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DOI: <https://doi.org/10.1063/5.0042435>

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ZORA URL: <https://doi.org/10.5167/uzh-209154>

Journal Article

Accepted Version

Originally published at:

Baumann, Noah; Lan, Jinggang; Iannuzzi, Marcella (2021). CO₂ adsorption on the pristine and reduced CeO₂ (111) surface: Geometries and vibrational spectra by first principles simulations. *Journal of Chemical Physics*, 154(9):094702.

DOI: <https://doi.org/10.1063/5.0042435>

CO₂ Adsorption on the Pristine and Reduced CeO₂ (111) Surface: Geometries and Vibrational Spectra by First Principles Simulations

Noah Baumann,¹ Jinggang Lan,¹ and Marcella Iannuzzi^{1, a)}

*Department of Chemistry, University of Zurich, 8057 Zurich,
Switzerland*

(Dated: 9 February 2021)

First principles simulations of carbon dioxide adsorbed on the ceria (CeO₂) (111) surface are discussed in terms of structural features, stability, charge transfer, and vibrational modes. For this purpose, different density functional theory (DFT) methods, such as PBE, PBE+U, hybrid functionals, and different basis sets have been applied and compared. Both the stoichiometric and the reduced (111) surface are considered, where the electronic structure of the latter is obtained by introducing oxygen vacancies on the topmost or the subsurface oxygen layer. Both the potential energy surfaces of the reduced ceria surface and of the adsorbate-surface complex are characterised by numerous local minima, of which the relative stability depends strongly on the electronic structure method of choice. Bent CO₂ configurations in close vicinity to the surface oxygen vacancy that partially re-oxidize the reduced ceria surface have been identified as the most probable stable minima. However, the oxygen vacancy concentration on the surface turns out to have a direct impact on the relative stability of possible adsorption configurations. Finally, the vibrational analyses of selected adsorbed species on both the stoichiometric and reduced surface show promising agreement with previous theoretical and experimental results.

^{a)}Electronic mail: Marcella.iannuzzi@chem.uzh.ch

I. INTRODUCTION

Rare earth metal oxides are used in numerous applications in catalysis. Preparation and pretreatment of metal oxides and of their surfaces are known to lead to significant differences in their catalytic properties, which are sometimes as large as differences between catalysts of different chemical compositions¹. In particular, CeO_2 is relatively cheap compared to other rare earth metal oxides and exhibits remarkable chemical and catalytic properties^{2,3}. The unusual redox behavior of ceria is already utilized in various fields^{1,4-8}. Applications such as three-way catalysis⁹ and syngas production^{4,10} are based on the distinctive feature of ceria to release and uptake oxygen in an entirely reversible fashion. This feature is a consequence of the uncomplicated reduction of Ce^{4+} to Ce^{3+} and vice versa.

Ceria crystallizes in a fluorite ($\text{Fm}\bar{3}\text{m}$) structure with four eight-coordinated Ce^{4+} and eight four-coordinated O^{2-} per unit cell. At high temperatures, oxygen is released to yield a non-stoichiometric, anion-deficient form of ceria¹¹, which preserves the fluorite structure. The stoichiometric (111) surface, with a terminal oxygen layer, has been shown, both theoretically and experimentally, to be the most stable low index CeO_2 surface¹²⁻¹⁴. The topmost O-Ce-O trilayer mainly determines its properties. The arrangement of the oxygen vacancies and associated excess charge (Ce^{3+}) at the reduced ceria surface has been addressed in several studies.¹⁵⁻¹⁸ The oxygen vacancy density can reach a minimum of 1.7% even for a maximally oxidized ceria (111) surface obtained with modern preparation techniques^{19,20}. Previous studies have shown that the isolated vacancies are most probably located at sub-surface sites, while the remaining excess electrons form polarons at Ce-sites, which are rather not first neighbors of the vacant site.^{21,22} The number of oxygen vacancies, their positions, and the localization of the cerium 4f states are then expected to be essential factors determining the reactivity of ceria surfaces²³. Recently, the dynamics at finite temperature of vacancies and associated polarons in the vicinity of the ceria surface has attracted new attention. Both experimental as well as theoretical studies have provided estimates of the energy barriers for polaron hopping and new insight into the microscopic understanding of the entangled migration of oxygen and Ce^{3+} at reduced ceria surfaces.^{17,24-27}

Ceria-based catalysts are promising for many catalytic cycles that lead to the conversion of CO_2 into valuable compounds, as the reverse water shift reaction²⁸, the methanol synthesis²⁹, and the dry forming of methane⁶. The limited use of CO_2 in the industry is caused by its

chemical inertness. The inert character is not only exhibited in terms of thermodynamics, but also in terms of kinetics. The stability of the carbon-oxygen bonds turns out to be reduced when CO_2 is chemisorbed in an anionic bent configuration on pure metal and metal oxide surfaces³⁰. The preferred configuration is known to depend strongly on the Lewis acidity of the surface³¹. Hence, an ideal catalyst would favour a bent configuration by charge transfer from the Lewis basic surface towards the carbon dioxide molecule to support the associative or dissociative substitution of the oxygen atoms.

It was reported, experimentally and theoretically, that linear, as well as bent configurations of CO_2 on the ceria surface are possible^{19,32,33}. Adsorption energies up to -1.85 eV for carbon dioxide were calculated based on density functional theory (DFT) simulations³²⁻³⁴. Especially reduced ceria surfaces are expected to exhibit desirable conditions to catalyze carbon dioxide reduction reactions. This because polarons are involved in the molecular adsorption process at oxide surfaces, providing an enhanced charge transfer that is the initial step of many chemical reactions and is therefore crucial in understanding the surface chemical reactivity.^{35,36} Indeed, lower adsorption energies on the reduced (111) ceria surface compared to the pristine surface were obtained by means of DFT+U simulations^{33,37}.

Infrared spectroscopy is a powerful technique for studying the microscopic structural properties of oxide surfaces, in particular the presence of defects or rearrangements, and is used as well to determine the adsorption geometries of adsorbates^{38,39}. In particular, Fourier transform infrared spectroscopy (FTIRS) has been used to characterize the adsorbed CO_2 on CeO_2 ^{19,34,40,41}. However, the assignments based on FTIRS are not always conclusive. Some peaks have been assigned to different configurations or are not explainable at all. Vayssilov et al.³⁴ and Reimers et al.³³ applied DFT vibrational analysis to several adsorbate configurations on ceria in order to better interpret the experimental spectral features. However, the resulting theoretical spectra cannot reproduce a complete correspondence to the experimental ones. In particular, Kong et al.¹⁹ did not find any evidence for monodentate or bidentate adsorption on the maximally oxidized (nearly stoichiometric) and reduced (111) CeO_2 surfaces. They only detected two peaks above 1200 cm^{-1} when they applied different doses of carbon dioxide on the maximally oxidized surface. One at 2362 cm^{-1} has its maximum intensity at 6 Langmuir and has been assigned to the linear physisorbed CO_2 molecule. The peak at 1292 cm^{-1} reaches its maximum intensity at 3 Langmuir. A further increase in intensity and a shift to 1288 cm^{-1} has been observed by increasing the O-vacancy

concentration to 14.3%. Based on this observation, it was proposed that the band at 1292 cm^{-1} corresponds to a CO_2^- species located over an oxygen vacancy, where a Ce^{3+} polaron provides the electron via: $\text{Ce}^{3+} + \text{CO}_2 \longrightarrow \text{Ce}^{4+} + \text{CO}_2^-$.

