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Spectroscopy of Ni-n(benzene)(m) anion complexes

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Total energy calculations based on the generalized gradient approximation to the density functional theory reveal that the Ni(benzene) and Ni(benzene)$_2$ anions are unstable against autodetachment of the additional electron while other anion complexes containing more than one Ni atom are stable. Although the adiabatic electron affinities increase with Ni content, they are significantly smaller than those in pure Ni clusters containing the same number of Ni atoms. The difference between adiabatic electron affinities and vertical detachment energies are around 0.2 eV in most cases, indicating that the equilibrium geometries of Ni_n(benzene)$_m^-$ are not significantly altered from their corresponding neutral geometries. The vertical transitions from the anion to the neutral provide new insight into the magnetic moment of these organometallic complexes. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1499954]

I. INTRODUCTION

Recently considerable attention has been given towards a fundamental understanding of the interaction of transition-metal atoms with organic complexes without having to deal with the complexities associated with solvents.[1–28] This is accomplished through gas phase studies where transition-metal atoms created by laser vaporization are allowed to cluster in the presence of organic molecules such as benzene (C_6H_6 or Bz). Experimental studies[1–20] of the mass spectra, dissociation energies, ionization potentials and mobilities of the organometallic complexes then provide information on their electronic structure and stability. One of the systems that has been studied systematically[20] involves $3d$ transition-metal atoms, M (M = Sc, Ti, V, Cr, Mn, Fe, Co, and Ni) interacting with benzene molecules.

Kaya and co-workers[20] observed that while the mass spectra of M_n(benzene)$_m$ are characterized by $m = n + 1$ for M = Sc, Ti, V, Cr, and Mn, those involving M = Fe, Co, and Ni behave very differently. Among these Ni_n(benzene)$_m$ complexes have the most unusual behavior: For example, the mass spectra of Ni_n(Bz)$_m$ possess peaks at $(n,m) = (1,2)$, (2,2), (3,2); (2,3), (3,3), (4,3), (5,3), (6,3); (6,4), (7,4), (8,4), (9,4), (10,4), and (10,5). No other transition-metal–benzene complex exhibits so many peaks in the mass spectra. The fact that the number of metal atoms can far exceed the number of benzene molecules indicates that the geometries of these clusters are most likely the one where the benzene molecules cage the metal cluster. Second, the ionization potential[20] of Ni_n(Bz)$_m$ complexes decrease rapidly from $(n,m) = (3,3)$ to (5,3), and then decrease again from $(n,m) = (5,3)$ to (7,4). To the best of our knowledge, no photodetachment spectroscopy experiments of $3d$ transition-metal–benzene complexes, with the exception of V(Bz) and Co(Bz),[29] have been systematically carried out. Motivated by our theoretical calculations of the spectroscopy of Ni_n(Bz)$_m$ cluster anions, Bowen's group has recently measured the photodetachment spectra of Ni-Bz complexes.[30]

Theoretical studies[21–26] of the $3d$ metal–benzene com-

plexes have mostly concentrated on either neutral or cationic species containing up to two benzene molecules and three metal atoms. Unlike the transition-metal–benzene complexes involving early part of the $3d$ series that have multidecker sandwich structures, the geometries[27,28] of neutral and cationic Ni_n(Bz)$_m$ complexes are characterized by Ni clusters caged between benzene molecules. Earlier calculations[25] on Ni_n(Bz)$_m$ anion complexes were restricted to $n = 1$ and $m = 2$ and that too having D_{6h} symmetry. The adiabatic electron affinities (that measure the energy difference between the ground states of the anion and neutral) were found to be negative for the Ni–benzene systems, indicating that $Ni(Bz)_1^-$ and $Ni(Bz)_2^-$ anions are unstable against autodetachment of the extra electron.

