

DFT Based Simulation of H₂S Gas Sensing Properties of Doped Graphene

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Abstract - The interactions of P- and S-doped graphene sheets with H₂S molecule are investigated based on density functional theory based simulations to analyze the reactivity of these doped graphenes towards H₂S. The energetically favourable adsorption configurations of H₂S on doped graphene sheets are determined and adsorption energies are calculated. Our results indicate that the structural properties of doped graphene sheets are not influenced much by the adsorption of H₂S. The results from charge distribution analysis, electronic band structures and density of states of H₂S adsorbed on the doped graphene sheets show that the interactions between H₂S and doped graphene sheets does not induce any significant changes in the electronic properties of P- and S-doped graphene.

Keywords: doped graphene, density functional theory, reactivity, H₂S, adsorption energies, structural properties, interactions, electronic properties

1. Introduction

Hydrogen sulphide (H₂S), a colourless gas with distinct odour of rotten eggs is an important environmental and industrial pollutant. H₂S is readily found in raw natural gas, in swamps and sewers, in waste gas streams from paper and petrochemical industry [1]. H₂S can cause a wide range of health effects [2]. Prolonged low-level H₂S exposure (20 ppm) may result in loss of appetite, poor memory, fatigue, headache, dizziness and irritability. H₂S in micro-amounts of 50-300 ppm can cause various respiratory difficulties ranging from rhinitis to acute respiratory failure. Exposure to concentrations of 500 ppm can cause loss of consciousness and concentrations as high as 700 ppm can cause instant death [3]. Being toxic, corrosive, flammable and explosive in nature, H₂S detection and control is inevitable in laboratories and for various processes such as coal or natural gas manufacturing.

Graphene has been widely used in gas sensors since the demonstration of the first graphene based micro sensor in 2007, due to its unique structural and electronic properties [4-7]. Previous theoretical studies have shown that pristine graphene (hereafter abbreviated as PG) can only physisorb gas molecules [8] and this limits the use of graphene in developing gas sensors. It was reported that the sensitivity of graphene could be improved by doping of graphene with other elements. The introduction of dopant atoms tunes the chemical reactivity of graphene by modifying the electronic properties of graphene.

Density functional theory (DFT) based calculations have shown weak binding of H₂S to PG [9]. Graphene doped with boron (B) and nitrogen (N) atoms were also not found to be promising routes for improving the adsorption of H₂S molecule on graphene surface [9]. Graphene doped with silicon (Si) can strongly adsorb H₂S molecule on the graphene surface through the formation of Si-S bond, compared to the weak physisorption of H₂S molecule onto PG and the B, N-doped graphene [9]. Another DFT study revealed increase in the sensitivity of graphene to H₂S molecule when doped with

aluminium (Al) and gallium (Ga), due to the chemisorptions of H₂S on these doped graphene with relatively large adsorption energies and small binding distances [3]. It was also found that graphene modified with transition metals such as calcium (Ca), cobalt (Co) and iron (Fe) show much higher sensing affinities towards H₂S molecule [9, 10]. Platinum (Pt)-doped graphene has also been studied as a promising adsorbent for H₂S detection, owing to the significantly enhanced interactions between graphene and H₂S on doping with Pt from the DFT calculations [10]. Theoretical calculations have predicted the application of graphene modified with Al, Si, Ga, Fe, Ca, Co, and Pt dopants as good sensors for the detection of H₂S.