In this study we apply different DFT-based model to describe the pristine and the reduced ceria (111) surface. We discuss the properties of the surface and how these influence the adsorption and activation of CO_2 . Our goal is to take into account also possible metastable configurations, which may appear under different conditions, and be important with respect to dissociation processes, since they represent the most active species. In particular, we propose one configuration that, according to the resulting IR spectrum, might be the one observed by Kong et al.¹⁹ at reduced ceria.

The manuscript is organised as follows. After the description of the computational methods, we first determine structure and electronic properties of the reduced ceria (111) surface. Then several possible adsorption configurations are discussed in terms of their electronic and structural properties. Finally, the vibrational spectrum of some possible adsorbates is calculated and compared to the experimental findings.

II. COMPUTATIONAL DETAILS

Describing the electronic properties of ceria is challenging at the DFT level because of the strongly localized empty 4f states located between 2.9 and 4.4 eV above the valence band^{42,43}. Indeed, standard DFT methods tend to delocalize the 4f electrons over the whole crystal. Several approaches have been proposed to overcome these delocalization issues, which are common for transition metal oxides. Common strategies are the empirical ad hoc correction based on including a repulsive local term based on a Hubbard mode (DFT+U model), or the more computationally demanding hybrid functional schemes. Both approaches still allow to simulate rather large systems for stoichiometric bulk and surface properties⁴⁴. Higher level quantum-chemistry methods which are able to capture strong correlations are in general restricted to small system models and used as reference. In the past years a few extensive studies appeared in the literature reporting thorough assessment and benchmarking of density functional theory approximations on the description of bulk CeO_2 structural and electronic properties^{45,46}. These studies also show that special care has to be used whenever polarons are formed and a reduction from Ce^{4+} to Ce^{3+} takes place, since the strongly

localized 4f states get occupied and gain in importance.

All simulations in this study were carried out by means of the CP2K program package^{47,48}. The electronic structure was described at the Kohn-Sham DFT level within the Gaussian and Plane Waves (GPW) framework. PBE⁴⁹, PBE+U^{50,51}, PBE0⁵² and HSE06⁵³ exchange-correlation functionals together with scalar relativistic norm-conserving Goedecker-Teter-Hutter (GTH) pseudopotentials⁵⁴ were applied. The cutoff and relative cutoff energies of the auxiliary plane wave basis sets were converged to energy differences smaller than 10^{-6} Hartree/atom. No additional correction for the dispersion interaction has been applied, which is justified by the good agreement of all the models in reproducing the equilibrium bulk lattice constant (see Table 1 in the SI). From test calculations of the physisorbed linear CO₂ molecules on the reduced ceria surface, we could verify that the optimized geometry does not change by augmenting the DFT+U model by the revised Vydrov-Voorhis⁵⁵ nonlocal correlation functional.

Two different types of basis sets were compared for Ce: Contracted and uncontracted 4f Gaussian orbital basis sets. In the contracted case, DZVP-MOLOPT-SR-GTH basis sets were used⁵⁶. They were always combined with DZVP-MOLOPT-SR-GTH oxygen basis sets for CeO₂. This approach is referred to as "CFM" (contracted 4f orbital method) in the following. It was applied for all standard PBE, PBE0, HSE06 and some PBE+U calculations. A cutoff energy of 1000Ry and a relative cutoff energy of 70Ry were applied for CFM simulations. An U_{eff} value of 4.5 eV for the 4f states of CFM PBE+U simulations was used. Uncontracted triple- ζ basis sets constructed by Hahn et al.⁵⁷ and modified (addition of a series of uncontracted Gaussian f orbital functions) by Wang et al.⁵⁸ were also used. They were always combined with TZVP-MOLOPT-GTH basis sets for CeO₂ oxygen. From now on, the uncontracted approach is called "UCFM" (uncontracted 4f orbital method). The UCFM, only applied for PBE+U simulations, requires a cutoff of 600Ry, a relative cutoff of 40Ry, and a U_{eff} value of 7.0 eV for 4f states. For the adsorbates (CO₂), TZVP-MOLOPT-GTH basis sets were applied in the CFM and UCFM case. The ADMM method was applied for hybrid functionals by introducing cpFIT3 auxiliary basis sets for C and O, and FIT3 auxiliary basis sets constructed by Hahn et al.^{32,57} for Ce.

All electronic structures have been obtained by unrestricted Kohn-Sham (spin-polarized) calculations at the Γ -point only, using sufficiently large supercell models. We used a $2 \times 2 \times 2$ super cell for bulk calculations. A $p(5 \times 5)$ ceria (111) surface slab system with three O-

Ce-O trilayers free to relax and one bottom trilayer fixed to mimic the bulk embedded in a five trilayer thick vacuum region was used for surface and adsorption simulations. For all visualizations of crystal and molecular structures, the VMD software was used⁵⁹. The presented settings have been assessed by means of bulk and pristine surface simulations and proved to be reliable in reproducing the expected structural, energetic and electronic properties (results are reported in the Supplementary Information).

III. RESULTS

A. Vacancy Formation at ceria (111)

The reduced ceria (111) surface is a theoretically well-studied system. For every formed oxygen vacancy, two reductions from Ce^{4+} to Ce^{3+} take place at relatively low vacancy concentrations. Previous theoretical calculations and experiments demonstrated that the vacancies are formed preferably in the subsurface and surface layer rather than in the bulk. Each reduction from Ce^{4+} to Ce^{3+} leads to the occupation of a strongly localized Ce_{4f} state and to the local distortion of the surrounding oxygen shell to screen the charge, forming a small polaron. It is known that the positions of the vacancy as well as of the two Ce^{3+} polarons have a critical impact on the formation energy of the defect. The Ce^{3+} is energetically favored if it is nearest-neighboring (NN) or next-to-nearest-neighboring (NNN) the oxygen vacancy in the topmost cerium layer^{57,60–64}. Figure 1 shows these Ce^{3+} positions relative to the surface and subsurface vacancies.

Standard GGA or LDA methods, such as PBE, are not capable of describing the localized d and f states of transition and rare earth metal oxides. They tend to delocalize the additional electron, which results in a metallic behavior. The localized states can only be described with extended methods, such as DFT+U or hybrid DFT^{65,66}. The geometry optimization for large systems with hybrid functionals is computationally hardly affordable. Therefore, DFT+U has been the method of choice in most theoretical descriptions of reduced ceria surfaces and bulk systems. DFT+U methods and any other method that promotes the single occupation of d or f states tend to give rise to metastable orbital occupations and locations^{67,68}. Additional local minima are introduced to the energy surface and computational optimization algorithms often get stuck in these metastable states⁶⁹. Metastability is

the main reason for the disagreement of theoretically proposed localized orbital occupation in uranium dioxide and reduced ceria surfaces.^{68,70,71}

The initial assumption of the 4f orbitals' occupation in the starting electronic distribution of a DFT simulation has a significant effect on the final result. The f orbitals' occupation influences the distances towards surrounding ions. Hence, a further stabilization of possibly wrong electronic structures might take place in a geometry optimization. There is a high probability that the initial electron density leads to the occupation of local minima with a sufficient energy barrier to prevent the system from finding the true ground state⁶⁸. The true Ce_{4f} orbital occupation is therefore hardly determinable.

