



On the Interactions of Sodium with Ammonia

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Abstract

The interactions of sodium with ammonia in the gas phase are investigated. The optimized equilibrium geometries obtained at the DFT/B3LYP level using the 6-31G(d,p) basis set show that stable compounds $\text{Na}(\text{NH}_3)_4$ and $\text{Na}(\text{NH}_3)_5$ may result with respective dissociation energies of 42.5 and 48.0 kcal.mol⁻¹ relative to their fragments Na and NH₃. Upon addition of diffuse functions on Na and N, one gets 33.2 kcal.mol⁻¹ for $\text{Na}(\text{NH}_3)_4$. The nature of the interactions was studied by NBO analysis through calculation of the second order perturbation energy. This showed that the most stabilizing interactions involve the donation of charge from the lone pairs of the ligands to Rydberg orbitals of Na and back-donation of charge from the singly occupied orbital of Na to the Rydberg orbitals of N and H and to the $\sigma^*_{\text{N-H}}$. An occupation of the $\sigma^*_{\text{N-H}}$ and of the Rydberg orbitals of N and H by the odd electron of Na is therefore observed, which places its electron density near the positions of these nuclei. The calculated small Wiberg bond indices and the van der Waals penetration distance are in accord with a non-covalent type of interactions of the kind Lewis acid-Lewis base.

Keywords: Sodium-ammonia complexes, density functional calculations, NBO analysis, charge-transfer interactions, charge distributions.

Introduction

The solubility of alkali metals in ammonia was first reported by Weyl in 1864¹. Since then, research in this area has evolved to include the alkaline earth metals (Mg, Ca, Ba, Sr), the lanthanides (Eu and Yb) and other solvents such as tetrahydrofuran (THF), polyamines and polyethers. Numerous experimental studies have been done on these metal solutions with the objective of gaining some insights into the nature of the solute. So, the dependence of the conductance, optical and magnetic properties of the solutions on temperature, solvent and metal concentrations has been extensively investigated²⁻⁵. The results revealed the presence of solvated metal cations and solvated electrons in dilute solutions while concentrated solutions may contain ionic clusters of these two species. Further work on these metal solutions yielded solid compounds such as $\text{Li}(\text{NH}_3)_4$, and others of stoichiometry $\text{M}^+\text{L}_n\text{e}^-$ and $\text{M}^+\text{L}_n\text{N}^-$ called respectively electrides and alkalides (M and N are alkali metals, L is a ligand)^{6,7,8}. Both the metal solutions and the solid compounds display interesting physical and chemical properties as powerful reducing agents^{9,10}. Alkalides and electrides are low temperature semiconductors.

There has been a growing interest in the charge distributions in these systems mainly in the structure of the odd electrons of the alkali metal atoms and where they are localized upon solvation and in the solid compounds. Some experimental studies on these aspects have been reported. Ionization energies have been measured in the gas phase for the systems

$\text{M}(\text{NH}_3)_n$ and $\text{M}(\text{H}_2\text{O})_n$ where M is Li, Na and Cs as well as those of negatively charged species $(\text{NH}_3)_n^-$, $\text{Li}(\text{NH}_3)_n^-$, $\text{Na}(\text{NH}_3)_n^-$ by photoelectron spectroscopy^{11,12,13,14}. The results indicated that the first ionization energies of the neutral systems decreased as n increased. The extrapolated experimental value at infinite coordination of 1.47 eV was in accord with the photoelectric threshold of liquid ammonia. These experimental findings, along with theoretical work by the authors by means of ab initio MO wave functions showed that the valence electron of the metal is delocalized over the ligands as n increases. E. Zurek et al. have done an extensive and comprehensive study on the geometries and charge distributions of several species that can be found in lithium-ammonia solutions by DFT and TD-DFT using a variety of high quality basis sets¹⁵. Their results on models of the solvated electron cluster consisting of negatively charged associations of an increasing number of ammonia molecules (n=1 to 14), which depict an electron trapped in the solvent moiety, locate the unpaired electron near the solvent molecules, thus weakening normal hydrogen bonding. This corroborates theoretical findings by other authors¹⁶. These theoretical results also show that wave functions of good quality can be constructed at the DFT level with selected basis sets, which can be used to properly describe the geometries and charge distributions in the metal-ammonia systems. We have done previous work on $\text{Li}(\text{NH}_3)_n$ (with n=1-4) at the UHF level with a basis set constructed from the standard 6-31+G (d,p) by omitting the polarization functions on Li and the diffuse sp set on N¹⁷. Computed spin density values of $\text{Li}(\text{NH}_3)_4$ indicated that 98% of the unpaired

