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Hydrogen Storage on Calcium-Coated Toroidal Carbon Nanostructure C_{120} modeled with Density Functional Theory

A. Cruz-Torres^a, F. de L. Castillo-Alvarado^a, J. Ortíz-López^a, and J. S. Arellano^b

^aEscuela Superior de Física y Matemáticas, Instituto Politécnico Nacional,
Edificio 9, Unidad Profesional Adolfo López Mateos, Col. San Pedro Zacatenco,
Delegación Gustavo A. Madero, México, 07738, D.F. México.

^bUniversidad Autónoma Metropolitana Azcapotzalco,
Av. San Pablo 180, Col. Reynosa Tamaulipas, México, 02200 D.F., México,
e-mail: jsap@correo.azc.uam.mx

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Ab initio density functional calculations are performed for a toroidal carbon C_{120} nanostructure doped with one to ten calcium atoms bonded to its outer surface. The calculations are based on DFT with the generalized gradient approximation PW91 (Perdew and Wang) as implemented in the Materials Studio v.4.3 code. Dmol³ module is used to calculate, among others, total energies, charge density, HOMO-LUMO and Mulliken population analysis. Based on these results, it is possible to propose that a single Ca atom is able to adsorb up to 6 H_2 molecules. The study is extended for a system with ten Ca atoms, which can adsorb up to 60 H_2 molecules. This leads to 6.16 weight percentage for the gravimetric hydrogen storage capacity which fulfills the US Department of Energy (DOE) target (6 wt%) for onboard hydrogen storage systems for the year 2010. Accordingly, the calcium-coated toroidal carbon C_{120} nanostructure is a good quality candidate for H_2 storage with higher adsorption energy than on pristine carbon nanotorus.

Keywords: Hydrogen storage; density functional theory calculation; toroidal carbon nanostructure.

Se realizan cálculos de primeros principios con la funcional de la densidad para una nanoestructura toroidal de carbono C_{120} dopada con uno y hasta diez átomos de calcio ligados a su superficie externa. Los cálculos se basan en la teoría del funcional de la densidad (DFT), con la aproximación de gradiente generalizado PW91 (de Perdew y Wang), como aparece en el código Materials Studio v.4.3. Se usa el módulo Dmol³ para calcular, entre otras, las energías totales, densidad de carga, orbitales moleculares ocupados más alto y más bajo y análisis de población de Mulliken. Basados en estos resultados, es posible proponer que un solo átomo de carbono es capaz de adsorber hasta 6 moléculas de hidrógeno, H_2 . Esto da lugar a un porcentaje en peso de 6.16 % para la capacidad gravimétrica de almacenamiento de hidrógeno, que satisface la meta establecida de 6% para sistemas móviles de almacenamiento de hidrógeno para el año 2010 establecida por el Departamento de energía (DOE) de los Estados Unidos de América. Por lo tanto, la nanoestructura toroidal de carbono C_{120} , es un candidato de buena calidad para almacenar H_2 , con una energía de adsorción más alta que en el nanotoro puro de carbono.

Descriptores: Almacenamiento de hidrógeno; cálculo con teoría funcional de la densidad; nanoestructura toroidal de carbono.

PACS: 71.15.Mb; 71.15.Nc; 81.05.Tp; 81.05.Uw

1. Introduction

Development of novel nanostructured materials for efficient hydrogen storage is of current technological interest because hydrogen is expected to replace hydrocarbons as energy source in the near future. The large surface area of the torus geometry in a given molecular species is ideal for hydrogen storage applications. Carbon nanostructures with toroidal geometry are expected to have other unusual physical properties that make them attractive for a wide range of technological applications. Dunlap proposed a toroidal carbon nanostructure with six-fold rotational symmetry in 1992 by connecting six straight nanotube segments [1]. In this work we study the all-carbon five-fold symmetric C_{120} torus as a good candidate for a hydrogen storage system. Ihara and coworkers [2] built the C_{120} nanotorus from 12 not equivalent carbon atoms.

In a recent theoretical study, Guangfen Wu *et al.* [3], investigate the feasibility of bare and metal-coated boron buckyball B_{80} with $M = Li, Na, K, Be, Mg, Ca, Sc, Ti,$ and V for hydrogen storage using density functional theory approach.

They find that $M = Ca$ or Sc are best candidates for hydrogen storage with moderate adsorption energy of H_2 and without clustering of Sc or Ca on B_{80} surface. Qiang Sun *et al* [4], based on gradient corrected density functional theory, show that Li decorated B doped heterofullerene ($Li_{12}C_{48}B_{12}$) has properties of a hydrogen storage material. On the other hand, Qian Wang *et al.* [5], by means of first principles calculations based on gradient corrected density functional theory and molecular dynamics simulations of Ca decorated fullerene indicate that $C_{60}Ca_{32}$ can absorb up to 62 H_2 molecules in two layers. In addition, T. Yildirim, *et al.* [6], performed a study about molecular and dissociative adsorption of multiple hydrogen molecules on transition metal decorated C_{60} , once the metals are adsorbed on C_{60} , each can bind up to four hydrogen molecules.

