Photoelectron spectroscopy of mixed metal cluster anions: NiCu⁻, NiAg⁻, NiAg₂⁻, and Ni₂Ag⁻

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Negative ion photoelectron spectra of NiCu⁻, NiAg⁻, NiAg₂⁻, and Ni₂Ag⁻ are presented for electron binding energies up to 3.5 eV. The metal cluster anions were prepared in a cold cathode dc discharge flowing afterglow source. The dimer spectra exhibit three low lying electronic states; the ground electronic states are vibrationally resolved. The dimer electron affinities are determined to be EA(NiCu)$=0.889\pm0.010$ eV and EA(NiAg)$=0.979\pm0.010$ eV. Two excited state electron configurations are assigned as $(d_{\mathrm{Ni}}^8 d_{\mathrm{Cu}}^{10}\sigma^2\sigma^{*1})$ and as $^4\Delta$ $(d_{\mathrm{Ni}}^9 d_{\mathrm{Cu}}^{10}\sigma^1\sigma^{*1})$. The NiCu⁻ ground state is assigned as $^3\Delta$ $(d_{\mathrm{Ni}}^9 d_{\mathrm{Cu}}^{10}\sigma^2\sigma^{*1})$, and has a vibrational frequency of 235 ± 25 cm⁻¹. The photoelectron spectrum of NiAg⁻ strongly suggests that the electronic configurations of the three observed states are the same as those of NiCu⁻. The NiAg ground state vibrational frequency is 235 ± 25 cm⁻¹ and the NiAg⁻ frequency is 185 ± 25 cm⁻¹. The chemical bonding in both NiCu and NiAg dimers is dominated by a $s\sigma$ molecular orbital, and the extra electron in the anions has primarily $s\sigma^*$ character. The photoelectron spectra of the trimers, NiAg₂⁻ and Ni₂Ag⁻, are remarkably similar to those obtained for the coinage metal trimers, and are consistent with a transition between a linear anion ground state and a linear excited state of the neutral. © *1996 American Institute of Physics.* [S0021-9606(96)00712-0]

I. INTRODUCTION

Spectroscopic studies have greatly enhanced our understanding of the electronic structure and chemical bonding of small transition metal clusters.[1,2] Negative ion photoelectron spectroscopy[3] can be used effectively to probe the chemical bonding and electronic structure of small metal clusters.[4,5] In recent years our laboratory has applied this technique to a variety of systems, including small clusters of the Cu group[6,7] and Ni group[8–10] atoms. The findings of these previous studies of the pure clusters provide an important motivation for this study of the mixed dimers and trimers.

The photoelectron spectra of the coinage metal clusters have been studied[6,7] for Cu$_n$ and Ag$_n$ ($n=1-10$) and Au$_m$ ($m=1-5$). Since the separated atomic ground states have the configuration $(d^{10}s^1)$, the dimers can bond only through the s orbitals, creating an $s\sigma$ and $s\sigma^*$ pair of orbitals and leaving the fully filled d "core" largely unperturbed. Thus the ground state of M$_2$ (M=Cu, Ag, Au) is $^1\Sigma_g^+(d^{20}\sigma_g^2)$. The additional electron in the anion occupies the σ^* orbital to make a $^2\Sigma_u^+(d^{20}\sigma_g^2\sigma_u^{*1})$ ground state of M$_2^-$. The photoelectron spectra of the coinage metal dimer anions display transitions from the anion ground state to the singlet ground state of the neutral and to the lowest triplet state, M$_2$ $^3\Sigma_u^+(d^{20}\sigma_g^1\sigma_u^{*1})$; no additional states appear due to detachment from the d orbitals. This is not a surprising result, since the free atom excitation energies to the (d^9s^2) are large (for example, 11 202 cm⁻¹ for copper). The electron configurations given above are further supported by photoelectron angular distributions and by thermochemical arguments based on the electron affinities and triplet term energies of the dimers. The transitions to the ground states of the coinage metal dimers are vibrationally resolved, yielding vibrational frequencies of the M$_2$ singlet ground states consistent with previous measurements by Morse[1] and of the M$_2^-$ ground states.

The photoelectron spectra[6,7] of Cu$_3^-$ and Ag$_3^-$ are remarkably simple, with a single, relatively narrow peak near 2.4 eV binding energy. This has been assigned as the transition to a linear excited state of the neutral (M$_3$ $^2\Sigma_u^+$) from the linear ground state of the anion (M$_3^-$ $^1\Sigma_g^+$), where the fully filled d orbitals remain unperturbed and the bonding occurs entirely through the s orbitals. The ground states of the neutral triatomics have been calculated[11,12] to be triangular while the same authors report anion ground states which are linear. The poor Franck–Condon overlap between these geometries makes direct observation of the neutral ground state infeasible, and the electron affinities of the trimers are estimated using the calculated term energies of the observed linear neutral states.

The nickel clusters differ from those of the copper group in that they lack fully filled d shells, making available a much larger number of low lying electronic states and resulting in more complicated anion photoelectron spectra. While the ground state of the free nickel atom has the (d^8s^2) configuration, the (d^9s^1) configuration lies only 204.8 cm⁻¹ higher in energy. The Ni$_2$ ground state is made up of two atoms in the higher state for a $(d^{18}\sigma^2)$ configuration with a formal bond order of 1. Despite the well-described electron configuration, the absolute identity of the ground state has proven difficult to assign[13,14] and the experimental state assignment has recently been reassigned;[14] this new assign-

ment is in agreement with *ab initio* and ligand field calculations.[13] The photoelectron spectrum[8] of Ni_2^- exhibits vibrationally resolved transitions to the ground state (although other states may also be present in this region) and unresolved transitions to a large number of additional electronic states covering most of the electron binding energy range from 1.7 to 3.5 eV. The photoelectron spectrum of Ni_3^- is similarly complex, showing relatively weak transitions to the ground state region of Ni_3 and unresolvable features starting near 1.8 eV binding energy and continuing past the photon energy (2.54 eV) of the previous study from our laboratory.[9] The authors of that study, after installing a new laser system using 3.53 eV photons, obtained the photoelectron spectrum of Ni_3^- at the new photon energy[15] which is reproduced here. The unresolvable features are shown in the new spectrum to reach a maximum near 2.3 eV and drop gradually to approach zero signal at 3.5 eV.

