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# The structure of lithium and potassium cations coordinated by ammonia molecules in the gas phase as revealed by ab initio SCF-MI calculations

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## Abstract

The structure and the energetics of lithium and potassium cations coordinated by ammonia molecules were calculated by an ab initio Hartree Fock study in the absence of basis set superposition error (BSSE). Complexes formed by clusters consisting of up to six ammonia molecules and  $\text{Li}^+$  or  $\text{K}^+$  ions were investigated. Gradient geometry optimizations were performed in the framework of the self consistent field for molecular interactions (SCF-MI) theory adopting the recently implemented generalization of the method. The intermolecular interaction energies and PES are a priori corrected for the BSSE. The 6-31 + G\* basis set was used. Ion clusters are stabilized by the metal-N bond and the interaction structure allows the formation of the maximum number of such bonds in the first solvation shell. All the properties studied change in a systematic manner upon addition of a further ammonia molecule.  $\text{Li}^+$  and  $\text{K}^+$  complexes exhibit no sign of hydrogen bonding between the molecules of the first coordination shell. However, the  $\text{Li}^+$  complexes with five and six ammonia molecules show the formation of hydrogen bonds between the coordinated molecules of first and second shells. From the results, it follows that both  $\text{Li}^+$  and  $\text{K}^+$  ions form similar complexes with up to four ammonia molecules. However, in the  $\text{Li}^+$  complexes, the first coordination shell saturates with four molecules and leads to conformations differing from those of the  $\text{K}^+$  complexes. In accordance with recent neutron diffraction experimental analysis of the structure of  $\text{Li}^+$  and  $\text{K}^+$  in  $\text{NH}_3$  solutions [J. Chem. Phys. 112 (2000) 7147], the lithium is tetrahedrally coordinated while potassium results octahedrally coordinated by solvent molecules. The theoretical results are acceptably consistent with the experiments and can furnish insight into the identification of some features of the clustering process. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Intermolecular interactions; Basis set superimposition error; Self consistent field for molecular interactions; Solvation effects

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## 1. Introduction

Ion solvation processes are of great importance in relation to a variety of applications. In order to

improve the knowledge and to characterize such processes, gas phase studies can be performed providing detailed information about individual interactions. These studies can explore changes in some properties between the complexes in the gas phase and the solvated systems in the liquid phase. Theoretical methods can thus provide valuable complementary information not accessible to experimental

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approaches both in the characterization of the complexes and in the specific mechanism of the involved interactions.

Since the first preparation of potassium in ammonia solution (Sir Humphrey Davy, in 1808) alkali metal–ammonia solutions have been at the center of theoretical and experimental interest. Novel properties include low density, high electrical conductivity, liquid–liquid phase separation, and a concentration driven metal–nonmetal transition [1–5]. A variety of electronic species has also been reported as a function of concentration, including polarons, bipolarons, and delocalized metallic [1–5]. As further motivation for studying this system, saturated lithium–ammonia solutions lie above a deep pseudoeutectic, at 88 K. This provides an important opportunity to study a low density liquid over a large temperature range [6].

The structure of Li and K ammonia solution has been recently studied by neutron diffraction experiments [6]. In this neutron diffraction study the technique of isotopic substitution has been successfully applied to obtain the N-centered first-order difference functions and corresponding real-space data sets for saturated solutions of lithium and potassium in ammonia, as well as for the pure solvent. The results show that for saturated lithium–ammonia solutions the cation is tetrahedrally solvated by ammonia molecules. This finding has also been seen in an earlier neutron diffraction study on saturated lithium–ammonia solutions [6] and predicted for lithium–ammonia solutions using computer simulations taking into account quantum effects. On the other hand, from the data of the microscopic structure of potassium–ammonia solutions, the potassium results octahedrally coordinated with ammonia molecules. The  $\text{Li}^+$  is a ‘structure making ion’ and  $\text{K}^+$  is a ‘structure breaking’ ion in alkali metal–ammonia solutions, as also found in aqueous solutions of lithium chloride and potassium chloride, respectively, [7,8]. In fact, from comparative studies of aqueous solutions, the lithium cations were found to be strongly coordinated with nearest-neighbor water molecules acting as a structure making ion [7,8] while a loose association between  $\text{K}^+$  and  $\text{D}_2\text{O}$  was observed for a 3.57 M aqueous solution of potassium chloride, i.e. the aqueous solution contains structure breaking  $\text{K}^+$  ions [9].

