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First-principles Studies of CO_2 and NH_3 Gas Molecules Adsorbed on Graphene Nanoribbons

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Abstract: We present first-principles studies of CO_2 and NH_3 adsorbed on graphene nanoribbons (GNRs). The electronic and transport properties are calculated based on density functional theory combined with non-equilibrium Green's function method. Absorption energy, density of states, electron density deformation, charge transfer, current-voltage characteristics, and transmission spectra were analyzed. It is found that CO_2 and NH_3 adsorbed on GNRs exhibit acceptor-like and donor-like behaviors, respectively. Both CO_2 and NH_3 molecules show physissorption on GNRs with low adsorption energies and small charge transfers. In other words, the interactions between CO_2 and NH_3 molecules and GRNs are very weak. The results suggest that the sensitivity and selectivity of GRN-based gas sensors could be improved by introducing the dopant, defect, or modification of electronic structures of graphene.

Keywords: First-principles, Graphene Nanoribbons, CO2 Adsorbed on Graphene, NH3 Adsorbed on Graphene.

1. Introduction

Graphene, the first truly 2D crystalline materials, has been attracting much attention since its successful fabrication in 2004 [1, 2]. It is a promising candidate for silicon replacement in semiconductor industry [3, 4] or gas sensing applications [5]. Graphene can be patterned into GNRs via lithographic [6, 7] or focus ion beam [8] techniques. GRNs have been investigated as alternative for gas sensors due to their high mobility, high surface area to volume ratio, easy micro fabrication, and controllable energy gap. The sensor properties are based on changes in resistivity due to molecules adsorbed on GRNs that act as donors or acceptors. A theoretical study of gas molecular adsorption on the infinite graphene surface has been reported recently [9]. The adsorption of ammonia (NH_3) and carbon dioxide (CO_2) on graphene sheet have been investigated in experiments [10, 11].

In this report, the adsorptions of CO_2 and NH_3 on GRNs have been investigated within the framework of density functional theory (DFT) in combination with non-equilibrium Green's function (NEGF) method. We focus on clarifying and evaluating the interaction between these gas molecules

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and GNRs. The study also contributes for understanding the atomistic mechanism of gas molecules adsorbed on GNRs to assist designing gas graphene-based sensors.

2. Model and computational method

First-principles calculations are performed to study the adsorption of CO_2 and NH_3 gas molecules on GNRs. The electronic and transport properties are calculated using the combination of DFT and NEGF methods. In particular, the electronic properties such as density of state (DOS), electron density, and charge transfer analysis are calculated based on DFT using Materials Studio/Dmol3 package [12]. The transmission spectra, current-voltage characteristics are calculated based on NEGF method which is implemented in the OpenMX package [13]. All calculations were carried out within the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) exchange-correlation functional [14]. The SCF energy convergence criterion is set to 10^{-6} Hartree. In the treatment of pseudo-potentials, the pseudo atomic orbital basis sets of C4.5-s2p1 for carbon and H4.5-s2 for hydrogen were used, where in the abbreviation of basis functions such as C4.5-s2p1, C stands for the atomic symbol, 4.5 the cutoff radius (bohr) in the generation by the confinement scheme, and s2p1 means the employment of two primitive orbitals for s and one primitive orbital for p [13]. These basis sets was chosen based on the optimized parameters calculations.

