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A DENSITY FUNCTIONAL STUDY OF THE ADSORPTION OF CARBON DIOXIDE MOLECULE ON GRAPHENE

The physisorption of a CO_2 molecule on a graphene sheet using ab initio density functional theory is investigated. The geometrical structure of graphene, including various parameters viz. the bond lengths and bond angles are calculated for a graphene sheet under the adsorption of a CO_2 gas. Additionally, the density of states of a graphene sheet is calculated with & without adsorption of CO_2 molecules. It is observed that the CO_2 molecule is adsorbed on the graphene sheet with the adsorption energy of about 61.7 meV or less. The HOMO-LUMO energy levels of the graphene sheet before and after the adsorption of a CO_2 molecule remain unaltered. Therefore, the graphene sheet cannot detect a CO_2 molecule owing to their weak interaction.

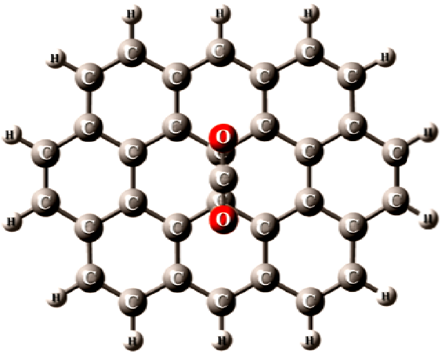
Keywords: graphene, adsorption; density functional theory, CO_2.

1. Introduction

The phenomenon of adsorption was discovered over two centuries ago [1, 2]. At present, the adsorption of gases on porous solid substrates is of increasing significance in both science and engineering. Various processes based on the adsorption principle, such as the gas sensing, separation of chemicals, biochemical processes *etc.*, have been devised and are constantly being improved. A consistent research, both experimental and theoretical, is being carried out to tailor new substrates for the efficient adsorption of gases. Semiempirical and *ab initio* methods [3] have been devised based on quantum mechanical laws, for the modeling of atoms, molecules, radicals, ions, and their interactions. In particular, the properties of a molecule in a ground electronic state are determined by the ground-state electron density instead of the wave function in the modeling on the basis of density functional theory [4–6].

Extensively studied molecular systems are carbon-based substrates, which include carbon nanotubes, graphene, and fullerenes. In particular, the interface between sp^2-bonded carbon materials, and other molecular species, is being widely studied both experimentally and theoretically for various promising applications for nanoelectronic devices and nanosensors.

Graphene, a member of sp^2-bonded carbon materials, is a flat single film of carbon atoms packed tightly into a two-dimensional (2D) honeycomb lattice, which exhibits fascinating electric and transport properties. Adsorption of various chemical species on graphene has been studied using the semiempirical and *ab initio* methods including density functional theory [7–12]. A. Montoya *et al.* [12] refer to experimental and theoretical studies, providing a further insight into the mechanism of CO_2 chemisorption



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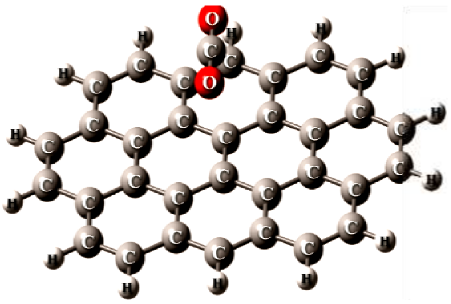

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Fig. 1. *A* – CO_2-graphene system with CO_2 adsorbed on site (*a*) (top view), wherein the CO_2 molecule is positioned in parallel to the graphene sheet. The grey spheres indicate carbon atoms, the red indicate the oxygen atoms, whereas the whitish grey spheres indicate the hydrogen atoms meant for terminating the dangling bonds; *B* – CO_2-graphene system with CO_2 adsorbed on site (*a*) (side view)

on carbonaceous surfaces using the density functional theory.

The carbon monoxide gas detection is studied on Al-doped graphene [13] by means of density functional theory, wherein it is reported that a large electrical conductivity change is observed after the adsorption of CO on Al-doped graphene. Thereby, Al-doped graphene may be used as an excellent candidate for sensing a CO gas. Earlier, the molecular dynamics approach [14] was used to carry out the physisorption of CO_2 on a graphite basal plane in the temperature range of 100 to 130 K. J. Zhao *et al.* [15] has reported the adsorption of various gas molecules on single-walled carbon nanotubes (SWNTs) and bundles using a first-principle method, wherein the equilibrium position, adsorption energy, charge transfer, and electronic band structures are obtained for different kinds of SWNTs. Adsorption of CO_2 and CH_4 at atmospheric pressure and at the temperature 300 K on a graphene sheet modified with titanium is reported [16] by I. Carrilla *et al.*

A search for available studies with reference to graphene as described above suggests that no study of the physisorption of a CO_2 molecule onto graphene at various adsorption sites has been attempted till date; instead, a few studies regarding either chemisorptions or physisorption of CO_2 on graphite [12], carbon nanotubes [15], and a graphene sheet modified with titanium [16] have been done. Accordingly, the present work is directed to use density functional theory to study the physisorption of (CO_2) molecule on a single graphene sheet at various adsorption sites. The calculations carried out in this work are based on density functional theory (DFT) and are performed, by using Gaussian 03 [17].

