

Supporting Information: Theoretical Investigation of the Adsorption Properties of CO, NO, and OH on Monometallic and Bimetallic 13-Atom Clusters: The Example of Cu₁₃, Pt₇Cu₆, and Pt₁₃

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ABBREVIATIONS: DFT, PBE, FHI-aims

KEYWORDS: Adsorption, Transition Metal Clusters, Density Functional Theory

A Gas-Phase Systems

The most important properties of CO, NO, and OH are summarized in Table S1 along with the experimental results.¹⁻⁴ The bond lengths, d_0 , are larger than the experimental results by about 1.0%,⁴ which is expected in DFT-PBE calculations,⁵ while the binding energies, E_b , are larger than experimental ones, in particular, for NO and OH (e.g., 5.2 % for CO, 14.8 % for NO, and 8.6 % for OH) due to the difficulties of plain DFT-PBE to describe the doublet states in NO and OH (i.e., 1 unpaired electron).⁵ The vibrational frequencies without anharmonic corrections are slightly smaller than the experimental results (e.g., around 2.0 % for CO, 0.9 % for NO, and 3.7 % for OH). The charge transfer among the chemical species were calculated using the electronic density dependent Hirshfeld scheme.^{6,7} For comparison we also calculated the charge population based on the Mulliken concept.^{8,9} Our results show that the magnitude of the Hirshfeld charges (Q_{Hirs}) are almost linearly proportional to the size of the Pauling electronegativity difference between the chemical species ($\Delta\chi = \chi_A - \chi_B$).¹⁰ For example, $Q_{\text{eff}}^{\text{O}} = -0.01 e$ (NO, $\Delta\chi = 0.40$), $-0.07 e$ (CO,

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Table S1: Diatomic molecule properties. Binding energy per atom, E_b , equilibrium bond length, d_0 , vibrational frequency, ν , spin multiplicity, M , dipole moment, μ , given in Debye (D), and the Hirshfeld charge, Q_{Hirs} . The experimental results¹⁻⁴ are indicated by \dagger .

Properties	CO	NO	OH
E_b (eV)	-5.84	-3.73	-2.39
	-5.55 †	-3.25 †	-2.20 †
d_0 (Å)	1.14	1.16	0.98
	1.13 †	1.15 †	0.97 †
ν (cm $^{-1}$)	2127	1887	3598
	2170 †	1904 †	3738 †
M	1.00	2.00	2.00
μ (D)	0.20	0.22	1.16
	0.11 †	0.16 †	1.66 †
Q_{Hirs} (e)	+0.07 ^C	+0.01 ^N	+0.15 ^H
	-0.07 ^O	-0.01 ^O	-0.15 ^O

$\Delta\chi = 0.89$), and $-0.15e$ (OH, $\Delta\chi = 1.22$). Furthermore, we obtained almost the same dipole moment, μ , for CO and NO, which is consistent with experimental results,^{1,2} while it is substantially larger for OH, and hence, it supports our charge transfer analysis among the chemical species based on the Hirshfeld scheme.

The energies of the molecular orbitals for the diatomic CO ($3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2$), NO ($3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 2\pi^{*1}$), and OH ($2\sigma^2 3\sigma^2 1p^3$) molecules in gas-phase are shown in Figure S1. For CO, the highest occupied molecular orbital (HOMO), $5\sigma^2$, has a bonding character and it is composed mainly by C states derived from s - and p -states, while the lowest unoccupied molecular orbital (LUMO), $2\pi^*$, is composed mainly by states from C p -states, with a HOMO-LUMO energy difference of 6.99 eV, which increases to 9.19 eV by using the hybrid Heyd-Scuseria-Ernzerhof (HSE06) functional.^{11,12} Nitrogen has an extra valence electron compared with C, and hence, the HOMO and LUMO states of NO have an antibonding character, $2\pi^*$, with a small energy separation of 0.28 eV, which increases to 2.77 eV using the HSE06 functional. For OH, the HOMO and LUMO states, 1π , are mainly composed by O p -states, as expected,

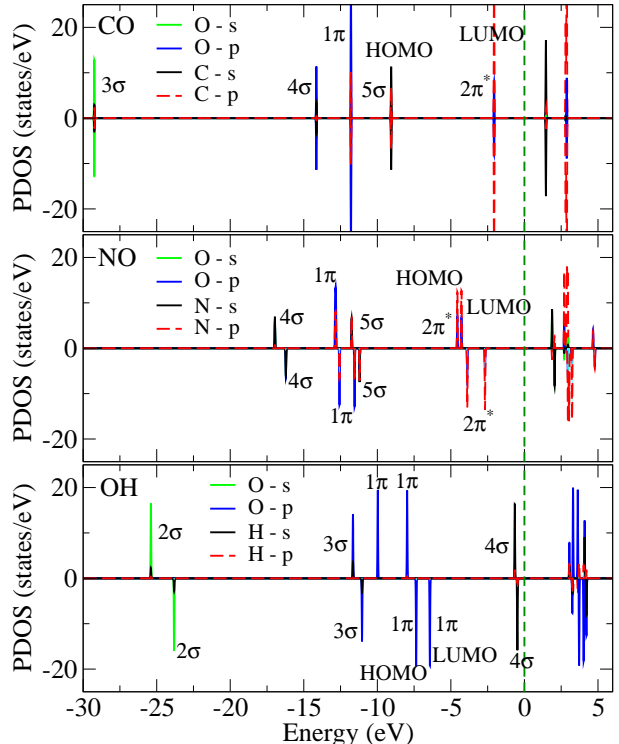


Figure S1: Molecular orbital energies and its decomposition into the s - and p -states for the CO, NO, and OH in gas-phase. The molecular orbitals are labeled and the HOMO and LUMO states are indicated for every molecule. The zero energy indicates the reference vacuum energy.

with an energy separation of 0.93 eV (4.06 eV using HSE06). The use of a hybrid exchange-correlation functional is expected to minimize the band-gap problem of DFT with standard functionals (e.g., GGA-PBE), by decreasing the charge delocalization error.¹³ However, even using such functional we obtained values which are smaller than available experimental results, obtained from the difference between ionization potentials and electron affinities, namely, differences within 27.5% (CO^{14,15}), 70.0% (NO^{16,17}) and 63.7% (OH^{18,19}).

The properties of the Cu₁₃, Pt₇Cu₆, and Pt₁₃ clusters in different charge states are summarized in Table S2. We found that the structural parameters calculated with the effective coordination concept,^{20,21} namely, the average weighted bond length, d_{av} , and the average effective coordination number (ECN) given in number of nearest neighbours (NNN), are

Table S2: Transition-metal 13-atom clusters properties. Average weighted bond length, d_{av} , average cluster effective coordination number, ECN, in number of nearest neighbours (NNN), binding energy per atom, E_b , spin multiplicity, M , and the center of gravity of the occupied d -states with respect to the HOMO state, ϵ_d .

	Cu ₁₃			Pt ₇ Cu ₆			Pt ₁₃		
	+	0	−	+	0	−	+	0	−
E_b (eV)	−2.54	−2.34	−2.43	−3.48	−3.30	−3.40	−4.11	−3.89	−3.97
ECN (NNN)	5.691	5.697	5.670	5.348	5.351	5.370	4.303	4.286	4.219
d_{av} (Å)	2.459	2.456	2.459	2.535	2.535	2.539	2.583	2.584	2.583
M	1.00	2.00	1.00	4.00	3.00	2.00	4.00	3.00	2.00
ϵ_d (eV)	−1.88	−1.85	−1.80	−1.96	−2.18	−2.20	−2.35	−2.47	−2.45

nearly the same for the cationic, neutral, and anionic clusters (i.e., differences of less than 2.0% in the worst cases). As expected, the binding energy depends on the charge state with differences from 0.1 eV to 0.2 eV per atom, with an enhancement of the binding energy by adding or releasing one electron from the neutral cluster. Cu₁₃⁰ has a $M = 2$ (doublet), and the release or addition of one electron yields a singlet state. In contrast with Cu₁₃⁰, the Pt₁₃⁰ cluster has higher multiplicity (e.g., $M = 3$), which increases by removing one electron. The center of gravity of the occupied valence Cu d -states are closer to the HOMO than the Pt d -states even though Cu d -states are filled, which can be explained by the localized nature of the Cu 3d-states and the larger bandwidth of the Pt 5d-states. For the bimetallic clusters, as expected, we obtained a center of gravity between both parent systems.

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Table S3: Adsorption energy of CO, NO, and OH on the Cu₁₃, Pt₇Cu₆, and Pt₁₃ clusters in the cationic (+), neutral (0), and anionic (−) charge states. For each system, a large number of configurations were calculated for onefold, twofold, threefold, and fourfold adsorptions sites. In this table, we report only the adsorption energy for the lowest energy configurations for each adsorption site. The triangledown symbols (∇) indicate all unstable configurations, i.e., molecules adsorbed initially on particular adsorption sites move away from those sites along the geometric optimization.

Adsorption Site		Cu ₁₃			Pt ₇ Cu ₆			Pt ₁₃		
		+	0	−	+	0	−	+	0	−
CO	Onefold	−1.37	−1.23	−1.33	−2.65	−2.65	−2.72	−2.48	−2.46	−2.41
	Twofold	−1.00	−1.04	−1.17	−2.17	−2.10	−2.22	−1.96	−2.02	−2.17
	Threefold	−0.96	−0.55	−1.20	−1.81	−1.81	−1.91	−1.44	−1.24	−1.70
	Fourfold	−0.74	−0.74	−0.69	∇	−1.30	∇	∇	∇	∇
NO	Onefold	−1.26	−1.25	−1.42	−2.92	−2.87	−2.90	−2.44	−2.42	−2.47
	Twofold	−1.28	−1.38	−1.56	−2.29	−2.24	−2.34	−2.49	−2.68	−2.69
	Threefold	−1.14	−1.44	−1.43	−2.21	−2.22	−2.23	−1.66	−1.71	−0.95
	Fourfold	−0.89	−1.06	−1.00	∇	∇	∇	∇	∇	∇
OH	Onefold	−2.72	−3.34	−3.41	−3.50	−3.59	−3.70	−3.16	−3.23	−3.37
	Twofold	−3.42	−3.70	−3.55	−3.66	−3.69	−3.69	−3.73	−3.60	−3.49
	Threefold	∇	∇	∇	−3.67	−3.39	∇	∇	∇	∇
	Fourfold	∇	∇	∇	∇	∇	∇	∇	∇	∇

Table S4: Hirshfeld population analysis of the adsorption process of CO, NO and OH on Cu₁₃, Pt₇Cu₆, and Pt₁₃ clusters in different charge states, namely, cationic (+), neutral (0), and anionic (−). $\Delta q(X)$ ($X = C, N, H, O, TM$ (Cu, Pt)) is the total charge variation on the corresponding X atom, on which $\Delta q > 0$ means loss of charge while $\Delta q < 0$ corresponds to gain.

		Cu ₁₃			Pt ₇ Cu ₆			Pt ₁₃		
		+	0	−	+	0	−	+	0	−
CO	$\Delta q(C)$	0.09	0.05	0.01	0.08	0.04	0.00	0.08	0.05	0.02
	$\Delta q(O)$	−0.03	−0.09	−0.14	−0.07	−0.12	−0.18	−0.07	−0.12	−0.16
	$\Delta q(TM)$	0.94	0.04	−0.87	0.99	0.08	−0.82	0.99	0.07	−0.86
NO	$\Delta q(N)$	−0.06	−0.09	−0.13	0.05	0.00	−0.04	−0.01	−0.03	−0.06
	$\Delta q(O)$	−0.03	−0.12	−0.17	0.02	−0.05	−0.12	−0.05	−0.12	−0.18
	$\Delta q(TM)$	1.09	0.21	−0.70	0.93	0.05	−0.84	1.06	0.15	−0.76
OH	$\Delta q(H)$	0.15	0.12	0.09	0.18	0.12	0.09	0.15	0.12	0.10
	$\Delta q(O)$	−0.31	−0.34	−0.36	−0.25	−0.28	−0.34	−0.24	−0.27	−0.29
	$\Delta q(TM)$	1.16	0.22	−0.73	1.07	0.16	−0.75	1.09	0.15	−0.81

