Density functional study of structural and electronic properties of bimetallic silver–gold clusters: Comparison with pure gold and silver clusters

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(Received 28 March 2002; accepted 20 May 2002)

Bimetallic silver–gold clusters offer an excellent opportunity to study changes in metallic versus “ionic” properties involving charge transfer as a function of the size and the composition, particularly when compared to pure silver and gold clusters. We have determined structures, ionization potentials, and vertical detachment energies for neutral and charged bimetallic AgₙAuₘ [3 ≤ (m + n) ≤ 5] clusters. Calculated VDE values compare well with available experimental data. In the stable structures of these clusters Au atoms assume positions which favor the charge transfer from Ag atoms. Heteronuclear bonding is usually preferred to homonuclear bonding in clusters with equal numbers of hetero atoms. In fact, stable structures of neutral Ag₃Au₁, Ag₅Au₃, and Ag₆Au₄ clusters are characterized by the maximum number of hetero bonds and peripheral positions of Au atoms. Bimetallic tetramer as well as hexamer are planar and have common structural properties with corresponding one-component systems, while Ag₄Au₉ and Ag₈ have 3D forms in contrast to Au₈ which assumes planar structure. At the density functional level of theory we have shown that this is due to participation of d electrons in bonding of pure Auₙ clusters while s electrons dominate bonding in pure Agₘ as well as in bimetallic clusters. In fact, Auₙ clusters remain planar for larger sizes than Agₘ. The latter are known from our earlier investigations. Density functional method and used for structural assignment in ion mobility measurements. There are similarities in the density functional method and used for structural assignment in ion mobility measurements. There are similarities between two components in bimetallic systems is not favorable, as shown in the example of Ag₅Au₃ cluster. We have found that the structures of bimetallic clusters with 20 atoms Ag₁₀Au₁₀ and Ag₁₂Au₈ are characterized by negatively charged Au subunits embedded in Ag environment. In the latter case, the shape of Au₈ is related to a pentagonal bipyramid capped by one atom and contains three exposed negatively charged Au atoms. They might be suitable for activating reactions relevant to catalysis. According to our findings the charge transfer in bimetallic clusters is responsible for formation of negatively charged gold subunits which are expected to be reactive, a situation similar to that of gold clusters supported on metal oxides. © 2002 American Institute of Physics.

I. INTRODUCTION

Increasing interest in structural and electronic properties of small gold clusters as function of their size has been initiated by the discovery of unusual catalytic activity of small supported gold clusters in contrast to the inert bulk material. Also, in the reaction study of combustion of CO on size-selected small monodispersed gold clusters supported on magnesia, it has been found that Au₈ is the smallest catalytically active cluster size. It has been shown that the anionic gold clusters with even number of atoms react with molecular oxygen having low values of electron affinities in contrast to those with odd number of atoms, thus exhibiting the even–odd oscillatory behavior as a function of the cluster size. The connection between electron affinity and activation of molecular oxygen by gold clusters at low temperature has been also established.

The experimental values of electron affinities, vertical detachment energies, and ionization potentials of pure gold clusters as function of their size are known from early investigations. Structural properties of small anionic and neutral Auₙ (n = 3–8) clusters have been theoretically investigated. In the case of cationic Auₙ⁺ (n < 14) clusters, the structures have been determined in the framework of the density functional method and used for structural assignment in ion mobility measurements. There are similarities for small clusters (n = 3, 4), but also significant differences between the structures of cationic gold and silver clusters larger than tetramers. The latter are known from our earlier work. This has been also confirmed by recent ion mobility measurements and calculations on cationic silver clusters. Since the calculated values of vertical detachment energies, electron affinities, and collision cross sections are
strongly structure dependent, the energy sequence of the isomers remains still an important issue and can strongly depend on the theoretical method applied. The experimental conditions, in particular the temperature, may also significantly influence the measured properties. Therefore, an accurate determination of structural properties of pure gold clusters is important in order to address aspects of their reactivity. In fact, the theoretical treatment of the gold clusters is much more demanding than of silver clusters, since in the former case fewer electrons are expected to participate in the bonding and in the latter case they are localized in the core of the Ag atoms and do not play a key role for structural properties.16

In contrast to the pure gold and silver clusters, considerably less information is available about structural and electronic properties of bimetallic silver–gold clusters. Exception is an experimental work on photodetachment of Ag$_{m}$Au$_{n}$ \((m+n\leq4)\) clusters\(^{17}\) and earlier\(^{18}\) as well as recent\(^{19}\) theoretical work on the mixed trimers. Several open questions have not been addressed yet. The role of the hetero-polar bonding versus homonuclear metallic bonding in small bimetallic clusters should be clarified, since the former can promote charge transfer from the Au to the Ag atoms. Charged gold species embedded in the Ag-surrorunding might be interesting systems for studying reactivity. It is known that metal oxide support which is responsible for the charge transfer plays a key role for generating the catalytic activity of supported Au catalysts. In this context, it is of particular interest to find the structural patterns promoting charge transfer in bimetallic clusters. For this purpose it is necessary to search for the given size and the composition of clusters which can give rise to negatively charged gold species embedded in the environment of silver atoms. In other words, the investigation of “ionic” versus metallic properties with charge transfer in bimetallic clusters is important for gaining an understanding about their possible role as reactive centers. In this regard it is also useful to compare the structural and electronic properties of bimetallic gold–silver clusters with those of gold and silver one-component systems.

