STRUCTURE AND REACTIVITY OF INDIUM CLUSTERS In$_n$ (n≤11) : A DFT STUDY

Leandro Fortunato, Gabriel Radivoy and Viviana Dorn

INQUISUR, Departamento de Química, Universidad Nacional del Sur (UNS)-CONICET, Av. Alem 1253, 8000 Bahía Blanca, Argentina, e-mail: leandro.fortunato@uns.edu.ar

Keywords: Indium nanoparticles, DFT, metallic clusters.

Introduction:

Recently there has been great interest in the study of small metallic clusters because they are considered as a completely new area which can bridge the gap between isolated atoms and bulk matter. It has been observed that nanoparticulate systems affected their catalytic properties are, since increases its surface area and modifies their electronic properties. Experimentally it is very difficult to accurately determine the disposition of atoms in a nanoparticle system, however, accurate theoretical calculations could provide a reliable information about the geometrical and electronic structures of small clusters. There is a wide variety of DFT studies on metallic systems of few atoms,[1, 2] however there are no bibliographic references of indium nanoparticles.

Indium nanoclusters have been experimentally studied keeping in view the importance of their physical and chemical properties. The former included: thermal stability,[3] plastic compatibility [4] and for their melting temperature as function of their size.[5] Indium nanoclusters optical properties have been explored,[6] for their applications in quantum devices [7] and quantum dots.[8] Besides, Indium nanoparticles have been applied as nanocatalizer in organic transformations. poner ref del RSC and references cited therein.

In this work, we present a systematic theoretical study about indium neutral clusters up to 11 atoms. We explore the lowest-energy structures and investigate their geometric and electronic properties including vertical electron affinity **(VEA)**, vertical ionization potential **(VIP)**, highest-occupied and lowest-unoccupied molecular orbital **(HOMO-LUMO)** gap, second differences of cluster energies **(Δ_2E)** and spin density **(SD)**, using the Gaussian 09 program, B3LYP and M06 functionals and Los Alamos pseudopotential and corresponding basis set (LANL2DZ).

Results and discussion:

Figure 1 show the optimized geometries of In$_n$ clusters up to 11 atoms (distance values in Å. The calculated electronic properties are summarized in **Table 1**.

Many planar (2D) and non-planar (3D) initial structures have been proposed until the local minimum of the total energies was found, including different isomers to check the stability, symmetry and geometrical parameters. The In-In distance was confined in 2.72-3.42 Å with a average bond length of 3.05Å. As the cluster size increases, the nanoparticles tend to adopt more compact structures. Additionally it is found that the lowest-energy structure of **In$_n$** can be obtained by capping an atom on the structure of **In$_{n-1}$**. Similar patterns are also found in previous works of Ga$_n$ cluster.[2]

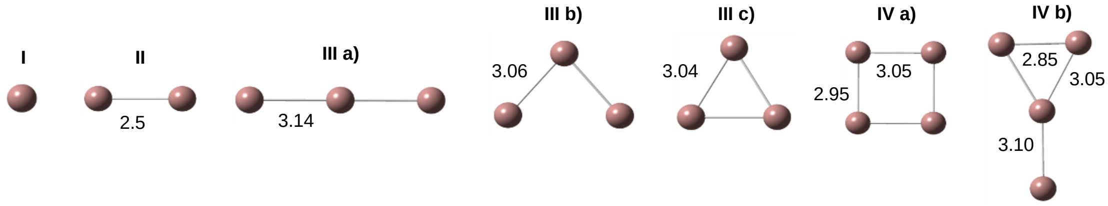

Figure 1. Optimised geometries for In$_n$ cluster (n=1-10). The In-In bond lenght, in Å are given in each cluster.

