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Electronic Supplementary Information

Computational investigation of structural and electronic properties of aqueous interfaces of GaN, ZnO, and a GaN/ZnO alloy

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Contents:

1. Optimized water dimer geometries
2. MP2 and CCSD(T) potential energy curves for water dimer
3. Bulk water diffusivity and system size effects
4. Optimized lattice parameters for bulk GaN and ZnO
5. Radial distribution functions of surface cations with O atoms in OH^- ions and water molecules
6. Spatial dependence of water structure at aqueous interfaces of GaN $(10\bar{1}0)$, ZnO $(10\bar{1}0)$, and GaN/ZnO $(1\bar{2}10)$ surfaces
7. References

1. **Optimized water dimer geometries**

The optimized geometries of water dimers in the hydrogen bonded and the repulsive configurations are given in Tables S1 and S2 respectively. The last entry labeled as “Infinity” in S1 and S2 corresponds to a water molecule.

TABLE S1. Optimized geometries of water dimers in hydrogen bonded configuration.

R_{O-O} (Å) /Atom	x (Å)	y (Å)	z (Å)
2.41079			
O1	1.202107	0.088983	-0.000194
H2	0.709489	-0.737788	-0.000038
H3	2.130961	-0.155958	0.001045
O4	-1.202103	-0.088969	0.000030
H5	-2.130994	0.155833	-0.000117
H6	-0.709486	0.737802	0.000423
2.51079			
O1	1.249773	-0.091943	0.022760
H2	0.743554	0.726443	0.061915
H3	2.161475	0.172426	-0.123985
O4	-1.253726	0.093049	-0.025431
H5	-2.153466	-0.199638	0.139938
H6	-0.719941	-0.708075	-0.056504
2.61079			
O1	-1.258167	-0.001544	0.120633
H2	-1.514395	-0.755823	-0.419444
H3	-1.512705	0.766684	-0.400245
O4	1.340962	0.001816	-0.125798
H5	1.924943	-0.009520	0.635907
H6	0.439793	-0.003516	0.225099
2.71079			
O1	1.289947	-0.000330	0.110531
H2	1.653285	0.763028	-0.349025
H3	1.654260	-0.760702	-0.353178
O4	-1.410595	0.000370	-0.124925
H5	-1.872927	-0.002304	0.716353
H6	-0.469432	-0.000347	0.101000
2.81079			
O1	1.338448	-0.000191	0.110410
H2	1.701716	0.762024	-0.351036
H3	1.702180	-0.760704	-0.353468
O4	-1.462578	0.000214	-0.123630
H5	-1.895548	-0.001357	0.733360
H6	-0.515304	-0.000147	0.076903
2.91079			
O1	0.001107	-1.391346	0.000000
H2	0.490574	-1.718787	0.760868

H3	0.490574	-1.718787	-0.760868
O4	0.001107	1.519440	0.000000
H5	-0.898219	1.856381	0.000000
H6	-0.100641	0.556443	0.000000
3.01079			
O1	-1.435894	-0.000008	0.109157
H2	-1.803854	-0.760494	-0.351057
H3	-1.803854	0.760546	-0.350945
O4	1.566073	0.000010	-0.121112
H5	1.954708	-0.000066	0.757291
H6	0.611567	-0.000003	0.040348
3.11079			
O1	1.484872	-0.000020	0.108304
H2	1.856267	0.760295	-0.349349
H3	1.856266	-0.760167	-0.349630
O4	-1.617531	0.000025	-0.119935
H5	-1.990274	-0.000165	0.765460
H6	-0.660987	-0.000005	0.026572
3.21079			
O1	-1.534476	-0.000181	0.108018
H2	-1.905507	-0.759328	-0.351779
H3	-1.905505	0.760482	-0.349270
O4	1.668278	0.000224	-0.118950
H5	2.029917	-0.001469	0.771139
H6	0.710681	-0.000029	0.017365
3.31079			
O1	1.583792	-0.000929	0.107159
H2	1.957859	0.762689	-0.342498
H3	1.957828	-0.756736	-0.355533
O4	-1.719331	0.001148	-0.117966
H5	-2.070550	-0.007657	0.776367
H6	-0.760820	-0.000049	0.008118
3.41079			
O1	1.630818	-0.000710	0.103824
H2	2.023819	0.761702	-0.331314
H3	2.023521	-0.757269	-0.341678
O4	-1.772865	0.000909	-0.116196
H5	-2.099132	-0.006272	0.787629
H6	-0.811835	0.000245	-0.015662
3.51079			
O1	-1.679709	-0.000245	0.102218
H2	-2.080135	-0.758421	-0.333410
H3	-2.079232	0.760255	-0.330177
O4	1.824344	0.000259	-0.115127
H5	2.139640	-0.001781	0.792678
H6	0.862650	-0.000161	-0.025817

