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## Conclusion

The determination of acidic and basic sites on solid surfaces is a multifaceted problem. Unfortunately, there exists no general theory of the acidity of solids that could serve as a basis for acidity determination. However, we have shown that a standardization

of the acidity of solids is possible. The consistent outlook of the found correlations as well as the wide range of the acid-base characteristics of our samples should allow classification a priori of any other simple oxide in a field of average heat of adsorption corresponding to a determined acidic or basic strength.

## Adsorption of Ammonia on Ni(111)

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The adsorption of ammonia on the [111] surface of Ni is treated by using a many-electron embedding theory to describe the electronic bonding, modeling the lattice as a 28-atom, three-layer cluster. Ab initio valence orbital CI calculations carried out on a local surface region permit an accurate description of bonding at the surface. Molecular  $\text{NH}_3$  adsorbed on the Ni(111) surface at an atop site and a fcc threefold site as well as a bridge site are of comparable stability, with adsorption energies of 19, 18, and 17 kcal/mol and with Ni-N equilibrium distances of 2.12, 2.78, and 2.74 Å, respectively; ammonia bonds to the substrate via the N atom with the H's pointing away from the surface. The equilibrium geometry of  $\text{NH}_3$  is calculated to have a pyramidal configuration with the molecular axis normal to the substrate, but tilting the molecular axis or rotating the molecule about the surface normal requires little energy. Calculated frequencies of the surface- $\text{NH}_3$  group vibration, perpendicular to the Ni(111) surface, are between 460 and 500  $\text{cm}^{-1}$ , and the H-N stretching frequency in  $\text{NH}_3$  on the surface is 3340  $\text{cm}^{-1}$ . The work function decreases by  $\approx 0.6$  eV on  $\text{NH}_3$  adsorption.

## 1. Introduction

Ever since the catalytic synthesis of ammonia was established on iron catalysts,<sup>1,2</sup> there has been interest in the behavior of ammonia on other transition metals. While each substrate-ammonia system is unique, knowing the behavior over a range of substrates may indicate some correlations of metal-ammonia bonding, i.e., the interaction between the metal valence electrons and the lone pair of ammonia. Recently both experimental and theoretical studies of  $\text{NH}_3$  vapor with a number of transition-metal surfaces at high vacuum have been reported.<sup>3-30</sup> It has been

observed that on several close-packed surfaces, such as Ni(111),<sup>3-9</sup> Ir(111),<sup>10</sup> Pt(111),<sup>11-13</sup> Al(111),<sup>14</sup> and Ru(001),<sup>15,16</sup> that  $\text{NH}_3$  is molecularly adsorbed on the clean surfaces and bonded to the substrate via the nitrogen atom with the hydrogens pointed away from the surface. On the other hand,  $\text{NH}_3$  dissociation by electron bombardment has been found on clean Ni(111),<sup>3</sup> Ru(001),<sup>17</sup> and Ni(110),<sup>20</sup> while thermal dissociation below room temperature has been established on clean Fe surfaces.<sup>24-28</sup>

The circular ESDIAD pattern of  $\text{NH}_3$  adsorbed on a clean Ni(111) surface provides evidence that a fractional  $\text{NH}_3$  monolayer adsorbed at 80 K and heated up to 150 K exhibits no preferred azimuthal orientation for the H atoms; the local bonding configurations of  $\text{NH}_3$  have a nearly random distribution.<sup>5,6,9</sup> Studies of the azimuthal ordering for  $\text{NH}_3$  adsorbed on a clean Ni(111) surface using angle-resolved UPS indicated that  $\text{NH}_3$  is freely rotating under the conditions of the experiment.<sup>4</sup> It is generally agreed that the geometry of the adsorbate is roughly pyramidal with the N atom bonding to the metal and the H's pointing away from the surface. The binding site of ammonia adsorbed on the surface has not been fixed unequivocally, primarily because of lack of strong evidence such as LEED data. There is a general agreement, however, that it could be a threefold site (fcc hollow) where the atom in the second layer is missing.<sup>5-7,10,11</sup> A 14 Ni atom cluster calculation on Ni(100) using an ab initio method has shown that  $\text{NH}_3$  is bonded to the nickel surface via

