Predicting the Photoelectron Spectra of Quasi Octahedral Al₆Mo⁻ Cluster

Paulo H. Acio[ia]

We have recently developed a computational methodology to separate the effects of size, composition, symmetry and fluxionality in explaining the experimental photoelectron spectra of mixed-metal clusters. This methodology was successfully applied first in explaining the observed differences between the spectra of Al₁₂⁻ and Al₁₂Ni⁻ and more recently to explain the measured spectra of AlₙMo⁻, \( n = 3–5,7 \) clusters. The combination of our approach and new synthesis techniques can be used to prepare cluster-based materials with tunable properties. In this work we use the methodology to predict the spectrum of Al₆Mo⁻. This system was chosen because its neutral counterpart is a perfect octahedron and it is distorted to a \( D_{3d} \) symmetry and was not observed in the recent experiments. This high symmetry cluster bridges the less symmetric Al₆Mo⁻ and Al₆Mo⁻ structures. The measured spectra of Al₆Mo⁻ has well defined peaks, while that of Al₆Mo does not. This can be explained by the fluxionality of Al₆Mo⁻, as at least 6 different structures lie within the range that can be reached by thermal effects. We predict that Al₆Mo⁻ has well defined peaks, but some broadening is expected as there are two low-lying isomers, one of \( D_{3d} \) and the second of \( D_{5h} \) symmetry that are only 0.052 eV apart.

1. Introduction

The unique properties of small atomic clusters that are very different from those of the bulk of the same element make these systems a one of a kind laboratory to design new materials with very specific characteristics. Cluster of metallic elements often do not display metallic properties until they reach a certain critical size.¹⁻¹³ This size dependence of the metallicity of a cluster has been well explored and a good account of the factors that affect metallicity in pure clusters can be found in Refs. 1–13 and references therein. The technological potential is substantially increased when these clusters contain more than one element. Adding a single metallic impurity to a pure metal cluster can have important effects such as increasing/decreasing their reactivity or enhancing/suppressing their magnetism. An excellent example of how dramatic these effects can be found in our recent work⁴⁻¹⁰ on the explanation of the evolution of the photoelectron spectra (PES) from a 12 atom pure aluminum cluster to the 13 atom Al₁₃⁻ and Al₁₃Ni⁻ clusters. The addition of an Al or Ni atom leads to substantially different spectra and we were able to separate the different effects of size, structure, symmetry, and composition. The spectrum of Al₁₂⁻ has three clear peaks at 2.8, 3.2, and 3.75 eV. The addition of an Al atom leads to a very symmetric Al₁₃⁻ cluster with one peak at 3.8 eV and a shoulder at around 4.1 eV. This dramatic change in spectrum is due to the conversion of the Al₁₂⁻ from a less symmetric Cs structure into a perfect icosahedron 13 atom cluster. This can be explained as a symmetry effect that leads to more degenerate energy levels. The spectrum of Al₁₃Ni⁻ has three broad peaks at 3.2, 3.75 and at 4.4 eV. Our computations showed that Al₁₃Ni⁻ is also a perfect icosahedron, but the explanation of such a different spectrum was due to the fact that the Ni atom brings 10 extra valence electrons and the interaction of these valence orbitals with those of Al₁₃⁻ explain the difference in spectrum. Another good example of the importance of bimetallic clusters can be found on the recent work of Khetrapal et al.¹⁵ in studying the structural evolution of mixed gold-aluminum clusters using PES and density functional theory (DFT) computations. The proper identification of the structural and electronic properties of mixed-metal clusters are therefore of great interest and shall be further explored. Another example is our work on mixed anionic aluminum-molybdenum clusters where we applied the analysis developed in ref. [14] to explain the measured spectrum of Al₅Mo⁻, \( n = 3–5,7 \) and to separate the effects of size, symmetry, composition to explain the changes in spectrum of Al₁₃⁻, Al₁₃⁻, and Al₅Mo⁻.

In this work we predict the photoelecronic spectrum of Al₆Mo⁻ and provide an explanation why this cluster was not observed in the experiment reported on ref. [16]. We present the lowest energy structure of the neutral and anionic Al₆Mo clusters with \( n = 1–7 \), their binding and vertical detachment energies, and use this analysis to explain the reason why the anionic Al₆Mo⁻ cluster was not observed in the experiment. In the next section, we present the methods used in this work. The results are presented in the following section and the last section is dedicated to concluding remarks.