Until now, it has been reported that N, B, and Si atoms can be successfully doped into graphene [11, 12]. Experimental works on the doping of graphene with P and S atoms have also been performed [13, 14]. Density functional theory (DFT) calculations on the adsorption of several gas molecules on P-doped graphene (hereafter abbreviated as PhG) have shown strong chemisorption of O₂, NO, NO₂ and SO₂ onto PhG through the formation of P-X (X = O, N, S) bonds, while weak physisorption was observed for H₂, H₂O, CO₂, CO, N₂ and NH₃ [15]. Liang *et al.* have demonstrated that S-doped graphene (hereafter abbreviated as SG) is highly selective to NO₂ in the presence of other gases such as NH₃, CO, SO₂, CH₄ [16]. SG has shown strong binding of NO₂ among other gas molecules such as NH₃, SO₂, H₂O, CO, CO₂, NO, H₂, O₂, according to DFT based analysis [17]. Faye *et al.* [18] studied H₂S adsorption on SG and concluded that H₂S exhibits a long range interaction with SG with no sign of any new bond formation, from the analysis of adsorption energy and charge transfer calculations. However, the effect of the P dopant on the reactivity of graphene towards H₂S has not been investigated. In this paper, the interactions between H₂S molecule and doped graphene such as PhG and SG have been investigated using first-principles density functional computations to analyze the sensitivity of PhG and SG towards H₂S molecule.

2. Computational Procedure

DFT calculations are performed using generalized gradient approximation (GGA) by Perdew *et al.* [19] for the exchange-correlation potential. A 4 × 4 graphene supercell containing 32 carbon (C) atoms with a doped atom substituting a C atom and a single H₂S molecule adsorbed onto it is constructed. In the direction normal to the graphene plane, 16 Å length in the supercell is considered to minimize the interaction between graphene layers. A plane wave basis set with a kinetic energy cutoff of 30 Ha is chosen in all simulations. The pseudopotentials were constructed using the Troullier and Martins scheme [20] to describe the valence electron interaction with the atomic core. The Brillouin zone is sampled using a 5 × 5 × 1 Monkhorst-Pack (MP) k-point [21]. A denser MP grid of 15 × 15 × 1 is used for the calculation of density of states (DOS). Broyden-Fletcher-Goldfarb-Shanno minimization [22] was employed to optimize the atomic coordinates and all atoms were allowed to relax until the forces were smaller than 5 × 10⁻⁴ Hartree/Bohr. All first-principles calculations are performed using the Abinit software package [23].

To evaluate the interaction between a H₂S molecule and doped graphene sheet, the adsorption energy (E_{ad}) is calculated as given in Eq. (1).

$$E_{ad} = E_{tot} - E_{dg} - E_{molecule}, \quad (1)$$

In Eq. (1), E_{tot} is the total energy of the doped graphene with a bound H₂S molecule, E_{dg} is the energy of doped graphene and $E_{molecule}$ is the energy of the isolated H₂S molecule. All energies were calculated for optimized atomic structures. Charge transfer analysis is based on the Hirshfeld method [24].

3. Results and Discussions

3.1. Structural and Energetic Properties

We first optimized the atomic geometries of isolated H₂S molecule and PG sheet. The structural parameters for H₂S molecule are determined with H-S bond length of 1.35 Å and the H-S-H angle measures 91.6°, which are close to the experimental values of 1.336 Å and 92.11°. The lattice constant and C-C bond length of PG are found to be 2.46 Å and 1.42 Å (Fig. 1), which are close to the previous results [25].

Substitution of a single C atom by P and S atoms in PhG and SG, respectively results in distortion of the structure due to the stress introduced by the bigger sized dopant atoms compared to the host carbon atoms. The obtained relaxed structures of PhG and SG are shown in Fig. 2, where the dopant atoms protrude out of the graphene sheet. The elevation of the P and S atoms is observed to be 1.107 and 1.005 Å and the bonds around the dopant atom expands to 1.76 Å (P-C

bond) and 1.74 Å (S-C bond) in PhG and SG respectively. These are in good agreement with the results reported in Ref. [15, 17].

