Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Stabilities of group-III phosphide (MP, M = B, Al, Ga and In) monolayers in oxygen and water environments

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In supporting information, additional results mainly about the calculated properties of two-dimensional (2D) and three-dimensional (3D) group-III phosphides (MPs) are presented. Table S1 provides the calculated and experimental structural properties of 3D MPs with a zinc-blende (ZB) structure, and Table S3 provides the calculated mechanical properties of the 2D GeS monolayer and graphene along with the theoretical values in literature. These two tables are used to examine the reliability of our method. The cohesive energies of the 2D V-BP, H-AlP, H-GaP and H-InP and their energy differences with corresponding 3D materials are listed in Table S2, which complements Table 1 in the main text. If not otherwise specified in this paper, the group-III phosphide (BP, AlP, GaP and InP) monolayers refer to the single layer H-BP, V-AlP, V-GaP and V-InP nanosheets.

Figure S1 displays the AIMD results of group-III phosphide monolayers in the vacuum. As shown in Figures S2-S9, the adsorption of an oxygen atom and molecule on the high-symmetry sites of group-III phosphide monolayers were carefully investigated to find their most favorable adsorption sites. Similarly, Figures S10-S21 represent the adsorption of a water molecule, H atom and OH group on the high-symmetry sites of group-III phosphide monolayers. In these figures, the values of ΔE are defined as the energy differences relative to corresponding most stable structure.

Table S1. Lattice constants (a) and bulk modulus (B) of 3D MPs with a ZB structure

	a (Å)		B (GPa)	
	Present work	Experimental	Present work	Experimental
BP	4.523	4.54[a]	174.0	173[b]
AlP	5.444	5.45[a]	91.2	86[a]
Gap	5.430	5.45[a]	88.5	91[c]
InP	5.863	5.87[a]	66.2	72[a]

[a] Data from Wyckoff,[1] [b] from Schroten et al,[2] and [c] from Bliss.[3]

Table S2. Cohesive energies (E_{coh}) of 2D V-BP, H-AlP, H-GaP and H-InP, and energy differences (E_d) between the 2D materials and corresponding 3D crystals at 0 K

	V-BP	H-AlP	H-GaP	H-InP
E_{coh} (eV atom^{-1})	-4.731	-3.565	-3.090	-2.752
E_d (eV atom^{-1})	0.803	0.685	0.638	0.653

Table S3. In-plane elastic stiffness (C_{11}, C_{22} and C_{12}), in-plane Young's modulus and Possion's ratio of 2D graphene and GeS monolayer at 0K

material	C_{11} (N m^{-1})	C_{22} (N m^{-1})	C_{12} (N m^{-1})	E_x (N m^{-1})	E_y (N m^{-1})	ν_{xy}	ν_{yx}
graphene (this work)	347.5	347.5	60.63	336.9	336.9	0.17	0.17
graphene (Topsakal et al.[4])	343.8	343.8	59.1	335	335	0.16	0.16
GeS (this work)	49.1	14.0	21.9	14.9	4.2	1.56	0.45
GeS (Qin et al.[5])	38.9	10.9	16.6	13.6	3.8	1.52	0.43

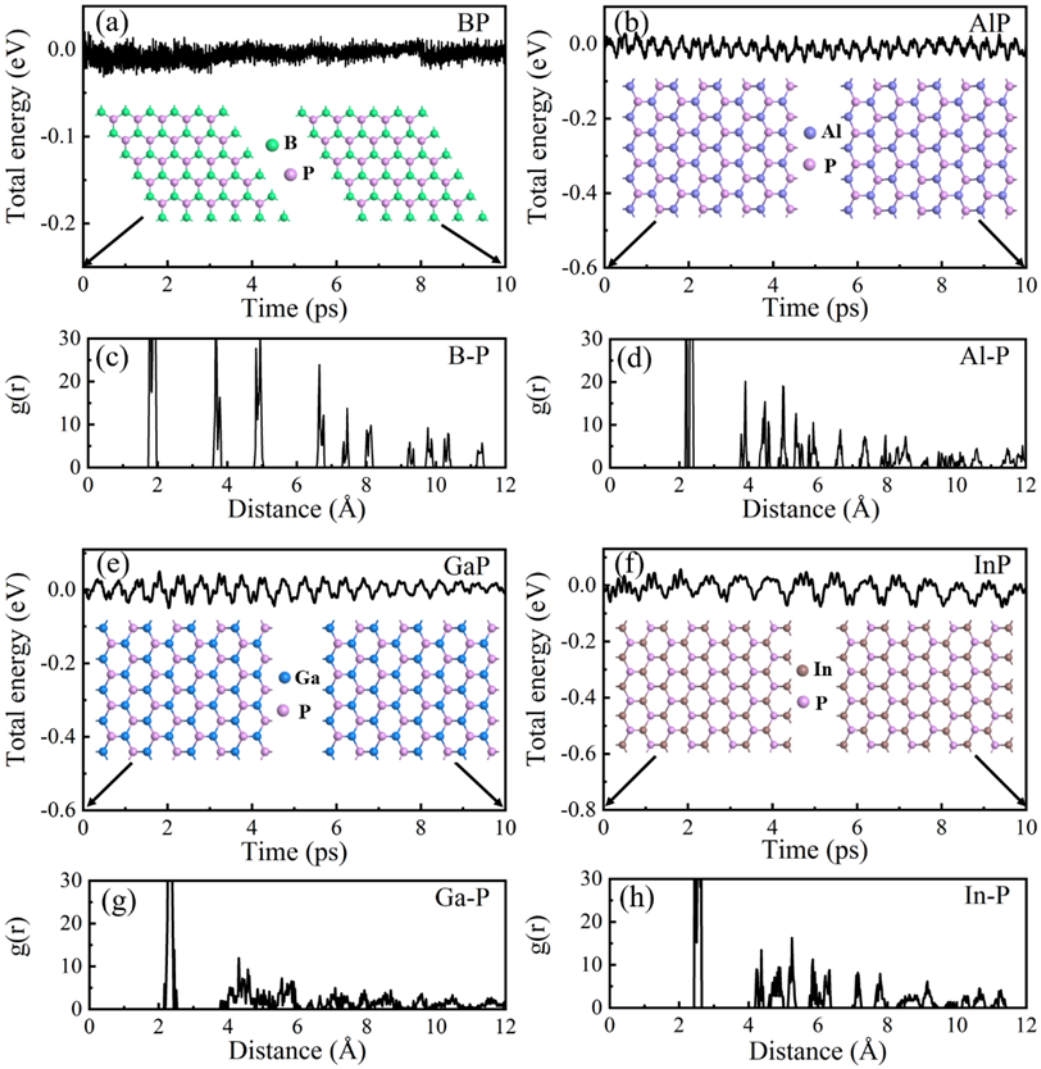

Fig. S1 The evolution of the relative total energies of the (a) BP, (b) AlP, (e) GaP and (f) InP monolayers in a vacuum in the AIMD simulations at 300 K and the snapshot structures of the 2D systems at 0 ps and 10 ps. The normalized radial distribution functions *g(r)* for (c) BP, (d) AlP, (g) GaP and (h) InP after annealing at 300 K for 10 ps.

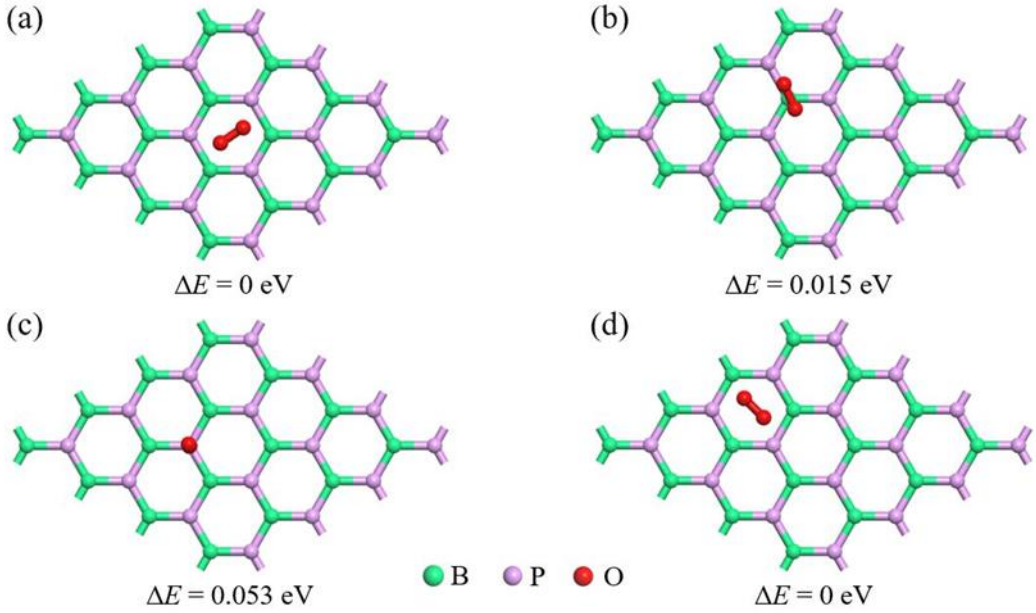

Fig. S2 Equilibrium structures of an oxygen molecule initially adsorbed on the (a) H, (b) T1, (c) T2, and (d) B sites of the BP monolayer. H, T1, T2 and B stand for hollow, top of B atom, top of P atom, and bridge, respectively. The values of ΔE are the energy differences relative to the most stable structure.