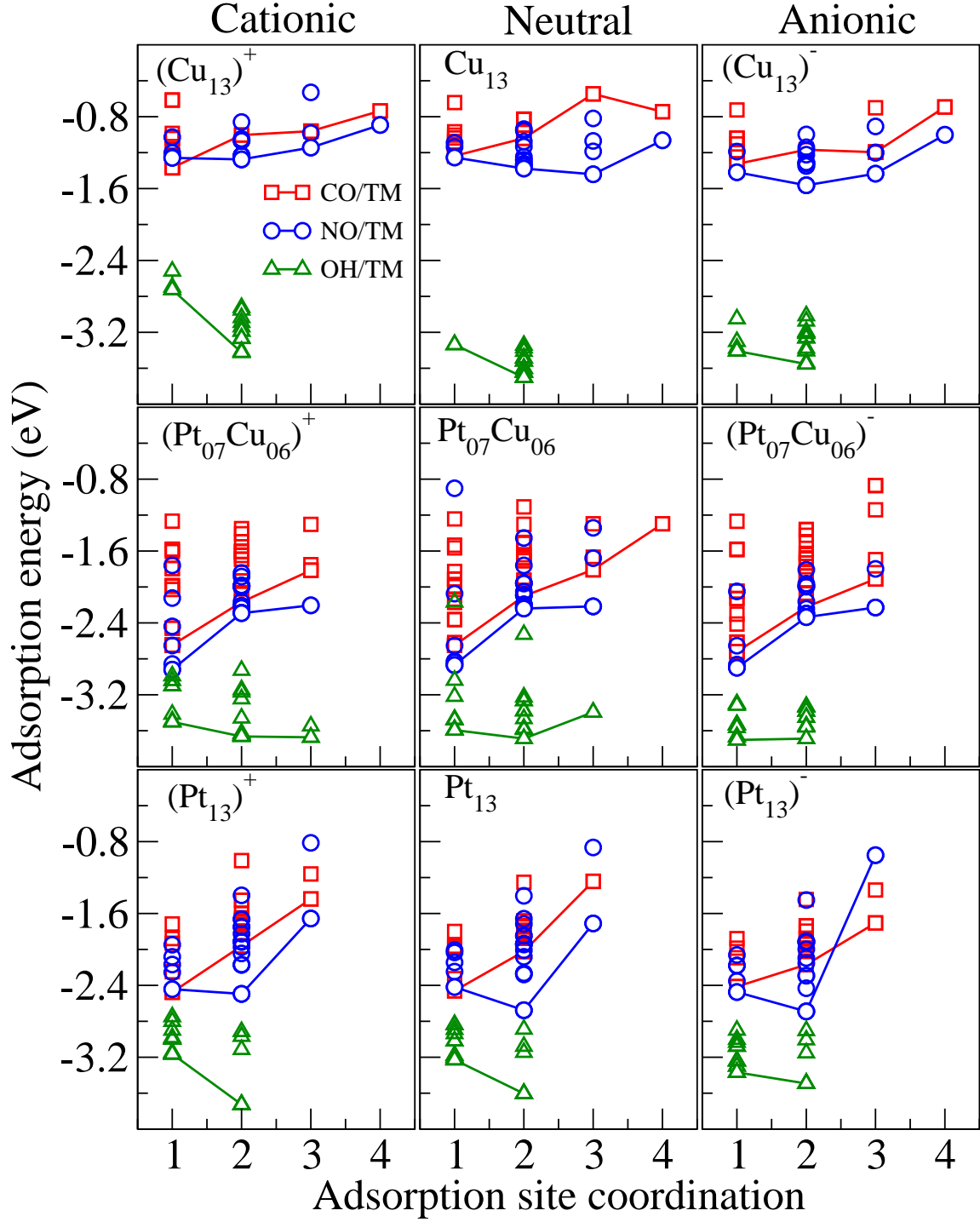


Figure S2: Adsorption energy of CO, NO and OH on the Cu_{13} , Pt_7Cu_6 , and Pt_{13} clusters in the cationic, neutral, and anionic states as a function of the coordination of the adsorption sites, namely, 1 (onelfold), 2 (twofold), 3 (threefold), and 4 (fourfold), for all calculated configurations. The continuos lines indicate the lowest energy configurations.

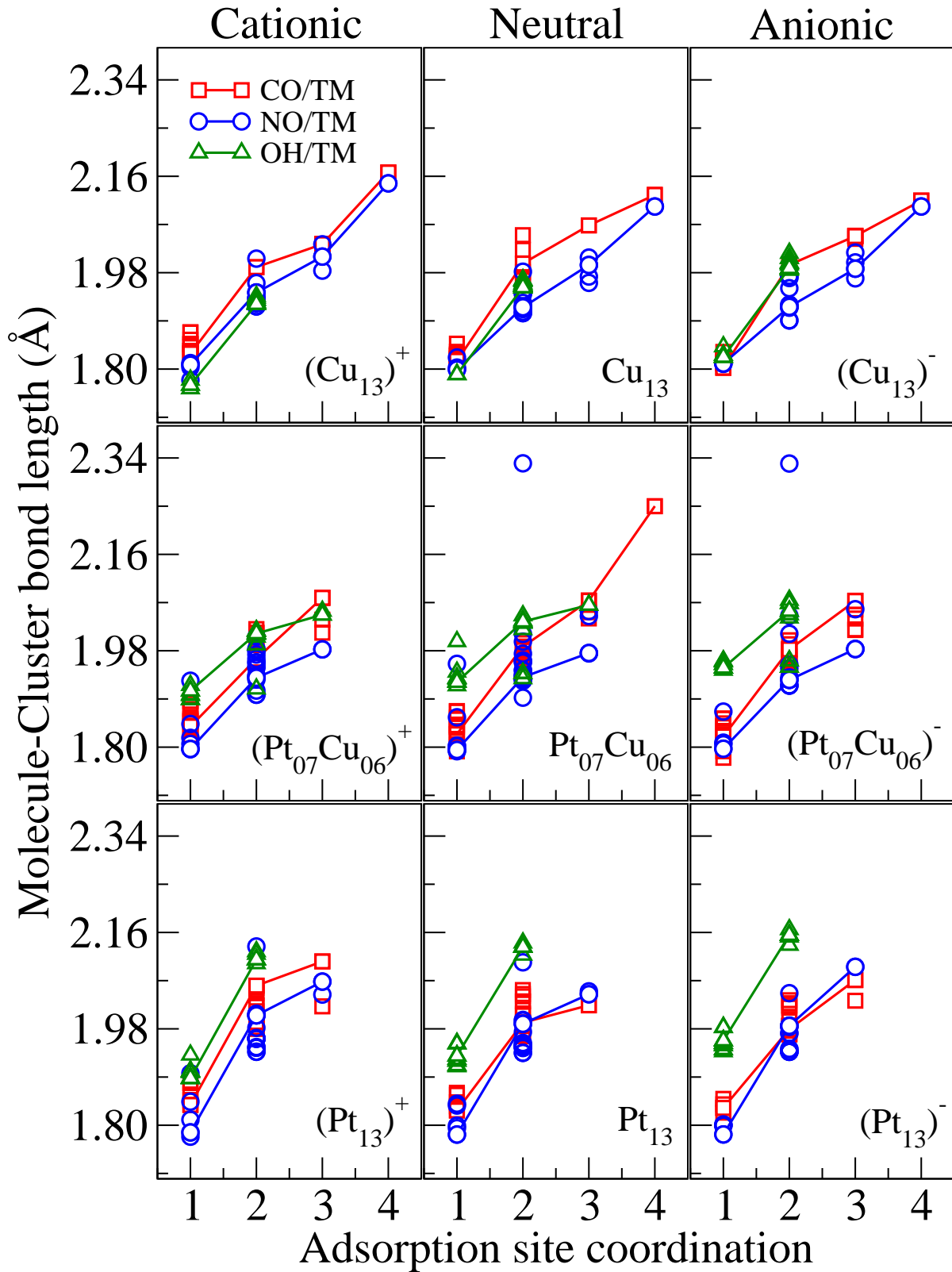


Figure S3: Equilibrium bond lengths between the molecules (CO, NO, OH) and the 13-atom clusters (Cu_{13} , Pt_7Cu_6 , Pt_{13}) in the cationic, neutral, and anionic charge states as a function of the coordination of the adsorption sites, namely, 1 (onelfold), 2 (twofold), 3 (threefold), and 4 (fourfold), for all calculated configurations. The continuous lines indicate the lowest energy configurations.

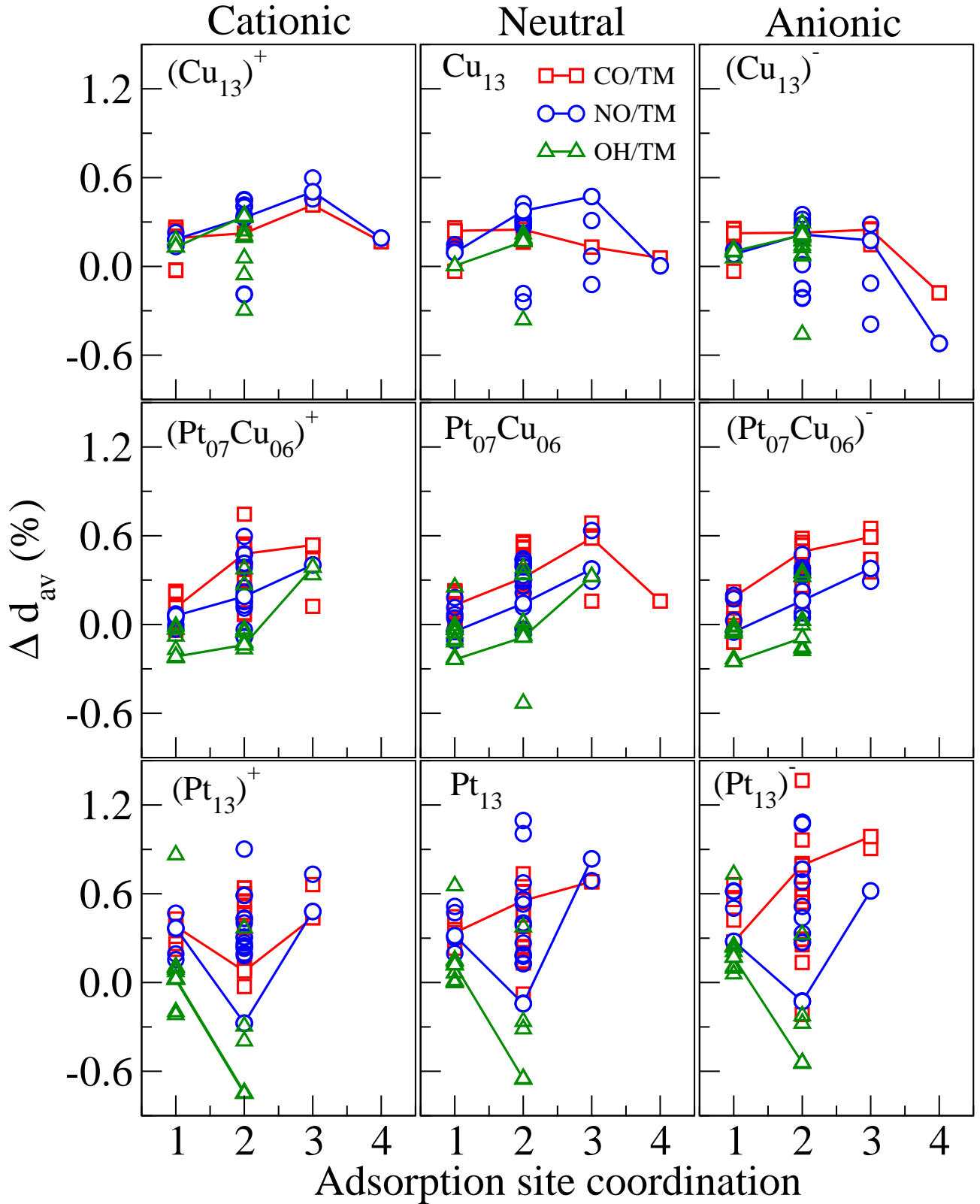


Figure S4: Relative deviations in the average weighted bond lengths, Δd_{av} , of the 13-atom clusters (Cu_{13} , Pt_7Cu_6 , Pt_{13}) upon the adsorption of the diatomic molecules (CO, NO, OH), for all calculated configurations in the cationic, neutral, and anionic charge states as a function of the coordination of the adsorption sites, namely, 1 (onefold), 2 (twofold), 3 (threefold), and 4 (fourfold). The relative deviations in percentage are given by $\Delta d_{av} = \frac{100(d_{av}^{\text{MO/TM}_{13}} - d_{av}^{\text{TM}_{13}})}{d_{av}^{\text{TM}_{13}}}$.

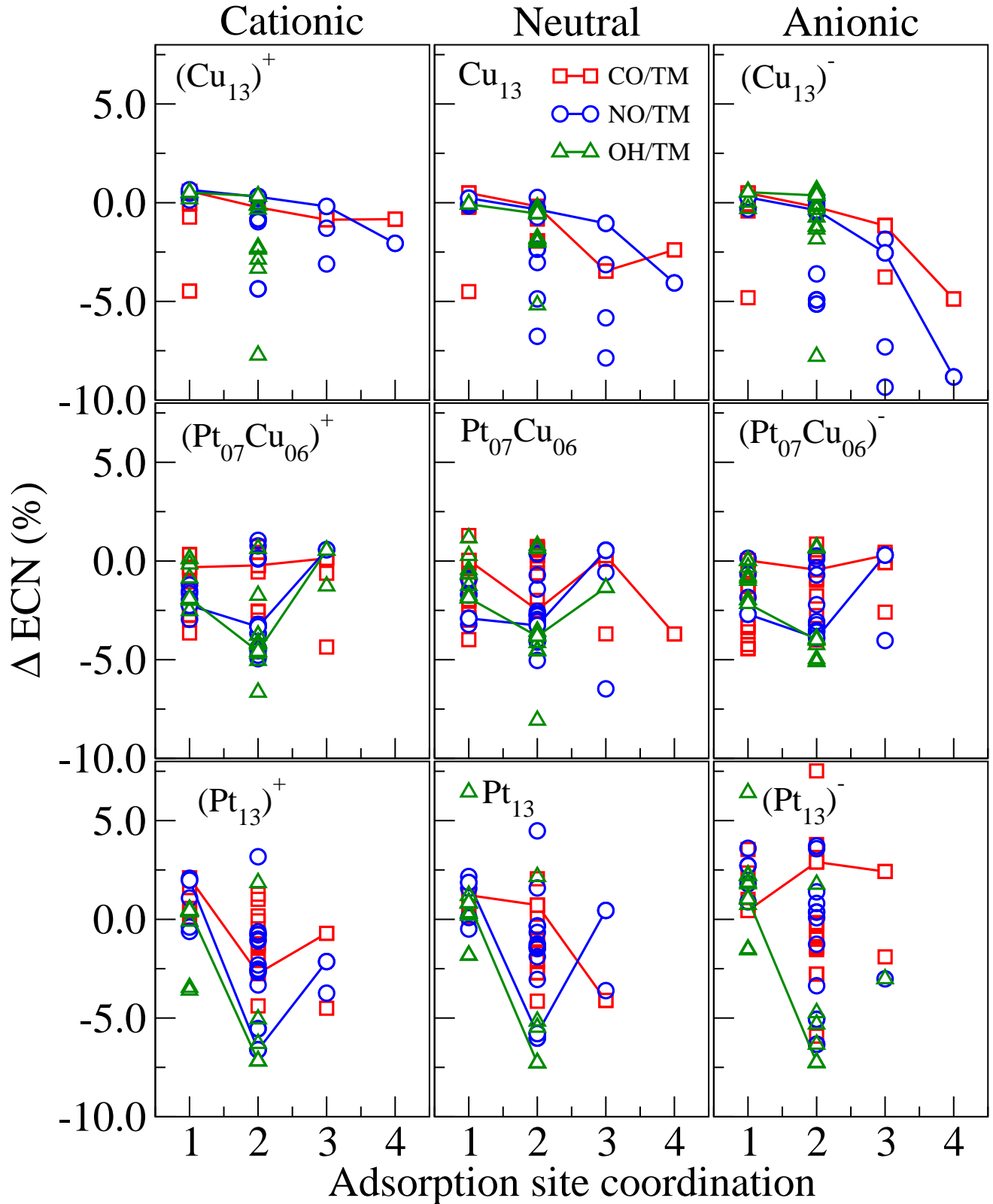


Figure S5: Relative deviations in the effective coordination number (ECN), ΔECN , of the 13-atom clusters (Cu_{13} , Pt_7Cu_6 , Pt_{13}) upon the adsorption of the diatomic molecules (CO, NO, OH), for all calculated configurations in the cationic, neutral, and anionic charge states as a function of the coordination of the adsorption sites, namely, 1 (onefold), 2 (twofold), 3 (threefold), and 4 (fourfold). The relative deviations in percentage are given by $\Delta ECN = \frac{100(ECN^{\text{MO/TM}_{13}} - ECN^{\text{TM}_{13}})}{ECN^{\text{TM}_{13}}}$.