In this work, we perform DFT calculations on C_{120} nanotorus with Dmol³ code [7,8] implemented in the Materials Studio program [9]. As a first step, the stability of the isolated C_{120} nanotorus and of each of the calcium-coated nanotori with nH_2 molecules ($n=1-6$) was investigated. Opti-

mized geometry of C₁₂₀ yields 4.159 and 11.740 Å for the inner and outer diameters, respectively, with a nearly circular cross section with diameter 4.623 Å. We report calculations of total energies, charge density, Mulliken population analysis and highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) energy gaps of these systems. The closed structure and large specific surface area of the C₁₂₀ toroidal geometry gives room to up to 10 Ca atoms, each of which can bond to up to six H₂ molecules, suggesting that they should be efficient H₂ storage systems.

2. Theoretical method

As Ihara and coworkers [2] describe, coordinates of the 120 carbon atoms of the nanotorus were obtained from a set of 12 non equivalent carbon atoms by successive five-fold rotations followed by a reflection and final rotation of $\pi/5$ radians. The structure consists of ten pentagonal, forty hexagonal and ten heptagonal rings. Five- and six-member rings follow the *isolated pentagon rule* [10,11]. The optimized geometry of C₁₂₀ torus is described in Table I.

We use the generalized gradient approximation of DFT implemented in the Materials Studio v.4.3 code, as proposed by Perdew and Wang (PW91) [12]. The Dmol³ module was used to calculate, among others, total energy, electronic charge density, HOMO-LUMO and Mulliken population analysis. To calculate the interaction energies of the hydrogen molecules with the C₁₂₀ nanotorus, the DFT is complemented with a double numerical plus polarization basis set, (DNP). For occupied orbitals, we consider two atomic orbitals in the basis set. For C and H atoms polarization, *d*-function and *p*-function are used, respectively. The employed basis set has the advantage to be equivalent to the analytical basis set 6-31G**.

3. Results, analysis and discussion

This work has been organized in two parts. The first one is the study of the capacity of C₁₂₀ doped with a single Ca atom externally attached (CaC₁₂₀) to adsorb H₂ molecules. We found that the maximum number is six, based on the corresponding average adsorption energy per H₂ (Table II). Based on this result, the second part of the present work consists on the study of C₁₂₀ doped with 10 Ca atoms, each of them associated with 6 H₂ molecules. We add one Ca atom (and its 6 H₂ molecules) at a time, and optimize the geometries of each system before adding the next Ca.

3.1. Hydrogen storage capacity of CaC₁₂₀

In this section, we study hydrogen adsorption capabilities of the toroidal carbon C₁₂₀ structure with a single Ca atom externally attached. Although a metal atom can occupy different sites of toroidal carbon C₁₂₀ nanostructure, we consider a Ca atom adsorbed between carbon atoms labeled 85 and 86, which neighbors in a pentagonal and hexagonal ring and the

respective bond length is 1.486 Å. The optimized structures of CaC₁₂₀–*n*H₂, for *n* = 1–6, are shown in Fig. 1. The geometry and energy information of calcium-toroidal carbon C₁₂₀ nanostructure are presented in Table II. The average C-C distances involving the C atoms closest to the Ca atom (C85 y C86 in Table I) are 2.649 and 2.656 Å, respectively. The average Ca-H distances are in the range of 2.623–2.721 Å. On the other hand, the average H-H bond distances of the H₂ molecules located near the Ca atom is of 0.773 Å, as the number of H₂ molecules increases from one to six. On the contrary the C85-C86 bond distance, slightly increases from 1.484 to 1.509 Å, as the number of H₂ molecules increases from one to six

The binding energy E_b of the Ca atom adsorbed on the outer surface of the bare nanotorus is defined as [13]

$$E_b = E_t(\text{Ca}) + E_t(\text{C}_{120}) - E_t(\text{C}_{120-\text{Ca}}) \quad (1)$$

TABLE I. Carbon atom numbering and coordinates x, y, z (Å) in C₁₂₀ nanotorus optimized structure.

C	x	y	z
1	2.052	0.000	0.362
2	2.364	0.000	1.767
3	2.076	2.385	2.321
4	2.909	1.239	2.321
5	4.353	1.283	2.165
6	2.564	3.745	2.166
7	5.006	0.000	1.818
8	3.889	3.734	1.558
9	4.754	2.546	1.559
10	5.818	0.001	0.617
11	5.365	2.444	0.240
12	3.982	4.346	0.239
13	0.634	-1.947	0.359
14	0.730	-2.245	1.765
15	2.909	-1.238	2.321
16	2.076	-2.384	2.321
17	2.565	-3.744	2.166
18	4.354	-1.282	2.165
19	4.754	-2.545	1.559
20	3.890	-3.733	1.558
21	3.983	-4.346	0.239
22	5.366	-2.443	0.240
23	0.730	2.246	1.765
24	1.547	4.760	1.819
25	1.661	-1.204	-0.356
26	1.548	-4.760	1.819
27	1.799	-5.532	0.617
28	-1.660	-1.205	0.356
29	-1.913	-1.390	1.760