To examine if the larger Ni_n(Bz)$_m^-$ clusters are stable against autodetachment as n increases and whether their geometries have D_{6h} symmetry, we have performed the first calculations based on the *ab initio* theory of the equilibrium geometries and total energies of Ni_n(Bz)$_m^-$ anion complexes ($n = 1–3$ and $m = 1,2$) without any symmetry constraint and for various spin multiplicities. These results, when compared with the total energies of the neutral complexes having the geometry of the anion, but of spin multiplicities differing from the anion by ± 1, yield vertical electron detachment energies. On the other hand, the difference in the ground-state energies of the anion and that of the neutral yield values of adiabatic electron affinities. Our results are consistent with the preliminary experimental results of Bowen and co-workers. In Sec. II we outline briefly our theoretical approach. The results are discussed and summarized in Sec. III.

II. THEORETICAL METHOD

Total energies and equilibrium geometries of Ni–benzene complexes are calculated using the molecular orbital approach and density functional theory. The atomic orbitals of the constituent atoms are represented by a set of Gaussian orbitals. We have used the split-valence LANL2DZ basis set[31,32] in the GAUSSIAN 98 code.[32] As this basis set uses
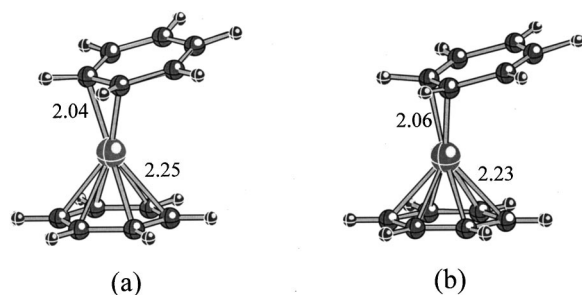
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FIG. 1. Comparison of ground-state geometries of Ni(Bz)$_2$ cluster obtained from (A) LANL2DZ and (B) 6-311++$G\ddagger$ basis sets.

an effective core potential for the core electrons for the Ni atom, the accuracy of the results obtained using this basis has been tested by repeating some of the calculations with an all-electron basis set. The exchange-correlation potential was incorporated using the generalized gradient approximation. We have used Becke–Perdew–Wang formulation[33] commonly referred to as BPW91 in the Gaussian code. The equilibrium geometries were obtained by searching for the lowest energy on the Born–Oppenheimer surface through the calculation of the forces at the atomic sites and moving the atoms around till the forces vanished. No symmetry was used in the calculation. The calculations were repeated for higher spin multiplicities starting with singlet states for even-electron and doublet for odd-electron systems to determine the preferred spin configuration of the cluster.

III. RESULTS AND DISCUSSIONS

A. Accuracy of the frozen core basis set

The computational complexity and the cost in optimizing the geometries of Ni$_n$(Bz)$_m$ neutral and anionic complexes containing up to three Ni atoms and two benzene molecules have forced us to choose an effective core potential for the core electrons leading to the LANL2DZ basis set. The accuracy of this basis set was tested earlier[28] while treating neutral and cationic Ni–benzene complexes. While the equilibrium geometries and C-C, C-H, and Ni-C distances remained essentially unaffected, the energies differed by no more than 0.3 eV. Since the electrons in a negatively charged cluster are more diffused, we have examined the effects of diffuse functions by performing calculations on Ni(Bz)$_2$ using the 6-311++G** basis, which contains both diffuse functions and polarizations. Figure 1 compares the geometries for this system obtained from the LANL2DZ basis and the extended all-electron basis. It is clear that the difference between the two geometries is almost negligible. The binding energies of Ni(Bz)$_2$ calculated with respect to its dissociation into a Ni atom and two benzene molecules are 2.61 eV and 2.67 eV, respectively for the LANL2DZ and the 6-311++G** basis sets. This comparison gives added confidence in the use of the effective core basis.