The past work from this laboratory on homonuclear metal cluster anions can be summarized by the observation that the copper group dimers and trimers display simple, readily interpreted spectra; the dimers and trimers of the nickel group, however, are characterized by numerous electronic states which make interpretation of the photoelectron spectra much more complicated. The added complexity in the nickel group spectra is attributed to the lack of a fully filled *d* shell on each atom and to the low promotion energy of the free atoms to excited electronic states. In the present work we expand our exploration of diatomic and triatomic metal clusters by reporting some photoelectron spectra of the mixed cluster anions of the copper and nickel groups. We examine the spectra of $NiCu^-$ and $NiAg^-$ with the objective of determining the effect on the electronic structure and bonding in metal dimers of a single *d* hole on only one of the atoms. The spectra of the mixed triatomics $NiAg_2^-$ and Ni_2Ag^- help elucidate the effect of stepwise introduction of *d* holes from zero to three in the series Ag_3^-, $NiAg_2^-$, Ni_2Ag^-, and Ni_3^-.

The electronic structure of NiCu has been studied by Shim[16] using *ab initio* Hartree–Fock and configuration interaction methods for a Ni atom in the ^3D ($3d^94s^1$) configuration bonded to a Cu atom in the ^2S ($3d^{10}4s^1$) configuration. The calculations revealed that the chemical bond in NiCu is best characterized by a bonding σ molecular orbital formed by 4*s* orbital overlap, with the 3*d* and 4*p* orbitals hardly participating in the chemical bonding. Spin–orbit coupling was considered in some detail. The ground state was found to be pure $^2\Delta_{5/2}$; however, strong mixing was found between the low lying $^2\Delta$, $^2\Sigma$, and $^2\Pi$ spin–orbit states of identical Ω.

The first experimental investigation into the structure of NiCu was performed by Fu and Morse[17] using resonant two-photon ionization (R2PI) spectroscopy in a jet-cooled molecular beam. This report was followed by a second R2PI experimental study by Spain and Morse[18] where they definitively assign the ground state of NiCu to be $^2\Delta_{5/2}$ ($d_{Ni}^9 d_{Cu}^{10}\sigma^2$). In an accompanying study, they determined that the ground states of NiAu and PtCu are also $^2\Delta_{5/2}$ ($d_A^9 d_B^{10}\sigma^2$).[19] They argue that the 3*d* orbitals do not participate significantly in

the bonding, since if they did a $^2\Sigma_{1/2}^+$ ground state would be expected in these dimers.[18] Detailed analysis of the NiCu R2PI spectrum yielded the following molecular constants for the ground state of NiCu: $r_e = (2.234 \pm 0.006)$ Å, $\omega_e = (273 \pm 1)$ cm^{-1}, and $D_0 = (2.05 \pm 0.01)$ eV. In a third study, Spain and Morse[13] also used ligand field theory to determine the electronic states of NiCu. They found that the theory could accurately predict the transitions to the $(3d_{Ni}^8 3d_{Cu}^{10}\sigma^2\sigma^{*1})$ manifold of states in their optical spectra. They also predicted several states of similar configuration that were outside the range of their spectral technique. In addition, they found ligand field theory gave good agreement with the *ab initio* calculations by Shim[16] for the low lying $(3d_{Ni}^9 3d_{Cu}^{10}\sigma^2)$ spin–orbit states. The results of these and other studies of Ni group and Cu group clusters are discussed in a recent comprehensive review by Morse.[20]

The experimental methods used in this study are reviewed in Sec. II. Experimental results and the quantitative conclusions that can be derived from the photoelectron spectra are presented in Sec. III, followed by a discussion, in Sec. IV, in terms of a molecular orbital picture of the metal–metal chemical bonding.

II. EXPERIMENTAL METHOD

The negative ion photoelectron spectrometer and the metal cluster anion source have been described in detail previously.[6–9] Essentially, a mass selected beam of metal cluster anions is crossed with 351.1 nm laser light. The laser system used in this system has been described previously.[7] The 351.1 nm (3.5312 eV) output of an argon ion laser is injected into an optical build up cavity encompassing the ion beam to provide 50–100 times the input laser power for photodetachment. The electron kinetic energies (eKE) of photodetached electrons are measured with a hemispherical electrostatic energy analyzer. Electron binding energies (eBE) associated with transitions between the initial anion state and the accessible neutral states are determined from the difference between the photon energy and the measured electron kinetic energy (eBE = $h\nu$ − eKE).

The absolute electron kinetic energy was determined by calibration with the known electron affinities of the metal atoms,[6,21] Ni, Cu, and Ag. Spectra were further corrected for a small energy scale compression by calibration with the known energy levels of atomic tungsten.[22] The instrumental resolution of the spectrometer was determined from the widths of isolated atomic lines to be ~10 meV.

The metal cluster anions were produced in a flowing afterglow ion source by cathodic sputtering[6,7] with a dc discharge. A mixture of 20% argon (Spectra-Gases, Ultra-purity 99.9995%) in helium (purified with a liquid nitrogen cooled molecular sieve trap) flowed over the metal cathode with a pressure of ~0.4 Torr. The flow rate was ~3.0 standard liters per minute. The cathode was fabricated from a nickel–copper alloy (Constantan foil, Goodfellows Corp.) in the NiCu case, and from high purity silver foil (Goodfellows Corp.) wrapped around a high purity nickel foil (Goodfellows Corp.) in the NiAg case. An alloy cathode was not

necessary for mixed cluster formation; the cluster anions are formed by gas-phase reactions. The cathode was typically biased at ~4 kV, producing a 10–15 mA discharge. Typical $NiCu^-$ and $NiAg^-$ currents were 0.5–1.0 pA. The metal clusters react rapidly with oxygen, and the presence of even trace amounts resulted in a substantial formation of metal oxide clusters. Considerable effort was required to reduce the oxygen contamination to acceptable levels required to obtain usable unoxidized anion beams.

The method of obtaining photoelectron angular distributions has been described previously.[10,23] The angular distribution for a given transition is measured by using linearly polarized light, and varying the angle between the polarizer and the electron detection direction. For the case of atomic photodetachment the intensity of photoelectrons at a given angle θ, I_θ, has been shown[24] to be given by $I_\theta = 1 + \beta P_2(\cos\theta)$, where $P_2(\cos\theta)$ is the second associated Legendre polynomial and β is the anisotropy parameter, which can vary between $-1 \leq \beta \leq 2$. Since photons carry one unit of angular momentum, detachment from a pure s orbital results in p wave detachment, giving $\beta = 2$. The angular distribution is expected to be more isotropic for d-electron detachment than s-electron detachment, and if the transition is not close to threshold, β for d-electron detachment is usually negative. Angular distributions of detachment from molecules are complicated by the loss of spherical symmetry, but normally β is positive for s-like orbital detachment and $\beta \sim 0$ for d-like orbital detachment. Angular distribution measurements of the photoelectron signal from $NiCu^-$ and $NiAg^-$ thus give some information about the symmetry of the molecular orbitals from which electrons are detached, as described in more detail in Sec. III A.

