Layered transition metal trichalcogenides MPX₃ (M: transition metal; X: S, Se) demonstrate a wide spectrum of properties and are widely proposed as effective materials for the water splitting reactions. Among these materials, NiPX₃ are the most promising ones because their electronic structures, band gaps and positions of the valence and conduction bands edges fit to the potentials characteristic for the oxygen and hydrogen evolution reactions. Here, first steps of a detailed theoretical description on the adsorption of water molecules on pristine and defected (chalcogen vacancies) surfaces of NiPX₃ are presented and it is shown that in all cases a physisorption takes the place with adsorption energies do not exceeding $-650 \text{ meV}$ and water dissociative adsorption is unfavorable. This work provides a general description for water molecules interaction with MPX₃ and can serve as a basis for further studies on more complicated water/MPX₃ reactions.

1. Introduction

Metal phosphorus trichalcogenides (MPX₃, with M: transition metal and X: S, Se) are the van der Waals (vdW) layered crystalline materials, where each monolayer adopts a $D_{2d}$ point symmetry (Figure 1a,b). Six M cations form a honeycomb lattice with a phosphorus dimer which perpendicularly crosses the center. The P–P dimers are covalently bound to six sulfur (or selenium) atoms to form an ethane-like $(P_2X_6)^{4-}$ unit, where each P-atom is tetrahedrally coordinated with three S (or Se) atoms. Meanwhile, each sulfur (or selenium) atom is coordinated with M sites and is covalently bonded to one P-atom. The 2D layers are identical across the MPX₃ family members, but their 3D stacking arrangement depends on cations and anions constituting the crystals. Most of them crystallize into monoclinic ($C2/m$)¹ or trigonal ($R3$)² crystallographic structures.

The unique crystal structure of MPX₃ with wide vDW gaps between the single layers and strong ionic bond between M cations and $(P_2X_6)^{4-}$ endows these materials with rich functionalities. For example, the comparatively large band gap ranging from 1.3 to 3.5 eV³,⁴ which is unavailable for other 2D materials, indicates their potential application in optoelectronics and photo(electro)chemical catalysis.⁵

In consequence of the small cleavage energy, MPX₃ crystals can be easily exfoliated into 2D honeycomb monolayers,¹⁰ making them attractive for the 2D materials community. Here, one of the research directions is motivated by potential application of MPX₃ in low-dimensional magnetic and spintronic devices⁶–⁹ and the detailed understanding of the electronic and magnetic properties of MPX₃ monolayers is expected from experimental and theoretical fundamental studies.

Until now the vast majority of the relevant works are theoretical calculations⁴,¹⁰–¹² whereas the experimental studies on magnetic properties are mainly focused on the MPX₃ bulk crystals.⁴,¹⁰–¹³ According to density functional theory (DFT) calculations, the 2D MPX₃ exhibit a variety of magnetic behaviors¹⁰ including ferromagnetism (FM), Néel anti-ferromagnetism (nAFM), zigzag anti-ferromagnetism (zAFM), and stripy anti-ferromagnetism (sAFM), which can be modulated through doping⁶,²⁰,²¹ or lattice strain effects.⁰ Surprisingly, the role of chalcogen vacancies, which may appear during exfoliation and processing was not taken into account. This kind of defects may deteriorate the performance of future MPX₃-based devices. At the same time, deviations from perfection can be useful in some applications, as they make it possible to tailor the local properties of material and to achieve new functionalities.

Presently, the focus in the studies of this class of materials is shifted to the applied-oriented investigations, while there are no basic and systematic studies on their electronic structure, which provide direct insight in the properties, which make MPX₃ family so promising candidates for different applications. For example, despite attempts to apply these materials for the water splitting reactions⁵,²² the fundamental studies on the interaction of transition-metal phosphorus trichalcogenides with a single water molecule are missed. The aim of our studies is to fill this lacuna.