The present paper focuses on the structural

properties of  $[\text{Li}(\text{NH}_3)_n]^+$  and  $[\text{K}(\text{NH}_3)_n]^+$  (with  $n = 1–6$ ) clusters. Stability and structure of  $[\text{Li}(\text{NH}_3)_n]^+$  and  $[\text{K}(\text{NH}_3)_n]^+$  (with  $n = 1–6$ ) clusters have been investigated ab initio by the self consistent field for molecular interactions (SCF-MI) method [10–13]. It is well known that the basis set superposition error (BSSE) [14–16] represents a serious drawback when variational procedures are adopted for interacting system studies. Regarding the elimination of this error, some remarks have to be made. First of all, the evaluation of the monomer energies at the dimer geometry involves a variable underestimate of the BSSE [17,18], which in some cases can account to up to 10% of the binding energy. It is therefore always mandatory to consider the effects of geometry deformation, which implies a considerable increase in computation time in the case of big systems. Moreover, it has been recently pointed out [19] that in order to compute equilibrium geometries and binding energies it is essential to operate within BSSE free potential surfaces. For example, the uncorrected potential energy surface (PES) of the hydrogen fluoride dimer at the MP2/6-31G\*\* level predicts only a minimum corresponding to the wrong cyclic structure. The correct quasi-linear minimum appears only after analysis of the CP corrected PES, showing the cyclic dimer as a transition state [19]. Moreover, the addition of the partner’s functions introduces the secondary superposition error, a spurious electrostatic contribution, which is not removed by the CP approach, due to improper modification of multipole moments and polarizabilities of the monomers. This is particularly important in the case of anisotropic potentials, where these errors can contribute to alter even more the shape of the PES and the resulting physical picture [20].

The SCF-MI approach is used, so as to ensure the absence of the BSSE. The SCF-MI method allows the elimination of BSSE occurrence by an a priori strategy at the HF level; basis set and size consistency is also ensured. The geometry is then optimized on a BSSE-free PES. The SCF-MI approach has led to quite accurate predictions of the properties of molecular dimers of biological interest [21–24]. In particular, it was demonstrated that the SCF-MI method can provide reliable results even with small basis set such as the 3-21G basis [25].

This work reports ab initio calculations for the

clusters formed by ammonia molecules with lithium and potassium ions in the gas phase performed with the SCF-MI method and using the 6-31 + G\* basis set. The clusters studied has the formula  $M(\text{NH}_3)_n$ , where  $M$  is either  $\text{Li}^+$  or  $\text{K}^+$  and  $n$  ranged from 1 to 6.  $\text{Li}^+$  saturation of the coordination shell was reached with fewer ammonia molecules. The results thus obtained can allow one to identify the effects of gradual solvation of the ions on some properties such as energies and geometries and vibrational frequencies. All computations were performed by using the GAMESS-US software package [26].

## 2. Theory

In this section we report an introduction to the most relevant elements of the SCF-MI approach; a more detailed account can be found elsewhere [10–13]. The validity of the method extends from the long range to the region of the minimum and of short distances.

According to the SCF-MI strategy, a supersystem of  $K$  closed shell interacting fragments  $a_1 \dots a_K$  containing  $2N$  electrons ( $N = N_1 + N_2 + \dots + N_K$ ) is described by the one determinant wave function

$$\Psi(1, \dots, 2N) = \mathcal{A}[\varphi_{1,1}(1)\bar{\varphi}_{1,1}(2) \dots \varphi_{K,N_K}(2N-1)\bar{\varphi}_{K,N_K}(2N)] \quad (1)$$

where  $\mathcal{A}$  is the total antisymmetrizer operator. The key of the method is the partitioning of the total basis

