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DFT Insights into the Detection of NH_3 , AsH_3 , PH_3 , CO_2 , and CH_4 Gases with Pristine and Monovacancy Phosphorene Sheets

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ABSTRACT: Density functional theory (DFT) calculations were employed to investigate the adsorption behavior of NH_3 , AsH_3 , PH_3 , CO_2 , and CH_4 molecules on both pristine and mono-vacancy phosphorene sheets. The pristine phosphorene surface shows weak physisorption with all the gas molecules, inducing only minor changes in its structural and electronic properties. However, the introduction of mono-vacancies significantly enhances the interaction strength with NH_3 , PH_3 , CO_2 , and CH_4 . These variations are attributed to substantial charge redistribution and orbital hybridization in the presence of defects. The defective phosphorene sheet also exhibits enhanced adsorption energies, along with favorable sensitivity and recovery characteristics, highlighting its potential as a promising gas sensor for NH_3 , AsH_3 , PH_3 , CO_2 , and CH_4 at ambient conditions.

KEYWORDS: Phosphorene; vacancy; defects; DFT; interaction; sensitivity

1 Introduction

Toxic gases possess serious health risks upon inhalation, with effects ranging from mild irritation to life-threatening conditions. Among them, ammonia (NH_3), arsine (AsH_3), phosphine (PH_3), carbon dioxide (CO_2), and methane (CH_4) are chemically different, yet they have significance in both environmental and industrial contexts. Ammonia, a colorless gas with a sharp, pungent odor, is naturally released during the decomposition of organic matter and is widely synthesized for use in fertilizers due to its high nitrogen content essential for plant growth. It is highly soluble in water, forming ammonium hydroxide, which is a common component in household cleaners. Although non-flammable under standard conditions, ammonia can form explosive mixtures with air at elevated concentrations. Exposure levels above 20 ppm are considered hazardous, potentially causing irritation to the eyes, skin, and respiratory system. A high concentration of toxic gases leads to severe burns, respiratory failure, or even death [1–4]. Arsine (AsH_3) is a colorless, highly toxic, and flammable gas composed of arsenic and hydrogen, primarily used in semiconductor manufacturing and chemical synthesis. Though it may emit a garlic-like odor at high concentrations, arsine is often undetectable at hazardous levels. Even minimal exposure can lead to hemolysis, abdominal pain, respiratory failure, and death, necessitating strict safety protocols [5]. Phosphine (PH_3), another highly toxic gas, consists of phosphorus and hydrogen. It is colorless and may have a garlic or fishy odor, though pure phosphine is odorless. It forms naturally in trace amounts through the anaerobic decay of phosphorus-rich



matter and is widely used as a fumigant and in electronics manufacturing. Exposure can cause symptoms ranging from nausea and chest tightness to pulmonary edema and fatality, demanding rigorous handling precautions [6].

Carbon dioxide (CO_2), while non-toxic at ambient concentrations, plays a central role in Earth's carbon cycle. Naturally produced through respiration, decomposition, and volcanic activity, CO_2 is also heavily emitted by human activities such as fossil fuel combustion and deforestation, contributing significantly to global climate change. In confined spaces, CO_2 accumulation can displace oxygen, posing suffocation risks. It is widely used across industries, including food processing, fire suppression, and refrigeration [7,8]. Methane (CH_4), the simplest hydrocarbon, is a colourless, odourless, and highly flammable gas formed naturally via anaerobic processes in wetlands and livestock digestion. As the primary component of natural gas, it is a critical fuel source. Although non-toxic, methane can cause oxygen displacement in enclosed environments, creating asphyxiation risks. Additionally, it is a potent greenhouse gas over 80 times more effective than CO_2 at trapping heat over a 20-year period, making it a major contributor to global warming. Despite their diverse industrial, agricultural, and energy-related applications, these gases pose significant health, safety, or environmental hazards, underscoring the need for careful monitoring and control strategies [9].

Due to the harmful nature of these gases, it is essential to develop a sensor that can detect these gases in small amounts. In the past decades, the two dimensional materials such as graphene, graphene oxide, boron nitride, MoS_2 , germanene and silicene have been widely investigated for the applications in the field of energy storage, gas sensors, molecular adsorption, and many other fields due to their high surface area, high carrier mobility, high chemical stability and fast response time [10–15]. Although graphene is the most explored 2D material, it has limited applications in fields such as magnetic field sensors and single-electron detectors. Using density functional theory (DFT), Leenaerts et al. [16] found that the weak interaction between graphene and common gas molecules such as NO , NH_3 , CO , and H_2O , limits its application towards single gas molecule detection. It has been found that MoS_2 has weak interaction with gas molecules like O_2 , H_2 , H_2O , and CH_4 etc. as there was no significant change in electronic properties found after adsorption of these gas molecules. Xia et al. [17] studied the adsorption of various gas molecules on germanene using DFT and found that NH_3 , NO , and NO_2 gas molecules strongly interact with germanene, while CO , H_2O and CO_2 gas molecules interact weakly. Wand et al. studied the adsorption H_2 , CO , CO_2 , H_2O , NO_2 , H_2S , NH_3 , and CH_4 gas molecules on the SnGe_2N_4 monolayer surface. Their results showed that all these molecules reveal low adsorption energies and adsorption lengths on the SnGe_2N_4 surface [18]. Even though these 2D materials have amazing properties, their zero band gap of graphene and low mobilities & heavy electron effective mass of MoS_2 limit their applications for high-performance devices. Similarly unstable nature of germanene and silicene in air restricts their applications in electronic devices.

Phosphorene is the quasi-2D knitted sheet of black phosphorus. It has a noticeable direct band gap, which is an advantage over graphene. Its electron mobility is large in comparison to transition metal dichalcogenides (TMD). Its conductance is anisotropic, and it also has optical responses. It has high flexibility, high mechanical strength, and anisotropic elasticity [19]. These properties distinguish the phosphorene from other 2D materials like isotropic graphene and TMDs. This makes the phosphorene a promising material for applications in the fields of nanoelectronics and optoelectronics [20,21]. Phosphorene possesses applications in the field of thin film solar cell [22], field effect transistors [23], and gas sensors [1].