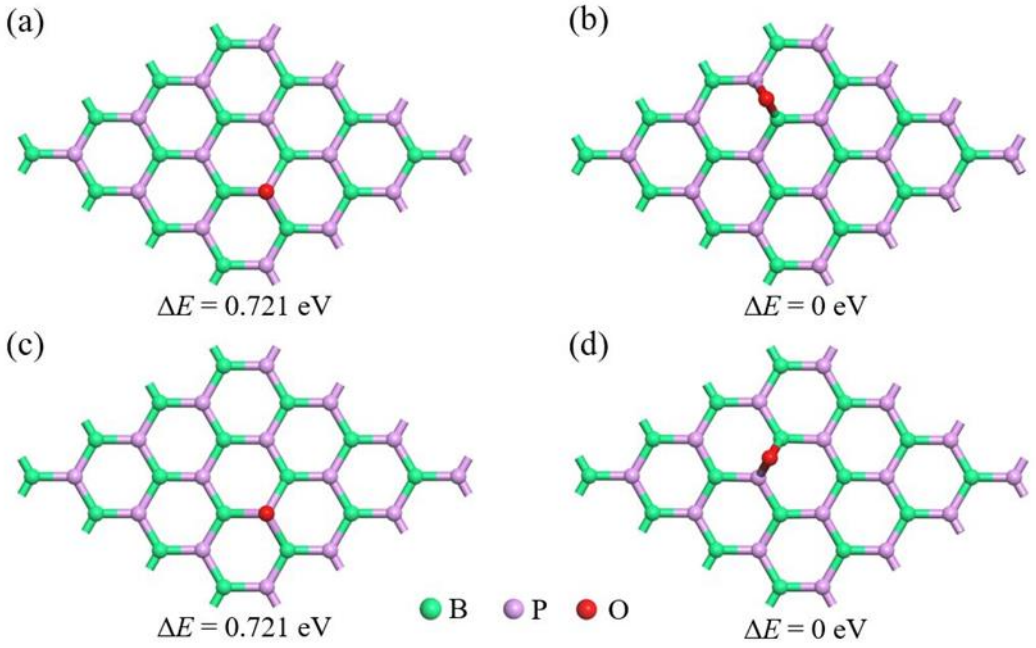

Fig. S3 Equilibrium structures of an oxygen atom initially adsorbed on the (a) H, (b) T1, (c) T2, and (d) B sites of the BP monolayer. H, T1, T2 and B stand for hollow, top of B atom, top of P atom, and bridge, respectively.

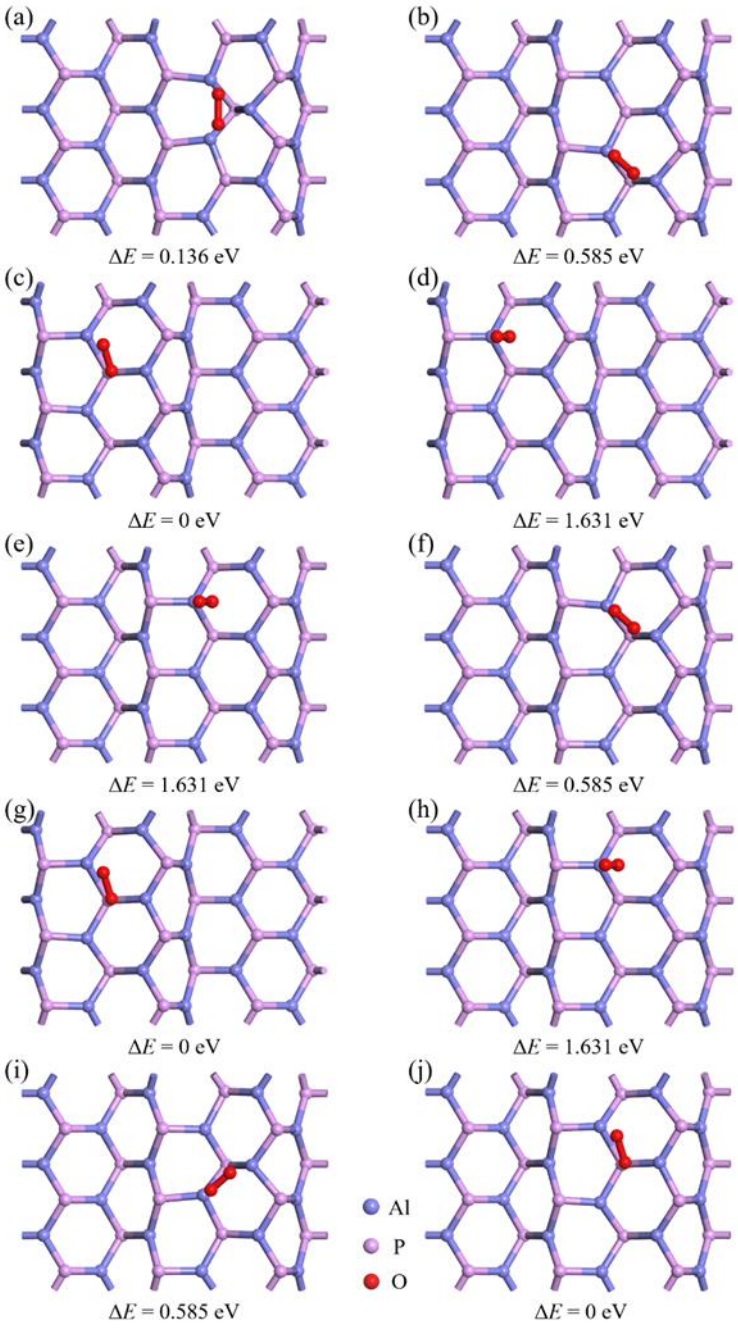

Fig. S4 Equilibrium structures of an oxygen molecule initially adsorbed on the (a) H1, (b) H2, (c) T1, (d) T2, (e) T3, (f) T4, (g) B1, (h) B2, (i) B3, and (j) B4 sites of the AlP monolayer. H, T1 (3), T2 (4) and B stand for hollow, top of Al atom, top of P atom, and bridge, respectively.

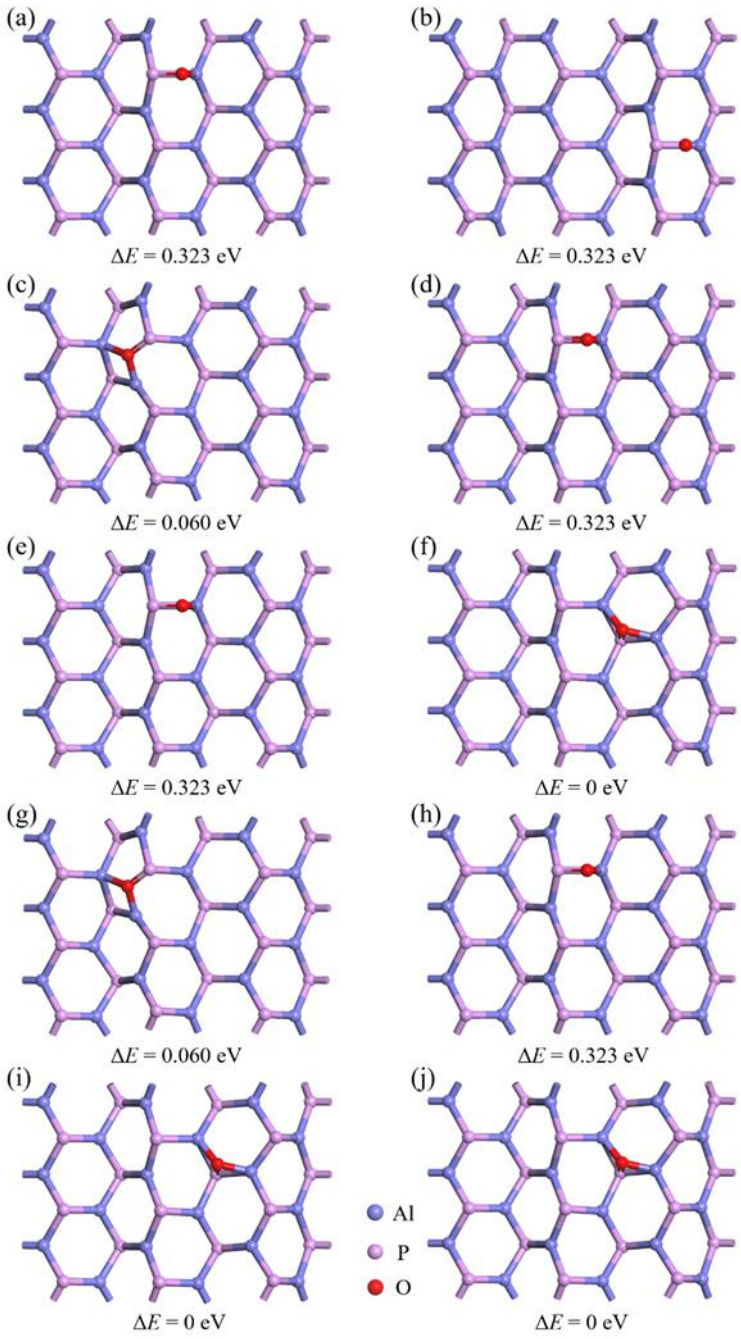

Fig. S5 Equilibrium structures of an oxygen atom initially adsorbed on the (a) H1, (b) H2, (c) T1, (d) T2, (e) T3, (f) T4, (g) B1, (h) B2, (i) B3, and (j) B4 sites of the AlP monolayer. H, T1 (3), T2 (4) and B stand for hollow, top of Al atom, top of P atom, and bridge, respectively.