- (1) Ertl, G. *Catal. Rev. Sci. Eng.* **1980**, *21*, 201.
- (2) Grunze, M. In *The Chemical Physics of Surfaces and Heterogeneous Catalysis*; King, D. A., Woodruff D. P., Eds.; Elsevier: Amsterdam, 1982; Vol. 4, p 143.
- (3) Seabury, C. W.; Rhodin, T. N.; Purtell, R. J.; Merrill, R. P. *Surf. Sci.* **1980**, *93*, 117; *J. Vac. Sci. Technol.* **1981**, *18*, 602.
- (4) Kang, W. M.; Li, C. H.; Tong, S. Y.; Seabury, C. W.; Jacobi, K.; Rhodin, T. N.; Purtell, R. J.; Merrill, R. P. *Phys. Rev. Lett.* **1981**, *47*, 931.
- (5) Madey, T. E.; Houston, J. E.; Seabury, C. W.; Rhodin, T. N. *J. Vac. Sci. Technol.* **1981**, *18*, 476.
- (6) Netzer, F. P.; Madey, T. E. *Phys. Rev. Lett.* **1981**, *47*, 928; *Surf. Sci.* **1982**, *119*, 422.
- (7) Fisher, G. B.; Mitchell, G. E. *J. Electron Spectrosc. Relat. Phenom.* **1983**, *29*, 253.
- (8) Bozso, F.; Arias, J. M.; Hanrahan, C. P.; Yates, J. T., Jr.; Metiu, H.; Martin R. M. *Surf. Sci.* **1984**, *138*, 488.
- (9) Dresser, M. J.; Lanzillotto, A.-M.; Alvey, M. D.; Yates, J. T., Jr. *Surf. Sci.* **1987**, *191*, 1. Lanzillotto, A.-M.; Dresser, M. J.; Alvey, M. D.; Yates, J. T., Jr. *Surf. Sci.* **1987**, *191*, 15.
- (10) Purtell, R. J.; Merrill, R. P.; Seabury, C. W.; Rhodin, T. N. *Phys. Rev. Lett.* **1980**, *44*, 1279.
- (11) Sexton, B. A.; Mitchell, G. E. *Surf. Sci.* **1980**, *99*, 523, 539.
- (12) Fisher, G. B. *Chem. Phys. Lett.* **1981**, *79*, 452.
- (13) Gland, J. L.; Killin, E. B. *J. Vac. Sci. Technol.* **1981**, *18*, 604.
- (14) Netzer, F. P.; Madey, T. E. *Chem. Phys. Lett.* **1981**, *88*, 315.
- (15) Madey, T. E.; Yates, J. T., Jr. *Proceedings of the 7th International Vacuum Congress and 3rd International Conference on Solid Surfaces*; R., Dobrozemsky, Ed.; Burger: Vienna, 1977; p 1187.
- (16) Danielson, L. R.; Dresser, M. J.; Donaldson, E. E.; Dickinson, J. T. *Surf. Sci.* **1978**, *71*, 599.
- (17) Danielson, L. R.; Dresser, M. J.; Donaldson, B. F.; Sandstrom, D. R. *Surf. Sci.* **1978**, *71*, 615.
- (18) Grunze, M.; Dowben, P. A.; Brundle, C. R. *Surf. Sci.* **1983**, *128*, 311.
- (19) Grunze, M.; Golze, M.; Driscoll, R. K.; Dowben, P. A. *J. Vac. Sci. Technol.* **1981**, *18*, 611.
- (20) Alvey, M. D.; Klauber, C.; Yates, J. T., Jr. *J. Vac. Sci. Technol. A3* **1985**, 1631.

- (21) Madey, T. E.; Benndorf, C. *Surf. Sci.* **1985**, *152/153*, 587.
- (22) Lee, L.; Arias, J.; Hanrahan, C.; Martin, R. M.; Metiu, H. *Surf. Sci.* **1986**, *165*, L95.
- (23) Bassignana, I. C.; Wagemann, K.; Kuppers, J.; Ertl, G. *Surf. Sci.* **1986**, *175*, 22.
- (24) Grunze, M.; Bozso, F.; Ertl, G.; Weiss, M. *Appl. Surf. Sci.* **1978**, *1*, 241.
- (25) Grunze, M.; Ertl, G. *Proceedings of the 7th International Vacuum Congress and 3rd International Conference on Solid Surfaces*; R., Dobrozemsky, Ed.; Burger: Vienna, 1977; p 1137.
- (26) Weiss, M.; Ertl, G.; Nitschke, F. *Appl. Surf. Sci.* **1979**, *3*, 614.
- (27) Drechsler, M.; Hoinkes, H.; Kaarman, H.; Wilson, K.; Ertl, G.; Weiss, M. *Appl. Surf. Sci.* **1979**, *3*, 217.
- (28) Kishi, K.; Roberts, M. W. *Surf. Sci.* **1977**, *62*, 252.
- (29) Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1985**, *83*, 3129.
- (30) Redondo, A.; Zeiri, Y.; Low, J. J.; Goddard, W. A. III. *J. Chem. Phys.* **1983**, *79*, 6410.

the nitrogen atom with pyramidal geometry, but only an atop atom adsorption site was considered.<sup>29</sup> Application of transition state theory to desorption from solid surfaces provides rate expressions to interpret the temperature-programmed desorption spectra of  $\text{NH}_3$  from  $\text{Ni}(111)$ .<sup>30</sup> This leads to an adsorption energy of  $D_0 = 21.0 - 3.7\theta$  kcal/mol, where  $\theta$  is the fraction of saturation coverage. Hartree-Fock calculations for  $\text{NH}_3$  adsorbed on the  $\text{Ni}(111)$  surface modeled with a  $\text{Ni}_{13}$  atom cluster were also reported in ref 30, but only the threefold adsorption site was considered.

The present work treats the adsorption of a single ammonia molecule on a  $\text{Ni}(111)$  surface in the context of a many-electron theory that permits calculations at an ab initio configuration interaction level. The adsorbate and local surface region are treated as embedded in the remainder of the lattice electronic distribution, which is modeled as a 28-atom, three-layer cluster, extracted from a 62-atom cluster by an orbital localization transformation.

In the investigation, our goal is to find the geometry, adsorption energy, vibrational frequency, and bonding properties of ammonia on the  $[111]$  surface of nickel. The construction of the cluster,  $\text{NH}_3$  adsorption sites, and  $\text{NH}_3$  binding properties are discussed in the following sections.

## 2. General Theory

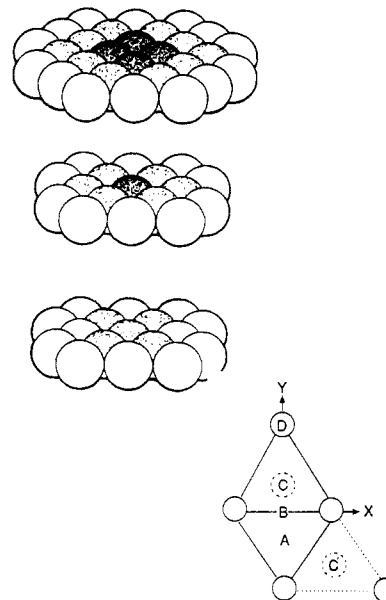
The objective of the embedding theory employed in this work is to treat adsorbed species and a surface region of the metal with sufficient accuracy to describe reaction energetics, while at the same time maintaining a proper coupling of the surface region to the bulk. In this approach, one proceeds to define a local region as an  $N$ -electron subspace extracted from the remainder of the lattice by a localization transformation.<sup>31-33</sup>

The adsorbate and local region are then treated at high accuracy as embedded in the Coulomb and exchange field of the remainder of the electronic system. There are various ways to carry out such calculations and the present approach is identical with that in ref 34. The use of electron exchange as the basis of a localization transformation is discussed in refs 31-33.