The main objects of this work are the typical representatives of the family of transition-metal phosphorus trichalcogenides—NiPS₃ and NiPSe₃. We start with the description of the electronic and magnetic properties of 2D NiPX₃ (X = S, Se). Here,
the chalcogen defects (Figure 1c–e) are addressed. Since NiPX₃ (among other MPX₃ materials) were proposed for the possible application in water-splitting reactions,²¹²³ on a first step, we performed detailed theoretical studies of water molecules adsorption on pristine and defected (S- and Se-vacancies) surface of NiPX₃. Also, these modelings are important taking in mind the future utilization of 2D NiPX₃ materials in real low-dimensional applications, where adsorption of H₂O molecules can drastically influence the electronic structure of 2D NiPX₃ (X = S, Se) and thus functionality of devices.

2. Results and Discussion

Bulk NiPS₃ crystallizes in the C2/m space group, while NiPSe₃ in R3 and both of them adopt the AFM ground state. (For optimized 3D structures and calculated ground-state properties, see Table S1 and Figure S1, Supporting Information). It is expected that individual NiPX₃ layers can be isolated by mechanical exfoliation. In this regard, the cleavage energy ($E_c$) of a layered material is an essential property that need to be considered. The calculated values, $E_c$(NiPS₃) = 0.19 J m⁻² and $E_c$(NiPSe₃) = 0.26 J m⁻² (see Figure S2, Supporting Information), are smaller than that of a bulk graphite (0.36 J m⁻²),¹³ which is used as an indicator for the feasibility of exfoliation of materials in experiments. It is also important to note that the obtained values agree with the previously published data for NiPS₃.¹⁴

When studying 2D NiPX₃ monolayers, we consider four different magnetic configurations of Ni²⁺ ions, which include FM, nAFM, zAFM, and sAFM configurations, as well as the non-magnetic states. According to our calculations, the energetically most favorable structure corresponds to the zAFM arrangement of magnetic moments for the both NiPS₃ and NiPSe₃ (Table 1). The both monolayers under study are indirect band gaps semiconductors: the VBM is located at the K point, while the CBM lies on the K to Γ path (see Figure S3, Supporting Information). Moreover, the top of the valence band is mainly formed by S/Se, whereas the bottom of the conduction band consists of S/Se and Ni. These observations are consistent with the data recently published for bulk NiPS₃, which was shown to be a charge-transfer insulator.²⁶ The band gaps calculated by means of Perdew–Burke–Ernzerhof (PBE)+U+D2 are $E_g$ = 2.19 and 1.85 eV for NiPS₃ and NiPSe₃, respectively (see Figure 2a and Figure S3, Supporting Information). Hybrid functional (here: HSE06) yields qualitatively similar results, albeit yielding wider gaps: 2.87 and 2.46 eV for 2D NiPS₃ and NiPSe₃ (see Figure S3, Supporting Information), which are consistent with previously published data (3.01 eV for NiPS₃).⁴

The calculated total energies for different magnetic configurations were used to estimate the exchange-coupling parameters ($J_1$, $J_2$, and $J_3$), describing the magnetic interactions between Ni²⁺ ions (Table 2). The obtained results can be understood on the basis of the Goodenough–Kanamori–Anderson (GKA) rules.²⁷²⁸ Two types of interactions have to be considered: Direct Ni–Ni couplings ($t_{2g}–t_{2g}$ orbital overlapping) and indirect Ni–X–Ni super-exchange couplings. The $t_{2g}$ orbitals are filled in NiPX₃, and direct couplings do not exist. The super-exchange interaction between nearest neighbors is through the two X atoms on edge-shared octahedra between neighboring Ni atoms. The respective Ni–X–Ni angle is 85.3° for X = S and 86.3° for X = Se, that is, close to 90°. Thus, according to the GKA rules, the considered interaction should be ferromagnetic ($J_1 > 0$). In the case of second neighbor coupling, no coplanar X atoms with overlapping orbitals exist, which results in $J_2 ≈ 0$. The super-super-exchange interaction involves a Ni–X–X–Ni bridge with two X atoms belonging to the same PX₃ sublayer. Thus, the third neighbor interaction is antiferromagnetic ($J_3 < 0$). Overall, the zAFM ground state is determined by 3NN super-super-exchange interaction. Our results are in good agreement with the previously published experimental data for NiPS₃.¹⁷

