

Doped Quantum Sized Gold Nanoclusters

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Abstract We have carried a combined Gupta (GP) potential and Density Functional Theory (DFT) study of endohedral doped tubular Au₂₄ cage with transition metal M (M=Au, Cu and Ag). The GP calculation predicts that endohedral Au doping makes the Au₂₄ cage more stable as compared to Cu and Ag atoms doping. However, DFT results predict that the Cu doped Au cage is more stable. The difference in the results of the two approaches can be explained by the observation that GP favors Au-Au bonding over Cu-Au and Ag-Au bonds. The study indicates that for the application of GP to small binary gold clusters its careful re-parameterization is called for.

Keywords: Doped Gold Clusters, Gupta Potential (GP), Density Functional Theory (DFT)

I. INTRODUCTION

Binary nanoclusters often present novel and interesting structures which are important to understand their chemical and physical properties. At present, a systematic search for global minimum (GM) structures for clusters involving more than 20 atoms is still extremely demanding for high-level calculations because of computational limitations in exploring vast areas of configuration space [1-3]. Empirical and semi empirical potentials have been developed to overcome such computational limitations. These potentials are believed to be suitable for modeling noble metals. It is, thus, important to check the predictions made by these potentials. An analysis in terms of structural families is particularly meaningful, as it allows one to roughly predict the order of stability among

structural motifs on the basis of a minimal number of calculations. Gold clusters Au_n exhibit intriguing geometrical structures and size-dependent evolution. They favor the two-dimensional planar structures up to $n = 13$, a perfect tetrahedron at $n=20$, tubular structures at $n = 24$ and 26 [4, 5]. The possibility to form a hollow tubular Au_n cluster by closing a segment of the SWGNT (Single Wall Gold Nanotube) has opened the possibilities of new stable doped structures in competition with other possible structures. The structural and magnetic properties of the tubular Au₂₄ doped with different 3d transition-metal atoms M (M = V, Cr, Mn, Fe, Co, and Ni) have been studied by Yang et al. using scalar relativistic DFT calculations. It is found that all of the M@Au₂₄ clusters retain their tubular structure while the dopant atom is located at the center of the Au₂₄ cluster [6].

The transition bimetallic clusters, particularly of Au, Ag, and Cu, have received much attention because of their particular physical and chemical properties and potential technological applications in solid-state chemistry, materials science, nanotechnology, catalysis, biology, and medicine. [7-9]. Structural and electronic properties of M₂⁻ doped Au_n (M = Ag, Cu; $n = 1-10$) clusters have been studied by Zhao et al. [10]. Although a number of studies have been carried out on gold clusters doped with Ag and Cu atoms, they are confined to a smaller size range. Also there is limited literature available on combining different approaches i.e., Semi empirical and Ab initio, to study Gold clusters and their doping. We have chosen Au₂₄ tubular cages for doping with

Cu and Ag atoms as these cages have already been studied by us [11]. In the present work, we study the endohedral doping of Au₂₄ tubular cage with transition metal (Au, Cu, Ag) and their effect on its structural stability by using an effective atom-atom potential, GP as well as DFT.

Our paper is organized as follows. The work done by Density Functional Theory (DFT) is discussed in Sec. 2. Details of work done by Semi empirical approach i.e. Gupta potential are presented in Sec. 3, starting with the analysis of the stability Au₂₄-II pure gold cages. Effect of doping is then studied and discussed. Lastly, our conclusions are summarized.

2. Calculations using Density Functional Theory (DFT)

2.1 Ab-initio approach

For DFT calculations, we have used the well known Spanish Initiative for Electronic Simulation with Thousands of Atoms computational code, SIESTA, based on Density Functional theory method. The electron density functional is treated by the generalized gradient approximation (GGA) with exchange correlation functional parameterized by Perdew, Zunger and Ernzerhof (PBE) scheme [16, 17]. Relativistic pseudo potentials are used for Au, Ag, and Cu atoms. The symmetry unrestricted geometry optimization is carried out using conjugate gradient and all the forces are less than 0.01eV/Å. We have verified the computational procedure by calculating the ionization potential (IP) for a gold atom and performing test calculations on Au₂ using DFT. The IP of the gold atom is found to be 8.90 eV which is in fair agreement with the experimental value of 9.22eV [18]. The calculated bond length for the Au-Cu dimer and Au-Ag dimer from DFT and GP are presented in Table 1. These numbers are in good agreement with experimental values [20, 21].

