Chemistry and Materials Research
ISSN 2224- 3224 (Print) ISSN 2225- 0956 (Online)
Vol.9 No.3, 2017

DFT Study of Small Gold Clusters Au_n (n=2-13): The Structural, Electronic, Thermodynamic and Spectral Properties

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Abstract

The structures and relative stabilities of small gold clusters Au_n (n=2-13) have been investigated at
The B3LYP/ CEP-121G level of density functional theory with exploitation Gaussian09 program. Relative stabilities of these clusters have been analyzed based on the variation of their binding energies (E_b), fragmentation energies (E_{frag}), ionization energies (VIP), electron affinities (EA), the energy gap (E_{gap}) and IR spectrum with cluster size (n). We note that the gold clusters Au_n (n=2, 4, 6, 8, 10, 12) have a special values of E_{gap}, VIP and E_{frag}, these indicates that these clusters are more stable than their neighbouring clusters. Binding Enthalpy (ΔH_b), Entropy (ΔS_b) and Gibbs free energy (ΔG_b) of Au_n clusters were computed at 298.15K.We note that these amounts decrease with increasing cluster size. We calculate IR spectra for gold clusters and compared our results with experimental data and we note that the clusters Au_n (n=6, 8, 10, 12) absorbed at lower wave length.

Keywords: Gold clusters, Density Functional theory (DFT), Bending energy, Fragmentation energy, Ionization energy, Electron affinity, Energy gap, Enthalpy, Entropy, Gibbs free energy, IR spectrum.

Introduction

In recent years, gold nanoclusters have received considerable attention due to their important role as building blocks in nanoscale electronic [1], optical and medical diagnostic devices [2], in particular small gold clusters have attracted interest as tips and contacts in molecular electronic circuit [3] and also as potential chemical catalysts [4].

The gold shows distinctively structural and electronic properties compared to its lighter congeners copper and silver [5], the exceptional and unique chemical and physical properties of gold are often caused by large relativistic effects [6].

There have been a number of papers dedicated to structure of both neutral and ionic gold clusters, Grönbeck and Andreoni compared Au_2 to Au_5 with spin polarized (Beck-three-Yang-parr) functional[7].

Bravo pérez et al investigated small gold clusters up to six atoms at ab initio Hartree-fock (HF) and post-HF levels [8]. Häkkinen and Land man have investigated the low energy structures of gold clusters and their anions for Au_n (n=2-10) using density functional theory (DFT) employing secular relativistic pseudo potentials for $5d^{10}6s^1$valance electrons of gold and generalized gradient approximation (GGA).Thy located the planer to 3D transition for neutral clusters at n=7[9]. Walker performed DFT calculations to determine the optimized geometries of neutral Au_n (n=2-11) and cationic Au_n^+ (n=2-9) clusters and found that the 2D to 3D transition for neutral clusters occurs at n=11 [10].

Computational method

The isomers of gold clusters Au_n (n=2-13) have been fully optimized using (DFT) theory and we have chosen the B3LYP functional which incorporates Becke's exchange and Lee-Yang-Parr correlations. In order to determine the best basis set to be used for the calculation, we made a comparative study of bond length(R), binding energy (E_b), fragmentation energies (E_{frag}), ionization energies (VIP), electron affinities (EA), the energy gap between highest occupied and the lowest unoccupied molecular orbital (E_{gap}) and wave number (ϖ) of gold dimer Au_2 using various basis sets and compared our results, the results are presented in table1.

The binding energy is computed from:

$$E_b = E(Au_n) - n E(Au)$$

Where $E(Au_n)$ is the energy of a cluster with n atoms and E(Au) is the energy of Au atom.

The fragmentation energy for the cluster has been calculated from:

$$E_{frag} = E(Au) + E(Au_{n-1}) - EAu_n$$

The ionization potential (VIP) and electron affinity (EA) are calculated as:

$$VIP = E(Au_n^+) - E(Au_n)$$

$$EA = E(Au_n^-) - E(Au_n)$$

Where $E(Au_n^+)$ and $E(Au_n^-)$ are the energy of the cationic and anionic clusters, respectively, at the optimized geometry of the neutral cluster.

The energy gap (E_{gap}) is calculated as:

$$E_{gap} = |\varepsilon_{HOMO} - \varepsilon_{LUMO}|$$

Where ε_{HOMO} is the energy of highest occupied molecular orbital and the ε_{LUMO} is the energy of lowest unoccupied molecular orbital.