To bypass these wrong minima, we employ an approach based on the manual control of the initial occupation matrix for the f orbitals⁷². This approach can overcome the metastability issues, but only with previous knowledge of the Ce_{4f} orbitals occupation and the location of the reduced cerium centers. Even though, the most stable Ce³⁺ and vacancy position have already been determined theoretically (subsurface vacancy with next-to-nearest-neighboring (NNN) Ce³⁺ position), the Ce_{4f} orbitals occupation has not.

The results for different 4f orbital occupations of the most stable configuration (subsurface vacancy with both Ce³⁺ in NNN positions) calculated with CFM PBE+U are listed in Table I. Based on the results for the work function (see SI), we used a four O-Ce-O trilayer system with the bottom trilayer fixed and a $p(5 \times 5)$ surface. A large enough slab is needed in order to prevent any polaron-polaron interactions. Moreover, an important aspect is the orbital symmetry of the polaron state, which is determined by the local environment. The correct hybridization and the relative stability of the polaronic orbital can be achieved only if the surrounding atoms are free to relax. These aspects have been discussed in previous works, where, for instance, an asymmetric slab of five Ti layers with the two bottom ones fixed turned out to be adequate to model the reduced rutile surface.⁷³ The occupation of the f orbitals was modified for two reduced cerium centers, only for a few electronic structure optimisation steps, until a convergence of 10^{-4} Hartree in the total energy. This selection of the two Ce³⁺ is obtained by modifying their position, thus increasing their distance from the surrounding oxygens, before starting the geometry optimization. No structural constrain is imposed during the optimisation. The vacancy formation energy E_{vac} is defined as

$$E_{\text{vac}} = \frac{1}{N_{\text{vac}}} (E_{\text{CeO}_{2-x}} + \frac{N_{\text{vac}}}{2} E_{\text{O}_{2,g}} - E_{\text{CeO}_2}). \quad (1)$$

$E_{\text{CeO}_{2-x}}$ is the total energy of the reduced system, N_{vac} is the number of vacancies, $E_{\text{O}_{2,g}}$ is the energy of an O_2 molecule calculated in the triplet state in a $20 \times 20 \times 20 \text{ \AA}$ vacuum cell, and E_{CeO_2} is the total energy of the fully oxidized stoichiometric system. The "Enforced orbital

Enforced orbital occupation	E_{vac} [eV]
f_3	2.67
f_2	2.58
f_1	2.87
f_0	2.94
f_{+1}	2.86
f_{+2}	2.58
f_{+3}	2.68

TABLE I: Comparison of the energies observed with different enforced occupations of Ce_{4f} orbitals computed with CFM PBE+U. The occupation of the f orbitals is forced towards the mentioned orbital up to a convergence of $1e - 4$ Hartree for the first electronic structure optimization. All simulations are performed in the triplet state.

occupation" column only gives the initially enforced occupation for CFM PBE+U. The finally obtained compositions of the 4f orbitals do deviate marginally. The lowest vacancy formation energy among them was achieved when the two additional electrons occupy states that are mainly composed of $\text{Ce}_{4f_{+2}}$ or Ce_{4f_2} orbitals. For these and all following surface and adsorption CMD PBE+U calculations, we applied an U_{eff} value of 4.5 eV. The choice is based on the results of bulk and pristine surface simulations, as discussed in the SI, and on some tests on the vacancy formation energy also reported in the SI.

All E_{vac} values obtained for different vacancy and relative Ce^{3+} positions with CFM PBE+U are listed in Table S2 (see SI). We assumed that the orbital occupation does not change significantly by changing positions of the Ce^{3+} cations. With the CFM PBE+U model, the lowest energy is found with both reduced cerium ions at NNN locations, consistent with the literature. The subsurface NNN-NNN system exhibits the lowest vacancy formation energy, followed by the surface NNN-NNN system. E_{vac} increases with the transfer of electrons to the NN position. The spin-density isosurface computed for the subsurface vacancy system with two cations in NNN position is shown in Figure 2(a).

The presence of a surface and a vacancy is expected to lead to a combination of fractionally occupied 4f orbitals due to crystal field splitting and structural disturbance caused by the two excess electrons. However, the contracted f orbital Gaussian basis sets for cerium do not allow fractional occupied 4f orbitals when the DFT+U method is applied. Wang et al. published an approach to overcome the restrictions of CFM PBE+U⁵⁸, by replacing the contracted 4f Gaussian functions in the basis sets of Hahn et al.^{13,32,57} with uncontracted ones. The flexibility gained by means of uncontracted functions allows for more freedom in the construction of 4f orbitals. We employed the UCFM basis set by Wang et al.⁵⁸ together with a modified approach for the optimization of the Ce³⁺ configuration. We performed a prerun with lanthanum substituting cerium at the two desired Ce³⁺ positions, using softer convergence criteria. The resulting configuration presents all cerium atoms in a 4+ and the two lanthanum cations in a 3+ oxidation state. Due to the larger ion radius, the La³⁺ ions push the oxygen anions slightly away from their lattice site. Starting from this geometry, replacing La with Ce, the additional electron is forced to localize on the desired sites because of the elongated distances from the neighbouring O atoms. The U_{eff} value of 7 eV was chosen comparing properties and electronic structure of the bulk system, as well as vacancy formation energy (see SI).

Overall, the vacancy formation energies are lower compared to CFM, and the predicted relative stability is slightly different. In the UCFM framework, the surface and subsurface vacancies with Ce³⁺ NNN do nearly exhibit the same stability, and the subsurface NN-NN system is the least stable one. The energy gaps $\Delta E_{O_{2p}-Ce_{4f}^{occ}}$ are up to 54% higher than experimental values⁷⁴. The energy difference between the two occupied cerium 4f states, Ce_{4f}^{occ} splitting, increases in most of the cases. Since the lowest energy f orbital occupation is nearly the same for both Ce³⁺ cations, the splitting is associated to the relative position of the Ce³⁺ ions with respect to the vacancy. The isosurface of the most stable singlet subsurface NNN-NNN system is represented in Figure 2(b). The lack of a full symmetrization of the electronic distribution suggests that also with UCFM PBE+U the optimisation gets stuck in local minima. Hence, we adopted the cheaper CFM PBE+U model for the study of CO₂ adsorption on the reduced surface.

The single-shot hybrid functionals calculations seem to better reproduce the expected vacancy formation energies according to References²³ and⁶². Since the full structure optimization at the hybrid functional level would be excessively demanding, the optimized

geometries obtained with CFM PBE+U calculations are used for these single point calculations with PBE0 and HSE06. The simulations were limited to the most stable (subsurface vacancy with both Ce^{3+} NNN to the vacancy) and the most unstable system (surface vacancy with both Ce^{3+} NN to the vacancy). The results are listed in Table S2 in the SI. PBE0 and HSE06 yielded very similar results. When hybrid functionals are applied, the defective structures are less stable compared to PBE+U. $\Delta E_{\text{O}_{2p}-\text{Ce}_{4f}^{\text{occ}}}$ is strongly overestimated compared to the experimental results⁷⁴. The f orbital occupations are similar to the ones obtained by CFM PBE+U, because the same geometries were used. The resulting occupied 4f orbitals do as well mainly consist of f_{+2} orbitals. Some tests were also performed with "neutral" geometries obtained by the lanthanum substitution method. They reveal that hybrid functionals are as well prone to metastable orbital occupations, although they seem to allow fractional orbital occupation.

