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

Water aggregation and dissociation on the ZnO(10□0) surface.

SUPPLEMENTARY INFORMATION

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In order to evaluate the impact of the GGA band gap problem on the water adsorption energies calculated using the PBE functional, benchmark calculations using the hybrid density functional HSE06 were carried out for structures with small unit cells. The adsorption energies were calculated at the HSE06 equilibrium lattice parameters for bulk ZnO, a = 3.261 Å, c/a = 1.607, u = 0.381 (PBE: a = 3.289 Å, c/a = 1.614, u = 0.379; expt.: a = 3.250 Å, c/a = 1.602, u = 0.382). The results are summarized in Table S1 and compared to PBE.

Table S1: Comparison of adsorption energies calculated using the hybrid DFT HSE06 with PBE

Structure	Supercell	# H2O	Coverage	E_{ads}		Difference	%
				HSE06	PBE		
C-M	(1x2)	1	1/2	-1.09	-1.01	-0.08	8.1%
C-D	(1x2)	1	1/2	-0.76	-0.68	-0.08	11.5%
R-M	(2x1)	1	1/2	-1.11	-1.02	-0.09	9.2%
R-D	(2x1)	1	1/2	-1.20	-1.06	-0.14	13.1%
1ML-M	(1x1)	1	1	-1.16	-1.07	-0.09	8.3%
1ML-D	(1x1)	1	1	-1.18	-1.07	-0.11	10.1%
1ML-MD	(2x1)	2	1	-1.29	-1.18	-0.11	9.6%
2ML1	(2x1)	4	2	-0.96	-0.93	-0.04	3.9%
½ML-DD	(2x1)	1	1/2	0.21	0.18	0.03	18.0%

The HSE06 results show a systematic strengthening of the water adsorption energies by -0.08 to -0.14 eV or 8-13 % as compared with PBE. More detailed analysis of the data may indicate a slight tendency towards stabilizing dissociated structures relative to molecular adsorption. However, this is a small effect and does not change the general trends regarding water aggregation or dissociation discussed in the paper. Only borderline cases with a driving force $\leq$ 0.01 eV may be affected. In the case of the 2 ML structure, 2ML1, the change in adsorption energy per water molecule (-0.04 eV) is smaller because only 2 of the 4 molecules are forming Zn-O_W bonds. The double dissociated structure, ½ML-DD, may be a special case due to the high-energy of this structure that is not bound (metastable) with respect to the clean surface and a water molecule in the gas phase.

Figure S1 shows the energy of isolated water molecules calculated with the PBE density functional as function of the O-H bond length. The VASP calculations used a cubic unit cell of 19 Å, dipole correction and a Fermi distribution with 0.1 eV width. The energy of the fully optimized structure is set to zero. When the bond length is stretched to more than 1.6 Å, spin polarization has to be taken into account. With this provision, the bond dissociation energy agrees with high-level [8,8]-CASSCF calculations using the aug-cc-pVTZ basis set and with the experimental value. For a detailed discussion of the bond dissociation curve of water see Frank Jensen, Introduction to computational chemistry, John Wiley & Sons, Chichester 1999, Chapter 11.5. For comparison the energies of frozen water molecules taken from the adsorbed structures, calculated with and without spin polarization are also shown.