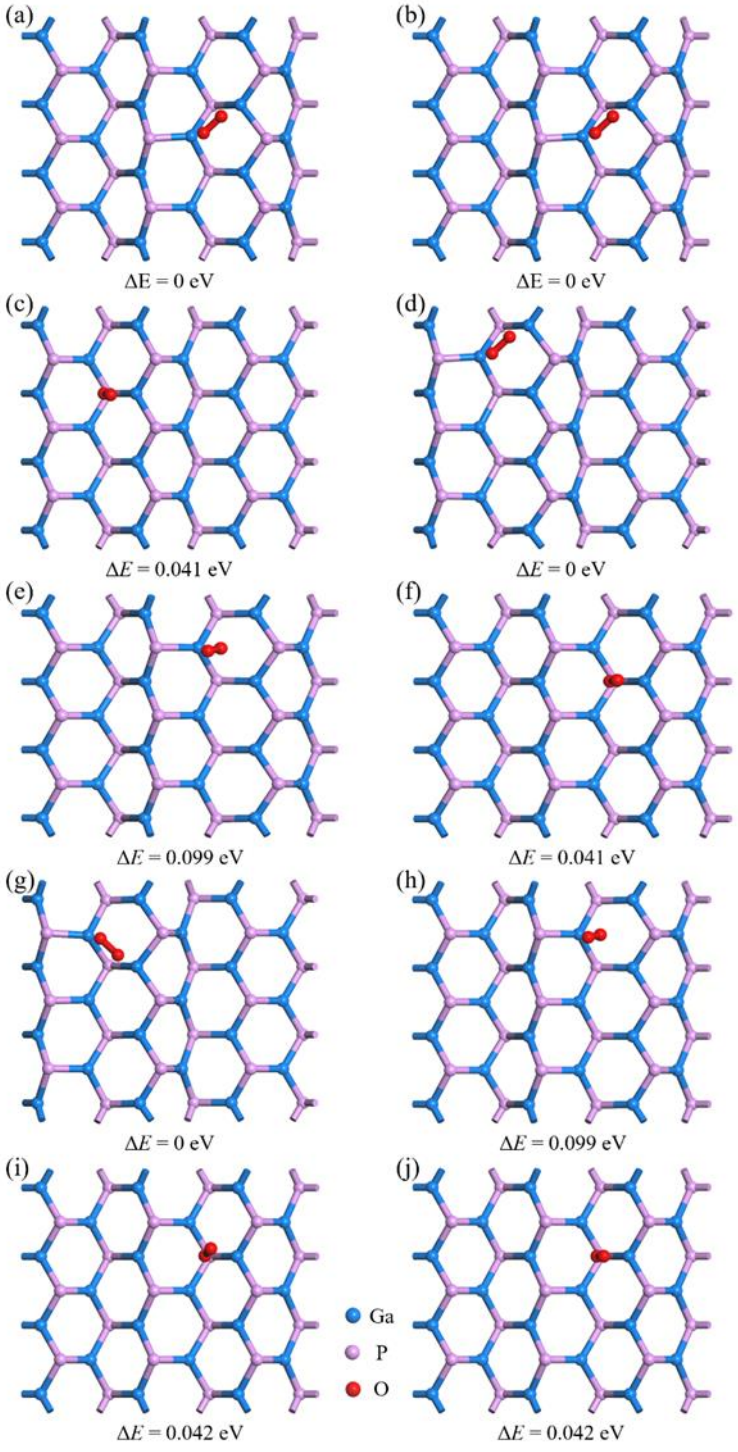

Fig. S6 Equilibrium structures of an oxygen molecule initially adsorbed on the (a) H1, (b) H2, (c) T1, (d) T2, (e) T3, (f) T4, (g) B1, (h) B2, (i) B3, and (j) B4 sites of the GaP monolayer. H, T1 (3), T2 (4) and B stand for hollow, top of Ga atom, top of P atom, and bridge, respectively.

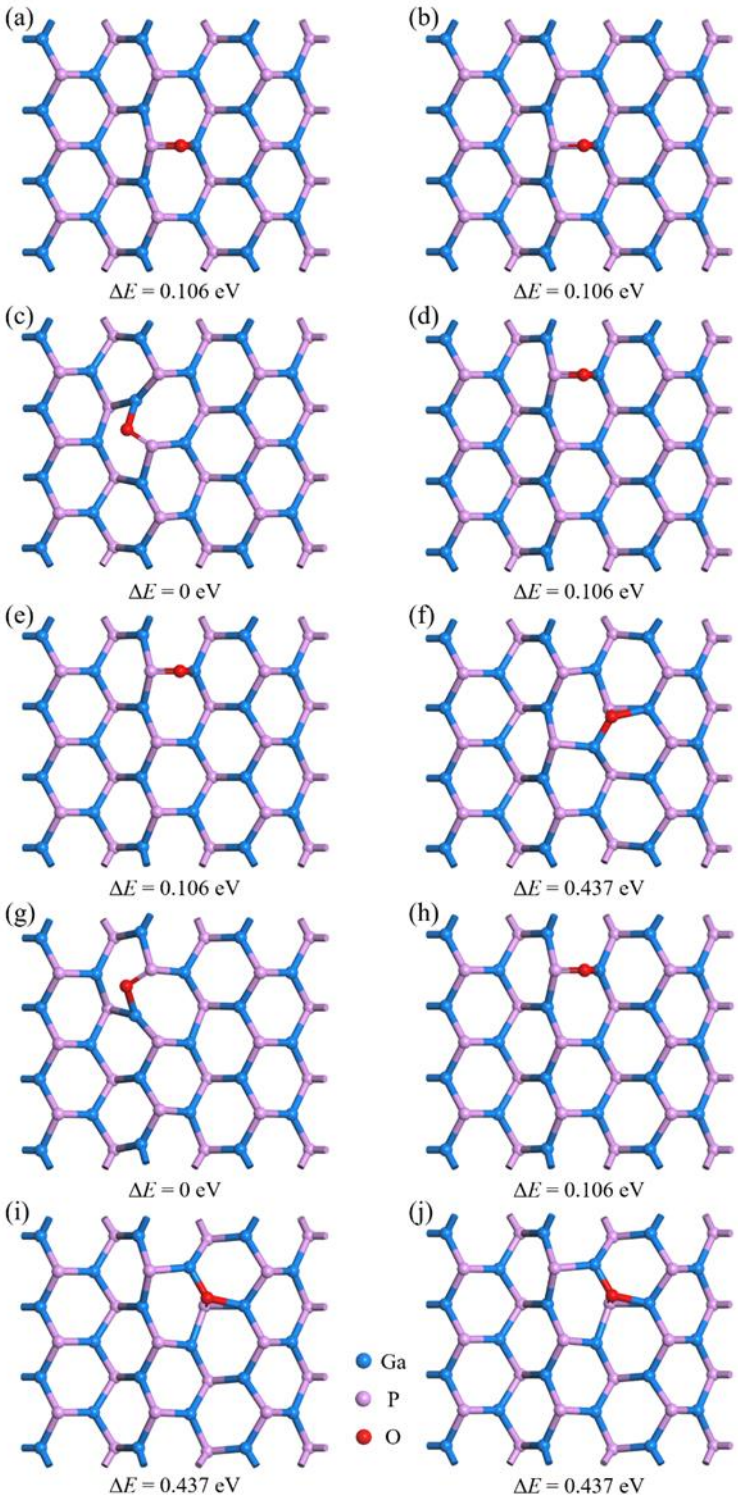

Fig. S7 Equilibrium structures of an oxygen atom initially adsorbed on the (a) H1, (b) H2, (c) T1, (d) T2, (e) T3, (f) T4, (g) B1, (h) B2, (i) B3, and (j) B4 sites of the GaP monolayer. H, T1 (3), T2 (4) and B stand for hollow, top of Ga atom, top of P atom, and bridge, respectively.