S. No.	Dimer	E _b (eV)	E _b (eV)		Bond length (Å) [20, 21]	Bond length (Å)	
			DFT	GP		DFT	GP
		Literature			Experimental		
1	Au-Cu	1.15** [20, 21]	1.590	1.6719	2.33	2.37	2.23
2	Au-Ag	1.92* [22]	1.429	1.8632	2.50	2.56	2.37

** Experimental value

* Theoretical value

Table1. The calculated bond length for the Au-Cu dimer and Au-Ag dimer from DFT and GP are presented in Table 1, in comparison with experimental and theoretical values, where E_b is average binding energy per atom.

2.2 Results and Discussions

2.2.1. Results from Density Functional theory (DFT)

The two initial structures of Au₂₄ tube i.e., Au₂₄-I and Au₂₄-II which have D_{3d} and D_{3h} symmetries respectively and which differ only in the relative orientation of the two triangular layers at each end are optimized using DFT amongst which Au₂₄-II has slightly higher binding energy (0.01 eV) compared to Au₂₄-I cage. Therefore we have considered only the Au₂₄-II structure for doping. The resultant optimized geometries are given in Fig. 1, and are the same as obtained by Gupta potential.

In case of M₁@ Au₂₄-II (M =Ag, Cu, Au) it is observed that doping with a single guest atom does not alter the host cage in any way and the guest atom just occupies the available empty space in the geometric centre of the cluster. For M₂@ Au₂₄-II, with the introduction of two guest atoms (M = Cu, Ag, Au) they occupy endohedral positions almost collinear with the axis of the cluster, which can now be called cage like as far as host gold atoms are concerned. The triangular layers adjacent to the central hexagon have now become hexagonal. Thus the gold atoms constitute a tube with three hexagonal layers and

triangular en caps. The guest atoms occupy symmetric positions along the tube axis. With three guest atoms introduced $M_3@ Au_{24-II}$, the host cage attains some distortion. However, the structure can still be described as core-shell type. The row of Cu atoms bends the host shell, whereas for three atoms Au or Ag doping, the third dopant atom becomes part of one of the caps (end layer).

Thus according to our DFT calculations, doping of Au and Ag guest atoms has not changed the binding energy of pure gold cage and core shell structure is appreciably maintained. The Cu doped Au_{24} clusters are found to be the most stable. These results are in agreement with the other DFT studies [10].

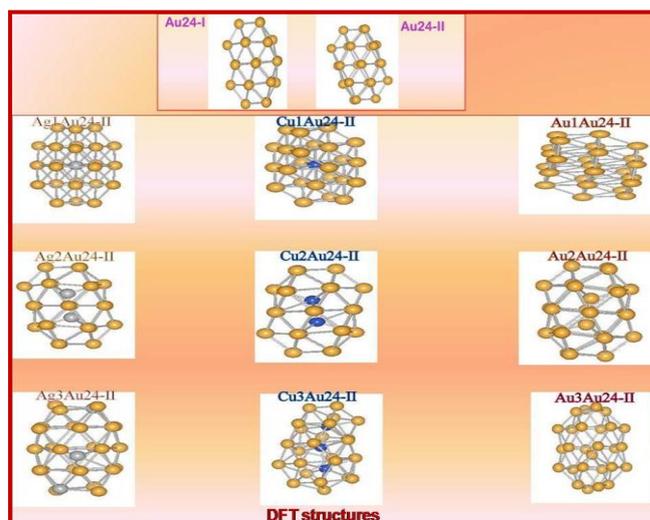


Table 2. Binding energy per atom (E_b) and bond lengths (R_{Au-Au} & R_{M-M}) of $M_n@ Au_{24-I, II}$ ($M = Ag, Cu$ and Au) clusters

Fig1: The optimized geometries of $M@ Au_{24}$ where M is Au, Cu and Ag . The yellow ball represents Au atom, grey ball is Ag atom and blue ball represents Cu atom.

