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

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Abstract. Ab initio density functional calculations were performed on a toroidal carbon C_{120} nanostructure with a single beryllium atom bonded to its outer surface. These calculations are based on DFT with the generalized gradient approximation PW91 (Perdew and Wang) as implemented in the Materials Studio v.4.3 code. The Dmol^3 module was used to calculate, among others, total energy, charge density, HOMO-LUMO and Mulliken population analysis. On the basis of these results, the beryllium-coated toroidal carbon C_{120} nanostructure appears to be a good candidate for H_2 storage with moderate adsorption energy.

Introduction

At the beginning of the 90's, a new carbon nanostructure with a toroidal shape was theoretically proposed by Dunlap [1]. The geometry and topology of this new carbon form, also called nanotorus, was created from dangling bonds in a carbon nanotube. Carbon nanostructures and graphene materials are of great interest for nanoscale device applications. In this work we study the C_{120} nanotorus, mainly as a hydrogen storage system. Besides the inherent hydrogen storage problems, the community looks with effort for novel forms of H_2 storage. This interest is because hydrogen is a clean energy source and very promising to reduce the world consumption of hydrocarbons. Metal hydrides allow a greater hydrogen storage respect to other storage forms such as compressed gas and liquefaction [2]. Nanofibers are another possibility under current experimental and theoretical study [3].

The nanotorus composed by 120 carbon atoms was built from 12 inequivalent carbon atoms as described by Ihara and coworkers [4]. We have focused our study on total energy, charge density, Mulliken population analysis and highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) energy gaps. The initial dimensions of the relaxed C_{120} nanotorus are 4.159 and 11.740 Å for the inner and outer diameters, respectively. The cross section of the nanotorus is close to a circle with diameter 4.623 Å.

In a recent theoretical study, Guangfen Wu et al [5], investigate the feasibility of bare and metal (M) 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.

In this work we present results of a DFT computational study on a C_{120} carbon nanotorus, using Dmol^3 code [6, 7] as implemented in the Materials Studio program [8]. First of all, we investigated the stability of the isolated C_{120} nanotorus and also for each one of the beryllium-coated nanotori with nH_2 molecules systems. As it occurs for carbon nanotubes, the nanotorus also has a peculiar texture and a large specific surface area. These characteristics suggest that they should be efficient for H_2 storage. It is believed that carbon nanostructures such as nanotubes and nanotorus will be widely used in technological new developments.

Method

To build the nanotorus we used the initial structure with only 12 carbon atoms, proposed by Sigeo Ihara and coworkers [4]. The coordinates of the 120 carbon atoms of the nanotorus were obtained by successive five-fold rotations of this set of 12 atoms followed by a reflection and final rotation of $\pi/5$ radians. The generated structure is composed by ten pentagonal, forty hexagonal and ten heptagonal rings [9]. Five- and six-member rings on the nanotorus surface meet the *isolated pentagon rule* [10, 11]: "no two pentagons can touch, but are always surrounded by hexagons".

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 Dmol^3 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 C_{120} nanotorus, the DFT is complemented with a double numerical plus polarization basis set, (DNP). For occupied orbitals, two atomic orbitals are considered 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**. Real frequencies were obtained for the isolated nanotorus. Hydrogen storage of the BeC_{120} systems was studied after these calculations were performed.

Table 1 contains the type of ring (pentagonal, hexagonal or heptagonal) for a pair of carbon atoms identified by their labels. For example, carbon atoms labeled 27 and 78 are neighbors in a pentagonal ring and the respective bond length is 1.458 Å, with a Mulliken bond order of 0.875, which makes difficult to assign either single or double bond character. For comparison, for ethane and ethane molecules C-C bond lengths turn out to be 1.523 and 1.369 Å, while Mulliken bond orders are 1.050 and 0.742, respectively. For the pentagonal, hexagonal and heptagonal rings, the average bond lengths are 1.460, 1.452 and 1.447 Å, respectively.

