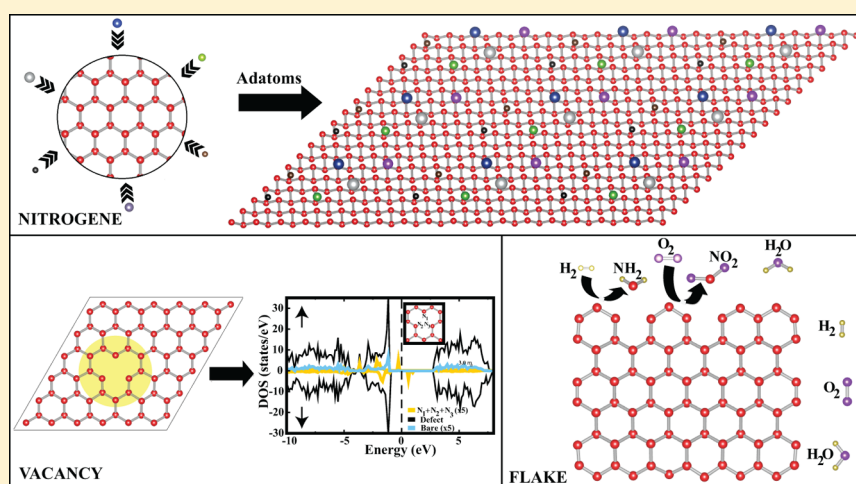


Functionalization of Single-Layer Nitrogen by Vacancy, Adatoms, and Molecules

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ABSTRACT: Despite its strong N_2 molecule, recent studies have shown that nitrogen, the lightest group V element, remains stable in the free-standing, single-layer buckled honeycomb structure with two-dimensional (2D) hexagonal lattice. This structure is called nitrogen and is predicted to be a nonmagnetic, wide band gap semiconductor or insulator. In this paper, we investigated the formation of a single vacancy, as well as the adsorption of selected single adatoms and molecules on 2D nitrogen, using the supercell method within the density functional theory. Through the consideration of large supercells, the couplings between adjacent vacancies and adspecies are minimized; hence, the results are taken to represent single, isolated defect and adspecies. We found that a single vacancy contributes a local magnetic moment and filled and empty localized gap states at low temperature but is prone to instability due to thermal excitations. Adatoms are bound to the surface of nitrogen and form localized gap states contributing a diversity of electronic and magnetic properties. Adsorption of adatoms, such as B, C, Si, and N, however, give rise to local and strong reconstruction in nitrogen in their close proximity. Notably, a N adatom forms a strong N_2 molecule by removing one N atom from nitrogen and leaves a vacancy behind. Conversely, the interactions between selected molecules, such as H_2 , O_2 , H_2O , and N_2 , and the surface of nitrogen are rather weak and do not induce any change in the physical properties. However, H_2 and O_2 can be dissociated at the edges of a nitrogen flake and concomitantly can remove host N atoms to form NH_2 and NO_2 molecules. Calculated properties of adatoms adsorbed to nitrogen differ dramatically from the properties of those adsorbed to single-layer structures of other group V elements.

INTRODUCTION

Following the synthesis of very thin phosphorene and field effect transistor fabricated thereof,¹ recent theoretical studies have shown the stability of single-layer (SL), free-standing structures of group V elements or pnictogens (N, P, As, Sb, and Bi). These SL structures are nitrogen,^{2,3} phosphorene,⁴ arsenene,⁵ antimonene,^{6,7} and bismuthene.⁸ Among pnictogens, nitrogen has a liquid phase at 77 K and molecular/nonmolecular solid phases^{9–14} and three-dimensional (3D) cubic gauche (cg-N) crystalline phase^{15,16} at extreme conditions,

but normally it is gaseous at room temperature and forms the strongest molecule in nature, N_2 . It was surprising that nitrogen can also form a stable, two-dimensional (2D) crystalline phase with hexagonal lattice in SL, buckled honeycomb structure termed *nitrogen*.² While the N_2 molecule is triple-bonded, nitrogen is constructed from single-bonded N atoms similar to

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the 3D cg-N crystalline phase. Furthermore, it was predicted that nitrogen can remain stable above room temperature and can form stable nanoribbons, bilayers, and 3D graphitic structures named *nitrogenite*.² Unlike semimetallic graphene¹⁷ or silicene^{18,19} having perfect electron–hole symmetry, nitrogen is a nonmagnetic, wide band gap semiconductor or insulator. Experimentally, Harada et al. reported the epitaxial growth of 2D nitrogen atomic sheet in GaAs.²⁰ Also, the structure of the monolayer consisting of N₂ molecules adsorbed on MgO(100) powder was investigated at 10–60 K.²¹

In this paper we investigate single-vacancy and divacancy defects of SL nitrogen, as well as the adsorption of 13 selected single adatoms (i.e., H, Li, O, Al, P, Cl, Ti, As, Sb, B, C, Si, and N) and physisorption of 4 molecules (i.e., H₂, O₂, H₂O, and N₂). These adatoms and molecules were known to engage in chemical interactions with various SL structures, like graphene, silicene, BN, MoS₂,^{22–31} antimonene,³² and arsenene,³³ and give rise to novel functional properties. For example, Ti and Li adatoms were shown to be crucial in high-capacity hydrogen storage when adsorbed on graphene.^{23,24,26} Some of these adatoms by themselves (N, C, Si, P, As, and Sb) can form free-standing, honeycomb structures with a 2D hexagonal lattice.

Our objectives in this paper are three-fold: (i) We first test whether the stability of nitrogen is maintained after the creation of point defects, such as a vacancy, and after the adsorption of single adatoms. (ii) We reveal the modification of the properties of nitrogen after the creation of vacancy and adsorption of single adatoms. In this way we explore the functionalization of nitrogen. (iii) The edges of a nitrogen flake have 2-fold coordinated N atoms behaving as active sites, which may lead to the dissociation of certain molecules. We examine the interaction of these active sites with selected molecules and explore whether a dissociative reaction can take place and lead to a hydrogen evolution process.

