JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

ARTICLE

pubs.acs.org/JACS

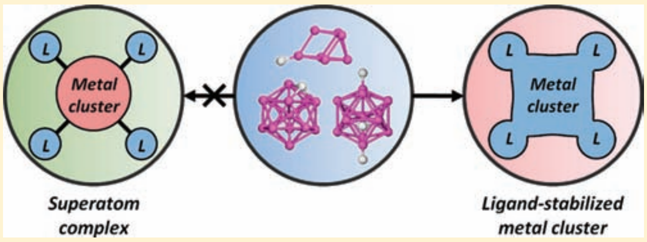
Can an Electron-Shell Closing Model Explain the Structure and Stability of Ligand-Stabilized Metal Clusters?

Jaehoon Jung,[†,§] Hyemi Kim,[†] and Young-Kyu Han[*,‡]

[†]Corporate R&D, LG Chem., Ltd., Research Park, Daejeon 305-380, Republic of Korea

[‡]Division of Materials Science, Korea Basic Science Institute, Daejeon 305-333, Republic of Korea

S *Supporting Information*



ABSTRACT: We investigated the structure and stability of several aluminum hydride complexes to understand the essence of "superatom chemistry" and to gain a right perspective on the ligand (L)-stabilized metal (M) clusters. We successfully interpret the structure and stability using molecular orbital analysis, which clearly shows the failure of an electron-shell closing model (or a superatom model) to explain it. The structure and stability of Al_mH_n are closely associated with the molecular orbital stabilization owing to the effective orbital overlap between Al_m (M_m) and nH (nL). The importance of retaining the electronic structural integrity of M_m in M_mL_n—within an electron-shell closing model—has been underestimated or even disregarded, and this has created the current controversies in the scientific community.

INTRODUCTION

Metal clusters of a given element can have chemical and electronic properties resembling those of a different atom. Such clusters, or "superatoms", can be described using an electron-shell closing model that results from quantum confinement of the valence electrons, which parallels the electron-shell closure of atoms. Ligand-stabilized metal clusters have been a subject of great interest in recent years due to their highly structured optical absorption, intense circular dichroism, luminescence visible to the eye, sizable nonlinear optical properties, and nanoscale catalytic activities.[1]

Bergeron et al.[2] reported that Al_{13} and Al_{14} are halogen-like and alkaline earth-like superatoms in the $Al_{13}I_n^-$ ($n = 1-12$) and $Al_{14}I_n^-$ ($n = 1-11$) complexes, respectively; the authors suggested a new form of "superatom chemistry" in which a superatom behaves like an atom when it reacts with other molecules. Since then, a variety of studies on superatom complexes have been actively pursued.[3] Kiran et al.[4] reported that H atoms select between the on-top and bridge (or face) sites on the Al clusters of the most stable Al_mH_n complexes ($m/n \geq 2$) in a way that makes the total number of valence electrons attain electronic shell closure. Walter et al.[5] showed that the superatom model straightforwardly accounts for the particular stability of thiolate (RS)-coordinated gold clusters such as $Au_{25}(SR)_{18}^-$ and $Au_{102}(SR)_{44}$. This demonstrates that the number of available Au 6s electrons must be a "magic number" obtained by filling shells quantized by angular momentum. The superatom model or electron-shell closing model, therefore, has been widely regarded as a simple and powerful tool for explaining the structures and stabilities of many ligand-stabilized metal clusters M_mL_n (M = metal and L = ligand).

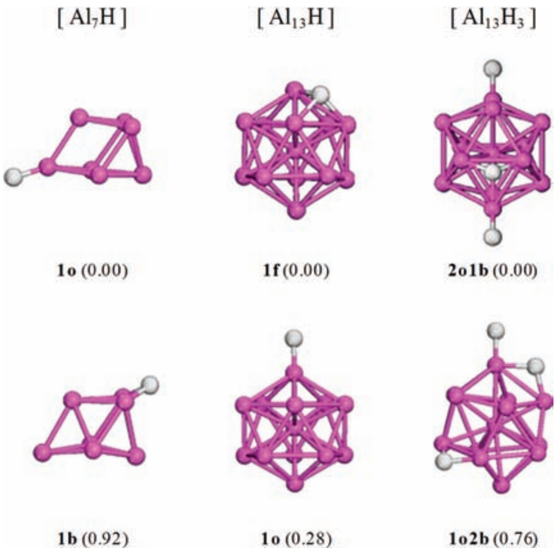


Figure 1. Optimized structures of Al_7H, $Al_{13}H$, and $Al_{13}H_3$ along with the relative energies (in eV).

