ORIGINAL PAPER

Interaction between an icosahedron Li_{13} cluster and a graphene layer doped with a hydrogen atom

Eduardo Rangel · Gerardo Vázquez · Fernando Magaña · Enrique Sansores

Abstract It is known that graphene reacts with atomic hydrogen to form a hydrogenated sheet of graphene. In order to understand the nature of the interaction between hydrogen and lithium in hydrogenated samples, we have carried out first principle calculations. Density functional theory and molecular dynamics were used to study the interaction between an icosahedron Li_{13} cluster, and a graphene layer doped with a hydrogen atom. It was found that a hydrogen atom is levitated from the graphene layer and absorbed into the cluster of Li at 300 K and atmospheric pressure, with a binding energy far exceeding that of the adsorption energy of a hydrogen atom on the graphene layer.

Keywords Adsorption · Graphene · Hydrogenated samples · Lithium

Introduction

Recently, considerable theoretical and experimental research focused on hydrogen storage in solids has been undertaken. In particular, several works tackled the problem of hydrogen storage on graphene [1–6]. These efforts have been motivated with the intention of achieving hydrogen storage in a safe and efficient way to be employed as fuel aboard a

E. Rangel (✉) · E. Sansores
Instituto de Investigaciones en Materiales,
Universidad Nacional Autónoma de México,
Apartado Postal 70-360,
C.P. 04510 Mexico, DF, Mexico
e-mail: kovoldedu@yahoo.com.mx

G. Vázquez · F. Magaña
Instituto de Física, Universidad Nacional Autónoma de México,
Apartado Postal 20-364,
C.P. 01000 Mexico, DF, Mexico

vehicle. It is a well established fact that for practical applications it is necessary to have a hydrogen storage capacity of 6 wt. % or more [7].

Subrahmanyam and coworkers [8] prepared few-layer graphene samples by exfoliation of graphite oxide (EG) and arc evaporation of graphite under hydrogen (HG). Then, they used lithium in liquid NH_3, reacting on the graphene layers (this reaction is known as Birch reduction), and got hydrogenated graphene. The prepared samples have an atomic hydrogen content around 5 wt. %.

On the other hand, in the last 20 years there has been research interest in the properties of lithium clusters. It is known now, that they could be a promising material for hydrogen storage. The nature of the interaction of hydrogen with the lithium cluster has been studied theoretical and experimentally. Furthermore, there is experimental information on hydrogenated lithium clusters. This information includes ionization potential, binding energy, and dissociation channels [8–10]. The aim of this study is to reveal the nature of the interaction between the hydrogen atoms and a lithium cluster in the hydrogenated samples. In particular, we are interested in studying the ability of a lithium cluster, adsorbed on a graphene layer, to adsorb atomic hydrogen, which is already adsorbed on the graphene layer. We focused on the icosahedron Li_{13} cluster because it was apparent that the icosahedral structure represents the most favorable geometry for Li_{13}. These results concur with those described by other authors [11–13]. Research on Li_{13} indicates particularly stable cluster structures, and the high value referring to its lowest vibrational (147 cm^{-1}) indicates that it is comparatively rigid [12].

The following sections describe the methods we have used, the results we have obtained, the corresponding discussion and our conclusions.

Methods

Density functional theory (DFT) with local density approximation (LDA) [14], molecular dynamics (MD) [15, 16], within Born-Oppenheimer approximation and quantum espresso code [17] were all applied to this problem. In order to reveal exchange-correlation energies, the Perdew-Zunger expression [18] was employed. We also made use of a norm conserving Troullier-Martins pseudo potentials [19], in the fully separable form of Kleinman-Bylander [20]. We considered valence electronic states for hydrogen as 1 s, for carbon as $2s^2 2p^2$ and for lithium as $2 s^1$.

The cut-off energy was 1360 eV, and we used 34 k points within the Monkhorst-Pack special k point scheme [21]. The threshold energy convergence was 0.1 meV.

