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Adsorption Characteristics of DNA Nucleobases, Aromatic Amino Acids and Heterocyclic Molecules on Silicene and Germanene Monolayers

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Highlights

We have probed the adsorption mechanism of nucleobases, amino acids and heterocyclic molecules on silicene and germanene monolayers for the application of sensing of biomolecules. The salient outcomes of the current study are:

1. Nucleobases, amino acids and heterocyclic molecules are interacting with silicene and germanene under both physisorption and chemisorption process.
2. BEN physisorbed on the monolayer substrates and thereby adopts a planar conformation as that of free standing BEN. While the rest of the molecules chemisorb and thereafter, bend upon chemical binding or charge transfer.
3. In nucleobases, G has higher binding affinity with silicene and germanene whereas TRP and TYR have strong affinity towards silicene and germanene respectively.
4. Five membered heterocyclic molecules PYE has strong adsorption on silicene and germanene and PYRI, THP has strong adsorption on silicene and germanene respectively.
5. During the adsorption process a fraction of electronic charge is exchanged between the monolayers (silicene/germanene) and the incident molecules. The charge transfer varies from a minimum of 0.01 e (for BEN on silicene) to a maximum of 0.95 e (for PYN on silicene)
6. The binding characteristics governed by the charge transfer mechanism of bio molecules also alters the electronic properties of both silicene and germanene nano sheets.

Based on the findings mentioned above, we conclude that the both silicene and germanene could be promising monolayers for the detection and capture of a variety of bio molecules.

Abstract

Binding of DNA/RNA nucleobases, aromatic amino acids and heterocyclic molecules on two-dimensional silicene and germanene sheets have been investigated for the application of sensing of biomolecules using first principle density functional theory calculations. Binding energy range for nucleobases, amino acids and heterocyclic molecules with both the sheets have been found to be (0.43-1.16 eV), (0.70-1.58 eV) and (0.22-0.96 eV) respectively, which along with the binding distances show that these molecules bind to both sheets by physisorption and chemisorption

process. The exchange of electric charges between the monolayers and the incident molecules has been examined by means of Bader charge analysis. It has been observed that the introduction of DNA/RNA nucleobases, aromatic amino acids and heterocyclic molecules alters the electronic properties of both silicene and germanene nano sheets as studied by plotting the total (TDOS) and partial (PDOS) density of states. The DOS plots reveal the variation in the band gaps of both silicene and germanene caused by the introduction of studied molecules. Based on the obtained results we suggest that both silicene and germanene monolayers in their pristine form could be useful for sensing of biomolecules.

Keywords: Adsorption Characteristics

DNA Nucleobases,

Aromatic Amino Acids

Heterocyclic Molecules

Introduction

Graphene has attracted the attention of both experimentalists and theoreticians due to its unusual properties such as high surface area, robust electron mobility, low electrical noise¹⁻³ and its sensitivity to the chemical environments. The maximized surface-to-volume ratio of 2D materials is particularly appealing for chemical gas sensors to achieve the ultimate level of sensitivity. Reported experimental studies demonstrated that one can attain the sensitivity in the order of 1 part per billion (1 ppb) by using carbon nanotube sensors while conventional sensors only shows the highest sensitivity in the range of 1 part per million (1 ppm). Due to the stated benefits, graphene is practically feasible for detecting various types of sensors for the small^{4,5} and biomolecules.⁶⁻⁸ In addition to that, noncovalent functionalization of graphene have been

carried out for novel properties of these new nanocomposite materials.^{9,10} Recently graphene analogues such as silicene and germanene has caught significant attraction to the researchers because of high carrier mobility, quantum hall effect and half metallicity. Silicene were successfully grown experimentally on Ag¹¹⁻¹⁴, Ir¹⁵ and ZrB₂¹⁶ substrate and germanene has also been grown experimentally on Pt (111) surface.¹⁷ Notably, their crystal structures do not exactly resemble graphene, they exhibit the buckled honeycomb structures instead of the flat honeycomb phase¹⁸. Intriguingly, the tilting geometry intrinsically provides sp^3 bonding to strengthen chemical bonding. Both silicene and germanene are more reactive than graphene due to their buckled honeycomb structure¹⁸ therefore, atoms and molecules are strongly¹⁹⁻²³ bind with silicene and germanene than graphene making these monolayers as a potential materials for batteries²², catalyst²³ and sensor^{21,22}. There have been numerous studies on silicene and germanene based sensors to detect some environmentally and industrially important gas molecules such as CO, NO, NH₃ and NO₂, H₂S, CO₂ and SO₂ molecules on silicene²⁴⁻²⁶ and germanene^{27,28} for the application of gas sensing and the results shows SO₂ and NO₂ molecule strongly binds to the silicene and germanene respectively. Although the interaction of various gas molecules has been extensively studied with both silicene and germanene monolayers, however their interaction with biomolecules such as DNA nucleobases, amino acids are very limited. To bridge this void in this study we have performed DFT calculations for the adsorption of DNA nucleobases, aromatic amino acids with silicene and germane for the bio sensing applications and with various heterocyclic molecules (with O, N, S) for the new composite material for the sensing/capture applications.

Computational methods

All the calculations in this study were performed by using DFT in the generalized gradient approximation (GGA)²⁹ with Perdew–Burke–Ernzerhof (PBE) exchange functional as implemented in VASP³⁰. It is well known fact that simple GGA-PBE underestimates the binding energies especially where the van der Waals binding effect is present. Thus to incorporate the van der Waals correction, we employed the DFT-D2³¹ method of Grimme as implemented in VASP. According to DFT-D2 approach the self-consistent total energy is obtained from Kohn-Sham DFT (E_{KS-DFT}) additionally corrected by E_{disp} as follow:

$$E_{\text{DFT-D2}} = E_{\text{KS-DFT}} + E_{\text{disp}}$$

Here, the underlying E_{disp} is a pairwise term accounting for the long-range van der Waals (vdW) interactions and it is defined as

$$E_{\text{disp}} = -s_6 \sum_{i=1}^{N_{\text{at}}} \sum_{j=1}^{N_{\text{at}}} \sum_L' \frac{C_6^{ij}}{|r^{i,0} - r^{j,L}|^6} f(|r^{i,0} - r^{j,L}|)$$

where $C_6^{ij} = \sqrt{C_6^i C_6^j}$ represents the dispersion coefficient, $R^{ij} = R^i + R^j$ is the vdW radius and $f(r^{ij})$ is the damping function. We have added this useful information to the revised manuscript.