3.61079			
O1	-1.728357	-0.001849	0.100158
H2	-2.138439	-0.752981	-0.338588
H3	-2.136680	0.765238	-0.311809
O4	1.876073	0.002243	-0.113961
H5	2.179623	-0.016036	0.797684
H6	0.913766	0.000628	-0.036862
3.71079			
O1	-1.777233	-0.000583	0.098515
H2	-2.194987	-0.756816	-0.323851
H3	-2.192082	0.761249	-0.316596
O4	1.927528	0.000514	-0.112854
H5	2.219954	-0.003939	0.802665
H6	0.964753	0.000050	-0.047507
3.81079			
O1	-1.825700	-0.002510	0.095876
H2	-2.254337	-0.750448	-0.330255
H3	-2.252088	0.766984	-0.292458
O4	1.979427	0.003131	-0.111649
H5	2.260292	-0.023179	0.807138
H6	1.016320	0.001677	-0.058238
3.91079			
O1	-1.874712	-0.001481	0.093100
H2	-2.313192	-0.753975	-0.313917
H3	-2.311790	0.763732	-0.291080
O4	2.030729	0.001911	-0.111281
H5	2.308670	-0.014234	0.808925
H6	1.068175	0.001034	-0.058479
Infinity			
O1	1.349074	0.113839	0.000000
H2	1.680963	-0.375420	-0.758092
H3	1.680963	-0.375420	0.758092

TABLE S2. Optimized geometries of water dimers in repulsive configuration.

R_{O-O} (Å) /Atom	x (Å)	y (Å)	z (Å)
2.91079			
O1	0.000000	0.000000	-1.455304
H2	0.000000	0.756239	-2.049880
H3	0.000000	-0.756239	-2.049880
O4	0.000000	0.000000	1.455391
H5	0.756417	0.000000	2.049531
H6	-0.756417	0.000000	2.049531
3.01079			
O1	1.505232	-0.000017	0.000000
H2	2.099787	0.000000	0.756451
H3	2.099787	0.000000	-0.756451
O4	-1.505455	-0.000103	0.000000
H5	-2.099544	-0.756220	0.000000
H6	-2.098244	0.757178	0.000000
3.11079			
O1	1.555335	-0.000039	0.000000
H2	2.148851	-0.000009	0.756794
H3	2.148851	-0.000009	-0.756794
O4	-1.555348	-0.000191	0.000000
H5	-2.150227	-0.755956	0.000000
H6	-2.147376	0.757822	0.000000
3.21079			
O1	1.605339	-0.000062	0.000000
H2	2.198309	-0.000013	0.757125
H3	2.198309	-0.000013	-0.757125
O4	-1.605344	-0.000313	0.000000
H5	-2.200586	-0.755634	0.000000
H6	-2.195992	0.758655	0.000000
3.31079			
O1	-1.655340	-0.000091	0.000000
H2	-2.248035	-0.000023	-0.757248
H3	-2.248035	-0.000023	0.757249
O4	1.655342	-0.000458	0.000000
H5	2.251480	-0.755035	0.000000
H6	2.244579	0.759473	0.000000
3.41079			
O1	-1.705340	-0.000124	0.000000
H2	-2.297683	-0.000024	-0.757465
H3	-2.297683	-0.000025	0.757465
O4	1.705343	-0.000675	0.000000
H5	2.302549	-0.754238	-0.000001
H6	2.292794	0.760679	0.000001
3.51079			

