



Quantum-based first-principles study of gas molecules (O₂, CO₂, NO₂) interaction on monolayer germanene

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Abstract

We perform calculations of the adsorption energy of O₂, CO₂, and NO₂ molecules on germanene by using the density functional theory (DFT). We find two favorable configurations for O₂, the U-site and V-site configurations with similar adsorption energies of -4.10 and -4.32 eV. As for NO₂, we find two favorable configurations, the T-site and DB-site configurations. The T-site configuration is 0.98 eV more stable than the IB-site one, and both configurations are chemically adsorbed by germanene. On the contrary for CO₂, we find a T-site configuration with adsorption energy of 0.42 eV and the configuration physically adsorbed by germanene.

1. Introduction

Graphene, successfully fabricated for the first time in 2004 by Novoselov *et al.* [1], inspires many findings in two-dimensional (2-D) materials, particularly Group IVA materials resulting in other 2-D materials such as silicene and germanene. Graphene has planar structures while silicene and germanene, from previous studies [2-7], are addressed to have buckled structures. These two 2-D materials have similar properties as graphene and also have potential as stable materials [8-11]

Recently, germanene has been extensively studied for its potential to be a semiconductor material by adsorption of small molecules [12], giving defects [13,14], or giving vacancies [15,16]. The tunable bandgap behavior of germanene and the higher carrier mobility of germanene [17,18] make germanene a plausible candidate as an active layer of high-performance electronic devices such as the field-effect transistor [19,20].

Wang *et al.* [12] studied the adsorption of small organic molecules on germanene by using the density functional theory (DFT). They found that the adsorption energies are lower than those in silicene, indicating that such molecules are strongly bound in germanene. Liu *et al.* [5] and Xia *et al.* [21] studied the interaction of O₂ on germanene and showed an enhancement of the stability of germanene in air. This stability of the free-standing germanene is an important part of the study of two-dimensional material-based electronic devices. The application of germanene as a gas-sensing material is studied

extensively, especially for toxic gas sensing [22-24]. Therefore, the study of gases-based molecule adsorption on germanene is necessary.

The interaction of an individual gas molecule such as O₂ with germanene was studied [5,21], however, the adsorption comparison of some gas molecules on germanene needs to be investigated. In the present work, we carry out quantum-based DFT calculations to study the adsorption of O₂, CO₂, and NO₂ on germanene. We use a 32-sites supercell and model some possible configurations. To check the stability of the configurations, we calculate the adsorption energies of O₂, CO₂, and NO₂ on monolayer germanene. We fully relaxed atoms and parallelly optimized the system using energy and atomic force criteria to obtain accurate results.

2. Methodology

We perform the DFT calculations to investigate the adsorption of oxygen and nitrogen gases on germanene. We use a quantum-based code PHASE/0 [25-29] employing the plane wave basis sets. We apply the generalized gradient approximation as an exchange-correlation functional with the norm-conserving pseudopotential. The cut-off energy wave-function and charge-density are 15 Ry and 60 Ry, respectively. The cut-off energy is the number of plane-wave functions as basis functions. A 4 × 4 × 1 mesh grid point and a vacuum of 15 Å are applied for the lattice constant calculation. The optimized lattice constant is obtained to be 4.1 Å, which is in agreement with the previous results [21,30]. To model the gas-adsorbed germanene,

we carry out a supercell containing 32 atomic sites and initially place O₂, CO₂, and NO₂ molecules on several sites on germanene such as at hollow, top, and bridge sites, shown in Figure 1. For the graphical illustrations of the atomic structure, we employ VESTA [31].

During relaxation, gas molecules diffuse from the initial to optimized positions, which are their favorable configurations. The optimized geometry, which is the ground state of the system is reached by relaxing atoms in the supercell so that the atomic force and energy criteria are less than 10⁻⁴ Ha.bohr⁻¹ and 10⁻⁶ Ha, respectively. The atomic relaxation is applied in all directions (x, y, z-axes) to obtain reliable calculational results. We next examine the stability of the configurations by calculating adsorption energies E_{ads} given by:

$$E_{\text{ads}} = E_{\text{Ge+gas}} - E_{\text{Ge}} - E_{\text{gas}} \quad (1)$$

where $E_{\text{Ge+gas}}$, E_{Ge} , and E_{gas} are the total energies of the gas-adsorbed germanene, pristine germanene, and isolated gas, respectively.

