Joint photoelectron and theoretical study of \((\text{Rh}_m\text{Co}_n)^-\) \((m = 1–5, \ n = 1–2)\) cluster anions and their neutral counterparts†

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Anion photoelectron spectroscopic experiments and calculations based on density functional theory have been used to investigate and uniquely identify the structural, electronic, and magnetic properties of both neutral and anionic \((\text{Rh}_m\text{Co}_n)^-\) and \((\text{Rh}_m\text{Co}_n)^-\) \((m = 1–5, \ n = 1–2)\) clusters, respectively. Negative ion photoelectron spectra are presented for electron binding energies up to 3.493 eV. The calculated electron affinities and vertical detachment energies are in good agreement with the measured values. Computational results for geometric structures and magnetic moments of both cluster anions and their neutrals are presented.

I. Introduction

For both scientific and technological reasons, interest in atomic clusters has grown in recent years. In particular, transition metal (TM) clusters have novel and highly size dependent electronic, chemical, optical, and magnetic properties at the nanometric scale, reflecting the important role played by their structures. In some cases, a single size cluster is found to possess unexpected properties, such as multiple reaction rates or multiple ionization potentials, and these have been attributed to the presence of geometric isomers, each having its own properties. Combined experimental and computational investigations of the structures and properties of clusters support this interpretation. The determination of the geometric structure of transition metal (TM) clusters is a vital step towards understanding cluster properties, such as catalytic and magnetic properties. Particularly interesting among TM clusters are those containing cobalt, since small cobalt clusters exhibit magnetic moments that are considerably larger than that of bulk cobalt. (Cobalt clusters preserve the atomic magnetic moment value of 2 \(\mu_B\) per atom up to clusters with diameters of ~1.5 nm.) In general, the enhancement of magnetism in clusters can be qualitatively understood as a consequence of the reduction of local coordination number, which in turn results in a stronger localization of 3d electrons, and in a reduction of the effective d band width. Also, the size dependence of the interatomic distances, typically 20% smaller than those in bulk crystals, plays an important role in determining the ground state magnetic moments. Finally, finite size effects and reduced symmetry are also responsible for the magnetic anisotropy energies per atom found in TM clusters.

While many experimental and theoretical studies have already been carried out on homonuclear TM clusters, very few investigations have focused on mixed (alloy) clusters. Heteronuclear clusters exhibit a much wider variety of magnetic behaviors due to more variables coming into play. For example, recent experimental studies have shown that rhodium/cobalt nanoparticles exhibit enhanced average magnetizations per atom compared to macroscopic rhodium/cobalt alloys of similar compositions. They are also expected to show larger magnetic anisotropies compared to pure 3d TM clusters due to the stronger spin orbit coupling at the 4d atoms. Consequently, a comprehensive study of the properties of mixed 3d-4d TM clusters should be valuable.

Here, we report a negative ion photoelectron spectroscopy (PES) study combined with theoretical calculations done with density functional theory (DFT) using the generalized gradient approximation (GGA) for exchange–correlation functional for the anionic and neutral clusters, \((\text{Rh}_m\text{Co}_n)^-\) and \((\text{Rh}_m\text{Co}_n)^-\) \((m = 1–5, \ n = 1–2)\), respectively. Previous computational work has examined magnetic and structural aspects of several rhodium/cobalt neutral clusters. The present work incorporates an experimental (and its complementary computational) component by considering rhodium/cobalt anionic clusters, while at the same time providing a more complete picture of the geometries, electronic structure, and magnetic properties of both of these anionic and neutral rhodium/cobalt clusters.
II. Methods

A Experimental

Negative ion photoelectron spectroscopy is conducted by crossing a beam of mass selected anions with a fixed-frequency photon beam and energy analyzing the resultant photo-detached electrons. The photodetachment process is governed by the energy conserving relationship, \( h\nu = E\text{BE} + E\text{KE} \), where \( h\nu \) is the photon energy, EBE is the electron binding energy, and EKE is the electron kinetic energy. Our apparatus has been described previously elsewhere.\(^{30}\) Briefly, the apparatus consists of an ion source, a linear time-of-flight (TOF) mass spectrometer, a Nd:YAG (yttrium aluminium garnet) photodetachment laser, and a magnetic bottle photoelectron spectrometer (MB-PES). The instrumental resolution of the MB-PES is \( \sim 35 \text{ meV} \) at 1 eV EKE. The third harmonic (355 nm, 3.493 eV) of a Nd:YAG was used to photodetach the cluster anions of interest. Photoelectron spectra were calibrated against the well known atomic transitions of Cu\(^+\).

