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## Structure and bonding of $Au_5M$ ( $M=Na, Mg, Al, Si, P,$ and $S$ ) clusters

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The atomic and electronic structure of  $Au_5M$  ( $M=Na, Mg, Al, Si, P, S,$  and  $Au$ ) clusters have been investigated using generalized gradient approximation to the density functional theory. Depending on the nature of interaction with different impurity elements a structural transition from planar to nonplanar configuration has been observed in  $Au_5M$ . With the exception of  $S$ , impurities with  $p$  electrons ( $Al, Si, P$ ) yield nonplanar geometries of  $Au_5M$  clusters, while those with  $s$  electrons ( $Na, Mg$ ) yield planar geometries. The properties of  $Au_5S$  cluster are anomalous: The cluster not only has a planar geometry, but also is chemically most stable with the highest vertical ionization potential among all the clusters studied. The origin of these anomalous properties of  $Au_5S$  cluster is attributed to the delocalization of electronic wave function associated with the highest occupied molecular orbital.

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### INTRODUCTION

During the last three decades there has been considerable interest in understanding the structure and properties of atomic clusters. This new phase of matter, intermediate between atoms and bulk, possesses unique and novel size and composition-based specific properties. More importantly, their structure and properties can be altered one atom at a time.<sup>1,2</sup> A fundamental understanding of the atomic structure and stability of clusters has been one of the central goals of current research. For example, the relative stability of alkali metal clusters can be understood from the electronic shell model<sup>3</sup> where clusters containing 2, 8, 20, and 40, atoms are unusually stable due to electronic shell closure. Their geometries are planar up to five-atom clusters and adopt three-dimensional (3D) structures as the size grows. The electronic structure of coinage metal clusters such as  $Cu, Ag,$  and  $Au$  also follow the electronic shell model, however, their geometries can differ significantly from that of the alkali metal clusters. This is essentially due to the effect of core  $d$ -electrons in coinage metals, which can easily hybridize with outer  $s$ -electrons. Further, addition of hetero-atoms to coinage metal clusters can have significant effects on their geometries and stability.

Among the coinage metal clusters, gold nanoclusters have received much attention and have been a subject of interest in numerous experimental and theoretical studies. This interest is brought about due to their novel catalytic, magnetic, and structural properties. Recently, Hakkinen and Landman<sup>4</sup> showed that neutral and anion gold clusters are planar for  $n \leq 8$  and  $\leq 7$ , respectively. Further, they predicted that anion clusters can undergo a structural transition from  $n=9$  onward. However, the subsequent experiment<sup>5</sup> by ion-mobility measurements showed discrepancy with earlier prediction and provided evidence of planar structures for  $n=7$  and  $11$ , for cation and anion clusters, respectively. Recent studies<sup>6-9</sup> have shown that the ground state structures of small gold clusters clearly differ from that of the other coinage metal clusters. In particular, neutral gold clusters are planar up to

size  $n=11$ , while the 2D to 3D transition for anionic gold clusters occurs at size  $n=12$ . However, in the case of silver and copper clusters, the 2D to 3D transition occurs at  $n=6$  for neutral and at  $n=5$  for anionic clusters.<sup>9</sup> The reason for the preference of planar structures by gold clusters up to large cluster sizes was attributed to the relativistic effects that cause a shrinking of the size of the  $s$  orbitals and thus enhance the  $s$ - $d$  hybridization. Apart from the unusual preference for planar structures, the interest in gold clusters is based on its various applications in molecular electronic devices, catalysts, and biological diagnostics.<sup>10</sup>

