

# Electronic Properties of the Silver—Silver Chloride Cluster Interface

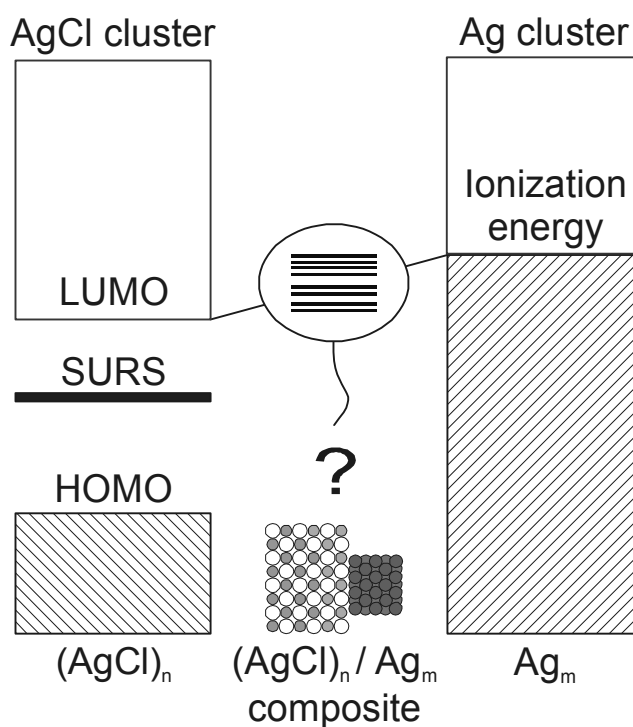
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The objective of this study was to gain insight into the electronic structure of silver-silver chloride cluster composites and especially into the metal-semiconductor interface. For this purpose a theoretical study of  $(\text{AgCl})_n$  ( $n = 4, 32, 108, 192,$  and  $256$ ), of  $\text{Ag}_m$  ( $m = 1 - 9, 30, 115, 276,$  and  $409$ ), and of the cluster composites  $\text{Ag}_{115}\text{---}(\text{AgCl})_{192}$  and  $\text{Ag}_{409}\text{---}(\text{AgCl})_{192}$  has been carried out. Density of levels (DOL), local density of levels (*l*-DOL), projection of surface states, as well as projection of properties of individual atoms or groups of atoms obtained in molecular orbital calculations are shown to be powerful tools for gaining deep insight into properties of these large systems. The  $\text{Ag}_{115}\text{---}(\text{AgCl})_{192}$  aggregate, consisting of a cubic  $\text{Ag}_{115}$  cluster without corner atoms on top of a cubic  $(\text{AgCl})_{192}$  cluster was found to be remarkably stable with a cluster to cluster distance of about 280 pm and a geometry in which the number of bonding interactions between the silver atoms of  $\text{Ag}_{115}$  and the chloride ions of  $(\text{AgCl})_{192}$  is at its maximum. A sharp jump in charge distribution occurs at the  $\text{Ag}_{115}\text{---}(\text{AgCl})_{192}$  composite interface. The first AgCl slab picks up negative charge from the two adjacent silver slabs, so that in total the silver cluster is positively charged. In addition, the core of the silver cluster is positively charged with respect to its outermost layer. The main reason for the charge transfer from the silver cluster to the silver chloride are the newly formed MIGS (metal induced gap states) in the energy gap range of the silver chloride and the MIdS (metal induced d states) in the d-orbital region. Their wave functions mix with orbitals of the silver cluster and with both the orbitals of the silver- and the chloride ions of the silver chloride. The MIGS and the MIdS are of quite localized nature. In them nearest neighbor interactions dominate, with the exception of close lying silver chloride surface states

which mix in to a large extent. We conclude that especially the MIGS not only influence the photochemical properties of silver chloride but that their existence might be probed by appropriate spectroscopic measurements.



**Figure:** Energy level diagram of a  $Ag_m$  and a  $(AgCl)_n$  cluster. The figure illustrates schematically the new states built up at the interface upon interaction of the clusters. These interface levels (metal induced gap states) influence the electronic properties of the cluster composite and are the main point of interest in our study.

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