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Adsorption Energies Calculations of Hydrogen Storage on Cs Doped Graphene: ab initio Study

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Abstract:

We reported hydrogen adsorption on Cesium (Cs) doped graphene by applying density functional theory (DFT) calculations.The four hydrogen molecules can able to binds Cesium atom with graphene. The evaluated binding energy found in the range -0.502 to-0.606 eV/H2. The Partial density of states (PDOS) of Gr-Cs system determined. The s and d orbitals of H_2 molecule and Cs atom at -0.2eV overlaps of main peaks indicates strong hybridizing and binding of s and d orbitals of H_2 and Cs atom accordingly.

Keywords: Cesium, Density functional theory,Graphene,Adsorption energies

1. Introduction

There is urgent need to increase the specific solution on energy consumption via its productivity and economic growth .our target is to find alternative solution to replace oil consumption by using new energy sources. The suitable solution is molecular hydrogen is alternative energy resource due applications in various fields [1-3]. In 21st century the major challenge is efficient and clean energy.

Considering eco-friendly nature one of the good alternatives of energy source in future is hydrogen energy [4].

Our prime goal is to find safe, efficient and effective stores for H_2 gas, and replace current technologies based around the compression of H_2 as a liquid or as a gas using cryogenic [5]. The theoretical work elucidated in terms of poor capacity of H_2 adsorption on monolayer graphene surface[3]. The obtained results from quantum chemical calculations shows the adsorption energy (E_{ad}) of H_2 on graphene sheets found approximately 4.9 kJ/mol [2], which is far from the recommended E_{ad} (20-40 kJ/mol or 0.2-0.6 eV/Hydrogen molecule) for use of practical applications [6].However, adsorption energy of hydrogen on surface of graphene could improve its uptake at room temperature [2]. The modelling and simulation results play the vital role leading to low H_2 adsorption capacity of pristine graphene [7] is weak binding between graphene sheets and H_2 atoms under ambient conditions.

The doping of graphene (Gr) sheets is considered as one of the promising methods for hydrogen uptake improvement at ambient temperature [8,9]. The palladium (Pd) transition metal [10], calcium (Ca) [11] , The adsorption of hydrogen on alkali (Cesium) doped C_{60} with its effect on H2 molecule for application of physisorption energy[12]. doped graphene indicates the hydrogen storage capacity increases by doping the boron atom [13].

To cater the need of energy in vehicular system, the suitable path way for production of renewable source is hydrogen storage a air pollution free substitute for energy. In this article we reported possibility of hydrogen storage for daily life utility.

In our findings for a considered complex system, we adsorbed hydrogen atoms on the surface of Cesium doped Graphene. The Cs atom doped structure of graphene sheets responsible to improve the hydrogen storage capacity on the surface of the complex system. During the process of hydrogen adsorption, Cesium able to increase the adsorption of dissociated hydrogen atoms. Cesium doping most suitable and practical method for application of hydrogen storage utility in daily life.

2. Methods

We considered the model [14] and further quantum chemical calculations were applied by using density functional theory. We applied Vienna ab initio simulation code (VASP) [15-16] within PAW method. The exchange and correlation within local density approximation have been selected for our studied system. To interpret all the characteristics of molecular interactions no density functional theory describes

it accurately, particularly Van der Waals (VdW) interactions [17-18]. The LDA method employed to study the physisorption energies of H_2 on CNT and graphene are in good agreement with experimental values [19-20].

However, the overestimate of the binding energy by LDA is compensated by the ignored van der Waals interactions [21-22]. The electron wave functions are expanded by plane waves with a kinetic energy cutoff of 450 eV to attain the required convergence. All of the self-consistent loops are iterated until the total energy difference of the systems between the adjacent iterating steps is less than 10^{-7} eV. The Brillouin zone is sampled by 5 × 5 × 1 mesh points in k-space based on Monkhorst-Pack scheme [23-24]. The effective range of the kinetic energy cutoff and the validity of the mesh density used in this calculation are determined by a convergence test using the theoretically estimated lattice constants of the pristine graphene, 2.46 Å. To avoid the interactions of adjacent slabs, the vacuum space of 20 Å is introduced for 4 × 4 supercell which contains 54 carbon & 20 hydrogen atoms.

