Ideal, Defective, and Gold–Promoted Rutile TiO$_2$(110) Surfaces: Structures, Energies, Dynamics, and Thermodynamics from PBE+U

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Extensive first principles calculations are carried out to investigate gold-promoted TiO$_2$(110) surfaces in terms of structure optimizations, electronic structure analyses, *ab initio* thermodynamics calculations of surface phase diagrams, and *ab initio* molecular dynamics simulations. All computations rely on density functional theory in the generalized gradient approximation (PBE) and account for on-site Coulomb interactions via inclusion of a Hubbard correction, PBE+U, where U is computed from linear response theory. This approach is validated by investigating the interaction between TiO$_2$(110) surfaces and typical probe species (H, H$_2$O, CO). Relaxed structures and binding energies are compared to both data from the literature and plain PBE results, thus allowing the performance of the PBE+U approach for the specific purpose to be verified. The main focus of the study is on the properties of gold-promoted titania surfaces and their interactions with CO. Both PBE+U and PBE optimized structures of Au adatoms adsorbed on stoichiometric and reduced TiO$_2$ surfaces are computed, along with their electronic structure. The charge rearrangement induced by the adsorbates at the metal/oxide contact is also analyzed in detail and discussed. By performing PBE+U *ab initio* molecular dynamics simulations, it is demonstrated that the diffusion of Au adatoms on the stoichiometric surface is highly anisotropic. The metal atoms migrate either along the top of the bridging oxygen rows, or around the area between these rows, from one bridging position to the next along the [001] direction. No translational motion perpendicular to this direction is observed. Approximate *ab initio* thermodynamics predicts that under O–rich conditions, structures obtained by substituting a Ti$_{5c}$ atom with an Au atom are thermodynamically stable over a wide range of temperatures and pressures that are relevant to applications in the realm of catalysis. Finally, it is shown that TiO$_2$(110) surfaces containing positively charged Au ions activate molecular CO, whereas a single negatively charged Au$^{-4}$ species bound to an O vacancy only weakly interacts with CO. Despite this, the calculations predict that the reactivity of gold nanoparticles nucleated at O vacancies can be recovered for cluster sizes as small as Au$_2$.

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I. INTRODUCTION

Titania, TiO$_2$, is a metal oxide of both fundamental interest and technological importance. It is used in several key technologies including pigments, coatings, electronic devices, implants, gas sensors, photochemical reactions, and catalysis. One of the most important properties of titania is that it can be easily reduced (see e.g. Ref. 9 for a concise presentation), strongly affecting its chemical properties in general and its reactivity in particular. One way to reduce the TiO$_2$ surface is to remove surface oxygen atoms, thereby creating O vacancies. The removal of an O atom gives rise to two excess electrons and the appearance of new electronic states within the band gap at about 0.7 to 0.9 eV below the conduction band edge, thus creating an $F$–center. By this process, two substrate Ti$^{4+}$ ions change formally to a Ti$^{3+}$ oxidation state; see Ref. 10 for recent literature and a detailed picture of the (de–)localization dynamics of the excess electrons. Alternatively, the TiO$_2$ surface can be reduced by hydroxylation of surface O atoms via adsorption of hydrogen. The interaction of TiO$_2$ with water is an important process which has to be taken into account, since it occurs easily, even in well–controlled UHV experiments. The adsorption of water on TiO$_2$ has been investigated extensively, both experimentally and theoretically; in particular see Refs. 10,19 for the most recent reviews of this literature.

Most relevant to catalysis is the interaction of Au and CO with stoichiometric or reduced TiO$_2$ surfaces and, in particular, the interaction of titania–supported gold particles with CO molecules. A detailed understanding of the process of CO adsorption is required to best comprehend its wide variety of applications, such as CO oxidation at low temperature, the water gas shift reaction, and CO hydrogenation. In a recent paper, we investigated the interaction of CO with the stoichiometric TiO$_2$(110) surface using a combination of density functional theory (DFT) and post Hartree-Fock methods. For a single CO molecule in the (4 $\times$ 2) surface unit cell of our slab, we found that the upright position above the fivefold coordinated Ti sites, Ti$_{5c}$, remains the preferential adsorption geometry, even without enforcing symmetry. On the reduced titania surface, results from temperature–programmed desorption (TPD) experiments suggested that, at low coverages, CO adsorption occurs at non-adjacent Ti$_{5c}$ sites. These findings were supported by various calculations. However, earlier studies implicated bridge–bonded oxygen vacancies as adsorption sites for CO, a conclusion corroborated by some theoretical investigations as well.

The seminal work of Haruta and coworkers has...
shown that the low–temperature oxidation of molecular CO can be efficiently catalyzed by highly dispersed Au nanoparticles supported on TiO$_2$ surfaces. It is now recognized that gold nanoclusters, prepared in different ways and supported on various metal oxides, are able to catalyze a number of reactions, and that the size of the gold particles substantially affects the catalytic activity. The gold clusters should be smaller than about 5 nm for high catalytic activity to occur, suggesting the key importance of metal/support interfacial interactions on a nanometer scale. Extensive studies of the Au/TiO$_2$ system link the peculiar catalytic activity of gold nanoparticles on titania to several factors: high concentration of low–coordination sites, quantum size effects of two–layer Au islands, active perimeter sites of the nanoparticles, and charge transfer between the gold particles and the supporting oxide.