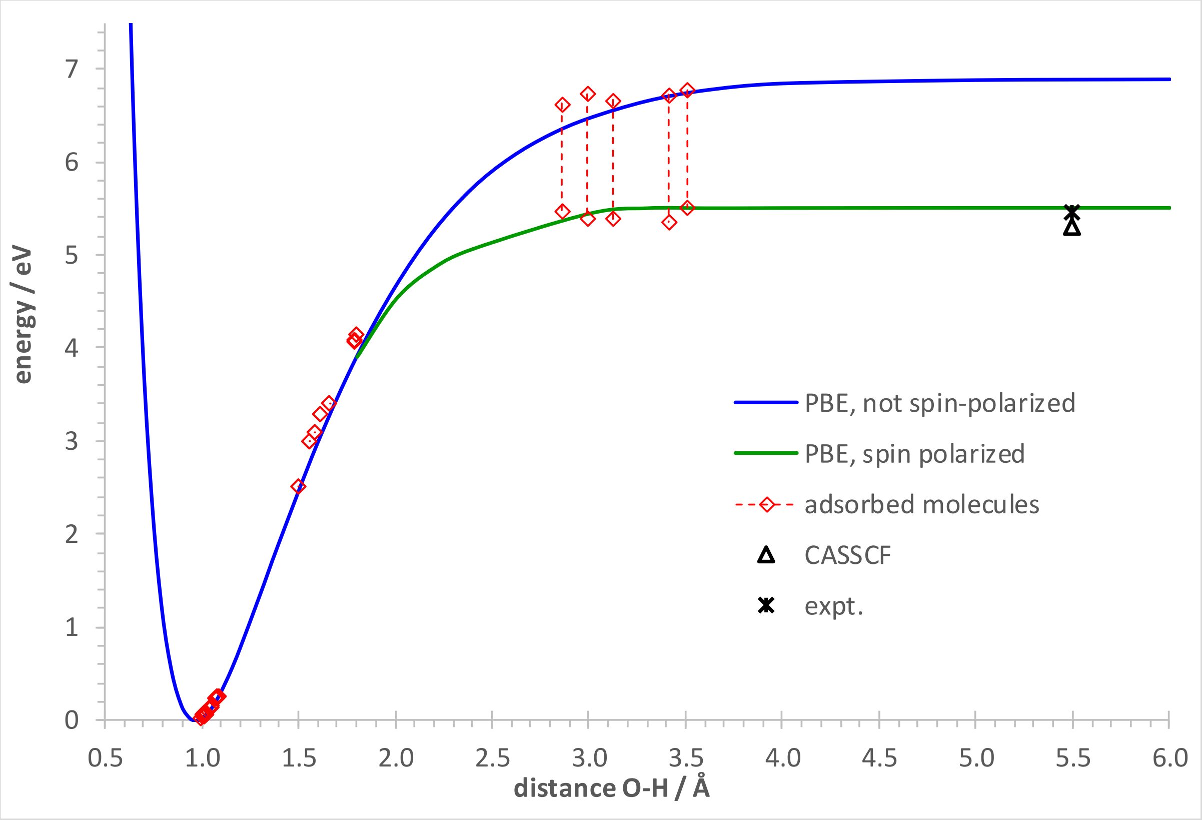

Figure S1: Bond dissociation curve of water calculated using PBE without (blue) and with (green) spin polarization. For comparison, the [8,8]-CASSCF/aug-cc-pVTZ and experimental dissociation energies (black) are included and the relaxation energies of the frozen water molecules taken from the adsorbed structures (red).

The structures of doubly dissociated water molecules (Figure S2) have oxygen atoms in a bridging position between two surface zinc sites. The Zn-$\mathrm{O_W}$ bonds are 1.9-2.0 Å. Dissociation ontop of ZnO surface dimers is preferred (I-DD1) over dissociation across the trench (I-DD2 and I-DD3) in spite of the longer O-$\mathrm{H_S}$ distances (2.635 Å in I-DD1, compared to 2.285 Å in D-DD3). The most stable structure for a double dissociated isolated water molecule, I-DD1, resembles that reported for adsorption of H_2S on ZnO (J. Goclon, B. Meyer, Phys.Chem.Chem.Phys., 2013, 15, 8373-8382). However for water, double dissociation is very unfavorable and all structures in Figure S2 are not stable with respect to desorption (endothermic adsorption energies, $E_{ads} > 0$). The arrangement in columns (C-DD) is even more unfavorable, while arrangement in rows (R-DD) or as half monolayer (½ML-DD) is somewhat less unfavorable than the isolated structure I-DD1.