3. Results and discussion

3.1 Pristine graphene (PGr) model

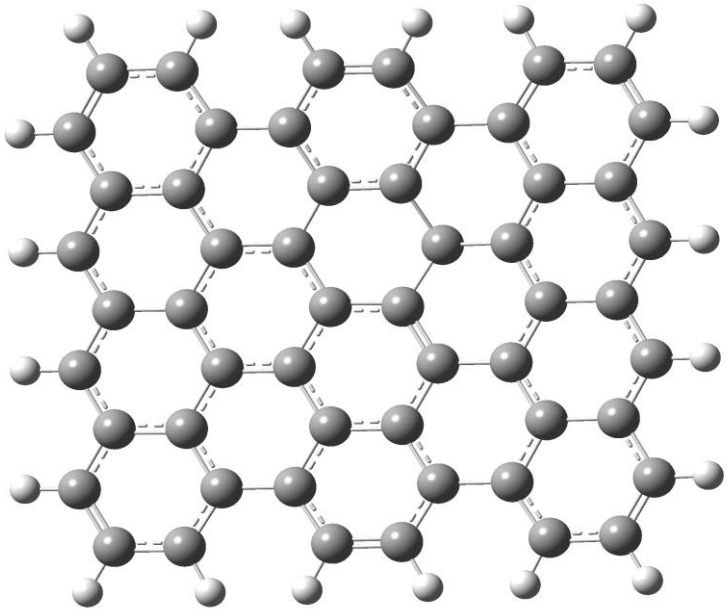


Figure 1. The simulated structure of Pristine Graphene(PGr) model considered with C-54 & H 20 atoms.

Figure 1 shows the pristine graphene sheet constitute with C-54 atoms and H-20 atoms.

3.2 Adsorption of Cesium(Cs) atom on Graphene

We considered that Cs atoms distributed uniformly on graphene (Gr) sheet, the adsorption mechanism of Cs on pristine graphene sheet determined using below equation. The adsorption energy (E_{ad}) of Cs on graphene (Gr) can be calculated as:

$$E_{ad-Cs} = E_{Cs/Gr} - E_{Cs} - E_{Gr} \quad (1)$$

Where $E_{Cs/Gr}$, E_{Cs}, and E_{Gr} are evaluated total energies of the complex Cs-doped graphene sheet, isolated Cs atom and pristine graphene (Gr) sheet. We found the favorable adsorption site for Cesium atom on surface of Gr sheet has at the centre of a hexagonal ring. The evaluated value of the adsorption energy (E_{ad}) of Cs on graphene (E_{ad-Cs}) is -2.74 eV.

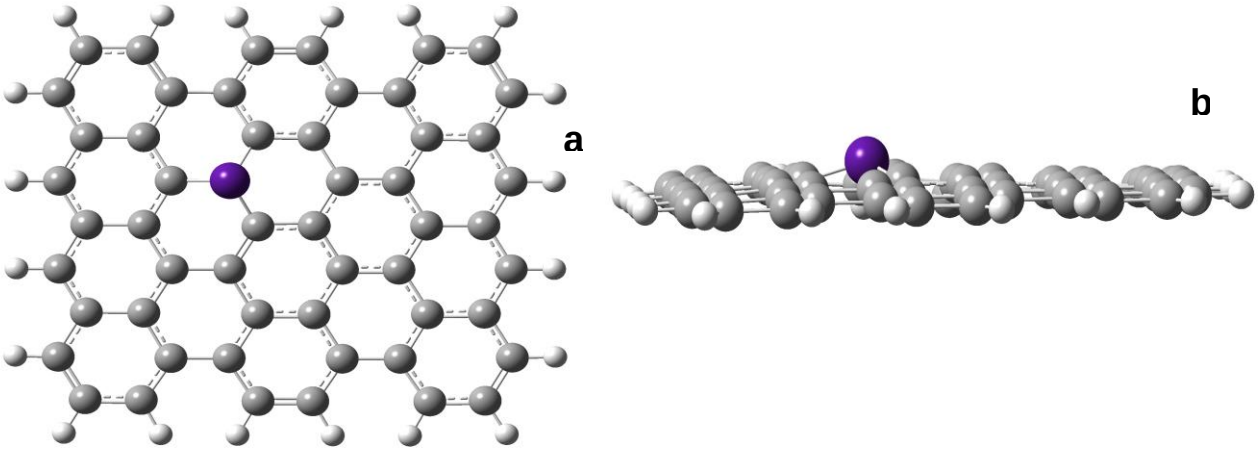


Figure 2. The optimized Cs doped Graphene with C-54 ,Cs-01 & H-20 atoms for a complex system Top view (a) and side view (b).