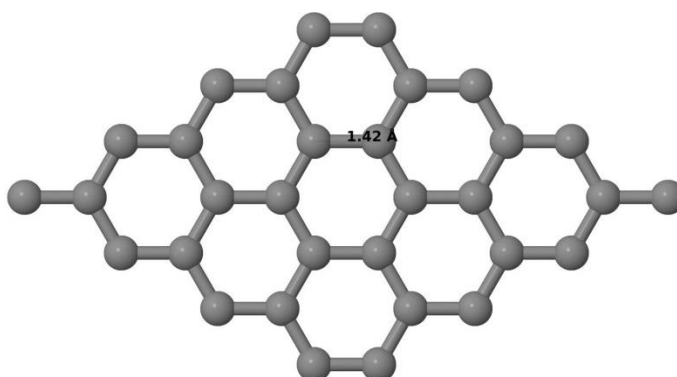


Fig. 1: Optimized structure of PG sheet.

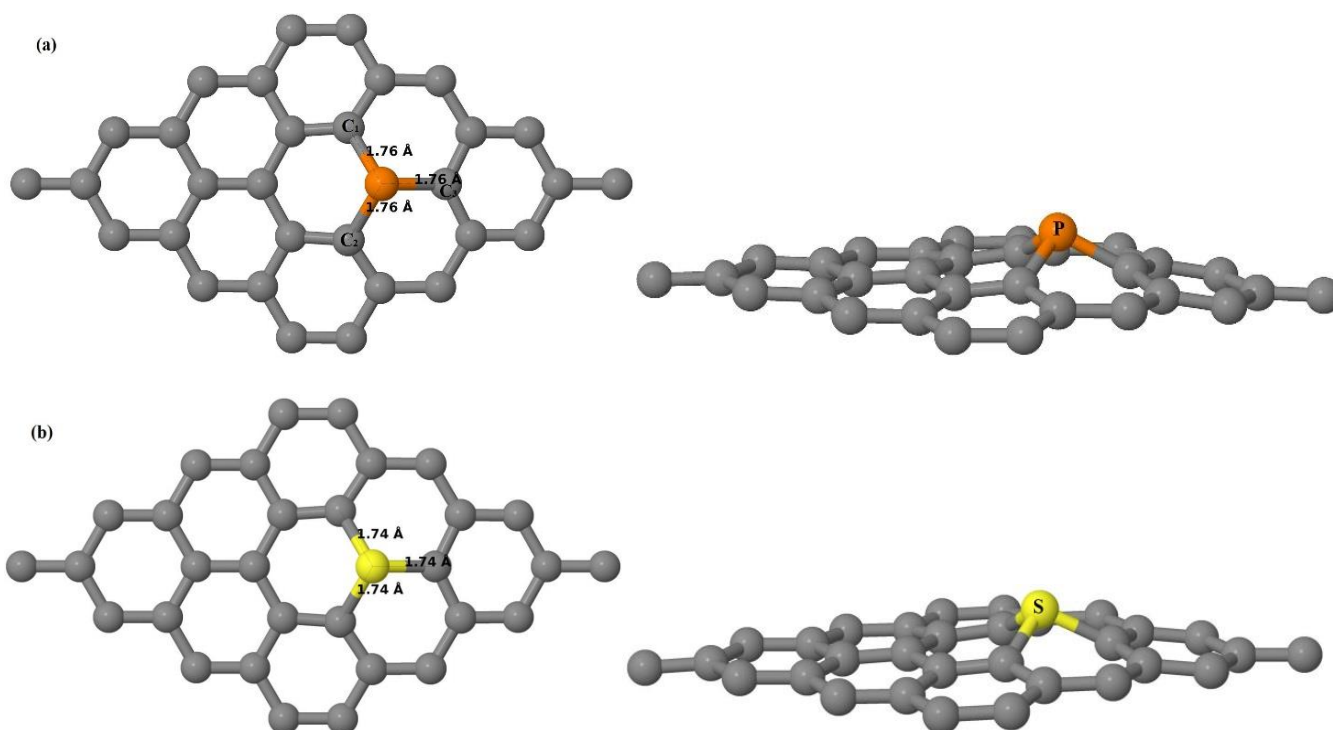


Fig. 2: Top (left) and side (right) views of optimized structures of (a) PhG and (b) SG sheets.

