63	-49.12
-40.75	-45.81	-35.61	-45.27
-38.04	-42.99	-34.29	-77.16

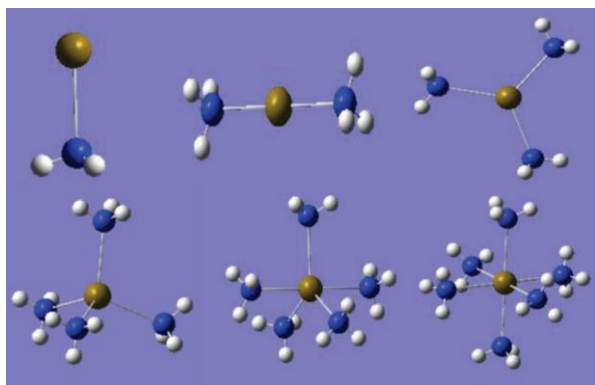
These result also indicate effect of electron correlation to be expected during the simulation. As can be observed from Table 1, the average solvation energy values differ slightly for HF, MP2, and CCSD, but the difference is quite considerable in the case of B3LYP. However, neither MP2 nor CCSD is computationally affordable for simulation at present, so we prefer to use HF as the level of theory for the QM calculation. The relative scale lists the average binding energies per ligand descending from highest to lowest is  $\text{HF} > \text{CCSD} > \text{MP2} > \text{B3LYP}$ .

Ab initio HF SCF or density functional theory (DFT) are manageable, considering the necessary computational effort. In recent investigations of similar ionic systems, results of HF calculations were in good agreement with experimental data, whereas simple DFT methods always failed, and even the more suitable hybrid B3LYP functional sometimes yielded wrong descriptions or, at best, a proper description of the system without any time saving effect.

**Table 2.** Average Sr-N Distances in Å for  $\text{Sr}(\text{II})-\text{NH}_3$  Clusters of Different Size Obtained from HF, MP2, CCSD, and B3LYP Calculations

n	HF	MP2	CCSD	B3LYP
1	2.64	2.44	2.53	2.57
2	2.69	2.44	2.65	2.64
3	2.70	2.44	2.65	2.65
4	2.73	2.44	2.75	2.75
5	2.76	2.44	2.69	2.70
6	2.76	2.44	2.76	2.82

The average bond distances resulting from the different calculations are in good agreement, the B3LYP method showing the largest deviation. Based from the experiment distance from  $\text{Sr}^{2+}-\text{N}$  is 2,62 [15]. HF is in excellent agreement with experimental data. The relative scale of the average  $\text{Sr}^{2+}-\text{N}$  distances from highest to lowest is  $\text{HF} > \text{CCSD} > \text{B3LYP} > \text{MP2}$ .



**Figure 1.** Optimized geometries of  $\text{Sr}^{2+}(\text{NH}_3)_n$  ( $n=1-6$ )

Based on the Table 1 and 2, there is slightly difference in energy and distance from several method. The result not depend on correlation interaction because doesn't give significant contribution. MP2, B3LYP, and CCSD have high accuracy for simulation because correlation interaction effect, but HF used for calculation method. HF is the simplest method which spend shorter time than MP2, B3LYP, and CCSD. Optimized geometries can be seen in Figure 1.

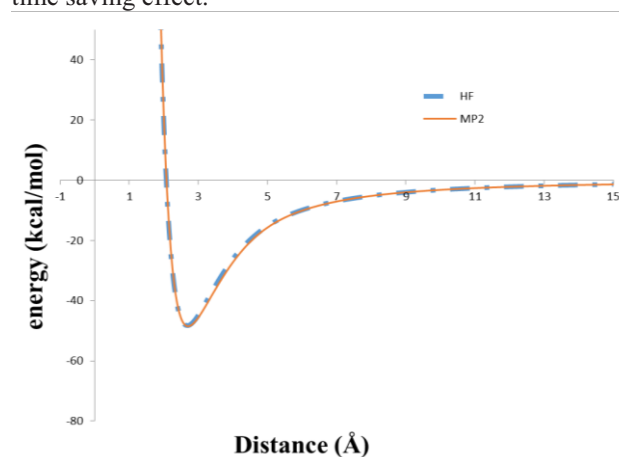
Tables 1 and 2 list the binding energy as well as the Sr-N distance obtained for geometry optimization of  $[\text{Sr}(\text{NH}_3)_n]^{2+}$  ( $n = 1-6$ ) clusters at various levels of theory employing the above mentioned basis sets SV(P). the deviations obtained for the binding energies are in the order of about 1 kcal/mol except for B3LYP, which shows larger values at lower coordination number. The average bond distances resulting from the different calculation are in good agreement, the B3LYP method showing the largest deviation. The good agreement of the ab initio HF SCF method with correlated methods for the description of solvated ions has been demonstrated recently in similar investigation of the solvated ions Li (I). Based on these investigations and the results of the geometry optimizations the Sr(II) ammonia the ab initio HF-SCF method was to be preferred in the construction of the pair and three body interaction potentials as this method is more accurate in the case of the mono- and diammine than the DFT method. Due to compatibility, the ab initio HF scheme had to be applied in QM part of the simulation as well. As a general conclusion one can state the influence of electron correlation is minor for such system and that many body effect are less pronounced for monovalent ions than for those with higher charges

HF delivers strontium ion-ammonia distances close to the values derived by CCSD calculations, although the stabilization energy is too small. The difference becomes smaller with increasing number of ligand. Simulation in solution with abundance of ligands is favorable. The MP2 calculations are in good agreement with CCSD ones. The energy of strontium(II) clusters is underestimated to a similar extent as by HF, whereas the binding distances are too small again. The inclusion of dispersion terms (B3LYP) yield better result, but more recent B3LYP approach leads to too rigid hydrogen bonds and make slowing down the dynamics[16].