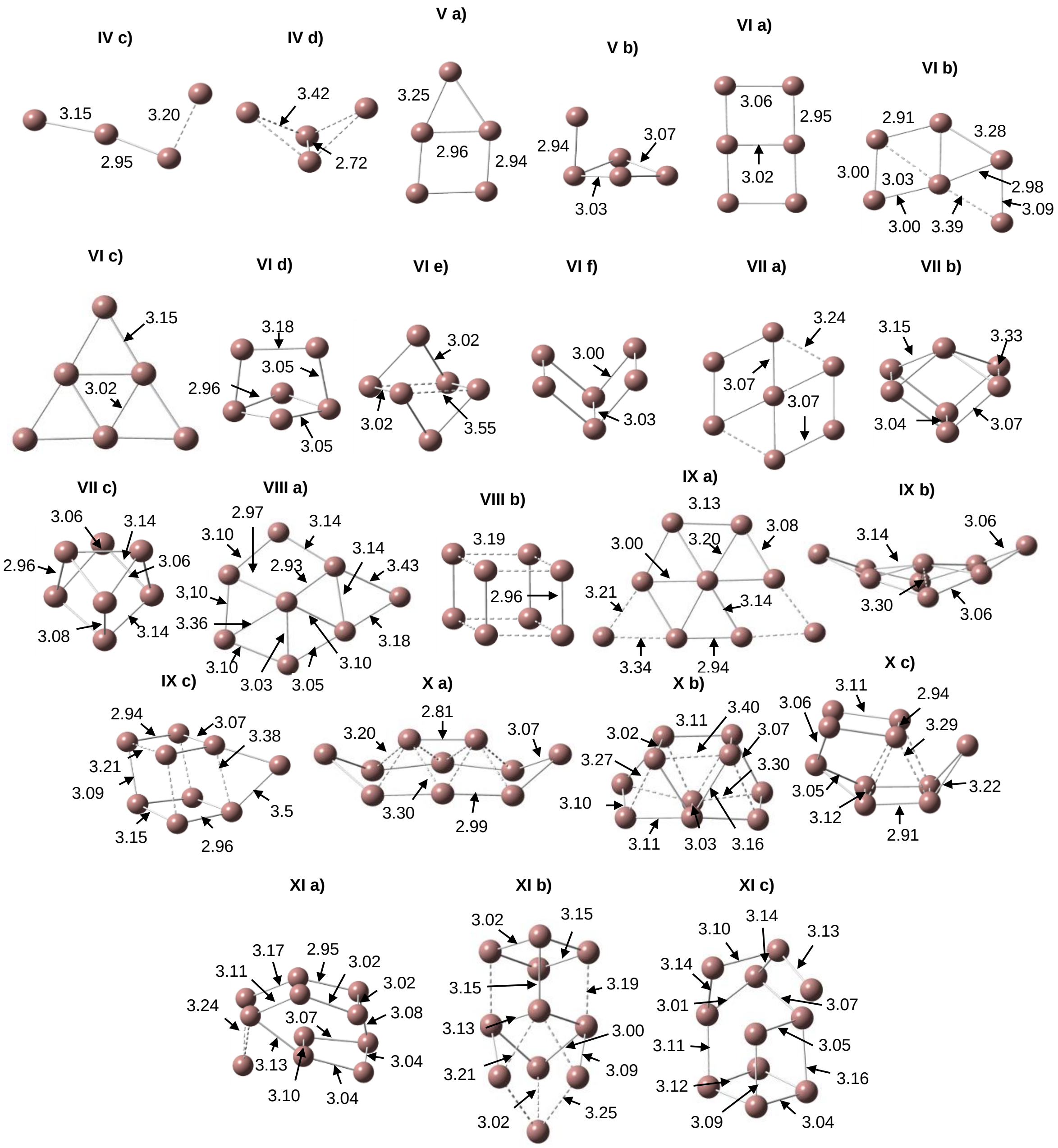

Figure 1 Cont.

At first, we calculate the relative energy (∆**E**) for each isomer clusters. The lowest-energy structure are in bold in **Table 1**. Using different functionals (B3LYP and M06 respectively) the same result was obtained, except for In_3 systems. Calculations using the B3LYP functional and LANL2DZ pseudopotential predict a linear structure as lowest-energy In_3 cluster, with the equilateral and isosceles triangle clusters 0.094 and 0.015 eV higher in energy, respectively. However, at the M06/LANL2DZ level of theory, the lowest-energy In_3 structure is a equilateral triangle, with the linear cluster 0,164 eV higher in energy.

TABLE 1. Calculated Electronic Structures Properties of DFT-Optimized In_n cluster