In this article after a brief outline of computational approach in Sec. II, which is based on the density functional method with two different effective core potentials and corresponding AO basis sets, we present structures and binding energies of the neutral gold clusters Au$_n$ \((n=2-10)\) in Sec. III. Results on anionic, neutral, and cationic bimetallic trimers, tetrarners, and pentamers are given in Sec. IV. Properties of neutral larger bimetallic clusters such as Ag$_3$Au$_1$, Ag$_3$Au$_4$, Ag$_5$Au$_5$, Ag$_{10}$Au$_{10}$, and Ag$_8$Au$_{12}$ are presented in Sec. V. The occurrence of charge transfer and formation of negatively charged gold subunits which can serve as reactive centers are addressed. Comparison of bimetallic with pure gold and silver one-component systems allows us to show different roles of \(s\) and \(d\) electrons for bonding in these systems. Conclusions and outlook are given in Sec. VI.

II. COMPUTATION

The gradient corrected density functional method with relativistic effective core potentials (RECP) is used throughout the article. The aim is to investigate structural properties of bimetallic Ag$_m$Au$_n$ clusters as a function of the size and the composition for \(3 \leq (m+n) \leq 20\) and compare them with the properties of pure Ag$_m$ and Au$_n$ clusters. Therefore, we proceeded in two directions taking into account either one valence electron per atom (1e-RECP) or 19 valence electrons per Au and Ag atom (19e-RECP).

Recently we developed 1e-RECP for the Au atom and revised the corresponding 1e-RECP for the Ag atom together with small AO basis sets\(^{19}\) based on DFT calculations with Becke and Lee, Young and Parr (BLYP) exchange,\(^{20}\) and correlation\(^{21}\) functionals. As described in Ref. 19, the 1e-RECPs were derived by starting from our 11e-RECP for the Ag atom\(^{16}\) with original uncontracted 6\(s\)5\(p\)5\(d\) AO basis set and from 19e-RECP of Hay and Wadt\(^{22}\) for the Au atom with their 8\(s\)6\(p\)4\(d\) uncontracted basis set. Our 1e-RECPs are semiempirical because atomic and diatomic data have been used in the fitting procedure. Comparison of the ground state properties of homo- and hetero-nuclear neutral and charged dimers obtained employing 1e-RECP BLYP method with available experimental data shows that the calculated bond distances are in very satisfactory agreement with experimental values (cf. Table I and Ref. 19). Ionization potentials (IP), electron affinities (EA), vertical detachment energies (VDE), and dissociation energies deviate mostly by \(-0.2\) eV from the measured ones except for the IP of Au$_2$ for which this deviation is slightly larger (cf. Table I and Ref. 19).

In order to determine influence of \(d\)-electrons on bonding properties in Au clusters and in bimetallic clusters we employ 19e-RECP from the Stuttgart group\(^{23}\) with the [9\(s\)7\(p\)5\(d\)1\(f\)]/[7\(s\)5\(p\)3\(d\)1\(f\)] for Au atom and with [8\(s\)7\(p\)5\(d\)1\(f\)]/[6\(s\)5\(p\)3\(d\)1\(f\)] for Ag atom in the framework of DFT with the S-VWN and Becke–Perdew\(^{24}\) parametrization (BP-86) as in Refs. 12 and 15. We have shown previously\(^{16}\) that 1e-RECP configuration interaction method allows for adequate description of the ground state properties of pure Ag clusters\(^{13,14}\) and compares well with results obtained with 11e-RECP coupled cluster method.\(^{16}\) The \(d\) electrons are localized in the atomic cores and do not participate directly in bonding. This has been confirmed recently for the cationic Ag clusters experimentally and theoretically,\(^{15}\) as well as for the neutral clusters.\(^{25}\) The bond distances, frequencies and dissociation energies for homonuclear and heteronuclear neutral and charged dimers obtained with 1e-RECP BLYP and 19e-RECP BP86 approaches are given in Table I and compared with available experimental data.\(^{26–31}\) Bond distance obtained from 1e-RECP BLYP are in better agreement with experimental data than those of 19e-RECP BP86 procedure. The latter give rise to distances slightly larger than the experimental ones which might influence computed structural properties, particularly of very small systems. Dissociation energies \((D_e)\) for silver and mixed dimers obtained from both treatments are in satisfactory agreement with the available experimental data. \(D_e\) for Au$_2$ calculated with 19e-RECP BP86 is in better agreement with the experimental value. Concerning the accuracy of IP values, considerable
deviations from the experimental results are found for Au$_2$ at 1e-RECP BLYP level and for Au and Ag atom as well as for Ag$_2$ at the 19e-RECP BP86 level of calculations. The VDE values from 1e-RECP BLYP are in good agreement with experimental data, while 19e-RECP BP86 values are in general larger than experimental ones. Since the $s$–$d$ excitation for Au and Ag atom is 1.74 and 3.97 eV, respectively, it is not surprising that inclusion of $d$ electrons is important for the pure Au clusters while the 1e-RECP BLYP provides reliable results for Ag clusters. Therefore, for the neutral gold clusters we carried out 19e-RECP BP86 calculations which are presented in Sec. III. Comparison of the results obtained with 1e-RECP BLYP procedure shows that the most stable structures obtained from both treatments differ for cluster sizes $6 \leq n \leq 10$.