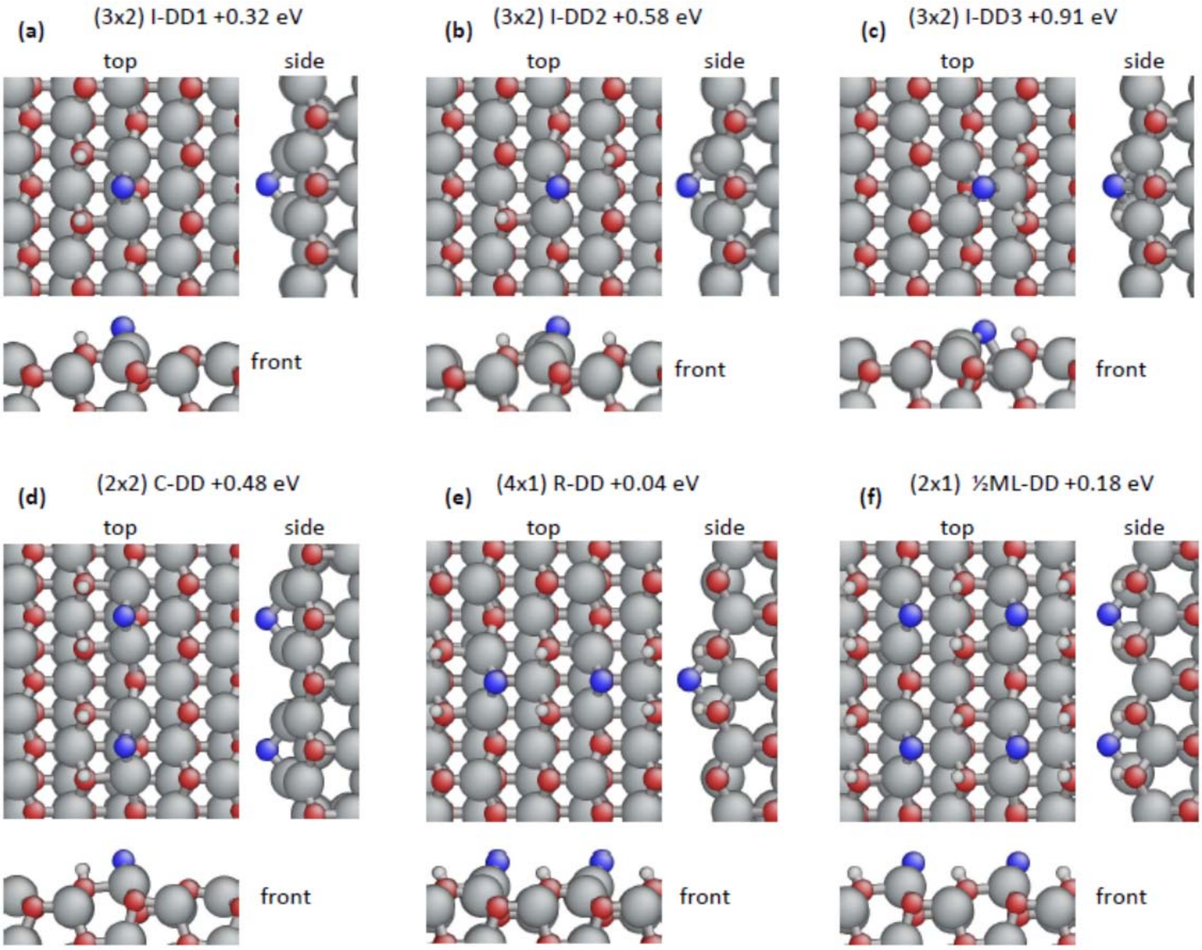

Figure S2: Top, front and side views of doubly dissociated water molecules adsorbed on the ZnO($10\bar{1}0$) surface: (a) – (c) isolated I-DD1 to I-DD3, (d) column C-DD, (e) row (R-DD, (f) half monolayer ML-DD. Zinc atoms grey, oxygen atoms of ZnO red, oxygen atoms of water molecules blue, hydrogen atoms white.

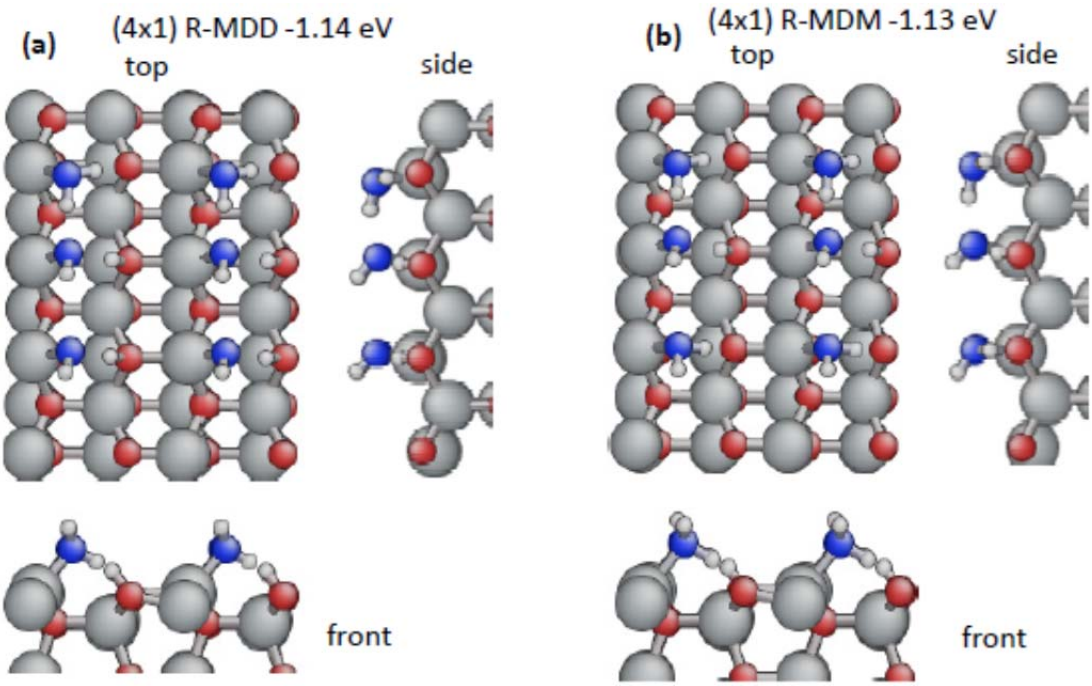

Figure S3: **Top, front and side views of partially dissociated water aggregates on the ZnO(10$\bar{1}$0) surface: (a) ladder-like row of trimers with MDD sequence R-MDD, (b) ladder-like row of trimers with MDM sequence R-MDM. Zinc atoms grey, oxygen atoms of ZnO red, oxygen atoms of water molecules blue, hydrogen atoms white.**

