We use density functional theory calculations with Hubbard corrections (DFT+U) to investigate electronic aspects of the interaction between ceria surfaces and gold atoms. Our results show that Au adatoms at the (111) surface of ceria can adopt Au\(^{0}\), Au\(^{+}\) or Au\(^{2+}\) electronic configurations depending on the adsorption site. The strongest adsorption sites are on top of the surface oxygen and in a bridge position between two surface oxygen atoms, and in both cases charge transfer from the gold atom to one of the Ce cations at the surface is involved. Adsorption at other sites, including the hollow sites of the surface, and an O–Ce bridging site, is weaker and does not involve charge transfer. Adsorption at an oxygen vacancy site is very strong and involves the formation of an Au\(^{+}\) anion. We argue that the ability of gold atoms to stabilise oxygen vacancies at the ceria surface by moving into the vacancy site and attracting the excess electrons of the defect could be responsible for the enhanced reducibility of ceria surfaces in the presence of gold. Finally, we rationalise the differences in charge transfer behaviour from site to site in terms of the electrostatic potential at the surface and the coordination of the species.

1. Introduction

Metal–oxide supported gold catalysts are known to be highly active in technologically important reactions, including the low-temperature oxidation of carbon monoxide\(^1\)–\(^3\) and the water gas shift (WGS) reaction.\(^4\),\(^5\) A widely debated issue in heterogeneous gold catalysis is the oxidation state of the active gold species in the supported catalyst. Fu et al.\(^6\) have shown that the activity of a gold/ceria catalyst in the WGS reaction is retained if all the metallic gold is removed from the catalyst, leaving only cationic gold species. Hutchings et al.\(^7\) have performed spectroscopic studies which indicate that cationic gold species are central in the catalytic mechanism of CO oxidation, while Zhang et al.\(^8\) and Guzman and Gates\(^9\) have also suggested that Au(III) is the active species in hydrogenation reactions. However, other authors have disputed the role of the cationic gold species. An XAS study by Schwartz et al.,\(^10\) for example, has indicated that oxidized Au species are not necessary to achieve high activities of CO oxidation with a Au/TiO\(_2\) catalyst. In the case of the WGS reaction, Tibelli et al.\(^1\) have reported that, although a fresh Au/CeO\(_2\) catalyst contains isolated gold cations, only metallic gold could be detected by XANES measurements under reaction conditions.

It is clear that a fundamental understanding of the interaction of gold with ceria surfaces is required to rationalise the experimental information on this topic, and computer modelling is well suited to play a major role in this effort. Recent simulation studies have shown that gold cations doped in the lattice positions of various oxides significantly increase the reducibility of the surfaces,\(^11\)–\(^13\) whereas a density functional theory (DFT) investigation by Liu et al.\(^14\) has also concluded that gold atoms become positively charged upon deposition at the ceria (111) surface. However, the latter work was performed using the generalised gradient approximation (GGA), which is known to provide an essentially incorrect description of the highly localised 4f orbitals of reduced Ce cations. In order to overcome this limitation of the DFT method in the description of CeO\(_2\) oxides, different approaches are available. One is the so-called DFT + U method,\(^15\),\(^16\) which in the case of ceria introduces an energy term that penalises the hybridisation of the Ce f orbitals with the O ligands, thereby forcing the localisation of the f electron.\(^17\)–\(^19\) Another alternative, which is computationally much more demanding, is the use of a hybrid functional that partially corrects the self-interaction problem of DFT by substituting a certain fraction of the DFT exchange term with non-local Hartree–Fock exchange,\(^20\) which also yields a correct description of Ce f electrons.\(^21\) In a previous work, we have shown that some correction of the DFT functional is indeed essential to describe the interaction of ceria surfaces with adsorbed metals, and the DFT + U method correctly predicts charge transfer from Pd adatoms to the ceria cations, in agreement with experimental observations, but contrasting with pure GGA calculations.\(^22\) A recent DFT simulation\(^23\) of the interaction of gold with ceria surfaces has provided energetic data about the adsorption, but a discussion of the electronic aspects of the adsorption was not included, even when this is important for the catalytic applications. Zhang et al.\(^24\) have recently published another investigation of the interaction between gold and ceria surfaces, where they found that the strongest interaction of gold with the stoichiometric surface occurs when the adatom is in a bridging position between two oxygen atoms.

