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NH_3 adsorption around Ni_n ($n \leq 4$) clusters

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Abstract

The attachment of NH_3 to Ni_n clusters was studied both theoretically and experimentally. Experiments were conducted by generating the clusters in a flow tube reactor and reacting them with NH_3 gas. The experimental mass spectra show that in Ni_n–$(NH_3)_m$, the dominant products for cations occur at 1:2, 1:3, 3:3, 4:4, 5:5 and 6:6. This paper also reports the results of theoretical ab initio density functional calculations, which were carried out to examine the nature of binding, stability and the effect of NH_3 on the electronic and magnetic behavior of Ni_n clusters. It is shown that the binding energy (BE) of NH_3 to Ni_n clusters changes non-monotonically with size and that the observed peaks in the mass spectrum of Ni_n–$(NH_3)_m$ clusters can be understood from the theoretical energetics. Although the magnitude of the bond energies is greater for ammonia bound to Ni^+ than to the neutral atom, based on the energetics, the trend leading to a truncation in the cluster distribution is expected to be the same in accord with the experimental findings. Theoretical attention was also directed to a study of the trends in the magnetic properties of the system. We show that the absorption leads to a gradual quenching of the Ni_n moments. In some cases, however, the moments can reappear at higher coverage. This reappearance of magnetism is shown to be a consequence of the variation of Ni–N distance with coverage of the adsorbent. (Int J Mass Spectrom 220 (2002) 171–182)

Keywords: NH_3 adsorption; Ni_n clusters; Magnetic Moment; $NiNH_3$ clusters

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1. Introduction

It is now fairly well established that the geometry, electronic, chemical, and magnetic properties of clusters are different from those of the individual atoms or the solids [1,2]. For example, clusters of noble metals can be highly reactive while the reactivity of transition metal clusters can change by orders of magnitude with size [3]. The electronic features are also very different. For example, size selected clusters of simple metal atoms (e.g., Al_{13}) can have properties resembling those of halogen atoms [4]. The magnetic properties of clusters are also quite unique. Small clusters of ferromagnetic solids can exhibit superparamagnetic relaxations [5] while clusters of paramagnetic solids can be magnetic [6,7]. These developments are redefining the limits of material science and the possibility of forming materials using clusters as the building blocks does not seem too distant [8]. The stumbling block of this dream has been the reality that almost all clusters generally coalesce to form bigger units when assembled. One of the ways to get around this problem is to coat the clusters with ligands before assembly. This has generated considerable interest in studies of the effects of ligands on the behavior of clusters. The study of ligated clusters is

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also important for another reason. One of the fundamental problems that has remained largely unsolved is the determination of the geometrical structure of clusters. Generally clusters are too small for using microscopic techniques but too large for spectroscopic studies. Cluster structure determination, therefore, has to rely on indirect methods, for example the chemical approach [9]. Here, one exposes the cluster to non-invasive gases and studies the equilibrium coverage as a function of temperature and pressure. The plateaus in the uptake data can then provide information on the number of different kinds of sites and this can be used to derive structural information. This approach implicitly assumes that the geometry of clusters is unaffected by the adsorbed species. A study of the ligated clusters is needed to examine the applicability of these methods.

The 3d transition metals and in particular Ni have recently drawn attention because of their important catalytic and magnetic properties. Nickel is one of the widely used catalysts in large-scale industrial processes such as the Fischer–Tropsch reaction of carbon monoxide hydrogenation and ethylene hydrogenation. Ni is also interesting because of its magnetic properties. It is one of the three itinerant 3d ferromagnetic solids. Studies of small clusters have suggested that the magnetic moments per atom of Ni_n clusters are enhanced from the bulk value [10] and change non-monotonically with size [11]. In fact some of the small clusters have magnetic moments per atom that are even larger than bulk Co.

In addition to magnetism, the geometrical structure of nickel clusters has been investigated using chemical methods. Riley and co-workers have used NH_3 [12] and N_2 [13,14] to probe the structures of several small to medium size neutral nickel clusters. They have measured the adsorption profiles as a function of temperature and assuming that different sites have different binding energies, and that sites with lower coordination can attach multiple molecules, the plateaus in the experimental adsorption profiles have been used to deduce their structures. As mentioned above, they assume that the adsorbed species does not change the structure of the clusters.

The Ni_n clusters have also been the subject of numerous theoretical studies using ab initio techniques with core potentials [5,15], semi-empirical methods such as complete neglect of differential overlap (CNDO) [16], tight binding methods [17], effective medium theories [18], and density functional approaches [19]. All these methods generally agree that the small clusters have compact structures that differ from the bulk arrangements. The studies also agree that the magnetic moment per atom in clusters is higher than in the bulk and changes non-monotonically with size. There are however, only limited attempts to study the effects of ligands on the geometry, electronic structure, and magnetic properties.

In this paper, we present experimental studies of the attachment of ligands to Ni_n cation clusters. The experimental studies are accompanied by ab initio theoretical calculations on neutral nickel clusters that confirm some of the experimental findings and further provide explanations of the mass spectra peak abundances and the truncations of series adducts to nickel clusters of certain sizes, as well as possible structural configurations of Ni–ligand complexes. We use the NH_3 reaction as a case study. Experimental results also indicate that the alcohol systems are analogous to NH_3. The results of NH_3 reactions with nickel are, therefore, also applicable to CH_3OH and C_2H_5OH. We are able to show that geometric properties as well as the electronic energy states are the determining factors for the formation of cluster–ligand complexes. We will particularly focus on the changes in the magnetic moment of transition metal clusters upon adsorption of NH_3 and show that the adsorption of NH_3 can lead to quenching of the NH_3 moments and that in some cases, the moments reappear after further coverage. In some cases, the adsorption can lead to the fracture of NH_3 molecules. Since the products remain attached to the clusters, such fragmentations will not be observed in experiments that depend on mass changes to signify reactions.