In this study, we found that a single vacancy can contribute a local magnetic moment of 3 μ_B and spin-polarized localized states in the gap. Adatoms, such as H, Li, O, Al, P, Cl, Ti, As, and Sb, adsorbed on the surface of 2D nitrogen can form strong bonds inducing minute or moderate local deformations in the structure of substrate and leading to diversity of electronic and magnetic properties. However, the adsorption of B, C, Si, and N results in massive local reconstruction; even a hole can be created in nitrogen. The molecules, such as H₂, O₂, H₂O, and N₂, interact weakly with the surface nitrogen. However, H₂ and O₂ form NH₂ and NO₂ molecules, respectively, upon their dissociation at the edges of a nitrogen flake.

■ COMPUTATIONAL DETAILS

The predictions of this study are obtained by carrying out first-principles plane wave calculations based on spin-polarized density functional theory (DFT)³⁴ within supercell geometry using periodic boundary conditions. A single vacancy is created or single adatom (molecule) is adsorbed at its specific equilibrium positions of each (6 × 6) supercell of nitrogen, so that a 2D regular array of vacancy or adspecies is obtained. The details of supercell geometry will be given in forthcoming sections. The Perdew–Burke–Ernzerhof functional (PBE) is used for the exchange–correlation potential in generalized gradient approximation (GGA),³⁵ and the PAW pseudopotentials are adopted.^{36,37} In all calculations, corrections of van der Waals (vdW) interactions in the DFT-D2 level³⁸ are included. Different methods of the vdW corrections have been discussed

in the literature.^{39–41} While the DFT-D2 method overbinds by ~8% and hence underestimates the interlayer spacing of graphite and 2h-MoS₂, the first-principles DFT-DF⁴¹ method slightly underbinds, but is sophisticated to use.

The electron wave functions were expanded in plane waves up to a kinetic energy cutoff of 550 eV. The Brillouin zone (BZ) is sampled using a Monkhorst–Pack scheme⁴² by (5 × 5 × 1) mesh in the *k*-space. The energy convergence criterion is taken as 10^{−5} eV between two successive iterations. The maximum pressure on the unit cell is reduced to less than 1 kbar. Calculations from the first principles were performed using Vienna Ab Initio Simulation Package (VASP).^{43,44} Caution was taken in the optimization of systems having magnetic ground state. To this end we performed a series of total energy calculations for single vacancy in nitrogen (ntrgn +V) or single adatom adsorbed to nitrogen (ntrgn+A), each having different, fixed magnetic moment. Then the magnetic moment of the optimized structure is determined as the magnetic moment corresponding to that of the minimum total energy.

Calculation of the binding energy is crucial for the interaction of adatom or molecule with 2D nitrogen. A binding energy larger than ~1 eV usually implies the chemisorption of adatom with the exchange of charge with nitrogen. When compared with this binding energy, the contribution of vdW interaction is minute. However, in the case of physisorption, the binding energy is weak and ranges between ~40 and 110 meV for molecules considered in this study. In contrast to chemisorption, the contribution of vdW interaction dominates the physisorption energy. In forthcoming sections we present the contribution of vdW interaction in typical chemisorption and physisorption bonds.

The binding energy E_b , (or physisorption energy, E_a) is obtained from the expression, $E_b(E_a) = E_T[A(M)] + E_T[\text{bare} \sim \text{ntrgn}] - E_T[\text{ntrgn}+A(M)]$ in terms of the total, spin-polarized energies of the free adatom (molecule), bare nitrogen, and the system of adatom adsorbed (molecule physisorbed) to the nitrogen. Here A(M) denotes adatom (molecule). Because the initial configuration of the molecule relative to the substrate is crucial for physisorbed molecules, various orientations have been also tested to achieve the highest physisorption energy. The energy released after the formation of a new molecule NM = NH₂ or NO₂ following the dissociation of one N atom from the edge of nitrogen and the dissociation of molecule M = H₂ or O₂ at the edge of the nitrogen flake is calculated $E_f = E_T[\text{bare} \sim \text{ntrgn}] + E_T[M] - E_T[\text{ntrgn}+NM]$, where $E_T[\text{ntrgn}+NM]$ is the optimized total energy of the flake with one N atom removed from edge plus the new molecule formed in the process. This energy corresponds to the formation energy of the new molecule, NM, at *T* = 0 K. We note that in this study the calculated positive values of E_b , E_a , cohesive energy E_C , and formation energy E_f indicate that the process under study is favorable energetically.

The formation energy of a single vacancy is obtained from $E_v = E_T[\text{ntrgn}+V] - \frac{m-1}{m}E_T[\text{bare} \sim \text{ntrgn}]$ ⁴⁵ in terms of the total energy of the cell containing a vacancy and of bare nitrogen. Here *m* is the number of atoms in the SL nitrogen. The stability of the single vacancy in nitrogen has been tested by performing finite temperature ab initio molecular dynamics (MD) calculations with time steps of 2 fs. We performed MD simulations using Nosé thermostat for the duration of 2 ps at

