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Supporting Information: Adsorption of Water and Ethanol on Noble and Transition-Metal Substrates: A Density Functional Investigation within van der Waals Corrections

Rafael L. H. Freire,[†] Adam Kiejna,[‡] and Juarez L. F. Da Silva[*,¶]

São Carlos Institute of Physics, University of São Paulo, PO Box 369, 13560-970, São Carlos, SP, Brazil, Institute of Experimental Physics, University of Wrocław, Plac M. Borna 9, 50-204 Wrocław, Poland, and São Carlos Institute of Chemistry, University of São Paulo, PO Box 780, 13560-970, São Carlos, SP, Brazil

E-mail: juarez_dasilva@iqsc.usp.br

[*]To whom correspondence should be addressed
[†]University of São Paulo
[‡]University of Wrocław
[¶]University of São Paulo

I Extra Results and Analysis

Table 1: Equillibrium lattice constant (a_0), in Å, for the transition metals Cu, Pt and Au. In parenthesis we show the deviation from experimental results.[1]

Bulk	PBE		PBE+D3	
Cu	3.63	(0.55 %)	3.56	(−1.39 %)
Pt	3.97	(1.28 %)	3.92	(0.00 %)
Au	4.15	(1.72 %)	4.10	(0.49 %)

Table 2: Geometric parameters of ethanol molecule in the gas phase. We presented the bond lengths and angles for the molecule atoms calculated using PBE and PBE+D3. Some results are compared with experimental. The atoms in molecule are labeled in accordance with Fig. 1.

	Ethanol distances (Å)								
	Isomer	C^1–C^2	C^1–O	O–H^1	C^1–H^5	C^1–H^6	C^2–H^2	C^2–H^3	C^2–H^4
PBE	Anti	1.52	1.44	0.97	1.11	1.11	1.10	1.10	1.10
PBE+D3		1.52	1.44	0.97	1.11	1.11	1.10	1.10	1.10
PBE	Gauche	1.52	1.43	0.97	1.10	1.11	1.10	1.10	1.10
PBE+D3		1.52	1.43	0.97	1.10	1.11	1.10	1.10	1.10
Expt.		1.51	1.43	0.97	1.10	1.10	1.09	1.09	1.09

	Ethanol angles (°)							
	Isomer	$H^1O^1C^1$	$O^1C^1C^2$	$H^5C^1O^1$	$H^6C^1O^1$	$H^5C^1H^6$	$H^5C^1C^2$	$H^6C^1C^2$
PBE	Anti	108.36	108.03	110.42	110.42	107.67	110.16	110.16
PBE+D3		108.53	107.79	110.51	110.51	107.65	110.19	110.19
PBE	Gauche	108.05	113.10	104.86	110.58	107.17	110.50	110.34
PBE+D3		108.05	113.10	104.86	110.58	107.17	110.50	110.34
	Isomer	$C^1C^2H^2$	$C^1C^2H^3$	$C^1C^2H^4$	$H^2C^2H^3$	$H^2C^2H^4$	$H^3C^2H^4$	
PBE	Anti	110.27	110.67	110.67	108.44	108.44	108.27	
PBE+D3		110.48	110.57	110.57	108.46	108.46	108.21	
PBE	Gauche	110.64	110.86	111.15	108.39	107.45	108.22	
PBE+D3		110.64	110.86	111.15	108.39	107.45	108.22	

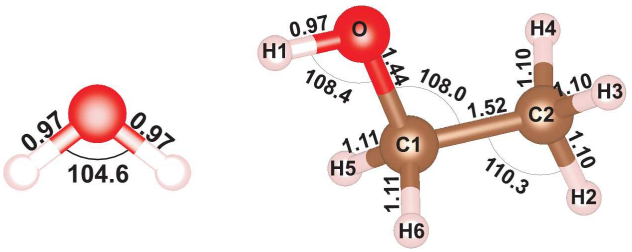

Figure 1: (a) Water and (b) ethanol geometric properties and definitions evaluated in the gas phase using PBE. Additional measurements for ethanol are presented in Table 2.

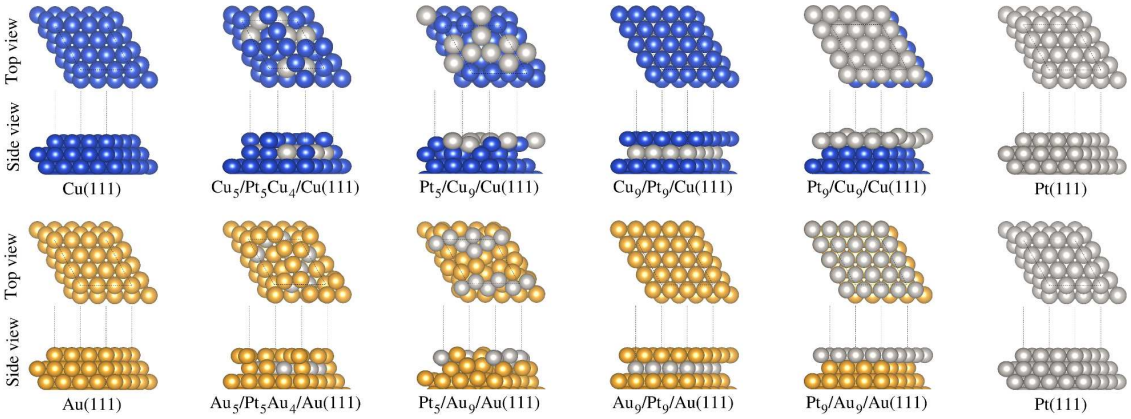

Figure 2: Close-packed, Cu(111), Pt(111), Au(111), defected, Cu_5/Pt_5Cu_4/Cu(111), Pt_5/Cu_9/Cu(111), Au_5/Pt_5Au_4/Au(111), Pt_5/Au_9/Au(111), and Pt-strained, Cu_9/Pt_9/Cu(111), Pt_9/Cu_9/Cu(111), Au_9/Pt_9/Au(111), Pt_9/Au_9/Au(111), lowest energy substrates for PBE+D3.

Table 3: Water adsorption properties for all lowest energy configurations. E_{ad}, in meV, is the adsorption energy, $d_{\mathrm{O-TM}}$, in Å, is the distance between O from molecules and its TM nearest neighbor in the surface, which is showed in parentheses (TM). Δ_{O}, in Å, is the lateral displacement of the O atoms from the nearest TM on-top site. β, in degrees, is the angle between O−H bonds and the substrate surface, the two O−H bonds are presented. Negative angle indicates the O−H bond orientation towards to the surface, while positive is oriented outwards. All parameters are defined in the main text.