On the other hand, there have been totally different viewpoints for ligand-stabilized metal clusters. Han et al.[6] showed

Received: February 8, 2011
Published: March 28, 2011

dx.doi.org/10.1021/ja201205k

that Al_{13} and Al_{14} have no superatomic characteristics in $Al_nI_2^-$ and $Al_nI_3^-$ (n = 11−15) complexes, respectively. Zhang et al.[7] also reported that Al_{13} cannot be simply considered as a superatom when it interacts with sulfur for Al_nS^- (n = 3−15) and $Al_nS_2^-$ (n = 7−15) complexes. In terms of the exceptional stability of $Au_{102}(SR)_{44}$, Reimers et al.[8] reported that the superatom model is inadequate for predicting of the thermodynamic stability of sulfur-stabilized gold nanoparticles. Instead, the authors showed that local structural effects dominate the chemistry.

To understand the essence of such controversies, we used first-principles calculations to investigate the structure and stability of M_mL_n (M = Al and L = H) complexes, as a contentious issue and a representative example: **1o**, **1b** Al_7H, **1f**, **1o** $Al_{13}H$, and **2o1b**, **1o2b** $Al_{13}H_3$ (see Figure 1; **o**: on-top, **b**: bridge, **f**: face). The work of Kiran et al.[4] mentioned above needs to be focused in that their electron counting rule (hereafter the KEC rule), based on an electron-shell closing model, determines the structure as well as the stability of ligand-stabilized metal clusters. It is very challenging to clearly analyze the electronic structures of ligand-stabilized metal clusters because of their complexity. We successfully interpret the structure and stability using molecular orbital (MO) analysis and show that there is no relationship between the electron-shell closing model (or a superatom model) and the stable structures of the Al_mH_n complexes. Instead, our results confirm that the structure and stability of Al_mH_n complexes are closely associated with the effective orbital overlap between M_m and nL and the resulting MO stabilization by the attached ligands.

Table 1. Energy Differences between On-Top and Bridge (or Face) Forms for Al_7H, Al_7I, $Al_{13}H$, and $Al_{13}I$. Units are in eV

	on-top	bridge (or face)[a]
Al_7H	0.00	0.92
Al_7I	0.00	0.58
$Al_{13}H$	0.28	0.00
$Al_{13}I$	0.23	0.00

[a] Bridge, Al_7H, Al_7I, $Al_{13}I$; and face, $Al_{13}H$.

COMPUTATIONAL DETAILS

Kohn−Sham density functional theory (DFT) was used to investigate the detailed electronic structures of Al_mH_n clusters. DFT calculations were performed with the gradient-corrected exchange-correlation functional proposed by Perdew, Burke, and Ernzerhof (PBE)[9] and the correlation-consistent triple-ζ (cc-pVTZ)[10] basis set. Scalar relativistic effects were treated with the energy-consistent small-core (25 valence electrons) pseudopotential (PP) for iodine.[11] The correlation-consistent triple-ζ (cc-pVTZ-PP) basis set was used for iodine.[12] For each specific cluster size, an exhaustive search for minimum energy structures was carried out without any symmetry constraint.[13] To judge whether the obtained structures are local minima, all of the vibrational frequencies were calculated using the analytic second derivatives evaluation of the energy with respect to nuclear coordinates. We present all the orbital

