J. Phys. Chem. A **2000,** *104,* 6817−6823

Theoretical Study on the Adsorption of NH_3 to Alkali Halide Clusters

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Received: October 19, 1999; In Final Form: April 11, 2000

The adsorption of ammonia to the metal halide clusters Na_nF_n, Na_nCl_n, and Li_nF_n and the positively charged clusters $Na_nF_{n-1}^+$, $Na_nCl_{n-1}^+$, and $Li_nF_{n-1}^+$ was studied by the ab initio method for cluster sizes from 1 to 14. The positively charged clusters were more reactive than the neutral clusters. The ammonia molecule is adsorbed into a basket vacancy for the $Na_{13}Cl_{12}^+$ and $Na_{13}F_{12}^+$ clusters.

1. Introduction

A cluster is a small piece of material containing from three to several hundred atoms. Small clusters show properties very different from those of bulk material because of their small particle size. As cluster size increases, there will appear structures where all atoms can fill an ideally truncated lattice, so that there are only perfect nanocrystalline surfaces. The nanosurfaces of small clusters may show chemical properties different from those of bulk material, because of their large surface-to-volume ratio and the large step and defect density. There is a relation between the cluster size and chemical properties; for example, a particular cluster size is very reactive but the next size is inert. A large enough cluster has bulklike structure and chemical behavior. In addition to these interesting items, studies on the chemistry on nanocrystalline surfaces of clusters provide a new way to study surface processes. Defect sites, such as steps, adatoms, and vacancies, play important roles in solid-surface reactions.[1−3] Studies by using size-selected inorganic clusters may generate further insight into the fundamental steps of complicated chemical processes on defect surfaces as well as those on perfect surfaces.

Homer et al. reported the adsorption of NH_3, H_2O, etc., which have a lone pair of electrons, to alkali metal halide clusters.[4,5] They found that the reactivity depends on the cluster size and the alkali metal, and positively charged clusters $M_nX_{n-1}^+$ are much more reactive than neutral and negatively charged clusters. KF, NaF, and NaCl clusters have the same reactivity patterns. Cuboidal nanocrystals (cluster sizes $n = 14$, 23, 32, 38, and 53) of positively charged clusters are nonreactive toward NH_3 adsorption, whereas basketlike clusters ($n = 13$ and 22), which have defect sites, completely react with NH_3. Molecular NH_3 has been suggested to fill the basket defect. $Na_nF_{n-1}^+$ clusters are the most reactive, while the $Li_nF_{n-1}^+$ cluster shows a different reactivity pattern than other positively charged alkali halide clusters.

There have been many theoretical studies on the relationship between the structure and size of metal halide clusters.[6−14] Barnett et al. studied water adsorption and reactions on small sodium chloride clusters and reported a water molecule adsorbed at the halide-vacant (F-center) site.[15]

I previously investigated the structure and energetics for the metal halide clusters Na_nF_n, Na_nCl_n, and Li_nF_n and the positively charged clusters $Na_nF_{n-1}^+$, $Na_nCl_{n-1}^+$, and $Li_nF_{n-1}^+$ by the ab initio method for cluster sizes from 1 to 14.[16] The magic numbers for all of the smaller neutral clusters, $n < 9$, were 4, 6, and 8. A smaller neutral Li_nF_n cluster, $n < 9$, showed characteristics different from those of similar-sized Na_nF_n and Na_nCl_n clusters. The geometries of the most stable isomers for each cluster size were almost the same for the three positively charged clusters $Na_nF_{n-1}^+$, $Li_nF_{n-1}^+$, and $Na_nCl_{n-1}^+$. The magic numbers were 5 and 8, and their structures were close to an ideal cuboid with (100) facets. Basket structures were the most stable for cluster size $n = 13$ for the three positively charged clusters $Na_{13}F_{12}^+$, $Li_{13}F_{12}^+$, and $Na_{13}Cl_{12}^+$.

I report here the differences among these clusters with regard to the size-dependence of NH_3 adsorption for cluster sizes from 1 to 14.

2. Model and Calculational Method

I examined the adsorption of molecular ammonia to the alkali halide neutral and positively charged clusters LiF, NaF, and NaCl. The following basis sets were used for the Li, Na, F, Cl, N, and H atoms:

Li: (10s)/[3s] set + polarization *p* function ($\zeta_p = 0.076$)
Na: (11s5p)/[5s2p] set + polarization *p* function ($\zeta_p = 0.061$)
F: (10s7p)/[3s2p] set + polarization *d* function ($\zeta_d = 1.496$)
Cl: (11s8p)/[4s3p] set + polarization *d* function ($\zeta_d = 0.514$)
N: (10s7p)/[3s2p] set + polarization *d* function ($\zeta_d = 0.864$)
H: (4s)/[2s] set + *p*-type function (first derivatives[17,18] of the [2s] set)

All of these basis sets were taken from Huzinaga and Dunning[19,20] with a few modifications. Hartree−Fock (HF) and second-order Møller−Plesset perturbation theory (MP2) calculations were performed using the Gaussian 94 program.[21]

I have investigated the structures and energetics of all isomers for each of the cluster sizes,[16] and the other calculational studies have done the same for most of the structures and energetics of all of the clusters in this study.[6−15] I will not discuss the details of their geometries or the Mulliken atomic charges for each of the clusters.

Homer et al. measured the reactivity of clusters on NH_3 adsorption at 300−335 K.[5] I supposed that the most stable isomers exist mainly in this temperature region. I therefore only studied the adsorption to the most stable isomers for each cluster size.

