

Adsorption of ammonia on the Al(111) surface: Theoretical studies

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Model calculations on $\text{Al}_{10}\text{NH}_3$ clusters are used to study the chemisorptive interaction of NH_3 with the Al(111) surface. It is assumed that the ammonia molecule stabilizes on the surface with the N center pointing towards the metal and two different surface sites, on top and threefold hollow, are examined. The energetics of the NH_3 -Al interaction are described in detail. The interaction between the frozen charge distributions of the NH_3 and Al_{10} subunits is repulsive for both sites. However, the repulsion is much larger in the threefold hollow site than in the on-top site. The charge rearrangements that are important for the bonding are the intra-unit polarizations of both NH_3 and Al_{10} in the presence of the other (frozen) subunit. These polarizations make attractive electrostatic contributions. They are larger for the on-top site. As a consequence, the NH_3 -Al interaction leads to a 0.8 eV binding in the on-top site whereas the threefold hollow site is repulsive. In both sites, NH_3 to metal a_1 donation is of minor importance. This is in contrast to the bonding scheme suggested from photoemission on NH_3 /metal systems. A large differential shift of the $3a_1$ ionization potential (IP) for adsorbed NH_3 has been interpreted as major involvement of the NH_3 $3a_1$ orbital in the NH_3 -metal bond. We show that the differential $3a_1$ IP shift is not related to its involvement in the bonding.

I. INTRODUCTION

An understanding of the chemisorptive interaction between ammonia and metal surfaces is important as a first step in the microscopic description of NH_3 reactions, in particular decomposition and synthesis, in the presence of catalysts. In technologically important processes involving ammonia reactions,¹ catalysts containing both simple-metal and transition-metal complexes are used. Therefore it is necessary to understand the interaction of NH_3 with surfaces of both types of metals. In particular, one should be able to describe differences and similarities in the chemisorptive behavior between the two groups.

The bonding between ammonia and transition-metal surfaces [Ni (Refs. 2 and 3), Fe (Ref. 4), and Cu (Ref. 6)] has been examined previously on the basis of cluster models. Extended analyses⁵⁻⁷ for Al_4NH_3 and Cu_5NH_3 cluster using the constrained space orbital variation (CSOV) method⁵ show that the metal- NH_3 bonding is characterized as mostly electrostatic and arising mainly as a consequence of the large NH_3 dipole moment. The formation of dative covalent chemical bonds involving the NH_3 lone pair $3a_1$ orbital is of minor importance. However, note that the metals to which we have applied the CSOV analysis to reach this conclusion about the NH_3 donation do not have open d shells. For the metal-carbonyl interaction, transition metals with open d shells have been investigated.^{8,9} When the d shell is open, the CO-to-metal σ donation is more important for the bonding although it still does not make the major contribution. For the bonding of NH_3 with open- d -shell transition metals, the $3a_1$ donation to $d\sigma$ may have some importance.

The interaction of NH_3 with the (simple metal) Al(111) surface, represented by an Al_4NH_3 cluster,⁵ is quite similar in character to the NH_3 -Cu bonding.⁶ However, the quantitative results differ between the two systems due to the fact that Al, being an sp metal, has a larger number of sp valence electrons compared to Cu.

In the present paper we extend our study of the chemisorptive NH_3 -Al interaction to a larger substrate cluster, $\text{Al}_{10}\text{NH}_3$, modeling the Al(111) surface. Here it is possible to study different adsorption sites of ammonia which should give further insight into the details of the interaction. *Ab initio* Hartree-Fock-LCAO calculations for $\text{Al}_{10}\text{NH}_3$ show that NH_3 stabilizes on the Al(111) surface in an on-top site with the nitrogen end pointing towards the metal. The adsorbate is bound by 0.8 eV at an equilibrium separation (between the N center and the topmost surface Al atom) of $d=4.05$ bohr. In contrast, NH_3 does not bind in the threefold hollow site of the Al(111) surface; at a surface-N separation $d=4.05$ bohr, the NH_3 -Al interaction is repulsive by 1.3 eV. The difference between the two sites can be understood on the basis of a CSOV analysis. First, the frozen orbital (FO) repulsion between Al_{10} and NH_3 is much larger in the threefold hollow than in the on-top site. Second, the energy gain by the intra-unit polarization of the Al_{10} in the presence of the fixed charge distribution of free NH_3 is smaller in the threefold hollow site compared with the on-top site. The a_1 charge donation from NH_3 to Al_{10} makes a smaller contribution to the interaction than the intra-unit charge rearrangements for both sites.

The effect of the adsorbate-substrate interaction on the adsorbate derived ionization potentials (IP) in $\text{Al}_{10}\text{NH}_3$ is

studied on the basis of a frozen orbital or Koopmans' approximation. With these IP's, we consider only initial-state effects and neglect effects due to final-state relaxation.¹⁰ We include results from calculations on smaller clusters, Al_1NH_3 and Al_4NH_3 , in order to show the influence of cluster size on the IP's. It is found that the NH_3 -derived cluster IP's are all shifted to larger values with respect to the free molecule. For a given Al_nNH_3 cluster, this shift is constant among the NH_3 -type orbitals except for the lone-pair orbital $3a_1$ where it is much larger. This differential shift of the $3a_1$ IP is observed in photoemission experiments of ammonia adsorbed on transition-metal surfaces^{11,12} and has been interpreted as a bonding shift arising from a dominant participation of the NH_3 $3a_1$ orbital in the NH_3 -metal bond. However, our CSOV analysis on the Al_nNH_3 clusters shows that the mixing of the NH_3 $3a_1$ with unoccupied Al valence sp orbitals does not contribute significantly to the energetics of the Al-NH₃ bond. There is strong mixing between the fully occupied orbitals of the two subunits, Al_n and NH_3 , but this leads to bonding and antibonding mixtures which do not contribute to the Al_n -NH₃ bond strength.

