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Competition between Pauli Exclusion and H-Bonding: H_2O and NH_3 on Silicene

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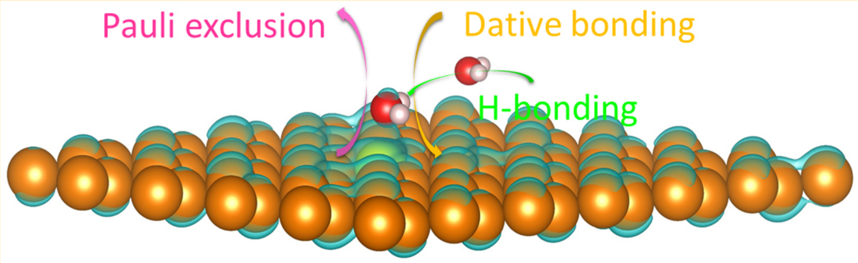
Ⓢ *Supporting Information*



ABSTRACT: We demonstrate that the competition between Pauli exclusion and H-bonding dominates the adsorption of H_2O on silicene through first-principles calculations. It explains the bewildering problem that isolated H_2O is inert on silicene while isolated NH_3 tends to chemisorption. Moreover, Pauli exclusion can be overcome by the synergetic effect of Si⋯O dative bonding and intermolecular H-bonding. As a result, H_2O molecules are readily to chemisorb in clusters. It is expected that the competition is in general polar molecule adsorption on silicene and, thus, crucial for the adsorption mechanism.

1. INTRODUCTION

Silicene, as a counterpart of graphene, has attracted enormous interests due to its good compatibility with current Si-based nanoelectronics, and its unique properties naturally inherit graphene, such as massless Dirac Fermions, quantum spin Hall effect, high carrier mobility, and so on.[1−4] Fundamentally, these commonalities lie in the unique symmetry of hexagonal π-orbital network,[5] which is derived from the honeycomb lattice and similar valence electron configurations of C ($2s^2 2p^2$) and Si ($3s^2 3p^2$).

Nevertheless, recent studies indicate that silicene possesses higher chemical reactivity to foreign atoms and molecules. For example, the metal atoms were reported to have stronger binding strength on silicene.[5−9] In particular, the binding energy of Au atom is about 23 times greater than that on graphene.[5,10] Some common gas molecules, like NH_3, NO, NO_2, SO_2, and O_2 were chemically inert to graphene,[11−13] but all of them tend to chemisorption on silicene.[14−16] Remarkably, the binding energies of NO_2, O_2, and SO_2 on silicene are greater than 1 eV.[14,15,17] In some extent, it can be explained from the strength of formed π-orbital network of these two materials. In silicene (graphene), the π bond originates from the overlapping of $3p_z$ ($2p_z$) electrons. Because the overlapping of $3p_z$ electrons is relatively weaker as compared to $2p_z$ electrons,[18,19] the π bond of silicene is easily broken by the adsorption of foreign adsorbates and, thus, accompanied by larger heat of adsorption.

To one's surprise, H_2O molecule, despite similar to NH_3, for example, containing lone pair of electrons, was reported to be inert to silicene, in contrast to the chemisorption of NH_3.[14,20] Moreover, this is different from their adsorption on graphene, where both are chemically inert.[11] It suggests that the explanation merely from the strength of π-orbital network is not complete, and the adsorption mechanism on these two-dimensional (2D) materials needs further investigations. Meanwhile, we note that Si(100)-2 × 1 surface shares the similar building block with silicene: buckled Si−Si bond. It is, for both substrates, composed of a σ bond and a π bond.[10,21,22] H_2O and NH_3 molecules, however, show stronger interaction on Si(100).[23−26] It implies that silicene can be treated as a prototype for unveiling the adsorption mechanism on these analogous 2D materials, including graphene and germanene, via comparing the adsorption of H_2O and NH_3 on silicene and Si(100). In addition, intermolecular H-bonding is also an important factor, which is found to promote the clustering of H_2O and NH_3 on Si(100) surface in the previous studies.[24,27−29] In this regard, H-bonding should be included in the theoretical investigations for the adsorption of H_2O and NH_3 on silicene.

In this article, we first confirm that the isolated H_2O molecule is chemically inert, while isolated NH_3 tends to chemisorption on silicene. Then we find that two H_2O molecule can be chemisorbed on silicene when H-bonding is introduced. To shed light on this phenomenon, we conduct electronic structure analysis on three most stable systems: H_2O/silicene, NH_3/silicene, and $2H_2O$/silicene. It confirms

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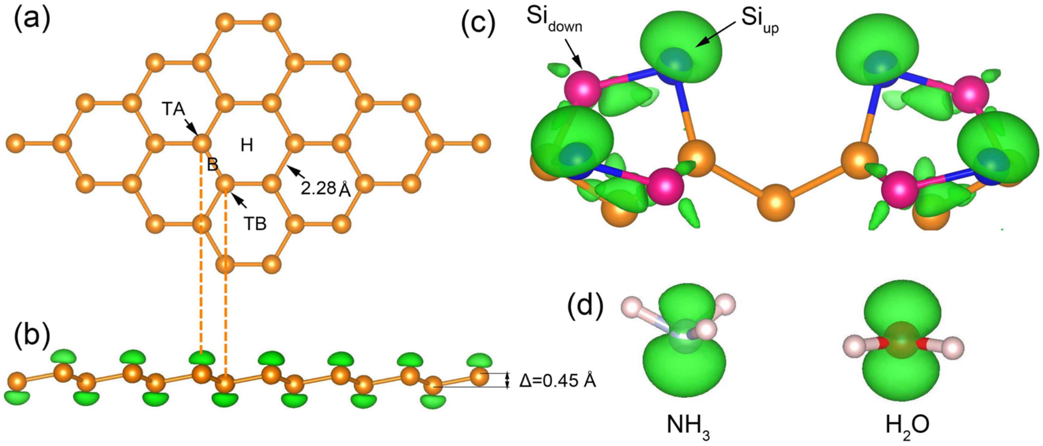