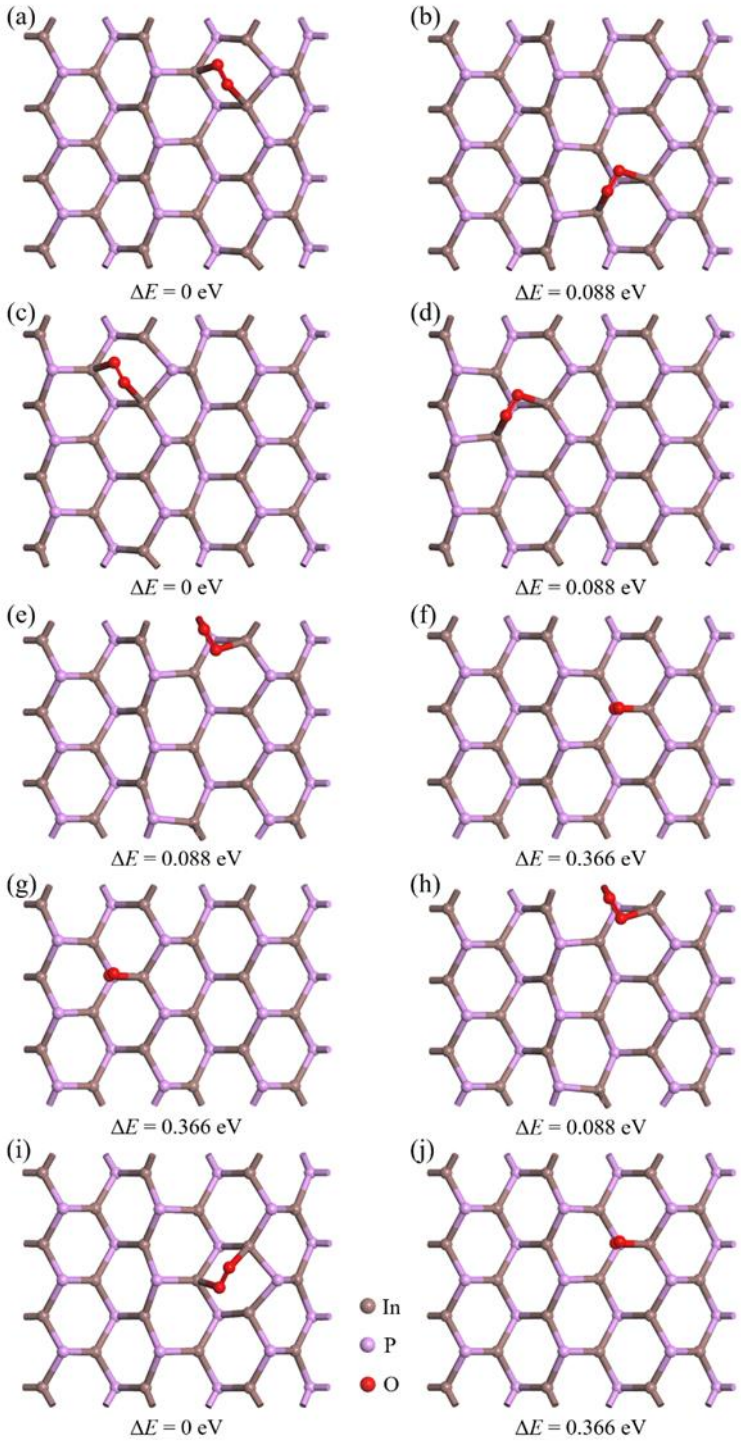

Fig. S8 Equilibrium structures of an oxygen molecule initially adsorbed on the (a) H1, (b) H2, (c) T1, (d) T2, (e) T3, (f) T4, (g) B1, (h) B2, (i) B3, and (j) B4 sites of the InP monolayer. H, T1 (3), T2 (4) and B stand for hollow, top of In atom, top of P atom, and bridge, respectively.

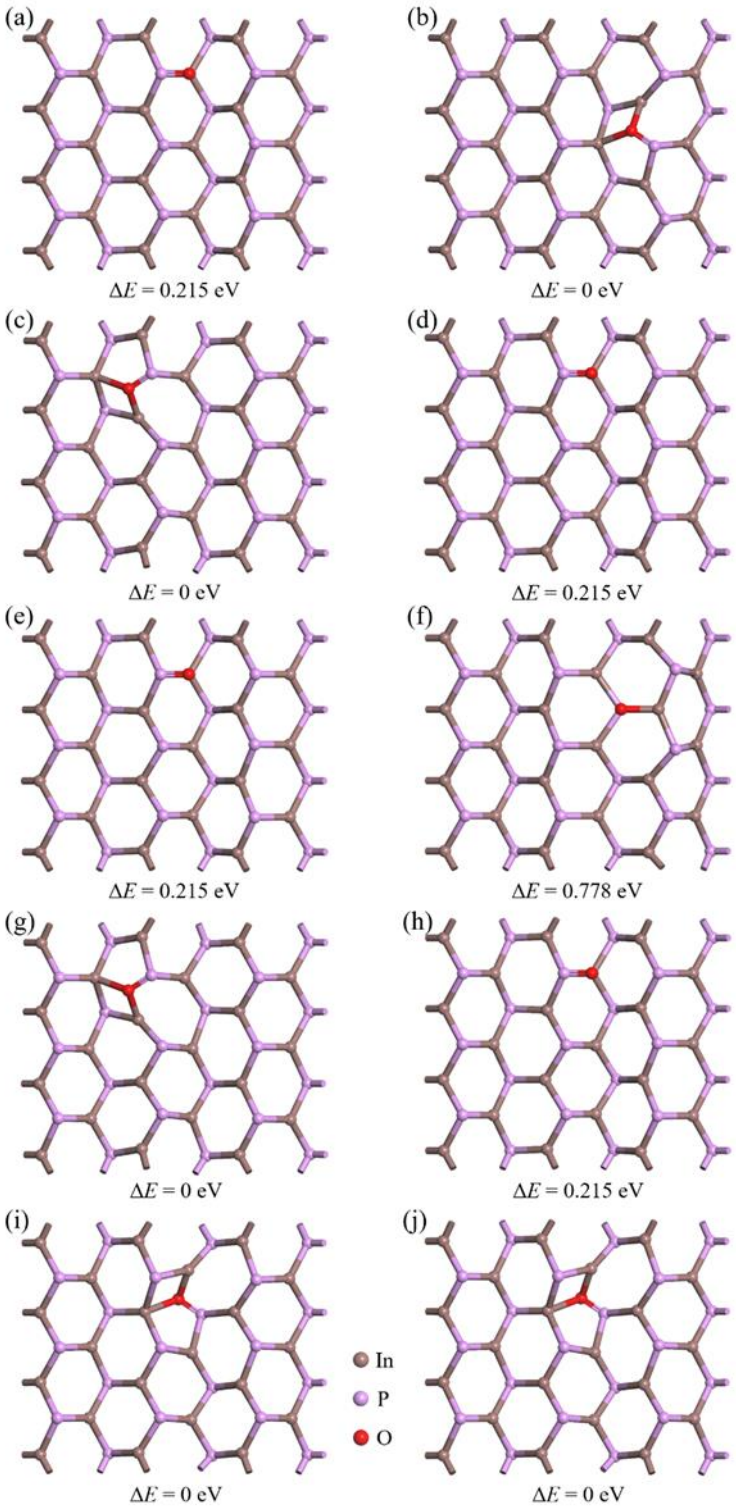

Fig. S9 Equilibrium structures of an oxygen atom initially adsorbed on the (a) H1, (b) H2, (c) T1, (d) T2, (e) T3, (f) T4, (g) B1, (h) B2, (i) B3, and (j) B4 sites of the InP monolayer. H, T1 (3), T2 (4) and B stand for hollow, top of In atom, top of P atom, and bridge, respectively.

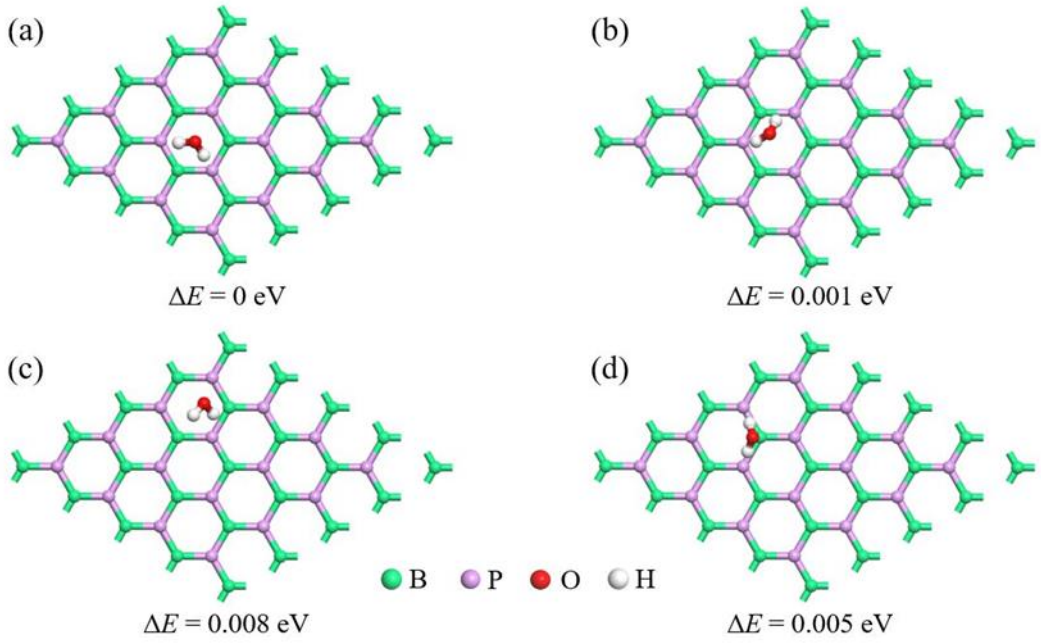

Fig. S10 Equilibrium structures of a water molecule initially adsorbed on the (a) H, (b) T1, (c) T2, and (d) B sites of the BP monolayer. H, T1, T2 and B stand for hollow, top of B atom, top of P atom, and bridge, respectively. The values of Δ*E* are the energy differences relative to the most stable structure.

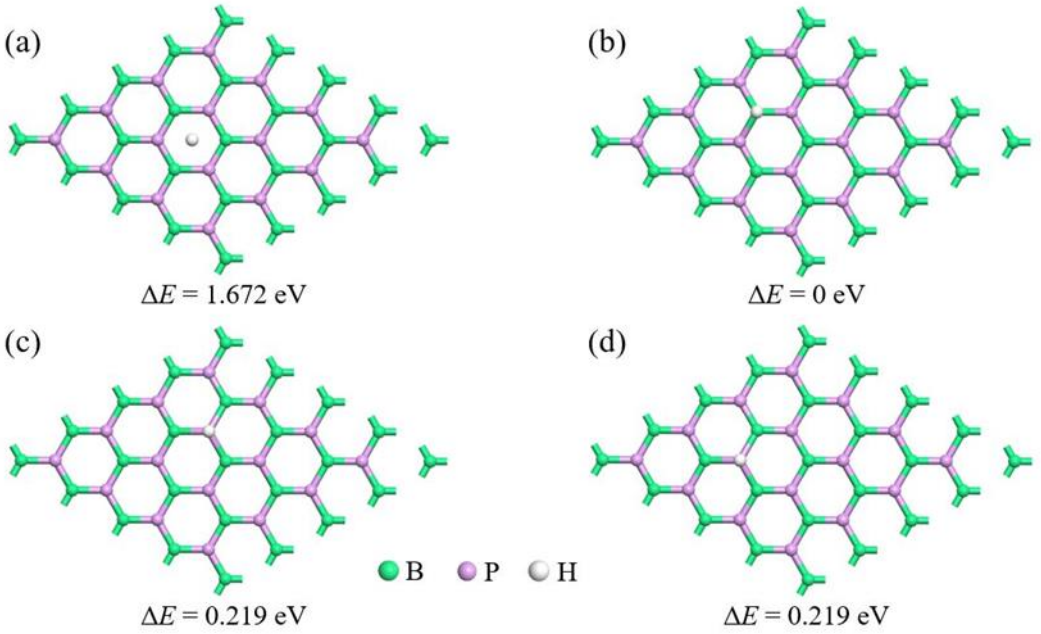

Fig. S11 Equilibrium structures of a hydrogen atom adsorbed on the (a) H, (b) T1, (c) T2, and (d) B sites of the BP monolayer. H, T1, T2 and B stand for hollow, top of B atom, top of P atom, and bridge, respectively.