Table 2 contains, for the pentagonal, hexagonal and heptagonal rings, the angle formed by three adjacent carbon atoms. For example, for atoms 27, 78 and 74, the angle is 107.3°. In a similar way as for the bond length, the average angle for each type of ring, pentagonal, hexagonal and heptagonal, is 107.5°, 118.9° and 118.0°, respectively.

Results

We first investigate hydrogen adsorption on the bare toroidal carbon C_{120} nanostructure. For example, the adsorption energy of a single H_2 to the outer wall of C_{120} is only 0.115 eV. This means that pure C_{120} nanotorus is not a good candidate for hydrogen storage directly.

Next, we study hydrogen adsorption capabilities of the toroidal carbon C_{120} structure with a single Be atom externally attached. Although Be atom can occupy different sites outside the toroidal carbon C_{120} structure, we consider it adsorbed between carbon atoms labeled 88 and 86, which belong to neighboring pentagonal and hexagonal rings with a bond length of 1.473 Å. The optimized structures of BeC_{120}-$n$$H_2$, for n = 1-3, are shown in Figure 1. The geometry and energy information of Beryllium-toroidal carbon C_{120} are presented in Table 3.

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

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

where E_t (Be), E_t (C_{120}) and E_t (C_{120}-Be) are the total energies of a free Be atom, the pure C_{120} and the C_{120}-Be system, respectively. Eb was found to be equal to 2.948 (eV), which indicates that the C_{120}-Be system is strongly bonded. The strength of the interaction is consistent with the formation of a C-Be bond, which indicates that the whole system can be considered as one single species.

Table 1. C-C bond lengths (Å) and Mulliken bond orders for pentagonal, hexagonal and heptagonal rings in the optimized C_{120} nanotorus.

C-C Atom label and ring type			C-C bond lengths (Å) and ***Mulliken bond orders***		
Pentagon	Hexagon	Heptagon	Pentagon	Hexagon	Heptagon
27-78	33-35	91-104	1.458 ***0.875***	1.457 ***0.867***	1.440 ***0.891***
78-74	35-36	104-105	1.458 ***0.846***	1.470 ***0.917***	1.463 ***0.814***
74-75	36-32	105-92	1.470 ***0.917***	1.458 ***0.866***	1.417 ***0.959***
75-77	32-31	92-80	1.458 ***0.845***	1.454 ***0.813***	1.462 ***0.811***
77-27	31-30	80-79	1.457 ***0.874***	1.417 ***0.962***	1.439 ***0.894***
	30-33	79-40		1.454 ***0.816***	1.456 ***0.806***
		40-91			1.456 ***0.807***
Average bond lengths			1.460	1.452	1.447

Table 2. Angle (degrees), formed by three adjacent carbon atoms for the pentagonal, hexagonal and heptagonal rings in the optimized C_{120} nanotorus.

C-C-C Atom labels and ring type			Angle (degree)		
Pentagon	Hexagon	Heptagon	Pentagon	Hexagon	Heptagon
27-78-74	33-35-36	91-104-105	107.3	122.7	116.9
78-74-75	35-36-32	104-105-92	107.6	122.7	117.7
74-75-77	36-32-31	105-92-80	107.7	110.0	117.7
75-77-27	32-31-30	92-80-79	107.2	124.0	116.8
77-27-78	31-30-33	80-79-40	107.7	124.1	122.6
	30-33-35	79-40-91		110.0	111.7
		40-91-104			122.5
Average angle			107.5	118.9	118.0

The spatial HOMO-LUMO distributions for the bare BeC_{120} and hydrogenated BeC_{120}-nH_2 system, for n = 1-3 are shown correspondingly in figures: 2, 3, 4 and 5. Blue lobes show the positive and yellow lobes show the negative values of the wave function.