Due to its puckered surface, phosphorene has good absorption properties for several gas molecules. For example, Ghambarian et al. [24] investigated the adsorption of phosgene gas on pristine and defected phosphorene through DFT HSE calculations and found that defective phosphorene is a highly suitable and reusable gas sensor for the detection of phosgene gas. Luo et al. [6] studied the adsorption of hazardous gases NH_3 , PH_3 , AsH_3 on the graphene and rare earth metal-doped graphene. They found that pristine graphene

show weak physisorption towards NH_3 , PH_3 , and AsH_3 gas molecules. But the rare-earth metal-doped graphene shows enhanced chemisorption toward NH_3 and weakened adsorption toward AsH_3 . They found the sensitivities below 40% for the detection of NH_3 , PH_3 , and AsH_3 . In the present work, we have studied the sensing properties of pristine and mono-vacancy phosphorene towards ammonia, arsine, phosphine, carbon dioxide, and methane by analyzing interaction energy, energy band gap, Bader charge transfer, sensitivity, recovery time, and work function.

2 Computational Methods

Density functional theory (DFT) [25] based calculations were performed using the Quantum ESPRESSO [26] package. We used generalized gradient approximation (GGA) [27] with Perdew-Burke-Ernzerhof (PBE) functional [28] for the exchange-correlation energy of electronic interactions. The Van der Waals (VdW) corrections were included using the Grimme-D3 [29] method to consider the long-range interactions. The Brillouin zone was sampled employing a Monkhorst-Pack grid [30] corresponding to a $5 \times 4 \times 1$ k-point grid for all calculations of geometric optimizations and electronic properties for a $3 \times 3 \times 1$ supercell consisting of 36 atoms. Along the z-direction (perpendicular to 2d sheet), a 20 Å vacuum thickness was added to avoid the neighboring interactions. The interaction energy, E_{int} , of different gases on the pristine phosphorene sheet (P) and mono-vacancy phosphorene sheet (MVP) was calculated as

$$E_{\text{int}} = E_{\text{X-G}} - (E_{\text{X}} + E_{\text{G}}) \quad (1)$$

where $E_{\text{X-G}}$, E_{X} , and E_{G} are the energies of a gas molecule adsorbed over the P/MVP sheet, P/MVP adsorption substrate, and gas molecules, respectively. A value of $E_{\text{int}} < 0$ signifies that the interaction process is exothermic, and gas interaction happens concurrently.

The sensing quality of a sensor can be determined in terms of sensitivity (S , %) [6], which is defined as

$$S = \left| \frac{\sigma_{\text{s-g}} - \sigma_{\text{s}}}{\sigma_{\text{s}}} \right| \times 100 \quad (2)$$

where $\sigma_{\text{s-g}}$ and σ_{s} are the electrical conductivity of the operating sensor with gas adsorption and without gas adsorption, respectively. The electrical conductivity is related to the band gap (E_{g}) and can be described by Eq. (3) [1].

$$\sigma = AT^{\frac{3}{2}} \exp \left[-\frac{E_{\text{g}}}{2k_{\text{B}}T} \right] \quad (3)$$

here, σ is the electrical conductivity, A is a material-dependent prefactor containing density-of-states and mobility terms, T is absolute temperature, E_{g} is the band gap, and k_{B} is Boltzmann's constant.

The recovery duration was evaluated using the Van't-Hoff-Arrhenius equation [1] given by

$$\tau = \frac{1}{\nu_0} e^{\left(-\frac{E_{\text{a}}}{k_{\text{B}}T} \right)} \quad (4)$$

In this equation, ν_0 represents the apparent frequency factor (10^{12} Hz) [31], T signifies the operational temperature, k_{B} stands for the Boltzmann constant, and E_{a} indicates the energy barrier for desorption. It is commonly assumed that E_{a} is equivalent to E_{int} , given that desorption is the opposite of adsorption. This common practice also used by Kumar et al. [1], Kharb et al. [31], Cui et al. [32] and Kalwar et al. [33].

The interaction of gas molecules with P/MVP sheet can lead to alterations in the work function and is determined using Eq. (5) [1].

$$\varphi = E_{\text{vac}} - E_{\text{F}} \quad (5)$$

where E_{vac} represents the vacuum energy level and E_{F} denotes the Fermi energy of the system. The efficiency of the sensor can also be derived from the relative variation in its work function, as described by Eq. (6) [1].

$$\varepsilon = 100 \times \left| \frac{\varphi_{\text{X-G}} - \varphi_{\text{X}}}{\varphi_{\text{X}}} \right| \quad (6)$$

where $\varphi_{\text{X-G}}$ and φ_{X} represent the work functions of P/MVP sheet following the adsorption of the gas molecule and prior to gas adsorption, respectively.

The Bader charge [34] analysis was performed to analyze the electron transport dynamics between the gas molecule and the P/MVP sheet. The quantity of charge transfer (Q_t) indicates the changes in electronic characteristics on the surface of P/MVP when interacting with the gas molecules, as defined below:

$$Q_t = Q_{\text{adsorbed(gas)}} - Q_{\text{isolated(gas)}} \quad (7)$$

In this context, $Q_{\text{adsorbed(gas)}}$ and $Q_{\text{isolated(gas)}}$ refer to the charge associated with a gas molecule after it has adsorbed and that of an isolated gas molecule, respectively.

3 Results and Discussions

3.1 Geometric Structure of Pristine Phosphorene (P) and Mono-Vacancy Phosphorene (MVP)

The unit cell of phosphorene consists of four phosphorus atoms in an orthorhombic space group, as shown in Fig. 1A, with a lattice parameter of 4.61 and 3.29 Å, which is in good agreement with the previous reports [1]. We used a 3×3 supercell consisting of 36 atoms to model the gas molecule interaction studies as shown in Fig. 1B, with lattice dimensions of 13.85 Å $\times$ 9.89 Å. As can be seen, the structure of pristine phosphorene is anisotropic along the x and y directions, which are labeled as armchair and zigzag directions, respectively. After relaxation, the bond length of the P-P bond [d_1 (inter-layer distance)] was 2.26 Å in the armchair direction and 2.22 Å [d_2 (intra-layer distance)] in the zigzag direction, which are consistent with the literature [1]. Here, d_1 and d_2 are found to be slightly different but are very close to each other due to the covalent bonds between phosphorus 3p orbitals.