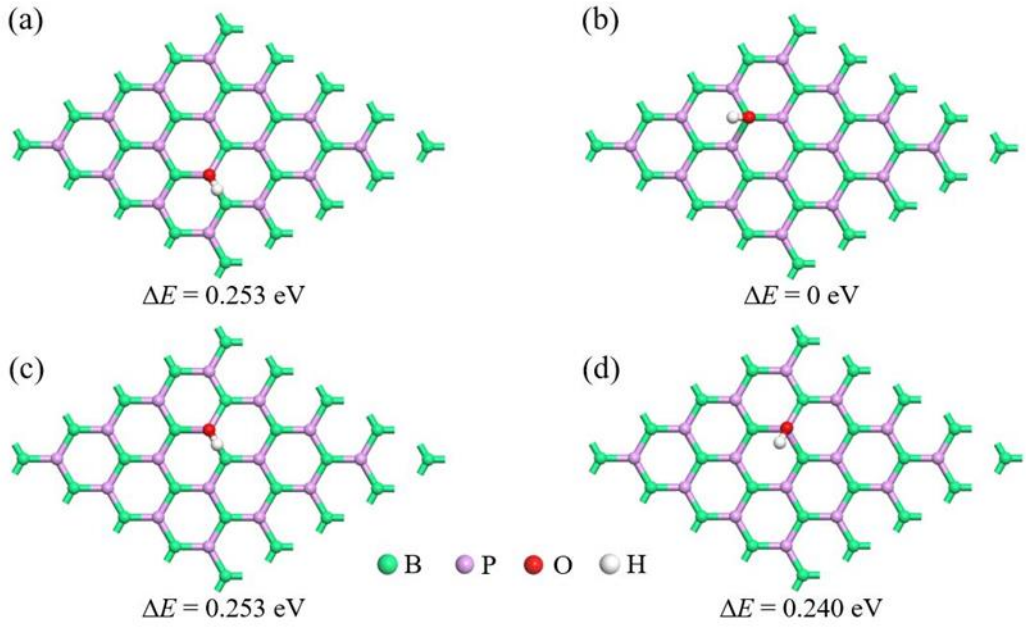

Fig. S12 Equilibrium structures of an OH group initially adsorbed on the (a) H, (b) T1, (c) T2, and (d) B sites of the BP monolayer. H, T1, T2 and B stand for hollow, top of B atom, top of P atom, and bridge, respectively.

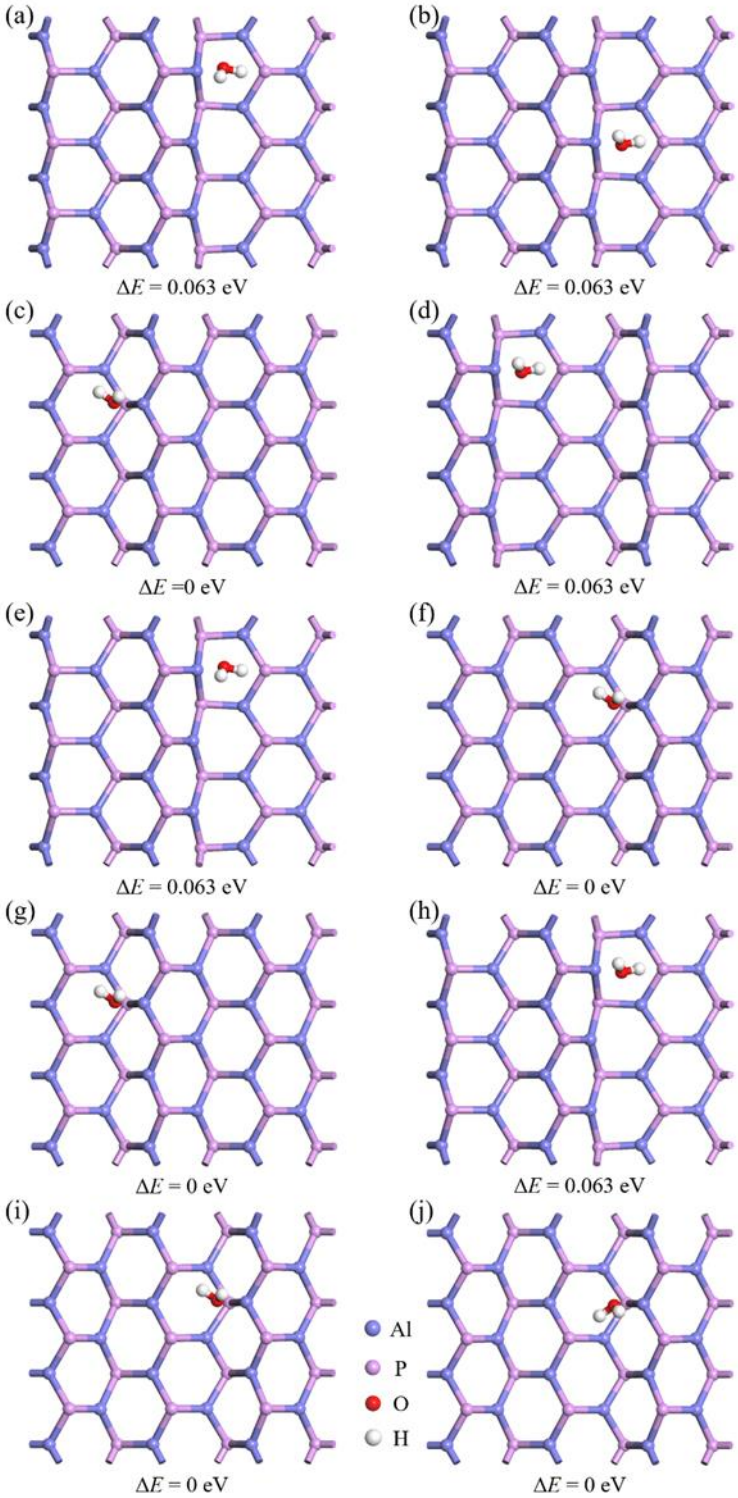

Fig. S13 Equilibrium structures of a water molecule initially adsorbed on the (a) H1, (b) H2, (c) T1, (d) T2, (e) T3, (f) T4, (g) B1, (h) B2, (i) B3, and (j) B4 sites of the AlP monolayer. H, T1 (3), T2 (4) and B stand for hollow, top of Al atom, top of P atom, and bridge, respectively.

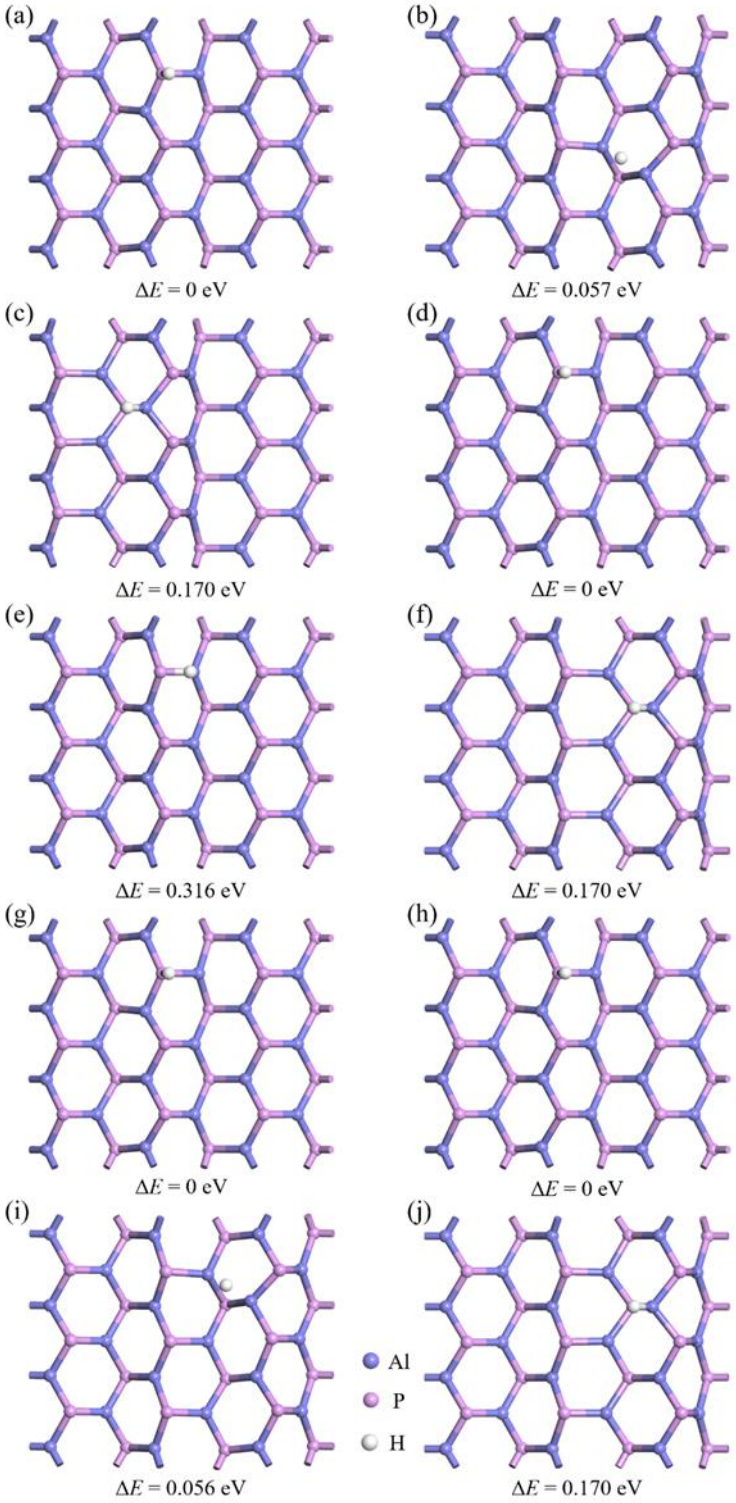

Fig. S14 Equilibrium structures of a hydrogen atom initially adsorbed on the (a) H1, (b) H2, (c) T1, (d) T2, (e) T3, (f) T4, (g) B1, (h) B2, (i) B3, and (j) B4 sites of the AlP monolayer. H, T1 (3), T2 (4) and B stand for hollow, top of Al atom, top of P atom, and bridge, respectively.

