First-principles study on the structural and electronic properties of graphene upon benzene and naphthalene adsorption

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ABSTRACT

Within the framework of the local density approximation (LDA) of the density functional theory (DFT) and the pseudopotential method, we have carried out ab initio calculations to investigate the structural and electronic properties of graphene upon the adsorption of benzene and naphthalene molecules. Our total-energy calculations suggest that, for both benzene and naphthalene adsorbed on graphene, the stack configuration is the most stable structure. The corresponding adsorption energies at different sites are estimated for both molecular adsorbates. The equilibrium parameters and the electronic band structure for the stable geometries have been calculated and compared with the available findings.

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1. Introduction

The unique and exotic structural, electronic, and mechanical properties of graphene [1], a two-dimensional sheet of carbon atoms, have attracted enormous interest [2,3,4]. Generally, the electronic structure of graphene stands on sp²-bonded carbons with ‘bonding’ π and ‘anti-bonding’ π* degenerated states at the K edge of its hexagonal Brillouin zone. Moreover, the linear band dispersion at the so-called Dirac point is considered as a special feature of graphene, leading to high mobility charge carriers. These properties have led the graphene to become a promising candidate for potential applications, such as spintronics and optical devices.

The chemical interaction between graphene and molecules is considered as the main resource for various electrical and optical applications. Therefore, molecular adsorption on graphene has been the subject of various theoretical and experimental [5,6,7] studies. The adsorption of benzene and naphthalene molecules on graphene has been the subject of various theoretical [5–12] and experimental [13,14] studies. Wehling et al. [7] have presented first-principles studies of water adsorption on graphene and the influence of SiO₂ substrate. These investigations suggested that graphene on the SiO₂ substrate is more sensitive to water adsorbates than perfect suspended graphene. Nakamura and co-workers [8,9] have investigated the structural and electronic properties of the graphene sheet upon oxygen adsorption. Their first-principles calculations predicted that the oxygen-adsorbed graphene shows the structural bistability between the epoxy and ether group phases. They suggested that the ether group structure is the most energetically preferable for adsorption involving both sides of the sheet, while the one-side adsorption structure appears only as a meta-stable phase, with a finite energy gap at the K point emerges and its value increases as the ratio O/C increases. Further, Leenaerts et al. [10,11] have reported on the main charge transfer mechanisms upon adsorption of small molecules on graphene, such as NH₃ and NO₂. It has been found that when molecules adsorb on graphene, charge transfer occurred by two mechanisms. Small charge transfer takes place due to orbital hybridisation (orbital mixing) for all molecules. Large charge transfer takes place when the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the molecules lie close enough to the Dirac point. Moreover, graphene (hydrogen-passivated graphene) has also been considered in many theoretical and experimental studies [15–18]. Sofo et al. [15] have studied the adsorption of hydrogen atoms on both sides of the graphene plane in an alternating manner, leading to both the chairlike and boatlike configurations. Their total-energy calculations indicated that the chairlike is more energetically preferable than the boatlike structure, suggesting semiconducting behaviour with 3.5 eV and 3.7 eV for the chairlike and boatlike, respectively.

Moreover, the adsorption of organic molecules on graphene has attracted immense attention due to the significant change in the electronic properties of graphene [19,20]. Chakarova-Kack et al. [21] have deduced van der Waals density functional (vdW-DF) calculations for the binding energies of benzene and naphthalene on an infinite sheet of graphite. However, the mechanism of charge transfer and structural and electronic changes of graphene due to these adsorbates are still not resolved. Recently,
Pinto et al. [22] have presented local density investigation of the electronic properties of graphene upon the adsorption of tetrafluoro-tetracyanoquinodimethane (F4-TCNQ). Their calculations reveal that the F4-TCNQ molecule is a p-type dopant for graphene with electronic transfer of 0.3 e/molecule from the HOMO of graphene to the LUMO of the molecule. Very recently, Zhang et al. [23] have investigated the binding of organic electron donor and acceptor molecules on graphene sheets using the density functional theory. It has been found that the adsorption of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and tetrathiafulvalene (TTF) induce hybridization between the molecular levels and the graphene valence bands, leading to transforming the zero-gap semiconductor graphene into metallic graphene. Despite much available studies, there is still incredible need for thoroughly investigations and deeply understanding of the electronic and atomic changes of graphene upon organic molecular adsorption.