We would like to add that while the current experiments are done on cations, most of the theoretical calculations are carried out on neutral species where there is interest in the changes in the magnetic properties of Ni_n clusters upon adsorption. The magnetic moments of clusters are measured via Stern–Gerlach experiments. Such studies can only be carried out on neutral clusters since any net charge will produce a large Lorentz force. As we will show, the trend in the energetics calculated for the neutral clusters are the same as those of the cationic clusters.

2. Experimental techniques

The details of the experimental setup are described elsewhere [20,21]. Briefly, Ni clusters are produced via a laser evaporation source located at the end of a flow tube reactor, which is operated under well-defined laminar flow conditions. An excimer laser is used to ablate a 1/4″ Ni rod turned by a step motor to maintain a fresh Ni surface. Ni clusters are carried by the He carrier gas (99.997% from Matheson) to the flow tube reactor through a 1 mm orifice. The Ni rod we used (99.9% from Alfa), has the naturally occurring isotopes of 58 and 60 amu. The He carrier gas passes through a series of molecular sieves and a liquid nitrogen trap to remove any impurities before it reaches the source chamber or flow tube reactor. The reactant gas is introduced into the flow tube reactor from a reactant gas inlet (RGI). NH_3 gas from Matheson (with 99.99% purity) is introduced from the RGI without helium dilution. CH_3OH and C_2H_5OH (from Alfa, with purity as 99.7%) are introduced into the RGI after the reaction line is cleaned up by a technique called pump–thaw cycle. We first freeze the liquid reactant in the test tube connected to the RGI with liquid nitrogen and then pump the pipes between the RGI and reactant gas container to the desired low pressure. The liquid nitrogen is then taken out, the reactant is thawed, and then the line between the reactant, reactant container, and the RGI port is flushed before we pump the line again. We freeze the reactant for the second time and perform the pump–thaw cycle at least three times to ensure that the reactant gas line is flushed clean. The pressure in the flow tube reactor is around 0.3 Torr. It is pumped by the root pump as well as the two diffusion pumps, which keep the detection chamber pressure at 1×10^{-5} Torr. The signals are detected by the Electron Multiplier (Norland Inc., Model #1710).

3. Theoretical method

The theoretical calculations were carried out using a linear combination of atomic–molecular orbital approach within the density functional formalism. Briefly, the molecular orbitals are expressed as a linear combination of atomic orbitals centered at the atomic sites. The atomic orbitals are formed from a linear combination of Gaussian functions. The molecular integrals required in the solution of the Kohn–Sham equation are carried out numerically over a carefully chosen mesh. The actual calculations were carried out using the NRLMOL set of codes developed by Pederson and co-workers [22] and the reader is referred to original papers for details. The exchange correlation contributions were included via a gradient corrected functional proposed by Perdew et al. [23] and all the calculations were carried out at the all electron level.

We have studied Ni_n clusters containing up to 4 Ni and 6 NH_3 molecules. The basis set for Ni had 20 primitive Gaussians contracted into 7s, 5p, and 4d Gaussians, for N there were 13 primitive Gaussians contracted into 5s, 4p, and 3d Gaussians, and for H there were six primitive Gaussians contracted into 4s, 3p, and 1d Gaussians [22]. The ground state determination involves optimization of geometry for various spin multiplicities. This is a daunting task and to render calculations manageable, we initially assumed symmetry constraints and then relaxed the constraint to allow complete optimization. The final structures therefore include all possible distortions. In some cases, the relaxation of the constraints did lead to very different structures.

4. Results and discussions

4.1. Experimental results

Fig. 1 is a typical Ni cation mass spectrum from our mass spectrometry apparatus. Each peak is identified

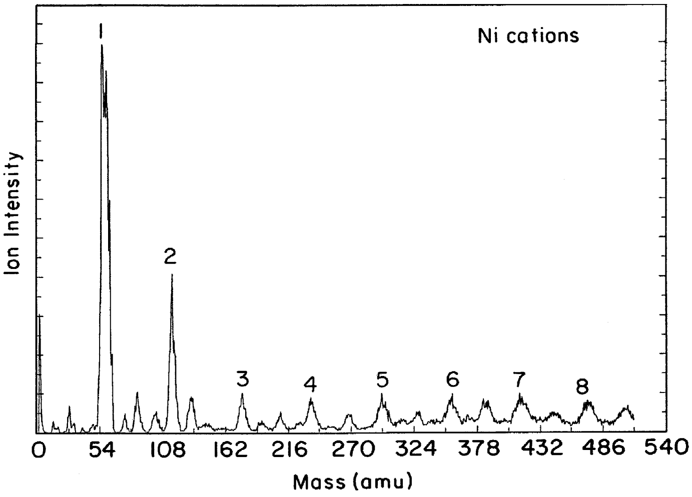

Fig. 1. Mass spectrum of cationic Ni_n clusters. The number of atoms for different sizes is marked.

with the calibrated Ni atomic mass and the Ni cluster isotope patterns. The small peaks between the Ni cluster are the Ni oxides with one or two oxygen adducts. It is believed that the oxygen is from the Ni rod.

