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Understanding the Reactivity Properties of Au_n ($6 \leq n \leq 13$) Clusters Using Density Functional Theory Based Reactivity Descriptors

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Relativistic density functional theory (DFT) based calculations have been performed on gold clusters with six to thirteen atoms (Au_n ; $n = 6–13$). The ground state geometries of these clusters as obtained from our calculations are presented and discussed. This work proposes that atoms in a ground state conformation can be classified into distinct types of reactive sites in a given geometry. Based on symmetry, susceptibility of various types of reactive sites in the ground state geometry toward an impending electrophilic and/or a nucleophilic attack has also been studied using DFT based reactivity descriptors. The studies have also been extended to high energy isomers in these cluster sizes. The reactivity of various sites as a function of cluster size and shape was thus analyzed. The study shows that as a general rule the size and shape of the cluster influences the number and position of available sites for an electrophilic and/or nucleophilic attack. This makes the reactivity patterns of these clusters highly complex. The study also highlights as to how for a cluster with seven atoms (Au_7) various conformations are likely to coexist indicating that the reactivity patterns of various high energy conformations are also important while dealing with small sized Au clusters.

I. Introduction

Gold clusters with six atoms and above exhibit different chemical properties as compared to their bulk counterpart. Some of the unique properties observed in these gold clusters are high catalytic activity,^{1–4} better response properties,^{5–7} and different melting behavior,⁸ to name a few. The first two distinct properties have led to an exponential amount research on their applications in the areas of material science,⁹ medicine,¹⁰ and especially catalysis.^{11–15} Although it was well-known that the catalytic properties of the nanoclusters vary with the size of the cluster, what came as a surprise in the subnanocluster size range (clusters with 2–100 atoms) is the fact that addition or removal each atom is seen to alter these properties dramatically. The results varied depending upon the support, host molecule, geometry, and shape of the Au clusters. A detailed analysis of these aspects has been discussed in one of the recent reviews.¹⁶ Hence, several theoretical^{17–30} and experimental studies in conjunction with theoretical calculations^{30–33} were carried out to understand the structural and electronic properties of Au clusters as a function of size and charge. These reports have brought out interesting and sometimes conflicting details on the lowest energy structure and reactivity trends for small Au clusters. One of the most debated issues has been the exact cluster size where the 2D–3D transition occurs in Au clusters. This transition is seen to be at a much larger cluster size range as compared to that of Pt, Pd, Ag, and Cu clusters.^{34–36} Ion mobility experiments and photoelectron spectroscopy studies in combination with density functional theory (DFT) calculations have shown that Au anions and cations retain their planarity up to 12 and 8 atoms,^{37,38} respectively. However, there are no experimental records for neutral clusters. CCSD(T) calculations place this value to be 8 for neutral clusters²² and DFT

calculations report this value to be between 11–15 atoms.^{23–29} Complete reviews are available which mention several theoretical studies carried out to investigate the lowest energy geometry of Au clusters.^{39–42} Apart from the study on the lowest energy conformation, many researchers have been interested in the catalytic activity of Au clusters in the size range of 6–13 atoms. One of the important applications of Au clusters has been for CO oxidation. This requires the simultaneous reduction of O_2 molecule and CO oxidation. In this context, the interaction of ground state geometry of Au clusters with O_2 ^{43–48} and CO^{49,50} has been widely studied. However, detailed information on the reactivity of various Au clusters and the reacting sites within them has not yet been clearly obtained. Moreover, it has now recently been reported that in some cases the higher energy conformations have better adsorption properties as compared to the ground state cluster.^{50,51} Many additional reports have shown that the activity of neutral clusters depends upon the type of sites exposed and their ability to absorb or donate electrons. Thus, the catalytic activity of gold clusters is more complex and is closely related to the basic electrophilicity and nucleophilicity of various sites in a given cluster. The number of electrophilic or nucleophilic sites is in turn dependent on the size and shape of the cluster.

Hence, in this work, we propose to analyze in depth the response of various sites toward an impending electrophilic attack (which describes as to how easily it will donate the electrons) or an nucleophilic attack (which describes as to how easily it will accept the electrons). For this purpose, the ground state structure as well as few characteristic high energy isomers of Au_n ($n = 6 – 13$) were considered. The relative nucleophilicity and electrophilicity of the above conformations were calculated and an analysis of this is presented in Section 3. Our results show that for gas phase clusters, the ground state geometries with alternating nucleophilic and electrophilic sites are best suited for catalysis. In contrast, nonplanar geometries are better candidates for adsorbing on supports and subsequent

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catalysis. An analysis of infrared spectrum of Au₇ isomers clearly demonstrates that in this cluster size range, ground state conformations as well as some high energy conformations are likely to coexist indicating that above aspects could play an important role in the overall reactivity of these clusters.

II. Theoretical Methods

The ground-state energy of an atom or a molecule, in density functional theory, can be expressed in terms of electron density, $\rho(\mathbf{r})$, as⁵²

$$E[\rho] = F_{\text{HK}}[\rho] + \int v(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r} \quad (1)$$

where $v(\mathbf{r})$ is the external potential, and F_{HK} , the universal Hohenberg–Kohn functional is the sum of electronic kinetic energy ($T[\rho]$) and electron–electron interaction energy ($V_{ee}[\rho]$).

$$F_{\text{HK}}[\rho] = T[\rho] + V_{ee}[\rho] \quad (2)$$

The first partial derivative of $E[\rho]$ with respect to the number of electrons N under constant external potential $v(\mathbf{r})$ is defined as the chemical potential,⁵³ μ , for a system

$$dE = \mu dN + \int \rho(\mathbf{r})dv(\mathbf{r}) \, d\mathbf{r} \quad (3)$$

where

$$\mu = \left(\frac{\partial E[\rho]}{\partial N} \right)_v = \left(\frac{\partial E}{\partial \rho(\mathbf{r})} \right)_v \quad (4)$$

For the calculation of curvature of E with respect to N at a given value of N at 0 K, using the finite difference method

$$\mu = \left(\frac{\partial E[\rho]}{\partial N} \right)_v \approx \frac{E(N+h) - E(N-h)}{2h} \quad (5)$$

