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Conformers of Al_{13}, $Al_{12}M$, and $Al_{13}M$ (M=Cu, Ag, and Au) clusters and their energetics

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The candidate structures for the ground-state geometry of the Al_{13}, $Al_{12}M$, and $Al_{13}M$ (M=Cu, Ag, and Au) clusters are obtained within the spin-polarized density-functional theory with a three-parameter hybrid functional to describe the exchange-correlation effects. Binding energy, vertical ionization potential, vertical electron affinity, and the energy gap between the highest-occupied molecular-orbital level and the lowest-unoccupied molecular-orbital level have been calculated to investigate the stability of these clusters. These results are compared with those of the alkali doped Al_{12} and Al_{13} clusters. The adatom energies (defined as the energy gained upon adding the atom to the host Al_{13} clusters) are found to be substantially larger for the coinage metal atom than those for alkali and Al atoms. The natural population analysis was carried out to get a qualitative picture of the bonding in these clusters.

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I. INTRODUCTION

Cluster physics has been a subject of intense research activities in recent years due to the potential technological applications like fabrication of materials with desired properties [1,2]. Clusters with some particular number of valence electrons show enhanced stability against dissociation. These clusters are termed as magic clusters. Such stable "magic" clusters can be used in the manufacture of novel materials. One of the way to obtain a magic cluster is to dope the pure clusters with a suitable dopant. Recently a few studies, both theoretical as well as experimental, of aluminum clusters doped with alkali metals have been reported [3–9]. These studies have shown that, in general, doping of Al clusters with alkali atoms results in lowering of the ionization potential of pure Al clusters. Some theoretical works have shown that the stability of Al_{13} is found to be enhanced upon doping with single alkali atom [5,8]. This increase in stability upon doping can be rationalized with the help of the spherical jellium model (SJM). The SJM predicts that the clusters with 2, 8, 20, 40,... valence electrons have higher stability due to the closure of electronic shells [10,11]. Pure Al_{13} cluster is a 39 electron system with two energetically degenerate structures. Doping of Al_{13} with a single alkali atom results in the required "magic" number of valence electrons for shell closure. These clusters are found to be ionic, i.e., the bonding can be explained as $Al_{13}^{-}A^{+}$ where A is the alkali metal atom that remains outside the Al cage. It is surmised that such clusters can be used to form extended solids [4].

In this paper, we present our *ab initio* results of the stabilities of Al_{12} and Al_{13} clusters doped with coinage metal atoms. This study is interesting on the account of the similarities and differences of coinage atoms with alkali atoms. The similarities lie in that both alkali and coinage metal atoms have one *s* electron in their outmost shells. Also, the pure clusters of the coinage metal atoms are similar in structure to those of alkali atoms. If these impurities act like monovalent impurity then the $Al_{13}M$ (M=Cu, Ag, and Au) clusters with 40 valence electrons should be particularly stable. On the other hand, 13-atom systems are geometrically stable. Adding an impurity to Al_{12} cluster should make it geometrically more stable. In this case, it is interesting to see the resultant geometry and the bonding. However, in case of the coinage atoms, the *d* electrons may play some role in bonding and also on some electronic properties. For example, the inclusion of *d* electrons in the calculation was found to be necessary for the description of photoabsorption spectra for silver clusters [12]. It is, therefore, interesting to examine the effect of doping the Al_{12} and Al_{13} clusters with a single coinage metal atom on the structure, stability, and electronic properties of the host aluminum clusters, and also to compare the results with their alkali-atom doped counterparts.

In the following section, we briefly outline the computational methodology. The results are presented and discussed in Sec. III.

II. METHODOLOGY AND COMPUTATIONAL DETAILS

The structure optimization and electronic-structure calculation is performed using molecular-orbital approach within the framework of spin-polarized density-functional theory [13]. The geometry optimization was carried out by starting with several-possible ionic configurations for each cluster, including those obtained earlier for Al_nNa using simulated annealing technique [9]. We have employed the LANL2DZ basis set with the small-core relativistic effective-core potential (RECP) due to the Hay and Wadt [14]. The accuracy of this basis set has been established for Al clusters [15]. The relativistic effects are important especially for Au. The use of