Having determined the most stable structures of doped graphene sheets, we next discuss the adsorption of H_2S on PhG and SG. H_2S molecule is initially placed on the top of the doping atoms. Different orientations of the H_2S molecule with respect to graphene surface are considered by starting from S atom with H-S bonds parallel, pointing up and down. The system is allowed to relax for all the considered adsorption configurations and the adsorption energy and the binding distance (equilibrium graphene-gas molecule distance) are calculated for these configurations. After H_2S adsorption, we find that there is no significant change in the structure of PhG and SG (Fig. 3). Fig. 3 demonstrates the fully relaxed structures of H_2S adsorbed-PhG and -SG systems. After relaxation, the most stable adsorption configuration is found to be the one in which is H_2S is oriented downwards with both H-atoms close to the graphene plane than the S-atom, according to the calculations. After structural relaxation of the H_2S adsorbed-PhG and -SG systems, the H_2S molecule is located at a

distance larger than 3.5 Å above the doped graphene sheets (Fig. 3). The elevation of P atom decreases to 1.025 Å with decreased P–C bond length of 1.75 Å on H₂S adsorption (Fig. 3). Similarly in the case of SG, the elevation of S atom decreases to 0.901 Å with the same S–C bond length of 1.74 Å. Thus both the dopant atoms are slightly pushed downwards by the adsorbed H₂S, which indicates the repulsive force between the dopant atoms and the H₂S molecule.

The energetic behaviour of H₂S adsorptions on PhG and SG are studied by calculating the adsorption energies and are presented in Table 1. The negative E_{ad} values in both cases indicate that H₂S adsorption is energetically favourable. The relatively low values of adsorption energies (-0.037 eV for PhG and -0.011 eV for SG) and large binding distances (3.97 Å for PhG and 4.23 Å for SG) show that the interactions of H₂S with PhG and SG are weak and H₂S adsorbed-PhG and -SG systems are in the very weak physisorption region. The observed physisorption of H₂S on SG agrees well with the recent findings by Faye *et al.* [18].