Since only integral values of N can be observed from data of ionization potentials (I) and electron affinity (A), the infinitesimally small quantity h , can be set equal to unity and through rearrangement, followed by using electron densities of N_0 , $N_0 + 1$, and $N_0 - 1$ electron systems, the equation is modified as

$$\mu = \frac{E(N+1) - E(N-1)}{2h} = -\frac{I+A}{2} \quad (6)$$

The second derivative of energy with respect to N at 0 K as obtained from 4 gives the definition of hardness, η

$$\eta = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right)_v = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_v \quad (7)$$

and applying three point finite difference approximation, we obtain the formula

$$\eta = \frac{I-A}{2} \quad (8)$$

From the understanding of MO theory, within the framework of density functional theory, applying Koopmans' approximation to Kohn–Sham orbitals instead of canonical Hartree–Fock molecular orbitals,⁵⁴ eqs 6 and 8 can be further simplified using the MO eigenvalues (ϵ) of the highest occupied (ϵ_{HOMO}) and lowest occupied (ϵ_{LUMO}) molecular orbitals. In that case, eqs 6 and 8 simplify as

$$\mu = \frac{\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}}}{2} \quad (9)$$

$$\eta = \frac{\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}}{2} \quad (10)$$

Continuing from eq 3, the function $f(\mathbf{r})$ is defined as the derivative of chemical potential μ against external potential at constant electronic framework or the slope of density against number of electrons, N , at constant perturbation

$$f(\mathbf{r}) \equiv \left(\frac{\delta \mu}{\delta v(\mathbf{r})} \right)_N = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_v \quad (11)$$

$f(\mathbf{r})$ is called the Fukui function or frontier function for a molecule.⁵⁵ Thus, the Fukui function can be interpreted either as the change of electron density at each point \mathbf{r} when the total number of electrons is changed or as the sensitivity of chemical potential of a system to an external perturbation at a particular point \mathbf{r} . The N discontinuity problem of atoms and molecules⁵⁶ in eq 4 leads to the introduction of both right- and left-hand-side derivatives at a given number of electrons, N_0 ($\equiv N$)

$$f^+(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_v^+ \quad (12)$$

for nucleophilic attack and

$$f^-(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_v^- \quad (13)$$

for electrophilic attack.

By the finite difference method, using electron densities of N_0 , $N_0 + 1$, and $N_0 - 1$ electron systems, Fukui functions for nucleophilic and electrophilic attack can be defined respectively as

$$f^+(\mathbf{r}) \approx \rho_{N_0+1}(\mathbf{r}) - \rho_{N_0}(\mathbf{r}) \quad (14)$$

$$f^-(\mathbf{r}) \approx \rho_{N_0}(\mathbf{r}) - \rho_{N_0-1}(\mathbf{r}) \quad (15)$$

and for radical attack

$$f^0(\mathbf{r}) \approx \frac{1}{2} (\rho_{N_0+1}(\mathbf{r}) - \rho_{N_0-1}(\mathbf{r})) \quad (16)$$

To describe the site reactivity or site selectivity, Yang et al.⁵⁷ proposed the atom condensed Fukui function, based on the idea of electronic population around an atom in a molecule, similar to the procedure followed in the population analysis technique. The condensed Fukui function for an atom k undergoing

nucleophilic, electrophilic, or radical attack can be defined respectively as

$$f_k^+ \approx q_k^{N_0+1} - q_{N_0}^k \quad (17)$$

$$f_k^- \approx q_k^{N_0} - q_{N_0-1}^k \quad (18)$$

$$f_k^0 \approx \frac{1}{2}(q_k^{N_0+1} - q_{N_0-1}^k) \quad (19)$$

where q^k values are electronic population of the k th atom of a particular species.

To determine the relative nucleophilicity indices, Roy et al. proposed the relative nucleophilicity as^{58,59}

$$f_{nu} \approx \frac{f_k^+}{f_k^-} \quad (20)$$

$$f_{el} \approx \frac{f_k^-}{f_k^+} \quad (21)$$

where f_{el} is the relative electrophilicity. This quantity is quite useful to identify the reactive site at which the reaction takes place. For intramolecular reactivity, f_{nu}/f_{el} has the importance in comparing reactivity across the same molecule. Further the relative difference between the values of f_{nu} and f_{el} is also of importance. A site for which $f_{nu} \gg f_{el}$ is a site favorable for a nucleophilic attack, while a site for which $f_{el} \gg f_{nu}$ is clearly a site favorable toward an electrophilic attack. A site for which f_{el} is nearly equal to f_{nu} is likely to both give or take electrons easily making it an amphiphilic site, likely to participate in both oxidation and reduction chemical reactions.

III. Computational Details

All calculations have been performed using *deMon.2.2.6* code.⁶⁰ The geometries of all of the clusters have been optimized using B88 exchange and Lee, Yang, and Parr correlation functional⁶¹ followed by the calculation of harmonic vibrational frequencies. All of the frequencies were found to be positive, confirming the structure to be a minima. The basis set used for the relativistic calculations is RECP quality with 1997 Stuttgart-Dresden RECP for 19 valence electrons treatment.⁶² The A2 auxiliary functions were set to fit the charge density.⁶³ No additional polarization functions have been added. It may be noted that these ECPs are well documented for accurate prediction of structure as well as spectroscopic properties of Au clusters.^{64,65} The convergence of the geometries were based on gradient and displacement criteria with a threshold value of 10^{-5} au and the criteria for convergence of SCF cycles was set to 10^{-9} . The FFs were calculated on the basis of Lowdin population analysis.⁶⁶ Only one spin multiplicity has been investigated depending upon the cluster size. Only the lowest spin state has been considered for all the Au clusters. The spin multiplicities for even electron (even number of Au atoms) clusters are singlets and doublets for odd electron (odd number of Au atoms) clusters. It has also been reported in an earlier literature that Au clusters prefer to be in their lowest spin state.⁶⁷

TABLE 1: Structural, Electronic, and Reactivity Parameters of Au_6 Conformations^a

	Structure	ΔE (eV)	No. of Unique sites	Site	Charge	f_{nu}	f_{el}
I		0.00	2	A	-0.16	1.26	0.79
				B	0.16	0.78	1.29
II		0.90	2	A	0.05	1.00	1.00
				B	-0.24	0.85	1.18
III		1.53	5	A	0.12	1.94	0.52
				B	-0.11	1.83	0.55
				C	0.03	0.48	2.09
				D	-0.17	0.52	1.91
				E	0.01	0.46	2.17
IV		1.62	2	A	0.06	1.09	0.91
				B	-0.12	0.75	1.33

^a The values in red, blue, and black correspond to electrophilic, nucleophilic, and amphiphilic attack sites, respectively. The values given next to the conformations in column II of the table correspond to the inter-atomic distances (in Å) between various unique sites.

