

Supporting Information for Publication

CO₂ Adsorption on Stoichiometric Ceria (110) Revisited

Rolando Saniz^{1,3}, Shangkun Li^{1,2,3}, Dirk Lamoen⁴, Annemie Bogaerts^{2,3}, and Bart Partoens^{1,3}

¹CMT, Departement Fysica, Universiteit Antwerpen, B-2020 Antwerpen, Belgium

²PLASMANT, Departement Chemie, Universiteit Antwerpen, Universiteitsplein 1, B-2610 Antwerpen, Belgium

³PLASMA Centre of Excellence, Universiteit Antwerpen, Universiteitsplein 1, B-2610 Antwerpen, Belgium

⁴EMAT, Departement Fysica, Universiteit Antwerpen, B-2020 Antwerpen, Belgium

S1 Bulk CeO₂

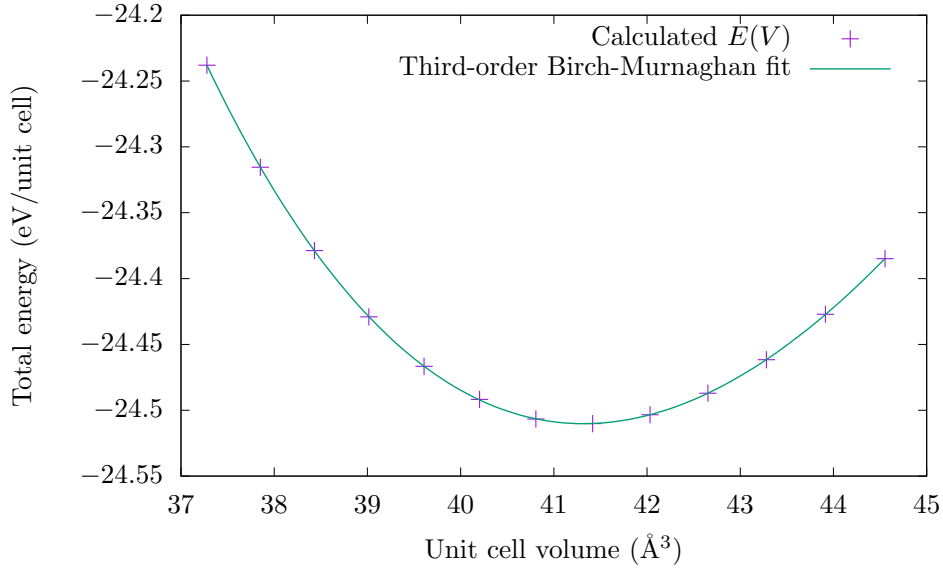


Figure S1: Plot of the Birch-Murnaghan fit used to determine the lattice parameter of bulk CeO₂ ($Fm\bar{3}m$, #225). The total energy calculations were done with the PBE+ U approach, with $U = 5$ eV, as explained in the main text. The results are: Equilibrium energy = -24.5102 eV; Equilibrium volume = 41.3183 Å³; Equilibrium lattice constant = 5.478 Å³ (recall the FCC unit cell volume is one 1/4 of the volume of the conventional cubic cell).