FIG. 1. Photoelectron spectra of (a) Cu_2^-, (b) $NiCu^-$, and (c) Ni_2^- obtained at 351.1 nm (3.531 eV) with 10 meV instrumental resolution. The $NiCu^-$ spectrum was obtained with the laser polarization parallel to the electron collection angle. The Cu_2^- and Ni_2^- spectra are adapted from previous publications from this laboratory (Refs. 7, 8).

III. RESULTS AND ANALYSIS

A. Dimers: $NiCu^-$ and $NiAg^-$

Photoelectron spectra of Cu_2^-, $NiCu^-$, and Ni_2^- are shown in Fig. 1, in which the photoelectron counts are plotted as a function of electron binding energy over the full binding energy range between 0 and 3.5 eV. Similar Ag_2^-, $NiAg^-$, and Ni_2^- spectra are shown in Fig. 2. The remarkable similarity of the $NiCu^-$ and $NiAg^-$ photoelectron spectra to those of Cu_2^- and Ag_2^- reflects a corresponding similarity in the chemical bonding and electronic structure of these species. The features at ~0.9 eV binding energy of the Cu_2^-, Ag_2^-, and Ni_2^- spectra have been previously identified as corresponding to detachment from the σ^* orbital to form the $^1\Sigma_g^+$ ($d^{20}\sigma_g^2$) (Cu_2, Ag_2) or the ($d^{18}\sigma_g^2$) (Ni_2) ground states, and the feature at ~2.8 eV binding energy in the Cu_2^- and Ag_2^- spectra has been shown to arise from σ orbital detachment to form the $^3\Sigma_u^+$ ($d^{20}\sigma_g^1\sigma_u^{*1}$) state. The similarity in position and appearance of the major features in the $NiCu^-$ and $NiAg^-$ spectra strongly suggests a similar interpretation, where the ground state has a ($d_{Ni}^9 d_M^{10}\sigma^2$) configuration (M = Cu, Ag) while the state at ~2.8 eV binding energy has a ($d_{Ni}^9 d_M^{10}\sigma^1\sigma^{*1}$) configuration. An additional feature at ~2.1
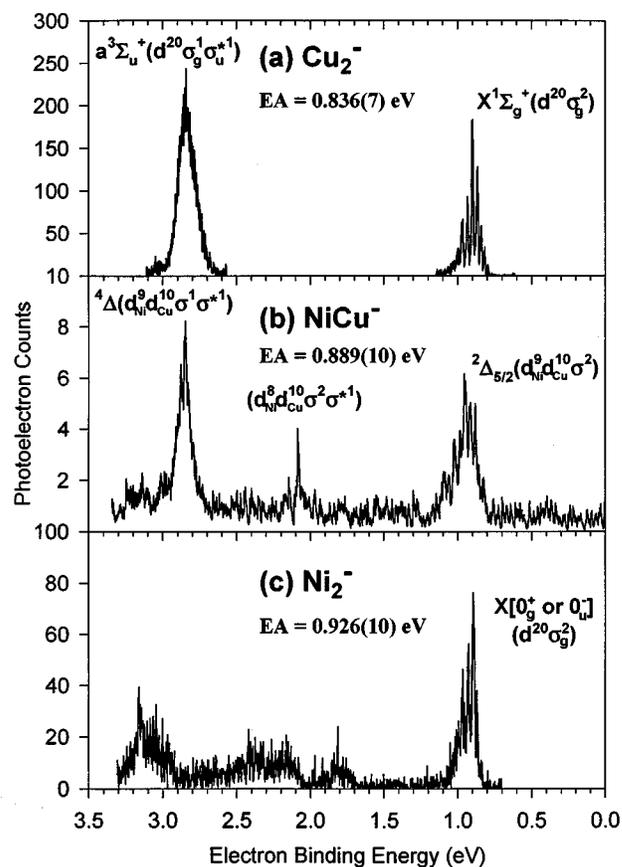
eV in the $NiCu^-$ and $NiAg^-$ spectra may be associated with d-electron detachment, similar to the intermediate features in the Ni_2^- spectrum.

Photoelectron angular distributions provide further evidence to support the preliminary findings presented above. For example, for Cu_2^-, the anisotropy parameters measured[8] for the transitions to the neutral $^1\Sigma_g^+$ (σ_u^* detachment) and $^3\Sigma_u^+$ (σ_g detachment) states are 0.8 and 1.5, respectively. Detachment from the nearly spherical σ_g orbital is therefore more s-like than detachment from the σ_u^* orbital. The anisotropy parameters measured for the $NiCu^-$ and $NiAg^-$ spectra, presented in Tables I and II, respectively, show similar behavior for the features at similar positions, suggesting that detachment to form the ground state is also from a σ^*-type orbital while formation of the excited state at 2.8 eV binding energy follows σ orbital detachment. The intermediate state at ~2.1 eV binding energy has a lower β for both $NiCu^-$ and $NiAg^-$, consistent with detachment from an orbital with substantial d character.

Franck–Condon simulations of the NiCu and the NiAg doublet ground states are presented in Fig. 3. The Franck–Condon analysis procedure has been described
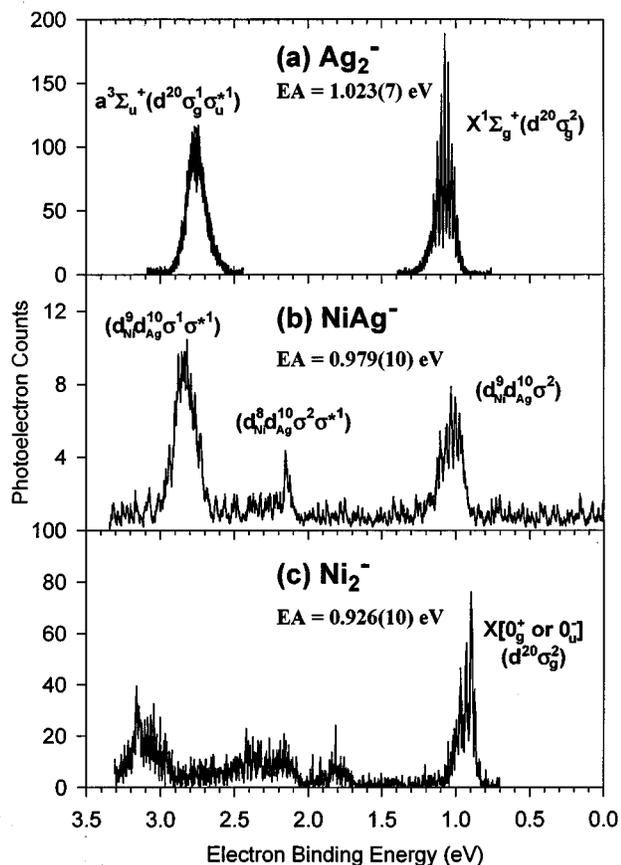
FIG. 2. Photoelectron spectra of (a) Ag_2^-, (b) $NiAg^-$, and (c) Ni_2^- obtained at 351.1 nm (3.531 eV) with 10 meV instrumental resolution. The $NiAg^-$ spectrum was obtained with the laser polarization parallel to the electron collection angle. The Ag_2^- and Ni_2^- spectra are adapted from previous publications from this laboratory (Refs. 7, 8).

