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# Density functional study of $H_2S$ binding on small cationic $Ag_nAu_m^+$ $(n + m \leqslant 5)$ clusters

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ABSTRACT

Density functional theory calculations were performed to investigate the structural and energetic properties of $H_2S$ binding on small cationic $Ag_nAu_m^+$ clusters $(n + m \leqslant 5)$. The adsorbates prefer binding to Au atoms when both Au and Ag co-exist in the cluster with the exceptions of $Ag_4Au^+$ and $Ag_3Au_2^+$. The binding energy decreases as the cluster size grows and is further correlated with the LUMO energy of bare $Ag_nAu_m^+$ clusters. Our calculation suggests that the $Ag_nAu_m^+$ cations may react with $H_2S$ dissociatively by way of a $H_2$ molecule loss. The S—H and M—S vibrational frequencies are highly related to whether S atom is attached to Au or Ag atoms.

## 1. Introduction

The bimetallic Ag/Au clusters and nanoparticles have attracted considerable interest both experimentally and theoretically since they play an important role in colloidal chemistry, medical science and catalysis [1–9]. A new class of highly efficient optical materials based on Ag/Au clusters, showing vastly enhanced optical nonlinearity over the bulk metals, has been synthesized [1]. The photoelectron spectroscopy of $Ag_mAu_n^-$ $(m + n \leqslant 4)$ indicated that electron affinities of those cluster anions tend to increase with increasing gold composition [2]. Pyridine prefers binding to Ag when both Au and Ag atoms co-exist at active sites of a mixed Ag/Au cluster [3]. Our previous theoretical study indicated that the adiabatic ionization potentials, electron affinities and hydrogen binding energies of bimetallic Ag/Au cluster hydrides increase as the Au content increases [4].

$H_2S$ is one of the most useful gas sensors and yet one of the most common surfactants in hydrodesulfurization of hydrocarbons [10,11]. The interaction of $H_2S$ with gold and silver surface is widely used as a model system to understand the various reasons for the poisoning of metals by sulfur compounds [12,13]. The Fourier-transform ion-cyclotron resonance (FT-ICR) mass spectrometry has been performed to investigated the reactions of gold cluster cations $Au_n^+$ $(n = 1–12)$ with $H_2S$ at room temperature [14]. Most $Au_n^+$ clusters are reactive towards $H_2S$ except for $Au^+$ and $Au_3^+$. Sequential sulfuration reactions of $Au_nS^+$ produced $Au_nS_m^+$ and finally stopped at $Au_nS_{m+x}H_2^+$ when $H_2$ release did not occur. While unambiguous determination of the geometric and energetic properties of a small atomic cluster is an almost impossible task from experiments alone, quantum-chemical studies may shed light on the understanding of the catalytic activity of small metal clusters. The theoretical studies of $H_2S$ adsorption on coinage metal clusters have also been appeared [15–19]. The $H_2S$ adsorption energies on cationic $Au_n^+$ clusters $(n = 1–8)$ are generally greater than those on the corresponding neutral $Au_n$ clusters [15]. The small gold cluster would like to bond with sulfur in the same plane and the $H_2S$ molecule prefers to occupy the on-top and single fold coordination site in the $Au_nH_2S$ $(n = 1–13)$ clusters [16]. Hamilton et al. have performed a theoretical calculation on the decomposition channels of $M_nH_2S^+$ complex $(M = Cu, Ag, Au, n = 1–4)$ involving loss of an H atom, $H_2$ molecule, M atom or $M_2$ dimer [17]. Alloying neutral $Au_k$ with copper and silver decreases the attraction of Au towards $H_2S$, while alloying $Ag_k$ and $Cu_k$ by gold increases the attracting of Ag and Cu towards $H_2S$ with $k = 1–3$ [18]. Compared to neutral clusters, experimentally, it is much more straightforward to study the properties of ionic clusters. To our knowledge, there is no theoretical report about the interaction between $H_2S$ and the cationic $Ag_nAu_m^+$ clusters available. In this contribution, we systematically investigate the interaction between $H_2S$ and small $Ag_nAu_m^+$ $(n + m \leqslant 5)$ cluster cations using the first principles methods on the basis of density functional theory (DFT). The goal of this work is to have a better understanding of the correlation between the energetic properties of the cationic Ag/Au clusters and their structure, composition and size. Moreover, to fully understand the catalytic activity of bimetallic clusters for a

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specific reaction, it is important to study the interaction between bimetallic clusters and the reactant and product molecules. The results of geometry, binding energy, dissociation channel and vibrational frequency for bimetallic and monometallic clusters were analyzed and discussed in Section 3. Before presenting the results, we summarize the computational details in Section 2. Finally, the conclusion is drawn in Section 4.

## 2. Computational details

The calculations were carried out using Gaussian 03 package [20]. The PW91PW91 [21] exchange and correlation functional was employed for all the calculations in this study. The Los Alamos relativistic effective core potential (RECP) plus DZ basis set [22] was used for Ag and Au atoms. The 6-311++G(d, p) basis set was used on H and S atoms. All calculations were performed with (99, 590) pruned grid (ultrafine grid as defined in Gaussian 03). Natural bond orbital (NBO) [23] analysis was used to provide the natural charge distribution. Vibrational frequency calculations including thermochemical analysis were carried out at 298.15 K and 1 atmosphere of pressure. These frequency calculations also guarantee the optimized structures locating the minima, not as transition structures.