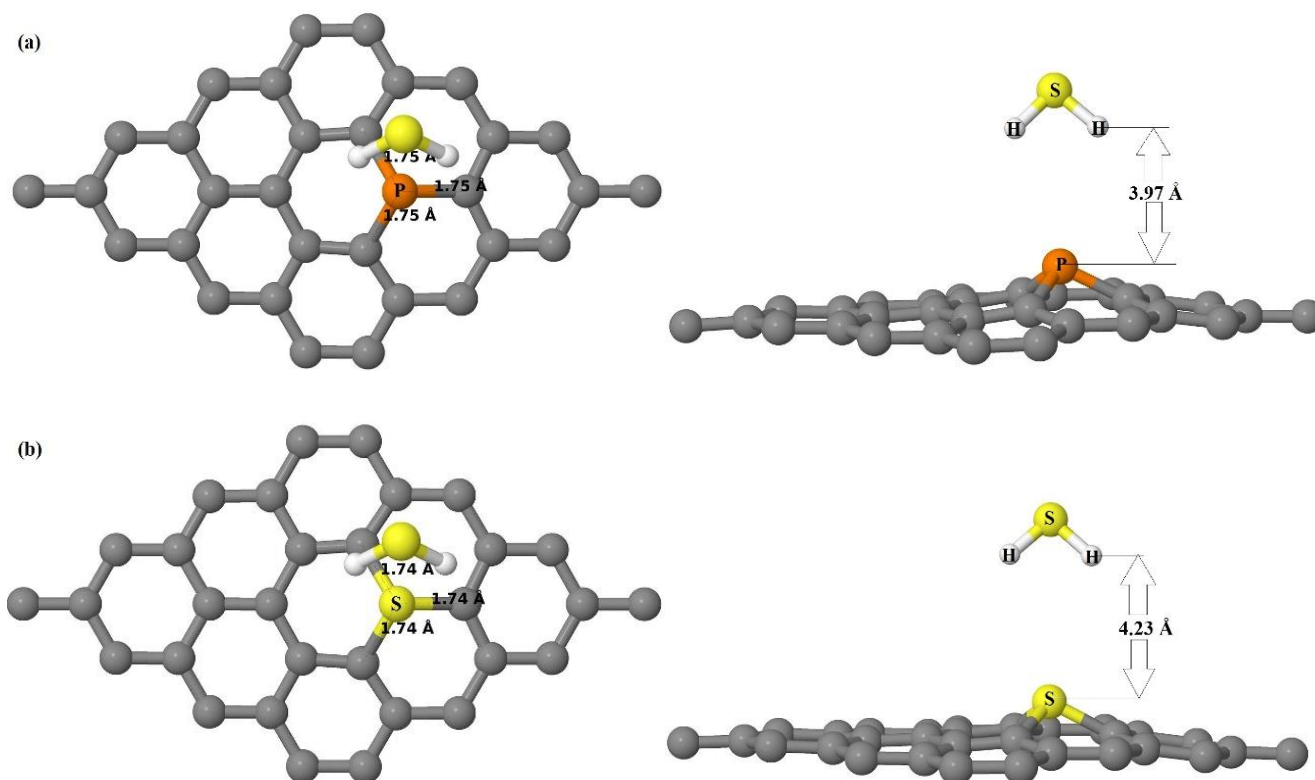


Fig. 3: Top (left) and side (right) views of optimized structures of H₂S molecule on (a) PhG and (b) SG sheets.

Table 1: Values of adsorption energy and binding distance of H₂S molecule above PhG and SG sheets.

System	PhG	SG
E_{ad} in eV	-0.037	-0.011
d in Å	3.97	4.23

3.2. Electronic Properties

Table 2 presents the results of the charge distribution analysis of the doped graphene sheets before and after H₂S adsorption, which shows the electronic charge state of the dopant atoms, three neighbouring C atoms of the dopant atom and the adsorbed H₂S molecule. In PG, all the carbon atoms are in neutral state and hence they possess zero charge. Upon replacing C atom with P atom, the three C atoms surrounding the P-dopant catch electrons from the dopant atom due to their high electron affinity, whereas a decrease in electron density is observed on P-dopant. Thus the neighbouring dopant atoms gain a charge state of -0.046 in PhG and the P-dopant lose electronic charge of 0.172. Even though both carbon and sulphur atoms have almost the same electronegativity, the smaller size of C makes it more electronegative than S. Hence

the nearest C neighbours attract electrons from S and gain a charge state of -0.037, whereas S dopant loses electrons with a charge state of 0.300.

Upon H₂S adsorption on PhG and SG, it was observed that there is only a very slight increase and decrease in the electronic charge states of the nearest C neighbours and the dopant atoms respectively. As the adsorption of H₂S does not result in significant change in the charge state of dopant atoms in PhG and SG, the charge transfer between the doped graphene sheets and H₂S is negligible. The negligible charge transfer between H₂S and SG that point towards a weak interaction between H₂S and SG is in agreement with the results reported in Ref. [18].

Table 2: Hirshfeld charge distribution analysis of the dopant atom, three C atoms around dopant atom and the adsorbed H₂S molecule on the surface of PhG and SG^a.

System	C ₁	C ₂	C ₃	P	S	H ₂ S
PG	0	0	0	-	-	-
PhG	-0.0460	-0.0460	-0.0460	0.1715	-	-
SG	-0.0370	-0.0370	-0.0370	-	0.3004	-
H ₂ S-PhG	-0.0463	-0.0464	-0.0468	0.1797	-	-0.014
H ₂ S-SG	-0.0374	-0.0371	-0.0376	-	0.3013	-0.008

a. A negative sign indicates electrons gained, whereas positive sign implies electron lost by the atom (the unit of charge is electron).