In Fig. 2, the density distribution in the LUMO of BeC_{120} systems is mainly located in the neighborhood of the Be atom, indicating that the adsorption of the first H_2 molecule is expected to take place in this region. For the BeC_{120}-nH_2 systems with n = (1-2) the HOMO density is concentrated in the vicinity of the Be atom, suggesting that the second and third molecules of H_2 would also be absorbed in this region. However, there is no density concentration on the vicinity of Be for the BeC_{120}-$3H_2$ system. This suggests that the fourth H_2 molecule, and probably any other after that, would be absorbed in a non-coated region of the toroid. Therefore their binding energies are expected to be of similar magnitude that those involving H_2 adsorptions on the surface of bare toroidal carbon C_{120} nanostructure.

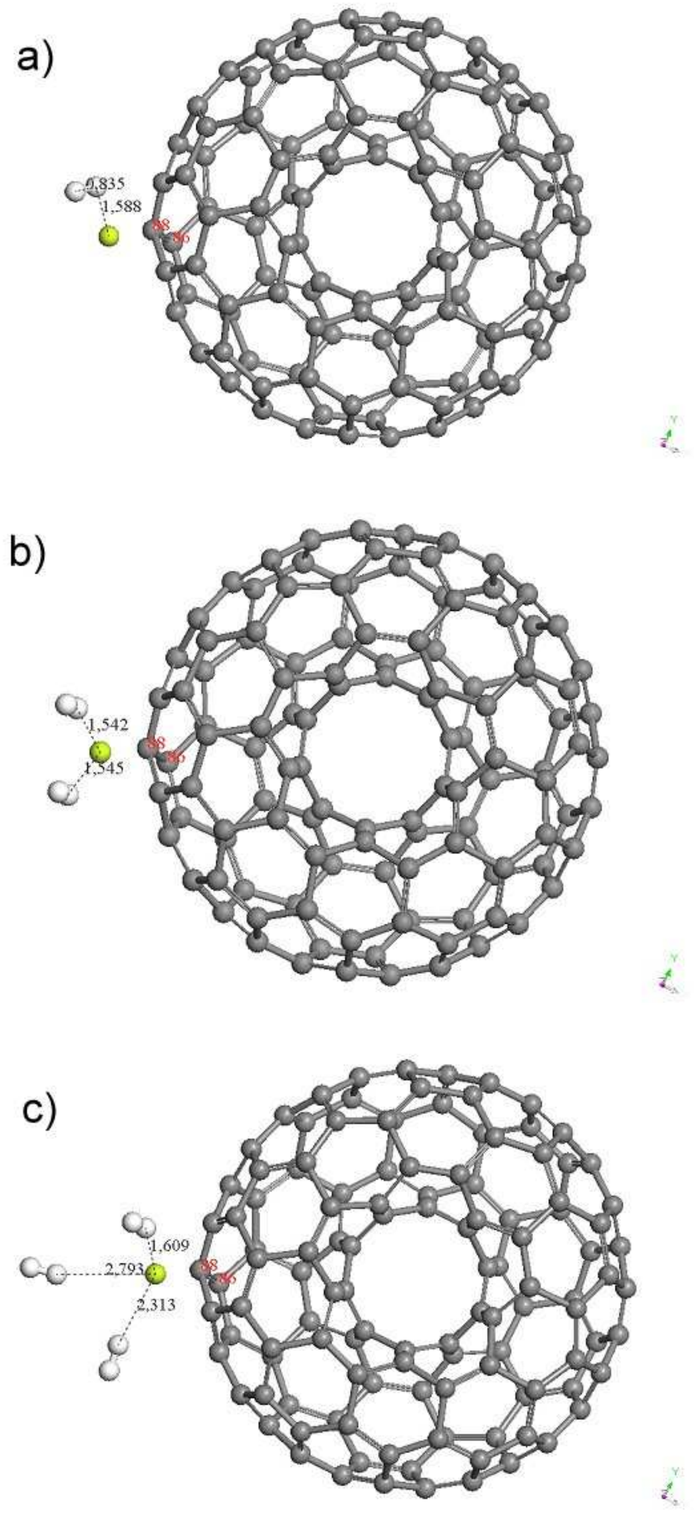

Figure 1. a, b and c. Optimized structures of BeC_{120}-nH_2 systems, for $n = 1, 2$ and 3, respectively.