set

$$\chi = (\chi_1 | \chi_2 | \dots | \chi_K) \quad (2)$$

where  $M = M_1 + \dots + M_K$  is the basis set size, so as the MOs of different fragments are expanded in different subsets centered on each fragment. In this way, the  $N_K$  doubly occupied molecular orbitals of the fragment  $K$ ,  $\varphi_K = (\varphi_{K,1} \dots \varphi_{K,N_K})$ ,

$$\varphi_K = \chi_K T_K \quad (3)$$

are expanded in the proper set  $\chi_K = (\chi_{K,1} \dots \chi_{K,M_K})$ , where  $T_K$  is an  $M_K \times N_K$  matrix and  $M_K$  is the number of basis orbitals centered on the fragment  $K$ . The orbitals of different fragments are free to overlap with each other; the non orthogonality problem is solved so as not to involve any particularly severe computational difficulty. The total  $(M \times N)$  matrix of the partitioned molecular orbital coefficients  $\mathbf{T}$ , defined as

$$\varphi = (\varphi_1 | \varphi_2 | \dots | \varphi_K) \quad \varphi = \chi T \quad (4)$$

is assumed in a block diagonal form where the diagonal blocks are the  $T_1, \dots, T_K$  matrices while the other blocks are null matrices (see Fig. 1 for the case of three interacting fragments).

The energy corresponding to the SCF-MI wavefunction (1)

$$E = \text{Tr}[\mathbf{D} \cdot \mathbf{h}] + \text{Tr}[\mathbf{D} \cdot \mathbf{F}(\mathbf{D})] \quad (5)$$

is written in term of  $F$  and  $h$ , the usual Fock and one-electron integral matrices expressed in the atomic orbitals basis set, and of the density matrix  $\mathbf{D}$  defined

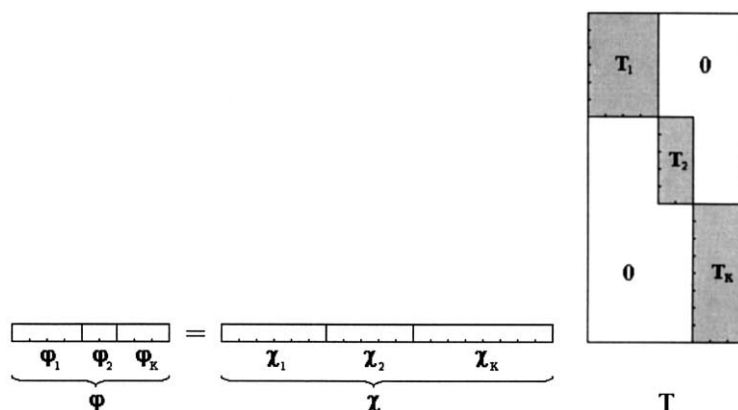


Fig. 1. Atomic and molecular orbitals in a case of  $K = 3$  fragments.

as

$$\mathbf{D} = \mathbf{T}(\mathbf{T}^\dagger \mathbf{S} \mathbf{T})^{-1} \mathbf{T}^\dagger \quad (6)$$

and satisfying the general idempotency condition

$$\mathbf{DSD} = \mathbf{D} \quad (7)$$

The appearance of the BSSE is avoided by assuming and maintaining the orbital coefficient variation matrix in a block diagonal form. The general stationary condition  $\delta E = 0$  becomes equivalent to  $K$  secular problems

$$\begin{cases} F_k' T_k' = S_k' T_k' L_k \\ T_k'^\dagger S_k' T_k' = 1^{N_k} \end{cases} \quad (8)$$

in terms of effective Fock and overlap matrixes  $F_k'$  and  $S_k'$ . It is substantial to recognize that these matrices are Hermitian and possess the correct asymptotic behavior: that is, in the limit of infinite separation of the fragments,  $F_k'$  and  $S_k'$  become exactly the Fock and overlap matrixes of the individual systems.

The binding energy is

$$\Delta E_{\text{SCF-MI}} = E_{\text{SCF-MI}} - \sum_{k=1}^K E_{\text{SCF}}^K \quad (9)$$

and takes properly account of the geometry relaxation effects.