We have used 5×5 model supercell of both silicene and germanene monolayers having 50 atoms for each supercell. The energy cutoff was set to be 500 eV and to minimize the possible interaction between nearby sheet a vacuum space about 20 Å were used in Z direction. Brillouin zone was sampled with $3 \times 3 \times 1$ k -points by using Monkhorst-pack scheme,³² the energy and force convergence of 10^{-6} eV and 0.001 eV/Å have been used respectively. Charge transfer was calculated using Bader charge analysis. The charge enclosed within the Bader volume is a mature approximation to the total electronic charge of an atom. Therefore, Bader analysis can be used to estimate the charge transfer. We have amended this explanation into the revised manuscript. The binding energy of DNA nucleobases, aromatic amino acids and heterocyclic molecules with silicene and germanene was calculated by using the following relation:

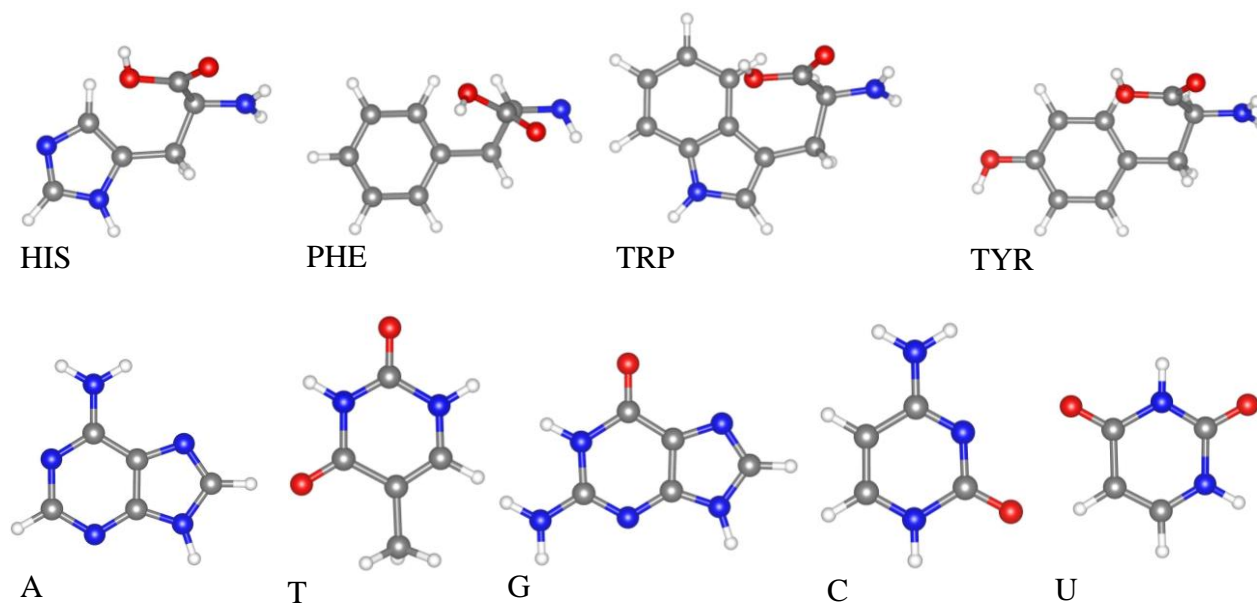
$$\text{Binding energy} = E_{\text{sheet+molecule}} - (E_{\text{sheet}} + E_{\text{molecule}})$$

Where $E_{\text{sheet+molecule}}$, E_{sheet} and E_{molecule} are total energy of sheet with molecule, pristine sheet and the molecule respectively. The negative values of binding energy account for favorable binding while the positive values represent unfavorable binding.

Results and discussion

Binding of DNA nucleobases on Silicene and Germanene

The calculated Si-Si bond length of buckled silicene is 2.27 Å and Ge-Ge bond length of germanene is 2.44 Å which has good agreement with previous studies.^{25,27} Molecules can bind either perpendicular or parallel to the silicene and germanene sheet, since parallel binding is more favorable than perpendicular binding in the earlier reports⁶ of binding of small and large molecules on graphene and graphane, we have considered only parallel binding of DNA nucleobases, aromatic amino acids and heterocyclic molecules on both sheets. Model system of DNA nucleobases (A, T, G, C and U), aromatic amino (histidine (HIS), phenylalanine (PHE), tryptophan (TRP), and tyrosine (TYR)) acids and heterocyclic molecules are depicted in **Figure1**. The comprehensive details of these bio-molecules with silicene and germanene will be consecutively presented.