Doping of gold clusters with different atoms was expected to open up new channels, wherein one can tailor the properties of the clusters by varying the nature of the dopant atom. Pykko and Runeberg initially predicted<sup>11</sup> the existence of a highly stable  $WAu_{12}$  cluster with a large HOMO-LUMO gap, which was later confirmed by the photoelectron spectroscopy based experiments.<sup>12</sup> The enhanced stability of the metal-doped  $Au_{12}$  cluster was attributed to the aurophilic attractions, relativistic effects, and closed-shell electron configuration. Following this prediction and subsequent confirmation of the existence of highly stable  $M$  at  $Au_{12}$  ( $M=W$  and  $Mo$ ) clusters, a considerable amount of experimental and theoretical work has been carried out on  $Au$  clusters doped with impurity atoms.<sup>13-26</sup> Most of these studies have focused on the interaction of transition metal atoms with gold clusters. The evidence of enhanced stability for specific cluster sizes has been explained based on the electronic shell-model and assuming that the valence electrons are delocalized. In this series,  $Au_5X^+$  ( $X=V, Cr, Mn, Fe, Co,$  and  $Zn$ ) clusters showed extra stability, which was explained based on the structural planarity and the delocalized electrons, with six delocalized electrons being defined as magic number for two-dimensional systems.<sup>16,17</sup> The delocalization of electrons in a planar geometry leads to magnetic shielding which in turn enhances the stability. This effect is evident from the unusual high stability of  $Au_5Zn^+$  cluster, which has further been attributed to  $\sigma$ -aromaticity.<sup>18</sup> It may be noted that in all these studies the ground state geometry of the  $Au$  clusters

remained planar even after doping it with an impurity atom. In another interesting study, halogenlike behavior of Au atoms was observed in  $MAu_4$  clusters where  $M=Ti, Hf, Zr, Th,$  and  $U$ . Interestingly, these clusters prefer nonplanar tetrahedral configuration as their lowest energy isomers.<sup>19</sup> The hydrogen-like behavior of Au atoms was reported by Kiran *et al.*,<sup>27</sup> in which the analogy between the  $SiH_4$  and  $SiAu_4$  was verified using the photoelectron spectroscopy and theoretical studies. In another theoretical study<sup>25</sup> on the positively charged transition metal-doped gold clusters, planar structures were predicted up to  $n=6$ , while the nonplanar structures took over from  $n \geq 7$ . In a recent study<sup>28</sup> it was found that neutral and anionic  $Au_6M$  ( $M=Ti, Cr,$  and  $V$ ) clusters not only form planar structures, but also the dopant metal atoms possess atom-like magnetism.

From the above discussion it is clear that the ground state geometries of impurity-atom-doped Au clusters can be widely different. The reason for such differences is due to the nature of bonding between the dopant atom and the gold clusters. Although most of the studies have focused on the interaction of Au clusters with transition metal atoms, few are available to show the interactions of  $s$ - and  $p$ -block elements with Au clusters.<sup>29</sup> In this work, we have investigated the atomic and electronic structure of  $Au_5M$  clusters where  $M$  atoms represent Na, Mg, Al, Si, P, and S. The reason for choosing these atoms from the same row of the periodic table is that their principle quantum numbers remain the same while increasing the valence electrons in steps of 1. The results reveal two most important features: (i) very high ionization potential of  $Au_5S$  which is an odd electron system and (ii) nonplanar geometry of metal-doped  $Au_6(Au_5Al)$  cluster.

### COMPUTATIONAL DETAILS

All calculations on  $Au_5M$  clusters were performed within the framework of generalized gradient approximation to the density functional theory (GGA-DFT). The geometry optimization has been performed in two steps. First, we carried out an initial search to identify a few low lying isomers of each  $Au_5M$  clusters using the plane wave based pseudopotential method.<sup>30</sup> The PAW potentials have been used to account for the electron-ion interactions.<sup>31</sup> A simple cubic cell of 15 Å dimension with the  $\Gamma$  point for the Brillouin zone integration was considered for these calculations. The geometries are considered to be converged when the force on each ion becomes 0.01 eV/Å or less. In the second step, the total energies and geometries of low-lying isomers (within energy difference of 1.0 eV) were further evaluated using the LCAO-MO based approach using the gradient corrected exchange and correlation functional of Perdew and Wang (termed as PW91PW91)<sup>32</sup> as implemented in the GAUSSIAN03 software code.<sup>33</sup> The triple- $\zeta$  basis set (6-311G\*) was used for Na, Mg, Al, Si, P, and S atoms, while a relativistic frozen core potential with a 19 electron valence basis set (SDD) was adopted for Au atoms.<sup>34</sup> The accuracy and reliability of the PW91PW91 functional form for small gold clusters has been verified by earlier studies.<sup>35</sup> Different structural configurations of  $Au_5M$  clusters were re-

