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Sincerest form of flattery: The frontier orbitals and optical absorption spectra of the  $AlAu_4^-$  anion are reported. By using density functional theory, it is shown that  $AlAu_4$  not only mimics the chemistry of halogens, but also, with a vertical detachment energy (VDE) of 3.98 eV in its anionic form, that it is a superhalogen.



T. Zhao, Y. Li, Q. Wang,\* P. Jena

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All-Metal Clusters that Mimic the Chemistry of Halogens

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DOI: 10.1002/cphc.201300511

# All-Metal Clusters that Mimic the Chemistry of Halogens

Tianshan Zhao,<sup>[a]</sup> Yawei Li,<sup>[b]</sup> Qian Wang,<sup>\*[a, c]</sup> and Puru Jena<sup>[c]</sup>

Owing to their s<sup>2</sup>p<sup>5</sup> electronic configuration, halogen atoms are highly electronegative and constitute the anionic components of salts. Whereas clusters that contain no halogen atoms, such as AlH<sub>4</sub>, mimic the chemistry of halogens and readily form salts (e.g., Na<sup>+</sup>(AIH<sub>4</sub>)<sup>-</sup>), clusters that are solely composed of metal atoms and yet behave in the same manner as a halogen are rare. Because coinage-metal atoms (Cu, Ag, and Au) only have one valence electron in their outermost electronic shell, as in H, we examined the possibility that, on interacting with Al, in particular as  $AIX_4$  (X = Cu, Ag, Au), these metal atoms may exhibit halogen-like properties. By using density functional theory, we show that AlAu<sub>4</sub> not only mimics the chemistry of halogens, but also, with a vertical detachment energy (VDE) of 3.98 eV in its anionic form, is a superhalogen. Similarly, analogous to XHX superhalogens (X = F, Cl, Br), XAuX species with VDEs of 4.65, 4.50, and 4.34 eV in their anionic

### 1. Introduction

Owing to their large electron affinities (EAs), halogen atoms play an important role in chemistry as oxidizing agents and form the anionic components of many salts. Almost 50 years ago<sup>[1]</sup> it was discovered that clusters that consist of a core metal atom that is surrounded by halogen atoms (e.g., PtF<sub>6</sub>), the number of which exceeds the maximum valence of the metal atom by one, not only mimic the chemistry of halogen atoms but also that their EAs are larger than those of halogen atoms. Gutsev and Boldyrev<sup>[2]</sup> named such species "superhalogens". Over the last few years,<sup>[3–5]</sup> research has shown that clusters completely devoid of metal or halogen atoms can also have superhalogen properties. However, clusters that only contain metal atoms but mimic the chemistry of halogen atoms are rare. The only reported examples of all-metal superhalogens are Al<sub>13</sub>, Sc@Au<sub>14</sub> and TaAu<sub>12</sub>.<sup>[6–9]</sup>

[a]	T. Zhao, Prof. Q. Wang
	Center for Applied Physics and Technology
	College of Engineering
	Peking University
	Beijing 100871 (PR China)
[b]	Y. Li
	Department of Materials Science and Engineering
	College of Engineering
	Peking University
	Beijing 100871 (PR China)
[c]	Prof. Q. Wang, Prof. P. Jena
	Department of Physics

Department of Physics Virginia Commonwealth University Richmond, VA 23284 (USA) E-mail: qianwang2@pku.edu.cn form, respectively, also form superhalogens. In addition, Au can also form hyperhalogens, a recently discovered species that show electron affinities (EAs) that are even higher than those of their corresponding superhalogen building blocks. For example, the VDEs of  $M(A|Au_4)_2^-$  (M=Na and K) and anionic (FAuF)–Au–(FAuF) range from 4.06 to 5.70 eV. Au-based superhalogen anions, such as  $A|Au_4^-$  and  $AuF_2^-$ , have the additional advantage that they exhibit wider optical absorption ranges than their H-based analogues,  $A|H_4^-$  and  $HF_2^-$ . Because of the catalytic properties and the biocompatibility of Au, Au-based superhalogens may be multifunctional. However, similar studies that were carried out for Cu and Ag atoms have shown that, unlike  $A|Au_4$ ,  $A|X_4$  (X=Cu, Ag) clusters are not superhalogens, a property that can be attributed to the large EA of the Au atom.