Summarizing briefly the approach, a 62-atom cluster consisting of a  $\text{Ni}_{28}$  interior and all of its nearest neighbor atoms in the first three layers at unperturbed fcc lattice sites is used to model the  $[111]$  surface, see Figure 1. Only the  $s$  band of this cluster is treated initially and it is described simply by using a single  $4s$  orbital per atom and a pseudopotential for all core and  $d$ -type electrons ( $d$  electrons on surface  $\text{Ni}$  atoms are explicitly treated in a subsequent step). A SCF calculation on this system, followed by a localization of the cluster (molecular) orbitals is used to define the number of electrons of  $\text{Ni}_{28}$  strongly involved in bonding with other atoms; the latter atoms are referred to as the bulk. Orbitals are localized by exchange maximization with the bulk atoms.

A set of occupied localized orbitals large enough to neutralize the nuclear charge on the boundary atoms is then selected; in the present problem this corresponds to the accommodation of  $62 - 28 = 34$  electrons. Analysis of the electron density of these orbitals shows that, in addition to covering the boundary atoms, the density spreads partly onto the neighboring atoms of the 28-atom cluster. This spread in density can be thought of as the fraction of the 28-atom cluster strongly bound to the remainder of the lattice. The objective is to modify the boundary atoms of  $\text{Ni}_{28}$  to take into account the fact that these atoms should be bonded to the remainder of the lattice.

In the present work, that fraction of the boundary atom density that is tightly bound to the remainder of the lattice is described by a spherical density  $f s(1) s(1)$  where  $s$  is a normalized linear combination of gaussians and  $f$  is the fraction of assigned charge.<sup>35</sup> The Coulomb and exchange fields of the bulk electron distribution



**Figure 1.** Cluster geometry and local region of the nickel cluster used to model the  $(111)$  crystal face of nickel. The three-layer, 62-atom cluster consists of a surface layer of 28 atoms, a second layer of 17 atoms, and a third layer of 17 atoms. Embedding theory is used to reduce the  $\text{Ni}_{62}$  cluster to a 28-atom model depicted as shaded atoms. Surface sites are A, the hollow threefold site where there is no second-layer nickel atom underneath (fcc extension of the lattice); C, the filled threefold site with a second-layer nickel atom underneath (hcp extension of the lattice); B, the bridge site; and D, the atop atom site. Atoms surrounding the four central atoms in the surface layer and the one central atom in the second layer are described by effective potentials for  $(1s-3p \text{ core})(3d)^9(4s)^{1/2}$  and  $(1s-3p \text{ core})(3d)^9(4s)^{1/4}$  configurations, respectively. Effective potentials for the shaded atoms in the third layer describe the  $(1s-3p \text{ core})(3d)^9(4s)^{3/5}$  configuration. Unshaded atoms have neutral atom  $(1s-3p \text{ core})(3d)^9(4s)^1$  potentials. All atoms have Phillips-Kleinman projectors  $\sum |Q_m\rangle \langle Q_m| (-\epsilon_m)$  for the fixed electronic distribution. The nearest neighbor Ni-Ni distance is 2.48 Å.

are represented by neutral atom potentials including a Phillips-Kleinman term,  $\sum_k |\Phi_k\rangle \langle \Phi_k| (-\epsilon_k)$ , where  $\Phi_k$  is an atomic orbital. Figure 1 gives the fraction of charge for each boundary atom assigned to the effective potential and depicts the three-layer geometry. Further details are given in ref 34 and work to be published on the representation of boundary potentials.<sup>36</sup>

The same set of effective potentials is used in all subsequent calculations on the  $\text{Ni}(111)$  surface and for all  $\text{NH}_3$  adsorption calculations.

## 3. Calculations

The cluster model of the  $[111]$  surface of  $\text{Ni}$  described in the previous section is shown in Figure 1; it consists of three layers, the surface layer of 14 atoms, a second layer of 9 atoms, and a third layer of 5 atoms. For the local surface region of four nickel atoms, see Figure 1, a  $[1s-3p]$  core potential is used and valence  $d$  orbitals are explicitly included. Other  $\text{Ni}$  atoms are described by an effective core potential for  $[1s-3d]$  electrons. For all boundary atoms, and those in the third layer, the core potential is further modified to account for bonding to the bulk region, as described in Section 2 and refs 34 and 35. The  $\text{Ni}$  core basis and core density and exchange expansions are the same as used in a previous study of nickel surface states,<sup>37,38</sup> and the  $\text{Ni}$  and  $\text{H}$  basis sets are the same as used in previous calculations on  $\text{H}/\text{Ni}(111)$ .<sup>34</sup>  $\text{Ni}$   $4p$  functions perpendicular to the surface were included on the four atoms in the local region; however, in plane  $\text{Ni}$   $4p$  functions were excluded due to their near linear dependency with combinations of  $\text{Ni}$   $4s$  functions on surrounding nuclei. The

(31) Whitten, J. L.; Pakkanen, T. A. *Phys. Rev. B* **1980**, *21*, 4357.

(32) Whitten, J. L. *Phys. Rev. B* **1981**, *24*, 1810.

