Photoelectron spectroscopy of small chromium clusters: Observation of even-odd alternations and theoretical interpretation

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(Received 6 February 1997)

We report an extensive photoelectron-spectroscopy study of size-selected Cr_n^- ($n=2-70$) clusters. Even-odd alternations are observed for the small Cr_n clusters and their electron affinities. The spectra of clusters with an even number of atoms show less density of states near the threshold, while those with odd clusters show more complex features. A dimer growth path found in a previous theoretical study is used to interpret the data and accounts well for the even-odd effects. The work provides a key contribution to the understanding of the complicated electronic structure of the Cr clusters. [S0163-1829(97)05919-5]

The open d shells of transition metals (TM's) have presented considerable challenges in the study of TM clusters. Limited progress has been made in our understanding of the structure and bonding of the TM clusters, while significant progress has been made with regard to simple clusters involving alkali and coinage metals and semiconductors.[1–3] The open d shells give rise to strong electron correlation effects, and the number of electrons in the TM clusters increases rapidly with cluster size. Thus it has been very difficult to calculate the electronic structure of the TM clusters.[4–6] The lack of theoretical interpretations and the enormous complexity of TM clusters have also limited experimental efforts.[7,8] In this paper, we report an extensive and systematic photoelectron spectroscopic study of size-selected Cr clusters (Cr_n^-, $n=2-70$) to probe their electronic structure. We observe a surprising even-odd alternation in the electronic structure of small chromium clusters, and show that this can be well explained by a previous density-functional-theory (DFT) study.

Chromium clusters have attracted broad interest. In particular, the Cr_2 dimer has drawn considerable attention as a prototype system to understand d-d bonding.[4,7,9–11] The magnetic properties of Cr clusters are also important.[12] Several calculations have been performed on selected Cr clusters by assuming the bulk body-centered-cubic (bcc) lattice to gain insight into the structure-properties relationships and the cluster-bulk analogies.[12] Additionally, a few experimental studies have focused on small chromium clusters. These include dissociation studies on the Cr_n^+ ($n=2-21$) clusters to probe their structure and bonding, and a Stern-Gerlach experiment on the magnetic properties of Cr_n ($n=9-31$) clusters.[13,14] However, there has been a lack of studies which systematically address the electronic structure and bonding in the small Cr clusters, despite the extensive research done on the Cr_2 dimer.[4,7,9–11] In conjunction with our experimental photoelectron spectroscopy (PES) study on the Cr clusters,

we recently carried out a series of electronic structure calculations for Cr_n ($n=2-15$) clusters based on the local-spin-density approximation by fully optimizing the possible cluster structures. We found an interesting dimer growth route for the small clusters and a structural transition from the dimer growth to bulklike structures.[15] The purpose of the current work is to present our extensive and systematic PES studies on size-selected Cr anion clusters (Cr_n^-, $n=2-70$) and to provide a detailed interpretation on the PES spectra based on the theoretical results, thus providing a systematic understanding of the electronic and atomic structures of a complicated TM cluster series.

The magnetic-bottle PES apparatus used in this work has been described previously.[16,17] Briefly, laser vaporization is employed to generate the desired cluster anions with a time-of-flight (TOF) mass spectrometer to separate the cluster sizes. In the current study, PES spectra of size-selected Cr_n^- anions are obtained at three photon energies: 3.49, 4.66, and 6.42 eV. Lower photon energies give better spectral resolution due to the dependence of resolution on photoelectronic kinetic energies while higher photon energies allow more valence states to be probed. The mass intensities for the smallest clusters are quite weak. In particular, Cr_2^- and Cr_4^- show unusually low abundance. The PES spectra for the low abundance clusters are taken at slightly lower resolution with poorer counting statistics. The resolution of the spectrometer is typically better than 30 meV at 1-eV electron kinetic energy. All the raw photoelectron TOF spectra are calibrated with the known spectra of Cu^-. The obtained kinetic-energy spectra are smoothed with a 5 meV (for the 3.49-eV spectra) or 10 meV (for the 4.66- and 6.42-eV spectra) window function and then subtracted from the respective photon energies to obtain the presented binding-energy (BE) spectra.