previously.[6,7,23] The spectral simulation can yield the vibrational frequency of the anion and the neutral, bond length changes between the anion and the neutral, and the anion vibrational temperature, which was 500 ± 150 K for both $NiCu^-$ and $NiAg^-$. In the case of $NiCu^-$, the vibrational frequency of the neutral (273 cm^{-1}) and the equilibrium bond length (2.234 Å) were fixed at the values obtained by Spain and Morse,[18] and the anion frequency and bond length were extracted. Similarly, the NiAg ground state bond length

was fixed at the preliminary value calculated by Brocławik.[25] The results obtained from the Franck–Condon simulation for NiCu and NiAg are presented in Tables I and II, respectively. The direction of the bond length change cannot be determined from the simulation; however, since both the vibrational frequency and the dissociation energy (discussed below) of the anion are lower than those of the neutral, the neutral NiCu and NiAg bond lengths are surely shorter than the anion bond lengths, as reported in Tables I and II. This conclusion is also consistent with the observations presented above which indicate detachment from a σ^* orbital to form the ground state of the neutral.

The adiabatic electron affinity (EA), which is the energy difference between the ground electronic and vibrational states of the anion and of the neutral, can only be precisely determined from the photoelectron spectra when the vibrational origin can be identified.[7] Since vibrational structure was resolved in the low binding energy feature in both the $NiCu^-$ and the $NiAg^-$ spectra, we are able to identify the origin and obtain an accurate measure of the electron affinity. The electron affinities for NiCu and NiAg are found to be 0.889 ± 0.010 and 0.979 ± 0.010 eV, respectively.

Vertical term energies for the excited states at ~2.8 eV binding energy in the $NiCu^-$ and $NiAg^-$ spectra are also reported in Tables I and II. Vibrational structure is not resolved in these states, suggesting a vibrational frequency of $\omega_e \leqslant 150$ cm^{-1} for both NiCu and NiAg.

Recently, Morse and co-workers reported $D_0(NiCu)$ to be 2.05 ± 0.01 eV.[13] This can be used with the electron affinity of NiCu and the known electron affinities of Ni and Cu to determine the dissociation energy of $NiCu^-$. Since the EA of Cu (1.235 ± 0.005 eV)[6] is larger than that of Ni (1.156 ± 0.010 eV)[21] the minimum energy dissociation path is $NiCu^-\rightarrow Ni+Cu^-$, therefore, the relationship $D_0(NiCu^-)+EA(Cu)=D_0(NiCu)+EA(NiCu)$ can be used to determine $D_0(NiCu^-)=1.70\pm0.02$ eV. The dissociation limit of the excited $(d_{Ni}^9 d_{Cu}^{10}\sigma^1\sigma^{*1})$ configuration is to the same atomic states as is the ground state, so the dissociation energy of the NiCu excited state at ~2.8 eV binding energy can be estimated as 0.11 ± 0.05 eV, given the measured term energy (1.94 eV) and the ground state NiCu dissociation energy. The dissociation energy for neutral NiAg has not been

TABLE I. Measured molecular constants of NiCu electronic states.

	State	Vertical detachment energy (eV)	Term energy (cm^{-1})	ω_e (cm^{-1})	r_e (Å)	D_0 (eV)	Anisotropy parameter, β[a]
$NiCu^-$	$X\,^3\Delta\ (d_{Ni}^9 d_{Cu}^{10}\sigma^2\sigma^{*1})$	0	0	235 ± 25	2.36 ± 0.01[b]	1.70 ± 0.02	
NiCu	$X\,^2\Delta_{5/2}\ (d_{Ni}^9 d_{Cu}^{10}\sigma^2)$	0.95 ± 0.01	0	273 ± 1[c]	2.2346 ± 0.0005[c]	2.05 ± 0.05[c]	1.2 ± 0.3
	$(d_{Ni}^8 d_{Cu}^{10}\sigma^2\sigma^{*1})$	2.09 ± 0.01	$9,680\pm150$				0.8 ± 0.3
	$^4\Delta\ (d_{Ni}^9 d_{Cu}^{10}\sigma^1\sigma^{*1})$	2.83 ± 0.02	$15,650\pm150$	$\leqslant150$		0.11 ± 0.05	1.5 ± 0.3

[a]Anisotropy parameter $\beta=(I_0-I_{90})/(\frac{1}{2}I_0+I_{90})$, where I_0 and I_{90} are the intensities of photoelectron signal collected with the laser polarization oriented parallel and perpendicular to the electron collection direction, respectively.
[b]Based on this work and that of Morse (Ref. 20).
[c]From Morse (Ref. 20).

TABLE II. Measured molecular constants of NiAg electronic states.

	State[a]	Vertical detachment energy (eV)	Term energy (cm⁻¹)	ω_e (cm⁻¹)	r_e (Å)	D_0 (eV)	Anisotropy parameter, β[b]
NiAg⁻	$X\ ^3\Delta$ ($d^9_{Ni}d^{10}_{Cu}\sigma^2\sigma^{*1}$)	0	0	185±25	2.40+0.121[c]	D_0(NiAg)−0.32	
NiAg	$X\ ^2\Delta$ ($d^9_{Ni}d^{10}_{Cu}\sigma^2$)	1.04±0.01	0	235±25	2.40[d]	1.96[d]	0.6±0.3
	($d^8_{Ni}d^{10}_{Cu}\sigma^2\sigma^{*1}$)	2.15±0.01	9,440±150				0.4±0.3
	$^4\Delta$ ($d^9_{Ni}d^{10}_{Cu}\sigma^1\sigma^{*1}$)	2.86±0.05	15,160±400	≤150		D_0(NiAg)−1.88	1.0±0.3

[a]Term symbol assignments are tentative.
[b]Anisotropy parameter $\beta=(I_0-I_{90})/(\frac{1}{2}I_0+I_{90})$, where I_0 and I_{90} are the intensities of photoelectron signal collected with the laser polarization oriented parallel and perpendicular to the electron collection direction, respectively.
[c]Based on this work and preliminary calculations by Brocławik (Ref. 25).
[d]From preliminary calculations by Brocławik (Ref. 25).

measured experimentally, but has been calculated recently by Brocławik[25] as D_0(NiAg)≈1.96 eV using density functional theory. Since the EA for Ag (1.302±0.007 eV)[21] is larger than that for NiAg (0.979 eV) we can conclude that the anion bond is weaker than the neutral bond by ∼0.32 eV; combining this finding with the calculated dissociation energy of NiAg we estimate D_0(NiAg⁻)≈1.96−0.32 eV≈1.64 eV. The

dissociation energy of the NiAg ($d^9_{Ni}d^{10}_{Cu}\sigma^1\sigma^{*1}$) excited state is estimated as 0.08 eV by subtracting the term energy of this state (1.88 eV) from the calculated dissociation energy of the ground state.