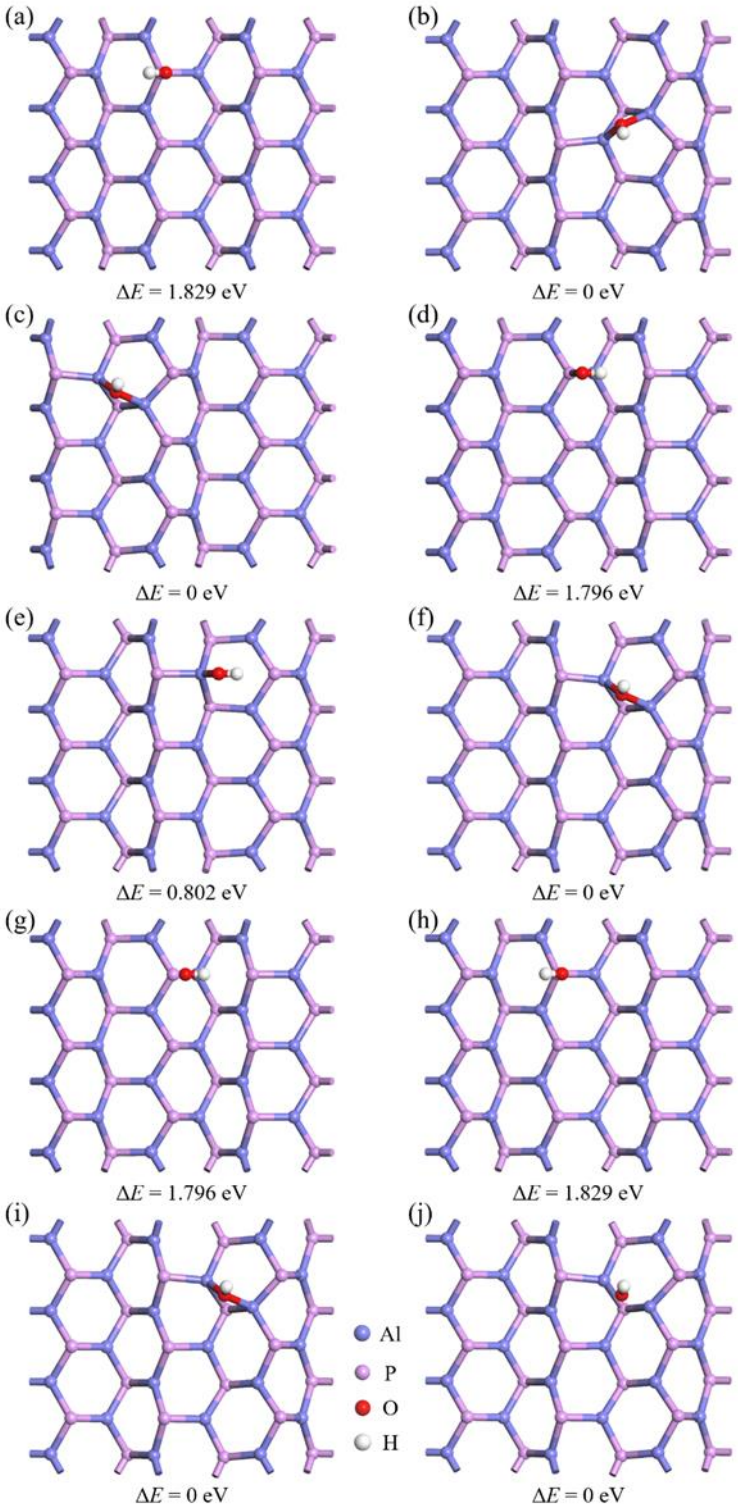

Fig. S15 Equilibrium structures of an OH group initially adsorbed on the (a) H1, (b) H2, (c) T1, (d) T2, (e) T3, (f) T4, (g) B1, (h) B2, (i) B3, and (j) B4 sites of the AlP monolayer. H, T1 (3), T2 (4) and B stand for hollow, top of Al atom, top of P atom, and bridge, respectively.

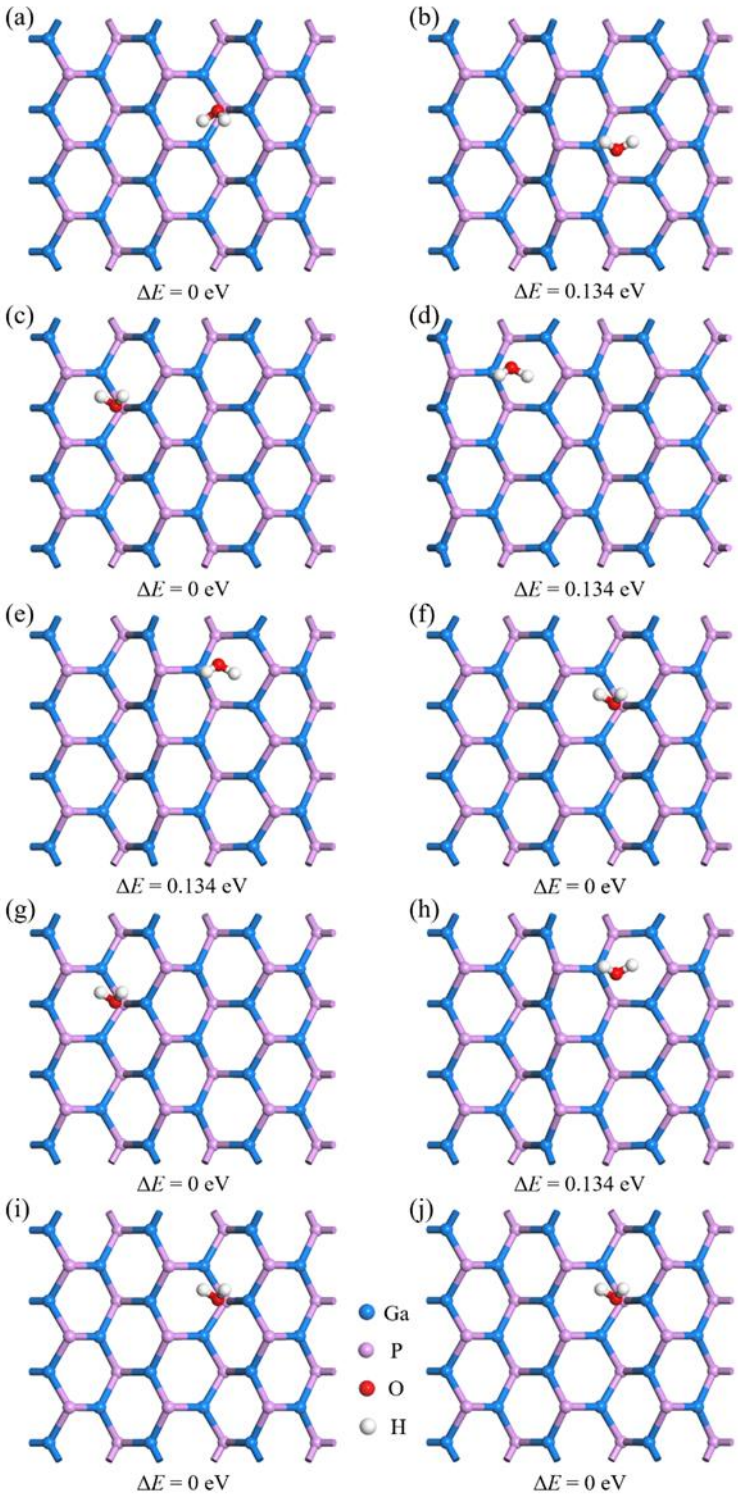

Fig. S16 Equilibrium structures of a water molecule initially adsorbed on the (a) H1, (b) H2, (c) T1, (d) T2, (e) T3, (f) T4, (g) B1, (h) B2, (i) B3, and (j) B4 sites of the GaP monolayer. H, T1 (3), T2 (4) and B stand for hollow, top of Ga atom, top of P atom, and bridge, respectively.