30	-0.279	-3.148	2.318				
31	-1.626	-2.711	2.318	77	0.668	-5.858	-0.241
32	-2.769	-3.597	2.169	78	2.906	-5.131	-0.242
33	0.128	-4.536	2.167	79	-2.051	0.000	-0.362
34	-4.051	-2.943	1.824	80	-2.362	0.000	-1.767
35	-0.950	-5.307	1.560	81	-2.075	-2.385	-2.321
36	-2.349	-4.855	1.562	82	-2.908	-1.239	-2.321
37	-4.708	-3.420	0.621	83	-4.352	-1.283	-2.165
38	-2.903	-5.131	0.243	84	-2.563	-3.745	-2.166
39	-0.665	-5.858	0.241	85	-5.004	-0.001	-1.818
40	-1.660	1.204	0.356	86	-3.888	-3.734	-1.558
41	-1.913	1.389	1.760	87	-4.752	-2.546	-1.559
42	-3.082	-0.708	2.318	88	-5.816	-0.001	-0.617
43	-3.082	0.707	2.318	89	-5.364	-2.444	-0.240
44	-4.278	1.522	2.170	90	-3.981	-4.346	-0.239
45	-4.277	-1.523	2.170	91	-0.632	1.947	-0.359
46	-4.052	2.943	1.824	92	-2.908	1.238	-2.321
47	-5.343	-0.736	1.561	93	-4.352	1.282	-2.165
48	-5.344	0.735	1.561	94	-4.753	2.545	-1.559
49	-4.708	3.420	0.621	95	-3.981	4.346	-0.239
50	-5.778	1.176	0.242	96	-5.364	2.443	-0.240
51	-5.778	-1.177	0.242	97	1.662	1.205	-0.356
52	-1.627	2.711	2.318	98	0.634	1.948	0.359
53	-2.770	3.597	2.169	99	-0.279	3.148	2.318
54	-2.350	4.855	1.562	100	0.127	4.536	2.167
55	-2.904	5.131	0.242	101	-0.951	5.306	1.560
56	1.915	-1.389	-1.760	102	1.798	5.532	0.617
57	3.083	0.708	-2.318	103	-0.666	5.858	0.241
58	3.083	-0.707	-2.318	104	-0.729	2.245	-1.765
59	4.279	-1.522	-2.170	105	-2.075	2.384	-2.321
60	4.279	1.523	-2.170	106	-2.564	3.744	-2.166
61	4.053	-2.943	-1.824	107	-1.546	4.760	-1.819
62	5.345	0.736	-1.561	108	-3.889	3.733	-1.558
63	5.345	-0.735	-1.561	109	-1.798	5.532	-0.618
64	4.710	-3.420	-0.621	110	1.915	1.389	-1.760
65	5.780	-1.176	-0.242	111	0.280	3.148	-2.319
66	5.780	1.177	-0.242	112	1.628	2.711	-2.318
67	-0.632	-1.948	-0.359	113	2.770	3.597	-2.169
68	-0.728	-2.246	-1.765	114	-0.126	4.536	-2.167
69	1.628	-2.711	-2.318	115	4.052	2.943	-1.824
70	0.280	-3.148	-2.318	116	0.951	5.307	-1.560
71	-0.125	-4.536	-2.167	117	2.350	4.855	-1.562
72	2.771	-3.597	-2.169	118	4.709	3.420	-0.621
73	-1.545	-4.760	-1.819	119	2.905	5.131	-0.243
74	2.351	-4.855	-1.562	120	0.666	5.858	-0.241
75	0.952	-5.306	-1.560				
76	-1.797	-5.532	-0.617				

where E_t (Ca), E_t (C_{120}) and E_t (C_{120-Ca}) are the total energies of a free Ca atom, the pure C_{120} and the C_{120-Ca}

system, respectively. E_b is found to be equal to 4.630 (eV), which indicates that the C_{120} -Ca system is strongly bonded. The strength of the interaction is consistent with the formation of a C-Ca bond, which indicates that the whole system can be considered as one single species.

We have also computed the average adsorption energy per H_2 , [3]

$$E_{ave} = \{E[CaC_{120}] + nE[H_2] - E[CaC_{120} - nH_2]\} / n \quad (2)$$

and consecutive adsorption energy of H_2

$$E_t = E[CaC_{120} - (n-1)H_2] + E[H_2] - E[CaC_{120} - nH_2] \quad (3)$$

where $E[CaC_{120}]$, $E[H_2]$, $E[CaC_{120} - nH_2]$ and $E[CaC_{120} - (n-1)H_2]$ are the total energies of relaxed CaC_{120} , H_2

molecule, $CaC_{120} - nH_2$ and the $CaC_{120} - (n-1)H_2$ system, respectively, and n is the number of H_2 molecules, see Table II. Although the adsorption energy of the first H_2 on CaC_{120} reaches up to 0.151 eV, that of the second H_2 is 0.201 eV. The stronger binding of H_2 to CaC_{120} and the relatively larger HOMO-LUMO gap of $CaC_{120} - H_2$ imply that this structure is of high stability. Thus, the second H_2 is very easy to adsorb. For the other H_2 molecules, the value of adsorption energy slightly decreases from 0.201 for two H_2 molecules to 0.084 eV, for six H_2 molecules. However, even for the latter there is a strong binding of H_2 to CaC_{120} . Accordingly, the system $CaC_{120} - 6H_2$ is stable and expected to be a good alternative for hydrogen storage.

