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INTERACTION POTENTIAL BETWEEN BERYLLIUM (II) ION AND AMMONIA DERIVED FROM AB-INITIO CALCULATIONS

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ABSTRACT

An analytical pair potential function for beryllium (II) ion interacting with ammonia was constructed by fitting process of well-selected 150 interaction-data points. The potential interactions were calculated by means of ab initio SCF-LCAO-MO method, based on the double zeta basis function including polarization.

INTRODUCTION

In the subject of solution chemistry, aqueous electrolyte solutions seem to be of most interest, because they involve with the biological bodies. In general, the squeous solution are composed of many existing species and it can be possibly classified by three pairs of interactions e.g. the interactions between (i) water and water[1-2] (ii) ions and polar solvents[3-8] and (iii) polar solvents and some organic molecules,[9-10] which were investigated by quantum chemical calculations. According to the toxicity of ammonia which can form complex with alkaline metal, the interaction energy between alkaline metal and ammonia was then studied.[11] The information of interaction potential between beryllium (II) ion and neutral molecule was hardly ever studied, yet its role is of interest. However, the strong charge such as beryllium (II) ion frequently makes doubtful its interaction with polar molecule.[12] It may be caused from the large charge-to-radius ratio of the beryllium (II) ion and the polarity of the polar molecule.

In this work the interaction potential between beryllium (II) ion and ammonia was therefore investigated and also constructed as an analytical formula. The analytical potential function obtained from this work can be used in the computer simulations such as Monte Carlo (MC)[13-20] and molecule dynamics (MD)[21-27] techniques.

METHOD OF COMPUTATIONS

The stabilisation energies between Be^{2+} and NH_3 were obtained from ab initio calculations with the basis function of DZP (Double Zeta plus Polarization function of exponents (0.21, 0.80), (1.00) and (0.06, 0.05) for N, H and Be^{2+} respectively). The DZP selected from the option of the HONDO Programme [25, 26] was examined and regarded

as the most appropriate basis function for Be^{2+}/NH_3 system. The geometrical parameters of ammonia molecule used in the calculations were taken from reference 27; N-H bond and HNH angle of ammonia molecule are 1.0124 Å and 106.7° respectively.

The three vertical planes along molecular axis (z-axis) defined as the plane A (xz-plane), plane B (θ = 30°) and plane C (θ = 60°) (see Fig.1) were introduced. The seventeen different orientations of beryllium (II) ion around ammonia molecule which mostly represent whole space of energy surface were performed.

The final form of the analytical pair potential function has been carried out by fitting 150 energy surface points of the beryllium (II) / ammonia interaction, situated within one sixth of whole space around ammonia molecule. The fitting was proceeded by ESNIT programme.[28]

Quantum chemical computations were performed on the IBM 3031/08 Computer Centre of Chulalongkorn University and the fitting process was carried out on the NEC 286 Personal Computers, Research Affairs, Chulalongkorn University.

RESULTS AND DISCUSSION

The form of the pair potential function between beryllium (II) ion and ammonia, obtained from the fitting (in the unit of kJ/mole) is given by

$$\Delta E\,(Be^{2+},NH_3) = \sum_{j=1}^{4} \left[\frac{B_{ij}}{r_{ij}^{12}} - \frac{A_{ij}}{r_{ij}^{6}} + \frac{C_{ij}}{r_{ij}^{2}} + \frac{D_{ij}}{r_{ij}^{3}} + \frac{E_{ij}}{r_{ij}^{4}} + \frac{F_{ij}}{r_{ij}^{5}} + q_i q_j \frac{G_{ij}}{r_{ij}} \right]$$

Eq. (1)

where A_{ij}, B_{ij}, C_{ij}, D_{ij}, E_{ij}, F_{ij} and G_{ij} are the fitted-model parameters (Table 1), r_{ij} is the distance between Be^{2+} ion and an atom j of the ammonia molecule (in atomic units), q_1 and q_j are the net charges of Be^{2+} ion and atoms j (in atomic units) of the isolated molecule, respectively. The net charges of these atoms were obtained from the Mulliken population analysis.[29] This potential function can be regarded as a form of polynomial character consisting of the extended term and the Lennard-Jones-type function. The shapes of the extended and the Lennard-Jones-type functions are the terms of $C_{ij}/r_{ij}^2 + D_{ij}/r_{ij}^3 + E_{ij}/r_{ij}^4 + F_{ij}/r_{ij}^5$ and $B_{ij}/r_{ij}^{12} - A_{ij}/r_{ij}^6$ respectively.