In order to validate our pseudo potentials, the following calculations were carried out. We calculated the length of the hydrogen molecule bond by applying energy minimization, and obtained 0.766 Å. The corresponding experimental value is 0.742 Å [19]. In this way, the length of the lithium bond was obtained: 3.49 Å (the experimental value is 3.51 Å [22]) and the cohesive energy was found to be 1.9 eV (the experimental value is 1.63 [22]). Applying a similar approach, we obtained the carbon bond-length for graphite as 1.408 Å, and the interlaminar distance as 3.320 Å (the experimental values are 1.415 Å and 3.350 Å, respectively [22]).

Next, the interaction of a lithium cluster with a graphene sheet was studied. For this purpose, we have taken into account two different systems of hydrogenated graphene. In the first one, atomic hydrogen is attached to a carbon atom on the graphene layer. For the second one, the hydrogen atom is placed in a substitutional position on the graphene layer. In both systems, we studied only one side of the graphene.

We started by focusing on one icosahedron Li_{13} cluster per 50 carbon atoms (49 carbon atoms for the second system). The system was represented by a hexagonal unit cell with $a = b = 12.19$ Å and $c = 20$ Å and periodic conditions. The magnitude of c was large enough to avoid undesired interactions between adjacent layers along this direction. It was found that the lithium cluster is adsorbed on this graphene sheet, and subsequently the adsorption energy was calculated.

Using the same system, the interaction between a H atom and a graphene sheet was studied and the adsorption energy calculated.

Afterward, we began to explore the capacity of this lithium cluster, when it had been adsorbed into a graphene sheet for trapping adsorbed hydrogen atoms. Subsequently, we took into account the effect of temperature on hydrogen adsorption.
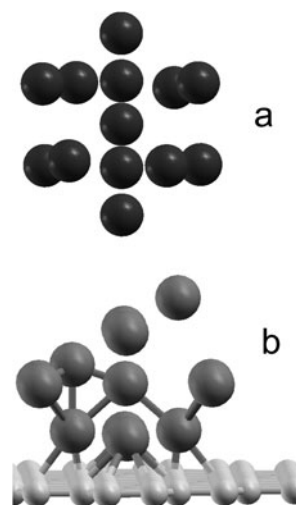
Fig. 1 Optimized system of hydrogenated graphene and a Li cluster with a hydrogen atom attached to a carbon atom on the graphene layer. We can see the distortion of the lithium cluster. In the undistorted cluster (**a**), the average distance from the central lithium atom, to any other atom is 2.90 Å. For the distorted cluster (**b**), the corresponding average distance is 2.82 Å

Results and discussion

First the system was optimized; it was found that the lithium cluster is adsorbed by the graphene. The original lithium cluster became distorted when it was adsorbed, see Fig. 1.

We calculated the binding energy of the lithium cluster on pristine graphene. For the definition of the adsorption energy, we applied the equation:

$$\Delta E = E(\text{graphene} + Li_{13}) \\ - [E(\text{graphene}) + E(Li_{13})], \qquad (1)$$

where $E(\text{graphene} + Li_{13})$ is the energy of the final optimized configuration; $E(\text{graphene}) + E(Li_{13})$ is the energy of the initial system, which is graphene alone plus the energy of the lithium cluster alone, when no interaction takes place
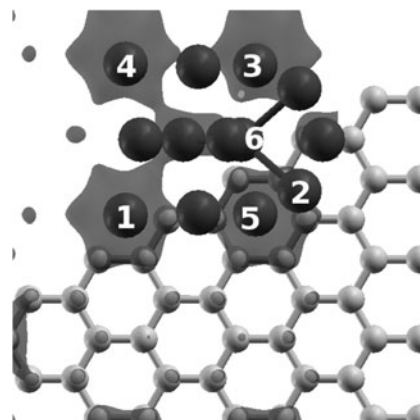
**Fig. 2** Charge transfer from lithium atoms (1-5) to the carbon atoms
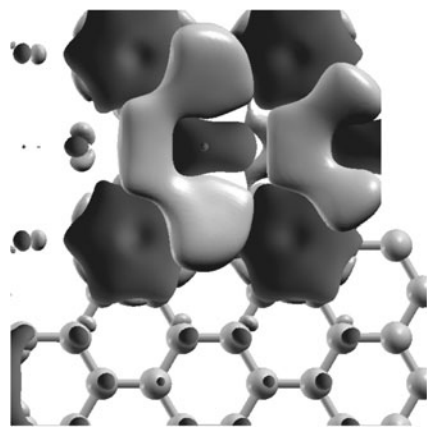
Fig. 3 Another view of the charge transfer from lithium atoms (1-5) to the carbon atoms

between them. The icosahedron Li_{13} cluster was optimized and we found that the icosahedral structure is the most favorable geometry for Li_{13}.