We present here a theoretical investigation, based on the DFT + U method, of the adsorption of gold atoms at the stoichiometric and oxygen-deficient CeO\(_2\) (111) surfaces, where we show that important variations in the electronic behaviour take place among the different adsorption sites. We will attempt to explain the physical origin of these variations,
and discuss the implications of this behaviour for the redox properties of gold/ceria catalysts.

2. Methodology

All the calculations were performed using the VASP code,\textsuperscript{25,26} where we have used the generalized gradient approximation (GGA), with a density functional built from the Perdew and Zunger\textsuperscript{27} local functional, and the gradient corrections by Perdew \textit{et al}.\textsuperscript{28} In the DFT+U functional a Hubbard parameter $U_{\text{eff}} = 5$ eV is typically used in studies of ceria surfaces\textsuperscript{22,29} and this is also the value recommended by Andersson \textit{et al}.\textsuperscript{17} based on a systematic study of CeO$_2$ oxides. Previous work has also shown that the correct localisation of excess electrons on Ce ions is only achieved for $U_{\text{eff}} = 5$ eV and greater.\textsuperscript{29} Since we are interested in the description of localised Ce f states, in this case arising from any charge transfer from the metal adatom, we will follow these authors and use the same value of the Hubbard parameter.

The interaction between the valence electrons and the core was described with the projected augmented wave (PAW) method\textsuperscript{30} in the implementation of Kresse and Joubert.\textsuperscript{31} The core levels up to 4f in Au, 4d in Ce and 1s in O were kept frozen in their atomic reference states. Scalar relativistic effects are included in these potentials, which is necessary for the correct description of the electronic structure of the heavy Au atoms. The number of plane waves in VASP is controlled by a cut-off energy, which in our calculations was set to $E_{\text{cut}} = 415$ eV. We have carried out test calculations with an increased cutoff energy of 500 eV and found that this changed the adsorption energies by only a few meV, while the electronic details of the interaction were unaltered.

The CeO$_2$ (111) surface is represented in our calculations by oxygen-terminated slabs, which repeat periodically in the direction perpendicular to the surface, separated by a vacuum gap of $\sim 15$ Å. Based on the results of our previous work on both ceria (111) and the isostructural cubic zirconia (111) surface, each slab contains nine atomic layers (three O-Ce-O tri-layers), which we found to be sufficient to obtain convergence of the surface properties.\textsuperscript{22,32} Parallel to the surface, the supercell consists of a $2 \times 2$ array of hexagonal surface unit cells. Each unit cell contains one CeO$_2$ unit at the surface, and therefore the three-layer simulation supercell contains 36 atoms in total, with four oxygen ions at each surface (Fig. 1). In all calculations, the positions of the four atomic layers at the bottom of the slab were kept fixed at the bulk positions, while the first five layers of the top face, where we deposit the metallic atoms, were fully relaxed. Structural optimizations were performed using a conjugate gradients technique in which the iterative relaxation of atomic positions was stopped when the forces on the atoms were all less than 0.01 eV Å$^{-1}$. For all geometry optimization calculations a $3 \times 3 \times 1$ k-point mesh was used to sample the reciprocal space, while at the final single-point runs for the calculation of the electronic density of states, a denser mesh of $5 \times 5 \times 1$ k-points was employed.