TABLE 1. Bond length(R), binding energy (E_b), fragmentation energy (E_{frag}), ionization energy (VIP), electron affinity (EA) and wave number (ϖ) of gold dimer Au_2

Method	R (Å)	E_b (eV)	VIP (eV)	EA (eV)	ϖ (cm^{-1})
DFT/B3LYP(CEP-4G)	2.5706	1.90567	9.149196	1.818839	164.744
DFT/B3LYP(CEP-31G)	2.5706	1.90567	9.149196	1.818839	164.744
DFT/B3LYP(CEP-121G)	2.5706	1.90567	9.149196	1.818839	164.744
DFT/B3LYP(LANL2MB)	2.6757	1.53236	9.303302	1.986614	143.817
DFT/B3LYP(LANL2DZ)	2.573	1.87258	9.424427	2.027354	162.497
DFT/B3LYP(SDDALL)	2.5789	1.85963	9.267366	1.955103	163.915
Experimental values *	2.47[a]	2.30[b]	9.5[b]	1.94[b]	191[c]

Experimental values (a), (b) and (c) are taken from [11], [12] and [13] respectively.

We note from the table (1) that the values from DFT/B3LYP(CEP-121G) are agree with the experimental values so we will use this basis set in all calculations.

Results and discussion

1-Structural data:

In our resent work [14]: we investigate a number of low-lying energy structures of Au_n (n=2-10) clusters are calculated at B3LYP/CEP-121G level to obtain the corresponding global minimum structures. Figure1. shows the optimized geometries and their bond lengths and angles.

In this work: the DFT/B3LYP/CEP-121G groundstates and a number ofisomers of Au_n (n=11-13) clusters are presented in figure 2, where their relative energies from ground state are displayed below the structures. We notice from figure 1 and 2 that all stable structures prefer to be planner.