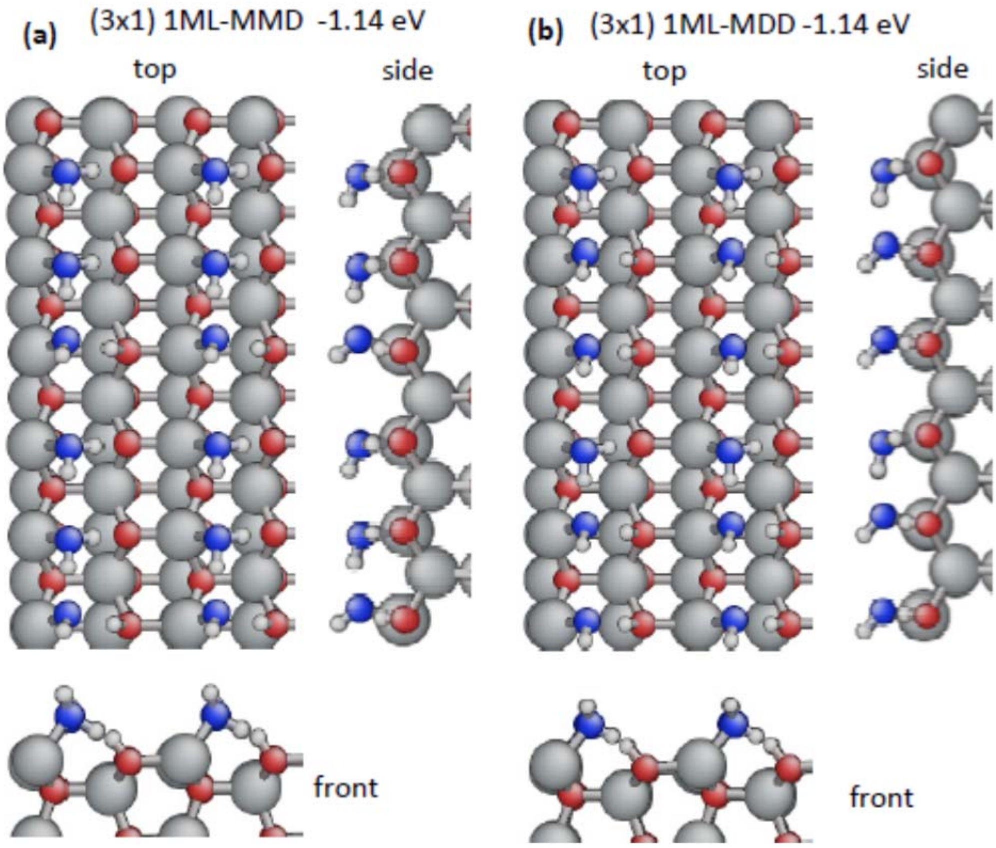

Figure S4: Top, front and side views of partially dissociated water monolayers on the ZnO($10\bar{1}0$) surface with: (a) 1/3 dissociated molecules 1ML-MMD, (b) 2/3 dissociated molecules 1ML-MDD. Zinc atoms grey, oxygen atoms of ZnO red, oxygen atoms of water molecules blue, hydrogen atoms white.

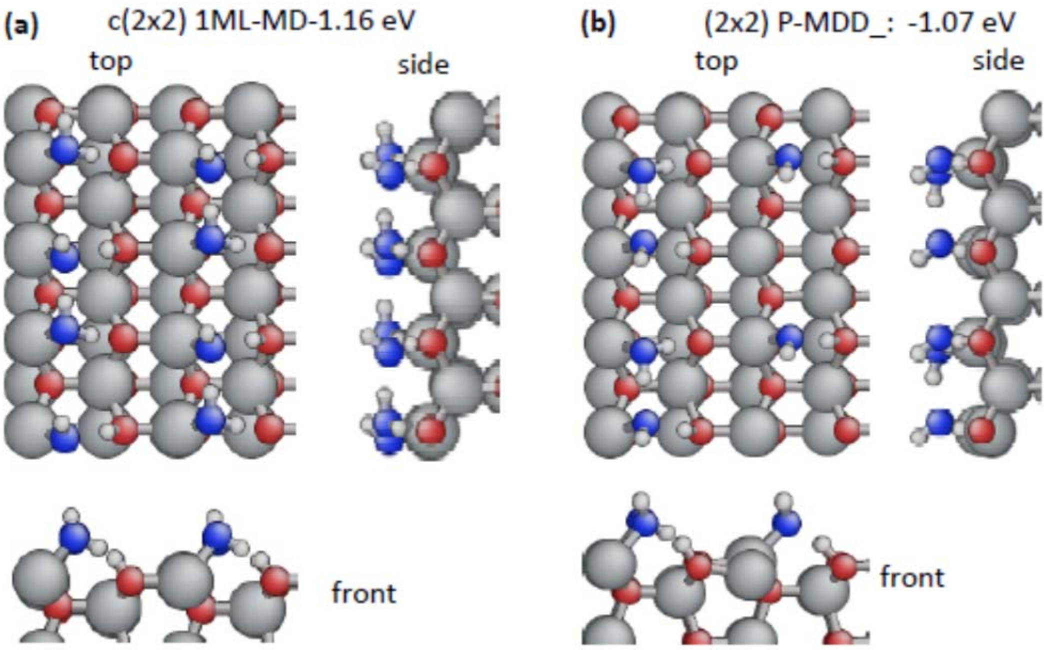

Figure S5: Top, front and side views of partially dissociated water layers on the ZnO($10\bar{1}0$) surface: (a) half-dissociated monolayer with c(2x2) periodicity 1ML-MDDM, (b) monolayer with point-defect P-MDD_. Zinc atoms grey, oxygen atoms of ZnO red, oxygen atoms of water molecules blue, hydrogen atoms white.