The cohesive energy of complex system in solid phase of Cesium found -3.32 eV/atom is greater than evaluated adsorption energy of Cesium atom on PGr sheet. It signifies that the Cesium atoms forms cluster. Studied system is fully relaxed to achieve stable configuration .The Cs atom is at para position the distance between para to meta (carbon atom) is 1.421 Å, It tends to stay top site near the carbon (C) atom as shown in figure 3. The distance between C-C 1.418Å whereas the distance between Cs and C atom(meta) is 1.555Å.

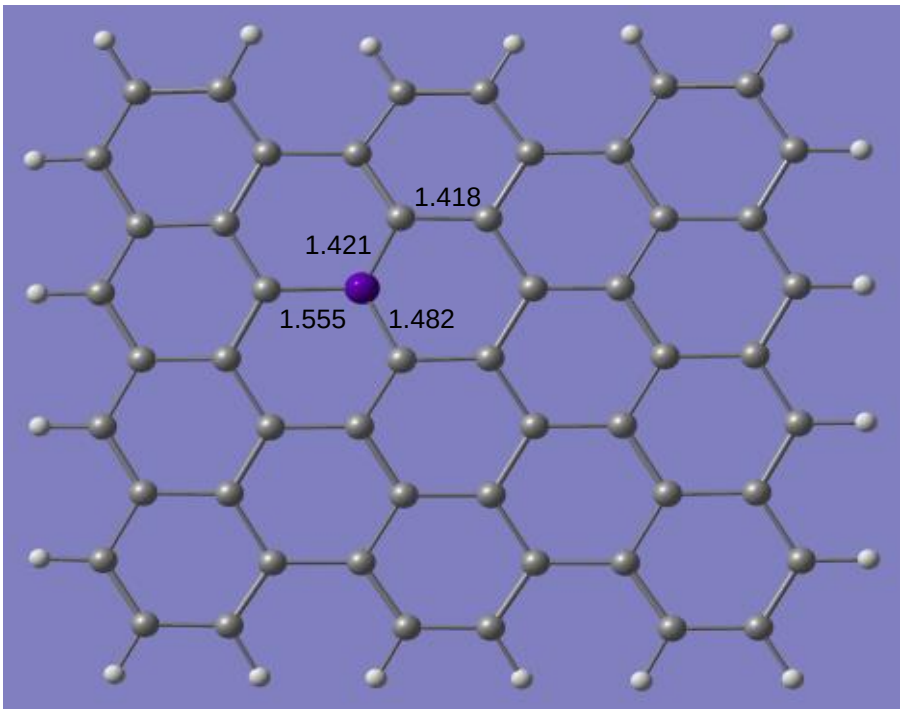


Figure 3 .The bond distance between Cs & C-C in Å

The investigated simulation result shows the adsorption energy of Cs doped atom Gr sheet is -3.32 eV/atom is greater than bulk or complex solid phase magnesium cohesive -3.02 eV/atom.

The magnitude of charges and distance between the centers of positive and negative charges i.e.diplole moment of the complex system (CsC54H20) is 5.43428 Debye evaluated by B3LYP method using 6-31G basis set within Gaussian 09 code [23].

3.3 Adsorption of hydrogen on Cs doped graphene

The complex system of Cesium doped graphene sheet reported for the practical application of hydrogen storage. The adsorption of hydrogen (H_2) molecules on Cesium doped graphene sheet as discussed briefly

After full relaxation optimized configurations of all H_2 molecules demonstrates in Figures 4 a-d (Top view).Figures 4a-d(side view) reveals the H_2 molecules prefers takes sites near to Mg atoms as well and vertical distance between first molecule and graphene sheet reported is 2.50 The other molecules exhibit same distance with the graphene sheet. The average bond length d_{Avg}=H-H is 0.925 Å which is elongated as shown in figure 3a, in gas phase bond length is 0.74 Å of the H_2 molecules.