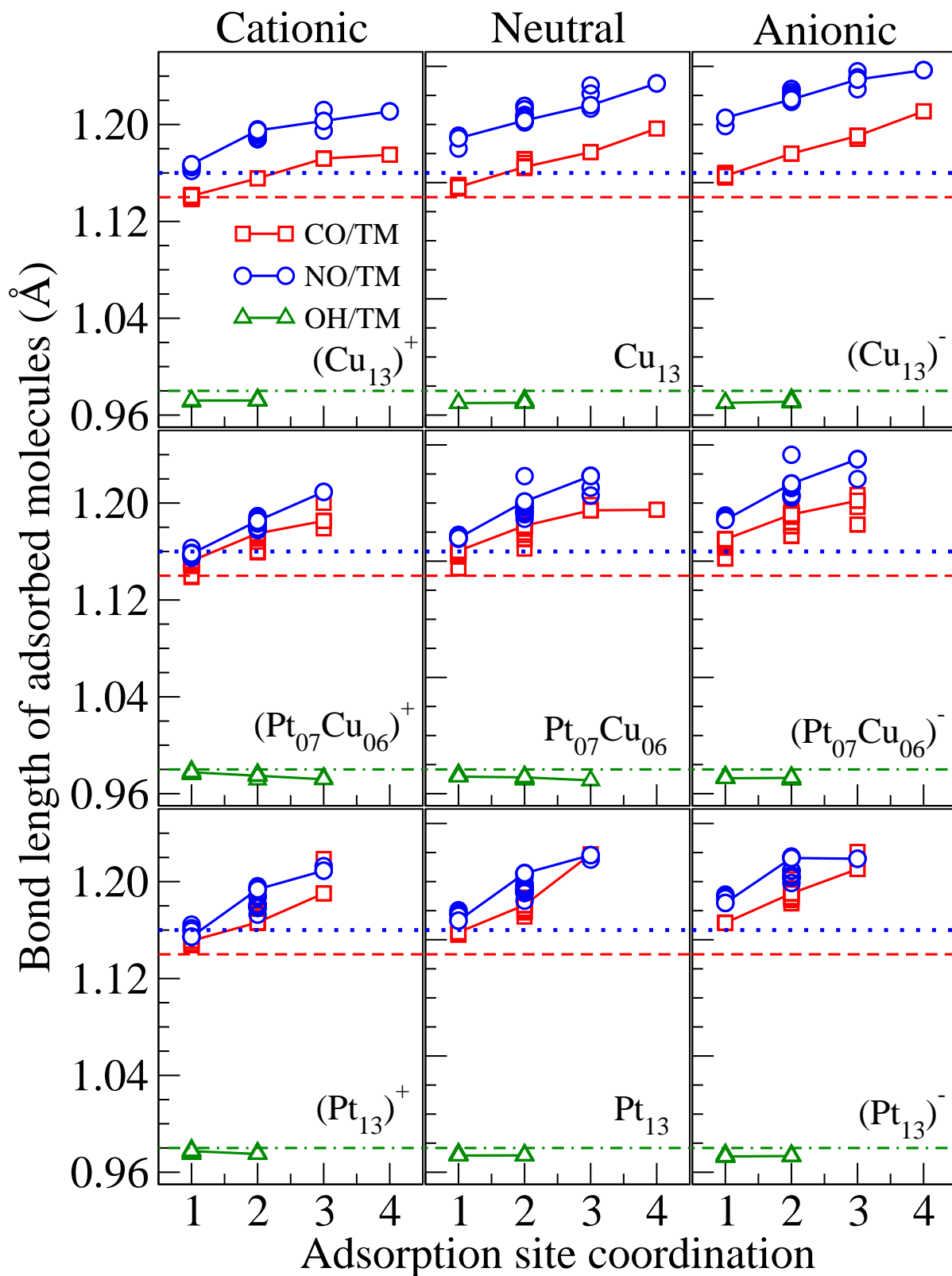


Figure S6: Equilibrium bond lengths of the adsorbed molecules (CO, NO, OH) upon the adsorption on the 13-atom clusters (Cu₁₃, Pt₇Cu₆, Pt₁₃) for all calculated configurations in the cationic, neutral, and anionic charge states, as a function of the coordination of the adsorption sites, namely, 1 (onefold), 2 (twofold), 3 (threefold), and 4 (fourfold). The horizontal red dashed line, blue dotted line and green dot-dashed line correspond, respectively, to our calculated value for the CO, NO and OH equilibrium bond length in the gas-phase.

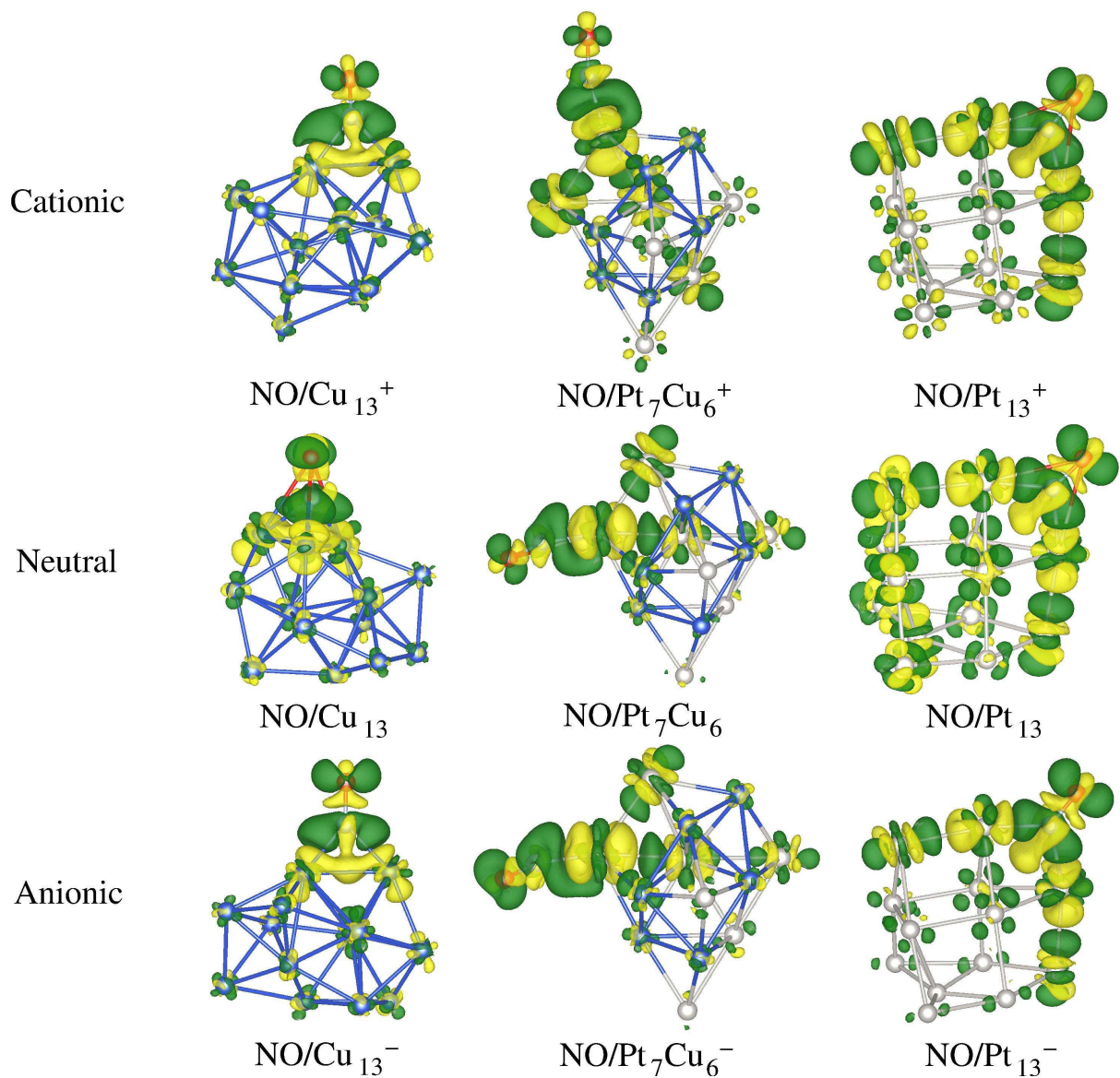


Figure S7: Charge density difference due to the NO adsorption process on the 13-atom clusters (Cu_{13} , Pt_7Cu_6 , Pt_{13}) for all lowest-energy configurations in the cationic, neutral, and anionic charge states. Green isosurfaces correspond to gain of charge while yellow isosurfaces are regions related with loss of charge due to the adsorption.

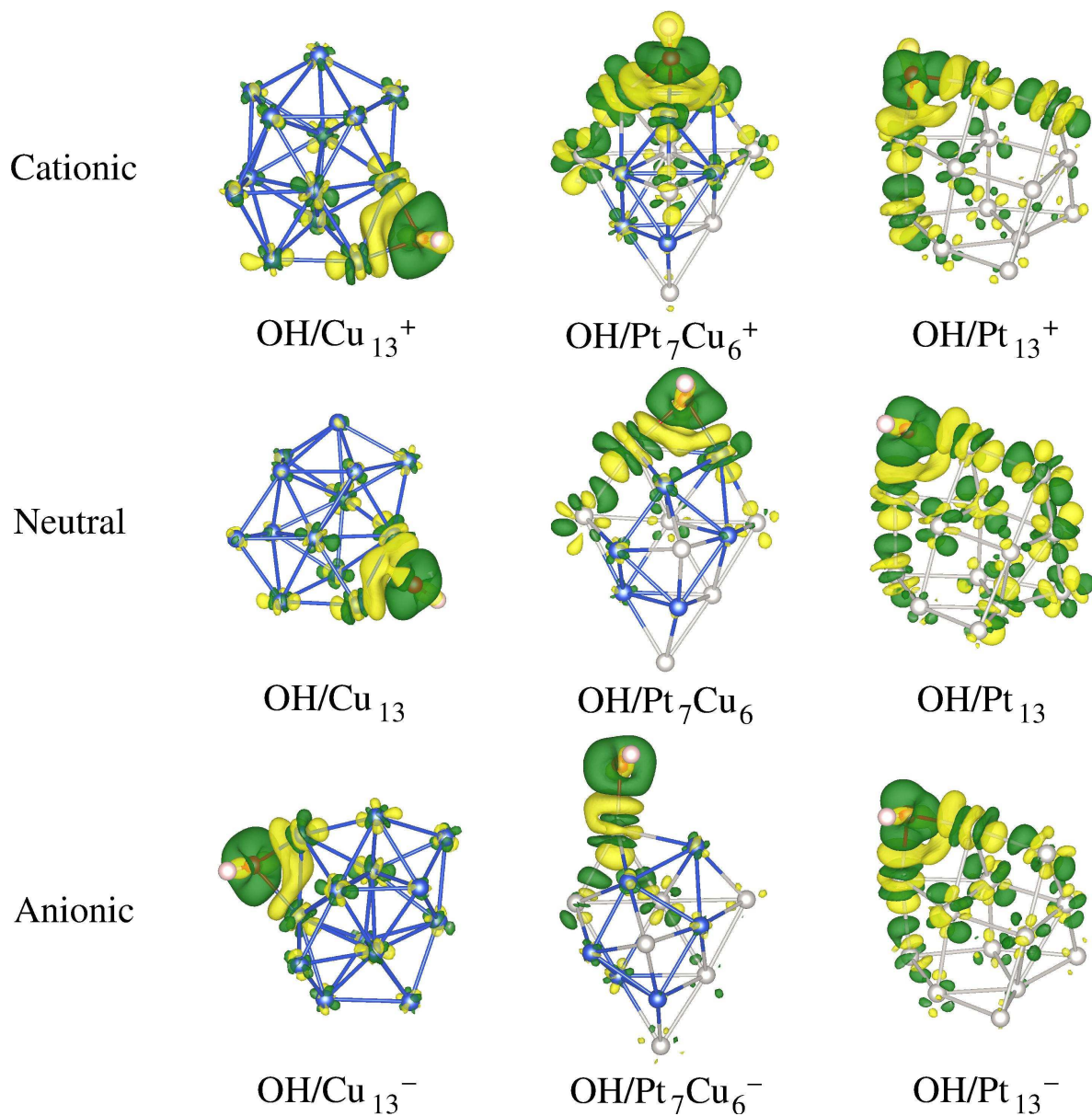


Figure S8: Charge density difference due to the OH adsorption process on the 13-atom clusters (Cu_{13} , Pt_7Cu_6 , Pt_{13}) for all lowest-energy configurations in the cationic, neutral, and anionic charge states. Green isosurfaces correspond to gain of charge while yellow isosurfaces are regions related with loss of charge due to the adsorption.