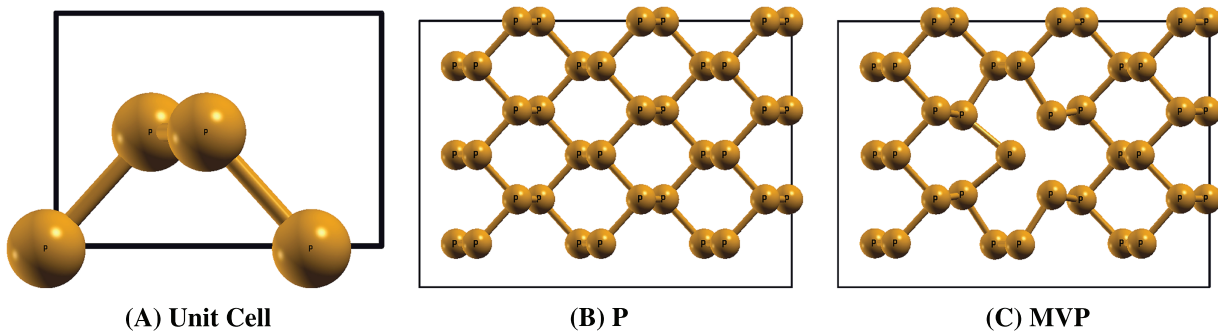


Figure 1: Relaxed structure of (A) Unit cell of phosphorene, and 3×3 super cell of (B) Pristine phosphorene sheet and (C) Mono-vacancy phosphorene sheet

In order to investigate the mono-vacancy, we removed one phosphorus atom from the 3×3 supercell structure. The structure of the MVP is shown in Fig. 1C. The formation energy (E_f) of the mono-vacancy configuration was computed using the relation $E_f = E_{MVP} - N_p E_p$, where E_{MVP} denotes the energy of phosphorene containing a single vacancy, N_p is the number of phosphorus atoms in the defective model, and E_p corresponds to the per-atom energy extracted from pristine phosphorene. The calculated formation energy is 2.07 eV, indicating that vacancy creation is endothermic but energetically feasible. This value is in excellent agreement with earlier work by Ramachandran et al. [35], who reported a formation energy of 2.09 eV using DFT-GGA. The relatively low value implies that mono-vacancies can be introduced experimentally and may play an active role in modulating the sensing performance of phosphorene.

Close to this defect, the armchair bond length of P-P bond measures 2.26 Å, while in zig-zag direction, it was 2.34 Å. In contrast, the bond lengths away from the defect region were 2.26 and 2.22 Å along armchair and zig-zag directions, respectively, which are comparable to those of phosphorene.

We next investigated the interaction of phosphorene sheets with different molecules by placing molecules close to the sheet in the orientation as shown in the Fig. 2. Interaction lengths between different gas molecules and P & MVP sheets is shown in Fig. 3, while geometry of gas molecules after interaction with sheets is shown in the Figs. 2 and 4, respectively. First, the interaction was investigated on a pristine phosphorene sheet, where we found almost no change in P-P bond length. We found that the interaction length (d) between NH_3 , AsH_3 , PH_3 , CO_2 and CH_4 and the pristine phosphorene sheet was 3.01, 3.45, 3.40, 3.62 and 3.19 Å, respectively with calculated interaction energies to be -0.166, -0.163, -0.157, -0.112 and -0.104 eVs for respective gases showing weak physisorption interactions. The interaction energy data suggest that the interaction ability of these five gas molecules on pristine phosphorene is in the order $\text{NH}_3 > \text{AsH}_3 > \text{PH}_3 > \text{CO}_2 > \text{CH}_4$. In a pristine phosphorene sheet, each phosphorus atom is covalently bonded with three neighboring phosphorus atoms. Each phosphorus atom has five valence electrons ($3s^2 3p^3$). Three of these electrons form three σ bonds with adjacent phosphorus atoms. The remaining two valence electrons create a lone pair that resides in an out-of-plane orbital. This arrangement gives rise to the distinctive puckered honeycomb structure. When a gas molecule interacts with a pristine phosphorene sheet, then Van der Waals interaction between the gas molecules and P sheet leads to higher values of interaction length.

Next, we studied the interaction of various gases on a mono-vacancy phosphorene (MVP) sheet by placing a gas molecule near the vacancy of MVP and allowing the system to relax without any constraints. The interaction lengths between gas molecules and the MVP sheet were 0.69, 1.26, 1.07, 2.58 and 2.04 Å for NH_3 , AsH_3 , PH_3 , CO_2 , CH_4 gases, respectively. In case of MVP, at the vacancy site each phosphorus atom is bonded with only two adjacent phosphorus atoms compared to three phosphorus atoms in pristine phosphorene sheet. This creates the local deformation and changes in orbital hybridization (Figs. S2 and S3). When NH_3 , AsH_3 , or PH_3 gas atoms interact with MVP sheet then these gas atoms covalently bind with phosphorus atoms close to the vacancy site. This results in strong interaction and a remarkable reduction in the interaction length. As compared to the pristine phosphorene sheet (P), we observed stronger interactions between vacancy-defected phosphorene sheet and different molecules. The relaxed structures of the MVP sheets after adsorption of NH_3 , AsH_3 , PH_3 , CO_2 and CH_4 gas molecules are shown in Fig. 4A–J.

In case of mono-vacancy phosphorene, the interaction energies of NH_3 , AsH_3 , PH_3 , CO_2 , CH_4 gas molecules were -0.343, -0.045, -0.272, -0.522, and -0.519 eV, respectively. The interaction ability of these five gas molecules on MVP is in the order $\text{CO}_2 > \text{CH}_4 > \text{NH}_3 > \text{PH}_3 > \text{AsH}_3$.

On comparing the interaction energies of NH_3 , AsH_3 , PH_3 , CO_2 , and CH_4 gas molecules on pristine phosphorene and MVP, it was found that vacancy could enhance the bonding strength of all the gas molecules except AsH_3 . We have given a comparison of the interaction energies of NH_3 , AsH_3 , PH_3 , CO_2 , and CH_4 gas molecules on pristine phosphorene (P) (blue color) and mono vacancy phosphorene (MVP) in Fig. S1.

