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

Supporting Information: The Role of Charge Transfer in the Oxidation State Change of Ce Atoms in the $TM_{13}/CeO_2(111)$ systems (TM = Pd, Ag, Pt, Au): A DFT+U Investigation

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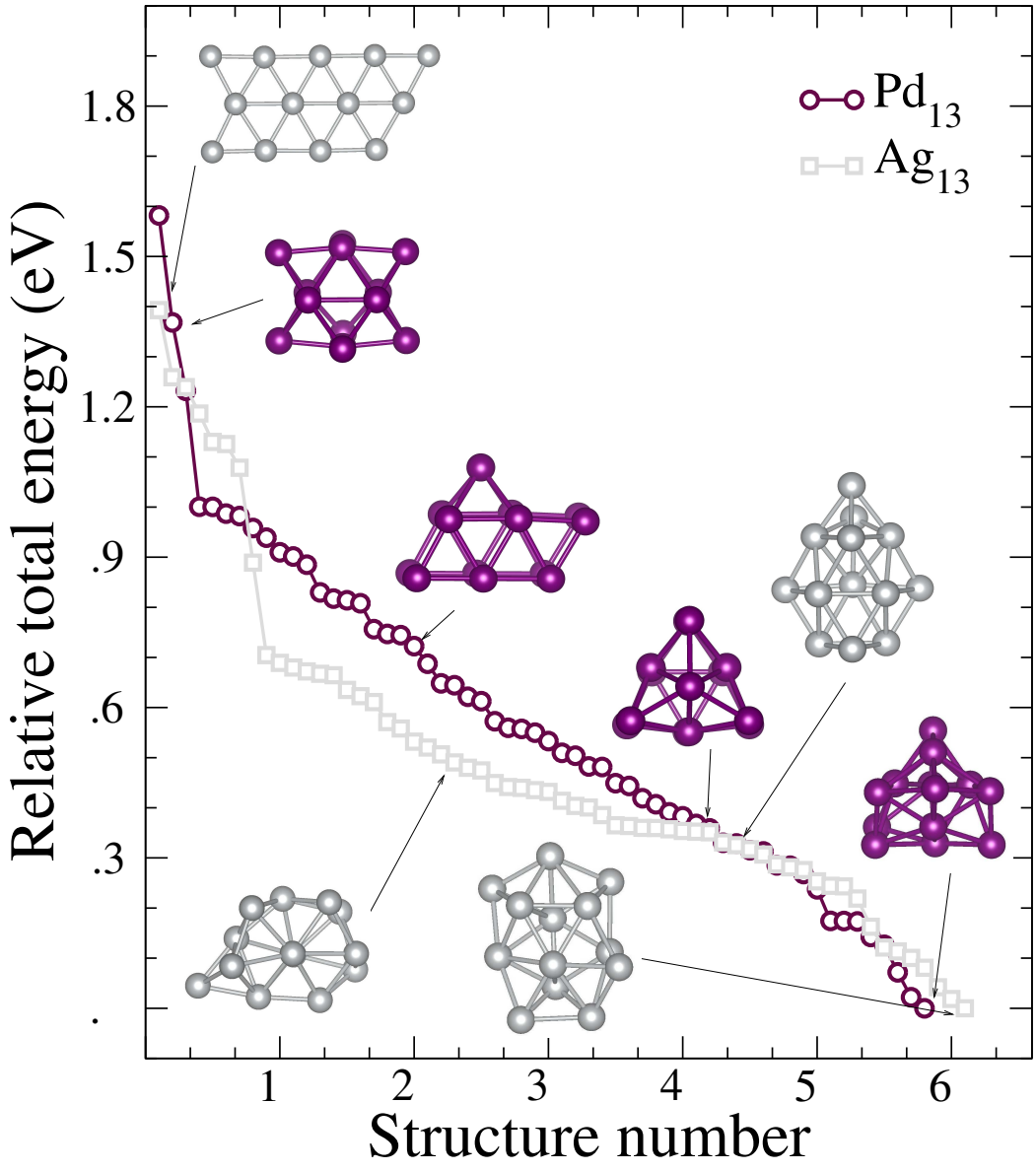

Figure 1: Relative total energy calculated for all the 13-atom Pd_{13} and Ag_{13} configurations. $\Delta E_{\text{tot}} = E_{\text{tot}}^{\text{Config-i}} - E_{\text{tot}}^{\text{lowest}}$, where $E_{\text{tot}}^{\text{Config-i}}$ is the total energy of a given configuration and $E_{\text{tot}}^{\text{lowest}}$ is the total energy of the lowest energy configuration. Representative atomic structures are also indicated within the figure.