(33) Cremaschi, P.; Whitten, J. L. *Surf. Sci.* **1985**, *149*, 273 and references contained therein.

(34) Yang, Hong; Whitten, Jerry L. *J. Chem. Phys.* **1988**, *89*, 5329.

(35) Cremaschi, P.; Whitten, J. L. *Theor. Chim. Acta* **1987**, *72*, 485.

(36) Chattopadhyay, A.; Whitten, J. L. Ph.D. Thesis, The State University of New York, at Stony Brook, 1988.

(37) Madhavan, P. V.; Whitten, J. L. *Chem. Phys. Lett.* **1986**, *127*, 354.

(38) Trentini, F. v.; Madhavan, P. V.; J. L. Whitten *Prog. Surf. Sci.* **1987**, *26*, 201.

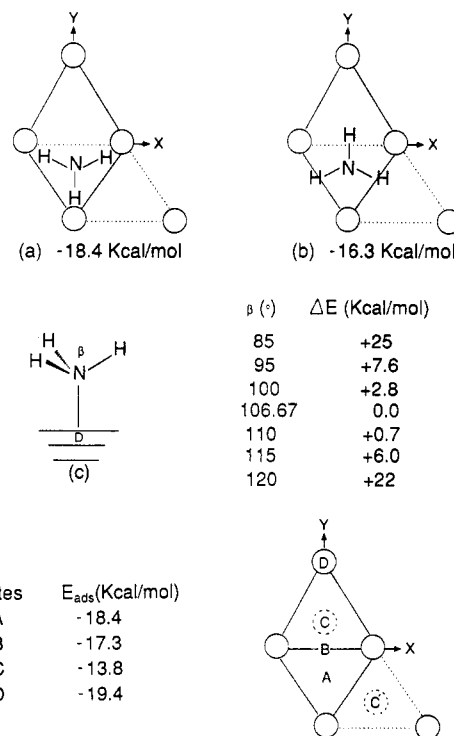
nitrogen basis was taken from Whitten,<sup>39</sup> with the p orbitals described by a split basis. This simple double  $\zeta$  s, p basis for nitrogen, along with the double  $\zeta$  s basis for hydrogens, gives erroneous results for the inversion of ammonia; the planar geometry is found to be more stable than the experimental (pyramidal) one, which is consistent with Kaldor and Shavitt's findings.<sup>40</sup> However, addition of a set of d polarization functions (exponent of 1.5) to the basis gives the right inversion barrier. It was found that the two d orbitals,  $d_{xz}$  and  $d_{yz}$ , are the ones responsible for stabilizing the pyramidal geometry in preference to the planar ones. In all calculations involving  $\text{NH}_3$  on the nickel surface, these two d orbitals are explicitly included.

Calculations are performed by first obtaining self-consistent-field (SCF) solutions for the nickel cluster plus  $\text{NH}_3$ . The occupied and virtual orbitals of the SCF solution are then transformed separately to obtain orbitals spatially localized about the four-atom surface region shown in Figure 1 and the  $\text{NH}_3$  adsorbate. This unitary transformation of orbitals is based on exchange maximization with the valence orbitals of atoms belonging to the surface region<sup>31-33</sup> and is designed to enhance convergence of the configuration interaction (CI) expansion. The CI calculations involve excitation within a 30-electron subspace to 28 possible virtual localized orbitals. All configurations arising from single and double excitations with an interaction energy greater than  $1 \times 10^{-5}$  hartree with the parent SCF configuration are explicitly retained in the expansion; contributions of excluded configurations are estimated by using second-order perturbation theory. For all sites calculated, the SCF solution is the only dominant configuration. Details of the procedure are given in ref 41. Basis superposition contributions to the adsorption energy were investigated by calculating the energy of the Ni cluster with the  $\text{NH}_3$  virtual basis present (but not the nucleus) for points near the equilibrium geometries.

Since there is some uncertainty in the assignment of the boundary electron density and its representation by a spherical effective potential, it is important to examine the SCF solution of the final 28-atom cluster model. These results are reported in ref 34. The calculated 4s-band width of the  $\text{Ni}_{28}$  cluster is 9.0 eV, which is reasonably close to the width measured by photoemission of 10 eV.<sup>42</sup> The ionization energy or work function of 5.30 eV of the cluster, calculated by CI as  $E_{\text{Ni}}^+ - E_{\text{Ni}}$  (5.38 eV calculated by Koopmans' theorem) is close to the range observed experimentally of 5.15–5.35 eV for Ni(111).<sup>43-45</sup> In addition, the calculated eigenvalue spectrum for the 4s band is moderately dense, particularly near the Fermi level, which is important to assure charge flow on adsorption. The present model thus gives a good account of the essential features of the nickel 4s band.

#### 4. $\text{NH}_3$ Adsorption

The sites considered for  $\text{NH}_3$  adsorption are as follows: a hollow threefold site with no second-layer nickel atom underneath (fcc extension of the lattice), a filled threefold site with a second layer nickel atom underneath (hcp extension of the lattice), a bridge site, and an atop atom site, denoted by A, C, B, and D, respectively, in Figure 1. In the initial nitrogen-surface distance optimization, the N–H bond lengths are fixed at 1.01 Å and the HNH angle at 106.67°, which are the gas-phase experimental values,<sup>46</sup> and the  $\text{NH}_3$  molecule has pyramidal geometry with the molecular axis normal to the surface. Two hydrogen orientations in  $\text{NH}_3$  are considered for  $\text{NH}_3$  at threefold sites: the H's pointing either



**Figure 2.**  $\text{NH}_3$  adsorption sites on Ni(111) and calculated energies. The adsorption energy of  $\text{NH}_3$  at the most stable atop atom site D is 19 kcal/mol. In c the variation in energy with HNH angle  $\beta$  is shown. Adsorption energies for sites A–D are for  $\text{NH}_3$  perpendicular to the surface with a pyramidal geometry and a symmetric HNH angle of 106.67°.

