Coverage effect of the CO_2 adsorption mechanisms on CeO_2(111) by first principles analysis

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Supporting Information

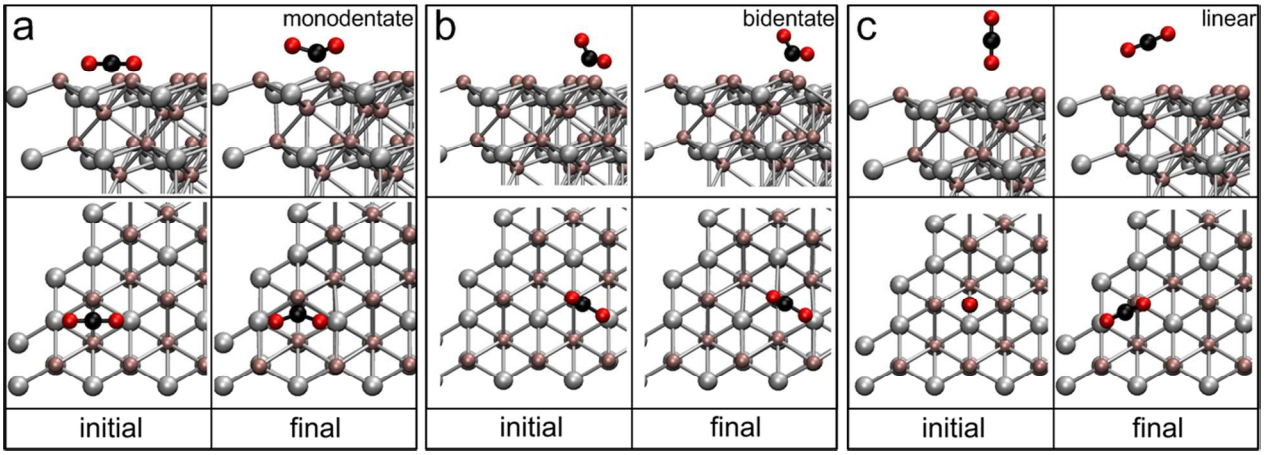

Figure S1. Initial and final configurations for stable configurations of CO_2 on CeO_2(111). When the linear CO_2 molecule was initially placed close to the surface (1.7 Å), the molecule spontaneously bent to form a monodentate species (a).