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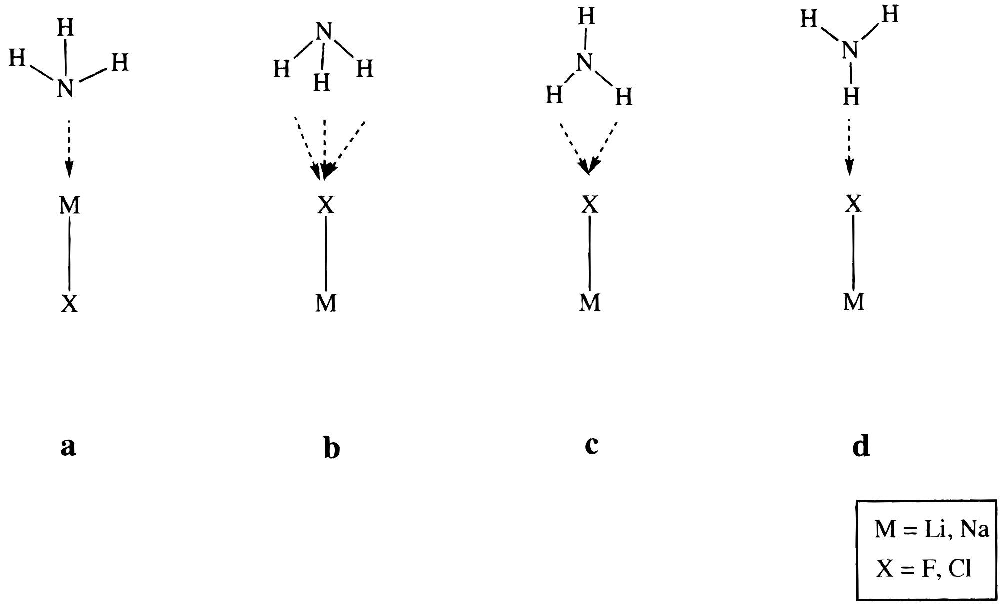

Figure 1. Supposed structures for the adsorption of ammonia to LiF, NaF, and NaCl clusters.

TABLE 1: Geometries and Mulliken Atomic Charges of Alkali Halide Clusters ($n = 1-3$) Computed with the MP2 Method

MX[a]	r, ∠XMX, ∠MXM[b]	Mulliken atomic charge
LiF	$r = 1.664$	±0.89
expt	$r = 1.564$	
NaF	$r = 1.982$	±0.91
expt	$r = 1.917$	
NaCl	$r = 2.356$	±0.68
expt	$r = 2.360$	
Li_2F_2	$r = 1.818$, ∠XMX = 95.5, ∠MXM = 84.6	±0.91
expt	$r = 1.680$	
Na_2F_2	$r = 2.141$, ∠XMX = 91.4, ∠MXM = 88.7	±0.92
Na_2Cl_2	$r = 2.541$, ∠XMX = 101.6, ∠MXM = 78.2	±0.66
Li_3F_3	$r = 1.781$, ∠XMX = 123.2, ∠MXM = 116.0	±0.91
Na_3F_3	$r = 2.138$, ∠XMX = 121.2, ∠MXM = 119.0	±0.93
Na_3Cl_3	$r = 2.500$, ∠XMX = 134.0, ∠MXM = 105.8	±0.66

[a] M and X = alkali metal and halogen atoms, respectively. [b] Bond distances and angles are in angstroms and degrees, respectively.

The geometry of each cluster was fixed during geometry optimization performed using the energy gradient method at the HF level. A relaxation effect of clusters might be important in adsorption. However, since the clusters have a large number of degrees of freedom, a formidably large calculation is necessary if such effects are included. Therefore I did not include the effect of relaxation of clusters except in the case of basket cluster.

3. Ammonia Adsorption to Neutral Clusters, M_nX_n

I first investigated the adsorption of NH_3 to the neutral clusters LiF, NaF, and NaCl. The bond distance and Mulliken atomic charge of these clusters are shown in Table 1. At first I supposed five adsorbed structures as shown in Figures 1 and 2 and tried to find out the stable structures. The nitrogen atom of the ammonia molecule interacts with the metal atom of the cluster in structure **a**. Three, two, and one hydrogen atom of ammonia interact with the halogen atom of the cluster in structures **b**, **c**, and **d**. The nitrogen and one hydrogen atom interact with the metal and halogen atoms at the same time in structure **e**. The adsorption energies of structures **b**, **c**, and **d** are almost zero. The structures **a** and **e** are stable.

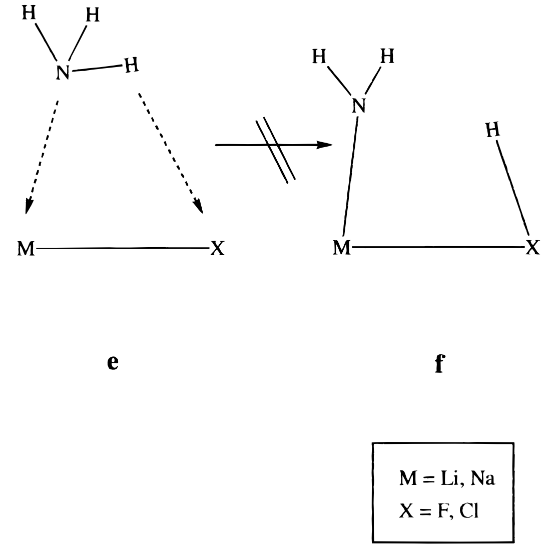

Figure 2. Adsorption of ammonia to LiF, NaF, and NaCl clusters. The ammonia molecule is adsorbed via the association of the nitrogen and hydrogen atoms with the metal and halogen atoms, respectively, of the clusters. Structure **f** shows dissociative adsorption of an ammonia molecule.

