Adsorption Behavior of Toxic Carbon Dichalcogenides (CX₂; X = O, S, or Se) on β₁₂ Borophene and Pristine Graphene Sheets: A DFT Study

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Abstract: The adsorption of toxic carbon dichalcogenides (CX₂; X = O, S, or Se) on β₁₂ borophene (β₁₂) and pristine graphene (GN) sheets was comparatively investigated. Vertical and parallel configurations of CX₂···β₁₂/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 CX₂···β₁₂/GN complexes decreased in the order CSe₂ > CS₂ > CO₂, indicating that β₁₂ and GN sheets showed significant selectivity for the CSe₂ molecule with superb potentiality for β₁₂ sheets. Bader charge transfer analysis revealed that the CO₂···β₁₂/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 β₁₂ 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 β₁₂ 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 β₁₂ phase with 1/6 vacancy concentration and the χ₃ 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 β₁₂ borophene (β₁₂) [37,41]. Therefore, the sensing and trapping of greenhouse gases and other atmospheric pollutants (e.g., CO₂, CH₄, NH₃, and NOₓ) using the β₁₂ sheet has grown significantly [42–45].

Hence, this work was accordingly designed in order to deeply understand the potentiality of β₁₂ and GN sheets to adsorb CX₂ toxic molecules by employing density functional theory (DFT) calculations. In that spirit, the CX₂ ⋅ β₁₂/GN complexes (CX₂: X = O, S, or Se) were characterized in both vertical and parallel configurations (Figure 1). The geometric structures of CX₂ ⋅ β₁₂/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 ⋅ β₁₂/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 β₁₂ and GN.

**Figure 1.** CSe₂ ⋅ GN complex as an illustration for the CX₂ ⋅ 2D sheet complexes (where CX₂ = CO₂, CS₂, or CSe₂ and the 2D sheet = β₁₂ or GN) within vertical and parallel configurations from the side and top representations.
2. Computational Methods

Geometric optimization and energy calculations of the CX$_2$···β$_{12}$/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 CX$_2$···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):

$$E_{ads} = E_{CX_2 \cdot \cdot 2D\, sheet} - (E_{CX_2} + E_{2D\, sheet})$$  \hspace{1cm} (1)

where $E_{CX_2 \cdot \cdot 2D\, sheet}$, $E_{CX_2}$, and $E_{2D\, sheet}$ represent the energies of complexes, adsorbed CX$_2$ molecules, and 2D sheets, respectively. The charge density difference ($\Delta \rho$) calculations were estimated using Equation (2):

$$\Delta \rho = \rho_{total} - (\rho_{CX_2} + \rho_{2D\, sheet})$$  \hspace{1cm} (2)

where $\rho_{total}$, $\rho_{CX_2}$, and $\rho_{2D\, sheet}$ are the charge densities of complexes, adsorbed CX$_2$ 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):

$$Q_t = Q_{combined\, 2D\, sheet} - Q_{isolated\, 2D\, sheet}$$  \hspace{1cm} (3)

where $Q_{combined\, 2D\, sheet}$ indicates the total charge of the 2D sheets after the adsorption process, and $Q_{isolated\, 2D\, sheet}$ 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, $\Gamma$ (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 CX$_2$ 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].
According to the equilibrium structures displayed in Figure 2, four probable adsorption sites were identified in the $\beta_{12}$ 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 $\text{CX}_2 \cdots \beta_{12} / \text{GN}$ complexes (where $X = \text{O, S, or Se}$) was unveiled at variant sites (Figure 2). The $\text{CX}_2 \cdots \beta_{12} / \text{GN}$ complexes were first relaxed, and the obtained structures are given in Figure S1. The adsorption energies ($E_{\text{ads}}$) for all relaxed complexes were then assessed and are gathered in Table 1. The most desirable relaxed structures of the $\text{CX}_2 \cdots \beta_{12} / \text{GN}$ complexes are provided in Figure 3.