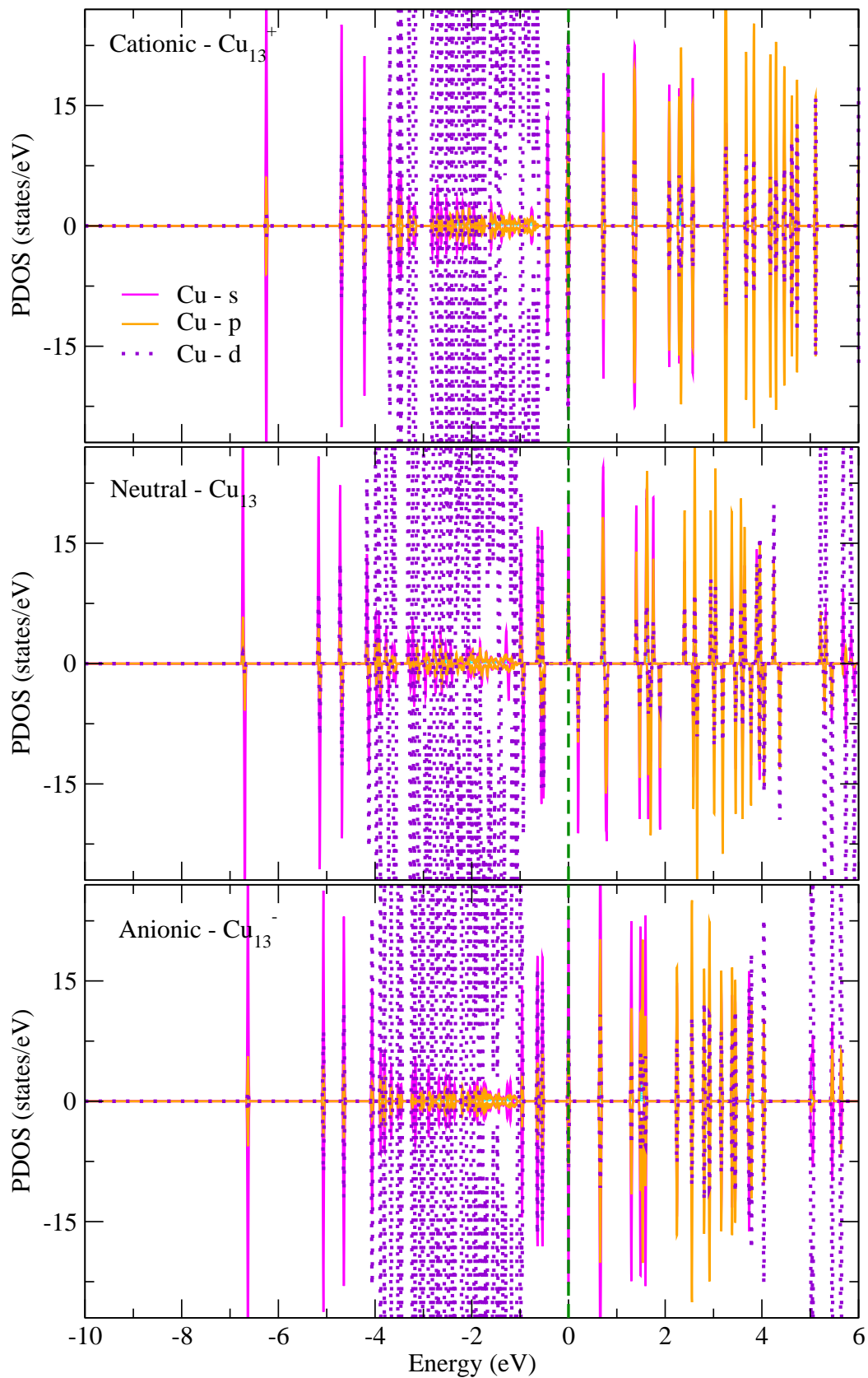


Figure S9: Projected Density of States (PDOS) for the gas-phase Cu_{13} clusters for each lowest-energy configurations in the cationic, neutral, and anionic charge states. The vertical green dashed line corresponds to the HOMO energy (0 eV).

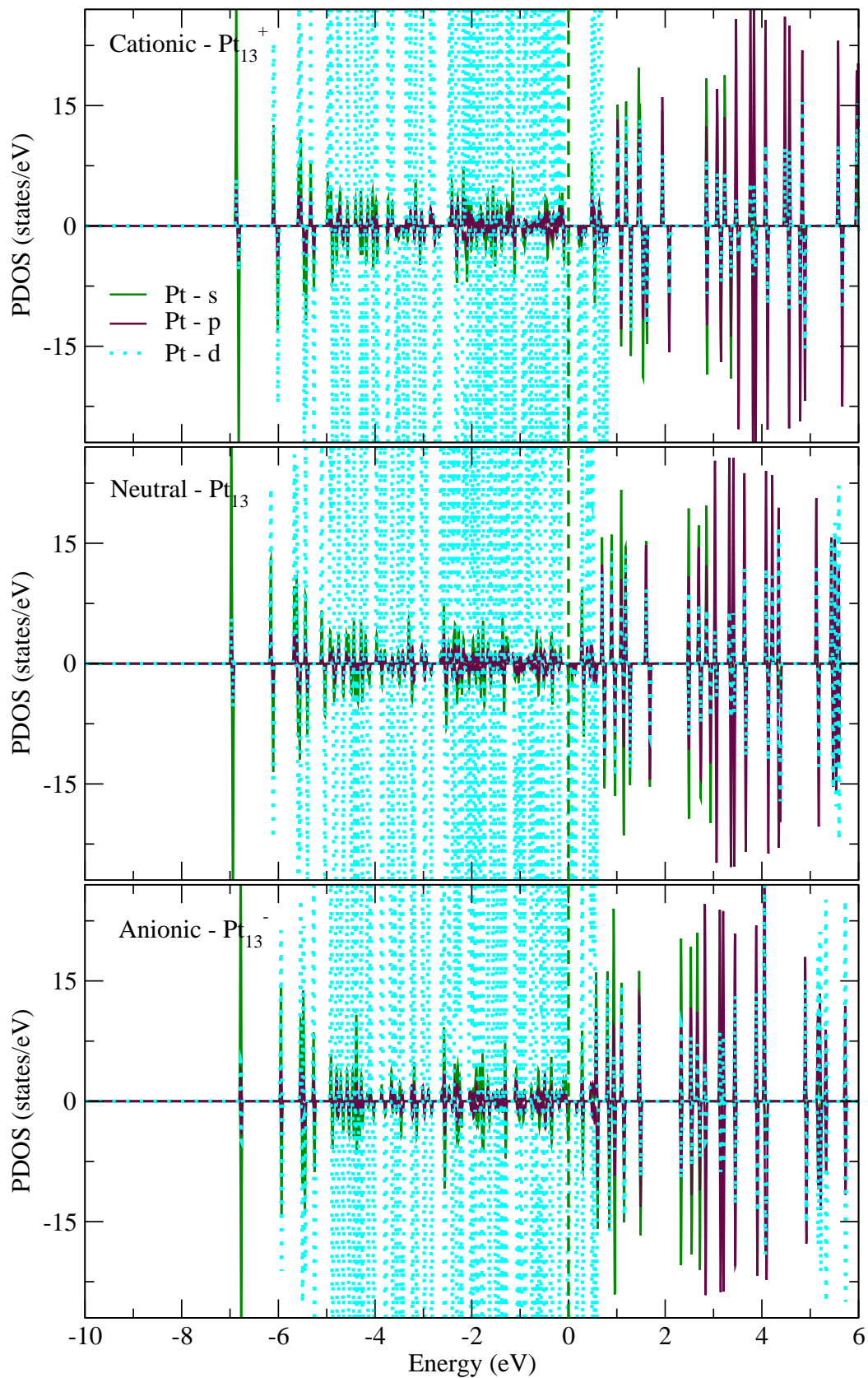


Figure S10: Projected Density of States (PDOS) for the gas-phase Pt_{13} clusters for each lowest-energy configurations in the cationic, neutral, and anionic charge states. The vertical green dashed line corresponds to the HOMO energy (0 eV).

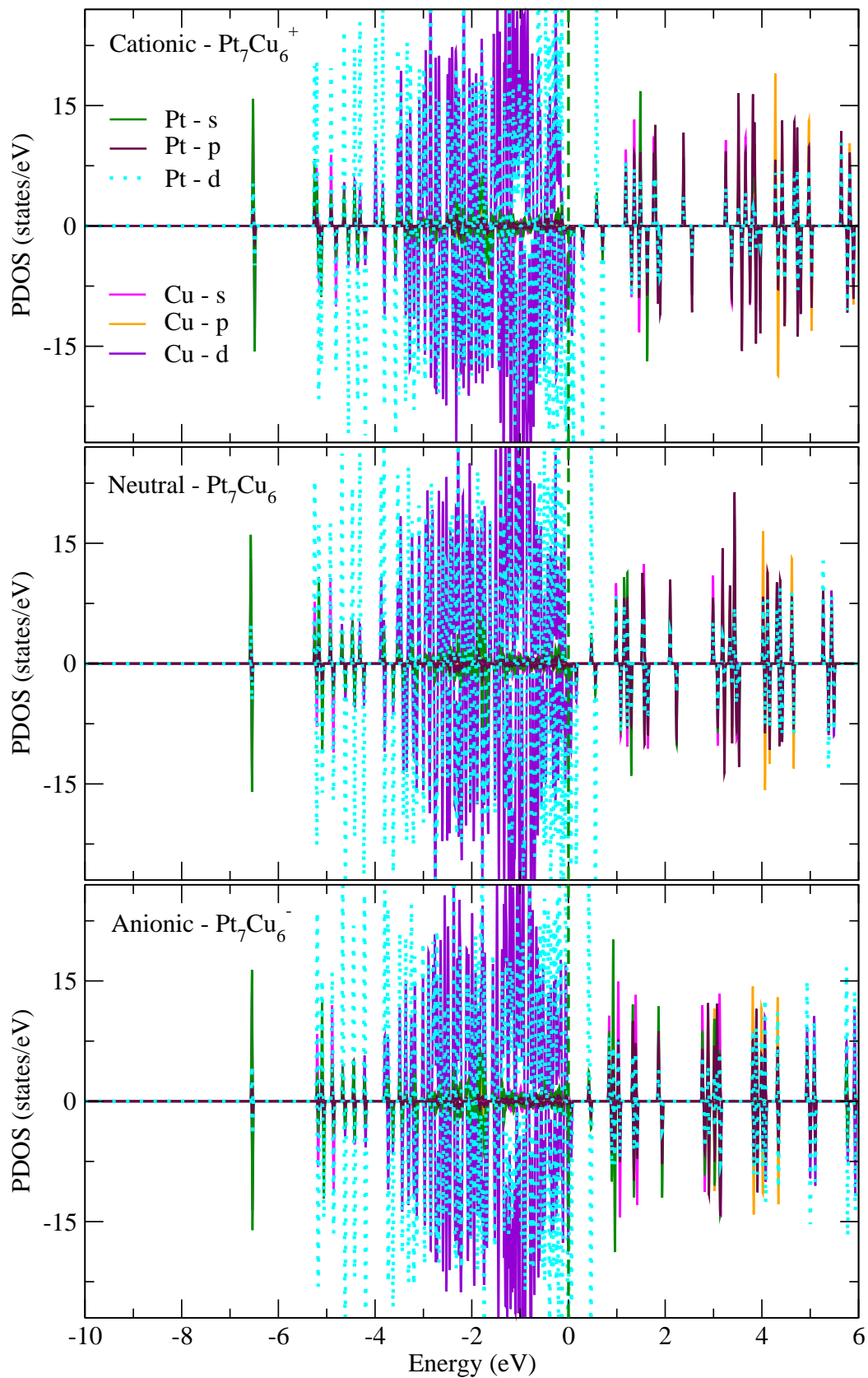


Figure S11: Projected Density of States (PDOS) for the gas-phase Pt_7Cu_6 clusters for each lowest-energy configurations in the cationic, neutral, and anionic charge states. The vertical green dashed line corresponds to the HOMO energy (0 eV).