IV. Results

A. Au_6 . The structural, electronic and reactivity parameters of the lowest energy structure and a few characteristic high energy conformations of Au_6 are given in Table 1. We begin with an analysis of structural and electronic properties of the ground state Au_6 geometry shown in Table 1 (conformation(I)). The values given next to the conformations in column II Table 1 correspond to the interatomic distances (in Å) between various unique sites. Consistent with the earlier reports,^{28,29} the lowest energy conformation is a planar triangle with D_{3h} point group. Depending upon the symmetry, various atoms in this conformation have been grouped together as distinct reactive site types. This particular arrangement of six atoms results in 2 types of reactive sites having distinct chemical environments viz., (i) atoms forming an inner triangle “A” and (ii) atoms capping each edge of this triangle, “B”. The inner triangle (AAA) is a perfect equilateral triangle. On the other hand, the outer triangles (BAA) are deformed equilateral triangles with the B–A–A angles reduced to 57.5° and the angle A–B–A increased to 64° . These structural features are an outcome of the charge redistribution among the six atoms. The inner triangular atoms (“A” atoms) absorb some charge from the atoms capping them (“B” atoms). As result the inter atomic distances in the inner triangle increase to nearly 2.92 Å (higher than the bulk Au–Au inter atomic distance of 2.88 Å) indicating

TABLE 2: Structural, Electronic, and Reactivity Parameters of Au₇ Conformations^a

	Structure	ΔE (eV)	No. of Unique sites	Site	Charge	f_{nu}	f_{el}
I		0.00	7	A B C D E F G	0.04 -0.10 0.15 -0.14 0.18 -0.25 0.12	1.07 1.94 1.06 0.98 1.01 0.90 0.97	0.93 0.98 0.94 1.02 0.99 1.11 1.03
II		0.37	3	A B C	0.05 -0.31 0.05	1.00 0.94 1.02	1.00 1.07 0.98
III		0.46	4	A B C D	0.10 -0.22 0.19 -0.13	1.04 0.91 1.04 1.06	0.96 1.10 0.96 0.95
IV		0.68		A B C D E		1.00 0.98 1.01 1.00 1.01	0.99 1.02 0.99 1.00 0.99
V		0.74	2	A B	0.06 -0.14	1.00 1.00	1.00 1.00

^a The values in red, blue, and black correspond to electrophilic, nucleophilic, and amphiphilic attack sites respectively. The values given next to the conformations in column II of the table correspond to the inter-atomic distances (in Å) between various unique sites.

these atoms to be bonded through metallic bonds. The outer cap atoms are bonded to the equilateral triangle through bond lengths of 2.77 Å. This is in between the covalent bond length (Au dimer has an inter atomic bond distance of 2.59 Å)⁶⁸ and metallic bond length seen in bulk Au.

The next high lying isomer (0.90 eV) is a nonplanar conformation, a capped pentagon with C_{5v} point group (conformation II) and two unique reactive sites. The central atom (atom with highest co-ordination) in this configuration is negatively charged and the atoms surrounded are positively charged. In this case, the central atom is connected to the surrounding atoms with shorter inter atomic distances as compared to inter atomic distances between the edge atoms. All other conformations lie about 1.5–1.6 eV higher than the lowest energy conformation. Two such characteristic conformations are shown in Table 1. One conformation (conformation III) has nearly five types of reactive sites and has an open dangling trimer attached to a closed trimer. The other conformation analyzed (conformation IV) has two types of reactive sites. The trend of atoms with higher co-ordination (which are mostly

the central atoms) being negatively charged is consistently observed in these two structures too.

The final interest in all these clusters is to understand their response toward an impending electrophilic or a nucleophilic attack which is analyzed using relative reactivity descriptors discussed in section II. It is noteworthy, that these reactivity descriptors need not follow the charges necessarily as they are indicative of the tendency of an atom to accept or loose additional charge. On the other hand, charge is a measure of the amount of electrons the atom has lost or gained within the conformation. In conformation I, the atoms forming the caps (called as cluster tips in earlier works)⁷⁴ are favorable for the adsorption of an electrophilic guest molecule such as O₂ or an oxide support. The atoms forming the inner equilateral triangle in contrast are favorable for an attack by a nucleophilic molecule such as CO, H₂O. The reactivity trends observed in our study within the ground state isomer of Au₆ are interestingly corroborated by results from a recent work, which reported that O₂ molecule binds with Au₆ only when it collides with the tips of the cluster and not along the edges while CO prefers the