B. Geometries

In Figs. 2(A), 2(B), and 2(C) we plot the equilibrium geometries of neutral, cationic, and anionic clusters, respec-

tively, involving up to three Ni atoms and two benzene molecules. We note that, in general, the structures remain relatively unchanged following an electron attachment (negative ions) or electron detachment (positive ions). The structure of Ni(Bz) is that of a metal atom sitting on top of the benzene molecules along the C_{6v} symmetry axis. The distance of the metal atom from the top of the benzene plane increases from 1.58 Å in the case of neutral Ni(Bz) to 1.70 Å in the case of a negative ion and to 1.76 Å in the positive ion. In the Ni$_2$(Bz) complex the Ni atoms sit atop the benzene molecule irrespective of its charge state, but the Ni–Ni bond distance increases from 2.27 Å in the neutral to 2.38 Å in the anion and 2.36 Å in the cation. A similar trend is also observed for Ni$_3$(Bz). The maximum distortion in the structure is found in Ni(Bz)$_2$ where the two benzene planes are nearly parallel in the cation but are tilted maximally with respect to each other in the anion. The geometries of Ni$_2$(Bz)$_2$ and Ni$_3$(Bz)$_2$ are essentially the same among the neutral, cation, and anion configurations. These small changes are reflected in the energetics of these clusters.

C. Adiabatic electron affinity and vertical detachment energies

In a photodetachment experiment, the added electron of a mass-selected negative-ion cluster is photodetached by a fixed frequency laser. The analysis of the kinetic energy of the photodetached electron provides the adiabatic electron affinity (AEA),

$$\text{AEA} = E^- - E^0,$$

and the vertical detachment energies. The AEA measures the difference in the total energy of the anion, E^-, and that of its neutral, E^0, in their respective ground-state configuration. The vertical detachment energy, on the other hand, measures the difference in the energy of the anion in its ground state and that of its neutral in having the same geometry as the anion, i.e., by not allowing the neutral to relax to its ground state. The vertical detachment, in general, can produce two prominent transitions where the spin multiplicities of the neutral differ from the anion by ± 1. There are other transitions as well that could result from the electronic or vibronic excited states.

In Table I we list the adiabatic ionization potentials (the difference in the total energies between the neutral and the cation corresponding to their ground-state configuration) and the vertical ionization potentials (the difference in ground-state energy of the neutral and the cation having the ground-state geometry of the neutral) of Ni$_n$(Bz)$_m$ complexes. Note that the vertical ionization potentials, with the exception of Ni(Bz)$_2$ and Ni$_2$(Bz)$_2$, are within 0.2 eV of the adiabatic ionization potential. This small energy difference mirrors the small changes in the geometries seen in Fig. 2. This has been discussed earlier in detail and is not elaborated here. In this paper we focus on the anions.