Figure 1. (a, b) Top and side views of silicene with four unequal adsorption sites marked as TA, TB, H, and B. The bond length and vertical height of Si−Si bond are 2.28 and 0.45 Å, respectively. (b, c) Partial charge densities of silicene and Si(100). It is evaluated in the energy range of [−1, 0] eV relative to the valence band maximum. The isosurface levels of silicene and Si(100) are set to 0.003 and 0.01 e/bohr^3, respectively. (d) HOMO of NH_3 and H_2O molecules at isosurface level 0.04 e/bohr^3. The balls in pink denote Si_{down} atoms, and those in blue represent Si_{up} atoms.

that the inert of an isolated H_2O to silicene is stemmed from Pauli exclusion, while it can be overcome with the promotion of H-bonding. In addition, we investigate the adsorption of H_2O and NH_3 on Al and P doped silicene to further confirm the proposed adsorption mechanism.

2. COMPUTATIONAL DETAILS

Geometry optimization and electronic structure were calculated by using the generalized gradient approximation (GGA) in the form of Perdew, Burke, and Ernzerhof (PBE)[30] for exchange-correlation potentials, the projector augmented waves (PAW) method and a plane-wave basis set of 400 eV, as implemented in Vienna ab initio simulation package (VASP) with consideration of spin-polarization.[31] Dispersion correction, which takes van der Waals interaction into account, is adopted at DFT-D2 level of Grimme method,[32] which is known to give a better description of geometries and corresponding energies than those from the standard DFT.[33]

A 4 × 4 supercell is adopted throughout our calculations. Since silicene is at a low-buckled state, we denote its sublattices with A (up) and B (down), as shown in Figure 1. The optimized bond length of Si−Si is 2.28 Å, and the buckled height is 0.45 Å, in good agreement with previous DFT calculations.[2,6,18] Four different sites have been considered for the adsorption: the hollow site (H) above the center of a hexagon, the top site (TA) above a Si atom of sublattice A, the top site (TB) above a Si atom of sublattice B, and the bridge site (B) above the midpoint of a Si−Si bond. The corresponding geometries are named as configurations H, TA, TB, and B for short, respectively.

The variation in adsorption energies of a H_2O dimer adsorbed on TA with increasing k-mesh from 4 × 4 × 1 to 6 × 6 × 1 is within 2 meV. Hence, a 4 × 4 × 1 gamma-centered k-mesh is adopted in our following studies. All structures are fully relaxed until the force on each atom is smaller than 0.02 eV/Å. The vacuum space in the Z direction is about 11 Å to separate the interaction between the neighboring slabs. The total energy of a H_2O dimer located at the TA site with vacuum layer ongoing from ∼11 to ∼21 Å is within 8 meV. Dipole correction is employed to cancel the errors of electrostatic potential, atomic forces and total energy, caused by periodic boundary condition. For the charge transfer analysis, the effective charge on the atoms is obtained by the Hirshfeld method implemented in DMol^3 package[34] combined with exchange-correlation function of GGA(PBE).

3. RESULTS AND DISCUSSION

3.1. Adsorption of an Isolated H_2O or NH_3 on Silicene.

We first investigate the stable adsorption configuration of a single H_2O or NH_3 molecule on silicene. The adsorption energy E_{ads} is obtained through subtracting the sum of total energies of clean silicene and an isolated molecule (H_2O or NH_3) from the total energy of optimized configuration of silicene with adsorbed molecule, as listed in Table 1.

Table 1. Adsorption Energies (E_a) of Molecules (H_2O and NH_3) Located at H, TA, TB, and B Sites, Respectively[a]

molecule	site	E_a (eV)	E_a (eV) − vdW	d_{M-Si} (Å)
H_2O	H	0.06	0.17	3.55
	TA	0.07	0.16	2.67
	TB	0.05	0.14	3.79
	B	0.05	0.14	3.17
NH_3	H	0.02	0.15	3.70
	TA	0.46	0.61	2.05
	TB	0.27	0.44	2.02
	B	→TA	→TA	→TA

[a] d_{M-Si} denotes the distance between the O (N) atom and the nearest Si atom.

Overall, an isolated H_2O molecule has comparable heat of adsorption at these four sites on silicene, ∼0.07 eV. For TA configuration, the O atom is located right above Si atom with a Si···O distance of 2.67 Å. The bond lengths and bond angle of H_2O are 0.98 Å and 104.8°, nearly unchanged from the free state. Three nearest Si−Si bonds (bond1) are slightly elongated by 0.01 Å, as shown in Figure 2a and 2b. These features indicate that H_2O molecule has a rather weak interaction with silicene.