3. Results and discussion

Adsorption at the stoichiometric surface

We first performed a systematic search for stable adsorption configurations at the non-defective (111) surface, by simultaneously relaxing the positions of the surface ions and the gold adatom, starting from different geometries and without applying any symmetry constraints. Besides the high-symmetry sites (on top of Ce, on top of the surface oxygen $O_u$ and above the subsurface oxygen $O_d$, see Fig. 1), we also started the optimisations from less symmetric positions, including the centre of the Ce–$O_u$–$O_d$ “triangle”, and in the middle between each pair of sites ($O_u$–Ce, $O_u$–$O_d$, Ce–$O_d$). Such a systematic probing of all non-symmetric sites has proved to be essential for the determination of the adsorption ground-state in this and similar surfaces.\textsuperscript{22,32}

Not all tested sites provided local energy minima for adsorption, with relaxation leading to five types of adsorption configurations: (i) Ce (Fig. 2a) and (ii) $O_d$ (Fig. 2b) hollow sites, where the adatom is coordinated to three surface $O_u$ ions, (iii) $O_u$–Ce site (Fig. 2c), where the adatom is coordinated to only one $O_u$ atom, but it is tilted towards a Ce ion, effectively forming a $O_u$–Au–Ce bridge, (iv) top site configurations where Au is coordinated mainly to one $O_u$ atom at the surface (Fig. 2d,e), and (v) $O_d$–$O_u$ bridging configurations (Fig. 2f–h), where Au is coordinated to two $O_u$ surface ions. Some relevant properties of the different configurations are listed in Table 1.

The integration of the spin densities within spheres (magnetic moments $\mu$) around each of the four Ce atoms at the surface allows us to distinguish between Ce$^{4+}$ (4f$^0$, non-magnetic) and Ce$^{3+}$ (4f$^1$, magnetic) cations. We observe that in the two hollow sites (Ce and $O_d$) and in the $O_u$–Ce site all the Ce atoms at the surface remain as Ce$^{4+}$, whereas the adsorption on top of the $O_u$ or in a bridging $O_u$–$O_d$ site does involve the reduction of one of the surface cerium atoms, as indicated by magnetic moments between 0.82 and 0.97 $\mu_B$ (which are close to the ideal value of 1 $\mu_B$ for the spin moment of one unpaired electron). The local environment of the Ce atoms also changes upon reduction, with an increased average distance to the neighbouring oxygen ions of $\sim 2.5$ Å, compared to an average of $\sim 2.35$ Å for Ce$^{4+}$–O at the clean surface. A similar local distortion is observed upon the

![Fig. 1](image-url) Slab model for the (111) surface of ceria, showing the high-symmetry sites $O_u$, $O_d$ and Ce.
The hollow site, the Au atom is nearly neutral (\(3^+\)). labelled with a ‘+’ sign, and the reduced cerium atom is labelled.

Fig. 2 Different configurations of adsorption of a gold atom at the stoichiometric CeO\(_2\) (111) surface. The schemes only show the last three atomic layers, but models with 9 atomic layers were employed in the calculations, as shown in Fig. 1. Yellow balls are gold adatoms, small red balls are subsurface oxygen ions (O\(_d\)), large red balls are surface oxygen ions (O\(_u\)), and white balls are cerium ions. In configurations where charge transfer is predicted, the oxidised gold atom is labelled ‘+’, and the reduced cerium atom is labelled ‘3+’.

The reduction of a Ce atom is accompanied by the oxidation of the gold adatom, as we have checked by calculating the Bader charges. For example, after adsorption on the hollow site, the Au atom is nearly neutral (–0.05 e\(^-\) and –0.07 e\(^-\) for Ce and O\(_d\) sites, respectively), but positive charges of \(\sim 0.33\) e\(^-\) are obtained for gold adatoms at O\(_u\) and O\(_u\)-O\(_u\) sites. The configurations involving charge transfer are also the most stable, with adsorption energies between –0.86 eV and –1.15 eV, compared to values from –0.38 to –0.75 eV in the configurations without charge transfer.