Water/Substrate	E_{ad}^{PBE}	$E_{ad}^{\mathrm{PBE+D3}}$	$d_{\mathrm{O-TM}}^{\mathrm{PBE}}$	$d_{\mathrm{O-TM}}^{\mathrm{PBE+D3}}$	β^{PBE}	$\beta^{\mathrm{PBE+D3}}$	$\Delta_{\mathrm{O}}^{\mathrm{PBE}}$	$\Delta_{\mathrm{O}}^{\mathrm{PBE+D3}}$
$Cu_9/Cu_9/Cu(111)$	−185	−433	2.35 (Cu)	2.34 (Cu)	8.34	3.12	0.05	0.20
					9.30	2.87		
$Pt_9/Pt_9/Pt(111)$	−271	−500	2.37 (Pt)	2.36 (Pt)	6.08	3.88	0.14	0.19
					6.10	5.01		
$Au_9/Au_9/Au(111)$	−106	−303	2.84 (Au)	2.88 (Au)	1.04	−10.15	0.21	0.78
					0.34	−8.24		
$Cu_5/Pt_5Cu_4/Cu(111)$	−450	−992	2.15 (Cu)	2.16 (Cu)	−23.80	−30.28	1.74	1.89
					−14.69	−18.72		
$Pt_5/Cu_9/Cu(111)$	−458	−587	2.28 (Pt)	2.22 (Cu)	−18.52	18.69	2.05	0.95
					−18.18	−18.27		
$Au_5/Pt_5Au_4/Pt(111)$	−253	−538	2.56 (Au)	2.60 (Au)	−40.54	−37.07	2.13	2.30
					−9.42	−20.30		
$Pt_5/Au_9/Pt(111)$	−572	−832	2.25 (Pt)	2.23 (Pt)	−2.56	−7.90	1.76	1.79
					−24.64	−22.99		
$Cu_9/Pt_9/Cu(111)$	−181	−429	2.30 (Cu)	2.32 (Cu)	8.78	1.36	0.08	0.39
					9.99	1.09		
$Pt_9/Cu_9/Cu(111)$	−91	−348	2.95 (Pt)	2.95 (Pt)	−3.75	−4.76	0.13	0.08
					−3.53	−3.36		
$Au_9/Pt_9/Pt(111)$	−134	−346	2.75 (Au)	2.73 (Au)	6.88	−2.70	0.07	0.62
					6.84	−7.03		
$Pt_9/Au_9/Pt(111)$	−319	−526	2.35 (Pt)	2.36 (Pt)	1.77	1.94	0.34	0.31
					2.14	2.16		

Table 4: Ethanol adsorption properties for all lowest energy configurations. The parameters E_{ad}, $d_{\mathrm{O-TM}}$ and $\Delta_{\mathbf{O}}$ are given as in Table 3. α, in degrees, is the angle between the C−C bond and substrate surface considered. Negative angles indicate a C−C bond oriented towards to the surface, where $\mathbf{C^2}$ is closer to the surface than $\mathbf{C^1}$ (see Figure 1). Positive angles indicate the opposite.

Ethanol/Substrate	E_{ad}^{PBE}	$E_{ad}^{\mathrm{PBE+D3}}$	$d_{\mathrm{O-TM}}^{\mathrm{PBE}}$	$d_{\mathrm{O-TM}}^{\mathrm{PBE+D3}}$	α^{PBE}	$\alpha^{\mathrm{PBE+D3}}$	$\Delta_{\mathrm{O}}^{\mathrm{PBE}}$	$\Delta_{\mathrm{O}}^{\mathrm{PBE+D3}}$
$Cu_9/Cu_9/Cu(111)$	−185	−723	2.31 (Cu)	2.31 (Cu)	75.19	7.05	0.19	0.29
$Pt_9/Pt_9/Pt(111)$	−305	−875	2.33 (Pt)	2.33 (Pt)	73.99	9.55	0.20	0.28
$Au_9/Au_9/Au(111)$	−114	−559	2.79 (Au)	2.78 (Au)	74.99	7.18	0.20	0.19
$Cu_5/Pt_5Cu_4/Cu(111)$	−468	−1277	2.13 (Cu)	2.14 (Cu)	32.10	18.88	1.42	1.54
$Pt_5/Cu_9/Cu(111)$	−866	−799	2.49 (Pt)	2.16 (Cu)	73.21	−1.15	0.26	1.09
$Au_5/Pt_5Au_4/Pt(111)$	−222	−862	2.49 (Au)	2.82 (Au)	−0.15	23.00	0.28	0.67
$Pt_5/Au_9/Pt(111)$	−619	−1264	2.21 (Pt)	2.20 (Pt)	58.39	39.90	1.59	1.76
$Cu_9/Pt_9/Cu(111)$	−179	−725	2.29 (Cu)	2.28 (Cu)	75.82	9.77	0.22	0.33
$Pt_9/Cu_9/Cu(111)$	−97	−677	3.00 (Pt)	2.98 (Pt)	10.71	2.99	0.12	0.69
$Au_9/Pt_9/Pt(111)$	−153	−627	2.66 (Au)	2.62 (Au)	77.35	6.15	0.16	0.39
$Pt_9/Au_9/Pt(111)$	−360	−892	2.32 (Pt)	2.30 (Pt)	77.21	6.31	0.20	0.35

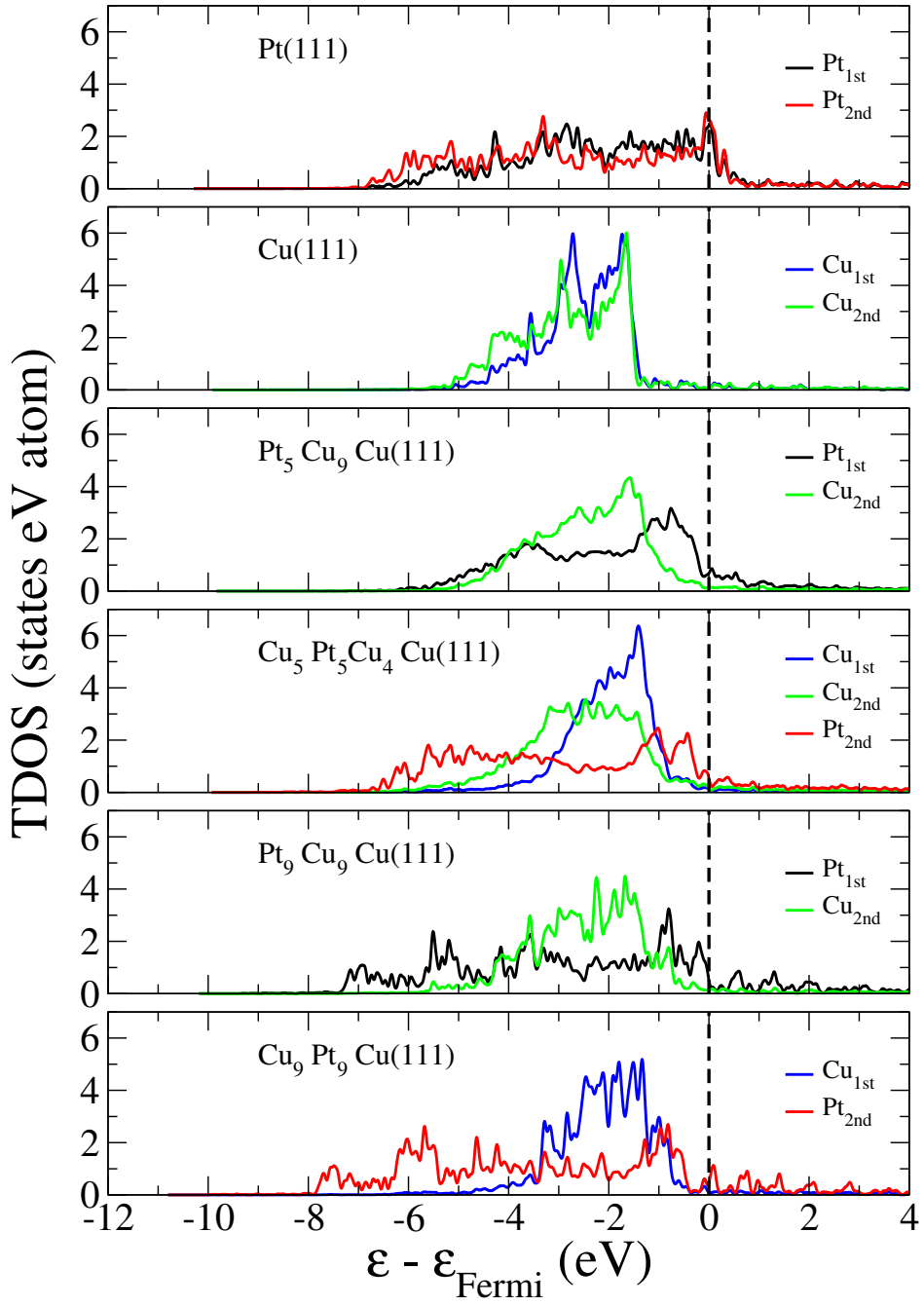

Figure 3: Local density of states for Pt/Cu(111) substrates calculated using PBE. Here and in the following figures, the indices "1st" and "2nd" indicate species which lie in one or two of the two outermost substrate layers, where "1st" is the topmost substrate layer and "2nd" is the underlying layer.