B. CO_2 Adsorption on Ceria(111)

1. *Adsorption on Pristine Ceria (111)*

Before considering the reduced surface, we evaluate our computational approach on the adsorption of CO_2 on pristine ceria (111). In particular, we take into consideration the three monomer adsorption geometries already proposed in previous recent works^{32–34,37}: The monodentate species (Figure 3(a)), the bidentate species (Figure 3(b)) and the linear species (Figure 3(c)).

The adsorption energies E_{ads} is obtained as:

$$E_{\text{ads}} = \frac{1}{n}(E_{n\text{CO}_2/\text{surf}} - E_{\text{surf}} - nE_{\text{CO}_2,g}) \quad (2)$$

where $E_{n\text{CO}_2/\text{surf}}$ is the total energy of the adsorbates-surface complex, E_{surf} is the energy of the bare surface, n is the number of adsorbates, and $E_{\text{CO}_2,g}$ is the energy of CO_2 in vacuum (simulated in a $20 \times 20 \times 20$ Å cell). Mulliken population analysis⁷⁵ was used to calculate the charge transfer between surface and adsorbate.

We notice that the contraction of the 4f orbital Gaussian functions has a marginal influence on the geometry, stability, and charge transfer of the three adsorption species. The bond length of the carbon atom to the surface oxygen $d_{\text{C-O}_{\text{surf}}}$ of the monodentate species (1.37 Å) is in the range of a partial double bond. Moreover, the intramolecular C-O bonds

Method	C.	E_{ads} [eV]	$d_{\text{C-O1}}$ ($d_{\text{C-O2}}$) [$\text{\AA}$]	$d_{\text{C-O}_{\text{surf}}}$ ($d_{\text{O1-surf}}$) [$\text{\AA}$]	α_{OCO} [$^\circ$]	Charge [e]
CFM	M.	-0.56	1.27 (1.27)	1.37	128.6	-0.43
PBE+U	B.	-0.32	1.30 (1.22)	1.42	129.3	-0.40
	L.	-0.08	1.18 (1.17)	(2.35)	177.7	0.01
UCFM	M.	-0.63	1.27 (1.27)	1.37	128.9	-0.45
PBE+U	B.	-0.37	1.30 (1.22)	1.43	130.0	-0.40
	L.	-0.15	1.18 (1.17)	(2.35)	177.6	0.01

TABLE II: Adsorption energies (E_{ads}), geometric properties (explained in Figure 3) and total charge of the adsorbed CO_2 molecule in different configurations on the stoichiometric CeO_2 (111) surface. The values in parentheses correspond to the header in parentheses. Calculations were performed with CFM and UCFM PBE+U for the monodentate (M.), bidentate (B.) and linear (L.) adsorption configuration (C.).

are elongated to 1.27 $\text{\AA}$, implying a relatively strong deformation. The charge transfer of -0.43 e (CFM PBE+U) or -0.45 e (UCFM PBE+U) from the surface into the adsorbate's hybridized orbital leads to the bent anionic $\text{CO}_2^{\delta-}$ species (Figure 4(a)). The resulting orbital exhibits bonding character between the C and O_{surf} and anti-bonding character within the CO_2 molecule. This anti-bonding character can be associated to an increase in reactivity³⁰.

The $d_{\text{C-O}_{\text{surf}}}$ bond distance of the bidentate species corresponds to a single C-O bond. The molecular C-O1 bond turns out to be more elongated than C-O2. The charge density difference (Figure 4(b)) indicates charge accumulation between a surface cerium atom and O1, while the hybridized orbital is similar to the one observed for the monodentate species. The linear species is physisorbed and remains at 2.35 $\text{\AA}$ above the surface. The PDOS computed for the three configurations are reported in the SI.

2. *Single CO_2 Adsorption above an Oxygen Vacancy*

We limited the calculations with a single adsorbate on a single oxygen vacancy to two surface configurations: The most stable one in the subsurface with both reduced cerium ions in NNN position, and the surface vacancy with both Ce^{3+} polarons in NN position.

The latter can be expected to be the most reactive, since the vacancy in the surface layer and the Ce^{3+} polarons in close proximity should make this configuration the most prone to (partial) re-oxidations. This choice obviously does not exhaustively cover all possible binding conformations of CO_2 on reduced ceria (111). Indeed, both oxygen vacancy as well as polarons are known to have quite high mobility at finite temperature^{26,27} and the presence of the adsorbate can affect the specific stability of the defective surface, thus favouring transitions to unexpected structures. On the other hand, we aim at identifying a reactive arrangement at the reduced surface that can induce a significant charge transfer with the consequent stabilization of the adsorbate, and that can be associated to the species observed by Kong et al.¹⁹

On the reduced surface with a subsurface vacancy and NNN-NNN Ce^{3+} sites, the monodentate, bidentate and linear CO_2 configurations have been optimised. The goal is to identify possible effects of the vacancy and of the localized 4f states on the adsorbate's properties. The simulations were performed with CFM PBE+U, an orbital occupation constrained to f_{+2} , and multiplicity 1 (antiferromagnetic coupling). Some tests in the triplet state (ferromagnetic coupling) showed that the difference of spin-state barely affects the stability or the geometry of the systems. The following initial positions of CO_2 have been considered (see also Figure 5):

- (1) Nearest to the vacancy with largest possible distance to Ce^{3+}
- (2) Nearest to the vacancy with smaller distance to the reduced cerium centers
- (3) Nearest to Ce^{3+} with larger distance to the vacancy
- (4) Position far away from vacancy and reduced ceria centers

The adsorption energies are given relative to the reduced CeO_2 (111) surface with both occupied 4f orbitals in NNN position (Equation 2).

The interaction with the vacancy induces significant rearrangements in the adsorbate's configuration. When physisorbed as linear CO_2 , the molecule rotates with respect to the orientation observed on the pristine surface, as shown in Figure 5, and it is more stable by placing it closer to the Ce^{3+} ions. The bidentate configuration is destabilised by the vacancy and it optimises to a monodentate geometry. A stable bidentate configuration is only observed when the molecule is placed far away from the vacancy. The monodentate

species gets slightly stabilized with decreasing distance to the Ce^{3+} ions, as observed for the linear configurations.

C.	E_{ads} [eV]	$d_{\text{C-O1}}$ ($d_{\text{C-O2}}$) [$\text{\AA}$]	$d_{\text{C-O}_{\text{surf}}}$ ($d_{\text{O1-surf}}$) [$\text{\AA}$]	α_{OCO} [$^\circ$]	Charge [e]
M. (1)	-0.53	1.26 (1.26)	1.40	131.3	-0.42
M. (2)	-0.60	1.27 (1.26)	1.39	131.0	-0.43
M. (3)	-0.63	1.27 (1.28)	1.38	128.3	-0.46
M. (4)	-0.56	1.27 (1.27)	1.38	129.2	-0.42
B. (4)	-0.45	1.30 (1.22)	1.42	129.7	-0.40
L. (1)	0.16	1.18 (1.17)	(2.37)	177.6	0.01
L. (2)	-0.11	1.18 (1.17)	(2.37)	177.6	0.01
L. (3)	-0.14	1.18 (1.17)	(2.38)	177.1	0.02
L. (4)	-0.08	1.18 (1.17)	(2.35)	177.9	0.01

TABLE III: Adsorption energies, geometric properties, and total charge of different adsorption configurations relative to the vacancy and reduced cerium ions on the reduced ceria (111) surface. The values in parentheses correspond to the header in parentheses. Calculations were performed with CFM PBE+U for the monodentate (M.), bidentate (B.) and linear (L.) adsorption configurations (C.). The numbering is explained in Figure 5.