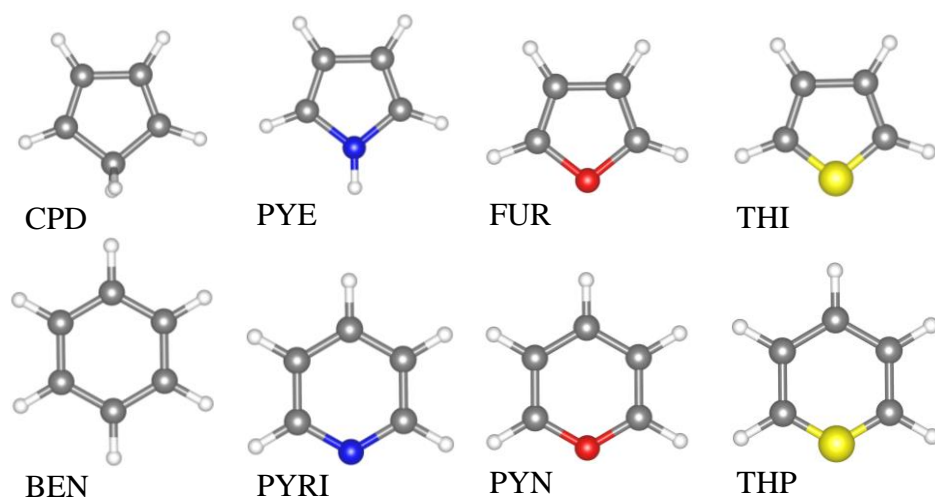
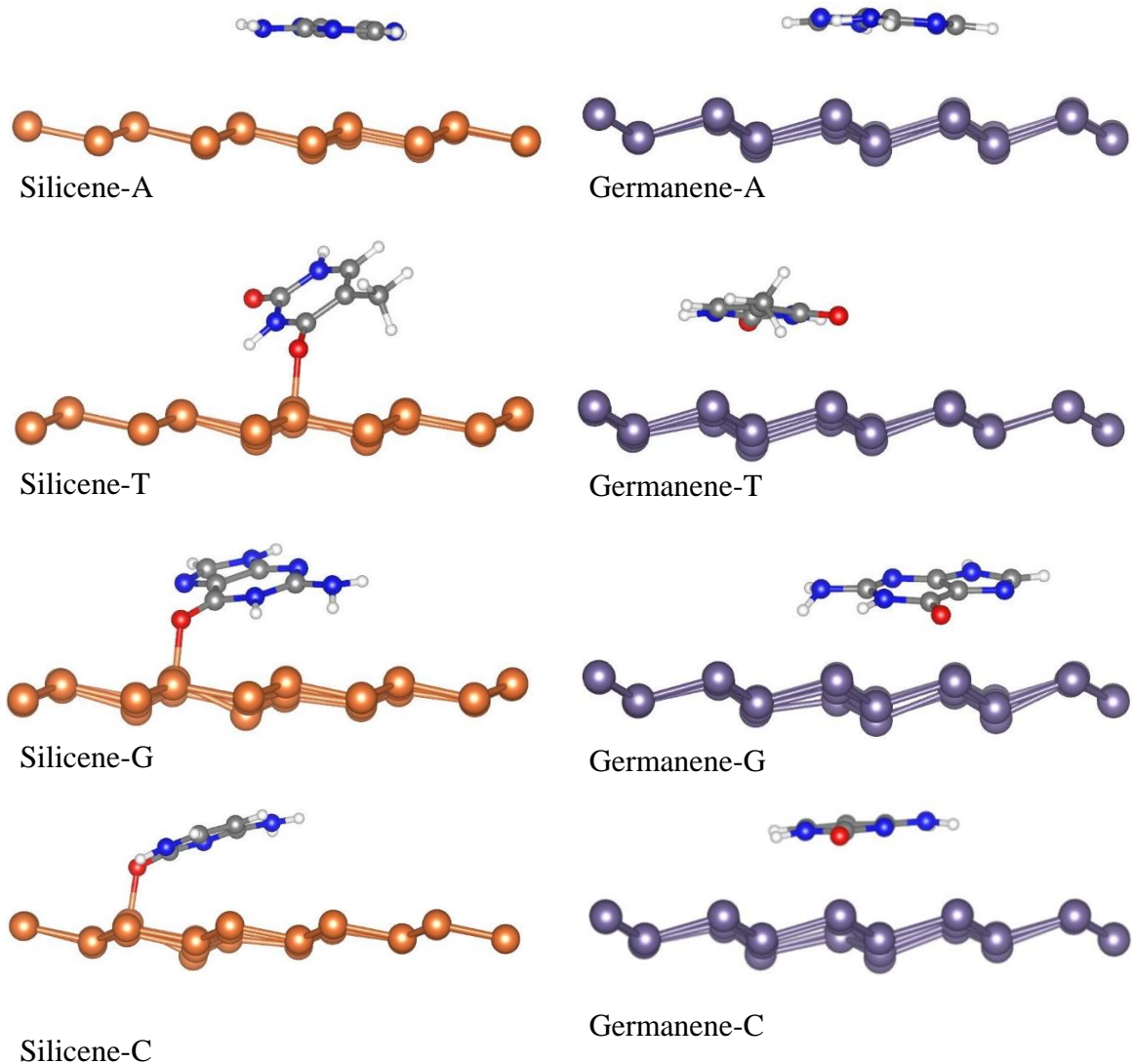


Figure1. Nucleobases (A, T, G, C and U), aromatic amino acids (HIS, PHE, TRP and TYR), and heterocyclic (CPD, PYE, FUR, THI, BEN, PYRI, PYN, and THP) molecule models for calculations (grey: C, white: H, blue: N, red: O, yellow: S)

In the following sections we discuss about structure and energetics of binding of DNA nucleobases with silicene and germanene sheet. Energy minimized structures of nucleobases with silicene and germanene sheet are shown in **Figure 2**. It is apparent that nucleobase A energetically adopts a parallel orientation whereas T, G, C and U have tilted orientation towards silicene and germanene. This is because of the absence of oxygen atom in A, whereas in other nucleobases oxygen atom strongly interacting with Si, Ge atom of silicene and germanene respectively. The calculated vertical heights between A, T, G, C and U with silicene are about 3.22, 1.85, 1.82, 1.81 and 3.13 Å respectively and the binding energies are 0.54, 0.7, 1.16, 1.13 and 0.43 eV respectively. Binding energy of T, G and C is higher than A and U due to strong affinity of O atom in T, G, U with silicon atom of silicene and that silicon atom is pulled towards the O atom of nucleobases. Order of binding energies of A, T, G, C and U with silicene is $G > C > T > A > U$, which is different from graphene, MoS₂ and WS₂ monolayer ($G > A > T > C > U$) calculated by using DFT-D2 method.^{7,8} We have analyzed charge transfer mechanism through Bader charge analysis as implemented in VASP and the results shows T, G, C and U gain 0.11,

0.07, 0.03 and 0.03e from silicene surface, however there is no charge transfer between A and silicene. In the case of germanene monolayer the calculated vertical heights and binding energies for A, T, G, C and U are 3.05, 3.02, 2.26, 3.09, 3.12 Å and 0.70, 0.57, 0.95, 0.56, 0.51 eV respectively and the order of binding energies is $G > A > T > C > U$ which resembles to that of graphene, MoS₂ and WS₂ monolayer.⁸ It can be concluded from the findings that G strongly interacts with both silicene and germanene, but U shows the opposite.