3. Results and discussion

We set the hollow site's initial condition in which the O₂ molecule floats 1.03 Å above the germanene sheet (Figure 2(a)). We first optimized the O₂ molecule and obtained that the bond length (O-O) is 1.16 Å which is somewhat smaller than the O₂ bond length in vacuum (1.21 Å) [32]. In the optimized condition, two oxygen atoms are separated and then bounded by germanium atoms, resulting in the U-site configuration (Figure 2(b)).

We variate another initial condition by positioning the O₂ molecule at the top site of germanene, illustrated in Figure 3(a). In this case, one of the oxygen atoms of the O₂ molecule has a bond with the germanium atom. The bond length between these atoms (O-Ge) is 1.96 Å. Both in the U-site and V-site configuration the O₂ molecule breaks their bond and each oxygen atom bonds with germanium atoms. As depicted by Figure 2(b), each oxygen atom finds the minimum energy of the system in the nearest Ge-Ge bond. In the optimized V-site configuration, a Ge atom is distorted upward (ordinate direction) from the germanene sheet (Figure 3(b)).

During optimization, O₂ diffuses from the initial state to the transition state and finally forms the final state. These states are illustrated by the reaction coordinate diagram in Figure 4 and Figure 5. The coordinate diagrams depict the configuration evolution from the highest energy, the midpoint energy, and the lowest energy. The energy values in the reaction coordinate diagram are subtracted by the highest energy in the system. The diffusion of O₂ can be explained in three steps. Firstly, O₂ dissociates to be two single oxygen atoms approaching Ge, forming an O-Ge bond of about 1.9 Å for the U-site and 2.1 Å for the V-site in the transition state. Secondly, each oxygen atom moves to the Ge-Ge bond. Finally, the two single oxygen atoms approach a Ge atom forming a strong O-Ge-O bond. The calculated bond length of O-Ge is around 1.88 Å for the U-site and 1.9 Å for the V-site. Meanwhile, the distance of O-O is found to be 4.02 Å for U-site and 3.02 Å for V-site, which is far enough compared to its value in vacuum (1.21 Å). Thus, the O₂ molecule dissociated to be two single oxygen atoms. In this site, O₂ is very reactive and strongly bounded via covalent bonds. This result is in agreement with that of the previous studies [5,21].

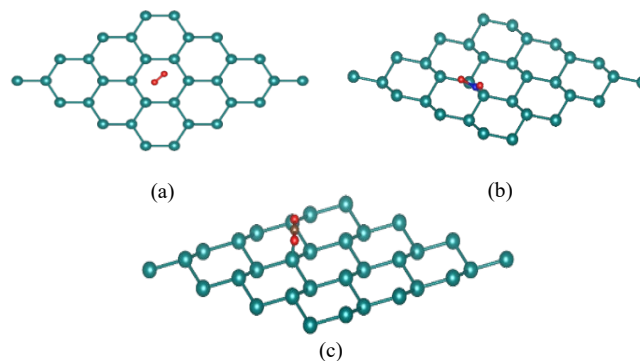


Figure 1. The initial configurations of (a) hollow site, (b) bridge site, and (c) top site.

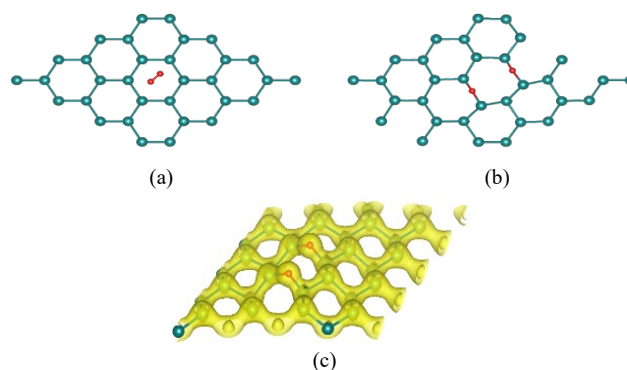


Figure 2. Optimized geometries of O₂ in (a) hollow site initial configuration, (b) U-site final configuration, and (c) the charge density distribution of the U-site configuration.