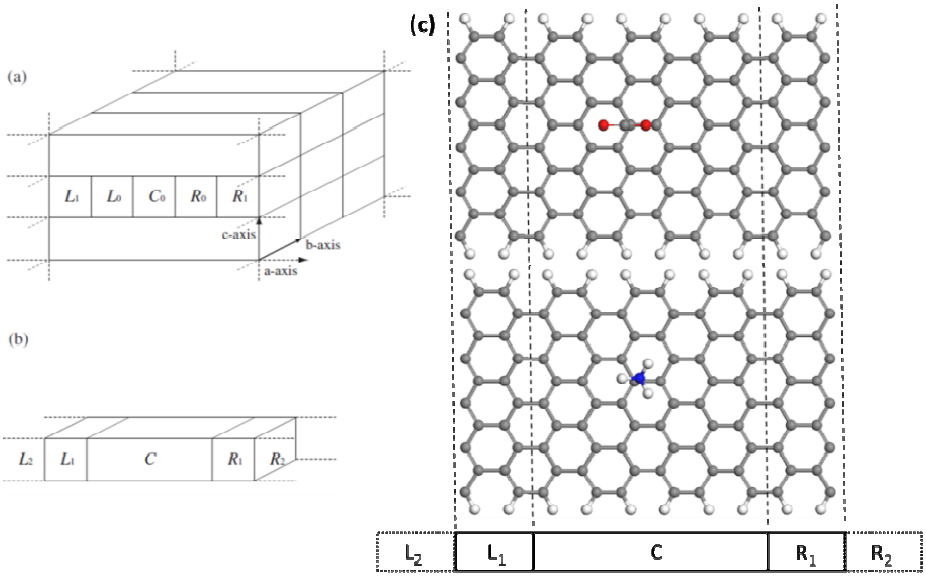

Figure 1. (a) Configuration of the system treated by NEGF method. (b) One dimensional system derived from the configuration of (a) where the region C is an extended central region consisting of L_0, C_0, and R_0. (c) Structure model of GNRs with CO_2 and NH_3 gas molecules adsorption.

For quantum transport calculations in OpenMX, a system consisting of a central region connected to left and right leads with infinite size, as shown in Fig. 1a, is treated by the NEGF method. By considering the two dimensional periodicity in the bc-plane, the system can be cast into a one-dimensional problem, as show in Fig. 1b. The electronic transport is assumed to occur along the *a*-axis. The structure model of CO_2 and NH_3 gas molecules adsorbed on the center of 10-AGRN (Fig. 1c) and 9-ZGNR were used. In the model, the edges of GNRs were terminated by hydrogen to avoid effect of edge dangling bonds.

3. Results and discussion

3.1. Geometry optimization and adsorption energy

The previous DFT calculation study of CO_2 adsorbed on Armchair GNRs (AGNRs) shows that the C-C and C-O distances are 1.51 Å and 1.26Å, respectively, and the C-O-C angle is 127° [15]. Therefore, the similar structure was used for initial configuration (Fig. 2a). For the adsorption of NH_3 on AGNR, the initial structure was built as show in Fig. 2c, in which adsorbed NH_3 molecule sits 1.49Å away from AGNR sheet, the H-N distance is 1.03Å, and the dihedral angle is about 21° between the C-N bond and the AGNR plane [15]. The optimized structures are show in the Fig. 2b and 2d. One can see that both CO_2 and NH_3 molecules go far away from AGNRs in comparison with initial structures. In particular, the distance between CO_2, NH_3 molecules and the AGNR sheet are 2.82Å, 2.80Å, respectively.

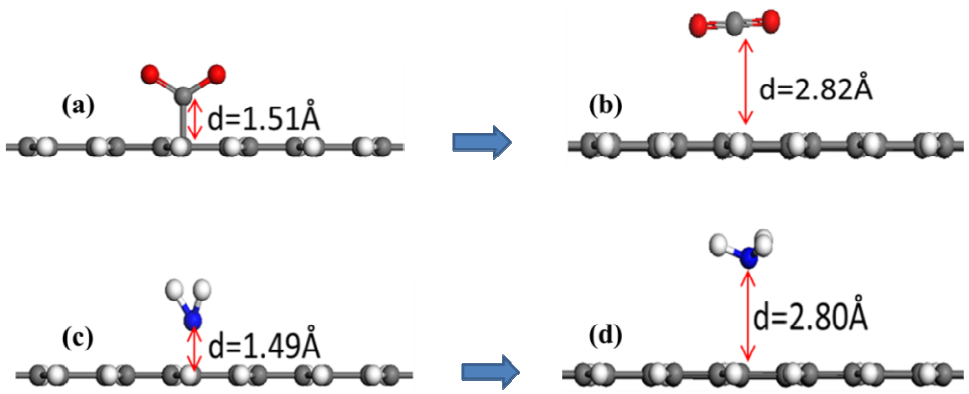

Figure 2. (a), (c) initial structures; and (b), (d) optimized structures of AGNR adsorbed CO_2 and NH_3, respectively.

For Zigzag GNRs (ZGNRs) adsorption cases, the initial structures are built by putting a relax CO_2 (NH_3) molecule on the ZGNRs sheet with distance of 1.5Å as show in the Fig. 3a and 3c. Similarly to the AGNR adsorption cases, the optimized structures show that the adsorbed molecules tend to go far away from the ZGNR sheets. The distance between CO_2 and NH_3 molecules and the ZGNR sheet are 2.86Å and 3.05Å, respectively.