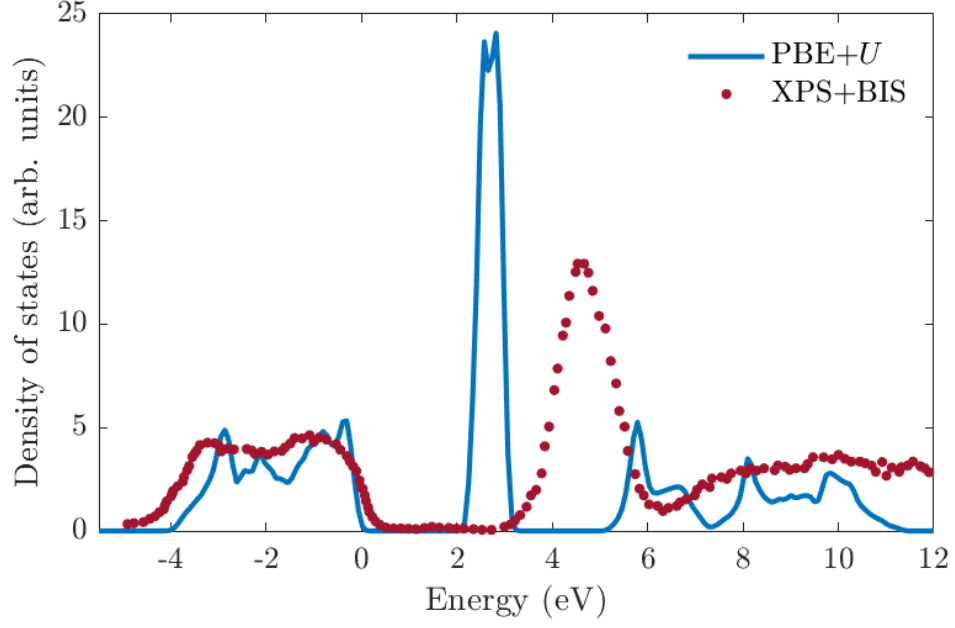


Figure S2: Calculated density of states (DOS) of bulk CeO₂ overlaid on top of XPS+BIS data. The pronounced peak above 2 eV, due to Ce 4*f* states, is too low compared to experiment. It lies sufficiently high above the VBM (set at 0 eV) that the discrepancy is not relevant to our findings in the main text. Our DOS result is in agreement with previous theoretical calculations [1].

S2 CeO₂ slab

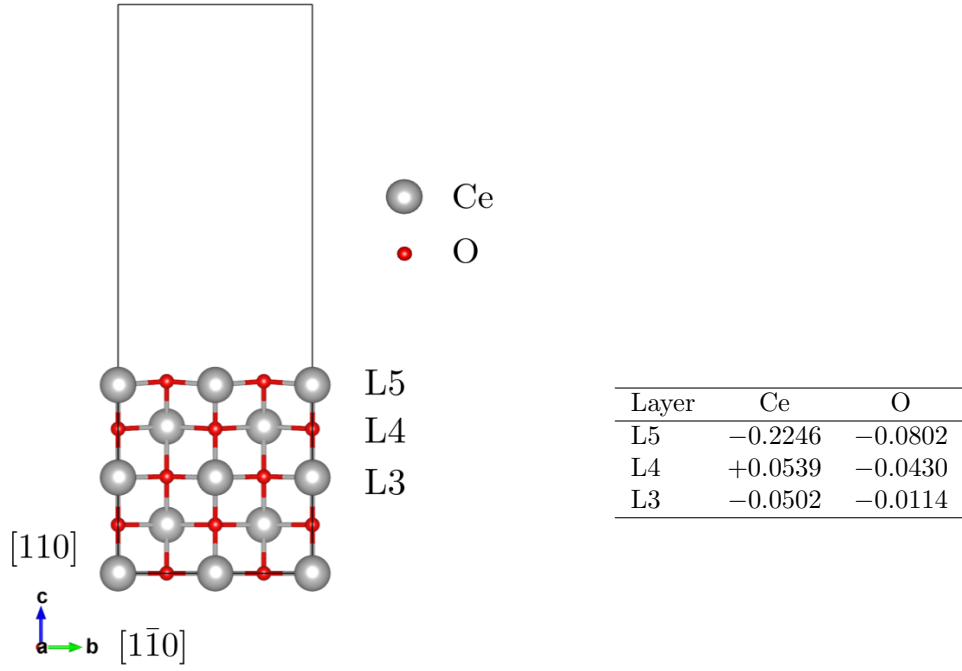


Figure S3: The figure shows a side view ($[001]$ direction) of the 5 layer relaxed slab surface model used in our calculations. The table gives the change of the coordinate value in the c -direction (in Å) of the Ce and O atoms positions in the upper three layers with respect to their value in the unrelaxed slab.

S3 Adsorption starting from exact positions

Table S1: CO₂ adsorption states reached starting the calculations exactly at the locations indicated in Fig. 2(a) in the main text. Nine out of the fifteen states are metastable. These are indicated by the superindex ^m.

