Electronic and structural evolution of Co_n clusters ($n=1-108$) by photoelectron spectroscopy

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Well-resolved photoelectron spectra are reported for Co_n^- ($n=1-108$) clusters. The data provide evidence for structural transitions and reveal in detail the molecular to bulk electronic evolution in Co clusters. Clusters with $n<20$ behave molecularlike with discrete transitions and dramatic size variations. Clusters with $n\geq20$ behave bulklike with broad spectral features and smooth-size evolution. But discrete and well-resolved spectral features are observed around $n=55$, evident of a highly symmetric Co_{55} cluster. The molecularlike to bulklike transition is also shown in the electron affinities as a function of size, which obey the metallic-droplet model above Co_{20} and extrapolate to the bulk workfunction.

Clusters consist of a few to few-hundred atoms (∼2 nm) cover a critical-size range, in which the finite-sized systems evolve from molecularlike species to nanoparticles. Advances in nanotechnology have made it possible to examine ever smaller systems from the nanometer size regime down to atomic scales. However, in the critical-size range between the transition from atomic clusters to nanoparticles gas-phase techniques are still advantageous, permitting systematic examinations of quantum-size effects atom by atom without influence of any substrates. Transition-metal clusters have been of special interest because of their diverse physical and chemical properties,[1] but they have been most challenging due to the complexity of the underlying electronic structures.[2] Cobalt clusters are particularly interesting because of their magnetic properties[3,4] and the importance of cobalt nanoparticles in magnetic storage devices. Yet, the electronic structure of small cobalt clusters and how it evolves with cluster size have not been well established, despite extensive previous gas-phase investigations.[3-14]

Photoelectron spectroscopy of size-selected anions has emerged as one of the most powerful experimental techniques in probing the electronic structure of bare clusters. It yields directly the valence electronic density of states of the underlying clusters and is capable of providing an atom-by-atom view of how the electronic structure of clusters evolves from that of the atoms to that of finite-sized clusters and nanoparticles. However, it is much more demanding to investigate the transition-metal cluster systems because of their intrinsic high density of electronic states even for the smallest cluster sizes.[15] Recent advances in our laboratory to improve the energy resolution of the photoelectron spectroscopic technique and in our ability to control the cluster temperatures have allowed us to obtain well-resolved electronic features of size-selected atomic clusters from few atoms up to more than 100 atoms.[16-18] In the present report, we report an investigation of small Co_n^- clusters from the atom up to $n=108$, clusters with sizes already larger than 1 nm. Well-resolved electronic features and their size evolution are observed. Small clusters with $n<20$ are shown to be

molecularlike with discrete electronic transitions and dramatic size variations. Evidence is also obtained for a high symmetry icosahedral Co_{13}. For clusters with $n\geq20$, the electronic density of states becomes high enough so that no discrete electronic transitions are able to be resolved except around $n=55$, where discrete spectral features are observed from about $n=50-57$ and are attributed to the icosahedral packing effect and a highly symmetric icosahedral Co_{55}. The observed electron affinities as a function of size are shown to follow the metallic droplet model precipitously from Co_{20}, consistent with the onset of bulklike electronic structures at this cluster size.

The experiment was performed using a magnetic-bottle time-of-flight photoelectron spectroscopy apparatus with a laser-vaporization supersonic cluster-beam source.[19] A pure Co disk target was vaporized by a pulsed laser beam. The laser-generated plasma was mixed with an intense high-pressure helium carrier gas pulse. Clusters formed in the nozzle were entrained in the carrier gas and underwent a supersonic expansion. Negatively charged clusters in the beam were extracted perpendicularly into a time-of-flight mass spectrometer. A given cluster of interest was selected and decelerated before photodetachment by either a Nd:YAG laser beam (355 and 266 nm) or an ArF excimer laser (193 nm). The energy resolution of the apparatus is about 2.5% ($\Delta E_k/E_k$), i.e., about 25 meV for 1 eV electrons. As shown previously for Al_n^- clusters, we found that the cluster temperatures from our cluster source span a wide range, depending on the residence time of the clusters in the nozzle.[16-18] Those clusters coming out of the nozzle late (long residence time) tend to be colder. Significant temperature effects were observed even for relatively small clusters—hot clusters in general result in broad spectral features, smearing out discrete electronic transitions even under high-instrumental resolution. All the data presented here were taken at the cold-temperature regime, which was estimated to be at or slightly below room temperature based on our previous results for small Al_n^- clusters.[17]

