A densityfunctional study of cluster reactivity. III. NH3 on a free Ga5As+ 5 cationic cluster

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A density-functional study of cluster reactivity. III. NH$_3$ on a free Ga$_5$As$_5^+$ cationic cluster

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Ammonia chemisorption on a small and positively charged gallium arsenide cluster in the gas phase has been investigated using density-functional methods. The reactivity at various cluster sites are characterized in terms of binding energy and charge transfer from the adsorbate to the cluster with a strong correlation shown between the latter two quantities. The calculations show a strong dependence of the reactivity of the cluster on its charge state. Ionizing the bare cluster to a cationic charge state enables multiple chemisorption of ammonia, which is much less favored by a neutral cluster and can be prohibited on a negatively charged cluster. © *1996 American Institute of Physics.* [S0021-9606(96)01504-1]

I. INTRODUCTION

Gallium arsenide crystals are vastly used in fast microelectronic devices and are among the most important materials in general semiconductor technology. The surface properties of gallium arsenide are of general interest and have been studied in the form of small free clusters produced by laser-beam technologies.[1−8] Unique to these free clusters are the availability of a wide range of chemical compositions and a large surface-to-volume ratio. Small gallium arsenide clusters can also be conveniently studied using sophisticated electronic structure methods.[9−13]

Recent experiments show that reactivities of small gallium arsenide clusters depend strongly on cluster size, Ga/As composition ratio, and cluster charge state. For positively charged Ga$_x$As$_y^+$ clusters in the size range from $x+y=6-16$, it is shown that the ammonia sticking rates are much higher at the cluster size $x+y$ being an even number than an odd number, and the rates peak at (or near) stoichiometric compositions $x=y$.[4] Moreover, the adsorption of NH$_3$ molecules on these cationic clusters occur sequentially as a function of exposure time with a saturation limit of four NH$_3$ molecules in most cases. On the other hand, it has been experimentally found that small gallium arsenide clusters with negative charges do not react with ammonia.[14]

In two previous papers,[15,16] we have studied the chemisorption of NH$_3$ on a ten atom gallium arsenide cluster, with no charges (either positive or negative) on it, and found that the NH$_3$ tends to be bound more strongly over a gallium site than an arsenic site. As a general observation, charges are withdrawn from gallium sites to nearby arsenic sites due to an alternating Ga-As bonding arrangement typically existing in small gallium arsenide clusters.[4,9,11,12] The neutral cluster is also found to allow a second NH$_3$ to be bound on a different atomic site after the initial adsorption. The total charge transferred to the bare cluster is however not increased as much with the addition of the second ammonia, which suggests that some degree of saturation has been reached in the bare cluster. The binding energy of a second ammonia with a neutral cluster is small compared to that of the first ammonia. In terms of "adsorbate−adsorbate" interaction, multiply adsorbed ammonia on a neutral cluster appear to be repulsive to each other. A strong correlation between the adsorbate-cluster binding energy and the charge transfer to the cluster has been demonstrated. Since the chemisorption experiments were mostly performed on clusters with positive charges, it is of interest to investigate the details of interaction of NH$_3$ with charged bare clusters particularly those in a cationic charge state.

In this paper, we provide details on ammonia interacting with a +1 cationic gallium arsenide cluster. Our goal is to illuminate further the general nature and mechanisms of ammonia reactivity with small GaAs clusters. In particular, the dependence of site reactivity on the ionization charge of the bare cluster is investigated. In Sec. II we outline the calculational method. The geometric and electronic parameters used to characterize NH$_3$ chemisorption are detailed in Sec. III. In Sec. IV we discuss the results.

II. THEORY

The calculations are performed in the framework of local-spin-density (LSD) approximation using a recently developed computer program[17] for an *ab initio* determination of the geometric and electronic structure of the Ga$_5$As$_5$(NH$_3$)$_x^+$ cluster complexes. The algorithms used in the program are capable for execution on scalable parallel computers. Three-dimensional integrations and a multipole representation of the electrostatic potential[18,19] suitable for streamlined processing are utilized. The LSD exchange-correlation potential of Barth and Hedin has been used throughout.[20] The same basis set as in the previous calculation[15,16] is used which for N, Ga, and As are composed of occupied atomic orbitals of the ground state atoms and the valence orbitals of a 2+ ionic state, plus a single

d-type polarization function. For hydrogen, the basis set is composed of the H $1s$ orbital and an additional s function, and a p function.