The adiabatic electron affinities of Ni$_n$(Bz)$_m^-$ complexes are also given in Table I. We note that complexes containing one Ni atom have negative electron affinities, i.e., they are unable to attach an electron. Note that the electron affinity of a Ni atom is 1.156 eV. Thus adding one or more benzene
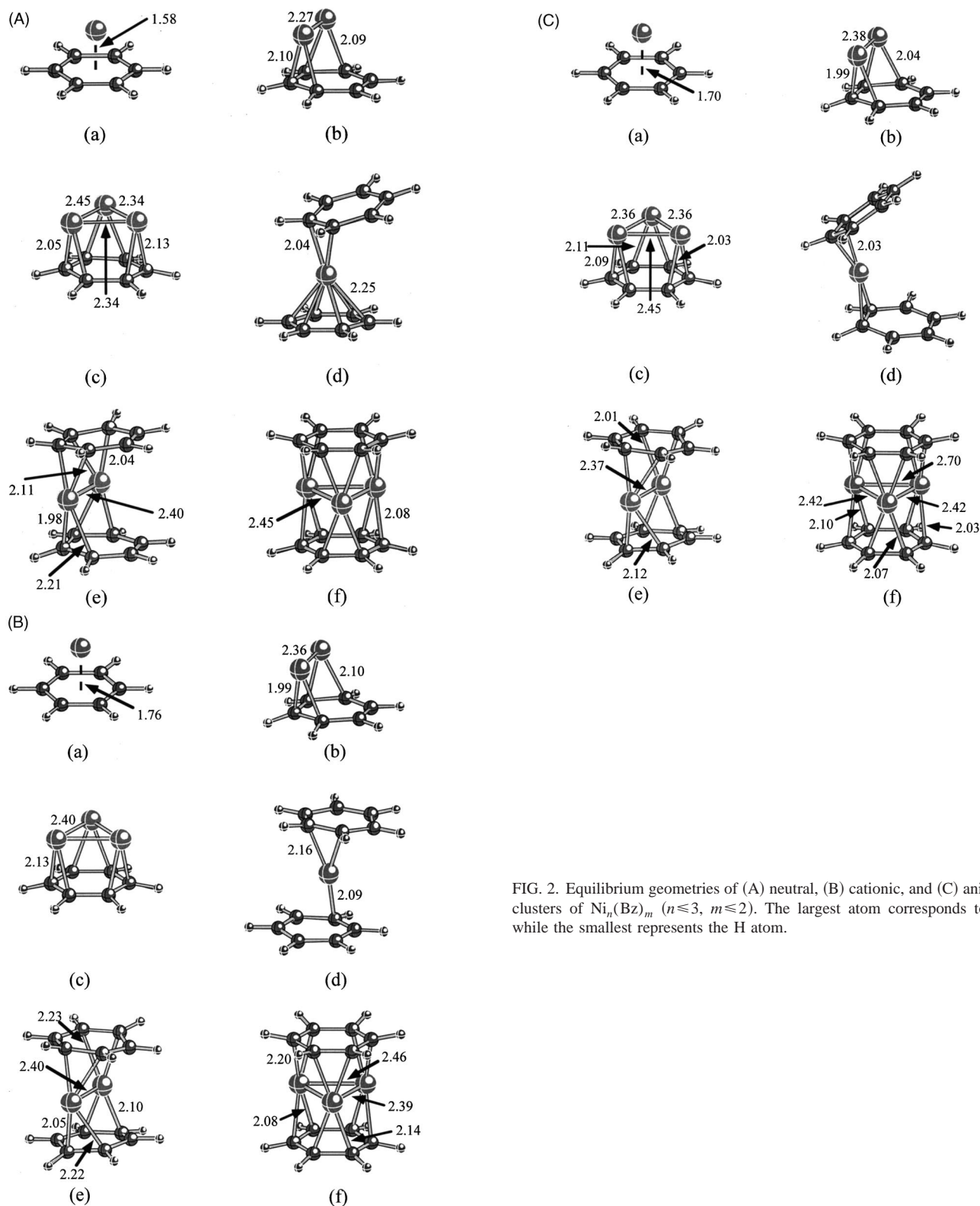
FIG. 2. Equilibrium geometries of (A) neutral, (B) cationic, and (C) anionic clusters of $Ni_n(Bz)_m$ ($n \leqslant 3$, $m \leqslant 2$). The largest atom corresponds to Ni while the smallest represents the H atom.

molecules reduces this electron affinity to the point at which they are negative. This is understandable since the electron affinity of benzene is negative. These results are consistent with the recent experiments of Bowen and collaborators,[30] who did not observe the spectra of $Ni(Bz)_m^-$ and $Ni(Bz)_2^-$. Second, we note that the electron affinity increases as the number of metal atoms increases for fixed benzene content. For example, the adiabatic electron affinities of $Ni_2(Bz)$ and $Ni_3(Bz)$ are, respectively, 0.48 and 0.78 eV. These electron affinities are, however, smaller than those of Ni_2 and Ni_3, which are 0.926 ± 0.01 and 1.41 ± 0.05 eV,[34] respectively. Once again, addition of benzene reduces the electron affini-

TABLE I. Vertical and adiabatic ionization potentials and electron affinities of Ni$_n$(Bz)$_m$ clusters (in eV).