The magnitude of the adsorption energy of the lithium cluster on pristine graphene is 1.053 eV. This result shows that the lithium cluster is adsorbed with a small amount of energy. On the other hand, the magnitude of the adsorption energy of a lithium atom on pristine graphene is 1.02 eV and our result for the lithium atom cohesive energy is 1.9 eV. This result is near to the corresponding experimental value, 1.63 eV. Thus, the binding energy of the lithium atom to pristine graphene is less than its cohesive energy, which may result in lithium clustering on pristine graphene.

In the Li_{13}–graphene system, there is an electronic charge transfer from the lithium atoms 1–5 (see Fig. 2) to the carbon atoms. From a Löwdin population analysis, we found that the lithium atoms (1–5) have a net positive charge
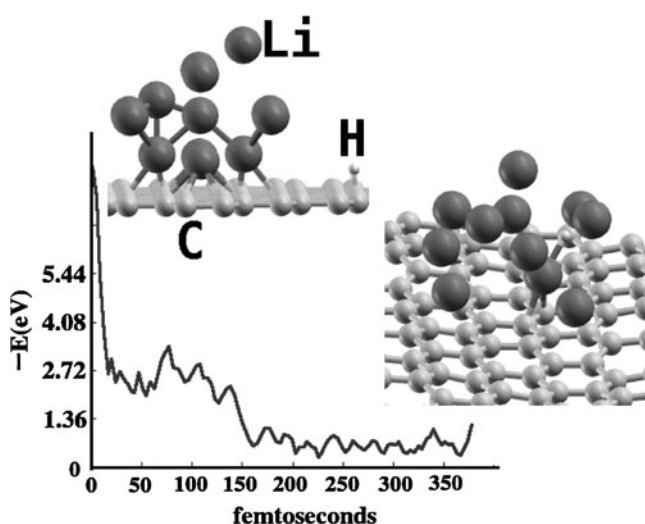
Fig. 4 Time evolution, at 300 K, of the system made by a lithium cluster anchored on a graphene layer, with a hydrogen atom bound to a carbon atom
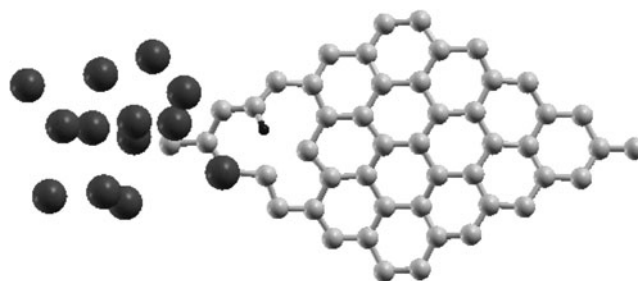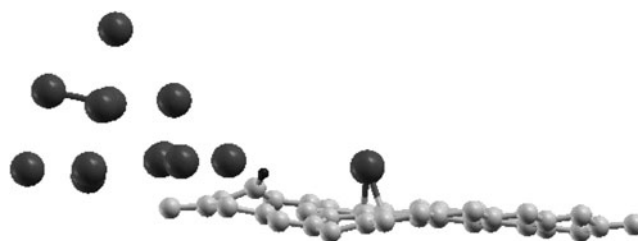

Fig. 5 Optimized system of hydrogenated graphene and a Li cluster with a hydrogen atom, placed in a substitutional position on the graphene layer

of +0.20, +0.16, +0.22, +0.28 and +0.20, respectively. The carbon atoms nearest to the lithium cluster present a net negative charge. In Fig. 2 we have plotted a surface of constant electron-density difference for a Li cluster adsorbed on graphene. The isosurface corresponds to $+1.0\times10^{-3}$ e / a. u^3. The dark surface is the region where electronic charge concentrates, following the interaction between the Li cluster and graphene sheet. The maximum and minimum values, not plotted here are 6.5 and -2.5×10^{-3} e/a. u^3, respectively. Figure 3 shows the isosurfaces corresponding to -9.0, $+9.0\times 10^{-4}$ e/a. u^3 respectively.