To have the results of bare clusters and complex clusters for comparison, we also studied the geometries and properties of bare Ag/Au clusters in cationic charge state up to five atoms. The most stable $Ag_nAu_m^+$ ($n + m \leqslant 5$) clusters taken from our previous work [4] are displayed in Fig. 1. Small cationic $Ag_nAu_m^+$ clusters tend to be planar structures up to four atoms. The lowest energy isomer of $Ag_5^+$ cation has three-dimensional $D_{2d}$ structure while the most stable $Au_5^+$ is a twisted X-shaped geometry with $D_{2h}$ symmetry. The most stable $Ag_4Au^+$, $Ag_2Au_3^+$ and $AgAu_4^+$ isomers can be viewed as the replace of Ag with Au atoms in the $Ag_2$ unit of the $D_{2d}$ structure, while the lowest energy form of $Ag_3Au_2^+$ is trigonal bipyramid with $D_{3h}$ symmetry. Those structures of $Ag_nAu_m^+$ cations are in good agreement with previous theoretical reports [24,25].

## 3. Results and discussion

### 3.1. Structures and population analysis

Previous theoretical studies indicated that small metal clusters prefer to bond with the S atom of $H_2S$ rather than to bond with hydrogen or to bond with both S and H atoms [15–19]. Thus, the $H_2S$ was constrained to S atom binding in this calculation. The most stable Au-binding structures are listed in Fig. 2 and the most stable Ag-binding structures are listed in Fig. 3 (more structures can be seen in the supporting information for the conciseness of the text). Consistent with previous studies, the S atom is bonded to only one metal atom of the clusters and $H_2S$ molecule is only slightly perturbed despite the strong M—S bond. The Au—S distances range from 2.37 to 2.50 Å and the Ag—S distances range from 2.52 to 2.59 Å. The lanthanide contraction makes the gold atom has a radius very close to that of silver atom. If the difference of Au—S and Ag—S distance is due to the bonding interaction, it is expected that in all cases the Au—S bond is stronger than the Ag—S bond. However, there are two exceptions of $Ag_4AuS^+$ and $Ag_3Au_2S^+$ clusters whereby the Ag-binding is more favorable than Au-binding. We also note that the lowest-energy structures of $Ag_nAu_mH_2S^+$ complex are related to the ground-state isomers of bare $Ag_nAu_m^+$ clusters except for $Ag_3Au^+$ and $Ag_2Au_2^+$. The competition of the stability here is between two processes: larger electrostatic interaction between Au and S atom and the tendency for the metal framework in complex to keep the similar shape to the ground states of the bare clusters.

To further understand the interaction between the metal cluster and adsorbate, Table 1 tabulates the electron populations of the atomic orbitals for $Ag_2^+$, $Ag_2H_2S^+$, $AgAu^+$, $AgAuH_2S^+$, $Au_2^+$ and $Au_2H_2S^+$ clusters. It is observed that irrespective of binding sites, the adsorbate bares a certain amount of positive charge. Higher charge transfer is observed when the S atom is attached to the Au atom (which usually have higher binding energies) than when the S atom is attached to the Ag atom. This can be simply understood by the larger electronegativity of Au than Ag (2.54 *versus* 1.93). After binding, the *p* population of the S atoms shows the most dramatic decrease, while the *s* and *d* populations almost remain intact. The decrease of the *s* orbital of H is less pronounced but still noticeable. Regarding the metal part, the *s* populations of both the two metal atoms increase, whereas the *d* population decreases. The *p* populations of the metal atom connected to S atom are also higher in comparison with that in bare dimers. Thus, on the one hand, electrons are transferred from the *d* level of S and *s* level of H to the *s* and *p* level of metal atoms. On the other hand, electrons are back transferred from the *d* level of metal atoms to the adsorbate. This cooperative donation and back-donation may be responsible for the bending of the M—M—S axis in the complex clusters. Previous theoretical study of neutral $Au_nH_2S$ ($n = 1–8$) systems also indicated that the bending of Au—Au—S axis results in a better overlap of the *p* orbital of S and the *sd*-hybridized orbitals of Au [15].

### 3.2. Binding energies

The $H_2S$ binding energy (BE) is defined by the follow equation:

$$BE = E(Ag_nAu_m^+) + E(H_2S) - E(Ag_nAu_mH_2S^+)$$

where $E(Ag_nAu_m^+)$ and $E(Ag_nAu_mH_2S^+)$ are the total energies of the bare cluster and the complex cluster, respectively. The more positive the BE is, the stronger the bond is. The calculated binding energies for all the complex clusters studied above are given in Figs. 2 and 3, together with the amount of the charge transfer. One can

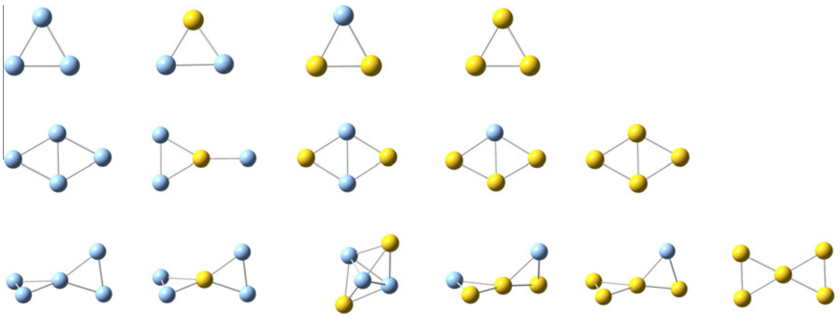

**Fig. 1.** Optimized geometries of the most stable cationic $Ag_nAu_m^+$ clusters, with $n + m \leqslant 5$. The structures are arranged in the order of increasing Au composition.