



# The $\text{Ag}_x\text{Si}_y$ ( $x=1-5$ , $y=1-5$ , $x+y=5$ ) Clusters

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**Abstract:** In this paper are presented the theoretical work for clarify the structure of all cluster which levels of theory describe better the propriety of the  $\text{Ag}_x\text{Si}_y$  cluster. For  $\text{Ag}_x\text{Si}_y$  are reach different value of the bond, ionization potentials and frequencies, electron affinities and binding energy method employed ab initio and relativistic bases. Are optimization with PBE/LANL2DZ level of theory. I employed relativistic LANL2DZ bases in this work and PBE functional of exchange and correlation Perdew-Burke-Ernzerhof who employed the GGA (Generalized Gradient Approximation), this are better for the energy, and different energy structure.

**Keywords:**  $\text{Ag}_x\text{Si}_y$  clusters, Electronic Properties, Binding Energy, Electron Affinity and Ionization Potentials

## 1. Introduction

Many series of elemental clusters have been characterized in detail with a variety of different levels of theory and experimental techniques. Very little is known about the structure  $\text{A}_x\text{B}_y$  of clusters in general. Elucidating of this structure is a challenging problem that requires piecing together informations from different experiments and theory. The study of  $\text{Ag}_x\text{Si}_y$  is important for the practical importance in the new electronic materials. Are mentioned in the papers the structure and another properties of silver and silicon clusters. The people are now the difference of the clusters and bulk-state. Ideas like “super-atoms”, “magic numbers” or “fission” in clusters provokes a wider class of scientists to study this “relatively” new area of the physical sciences. Growing interest in the stabilities of small clusters and the evolution of bulk properties from cluster properties is also due to the emergence of new science.

Ab initio effective core potentials (ECPs) have been generated to replace the Coulomb, exchange, and core-orthogonality effects of the chemically inert core electron in the transition metal atoms.

In LANL2DZ the relativistic mass-velocity and Darwin effect on the valence electrons are incorporated in the relativistic ECP's generated for the heavier ( $Z>36$ ) elements.

The “core” ns and np orbitals do not play any direct role in the chemical bonding in this species, since their binding energies are much larger than electrons in the valence

shell. The core electrons:  $\text{Ag}[\text{core}]4s^24p^64d^{10}5s^1$ . The calculations are with the program Gaussian 03.

In this study are important now the influence of d-electrons at the outer orbitals, overlapped by the partially filled s-orbitals, which makes the study of silver clusters interesting and challenging. The dissociation energies for the loss of an atom showed strong odd-even alternation. The electronic properties of silver cluster and the stability of the clusters are strongly dominated by the filled d electrons screening the oscillator strength of valence electrons but are not known for  $\text{Ag}_x\text{Si}_y$ . The majority of spectroscopic phenomena can be explained in terms of s electrons. Topologically different clusters and clusters belonging to different symmetry groups have been identified and studied in detail for  $\text{Ag}_x\text{Si}_y$  clusters. In the potential energy surface (PES) the local minimum, meaning that it is the lowest point in some limited region of the potential surface, or it can be the global minimum, the lowest energy point anywhere on the potential surface. Different minima corresponding to different conformations or structural isomers in the case of single molecules. A point which is a maximum in one direction and a minimum in the other is called a saddle point. A saddle point corresponds to a transition structure connecting the two equilibrium structure. A point on the potential energy surface where the force are zero is called a stationary point. By definition, a structure which has n imaginary frequencies is an  $n^{\text{th}}$  order saddle point. In this work are not reported all transition structure with imaginary

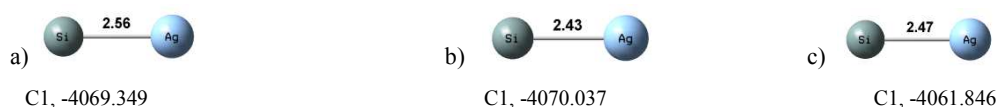
frequencies that are important for path of reaction between the minima local point in the PES. Are studie all proprieties because are important for the chemical reaction when are possible form secondary product because this structure are more energy and exist for little timp for transformation in another structure or reacting.

## 2. Results and Discussion

In this work full geometry optimizations have been carried out and are reported only the must stable structure with the positive frequencies values.

The local density approximation (LDA) in density-functional theory (DFT) has been used successfully to calculate the structural properties of solids, including the calculations of the stability, lattice constant, bulk moduli, and phonon spectra, for the last two decades, for this motive I used in this paper PBE theory.

The overestimation of binding energy of the molecule or solids and the underestimation of the gap in insulators and bond lengths are well known deficiencies of the LDA which limits its further application. Computationally, it is simple to extend the LDA functional to the GGA functional with simple gradient calculations of the density at minimal cost.



**Fig. 1.** The structure of dimer clusters with PBE/LANL2DZ: a) neutral; b) anions; c) cations. Are reported symmetrie and electronic state. The energy of clusters in eV.

Are observed that the anion and cation cluster are minor distance that the neutral cluster. The cluster Fig. 1 a) are the  $\alpha$  orbital HOMO with -0.163 energy and  $\beta$  orbital HOMO with -0.143 energy, degenerate; the LUMO orbital  $\alpha$  are -0.158 energy and  $\beta$  orbital LUMO with -0.111 energy. The HOMO for cation cluster are 0.057 for  $\alpha$  and  $\beta$  and LUMO 0.037 energy. For anion cluster -0.415 for HOMO and -0.386 energy for LUMO. For this degenerate orbital the distance in neutral cluster are minor that cation and anion cluster. In literatura for silver cluster are not reported this tip of distance and variation of distance between neutral, anion and cation cluster [5].

### 3.2. Neutral Trimer, Neutral, Anions and Cations

For the structure in Fig. 2 a) I the HOMO are -0.114 and LUMO -0.133 energy, for 2 a) II -0.151 and -0.193 hartree, for 2 a) III -0.178 hartree and -0.150 hartree and 2 a) IV the

Ortiz and Ballone applied the earlier version of the GGA functional to atoms, molecules, and solids and characterized the basic properties of the GGA functional [1, 2]. In this paper we consider the simplified version of the GGA functional by Perdew, Burke, and Ernzerhof (PBE)[3] which satisfies many exact properties of DFT. I employed SCF=QC, quadratically convergent SCF procedure [4], for optimization in Gaussian for all structure neutral, anions and cations.

According to molecular orbital (MO) theory the ionization potential of a molecule is simple the orbital energy of the HOMO and the electron affinity is the orbital energy of the LUMO, with change in sign:

$$I = -\epsilon_{\text{HOMO}}$$

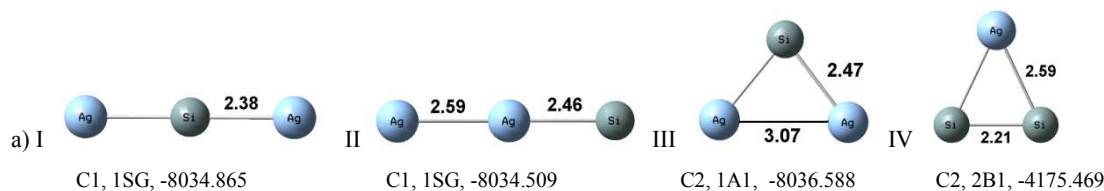
$$A = -\epsilon_{\text{LUMO}}$$

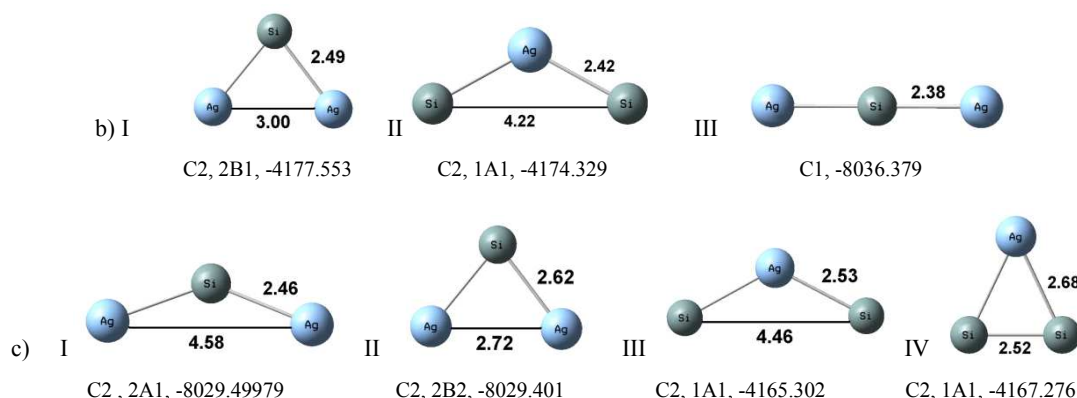
These are consequences of Koopmans theorem.

## 3. Distance in Clusters

### 3.1. Neutral Dimers, Neutral Anions and Cations

HOMO are -0.187 and LUMO are -0.113 hartree. In this cluster are present the Jahn –Teller effect, for Fig. 2 b) I when  $\alpha$  HOMO are 0.019 hartree and  $\beta$  HOMO are 0.000 hartree, the LUMO are 0.061 and 0.057 hartree. In Fig. 2 b) II the HOMO are 0.021 and LUMO 0.010. In the Fig. 2 b) III the cluster for  $\alpha$  HOMO are 0.040 and  $\beta$  HOMO 0.048 hartree, for LUMO  $\alpha$  and  $\beta$  0.007 and 0.055 hartree. In Fig. 2 c) I -0.360  $\alpha$  HOMO and -0.326  $\beta$  HOMO, for LUMO are -0.340 and -0.319 hartree. In Fig. 2 c) II -0.380  $\alpha$  HOMO and -0.350  $\beta$  HOMO, for LUMO are -0.351 and -0.340 hartree. In Fig. 2 c) III HOMO -0.343 and LUMO -0.352 hartree and Fig. 2 c) IV for HOMO -0.380 and LUMO -0.387 hartree. In Fig. 2 c) I the obtuse triangle are more distance that in Fig. 2 b) II for the Jahn Teller effect. The structure in Fig. 2 a) I are the same distance with the Fig. 2 b) III for anion cluster. For neutral structure the isoscele Fig. 2 a) III are minor energy, for anion the linear structure and cation the obtuse triangle.



