

Cobalt–benzene cluster anions: Mass spectrometry and negative ion photoelectron spectroscopy

M. Gerhards,^{a)} O. C. Thomas, J. M. Nilles, W.-J. Zheng, and K. H. Bowen, Jr.^{b)}
Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218

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(Cobalt)_{*n*}(benzene)_{*m*}[−] cluster anions, (*n,m*) were generated by laser vaporization and studied by both mass spectrometry and anion photoelectron spectroscopy. Our assignment of the photoelectron spectrum of the (1,2) cluster anion suggests that it possesses a sandwich structure with the cobalt atom located between two parallel benzene rings, that the ground state of this anion is a singlet, and that the ground state of its corresponding neutral is a doublet. The photoelectron spectra of cobalt-rich cluster anions of the form (*n*,1) are interpreted as cobalt metal cluster anions which have been solvent-stabilized by their interaction with, in each case, a single benzene molecule. The photoelectron spectra of the benzene-rich cluster anions, (2,3), (2,2), and (3,3), are tentatively interpreted as suggesting extended sandwich structures for these anion complexes. © 2002 American Institute of Physics. [DOI: 10.1063/1.1477924]

I. INTRODUCTION

The interaction of metals with organic molecules is of fundamental interest to chemical and materials science. Compounds consisting of single metal atoms and multiple organic molecules are prevalent in classical organometallic and coordination chemistry, and more recently, the interaction of small metal clusters with organic molecules has become an important topic in bioinorganic chemistry. In addition, the interaction of transition metal clusters with organic substrates may soon become a significant issue in nanoscience. In this paper we focus on complexes of cobalt atoms and clusters with benzene as an example of a model system for investigating such interactions.

Transition metal sandwich compounds, in which a metal atom lies between two parallel or nearly parallel carbocyclic ring systems, have been of interest to chemists for some time. Ferrocene¹ and dibenzene chromium² are classic examples, and the number and diversity of these compounds has grown dramatically with the recent application of gas phase synthetic strategies.^{3–13} An overview of recent work on organometallic compounds in the gas phase, including a review of work performed on transition metal–benzene clusters, has been provided by Nakajima and Kaya.¹⁴ These investigators have explored photofragmentation processes,^{11,12} binding energies,^{13,14} structures, electron affinities,^{15,16} and ionization energies³ for various transition metal–aromatic molecular complexes.

In the case of cobalt/benzene clusters, their ionization energies and mass spectral intensities have been explained in terms of two basic structural types. Co_{*n*}(benzene)_{*m*} (*m* = *n* + 1 and *n* = 1–3) clusters are described as multiple-decker sandwiches, whereas Co_{*n*}(benzene)_{*m*} (*n* ≥ 4) form *n* atom

metal clusters coated by *m* benzene molecules.³ The diverse structures of cobalt-benzene clusters make them attractive candidates for further study. Benzene-coated clusters can function as model systems for understanding the interactions between small metal clusters and substrates.¹⁷ Cobalt-benzene sandwich complexes, on the other hand, are important as basic models of *d*– π bonding interactions as well as being potential precursors of extended metal–aromatic polymers.¹⁴

Here, we report the application of negative ion photoelectron spectroscopy and mass spectrometry to cobalt–benzene anionic clusters. Clusters containing *n* cobalt atoms and *m* benzene molecules are abbreviated as (*n,m*). Cobalt_{*n*}benzene₁ (*n* = 2–5) clusters are referred to as cobalt-rich clusters, whereas clusters for which *m* ≥ *n* are referred to as benzene-rich.

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 $h\nu = \text{EKE} - \text{EBE}$, where $h\nu$ 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.¹⁸ 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 ion source consisted of an aluminum laser vaporization block with a rotating, translating cobalt rod (ESPI Company, purity 3N5) inside, a laser beam entrance port, and a gas expansion exit nozzle. A pulsed gas valve (General Valve, Iota One series 9) was mounted on the outside of this

^{a)}Permanent address: Heinrich-Heine Universitaet Duesseldorf, Universitaetstrasse 26.43.02, 40225 Duesseldorf, Germany.