Following the scheme proposed by Gerratt and Mills [27], see also Pulay [28] and Yamaguchi et al. [29], the calculation of first and second derivatives was easily implemented [10–13,26].

The version of the SCF-MI code inserted into GAMESS-US package can perform single point conventional and direct SCF-MI energy calculation, analytic gradient, numerical Hessian evaluation and geometry optimization; vibrational analysis is also available. Increase in complication and computation time with respect to standard SCF algorithms is minimal. Level shifting technique [30] has been adopted to increase the convergence performance. The SCF-MI option is also incorporated in the particularly efficient PC GAMESS version [31] of the GAMESS-US [26] quantum chemistry package.

### 3. Computational details

All calculations were performed ab initio with the SCF and SCF-MI procedures implemented in the GAMESS-US package [26]. Stability and structure of  $[\text{Li}(\text{NH}_3)_n]^+$  and  $[\text{K}(\text{NH}_3)_n]^+$  (with  $n = 1-6$ ) clusters were optimized by using the energy gradient method in the framework of the SCF-MI theory. The structure of each of the complexes studied was fully optimized by searching for a minimum in its potential hypersurface. The starting geometries were chosen on the basis of chemical intuition and also from geometries obtained from the literature [32–35]. No symmetry restrictions were imposed during optimizations. The vibrational analysis using the SCF-MI second-derivative matrix was carried out to characterize the nature of the stationary points. The standard split valence 6-31 + G\* basis set [26,36] was employed, with all the electrons considered explicitly. The basis set contains diffuse s and p functions on metals and  $N$  atoms that are expected to provide enough flexibility to describe the clusters.

The interaction energy at each minimum was calculated by using the supermolecule method described in section 2. The intermolecular interaction energy for a cluster  $M(\text{NH}_3)_n \cdot \text{Li}^+$ , is the difference between the energy at the minimum of the potential energy surface for the cluster in a completely relaxed geometry and the sum of the energies for its  $n + 1$  individual components in their relaxed conformation. Thus, for a cluster of  $K$  molecules, the intermolecular interaction energy is given by (9)

$$\Delta E_{\text{SCF-MI}} = E_{\text{SCF-MI}} - \sum_{k=1}^K E_{\text{SCF}}^K$$

where all the terms are fully optimized.

As already underlined, all SCF-MI interaction energies result to be corrected for the BSSE by definition [10–13] providing an accurate estimate of the interaction energy. The SCF-MI interaction energy takes account of the distortion undergone by the isolated molecules in adopting the fully optimized cluster geometry (deformation energy) [17–19]. As the magnitude of the interaction energy is substantial, the deformation energy can be expected to be significant.

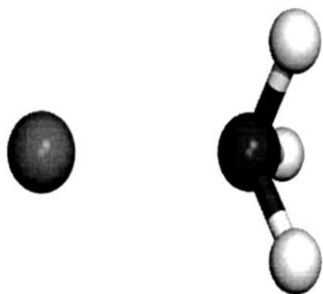


Fig. 2. Lowest energy SCF-MI optimized structure of the  $K^+$  or  $Li^+$  cation with one ammonia molecules.

#### 4. Results and discussion

This section presents and discusses the results obtained in our study of the  $[Li(NH_3)_n]^+$  and  $[K(NH_3)_n]^+$  (with  $n = 1-6$ ) systems using the SCF and SCF-MI methods with the  $6-31 + G^*$  basis set. The geometries of the minima located are discussed and the corresponding interaction energies are then commented on.

##### 4.1. Optimized structures for the $[K(NH_3)_n]^+$ clusters

The SCF and SCF-MI computational methods tested lead to similar spatial arrangement of molecules in each type of cluster. Only the figures corresponding to the SCF-MI method are thus shown. In describing the different conformations of each complex, we shall refer to the arrangement adopted by the nitrogen atoms around the central cation.