The atomic charge and the net charge transfer into the cluster, both of which will be used to characterize the ammonia–GaAs cluster interaction, are obtained from Mulliken population analysis. Although arbitrariness is unavoidable whenever a scheme is adopted to partition charges in a molecular system to atomic centers, we believe that the result given by this charge analysis method should be sufficient for a *qualitative* description of the chemisorption of concern.

III. RESULTS

A. The bare cluster

The bare $Ga_5As_5^+$ cluster used in this calculation has a tetracapped trigonal prism (TTP) structure in the C_s point group symmetry. For the neutral Ga_5As_5 cluster, this TTP structure corresponds to the most stable isomer. The final structures of the $Ga_5As_5(NH_3)_x^+$ $(x=1,2)$ cluster complexes with configurations corresponding to ammonia adsorbed on different cluster sites are approached to by first placing the NH_3 at approximately 1.5 Å away from the cluster with the negative side (N atom) pointing towards the designated site, and then allowing for full relaxation until the maximum force on the nuclei becomes smaller than 0.001 atomic units. Due to the restrictions made on the initial position of ammonia, the potential energy surface has been explored only partially in this work; those regions related to, for instance, the binding of NH_3 with orientations other than the head-on position and the NH_3 dehydrization on cluster surface are excluded. Dative bonding between ammonia and the cluster is presumed.

The existence of the C_s symmetry in the bare cluster causes fewer atomic sites to be unique to NH_3 adsorption. Among the symmetry unique atomic sites, three are arsenic: As-1 (As-2), As-3, and As-4 (As-5), and four are gallium: Ga-6 (Ga-7), Ga-8, Ga-9, and Ga-10 [see Fig. 1(a)]. For single NH_3 adsorptions on the in-plane sites As-3, Ga-8, Ga-9, and Ga-10, the C_s symmetry is used in the relaxation of the structure of the corresponding ammonia-cluster complexes. In all the other cases, no symmetry constraints are imposed.

The singly ionized $Ga_5As_5^+$ cluster has a doublet ground state $^2A_1$ due to the unpaired electron. The TTP structure is maintained in the $+1$ charge state of the cluster [Fig. 1(a)]. But changes in local bonding details appear to be quite large: e.g., the change in bond length can range from 0.2–1.3 Å (mostly becoming longer). A comparison of Mulliken atomic charges between the ionized cluster and the neutral cluster is given in Table I. The $+1$ charge is unevenly divided, and mostly localized at the gallium sites.

B. Single NH_3 adsorption

In Table II, the binding energy E^s, the amount of charges transferred from the adsorbed NH_3 to the cluster ΔQ, and the adsorbate-cluster bond distance R are listed for single-NH_3
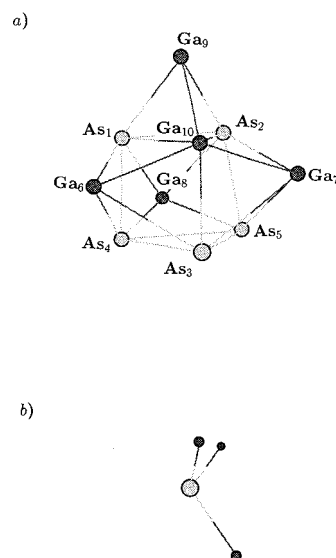

FIG. 1. (a) The $Ga_5As_5^+$ bare cluster in the tetracapped trigonal prism (TTP) form, with light circles representing arsenic atoms and dark circles gallium atoms; (b) a free NH_3 molecule.

adsorptions on all the seven unique cluster sites. The binding energy E^s is defined as the energy to remove the NH_3 from the cluster to a large distance and is calculated as the energy difference between the $Ga_5As_5NH_3^+$ cluster complex and the free fragments $Ga_5As_5^+$ and NH_3. The value of ΔQ is obtained by taking the sum of the Mulliken charges at the N and H sites of the adsorbed ammonia. As can be seen from the table, this quantity correlates well with the binding energy. In contrast, charges obtained for each individual atomic centers (either at the cluster site or the nitrogen) do not correlate with the binding energy. Generally, NH_3 tends to form stronger bonds with gallium atoms in the cluster than with the arsenic atoms as is indicated by the calculated binding energies on the respective sites. The same tendency was found in the NH_3 adsorption on a neutral Ga_5As_5 cluster.[15,16]

The most stable site in the TTP $Ga_5As_5^+$ cationic cluster for NH_3 adsorption is the Ga-9 atom. This atom connects strongly with three neighboring atoms (Ga-10, As-1 and As-2). The bond lengths are all short (<2.75 Å). The amount of charges transferred into the cluster is large.