The spatial HOMO-LUMO distributions for the bare CaC_{120} and hydrogenated $CaC_{120} - 6H_2$ system are shown correspondingly in Figs. 2 and 3, respectively. Blue lobes

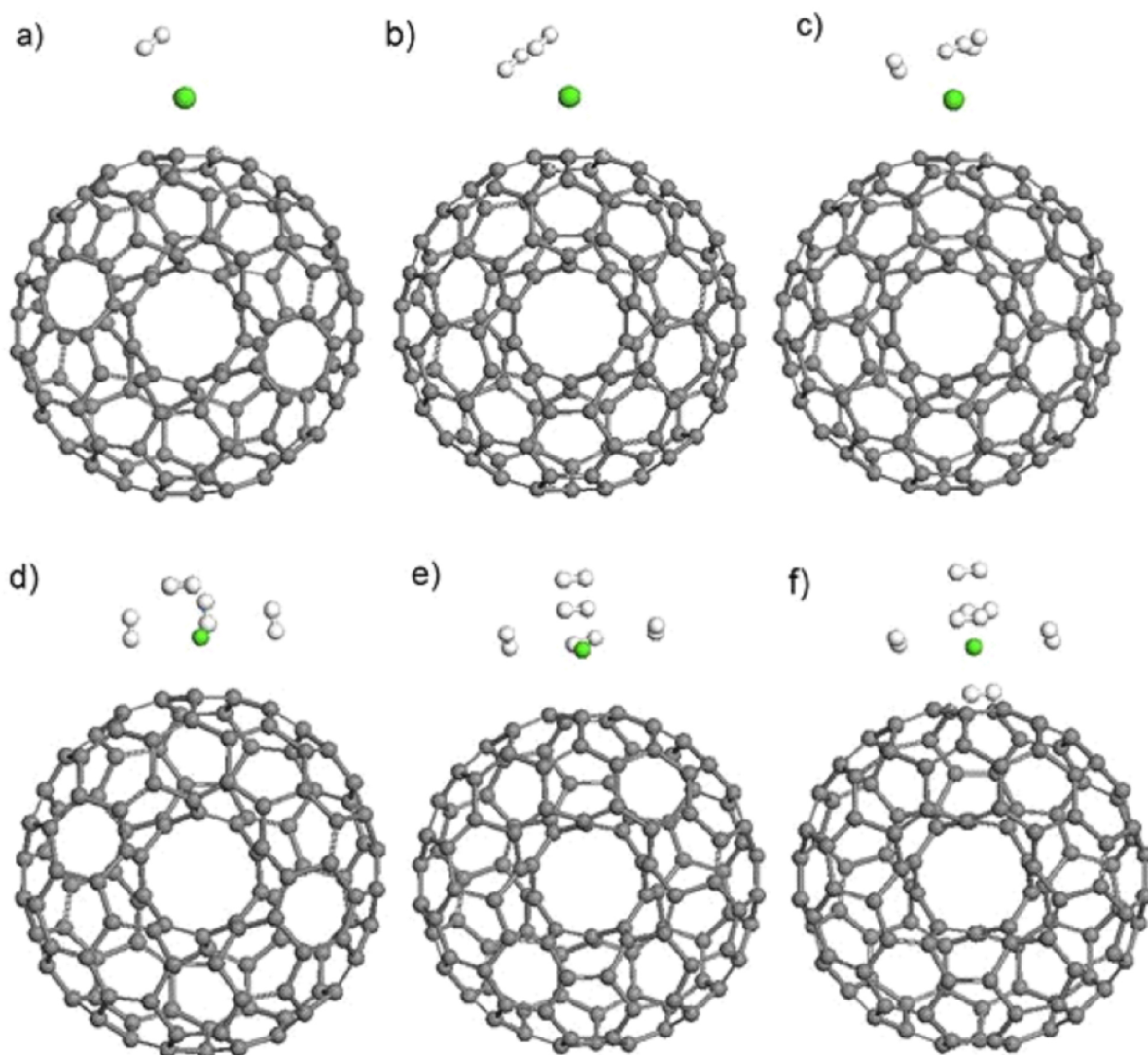


FIGURE 1. (a - f) Optimized structures of $CaC_{120} - nH_2$ systems, for $n = (1-6)$ respectively.

TABLE II. Total energy, average adsorption energy per H_2 and consecutive adsorption energy (in parentheses) of H_2 , and geometrics parameters of CaC_{120} and $CaC_{120} - nH_2$ $n = (1-6)$ systems.