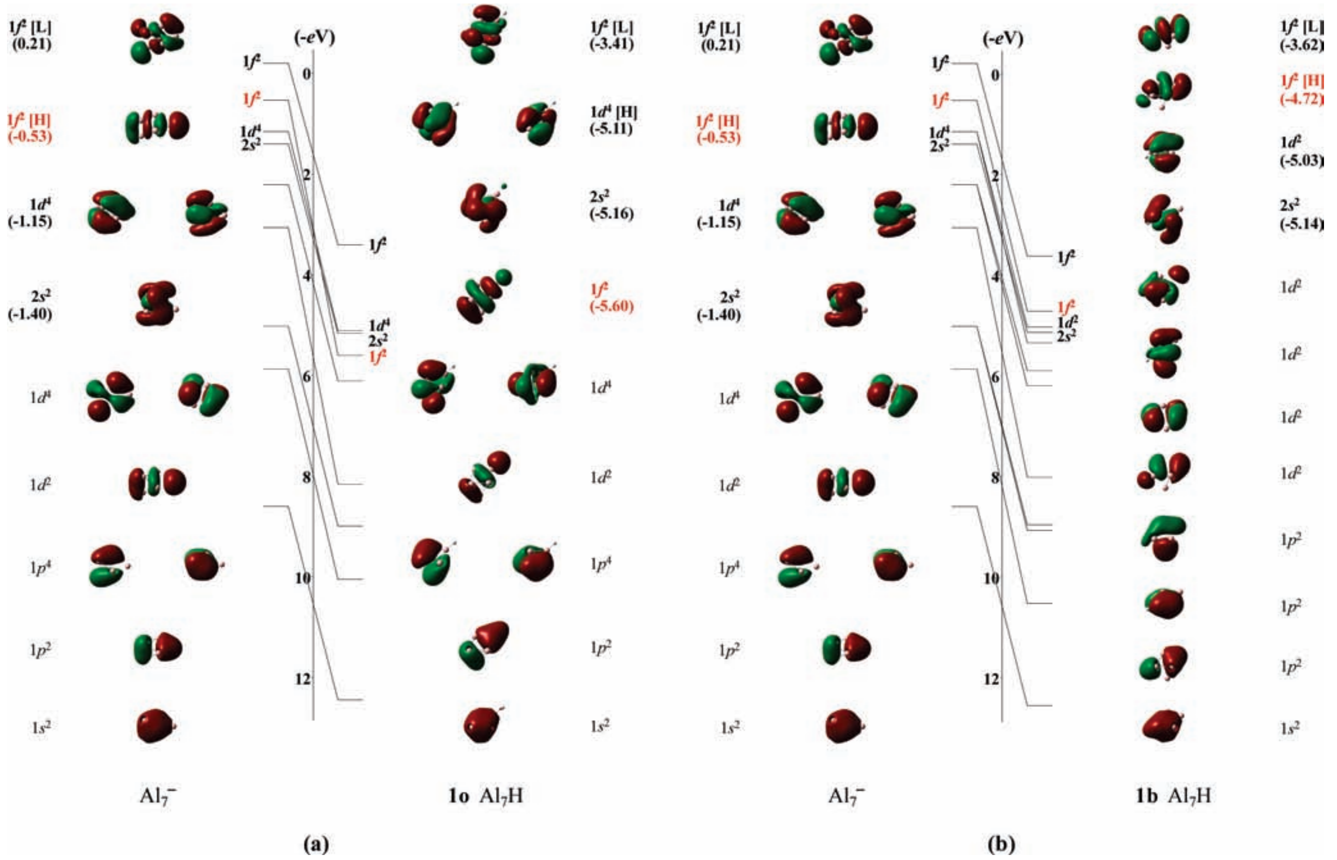


Figure 2. Molecular orbital diagrams for (a) Al_7^- and **1o** Al_7H and (b) Al_7^- and **1b** Al_7H.