^{b)}Author to whom correspondence should be addressed; electronic mail: kitbowen@jhunix.hcf.jhu.edu

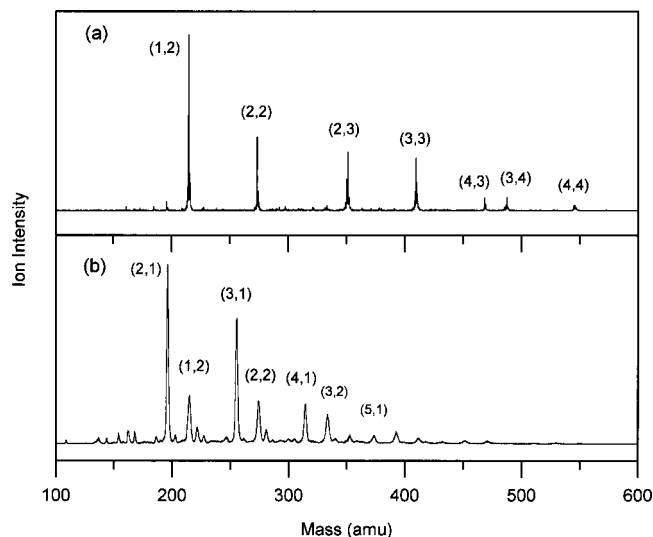


FIG. 1. Mass spectra of the $\text{Co}_n(\text{benzene})_m^-$ cluster anions recorded under conditions with (a) relatively high benzene partial pressure and (b) relatively low benzene partial pressure. The cluster anions are identified by the symbols (n,m) , which are abbreviations for number of cobalt atoms and number of benzene molecules.

block. Typically, helium gas at 4 bar was expanded over benzene in synchronization with laser ablation pulses in order to generate the cobalt/benzene cluster anions of interest. The benzene was maintained at room temperature to achieve cobalt-rich conditions and at 60 °C to provide benzene-rich conditions. The cobalt rod was ablated with the second harmonic (532 nm) of a Nd:YAG laser. Both second (532 nm) and third (355 nm) harmonics of a second Nd:YAG laser were used to photodetach the cluster anions of interest. Photoelectron spectra were calibrated against the atomic lines of copper and cobalt.

III. RESULTS AND DISCUSSION

A. Mass spectra

The mass spectra of the Co_nBz_m^- clusters are shown in Figs. 1(a) and 1(b). The spectrum given in Fig. 1(a) is recorded under benzene-rich conditions. This spectrum contains prominent peaks for the (1,2), (2,2), (2,3), (3,3), (3,4), (4,3), and (4,4) clusters. Each Co_nBz_m^- cluster exhibits a single peak followed by a small shoulder resulting from the cumulative effect of the natural abundance of C^{13} (1.1%). No impurities are observed. The spectrum roughly represents the alternating addition of cobalt atoms and benzene molecules to the (1,2) cluster. This pattern of addition is consistent with the formation of extended sandwich clusters.

The mass spectrum shown in Fig. 1(b) is recorded under cobalt-rich conditions. It exhibits prominent peaks for the (2,1), (3,1), (3,2), and (4,1) clusters. Peaks of the (1,2) and (2,2) clusters are also in evidence, but no clusters with $m - n > 1$ are observed. This ion intensity profile is consistent with the sequential addition of cobalt atoms to the (2,1) and (1,2) clusters. This addition process is consistent with the formation of cobalt cluster anions solvated by one and two benzene molecules, respectively.

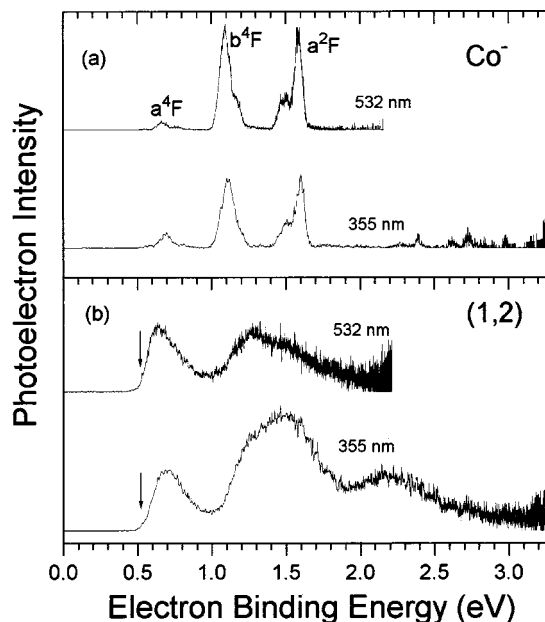


FIG. 2. (a) Photoelectron spectra of the Co^- anion recorded at a photodetachment wavelength of 532 nm (upper trace) and 355 nm (lower trace). Term symbols for the neutral (terminal) states are indicated above or next to the main features. (b) Photoelectron spectrum of the (1,2) cluster recorded at photodetachment wavelengths of 532 nm (upper trace) and 355 nm (lower trace). Arrows indicate the assigned spectroscopic origins and thus the electron affinities.