Subsequently, we began to explore the capacity of the lithium cluster to adsorb a hydrogen atom. For the first system, we started by optimizing the geometry for a hydrogen atom on the Li_{13} − graphene system. We considered three positions of the H atom: on top of a carbon atom (configuration A), located on an external lithium atom (configuration B), and centered in the lithium cluster (configuration C). We found that these three positions of the hydrogen atom in the lithium cluster-graphene system are stable.

The adsorption energy of an H atom is calculated by taking the difference of the total energies of the separated subsystems and the combined system, $\Delta E = E(graphene + Li_{13} + H) - [E(graphene) + E(Li_{13}) + E(H)]$. The value is 2.69, 3.66, and 3.96 eV for configurations A, B and C respectively. Clearly, this means that the most stable position of the hydrogen atom would be inside the lithium cluster. On the other hand, for comparison, we calculated

Fig. 6 Final configuration of the hydrogenated graphene and a Li cluster with a hydrogen atom placed in a substitutional position on the graphene layer

the energy in the hydrogen-lithium bonding in LiH and obtained 2.65 eV. The corresponding hydrogen energy bonding in CH_3Li is 5.05 eV.

Likewise, our result for the adsorption energy of one hydrogen atom on a pristine graphene layer is 1.49 eV. The stable position is on top of a carbon atom and the equilibrium C-H distance is 1.13 Å concurring with results from other authors [11, 23]. There is a change in the C-C distance after hydrogenation, for the C atoms neighboring to the hydrogen atom. The C-C distance before hydrogenation is 1.415 Å, and after hydrogenation, the distance becomes 1.485 Å. On the other hand, after hydrogenation, there are small changes in the general density of states (DOS). The value of the Fermi energy changes from -1.8136 eV to -1.9427 eV. Furthermore, near the Fermi energy, there are not changes in the DOS. From a Löwdin population analysis, we found that the H atom has a net positive charge of +0.21. Clearly, when the lithium cluster is anchored to the graphene, it promotes the adsorption of the hydrogen atom. The negative charge on the carbon atoms promotes the interaction between the hydrogen atoms that are adsorbed in the region of the graphene layer and the lithium cluster. The results indicate that hydrogen can migrate and penetrate rather easily into the Li cluster. In all configurations H attracts electrons. We repeated our calculations taking into account the spin. We obtained the same results.

Casassa and Pisani [24] demonstrated that hydrogen is adsorbed into a lithium surface (001) with appreciable energy (2.60-3.46 eV) and can migrate almost freely in the surface layer; its deeper penetration into the lattice seems to require overcoming a modest but not negligible activation barrier (0.43-0.65 eV). Ray and Hira [25] performed a series of *ab initio* calculations on the interactions of a hydrogen atom with only lithium clusters. The chemisorption energies for the on-top approach positions studied, average 1.2 eV for bcc (100) symmetry and 1.6 eV for bcc (110) symmetry. In the case of the open-site approach, averages are 2.06 eV for bcc (100) and 1.88 eV for bcc (110), whereas, the corresponding values for the bridge positions are 2 eV and 2.5 eV. The experimental value is known to be 1.66 eV [26]. Our results concur with most published in the literature referring to the chemisorption energy between H and an isolated lithium cluster.