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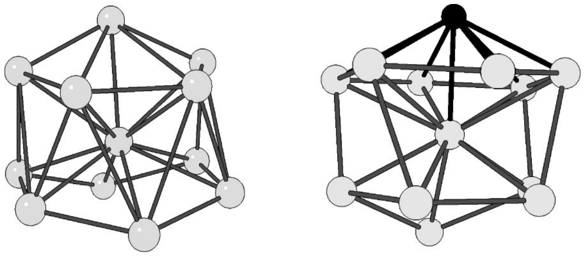

FIG. 1. Lowest-energy structure of the Al_{12} and $Al_{12}Cu$ clusters. The dark circle represents the impurity atom. The structures of the lowest-energy $Al_{12}Ag$ and $Al_{12}Au$ are similar to that of $Al_{12}Cu$.

small-core RECP is found to provide the results that are in excellent agreement with all-electron relativistic calculation for Au and its compounds [16]. The *d* electrons along with the outermost core *s* and *p* electrons were treated on equal footing with the valence electrons in all the three impurity atoms. The exchange-correlation effects were described by the Becke's three-parameter functional, which uses part of Hartree-Fock exchange [but calculated using Kohn-Sham (KS) orbitals] and Becke-exchange functional [17] in conjunction with the Lee-Yang-Parr [18] (B3LYP) functional for correlation. This approach is based on the adiabatic connection method, and at present, is one of the most powerful density-functional scheme that provides results close to those obtained by most refined post-Hartree-Fock methods [19]. The optimization was performed for the two lowest values of spin multiplicities for each cluster, multiplicity being 1 for clusters with even number of electrons and 2 for the odd electron clusters. However, for clusters containing Cu impurity, the search was carried out for the lowest four values of spin multiplicity. All calculations are carried out using GAUSSIAN98 [20] suite of programs.

III. RESULTS AND DISCUSSION

We fist discuss the geometries of pure Al_{12} and pure Al_{13} clusters. Although there exist quite a few studies of structures of these clusters, there are differences concerning the lowest-energy structure of Al_{13}. Since this is crucial for the determination of the structures of doped clusters and for the adsorption energy of the impurity atom, we have also carried out the geometry optimization for these clusters at the B3LYP/LANL2DZ level of theory. The lowest-energy[1] structure of Al_{12} is shown in Fig. 1 and is in agreement with that obtained by Rao and Jena [15]. The 13 atom clusters are interesting because they have geometrical shell closure. Some earlier calculations were performed assuming the geometry to be an icosahedron. It was shown by Rao and Jena [8] that the decahedral structure is also an energetically degenerate structure for Al_{13}. In the present calculation, an icosahedron, a decahedron, and a cubotahedron structure were used as starting geometries for Al_{13}. At B3LYP/LANL2DZ level of theory, we find the decahedral structure to be the lowest-energy structure for Al_{13}. The distorted icosahedron is a low-lying isomer, 0.41 eV above the decahedron, while cuboctahedral structure is higher in energy by 0.98 eV. This order of isomers agrees with those reported at a lower level of theory (BPW91/LANL2DZ) by Rao and Jena [8]. They found the decahedral structure to be lower than the icosahedral one with similar energy difference (0.43 eV). The all-electron calculation by them, however, showed the icosahedral structure to be preferred over the decahedral one. Similar results were reported by several other groups [21]. Rao and Jena [8], however, concluded that the decahedral structure to be the lowest-energy structure on the basis of comparison of theoretical ionization potential with the experimental one. Our all-electron calculations (B3LYP/6-311G**) of various isomers of Al_{13} cluster also confirms this order of isomers.

The optimization of the $Al_{12}M$ (M=Cu, Ag, and Au) clusters were carried out starting with the geometry of the Al_{13} clusters where one peripheral atom was replaced by the impurity atom. The same procedure was repeated by replacing the central Al atom by the impurity. We also carried out the optimization starting with the geometry of the $Al_{12}Na$ obtained earlier [9] by simulated annealing technique with the alkali atom replaced by the impurity atom. The lowest-energy structures of the $Al_{12}M$ clusters are similar and, therefore, only that of $Al_{12}Cu$ is presented in Fig. 1. Several earlier calculations have considered geometrically stable icosahedral structures with the dopant atom at the center [22]. However, in case of $Al_{12}A$, where *A* is an alkali atom, the structure is totally different. In this case the alkali atom resides on the surface of the Al_{12} cage [3,9]. Our results also show that in the present case of $Al_{12}M$ (for M=Cu, Ag, and Au), the lowest-energy structure has the impurity atom on its surface. However, unlike the case of alkali-atom doped Al_{12} clusters, the structures with impurity atom at the center of icosahedron are stable, i.e., the impurity atom remains inside the cage of Al atoms. This icosahedral structure with the coinage metal atom at near center position is higher in energy than the lowest-energy structure by 0.14, 0.40, and 0.65 eV for Cu, Ag, and Au, respectively.