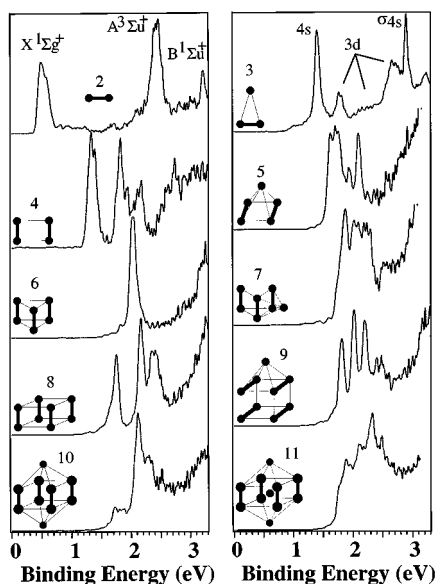Figures 1 and 2 display the PES spectra of Cr_n^- ($n=2-25$) at 3.49 eV. Extensive discrete spectral features

FIG. 1. Photoelectron spectra of Cr_n^- from $n=2$ to 11 at 3.49-eV photon energy. Note the difference between the even and odd clusters. The structure of each cluster from Ref. 15 is included schematically.

are observed for the smaller clusters. The spectra become more congested as cluster size increases.[18] Interestingly, the spectra of the smaller clusters seem to exhibit an even-odd alternation: the even ones ($n=2-10$, Fig. 1, left column) give simpler spectra with fewer features near the threshold and a distinct gap; the odd ones ($n=3-11$, Fig. 1, right column) show more complicated spectra with congested features near the threshold, particularly for $n=5, 7$, and 11. Although the spectra of Cr_9^- is well resolved with five sharp peaks, it exhibits an apparent similarity to the spectra of the other odd clusters. This even-odd alternation in the PES spectra disappears above Cr_{12}^- (Fig. 2), where a sharp
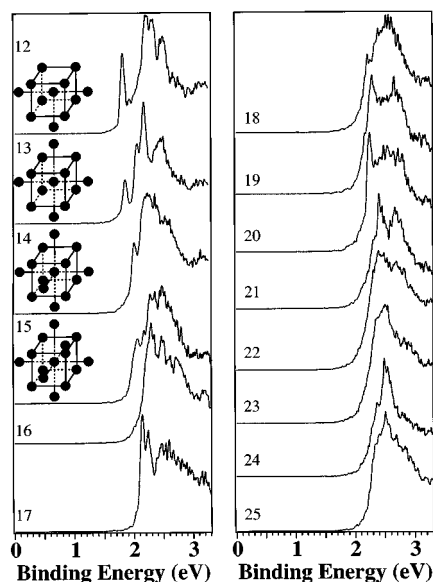

FIG. 2. Photoelectron spectra of Cr_n^- from $n=12$ to 25 at 3.49-eV photon energy. The structures of Cr_{12}-Cr_{15} from Ref. 15 are included schematically.
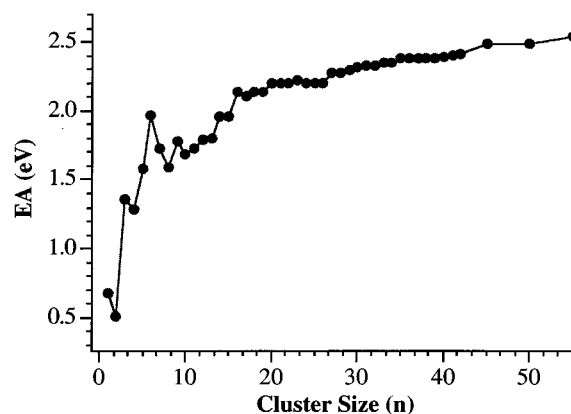

FIG. 3. Electron affinity of Cr_n ($n=1-55$) clusters vs cluster size n. Note the even-odd alternations between $n=1-11$ and the local maximum at $n=6$.

threshold feature is observed. This sharp feature evolves toward high BE, and overlaps with higher BE features as cluster size increases.[18] The even-odd alternation is seen more clearly in the electron affinity (EA) of the clusters, as shown in Fig. 3:[19] except for Cr_6, all the even clusters from $n=2$ to 10 have lower EA's than their neighboring odd ones.