Cluster		**n**	**ΔE (eV)**		**E_b (eV/n)**		**VEA (eV)**		**VIP (eV)**	
			B3LYP	**M06**	**B3LYP**	**M06**	**B3LYP**	**M06**	**B3LYP**	**M06**
1	2D	1	**0.000**	**0.000**	0.000	0.000	-0.071	-0.623	5.739	5.152
2	2D	2	**0.000**	**0.000**	0.136	-0.018	1.229	1.036	5.431	...
3 a)	2D	3	**0.000**	0.164	0.676	0.466	1.216	1.128	5.206	5.060
3 b)	2D	3	0.015	...	0.671	...	1.257	...	5.832	...
3 c)	2D	3	0.094	**0.000**	0.645	0.521	1.301	1.421	5.807	6.095
4 a)	2D	4	**0.000**	**0.000**	0.824	0.722	2.054	1.905	5.649	5.667
4 b)	2D	4	0.113	0.149	0.796	0.685	1.536	...	5.405	...
4 c)	2D	4	0.369	0.694	0.732	0.549	1.551	...	5.030	...
4 d)	3D	4	0.050	0.017	0.812	0.718	1.408	...	5.603	...
5 a)	2D	5	0.004	0.117	0.990	0.903	1.897	...	5.710	...
5 b)	3D	5	**0.000**	**0.000**	0.989	0.927	1.801	1.830	5.732	5.809
6 a)	2D	6	0.229	0.384	1.078	1.015	1.852	...	5.572	...
6 b)	2D	6	0.492	0.500	1.035	0.996	1.919	...	5.632	...
6 c)	2D	6	0.307	0.353	1.065	1.021	1.911	...	5.725	...
6 d)	3D	6	0.120	0.067	1.097	1.068	1.924	...	5.880	...
6 e)	3D	6	0.257	0.125	1.074	1.059	1.634	...	5.976	...
6 f)	3D	6	**0.000**	**0.000**	1.117	1.079	1.693	1.733	5.877	5.933
7 a)	2D	7	0.354	0.365	1.160	1.146	2.205	...	5.778	...
7 b)	3D	7	0.697	...	1.111	...	2.392	...	5.598	...
7 c)	3D	7	**0.000**	**0.000**	1.211	1.199	1.740	1.835	5.654	5.639
8 a)	2D	8	0.572	0.625	1.195	1.194	1.811	...	5.570	...
8 b)	3D	8	**0.000**	**0.000**	1.266	1.272	1.908	1.828	5.872	6.049
9 a)	2D	9	0.570	0.482	1.186	1.197	2.103	...	5.365	...
9 b)	2D	9	**0.626**	**0.693**	1.179	1.174	1.995	...	5.074	...
9 c)	3D	9	**0.000**	**0.000**	1.249	1.251	2.083	2.227	5.605	5.590
10 a)	3D	10	0.511	0.819	1.239	1.251	1.875	...	5.571	...
10 b)	3D	10	**0.000**	**0.000**	1.290	1.333	1.959	1.866	5.619	5.823
10 c)	3D	10	0.199	...	1.270	...	1.824	...	5.554	...
11 a)	3D	11	**0.000**	**0.000**	1.300	1.350	2.288	2.398	5.510	5.527
11 b)	3D	11	0.117	0.172	1.289	1.335	2.093	2.215	5.366	5.349
11 c)	3D	11	0.052	0.008	1.295	1.349	2.069	2.149	5.408	5.329

Relative Energies (ΔE), Binding energies per atom (E_b), Vertical Electron Afinities (VEA) and Vertical Ionization Potential (VIP). Calculations carried out using the LANL2DZ basis set and either the B3LYP and M06 functionals. The calculated lowest-energy structures are in bold.

Figure 2 display the calculated Binding Energy per atom (**E_b**) or Cohesives Energies (**E_{coh}**) of the neutral clusters using B3LYP functional. Eb is defined by:

$$E_b = - [E_n / n - E_0] \qquad (1)$$

where **E_n** is the total energy of the In_n cluster and **E_0** is the energy of In_1.

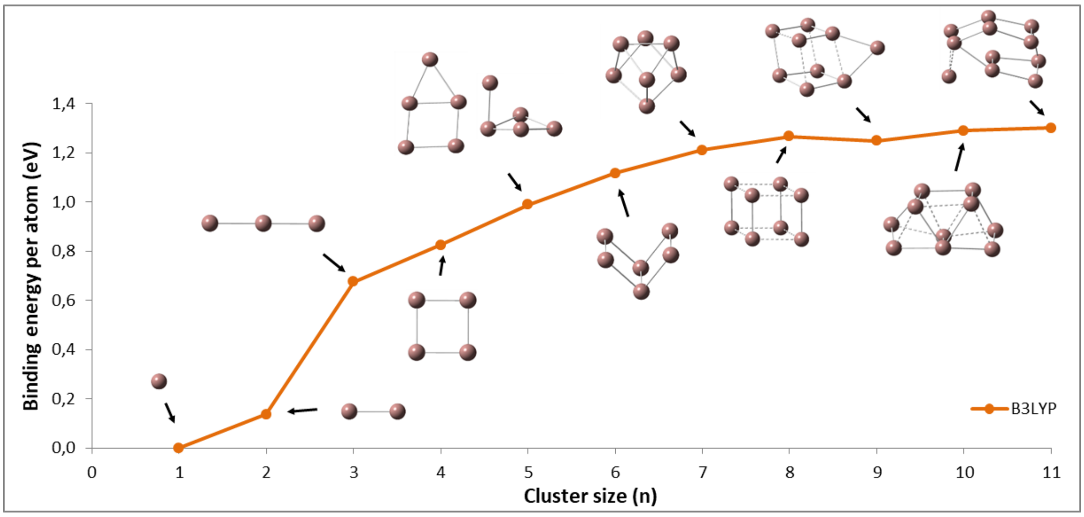

Figure 2. Binding energy per atom as a function of cluster size for lowest-energy structures In_n (n=1-11) using B3LYP functional. Calculations predict two nearly degenerate structures for In_5 clusters.