System	Total Energy (Ha)	Average adsorption energy per H_2 (eV)	Distances (Å)				Average H-H bond lengths (Å)
			C86-Ca	C85-Ca	Average Ca-H	C85-C86	
CaC_{120}	-5251.436127	–	2.674	2.696	–	1.484	–
$CaC_{120}-H_2$	-5252.610773	0.151	2.611	2.631	2.721	1.493	0.772
$CaC_{120}-2H_2$	-5253.787271	0.176 (0.201)	2.676	2.686	2.623	1.485	0.774
$CaC_{120}-3H_2$	-5254.962808	0.176 (0.175)	2.709	2.662	2.633	1.487	0.774
$CaC_{120}-4H_2$	-5256.139268	0.182 (0.200)	2.643	2.638	2.631	1.488	0.773
$CaC_{120}-5H_2$	-5257.315292	0.183 (0.188)	2.657	2.634	2.659	1.487	0.772
$CaC_{120}-6H_2$	-5258.487476	0.167 (0.084)	2.624	2.595	2.643	1.509	0.772

TABLE III. HOMO-LUMO energies and gap (Δ) of CaC_{120} and $CaC_{120} - nH_2$ $n = (1-6)$ system in eV.

System	HOMO	LUMO	(Δ)
CaC_{120}	-5.57	-4.59	0.98
$CaC_{120}-H_2$	-5.57	-4.59	0.98
$CaC_{120}-2H_2$	-5.58	-4.59	0.99
$CaC_{120}-3H_2$	-5.58	-4.60	0.98
$CaC_{120}-4H_2$	-5.58	-4.60	0.98
$CaC_{120}-5H_2$	-5.58	-4.60	0.98
$CaC_{120}-6H_2$	-5.57	-4.59	0.98

show the positive and yellow lobes show the negative values of the wave function.

In Fig. 2, the density distribution in the LUMO of CaC_{120} systems is mainly located in the neighborhood of the Ca atom, indicating that the adsorption of the first H_2 molecule is expected to take place in this region. The Fig. 3 shows the $CaC_{120}-6H_2$ system. The LUMO density is also concentrated in the vicinity of the Ca atom, suggesting that the second molecule of H_2 would also be absorbed in this region.

The HOMO-LUMO energy gaps (Δ) of CaC_{120} and $CaC_{120} - nH_2$ $n = (1-6)$ system are reported in Table III. They are very similar for all the reported systems with average values of 0.98 eV.

The values for the Mulliken population analysis are on Table IV. According to them for the system with only one atom of Ca without H_2 molecules, the value is 0.993 electrons. This means there is a very high charge transfer from this atom to the C atoms that are closer and labeled with numbers 85, 86, 88 and 89. For the rest of the Ca atoms, as the number of H_2 molecules increases the value of its charge transfer lowers from 0.979 for one H_2 molecule to 1.016 electrons for 6 hydrogen molecules.

From Table IV it is also possible to observe that when 1 to 5 molecules of H_2 are adsorbed, the charge transfer to these carbon atoms is almost the same for all (-0.135 electrons in average). But when the number of hydrogen molecules in-

crease to 6, then the charge transfer also increase towards the carbon atoms labeled with numbers 85 and 86 (-0.297 electrons in average). Regarding the hydrogen, these transfer their charge and stabilize in an average value of 0.016 electrons.

3.2. Hydrogen storage capacity of $10CaC_{120}$

Now we know that a single atom of Ca can adsorb up to six molecules of H_2 . In this section of our study, we cover C_{120}

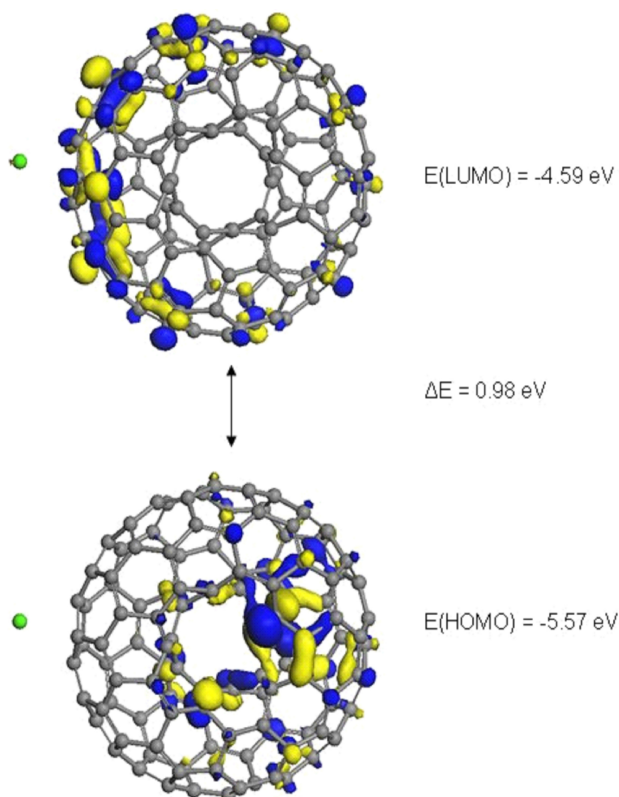


FIGURE 2. HOMO-LUMO energy gap (Δ) for the CaC_{120} system. Above: $E(LUMO) = -4.59$ eV. Below: $E(HOMO) = -5.57$ eV. $\Delta E = 0.98$ eV.

