

Transition from exo to endo Cu absorption in Si_nCu clusters: A Genetic Algorithms Density Functional Theory (DFT) Study

Ofelia B. Oña,^a Marta B. Ferraro^a and Julio C. Facelli^{b, c}

^aDepartamento de Física, Facultad de Ciencias Exactas y Naturales,
Universidad de Buenos Aires, Argentina, ofelia@df.uba.ar; ferraro@df.uba.ar

^bDepartment of Biomedical Informatics and ^cCenter for High Performance Computing,
University of Utah, 155 South 1452 East Rm 405, Salt Lake City,
Utah 84112-0190, julio.facelli@utah.edu

ABSTRACT

The characterization and prediction of the structures of metal silicon clusters is important for nanotechnology research because these clusters can be used as building blocks for nano devices, integrated circuits and solar cells. Several authors [1-3] have postulated that there is a transition between *exo* to *endo* absorption of Cu in Si_n clusters and showed that for *n* larger than 9 it is possible to find *endohedral* clusters. Unfortunately, no global searchers have confirmed this observation based on plausible structures. Here we use our parallel Genetic Algorithms (GA), [4,5] as implemented in our MGAC software, [6-8] directly coupled with DFT energy calculations to show that the global search of Si_nCu cluster structures does not find endohedral clusters for *n* < 8 and finds them for *n* = 10

Keywords: copper-silicon clusters, genetic algorithms, global optimization.

1 METHODOLOGY

In order to find the most stable Cu@Si_n isomers, we employed the MGAC methodology, [6-8] which employs parallel genetic algorithms (GA). The GA methods are based in the principle of survival of the fittest, considering that each string or *genome* represents a set of trial solutions candidate that at any generation compete with each other in the population for survival and produce offspring for the next generation by prescribed propagation rules. [4, 5] The clusters are represented by a genome of dimension 3N, where N is the number of atoms in the cluster. Operators analogous to crossover, mutation, and natural selection are employed to perform a search able to explore and learn the multidimensional parameter space and determine which regions of that space provide good solutions to the problem. MGAC uses DFT local energy minimizations, provided by the CPMD [9] code, as merit function. In this study we used the Goedecker *et al.* [10] pseudopotential, the PBE (Perdew-Burke-Ernzerhof) [11] exchange correlation functional with an energy cutoff (Ecut) of 100 Ry, and a cell length of 4 Å plus the largest dimension of the cluster

on each side. The pseudopotential was selected after comparing the rms (root mean square) between experimental and predicted bond lengths, binding energies, and vibrational frequencies, for Si₂, Cu₂, and SiCu, employing different density functional methods implemented in the CPMD code and several all electron methods. The results of this comparison are presented in Table I, which shows that the selected combination, PBE/GO, is as good or better than any other DFT approach and better than most of the all electron approaches considered here.

TABLE I. rms between experimental and calculated geometry parameters (Re), binding energy (Eb), and vibrational frequencies (Freq) for Si₂, Cu₂ and SiCu systems with Ecut=100 Ry.

<i>Method</i>	Re [Å]	Eb [eV]	Freq [cm-1]
PBE/GO	0.070	0.301	53
BP/GO	0.070	0.277	56
LDA/GO	0.098	0.547	62
B3LYP/GEN	0.040	0.162	16
LCGTO-LSD	0.020	0.520	49
LCGTO-GGA	0.050	0.180	60
All electron calculations			
B3LYP/6-311+G(d)	0.043	0.217	19
MP4(6s,5p,3d,1f)	0.019	0.149	2
QCISD/6-311+G(d)	0.038	0.420	16
QCISD(T)/6-311+G(d)	0.045	0.463	5
CASSCF/CASPT2	0.010	0.265	56
CASSCF/CASPT2+DK	0.081	0.058	64

The number of generations needed to achieve convergence was between 15 and 100 and the total number of computer processors employed ranges from 49 to 200.

2 RESULTS AND DISCUSSION

In this paper we report the structures and relative stabilities in the homologous series Cu@Si_n ($n=6, 8, 10$). We analyzed all the different isomers found by MGAC/CPMD methodology and calculated their vibration frequencies to discriminate transition states from structures that correspond to true local minima of the energy.