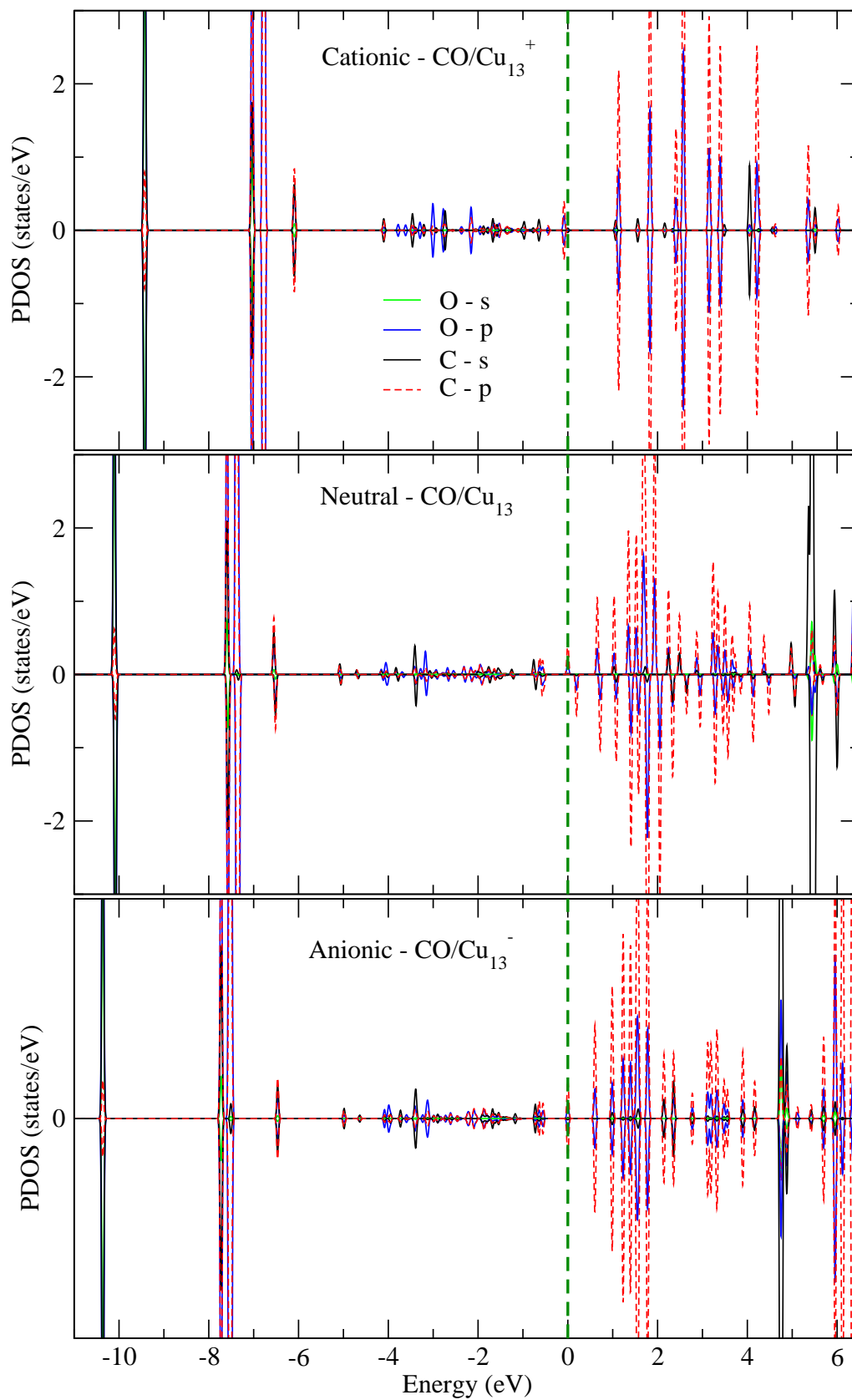


Figure S12: Projected Density of States (PDOS) for the CO-states of the CO adsorption on the Cu_{13} clusters for each lowest-energy configurations in the cationic, neutral, and anionic charge states. The vertical green dashed line corresponds to the HOMO energy (0 eV).

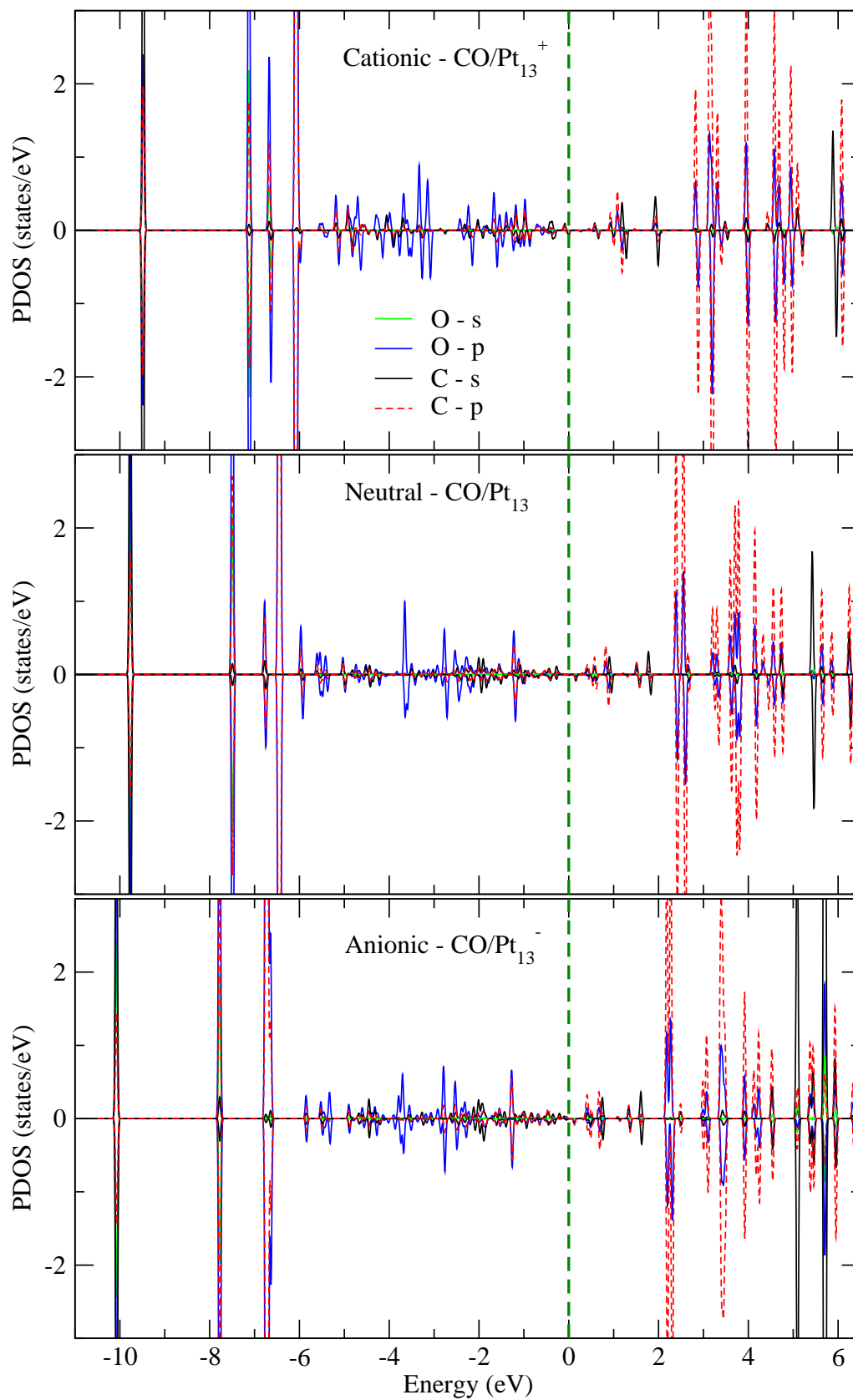


Figure S13: Projected Density of States (PDOS) for the CO-states of the CO adsorption on the Pt_{13} clusters for each lowest-energy configurations in the cationic, neutral, and anionic charge states. The vertical green dashed line corresponds to the HOMO energy (0 eV).

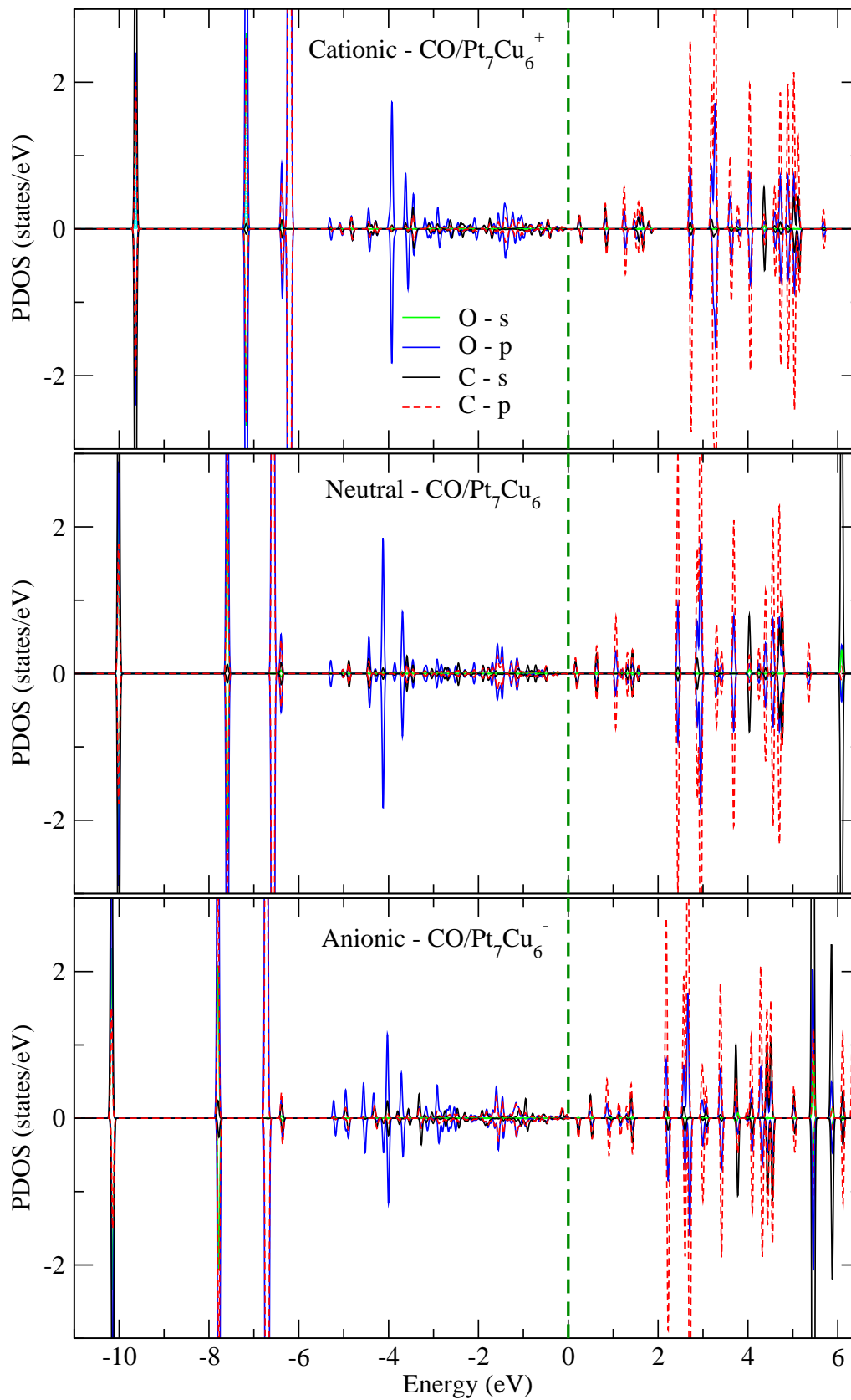


Figure S14: Projected Density of States (PDOS) for the CO-states of the CO adsorption on the Pt_7Cu_6 clusters for each lowest-energy configurations in the cationic, neutral, and anionic charge states. The vertical green dashed line corresponds to the HOMO energy (0 eV).

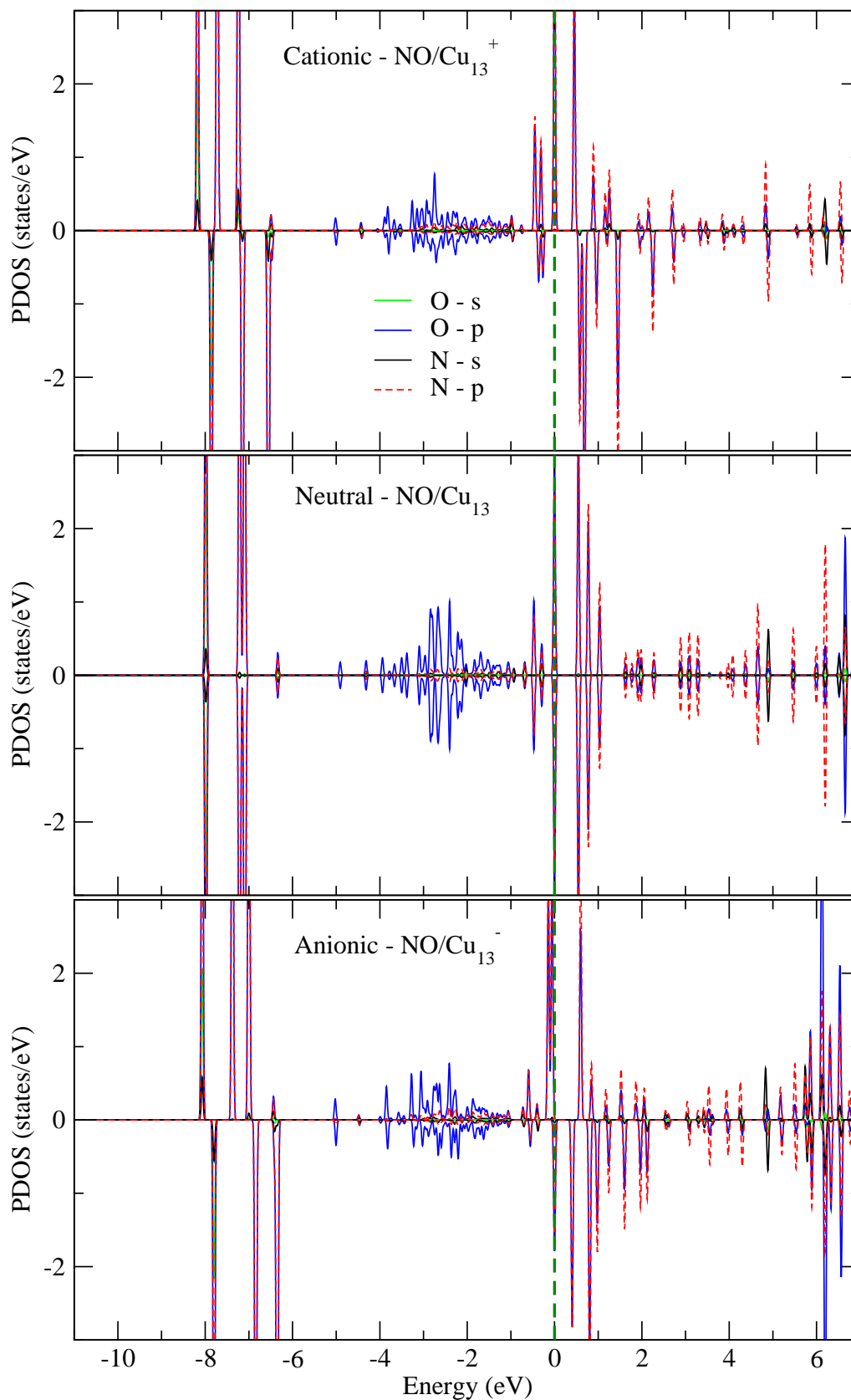


Figure S15: Projected Density of States (PDOS) for the NO-states of the NO adsorption on the Cu_{13} clusters for each lowest-energy configurations in the cationic, neutral, and anionic charge states. The vertical green dashed line corresponds to the HOMO energy (0 eV).