It is found that the binding energy increases with cluster size up to n=7 remaining approximately constant about 1.27 eV/atom. Furthermore it is observed that planar structures are energetically favored for In_n cluster up to n≤4. With n=5 calculations using B3LYP functional predict two nearly degenerate lowest-energy structures: the square-triangle (planar) and square pyramid (non-planar) (see **Fig.2**), and from this point a 2D-to-3D (two dimensional to three dimensional) transition takes place. However, calculations carried out with M06 functional predict that the 2D-to-3D crossover should occur at In_5 (see **Table 1**).

Electron Affinity (**EA**) and Ionization Potential (**IP**) are very important parameters that provide fundamental insight into the electronic structure of the cluster. In this work, we study the **Vertical Electron Affinities** (**VEA**) and the **Vertical Ionization Potential** (**VIP**) of In_n clusters. The **VEA** is the amount of energy released when the system gains an electron from its neutral state and the **VIP** is the energy needed to remove an electron from the neutral cluster, assuming that the geometry of the charged cluster remains unchanged, for both electronic properties. The results are given in **Table 1**. **Fig. 3 a)** and **b)** show the calculated vertical electron affinities and vertical ionization potential, respectively as a function of cluster size for lowest-energy structures. According to our knowledge, there is no experimental evidence of these properties in In_n clusters.

According to the analysis of the **VEA** exposed in **Fig. 3a)**, a similar behavior is observed regardless of the functional chosen: the electronic affinity increases with the cluster size up to In_4, then it decreases very slowly to a minimum in In_6 and finally increases again until getting another maximum in In_9. There are small differences in behavior for In_n clusters with n<4 according to the chosen functional: mainly from n=2 and n=3; that is **EA** remains approximately constant when using B3LYP, while with M06 increased by 40%. However, we can say that these changes do not significantly affect the overall trend obtained.

When we study the ionization potential as function of the cluster size, we observed that it shown singular results for n<4 using different functionals. Using B3LYP we observed that the **IP** decreases with the clusters size,to getting a local minimum in In_3; while, using M06, it is assumed that increases with the size, besides, the three atoms system, is a local maximum. In regard to In_2, its cation is very unstable and we could not obtain the corresponding energy. Excluding In_4 cluster, the **IP** is independent of the functional , since the trend is similar for both with maximums in In_6 and In_8 respectively.