In contrast, NH_3 molecule is found to be active on silicene, despite sharing the similar characteristics with H_2O, for example, lone pair of electrons. It prefers to bond with Si atom at TA site, with E_{ads} = 0.46 eV. The Si···N distance is 2.05 Å, close to 1.98 Å of Si_{down}···N dative bond on Si(100).[27,35]

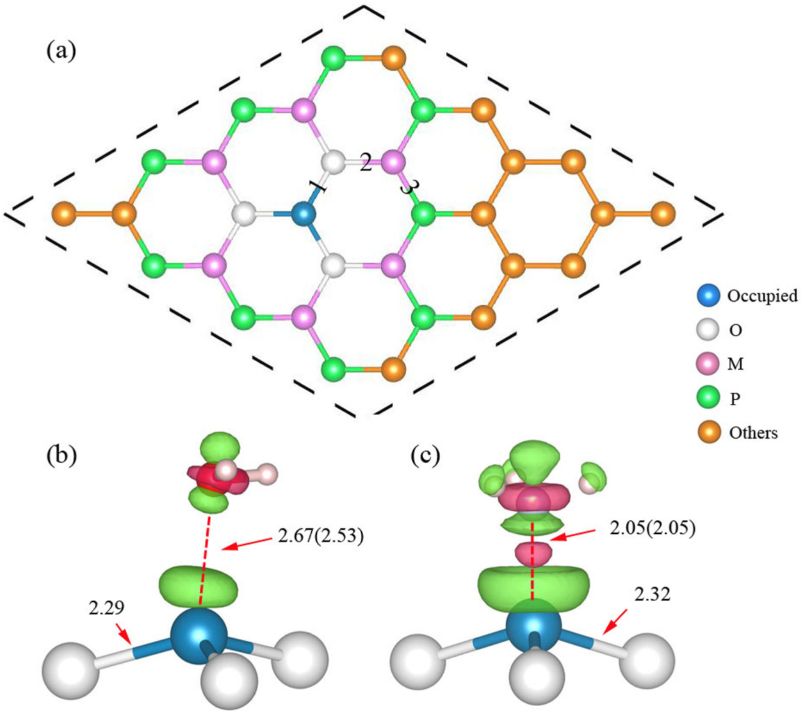

Figure 2. (a) Relative positions of Si atoms in TA configuration of H_2O or NH_3. The light blue ball denotes the occupied Si atom. The white, pink, and green balls represent the first (ortho), second (meta), and third (para) neighboring Si atoms (denoted by O, M, and P), relative to the occupied Si atom, respectively. Correspondingly, bonds marked in 1, 2, and 3 denote the Si−Si bonds in the first, second, and third nearest neighbors, respectively. The other Si atoms are in brown. (b, c) Charge density differences of TA configurations of H_2O and NH_3. It is obtained via subtracting the total charge densities of adsorbed H_2O (NH_3) and silicene from that of TA configuration of H_2O (NH_3). Isosurface level is ± 0.006 e/bohr^3. The light purple denotes electron accumulation, and the light green denotes electron depletion. Values in brackets are revised by vdW correction.

Three nearest Si−Si bonds are all elongated from 2.28 to 2.32 Å, seen in Figure 2c. The TB configuration is less stable, with E_{ads} = 0.27 eV. Adsorption at B site is not stable, it would transform to TA site spontaneously after relaxation.

Furthermore, we calculate the charge density difference of TA configurations of H_2O and NH_3. As displayed in Figure 2b,c, there is hardly any charge accumulated between O and Si atoms, but significantly between N and Si atoms in the same isosurface level of ± 0.006 e/bohr^3. It suggests that Si⋯N bonding possesses characteristics of covalent bond to some extent, exhibiting a distinct adsorption behavior to H_2O. In addition, we have investigated the effect of van der Waals (vdW) interaction on the adsorption of isolated H_2O and NH_3 on silicene. It is found that the tendency is unchanged before and after vdW corrections. These results are in good agreement with the previous studies.[14,20]

3.2. Comparison of Adsorption (H_2O and NH_3) between Silicene and Si(100).

Considering the low-buckled structure of silicene, we associate it with Si(100)-2 × 1 surface, since they share nearly the same structural building block: buckled Si−Si bond. Each Si−Si bond on these two substrates is composed of a strong σ-bond and a weak π-bond. However, the Si(100) surface shows a higher reactivity toward H_2O and NH_3 molecules. For example, E_{ads} of H_2O and NH_3, with X (X = O, N) atom binding with Si_{down} atom are as large as ∼0.71 and ∼1.27 eV on Si(100), respectively,[23−26] about 0.7 eV greater than those of TA configurations of H_2O and NH_3 on silicene.

Here it should be stressed that Si_{down} atoms on Si(100) are electron-deficient because of charge transfer from the Si_{down} atom to the Si_{up} atom in the buckled Si−Si bond.[36] In comparison, Si atoms on silicene are electron-neutral since the equivalence of two sublattices. This can be seen clearly from partial charge density (PCD) evaluated at the energy range of [−1, 0] eV relative to the valence band maximum. As displayed in Figure 1b, equal PCD are localized at two bonded Si atoms on silicene, but there is hardly any PCD localized at Si_{down} atom with respect to Si_{up} atom at isosurface level of 0.01 e/bohr^3 (cf. Figure 1c).

The highest occupied molecular orbital (HOMO) of H_2O or NH_3 is contributed from lone pair of electrons, shown in Figure 1d. Note that for H_2O, NH_3, and Si atom of silicene, they all can be viewed as closed-shell systems. Thus, when H_2O (NH_3) approaches silicene, the charge overlapping derived from the lone pair of electrons of X atom (X = O, N) and electron of Si is likely to happen and, therefore, results in Pauli exclusion. In comparison, since the Si_{down} atom is electron-deficient, the Pauli exclusion between X and Si_{down} atoms should be relatively weaker with respect to that on silicene. Furthermore, the electron-deficient makes Si_{down} atom able to provide empty orbitals to accept the charge of a lone pair of electrons of X atom via Lewis acid−base interaction,[37−39] that is, dative bonding. Consequently, the adsorption of H_2O and NH_3 on Si(100) are accompanied by a larger heat of adsorption. From this point, we speculate that Pauli exclusion may be a key factor for understanding the adsorption of H_2O and NH_3 on silicene.