In Sec. II we describe briefly the computational details, and in Sec. III we discuss our results. In Sec. IIIA we consider the Al-NH₃ bonding in detail on the basis of a CSOV analysis, while the consequences of the bonding for the cluster IP's are considered in Sec. IIIB. Section IV summarizes our conclusions, stressing those features that are pertinent for comparison with adsorption experiments.

II. COMPUTATIONAL DETAILS

A. Geometries and basis sets

Two different adsorption sites on the Al(111) surface was modeled with an Al_{10} cluster. For adsorption in the on-top site directly above an Al surface atom, the cluster consists of the central surface atom, its six nearest neighbors in the first layer and its three neighbors in the second layer, yielding $\text{Al}_{10}(7,3)$; see Fig. 1(a). For adsorption in the threefold hollow site this cluster is inverted yielding $\text{Al}_{10}(3,7)$. Thus, the three first layer Al atoms which are nearest the NH_3 and their nearest neighbors in the second layer are included; see Fig. 1(b). The Al-Al nearest neighbor distance of the bulk, $a_0=2.86$ Å, is used. The adsorption of NH_3 in the on-top and threefold sites was assumed to occur with the threefold symmetry axis of NH_3 being perpendicular to the substrate surface and with N pointing towards the surface. The geometry of the NH_3 unit of $\text{Al}_{10}\text{NH}_3$, $d(\text{N-H})=1.00$ Å and $\angle \text{H-N-H}=107.2^\circ$, is taken from an optimization on the free molecule, which yields results close to experiment.¹³ We also performed a limited re-optimization of the NH_3 geometry for the AlNH_3 cluster and found $d(\text{N-H})=1.00$ Å and $\angle \text{H-N-H}=108.1^\circ$. These are not significantly different from the free-molecule values, indicating that the Al-NH₃ interaction does not lead to major changes in the NH_3 geometry. This is consistent with the dominantly electrostatic, as opposed to covalent, character of the bonding which is described in the following section.

Self-consistent field (SCF) analytic basis set Hartree-Fock calculations for various electronic states of $\text{Al}_{10}\text{NH}_3$

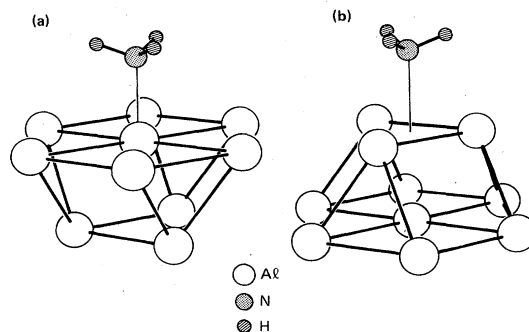


FIG. 1. Geometries of the $\text{Al}_{10}\text{NH}_3$ clusters used in this study: (a) shows $\text{Al}_{10}(7,3)\text{NH}_3$ modeling the on-top adsorption site; (b) shows $\text{Al}_{10}(3,7)\text{NH}_3$ modeling the threefold hollow adsorption site on the Al(111) surface.

and of the free- NH_3 molecule were carried out using the *ALCHEMY-MOLECULE*¹⁴ program system with suitable extensions to handle pseudopotentials.¹⁴ The contracted Gaussian basis set for N was taken from van Duijneveldt's atom optimization,¹⁵ where a $(9s,5p)$ basis was contracted to $(4s,3p)$. The H basis set consisted of $(4s,1p)$ contracted to $(2s,1p)$.¹⁶ The basis set of the central Al atom of the 7 atom layer was an all electron basis consisting of $(10s,6p)$ contracted to $(4s,3p)$. The contraction is single zeta for the Ne core and double zeta for the $3s$ and $3p$ valence regions; for further details see Ref. 17. In the other nine Al atoms the Ne core was described by a pseudopotential¹⁸ while the valence basis set was $(4s,3p)$ contracted to $(2s,1p)$.¹⁸ The use of pseudopotentials in Al_n -ligand clusters has been tested extensively and found to introduce only very small errors in the Al-ligand bonding^{18,19} compared to all electron calculations. The symmetry of the present clusters is described by the C_{3v} point group, and the cluster wave functions and orbitals are labeled according to the irreducible representations of C_{3v} .

B. Constrained space orbital variation

Our interpretation of the Al-NH₃ bonding is largely based on the constrained space orbital variation (CSOV) analysis.⁵ In this analysis, the orbitals arising from one of the units, Al_{10} or NH_3 , are held fixed and those from the other unit, denoted X , are allowed to vary. The variational space of these orbitals, denoted Y , may be constrained so that only a subset of the full space is used. Such a CSOV step is described as $V(X;Y)$.

The CSOV analysis allows the division of the interaction into charge rearrangement within a unit, intra-unit polarization, and charge donation between units, inter-unit charge transfer. The intra-unit polarization can, in general, have two effects: (1) to reduce the overlap repulsion between the ligand and metal,^{5,6,17} and (2) to enhance the electrostatic interaction between metal and ligand units.^{5,6} The inter-unit charge transfer includes both metal-to-ligand and ligand-to-metal donations. With the CSOV analysis it becomes possible to determine the energetic importance of the two donations separately.^{5,6,20} The CSOV analysis starts from the interaction of the frozen orbitals of the separate units followed by six dif-

ferent CSOV steps.

Step 1: $V(\text{Al}_{10}; \text{Al}_{10})$. Here the NH_3 orbitals are fixed at their free molecule character and polarization of the Al_{10} orbitals in the Al atom-centered basis set is allowed.