The ability of the noble metal to donate one electron to the surface Ce ions and the relative stability of the charge transfer solution compared to the neutral gold adsorption is similar to what has been theoretically and experimentally observed for Pd/ceria interactions. The weaker adsorption at the hollow sites, and the occurrence of charge transfer when gold is adsorbed at the top and bridging sites, has also been reported recently by Zhang et al. However, in contrast with the results reported in that work, we have found here that different electronic solutions can be stable for similar adsorption geometries. For example, in ref. 24 only one mode of adsorption at the top (O\(_u\)) site was found, where the reduced Ce atom was the nearest one to the Au–O\(_u\) bond, while other locations for the transferred electron could not be stabilised. In our work, we were able to obtain stable O\(_u\) adsorption solutions in which the electron is located either far from (Fig. 2d) or near (Fig. 2e) the Au–O\(_u\) bond, and in fact we found that the first case is slightly more stable (by \(\sim 0.04\) eV). Furthermore, it can be argued that the O\(_u\)-Ce site of Fig. 2c, which was not reported in ref. 24, is yet another mode of adsorption on top of O\(_u\), in this case without charge transfer. This adsorption geometry is similar to the most stable adsorption configuration of gold on the (111) surface of cubic zirconia, where charge transfer is prevented by the low reducibility of Zr\(^{4+}\) cations. For the O\(_u\)-O\(_u\) bridging site we also found three stable configurations, which differ from each other in the location of the reduced Ce\(^{3+}\) cation (Fig. 2f, g, and h), and show appreciable variations in the adsorption energy.

We should mention that, in order to obtain these solutions, it is generally not enough to assign the desired initial position of the magnetic moment, as the final location of the unpaired electron can change upon electronic relaxation. In order to force a solution with a particular position of the reduced cerium cation, one has to distort the geometry in a way consistent with the oxidation state of the cations (for example, larger Ce–O distances for Ce\(^{3+}\) compared to Ce\(^{4+}\)). In particular, we have checked that, when a calculation is started from the geometry corresponding to a particular position of

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### Table 1

<table>
<thead>
<tr>
<th>Site</th>
<th>(E_{\text{ads}}) (\text{eV})</th>
<th>(d[\text{Au–O}])</th>
<th>(d[\text{Au–Ce}])</th>
<th>(\mu)</th>
<th>(\mu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>–0.38</td>
<td>3(\times) 3.14</td>
<td>1(\times) 2.99</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>O(_u)</td>
<td>–0.61</td>
<td>3(\times) 2.76</td>
<td>3(\times) 3.27</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>O(_u)-Ce(_u)</td>
<td>–0.75</td>
<td>2.17</td>
<td>1(\times) 3.16</td>
<td>0.02</td>
<td>0.00</td>
</tr>
<tr>
<td>O(_u) (conf. 1)</td>
<td>–0.96</td>
<td>1.96</td>
<td>2(\times) 3.85</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>O(_u) (conf. 2)</td>
<td>–0.92</td>
<td>2.06</td>
<td>2(\times) 3.50</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>O(_u)-O(_u) (conf. 1)</td>
<td>–1.15</td>
<td>2(\times) 2.15</td>
<td>1(\times) 2.83</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>O(_u)-O(_u) (conf. 2)</td>
<td>–1.00</td>
<td>2.15</td>
<td>1(\times) 3.37</td>
<td>0.06</td>
<td>0.00</td>
</tr>
<tr>
<td>O(_u)-O(_u) (conf. 3)</td>
<td>–0.86</td>
<td>2(\times) 2.21</td>
<td>1(\times) 2.87</td>
<td>0.05</td>
<td>0.00</td>
</tr>
</tbody>
</table>
the reduced Ce ion, the calculation always converges to the configuration corresponding to that geometry, even if the initial magnetic moment is assigned in a different way. This might be the reason why other authors have not obtained these solutions before. Similar arguments have been offered recently by Ganduglia-Pirovano et al.,33 in connection with the distribution of the excess electrons associated to an oxygen vacancy in the (111) surface of ceria: previous calculations had concluded that the electrons localise on the Ce atoms neighbouring the vacancy, but a careful sampling of the possible configurations in ref. 33 showed that the ground state is actually one in which the electrons localised at the next-nearest Ce ions. In other words, there is a strong coupling in this system between the electronic and geometric degrees of freedom, and therefore the final electronic configurations depend very sensitively on the initial local geometry.