We also note that the (1,1) cluster is not observed under any of the conditions employed in our experiment. The (1,1) neutral cluster has been observed previously, and we take its absence in the anion mass spectra to be a strong indication that the electron affinity of this cluster is nonpositive. Calculations by Rao and co-workers¹⁷ found the electron affinity of the (1,1) cobalt/benzene cluster to be very near zero.

B. Photoelectron spectra of the (1,2) cobalt/benzene cluster anion

The photoelectron spectra of the Co^- atomic anion and the (1,2) cluster anion are compared in Fig. 2. Spectra were taken at both 532 (2.33 eV) and 355 (3.49 eV) nm. The photoelectron spectrum of (1,2), taken with a photodetachment wavelength of 355 nm, exhibits transitions centered at 0.70, 1.45, and 2.20 eV. The photoelectron spectrum of Co^- exhibits five clear transitions, these occurring at 0.69, 0.78, 1.09, 1.50, and 1.59 eV. A sixth feature at 1.18 eV is observed as a shoulder in our photoelectron spectrum. Our Co^- spectrum is in agreement with that measured previously by Lineberger and coworkers.¹⁹ The electronic transitions of the Co^- anion can be arranged into three groups, describing transitions from the 3F ground state of the anion to the a^4F (0.69 and 0.78 eV), b^4F (1.09 and 1.18 eV), and a^2F (1.50 and 1.59 eV) states of the neutral atom. The splitting observed in each of these transitions is due to spin-orbit coupling. The 3F ground state of the cobalt anion corresponds to a $(3d^8 4s^2)$ electronic configuration. The a^4F ground state of the neutral atom corresponds to a $(3d^7 4s^2)$ electronic configuration, while the b^4F and a^2F excited states of the neutral correspond to $(3d^8 4s^1)$. In accordance with Hund's first rule, the b^4F state is lower in energy than a^2F .

TABLE I. Spectral assignment of the (1,2) cobalt/benzene anion photoelectron spectrum.

Peak location (eV)	Assignment
0.70	$(3de_{2g})^4(4sa_{1g})^2(3de_{1g})^4(3da_{1g})^0$ $\rightarrow(3de_{2g})^4(4sa_{1g})^2(3de_{1g})^3(3da_{1g})^0$
1.45	$(3de_{2g})^4(4sa_{1g})^2(3de_{1g})^4(3da_{1g})^0$ $\rightarrow(3de_{2g})^4(4sa_{1g})^1(3de_{1g})^4(3da_{1g})^0$
2.20	$(3de_{2g})^4(4sa_{1g})^2(3de_{1g})^4(3da_{1g})^0$ $\rightarrow(3de_{2g})^3(4sa_{1g})^2(3de_{1g})^4(3da_{1g})^0$

The first transition observed in the photoelectron spectrum of the (1,2) cluster is centered at 0.70 eV and is comparable in electron binding energy to the peaks of the ${}^3F \rightarrow a^4F$ transitions (0.69 eV, 0.78 eV) in the Co^- spectrum. A second broad feature is centered at 1.45 eV. The maximum of this feature (in the 532 nm spectrum) is nearly equidistant in energy between the ${}^3F \rightarrow b^4F$ and ${}^3F \rightarrow a^2F$ transitions observed in the pure Co^- anion. A third feature is evident in the 355 nm spectrum of (1,2). Its center is located at an electron binding energy of 2.20 eV.