O1	-0.000536	-1.755339	0.000000
H2	-0.000532	-2.347676	0.757405
H3	-0.000532	-2.347676	-0.757405
O4	-0.000536	1.755345	0.000000
H5	-0.752558	2.354682	0.000000
H6	0.762203	2.340624	0.000000
3.61079			
O1	0.000762	-1.805341	0.000000
H2	0.000758	-2.397136	-0.757802
H3	0.000758	-2.397136	0.757802
O4	0.000762	1.805343	0.000000
H5	0.750877	2.406478	0.000000
H6	-0.764592	2.387780	0.000000
3.71079			
O1	-1.855331	0.000000	-0.000299
H2	-2.447627	0.757361	-0.000085
H3	-2.447627	-0.757361	-0.000085
O4	1.855351	0.000000	-0.001611
H5	2.459934	0.000000	-0.749556
H6	2.435160	0.000000	0.765004
3.81079			
O1	-1.905338	0.000000	-0.000355
H2	-2.496769	0.758027	-0.000059
H3	-2.496769	-0.758027	-0.000059
O4	1.905350	0.000000	-0.002233
H5	2.512334	0.000000	-0.747429
H6	2.481106	0.000000	0.768254
3.91079			
O1	-1.955327	0.000000	-0.000450
H2	-2.547398	0.757489	-0.000102
H3	-2.547398	-0.757489	-0.000102
O4	1.955357	0.000000	-0.002720
H5	2.567169	0.000000	-0.744437
H6	2.527384	0.000000	0.769998
Infinity			
O1	1.349074	0.113839	0.000000
H2	1.680963	-0.375420	-0.758092
H3	1.680963	-0.375420	0.758092

2. **MP2 and CCSD(T) potential energy curves for water dimer**

The interaction energy curves ($E_{dimer} - 2E_{monomer}$) are plotted in Figure S1 and the corresponding potential energy raw data is given in Tables S3 and S4. As described in the main text, the basis set superposition error (BSSE) corrections are applied in MP2/aug-cc-pVTZ optimizations as well as final CCSD(T) calculations using the MP2 optimized geometries. The two point extrapolation scheme is then used to extrapolate the BSSE-corrected energies to the complete basis set (CBS) limit using aug-cc-pVTZ results and additional aug-cc-pVDZ calculations using aug-cc-pVTZ optimized geometries.[1, 2]

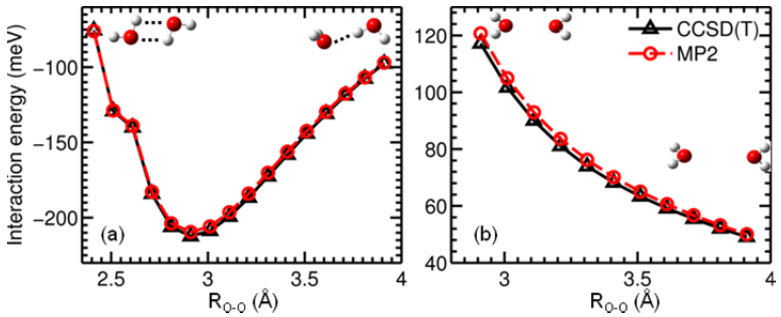

Figure S1. Interaction energy of water dimer as a function of the separation between oxygen atoms. (a) Hydrogen bonded configuration. (b) Repulsive configuration.

TABLE S3. Potential energy of water dimers in hydrogen bonded configuration.

R_{O-O} (Å)	MP2 Energies (eV)		CCSD(T) Energies (eV)	
	BSSE-corrected	CBS-extrapolated	BSSE-corrected	CBS-extrapolated
2.41079	-152.6603229627	-152.7181460874	-152.6869004301	-152.7450840262
2.51079	-152.6623524793	-152.7200810519	-152.6889787986	-152.7470608561
2.61079	-152.6626349020	-152.7204551997	-152.6892594709	-152.7474587279
2.71079	-152.6643348366	-152.7220643195	-152.6909814932	-152.7490765873
2.81079	-152.6652061714	-152.7228392801	-152.6918982460	-152.7498839160
2.91079	-152.6654945067	-152.7230528524	-152.6922141864	-152.7501143509
3.01079	-152.6654138899	-152.7229156867	-152.6921476935	-152.7499830906
3.11079	-152.6651108886	-152.7225702284	-152.6918489880	-152.7496350271
3.21079	-152.6646831544	-152.7221116300	-152.6914192682	-152.7491688514
3.31079	-152.6641964915	-152.7216037392	-152.6909264167	-152.7486501830
3.41079	-152.6636945080	-152.7210881068	-152.6904154717	-152.7481218735
3.51079	-152.6632011402	-152.7205850525	-152.6899129296	-152.7476066788
3.61079	-152.6627334366	-152.7201110465	-152.6894361386	-152.7471212471
3.71079	-152.6622997507	-152.7196729114	-152.6889942230	-152.7466730383
3.81079	-152.6619035227	-152.7192741687	-152.6885903319	-152.7462651965
3.91079	-152.6615435069	-152.7189142055	-152.6882228371	-152.7458967029
Infinity	-152.6579846469	-152.7153499839	-152.6846508800	-152.7423105592

