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Structural properties and reactivity of bimetallic silver-gold clusters

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Abstract. Bimetallic silver-gold clusters are well suited to study changes in metallic *versus* "ionic" properties involving charge transfer as a function of the size and the composition. We present structures, ionization potentials (IP) and vertical detachment energies (VDE) for neutral and charged bimetallic $\mathrm{Au}_n\mathrm{Ag}_m$ $(2 \leq (n+m) \leq 5)$ clusters obtained from density functional level of theory. In the stable structures of these clusters Au atoms assume positions which favor charge transfer from Ag atoms. In clusters with equal numbers of hetero atoms $(n = m = 1-4)$ heteronuclear bonding is preferred to homonuclear bonding, giving rise to large values of ionization potentials. For larger clusters $(n = m = 5, 10)$ stable structures do not favor neither hetero bonding nor segregation into the single components, although they exhibit more metallic than ionic features. This remains valid also for $\mathrm{Au}_8\mathrm{Ag}_{12}$ cluster characterized by strong charge transfer to gold subunit. The influence of doping of pure gold clusters with silver atoms on VDE and IP values is discussed in context of their reactivity towards O_2 and CO molecules. As a starting point we consider reactivity towards CO and O_2 molecules on the example of AgAu^- dimer. The results show that the catalytic cycle can be fullfilled.

PACS. 31.15.Qg Molecular dynamics and other numerical methods – 31.15.Ar Ab initio calculations

1 Introduction

In contrast to extensively investigated structural and electronic properties of gold [1–5] and silver clusters [6–9], considerably less information is available about bimetallic silver-gold clusters [10,11]. The role of the hetero-polar bonding *versus* homonuclear metallic bonding in small bimetallic clusters is of considerable interest, since the former can promote charge transfer from the Ag to the Au atoms. In the context of the reactivity, it is important to find the structural patterns favorable for charge transfer in bimetallic clusters. Therefore the investigation of "ionic" *versus* metallic properties in these clusters as a function of their size and composition provides an information about their reactive properties. In this regard it is also useful to compare the structural and reactivity properties of gold-silver clusters with those of gold [12–15] and silver one-component systems. According to our density functional results the role of *d*-electrons in determining structural properties drastically increases from silver and bimetallic clusters towards gold clusters due to a decrease in the *s*-*d* energy separation [11]. Consequently silver and bimetallic clusters assume related structures in contrast to gold clusters which tend to remain planar for larger sizes [5,16]. In this contribution we present the ground state properties of small neutral and charged bimetallic $\mathrm{Au}_n\mathrm{Ag}_m$ clusters $(2 \leq (n+m) \leq 5)$ in which the influence of increasing Ag-component on their reactivity has been considered. IP values for selected bimetallic clusters with equal number of hetero atoms $(m = n = 1{-}5)$ are then compared with those obtained for pure gold clusters. Characteristic features of $\mathrm{Au}_{10}\mathrm{Ag}_{10}$ and $\mathrm{Au}_8\mathrm{Ag}_{12}$ clusters are discussed. Finally we address the reactivity of AgAu^- towards CO and O_2 molecules.

2 Computational methods

We use gradient corrected density functional theory (DFT) combined with relativistic effective core potentials. Previous studies of the structural properties of the charged [8,16] and neutral [11] gold clusters have shown that explicit treatment of the *d*-electrons is mandatory for proper description of the structural properties of pure gold clusters.

Therefore, we determined them using the Stuttgart group [17] relativistic effective core potentials with

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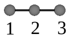
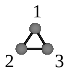
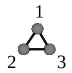
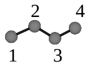
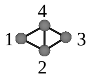
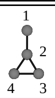
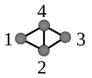
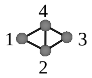
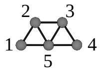
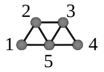
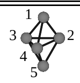
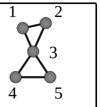
Table 1. Topologies of the stable structures of pure and mixed clusters with labels of atoms are shown allowing to identify positions of hetero atoms.