We have also computed the average adsorption energy per H_2, [5]

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

and consecutive adsorption energy of H_2

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

where $E[BeC_{120}]$, $E[H_2]$, $E[BeC_{120}\text{-}nH_2]$ and $E[BeC_{120}\text{-}(n\text{-}1)H_2]$ are the total energies of relaxed BeC_{120}, H_2 molecule, $BeC_{120}\text{-}nH_2$ and the $BeC_{120}\text{-}(n\text{-}1)H_2$ system, respectively, and n is the number of H_2 molecules, see Table 4.

Table 3. Bond length, HOMO-LUMO Gap (Δ) and Mulliken atomic charges of $BeC_{120}\text{-}nH_2$ system.

Number of H_2 molecules (n)	C(88)-Be distance (Å)	C(86)-Be distance (Å)	Be-H distance (Å)	H-H bond length (Å)	Δ (eV)	Mulliken atomic charges
Be 0 H_2	1.840	1.808	-	-	0.78	Be 0.039
Be 1 H_2	1.807	1.778	H1 1.532 H2 1.500	0.895	0.31	Be -0.019 H1 0.079 H2 0.062
Be 2 H_2	1.852	1.810	H1 1.544 H2 1.539 H3 1.542 H4 1.551	0.856 0.855	0.45	Be -0.098 H1 0.089 H2 0.082 H3 0.087 H4 0.085
Be 3 H_2	1.845	1.808	H1 1.609 H2 1.602 H3 2.313 H4 3.082 H5 2.793 H6 3.524	0.827 0.775 0.765	0.70	Be -0.041 H1 0.098 H2 0.104 H3 -0.035 H4 0.018 H5 0.025 H6 -0.033

Table 4. Average adsorption energy per H_2 and consecutive adsorption energy (in parentheses) of H_2 for $BeC_{120}\text{-}nH_2$, n = (1-3) system.

System	Be	Be H_2	Be $2H_2$	Be $3H_2$
Average adsorption energy per H_2 (eV)	-	0.261	0.310 (0.359)	0.203 (-0.011)

Although the adsorption energy of the first H_2 on BeC_{120} reaches up to 0.261 eV, that of the second H_2 is 0.359 eV. The stronger binding of H_2 to BeC_{120} and the relatively larger HOMO-LUMO gap of $BeC_{120}\text{-}H_2$ imply that this structure is of high stability. Thus, the second H_2 is very easy to adsorb.

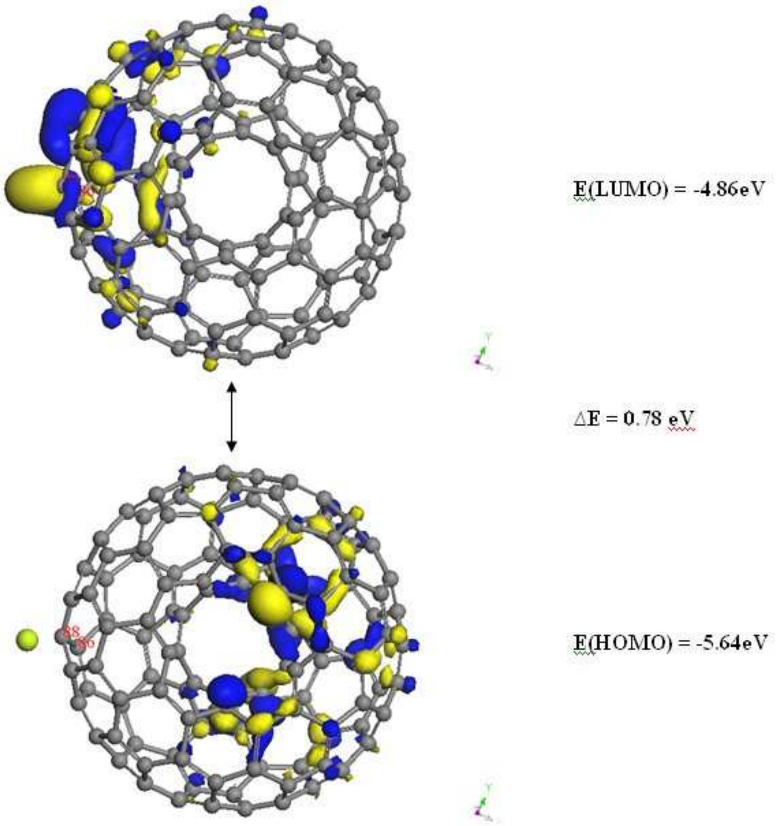

Figure 2. HOMO-LUMO for the BeC_{120} system.