Step 2: $V(\text{Al}_{10}; \text{Al}_{10}, \text{full } a_1 \text{ basis})$. The NH_3 virtual orbitals of a_1 symmetry are included in the Al_{10} variational space and Al_{10} -to- NH_3 a_1 donation is possible.

Step 3: $V(\text{Al}_{10}; \text{full basis})$. The NH_3 virtual orbitals of both a_1 and e symmetry are included in the Al_{10} variational space. Now Al_{10} -to- NH_3 e donation is possible.

Step 4: $V'(\text{NH}_3; \text{NH}_3)$. Here the Al_{10} orbitals of step (3), i.e., those including polarization and donation to NH_3 , are fixed, and polarization of the NH_3 orbitals in their basis set is allowed. This variation and the following ones are denoted by V' to indicate that the frozen Al_{10} subunit is taken from CSOV step (3) rather than as free Al_{10} . (The notation V' was not used in earlier work⁵⁻⁷ although the same variational procedure was also used there. The prime has been added in order to stress the fact that polarized metal orbitals, rather than free metal ones, were used and frozen in this CSOV step.)

Step 5: $V'(\text{NH}_3; \text{NH}_3, \text{full } a_1 \text{ basis})$. The Al_{10} virtual orbitals of a_1 symmetry are included in the NH_3 variational space and NH_3 -to- Al_{10} a_1 donation becomes possible.

Step 6: $V'(\text{NH}_3; \text{full basis})$. All Al_{10} virtual orbitals are included in the variational space. Now NH_3 -to- Al_{10} e donation is allowed.

The results of step 6 are compared to an unconstrained SCF calculation on the $\text{Al}_{10}\text{NH}_3$ cluster. If the two results are close to each other the CSOV analysis includes all the important bonding effects. This near agreement has been found to occur in a number of metal-closed-shell ligand systems^{5,6} and is also the case for the present systems.

III. RESULTS AND DISCUSSION

A. Adsorbate-substrate bonding

For the bare substrate cluster $\text{Al}_{10}(7,3)$, several electronic states have been considered. The three lowest energy states are

$${}^3A_2(8a_1^2 6e^2 1a_2^2), \quad E_{\text{tot}} = -259.0378 \text{ hartree},$$

$${}^3E(9a_1^1 6e^1 1a_2^2), \quad E_{\text{tot}} = -259.0375 \text{ hartree},$$

$${}^1A_1(9a_1^2 5e^4 1a_2^2), \quad E_{\text{tot}} = -259.0235 \text{ hartree}.$$

The two lowest states, 3A_2 and 3E , are different in energy by only 0.008 eV. Therefore, on the basis of a total energy criterion it is impossible to decide which electronic state one should use to represent the interaction of NH_3 with Al(111). However, test calculations for the on-top site with the $\text{Al}_{10}(7,3)\text{NH}_3$ cluster show a moderate bonding starting from the $\text{Al}_{10} {}^3A_2$ state while the $\text{Al}_{10}\text{-NH}_3$ interaction is repulsive for the 3E state; see Ref. 17 for an explanation of this difference in the similar case of Al_4 . Therefore, we restrict ourselves to a discussion of the 3A_2 cluster results. The ground state configuration of free NH_3 is ${}^1A_1(3a_1^2 1e^4)$. It is expected that the $\text{Al}_{10}\text{NH}_3$

cluster orbitals have much of the character of either subunit, Al_{10} or NH_3 . Therefore, the electronic configuration of $\text{Al}_{10}\text{NH}_3$ is formed by combining the orbitals of the $\text{NH}_3 {}^1A_1$ ground state with those of the $\text{Al}_{10} {}^3A_2$ state. This yields a $11a_1^2 7e^2 1a_2^2$ configuration for both the on-top site, $\text{Al}_{10}(7,3)\text{NH}_3$, and the threefold hollow site, $\text{Al}_{10}(3,7)\text{NH}_3$, clusters. The total symmetry of these clusters is 3A_2 ; the same as for bare Al_{10} .

Figure 2 shows the binding energies E_B of the $\text{Al}_{10}\text{NH}_3$ clusters as a function of the $\text{Al}_{10}\text{-NH}_3$ separation d . Here d is defined as the distance between the nitrogen center of NH_3 and the plane through the nuclei of the first-layer Al atoms. The binding energy E_B is calculated from total energy differences

$$E_B(d) = E_{\text{tot}}(\text{Al}_{10}\text{NH}_3, d) - E_{\text{tot}}(\text{Al}_{10}) - E_{\text{tot}}(\text{NH}_3). \quad (1)$$

It is obvious from Fig. 2 that the NH_3 molecule stabilizes in the on-top side of the Al_{10} cluster. The equilibrium separation is $d_{\text{min}} = 4.05$ bohr with a binding energy of 0.80 eV. The excitation energy $\hbar\omega$ for vibrations of the rigid NH_3 molecule perpendicular to the surface can be calculated in the harmonic approximation from the curvature of the $E_B(d)$ curve at its minimum. Here, a value $\hbar\omega = 40.2$ meV is obtained assuming a rigid Al_{10} substrate cluster of infinite mass. The interaction curve for NH_3 approaching the Al_{10} cluster in a threefold hollow site is always repulsive with respect to the infinite $\text{Al}_{10}\text{-NH}_3$ separation as can be seen from Fig. 2. At a separation $d = 4.05$ bohr (where the on-top site binding is largest) the repulsion energy is 1.3 eV. Thus, the ammonia molecule interacts quite differently with the Al_{10} substrate in the two surface sites. In order to understand this different behavior we have carried out a CSOV analysis of the Al- NH_3 interaction for both $\text{Al}_{10}(7,3)\text{NH}_3$ and $\text{Al}_{10}(3,7)\text{NH}_3$. The analyses for the two sites were performed at similar NH_3 -surface distances; $d = 4.05$ bohr for the on-top site, $\text{Al}_{10}(7,3)\text{NH}_3$, and $d = 4.082$ bohr for the threefold site, $\text{Al}_{10}(3,7)\text{NH}_3$.