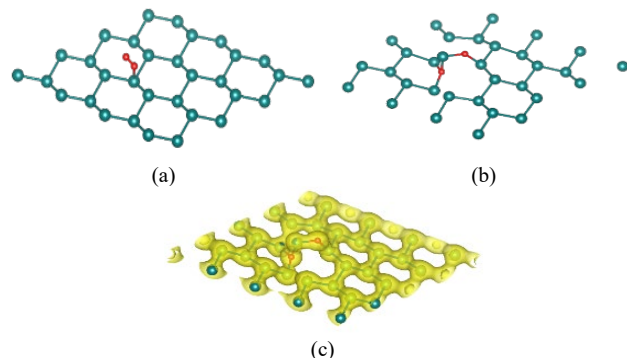


Figure 3. Optimized geometries of O₂ in (a) top site initial configuration, (b) V-site final configuration, and (c) the charge density distribution of the V-site configuration.

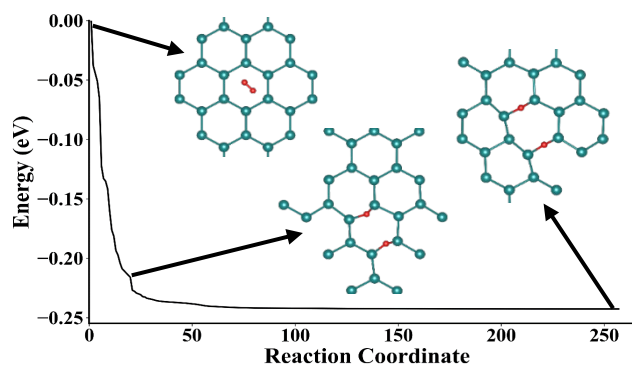


Figure 4. Reaction coordinate diagram of O₂ U-site configuration.

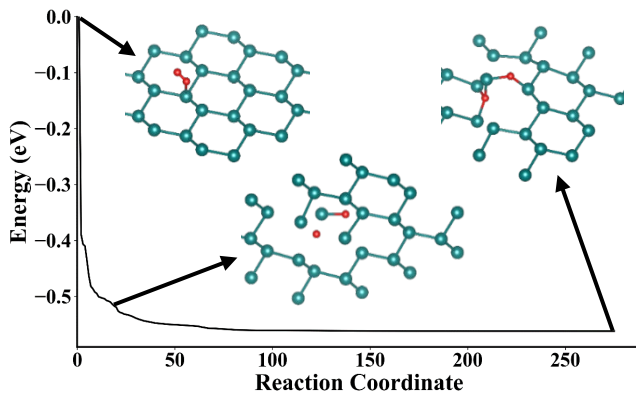


Figure 5. Reaction coordinate diagram of O_2 V-site configuration.

We set an initial configuration for the CO_2 molecule with top site configuration as shown in Figure 6(a). The C atom in the CO_2 molecule bonds with the Ge atom in the germanene sheet. This bond is placed at a distance of 1.9 Å. During optimization to find the minimum energy of the system, the CO_2 molecule shows a phenomenon called physical adsorption (physisorption) in which the germanene sheet is undisturbed by the presence of a CO_2 molecule. This result is in accord with the previous study [33]. Instead of creating a bond with the germanene sheet, CO_2 repels away at a distance of 3.68 Å in the final state, namely a T-site configuration (Figure 6(b)). The reaction coordinate diagram of the T-site configuration of the CO_2 molecule in Figure 7 shows the initial state, the transition state, and the final state. The difference between the transition state and the final state is the distance in the ordinate direction.

We model two initial configurations for the NO_2 molecule at the hollow site and the bridge site. For the hollow site, we place the NO_2 molecule in the middle of the honeycomb germanene structure as illustrated in Figure 8(a). In the bridge site's initial configuration, we lay the NO_2 molecule in the Ge-Ge bond (Figure 9(a)). We find a T-site configuration where one of the oxygen atoms is bonded with the Ge atom (Figure 8(b)). The bond length between these atoms is 1.94 Å. The bond lengths between the nitrogen atom and oxygen atom are 1.12 Å and 1.67 Å for the oxygen atom that bonded with the Ge atom. Therefore, the interaction between the NO_2 molecule and germanene is chemical adsorption (chemisorption).

In the case of the bridge site's initial configuration, we find the DB-site configuration. The bond of the NO_2 molecule breaks to be NO molecule unbonded with Ge atom and oxygen atom bonded with Ge atoms. The oxygen atom is reactive moving to the nearest Ge atoms and bonding with them (Figure 9(b)).