Au_mAg_n	Anion			Neutral	Cation	
						
Au_3		Au(1-3)		Au(1-3)	Au(1-3)	
Au_2Ag		Au(1,3)		Au(2,3)	Au(2,3)	
$AuAg_2$		Au(1)		Au(1)	Au(1)	
Ag_3		Ag(1-3)		Ag(1-3)	Ag(1-3)	
						
Au_4	Au(1-4)			Au(1-4)	Au(1-4)	
Au_3Ag			Au(1,3,4)	Au(1-3)	Au(1-3)	
Au_2Ag_2		Au(1,3)		Au(1,3)	Au(1,3)	
$AuAg_3$		Au(1)		Au(1)	Au(1)	
Ag_4		Ag(1-4)		Ag(1-4)	Ag(1-4)	
						
Au_5		Au(1-5)		Au(1-5)	Au(1-5)	
Au_4Ag		Au(1-4)		Au(1-4)	Au(1-4)	
Au_3Ag_2		Au(1,3,4)		Au(1,3,4)	Au(2-4)	
Au_2Ag_3		Au(1,4)		Au(1,3)		Au(1,5)
$AuAg_4$		Au(1)		Au(1)	Au(3)	
Ag_5		Ag(1-5)		Ag(1-5)	Ag(1-5)	

explicit treatment of 19 valence electrons (19e-RECP) and [$9s7p5d1f$]/[$7s5p3d1f$] basis set [5,17] with the S-VWN and Becke-Perdew [18,19] parametrization labeled as BP86. In the case of bimetallic gold-silver clusters comparison of the results obtained with 19e-RECP and our recently developed one electron effective core potential (1e-RECP) [20] has shown that structural and electronic properties of these species are largely independent on the explicit treatment of d-electrons. For example the values of IP's obtained with 1e-RECP are by ~0.2 eV lower then those calculated with 19e-RECP. Therefore, in order to extend our study to larger cluster sizes we employed our 1e-RECP with the BLYP functional [11], to determine *e.g.* trends in the IP's for clusters with equal number of hetero atoms. All structures have been fully optimized and vibrational frequency analysis have been performed in order to identify local minima. For reactivity study towards CO and O_2 molecules 19e-RECP and B3LYP parametrization were used.

3 Results and discussion

3.1 Bimetallic silver-gold clusters; comparison with pure gold

We present the results of systematic investigation of the ground state properties for neutral and charged bimetallic clusters in context with their reactivity properties. The IP and electron affinity values of Au atom are higher than those of Ag atom which gives rise to the larger electronegativity value for Au. Therefore it is to expect that significant charge transfer may occur from silver to gold atoms. The structures of the Au_nAg_m ($2 \leq (m+n) \leq 5$) bimetallic clusters are shown in Table 1. It has been found that gold atoms prefer positions which allow large charge transfer from silver. Since the reactivity of metallic clusters with small molecules such as CO and O_2 is correlated with the IP and VDE values [14], the influence of the doping of pure gold clusters with Ag atoms has been studied. As it can be seen from Figure 1, by varying the composition of the clusters VDE's and IP's can be tuned in a broad range, allowing to influence their capability to bind cooperatively CO and O_2 species. The VDE values plotted in Figure 1a decrease with increasing number of Ag atoms and agree well with the available experimental data [10]. Anionic tetramers with odd number of electrons have lowest VDE values. A particular decrease occurs for the $Au_2Ag_2^-$ species with "ionic" character due to the maximum number of hetero bonds and large charge transfer from Ag to Au atoms. Since it is experimentally known that clusters with low VDE's bind strongly O_2 molecule [14] we can conclude that this will be the case for $Au_2Ag_2^-$, $AuAg_3^-$, Ag_4^- species. The IP values shown in Figure 2b decrease with increasing number of Ag atoms as well. The largest values for IP have been calculated again for tetramers in particular for Au_4, Au_3Ag and Au_2Ag_2 clusters. Bonding of CO molecule is due to cooperative effects of σ-donation and π-back donation nature especially with transition metals. Since s-electrons dominate bonding in bimetallic tetramers and in Au_4 with high IP values it is to expect that CO will act as σ donor and therefore binds stronger to these species. Proper combination of low VDE and high IP values may induce cooperative binding of O_2 and CO. Values of the IP's for the clusters with equal