**TABLE I:  $\text{NH}_3$  Adsorption on Ni(111). Adsorption Energies, Equilibrium Distances,  $\text{NH}_3$  Vibrational Frequencies, and N–H Stretching Frequencies from CI Calculations on  $\text{NH}_3$  Adsorbed at Different Sites on a Cluster Model of the Ni(111) Surface. Energies in Parentheses Are Uncorrected for Basis Superposition Effects**

site <sup>a</sup>	$R_{\text{N-surface}}$ , <sup>b</sup> Å	$R_{\text{Ni-Ni}}$ , <sup>c</sup> Å	$E_{\text{ads}}$ , kcal/mol	$\text{NH}_3$ –Ni stretch, $\text{cm}^{-1}$	N–H stretch, $\text{cm}^{-1}$
threefold (A)	2.38	2.78	18 (20)	470	
bridge (B)	2.44	2.74	17 (19)	500	
threefold (C)	2.37	2.77	14 (16)	461	
atop (D)	2.12	2.12	19 (21)	503	3340
exptl			17 <sup>d</sup>	450 <sup>e</sup>	3360 <sup>f</sup>

<sup>a</sup> Hollow site, A; filled site, C; bridge site, B; atop atom site, D; see Figure 1. <sup>b</sup> Nitrogen perpendicular distance to the surface. <sup>c</sup> Distance from nitrogen to nearest surface Ni. <sup>d</sup> Reference 6 and 9. <sup>e</sup> EELS assignment for  $\text{NH}_3$  adsorbed on Ni(110) surface, ref 23. <sup>f</sup> Reference 7.

toward the nearest Ni atoms or toward the Ni–Ni bond centers, as shown in Figure 2a and 2b. Our previous  $\text{CH}_3/\text{Ni}(111)$  calculations<sup>47</sup> and Hoffmann and co-workers' results for  $\text{CH}_3$  adsorbed on metal surfaces<sup>48</sup> indicated that the most stable geometry of  $\text{CH}_3$  at a threefold adsorption site is for the H's pointing toward the nearest metal atoms. Therefore, the initial optimization reported below is based upon a  $\text{NH}_3$  pyramidal geometry with the H's oriented toward the nearest Ni atoms at the threefold sites A and C. The  $\text{NH}_3$  molecule was translated in the y direction from the fcc threefold site A (Figure 2) to obtain the bridge site, B, and the atop atom site, D, geometries. Other geometries for  $\text{NH}_3$  will be discussed in detail in a subsequent section.

Calculated adsorption energies, nickel–nitrogen equilibrium distances, and  $\text{NH}_3$  vibrational frequencies are reported in Table I. From the present results, several conclusions may be drawn. First, regarding the stability of the sites investigated, the calcu-

(39) Whitten, J. L. *J. Chem. Phys.* **1966**, *44*, 359.

(40) Kaldor, U.; Shavitt, I. *J. Chem. Phys.* **1966**, *45*, 888.

(41) Madhavan, P. V.; Whitten, J. L. *J. Chem. Phys.* **1982**, *77*, 2673.

(42) Herman, F.; Dalton, N. M.; Keohler, T. R. *Computational Solid State Physics*; Plenum Press: New York-London, 1972; p 39.

(43) Baker, B. G.; Johnson, E. B.; Marie, G. I. C. *Surf. Sci.* **1971**, *24*, 572.

(44) Himpsel, F. J.; Knap, J. A.; Eastman, D. E. *Phys. Rev. B* **1979**, *19*, 2872.

(45) Demuth, J. E. *Surf. Sci.* **1977**, *65*, 369.

(46) Herzberg, G. *Electronic Spectra of Polyatomic Molecules*; D. Van Nostrand Company, Inc.: Princeton, NJ, 1967; p 609.

(47) Yang, Hong; Whitten, Jerry L. *ACS Symp. Ser.* **1989**, No. 394.

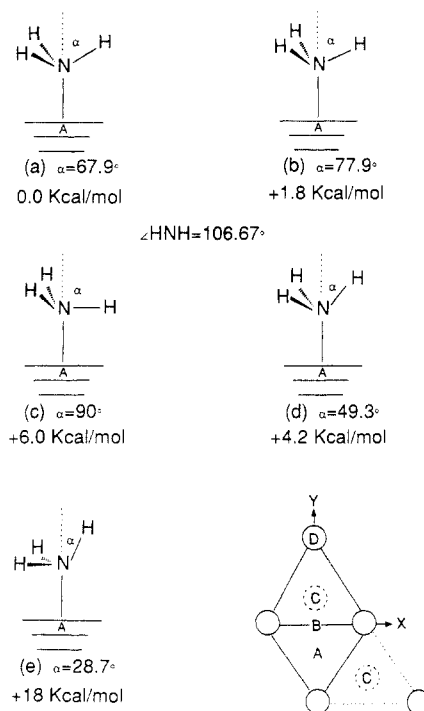
(48) Zheng, C.; Apeloig, Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1988**, *110*, 749.