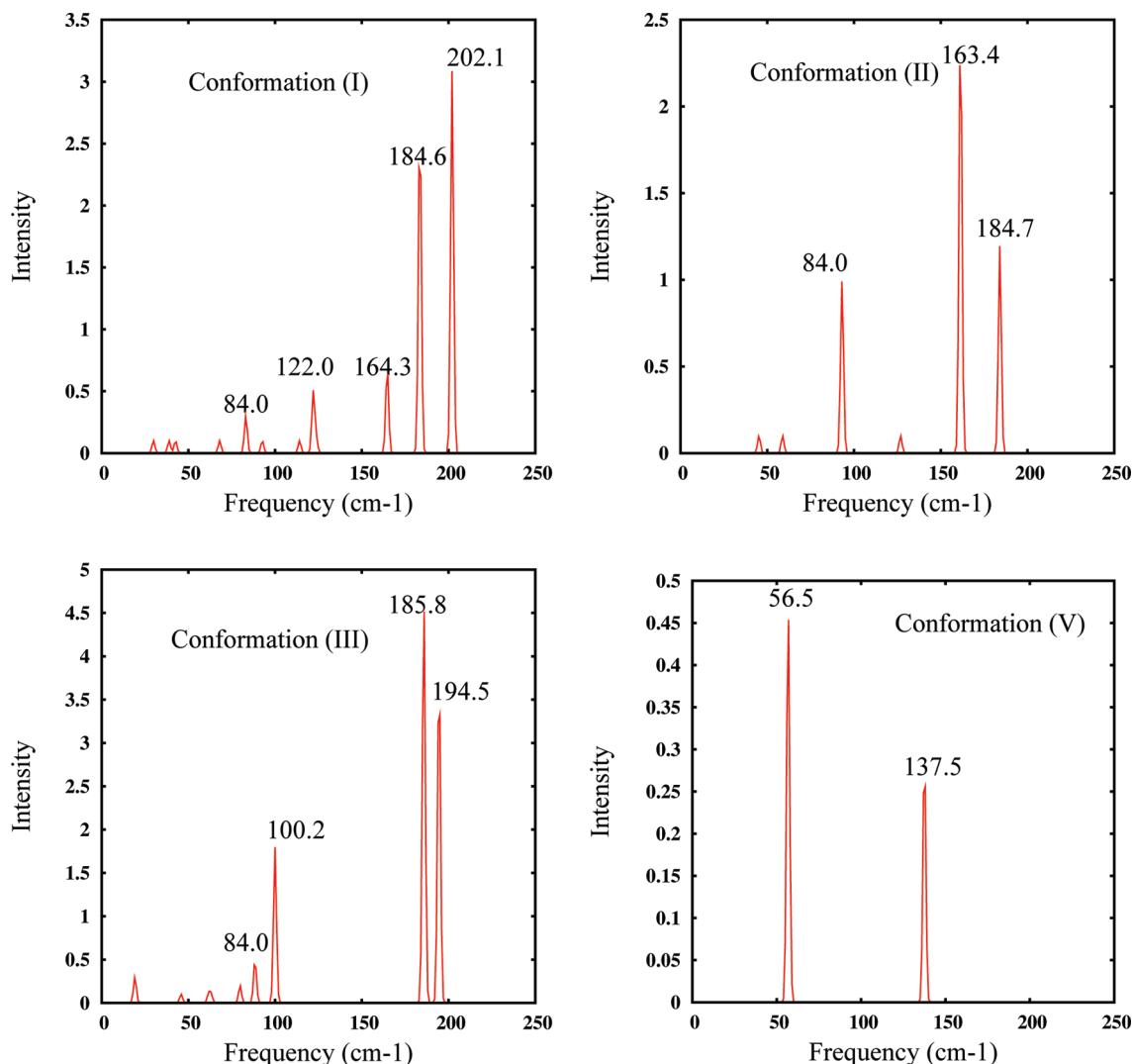


Figure 1. Calculated infrared vibration spectra for various conformations of Au_7 .

inner-triangular atoms.^{74,75} In conformation III, the atoms “C”, “D”, and “E” forming the open triangle are more favorable for O_2 adsorption. Rest of two chemical sites (“A” and “B”) are favorable for a nucleophilic attack. Conformations II and IV differ from conformations I and III as in the former two, it is the inner or central atoms (sites “B”) that are more viable for an electrophilic attack.

B. Au_7 . In Table 2, we present the structural and electronic properties of the ground state and a few characteristic high lying geometries of Au_7 . The lowest energy conformation is built upon Au_6 -conformation(I) and is consistent with several earlier reports.³² The additional atom “G” breaks down the symmetrical structure of Au_6 leading to 7 unique reactive sites. As a consequence, the inner triangle (B–F–D) is no longer equilateral. The atom F in inner triangle absorbs some charge from the new atom G, becoming the most negatively charged center and consequently increasing the bond distances between it and other two central atoms (“B” and “F”). Thus, “A”–“F” and “B”–“F” increase from 2.71 Å in Au_6 to 2.79 Å and from 2.92 to 3.14 Å, respectively. However, rest of the inter atomic distances remain between 2.71–2.74 Å. As in case of Au_6 conformation I, central atoms (“F”, “B”, and “D”) having maximum atomic coordination have a negative charge on them. Rest of the four discussed structures of Au_7 are nonplanar. Conformation II is the first high energy conformation and lies 0.37 eV above the lowest energy conformation in our calculation

and is consistent with a recent report.³² Thus, the gap between the planar and nonplanar conformation has reduced considerably in Au_7 as compared to Au_6 . This geometry, based on symmetry has three unique reactive sites. The central atom is negatively charged. This trend is also consistent in conformations III, IV, and V where atoms with higher co-ordination number (central atoms) are negatively charged. Further, these negatively charged centers are bonded to each other through the largest inter atomic bond distances in the range of 2.90–3.00 Å.

In a recent work, experimental infrared (IR) vibrational modes of neutral Au_7 have been reported. Hence, we found it interesting to analyze the IR spectrum of the above-mentioned isomers and compare them with the earlier reported theoretical as well as experimental studies.³² In Figure 1, we show the IR spectra of the five conformations given in Table 2. The experimental IR spectra has been reported to have small peaks around 56, 65, 75, 100, 120, 165, and 201 cm⁻¹ and one prominent peak around 186 cm⁻¹. A quick observation shows that none of the isomers show the same features. However, three isomers, viz., conformations I, II, and III, show prominent peaks around 185 cm⁻¹. Conformation II shows a peak around 56 cm⁻¹. Conformation I shows peaks around 120, 165, and 201 cm⁻¹. Conformation III shows a peak around 100 cm⁻¹. Conformation IV does not have show any appearance in experimental spectrum and Conformation V shows a peak around 56 cm⁻¹. This is in contrast to earlier observations in Au_{19} and Au_{20} ,

TABLE 3: Structural, Electronic, and Reactivity Parameters of Au₈ Conformations^a

	Structure	ΔE (eV)	No. of Sites	Site	Charge	f_{nu}	f_{el}
I		0.00	2	A	0.17	1.06	0.94
				B	-0.17	0.92	1.08
II		0.44	5	A	-0.29	1.31	0.77
				B	0.06	1.03	0.97
				C	0.10	0.89	1.13
				D	-0.09	0.89	1.12
				E	0.15	1.00	1.00
III		0.54	6	A	0.19	0.99	1.01
				B	-0.35	0.52	1.91
				C	-0.14	0.90	1.10
				D	0.18	1.01	0.99
				E	-0.14	0.96	1.04
				F	0.19	1.69	0.59
IV		0.57	4	A	0.15	1.04	0.96
				B	0.10	1.08	0.92
				C	-0.20	0.86	1.16
				D	0.04	1.02	0.99
				E	-0.04	0.97	1.03
V		0.78	2	A	0.17	1.10	0.91
				B	-0.17	0.98	1.02

^a The values in red, blue, and black correspond to electrophilic, nucleophilic, and amphiphilic attack sites respectively. The values given next to the conformations in column II of the table correspond to the inter-atomic distances (in Å) between various unique sites.

where IR spectrum of the ground state geometry is seen to closely match with the experimentally predicted one.^{32,65} Thus, it is more likely that in these cluster ranges, various conformations are likely to coexist leading to a mixed experimental spectrum.

The relative reactivity indices show that atoms A, B, and C in conformation I are good nucleophilic sites and the central edge atoms F and G are good electrophilic sites. Sites "D" and "E" are amphiphilic site as noted from the relative f_{nu} and f_{el} sites. An analysis of the reactivity descriptors of high energy conformations reveals that all the sites in conformations IV and V are favorable for both electrophilic and nucleophilic attack. In conformations II and III, the central atoms "B" is viable for an electrophilic attack.