The energetic preference for oxidised states of gold at ceria surfaces agrees with a number of experimental studies showing the presence of Au cations in gold/ceria systems.37 For example, Fu et al.,6 used XPS spectroscopy to demonstrate the occurrence of both Au + and Au 3+ oxidation states in a gold/ceria catalyst, although the presence of the 3+ species argues in favour of lattice substitution rather surface deposition. Recent experimental studies of the interaction of gold with the (111) surface of ceria under more controlled conditions are not conclusive. Rodriguez et al.,38 studied the properties of gold nanoparticles supported at the CeO2(111) surface, but they did not obtain any evidence of oxidised gold, probably due to the pre-treatment of the samples under reducing WGS reaction conditions. In a more recent photoelectron spectroscopy study, Škoda et al. observed the formation of Ce 3+ ions upon gold deposition at the (111) surface, which associated with the formation of Au + species. Our theoretical results provide support for this interpretation. However, it should be noted that in the experimental studies in ref. 38 and 39, gold is forming nanoclusters at the ceria surface, while our theoretical investigation refers to atomically dispersed Au atoms. Considering the current debate about the role of Au 3+ cations in gold catalysis, an experimental investigation of the interaction of individual gold atoms with ceria surfaces would be very desirable.

**Adsorption at the defective surface**

In order to investigate the adsorption of gold atoms at the defective sites, we first calculated the formation energies of the oxygen vacancies, which were 2.45 eV for an O d vacancy and 2.56 for an O a vacancy, in fair agreement with values reported by other authors.19,23,33,40 Upon vacancy formation, two surface Ce 3+ cations are reduced to Ce 3+, orienting their magnetic moments in antiparallel directions, as represented in the DOS plot of Fig. 3a. We have not investigated here all the possible distributions of the excess electrons associated with the vacancy, as in ref. 33, but we discuss below the localisation of the excess electrons of the defective surface upon gold adsorption.

Our calculations show that the adsorption of gold atoms on top of the O a vacancy releases an energy comparable with the adsorption at the clean surface (−0.55 eV), but the adsorption on top of the O u vacancy is much more exothermic, with \( E_{\text{ads}} = -2.41 \) eV. In both cases, the charge transfer occurs in the opposite direction compared to the adsorption at the O a and the O u–O u sites of the stoichiometric surface, with the electron now going from one of the reduced Ce cations to the adsorbed gold atom. The DOS plot of Fig. 3b shows clearly that when a gold atom is adsorbed on top of the vacancy site, both Au 6s levels become occupied, which means that the adatom has adopted an Au + configuration. The DOS also shows that one of the reduced cations originally associated with the vacancy has reoxidised to the 4+ state upon gold adsorption (no f peak below the Fermi level), while the other Ce 3+ cations keeps its reduced electronic state. We have also investigated the variation of the Au adsorption energy with the position of the reduced Ce cation, and we find that when the excess electron is localised on the next-nearest neighbour (NNN) Ce atom, instead of on the nearest neighbour (NN) Ce atom, the total energy decreases significantly, by 0.23 eV. This is in line with the recent report by Ganduglia-Pirovano et al.,33 which shows that in a defective ceria surface, the localisation of the excess electrons on one NN and one NNN Ce atoms is more stable than the localisation on two NN atoms. In their work, the energy difference between the two cases was found to be \( \sim 0.2 \) eV using GGA+U and hybrid methods. Our results indicate that this energy difference is roughly conserved after Au adsorption on top of the O vacancy, provided that the electron transferred to the adatom comes from the NNN Ce 3+ cation. Therefore, the adsorption energy of gold at the vacancy site is not affected by the initial distribution of the excess electrons associated with the defect.