The 150 data points of stabilisation energy used in the fitting procedure was sufficient to be relied.[11] Eq. (1) extracted from twenty-one models is the most appropriate function to represent the interaction between Be^{2+} and NH_3.

Total standard deviation, σ_{Total} = 20.1 kJ/mol, obtained from the fitting could be statistically acceped as comparison with the accuracy of the DZP-ab initio calculations and used in the computer simulation such as MC and MD simulations. The theoretical chemical studies such as MC and MD simulations normally require the potential function of which the low energies are more accurate than the higher energies. Therefore, the weighting

technique of the fitting process was used in order to enhance the accuracy of the lower energies; it is reflected by the standard deviation of various energy-intervals as shown in Table 2.

The energy correlation between the stabilisation energies obtained from the SCF-MO calculations ($\triangle E_{SCF\text{-}MO}$) and the energies obtained from the potential function of equation (1) with the parameters of Table 1 ($\triangle$ EFIT) is shown in Figure 2. Figure 2 demonstrates that the lower energies are slighly deviated from the linear curve.

If the structural results obtained from MC and MD simulations depend rather on the relative potential than the absolute interaction energies, then the sequence of the energy curves and their mininum positions (according to both of $\triangle E_{SCF\text{-}MO}$ and $\triangle E_{FIT}$) should be significant. Figure 3 shows that the energy minima of SCF-MO curves are located at the same position of the fitted curve. Curves d, e and f of Fig. 3 obtained from the potential function of eq. (1) show the large deviation of energies comparing with those values obtained from the quantum chemical calculations, but their energies are less important than the curves a, b and c. However, the DZP-ab initio calculations on the energies of curves c, d, e and f were under-estimated but for the curves a and b seem to be over-estimated. The under and over-estimations may be caused by the Be^{2+} located near the ammonia hydrogen atoms and the nitrogen atom, respectively.

The lowest energy of Be^{2+} / NH_3 complex is in the potential direction of (Θ, ϕ) = (0°, 0°), which Be^{2+} is positioned at 1.96 Å from N-atom of ammonia molecule along the molecular axis (z-axis). However, the most preferable structure is the configuration of the ammonia pointing with its nitrogen atom towards to the Be^{2+} ion. According to the DZP-ab initio calculations on the Be^{2+} / NH_3 system, we can remarkably conclude that (i) the most stable structure of Be^{2+} / NH_3 complex is the configuration of Be^{2+} located at (Θ, ϕ, r) = (0°, 0°, 1.96 Å) (stabilized by the interaction energy of -669 kJ/mol), (ii) at long distance (5-7 Å far from ammonia-nitrogen atom), the interaction potential is valid within the range of -75 to -134 kJ/mol , and (iii) the potential-energy curve of the positive value throughout the curve is not found.

Although the well-selected DZP-basis set was used in the SCF-calculations, the interaction potential for Be^{+2} / NH_3 system is not absolutely justified. The extended basis function of SCF-MO calculations on Be^{2+} / NH_3 should be recalculated as the future work.

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บทคัดย่อ

การสร้างฟังก์ชันพลังงานศักย์ของอนุภาคคู่ ระหว่าง Be^{2+} กับ NH_3 โดยการฟิต (fitting) โดยใช้ข้อมูลที่เป็นพลังงานศักย์ของอนุภาคคู่ซึ่งได้มาจากการคำนวณทางเคมีควอนตัมโดยวิธี ab initio SCF-LCAO-MO โดยใช้ DZP เป็น basis function

TABLE 1 Model parameters for Be^{2+} interacting with ammonia molecular atoms ($q_N = -0.742$ and $q_H = 0.247$, in atomic units) based on atomic length units for distance r and kJ/mol for interaction energy.

Pair of interaction	Parameters A	B	C	D	E	F	G
$Be^{2+} - N$	−0.11702E+08	−0.93386E+07	0.53888E+06	−0.33709E+07	0.10925E+08	−0.17781E+08	0.31540E+05
$Be^{2+} - H$	0.10694E+07	0.12208E+06	−0.12128E+06	0.61267E+06	−0.15974E+07	0.20801E+07	0.26058E+06

TABLE 2 Standard deviation σ of the fitted potential energies (kJ/mol).

