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Theoretical insights into H_2O adsorption on $CuAlO_2(11\bar{2}0)$ surface: from low to high coverage

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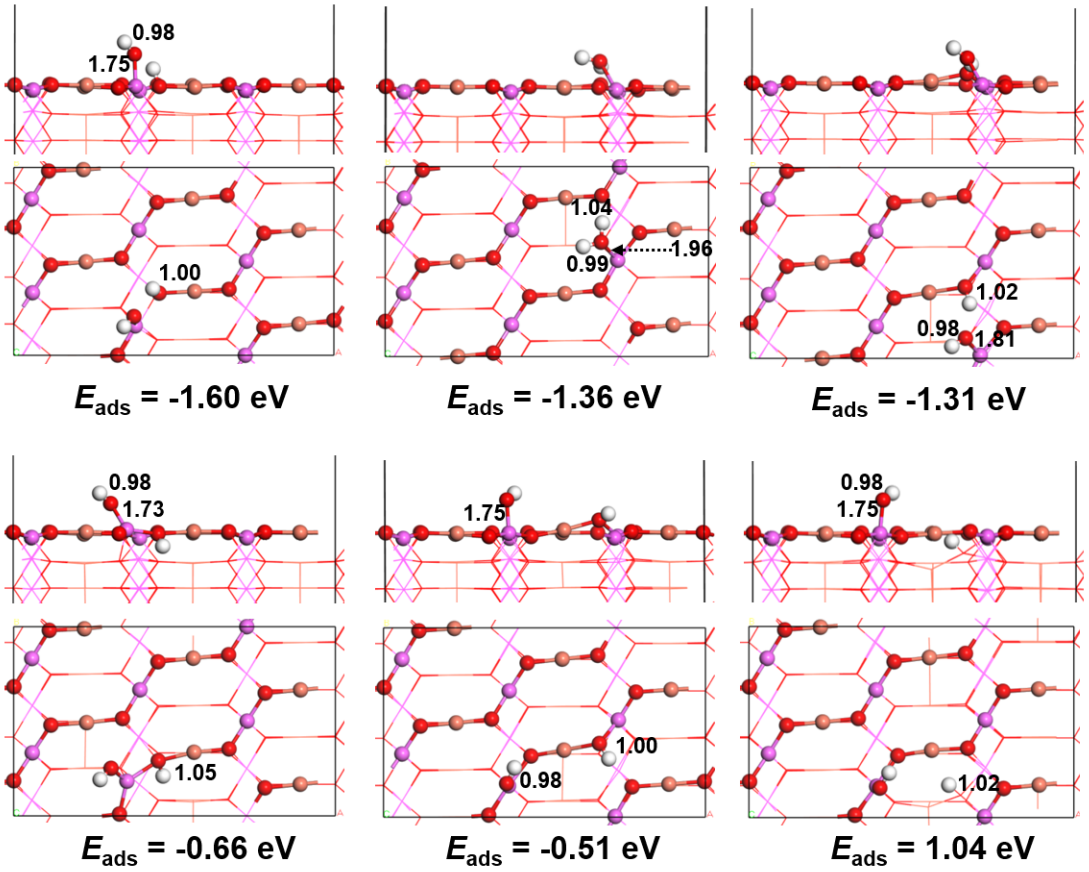

Figure S1. The stable configurations of H_2O adsorption on the perfect $CuAlO_2(11\bar{2}0)$ surface after relaxation. H, O, Al, and Cu atoms are in white, red, pink, and copper, respectively. The adsorption energies (E_{ads}, in eV) are below the corresponding geometries.