The Figs. 2–7 show the structural arrangement of the minima located for the  $[K(NH_3)_n]^+$  clusters. As can be seen, the ammonia molecules surround the central ion to form the so-called ‘interior’ structures [32–35]. The molecules orientate so as the nitrogen atom lone pair faces the cation, as expected from the positive charge of the ion and the electronegative character



Fig. 3. Lowest energy SCF-MI optimized structure of the  $K^+$  or  $Li^+$  cation with two ammonia molecules.

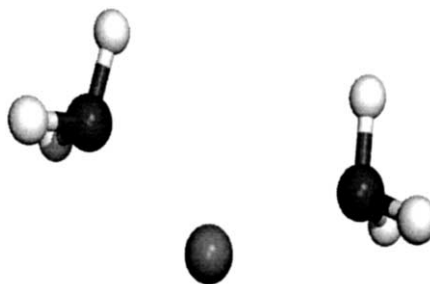


Fig. 4. Lowest energy SCF-MI optimized structure of the  $K^+$  or  $Li^+$  cation with three ammonia molecules.

of nitrogen. The dipole moment of ammonia points towards the positive charge of the ion, favoring charge-dipole interaction, which is the main contribution to the interaction. In all clusters considered, ammonia molecules try to orientate in such a way that dipole moments point to the ion. The  $[K(NH_3)_2]^+$  complex possesses a linear structure, i.e. it exhibits a linear N–K–N atom sequence (Fig. 3). In

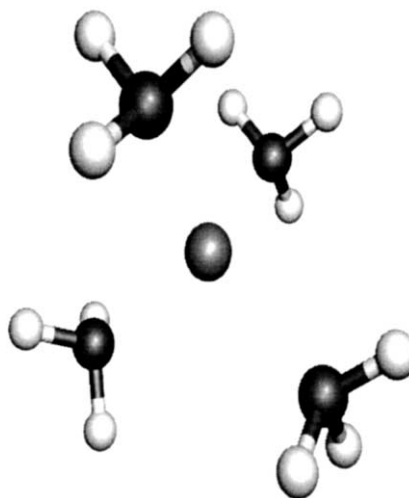


Fig. 5. Lowest energy SCF-MI optimized structure of the tetrahedral complex of the  $K^+$  or  $Li^+$  cations with four ammonia molecules.

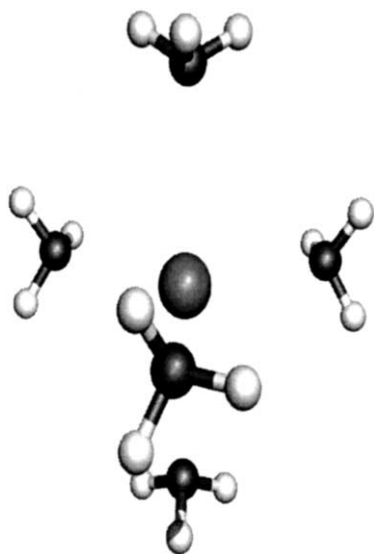


Fig. 6. Lowest energy SCF-MI optimized structure of the bipyramidal complex of the  $K^+$  cation with five ammonia molecules.

the cluster with  $n = 3$  (Fig. 4), the solvent molecules lie symmetrically around the central cation; this is an almost planar structure, where the three nitrogen atoms form an equilateral triangle. The  $[K(NH_3)_4]^+$  complex is tetrahedral (Fig. 5), with the hydrogen

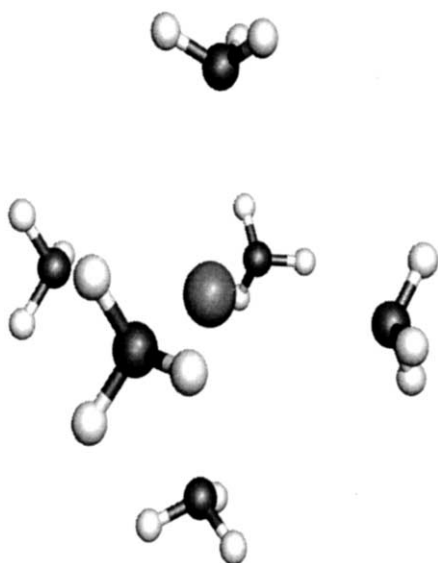


Fig. 7. Lowest energy SCF-MI optimized structure of the octahedral complex of the  $K^+$  cation with six ammonia molecules.