We obtained the photoelectron spectra of Co_n^- from $n=1$ to 108 atom by atom at the three detachment laser wave-
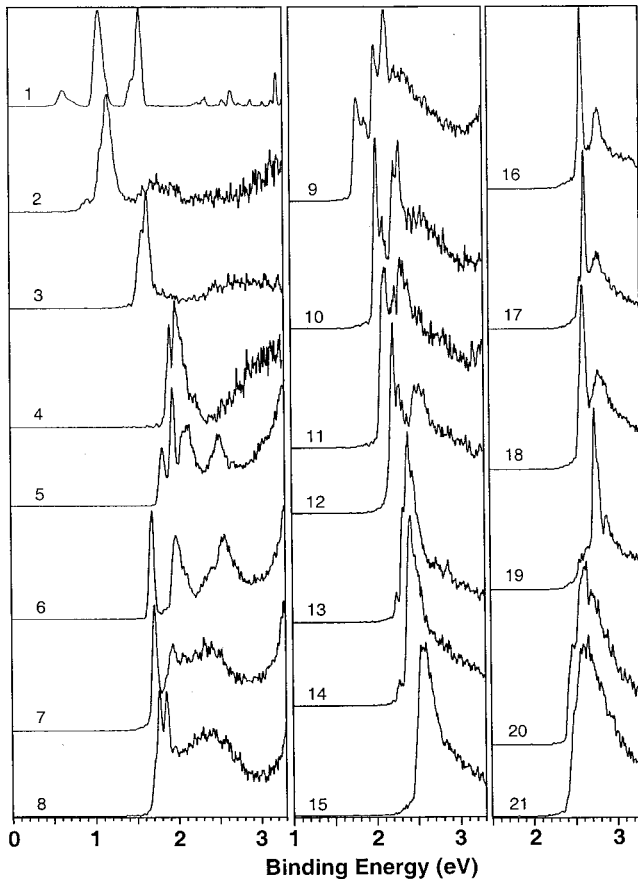
FIG. 1. Photoelectron spectra of Co_n^- ($n=1-21$) at 355 nm (3.496 eV).

FIG. 2. Photoelectron spectra of Co_n^- ($n=25-108$) at 266 nm (4.661 eV).

lengths. The spectra for $n=1-21$ at 355 nm are shown in Fig. 1 and those for $n=25-108$ at 266 nm are shown in Fig. 2. For $n<20$, a strong size dependence and sharp electronic features are observed. The spectra for $n<12$ exhibit no resemblance to each other. There is an abrupt change from Co_{12}^- to Co_{13}^-, whose spectrum becomes narrower, yet with discernible fine features. The spectra of Co_{14}^- and Co_{15}^- are similar to that of Co_{13}^-, except that they become slightly more diffuse. A dramatic spectral change occurs again from Co_{15}^- to Co_{16}^-, which shows a surprisingly sharp threshold peak and a broader higher-energy feature. The sharp peak also appears in the spectra of $Co_{17}^--Co_{19}^-$, whose spectra are similar to that of Co_{16}^- except that weaker lower binding-energy features seem to be present in the spectra of the larger clusters. An abrupt spectral change is observed yet again from Co_{19}^- to Co_{20}^-, where suddenly the spectral features become more congested and no sharp peaks can be resolved. The spectra for $n \geq 20$ are all similar, becoming increasingly congested and broad. Weak low-energy features appear to be present in the spectra of $Co_{34}^--Co_{37}^-$. Most interestingly, a sharp threshold peak begins to be resolved starting at Co_{50}^-. The spectral features become better defined with increasing size and three distinct features are resolved in the spectra of $Co_{52}^--Co_{56}^-$. The well-resolved spectral features disappear beyond Co_{57}^-, but a threshold peak is still discernible in several larger clusters, notably around Co_{63}^-, Co_{80}^-, and Co_{90}^-.
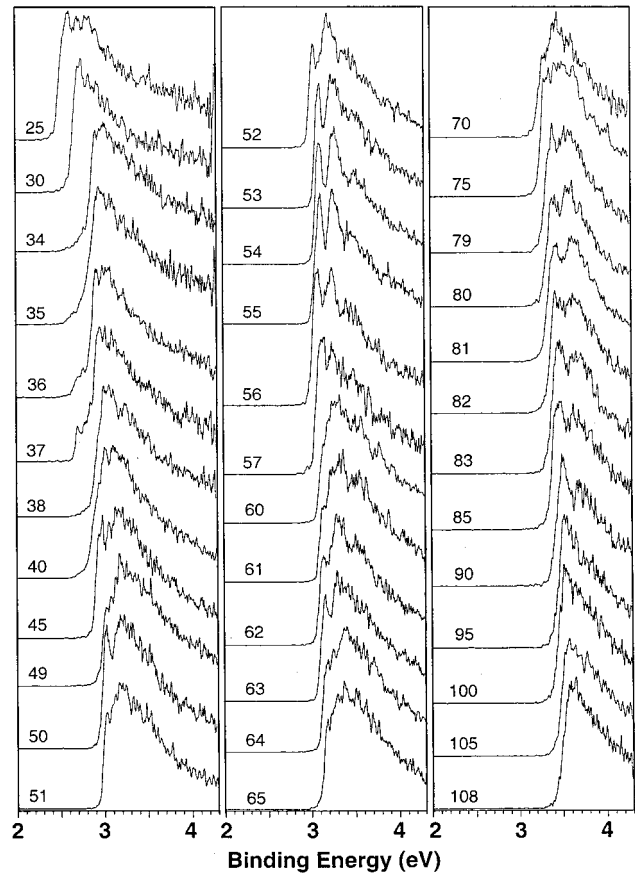
The electron affinities determined from the detachment thresholds are plotted in Fig. 3 as a function of size. Large-size variations are observed for $n<20$, beyond which the electron affinity changes with the cluster size rather
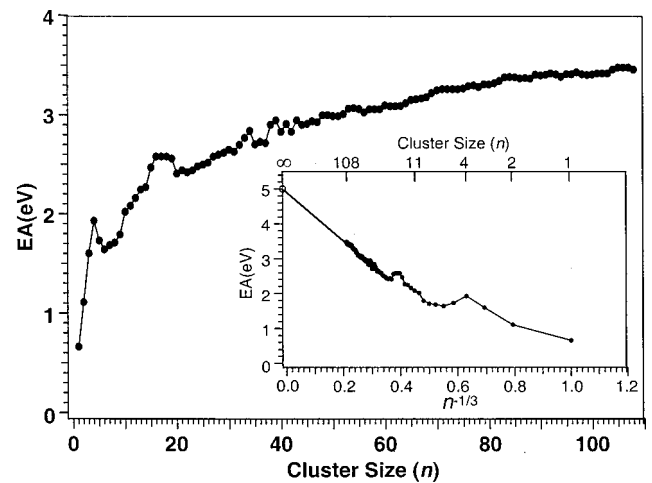