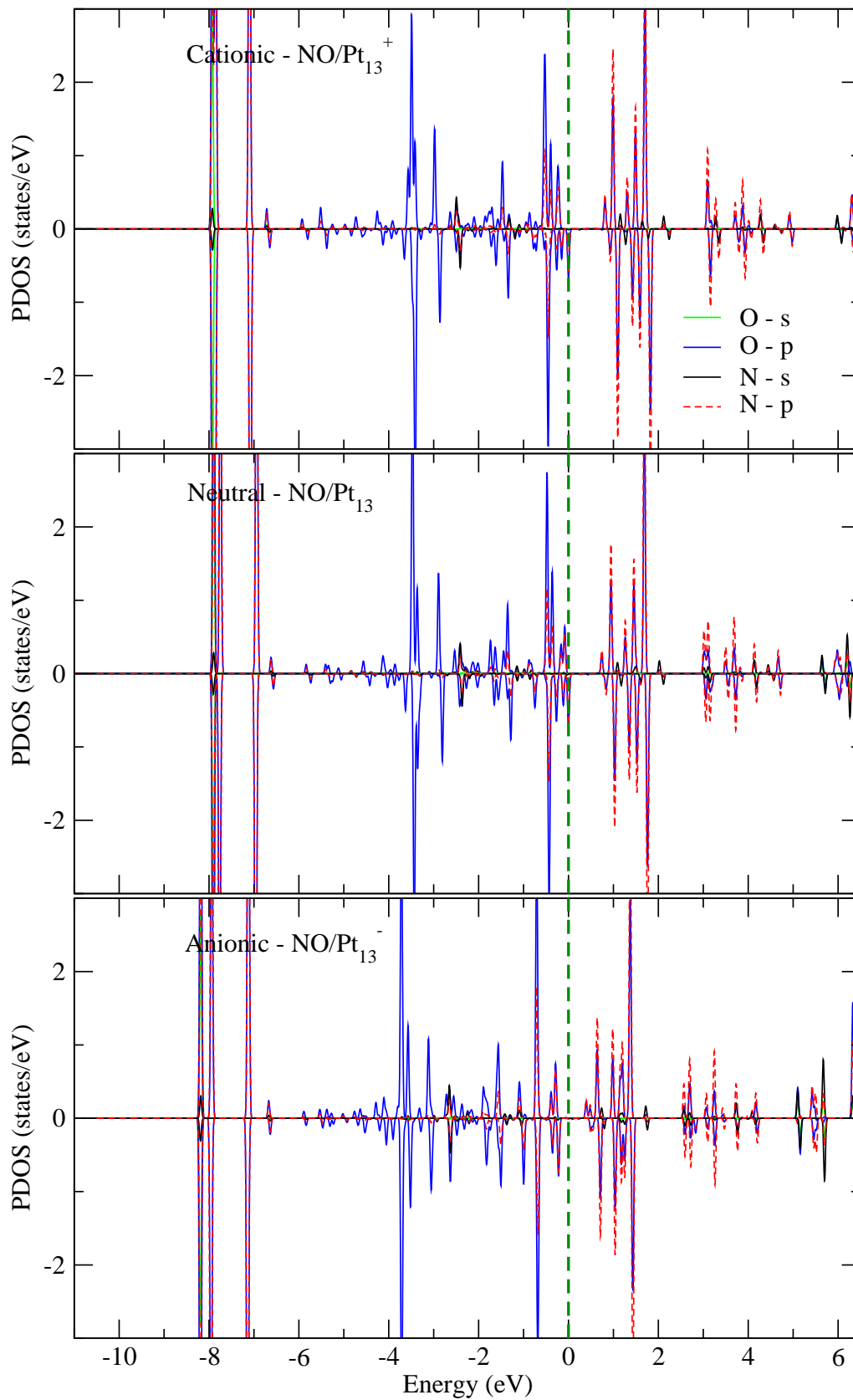


Figure S16: Projected Density of States (PDOS) for the NO-states of the NO adsorption on the Pt_{13} clusters for each lowest-energy configurations in the cationic, neutral, and anionic charge states. The vertical green dashed line corresponds to the HOMO energy (0 eV).

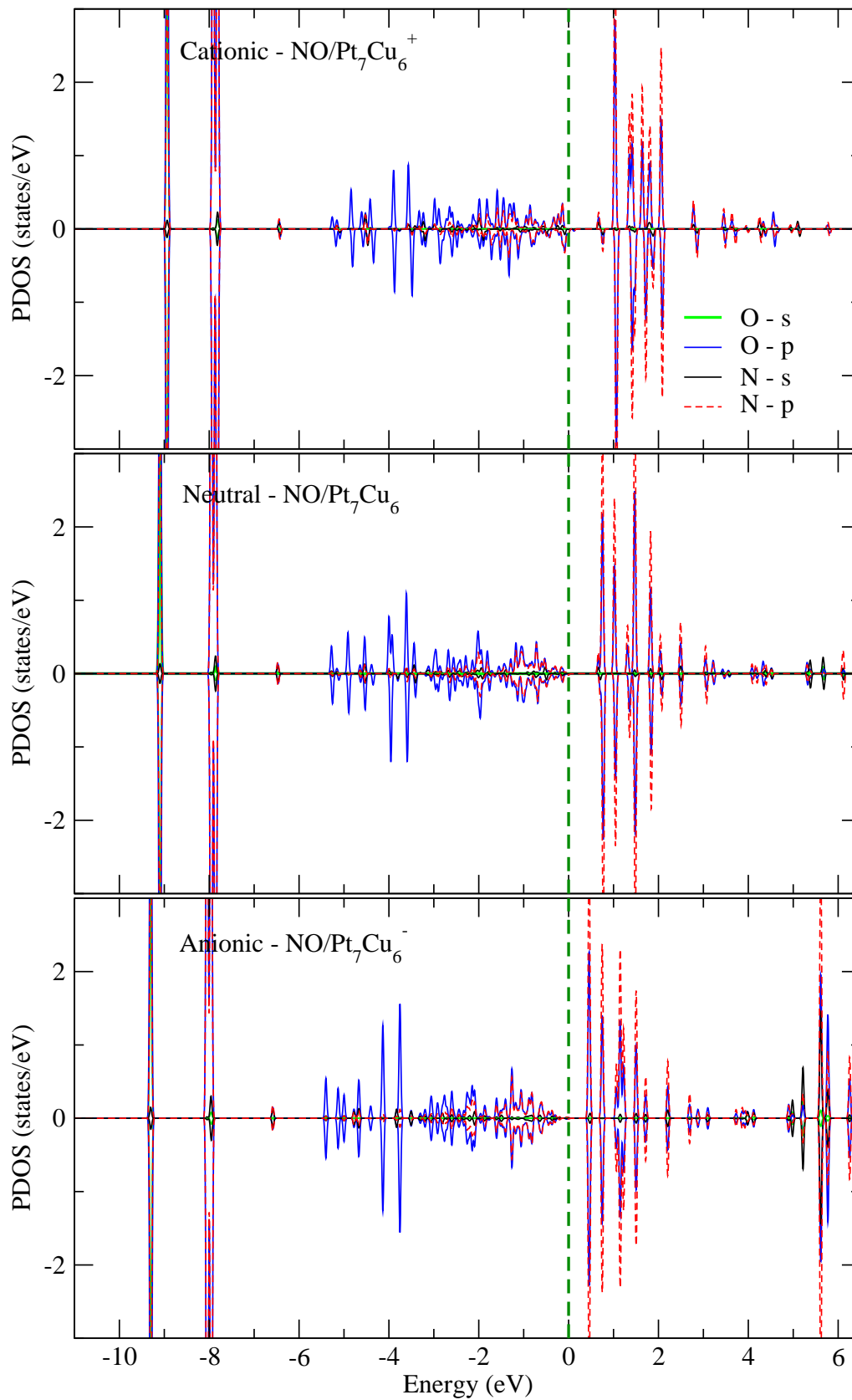


Figure S17: Projected Density of States (PDOS) for the NO-states of the NO adsorption on the Pt_7Cu_6 clusters for each lowest-energy configurations in the cationic, neutral, and anionic charge states. The vertical green dashed line corresponds to the HOMO energy (0 eV).

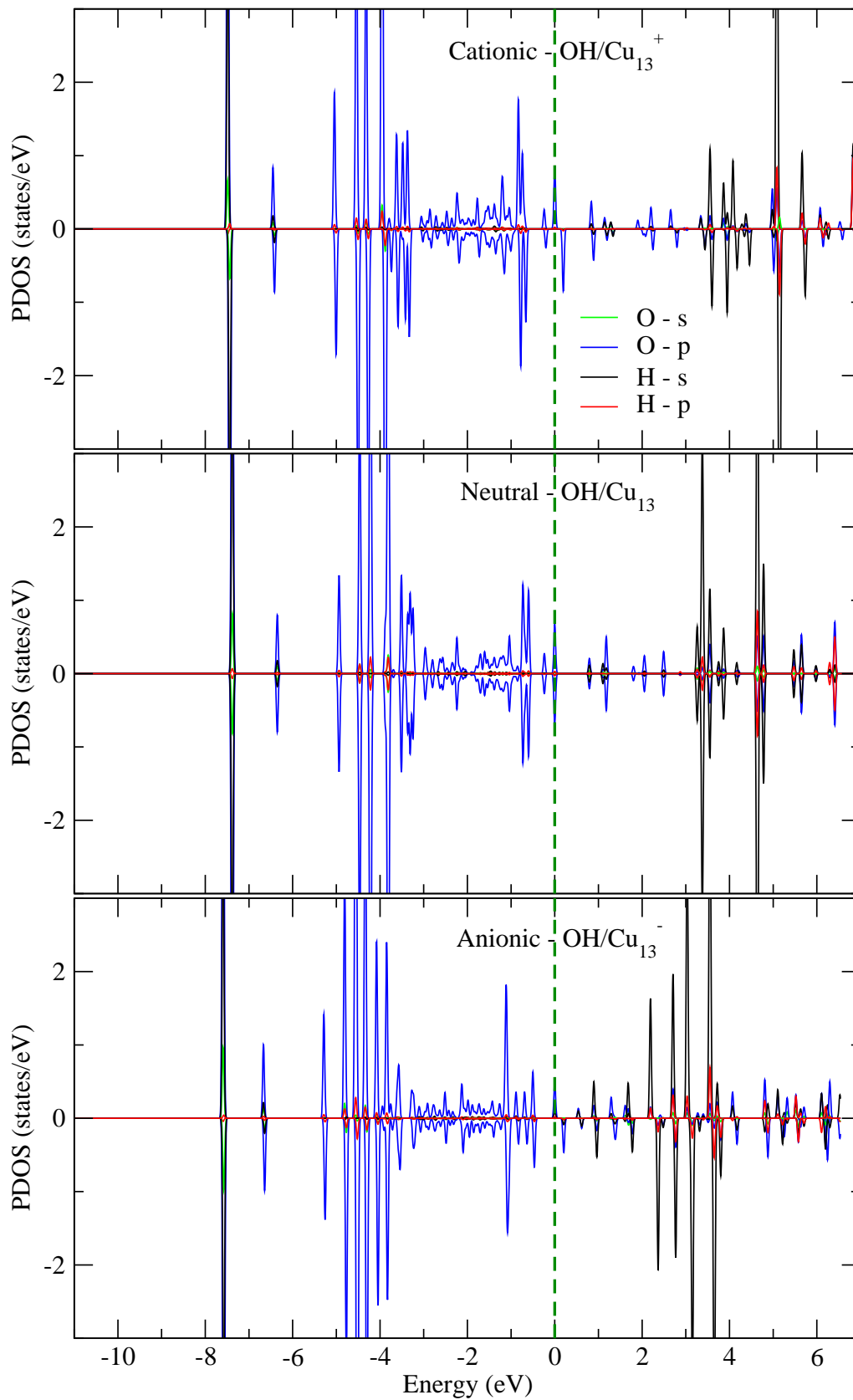


Figure S18: Projected Density of States (PDOS) for the OH-states of the OH adsorption on the Cu_{13} clusters for each lowest-energy configurations in the cationic, neutral, and anionic charge states. The vertical green dashed line corresponds to the HOMO energy (0 eV).