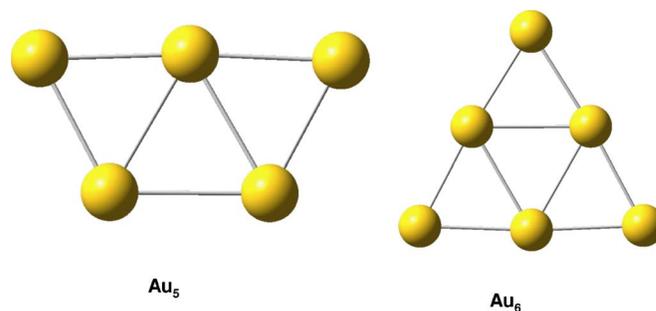


FIG. 1. (Color online) The ground state geometries of the  $Au_5$  and  $Au_6$  clusters.

optimized without any symmetry constraints. In the geometry optimization procedure, the convergence criteria for gradient force and energy are set to  $10^{-4}$  hartree/Å and  $10^{-9}$  hartree, respectively. The stability of the optimized geometries was confirmed by computing vibrational frequencies at the same level of theory.

### RESULTS AND DISCUSSION

In this section we discuss the structural details of a few low-lying isomers of  $Au_5M$  clusters which were obtained during an exhaustive search for the ground state geometries. The lowest energy structures of  $Au_5M$  clusters were obtained by placing the  $M$  atom on each possible site of the  $Au_5$  host cluster as well as by substituting one Au by  $M$  atom from the  $Au_6$  cluster.

To begin with, we present the ground state geometries of  $Au_5$  and  $Au_6$  clusters as shown in Fig. 1. The lowest energy geometries of  $Au_5$  and  $Au_6$  clusters form planar “W” and stacked triangle structures, respectively. This is in agreement with previously reported results using different theoretical techniques.<sup>12–16</sup> The ground state and low-lying isomers of  $Au_5M$  ( $M=Na, Mg, Al, Si, P,$  and  $S$ ) clusters are shown in Fig. 2. In order to illustrate the structural features of the lowest energy structures, we have listed the point group symmetry, smallest bond lengths for Au-Au and Au- $M$ , spin multiplicity, and the electronic charges on  $M$  atoms in Table I. The  $Au_5Na$  cluster has a planar structure, with Na atom occupying the fourfold coordination site. Another planar triangular structure, in which the dopant atom is twofold coordinated, was found to be 0.58 eV higher in energy than the ground state geometry. It is to be noted here that though the Na atom prefers fourfold coordination, all four Au-Na bonds (2.93 and 2.99 Å) are considerably weakened when compared to the AuNa dimer bond (2.62 Å). The Mg atom, similar to Na, also prefers to occupy the fourfold site in its ground state geometry which is again a planar triangle. Similar to Na atom, Mg forms two different sets of bonds with Au atoms: one with the Au atoms on the same side of the triangle (2.56 Å), and the other with the fourfold coordinated Au atoms (2.65 Å). We note that the Au-Mg bond length in  $Au_5Mg$  has increased from that in the  $AuMg$  dimer (2.49 Å). The second higher energy isomer ( $\Delta E=0.49$  eV) of  $Au_5Mg$  differs from  $Au_5Na$ , where the planar triangular structure is