| | Ionization potential (eV) | | | Electron affinity (eV) | |
| | Vertical | | | | |
Cluster	Theory	Experiment	Adiabatic	Vertical	Adiabatic
Ni(Bz)	6.36	5.99–6.42	6.17	⋯	−0.35
Ni$_2$(Bz)	5.81		5.70	0.72	0.48
Ni$_3$(Bz)	5.70		5.62	0.81	0.78
Ni(Bz)$_2$	6.12	5.86	5.68	⋯	−0.39
Ni$_2$(Bz)$_2$	6.37		5.76	0.44	0.17
Ni$_3$(Bz)$_2$	6.34		6.12	0.61	0.40

ties of metal–benzene complexes compared to the pure metal clusters. Similar systematics are seen in Ni$_n$(Bz)$_2$ complexes where the electron affinities increase with n, but are smaller than those in Ni$_n$(Bz) complexes. We have refrained from making a quantitative comparison of these results with the experiment of Bowen and co-workers, as their experimental analysis is preliminary. However, Bowen's group has observed the anion spectra of Ni–benzene complexes containing more than one Ni atom.[30]

D. Spin multiplicities ($M = 2S + 1$)

In Table II the spin multiplicities of these anionic complexes corresponding to the ground-state configurations are given and are compared with those of the neutral and cationic complexes. The ground-state multiplicities of neutral complexes with the exception of Ni$_2$(Bz) and Ni$_3$(Bz) are singlets, i.e., their total magnetic moments are zero. Note that Ni as a free atom possesses a magnetic moment of $2\mu_B$ and the bulk is ferromagnetic with a magnetic moment of $0.6\mu_B$/atom. Ni clusters are ferromagnetic as well with magnetic moments/atom values intermediate between the free atom and the bulk that generally decrease with cluster size. However, in most Ni–benzene complexes, the magnetic moments are quenched. This quenching is brought about by the interaction of Ni $3d$ eletrons with the π electrons of benzene. As the Ni content increases with fixed benzene content as in Ni$_2$Bz and Ni$_3$Bz, the clusters do develop a magnetic moment, namely $2\mu_B$ each, but they are again quenched as more benzene molecules are added [see Ni$_2$(Bz)$_2$ and Ni$_3$(Bz)$_2$ results in Table II]. Note that the magnetic moments of pure Ni$_2$ and Ni$_3$ clusters are $2\mu_B$ each. Thus, we expect that larger Ni-Bz clusters such as Ni$_9$(Bz)$_4$ will possess a net magnetic moment, although it may be less than that of pure Ni$_9$.

TABLE II. Spin multiplicities of neutral, anionic, and cationic Ni$_n$(Bz)$_m$ complexes.

Cluster	Neutral Ni$_n$(Bz)$_m$	Anion Ni$_n$(Bz)$_m^-$	Cation Ni$_n$(Bz)$_m^+$
Ni(Bz)	1	2	2
Ni$_2$(Bz)	3	2	2
Ni$_3$(Bz)	3	2	4
Ni(Bz)$_2$	1	2	2
Ni$_2$(Bz)$_2$	1	2	2
Ni$_3$(Bz)$_2$	1	2	2

As these clusters are charged either by removing or adding an electron, the total number of valence electrons becomes odd, and thus the lowest magnetic moment (spin multiplicities) can be as small as $1\mu_B$. Note that except in the case of Ni$_3$Bz$^-$ this is indeed the case, and the magnetic moment of Ni$_3$Bz$^-$ is $3\mu_B$ and hence there is a spin multiplicity of 4.

No experiments are available to verify the predicted spin multiplicities of these clusters. The only experimental technique that has been used to study the magnetism of free atomic clusters involves the deflection of the neutral cluster beam in a Stern–Gerlach magnetic field.[35] However, clusters with zero magnetic moments cannot be deflected. In addition, the quantitative nature of the measured magnetic moment in the Stern–Gerlach experiment has been problematic as one usually invokes the superparamagnetic model to extract the magnetic moment. This procedure relies on the knowledge of the temperature of the cluster in addition to measuring small deflections accurately, and the precise value of the cluster's temperature has been a source of controversy.