We explain the bonding of the gas molecules on germanene using charge density distribution. The charge density is plotted for each system shown in Figure 2-3, Figure 6, Figure 8, and Figure 9(c). The yellow surface represents the electron cloud, representing strong bonds between atoms. In the optimized U-site and V-site configurations, oxygen atoms are reactive and make strong bonds with their adjacent germanium atoms (Figures 2 and Figure 3(c)). From Figure 6(c), the CO_2 molecule is floating with no charge cloud in between CO_2 and germanene. This indicates a weak interaction between CO_2 and germanene. In the case of the NO_2 molecule, the charge cloud binds germanium and oxygen atoms (Figures 8 and Figure 9(c)).

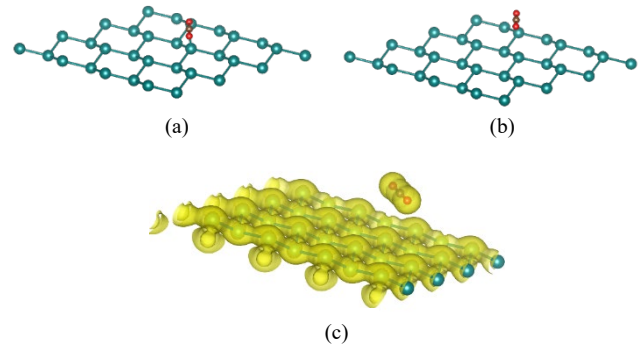


Figure 6. Optimized geometries of CO_2 in (a) top site initial configuration, (b) T-site final configurations, and (c) the charge density distribution of the T-site configuration.

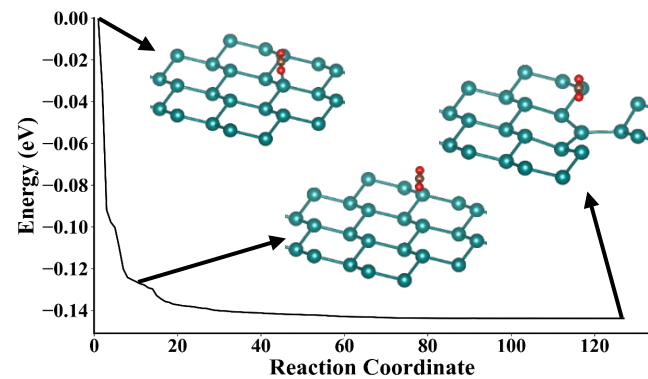


Figure 7. Reaction coordinate diagram of CO_2 T-site configuration.

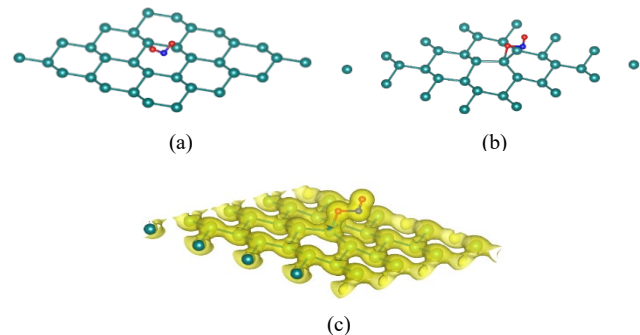


Figure 8. Optimized geometries of NO_2 in (a) hollow site initial configuration, (b) T-site final configuration, and (c) the charge density distribution of the T-site configuration.

The reaction coordinate diagrams in Figure 10 and Figure 11 show the dynamics of configuration associated with the energy of T-site configuration and DB-site configuration, respectively. DB-site configuration needs more energy than the T-site configuration to find the optimized configuration. In Figure 10, we can see that at the transition state, one of the oxygen atoms is attracted to the Ge atom. This drags atom N and other O to construct the final state configuration. On the other side, from Figure 11, we can see that in the transition state one of the oxygen atoms from the NO_2 molecule bonds with the Ge atom. Because oxygen is reactive, it bonds with another Ge atom. So, oxygen bonds with two Ge atoms in the final state configuration.