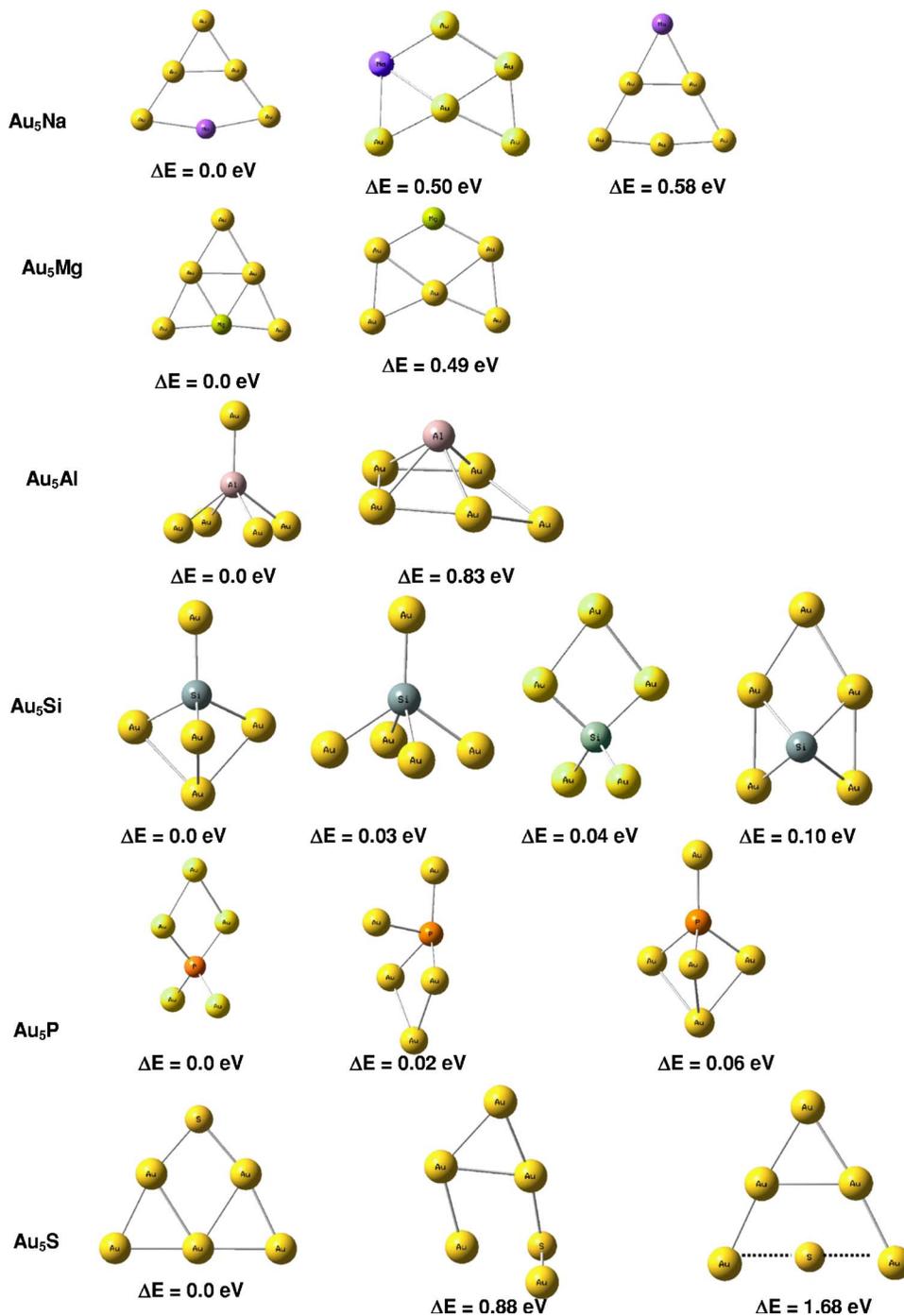


FIG. 2. (Color online) Low-lying isomeric structures Au<sub>5</sub>M clusters ( $M = \text{Na, Mg, Al, Si, P, and S}$ ). The relative stabilities of each isomer have been expressed in terms of the difference in total energy with respect to the lowest energy isomer.

deformed by opening the acute angle and causing the farthest Au atom to come close to the Mg atom.

The first important structural change occurs for Au<sub>5</sub>Al cluster, where it favors a nonplanar geometry. The lowest energy isomer of the Au<sub>5</sub>Al cluster can be seen as a Au<sub>4</sub>Al square pyramid subunit with the fifth Au atom connected to the Al at the top, thus adopting the C<sub>4v</sub> point group symmetry. The next higher energy isomer is significantly higher in energy ( $\Delta E = 0.83 \text{ eV}$ ) but follows the trend of nonplanar structural motif. It may be mentioned at this point that several planar geometries were optimized to verify the preference of Au<sub>5</sub>Al cluster to adopt a nonplanar structure and few of the planar structures ultimately converged to a nonplanar