On the other hand, H-bonding was reported to have a significant influence on the adsorption of H_2O and NH_3 on Si(100). An obvious change to the preadsorbed H_2O or NH_3 on Si(100) is the contraction of Si⋯O or Si⋯N distance when H-bonding with the additional H_2O or NH_3 molecules. For example, Si⋯O (Si⋯N) distance is shortened by 0.15 (0.06) Å when H-bonded with the second H_2O (NH_3) molecule.[24,27] It implies that whereas isolated H_2O is chemically inert to silicene, intermolecular H-bonding is probably to affect its adsorption behaviors and is, thus, beneficial for revealing this confusing problem.

3.3. Clustering of H_2O or NH_3 Molecules on Silicene.

To take intermolecular H-bonding into consideration, we investigated two scenarios of adsorption based on TA configurations of H_2O and NH_3: (i) dispersed on silicene; (ii) clustered via H-bonding. For the former case, we considered three unequal sites named as *ortho-*, *meta-*, and *para*-positions (O, M, and P for short), relative to the occupied Si atom, corresponding to the first, second, and third neighboring Si atoms, respectively, as shown in Figure 2a. The optimized configurations are named as D-O, D-M, and D-P. For the latter case, we considered three unequal H-bond directions, which are nearly along the connection between the occupied Si atom and Si atom at O, M, or P site in the top view, respectively, as shown in Figure 3. The optimized configurations are named as C-O, C-M, and C-P. The adsorption energy E_{ads} is defined as

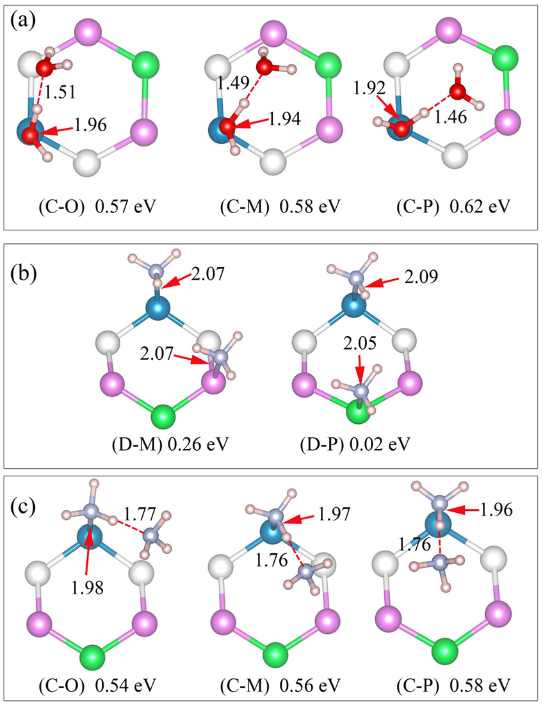

Figure 3. Clustered (a) H_2O and (c) NH_3 molecules on silicene with three different H-bond directions. (b) Two NH_3 molecules adsorb dispersedly on silicene.

$$E_{ads} = E_M + E_{TA} - E_{TA+M}$$

where E_M, E_{TA}, and E_{TA+M} represent total energies of isolated molecule (H_2O or NH_3), TA configuration, and TA configuration with an additional molecule, respectively.

To one's surprise, the additional H_2O molecule located at the O, M, or P site at the beginning, despite with different orientations, is found to move spontaneously toward the preadsorbed H_2O along the H-bonding direction during the optimization. Meanwhile, the Si···O distance and H-bond are both shortened, showing a synergetic effect. It leads to the clustering of H_2O molecules on silicene eventually. The formed three H_2O cluster configurations are similar to those optimized directly from scenario-ii, as shown in Figure 3a. For the most stable cluster configuration, that is, C−P, the Si···O distance is dramatically reduced from 2.67 to 1.92 Å, and the H-bond is shortened from 1.88 Å (a free H_2O dimer) to 1.46 Å (cf. Figure 4a). In particular, E_{ads} of these three configurations reach up to 0.57−0.62 eV, enhanced by nearly an order of magnitude with respect to 0.07 eV of the preadsorbed H_2O.

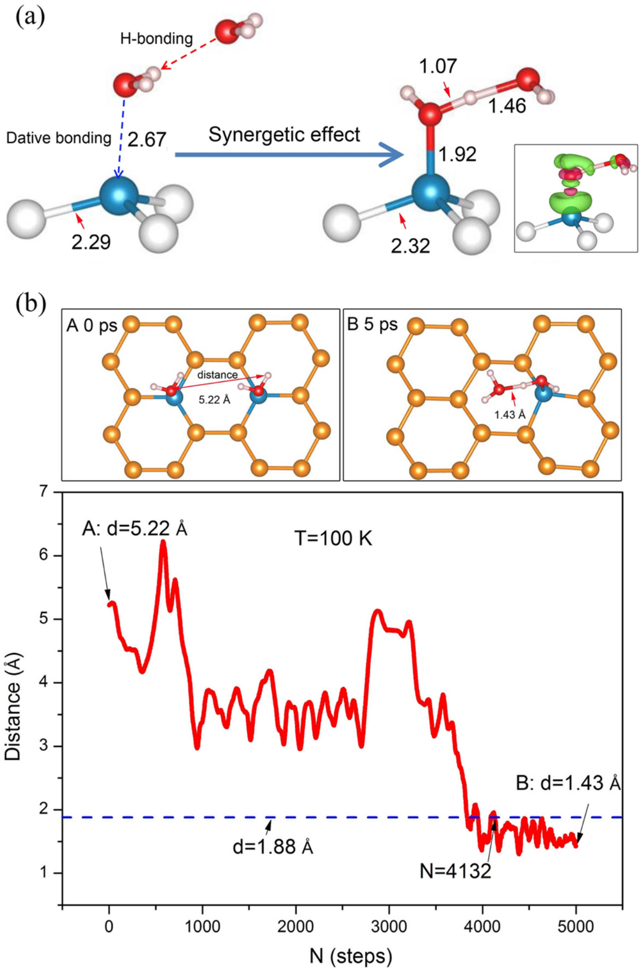

Figure 4. (a) Schematic plot of synergetic effect between H-bonding and dative bonding during the adsorption of a H_2O dimer on silicene. The clustered configuration is C-P. The inset is its isosurface plot of charge density difference, which is obtained via subtracting the sum of charge densities of adsorbed $2H_2O$ and silicene from that of configuration C-P. Isosurface level is set to ±0.006 e/bohr^3. Light purple and light green regions denote electron accumulation and depletion, respectively. (b) The clustering of two H_2O molecules on silicene at 100 K from the first-principle molecular dynamics simulations. The two insets correspond to snapshots from MD at 0 and 5 ps, respectively.

