s-p Hybridization and Electron Shell Structures in Aluminum Clusters: A Photoelectron Spectroscopy Study

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Using photoelectron spectroscopy of size-selected Al_x^- (x = 1-162) clusters, we studied the electronic structure evolution of Al_x and observed that the Al 3*s*- and 3*p*-derived bands evolve and broaden with cluster size and begin to overlap at Al₉. Direct spectroscopic signatures were obtained for electron shell structures with spherical shell closings at Al_{11}^- , Al_{13}^- , Al_{19}^- , Al_{23}^- , Al_{35}^- , Al_{37}^- , Al_{46} , Al_{52} , Al_{55}^- , Al_{56} , Al_{66} , and Al_{73}^- . The electron shell effect diminishes above Al_{75} and new spectral features appearing in Al_x^- (x > 100) suggest a possible geometrical packing effect in large clusters. [S0031-9007(98)06997-X]

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The electronic structure of alkali metal clusters can be described well by the jellium model [1-3]. Valence electrons of the metal atoms are delocalized in the volume of the clusters and move in a spherical jellium potential created by the ionic cores. The electrons are quantized according to the spherical orbitals $|nl\rangle$, leading to the wellknown electron shell structures. Shell structures were first observed in the mass spectra of Na_n clusters [1], where particular abundant clusters (magic numbers) were observed at n = 8, 20, 40, 58, and 92. Trivalent aluminum is a nearly free electron metal [4]. Thus the electronic structure of Al clusters were expected to be described by the jellium model. Figure 1 shows a set of Al clusters (neutrals and anions) which should exhibit shell closings under the spherical jellium model [2]. However, there are two important issues concerning the Al clusters compared to clusters of the monovalent alkali atoms. First, the electronic structure of the Al atom is $[Ne]3s^23p^1$ and the energy separation between the 3s and 3p orbitals is about 3.6 eV [5]. For the shell model to hold, one of the 3s electrons has to be promoted to a 3p orbital. This is unlikely in small clusters due to the large 3p-3s energy separation. Therefore, there should exist a critical cluster size range where the separate s and p "bands" overlap and the shell model starts to be valid for the larger clusters. Second, the +3 ionic cores of the Al clusters may show larger perturbations to the spherical jellium potential. Thus deviations from the jellium model might be expected at certain cluster sizes. Extensive experimental and theoretical studies have been focused on Al clusters to understand their electronic and structural properties [6-14]. However, there is still no general consensus regarding the above issues. Photoionization experiments suggested a set of shell closings partially consistent with the shell model [8], whereas nonjellium behavior was suggested from static dipole polarizability data [7].

Using photoelectron spectroscopy (PES) of size selected anions, we obtained precise information about the s-p hybridization and direct spectroscopic signatures about the electronic shell closings of Al clusters. Previous PES studies of Al_x^- were all done with limited cluster sizes or poor energy resolution [9]. No PES data are available above Al_{32} , beyond which an extensive set of closed shell clusters is expected (Fig. 1). We have performed an extensive PES study of Al_x^- (x = 1-162) clusters at 6.42 eV photon energy. Our experiments were performed with an improved magnetic-bottle photoelectron analyzer and a laser vaporization cluster source [15]. Briefly, an aluminum disk target was vaporized at 532 nm (5–10 mJ/pulse) from a Nd:YAG laser. The laser produced plasma was mixed with a He carrier gas pulse at



FIG. 1. Spherical shell closings and the corresponding closed shell neutral and negative clusters of trivalent Al. The number in the parentheses after each shell index indicates the occupation number, 2(2l + 1).

a 10 atm backing pressure. A cold cluster beam was produced by a supersonic expansion of the cluster/carrier gas mixture through a 2 mm diam nozzle and collimated by a 6 mm diam skimmer. The anions were extracted from the beam at 90° and mass analyzed by a time-of-flight (TOF) mass spectrometer. The clusters of interest were size selected and decelerated before irradiated by a 193 nm photon beam from an ArF excimer laser. Photoelectron TOF spectra were collected for each size-selected cluster for 10000 to 30000 laser shots at 20 Hz repetition rate. The vaporization laser was off at alternating detachment laser shots for background subtraction. For the very small clusters, the anion mass abundance was weak and higher photon flux was needed, causing a more severe noise problem (see Fig. 2). The electron TOF spectra were converted to kinetic energy (K_e) spectra calibrated by the known spectra of Cu⁻. The presented binding energy (BE) spectra were obtained by subtracting the K_e spectra from the photon energy (6.42 eV). The electron energy resolution of our apparatus was about 30 meV at 1.5 eV K_e and deteriorates according to $(K_e)^{3/2}$ for high K_e (low BE) features.