C. Au₈. Table 3 gives structural, electronic, and reactivity parameters of Au₈ conformations. The lowest energy conformation I is a planar one with four caps ("A") to each edge of a square made up of atoms "B" as seen in Table 3. This is the only cluster size among Au_n ($n = 6-13$) clusters whose lowest energy conformation is not built upon Au₆ ground state geometry. This configuration has been reported to be the lowest energy configuration also in earlier literature reports.^{28,29} The inner atoms "B" are negatively charged and bonded to each other through reasonably long bond distances of 2.88 Å. The first high energy conformation (conformation II) is a planar conformation and is built upon Au₇ conformation I. It has a C_{2v} symmetry. Due to increased symmetry, this conformation has just five distinct reactive sites. The central atoms (A–D–D)

TABLE 4: Structural, Electronic, and Reactivity Parameters of Au₉ Conformations^a

	Structure	ΔE (eV)	No. of Sites	Site	Charge	f_{nu}	f_{el}
I		0.00	6	A	0.05	0.92	1.09
				B	0.10	0.98	1.02
				C	-0.29	0.88	1.13
				D	-0.05	1.11	0.90
				E	-0.20	0.93	1.07
				F	0.17	0.92	1.08
II		0.10	4	A	0.16	1.00	1.00
				B	-0.06	1.02	0.98
				C	0.14	0.98	1.02
				D	-0.36	0.97	1.03
III		0.48	9	A	0.19	1.06	0.95
				B	-0.18	0.92	1.09
				C	-0.11	0.95	1.05
				D	-0.06	1.02	0.98
				E	0.20	1.06	0.94
				F	-0.02	1.05	0.96
				G	-0.18	0.92	1.09
				H	-0.03	0.98	1.02
				I	0.18	1.02	0.98
IV		0.74	6	A	0.15	1.00	1.00
				B	0.10	0.99	1.01
				C	-0.14	1.00	1.00
				D	0.18	1.01	0.99
				E	-0.02	0.99	1.00
				F	0.10	0.99	1.00

^a The values in red, blue, and black are electrophilic, nucleophilic, and amphiphilic attack sites respectively. The values given next to the conformations in column II of the table correspond to the inter-atomic distances (in Å) between various unique sites.

form an equilateral triangle and are bonded to each other with the largest inter atomic distances within the cluster. Atom "A" with maximum co-ordination remains negatively charged. Among the two nonlinear structures considered, one of them has 6 unique reactive sites. The other nonlinear conformation has D_{5h} symmetry and 2 types of reactive sites.

Analysis of the reactivity parameters indicates that the four cap atoms in the conformation I are favorable for a nucleophilic attack, while the atoms in the square are preferable for an electrophilic attack. Thus, the structure has alternating electrophilic and nucleophilic sites. First high energy conformation II has electrophilic sites located at the edges of the upper triangle while the central atom is a nucleophilic attack preferring site. The other planar conformation IV has favored sites of electrophilic attack inner triangle (C–C–E) surrounded by favored sites for nucleophilic attack. This arrangement is likely to be favorable for C=O oxidation which requires a simultaneous O₂

reduction and C=O oxidation. The other two nonplanar conformations also show similar arrangement of the reactivity sites.

D. Au₉. The lowest two conformations of Au₉ are built upon the lowest energy conformations of Au₆ and Au₇ as shown in Table 4. Conformation I is made up of one additional atom to the first high energy isomer of Au₈, with six unique reactive sites. As in the earlier clusters, the central atoms are negatively charged.

First high energy isomer is also planar and looks like two Au₆ configurations fused at the bottom. The structure has C_{2v} symmetry and four unique reactive sites. The other two conformations given in the Table 4 are the lowest nonplanar structures in the present study with a flat cage shape. It is noteworthy, that from Au₉ onward we begin to see nonplanar structures having a flat cage conformation. One of the nonplanar conformations with C_1 symmetry has nine distinct reactive sites.

TABLE 5: Structural, Electronic and Reactivity Parameters of Au₁₀ Conformations^a

	Structure	ΔE (eV)	No. of Sites	Site	Charge	f_{nu}	f_{el}
I		0.00	4	A	0.06	0.75	1.33
				B	0.09	1.04	0.96
				C	0.02	1.47	0.68
				D	-0.25	0.86	1.17
II		0.31	5	A	0.16	0.52	1.91
				B	-0.07	0.26	3.80
				C	-0.08	0.84	1.19
				D	0.23	2.02	0.50
				E	-0.17	1.67	0.60
III		0.67	6	A	0.12	1.32	0.76
				B	-0.07	1.10	0.91
				C	-0.16	1.19	1.19
				D	-0.06	0.91	0.91
				E	0.18	1.35	1.35
				F	0.12	1.32	0.76

^a The values in red, blue, and black are electrophilic, nucleophilic, and amphiphilic attack sites respectively. The values given next to the conformations in column II of the table correspond to the inter-atomic distances (in Å) between various unique sites.

As in earlier cases, atoms with the higher co-ordination are negatively charged and are bonded to each other with largest inter atomic bond distances in all of the above configurations.

The number and types of reactive sites in each of these three clusters are given in Table 4. All of the atoms in the lowest energy structure except “B” and “D” sites are viable for an electrophilic attack. The other planar conformation (conformation II) in contrast has the central atom clearly preferable for electrophilic attack with rest of atoms being amphiphilic in nature. Conformation IV, which is more symmetric of the two nonplanar has all the atoms with amphiphilic behavior. On the other hand, another conformation III has 6 chemically distinct reactive sites of which the four corner atoms “A”, “E”, “F”, and “I” are favorable for an nucleophilic attack. Thus, conformation III, which is a high energy isomer, offers more sites susceptible to nucleophilic attack as compared to the ground state conformation.

E. Au₁₀. Table 5 gives the structural details and reactivity parameters for Au₁₀ cluster. The lowest energy conformation is built upon Au₉ conformation I. The geometry does not change significantly from that of Au₉ in spite of one additional atom. However, it increases the symmetry of the structure to C_{2v} there by reducing the atoms with distinct chemical environment to four. As in case of earlier clusters, the central atoms are negatively charged. The two nonplanar structures are reasonably symmetric and lie about 0.3 and 0.7 eV higher than the planar ground state configuration.

In conformation I, the outer edge atoms B–C–B are most vulnerable for an nucleophilic attack, while the atoms forming an inner edge A–D–D–A are better for an electrophilic attack. The lowest nonlinear conformation II is a very interesting geometry where its entire upper part (A–B–B–C) is highly favorable for an electrophilic attack leaving only three atoms at the bottom, D–E–D, for a nucleophilic attack. Another nonlinear conformation III, in contrast has only four atoms, two C sites and two E sites for an electrophilic attack. Thus, the nonplanar cluster is a better alternative for adsorption of molecules seeking electrons, while the lower planar structure is better for adsorption of electron donating molecules such as CO.

F. Au₁₁. Table 6 gives the details of Au₁₁ conformations. Conformations I and II are lowest energy configurations with C_1 point group and are built upon Au₁₀ conformation. Both of them have 11 unique reactive sites. The two central atoms and the atoms bonded to the new additional atom I in both cases are negatively charged. The two lowest nonplanar configurations shown are very similar except for the position of the top cap atom which makes configuration IV more symmetric as compared to the configuration III.