Ga-10 is the second stable site following Ga-9. This site has three immediate gallium neighbors (Ga-6,7,9) and an

TABLE I. Mulliken atomic charge. Q^0 and Q^{+1} denote the charge on each atom of the Ga_5As_5 and $Ga_5As_5^{+1}$ clusters, respectively. $\Delta Q = Q^{+1} - Q^0$.

Site	Q^0(e)	Q^{+1}(e)	ΔQ(e)
As-1,2	-0.180	-0.126	0.054
As-3	-0.088	-0.012	0.076
As-4,5	-0.075	0.010	0.085
Ga-6,7	0.149	0.291	0.142
Ga-8	0.171	0.304	0.133
Ga-9	0.198	0.320	0.122
Ga-10	-0.071	0.037	0.108

TABLE II. Binding energy E^s, ammonia-cluster site bond distance R, net charge transfer to the cluster ΔQ^s, and charge on the nitrogen atom Q_N for single-ammonia adsorption on a $Ga_5As_5^+$ cationic cluster. Values in parentheses are those for a Ga_5As_5 neutral cluster.

Site	$-E^s$ (eV)	R(Å)	ΔQ^s(e)	$-Q_N$(e)
As-1,2	0.87 (0.24)	2.35 (2.36)	0.23 (0.20)	0.80 (0.80)
As-3	1.03 (1.30)	2.17 (2.4)	0.24 (0.17)	0.87 (0.78)
As-4,5	0.58 (0.27)	2.22 (3.2)	0.28 (0.21)	0.84 (0.82)
Ga-6,7	0.73 (1.72)	2.27 (2.1)	0.28 (0.27)	0.83 (0.92)
Ga-8	1.28 (1.50)	2.08 (2.3)	0.30 (0.19)	0.92 (0.84)
Ga-9	2.23 (1.83)	2.12 (2.1)	0.40 (0.33)	0.94 (0.93)
Ga-10	2.02 (2.12)	1.99 (2.1)	0.41 (0.32)	0.95 (0.91)

arsenic atom (As-3) at a larger distance. The fact that the local environment is gallium rich might be responsible for the large charge transfer from NH_3 to the cluster at this site. The ammonia-cluster bond distance is also shortened by $\simeq 0.1$ Å compared to other Ga sites.

The NH_3 adsorption on the Ga-8 site is moderate. The connections between the Ga-8 atom and the neighboring atoms are rather loose with longer than average bond lengths ($\geqslant 2.75$ Å). The net charge transfer is much reduced compared to those involved in the previous two cases. The bond distance between N and Ga-8 is also short.

The Ga-6 site (and its symmetric equivalent Ga-7) is rather passive. The NH_3 binding energy on this site is only 1/4 of that of the Ga-9 site. The Ga-6 has only two close-neighbor atoms (Ga-10 and As-4). The C_s symmetry is lost when the site is bound with an ammonia. The N-Ga(6) bond distance 2.27 Å is the longest of all the four N-Ga distances. The net charge transfer is the smallest of the four gallium sites.

Ammonia binds relatively weakly to arsenic sites compared to the gallium sites. The largest binding energy is found on the site As-3, which is only half of the binding energy of Ga-9 or Ga-10, but similar to the binding energy on the Ga-8 site. The As-3 is located in the C_s mirror plane of the bare cluster. The other arsenic sites are rather passive and like the Ga-6 and 7, located off the mirror plane.

C. Double NH_3 adsorption

In the previous calculation,[16] it has been found that multiple NH_3 adsorption on a neutral gallium arsenide cluster is energetically possible. However, the binding energy of a second NH_3 is considerably less than the binding energy of the first ammonia. The adsorbate–adsorbate interaction between

the two ammonia molecules chemisorbed on the neutral cluster is repulsive. Here we show that on a positively charge gallium arsenide cluster, the second NH_3 can be bound more stably than it could on a bare cluster, showing attractive ammonia-ammonia interactions.

Listed in Table III are some of the electronic and geometric parameters used to characterize double ammonia adsorption on the $Ga_5As_5^+$ cluster. E^d is the binding energy for two NH_3 molecules adsorbed on sites A and B. E_{ad-ad} is the adsorbate–adsorbate interaction energy and is defined as the difference between E^d and the sum of the two single-NH_3 binding energies E_A^s and E_B^s for site A and site B respectively. ΔQ^d denotes the total charge transfer from the two adsorbed NH_3 molecules to the cluster. R_A (R_B) is the nitrogen-cluster bond distance for the site A (B). R_{N-N} gives the ammonia–ammonia separation measured between the N atoms.