TABLE 2: NH_3 Adsorption Energies ΔE [kcal/mol][a], and N−M (M = Li and Na atoms) and H−X (X = F and Cl atoms) Distances R [Å] for LiF, NaF, and NaCl Clusters

	a		e		
	ΔE	R(N−M)	ΔE	R(N−M)	R(H−X)
LiF	−20.7	2.09	−19.2	2.06	2.73
NaF	−16.4	2.47	−17.6	2.40	2.08
NaCl	−17.6	2.44	−19.1	2.39	2.53

[a] The adsorption energies ΔE were calculated as $\Delta E = E$(adsorbed structure) − E(LiF, NaF, or NaCl) − $E(NH_3)$.

The adsorption energy and nitrogen−metal (metal = Li and Na atoms) and hydrogen−halogen (halogen = F and Cl atoms) distances in structures **a** and **e** are shown in Table 2. The adsorption energy was calculated as

$$\Delta E = E(\text{adsorbed structure}) - E(\text{cluster}) - E(NH_3)$$

The metal−halogen and nitrogen−hydrogen bond lengths are the same before and after adsorption for structures **a** and **e**. The

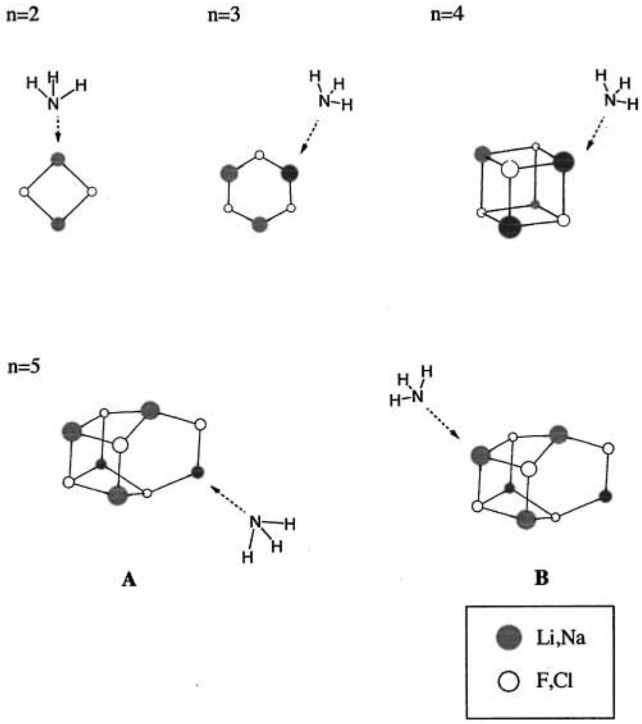

Figure 3. Adsorption of ammonia to Li_nF_n, Na_nF_n, and Na_nCl_n clusters, $n = 2-5$.

TABLE 3: NH_3 Adsorption Energies ΔE^a [kcal/mol] for Li_nF_n, Na_nF_n, and Na_nCl_n clusters, $n = 2-5$

n	Li_nF_n	Na_nF_n	Na_nCl_n
2	−15.8	−12.8	−15.2
3	−13.1	−11.2	−14.4
4	−15.8	−12.3	−14.6
5 (**5A**)	−16.1	−14.3	−15.9
5 (**5B**)	−14.8	−13.2	−15.8

[a] The adsorption energies ΔE were calculated as $\Delta E = E$(adsorbed structure) $-$ E(Li_nF_n, Na_nF_n, or Na_nCl_n) $-$ $E(NH_3)$.

adsorption energies of structures **a** and **e** are almost the same for all of the clusters. Dissociation of the N−H bond of ammonia, as shown in Figure 2, does not occur for all of the clusters.

I next investigated slightly larger clusters ($n = 2-5$), and focused only on the adsorption of the nitrogen atom of ammonia to a metal atom, as shown in Figure 3. All structures were found to be local minima in geometry optimization. The geometry and Mulliken atomic charge of these clusters are shown in Table 1. The coordination number of metal atoms adsorbed by ammonia is 2 at cluster sizes $n = 2$ and 3. The coordination number of metal atoms is 3 for cluster size $n = 4$. The coordination numbers of metal atoms are 2 and 3 for A and B, respectively, in cluster size $n = 5$, as shown in Figure 3. The adsorption energies are shown in Table 3.

The adsorption energy does not depend on the cluster size or the coordination number and the differences among three clusters are within a few kilocalories.

4. Ammonia Adsorption to Positively Charged Clusters, $M_nX_{n-1}^+$

4.1. Cluster Size $n = 2-9$. I next examined the adsorption of ammonia to the positively charged clusters $M_nX_{n-1}^+$ for $n = 2-9$. The geometries and Mulliken atomic charges of small clusters ($n = 2-5$) are shown in Tables 4 and 5, respectively.

I first investigated the adsorption to M_2X^+ clusters. I supposed five adsorbed structures as shown in Figures 4 and 5 and tried to find out the stable structures. The nitrogen atom of ammonia is adsorbed to the metal atom of each cluster in structure **a**. Three, two, and one hydrogen atoms are adsorbed to the halogen atom for structures **b**, **c**, and **d**, respectively. The nitrogen and one hydrogen atoms interact with the metal and halogen atoms at the same time in structure **e**. The ammonia molecule is not adsorbed in structures **b**, **c**, **d**, and **e**. Dissociation of the N−H bond of ammonia also does not occur. Only structure **a** is stable. The adsorption energy and the distance between the nitrogen and metal atoms for structure **a** are shown in Table 6.