Analysis of the relative reactivity descriptors shows that in conformation I, the two central atoms “D” and “E” and the projecting atom “I” are most viable atoms for an nucleophilic attack, while, the atoms forming the left edge “B”, “C”, “F”, and “G” are favorable for an electrophilic attack. In contrast, conformation II has only one site for a nucleophilic attack which

TABLE 6: Structural, Electronic, and Reactivity Parameters for Au₁₁ Conformations^a

	Structure	ΔE (eV)	No. of Sites	Site	Charge	f_{nu}	f_{el}
I		0.00	11	A	0.06	1.00	0.99
				B	0.09	0.97	1.03
				C	0.00	0.91	1.10
				D	-0.21	1.09	0.92
				E	-0.24	1.15	0.87
				F	0.09	0.98	1.03
				G	0.11	0.99	1.01
				H	-0.05	0.99	1.01
				I	0.17	1.03	0.97
				J	-0.13	0.93	1.08
				K	0.11	1.01	0.98
II		0.06	11	A	0.06	1.00	1.00
				B	0.09	1.01	0.99
				C	0.02	1.02	0.99
				D	-0.26	0.97	1.03
				E	-0.23	1.03	0.97
				F	0.13	1.00	1.00
				G	-0.08	1.00	1.00
				H	-0.05	1.00	1.00
				I	0.15	0.99	1.01
				J	0.05	0.98	1.02
				K	0.10	1.01	0.98
III		0.53	8	A	0.23	1.08	0.93
				B	-0.02	0.92	1.09
				C	-0.14	0.89	1.12
				D	-0.13	1.08	0.92
				E	0.18	1.01	0.99
				F	-0.05	1.02	0.98
				G	-0.05	1.02	0.98
				H	0.21	1.07	0.94
IV		0.64	5	A	0.01	1.02	0.98
				B	0.17	1.03	0.97
				C	-0.08	1.00	1.00
				D	-0.05	0.97	1.03
				E	-0.19	0.98	1.01

^a The values in red, blue, and black are electrophilic, nucleophilic, and amphiphilic attack sites respectively. The values given next to the conformations in column II of the table correspond to the inter-atomic distances (in Å) between various unique sites.

is the central atom “E”. Thus, difference in position of a single atom modifies the number and type of reactive sites in a cluster. Going to a nonplanar conformation III results in a geometry with several sites (six unique sites) favorable for a nucleophilic attack (eight atoms). Rest of the three atoms “B” and “C” are

favorable sites for an electrophilic attack. However, the more symmetric nonplanar structure has only two central atoms favorable for an electrophilic attack, viz., “D”. The two edge atoms on both sides, “B” and “F”, are favorable for an nucleophilic attack.

TABLE 7: Structural, Electronic, and Reactivity Parameters of Au₁₂ Conformations^a

	Structure	ΔE (eV)	No. of Sites	Site	Charge	f_{nu}	f_{el}
I		0.00	3	A	0.10	1.05	0.95
				B	-0.01	0.60	1.66
				C	-0.19	1.83	0.55
II		0.52	5	A	-0.05	0.82	1.21
				B	0.21	1.23	0.81
				C	-0.08	1.26	0.79
				D	-0.20	0.84	1.19
				E	-0.16	1.03	0.97
III		0.73	8	A	0.06	1.24	0.81
				B	0.11	1.03	0.98
				C	-0.28	0.93	1.08
				D	0.03	0.74	1.35
				E	-0.19	1.26	0.79
				F	-0.01	1.22	0.82
				G	-0.21	0.73	1.37
				H	0.17	1.06	0.95
IV		0.91	9	A	0.06	0.69	1.46
				B	0.10	0.63	1.60
				C	0.04	1.04	0.96
				D	-0.02	1.14	0.88
				E	0.20	1.13	0.88
				F	-0.21	1.54	0.65
				G	-0.04	1.22	0.82
				H	-0.38	0.71	1.41
				I	0.09	0.99	1.01

^a The values in red, blue, and black are electrophilic, nucleophilic, and amphiphilic attack loving sites respectively. The values given next to the conformations in column II of the table correspond to the inter-atomic distances (in Å) between various unique sites.

G. Au₁₂. Table 7 describes the lowest energy geometry and a few higher energy conformers of Au₁₂. Conformation I is planar and is the lowest energy structure with a symmetry of D_{3h} . The high symmetry of the structure reduces the number of chemically distinct sites to three. Other planar structure of Au₁₂

which is also built upon the structure of Au₁₁ is less symmetric than Conformation I with 8 distinct reactive sites and C_{2v} symmetry. Conformation III is the lowest energy of all nonplanar ones and corresponds to the flat cage. This structure is also built upon the lowest energy nonplanar structure of Au₁₁ and has 5

distinct reactive sites. Conformation IV is the higher energy nonplanar structure of Au₁₂ with a point group of C_s . It has one mirror plane passing through the atoms A, B, C, H and I thereby dividing the cluster into two halves due to which distinct reactive sites reduces to 9.

The lowest energy conformation of Au₁₂, which is a Au₆ cluster with 2 atoms capping each edge has one reactive site "B", which is favorable for an electrophilic attack. The three central atoms, "C", are the only atoms favorable for a nucleophilic attack. The next low lying planar configuration, conformation II, results in one less site for an nucleophilic attack with the central atom, "C", atoms "D" and "E" site preferring an electron loving guest. In the nonplanar conformation, conformation III, all the atoms with maximum coordination, viz., "D" and "A", prefer an electrophilic attack, with rest of the atoms favoring and nucleophilic attack. The other nonplanar structure shows an interesting feature where the entire lower part of the structure is a electron loving region, thereby preferring to react with electron donating molecules, leaving the upper three atoms "A", "B", and "H" for a electrophilic attack. Thus, interestingly, most of the Au₁₂ clusters are favorable for an nucleophilic attack.

H. Au₁₃. Table 8 gives the lowest energy structure and a few characteristic high energy conformations of Au₁₃. It is clearly seen that there are two lowest nearly degenerate planar conformations which are both built upon planar conformation of Au₁₂. Conformation III, is the lowest energy structure among the all nonplanar conformations and is built upon the lowest nonplanar conformation of Au₁₂. There are no major changes in the inter atomic bond distances due to the additional atom. Structure IV is a higher energy conformer which is non planar with no clear symmetry (C_1) and thus has 13 distinct sites.

Analysis of the reactivity parameters indicates that most of the sites in the lowest energy planar configuration and two nonplanar configurations are amphiphilic in nature. The planar configuration nearly degenerate to the ground state conformation has alternating electrophilic and nucleophilic loving sites. This arrangement of amphiphilic sites or alternating electrophilic and nucleophilic sites makes them ideal catalysts for CO reduction as discussed before.