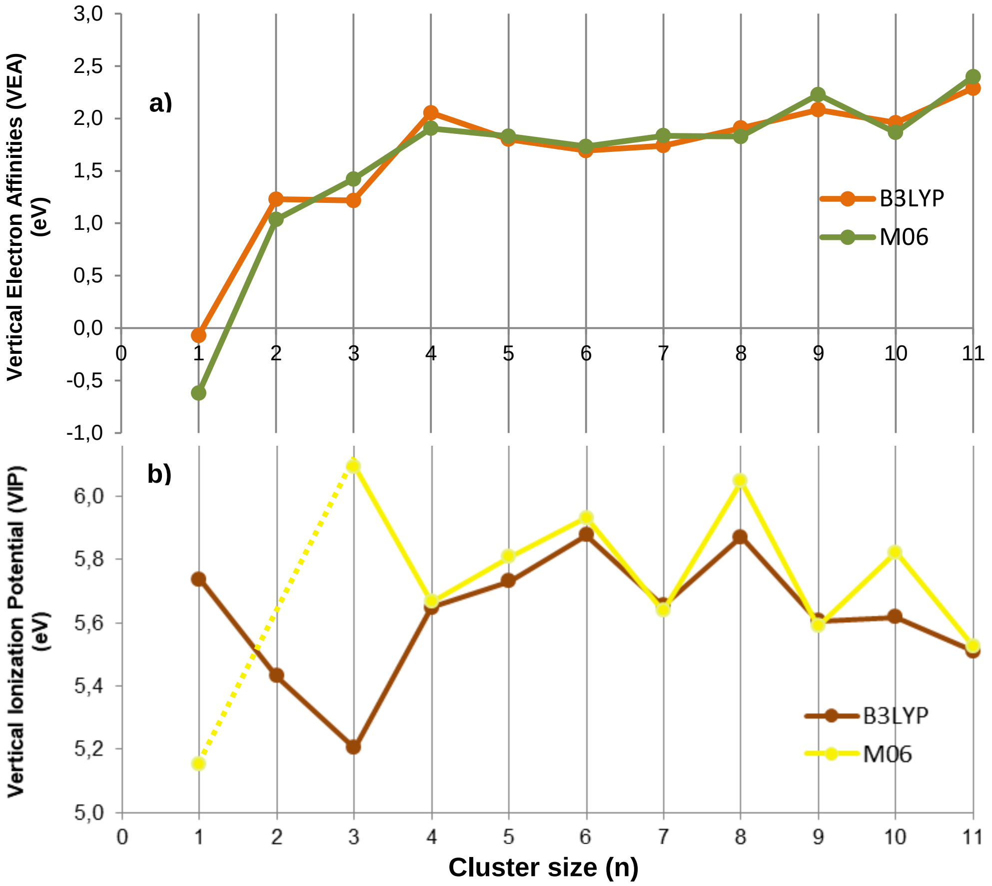

Figure 3. (a) Vertical Electron Affinities (VEA) and (b) Vertical Ionization Potential (VIP) as a function of cluster size In_n (n=1-11)

Previous works of Ga_n[2] analyze these parameters for cluster up to 26 atoms and clearly shows that, our results obtained using B3LYP correlate much better with their results than those provided by M06. In this paper, all calculations were performed using the DMOL program based on DFT method with GGA for the exchange-correlation functional (PW91).

Both the **HOMO-LUMO** gap and the second difference of total energies $\Delta_2 E_n$ are the values that estimate the stability of cluster against its neighbors more next. **Fig 4. (a)** and **(b)** display the results for lowest-energy structures as a function of the cluster size.

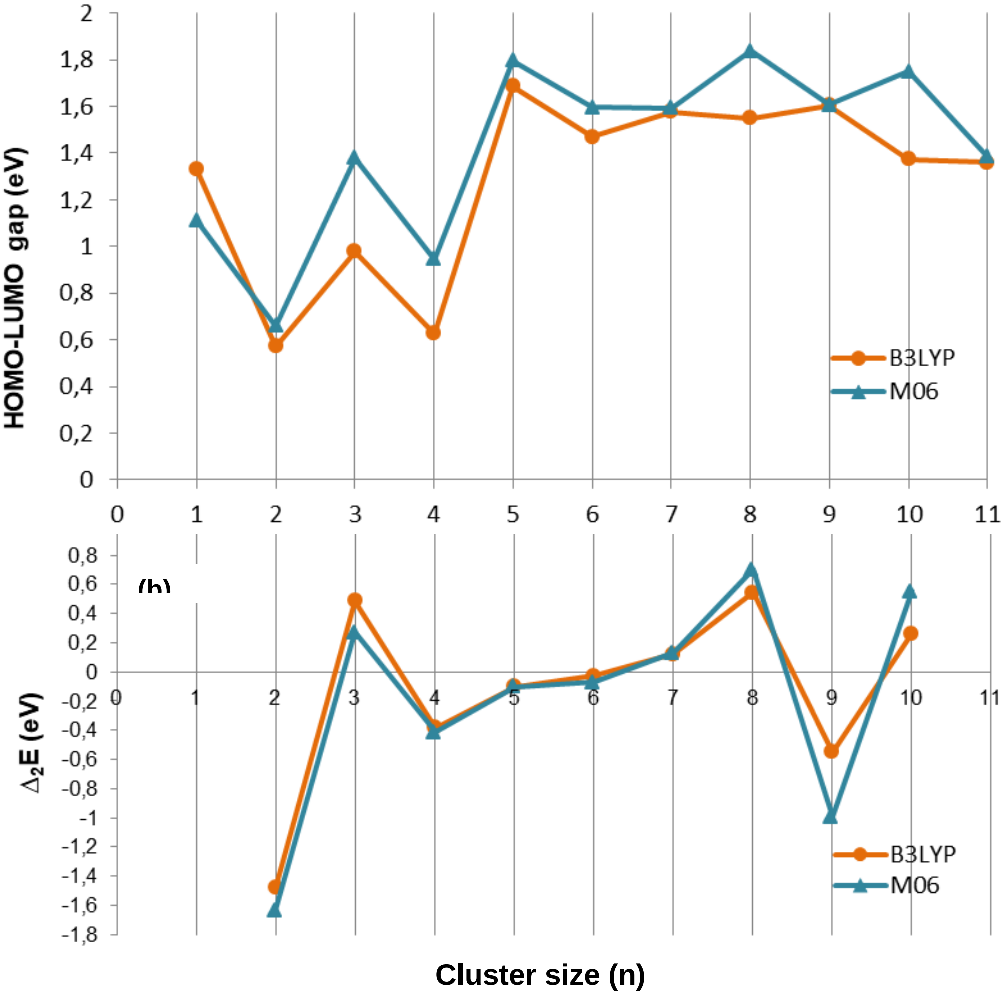

Figure 4. (a) HOMO-LUMO gap and (b) Second differences of cluster energies Δ_2E as a function of the cluster size In_n (n=1-11)

