



Article Adsorption Behavior of Toxic Carbon Dichalcogenides (CX₂; X = O, S, or Se) on β_{12} Borophene and Pristine Graphene Sheets: A DFT Study

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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). **Abstract:** The adsorption of toxic carbon dichalcogenides (CX₂; X = O, S, or Se) on β_{12} borophene (β_{12}) and pristine graphene (GN) sheets was comparatively investigated. Vertical and parallel configurations of $CX_2 \cdots \beta_{12}$ /GN complexes were studied herein via density functional theory (DFT) calculations. Energetic quantities confirmed that the adsorption process in the case of the parallel configuration was more desirable than that in the vertical analog and showed values up to -10.96 kcal/mol. The strength of the $CX_2 \cdots \beta_{12}/GN$ complexes decreased in the order $CSe_2 > CS_2 > CO_2$, indicating that β_{12} and GN sheets showed significant selectivity for the CSe₂ molecule with superb potentiality for β_{12} sheets. Bader charge transfer analysis revealed that the CO₂ \cdots β_{12} /GN complexes in the parallel configuration had the maximum negative charge transfer values, up to -0.0304 e, outlining the electron-donating character of CO₂. The CS₂ and CSe₂ molecules frequently exhibited dual behavior as electron donors in the vertical configuration and acceptors in the parallel one. Band structure results addressed some differences observed for the electronic structures of the pure β_{12} and GN sheets after the adsorption process, especially in the parallel configuration compared with the vertical one. According to the results of the density of states, new peaks were observed after adsorbing CX₂ molecules on the studied 2D sheets. These results form a fundamental basis for future studies pertaining to applications of β_{12} and GN sheets for detecting toxic carbon dichalcogenides.

Keywords: graphene; borophene; carbon dichalcogenides; adsorption process; DFT

1. Introduction

Recently, the emission of greenhouse gases and toxic molecules into the environment has gathered unprecedented attention from the scholarly community. These molecules might cause severe heart and lung conditions and contribute to the greenhouse impact and the destruction of the ozone layer [1–4]. Among these harmful molecules, carbon dioxide (CO₂) is a crucial gas because of its high concentration in the atmosphere as a result of the combustion of petroleum, coal, and other fossil fuels [5]. Carbon disulfide (CS₂) is another toxic gas that adversely affects human health. It was documented that exposure to CS₂ gas leads to many problems, including paucity of vitamin B₆ and an increase in heart attack risk [6,7]. In the same vein, the carbon diselenide (CSe₂) molecule is well recognized as a highly toxic molecule with unpleasant properties [8,9]. Because of its high toxicity, the CSe₂ molecule must be handled with utmost care [10]. Many researchers have accordingly focused their efforts on developing various effective sensors for monitoring such toxic molecules. Two-dimensional (2D) materials are a topic of interest for sensing purposes due to their vital physical and chemical properties. Graphene (GN), the first 2D form of carbon produced experimentally in 2004 [11], has received sustained attention due to its superior optical and mechanical properties [12–17]. Based on the electronic properties of 2D materials, the GN sheet was previously nominated as a Dirac material and could be recognized by defining its pseudomobility energy edges, energy spectrum surrounding the Fermi energy, and zero-energy confined state modes [18].

Crucially, GN has been used in many fields such as gas sensors [19], energy production [20], and spintronic devices [21]. The utilization of pristine and doped GN in detecting toxic gases, such as CO, NO, NO₂, and NH₃, has been investigated [14,22,23].

In addition to GN, many 2D materials have been developed, like molybdenum disulfide [24–26], phosphorene [27,28], silicene [29,30], and germanene [31,32], as active nanomaterials. Among the new 2D materials, borophene [33] has aroused the interest of the academic community. Indeed, borophene has been well characterized with versatile superior properties, including superconductivity, chemical complexity, low density, large bulk modulus, and high carrier mobility [34–36]. Borophene was earlier synthesized on a silver (111) surface in an ultrahigh vacuum [33]. Two phases of borophene have been observed using various deposition temperatures: the β_{12} phase with 1/6 vacancy concentration and the χ_3 phase with 1/5 vacancy concentration [37]. From the literature, experimental and theoretical studies have revealed that all phases of borophene are metallic and exhibit superb electronic conductivity [37,38]. Further electronic properties of borophene as a Weyl 2D material, including high anisotropy and topological character, were also revealed [39,40].

The most stable type of borophene was reported to be β_{12} borophene (β_{12}) [37,41]. Therefore, the sensing and trapping of greenhouse gases and other atmospheric pollutants (e.g., CO_x, CH₄, NH₃, and NO_x) using the β_{12} sheet has grown significantly [42–45].

Hence, this work was accordingly designed in order to deeply understand the potentiality of β_{12} and GN sheets to adsorb CX₂ toxic molecules by employing density functional theory (DFT) calculations. In that spirit, the CX₂··· β_{12} /GN complexes (CX₂; X = O, S, or Se) were characterized in both vertical and parallel configurations (Figure 1). The geometric structures of CX₂··· β_{12} /GN complexes were first subjected to relax calculations to obtain the minimum structures. The adsorption energies were then computed upon the relaxed structures of all the complexes under study. For most stable CX₂··· β_{12} /GN complexes, charge transfer, electronic band structure, and density of state (DOS) analyses were performed to clearly elucidate the effect of the adsorption process on the features of the inspected 2D sheets. The findings of this study form a basis for future studies relevant to the applications of β_{12} and GN.



Figure 1. $CSe_2 \cdots GN$ complex as an illustration for the $CX_2 \cdots 2D$ sheet complexes (where $CX_2 = CO_2$, CS_2 , or CSe_2 and the 2D sheet = β_{12} or GN) within vertical and parallel configurations from the side and top representations.