TABLE 4: Geometries of the Most Stable Isomers $M_nX_{n-1}^+$ ($n = 1-3$) Computed with the MP2 Method

MX	bond length[a,b] angle[c]
Li_2F^+	$r_{M1-X2} = 1.752$
Na_2F^+	$r_{M1-X2} = 2.076$
Na_2Cl^+	$r_{M1-X2} = 2.464$
$Li_3F_2^+$	$r_{M2-X2} = 1.787$, $r_{M1-X2} = 1.729$
$Na_3F_2^+$	$r_{M2-X2} = 2.171$, $r_{M1-X2} = 2.050$
$Na_3Cl_2^+$	$r_{M2-X3} = 2.652/\alpha_{X3M2X3} = 81.5$, $\alpha_{M2X3M2} = 82.1$
$Li_4F_3^+$	$r_{M2-X3} = 1.872$, $r_{M3-X3} = 1.938/\alpha_{X3M3X3} = 87.3$, $\alpha_{X3M2X3} = 91.2$, $\alpha_{M3X3M2} = 86.5$
$Na_4F_3^+$	$r_{M2-X3} = 2.201$, $r_{M3-X3} = 2.283/\alpha_{X3M3X3} = 83.9$, $\alpha_{X3M2X3} = 87.9$, $\alpha_{M3X3M2} = 89.1$
$Na_4Cl_3^+$	$r_{M2-X3} = 2.593$, $r_{M3-X3} = 2.652/\alpha_{X3M3X3} = 93.0$, $\alpha_{X3M2X3} = 95.8$, $\alpha_{M3X3M2} = 83.7$
$Li_5F_4^+$	$r_{M2-X3} = 1.844$, $r_{M4-X3} = 1.949/\alpha_{X3M4X3} = 90.0$, $\alpha_{X3M2X3} = 96.6$, $\alpha_{M4X3M2} = 86.7$
$Na_5F_4^+$	$r_{M2-X3} = 2.201$, $r_{M4-X3} = 2.334/\alpha_{X3M4X3} = 90.0$, $\alpha_{X3M2X3} = 97.2$, $\alpha_{M4X3M2} = 86.4$
$Na_5Cl_4^+$	$r_{M2-X3} = 2.555$, $r_{M4-X3} = 2.791/\alpha_{X3M3X3} = 90.0$, $\alpha_{X3M2X3} = 97.4$, $\alpha_{M3X3M2} = 86.3$

[a] Bond distances r_{Mc-Xc} and angles α_{XcMcXc} and α_{McXcMc} are in angstroms and degrees, respectively. [b] Bond distance between the metal (M_c) and halide atoms (X_c). c indicates the coordination number of the metal or halide atom. [c] Bond angles $X_c-M_c-X_c$ and $M_c-X_c-M_c$. c indicates the coordination number of the metal or halide atom.

TABLE 5: Mulliken Atomic Charges on the Atoms (M*c* and X*c*)[a] of the Most Stable Isomers $M_nX_{n-1}^+$ ($n = 1-3$) Computed with the MP2 Method

MX	Mulliken atomic charge
Li_2F^+	M1 = +0.97, X2 = −0.93
Na_2F^+	M1 = +0.97, X2 = −0.94
Na_2Cl^+	M1 = +0.84, X2 = −0.68
$Li_3F_2^+$	M2 = +0.94, M1 = +0.96, X2 = −0.93
$Na_3F_2^+$	M2 = +0.94, M1 = +0.97, X2 = −0.94
$Na_3Cl_2^+$	M2 = +0.72, M1 = +0.81, X2 = −0.67
$Li_4F_3^+$	M3 = +0.89, M2 = +0.96, X3 = −0.92
$Na_4F_3^+$	M3 = +0.88, M2 = +0.96, X3 = −0.92
$Na_4Cl_3^+$	M3 = +0.63, M2 = +0.76, X3 = −0.63
$Li_5F_4^+$	M4 = +0.92, M2 = +0.94, X3 = −0.93
$Na_5F_4^+$	M4 = +0.92, M2 = +0.96, X3 = −0.94
$Na_5Cl_4^+$	M4 = +0.56, M2 = +0.76, X3 = −0.65

[a] Mulliken atomic charge on the atom with coordination number c.

TABLE 6: NH_3 Adsorption Energies ΔE^a [kcal/mol] and N−M (M = Li and Na atoms) Distances R [Å] for Li_2F^+, Na_2F^+, and Na_2Cl^+ Clusters

	ΔE	R(N−M)
LiF	−29.8	2.06
NaF	−19.6	2.41
NaCl	−23.0	2.40

[a] The adsorption energies ΔE were calculated as $\Delta E = E$(adsorbed structure) $-$ E(Li_2F^+, Na_2F^+, or Na_2Cl^+) $-$ $E(NH_3)$.