![Figure 1. (left panel) a) Top and b) side views of a single layer of MPX₃. (right panel) Structure of the considered chalcogen defects: c) Vₓ@1L; d) Vₓ@2L; e) Vₓ@2L. Spheres of different size/color represent ions of different type.](image)

| System       | State  | $E$   | $ΔE$ | $M$  | $E_g$ |
|--------------|--------|-------|------|------|------|
| NiPS₃        | nAFM   | -89.443 | 13    | 1.59 | 2.26 |
|              | zAFM   | -89.456 | 0     | 1.59 | 2.19 |
|              | sAFM   | -89.337 | 119   | 1.60 | 1.69 |
|              | FM     | -89.357 | 99    | 1.60 | 2.34/2.21 |
|              | NM     | -83.321 | 6135  | 0    | 0.00 |
| NiPSe₃       | nAFM   | -80.109 | 24    | 1.54 | 1.89 |
|              | zAFM   | -80.133 | 0     | 1.53 | 1.85 |
|              | sAFM   | -79.996 | 137   | 1.56 | 1.32 |
|              | FM     | -80.031 | 102   | 1.56 | 1.35/1.78 |
|              | NM     | -74.835 | 5298  | 0    | 0.00 |

*²Two values for the spin-up and spin-down channels are indicated.*

Table 1. Ground-state properties as obtained for the different magnetic states of 2D NiPS₃ and 2D NiPSe₃ with PBE+U+D2: $E$ (in eV) is the total energy, $ΔE$ (in meV per (2x1) supercell) is the difference between the energy calculated for the magnetic states and the energy calculated for the zAFM state, $M$ is magnetic moment (in μB per Ni ion), $E_g$ (in eV) is the band gap.
available experimental results ($T_N$ is 155\textsuperscript{[17]} and 206 K\textsuperscript{[29]} for NiPS\textsubscript{3} and NiPSe\textsubscript{3}, respectively).

Mechanical exfoliation, usually utilized for monolayers production, can lead to formation of chalcogen vacancies. Therefore, we consider three different kinds of defects: i) one vacancy at X-site, named as VS\textsubscript{x}@1L or VSe\textsubscript{x}@1L with a defect concentration about 2.5% (Figure 1c); ii) two vacancies at the neighboring X-sites of the same chalcogen sub-layer named as VS\textsubscript{2}@1L or VSe\textsubscript{2}@1L with a concentration about 5% (Figure 1d); iii) two vacancies at X-sites of the different chalcogen sub-layers named as VS\textsubscript{2}@2L or VSe\textsubscript{2}@2L with a concentration about 5% (Figure 1e).

The defect formation energies ($\Delta E_{\text{def}}$) are presented in Table 3. Overall, $\Delta E_{\text{def}}$ are in the same range that those of transition metal dichalcogenides—sulfur vacancies in, for example, FeS\textsubscript{2} ($\Delta E_{\text{def}} = 2.25$ eV\textsuperscript{[30]}\textsuperscript{)} and MoS\textsubscript{2} (2.12 eV\textsuperscript{[11]}\textsuperscript{)} and of reducible oxides—oxygen vacancies in, for example, Fe-oxides ($\Delta E_{\text{def}} = 1.72 \ldots 3.51$ eV\textsuperscript{[32,33]}\textsuperscript{)}\textsuperscript{.} For the same defect type, Se vacancy is more likely to occur compared to S vacancy, which correlates with the respective electronegativity values. For the same X, the difficulty of defect formation is VS\textsubscript{2}@1L > VSe\textsubscript{2}@2L > VSe\textsubscript{2}@1L and from now on we will focus on detailed consideration of VS\textsubscript{x}@1L.