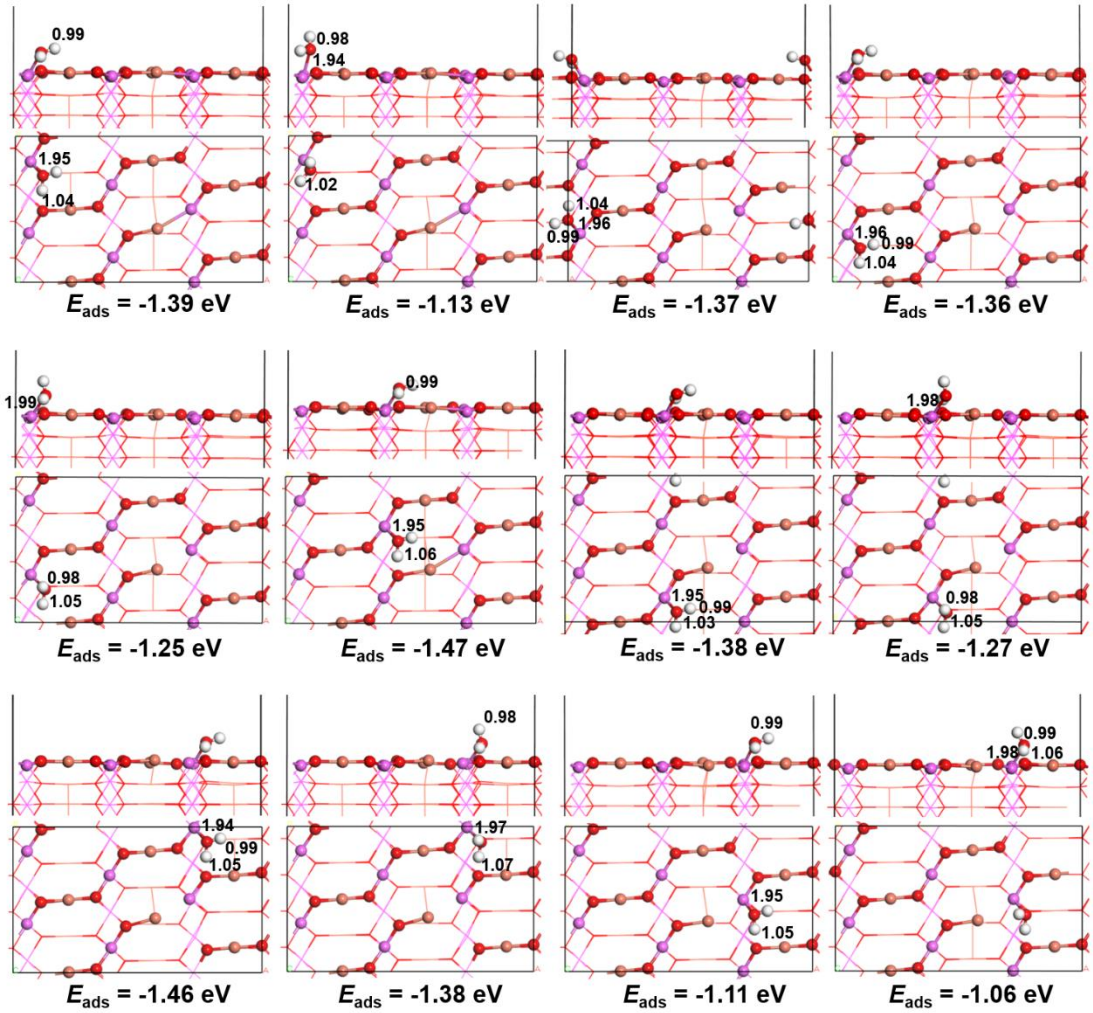

Figure S2. The stable configurations of molecular H_2O adsorption on the $CuAlO_2(11\bar{2}0)$-O_v surface after relaxation. The adsorption energies (E_{ads}, in eV) are below the corresponding geometries.

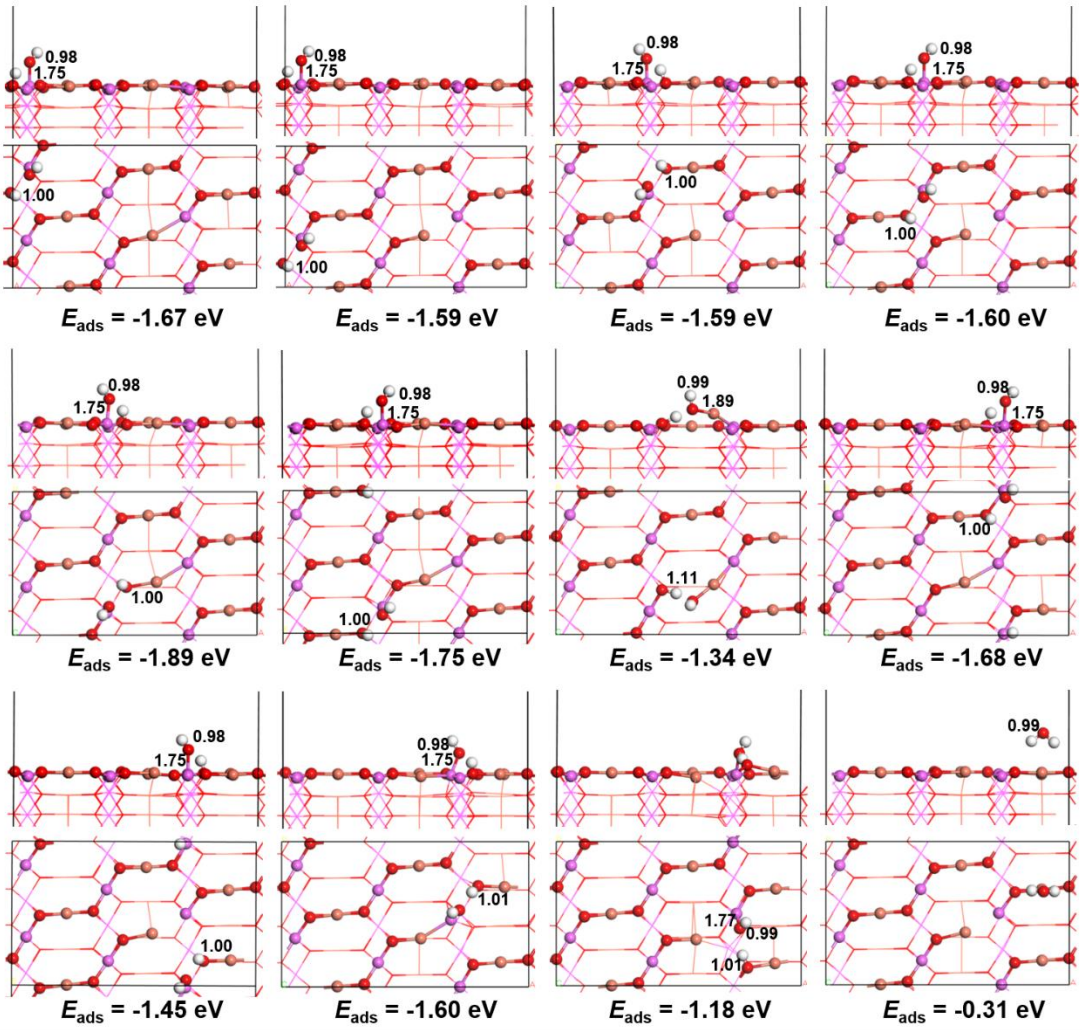

Figure S3. The stable configurations of dissociative and physisorbed H_2O on the $CuAlO_2(11\bar{2}0)$-O_v surface after relaxation. The adsorption energies (E_{ads}, in eV) are below the corresponding geometries.