Apparently, the relaxed structures of the $\text{CX}_2 \cdots \beta_{12} / \text{GN}$ complexes showed the ability of the $\beta_{12}$ and GN sheets to adsorb toxic $\text{CX}_2$ molecules (Figure S1), resulting in significant negative adsorption energies (Table 1). From Figure 3 and Table 1, the $\text{CX}_2$ $\beta_{12}$ 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 $\text{CX}_2$ molecules on the $\beta_{12}$ sheet in the vertical configuration, the $\text{CS}_2 \cdots \beta_{12}$ and $\text{CSe}_2 \cdots \beta_{12}$ complexes exhibited the most significant negative adsorption energies with values of $-4.25$ and $-6.73$ kcal/mol, respectively. For the $\text{CO}_2 \cdots \beta_{12}$ complexes, the most favorable adsorption energy value of $-2.13$ kcal/mol was obtained at the Br2 adsorption site of the $\beta_{12}$ sheet (Table 1). In the parallel configuration, it was observed that the most favorable adsorption site on the $\beta_{12}$ sheet for adsorbing all the $\text{CX}_2$ molecules was the $\text{H} \cdots \beta_{12}$ site (Figure 3). Notably, the $\text{CSe}_2 \cdots \beta_{12}$ complex had the largest negative adsorption energy, followed by the $\text{CS}_2 \cdots \beta_{12}$ and $\text{CO}_2 \cdots \beta_{12}$ complexes, with values of $-10.96$, $-6.53$, and $-4.42$ kcal/mol, respectively (Table 1).

Similar to the $\text{CX}_2 \cdots \beta_{12}$ complexes, the most considerable negative adsorption energies were generally observed in the case of $\text{CSe}_2 \cdots \text{GN}$ complexes. In the case of the vertical configuration, the $E_{\text{ads}}$ values of the studied complexes were noticed to decrease in the order $\text{CX}_2 \cdots \text{H} \cdots \text{GN} > \text{Br} \cdots \text{GN} > \text{T} \cdots \text{GN}$, showing the favorability of the $\text{H} \cdots \text{GN}$ site. Numerically, the $E_{\text{ads}}$ values of $\text{CS}_2 \cdots \text{H} \cdots \text{GN}$, $\text{CSe}_2 \cdots \text{Br} \cdots \text{GN}$, and $\text{CS}_2 \cdots \text{T} \cdots \text{GN}$ were found to be $-3.28$, $-3.14$, and $-3.13$ kcal/mol, respectively. For the
parallel configuration, the favorability of the \( \text{CX}_2 \cdots \beta_{12}/\text{GN} \) complexes increased in the order of \( \text{CX}_2 \cdots \text{H}@\text{GN} < \text{CX}_2 \cdots \text{T}@\text{GN} < \text{CX}_2 \cdots \text{Br}@\text{GN} \). It was also observed that the \( \text{CSe}_2 \cdots \text{Br}@\text{GN} \) complex with an equilibrium distance of 3.47 Å had the most significant \( E_{\text{ads}} \), with a value of \(-6.91\) kcal/mol (Table 1).

Ultimately, all the studied carbon dichalcogenides (\( \text{CX}_2; X = \text{O}, \text{S}, \text{or Se} \)) showed negative values of \( E_{\text{ads}} \), indicating greater preferentiality of the parallel configuration of the \( \text{CX}_2 \cdots \beta_{12}/\text{GN} \) complexes compared with the vertical one.

Table 1. Adsorption energies (\( E_{\text{ads}} \), kcal/mol) and equilibrium distances (\( d \), Å) for the vertical and parallel configurations of the \( \text{CX}_2 \cdots \beta_{12}/\text{GN} \) complexes (where \( X = \text{O}, \text{S}, \text{or Se} \)), in addition to the charge transfer differences (\( Q_t \), e) for the investigated 2D sheets after adsorbing the \( \text{CX}_2 \) molecules.