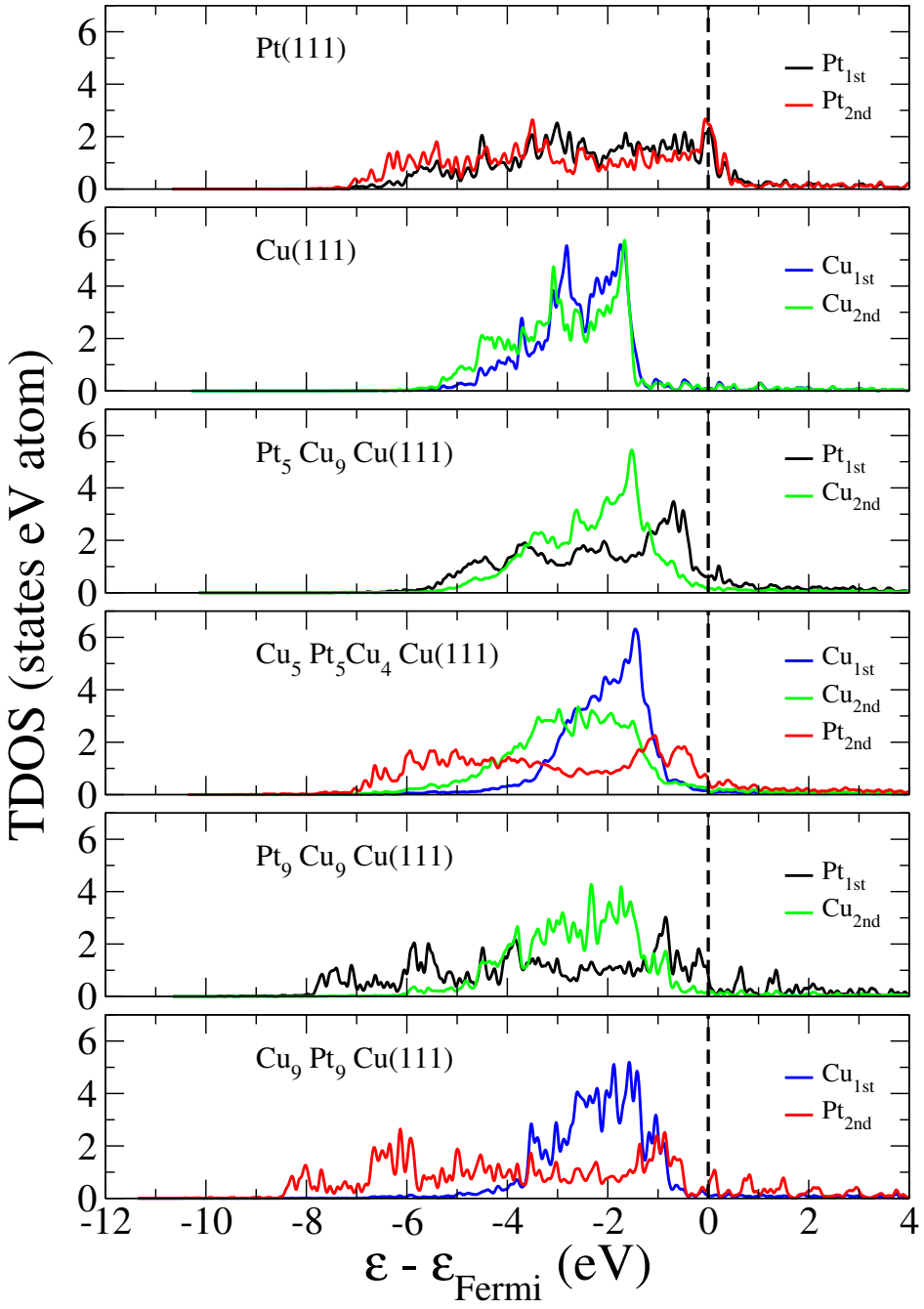

Figure 4: Local density of states for Pt/Cu(111) substrates calculated using PBE+D3.

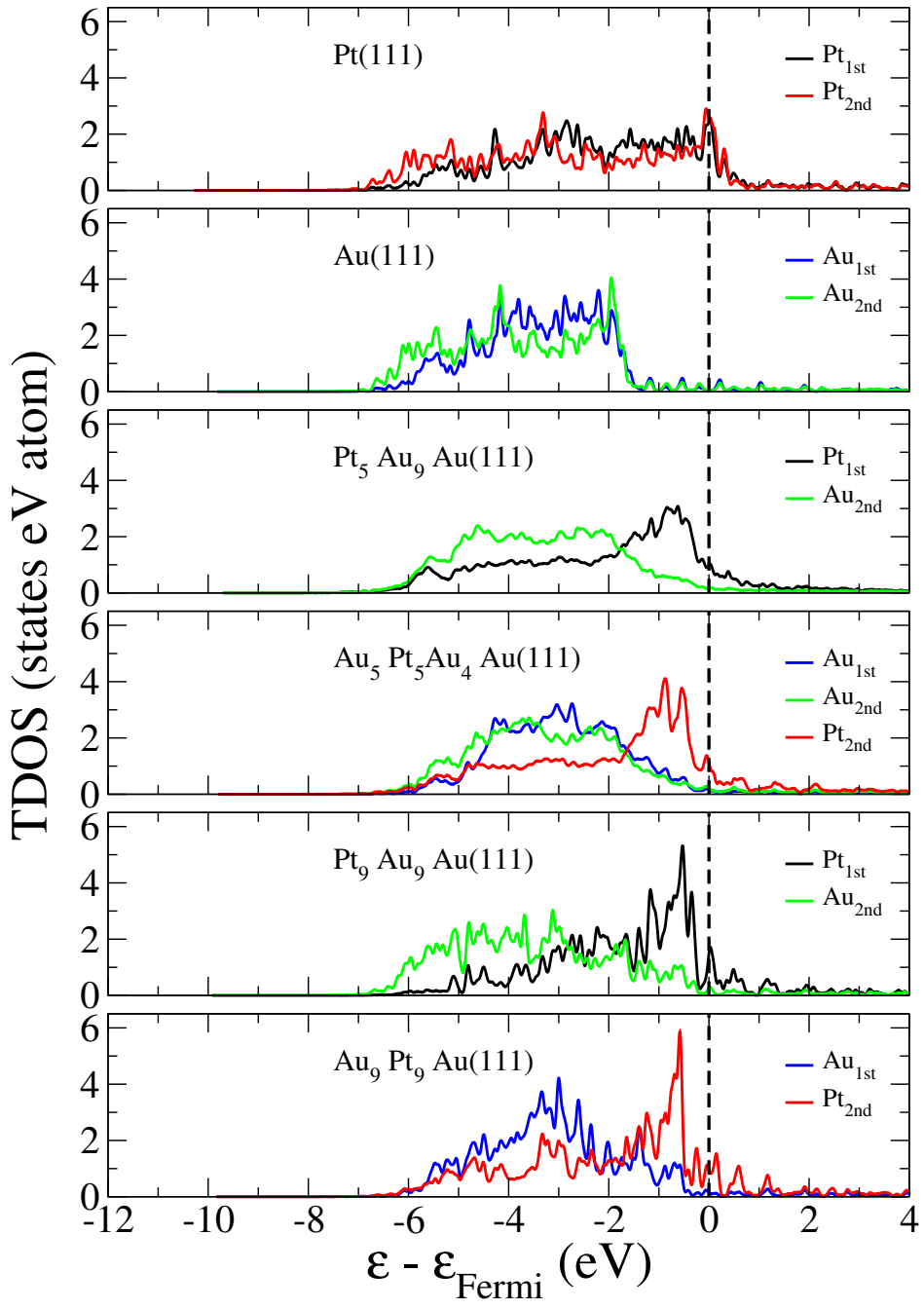

Figure 5: Local density of states for Pt/Au(111) substrates calculated using PBE.