Vibrational structure is not observed in the intermediate transitions at ∼2.1 eV binding energy in the NiCu⁻ and NiAg⁻ spectra. Consequently, vertical detachment energies, VDE, were determined from the maxima in the spectra. These were then used to determine vertical term energies, T_v=VDE−EA, which are included in Tables I and II for NiCu and NiAg, respectively.

B. Trimers: NiAg₂⁻ and Ni₂Ag⁻

The photoelectron spectra of Ag₃⁻, NiAg₂⁻, Ni₂Ag⁻, and Ni₃⁻ are presented in Fig. 4. The Ag₃⁻ spectrum, Fig. 4(a), contains a single intense feature at 2.43(1) eV binding energy which corresponds to the transition from the linear ground state of Ag₃⁻ to a linear electronic state of the neutral. The Ag₃ ground state has a triangular geometry according to *ab initio* calculations,[12,26] and so has poor Franck–Condon overlap with the anion ground state and is not observable in the Ag₃⁻ photoelectron spectrum. The electron affinity is estimated[7] to be 2.32 eV by subtracting the calculated term energy[12,26] of the linear Ag₃ $^2\Sigma_u^+$ state from the observed VDE. The Ni₃⁻ photoelectron spectrum in Fig. 4(d) contains features corresponding to transitions to numerous Ni₃ electronic states,[9] but in this case the anion is slightly bent and a transition to the ground state is observable at 1.41(5) eV. The largest feature in the nickel trimer photoelectron spectrum, however, is centered at 2.32(1) eV binding energy, remarkably close to the single peak in the Ag₃⁻ spectrum. The similarity in the positions of the peaks becomes more striking when compared further to the NiAg₂⁻ [Fig. 4(b)] and Ni₂Ag⁻ [Fig. 4(c)] photoelectron spectra. One major feature is apparent in each of these spectra at 2.37±0.01 and 2.39±0.01 eV in the NiAg₂⁻ and Ni₂Ag⁻ spectra, respectively; these values are intermediate between the VDE of the major peaks in the Ag₃⁻ and Ni₃⁻ photoelectron spectra. Additionally, the NiAg₂⁻ spectrum contains a smaller, broad feature at higher binding energy than the major peak, and the Ni₂Ag⁻ spectrum contains a similar, slightly more prominent, feature. Comparison of all four spectra reveals that this feature is repeated in the
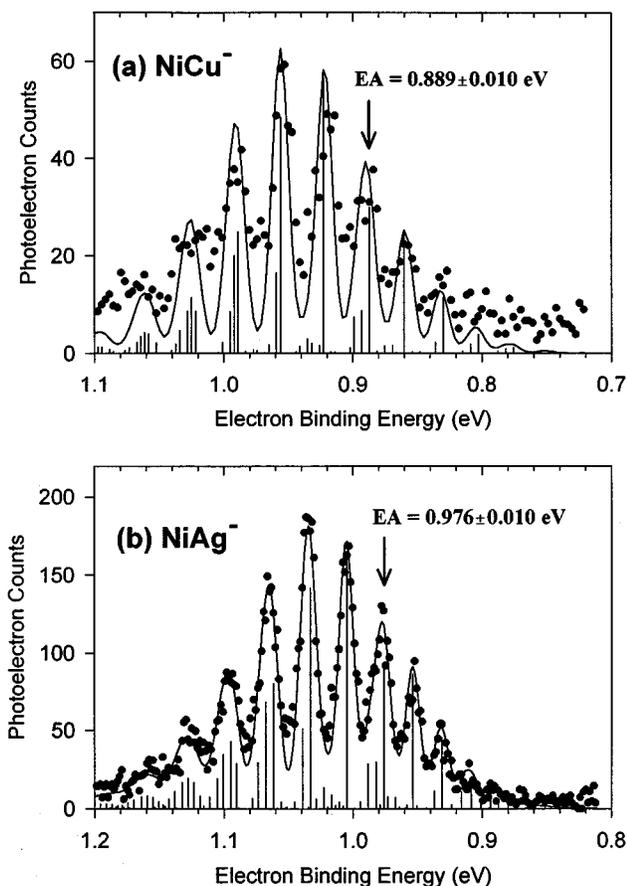

FIG. 3. Franck–Condon simulations of the transitions to the ground states of (a) NiCu and (b) NiAg. The points represent the experimental data and the solid curve is the result of the Franck–Condon simulation. The individual vibrational transitions are marked with sticks, and the origin is marked with a vertical arrow.
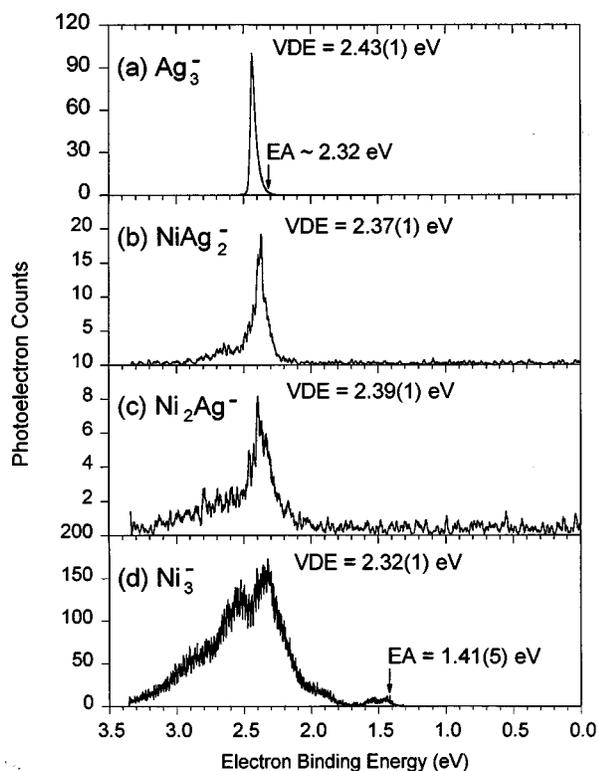
FIG. 4. Photoelectron spectra of (a) Ag_3^-, (b) $NiAg_2^-$, (c) Ni_2Ag^-, and (d) Ni_3^- obtained at 351.1 nm (3.531 eV) with 10 meV instrumental resolution. The spectra were obtained with the laser polarization at the magic angle (54.7°) with respect to the electron collection direction. The Ag_3^- spectrum is adapted from a previous publication from this laboratory (Ref. 7) and the Ni_3^- was obtained in this laboratory (Ref. 15).