A chalcogen vacancy formation leads to a strong modification of the local crystallographic and electronic structures (Figure 2). Thus, the phosphorus dimer is shifted from its original position. Notably, it is tilted toward the vacancy and its angle with the...
Figure 3. a–c) Top and side views of the relaxed structures obtained after water adsorption on a) pristine NiPS$_3$ (molecular adsorption); b) defective NiPS$_3$ (molecular adsorption); c) defective NiPS$_3$ (dissociative adsorption). Side view are superimposed with electron density redistribution maps. Electron density accumulation (depletion) is shown in red (blue). Green, violet, and orange spheres represent Ni, P, and S atoms, respectively. The water molecule is shown with red and light-blue spheres, for O and H, respectively. d–f) Site-projected density of states after water adsorption for d) pristine NiPS$_3$ (molecular adsorption); e) defective NiPS$_3$ (molecular adsorption); f) defective NiPS$_3$ (dissociative adsorption). The molecular orbitals of a gas-phase H$_2$O molecule are indicated by horizontal dashed lines. These are obtained by aligning the $2\sigma_1$ core level of the gas-phase and adsorbed H$_2$O molecules.

vertical direction is 2.8 or 4.3 degrees for X = S or Se, respectively. Furthermore, this dimer is pulled out from the entire layer, while keeping the P–P distance almost unchanged with respect to the pristine structure. All P–X distances are slightly elongated and this effect is more pronounced for the defective sublayer (Table 3).

Upon removal of a chalcogen atom, the left behind electrons occupy the easily available electronic states of a (P$_x$X$_{3-x}$) entity. As a result, in the calculated density of states (DOS) of the NiPS$_{3-x}$ monolayer a localized defect state appears in the energy gap just below $E_F$ (Figure 2b,c) and the electron density is delocalized between the P and S atoms of the defective sublayer (Figure 2c,d). One more state is formed in the energy gap above $E_F$ and it has Ni-3d character (Figure 2c,e). The magnetic moments of the Ni$^{2+}$ ions nearby the vacancy are coupled ferromagnetically and the both considered states appear in the spin-up channel. In the case of X = Se the occupied state is not well-localized, although its signature can be visible in the vicinity of $E_F$ (Figure 2c). Naturally, these modifications yield a decrease of the energy gap width: $E_g = 1.36$ and 1.29 eV for the defective NiPS$_3$ and NiPSe$_3$, respectively.

In the next step we investigate the adsorption of a single H$_2$O molecule on pristine NiPX$_x$ (X = S, Se) monolayers. Various high-symmetry adsorption sites and adsorption orientations are considered (see Table S2 and Figure S5, Supporting Information). All adsorption configurations have similar adsorption energies which range from −115 to −173 meV and from −109 to −176 meV for NiPS$_3$ and NiPSe$_3$, respectively. In the most stable adsorption structures, the oxygen atom of a water molecule stays directly above of an P atom [d(P–O) = 3.17 and 3.34 Å for NiPS$_3$ and NiPSe$_3$, respectively] and the H atoms are directed toward the neighboring X atoms as it is shown in Figure 3a. In accordance with the weak interaction, the structural parameters of H$_2$O as well as of the studied monolayer undergo insignificant changes.

To shed more light on the adsorbate mode, we have investigated the electron density redistribution upon adsorption ($\Delta \rho$). The $\Delta \rho$ and DOS plots are shown in Figure 3a,d. When molecular water adsorbs on the pristine NiPX$_x$ monolayer, the main charge rearrangement takes place between O and P atoms. Charge accumulation in the p-orbital of P on the side of the adsorbate indicates that it is the main orbital participating in the bonding. The electron density accumulation between H$_2$O and NiPX$_x$ is accompanied with a depletion at the hydrogen positions. Furthermore, there is some signature for the interaction between water hydrogens and the neighboring chalcogen atoms.