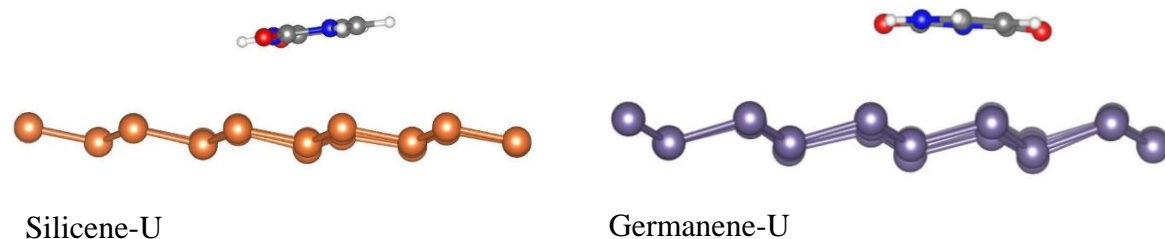
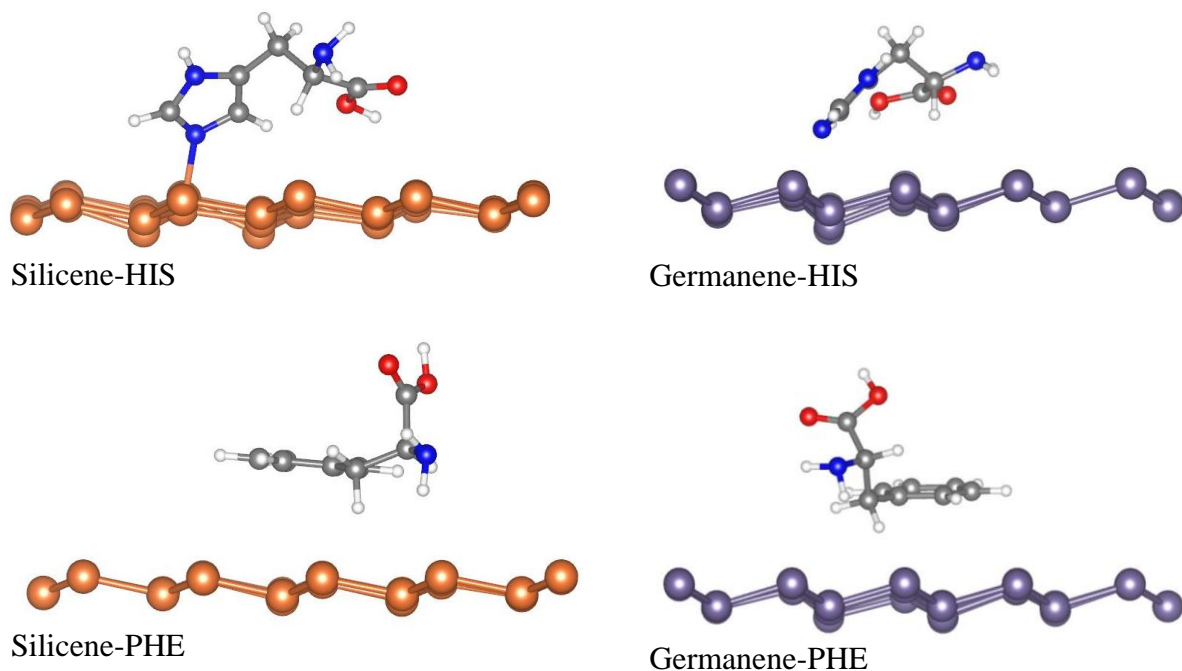


Figure 2. Optimized structures of different nucleobases with silicene and germanene sheet (orange: Si, purple: Ge, grey: C, white: H, blue: N, and red: O).

Binding of aromatic amino acids on Silicene and Germanene

The lowest energy structures of HIS, PHE, TRP and TYR with silicene and germanene obtained through relaxation are shown in **Figure 3**.