TABLE S4. Potential energy of water dimers in repulsive configuration.

R_{O-O} (Å)	MP2 Energies (eV)		CCSD(T) Energies (eV)	
	BSSE-corrected	CBS-extrapolated	BSSE-corrected	CBS-extrapolated
2.91079	-152.6534639880	-152.7109141842	-152.6802461720	-152.7380051846
3.01079	-152.6540570446	-152.7114938451	-152.6808290201	-152.7385723263
3.11079	-152.6545092668	-152.7119349989	-152.6812707358	-152.7390008388
3.21079	-152.6548614708	-152.7122770690	-152.6816127637	-152.7393307030
3.31079	-152.6551428860	-152.7125492140	-152.6818842987	-152.7395910818
3.41079	-152.6553739387	-152.7127722255	-152.6821065438	-152.7398035920
3.51079	-152.6555683218	-152.7129600817	-152.6822925472	-152.7399816253
3.61079	-152.6557360990	-152.7131224735	-152.6824537936	-152.7401362533
3.71079	-152.6558831596	-152.7132656396	-152.6825937094	-152.7402713026
3.81079	-152.6560153843	-152.7133947053	-152.6827216726	-152.7403953086
3.91079	-152.6561346255	-152.7135117439	-152.6828352466	-152.7405060727
Infinity	-152.6579846469	-152.7153499839	-152.6846508800	-152.7423105592

3. **Bulk water diffusivity and system size effects**

We analyse the dynamical properties of the simulated water by means of the self- diffusion coefficient calculated using the Einstein relation

$$D_{PBC} = \frac{1}{6}\lim_{t\to\infty}\frac{d}{dt}\langle|r_i(t) - r_i(0)|^2\rangle.$$

The subscript 'PBC' is used to emphasize the use of periodic boundary conditions (PBCs). The self-diffusion coefficient corrected for the PBCs is given by

$$D_0 = D_{PBC} + \frac{k_B T\xi}{6\pi\eta L}$$

where a numerical coefficient $\xi = 2.837297$, L is the box size, and η is the translational shear viscosity.[3, 4] The value of η for heavy water under ambient conditions is 1.095×10^{-3} Pa·s.[5] The mean square displacements (MSDs) of oxygen atoms in 32 H_2O cell simulated at 325 K and 350 K for 25 ps are shown in Figs. S2a and S2b, respectively. D_{PBC} is evaluated by averaging over the 7 ps segments equally spaced by 2.5 ps intervals.[6, 7] The initial transient of 1 ps is excluded while calculating the slope of the MSD.[8] The calculated values of D_{PBC} and D_0 are given in Table S5. D_0 increases significantly when the simulation temperature is raised from 325 K to 350 K. The experimental value of self-diffusion coefficient of heavy water is 1.8×10^{-5} cm^2/s,[9] which is close to the value of D_0 obtained from MD simulation at 350 K.