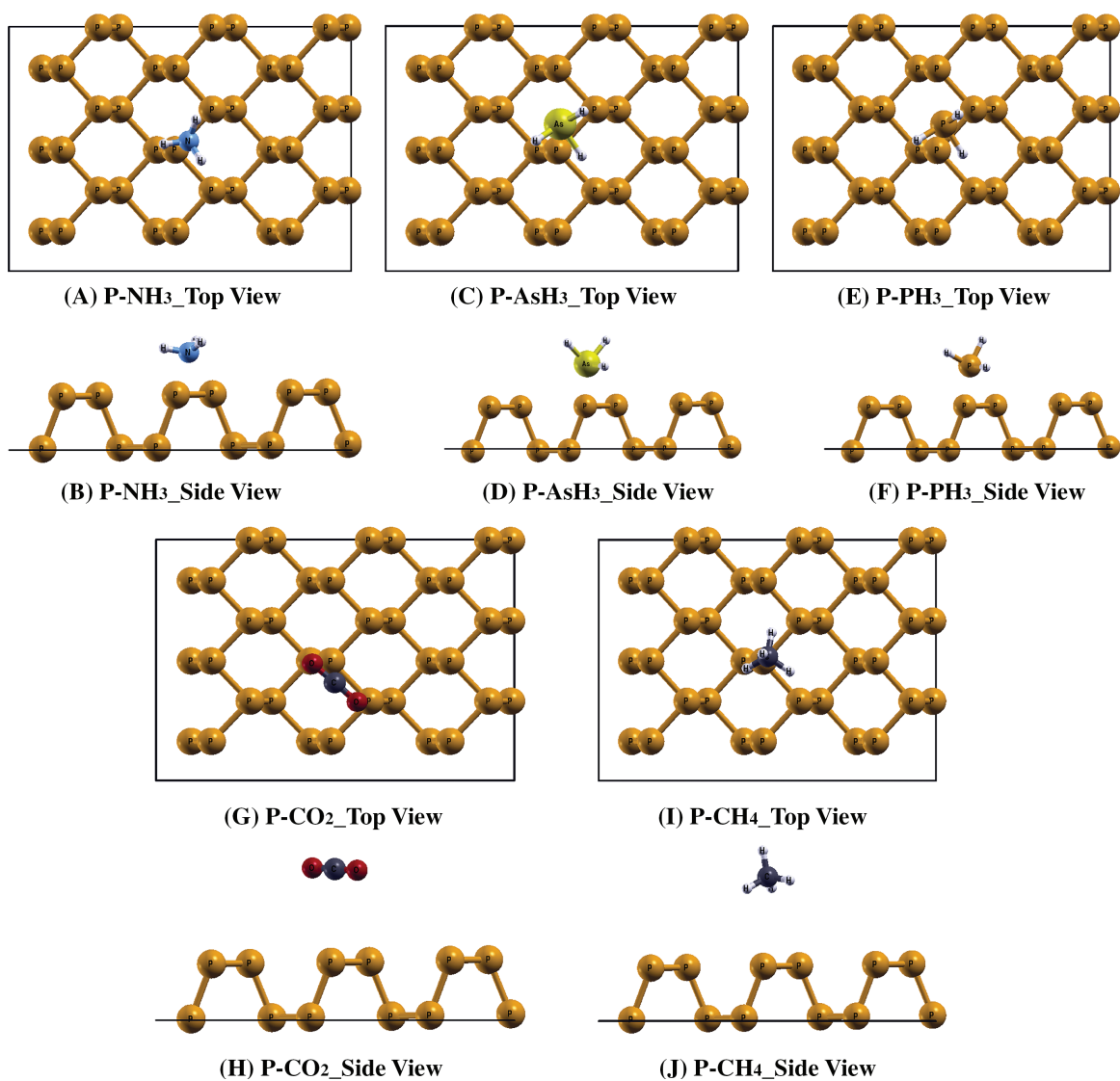


Figure 2: The relaxed structures of (A, B) P-NH₃, (C, D) P-AsH₃, (E, F), P-PH₃, (G, H) P-CO₂, (I, J) P-CH₄, respectively