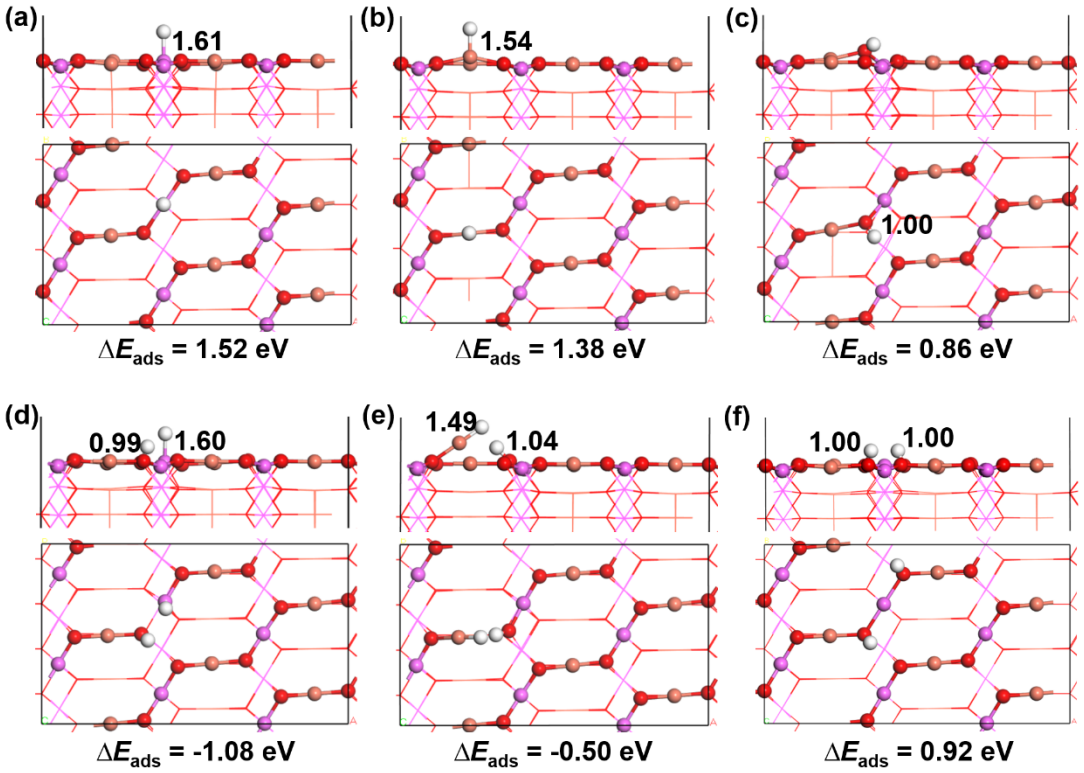

Figure S4. The stable configurations of single H atom and two H atoms adsorptions on the (a) Al site, (b) Cu site, (c) O site, (d) Al-O site, (e) Cu-O site, and (f) O-O site of perfect $CuAlO_2(11\bar{2}0)$ surface after relaxation, respectively. The stepwise adsorption energies (ΔE_{ads}, in eV) are below the corresponding geometries.