| 2D Sheet | Adsorption Site |  | Carbon Dichalcogenides (\( \text{CX}_2 \)) |  |  | Carbon Dichalcogenides (\( \text{CX}_2 \)) |
|----------|----------------|---|-------------------------------------------|---|---|-------------------------------------------|
|          |                | \( \text{CO}_2 \) | \( \text{CS}_2 \) | \( \text{CSe}_2 \) | \( \text{CO}_2 \) | \( \text{CS}_2 \) | \( \text{CSe}_2 \) |
|          |                | \( E_{\text{ads}} \) (kcal/mol) | \( d \) (Å) | \( Q_t \) b (e) | \( E_{\text{ads}} \) (kcal/mol) | \( d \) (Å) | \( Q_t \) b (e) | \( E_{\text{ads}} \) (kcal/mol) | \( d \) (Å) | \( Q_t \) b (e) |
| Vertical Configuration \( ^c \) | \( \beta_{12} \) | T | \(-2.05\) | \(3.24\) | \(-0.0117\) | \(-3.54\) | \(3.35\) | \(-0.0219\) | \(-5.35\) | \(3.30\) | \(-0.0127\) |
|        |                | H | \(-1.76\) | \(3.14\) | \(-0.0122\) | \(-4.25\) | \(3.09\) | \(-0.0199\) | \(-6.73\) | \(3.04\) | \(-0.0036\) |
|        |                | Br1 | \(-\) | \(3.17\) | \(-0.0120\) | \(-3.47\) | \(3.34\) | \(-0.0233\) | \(-5.04\) | \(3.33\) | \(-0.0189\) |
|        |                | Br2 | \(-2.13\) | \(3.17\) | \(-0.0120\) | \(-3.47\) | \(3.34\) | \(-0.0233\) | \(-5.04\) | \(3.33\) | \(-0.0189\) |
|        |                | GN | T | \(-1.77\) | \(3.16\) | \(-0.0055\) | \(-3.13\) | \(3.31\) | \(-0.0077\) | \(-4.39\) | \(3.31\) | \(-0.0051\) |
|        |                | H | \(-1.95\) | \(3.03\) | \(-0.0059\) | \(-3.28\) | \(3.23\) | \(-0.0097\) | \(-4.49\) | \(3.26\) | \(-0.0072\) |
|        |                | Br | \(-1.79\) | \(3.14\) | \(-0.0055\) | \(-3.14\) | \(3.29\) | \(-0.0072\) | \(-4.39\) | \(3.30\) | \(-0.0040\) |
|        |                | \( ^d \) | \( ^d \) | \( ^d \) | \( ^d \) | \( ^d \) | \( ^d \) | \( ^d \) | \( ^d \) | \( ^d \) | \( ^d \) |
|        |                | GN | T | \(-3.64\) | \(3.19\) | \(-0.0155\) | \(-5.17\) | \(3.46\) | \(-0.0100\) | \(-6.81\) | \(3.49\) | \(0.0063\) |
|        |                | H | \(-3.29\) | \(3.26\) | \(-0.0114\) | \(-4.83\) | \(3.52\) | \(0.0008\) | \(-6.45\) | \(3.55\) | \(0.0118\) |
|        |                | Br | \(-3.77\) | \(3.14\) | \(-0.0146\) | \(-5.31\) | \(3.42\) | \(-0.0199\) | \(-6.91\) | \(3.47\) | \(0.0068\) |
| Parallel Configuration \( ^c \) | \( \beta_{12} \) | T | \(-3.86\) | \(3.41\) | \(-0.0213\) | \(-5.49\) | \(3.49\) | \(0.0044\) | \(-8.54\) | \(3.43\) | \(0.0513\) |
|        |                | H | \(-4.42\) | \(3.17\) | \(-0.0271\) | \(-6.53\) | \(3.32\) | \(0.0139\) | \(-10.96\) | \(3.26\) | \(0.0724\) |
|        |                | Br1 | \(-3.78\) | \(3.22\) | \(-0.0304\) | \(-6.29\) | \(3.38\) | \(-0.0039\) | \(-9.54\) | \(3.34\) | \(0.0335\) |
|        |                | Br2 | \(-2.96\) | \(3.37\) | \(-0.0225\) | \(-5.69\) | \(3.44\) | \(0.0044\) | \(-8.74\) | \(3.39\) | \(0.0484\) |
|        |                | GN | T | \(-3.64\) | \(3.19\) | \(-0.0155\) | \(-5.17\) | \(3.46\) | \(-0.0100\) | \(-6.81\) | \(3.49\) | \(0.0063\) |
|        |                | H | \(-3.29\) | \(3.26\) | \(-0.0114\) | \(-4.83\) | \(3.52\) | \(0.0008\) | \(-6.45\) | \(3.55\) | \(0.0118\) |
|        |                | Br | \(-3.77\) | \(3.14\) | \(-0.0146\) | \(-5.31\) | \(3.42\) | \(-0.0199\) | \(-6.91\) | \(3.47\) | \(0.0068\) |
|        |                | \( ^d \) | \( ^d \) | \( ^d \) | \( ^d \) | \( ^d \) | \( ^d \) | \( ^d \) | \( ^d \) | \( ^d \) | \( ^d \) |

\( a \) All adsorption sites on the \( \beta_{12} \) 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 \( \text{CX}_2 \cdots \beta_{12}/\text{GN} \) complexes. \( d \) No favorable adsorption was observed.

