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

Supplementary Data

Hydrogen Adsorption on Various Transition Metal (111) Surfaces in Water: A DFT Forecast

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Figures

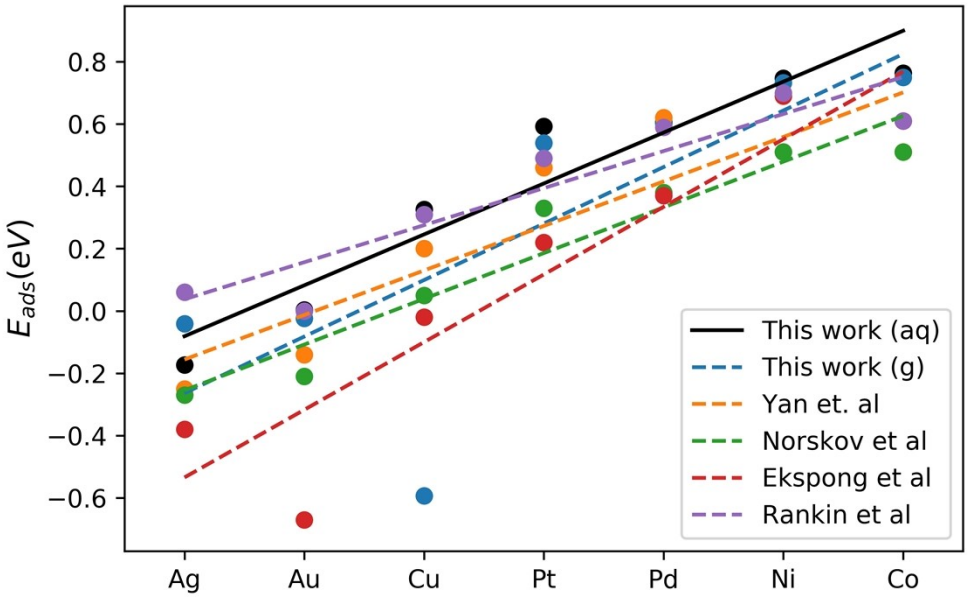


Figure S1: The adsorption-free energies of hydrogen on various metal (111) surfaces.

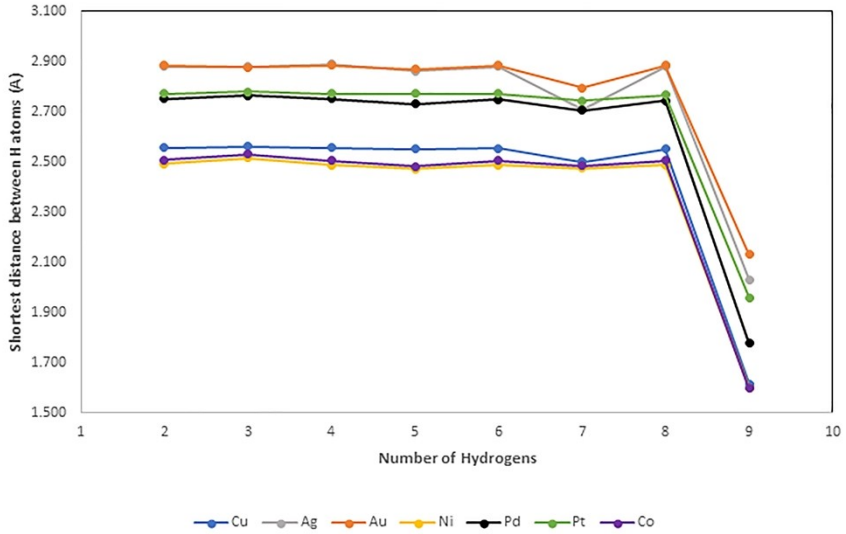


Figure S2: The shortest distance between hydrogen atoms (Å) on the M(111) under different surface coverage.