2. Computational Methods

Geometric optimization and energy calculations of the $CX_2 \cdots \beta_{12}/GN$ complexes $(CX_2; X = O, S, or Se)$ were carried out in accordance with density functional theory (DFT) [46,47] via the Quantum ESPRESSO 6.4.1 package [48,49]. To describe the electronic interactions, the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional of the Generalized Gradient Approximation (GGA) was applied [50]. Ultrasoft pseudopotential was adopted for describing the interaction of valence electrons and the atomic cores [51]. The Grimme (DFT-D2) algorithm [52] was applied to correct the dispersion energy of the van der Waals interactions. In all the executed computations, the energy cutoff was set to 50 Ry, and the charge density cutoff was 500 Ry. The structures were optimized at energy and force convergence of 10^{-5} eV and 10^{-4} eV/Å, respectively. To sample and analyze the first Brillouin zone (BZ), Monkhorst–Pack grids were utilized with $6 \times 6 \times 1$ k-points for geometric optimization and adsorption energy calculations. For the electronic structure calculations, $12 \times 12 \times 1$ k-points were utilized. The Marzari–Vanderbilt smearing technique was performed to speed up the convergence [53]. To avoid interactions between neighboring atoms in the *z*-direction of the β_{12} and GN sheets, a vacuum layer with 20 Å was used. Supercells of $3 \times 4 \times 1$ and $6 \times 5 \times 1$ were modeled to calculate the adsorption energy of β_{12} - and GN-containing complexes, respectively, containing 60 atoms in both sheets. For the CX₂··· β_{12} /GN complexes, both vertical and parallel configurations were considered, as depicted in Figure 1. The adsorption energy (E_{ads}) of all the studied complexes was computed using Equation (1):

$$E_{\text{ads}} = E_{\text{CX}_2 \dots \text{2D sheet}} - \left(E_{\text{CX}_2} + E_{\text{2D sheet}}\right) \tag{1}$$

where $E_{CX_2...2D \text{ sheet}}$, E_{CX_2} , and $E_{2D \text{ sheet}}$ represent the energies of complexes, adsorbed CX₂ molecules, and 2D sheets, respectively. The charge density difference ($\Delta \rho$) calculations were estimated using Equation (2):

$$\Delta \rho = \rho_{\text{total}} - \left(\rho_{\text{CX}_2} + \rho_{\text{2D sheet}}\right) \tag{2}$$

where ρ_{total} , ρ_{CX_2} , and $\rho_{2\text{D sheet}}$ are the charge densities of complexes, adsorbed CX₂ molecules, and 2D sheets, respectively. The Visualization for Electronic and Structural Analysis (VESTA) package was used to generate the $\Delta\rho$ maps [54]. Analysis of the Bader charge [55] was utilized to determine the charge transfer (Q_t) to or from the 2D sheets according to Equation (3):

$$Q_{\rm t} = Q_{\rm combined \ 2D \ sheet} - Q_{\rm isolated \ 2D \ sheet} \tag{3}$$

where $Q_{\text{combined 2D sheet}}$ indicates the total charge of the 2D sheets after the adsorption process, and $Q_{\text{isolated 2D sheet}}$ represents the total charge of the 2D sheets before the adsorption process. To elucidate the electronic properties, the electronic band structure and the total and projected density of states (TDOS and PDOS) calculations were determined for the inspected 2D sheets. For the band structure calculations, high-symmetry points—namely, Γ (0.0, 0.0, 0.0), Y (0.5, 0.0, 0.0), S (0.5, 0.5, 0.0), and X (0.0, 0.5, 0.0)—were selected, and 50 points were taken between each high-symmetry point.

3. Results and Discussion

3.1. Geometric Structures

The structures of the β_{12} and GN sheets were fully relaxed prior to the adsorption of the CX₂ molecules on their surfaces, and the obtained structures are given in Figure 2.

After the relaxation of the β_{12} and GN sheets, the optimized lattice parameters of their primitive cells were a = 5.06 Å and b = 2.93 Å for β_{12} sheets (Figure 2), while a and b had a similar value of 2.47 Å in the case of GN sheets. The obtained findings were compatible with experimental and theoretical evidence [33,37,56,57].



Figure 2. Side and top representations for optimized structures of $3 \times 4 \times 1 \beta_{12}$ and $6 \times 5 \times 1$ GN with the modeled adsorption sites. T, Br, and H refer to top, bridge, and hollow sites.

According to the equilibrium structures displayed in Figure 2, four probable adsorption sites were identified in the β_{12} sheet—namely, top (T), hollow (H), and two bridge (Br1 and Br2) sites. For GN sheets, the top (T), bridge (Br), and hollow (H) sites were located above the carbon atom, C–C bond, and center of the hexagonal ring, respectively.

3.2. Adsorption Energy Calculations

The adsorption process within the vertical and parallel configurations of the $CX_2 \cdots \beta_{12}/GN$ complexes (where X = O, S, or Se) was unveiled at variant sites (Figure 2). The $CX_2 \cdots \beta_{12}/GN$ complexes were first relaxed, and the obtained structures are given in Figure S1. The adsorption energies (E_{ads}) for all relaxed complexes were then assessed and are gathered in Table 1. The most desirable relaxed structures of the $CX_2 \cdots \beta_{12}/GN$ complexes are provided in Figure 3.

Apparently, the relaxed structures of the CX₂··· β_{12} /GN complexes showed the ability of the β_{12} and GN sheets to adsorb toxic CX₂ molecules (Figure S1), resulting in significant negative adsorption energies (Table 1). From Figure 3 and Table 1, the CX₂ β_{12} and GN equilibrium distances were found to be in the ranges 3.04–3.49 and 3.03–3.55 Å, respectively.