The plot of charge density difference of configuration C−P shows that there is a significant charge transfer between the H_2O dimer and silicene. Significantly, there are charges accumulated between Si and O atoms at the isosurface level of ±0.006 e/bohr^3, in contrast to that of TA configuration (cf. Figure 2b), as shown in Figure 4a. It suggests that the H_2O dimer is chemisorbed on the silicene.

For the additional adsorption of NH_3, it is found that the NH_3 molecule located at site O initially tends to H-bond with

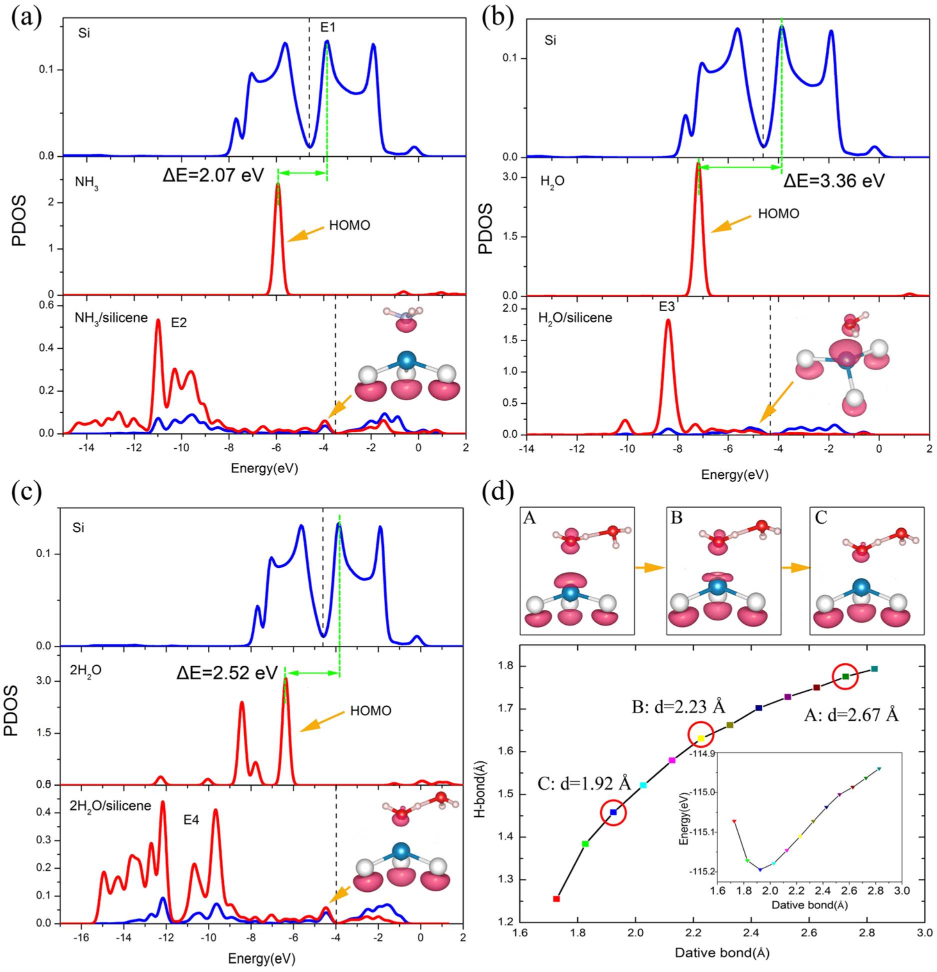

Figure 5. PDOS to illustrate the level coupling due to the molecule adsorption on silicene. (a), (b), and (c) correspond to the adsorption of NH_3, H_2O, and $2H_2O$ on silicene, respectively, with the levels aligned with respect to the vacuum level (set to zero here). Blue line denotes the p_z orbital of the Si atom. Red line represents p_z orbital of N or O atom, except the $2H_2O$ in (c), where it denotes the sum of p orbitals ($p_x + p_y + p_z$) of adsorbed O atom. The dashed line shows the position of Fermi level. (d) Variation of H-bond with the change of dative bond. The Si···O distance is fixed during the optimization. Insets in (a), (b), (c), and (d) are partial charge density (PCD) evaluated in the energy range of [−1, 0] eV relative to Fermi level, with the same isosurface level of 0.005 e/bohr^3.

the preadsorbed NH_3 and transform to configuration C−O spontaneously during optimization. While for the ones located at M and P sites, they would keep isolated with E_{ads} = 0.26 and 0.02 eV, respectively, as shown in Figure 3b. In contrast, configurations C-O, C-M, and C-P are significantly stabilized, with E_{ads} = 0.54−0.58 eV, which are even ∼0.12 eV larger than that of preadsorbed NH_3. The synergetic effect is also reflected. In the most stable configuration, that is, configuration C-P, with the H-bond decreased from 2.22 Å (a free NH_3 dimer) to 1.76 Å, the length of Si−N bond is shortened from 2.05 to 1.96 Å.