I supposed some adsorbed geometries of smaller clusters ($n = 3-5$) as shown in Figure 6 and optimized the geometry parameters to find out the local minima. The adsorption energies are shown in Table 7. The most stable isomer for $Na_3Cl_2^+$ is

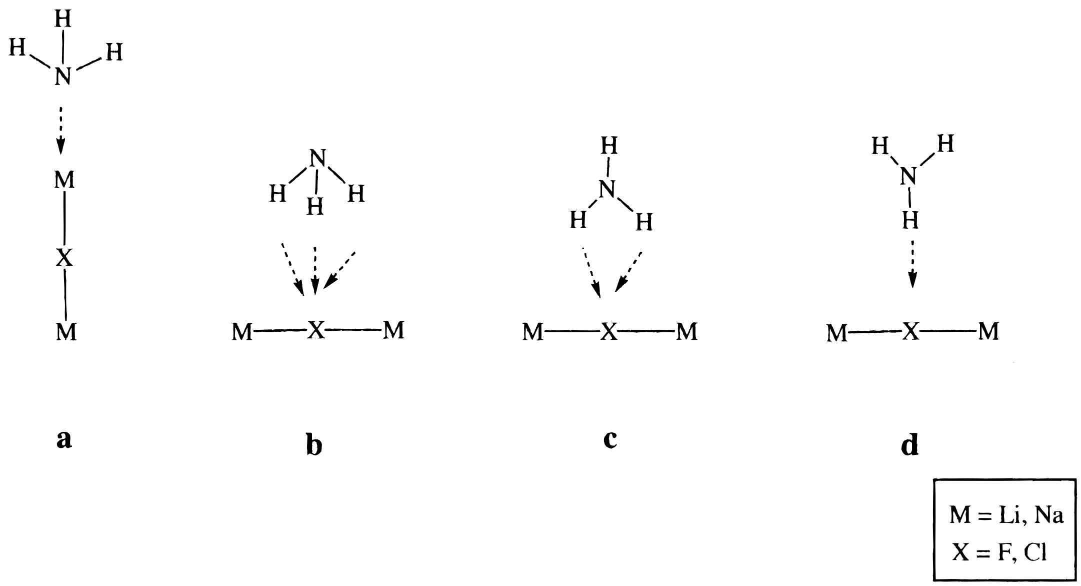

Figure 4. Supposed structures for the adsorption of ammonia to Li_2F^+, Na_2F^+, and Na_2Cl^+ clusters.

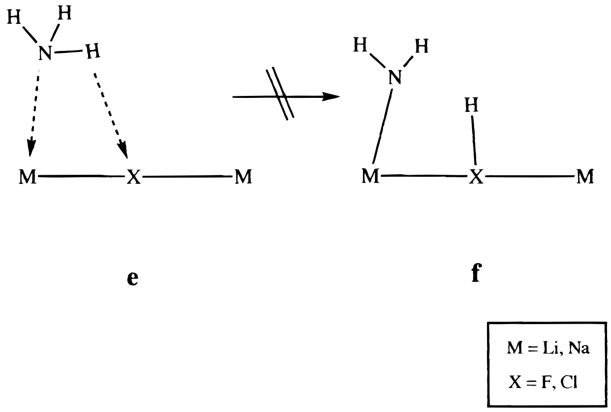

Figure 5. Adsorption of ammonia to Li_2F^+, Na_2F^+, and Na_2Cl^+ clusters. The ammonia molecule is adsorbed via the association of the nitrogen and hydrogen atoms with the metal and halogen atoms, respectively, of the clusters. Structure **f** shows dissociative adsorption of an ammonia molecule.

different from those for the other two clusters ($Na_3F_2^+$ and $Li_3F_2^+$), and this isomer is identified as structure **3c** in Table 7 and Figure 6. The coordination numbers of the metal atoms adsorbed by ammonia for structures **3a**, **3b**, and **3c** are 1, 2, and 2, respectively. The adsorption energy of **3a** is greater than that of **3b**.

The coordination numbers for structures **4b** and **4c** are 3 and 2, respectively. The difference in adsorption energy between structures **4b** and **4c** is small. The nitrogen atom is positioned at the halogen defect site in structure **4a**. The adsorption energy of structure **4a** is quite small compared to those of structures **4b** and **4c**.

The coordination numbers for structures **5a** and **5b** are 2 and 4, respectively. The adsorption energy of structure **5a** is greater than that of structure **5b**.

There is a relation between the coordination number and the net atomic charge on metal atoms for all of the clusters $M_nX_{n-1}^+$: atoms with smaller coordination numbers have larger atomic charges[16] as shown in Table 5. The adsorption energy of ammonia is also related to the coordination number of the adsorbed metal atom: the adsorption energy to the metal atom decreases with the coordination number.

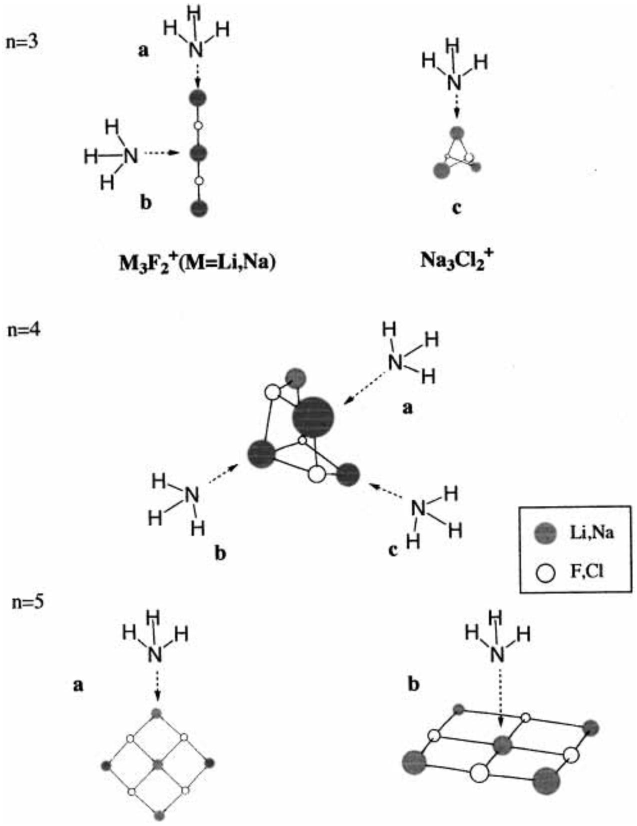

Figure 6. Adsorption of ammonia to $Li_nF_{n-1}^+$, $Na_nF_{n-1}^+$ and $Na_nCl_{n-1}^+$ clusters, $n = 3-5$.