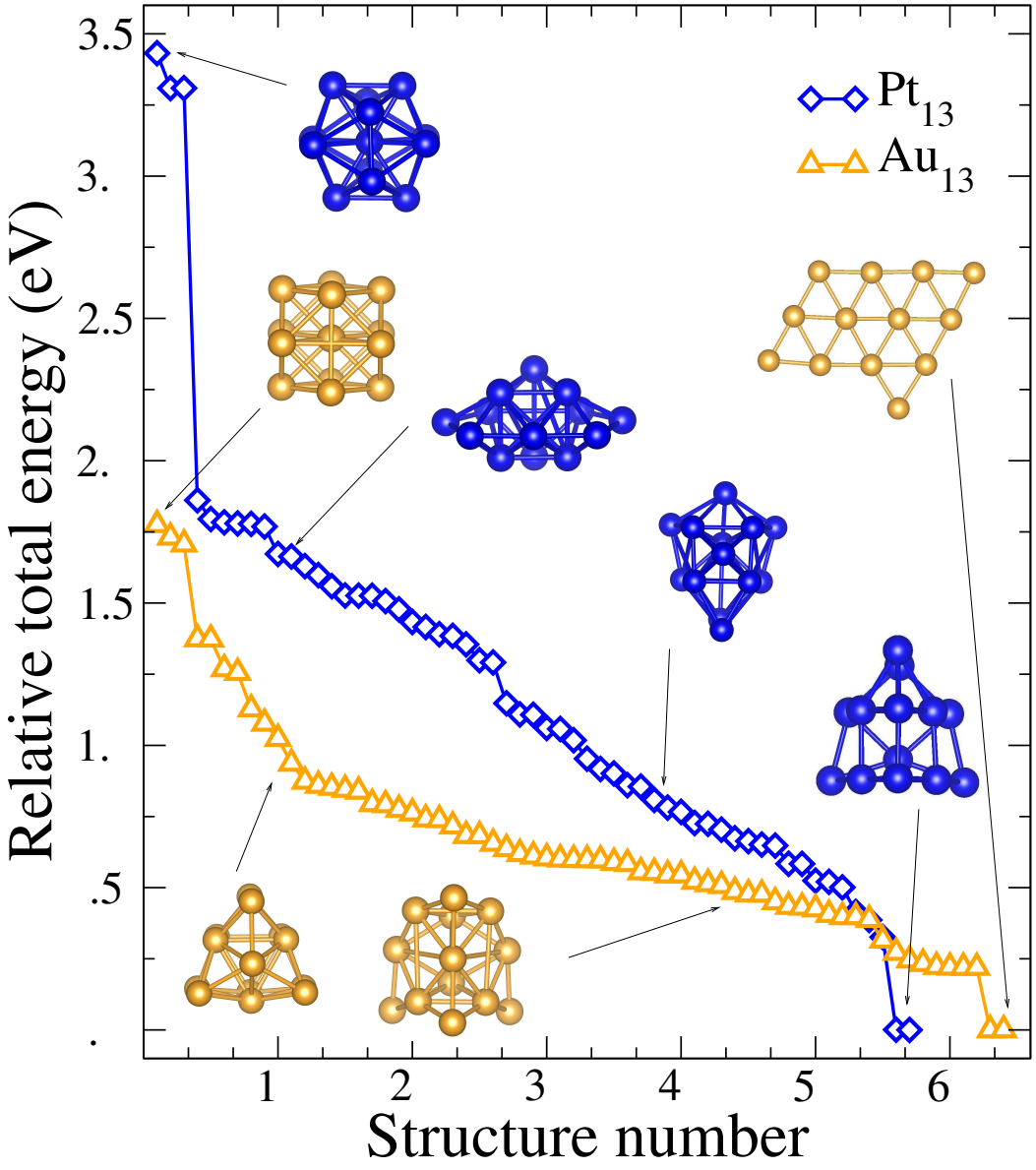

Figure 2: Relative total energy calculated for all the 13-atom Pt_{13} and Au_{13} configurations. $\Delta E_{\rm tot} = E_{\rm tot}^{\rm Config\text{-}i} - E_{\rm tot}^{\rm lowest}$, where $E_{\rm tot}^{\rm Config\text{-}i}$ is the total energy of a given configuration and $E_{\rm tot}^{\rm lowest}$ is the total energy of the lowest energy configuration. Representative atomic structures are also indicated within the figure.