In general terms, the **HOMO-LUMO** gap exhibit odd-even oscillations. For both, B3LYP and M06 functionals, the calculations show a similar behaviors up to n=6: the odd numbered clusters have a larger gap that their even-sized ones neighbors. Nevertheless, these results do not agree with the expected according to previous works for other metals.[9-12] They suggest that the odd-even oscillation can be understood by **electron-pairing effect**. For even cluster, all electrons are paired, giving a closed-shell electronic structure and therefore greater stability. In contrast, all odd clusters should be more reactives because have open-shell electronic structures. On the other hand, a greater difference in energy between the orbital borders confers to the particle greater stability, therefore it is believed that those clusters containing an even number of atoms will have a larger gap. However, our calculations turned out to be completely opposed. The reason why gap behavior does not match the expected pattern may be due to the great role of geometric effects in smaller clusters.

For n=6-11 we found different results according to the functional chosen: using B3LYP, the **HOMO-LUMO** gap does not strongly depends of the cluster size, containing two minor bumps at n=8 and 10. Instead, using M06, the gap show maximum at the even numbered clusters (n=8 and 10), as predicts the electron-pairing effect previously commented. For In_n clusters with n>11 will be studied coming soon.

To complete the study about the relative stability of the systems, we analyse the Δ_2**E** energy.By definition:

$$\Delta_2 E_n(n) = E_{n+1} + E_{n-1} - 2\, E_n \qquad (2)$$

and their peaks indicates “***magic cluster sizes”*** (i.e., very stable cluster sizes that can lead to higher intensities in their synthesis). Regardless the functional chosen, the Δ_2**E** display similar behaviors. It is particularly large for In_3 and In_8, indicating that this clusters are relatively more stables than their even- and odd- numbered neighbors, respectively, in agreement with those calculated by Song and Cao.[2] However, previous works of tin clusters do not coincide with this pattern.[13] Assadollahzadeh and co-workers have shown that most even-numbered clusters are more stables than odd-sized ones, except for Sn_8 and Sn_{12} systems. They propose that low stability of Sn_8 is due to geometric effects. While Sn_7 adopt a pentagonal bipyramid and Sn_9 a symmetrically bicapped, Sn_8 lies structurally in-between and does not adopt a flat pentagonal motif. On the other hand, our calculations suggest that the lowest-energy cluster for In_8 is a cubic estructure (see **Fig 1 VIII b)**).

The trend in Δ_2**E** can only be interpreted reasonably if the global minimum structures were correctly identified. For larger clusters, that have more degrees of freedom, it is more difficult to find the minimal structure, so the analysis of Δ_2**E** is complicated and undesired results are obtained..

Some interesting conclusions can be drawn by compared both graphs in **Figure 4**:

- The gap is particularly large for In_3 and In_5 compared to their nearest neighbors, regardless of the functional chosen. In addition, with M06, a large gap is observed for In_8 and In_{10}.
- As mentioned above, In_3 and In_8 are the group of *“magic cluster sizes”* so that there is a greater correlation between the **HOMO-LUMO** gap and Δ_2**E** using M06 but...
- ... the correlation **is not total**, because the In_5 cluster has a large gap but is not a component of the "*magic*" group. This highlights that **HOMO-LUMO** gap should not be used exclusively to discuss the stabilities of clusters.

The spin density (**SD**) is a sensitive value to provide fundamental insight about to reactivity of metallic clusters. All open-shell electronic structures present a total spin density equal to 1 (one unpaired electron), however there are inherent polarizations within each particle that generate electronic differences at the atoms. **Figure 5** displays the spin spatial distribution for the odd clusters and the values of **SD** obtained from the NBO method, as a difference between **β** and **α** spin densities respectively. An excellent qualitative correlation between the graphs and the calculated values is observed.

It is necessary to bear in mind that, those particles with an even number of atoms possess all its paired spines and therefore spin density equal to zero, it is for this reason that the analysis is only presented particles with an odd number of atoms.