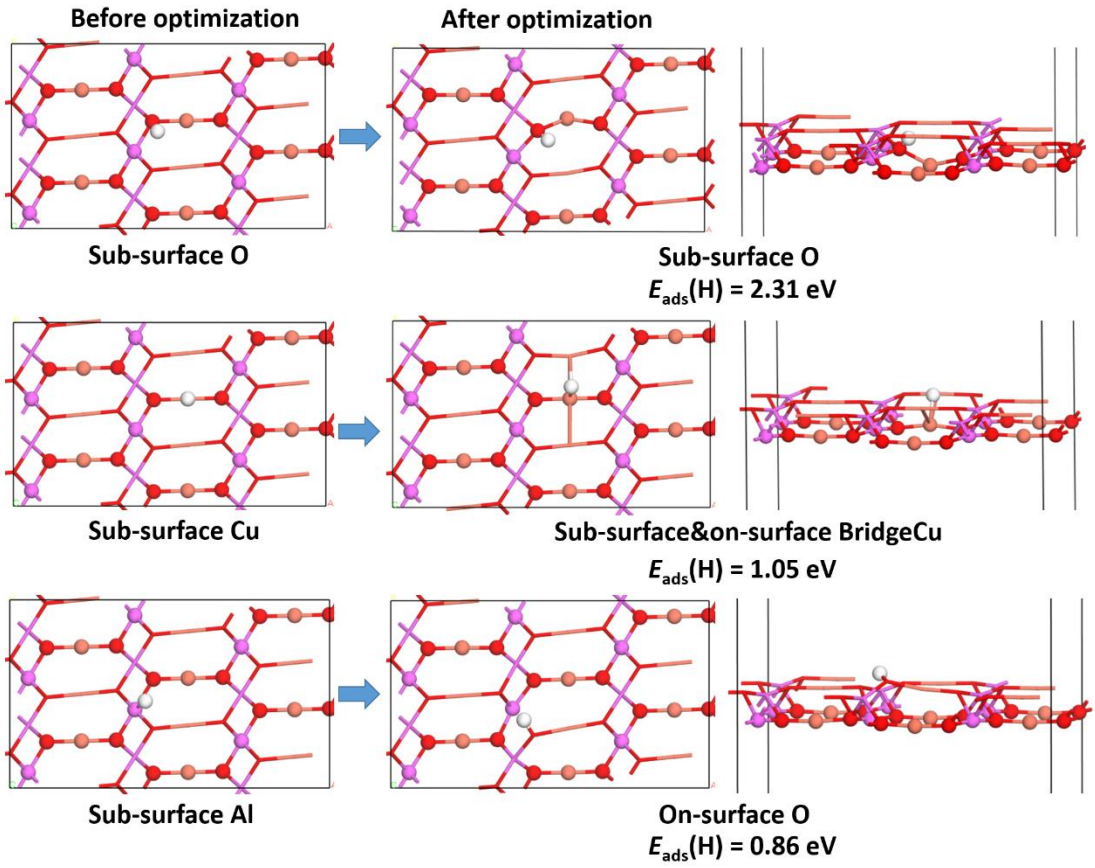

Figure S5. The structure before and after the optimization of H adsorption in the sub-surface layer. The structural diagram only displays the atoms in the on-surface and sub-surface layers. In the model, the on-surface atoms are represented using the stick model, while the sub-surface atoms are displayed using the ball-and-stick model.

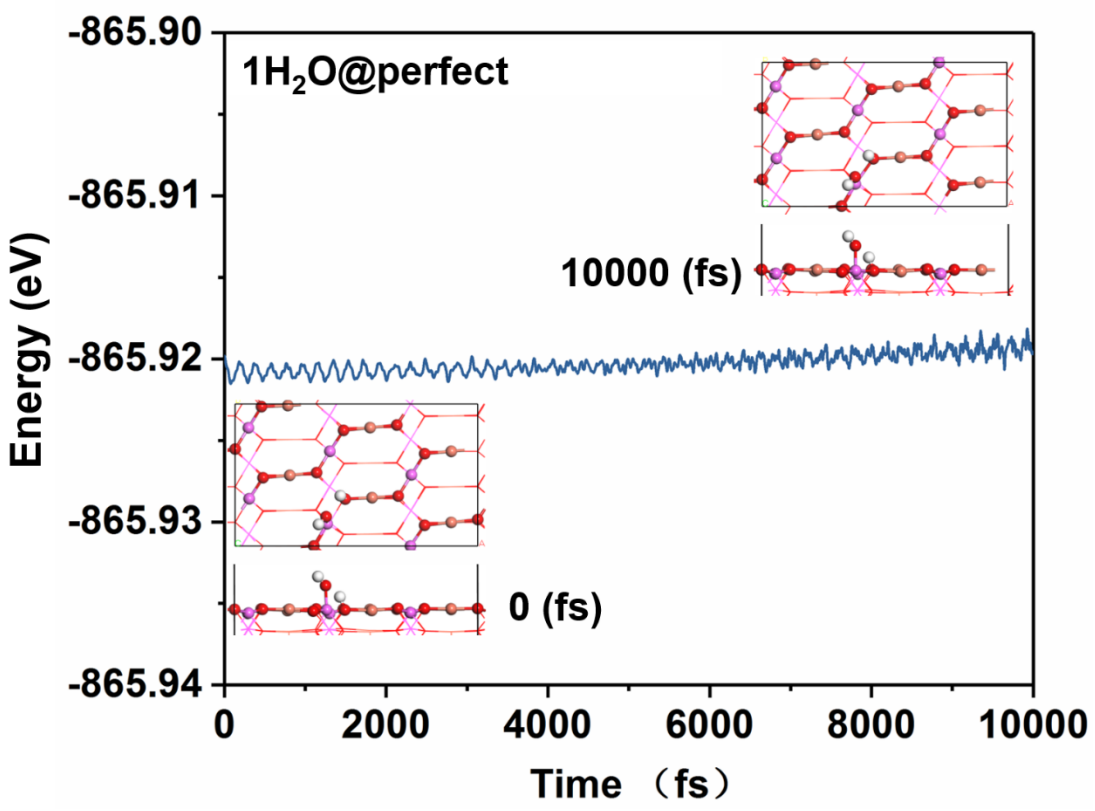

Figure S6. AIMD simulations (NVT ensemble) of single H_2O adsorption on the perfect $CuAlO_2(11\bar{2}0)$ surface with time scale of 10 ps at 298 K.