[a] Dr. P. H. Acioi
Department of Physics and Astronomy
Northeastern Illinois University
Chicago, Illinois, 60625 (USA)
E-mail: p-acioi@neiu.edu

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2. Computational Methods

All the computations are performed within density functional theory using Gaussian 03. We used the Becke exchange[17] and Perdew86 correlation[18] functions (BP86), and the Stuttgart (SDDALL) suite of pseudopotentials with the corresponding basis set as implemented in Gaussian 03.[19] The selection of the BP86 exchange-correlation functional and pseudopotentials is based on extensive tests that included a variety of alternative choices and are presented in detail in Ref. [16]. Stable structures were obtained by performing unconstrained gradient-based minimization. Normal mode analysis was performed to distinguish between stable structures and transition state candidates. To obtain the photoelectron spectra we used a correction scheme to convert Kohn-Sham (KS) single-electron eigenvalues into electron binding energies.[20] In this scheme the electron binding energy is obtained as

\[ BE_i(N) = -\varepsilon_i(N) + \Delta_i(N) \]  

(1)

where \( BE_i(N) \) is the binding energy corresponding to the \( i \)th Kohn-Sham energy level \( \varepsilon_i(N) \) of the \( N \)-electron system, and \( \Delta_i(N) \) is the correction. The correction term is defined as a linear interpolation between correction terms of the \( i \)th energy level of the \( N-1 \) electron system and the \( i+1 \)th term of the \( N \) electron system as indicated below:

\[ \Delta_i(N) = \Delta_i(N-1) + [\Delta_{i+1}(N) - \Delta_i(N-1)]\alpha_i(N) \]  

(2)

Where

\[ \alpha_i(N) = \frac{\varepsilon_i(N) - \varepsilon_i(N-1)}{\varepsilon_{i+1}(N) - \varepsilon_i(N-1)} \]  

(3)

In order to determine all the corrections, one must compute the corrections to the highest occupied molecular orbital (HOMO) of the 1, 2, ..., \( N \) electron system and recursively compute the corrections to the inner electrons. A full description of this method can be found in ref. [20]. As discussed in earlier work,[16–19] this scheme is robust, accurate, and can be applied to any DFT exchange-correlation functional. The full scheme has been successfully applied to clusters and molecules.[5–14]

We have shown in ref. [16] that this methodology reproduces well the PES of \( \text{Al}_n\text{Mo} \), \( n = 3-5,7 \). In this work we focus in predicting the PES of \( \text{Al}_n\text{Mo} \).

3. Results and Discussion

3.1. Structural Properties

In this section we report the lowest energy structures of neutral (Figure 1) and anionic (Figure 2) \( \text{Al}_n\text{Mo} \) clusters, \( n = 1–7 \). In many cases, the lowest energy isomer of the neutral and anionic clusters have the same packing. The exceptions are \( \text{Al}_2\text{Mo}, \text{Al}_3\text{Mo}, \text{Al}_5\text{Mo}, \text{Al}_6\text{Mo} \). In the neutral \( \text{Al}_n\text{Mo} \) the molybdenum atom is bonded to both Al in a \( C_{2v} \) structure, while in the anionic form the Mo is bonded to a single Al in a \( C_{nv} \) arrangement. We should note, however, that a \( C_{2v} \) structure similar to the neutral lowest energy isomer is found only 0.013 eV higher in energy, it is therefore expected that both structures would contribute to the photoelectron spectrum. The neutral \( \text{Al}_n\text{Mo} \), the main objective of this study, is a perfect octahedron in a closed shell configuration. This hints to a magic number system with enhanced stability. The anionic \( \text{Al}_n\text{Mo} \) is distorted from the \( O_6 \) symmetry into a lower energy \( D_{3d} \) symmetry cluster. Given the possibility of a magic number cluster, one should expect that the electron affinity or the vertical detachment energy of this system to be lower as compared to their neighboring \( \text{Al}_n\text{Mo} \) and \( \text{Al}_n\text{Mo} \) clusters. We will discuss this subject in the next subsection. The neutral \( \text{Al}_n\text{Mo} \) cluster is a \( C_{2v} \) structure obtained by adding an Al atom to the \( \text{Al}_n\text{Mo} \) \( O_6 \) structure, while the anion seems to be derived by the addition of 2 Al atoms to the \( \text{Al}_n\text{Mo} \) \( C_{2v} \) structure. This will probably have effects on the stability of the clusters. It is interesting to note that in both the neutral and charged forms the clusters start with a high spin state that is reminiscent from the electronic structure of the Mo atom that has a 4d\(^5\)s\(^1\) ground state. As the clusters grow in size Mo bonds to more Al atoms leading to lower spin states. In the neutral case, we first...
observe a zero spin ground state at Al₆Mo, while in the anions this happens for Al₇Mo.