I. HOMO–LUMO Energy Gap. The HOMO–LUMO energy gap reflects the possibility of electrons to jump from the occupied orbitals to unoccupied orbitals and is a fair indicator of the electronic stability of the cluster. It partially indicates the electronic perturbation required to lose the assembly of molecule undergoing a chemical reaction or a thermal isomerization. Table 9 gives the HOMO–LUMO energy gaps for various conformations of Au clusters. From the values of HOMO–LUMO energy gap as obtained, the planar Au₆ has a very noticeable value for E_{gap} which is in well agreement with the literature⁶⁹ and calculations performed by Wang et al.⁷⁰ The experimental⁷¹ value of HOMO–LUMO transition energy has been reported to be 2.5 eV which is in reasonable accordance with our calculated value of 2.2 eV.

Thus, the HOMO–LUMO energy gap of Au₆ ground state conformation is found to be higher than that of two most stable Au clusters reported to date, viz., Au₂₀ (with a reported energy gap of 1.77 eV experimentally⁷² and 1.85 eV theoretically⁷³) and Au₂ (1.97 eV from our calculations against 1.96 eV in literature.⁶⁹) The Au₆ ground state conformation also has a much higher energy gap value as compared to the corresponding values of Au₇–Au₁₃ ground state conformations. The order of electronic stability of the ground state conformation as understood from the HOMO–LUMO energy gap is Au₆ > Au₂ > Au₂₀ > Au₈ > Au₇ > Au₁₀ > Au₁₁ > Au₁₂ > Au₁₃, with also Au₆

as the most stable cluster among Au_n ($n = 1$ –20) clusters. The higher energy conformations of Au₆ have much lower E_{gap} values, indicating that Au₆ ground state conformation is also exceptionally stable compared to its higher energy conformations.

In the context of higher energy clusters of Au₇, conformation I shows the highest stability followed by nonplanar conformation IV and V. The nonplanar conformation V of Au₈ is the most stable one, having stability higher than the lowest energy conformation of Au₇ and is followed by conformations III and I. Conformation I of Au₉ is the most stable one followed by the conformations III and IV. This also indicates that the most stable conformation of Au₉ is a planar one in contrary to the results of nonrelativistic CCSD (T).²² Au₁₀ has the lowest energy conformation which is planar and first three conformations show similar stability. Continuing to the higher numbered cluster Au₁₁, the relativistic DFT calculation shows that the lowest energy conformation is electronically more stable with HOMO–LUMO energy difference as 0.99 eV. The next higher energy conformation is III which is close to structure I in terms of stability. Furthermore, for Au₁₂ cluster, all the clusters show similar stability in terms of HOMO–LUMO energy gap and hardness which is further calculated from the energy gap. For Au₁₃ cluster, conformation III shows the maximum hardness followed by conformations I, IV, and II.

It is thus observed that even-numbered gold clusters are more stable electronically as compared to the odd numbered ones. Moreover the stability reduces as the number of atoms in the cluster increases and so is the odd–even oscillation which has been displayed in Figure 2. This may suggest that the even numbered clusters up to ten atoms are relatively more stable as compared to their neighboring odd numbered ones.

V. Discussion on the Shape Sensitivity of Reactivity in Au_n ($n = 6$ –13) Clusters

From the above results, it is seen that the lowest energy conformation is a planar one within the studied cluster range. All of these planar configurations have an alternating arrangement of nucleophilic and electrophilic attack loving sites (a central nucleophilic sites surrounded by electrophilic sites or vice-versa). Interestingly in odd-atom clusters, the electrophilic attack loving sites form the tips or easily accessible edges of the clusters. This feature, in conjunction with the odd unpaired electron within them makes them more favorable for reactions such as O₂ reduction. The presence of nearby nucleophilic sites facilitates the adsorption of CO molecules and its subsequent oxidation following the for O₂ reduction. These could be key factors to why the odd-planar Au gas phase clusters in this size range as favorable catalysts for CO oxidation among many experimentalists. The even-atom clusters are seen to have most of the electrophilic sites located in the interior/inner locations of the cluster. One exception to this case is Au₆ whose edges are electrophilic sites. Interestingly, Au₂ and Au₆ are the two even-atom clusters, which show high binding energies with O₂ molecule.^{74–76}

However, it may be recalled that Au clusters adsorbed on oxide surfaces are more efficient catalysts for O₂ reduction.⁷⁷ This has been attributed to the additional electrons which the cluster absorbs from the oxide support making it more feasible for conversion of O₂ molecule to superoxide (O₂[–]). This type of adsorption involves most nucleophilic loving Au site orienting toward the oxide surface. Thus, it can be envisaged from the reactivity descriptors that the planar configurations consisting of both electrophilic and nucleophilic reactive sites are not the best candidates for this case. Instead, a structure, consisting of a nucleophilic attack loving base and few

TABLE 8: Structural, Electronic, and Reactivity Parameters of Au₁₃ Conformations^a

	Structure	ΔE (eV)	No. of Sites	Site	Charge	f_{nu}	f_{el}
I	<p>Detailed description: This diagram shows a complex 3D arrangement of 13 gold atoms (Au) labeled A through M. The atoms are represented by spheres of varying sizes, indicating their relative atomic positions. Bond lengths between adjacent atoms are labeled in Angstroms (Å). For example, bond lengths range from 2.71 to 2.98 Å.</p>	0.00	13	A	0.19	0.98	1.02
				B	-0.05	1.00	0.99
				C	0.15	1.01	0.99
				D	-0.14	1.03	0.97
				E	-0.18	0.99	1.01
				F	-0.01	1.02	0.98
				G	0.10	0.99	1.00
				H	-0.15	0.99	1.00
				I	-0.19	1.00	1.00
				J	0.10	1.00	1.00
				K	0.10	0.99	1.00
				L	-0.01	1.03	0.98
				M	0.01	0.97	1.03
II	<p>Detailed description: This diagram shows a smaller 3D arrangement of 8 gold atoms (Au) labeled A through H. Bond lengths are labeled in Angstroms (Å).</p>	0.04	8	A	0.15	0.99	1.01
				B	-0.04	1.05	0.96
				C	0.03	0.94	1.07
				D	-0.16	1.02	0.98
				E	0.11	1.03	0.98
				F	-0.19	0.93	1.07
				G	0.99	1.04	0.96
				H	0.00	1.00	1.01
III	<p>Detailed description: This diagram shows a 3D arrangement of 13 gold atoms (Au) labeled A through M. Bond lengths are labeled in Angstroms (Å).</p>	0.47	13	A	0.01	1.00	1.00
				B	0.22	1.00	1.00
				C	-0.18	0.97	1.03
				D	0.21	1.05	0.95
				E	0.01	0.92	1.08
				F	-0.28	0.96	1.05
				G	-0.16	1.02	0.98
				H	-0.12	0.95	1.06
				I	0.11	1.03	0.97
				J	-0.18	1.05	0.95
				K	0.24	1.00	1.00
				L	-0.17	0.95	1.06
				M	0.20	1.06	0.94
IV	<p>Detailed description: This diagram shows a 3D arrangement of 9 gold atoms (Au) labeled A through I. Bond lengths are labeled in Angstroms (Å).</p>	0.99	9	A	0.16	1.01	1.00
				B	-0.03	1.01	0.99
				C	-0.01	0.99	1.01
				D	0.09	0.95	1.05
				E	-0.16	1.03	0.97
				F	0.07	1.01	0.99
				G	0.02	0.98	1.02
				H	-0.10	1.02	0.98
				I	0.02	1.01	0.99