The fact that the adsorption energy of gold at the surface vacancy site has an absolute value similar to the formation energy of the oxygen vacancy, suggests that the reduction of the surface can be significantly enhanced by gold adsorption at these sites. Furthermore, since the adsorption at the vacancy site is much stronger than at the stoichiometric sites, we could envisage an activated mechanism of oxygen release by which the presence of vacancies at this surface is thermodynamically favoured by the diffusion of adsorbed gold atoms from stoichiometric sites (where gold is Au 3+ or Au 6+) to the vacancy sites (where gold is Au +). We calculate that the formation energies for oxygen vacancies following this type of mechanism would be between 0.53 and 1.07 eV (depending on the initial adsorption site). These values are much lower than the formation energy of the vacancy at the clean surface (2.56 eV), and therefore a higher concentration of vacancies should be expected in the presence of deposited gold. This mechanism of Au-assisted oxygen vacancy formation is similar to the one that we have suggested recently for the improved reducibility of zirconia surfaces upon gold doping, where the reduction was aided by the Au 3+ → Au + transition in the dopant.11 However, in the mechanism that we are proposing here, the gold atom would not need to occupy lattice positions in order to improve the reducibility of the surface, and the relevant transition would be from Au + or Au 3+ to the Au + oxidation state. This model agrees with recent suggestions based on experimental evidence that the presence of admetals favours the formation of oxygen vacancies in ceria.38 Ce 3d core-level XPS spectra obtained in that work showed partial reduction of
the ceria support after exposing Au/CeO$_2$(111) to CO, a reduction that was not seen when pure CeO$_2$(111) was exposed to the gas.

Rationalising the differences in charge transfer behaviour: electrostatic potential and orbital hybridisation

The dependence of the adatom charge on the site of adsorption suggests that the occurrence of charge transfer is not simply determined by the balance between the ionisation potential of gold atoms and the electron affinity of the Ce cations in the oxide, but that there must be some site-specific interactions controlling the charge transfer behaviour. One clear difference between the surface sites is the value of the electrostatic potential above the surface (Fig. 4a), which is much more negative on top of the Ou sites than at the rest of the surface, thus stabilising the adsorption of a positive ion at that site. Conversely, the least negative electrostatic potential at the surface is achieved in the presence of oxygen vacancies (Fig. 4b), which we have seen corresponds to a negative charge of the adatom upon adsorption.

The general correlation between the charge transfer and the electrostatic potential at the site is illustrated in Fig. 4c. However, the case of the bridging Ou–Ou site represents an obvious departure from the general trend. The electrostatic potential created by the surface at this site is not as negative as at the Ou site, but has instead an intermediate value, similar to the value obtained at the hollow Ce site, where gold adsors as Au$^0$. Still, the oxidation of gold when adsorbed at the bridging Ou–Ou site is apparent from the calculated Bader charge on Au ($+0.34\,|e|$) and the magnetic moment of $0.97\,\mu_B$ on a Ce ion at the surface. The electronic densities of states projected on the atoms involved in the adsorption at the Ce and at the Ou–Ou sites are compared in Fig. 5. The gold adatom on top of Ce retains the atom-like 6s$^1$ configuration (Au$^0$), and in this case the Ce 4f levels are all above the Fermi energy. However, when gold is adsorbed at the Ou–Ou site, one 4f level of a surface Ce clearly becomes occupied.

![Fig. 3](image1.png) The CeO$_2$ (111) surface with an Ou oxygen vacancy, (a) before and (b) after the adsorption of a gold atom on top of the vacancy site.