Ni_3^- case, except here it is almost as prominent as the 2.32 eV peak. All these observations strongly suggest that, while the density of electronic states increases dramatically as the number of d-orbital holes increases, the well-defined linear anion to linear neutral transition in the Ag_3^- spectrum is also the most important feature in the other spectra in Fig. 4.

IV. DISCUSSION

A. Dimers: NiCu⁻ and NiAg⁻

The spectra of NiCu⁻ and NiAg⁻, Figs. 1(b) and 2(b), are remarkably similar. Both spectra show two intense features and a weaker intermediate feature. They are markedly simpler than the Ni_2^- spectrum [Figs. 1(c) and 2(c)], which contains many unassigned features.[8] The two dominant features in the NiCu⁻ and NiAg⁻ spectra are similar to the two features observed for Cu_2^- [Fig. 1(a)] and Ag_2^- [Fig. 2(a)], suggesting that they are due to similar photoelectron transitions. The presence of a weaker intermediate state at $T_0 \approx 1.2$ eV is almost certainly a consequence of the open-shell d-electron structure of these two mixed metal dimers.

In the coinage metal dimer spectra, two features were observed.[7] The low binding energy feature was assigned to detachment of an electron from an σ^* orbital leaving the singlet ground state of the neutral coinage metal dimer, $^1\Sigma_g^+$ $(d^{20}\sigma_g^2)$. The high binding energy feature was then as-

signed to detachment of a σ orbital electron leaving the triplet excited state, $^3\Sigma_u^+$ $(d^{20}\sigma_g^1\sigma_u^{*1})$. Vibrational structure was not resolved in the transition to the Cu_2 and Ag_2 $^3\Sigma_u^+$ states, suggesting that the vibrational frequencies of these states are not more than ~ 120 cm^{-1}, substantially less than the frequencies[1] of the $^1\Sigma_g^+$ ground states of Cu_2 (266.43 cm^{-1}) and Ag_2 (192.4 cm^{-1}). The substantial reduction in vibrational frequency between the singlet and triplet state is consistent with a dramatic reduction in formal bond order from one to zero. Despite the formal bond order of zero, the triplet state of Cu_2 is weakly bound with an estimated bond energy of 0.1 eV.

1. The neutral $(d_{Ni}^9 d_M^{10}\sigma^2)$ and anion $(d_{Ni}^9 d_M^{10}\sigma^2\sigma^{*1})$ ground states

The ground state of NiCu has been definitively assigned by both experiment[17,18,20] and theory[13,16] to be $^2\Delta_{5/2}(d_{Ni}^9 d_{Cu}^{10}\sigma^2)$. This state correlates in the separated atom limit with a ground state copper atom, ^2S $(3d^{10}4s^1)$ and a nickel atom in its first excited state, $^3D_3(3d^94s^1)$. The $^3D_3(3d^94s^1)$ atomic state of Ni lies only 204.8 cm^{-1} above the ground state, $^3F_4(3d^84s^2)$.[22] Although the presence of the open d shell creates the possibility of d orbital participation in the bonding of NiCu, both theory and experiment suggest that the chemical bonding in the ground electronic state results primarily from the interaction of the $4s$ orbitals.

This interaction of the $4s$ orbitals of Ni and Cu results in the formation of a bonding $s\sigma$ and antibonding $s\sigma^*$ pair of orbitals. Three observations in the present work indicate strongly that the low binding energy transition in the NiCu spectrum results from detachment of the electron from the $s\sigma^*$ orbital: (1) The photoelectron angular distribution results for this transition are consistent with detachment of an electron from an $s\sigma^*$ orbital. (2) The vibrational frequency of the anion is lower, 235 cm^{-1}, than that of the neutral, 273 cm^{-1}, suggesting the loss of an electron from an antibonding $s\sigma^*$ orbital and a resulting increase in bond order. (3) The NiCu anion bond strength, 1.70 eV, is found to be weaker than that for the neutral, 2.05 eV, again suggesting a reduced bond order for the anion. These observations strongly support the assignment of the anion ground state electron configuration as $(d_{Ni}^9 d_{Cu}^{10}\sigma^2\sigma^{*1})$, where the extra electron has $s\sigma^*$ character and the formal σ bond order of the anion is 0.5.

The d orbital configuration in the anion is not known; however, the extra antibonding $s\sigma^*$ electron would not be expected to significantly perturb the d orbitals, indicating that the anion ground state is either $^1\Delta$ or $^3\Delta$, given that the neutral is $^2\Delta_{5/2}(d_{Ni}^9 d_{Cu}^{10}\sigma^2)$. This is also consistent with the selection rule for photoelectron detachment transitions that requires the spin multiplicity to change by ± 1, and with two major propensity rules,[27,28] namely: (a) Single electron processes, in which there is no reorganization of the electron configuration, are expected to dominate; and (b) Processes involving s electron detachment are expected to be stronger than those involving d electron detachment. Further exami-

nation of the NiCu$^-$ spectrum (Sec. IV A 2) will enable the further specification of the NiCu$^-$ ground state as $^3\Delta$.

The ground state of NiAg has not been determined spectroscopically; however, since both NiCu and NiAu[19] have $^2\Delta_{5/2}(d_{Ni}^9 d_M \sigma^2)$ ground states it would seem likely that NiAg has the same symmetry. Recent density functional calculations,[25] however, have suggested a $^2\Pi$ ground state, and low lying $^2\Delta$ and $^2\Sigma$ states. The photoelectron spectra presented here cannot distinguish between these orientations of the d hole. The angular distribution results for NiAg and the changes between the anion and the neutral in bond length, bond strength, and vibrational frequency, reported in Table II, are again consistent with detachment from an antibonding $s\sigma^*$ orbital. In a manner analogous to the NiCu case we assign the low binding energy feature to a $(d_{Ni}^9 d_{Ag}^{10}\sigma^2)\leftarrow(d_{Ni}^9 d_{Ag}^{10}\sigma^2\sigma^{*1})$ transition, but in this case do not assign term symbols, pending further experimental or theoretical investigations.