Starting from a substrate with a surface vacancy and NN-NN Ce^{3+} ions, we performed CFM PBE+U calculations based on the stable adsorption species proposed by Lu et al.³⁷ and Reimers et al.³³. We employed a larger $p(5 \times 5)$ ceria (111) slab with respect to those previous studies and overall a multiplicity of three. Our model did not reproduce the same stable configurations as previously reported. We obtained instead three possible metastable configurations, which are shown in Figure 6. The corresponding adsorption energies, computed with respect to the most stable NNN-NNN surface vacancy system, are 0.70 eV (MS 1), 0.56 eV (MS 2) and 0.84 eV (MS 3).

Obviously, the resulting adsorption energy is strongly influenced by the stability of the reference reduced ceria surface systems. If the vacancy formation energy is underestimated, the stability of the reduced surface is probably overestimated. Neither Lu et al.³⁷, nor Reimers et al.³³ provided any information about the reduced ceria surface system they used as reference. As discussed above, hybrid functional methods predict a higher vacancy

formation energy. In particular, the vacancy formation energies for the reference surface NNN-NNN systems are 4.63 eV for PBE0 and 4.68 eV for HSE06, while PBE+U gives 2.71 eV. Therefore, single point simulations with hybrid functionals (PBE0 and HSE06) for the geometries as obtained from the CFM PBE+U simulations provide quite different outcomes. The resulting E_{ads} for MS 1, MS 2, and MS 3 suggest indeed significantly more stable structures, if computed at this level of theory, reflecting more clearly the oxidative effect of the adsorbate.

Method	Config.	E_{ads} [eV]	$d_{\text{C-O1}}$ ($d_{\text{C-O2}}$) [$\text{\AA}$]	α_{OCO} [$^\circ$]	Charge [e]
CFM	MS 1	0.70	1.30 (1.30)	117.9	-0.58
PBE+U	MS 2	0.56	1.28 (1.28)	126.2	-0.58
	MS 3	0.84	1.38 (1.25)	114.8	-0.68
PBE0	MS 1	-1.44	-	-	-0.64
	MS 2	-1.51	-	-	-0.65
	MS 3	-1.28	-	-	-0.74
HSE06	MS 1	-1.23	-	-	-0.64
	MS 2	-1.32	-	-	-0.64
	MS 3	-1.07	-	-	-0.74

TABLE IV: Adsorption energies, geometric properties and total charge of adsorption species MS 1, MS 2 and MS 3. The values in parentheses correspond to the header in parentheses. The geometry optimizations were only performed with CFM PBE+U. Only single point calculations were performed for PBE0 and HSE06, therefore, the distances and angles are equivalent to CFM PBE+U.

The MS 1 configuration is characterised by two equal CO bonds of 1.3 $\text{\AA}$ and a bond angle of 117 $^\circ$. These values suggest an even stronger activated molecule than the monodentate species. The charge density difference map reported in the SI (Figure S7) shows that the electron density is mainly transferred from the three NN cerium atoms towards the molecule. A distinctive HOMO lobe of the MS 1 species towards one cerium ion is visible and some additional accumulation of charge is present between the CO₂-oxygen atoms and the other two Ce atoms. The MS 1 structure can be classified as a carboxylate because of the pronounced interactions of the carbon atom with the surface. The MS 2 configuration

is characterized by CO bond lengths of 1.28 Å and a bond angle of 126.2°. The electronic charge transferred from the surface to the molecule is mainly accumulated in a CO₂ HOMO lobe orientated towards the middle between two surface Ce cations, which exhibit a pronounced loss in electron density. Hence, MS 2 can be classified as a carboxylate as well. In the MS 3 structure one of the CO₂-oxygen atoms partially occupies the vacancy and the corresponding $d_{\text{C-O1}}$ is 1.38 Å long. The carbon atom is oriented in the direction of an NN surface cerium atom, while the other two NN cations interact with the oxygen occupying the vacancy. This strongly distorted configuration is the least stable and this might facilitate associative or dissociative reactions. The PDOS computed from these structures are reported in Figure S8 of the SI.

3. Vacancy Concentration and Coverage

Other aspects can affect the adsorption and activation of CO₂ on ceria (111). One important factor is the abundance of oxygen defects, i.e., the degree of reduction. For instance, it has been reported that at higher temperature aligned or triangular defect arrays may be observed⁶⁴. Most of previous theoretical studies have been carried out with a $p(2 \times 2)$ model containing one vacancy, i.e., corresponding to a 25% concentration^{33,37}. In order to address the role of the vacancy concentration, we considered four different models corresponding to 4.0%, 6.3%, 11.1%, and 25% (Table V) and an ideal distribution of defects. To this end, we used models of different size, i.e., a $p(5 \times 5)$ for 4.0%, a $p(4 \times 4)$ for 6.3% and 25%, and a $p(3 \times 3)$ surface for 11.1%. In the case of 4.0%, 6.3% and 11.1%, it was possible to construct an NNN-NNN surface vacancy system. An NNN-NN surface vacancy system has been used for calculations with 25.0% vacancy concentration. The formation energy $E_{\text{vac}}/\text{vacancy}$ has been calculated relative to the corresponding fully oxidized systems. While a marginal difference in vacancy formation energy results between the two more diluted cases, at 11.1% we obtained a difference of 6.4% per vacancy, and at the highest concentration it increased by 11.1%.

One CO₂ molecule has been placed on each surface, assuming the MS 1 configuration. The adsorption energies are computed using as reference the corresponding reduced surface. All values are reported in Table V. The destabilising effect of higher vacancy concentration is partially compensated by the adsorption of CO₂ up to the 11.1% model. For the smallest

model, corresponding to 25% vacancy concentration, the counter-effect of the adsorbate-adsorbate interaction leads to an overall destabilization of the system.

Vacancy conc. [%]	$E_{\text{vac}}/\text{vacancy}$ [eV]	$E_{\text{ads}}/\text{molecule}$ [eV]
4.0%	2.71	0.70
6.3%	2.75	0.69
11.1%	3.00	0.41
25.0%	3.30	0.56

TABLE V: Influence of the vacancy concentration (conc.) on the vacancy formation energy $E_{\text{vac}}/\text{vacancy}$ and the adsorption energy per CO_2 molecule $E_{\text{ads}}/\text{molecule}$. To allow an equal distribution of vacancies, different systems had to be applied: a $p(5 \times 5)$ for 4.0%, a $p(4 \times 4)$ for 6.3% and 25%, and a $p(3 \times 3)$ surface for 11.1%. The simulations were done using CFM PBE+U.

Another parameter to be considered is also the CO_2 concentration. Additional CO_2 molecules over already (partially) covered surfaces (by chemisorbed bent CO_2) are expected to mainly physisorb with a linear configuration³² and might have a stabilizing effect. This eventuality was examined by placing one or two linear molecules above the MS 1 structure. The corresponding adsorption energies are listed in Table VI. Though the linear molecules seem to accept some electron density from the chemisorbed molecule, the stabilizing effect appears not to be significant, at least at this low number of co-adsorbates.

CO_2 Molecules	$E_{\text{ads}}/\text{molecule}$ [eV]	Charge linear CO_2 [e]
MS 1	0.70	-
MS 1 + linear	0.59	-0.01
MS 1 + 2 linear	0.46	-0.02

TABLE VI: Average adsorption energy per molecule $E_{\text{ads}}/\text{molecule}$ for three different mixed coverages. The "Charge linear CO_2 " column indicates the total charge accepted by the linear CO_2 molecule(s). The simulations were done using CFM PBE+U.