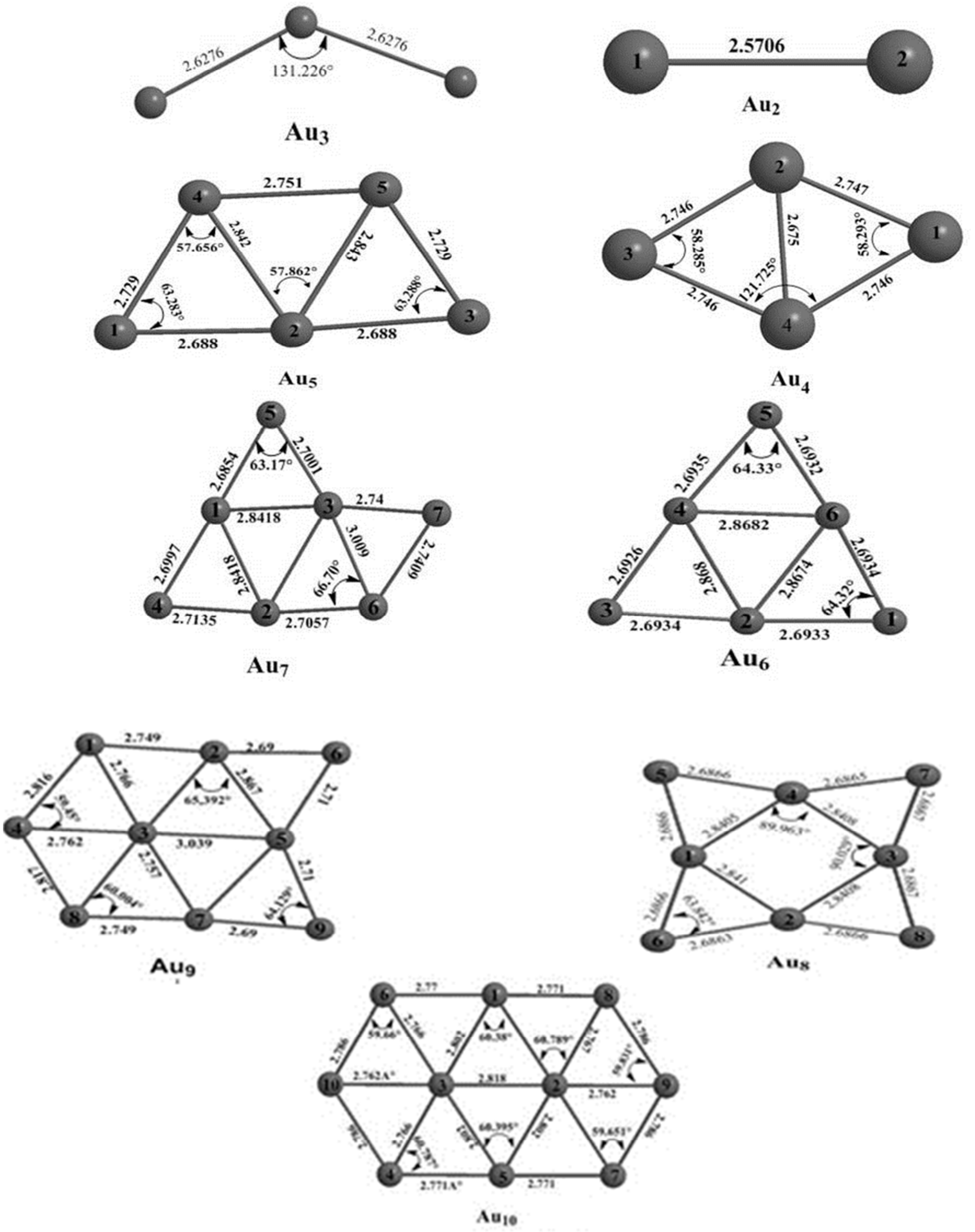


Fig 1. B3LYP/CEP-121G optimized geometries of Au_n clusters (n=2-10) and their angles and bond lengths.

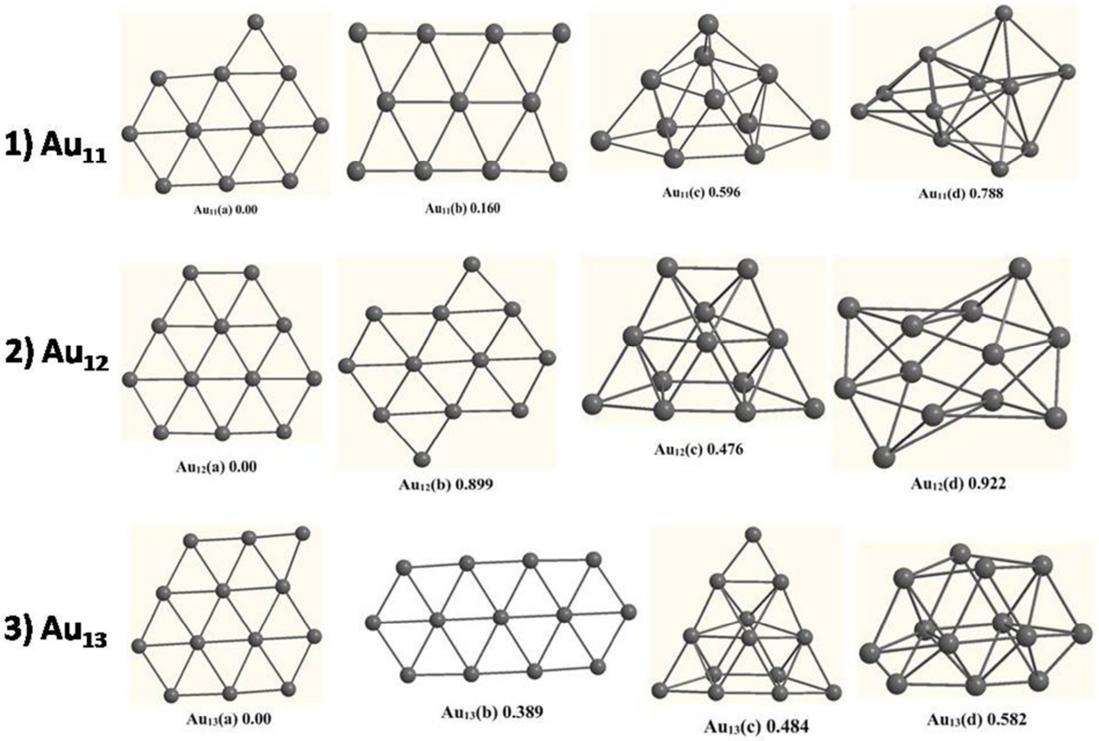


Fig 2. B3LYP/CEP-121G optimized geometries of Au_n clusters (n=11-13). The relative energies (eV) are indicated below the structures

2-Electronic properties:

The binding energies E_b, fragmentation energies (E_{frag}), ionization energies (VIP), electron affinities (EA) and the energy gap (E_{gap}) for the gold clusters Au_n(n=2-13) are collected in table 2.