The observation of such even-odd alternations is quite unusual among transition-metal clusters, and must be indicative of the unique electronic structure of the Cr clusters. The uniqueness of the Cr clusters among the transition metals originates from the special atomic ground-state configuration of Cr, $3d^54s^1$. This half-filled configuration is ready to form bonds without the need of a $4s \rightarrow 3d$ promotion as required for other TM elements. This results in a very high bond order of six in Cr_2 dimer in which all the electrons are paired ($\sigma_{3d}^2\pi_{3d}^4\delta_{3d}^4\sigma_{4s}^2\sigma_s^*$, $^1\Sigma_g^+$) and an extremely short bondlength (1.68 Å).[9–11] The unusual bonding in Cr_2 has been the subject of extensive research, and is now well understood.[4,7,9–11] However, one key question that remains unanswered is how larger clusters evolve from the dimer to the bulk where the Cr-Cr distance is much longer. Through an extensive DFT theoretical study, we have recently shown that the dimer maintains its identity in the larger clusters up to Cr_{11}.[15] These clusters essentially follow a dimer growth route, in which the even clusters are composed of dimers and the odd clusters are formed by attaching a single atom to the preceding even clusters. Above Cr_{11}, the clusters begin to assume more bulk-like bcc structures. These structures are shown schematically in Figs. 1 and 2 along with the PES spectra. The dimer growth in the small Cr clusters is essentially the cause of the even-odd alternation observed in the PES spectra (Fig. 1) and the EA's (Fig. 2). The details of the DFT calculations and the cluster structures were discussed previously.[15] We will show in the following that the PES spectra and the even-odd alternations can be well understood based on the electronic structure information obtained from the DFT calculations.

The closed-shell electronic configuration of Cr_2 results in a large energy gap between the highest occupied molecular orbital (HOMO) σ_{4s}, and the lowest unoccupied MO (LUMO) σ_{4s}^*, as indicated by the gap between the X and A states of the Cr_2^- ($...\sigma_{4s}^2\sigma_{4s}^{*1}$, $^2\Sigma_g^+$) spectrum in Fig. 1.

A vibrationally resolved PES spectrum of Cr_2^- has been obtained previously for the X and A states.[9] The current spectrum taken at 3.49 eV allows the observation of the B state, which is produced by removing a spin-up electron from the σ_{4s} orbital, similar to the A state formed by removing a spin-down σ_{4s} electron.

The Cr_3 trimer is basically composed of a dimer plus a loosely bonded atom with an overall C_{2v} symmetry. The electronic configuration of Cr_3 obtained from the DFT calculations can be approximately described as $(\sigma_{3d}^2 \pi_{3d}^4 \delta_{3d}^4 \sigma_{4s}^2)3d^5 4s^1$, with the third atom maintaining all its six unpaired electrons. The orbitals in the parentheses are from the dimer. Of course, all the orbital degeneracy will be lifted under the C_{2v} symmetry and, in particular, the $3d$ orbitals of the odd atom are split into five nondegenerate orbitals. The energy gaps between the adjacent electronic states are small, reflecting the weak interactions between the dimer and the odd atom. This is clearly shown in the PES spectrum of Cr_3^- in Fig. 1. The $4s$ orbital of the odd atom has some mixing with the σ_{4s} orbital of the dimer, and becomes the HOMO of Cr_3. The extra electron in the anion resides in the $4s$ orbital of the odd atom. The first feature of the Cr_3^- PES spectrum at 1.4 eV is mainly due to the removal of a $4s$ electron from the odd atom. The sharp peak near 2.9 eV is actually due to the removal of a σ_{4s} electron, and is of the same orbital origin as the A state in the dimer spectrum. This state is shifted slightly to a higher BE value in Cr_3 due to the interaction between the σ_{4s} orbital on the dimer and the $4s$ orbital on the third atom. All the features in between the first peak and the 2.9-eV peak are due to the $3d$ electrons of the odd room. *It is important to point out that all the states arising from the odd atom in Cr_3 are in fact falling in between the HOMO-LUMO gap of the Cr_2 dimer.* This is essential in understanding the larger odd clusters, where similar electronic characters arise, leading to the more complicated features in their PES spectra.

The PES spectra of Cr_4^- and Cr_8^- suggest that the neutrals are closed shell, each with a HOMO-LUMO gap of about 0.48 and 0.41 eV, respectively. The spectrum of Cr_6^- is unusual with an intense threshold peak and an abnormally high EA (Figs. 1 and 2). These can all be accounted for by the DFT calculations, which show that both Cr_4 (D_{4h}) and Cr_8 (D_{4h}) are indeed closed shell. However, Cr_6 (D_{3h}) is found to be open shell with two electrons in a doubly degenerate HOMO. The d electrons in Cr_6 are all paired in the three dimers, and the six $4s$ orbitals combine to form four MOs: two nondegenerate orbitals with lower energies and two doublet degenerate orbitals with higher energies. The two nondegenerate MOs are filled with two electrons each. The remaining two electrons fill one of the degenerate MOs, resulting in the open-shell configuration for Cr_6 with a triplet ground state. The extra electron in the anion enters into the partially filled HOMO, in contrast to Cr_4^- and Cr_8^-, where the extra electron occupies the empty LUMO of the neutral clusters.[20] This results in a very high EA for Cr_6, compared to Cr_4 and Cr_8, in excellent agreement with the experimental observation.