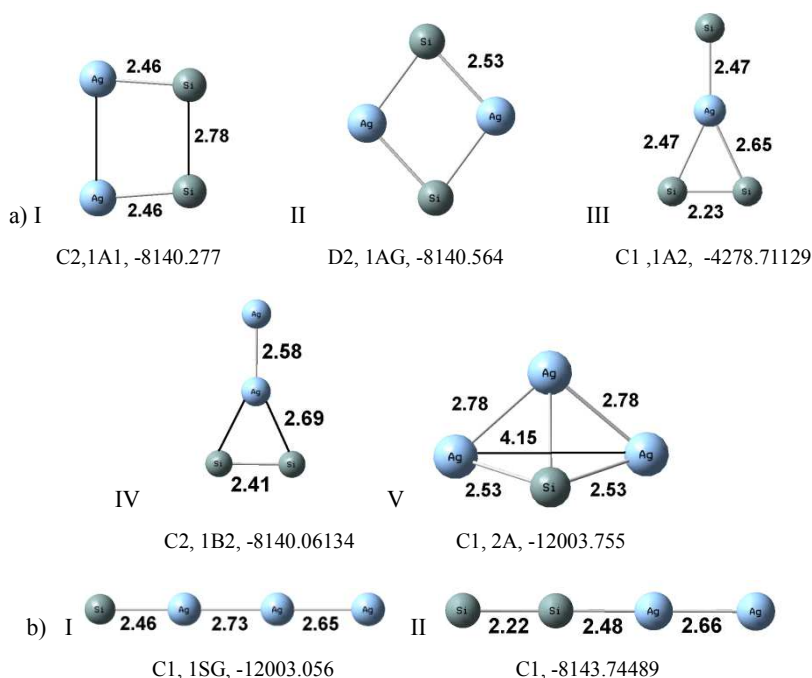


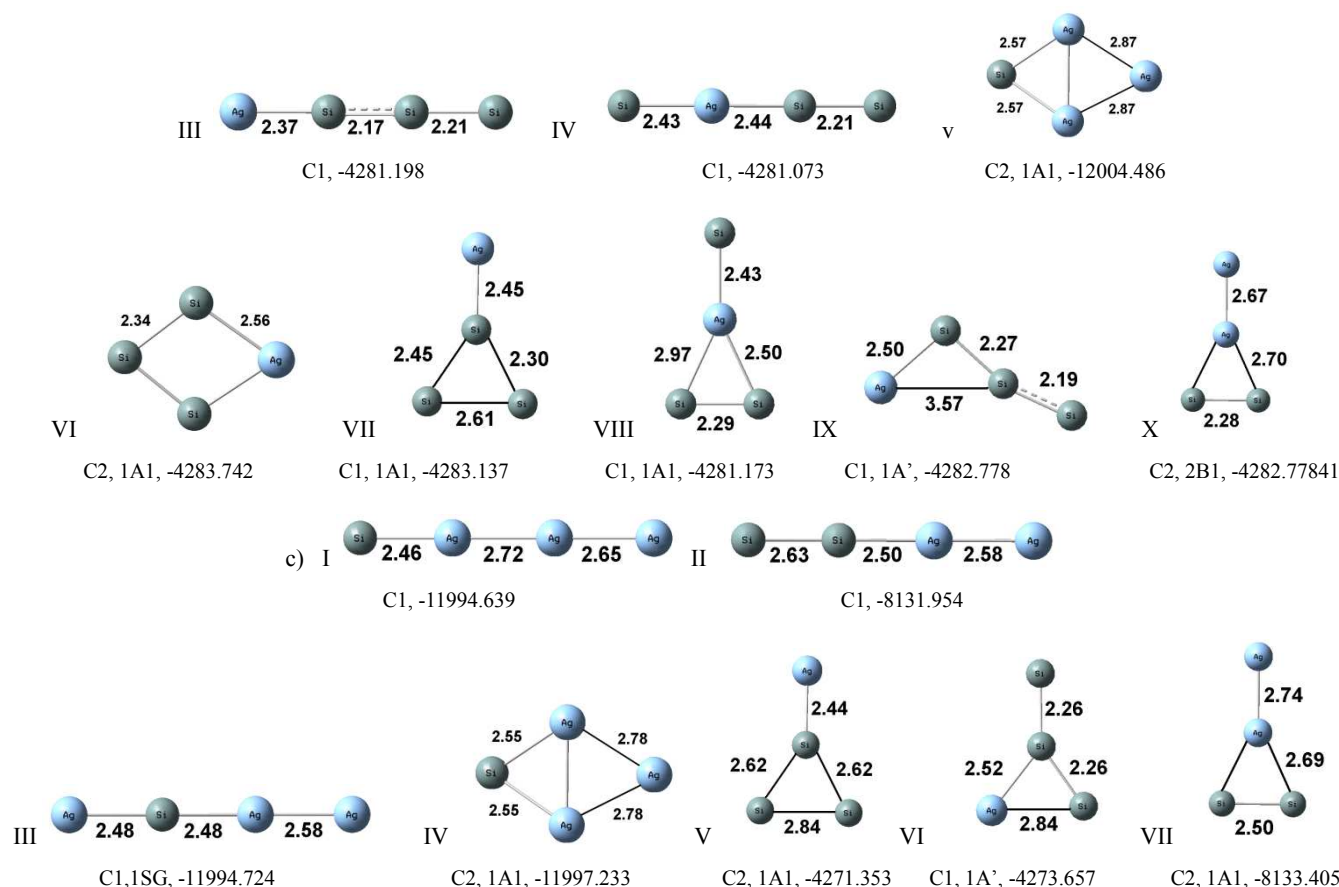
**Fig. 2.** The structure of trimer clusters with PBE/LANL2DZ; a) neutral; b) anions; c) cations. Are reported symmetrie and electronic state. The energy of clusters in eV.

### 3.3. Tetramer, Neutral, Anions and Cations

In the Fig. 3a) I the HOMO are -0.157 hartree and LUMO -0.179 hartree, Fig. 3a) II the HOMO are -0.154 hartree and LUMO -0.169 hartree. In Fig. 3 a) III the  $\alpha$  HOMO are -0.184 and  $\beta$  HOMO are -0.178 hartree, for LUMO are -0.173 and -0.172 hartree. In Fig. 2 a) IV the HOMO are -0.161 and LUMO -0.221 hartree. In Fig. 3a) V the  $\alpha$  HOMO are -0.161 and  $\beta$  HOMO are -0.133 hartree, for LUMO are -0.104 and -0.097 hartree, are degenerate orbital. In the Fig. 3 b) I the HOMO are 0.022 and LUMO -0.002 hartree, Fig. 3 b) II for anion cluster  $\alpha$  HOMO occupied with one electron are -0.029 and  $\beta$  HOMO are -0.027, for  $\alpha$  LUMO 0.035 and  $\beta$  LUMO are 0.056 hartree. In Fig. 3 b) III the HOMO are 0.023 and LUMO -0.005 hartree, in Fig. 3 b) IV the HOMO are -0.022 and LUMO are -0.013 hartree. In Fig. 3 b) V the HOMO are 0.007 and LUMO 0.00 Hartree, in Fig. 3 b) VI the HOMO are -0.022 and LUMO are 0.041 hartree. In Fig. 3 b) VIII the HOMO are -0.013 and LUMO -0.009, in Fig. 3 b IX the HOMO are -0.008 the LUMO are 0.008 hartree, the 2 electron with oposite spin

are occupied the same orbital. The Fig. 3 b) X the  $\alpha$  HOMO are -0.019 and  $\beta$  HOMO are -0.026, but the  $\alpha$  LUMO are positive values 0.039 and  $\beta$  LUMO are 0.048. The Fig. 3 c) I are cation cluster when HOMO are -0.331 and LUMO are -0.348, in Fig. 3 c) II  $\alpha$  HOMO are -0.312 and  $\beta$  HOMO -0.379, for  $\alpha$  LUMO are -0.390 and  $\beta$  LUMO are -0.361 hartree. In Fig. 3 c) III the HOMO occupied with 2 electrons are -0.316 energy and LUMO are -0.362 hartree, Fig. 3 c) IV for HOMO are -0.375 and for LUMO are -0.324 hartree, Fig. 3 c) V for HOMO are -0.345 and LUMO -0.383 hartree, Fig. 4 c) VI for HOMO are -0.378 and for LUMO are -0.337 hartree and Fig. 3 c) VII for  $\alpha$  HOMO are -0.348 and  $\beta$  HOMO are -0.366 hartree. In Fig. c) II and Fig. b) II are view that in anion cluster are more greater the distance between Si-Si. Compared Fig. 3 c) VII, b) X and 3 a) IV the anion are more greater distance between the atoms in this sens are covalent simple bidding more that another structure. The structure 3 b) III and 3 b) IX are the  $\frac{1}{2} \pi$  covalent bidding, for this motive in both structure the distance are minor that the simple covalent bidding.



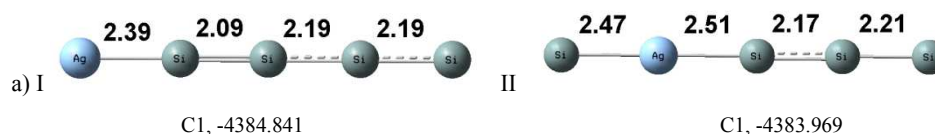


**Fig. 3.** The structure of tetramer clusters with PBE/LANL2DZ: a) neutral; b) anions; c) cations. Are reported symmetrie and electronic state. The energy of clusters in eV.

