Photoelectron spectroscopy of nickel-benzene cluster anions

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$(\mathrm{Nickel})_n(\mathrm{benzene})_m^-$ cluster anions were studied by both mass spectrometry and anion photoelectron spectroscopy. Only $\mathrm{Ni}_n(\mathrm{Bz})_m^-$ species for which $n \geqslant m$ were observed in the mass spectra. No single-nickel $\mathrm{Ni}_1(\mathrm{Bz})_m^-$ species were seen. Adiabatic electron affinities, vertical detachment energies, and second transition energies were determined for $(n,m)=(2,1)$, (2,2), (3,1), and (3,2). For the most part, calculations on $\mathrm{Ni}_n(\mathrm{Bz})_m^-$ species by B. K. Rao and P. Jena [J. Chem. Phys. **117**, 5234 (2002)] were found to be consistent with our results. The synergy between their calculations and our experiment provided enhanced confidence in the theoretically implied magnetic moments of several nickel-benzene complexes. The magnetic moments of small nickel clusters were seen to be extremely sensitive to immediate molecular environmental effects. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1839864]

I. INTRODUCTION

Chemists have studied metal-benzene bonding in condensed phases and on surfaces for many years.[1–3] In the gas phase, metal-benzene complexes have also received substantial attention. Armentrout and co-workers[4,5] studied $M^+-\mathrm{Bz}_2$ ($M=$Ti–Cu, Ag; Bz=benzene) via collision-induced dissociation experiments. Duncan and co-workers[6,7] conducted photodissociation studies of $M^+-\mathrm{Bz}$ ($M=$Fe, Mg, Ag, and Bi) and infrared absorption spectroscopy on $V^+\mathrm{Bz}$. Bowers and co-workers[8] investigated vanadium/benzene cation clusters using ion mobility spectrometry. Freiser and co-workers[9] used Fourier transform-ion cyclotron resonance (FT-ICR) to study the dissociation of $\mathrm{Mn}^+\mathrm{Bz}$ and $\mathrm{Cr}^+\mathrm{Bz}$. Nakajima, Kaya, and co-workers[10–13] performed mass spectrometric and photoionization studies on $M-\mathrm{Bz}$ clusters and their cations ($M=$Sc–Cu) as well as photoelectron studies of vanadium-arene anion complexes. Eberhardt and co-workers[14] carried out photoelectron studies of $M_2\mathrm{Bz}^-$ ($M=$Pt,Pd,Pb) cluster anions. Our group[15–17] conducted photoelectron spectroscopy studies of $M_n(\mathrm{Bz})_m^-$ ($M=$Co,Fe,Ti) and on $\mathrm{Co}_n(\mathrm{pyridine})_m^-$ cluster anions. Broyer and co-workers[18] measured the electric dipole moment of $M\mathrm{Bz}_2$ ($M=$Sc, Ti, V, Co, Ni, Nb, Ta, and Zr) complexes.

In addition, several theoretical calculations have been conducted. Binding energies and geometries of transition metal cation-benzene complexes have been calculated by Bauschlicher, Partridge, and Langhoff,[19] by Koch and co-workers,[20] by Chaquin *et al.*,[21] and by Rao and co-workers.[22] Geometric structures of neutral transition metal-benzene complexes were investigated by Froudakis, Andriotis, and Menon,[23] Rao and co-workers,[22] and Yabushita and co-workers,[24] while Pandey and co-workers[25] explored the magnetic moments for such systems. Anions of transition metal-benzene complexes have been studied extensively by Rao, Pandey, Jena, and co-workers.[22,26,27]

By contrast, there have been fewer experimental and theoretical studies of nickel-benzene complexes. Experimental studies by Nakajima and Kaya[10,12] and by Broyer and co-workers[18] have investigated neutral and cationic nickel-benzene clusters. Theory has considered neutral,[21–26] cationic,[19,21,22,25,26] and anionic[22,25,27] charge states of nickel-benzene clusters. Both experiment[12] and theory[27] agreed that nickel-benzene clusters are best described as nickel cluster cores caged by benzene molecules. The calculations on nickel-benzene cluster anions are of particular relevance to the present work. Here, we report our mass spectrometric and photoelectron spectroscopic study of nickel-benzene cluster anions, $\mathrm{Ni}_n(\mathrm{Bz})_m^-$, focusing, with the aid of calculations by Rao and Jena,[27] on the implied magnetic properties of neutral nickel-benzene complexes.