Mixed rhodium-cobalt cluster anions were generated in a laser vaporization disk source. First, a cobalt disk was made by pressing pure cobalt powder under a pressure of \( \sim 170 \text{ MPa} \). Then a layer of rhodium powder was deposited on top of the cobalt disk, and pressed again under the same pressure of \( \sim 170 \text{ MPa} \). We then assured that the laser would vaporize both components, this particular procedure has been done to avoid diluting the Rh too much. This rhodium/cobalt disk was then ablated by a pulsed laser beam of 532 nm photons from a Nd:YAG laser. The plasma was cooled by supersonically expanding a plume of helium carrier gas issuing from a pulsed valve with a backing pressure of \( \sim 1 \text{ MPa} \). The negatively charged clusters were then extracted into our spectrometer for photoelectron spectroscopy studies.

B Computational

A structural optimization and frequency analysis has been performed on (Rh\(_m\)Co\(_n\))^– and Rh\(_m\)Co\(_n\) (\( m = 1–5, n = 1–2 \)) clusters using density functional theory (DFT) calculations using generalized gradient approximation (GGA)\(^{25}\) for the exchange-correlation functional. We present results for the Perdew Burke Ernzerhof (PBE)\(^{31}\) GGA in this paper. Other exchange and correlation functionals have also been tested but not presented in this work. In order to perform the calculations we used double zeta plus valence polarization (DZVP) all-electron basis sets.\(^{32}\) DZVP means that each atomic orbital is expressed as the sum of two Slater-type orbitals (STOs), (Z) zeta value accounts for how diffuse (large) the orbital is. As it takes too much effort to calculate a double-zeta for every orbital, instead, many scientists simplify matters by calculating a double-zeta only for the valence orbital. Since the inner-shell electrons aren’t as vital to the calculation, they are described with a single Slater orbital. This method is called a split-valence basis set, and is written as DZV. Finally, (P) stands for polarization, to acknowledge and account for the fact that sometimes orbitals share qualities of ‘s’ and ‘p’ orbitals or ‘p’ and ‘d’, etc., and not necessarily have characteristics of only one or the other. As atoms are brought close together, their charge distribution causes a polarization effect (the positive charge is drawn to one side while the negative charge is drawn to the other) which distorts the shape of the atomic orbitals. In this case, ‘s’ orbitals begin to have a little of the ‘p’ flavor and ‘p’ orbitals begin to have a little of the ‘d’ flavor.

To locate different minima on the potential energy surface of the neutral, cationic and anionic clusters, a quasi-Newton method\(^{33}\) with analytic energy gradients was used for the structure optimization. The convergence was based on the gradient and displacement vectors with a threshold of \( 10^{-4} \text{ a.u.} \) The exchange-correlation potential was numerically integrated on an adaptive grid.\(^{34}\) The grid accuracy was set to \( 10^{-6} \) in all calculations. The Coulomb energy was calculated by the variational fitting procedure previously described by Dunlap, Connolly and Sabin.\(^{35,36}\) The auxiliary density was expanded in primitive Hermite Gaussian functions using the GEN-A2 auxiliary function set that contains s, p, d, f and g auxiliary functions, and adapts automatically to the chosen orbital basis set.\(^{37}\) The exchange and correlation potential was calculated with the orbital density including zero point energy corrections. The convergence was based on the gradient and displacement vectors with a threshold of \( 10^{-5} \text{ a.u.} \). For the vibrational analysis, the second derivatives were calculated by numerical differentiation (two-point finite difference) of the analytic energy gradients using a displacement of 0.002 a.u. from the optimized geometry for all 3N coordinates. The harmonic frequencies were obtained by diagonalizing the mass-weighted Cartesian force constant matrix. In the study of the cluster magnetic properties, only the atomic spin magnetic moments were computed, i.e. spin orbit interactions were not taken into account. While this is obviously an approximation, this may be justified on two grounds. Firstly, we are not interested in calculating the value of the magnetic anisotropy energy. Secondly, we are still able to identify the ground state structures of the clusters, as good agreement with experimental numbers for AEA shows. All calculations were performed using the density functional theory (DFT) deMon2k program.\(^{38}\)

III. Results and discussion

In Fig. 1, we present the anion photoelectron spectra of Rh\(_m\)Co\(_n\)\(^+\) (\( m = 1–5 \)) and Rh\(_m\)Co\(_n\)\(^–\) (\( m = 1–2 \)) clusters, each recorded with 355 nm photons. Peaks in the spectra are due to transitions from the ground electronic state of the anion to the ground and excited electronic and vibrational states of the resulting neutral species. In each of the photoelectron spectra, several transitions were observed. The EBE value in the onset (threshold) region of the lowest energy and the electronic transition (lowest EBE peak) in the spectrum give an estimate of the adiabatic detachment energy (ADE) of anion. The ADE is the energy difference between an anion and its corresponding neutral with the neutral relaxed into its nearest local minimum. In these cases, the ADE is also the adiabatic electron affinity (AEA) when both the anion and its corresponding neutral are in their ground states. The EBE value of the intensity maximum in the lowest EBE transition (peak) in the spectrum is the vertical detachment energy (VDE), which is defined as the
The geometry of the ground state structures obtained for the neutral Rh$_m$Co$_n$ (m = 1–5, n = 1–2) clusters is shown in Fig. 2. At the right hand side of each figure, (a) through (g), is plotted the charge density of the HOMO–LUMO Kohn–Sham molecular orbitals (MOs), where light grey corresponds to regions with excess electrons and dark grey corresponds to electron deficit regions.