Herein, we demonstrate the possibility that combinations of Au with simple metal atoms, such as Al, may be good candidates for forming superhalogens. This choice was motivated by the following facts: with an EA of 4.04 eV, AlH<sub>4</sub> is a superhalogen.<sup>[10]</sup> It forms a stable salt, namely, NaAlH<sub>4</sub>, which has been widely studied for its ability to reversibly store large amounts of H<sub>2</sub>.<sup>[11]</sup> H and Au share similar valence-electron configurations, namely, 1s<sup>1</sup> and 6s<sup>1</sup>, respectively. Both elements are electronegative, with EAs of 0.754 eV<sup>[12]</sup> and 2.309 eV<sup>[13]</sup> for H and Au, respectively; the EA of Au is the highest of all of the metal atoms in the periodic table.<sup>[14]</sup> Almost a decade ago, Buckart and co-workers found that the photoelectron spectra (PES) of the  $Au_n^-$  and  $Au_{n-1}H^-$  anions were remarkably similar,<sup>[15]</sup> which showed that H contributed its electron into the "valence pool" with the Au atoms. Later, a single Au atom was also found to behave in the same manner as a H atom in aurosilane and in other Si-Au clusters.<sup>[16,17]</sup> Thus, one would expect AlAu<sub>4</sub> to have similar chemistry to AlH<sub>4</sub>. However, the physical and chemical properties of H and Au are quite different in many cases. For example, H<sub>2</sub> is gaseous at room temperature, whereas Au forms a solid. H has a unique electronic structure in the sense that it can attract an electron to form a H<sup>-</sup> ion, donate an electron to form H<sup>+</sup>, or share its electron to form covalent bonds, as in H<sub>2</sub>. Under very high pressures, H can be a metal, but, under ambient conditions, it can form covalent, ionic, or H-bonds. Au, on the other hand, is a metal, but, unlike other metals, it is chemically inert. Thus, Au and H are not expected to show similar chemical behavior, which would seem to gues-

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tion our hypothesis that  $AIAu_4$ , like  $AIH_4$ , may be a superhalogen.

Herein, we show that Au and H indeed exhibit similar chemistry on interaction with Al and halogen atoms and form superhalogens. In addition, Au can also form hyperhalogens,<sup>[18,19]</sup> which are molecules with EAs that are even larger than those of their superhalogen building blocks. Notably, in the numerous reported methods for the design and synthesis of superhalogens and hyperhalogens, hydrogen can be used as either the core atom or as the surrounding ligands. For instance, in AlH<sub>4</sub><sup>-</sup>, H atoms act as ligands, whereas, in XHX<sup>-</sup>-type (X = F, Cl, and Br) superhalogen anions,  $^{\left[ 20,21\right] }$  the H atom acts as the core atom, surrounded by halogen ligands. More importantly, these two types of H-based superhalogens can further bind with a metal atom to form hyperhalogens.<sup>[22]</sup> Because Au<sub>n</sub><sup>-</sup> clusters have been shown to have the same electronic structure as  $Au_{n-1}H^{-,[15]}$  the question then arises: can Au be used in the place of H to design and synthesize superhalogen and hyperhalogen complexes? If this theory were true, it would open new pathways to design new superhalogens for oxidizing agents, biocatalysts, salts, and high-energy-density materials, because Au has very unique chemical and physical properties, owing to strong relativistic effects.<sup>[23, 24]</sup> Herein, we provide the answer to this question by examining AlAu<sub>4</sub><sup>-</sup>,  $XAuX^{-}$  (X = F, Cl, Br), and M(AlAu<sub>4</sub>)<sub>2</sub><sup>-</sup> clusters (M = Li, Na, K), as well as examining the potential of other coinage-metal atoms, such as Cu and Ag, to form super- and hyperhalogens.

### **Computational Methods**

We used density functional theory (DFT), as implemented in Gaussian 09,<sup>[25]</sup> with the Stuttgart quasi-relativistic pseudo-potential, the SDD basis set for Au atoms,  $^{\rm [26]}$  and the 6-311G\* basis set for B, Al, Ga, Li, Na, K, F, Cl, and Br atoms.<sup>[27,28]</sup> We tested a number of hybrid and pure density functionals, including BLYP,<sup>[29]</sup> B3LYP,<sup>[30]</sup> PBE0,<sup>[31]</sup> and PW91PW91.<sup>[32]</sup> We found that the PW91PW91 functional could better reproduce the EA of Au (2.36 eV) and the ionization potential (IP) of AI (6.10 eV), which were guite close to the experimental values of 2.309 and 5.986 eV, respectively.<sup>[13,33]</sup> Frequency analyses were performed to ensure the dynamic stability of the computed structures. The vertical detachment energy (VDE) values were calculated by taking the difference in the energy between the ground state of an anion and its corresponding neutral form with the anion geometry. Because Au nanostructures have special optical properties, we studied the UV/Vis absorption spectra of the Aubased superhalogens by using time-dependent DFT (TD-DFT),<sup>[34]</sup> with the Stuttgart quasi-relativistic pseudo-potential and the SDD basis set for Au atoms, which have been reported to be appropriate for the calculations of optical properties.[16, 17]