Cluster	E_b (eV)	R (Å)	
		Au-Au	M - M
Au_{24-II}	3.045	2.73-2.84	---
Au_1Au_{24-II}	3.058	---	---
Au_2Au_{24-II}	3.041	2.70-2.95	2.688
Au_3Au_{24-II}	3.067	2.72-2.89	No bonds
Cu_1Au_{24-II}	3.085	2.76- 2.85	---
Cu_2Au_{24-II}	3.109	2.77-2.88	2.40
Cu_3Au_{24-II}	3.156	2.73-2.91	2.59-2.64
Ag_1Au_{24-II}	3.054	2.74- 2.91	---
Ag_2Au_{24-II}	3.044	2.75-2.97	2.81
Ag_3Au_{24-II}	3.047	2.75-2.83	3.97-5.49

2.2.2. Bond length

The ranges of bond distances between Au-Au atoms in doped gold cages are almost same as the empty gold cage while the bond distance of Ag-Ag atom is larger than that of Cu-Cu atom given in Table 2. In Ag_3Au_{24} , the Ag -Ag bond distances have become greater than the interlayer (hexagons along the length of the Au_{24} tube) distances of the original cage and Ag atoms have come out on the surface of the cage. Similar size mismatch can be observed in case of Au_3Au_{24} clusters where Au atoms have come out of the cage. The distance between the Cu atoms in $M@Au_{24-II}$ structures is comparable with the interlayer distance Au-Au atoms. Hence it can be inferred that Cu atoms are more suitable for endohedral doping in the Au tubular cage. Similar prediction can be made after observing the binding energy (BE) values provided in Table 2.

3. Calculations using Model Potential

3.1 Theory and Computational Details

Gupta potential (GP) [12] was adopted to describe the interatomic interactions which is a many body potential developed on the basis of second moment approximation of the tight binding or linear combination of atomic orbitals (LCAO) scheme. This is a very ‘chemical’ point of view as it is related in a natural way to yield the metallic character of cohesive energy. The total energy of the system is written as eqn.1

$$V = \sum_{i=1}^N \left[\sum_{j=1}^N A \exp \left(-p \left[\frac{r_{ij}}{r_0} - 1 \right] \right) - \sqrt{\sum_{j=1}^N \xi^2 \exp \left(-2q \left[\frac{r_{ij}}{r_0} - 1 \right] \right)} \right] \quad (1)$$

where r_{ij} is the distance between atoms i and j . r_0 is the bulk first neighbor distance. A , p , q and ξ are parameters fitted to experimental values of the cohesive energy, lattice parameters, and independent elastic constants for the crystal structure at 0K. For GP the parameters for Au-Au, Au-Cu and Au-Ag clusters are taken from the literature [13-15]. The appropriateness of this potential to describe transition and noble metal structures is well recognized [15].

Energy per atom is calculated using the potential in eq.1 and the total energy is given by eq. 2.

$$U = \frac{1}{2} \sum_{ij} V(r_{ij}) \quad (2)$$

3.2 Results from Gupta Potential

3.2.1 Pure gold clusters

The same structures discussed in DFT study will now be optimized using GP. Out of the two cages, Au_{24-II} is slightly more stable than Au_{24-I} cage. The difference in binding energy per atom is 0.006 eV. This signifies that the orientation of the end capping is important only marginally in determining the stability of the structure. One major difference observed in the optimized structures using GP (fig. 2) as compared to DFT structures in fig. 1, is their distortion.

After optimization, the triangular layers adjacent to the caps are no longer planar. The structure looks like a buckled or caved in tube.