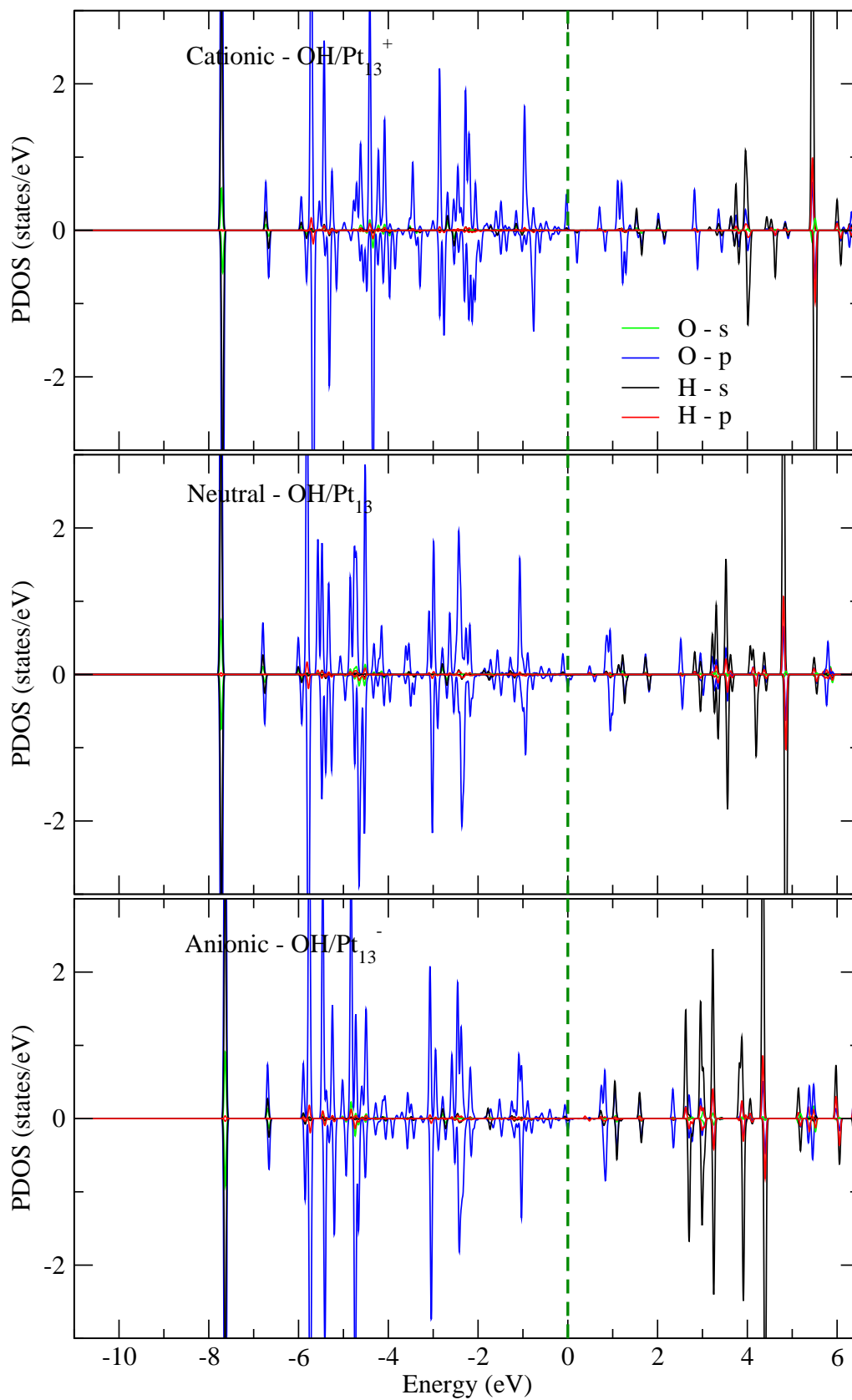


Figure S19: Projected Density of States (PDOS) for the OH-states of the OH adsorption on the Pt_{13} clusters for each lowest-energy configurations in the cationic, neutral, and anionic charge states. The vertical green dashed line corresponds to the HOMO energy (0 eV).

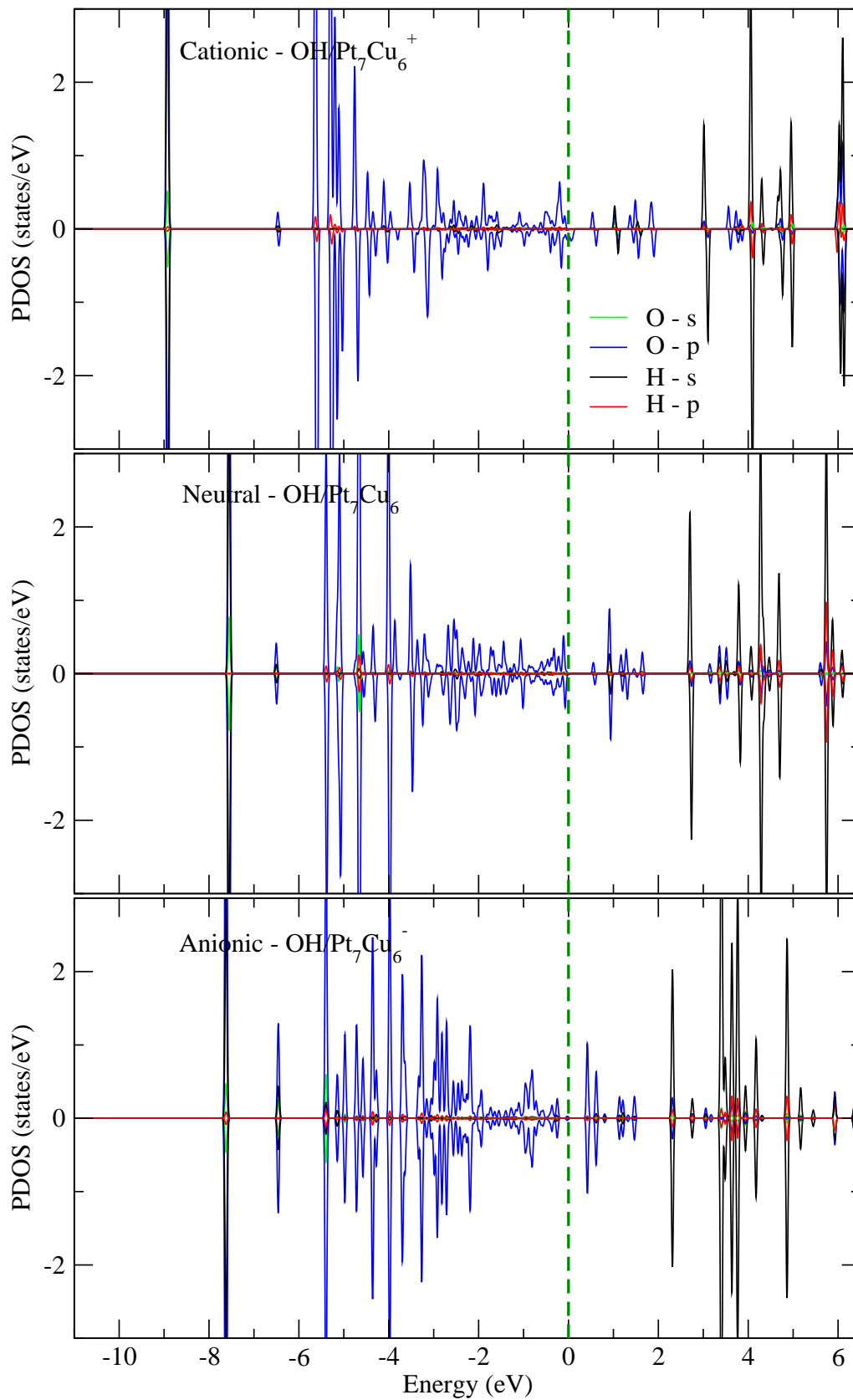


Figure S20: Projected Density of States (PDOS) for the OH-states of the OH adsorption on the Pt_7Cu_6 clusters for each lowest-energy configurations in the cationic, neutral, and anionic charge states. The vertical green dashed line corresponds to the HOMO energy (0 eV).

Table S5: Mulliken analysis of the adsorption process of CO on Cu₁₃, Pt₇Cu₆, and Pt₁₃ clusters in different charge states, namely, cationic (+), neutral (0), and anionic (−). Δq is the charge variation on the corresponding atom, where Δq > 0 means loss of charge while Δq < 0 corresponds to gain. Δq(M) (M = C, O, Cu and Pt) is the total charge variation of the M atom, while Δq(M)^s, Δq(M)^p, Δq(M)^d and Δq(M)^f indicate the charge variation of the *s*, *p*, *d* and *f* orbitals of the corresponding M atom. ΔqTM corresponds to the total charge variation of the TM cluster.

		Cu ₁₃			Pt ₇ Cu ₆			Pt ₁₃		
		+	0	−	+	0	−	+	0	−
CO	Δq(C)	0.30	0.28	0.24	0.22	0.17	0.11	0.25	0.21	0.14
	Δq(O)	−0.08	−0.15	−0.20	−0.11	−0.17	−0.23	−0.11	−0.17	−0.22
	Δq(C) ^s	0.64	0.62	0.61	0.70	0.67	0.63	0.71	0.68	0.62
	Δq(C) ^p	−0.18	−0.17	−0.20	−0.27	−0.29	−0.31	−0.26	−0.27	−0.28
	Δq(C) ^d	−0.14	−0.14	−0.15	−0.18	−0.18	−0.17	−0.17	−0.17	−0.16
	Δq(C) ^f	−0.02	−0.02	−0.02	−0.03	−0.03	−0.02	−0.03	−0.03	−0.02
	Δq(O) ^s	0.27	0.28	0.29	0.27	0.28	0.28	0.27	0.28	0.28
	Δq(O) ^p	−0.29	−0.36	−0.42	−0.32	−0.39	−0.46	−0.33	−0.39	−0.45
	Δq(O) ^d	−0.06	−0.06	−0.06	−0.05	−0.05	−0.05	−0.05	−0.05	−0.05
	Δq(O) ^f	−0.01	−0.01	−0.01	−0.01	−0.01	−0.01	−0.01	−0.01	−0.01
	Δq(Cu) ^s	2.31	1.46	0.37	1.63	1.52	1.35			
	Δq(Cu) ^p	−4.79	−4.85	−4.67	−2.55	−2.50	−2.39			
	Δq(Cu) ^d	3.64	3.63	3.62	1.73	1.65	1.62			
	Δq(Cu) ^f	−0.25	−0.25	−0.24	−0.18	−0.18	−0.18			
	Δq(Pt) ^s				1.07	0.80	0.41	2.34	1.95	1.44
	Δq(Pt) ^p				−2.14	−2.14	−2.14	−5.22	−5.15	−5.10
	Δq(Pt) ^d				1.95	1.46	1.04	5.03	4.43	3.98
	Δq(Pt) ^f				−0.36	−0.35	−0.34	−0.86	−0.84	−0.83
	Δq TM	0.78	−0.13	−1.03	0.89	0.00	−0.88	0.87	−0.04	−0.92

Table S6: Mulliken analysis of the adsorption process of NO on Cu₁₃, Pt₇Cu₆, and Pt₁₃ clusters in different charge states, namely, cationic (+), neutral (0), and anionic (−). Δq is the charge variation on the corresponding atom, where Δq > 0 means loss of charge while Δq < 0 corresponds to gain. Δq(M) (M = N, O, Cu and Pt) is the total charge variation of the M atom, while Δq(M)^s, Δq(M)^p, Δq(M)^d and Δq(M)^f indicate the charge variation of the *s*, *p*, *d* and *f* orbitals of the corresponding M atom. ΔqTM corresponds to the total charge variation of the TM cluster.

		Cu ₁₃			Pt ₇ Cu ₆			Pt ₁₃		
		+	0	−	+	0	−	+	0	−
NO	Δq(N)	−0.05	−0.13	−0.08	0.21	0.17	0.12	0.10	0.07	0.05
	Δq(O)	−0.02	−0.12	−0.19	−0.01	−0.07	−0.14	−0.08	−0.15	−0.21
	Δq(N) ^s	0.43	0.45	0.45	0.54	0.53	0.51	0.50	0.50	0.49
	Δq(N) ^p	−0.30	−0.37	−0.36	−0.14	−0.18	−0.21	−0.18	−0.20	−0.22
	Δq(N) ^d	−0.15	−0.18	−0.14	−0.16	−0.15	−0.15	−0.19	−0.19	−0.18
	Δq(N) ^f	−0.02	−0.02	−0.02	−0.02	−0.02	−0.02	−0.03	−0.03	−0.03
	Δq(O) ^s	0.24	0.25	0.25	0.24	0.24	0.25	0.24	0.24	0.25
	Δq(O) ^p	−0.17	−0.28	−0.34	−0.17	−0.24	−0.31	−0.23	−0.31	−0.37
	Δq(O) ^d	−0.07	−0.07	−0.08	−0.07	−0.07	−0.07	−0.07	−0.07	−0.07
	Δq(O) ^f	−0.01	−0.01	−0.01	−0.01	−0.01	−0.01	−0.01	−0.01	−0.01
	Δq(Cu) ^s	2.41	1.56	0.52	1.54	1.44	1.30			
	Δq(Cu) ^p	−4.68	−4.65	−4.57	−2.56	−2.39	−2.51			
	Δq(Cu) ^d	3.73	3.72	3.68	1.85	1.71	1.62			
	Δq(Cu) ^f	−0.26	−0.26	−0.26	−0.18	−0.18	−0.17			
	Δq(Pt) ^s				1.00	0.62	0.23	2.25	1.89	1.38
	Δq(Pt) ^p				−2.24	−2.25	−2.22	−5.04	−5.01	−4.91
	Δq(Pt) ^d				2.04	1.71	1.27	5.08	4.48	3.94
	Δq(Pt) ^f				−0.38	−0.38	−0.37	−0.87	−0.86	−0.84
	Δq TM	1.06	0.25	−0.74	0.79	−0.10	−0.98	0.99	0.08	−0.84

Table S7: Mulliken analysis of the adsorption process of OH on Cu₁₃, Pt₇Cu₆, and Pt₁₃ clusters in different charge states, namely, cationic (+), neutral (0), and anionic (-). Δq is the charge variation on the corresponding atom, where $\Delta q > 0$ means loss of charge while $\Delta q < 0$ corresponds to gain. $\Delta q(M)$ ($M = H, O, Cu$ and Pt) is the total charge variation of the M atom, while $\Delta q(M)^s$, $\Delta q(M)^p$, $\Delta q(M)^d$ and $\Delta q(M)^f$ indicate the charge variation of the s , p , d and f orbitals of the corresponding M atom. Δq^{TM} corresponds to the total charge variation of the TM cluster.