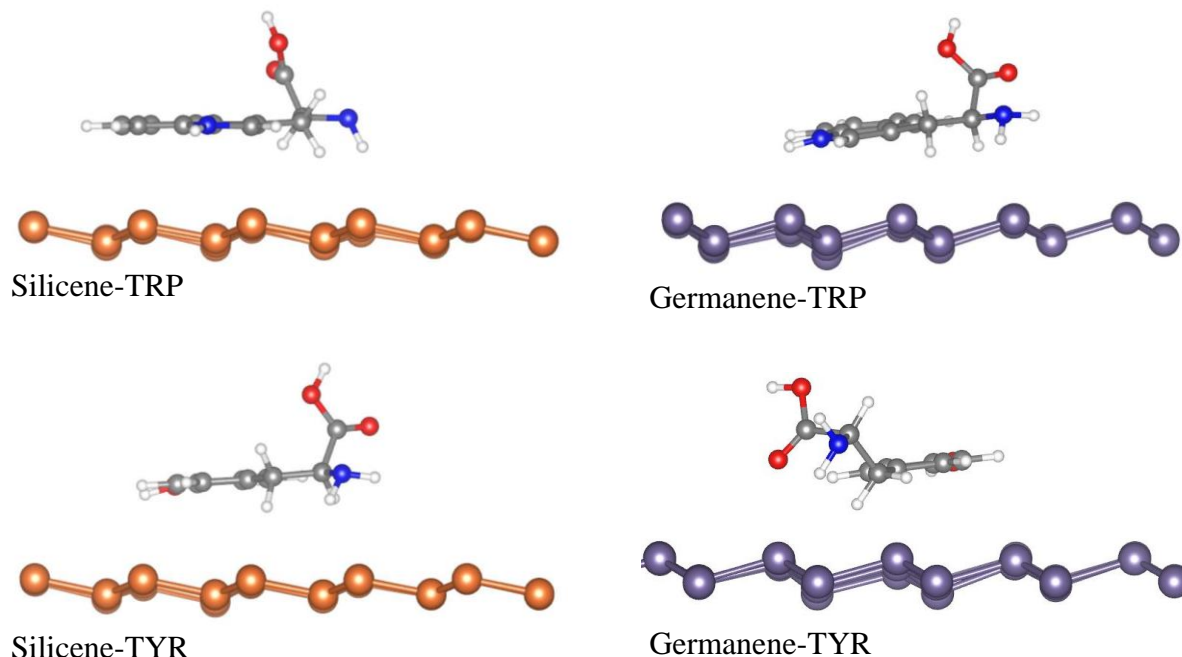


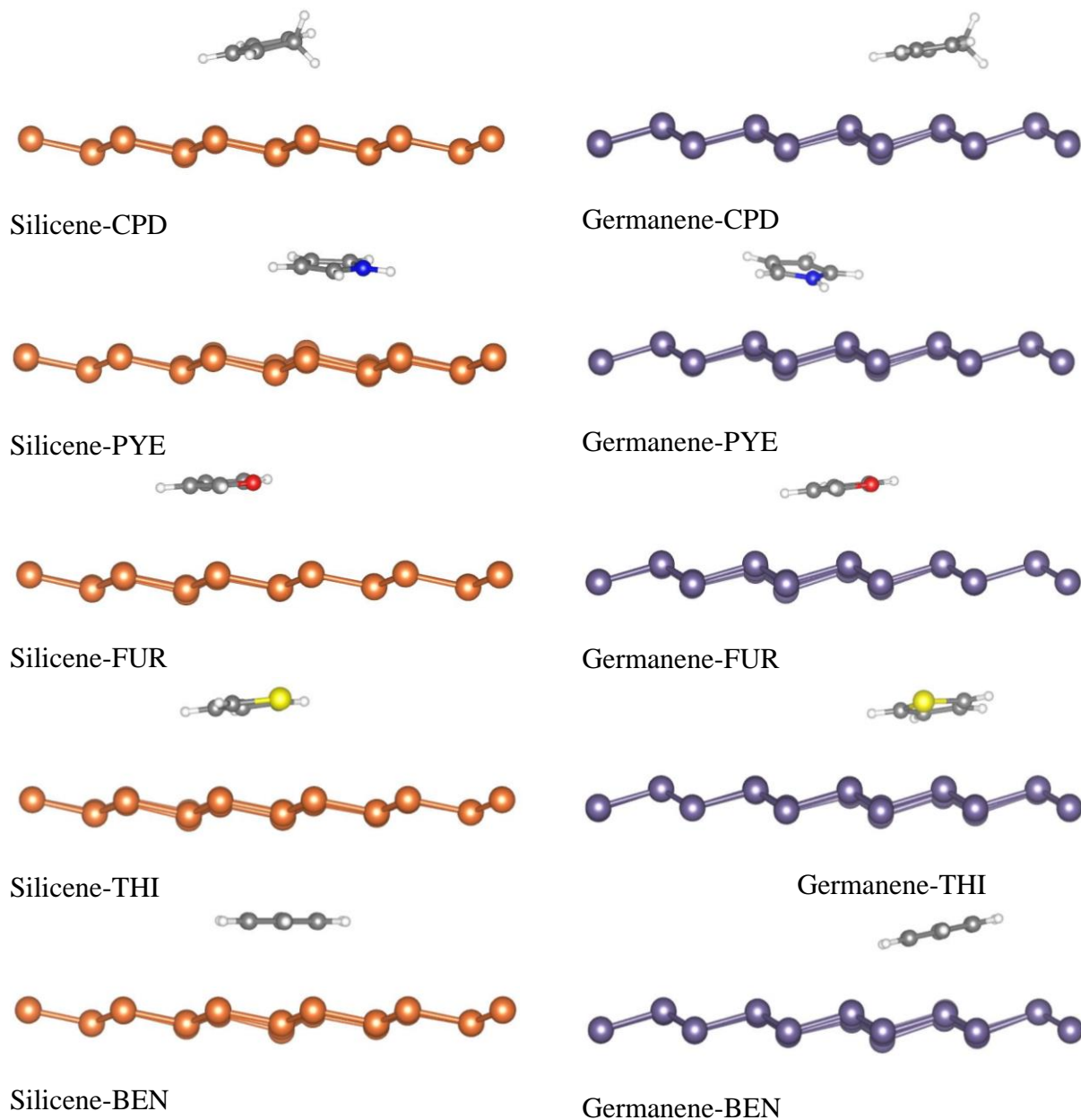
Figure 3. Optimized structures of aromatic amino acids with silicene and germanene sheet (orange: Si, purple: Ge, grey: C, white: H, blue: N, and red: O)

After complete optimization the vertical heights of HIS, PHE, TRP and TYR are 1.93, 2.98, 2.84 and 2.85 Å respectively with silicene and 2.19, 2.93, 2.71 and 3.09 Å respectively with germanene. PHE, TRP and TYR have parallel orientation with surface of silicene and germanene but HIS does not have parallel orientation because of the nitrogen atom in the imidazole ring of HIS has strong interaction with Si and Ge atom of substrate monolayers. The calculated binding energies of HIS, PHE, TRP and TYR are 1.21, 1.02, 1.39 and 1.28 eV respectively with silicene and 1.05, 0.70, 1.04 and 1.58 eV respectively with germanene, which are higher than graphene and carbon nanotube³³. The trend in the binding energies were found to be TRP > TYR > HIS > PHE with silicene but for the germanene a different trend like TYR > HIS > TRP > PHE. From the Bader charge analysis HIS, PHE and TYR acts as acceptor and accepts 0.04, 0.04, 0.02e from silicene, TRP acts as donor and it's donate 0.06e to the silicene monolayer. In the case of

germanene, HIS act as electron donor by donating 0.06e to substrate, other amino acids PHE, TRP and TYR attracts 0.30, 0.30 and 0.05e from substrate.

Binding of heterocyclic on Silicene and Germanene

The relaxed structures of unsaturated heterocyclic molecule on silicene and germanene surface have been shown in **Figure 4**.