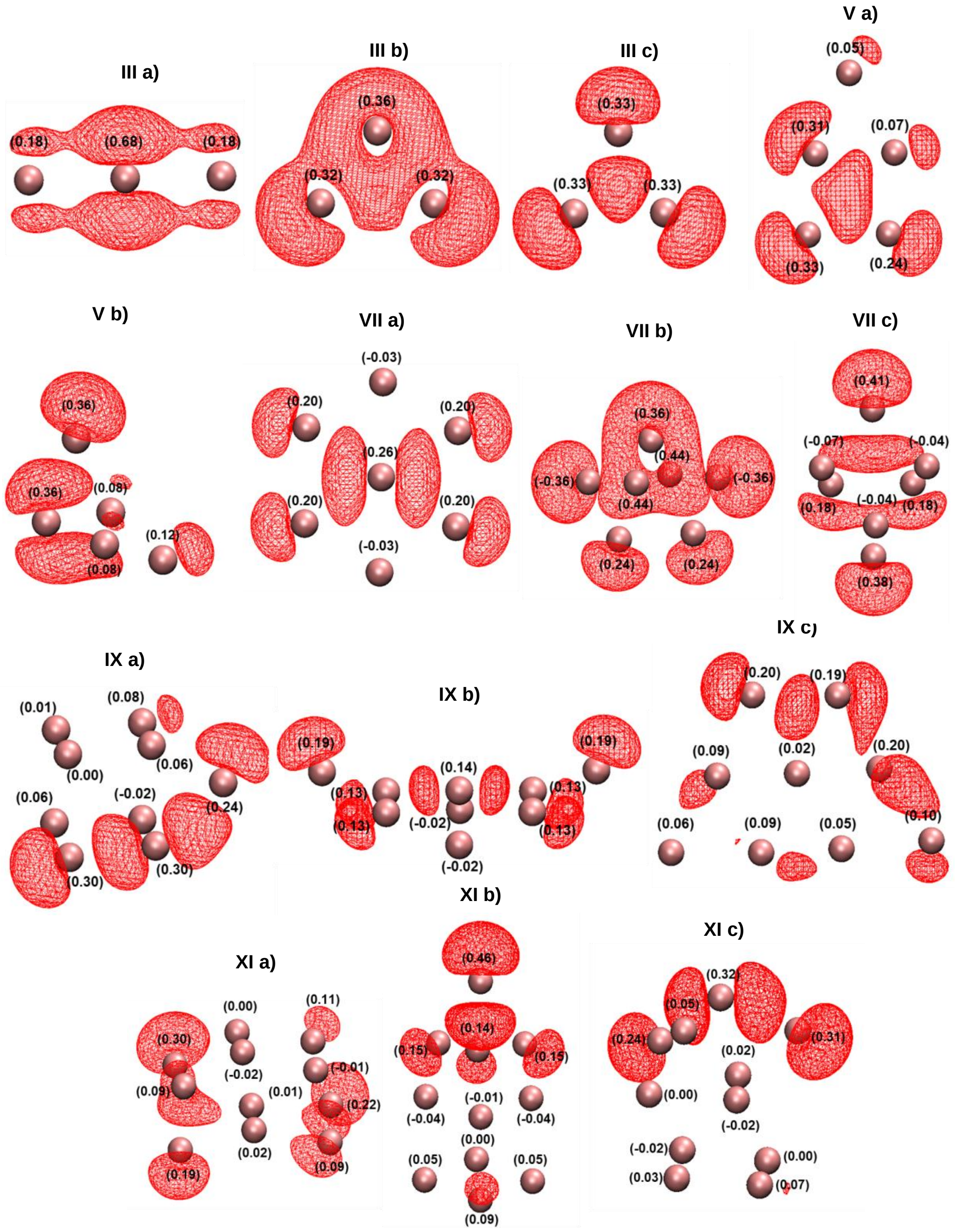

Figure 5. Spin densities (SD) for clusters with open-shell electronic structure (odd clusters). The values in parentheses correspond to the differences between β and α spin densities obtained from NBO method.

According to the **Figure 5**, in the linear In_3 (**III a)**), the spin density concentrates on the central atom (0.68), which makes it a possible reactive center against free radicals. In contrast, in the In_3 triangular cluster, (**III b)** or **III c)**) the spin is distributed between its three atoms almost in the same proportion. For this reason, it is necessary consider that, although the study of this property gives evidence of the molecule reactivity, such spin distribution change considerably regarding to small changes in the cluster geometry.

For n ≥ 5 the **SD** analysis is complicate due to the geometric distribution of the atoms in the different clusters. For In_5 planar particle (**V a)**), it is appreciated that the spin is straggling over the three atoms with an average of 0.30, while in the In_5 non-planar cluster (**V b)**) the spin is concentrated only over two atoms with a value of 0.36.

For n=7 the **SD** presents different characteristics as a function on the geometry of the particle. In the planar and symmetrical system (**VII a)**) there are five reactive centers, while two of them have a slightly **SD**. On the other hand, the **Fig. VII b)** shows that, all atoms could be reactive to free radicals, with spin values 0.24-0.44. Finally, **Fig. VII c)** shows that the spin is distributed mainly between two of its seven atoms, arranged in the tip position within the cluster.