Table I lists the results for the interaction energies E_{int} of the various steps in our CSOV analysis. Here E_{int} is defined by the total energy difference

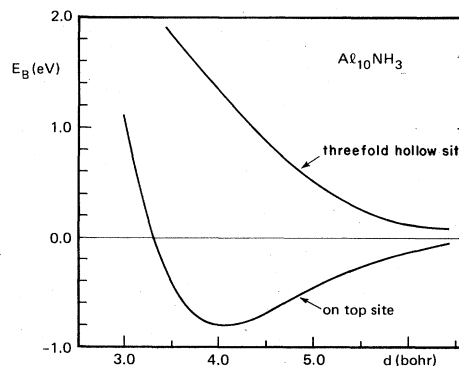


FIG. 2. Binding curves of the $\text{Al}_{10}(7,3)\text{NH}_3$ (on-top site) and the $\text{Al}_{10}(3,7)\text{NH}_3$ (threefold hollow site) clusters. For a definition of the binding energy E_B and the $\text{Al}_{10}\text{-NH}_3$ separation d , see text.

$$E_{\text{int}}(\text{step } k) = E_{\text{tot}}(\text{Al}_{10}) + E_{\text{tot}}(\text{NH}_3) - E_{\text{tot}}(\text{Al}_{10}\text{NH}_3, \text{step } k). \quad (2)$$

Thus E_{int} is positive (negative) if the CSOV step leads to a cluster state which is bound (unbound) with respect to the separate components. [Note, $E_{\text{int}} = -E_B$ as defined in Eq. (1).]

We will first concentrate on the results for the on-top site cluster. In the zeroth step of our analysis, denoted frozen orbital (FO), the cluster wave function is constructed from orbitals of the separate subunits, NH_3 and Al_{10} , which are orthonormalized for the finite separation d . The corresponding total energy contains all electrostatic effects including the exchange between the subunits leading to an interaction energy $E_{\text{int}} = -1.28$ eV. If we neglect the fact that the Al_{10} and NH_3 charge distributions interpenetrate, this FO E_{int} can be represented by an expansion in terms of the multipole moments of the separate subunits. Since the subunits are neutral, the lowest contribution to E_{int} comes from the dipole-dipole interactions. This contribution is, however, negligible since the dipole moment of Al_{10} ($\mu = 0.03$ a.u. from the present calculations) is quite small. However, the interpenetration between the NH_3 and Al_{10} charge distributions reduces the screening of the nucleus of the adsorption-site Al atom for the NH_3 dipole moment. This leads to an effective charge-dipole interaction.^{5,6,21} The dipole moment of NH_3 , N^-H^+ , is such that this interaction is attractive. However, there is also a repulsion arising from the overlap of the Al_{10} and NH_3 charge distributions; this repulsion has been shown to arise largely from the metal a_1 electrons and the ligand lone pair, $3a_1$ of NH_3 .^{5,6} The balance of the electrostatic effective charge-dipole attraction and the overlap repulsion leads to an overall repulsive $E_{\text{int}}(\text{FO})$.

In the first CSOV step, $V(\text{Al}_{10}; \text{Al}_{10})$, the negative value of E_{int} from the frozen orbital superposition is reduced by 0.98 eV, yielding $E_{\text{int}} = -0.30$ eV (cf. Table I). This is due to a charge rearrangement in the Al_{10} subunit in response to the presence of the rigid NH_3 charge distribution. The reasonably large reduction can be explained by the fact that the sp valence electrons of Al_{10} are rather diffuse and can therefore easily be polarized. This is reflected by the large polarizability α of the Al_{10} subunit; $\alpha = 290$ a.u. from the present SCF calculations. In the second step, $V(\text{Al}_{10}; \text{Al}_{10}, \text{full } a_1)$, charge transfer (donation) from Al_{10} to a_1 -type orbitals of NH_3 is allowed and leads to a further reduction of E_{int} by 0.19 eV, yielding $E_{\text{int}} = -0.11$ eV. The third step, $V(\text{Al}_{10}; \text{full basis})$, includes, in addition, donation from Al_{10} to e -type NH_3 orbitals resulting in a 0.31 eV increase in E_{int} by which the $\text{Al}_{10}(7,3)\text{NH}_3$ cluster becomes stable ($E_{\text{int}} = +0.20$ eV, see Table I). A comparison of the second and third CSOV steps suggests that the metal-to- NH_3 e donation is energetically much more important than a_1 donation. This is, however, an artifact of the calculation. As a consequence of the change in the variational space between the CSOV steps, the error in the wave-function representation by a limited basis set^{5,6} varies and this affects the interaction energies. This basis set superposition error^{5,22} has been estimated with calculations for each subunit, Al_{10} and NH_3 ,

TABLE I. Results of the CSOV analysis for $\text{Al}_{10}(7,3)\text{NH}_3$ (on top) with $d = 4.05$ bohr and for $\text{Al}_{10}(3,7)\text{NH}_3$ (threefold hollow) with $d = 4.082$ bohr. The interaction energies E_{int} are given in eV and are defined in the text.