Figure 2 shows the PES spectra of Al_x^- for x = 1-12. We measured spectra of size-selected Al_x^{-1} for x = 1to 162 systematically. For the very large clusters, the spectra became broad with few changes between spectra of neighboring clusters. The Al⁻ anion has an electron configuration of $[Ne]3s^23p^2$. The peak labeled "p" in the spectrum of Al⁻ corresponds to the detachment of a 3p electron, giving rise to the ground state of the Al atom $(3s^23p^1, {}^2P)$. The peak labeled "s" corresponds to the removal of a 3s electron, resulting in an excited Al atom $(3s^13p^2, {}^4P)$. The measured separation (3.6 eV) between the "p" and "s" bands agrees with the optical measurement of the ${}^{2}P{}^{-4}P$ separation for Al atoms [5]. However, bulk Al is known to have a completely hybridized s-p band with nearly free electron characters [4]. Thus, we anticipated that the p- and s-derived orbitals in small Al clusters would broaden and approach each other, eventually forming a unified s-p hybridized band at very large sizes.

In small Al clusters, the 3*s* orbitals of Al form bonding and antibonding molecular orbitals (MOs) which are fully occupied, whereas only the bonding MOs derived from the 3*p* are partially filled. The PES features from *p*and *s*-derived MOs are labeled in Fig. 2 with "*p*" and "*s*", respectively. The *s* features are characterized by their high binding energies and low detachment cross sections. The gap between the *p*- and *s*-"bands" is seen to be reduced significantly in Al₂, and rapidly approaches each other with increasing cluster size. At Al₈, the *p*and *s*-derived features already begin to overlap partially, and they are completely mixed starting at Al₉. Detailed quantum calculations have been performed for the atomic structures of small Al clusters [12,14]. Those with n < 6were found to be planner. A 2D to 3D structural transition



FIG. 2. Photoelectron spectra of Al_x^- (x = 1-12) at 6.42 eV. The "p" and "s" labels indicate features derived from the Al 3p and 3s, respectively. Note the overlap of the p- and s-derived features in Al₉.

occurs between Al_5 and Al_6 . The rapid *s*-*p* convergence is accompanied by the structural changes. The complete *s*-*p* mixing starting at Al_9 is probably due to the high coordination numbers possible for the larger clusters.

According to Fig. 1, the first spherical shell closing occurs at Al_{11}^{-} with the filling of the 1*f* shell. The PES spectrum of Al_{11}^{-} does show a slightly higher binding energy relative to its neighbors with numerous well-resolved features. However, the shell closing effect in Al_{11}^{-} is not as strong as observed in the larger clusters (Fig. 2), probably because Al_{11}^{-} is still quite small and its electronic structure is likely to be dictated more by its detailed molecular structure. A much stronger shell closing effect was observed at Al_{13}^{-} and larger clusters as shown in Figs. 3 and 4. Figure 3 shows the PES spectra of the closed shell anions (left column) compared to those one atom larger (right column). The closed shell anion clusters (Al_x^{-}) exhibit high binding energies



FIG. 3. Photoelectron spectra of the expected closed shell Al_x^- anions compared to those of the Al_{x+1}^- clusters. Note the high binding energies of the closed shell Al_x^- clusters and the appearance of low binding energy features and energy gaps in the Al_{x+1}^- clusters.