Fig. 4 (a)-(c) present the electronic band structures of PG, PhG and SG along the high symmetry points (Γ -K-M- Γ) of the hexagonal Brillouin zone of graphene. The DOS of PG, PhG and SG are shown in Fig. 5 (a)-(c). In PG, the valence and conduction bands cross at the K-point with zero energy band gap (Fig. 5 (a)) and the linear dispersion of valence and conduction bands around the Fermi level seen in Fig. 4 (a) is in accordance with the reported results [3]. Since both P (Group V) and S (Group VI) atoms have one and two valence electrons more than the host C atoms, these elements act as donors of electrons in graphene [26] and thus modify the electronic structure of graphene as seen in Fig. 4 (b), (c) and Fig. 5 (b), (c). Substitutional doping with P and S atoms in graphene lattice results in band gap opening in graphene. The calculated band structure plots of PhG and SG agree well with those in previous reports [27]. Doping with P and S introduce band gaps of 0.658 eV (Fig. 4 (b)) and 0.583 eV (Fig. 4 (c)) respectively in graphene. The observed band gap values are very close to the previously reported band gap values of 0.67 and 0.57 eV [27].

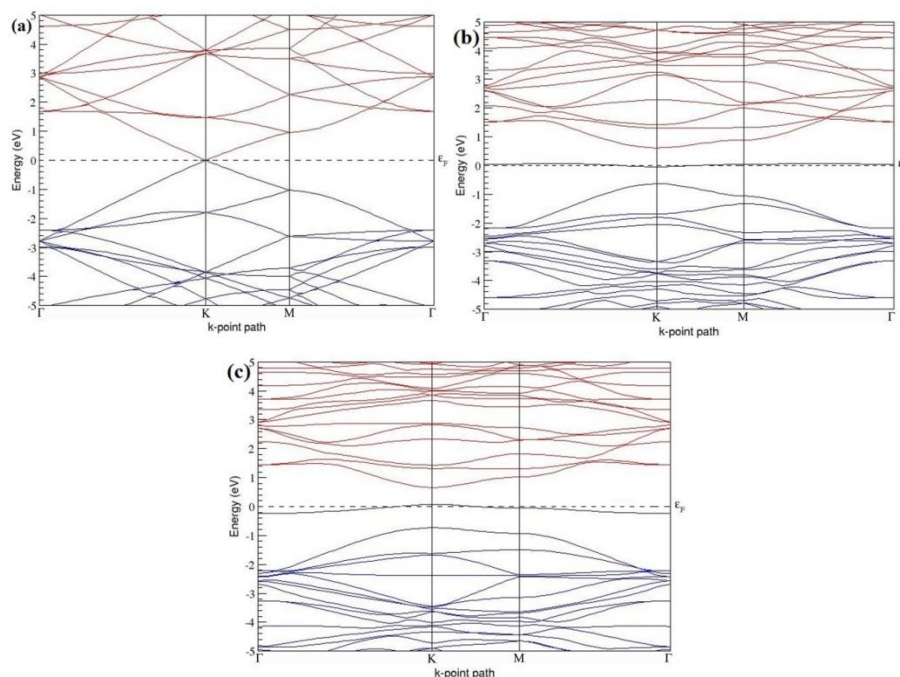


Fig. 4: Electronic band structures of (a) PG, (b) PhG, and (c) SG.