Table 2. Binding energies E_b, fragmentation energies (E_{frag}), ionization energies (VIP), electron affinities (EA) and the energy gap (E_{gap}) for the gold clusters Au_n (n=2-13**).**

Cluster size(n)	**E_b (eV)**	**E_{gap} (eV)**	**VIP (eV)**	**EA (eV)**	**E_{frag} (eV)**
2	-1.919	3.195	9.1491	1.8188	1.91
3	-2.878	2.926	7.0254	3.4054	0.96
4	-4.909	1.911	7.7249	2.4418	2.03
5	-6.732	2.448	7.0544	2.952	1.82
6	-9.973	3.361	8.2211	2.0256	2.64
7	-10.535	2.172	7.0117	3.1976	1.16
8	-12.970	2.684	7.6195	2.6589	2.43
9	-14.245	1.7381	6.8494	3.3611	1.27
10	-16.558	2.227	7.385	2.7477	2.31
11	-18.122	1.916	6.846	3.591	1.51
12	-20.463	1.767	7.232	3.154	2.34
13	-22.002	1.489	6.736	3.695	1.54

Figure 3. describes the binding energy per atom E_b/n. Notice that the binding energy increases with size of clusters when (n<5) whereas for (n≥5) we note that the even numbered clusters have the highest binding energy than the odd numbered size. These indicates to the higher stability of even numbered clusters than the odd numbered clusters and this agree will with resent theoretical study of Decka [15].

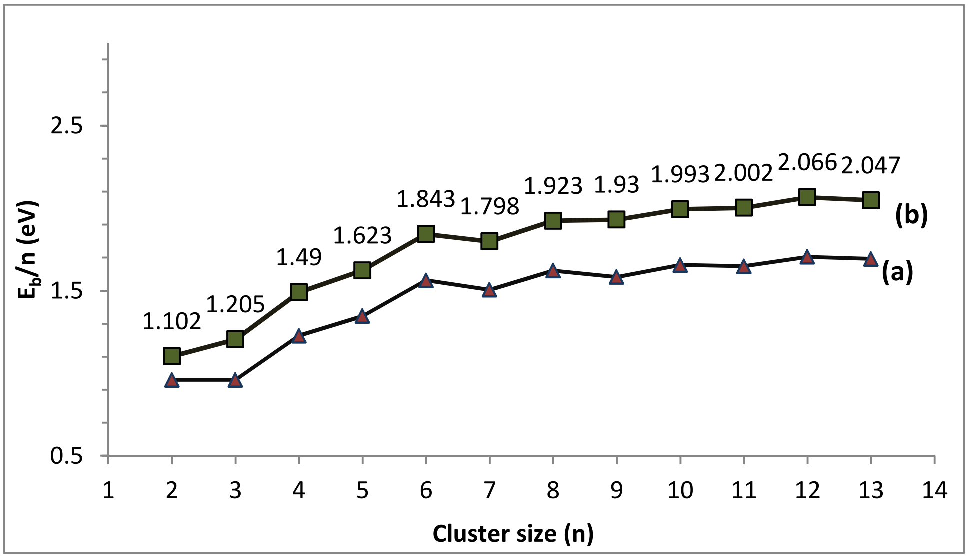


Fig.3 Size dependence of the binding energy per atom E_b/n for the lowest-energy structures of Au_n clusters. (a) Denotes to the values in this work and (b) denotes to the values which calculate by B3LYP/DNP [15].

The size dependence of fragmentation energies for the lowest-energy clusters Au_n are shown in Fig 4. Clearly, there are five remarkable peaks at cluster sizes with (n = 4, 6, 8, 10, 12). These clusters have enhanced stabilities as compared to their neighbors and the cluster Au_6 has the highest value of fragmentation energy indicating high stability of cluster which agree with Decka [15].