It is worthwhile to fully understand the possibility of detection of a CO_2 molecule by graphene, which means, in turn, that it is important to understand the interaction between graphene and a CO_2 molecule. The present study aims at understanding this interaction between graphene and CO_2 using density functional theory. We determine the exact orientation of a CO_2 molecule on the graphene sheet along with its favored adsorption sites by calculating CO_2 molecule's binding energy.

2. Computational Details

It is known that density functional theory predicts a molecular structure with high accuracy as compared to the predictions drawn from other methods. In the present study, a single sheet of graphene was built using Gaussview 4.1.2, wherein a limited size graphene model with 32 carbon atoms and 14 hydrogen atoms was obtained. The hydrogen atoms are meant for terminating the dangling bonds of carbon atoms at the edges. The atomic positions in the graphene sheet of one-carbon-atom in thickness were optimized using the DFT method with local spin density approximation (LSDA) and PBEPBE density functional, which is the pure GGA functional, along with the 6-311++G(d, p) basis set until the total energy change becomes less than 0.0001 eV.

A carbon dioxide molecule was separately optimized in a manner similar to the graphene sheet as described above and then positioned in a close proximity to the optimized graphene sheet forming a CO_2-graphene system as shown in Fig. 1. The CO_2 molecule was placed at nine different sites on a graphene sheet as shown in Fig. 2. The so-obtained CO_2-graphene systems were again optimized in a manner similar to that described above for a graphene sheet with LSDA and GGA functionals and 6-311++G(d, p) basis set. A comparison of the geometry of optimized CO_2-graphene system and with that of optimized pristine graphene (without CO_2) was carried out. Further, the optimized CO_2-graphene system and optimized pristine graphene was utilized for calculating the adsorption energy and the density of states.

3. Results and Discussions

The structures of graphene with adsorbed CO_2 for all nine combinations are displayed in Fig. 2. It is observed that the graphene sheet retains its original shape, with negligible changes in the bond lengths and the bond angles between atoms which are in a close proximity to the CO_2 molecule. Further, the adsorption energies of a CO_2 molecule adsorbed onto the graphene sheet at the nine sites are calculated using the equation

$$E_{\text{adsorptionenergy}} = E_{\text{graphene}} + \text{CO}_2 - (E_{\text{CO}_2\text{-graphene}}). \quad (1)$$

The adsorption energies are calculated for the nine adsorption sites with LSDA, unrestricted-LSDA, GGA, and unrestricted-GGA with 6-311++G (d, p) basis set. It is found that the adsorption energies for restricted and unrestricted functionals are exactly the same. Hence, only LSDA and GGA are reported and tabulated in Table 1 along with the perpendicular distance (d) between the CO_2 molecule and the graphene sheet after optimization.

It is found that the adsorption energy of the CO_2 molecule is higher for adsorption sites (a) to (f) as compared to that for adsorption sites (g) to (i) with a difference of about 24 meV for LSDA and about 20 meV for GGA. This means that the adsorption sites (a) to (f) are more stable as compared to the adsorption sites (g) to (i). Figure 3 is a graph of adsorption energies versus the position or orientation (adsorption sites) of a CO_2 molecule on the graphene sheet. A comparison of the adsorption energies calculated by LSDA and GGA shows that there

