Silver Sulfide Nanoclusters and the Superatom Model

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The superatom model of electron-shell closings has been widely used to explain the stability of noble metal nanoclusters of few nanometers, including thiolate-protected Au and Ag nanoclusters. The presence of core sulfur atoms in the silver sulfide (Ag-S) nanoclusters render them as a class of clusters with distinctive properties as compared to those of typical noble metal clusters. Here, it is natural to ask whether the superatom model is still applicable for the Ag-S nanoclusters with mixed metal and non-metal core atoms? To address this question, we apply density functional simulations to analyze a series of Ag-S nanoclusters: $Ag_{14}S(SPh)_{12}(PPh_3)_8$, $Ag_{14}(SC_6H_3F_2)_{12}(PPh_3)_8$, $Ag_{70}S_{16}(SPh)_{34}(PhCO_2)_4(triphos)_4$ and $[Ag_{123}S_{35}(S\mathit{t}Bu)_{50}]^{3+}$ [1]. We observe that superatomic orbitals are still present in the conduction band of these Ag-S clusters where the cluster cores comprise mostly silver atoms. In contrast to these Ag-S clusters, $[Ag_{62}S_{12}(S\mathit{t}Bu)_{32}]^{2+}$ has superatomic orbitals in both of its valence and conduction bands. This contrasting feature is ascribed to the existence of effective delocalized electrons and the unique core-shell structure of the Ag_{62} cluster [2].

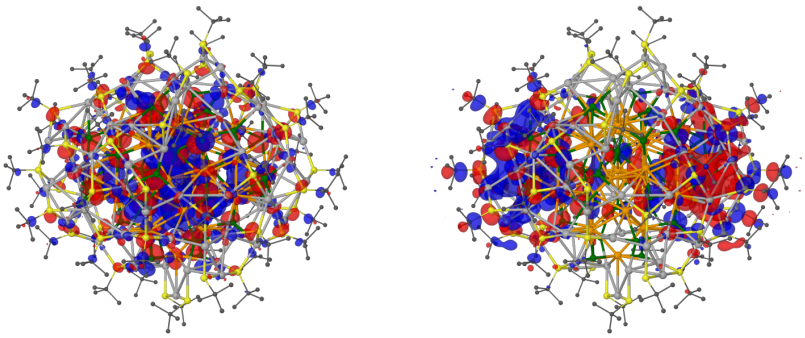

Figure 1: (left) LUMO and (right) LUMO+1 orbitals of $[Ag_{123}S_{35}(S\mathit{t}Bu)_{50}]^{3+}$ cluster correspond to 1S and 1P superatomic states, respectively.

[1] J.-Q. Goh, S. Malola, H. Häkkinen, and J. Akola. Silver Sulfide Nanoclusters and the Superatom Model. *J. Phys. Chem. C*, **2015**, 119, 1583 – 1590.

[2] J.-Q. Goh, and J. Akola. Superatom Model for Ag–S Nanocluster with Delocalized Electrons.. *J. Phys. Chem. C*, **2015**, 119, 21165 – 21172.