electron density is in the diffuse s orbital of Li. These data, although qualitative because electron correlation effects were not added, show however the diffuse character of the spatial distribution of this charge. Other theoretical studies have been done on the metal-ammonia systems but have focused on the structural and energetic aspects^{18,19,20}.

Although a tremendous amount of theoretical and experimental work has been done, there is still no neat understanding of whether the unpaired electron of the metal is free or associated with the solvent molecules in these systems. Moreover, little theoretical work has been done on other metal-ammonia systems to enlighten findings on those of lithium-ammonia.

Here we present theoretical results of investigations on the geometric and electronic structures of some sodium-ammonia complexes. An analysis by the Natural Bond Orbital (NBO) technique is also done in afford for understanding the nature of the metal-ligand interactions.

Material and Methods

Calculations on the geometric and electronic structures of $\text{Na}(\text{NH}_3)_n^+$ and NaNH_3 (with $n=1,4$ and 5) were done at the DFT level by using the "Gaussian 09 software package"²¹. The gradient-corrected hybrid functional B3LYP method was chosen along with the standard 6-31G(d,p) and 6-31+G(d,p) basis sets²². For all the systems studied, a vibration frequency calculation was carried out at each stationary point to characterize its nature as a minimum and to correct the energies for zero-point vibration contribution. The optimized geometries were visualized with the "Gauss View visualization program". The analysis of Fock Matrix elements in Natural Bond Orbital (NBO) basis was done by second order perturbation theory for the different optimized molecular geometries with the NBO codes provided by the "Gaussian 09 package".

Results and Discussions

Geometries and energies: The calculations have been performed with spin-restricted and spin-unrestricted DFT wave functions for the cationic and the neutral complexes respectively. According to the previous work on the metal-ammonia complexes, the interactions are more attractive when the NH_3 molecule approaches the metal atom by the N end; so this directional approach was maintained. Table-1 and table-2 give the geometrical parameters of the optimized structures obtained with the selected basis sets. One observes that the experimental geometry of ammonia is quite well reproduced. NaNH_3^+ and NaNH_3 have stable C_{3v} structures with Na-N bond length of 2.3 Å and 2.4 Å respectively. There is no experimental data on the geometry of the