I next investigated the adsorption site with the smallest coordination number for cluster sizes from six to nine as shown in Figure 7, and the adsorption energies are shown in Table 7. The coordination numbers of the metal atoms adsorbed by ammonia are 2 for cluster sizes $n = 6$ and 8 and 3 for cluster sizes $n = 7$ and 9. The cluster size $n = 8$ is more reactive compared to the neighbor cluster sizes $n = 7$ and 9 due to the difference of coordination number of adsorption site.

The adsorption energies of $Li_nF_{n-1}^+$ clusters are the greatest at each cluster size, while $Na_nF_{n-1}^+$ clusters have the lowest adsorption energies. The interaction between N and Na atoms is ionic-dipole, while the Li−N bond is not only ionic but also

TABLE 7: NH_3 Adsorption Energies ΔE^a [kcal/mol] for $Li_nF_{n-1}^+$, $Na_nF_{n-1}^+$, and $Na_nCl_{n-1}^+$ Clusters, $n = 3-9$

	$Li_nF_{n-1}^+$	$Na_nF_{n-1}^+$	$Na_nCl_{n-1}^+$
		$n = 3$	
3a	−28.4	−20.6	
3b	−14.4	−10.6	
3c			−22.4
		$n = 4$	
4a	−11.2	−3.6	−6.6
4b	−24.1	−16.9	−19.2
4c	−25.3	−17.4	−19.1
		$n = 5$	
5a	−23.3	−16.7	−18.9
5b	−15.0	−10.7	−14.0
		$n = 6$	
6	−22.3	−13.3	−14.2
		$n = 7$	
7	−23.4	−15.4	−17.7
		$n = 8$	
8	−23.6	−17.1	−19.4
		$n = 9$	
9	−23.4	−12.3	−15.6

[a] The adsorption energies ΔE were calculated as $\Delta E = E$(adsorbed structure) − $E(Li_nF_{n-1}^+$, $Na_nF_{n-1}^+$, or $Na_nCl_{n-1}^+)$ − $E(NH_3)$.

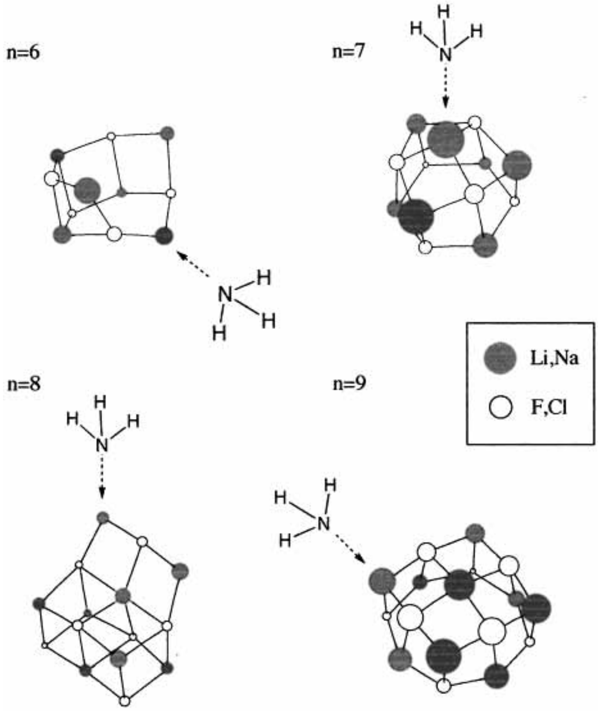

Figure 7. Adsorption of ammonia to $Li_nF_{n-1}^+$, $Na_nF_{n-1}^+$, and $Na_nCl_{n-1}^+$ clusters, $n = 6-9$.

covalent. The *s* and *p* unoccupied orbitals of Li atom mix with the orbital filled with the lone-pair of electrons of NH_3 molecule and the covalent bond is formed. This makes the adsorption energy of $Li_nF_{n-1}^+$ clusters lager than the others.

The adsorption energy for $Li_nF_{n-1}^+$ clusters is not size-dependent. On the other hand, the adsorption energies for $Na_nF_{n-1}^+$ and $Na_nCl_{n-1}^+$ clusters show size dependency.

4.2. NH_3 Adsorption to Basket-Structure Clusters, $M_{13}X_{12}^+$. Basket structures, which have a defect site as shown in Figure 8, are the most stable for cluster size $n = 13$.[16] Homer et al.[4,5] also suggested that the basket structure was the most stable for this cluster size. They have compared the thermal stabilities of structural isomers for $Na_{13}F_{12}^+$ by using Monte Carlo simulations. The simulation shows that the basket isomer is the lowest energy isomer and that if the other isomers are heated their structures collapse into the basket structure. They think that this structure is highly reactive for the adsorption of molecular NH_3, which may be adsorbed into the basket vacancy.