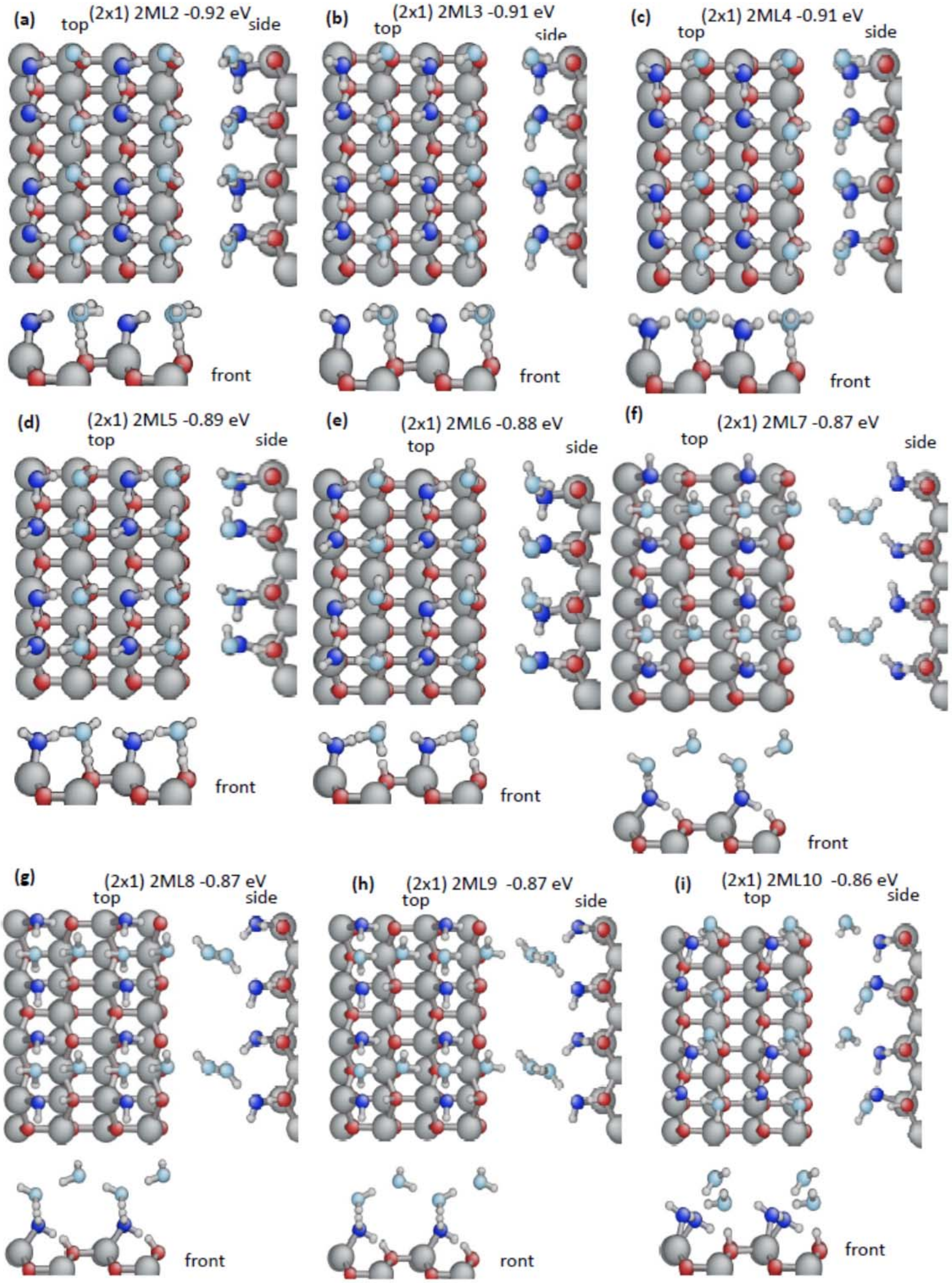

Figure S6: Top, front and side views of partially dissociated water double monolayers on the ZnO(10$\bar{1}$0) surface. Zinc atoms grey, oxygen atoms of ZnO red, oxygen atoms of water molecules blue, hydrogen atoms white. For better visualization, the oxygen atoms of water and OH-groups bound to Zn are dark blue, while the oxygen atoms of additional H-bonded molecules are sky-blue.

Table S2: H-bond topology, number of dangling OH-bonds and contributions to the binding energy of the ten most stable structures with 2 ML.

Structure	2ML1	2ML2	2ML3	2ML4	2ML5	2ML6	2ML7	2ML8	2ML9	2ML10
H-bond topology [a]	6-rings	6-rings	6-rings	6-rings	4-rings	4-rings	chains	chains	chains	chains
OH dangling bonds	0	0	0	0	0	2	2	2	2	2
E(W/ZnO)	-1.91	-1.99	-1.84	-1.93	-1.92	-2.02	-1.70	-1.71	-1.70	-1.83
E(W/W)	-0.66	-0.58	-0.70	-0.65	-0.58	-0.47	-0.40	-0.40	-0.40	-0.65
$E^{relax}(ZnO)$	0.22	0.23	0.21	0.23	0.21	0.21	0.24	0.24	0.24	0.21
$E^{relax}(W_1)$ [b]	5.38	5.38	5.30	5.35	5.38	5.34	3.73	3.75	3.74	5.38
$E^{relax}(W_2)$ [c]	0.16	0.17	0.20	0.30	0.11	0.10	0.14	0.14	0.13	0.21
$E^{relax}(W_3)$ [d]	0.11	0.11	0.08	0.08	0.10	0.11	0.09	0.09	0.09	0.04
$E^{relax}(W_4)$ [d]	0.05	0.04	0.05	0.05	0.05	0.04	0.01	0.01	0.01	0.01
E_{ads} [e]	-0.93	-0.92	-0.91	-0.91	-0.89	-0.88	-0.87	-0.87	-0.87	-0.86

a 1D-Chain or ring size(s) of the H-bond network. *b* W_1 is the dissociated water molecule adsorbed on a surface Zn site. *c* W_2 is the undissociated water molecule adsorbed on a surface Zn site. *d* W_3 and W_4 are additional water molecules not bound to surface Zn sites. *e* The average of the water relaxation energies $E^{relax}(W_i)$ contributes to E_{ads}.