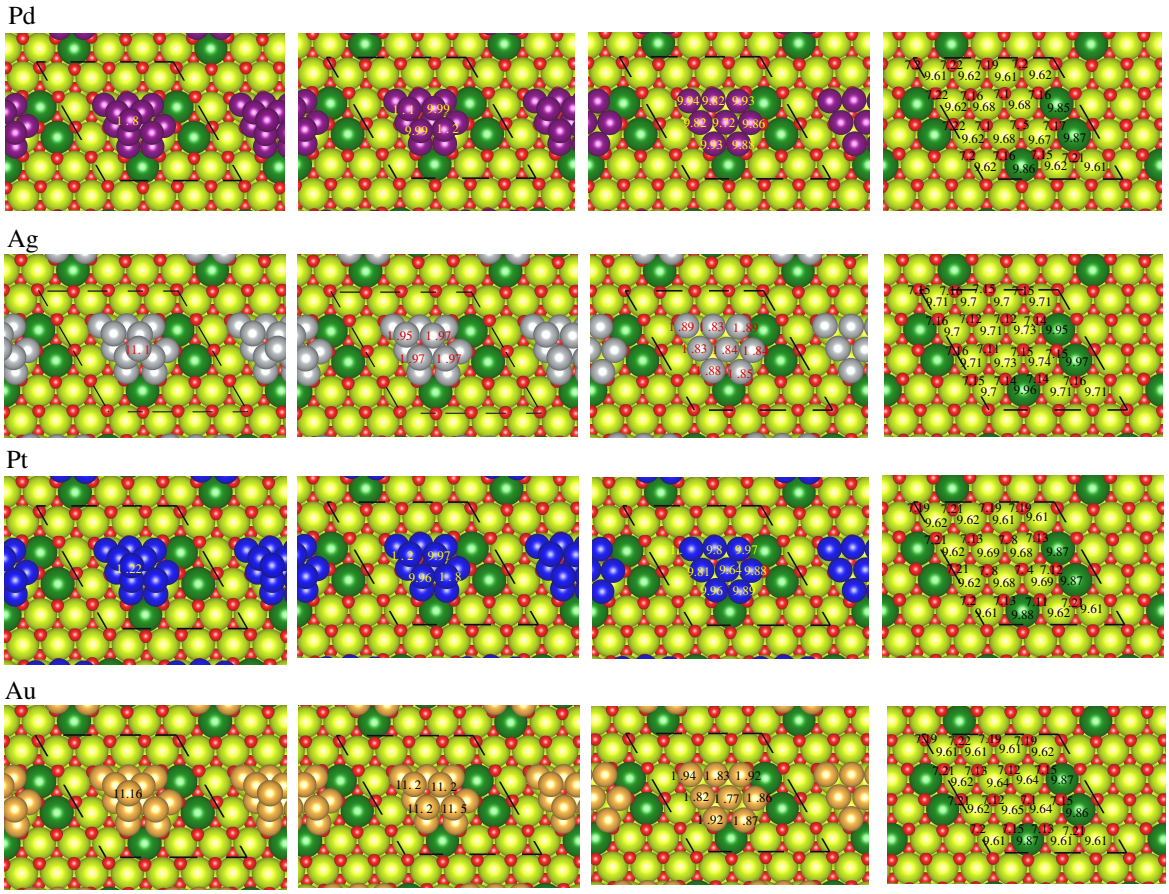

Figure 3: Layer resolved maping of the Bader charges on the TM, Ce^{III}, Ce^{IV}, and O atoms in the lowest energy configuration for the $TM_{13}/CeO_2(111)$ systems (TM = Pd, Ag, Pt, Au). For the TM atoms, the Bader charges are indicated for every TM atom in the top, middle, and bottom layer in the 13-atom clusters. For the Ce^{III}, Ce^{IV}, and O atoms, the Bader charges were calculated only for the tomost Ce and O layers in the $TM_{13}/CeO_2(111)$ system. The O, TM, and Ce atoms are indicated by small (red), medium (purble (Pd), gray (Ag), blue (Pt), and yellow-orange (Au)), and large spheres. The Ce atoms are separated into two groups, namely, Ce^{III} (dark green) and Ce^{IV} (light green).