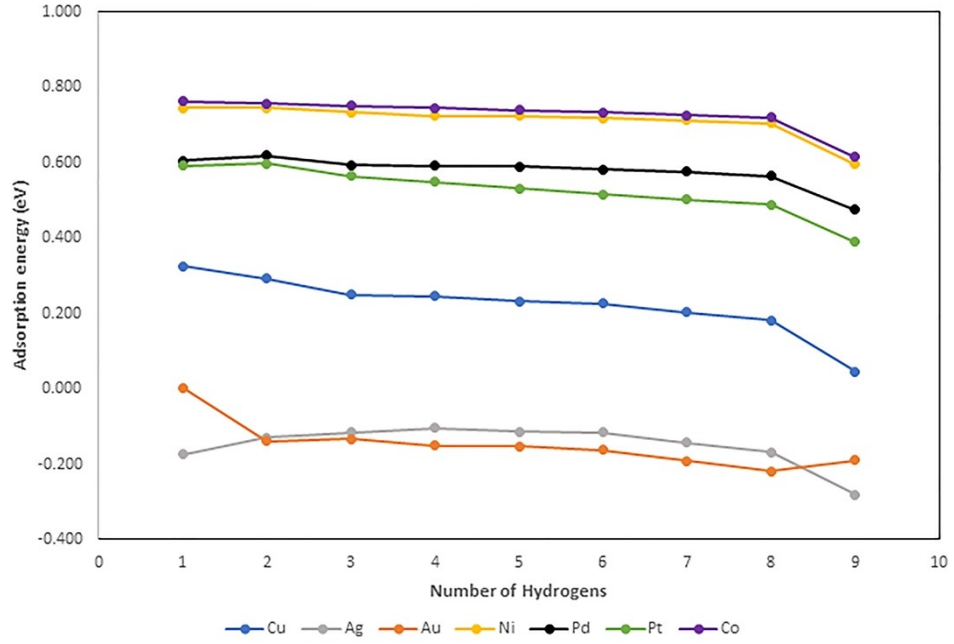


Figure S3: The adsorption energies (E_{ads}) of hydrogens on M(111) surface

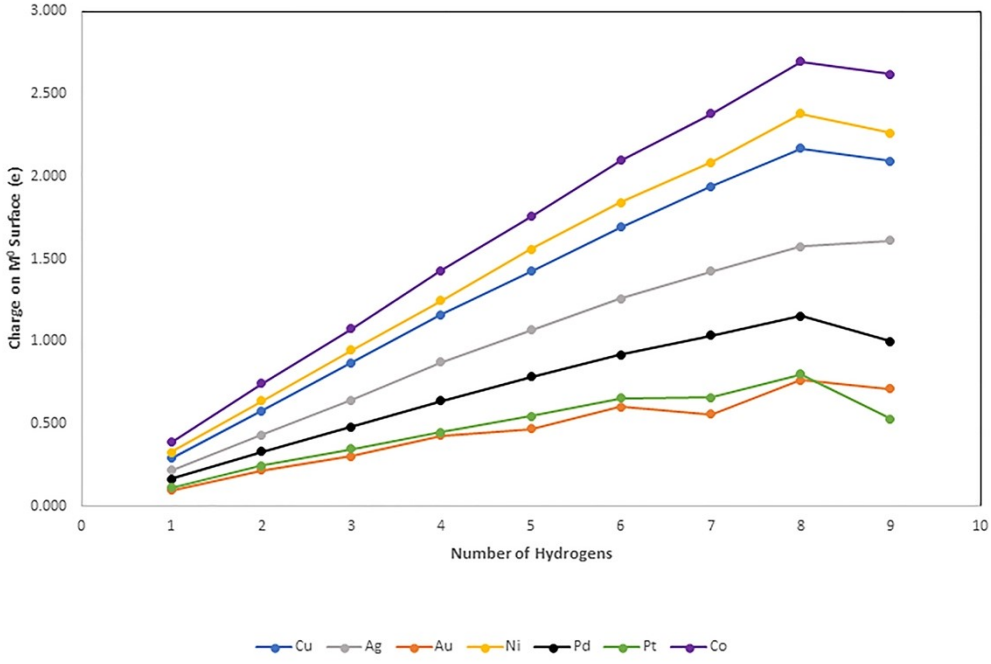


Figure S4: The charge on M(111) surface at different surface coverage of hydrogens.