sodium-ammonia complexes either in gas phase or in condensed medium. However K. Hashimoto et al. have done a study on the clusters $\text{Na}(\text{NH}_3)_n^+$ and $\text{Na}(\text{NH}_3)_n$ (with $n=1-6$) with emphasis on the search for the optimal coordination number, the minimal geometries and corresponding binding energies²⁷. The geometries were optimized at the HF/6-31+G(d) level, then, single-point calculations at the MP2 frozen core level was done. For the neutral clusters of interest here, they found a stable tetrahedral D_{2d} structure for $\text{Na}(\text{NH}_3)_4$ and a trigonal bipyramidal one of C_{3v} symmetry for $\text{Na}(\text{NH}_3)_5$. Their results also gave evidence that the first-solvation-shell of Na and Na^+ is completed with 4 or 5 molecules of ammonia in accord with experimental and theoretical findings on Na^+ -ammonia systems^{23,24,25}. Our present work on $\text{Na}(\text{NH}_3)_4^+$ and $\text{Na}(\text{NH}_3)_4$ indicates that both complexes have T_d equilibrium symmetry with a tetrahedral arrangement of the amine groups around the metal atom. Figure-1 and figure-2 picture the stable structures of $\text{Na}(\text{NH}_3)_4$ and $\text{Na}(\text{NH}_3)_5$ obtained with 6-31G(d,p). For $\text{Na}(\text{NH}_3)_5^+$ and $\text{Na}(\text{NH}_3)_5$, we have used no symmetry constrains in order to allow more flexibility in the positions of the NH_3 molecules. These two complexes showed several geometrical isomers very close in energy due to the small energy required for rotation of the NH_3 groups. Therefore precise minima could hardly be found with our basis sets except for $\text{Na}(\text{NH}_3)_5$ with 6-31G(d, p). Geometries of some saddle points with one imaginary frequency are also given in table-1 and table-2. One can observe that the pyramidal structure of NH_3 is retained in all complexes although the stronger attractive interactions in the cations cause a sensible reduction of Θ_{HNNH} compared to that in free NH_3 . The bond lengths $R_{\text{Na-N}}$ have values of 2.41 Å and 2.45 Å for $\text{Na}(\text{NH}_3)_4$ and $\text{Na}(\text{NH}_3)_4^+$ with 6-31G(d,p). Similar values are obtained with 6-31+G(d,p). The bond lengths $R_{\text{Na-N}}$ and bond angles (Θ_{HNNH} and Θ_{NANH}) obtained with our basis sets are in accord with those reported by K. Hashimoto et al.¹⁹. An elongation of the Na-N bond with increase in coordination number is observed as expected, due to increased steric effects caused by the approaching NH_3 molecules. It is however smaller for the high coordinated complexed cations than for the neutral and that reflects the smaller size of Na^+ compared to that of Na.

One may also notice that in $\text{Na}(\text{NH}_3)_5$ and $\text{Na}(\text{NH}_3)_5^+$, Θ_{NANAN} and $R_{\text{Na-N}}$ are different for the ligands in equatorial and in axial positions. The distance between Na and N are slightly longer for the axial NH_3 groups. The angles Θ_{NANAN} indicate a slight deviation from an ideal bipyramidal geometry due probably to rearrangement of the ligands in the coordination sphere of $\text{Na}(\text{NH}_3)_4$ or $\text{Na}(\text{NH}_3)_4^+$ to accommodate the extra NH_3 molecule. This might suggest that the first solvation shell of Na could have an optimum number of four ammonia molecules during a reaction in the gas phase.

Table-1
Energies and geometries with 6-31G(d,p)

System	E(au)	ΔE (kcal.mol ⁻¹)	R_{Na-N} (Å)	R_{N-H} (Å)	Θ_{NNaN} (°)	Θ_{NaNH} (°)	Θ_{HNH} (°)
NH ₃ , C _{3v}	-56.523327	-	-	1.018	-	(111.867)	105.746
NH ₃ , experimental	-	-	-	1.012	-	-	106.7
NaNH ₃ , C _{3v}	-218.820424	10.80	2.407	1.021	-	112.227	106.581
NaNH ₃ ⁺ , C _{3v}	-218.656490	32.582	2.329	1.021	-	113.564	105.087
Na(NH ₃) ₄ , T _d	-388.440854	42.452	2.414	1.022	109.471	112.329	106.468
Na(NH ₃) ₄ ⁺ , T _d	-388.334164 (-388.331812) ^a	100.147 (68.412) ^b	2.448	1.019	109.471	113.245	105.448
Na(NH ₃) ₅ , C ₁	-444.973064	48.025	2.49(ax) 2.46(eq)	1.02	87.7; 92.5(ax/eq) 117.8;121.3(eq/eq)	110.4-113.5(ax) 108.9-118.2(eq)	106.2-106.7
Na(NH ₃) ₅ ⁺ , C ₁ 1 imaginary frequency	-444.872534 (-444.868512) ^a	109.585	2.54(ax) 2.50(eq)	1.02	90.0 120.0	113.4 112.7	105.5

^a Single point calculation at the geometry of the neutral species; ^b Vertical ionization energy; E(Na) = -162.279881 H; E(Na⁺) = -162.081230 H;

Table-2
Energies and geometries with 6-31+G(d,p)