CSOV step	E_{int}	
	On top	Threefold hollow
Step 0, frozen orbital	-1.28	-2.41
Step 1, $V(\text{Al}_{10}; \text{Al}_{10})$	-0.30	-1.95
Step 2, $V(\text{Al}_{10}; \text{Al}_{10}, \text{full } a_1)$	-0.11	-1.66
Step 3, $V(\text{Al}_{10}; \text{full basis})$	+0.20	-1.60
Step 4, $V'(\text{NH}_3; \text{NH}_3)$	+0.46	-1.49
Step 5, $V'(\text{NH}_3; \text{NH}_3, \text{full } a_1)$	+0.74	-1.36
Step 6, $V'(\text{NH}_3; \text{full basis})$	+0.75	-1.32
Step 7, SCF	+0.80	-1.27

for the geometries of both $\text{Al}_{10}(7,3)\text{NH}_3$ and $\text{Al}_{10}(3,7)\text{NH}_3$; the estimates are made following the description in Ref. 5. These error estimates give a reliable indication of the extent to which the inter-unit CSOV steps, steps 2, 3, 5, and 6, give too large values for the charge transfer contributions to E_{int} . Except for one case, the basis set superposition errors are quite small, ≤ 0.01 eV. This case is the improvement of the description of the Al_{10} cluster by the NH_3 virtual orbitals of e symmetry for the $\text{Al}_{10}(7,3)\text{NH}_3$ geometry. It affects the Al-to- NH_3 e charge transfer (CSOV step 3); the superposition error is 0.12 eV. Thus, an appropriate value for the gain in E_{int} due to Al-to- NH_3 e donation is 0.2 eV rather than the directly calculated 0.3 eV. The energetic importance of both of these donations from Al, a_1 , and e , are similar (although somewhat larger) than the values obtained previously for $\text{Al}_4(1,3)\text{NH}_3$.⁵ The Al e donation for either $\text{Al}_4(1,3)\text{NH}_3$ or $\text{Al}_{10}(7,3)\text{NH}_3$ is much smaller than that for Al to CO which, for $\text{Al}_4(1,3)\text{CO}$, is 0.76 eV.⁵ This is to be expected since CO is a good π acceptor while NH_3 is not; the first unoccupied e level of NH_3 is Rydberg-type.¹³ For the on-top site, the most important Al charge rearrangement is the intra-unit polarization, CSOV step 1. This polarization reduces the FO repulsion by reducing the overlap between the orbitals of the subunits; the polarized metal charge may also enhance the attractive effective dipole-dipole interaction⁵ between Al_{10} and NH_3 . The Al-to- NH_3 charge donation contribution to E_{int} , CSOV steps 2 and 3, is much smaller than the 1.0 eV contribution from the Al intra-unit polarization.

The fourth step of the analysis, $V'(\text{NH}_3; \text{NH}_3)$, describes the polarization of the NH_3 subunit in the presence of the (polarized) Al_{10} subunit. The change in E_{int} is 0.26 eV, leading to a further increased stability of $\text{Al}_{10}(7,3)\text{NH}_3$ (see Table I). It involves a small additional polarization of NH_3 charge towards Al_{10} . In the fifth step, $V'(\text{NH}_3; \text{NH}_3, \text{full } a_1)$, where a_1 donation from NH_3 to Al_{10} is allowed, the interaction energy increases by 0.28 eV. This is the largest of all contributions due to inter-unit donation in $\text{Al}_{10}\text{NH}_3$ and reflects the (smaller) importance of the involvement of the NH_3 $3a_1$ lone pair orbital in the NH_3 - Al_{10} interaction. From a naive molecular orbital (MO) picture, one would expect the NH_3 $3a_1$ orbital to participate dominantly in a metal- NH_3 bond of the present geometry. This bonding scheme has also been proposed

on the basis of photoemission experiments on NH_3 /metal adsorbate systems^{11,12} as will be discussed below. Our analysis shows, however, that the NH_3 $3a_1$ involvement in the NH_3 -Al interaction (resulting in a noticeable mixing or hybridization with occupied Al_{10} sp orbitals) is energetically much less important than the sum of the intra-unit polarizations (1.24 eV gain from steps 1 and 4). This result seems to be general and is found in similar analyses of the NH_3 -metal bonding in $\text{Al}_4(1,3)\text{NH}_3$ (Ref. 5) and in $\text{Cu}_5(1,4)\text{NH}_3$ (Ref. 6).

In the sixth step, $V'(\text{NH}_3; \text{full basis})$, donation from NH_3 to Al_{10} e -type orbitals is included in addition. As expected, this leads to a very small change in E_{int} , 0.01 eV, which is explained by the fact that the highest occupied e orbital, $1e$, in NH_3 (responsible for part of the $\text{N}-\text{H}_3$ bond) cannot donate charge into the metal without substantially modifying (reducing) the intra-unit bonding in NH_3 . As a seventh step, denoted SCF, Table I contains the E_{int} value of the fully self-consistent calculation for $\text{Al}_{10}(7,3)\text{NH}_3$. This value is quite close to the result of the last CSOV step (step 6) and shows that the sequence of CSOV steps described here includes all the important features of the NH_3 -Al interaction.