Figure 3. Side and top representations for the relaxed structures of the vertical and parallel configurations of the \( \text{CX}_2 \cdots \beta_{12}/\text{GN} \) complexes (where \( X = \text{O}, \text{S}, \text{or Se} \)), in addition to the charge transfer differences \( (Q_t, e) \) for the investigated 2D sheets after adsorbing the \( \text{CX}_2 \) molecules.

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 CO$_2$, CS$_2$, and CSe$_2$ molecules on the electronic features of the $\beta_{12}$ 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 $\Gamma$-Y-S-X-$\Gamma$ and Y-S-X-$\Gamma$-Y paths were selected for band structures of the $\beta_{12}$ and GN sheets, respectively. Figure S2 illustrates the band structures of the pure $\beta_{12}$ and GN sheets. The electronic band structure calculations of the adsorbed CX$_2$ molecules at the most favorable adsorption sites on the $\beta_{12}$ and GN sheets were plotted and are shown in Figure 4.

According to Figure S2, the electronic band structure of the pure $\beta_{12}$ 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 $\Gamma$ 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 $\beta_{12}$ and GN sheets (see Figure S2). Such an observation outlines that $\beta_{12}$ and GN cannot be highly effective CO$_2$ sensors, which agrees with evidence from previous studies [44,58]. In contrast, the adsorption of the CS$_2$ and CSe$_2$ molecules in vertical and parallel configurations on the $\beta_{12}$ 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 $\beta_{12}$ moved far away from each other after adsorbing CS$_2$ and CSe$_2$ molecules, confirming the strong adsorption of these molecules on the $\beta_{12}$ sheet. In detail, the resultant band structures after the adsorption of CS$_2$ molecules on $\beta_{12}$ 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 CSe$_2$ $\cdots$ $\beta_{12}$ complexes strongly affirmed the more evident impact of the adsorbed CSe$_2$ molecules on the electronic characteristics of the $\beta_{12}$ sheet in the parallel configuration compared with the vertical analog. For adsorption of the CSe$_2$ 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$_2$····β$_{12}$/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 CSe$_2$····β$_{12}$ complexes were more favorable than the CS$_2$····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 CX$_2$ molecules were improved in the order CO$_2$····β$_{12}$/GN < CS$_2$····β$_{12}$/GN < CSe$_2$····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 CX$_2$ molecules with the investigated 2D sheets. In addition, the presence of the Dirac point was not affected by the adsorption of CX$_2$ molecules on the GN sheet, confirming the physical adsorption of CX$_2$ 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 CX$_2$····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 CX$_2$ molecules to the 2D sheet and from the 2D sheet to the adsorbed CX$_2$ molecules, respectively.
According to the $Q_t$ values recorded in Table 1, adsorption of the $\text{CX}_2$ molecules in the vertical configuration at different adsorption sites on the $\beta_{12}$ sheet was noticed with negative values of $Q_t$. For instance, the $\text{CO}_2\cdots\cdot\beta_{12}$ complexes at the $\text{T}$ site exhibited $Q_t$ values of $-0.0117$, $-0.0219$, and $-0.0127\ e$, respectively. These negative values demonstrate that the $\beta_{12}$ sheet behaved as an electron acceptor.