CuSi₆ and CuSi₈

Figures 1 and 2 show the structures of the six lowest energy isomers of CuSi_6 and CuSi_8 . Structures CuSi_6 -d, CuSi_6 -f and CuSi_8 -a correspond to transition states, but several structures in the figures are structures that have not been previously reported; only CuSi_6 -a, CuSi_6 -b and CuSi_8 -a have been reported previously in the literature. [1]

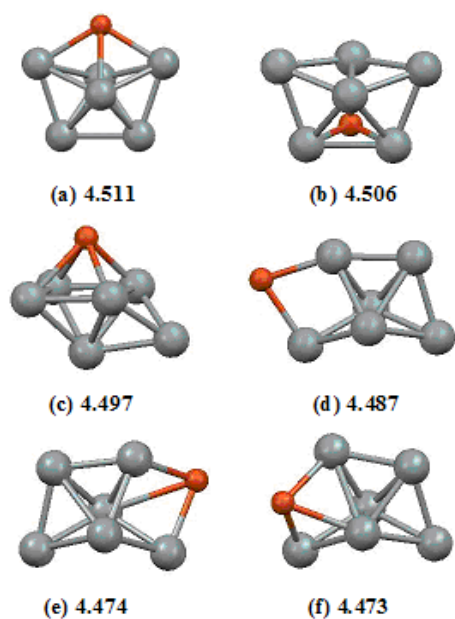


Figure 1: CuSi_6 structures obtained by the MGAC/CPMD and binding energy per atom. All energies in eV based on a Si atomic energies of -101.319 eV and Cu atomic energies of -1289.34 eV.

The vibrational spectra corresponding to structures CuSi_6 -b and CuSi_8 -b are depicted in Figure 3. It is observed that the CuSi_6 -b structure is similar to the structure of CuSi_6^+ reported by Gruene *et al.* [12], our predicted vibrational spectra for CuSi_6 -b with the principal vibration mode, of about 450 cm^{-1} , is close to the corresponding principal vibration mode, about 430 cm^{-1}

predicted for the CuSi_6 cation. [12] Our predicted vibration spectra for CuSi_8 -b is very similar to the experimental spectra reported on reference [12] for CuSi_8^+ . The four predicted and experimental modes are, 250 cm^{-1} , 310 cm^{-1} , 360 cm^{-1} and 440 cm^{-1} ; and 275 cm^{-1} , 325 cm^{-1} , 350 cm^{-1} , $400\text{-}450 \text{ cm}^{-1}$, respectively. However, the theoretical structure shown by Gruene *et al.* [12] is different from CuSi_8 -b. In fact, we are reporting a new structure, CuSi_8 -b, whose theoretical spectrum reproduces better the experimental spectrum than that predicted by Gruene *et al.* [12] for Si_8Cu^+ .

From Figures 1 and 2 it is apparent that all the low energy structures predicted here have the Cu atom in the periphery of the cluster, because the MGAC/CPMD perform a global search over all possible cluster configurations, this is very strong evidence that endohedral configurations are not energetically favorable for these clusters.

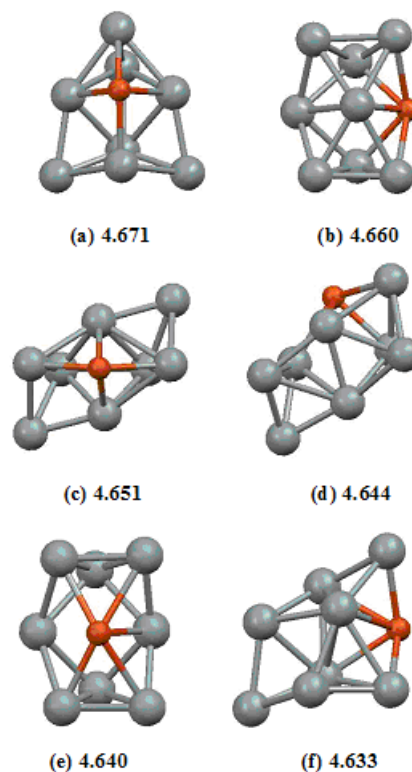


Figure 2. CuSi_8 structures obtained by the MGAC/CPMD and binding energy per atom. All energies in eV based on a Si atomic energies of -101.319 eV and Cu atomic energies of -1289.34 eV.