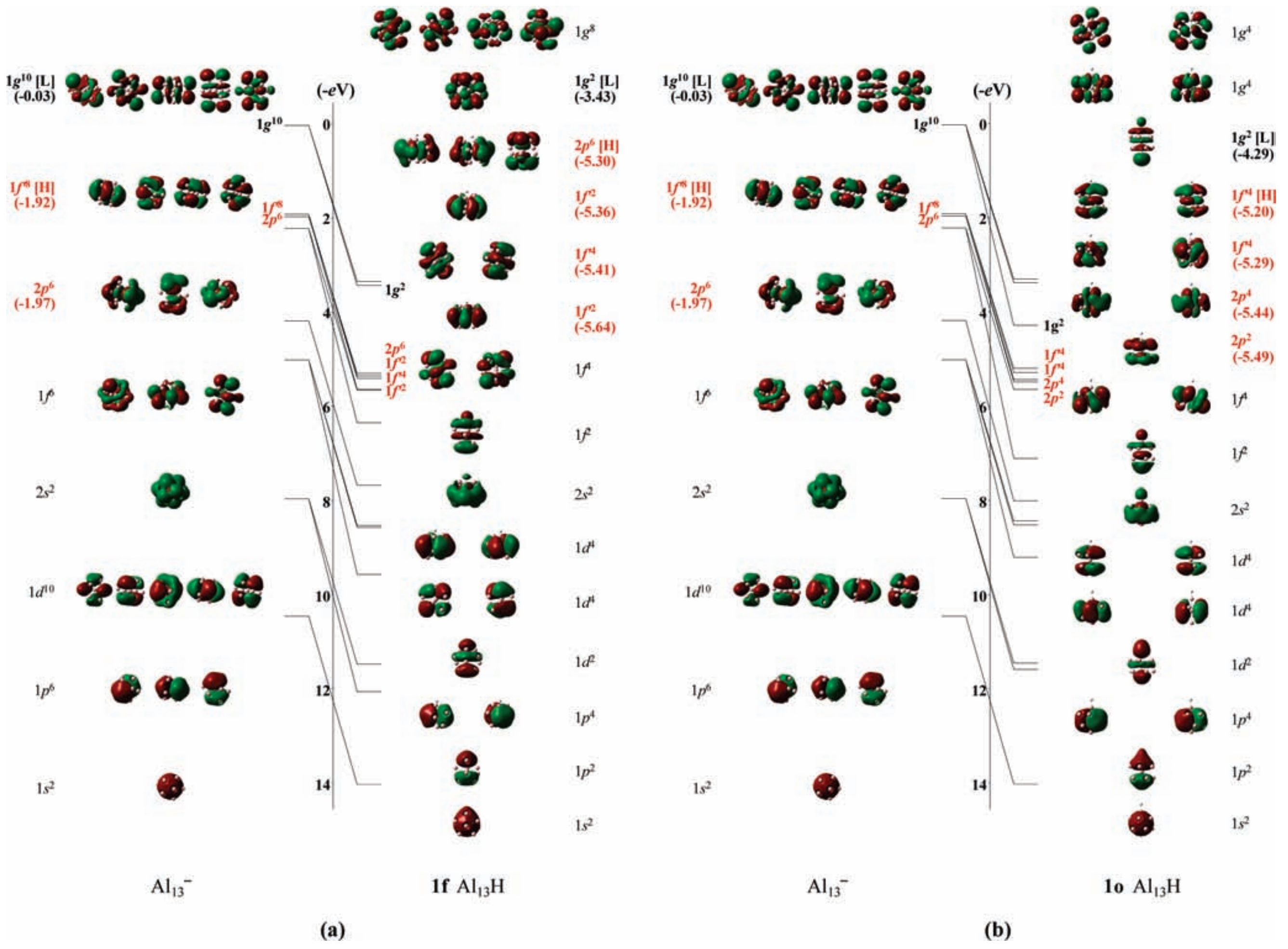


Figure 3. Molecular orbital (MO) diagrams for (a) Al_{13}^- and **1f** $Al_{13}H$ and (b) Al_{13}^- and **1o** $Al_{13}H$.

energies of the systems considered here in the Supporting Information. All the calculations were carried out with the Gaussian 03 program.[14]

■ RESULTS AND DISCUSSION

The lowest-energy structures of **2b** Al_6H_2, **1o** Al_7H, **2o1b** Al_7H_3, **4o** Al_8H_4, **1f** $Al_{13}H$, and **2o** $Al_{14}H_2$ clusters fulfilled the predictions of KEC rule, i.e., the number of valence electrons N equals the electron-shell closing number, the magic number 20 or 40. Simple electron counting as $N = 3$, 1, and -1 for Al, bridge (or face) H, and on-top H, respectively, and the valence electrons in the six Al_mH_n complexes can satisfy the electron-shell closing model.[4] Furthermore, Reveles et al.[15] also reported that Al_7 is a multivalent superatom based on DFT calculations. Interestingly, hot-issued aluminum iodide complexes Al_7I and $Al_{13}I$ also have on-top and bridge forms, respectively, similar to the aluminum hydride complex analogues (see Table 1). This leads us to believe that our results and discussion are valid for various M_mL_n complexes.

Can an electron-shell closing model or superatom model really determine the structure and stability of Al_mH_n complexes? To answer this question, we first performed MO analysis for the **1o** and **1b** Al_7H structures. All of the optimized structures considered in this work are shown in Figure 1, along with the relative energies. The **1o** isomer is more stable than the **1b** form by 0.92 eV (21 kcal/mol). According to the KEC rule, the N value for the lowest-energy **1o** form is the magic number of 20 $[3(\mathrm{Al}) \times 7 - 1(\text{on-top H})]$, while it is 22 $[3(\mathrm{Al}) \times 7 + 1(\text{bridge H})]$ for the **1b** form. We present the molecular orbitals and orbital energies of **1o** and **1b** Al_7H in Figure 2, and include the MO analysis results of Al_7^- for comparison. If a minor perturbation of the metal cluster by H attachment would leave the electronic shell structures virtually unchanged, then the electron-shell closing (or superatom) model should remain valid. However, our MO analysis shows that even one H attachment leads to a significant loss of degeneracy of the electronic states in the cluster orbital shells. It is worth noting that the highest occupied molecular orbitals (HOMOs) of Al_7^-, 1f orbital, forms a stable bonding MO with the on-top H atom, resulting in a low orbital energy of -5.60 eV, even below the $1d^4$ (-5.11 eV) and $2s^2$ (-5.16 eV) orbitals in **1o** Al_7H. This indicates that Al_7 overlaps with H very effectively, when the H atom occupies the on-top position. On the other hand, for **1b** Al_7H, the $1f^2$ HOMO (-4.72 eV) is still located above the $1d^2$ (-5.03 eV) and $2s^2$ (-5.14 eV) orbitals, similar to Al_7^-. The MO reordering does not occur, despite the slight loss of orbital degeneracy due to the attachment of a bridge H atom. Hence, the gap between the HOMO and the lowest unoccupied molecular orbital (LUMO) of **1b** Al_7H (1.10 eV), a factor determining the stability of the complex, is much lower than 1.70 eV of **1o** Al_7H. We note that the **1b** Al_7H is