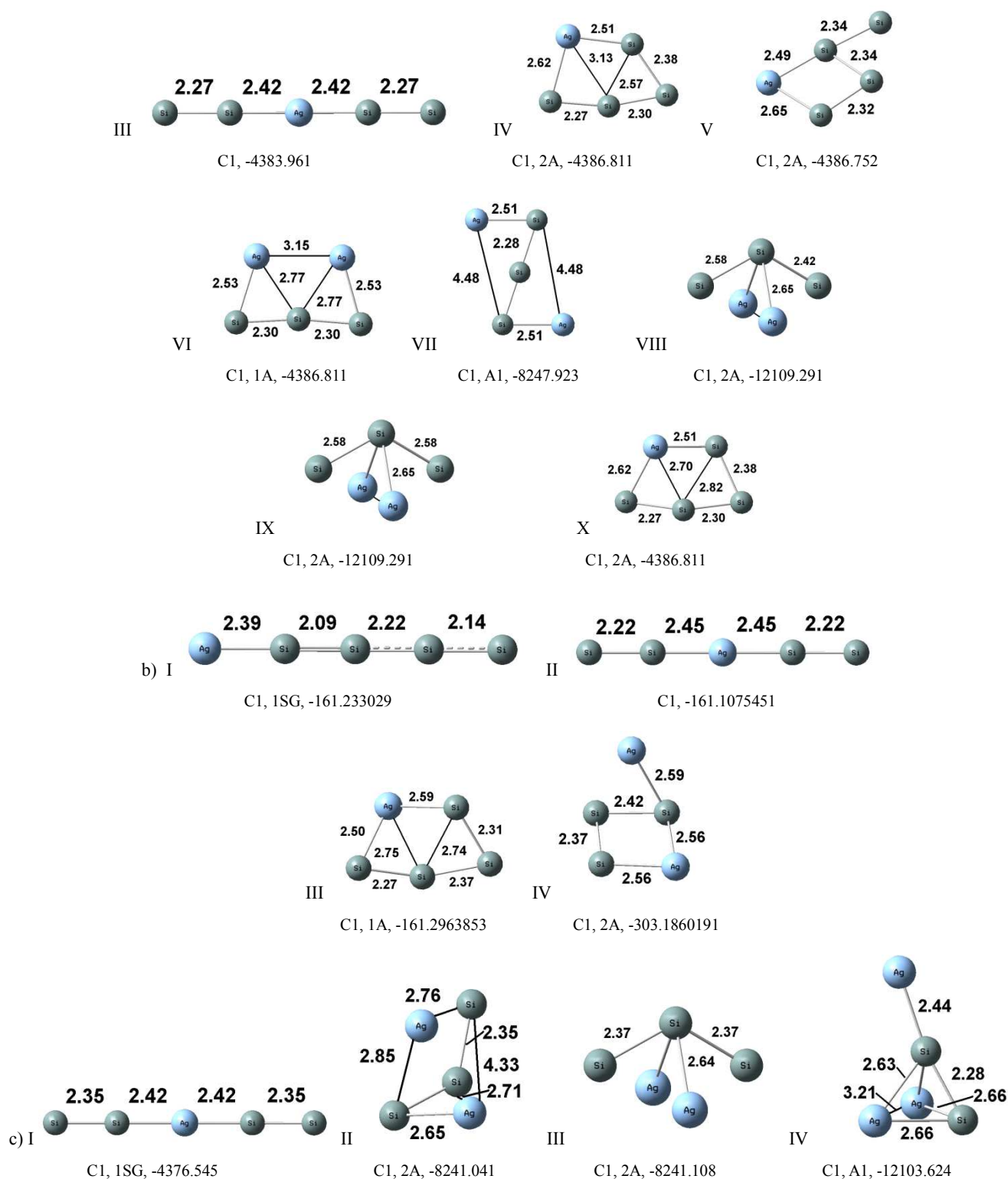
### 3.4. Pentamer, Neutral, Anions and Cations

In Fig. 4 a) I the  $\alpha$  HOMO are -0.172 and  $\beta$  HOMO are -0.163 hartree, for  $\alpha$  LUMO are -0.158 and  $\beta$  LUMO -0.156 hartree, Fig. 4 a) II the  $\alpha$  HOMO are -0.175 and  $\beta$  HOMO are -0.165 hartree and for  $\alpha$  LUMO are -0.171 -0.155 and  $\beta$  LUMO, Fig. 3 a) III the  $\alpha$  HOMO are -0.201 and  $\beta$  HOMO are -0.196 for  $\alpha$  LUMO are -0.200 and  $\beta$  LUMO -0.185. In Fig. 4 a) IV the  $\alpha$  HOMO are -0.177 and  $\beta$  HOMO are -0.150 hartree for  $\alpha$  LUMO are -0.148 and  $\beta$  LUMO -0.144, Fig. 4 a) V for  $\alpha$  HOMO are -0.167 and  $\beta$  HOMO are -0.138, for  $\alpha$  LUMO are -0.139 and  $\beta$  LUMO are -0.136. For Fig. 4 a) VI for HOMO are -0.187 hartree and LUMO -0.146, Fig. 4 a) VII for HOMO are -0.192 and LUMO -0.145. For Fig. 4 a) VIII for  $\alpha$  HOMO are -0.149 and  $\beta$  HOMO are -0.129, for  $\alpha$  LUMO are -0.116 and for  $\beta$  LUMO are -0.113. For Fig. 4 a) IX for  $\alpha$  HOMO are -0.149 and  $\beta$  HOMO are 0.129, for  $\alpha$  LUMO are -0.116 and  $\beta$  LUMO are -0.113. For Fig. 4 a) X

for  $\alpha$  HOMO are -0.177 and  $\beta$  HOMO are -0.151, for  $\alpha$  LUMO are -0.148 and  $\beta$  LUMO are -0.144. For Fig. 4 b) I the HOMO are -0.022 and LUMO are -0.029, in Fig. 4 b) II  $\alpha$  HOMO are -0.201 and  $\beta$  HOMO are -0.196, for  $\alpha$  LUMO are -0.200 and  $\beta$  LUMO are -0.185. In Fig. 4 b) III the HOMO are -0.011 and LUMO are 0.023, in Fig. 4 b) IV the  $\alpha$  HOMO are -0.005 and  $\beta$  HOMO are 0.019, for  $\alpha$  LUMO are 0.031 and  $\beta$  LUMO are 0.038. In Fig. 4 c) I are -0.350 hartree for HOMO and -0.342 hartree for LUMO, in Fig. 4 c) II the  $\alpha$  HOMO are -0.338 and  $\beta$  LUMO are -0.312, but  $\alpha$  LUMO are -0.317 and  $\beta$  LUMO are -0.308, in Fig. 4 c) III the  $\alpha$  HOMO are -0.337 and  $\beta$  HOMO are -0.310, the  $\alpha$  LUMO are -0.313 and  $\beta$  LUMO are -0.306, in Fig. 4 c) IV the HOMO are -0.360 and LUMO -0.264. In the Fig. 4 a) I and II and b) I are un  $2\frac{1}{2}\pi$  bidding and one double bidding with minor distance that single bidding covalent. For this reason this cluster are transformed in another cluster or reaction very quick.







**Fig. 4.** The structure of pentamer clusters with PBE/LANL2DZ: a) neutral; b) anions; c) cations. Are reported symmetry and electronic state. The energy of clusters in eV.

## 4. Biding Energy for Atom

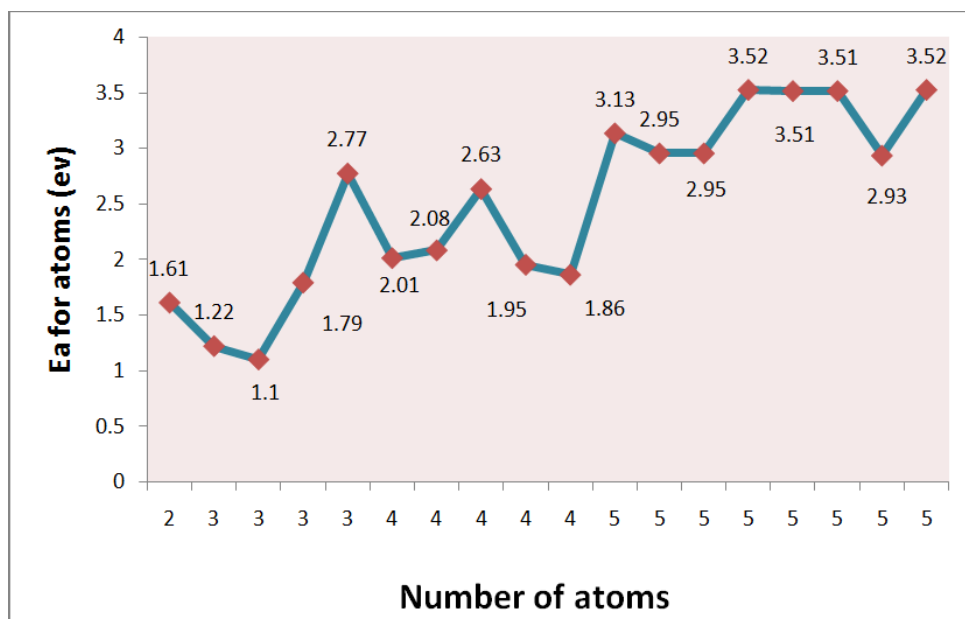
Is important to study the biding energy for atom because to refer at stability of clusters. Are graphical the value of the biding energy of the neutral cluster, anions and cations, Fig. 5-

7.

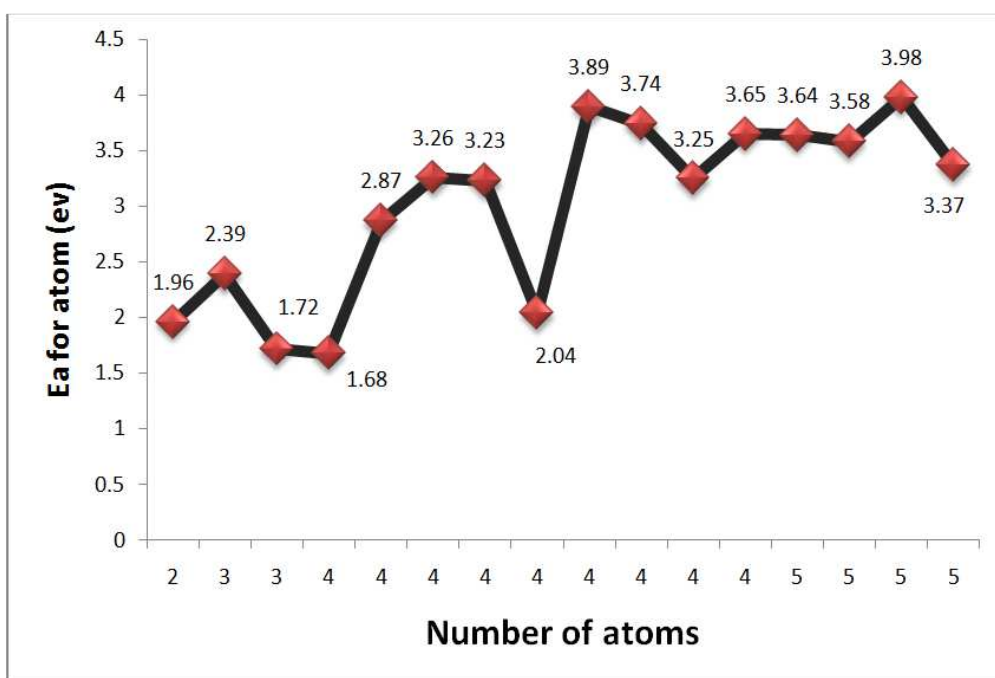
Calculate with  $\frac{E_b}{n} = \frac{x E_x + y E_y + \dots + m E_m - E_n}{n}$ , where  $E_n$  are the total energy for the neutral species optimized with n atoms ( $\text{Ag}_x\text{Si}_y$  in this work);  $\frac{E_b^\pm}{n} = \frac{x E_x + y E_y + \dots + m E_m - E_n^\pm}{n}$ , where n are

the number of the total atoms in the cluster,  $x$  are the number of the atom of element  $x$  (Ag in this work)  $y$  are the number of atom for the another element (Si in this work), the  $E_x$  are the energy of the neutral element  $x$  and  $E_y$  are the energy of the neutral element  $y$ ,  $m$  are the number of atom of element  $m$  and  $E_m$  are the energy of the neutral element  $m$ , and  $E_n^\pm$  are the energy of the anion or cation cluster ( $\text{Ag}_x\text{Si}_y$  in this work). The binding energy of anion per atom for the anion and cation cluster are employed with this equation because the cluster are charge negative or positive with the sum of the charge of all atoms in the cluster. In Fig. 5 are observed the binding energy per atom for neutral structure, Fig 2a) IV, are greater 2.77 eV

that another cluster with 3 atoms and 4 atoms. For 5 atoms the binding energy are grater in comparison with 2, 3 and 4 atoms. For Fig 4a) I with the frecuencies negative are 3.15 eV and are greater that another linear structure 4a) III and the trapezoidal form are the same energy with the another structure. The linear form Fig. 3a) IV are little binding energy 2.04 near with the structure with 2 atoms, Fig. 6. The form T for cluster with 4 atoms are very near energy with the structure with 5 atoms, this speak the form in the same time this structure and necessitaed greater energy. In Fig. 7 the cation cluster of the Fig. 3c) VI are greater values 1.57 eV. For the anion and cation, Fig. 7, the values are very near.