$\sigma_{<-500}$	$\sigma_{<-400}$	$\sigma_{<-300}$	$\sigma_{<-200}$	$\sigma_{<-100}$	$\sigma_{<0}$	$\sigma_{<100}$
17.8	20.6	22.7	25.3	22.4	21.2	20.6

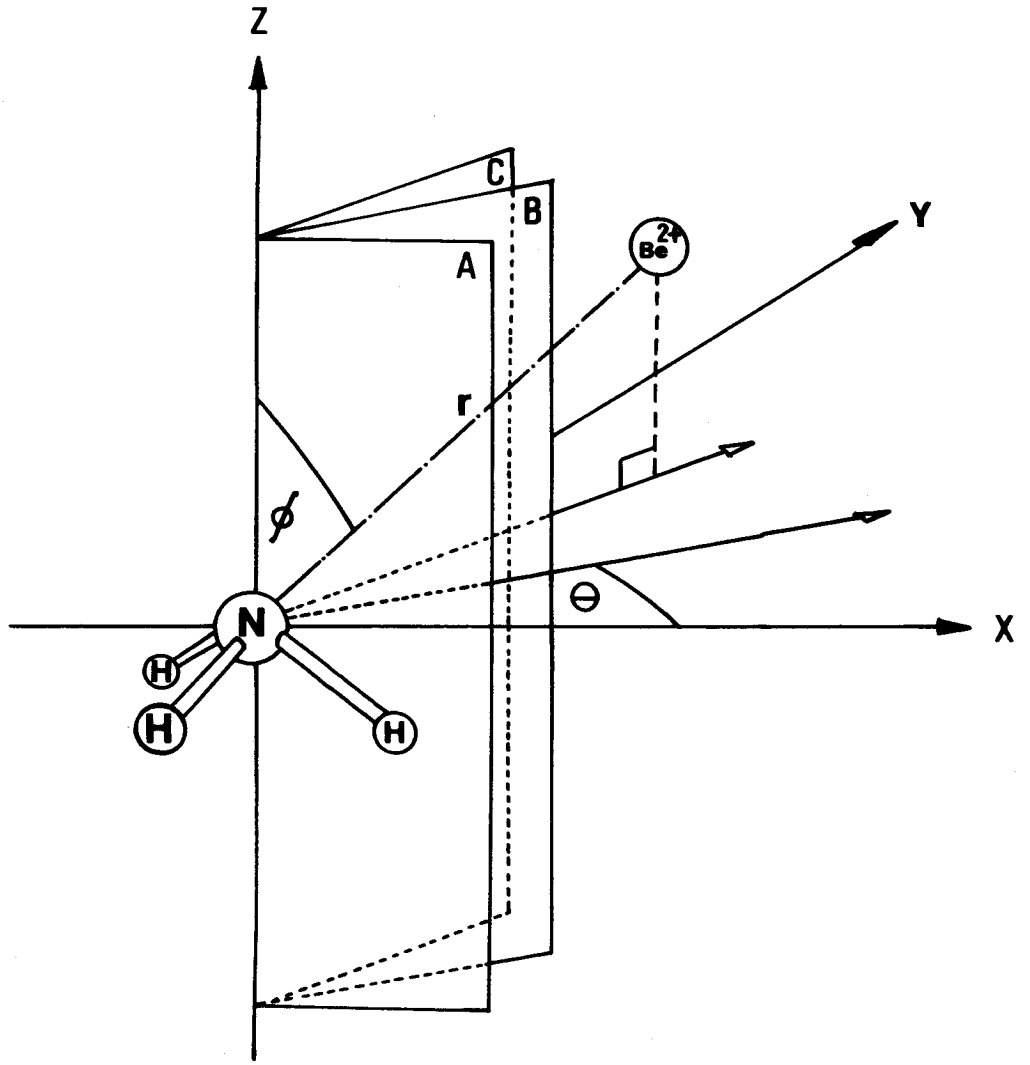

Fig. 1 Definition of geometric parameters, Θ, ϕ and r for the configurations of beryllium (II)/ammonia, and the molecular planes of ammonia molecule are defined as the plane A (xz-axis), plane B (Θ = 30°) and plane C (Θ = 60°).