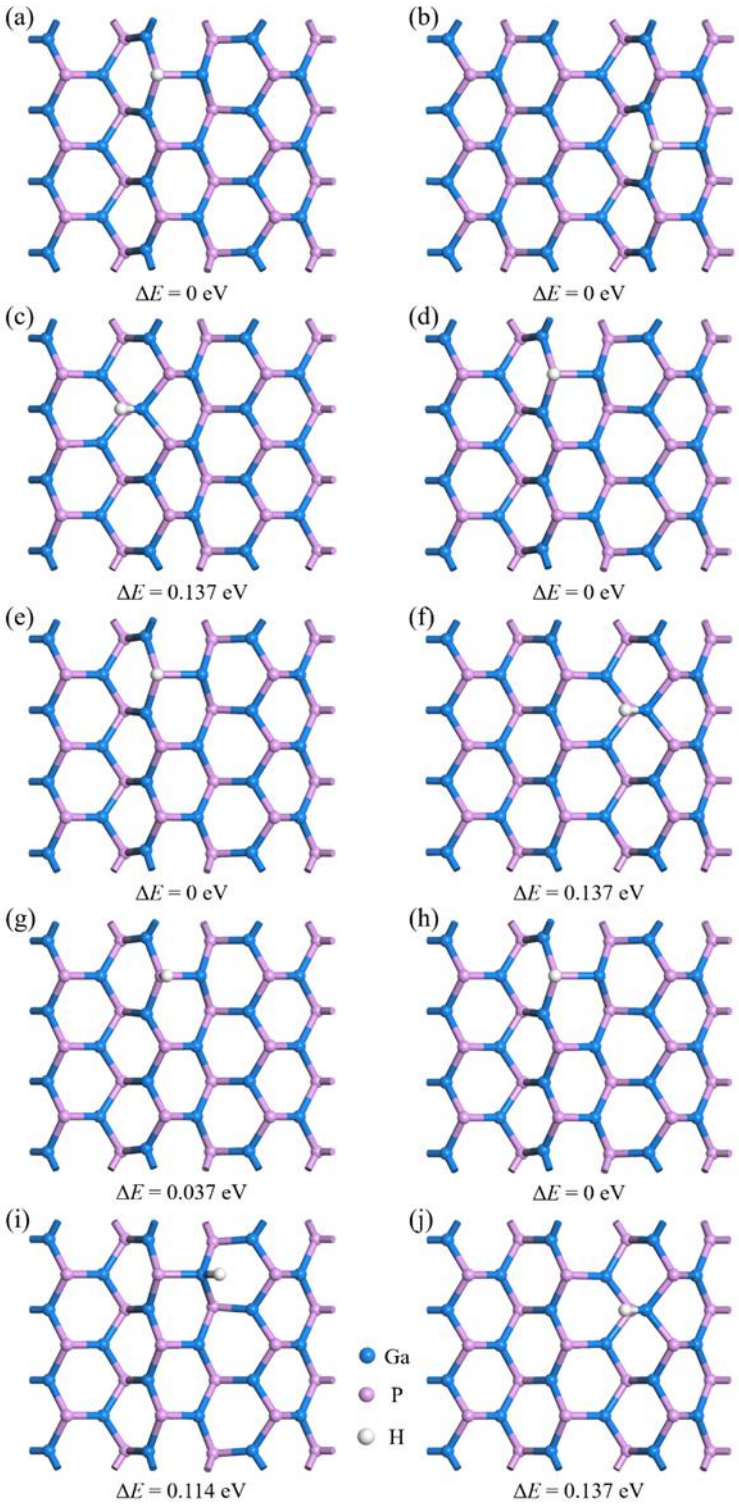

Fig. S17 Equilibrium structures of a hydrogen atom initially adsorbed on the (a) H1, (b) H2, (c) T1, (d) T2, (e) T3, (f) T4, (g) B1, (h) B2, (i) B3, and (j) B4 sites of the GaP monolayer. H, T1 (3), T2 (4) and B stand for hollow, top of Ga atom, top of P atom, and bridge, respectively.

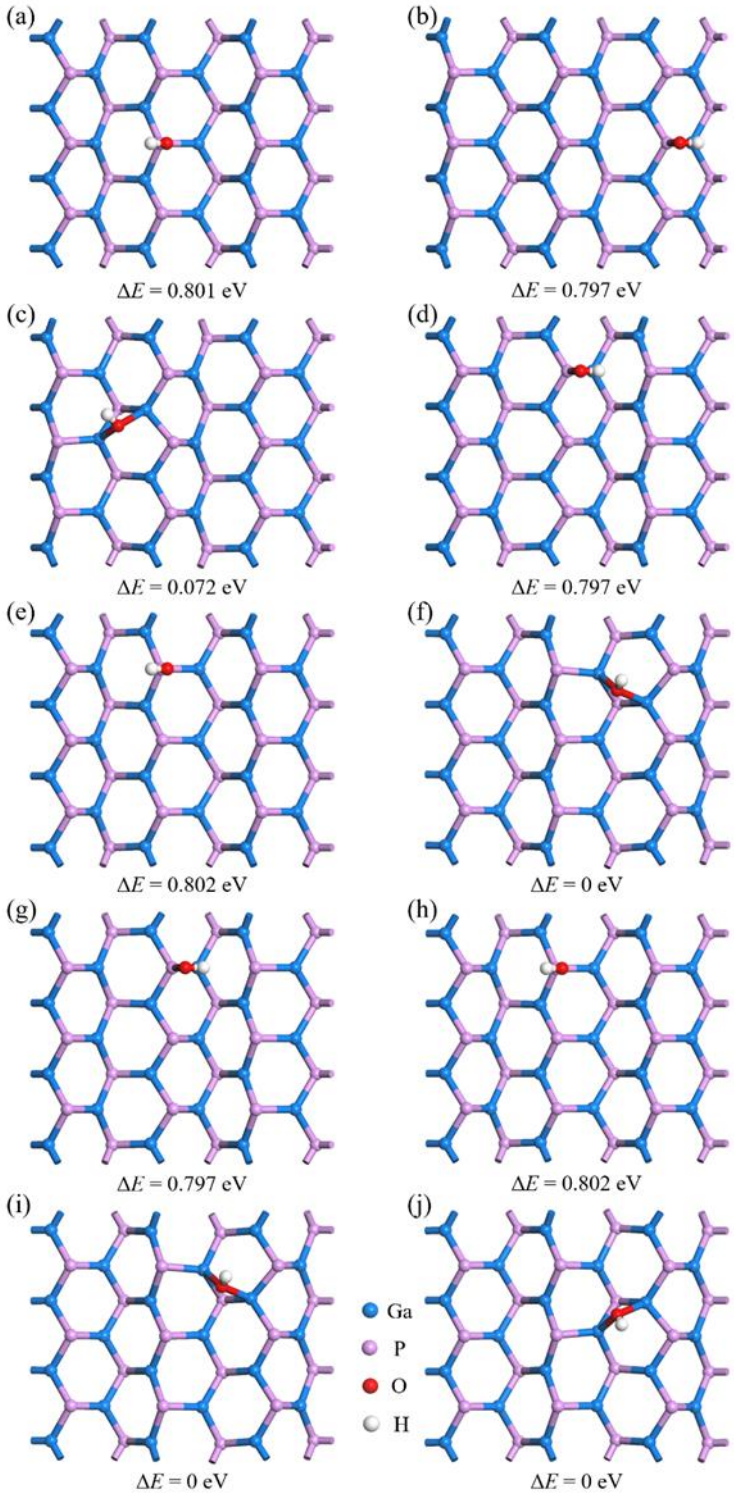

Fig. S18 Equilibrium structures of an OH group initially adsorbed on the (a) H1, (b) H2, (c) T1, (d) T2, (e) T3, (f) T4, (g) B1, (h) B2, (i) B3, and (j) B4 sites of the GaP monolayer. H, T1 (3), T2 (4) and B stand for hollow, top of Ga atom, top of P atom, and bridge, respectively.