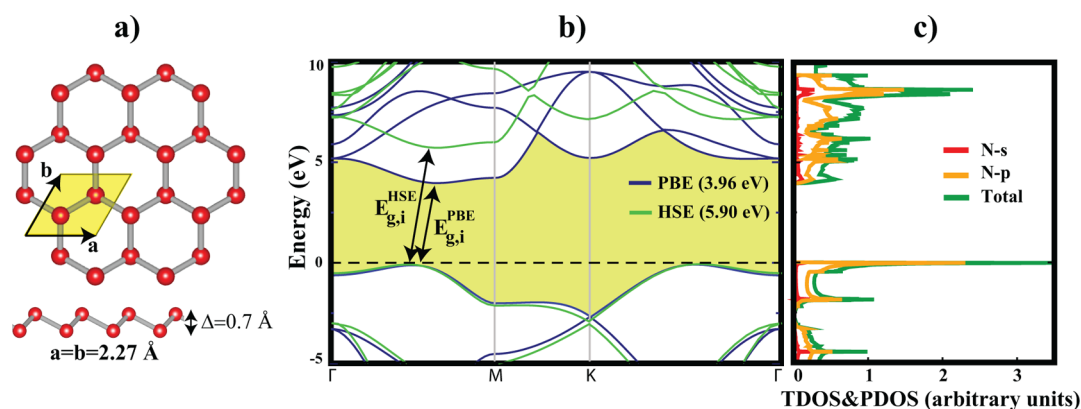


Figure 1. Free standing SL nitrogen: (a) top and side views of buckled honeycomb structure. The primitive unit cell of the 2D hexagonal lattice is shaded, and lattice constants a and b are indicated. (b) Electronic energy band structure calculated using PBE and HSE (see text). The fundamental band gap calculated by PBE is shaded. (c) Total and s- and p-orbital projected density of states, TDOS and PDOS, respectively. The zero of energy is set at the top of the valence band.

different constant temperature levels, where the velocities were normalized after each 40 time steps.

NITROGENE

That nitrogen atoms form 2D single-layer, stable, wide band gap semiconductor (or insulator) with hexagonal lattice was first predicted by Özçelik et al.² For the sake of completeness, part of their results relevant to the present study is reproduced here. We start with reproducing the atomic and electronic structure of nitrogenene, because it is essential in the analysis of its interaction with adatoms and molecules.

The cohesive energy of the structure optimized nitrogenene is $E_C = 3.67$ eV. The atomic configuration and primitive cells of nitrogenene in buckled honeycomb structure is shown in Figure 1a together with the lattice constants of its 2D hexagonal lattice. Because of buckling, nitrogenene consists of two atomic planes of nitrogen atoms, which are separated by 0.7 Å. The electronic energy band structure of bare nitrogenene calculated by PBE is presented in Figure 1b. Accordingly, nitrogenene is a wide band gap semiconductor with an indirect band gap of $E_{g,i} = 3.96$ eV occurring between conduction and valence band along the Γ – M direction of BZ. This band gap increases to $E_{g,i} = 5.90$ eV after the HSE06 correction.^{46,47} The total and s- and p-orbital projected densities of states presented in Figure 1c indicates that the edges of valence and conduction band are composed of predominantly p-orbitals.

SINGLE VACANCY

Single vacancy in nitrogenene, i.e., ntrgn+V, is created by removing one N atom from each (6×6) supercell of the buckled honeycomb structure and subsequently by optimizing the defected structure. In this process, the vacancy formation energy is calculated to be $E_v = 1.19$ eV. Through the uncompensated spins of missing nitrogen atom, ntrgn+V attains a permanent magnetic moment of $3 \mu_B$ at the vacancy site. We note that the earlier calculation,² which predicted the formation energy of a single vacancy as 5.90 eV, used a formal definition which is different from that in the present study.

The effect of the vacancy on the electronic structure is analyzed using density of states. In Figure 2, the calculated spin-polarized densities of states of ntrgn+V are presented. A single vacancy gives rise to spin-polarized states in the fundamental band gap. These states are localized at the vacancy site, in

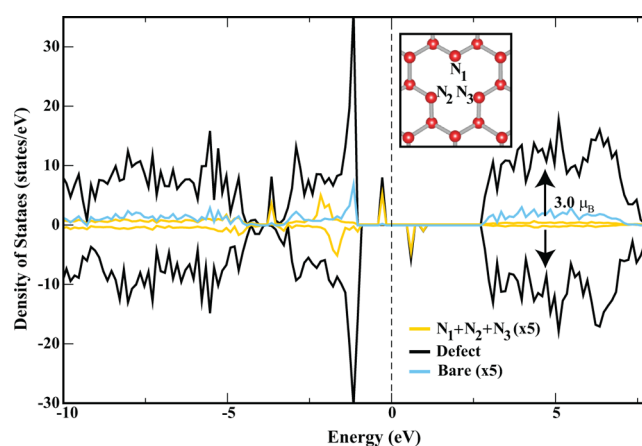


Figure 2. Spin-polarized density of states of nitrogen with a single vacancy, i.e., ntrgn+V. Atomic structure of the vacancy and three 2-fold coordinated N atoms, N_1 , N_2 , and N_3 , are shown in the inset. The sum of local density of states on three N atoms surrounding the vacancy (yellow lines) and the local density of states on a host N atom of nitrogenene farthest from the vacancy (light blue lines) are also presented. The latter local density of states represents the total density of states of "bare" and extended nitrogenene. The zero of energy is set to the Fermi level of ntrgn+V.

particular at N atoms surrounding the vacancy. In addition, resonance states due to the vacancy can occur in the band continua. The energy shifts of vacancy-induced localized states relative to the "bare" and extended nitrogenene having single vacancy can be retrieved by calculating the local density of states (LDOS) at a host N atom in the supercell, which is farthest from the vacancy. This state density is specified in Figure 2 as bare nitrogenene. In the band gap, localized spin up states due to the vacancy are filled, while localized spin down states are empty; the gap between them is 0.5 eV. Apparently, this situation indicates a dramatic effect of vacancy, whereby the wide band gap of bare nitrogenene is reduced to a narrow band gap.

Based on finite temperature, ab initio MD calculations in the temperature range between 0 and 500 K, the single vacancy in nitrogenene is found to be stable at 0 K, but it is prone to severe deformations under thermal excitations at and above 300 K. These results imply that the single vacancy can remain stable at low temperature; however, instabilities can occur at room

temperature and above. Similar calculations resulted in the structural instability of divacancy in nitrogen.

■ ADSORPTION OF ADATOMS

In our study of the adsorption of adatoms (H, Li, O, Al, P, Cl, Ti, As, Sb, B, C, Si, and N) to nitrogen, we first determine the equilibrium site (or geometry) by the optimization of the atomic structure of adatom and nitrogen underneath. Using the optimized atomic structure corresponding to the equilibrium geometry, we calculate electronic and magnetic structure together with the adatom-induced localized states. In this way we reveal the functionalization of nitrogen through modifications of its electronic and magnetic properties.