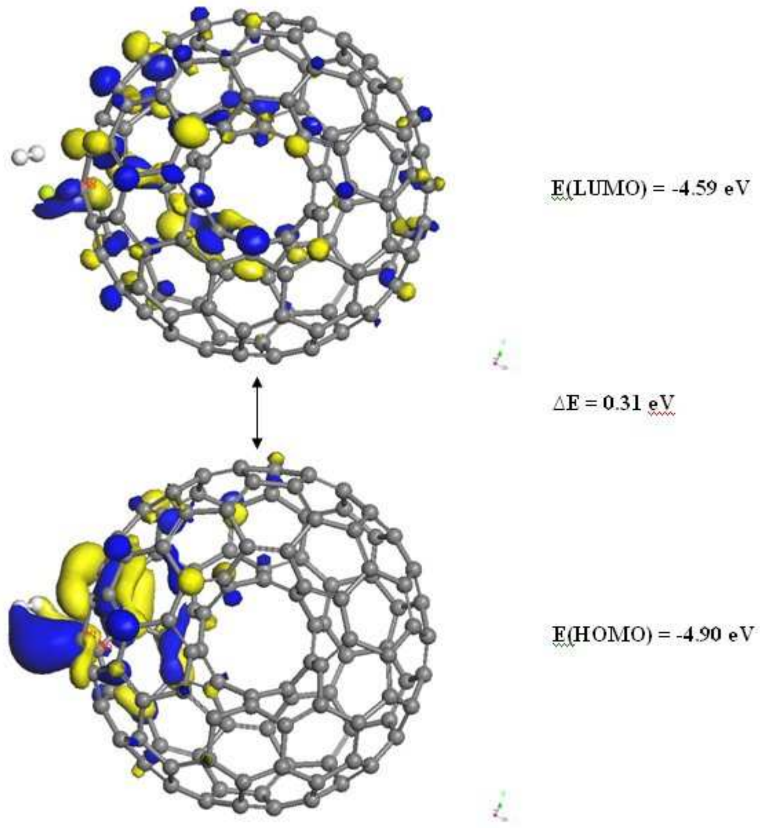

Figure 3. HOMO-LUMO for the BeC_{120}-nH_2 system, n =1.