### 2. Results and Discussions

We began with AlAu<sub>4</sub>, in which Au atoms act as the surrounding ligands. The search for the lowest-energy configurations of neutral and anionic AlAu<sub>4</sub> was performed starting from different isomers and fully optimizing the geometries without symmetry constraints. The low-lying energy isomers are shown in Figure 1. The ground-state geometry of neutral AlAu<sub>4</sub> has  $C_s$ symmetry, whereas the AlAu<sub>4</sub><sup>-</sup> anion has  $T_d$  symmetry and



**Figure 1.** Optimized geometries of the low-lying isomers of neutral  $(a_1, a_2)$  and anionic AlAu<sub>4</sub> clusters  $(b_1, b_2)$ . The central and outer spheres represent Au and Al atoms, respectively. The energies  $(\Delta E)$  of the isomers are measured with respect to the lowest-energy configuration. Al–Au and Au–Au bond lengths [Å] and the Al–Al–Au angle are also shown.

mimics the geometry of  $\text{AlH}_4^-.$  The calculated VDE of  $\text{AlAu}_4^-$  is 3.98 eV, which is comparable to that of  $AIH_4^-$ , namely, 4.04 eV. Because these values are larger than that of Cl- $(3.617(\pm 0.003) \text{ eV})$ ,<sup>[35]</sup> AlAu<sub>4</sub>, just like AlH<sub>4</sub>, can be classified as a superhalogen. Its superhalogen behavior can be understood as follows. In AlAu<sub>4</sub><sup>-</sup>, the Al<sup>3+</sup> ion would have a core configuration of 2s<sup>2</sup> 2p<sup>6</sup> and all of the Au atoms would have the [Xe] 4f<sup>14</sup> 5d<sup>10</sup> 6s<sup>1</sup> electronic configuration. AlAu<sub>4</sub><sup>-</sup> can be thought of as having  $3+4\times1+1=8$  electrons and, hence, can be presumed stable owing to the octet rule, which governs the superhalogen behavior of AlAu<sub>4</sub>. Figure 2 shows the HOMO and LUMO of AlAu<sub>4</sub><sup>-</sup>. We see that the central Al and Au ligands contribute to the frontier orbitals. To examine the dynamic stability of AlAu<sub>4</sub><sup>-</sup>, we performed frequency calculations. The calculated results showed that no imaginary frequencies exist, thus indicating that AlAu<sub>4</sub><sup>-</sup> is dynamically stable.



Figure 2. a) HOMO and b) LUMO of the AlAu<sub>4</sub> anion.

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**Figure 3.** Equilibrium geometries of a) the anionic BAu<sub>4</sub> and b) the anionic GaAu<sub>4</sub> clusters. The outer spheres represent Au atoms and the inner sphere in a) represents a B atom and in b) represents a Ga atom. The VDEs and the B–Au and Ga–Au bond lengths [Å] are also shown.

Because B and Ga belong to the same Group as Al in the Periodic Table, we also studied BAu<sub>4</sub> and GaAu<sub>4</sub> to see whether they too were superhalogens. Figure 3 shows the ground-state geometries of anionic BAu<sub>4</sub> and GaAu<sub>4</sub>. They both have  $T_d$  symmetry, as does AlAu<sub>4</sub><sup>-</sup>. The VDEs of BAu<sub>4</sub><sup>-</sup> and GaAu<sub>4</sub><sup>-</sup> were calculated to be 3.56 eV and 3.93 eV, respectively. Thus, whereas BAu<sub>4</sub> is not a superhalogen, GaAu<sub>4</sub> is.