An interesting feature of doping with an alkali atom is the lowering of the ionization potential of the pure Al clusters [3,6]. We have calculated the vertical ionization potentials (VIP's) of these clusters and compared them with that of pure Al_{12} clusters. The values are presented in Table I. In this case also the ionization potential of the pure Al cluster is lowered upon doping with the coinage metal atoms (except for $Al_{12}Cu$ isomers). Amongst the lowest-energy structures, the lowering of IP is maximum for Ag impurity (0.64 eV), while it is comparable for Cu (0.47 eV) and Au (0.44 eV). Thus, in the case of Al_{12}, the doping with coinage metal atom mimics that of alkali atoms. For the sake of comparison, we also present the VIP's for the icosahedral structures in which the impurity atom occupies an internal position near the center. The VIP's for these positions are higher than for surface positions, except for $Al_{12}Au$, in which case the values are same for both the positions of the impurity atom. In the same table, we also present the binding energies (BE) per

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[1] By lowest-energy structures, we mean, the ionic configurations corresponding to the lowest energy in the present (not exhaustive) search.

TABLE I. The values of vertical ionization potentials, binding energies, adsorption energies, and the HOMO-LUMO gap of Al_{12} and $Al_{12}M$ (M=Cu, Ag, and Au) in eV. "Ico" in the structure column refers to the icosahedral structure. The "central" in the position column refers to a near-center position of the impurity atom.

System	Structure	Position	vIP	BE	E_{ad}	Gap
Al_{12}			6.43	1.59		
$Al_{12}Cu$	Ico	Central	6.41	1.73	1.90	1.52
$Al_{12}Cu$		Surface	5.96	1.74	2.00	1.65
$Al_{12}Ag$	Ico	Central	6.30	1.61	0.37	1.02
$Al_{12}Ag$		Surface	5.79	1.69	1.36	1.59
$Al_{12}Au$	Ico	Central	5.99	1.71	1.60	1.09
$Al_{12}Au$		Surface	5.99	1.76	2.21	1.57

atom, the adsorption energy E_{ad} of the impurity and the energy difference between the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO). The BE is maximum for $Al_{12}Au$ and is the least for the silver-doped cluster. From the BE values it can be seen that impurity on the surface makes the cluster structurally more stable than when it occupies an internal position. The adsorption energy values follow the same trend shown by the BE values with the highest value for Au and the lowest value for Ag. The HOMO-LUMO gap indicates the reactivity of the clusters, in that, the clusters with higher HOMO-LUMO gap are less reactive. Table I shows that the Cu-doped cluster is less reactive than the other two. The energetics show that Au- and Cu-doped Al_{12} clusters are structurally more stable than that doped with silver.

The optimized lowest-energy structures of the $Al_{13}Cu$, $Al_{13}Ag$, and $Al_{13}Au$ are shown in Fig. 2. The optimization was carried out for each of decahedral and icosahedral structures putting the impurity atom at a peripheral position and was repeated again by keeping the impurity atom at the center. The icosahedral structure capped by impurity, which is a stable isomer for $Al_{13}A$ with A being alkali atom other than Rubidium, is not found to be stable in the present work. This structure upon optimization transforms to the impurity-capped decahedral structure. Although we refer to these structures as capped decahedral or icosahedral, they are distorted during the optimization. This distortion is mild for the structures containing decahedral cage. The icosahedral-like structure with impurity near center are significantly distorted in comparison with the capped icosahedral Al_{14} structure. Further, similar to $Al_{12}M$ and unlike $Al_{13}A$ (A is an alkali atom) we find that the structures with an impurity at or near the center of the decahedron or icosahedron to be stable in the sense that it does not transform to any other structure upon optimization. In general, the energy differences between the various isomers are very small.