For adsorption of the CX₂ molecules on the β_{12} sheet in the vertical configuration, the CS₂··· and CSe₂··· H@ β_{12} complexes exhibited the most significant negative adsorption energies with values of -4.25 and -6.73 kcal/mol, respectively. For the CO₂··· β_{12} complexes, the most favorable adsorption energy value of -2.13 kcal/mol was obtained at the Br2 adsorption site of the β_{12} sheet (Table 1). In the parallel configuration, it was observed that the most favorable adsorption site on the β_{12} sheet for adsorbing all the CX₂ molecules was the H@ β_{12} site (Figure 3). Notably, the CSe₂···H@ β_{12} complex had the largest negative adsorption energy, followed by the CS₂···H@ β_{12} and CO₂···H@ β_{12} complexes, with values of -10.96, -6.53, and -4.42 kcal/mol, respectively (Table 1).

Similar to the $CX_2 \cdots \beta_{12}$ complexes, the most considerable negative adsorption energies were generally observed in the case of $CSe_2 \cdots GN$ complexes. In the case of the vertical configuration, the E_{ads} values of the studied complexes were noticed to decrease in the order $CX_2 \cdots H@GN > \cdots Br@GN > \cdots T@GN$, showing the favorability of the H@GN site. Numerically, the E_{ads} values of $CS_2 \cdots H@GN$, $CS_2 \cdots Br@GN$, and $CS_2 \cdots T@GN$ were found to be -3.28, -3.14, and -3.13 kcal/mol, respectively. For the parallel configuration, the favorability of the CX₂···GN complexes increased in the order of CX₂···H@GN < CX₂···Br@GN. It was also observed that the CSe₂···Br@GN complex with an equilibrium distance of 3.47 Å had the most significant E_{ads} , with a value of -6.91 kcal/mol (Table 1).

Ultimately, all the studied carbon dichalcogenides (CX₂; X = O, S, or Se) showed negative values of E_{ads} , indicating greater preferentiality of the parallel configuration of the CX₂··· β_{12} /GN complexes compared with the vertical one.

Table 1. Adsorption energies (E_{ads} , kcal/mol) and equilibrium distances (d, Å) for the vertical and parallel configurations of the CX₂··· β_{12} /GN complexes (where X = O, S, or Se), in addition to the charge transfer differences (Q_t , e) for the investigated 2D sheets after adsorbing the CX₂ molecules.

	Adsorption Site ^a	Carbon Dichalcogenides (CX ₂)								
2D Sheet		CO ₂			CS ₂			CSe ₂		
		E _{ads} (kcal/mol)	d (Å)	Q _t ^b (e)	E _{ads} (kcal/mol)	d (Å)	Q_t^{b} (e)	E _{ads} (kcal/mol)	d (Å)	$Q_t^{b}(e)$
Vertical Configuration ^c										
β ₁₂	T H Br1 Br2	-2.05 -1.76 -d -2.13	3.24 3.14 d 3.17	$-0.0117 \\ -0.0122 \\ ^{d} \\ -0.0120$	-3.54 -4.25 d -3.47	3.35 3.09 ^d 3.34	$-0.0219 \\ -0.0199 \\ -d \\ -0.0233$	-5.35 -6.73 d -5.04	3.30 3.04 ^d 3.33	-0.0127 -0.0036 -d -0.0189
GN	T H Br	$-1.77 \\ -1.95 \\ -1.79$	3.16 3.03 3.14	-0.0055 -0.0059 -0.0055	-3.13 -3.28 -3.14	3.31 3.23 3.29	-0.0077 -0.0097 -0.0072	$-4.39 \\ -4.49 \\ -4.39$	3.31 3.26 3.30	$-0.0051 \\ -0.0072 \\ -0.0040$
Parallel Configuration ^c										
β ₁₂	T H Br1 Br2	-2.86 -4.42 -3.78 -2.96	3.41 3.17 3.22 3.37	$\begin{array}{r} -0.0213 \\ -0.0271 \\ -0.0304 \\ -0.0225 \end{array}$	-5.49 -6.53 -6.29 -5.69	3.49 3.32 3.38 3.44	0.0044 0.0139 -0.0039 0.0044	-8.54 -10.96 -9.54 -8.74	3.43 3.26 3.34 3.39	0.0513 0.0724 0.0335 0.0484
GN	T H Br	-3.64 -3.29 -3.77	3.19 3.26 3.14	$-0.0155 \\ -0.0114 \\ -0.0146$	-5.17 -4.83 -5.31	3.46 3.52 3.42	-0.0010 0.0008 -0.0019	-6.81 -6.45 -6.91	3.49 3.55 3.47	0.0063 0.0118 0.0068

^a All adsorption sites on the β_{12} and GN surfaces are shown in Figure 2. ^b Q_t was estimated using Equation (3). ^c Figure S1 displays all relaxed structures of the CX₂··· β_{12} /GN complexes. ^d No favorable adsorption was observed.



Figure 3. Cont.



Figure 3. Side and top representations for the relaxed structures of the vertical and parallel configurations of the $CX_2 \cdots \beta_{12}/GN$ complexes (where X = O, S, or Se) at the most favorable energetic sites. Equilibrium distances (d) are given in Å.

3.3. Band Structure Calculations

To trace the influence of the adsorbed CO₂, CS₂, and CSe₂ molecules on the electronic features of the β_{12} and GN sheets, electronic band structure analysis was performed for the pure and combined 2D sheets. The PBE functional was used to calculate the band structure on the high-symmetry path of the BZ. The Γ -*Y*-*S*-*X*- Γ and *Y*-*S*-*X*- Γ -*Y* paths were selected for band structures of the β_{12} and GN sheets, respectively. Figure S2 illustrates the band structures of the pure β_{12} and GN sheets. The electronic band structure calculations of the adsorbed CX₂ molecules at the most favorable adsorption sites on the β_{12} and GN sheets were plotted and are shown in Figure 4.

According to Figure S2, the electronic band structure of the pure β_{12} surface showed a metallic character that was attributed to the presence of many bands that crossed the Fermi level along the high-symmetry path. In comparison, the Dirac point on the pure GN surface between points *X* and Γ indicated that the GN exhibited a semiconductor amplitude that was consistent with that in previous work [17].