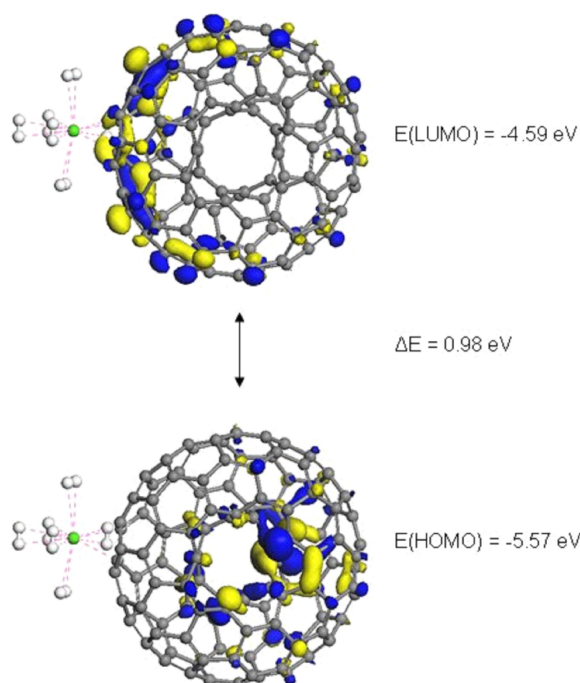


FIGURE 3. HOMO-LUMO energy gap (Δ) for the $\text{CaC}_{120}\text{-6H}_2$ system. Above: $E(\text{LUMO}) = -4.59$ eV. Below: $E(\text{HOMO}) = -5.57$ eV. $\Delta E = 0.98$ eV.

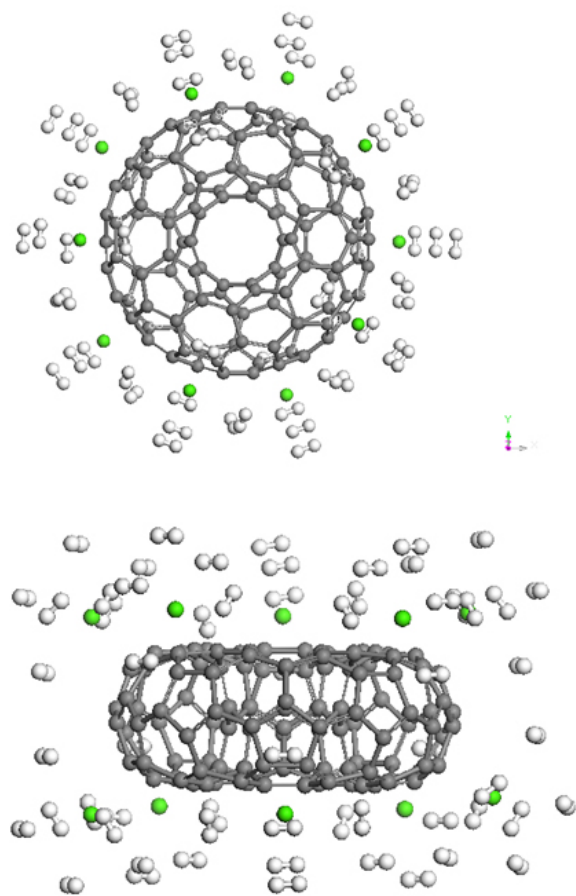


FIGURE 4. Optimized structure of $10\text{CaC}_{120}\text{-60H}_2$ system. Upper view (above) and side view (below).

TABLE IV. Mulliken population analysis of CaC_{120} and $\text{CaC}_{120} - n\text{H}_2$ $n = (1-6)$ system.

System	Mulliken charge (electron)		
	Ca atom	H atom Average	C atom
CaC_{120}	0.933	–	C85 -0.131 C86 -0.139 C88 -0.171 C89 -0.150
$\text{CaC}_{120}\text{-H}_2$	0.979	-0.015	C85 -0.161 C86 -0.171 C88 -0.148 C89 -0.141
$\text{CaC}_{120}\text{-2H}_2$	1.016	-0.019	C85 -0.135 C86 -0.133 C88 -0.169 C89 -0.160
$\text{CaC}_{120}\text{-3H}_2$	1.072	-0.021	C85 -0.137 C86 -0.109 C88 -0.160 C89 -0.193
$\text{CaC}_{120}\text{-4H}_2$	1.086	-0.016	C85 -0.154 C86 -0.151 C88 -0.157 C89 -0.160
$\text{CaC}_{120}\text{-5H}_2$	1.085	-0.014	C85 -0.155 C86 -0.146 C88 -0.147 C89 -0.160
$\text{CaC}_{120}\text{-6H}_2$	1.016	-0.014	C85 -0.309 C86 -0.286 C88 0.036 C89 0.033

with more Ca atoms and thus we find up to now and without external pressure, that the maximum number is 10 (10CaC_{120}), giving us 60 H_2 molecules. This represents a 6.16 percentage in weight, which complies with the U.S. Department of Energy (USDOE) goal for the year 2010 (6 wt%) for materials designed to store hydrogen.

Figure 4 shows many sites around the middle plane of the nanotorus that can be coated with more calcium atoms and hydrogen molecules. This will be explored with the application of external pressure and will be reported elsewhere. A second group of hydrogen molecules around the first one could possibly be bonded in addition but with an expected binding energy less than for the nearest hydrogen molecules to the calcium and carbon atoms.