Optimized Structure and Energetics of Adsorbed Adatoms. In Figure 3 we describe our models of supercells of

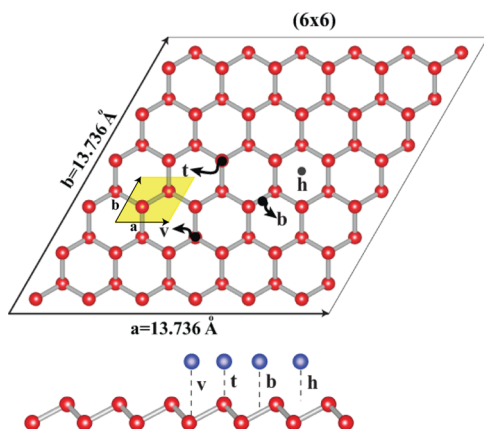


Figure 3. Top and side views of the atomic configuration of the (6×6) supercell of nitrogen, which is used to treat single vacancy, adsorbed adatoms, and physisorbed molecules. The 2D hexagonal primitive unit cell of nitrogen is delineated and shaded. Possible adsorption sites are the top site (t), where the adatom is on top of a host N atom; the bridge site (b), where the adatom is above the center of the N–N bond; the hollow site (h), where the adatom is located above the center of hexagons of the host N atoms; and the valley site (v), where the adatom is placed on top the low-buckled host N atom. Host N atom and adatom are represented by red and blue balls, respectively. Optimized lattice constants of the supercell are $a = b = 13.736$ Å.

2D nitrogen showing possible sites of adsorption or physisorption [such as top (t), bridge (b), hollow (h), and valley (v) sites] above the substrate plane. The supercells are constructed from a (6×6) supercell comprising 36 primitive cells of 2D nitrogen, which is found to give rise to negligible coupling between adjacent adatoms. The minimum energy adsorption site corresponding to the equilibrium structure of an adatom (molecule) together with the atomic configuration of the underlying nitrogen is determined through a comprehensive optimization process. To this end, each adatom or molecule is placed to all possible sites described in Figure 3 at a distant height from nitrogen. Subsequently, all atomic positions including the height of the adatom or molecule and atomic positions of substrate atoms are relaxed to attain the minimum total energy, $E_T[\text{ntrgn} + \text{A}(\text{M})]$ and minimum forces on each atom. The site yielding the minimum value among the total energies calculated for a particular adatom is taken as the equilibrium adsorption site of this adatom. It should be noted that contrary to the case of the large supercell in this study, adatoms treated using small supercells lead to high coverage,

namely $\Theta \sim 1$, and result in specific decorations of nitrogen. Under these circumstances, the coupling among adsorbed adatoms increases, and at the same time the interaction between an adatom and substrate can be modified. At the end, the physical properties of the adatom overlayer and of nitrogen can be modified significantly depending on the coverage. In particular, the localized electronic states originated from adatoms can form energy bands at high coverage. In the present situation using (6×6) supercells, small adatom–adatom coupling lets us interpret our results as if they correspond to isolated single adatom adsorption (or dilute doping).

All adatoms treated in this paper form chemical bonds with nitrogen. For adatoms H, Li, O, Al, P, Cl, Ti, As and Sb, only local deformations of nitrogen at the proximity of adsorbate have occurred, but overall honeycomb geometry has been retained. However, the adsorption of adatoms B, C, and N in the first row, as well as Si gives rise to local reconstruction in nitrogen followed by bond breaking, even dissociation of the host N atoms. We therefore examine the adsorption of adatoms in two categories.

In the first category, the equilibrium adsorption geometries of H, Li, O, Al, P, Cl, Ti, As, and Sb are presented in Figure 4. The hydrogen atom is adsorbed to t-site with a binding energy of 2.09 eV and contribute a local magnetic moment of $1.0 \mu_B$. The van der Waals contribution to the binding energy is a small

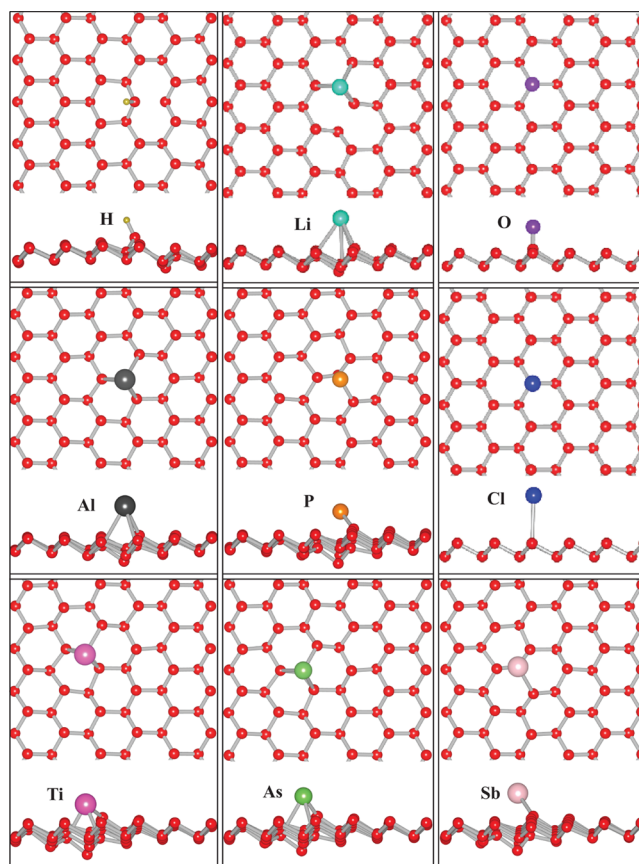


Figure 4. Top and side views of the equilibrium atomic configuration of the adatoms H, Li, O, Al, P, Cl, Ti, As, and Sb adsorbed to nitrogen. Despite deformations at the close proximity of adatoms, the overall honeycomb geometry of nitrogen is retained. Host N atoms of nitrogen are described by small, red balls.