Figure 4 shows that the electronic properties of 2D sheets were marginally affected by the adsorption of the CO_2 molecule in both studied configurations on the surfaces of the β_{12} and GN sheets (see Figure S2). Such an observation outlines that β_{12} and GN cannot be highly effective CO_2 sensors, which agrees with evidence from previous studies [44,58]. In contrast, the adsorption of the CS₂ and CSe₂ molecules in vertical and parallel configurations on the β_{12} and GN sheets resulted in the appearance of many new bands in valence and conduction regions, as illustrated in Figure 4. The band structure plots showed that the bands of β_{12} moved far away from each other after adsorbing CS₂ and CSe₂ molecules, confirming the strong adsorption of these molecules on the β_{12} sheet. In detail, the resultant band structures after the adsorption of CS₂ molecules on β_{12} showed extra conduction bands in the vertical and parallel configurations at around 2.3 and 1.8 eV, respectively. Besides this, new valence bands were noticed at -1.8 and -2.0 in the vertical and parallel configurations, respectively. For $CS_2 \cdots GN$ complexes, additional conduction and valence bands in both configurations were found at 1.5 and -2.5 eV, respectively. The band structures of the CSe₂··· β_{12} complexes strongly affirmed the more evident impact of the adsorbed CSe₂ molecules on the electronic characteristics of the β_{12} sheet in the parallel configuration compared with the vertical analog. For adsorption of the CSe₂ molecule in the parallel configuration at the $H@\beta_{12}$ site, new bands were observed at 1.35, 1.55, and



1.65 eV in the conduction region. In addition, new bands at -0.4, -0.65, and -1.75 eV appeared in the valence region, as depicted in Figure 4.

Figure 4. The plots of band structure for the relaxed structures of the vertical and parallel configurations of the $CX_2 \cdots \beta_{12}$ /GN complexes (where X = O, S, or Se) at the most favorable energetic sites on the high-symmetry path of the Brillouin zone (BZ). The Fermi level is located at zero energy.

Conspicuously, the results regarding the band structure demonstrated that the CSe₂··· β_{12} complexes were more favorable than the CS₂··· β_{12} complexes, as revealed by the bands that moved toward the Fermi level. To sum up, the electronic characteristics of the studied 2D sheets after adsorbing CX₂ molecules were improved in the order CO₂··· β_{12} /GN < CS₂··· β_{12} /GN < CSe₂··· β_{12} /GN, which is consistent with the results regarding the adsorption energies (Table 1). The appearance of new valence and conduction bands indicates the interaction of the CX₂ molecules with the investigated 2D sheets. In addition, the presence of the Dirac point was not affected by the adsorption of CX₂ molecules on the GN sheet, confirming the physical adsorption of CX₂ on the GN sheet.

3.4. Charge Transfer Calculations

Bader charge analysis is considered an informative method for deducing the charge transfer throughout the adsorption process [55,59]. Thus, the charge transfer (Q_t) was calculated for the vertical and parallel configurations of the CX₂··· β_{12} /GN complexes at variant sites, and the results are given in Table 1. Negative and positive signs of the Q_t values indicate the transference of charge from the CX₂ molecules to the 2D sheet and from the 2D sheet to the adsorbed CX₂ molecules, respectively.

According to the Q_t values recorded in Table 1, adsorption of the CX₂ molecules in the vertical configuration at different adsorption sites on the β_{12} sheet was noticed with negative values of Q_t . For instance, the CO₂···, CS₂···, and CSe₂··· β_{12} complexes at the T site exhibited Q_t values of –0.0117, –0.0219, and –0.0127 *e*, respectively. These negative values demonstrate that the β_{12} sheet behaved as an electron acceptor.

The adsorption of the CO₂ molecule on the β_{12} sheet, in the case of the parallel configuration, had negative values of Q_t , demonstrating the electron donor character of the CO₂ molecule. Moreover, the adsorption of the CS₂ and CSe₂ molecules on the β_{12} sheet showed positive Q_t values, proposing that the CS₂ and CSe₂ molecules acted as electron acceptors. Numerically, Q_t values of 0.0044 and 0.0513 *e* were shifted from the β_{12} sheet toward the CS₂ and CSe₂ molecules at the T@ β_{12} site, respectively. In line with the adsorption energy results, the CSe₂···H@ β_{12} complex, the most favorable adsorption system in the parallel configuration, was found to have the largest positive Q_t value of 0.0724 *e*.

For the vertical configuration of the $CX_2 \cdots GN$ complexes, the H@GN site showed the highest negative Q_t values, consistent with its energetic preferentiality. Notably, all the $CX_2 \cdots GN$ complexes showed negative values of Q_t , illustrating the potent ability of the GN sheet to accept electrons from the CX_2 molecules.

Negative Q_t values were observed for the parallel configuration of the CO₂···T/H/Br@GN complexes, while both negative and positive Q_t values were found at the studied adsorption sites in the case of the CS₂···GN complexes. For adsorption of the CSe₂ molecule, it can be seen that the charge was transferred from the GN sheet to the adsorbed CSe₂, as indicated by the positive Q_t values shown in Table 1.

At the most favorable energetic sites, the charge density difference ($\Delta \rho$) maps of the CX₂··· β_{12} /GN complexes were plotted and are depicted in Figure 5.

As seen in Figure 5, the $\Delta\rho$ maps of the $CX_2 \cdots \beta_{12}$ complexes in the vertical configuration showed that the CX_2 molecules acted as electron donors, as demonstrated by the negative Q_t values (Table 1). In the case of the parallel configuration, the charges were shifted from the CO_2 to the β_{12} sheet, as seen from the charge accumulation region existing below the CO_2 (cyan region) and corroborated by the negative Q_t value in Table 1 (-0.0271 e). A depletion region (i.e., yellow color) was clearly observed above the β_{12} sheet in the case of the adsorption of CS_2 and CSe_2 molecules in the parallel configuration, which was consistent with the positive Q_t values stated in Table 1. This observation emphasized that CS_2 and CSe_2 molecules have the potential to draw charge from the β_{12} sheet.