A series of experiments were run with increasingly longer concentrations, where upon nickel–ammonia clusters were generated. At high concentrations (e.g., typically about 100 standard cubic centimeters per minute flow rates) the distribution reached a "saturated" condition; that is, the cluster-size ratios did not further shift to larger sizes and no further ligand addition took place. Fig. 2a and b (insert)

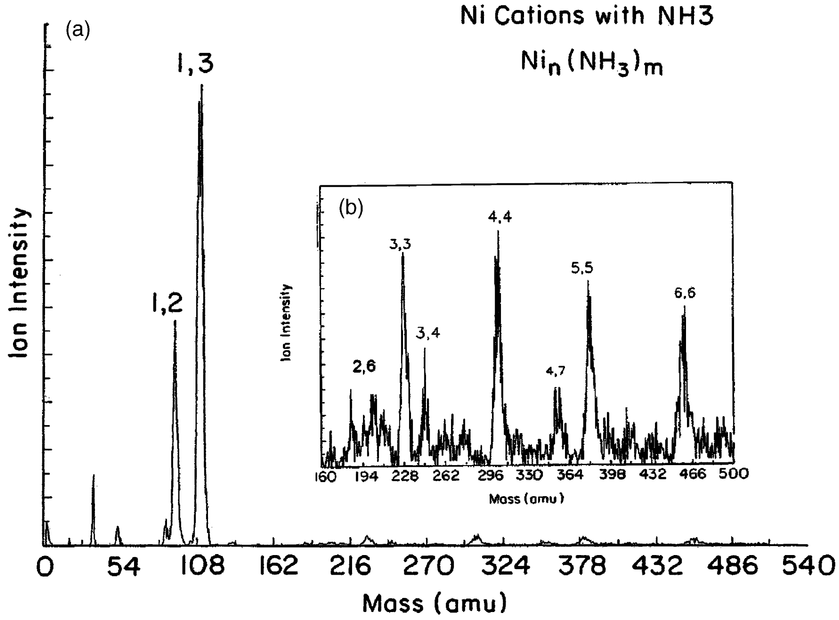

Fig. 2. (a) Ni cation reactions with NH_3, the peaks corresponding to Ni_n–$(NH_3)_m$ sizes are labeled by *n*, *m* in the mass spectrum. (b) Larger clusters are displayed in the insert.

show the final products of the Ni–NH_3 at the saturated NH_3 condition. There are two distinct features. Fig. 2a is the Ni–NH_3 reaction mass spectrum. Nickel monomer association of NH_3 is dominated by the peaks of Ni:ligand = 1:2 and 1:3. This shows that it is difficult to attach more than three NH_3 molecules to a single Ni site under the present, well thermalized, experimental conditions which do not involve expansion techniques normally used to affect cluster formation and growth. The second noticeable feature is the dominating 1:1 stoichiometric ratio products beginning with nickel trimer shown in Fig. 2b. There are also additional secondary peaks at Ni_3–$(NH_3)_4$ and Ni_4–$(NH_3)_7$. Fig. 3 shows the pattern for the association of nickel with alcohols. The prominence of the 1,3 peak is similar to the pattern seen for the NH_3 as are most of the larger complexes as seen by comparing Fig. 2b and the insert in Fig. 3. The only notable difference is that there is also some modest intensity of the 1,4 and 2,4 species observable in the spectra. Very similar distribution patterns were seen for both alcohols, CH_3OH and C_2H_5OH, binding to nickel clusters.

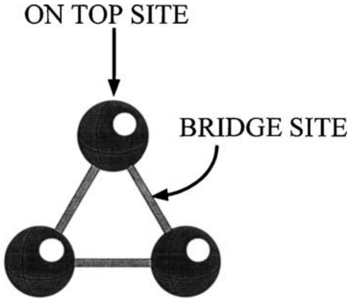

Fig. 4. Top and bridge sites in a nickel trimer.

The active sites of the Ni probed are nearly independent of the ligands used here, and the observations raise interesting questions about the binding of ligands to clusters and in particular the ground state geometries and the spin multiplicities. First of all, we want to answer the question of whether the binding sites of NH_3 to Ni clusters is on a bridge site or on a top site (see Fig. 4).

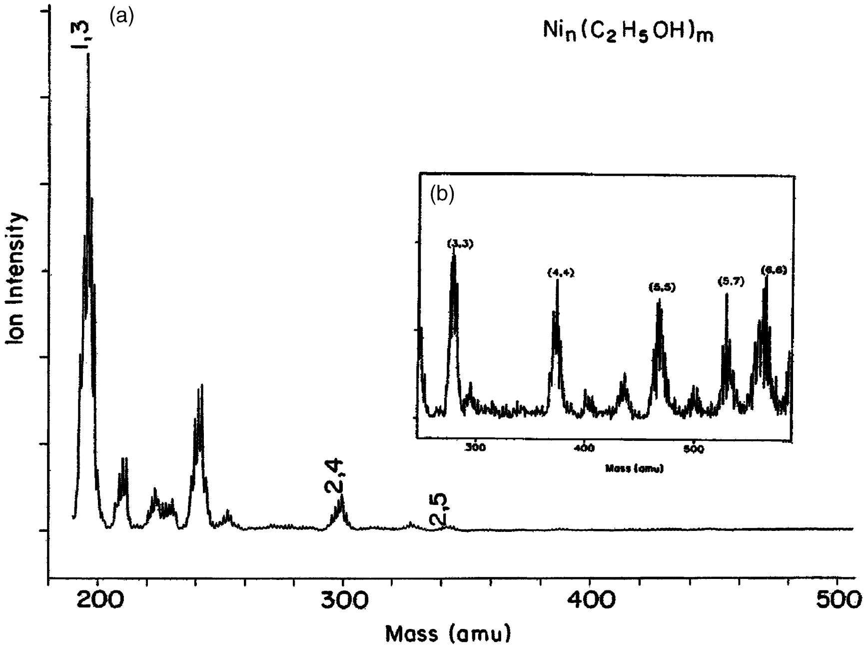

Fig. 3. (a) Ni cation reactions with C_2H_5OH, $Ni_n(C_2H_5OH)_m$ peaks are labeled by n, m in the mass spectrum. (b) Insert: Ni cation reactions with CH_3OH in the high mass range, $Ni_n(CH_3OH)_m$ peaks are labeled by n, m in the mass spectrum.