The general appearance of the (1,2) spectrum can be understood in terms of the molecular orbitals and spin multiplicities of the neutral cluster and its anion. Here, we assume the (1,2) cluster to form a sandwich compound in which the cobalt atom lies between two parallel and eclipsed benzene rings. This results in a D_{6h} symmetry. Though there have been no experimental determinations of the molecular point group for cobalt(benzene)₂, dibenzene chromium has been shown through x-ray studies to exhibit D_{6h} symmetry in the crystalline state.²⁰ The degeneracy of the five 3d orbitals of cobalt is broken in a D_{6h} field, the d_{xy} and $d_{x^2-y^2}$ orbitals forming an e_{2g} set, the d_{xz} and d_{yz} orbitals forming an e_{1g} set, and the d_{z^2} orbital forming an a_{1g} orbital. The 4s orbital of cobalt is also assigned as a_{1g} . By assuming the $3da_{1g}$ orbital to be higher in energy than the $3de_{2g}$ and $3de_{1g}$ orbitals, one obtains an electronic configuration for the (1,2) cluster that is consistent with both the photoelectron spectra presented here and spin multiplicities calculated for both the anion and neutral (1,2) sandwich compound by Rao and co-workers.²¹ The valence electronic configurations assigned to the ground states of the anions and neutral of the (1,2) cluster are $(3de_{2g})^4(4sa_{1g})^2(3de_{1g})^4(3da_{1g})^0$ and $(3de_{2g})^4(4sa_{1g})^2(3de_{1g})^3(3da_{1g})^0$, respectively. These correspond to spin multiplicities of 1 and 2, respectively. The configurations of the first and second excited states of the neutral are $(3de_{2g})^4(4sa_{1g})^1(3de_{1g})^4(3da_{1g})^0$ and $(3de_{2g})^3(4sa_{1g})^2(3de_{1g})^4(3da_{1g})^0$, respectively. In Table I, the observed peaks in the spectrum are correlated with anion-to-neutral transitions involving these configurations.

We have determined the electron affinity (EA) of the (1,2) cluster to be 0.50 eV by assigning the origin to lie on the low EBE side of the lowest EBE feature of the spectrum. This is slightly less than the literature value for the EA of Co (0.66 eV) and is contrary to the theoretical prediction for the EA of the (1,2) cluster.^{21,22} This photoelectron spectrum has been interpreted in terms of a molecular orbital picture and is consistent with the (1,2) cluster being a sandwich complex which, as an anion, possesses a ground state spin multiplicity

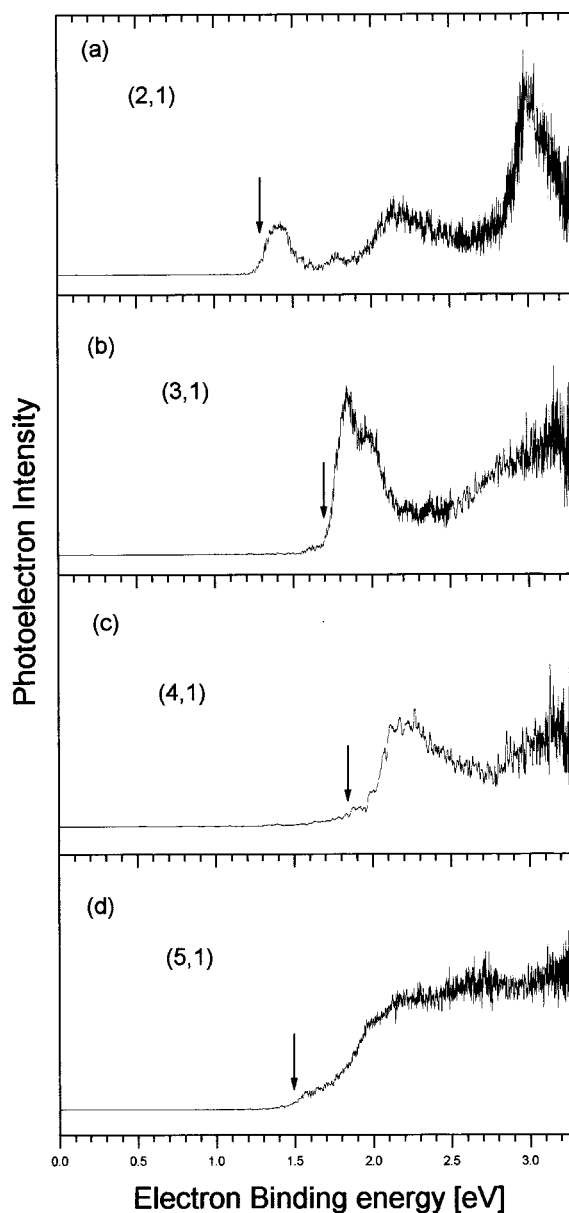


FIG. 3. Photoelectron spectra of (a) (2,1), (b) (3,1), (c) (4,1), and (d) (5,1) cluster anions each recorded at a wavelength of 355 nm (3.49 eV). Arrows indicate the assigned spectroscopic origins and thus the electron affinities.