Over the past decade, DFT–based calculations have been extensively employed to study the interaction between gold and the TiO$_2$(110) surface. Most of the existing theoretical studies provide information on stable adsorption sites of Au on the stoichiometric and reduced titania studies, while less effort has been devoted to the study of the O–rich Au/TiO$_2$(110) system and the diffusion of Au adatoms on the stoichiometric and reduced TiO$_2$(110) surface. A wide variation in the lowest–energy positions of Au on titania are reported in the literature, which can be explained in part by considering that Au can diffuse rather easily on the stoichiometric surface. The potential energy surface (PES) of a single Au adatom deposited on the stoichiometric TiO$_2$(110) surface or adsorbed into a surface O vacancy has been explored using static calculations. It has been shown that Au migration on the stoichiometric surface is two–dimensional, with a relatively flat profile. The scenario where an Au atom is substituted for a surface Ti$_{5c}$ site, has been demonstrated that the Au atom is capable of weakening bonds of surface oxgens with the oxide.

Most of the density functional theory studies available in the literature dealing with defects and/or molecules adsorbed on titania substrates using reasonably sized supercells make use of local (LDA) or semilocal (GGA) functionals. Despite widespread use, such functionals are known to often (but not always) fail to predict qualitatively correct electronic structures for reduced transition metal oxides, due to the self–interaction error inherent in the functionals. To partially correct for the self–interaction error, different computational methods can be used: perturbative many–body theories such as “GW”, LDA plus dynamical mean field theory (DMFT), pseudo self–interaction–correction schemes (pSIC), LDA plus U, and other methods that rely on hybrid functionals. Recently, GGA+U approaches have been applied with promising results in studies of intrinsic electron transport in TiO$_2$ bulk and in the investigation of the charge (de–)localization dynamics induced by surface oxygen vacancies on the (110) surface.

The TiO$_2$(110) surfaces were modeled by four O– Ti$_2$O$_2$–O trilayer (4x2) supercell slabs separated by more than 10 Å of vacuous space normal to the surface. The bottom of the slab was passivated with pseu-
dohydrogen atoms of nuclear charge +4/3 and +2/3 in order to achieve well–converged results. This is our so–
called “standard setup” which has been previously care-
fully constructed by performing extensive tests on the
convergence of surface energies as well as hydrogen and
water adsorption energies, with respect to both the num-
ber of relaxed outermost trilayers and the thickness of the
slab itself (see tables and graphs in22 for detailed compar-
isons). The system size employed in our calculations,
corresponding to 208 atoms for the stoichiometric slab,
belongs to the largest systems used so far in order to
model the surface, in particular when it comes to per-
forming ab initio molecular dynamics. In order to fur-
ther check the convergence we optimized two five trilayer
slabs (one with an empty surface O vacancy and one with
an Au adatom at this vacancy) and confirmed that the
resulting spin density and excess charge localization is
the same as reported herein for our “standard setup”.

The gradient–corrected Perdew-Burke-Ernzerhof func-
tional (PBE) was employed to describe semilocal the
exchange–correlation effects. The spin–polarized Kohn-
Sham equations were solved in the plane wave / pseu-
dopotential framework using Vanderbilt’s ultrasoft pseu-
dopotential with a cutoff of 25 Ry using the Γ–point.
The Ti pseudopotential was constructed from an ionic
3d⁸ 4s² configuration and the 3s and 3p semicore elec-
trons were treated as fully valence states. It is well es-
stablished that adding a Hubbard U term greatly improves the quality of LDA or
GGAs in describing the electronic structure of both ox-
idized and reduced titania surfaces. Following our previous work11,17,19,60,63–65, we used a self–consistent linear
response formalism19,61 to compute the Hubbard term,
which turns out to be U = 4.2 eV for this particular
setup; the occupations of the d orbitals were calculated
using atomic–like wave function projectors. It will not
have escaped attention that our value of the U param-
eter is larger than that recently derived by Mattioli et
al.23 (i.e. U = 3.25 eV). This can be attributed to the
different d–orbitals used as projectors for the integration of the d–orbital occupation numbers. The U value
of 3.25 eV obtained in23 was derived using the d–orbital of
the neutral Ti atom as a projector, whereas our value,
U = 4.20 eV, is computed by using Ti⁺¹ as a reference,
which in our opinion more closely resembles the charge
state of Ti in the TiO₂(110) surface. At this point it
should be noted that we also obtained U = 3.20 eV when
using the d–orbital of the neutral Ti atom as the projector
instead, which is in agreement with the U value reported
in23. Similarly, performing the calculations of FeO Pick-
ett et al.22 showed that the calculated Hubbard energy
strongly depends on the choice of d–orbital. Using the d–
orbital of the neutral Fe atom they obtained U = 4.6 eV
whereas using the Fe⁺² dication yields a substantially
larger value of U = 7.8 eV. This is a well–known and
still poorly understood shortcoming of the U parameter
derivation procedures that use atomic–like d–orbitals as
projectors for the integration of the occupations of the
d–orbitals in solids, which, in turn, is an input for the
computation of the Hubbard correction to LDA/GGA density functionals. The static optimizations for the
different TiO₂(110) surface structures were carried out using the Quantum Espresso code. All structures were
relaxed by minimizing the atomic forces, where conver-
gence was assumed to have been achieved when the max-
imum component of the residual forces on the ions was
less than 0.02 eV/Å. Here, only the lowest trilayer atoms
were constrained to their equilibrium positions while all
other atoms were free to move during optimization. All
ab initio molecular dynamics (AIMD) simulations were
carried out using the same spin–polarized PBE+U ap-
proach, together with the Car–Parrinello propagation scheme using a fictitious electron mass of 700 a.u. and
a time step of 0.145 fs. Our in-house modified version of the CPMD code was used for this purpose.