4.2. Binding of NH_3 molecules to Ni atom

Before we discuss the binding of NH_3 molecules to Ni clusters let us briefly recall the properties of pure Ni_n clusters. Small Ni_n clusters have been the subject of numerous theoretical investigations over the past few years and the reader is referred to a recent paper by Reddy et al. [24] for details. In Fig. 5, we show ground state geometries, binding energies and multiplicities of pure Ni_n clusters containing up to 4 atoms calculated using the NRLMOL. The ground state of Ni_2 is a spin triplet with a binding energy (BE) of 2.86 eV and an equilibrium bond length of 2.12 Å. For Ni_3, we obtain an equilateral triangle with a bond length of 2.24 Å and a BE of 5.54 eV. The ground state of Ni_4 is a D_{2d} structure. It has a multiplicity of 5 and a BE of 8.52 eV. All the results are in good agreement with recent density functional calculations [24].

To investigate the nature of Ni–NH_3 bonding, we begin with a consideration of the binding of a single NH_3 molecule to Ni. The NH_3 molecule can bind head on with N towards the Ni atoms as an upside down umbrella as depicted in Fig. 6a or with the H atoms toward the Ni atom as right side up umbrella shown in Fig. 6b. We found that even when the NH_3 is given the chance to have H approach Ni first, the configuration

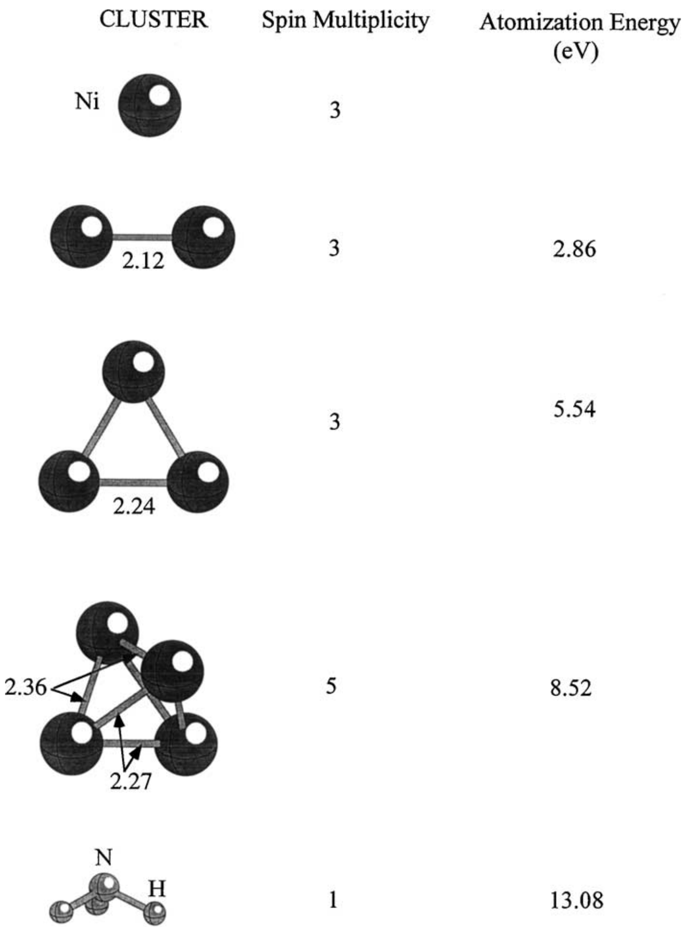

Fig. 5. The ground state geometries, spin multiplicities and atomization energies (AE) of the pure Ni_n and NH_3 clusters. The bond lengths are in angstrom (Å) and the binding energies are in electron volts (eV).

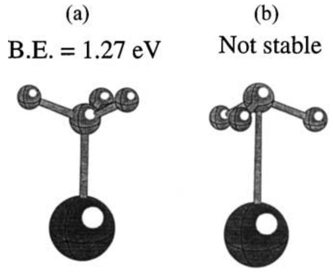

Fig. 6. Umbrella configurations of Ni bonding with NH_3.

flipped back to the N–Ni bonding configuration after the optimization. The ground state of Ni–NH_3 is therefore a spin singlet with N attached to Ni atoms as shown in Fig. 6a. The Ni–N–H diheral angle was found to be 110°.

The NH_3 BE is defined as

$$\text{Ni–NH}_3 \rightarrow \text{Ni} + \text{NH}_3$$

$$\text{BE} = E(\text{Ni}) + E(\text{NH}_3) - E(\text{Ni–NH}_3) \quad (1)$$

We find a BE of 1.27 eV. We also find a spin triplet with a Ni–N bond length of 2.05 a.u. and a BE of 0.82 eV. In order to further probe the nature of bonding, we carried out an analysis of the resulting electronic charge density by calculating the total charge within radii of appropriate sizes drawn around the various atoms. We found that the Ni sites gain around 0.78 e^-. The Ni–NH_3 molecule was found to have a dipole moment of 1.03 Debye. This shows that the binding has an appreciable ionic character.