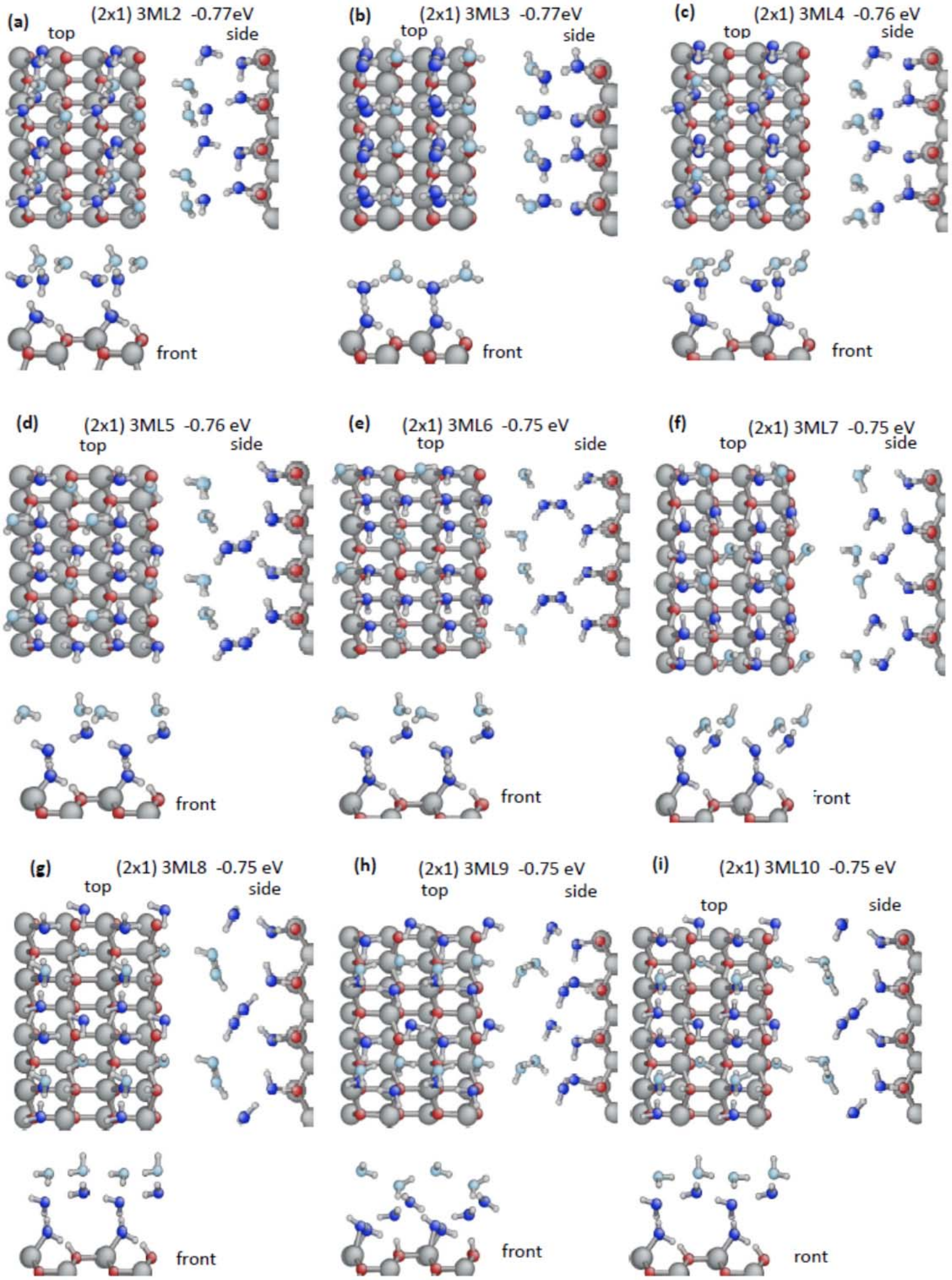

Figure S7: Top, front and side views of partially dissociated water films with 3 ML coverage on the ZnO(10$\bar{1}$0) surface. Zinc atoms grey, oxygen atoms of ZnO red, oxygen atoms of water molecules blue, hydrogen atoms white. For better visualization, the oxygen atoms of water and OH-groups bound to Zn and in the middle layer are dark blue, while the oxygen atoms of molecules in the outermost layer are sky-blue.

In order to analyse the driving forces for water aggregation and dissociation, the focus should be on comparable structures. In particular, for aggregation structures with identical dissociation degree should be compared, while for dissociation only aggregates with comparable size and shape should be compared.

