Sincerest form of flattery: The frontier orbitals and optical absorption spectra of the $\text{AlAu}_4^-$ anion are reported. By using density functional theory, it is shown that $\text{AlAu}_4$ 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.
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All-Metal Clusters that Mimic the Chemistry of Halogens
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Owing to their s²p² electronic configuration, halogen atoms are highly electronegative and form the anionic components of many salts. Whereas clusters that contain no halogen atoms, such as AlH₄, mimic the chemistry of halogens and readily form salts (e.g., Na⁺(AlH₄)⁻), clusters that 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 AlX₄ (X = Cu, Ag, Au), these metal atoms may exhibit halogen-like properties. By using density functional theory, we show that AlAu₄ 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 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(AlAuF)₃⁻ (M = Na and K) and anionic (FAuF)⁻–Au⁻(FAuF) range from 4.06 to 5.70 eV. Au-based superhalogen anions, such as AlAuF⁻ and AuF₃⁻, have the additional advantage that they exhibit wider optical absorption ranges than their H-based analogues, AlH⁻ and HF⁻. 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 AlAu₄, XAuX (X = Cu, Ag) clusters are not superhalogens, a property that can be attributed to the large EA of the Au atom.

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, it was discovered that clusters that consist of a core metal atom that is surrounded by halogen atoms (e.g., PF₃), 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 named such species “superhalogens”. Over the last few years, 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 Al₁₃, Sc@Au₁₄ and TaAu₁₂.[6–9]

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, AlH₄ is a superhalogen.[10] It forms a stable salt, namely, NaAlH₄, which has been widely studied for its ability to reversibly store large amounts of H₂.[11] H and Au share similar valence-electron configurations, namely, 1s¹ and 6s¹, respectively. Both elements are electronegative, with EAs of 0.754 eV[12] and 2.309 eV[13] for H and Au, respectively; the EA of Au is the highest of all of the metal atoms in the periodic table.[14] Almost a decade ago, Buckart and co-workers found that the photoelectron spectra (PES) of the Au⁻ and Au⁺, H⁻ anions were remarkably similar,[15] 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.[16,17] Thus, one would expect AlAu₄ to have similar chemistry to AlH₄. However, the physical and chemical properties of H and Au are quite different in many cases. For example, H₂ 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⁻ ion, donate an electron to form H⁺, or share its electron to form covalent bonds, as in H₂. 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 ques-

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tion our hypothesis that AlAu₄, like AlH₄, 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,[22, 23] 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 AlH₄⁻, H atoms act as ligands, whereas, in XH⁻⁻type (X = F, Cl, and Br) superhalogen anions,[20, 21] 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.[22] Because Auₙ⁻ clusters have been shown to have the same electronic structure as Auₙ⁻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.[23, 24] Herein, we provide the answer to this question by examining AlAu₄⁻, XAuX⁻ (X = F, Cl, Br), and M(AlAu₄)₂⁻ 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,[25] with the Stuttgart quasi-relativistic pseudo-potential, the SDD basis set for Au atoms,[26] and the 6-311G* basis set for B, Al, Ga, Li, Na, K, F, Cl, and Br atoms.[27, 28] We tested a number of hybrid and pure density functionals, including BLYP,[29] B3LYP,[30] PBE0,[31] and PW91PW91.[32] We found that the PW91PW91 functional could better reproduce the EA of Au (2.36 eV) and the ionization potential (IP) of Al (6.10 eV), which were quite close to the experimental values of 2.309 and 5.986 eV, respectively.[23, 24] 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 neutral and anionic AlAu₄ clusters (b 1, b 2). The central and outer spheres represent Au and Al atoms, respectively. The energies (ΔE) of the isomers are measured with respect to the lowest-energy configuration. Al−Au and Au−Au bond lengths (r) and the Al−Al−Au angle are also shown.

2. Results and Discussions

We began with AlAu₄, in which Au atoms act as the surrounding ligands. The search for the lowest-energy configurations of neutral and anionic AlAu₄ 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 AlAu₄ has Cs symmetry, whereas the AlAu₄ anion has Tₙ symmetry and mimics the geometry of AlH₄⁻. The calculated VDE of AlAu₄⁻ is 3.98 eV, which is comparable to that of AlH₄⁻, namely, 4.04 eV. Because these values are larger than that of Cl⁻ (3.617 ± 0.003 eV),[33] AlAu₄ just like AlH₄ can be classified as a superhalogen. Its superhalogen behavior can be understood as follows. In AlAu₄⁻, the Al¹⁺ ion would have a core configuration of 2s² 2p⁶ and all of the Au atoms would have the [Xe] 4f¹⁴ 5d¹⁰ 6s¹ electronic configuration. AlAu₄⁻ can be thought of as having 3.4×1.4×1 = 6 electrons and, hence, can be presumed stable owing to the octet rule, which governs the superhalogen behavior of AlAu₄. Figure 2 shows the HOMO and LUMO of AlAu₄⁻. We see that the central Al and Au ligands contribute to the frontier orbitals. To examine the dynamic stability of AlAu₄⁻, we performed frequency calculations. The calculated results showed that no imaginary frequencies exist, thus indicating that AlAu₄⁻ is dynamically stable.
Because B and Ga belong to the same Group as Al in the Periodic Table, we also studied BAu4 and GaAu4 to see whether they too were superhalogens. Figure 3 shows the ground-state geometries of anionic BAu4 and GaAu4. They both have Td symmetry, as does AlAu4-. The VDEs of BAu4- and GaAu4- were calculated to be 3.56 eV and 3.93 eV, respectively. Thus, whereas BAu4 is not a superhalogen, GaAu4 is.