Site	E_a (eV)	H (Å)	ℓ_{C-O} Å	\angle_{O-C-O} (°)
dh _a ^m	-0.072	3.6	1.174	179.9
ot _a ^m	-0.299	2.8	1.178-1.171	176.3
oo _a ^m	-0.290	3.0	1.173	177.7
hh _a ^α	-0.549	2.4	1.173	177.0
ct _a ^m	-0.071	3.6	1.174	178.8
dh _b ^α	-0.551	2.5	1.176	173.9
ot _b ^α	-1.765	1.3	2×1.278,1.347	2×116.4,126.7
oo _b ^α	-0.514	2.2	1.177	171.2
hh _b ^m	-0.120	3.2	1.174	179.5
ct _b ^m	-0.091	3.7	1.174	178.9
dh _c ^m	-0.127	2.9	1.174,1.172	180.0
ot _c ^α	-1.765	1.3	2×1.279,1.347	2×116.4,126.6
oo _c ^m	-0.060	3.2	1.173,1.175	180.0
hh _c ^m	-0.141	2.2	1.173,1.175	180.0
ct _c ^α	-0.266	2.8	1.173,1.169	180.0

S4 Density of states: bulk vs slab

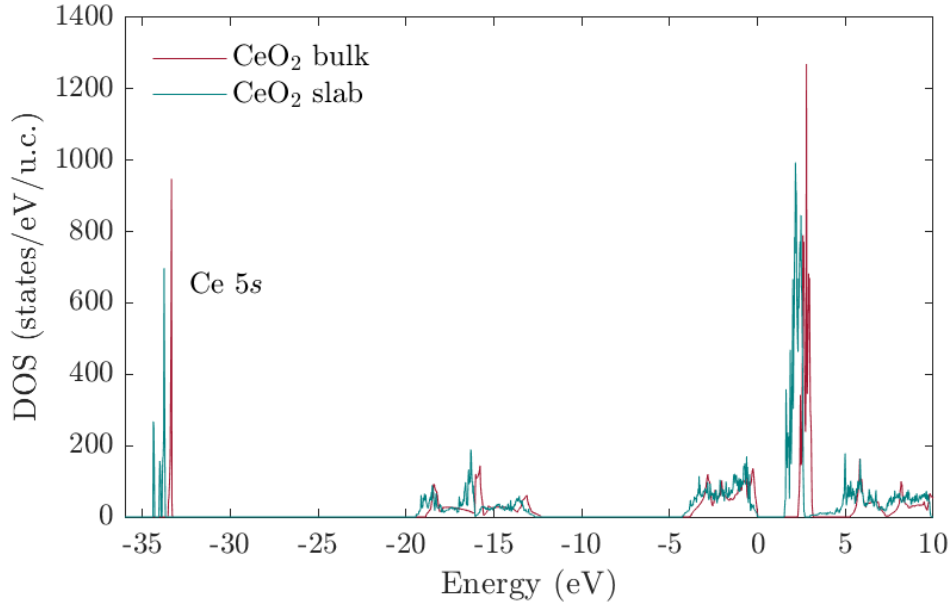


Figure S4: In the slab, the Ce and O atoms in the different slabs are no longer equivalent, thus lifting their energy degeneracy. This is clearly seen in the DOS plot of the slab, where there are five Ce 5s peaks instead of only one (it appears like there are only three, but this is only due to the resolution of the plot). In addition, the contraction of the distance between the atoms in the upper layers causes the band widths to increase and the band gap to decrease.