II. EXPERIMENT

Negative ion photoelectron spectroscopy is conducted by crossing a mass-selected beam of anions with a fixed frequency photon source and energy analyzing the resultant photodetached electrons. This technique is governed by the energy-conserving relationship $h\upsilon=\mathrm{EKE}+\mathrm{EBE}$, where $h\upsilon$ is the photon energy, EKE is the measured electron kinetic energy, and EBE is the electron binding energy. The details of our apparatus have been described elsewhere.[28] Briefly, both mass spectra and anion photoelectron (photodetachment) spectra were collected on an apparatus consisting of a laser vaporization source, a linear time-of-flight mass spectrometer for mass analysis and selection, and a magnetic bottle photoelectron spectrometer for electron energy analysis. (The instrumental resolution is ~35 meV at 1 eV EKE.) The third harmonic (355 nm, 3.493 eV) of a Nd:YAG (YAG—yttrium aluminum garnet) laser was used to photodetach the cluster anions of interest. Photoelectron spectra were calibrated against the atomic lines of Cu-.

Nickel-benzene cluster anions were generated in a laser vaporization source. A rotating, translating nickel rod (1/4 inch diameter, ESPI Company, 3*N* purity) was utilized as target in the laser vaporization source. It was ablated with the second harmonic (532 nm, 2.33 eV) of another pulsed Nd:YAG laser using ≈10 mJ of power per pulse. Helium gas

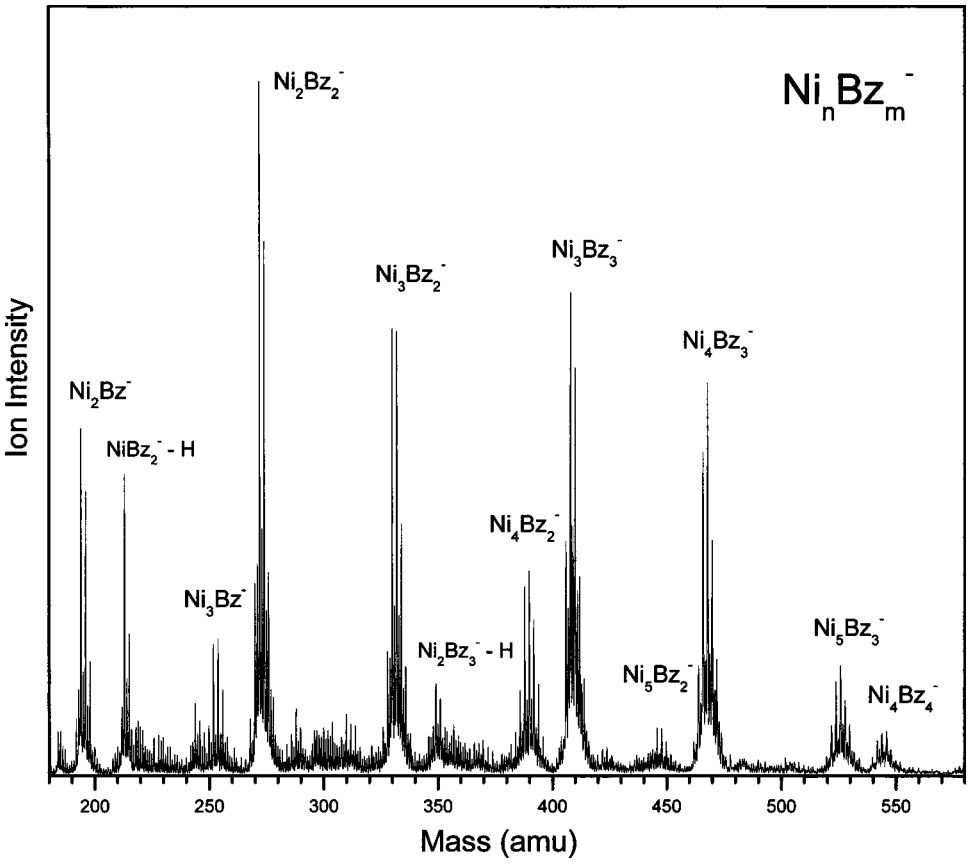

FIG. 1. A typical mass spectrum of nickel-benzene cluster anions.

at ~4 atm, seeded with benzene vapor, was expanded through a pulsed valve into the source, thus generating and cooling the resultant nickel-benzene cluster anions.