System	E(H)	ΔE (kcal.mol ⁻¹)	R_{Na-N} (Å)	R_{N-H} (Å)	Θ_{NNaN} (°)	Θ_{NaNH} (°)	Θ_{HNH} (°)
NH ₃ , C _{3v}	-56.532613	-	-	1.016	-	(116.735)	108.08
NH ₃ , experim.	-	-	-	1.012	-	-	106.7
NaNH ₃ , C _{3v}	-218.824232	7.345	2.445	1.021	-	111.98	106.85
NaNH ₃ ⁺ , C _{3v}	-218.658326	27.898	2.341	1.021	-	113.49	105.17
Na(NH ₃) ₄ , T _d	-388.463212	33.157	2.434	1.022	109.5	112.31	106.49
Na(NH ₃) ₄ ⁺ , T _d	-388.344879 (-388.342954) ^a	83.556 (75.448) ^b	2.46	1.019	109.5	113.12	105.59
Na(NH ₃) ₅ , C ₁ 1 imaginary frequency	-445.003393	37.905	2.54(ax) 2.48(eq)	1.02	88.3; 91.5(ax/eq) 119.6;120.1(eq/eq)	112.0-112.4(ax) 111.3-114.5(eq)	106.4-106.6
Na(NH ₃) ₅ ⁺ , C ₁ 1 imaginary frequency	-444.888384	90.390	2.57(ax) 2.51(eq)	1.02	89.4; 90.6(ax/eq) 119.6;120.0(eq/eq)	112.8-113.0	105.8

^a Single point calculation at the geometry of the neutral species; ^b Vertical ionization energy; E(Na) = -162.279911 H; E(Na⁺) = -162.081246 H