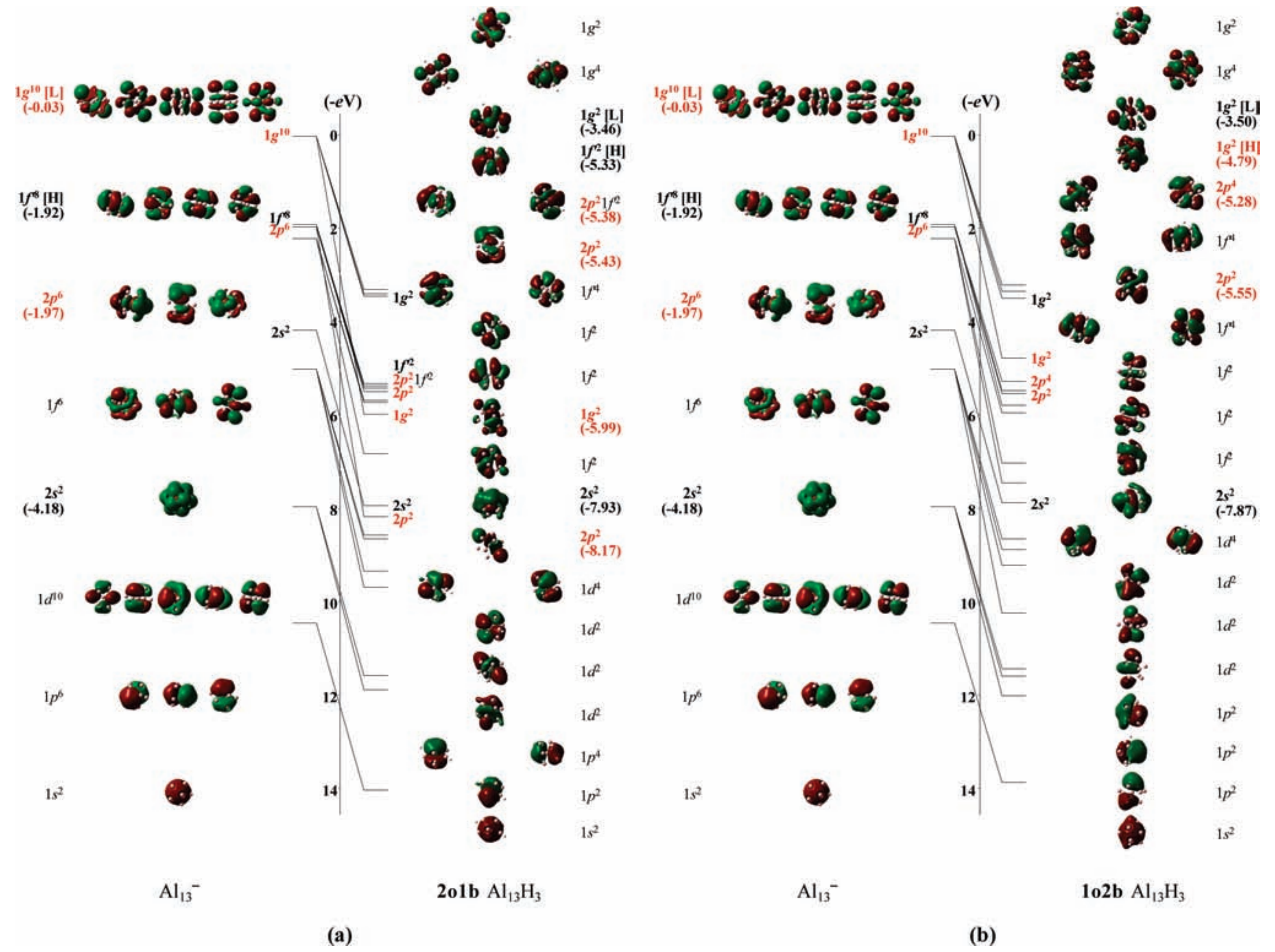


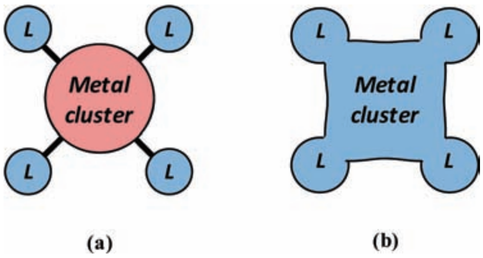
Figure 4. Molecular orbital (MO) diagrams for (a) Al_{13}^{-} and **2o1b** $Al_{13}H_3$ and (b) Al_{13}^{-} and **1o2b** $Al_{13}H_3$.

unstable, because it has a shell-structure similar to that of Al_7^{-}, that is, the small perturbation of the Al_7 cluster by an attached H atom.