Notably, the AlAu<sub>4</sub><sup>-</sup> anion has the highest VDE among the three Au-based MAu<sub>4</sub><sup>-</sup> (M=B, Al, and Ga) clusters. This result is consistent with the IPs of B, Al, and Ga, which are 8.298,<sup>[36]</sup> 5.986,<sup>[33]</sup> and 5.999 eV, respectively.<sup>[37]</sup> The reason Al possesses a lower IP than Ga is that the closed-shell 3d electrons of Ga have a weak shielding effect on the valence 4s and 4p electrons, thus leading to stronger valence-electron localization, which results in a larger IP for Ga compared to that of Al. Therefore, the valence electrons of Al can be more-easily transferred on bonding with Au and the extra electron can easily delocalize around the four Au atoms in the tetrahedral AlAu<sub>4</sub><sup>-</sup>. Thus, a stable structure with a large VDE is formed.

Next, we studied whether these superhalogens, denoted "Y" ( $Y = AIAu_4$  and  $GaAu_4$ ), could form the building blocks of hyperhalogens with alkali atoms, denoted "M" (M = Li, Na, and K), as the core atom with the composition MY<sub>2</sub>. The lowest-energy configurations and frontier orbitals of the  $MY_2$  anions for Y =AlAu<sub>4</sub> and GaAu<sub>4</sub> are shown in Figure 4 and Figure 5, respectively. The VDEs of the anionic Li(AlAu<sub>4</sub>)<sub>2</sub>, Na(AlAu<sub>4</sub>)<sub>2</sub>, K(AlAu<sub>4</sub>)<sub>2</sub>, Li(GaAu<sub>4</sub>)<sub>2</sub>, Na(GaAu<sub>4</sub>)<sub>2</sub>, and K(GaAu<sub>4</sub>)<sub>2</sub> clusters were calculated to be 3.75, 4.16, 4.06, 3.71, 4.03, and 4.05 eV, respectively; the calculated results are summarized in Table 1 for clarity. Notably, the VDEs of  $Li(AIAu_4)_2^{-1}$ and  $Li(GaAu_4)_2^-$  were smaller than those of AlAu<sub>4</sub><sup>-</sup> and GaAu<sub>4</sub><sup>-</sup>, respectively. Thus, Li(AlAu<sub>4</sub>)<sub>2</sub> and Li(GaAu<sub>4</sub>)<sub>2</sub> cannot be classified as hyperhalogens. On the other hand, the VDEs of M(AlAu<sub>4</sub>)<sub>2</sub><sup>-</sup> and M(GaAu<sub>4</sub>)<sub>2</sub><sup>-</sup> (M = Na, K) were marginally larger than those of their corresponding superhalogen building blocks and their neutral counterparts can technically be termed as hyperhalogens. The HOMO and LUMO are plotted in Figure 4 and 5, respectively, and show a similar feature, that is, the main contribution to the frontier orbitals in all of the Au-based hyperhalogens comes from the superhalogen (AlAu<sub>4</sub> or GaAu<sub>4</sub>) instead of the central alkalimetal atom.

We further investigated the  $XAuX^{-}$  complexes (X = F, CI, and Br) to examine whether Au could play the same role of a central atom in forming a superhalogen anion as H does in XHX<sup>-</sup> species. The optimized geometries are shown in Figure 6. The VDEs of AuF<sub>2</sub><sup>-</sup>, AuCl<sub>2</sub><sup>-</sup>, and AuBr<sub>2</sub><sup>-</sup> were calculated to be 4.65, 4.50, and 4.34 eV, respectively. Therefore, their neutral counterparts all are superhalogens, because their VDEs are larger than those of their corresponding halogen anions. Clearly, XAuX<sup>-</sup> species have the same chemistry as XHX<sup>-</sup> species. Notably, AuF<sub>2</sub><sup>-</sup> exhibited a larger VDE compared to that of AuCl<sub>2</sub><sup>-</sup>, although F has a smaller EA than Cl. This result was because the smaller size of F allows it to form a stronger bond with Au. For comparison, we also calculated the VDEs of FHF<sup>-</sup>, CIHCI<sup>-</sup>, and BrHBr<sup>-</sup>, because no theoretical results at the same computational level were available. The calculated values of 5.60, 5.09, and 4.74 eV for XHX<sup>-</sup> (X = F, Cl, and Br) were larger than those of XAuX $^-$  (X = F, Cl, and Br).  $^{\scriptscriptstyle [38]}$  This result was consistent with the comparative sizes of H and Au and with the above discussion on the hyperhalogen properties of M(AlAu<sub>4</sub>)<sub>2</sub> (M = Na and K). The HOMO and LUMO of  $XAuX^{-}$  (X = F, Cl, and Br) are shown in Figure 6, which clearly shows that the d orbitals of Au participate in the bonding interactions with F, Cl, and Br.