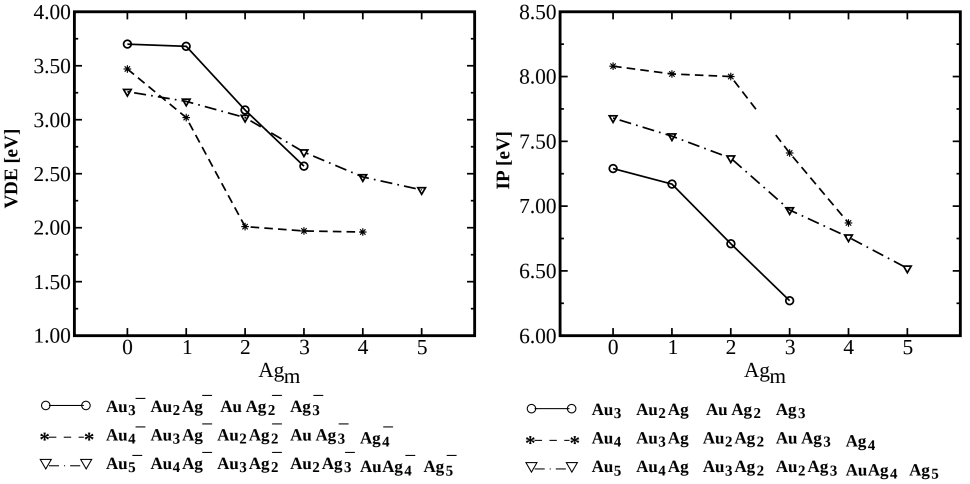


Fig. 1. Calculated VDE and IP values for Au_nAg_m ($n + m = 3, 4, 5$) varying the number of Ag atoms m.

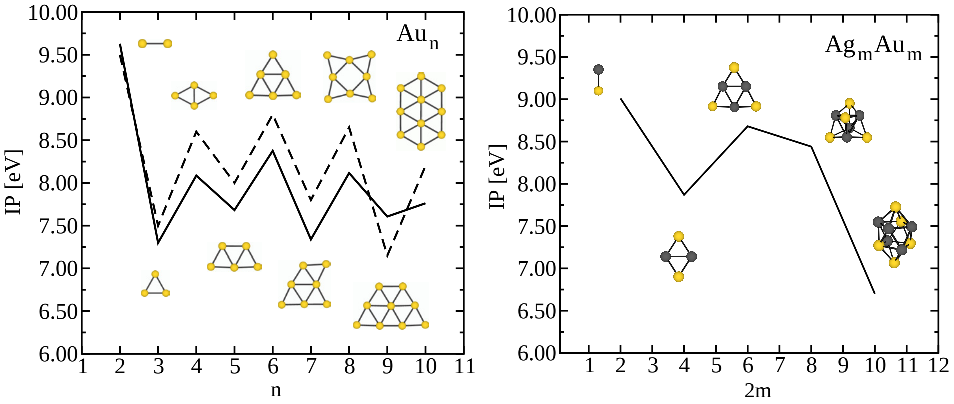


Fig. 2. (Left side) Calculated (full line) and experimental (dashed line, Ref. [21]) vertical ionization potentials and the most stable structures for Au_n ($2 \leq n \leq 10$). (Right side) Vertical ionization potentials and structures for Ag_mAu_m ($m = 1, 2, 3, 4, 5$). Light circles indicate Au atom(s) and dark ones Ag atom(s).

numbers of silver and gold atoms and comparison with those calculated for the pure gold clusters are shown in Figure 2. The IP's for Ag_3Au_3 and Ag_4Au_4 assume higher values then for Au_6 and Au_8, respectively, indicating pronounced ionic character of the bonding in these systems, since the Ag-component by itself should significantly decrease the IP values. The stable structure of Ag_4Au_4 assumes 3D form with maximal number of heteronuclear bonds in contrast to pure gold clusters which remain planar even for larger sizes. Our calculated vertical ionization potentials for gold clusters are slightly lower then the measured IP's [21] with exception of Au_9. Agreement between theoretical and experimental data is in general satisfactory. The transition from the "ionic" to metallic properties occurs for Ag_5Au_5 and can be inferred from the low values of ionization potential (*cf.* Fig. 2). This remains also valid for $Ag_{10}Au_{10}$ and $Ag_{12}Au_8$ in which negatively charged Au subunits are embedded in the Ag-surrounding containing exposed gold atoms, particularly in the latter case. The Au_8 subunit in $Ag_{12}Au_8$ cluster has common structural property with the Au_8 cluster deposited on magnesium-oxide which has been found to be particularly reactive species towards CO and O_2. Therefore $Ag_{12}Au_8$ might be a suitable candidate for activating reactions relevant for catalysis (*cf.* Ref. [11]).