structure. In the case of Au<sub>5</sub>Si cluster, three nonplanar structures, which are energetically degenerate, are found to be the most preferred structures. The lowest energy isomer is a capped tetrahedron, where the tetrahedral arrangement of Au<sub>4</sub>Si cluster is capped with the fifth Au atom on one triangular face of the tetrahedron (C<sub>3v</sub> symmetry). This capping of the triangle formed by the Au atoms has resulted in opening up of the tetrahedral moiety. The top-capped square pyramid structure (C<sub>4v</sub>), the lowest energy isomer in Au<sub>5</sub>Al, is only 0.03 eV higher in energy than the lowest energy isomer. A C<sub>2v</sub> symmetric tetrahedral isomer, in which the dopant atom has a tetrahedral coordination and the additional Au atom is twofold coordinated with two gold atoms is found to

TABLE I. Geometrical parameters (smallest Au-Au and Au- $M$  bond lengths) of the lowest energy isomers of  $Au_5M$  clusters. The atomic charge on  $M$  atoms obtained through mulliken population analysis is listed in column 5. The multiplicity of the lowest energy isomer is listed in the last column.

System	Symmetry	Au-Au	Au- $M$	Charge on $M$	$2S+1$
$Au_6$	$C_{2v}$	2.67			1
$Au_5Na$	$C_{2v}$	2.60	2.93	+0.853	1
$Au_5Mg$	$C_{2v}$	2.72	2.56	+0.952	2
$Au_5Al$	$C_{4v}$	2.85	2.35	+1.753	1
$Au_5Si$	$C_{3v}$	2.84	2.34	+1.034	2
$Au_5P$	$C_{2v}$	2.74	2.28	+0.249	1
$Au_5S$	$C_{2v}$	2.66	2.33	-0.153	2

be 0.04 eV higher in energy than the lowest energy configuration. These energy differences are within the uncertainty of our current calculations, and hence one cannot distinguish the correct ground state geometry among these three isomers. Moreover, the small energy difference between these isomers indicates a possible structural transition of the  $Au_5Si$  cluster under perturbation of an external field. This trend of forming the three-dimensional structural pattern continues for  $Au_5P$  cluster. The tendency to prefer the three-dimensional structural motifs over planar geometries as we move from Na, Mg to Al, Si, and P can be attributed to the fact that Al, Si, and P, in general, prefer  $sp^3$  hybridized structures, thus nonplanar geometries. Interestingly, for  $Au_5S$  cluster, the trend gets reversed due to the preference of planar structures again. The lowest energy isomer of  $Au_5S$  cluster forms planar triangular structure where S atom occupies the apex site of the triangle, with twofold coordination. It should be pointed out that although  $Au_5Na$  and  $Au_5Mg$  clusters favor planar conformation, the impurity atoms occupy higher coordination site. In fact for  $Au_5S$  cluster with S atom at the fourfold site, similar to that of  $Au_5Na$  and  $Au_5Mg$  isomers, is 1.68 eV higher in energy to that of the lowest energy isomer. The preference of twofold coordination by S and fourfold coordination sites by Na and Mg, for similar structural conformers reflects the bonding of covalent (directional bonding) and metallic bonding (higher coordination), respectively. In this context it may be mentioned that for a covalent bond the electrons align along the bond axis, and therefore, directional in nature. However, for organic molecules which are particularly aromatic in nature, delocalization of electronic wave functions are found across the molecule. Based on the above-discussed points, it can be argued that the structural planarity of the  $Au_5S$  cluster has resulted from the delocalization of electrons over all the constituent atoms.

Since, the binding energy (BE) of a given cluster is a measure of its thermodynamic stability, we have analyzed the stability of these clusters by calculating the BE and the interaction energy of the dopant atom with the  $Au_5$  cluster. The BE of a given cluster is calculated as  $[E(Au_5M) - 5E(Au) - E(M)]$ , while the interaction energy of the dopant atom is defined as  $[E(Au_5M) - E(Au_5) - E(M)]$ . The calculated BE and the interaction energies of

TABLE II. The binding energy  $[BE(Au_5M) = E(Au_5M) - 5E(Au) - E(M)]$ , interaction energy  $[E_{int}(Au_5M) = E(Au_5M) - E(Au_5) - E(M)]$  of  $M$  atoms, and vertical ionization potential  $[VIP = E(Au_5M) - E(Au_5M)^+]$  of the  $Au_5M$  clusters.