**Fig. 5.** Biding energy for atom for neutral clusters. The cluster for 2 atoms are: Fig 1 a); for 3 atoms: Fig. 2 a)I, a)II, a)III, a)IV, and a)V; for 4 atoms are: Fig. 3 a)I, a)II, a)III, a)IV, a)V, and a)VI; for 5 atoms are: Fig. 4 a)I, a)II, a)III, a)IV, a)V, a)VI, a)IX, and a)X. The values are in the figure.



**Fig. 6.** Biding energy for atom for anion clusters. The clusters for 2 atoms are: Fig.1 b); for 3 atoms are: Fig. 2 b)I, b)II, and b)III; for 4 atoms are: Fig. 3 b)I, b)II, b)III, b)IV, b)V, b)VI, b)VII, b)VIII, and b)IX, The clusters for 5 atoms are: Fig. 4 b)I, b)II, b)III, and b)IV. The values are in the figure.

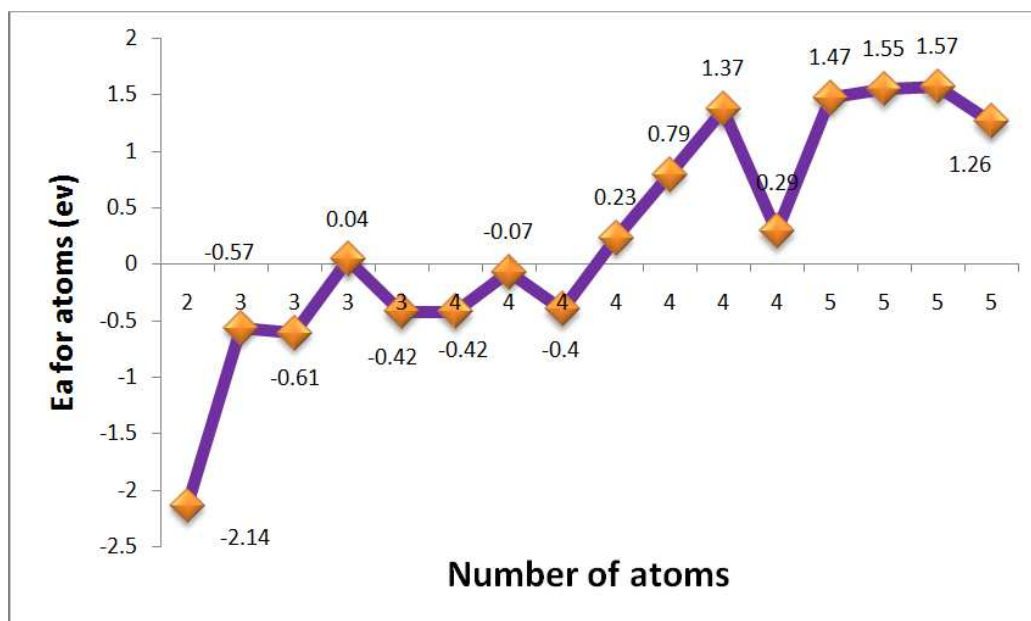


Fig. 7. Biding energy for atom for cation clusters. The clusters for 2 atoms are: Fig. 1 c); for 3 atoms are: Fig. 2 c)I, c)II, c)III, and c)IV; for 4 atoms are: Fig. 3 c)I, c)II, c)III, c)IV, c)V, c)VI, and c)VII; for 5 atoms are: Fig. 4 c)I, c)II, c)III, c)IV and c)V. The values are in the figure.

## 5. Ionization Potential and Electronic Affinity

### 5.1. Vertical and Adiabatic Electronic Affinity

The calculus for electronic affinities has been calculated with  $A = E_n - E_n^-$ , where  $E_n$  is the total energy for neutral species optimized and  $E_n^-$  is the total energy for the anion species after optimized. For the vertical electronic affinities are calculated with the neutral form optimized and single

point for anion and cation cluster.

The value -1.14 in Fig. 8 for cluster with 3 atoms speak that this cluster are not stable. For 5 atoms are need very large value 4.07, 4.26 eV, Fig. 8.

In Fig. 9 for structure with 5 atoms the vertical electronic affinity are little, the very large value are for Fig. 4 a) III, 3.11 eV. The tendency and values for adiabatic and vertical electron affinity are different. Are not experimental date. For the vertical electronic affinity are variation odd even in the cluster.

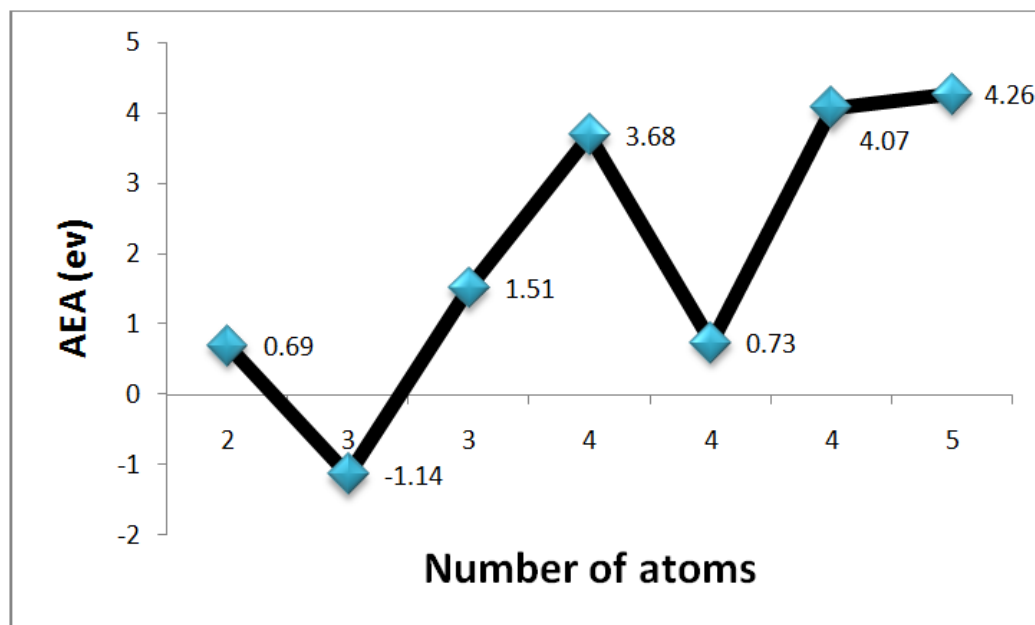


Fig. 8. Adiabatic electronic affinity for silver cluster employed. Vs. Number of atoms in the cluster.

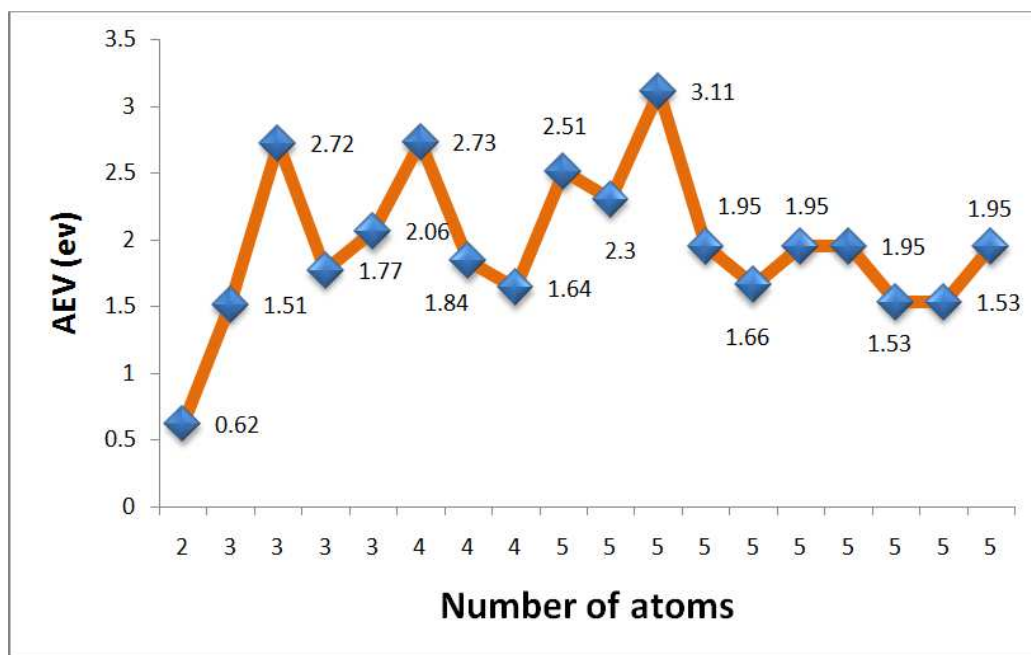


Fig. 9. Vertical electronic affinity for silver cluster employed DFT. Vs. Number of atoms in the cluster.

### 5.2. Vertical and Adiabatic Ionization Potential

The adiabatic ionization potential are defined how the energy of transition in origin between the basal state of cation and the basal state of neutral with  $I = E_n^+ - E_n$ , where  $E_n^+$  is the total energy of species of cations after optimization the structure and  $E_n$  is the total species neutral optimized. For vertical ionization potential are employed the neutral values

for the structure optimized and for the cation sigle point with the neutral structure.

In Fig. 10 are view the mas greater value ar for cluster with 5 atoms, 10.27 eV and for 3 atoms are 10.17 eV. In figure 11 are see the cluster with 5 atoms are very near value with compared with the another structure. Are not experimental data.