The accuracy of electron correlation treatment at the DFT level of theory for Au clusters in the framework of 19e-RECP is difficult to judge. It seems that DFT procedure gives rise to relatively small $s$–$d$ energy gap which might lead to overestimated hybridization effects. The only computationally convenient alternative to the DFT treatment of 19 electrons per atom is offered by Møller–Plesset method (MP2) which is known to be less adequate for delocalized than for directional bonding. Both methods have been used with 19e-RECP for determination of structures of the cationic Ag$_m^+$ clusters. The MP2-method gave rise to the 3D structure of Ag$_7^+$ (pentagonal bipyramid) and DFT to the 2D planar structure although the energy difference between both structures is very small. The 3D structure is in better agreement with ion mobility measurements. In general MP2 and DFT yield similar results for cationic Ag clusters for which the correlation of $d$ electrons is not very important. In contrast, cationic gold clusters are predicted by DFT to be planar for larger sizes (e.g., Au$_4^+$) in agreement with ion mobility measurements, while MP2 predicts a 3D structure for Au$_2$ similar to that of Ag$_4^+$. This indicates that MP2 might underestimate contribution of $d$ electrons to bonding in Au$_2$ cluster. In fact, based on combined experimental and theoretical work conclusion has been drawn that the number of bonds in stable structures of cationic silver clusters is larger than in those of cationic gold clusters for sizes $5 \leq n \leq 11$. Therefore, the DFT description might be more realistic for Au clusters than that offered by MP2 approach. We also carried out several comparisons between DFT and MP2 results for neutral Au and for Ag clusters and they showed that the two methods disagree mainly for gold systems. This discrepancy is particularly large, for example in the case of Au$_8$ for which the DFT energy difference between the most stable planar structure and the 3D-T$_d$ form is $\approx 0.5$ eV, while MP2 yields T$_d$ structure by $\approx 0.81$ eV lower than the planar one. Since MP2 has tendency to produce similar structures for gold and silver clusters, it seems that the correlation effects for $d$ electrons in the case of Au clusters are not sufficiently taken into account. Based on these findings the DFT method is used throughout the article. However, there is no proof about its accuracy, particularly concerning the determination of the cluster size at which the transition from 2D to 3D structure occurs in the case of pure Au clusters.

In order to check the accuracy of the 1e-RECP BLYP procedure for determination of structural properties of bimetallic clusters we have carried out comparison with the 19e-RECP BP86 approach for the smaller clusters $3 \leq (m+n) \leq 8$. As it will be shown in Secs. IV and V, the structural properties of bimetallic clusters are well described by the 1e-RECP BLYP procedure, particularly neutral species, since the $s$–$d$ hybridization is considerably smaller than in the pure Au clusters. All geometries have been fully optimized and vibrational analysis has been carried out for the majority of structures in order to determine the local minima on the energy surfaces. We refer throughout the article to 19e-RECP with BP86 parametrization as 19e-RECP and to 1e-RECP with BLYP functional as 1e-RECP. Calculations have been carried out using GAMESS-UK and GAUSSIAN 98 program packages.

### Table I. Ground state properties of the atoms and dimers obtained with the 1e-RECP BLYP and the 19e-RECP BP96 (in square brackets) methods.

<table>
<thead>
<tr>
<th></th>
<th>$r_e$ (Å)</th>
<th>$r_e$ (expt.) (Å)</th>
<th>$\omega_e$ (cm$^{-1}$)</th>
<th>$\omega_e$ (expt.) (cm$^{-1}$)</th>
<th>$D_e$ (eV)</th>
<th>$D_e$ (expt.) (eV)</th>
<th>IP (eV)</th>
<th>IP(expt.) (eV)</th>
<th>VDE (eV)</th>
<th>VDE(expt.) (eV)</th>
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<tr>
<td>Au</td>
<td>2.473</td>
<td>2.4713</td>
<td>180.0 [172.0]</td>
<td>190.0$^b$</td>
<td>2.52$^b$</td>
<td>2.29$^b$</td>
<td>9.25</td>
<td>9.23$^{a}$</td>
<td>2.27</td>
<td>2.44</td>
</tr>
<tr>
<td>Ag</td>
<td>2.674</td>
<td>2.6266</td>
<td>116.0 [147.0]</td>
<td>1.92 [2.43]</td>
<td></td>
<td></td>
<td>7.58</td>
<td>7.58$^{a}$</td>
<td>1.23</td>
<td>1.54</td>
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<td>Au$_2$</td>
<td>2.543</td>
<td>2.5303</td>
<td>197.0 [188.4]</td>
<td>192.4$^d$</td>
<td>1.83 [1.74]</td>
<td>1.65$^c$</td>
<td>7.83</td>
<td>7.89$^{d}$</td>
<td>0.92</td>
<td>1.18</td>
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<td>Ag$_2$</td>
<td>2.776</td>
<td>2.7022</td>
<td>124.0 [132.4]</td>
<td>1.57 [1.78]</td>
<td></td>
<td></td>
<td>1.27</td>
<td>1.27$^{c}$</td>
<td>1.43$^{c}$</td>
<td></td>
</tr>
<tr>
<td>AgAu</td>
<td>2.493</td>
<td>2.496$^d$</td>
<td>198.0 [183.0]</td>
<td>2.00 [2.10]</td>
<td></td>
<td></td>
<td>2.27</td>
<td>2.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AgAu$^+$</td>
<td>2.706</td>
<td>2.709$^d$</td>
<td>123.0 [139.0]</td>
<td>1.10 [1.40]</td>
<td></td>
<td></td>
<td>1.27</td>
<td>1.27$^{c}$</td>
<td>1.43$^{c}$</td>
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<tr>
<td>AgAu$^-^+$</td>
<td>2.623</td>
<td>2.681$^d$</td>
<td>138.0 [135.0]</td>
<td>1.30 [1.30]</td>
<td></td>
<td></td>
<td>1.27</td>
<td>1.27$^{c}$</td>
<td>1.43$^{c}$</td>
<td></td>
</tr>
</tbody>
</table>