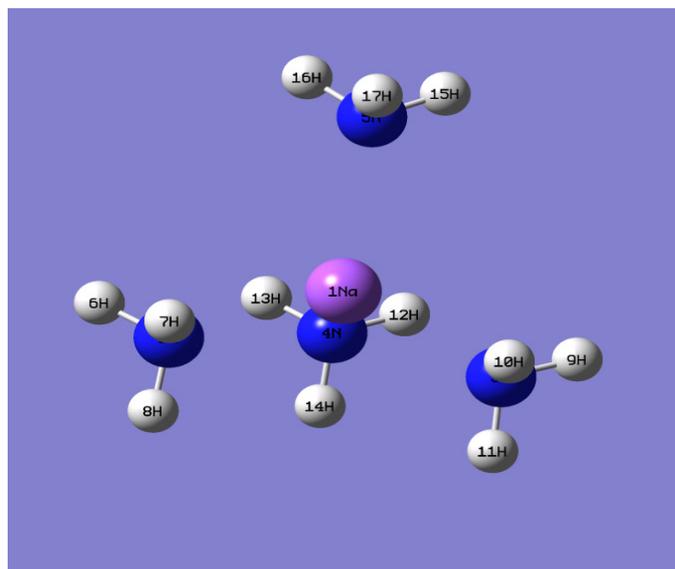


Figure-1

Optimized geometry of $\text{Na}(\text{NH}_3)_4$ at the B3LYP/6-31G(d,p) level

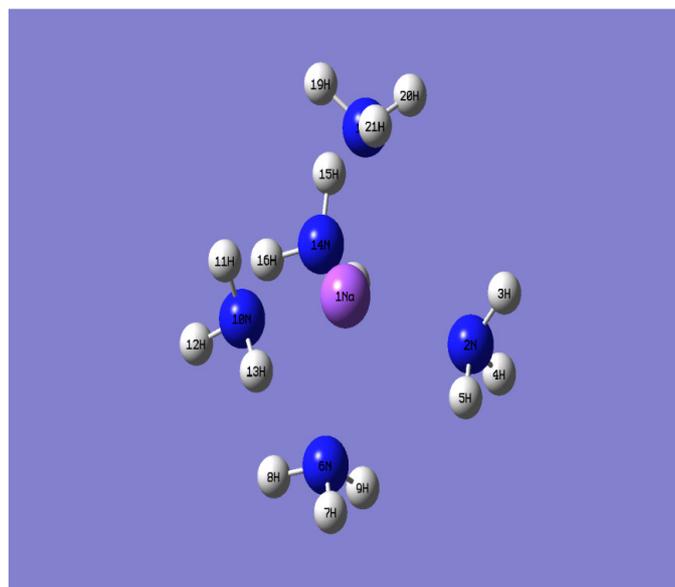


Figure-2

Optimized geometry of $\text{Na}(\text{NH}_3)_5$ at the B3LYP/6-31G(d,p) level

The dissociation energies ΔE_n of the complexes relative to the isolated metal atom or ion and the ligand molecules given by the following expression are also listed in table-1 and table-2. They indicate that the reactions of formation of these systems are all exoergic.

$$\Delta E_n = E(\text{M}) + n E(\text{NH}_3) - E[\text{M}(\text{NH}_3)_n]$$

where M is Na or Na^+ .

ΔE_n values of 10.8, 42.5, 48.0 kcal.mol⁻¹ are obtained for the neutral complexes with $n = 1$, $n = 4$ and $n = 5$ respectively at the 6-31G(d,p) level. Those of the corresponding cations are 32.6, 100.1 and 109.6 kcal.mol⁻¹. Upon addition of diffuse functions on Na and N, one gets 7.3 kcal.mol⁻¹ for NaNH_3 , 27.9 kcal.mol⁻¹ for NaNH_3^+ , 33.2 kcal.mol⁻¹ for $\text{Na}(\text{NH}_3)_4$ and 83.6 kcal.mol⁻¹ for $\text{Na}(\text{NH}_3)_4^+$. Our B3LYP/6-31G(d,p) results are quite in good agreement with the data of K. Hashimoto et al. collected at the MP2 frozen core level and reflect the relative strength of the interactions of the neutral atom and its cation with the ligands¹⁹. The interaction energy of each ammonia molecule with the atom or the ion weakens as n increases. With 6-31G(d,p), the computed first ionization energy of Na is 5.4 eV and the vertical ionization energies of $\text{Na}(\text{NH}_3)_4$ and $\text{Na}(\text{NH}_3)_5$ are respectively 2.97 and 2.84 eV. Inclusion of diffuse functions in the basis set leads to a vertical ionization energy of 3.27 eV for $\text{Na}(\text{NH}_3)_4$. They are in agreement with measured and computed values of 5.14 eV for Na and 2.9 eV for the studied complexes and indicate that upon complexation of the Na atom, the odd electron becomes loosely bound^{11,19}.

Charge distributions: In the natural atomic orbital (NAO) basis, the natural population on an atom (A) is the sum over all contributing NAOs of the natural population $q_i(\text{A})$ of orbital $\phi_i(\text{A})$. The natural charge $Q(\text{A})$ is then the difference between its natural population and its atomic number $Z(\text{A})$ ²⁶. $q_i(\text{A})$ satisfies the Pauli principle that is $0 \leq q_i(\text{A}) \leq 2$. Table-3 displays the natural charges given by our analysis. For the metal atom in the complexed cations, the values are consistent with its charge and the decrease observed as n augments, suggests a continuous transfer of negative charge from the ligand to the metal center. The negative charge acquired by Na in the neutral complexes can be explained on the same grounds. The diffuse functions offer more flexibility in the description of these species as outlined in previous work and indeed the charges are greater when these functions are added in the basis set. The small but positive charge on Na (0.0043 a.u.) in $\text{Na}(\text{NH}_3)_4$ may be caused by a balance in the process of transfer of charge between the metal atom and the ligand. Polarization of the hydrogen atoms occur for all complexes ($Q(\text{H}) \sim 0.4$ a.u.). We have also given in table-3 the spin densities and the isotropic Fermi contact couplings at each atomic center of the studied complexes. One should note that these two properties are results of Mulliken population analysis. The variation of the spin densities at the nuclei, although qualitative and small, indicates that about 20 % of the odd electron is transferred onto the H atoms in $\text{Na}(\text{NH}_3)_4$ and $\text{Na}(\text{NH}_3)_5$.