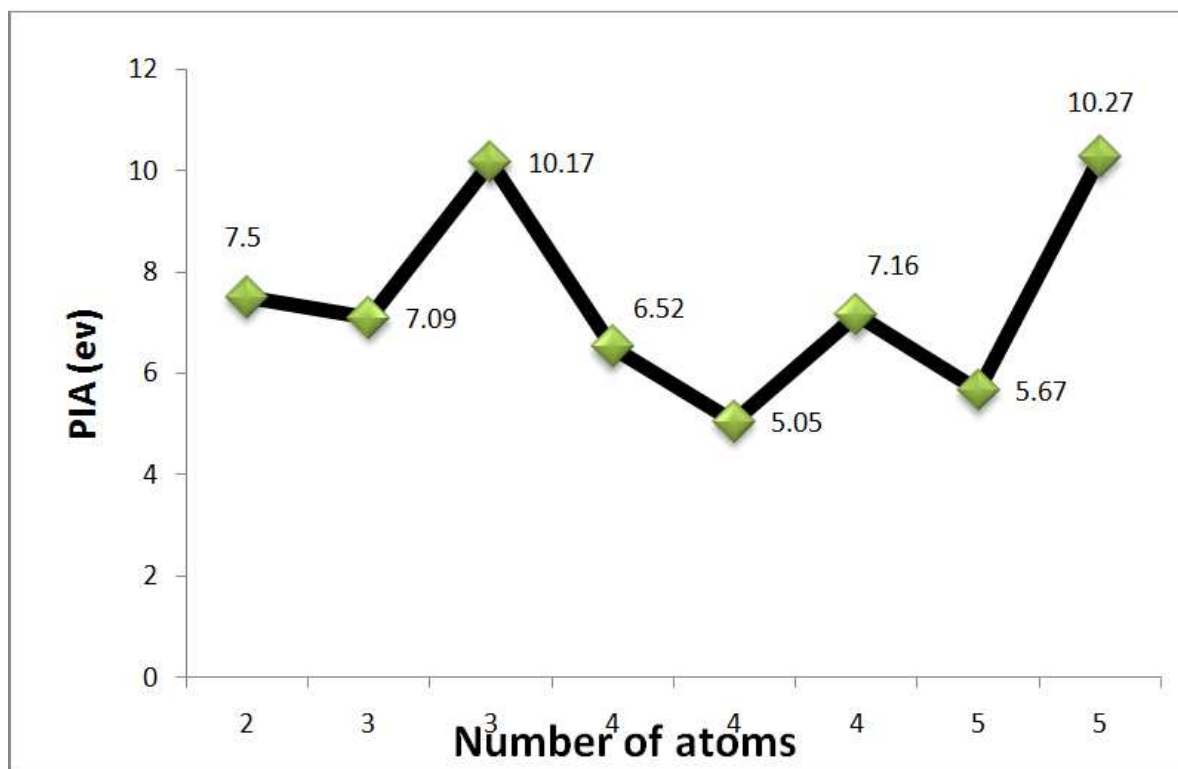


Fig. 10. Adiabatic electronic potential for silver cluster employed HF. Vs. Number of atoms in the cluster.



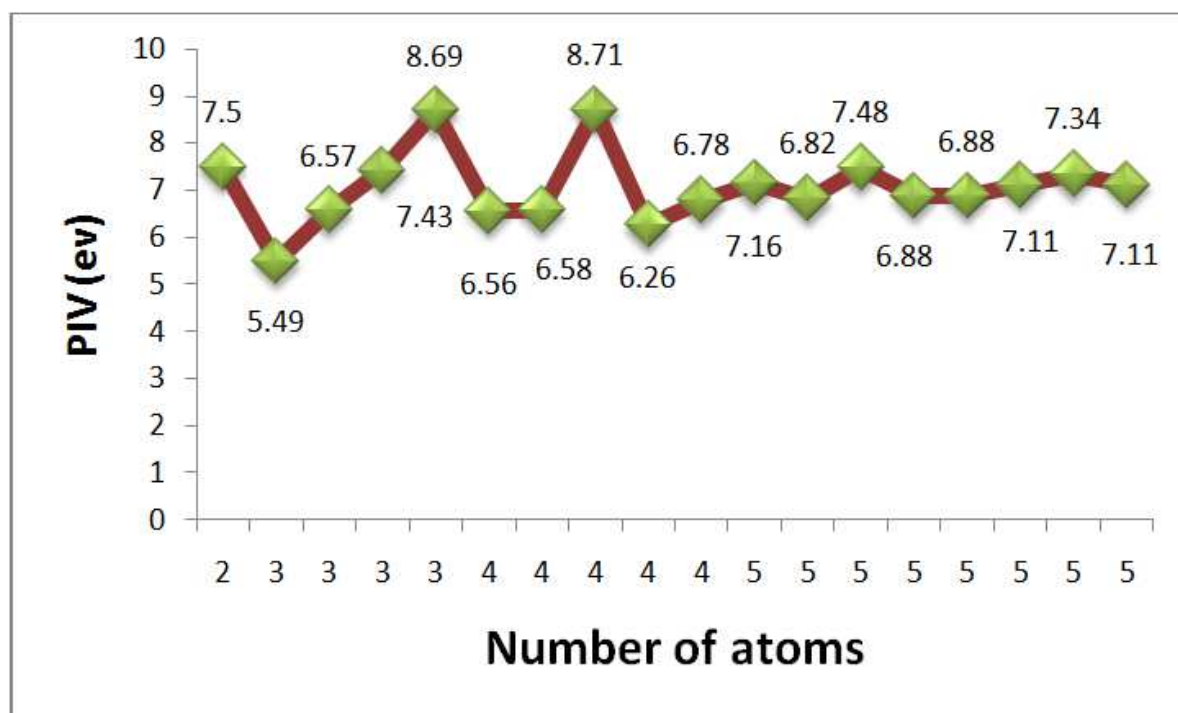


Fig. 11. Vertical ionization potential for silver cluster employed HF. Vs. Number of atoms in the cluster.

## 6. Frequencies

The Table 1-9 are show the values of frequencies for all structure. Are not experimental data for this clusters.

Table 1. The armonic frecuencia (in cm-1) of the more stable cluster with 2 atoms.

289.4678	277.5002	296.4516




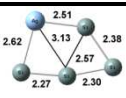
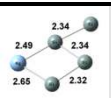
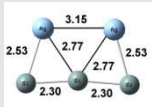
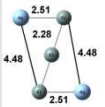
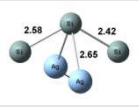
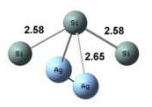
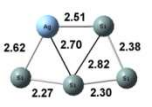
Table 2. The armonic frecuencia (in cm-1) of the more stable neutral cluster with 3 atoms.

61.2540	60.2707	61.8344	176.3551
61.2541	60.2708	248.7972	217.6540
170.2134	169.3103	310.9345	515.8439
296.2584	295.4917		

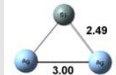
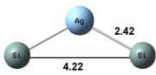

Table 3. The armonic frecuencia (in cm-1) of the more stable neutral cluster with 4 atoms.

38.0908	77.1104	17.8624	59.1809	39.1314
50.6923	89.2589	40.3779	86.6282	114.5355
164.9246	195.5846	95.1723	121.3310	120.2875
247.1882	220.0214	176.0888	170.4721	124.9824
293.9536	254.1555	265.6528	202.6184	265.6886
302.3129	297.3688	481.6978	270.0633	277.5728

**Tabla 4.** The armonic frecuencia (in  $\text{cm}^{-1}$ ) of the more stable neutral cluster with 5 atoms.

				
-236.8834	-80.1811	14.0899	12.9207	9.2402
-151.8604	-79.6265	15.8942	65.3879	77.4790
15.6640	-13.0682	32.9491	91.4487	101.7284
18.7908	3.1019	33.0328	178.9619	136.2930
40.3831	61.0194	79.5248	196.0907	178.7018
56.0134	79.1126	83.7637	290.4534	283.4256
157.7148	137.7432	174.3788	315.8554	319.6353
345.1747	290.1538	233.0432	391.5700	425.2164
573.4102	403.8842	526.0766	523.5121	463.9279
704.7066	645.2857	533.6174		
				
44.5211	46.2706	42.5642	42.5235	12.9198
46.3601	48.4521	56.5977	56.5819	65.3880
47.3449	50.9229	86.7292	86.6928	91.4480
50.6924	55.6019	108.8476	108.8389	178.9616
207.2891	163.8514	126.1458	126.1673	196.0907
237.6018	240.4322	173.1967	173.1943	290.4533
239.0585	253.9025	174.5014	174.5041	315.8557
342.0927	338.1119	259.1049	259.1378	391.5712
520.2694	542.0504	363.8282	363.8347	523.5129

**Tabla 5.** The armonic frecuencia (in  $\text{cm}^{-1}$ ) of the more stable anion cluster with 3 atoms.

		
66.5929	79.0991	142.5894
224.6393	291.0727	149.8741
294.4007	297.0563	173.4504
		428.1234

**Tabla 6.** The armonic frecuencia (in  $\text{cm}^{-1}$ ) of the more stable anion cluster with 4 atoms.

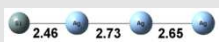




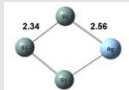
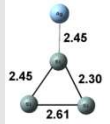
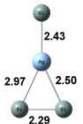
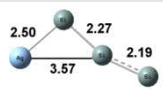
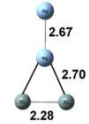
				
-35.7619	32.0682	15.84671	21.3784	60.7644
15.9426	32.0683	15.9426	21.3784	100.7143
16.1103	117.0570	16.1103	37.4810	137.3905
41.5201	117.0570	41.5201	37.4810	171.9527
92.9930	128.1290	92.9930	198.5703	276.8247
171.0834	195.7475	171.0834	312.4121	509.6182
269.0548	500.8718	269.0548	562.9725	
				
60.7644	76.0321	39.2116	34.2301	29.6476
100.7143	94.3214	43.4734	37.2942	59.2076
137.3905	166.4394	95.2697	101.2605	124.2080
171.9527	261.1436	237.2955	264.6299	159.2207
276.8247	417.1202	314.4356	353.4079	184.4937
509.6182	523.8034	501.0188	592.1600	417.3119

Tabla 7. The armonic frecuencia (in cm-1) of the more stable anion cluster with 5 atoms.



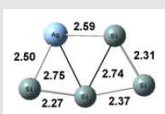
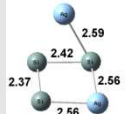
			
26.8717	17.0737	73.9663	29.0310
26.8718	18.1317	78.3110	67.3016
70.2514	30.6007	126.0094	113.5095
70.2514	46.8288	163.0146	143.6832
158.8308	69.9188	205.4782	177.1583
346.4953	90.2902	263.5087	212.7936
606.3442	172.2952	302.1305	268.4456
707.2207	228.9392	417.9950	330.9471
990.1063	553.4645	502.9446	394.1821
990.1911	560.2593		

Tabla 8. The armonic frecuencia (in cm-1) of the more stable cation cluster with 3 atoms.