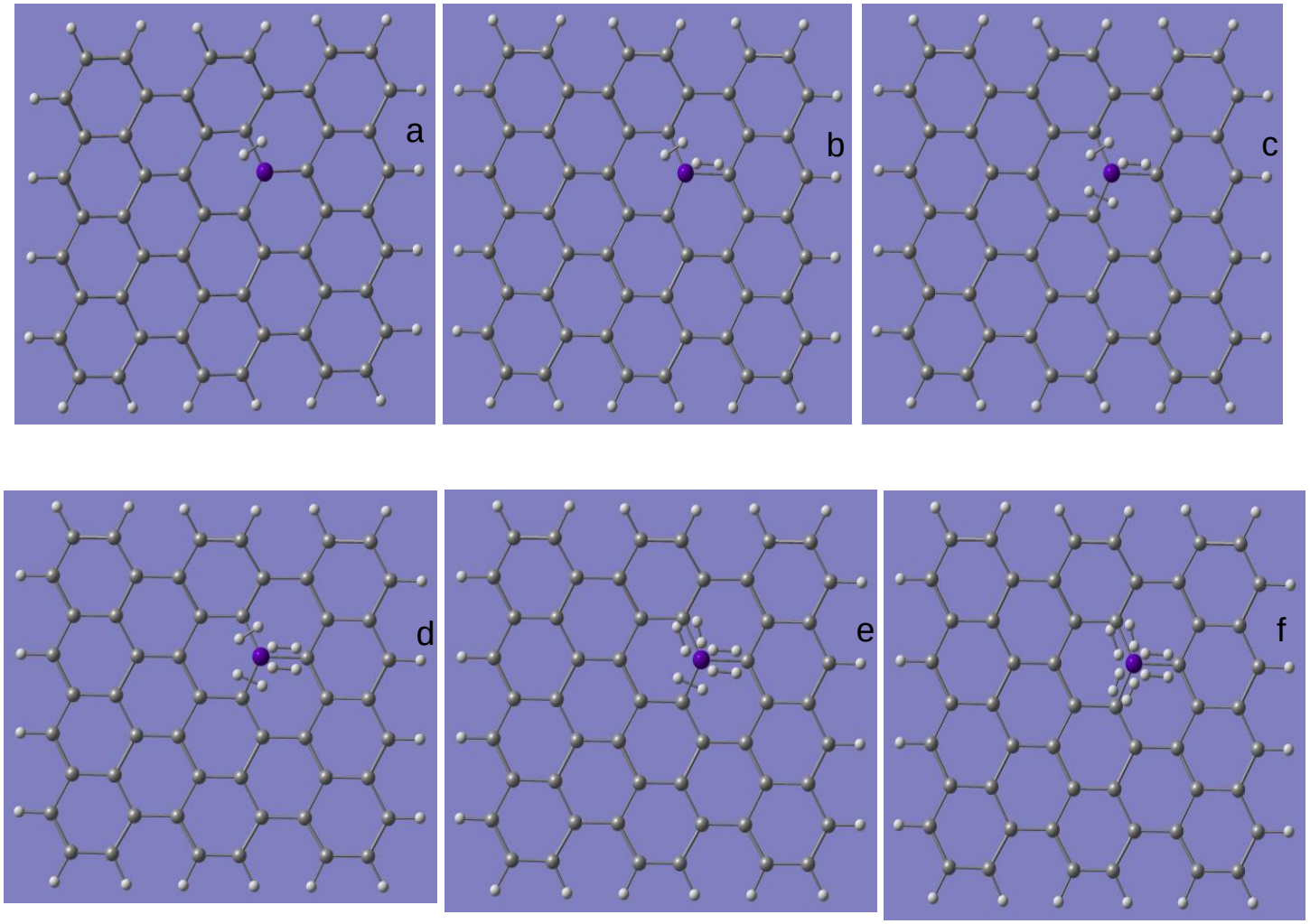


Fig.4 a-f. The optimized structures of H_2 molecules adsorbed on Cs doped Graphene top view

Figure 4a-f results shows, there is slight distortions in all configurations. Particularly, in plane distortion to the graphene sheet. The lattice distortion in graphene layer [8] by means of adsorption of 3d-trasition metals confirms the reported slight distortions in Graphene sheet. The stability of H_2 molecules adsorbed on modified graphene sheet; we evaluated average adsorption energy of H_2 molecules using formula 3.