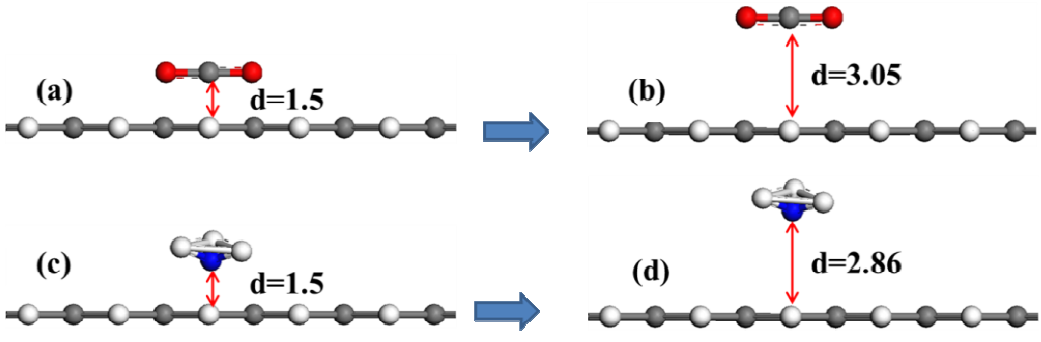

Figure 3. (a), (c) initial structures, and (b), (d) optimized structures of ZGNR adsorbed CO_2 and NH_3, respectively.

Adsorption energy (ΔE_{ads}) is a key quantity in predicting adhesive property of an adsorption system. As is known, the adsorption energy is defined as

$$\Delta E_{ads} = E_{GRN_{Gas}} - (E_{GRN} + E_{Gas}) \quad (1)$$

Where E_{GNR_Gas} is the total energy of the GNR with gas molecule adsorption. E_{GNR}, E_{Gas} are the energies of isolated GNR and isolated corresponding gas molecule, respectively. In general, a negative ΔE_{ads} indicates that the molecule adsorption is exothermic and thus the adsorption system is energetically stable.

Table 1. Adsorption energies (eV) of CO_2 and NH_3 on GNRs

	CO_2	NH_3
AGNR	-0.186	-0.153
ZGNR	-0.157	-0.175

The adsorption energies of CO_2 and NH_3 molecules on GNRs are shown in the Table 1. We can see that all adsorption energies are negative with absolute smaller than 0.5eV per molecule in both AGNR and ZGNR cases. It implies that the interaction between these adsorbed gas molecules and GNRs are physisorption. In the other words, these interactions are very weak.