FIG. 3. Electron affinities (EA) of Co_n ($n=1-108$) as a function of cluster size, n. The inset shows EA versus $n^{-1/3}$ (proportional to $1/r$, r being the cluster radius), demonstrating that the EA is proportional to $1/r$ starting at $n=20$ and extrapolates to the bulk work-function (5.0 eV).

smoothly. The more visible variation between $n = 34–38$ is caused by the weak lower binding-energy features in the spectra of Co_{35}^{-}–Co_{37}^{-} (Fig. 2). The inset of Fig. 3 shows the electron affinities versus $n^{-1/3}$, which is proportional to $1/r$ (r = cluster radius). The electron affinities are observed to follow approximately a straight line after $n = 20$ and extrapolate smoothly to the bulk workfunction (5.0 eV).

Photoelectron spectroscopy of size-selected clusters involves photodetachment transitions from the ground state of the anions to the ground and low-lying states of the neutral clusters. The photoelectron spectra shown in Figs. 1 and 2 reveal the valence electronic density of states of the cobalt clusters and how it evolves with cluster size. The detailed electronic features resolved in this study are unprecedented,[8] particularly considering the anticipated complexity of the electronic structure of these clusters and the high density of electronic states. The well-resolved spectra are due to the colder cluster anions produced from our laser-vaporization cluster source. Here we will focus on two aspects of the experimental results pertaining to the overall spectral changes with cluster size and the structural implications of the sudden spectral variations from one size to another.

The spectra for clusters with $n < 20$ all exhibit sharp and discrete spectral transitions and considerable size variations. The strong size effect in the smaller clusters is also displayed in the electron affinities shown in Fig. 3. These observations reveal the molecular nature of the small clusters, which should be viewed as individual molecules expected to possess molecularlike discrete electronic states. However, abruptly starting at Co_{20}^{-} the photoelectron spectra become congested and featureless with two exceptions around Co_{36}^{-} and Co_{55}^{-}. The weak low-energy features observed in the spectra of Co_{35}^{-}–Co_{37}^{-} are attributed to possible isomers of the negatively charged clusters that have lower electron affinities. Indeed, the main features of the spectra in this size range show no dramatic differences from their neighbors. The well-resolved spectral features around Co_{55}^{-} are attributed to an icosahedral packing effect, as discussed below. Besides these two exceptions, the spectral changes for $n \geqslant 20$ are rather gradual and smooth, suggesting the electronic structure of the large clusters begins to behave bulklike. They are bulklike in the sense that they have high density of electronic states and the addition of one atom does not induce dramatic spectral or structural changes. The onset of bulklike behavior at Co_{20} is supported by the electron affinities versus size curve displayed in Fig. 3, which shows that the electron affinities of the clusters obey the metallic droplet model[20] precipitously starting at Co_{20} and extrapolate to the bulk workfunction. This is also consistent with previous photoelectron spectroscopic investigations on transition-metal clusters, showing that the onset of bulklike electronic behavior in general takes place at rather small-size regime for these clusters.[19,21,22] It is expected that not all the properties of the clusters in this size regime will be bulklike. For example, the magnetic properties[3,4] and chemical reactivities[12,13] in this size regime are still considerably different from that of the bulk, because these properties are much more sensitive to the surfaces of the clusters.[23]