For the odd clusters from Cr_5 to Cr_9, their electronic configuration can be described as due to the coupling between the electronic structure of the even cluster and that of the odd atom. As expected, the energy levels of the odd atom are all congested near the HOMO and in between the HOMO-LUMO gap of the corresponding even cluster, similar to the situation in Cr_3. These lead to the complicated features in the PES spectra and higher EA's for the odd clusters compared to their even neighbors (except Cr_6), since the extra electron enters into the open-shell HOMO in the odd clusters. The interactions between the odd atom and the corresponding even cluster increase from Cr_5 to Cr_9, resulting in a systematic shift of some $3d$ levels of the odd atom to higher BE. This is evident in the well-resolved spectrum of Cr_9^-, where the $3d$ level shifts lead to less density of states near the HOMO, compared to Cr_5 and Cr_7.

Cr_{10} and Cr_{11} deviate slightly from the expected dimer growth structures,[15] each with only four dimers instead of five. In Cr_{10} the four dimers form a cubic framework with two capping atoms, giving an overall D_{4h} symmetry. Cr_{11} (D_{4h}) is similar to Cr_{10}, except that the eleventh atom sits in the center of the cube, forming a structure resembling a bcc fragment. The interpretations of their PES spectra are less straightforward compared to the smaller ones. Nevertheless, they each seem to resemble the smaller ones, fitting nicely in the even-odd pattern both in their EA's (Fig. 3) and their PES spectral patterns (Fig. 1).

From Cr_{12} to Cr_{15}, the DFT results suggest that a significant structural change takes place and the cluster structures begin to resemble the bulk bcc structure (Fig. 2). Thus the dimer growth pattern disappears. Experimentally, we observe that the even-odd alternations in the PES spectra and the EA's also disappear abruptly at the same size, in excellent agreement with the theoretical predictions. The PES spectra of the larger clusters begin to exhibit similarities, all with a sharp feature near the threshold. This feature slowly merges with the higher BE features from Cr_{12} to Cr_{15}, as seen in Fig. 2. The well-resolved features at the higher BE's as observed in Cr_{12} and Cr_{13} become hard to resolve in the larger clusters due to increasing electronic density of states. Discrete spectral features still can be resolved up to Cr_{24}, beyond which only one broad band is observed near the threshold at the 3.49- and 4.66-eV photon energies.[18] The spectra in this size range resemble the first bulk feature to a significant degree where a sharp feature near the Fermi level is followed by a broad surface feature.[21] At 6.42 eV, a second band is further revealed at a much higher BE (>5 eV) and the overall spectral features begin to resemble the full bulk valence photoemission spectrum.[21]

Finally, it is noteworthy that even-odd alternations have been observed for alkali- and coinage-metal clusters, where they are explained by the ellipsoidal jellium model due to the itinerary nature of the valence s electrons of these elements.[1] However, we show that the even-odd alternation found in Cr clusters is completely different in nature. Here it is due to the special dimer growth of the small Cr clusters and the even-odd alternations disappear as the cluster structure changes from dimer growth to bulklike bcc structures.

In conclusion, even-odd alternations in photoelectron spectroscopy and electron affinity are observed for clusters of a TM element. These reflect the even-odd nature of the underlying electronic structures of the Cr clusters and are satisfactorily interpreted based on a dimer growth route found in a previous density-functional theory study. The cur-

rent work presents a rather complete picture of the structure and bonding of the small chromium clusters, and shows that photoelectron spectroscopy coupled with appropriate theoretical calculations opens the possibility to completely understand the complicated structure and bonding of transition metal clusters.

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[18] We have obtained PES spectra for Cr_n^- up to $n=70$. The PES spectra above $n=25$ exhibit no sharp features. At 3.49 and 4.66 eV, one broadband similar to that of Cr_{25}^- is observed for all the higher clusters, while at 6.42-eV photon energy a second band at higher BE is also observed.

[19] The EA is systematically estimated by drawing a straight line along the leading edge of each spectrum. The intercept with the Be axis plus a constant of 0.06–0.10 eV (for compensation of finite resolution and thermal broadening) is taken as the adiabatic EA. The uncertainty for the EA values is ±0.06 eV or better depending on the sharpness of the leading edge.

[20] A Jahn-Teller effect is anticipated for the Cr_6^- anion. The PES spectrum suggests that this effect is rather small and gives rise to a slight broadening of the PES feature in Cr_6^-. A similar effect is expected to occur in Cr_8^- because the LUMO of neutral Cr_8, where the extra electron enters, is doubly degenerate. The slight broadening in the first feature of the Cr_8^- spectrum is consistent with a weak Jahn-Teller effect in Cr_8^-.

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