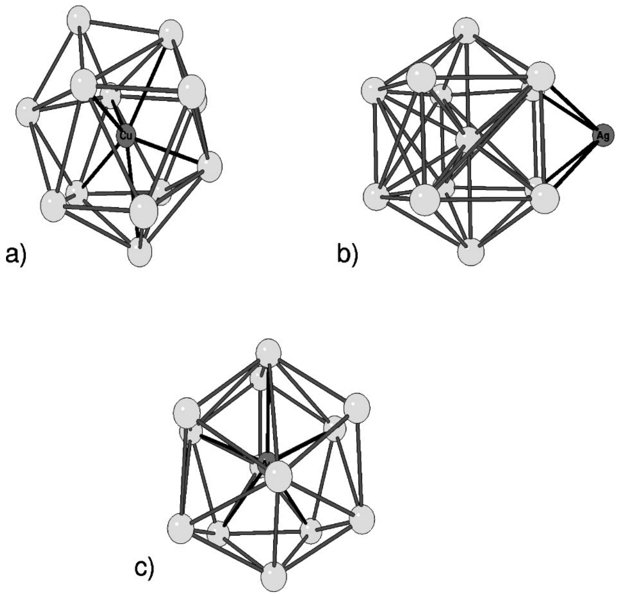

FIG. 2. The lowest-energy structures of (a) $Al_{13}Cu$, (b) $Al_{13}Ag$, and (c) $Al_{13}Au$ respectively (beginning from upper left). The impurity atom is shown as a dark circle.

The decahedron and icosahedron structures of $Al_{13}Cu$ with Cu at the center are energetically degenerate. The third isomer has Cu lying on the surface of the decahedral cage and is higher in energy by 0.75 eV than the other two. In case of $Al_{13}Ag$, the lowest-energy structure has the Ag atom capping the decahedral cage of Al atoms. The structures with the Ag atom at center of decahedron- and icosahedron-like structures are higher in energy by 0.41 and 0.2 eV, respectively. The lowest-energy structures for $Al_{13}Au$ has Au atom sitting inside the icosahedral-like cage of Al atoms. This cluster has two energetically nearly degenerate isomers that are higher than the lowest-energy isomer by 0.21 eV. One of them is decahedral in form with Au occupying inner position, while the other one has Au at a peripheral or surface position. The energy difference between these two structures are very small, ~0.005 eV. Thus, although coinage metal atoms, similar to alkali atoms, have larger ionic radii than the host Al atoms, the structures wherein a coinage atom occupies near-central position in the cage of Al atoms are not only stable but also are candidates for the lowest-energy structures. Further, the energy differences between the various isomers (except for the Cu capping the decahedral cage of Al_{13}) being small, these clusters can be said to be energetically degenerate at the accuracy of the present B3LYP/LANL2DZ level of theory.

The VIP, vertical electron affinity (VEA), binding energy, adsorption energy, and the HOMO-LUMO gap calculated for

TABLE II. The values of binding energies, adsorption energies, vertical ionization potentials, vertical electron affinities, and the HOMO-LUMO gap of Al_{13} and $Al_{13}M$ (M=Cu, Ag, and Au) in eV. "Ico" and "Dec" in the structure column refer to the icosahedral and decahedral structures, respectively and "central" in the position column refers to a near-center position of the impurity atom.

System	Structure	Position	BE	E_{ad}	vIP	vEA	Gap
Al_{13}	Dec		1.72		6.43		1.83
$Al_{13}Cu$	Dec	Central	1.88	3.86	7.20	1.82	2.30
$Al_{13}Cu$	Dec	Surface	1.82	3.12	6.51	1.41	2.40
$Al_{13}Cu$	Ico	Central	1.88	3.86	6.50	1.83	2.30
$Al_{13}Ag$	Dec	Central	1.75	2.07	6.30	1.93	1.99
$Al_{13}Ag$	Dec	Surface	1.78	2.48	6.57	1.01	2.40
$Al_{13}Ag$	Ico	Central	1.76	2.28	6.30	1.99	2.02
$Al_{13}Au$	Dec	Central	1.84	3.38	6.30	1.91	2.10
$Al_{13}Au$	Dec	Surface	1.84	3.38	6.36	1.28	2.20
$Al_{13}Au$	Ico	Central	1.86	3.59	6.40	1.98	2.10