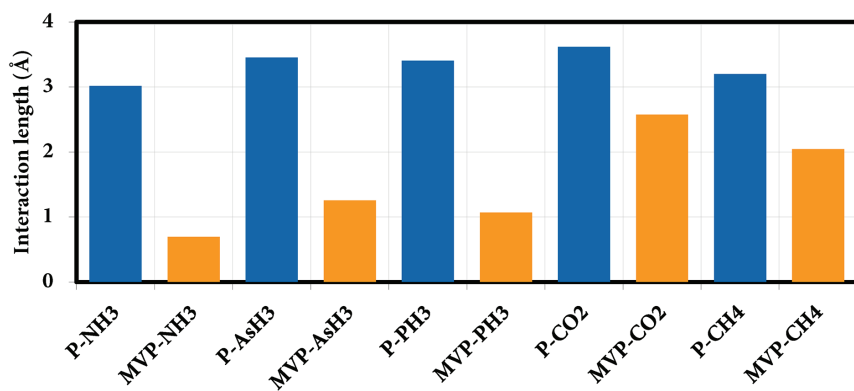


Figure 3: Interaction length between different gas molecules and P & MVP sheets

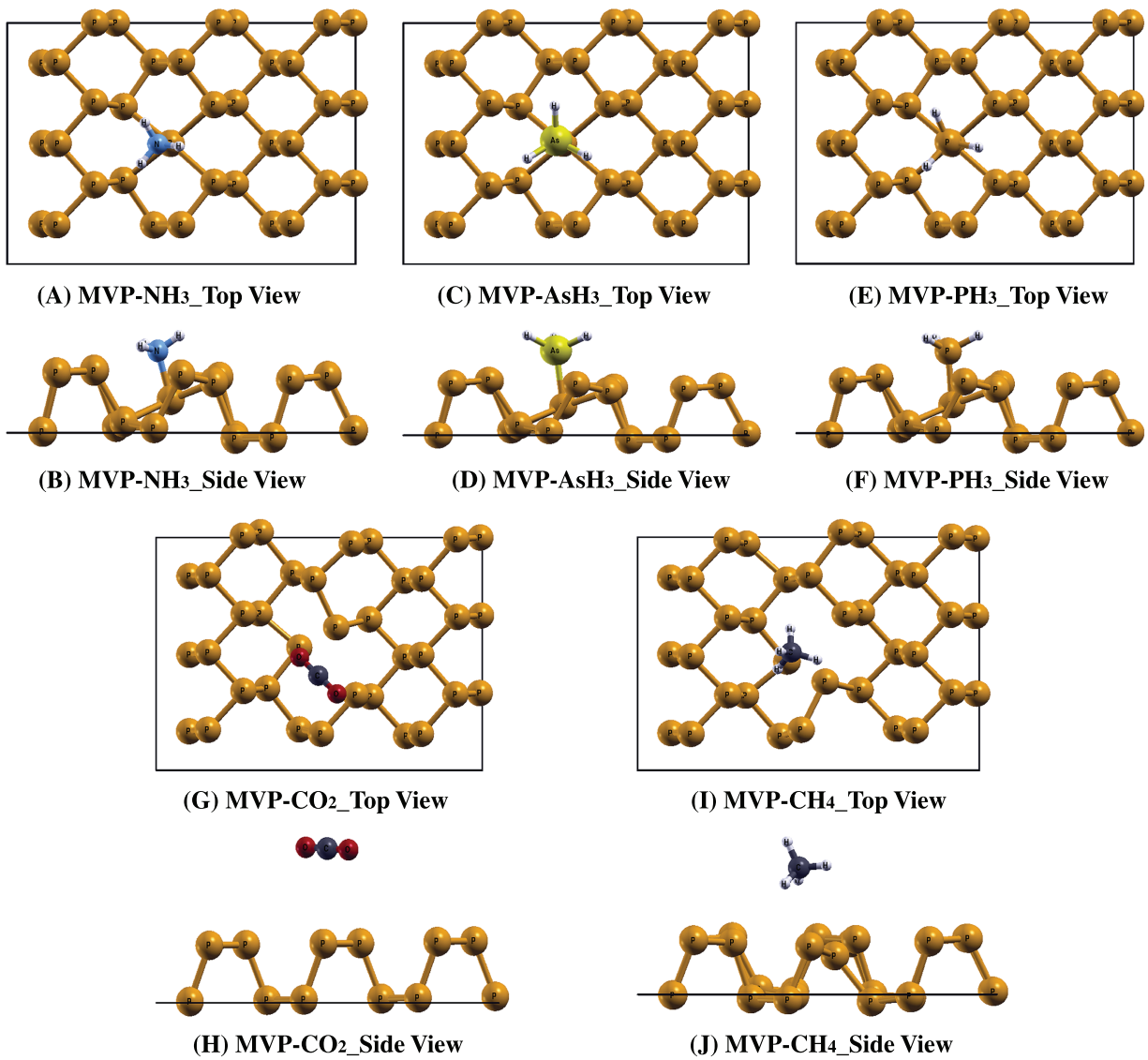


Figure 4: The relaxed structures of (A, B) MVP-NH₃, (C, D) MVP-AsH₃, (E, F), MVP-PH₃, (G, H) MVP-CO₂, (I, J) MVP-CH₄, respectively

This exception in the case of AsH₃ arises mainly due to electronic and structural factors. The mono-vacancy introduces unsaturated phosphorus atoms with dangling bonds that generally promote charge transfer and covalent bonding with incoming gas molecules. However, AsH₃ possesses a larger atomic radius and weaker electronegativity compared to NH₃ and PH₃, leading to poor orbital overlap between As-4p and P-3p states at the defect site. As a result, AsH₃ fails to form a strong P-As bond and instead exhibits lower interaction energy and a negative Bader charge transfer value (-0.469 e^-) (discussed in next section), indicating electron withdrawal rather than bond stabilization. Therefore, unlike other gases, AsH₃ interacts less strongly with the defective phosphorene sheet.

In the chemisorbed cases (NH₃, PH₃, and to a lesser extent AsH₃ on MVP), the interaction is predominantly covalent in nature. The mono-vacancy creates unsaturated phosphorus atoms with dangling bonds, which act as active sites for adsorption. The lone-pair electrons on N or P atoms in NH₃ and PH₃ interact with the P-3p orbitals at the vacancy site, leading to dative (coordinate) covalent bond formation.

This is confirmed by the significant reduction in adsorption distance (0.69–1.07 Å), large negative adsorption energies (−0.272 to −0.343 eV), and notable Bader charge transfer (0.256 e^- for NH_3 and −0.362 e^- for PH_3) (discussed in next section). In contrast, AsH_3 shows a weakly chemisorbed or transition-type interaction due to poor orbital overlap between the larger As-4p orbitals and P-3p defect orbitals, which explains its lower adsorption energy. Meanwhile, CO_2 and CH_4 exhibit van der Waals-type physisorption, as indicated by larger adsorption distances (>2.0 Å), small charge transfer, and minimal deformation of the MVP lattice.

3.2 Electronic Characteristics of Pristine and Mono-Vacancy Phosphorene Sheets and the Effect of Gas Molecule Interaction

To investigate further the gas molecule interaction and their sensing properties, we studied the electronic properties of systems by analysing their electronic band structures (Fig. 5). Fig. 5A shows the band structure of pristine phosphorene, while Fig. 5B–F shows the band structure of the phosphorene sheets after their interaction with gas molecules NH_3 , AsH_3 , PH_3 , CO_2 , and CH_4 , respectively. We observed that due to the weak interaction between different gas molecules and the pristine phosphorene sheet, the electronic bands profile remains almost unaltered.

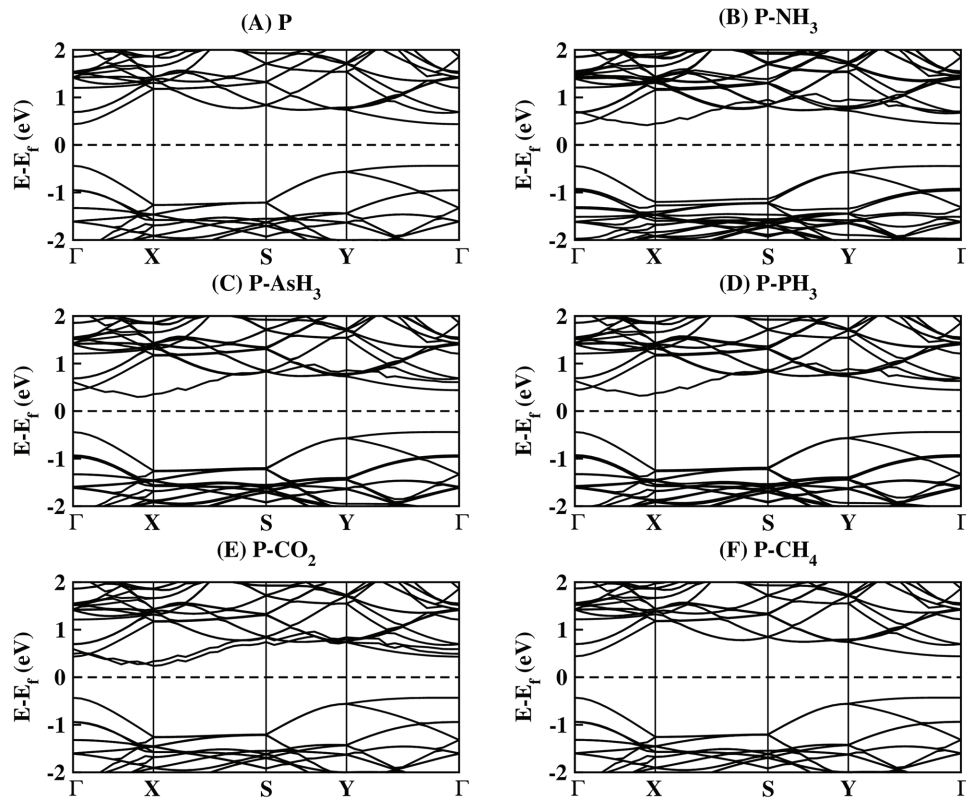


Figure 5: The band structure of (A) Phosphorene, (B) P- NH_3 , (C) P- AsH_3 , (D) P- PH_3 , (E) P- CO_2 , and (F) P- CH_4 Systems

We have given the band structures of MVP sheets before and after gas molecule interaction in Fig. 6. The presence of the defect is shown to induce hole doping within the phosphorene, evidenced by the Fermi level shifting upwards towards the valence band. The band gap identified was indirect, measuring approximately 0.77 eV. Additionally, it was observed that the defect creates localized states in the valence band, indicated

by the relatively flat band just below the Fermi level. These localized states act as possible active states for interacting with gas molecules.