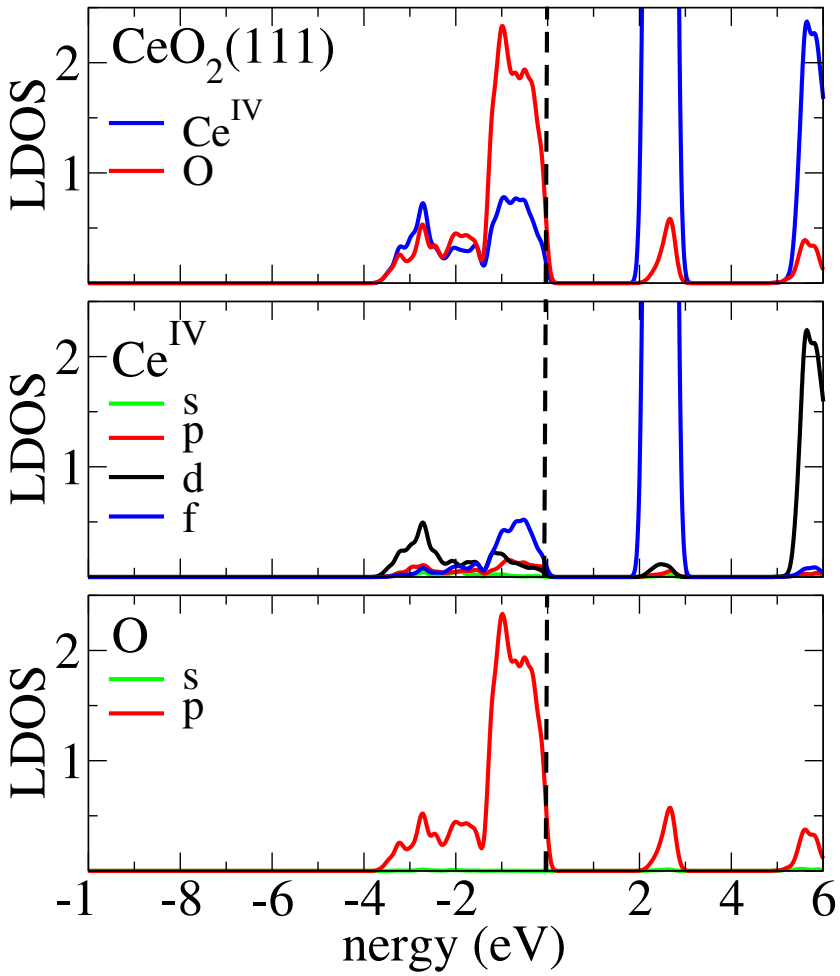

Figure 4: Atom resolved average local density of states (LDOS) of the Ce^{IV} and O atoms in the clean $CeO_2(111)$ surface in the lowest energy configuration. The Ce^{IV} and O LDOS are the average over only the Ce^{IV} and O atoms in the topmost Ce and O layers in the clean $CeO_2(111)$ surface. The decomposition of the LDOS into *s*-, *p*-, *d*-, and *f*-states are also shown for the respective atoms. The vertical dashed lines in black indicate the Fermi energy.