The adsorption energy $E_{\text{ads}}^H$ per H atom on the stoichiometric TiO₂(110) surface is computed from

$$E_{\text{ads}}^H = \frac{1}{N_H} \left[ E_{\text{tot}}^{\text{H-ads}}(N_H) - \left( E_{\text{tot}}^{\text{slab-TiO}_2} + \frac{N_H}{2} E_{\text{H}_2} \right) \right],$$

where $E_{\text{tot}}^{\text{H-ads}}(N_H)$ is the total energy of the slab satu-
rated with $N_H$ H adatoms; here $E_{\text{tot}}^{\text{slab-TiO}_2}$ is the energy
of the stoichiometric slab, which we take as a reference, and $E_{\text{H}_2} / 2$ is the energy of a H₂ molecule. When
dealing with CO, H₂O, and Au, the adsorption energies on stoichiometric and reduced TiO₂(110) surfaces were
calculated according to

$$E_{\text{ads}} = E_{\text{tot}}^{\text{sub+X}} - \left( E_{\text{tot}}^{\text{sub}} + E_X \right),$$

where $E_{\text{tot}}^{\text{sub+X}}$, $E_{\text{tot}}^{\text{sub}}$, and $E_X$ are the total energies of the combined system, the (Au/)TiO₂(110) surface in a
certain oxidation state, and the isolated X adsorbate, re-
spectively. The adsorption energies were calculated with
and without inclusion of the Hubbard U term correction to the standard density functional, i.e. using the plain
PBE and the PBE+U approaches. The O-vacancy for-
mation energy was calculated using

$$E_{\text{V}}^0 = E_{\text{tot}}^{\text{O-}} - \left( E_{\text{tot}}^{\text{slab-TiO}_2} - \frac{1}{2} E_{\text{O}_2} \right),$$

where $E_{\text{tot}}^{\text{slab}}$ and $E_{\text{O}_2}$ represent the total energy of the
defective system and of the O atom, respectively. Because (semi)local functionals are known to overbind
molecular O₂, the total energy of the O atom was ad-
justed in the manner of our previous work2.2

In order to analyze the thermodynamic stability of our
different structures in the presence of H adatoms, we em-
ploy the formalism of approximate ab initio thermody-
namic37,101 by assuming that the surfaces can exchange
H atoms with a surrounding gas phase. Assuming ther-
modynamic equilibrium, the most stable surface compos-
ation at a given temperature $T$ and pressure $p$ is given by
the minimum of the surface Gibbs free energy. Since
we are only interested in the relative stabilities of surface structures, we directly compute the differences in the surface Gibbs free energies $\Delta G_{\text{ads}}(T, p)$ between the defective and the ideal surface according to

$$
\Delta G_{\text{ads}}(T, p) = \frac{1}{A} \left[ E_{\text{H-ads}}^H(N_H) - \left( E_{\text{slab-TiO}_2} + \Delta N_H \mu_H(T, p) \right) \right],
$$

where $A$ is the surface area, $\Delta N_H$ is the difference in the number of H atoms between the two surfaces, and $\mu_H(T, p)$ is the chemical potential representing the Gibbs free energy of the gas phase with which the H atoms are exchanged. Assuming that all differences in entropy and volume contributions in $\Delta G_{\text{ads}}(T, p)$ are negligible, the Gibbs free energies are approximated by their respective total energies of our DFT slab calculations as usual 99–101.

The upper bound for the chemical potential $\mu_H(T, p)$ is given by the total energy of its most stable elemental phase, that is, molecular hydrogen ($\frac{1}{2}E_H^{\text{2h}}$). This upper bound is taken as the zero of our energy scale by using $\Delta \mu_H = \mu_H(T, p) - \frac{1}{2}E_H^{\text{2h}}$.

In a similar way, the effect of temperature and pressure on the relative stability of the Au/TiO$_2$(110) surface structures is studied by employing the formalism of approximate ab initio thermodynamics 99–101. The free energy of formation of the Au/TiO$_2$(110) surface structures $\Delta G_{\text{ads}}(T, p)$ is assumed to depend on the temperature and pressure only via the oxygen chemical potential $\mu_O(T, p)$ given by

$$
\mu_O(T, p) = \mu_O(T, p^0) + \frac{1}{2}kT \ln \left( \frac{p}{p^0} \right),
$$

Equation (5) represents the thermodynamics reservoir of the O$_2$ environment that is in contact with the surface under consideration. The free energy differences will be calculated as a function of $\Delta \mu_O(T, P) = \mu_O(T, p) - \mu_O(T = 0 \text{ K}, p^0)$, corresponding to changes of the oxygen chemical potential with respect to a zero reference state. The latter is set to the total energy of the O atom at $T = 0 \text{ K}, \mu_O(T = 0 \text{ K}, p^0) = 1/2E_O^{\text{2h}} = 0$. Assuming thermodynamic equilibrium of the surfaces with an O$_2$ gas phase, the chemical potential can be converted into a pressure scale for different temperatures by using experimental thermochemical reference data or by applying the ideal gas equation 99–101. Vibrational and rotational entropic contributions to $\mu_O(T, p)$ are included by means of thermodynamic tables as described in Ref. 99. Under these assumptions and neglecting entropic contributions of the solids involved, the free energy of formation as a function of pressure and temperature assumes the expression