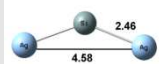
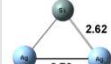
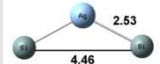
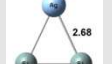
			
45.9334	133.0302	74.3294	142.2687
232.0150	142.8373	279.4977	198.9206
314.5689	250.5726	297.7459	361.7706

Tabla 9. The armonic frecuencia (in cm-1) of the more stable cation cluster with 4 atoms.

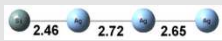


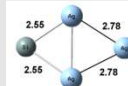
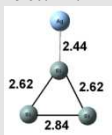
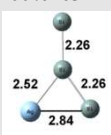
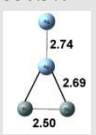

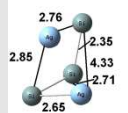

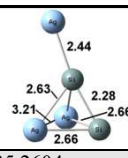
			
-37.2755	-56.3408	21.3554	42.8461
-37.2752	19.4096	21.3554	84.9234
35.1106	33.1875	90.3077	109.0936
35.1284	119.7142	130.6749	126.8424
90.8406	204.2132	130.6749	242.1449
167.8173	252.7979	196.0670	279.4739
290.7447	299.6463	336.3791	
			
88.5063	29.7044	46.2545	
93.1119	35.5871	81.9702	
126.9542	88.6014	103.8632	
169.5154	198.3702	161.8707	
343.8686	380.1266	169.7107	
1797.5510	576.0177	267.2918	

Tabla 10. The armonic frecuencia (in cm-1) of the more stable cation cluster with 5 atoms.

			
17.8133	45.8941	46.1342	35.2604
17.8154	67.2050	81.8008	39.0983
50.1703	98.8833	110.2659	48.6425
50.1704	123.4610	117.9379	142.1119
98.9028	133.9406	146.8410	153.3828
98.9040	182.7599	196.8942	198.7799
168.4277	203.8192	199.0689	210.9414
224.8271	358.7617	373.6800	240.2301
484.1511	463.6575	418.7158	531.4017
493.3514			

## 7. Hardness

Are calculated hardness with the objective see the reactivity of the cluster taken in account the relativistic effects and electronic correlation and see what silver cluster digest how soft acid or soft base or hard acid or hard base. The hardness are calculated with  $\eta = (PI - AE)/2$ , where PI are the adiabatic ionization potential and AE are the adiabatic

electron affinity.

In the Table 13-15 are the value obtained for the difference HOMO-LUMO (gap) for the clusters employed the Klopman theorie [6].

In Fig 12 the cluster with 3 atoms are hard and with 5 atoms are soft. This value a speak the energy for accepted electron in cluster. The tendencies in HOMO-LUMO are different for anion, cation and neutral cluster.

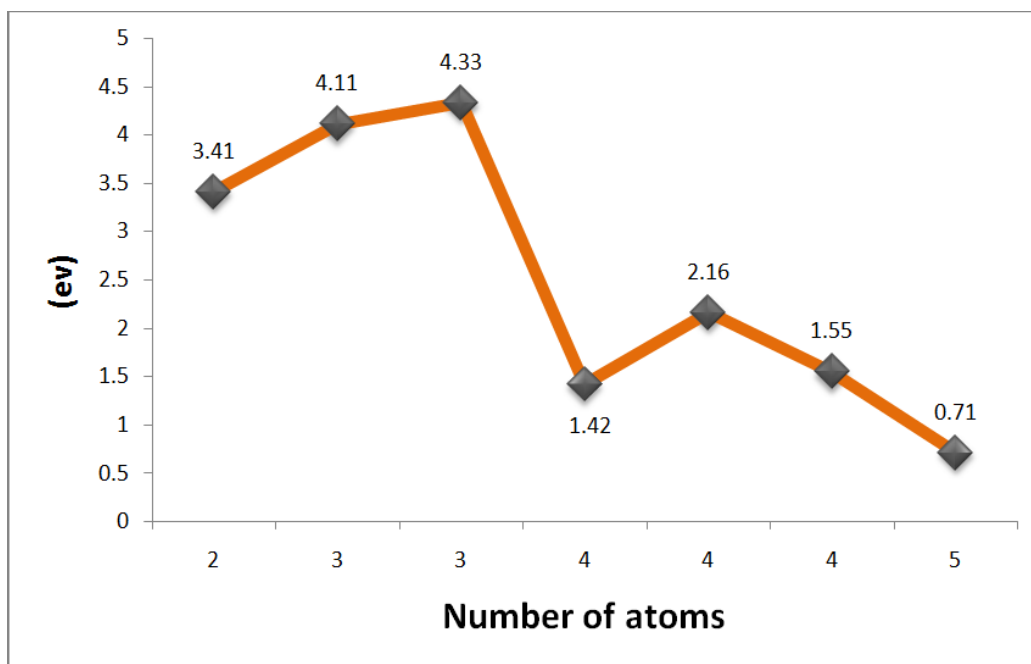


Fig. 12. Hardness ( $\eta$ ) for  $\text{Ag}_x\text{Si}_y$  cluster. Vs. Number of the atoms in the cluster.

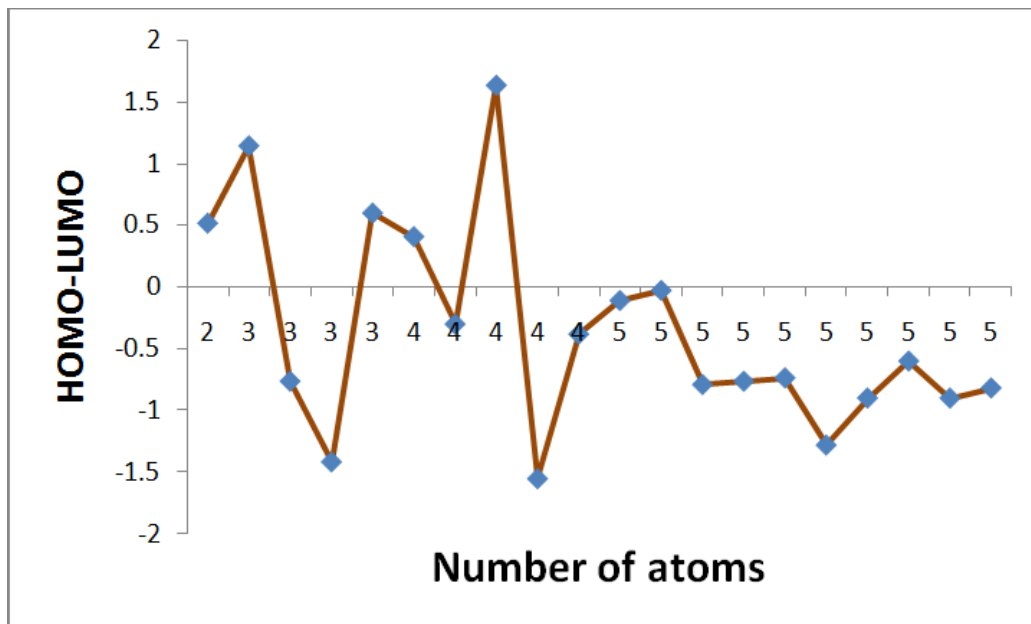


Fig. 13. HOMO-LUMO for  $\text{Ag}_x\text{Si}_y$  neutral cluster. Vs. Number of the atoms in the cluster.

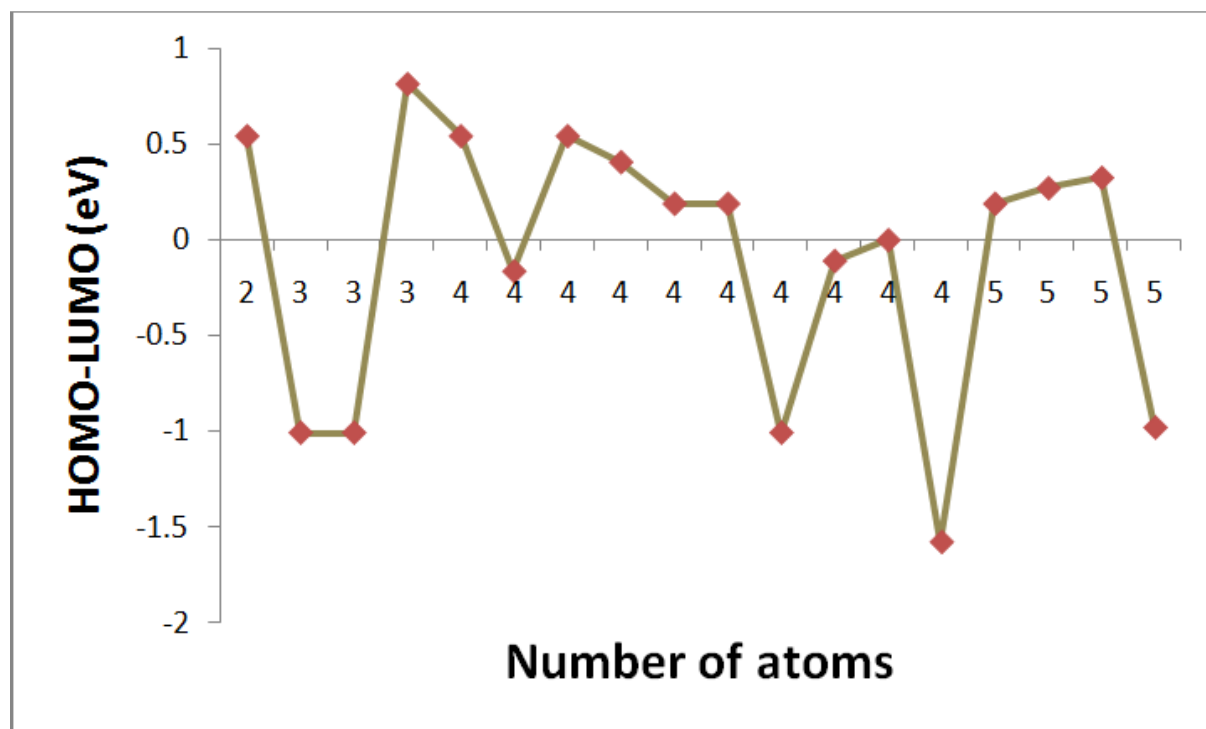


Fig. 14. HOMO-LUMO for  $Ag_xSi_y$  anion cluster. Vs. Number of the atoms in the cluster.