The dramatic electronic structure changes as revealed by the photoelectron spectra are also expected to be accompanied by transformations in the underlying cluster atomic structures. However, there is not yet direct experimental means to determine the structures of free transition metal clusters, although recent advances in electron diffraction of trapped cluster ions appear to be a promising technique.[24] Because of the enormous complexity of the electronic structure pertaining to the transition-metal clusters,[1,2] theoretical predictions of the Co cluster structures are few[14] and none for clusters containing more than a few atoms. However, there have been extensive investigations using chemisorption as a structural probe for the transition-metal clusters.[10–12] Although the structural changes induced by the chemisorption are not completely understood, the chemical probes have yielded very interesting information and suggestions for possible structures of the Co clusters.[10–12] For example, chemisorption experiments using NH_3 suggested that Co_{19} has an octahedron-type structure and there is a transition from octahedral to polyicosahedral structures for clusters beyond Co_{19}.[11] Our observation of the sudden photoelectron spectral change from Co_{19}^{-} to Co_{20}^{-} is consistent with the suggested structural change. More significantly, the discrete spectral features that we observe around Co_{55}^{-} provide the most convincing evidence for the icosahedral packing for the larger clusters.

The well-resolved spectral features in these large clusters are remarkable. They represent the largest transition metal cluster systems, in which we have been able to resolve discrete electronic features.[19,22] These observations were not expected, considering the general complexity of the electronic structure of the transition-metal clusters, and they are due to the cold cluster-anions produced from our laser-vaporization cluster source. These sharp features suggest that these clusters possess high-symmetry structures with high electronic degeneracy, consistent with the icosahedral packing suggested from the previous chemisorption studies,[10,11] Co_{55} would have the highest symmetry with a perfect icosahedral structure with two complete atomic shells and a central atom, consistent with the fact that the spectrum of Co_{55}^{-} is the best resolved in this size range. The clusters with $n < 55$ probably have an incomplete second atomic shell while those with $n > 55$ will start to nucleate the third atomic shell.[11]

The extremely sharp peak observed in the spectra of Co_{16}^{-}–Co_{19}^{-} is also remarkable. In fact, they are almost like atomic transitions since the peak width in the spectra of Co_{16}^{-} and Co_{17}^{-} is only slightly larger than the instrumental resolution in the respective energy ranges. This observation suggests that the sharp peak is due to ionization of nonbonding electrons. The similarity of the spectra for Co_{16}^{-}–Co_{19}^{-} also suggests that they are likely to have similar atomic structures, and they may all fall into the octahedral-type as suggested for Co_{19}^{-} from the chemisorption studies.[11]

The narrow spectral feature of Co_{13}^{-} and the abrupt change from Co_{12}^{-} to Co_{13}^{-} suggest that the Co_{13} cluster may also have a very high symmetry structure. In fact, the Co_{13}^{-} spectrum even contains discrete and reproducible fine features. It

is very likely that Co_{13} also possesses a highly symmetric icosahedral structure with a central atom and a single atomic shell, similar to that of Co_{55}^-, although previous chemisorption studies by N_2 uptake suggested that Co_{13} may have an octahedral-type structure (the chemisorption may have favored the octahedral clusters over the icosahedral structure since it was observed that the adsorption of N_2 did cause most cobalt clusters to change structures).[12] Based on the similarity of the spectra of Co_{14}^- and Co_{15}^- to the spectrum of Co_{13}^-, the larger clusters may have similar icosahedral structures with the initiation of a second atomic shell. Thus, it seems that there exists a structural transition from icosahedral (Co_{15}^-) to octahedral (Co_{16}^-) packing, and another change from octahedral (Co_{19}^-) to icosahedral packing again beyond Co_{19}^-. Such dramatic electronic and structural transformations induced by just one atom is remarkable, but common in small clusters, and would be desirable to be verified by *ab initio* calculations or future trapped-ion electron-diffraction experiments.[24]

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