The contact density of the electron at the nuclei for these complexes markedly decreased from that of the free atom and shows larger values at N and smaller ones at H. Our results agree with those of NMR Knight shift experiments for solutions of metals in ammonia and with other theoretical findings and may arise from the nature of the wave function of the odd electron^{15,27,28}.

Table-3
Atomic properties of the studied complexes with 6-31G(d,p) and 6-31+G(d,p) (in parenthesis)

System	Natural charge (e)			Spin densities (a.u.)			Isotropic Fermi contact couplings (a.u.)			Wiberg bond index		
	Na	N	H	Na	N	H	Na	N	H	Na-N	Na-H	N-H
Na	0.0	-	-	1.0	-	-	0.533	-	-	-	-	-
NH ₃ C _{3v}		-1.13 (-1.18)	0.38 (0.39)	-	-	-	-	-	-	-	-	0.86
NaNH ₃ C _{3v}	-0.0044 (-0.0051)	-1.20 (-1.24)	0.40 (0.41)	0.97	0.0025	0.011	0.403	0.165	0.0003	0.046	0.0069	0.83
NaNH ₃ ⁺ C _{3v}	0.97 (0.98)	-1.26 (-1.29)	0.43 (0.44)	-	-	-	-	-	-	0.063	0.0004	0.81
Na(NH ₃) ₄ T _d	0.0043 (-0.0019)	-1.18 (-1.23)	0.39 (0.41)	0.84	-0.11	0.017	0.085	0.163	0.0001	0.080	0.011	0.83
Na(NH ₃) ₄ ⁺ T _d	0.75 (0.78)	-1.17 (-1.21)	0.41 (0.42)	-	-	-	-	-	-	0.12	0.0005	0.83
Na(NH ₃) ₅ C ₁	-0.013 (-0.038)	-1.16 (-1.21)	0.39 (0.41)	0.83	-0.010	0.016	0.062	0.14(eq) 0.16(ax)	-0.00006 0.00020	0.084(eq) 0.080(ax)	0.010	0.83
Na(NH ₃) ₅ ⁺ C ₁	0.71 (0.74)	-1.15 (-1.19)	0.40 (0.42)	-	-	-	-	-	-	0.114(eq) 0.106(ax)	0.0006	0.84

Natural bond orbital (NBO) analysis: The methodology of NBO analysis is well documented^{26,29}. It transforms an input basis set to orthonormal localized basis sets: natural atomic orbitals (NAOs) and natural hybrids orbitals (NHOs). These orbitals are subsequently used to construct orthonormal natural bond orbitals (NBOs) and natural localized molecular orbitals (NLMOs) with a requirement of maximum occupancy. The natural bond orbitals well describe the electron distributions in chemical substances and provide their best Lewis structures. Another aspect of the analysis is that it can be used to study intra- and intermolecular interactions. Electron delocalization effects can be accessed from the interactions between the filled NBOs of a donor group and the unfilled ones of an acceptor. The stabilizing interaction energy is provided by the second order perturbation energy $E^{(2)}$ given by an analysis of the Fock matrix in the NBO basis using the following expression:

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F_{ij}^2}{\epsilon_j - \epsilon_i}$$

in which q_i is the occupancy of the donor NBO, F_{ij} is the off-diagonal Fock matrix element and ϵ_i and ϵ_j are the NBOs energies. The results of such an analysis for Na(NH₃)₄ and Na(NH₃)₅ with the used basis sets are presented in table-4 and table-5. As can be seen from these data, the stabilizing interactions in the complexes involve mainly LP(1)Na (the singly occupied orbital of Na) with the antibonding orbitals σ_{N-H}^* ($\Delta E_{ij} \sim 3 \text{ kcal.mol}^{-1}$) and LP(1)N (the lone pair of the ligand) with antibonding NHOs and Rydberg orbitals of Na ($0.84 \leq \Delta E_{ij} \leq 6.8 \text{ kcal.mol}^{-1}$). Less strong interactions occur between LP(1)Na and Rydberg orbitals of N and H (ΔE_{ij} as high as 1.73