$a$Reference 26.
$b$References 6, 27, and 28.
$c$Ref. 29.
$d$Reference 31.
$e$Adiabatic ionization potentials.
$f$Reference 17.
III. NEUTRAL GOLD CLUSTERS \( \text{Au}_n \) (\( n = 2 - 10 \))

The binding energies per atom obtained from the 19e-RECP as a function of the cluster size calculated for the most stable structures are presented in Fig. 1. The lowest energy structures as well as those corresponding to almost degenerate isomers are also shown in Fig. 1. The geometries and energies of all optimized structures corresponding to different isomers for each cluster size are available in the electronic form as supplement to this article (Ref. 34). The lowest energy structures of \( \text{Au}_n \) up to \( n = 10 \) are planar at the DFT level of theory and they are not directly related to sections of the bulk phase. Since large numbers of structures have been investigated for each cluster size, we are confident that the global minima have been identified for the majority of clusters investigated. The binding energies per atom increase with the cluster size, exhibiting pronounced even–odd alternation which indicates larger stability of clusters with the even number of electrons than of those with odd number of electrons. This is a common feature for all clusters of Ia and Ib elements.

The stable structures are well separated in energy from other isomers in all cases with the exception of \( \text{Au}_3 \), \( \text{Au}_4 \), and \( \text{Au}_7 \) (cf. Fig. 1). For trimer the linear and isoceles triangular geometries are almost degenerate, for tetramer the rhombic and T-form are very close in energy, and for the heptamer two planar geometries with different patterns are competing in stability. The energy ordering of close lying isomers can depend on the details of the theoretical treatment. This has been illustrated by the study carried out on structures of \( \text{Au}_3 \) employing different methods.\(^{35} \) The isoceles triangular geometry is the most stable structure at the level of the coupled cluster theory including single, double and triple excitations CCSD(T) with the two states, the \( ^2A_1 \) and \( ^2B_2 \) close in energy, arising from the Jahn–Teller effect. The linear form is slightly higher in energy. In the present DFT study the 1e-RECP gives rise to very similar results, but the energy of the linear form is slightly lower when the 1e-RECP is used (cf. Ref. 34). This confirms that accurate determination of the bond lengths such as at 1e-RECP DFT level might be very important for structural properties of small systems such as \( \text{Au}_3 \), as pointed out in Sec. II.

At this point it is useful to address the role of \( d \) electrons for bonding in Au clusters. The rhombic and T-form of the tetramer are closer in energy if the \( d \) electrons are accounted for with 19e-RECP, but the former remains the most stable structure as in the 1e-RECP treatment. In contrast, 19e-RECP predicts planar structures of the heptamer to be considerably lower in energy (by 0.9 eV) than the 3D structures (cf. Ref. 34), while the 1e-RECP gives rise to the pentagonal bipyramid as the most stable form. Discrepancies between the two approaches in predicting the transition from 2D to 3D structures indicate that the inclusion of \( d \) electrons in the treatment is important for the ground state properties of the pure Au clusters with nuclearity larger than 6. This finding is also supported by the investigations carried out on the cationic Au clusters using the same 19e-RECP BP86 treatment as in this article. Therefore a comparison of our results obtained for the neutral Au clusters can be made with those of Ref. 12 on cationic species.

The stable structures of the neutral Au clusters presented in Fig. 1 differ from those found for the cationic clusters, with the exception of the tetramer and the hexamer which assume rhombic and the planar triangular forms in both cases. According to Ref. 12 cationic Au clusters larger than heptamer have 3D forms related to the sections of the bulk phase, which indicates a substantial influence of the positive charge on the structures of gold clusters. This is also evidenced by the form of the stable planar structures of the neutral Au clusters (cf. Fig. 1) which favor maximum number of exposed atoms accommodating negative charge. The lowest energy structures of \( \text{Au}_n \) \( (n = 4 - 7) \) can be derived by adding a single atom to the lowest energy structure of \( \text{Au}_{n - 1} \) cluster, thus forming an additional triangular subunit. This pattern changes for the most stable structure of \( \text{Au}_8 \) in which the square subunit is capped by four atoms on each side. The structural motive changes again for \( \text{Au}_9 \) and \( \text{Au}_{10} \). In the former case the single atom assumes central position and therefore is highly coordinated, and in the latter case two centered highly coordinated atoms are present (cf. Fig. 1).

What is the reason for the 2D forms of \( \text{Au}_n \) clusters? The \( s - d \) energy separation in Au atom is relatively small and as a consequence the \( d \) electrons might participate in bonding. However, the degree of their participation seems to be dependent upon structural properties. We have carried out the analysis of DFT density of states (DOS) in terms of \( s-\), \( p-\), and \( d-\)contributions which allowed us to identify them in the energy interval important for the bonding. Two different characteristic features have been identified for the 2D and 3D structures, for example in the case of \( \text{Au}_8 \). The DOS corresponding to the HOMO of the planar structure is dominated by the \( d \)-contributions and the energy gap with respect to other DOS with mixed \( s \)- and \( d \)-character is very small. In contrast, DOS obtained for the \( T_d \) structure corresponding to the HOMO has larger \( s \)- than \( d \)-contributions and is strongly separated from lower energy DOS which are dominated by \( d \)-contributions. The above analysis indicates that the higher
stability of the planar structure of $\text{Au}_8$ is due to larger contributions of $d$ electrons to the bonding than in the case of the $T_d$-3D structure. This explains qualitatively also why the neutral silver clusters which are characterized by $s$-type bonding assume 3D structures already for larger sizes than hexamer.