S5 Band structures

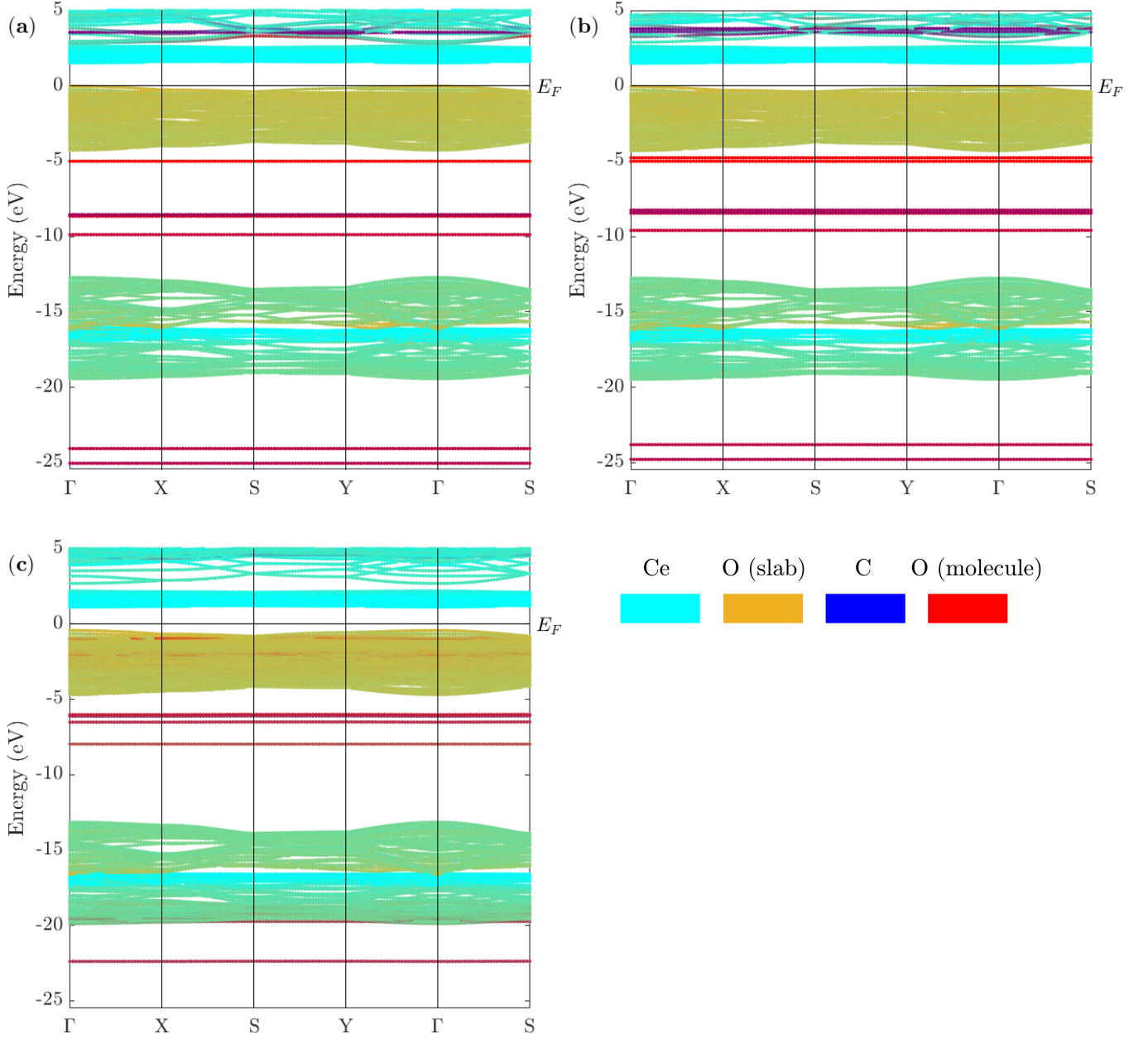


Figure S5: Projected band structure for cases ct_c^α , dh_b^α , and ot_b^α , in Figs. (a), (b), and (c), respectively. In Figs. (a) and (b) there is no hybridization between the molecule (blue and red) and slab states, consistent with the fact that these are physisorption cases. Hybridization is evident in the chemisorption case, in Fig. (c), specially in the $[-5, 0]$ eV interval, where the molecule and slab oxygen states strongly mix. It also occurs in the lower valence band, at places in the interval roughly between -20 and -13 eV, but somewhat more difficult to see. These plots complement and confirm what is seen in the DOS plots in the main text.