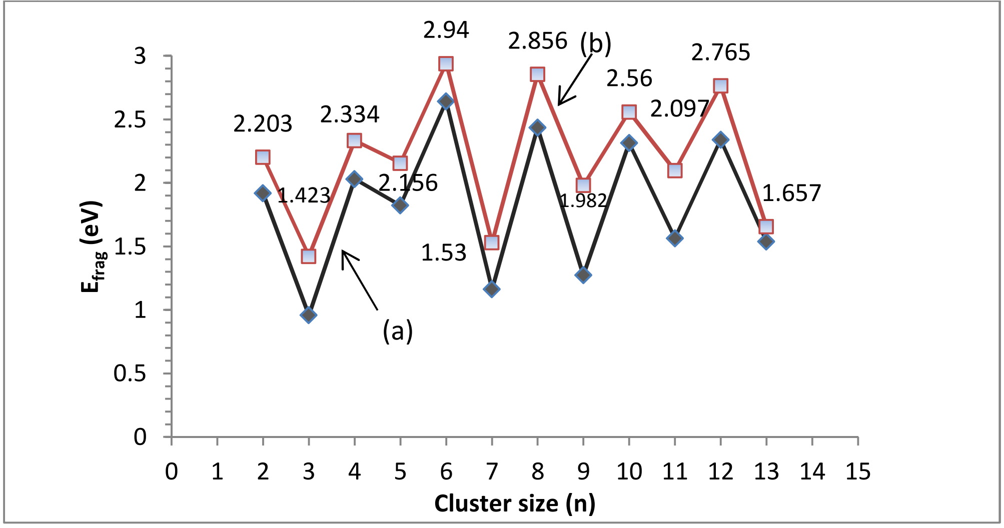


Fig 4. Size dependence of the fragmentation energy E_{frag} of the lowest-energy structures of Au_n clusters. (a) Denotes to the values in this work and (b) denotes to the values which calculate byB3LYP/DNP [15].

The energy gap for gold clusters is considered to be an important parameter in terms of the electronic stability of small clusters. The E_{gap} as function of cluster size is shown in figure.5. As seen from the figure.5 the E_{gap} shows an odd-even oscillation for (n>4). The even numbered clusters (n=6, 8, 10, 12) have larger E_{gap} and are relatively more stable than the odd-numbered neighbours.

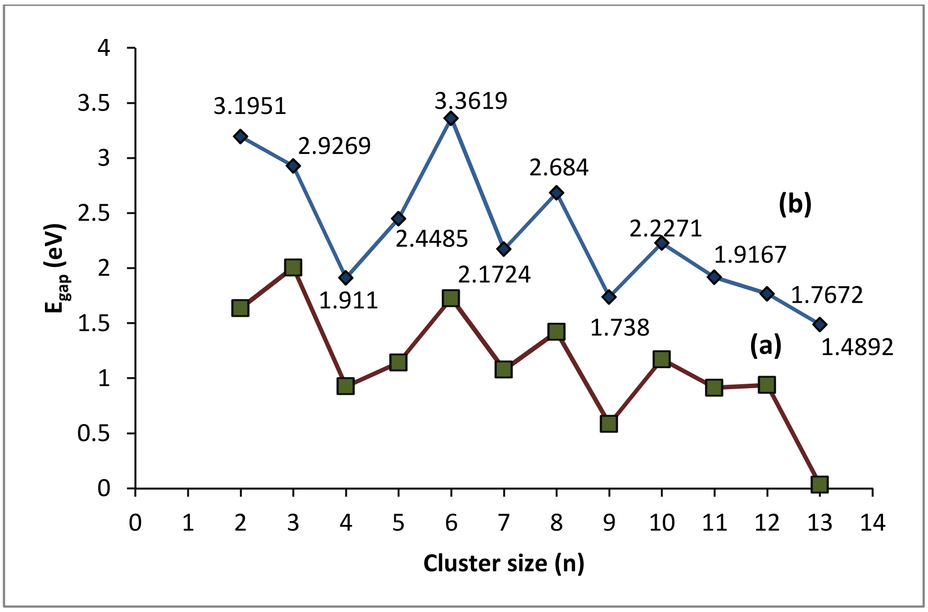


Fig 5. Size dependence of the E_{gap} of the lowest-energy structures of gold clusters. (a) denotes to the values in this work and (b) denotes to the values which calculated by B3LYP/DNP[15].

In figure 6. The calculated vertical ionization potential values of gold clusters are compared with the experimental values [16] and the theoretical values for Decka [15]. The trend of VIP shows a remarkable odd-even oscillation which implies that the clusters with even numbers of atoms (n=2,4,6,8,10,12) have higher VIP than the neighbor clusters with odd numbers of atoms.