For the vertical configuration of the $CX_2 \cdots GN$ complexes, the existence of regions with accumulated charge ensures the adsorption of CX_2 molecules on the β_{12} and GN sheets. The accumulated charge above the GN sheet within the $CO_2 \cdots$ and $CS_2 \cdots GN$ complexes in the parallel configuration indicated that electrons were transferred from the CO_2 and CS_2 molecules to the GN sheet (Figure 5). In comparison, the depletion region above the GN sheet in the case of adsorption of the CSe_2 molecule revealed the ability of the molecule to attract charge from the sheet.

To recapitulate, the Bader charge findings revealed that the charge was transferred from the CX₂ molecules to the studied 2D sheets in the vertical configuration, indicating the electron-donating character of the CX₂ molecules. The CO₂··· β_{12} /GN complexes in the case of parallel configuration had the largest negative Q_t values, followed by CS₂··· β_{12} /GN, then CSe₂··· β_{12} /GN complexes. The small Q_t values confirmed physical adsorption between the CX₂ molecules and the investigated 2D sheets. Consistent with the literature, the electronic properties of the β_{12} and GN sheets were changed by transferring electronic charge to or from the adsorbed molecules, indicating their potential for use as sensors [60–62].



Figure 5. Side and top representations of the charge density difference ($\Delta \rho$) maps for the relaxed structures of the vertical and parallel configurations of the CX₂··· β_{12} /GN complexes (where X = O, S, or Se) at the most favorable energetic sites. The charge accumulation and depletion are represented by the cyan and yellow colors, respectively. The isosurface values were determined in ($e/Å^3$) for each complex. Dark green, brown, red, yellow, and pale green balls refer to boron, carbon, oxygen, sulfur, and selenium atoms, respectively.

3.5. Density of State Calculations

For pure and combined 2D sheets, density of state (DOS) analysis was carried out in terms of total and projected DOS (TDOS and PDOS). The TDOS and PDOS of the pure β_{12} and GN surfaces are illustrated in Figure S3.

From the data in Figure S3, the TDOS peaks of the pure β_{12} sheet at the Fermi level had high DOS, demonstrating that the β_{12} sheet had a metallic property. In the case of the GN

surface, the TDOS peaks reached zero at the Fermi level, showing the presence of the Dirac point on the pure GN surface. The DOS results confirmed the band structures in Figure S2. For β_{12} and GN surfaces before adsorbing CX₂ molecules, the major contributions to the DOS were ascribed to the PDOS of B_p and C_p, respectively.

Figure 6 shows the TDOS and PDOS for the β_{12} and GN sheets within the vertical and parallel configurations of the CX₂··· β_{12} /GN complexes (where X = O, S, or Se) at the most favorable energetic sites. For adsorption of the CO₂ molecule on the β_{12} sheet in both configurations, a significant hybridization between the PDOS of O_p and B_p peaks was observed in the valence region between -3.9 and -4.5 eV. In addition, the TDOS and PDOS peaks of adsorption of the CO₂ molecule on the GN sheet in both configurations demonstrated the occurrence of a weak physical adsorption process. Hence, the appearance of the PDOS of O_p peaks within the CO₂··· GN complexes in both configurations was noticed in the valence and conduction regions ranging from -4.5 to -5.6 eV and from 3.5 to 4.0 eV, respectively.



Figure 6. Total and projected densities of states (TDOS/PDOS) for the relaxed structures of the vertical and parallel configurations of the $CX_2 \cdots \beta_{12}$ /GN complexes (where X = O, S, or Se) at the most favorable energetic sites. The contributions of the *p*-orbital for boron (B), carbon (C), oxygen (O), sulfur (S), and selenium (Se) atoms in the adsorption process are represented by B_p, C_p, O_p, S_p, and Se_p, respectively.

Conspicuously, the PDOS of S_p was the major contributor to the adsorption within both modeled configurations of the $CS_2 \cdots \beta_{12}/GN$ complexes. For both configurations of $CS_2 \cdots \beta_{12}$ and \cdots GN complexes, the appearance of the PDOS of S_p peaks was observed in the valence region with values from -1.5 to -2.5 eV and from -2.0 to -3.0 eV, respectively.

For both configurations of $CSe_2 \cdots \beta_{12}/GN$ complexes, the PDOS of Se_p peaks appeared in the valence region in the range from -1.0 to -2.2 eV within the $CSe_2 \cdots \beta_{12}$ complexes and from -1.5 to -2.3 eV within the $CSe_2 \cdots GN$ complexes.

Overall, the DOS results outlined that the electronic properties of the β_{12} and GN sheets were changed after adsorbing the CX₂ molecules in vertical and parallel configurations. The appearance of the new DOS peaks indicated the occurrence of adsorption of the CX₂ molecules on the investigated 2D sheets.

4. Conclusions

The adsorption of toxic carbon dichalcogenides (CX₂; X = O, S, or Se) on β_{12} and GN sheets was assessed via DFT calculations. After geometric relaxation, adsorption energy calculations and electronic analyses were carried out for vertical and parallel configurations of all $CX_2 \cdots \beta_{12}/GN$ complexes. The favorability of $CX_2 \cdots \beta_{12}/GN$ complexes was more obvious in the parallel configuration compared with the vertical one. The CSe₂··· H@ β_{12} complex in the parallel configuration was the most promising complex, with an adsorption energy value of -10.96 kcal/mol. The electronic properties of the β_{12} and GN surfaces were notably changed after the adsorption of CS_2 and CSe_2 molecules. In comparison, the electronic characteristics of the β_{12} and GN surfaces were slightly changed after adsorbing the CO_2 molecule. Based on Bader charge analysis, an electron-donating character was observed for all the CX₂ molecules in vertical configuration within the CX₂··· β_{12} /GN complexes. In comparison, the CS₂ and CSe₂ molecules acted as electron acceptors within the parallel configuration of the CS₂··· and CSe₂··· β_{12} /GN complexes. The results of the electronic band structure, TDOS, and PDOS demonstrated that adsorption of the CX_2 molecules on the β_{12} and GN sheets boosted their electronic properties. The appearance of new bands and DOS peaks affirmed the interaction of the CX_2 molecules with the investigated 2D sheets. Based on the findings of the present study, it appears promising to use the β_{12} and GN sheets as a suitable sensor for CX₂ molecules, particularly CS₂ and CSe₂ molecules.