The most stable double-NH_3 adsorptions are on the sites Ga-10 and Ga-8. Since the total binding energy exceeds the sum of two separate single-ammonia adsorption binding energies, the adsorbate–adsorbate interaction energy as defined above changes sign to become "attractive." Expressed differently, the adsorption of an ammonia at either of these two sites can enhance the receptivity of the cluster to a second ammonia at the other site. In the other two cases, Ga-9/As-3 and Ga-9/Ga-10, "repulsive" interactions between the two adsorbed ammonia molecules are obtained.

The binding energy and net charge transfer of double-ammonia adsorption on a neutral bare cluster (TTP Ga_5As_5) obtained previously[16] are also listed in Table III, quoted in parentheses. These net charge transfer values are only half of those for the ionized bare cluster. The ΔQ^d value is particularly large for the Ga-8/Ga-10 site chemisorption on the cationic bare cluster, which is 0.83e compared to 0.78e and

TABLE III. Binding energy E^d, ammonia–ammonia interaction energies E_{ad-ad}, net charge transfer to the cluster ΔQ^d, ammonia-cluster bond distances R_A and R_B, and inter-ammonia distance R_{N-N} for double-ammonia adsorption on a $Ga_5As_5^+$ cationic cluster at atomic sites A and B. See text. Values in parentheses are those for a Ga_5As_5 neutral cluster.

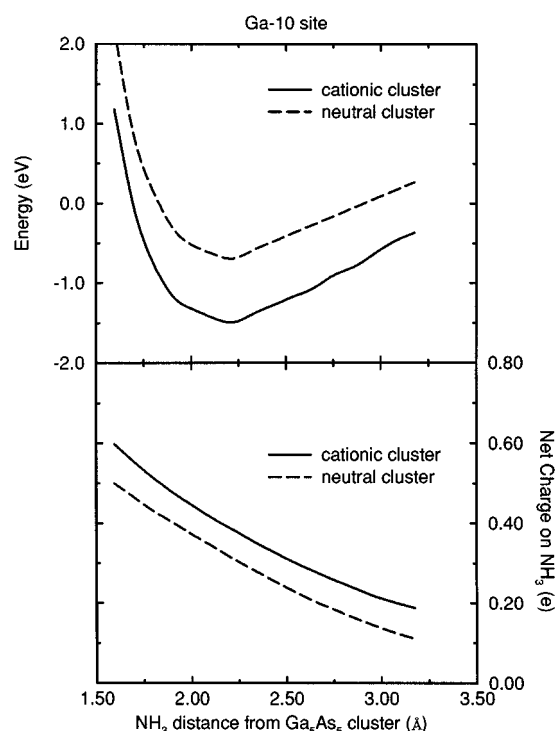| Sites A/B	$-E^d$ (eV)	E_{ad-ad} (eV)	ΔQ^d (e)	R_A (Å)	R_B (Å)	R_{N-N} (Å)
Ga-10/Ga-8	3.43(2.60)	−0.13(1.02)	0.83(0.36)	2.02(2.1)	2.00(2.2)	7.90(7.4)
Ga-9/As-3	2.99(2.11)	0.26(1.01)	0.67(0.38)	2.02(2.1)	2.97(3.4)	7.05(7.6)
Ga-6/Ga-7	−0.66(1.60)	2.12(1.84)	0.48(0.15)	2.13(2.1)	2.13(2.1)	3.63(5.4)
Ga-10/Ga-9	3.03	1.22	0.78	2.09	2.01	5.93

FIG. 2. Binding energy profile and adsorbate-cluster charge transfer for NH_3 rigid translation towards the Ga-10 site. The zero of energy is given by the sum of the total energies of a free NH_3 and the Ga_5As_5 cluster.

$0.67e$ for the Ga-9/Ga-10 and Ga-9/As-3 site combinations respectively. The reduced charge transfer for ammonia chemisorption on the neutral clusters suggest that charge saturation may be a limiting factor in multiple ammonia chemisorption on the cluster.

D. Vibrations of the adsorbed NH_3

As is already shown, the net charge transfer ΔQ to a positively charged cluster is generally different from that to a neutral cluster. This could affect the vibrational motion of the adsorbed NH_3 molecule.