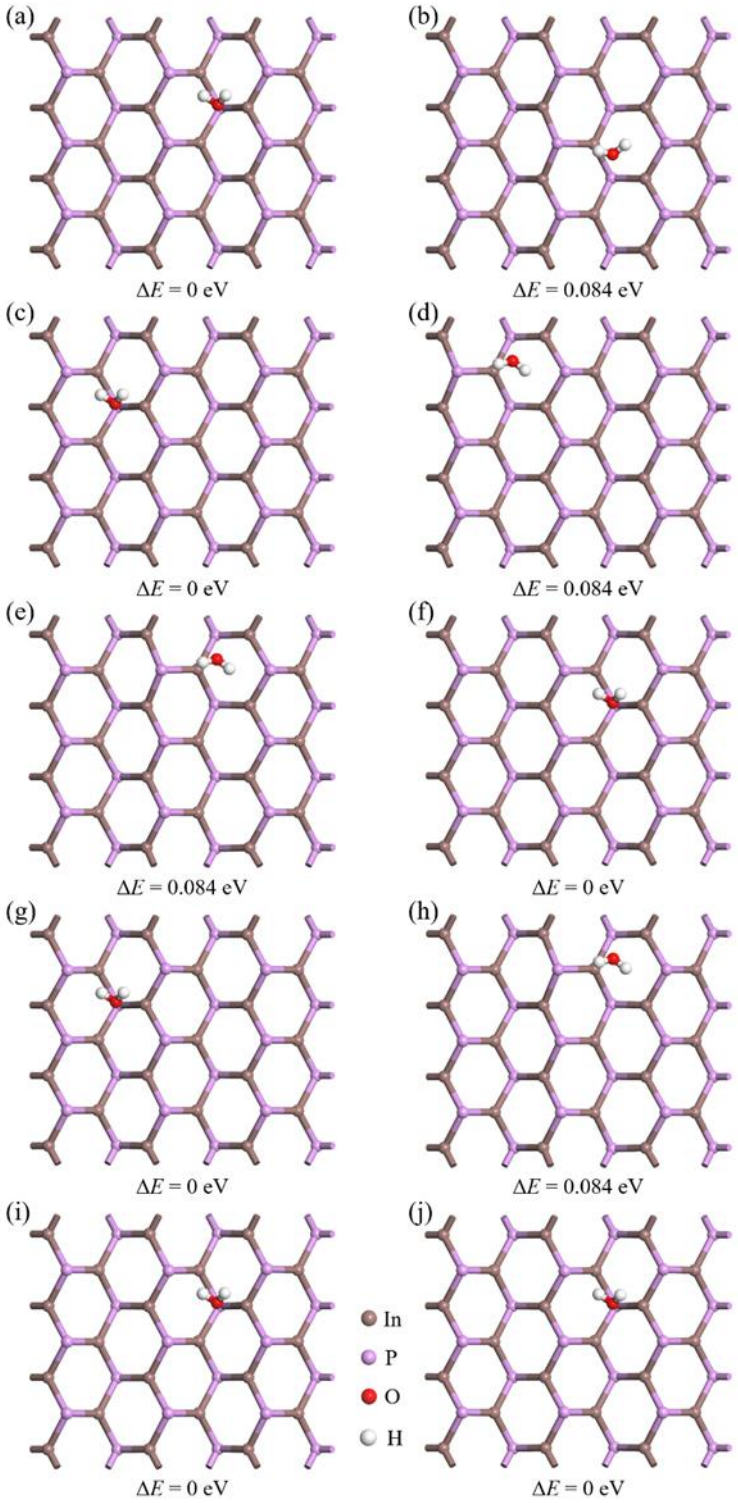

Fig. S19 Equilibrium structures of a water molecule initially adsorbed on the (a) H1, (b) H2, (c) T1, (d) T2, (e) T3, (f) T4, (g) B1, (h) B2, (i) B3, and (j) B4 sites of the InP monolayer. H, T1 (3), T2 (4) and B stand for hollow, top of In atom, top of P atom, and bridge, respectively.

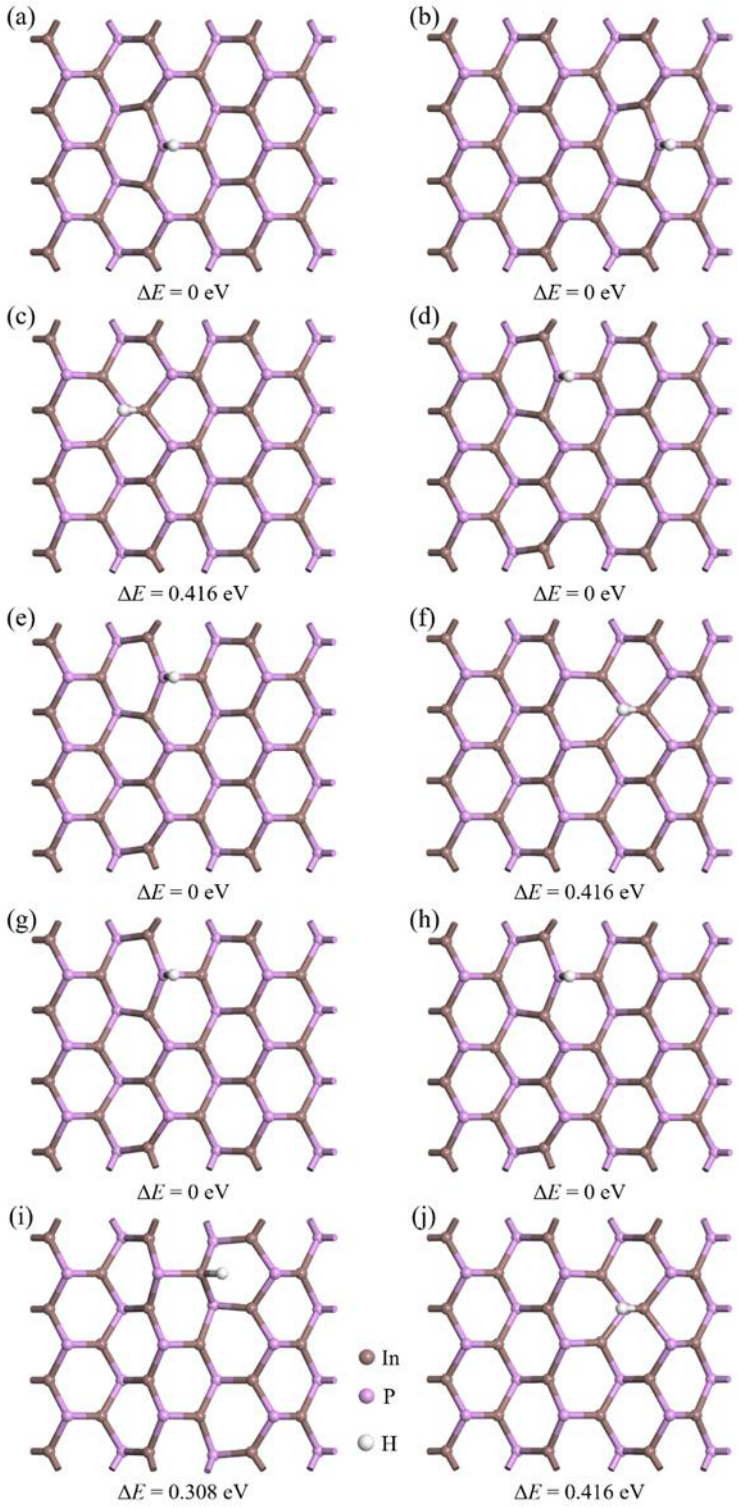

Fig. S20 Equilibrium structures of a hydrogen atom initially adsorbed on the (a) H1, (b) H2, (c) T1, (d) T2, (e) T3, (f) T4, (g) B1, (h) B2, (i) B3, and (j) B4 sites of the InP monolayer. H, T1 (3), T2 (4) and B stand for hollow, top of In atom, top of P atom, and bridge, respectively.

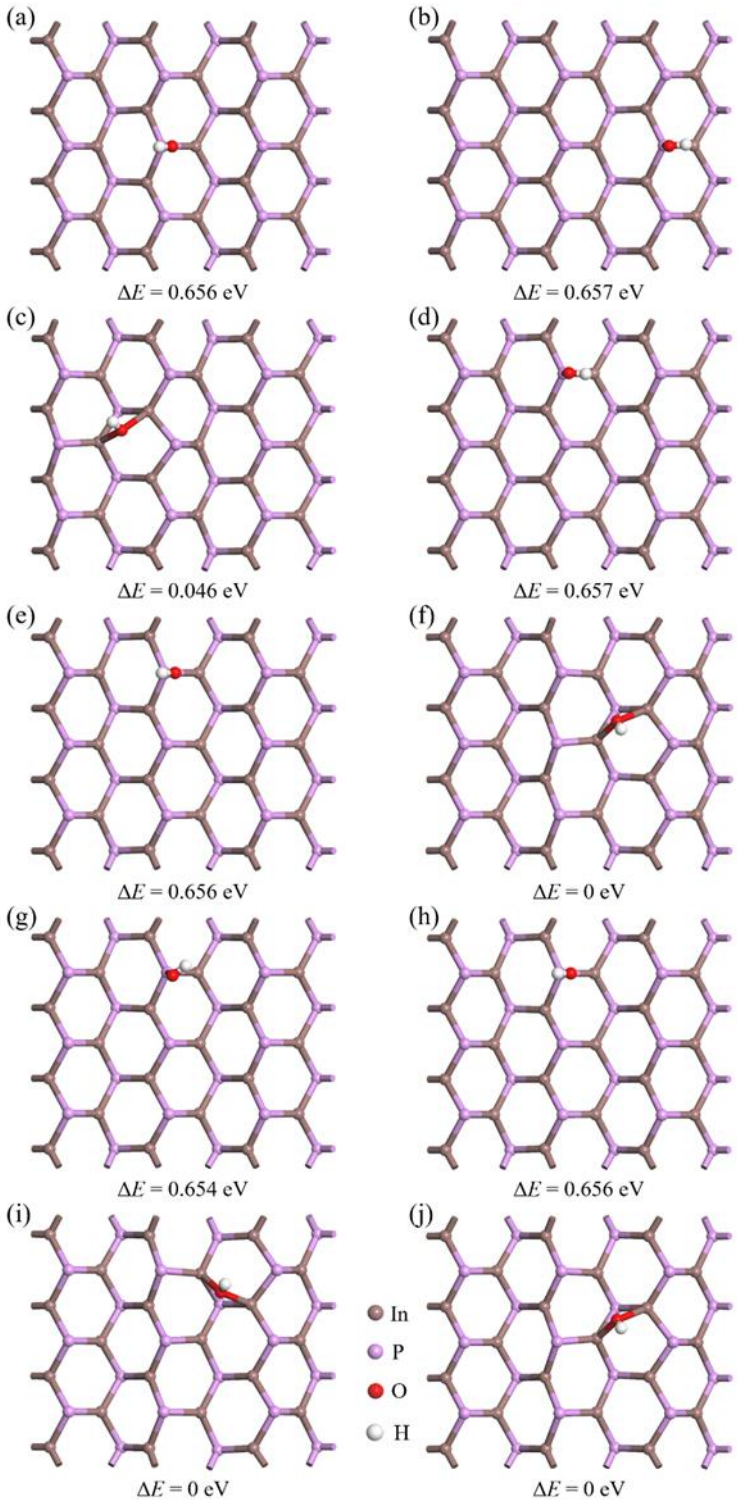

Fig. S21 Equilibrium structures of an OH group initially adsorbed on the (a) H1, (b) H2, (c) T1, (d) T2, (e) T3, (f) T4, (g) B1, (h) B2, (i) B3, and (j) B4 sites of the InP monolayer. H, T1 (3), T2 (4) and B stand for hollow, top of In atom, top of P atom, and bridge, respectively.

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