these structures are given in Table II. It is evident from the binding energies per atom shown in the table that the $Al_{13}Cu$ clusters are the most stable, followed by $Al_{13}Au$ clusters. The BE energies of these clusters are larger than the BE of Al_{13} and also of Al_{14}(1.75 eV). The values of adsorption energies, which is the energy gained upon the addition of the impurity atom M to the $Al_{13}M$ clusters, are significantly large especially for the structures wherein Au and Cu impurity occupy internal position and indicate the enhanced stability of these clusters. These values are larger than the adsorption energies of alkali atoms in $Al_{13}A$ clusters [8]. The difference would be actually further large as the adsorption energies of alkali atoms in Ref. [8] are calculated at BPW91/LANL2DZ level, which is likely to overestimate the energies than the B3LYP/LANL2DZ level of theory used in the present calculation. For example, the BE of the decahedral structure of Al_{13}, calculated at BPW91/LAN2DZ level of theory is 2.12 eV, while B3LYP/LANL2DZ yields 1.72 eV. The ionization potential of the lowest-energy clusters of pure Al_{13} is 6.43 eV. This value is comparable to the IP of $Al_{13}M$ clusters and it is difficult to say if the doping increases or decreases the IP of Al_{13} clusters. Rao and Jena also have similar conclusion about the decrease/increase in IP of Al_{13} upon doping with alkali atoms [8]. The effect of doping Al_{13} with a coinage metal atom (M=Cu, Ag, and Au) upon the VIP and also on structure is different than doping it with alkali atom. The values of VEA suggests that clusters with the impurity atom at the center have high electron affinity, while that of those with the impurity on the surface is significantly lower. However such a clear trend is not seen in the VIP values except in $Al_{13}Ag$. The other point to be noted from the Table II is that the clusters with M atom on the periphery also have larger HOMO-LUMO gap than their isomers with impurity atom M at or near the center, indicating the lower reactivity of the $Al_{13}M$ clusters with M at periphery. This difference is especially prominent between $Al_{13}Ag$ decahedral structure capped by Ag and its isomers. The former structure, which also corresponds to the lowest-energy structure of $Al_{13}Ag$, has the HOMO LUMO larger by 0.3–0.4 than its isomers. It has the highest VIP and the lowest VEA. This structure is, therefore, chemically least reactive amongst all the $Al_{13}M$ clusters. The difference in VIP of the lowest-energy structure of $Al_{13}Ag$ and its isomers is about 0.27 eV. Thus, an accurate experimental measurement of the VIP performed at sufficiently low temperature can distinguish between the isomers of $Al_{13}Ag$. Such a correlation between the HOMO-LUMO gap, VEA, and BE is not seen for $Al_{13}Cu$ and $Al_{13}Au$ clusters. It can be pointed out here that the values of VIP of the $Al_{13}Cu$ with Cu at the central positions of the decahedral and the icosahedral structures are widely different while their total energies are degenerate. An experimental measurement of the ionization potential can help in selecting the lowest-energy structure in this case.

The Mulliken population analysis [23] and natural population analysis (NPA) [24] have been carried out to get some idea about the charge transfer between the impurity atom M and the host Al atoms in both $Al_{12}M$ and $Al_{13}M$ clusters. Such type of analysis is arbitrary but is useful in getting qualitative information about charge distribution. We present the charges calculated by NPA scheme as it is found to provide more realistic description of covalent as well as ionic systems with an additional advantage of being also relatively less basis-set dependent when compared with Mulliken scheme [24]. In the present case, we find that Mulliken population analysis puts relatively more negative charge on impurity atoms that is somewhat unrealistic. The charge on impurity atom M obtained by NPA scheme is given in Table III. In case of $Al_{12}M$, for all cases of M except for $Al_{12}Au$ with Au at center, the charge $q(M)$ on M is positive indicating transfer of charge from the impurity atom to the Al cage. The charge transfer is more when the impurity is on the surface. This is similar to the case of alkali-doped Al clusters where the charge transfer takes place from the impurity to the host. The bonding in this case can be taken as $Al_{12}^{-}M^{+}$ similar to the case of alkali-doped Al_{13} clusters. Similar trends are also seen in $Al_{13}M$ clusters again with the exception of $Al_{13}Au$ with Au at the center. For the structures wherein the impurity atom is on the surface, the charge on the central Al atom is roughly −1.54, and is of the similar (−1.6) magnitude of the charge on central Al atom in Al_{13} and $Al_{13}A$ (A≡alkali at-

TABLE III. The charges on the impurity atom in the $Al_{12}M$ and $Al_{13}M$ (M=Cu, Ag, and Au) clusters obtained by natural population analysis.