lations predict a nearly flat potential surface for  $\text{NH}_3$  chemisorption on the Ni(111) surface. The adsorption energies obtained in the present work are 18 kcal/mol (fcc threefold site A), 17 kcal/mol (bridge site B), 14 kcal/mol (hcp threefold site C), and 19 kcal/mol (atop atom site D). The calculated adsorption energy for  $\text{NH}_3$  at the hollow threefold site A (with no second-layer Ni atom underneath) is 4 kcal/mol lower in energy than that at the threefold site C (with the second-layer Ni atom underneath). The stability of the threefold site is consistent with the experimental suggestion of  $\text{NH}_3$  adsorption at the fcc threefold site on Ni(111),<sup>5-7</sup> Ir(111),<sup>10</sup> and Pt(111);<sup>11</sup> however, the relatively large 4 kcal/mol difference between sites is not supported by experiment; see subsequent discussion. In addition, our calculations show that the atop atom site, the fcc threefold site, and the bridge site are all of comparable stability, with a maximum energy difference between sites only 2 kcal/mol. In general, the present values are in excellent agreement with the experimental value of 17 kcal/mol for  $\text{NH}_3$  chemisorption on Ni(111)<sup>6,9</sup> and is close to the theoretical prediction of 21.0 kcal/mol for  $\text{NH}_3$  adsorption on Ni(111) at very low coverage.<sup>30</sup> In the latter work, Goddard and co-workers, using potential parameters from a combination of experiment and ab initio calculations, applied the rate expressions drawn from their transition state theory to evaluate the temperature-programmed desorption spectra of  $\text{NH}_3$  from Ni(111) and predicted an adsorption energy of  $D_0 = 21.0 - 3.7\theta$  kcal/mol, where  $\theta$  is the fraction of saturation coverage. They have also performed Hartree-Fock calculations for  $\text{NH}_3$  adsorbed on the threefold site of the Ni(111) surface modeled with a  $\text{Ni}_{13}$  atom cluster. The adsorption energy obtained in ref 30 varies between 10 and 30 kcal/mol with different basis sets. Using an ab initio SCF plus CI method and modeling the nickel surface as 14 atom cluster, Bauschlicher obtained an 8.1 kcal/mol adsorption energy for  $\text{NH}_3$  on Ni(100),<sup>29</sup> substantially less than the present value.

The nickel-nitrogen equilibrium distances calculated in the present work are 2.78, 2.74, 2.77, and 2.12 Å for  $\text{NH}_3$  at sites A, B, C, and the atop site D, respectively. Goddard and co-workers obtained 2.13 Å for the nearest neighbor Ni-N distance for  $\text{NH}_3$  at the three-coordinate Ni(111) site surface by performing Hartree-Fock calculations and modeling the nickel surface as 13-atom cluster.<sup>30</sup> Bauschlicher obtained 2.29 Å for the Ni-N bond length for  $\text{NH}_3$  at the atop atom site for his cluster model of Ni(100).<sup>29</sup> No experimental data for distances are available for either the [100] or [111] surface.

Calculated frequencies of the surface- $\text{NH}_3$  group vibration, perpendicular to the Ni(111) surface, are 470, 500, 461, and 503  $\text{cm}^{-1}$  for  $\text{NH}_3$  adsorbed at the fcc threefold site A, the bridge site B, the hcp threefold site C, and the atop atom site D, respectively. Although the surface- $\text{NH}_3$  stretch was not detected by EELS for  $\text{NH}_3$  chemisorbed on Ni(111)<sup>7</sup> and Pt(111),<sup>11</sup> the present results generally agree with the metal-N stretching mode near 500  $\text{cm}^{-1}$  in inorganic complexes containing metal- $\text{NH}_3$  species.<sup>49</sup> In addition, our calculations values are not far from the energy loss peak of 450  $\text{cm}^{-1}$  attributed recently to the surface- $\text{NH}_3$  stretch on Ni(110) by Ertl and co-workers<sup>23</sup> (the energy loss peak of 570  $\text{cm}^{-1}$  assigned previously to the surface- $\text{NH}_3$  stretch on Ni(110) by Fisher and Mitchell<sup>7</sup>). The present values are also similar to the ammonia-surface stretch frequency of 417  $\text{cm}^{-1}$  calculated by Goddard et al.,<sup>30</sup> in which  $\text{NH}_3$  was considered as adsorbed at a threefold site on a  $\text{Ni}_{13}$  cluster. We calculate a H-N stretching frequency for  $\text{NH}_3$  on the Ni(111) surface at 3340  $\text{cm}^{-1}$ , in agreement with electron energy loss assignments for N-H of 3360  $\text{cm}^{-1}$  for  $\text{NH}_3$  adsorbed on Ni(111).<sup>7</sup>

The above results assume an orientation of the  $\text{NH}_3$  pyramidal geometry with the H's pointing toward the nearest Ni atoms at the threefold sites A and C and bridge and atop atom geometries obtained by translation of the threefold site A orientation. Rotating the H's by 180° about the surface normal to orient the N-H bonds between neighboring nickel atoms for  $\text{NH}_3$  at the threefold sites A and C, and a corresponding shift of the site A geometry



**Figure 3.** Geometries and energies of  $\text{NH}_3$  intermediates on Ni(111). Energies are for the fcc threefold adsorption site and are relative to that of the stable geometry depicted in a, which corresponds to adsorption at the fcc threefold site A with  $E_{\text{ads}} = 18$  kcal/mol. All HNH angles are kept equal to 106.67° and the angle between the NH axis and the surface normal is denoted by  $\alpha$ .

to the bridge site B and the atop from site D, gives energy differences of +2.1, +1.7, +1.6, and +1.1 kcal/mol for  $\text{NH}_3$  at the hollow threefold site A, the bridge site B, the filled threefold site C, and the atop atom site D, respectively. Since distances and angles are not optimized for these rotations, the calculated barriers are upper bounds. The smallest barrier is for an atop site but all of the values are near the limit of computational precision and should be interpreted as showing that the barrier to rotation about the surface normal is very low for each site. Circular ESDIAD measurements<sup>5,6,9</sup> show barriers significantly smaller than those calculated.