III. RESULTS

A. Mass spectra

A typical mass spectrum of nickel-benzene cluster anions, $Ni_nBz_m^-$, is presented in Fig. 1. It is dominated by the following species; Ni_2Bz^-, $Ni_2Bz_2^-$, Ni_3Bz^-, $Ni_3Bz_2^-$, $Ni_3Bz_3^-$, $Ni_4Bz_2^-$, $Ni_4Bz_3^-$, $Ni_4Bz_4^-$, and $Ni_5Bz_3^-$. The species, $Ni_2Bz_2^-$ and $Ni_3Bz_3^-$ always exhibited the highest intensities, suggesting enhanced stabilities for these particular species. Even more interesting, it was always true that $n \geqslant m$ among these species. For example, neither $NiBz_2^-$, $Ni_2Bz_3^-$, nor $Ni_3Bz_4^-$ were observed. In fact, no single-nickel species were observed, and this even included $NiBz^-$, where $n=m$.

It is interesting to compare the mass spectra of $Ni_nBz_m^-$ cluster anions with the mass spectra of $Co_nBz_m^-$ cluster anions. Unlike $Ni_nBz_m^-$ species, which strictly adhere to the relationship, $n \geqslant m$, in their mass spectra, $Co_nBz_m^-$ species with $m>n$ are routinely observed under certain source conditions.[15] The $m>n$ pattern is consistent with an extended sandwich structure. The fact that $Ni_nBz_m^-$ species do not exhibit such a pattern suggests that they do not have a sandwich structure and is consistent with the structure proposed by both Kaya[12] and Rao[27] in which a nickel cluster core is caged by benzene molecules.

Due to nickel's five naturally occurring isotopes, the mass spectrum of nickel-benzene cluster anions is relatively complex. Because our apparatus has unit mass resolution up to about 500, however, this does not present a serious problem. This allows us to distinguish all of the mass peaks belonging to nickel-benzene cluster anions up to sizes as large as $Ni_4(Bz)_3^-$. The combination of unit mass resolution and careful attention to the isotopic peak-height ratios in a given species profile insured that we avoided cluster anions which had lost hydrogen atoms due to dissociative attachment of electrons to the benzene moiety, viz., $[Ni_n(Bz_m-H_x)]^-$. We always recorded photoelectron spectra of a given cluster species by selecting the mass peak having the least possibility of hydrogen-loss contamination. We estimate that contamination from $[Ni_n(Bz_m-H_x)]^-$ "impurities" was kept well below 5% in all cases studied.

B. Photoelectron spectra

The photoelectron spectrum of the four $Ni_n(Bz)_m^-$ cluster anions studied here are presented in Fig. 2. Each of these spectra depict transitions from the electronic ground state of that particular cluster anion to the electronic ground state and energetically accessible, excited states of its corresponding neutral cluster. The peaks are broadened by the vibrational/rotational manifold associated with each electronic state. The lowest EBE peak in each spectrum corresponds to the transition from the ground electronic state of that cluster anion to the ground electronic state of its corresponding neutral cluster. The EBE of the peak maximum is the vertical detach-