System	BE (eV)	$E_{int}$ (eV)	VIP (eV)
$Au_6$	10.92		8.42
$Au_5Na$	11.16	3.21	8.17
$Au_5Mg$	10.65	2.69	6.14
$Au_5Al$	12.83	4.88	7.98
$Au_5Si$	12.69	4.74	6.98
$Au_5P$	11.35	3.39	7.54
$Au_5S$	11.85	3.90	8.29

$Au_5M$  ( $M=Na, Mg, Al, Si, P,$  and  $S$ ) are listed in Table II. The  $Au_5Al$  cluster, being a closed-shell eight electron system (one electron from each Au and three electrons from Al), is found to be the most stable cluster among all the clusters under study, while  $Au_5Mg$  is the least stable. Among the planar clusters,  $Au_5S$  is found to be the most stable cluster. It should be noted that the energy gain in adding a gold atom to  $Au_5$  is 2.97 eV which, with the exception of Mg, is smaller than the energies gained due to the addition of all other dopant atoms. The weaker binding of Mg to Au is due to the filled  $3s^2$  orbital of Mg. It has recently been shown that the strong binding of Au cluster to S can be used for the separation of S-containing amino acids.<sup>36</sup>

In order to understand the nature of chemical bonding in these systems we have plotted the spatial orientation of the highest occupied molecular orbital (HOMO) energy level for all  $Au_5M$  clusters. The spatial orientations of the HOMO energy levels are depicted in Fig. 3. It is found that although  $Au_5Na$ ,  $Au_5Mg$ , and  $Au_5S$  clusters favor planar structures, only in the  $Au_5S$  cluster, the HOMO is strongly delocalized with a contribution from all the atoms in the cluster. It may be argued that the delocalization of electrons and covalent bonding may be contradictory. However, it may be noted that organic aromatic molecules having strong covalent character are known to be extra stabilized by the delocalization of electronic wave function. The electron delocalization observed in the  $Au_5S$  is similar to that reported earlier<sup>18</sup> for  $Au_5Zn^+$  cluster, where the electron delocalization was attributed as one of the factors in stabilizing the planar structure. For  $Au_5Al$ ,  $Au_5Si$ , and  $Au_5P$  clusters which form nonplanar structures, the preference of directional bonding is reflected from the spatial orientation of their molecular orbitals.

Ionization potential (IP) is another parameter, which is used to define the chemical stability of small clusters. The larger the vertical ionization potential (VIP), the deeper is the HOMO energy level, which leads to less reactivity or higher chemical stability. The VIPs of  $Au_5M$  clusters are shown in Fig. 4. It is seen that  $Au_5Mg$  and  $Au_5Si$  clusters have lower VIP in comparison to others. This can be explained based on their odd number of electrons. As expected, the  $Au_5Na$ ,  $Au_5Al$ , and  $Au_5P$  clusters with closed-shell electrons have larger IPs than the clusters with an odd-number of electrons. Remarkably, in contrast to the trends followed by  $Au_5M$  clusters ( $M=Na, Mg, Al, Si,$  and  $P$ ), it is found that  $Au_5S$