atoms as far as possible from one another. The cluster with  $n = 5$  adopts a bipyramidal conformation and that with  $n = 6$  an octahedral one (Figs. 6 and 7). Also, it can be observed from the structures shown in Figs. 2–7 that no hydrogen bonds can be formed in the clusters. The variation of the average K–N distance with  $n$  (the number of solvent molecules) for each cluster increases with increasing number of solvent molecules as the result of steric effects between ammonia molecules and of repulsion between the permanent dipoles.

The variation of Lowdin atomic charge of  $K^+$  with the number of ammonia molecules in the cluster show that the cation possesses a smaller charge in the cluster than in isolation, so a part of the charge is transferred from the  $NH_3$  molecules to an extent that increases with increasing cluster size.

#### 4.2. Optimized structures for the $[Li(NH_3)_n]^+$ clusters

Because the ionic radius of  $Li^+$  is smaller than that of  $K^+$ , the  $Li^+$  cation allows solvent molecules to come closer to it; as a result, such molecules will feel a stronger electric field than those around  $K^+$  causing also stronger interaction. This was in fact reflected in the results for all the  $[Li(NH_3)_n]^+$  systems. In addition because of its smaller size,  $Li^+$  is able to accommodate fewer ammonia molecules in its first coordination shell.

The optimized structures for  $[Li(NH_3)_n]^+$  are shown in Figs. 2–5, 8 and 9. The lowest energy

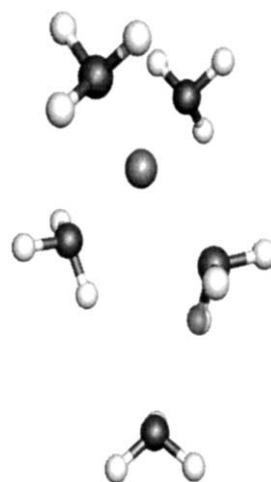


Fig. 8. Lowest energy SCF-MI optimized structure of the complex of the  $Li^+$  cation with five ammonia molecules.

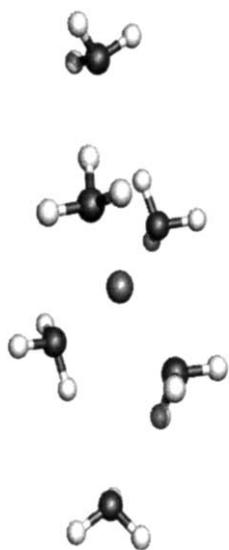


Fig. 9. Lowest energy SCF-MI optimized structure of the complex of the  $\text{Li}^+$  cation with six ammonia molecules.

molecular arrangements for the clusters of  $n = 1$ –4 were identical with those for the  $\text{K}^+$  complexes (Figs. 2–5). The complex with  $n = 5$  (Fig. 8), however, exhibited some differences from the  $[\text{K}(\text{NH}_3)_5]^+$  system owing to the small size of  $\text{Li}^+$ , which, as noted before accommodates fewer solvent molecules in its first solvation shell. The results obtained for the complex of  $n = 5, 6$  indicate that the fifth and sixth molecules are located in the second coordination shell. As a consequence, they interact strongly with some molecules of the first solvation sphere forming bifurcated H-bonds (Figs. 8 and 9).

Both SCF and SCF-MI methods provide other structures for the complexes with five and six ammonia molecules that correspond to secondary minima of the potential surface. In the secondary minimum with five  $\text{NH}_3$ , the solvent molecules adopt a bipyramidal structure similar to that found in  $\text{K}^+$  complex (Fig. 6). In the secondary minimum with six  $\text{NH}_3$ , the solvent molecules adopt an octahedral structure similar to that found in the corresponding  $\text{K}^+$  complex (Fig. 7). As in the case of  $\text{K}^+$  complexes, the systems with less than five ammonia molecules cannot form hydrogen bonds between the solvent molecules. From the computed Lowdin charge of  $\text{Li}^+$  for clusters of different sizes, it results that  $\text{Li}^+$  complexes behave as  $\text{K}^+$  complexes though a greater amount of charge is transferred in this case.