and high degeneracy, whereas those clusters one atom larger (Al_{x+1}) show weak low energy features with energy gaps, suggesting partial occupation of the next higher shells according to Fig. 1. Al_{13}^{-} , with 40 valence electrons, exhibits the strongest shell closing effect. The electron affinity derived for Al_{13} is 3.62 eV, the highest of all the Al clusters we investigated. The spectrum of Al₁₃⁻ shows the fewest features, indicating a high degeneracy and high symmetry, consistent with the known icosahedral geometry (I_h) for Al₁₃ [12,13]. Al₁₄⁻, with 43 valence electrons, was expected to partially fill the 1gshell, which should undergo ellipsoidal splitting [16]. The spectrum of Al_{14}^- is almost identical to that of $Al_{13}^$ except for the three weak low energy features (Fig. 3) which are consistent with the anticipated splitting of the 1g level. Ellipsoidal distortion in open-shell clusters leads to subshell structures and subshell closings [16]. The



FIG. 4. Photoelectron spectra of Al_x^- anions for which the corresponding neutrals are expected to be closed shell and those of larger Al_x^- clusters (x = 99-112).

PES spectra of the other Al_{x+1}^{-} clusters in Fig. 3 suggest that the neutral Al_{x+1} clusters are all closed shell with a substantial energy gap. In particular, Al₃₆ exhibits an unusually large energy gap (1.02 eV). The PES spectra of those clusters, for which the neutrals were expected to be closed shell in the spherical shell model (Fig. 1), are shown in Fig. 4 along with those of several large clusters. For Al₄₆⁻, Al₅₂⁻, and Al₆₆⁻, a weak low energy feature was clearly resolved with a significant energy gap, indicating the neutral clusters are indeed closed shell. For Al₅₆⁻ alone, the weak low energy feature was not well resolved and only a shoulder was observed, suggesting a smaller energy gap between the 4s and 1j shells (Fig. 1). We observed additional closed shell neutral clusters, Al₂₆, Al₂₈, Al₃₂, Al₄₂, Al₅₄, Al₆₈, and Al₇₂, probably due to subshell closings.

However, the spectra of Al_{78}^- and Al_{80}^- (Fig. 4) do not show a similar energy gap even though the

corresponding neutral clusters were expected to be closed shell (Fig. 1). This could be due to the fact that the ordering of the higher electron shells is different from that shown in Fig. 1, giving a different set of spherical shell closings. However, we did not observe any electronic features resembling shell closings in the clusters larger than Al₇₅⁻. The PES spectra for the larger clusters showed broad features similar to those of Al₇₈⁻ and Al₈₀⁻ up to Al_{99}^{-} (Fig. 4). Starting at Al_{100}^{-} , a new low energy feature appeared abruptly. The new feature persisted and grew in intensity until Al112⁻ where it merged with the higher energy features. The PES spectra then again became broad and featureless. Instead of suggesting a shell closing at Al_{100} , the new PES feature appeared in Al_{100}^{-} and the larger clusters seemed to indicate a geometrical packing effect. The new PES feature may suggest the onset of a new atomic shell and the intensity of this feature increased as the shell was being filled. In fact, octahedral atomic shell packing has been suggested for large aluminum clusters [17]. Clearly, the nature of the spectral transition between Al_{75}^{-} and Al_{100}^{-} and the spectral evolution at larger clusters deserve further investigation.

The observation of electron shell structures starting from about Al_{13}^{-} is consistent with our observation of the *s*-*p* hybridization starting from Al₉. All the shell closings observed in our data agree with those assigned from previous photoionization studies [8]. However, more closed shell clusters were observed in our experiments, due to the direct electronic structure signatures of energy gaps evidenced in the PES data. Quantitative understanding of the fine electronic features contained in the PES spectra will no doubt require accurate quantum calculations by taking into account detailed cluster geometrical structures, particularly for the small clusters. However, the shell model does provide a qualitative picture and predict the closed shell clusters well. The evolution of the PES spectra beyond Al₇₅ and the fact that no shell closings seemed to exist are intriguing. Previous theoretical studies suggested that for Al₅₅ a face-centered cubic structure was already energetically comparable to an I_h cluster [13]. It is thus reasonable to assume that for larger clusters lattice based structures may dominate [10,17] and the simple electron shell model is no longer adequate.

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