$$
\Delta G_{\text{ads}}(T, p) = \frac{1}{A} \left[ E_{\text{sub+X}}^{\text{bulk}} - E_{\text{slab-TiO}_2} + N_V \mu_O(T, p) + N_T \left( E_{\text{TiO}_2}^{\text{bulk}} - 2\mu_O(T, p) - \mu_{\text{Au}} \right) \right],
$$

where $E_{\text{TiO}_2}^{\text{bulk}}$ is the energy of a formula unit of the TiO$_2$ bulk phase. The quantities $N_V$ and $N_T$ represent the number of O or Ti vacancies that are present in the structure under consideration. Therefore, the energy cost for the formation of surface defects is taken into account in Eq. (6) via the chemical potential of O atoms and of bulk TiO$_2$. Finally, the chemical potential of Au, $\mu_{\text{Au}}$, is set to be the total energy per atom of the bulk Au crystal. The upper bound for the chemical potential $\mu_O$ is given by the total energy of its most stable elemental phase, that is, molecular oxygen ($\frac{1}{2}E_O^{\text{2h}}$). This upper bound is used to define $\Delta \mu_O(T, P) = \mu_O - \frac{1}{2}E_O^{\text{2h}}$. A lower bound for $\Delta \mu_O$ is given by minus half of the formation energy of bulk TiO$_2$, i.e., $E_{\text{TiO}_2} = E_{\text{bulk}}^{\text{TiO}_2} + E_{\text{Ti}}^{\text{bulk}} - E_{\text{bulk}}^{\text{Ti}}$, for which we have taken the theoretical value of 4.8 eV from our PBE calculations; here $E_{\text{bulk}}^{\text{TiO}_2}$ and $E_{\text{bulk}}^{\text{Ti}}$ are the energies of one bulk unit cell of TiO$_2$ and metallic Ti, respectively 99–101.

Finally, the bonding charge density has been evaluated using the expression

$$
\Delta \rho(\vec{r}) = \rho_{\text{sub+X}} - (\rho_{\text{sub}} + \rho_X)
$$

where the $\rho$’s are the respective valence electronic charge densities at position $\vec{r}$ in space.

### III. SMALL MOLECULES ON TITANIA: REFERENCE CALCULATIONS USING PBE+U

Computationally efficient implementations of DFT based on local/semilocal LDA/GGA density functionals predict rather delocalized defect levels for excess electrons in the case of reduced transition metal oxides in general, and for titania in particular. Thus, more sophisticated techniques such as hybrid functionals or GGA+U approaches are necessary to properly account for the strong correlation effects of these $d$-electrons, resulting in localization of the excess charge on $3d$-orbitals of reduced Ti atoms. However, before using PBE+U to investigate the properties of gold on titania, it is necessary to confirm that this approach does not destroy the agreement between previously reported plain PBE results (mainly optimized structures and relative energies) and experimental observations. The purpose of this section is therefore twofold: first, to validate the PBE+U approach using a test set that probes the physics and chemistry of titania surfaces interacting with adspecies relevant to heterogeneous catalysis; and, second, to check how PBE+U performs compared to plain PBE investigations for the very same systems. Thus, the interaction of H, H$_2$O, and CO with the TiO$_2$(110) substrate is investigated in the following section using the PBE+U approach where a large set of both experimental and previous theoretical data are available.

Many theoretical and experimental studies have been devoted to understanding the interaction between hydrogen atoms 9,15–18,102 or water 9,10,19–36 and the TiO$_2$(110) surface. In experiments, hydrogen atoms, when adsorbed
on TiO$_2$(110), stick to the bridging oxygens and a maximum surface saturation limit of ~0.7 ML is observed\textsuperscript{18}. These findings have been confirmed on purely theoretical grounds within the framework of standard GGA calculations using the PBE functional\textsuperscript{9}. In-depth \textit{ab initio} thermodynamics considerations reveal a maximum saturation level of hydrogen on this oxide surface of about 60–70\%, in excellent agreement with the above-mentioned experimental observations. Adsorption of hydrogen on the stoichiometric surface results in its reduction by introducing one electron per adsorbed H atom into the substrate.

We first consider the interaction of H with the stoichiometric TiO$_2$(110) surface. The hydroxylated surface has been investigated for a wide range of H coverages using both PBE+U and PBE. In agreement with both plain PBE calculations and experimental results, we find that H atoms preferentially adsorb on top of surface O$_b$ atoms of the stoichiometric titania surface, leading to the formation of OH groups with O–H bond lengths of ~1 Å. In addition, our PBE+U calculations predict that one electron per H atom adsorbed on the surface is transferred to the substrate, leading to the formation of Ti$^{3+}$ ions (see Table \textbf{I}). The newly-formed OH groups are found to be tilted by about 20–50\(^\circ\) in opposite [1 $\bar{1}$ 0] and [1 0 1] directions, and at room temperature OH groups will be fully disordered with respect to their axes because of the tiny barrier that must be overcome in order to flip their orientation.

At all coverages, the PBE+U adsorption energies are found to be significantly lower, by about $-0.3$ to $-0.6$ eV, compared to the PBE data in Table \textbf{I}. However, the same stability trend obtained by employing the PBE+U functional is obtained using the standard PBE functional, i.e. a decrease of the adsorption energy with increasing coverage. Nevertheless, even at full monolayer coverage, the adsorption energy per atom is still significant and must be overcome in order to flip their orientation.