fraction of the binding energy and is only 90 meV. Lithium prefers to v-site and forms a strong bond with binding energy of 2.51 eV and local magnetic moment of $1.0 \mu_B$. Oxygen at t-site forms even stronger bonds with host N atom. Group V elements or pnictogens, P, As, and Sb atoms can be viewed as a subgroup; they are adsorbed at a t-site but slightly shifted toward v-sites and form bonds with binding energies ranging from ~ 1.1 to 1.5 eV with $1.0 \mu_B$ local magnetic moment. Chlorine at t-site forms a weak bond with a binding energy of 0.51 eV at the t-site. In contrast, Ti at a v-site forms a strong bond and causes local deformation and higher local magnetic moment of $2.0 \mu_B$. Calculated binding energies and relevant structural parameters and local magnetic moments related to these adatoms are presented in Table 1.

Table 1. Values Calculated for the Adsorption Adatoms H, Li, O, Al, P, Cl, Ti, As, and Sb to Nitrogen^a

adatom (A)	site	E_b (eV)	h (Å)	d_{A-N} (Å)	μ (μ_B)
H	t	2.09	1.72	1.04	1.0
Li	v	2.51	1.65	1.97	1.0
O	t	3.24	1.43	1.20	0.0
Al	v	2.29	1.65	2.23	1.0
P	v-b	1.46	1.13	1.69	1.0
Cl	t	0.51	2.52	2.56	1.0
Ti	v	4.76	1.10	1.98	2.0
As	v	1.13	1.48	1.87	1.0
Sb	v	1.30	1.65	2.09	1.0

^aAdsorption site; binding energy, E_b ; height (distance) of the adatom from the original, high-lying N atomic plane of nitrogen, h ; the smallest distance between the adatom and host N atom of nitrogen, d_{A-N} ; the local magnetic moment, μ .

As shown in Figure 5, B adatom in the second category causes massive local reconstruction in nitrogen at the close proximity of adsorption site. N–N bonds are broken to form a B–N–N atomic string; hence, a hexagon is destroyed to open a hole in nitrogen. The bonding is strong with the binding energy of 5.67 eV and local magnetic moment of $1 \mu_B$. Carbon and silicon adatoms cause similar effects in nitrogen with binding energies 5.11 and 5.69 eV, respectively. A nitrogen atom forms a N_2 molecule by removing one N atom of nitrogen and leaves the substrate by creating a single vacancy behind. Calculated values regarding these adatoms are presented in Table 2.

Electronic and Magnetic Properties. Our main objective in the doping of nitrogen is to modify its electronic and magnetic properties and hence to make it more functional. Adsorbed adatoms can modify the electronic and magnetic structure of nitrogen locally. In the doping at very low coverage, single adsorbed or substituted foreign atoms give rise to localized states in the fundamental band gap and/or resonance states in the band continua.

The present analysis uses a scheme to deduce the effects of adsorption, in particular, energy shifts of adatom induced localized states relative to the “bare” extended substrate (ntrgn). Here, the total and adatom projected densities of states are examined to reveal the energy locations of dopant states relative to the fundamental band gap of the bare extended substrate, as shown in Figure 6. The density of states of the bare extended substrate and the energy position of its fundamental band gap is retrieved from the local density of states, LDOS, calculated at a N host atom, which is farthest

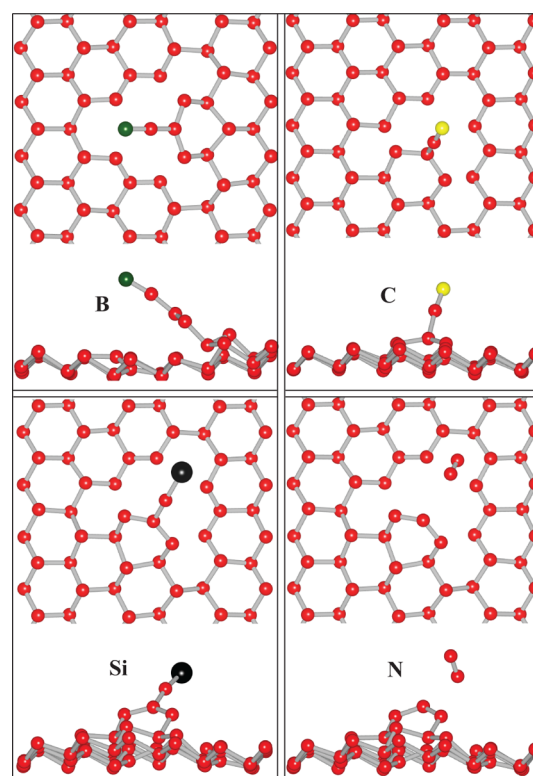


Figure 5. Top and side views of the equilibrium atomic configuration of the adatoms B, C, Si, and N adsorbed to nitrogen. Upon adsorption, massive reconstruction and/or dissociation have occurred by destroying one hexagon of the substrate and creating a single vacancy. Host N atoms of nitrogen are described by small, red balls.

Table 2. Calculated Values of Adatoms B, C, Si, and N Adsorbed to Nitrogen^a

adatom (A)	E_b (eV)	h (Å)	d_{A-N} (Å)	μ (μ_B)
B	5.67	3.07	1.25	1.0
C	5.11	2.88	1.19	2.0
Si	5.69	3.33	1.58	0.0
N	8.22	4.14	3.29	1.0

^aBinding energy, E_b ; height (distance) of the adatom from the original, high-lying N atomic plane of nitrogen, h ; the smallest distance between the adatom and N host atom of nitrogen, d_{A-N} ; the local magnetic moment, μ .

from the adatom in the supercell. This way, the energy positions of adatom-induced localized states can be determined relative to the band edges of the bare extended substrate with reasonable accuracy. The common Fermi level at $T = 0$ K (also the zero of energy), that is, the energy level separating the filled states from the empty states of ntrgn+A system, is normally within the fundamental band gap; it can move toward the band edges depending on the character of the localized states. Notably, for the systems containing very dilute adatoms or dopants, the Fermi level has to be determined through the chemical potential of the Fermi–Dirac distribution. We note that because of the finite size of the supercell the coupling between farthest host N atom and a few specific adatoms can give rise to small uncertainties in the exact position of band edges. Nevertheless, these uncertainties do not affect our discussion here.