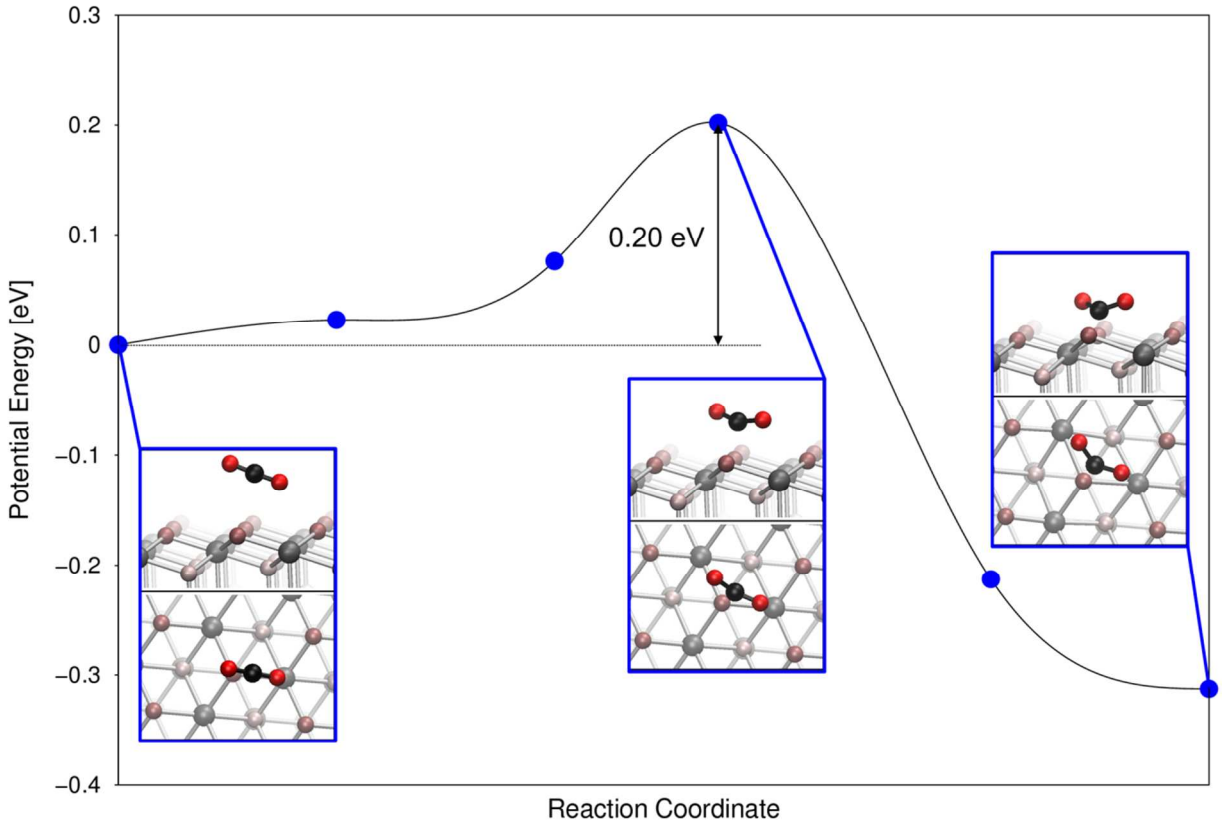

Figure S2. Potential energy surface for the transition of the linear CO2 molecule at 3.5 Å above the surface to the monodentate configuration of CO_2 obtained from nudged elastic band calculations. For the adsorption of CO_2 in the bent monodentate configuration, an activation energy of 0.2 eV is determined. In the transition state the O-C-O angle decreases to 152.1° and the C-O bond length elongates to 1.20 Å.