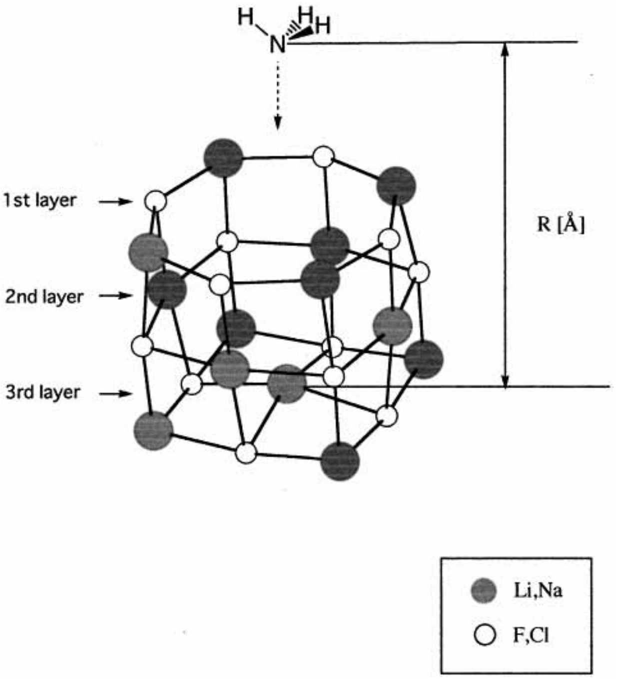

Figure 8. Approach of an ammonia molecule to the basket clusters $Li_{13}F_{12}^+$, $Na_{13}F_{12}^+$, and $Na_{13}Cl_{12}^+$.

I first investigated the adsorption energy of ammonia to clusters at the metal atom with a coordination number of 2. The adsorption energies for the $Li_{13}F_{12}^+$, $Na_{13}F_{12}^+$, and $Na_{13}Cl_{12}^+$ clusters are 15.5, 13.0, and 15.3 kcal/mol, respectively. These adsorption energies are smaller than those of smaller clusters.

I next examined the approach of an ammonia molecule to the basket vacancy, as shown in Figure 8. The energy diagrams are shown in Figure 9. Ammonia does not fit in the vacancy site of the $Li_{13}F_{12}^+$ and $Na_{13}F_{12}^+$ clusters. The adsorption energy for the $Na_{13}Cl_{12}^+$ cluster is 16.3 kcal/mol. The averaged diameters of the basket for the $Li_{13}F_{12}^+$, $Na_{13}F_{12}^+$, and $Na_{13}Cl_{12}^+$ clusters are 4.72, 5.53 and 6.85 Å, respectively. Therefore, the baskets of the $Li_{13}F_{12}^+$ and $Na_{13}F_{12}^+$ clusters are too small to accommodate an ammonia molecule. Then the geometry of $Na_{13}Cl_{12}^+ \cdot NH_3$ was fully optimized and shown in Figure 10. The adsorption energy is 17.0 kcal/mol. The averaged diameter of the first layer of cluster is 6.89 Å, which is almost the same as that of the cluster before NH_3 adsorption, 6.85 Å. The averaged diameter of the second layer of cluster is 7.31 Å, which is about 0.2 Å longer than that of the cluster before NH_3 adsorption. The N−H distance is 2.57 Å and the averaged H−Cl distance is 3.20 Å. The lone-pair of electrons of the nitrogen atom is located at the anion vacancy and interacts with the four metal atoms, and the hydrogen atoms interact with four halogen atoms.

The electron correlation effect was included by the MP2 method. The adsorption energies for the $Na_{13}F_{12}^+$ and $Na_{13}Cl_{12}^+$ clusters were calculated by the MP2 method with their geometries optimized at the HF level. The adsorption energies for the $Na_{13}F_{12}^+$ and $Na_{13}Cl_{12}^+$ clusters are 20.3 and 40.3 kcal/mol, respectively. The adsorption energies at the metal atom with the smallest coordination number were 8.4 and 9.4 kcal/mol, respectively.

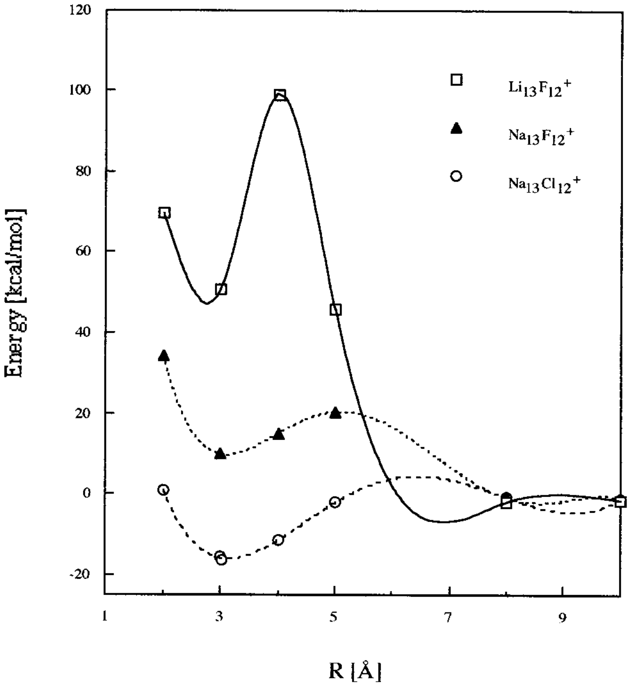

Figure 9. Energy diagrams for the adsorption of ammonia to the basket clusters $Li_{13}F_{12}^+$, $Na_{13}F_{12}^+$, and $Na_{13}Cl_{12}^+$. The white square, black triangle, and white circle denote the $Li_{13}F_{12}^+$, $Na_{13}F_{12}^+$, and $Na_{13}Cl_{12}^+$ clusters, respectively.