We now consider the binding of two NH_3 to Ni. It can either be by direct binding of Ni to the two NH_3 molecules or alternatively whereby one NH_3 binds to Ni and the second NH_3 binds with the first NH_3. The ground state corresponds to the first situation and in Fig. 7, we have shown the ground state geometry for the spin singlet and triplet multiplicities. The BE for the two NH_3

$$\text{Ni(NH}_3)_2 \rightarrow \text{Ni} + 2\text{NH}_3$$

$$\text{BE} = E(\text{Ni}) + 2E(\text{NH}_3) - E(\text{Ni–(NH}_3)_2) \quad (2)$$

molecules is 2.93 eV which corresponds to a BE per atom of 1.47 eV. This is higher than the case of a single NH_3 molecule and shows that the binding increases as a molecule is added.

For the case of Ni–$(NH_3)_3$, we tried two possible geometries. One where all the NH_3 are directly attached with Ni and the other where NH_3 binds with NH_3 through an NH_3–NH_3 bond instead of with a Ni. Surprisingly, the ground state corresponds to a spin singlet (Fig. 7) with one NH_3 weakly bound to another NH_3 and Ni. This is a highly asymmetric structure and the BE for the additional NH_3 is only 0.25 eV. We also find that the three NH_3 can bind to Ni in a higher multiplicity state however, the BE of this state is lower than the previous one.

In the case of Ni–$(NH_3)_4$, we considered various geometries. It is interesting that in its ground state, the Ni–$(NH_3)_4$ does prefer to have NH_3 in a nearly planar shape somewhat similar to the case of the solutions where it is a square structure [25]. The ground state is again a spin singlet and the BE of the additional NH_3 is only 0.19 eV. This shows that the attachment of NH_3 to a single Ni site becomes progressively less stable as NH_3s are added beyond Ni–$(NH_3)_2$. We also found that the ground state for the spin triplet is a tetrahedral configuration, however, this state is lower in energy than the singlet state.

One of the common features of all the structures is that the Ni–NH_3 bond length in the singlet structures is around 1.8–1.9 Å while in all the triplet configurations the bond lengths are 2.05–2.19 Å. This shows that while the attachment of NH_3 quenches the Ni moments, if one could stabilize the structures with the Ni–NH_3 bond lengths around 2.04 Å, the clusters would maintain a high spin state. Does it really happen?

Before proceeding further, we would like to add that for all the Ni–$(NH_3)_n$, we also carried out calculations on cationic clusters to examine if the energetics would be affected by the charged state. This is needed since the adsorption experiments are carried out on cationic clusters. The results showed that the ground states have the lowest spin multiplicity as in the neutral clusters. The energy gain in adding one, two and three NH_3 for the cationic clusters are 2.97, 2.47 and 0.97 eV, respectively, compared to 1.27, 1.66

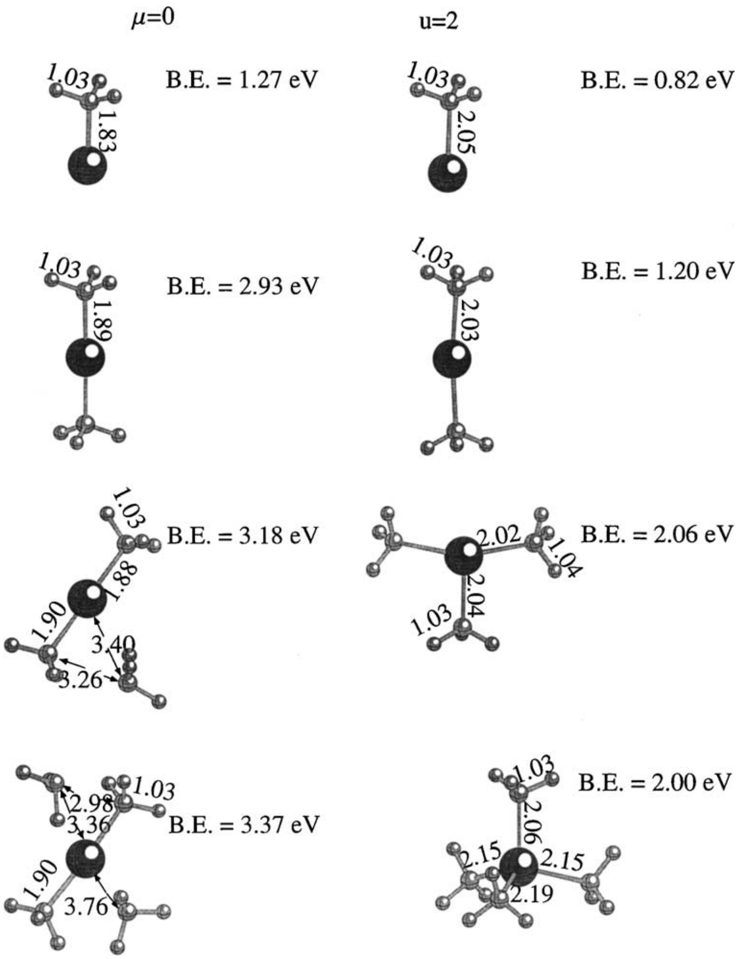

Fig. 7. Ground state geometries and the total binding energy of NH_3 clusters to a single Ni atom for various multiplicities. The bond lengths are in angstrom (Å) and the binding energies are in electron volts (eV).

and 0.25 eV for the neutral clusters. Note that in both cases, the energy for adding the third NH_3 is lower than the first two indicating that the energetic trends are similar. Since the charging effects are expected to be most dominant at smaller sizes, we believe that our studies on the larger neutral clusters will be applicable to the adsorption experiments on cationic clusters. As pointed out before, the theoretical calculations are carried out on neutral clusters since most of the emphasis here is on the changes in magnetic moment and the magnetic experiments are carried out on neutral clusters.