The present work reports on ab initio results of the effect of adsorption of benzene and naphthalene molecules upon the atomic and electronic properties of pristine graphene. The calculations have been performed in the framework of the density functional theory (DFT) with a plane wave basis set as implemented in the QUANTUM ESPRESSO simulation package [25]. The electron–electron interactions were treated within the local density approximation of Perdew–Zunger scheme [26]. The electron–ion interaction was treated by using the ultrasoft pseudopotential for carbon and hydrogen [27]. The single-particle Kohn–Sham [28] wave functions were expanded in the framework of a plane wave basis set with a kinetic energy cutoff of 30 Ryd. Self-consistent solutions of the Kohn–Sham equations were obtained by employing the $4 \times 4 \times 1$ K points Monkhorst–Pack set [29] within the hexagonal Brillouin zones. For modelling graphene using the supercell technique, we considered a $6 \times 6 \times 1$ unit cell containing 72 carbon atoms. The in-plane lattice parameter $a = 2.45$ Å for graphene agrees well with theoretical value [9,30,31] and experimental value for bulk graphite [32]. The vertical separation between the graphene sheet and its periodic image in the surface normal direction was taken to be 14.65 Å. These parameters have been carefully chosen after several convergence test calculations. Relaxed atomic positions for carbon and hydrogen atoms were obtained by using the total-energy and force minimisation methods. The equilibrium atomic positions were determined by relaxing all atoms except the carbon atom at the origin, which was kept in its bulk position. The adsorption energies of the organic molecules on graphene sheet were estimated using the following formula:

$$E = E_{\text{molecule/graphene}} - E_{\text{pristine graphene}} - E_{\text{molecule}},$$

where $E_{\text{molecule/graphene}}$, $E_{\text{pristine graphene}}$, and $E_{\text{molecule}}$ are the total energies of the fully relaxed systems containing the molecule/graphene, only graphene, and only molecule, respectively.

3. Results and discussion

Fig. 1 shows two possible configurations for the adsorption of benzene and naphthalene on pristine graphene. For each molecule we have considered a hollow (denoted as B1 and N1 in Fig. 1) and a stack (referred to as B2 and N2 in Fig. 1) adsorption sites. Our total-energy calculations indicate that the stack configuration
is energetically more preferable than the hollow structure by an energy gain of 0.05 eV and 0.08 eV for benzene and naphthalene, respectively. The adsorption energy of the stack (hollow) configuration for benzene/graphene is found to be $-0.30$ eV ($-0.25$ eV), which is slightly smaller than the theoretical value obtained by Zhang et al. [23] of $-0.24$ eV ($-0.16$ eV). However, we refer such inconsistency in the values of adsorption energy in the present work and the previous work [23] to the smaller cutoff energy chosen in their calculations (17.60 Ryd). According to our convergence test in a previous work [18], consistent with other works [21,22], using ultrasoft pseudopotential, well converged total-energy values were obtained for energy cutoff values of 30 Ryd or higher up to 55 Ryd. The adsorption energy of naphthalene, on the other hand, is determined to be $-0.47$ eV ($-0.39$ eV) for the stack (hollow) configuration.