The results of the CSOV analysis for the threefold hollow site $\text{Al}_{10}(3,7)\text{NH}_3$ are given in the second column of Table I. The FO superposition (step 0) yields an interaction energy $E_{\text{int}} = -2.41$ eV which is more negative by 1.1 eV than the value for the on-top site cluster. Obviously, the electrostatic repulsion between the interpenetrating charge distributions of NH_3 and Al_{10} is larger in the hollow than in the on-top site. The gain in E_{int} by polarization of Al_{10} in the presence of the rigid NH_3 (CSOV step 1) is 0.46 eV in the hollow site, about half on the on-top site value. Charge donation from Al_{10} to NH_3 a_1 -type orbitals, accounted for in the second CSOV step, results in an E_{int} reduction of 0.29 eV for the hollow site. The Al_{10} -to- NH_3 e donation (step 3) is negligible (0.06 eV) in the threefold site. Polarization of the NH_3 in the presence of the (polarized) Al_{10} (cf. step 4) leads to a 0.11-eV reduction of E_{int} in the hollow site which is roughly half the value of the on-top site. Charge donation from the NH_3 to Al_{10} a_1 orbitals, allowed for in the fifth CSOV step, contributes 0.13 eV to E_{int} in the hollow site. This value is smaller than the result for the on-top site which indicates a reduced involvement of the NH_3 $3a_1$ orbital in the NH_3 -Al interaction at the hollow site. Donation from NH_3 to Al_{10} e orbitals (see CSOV step 6) has a negligible effect (0.04 eV) on E_{int} for the hollow site; the reasons are the same as given for the on-top site. From Table I, the interaction energy E_{int} of the SCF calculation for $\text{Al}_{10}(3,7)\text{NH}_3$ is very similar to the value of the sixth CSOV step.

Overall, both the intra-unit polarizations and the inter-unit charge transfers make reasonably small contributions to the Al- NH_3 interaction at the threefold site; their sum is one-half of that for the on-top site. This is not sufficient to overcome the large, 2.4 eV, FO repulsion and the total SCF interaction is repulsive by 1.3 eV. We note that the environment of Al atoms nearest NH_3 is different for the threefold site cluster than for the on-top site cluster. The on-top adsorption-site Al atom has its six surface

layer nearest neighbors as well as three second layer nearest neighbors; the threefold adsorption-site Al atoms have only second layer neighbors and none in the surface layer. It is possible that there could be greater lateral polarization of the charge of the adsorption-site Al atoms for the on-top site than for the threefold if the surface-layer atoms are significantly involved in this lateral polarization. Thus, our calculated E_{int} for the threefold hollow site could be too small at the $V(\text{Al}_n; \text{Al}_n)$, intra-unit Al_n polarization, CSOV step with the $\text{Al}_{10}\text{NH}_3$ cluster. For the on-top site, a measure of the magnitude of this lateral polarization to surface layer atoms can be made by comparing results for the one surface layer atom $\text{Al}_4(1,3)\text{NH}_3$ cluster⁵ with those for $\text{Al}_{10}(7,3)\text{NH}_3$. The change in E_{int} at the $V(\text{Al}_n; \text{Al}_n)$ CSOV step is quite similar for these two clusters. This indicates that the first layer neighbors of the adsorption site atom do not make a major contribution to the lateral polarization of the Al atoms in the case of interaction with NH_3 . It suggests that the threefold site results would not change significantly if these first layer neighbors were included in, for example, an $\text{Al}_{19}(12,7)\text{NH}_3$ cluster.

B. Ionization potential changes due to the adsorbate-substrate interaction

In this section we examine the adsorption-induced changes in the SCF orbital energies ϵ of the clusters. These changes are obtained from differences in ϵ between the separate Al_n and NH_3 and the combined Al_nNH_3 clusters. Our discussion will be based on results for the on-top site $\text{Al}_{10}(7,3)\text{NH}_3$ and the threefold hollow site $\text{Al}_{10}(3,7)\text{NH}_3$ clusters. We also include results for the smaller on-top site clusters, $\text{Al}_4(1,3)\text{NH}_3$ and $\text{Al}_1(1)\text{NH}_3$, in order to show the cluster-size dependence of the effects.

The orbital energies ϵ are closely related to the FO ionization potentials (IP's). For Al_nNH_3 and both $\text{Al}_{10}\text{NH}_3$ clusters, the initial state is 3A_2 . The final state for ionization from one of the closed shells is either a doublet or a quartet spin state. As a consequence the closed shell ϵ 's are the multiplicity weighted averages^{10,23} of the different final state FO IP's, I_i^{FO} ,

$$\epsilon_i = -\frac{1}{6} [2I_i^{\text{FO}}(\text{doublet}) + 4I_i^{\text{FO}}(\text{quartet})] . \quad (3)$$

For ionization from the open e shell there is only a doublet ionic state and for this shell one obtains

$$\epsilon_i = -I_i^{\text{FO}} . \quad (4)$$

For the 2E initial state of Al_1NH_3 , the ϵ_i 's are also the weighted averages of the spatial multiplets arising from ionization out of the i th molecular orbital.^{10,23} The situation is slightly more complicated since for ionization from the closed shells of e symmetry spatial coupling to multiplets of A_1 , A_2 , and E total symmetry must be considered.

In cluster studies of CO chemisorption on Ni surfaces¹⁰ it was found that this multiplet splitting, which is a cluster artifact and does not represent the actual surface situation, is rather small. Therefore, we will use the average FO IP's given by ϵ_i . The IP's observed in photoemission

spectra (PES) contain final state relaxation effects not included in the FO approximation. This can lead to large differences between the FO IP and the observed value. However, initial state effects may account for a very large part of the change in the IP between the separated and the combined substrate and adsorbate systems. This has, indeed, been found to be the case in previous studies^{4,10} of the interaction of CO and NH₃ with Ni. Assuming that the relative changes in the IP's are also largely initial state effects for the Al-NH₃ interaction, we will use the changes in the ϵ_i to study the adsorption induced IP changes.