Subsequently, we considered the system made by a lithium cluster anchored on a graphene layer, with a hydrogen atom bound to a carbon atom (configuration A mentioned above). We allowed this system to follow an evolutionary process using molecular dynamics with a temperature of 300 K at atmospheric pressure for a time step of one femtosecond. In order to maintain the system at the correct temperature, we used the velocity rescaling method. At this temperature the H atom migrated from on top of the carbon atom (configuration A) into the Li cluster (configuration B or C) as presented in Fig. 4. At step 50 of the 150 referring to the dynamics, the H atom retreats from position A to be introduced inside the Li cluster. Thus, the hydrogen atom is adsorbed into the lithium cluster, from its original stable position on top of a carbon atom. Diffusion of Li is not observed on the surface of the graphene.

In the case of the second system, we placed the hydrogen atom in a substitute position, see Fig. 5, and repeated all the calculations made for the first system. In this case, the cluster of Li never levitated the hydrogen atom from the graphene layer. However, we were able to observe that one lithium atom had been removed from the cluster and that it had been physisorbed onto the graphene sheet. As shown in Fig. 6, another effect of the interaction between the Li cluster and the hydrogenated graphene is that the graphene layer became wrinkled.

References

1. Miura Y, Kasai H, Diño WA, Sugimoto T (2003) J Phys Soc Jpn 72:995–997
2. Arellano JS, Molina LM, Rubio A, Alonso JA (2000) J Chem Phys 112:8114–8119
3. Okamoto Y, Miyamoto Y (2001) J Phys Chem B 105:3470–3474
4. Lai-Peng M, Zhong-Shuai W, Li J, Er-Dong W, Wen-Cai R, Hui-Ming C (2009) Int J Hydrogen Energ 34:2329–2332
5. Srinivas G, Zhu Y, Piner R, Skipper N, Ellerby M, Ruoff R (2010) Carbon 48:630–635
6. Kim G, Jhi S, Lim S, Park N (2009) Appl Phys Lett 94:173102–173103
7. US Department of Energy (2006) DOE Hydrogen program, annual program report
8. Gautam S, Dharamvir K, Goel N (2011) J Phys Chem A 115:6383–6389
9. Antoine R, Dugourd Ph, Rayane D, Broyer M (1996) J Chem Phys 104:110–119
10. Chen J, Kuriyama N, Xu Q, Takeshita HT, Sakai T (2001) J Phys Chem B 105:11214–11220
11. Subrahmanyama KS, Kumara P, Maitraa U, Govindaraja A, Hembramb KPSS, Waghmareb UV, Rao CNR (2011) P N A S 108:2674–2677
12. Fournier R, Bo Yi Cheng J, Wong A (2003) J Chem Phys 119:9444–9454
13. Pacchioni G, Koutecký J (1984) J Chem Phys 81:3588–3593
14. Parr RG, Yang W (1989) Density-functional theory of atoms and molecules. Oxford University Press, Oxford
15. Marx D, Hutte J (2000) Modern methods and algorithms of quantum chemistry. In: Grotendorst J, editor. NIC Series, Vol 1.Jülich. John von Neumann Institute for Computing, pp 301- 449
16. Car R, de Angelis F, Giannozzi P, Marzari N (2005) Handbook of materials modeling, chapter 1. Springer, Dordrecht, The Netherlands, pp 59–76
17. Giannozzi P, Baroni S, Bonini N, Calandra M, Car R, Cavazzoni C et al (2009) J Phys Condens Matter 21:395502–395519

18. Perdew JP, Zunger A (1981) Phys Rev B 23:5048–5079
19. Troullier N, Martíns JL (1991) Phys Rev B 43:1993–2006
20. Gonze X, Kackell P, Scheffler M (1990) Phys Rev B 41:12264–12267
21. Monkhorst HJ, Pack JD (1976) Phys Rev B 13:5188–5192
22. Lide DR (2000) Handbook of chemistry and physics. CRC, Boca Raton FL
23. Casolo S, Martin Lovvik O, Martinazzo R, Tantarrdini G (2009) J Chem Phys 130:054704–054710
24. Casassa S, Pisani C (1995) Phys Review B 51:7805–7816
25. Ray AK, Hira AS (1988) Phys Review B 37:9943–9950
26. Gshneider KA (1964) In: Seitz F, Turnbull D (eds) Solid state physics, vol 16. Academic, New York