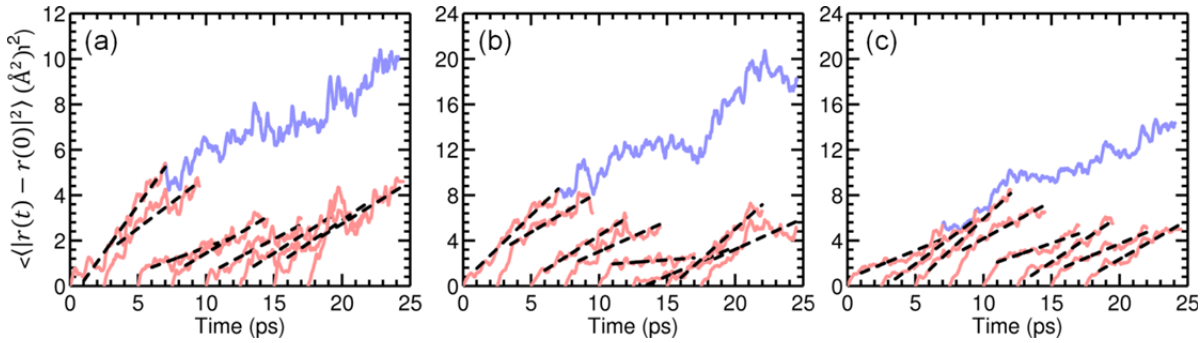

Figure S2. Mean square displacement (MSD) of oxygen atoms obtained from various MD simulations. (a) 32 H_2O at 325 K, (b) 32 H_2O at 350 K, and (c) 64 H_2O at 350 K. MSD for the entire trajectory of 25 ps is shown in blue and the MSDs for smaller 7 ps segments equally spaced by 2.5 ps intervals are shown in red. The dotted lines are the straight line fits to the linear diffusive regimes.

TABLE S5. Calculated self-diffusion coefficients

System Size			Diff. Coeff. ($\times 10^{-5}$ cm^2/s)	
# H_2O	L (Å)	T (K)	D_{PBC}	D_0
32	9.86	325	0.70	1.27
		350	1.13	1.70
64	12.41	350	1.16	1.62

To investigate the system-size effects, we compare the oxygen-oxygen radial distribution functions ($g_{OO}(r)$) and self-diffusion coefficients obtained from simulations with 32 and 64 water molecules at 350 K. The density of water in both simulations is the same as the ambient density (1 g/cm^3) of liquid water. The linear diffusive regimes in MSD plots for the 64 H_2O simulation (Figure S2c) are much more well defined and uniform compared to that for the 32 H_2O simulation (Figure S2b) at 350 K. However, the final values of D_0 from both simulations compare well with each other (Table S5). Additionally, the difference between $g_{OO}(r)$ calculated from 32 H_2O and 64 H_2O simulations is also negligible as shown in Figure S3.

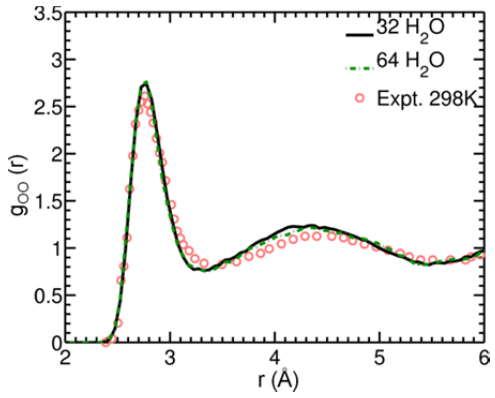

Figure S3. Oxygen-oxygen radial distribution function of 32 water molecule (solid line) and 64 water molecule (dash-dotted line) cells calculated using optB88-vdW functional at the MD simulation temperature of 350 K. The experimental data are shown by the hollow circles.[10]

4. **Optimized lattice parameters for bulk GaN and ZnO**

The optimized lattice parameters and band gaps calculated using different functionals are given in Table S6 along with the experimental data. All calculations are carried out using a 9×9×6 Γ-centered k-point grid, 600 eV plane-wave cutoff, and onsite Coulomb interaction corrections of U_{Ga} = 3.9 eV and U_{Zn} = 6.0 eV.[11] The equilibrium lattice volume is obtained by varying the cell volume isotropically (keeping the c/a ratio fixed at its experimental value) within 10 % of the experimental value and fitting the energy-volume curve to the Murnaghan equation of state.[12] The final lattice geometry is obtained by fully relaxing the unit cell keeping the volume fixed at the equilibrium cell volume obtained from the Murnaghan fit.