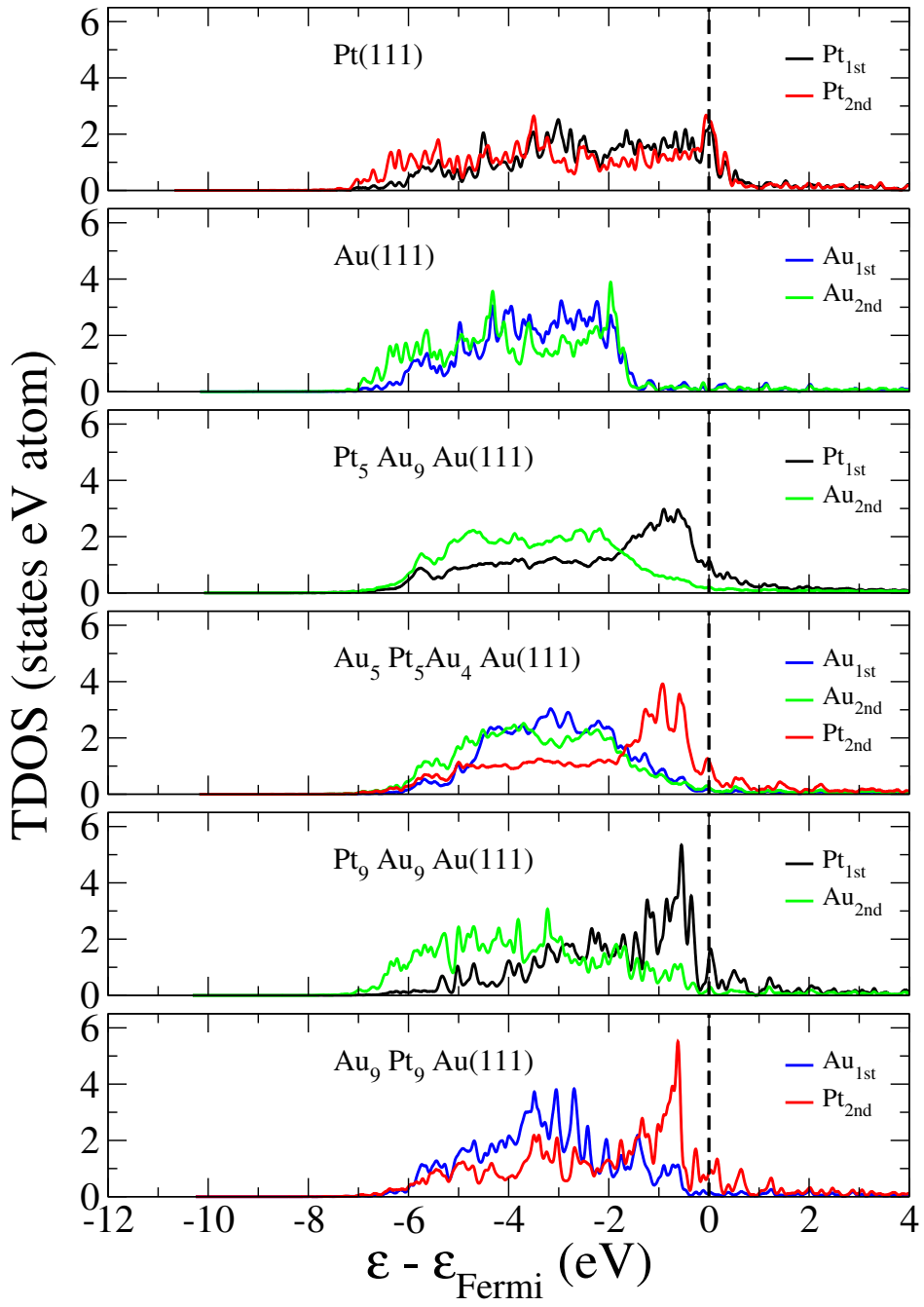

Figure 6: Local density of states for Pt/Au(111) substrates calculated using PBE+d3.

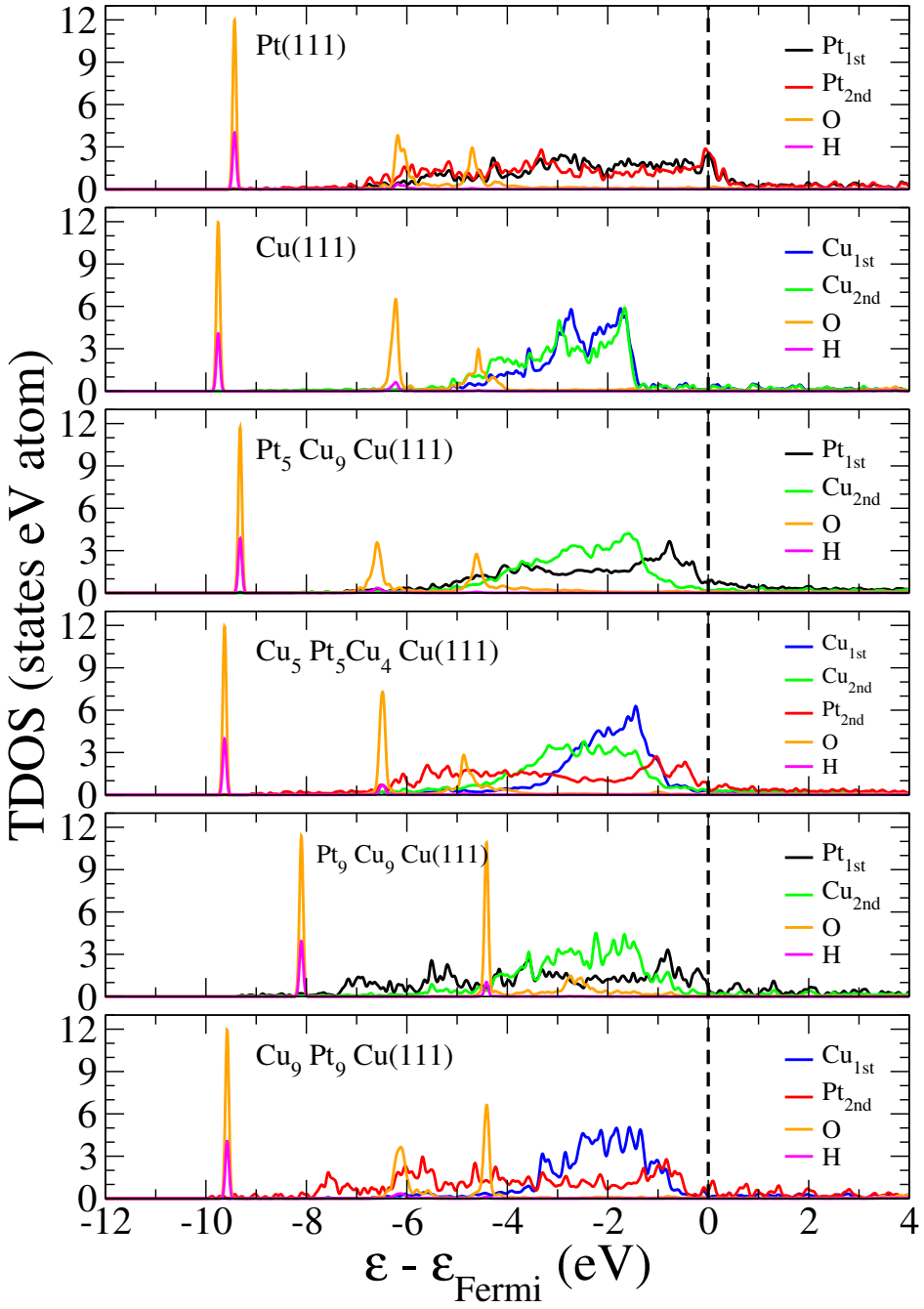

Figure 7: Total density of states for water adsorbed on Pt/Cu(111) substrates calculated using PBE.