We also used Au as the central atom to bind together two  $FAuF^-$  moieties to form the (FAuF)-Au-(FAuF) anion, as shown



Figure 4. Geometries, HOMOs, and LUMOs of the anionic M(AIAu₄)<sub>2</sub> [M = Li (a), Na (b), and K (c)] clusters. ●, ●, and ● spheres represent Li, Na, and K atoms, respectively.



Figure 5. Geometries, HOMOs, and LUMOs of the anionic M(GaAu<sub>4</sub>)<sub>2</sub> [M=Li (a), Na (b), and K (c)] clusters.

Table 1. Calculated symmetries, VDEs, and HOMO–LUMO gaps $\Delta E_{\rm gap}$ for the Au-based clusters.				
Cluster	Symmetry	VDE [eV]	$\Delta E_{\rm gap}$ [eV]	
BAu <sub>4</sub> <sup>-</sup>	T <sub>d</sub>	3.56	1.94	
AlAu <sub>4</sub> <sup>-</sup>	$T_d$	3.98	2.21	
GaAu <sub>4</sub> <sup>-</sup>	$T_d$	3.93	1.85	
Li(AlAu <sub>4</sub> ) <sub>2</sub> <sup>-</sup>	<i>C</i> <sub>1</sub>	3.75	1.76	
$Na(AIAu_4)_2^-$	<i>C</i> <sub>1</sub>	4.16	1.62	
K(AlAu <sub>4</sub> ) <sub>2</sub> <sup>-</sup>	<i>C</i> <sub>1</sub>	4.06	1.54	
Li(GaAu <sub>4</sub> ) <sub>2</sub> <sup>-</sup>	<i>C</i> <sub>1</sub>	3.71	1.51	
Na(GaAu <sub>4</sub> ) <sub>2</sub> <sup>-</sup>	<i>C</i> <sub>1</sub>	4.03	1.12	
K(GaAu <sub>4</sub> ) <sub>2</sub> <sup>-</sup>	<i>C</i> <sub>1</sub>	4.05	1.20	

in Figure 7a. The calculated VDE of this complex was 5.72 eV, thus suggesting that neutral (FAuF)–Au–(FAuF) is a hyperhalogen, similar to the (FHF)–H–(FHF) system.<sup>[9,21]</sup> From the frontier orbitals, as shown in Figure 7 b and c, we also see that the Au d orbitals, as well as the F 2p orbitals, contribute to the

HOMO and LUMO of the hyper-

halogen anion. From these above results, we have shown that Au can behave in the same manner as H in forming superhalogens and hyperhalogens, with Au either acting as a ligand or as a central atom. Au-based superhalogens can not only be used as strong oxidizing agents, but that they also have additional merits; they are biocompatible, have new optical properties, and can be used as catalysts. These unique features would make the Au-based negative ions multifunctional. Because Au

nanostructures have been found to display rich, tunable optical properties with applications in cancer-cell imaging, photothermal therapy, and DNA detection,<sup>[39]</sup> we studied the optical absorption spectra of  $AIAu_4^-$  and  $AuF_2^-$  and compared them with those of their corresponding H-based analogues, namely,  $AIH_4^-$  and  $HF_2^-$ , respectively. As shown in Figure 8, there are two typical peaks for the  $AIAu_4$  anion, at 350 and 530 nm, which are much larger than those of  $AIH_4^-$ , at 210 and 280 nm, thus suggesting that  $AIAu_4^-$  can absorb light in the UV/Vis region, whereas  $AIH_4^-$  can only absorb visible light. The absorption peak of  $AIF_2^-$  is calculated to be at 240 nm, whereas the main peak of  $HF_2^-$  is found at 140 nm, thus indicating that the Au-based superhalogen anions can absorb light with longer wavelengths.