kcal.mol^{-1}). Many other much weaker interactions ($\Delta E < 0.30 \text{ kcal.mol}^{-1}$) of the NH₃ groups with Na are given by the analysis. Therefore as the ligands approach Na, bonding and back bonding of the lone pairs on both sides with unfilled NBOs is observed. The occupancies of the alpha spin-orbitals provided by table-4 suggest in the case of Na(NH₃)₄ at the 6-31G(d,p) level, that more charge is sent over the ligand during the interactions and this might explain the positive charge on Na. The relative orientation of the interacting orbitals has an effect on the strength of the interactions. This may be the reason for the relatively higher gain in interaction energy in Na(NH₃)₅ compared to that in Na(NH₃)₄. The nature of the interacting NBOs can be seen from the data in table-5. The LP(1) of Na is mainly the 3s orbital and the Rydberg orbitals (LP*(1,2,3)Na and RY*(1)Na) are its 3p_{xyz} and 4s NAOs respectively. σ_{N-H}^* (BD*(1)N-H) are formed from 2s2p³ hybrids on N and the 1s orbitals on H. In the 6-31+G(d,p) description, there is more contribution of the polarization functions on these two atoms. The RY*(1)N is a 3s3p_{xyz} hybrid mixed with polarization functions. It has more p character in the 6-31+G(d,p) description and interacts better with LP(1)Na. RY*(1)H is a 2s2p_{xyz} hybrid which, with the 6-31+G(d,p) basis set has more p character and this causes a noticeable decrease in its occupancy. This might be the reason for the reported small Knight shift experimentally observed. So, the odd electron could be found near the nitrogen and hydrogen atoms through occupation of their Rydberg orbitals and the σ_{N-H}^* . Both the 2s and 3s of N contribute to describe these NBOs and that may give the high contact density observed at N.

Table-4

The principal NBOs contributing to the stabilization of Na(NH₃)₄ as given by the second order perturbation theory analysis

System	alpha spin orbitals		6-31G(d,p)		6-31+G(d,p)	
	Donor NBO(i)	Acceptor NBO(j)	Occupancies of alpha spin orbitals NBO(i)/NBO(j)	E ⁽²⁾ (kcal.mol ⁻¹)	Occupancies of alpha spin orbitals NBO(i)/NBO(j)	E ⁽²⁾ (kcal.mol ⁻¹)
Na(NH ₃) ₄	LP(1) Na	BD*(1)N-H	0.827/0.0133	3.43	0.853/0.0105	2.61
	LP(1) Na	RY*(1)N	0.827/0.00172	0.33	0.853/0.00431	1.73
	LP(1) Na	RY*(1)H	0.827/0.00134	0.45	0.853/0.0007	0.43
	LP(1) N	LP*(2) Na	0.982/0.0182	1.80	0.984/0.0175	1.70
	LP(1) N	LP*(3) Na	0.982/0.0182	1.80	0.984/0.0175	1.70
	LP(1) N	LP*(4) Na	0.982/0.0182	1.80	0.984/0.0175	1.70
	LP(1) N	RY*(1) Na	0.982/0.0128	1.16	0.984/0.0080	0.86
	Na(NH ₃) ₅	LP(1) Na	BD*(1)N-H	0.796/0.017	3.37-3.76	
LP(1) Na		RY*(1)N	0.796/0.0029	0.10-0.51		
LP(1) Na		RY*(1)H	0.796/0.0016	0.29-0.42		
LP(1) N		LP*(2) Na	0.98/0.029	6.08-6.79		
LP(1) N		LP*(3) Na	0.98/0.024	1.37-6.58		
LP(1) N		LP*(4) Na	0.98/0.023	4.48-4.99		
LP(1) N		RY*(1) Na	0.98/0.014	0.84-1.40		

Table-5

Contribution of NAOs to selected NBOs for Na(NH₃)₄ with 6-31G(d,p) and 6-31+G(d,p)(in parentheses)