Cluster	E_b (eV)	R (A°)	
		Au-Au	M - M
Au_{24-II}	1.6668	2.63 -2.91
Au_1Au_{24-II}	1.6813	2.68-2.94
Au_2Au_{24-II}	1.6853	2.59 -2.88	2.79
Au_3Au_{24-II}	1.6847	2.63 -2.98	2.81-2.98
Cu_1Au_{24-II}	1.5244	2.48- 2.59 (1)
Cu_2Au_{24-II}	1.528	2.39- 2.79	3.97
Cu_3Au_{24-II}	1.524	2.38- 2.63	2.42 - 2.48
Ag_1Au_{24-II}	1.4702	2.71 -2.89
Ag_2Au_{24-II}	1.4732	2.61 - 2.88	2.79
Ag_3Au_{24-II}	1.4711	2.60 - 2.89	2.67 -2.74

Table 4. Average Binding Energy per Atom (E_b) for $M_n @ Au_{24-II}$ ($M = Au, Cu, Ag$) cages, Average Distances of Dopants from the bonded Au atoms in the shell (R) using GP

3.2.2 Doped Au_{24-II} cage ($M_n @ Au_{24-II}$) - Structures compared with DFT

In case of $M_1 @ Au_{24-II}$ ($M = Ag, Cu, Au$) it is observed that doping with a single guest atom does not alter the host cage and the guest atom just occupies the available empty space in the geometric centre of the Au_{24-II} tubular cluster similar to the DFT result. For $M_2 @ Au_{24-II}$, with the introduction of two guest atoms ($M = Cu, Ag, Au$) Ag and Au occupy endohedral positions almost collinear with the axis of the cluster, which can now be called cage like as far as host gold atoms are concerned. For Cu atoms the host Au cage is somewhat distorted. The triangular layers adjacent to the central hexagon have now become hexagonal. Thus the gold atoms constitute a tube with three hexagonal layers (centre not occupied), which

now contain a line of guest atoms. With three guest atoms introduced $M_3@Au_{24-II}$, the host cage attains some distortion. However, the structure can still be described as a core shell type. The row of Ag atoms bends the host shell, whereas for three atom Au or Cu doping, the third dopant atom becomes part of one of the caps (end layer).

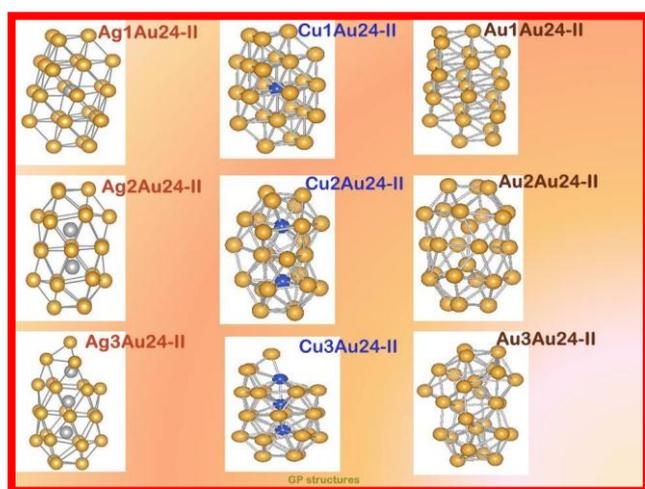


Fig 2: The optimized geometries of $M_n@Au_{24-II}$ where M is Ag, Au, Cu and n = 1-3.

The yellow ball represents Au atom, grey ball is Ag atom and blue ball represents Cu atom.

3.2.3. Remarks for both approaches

At the end we can comment that though the trend in binding energies of the $M@Au_{24}$ clusters differs in both GP and DFT calculations, the structural predictions are quite in agreement quantitatively with each other. The gupta parameters used for Au-Ag and Au-Cu were earlier applied to Au-Ag and Au-Cu alloys and were not tested for small clusters. The discrepancies in the binding energy values calculated from GP can be explained due to the above reason. But our results suggest that by careful re-parameterization of gupta parameters the results can be improved.

4. CONCLUSION

We have performed a comparative study of the structures and binding energy values from DFT and GP calculations of M_nAu_{24} clusters (M= Au, Cu, Ag, n= 1- 3). The two approaches give different results in terms of favoring the choice of dopant atoms. There is considerable difference in the stability prediction of doped cluster as per binding energy is concerned but the structural changes predicted by both approaches are somewhat similar. The GP favors Au doping while DFT study prefers Cu atom doping in gold tubular cages. Our study signifies in order to give accurate results from GP we need to do its careful reparameterization for its application to binary gold clusters.

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