of 1 and as a neutral, possesses a ground state spin multiplicity of 2. In the case of the ground state neutral, this implies a spin magnetic moment of $1 \mu_B$. This is a reduction in magnetic moment relative to atomic cobalt, which possesses a magnetic moment of $3 \mu_B$, and it is a measure of the influence of the two benzene molecules in this complex on the magnetic properties of the cobalt atom. This assignment of magnetic moment has also been corroborated by theory, and it further demonstrates the feasibility of obtaining magnetic moment information from electronic structure via anion photoelectron spectroscopy.^{17,23,24}

C. Photoelectron spectra of the cobalt-rich clusters ($n,1$); $n=2-5$

The photoelectron spectra of the (2,1), (3,1), (4,1), and (5,1) clusters are shown in Figs. 3(a)–3(d). For all spectra

TABLE II. Electron affinities and electronic transitions of $\text{Co}_n(\text{benzene})_m$ clusters.

Cluster size (m,n)	Electron affinity (eV) ^{a,b}	Electronic transitions (eV) ^a
(2,1)	1.31	1.43, 1.79, 2.25, 3.05
(3,1)	1.70	1.83, 1.98
(4,1)	1.85	2.20
(5,1)	1.50	1.90
(1,2)	0.50	0.70, 1.45, 2.20
(2,2)	1.00	1.11, 1.50, 1.79
(2,3)	0.68	0.95, 1.30, 1.75, 2.45
(3,3)	1.10	1.20, 1.60, 1.80, 2.18
(4,3)	1.20	2.22
(3,4)	1.05	

^aValues given have an uncertainty of ± 0.100 eV.

^bElectronic transitions are the electron binding energies of the centers of peaks observed in each spectrum.

shown, a photodetachment wavelength of 355 nm (3.49 eV) was used. Spectra obtained with 532 nm (2.33 eV) and 355 nm have been compared in the region below ~ 2.2 eV, and no differences with respect to electronic transitions were observed. This indicates that electronic features within this region are not the result of resonances excited by the 355 nm light. Electron affinities and the centers of prominent peaks are given in Table II.

We interpret the photoelectron spectra of the $(n,1)_{n=2-5}$ clusters through a comparison to the relevant photoelectron spectra of the Co_n^- clusters.²⁵ The $(n,1)_{n=2-5}$ spectra resemble the spectra of Co_n^- clusters, except for being shifted to higher electron binding energies. A shift to higher electron binding energies with respect to the pure cobalt clusters is interpreted as a solvent-induced stabilization. In other words, the solvent benzene molecule acts to stabilize the anion of the naked cobalt cluster.

The spectrum of the (2,1) cluster contains four transitions centered at 1.43, 1.79, 2.25, and 3.05 eV, respectively. The electron affinity of the (2,1) cluster was determined from our spectrum to be 1.31 eV. From the photoelectron spectrum of Leopold and Lineberger, the EA of Co_2 has been determined to be 1.11 eV.²⁶ Thus the anion of (2,1) is stabilized with respect to the Co_2^- anion by about 0.2 eV. The photoelectron spectrum of the Co_2^- anion exhibits electronic transitions centered at 1.18 and 1.74 eV. The transitions centered at 1.43 and 1.79 eV in our (2,1) cluster spectrum can be correlated to the transitions centered at 1.18 and 1.74 eV in the Co_2^- anion spectrum. Interestingly, a significant increase in electron binding energy is observed only for the lowest EBE peak.

No direct structural information is obtained from the photoelectron spectra of the $(n,1)$ clusters. However, through a comparison to theoretical and experimental investigations on both pure Co clusters and transition metal/benzene clusters, we can consider plausible structures. In the case of the (2,1) cluster, three idealized structures come to mind. The axis of the Co_2^- anion may lie (a) parallel or (b) perpendicular to the plane of the atomic ring, or (c) the Co_2^- anion may interact with benzene from the side. Transition metal/benzene complexes, where the transition metal forms very stable bonds to the π -cloud of benzene are well

known.^{27,28} In these complexes transition metal atoms may act as both electron donors and acceptors to the π and π^* orbitals of benzene. Thus we believe structures (a) and (b) to be more likely than the side-bonded arrangement (c). Furthermore, a structure which contains separated cobalt atoms seems unlikely, since there is no indication of transitions of atomic cobalt in the photoelectron spectrum.