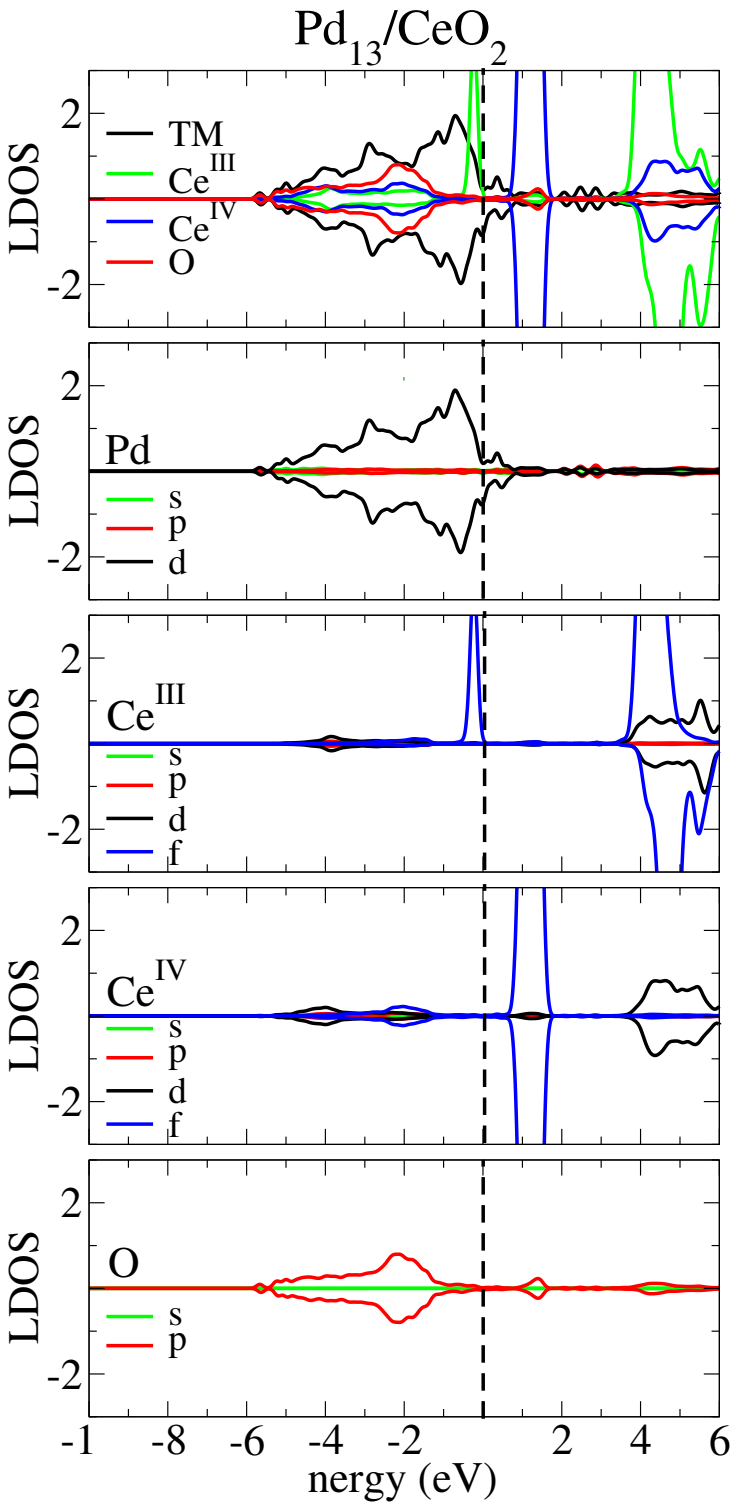

Figure 5: Atom resolved average local density of states (LDOS) of the Pd, Ce^{III}, Ce^{IV}, and O atoms in the $Pd_{13}/CeO_2(111)$ system in the lowest energy configuration. The Pd LDOS is the average over all the Pd atoms in the 13-atom cluster, while the Ce^{III}, Ce^{IV}, and O LDOS are the average over only the Ce^{III}, Ce^{IV}, and O atoms in the topmost Ce and O layers in the $CeO_2(111)$ surface. The decomposition of the LDOS into *s*-, *p*-, *d*-, and *f*-states are also shown for the respective atoms. The vertical dashed lines in black indicate the Fermi energy.