It is well-known that the investigated surface contains a significant number of oxygen vacancies (\~{}5\%), not just in ill-defined industrial situations, but even under well-controlled experimental conditions\textsuperscript{2}. Therefore, the investigation of the adsorption of water molecules on the reduced TiO$_2$(110) surface is of great importance in the frame of addressing the fundamental issue of dissociative \textit{versus} molecular adsorption modes\textsuperscript{9,10,19,21}. We thus consider the interaction between H$_2$O and the TiO$_2$ surface. We have performed systematic PBE+U and PBE calculations of H$_2$O adsorbed on the reduced TiO$_2$ surface, considering a titania surface containing a single V$_O$ vacancy; this greatly extends our recent comprehensive work\textsuperscript{10} concerning water on the stoichiometric surface using plain PBE.

The specific adsorption configurations for a water molecule on the reduced surface, which we consider in

| Configuration | $E_{\text{ads}}$(PBE+U) | Ti$^{3+}$ | $E_{\text{ads}}$(PBE) |
|---------------|-------------------------|----------|---------------------|
| 1H            | -0.91                   | 1        | -0.56               |
| 2H            | -0.86                   | 2        | -0.40               |
| 4H            | -0.77                   | 4        | -0.24               |
| 6H            | -0.68                   | 6        | -0.15               |
| 8H            | -0.37                   | 8        | -0.04               |

TABLE I: Adsorption energies $E_{\text{ads}}$ (in eV) per H atom for adsorption of hydrogen at different coverages as indicated. In the second column the number of reduced Ti$^{3+}$ ions which are present in the substrate is reported.

\[ \Delta G_{\text{ads}}(T, p) \] for H adsorption on TiO$_2$(110) stoichiometric surfaces with different hydrogen coverages as a function of the hydrogen chemical potential $\Delta \mu _H$. Conversion to hydrogen partial pressures $p_H$ (upper axis) has been carried out at $T=400$ K (see text). The red and blue lines represent the PBE+U and PBE results, respectively.

\[ \Delta G_{\text{ads}}(T, p) \] for H adsorption on TiO$_2$(110) stoichiometric surfaces with different hydrogen coverages as a function of the hydrogen chemical potential $\Delta \mu _H$. Conversion to hydrogen partial pressures $p_H$ (upper axis) has been carried out at $T=400$ K (see text). The red and blue lines represent the PBE+U and PBE results, respectively.

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\[ \Delta G_{\text{ads}}(T, p) \] for H adsorption on TiO$_2$(110) stoichiometric surfaces with different hydrogen coverages as a function of the hydrogen chemical potential $\Delta \mu _H$. Conversion to hydrogen partial pressures $p_H$ (upper axis) has been carried out at $T=400$ K (see text). The red and blue lines represent the PBE+U and PBE results, respectively.
The Ti\(_{5c}\) surface sites are labeled in relation to the V\(_0\) vacancy, where site Ti0 denotes a nearest-neighbor Ti\(_{5c}\) atom and sites Ti1 and Ti2 are the second and third nearest-neighbour Ti\(_{5c}\) sites parallel to the O\(_b\) row containing the V\(_0\) site; see panel (a) of Fig. [2]. In agreement with experimental data, we find that on the reduced surface, H\(_2\)O molecules prefer to dissociatively adsorb at V\(_0\) vacancy sites, leading to a configuration with two surface OH groups as shown in panel (b) of Fig. [2]. We therefore end up with a stoichiometric titania surface with two H atoms adsorbed on two surface O\(_b\) atoms. Once the water molecule dissociates at the oxygen defect through proton transfer to an adjacent O\(_b\) atom, the PBE+U (PBE) adsorption energy is −1.61 eV (−1.18 eV). A projected PDOS analysis reveals that upon dissociation of water at the V\(_0\) site, two second-layer Ti\(^{3+}\) ions are present in the substrate. This value of \(E_{\text{ads}}\) is ∼0.4 eV lower than the corresponding plain PBE value and previously reported values,\(^{35,36,103}\) which are between −0.94 and −1.1 eV. The energy value derived from a water desorption peak at 520 K in TDS experiments,\(^{104}\) using the simple Redhead formula,\(^{105}\) is about −1.4 eV, which is between the PBE+U and PBE values. However, the estimation of desorption energies using the Redhead formula can be biased by as much as 25%, which implies that both values must be considered to be consistent with experiment.

We now turn our attention to the adsorption and dissociation of water at Ti\(_{5c}\) sites next to V\(_0\). We anticipate that, as observed in the case of H\(_2\)O dissociatively adsorbed at the V\(_0\) site, the interaction between water and the Ti\(_{5c}\) sites does not further reduce the metal oxide support. All PBE+U calculations predict the presence of two reduced Ti\(^{3+}\) ions before and after the adsorption of H\(_2\)O at Ti\(_{5c}\) sites. Water molecules can be adsorbed either dissociatively (labeled as “D”) or molecularly ("M") at the various Ti\(_{5c}\) sites (i.e. Ti0, Ti1, and Ti2) next to V\(_0\) (see Fig. [2]). When H\(_2\)O dissociates at a Ti\(_{5c}\) site, the resulting configuration contains an OH group bonded to a Ti\(_{5c}\) atom and an H atom bonded to a nearest-neighbor O atom of the Ti\(_{5c}\) in the [110] direction. We have considered two different topologies: first, where the H atom coming from the dissociated water molecule binds to an O atom belonging to the O\(_b\) row in which the V\(_0\) vacancy site is present (labeled configuration “A”); and second, with the H atom bonded to O atoms belonging to an adjacent O\(_b\) row parallel to the O\(_b\) row that hosts V\(_0\) (configuration “B”). See Table [II] for the corresponding adsorption energies.