Table 1

SCF-MI interaction energies and the corresponding variations with the number of complexing ammonia molecules for  $[\text{K}(\text{NH}_3)_n]^+$  and  $[\text{Li}(\text{NH}_3)_n]^+$  clusters

$n$	$[\text{K}(\text{NH}_3)_n]^+$	Variation	$[\text{Li}(\text{NH}_3)_n]^+$	Variation
1	19.47		39.73	
2	36.70	17.23	74.21	34.48
3	51.53	14.83	98.48	24.27
4	63.79	12.26	114.54	16.07
5	71.86	8.07	122.36	7.82
6	78.55	6.69	129.59	7.23

#### 4.3. Interaction energy of $[\text{K}(\text{NH}_3)_n]^+$ and $[\text{Li}(\text{NH}_3)_n]^+$ clusters

Tables 1 and 2 show the values of the SCF and SCF-MI interaction energy for the  $[\text{K}(\text{NH}_3)_n]^+$  and  $[\text{Li}(\text{NH}_3)_n]^+$  complexes with  $n = 1$ –6. Overall, the results provided by the SCF and SCF-MI methods are consistent. As can be seen from the tables, the interaction energy increases as the size of the cluster grows (Figs. 10 and 11). In order to examine the variation of the interaction energy in the process of formation of the clusters, the difference between the energy in the clusters containing  $n$  and  $n - 1$  ligands was plotted against the number of ligands (Fig. 11).

As can be seen, the magnitude of the stabilizing effect of each new molecule in the cluster diminished with increasing  $n$  (Tables 1 and 2). Consequently, while the total binding energy of the complex increases as further molecules are incorporated into the cluster, the interaction of each ammonia molecule with the ion gradually weakens, as one would expected.

It is evident that for  $[\text{Li}(\text{NH}_3)_n]^+$  clusters the interaction energies are much greater than those obtained for the  $\text{K}^+$  complexes, consistent with the smaller size

Table 2

SCF interaction energies for  $[\text{K}(\text{NH}_3)_n]^+$  and  $[\text{Li}(\text{NH}_3)_n]^+$  clusters

$n$	$[\text{K}(\text{NH}_3)_n]^+$	Variation	$[\text{Li}(\text{NH}_3)_n]^+$	Variation
1	19.70		41.72	
2	37.07	17.38	77.64	35.92
3	52.00	14.92	102.36	24.72
4	64.36	12.36	119.17	16.81
5	72.67	8.32	127.50	8.33
6	79.79	7.11	135.51	8.01



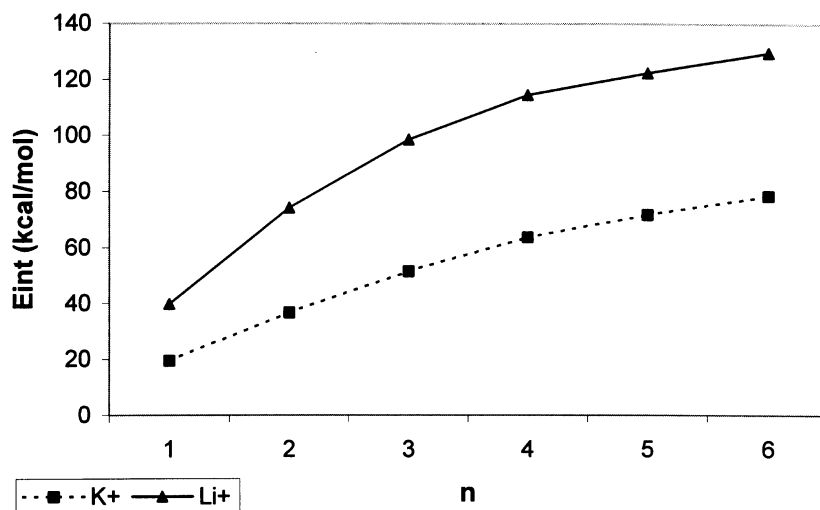


Fig. 10. Variation of SCF-MI interaction energies with the number of complexing ammonia molecules.

of  $\text{Li}^+$  ion, which establishes stronger interactions with the ligands. Fig. 11 shows changes in interaction energy caused by the incorporation of successive ammonia molecules.