From the perspective of thermodynamics, H_2O and NH_3 molecules are both inclined to cluster with the preadsorbed one via H-bonding, rather than adsorb dispersedly on the silicene. It suggests that H_2O and NH_3 molecules are likely to cluster via H-bonding if the kinetic energy of the molecules is not big enough, that is, at low temperatures. To demonstrate this point, we performed a molecular dynamics (MD) simulation within the NVT ensemble. The MD at 100 K lasted for 5 ps (cf. Figure 4b), with a time step of 1 fs. Two H_2O molecules are initially located on silicene with a distance of 5.22 Å. After about 4.1 ps, the length of H-bond is shortened within 1.88 Å (a free H_2O dimer), indicating that H_2O molecules are clustered. At 5 ps, the length of the H-bond is 1.43 Å, as seen in Figure 4b.

3.4. Adsorption Mechanism of H_2O or NH_3 Molecules on Silicene.

On silicene, an isolated H_2O is chemically inert, but two H_2O molecules can be chemisorbed through H-bonding. Note that the interaction is localized at the Si and O atoms; the following questions are naturally raised: (i) Is the chemically inert H_2O resulted from a Pauli exclusion? (ii) If so, is the Pauli exclusion overcome by the promotion of H-bonding for the clustered H_2O? (iii) Why can't the Pauli exclusion prevent the chemisorption of an isolated NH_3?

To explain the questions above, we calculated the projected density of states (PDOS) of atoms involved in binding for TA configurations of H_2O and NH_3, and C-P configuration of H_2O (H_2O/silicene, NH_3/silicene, and $2H_2O$/silicene for short), that is, O or N, and Si, as shown in Figure 5. On such a surface, the adsorption energy is a result of the coupling between the HOMO level of molecule (NH_3, H_2O, or H_2O dimer) and the highly localized E1 state of silicene. Here the HOMO level is primarily the occupied N or O lone pair state, while the E1 state is primarily the empty state of pristine silicene contributed by the p_z orbital of Si. The separation between HOMO level of NH_3 and E1 is about 1.29 eV smaller than that between H_2O and E1. Consequently, the coupling between HOMO level of NH_3 and E1 is significantly larger, as evidenced by the lower

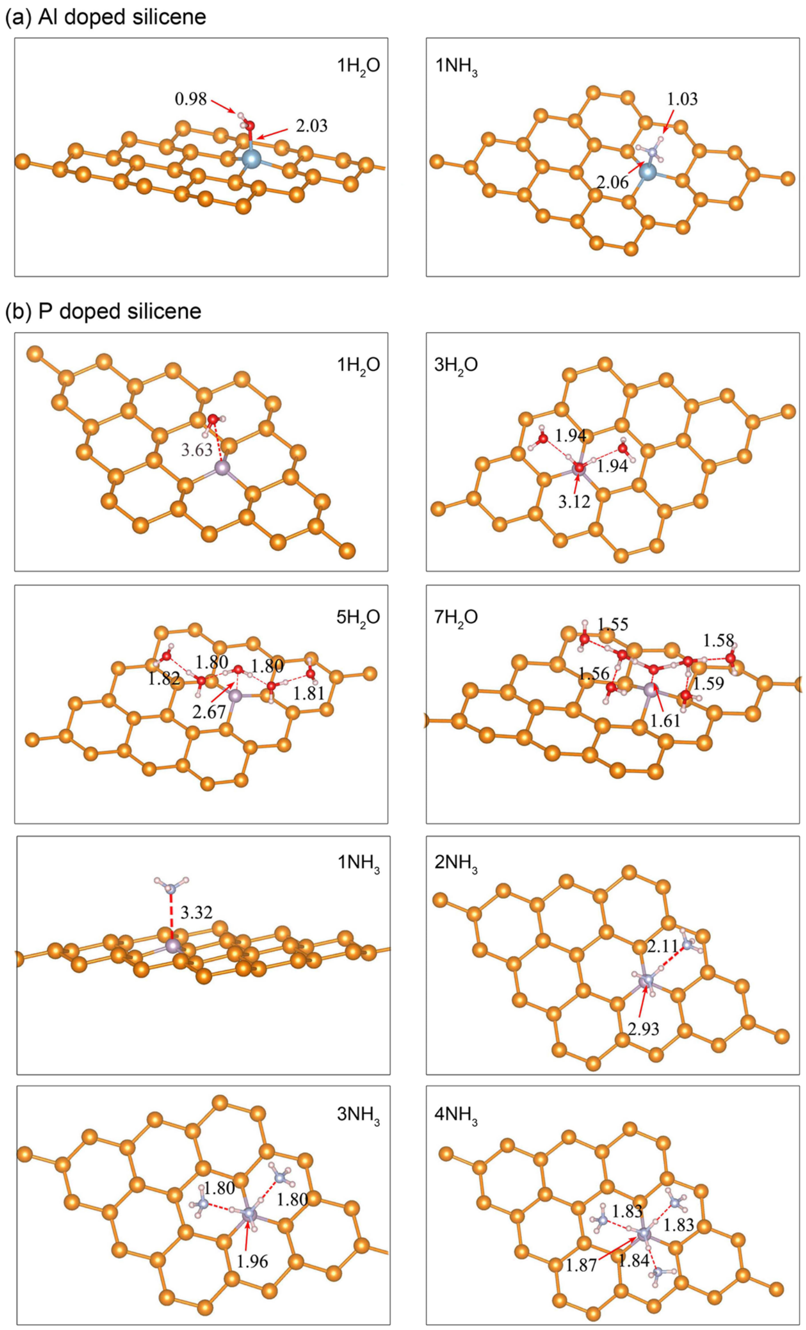

Figure 6. Optimized configurations of H_2O and NH_3 on (a) Al and (b) P atom doped silicene.

hybridized states E2 with respect to E3 of H_2O/silicene. Especially, the E3 states with few hybridized states in H_2O/silicene shifts slightly downward compared to the HOMO level of H_2O, indicating a weak interaction. However, due to the intermolecular H-bonding, the separation between the HOMO level of a H_2O dimer and E1 state of silicene decreases significantly, about 0.84 eV smaller with respect to the case of H_2O and silicene and, thus, results in strong hybridized states of E4 at lower energies.