Figure 2(a) shows the interaction potential between a rigid molecule and a rigid cluster in different charge states,

fixed in their fully relaxed forms as in the cluster complex. The translation between the two entities is in the direction of the original N-cluster site bond (here the cluster site is Ga-10). Figure 2(b) shows the charge that is transferred from the molecule to the cluster, as a function of the N-Ga(10) bond distance. The difference between the charge transfer to a neutral cluster and a cationic cluster is constant over a range of distance. The potential energy profiles also show a similar constant shift for different cluster charge states. We suspect that the electrostatic potential due to the ionic charge on the cluster could have an effect on the approaching molecule to lower the reaction barrier in addition to an increase of the binding energy.

Table IV lists the frequencies of the internal and collective vibrational modes of the NH_3 in the $Ga_5As_5NH_3^{\delta}$ cluster complex with $\delta = -1$, 0 and $+1$. The chemisorption site is chosen to be Ga-10. The vibrational frequencies are obtained from calculating the full force constant matrix for the cluster complex. The internal vibrational modes of the cluster are all below 300 cm^{-1} and can be considered decoupled from those of the adsorbate. We see from Table IV that in going through the cluster charge states from -1 to 0 to $+1$, the vibrational frequency of one of the symmetric modes of the adsorbed NH_3 (marked with an asterisk *) increases by 100 cm^{-1} in each ionization step, whereas the other internal modes show no significant change. In this particular vibrational mode, the center of mass of the three H atoms moves in the opposite direction to the N nucleus. The shift of vibrational frequency is therefore indicative of an increased repulsive potential for the deformation of N–H bonds caused by the charge transfer from molecule to the cluster. The chemisorption on a negatively charged cluster will be discussed in Sec. IV.

We also include in Table IV the vibrational mode that corresponds to a translation of NH_3 relative to the bare cluster. In this mode, the NH_3 molecule moves as a whole in the direction opposite to that of the Ga-10 site in the cluster, with the other cluster sites not in motion. The larger frequency value for the cationic cluster complex in this mode is consistent with the stronger bonding between the adsorbate and the cluster.

TABLE IV. Vibrational frequencies (in cm^{-1}) of an adsorbed NH_3 molecule. The symmetry of the adsorbed NH_3 is lowered to C_s from C_{3v} for a free molecule. The mode marked with an * is charge sensitive. The mode labeled ''vertical'' is the one in which the NH_3 moves as a whole in the direction of the N–cluster site bond, see the text. The experimental data is quoted from W. J. Hehre, L. Radom, P. v.R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley, New York, 1986).

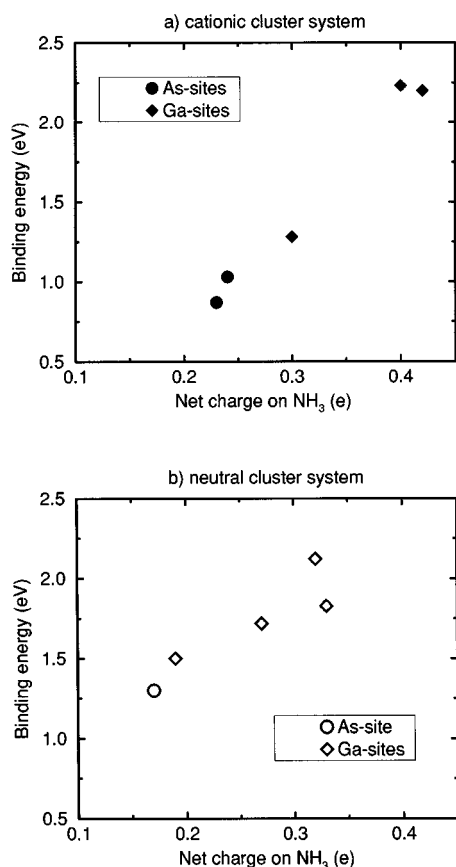|	NH_3 (C_{3v})		NH_3-$Ga_5As_5^{\delta}$ (C_s)		
Modes	Calc.	Expt.	$\delta=-1$	$\delta=0$	$\delta=+1$
s-stretch	3393	3337	3346	3368	3370
s-deform*	1020	950	1024	1106	1218
d-stretch	3527	3444	3489	3496	3478
			3522	3525	3516
d-deform	1585	1627	1527	1552	1560
			1560	1563	1579
''vertical''			351	369	434

FIG. 3. (a) Binding energy versus net charge transfer into the cluster for single-ammonia adsorptions on the TTP $Ga_5As_5^+$ cationic cluster; and (b) that on the TTP Ga_5As_5 neutral cluster.