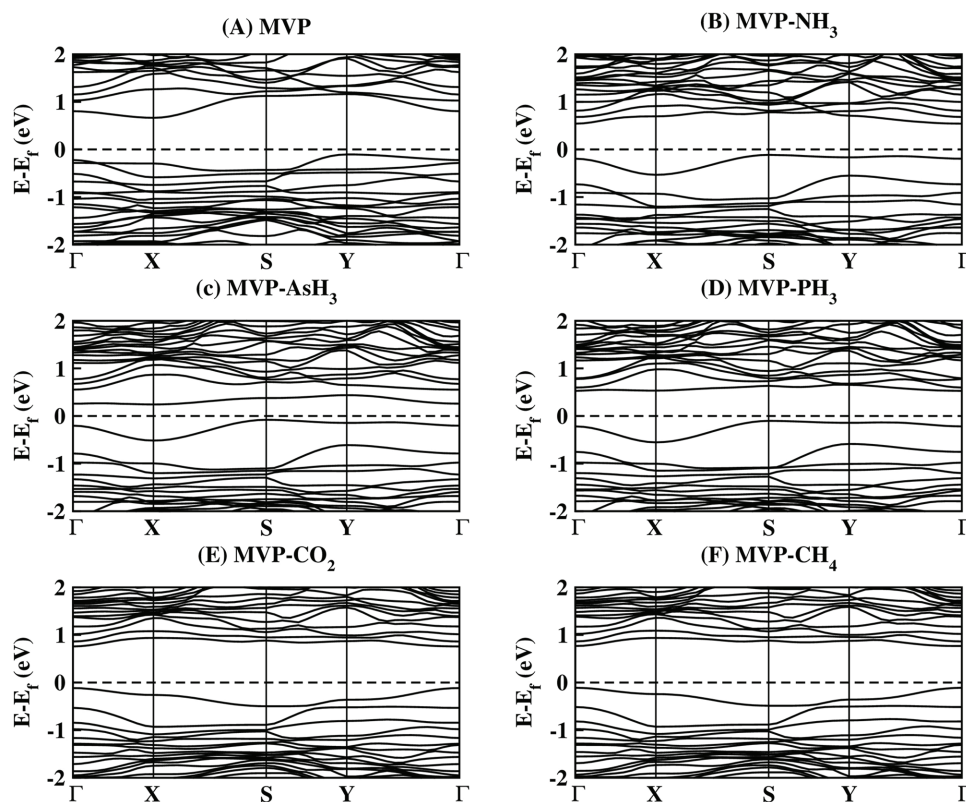


Figure 6: The band structure of (A) MVP, (B) MVP-NH₃, (C) MVP-AsH₃, (D) MVP-PH₃, (E) MVP-CO₂, and (F) MVP-CH₄ systems

The band gaps of P-sheet, MVP sheet, and the ad-systems are shown in Table 1. The band gap of the pristine phosphorene sheet was found to be 0.87 eV, which reduces to 0.77 eV in the MVP sheet as a result of vacancy. As in the case of pristine phosphorene sheet all gases show weak physisorption interactive nature with no chemical bond formation between molecule and the sheet, a similar interaction is reflected in the electronic band gap analysis, where we observed that band gap remains almost unaltered after different gas molecules interaction (Table 1) indicating very low amount of charge transfer between pristine phosphorene sheet and gas molecules. We have presented a comparative chart of the band gap in Fig. 7. In the case of gas molecules interacting with the MVP sheet, we see significant changes in the band gap values as a result of molecule interaction. The band gap of MVP changes from its original value of 0.77 eV to 0.66, 0.41, 0.65, 0.87, and 0.88 eV after interaction of gas molecules NH₃, AsH₃, PH₃, CO₂, and CH₄, respectively, which reflects larger charge transfer compared to that in the pristine phosphorene sheet. This was again confirmed through the Bader charge transfer analysis, where a considerable amount of charge transfer is observed between different molecules and the MVP sheet.

In order to gain a deeper insight into the electronic characteristics, the density of states (DOS) plots for all systems were analyzed (Fig. 8). We found that when NH₃, AsH₃, PH₃ gas molecules interact with pristine phosphorene, there is a slight change in DOS of pristine phosphorene and the Bader charge transfer are -0.039 , -0.011 , and -0.013 e⁻, respectively, which shows that there is less transfer of charge from the sheet to gas molecules, behaving NH₃, AsH₃, PH₃ are electron acceptors. While in the case of CO₂ and CH₄

gas molecules interaction with pristine phosphorene, there are significantly higher values of DOS in the conduction band, and CO₂ and CH₄ gas molecules interaction show the electron donor characteristics, as the Bader charge transfer are 0.017 and 0.006 e⁻, respectively.