The estimation of the influence of the basis set superposition error (BSSE) was performed for  $\text{Sr}^{2+}-\text{NH}_3$

(see Table 3). The BSSE (basis set superposition error) calculations were also performed for the Sr(II)-NH<sub>3</sub> different levels of theory and were included in Table 3. The data indicates that BSSE and electron correlation do not have any significant contribution for the system of interest.

With respect to the level of theory for the QM region, either ab initio HF SCF or density functional theory (DFT) are manageable, considering the necessary computational effort. In recent investigations of similar ionic system, result of HF calculation were in good agreement with experimental data, whereas simple DFT method such, B3LYP always failed and even the more suitable hybrid B3LYP functional sometimes yielded wrong descriptions or at best, a proper description of the system without any time saving effect.



**Figure 2.** Interaction Energy Curve of  $\text{Sr}^{2+}-\text{NH}_3$

Correlated method such as full MP2 and CCSD are still computationally too demanding. HF less costly than conventional MP2. MP2 accounts for electron correlation.

An approximate way of assessing BSSE is the counterpoise correction. In this method the BSSE is estimated as the difference between monomer energies as the difference between monomer energies with the regular basis and the energies calculated with the full set of basis functions for the whole complex. Consider two molecules A and B, each having regular nuclear-centred basis sets denoted with subscript a and b, and the complex AB having the combined basis set ab. The geometries of the two isolated molecule and of the complex are first optimized or otherwise assigned. The geometries of the A and B molecules in the complex will usually be slightly different than for the isolated species, and the complex geometry will denoted with a\*. The dimer energy minus the monomer is the directly calculated complexation energy.

$$\Delta E_{\text{complexation}} = E(\text{AB})_{ab}^* - E(\text{A})_a - E(\text{B})_b \quad (3)$$

To estimate how much of this complexation energy is due to BSSE, four additional energy calculations are needed. Using the a basis set for A and the b basis set for B, the energies of each of the two fragments are calculated with the geometry they have in the complex. Two additional energy calculations of the fragments at the complex geometry are then carried out with the full

<sup>a</sup> Corresponding author: ika.nur.f@mail.ugm.ac.id

ab basis set. This means that the energy of A is calculated in the presence of both the normal a basis functions and with the b basis function of fragment B located at the corresponding nuclear positions, but without the B nuclei present, and vice versa. Such basis functions located at fixed points in space are often referred to as ghost orbital. The fragment energy for A will be lowered due to these ghost functions, since the a basis becomes more complete. The counterpoise correction is defined in eq 4.

$$\Delta E_{cp} = E(A)_{ab}^* + E(B)_{ab}^* - E(A)_a - E(B)_b \quad (4)$$

The counterpoise-corrected complexation energy is then given in the eq 5.

$$\Delta E_{complexation} - \Delta E_{cp} \quad (5)$$

For regular basis sets, this typically stabilizes at the basis set limiting value much earlier than uncorrected values, but this is not necessarily the case if diffuse function are included in the basis set. Delta ECP is an approximate correction and gives an estimate of the BSSE effect but does not provide either an upper or lower limit [17].

It is usually observed that the counterpoise-correction for methods including electron correlation is larger and more sensitive to the size of the basis set than at the HF or DFT level. This is in line with the fact that the HF wave function converges much faster with respect to the size of the basis set than correlated wave functions.

**Table 3.** Basis Set Superposition Error According to Boys-Bernardi Procedure for Sr(II)-NH<sub>3</sub> Obtained from HF, MP2, CCSD, and B3LYP calculations

BSSE (in kcal/mol)	
HF	0.53
MP2	3.82
CCSD	3.78
B3LYP	1.03

BSSE HF is lower than MP2, CCSD, and B3LYP. From this BSSE value, HF is reliable because the fault in calculation of interaction energy was small.

The HF and MP2 curve are good in agreement with the Lennard-Jones interaction curve, as can be seen in Fig 2. The value of interaction energy gives positive value in short distance due to repulsive among particles. The interaction energy decreases until optimum distance with negative value. The interaction energy of HF method is good in agreement with MP2 method with slightly different in interaction energy.

## 4 Conclusion

The paper provides calculation of binding energy, distance, and BSSE at level ab initio used G09 methods for the solvation of Sr<sup>2+</sup> ion. The present study suggests SV(P) and DZP basis set with HF method is the lowest energy conformer of solvated Sr<sup>2+</sup> ion in liquid ammonia. HF level of theory promised to yield the best compromise between computational effort and accuracy.

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