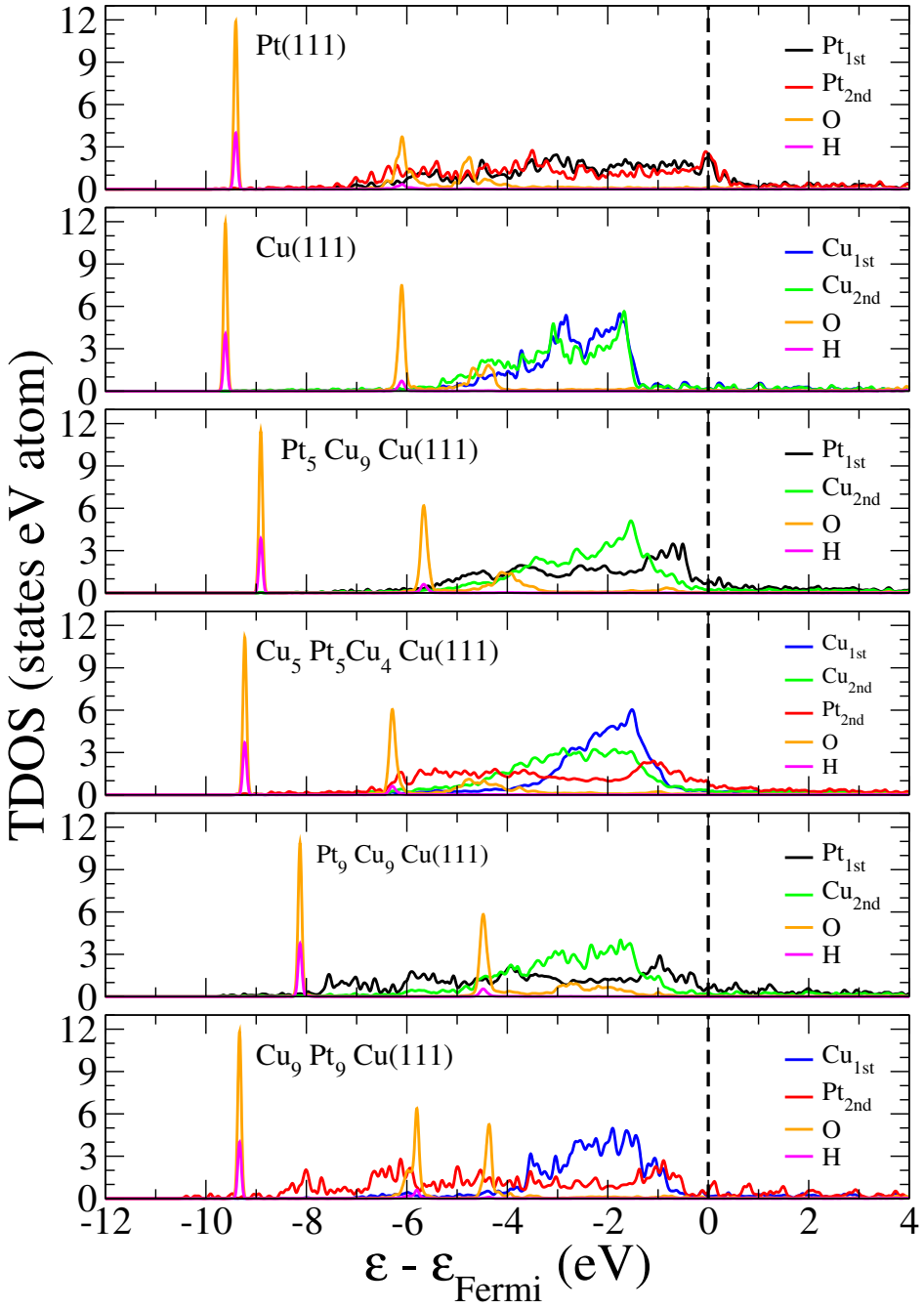

Figure 8: Total density of states for water adsorbed on Pt/Cu(111) substrates calculated using PBE+D3.

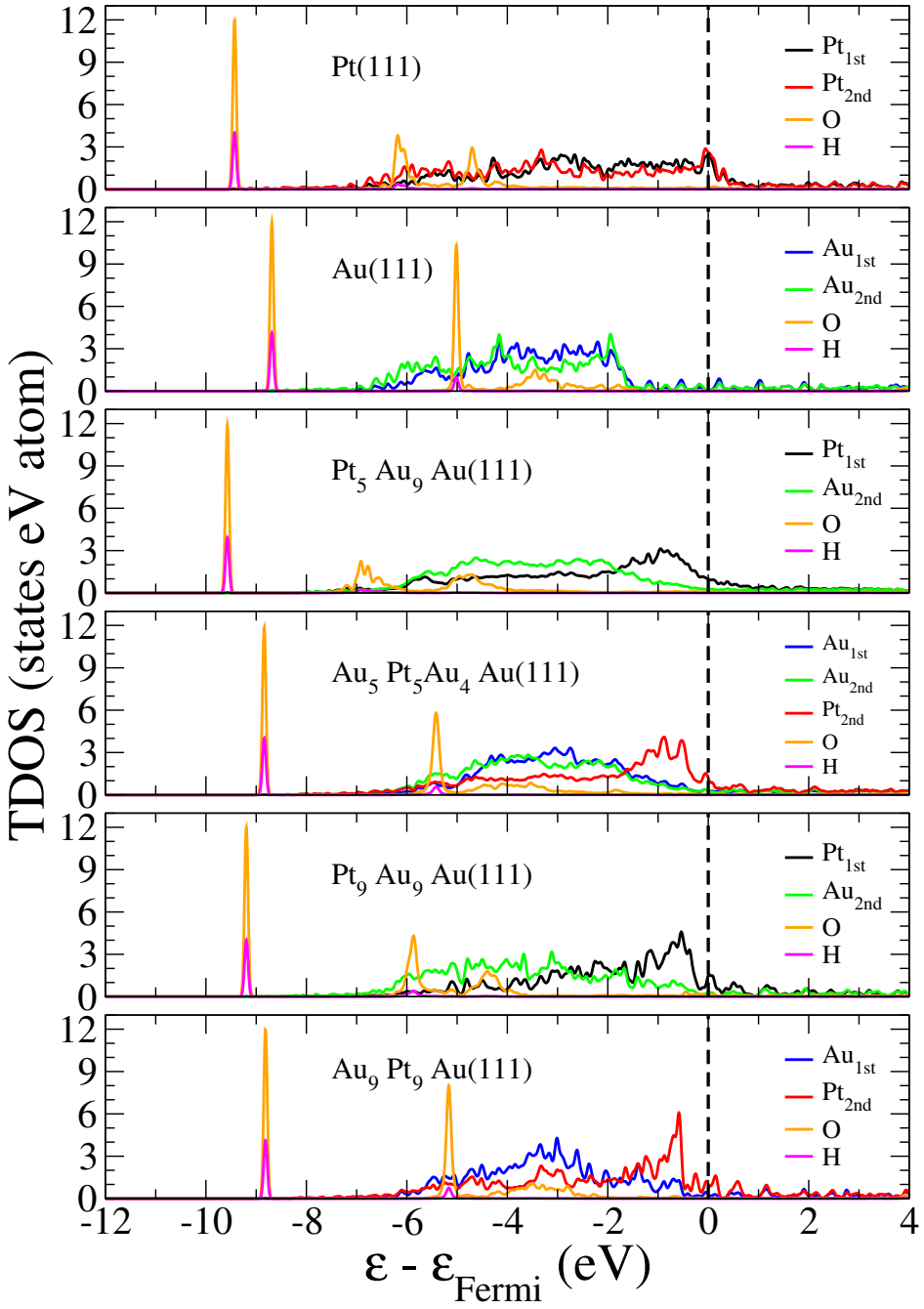

Figure 9: Total density of states for water adsorbed on Pt/Au(111) substrates calculated using PBE.