Supplementary Materials: The following supporting information can be downloaded at: https:// www.mdpi.com/article/10.3390/nano12193411/s1, Figure S1: Side and top representations for the relaxed structures of the vertical and parallel configurations of the CX₂··· β_{12} /GN complexes (where X = O, S, or Se) at all the adsorption sites. Equilibrium distances (d) are given in Å. Figure S2: Band structure plots of β_{12} and GN sheets along the high-symmetry points of the Brillouin zone. The Fermi energy is located at zero-energy. Figure S3: Total and projected densities of states (TDOS/PDOS) plot for the pure surfaces of β_{12} and GN sheets, assuming the Fermi level as the reference level. The contributions of the *p*-orbital for boron (B) and carbon (C) atoms are represented by B_p and C_p, respectively.

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References

- 1. Wang, H.; Lustig, W.P.; Li, J. Sensing and capture of toxic and hazardous gases and vapors by metal-organic frameworks. *Chem. Soc. Rev.* **2018**, *47*, 4729–4756. [CrossRef] [PubMed]
- Zhao, B.; Wang, S.X.; Liu, H.; Xu, J.Y.; Fu, K.; Klimont, Z.; Hao, J.M.; He, K.B.; Cofala, J.; Amann, M. NO_x emissions in China: Historical trends and future perspectives. *Atmos. Chem. Phys.* 2013, *13*, 9869–9897. [CrossRef]
- DeCoste, J.B.; Peterson, G.W. Metal-organic frameworks for air purification of toxic chemicals. *Chem. Rev.* 2014, 114, 5695–5727. [CrossRef]
- Mannucci, P.M.; Harari, S.; Martinelli, I.; Franchini, M. Effects on health of air pollution: A narrative review. *Intern. Emerg. Med.* 2015, 10, 657–662. [CrossRef] [PubMed]
- Quadrelli, R.; Peterson, S. The energy-climate challenge: Recent trends in CO₂ emissions from fuel combustion. *Energy Policy* 2007, 35, 5938–5952. [CrossRef]
- 6. Zhang, C.H.; Derakhshandeh, M. CS₂ adsorption on pristine and Al-doped graphynes: A DFT study. *Comput. Theor. Chem.* **2021**, 1204, 113380. [CrossRef]
- 7. Roohi, H.; Ardehjani, N.A. Adsorption behaviour of NO, NO₂, CO and CS₂ molecules on the surface of carbon-doped gallium nitride nanosheet: A DFT study. *Surf. Sci.* **2022**, *717*, 121988. [CrossRef]
- 8. Khan, M.D.; Aamir, M.; Akhtar, J.; Malik, M.A.; Revaprasadu, N. Metal selenobenzoate complexes: Novel single source precursors for the synthesis of metal selenide semiconductor nanomaterials. *Mater. Today Proc.* **2019**, *10*, 66–74. [CrossRef]
- 9. Wittig, C.; Smith, I.W.M. Carbon monoxide chemical laser from the reaction $O + Cse \rightarrow CO^{\dagger} + Se$. *Appl. Phys. Lett.* **1972**, 21, 536–538. [CrossRef]
- Pan, W.-H.; Fackler, J.P.; Chen, H.W. Preparations and proton, carbon-13, and phosphorus-31 nuclear magnetic resonance studies of some N,N-dialkyldiselenocarbamate complexes and their phosphine derivatives. X-ray crystal structure of Pt(Se₂CN(i-Bu)₂)₂. *Inorg. Chem.* **1981**, 20, 856–863. [CrossRef]
- 11. Novoselov, K.S.; Geim, A.K.; Morozov, S.V.; Jiang, D.; Zhang, Y.; Dubonos, S.V.; Grigorieva, I.V.; Firsov, A.A. Electric field effect in atomically thin carbon films. *Science* 2004, 306, 666–669. [CrossRef]
- 12. Novoselov, K.S.; Fal'ko, V.I.; Colombo, L.; Gellert, P.R.; Schwab, M.G.; Kim, K. A roadmap for graphene. *Nature* 2012, 490, 192–200. [CrossRef]
- Schedin, F.; Geim, A.K.; Morozov, S.V.; Hill, E.W.; Blake, P.; Katsnelson, M.I.; Novoselov, K.S. Detection of individual gas molecules adsorbed on graphene. *Nat. Mater.* 2007, *6*, 652–655. [CrossRef]
- 14. Leenaerts, O.; Partoens, B.; Peeters, F.M. Adsorption of H₂O, NH₃, CO, NO₂, and NO on graphene: A first-principles study. *Phys. Rev. B Condens. Matter* **2008**, *77*, 125416–125421. [CrossRef]
- Castro Neto, A.H.; Guinea, F.; Peres, N.M.R.; Novoselov, K.S.; Geim, A.K. The electronic properties of graphene. *Rev. Mod. Phys.* 2009, *81*, 109–162. [CrossRef]
- 16. Raccichini, R.; Varzi, A.; Passerini, S.; Scrosati, B. The role of graphene for electrochemical energy storage. *Nat. Mater.* **2015**, 14, 271–279. [CrossRef]
- Ibrahim, M.A.A.; Mahmoud, A.H.M.; Soliman, K.A.; Mekhemer, G.A.H.; Ahmed, M.N.; Shawky, A.M.; Abourehab, M.A.S.; Elkaeed, E.B.; Soliman, M.E.S.; Moussa, N.A.M. Borophene and Pristine Graphene 2D Sheets as Potential Surfaces for the Adsorption of Electron-Rich and Electron-Deficient pi-Systems: A Comparative DFT Study. *Nanomaterials* 2022, 12, 1028. [CrossRef]
- 18. Naumis, G.G. Electronic properties of two-dimensional materials. In *Synthesis, Modeling, and Characterization of 2D Materials, and Their Heterostructures*; Yang, E.-H., Datta, D., Ding, J., Hader, G., Eds.; Elsevier: Amsterdam, The Netherlands, 2020; pp. 77–109.
- 19. Lee, Y.; Lee, S.; Hwang, Y.; Chung, Y.-C. Modulating magnetic characteristics of Pt embedded graphene by gas adsorption (N₂, O₂, NO₂, SO₂). *Appl. Surf. Sci.* **2014**, *289*, 445–449. [CrossRef]
- 20. Shao, Y.; Zhang, S.; Engelhard, M.H.; Li, G.; Shao, G.; Wang, Y.; Liu, J.; Aksay, I.A.; Lin, Y. Nitrogen-doped graphene and its electrochemical applications. *J. Mater. Chem.* **2010**, *20*, 7491–7496. [CrossRef]
- 21. Tang, Y.A.; Yang, Z.X.; Dai, X.Q. Noble metals induced magnetic properties of graphene. J. Magn. Magn. Mater. 2011, 323, 2441–2447. [CrossRef]
- Zhang, Y.H.; Chen, Y.B.; Zhou, K.G.; Liu, C.H.; Zeng, J.; Zhang, H.L.; Peng, Y. Improving gas sensing properties of graphene by introducing dopants and defects: A first-principles study. *Nanotechnology* 2009, 20, 185504. [CrossRef]
- 23. Dai, J.Y.; Yuan, J.M.; Giannozzi, P. Gas adsorption on graphene doped with B, N, Al, and S: A theoretical study. *Appl. Phys. Lett.* **2009**, *95*, 232105. [CrossRef]
- Azhagurajan, M.; Kajita, T.; Itoh, T.; Kim, Y.G.; Itaya, K. In Situ Visualization of Lithium Ion Intercalation into MoS₂ Single Crystals using Differential Optical Microscopy with Atomic Layer Resolution. J. Am. Chem. Soc. 2016, 138, 3355–3361. [CrossRef] [PubMed]
- Hwang, H.; Kim, H.; Cho, J. MoS₂ nanoplates consisting of disordered graphene-like layers for high rate lithium battery anode materials. *Nano Lett.* 2011, 11, 4826–4830. [CrossRef] [PubMed]
- Zhao, S.J.; Xue, J.M.; Kang, W. Gas adsorption on MoS₂ monolayer from first-principles calculations. *Chem. Phys. Lett.* 2014, 595–596, 35–42. [CrossRef]