Recently an alternative method has been suggested[36] to determine the magnetic moment unambiguously that avoids the issue of cluster temperature or the use of a Stern–Gerlach field. This procedure requires a synergy between photodetachment spectroscopy and theoretical calculations. We briefly summarize this procedure. Consider a cluster anion to have a spin multiplicity of M. As the electron is photodetached, the resulting neutral cluster should have spin multiplicity $M' = M \pm 1$. Thus, there should be at least two transitions in the photodetached spectra if $M > 1$. There could, however, be other transitions resulting from vibrationally and/or electronically excited states or the existence of isomers. If the neutral cluster is further ionized, the resulting cationic cluster can have spin multiplicities of $M'' = M' \pm 1$. Here M' refers to the ground-state spin multiplicities of the neutral cluster. These transition energies can be calculated theoretically, and a good agreement between these transition energies and experiment can illustrate the spin multiplicities of the neutral cluster without any ambiguity. This procedure has been successfully used[35] for deriving the magnetic moment of Fe$_3$ and Ni$_5$ clusters. Here we apply the same procedure to further illustrate the magnetism or lack of it in Ni–benzene complexes.

In Fig. 3 we show the transition energies from the ground state of the anion to the neutral having the same geometry as the anion but with spin multiplicities that differ
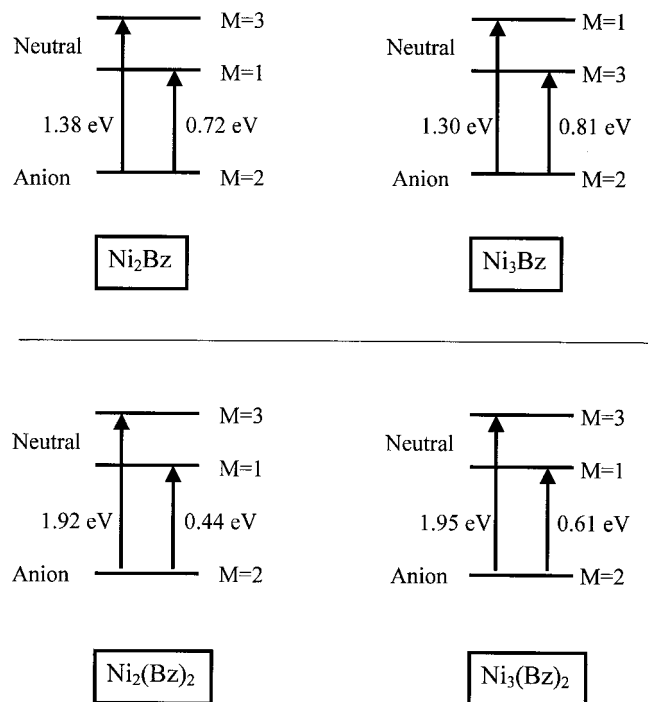
FIG. 3. Transition energies from the ground state of the anion $Ni_n(Bz)_m^-$ complexes to the corresponding neutral species having the same geometry as the anion, but with spin multiplicities differing by ± 1.
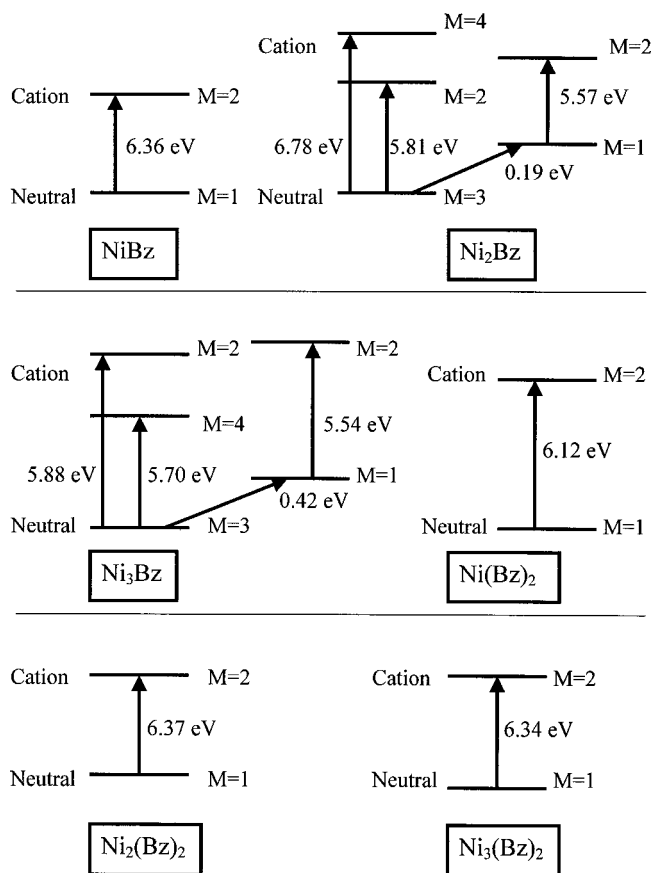