The main effects in DOS expected due to the interaction between H$_2$O and NiPX$_x$ are a shift of position and change in width of the molecular levels of the adsorbate. Analysis of the partial DOS (Figure 3d) shows that the bonding to the monolayer is mainly due to the $1b_1$ molecular orbital (MO) of H$_2$O (the water lone pair). This orbital undergoes some broadening due to hybridization with p states of P. In addition, a slight upward shift
with respect to the MO of gas phase water molecule is observed for this MO. (For the DOS of H2O/NiPSe3, see Figure S6, Supporting Information).

The chalcogen defect binds the H2O molecule more strongly: \(E_{\text{ads}} = -572\) and \(-637\) meV for \(X = S\) and Se, respectively. This is related to the higher coordination of the molecule in the vacancy than on the pristine monolayer. The water molecule is coordinated between two Ni ions as it is shown in Figure 3b. Additional stability is due to the quite strong interaction between the water H atom and the P atom [\(d(P - H) = 1.79\) Å], which lost the chalcogen neighbor. In accordance with the stronger interaction as compared to the adsorption on the pristine monolayer, some changes in the molecular structure can be observed. These are: a significant elongation of the H–O bond from 0.97 Å for the gas-phase molecule to 0.98/1.04 Å and 0.98/1.04 Å for the adsorbed molecule on NiPS3−x and NiPSe3−x, respectively. As a result of the interaction with the monolayer, the angle H–O–H is enhanced to 109.8° and 109.3° versus 104.5° in the case of H2O/NiPS3−x and H2O/NiPSe3−x, with respect to the gas phase H2O molecule.

As a further confirmation of strong interaction between the molecule and the monolayers, we find a strong accumulation of electron density between O and two Ni atoms as well as between H and P atoms (Figure 3b). Analysis of the partial DOS (Figure 3e) shows that, the orbitals of water contribute significantly to the NiPX3 defect states. Furthermore, the 1b and 3a1 MOs participate in the bonding to the monolayer. (For the DOS of H2O/NiPSe3−x, see Figure S6, Supporting Information). The X-defect formation energy is lowered from 1.48 eV (1.28 eV) for the dry monolayer to 1.08 eV (0.82 eV) for the surface with an adsorbed water molecule, in case of \(X = S\) (Se) respectively.

In addition to the molecular adsorption structures, dissociated structures were also investigated. In the case of pristine monolayers, all of them are characterized by positive adsorption energies and we do not discuss them here. Yet, the O–H bond elongation observed for the adsorption on defective monolayer, can serve as an indication for the possible dissociation of H2O. Indeed, in the case of NiPS3−x the dissociative adsorption is exothermic process. Consistently with the electronic structure of the defective monolayer, upon molecule dissociation, hydrogen substitutes the P-dangling bond and the OH fragment is bonded to Ni2+ ions \([d(Ni = O) = 2.04\) Å] (Figure 3c). The hydroxyl group in the vacancy shows an accumulation in the 1σ orbital and depletion in the 3σ orbital (Figure 3c). Charge accumulation between P and H is also detected. The observed phenomena can also be seen in partial DOS (Figure 3f). Still, the corresponding adsorption energy \(E_{\text{ads}} = -355\) meV for NiPS3 is lower in magnitude as compared with the value obtained for molecular adsorption structure, making the dissociative adsorption less favorable. The same trend was observed when studying adsorption of water on CrPX3 monolayers.\[43\]