The electron affinities in Tables I and II, as determined from the assigned origin for the low binding energy state, are substantially lower for both NiCu (0.889 ± 0.01 eV) and NiAg (0.976 ± 0.01 eV) than those for the separated atoms.[6,21] The assignment of the low binding energy states in the photoelectron spectra of NiCu$^-$ and NiAg$^-$ to detachment from an $s\sigma^*$ orbital is consistent with this, since the destabilization of the $s\sigma^*$ orbital due to the interaction between the atomic s orbitals will reduce the energy required to remove the extra electron from the dimer relative to the free atoms. This is in accord with our findings for Cu$_2^-$ and Ni$_2^-$.

The results presented above confirm that the chemical bonding in the ground states of NiCu and NiAg is dominated by s orbital overlap to form a doubly occupied bonding orbital and an empty antibonding σ^* orbital. The d orbitals play only a minor role, if any, in the chemical bonding. Electron repulsion ensures that the anion ground state is obtained by the addition of an extra electron to the antibonding σ^* orbital.

2. The ($d_{Ni}^9 d_M^{10}\sigma^1\sigma^{*1}$) excited states

Comparison of the NiCu$^-$ and NiAg$^-$ photoelectron spectra with those of Cu$_2^-$ and Ag$_2^-$ suggests strongly that the high binding energy feature at 2.8 eV in each spectrum is due to a similar photodetachment transition. This feature in the NiCu$^-$ and NiAg$^-$ spectra can therefore be assigned straightforwardly as detachment of an electron from a σ orbital, NiM $(d_{Ni}^9 d_M^{10}\sigma^2\sigma^{*1})\leftarrow$NiM$^-(d_{Ni}^9 d_M^{10}\sigma^2\sigma^{*1})$, with further support given by four more considerations: (1) The anisotropy parameter β is relatively large for this transition (Tables I and II), consistent with detachment of an electron from a σ orbital. (2) The lack of resolved vibrational structure in this feature in both the NiCu$^-$ and the NiAg$^-$ spectra suggests a low (≤150 cm^{-1}) vibrational frequency for this state. (3) The dissociation energies for this state are very small (0.11 ± 0.05 and ~0.08 eV for NiCu and NiAg, respectively), consistent with the expected (for the proposed assignment) formal bond order of zero. (4) Detachment of an electron from

a σ orbital is consistent with the propensity rules for photoelectron spectroscopy described in Sec. IV A 1.

The similarities between the homonuclear coinage metal diatomic anion spectra and those of NiCu$^-$ and NiAg$^-$ can also help assign the spin multiplicities of the common electronic states. As mentioned in Sec. IV A 1, the NiCu$^-$ ground state is either $^1\Delta$ or $^3\Delta$ since the neutral ground state is $^2\Delta_{5/2}$. The $(d_{Ni}^9 d_M^{10}\sigma^1\sigma^{*1})$ state is clearly the opposite spin component of the NiCu ground state, in analogy with the singlet and triplet states of Cu$_2$ and Ag$_2$; therefore the excited state is $^4\Delta$. Since transitions in photoelectron spectroscopy require $\Delta S=\pm1$, the only possibility for the anion ground state is $^3\Delta$. The spin–orbit components of this state are probably inverted to give a $^3\Delta_3$ ground state of NiCu$^-$; however, we do not have enough evidence to make this assignment. The NiAg states are most likely exactly analogous to those of NiCu: the ground state is a doublet, the excited state is a quartet made up of the opposite spin component of the ground state, and the ground state of the anion is a triplet. Term symbols of NiAg cannot be definitively assigned since unambiguous experimental or theoretical evidence does not exist to provide definitive information on the Ni d-hole orientation; therefore the state assignments in Table II are tentative.

The energy spacing between the transitions to the ground states and to the $(d_{Ni}^9 d_M^{10}\sigma^1\sigma^{*1})$ states of NiCu (1.94 eV) and NiAg (1.88 eV) gives a direct measure of the HOMO-LUMO energy spacings for these species. As can be seen in Figs. 1 and 2, the term energies of the $(d_{Ni}^9 d_M^{10}\sigma^1\sigma^{*1})$ excited states are remarkably similar to those of the Cu$_2$ and Ag$_2$ $(d_M^{10} d_M^{10}\sigma^1\sigma^{*1})$ states. The HOMO-LUMO energy spacings of all these species, therefore, are very close, suggesting that the bonding interactions are nearly identical in all cases.

3. The $d_{Ni}^8 d_M^{10}\sigma^2\sigma^{*1}$ excited states

The intermediate state at 1.20 ± 0.02 eV (9680 ± 150 cm^{-1}) above the ground state in the NiCu$^-$ and NiAg$^-$ spectra, Figs. 1 and 2, was not observed in the Cu$_2$ and Ag$_2$ spectra, suggesting that it must be related to the d hole present in NiCu and NiAg.

In a recent paper,[13] Spain and Morse used ligand field theory to calculate term energies for the $(d_{Ni}^8 d_{Cu}^{10}\sigma^2\sigma^{*1})$ manifold of states of NiCu. They found that the calculations are in good agreement with the optical transitions that they observe in their spectra,[18] and they predict an additional manifold of six states between 9664 and 10 343 cm^{-1} above the ground state, energies outside their accessible spectral region. The photoelectron spectrum does not contain the necessary information to ascribe the observed peak to any one (or more) of these states; consequently, we can tentatively ascribe the intermediate transition in the NiCu$^-$ spectrum to a NiCu$(d_{Ni}^8 d_{Cu}^{10}\sigma^2\sigma^{*1})\leftarrow$NiCu$^-(d_{Ni}^9 d_{Cu}^{10}\sigma^2\sigma^{*1})$ transition, but cannot distinguish between the states predicted by Spain and Morse. The assignment is consistent with the propensity rule for photoelectron detachment in that it is a single electron transition and the lower intensity of the peak relative to the others in the NiCu$^-$ spectrum is consistent with detachment

from a d orbital. Of the six states predicted in this region by Spain and Morse, the two closest to 9680 cm^{-1} have Ω values of 2.5 (9649 cm^{-1}) and 3.5 (9751 cm^{-1}). Since the ground state of NiCu$^-$ is probably $^3\Delta_3$, these states would also be the most likely to appear in the photoelectron spectrum ($\Delta\Omega = \pm 1/2$), lending further evidence that these may be the observed state and that the ground state is indeed $^3\Delta_3$.