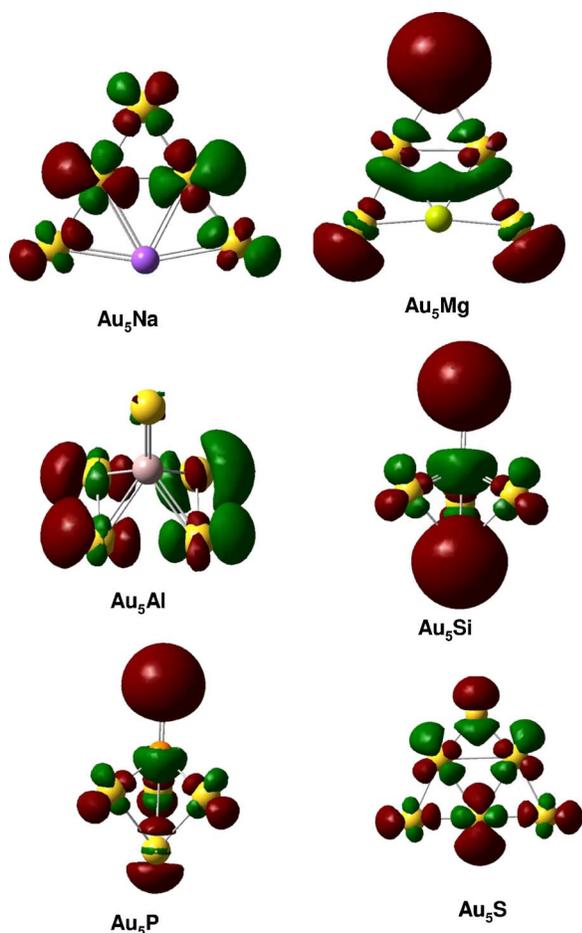


FIG. 3. (Color online) The spatial orientation of the highest occupied molecular orbital of Au<sub>5</sub>M ( $M$ =Na, Mg, Al, Si, P, and S) clusters.

cluster has the largest IP in this series of clusters. At this point it should be emphasized that Au<sub>5</sub>S consists of an odd number of electrons for which the highest occupied molecular orbitals are generally less bound and hence the IP is expected to be lower than the closed-shell clusters. To verify this fact, we have compared the HOMO energy of all these Au<sub>5</sub>M clusters. It is found that the HOMO energy levels follow the trend of the VIP as shown in Fig. 4 leading to the extraordinary stabilization of the HOMO for the Au<sub>5</sub>S cluster. This unusual stability of the Au<sub>5</sub>S cluster is attributed to its structural integrity and strong delocalization of electrons over all the atoms as shown in Fig. 3.

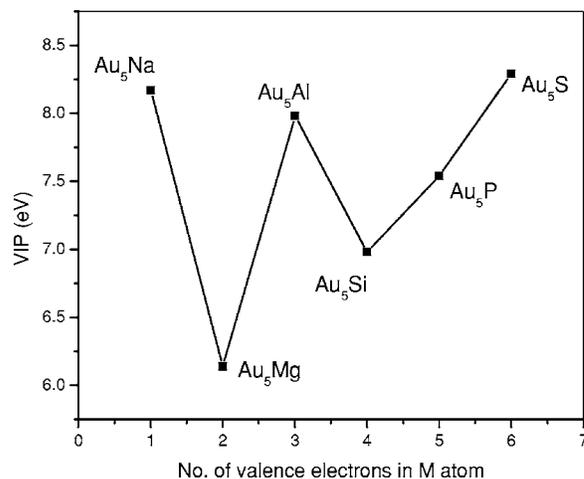


FIG. 4. The variation in the vertical ionization potential of Au<sub>5</sub>M ( $M$ =Na, Mg, Al, Si, P, and S) clusters.

### CONCLUSION

In conclusion, we have calculated the optimized geometries and electronic structures of Au<sub>5</sub>M ( $M$ =Na, Mg, Al, Si, P, and S) clusters using GGA-DFT. While Au<sub>5</sub>Na, Au<sub>5</sub>Mg, and Au<sub>5</sub>S clusters prefer planar triangular structures similar to that of Au<sub>6</sub> cluster, Au<sub>5</sub>Al, Au<sub>5</sub>Si, and Au<sub>5</sub>P clusters have three-dimensional geometries. Based on this structural trend it is inferred that while  $s$ -electron interaction with Au<sub>5</sub> cluster retains the planar configuration of Au<sub>6</sub> cluster, atoms with  $p$ -electrons in the outermost orbital adopt nonplanar configurations. The exception to this trend occurs for Au<sub>5</sub>S cluster, which adopts planar triangular structure where the S atom is placed at the apex position. Moreover, the Au<sub>5</sub>S cluster shows unusually high ionization potential despite being an odd electron system, which in turn reflects the stabilization of the highest occupied energy level. The reason for such behavior of the Au<sub>5</sub>S has been attributed to the structural planarity and the delocalization of electronic wave function over all the atoms at the HOMO energy level.

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