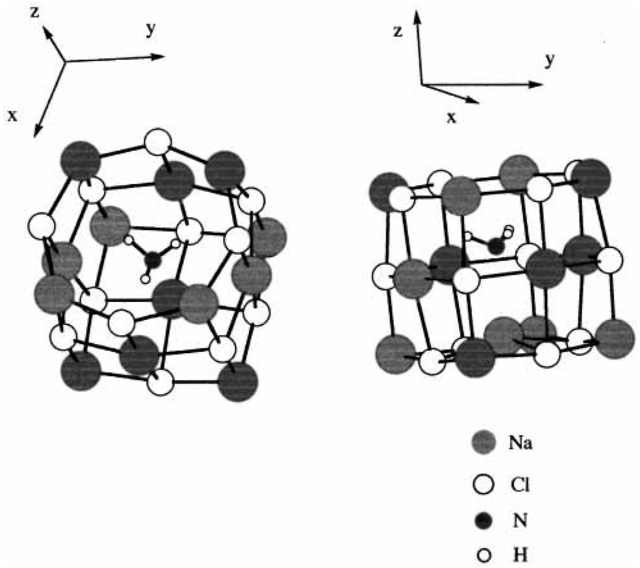

Figure 10. Fully optimized geometries of the adsorption of ammonia to the $Na_{13}Cl_{12}^+$ cluster.

I next investigated the adsorption of ammonia to the vacancy of $M_9X_8^+$ clusters, which have basketlike structures. However, the adsorption energies for all of the clusters are around 5 kcal/mol. The lone-pair of electrons of the nitrogen atom is located at the anion vacancy and interacts with the four metal atoms, while there is no interaction between the hydrogen and halogen atoms as in the adsorption to basket clusters, $n = 13$.

Finally, I investigated the adsorption to $M_{12}X_{11}^+$ and $M_{14}X_{13}^+$ clusters. I selected metal atoms with the smallest coordination numbers as the adsorption site. The coordination numbers for the $M_{12}X_{11}^+$ and $M_{14}X_{13}^+$ clusters are 2 and 3, respectively. The adsorption energies are shown in Table 8. The structure of the $M_{14}X_{13}^+$ cluster is a cube, 3 × 3 × 3. The adsorption energies for these clusters are slightly smaller than those of the other clusters, since they are cuboidal nanocrystals.

TABLE 8: NH_3 Adsorption Energies ΔE^a [kcal/mol] for $Li_nF_{n-1}^+$, $Na_nF_{n-1}^+$, and $Na_nCl_{n-1}^+$ Clusters, $n = 12-14$

n	$Li_nF_{n-1}^+$	$Na_nF_{n-1}^+$	$Na_nCl_{n-1}^+$
12	−22.2	−16.1	−18.1
13^b	−15.5	−13.0	−16.3
14	−18.4	−13.1	−16.2

[a] The adsorption energies ΔE were calculated as $\Delta E = E$(adsorbed structure) − E($Li_nF_{n-1}^+$, $Na_nF_{n-1}^+$, or $Na_nCl_{n-1}^+$) − E(NH_3). [b] All adsorption energies were calculated for adsorption on the metal atom with the smallest coordination number expect for the $Na_{13}Cl_{12}^+$ cluster. Molecular ammonia fits in the basket vacancy of the $Na_{13}Cl_{12}^+$ cluster.

5. Summary

The adsorption of NH_3 molecule onto neutral M_nX_n ($n = 1-5$) and positively charged $M_nX_{n-1}^+$ ($n = 2-9$ and $12-14$) clusters was examined. Homer et al. studied the molecular adsorption of ammonia on alkali metal halide clusters and nanocrystals by using experimental methods.[4,5] The calculation results in this study are compared with their experimental results in this section.

The nitrogen atom of ammonia is adsorbed to a metal atom of both neutral and positively charged clusters. The adsorption energy does not depend on the cluster size or the coordination number for neutral clusters. The differences of adsorption energy among three neutral clusters, Li_nF_n, Na_nF_n, and Na_nCl_n clusters, are within a few kilocalories per mole.

Positively charged clusters are more reactive than neutral clusters, and present results are in accord with the experimental results, in which the positively charged clusters are more reactive than neutral and negatively charged clusters.[4,5] The adsorption energy to metal atoms decreases with the coordination number for small positively charged clusters, $n < 5$, and the adsorption energy is in the order $Li_nF_{n-1}^+ > Na_nCl_{n-1}^+ > Na_nF_{n-1}^+$.

Ammonia fits into the basket vacancy of the $Na_{13}Cl_{12}^+$ and $Na_{13}F_{12}^+$ clusters in the present study. In addition, the lone-pair of electrons of the nitrogen atom is located at the anion vacancy and interacts with the four metal atoms, and the hydrogen atoms are found to interact with four halogen atoms. The adsorption energy are 20.3 and 40.3 kcal/mol for $Na_{13}F_{12}^+$ and $Na_{13}Cl_{12}^+$ clusters, respectively. Present results show good agreement with the experimental results which the basket clusters, $n = 13$, 22, 31, and 37, are more reactive than their neighboring size clusters for positively charged NaF and KF clusters.

The smallest clusters are the most reactive, and reactivity tends to decrease with size. The ammonia does not get into the basket vacancy of $Li_{13}F_{12}^+$ cluster because of the small size of the basket vacancy. These results about $Li_nF_{n-1}^+$ clusters are in accord with the experimental results.[4,5]

Including relaxation of the geometry of basket clusters due to the adsorption of ammonia may change the adsorption energy; however, the tendency of reactivities of clusters will not be changed. Further studies for larger clusters are expected to identify other trends in cluster reactivity.

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