4.3. *Binding of NH_3 to Ni_2*

Ni_2 presents the most interesting example of the interplay between adsorption and magnetism. The ground state of Ni_2 is a spin triplet. The first NH_3 molecule binds in "on-top" mode (Fig. 8). The ground state is a spin triplet and it is 0.59 eV more stable than the singlet configuration. The NH_3 molecule is bound by 0.84 eV which is smaller than the BE of an NH_3 to a single Ni site. The ground state for Ni_2–$(NH_3)_2$ is a chair configuration where the NH_3s bind at on-top sites. The BE per NH_3 molecule is 0.86 eV and the

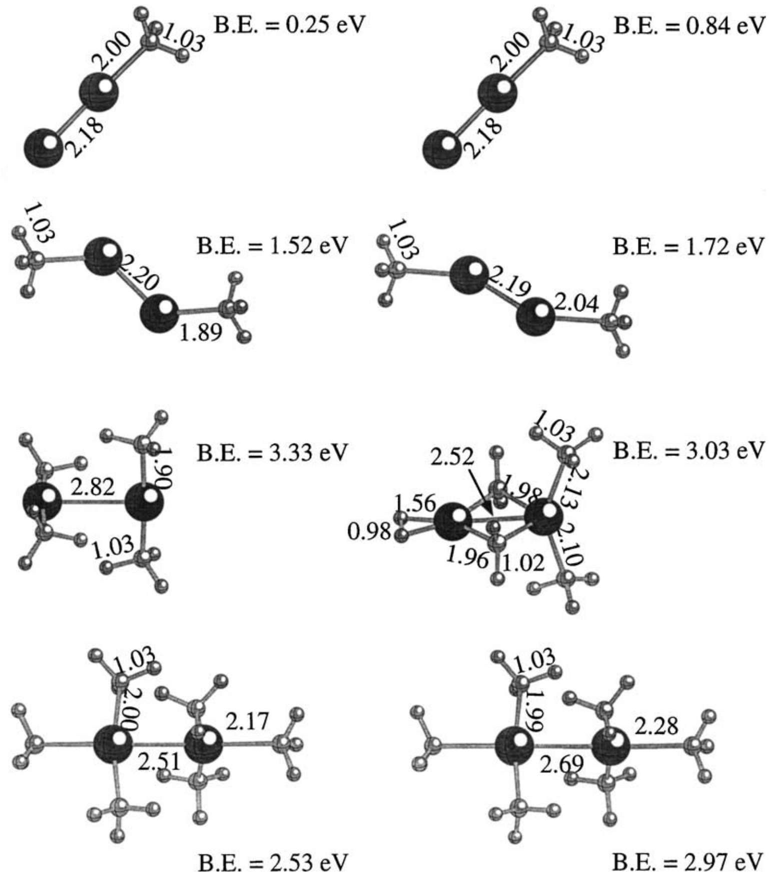

Fig. 8. Ground state geometries and the total binding energy of NH_3 clusters to a Ni_2 molecule for various multiplicities. The bond lengths are in angstrom (Å) and the binding energies are in electron volts (eV).

BE of the additional NH_3 is 0.88 eV compared to 0.84 eV for the first molecule. The ground state is a spin triplet and it is more stable than the singlet by 0.20 eV. This is a highly asymmetric configuration.

For Ni_2–$(NH_3)_4$, we tried several configurations. The ground state now corresponds to a spin singlet conforming to our earlier result that the addition of NH_3 generally leads to a quenching of the Ni moments. The BE per NH_3 is 1.01 eV. What is interesting is that the ground state of the spin triplet configuration corresponds to a situation where the NH_3 molecule breaks into NH_2 and an H atom and the two H atoms form the NH_2 molecules attached in the bridge site to form an H_2 molecule. Since this is not the ground state configuration it will not be observed. However, it does show that these kinds of processes are possible but will be undetectable in ordinary experiments.

While the experimental mass spectra show a dominant peak at 2:4 adducts, the 2:6 adduct is very weak. To examine this, we carried out calculation on Ni_2–$(NH_3)_6$. The ground state configuration corresponds to NH_3 adsorbed on on-top sites. There are, however, two interesting features. Firstly, the spin triplet is more stable than the spin singlet. This reappearance of magnetism on continuous adsorption is, in our view, a unique feature. Note that the Ni–N bond length in the spin triplet state is larger than in the spin singlet configuration. We will come to this point later. The other point is that the BE of the six NH_3 molecules is less than for Ni–$(NH_3)_4$ cluster. It is therefore energetically favorable for the Ni_2–$(NH_3)_6$ cluster to fragment to Ni_2–$(NH_3)_4$ and two NH_3 molecules. We believe that this energetic instability is responsible for the weak peak corresponding to Ni_2–$(NH_3)_6$ in the mass spectrum of Ni_2–$(NH_3)_m$ clusters.

4.4. *Binding of NH_3 to Ni_3 and Ni_4*

For the case of Ni_3 and Ni_4, we only examined limited compositions. For Ni_3 only the (3,3) peak is observed in the experimental mass spectrum. We therefore carried out studies on Ni_3–$(NH_3)_3$ and Ni_3–$(NH_3)_4$ clusters. Various geometries were tried and in Fig. 9, we show the corresponding minimum energy configurations for various multiplicities. For Ni_3–$(NH_3)_3$, the ground state corresponds to an on-top arrangement and the ground state structure is a planar structure. The ground state is a spin triplet and the BE of the NH_3 molecules is 8.67 eV. Addition of an NH_3 molecule leads to a complete rearrangement of the structure. The Ni_3 assumes a linear structure and the four NH_3 molecules bind to the outer atoms. The BE of the NH_3 molecules is however less than in the case of Ni_3–$(NH_3)_3$. Any Ni_3–$(NH_3)_4$ will therefore lose an NH_3 and assume a more stable structure. This explains the weakness of the 3:4 adduct in the mass spectrum. Another surprising feature is that the ground state is a spin singlet. The magnetic moment per Ni atom in a bare linear Ni_3 cluster is higher