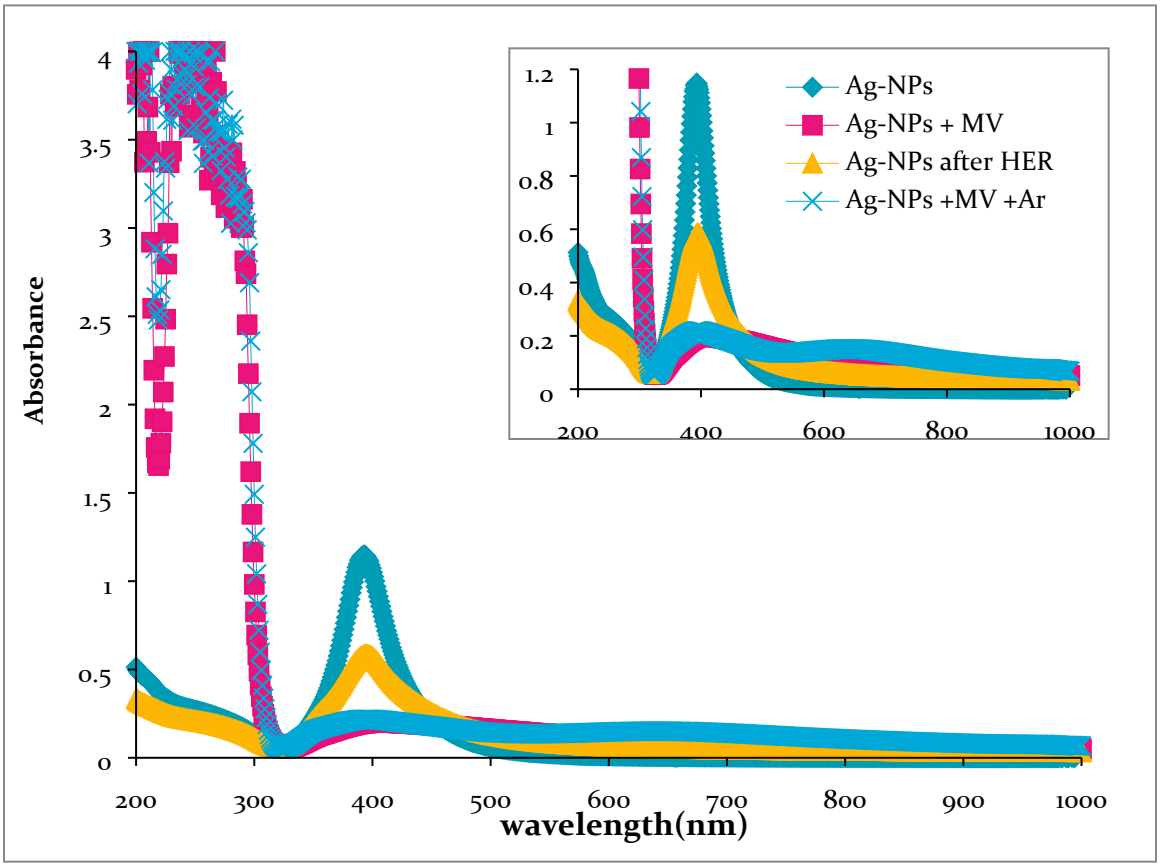


Figure S5: UV-Vis spectra of 3.8nm Ag^0-NPs ( ) Ag^0-NPs before HER, maximum absorption 395 ± 2 nm. ( ) Ag^0-NPs after HER, maximum absorption 394 ± 2 nm. ( ) Ag^0-NPs after HER with methyl-viologen, [MV]= 1mM. ( ) Ag^0-NPs after HER with methyl-viologen [MV]= 1mM in argon atmosphere, maximum absorption 637 ± 2 nm.

Tables

Table S1: Hydrogen binding energies (eV) on different adsorption sites on M(111) surface.