Figure 4 shows the geometry optimized system $10\text{CaC}_{120}\text{-60H}_2$. The total energy values obtained for all systems from

TABLE V. Total energy, HOMO-LUMO energy gap (Δ) and geometrics parameters of CaC_{120} and $n\text{CaC}_{120}-(6n)\text{H}_2$ $n=1-10$ systems.

System	Total Energy (Ha)	(Δ) (eV)	Distances (\AA)			Average H-H bond lengths (\AA)
			Average C-Ca	Average Ca-H	Average C(1)-C(2)	
CaC_{120}	-5251.436127	0.98	2.688	–	1.509	–
$\text{CaC}_{120}-6\text{H}_2$	-5258.487476	0.98	2.609	2.643	1.509	0.772
$2\text{CaC}_{120}-12\text{H}_2$	-5943.243964	0.92	2.608	2.647	1.510	0.773
$3\text{CaC}_{120}-18\text{H}_2$	-6627.999257	0.88	2.596	2.683	1.512	0.773
$4\text{CaC}_{120}-24\text{H}_2$	-7312.753049	0.87	2.611	2.698	1.512	0.773
$5\text{CaC}_{120}-30\text{H}_2$	-7997.505069	0.86	2.593	2.695	1.512	0.776
$6\text{CaC}_{120}-36\text{H}_2$	-8682.255838	0.81	2.593	2.695	1.511	0.775
$7\text{CaC}_{120}-42\text{H}_2$	-9367.008956	0.11	2.591	2.679	1.509	0.775
$8\text{CaC}_{120}-48\text{H}_2$	-10051.756726	0.12	2.590	2.676	1.508	0.776
$9\text{CaC}_{120}-54\text{H}_2$	-10736.504581	0.12	2.583	2.686	1.507	0.776
$10\text{CaC}_{120}-60\text{H}_2$	-11421.253482	0.21	2.592	2.677	1.507	0.776

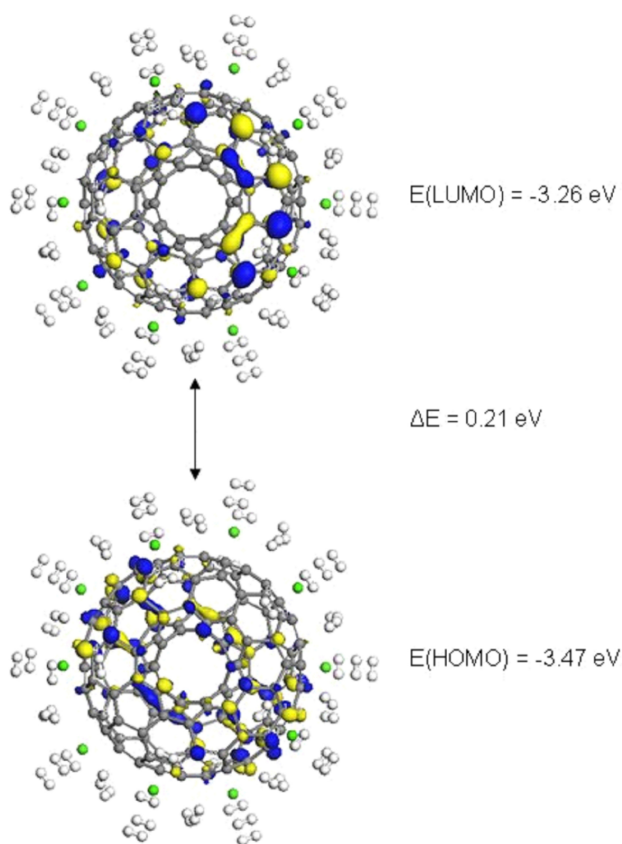


FIGURE 5. HOMO-LUMO energy gap (Δ) for the $10\text{CaC}_{120}-60\text{H}_2$ system. Above: $E(\text{LUMO}) = -3.26$ eV. Below: $E(\text{HOMO}) = -3.47$ eV. $\Delta E = 0.21$ eV.

one to 10 Ca atoms is on Table V. The values HOMO-LUMO energy gaps (Δ) and geometric parameters of optimization are given.

From values in Table V, it is possible to conclude that as the number of calcium atoms increases, the gap value de-

TABLE VI. Mulliken population analysis of CaC_{120} and $n\text{CaC}_{120}-(6n)\text{H}_2$ $n=1-10$ systems.

System	Mulliken charge (electron)		
	Ca atom Average	H atom Average	C atom Average
CaC_{120}	0.933	–	-0.121
$\text{CaC}_{120}-6\text{H}_2$	1.016	-0.023	-0.297
$2\text{CaC}_{120}-12\text{H}_2$	1.014	-0.031	-0.299
$3\text{CaC}_{120}-18\text{H}_2$	1.017	-0.025	-0.304
$4\text{CaC}_{120}-24\text{H}_2$	1.015	-0.028	-0.306
$5\text{CaC}_{120}-30\text{H}_2$	1.013	-0.020	-0.305
$6\text{CaC}_{120}-36\text{H}_2$	1.010	-0.021	-0.302
$7\text{CaC}_{120}-42\text{H}_2$	1.010	-0.027	-0.282
$8\text{CaC}_{120}-48\text{H}_2$	1.011	-0.031	-0.289
$9\text{CaC}_{120}-54\text{H}_2$	1.010	-0.034	-0.293
$10\text{CaC}_{120}-60\text{H}_2$	1.009	-0.032	-0.290

creases from 0.98 to 0.21 eV, for 1 and 10 Ca atoms, respectively. Note that for seven Ca atoms there is a minimal gap value of 0.11 eV. This means that the chemical reactivity of the system increases. The distance is inside the same range; except for the average of the H-H bond, that with single Ca atom is 0.772 \AA . As the number of Ca atoms increases, the bond length increases slightly up to 0.776 \AA with 10 Ca atoms.