- 27. Li, Y.; Wu, W.; Ma, F. Blue phosphorene/graphene heterostructure as a promising anode for lithium-ion batteries: A first-principles study with vibrational analysis techniques. *J. Mater. Chem. A* 2019, *7*, 611–620. [CrossRef]
- Cai, Y.Q.; Zhang, G.; Zhang, Y.W. Electronic Properties of Phosphorene/Graphene and Phosphorene/Hexagonal Boron Nitride Heterostructures. J. Phys. Chem. C 2015, 119, 13929–13936. [CrossRef]
- Aufray, B.; Kara, A.; Vizzini, S.; Oughaddou, H.; Leandri, C.; Ealet, B.; Le Lay, G. Graphene-like silicon nanoribbons on Ag(110): A possible formation of silicene. *Appl. Phys. Lett.* 2010, *96*, 183102. [CrossRef]
- Du, Y.; Zhuang, J.; Liu, H.; Xu, X.; Eilers, S.; Wu, K.; Cheng, P.; Zhao, J.; Pi, X.; See, K.W.; et al. Tuning the band gap in silicene by oxidation. ACS Nano 2014, 8, 10019–10025. [CrossRef] [PubMed]
- Cahangirov, S.; Topsakal, M.; Akturk, E.; Sahin, H.; Ciraci, S. Two- and one-dimensional honeycomb structures of silicon and germanium. *Phys. Rev. Lett.* 2009, 102, 236804. [CrossRef]
- 32. Derivaz, M.; Dentel, D.; Stephan, R.; Hanf, M.C.; Mehdaoui, A.; Sonnet, P.; Pirri, C. Continuous germanene layer on Al(111). *Nano Lett.* **2015**, *15*, 2510–2516. [CrossRef]
- Mannix, A.J.; Zhou, X.F.; Kiraly, B.; Wood, J.D.; Alducin, D.; Myers, B.D.; Liu, X.; Fisher, B.L.; Santiago, U.; Guest, J.R.; et al. Synthesis of borophenes: Anisotropic, two-dimensional boron polymorphs. *Science* 2015, 350, 1513–1516. [CrossRef]
- Li, H.; Jing, L.; Liu, W.; Lin, J.; Tay, R.Y.; Tsang, S.H.; Teo, E.H.T. Scalable Production of Few-Layer Boron Sheets by Liquid-Phase Exfoliation and Their Superior Supercapacitive Performance. ACS Nano 2018, 12, 1262–1272. [CrossRef]
- Ranjan, P.; Sahu, T.K.; Bhushan, R.; Yamijala, S.S.; Late, D.J.; Kumar, P.; Vinu, A. Freestanding Borophene and Its Hybrids. *Adv. Mater.* 2019, 31, e1900353. [CrossRef]
- Zhou, H.B.; Cai, Y.Q.; Zhang, G.; Zhang, Y.W. Superior lattice thermal conductance of single-layer borophene. NPJ 2D Mater. Appl. 2017, 1, 14. [CrossRef]
- 37. Feng, B.; Zhang, J.; Zhong, Q.; Li, W.; Li, S.; Li, H.; Cheng, P.; Meng, S.; Chen, L.; Wu, K. Experimental realization of twodimensional boron sheets. *Nat. Chem.* 2016, *8*, 563–568. [CrossRef]
- Zhang, Z.; Yang, Y.; Gao, G.; Yakobson, B.I. Two-dimensional boron monolayers mediated by metal substrates. *Angew. Chem.* 2015, 54, 13022–13026. [CrossRef]
- Li, X.B.; Xie, S.Y.; Zheng, H.; Tian, W.Q.; Sun, H.B. Boron based two-dimensional crystals: Theoretical design, realization proposal and applications. *Nanoscale* 2015, 7, 18863–18871. [CrossRef]
- 40. Penev, E.S.; Kutana, A.; Yakobson, B.I. Can Two-Dimensional Boron Superconduct? Nano Lett. 2016, 16, 2522–2526. [CrossRef]
- Xu, S.G.; Zhao, Y.J.; Liao, J.H.; Yang, X.B.; Xu, H. The nucleation and growth of borophene on the Ag (111) surface. *Nano Res.* 2016, 9, 2616–2622. [CrossRef]
- Qin, G.Q.; Cui, Q.Y.; Du, A.J.; Sun, Q. Borophene: A metal-free and metallic electrocatalyst for efficient converting CO₂ into CH₄. ChemCatChem 2020, 12, 1483–1490. [CrossRef]
- Tan, X.; Tahini, H.A.; Smith, S.C. Borophene as a promising material for charge-modulated switchable CO₂ capture. ACS Appl. Mater. Interfaces 2017, 9, 19825–19830. [CrossRef] [PubMed]
- 44. Ta, L.T.; Hamada, I.; Morikawa, Y.; Dinh, V.A. Adsorption of toxic gases on borophene: Surface deformation links to chemisorptions. *RSC Adv.* **2021**, *11*, 18279–18287. [CrossRef]
- Huang, C.S.; Murat, A.; Babar, V.; Montes, E.; Schwingenschlogl, U. Adsorption of the gas molecules NH₃, NO, NO₂, and CO on borophene. J. Phys. Chem. C 2018, 122, 14665–14670. [CrossRef]
- Kresse, G.; Furthmuller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev.* B Condens. Matter 1996, 54, 11169–11186. [CrossRef] [PubMed]
- 47. Kresse, G.; Furthmuller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comp. Mater. Sci.* **1996**, *6*, 15–50. [CrossRef]
- Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G.L.; Cococcioni, M.; Dabo, I.; et al. QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials. *J. Phys. Condens. Matter* 2009, *21*, 395502. [CrossRef]
- Giannozzi, P.; Andreussi, O.; Brumme, T.; Bunau, O.; Buongiorno Nardelli, M.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Cococcioni, M.; et al. Advanced capabilities for materials modelling with Quantum ESPRESSO. *J. Phys. Condens. Matter* 2017, 29,465901. [CrossRef]
- 50. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, 77, 3865–3868. [CrossRef]
- 51. Vanderbilt, D. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Phys. Rev. B Condens. Matter* **1990**, 41, 7892–7895. [CrossRef]
- 52. Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* **2006**, *27*, 1787–1799. [CrossRef]
- 53. Marzari, N.; Vanderbilt, D.; De Vita, A.; Payne, M.C. Thermal contraction and disordering of the Al(110) surface. *Phys. Rev. Lett.* **1999**, *82*, 3296–3299. [CrossRef]
- Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. J. Appl. Crystallogr. 2011, 44, 1272–1276. [CrossRef]
- 55. Henkelman, G.; Arnaldsson, A.; Jonsson, H. A fast and robust algorithm for Bader decomposition of charge density. *Comp. Mater. Sci.* **2006**, *36*, 354–360. [CrossRef]