Accompanied with this process, the Fermi levels of NH_3/silicene, $2H_2O$/silicene, and H_2O/silicene are found to shift upward by about 1.10, 0.63, and 0.35 eV, respectively, when compared to the pristine silicene. This is ascribed to the partially occupied antibonding levels resulting from the interaction between the HOMO level of molecules and the Si p_z of the silicene.

We note that there are some hybridized peaks, attributed to the interaction of p_z orbitals of X (N or O) and Si atoms, appearing in the energy range of [−1, 0] eV relative to the Fermi level in these three cases. Their partial charge density (PCD) distributions in real space are shown in the insets of Figure 5a−c. A significant difference between H_2O/silicene and the other two cases lies in that there is hardly any PCD accumulated at Si atom for NH_3/silicene and $2H_2O$/silicene, but prominent in the case of H_2O/silicene at the isosurface level of 0.005 e/bohr^3.

Given the difference between $2H_2O$/silicene and H_2O/silicene, we speculate that H-bonding is likely a critical factor for the adsorption of H_2O. Therefore, we investigate the

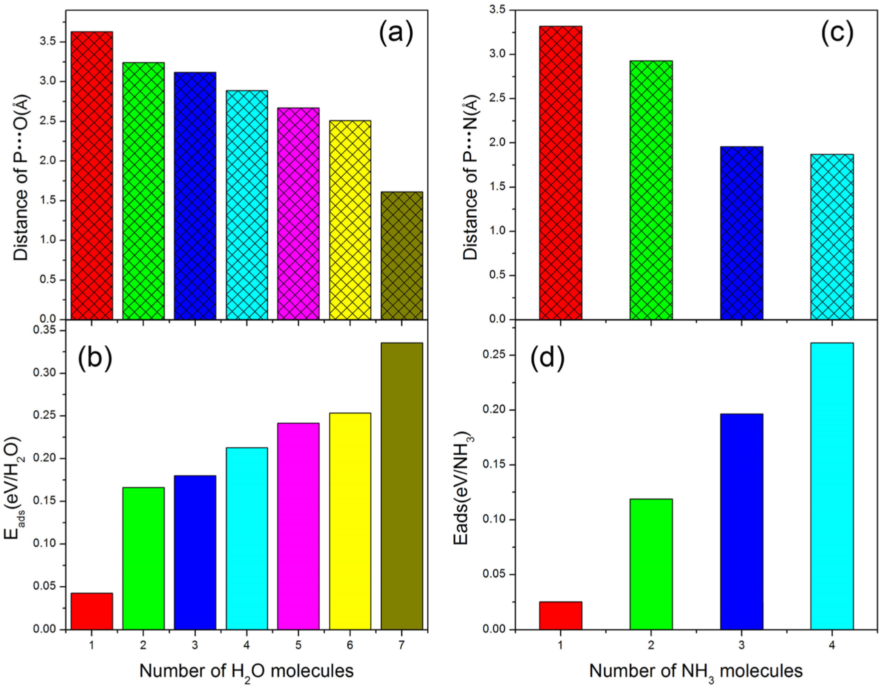

Figure 7. (a) Distance of P···O and (b) average adsorption energies of H_2O on P-doped silicene as a function of the number of H_2O molecules. (c) Distance of P···N and (d) average adsorption energies of NH_3 on P-doped silicene as a function of the number of NH_3 molecules.

variation of H-bond length with the change of Si···O distance, as shown in Figure 5d. It is found that the total energy of system decreases without any barrier when Si···O distance shortened from 2.67 to 1.92 Å. It is resulted from the synergistic effect as discussed above. Here 2.67 and 1.92 Å are the distances between the occupied Si atom and the adsorbed O atom for H_2O/silicene and $2H_2O$/silicene, respectively. Moreover, the H-bond is nearly showing a linear relation with Si···O distance in the range of [2.23, 2.83] and [1.92, 2.23] Å. A large slope in the latter case suggests that the synergistic effect is strengthened.

To further shed light on this phenomenon, we choose three states, labeled in A, B, and C in Figure 5d, and calculate their PCDs in the energy range of [−1, 0] eV relative to the Fermi level. The Si···O distances in configurations A, B, and C are 2.67, 2.23, and 1.92 Å, respectively. As displayed in Figure 5d, there is obvious PCD accumulated at the Si atom in configuration A, in which the H-bond is as large as 1.77 Å. However, with the shortening of the H-bond, the PCD gradually diminishes, as shown in PCD from configuration A, B to C. It indicates that the inert of an isolated H_2O to silicene is stemmed from Pauli exclusion. However, it can be overcome with the promotion of H-bonding.

The decreasing of PCD at occupied Si atom suggests that part of its p_z electron is transferred to the neighboring atoms, and thus becomes electron-deficient. In this respect, the occupied Si atom is similar to the Si_{down} atom on Si(100) surface in some extent. Therefore, it can provide empty orbitals for accepting charge from lone pair of electrons of O atom, that is, dative bonding. The charge distribution analysis indicates that H_2O dimer and the occupied Si atom lose 0.21 and 0.12 *e*, respectively. Three nearest Si atoms get the most significant and the equal amount of charge (cf. Figure S1 and Table S1). Meanwhile, accompanied by the charge transfer, three nearest Si−Si bonds (bond 1) are elongated from 2.29 to 2.32 Å, indicating that π-bonds are broken to some extent.