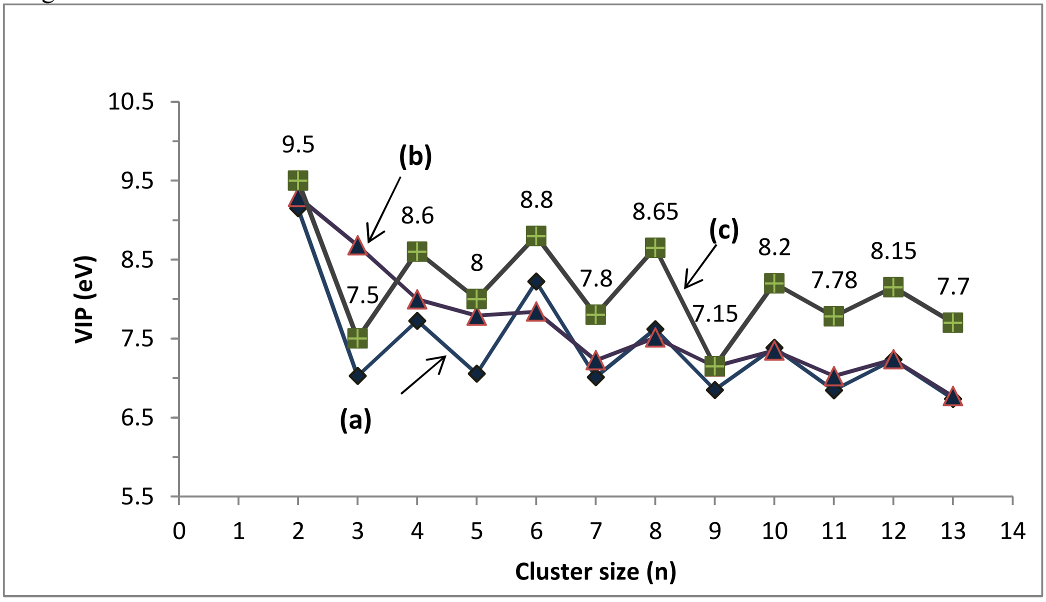


Fig 6. Size dependence of the vertical ionization potential (VIP) of the lowest-energy structures of gold clusters. Where (a) denotes to the values in this work, (b) denotes to the values which calculate by B3LYP/DNP[15] and (c) denotes to the experimental values[16].

The calculated electron affinities (EA) of gold clusters are compared with the experimental electron affinity [17] and plotted in figure 7. Similar to the ionization potentials the electron affinities show an odd-even alterative behavior but in this case the nature is opposite the even-sized clusters n=(2,4,6,8,10,12) have lower values of electron affinity compared to the odd-sized one.

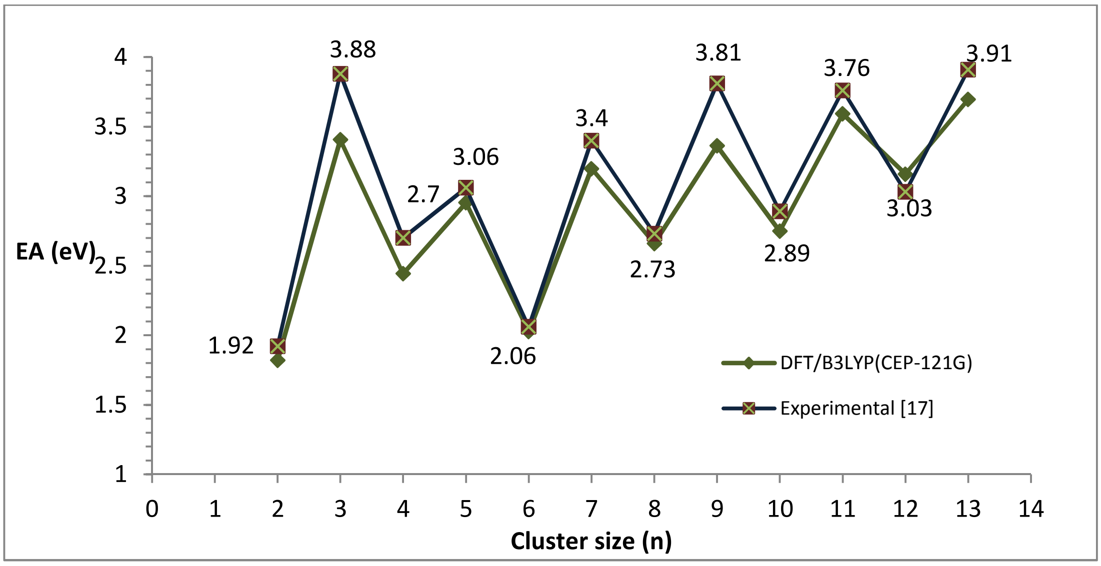


Fig.7. Size dependence of the electron affinities (EA) of the lowest-energy structures of gold clusters.

3-Thermodynamic properties:

Binding Enthalpies (ΔH_b) Entropies (ΔS_b) and Gibbs free energies (ΔG_b) of formation of the Au_n clusters from Au atoms, were computed at 298.15 K. The calculated values of ΔH_b, ΔS_b andΔG_b have been summarized in Table 3.

The binding enthalpy is computed from:

$$\Delta H_b = (H+E_i)_{(Aun)} - n(H+E_i)_{(Au)}$$

Where $H(Au_n)$ is the enthalpy for gold clusters and H(Au) the enthalpy for gold atom.

The binding Entropy free energy is calculated from:

$$\Delta S_b = S(Au_n) - nS(Au)$$

Where $S(Au_n)$ is the entropy for gold clusters and S(Au) the entropy for gold atom.