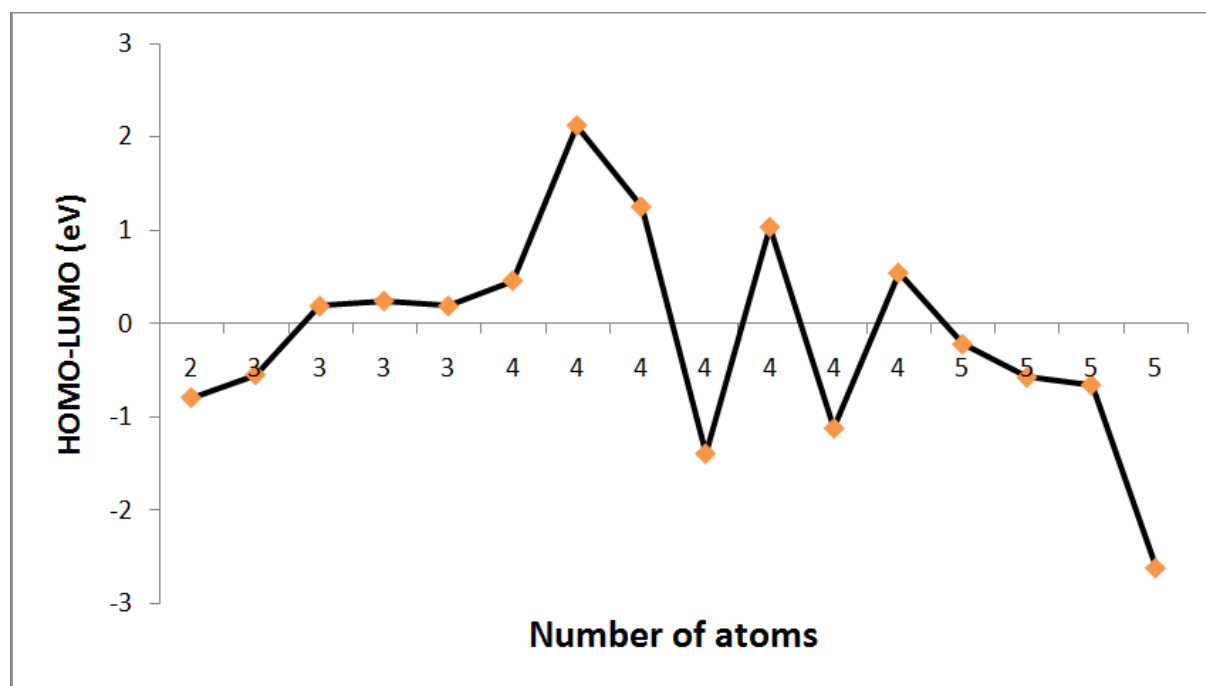


Fig. 15. HOMO-LUMO for  $Ag_xSi_y$  anion cluster. Vs. Number of the atoms in the cluster.

## 8. Enthalpies and Free Energy

The enthalpies and free energy, are speak of the tip of reaction endothermic and exothermic when this cluster are reactioned with another structure, Fig. 16-21. The value are near of 100-3000 Kcal/mol. The tendency for free energy and enthalpies are the sam for anion, cation and neutral cluster.

Very stable are the neutral structure in Fig. 4a) VIII and IX with near of  $-3000$  kcal/mol energy and piramidal structure for cluster with 4 atoms, Fig.16. In anion cluster with linear estructure are more stable, Fig. 17. For estructure rombic and linear in cation cluster are very stable with the trapezoidal form for structure with 5 atoms, Fig. 20.



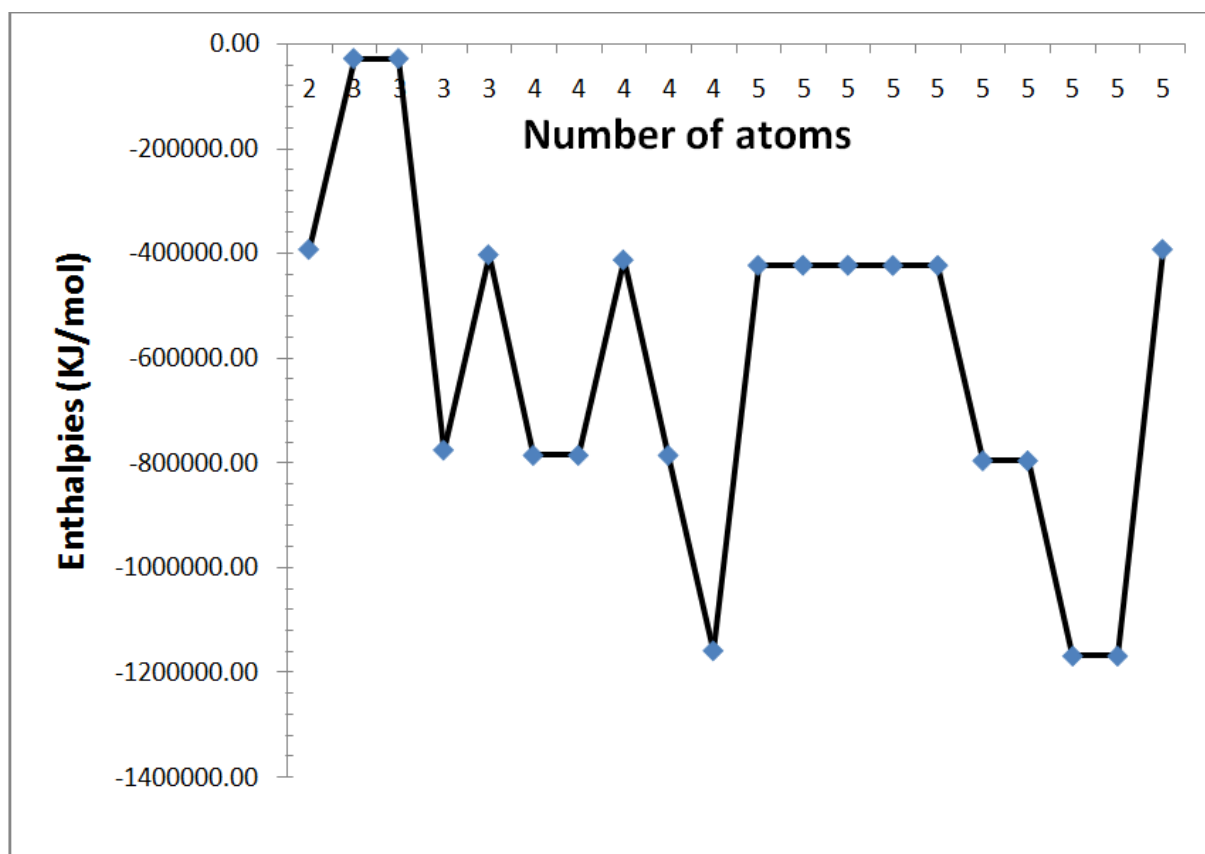


Fig. 16. Enthalpies for neutral clusters. Vs. Number of the atoms in the cluster.

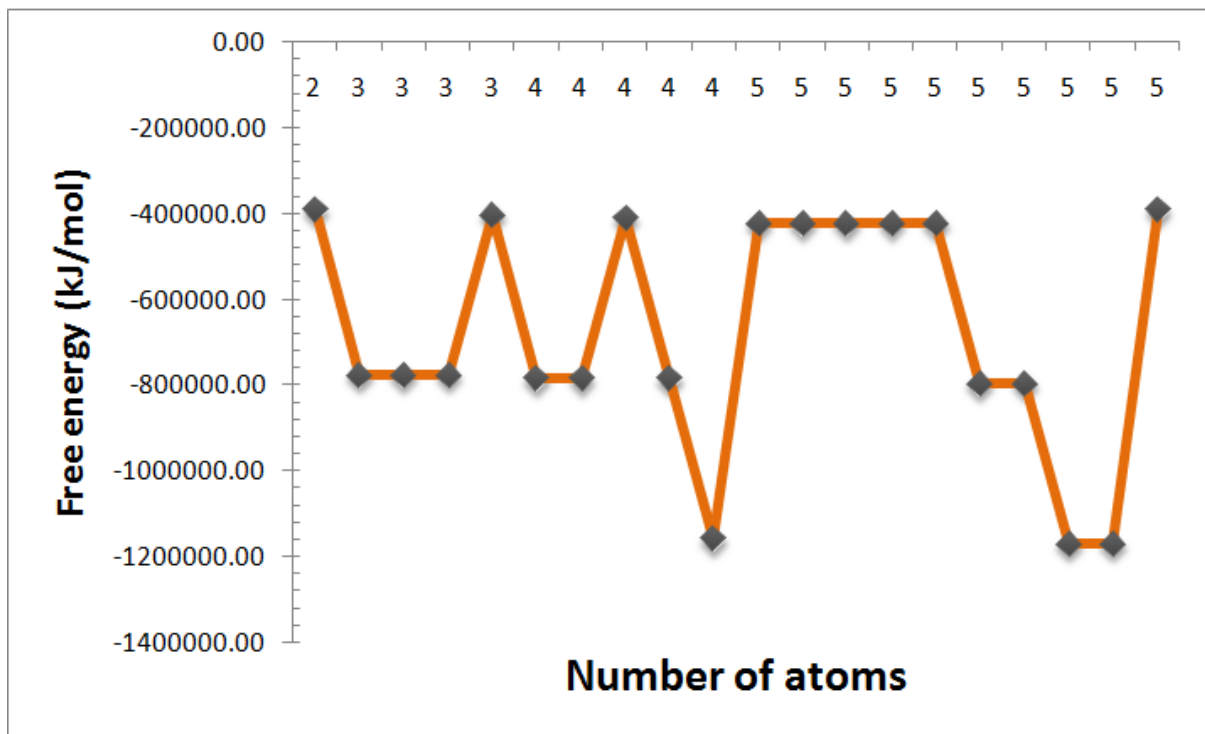


Fig. 17. Free energy for neutral clusters. Vs. Number of the atoms in the cluster.