In Figure 3 we present the binding energy per atom of the neutral and anionic clusters that were calculated according to:

\[ BE(Al_{6}Mo) = \frac{[nE(Al) + E(Mo) - E(Al_{6}Mo)]}{(n+1)} \]  
(4)

\[ BE(Al_{7}Mo^-) = \frac{[nE(Al) + E(Mo^-) - E(Al_{7}Mo^-)]}{(n+1)} \]  
(5)

where \( E(Al) \), \( E(Mo) \) and \( E(Mo^-) \) are the total energies of Al atom, Mo atom and of the Mo anion. Eqs. (4) and (5) refer to the binding energy of the neutral and anionic clusters, respectively. We chose the breakdown in energy in Eq. (5) because the electron affinity of Mo is higher than that of Al. The binding energy per atom for both neutral and negatively charged species seem to increase quickly from AlMo to Al₆Mo and then start to level off for the larger sizes. But, one can note that the graph seems to display a local maximum at the neutral Al₆Mo that is not seen on the anionic counterpart. This indicates that the Al₆Mo⁻ is relatively less stable than Al₆Mo when compared to the Al₆Mo and Al₇Mo counterparts. This can be viewed as a hint of why Al₆Mo⁻ is not seen in the experiment. It will indicate that the vertical detachment energy of Al₆Mo⁻ should be substantially lower than the ones observed for Al₇Mo⁻ and Al₇Mo⁻, further corroborating the idea of a magic cluster.

To more appropriately quantify the relative stability of the clusters we use the 2nd energy difference defined as:

\[ \Delta^2 E(Al_{n}Mo) = [E(Al_{n+1}Mo) - 2E(Al_{n}Mo) + E(Al_{n-1}Mo)] \]  
(6)

The results of the second difference are shown in Figure 4. As one can see the peaks are at \( n = 3 \) and 6. More importantly the neutral Al₆Mo displays a more pronounced peak than Al₇Mo, indicating that the neutral is more stable than the negatively charged form. Another indication on the difficulty of observing the Al₇Mo⁻ cluster.

3.2. Vertical Attachment and Detachment Energies

The photoelectron spectra peaks are manifestations of vertical processes, where the extracted electron transitions from the ground state of the anionic cluster into the frozen neutral counterpart. Thus, the need to compute the vertical detachment energies of the anionic clusters to compare with the experiment. In this work we also present the energy needed to add an electron to the frozen neutral cluster. We call it the vertical attachment energy. In Table 1 we present the vertical attachment and detachment energies for the neutral and anionic Al₄Mo clusters, \( n = 1 - 7 \). For the cases studies in reference [16] we also present the measured values of the 1st detachment energy and the adiabatic electron affinity. Comparing the computed values with the experiment one can see that there is very good agreement. In ref. [16] we estimated that the accuracy of our DFT calculations were within 0.1 eV, estimate confirmed by the numbers in Table 1. The vertical attachment energies to the neutral clusters for all sizes but Al₆Mo were slightly lower than the detachment energies of the corresponding anion. This is because the geometric and electronic structures of these clusters are very different. In addition, one can observe that the vertical electron detachment energy of Al₇Mo⁻ is substantially lower than those of Al₆Mo and Al₇Mo⁻. It is possible that this cluster converts into the neutral before the time-of-flight portion of the experiment, making its signal weaker and harder to observe.

![Figure 3. Binding energy per atom of neutral (red) and anionic (anion) Al₆Mo clusters, \( n = 1 - 7 \), computed using Eqs. (4) and (5).](image)

![Figure 4. Second energy difference (Eq. (6)) of neutral (red) and anionic (blue) Al₆Mo clusters, \( n = 1 - 7 \).](image)

| \( n \) | Computed VAE (eV) | VDE (eV) | Experiment EA | VDE |
|---|---|---|---|---|
| 1 | 1.016 | 1.255 | – | – |
| 2 | 1.523 | 1.691 | – | – |
| 3 | 1.941 | 2.229 | 2.05 | 2.25 |
| 4 | 1.971 | 2.131 | 2.15 | 2.20 |
| 5 | 2.035 | 2.163 | 2.20 | 2.30 |
| 6 | 1.735 | 1.872 | – | – |
| 7 | 1.929 | 2.644 | 2.50 | 2.65 |

Table 1. DFT computed vertical attachment (VAE) and detachment energies (VDE) of neutral and anionic Al₄Mo clusters. Also presented are the measured vertical detachment energy and adiabatic electron affinity (EA) of Al₇Mo⁻ (ref. [16]).
3.3. Photoelectron Spectrum of Al₇Mo⁻

In this section we will make a prediction of the photoelectron spectrum of Al₇Mo⁻. In order to place this spectrum in perspective, we reproduce here the measured spectra of Al₄Mo⁻ and Al₅Mo⁻ from our recently published work.