Second, we compare the MO diagrams of **1f** and **1o** $Al_{13}H$ with that of Al_{13}^{-} in Figure 3. In contrast to Al_7H, the **1f** form is more stable than the **1o** form by 0.28 eV (6.5 kcal/mol). According to the KEC rule, the *N* value for the lowest-energy **1f** form is the magic number of 40 ($3 \times 13 + 1$), while it is 38 ($3 \times 13 - 1$) for the **1o** form. It is worth noting that the quadruply degenerated HOMOs of Al_{13}^{-}, the 1f orbitals ($1f^8$), do not have a preference for a specific direction, unlike Al_7^{-} HOMO. The face H atom in **1f** $Al_{13}H$ provokes the MO reordering, that is, the $2p^6$ (-1.97 eV for Al_{13}^{-} and -5.30 eV for $Al_{13}H$) and $1f'^8$ (-1.92 eV for Al_{13}^{-} and -5.45 eV for $Al_{13}H$) orbital orders are exchanged; the $(2s)^2(1f)^6(\mathbf{2p})^6(\mathbf{1f'})^8$ valence orbitals of Al_{13}^{-} become the $(2s)^2(1f)^2(1f)^4(\mathbf{1f'})^2(\mathbf{1f'})^4(\mathbf{1f'})^2(\mathbf{2p})^6$ orbitals in **1f** $Al_{13}H$. On the other hand, no MO reordering was observed in the case of the less stable **1o** $Al_{13}H$ (see Figure 3b). It is noteworthy that one attached H atom on the *z*-axis significantly lowers the orbital energy of the unoccupied *z*-type 1g lowest unoccupied molecular orbitals (LUMOs) (-4.29 eV) of **1o** $Al_{13}H$, and slightly affects the *x*,*y*-type 1g orbitals. Thus, the HOMO−LUMO gap of **1o** $Al_{13}H$ (0.91 eV) becomes only half that of **1f** $Al_{13}H$ (1.87 eV).

Lastly, let us turn to the $Al_{13}H_3$ case, which does not fulfill the electron-shell closing model.[13] The **2o1b** $Al_{13}H_3$ complex is more stable than the **1o2b** form by 0.76 eV (18 kcal/mol). According to the KEC rule, the *N* value for the lowest-energy **2o1b** form is 38 ($3 \times 13 - 2 + 1$), while it is the magic number of 40 ($3 \times 13 - 1 + 2$) for the less stable **1o2b** form. We compare the MO of the lowest energy structure, **2o1b**, with Al_{13}^{-} MO in Figure 4a. Although the MO perturbation is more complex by three H attachment, the MO results can be explained in a way similar to the Al_7H and $Al_{13}H$ cases. The most notable thing is the significant energy lowering of $1g^2$. It is not surprising that the LUMO of Al_{13}^{-}, the 1g orbital (-0.03 eV for Al_{13}^{-} and -5.99 eV for $Al_{13}H_3$), forms a very stable bonding orbital with three H atoms because of the 42 (39 + 3) total valence electrons for $Al_{13}H_3$. The $2p^2$ orbital (-8.17 eV) is also significantly stabilized by the attachment of three H atoms, with a result below even that of the 2s orbital (-7.93 eV). As a result, there is a considerable MO reordering; the $(2s)^2(1f)^6(\mathbf{2p})^6(1f')^8(\mathbf{1g})^2$ valence orbitals of Al_{13}^{-} become the $(\mathbf{2p})^2(2s)^2(1f)^2(\mathbf{1g})^2(1f)^2(1f)^2(1f')^4$-$(\mathbf{2p})^2(\mathbf{2p})^2(1f')^2(1f')^2$ orbitals in **2o1b** $Al_{13}H_3$. On the other hand, the MO splitting by three hydrogen atoms is rather small, and the MO reordering occurs at a very restrictive level; that is, the $(2s)^2(1f)^6(\mathbf{2p})^6(1f')^8(\mathbf{1g})^2$ valence orbitals of Al_{13}^{-} become the $(2s)^2(1f)^2(1f)^2(1f)^2(1f')^4(\mathbf{2p})^2(1f')^4(\mathbf{2p})^4(\mathbf{1g})^2$ orbitals in the **1o2b** $Al_{13}H_3$, as shown in Figure 4b. We note that both the HOMO and LUMO are 1g orbitals and the HOMO(1g)−LUMO(1g) gap (1.29 eV) of the **1o2b** form is much lower than the HOMO(1f)−LUMO(1g) gap (1.87 eV) of the

Scheme 1. Schematic Diagrams for Two Different Viewpoints (a and b) for Ligand-Stabilized Metal Clusters (L: Ligand)



lowest-energy **2o1b** form. This can be interpreted as stemming from the significant energy lowering of 1g orbitals in the latter structure.