All our attempts to find a local minimum corresponding to the dissociative adsorption structure similar to one presented in Figure 3c were failed, when NiPSe3 is considered. Structure optimization yields spontaneous recombination of H and OH species into an H2O molecule. Presumably, this is due to the lower electronegativity of Se and bad localization of the corresponding defect state in the considered DOS (Figure 2c). Indeed, when considering iron oxides, which are known as effective materials for the water splitting, we noticed that the well-localized defect states in the DOS of respective defective surfaces are separated form the valence band states by \(\approx 300\) ... 600 meV and the dissociative adsorption on these surfaces is strongly favored (by 0.75 ... 1.23 eV) over the molecular.\[12,33\]

3. Conclusions

We present a comprehensive first-principles study of initial steps of adsorption of water on the pristine and defective NiPX3 (\(X = S, Se\)) trichalcogenide monolayers, also analyzing the underlying electronic mechanisms. On pristine monolayers a molecular adsorption is detected and the results obtained for \(X = S\) and Se are almost identical unless the chalcogen vacancy is created. Whereas a well-localized occupied defect state was detected in DOS of NiPS3, that was not revealed in DOS of NiPSe3. This can be a reason why water cannot follow the dissociation pathway in case of \(X = Se\). Although dissociation pathway is possible when \(X = S\), molecular adsorption is also energetically more favorable in this case. Overall, we found that in all cases the adsorption of water has a physisorption character with adsorption energies not exceeding \(-650\) meV. For both NiPX3, under study the X vacancy formation energy becomes lower by \(\approx 400\) meV if an adsorbed water molecule is present. The comparison of our data with previous results for transition-metal oxides allows us to conclude that dissociative water adsorption is connected with the strong localization (in space and in energy) of the defect state formed after creation of vacancy. The formation of such state, which is effectively energetically split from the valence band states, can be considered as a descriptor for the consideration of the possible water splitting on the pristine and defected surfaces of transition metal trichalcogenides. Our results are first steps on the consideration of the complicated H2O/MPX3 systems and the presented results can be used as a basis for further theoretical and experimental works.

4. Experimental Section

Spin-polarized DFT calculations based on plane-wave basis sets of 500 eV cutoff energy were performed with the Vienna ab initio simulation package (VASP).\[35–37\] The PBE exchange-correlation functional\[38\] was employed. The electron–ion interaction was described within the projector augmented wave method\[39\] with Ni (3p, 3d, 4s), P (3s, 3p), S (3s, 3p), and Se (4s, 4p) states treated as valence states. The Brillouin-zone integration was performed on Γ-centered symmetry reduced Monkhorst–Pack meshes using a Gaussian smearing with \(\sigma = 0.05\) eV, except for the calculation of total energies. For these calculations, the tetrahedron method with Blochl corrections\[40\] was employed. The 12 × 12 × 4 and 24 × 24 × 1 k-meshes were used for the studies of bulk and monolayer NiPX3, respectively, and the 12 × 12 × 1 k-mesh was used for the 2 × 2 × 1 supercells consisting of fourfold unit monolayers. The DFT + U scheme\[41,42\] was adopted for the treatment of Ni 3d orbitals, with the parameter \(U_{\text{eff}} = U - J\) equal to 6 eV. Dispersion interactions were considered adding a 1/8 8 atom-atom term as parameterized by Grimme (‘D2’ parameterization).\[43\] The selected approach yields structural parameters, which are in good agreement with available experimental data.\[22,26\] Furthermore the correct electronic state (charge-transfer insulator and width of the band gap)\[40\] and magnetic states (zAFM)\[44\] are reproduced. For comparison reasons, selected calculations were performed using the HSE06 functional.\[45\]

When modeling NiPX3 monolayers, the lattice constant in the lateral plane was set according to the optimized lattice constant of bulk NiPX3 and the positions of P and S were fully relaxed. A vacuum gap was set to
within the Metropolis algorithm with periodic boundary conditions.\[46\]