We next calculate the adsorption energies (Table 1) of the O₂, CO₂, and NO₂ molecules on the germanene sheet. In the case of the O₂ molecule, the obtained energies are -4.10 eV and -4.32 eV for U-site and V-site configuration, respectively. The adsorption energy of the NO₂ molecule also shows negative results, -1.22 eV for T-site configuration and -0.24 eV for DB-site configuration. On the other hand, the adsorption energy of the CO₂ molecule is positive, 0.42 eV. Here from the adsorption energy, we find that the O₂ and NO₂ molecules are chemisorption, and the CO₂ molecule is physisorption. The adsorption energy of the O₂ molecule is more stable than other molecules. These findings suggest that germanene has the potential to be material for gas sensing, especially O₂ and NO₂ gases.

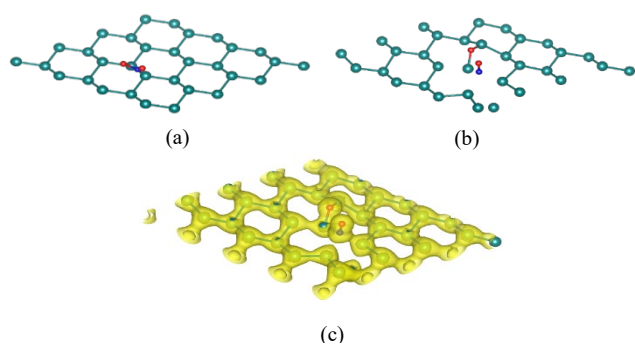


Figure 9. Optimized geometries of NO₂ in (a) bridge site initial configuration, (b) DB-site final configuration, and (c) the charge density distribution of the DB-site configuration.

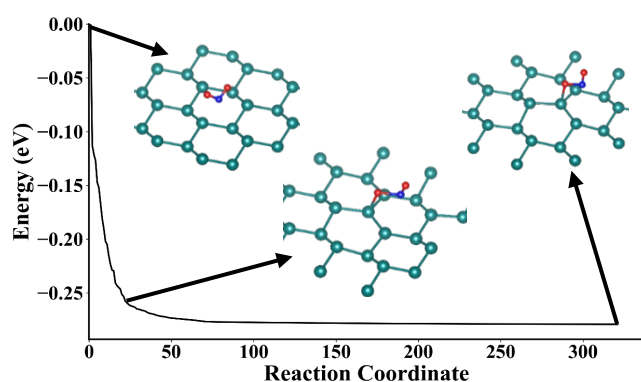


Figure 10. Reaction coordinate diagram of NO₂ T-site configuration.

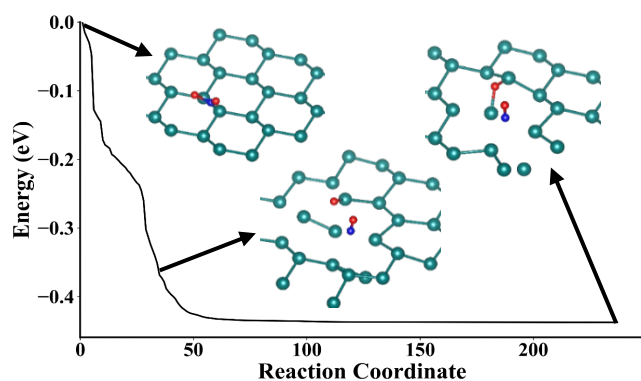


Figure 11. Reaction coordinate diagram of NO₂ DB-site configuration.

Table 1. Calculated adsorption energies of the gas-adsorbed germanene.

Molecule	Configuration	E _{ads} (eV)
O ₂	U-site	-4.10
	V-site	-4.32
CO ₂	T-site	0.42
NO ₂	T-site	-1.22
	DB-site	-0.24

4. Conclusions

To sum up, we have examined the adsorption of O₂, CO₂, and NO₂ gas molecules by using DFT calculations. All atoms in the supercell are fully relaxed in all directions through parallel energy-atomic force optimizations to obtain reliable results of calculations. In the O₂ case, we found two favorable configurations which are U-site and V-site, in which the V-site configuration is 0.22 eV more stable than the U-site configuration. As for the NO₂ molecule, we found that the T-site configuration is 0.98 eV more stable than the DB-site configuration. Both O₂ and CO₂ molecules are chemisorptions. On the contrary, we found that the CO₂ molecule is physisorption and repulsive with the germanene sheet indicated by a positive value in adsorption energy. These results are useful for future consideration of the study of the germanene-based electronic device.

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