4. *Vibrational Analysis*

Vibrational analyses have been performed for the monodentate, bidentate and linear species on the stoichiometric CeO_2 (111) surface using the CFM PBE+U model. The simulated IR spectra are reported in Figure 7. The peaks above 1000 cm^{-1} for the linear adsorption differ only marginally from the CO_2 molecule in vacuum. Both exhibit two stretching vibration modes at around 2345 cm^{-1} (asymmetric $\nu_{as}(\text{O1CO2})$) and 1315 cm^{-1} (symmetric $\nu_s(\text{O1CO2})$). The physisorbed species exhibit two additional scissoring vibration modes ($\delta_1(\text{CO}_3)$ and $\delta_1(\text{CO}_3)$) around 620 cm^{-1} . The monodentate species has due to its equally strong intramolecular bonds a comparably low asymmetric stretching mode (1572 cm^{-1}). The bidentate adsorption has an asymmetric stretching vibration mode at 1705 cm^{-1} . There is only one CO_2 -oxygen directly interacting with the surface, which makes the peak appear at higher energy than for the monodentate species. The monodentate and bidentate species exhibit additional stretching ($\nu(\text{CO}_{surf})$) and wagging ($\omega(\text{CO}_3)$) vibrations in the range of 748 cm^{-1} to 970 cm^{-1} . All three species have symmetric stretching vibration modes in the range of 1161 cm^{-1} to 1310 cm^{-1} . This mode is less sensitive to the configurational changes compared to the asymmetric stretching vibration. The results are in good agreement with previous DFT+U vibrational analyses performed on ceria nanoparticles³⁴ and experimental findings^{19,34,40,41,76,77}

The vibrational analyses for the metastable adsorbates on reduced ceria (111) reveals asymmetric stretching vibrations at approximately 1470 cm^{-1} for MS 2 and MS 3. The symmetric stretching appears at 868 cm^{-1} for MS 3 and at 1216 cm^{-1} for MS 2. The MS 1 species shows instead both symmetric and asymmetric stretching within the relatively narrow range from 1216 cm^{-1} to 1286 cm^{-1} , in good agreement with the RAIRS findings by Kong et al.¹⁹. We then suggest that the experimental peak between 1288 cm^{-1} and 1292 cm^{-1} may be interpreted as a superimposition of the asymmetric and symmetric stretching vibration peaks of the same species.

IV. CONCLUSIONS

Bulk ceria, as well as the pristine and reduced ceria (111) surface, were studied employing different DFT-based models. The properties of the reduced ceria (111) surface with an

oxygen vacancy strongly depend on the choice of the method. PBE+U overestimates the stability of the reduced surface, whereas hybrid functionals give vacancy formation energies in better agreement with experiments. The high number of local minima occurring with all methods that support localization of the f orbitals make the search for the lowest energy states complicated. The lowest energy solution has been found by forcing the f orbital occupation towards Ce_{4f+2} states. Though other solutions might involve even more complex f orbital occupation which are hard to capture since the geometry and the orbital occupation do strongly depend on each other. In general it can be assumed that the occurrence of metastable states is frequently ignored in literature. Our results indicate that contracted 4f orbital Gaussians in the cerium basis set in combination with initial constraints for the 4f orbital occupation might be considered a good choice to reproduce low energy solutions of the reduced surface with PBE+U.

We investigated the interactions of CO_2 molecules with the pristine and the reduced surface. On stoichiometric (111) surface we characterized the already proposed monodentate, bidentate and linear configurations, among which the monodentate turns out to be the most stable solution. Upon the formation of a subsurface vacancy, all three configurations become less stable if placed close to the vacancy site. On the other hand, the proximity to a reduced Ce^{3+} ions favours some charge transfer from the surface to the molecule, when the adsorbate is found in the monodentate configuration. On the ceria (111) surface with at least one oxygen vacancy, three more CO_2 adsorption configurations were investigated. All three do only occur if the oxygen vacancy is in the topmost surface oxygen layer. The three configurations are metastable when calculated with PBE+U. When applying hybrid functionals, the stability increases significantly, consistently with the reduced stability of the defective surface at this level of theory. This discrepancy stresses how the partial reoxidation of the reduced surface by CO_2 adsorption is only predictable in terms of stability if the stability of the reduced surface system is properly accounted for.

Finally, vibrational analyses have been carried out for some of the configurations to be compared to the experimental FTIRS data. The results for the monodentate, bidentate and linear adsorption species are in the expected range compared to experiments and previous theoretical findings. The simulated IR spectra of the MS 1 species do exhibit interesting similarities to the experimentally observed signals which have been recently assigned to a new adsorbate structure on the reduced ceria (111) surface.

V. SUPPLEMENTARY MATERIAL

The supplementary material contains: Some benchmarks of the computational models on the bulk ceria and the stoichiometric ceria (111) surface; A more complete description of the considered approaches to reproduce the formation of polarons by means of DFT+U; The full comparison of different possible configurations of the reduced surface locating the vacancy and the polarons at different sites and using different models; The PDOS of the reduced ceria (111) by changing the U parameter using the CFM PBE+U method; the PDOS of a few equilibrium configurations obtained by adsorbing CO₂ on the stoichiometric and on the reduced ceria surfaces; The charge density difference isosurfaces for the adsorbate configurations named MS 1, MS 2, and MS 3; The balls and sticks representation of the arrangement of a second linear CO₂ adsorbate added to the MS 1 structure.

Acknowledgments: The authors thank the generous allocation of computing resource from the Swiss National Supercomputing Center (CSCS) (project uzh1). We thank Professor Jürg Hutter for support and discussions.

Data availability Any data generated and analyzed for this study that are not included in this article and its Supplementary Information are available from the authors upon reasonable request.

REFERENCES

- ¹Hussein, G. A. M. *Journal of Analytical and Applied Pyrolysis* **1996**, *37*, 111–149.
- ²Mancheri, N. A.; Sprecher, B.; Bailey, G.; Ge, J.; Tukker, A. *Resources, Conservation and Recycling* **2019**, *142*, 101–112.
- ³Humphries, M. Rare Earth Elements: The Global Supply Chain. 2012.
- ⁴Chueh, W. C.; Falter, C.; Abbott, M.; Scipio, D.; Furler, P.; Haile, S. M.; Steinfeld, A. *Science* **2010**, *330*, 1797–1801.
- ⁵Laosiripojana, N.; Chadwick, D.; Assabumrungrat, S. *Chemical Engineering Journal* **2008**, *138*, 264–273.
- ⁶Sharma, S.; Sravan Kumar, K. B.; Chandnani, Y. M.; Phani Kumar, V. S.; Gangwar, B. P.; Singhal, A.; Deshpande, P. A. *The Journal of Physical Chemistry C* **2016**, *120*, 14101–14112.
- ⁷Abanades, S.; Flamant, G. *Solar Energy* **2006**, *80*, 1611–1623.
- ⁸Gorte, R. J. *AIChE Journal* **2010**, *56*, 1126–1135.
- ⁹Kapar, J.; Fornasiero, P.; Graziani, M. *Catalysis Today* **1999**, *50*, 285–298.
- ¹⁰Furler, P.; Scheffe, J. R.; Steinfeld, A. *Energy and Environmental Science* **2012**, *5*, 6098–6103.
- ¹¹Hayes, W.; Stoneham, A. M. *Defects and Defect Processes in Nonmetallic Solids*; Dover Publications: Mineola, New York, 2004.
- ¹²Siokou, A.; Nix, R. M. *The Journal of Physical Chemistry B* **1999**, *103*, 6984–6997.
- ¹³Hahn, K. Computer Simulations of Chemical Reactions on Metal Oxide Surfaces. Doctoral dissertation, University of Zurich, Zurich, 2013.
- ¹⁴Yang, Z.; Woo, T. K.; Baudin, M.; Hermansson, K. *The Journal of Chemical Physics* **2004**, *120*, 7741–7749.
- ¹⁵Esch, F.; Fabris, S.; Zhou, L.; Montini, T.; Africh, C.; Fornasiero, P.; Comelli, G.; Rosei, R. *Science* **2005**, *309*, 752 – 755.
- ¹⁶Murgida, G. E.; Ganduglia-Pirovano, M. V. *Physical Review Letters* **2013**, *110*, 246101.
- ¹⁷Sutton, J. E.; Beste, A.; Overbury, S. H. *Physical Review B* **2015**, *92*, 144105.
- ¹⁸Wu, X.-P.; Gong, X.-Q. *Physical Review Letters* **2016**, *116*, 086102.
- ¹⁹Kong, D.; Zhu, J.; Ernst, K.-H. *The Journal of Physical Chemistry C* **2016**, *120*, 5980–5987.