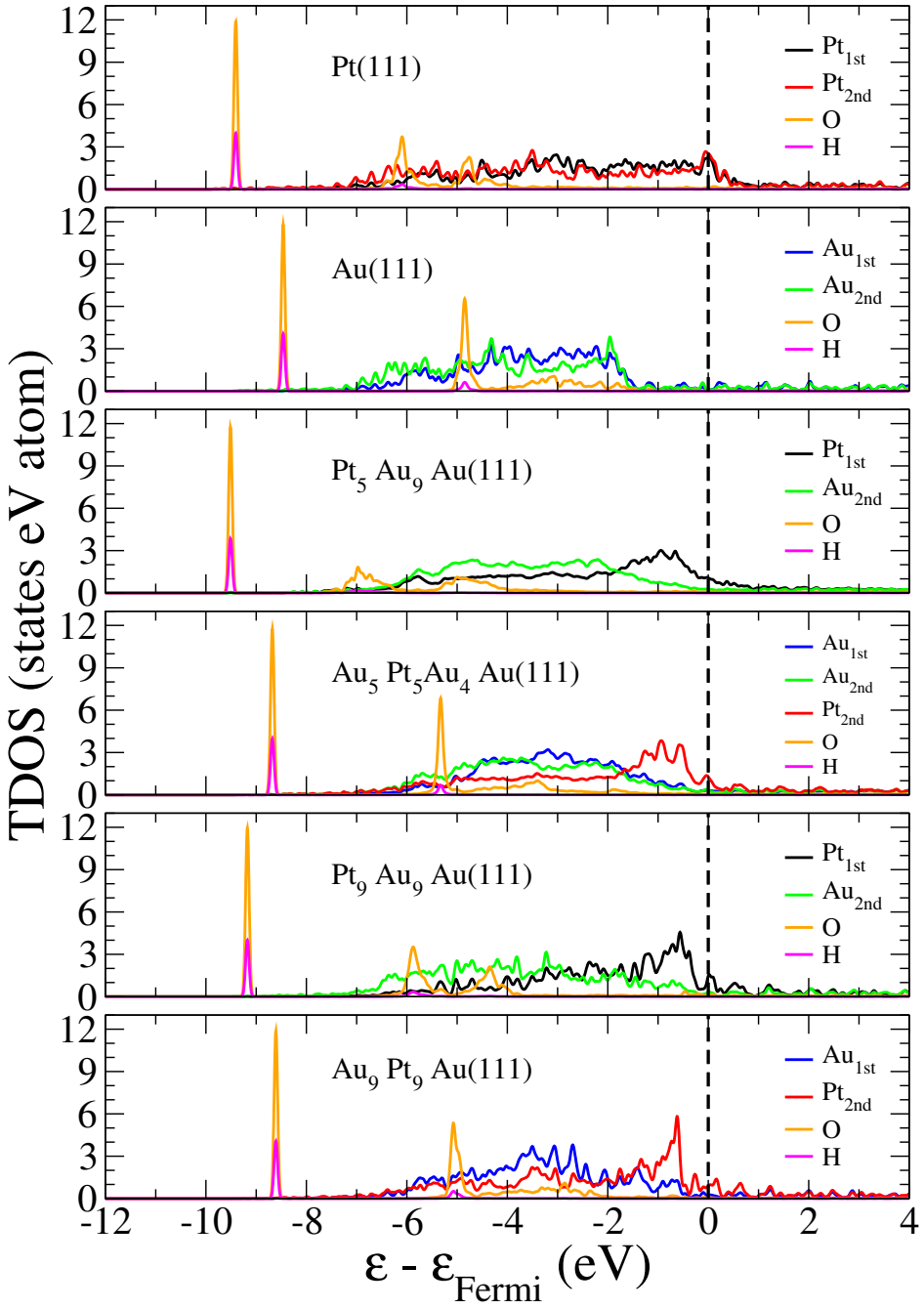

Figure 10: Total density of states for water adsorbed on Pt/Au(111) substrates calculated using PBE+D3.

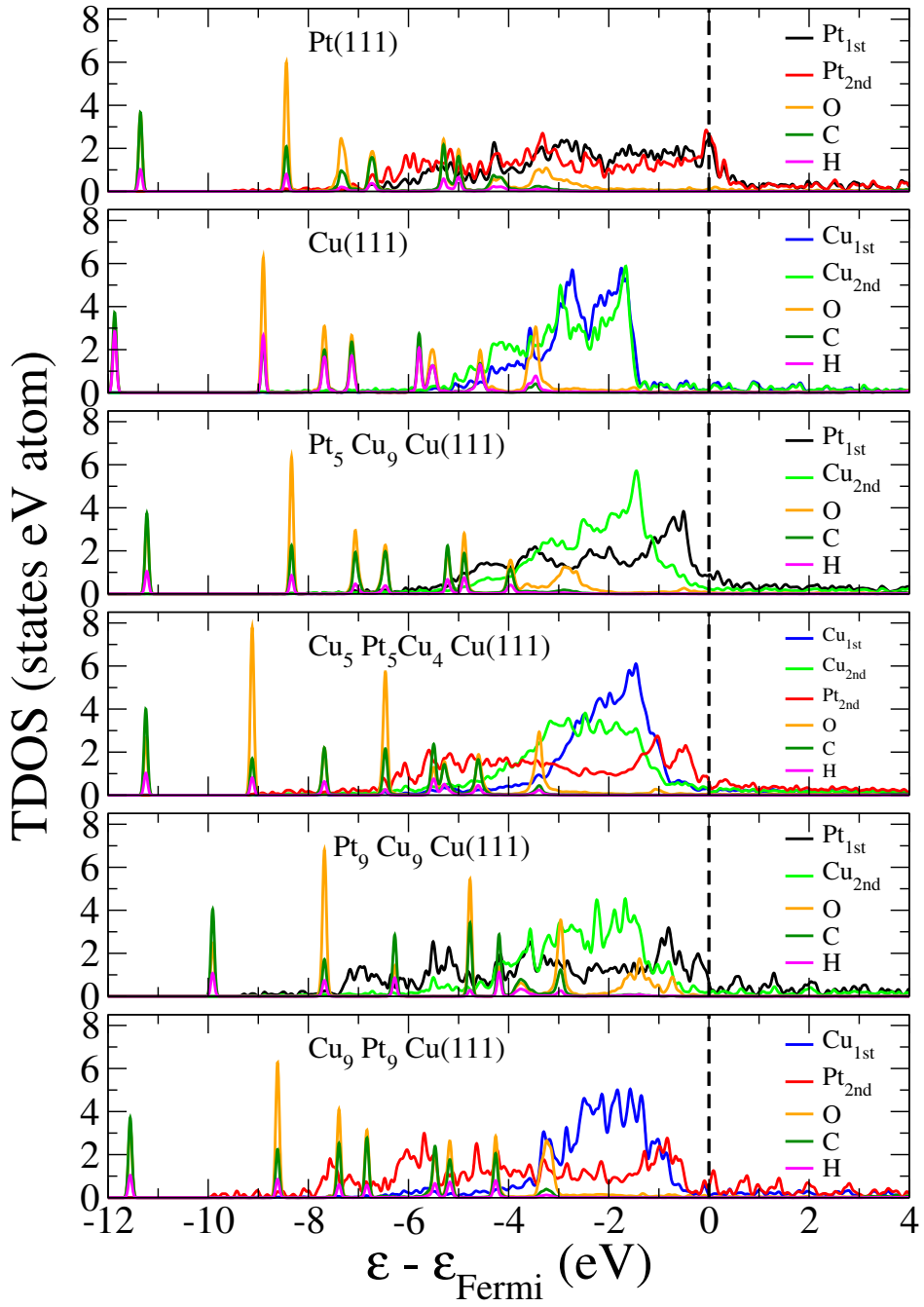

Figure 11: Total density of states for ethanol adsorbed on Pt/Cu(111) substrates calculated using PBE.