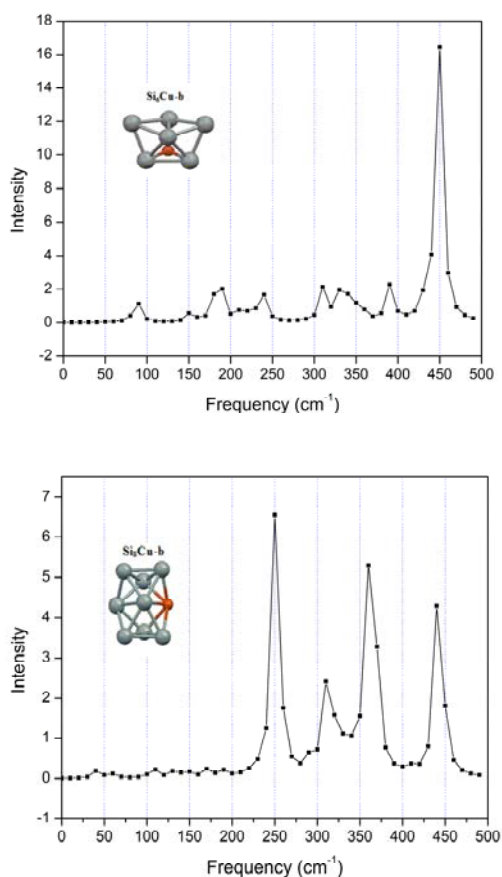


Figure 3. Vibrational spectra of $\text{CuSi}_6\text{-b}$ and $\text{CuSi}_8\text{-b}$ at B3LYP/6-31+G* level of theory.

CuSi_{10}

In Figure 4 we present the structures of the twelve lowest energy isomers for CuSi_{10} with their corresponding binding energies. The energetic and structural parameters of the clusters in Figures 1, 2 and 4 are given in Table II.

To compare our results with those from Ref. [14] the two cage structures, $\text{Cu@Si}_{10}\text{-h}$ and $\text{Cu@Si}_{10}\text{-l}$ were re-optimized using the B3LYP exchange correlation functional and the 6-31+G* basis set. $\text{Cu@Si}_{10}\text{-l}$ energy resulted only 0.044 eV lower than $\text{Cu@Si}_{10}\text{-h}$ energy, the same observation mentioned previously by Hossain *et al.* [13]. However $\text{Cu@Si}_{10}\text{-l}$ is a transition state and $\text{Cu@Si}_{10}\text{-h}$ is a stable isomer according to our calculations for B3LYP, while both of them are TS for GO/PBE.

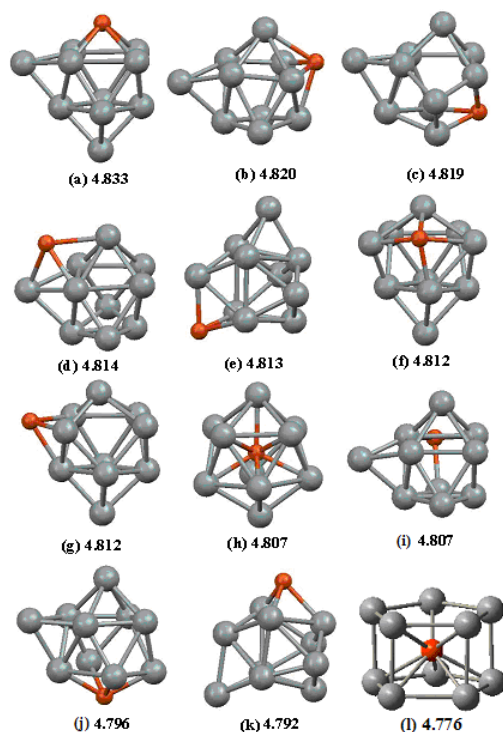


Figure 4. CuSi_{10} structures obtained by the MGAC/CPMD and binding energy per atom. All energies in eV based on a Si atomic energies of -101.319 eV and Cu atomic energies of -1289.34 eV.

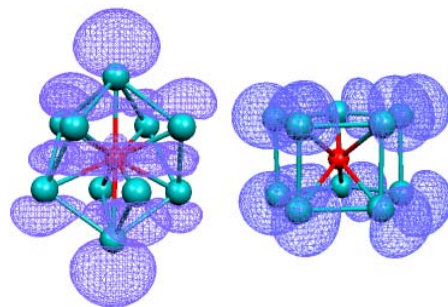


Figure 5. Spin density of $\text{Cu@Si}_{10}\text{-h}$ (right) and $\text{Cu@Si}_{10}\text{-l}$ (left) clusters obtained at B3LYP/6-31+G* level of theory. The isovalue of the contour map is at 0.001.

To verify that the structure $\text{Cu@Si}_{10}\text{-h}$ is a new structure that has not been reported in the literature before by King [14], we tried a local optimization of the structure of $\text{Cu@Si}_{10}\text{-h}$ enforcing the D_{4d} symmetry, as it was suggested by the topological model proposed in Ref. [14] but the optimization did not reach convergence for the model. This provides strong evidence that $\text{Cu@Si}_{10}\text{-h}$ is a truly new structure that has not been reported previously.