In order to determine the solvent-induced stabilization of the (3,1), (4,1), and (5,1) clusters, we compare them with the photoelectron spectra of the Co_{3-5}^- anions recorded by Kondow and coworkers.²⁵ The photoelectron spectrum of the (3,1) cluster contains two transitions centered at 1.83 and 1.98 eV, whereas the spectrum of the pure Co_3^- contains one sharp transition centered at 1.6 eV. The two transitions in the spectrum of the (3,1) cluster indicate an additional electronic state in the neutral cluster resulting from the interaction of the cobalt trimer with benzene. The electron affinity of the (3,1) cluster is 1.70 eV, which is 0.32 eV higher in energy than that of the Co_3 (1.38 eV) cluster.

The photoelectron spectra of the (4,1) and (5,1) clusters are very similar to the corresponding spectra of pure Co_4^- and Co_5^- . The electron affinity of the (4,1) cluster is determined from our data to be 1.85 eV which is about 0.20 eV higher in energy than the EA of the Co_4 cluster (1.65 eV). The electron affinity of the (5,1) cluster is determined from our data to be 1.50 eV. Though the EA value of Co_5 is not explicitly stated by Kondow and co-workers, it is indicated graphically to be ~ 1.4 eV.

From the photoelectron spectra of pure Co_n^- clusters and $(n,1)$ cobalt/benzene cluster anions, it can be concluded that a single benzene molecule acts to stabilize a $(n,1)$ cluster anion relative to its corresponding Co_n^- anion. However, the solvent stabilization energies are not uniform among small cobalt clusters, having values of 0.20, 0.32, 0.20, and 0.10 eV for the (2,1), (3,1), (4,1), and (5,1) clusters, respectively.

D. Photoelectron spectra of benzene-rich clusters (n,m) ($n>1,m>1$)

The photoelectron spectra of the (2,2), (2,3), (3,3), (3,4), and (4,3) clusters, recorded with a photodetachment wavelength of 355 nm (3.49 eV), are shown in Fig. 4. Spectra taken at 532 nm (2.33 eV) show no differences with respect to the observed electronic transitions, indicating that transitions occurring below ~ 2.2 eV are not the result of resonant phenomena. Table II presents the electron affinities of these clusters as well as the spectral positions of their observed electronic bands. It is interesting to note that, for clusters of constant cobalt content, electron affinities tend to decrease with the successive addition of benzene molecules.

Qualitatively, these spectra bear little resemblance to those of the $(n,1)$ cluster anions discussed in the previous section. Consider the following observations about the profiles of the benzene-rich cluster anion spectra. The spectra of (2,2), (2,3), and (3,3) are all highly structured, and multiple features are evident in each of these spectra in the region below 2 eV binding energy. The spectra of (2,2) and (3,3) are particularly similar in shape, with both spectra indicating multiple transitions in the region below 1.7 eV. The (2,2) spectrum has peaks centered at 1.11 and 1.50 eV and the