To conclude with the analysis it is observed that in In_9 and In_{11} systems, the **SD** is distributed mainly between three of their atoms, with values between 0.20 and 0.30 with the exception of the **XI b)** cluster where the spin is concentrated on a single atom (0.48). However, the most striking and interesting case is the In_9 structure showed in **IX b)**: it is observed that the spin is distribuited between all its atoms with values < 0.20, which implies that it does not have a really active center against radical species. We could estimated that when the cluster size increases, the system becomes less reactive against radicals, because the total **SD** is scattered between more atoms.

Conclusion:

In summary, using the DFT methods with both B3LYP and M06 functionals and pseudopotential LANL2DZ, the small In_n clusters up to 11 atoms have been studied, taking into account geometries in both two and three dimensions. We explore their geometric and electronic properties including electron affinity, ionization potential, **HOMO-LUMO** gap, $\Delta_2 E$ and spin density.

1) In order to predict the stability of these systems, we have calculated the binding energies. It has been observed that it increases gradually with the cluster size up to n=7 and then remains approximately constant at a value close to 1.27 eV/atom. Using both, B3LYP and M06 functional, the same lowest-energy structures are obtained, except for In_3 clusters which show a linear and a triangular geometry respectively. Additionally, we are found that the lowest-energy structure of In_n can be obtained by capping an atom on the structure of In_{n-1} and that as the cluster size increases, nanoparticles tend to adopt more compact structures. With regard to the stability between planar and non-planar structures, it is clearly observed that the 2D-3D crossover depends exclusively on the functional chosen: using B3LYP the transition ocurr at n=5 whereas with M06 arises in n=6.

2) The analysis of **EA** and **IP** is reliable with previous DFT results for other metals. Calculations using B3LYP and M06, present similar behaviors in the clusters up to 11 atoms. The exception is n<4, where the functional B3LYP give according to the bibliography.

3) The **HOMO-LUMO** gap exhibit odd-even oscillations. For both B3LYP and M06 functionals, the calculations show a similar behaviors up to n=6 but, according to previous works, these results do not correlate with the electron-pairing effect. On the other hand, this property depends fundamentally to the functional chosen: with B3LYP, the gap remains almost unchanged relative to the cluster size, while using M06, maximums are obtained in even-clusters (n=8,10), indicating a result more consistent with other works.

4) Regardless the functional chosen, the $\Delta_2 E$ show similar behaviors. It is particularly large for In_3 and In_8, indicating that this clusters are relatively more stables than their neighbors, in agreement with those calculated by other autors. This can be considered as a fundamental property to estimate the cluster stability.

5) It is assumed that as the spin density increases, the reactivity will be higher. Although the study of this property gives evidence of the molecule reactivity, such distribution of spin varies considerably with small changes in the structure of this one. Finally, as the cluster size increases, the system becomes less reactive, because of the total density is scattered between a larger number of atoms.

References:

[1] Viñes, F., Gomes, J. R. B., Illias, F. *Chem. Soc. Rev*. **2014**, 43, 4922.
[2] Song, B., Cao, P. *J. Chem. Phys.* **2005**, 123, 144312(1).
[3] Taglientea,M. A., Tapfer, L., Antisari, M.V., Mattei, G., Mazzoldi, P., *J. Non-Cryst. Solids* **2004**, 345, 663.
[4] Shi, F. F, Bulkowski, M., Hsieh K. C., *Nanotechnology* **2007**, 18, 1.
[5] Stenzel, O., Stendal, A., Roder, M., Borczyskowski, C.V., *Pure Appl. Opt.* **1997**, 6, 577.
[6] Liang, X. J., Li, J. L., Liu, X., Wang, J. Z., Liu, H., Xue, Q. K., Jia, J. F., *Surf. Interface Anal.* **2004**, 36, 100.
[7] Raman, P. S., Nair, K.G., Kesavamoorthy, R., Panigrahi, B. K., Dhara, S., Ravichandran, V., *Appl. Phys. A* **2007**, 87, 709.
[8] Heo, N.H., Park, J. S., Kim, Y. J., Lim, W. T., Jung, S. W., Seff, K., K, *J. Phys. Chem. B* **2003**, 107, 1120.
[9] Häkkinen, H. Landman, U., *Phys. Rev*. *B* **2000**, 62, R2287.
[10] Xiao, L., Wang, L., *Chem. Phys. Lett.* **2004**, 392, 452.
[11] Wu, X., Senapati, L., Nayak, S.K., Selloni, A. Hajaligol, M., *J. Chem. Phys* **2000**, 117, 4010.
[12] Walker, A.V., *J. Chem. Phys.* **2005**, 122, 94310.
[13] Assadollahzadeh, B., Schäfer, S., Schwerdtfeger, P, *J. Comput. Chem.* **2009**, 31, 929.