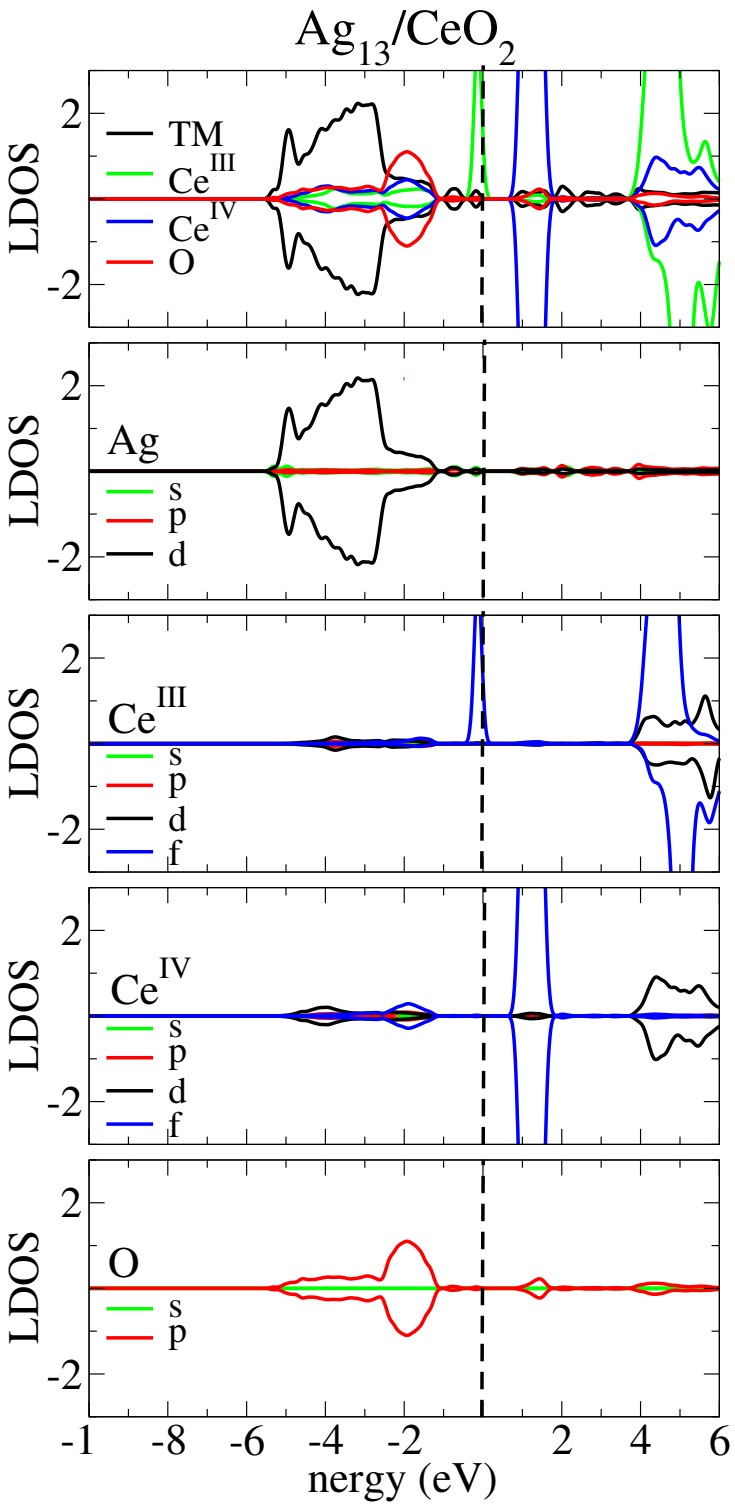

Figure 6: Atom resolved average local density of states (LDOS) of the Ag, Ce^{III}, Ce^{IV}, and O atoms in the $Ag_{13}/CeO_2(111)$ system in the lowest energy configuration. The Ag LDOS is the average over all the Ag atoms in the 13-atom cluster, while the Ce^{III}, Ce^{IV}, and O LDOS are the average over only the Ce^{III}, Ce^{IV}, and O atoms in the topmost Ce and O layers in the $CeO_2(111)$ surface. The decomposition of the LDOS into *s*-, *p*-, *d*-, and *f*-states are also shown for the respective atoms. The vertical dashed lines in black indicate the Fermi energy.