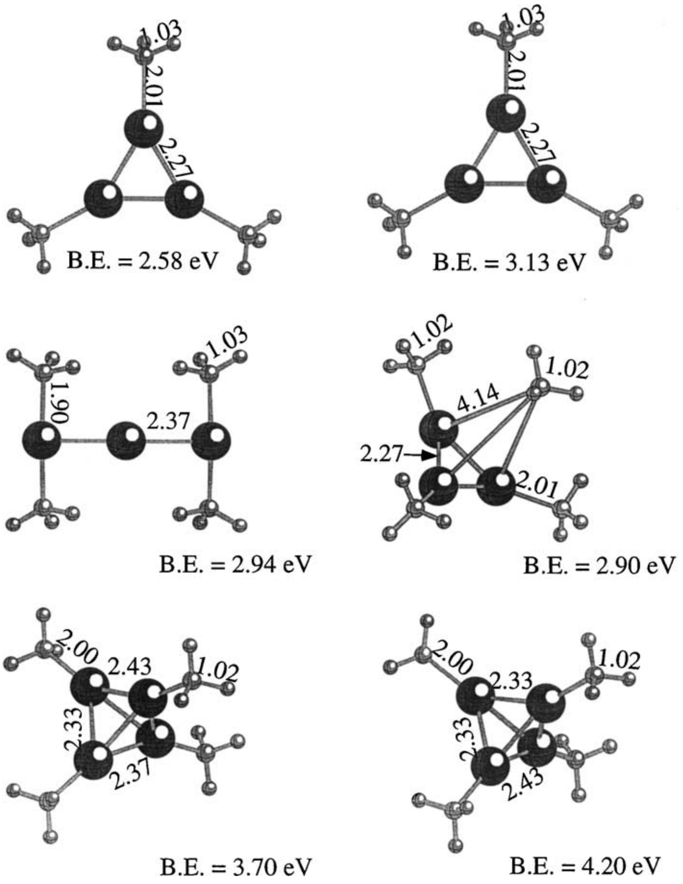

Fig. 9. Ground state geometries and the total binding energy of NH_3 clusters to Ni_3 and Ni_4 clusters for various multiplicities. The bond lengths are in angstrom (Å) and the binding energies are in electron volts (eV).

than in the triangular structure. The adsorption of NH_3, however, leads to a quenching of the magnetic moments.

For Ni_4–$(NH_3)_4$, the ground state is a tetrahedral Ni_4 with a NH_3 attached to each Ni atom in the on-top configuration. Although we optimized the geometry without any symmetry constraints, the final structure has a near D_{2d} symmetry. The ground state configuration is a spin triplet and the Ni–Ni bonds are stretched from those in the bare cluster. The BE per NH_3 is 1.06 eV which is comparable to that of other clusters.

The present results slightly deviate from the common trends regarding the binding of ligands to metal dimers. Recent studies have shown that for a majority of cases the metal cluster dimers form significantly stronger bonds with ligands such as NH_3, CO, and C_2H_4 than the corresponding metal atoms. For example, in the reactions of Ag_2 and Mo_2 with NH_3, 1:1 stoichiometry complex ratios are formed at high pressures and long residence times in the reactor [26]. It is believed that the Ag, Au, and Cu dimer complexes with NH_3 all have linear configurations because σ repulsion is alleviated. The second ligand stabilizes the binding, so the polarization induced by the first ligand is not the dominant factor. While our optimized results show a larger BE of the NH_3 to the Ni dimer, the difference from the binding to a single Ni is relatively small. We also found a switching reaction of NH_3 with the Ni dimer cation. The switching reaction was done with a double quadruple mass spectrometer apparatus in our group. It was found that NH_3 switches off one Ni atom when it reacts with the Ni dimer. We believe that this arises due to the attachment of two NH_3 molecules to the same Ni site. As our ab initio results show, the BE of two NH_3 molecules to a single Ni site is more than the BE of Ni_2. It is possible that the switching reaction by NH_3 is the reason we do not see a Ni_2–$(NH_3)_2$ peak in the mass spectrum.

Next, we consider the variation of the magnetic moment of Ni_n clusters upon adsorption of NH_3. In all cases we observe that the initial addition of NH_3 leads to a quenching of the magnetic moments. This quenching is consistent with the fact that the Ni–NH_3 bonding proceeds via a charge transfer from NH_3 to the Ni site. Note that the Ni–N bond lengths in the case of triplet lowest energy configurations are larger than in the case of the singlet configurations. We find that at high coverage Ni_2–$(NH_3)_m$ clusters can recover their lost magnetic moments. To understand these behaviors, we carried out a calculation of the singlet and triplet configurations of a Ni–NH_3 dimer as a function of Ni–N separation. For each separation and spin multiplicity, the positions of the H atoms were optimized. In Fig. 10, we show the variation of the total energy as a function of Ni–N separation for all these cases. Note that for larger Ni–N separations, the triplet state is more stable while at shorter separations the singlet state is more stable. The reappearance of magnetism in Ni–$(NH_3)_m$ clusters is associated with the increase in Ni–NH_3 separation at enhanced coverage.