The binding ΔG_b Gibbs free energy is calculated from:

$$\Delta G_b = \Delta H_b - T\Delta S_b$$

Where T is the temperature in Kelvin (T=298.15).

Table 3.The calculated binding enthalpies (ΔH_b), binding entropies (ΔS_b) and binding Gibbs free energies (ΔG_b) of formation the Au_n clusters from Au atom.

Cluster size (n)	**ΔH_b (kcal/mol)**	**ΔS_b kcal/mol.kelvin**	**ΔG_b (kcal/mol)**
2	-44.23	-0.021463	-37.83
3	-66.18	-0.039783	-54.73
4	-112.55	-0.069971	-91.69
5	-154.13	-0.094945	-125.82
6	-214.58	-0.125954	-177.03
7	-240.91	-0.149546	-196.33
8	-296.60	-0.17686	-243.87
9	-325.53	-0.205328	-264.31
10	-378.43	-0.23691	-307.79
11	-414.03	-0.263296	-335.52
12	-467.53	-0.294078	-379.85
13	-502.58	-0.321008	-406.87

To find out if the formation reactions of Au_n clusters from Au atoms is exothermic or not, we calculate ΔH_b from:

$$\Delta H_b = H(Au_n) - nH(Au)$$

Where $H(Au_n)$ is the thermal correction to enthalpy for gold clusters and H(Au) is the thermal correction to enthalpy for gold atom. The values of are collected in table 4. We note from the table that the formation reactions of Au_n clusters are endothermic processes when (n>3).

Table 4. The calculated ΔH_b of formation the Au_n clusters from Au atom.

Cluster size (n)	ΔH_b (kcal/mol)
2	-0.264808779
3	-0.250376073
4	0.075928584
5	0.395330642
6	0.731047934
7	1.043547394
8	1.376754649
9	1.684234038
10	2.004263605
11	2.328058227
12	2.654990393
13	2.975647469

4- Infrared-spectra (IR):

We calculated IR spectra for gold clusters Au_n (n=2-13) and compared our results with experimental values for Gruene et al [18]. The frequencies and IR intensities for IR active modes of gold clusters are presented in Tables 5 and 6 along with available experimental data. No IR-active mode is found in Au_2 while for Au_n (n=3,6,9,10,11,12,13), there is no experimental data to compare with our calculated results.Figure.8 shows the IR spectrum for gold clusters Au_n (n=3-13).

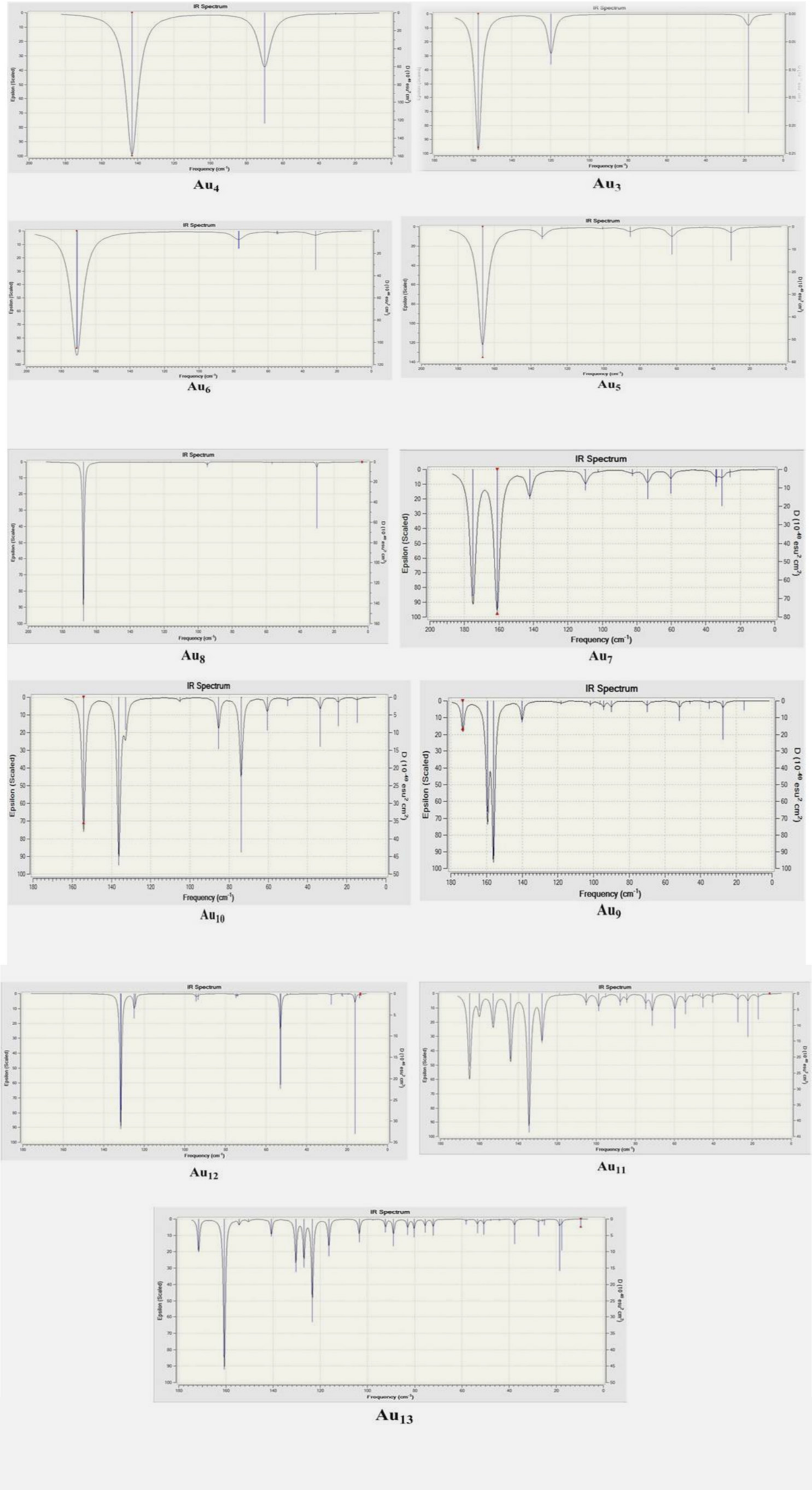
Table 5. Calculated IR intensities along with IR active frequencies at B3LYP/CEP-121G level of theory for Au_n(n=2-10).