Figure 5 depicts the spin density for Cu@Si₁₀-h and Cu@Si₁₀-l, in Cu@Si₁₀-l the density is mostly localized in the three silicon atoms at the top and bottom of the cage, whereas in Cu@Si₁₀-h the delocalization extends to the Cu atom.

TABLE II. Calculated binding energies, average Si-Si bond lengths, Si-Cu bond lengths, and α and β energy gaps for the Si_nCu clusters found by the MGAC-CPMD method. Their structures are given in Figs. 1, 2 and 4. The italicized entries correspond to those found by the MGAC-CPMD method that were not previously reported in the literature.

Isomer	E _b (eV)	α gap (eV)	β gap (eV)	Bond lengths	
				Si-Si	Si-Cu
CuSi₆-a	4.511	1.035	1.399	2.492	2.372
CuSi₆-b	4.506	1.207	1.392	2.439	2.323
<i>CuSi₆-c</i>	<i>4.497</i>	<i>1.194</i>	<i>1.174</i>	<i>2.475</i>	<i>2.399</i>
<i>CuSi₆-d</i>	<i>4.487</i>	<i>1.165</i>	<i>1.585</i>	<i>2.436</i>	<i>2.254</i>
<i>CuSi₆-e</i>	<i>4.474</i>	<i>1.218</i>	<i>1.490</i>	<i>2.448</i>	<i>2.452</i>
<i>CuSi₆-f</i>	<i>4.473</i>	<i>1.319</i>	<i>1.279</i>	<i>2.463</i>	<i>2.341</i>
CuSi₈-a	4.671	0.692	1.357	2.474	2.363
<i>CuSi₈-b</i>	<i>4.660</i>	<i>1.112</i>	<i>1.540</i>	<i>2.477</i>	<i>2.398</i>
<i>CuSi₈-c</i>	<i>4.651</i>	<i>0.696</i>	<i>1.336</i>	<i>2.504</i>	<i>2.352</i>
<i>CuSi₈-d</i>	<i>4.644</i>	<i>0.979</i>	<i>1.490</i>	<i>2.479</i>	<i>2.341</i>
<i>Si₈Cu-e</i>	<i>4.640</i>	<i>1.374</i>	<i>0.885</i>	<i>2.472</i>	<i>2.432</i>
<i>CuSi₈-f</i>	<i>4.633</i>	<i>0.897</i>	<i>0.956</i>	<i>2.491</i>	<i>2.429</i>
CuSi₁₀-a	4.833	1.395	1.377	2.493	2.349
<i>CuSi₁₀-b</i>	<i>4.820</i>	<i>1.298</i>	<i>0.965</i>	<i>2.461</i>	<i>2.338</i>
<i>CuSi₁₀-c</i>	<i>4.819</i>	<i>1.682</i>	<i>1.081</i>	<i>2.447</i>	<i>2.317</i>
<i>CuSi₁₀-d</i>	<i>4.814</i>	<i>1.982</i>	<i>0.754</i>	<i>2.517</i>	<i>2.365</i>
CuSi₁₀-e	4.813	1.777	0.798	2.513	2.232
<i>CuSi₁₀-f</i>	<i>4.812</i>	<i>1.445</i>	<i>1.217</i>	<i>2.486</i>	<i>2.308</i>
CuSi₁₀-g	4.812	1.346	1.211	2.507	2.310
<i>Cu@Si₁₀-h</i>	<i>4.807</i>	<i>1.938</i>	<i>0.780</i>	<i>2.580</i>	<i>2.352</i>
CuSi₁₀-i	4.807	1.719	0.830	2.480	2.333
<i>CuSi₁₀-j</i>	<i>4.796</i>	<i>0.895</i>	<i>1.392</i>	<i>2.492</i>	<i>2.309</i>
CuSi₁₀-k	4.792	0.909	1.171	2.502	2.268
Cu@Si₁₀-l	4.776	0.262	0.967	2.475	2.440

In agreement with previous reports the MGAC/CPMD method is able to find endohedral structures for CuSi₁₀, but in contrast with previous studies these structures are not postulated *a priori* and locally optimized, but are found automatically by the GA search.

CONCLUSIONS

Using the MGAC/CPMD method with the GO/PBE approach to calculate the energy we have shown that the GA search does not find any endohedral cluster for CuSi_n clusters with $n < 8$, but it is able to find them for $n = 10$. This has been previously postulated but the MGAC/CPMD method is able to find these structures without any *a priori* information on the approximate conformation of the clusters.

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