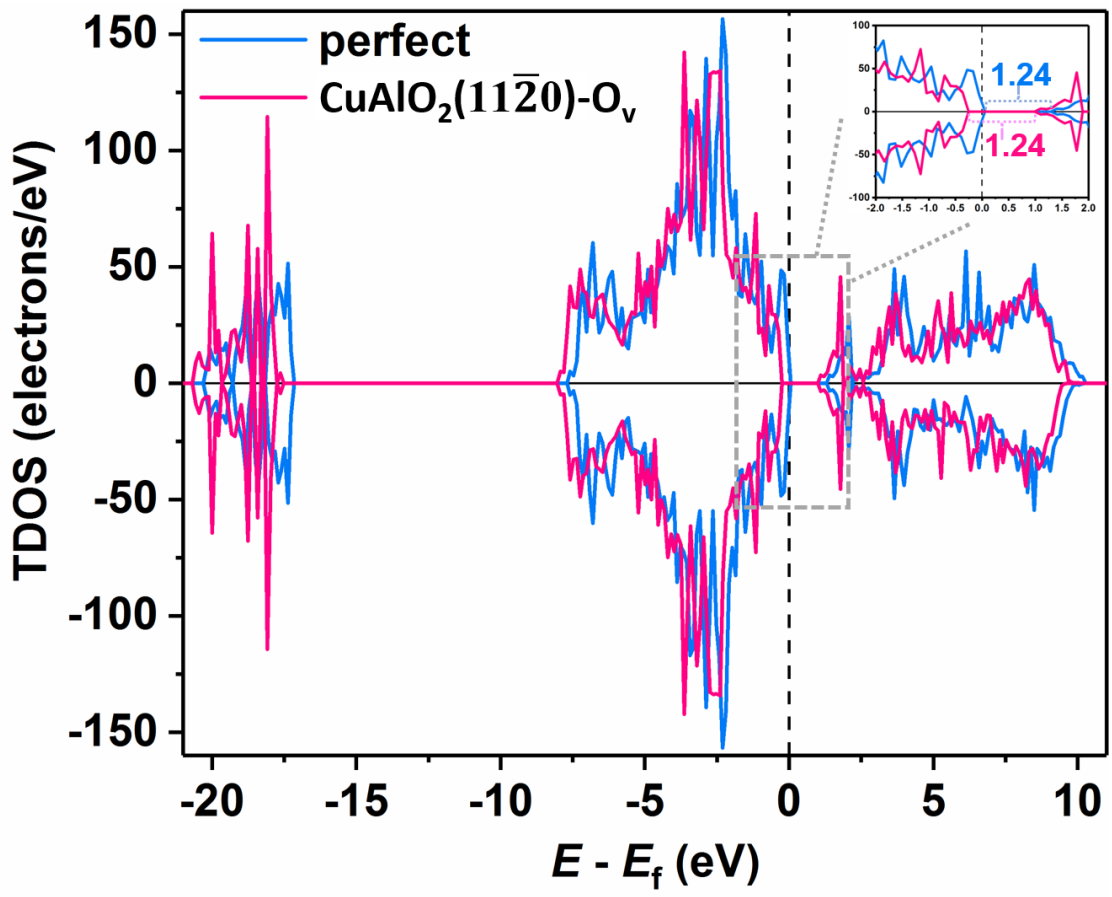

Figure S7. The TDOS of the perfect and $CuAlO_2(11\bar{2}0)$-O_v surfaces.

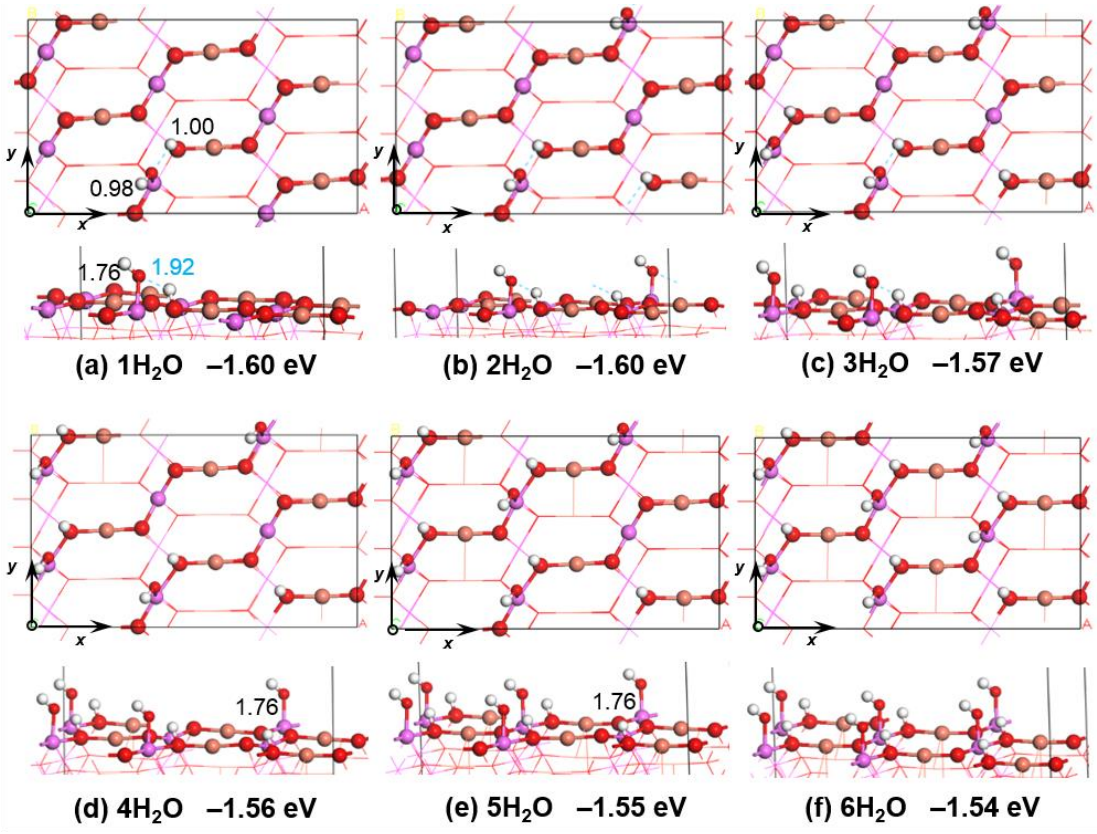

Figure S8. The first layer of nH$_2$O (n = 1-6) adsorbed on the perfect CuAlO$_2$(11$\bar{2}$0) surface. The bond distance and average adsorption energy are in Å and eV, respectively.