The ammonia adsorption calculations described thus far assume that the pyramidal axis of the  $\text{NH}_3$  molecule is normal to the surface (an axis through N and perpendicular to the plane of H's) with an HNH angle = 106.67°, as shown in Figure 2. The energetics as a function of  $\text{NH}_3$  geometry and orientation are shown in Figures 2 and 3. First, concerning the variation of the angle HNH,  $\beta$ , in  $\text{NH}_3$ , when  $\beta$  increases from 106.67° to 110°, 115°, 120°, see Figure 2c, the energy increases 0.7, 6.0, 22 kcal/mol at the atop adsorption site D. On decreasing  $\beta$  to 100°, 95°, then 85°, the energy increases by 2.8, 7.6, and 25 kcal/mol. Thus, the energy is essentially unchanged from 106.67° to 110°. We conclude that chemisorption of ammonia on the Ni(111) surface allows low-energy fluctuations in the HNH angle about an equilibrium value of  $108 \pm 2^\circ$ . A similar conclusion was drawn by Bauschlicher, based on an optimized HNH angle of 108.7° for  $\text{NH}_3$  adsorbed on Ni(100).<sup>29</sup> An optimum HNH angle of 104.8° was obtained by Goddard and co-workers.<sup>30</sup>

If the orientation of  $\text{NH}_3$  is changed, see Figure 3, such that the threefold axis of  $\text{NH}_3$  is tilted with the angle HNH kept equal to 106.67°, and with the  $\text{NH}_3$  adsorbed at fcc threefold site A, the energetics as a function of the angle  $\alpha$  between the NH axis and the surface normal and orientation are shown in Figure 3. If  $\text{NH}_3$  is perpendicular to the surface with a pyramidal geometry and a symmetric HNH angle of 106.67°, shown in Figure 3a,  $\alpha$  is equal to 67.9°. If  $\text{NH}_3$  is tilted at  $\alpha = 77.9^\circ$ , see Figure 3b, the energy increases 1.8 kcal/mol. When  $\alpha$  increases to 90°, see Figure 3c, such that only one hydrogen is on an axis parallel to the surface, the energy increases 6.0 kcal/mol. The opposite tilt

(49) Nakanoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1978; pp 197-202.

of decreasing  $\alpha$  from 67.9° to 49.3°, see Figure 3d, the energy increases 4.2 kcal/mol. Further decreasing  $\alpha$  to 28.7°, as shown in Figure 3e, such that two hydrogens are closer to the surface and are in a plane with the N parallel to the surface, increases the energy 18 kcal/mol. Although tilting calculations were not performed for at atop adsorption site, one would not expect significant stabilization in view of the types of tilting interactions investigated for the threefold site.

As discussed earlier, if the pyramidal geometry of NH<sub>3</sub> is distorted such that three hydrogens are in a plane parallel to the surface with an angle HNH of 120°, the energy is 22 kcal/mol higher than the minimum geometry in Figure 3e. Thus, our calculations suggest that the direct bonding between H ligands and the lattice is too weak to significantly attract one of the hydrogens toward the surface, i.e., there is no evidence of an agostic interaction in the present work. Only a small amount of energy is needed to tilt the NH<sub>3</sub> less than 10°, but the repulsion grows very quickly if the tilt is increased. Since the small angles of tilt for NH<sub>3</sub> on the surface requires little energy, it is easy to understand that adsorbate-adsorbate interactions can influence the structure of the overlayer when other species are coadsorbed.

On the question of the relative stability of NH<sub>3</sub> adsorption at different sites, the bridge site, threefold fcc site, and atop site all show comparable adsorption energies for optimized NH<sub>3</sub> geometries, 17–19 kcal/mol; however, for NH<sub>3</sub> at the threefold hcp site,  $E_{\text{ads}} = 14$  kcal/mol, 4 kcal/mol less than that for the threefold fcc site. The second-layer nickel atoms (there are nine explicitly included in the calculations) cannot have a direct effect at such long distances that exceed 4 Å, rather the atoms influence bonding at the surface through their interactions with the surface layer. For lone pair adsorbates such as NH<sub>3</sub>, the second layer affects the response of the 4s electron distribution as it shifts to avoid the lone pair distribution (a Pauli exclusion principle effect). The ability to form a site with less electron density could favor a hollow (fcc) threefold adsorption site for NH<sub>3</sub>. On the other hand, the 4 kcal/mol difference between sites is a fairly large relative energy difference, and while it is unlikely that calculational errors in relative binding energies could be this large, it is entirely possible that there might be an intrinsic bias in the cluster model of the surface. To explore this point, we consider calculations of H, OH, and H<sub>2</sub>O at each of the sites for the same cluster model. H adsorption is found to be slightly favored at the threefold hcp site (by 3 kcal/mol) and OH has essentially the same adsorption energy for the different threefold sites (within 0.1 kcal/mol). Comparisons with H<sub>2</sub>O/Ni(111) are probably more relevant. In recently published work,<sup>50</sup> we find that an atop Ni site is preferred for H<sub>2</sub>O with  $E_{\text{ads}} = 11$  kcal/mol, while the bridge, threefold fcc, and threefold hcp sites have H<sub>2</sub>O adsorption energies of 7, 8, and 6 kcal/mol, respectively. The latter two values are in accord with NH<sub>3</sub> results although the difference in energies is less by a factor of 2. These studies do not reveal any systematic bias to the cluster model that would easily explain the 4 kcal/mol difference in adsorption energies of NH<sub>3</sub> at the two different threefold sites. Of course, given the many uncertainties, differences in energy in the kcal range simply should not be taken too seriously.