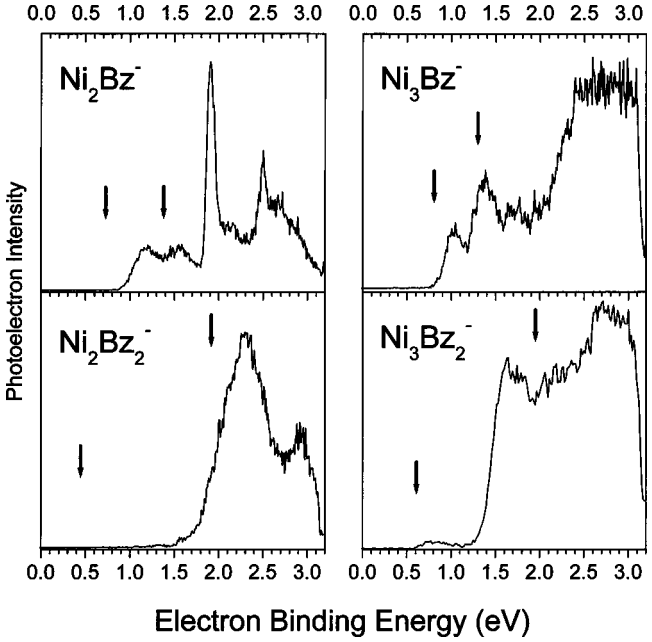

FIG. 2. The photoelectron spectra of Ni_2Bz^-, $Ni_2Bz_2^-$, Ni_3Bz^-, and $Ni_3Bz_2^-$ all recorded with 3.49 eV photons.

ment energy, VDE, i.e., the energy corresponding to maximum Franck–Condon overlap. If there is no vibrational excitation present in the cluster anion (hot bands), the EBE of the onset of electron intensity corresponds to the adiabatic electron affinity EA_a of the neutral cluster. However, since the cluster anions have internal energy corresponding to a significant temperature, the EBE that designates the EA_a value is typically interpreted as lying between the signal onset and the peak maximum. (We estimate the temperature of these cluster anions to be ~200 °C.) When the structure of the anion and its neutral are very similar, this peak is narrow (a Franck–Condon factor of almost one). Under such circumstances, EA_a would be approximately equal to VDE.

The photoelectron spectrum of Ni_2Bz^- in Fig. 2 exhibits at least six electronic transitions. The maximum of the lowest EBE peak occurs at 1.20 eV, which is the VDE. The EA_a value that we extracted from this peak is 1.0 eV. The maximum of the next higher EBE transition occurs at an EBE of 1.55 eV. The photoelectron spectrum of Ni_3Bz^- displays at least five electronic transitions. The maximum of the lowest EBE peak occurs at 1.00 eV, i.e., the VDE. The EA_a value that we extracted from this peak is 0.9 eV. The maximum of the next higher EBE transition occurs at an EBE of 1.35 eV. The spectrum of $Ni_2Bz_2^-$ exhibits two broad peaks, both at relatively high EBE values. The peak maximum for the lowest EBE feature occurs at 2.3 eV, and again, this is the VDE. The EA_a value is difficult to discern but is probably around 1.8 eV. The maximum of the next higher EBE peak occurs at an EBE of 2.9 eV. The spectrum of $Ni_3Bz_2^-$ exhibits three maxima, corresponding to at least three electronic transitions. The lowest EBE peak is much lower in intensity than the others. Its maxima occurs around 0.8 eV, i.e., the VDE. We did not assign a value for EA_a in this case. The maximum of the next higher EBE peak occurs at an EBE of 1.7 eV. Table I summarizes VDE, EA_a, and second transition energy values for the cluster systems studied here.

While the evidence is strong that nickel-benzene clusters have structures in which nickel cluster cores are caged by benzene molecules, a cluster ion-molecule solvation bonding model is clearly overly simplistic. Chemical, rather than physical, interactions dominate the bonding in these caged, cluster core structures. The failure of a nickel cluster anion-benzene molecule(s) solvation model becomes evident when one compares the photoelectron spectra and electron affinity values[29,30] of Ni_2 (0.926 eV) and Ni_3 (1.44 eV) with the spectra and our measured EA_a and VDE values for nickel-benzene clusters and their anions in Table I and Fig. 2.