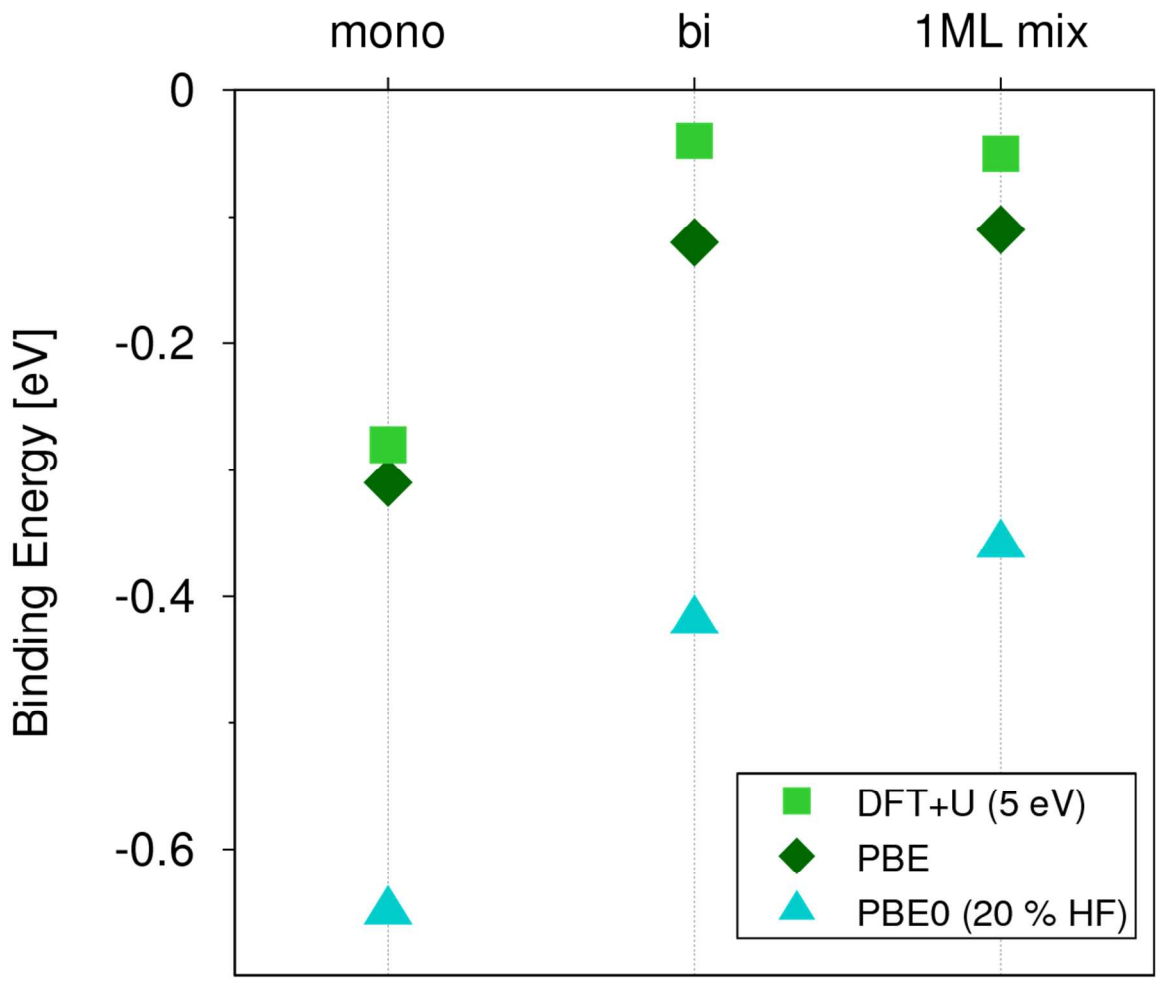

Figure S3. Binding energy of selected configurations (mono- and bidentate at 1/9 ML and mixed configuration of monodentate and linear species at 1 ML) of CO_2 adsorbed on CeO_2(111) calculated with DFT+U (U=5 eV), standard DFT using the PBE functional and PBE0. PBE0 calculations were performed using 20% exact exchange. All methods show the same trends for the stability of different adsorption mechanisms.

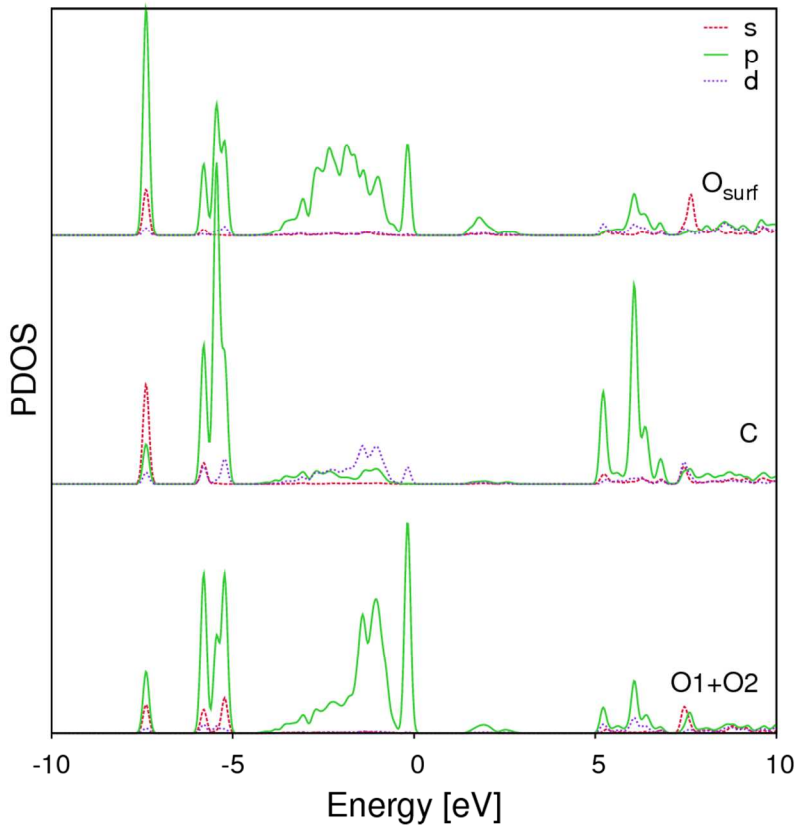

Figure S4. PDOS on s- (red lines), p- (green lines) and d-type (violet lines) orbitals of the O_{surf} atom and the C and O (O1 and O2) atoms of the CO_2 molecule adsorbed on CeO_2(111) in a monodenate configuration at 1/9 ML coverage. Binding of the CO_2 molecule at the valence band to the O_{surf} atom takes place through p-orbitals of the O atoms and hybridized orbitals of the C atom with d-character.