The adsorption of the $\text{CO}_2$ molecule on the $\beta_{12}$ sheet, in the case of the parallel configuration, had negative values of $Q_t$, demonstrating the electron donor character of the $\text{CO}_2$ molecule. Moreover, the adsorption of the $\text{CS}_2$ and $\text{CSe}_2$ molecules on the $\beta_{12}$ sheet showed positive $Q_t$ values, proposing that the $\text{CS}_2$ and $\text{CSe}_2$ molecules acted as electron acceptors. Numerically, $Q_t$ values of $0.0044$ and $0.0513\ e$ were shifted from the $\beta_{12}$ sheet toward the $\text{CS}_2$ and $\text{CSe}_2$ molecules at the $\text{T@}\beta_{12}$ site, respectively. In line with the adsorption energy results, the $\text{CSe}_2\cdots\cdot\text{H@}\beta_{12}$ 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 $\text{CX}_2\cdots\cdot\text{GN}$ complexes, the $\text{H@GN}$ site showed the highest negative $Q_t$ values, consistent with its energetic preferentiality. Notably, all the $\text{CX}_2\cdots\cdot\text{GN}$ complexes showed negative values of $Q_t$, illustrating the potent ability of the GN sheet to accept electrons from the $\text{CX}_2$ molecules.

Negative $Q_t$ values were observed for the parallel configuration of the $\text{CO}_2\cdots\cdot\text{T/H/Br@GN}$ complexes, while both negative and positive $Q_t$ values were found at the studied adsorption sites in the case of the $\text{CS}_2\cdots\cdot\text{GN}$ complexes. For adsorption of the $\text{CSe}_2$ molecule, it can be seen that the charge was transferred from the GN sheet to the adsorbed $\text{CSe}_2$, 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 $\text{CX}_2\cdots\cdot\beta_{12}/\text{GN}$ complexes were plotted and are depicted in Figure 5.

As seen in Figure 5, the $\Delta\rho$ maps of the $\text{CX}_2\cdots\cdot\beta_{12}$ complexes in the vertical configuration showed that the $\text{CX}_2$ 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 $\text{CO}_2$ to the $\beta_{12}$ sheet, as seen from the charge accumulation region existing below the $\text{CO}_2$ (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 $\beta_{12}$ sheet in the case of the adsorption of $\text{CS}_2$ and $\text{CSe}_2$ molecules in the parallel configuration, which was consistent with the positive $Q_t$ values stated in Table 1. This observation emphasized that $\text{CS}_2$ and $\text{CSe}_2$ molecules have the potential to draw charge from the $\beta_{12}$ sheet.

For the vertical configuration of the $\text{CX}_2\cdots\cdot\text{GN}$ complexes, the existence of regions with accumulated charge ensures the adsorption of $\text{CX}_2$ molecules on the $\beta_{12}$ and GN sheets. The accumulated charge above the GN sheet within the $\text{CO}_2\cdots\cdot\text{GN}$ complexes in the parallel configuration indicated that electrons were transferred from the $\text{CO}_2$ and $\text{CS}_2$ molecules to the GN sheet (Figure 5). In comparison, the depletion region above the GN sheet in the case of adsorption of the $\text{CSe}_2$ 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 $\text{CX}_2$ molecules to the studied 2D sheets in the vertical configuration, indicating the electron-donating character of the $\text{CX}_2$ molecules. The $\text{CO}_2\cdots\cdot\beta_{12}/\text{GN}$ complexes in the case of parallel configuration had the largest negative $Q_t$ values, followed by $\text{CS}_2\cdots\cdot\beta_{12}/\text{GN}$, then $\text{CSe}_2\cdots\cdot\beta_{12}/\text{GN}$ complexes. The small $Q_t$ values confirmed physical adsorption between the $\text{CX}_2$ molecules and the investigated 2D sheets. Consistent with the literature, the electronic properties of the $\beta_{12}$ 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 $\text{CX}_2 \cdot \cdot \cdot \beta_{12}$/GN complexes (where $X = \text{O, S, or Se}$) 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 $\beta_{12}$ and GN surfaces are illustrated in Figure S3.