TABLE S6. Lattice parameters and band gaps of Wurtzite GaN and ZnO

	GaN				ZnO			
	a (Å)	c/a	u	E_g (eV)	a (Å)	c/a	u	E_g (eV)
PBE	3.157	1.628	0.377	2.440	3.226	1.608	0.381	1.564
PBE-vdW	3.177	1.630	0.377	2.325	3.240	1.608	0.380	1.621
optB88-vdW	3.154	1.630	0.377	2.644	3.208	1.609	0.380	1.842
Expt.[a]	3.190	1.627	0.377	3.44	3.249	1.602	0.383	3.2

5. **Radial distribution functions of surface cations with O atoms in OH^- ions and water molecules**

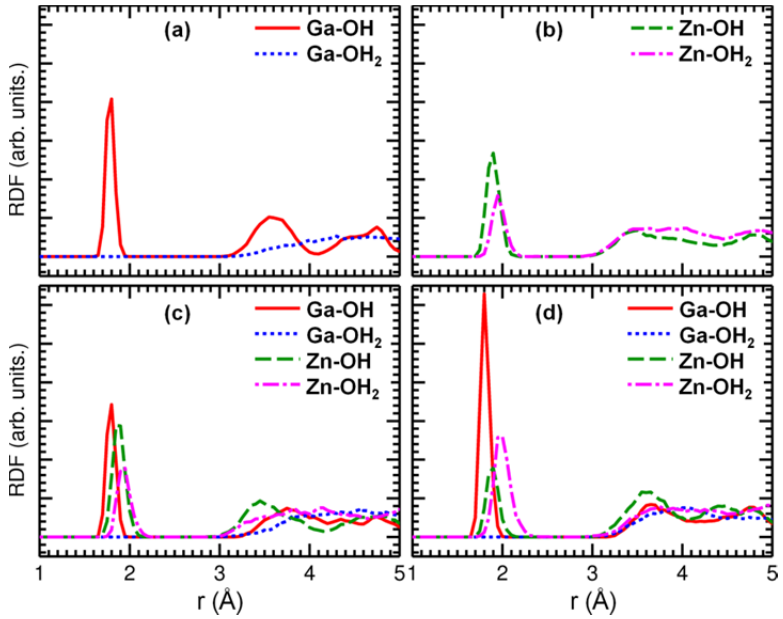

Figure S4. Radial distribution functions of surface cations with O atoms in OH^- ions and water molecules for (a) GaN $(10\bar{1}0)$, (b) ZnO $(10\bar{1}0)$, (c) GaN/ZnO $(10\bar{1}0)$, and (d) GaN/ZnO $(1\bar{2}10)$ interface simulations.

6. **Spatial dependence of water structure at aqueous interfaces of GaN $(10\bar{1}0)$, ZnO $(10\bar{1}0)$, and GaN/ZnO $(1\bar{2}10)$ surfaces**

The results for GaN $(10\bar{1}0)$, ZnO $(10\bar{1}0)$, and GaN/ZnO $(1\bar{2}10)$ surfaces are shown in Figs. S5, S6, and S7 respectively and are obtained using the same computational methods as those used to obtain the results for GaN/ZnO $(10\bar{1}0)$ surface shown in Figure 6 in the main text.