S6 Bader charges

Table S2: Bader charges (e) of the CO₂ molecule atoms in the five stable adsorption states discussed in the main text. The data in the last column are for the free molecule. The figures were rounded to two decimals.

	dh_b^α	ot_b^α	oo_b^α	hh_a^α	ct_c^α	CO ₂
C	1.92	1.89	1.95	1.81	1.92	2.00
OI	7.06	7.17	7.06	7.11	7.08	7.00
OII	7.06	7.17	7.06	7.11	7.00	7.00
Tot	16.04	16.23	16.07	16.03	16.00	16.00

S7 Hirshfeld charges

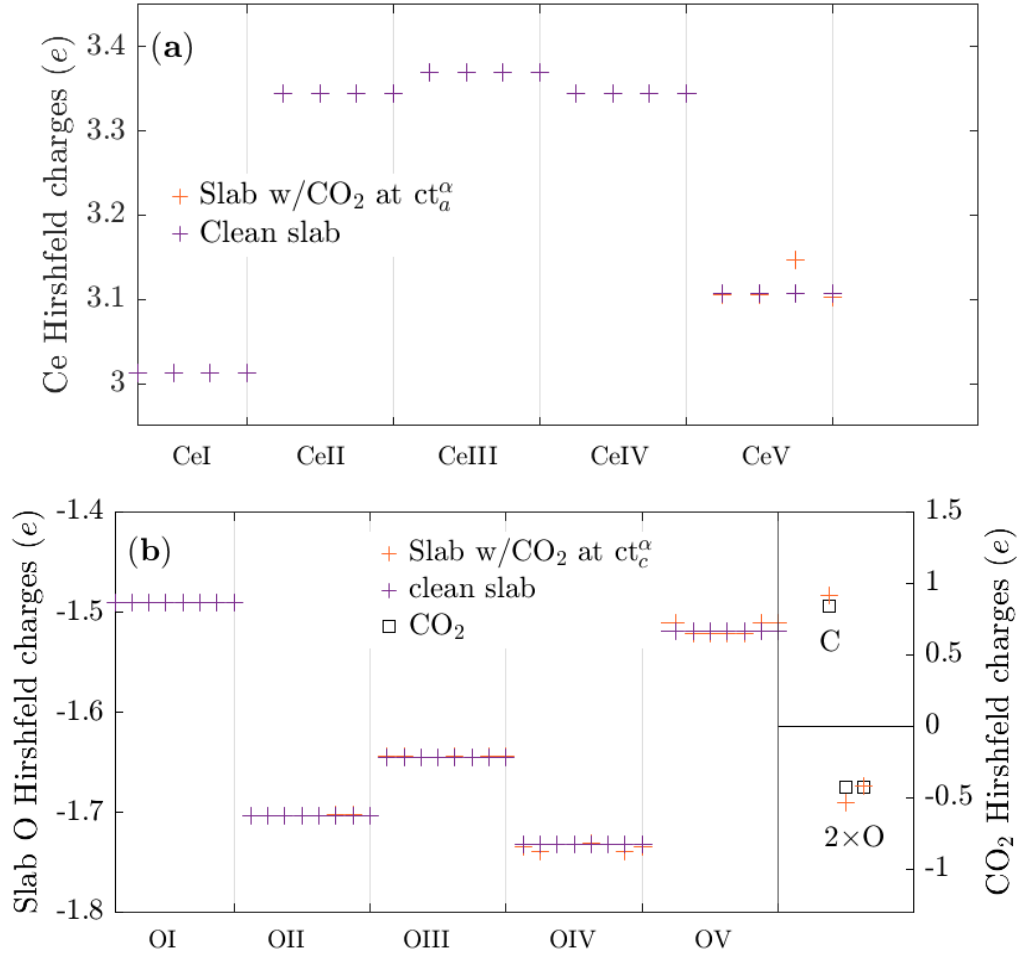


Figure S6: Hirshfeld charges in the ct_a^α state, corresponding to physisorption of moderate strength. The plot compares the charges of the clean slab with those of the slab with the adsorbed CO₂ molecule. (a) Ce charges. The label CeI represents the Ce atoms in the first layer (i.e., the bottom layer) in the slab. The CeII label represents those in the second layer, and so forth. The differences in charge are small, indicating a limited polarization change due a weak surface-molecule interaction. (b) Oxygen charges. There are two subplots: the one in the left side (left y -axis scale) shows the charges for the oxygen atoms in the slab, while the one in the right shows the charges for the carbon and oxygen atoms of the molecule. The polarization changes of the slab oxygen atoms of the slab are more evident than those of the Ce