Conclusively, the ligand H atoms are attached to the metal cluster (M_m) in a way that makes an effective orbital overlap between the metal cluster and ligands, and does not make the total number of valence electrons attain electron-shell closure. The effective orbital overlap between M_m and nL and the resulting MO stabilization by attached ligands are closely associated with the structure and stability of Al_mH_n complexes. Our MO interpretation clearly shows large MO splitting and concomitant MO reordering by attached ligands, which significantly deteriorates the superatom character, that is, the atom-like shell-type electronic structural character of pure metal clusters. Thus, there is no link between superatom-shell filling and the stable structures of Al_mH_n complexes.

We need to recognize two extremely different viewpoints to understand the characteristics of M_mL_n complexes (see scheme 1). From the first view, the structural integrity and chemical identity of M_m are retained and the influence of ligands is small (scheme 1a). Both the superatom model and electron-shell closing model are based on this viewpoint. From another point of view, the structural integrity and/or chemical identity of M_m disappears due to significant perturbation by ligands (scheme 1b). Most researchers recognize that a real complex system would have mixed characteristics of schemes 1a and 1b, and a superatom unit must retain its structural integrity in the assembled unit. However, the importance of retaining its electronic structural integrity has been underestimated or even disregarded, and this has created the current controversies in the scientific community. Our MO interpretation clearly confirms that a real complex system has characteristics very close to those of scheme 1b; that is, the perturbation by ligands is much more significant than generally believed.

It should be mentioned that Schnöckel et al.[1f] have synthesized various types of $Al_m{-}L_n$ complexes, where L is usually an electronegative ligand; The authors call the cluster type of scheme 1b "metalloid" clusters, because these clusters are metastable intermediates on the way to the metals.[16]

CONCLUSIONS

We investigated the structure and stability of several aluminum hydride complexes to understand the essence of superatom chemistry and further to provide a reasonable perspective on the ligand (L)-stabilized metal (M) clusters. Our elaborate MO analysis shows the failure of an electron-shell closing model (or a superatom model) in explaining the structure and stability of the ligand-stabilized metal clusters. Instead, the structure and stability of Al_mH_n can be well described by the MO stabilization owing to the effective orbital overlap between Al_m (M_m) and nH (nL). The influence of ligands on the electronic structure of M_m moieties should be investigated to deeply understand the structure and stability of M_mL_n complexes and to avoid further controversies concerning superatom chemistry in the scientific community. We suggest that our approach based on MO analysis is a powerful tool and theoretically sound for explaining and understanding the structure and stability of ligand-stabilized metal clusters.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Complete ref 14. Absolute electronic energies, optimized Cartesian coordinates, and all the orbital energies for the stable structures of Al_m^-, Al_mH_n, and Al_mI_n complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

ykhan@kbsi.re.kr

Present Addresses

[§]Department of Advanced Materials Science, The University of Tokyo, Chiba 277−8561, Japan and RIKEN Advanced Science Institute, Wako, Saitama 351−0198, Japan

ACKNOWLEDGMENT

This work was supported by the National Research Foundation of Korea Grant funded by the Korean Government (MEST) (NRF-2010-C1AAA001-0029018).

REFERENCES

(1) (a) Zhu, M.; Aikens, C. M.; Hendrich, M. P.; Gupta, R.; Qian, H.; Schatz, G. C.; Jin, R. *J. Am. Chem. Soc.* **2009**, *131*, 2490. (b) Ramakrishna, G.; Varnavski, O.; Kim, J.; Lee, D.; Goodson, T. *J. Am. Chem. Soc.* **2008**, *130*, 5032. (c) Zhu, Y.; Qian, H.; Drake, B. A.; Jin, R. *Angew. Chem., Int. Ed.* **2010**, *49*, 1295. (d) Wu, Z.; Gayathri, C.; Gil, R. R.; Jin, R. *J. Am. Chem. Soc.* **2009**, *131*, 6535. (e) Lopez-Acevedo, O.; Kacprzak, K. A.; Akola, J.; Häkkinen, H. *Nat. Chem.* **2010**, *2*, 329. (f) Schnöckel, H. *Chem. Rev.* **2010**, *110*, 4125. (g) Parker, J. F.; Fields-Zinna, C. A.; Murray, R. W. *Acc. Chem. Res.* **2010**, *43*, 1289. (h) Pei., Y.; Shao, N.; Gao, Y.; Zeng, X. C. *ACS Nano* **2010**, *4*, 2009.