The change in orbital energy $\Delta\epsilon_i$ of the cluster orbitals which have dominant NH₃ character is defined as

$$\Delta\epsilon_i = -\epsilon_i(\text{Al}_n\text{NH}_3) + \epsilon_i(\text{NH}_3). \quad (5)$$

Here, positive (negative) $\Delta\epsilon_i$ indicates that the IP of an electron in the i th orbital is larger (smaller) in the Al_{*n*}NH₃ cluster than in the separate unit. For the on-top site adsorption we report $\Delta\epsilon_i$ values using the Al-N equilibrium distance d found for the appropriate Al_{*n*}NH₃ cluster, while the results of the threefold hollow site cluster Al₁₀(3,7)NH₃ are for $d=4.082$ bohr; this is the same distance used in the bonding analysis of the preceding section.

The $\Delta\epsilon_i$ values for the dominantly NH₃-derived cluster orbitals are given in Table II. For all clusters, the $|\epsilon_i|$ are shifted to larger values by the Al-NH₃ interaction. The cluster $1\tilde{a}_1$, $2\tilde{a}_1$, and $1\tilde{e}$ orbitals (the tilde indicates that these orbitals are dominantly NH₃-type) are essentially unchanged from free NH₃; they do not mix significantly with Al_{*n*}. This is confirmed by the Mulliken population analyses of these orbitals where Al_{*n*} admixtures of less than 0.03 electrons are found. For any particular cluster, the IP shifts of the orbitals are almost the same. These shifts can thus be described as environmental shifts due to the Al_{*n*} potential seen by NH₃. There may also be contributions to the IP shifts from the small interunit charge donations (cf. Sec. III A). The approximately constant shifts are different for the different clusters because the Al_{*n*} potential seen by the NH₃ changes with the number and geometry of the Al atoms in Al_{*n*}.

The results are quite different for the NH₃ $3a_1$ orbital. This orbital is substantially modified by the interaction with Al_{*n*} and mixes considerably with one or more of the Al_{*n*} a_1 orbitals. Table II lists the $\Delta\epsilon_i$ value for the Al_{*n*}NH₃ orbital, $3\tilde{a}_1$, which has the largest amount of

NH₃ character. The NH₃ population of this orbital is also given. Although the specific value of this population is affected by artifacts of the population analysis,¹⁷ it can provide a useful qualitative guide to the extent to which the $3\tilde{a}_1$ orbital hybridizes or mixes with Al_{*n*} orbitals. An important result of Table II is that the $3\tilde{a}_1$ shift is considerably larger than for the other NH₃-derived orbitals. This differential shift for $3\tilde{a}_1$ is consistent with PES measurements for NH₃ chemisorbed on the (110) and (111) surfaces of Fe (Ref. 11) and Ni (Ref. 12) crystals. For these systems, there is a shift of the $3\tilde{a}_1$ PES peak toward the $1\tilde{e}$ peak such that the gas-phase $1e-3a_1$ separation is reduced by 0.7–1.5 eV. The $3\tilde{a}_1$ cluster orbital is a bonding combination of the NH₃ $3a_1$ with Al_{*n*} orbitals as shown by the overlap populations. However, the Al_{*n*} contributions to $3\tilde{a}_1$ must come mainly from the *occupied* orbitals of the Al_{*n*} subunit; the CSOV analysis of Sec. III A showed only a relatively small energy gain (cf. CSOV step 5) for NH₃ a_1 donation into unoccupied Al_{*n*} orbitals. As a consequence other, largely Al_{*n*}-type, occupied orbitals must admix NH₃ $3a_1$ -type contributions in an antibonding fashion in order to maintain orthogonality among the occupied orbitals. Mixing of fully occupied, closed shells can lead to changes in the orbital energies; the well-known view is that the orbital energies of the bonding combinations become more negative while those of the antibonding combinations become less negative. The view is consistent with the energy level diagram shown in Fig. 3. Here, we have compared the ϵ_i 's for the a_1 symmetry valence orbitals of the on-top site Al₁₀(7,3)NH₃ cluster with those of the separate subunits, Al₁₀ and NH₃. The level of the Al₁₀NH₃ orbital with dominant $3\tilde{a}_1$ character is connected with the NH₃ level while those of the Al₁₀-type orbitals in Al₁₀NH₃ are connected to the closest levels of Al₁₀. It is obvious from this picture that the downward shift of the $3\tilde{a}_1$ cluster orbital is accompanied by upward shifts of the other a_1 orbitals. One reason for the upward shifts is the formation of antibonding mixtures of Al₁₀ a_1 orbitals with the NH₃ $3a_1$ orbital. Other reasons can be the changed potential due to the presence of the NH₃ which acts on the Al₁₀ orbitals and, to a minor extent, a shift due to the fact that the small NH₃-to-Al₁₀ a_1 donation leads to a negatively charged Al₁₀ subunit.

The shifts $\Delta\epsilon_i$ of the NH₃-derived orbitals, given in Table II, show the same qualitative behavior for the three different on-top site Al_{*n*}NH₃ clusters and are expected to behave similarly in still larger on-top site clusters. This

TABLE II. Orbital energy difference $\Delta\epsilon_i$ of the NH₃-derived orbitals in AlNH₃ ($d=4.79$ bohr), Al₄(1,3)NH₃ ($d=3.94$ bohr), Al₁₀(7,3)NH₃ ($d=4.05$ bohr), and in Al₁₀(3,7)NH₃ ($d=4.082$ bohr). The $\Delta\epsilon_i$ are defined in the text. The orbital energies ϵ_i of free NH₃ are given for comparison. All energies are in eV. The numbers in parentheses give the NH₃ population of the $3\tilde{a}_1$ cluster orbital; this population is normalized to 2.0, the orbital occupation.