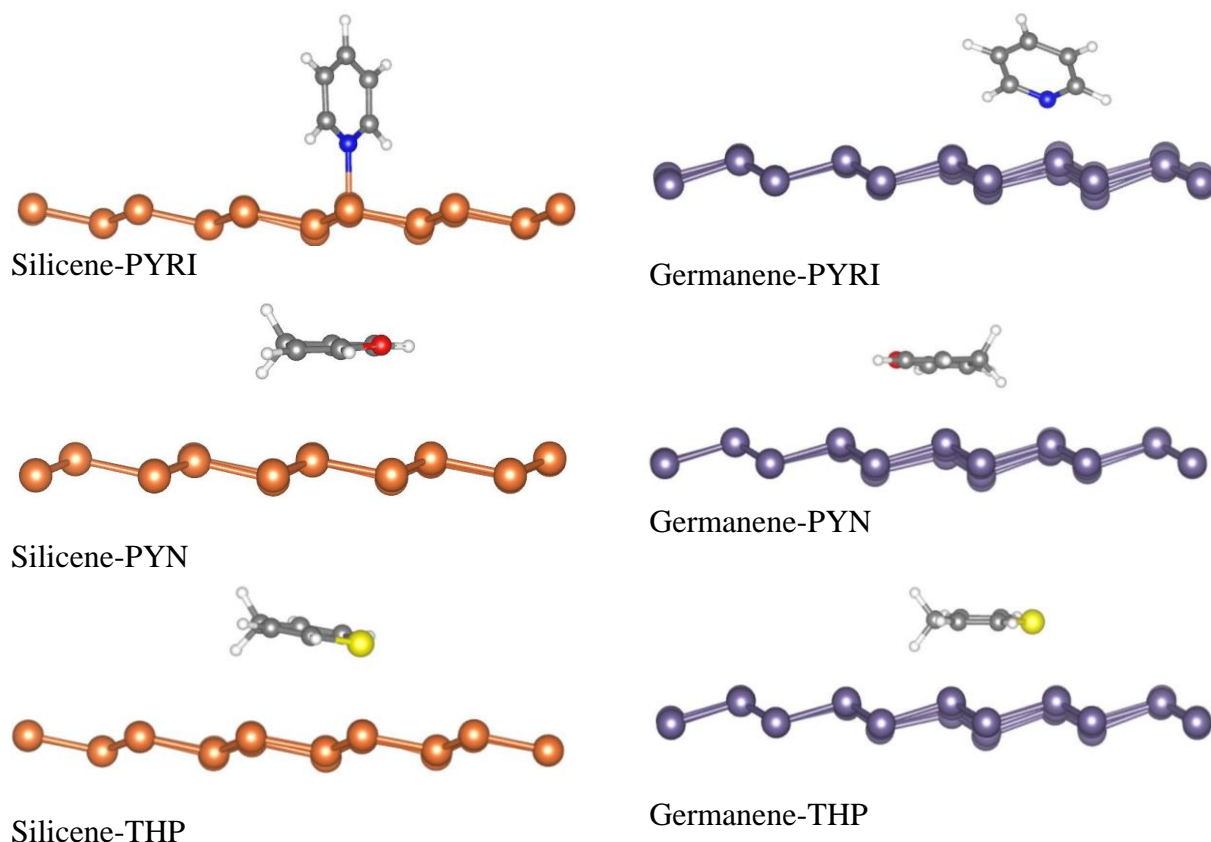


Figure 4. Optimized structures of five and six membered ring heterocyclic compounds with silicene and germanene sheet (orange: Si, purple: Ge, grey: C, white: H, blue: N, red: O, and yellow: S)

We consider five and six membered ring heterocyclic molecules such as cyclopentadiene (CPD), 1H-pyrrole(PYE), furan (FUR), thiophene (THI), benzene (BEN), pyridine (PYRI), 4H-pyran (PYN) and 4H-thiopyran (THP). All five membered ring molecules, have tilted orientation on silicene and germanene, the vertical distances of CPD, PYE, FUR and THI with silicene were found to be 2.86, 3.16, 3.35 and 3.43 Å respectively and 2.99, 2.82, 3.09 and 3.07 Å respectively with germanene. The calculated binding energies for the CPD, PYE, FUR and THI with silicene were 0.30, 0.33, 0.27, and 0.22 eV respectively and the same with germanene was 0.47, 0.53, 0.37, and 0.36 eV respectively. Therefore, PYE is the most reactive to both silicene and

germanene as evident by the highest binding energies. Noticeably, the binding energies of heterocyclic compounds with silicene are relatively less than those with germanene. This can be ascribed to the fact that the former possesses the smaller binding affinity. After adsorption on silicene, PYE donates 0.04e to the surface and other three molecules do not have significant charge transfer, CPD accepts 0.02e from germanene sheet and PYE donates 0.02e to the germanene sheet. As for as six membered ring molecules are concerned, only BEN has parallel orientation with silicene and other molecules (both five and six membered) do not have parallel orientation with silicene and germanene sheet. Vertical distances between BEN, PYRI, PYN and THP were 3.42, 1.96, 3.00, and 2.75 Å respectively with silicene and 3.16, 2.36, 3.27, and 3.00 Å respectively with germanene. The binding energies of these molecules with silicene were found to be 0.37, 0.96, 0.40 and 0.49 respectively and 0.24, 0.59, 0.52, and 0.70 eV respectively with germanene monolayer. The higher binding energy of PYRI with silicene was due to the strong interaction with silicon atom of the surface, which was reflected in calculated vertical distance (1.96 Å). BEN donates 0.01e and PYRI, PYN, THP accepts 0.01, 0.95 and 0.87e of charge respectively from the silicene surface. For germanene, we have not found charge transfer between BEN and the monolayer; PYRI accepts 0.03e while PYN and THP donates 0.68 and 0.67e of the charge to the surface.

Figure 5 shows the comparison of binding energies of nucleobases, amino acids and heterocyclic molecules with silicene and germanene.