- 56. Peng, B.; Zhang, H.; Shao, H.Z.; Ning, Z.Y.; Xu, Y.F.; Ni, G.; Lu, H.L.; Zhang, D.W.; Zhu, H.Y. Stability and strength of atomically thin borophene from first principles calculations. *Mater. Res. Lett.* **2017**, *5–6*, 399–407. [CrossRef]
- 57. Chakarova-Kack, S.D.; Schroder, E.; Lundqvist, B.I.; Langreth, D.C. Application of van der Waals density functional to an extended system: Adsorption of benzene and naphthalene on graphite. *Phys. Rev. Lett.* **2006**, *96*, 146107. [CrossRef]
- Lu, Y.H.; Xu, Y.J.; Zhang, J.A.; Zhang, Q.W.; Li, L.; Tian, J.L. Adsorption of Carbon Dioxide Gas by Modified Graphene: A Theoretical Study. *Chemistryselect* 2022, 7, e202104067. [CrossRef]
- 59. Bader, R.F.W. Atoms in Molecules: A Quantum Theory, 1st ed.; Clarendon Press: Oxford, UK, 1990; Volume XVIII, p. 438.
- Sun, Q.; Yang, Z.; Huo, Y.; Liu, R.; Xu, L.-C.; Xue, L.; Liu, X. Designing and optimizing β1-borophene organic gas sensor: A theoretical study. *Surf. Sci.* 2022, 719, 122030. [CrossRef]
- 61. Liu, W.J.; Zhang, C.; Deng, M.S.; Cai, S.H. The structural and electronic properties of metal atoms adsorbed on graphene. *Phys. E* **2017**, *93*, 265–270. [CrossRef]
- 62. Zhang, T.; Sun, H.; Wang, F.D.; Zhang, W.D.; Tang, S.W.; Ma, J.M.; Gong, H.W.; Zhang, J.P. Adsorption of phosgene molecule on the transition metal-doped graphene: First principles calculations. *Appl. Surf. Sci.* **2017**, *425*, 340–350. [CrossRef]