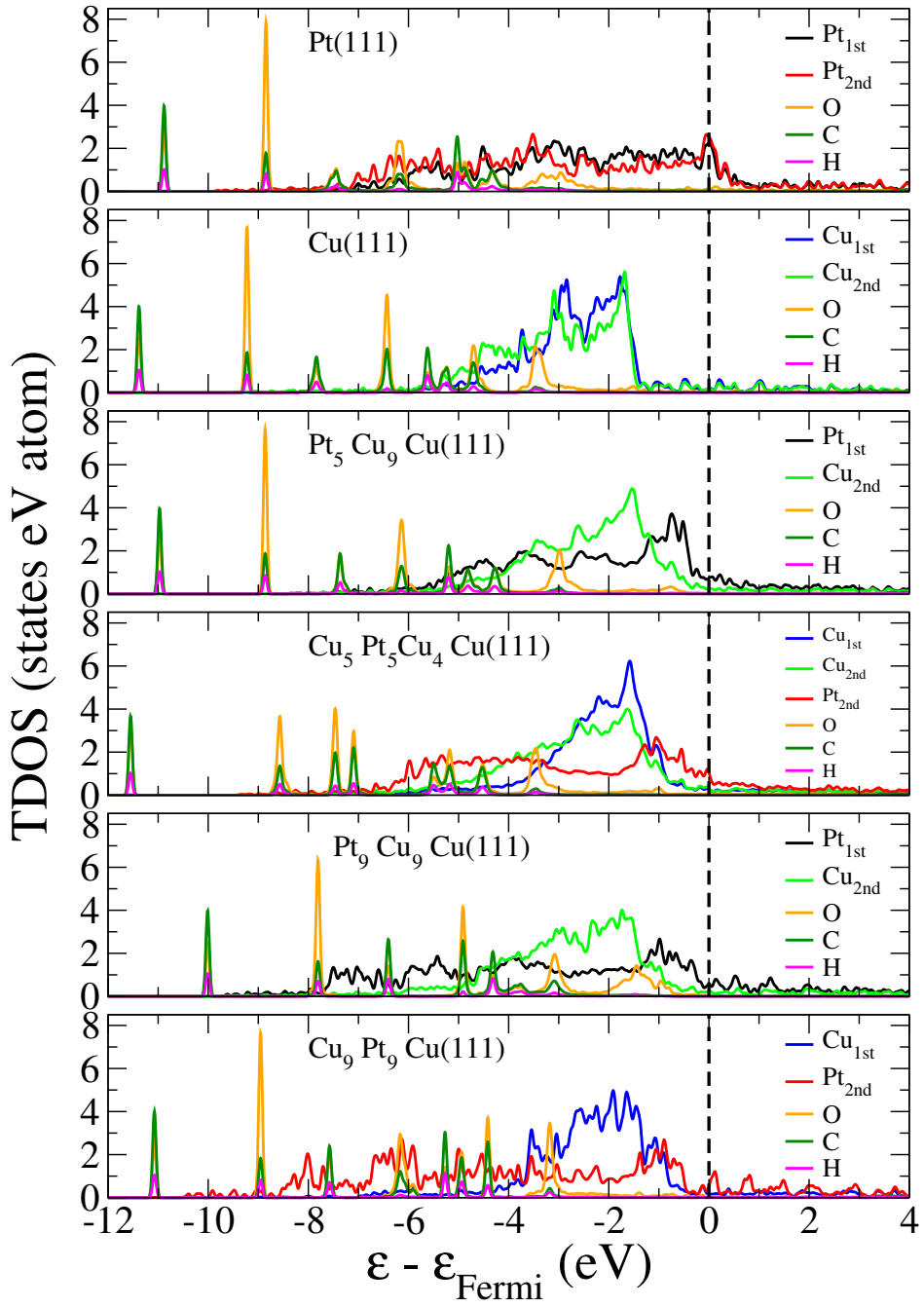

Figure 12: Total density of states for ethanol adsorbed on Pt/Cu(111) substrates calculated using PBE+D3.