Table 1: Fermi energy (E_F), band gap (E_g), work function (ϕ), interaction energy (E_{int}), and bader charge transfer (Q_t) and interaction length (d) of phosphorene, MVP, and their ad-systems

Structure	E_F (eV)	E_g (eV)	ϕ (eV)	E_{int} (eV)	Q_t (e ⁻)	d (Å)
P	-1.73	0.876	4.506	—	—	—
MVP	-2.5	0.77	5.199	—	—	—
P-NH ₃	-1.51	0.893	4.281	-0.166	-0.039	3.01
MVP-NH ₃	-1.81	0.657	4.545	-0.343	0.256	0.7
P-AsH ₃	-1.61	0.881	4.446	-0.163	-0.011	3.45
MVP-AsH ₃	-1.64	0.408	4.396	-0.045	-0.469	1.26
P-PH ₃	-1.58	0.886	4.401	-0.157	-0.013	3.4
MVP-PH ₃	-1.71	0.65	4.471	-0.272	-0.362	1.07
P-CO ₂	-1.64	0.867	4.492	-0.112	0.017	3.62
MVP-CO ₂	-2.2	0.875	4.989	-0.522	0.021	2.58
P-CH ₄	-1.67	0.871	4.478	-0.104	0.006	3.2
MVP-CH ₄	-2.3	0.878	5.049	-0.519	0.014	2.04

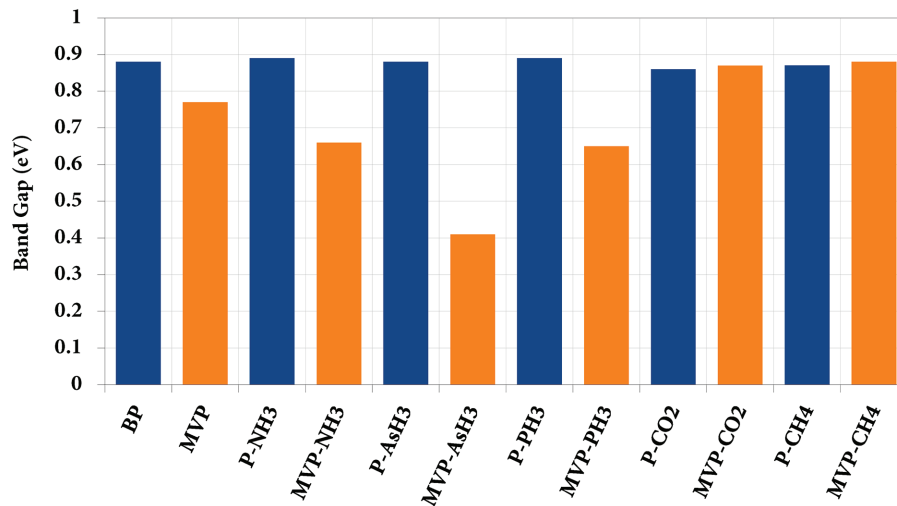


Figure 7: The comparative chart of band gap variations in pristine (P) and mono vacancy pristine (MVP) sheets as a result of interaction with different gas molecules

The DOS of the MVP sheet underwent significant modifications after the sheet's interaction with NH₃, AsH₃, PH₃, CO₂, and CH₄ gases. After NH₃ interaction, DOS of MVP increases significantly towards the lower energy side near the Fermi level, which further leads to a higher Bader charge transfer of 0.256 e⁻ showing electron donor properties of ammonia gas. AsH₃ and PH₃ interactions increase the DOS values in the vicinity of the Fermi level and lead to large Bader charge transfer of -0.469 and -0.362 e⁻, respectively that indicating the electron acceptor behavior of AsH₃ and PH₃ gas molecules. While CO₂ and CH₄ interaction slightly changes DOS of MVP towards the higher energy side near the Fermi level, and an increase in peak

value of DOS in the conduction band leads to a smaller Bader charge transfer with values 0.021, and 0.014 e^- . Hence, CO₂ and CH₄ molecules show the behavior of an electron donor.

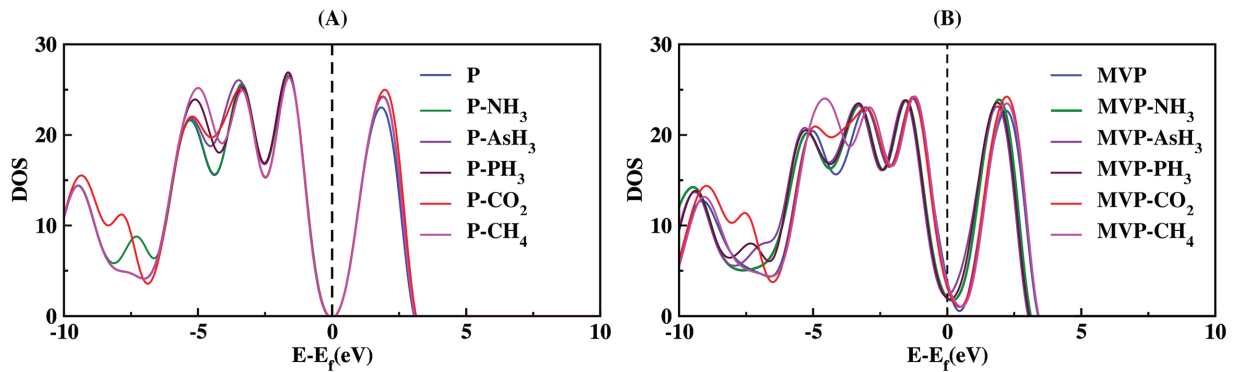


Figure 8: Comparison graph of DOS of (A) P and (B) MVP with their ad-systems.

Significant changes of DOS in the vicinity of the Fermi level are anticipated to lead to marked changes in the associated electronic properties. This is highly advantageous for gas sensing purposes. Therefore, the MVP demonstrates greater suitability for sensing NH₃, AsH₃, PH₃, CO₂, and CH₄ compared to pristine phosphorene. We have given projected-density-of-states (pdos) of NH₃ and AsH₃ molecules interacting with pristine and MVP sheets in Figs. S2 and S3, respectively. We note that a stronger overlap occurs, with noticeable As-sp³ mixing with defect-P (s-p hybrid) orbitals, indicating significant hybridization (Fig. S3).

3.3 Sensor Sensitivity, Recovery Time and Efficiency

The sensor responses for all the ad-systems were determined by analyzing the band gap before and after the interactions with the gases. Fig. 9 illustrates the sensitivity (S%), while Table 2 provides the sensitivities measured for NH₃, AsH₃, PH₃, CO₂, and CH₄ to be 39.65%, 10.34%, 17.7%, 15.62%, and 9.28%, respectively. For pristine phosphorene, the band gap shows nearly no changes following the interaction of AsH₃ and CH₄. However, there is a slight change in band gap noted after the interaction of NH₃, PH₃ and CO₂. Therefore, pristine phosphorene demonstrates a higher sensitivity towards NH₃, PH₃ and CO₂, while it has lower sensitivity towards AsH₃ and CH₄.