As pointed out in Sec. II, structural properties of Au clusters are very dependent on the particular method adopted for description of electron correlation effects. According to ion mobility measurements$^{12}$ on cationic Au clusters it is to be expected that also larger neutral Au clusters than hexamers assume planar structures as obtained from the DFT theory. Whether the neutral gold clusters are still planar until $n=10$ or not remains to be verified. Notice that the energy difference between 2D and 3D structures is smaller for $\text{Au}_9$ and $\text{Au}_{10}$ clusters ($\Delta E \approx 0.2$ eV) than for $\text{Au}_7$ and $\text{Au}_8$ ($\Delta E \approx 0.5$ eV) at the DFT level of calculations. Since DFT tends to favor planar structures of Au clusters, the error of $\sim 0.2$ eV can not be presently excluded.

The above findings are particularly important for the study of the structural and electronic properties of bimetallic clusters. The key role of the polar hetero bonds and a charge transfer to the gold atoms is of crucial importance for structural properties of these systems as it will be shown in the following sections.

IV. BIMETALLIC CHARGED AND NEUTRAL GOLD–SILVER TRIMERS, TETRAMERS, AND PENTAMERS

Systematic investigation of the structural and ground state properties of small bimetallic clusters have been carried out with the aim to establish the role of the heteronuclear versus homonuclear bonding in these systems. Due to larger electronegativity of the Ag than of the Au atom the charge transfer of $s$ electrons occurs to the gold atoms in bimetallic systems. Consequently, Au atoms prefer positions which allow the largest charge transfer from Ag atoms.

A. $\text{Ag}_m\text{Au}_n^{q+}\ (n+m=3)$

The results on trimers with one- and two-gold atoms obtained using 1e-RECP and 19e-RECP are summarized in Fig. 2. Both anionic trimers $\text{Ag}_2\text{Au}^-$ and $\text{AgAu}_2^-$ are linear with peripheral positions of Au atom(s) minimizing the repulsion of the excess electron localized at the ends of the chains. Both RECPs give rise to the same energy ordering of the isomers. The bond lengths are shorter in the former case (cf. Fig. 2) as pointed out in Sec. II. For neutral $\text{Ag}_2\text{Au}$ the linear form with two hetero bonds is close in energy with the isosceles triangular structure in both RECPs although their energy ordering changes; linear structure is more stable in 1e-RECP and the triangular form in 19e-RECP. In contrast, the neutral $\text{Ag}_2\text{Au}_2$ prefers obtuse triangular form in both treatments. The cationic trimers $\text{Ag}_2\text{Au}^+$ and $\text{AgAu}_2^+$ have obtuse and isosceles triangular geometries with positive charge localized at silver atoms (atom), respectively. The energies of all isomeric forms are given in Table II S of the supplement.$^{34}$ The vertical ionization potentials (IP$_v$) and vertical detachment energies (VDE) obtained from both 1e-RECP and 19e-RECP differ by $0.2\sim0.5$ eV (cf. Table II). The VDEs for $\text{Ag}_2\text{Au}^-$ are in acceptable agreement with the available experimental data$^{17}$ while for $\text{AgAu}_2^-$ the 19e-RECP yields VDE value which is closer to experiment$^{17}$ than that obtained with 1e-RECP (cf. Table II).

B. $\text{Ag}_m\text{Au}_n^{q+}\ (n+m=4)$

We present the structural and ground state properties of bimetallic tetramers starting with doping the silver trimer by one Au atom and then increasing the Au-content. In this manner the transition from “metallic” system doped by the one Au atom to the “ionic” $\text{AgAu}^- - \text{AgAu}$ versus segregated $\text{Ag}_2 - \text{Au}_2$ system back to the “metallic” species doped by the one Ag atom can be followed.

Since the 1e-RECP is applicable to considerably larger systems than the 19e-RECP, bimetallic tetramers offer a good opportunity to check the reliability of the 1e-RECP approach against the results obtained with 19e-RECP (cf.
TABLE II. Vertical ionization potentials (IP) and vertical detachment energies (VDE) for Ag\(_n\)Au\(_m\) (n + m = 2, 3, 4, 5), Ag\(_n\)Au\(_m\) (n = 3, 4, 5, 10), and Ag\(_{2}Au\) clusters obtained with 1e-RECP BLYP and 19e-RECP BP86 (in square brackets) methods.