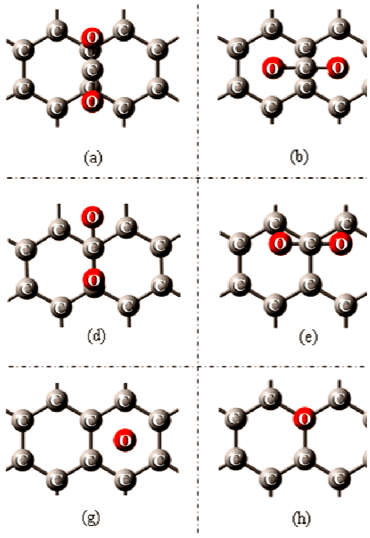


Fig. 2. Nine adsorption sites for CO_2 adsorbed on graphene [top view images], wherein at (a) to (f) adsorption sites, the CO_2 molecule is parallel to the graphene sheet and, at sites from (g) to (h), the CO_2 molecule is perpendicular to the graphene sheet. (a) T-B-T, (b) H-B-H, (c) T-H-T, (d) H-T-B, (e) H-T-H, (f) B-H-B (g) H (one oxygen atom downward and one upward with a carbon atom there between), (h) T (oxygen atom downward) and (i) B (oxygen atom downward between two carbon atoms). T, B and H denote top site of C atoms, bridge site of C-C bond, and hollow site of carbon hexagon, respectively. Grey and red spheres are denoted as C and O atoms, respectively

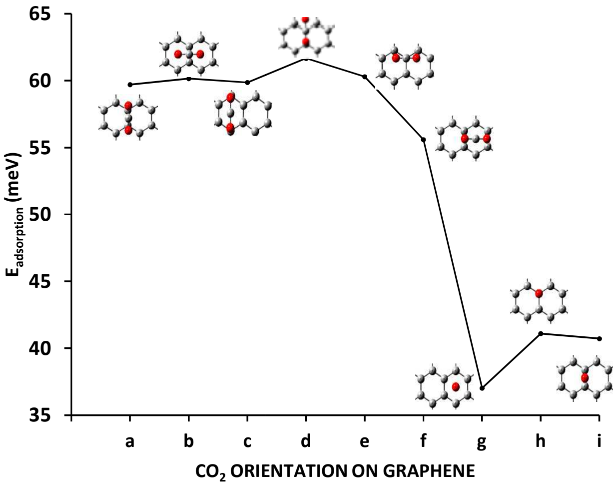
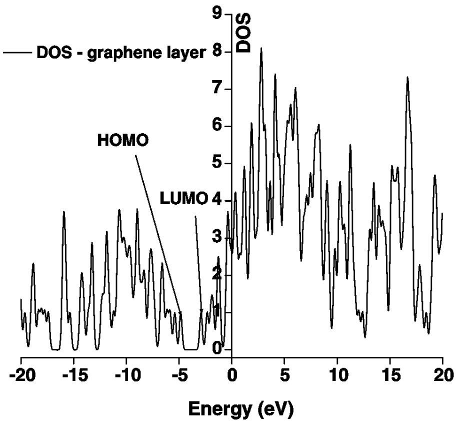


Fig. 3. Adsorption energies of the CO_2 molecule at orientations (a) to (i) are plotted. It is evident from the graph above that, for sites or orientations (a) to (f), the adsorption energies are high, which means that these sites are stable as compared to orientations (g) to (i) where the adsorption energies are less



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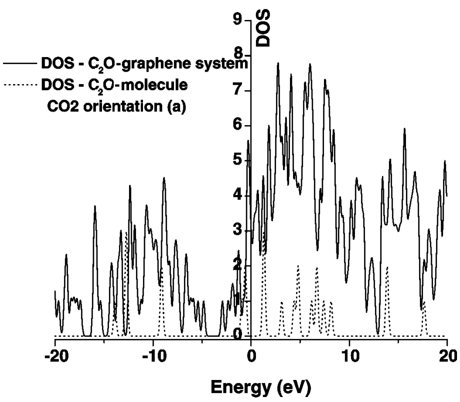

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Fig. 4. DOS for a pristine graphene sheet and a graphene sheet adsorbed with a CO_2 molecule on the adsorption site (*a*)

is a huge difference between the adsorption energies, wherein LSDA overestimates the adsorption energies. Further, the calculated values of adsorption energy of a CO_2 molecule on carbon nanotubes [15] using the first principles (various SWNTs) are tabulated in Table 1.

The adsorption energy values calculated herein agree with those in [15] in the order of magnitude: from 37 meV to 62 meV for the present calculations and from 89 to 110 meV reported in [15]. This difference is attributed to the fact that the carbon nanotubes are curved graphene surfaces, whereas, in the present case, the graphene sheet is flat.

The highest occupied molecular orbital (HOMO) and lowest unfilled molecular orbital (LUMO) are also calculated for each of nine combinations. It is found that the HOMO-LUMO levels and the HOMO-LUMO gap of a graphene sheet before and after the adsorption of CO_2 at all the sites do not change, which means that the HOMO-LUMO level and the HOMO-LUMO gap are independent of the orientation and the adsorption site of a CO_2 molecule. Further, it is found that the HOMO-LUMO gap has a value of 1.92 eV, and the Fermi level is found to be the same as the HOMO level and is numerically equal to −4.82 eV.