Based on the analysis above, it is convenient to give the physical picture of Pauli exclusion: for the adsorption of H_2O (NH_3) on silicene, there are three electrons taken part in the interaction, i.e., a p_z electron of Si atom and a lone pair of electrons of O (N) atom. However, as is well-known, a covalent bond is composed of one and only one pair of electrons. It suggests that in the process of Si−O (N) bonding an extra electron needs to be transferred to the other atoms and thereby introduces Pauli exclusion. Furthermore, we propose the adsorption mechanism of H_2O on silicene. It is composed of four processes: (i) H-bonding. (ii) Pauli exclusion; It is derived from the overlapping of a lone pair of electrons of O and the p_z electron of occupied Si. (iii) Dative bonding. The overcoming of Pauli exclusion is along with the p_z electron of occupied Si transferred to the neighboring Si atoms. As a result, the occupied Si becomes electron-deficient and, thus, can provide empty orbitals for accepting charge from a lone pair of electrons of the O atom, that is, dative bonding. (iv) Accompanied with the charge transfer, three nearest Si−Si bonds (bond 1) are elongated from 2.29 to 2.32 Å, indicating that π-bonds are broken to some extent. Processes (i) and (iii) are exothermal, while processes (ii) and (iv) are endothermic. Overall, if the heat release of (i) and (iii) is larger than the heat consumption of (ii) and (iv), the chemisorption can happen. Otherwise, physisorption is preferred. In this regard, a strong interaction of NH_3 with silicene is ascribed to a large heat release of process (iii), which is able to compensate for the heat consumption of processes (ii) and (iv).

3.5. Confirmation of Pauli Exclusion between H_2O or NH_3 and Silicene.

To further confirm the Pauli exclusion, we replaced the occupied Si atom with an Al or P atom. Similar to the Si atom, three valence electrons of Al and P atoms should take part in bonding with three nearest neighboring Si atoms. As a result, there is no extra electron left on the doped Al atom, while a lone pair of electrons is located on the doped P atom.

According to the mechanism above, it is expected that there is no obvious Pauli exclusion between H_2O (NH_3) molecule and the doped Al atom. Hence, they should be able to dative bond with Al. In contrast, for the P-doped case, the Pauli exclusion between O(N) and P is expected to be greater than that on pristine silicene, and thus, it would impede their adsorption. The average adsorption energy E_{ads} is defined as

$$E_{ads} = (E_{sub} + nE_M - E_{sub+nM})/n$$

where E_{sub}, E_M, and E_{sub+nM} denote the total energies of substrate (an Al or P atom doped silicene), isolated molecule (H_2O, NH_3), and substrate with adsorbed n molecules, respectively; n is the number of molecules.

For the adsorption on doped Al atom, E_{ads} of the first H_2O (NH_3) is 0.62 (1.01) eV, significantly larger than those on pristine silicene, while on the doped P atom, not only an isolated H_2O, but also H_2O dimer, trimer, tetramer, pentamer, and hexamer are all inert to the doped P atom (cf. Figures 6 and S2). The P···O distances are in the range of 2.5−3.7 Å, indicating a rather weak interaction with substrate. However, it is gradually shortened when H-bonded by more H_2O molecules, along with the average adsorption energy of H_2O gradually increased, as shown in Figure 7a,b. When H-bonded with the additional six H_2O molecules, the P···O distance reduces to 1.61 Å, and the average adsorption energy of H_2O increases to 0.34 eV, that is, chemisorbed. It indicates that Pauli exclusion has been overcome with the promotion of H-bonding.

In addition, it is found that an isolated NH_3 has also become inert to the doped P atom with E_{ads} as small as 0.03 eV, although it is readily to dative bond with Si on silicene. While with the preadsorbed NH_3 consecutively H-bonded by the additional NH_3, the average adsorption energies of NH_3 molecules increase from 0.03, 0.12, 0.20, to 0.26 eV, and the N···P distance is gradually shortened from 3.32, 2.93, 1.96, to 1.87 Å, indicating that the Pauli exclusion is gradually overcome by the compensation from H-bonding (c.f. Figure 7c,d). Overall, these results are well consistent with the mechanism proposed above, confirming that Pauli exclusion exists in the adsorption of H_2O and NH_3 on silicene. Significantly, it is generally for a wide class of molecules that contain OH or NH_2 group. Because of the lone pair of electrons of O or N, their adsorption on silicene would be affected by Pauli exclusion. Also, it is reasonable to speculate that the adsorption of H_2O and NH_3 on graphene and germanene follows the similar mechanism because of their similar geometric and electronic structures. Our calculations indicate that the adsorption of H_2O and NH_3 on free-standing germanene show the similar results to those on silicene (cf. Figure S3), while for the adsorption on graphene, H-bonding is unlike to overcome the Pauli exclusion because of the stronger resonant π-orbital network formed by $2p_z$ electrons of C atoms with respect to that of silicene or germanene.

4. CONCLUSIONS

In summary, we have studied the adsorption of H_2O and NH_3 on silicene taking H-bonding into consideration. We explained that the chemically inert of H_2O on silicene is ascribed to the Pauli exclusion between the lone pair of electrons of H_2O and p_z electron of Si of silicene. However, the H-bonding between H_2O molecules can overcome the Pauli exclusion to have H_2O chemisorbed on silicene. Both of H_2O and NH_3 molecules are energetically favored to cluster on silicene. This finding deepens the understanding of adsorption mechanism on silicene.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b05273.

> Charge distribution analysis for the systems of H_2O/silicene, NH_3/silicene, and $2H_2O$/silicene, as well as the optimized configurations of H_2O dimer, tetramer, and hexamer on P atom doped silicene (PDF).

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Notes

The authors declare no competing financial interest.

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