atoms, indicating that the former play a leading role in the molecule-surface interaction. The labels OI, OII, etc. indicate the layer to which the corresponding O atoms belong. The plot in the right side (right y -axis scale) shows the charges of the carbon and oxygen atoms of the molecule. The square symbols represent the free CO₂ molecule Hirshfeld charges. The polarization changes are stronger in the molecule. The carbon atom and upper lying oxygen atom increase their share of electrons ($0.073e$ and $0.004e$, respectively) while the lower lying oxygen atom sees its share increase ($0.112e$). This means that the CO₂ molecule has acquired a dipole moment.

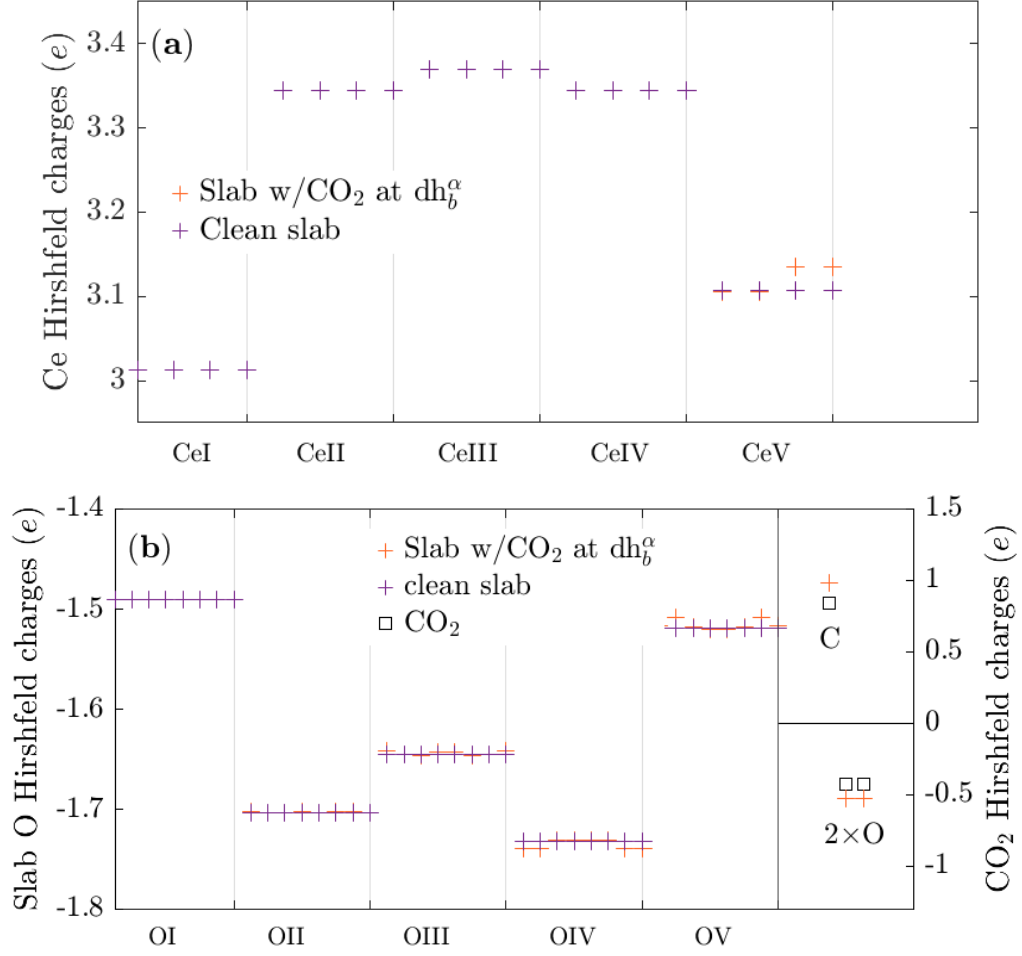


Figure S7: Hirshfeld charges in the dh_b^α state, i.e., a strong physisorption case. As in Fig. S6 (ct_c^α case), the plot compares the charges of the clean slab with those of the slab with the adsorbed CO_2 molecule, and the Ce and O labels have the same meaning. (a) Ce charges. The effect of the interaction with the CO_2 molecule is more pronounced. (b) Oxygen charges. The polarization changes in the molecule are stronger than in the ct_c^α case. The carbon atom loses $0.144e$ and the oxygen atoms gain $0.105e$ each. The molecule is bent (see Table 1 in the main text), i.e., there is an induced dipole moment.