- ²⁰Yang, C.; Yin, L.-L.; Bebensee, F.; Buchholz, M.; Sezen, H.; Heissler, S.; Chen, J.; Nefedov, A.; Idriss, H.; Gong, X.-Q.; Wll, C. *Physical Chemistry Chemical Physics* **2014**, *16*, 24165–24168.
- ²¹Han, X.; Amrane, N.; Zhang, Z.; Benkraouda, M. *The Journal of Physical Chemistry C* **2016**, *120*, 13325–13331.
- ²²Sun, L.; Huang, X.; Wang, L.; Janotti, A. *Physical Review B* **2017**, *95*, 245101.
- ²³Paier, J.; Penschke, C.; Sauer, J. *Chemical Reviews* **2013**, *113*, 3949–3985.
- ²⁴Tuller, H.; Nowick, A. *Journal of Physics and Chemistry of Solids* **1977**, *38*, 859–867.
- ²⁵Li, H.-Y.; Wang, H.-F.; Guo, Y.-L.; Lu, G.-Z.; Hu, P. *Chemical Communications* **2011**, *47*, 6105–6107.
- ²⁶Plata, J. J.; Mrquez, A. M.; Sanz, J. F. *The Journal of Physical Chemistry C* **2013**, *117*, 25497–25503.
- ²⁷Zhang, D.; Han, Z.-K.; Murgida, G. E.; Ganduglia-Pirovano, M. V.; Gao, Y. *Physical Review Letters* **2019**, *122*, 096101.
- ²⁸Liu, Y.; Li, Z.; Xu, H.; Han, Y. *Catalysis Communications* **2016**, *76*, 1–6.
- ²⁹Graciani, J.; Mudiyansele, K.; Xu, F.; Baber, A. E.; Evans, J.; Senanayake, S. D.; Stacchiola, D. J.; Liu, P.; Hrbek, J.; Sanz, J. F.; Rodriguez, J. A. *Science* **2014**, *345*, 546–550.
- ³⁰Freund, H.-J.; Roberts, M. *Surface Science Reports* **1996**, *25*, 225–273.
- ³¹Calatayud, M.; Markovits, A.; Menetrey, M.; Mguig, B.; Minot, C. *Catalysis Today* **2003**, *85*, 125–143.
- ³²Hahn, K. R.; Iannuzzi, M.; Seitsonen, A. P.; Hutter, J. *The Journal of Physical Chemistry C* **2013**, *117*, 1701–1711.
- ³³Reimers, W. G.; Baltans, M. A.; Branda, M. M. *Journal of Molecular Modeling* **2014**, *20*, 2270.
- ³⁴Vayssilov, G. N.; Mihaylov, M.; Petkov, P. S.; Hadjiivanov, K. I.; Neyman, K. M. *The Journal of Physical Chemistry C* **2011**, *115*, 23435–23454.
- ³⁵Dohnalek, Z.; Lyubinetsky, I.; Rousseau, R. *Progress in Surface Science* **2010**, *85*, 161–205.
- ³⁶Reticcioli, M.; Sokolovi, I.; Schmid, M.; Diebold, U.; Setvin, M.; Franchini, C. *Physical Review Letters* **2019**, *122*, 016805.
- ³⁷Lu, X.; Wang, W.; Wei, S.; Guo, C.; Shao, Y.; Zhang, M.; Deng, Z.; Zhu, H.; Guo, W. *RSC Advances* **2015**, *5*, 97528–97535.

- ³⁸Yang, C.; Will, C. *Advances in Physics: X* **2017**, *2*, 1–36.
- ³⁹Yang, C.; Wang, W.; Nefedov, A.; Wang, Y.; Mayerhfer, T. G.; Will, C. *Physical Chemistry Chemical Physics* **2020**, *22*, 17129–17133.
- ⁴⁰Jin, T.; Zhou, Y.; Mains, G. J.; White, J. M. *The Journal of Physical Chemistry* **1987**, *91*, 5931–5937.
- ⁴¹Li, C.; Sakata, Y.; Arai, T.; Domen, K.; Maruya, K.-i.; Onishi, T. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* **1989**, *85*, 1451.
- ⁴²Wuilloud, E.; Delley, B.; Schneider, W.-D.; Baer, Y. *Physical Review Letters* **1984**, *53*, 202–205.
- ⁴³Hay, P. J.; Martin, R. L.; Uddin, J.; Scuseria, G. E. *The Journal of Chemical Physics* **2006**, *125*, 034712.
- ⁴⁴Andersson, D. A.; Simak, S. I.; Johansson, B.; Abrikosov, I. A.; Skorodumova, N. V. *Physical Review B* **2007**, *75*, 035109.
- ⁴⁵Brugnoli, L.; Ferrari, A. M.; Civalleri, B.; Pedone, A.; Menziani, M. C. *Journal of Chemical Theory and Computation* **2018**, *14*, 4914–4927.
- ⁴⁶Castleton, C. W. M.; Lee, A.; Kullgren, J. *The Journal of Physical Chemistry C* **2019**, *123*, 5164–5175.
- ⁴⁷Hutter, J.; Iannuzzi, M.; Schiffmann, F.; VandeVondele, J. *Wiley Interdisciplinary Reviews: Computational Molecular Science* **2014**, *4*, 15–25.
- ⁴⁸Kühne, T. D. et al. *The Journal of Chemical Physics* **2020**, *152*, 194103.
- ⁴⁹Perdew, J. P.; Burke, K.; Ernzerhof, M. *Physical Review Letters* **1996**, *77*, 3865–3868.
- ⁵⁰Dudarev, S. L.; Manzh, D. N.; Sutton, A. P. *Philosophical Magazine B* **1997**, *75*, 613–628.
- ⁵¹Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y.; Humphreys, C. J.; Sutton, A. P. *Physical Review B* **1998**, *57*, 1505–1509.
- ⁵²Perdew, J. P.; Ernzerhof, M.; Burke, K. *The Journal of Chemical Physics* **1996**, *105*, 9982–9985.
- ⁵³Heyd, J.; Scuseria, G. E.; Ernzerhof, M. *The Journal of Chemical Physics* **2003**, *118*, 8207–8215.
- ⁵⁴Goedecker, S.; Teter, M.; Hutter, J. *Physical Review B* **1996**, *54*, 1703–1710.
- ⁵⁵Vydrov, O. A.; Voorhis, T. V. *Physical Review Letters* **2009**, *103*, 063004.
- ⁵⁶VandeVondele, J.; Hutter, J. *The Journal of Chemical Physics* **2007**, *127*, 114105.
- ⁵⁷Hahn, K. R.; Seitsonen, A. P.; Iannuzzi, M.; Hutter, J. *ChemCatChem* **2015**, *7*, 625–634.