States derived from a hydrogen adatom adsorbed to nitrogen are spin-polarized and appear in the gap near the

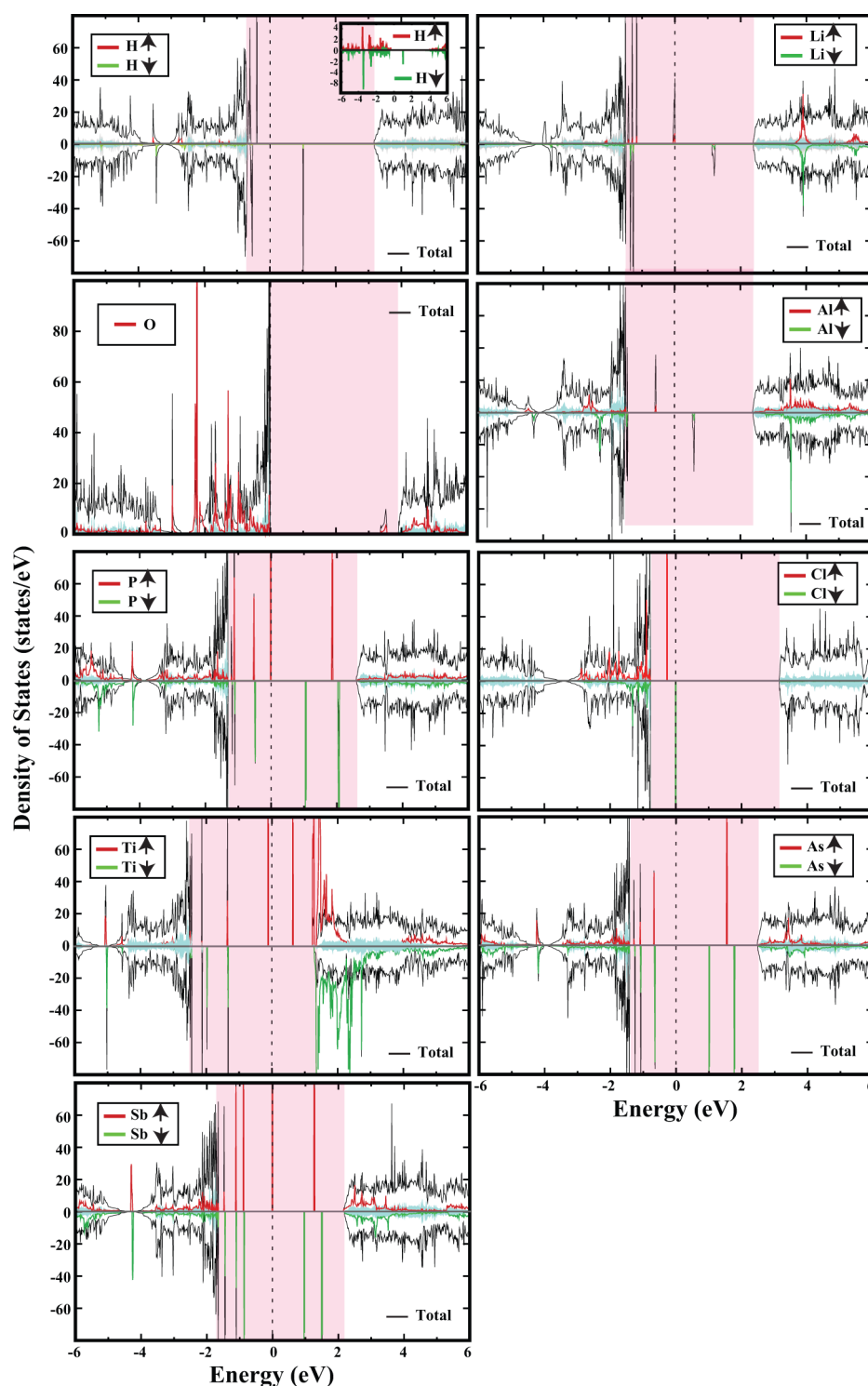


Figure 6. Densities of states calculated for an adatom adsorbed to each (6×6) supercell of nitrogen at equilibrium sites. Total density of states (TDOS) is shown by thin black lines. The density of states of the “bare” extended nitrogen substrate is obtained by projecting TDOS on a host N atom farthest from the adatom and is shown by light blue tone; its band gap is shown by the pink zone. Red and green lines indicate the densities of spin up and spin down states of TDOS projected to the adatom, respectively. The zero of the energy is set at the common Fermi level shown by the dashed vertical line. For clarity, the projected densities of states of H is shown in the inset.

edge of the valence band. Normally, Li adatom is used to donate part of its valence electrons to the conduction band states of the substrate, when the fundamental band gap is not wide. Here, Li-derived spin up localized states occur ~ 1.2 eV above the edge of the valence band of nitrogen. They are filled and set the Fermi level. The empty spin down states occur also

in the gap 1 eV above the Fermi level. The oxygen adatom forms strong bonds; hence, resonance states originating from O overlap with the valence band of bare nitrogen. Empty localized states are found in the gap, below the conduction band edge. States originating from Al are spin-polarized; localized, filled spin up and empty spin down states are found

in the gap. The localized, spin-polarized states originating from P, Cl, As, and Sb in the band gap of bare nitrogen share similar characters. Being a transition-metal atom, Ti exhibits differences with several localized and spin-polarized gap states leading to local magnetic moment relatively higher than others.

The local deformations resulted from the adsorption of the adatoms B, C, Si and N give rise to metastable atomic structures, which may undergo changes. Accordingly, the electronic properties of these metastable structures may not be uniquely determined.