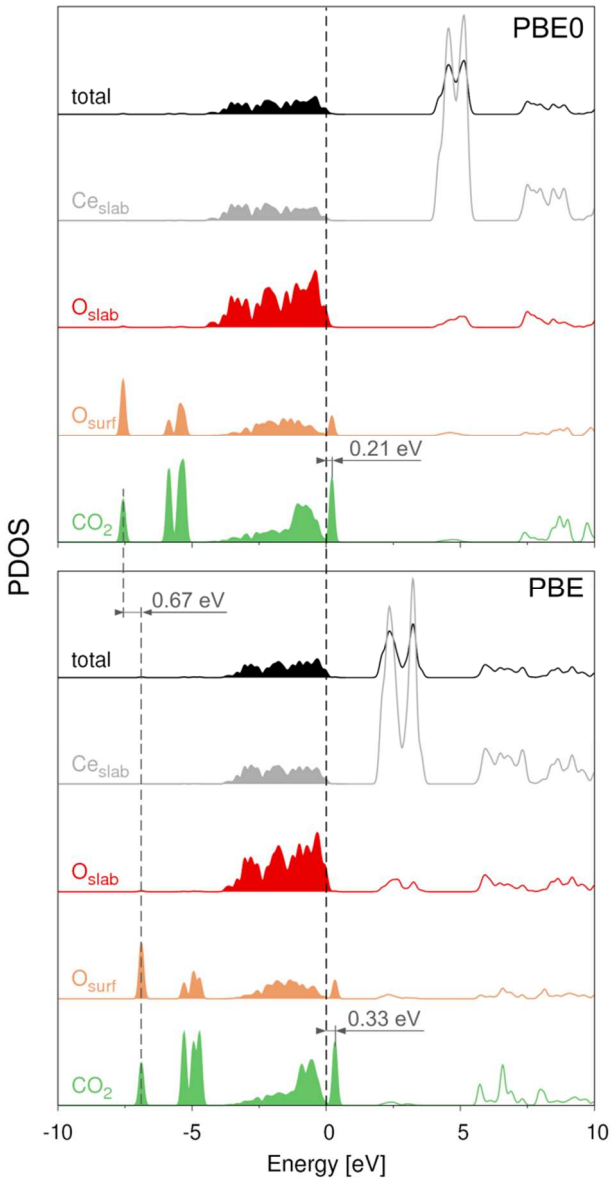

Figure S5. PDOS summed over all atoms (black) and on specific species (Ce_{slab}, O_{slab} and CO_2) of isolated (1/9 ML) CO_2 adsorbed on CeO_2(111) in a monodentate configuration calculated with PBE0 (top) and standard DFT (PBE, bottom). CO_2 orbitals ca. 6 eV below the valence band are found at lower energies (by 0.67 eV) for PBE0 than for PBE. Additional CO_2 states formed upon adsorption are found at 0.21 and 0.33 eV above the valence band of CeO_2 for PBE0 and PBE calculations, respectively.