Notably, the AlAu4- anion has the highest VDE among the three Au-based MAu4- (M = B, Al, and Ga) clusters. This result is consistent with the IPs of B, Al, and Ga, which are 8.298, 5.986, and 5.999 eV, respectively.[37] 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 AlAu4-. Thus, a stable structure with a large VDE is formed.

Next, we studied whether these superhalogens, denoted “Y” (Y = AlAu4, and GaAu4) could form the building blocks of hyperhalogens with alkali atoms, denoted “M” (M = Li, Na, and K), as the core atom with the composition MY2. The lowest-energy configurations and frontier orbitals of the MY2 anions for Y = AlAu4 and GaAu4, are shown in Figure 4 and Figure 5, respectively. The VDEs of the anionic Li(AlAu4)2, Na(AlAu4)2, K(AlAu4)2, Li(GaAu4)2, Na(GaAu4)2, and K(GaAu4)2 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(AlAu4)2- and Li(GaAu4)2- were smaller than those of AlAu4- and GaAu4-, respectively. Thus, Li(AlAu4)2 and Li(GaAu4)2 cannot be classified as hyperhalogens. On the other hand, the VDEs of M(AlAu4)2- and M(GaAu4)2- (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 (AlAu4 or GaAu4) instead of the central alkali metal atom.

We further investigated the XAuX- complexes (X = F, Cl, 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- species. The optimized geometries are shown in Figure 6. The VDEs of AuF2-, AuCl2-, and AuBr2- were calculated to be 4.65, 4.50, and 4.34 eV, respectively. Therefore, their neutral counterparts are all superhalogens, because their VDEs are larger than those of their corresponding halogen anions. Clearly, XAuX- species have the same chemistry as XHX- species. Notably, AuF2- exhibited a larger VDE compared to that of AuCl2-, 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 FH2-, CIH2-, and BrHBr-, 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- (X = F, Cl, and Br) were larger than those of XAuX- (X = F, Cl, and Br).[38] This result was consistent with the comparative sizes of H and Au and with the above discussion on the hyperhalogen properties of M(AlAu4)2 (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...
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.\[9, 21\] From the frontier orbitals, as shown in Figure 7b 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 hyperhalogen 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,\[39\] we studied the optical absorption spectra of AlAu4 and AuF2 and compared them with those of their corresponding H-based analogues, namely, AlH4 and HF2, respectively. As shown in Figure 8, there are two typical peaks for the AlAu4 anion, at 350 and 530 nm, which are much larger than those of AlH4, at 210 and 280 nm, thus suggesting that AlAu4 can absorb light in the UV/Vis region, whereas AlH4 can only absorb visible light. The absorption peak of AuF2 is calculated to be at 240 nm, whereas the main peak of HF2 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 AlAu4. The ground-state geometries of the AlCu4 and AlAg4 anions, as shown in Figure 9 and Figure 10, respectively, are square-pyramidal with C4v symmetry, instead of tetrahedral like the AlAu4 anion. Their VDEs were 2.66 and 2.80 eV, respectively, whereas that of AlAu4 was 3.98 eV. Hence, AlCu4 and AlAg4 are not superhalogens. The underlying reason for this result is that, owing to significant relativistic effects, Au exhibits very different properties to Cu and Ag. For example, the

<table>
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<th>(\Delta E_{\text{gap}}) [eV]</th>
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electron affinity of Au (2.309 eV)\(^{[13]}\) is significantly higher than those of Cu (1.236 eV) and Ag (1.304 eV).\(^{[40]}\) Among all of the elements with ns\(^1\) 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,\(^{[41]}\) next to H (13.59 eV). Namely, the relativistic contraction of 6s\(^1\) in Au makes it similar to 1s\(^1\) 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\(^+\)Au\(^{-}\).\(^{[42]}\)

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 AlH\(_4\)\(^-\) MAu\(_4\) (M = Al 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 with superhalogen moieties. Thus, MY\(_2\) (M = Na, K; Y = AlAu\(_4\), GaAu\(_4\)) 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 7](image7.png)

**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 [°] are also shown.

![Figure 8](image8.png)

**Figure 8.** Comparison of the optical absorption spectra of a) the AlAu\(_4\) and AlH\(_4\) superhalogen anions, and b) the AuF\(_2\) and AuH\(_2\) superhalogen anions.

![Figure 9](image9.png)

**Figure 9.** Geometries, symmetries, relative energies (ΔE), and VDEs of the AlCu\(_4\), anion.

![Figure 10](image10.png)

**Figure 10.** Geometries, symmetries, relative energies (ΔE), and VDEs of the AlAg\(_4\), anion.
the 6s\(^1\) orbital in Au, thus making it similar to the 1s\(^1\) 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.

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