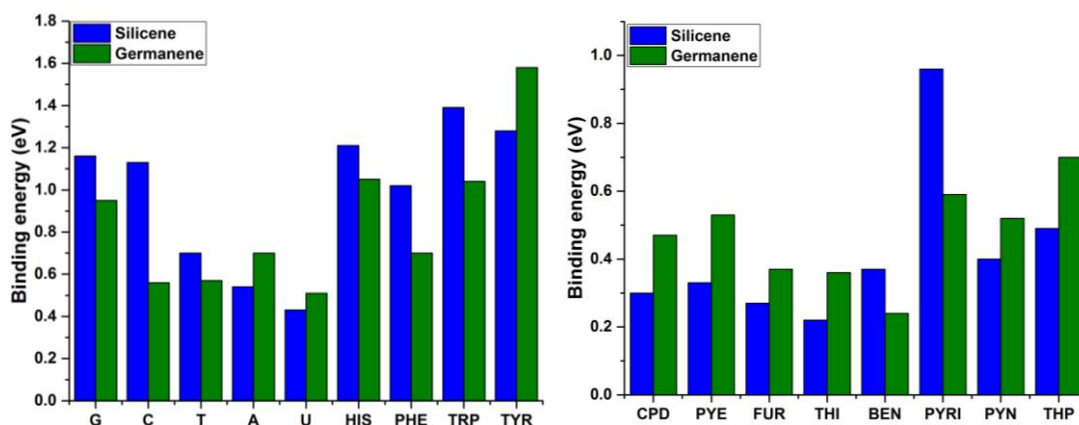


Figure 5. Comparison of binding energies of different molecules with silicene and germanene sheet

It is clear from figure (5) that the binding energies of G, C, and T with silicene are higher than that of germanene and the binding energies of A and U with germanene are higher than silicene. In case of amino acid (HIS, PHE and TRP) have higher binding energies with silicene than germanene, whereas TYR has higher binding with germanene than silicene. Binding energies of the five membered ring molecules (CPD, PYE, FUR, and THI) with germanene are higher than that of silicene but for six membered ring molecule both BEN and PYRI has higher binding energies with silicene than germanene, PYN and THP has higher binding energy with germanene than silicene.

Electronic properties

In addition to energetics analysis, the adsorption mechanism of various molecules/ligands on silicene and germanene has been further explained by means of plotting their total (TDOS) partial (PDOS) density of states. For comparison the TDOS and PDOS of pristine silicene and germanene sheets has been given in figure 6 (a), which indicates semi metallic nature of both the sheets. Although the use of GGA-PBE would underestimate the band gap due to its inability to approximate actual band gaps, however the use of more accurate hybrid functionals or even GW

approximations are computationally expensive and also beyond the scope of current study. It is evident from the upper and lower panel of figure 6 (a) that the valence and conduction

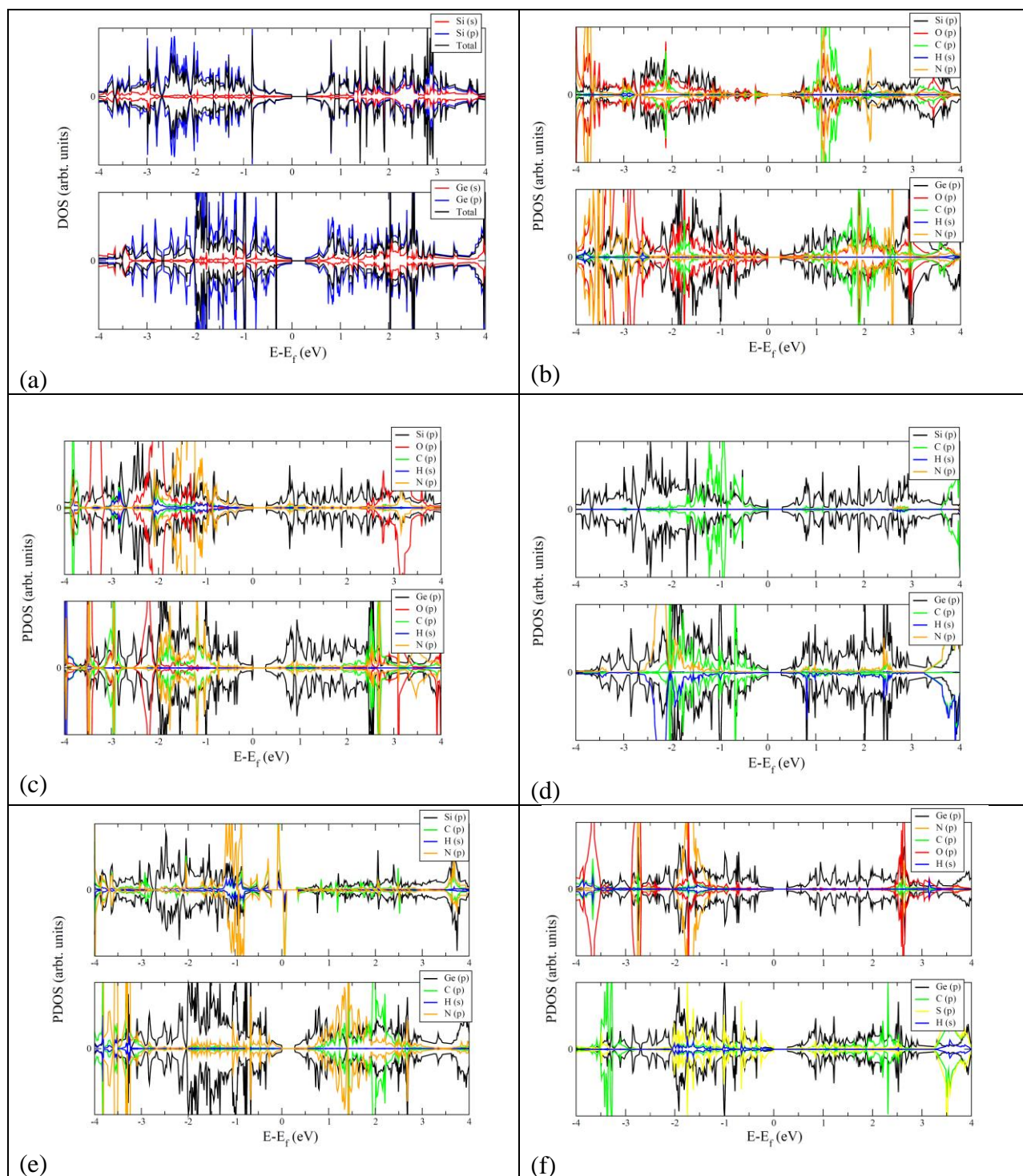


Figure 6. Total and partial density of states for the (a) pure silicene and germanene, (b) Silicene-G and Germanene-G, (c) Silicene-TRP, Germanene-TRP, (d) Silicene-PYE, Germanene-PYE, (e) Silicene-PYRI, and Germanene-PYRI (f) Germanene-TYR, Ge-THP