In Fig. 5 it can be seen that the HOMO and LUMO of the $10\text{CaC}_{120}-60\text{H}_2$ system are nearly uniformly distributed on the external surface of C_{120} .

We have computed the Mulliken populations for all the studied systems. The Mulliken charges on the Ca atom, H atom and C atom are in Table VI. We can conclude from this

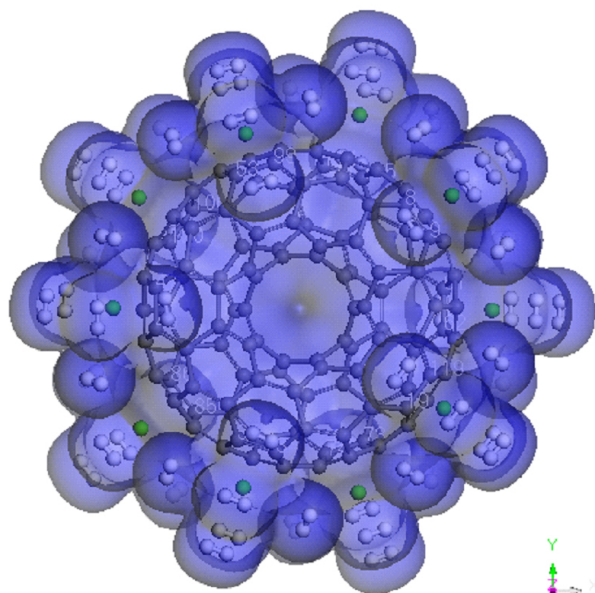


FIGURE 6. Top view of the calculated total charge density of 10CaC₁₂₀-60H₂. The gray and dark-gray atoms are H and C, respectively. (Blue color isovalue = 0.017).

table that for the system with a single Ca atom without H₂ molecules, there is a charge transfer of 0.933 electrons from Ca atom towards the C atom of -0.121 electrons (average of C atoms neighboring the Ca atom). For the systems with several Ca atoms that have H₂ molecules, there is also a charge transfer from the Ca atoms (1.012 average electrons) towards the C atoms (-0.297 average electrons) keeping all the values within the same range. In the case of the hydrogen atoms, it is observed that the average charge transfer is of -0.027 electrons.

Finally, the total charge density for the system with 60 H₂ molecules is in Fig. 6. The final equilibrium configuration for this case has a high symmetry distribution for all the atoms and in the charge density as well.

4. Summary

We have studied the hydrogen adsorption capabilities of toroidal carbon C₁₂₀ structure with a single metal (Ca) externally attached, these shows to be good candidate for hydrogen storage with higher H₂ adsorption energy than for pristine carbon nanotorus. The maximum number of H₂

molecules to be absorbed near the Ca atom is six. The system with 10 Ca atoms can adsorb up to 60 molecules of H₂, which represents 6.16 wt percentage, which fulfils the current requirement (6 wt %, in 2010, specified by US Department of Energy).

5. Conclusions

Geometry optimization and several properties of all the studied systems were calculated. The binding energy is calculated as function of the number of hydrogen atoms. The results let us to conclude that hydrogen storage is possible in the Ca-C₁₂₀ nanotorus system, reaching up to 6.16 wt %, for the system with 10 Ca atoms. Other possibilities to increase the quantity of hydrogen bounded to the system are under study. These results will be reported elsewhere.

The average H-H bond length is close to 0.774 Å for 1-10CaC₁₂₀ systems (see Table V). This length is a little bit greater than 0.7430 Å, the isolated length for the hydrogen molecule, as expected. In a recent work [14], hydrogen storage capacity is studied for a C₁₂₀ nanocapsule. They obtain -0.03 eV and 2.384 Å for the absorption energy of one hydrogen molecule on the outer surface of the tube and for the average C-H equilibrium distance, respectively. In our case, for only one hydrogen molecule we obtain for the system CaC₁₂₀H₂ absorption energy of 0.151 eV and 0.772 Å for the average H-H bond length.

B₈₀ fullerene coated with 12 Ca atoms can store 60 H₂ molecules with an average binding energy of 0.14 - 0.40 eV [15]. For a Ca covered B (9,0) nanotube, the hydrogen binding energy is 0.1-0.3 eV/H₂. A common and interesting feature of these systems with Ca atoms is that they became attractive for high hydrogen storage purposes.

Respect to other type of properties, it will be interesting to study for example, the possible semiconducting properties of cubic (fcc or sc) crystalline C₁₂₀ nanotorus and establish some comparison with the semiconducting properties exhibited by the fullerene C₆₀.

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