NBO	NAO							
	%s _{Na}	%p _{Na}	%d _{Na}	%s _N	%p _N	%d _N	%s _H	%p _H
LP(1)Na	100(3s) (100(3s))							
LP*(2)Na		100(3p _x) (99.91(3p _x))	(0.09)					
LP*(3)Na		100(3p _y) (99.91(3p _y))	(0.09)					
LP*(4)Na		100(3p _z) (99.91(3p _z))	(0.09)					
LP(1)N				25.60(2s) (24.11(2s))	74.35(2p _{xyz}) (75.85(2p _{xyz}))	0.05 (0.04)		
RY*(1)Na	100(4s) (100(4s))							
BD*(1)N-H 29.74%N;70.26%H (29.04%N;70.96%H)				24.79(2s) (25.25(2s))	75.14(2p _{xyz}) (74.67(2p _{xyz}))	(0.08)	100(1s) (99.89(1s))	(0.11(2p _{xyz}))
RY*(1)N				62.61(3s) (31.31(3s))	37.03(3p _{xyz}) (68.67(3p _{xyz}))	0.36 (0.02)		
RY*(1)H							94.97(2s) (93.27(2s))	5.03(2p _{xyz}) (6.73(2p _{xyz}))

The Wiberg bond indices provided by the NBO analysis and shown on table-3 indicate that except for the N-H bonds, no formal covalent bonds exist between the Na and N or Na and H atoms upon formation of these complexes. In addition, the Na-N bond length in the complexes shown in table-1 and table-2 are

longer than that expected for a covalent bond between Na and N (which would have a value around 2.27 Å). These observations reinforce the fact that these complexes are formed by charge transfer of the type found between Lewis acids and Lewis bases.

The values of the Na-N indices reflect the relative strength of the interactions.

There is apparently no interaction between Na and H in the complexed cations suggesting that the Na-H indices in the neutral complexes result from interactions involving the unpaired electron of Na. As pointed out elsewhere⁴⁰, there is a significant donor-acceptor character in a non-covalent type of bonding if the van der Waals penetration distance d_p ($d_p = d_{vdw} - d_{eq}$) is appreciably positive ($d_p \geq 0.1 \text{ \AA}$). By using the van der Waals radii of Na and N, one finds d_p values over 1.3 Å for both $\text{Na}(\text{NH}_3)_4$ and $\text{Na}(\text{NH}_3)_5$ with 6-31G(d,p) and 6-31+G(d,p) which support the donor-acceptor character of the bonding in these sodium-ammonia complexes^{29,30}.

Conclusion

We have presented here a theoretical study of the interactions of sodium with ammonia. The results indicate that in the gas phase, stable compounds $\text{Na}(\text{NH}_3)_4$ and $\text{Na}(\text{NH}_3)_5$ can be obtained with respective dissociation energies of 42.5 and 48.0 kcal.mol⁻¹ relative to their fragments Na and NH₃ at the DFT/B3LYP level by using the 6-31G(d,p) basis set. The cations $\text{Na}(\text{NH}_3)_4^+$ is also stable with a dissociation energy of 100.1 kcal.mol⁻¹ at the same level of theory. These energies are smaller when diffuse functions are added on Na and N in the basis set. Population analysis in the NBO basis showed that the interactions induce negative charges on the metal atom in these systems. The nature of the interactions was studied by NBO analysis. Our calculated second order perturbation energy revealed that the most stabilizing interactions involve on the one hand the donation of charge from the lone pairs of the ligands to Rydberg orbitals of Na and on the other hand the back donation of charge from the singly occupied orbital of Na to the Rydberg orbitals of N and H and to the $\sigma_{\text{N-H}}^*$. This leads to occupation of the $\sigma_{\text{N-H}}^*$ and of the Rydberg orbitals of N and H by the odd electron of Na thus placing its electron density near the positions of these nuclei. The calculated small Wiberg bond indices and the van der Waals penetration distance are in accord with a non-covalent type of interactions of the kind Lewis acid-Lewis base.

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