FIG. 4. Transition energies from the ground state of the neutral $Ni_n(Bz)_m$ complexes to the corresponding cationic species having the same geometry as the neutral, but having spin multiplicities that differ by ± 1.

by ± 1. These transitions are then referred to as the vertical transition energies. No results for $NiBz^-$ and $Ni(Bz)_2^-$ are given as these clusters are unstable against autodetachment of the extra electron. Note that for all clusters in Fig. 3 the transitions are from $M=2$ to $M'=1$ and 3. With the exception of Ni_3Bz, the lowest transition energy corresponds to the singlet state of the neutral. When photodetachment spectra are fully analyzed, results in Fig. 3 and Table I will provide three independent energies, namely, the adiabatic electron affinity and two vertical detachment energies with which theoretical results can be compared. Consequently, this will provide confidence in the predicted spin multiplicity of the anion.

To pinpoint the ground-state spin multiplicity of the neutral, one can further remove an electron from the neutral and measure the transition energies from the neutral to the cation. These are computed, and the results are shown in Fig. 4. We have computed, for this purpose, the total energy of the cation having the geometry of the neutral but with spin multiplicities $M''=M'\pm 1$. In the case of NiBz, the ground state is clearly a spin singlet state, and the vertical detachment energy to the spin doublet state of $NiBz^+$ is 6.36 eV. For Ni_2Bz the neutral has two isomers with the ground state having a spin multiplicity of 3. While the spin singlet state lies 0.19 eV above the ground states, the vertical transition from the spin triplet state lie at 5.81 and 6.78 eV, and the vertical transition from the spin singlet state lies at 5.57 eV. Similarly, there are two isomers of neutral Ni_3Bz, although the singlet state lies at a higher energy, namely 0.42 eV above the triplet ground state. The transitions from the triplet ground state to the quartet and doublet states of the neutral lie at 5.70 and 5.88 eV, respectively. The ground states of

$Ni_2(Bz)_2$ and $Ni_3(Bz)_2$ are singlets, and the corresponding vertical transitions are at 6.37 and 6.34 eV. We hope that these predictions will stimulate new experimental interest.

IV. CONCLUSIONS

In summary, we have calculated the electron affinity and vertical detachment spectra of $Ni_n(Bz)_m$ complexes from the anion to the neutral as well as from the neutral to the cation. While NiBz and $Ni(Bz)_2$ complexes are unable to attach an electron, the electron affinity is positive in larger complexes and increases as the Ni content increases for a fixed composition of benzene. For a given Ni content, addition of benzene lowers the electron affinity. The vertical transition energies are also calculated. It is argued that the comparison of the anion to neutral and neutral to cation detachment spectra with experiment can yield the spin multiplicities and, hence, the magnetic character of these clusters.

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