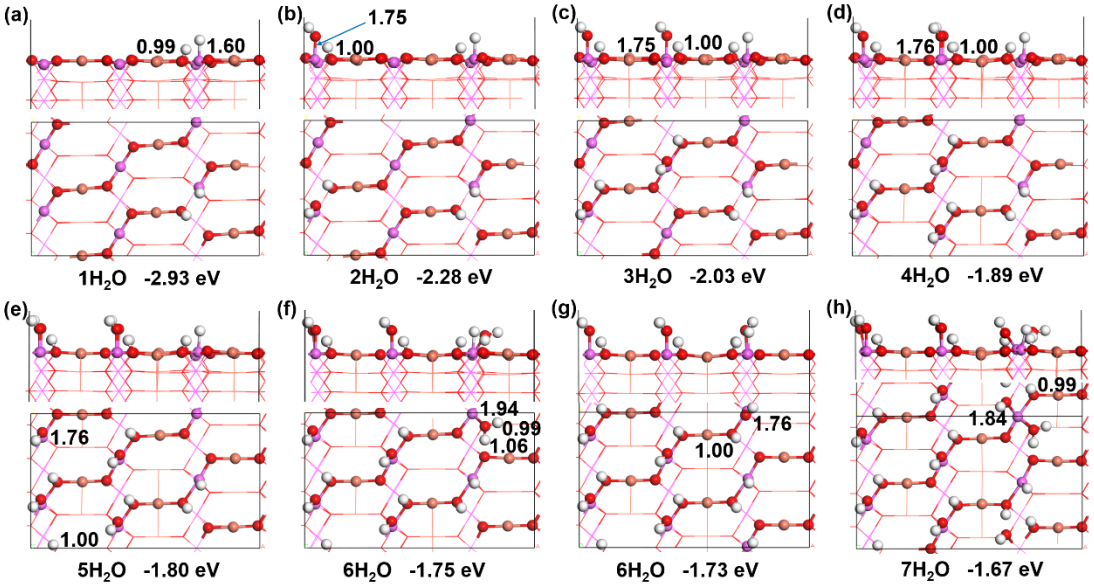

Figure S9. The stable adsorption configurations of nH$_2$O (n = 1-7) on CuAlO$_2$(11$\bar{2}$0)-O$_v$ surface. The bond distance and average adsorption energy are in Å and eV, respectively.

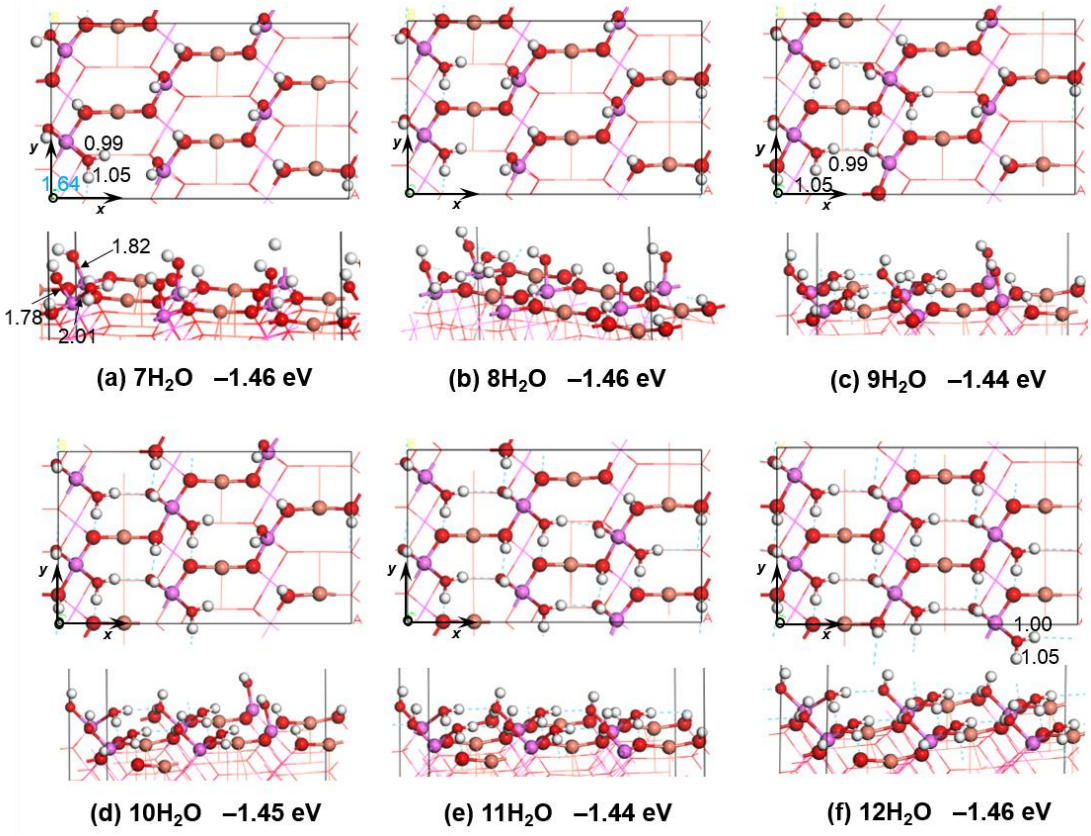

Figure S10. The second layer adsorption of nH$_2$O (n = 7-12) on the perfect CuAlO$_2$(11$\bar{2}$0) surface. The bond distance and average adsorption energy are in Å and eV, respectively.