<table>
<thead>
<tr>
<th>Ag(_n)Au(_m)</th>
<th>IP</th>
<th>VDE</th>
<th>VDE(expt.)*</th>
</tr>
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<tbody>
<tr>
<td>AgAu</td>
<td>9.01 [8.95]</td>
<td>1.27 [1.72]</td>
<td>2.47</td>
</tr>
<tr>
<td>Ag(_2)Au</td>
<td>6.94 [6.71]</td>
<td>2.78 [3.09]</td>
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<td>3.47 [3.68]</td>
<td>3.86</td>
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<td>Ag(_4)Au</td>
<td>7.14 [7.41]</td>
<td>1.56 [1.97]</td>
<td>1.66</td>
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<td>Ag(_5)Au</td>
<td>7.87 [8.00]</td>
<td>1.62 [2.01]</td>
<td>1.62</td>
</tr>
<tr>
<td>Ag(_4)Au(_1) (I) [II]</td>
<td>7.97 [8.02]</td>
<td>2.00 [2.17]</td>
<td>3.00</td>
</tr>
<tr>
<td>Ag(_4)Au(_1) (III) [I]</td>
<td>7.87 [8.00]</td>
<td>2.00 [2.17]</td>
<td>3.00</td>
</tr>
<tr>
<td>Ag(_4)Au(_1) (IV) [IV]</td>
<td>7.27 [7.3]</td>
<td>2.12 [2.37]</td>
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<td>Ag(_5)Au</td>
<td>6.45 [6.76]</td>
<td>2.18 [2.47]</td>
<td>2.47</td>
</tr>
<tr>
<td>Ag(_4)Au(_2)</td>
<td>6.71 [6.97]</td>
<td>2.44 [2.70]</td>
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<td>Ag(_5)Au(_2)</td>
<td>7.41 [7.54]</td>
<td>2.98 [3.17]</td>
<td>3.17</td>
</tr>
<tr>
<td>Ag(_4)Au(_3)</td>
<td>8.44</td>
<td></td>
<td>2.47</td>
</tr>
<tr>
<td>Ag(_5)Au(_3)</td>
<td>6.70</td>
<td></td>
<td>2.47</td>
</tr>
<tr>
<td>Ag(_5)Au(_5)</td>
<td>6.37</td>
<td></td>
<td>2.47</td>
</tr>
<tr>
<td>Ag(_4)Au(_5)</td>
<td>6.31</td>
<td></td>
<td>2.47</td>
</tr>
</tbody>
</table>

*Experimental results from Ref. 17.
†(I–IV), [I–IV] label isomers according to the energy sequence obtained with 1e-RECP and 19e-RECP, respectively.

Fig. 3). Therefore the structures and their energy ordering obtained from both treatments are given in Fig. 3 and energies are listed in Table III S of the supplement.34

Bimetallic neutral and charged tetramers tend to assume rhombic structures with a number of hetero bonds determined by the composition. The gold atoms prefer exposed positions while the silver atoms form a higher number of bonds. Such topologies are convenient for charge transfer and the neutral Ag\(_3\)Au the most stable structure is considerably lower in energy from all other isomers, independently from the treatment. In contrast, in the case of an anionic Ag\(_2\)Au\(_3\) cluster the 19e-RECP gives rise to small energy differences between the stable rhombic and other isomeric forms. Similarly, for Ag\(_2\)Au\(_3\) cluster, four isomers close in energy have been found. The structure with homonuclear bonding (Ag\(_3\)Au\(_3\)) is in competition with the hetero bonded one due to the lack of one electron and the energy sequence is influenced by the treatment.

Finally, the structures of tetramers with a single Ag atom are characterized by high coordination of Ag. For the neutral Ag\(_2\)Au\(_3\) and cationic Ag\(_2\)Au\(_3\) clusters the Ag atom is located at the short diagonal. In the case of the anion Ag\(_2\)Au\(_3\) the rhombic structure with the Ag atom at the short diagonal has almost the same energy as the T-form with the Ag atom in the central position at the 1e-RECP level of calculations. The 19e-RECP gives preference to the T-form with respect to the rhombic form. However, in both structures the Ag atom is three-coordinated. It seems that the energy ordering of the isomers for the neutral species is less dependent on the theoretical treatment employed than for the charged systems.

The calculated ionization potentials and VDEs are given in Table II. The values of the VDEs for the stable rhombic structures of Ag\(_3\)Au\(_2\) and Ag\(_2\)Au\(_3\) obtained from 1e-RECP are in excellent agreement with the experimental data,17 while the VDEs obtained from the 19e-RECP are higher than the measured ones. In the case of Ag\(_2\)Au\(_3\) the VDE value for the T-form is considerably closer to the experimental finding17 than the one for the rhombic structure, thus the 19e-RECP gives rise to an excellent agreement with experimental data.17

In conclusion, the determination of structural properties of the neutral bimetallic tetramers is not dependent on inclusion of d electrons, but for the charged tetramers the influence of d electrons on energy sequence of isomers might take place. However, the general trend concerning structural properties of bimetallic tetramers remains the same in both treatments. The Au atoms prefer hetero bonding than the homonuclear bonding and tend to take peripheral positions in order to withdraw charge from Ag atoms which are therefore higher coordinated.

C. Ag\(_m\)Au\(_n\)\(^{+,-}\) (n + m = 5)

Stable structures of anionic and neutral bimetallic pentamers assume planar trapezoidal structures with triangular subunits, in contrast to the cationic stable structures which prefer 3D forms as shown on Fig. 4. The energies of the stable structures as well as other isomeric forms obtained with 1e-RECP are given in Table IV S of the supplement.34 The calculations using the 19e-RECP have been carried out only for the cases for which the energies of the stable structures are very close to the other isomers. Both treatments give rise to the equivalent stable structures as shown in Fig. 4.