To extract the exchange interaction parameters between Ni ions spins, the Heisenberg Hamiltonian was considered

\[
H = \sum_{\langle \langle ij \rangle \rangle} J_{ij} \langle \langle \langle i \rangle \rangle \rangle \cdot \langle \langle \langle j \rangle \rangle \rangle
\]

where \( \langle \langle \langle i \rangle \rangle \rangle \cdot \langle \langle \langle j \rangle \rangle \rangle \) is the net spin magnetic moment of the Ni ions at site i, three different distance magnetic coupling parameters were estimated, considering one central Ni ions interacted with three nearest neighboring (NN, \( J_{ij} \)), six next-nearest neighboring (2NN, \( J_{ij} \)), and three third-nearest neighboring (3NN, \( J_{ij} \)) Ni ions, respectively. Here, the long-range magnetic exchange parameters \( J \) can be obtained as\[19\]

\[
J_1 = \frac{E_{FM} - E_{AFM} + E_{AFM} - E_{AFM}}{8S^2}
\]

\[
J_2 = \frac{E_{FM} + E_{AFM} - (E_{AFM} + E_{AFM})}{16S^2}
\]

\[
J_3 = \frac{E_{FM} - E_{AFM} - 3(E_{AFM} - E_{AFM})}{24S^2}
\]

where \( S \) is the calculated magnetic moment of the Ni ion and \( E_{FM}, E_{AFM}, E_{AFM}, E_{AFM} \) are the total energies in ferromagnetic, Néel antiferromagnetic, zigzag antiferromagnetic, and stripy antiferromagnetic configurations, respectively.

To estimate \( T_N \) temperature, Monte Carlo simulations were performed within the Metropolis algorithm with periodic boundary conditions.\[46\]

The three exchange parameters \( J_1, J_2, J_3 \) were used in a series of supercells \( L \times L \) \((L = 16, 32, 64)\) containing a large amount of magnetic sites to accurately evaluate the value. Upon the heat capacity \( C(T) = \langle \langle (E^2) - \langle E^2 \rangle \rangle \rangle / k_B T^2 \) reaching the equilibrium state at a given temperature, the \( T_N \) value can be extracted from the peak of the specific heat profile.

The electrically neutral vacancies were created by removing one or two X atoms from the \( (2 \times 2) \) supercells. Thereby, the distance between repeated vacancies in the nearest-neighbor cells was larger than 10 Å. The defect formation energy is defined as follows

\[
\Delta E_{def} = \frac{1}{n} \left[E(NiPX_{3-x}) + n \mu_X - E(NiPX_3)\right]
\]

where \( n \) is a number of defects, \( E(NiPX_{3-x}) \) and \( E(NiPX_3) \) are the energies of the 2D NiPX_{3-x} with and without vacancy, respectively, \( \mu_X \) is the chemical potential of X atom (\( \mu_X = -4.1279 \) eV and \( \mu_{25K} = -3.4895 \) eV)\[12\].

To study the adsorption of a single molecule, a \( (2 \times 2) \) supercell was used with one water molecule added. Adsorption energies were calculated as

\[
\Delta E_{ads} = E(A/NiPX_3) - (E(A) + E(NiPX_3))
\]

where \( E(NiPX_3) \) and \( E(A) \) are the energies of the relaxed isolated 2D NiPX_{3-x} and an adsorbate, and \( E(A/NiPX_3) \) is the energy of their interacting assembly.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

This work was supported by the National Natural Science Foundation of China (Grant No. 21970359). The authors appreciate the High Performance Computing Center of Shanghai University and Shanghai Engineering Research Center of Intelligent Computing System (No. 19DZ2252600) for providing the computing resources and technical support. Y.D. and E.V. thank the “ENSEMBLE3 - Centre of Excellence for Nanophotonics, Advanced Materials and Novel Crystal Growth-Based Technologies” project (GA No. MAB/2020/14) carried out within the International Research Agendas programme of the Foundation for Polish Science co-financed by the European Union under the European Regional Development Fund and the European Union’s Horizon 2020 research and innovation programme Teaming for Excellence (GA No. 857543) for support of this work.

**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**

density functional theory, trichalcogenides, water adsorption

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