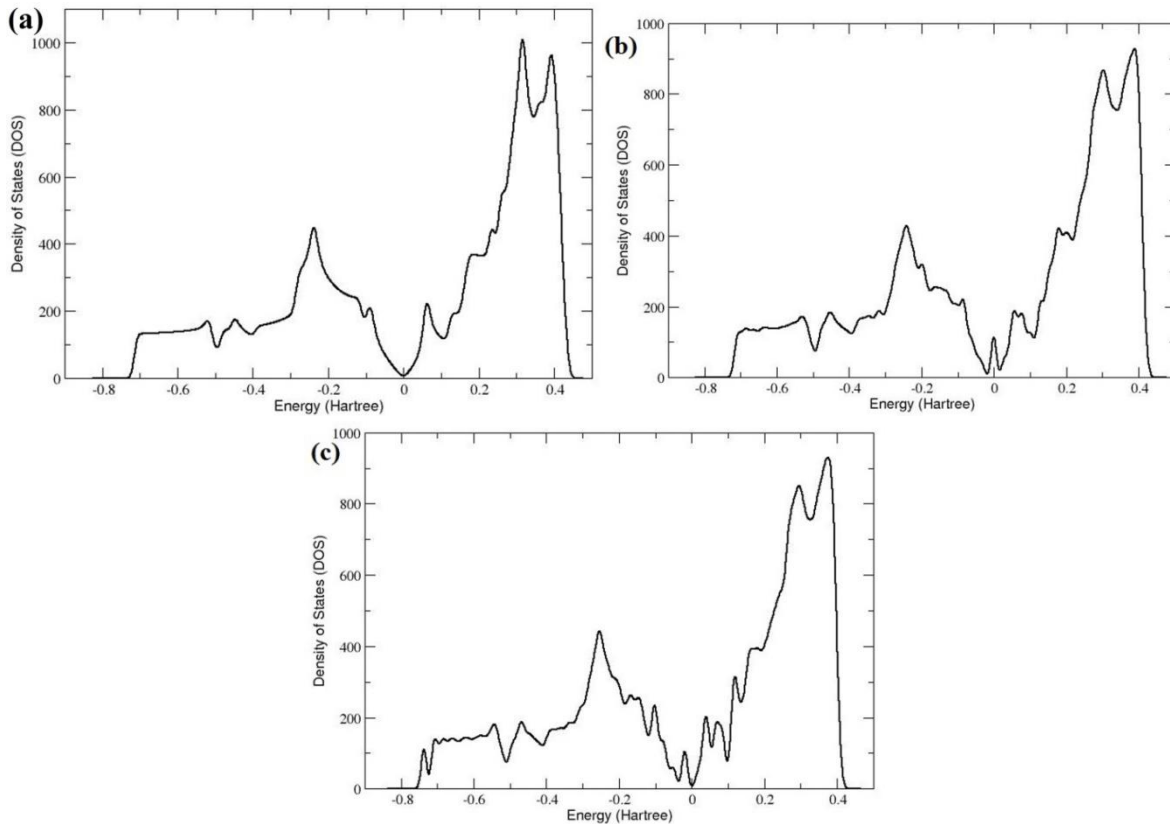


Fig. 5: The DOS of (a) PG, (b) PhG and (c) SG.

The band structures of H_2S molecule adsorbed on PhG and SG systems are shown in Fig. 6 (a) and (b). The band structures of PhG and SG are also found to be unaffected by their interaction with H_2S molecule as seen in Fig. 6 (a), (b). These results show that H_2S adsorption does not change the electronic structures of PhG and SG. The DOS of H_2S molecule adsorbed on PhG and SG systems are shown in Fig. 7 (a), (b). The DOS structures show little change near E_F after H_2S adsorption and the DOS of H_2S on PhG and SG systems are similar to that of PhG and SG respectively (Fig. 7 (a), (b)). The suggested weak interactions between PhG, SG and H_2S molecule from the calculations of adsorption energies are also evident in their DOS structures. The observed overlapping of the DOS profiles of SG and H_2S adsorbed SG system are similar to that reported in other studies [18].