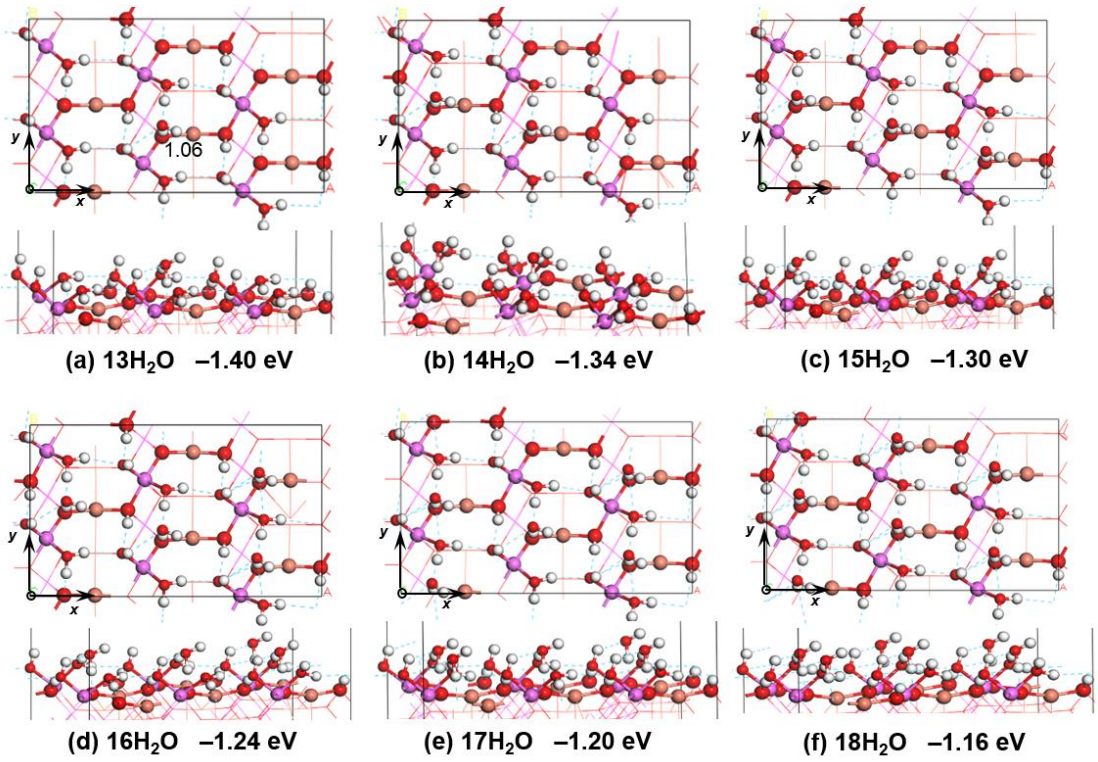

Figure S11. The third layer adsorption of nH$_2$O (n = 13-18) on the perfect CuAlO$_2$(11$\bar{2}$0) surface. The bond distance and average adsorption energy are in Å and eV, respectively.

Table S1. The adsorption energies for H_2O dissociative adsorption on (1×1), (1×2), (1×3), and (2×2) $CuAlO_2(11\bar{2}0)$ surface slab with six layers, respectively.

	(1×1)	(1×2)	(1×3)	(2×2)
$E_{ads}(H_2O)$ (eV)	-1.59	-1.60	-1.61	-1.61

Table S2. The variation of electron energy (per atom) of (1×2) $CuAlO_2(11\bar{2}0)$ surface slab with different relaxation layers (a total of 6 layers). ΔE(slab) = Eslab^n – Eslab^{n-1} (n, the number of relaxed layers). ΔE (per atom) = ΔE(slab) / 144.

n	ΔE(slab) (eV)	ΔE (per atom) (meV)
1	-3.93	-27.3
2	-1.04	-7.2
3	-0.14	-1.0
4	-0.10	-0.7

Table S3. The stepwise adsorption energies (ΔE(H)) of H and the total adsorption energies (eV) ($E_{ads}(H_2)$ and $E_{ads}(H_2O)$) of H_2 and H_2O adsorption on the perfect and $CuAlO_2(11\bar{2}0)$-O_v surfaces.

	ΔE(H)	$E_{ads}(H_2)$	$E_{ads}(H_2O)$
Al-O site	-1.74	-0.22	-2.93
Cu-O site	-1.05	0.33	-2.38
O-O site	-0.50	0.35	-0.94

Table S4. The stepwise ($\Delta E(H_2O)$) and average (E_{H2O}^{ave}) adsorption energies (eV) of $n$$H_2O$ (n = 1-18) adsorption on the perfect $CuAlO_2(11\bar{2}0)$ surface.