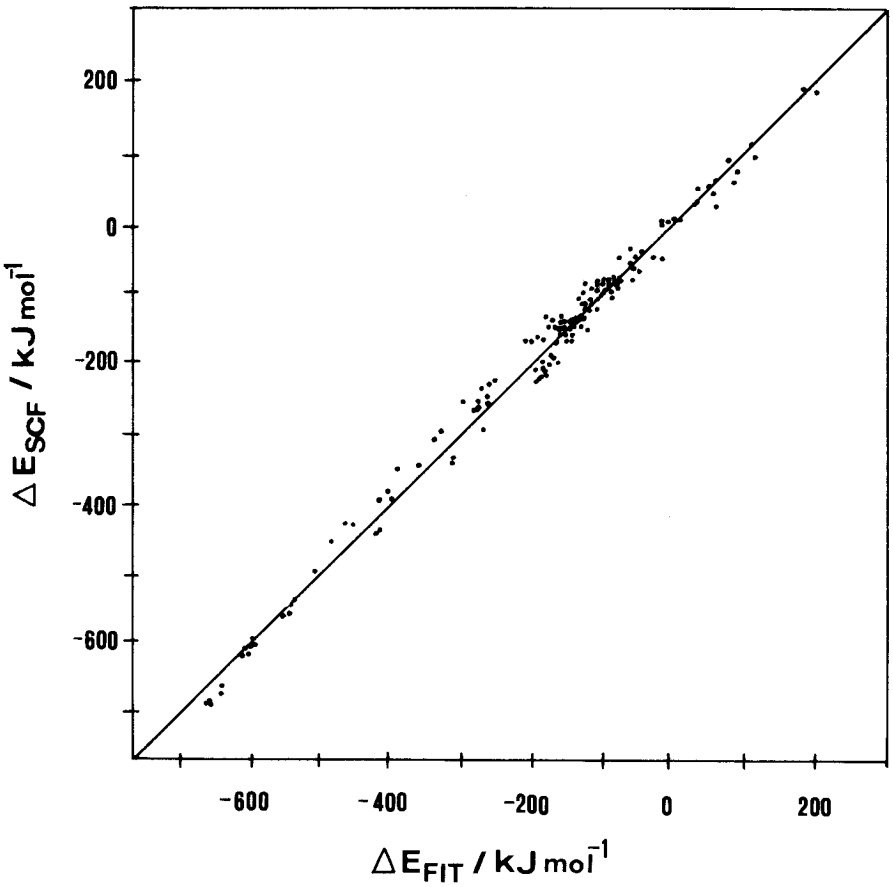

Fig. 2 Energy coorelation between SCF-MO calculated $\triangle E_{SCF}$ and fitted energies $\triangle E_{FIT}$ due to eq. 1 and its parameters given in Table 1.