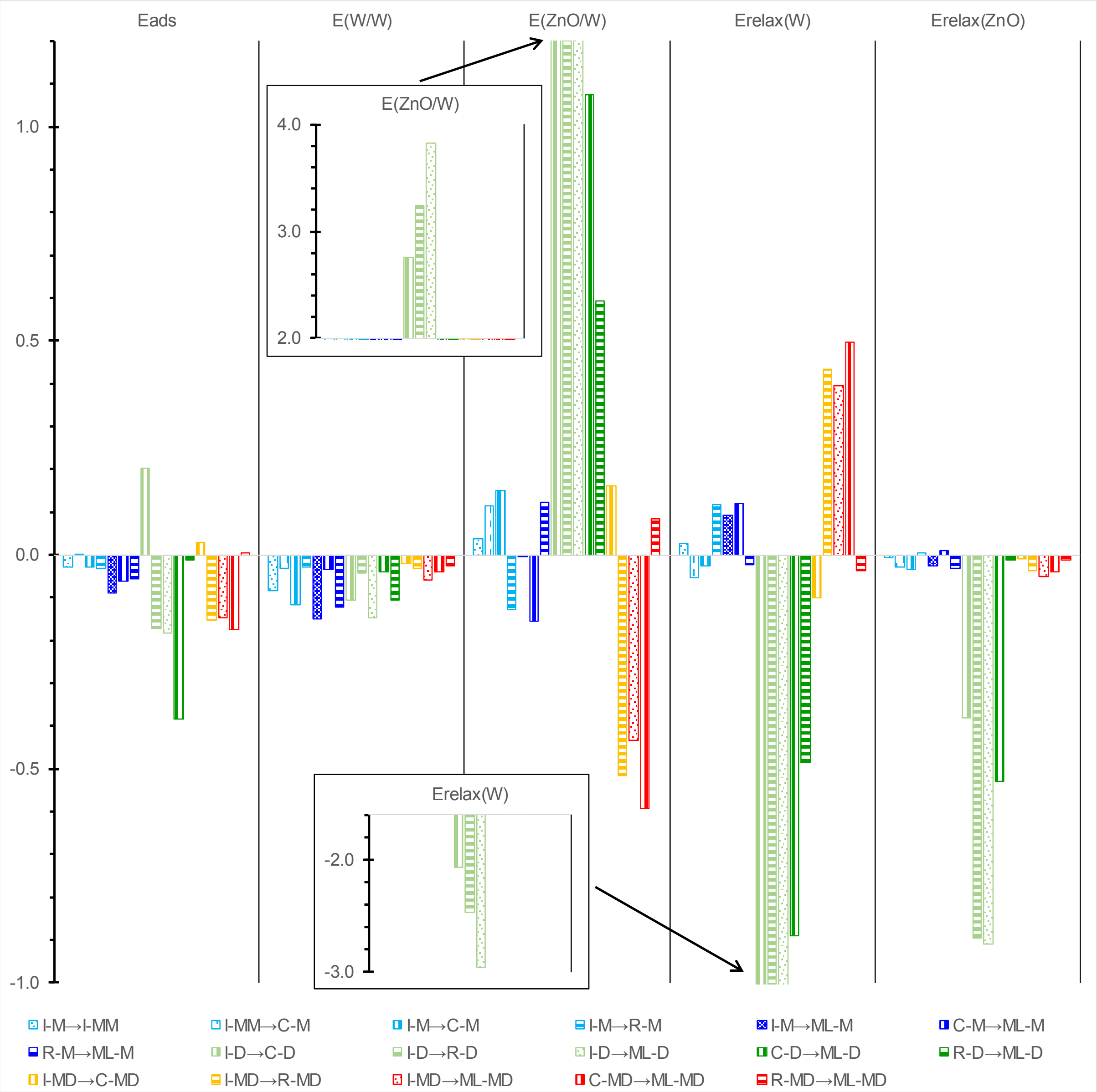

Figure S8: Changes in adsorption energies E_{ads}, water-water interaction energies, E(W/W), ZnO-water interaction energies, E(ZnO/W), water relaxation energies, E_{relax}(W) and ZnO relaxation energies E_{relax}(ZnO) for the aggregation processes listed in the Legend. I isolated molecule, C column, R row, ML monolayer, M undissociated water molecule, D dissociated water molecule.

Figure S8 shows an overview over the changes in the adsorption energies, water-water interaction energies, water-surface interaction energies, water relaxation energies and surface relaxation energies for 17 different water aggregation processes on the ZnO($10\bar{1}0$) surface. The abbreviations are explained in the Caption and the structures described in the Paper. In all cases, the direct water-water interaction energy favours formation of larger aggregates, even if the change in adsorption energy indicates that this process is unfavourable, as, e.g., in the case of forming columns of dissociated water molecules from isolated dissociated molecules: I-D → C-D. However, also energy changes due to adsorption and geometry changes contribute to the aggregation. In particular, the changes in the water-surface interactions and in the water relaxation energies can be very large. However, these two contributions have opposite sign and therefore cancel to a large extent (with one exception, the formation of a dimer from isolated molecules: I-M → I-MM). In general, changes in the relaxation energy of the ZnO surface favour aggregation. There are only two very minor exceptions. In summary, the driving force for aggregation comes from direct water-water interactions, as well as from surface mediated interactions. The final outcome, whether aggregation is favourable or not, depends on a subtle balance of water-water interactions, water-surface interactions and relaxation energies.