IV. DISCUSSION

A. Comparisons with theoretical predictions

We now compare our measured VDE, EA_a, and second transition energy values with those calculated by Rao and Jena.[27] These theorists found $Ni_1(Bz)_1$ to have a significantly negative adiabatic electron affinity value. Since we did not observe this species in our mass spectra, their prediction is consistent with our result. The arrows on the spectrum of $Ni_2(Bz)_1^-$ in Fig. 2 mark the theoretically predicted EBEs for the first (the VDE) and the second transition energies. While the agreement between theory and experiment in this case is not strong, it is significant, given the spacing between the predicted and measured transitions and the spectral energy range over which they both occur. In our judgement, theory and experiment are somewhat consistent in this case. The arrows on the $Ni_3(Bz)_1^-$ spectrum in Fig. 2 again mark the theoretical predictions for the two lowest EBE transitions. The agreement between theory and experiment in this case is very good, i.e., theory and experiment are consistent

TABLE I. Comparison between experimental and calculated transition energies (in eV).

Cluster	Adiabatic electron affinity		Vertical detachment energy		Second transition energy		Consistency between theory and experiment
	Theory[a]	Experiment[b]	Theory[a]	Experiment[b]	Theory[a]	Experiment[b]	
$Ni_1(Bz)_1$	−0.35	···	···	···	···	···	Yes
$Ni_2(Bz)_1$	0.48	1.0±0.1	0.72	1.20±0.05	1.38	1.55±0.05	Somewhat
$Ni_3(Bz)_1$	0.78	0.9±0.1	0.81	1.00±0.05	1.30	1.35±0.05	Yes
$Ni_1(Bz)_2$	−0.39	···	···	···	···	···	Yes
$Ni_2(Bz)_2$	0.17	1.8±0.2	0.44	2.3 ±0.1	1.92	2.9 ±0.1	No
$Ni_3(Bz)_2$	0.40	···	0.61	0.8 ±0.1	1.95	1.7 ±0.15	Yes

[a]Reference 27.
[b]This work.

for $Ni_3(Bz)_1^-$. Rao and Jena[27] found $Ni_1(Bz)_2^-$ to have a strongly negative EA_a value. Again, since we did not observe this species, their prediction is consistent with our experimental observations. A comparison of the first two theoretically predicted transitions for $Ni_2(Bz)_2^-$ with our experimentally measured ones shows strong disagreement (see Fig. 2). The first transition energy predicted by theory is far away in energy from any experimentally recorded photoelectron signal, even though the predicted EBE of the second transition is in the vicinity of a major peak in the spectrum. Theory and experiment are inconsistent for $Ni_2(Bz)_2^-$. One reason for performing these experiments is to provide benchmarks for theory, so that it can continue to develop. Higher level theoretical calculations are underway by Jena *et al.* to explore the source of the observed inconsistency. Comparison of the theoretically predicted transitions (see arrows) in the spectrum of $Ni_3(Bz)_2^-$ with those measured in this work shows generally good agreement. Theory and experiment are consistent in this case. Table I not only summarizes VDE, EA_a, and second transition energy values, it also tabulates the consistency or lack thereof between theory and experiment for the cluster systems studied here. Of the six $Ni_nBz_m^-$ cluster anions systems compared, the overall consistency is good, with four of them being highly consistent, with one of them showing itself to be somewhat consistent, but with only one failing to show credible consistency.

B. Magnetic moments from the synergy of experiment and theory

The substantial agreement between experiment and theory in the cases studied here makes it possible to draw inferences about the magnetic moments of specific cluster species. First, let us consider an example of why one might like to know this information. The clusters of several transition metals are known to exhibit higher magnetic moments per atom than the same metal in its bulk (macroscopic) state. The enhancement of magnetic moment with decreasing aggregate size first becomes significant in the size regime below about 500 atoms per cluster. As cluster size is reduced further, this enhancement continues to grow, resulting in increases in the magnetic moment per atom of 30%–60% over that for the same metal in bulk. These phenomena have been quantitatively demonstrated through the magnetic deflection (Stern-Gerlach) experiments of de Heer,[31] Bloomfield,[32] and Knickelbein[33] and through the theoretical work of Khanna, Jena, and others.[34] Based on these observations, one can imagine that small clusters of some transition metals may have potential for playing important roles in information storage and processing. For this aspect of subnanotechnology to advance, however, these clusters will likely have to be supported on appropriate substrates as quantum dots. During the course of developing such technology, several important questions would need to be addressed, among them, ''How will the interaction between transition metal clusters and their host substrate affect the magnetic moments of the clusters?'' The use of transition metal/molecular complexes as model systems together with the synergy between theory and experiment can contribute to answering this question. Here, we focus on nickel/benzene complexes, where the benzene molecules primitively mimic an organic surface.