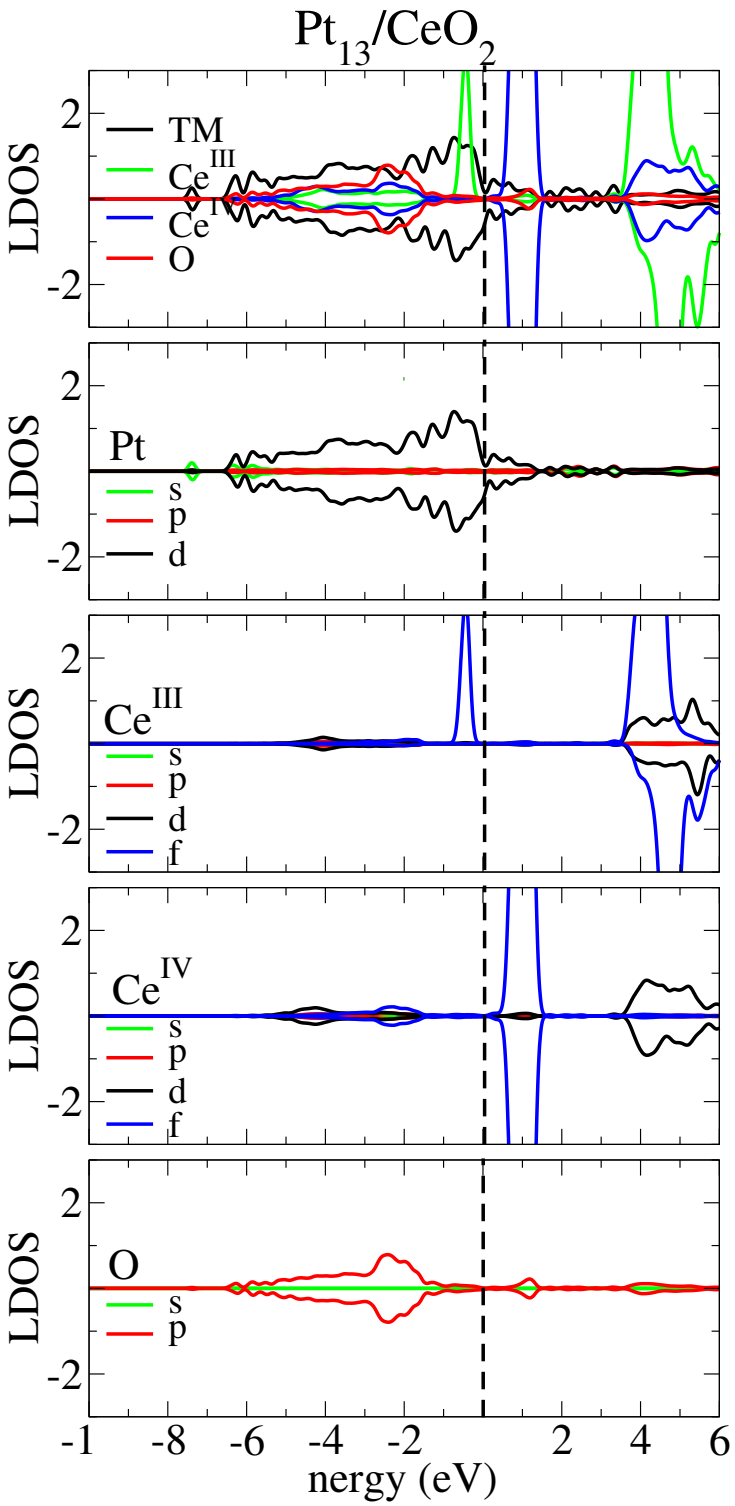

Figure 7: Atom resolved average local density of states (LDOS) of the Pt, Ce^{III}, Ce^{IV}, and O atoms in the $Pt_{13}/CeO_2(111)$ system in the lowest energy configuration. The Pt LDOS is the average over all the Pt atoms in the 13-atom cluster, while the Ce^{III}, Ce^{IV}, and O LDOS are the average over only the Ce^{III}, Ce^{IV}, and O atoms in the topmost Ce and O layers in the $CeO_2(111)$ surface. The decomposition of the LDOS into *s*-, *p*-, *d*-, and *f*-states are also shown for the respective atoms. The vertical dashed lines in black indicate the Fermi energy.