Fig. 3 Shows the anionic (Rh$_m$Co$_n$)$^{-1}$ (m = 1–5, n = 1–2) ground state clusters in a similar way as in Fig. 2. Each figure, (a) through (g), is followed by the charge density of the HOMO–LUMO Kohn–Sham molecular orbitals (MOs) at their right hand side. These structures are the result of an accurate determination of the lowest-energy points on the potential energy surface for these clusters. Isomers of different geometric forms, at each fixed stoichiometry, have been taken into consideration, followed by structures of fixed geometry that differ only in the distribution of the two types of atoms among the sites of the cluster. A reasonable set of starting geometries have been explored with all the possible nonequivalent sites of the cobalt atoms in the binary cluster. All the different possible configurations of the atomic spin magnetic moments (or multiplicities) for each geometry structure has been explored for both the anionic and the neutral systems.

As indicated above, all clusters were examined in detail using the DFT DeMon package.38 Analyzing both figures at the same time, one can see small structural differences (varying bond distances) as the cluster goes from the anionic state towards the relaxed neutral configuration. For the charge density, notice the changes in the charge distribution upon ionization. These differences are reflected in the changing appearance in the PS spectra (shown in Fig. 1) and clearly it is reflected in Fig. 4, where we show the energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for Rh$_m$Co (m = 1–5) and Rh$_m$Co$_2$ (m = 1–2). It is interesting that the HOMO–LUMO (H–L) gaps alternate in value between the neutrals and their corresponding anions after n = 2. In Fig. 5 we show graphically the behavior of the magnetic moments for Rh$_m$Co (m = 1–5) and Rh$_m$Co$_2$ (m = 1–2) clusters, which were obtained by combining the experimental PS spectra and the computational results (shown in Table 2, columns 4 and 5).

This is achieved through the quantitative agreement between the calculated (VDEs), from the anion ground state with multiplicity $M$ to neutral species (at the anion geometry) with multiplicity $M \pm 1$, with the experimental peaks. To extract this result we consider that the ionic cluster has an $N$ number of unpaired spins and thus a magnetic moment of $N\mu_B$ and a spin multiplicity of $M = N + 1$ (as knowing the spin multiplicity, one knows the spin magnetic moment $2S + 1 = M$). As an electron is detached the neutral cluster can have a spin multiplicity of $M + 1$ or $M - 1$, depending upon whether the electron was removed from the minority or majority state. One can observe an alternating behavior between anions and neutral clusters as a result of modifications in the Fermi energy and band filling. The variations in the magnetic moment are related to the relative position of the unoccupied spin up or down orbital, and thus it is a signature of the nature of the LUMOs in the parent cluster.39

Photoelectron spectroscopy is actually the most accurate energy difference between the anion and the neutral at the geometry of the anion. The ADE and VDE values, extracted from the experimental spectra, are listed in columns 2 and 3 of Table 1.

The ADE and VDE values of these species were also calculated in our DFT38 calculations. The calculated ADE and VDE are listed in columns 4 and 5 of Table 1, respectively. The calculated ADEs are also indicated by the vertical bars in Fig. 1. Quantitatively, the experimental and computational results are in good agreement. For example, in the case of RhCo, the EBE at the maximum of the most intense peak is 1.391 eV. These values are the experimental calculated value of 1.356 eV.

Table 1. Experimental and calculated adiabatic electron affinities (AEA) and vertical detachment energies (VDE) for neutral and anionic Rh$_m$Co ($m = 1–5$) and Rh$_m$Co$_2$ ($m = 1–2$) clusters, respectively.

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<th>Calculated</th>
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experimental method to provide information on the spin multiplicity and the ground state geometry when combined with theory. If the calculated energies agree with the experiment, quantitatively one can conclude that the multiplicity calculated by theory must be correct.26,27 Nevertheless, several considerations and complications have to be considered. First of all, one must be aware that in some cases the ground state structure of the anion and the neutral can be different, resulting in the broadening of the spectra. In addition, transitions from the anion to the vibrational or electronic excited states of the neutral can occur, which will produce further structures in the experimental spectra and complicate the interpretation of the peaks. And also the fact that both neutrals and anions could possess isomers that are energetically nearly degenerate. Therefore, for a good interpretation of the PES spectra the theoretical counterpart must comprehend the calculations of

Fig. 2 Figures (a) through (g) show the geometry configurations of Rh\textsubscript{m}Co (1 \leq m \leq 5) and Rh\textsubscript{m}Co\textsubscript{2} (m = 1, 2) for neutral clusters shown on the left, followed by the electronic charge distribution of the HOMO–LUMO molecular orbitals on the right hand side.