Finally, we examined the potential of Cu and Ag to serve as components of all-metal superhalogens. Calculations of these



systems were repeated by following the same procedure as discussed above for AlAu<sub>4</sub>. The ground-state geometries of the AlCu<sub>4</sub> and AlAg<sub>4</sub> anions, as shown Figure 9 in and Figure 10, respectively, are square-pyramidal with  $C_{4v}$  symmetry, instead of tetrahedral like the AlAu<sub>4</sub> anion. Their VDEs were 2.66 and 2.80 eV, respectively, whereas that of AlAu<sub>4</sub><sup>-</sup> was 3.98 eV. Hence, AlCu<sub>4</sub> and AlAg<sub>4</sub> are not superhalogens. The underlying reason for this result is that, owing to significant relativistic effects, Au exhibits very different properties to Cu and Aq. For example, the

Figure 6. Geometries, HOMOs, and LUMOs of the  $XAuX^{-}[X = F (a), CI (b), and Br (c)]$  superhalogens. The VDEs and the Au–F, Au–CI, and Au–Br bond lengths [Å] are also shown.

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Figure 7. a) Equilibrium geometry, b) HOMO, and c) LUMO of the (FAuF)–Au–(FAuF) anion. The F–Au bond lengths [Å] and Au-F-Au angles  $[^{\circ}]$  are also shown.

electron affinity of Au  $(2.309 \text{ eV})^{[13]}$  is significantly higher than those of Cu (1.236 eV) and Ag (1.304 eV).<sup>[40]</sup> Among all of the elements with *ns*<sup>1</sup> valence-electron configurations (H, Li, Na, K, Rb, Cs, Fr, Cu, Ag, and Au), Au is the only element that shows significant 6s orbital shrinkage, caused by relativistic effects, which results in strong interactions between the 6s electron and the core. Consequently, Au has a large IP of 9.226 eV,<sup>[41]</sup> next to H (13.59 eV). Namely, the relativistic contraction of 6s<sup>1</sup> in Au makes it similar to 1s<sup>1</sup> in H in some bonding environments, as found in experiments as well as in this study. Moreover, Au is the only metal that forms the negative component of a salt with Cs, namely, Cs<sup>+</sup>Au<sup>-</sup>.<sup>[42]</sup>

### 3. Conclusions

DFT calculations were performed to see whether Au and H exhibited a similar chemistry on interacting with Al and halogen atoms. Indeed, we found this theory to be the case, irrespective of whether Au and H were used as core atoms or as ligands. Similar to  $AIH_{4^{\prime}}$   $MAu_4$  (M=AI and Ga) clusters, in which Au atoms act as ligands, are superhalogens. In addition, XAuX complexes (X=F, Cl, and Br) in which Au plays the role of the central atom are also superhalogens, just as XHX (X=F, Cl, and Br) complexes are. The ability of these superhalogens to serve as the building blocks of hyperhalogens was further examined by using alkali-metal atoms at the core and decorating them



Figure 8. Comparison of the optical absorption spectra of a) the AlAu<sub>4</sub><sup>-</sup> and AlH<sub>4</sub><sup>-</sup> superhalogen anions, and b) the AuF<sub>2</sub><sup>-</sup> and AuH<sub>2</sub><sup>-</sup> superhalogen anions.

with superhalogen moieties. Thus,  $MY_2$  (M=Na, K; Y=AlAu<sub>4</sub>, GaAu<sub>4</sub>) complexes were found to be hyperhalogens. Analogous to (FHF)–H–(FHF), the neutral (FAuF)–Au–(FAuF) complex is a hyperhalogen with Au as a core atom. The underlying reason for Au behaving in the same manner as H in forming superhalogen and hyperhalogen compounds is the significant relativistic contraction of



Figure 9. Geometries, symmetries, relative energies ( $\Delta E$ ), and VDEs of the AlCu4 anion.



Figure 10. Geometries, symmetries, relative energies ( $\Delta E$ ), and VDEs of the AlAg<sub>4</sub> anion.

AuF

 $HF_2^{-}$ 

350

300

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200

 $\lambda / nm$ 

250

the 6s<sup>1</sup> orbital in Au, thus making it similar to the 1s<sup>1</sup> orbital in H in some bonding environments. Other coinage metals, such as Cu and Ag, do not form superhalogens on interacting with Al. Our studies imply that, with a judicious choice of ligands, new salts could be synthesized from the Au-based superhalogens and hyperhalogens with the corresponding cations. Furthermore, because Au-based superhalogens can absorb visible light, they have the potential for technological applications.

#### Acknowledgements

This research was supported by the National Natural Science Foundation of China (NSFC, Grant Nos. 11174014 and 21273012), the National Grand Fundamental Research 973 Program of China (Grant No. 2012CB921404), and the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering (Award No. DE-FG02-96ER45579).

**Keywords:** aluminum · cluster compounds · electronic structure · gold · superhalogens

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Received: May 30, 2013 Published online on ■■ ■, 2013