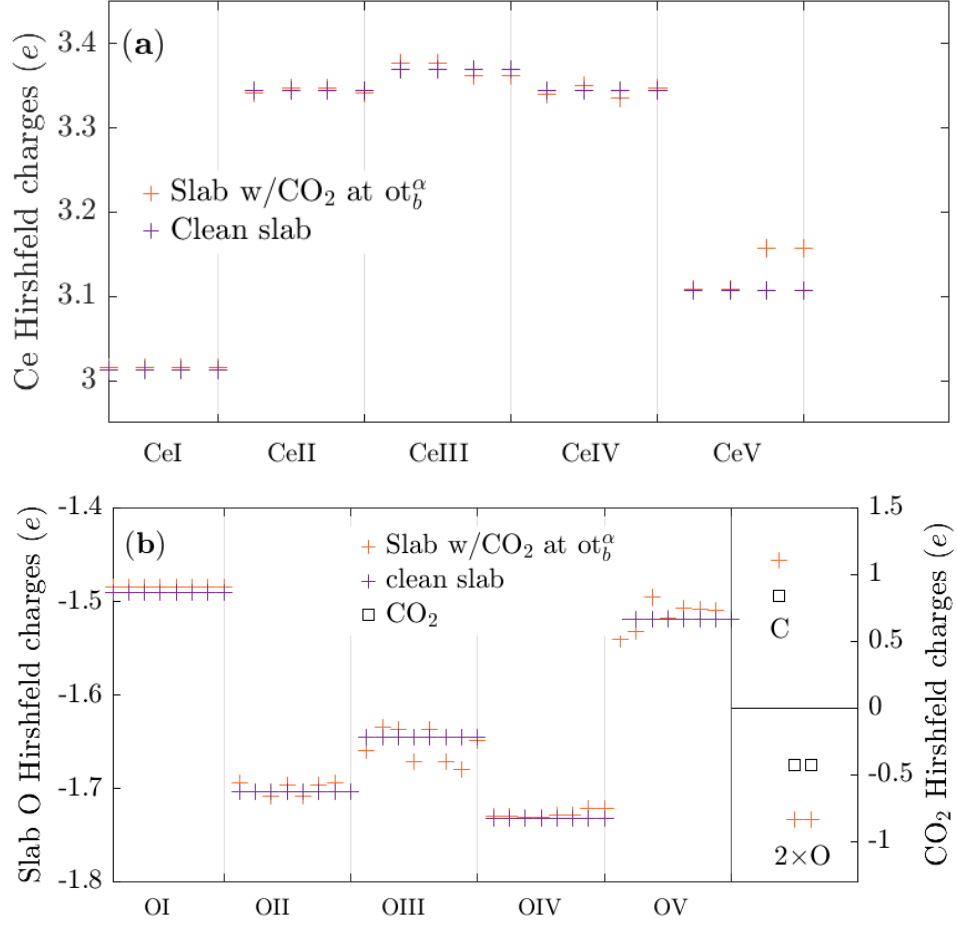


Figure S8: Hirshfeld charges in the ot_b^α state, which corresponds to the chemisorption case. Again, the plot compares the charges of the clean slab with those of the slab with the adsorbed CO_2 molecule, the Ce and O labels having the same meaning. (a) Ce charges. The effect of the interaction with the CO_2 molecule is clearly stronger. (b) Oxygen charges. There is not only polarization changes but also charge transfer with the surface. The carbon atom loses $0.268 e$ and each of the molecule oxygen atoms gain $0.413 e$. The surface oxygen atom forming the carbonate ion with the CO_2 molecule loses $0.409 e$.

References

- [1] H. Jiang, Phys. Rev. B **2018**, 97, 245132.