Our PBE+U and PBE calculations suggest that, in the presence of an oxygen vacancy, water molecules adsorb dissociatively or molecularly at Ti\(_{5c}\) sites with \(E_{\text{ads}}\) in the range of −0.45 to −0.92 eV. Once the water molecule dissociates at a Ti\(_{5c}\) site, it forms a pair of terminal hydroxyls. Therefore, in the dissociative case, we always end up with an OH group bonded to a Ti\(_{5c}\) site and a protonic H atom transferred to an adjacent O\(_b\) atom, the O\(_b\) atom belonging either to the O\(_b\) row that contains V\(_0\), or to the adjacent one that contains no oxygen vacancy. As shown in Table [II] the most stable dissociative configurations are those with the protonic H atom transferred to an O\(_b\) atom of an O\(_b\) row parallel to the row featuring the V\(_0\) site (configurations denoted “DB”) in Table [II] and Fig. [2]. The PBE+U/PBE calculations show that protons prefer to bind to O\(_b\) atoms belonging to an O\(_b\) row in absence of V\(_0\) sites, with \(E_{\text{ads}}\) ranging from −0.87 to −0.95 eV.

Otherwise, if we consider the case where, after water dissociation at a Ti\(_{5c}\) site, a proton transfers to an O\(_b\) atom belonging to an O\(_b\) row that includes a V\(_0\) site (configurations denoted “DA” in Table [II] and Fig. [2]), our calculations provide adsorption energies in the range of −0.45 to −0.71 eV; the same trend is observed with or without the inclusion of a Hubbard U term in the calculations. We note that the structure with an OH group adsorbed at a Ti\(_{5c}\) site and an H placed right at the V\(_0\) vacancy is unstable; the adsorption energy of this configuration \(E_{\text{ads}}\) is positive by 2.27 eV.

Our results show that on the reduced TiO\(_2\)(110) surface, water prefers to adsorb dissociatively onto Ti\(_{5c}\) sites. Once water molecules are molecularly adsorbed on the reduced surface, the binding energy of the surface is about 0.1 eV higher than it is when water is dissociated on the same substrate. These findings are in agreement with previous studies of H\(_2\)O interaction with the stoichiometric TiO\(_2\)(110) surface. However, as shown based on carefully converged calculations,\(^{106}\) molecular and dissociated configurations become essentially energetically degenerate at very low coverages, which explains why some studies favor molecular adsorption whereas others yield the dissociated state as the lowest energy configuration in this regime.\(^{106}\) Most experimental works, except a recent one\(^{107}\) claiming mixed adsorption, indicate molecular adsorption only. This gives rise to the well–known discrepancy between theoretical predictions and experimental results in providing a consistent and comprehensive picture of water adsorption on titanium dioxide surfaces, in particular at low coverages.

Last but not least, we focus on the interaction between CO and the TiO\(_2\)(110) surface. It is well known that, on the stoichiometric TiO\(_2\)(110) surface, the CO molecule adsorbs onto Ti\(_{5c}\) sites, thus forming Ti–C bonds. Because van der Waals dispersion interactions and non-

![Table II: Adsorption energies \(E_{\text{ads}}\) (in eV) in the case of adsorption of water on the reduced surface for PBE+U and plain PBE reported in parentheses; see Fig. [2] for labeling.](image-url)
FIG. 2: Ball and stick models of relevant configurations (see text) for an H$_2$O molecule adsorbed either molecularly (“M”) or dissociatively (“D”) in two configurations (“A” and “B”) on TiO$_2$(110) surfaces (top view) at V$_O$, Ti0, Ti1, and Ti2 sites (see panel (a) for site labeling) obtained using the PBE+U approach. Red, blue, violet, and yellow spheres are substrate O, Ti, water O, and H atoms, respectively, and the oxygen vacancy site $V_O$ is highlighted using a green sphere.

TABLE III: Adsorption energies $E_{\text{ads}}$ (in eV) of a CO molecule adsorbed on the reduced rutile TiO$_2$(110) surface at different sites, labeled according to Fig. 3. In the second column, the number of reduced Ti$^{3+}$ ions present in the substrate is reported.

| Configuration | $E_{\text{ads}}$(PBE+U) | Ti$^{3+}$ | $E_{\text{ads}}$(PBE) |
|---------------|--------------------------|-----------|----------------------|
| CO@V$_O$      | $-0.32$                  | 2         | $-0.29$              |
| CO@Ti0        | $-0.22$                  | 2         | $-0.28$              |
| CO@Ti1        | $-0.29$                  | 2         | $-0.30$              |
| CO@Ti2        | $-0.33$                  | 2         | $-0.29$              |

local electron correlations significantly influence this type of bonding, we have previously investigated the interaction of CO with the stoichiometric TiO$_2$(110) surface using a combination of DFT and post Hartree-Fock (“SCS-MP2”) methods. The CO binding energy has been found to vary significantly with coverage and increases upon reaching the saturation limit. The SCS-MP2 $E_{\text{ads}}$ computed values are $-0.20$ eV for the full saturated surface and $-0.36$ eV for a single CO molecule adsorbed on the surface. The PBE adsorption energy of a single CO molecule, $-0.32$ eV, is close to the SCS-MP2 value of $-0.36$ eV, and both energies are in accord with the experimental value obtained by means of thermal desorption spectroscopy. This demonstrates that PBE as such is able to describe the interaction of CO with the ideal (110) rutile surface in the limit of low coverages, which remains unaltered when using PBE+U, which gives $-0.31$ eV for the adsorption energy.

