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Investigation of H_2 Adsorption on Graphene by DFT Methods

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ABSTRACT

We optimized the geometries of the graphene and graphene with hydrogen using PW91VWN, PW91PL, MPWLYP, G96LYP, G96PL/3-21G,6-31G, 6-31G*levels of theory and compared our results with each other. We present the most important structural parameters determined for the addition of a hydrogen atom to graphene and the outward movement of the carbon atom that is bonded to hydrogen is 0.48 Å . Also we calculateed vibrational frequencies at the same levels. All thermodynamic parameters of including ΔG, ΔH, ΔS were calculated.

Keywords. Graphene; Adsorption; Hydrogen: DFT

INTRODUCTION

Since the 1950s carbon nanomaterials have been known and have gained increased interest since Iijima first described the structure of multi-walled carbon nanotubes. Because of their exceptional properties they became more and more attractive for scientific and industrial usage [1-5].

Carbon nanomaterials adsorb hydrogen very well because of their suggested suitability as materials for gas storage. This matter makes them attractive for hydrogen storage devices in fuel-cell-powered electric vehicles [6,7].

For understanding the storage mechanisms, capacity and necessary structure for hydrogen storage of carbon nanotubes (CNTs) and graphite nanofibers (GNFs),lots of studies have been carried out [8-22].

The synthesis of graphene sheets by Novoselov et al. opened a new era in nanotechnology. The outstanding mechanical, electrical and physical properties of graphene warrants its use in a variety of areas such as hydrogen technology, electronics, sensing and drug delivery, among many others [23-30].

The adsorption of gases on graphene surface has been studied using a wide range of techniques and methods because graphene is a two dimensional crystal with only a surface and no volume, which maximizes the effect of surface dopants.

The unusual properties of carriers in graphene are a result of the gapless and roughly linear electron dispersion at the vicinity of the Fermi level at two inequivalent points of the Brillouin zone.

In this work, we perform main calculations for the H atom adsorbated on graphen. Brillouin for studies and calculation of adsorption we used Density Functional Theory (DFT) approaches method.

COMPUTATIONAL METHOD

Chemists and physicist are interesting gases and graphene surface because of their important role

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in catalysis of many industrial processes as well as in car combustion.Hartree-Fock models treat the motions of individual electrons as independent of one another.This leads to overestimation of the electron-electron repulsion energy. The correlation energy is defined as the difference between the real energy and the Hartree-Fock energy. Several methodshave been developed to account for this correlation energy among which the most popular is probably the Müller-Plesset perturbation technique. Another solution to treat the correlation in many electrons systems is the density functional theory (DFT); see for example [31] for a review.This theory is based on the fact that all the properties of a system (in particular the energy) can be derived from the knowledge of its electronic density.The simplest DFT models are called local spin density and referred to as SVWN (Slater, Vosko,Wilk and Nusair). An improvement can be made by introducing an explicit dependence on the gradient of the electron density, in addition to the density itself. Within Spartan, it leads to the perturbative Becke-Perdew model (pBP) [32,33]. The DFT models available in Spartan use tabulated atomic solutions supplemented by d-type functions on heavy atoms instead of gaussian basis sets [34].The first principles calculations are performed using density functional theory (DFT) which has been successfully used for the study of adsorbates on graphene.

Five hybrid DFT methods are applied. Geometry optimization for graphene and related gas complexes has been carried out at the density functional theory; PW91VWN, PW91PL, MPWLYP, G96LYP, G96PL/3-21G, 6-31G, 6-31G* levels using the standard procedure in GUSSIAN 98 software package [35].

RESULTS AND DISCUSSION

Recent years have witnessed an ever growing interest in carbon-based materials. Carbon, being a small atom with a half-filled shell, is able to mix its valence s and p orbital to various degrees, thereby forming the building block for extended structures of incredibly different electronic, magnetic and mechanical properties.

Among them, those formed by sp^1 C atoms have attracted much attention in the last few years. They can be collective termed as graphitic compounds and comprise graphite, carbon nanotubes, fullerenes, Polycyclic Aromatic Hydrocarbons (PAHs), and recently graphene (the one-atom thick layer of graphite) and graphene nanoribbons (GNRs).

We optimized the geometries of the graphene and graphene with hydrogen using PW91VWN, PW91PL, MPWLYP, G96LYP, G96PL/3-21G, 6-31G, 6-31G* levels of theory and compared our results with each other. We present the most important structural parameters determined for the addition of a hydrogen atom to graphene. The structures determined for the graphene with a hydrogen atom is presented in Figure 1. The outward movement of the carbon atom that is bonded to hydrogen is 0.48 Å. This result is determined by Casolo *et al.*, using the plane wave code VASP [36] The values determined by us and by Casolo et al. are nearly twice as large as the one determined by Boukhvalov et al. (0.257 Å) [36, 37, 38].