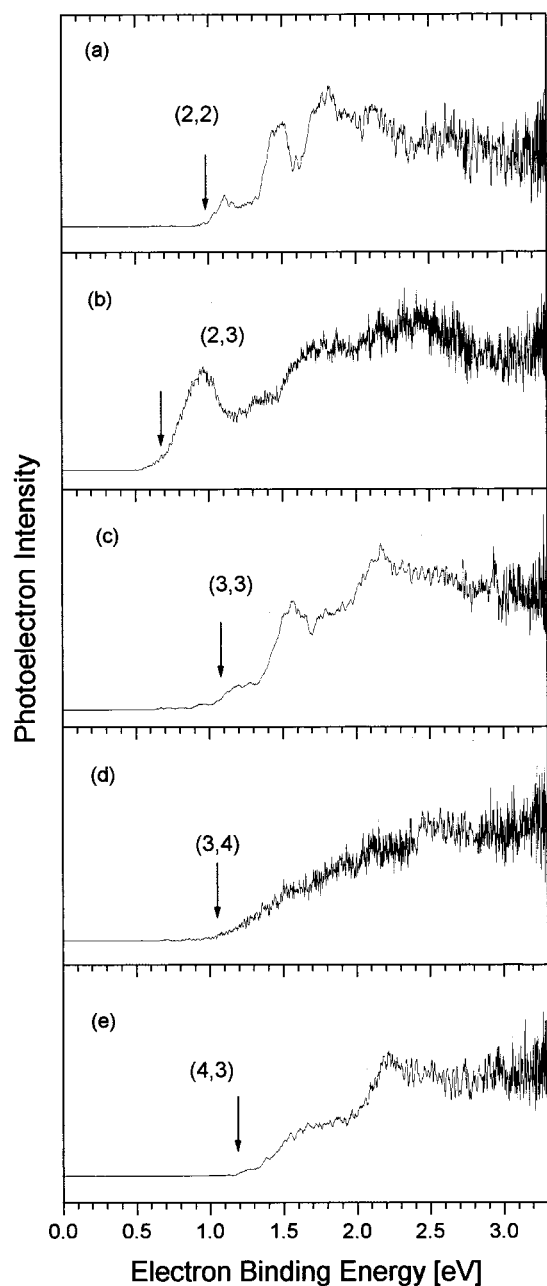


FIG. 4. Photoelectron spectra of (a) (2,2), (b) (2,3), (c) (3,3), (d) (3,4), and (e) (4,3) cluster anions each recorded at a wavelength of 355 nm (3.49 eV). Arrows indicate the assigned spectroscopic origins and thus the electron affinities.

(3,3) spectrum shows peaks centered at 1.20 and 1.60 eV with similar intensity ratios. The positions of these features are similar to those associated with the ${}^3F \rightarrow b^4F$ and ${}^3F \rightarrow a^2F$ transitions for Co^- which show peak maxima at 1.09 and 1.59 eV, respectively. The pattern of the lower EBE transitions in the (2,3) spectra is similar to that observed for the (1,2) cluster, except for being shifted to higher EBE. Electronic transitions appear in the (1,2) spectrum centered at 0.70, 1.45, and 2.20 eV, whereas similarly shaped features are apparent in the (2,3) spectrum centered at 0.95, 1.75, and 2.45 eV, the latter set of features being shifted to higher EBEs by ~ 0.25 eV.

Here, we speculate that the (2,2), (2,3), and (3,3) spectra

can be rationalized in terms of their anions being extended sandwich complexes. We propose that the (2,3) cluster anion is a double decker sandwich of the configuration, $|\bullet|\bullet|$. In this case, both cobalt atoms reside in chemical environments similar to the one occupied by cobalt in the (1,2) cluster anion. The increase in electron binding energy for (2,3) relative to (1,2) may be attributed to the delocalization of electrons along the axis of the cluster. Ionization energies for multiple decker $\text{Ti}_n(\text{benzene})_{n+1}$, $\text{V}_n(\text{benzene})_{n+1}$, and $\text{Cr}_n(\text{benzene})_{n+1}$ clusters have been explained in this way.²⁹

We suggest that the (2,2) and (3,3) cluster anions may exist as cobalt-capped sandwiches, having the configurations, $|\bullet|\bullet$ and $|\bullet|\bullet|\bullet$, respectively. This is supported by the appearance of the most prominent cobalt atomic-like features in the spectra of (2,2) and (3,3) cobalt/benzene cluster anions. In any case, it is clear that they are not benzene-coated cobalt cluster anions, given the close similarity between the (2,2) and (3,3) spectra and the dramatic differences between the spectra for pure Co_2^- and Co_3^- . Next, recalling that the multiplicity of the ground state of the (1,2) cluster anion was assigned as a singlet, it is interesting to consider the multiplicity of the ground states of the (2,2) and (3,3) cluster anions. The two features in the Co^- spectrum, which occur at similar electron binding energies to the low EBE peaks in the (2,2) and (3,3) spectra, terminate on neutral states of differing multiplicities. If the lower EBE peaks at issue in the (2,2) and (3,3) spectra also access neutral states of different multiplicities, then selection rules dictate that the ground state, cluster anions of (2,2) and (3,3) must have multiplicities of two or higher.

The (3,4) and (4,3) photoelectron spectra lack significant structure. Their spectral onsets are both in the vicinity of that of the (3,3) spectrum, and the energy range over which electrons are detached is similar for the spectra of both (3,4) and (3,3), with the profile of (4,3) showing some similarity to that of (3,3). Still, without distinct spectral features to guide us, it is difficult to speculate further about the structure of these two. We only note that benzene-coated clusters become more prevalent as these kinds of clusters become more complex.¹⁴

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