3.2 Reactivity of $AgAu^-$ dimer towards CO and O_2

Bimetallic anionic dimer was chosen as a model system in order to study the catalytic oxidation of CO and to investigate the role of the charge transfer on the catalytic activity of silver-gold clusters. It is expected that the charge transfer can promote catalytic activity and, as shown in the previous section, varying the composition of the clusters may offer the possibility to influence their reactivity more easily than in the case of pure clusters. As presented in Figure 3 binding of molecular oxygen is exothermic by -0.94 eV. The corresponding complex has silver atom bound to an oxygen atom of the superoxide unit. The binding of the molecular oxygen to the gold atom leads to the complex which is by 0.61 eV less stable. Since oxygen withdraws very strongly the charge from metal atoms, binding to gold is energetically unfavorable because gold

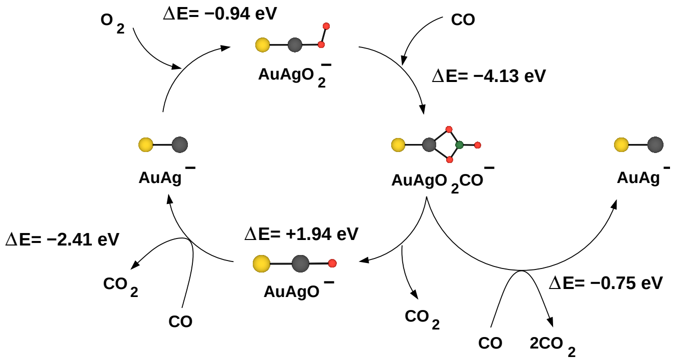


Fig. 3. Catalytic cycle for oxidation of CO on $AgAu^-$ dimer. Different atoms are labeled as: light large circle (Au), dark large circle (Ag), smallest dark circle (O), dark circle (C).

tends to keep negative charge due to its larger electronegativity. This feature might change for larger systems with adequate composition of hetero atoms. In the next step the complex $AuAgO_2^-$ can react with one CO molecule giving rise to the very stable complex with a carbonate-like unit bound to one silver atom. Once the complex is formed there are two possible pathways to close the catalytic cycle. In the first one the complex reacts with one CO molecule generating two CO_2 molecules and restoring the $AgAu^-$ dimer which therefore acts as a catalyst. This bimolecular reaction is exothermic by −0.75 eV. The second possible pathway is unimolecular dissociation which is endothermic by 1.94 eV and gives rise to one CO_2 molecule and to highly reactive $AgAuO^-$ species. The latter reacts then with one CO molecule giving CO_2 in an exothermic process of −2.41 eV, allowing to close the catalytic cycle.

4 Conclusion

We have shown that structural properties of bimetallic Ag-Au clusters are closer related to those of Ag than to those of Au clusters. This is due to large involvement of *d*-electrons in bonding only in the case of Au clusters. The charge transfer from Ag to Au plays a dominant role for structural and electronic properties of bimetallic clusters and is of importance for reactivity studies. In small Au_nAu_m $(3 \leq (n+m) \leq 5)$ clusters Ag atom(s) prefer to form more bonds than Au atom(s) but the Au atoms favor positions at which they withdraw the charge from Ag atoms. Therefore, ground state properties such as IP and VDE of these clusters can be tuned by varying number of atoms of one component for the given cluster size. Accordingly, bimetallic anionic tetramers $Au_2Ag_2^-$ and $AuAg_3^-$ with low VDE's are expected to be reactive towards O_2 and Au_2Ag_2 as well as Au_3Ag species with high IP's are capable to bind strongly CO. In clusters with equal number of hetero atoms high values of IP's indicate high stability of "ionic" species. In fact, the IP values for Ag_3Au_3 and Ag_4Au_4 are higher than for corresponding gold clusters. Segregation between two components in Au_5Ag_5 or $Au_{10}Ag_{10}$ is not favorable. In the case of $Ag_{12}Au_8$ a negatively charged Au_8 subunit embedded in Ag surrounding may serve as reactive center similarly to Au_8 supported on metal oxides [13]. We illustrated the reactivity aspect of bimetallic clusters for the catalytic cycle on the example of $AgAu^-$ interacting with CO and O_2 molecules. This result encouraged us to extend reactivity studies to larger bimetallic systems in the future.

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