Metal	fcc	hcp	bridge	atop
Cu	3.09	3.09	2.96	2.53
Ag	3.16	3.18	3.05	2.79
Au	3.30	3.25	3.27	3.12
Ni	4.11	4.09	3.96	3.53
Pd	3.98	3.94	3.85	3.51
Pt	3.91	3.86	3.87	3.93
Co	4.12	4.12	3.99	3.60

Table S2: The binding energies of a hydrogen atom on the fcc site of M(111) surfaces

Metal	H binding energy (eV)[a]				TPD H_2 desorption measurements (K) [1–7]
	This research		Greeley et al.[8]	Ferrin et al.[9]	
	In Aqueous Phase	In Gas Phase			
Cu	3.49	2.59	2.39	2.45	200-220
Ag	2.99	3.14	2.08	2.12	180
Au	3.17	3.15	2.22	2.18	108-111
Ni	3.91	3.91	2.89	2.94	335-370
Pt	3.76	3.72	2.72	2.72	270-300
Pd	3.77	3.78	2.88	2.88	300
Co	3.93	3.93	2.89	-	-

Table S3: The ZPE (eV) values of the metal surface before and after the adsorption of hydrogen atom in aqueous and gaseous medium.

M	Surface ZPE (aq) (eV)		Surface ZPE (gas) (eV)	
	Pristine	After H adsorption	Pristine	After H adsorption
Cu	2.86	3.24	2.57	3.08
Ag	0.90	1.08	1.06	1.06
Au	0.82	0.97	0.93	0.93
Ni	1.67	1.67	1.67	1.67
Pt	1.46	1.49	1.33	1.36
Pd	1.80	1.75	1.64	1.60
Co	1.70	1.71	1.69	1.69

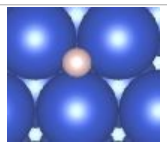
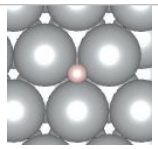
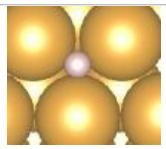
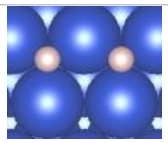
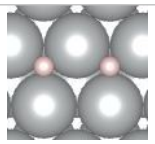
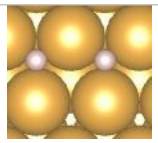
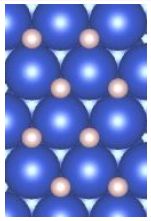
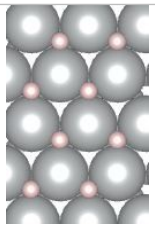
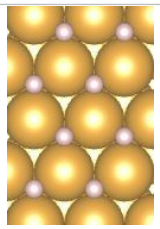
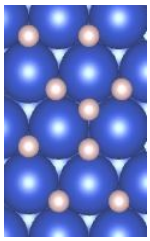
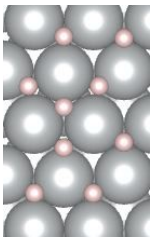
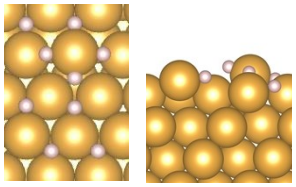
Table S4: The hydrogen binding energies and charge on H atoms with and without the presence of a co-adsorbed H_2O molecule.

M	H^* alone		H^* in presence of H_2O^*	
	H^* B.E (eV)	Charge on H^*	H^* B.E (eV)	Charge on H^*
Cu	3.49	-0.29	3.46	-0.30
Ag	2.99	-0.22	3.13	-0.22
Au	3.17	-0.10	3.14	-0.07
Ni	3.91	-0.33	3.90	-0.33
Pd	3.77	-0.16	3.79	-0.15
Pt	3.76	-0.12	3.72	-0.12
Co	3.93	-0.39	3.93	-0.38

Table S5: Charge on adsorbed hydrogen on a neutral and charged surface, Q is the charge of the surface.

M	Q = 0	Q = -1	Q = +1
Cu	-0.29	-0.33	-0.27
Ag	-0.22	-0.24	-0.20
Au	-0.10	-0.10	-0.07
Ni	-0.33	-0.36	-0.30
Pd	-0.16	-0.19	-0.15
Pt	-0.12	-0.14	-0.10
Co	-0.39	-0.42	-0.35

Table S6: The optimized geometries (top view*) of hydrogen adsorbed on Ag(111), Au(111) and Cu(111) surface.