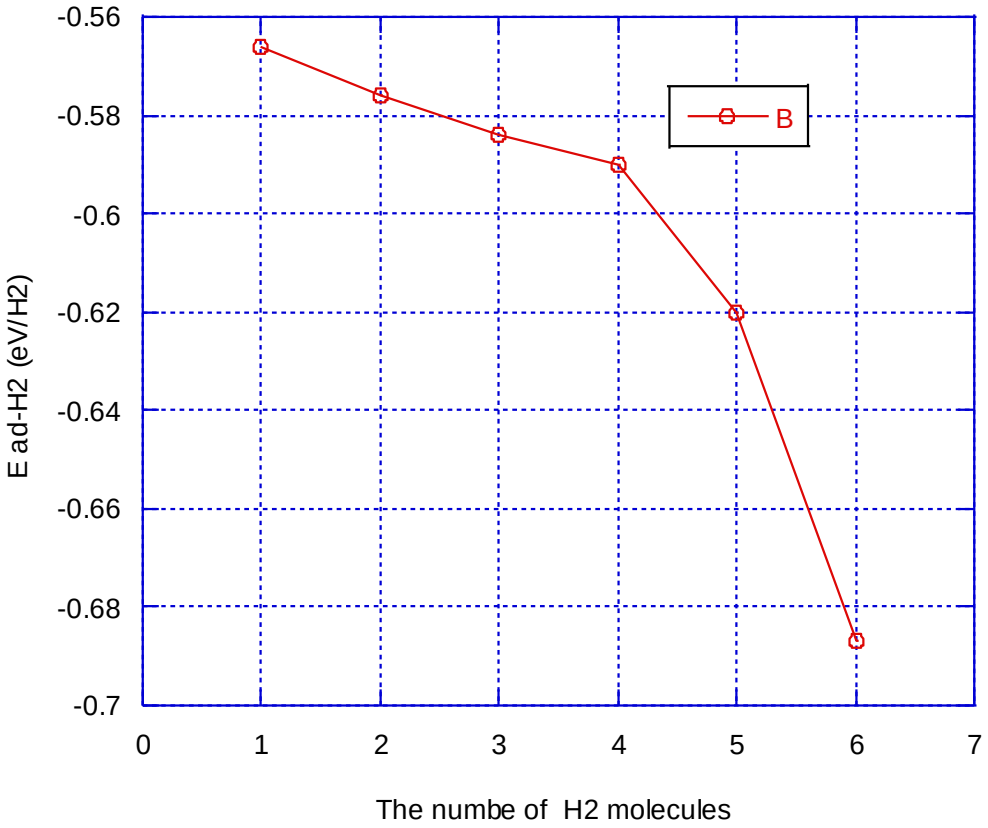
$$E_{ad-H2} = (E_{total} - E_{Cs/Gr} - nE_{H2})/n \qquad (3)$$

Serial Number	Number of H_2 molecules	Bond length of Cs/Gr in (Å)
1	$1H_2$	1.928
2	$2H_2$	2.289
3	$3H_2$	2.271
4	$4H_2$	2.021
5	$5H_2$	1.867
6	$6H_2$	2.199

Table 1 simulated bond lengths of the Cesium doped graphene (Cs/Gr) sheet for one to six adsorbed hydrogen molecules per Cs atom.

The calculated values of bond lengths in Å of graphene sheet for one to six hydrogen molecules per Cs atom are tabulated in table 1.The The extracted data indicates there is continuous increase in bond length, when hydrogen molecules adsorbed on Cs doped Gr sheet upto three hydrogen molecules afterwards slightly smaller in the fourth configuration (2.021Å in $4H_2$) ,fifth configuration (1.867 Å in $5H_2$),However, we increased adsorbed number of hydrogen molecules on surface of Cs doped Gr sheet, Howeve,slightly increase in bond length is observed at sixth configuration (2.199 Å in $6H_2$).

Table 1 .The average adsorption energies of H2 molecule on graphene



The average adsorption energies of hydrogen molecules on graphene sheet shown in fig.5.

From the plot highest value of adsorption energies is observed at $4H_2$ molecules, due to the Van der Walls interaction between the H_2 molecules and surface of the graphene [21]. Experimentally the 72% of adsorbed hydrogen is chemisorbed due to adsorption of hydrogen atoms.Then,how hydrogen molecule dissociate the on the surface of Cesium doped graphene? To resolve the problem, we used the NEB method to calculate the MEP of the hydrogen molecule dissociation on the surface of the Cs doped graphene[8].

Optimization process of complex system shows, we are able to evaluate the H-H and C-C bond lengths about 0.925 Å and 1.423 Å, as well. The quantum chemically evaluated values were compared with experimental values for H-H bond lengths is 0.74 Å [24] and 1.423 Å [26] for C-C bond lengths to check its validity.

4. Conclusions

The quantum chemical treatment including DFT within first principles method applied to Cesium doped graphene -hydrogen adsorption a complex system for hydrogen storage application. We report that cesium doped graphene by adsorption on Hydrogen molecules on its surface formed a cluster structure. Our simulated data shows, there is $6H_2$ molecules modified system can absorb with adsorption energy (E_{ad}) in the range between -0.502 to -0.606 eV/H_2. In the complex system, Cesium atom acts as doped agent interacting to H_2 surface and Gr, is responsible to enhance the adsorption capacity of graphene sheet for Hydrogen storage purpose. Our reported results of adsorption energies of a complex system studied definitely suitable for designing 2D Nanomaterial for hydrogen storage with outstanding potential.

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