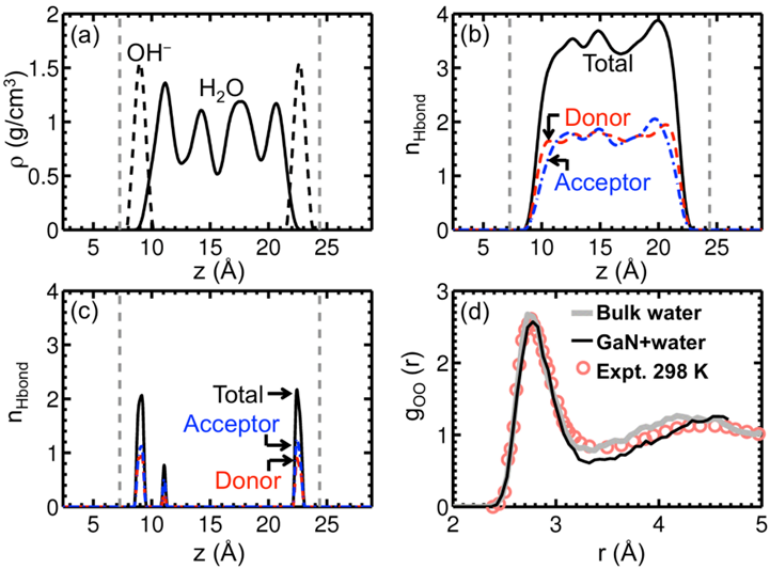

Figure S5. Structure of water as a function of distance from the GaN $(10\bar{1}0)$ surface. (a) Planar and time averaged density of water molecules and OH^- ions. Average number of donor (dashed line) acceptor (dash-dotted line) and total (solid line) hydrogen bonds per (b) water molecule and (c) OH^- ion. The vertical dashed lines in (a-c) indicate the nominal positions of the top and bottom semiconductor surfaces. (d) Oxygen-oxygen radial distribution function (RDF) calculated from a water layer consisting of water molecules more than 3 Å away from the semiconductor surface in GaN/ZnO-water interface simulation (dark line) along with the calculated (faint line) and experimentally derived (hollow circles) RDFs of bulk water. The RDFs of bulk water are the same as in Figure 2 in the main text.

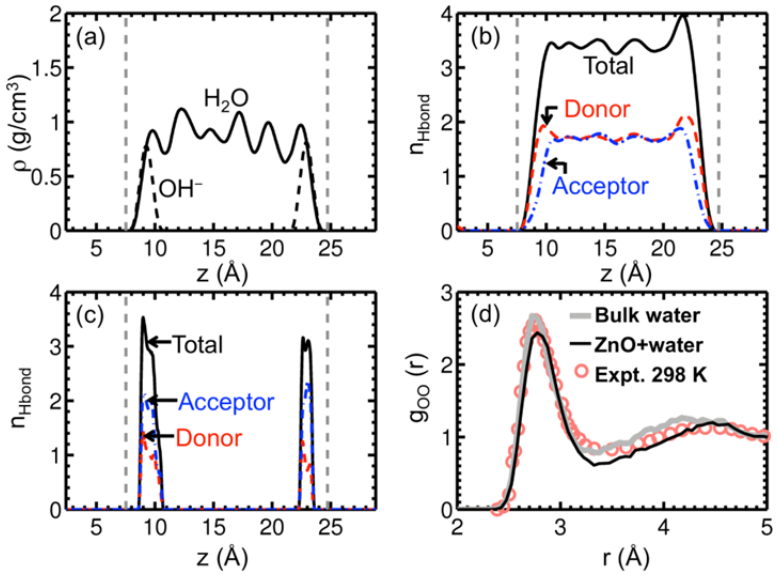

Figure S6. Same as Figure S4 but for the ZnO $(10\bar{1}0)$ surface.

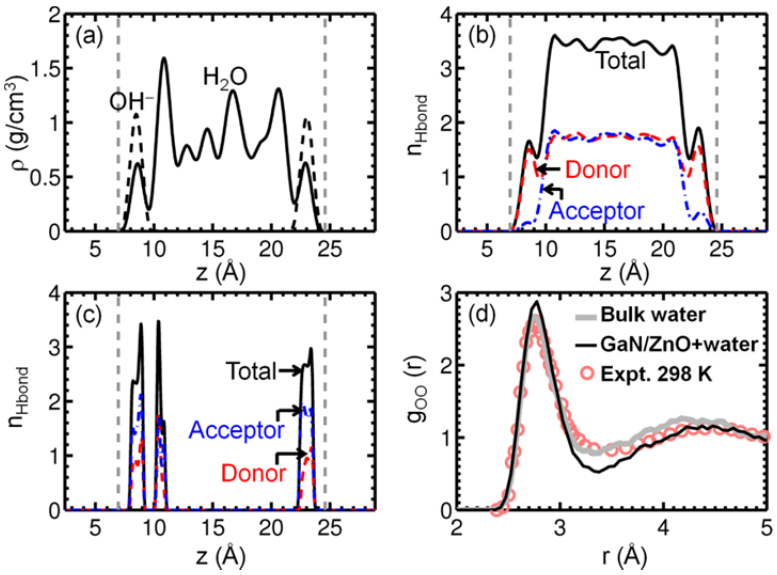

Figure S7. Same as Figure S4 but for the GaN/ZnO $(1\bar{2}10)$ surface.

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