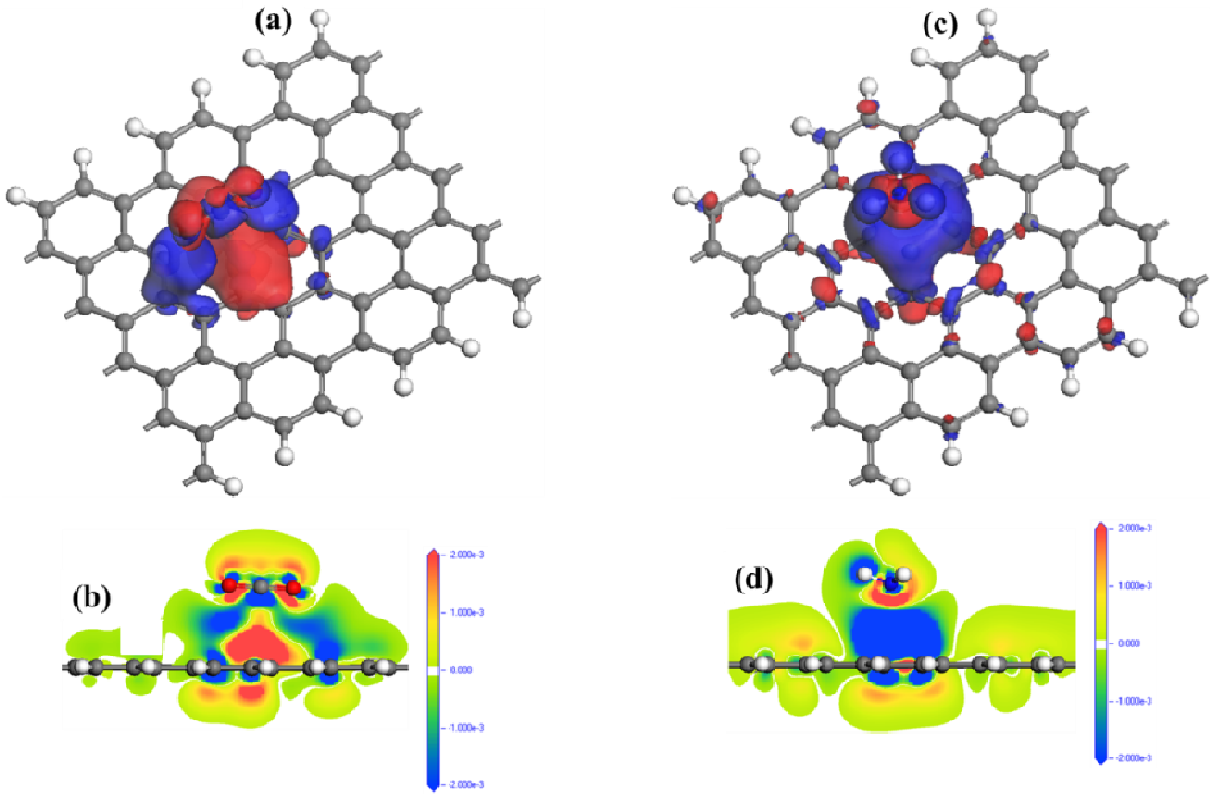

Figure 4. (a), (c) side view and (b),(d) cross-section view of electron density deformation of AGNR with CO_2 and NH_3 adsorptions, respectively, at the iso-value of 0.001 a.u.

3.2. Electron density deformation and charge transfer

In order to clarify the electronic interaction between adsorbed gas molecule and GNRs, electron density deformations have been analyzed. The electron density deformation is defined as the difference between the electron densities of GNR adsorbed gas molecule and sum of the electron densities of isolated GNR and of isolated gas molecule

$$\Delta\rho = \rho_{GRN_{Gas}} - (\rho_{GRN} + \rho_{Gas}) \quad (2)$$

Where ρ_{GNR_Gas} is electron density of GNR with gas molecule adsorption. ρ_{GNR}, ρ_{Gas} are the electron densities of isolated GNR and isolated corresponding gas molecule, respectively. Fig. 4 shows the electron density deformation of AGNR with CO_2 and NH_3 adsorptions. The red electron density deformation has positive value and blue one has negative value. It implies that there is an amount of electrons transferred from AGNR to CO_2. In opposite, electrons are transferred from NH_3 to AGNR. Our electron density deformation calculations for ZGRN with CO_2 and NH_3 adsorptions show similar results.

In order to understand the charge transfer quantity, Mulliken populations have been examined. It is found that there is small amount of 0.00868e (0.0843e) charge transferred from AGNR (ZGNR) to CO_2 molecule. It indicates that CO_2 adsorbed on GNRs acts as an acceptor-like (p-type). In contrast, there is a small amount of 0.08838e (0.08997e) charge transferred from NH_3 molecule to AGNR (ZGNR). In other works, NH_3 adsorbed on GNRs will act as a donor-like (n-type). These results are in good agreement with previous study [9]