$n$$H_2O$	$\Delta E(H_2O)$	E_{H2O}^{ave}	$n$$H_2O$	$\Delta E(H_2O)$	E_{H2O}^{ave}
$1H_2O$	-1.60	-1.60	$10H_2O$	-1.50	-1.45
$2H_2O$	-1.60	-1.60	$11H_2O$	-1.40	-1.44
$3H_2O$	-1.52	-1.57	$12H_2O$	-1.71	-1.46
$4H_2O$	-1.53	-1.56	$13H_2O$	-0.62	-1.40
$5H_2O$	-1.48	-1.55	$14H_2O$	-0.62	-1.34
$6H_2O$	-1.48	-1.54	$15H_2O$	-0.63	-1.30
$7H_2O$	-0.98	-1.46	$16H_2O$	-0.48	-1.24
$8H_2O$	-1.47	-1.46	$17H_2O$	-0.47	-1.20
$9H_2O$	-1.29	-1.44	$18H_2O$	-0.50	-1.16

Table S5. The Bader charge $|e|$ of $n$$H_2O$ (n = 0, 6, 12 and 18) adsorption on the perfect $CuAlO_2(11\bar{2}0)$ surface.

system	perfect	$1H_2O$ @perfect	$6H_2O$ @perfect	$12H_2O$ @perfect	$18H_2O$ @perfect
slab total	0.123	0.250	0.693	1.170	1.170
the first layer	0.268	0.369	0.788	1.043	0.998
all H_2O	/	-0.126	-0.564	-1.049	-1.048
average H_2O	/	-0.126	-0.094	-0.087	-0.058
O_s1	-1.453	-1.450	-1.423	-1.398	-1.430
O_s2	-1.453	-1.442	-1.429	-1.398	-1.424
O_s3	-1.442	-1.442	-1.366	-1.396	-1.399
O_s4	-1.442	-1.434	-1.366	-1.397	-1.393
O_s5	-1.448	-1.439	-1.431	-1.393	-1.419
O_s6	-1.448	-1.426	-1.428	-1.393	-1.415
O_s7	-1.440	-1.444	-1.382	-1.393	-1.395
O_s8	-1.440	-1.368	-1.369	-1.393	-1.396
O_s9	-1.449	-1.445	-1.421	-1.388	-1.397
O_s10	-1.449	-1.441	-1.431	-1.388	-1.396
O_s11	-1.439	-1.436	-1.518	-1.396	-1.396
O_s12	-1.439	-1.442	-1.367	-1.397	-1.396
Al1	2.397	2.398	2.442	2.464	2.463
Al2	2.397	2.400	2.439	2.465	2.462
Al3	2.399	2.399	2.440	2.458	2.464
Al4	2.399	2.437	2.440	2.457	2.465
Al5	2.396	2.399	2.438	2.461	2.461
Al6	2.396	2.398	2.439	2.461	2.461
Cu1	0.537	0.500	0.515	0.504	0.514
Cu2	0.537	0.519	0.515	0.501	0.514
Cu3	0.537	0.541	0.513	0.497	0.514
Cu4	0.537	0.514	0.515	0.496	0.513
Cu5	0.538	0.538	0.512	0.504	0.511
Cu6	0.538	0.536	0.514	0.505	0.510
H of O_wH1	/	0.625	0.617	0.623	0.627
H1	/	0.674	0.688	0.661	0.674
O_w of O_wH1	/	-1.425	-1.420	-1.394	-1.393
H of O_wH2	/	/	0.637	0.546	0.635
H2	/	/	0.681	0.654	0.653
O_w of O_wH2	/	/	-1.439	-1.318	-1.400
H of O_wH3	/	/	0.614	0.579	0.629
H3	/	/	0.680	0.666	0.683
O_w of O_wH3	/	/	-1.416	-1.352	-1.396
H of O_wH4	/	/	0.590	0.627	0.642
H4	/	/	0.679	0.666	0.680
O_w of O_wH4	/	/	-1.391	-1.399	-1.407

H of O_wH5	/	/	0.634	0.624	0.624
H5	/	/	0.695	0.659	0.672
O_w of O_wH5	/	/	-1.437	-1.395	-1.391
H of O_wH6	/	/	0.585	0.637	0.623
H6	/	/	0.825	0.653	0.655
O_w of O_wH6	/	/	-1.386	-1.408	-1.389
H of H_2O7	/	/	/	0.677	0.675
H of H_2O7	/	/	/	0.720	0.674
O_w of H_2O7	/	/	/	-1.460	-1.417
H of H_2O8	/	/	/	0.673	0.672
H of H_2O8	/	/	/	0.626	0.607
O_w of H_2O8	/	/	/	-1.362	-1.352
H of H_2O9	/	/	/	0.701	0.671
H of H_2O9	/	/	/	0.631	0.680
O_w of H_2O9	/	/	/	-1.393	-1.422
H of H_2O10	/	/	/	0.700	0.670
H of H_2O10	/	/	/	0.629	0.684
O_w of H_2O10	/	/	/	-1.390	-1.425
H of H_2O11	/	/	/	0.684	0.656
H of H_2O11	/	/	/	0.627	0.676
O_w of H_2O11	/	/	/	-1.375	-1.400
H of H_2O12	/	/	/	0.684	0.656
H of H_2O12	/	/	/	0.628	0.677
O_w of H_2O12	/	/	/	-1.376	-1.404
H of H_2O13	/	/	/	/	0.649
H of H_2O13	/	/	/	/	0.629
O_w of H_2O13	/	/	/	/	-1.285
H of H_2O14	/	/	/	/	0.639
H of H_2O14	/	/	/	/	0.647
O_w of H_2O14	/	/	/	/	-1.291
H of H_2O15	/	/	/	/	0.645
H of H_2O15	/	/	/	/	0.642
O_w of H_2O15	/	/	/	/	-1.295
H of H_2O16	/	/	/	/	0.646
H of H_2O16	/	/	/	/	0.624
O_w of H_2O16	/	/	/	/	-1.278
H of H_2O17	/	/	/	/	0.646
H of H_2O17	/	/	/	/	0.627
O_w of H_2O17	/	/	/	/	-1.282
H of H_2O18	/	/	/	/	0.650
H of H_2O18	/	/	/	/	0.646
O_w of H_2O18	/	/	/	/	-1.303