Clusters	Frequencies(cm^{-1})	Experimental frequency (cm^{-1})
Au_2	164.74	191
Au_3	17.94	
	119.79	
	157	
Au_4	30.78	76
	69.97	
	143.26	158
Au_5	30.04	
	47.16	
	62.54	53
	85.38	
	133.67	100
	166.44	192
Au_6	32.36	
	76.89	
	77.06	
	170.65	
	170.99	
Au_7	33.94	
	73.70	
	82.66	
	110.36	
	142.16	
	161.04	165
	175.01	186
		201
Au_8	30.11	
	50.14	46
	86.32	
	94.59	
	116.26	113
	167.5	193
	167.55	
Au_9	27.42	
	51.85	
	96.01	
	140.07	
	156.12	
	259.41	
	173.23	
Au_{10}	33.50	
	73.85	
	132.77	
	136.22	
	154.15	

Table 6.Calculated IR intensities along with IR active frequencies at B3LYP/CEP-121G level of theory for Au$_n$(n=11-13).

Clusters	Frequencies(cm^{-1})	Experimental frequency (cm^{-1})
Au$_{11}$	27.34	
	59.64	
	127.84	
	134.5	
	143.94	
	152.9	
	159.98	
	165.02	
Au$_{12}$	16.02	
	52.79	
	52.90	
	73.88	
	94.46	
	125.03	
	131.58	
Au$_{13}$	18.57	
	37.65	
	88.98	
	103.52	
	116.39	
	123.39	
	30.391	
	140.73	
	160.69	
	171.60	

We note from the tables 5 and 6 that the even numbered clusters Au$_n$ (n=6,8,10,12) absorbed at lower wavelength than the odd-sized clusters.



Au_4 Au_3

Au_6 Au_5

Au_8 Au_7

Au_{10} Au_9

Au_{12} Au_{11}

Au_{13}

Fig.8 IR of gold clusters Au_n (n=3-13).

Summary and conclusions

We have studied structural and electronic properties of gold clusters using Density functional theory at B3LYP/CEP-121G basis set. Gold clusters are observed to prefer planer structures. We note that the gold clusters Au_n (n=2, 4, 6, 8, 10, 12) have a special values of E_{gap}, VIP, EA and E_{frag}, these indicates that these clusters are more stable than their neighbouring clusters. Enthalpy and Gibbs free energy of Au_n clusters from Au atoms, were computed at 298.15K. We note that these amounts decrease with increasing of clusters size. We calculate IR spectra for gold clusters and compared our results with experimental data and we note that the clusters Au_n (n=6, 8, 10, 12) absorbed at lower wave lengths.

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