In case of MVP, the sensitivity for NH₃, AsH₃, PH₃, CO₂, and CH₄ are 88.71%, 99.9%, 90.13%, 86.82% and 87.56%, respectively. In this case, the increased value of S can be attributed to a significant alteration in the band gap. The changes in the band gap occur due to the interaction of NH₃, AsH₃, PH₃, CO₂, and CH₄ gas molecules on the MVP sheet, which leads to enhanced Bader charge transfer between the MVP and the gas molecules with values 0.256, −0.469, −0.362, 0.021, and 0.014 e^- , respectively in contrast to −0.039, −0.011, −0.013, 0.017 and 0.006 e^- in pristine phosphorene. Upon AsH₃ interaction with MVP, although the interaction energy is low, the sensitivity is very high. This indicates that AsH₃ is better sensed by MVP. The sensitivity of NO₂-doped graphene and Ti₃C₂ MXene is found to be 25.3% and 6.13%, respectively for NH₃ gas [36].

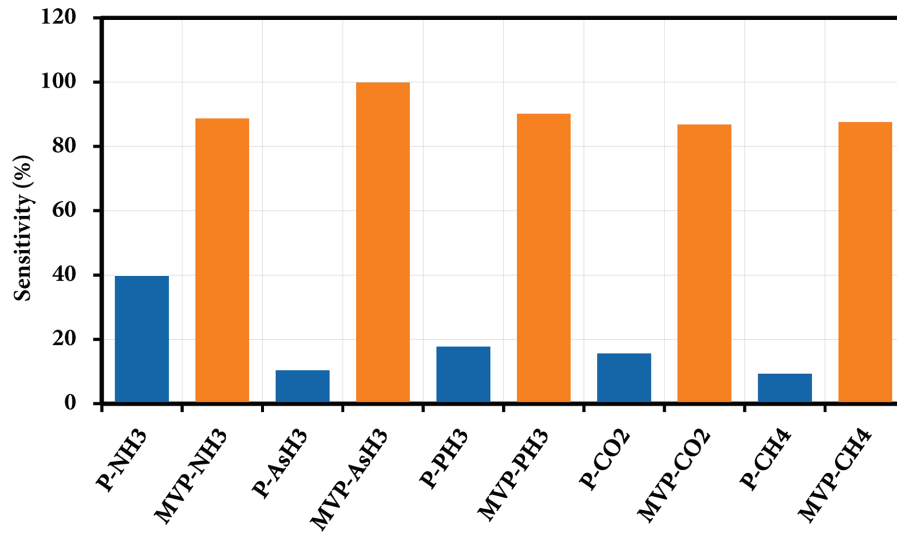


Figure 9: Sensitivity of NH₃, AsH₃, PH₃, CO₂, and CH₄ adsystems

Table 2: Sensitivity (S), estimated lower-bound recovery time (τ), and sensor efficiency (ϵ) of different systems

Structure	S (%)	τ	ϵ (%)
P-NH ₃	39.65	0.61 ns	4.99
MVP-NH ₃	88.71	0.56 μ s	12.58
P-AsH ₃	10.34	0.54 ns	1.15
MVP-AsH ₃	99.9	5.68 ps	15.44
P-PH ₃	17.7	0.43 ns	2.33
MVP-PH ₃	90.13	36.38 ns	14
P-CO ₂	15.62	75.51 ps	0.31
MVP-CO ₂	86.82	0.57 ms	4.04
P-CH ₄	9.28	55.45 ps	0.62
MVP-CH ₄	87.56	0.50 ms	2.88

We have also computed the recovery time using Eq. (4). A short recovery time is crucial because it ensures that the sensor is prepared for further measurements, improving the overall efficiency and reliability of gas detection, particularly in applications where gas concentrations fluctuate quickly. The recovery times for various ad-systems are presented in Table 2. The recovery time ranges from milliseconds to picoseconds. At room temperature, physisorbed systems (e.g., CO₂, CH₄ on P and on MVP) exhibit short lower-bound recovery times in the ps–ms range within the desorption energy approximation. By contrast, chemisorbed cases on MVP (notably NH₃, PH₃) can involve additional barriers arising from bond formation and local deformation; hence their practical recovery can be considerably longer than the lower-bound reported here and may benefit from temperature- or light-assisted desorption. The overall trend across gases and substrates remains unchanged. Consequently, both phosphorene-based sensors can be classified as reusable sensors, with MVP being slightly favored for its stable performance. This observation supports the conclusion that the MVP monolayer can be regarded as a highly sensitive and reusable sensor for these gases. For comparison,

the recovery time of $\text{Zr}_3\text{C}_2\text{O}_2$ -based gas sensor for NH_3 gas was found to be 1 ms and for W-doped graphene it was 10 s for CH_4 gas molecules [31].

The interactions between the surface and the adsorbate result in modifications to the work function of the nanomaterial. Therefore, we further determined the work function values and found that the interaction of these gas molecules on both P and MVP sensors caused a reduction in the work function. The work function values are presented in Table 2. The gas molecules NH_3 , AsH_3 , PH_3 , CO_2 , and CH_4 tend to exhibit weaker physisorption on pristine phosphorene, leading to only minor changes in the work function, although some modulation occurs due to decreased charge transfer. Consequently, the work function of pristine phosphorene sheet in the presence of these gases is found to be low. In contrast, the covalent adsorption of NH_3 , AsH_3 , and PH_3 on MVP leads to significant charge transfer, resulting in significant work function changes. Moreover, the physisorption of CO_2 and CH_4 on MVP causes lower charge transfer and, as a result, lower work function changes as well.

4 Conclusion

In this work, the adsorption behavior of NH_3 , AsH_3 , PH_3 , CO_2 , and CH_4 on pristine and mono-vacancy phosphorene sheets was systematically investigated using first-principles DFT calculations. Pristine phosphorene exhibits weak physisorption toward all gas molecules, resulting in negligible structural distortion, minimal charge transfer, and almost unchanged electronic properties. However, the introduction of a mono-vacancy significantly enhances the interaction strength for all gases (except AsH_3), due to the presence of unsaturated phosphorus atoms with dangling bonds and localized defect states near the Fermi level. These active defect sites promote stronger charge transfer, shorter adsorption distances, higher sensitivity, and noticeable modifications in band structure and density of states. Among all gases, CO_2 and CH_4 showed the highest interaction energies on MVP (−0.522 and −0.519 eV, respectively), while NH_3 and PH_3 induce significant modulation in the electronic properties. The MVP-based systems also exhibit high sensitivity (up to ~99.9%) and ultrafast recovery times ranging from picoseconds to microseconds, making them highly suitable for reusable room-temperature gas sensors.

Overall, the study reveals that mono-vacancy engineering in phosphorene dramatically improves its gas-sensing performance. Therefore, defective phosphorene, particularly MVP, can be considered a promising candidate for sensitive, selective, and reusable detection of NH_3 , AsH_3 , PH_3 , CO_2 , and CH_4 at room temperature.

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