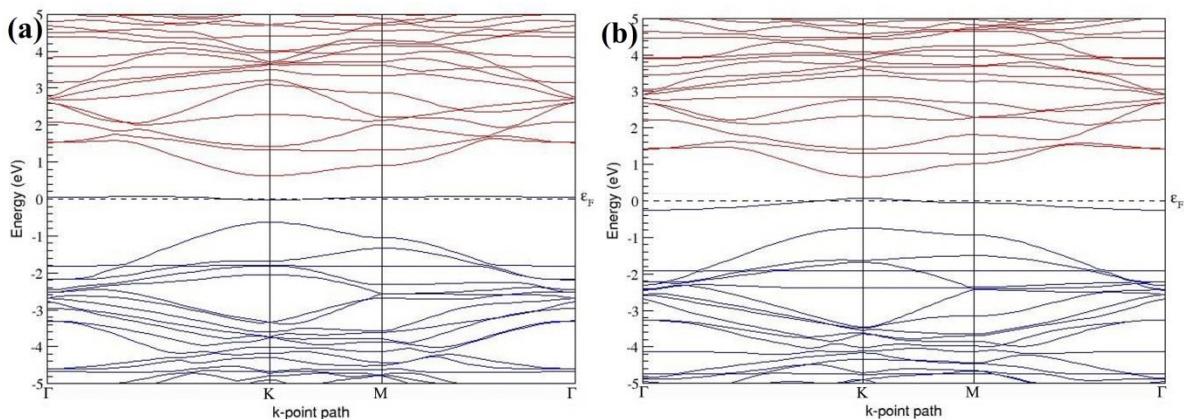


Fig. 6: Electronic band structures of H_2S adsorbed (a) PhG and (b) SG.

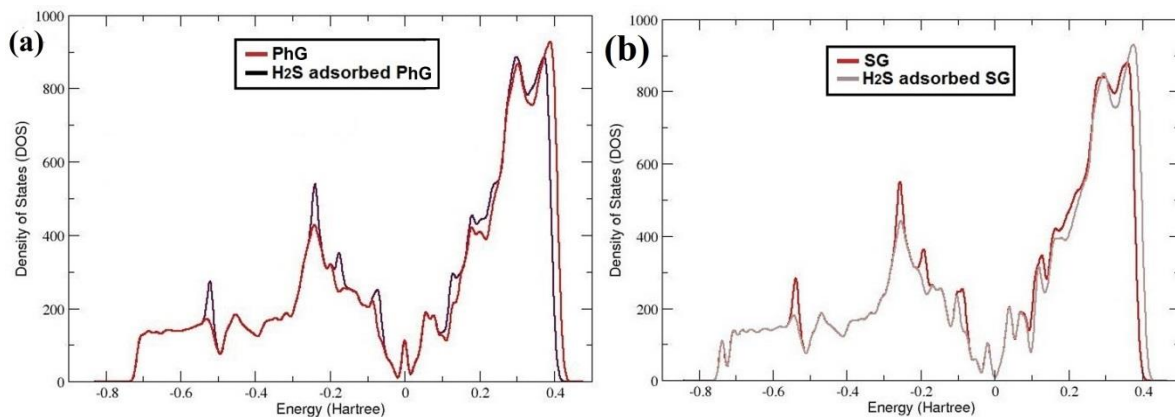


Fig. 7: The DOS of (a) PhG and H₂S adsorbed PhG and (c) SG and H₂S adsorbed SG.

4. Conclusion

The interactions between H₂S and doped graphene sheets such as P- and S-doped graphene have been investigated using first principles DFT method to analyze the gas sensing properties of these doped graphenes towards H₂S molecule. The structural and electronic properties of PhG and SG are found to be insensitive to the adsorption of H₂S. The Hirshfeld charge distribution analysis of the optimized structures also showed negligible charge transfer between H₂S and the doped graphene sheets. The electronic band structures and DOS of PhG and SG before and after H₂S adsorption indicate that H₂S adsorption would not result in significant change in the electrical conductances of PhG and SG.

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