In view of the lone pair 3a<sub>1</sub> orbital, the bonding of the ammonia to nickel would be expected to involve a small transfer of electronic charge from the ammonia to the surface. On the basis of Mulliken population analysis of the SCF solution, the electron transfer from NH<sub>3</sub> at the atop atom site D, to the substrate is only 0.2 e, which maintains an orientation of the NH<sub>3</sub> dipole with the negative end (the N atom) toward the surface. This transfer of electrons to the surface is consistent with the calculated work function decrease on NH<sub>3</sub> adsorption where decreases of 0.47, 0.38, 0.45, and 0.54 eV occur for adsorption sites A, B, C, and D, respectively, as calculated by Koopmans' theorem. The CI value of the work function change for NH<sub>3</sub> adsorbed at the atop atom site D is 0.62 eV, calculated as  $E_{\text{NiNH}_3^+} - E_{\text{NiNH}_3}$ . This 0.6-eV decrease in work function upon NH<sub>3</sub> chemisorption is in qualitative agreement with

work function change measurements showing a 1.6–1.7-eV decrease for NH<sub>3</sub> adsorbed on the Ni(111) surface.<sup>3,8</sup>

On bonding to the surface for an atop Ni adsorption site, the lone pair 3a<sub>1</sub> orbital of the gas-phase NH<sub>3</sub> molecule interacts strongly with the Ni 3d orbitals. The main NH<sub>3</sub> 3a<sub>1</sub>-bonding feature mixed with Ni 3d orbitals occurs at 11.3 eV below the Fermi level with populations (in percent) of [35NH<sub>3</sub>(3a<sub>1</sub>), 65Ni(3d)]. In addition, the weak interactions between the lone pair 3a<sub>1</sub> orbital and the Ni 3d orbitals occur at 11.7, 11.6, and 10.8 eV below  $E_F$  with populations (in percent) of [10NH<sub>3</sub>(3a<sub>1</sub>), 90Ni(3d)], [18NH<sub>3</sub>(3a<sub>1</sub>), 82Ni(3d)] and [10NH<sub>3</sub>(3a<sub>1</sub>), 90Ni(3d)], respectively. The 1e orbitals of the gas-phase NH<sub>3</sub> molecule are placed at 15.7 eV below  $E_F$  upon NH<sub>3</sub> chemisorption on the Ni(111) surface. UPS studies have led to the assignment of levels 6.7 and 11.0 eV below  $E_F$  as 3a<sub>1</sub>-bonding and 1e-bonding levels for NH<sub>3</sub> adsorption on Ni(111).<sup>3,8</sup> Although Koopmans' theorem would place the 3a<sub>1</sub> and 1e levels deeper than the UPS assignments, explicit treatment of the relaxation on ionization would likely bring the calculated ionization energies closer to the UPS values. The calculated spacing of the ionized 3a<sub>1</sub> and 1e states  $\Delta E(3a_1-1e)$  is 4.4 eV, in good agreement with the UPS value of 4.3 eV.<sup>3,8</sup> In an analogous system, Bagus et al.<sup>51</sup> have analyzed the bonding of NH<sub>3</sub> to a Cu<sub>5</sub> cluster at an atop Cu site. By constraining the mixing of orbitals in a series of SCF calculations, they show that the bonding can be viewed primarily as electrostatic, driven by the large dipole moment of NH<sub>3</sub>. Support for this interpretation can be found in the present calculations on Ni where the charge donation from NH<sub>3</sub> to the surface is only 0.2 e. The mixing with the 3d electrons of Ni is partly a resonant interaction that appears large but does not lead to a major increase in the adsorption energy. Further, in Figure 2 the fact that the energy increases significantly by 22 kcal/mol, when NH<sub>3</sub> becomes planar on the surface (a much larger increase than for the free molecule) is consistent with the importance of the NH<sub>3</sub> dipole moment and accompanying sp character of the 3a<sub>1</sub> lone pair.

## 5. Conclusions

The conclusions of the present study of the chemisorption of NH<sub>3</sub> on the [111] surface of nickel can be summarized as follows:

1. For molecular NH<sub>3</sub> adsorbed on the Ni(111) surface, the atop atom, the threefold fcc, and the bridge sites are of comparable stability, with adsorption energies of 19, 18, and 17 kcal/mol and with Ni–N equilibrium distances of 2.12, 2.78, and 2.74 Å, respectively, suggesting a nearly flat potential surface for ammonia on Ni(111). Ammonia bonds to nickel via the N atom with the H's pointing away from the surface. The hcp threefold site for NH<sub>3</sub> adsorption is 5 kcal/mol higher in energy than the most stable atop atom site.

2. The calculated equilibrium geometry of NH<sub>3</sub> has a pyramidal configuration with H's parallel to the surface, but tilting the hydrogens less than 10° or rotating the molecule by 180° about the surface normal changes the energy only slightly. The optimum HNH angle is in the range 108 ± 2°. The circular ESDIAD pattern of NH<sub>3</sub> molecularly adsorbed on the surface is consistent with these results.

3. The calculated surface–NH<sub>3</sub> vibrational frequencies, for group motion normal to the surface, are 470, 500, 461, and 503 cm<sup>-1</sup> at the adsorption sites A, B, C, and D, respectively. The H–N stretching frequency in NH<sub>3</sub> is 3340 cm<sup>-1</sup>.

4. The work function of the lattice decreases about 0.6 eV on NH<sub>3</sub> adsorption for this sparse level of coverage.

5. Analysis of bonding between ammonia and the surface shows major interactions of the Ni 3d and the lone pair 3a<sub>1</sub> orbital of ammonia. These interactions and a strong electrostatic interaction due to the ammonia dipole characterize the bonding to the surface.

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(50) Yang, Hong; Whitten, J. L. *Surf. Sci.* **1989**, *131*, 223.

(51) Bagus, P. S.; Hermann, K.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1984**, *81*, 1966.