■ PHYSISORPTION OF MOLECULES ON NITROGENE

Four molecules, H_2 , O_2 , H_2O , and N_2 , are attached to the surface of 2D nitrogen through weak and attractive vdW interaction; they do not engage in significant chemical interactions with nitrogen. Accordingly, the binding of these molecules are specified as physisorption, and associated energies are small. The physisorption of these four molecules are investigated by placing them in their different possible configurations above various sites in Figure 3 at large distances. Then the atomic positions of the whole system, namely, molecule and substrate atoms, are optimized to attain the minimum total energy as well as atomic forces. The optimized structures corresponding to minimum total energy are presented in Figure 7. Calculated values of physisorption energies, E_a , and molecule–substrate distances h and d are listed in Table 3.

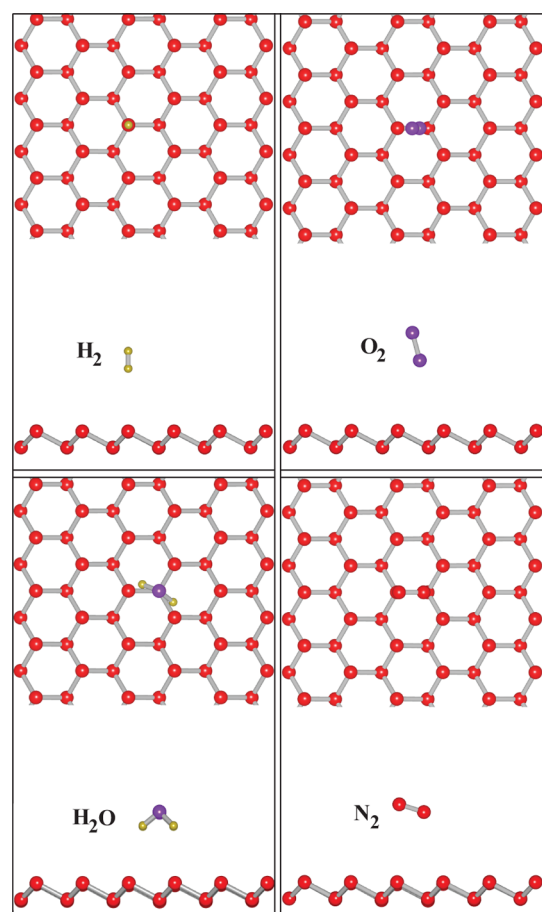


Figure 7. Top and side views of the equilibrium atomic configuration of the molecules H_2 , O_2 , H_2O , and N_2 physisorbed to nitrogen.

Table 3. Calculated Equilibrium Physisorption Energy, E_a ; Height from the Original Atomic Plane of Nitrogen, h ; Minimum Distance between Host N Atom and the Molecule (M) Physisorbed to Nitrogen

molecule (M)	E_a (meV)	h (Å)	$d_{\text{M-N}}$ (Å)
H_2	40	2.71	2.73
O_2	50	3.02	3.18
H_2O	110	2.47	2.60
N_2	50	3.02	3.31

The calculated binding (physisorption) energies are small and range between 40 and 110 meV. To test the contribution of vdW interaction to the binding, we calculated the binding energy of H_2O without vdW interaction. We found $E_a = -8$ meV. Even if this small energy marks the accuracy limits of DFT calculations, the interaction between H_2O and nitrogen is nonbonding without vdW interaction. In compliance with weak binding, the distances between molecules and nitrogen substrate are rather large. Accordingly, nitrogen is rather inert to H_2 , O_2 , H_2O , and N_2 molecules. Apparently, the electronic properties of nitrogen cannot be affected through the physisorption of these molecules.

Dissociation of Molecules at the Edges of Nitrogen.

It was shown that edges of flakes, vacancy defects, or specific adatoms adsorbed to graphene or MoS_2 constitute active sites, where dissociations of molecules, like H_2 , O_2 , and H_2O , can be mediated.^{30,48} In this section, we investigate the interaction of the edge of nitrogen with H_2 , O_2 , and H_2O . Our objective is to see whether the dissociations of these molecules are realized at the edges. We used the supercell geometry consisting of rectangular nitrogen flakes and vacuum space separating each flake from its neighbors. Nitrogen atoms at the zigzag and armchair edges of the flake are 2-fold coordinated and hence can act as chemically active sites.

The dissociation of molecules at the edges of the nitrogen flake in the present study is a complex process and depends on several conditions and parameters, such as the initial distance between molecule and N atom at the edge, the orientation of the molecule relative to the edge, the angle of approach, etc. In principle, molecules are usually dissociated if they become very close to the edges of the flake. Here, using only limited number of test simulations, we show that H_2 and O_2 molecules interacting with the specific edges of the nitrogen flake can dissociate into their constituent atoms under specific circumstances. Concomitantly, the nearest 2-fold coordinated N atom is removed from the edge, and eventually new molecules, NH_2 and NO_2 , are formed. This process can occur with positive formation energy even at $T = 0$ K either spontaneously or by overcoming a potential barrier.

In Figure 8, one sees that H_2 , O_2 , and H_2O molecules are situated near the zigzag, armchair edges of nitrogen flake. When H_2 is placed perpendicularly at a distance of 1.05–1.20 Å from the zigzag edge, it goes away in the course of structure optimization and eventually is physisorbed at a distance of 2.73 Å. The similar situation also occurs when H_2 is placed parallel to the zigzag edge facing a 2-fold coordinated host N atom. Upon structure optimization, it goes away and is physisorbed at a distance of 3.11 Å. However, H_2 is dissociated when it approaches the host N atom parallel to the edge as close as 1.02 Å. Concomitantly, a host N atom from the edge is removed and is implemented to form NH_2 molecule. Using the expression presented in Computational Details, the formation energy at T