The theoretical calculations on nickel/benzene cluster anions by Rao and Jena[27] provided geometric structures for both anions and neutrals, anion-to-neutral (photodetachment) transition energies, and spin multiplicities for each electronic state involved in these transitions. In effect, theory provides a predicted bar code of photodetachment transition energies, and when experiment finds a match between their EBEs, it becomes likely that the calculation has been correct in its predictions about the electronic properties, including the spin multiplicities. Knowing the spin multiplicity of a particular electronic state is important, because the value of its multiplicity implies the value of its spin magnetic moment. (Additional constraints on a match are that the spin multiplicity must change by ± 1, and only by ± 1, during a photodetachment transition, and that all transitions begin from the same state, i.e., the cluster anion's ground state.)

The spin magnetic moment is equal to the spin multiplicity minus one, $(2S+1)-1$ or $2S$, in units of Bohr magnetons, μ_B, i.e., each unpaired electron is worth one Bohr magneton of spin magnetic moment. Since the orbital magnetic moment is a small part ($\sim$15%) of the total magnetic moment in clusters, one has a working link between the (estimated) total magnetic moment per atom in clusters and their electronic multiplicities. Naturally, in considering the possibility of technological applications, it is most interesting to focus on the magnetic moment of the ground state of a given neutral cluster, since that is the one that would most likely be utilized in a practical situation. Thus, with the multiplicity of the neutral cluster's ground state known, the spin magnetic moment per atom in that cluster is implied, and this value is also an estimate of the total magnetic moment per atom in that cluster.

Let us now consider the three nickel/benzene cluster anions for which we found reasonable experimental/theoretical matches between their two lowest-lying electronic transitions. Matching the two lowest-lying transitions is enough to make it likely that the calculation has predicted the correct multiplicities. In the case of $Ni_2(Bz)_1^-$, Rao and Jena[27] predicted the anion to be a doublet, the neutral ground state to be a singlet, and the neutral's first excited state to be a triplet. This implies that the magnetic moment of the neutral ground state is quenched, i.e., zero. Since the magnetic moment of bare Ni_2 is 2 μ_B,[35] it appears that the role of benzene in $Ni_2(Bz)_1$ was to pair the two previously unpaired electrons of Ni_2. The case of $Ni_3(Bz)_1^-$ is also interesting. There, these same theorists predict the anion to be a doublet, the neutral ground state to be a triplet, and the neutral's first excited state to be a singlet. This implies that the magnetic moment of the neutral ground state is $2\mu_B$ or $2/3\mu_B$ per nickel atom. Since the magnetic moment of bare Ni_3 is also $2\mu_B$,[35] the net effect of benzene in $Ni_3(Bz)_1$ was to leave the magnetic moment unchanged. The third system for which theory and experiment found a match of the first two transitions is $Ni_3(Bz)_2^-$. There, Rao and Jena[27] predicted the anion to be a doublet, the neutral ground state to be a singlet, and the neutrals's first excited state to be a triplet. This, of course, implies that the magnetic moment of the neutral ground state

is quenched. Thus, while neutral ground state $Ni_3(Bz)_1$, with one benzene molecule, has a magnetic moment of $2\mu_B$, neutral ground state $Ni_3(Bz)_2$, with one additional benzene molecule, has lost its magnetic moment altogether. Magnetically, nickel trimer interacting with one benzene is very different from nickel trimer interacting with two benzene molecules. Thus, even a seemingly small change in the immediate molecular environment can cause a significant change in magnetic properties. In principle, this sensitivity to environmental effects could be used to design cluster-assembled magnetic materials with tailored properties. In summary, by combining the results of anion photoelectron experiments with those of theory, one can obtain considerable information about the multiplicities, and thus the magnetic moments, of clusters as a function of their size and composition.

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