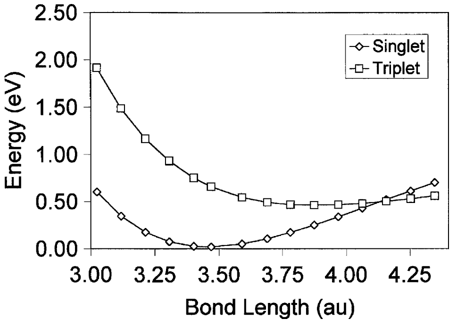

Fig. 10. The relative stability of the singlet and triplet spin configurations for a Ni–NH_3 cluster as a function of Ni–N separation.

In a recent paper [27], we had reported preliminary results of our investigations on Ni_n–$(NH_3)_m$ clusters using the Gaussian codes [28] and a smaller STO-3g basis. In that study pseudopotentials were used to replace the ionic cores. Those calculations were carried out using symmetry and therefore did not allow full variational freedom. While the present results do qualitatively agree with the previous results in that the initial NH_3 adsorption leads to a quenching of the Ni_n moments and that the moments can reappear at large coverage, the quantitative changes in the moments are different. This shows that it is necessary to perform symmetry-unrestricted calculations to get quantitatively accurate results.

5. Conclusion

The present results show that NH_3 reacts with Ni via direct binding on the top reaction site, with no bridge site being found in the ground state Ni_n–$(NH_3)_m$ clusters. The calculations show that the Ni_3 structure does not undergo reconstruction when it forms Ni_3–$(NH_3)_3$ but undergoes a substantial rearrangement when forming Ni_3–$(NH_3)_4$ clusters. Ni_4 is also found to have a similar structural framework as that of Ni_4–$(NH_3)_4$. The calculated binding energies explain the experimental mass peak abundance and the truncation of certain peaks in the mass spectra. The calculations of the Ni_2–$(NH_3)_n$ clusters also indicate that switching reactions occur in the Ni–NH_3 reaction which are similar to those observed with the flowtube reactor for Ni cluster cations. Our studies also show that the magnetic moments of Ni_n clusters are initially quenched upon adsorption of NH_3 but the moments reappear at high coverages. We have become aware that Knickelbein has performed Stern–Gerlach experiments on Ni_n clusters coated with NH_3 [29]. Their preliminary results indicate that the NH_3 adsorption quenches the magnetic moment of Ni_n clusters in agreement with current studies.

Acknowledgements

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References

[1] K. Sattler (Ed.), Cluster Assembled Materials, Trans Tech Publications, Zurich, Switzerland, 1996.
[2] H.H. Anderson (Ed.), Small Particles and Inorganic Clusters, Springer, New York, 1997.
[3] R.L. Whetten, D.M. Cox, D.J. Trevor, A. Kaldor, Phys. Rev. Lett. 54 (1985) 1494.
[4] X. Li, H. Wu, X.B. Wang, L.S. Wang, Phys. Rev. Lett. 81 (1998) 1090.
[5] S.N. Khanna, S. Linderoth, Phys. Rev. Lett. 67 (1991) 742.
[6] B.V. Reddy, S.N. Khanna, B.I. Dunlap, Phys. Rev. Lett. 70 (1993) 3323.
[7] A.J. Cox, J.G. Louderback, L.A. Bloomfield, Phys. Rev. Lett. 71 (1993) 923.
[8] S.N. Khanna, P. Jena, Phys. Rev. B51 (1995) 13705.
[9] E.K. Parks, S.J. Riley, Z. Phys. D33 (1995) 59.
[10] F.A. Reuse, S.N. Khanna, Chem. Phys. Lett. 234 (1995) 77.
[11] S.E. Apsel, J.W. Emmert, J. Deng, L.A. Bloomfield, Phys. Rev. Lett. 76 (1996) 1441.
[12] E.K. Parks, B.J. Winter, T.D. Klots, S.J. Riley, J. Chem. Phys. 94 (1991) 1882.
[13] E.K. Parks, L. Zhu, J. Ho, S.J. Riley, J. Chem. Phys. 100 (1994) 7206.
[14] E.K. Parks, L. Zhu, J. Ho, S.J. Riley, J. Chem. Phys. 102 (1995) 7377.
[15] J.W. Basch, M.D. Newton, J. Chem. Phys. 73 (1980) 4492.
[16] G. Blyhoder, Surf. Sci. 42 (1974) 249.
[17] A.N. Andriotis, N. Lathiotakis, M. Menon, Chem. Phys. Lett. 260 (1996) 15.
[18] M.S. Stave, A.E. Depristo, J. Chem. Phys. 97 (1992) 3386.
[19] M. Castro, C. Jamorski, D.R. Salahub, Chem. Phys. Lett. 271 (1997) 133.
[20] B. Chen, Ph.D. Thesis, Pennsylvania State University Press, 1997.
[21] R.E. Leuchtner, A.C. Harms, A.W. Castleman Jr., J. Chem. Phys. 92 (1990) 6527.
[22] M.R. Pederson, K.A. Jackson, Phys. Rev. B 41 (1990) 7453; K.A. Jackson, M.R. Pederson, Phys. Rev. B 42 (1990) 3276.
[23] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[24] B.V. Reddy, S.K. Nayak, S.N. Khanna, B.K. Rao, P. Jena, J. Phys. Chem. A1998 (1998) 1748.
[25] N.N. Greenwood, A. Earnshaw (Eds.), Chemistry of Elements, Pergoman Press, New York, 1984.
[26] P.M.W. Gill, L. Radom, J. Am. Chem. Soc. 110 (1988) 4931.
[27] B. Chen, A.W. Castleman Jr., S.N. Khanna, Chem. Phys. Lett. 304 (1999) 423.
[28] M.J. Frisch, et al., Gaussian 94, Gaussian Inc., Pittsburgh, PA, 1995.
[29] M. Knickelbein, Personal communication.