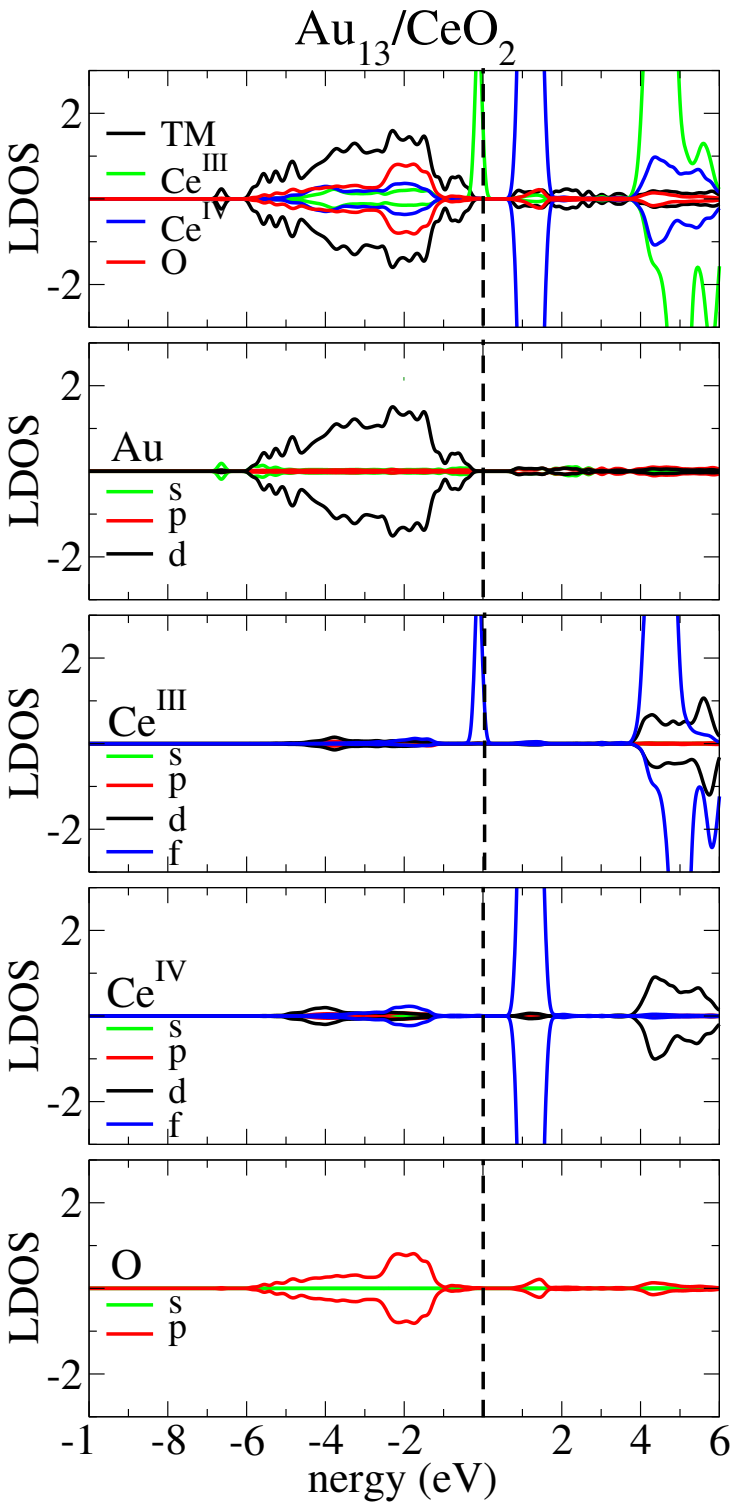

Figure 8: Atom resolved average local density of states (LDOS) of the Au, Ce^{III}, Ce^{IV}, and O atoms in the $Au_{13}/CeO_2(111)$ system in the lowest energy configuration. The Au LDOS is the average over all the Pt atoms in the 13-atom cluster, while the Ce^{III}, Ce^{IV}, and O LDOS are the average over only the Ce^{III}, Ce^{IV}, and O atoms in the topmost Ce and O layers in the $CeO_2(111)$ surface. The decomposition of the LDOS into *s*-, *p*-, *d*-, and *f*-states are also shown for the respective atoms. The vertical dashed lines in black indicate the Fermi energy.