^a The values in red, blue, and black are electrophilic, nucleophilic, and amphiphilic attack loving sites respectively. The values given next to the conformations in column II of the table correspond to the inter-atomic distances (in Å) between various unique sites.

electrophilic and nucleophilic attack loving sites as shown in Figure 3a or a 3D cluster with amphiphilic attack loving sites at the base

such as shown in Figure 3b are better suited for adsorption and subsequent catalytic reactions. Some of the earlier reports^{49,50}

TABLE 9: HOMO and LUMO Energies, the Corresponding Energy Gaps, and Hardness in Au Clusters

system	$-E_H$ (eV)	$-E_L$ (eV)	E_{gap} (eV)	hardness, (eV)
Au ₆ , I	6.041	3.837	2.204	1.102
Au ₆ , II	5.795	4.029	1.767	0.883
Au ₆ , III	5.514	5.117	0.397	0.199
Au ₆ , IV	5.270	4.496	0.774	0.387
Au ₇ , I	5.139	3.950	1.188	0.594
Au ₇ , II	4.632	4.550	0.081	0.041
Au ₇ , III	4.664	3.879	0.785	0.392
Au ₇ , IV	4.981	3.833	1.148	0.574
Au ₇ , V	4.866	3.943	0.924	0.462
Au ₈ , I	6.045	4.340	1.706	0.853
Au ₈ , II	5.461	4.623	0.837	0.419
Au ₈ , III	5.816	3.987	1.829	0.914
Au ₈ , IV	5.666	4.623	1.043	0.521
Au ₈ , V	5.823	3.903	1.921	0.960
Au ₉ , I	5.135	4.356	0.778	0.389
Au ₉ , II	4.706	4.530	0.176	0.088
Au ₉ , III	4.803	4.050	0.753	0.377
Au ₉ , IV	4.581	3.912	0.669	0.335
Au ₁₀ , I	5.735	4.439	1.297	0.648
Au ₁₀ , II	5.527	4.132	1.395	0.698
Au ₁₀ , III	5.396	4.178	1.218	0.609
Au ₁₁ , I	5.239	4.247	0.992	0.496
Au ₁₁ , II	4.468	4.468	0.541	0.271
Au ₁₁ , III	4.927	4.036	0.891	0.446
Au ₁₁ , IV	4.801	4.189	0.612	0.306
Au ₁₂ , I	5.642	4.707	0.935	0.467
Au ₁₂ , II	5.514	4.408	1.106	0.553
Au ₁₂ , III	5.599	4.556	1.044	0.522
Au ₁₂ , IV	5.219	4.380	0.839	0.420
Au ₁₃ , I	5.219	4.525	0.695	0.347
Au ₁₃ , II	4.991	4.780	0.210	0.105
Au ₁₃ , III	4.801	4.062	0.740	0.370
Au ₁₃ , IV	4.854	4.393	0.461	0.230

document the fact that mostly the 3D conformations are adsorbed on the surface.

VI. Summary and Conclusions

Our calculations show that the lowest energy structure is a planar one up to Au₁₃. The lowest energy conformations in Au clusters grow in a directional fashion by adding one atom to the ground state of the cluster of previous size from Au₆ to Au₁₃. However, analysis of IR spectra of various isomers of Au₇ and their comparison with the experimental Au₇ IR

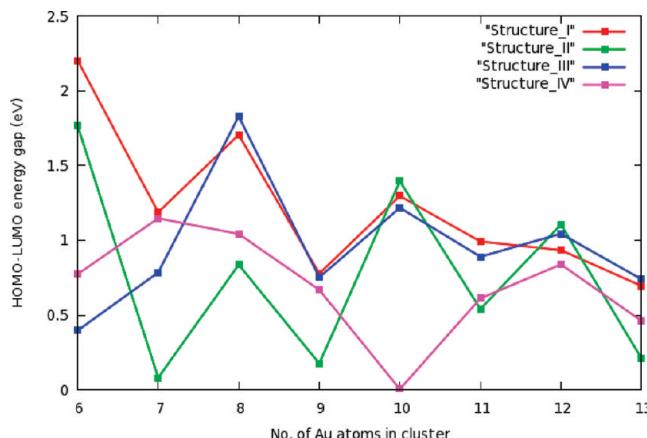


Figure 2. Size dependence of HOMO–LUMO energy gaps for the low-lying energy structures of Au cluster Some of the possible favorable Au cluster conformations for adsorption on oxide supports. Atoms in red, blue and black correspond to sites favorable for an electrophilic, nucleophilic, and amphiphilic attack respectively.

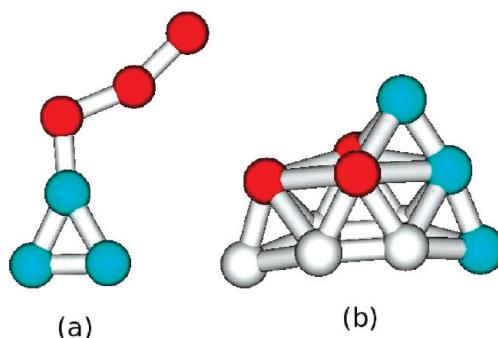


Figure 3. Some of the possible favorable Au cluster conformations for adsorption on oxide supports. Atoms in red, blue, and grey correspond to sites favorable for an electrophilic, nucleophilic, and amphiphilic attack respectively.

spectrum indicate that many conformations are likely to coexist in this cluster range. Interestingly, all the Au cluster conformations (planar as well as nonplanar) in Au_n ($n = 6–13$) have a central negatively charged core surrounded by positively charged atoms. These negatively charged centers are bonded through the largest interatomic bond distances. Finally, the reactivity of a cluster depends on the position and number of electrophilic and nucleophilic sites in a cluster. The reactivity descriptors indicate that while planar conformations are best suited gas phase catalysts for concomitant oxidation and reduction reactions, 3D conformations are better suited for adsorption on a surface and subsequent oxidation and reduction reactions.

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