FIG. 3: Ball and stick model of the TiO$_2$(110) surface (top view), with site labeling. Red and blue spheres are O and Ti atoms, respectively, and the oxygen vacancy site, V$_O$, within the bridging oxygen row, O$_b$, is highlighted using a green sphere.

We now turn our attention to CO adsorbed onto the O vacancy site, V$_O$, as well as on the fivefold coordinated surface sites, Ti$^5c$, at various distances from the vacancy. Note that the Ti$^5c$ site belongs to the Ti row next to the bridging O$_b$ row containing V$_O$ (see Fig. 3).
In each case, the CO molecule is placed perpendicular to the substrate, with the carbon atom pointing toward the surface. All the structures are fully relaxed according to our aforementioned convergence criterion. The computed adsorption energies ($E_{\text{ads}}$) are compiled in Table II. Interestingly, we do not see a significant variation in the adsorption energies computed for different structures. The PBE+U (PBE) adsorption energy for the CO molecule adsorbed at the surface O$_0$ vacancy site is $-0.32$ eV (−0.29 eV). CO adsorption at sites Ti1 and Ti2 results in adsorption energies of −0.29 eV (−0.30 eV) and −0.33 eV (−0.29 eV), respectively (see Fig. 3 for site labeling scheme). The computed values of $E_{\text{ads}}$ are in qualitative agreement with previous studies. We note that these values are close to those obtained when CO is adsorbed at the V$_O$ vacancy site (−0.32 eV) and on the stoichiometric surface, i.e. −0.31 eV (−0.32 eV) for PBE+U (PBE). When adsorbed at site Ti0, the adsorption energy of the CO molecule, computed with PBE+U, results in a distinctly higher value for $E_{\text{ads}}$ of −0.22 eV in agreement with Ref. 108, while the corresponding PBE value is −0.28 eV, comparable to the adsorption at sites Ti1 and Ti2. Our PBE+U results therefore confirm previous findings that CO molecules weakly interact with the reduced TiO$_2$(110) oxide surface, $E_{\text{ads}}$ being of the order of about −0.3 eV (see Refs. 39, 107, 108). The calculations indicate that CO adsorbs at both V$_O$ vacancies and Ti$_{5c}$ sites, but while PBE calculations give similar energy values for CO adsorption at V$_O$ vacancies and at Ti0, Ti1, and Ti2 sites, the inclusion of a Hubbard U term suggests that the adsorption of CO at Ti0 sites, the sites facing the V$_O$ vacancy, is discouraged. In this case, the adsorption energy $E_{\text{ads}}$ is found to be $\sim 0.1$ eV higher when compared to the adsorption energy values at sites Ti1 and Ti2. Upon CO adsorption on the reduced surface, the charge redistribution that results from attaching the molecule does not further reduce the oxide support: the PBE+U calculations yield two Ti$^{3+}$ ions before and after adsorption, which results in an insignificant change in the adsorption energies when switching from PBE to PBE+U calculations. This behavior is confirmed by the computed electronic density of states (DOS). In Fig. 4 we depict the electronic DOS and the bonding charge $\Delta \rho(z)$ at an isovalue of ±0.06 $e$/Å$^3$ where electron accumulation and depletion are represented by red and blue areas, respectively. The right panel shows the total DOS and atom-resolved projected DOS (PDOS) as indicated; here, energy values are with respect to the Fermi level, which is marked by a solid vertical line.

In conclusion, this detailed assessment convincingly demonstrates that although similar trends are observed in the adsorption energies with or without the inclusion of a Hubbard U correction, the PBE+U method is seen to significantly improve the description of the electronic structure whenever reduction occurs. In particular, the localization of excess charge on the titania substrate induced by O vacancies (F-centers) or upon H atom adsorption on bridging O atoms (hydroxylation), is correctly predicted by the PBE+U approach. Clearly, an adequate description of the electronic structure of such TiO$_2$(110) surfaces is crucial when dealing with metal-promoted oxide surfaces in the realm of catalysis.
IV. GOLD–PROMOTED TITANIA: ELECTRONIC STRUCTURE, DYNAMICS, AND THERMODYNAMICS FROM PBE+U

A. Au adatom adsorption on the stoichiometric TiO$_2$(110) surface

Having shown that the PBE+U formalism performs well for a set of reference calculations on the adsorption of H, H$_2$O, and CO on stoichiometric and reduced TiO$_2$(110) surfaces, and that it significantly improves the description of reduced titania surfaces, we now progress to investigating the interactions between gold and TiO$_2$(110) surfaces. The adsorption or substitution of gold induces strong charge rearrangements at the Au/oxide contact, which affects the electronic structure. Of particular interest in the realms of metal/support interactions and heterogeneous catalysis is the oxidation state of Au adatoms, which is determined by the site where the metal atom is adsorbed, as well as by the stoichiometry of the supporting oxide. As in previous GGA studies, two stable adsorption sites of a single Au adatom on the stoichiometric TiO$_2$(110) surface have been identified, the two structures differing by only $\sim 0.1$ eV in energy. The most stable adsorption site for an Au adatom deposited on this titania surface is a bridge site between an O$_b$ and a Ti$_{sc}$ atom as depicted in the central panel of Fig. 5 (B). The computed PBE+U (PBE) adsorption energy and the Au–O / Au–Ti bond lengths are $-0.58$ eV ($-0.41$ eV) and 2.30 (2.39) / 2.79 Å (2.88 Å ) respectively, in agreement with previous studies based on standard GGA calculations; see Table IV for a summary.