		Cu ₁₃			Pt ₇ Cu ₆			Pt ₁₃		
		+	0	-	+	0	-	+	0	-
OH	$\Delta q(H)$	0.22	0.19	0.17	0.23	0.18	0.15	0.21	0.18	0.15
	$\Delta q(O)$	-0.33	-0.37	-0.39	-0.32	-0.31	-0.39	-0.29	-0.31	-0.33
	$\Delta q(H)^s$	0.35	0.34	0.32	0.35	0.33	0.32	0.34	0.33	0.31
	$\Delta q(H)^p$	-0.12	-0.12	-0.13	-0.10	-0.13	-0.15	-0.11	-0.12	-0.13
	$\Delta q(H)^d$	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02
	$\Delta q(O)^s$	0.23	0.22	0.21	0.26	0.22	0.24	0.22	0.22	0.21
	$\Delta q(O)^p$	-0.52	-0.56	-0.57	-0.52	-0.48	-0.59	-0.46	-0.47	-0.49
	$\Delta q(O)^d$	-0.03	-0.03	-0.03	-0.05	-0.04	-0.03	-0.04	-0.04	-0.04
	$\Delta q(O)^f$	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01
	$\Delta q(Cu)^s$	2.47	1.61	0.52	1.65	1.49	1.35			
	$\Delta q(Cu)^p$	-4.65	-4.62	-4.47	-2.58	-2.53	-2.43			
	$\Delta q(Cu)^d$	3.69	3.57	3.53	1.85	1.72	1.59			
	$\Delta q(Cu)^f$	-0.27	-0.27	-0.26	-0.20	-0.19	-0.18			
	$\Delta q(Pt)^s$				1.09	0.74	0.37	2.26	1.86	1.38
	$\Delta q(Pt)^p$				-1.93	-1.98	-2.07	-5.03	-4.96	-4.84
	$\Delta q(Pt)^d$				1.85	1.51	1.22	5.17	4.51	3.88
	$\Delta q(Pt)^f$				-0.36	-0.37	-0.37	-0.88	-0.86	-0.84
	Δq^{TM}	1.11	0.18	-0.78	1.10	0.13	-0.77	1.08	0.13	-0.83

Table S8: Mulliken analysis of the neutral CO, NO, and OH in gas-phase. Δq is the charge variation on the corresponding atom, where $\Delta q > 0$ means loss of charge while $\Delta q < 0$ corresponds to gain. $\Delta q(M)$ ($M = C, N, H$ and O) is the total charge variation of the M atom, while $\Delta q(M)^s$, $\Delta q(M)^p$, $\Delta q(M)^d$ and $\Delta q(M)^f$ indicate the charge variation of the s , p , d and f orbitals of the corresponding M atom.

CO		NO		OH	
$\Delta q(C)$	0.14	$\Delta q(N)$	0.03	$\Delta q(H)$	0.26
$\Delta q(O)$	-0.14	$\Delta q(O)$	-0.03	$\Delta q(O)$	-0.26
$\Delta q(C)^s$	0.23	$\Delta q(N)^s$	0.15	$\Delta q(H)^s$	0.40
$\Delta q(C)^p$	0.04	$\Delta q(N)^p$	-0.01	$\Delta q(H)^p$	-0.12
$\Delta q(C)^d$	-0.10	$\Delta q(N)^d$	-0.10	$\Delta q(H)^d$	-0.02
$\Delta q(C)^f$	-0.01	$\Delta q(N)^f$	-0.02	$\Delta q(H)^f$	-0.00
$\Delta q(O)^s$	0.26	$\Delta q(O)^s$	0.24	$\Delta q(O)^s$	0.15
$\Delta q(O)^p$	-0.35	$\Delta q(O)^p$	-0.19	$\Delta q(O)^p$	-0.40
$\Delta q(O)^d$	-0.05	$\Delta q(O)^d$	-0.06	$\Delta q(O)^d$	-0.02
$\Delta q(O)^f$	-0.01	$\Delta q(O)^f$	-0.01	$\Delta q(O)^f$	-0.00

Table S9: Mulliken analysis of the Cu_{13} , Pt_7Cu_6 , and Pt_{13} gas-phase clusters in different charge states, namely, cationic (+), neutral (0), and anionic (−). Δq is the charge variation on the corresponding atom, where $\Delta q > 0$ means loss of charge while $\Delta q < 0$ corresponds to gain. $\Delta q(\text{X})$ ($\text{X} = \text{Cu}$ and Pt) is the summation of total charge variation over all X atoms in the cluster, while $\Delta q(\text{X})^s$, $\Delta q(\text{X})^p$, $\Delta q(\text{X})^d$ and $\Delta q(\text{X})^f$ indicate the charge variation of the s , p , d and f orbitals of the corresponding X atom. $\Delta q(\text{TM})$ corresponds to the total charge variation of the TM cluster.

		Cu_{13}	Pt_7Cu_6	Pt_{13}
Cationic	$\Delta q(\text{TM})$	1.00	1.00	1.00
	$\Delta q(\text{Cu})^s$	2.29	1.56	
	$\Delta q(\text{Cu})^p$	−4.50	−2.58	
	$\Delta q(\text{Cu})^d$	3.57	1.88	
	$\Delta q(\text{Cu})^f$	−0.24	−0.19	
	$\Delta q(\text{Pt})^s$		1.01	2.35
	$\Delta q(\text{Pt})^p$		−1.89	−4.96
	$\Delta q(\text{Pt})^d$		1.81	4.89
	$\Delta q(\text{Pt})^f$		−0.34	−0.84
Neutral	$\Delta q(\text{TM})$	0.00	0.00	0.00
	$\Delta q(\text{Cu})^s$	1.34	1.44	
	$\Delta q(\text{Cu})^p$	−4.52	−2.50	
	$\Delta q(\text{Cu})^d$	3.54	1.74	
	$\Delta q(\text{Cu})^f$	−0.24	−0.18	
	$\Delta q(\text{Pt})^s$		0.65	1.88
	$\Delta q(\text{Pt})^p$		−1.88	−4.92
	$\Delta q(\text{Pt})^d$		1.32	4.30
	$\Delta q(\text{Pt})^f$		−0.33	−0.83
Anionic	$\Delta q(\text{TM})$	−1.00	−1.00	−1.00
	$\Delta q(\text{Cu})^s$	0.12	1.28	
	$\Delta q(\text{Cu})^p$	−4.30	−2.36	
	$\Delta q(\text{Cu})^d$	3.52	1.65	
	$\Delta q(\text{Cu})^f$	−0.23	−0.18	
	$\Delta q(\text{Pt})^s$		0.16	1.30
	$\Delta q(\text{Pt})^p$		−1.84	−4.81
	$\Delta q(\text{Pt})^d$		0.85	3.73
	$\Delta q(\text{Pt})^f$		−0.32	−0.81

Table S10: Tests for different charge population analysis schemes, namely, basis-set dependent Mulliken and electron density dependent Hirshfeld schemes, for the study of the adsorption of CO on Cu₁₃, Pt₇Cu₆, and Pt₁₃ neutral clusters. Both population schemes are tested against different basis set sizes, namely, light or tight *tiers* 1, 2 or 3, according to the FHI-aims nomenclature. $\Delta q(X)^{Mull}$ and $\Delta q(X)^{Hirs}$ are respectively the Mulliken and Hirshfeld total charge variation on the corresponding X (X = TM (Pt, Cu), C, O) atom, where $\Delta q > 0$ means loss of charge while $\Delta q < 0$ corresponds to gain.

Basis set		CO/Cu ₁₃	CO/Pt ₇ Cu ₆	CO/Pt ₁₃
Light tier 1	$\Delta q(TM)^{Mull}$	−0.11	−0.01	−0.02
Light tier 2	$\Delta q(C)^{Mull}$	0.22	0.16	0.17
Light tier 2	$\Delta q(O)^{Mull}$	−0.11	−0.15	−0.15
Light tier 1	$\Delta q(TM)^{Hirs}$	0.04	0.07	0.07
Light tier 2	$\Delta q(C)^{Hirs}$	0.05	0.05	0.05
Light tier 2	$\Delta q(O)^{Hirs}$	−0.09	−0.12	−0.12
Light tier 2	$\Delta q(TM)^{Mull}$	0.02	−0.06	0.09
Light tier 3	$\Delta q(C)^{Mull}$	0.14	0.12	0.10
Light tier 3	$\Delta q(O)^{Mull}$	−0.16	−0.18	−0.19
Light tier 2	$\Delta q(TM)^{Hirs}$	0.04	0.08	0.07
Light tier 3	$\Delta q(C)^{Hirs}$	0.05	0.04	0.05
Light tier 3	$\Delta q(O)^{Hirs}$	−0.09	−0.12	−0.12
Tight tier 1	$\Delta q(TM)^{Mull}$	−0.17	−0.19	−0.19
Tight tier 2	$\Delta q(C)^{Mull}$	0.27	0.31	0.31
Tight tier 2	$\Delta q(O)^{Mull}$	−0.1	−0.12	−0.12
Tight tier 1	$\Delta q(TM)^{Hirs}$	0.02	0.07	0.07
Tight tier 2	$\Delta q(C)^{Hirs}$	0.06	0.05	0.05
Tight tier 2	$\Delta q(O)^{Hirs}$	−0.08	−0.12	−0.12
Tight tier 2	$\Delta q(TM)^{Mull}$	−0.13	0.00	−0.04
Tight tier 3	$\Delta q(C)^{Mull}$	0.28	0.17	0.21
Tight tier 3	$\Delta q(O)^{Mull}$	−0.15	−0.17	−0.17
Tight tier 2	$\Delta q(TM)^{Hirs}$	0.04	0.08	0.07
Tight tier 3	$\Delta q(C)^{Hirs}$	0.05	0.04	0.05
Tight tier 3	$\Delta q(O)^{Hirs}$	−0.09	−0.12	−0.12

Table S11: Tests for different charge population analysis schemes, namely, basis-set dependent Mulliken and electron density dependent Hirshfeld schemes, for the study of the CO, NO and OH in the gas-phase. Both population schemes are tested against different basis set sizes, namely, light or tight *tiers* 1, 2 or 3, according to the FHI-aims nomenclature. $\Delta q(X)^{Mull}$ and $\Delta q(X)^{Hirs}$ are respectively the Mulliken and Hirshfeld total charge variation on the corresponding X (X = C, N, H) atom, while $\Delta q(O)^{Mull}$ and $\Delta q(O)^{Hirs}$ correspond to the Mulliken and Hirshfeld total charge variation on oxygen atom. $\Delta q > 0$ means loss of charge while $\Delta q < 0$ corresponds to gain. The root mean square deviation (RMSD) was calculated for each system and scheme.

Basis set		CO	NO	OH
Light tier 1	$\Delta q(X)^{Mull}$	0.09	0.02	0.28
Light tier 1	$\Delta q(O)^{Mull}$	-0.09	-0.02	-0.28
Light tier 1	$\Delta q(X)^{Hirs}$	0.07	0.01	0.16
Light tier 1	$\Delta q(O)^{Hirs}$	-0.07	-0.01	-0.16
Light tier 2	$\Delta q(X)^{Mull}$	0.07	-0.04	0.30
Light tier 2	$\Delta q(O)^{Mull}$	-0.07	0.04	-0.30
Light tier 2	$\Delta q(X)^{Hirs}$	0.07	0.01	0.15
Light tier 2	$\Delta q(O)^{Hirs}$	-0.07	-0.01	-0.15
Light tier 3	$\Delta q(X)^{Mull}$	0.14	0.01	0.26
Light tier 3	$\Delta q(O)^{Mull}$	-0.14	-0.01	-0.26
Light tier 3	$\Delta q(X)^{Hirs}$	0.07	0.01	0.15
Light tier 3	$\Delta q(O)^{Hirs}$	-0.07	-0.01	-0.15
Tight tier 1	$\Delta q(X)^{Mull}$	0.09	0.02	0.29
Tight tier 1	$\Delta q(O)^{Mull}$	-0.09	-0.02	-0.29
Tight tier 1	$\Delta q(X)^{Hirs}$	0.08	0.01	0.16
Tight tier 1	$\Delta q(O)^{Hirs}$	-0.08	-0.01	-0.16
Tight tier 2	$\Delta q(X)^{Mull}$	0.08	-0.04	0.30
Tight tier 2	$\Delta q(O)^{Mull}$	-0.08	0.04	-0.30
Tight tier 2	$\Delta q(X)^{Hirs}$	0.07	0.01	0.15
Tight tier 2	$\Delta q(O)^{Hirs}$	-0.07	-0.01	-0.15
Tight tier 3	$\Delta q(X)^{Mull}$	0.14	0.03	0.26
Tight tier 3	$\Delta q(O)^{Mull}$	-0.14	-0.03	-0.26
Tight tier 3	$\Delta q(X)^{Hirs}$	0.07	0.01	0.15
Tight tier 3	$\Delta q(O)^{Hirs}$	-0.07	-0.01	-0.15
RMSD	Mulliken	0.034	0.018	0.017
RMSD	Hirshfeld	0.004	0.000	0.005