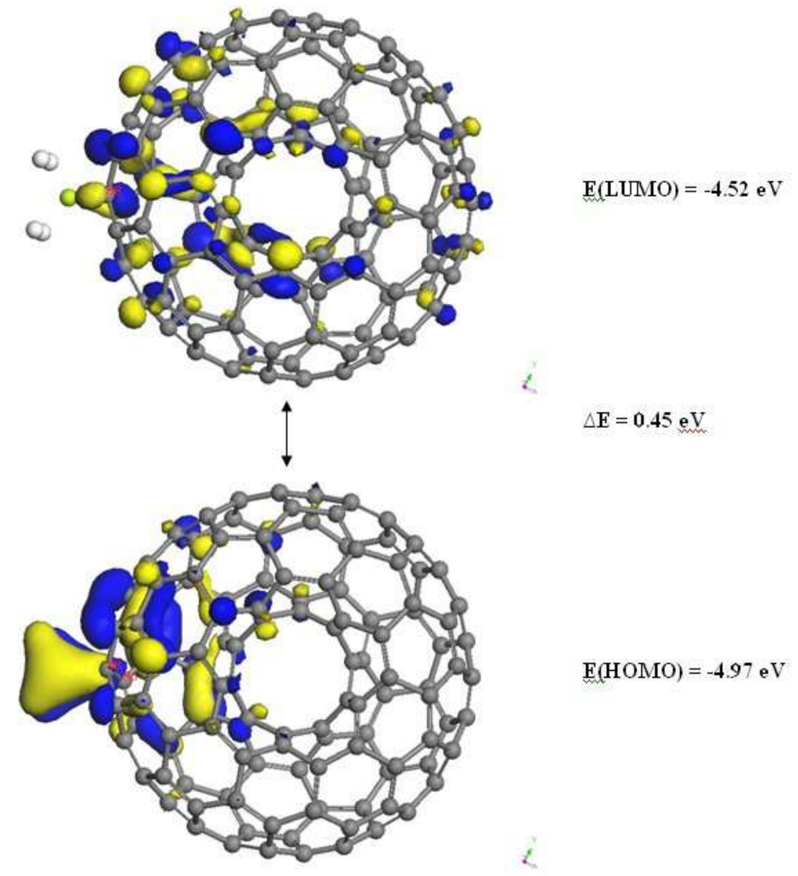

Figure 4. HOMO-LUMO for the BeC_{120}-nH_2 system, *n* =2.

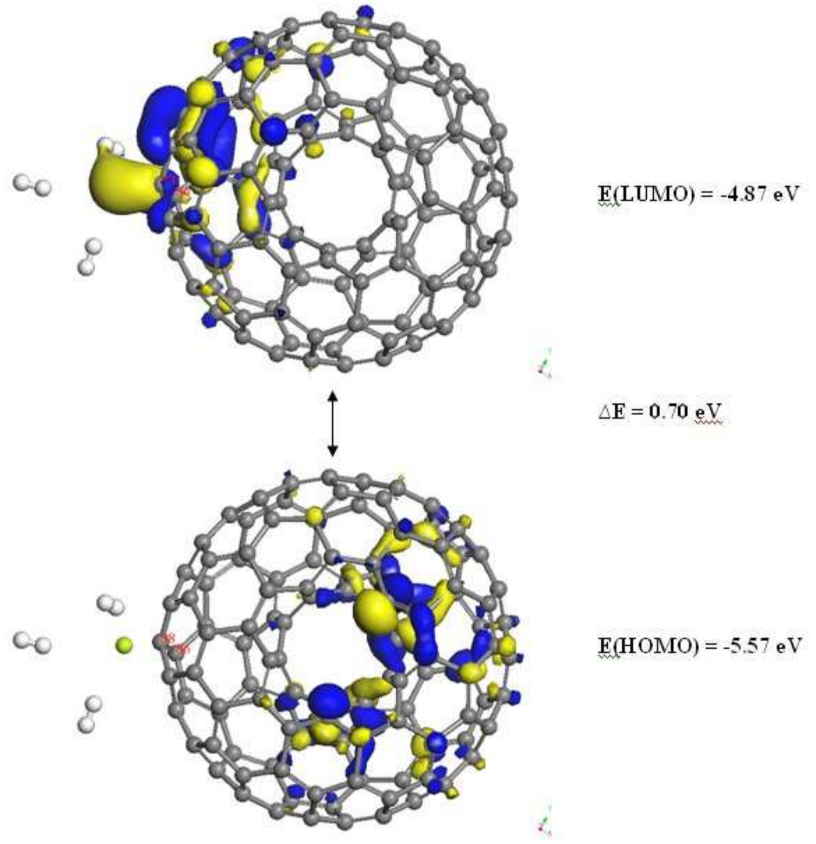

Figure 5. HOMO-LUMO for the BeC_{120}-nH_2 system, *n* =3.

Summary

In summary, we have studied the hydrogen adsorption capabilities of toroidal carbon C_{120} structure with a single Be alkaline-earth metal atom externally attached, which is demonstrated to be good candidate for hydrogen storage with moderate H_2 adsorption energy. The maximum number of H_2 molecules that are expected to be adsorbed near the Be atom is three. The adsorption of any other H_2 molecule would take place on a non-coated surface of the toroid.

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