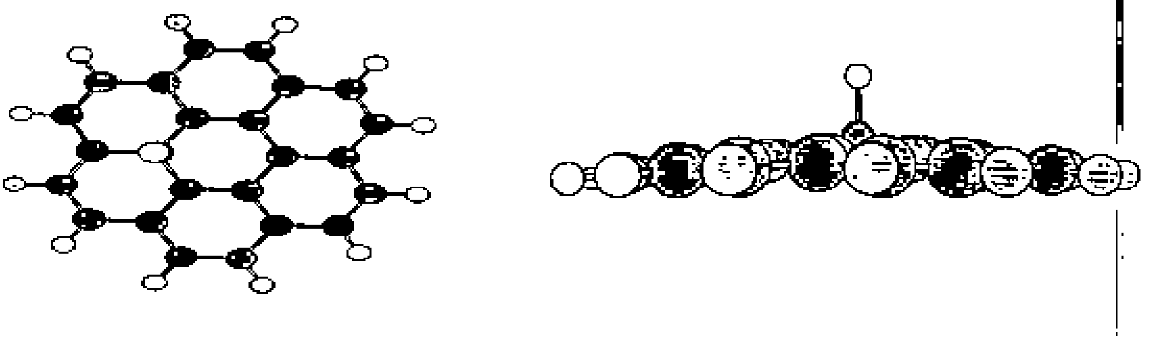

Fig. 1. Graphene with a hydrogen atom optimized by PW91VWN/6-31G* level of theory.

We studied the chemisorptions of hydrogen on geraphen containing 24 carbon atoms. The computed structural parameters vary with applied theory level. Considering our experience is in computing chemical structures with some kind of density functional theory methods. The geometric parameters in PW91VWN are 1.119A° for C-H bond, 1.532A°, 1.525A°, and 1.525A° for the C-C bond which are near the C-H chemisorptions. The C–H and C-C bond distances calculated for these chemisorptions are listed in Table 1.

Table 1. The C–H and C-C bond distances and E calculated for chemisorptions

method	E(cal/mol)	C-H (Å)	C-C (Å)	C-C (Å)	C-C(Å)
PW91VWN	-580172.067	1.119	1.532	1.525	1.525
PW91PL	-577854.965	1.122	1.535	1.528	1.528
MPWLYP	-575371.692	1.127	1.532	1.525	1.525
G96LYP	-575321.994	1.126	1.531	1.524	1.524
G96PL	-578319.060	1.121	1.536	1.529	1.529

The smallest value in all basis sets is related to PW91VWN and the largest one is related to MPWLYP. As expected, we have found that the energy of geraphen with H using PW91VWN method is smaller than the one experienced by the MPWLYP; the computed values are -580172.0675 and -575371.6925 calmol^{-1}, respectively.

Geometries of the graphene and graphene with hydrogen using B3LYP, PW91VWN, PW91PL, MPWLYP, G96LYP, G96PL/STO-3G, 3-21G, 6-31G, 6-31G* levels of theory was optimized and irrational frequencies obtained at the same levels. Entropy has been evaluated by standard statistical thermodynamic methods. Finally, Gibbs free energy of the reaction has been evaluated by using expression (1):

$$\Delta G\ (T) = \Delta H\ (T) - T\ \Delta S\ (T) \qquad (1)$$

The entropies, enthalpies and Gibbs free energies are important thermo chemical parameters for below reaction:

Geraphen + H→ Geraphen-H

The obtained results of thermo chemical studies are in figures (2,3,4) and in table (2) .In all methods ΔG, ΔH and ΔS increased from 3-21G to 6-31G*.

Table 2. The values of thermodynamic functions by different methods and basis sets

Thermodynamic functions	Method	3-21G	6-31G	6-31G*
ΔG(cal/mol)	PW91VWN	107.37	111.74	114.71
	PW91PL	121.11	125.36	128.34
	MPWLYP	121.31	126.8	129.25
	G96LYP	131.4	134.09	136.00
	G96PL	135.49	138.53	141.07
ΔH (cal/mol)	PW91VWN	108.74	112.4	116.47
	PW91PL	122.44	125.96	130.09
	MPWLYP	124.68	127.63	131.17
	G96PL	132.75	135.23	138.94
	G96P86	137.79	138.46	139.41
ΔS(kcal/ mol K)	PW91VWN	-54.61	-55.13	-55.14
	PW91PL	-54.91	-55.33	-55.18
	MPWLYP	-53.95	-54.56	-54.61
	G96LYP	-68.73	-68.90	-69.01
	G96PL	-68.51	-68.41	-68.22