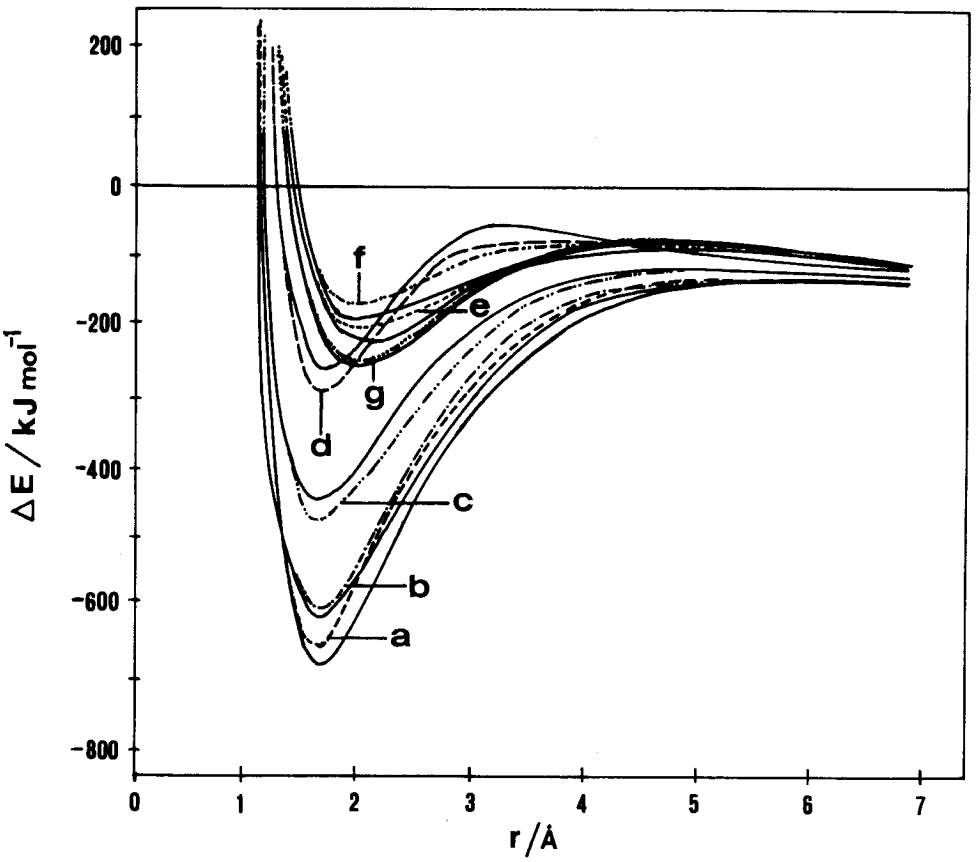

Fig. 3 Potential curves of different angles (plane C of Fig. 1) between DZP-ab initio computed energies (solid lines) and the fitted energies whose orientations of potential curve given by
a (ϕ = 0°, _ _ _ _ _ _), b (ϕ = 30°, ._._._._), c (ϕ = 60°, .._.._.._), d (ϕ = 90°, __ __ __ __), e (ϕ = 120°, ...), f (ϕ = 150°, .._ _.._ _..), and g (ϕ = 180°, _..._..._..._).

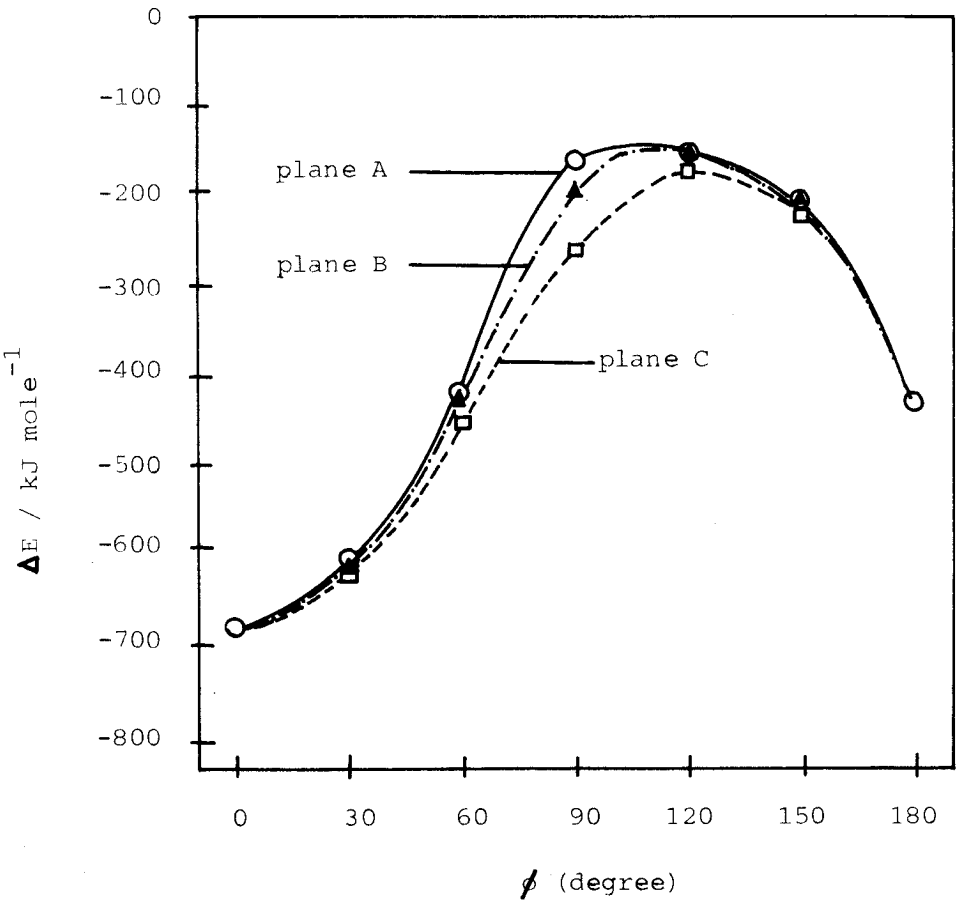

Fig. 4 Angular depencence of interaction potential between beryllium (II) ion and amonia in the plane A (_____), plane B (_._._._._.) and plane C (_ _ _ _ _ _).