Fig. 3 Figures (a) through (g) show the geometry configurations of the (Rh\textsubscript{m}Co)\textsuperscript{-} (1 \leq m \leq 5) and (Rh\textsubscript{m}Co\textsubscript{2})\textsuperscript{-} (m = 1, 2) anionic clusters on the left side, followed by the electronic charge distribution of the HOMO–LUMO molecular orbitals to their right.
all allowed spin states and all possible isomeric forms for both neutral and the anionic configurations.

Notice that our calculated magnetic moments for some of the Rh<sub>m</sub>Co<sub>n</sub> clusters also agree with previous calculations done via different theoretical approaches for RhCo where a value of 2.00 μB per atom is obtained, which is similar to the value obtained by Dennler et al.<sup>24</sup> and Lv et al.<sup>29</sup> For Rh₂Co and RhCo₂, a value of 1.67 μB is obtained by us and by Dennler et al.<sup>24</sup> However, our calculated value for the RhCo₂ is 2.0 μB, which, while agreeing with Dennler et al.’s result<sup>24</sup> does not agree with Lv et al.’s<sup>29</sup> value of 1.50 μB at the same geometry.

In Table 2 we show the binding energy per atom in column 2, binding energy (E<sub>b</sub>) of a cluster is defined as the energy gained in assembling the cluster from its isolated constituents atoms.

\[
E_b = \sum_{i} E_i(\text{atom}) - E_T(\text{cluster})
\]

where \(E_i(\text{atom})\) is the energy of the \(i\)th isolated atom, and \(E_T(\text{cluster})\) is the total energy of the cluster. In the case of our bimetallic clusters Rh<sub>m</sub>Co<sub>n</sub>, this quantity is calculated using the expression:

\[
E_b = (mE_{Rh} + nE_{Co} - E_{RhCo})(m + n)
\]

where, \(E_{RhCo}\), \(E_{Rh}\) and \(E_{Co}\) are the total energy of the bimetallic cluster, and the energies of an isolated Rh and Co atom, respectively. \(E_b\) can be used to establish the relative stability of clusters with different structures. Table 2 column 3 shows the adiabatic ionization potential, which involves the full minimization and search for minima of the positively charged clusters as a further reference. The magnetic moments found for all of the neutral structures are shown in Table 2 column 4, while column 5 shows the magnetic moments found for the anionic clusters. The largest magnetic moment per atom found is 2.5 μB for the (RhCo)<sub>1</sub> mixed dimer anion.

Columns 6 and 7 show the numerical values of the HOMO–LUMO gaps for the neutral and the anionic clusters. Finally, we calculated fundamental vibrational harmonic frequencies for all neutral clusters; the results are presented in Table 3. The fundamental vibrational harmonic frequencies for the negatively charged clusters are presented in Table 4. These values were used to guarantee that the structures obtained were actually local minima and not transitional states, and also to obtain the zero point energies which have been included in the results.

### IV. Conclusion

In the present work we have performed a comprehensive study of the energetic, structural, electronic, and magnetic properties of both anionic and neutral (Rh<sub>m</sub>Co<sub>n</sub>)<sup>−</sup> and Rh<sub>m</sub>Co<sub>n</sub> (\(m = 1–5\), \(n = 1–2\)) clusters, by using a synergistic approach which combined anion photoelectron spectroscopy and DFT based theoretical calculations. The total energy calculations quantitatively account for the photodetachment spectra and validates that the ground state structures of these clusters have...
can be explained by the s–d hybridization between rhodium
the lowest energy minima in neutral Rh
HOMO–LUMO gap found for
clusters are highly ordered and symmetric. The reduced
stability and dependence of these properties on the cluster
gaps have also been calculated for these structures. The
moments, vibrational frequencies, as well as the HOMO–LUMO

be extended the systems under current investigation to larger
stability of the alloyed cluster. It would be interesting to
enhancements in cluster magnetism due to the presence of a
rhodium clusters seems to increase the local magnetic moments
although the presence of a cobalt atom as an impurity in

Table 3 The calculated vibrational harmonic frequencies (cm

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Table 4 Calculated vibrational harmonic frequencies (cm

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References

1 J. L. Elkind, F. D. Weiss, J. M. Alford, R. T. Laaksonen and