![Fig. 4](image2.png) Electrostatic potential above the (111) surface of ceria: (a) stoichiometric surface, (b) surface with an oxygen vacancy in Ou position. (The distance from the plane to the surface termination is 1.8 Å, which is an intermediate value for the adsorption distance of Au atoms at different sites.) (c) Correlation between the Bader charge of the gold adatom and the electrostatic potential created by the surface at the point of adsorption.

The reason why the gold adatom becomes oxidised when adsorbed at the bridging site, while it remains neutral at the Ce site, even when the electrostatic potential is similar in both cases, can be understood in terms of the difference in coordination. It is well known that Au$^+$ cations show a marked preference for bi-coordinated environments. For example,
Au(I) has two ligands in both AuCl (ref. 41) and AuBr (ref. 42), and we have recently shown, using DFT calculations, that Au+ dopants at the zirconia surface distort their local environment to achieve a quasi-linear coordination to two oxygen atoms. The arguments used to explain this behaviour can then be turned around to explain the oxidation of gold to Au+ in a bridge coordination: according to a model originally proposed by Orgel, a bi-coordinated gold atom tends to hybridise its 5d\textsuperscript{z2} orbital (taking the z axis along the direction of coordination) with its 6s orbital, forming two new orbitals: one mainly localised in the z direction, between the gold atom and the ligands, and one more localised in the xy plane, away from the ligand. This orbital arrangement would be favourable for an Au\textsuperscript{+} cation because only the latter hybrid orbital would be occupied, while the former, which is more energetic because of the repulsion from the ligand electrons, would be empty. In other words, an Au atom in a O\textsubscript{u–Ou} bridging position prefers to be oxidised to a 1\textsuperscript{+} state because that allows a spatial redistribution of the charge in a way that minimises the repulsion between the filled orbitals of the gold atoms and those of the ligands. This can occur to a certain extent even when the ligands are not forming an exactly linear arrangement, as in the case we are discussing, where the O\textsubscript{u–Au–Ou} angle is \( \sim 130^\circ \). Fig. 5b shows that, indeed, a significant amount of sd hybridisation takes place in the gold adatom at the O\textsubscript{u–Ou} bridge. The empty Au peak at \( \sim 2.2 \) eV above the Fermi levels is not of pure 6s character as in an ideal d\textsuperscript{10} ion, but instead has a significant 5d contribution, as expected from the arguments above.

4. Conclusion

We have shown that gold atoms at a ceria (111) surface can adopt several oxidation states, depending on the site of adsorption. The strongest adsorption sites are on top of the surface oxygen, and bridged between two surface oxygen atoms. Both cases involve charge transfer from the gold atom to one of the Ce cations at the surface, resulting in the electronic configurations Au\textsuperscript{+} and Ce\textsuperscript{3+}. The adsorption energies are close to \(-1\) eV (\( \pm 0.15 \) eV depending on the precise configuration and the position of the reduced cerium cation with respect to the adatom). Adsorption at other sites, including the hollow sites of the surface, and an O–Ce bridging site, is weaker and does not involve charge transfer. However, if adsorbed near an oxygen vacancy, the gold adatom adopts the electronic configuration of an Au\textsuperscript{−} (d\textsuperscript{10}s\textsuperscript{2}) ion, with a very strong adsorption (\(-2.41\) eV). The energetic data suggest that the ability of ceria surfaces to release oxygen can be dramatically increased by the presence of gold adatoms near the defect sites, which stabilize the vacancies by attracting electrons left behind by the removed oxygen. We also suggest that the occurrence and direction of electron donation is affected by the value of the electrostatic potential at the surface, which explains much of the variations in charge transfer from site to site. However, the oxidation of gold at the bridging site between two O atoms cannot be explained in these terms, and we argue that in this case the driving force for oxidation is the large energy splitting between two sd hybrid orbitals due to the interaction with the ligands.

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