bands are formed by Si (p) and Ge (p) orbitals for silicene and germanene respectively. For convenience we have presented the electronic properties of specific species (selected members of each group like G, TRP, PYE, and PYRI) on silicene and germanene, which are discussed below one by one. While the main focus of the current study is to investigate the sensing properties of silicene and germanene nano sheets towards various selected species, hence the variations in the density of states around the Fermi level depicts the change in electronic properties.

In case of Silicene-G, a small band gap of 0.45 eV opens as shown in upper panel of figure 6 (b). Here the Si (p) states, which emerged close to Fermi level (E_f) on the left side in case of pristine sheet vanishes and there is no contribution from Si (p) orbitals between -1.0 eV to 0.60 eV on either side of E_f . Nevertheless hybridizations do exist among Si (p), N (p) and O (p) at -1.1 eV on the left and at 0.70 eV on the right of E_f . However the PDOS of germanene-G as shown in lower panel of figure 6 (b) displays a slightly different picture with more pronounced Ge (p) peaks hybridizing with O (p) at -1.0 eV, -0.60 eV and at -0.25 eV in the valence band region. Even on the right side of E_f , there is a small contribution from G and most of the peaks appearing are from Ge (p).

For silicene-TRP PDOS, as plotted in the upper panel of figure 6 (c), the system remain semi metallic despite the overlap between Si (p) and N (p) at several points between -0.80 eV to the edge of E_f in the valence band region. The shape of the conduction band remained similar to the case of pristine silicene with the contribution of mainly from Si (p) without altering the band gap. The orbital hybridization of Ge (p) with the constituent atoms of TRP is even smaller in

case of Ge-TRP PDOS as shown in the lower panel of figure 6 (c). Here majority of the contribution comes from Ge (p) on either side of E_f , except at -1.0 eV and -0.75 eV where peaks from N (p) appear without actually overlapping with Ge (p). Even here there is hardly any change in the band gap of the system as compared to the case of pristine germanene.

When it comes to PYE adsorption to the silicene sheet as given in upper panel of figure 6 (d), the PDOS looks similar to the case of silicene-G with a small band gap or around 0.50 eV. There is a reasonable hybridization of Si (p) and C (p) at -0.50 eV on the left of E_f in the valence band region. Apart from C (p), none of the constituent atoms of PYE contribute in the valence as well as in the conduction band region. For germanene-PYE, the band gap opening is rather small of around 0.35 eV, with a sharp contribution of C (p), which overlaps with Ge (p) at -0.55 eV on the left of E_f . Unlike silicene, here N (p) and H (s) also contributed in the PDOS but quite deep in the valence band at -1.8 eV and -2.2 eV respectively. There is also a small contribution of N (s) and H (s) in the conduction band at 0.80 eV.

In case of silicene-PYRI, which displays a very different behavior from all the other systems as shown in the upper panel of figure 6 (e). It is a metallic with significant contributions from N (p) right above and below the E_f overlapping with small peaks from Si (p) and H (s). Several sharp peaks of N (p) can also be seen between -1.1 eV and -0.80 eV somewhat hybridizing with Si (p), C (p) and H (s) however such overlap is not evident in the conduction band region on the right of E_f . The lower panel of figure 6 (e) shows PDOS of germanene-PYRI systems, which is semiconductor with a small band gap of 0.45 eV. The valence band on the left of E_f is dominated by the sharp peaks from Ge (p) and N (p) overlapping mainly at -0.75 eV, -0.45 eV and slightly at -0.25 eV. On the right of E_f there is hardly hybridization with the contributions from Ge (p), N (p) and C (p). Finally we describe the binding of TRP and THP on germanene as shown in upper

and lower panel of figure 6 (f) respectively. For TRP, we hardly see any contribution from its constituent element on either side of E_f except for O (p), which hybridize with Ge (p) at -0.75 eV and reduces the band gap of germanene to a small extent. In contrast to TRP, S (p) of THP has a significant contribution overlapping with Ge (p) at -1.0 eV and -0.50 eV on the left of E_f as shown in lower panel of figure 6 (f).

Based on the results obtained here, both silicene and germanene can be used to distinguish different nucleobases and amino acids, which is in the application of DNA sequencing and protein sequencing respectively. The interactions of heterocyclic molecules with silicene and germanene indicate that both sheets can be useful to understand the crystallization and heterogeneous catalysis.

Conclusions

In the summary, we have probed the adsorption mechanism of nucleobases, amino acids and heterocyclic molecules on silicene and germanene monolayers for the application of sensing of biomolecules. The salient outcomes of the current study are:

7. Nucleobases, amino acids and heterocyclic molecules are strongly interacting with silicene and germanene by physisorption and chemisorption process.
8. All molecules except BEN have tilted orientation towards the silicene and germanene monolayers.
9. In nucleobases, G has higher binding affinity with silicene and germanene whereas TRP and TYR have strong affinity towards silicene and germanene respectively.

10. Five membered heterocyclic molecules PYE has strong adsorption on silicene and germanene and PYRI, THP has strong adsorption on silicene and germanene respectively.
11. Due to difference of electronegativities, a fraction of electronic charge is exchanged between the monolayers (silicene, germanene) and the incident molecules.
12. The electronic properties of the both silicene and germanene changes upon the exposure of bio molecules.

Based on the findings mentioned above, we conclude that the both silicene and germanene could be promising monolayers for the detection and capture of a variety of bio molecules.

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