For the  $[\text{Li}(\text{NH}_3)_5]^+$  cluster, the stabilization gained in forming the bipyramidal complex was smaller than that for the structure where one molecule is placed out of the first solvation shell. In principle, the fifth molecule, which cannot interact directly with the ion, should have a considerably less marked stabiliz-

ing effect. However, because the molecules in the coordination shell are strongly polarized and distorted by the ion, the hydrogen-bonding with the outer molecule have a more stabilizing effect.

## 5. Conclusions

In this paper, a theoretical study of complexes formed by clusters of ammonia molecules and  $\text{Li}^+$

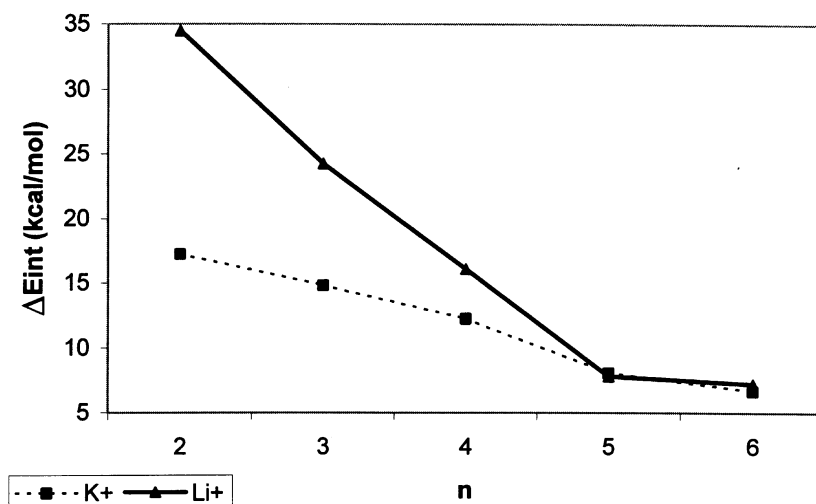


Fig. 11. Changes in the SCF-MI interaction energy of the systems upon addition of successive solvent molecules.

or  $K^+$  ions was performed by the ab initio SCF-MI method using the 6-31 +  $G^*$  basis set. Stability and structure of  $[Li(NH_3)_n]^+$  and  $[K(NH_3)_n]^+$  (with  $n = 1-6$ ) clusters have been investigated. The gradient geometry optimizations were performed adopting the recently implemented generalization of the SCF-MI method. Several stationary points for each cluster were thus located and were characterized as minima. Both the intermolecular interaction energies and the stationary point conformation result to be a priori corrected for the BSSE. From the results, it follows that both  $Li^+$  and  $K^+$  ions form similar complexes in the clusters with up to four ammonia molecules. In the  $Li^+$  complexes, the first coordination shell saturates with four molecules and leads to conformations differing from those of the  $K^+$  with  $n = 5, 6$ . All the properties studied change in a systematic manner upon addition of a further ammonia molecule; however, this trend is broken by the  $Li^+$  complexes with five and six ammonia molecules.  $Li^+$  and  $K^+$  complexes exhibit no sign of hydrogen bonding between the molecules of the first coordination shell. However, the  $Li^+$  complexes with five and six ammonia molecules show the formation of bifurcated hydrogen bonds between first and second shells. It is to be emphasized the accordance with recent neutron diffraction experimental analysis of the structure of  $Li^+$  and  $K^+$  in  $NH_3$  solutions [6], from which the lithium is tetrahedrally coordinated while potassium results octahedrally coordinated by solvent molecules. In conclusion, the theoretical results are consistent with the experiments and furnish insight into the identification of some features of the clustering process. The systematic comparison with the corresponding water and clusters will be the subject of following papers.

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