System	Str.	Position	$q(M)$	System	Str.	Position	$q(M)$
$Al_{12}Cu$	Ico	Central	0.16	$Al_{13}Cu$	Ico	Central	0.04
				$Al_{13}Cu$	Dec	Central	0.04
$Al_{12}Cu$		Surface	0.60	$Al_{13}Cu$	Dec	Surface	0.47
$Al_{12}Ag$	Ico	Central	0.20	$Al_{13}Ag$	Ico	Central	0.05
				$Al_{13}Ag$	Dec	Central	0.10
$Al_{12}Ag$		Surface	0.59	$Al_{13}Ag$	Dec	Surface	0.50
$Al_{12}Au$	Ico	Central	−0.38	$Al_{13}Au$	Ico	Central	−0.43
				$Al_{13}Au$	Dec	Central	−0.37
$Al_{12}Au$		Surface	0.21	$Al_{13}Au$	Dec	Surface	0.11

oms). Thus the charge transfer mainly takes place from the impurity atom to the outer Al atoms. On the other hand, the clusters with impurity at center have very small charge transfer. The ‘‘natural’’ electronic configuration of atoms (not presented) shows that in the clusters with impurity on surface, the charge transfer occurs from impurity to outer Al atoms, while for clusters with impurity atom at center, the higher p orbitals ($4p$, $5p$, and $6p$ for Cu, Ag, and Au) of impurity are populated with charge depleted from the outermost occupied s level. The bonding in the case of impurity atom on surface is, therefore, ionic type and for the clusters with impurity at center seems to be due to sharing of charge. The amount of charge transfer is of similar magnitude for Ag and Cu impurity, which may be due to the similar ionization potentials (7.73 eV for Cu and 7.58 for Ag [25]) of these atoms. The ionization potential of Au atom, on the other hand, is 9.22 eV [25]. The rather large electronegativity of the Au atom may be responsible for the large negative charge on the Au atom in the central position in both Al_{12} and Al_{13} clusters. In this case the charge transfer is reversed. The bonding with the Au atom is different from the other two impurities. The charge transfer from Au is relatively small when Au resides on the surface. However, the bond strength for AlAu is largest followed by AlCu and AlAg. The ionic radius of Ag is larger than Al, while it is comparable for Cu and Au [25]. The Ag atom due to its larger size prefer to be on the surface, while Cu and Au tend to occupy near-central position in Al_{13} clusters. This argument, however, does not explain why Cu and Au prefers to be on the surface in Al_{12} clusters. As the energy difference between the different structures are small it seems that the stability is governed by a somewhat intricate balance of all these factors.

To summarize, we have investigated the effect of doping Al_{12} and Al_{13} clusters with a coinage atom impurity. We have calculated the candidate structures for the ground-state geometry of these clusters together with the binding energies, the VIP’s and the VEA’s. It is found that the lowest-energy structure for $Al_{12}M$ have impurity atom M on the surface. The doping with coinage metal atom M reduces the VIP of host Al_{12} clusters. The effect of doping on Al_{13} clusters by a coinage metal atom is different from the doping with alkali atom. Unlike $Al_{13}A$ ($A\equiv$alkali-metal atom), the $Al_{13}M$ clusters with M atom at near central position are stable and are candidate structures for the ground-state geometry. The natural population analysis shows that bonding nature in these clusters is ionic type for the clusters with impurity on surface and, therefore, similar to that seen in alkali-doped Al_{13} clusters. The coinage metal-atom doped Al_{13} clusters with impurity atom at center shows nature of bonding to be more of shared-type than the ionic type. The large values of adsorption energies together with large values of the HOMO-LUMO gap and low values of VEA’s for $Al_{13}M$ clusters are due to the electronic shell closure and are indicative of chemical inertness of these clusters. These clusters, therefore, are possible candidates for forming the cluster-assembled novel materials.

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