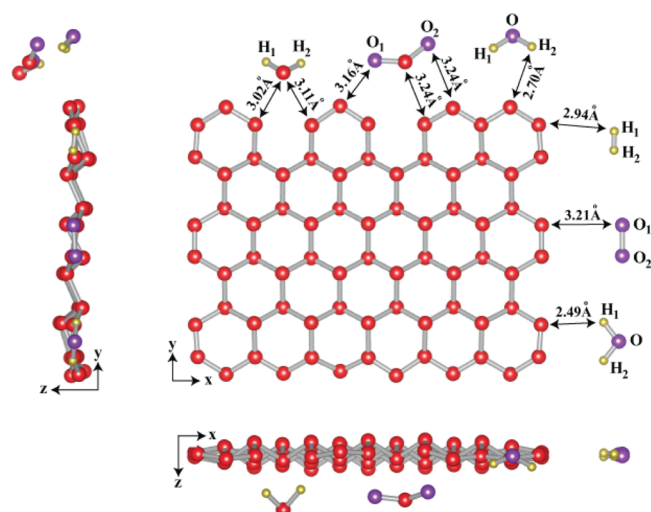


Figure 8. Top and two side views of the atomic configurations of H_2 , O_2 , and H_2O molecules interacting with the zigzag and armchair edges of a rectangular nitrogen flake. At the zigzag edge, 2-fold coordinated N atoms are implemented to dissociated H_2 and O_2 molecules to form eventually NH_2 and NO_2 molecules. H_2O remains intact at both edges.

$= 0$ K is calculated to be $E_f = 1.17$ eV, indicating that this process is exothermic and hence is favorable energetically. Alternatively, the formation energy E_f at $T = 0$ K can be calculated as 1.19 eV using the expression $E_f = 2E_T[\text{H atom}] + E_T[\text{N atom}] + E_C[\text{H}_2] + E_d[\text{N}] - E_T[\text{NH}_2]$, in terms of free atom total energies, the cohesive energy of H_2 molecule $E_C[\text{H}_2]$, the energy needed to remove a 2-fold N atom from the edge of the flake $E_d[\text{N}]$, and the total energy of NH_2 molecule. The energy $E_d[\text{N}]$ is estimated as $E_d[\text{N}] = 2E_C[\text{ntrgn}]/3$ from the cohesive energy of nitrogen. Our simulation of the formation of NH_2 following the dissociation of H_2 and N atom from the edge indicates that there exists a barrier between flake and H_2 molecule at about ~ 1.03 Å. Once this barrier is overcome, NH_2 can form spontaneously.

As for O_2 , it goes away from the edge if it is placed parallel to the edge at a distance of 1.85 Å. However, dissociation of O_2 and subsequently the formation of NO_2 can take place spontaneously if an O_2 molecule approaches parallel to the edge as close as 1.50 Å. The formation energy is calculated to be $E_f = 2.91$ eV. In terms of constituent free atom energies, cohesive energy of O_2 , and the dissociation energy of 2-fold N atom from the edge of the flake E_d , the formation energy of NO_2 molecule is estimated to be 2.95 eV; hence, it is exothermic and is favorable energetically.

The armchair edge of nitrogen appears to be less active than the zigzag edge; if H_2 and O_2 molecules are placed parallel to this edge at the same distances as in the case of the zigzag edge, both molecules go away and attain equilibrium binding at ~ 2.75 and ~ 3.10 Å from the edge. However, if they approach with an angle of 30° with the normal, the dissociation can occur spontaneously at appropriate distance from the edge N atoms. Contrary to H_2 and O_2 , H_2O remains intact as a molecule, even if it is placed close to the edges. Results of our simulation study related with the dissociation of specific molecules can be summarized as follows: (i) Because 2-fold coordinated N atoms at the zigzag and armchair edges of a nitrogen flake are chemically active and they can mediate dissociation of specific molecules, they deserve further attention. (ii) Depending on its orientation and distance from the host N atoms, H_2 and O_2

molecules can dissociate spontaneously and concomitantly can form NH_2 and NO_2 molecules. (iii) As compared to H_2 and O_2 molecules, H_2O molecule is relatively robust against dissociation at the edges of nitrogen.

CONCLUSIONS

We presented the analysis of the formation of a single vacancy as well as the interaction between selected single adatoms and molecules with nitrogen, a 2D single-layer buckled honeycomb structure of the lightest atom in group V family.

Upon formation of a vacancy, localized, filled, spin up states and empty spin down states occur in the fundamental band gap and a local permanent magnetic moment of $3 \mu_B$ is attained. However, structural instabilities can be induced by thermal excitations at room temperature.

Selected adatoms can form rather strong bonds at the surface of 2D nitrogen by exchanging electronic charges and give rise to local deformations. The honeycomb structure is maintained despite the local deformations induced by the adsorption of adatoms like H, Li, O, Al, P, Cl, Ti, As, and Sb. However, upon the adsorption of adatoms, B, C, Si, and N massive local deformations involving also bond breaking can occur; even a hole can form. For example, a N adatom approaching the surface of nitrogen surface can remove one host N atom and form N_2 molecule leaving behind a vacancy. The binding energies of adatoms are in the range of 1.1–5.7 eV. The chlorine adatom is an exception with binding energy smaller than 1 eV.

The adsorbed adatoms in dilute coverage can give rise to localized states in the fundamental band gap and resonance states in the band continua. In this way, the electronic structure near the band gap is modified. Most of the adatoms treated in this paper acquire local magnetic moments through their spin-polarized electronic states even though nitrogen is a nonmagnetic semiconductor.

Molecules like H_2 , O_2 , H_2O , and N_2 interact weakly with the surface of 2D nitrogen, and they are physisorbed to it through vdW interaction. Physical properties of nitrogen cannot be affected from the physisorption of these molecules. However, when placed at appropriate configuration and distance, H_2 and O_2 molecules are dissociated at the edge of a nitrogen flake, and concomitantly they form NH_2 and NO_2 molecules by removing host N atoms from the edge. In conclusion, vacancy and selected adatoms adsorbed to nitrogen surface contribute a diversity of electronic and magnetic properties, attaining functional properties. Some adatoms bring about instability upon adsorption.

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Notes

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