Table 1. **Calculated values of adsorption energy of CO_2 molecule on carbon nanotubes using first principles (various SWNT)**

Adsorption sites	$E_{adsorption}$ (meV)	Distance (*d*) A°	$E_{adsorption}$ (meV)	Distance (*d*) A°
a	209.19	2.98	59.70	3.54
b	211.18	2.99	60.15	3.49
c	209.11	2.97	59.86	3.54
d	212.13	3.05	61.66	3.65
e	211.25	3.03	60.29	3.62
f	207.24	3.07	55.59	3.60
g	185.46	2.92	37.02	3.42
h	189.25	2.90	41.10	3.38
i	188.24	2.87	40.72	3.37
$E_{adsorption}$ [15]	109	3.2		
	97	3.54		
	89	3.23		

Table 2. **The altered bond lengths and bond angles at the adsorption of a CO_2 molecule on the graphene sheet**

Bond	Bond Length	
	Graphene	CO_2-Graphene
C3–C4	1.43540	1.43577
C4–C8	1.42281	1.42292
C3–C7	1.42281	1.42292
C4–C5	1.42281	1.42292
C3–C2	1.42281	1.42292
Angle	Bond Angle	
C2–C3–C4	119.9874	119.9902
C3–C4–C5	119.9874	119.9902
C3–C4–C8	119.9874	119.9902
C4–C3–C7	119.9874	119.9902

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The altered bond lengths and bond angles at the adsorption of a CO_2 molecule on the graphene sheet are listed in Table 2.

It is found that the bond lengths and the bond angles of a graphene sheet with adsorbed CO_2 are perturbed only marginally for atoms in a close vicinity of the CO_2 molecule; however, the perturbation is very small. Table 2 presents only the perturbed bond lengths and the bond angles for carbon atoms in a very close vicinity of the CO_2 molecule for orientation (a) with GGA and 6-311++G (d, p) basis set.

The density of states of the CO_2-graphene sheet system: To verify the effects of the adsorption of a CO_2 molecule on the graphene sheet electronic properties, the total density of states (DOS) of the CO_2-graphene system are calculated for GGA level of theory with 6-311++G(d, p) basis set and are compared with those of the graphene sheet without CO_2. It is found that the orientation and the adsorption sites of a CO_2 molecule do not change the DOS appreciably for various orientations. The DOS for the graphene sheet without CO_2 is shown in Fig. 4, *A* and the DOS for the graphene sheet with CO_2 adsorbed on it at adsorption site (a) is shown in Fig. 4, *b*. Further, the analysis of DOS (Fig. 4, *A* and *B*) shows that the contribution of CO_2 electronic levels to the total density of states is localized between −14.7 to −11.8 eV and −10 to −8.28 eV in the valence bands and around 0.44 to 9 eV in the conduction bands, which are far away from the Fermi level or the HOMO-LUMO gap. This shows that the adsorption of CO_2 does not change the HOMO-LUMO gap. The same is the case for remaining eight adsorption sites (*b* to *i*) [for which the DOS is not shown].

4. Conclusions

The physisorption of CO_2 on graphene using *ab initio* density functional theory method has been investigated. It is observed that graphene with adsorbed CO_2 retains its original shape, and the bond angles are not altered significantly. The adsorption energy of a CO_2 molecule on the graphene sheet was found to be 61.7 meV or less, whereas the DOS analysis of pristine graphene and the graphene-CO_2 system provided a reason for the weak adsorption energy. Further, the HOMO-LUMO gap is independent of the orientation and the adsorption site of the CO_2 molecule. It may be concluded that the graphene sheet has very low sensitivity to CO_2 molecules.

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ДОСЛІДЖЕННЯ АДСОРБЦІЇ МОЛЕКУЛИ ВУГЛЕКИСЛОГО ГАЗУ НА ГРАФЕНІ МЕТОДОМ ФУНКЦІОНАЛА ЩІЛЬНОСТІ

Р е з ю м е

Досліджено фізісорбцію молекули CO_2 на пластині графену, виходячи з перших принципів теорії функціонала щільності. Розраховано геометричну структуру графену (довжини і кутів зв'язків) для адсорбції вуглекислого газу на пластині графену. Визначено щільність станів для пластини графену з адсорбцією і без неї. Показано, що енергія адсорбції CO_2 молекули дорівнює приблизно 61,7 меВ або менше. До і після адсорбції молекули вуглекислого газу рівні HOMO-LUMO пластини графену не змінюються. Тому пластина графену не може детектувати CO_2 молекулу внаслідок слабкої взаємодії.