From the data in Figure S3, the TDOS peaks of the pure $\beta_{12}$ sheet at the Fermi level had high DOS, demonstrating that the $\beta_{12}$ 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 $\beta_{12}$ and GN surfaces before adsorbing CX$_2$ 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 $\beta_{12}$ and GN sheets within the vertical and parallel configurations of the CX$_2$···$\beta_{12}$/GN complexes (where X = O, S, or Se) at the most favorable energetic sites. For adsorption of the CO$_2$ molecule on the $\beta_{12}$ 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 CO$_2$ 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 CO$_2$···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$_2$···$\beta_{12}$/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 $p_x$ was the major contributor to the adsorption within both modeled configurations of the $\text{CS}_2 \cdots \beta_{12}/\text{GN}$ complexes. For both configurations of $\text{CS}_2 \cdots \beta_{12}$ and $\cdots \text{GN}$ complexes, the appearance of the PDOS of $p_x$ 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 $\text{CSe}_2 \cdots \beta_{12}/\text{GN}$ complexes, the PDOS of $p_x$ peaks appeared in the valence region in the range from $−1.0$ to $−2.2$ eV within the $\text{CSe}_2 \cdots \beta_{12}$ complexes and from $−1.5$ to $−2.3$ eV within the $\text{CSe}_2 \cdots \text{GN}$ complexes.

Overall, the DOS results outlined that the electronic properties of the $\beta_{12}$ and GN sheets were changed after adsorbing the $\text{CX}_2$ molecules in vertical and parallel configurations. The appearance of the new DOS peaks indicated the occurrence of adsorption of the $\text{CX}_2$ molecules on the investigated 2D sheets.

4. Conclusions

The adsorption of toxic carbon dichalcogenides ($\text{CX}_2; X = O, S, \text{or Se}$) on $\beta_{12}$ 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 $\text{CX}_2 \cdots \beta_{12}/\text{GN}$ complexes. The favorability of $\text{CX}_2 \cdots \beta_{12}/\text{GN}$ complexes was more obvious in the parallel configuration compared with the vertical one. The $\text{CSe}_2 \cdots \text{H}@\beta_{12}$ 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 $\beta_{12}$ and GN surfaces were notably changed after the adsorption of $\text{CS}_2$ and $\text{CSe}_2$ molecules. In comparison, the electronic characteristics of the $\beta_{12}$ and GN surfaces were slightly changed after adsorbing the $\text{CO}_2$ molecule. Based on Bader charge analysis, an electron-donating character was observed for all the $\text{CX}_2$ molecules in vertical configuration within the $\text{CX}_2 \cdots \beta_{12}/\text{GN}$ complexes. In comparison, the $\text{CS}_2$ and $\text{CSe}_2$ molecules acted as electron acceptors within the parallel configuration of the $\text{CS}_2 \cdots \beta_{12}/\text{GN}$ and $\text{CSe}_2 \cdots \beta_{12}/\text{GN}$ complexes. The results of the electronic band structure, TDOS, and PDOS demonstrated that adsorption of the $\text{CX}_2$ molecules on the $\beta_{12}$ and GN sheets boosted their electronic properties. The appearance of new bands and DOS peaks affirmed the interaction of the $\text{CX}_2$ molecules with the investigated 2D sheets. Based on the findings of the present study, it appears promising to use the $\beta_{12}$ and GN sheets as a suitable sensor for $\text{CX}_2$ molecules, particularly $\text{CS}_2$ and $\text{CSe}_2$ 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 $\text{CX}_2 \cdots \beta_{12}/\text{GN}$ complexes (where $X = O, S, \text{or Se}$) at all the adsorption sites. Equilibrium distances ($d$) are given in Å. Figure S2: Band structure plots of $\beta_{12}$ 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 $\beta_{12}$ 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.

Author Contributions: Conceptualization, M.A.A.I.; methodology, A.H.M.M.; software, M.A.A.I., and M.E.S.S.; formal analysis, A.H.M.M.; investigation, A.H.M.M., and N.A.M.M.; resources, M.A.A.I. and A.M.S.; data curation, A.H.M.M.; writing—original draft, A.H.M.M.; writing—review and editing, M.A.A.I., G.A.H.M., A.M.S., M.E.S.S., and N.A.M.M.; visualization, A.H.M.M.; supervision, M.A.A.I. and G.A.H.M.; project administration, M.A.A.I. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Not applicable.

Acknowledgments: Ahmed M. Shawky would like to thank the Scientific Research at Umm Al-Qura University for supporting this work with grant No. 22UQU4331174DSR20. The computational work was partially completed with resources provided by the Science and Technology Development Fund (STDF), Egypt, grants No. 5480 and 7972 (Granted to Mahmoud A. A. Ibrahim).
Conflicts of Interest: The authors declare no conflict of interest.

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