FIG. 4. Adsorbate–adsorbate interaction energy as a function of $1/R_{N-N}$, the inverse of inter-adsorbate distance. Both quantities are as defined in the text.

IV. DISCUSSION

A. Effects of charge transfer

In order to understand the role of charge transfer in the chemisorption reactions (and site selection), we study the correlation between the adsorbate-cluster binding energy E and the net charge transferred from NH_3 into the cluster ΔQ for adsorption on the various sites. Figure 3 is a plot of E^s versus ΔQ^s for a single ammonia chemisorbed on a cationic and a neutral Ga_5As_5 cluster respectively. The circle represent Ga sites and the squares As sites. Only the sites that provide the strongest bond with NH_3 are included.

A few interesting points can be raised from inspecting this plot. First, we can see that the sites with larger charge transfer consistently have larger binding energies. A segregation of cluster sites based on their electronegativity is apparent. Second, we see that the correlation is not entirely linear. The increasing trend saturates at some ΔQ values, for both the cationic and the neutral bare clusters. This is evidence that the charges moved to the cluster from NH_3 can eventually saturate the cluster and therefore limit its reactivity. The finding of a cluster charge dependent charge saturation makes it interesting to also investigate the interaction between an ammonia molecule and a negatively charged cluster.
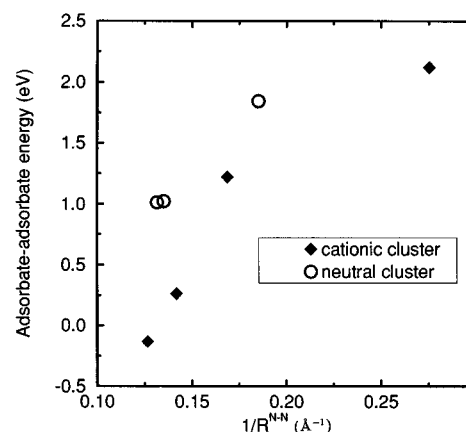
To extend our discussion to include anionic clusters, we performed calculations on NH_3 interacting with a $Ga_5As_5^-$ cluster ion over the site Ga-10, using a larger basis to account for the more diffuse charge distribution on the negatively charged cluster. A bound state was found for the anionic cluster complex $Ga_5As_5NH_3^-$. However, the total energy of this state is 8 eV higher than the energy of the dissociation products $Ga_5As_5^-$ and a free NH_3 molecule. The high adsorption barrier can effectively prevent the negatively charged bare cluster from reacting with the ammonia molecules as was observed in experiment. We have thus shown that by ionizing the cluster to the lowest anionic state -1, the cluster can be passivated.

B. Adsorbate–adsorbate interaction

To discuss the effects of inter-adsorbate interaction qualitatively we plot in Fig. 4 the adsorbate–adsorbate interaction energy E_{ad-ad} (defined in Sec. III) as a function of the inverse of inter-ammonia distance R_{N-N}. For both neutral and cationic clusters, E_{ad-ad} is large and repulsive for small R_{N-N}. At large separations, E_{ad-ad} remains positive for a neutral cluster but becomes negative, indicating an attractive interaction, for a positively charged cluster.

The nearly linear variation of E_{ad-ad} with $1/R^{N-N}$ indicates that the adsorbates are interacting with each other like charged particles. At small distances, one expects high steric repulsion between ammonia molecules to be the dominant interaction. At relatively large inter-adsorbate distances ($R_{N-N} \gtrsim 7.0$ Å), the steric repulsion is effectively screened out and the adsorbates interact more directly with the cluster. Therefore, at large ammonia–ammonia separations, the significant factor that will limit the chemisorption is the cluster charge.

V. CONCLUSIONS

By studying the interaction of ammonia molecules with a small gallium arsenide cluster ionized to a cationic charge state $+1$, we have demonstrated the dependence of reactivity

on the cluster's charge state. The gallium arsenide clusters can be activated to react with ammonia molecules by ionizing to a cationic charge state and passivated by ionizing to a negative charge state. The calculations also show that multiple ammonia adsorption is strongly favored on the cationic bare cluster. On this system, the ammonia–ammonia interaction can be attractive.

As in the case of ammonia reacting with different sites on a neutral cluster, the results show a strong correlation between ammonia-cluster binding energy and charge transfer from ammonia to a cationic cluster. We have also demonstrated that one of the internal vibrational modes of the chemisorbed ammonia molecule can be very sensitive to the charge state of the cluster.

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