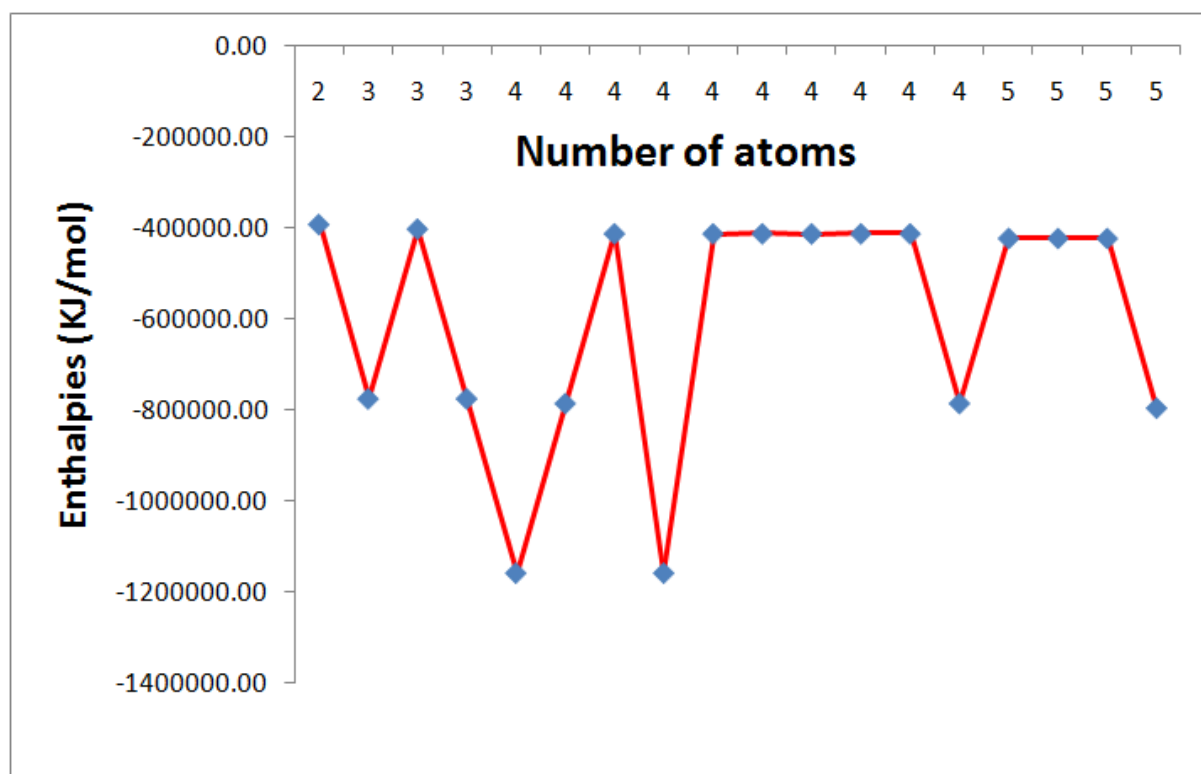


Fig. 18. Enthalpies for anion clusters. Vs. Number of the atoms in the cluster.

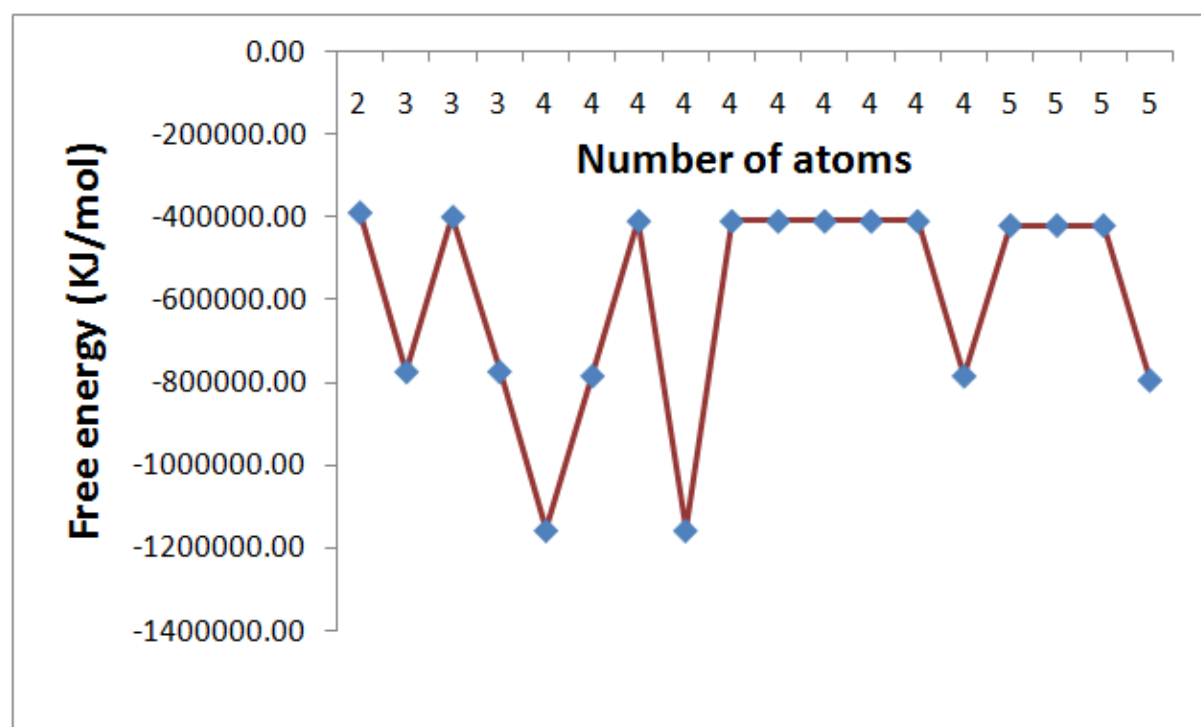


Fig. 19. Free energy for anion clusters. Vs. Number of the atoms in the cluster.

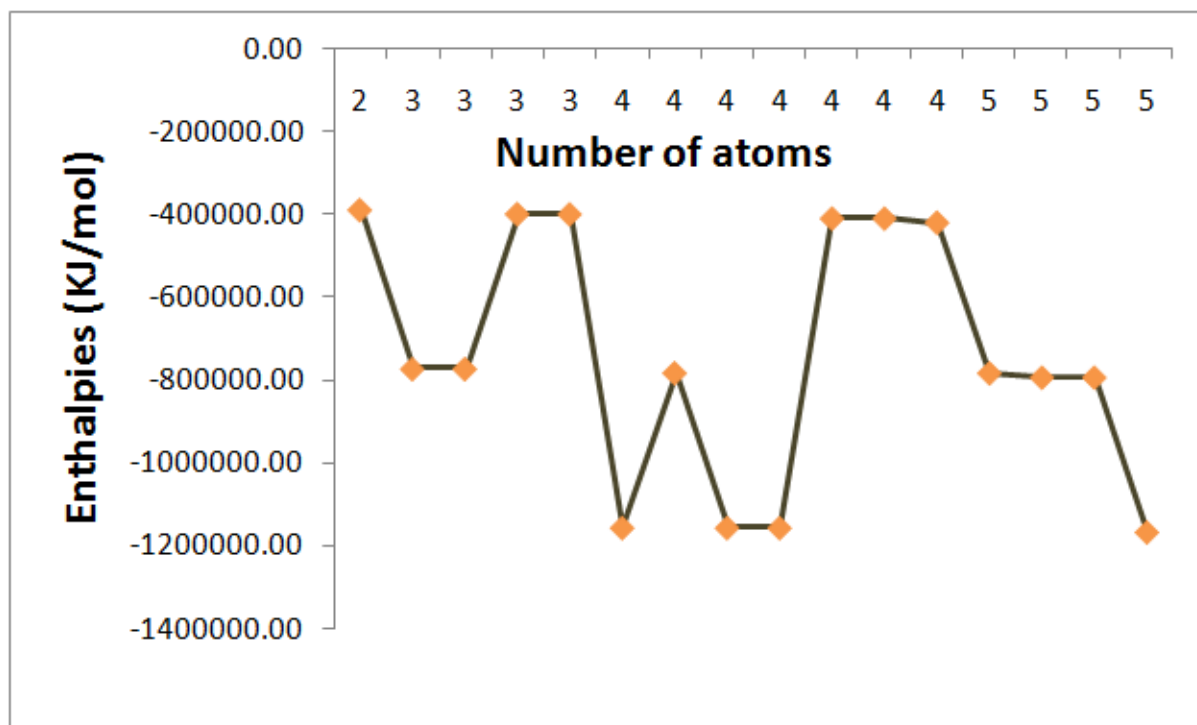


Fig. 20. Enthalpies for cation clusters. Vs. Number of the atoms in the cluster.

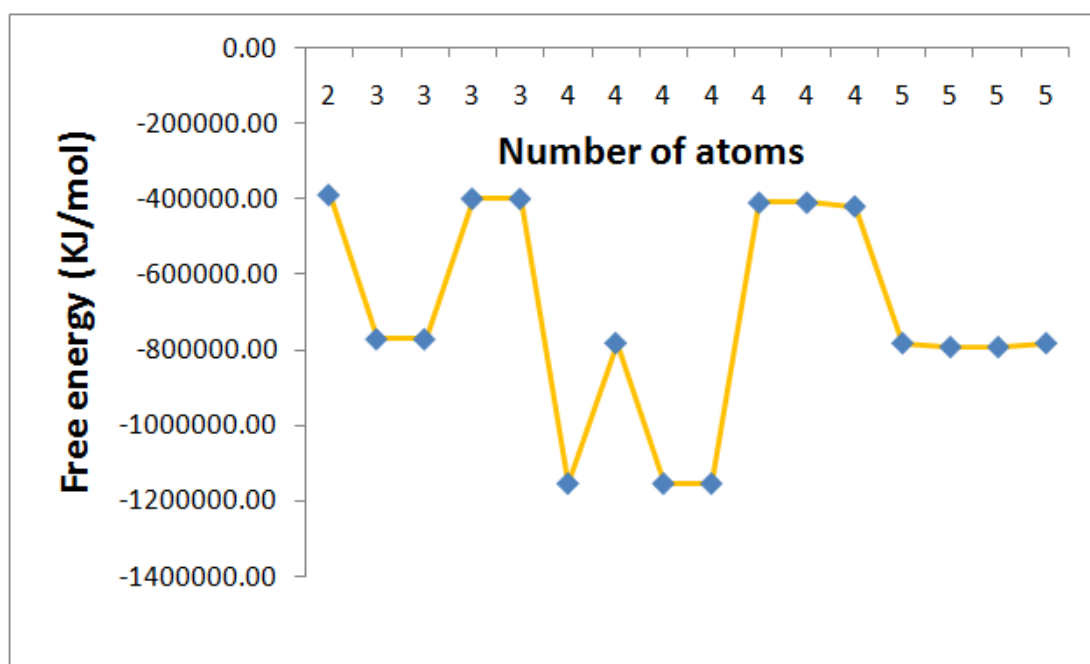


Fig. 21. Free energy for cation clusters. Vs. Number of the atoms in the cluster.

## 9. Conclusions

In this work are studied the cluster  $\text{Ag}_x\text{Si}_y$  structure and their properties employed the PBE/LANL2DZ level of theory with relativistic effect. For neutral trimer cluster C2, A1 structure isosceles are more stable, Fig. 2 a)III. In case of neutral cluster with 4 atoms the pyramidal structure are very stable. The Fig. 4 a)VII are very stable neutral cluster. For anion the linear structure are very stable, Fig. 2 b) III. In Fig.

5 b)4 the anion structure are very stable with -303.18 eV.

All  $\alpha$  HOMO orbital are occupied with one electron and HOMO and LUMO with 2 electron.

Are studied the frequencies, electronic affinity, electronic potential, binding energy for atom, enthalpies and free energy. The structure with negative frequencies are saddle point in PES.

The electronic affinity and electronic potential speak of the energy for accepted and grant electrons.

The values reported for enthalpies and free energy are normal values.

All structure are soft and are reactive. Polarization is easiest when the energy gap is small for each molecule.

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