Supplementary information to: Early stages of water/hydroxyl phase generation at transition metal surfaces - Synergetic adsorption and O−H bond dissociation assistance

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Table 1 The influence of the functional used on the energetic results (E_{ads}, ΔE and $\Delta E^{\ddagger}$ for the O−H scission, expressed in eV) is probed on two extreme cases (Rh and Pt) using GGA functionals (PW91, PBE), Grimme correction for dispersion (PBE+D2) and a van der Walls functional (optB86B, see J. Klimes, D.R. Bowler, A. Michaelides, *Phys. Rev. B.* **83**, 195131, (2011))

		PW91	PBE	PBE+D2	optB86B
Rh					
θ =1/9 ; monomer	E_{ads}	-0.41	-0.37	-0.67	-0.62
θ =2/9 ; monomers	E_{ads}	-0.77	-0.69	-1.31	-1.19
θ =2/9 ; dimer	E_{ads}	-1.00	-0.93	-1.51	-1.35
θ =1/9 ; monomer	ΔE	-0.01	0.03	0.00	-0.05
	$\Delta E^{\ddagger}$	0.90	0.91	0.88	0.89
θ =2/9 ; dimer donor	ΔE	0.10	0.14	0.09	-0.02
	$\Delta E^{\ddagger}$	1.12	1.14	0.96	0.92
θ =2/9 ; dimer acceptor	ΔE	0.10	0.14	0.09	-0.02
	$\Delta E^{\ddagger}$	0.64	0.73	0.62	0.57
Pt					
θ =1/9 ; monomer	E_{ads}	-0.28	-0.25	-0.67	-0.49
θ =2/9 ; monomers	E_{ads}	-0.51	-0.45	-1.31	-0.92
θ =2/9 ; dimer	E_{ads}	-0.84	-0.78	-1.61	-1.20
θ =1/9 ; monomer	ΔE	0.67	0.70	0.76	0.64
	$\Delta E^{\ddagger}$	0.96	0.96	0.98	0.92
θ =2/9 ; dimer donor	ΔE	0.78	0.80	0.89	0.73
	$\Delta E^{\ddagger}$	1.18	1.15	1.17	1.12
θ =2/9 ; dimer acceptor	ΔE	0.45	0.48	0.46	0.38
	$\Delta E^{\ddagger}$	0.97	0.88	0.85	0.77

Table 2 The water dimer adsorbed at a metallic surface has been split into three systems keeping the geometries fixed: the donor, the acceptor and the surface. This table provides the adsorption energy analysis (expressed in eV) in term of two bodies and three bodies decompositions. The synergy is the difference between the three-bodies term and the two bodies terms.

Metal	Acceptor-slab	Donor-slab	Acceptor-Donor	Three-body	Synergy
Ru	-0.13	-0.46	-0.26	-1.10	-0.26
Co	-0.13	-0.38	-0.28	-1.00	-0.21
Rh	-0.12	-0.46	-0.25	-1.09	-0.27
Ir	-0.09	-0.35	-0.25	-1.00	-0.31
Ni	-0.12	-0.40	-0.27	-1.02	-0.23
Pd	-0.13	-0.32	-0.25	-0.95	-0.24
Pt	-0.11	-0.28	-0.25	-0.92	-0.28

Table 3 Electronic population of the LUMO of the adsorbed entity after adsorption. For the magnetic surfaces, the α and β populations are provided successively.

Metal	H_2O	$(H_2O)_2$
Ru	0.305	0.376
Co	0.306/0.266	0.433/0.373
Rh	0.283	0.311
Ir	0.322	0.339
Ni	0.289/0.271	0.341/0.364
Pd	0.241	0.289
Pt	0.272	0.293

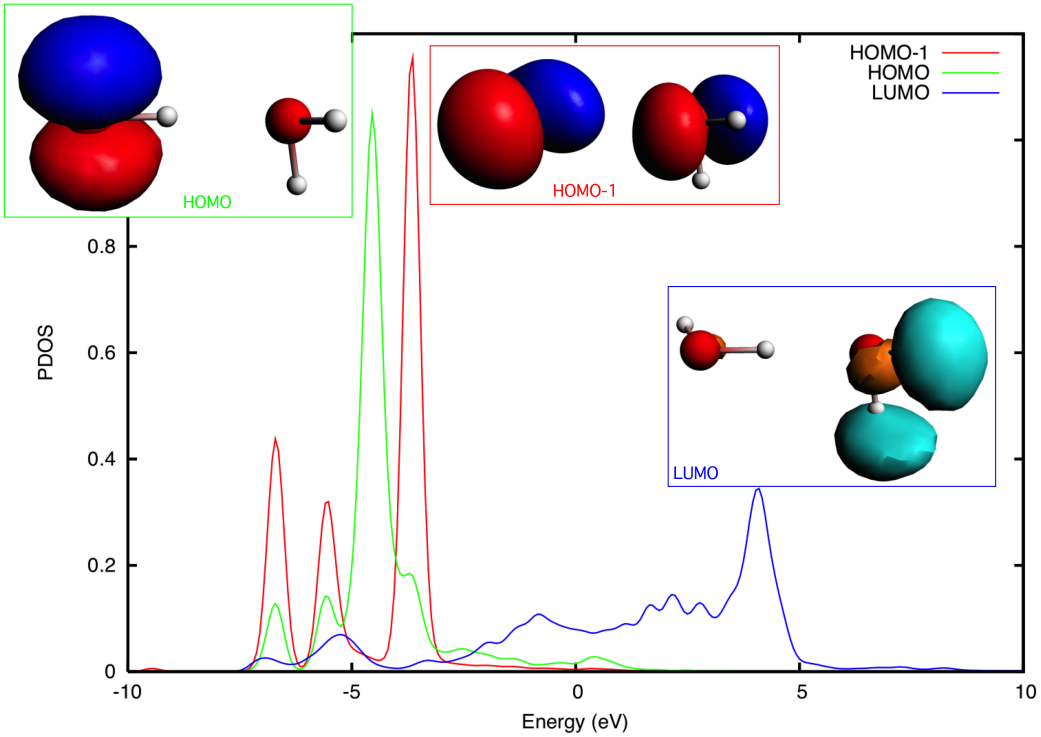

Fig. 1 Density of state of the water dimer adsorbed at a Rh(111) surface projected on the HOMO-1, the HOMO and the LUMO orbitals of the water dimer. The corresponding orbitals are represented close to the corresponding peak density: in green, left handside, the HOMO ; in red, middle, the HOMO ; in blue, right handside, the LUMO.