In all anionic and neutral stable trapezoidal structures of pentamers one Ag atom remains four-coordinated independently from the composition. In fact, the common structural properties of anionic and neutral pentamers concerning posi-
FIG. 3. Structures of charged and neutral bimetallic tetramers $\text{Ag}_m\text{Au}_n$ ($m+n=4$) optimized at the 1e-RECP BLYP and 19e-RECP BP86 level of theory. The energy differences with respect to the most stable structure obtained from the former and the latter approach are given in the round and square brackets, respectively. I–IV denote energy sequence of the isomers according to 1e-RECP BLYP results. Labels of the symmetry group and of the ground electronic states are also given. Dark circles indicate Au atom(s) and light ones Ag atom(s). For energies cf. Table III S of Ref. 34.
tions of hetero atoms are present with the exception of Ag₃Au₂ and Ag₃Au₂⁺ as can be depicted from Fig. 4. Even in this case Au atoms prefer hetero bonding, which means that no segregation between the silver and the gold subunits occur for the compositions \( 3+2 \) and \( 2+3 \).

The stable structures of cationic bimetallic pentamers tend to deviate from planarity. The lowest energy structures of Ag₄Au⁺, Ag₂Au₃⁺, and AgAu₄⁺ assume double triangular forms sharing the Au atom (cf. Fig. 4). In the case of Ag₃Au₂⁺ the trigonal bipyramid with peripheral positions of Au atoms competes in energy with the double triangular form.

### D. Ionization potentials and vertical detachment energies

Results obtained from both 1e-RECP and 19e-RECP for bimetallic AgₙAuₙ clusters are summarized in Figs. 5 and 6. They are plotted as a function of the number of Ag atoms \( n \) for the fixed number of gold atoms \( m = 5 \). Both VDE and IP⁺ values show in general even–odd behavior with increasing \( m \). An exception is almost equal VDE values for AgAu₃⁺ and Ag₂Au₃⁺ (cf. Fig. 6). The VDEs obtained from 19e-RECP are on average by \( \sim 0.4 \) eV higher than those obtained from the 1e-RECP and the available experimental values lay in between. The ionization potentials obtained from both treatments are in fairly good agreement (cf. Fig. 6). These results indicate that the 1e-RECP at the DFT level is also suitable for determination of the ground state properties of the bimetallic clusters since in this case the \( s–d \) hybridization is not so strong as for the pure Au clusters. The absolute values of VDE for the given cluster size increase with the number of Au atoms, as expected. The values of ionization potentials can serve as an indicator of the "ionic" character of the cluster when compared with the IP of the AgAu dimer which is \( \sim 9 \) eV. In fact, the IP⁺ values above 7.5 eV have been obtained for Ag₂Au₂ and Ag₃Au₃ clusters which assume planar structures with maximum number of hetero bonds as shown in Fig. 7. The properties of Ag₃Au₃ will be addressed in the next section.
V. NEUTRAL BIMETALLIC SILVER–GOLD

The study of the bimetallic clusters with equal number of silver and gold clusters aims to find out the preference for charge transfer in different structural patterns which include maximal number of hetero bonds and segregation or embedding of two components. The other aspect of this investigation is connected with the transition from 2D to 3D structures which occurs for one-component systems at different cluster sizes. For the neutral clusters Ag₇ assumes the 3D pentagonal bipyramid form and gold clusters are planar up to ten atoms as shown in Sec. III. In addition to systems with equal number of silver and gold atoms the investigation of the Ag₁₂Au₈ cluster serves as a model for studying embedding of Au₈ in the surrounding of silver atoms in connection with the possible reactivity of bimetallic species.

The results for Ag₃Au₃ and Ag₄Au₄ are presented on Fig. 8. Both systems have been calculated using the 1e-RECP and 19e-RECP approaches. The most stable structure of the Ag₃Au₃ is the planar triangular form with negatively

FIG. 8. Structures of neutral bimetallic Ag₃Au₃ and Ag₄Au₄ clusters optimized at 1e-RECP BLYP and 19e-RECP BP86 level of theory. The energy differences with respect to the most stable structure (in eV) obtained from the former and latter approach are given in round and square brackets, respectively. I–IV denote the energy sequence of isomers according to 1e-RECP BLYP results. Labels of the symmetry group and the ground electronic states are also given. Dark circles indicate Au atom(s) and light ones Ag atom(s).
charged Au atoms located at the peripheral position independent from the treatment. The pentagonal pyramid and tetrahedral type of structures with different locations of hetero atoms have been systematically investigated at the 1e-RECP level. Several 3D structures optimized with 19e-RECP are for illustration shown in Fig. 8, but all of them also have substantially higher energies than the planar Ag₈Au₃. In contrast, the Ag₁₄Au₄ assumes 3D tetrahedral type of structure with negatively charged Au atoms located at the outside tetrahedron capping the inner silver tetrahedron and forming hetero bonds. Again systematic investigation of different 3D and 2D structures has been carried out with the 1e-RECP and energy ordering of several structures was checked against 19e-RECP results as shown in Fig. 8. All of them lie energetically above the bimetallic T₃ structure. The pure Ag₈ assumes also the T₃ structure in contrast to the planar form of Au₈. In other words, the hetero bonding influences substantially the structural properties of gold octamer. Since the s–d separation in bimetallic systems is substantially larger than in the pure Au clusters, as evidenced by analysis based on DFT density of states (DOS), the structural properties of Ag₄Au₄ are closer to the ones obtained for Ag₈. Moreover, the “ionic” nature of Ag₃Au₁ and Ag₄Au₃ is evidenced by large values of ionization potentials. They are only by 0.25 and 0.5 eV lower than the IP value of the hetero dimer AgAu as shown in Fig. 7.