- ⁵⁸Wang, Y.-G.; Mei, D.; Li, J.; Rousseau, R. *The Journal of Physical Chemistry C* **2013**, *117*, 23082–23089.
- ⁵⁹Humphrey, W.; Dalke, A.; Schulten, K. *Journal of Molecular Graphics* **1996**, *14*, 33–38.
- ⁶⁰Su, Y.-Q.; Filot, I. A. W.; Liu, J.-X.; Tranca, I.; Hensen, E. J. M. *Chemistry of Materials* **2016**, *28*, 5652–5658.
- ⁶¹Mullins, D. R. *Surface Science Reports* **2015**, *70*, 42–85.
- ⁶²Ganduglia-Pirovano, M. V.; Da Silva, J. L. F.; Sauer, J. *Physical Review Letters* **2009**, *102*, 026101.
- ⁶³Li, H.-Y.; Wang, H.-F.; Gong, X.-Q.; Guo, Y.-L.; Guo, Y.; Lu, G.; Hu, P. *Physical Review B* **2009**, *79*, 193401.
- ⁶⁴Han, Z.-K.; Yang, Y.-Z.; Zhu, B.; Ganduglia-Pirovano, M. V.; Gao, Y. *Physical Review Materials* **2018**, *2*, 035802.
- ⁶⁵Fabris, S.; de Gironcoli, S.; Baroni, S.; Vicario, G.; Balducci, G. *Physical Review B* **2005**, *71*, 041102.
- ⁶⁶Esch, F.; Fabris, S.; Zhou, L.; Montini, T.; Africh, C.; Fornasiero, P.; Comelli, G.; Rosei, R. *Science* **2005**, *309*, 752–755.
- ⁶⁷Rabone, J.; Krack, M. *Computational Materials Science* **2013**, *71*, 157–164.
- ⁶⁸Allen, J. P.; Watson, G. W. *Physical Chemistry Chemical Physics* **2014**, *16*, 21016–21031.
- ⁶⁹Geng, H. Y.; Chen, Y.; Kaneta, Y.; Kinoshita, M.; Wu, Q. *Physical Review B* **2010**, *82*, 094106.
- ⁷⁰Dorado, B.; Freyss, M.; Amadon, B.; Bertolus, M.; Jomard, G.; Garcia, P. *Journal of Physics: Condensed Matter* **2013**, *25*, 333201.
- ⁷¹Zhu, S.; Guo, L.; Li, P.; Zhang, B.; Zhao, G.; He, T. *Catalysis Today* **2018**, Article not published. Available from: <https://doi.org/10.1016/j.cattod.2018.11.056>.
- ⁷²Dorado, B.; Amadon, B.; Freyss, M.; Bertolus, M. *Physical Review B* **2009**, *79*, 235125.
- ⁷³Reticcioli, M.; Setvin, M.; Schmid, M.; Diebold, U.; Franchini, C. *Physical Review B* **2018**, *98*, 045306.
- ⁷⁴Jerratsch, J.-F.; Shao, X.; Nilius, N.; Freund, H.-J.; Popa, C.; Ganduglia-Pirovano, M. V.; Burow, A. M.; Sauer, J. *Physical Review Letters* **2011**, *106*, 246801.
- ⁷⁵Mulliken, R. S. *The Journal of Chemical Physics* **1955**, *23*, 1833–1840.
- ⁷⁶Li, C.; Sakata, Y.; Arai, T.; Domen, K.; Maruya, K.-i.; Onishi, T. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* **1989**, *85*, 929.

⁷⁷Binet, C.; Badri, A.; Boutonnet-Kizlingt, M.; Lavalley, J.-C. *Journal of the Chemical Society, Faraday Transactions* **1994**, *90*, 6.

FIG. 1: Labeling of cerium atoms around the oxygen vacancy. Upper figures show the top view on the surface; lower figures show the side view. The dark grey spheres indicate the vacancy positions, white spheres Ce, blue spheres the surface oxygen layer and red spheres the subsurface oxygen layer. NN labels nearest-neighboring and NNN next-to-nearest-neighboring Ce centers. Only the surface trilayer is shown for clarity reasons.

FIG. 2: Isosurfaces of the spin-densities of the subsurface vacancy system with two Ce^{3+} cations in NNN position observed with CFM (triplet state) and UCFM (singlet state) PBE+U. For CFM, the Ce_4f orbitals are enforced to occupy the f_{+2} orbitals up to a SCF convergence of $1e - 4$ Hartree. No occupation constraint is applied for the UCFM simulation. The distances are given in Å.

FIG. 3: Stable adsorption configurations on the stoichiometric CeO_2 (111) surface obtained with CFM PBE+U. The red spheres indicate oxygen, white spheres Ce^{4+} , and black spheres carbon atoms. For clarity reasons, only one trilayer of the relaxed surface is shown. The bond lengths and angles for CFM and UCFM PBE+U are listed in Table II.

FIG. 4: Isosurface of the charge density difference at $0.01 \text{ e}/\text{\AA}^3$ computed for the monodentate and bidentate CO_2 species. The cyan lobes indicate accumulation and the orange lobes loss of electron density. For clarity reasons only one trilayer of the relaxed surface is shown. Calculations were performed with CFM PBE+U.

FIG. 5: Comparison of different adsorption sites on the reduced CeO_2 (111) surface in its most stable configuration. The numbered CO_2 molecules were simulated separately in different slab systems with CFM PBE+U. The red spheres indicate oxygen, white spheres Ce^{4+} , cyan spheres Ce^{3+} , black spheres carbon atoms, and the bigger grey spheres the vacancy. The transparent CO_2 molecules indicate the starting configuration previous to the geometry optimization, the solid molecules indicate the resulting geometry optimized structures. In the case of the bidentate adsorption, structures (1) to (3) result in monodentate adsorption. In these three cases, geometry optimized structures are not visualized. For clarity reasons, one unrelaxed trilayer is shown in the background.

FIG. 6: Possible adsorption species on the reduced CeO_2 (111) surface. The red spheres indicate oxygen, white spheres Ce^{4+} , black spheres carbon atoms, and grey spheres the oxygen vacancy. The geometry optimizations were performed with CFM PBE+U

FIG. 7: Simulated IR spectra of the three stable adsorption species on the stoichiometric (monodentate, bidentate, linear), and the three species on the reduced ceria (111) surface (MS 1, MS 2, MS 3) calculated with CFM PBE+U. $\nu_{as}(O1CO2)$ specifies asymmetric and $\nu_s(O1CO2)$ indicates symmetric stretching vibration modes. $\nu(CO_{surf})$ indicates an additional stretching vibration mainly between C and the surface oxygen O_{surf} . $\omega(CO_3)$ represents a wagging vibration, $\delta_1(CO_3)$, $\delta_2(CO_3)$, and $\delta(CO_2 - Surf)$ indicate scissoring modes.