No. of Hydrogens	Cu(111)	Ag(111)	Au(111)
1			
2			
8			
9			

*** In the last row a side view is given for Au, to show the deformation of Au(111) in 9/8 coverage ratio.**

Table S7: The optimized geometries of hydrogen adsorbed on Co(111), Ni(111), Pd(111) and Pt(111) surface.

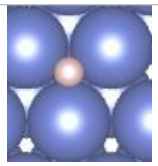
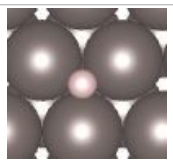
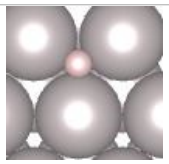
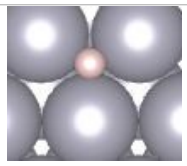
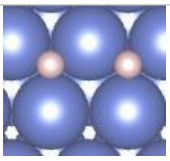
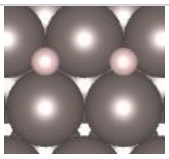
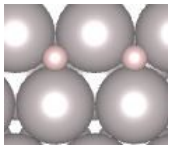
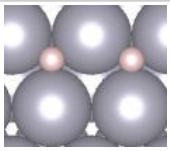
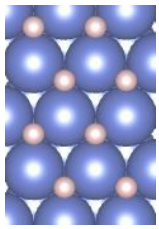
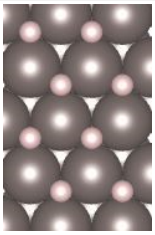
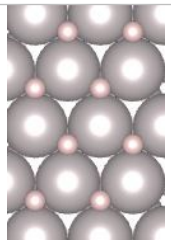
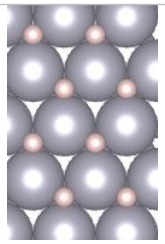
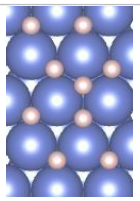
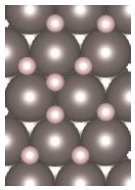
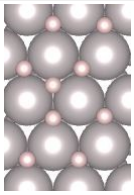
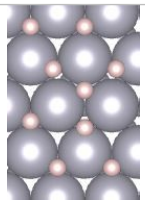
No. of Hydrogens	Co(111)	Ni(111)	Pd(111)	Pt(111)
1				
2				
8				
9				

Table S8: $^{\Delta G_{H_2(aq)}}$ ***values on neutral and charged M(111) surfaces, Q is the charge of the surface.***

M	No. of Hydrogens	$^{\Delta G_{H_2(aq)}}$ (eV)	
		Q = 0	Q = -1
Cu	8	0.09	0.10
	9	-1.02	-1.13
Ag	9	-1.52	-1.60
Au	7	-0.58	-0.60
Ni	9	0.37	0.25
	10	-0.61	-0.78
Pd	9	0.25	0.14
	10	-0.45	-0.66

Pt	8	0.82	0.73
	9	0.00	-0.09
Co	9	0.46	0.38
	10	-0.28	-0.39

Table S9: The E_a barriers for the H_2 evolution from M(111) surfaces at 10/8 ML coverage.

M(111)	**E_a (eV)**	
	Q = 0	**Q = -1**
Pd	0.36	0.34
Ni	0.38	0.43
Co	0.26	0.32

Table S10: The E_a barriers (eV) for the H_2 dissociation and formation from M(111) surfaces at 2/8 ML coverage: * +$H_{2(aq)}$ → 2*H

M	**H_2 dissociation barriers**	**H_2 formation barrier**
Cu	0.29	0.94[a]
Ag	1.13[a]	0.79
Au	0.64[a]	0.65
Ni	0.18	1.04[a]
Pd	0.00	1.19[a]
Pt	0.00	1.45[a]
Co	0.00	1.67[a]

[a] *These reactions are endergonic.*

VASP INCAR File

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EDIFF = 1E-04
ISMEAR = 1
NELM = 120
IVDW = 1          #dispersion correction
LSOL = .TRUE.     #solvation

#Ionic Relaxation
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NSW = 150
ISIF = 2

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NFREE = 2
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NSW = 1

#DOS calculation (changes and additions in the INCAR)
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References

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679–689. https://doi.org/10.1016/j.susc.2011.12.017.