Orbital	$-\epsilon_i(\text{NH}_3)$	AlNH ₃	$\Delta\epsilon_i$		Threefold site Al ₁₀ NH ₃
			On-top site Al ₄ NH ₃	Al ₁₀ NH ₃	
$1\tilde{a}_1(\text{N } 1s)$	422.5383	1.54	3.72	3.28	2.25
$2\tilde{a}_1$	31.2674	1.47	3.67	3.26	2.44
$3\tilde{a}_1$	11.3979	2.61 (1.76)	5.95 (1.60)	4.93 (1.34)	4.27 (1.20)
$1e$	17.1739	1.42	3.51	3.18	2.41

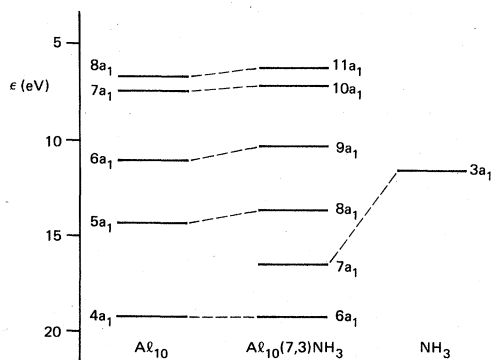


FIG. 3. Energy level diagram of the a_1 valence orbitals in Al_{10} , NH_3 , and $\text{Al}_{10}(7,3)\text{NH}_3$. The connecting lines indicate the correlation between the orbitals of the different components. The energies are given in eV.

should also apply to threefold hollow site Al_nNH_3 clusters of larger size. Thus, the similarity between the $\Delta\epsilon_i$ results of the on-top site and those of the threefold hollow site suggests that PES measurements of NH_3 adsorbed on the Al(111) surface cannot be used by themselves to distinguish between different adsorption sites. This might be true also for other Al surfaces and different metal substrates.

The observed shift of the $3\bar{a}_1$ IP for chemisorbed NH_3 has been ascribed to the involvement of the $3a_1$ orbital in the bonding.^{11,12} Analogous shifts of the CO $5\bar{\sigma}$ orbital for CO/Ni(100) have been interpreted to mean that the metal-ligand bond arises almost entirely from the lone-pair-metal interaction and mixing.²⁴ However, the CSOV results give an unambiguous measure of the importance of the NH_3 a_1 donation for the bonding. For the Al- NH_3 interaction, and for many other systems,^{5,6} it is small but there is a large differential shift of the $3a_1$ IP as shown in Table II and Fig. 3. Obviously, there must be a different origin for this shift. The mixing of the occupied orbitals of the subunits provides a partial explanation; the bonding and antibonding combinations of these orbitals shift in opposite directions as shown in Fig. 3. Of course, mixing of closed shell, occupied orbitals does not contribute to bonding; if it did the rare gas dimers, for example, would be more strongly bound by chemical rather than by weak van der Waals bonding. Other contributions come from the electrostatic potential due to the metal seen by the lone pair of the ligand. The different spatial distribution of this orbital, closer to the metal, leads to a different environmental shift for this orbital. A detailed study of the contributions to the FO IP shift for the CO 5σ lone pair orbital based on a CSOV analysis is given elsewhere.²⁵

IV. CONCLUSIONS

In summary, the CSOV analyses give a clear picture of the NH_3 -Al interaction in the on-top and threefold sites. The attractive part is, for both adsorption sites, mainly due to electrostatic interactions and polarization of the subunits; covalent contributions from an involvement of the NH_3 $3a_1$ orbital in the NH_3 -Al bonding play a minor role. In the on-top site cluster, $\text{Al}_{10}(7,3)\text{NH}_3$, the attractive part of the NH_3 -Al interaction is strong enough to overcome the frozen orbital repulsion between the subunits, resulting in an overall attractive interaction of 0.8 eV at equilibrium. In contrast, the frozen orbital repulsion in the threefold hollow site cluster, $\text{Al}_{10}(3,7)\text{NH}_3$, is larger than the attractive contributions of the NH_3 and Al_{10} charge rearrangements so that NH_3 cannot stabilize in the threefold hollow site. The main differences between the interactions of the two sites can be characterized by two results. First, the frozen orbital repulsion in the threefold hollow site is twice as large as in the on-top site. Second, polarization contributions to the attractive part of the NH_3 -Al interaction are smaller in the threefold hollow than in the on-top site.

Our analysis definitely shows that the so-called bonding shift^{10,24} of the adsorbate lone-pair orbital binding energy is *not* a measure of the contribution of this orbital to the bonding between the metal and NH_3 . It confirms the general validity of similar conclusions obtained in studies of the metal-CO interaction.^{17,25} The differential IP shift of the $3\bar{a}_1$ orbital may, however, be used as a measure of the adsorbate geometry on the surface. If the NH_3 were adsorbed with its H atoms pointing toward the surface, one would expect that the $3\bar{a}_1$ IP would shift by an amount similar to those of $1\bar{e}$ and $2\bar{a}_1$ IP's. We have examined the NH_3 -derived orbital energy shifts as a function of the Al_n - NH_3 separation d . The differential shift on the $3\bar{a}_1$ orbital increases as d decreases and the Al_n - NH_3 coupling increases. This is consistent with earlier results¹⁷ for the $5\bar{\sigma}$ differential shift of adsorbed CO. Thus, the agreement between our computed relative $3\bar{a}_1$ IP shift and the observed PES shifts for chemisorbed NH_3 (Refs. 11 and 12) provide strong support for an NH_3 -adsorption geometry with the N atom pointing toward the metal. The strong similarity between the relative $3\bar{a}_1$ IP shifts for the on-top and threefold sites suggests that the PES measurement may not be able to provide information to differentiate between adsorption at these sites.

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