3.3. Density of states, transmission spectra, and current-voltage characteristics

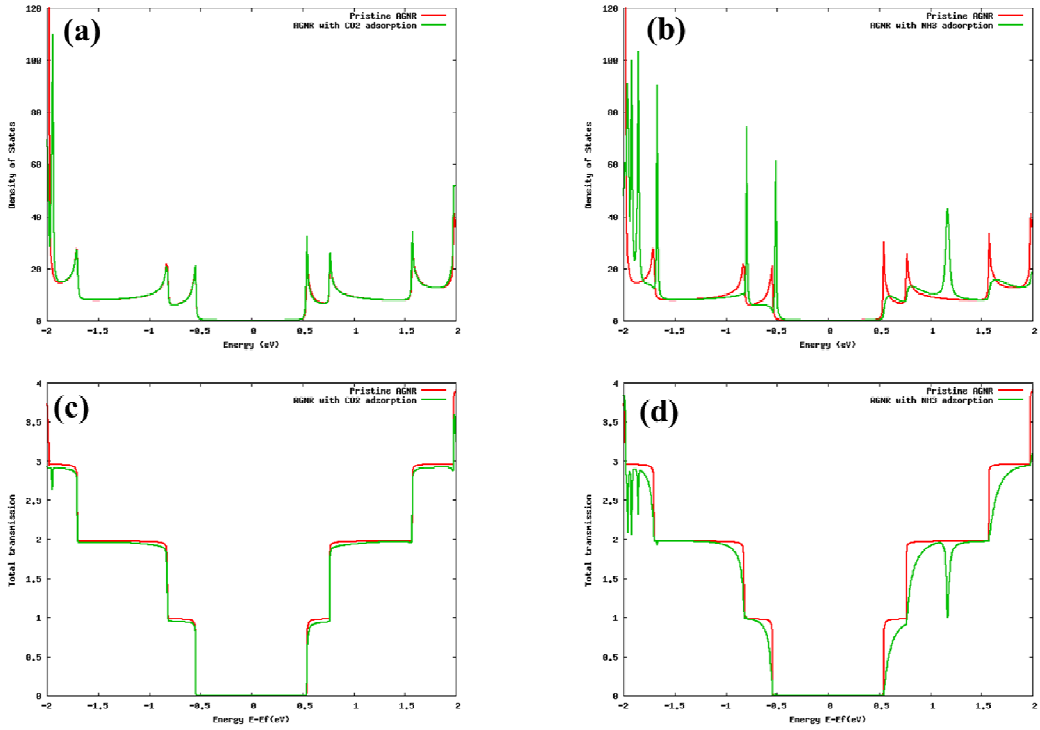

Figure 5. (a), (b) DOS (eV^{-1}) and (c), (d) corresponding transmission spectra of AGNRs with CO_2, and NH_3 adsorptions, respectively (green lines), in comparison to AGNRs without adsorption (red lines).

Figure 5 shows the DOS and corresponding transmission spectra of AGNR within CO_2 and NH_3 adsorptions in comparison to AGNR without adsorption.

In the case of AGNR without adsorption, we can see that DOS shows multiple sharp peaks which are caused by lateral quantization of electronic states in the one-dimensional AGNRs. Therefore, the corresponding transmission spectrum has a step-shape.

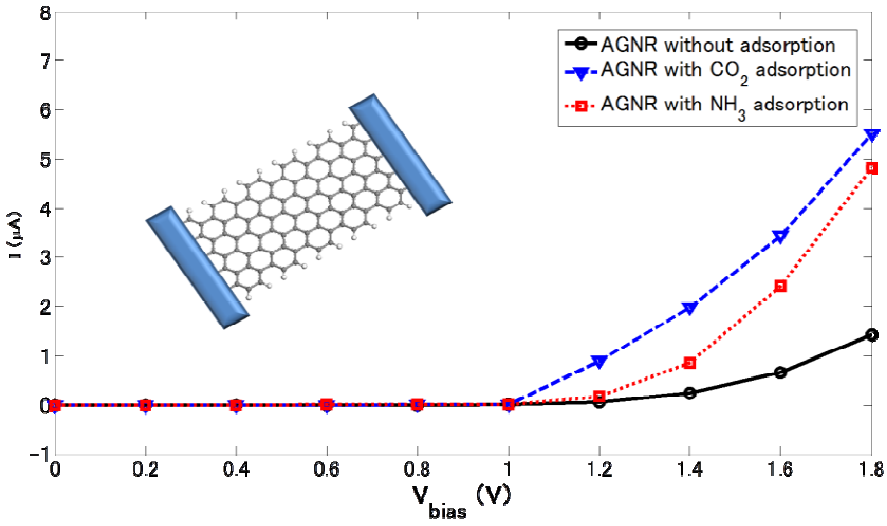

Figure 6. Current-voltage characteristics for AGNR sensor without and with adsorptions of CO_2 and NH_3. The inset shows the schematics of such a AGRN sensor.

In the case of AGNR with CO_2 adsorption, the DOS are almost unchanged in comparison to AGNR without adsorption because of very weak interaction between CO_2 molecule and ANGR. This caused transmission spectra almost unchanged. However, these transport features are slightly changed with the presence of an adsorbed NH_3 molecule. Sharp peaks at the lowest unoccupied molecular orbital (LUMO) energy cannot be seen in DOS, and the transmission rate is reduced near the LUMO edge. The changes of transmission spectra effect on their current-voltage characteristics, which are shown in the Fig. 6. This demonstrated that GRNs can be used as a gas sensor to detect CO_2 and NH_3. However, the sensitivity and selectivity of the GRN-based sensors are low due to the weak interaction between GRN and these adsorbed gas molecules.

4. Conclusion

First-principles calculations were performed to study the adsorption of CO_2 and NH_3 gas molecules on GNRs. The analysis of electron deformation densities and charge transfers demonstrates that CO_2 and NH_3 adsorbed on GNRs exhibit acceptor-like and donor-like behavior, respectively. The obtained results show that both CO_2 and NH_3 gas molecules show physisorption on GNRs with low adsorption energies and small charge transfer. It implied that the interaction between CO_2 and GNRs are very weak. The results suggest that the sensitivity and selectivity of graphene-based gas sensors could be improved by introducing the dopant, defect, or modification of electronic structure of graphene.

Acknowledgments

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