After the transition to 3D structures has been determined we employed the 1e-RECP for larger systems which are computationally more demanding. Since we found that the stable structure of Ag₄Au₄ is closer related to the structure of the silver than of the gold octamer, the optimization of Ag₁₀ and Ag₂₀ has been first carried out and the corresponding structures were used as the starting point for consideration of the bimetallic structures. Of course for the cluster of this size it cannot be guaranteed that the absolute minimum has been found.

For Ag₁₀ two lowest energy structures can be derived by bicapping the T₄ and antiprism subunits, respectively. The other higher lying isomers contain a pentagonal bipyramid capped by three atoms in different ways. A systematic investigation of Ag₅Au₅ has been carried out by placing Au atoms at different positions searching for the segregation between two components versus other patterns, e.g., such as achieving the largest charge transfer to the Au atoms. The latter proved to be more successful. The lowest energy structure found for Ag₅Au₅ is deformed bicapped antiprism with a chain of Au atoms at the peripheral positions attracting the negative charge as shown on Fig. 8. Other structures with segregation pattern or with larger number of hetero bonds have substantially higher energies. Correspondingly, the value of IP for Ag₅Au₅ is considerably lower than the one obtained for the T₄ structure of Ag₄Au₄ with the maximum number of hetero bonds (cf. Fig. 8).

In the case of 20-atoms we investigated first the structural properties of Ag₂₀ and Au₂₀ clusters and found that the C₃ form with the icosahedral subunit capped by seven atoms has lower energy than different C₂₀ and T₄ type of structures. For the bimetallic Ag₁₀Au₁₀ cluster, structures with lowest energies contain Au atoms distributed in the icosahedral subunit of the deformed C₃ structure as shown in Fig. 9. The three structures labeled by a, b, and c are close in energy and they differ only in differently placed Au atom(s) within the icosahedral subunit. The structure labeled by d contains one Au atom outside the icosahedra and has by 0.2 eV higher energy with respect to the structure a. The lowest energy structure exhibits the largest charge transfer from the silver to gold atoms. All Au atoms except of the central one have negative charge while Ag atoms are positively charged. The Au₁₀ subunit with one central atom is embedded in the surrounding of Ag atoms.

This pattern remains valid for the lowest energy structure found for Ag₁₂Au₈ as shown in Fig. 10. In this case the
Au₈ assumes the pentagonal bipyramidal structure capped by one atom and is also a part of an icosahedral subunit. All Au surface atoms are negatively charged. This Au₈ subunit embedded in Ag₉Au₂ represents a good candidate for the reactive center, since three exposed Au atoms labeled by 1,2,3 in Fig. 10 have convenient positions to react with molecules. In fact, such three-atomic facets of Au₈ have been found also in the model calculations of gold clusters supported on magnesium and used for the reactivity study with O₂ and CO molecules. Notice that the structure b in Fig. 10, which does not contain Au₁₂-facet, has by ~0.13 eV higher energy than to the structure a. In the structure c, which has even higher energy, one Au atom lies outside the icosahedral subunit. This indicates that the lowest energy structure a of Ag₁₂Au₈ represents an interesting model for studying the reactivity of bimetallic clusters.

VI. CONCLUSIONS

Our density functional study of structural properties of bimetallic silver–gold clusters and their comparison with one-component systems allows us to draw following conclusions:

1. The charge transfer from Ag to Au atom(s) plays dominant role for structural properties of bimetallic clusters. The degree of s–d hybridization lies between the low one for Ag and the large one for Au clusters.

2. In small bimetallic clusters 3 ≤ (n + m) ≤ 5 a general tendency can be observed that Ag atom(s) prefer to form more bonds than Au atom(s) as in the case of pure Ag and Au clusters, respectively. However, Au atoms favor positions at which it is convenient to withdraw the charge from Ag atoms.

3. Formation of hetero bonds is more favorable than of homo bonds as shown for Ag₉Au₈ (n = 2,3,4) species giving rise to high ionization potentials and stability of “ionic” species.

4. Segregation between two components is not energetically favorable.

5. In both studied clusters with 20 atoms, Ag₁₀Au₁₀ and Ag₁₂Au₈, a negatively charged Au₁₀ or Au₈ subunit is embedded in the Ag environment.

6. In the case of Ag₁₂Au₈ the shape of Au₈ corresponds to the pentagonal bipyramid capped by one atom in which three exposed gold atoms form a facet capable of interacting with reactants. Small gold negatively charged subunits embedded in Ag surroundings might serve as reactive centers similarly to gold clusters supported on metal oxides.

7. Structural properties of bimetallic clusters are closer related to those of Ag than to those of Au clusters. The d electrons are involved in the bonding in Au clusters while the s electrons are primarily responsible for formation of bonds in Ag clusters. Consequently, there are structural differences between neutral Ag and Au species for sizes larger than hexamers and for cationic clusters even for sizes larger than tetramers according to Refs. 12 and 15. Stable structures of pure Au clusters have smaller number of bonds and tend to remain planar while the structures of Ag clusters have a larger number of bonds and tend to become three-dimensional for smaller sizes, similarly as bimetallic clusters.

In summary, we have shown that bimetallic silver–gold clusters own interesting properties which can be important for reactivity studies. This finding might stimulate further experimental work in this area.

ACKNOWLEDGMENTS

This work was supported by the Deutsche Forschungsgemeinschaft SFB 450. We thank Professor M. Kappes for communicating the results prior to publication.

See EPAPS Document No. E-JCPSA6-117-303231 for investigated structures and energies (Table I S) of gold clusters. The energies of bimetallic clusters are given in Tables II S–IV S. This document may be retrieved via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.