At present there are no published experimental or theoretical results for NiAg that can assist in the assignment of the NiAg$^-$ photoelectron spectrum; however, the similarity of the spectrum to that of NiCu$^-$ strongly suggests that the intermediate state corresponds to an analogous transition. We thus assign the transition to d-electron detachment, NiAg $(d_{Ni}^8 d_{Ag}^{10} \sigma^2 \sigma^{*1}) \leftarrow$ NiAg$^- (d_{Ni}^9 d_{Ag}^{10} \sigma^2 \sigma^{*1})$. The term symbol cannot be suggested, since we have no information of the configuration of the d orbitals.

In both the NiCu$^-$ and NiAg$^-$ spectra the intermediate state at 1.2 eV above the ground state is much sharper than the two dominant transitions, suggesting that a nonbonding electron has been detached. This finding is consistent with the suggestion that s orbital overlap dominates chemical bonding, and that the d orbitals are essentially nonbonding in nature, so that detachment of an electron from a d orbital does not significantly alter the bond length. The appearance of only one feature is somewhat surprising, however, since we would expect transitions to at least two, and possibly as many as six, electronic states in this energy region. The observation of only one state is probably a result of the low signal level in the spectrum, and weaker transitions to other states may be present.

B. NiAg$_2^-$ and Ni$_2$Ag$^-$

The spectra of the NiAg$_2^-$ and Ni$_2$Ag$^-$ trimers are remarkably similar to that of Ag$_3^-$ [Fig. 4(a)]. The single feature in the Ag$_3^-$ spectrum is due[7] to a transition between the linear ground state of the anion and a linear excited state of the neutral. The ground state of the neutral trimer is bent, and so has a very weak Franck–Condon overlap with the linear ground state of the anion. The measured VDE therefore does not correspond to the adiabatic electron affinity of the trimer, and the calculated[12] term energy of the linear state of Ag$_3$ was subtracted from the VDE to estimate the EA. The similarity of the spectra of NiAg$_2^-$ and Ni$_2$Ag$^-$ to that of the silver trimer anion suggests a similar interpretation. The observed transitions in the NiAg$_2^-$ and Ni$_2$Ag$^-$ spectra are thus assigned to a linear to linear transition between the ground state of the anion and a linear excited state of the neutral clusters. The adiabatic electron affinities of the mixed trimers cannot be estimated, however, since calculations of the term energies of the linear excited states are not available.

The complexity of the Ni$_3^-$ photoelectron spectrum [Fig. 4(d)] is attributable to the presence of an open d shell which results in a markedly higher density of low lying states, as discussed in detail in a previous publication.[9] Transitions to several low lying electronic states of the neutral are observed, reflecting the fact that the low lying states of the anion and of the neutral adopt both linear and triangular geometries. A much wider range of transitions is therefore observed. The adiabatic electron affinity of Ni$_3^-$ was estimated to be 1.41$\pm$0.05 eV from the spectrum, although the ground state could not be definitively assigned. The comparison of the Ni$_3^-$ spectrum with those of Ag$_3^-$, NiAg$_2^-$, and Ni$_2$Ag$^-$ presented in Fig. 4, however, enables the extraction of further qualitative information about the structure of the nickel trimer: the position of the largest peak in the Ni$_3^-$ spectrum coincides almost precisely with the largest peaks in the other spectra, implying that the linear anion to linear neutral transition appears at the same binding energies even with the successive addition of d orbital holes. The electron affinity apparently changes substantially ($\sim$2.32 and 1.41 $\pm$0.05 eV for Ag$_3$ and Ni$_3$, respectively), as does the density of electronic states, but the linear geometry of the anion, and the binding energy of an electron to this a linear neutral state, is nearly invariant in all of these triatomics.

V. CONCLUSIONS

Negative ion photoelectron spectra obtained at 351.1 nm for NiCu$^-$, NiAg$^-$, NiAg$_2^-$, and Ni$_2$Ag$^-$ give direct information about the low lying states of the anion and the neutral mass selected clusters. The objective of the study was to investigate the effect of successive addition of d holes on the bonding and electronic structure of small metal clusters.

The photoelectron spectra of NiCu$^-$ and NiAg$^-$ are remarkably similar to those obtained for the coinage metal dimers, Cu$_2^-$ and Ag$_2^-$, except that a weak transition is observed at intermediate energy which we have assigned to d electron detachment. The two principal transitions in the dimer spectra are assigned to $s\sigma^*$ and $s\sigma$ detachments to form the $^2\Delta_{5/2}$ ground states and $^4\Delta$ excited states, respectively. The data show that the bonding of both species is dominated by s orbital overlap to form $s\sigma$ bonding and $s\sigma^*$ antibonding pairs, and that the d and p orbitals participate to only a minor extent in the bonding. Since the NiCu ground state is $^2\Delta_{5/2}(d_{Ni}^9 d_{Cu}^{10} \sigma^2)$, and the extra electron in the anion has $s\sigma^*$ character, the electron configuration of the NiCu$^-$ ground state is assigned as $(d_{Ni}^9 d_{Cu}^{10} \sigma^2 \sigma^{*1})$. Also, the similarity between the photoelectron spectra corresponding to the Cu$_2$ $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states and the NiCu $^2\Delta_{5/2}$ and $^4\Delta$ states suggests the anion is $^3\Delta$, with the Ω=3 component probably lowest in energy. The electron configuration of the NiAg neutral ground state is $(d_{Ni}^9 d_{Ag}^{10} \sigma^2)$ and the NiAg$^-$ ground state is $(d_{Ni}^9 d_{Ag}^{10} \sigma^2 \sigma^{*1})$; however, since the d orbital configuration is unknown the term symbols can be assigned only tentatively, by analogy with the NiCu state term symbols. Additional states of NiCu and NiAg, formed by $d \rightarrow s$ electron promotion to give the $(d_{Ni}^8 d_M^{10} \sigma^2 \sigma^{*1})$ electron configuration, are observed.

The transitions to the NiCu and NiAg ground states exhibit resolved vibrational structure. Franck–Condon simulations yield molecular constants reported in Tables I and II, and the electron affinities of NiCu and NiAg are obtained from the assigned vibrational origins as EA(NiCu)=0.889 $\pm$0.010 eV and EA(NiAg)=0.976$\pm$0.010 eV.

The photoelectron spectra of the trimers, $NiAg_2^-$ and Ni_2Ag^-, are similar to those obtained for the coinage metal trimers. A single transition is observed which is assigned to the linear to linear transition between a linear anion ground state and a linear excited state of the neutral trimer. The VDEs are remarkably similar to those of the coinage metal trimers, and the most intense feature in the Ni_3^- spectrum. The density of electronic states increases dramatically in the same order as the number of d holes, $Ag_3^- < NiAg_2^- < Ni_2Ag^- < Ni_3^-$; however, the binding energy of an electron to the linear trimer is nearly invariant between all these species, and the anion ground states are probably all linear.

ACKNOWLEDGMENTS

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