An overview of the changes in adsorption energies and their decomposition is shown in Figure S9 for dissociation of 9 different aggregates. The changes in adsorption energy indicate favourable as well as unfavourable examples with negative and positive differences, respectively. For dissociation, the decomposition terms show a very regular behaviour. Remarkably, the change in water-water interactions is negligible. Direct water-water interactions do not contribute to dissociation. This is surprising as the type of aggregate determines whether dissociation is favourable or not. The water-surface interactions always increase upon dissociation. This reveals the driving force for dissociation of adsorbed water. On the other hand, the water relaxation energies and the surface relaxation energies increase upon dissociation and therefore oppose it.

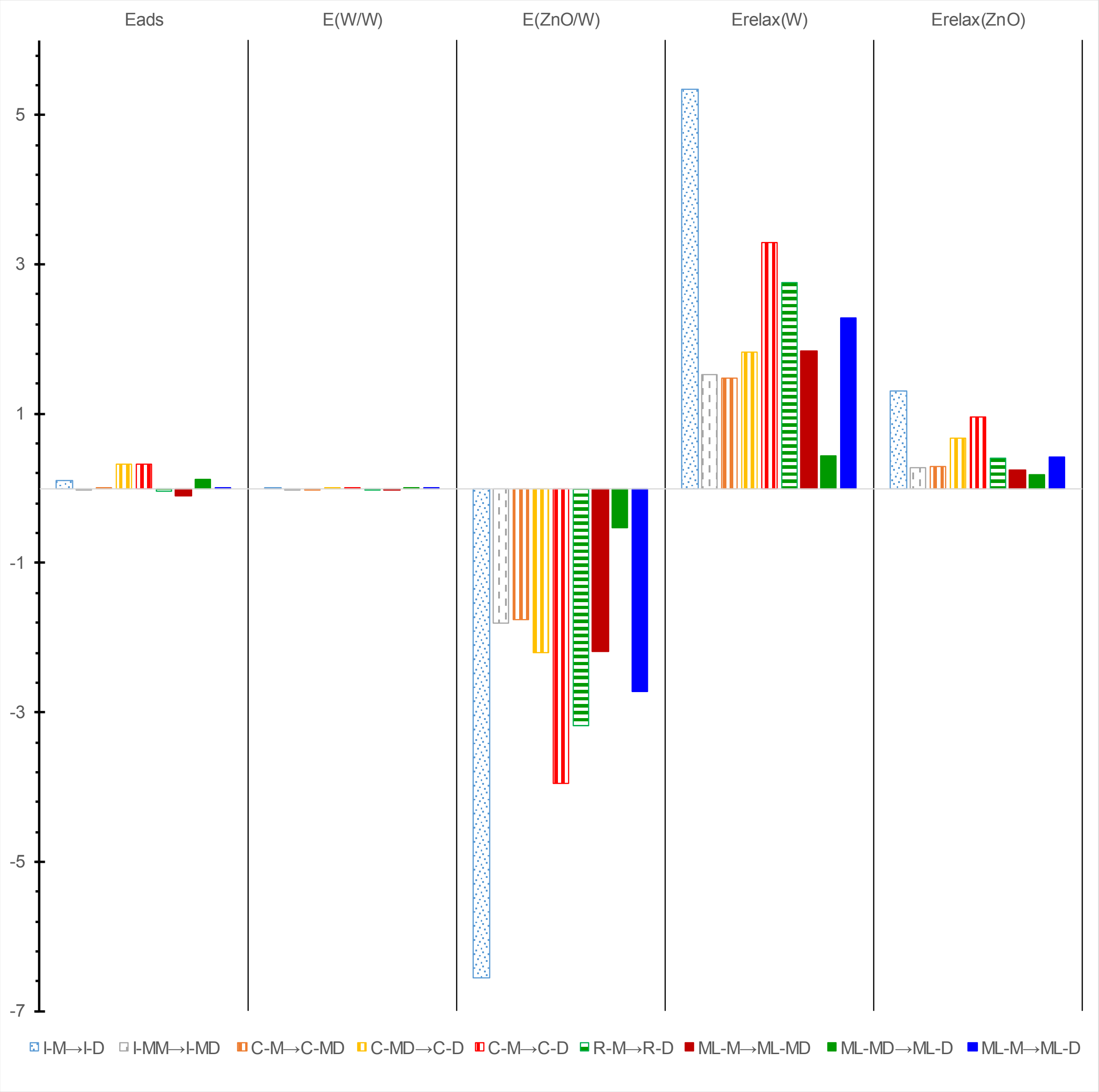

Figure S9: Changes in adsorption energies E_{ads}, water-water interaction energies, E(W/W), ZnO-water interaction energies, E(ZnO/W), water relaxation energies, E_{relax}(W) and ZnO relaxation energies E_{relax}(ZnO) for the dissociation processes listed in the Legend. I isolated molecule, C column, R row, ML monolayer, M undissociated water molecule, D dissociated water molecule.