The relaxed geometries with the basic structural parameters of the preferable configurations for the molecule/graphene structures are shown in Fig. 2. As an initial step towards the structural optimisation, we have assumed a $6 \times 6$ planar sheet of graphene with molecular atoms which are 1.5 Å above the graphene atoms. Under relaxation process, the benzene (naphthalene) molecule adopts an approximately planar geometry 3.52 Å (3.54 Å) above the graphene sheet. These values are in excellent agreement with the estimated value of 3.6 Å from the binding energy curves performed by Chakarova-Käck et al. [21] and slightly larger than the value obtained in Ref. [23] of 3.17 Å due to the energy cutoff used in their calculations. Furthermore, our calculated C–C and C–H bond lengths of benzene on the top of graphene (shown in Fig. 2(a)) are measured to be 1.39 Å and 1.10 Å, respectively. These values are quite similar to the typical bond lengths in the isolated benzene molecule (and typical hydrocarbons) of 1.40 Å and 1.10 Å for C–C and C–H bonds, consequently. From these calculations we have also obtained that the C–C–C and C–C–H angles are identical and equal to $120^\circ$, suggesting a planar orientation of the molecule above the graphene as noted for F4-TCNQ [22] which also indicate similar adsorption mechanism for organic molecules on graphene. Despite that no appreciable change in C–H bond length is noted, we have observed remarkable changes in the C–C bond lengths of the molecule components for the naphthalene/graphene compared to the benzene adsorbed system. These bond lengths can be classified into three categories as shown in Fig. 2(b): 1.37 Å, 1.40 Å, and 1.43 Å. These values are close enough to the typical bond lengths of isolated naphthalene molecule (1.36–1.42 Å). The C–C–C and C–C–H angles range between 121–122° and 118–120°, respectively. This obser-

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**Fig. 2.** Key structural parameters of the the relaxed (a) benzene and (b) naphthalene molecules on the top of the graphene. The bond lengths are measured in Å and angles in degrees.

**Fig. 3.** Electronic band structure of (a) pristine graphene, (b) benzene/graphene, and (c) naphthalene/graphene along the high symmetry directions of the hexagonal Brillouin zone of graphene. The Fermi level is set to zero.
vation indicates a very tiny amount of vertical tilt in the carbon planes. Having looked at the substrate (graphene) for both systems, we find that the C–C bond lengths of 1.41 Å and the C–C–C angles of 120° preserve the ideal C–C bond lengths (1.42 Å) and C–C–C angles (120°) of the pristine graphene.

The calculated electronic band structure of the ideal graphene, benzene/graphene, and naphthalene/graphene are depicted in Fig. 3. Fig. 3(a) shows the band structure of graphene sheet which indicates the zero-gap semiconducting nature. Due to the band folding in the used supercell, the top of the valence (bonding π) and the bottom of the conduction states (antibonding π*) degenerate at the Γ' edge (Dirac point) instead of the K point of the hexagonal Brillouin zone. These two bands, however, obey a linear in-plane dispersion relation near the Fermi energy at the Γ' point of the Brillouin zone.

Upon the benzene and naphthalene adsorption, the electronic band structure calculations are depicted in panels (b) and (c) of Fig. 3, respectively. In both calculations the Fermi level is set at the zero. It is clearly noted that the Dirac point of the molecule/graphene systems is coincided with the Fermi level, indicating that neither molecule leads to any considerable amount of charge transfer. We refer such an observation to that only the states very far below/above the Dirac point of graphene are perturbed by the molecular adsorption. However, this conclusion is supportive of the result obtained in a previous ab initio work for the adsorption of benzene on graphene [23]. In their calculations, Zhang et al. found that the adsorption of benzene on pristine graphene results in a very little amount of electronic charge to be transferred from the molecule to the graphene sheet. Moreover, both molecule/graphene systems have a zero-gap feature, suggesting that pristine graphene band gap is not changed upon the benzene or naphthalene adsorption. Despite that the band structure for the benzene/graphene system looks very similar to the pristine graphene within the energy range ±2.0 eV, the band structure for the naphthalene/graphene system conducts a little change below the Fermi level. As shown in Fig. 3(c), a new flat (nondispersive) band appears at $E_F$ − 1.3 eV which is believed to be originated from the molecule states.

4. Summary and conclusion

The present ab initio calculations investigate the structural and electronic properties of graphene, resulting from benzene and naphthalene adsorbates. Using the plane-wave pseudopotential method and the density functional theory within the local density approximation we have shown that, for the adsorption of benzene and naphthalene on graphene, the stack configuration is more stable than the hollow structure by an energy gain of 0.05 eV and 0.08 eV, respectively. Both molecules adopt a planar geometry with a vertical distance of 3.52–3.54 Å above the graphene which is in agreement with binding energy curves performed in a previous work. We have noted that the Dirac point of graphene upon benzene and naphthalene adsorption is coincided with the Fermi level, indicating that no significant amount of electronic charge being transferred. Overall, graphene’s low energy electronic properties remain unchanged upon benzene and naphthalene adsorption.

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References