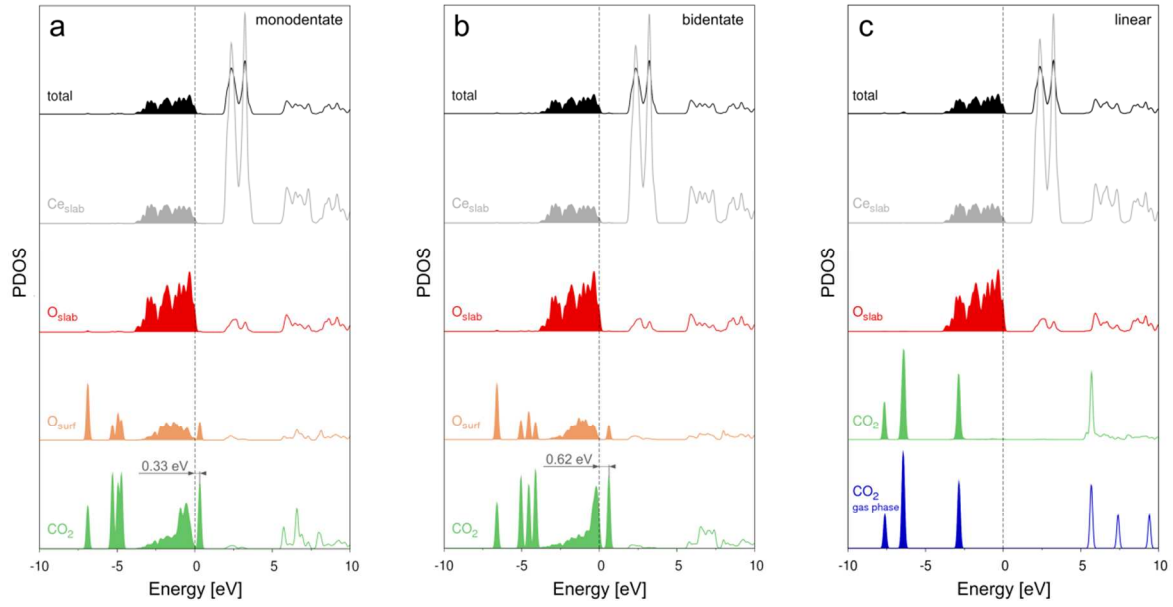

Figure S6. PDOS summed over all atoms and on the orbitals of substrate Ce (Ce_{slab}, grey lines) and O (O_{slab}, red lines) atoms upon adsorption of CO_2 (green lines) as (a) monodentate, (b) bidentate and (c) linear species. In the case of linear adsorption, additionally the DOS of linear CO_2 in the gas phase (blue line) is shown, where the energy levels have been shifted to match the energy levels of linear CO_2 physisorbed on CeO_2(111). The reference 0 eV has been set to the valence band of the CeO_2 substrate. One additional state evolves above the valence band of CeO_2 in the case of mono- and bidentate CO_2 adsorption. This can be attributed to the hybridized HOMO of gas phase CO_2 and lies 0.33 and 0.62 eV above the CeO_2 valence band in the mono- and bidentate configuration, respectively.

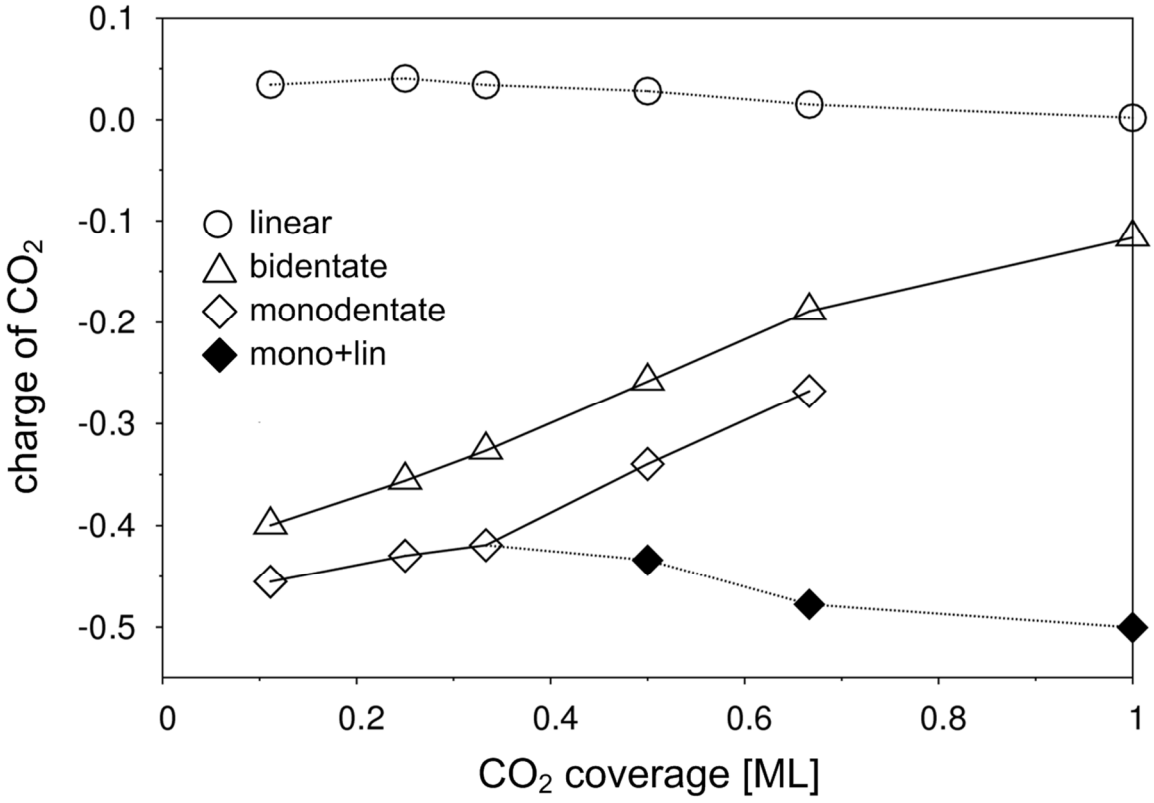

Figure S7. Average charge per CO_2 molecule adsorbed linearly (circles), as bidentate (triangles) and monodentate (diamonds) species as a function of the CO_2 coverage. Filled diamonds show the charge of monodentate species (1/3 ML) when additional CO_2 is adsorbed as linear species. In this case, the charge of the monodentate species even decreased slightly with increasing amount of linear CO_2 indicating an additional charge transfer from linear to monodentate CO_2 species.