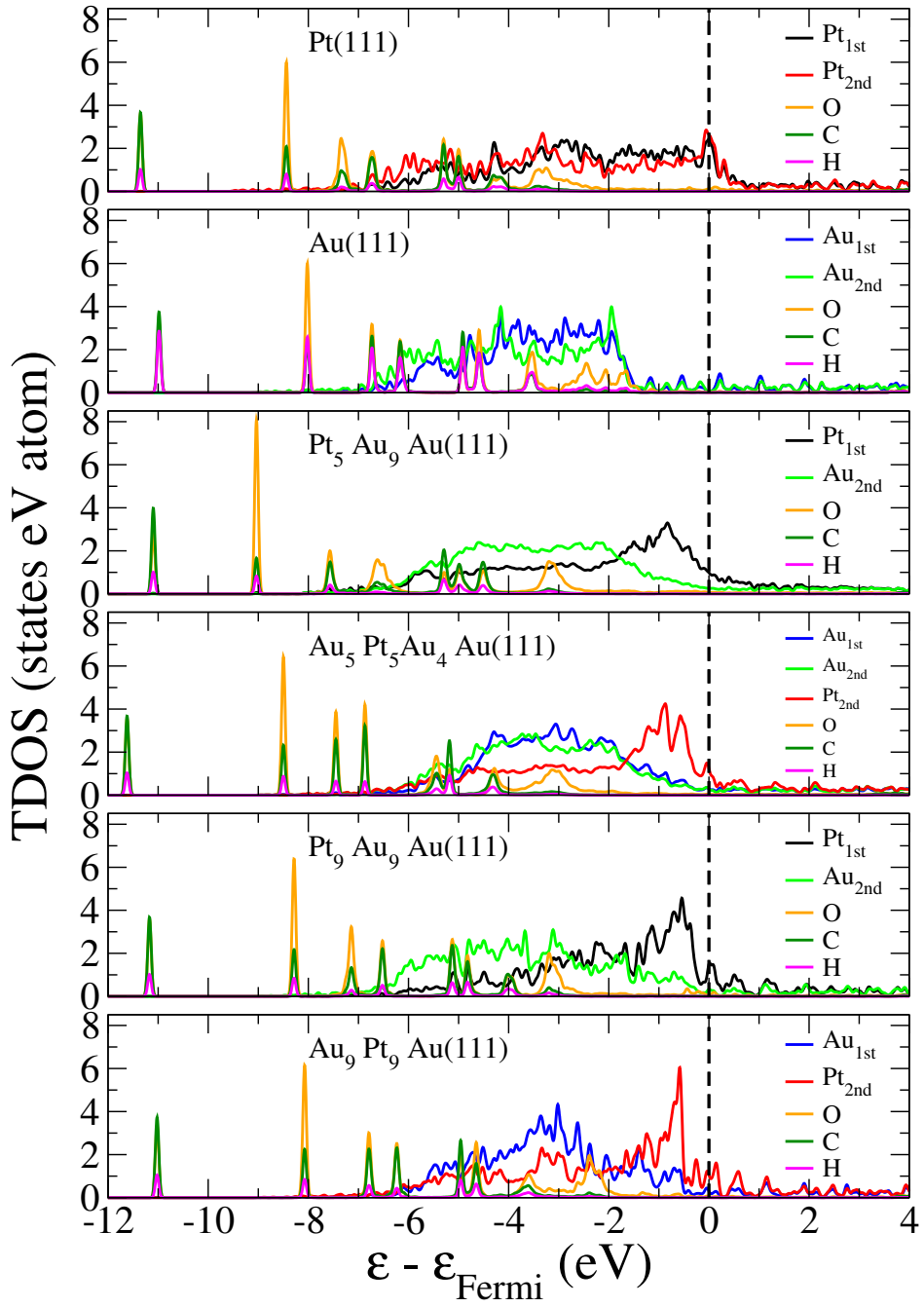

Figure 13: Total density of states for ethanol adsorbed on Pt/Au(111) substrates calculated using PBE.

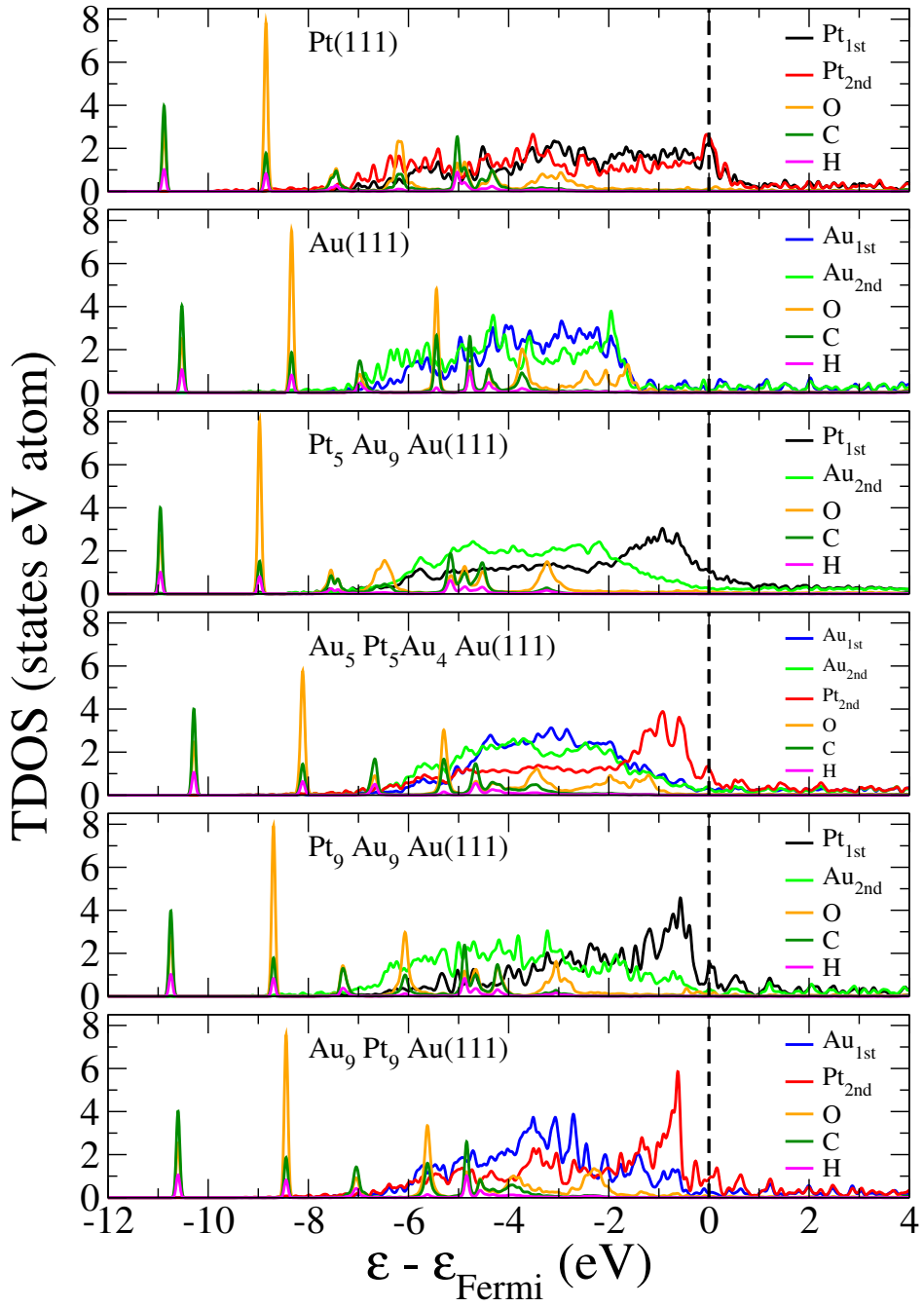

Figure 14: Total density of states for ethanol adsorbed on Pt/Au(111) substrates calculated using PBE+D3.

II Bader Analysis

Table 5: Bader charge analysis for water adsorbed systems. The main atoms affected by the adsorption are presented. The Q_M charge is the charge of the transition metal from the surface which is the O nearest neighbor, and whose specie is indicated in parenthesis. All charges are in e units.

Water/Substrate	Q_O^{PBE}	Q_O^{vdW}	$Q_{H_1}^{PBE}$	$Q_{H_1}^{vdW}$	$Q_{H_2}^{PBE}$	$Q_{H_2}^{vdW}$	Q_M^{PBE}	Q_M^{vdW}
Free-molecule	−1.19	−1.19	0.59	0.59	0.60	0.60		
$Cu_9/Cu_9/Cu(111)$	−1.23	−1.21	0.62	0.61	0.62	0.61	0.11 (Cu)	0.11 (Cu)
$Pt_9/Pt_9/Pt(111)$	−1.15	−1.15	0.62	0.62	0.63	0.62	0.08 (Pt)	0.08 (Pt)
$Au_9/Au_9/Au(111)$	−1.18	−1.17	0.60	0.60	0.60	0.59	0.03 (Au)	0.03 (Au)
$Cu_5/Pt_5Cu_4/Cu(111)$	−1.21	−1.21	0.62	0.59	0.60	0.60	0.29 (Cu)	0.29 (Cu)
$Pt_5/Cu_9/Cu(111)$	−1.17	−1.21	0.60	0.61	0.62	0.60	−0.06 (Pt)	0.37 (Cu)
$Au_5/Pt_5Au_4/Pt(111)$	−1.17	−1.17	0.61	0.60	0.61	0.61	0.08 (Au)	0.08 (Au)
$Pt_5/Au_9/Pt(111)$	−1.16	−1.15	0.63	0.63	0.61	0.60	0.08 (Pt)	0.08 (Pt)
$Cu_9/Pt_9/Cu(111)$	−1.22	−1.21	0.61	0.61	0.62	0.61	0.26 (Cu)	0.25 (Cu)
$Pt_9/Cu_9/Cu(111)$	−1.18	−1.23	0.60	0.60	0.60	0.65	−0.13 (Pt)	−0.18 (Pt)
$Au_9/Pt_9/Pt(111)$	−1.17	−1.18	0.61	0.61	0.60	0.60	0.07 (Au)	0.07 (Au)
$Pt_9/Au_9/Pt(111)$	−1.14	−1.16	0.62	0.62	0.62	0.64	0.04 (Pt)	0.04 (Pt)

References

(1) Kittel, C. *Introduction to Solid State Physics, 8th Edition*; John Wiley & Sons, Inc., New York, 2004.