In Figure 5 we present the spectra of Al₄Mo⁻ and Al₅Mo⁻. As discussed in ref., the first isomer of Al₄Mo⁻ does reproduce qualitatively as well as quantitatively the peaks of the measured spectrum, the largest discrepancy is 0.1 eV. The lines corresponding to the second isomer, lying 0.283 eV higher in energy, also fall under the measured spectrum, but the features are different. This is a great indication that for this case we only need to invoke the lowest energy isomer to explain the measured spectrum.

In Figure 5b) we present the measured spectra of Al₅Mo⁻. The features in the experimental spectrum in this case are less defined than the case of Al₄Mo⁻. Although one could argue three or four different peaks, the overlap between them result in a broader peak centered around 3 eV with a width of roughly 1 eV. One should expect that this could be a result of many different isomers contributing to the final spectrum. In fact, as discussed in reference the first six isomers of Al₅Mo⁻ are separated by about 0.184 eV which is substantially lower than the corresponding thermal energy at room temperature of 0.465 eV. If we invoked just the first isomer, the spectrum should have 3 well defined peaks. However, as we include all the isomers, the overlap of all the peaks would be enough to spread the features and have a less well defined spectrum that is observed in the experiment.

The question that we want to ask is whether the Al₇Mo⁻ spectrum has well defined peaks like Al₅Mo⁻ or more spread like Al₄Mo⁻. Given that the Al₇Mo⁻ lowest energy isomer is highly symmetrical we expect it to have well defined peaks, but in order to answer it more definitely we must look for other low-lying isomers as seen in Figure 6. A thorough search yielded only two structures within the computed thermal energy at room temperature. They are a D₃d structure that is slightly distorted from the perfect octahedron and a D₃h structure that corresponds to a 60° rotation of one of the Al₇ trimers around the original C₃ axis of the D₃d structure. This second structure is only 0.052 eV higher in energy, and is therefore expected to contribute to the PES spectrum. In Figure 7 we represent the line spectrum (vertical lines) representing individual electron binding energies and a simulated spectrum (red line) resulting from a 0.1 eV broadening of the computed lines. If measurements are made in Al₇Mo⁻ the spectrum will clearly have a sharp peak centered about 1.9 eV and then a second broad peak around 2.6 eV and a smaller peak at around 3.2 eV. This peak is a result of lines from the second isomer. These lines are also present in the D₃d isomer, but they lie beyond the energy range of the experiment described in ref. [16].

![Figure 5](image1.png)

**Figure 5.** a) Measured photoelectron spectrum of Al₄Mo⁻. b) Measured photoelectron spectrum of Al₅Mo⁻. Data from our earlier work of ref. [16].

![Figure 6](image2.png)

**Figure 6.** Low energy isomers of Al₇Mo⁻.

![Figure 7](image3.png)

**Figure 7.** DFT computed electron binding energy spectrum of Al₇Mo⁻. The solid lines correspond to the D₃d lowest energy isomer and the dashed lines correspond to the D₃h 2nd isomer. The red continuous line corresponds to a 0.1 eV Gaussian broadening of the computed (vertical lines) of the two low energy isomers.
4. Conclusions

We presented structural and electronic properties of neutral and anionic Al\textsubscript{7}Mo \((n = 1-7)\) mixed clusters. The binding energy per atom and the 2\textsuperscript{nd} energy difference points to an enhanced neutral Al\textsubscript{7}Mo cluster, while the anionic counterpart seems to have similar energetic properties as the Al\textsubscript{7}Mo and Al\textsubscript{7}Mo\textsuperscript{-}. Therefore, Al\textsubscript{7}Mo\textsuperscript{-} has a relatively low vertical detachment energy that does not follow the increasing trend as a function of cluster size. This is an indication that the neutral Al\textsubscript{7}Mo cluster can be viewed as closing the magic number of valence electrons resulting on a very symmetric \(O_h\) structure. The lowest energy structure of the anionic counterpart is a distortion from \(O_h\) to the lower \(D_{3d}\) group. We also found a \(D_{3d}\) structure that is a trigonal prism with a Mo atom in the center. This structure is 0.052 eV less stable than the first isomer. Because of the relatively low vertical detachment energy, the signal in the time-of-flight spectrum might be too low and this could explain the difficulty of getting a well-defined photoelectron spectrum for this system. Nevertheless, we believe that having an idea of the predicted spectrum might help identifying this spectrum in a future experiment. Our simulated spectrum (Figure 7) results from a 0.1 eV broadening of the computed lines for the two low energy forms of Al\textsubscript{7}Mo\textsuperscript{-} we found in this study. The main features identified in this work are one peak centered at 1.9 eV a second broader peak around 2.6 eV and a smaller peak at 3.2 eV.

Supplementary Information

See supplementary material for the full structure of the lowest energy isomer of Al\textsubscript{7}Mo.

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Conflict of Interest

The authors declare no conflict of interest.

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