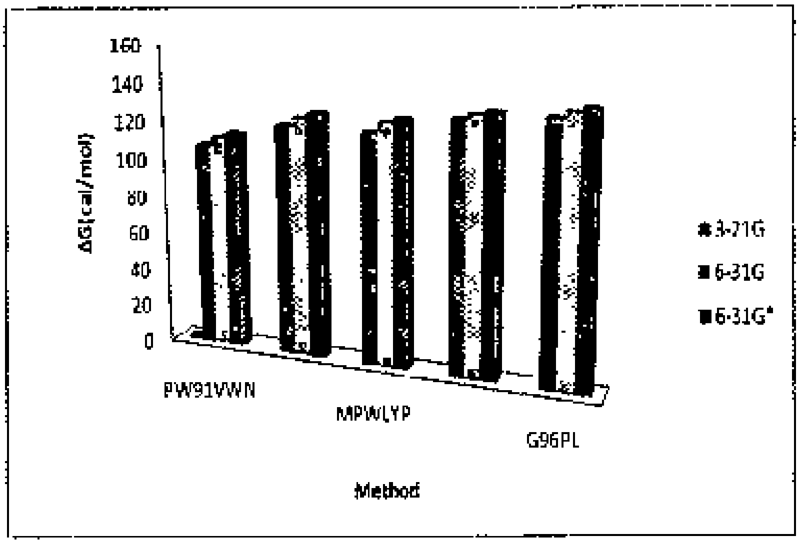

Fig. 2. The values of ΔG by different methods and basis sets.

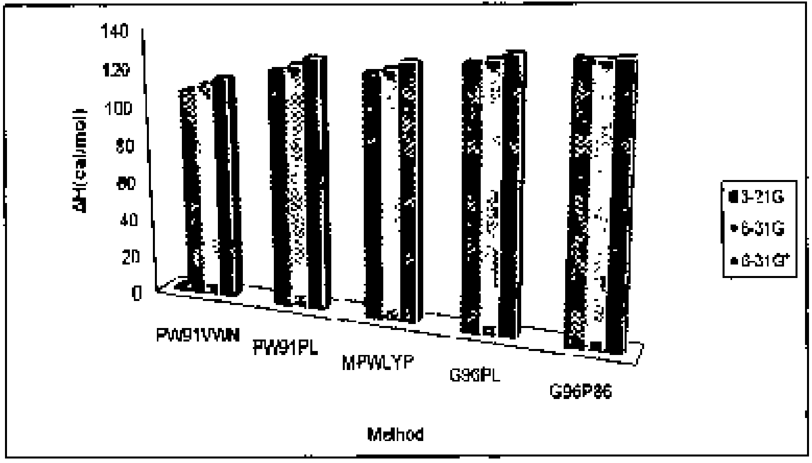

Fig. 3. The values of ΔH by different methods and basis sets.

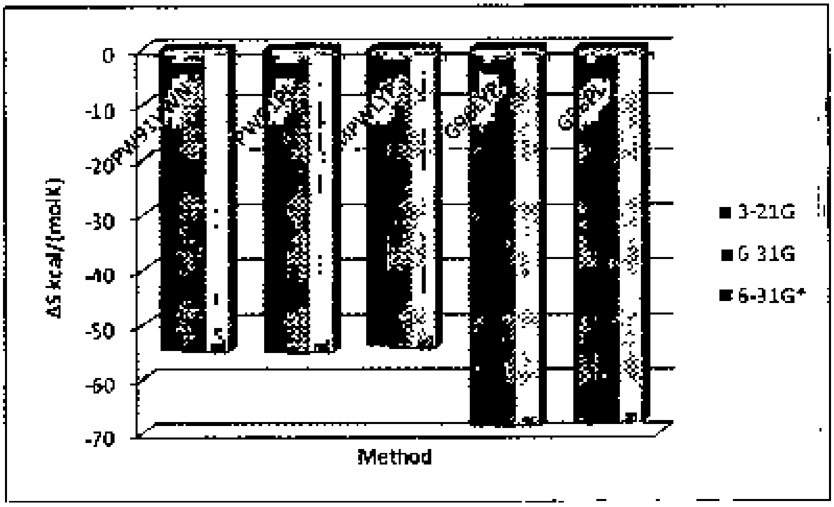

Fig. 4. The values of ΔS by different methods and basis sets

CONCLUSION

We have investigated the addition of hydrogen to graphene. Structural parameters determined were in excellent agreement with our 5 methods and 3 basis sets. The free energy change for the single H addition to graphene at 298 K and enthalpy and entropy changes were determined.

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