(2) Bergeron, D. E.; Roach, P. J.; Castleman, A. W., Jr.; Jones, N. O.; Khanna, S. N. *Science* **2005**, *307*, 231.

(3) (a) Roach, P. J.; Woodward, W. H.; Castleman, A. W., Jr.; Reber, A. C.; Khanna, S. N. *Science* **2009**, *323*, 492. (b) Castleman, A. W., Jr.; Khanna, S. N.; Sen, A.; Reber, A. C.; Qian, M.; Davis, K. M.; Peppernick, S. J.; Ugrinov, A.; Merritt, M. D. *Nano Lett.* **2007**, *7*, 2734. (c) Roach, P. J.; Reber, A. C.; Woodward, W. H.; Khanna, S. N.; Castleman, A. W., Jr. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 14565. (d) Castleman, A. W., Jr.; Jena, P. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 10554. (e) Johnson, G. E.; Mitrić, R.; Tyo, E. C.; Bonačić-Koutecký, V.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **2008**, *130*, 13912. (f) Claridge, S. A.; Castleman, A. W., Jr.; Khanna, S. N.; Murray, C. B.; Sen, A.; Weiss, P. S. *ACS Nano* **2009**, *3*, 244. (g) Qian, M.; Reber, A. C.; Ugrinov, A.; Chaki, N. K.; Mandal, S.; Saavedra, H. M.; Khanna, S. N.; Sen, A.; Weiss, P. S. *ACS Nano* **2010**, *4*, 235. (h) Reveles, J. U.; Clayborne, P. A.; Reber, A. C.; Khanna, S. N.; Pradhan, K.; Sen, P.; Pederson, M. R. *Nat. Chem.* **2009**, *1*, 310. (i) Reber, A. C.; Khanna, S. N.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **2007**, *129*, 10189. (j) Yang, L.; Ding, Y.; Sun, C. *J. Am. Chem. Soc.* **2007**,

129, 1900. (k) Bergeron, D. E.; Roach, P. J.; Castleman, A. W., Jr.; Jones, N. O.; Reveles, J. U.; Khanna, S. N. *J. Am. Chem. Soc.* **2005**, *127*, 16048. (l) Shimojo, F.; Ohmura, S.; Kalia, R. K.; Nakano, A.; Vashishta, P. *Phys. Rev. Lett.* **2010**, *104*, 126102. (m) Müller, M.; Lesanovsky, I.; Weimer, H.; Büchler, H. P.; Zoller, P. *Phys. Rev. Lett.* **2009**, *102*, 170502.

(4) Kiran, B.; Jena, P.; Li, X.; Grubisic, A.; Stokes, S. T.; Ganteför, G. F.; Bowen, K. H.; Burgert, R.; Schnöckel, H. *Phys. Rev. Lett.* **2007**, *98*, 256802.

(5) Walter, M.; Akola, J.; Lopez-Acevedo, O.; Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Whetten, R. L.; Grönbeck, H.; Häkkinen, H. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 9157.

(6) Han, Y.-K.; Jung, J. *J. Am. Chem. Soc.* **2008**, *130*, 2.

(7) Zhang, Z.-G.; Xu, H.-G.; Feng, Y.; Zheng, W. *J. Chem. Phys.* **2010**, *132*, 161103.

(8) Reimers, J. R.; Wang, Y.; Cankurtaran, B. O.; Ford, M. J. *J. Am. Chem. Soc.* **2010**, *132*, 8378.

(9) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(10) (a) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007. (b) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

(11) Peterson, K. A.; Figgen, D.; Goll, E.; Stoll, H.; Dolg, M. *J. Chem. Phys.* **2003**, *119*, 11113.

(12) Peterson, K. A.; Shepler, B. C.; Figgen, D.; Stoll, H. *J. Phys. Chem. A* **2006**, *110*, 13877.

(13) Jung, J.; Han, Y.-K. *Phys. Rev. Lett.* **2008**, *100*, 199701.

(14) Frisch, M. J.; et al. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(15) Reveles, J. U.; Khanna, S. N.; Roach, P. J.; Castleman, A. W., Jr. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 18405.

(16) (a) Schnepf, A.; Stösser, G.; Schnöckel, H. *J. Am. Chem. Soc.* **2000**, *122*, 9178. (b) Schnöckel, H. *Dalton Trans.* **2005**, 3131. (c) Schnöckel, H.; Schnepf, A.; Whetten, R. L.; Schenk, C.; Henke, P. *Z. Anorg. Allg. Chem.* **2011**, *637*, 15.