The bonding charge density analysis reveals that 0.11 $|e|$ are transferred from the metal atom to the oxide substrate, thus indicating a very weak oxidation of Au. The excess charge in the substrate is mostly localized around the O$_b$ bonded to the Au adatom. This value of the charge transfer has been obtained by integrating the bonding charge density on planes parallel to the surface from the center of the vacuum region to the center of the O–Au–Ti bond (see left panel of Fig. 5 (B)). As demonstrated by the PDOS analysis shown in the right panel of Fig. 5 (B), in this configuration all the Ti ions belonging to the substrate preserve their formal oxidation state Ti$^{4+}$.

The second identified stable site is a top site (see central panel of Fig. 5 (C)), where the Au adatom is adsorbed on top of an O$_b$ atom. The corresponding PBE+U (PBE) adsorption energy and the Au–O bond length are $-0.48$ eV ($-0.29$ eV) and 2.00 Å (2.16 Å ), akin to previous GGA studies. Again, a net charge transfer from metal to surface, leading to a positively charged Au$^{4+}$ ion, is observed. In this case, however, the magnitude of the charge transfer, 0.35 $|e|$, is more significant, i.e. three times larger than in the previous case. The excess charge in the substrate is now mostly localized around the surface O$_b$ atom bound to the Au$^{4+}$ and a second–layer Ti ion which reduces Ti$^{4+}$ $\rightarrow$ Ti$^{3+}$ (see Fig. 5 (C)). The reduced Ti$^{3+}$ ion is located at a site adjacent to the Au$^{5+}$ adatom in the second subsurface layer under the Ti$_{sc}$. These findings are corroborated by the computed DOS plotted in Fig. 5 (C), which displays two features in the band gap. The projected DOS analysis reveals that the filled state below the Fermi level and closest to the valence band results from the charge transferred from the metal to the substrate being localized on a second–layer reduced Ti$^{3+}$ atom. The unoccupied level closest to the conduction band is instead related to the Au–O bonding. The 6s levels of Au are partially empty and are located above the Fermi level, leading to the Au oxidation.

In summary, the PBE+U calculations predict two lowest–energy configurations for Au adsorption on the stoichiometric TiO$_2$(110) surface: a bridge site with the Au adatom adsorbed between O$_b$ and Ti$_{sc}$ atoms and a top site with the Au adatom adsorbed on top of an O$_b$ atom. Once adsorbed at the bridge site, a very weak oxidation of the Au adatom is observed. On the other hand, the adsorption process of Au on top of an O$_b$ atom induces a net charge transfer from the adsorbate to the substrate, leading to the formation of a distinctly positively charged Au$^{5+}$ species where about a third of an electron is transferred from the metal atom to the oxide substrate. A qualitatively similar scenario has been observed in recent studies of the related Au/CeO$_2$ system. However, unlike titania, with ceria the charge transfer involved in the adsorption of Au on the stoichiometric oxide surface always leads to the reduction of a substrate Ce ion. In addition, the fact that the excess charge $\delta$–, stemming from Au in the present case, localizes on a second–layer Ti ion is in line with our recent findings on reduced titania surfaces.
FIG. 5: Electronic structure analyses (based on the PBE+U approach) of an Au adatom (B) supported by the stoichiometric TiO$_2$(110) surface in the bridge position, (C) supported by the stoichiometric TiO$_2$(110) surface in the top position, (D) adsorbed on a surface V$_O$ vacancy on the TiO$_2$(110) surface, and (E) substituting a surface Ti$_{5c}$ atom in the presence of a surface V$_O$ vacancy in a bridging position on the TiO$_2$(110) surface (see Fig. 9). Left panels represent the bonding charge $\delta \rho (z)$ integrated over planes perpendicular to the surface and plotted as a function of the height from the surface. Central panels display the bonding charge $\Delta \rho(\vec{r})$ at an isovalue of $\pm 0.06$ $|e|/\AA^3$ where electron accumulation and depletion are represented by red and blue areas, respectively. Right panels show the total DOS and atom resolved projected DOS (PDOS) as indicated, where energy values are with respect to the Fermi level, which is marked by a solid vertical line.
B. Au adatom diffusion on the stoichiometric 
TiO$_2$(110) surface

Several previous theoretical studies explored the PES of a single Au adatom deposited on the stoichiometric TiO$_2$(110) surface or adsorbed onto a V$_0$ vacancy site using static calculations, including nudged elastic band (NEB) mappings. A key finding of these investigations is that the PES for Au migration is quite flat, with low energy barriers. This indicates that Au might diffuse rather easily on the stoichiometric surface. The estimated values of the energy barriers agree with the experimental observation of facile Au diffusion on the oxide surface even at temperatures as low as 140 K, as well as the estimates for the binding energy of 0.5 eV and small migration barriers of 0.07 eV (see Refs. 12,50).

Inspired by these findings, we decided to perform explicit dynamics using unconstrained \textit{ab initio} molecular dynamics in order to reveal the mechanism of diffusion of an Au adatom on the stoichiometric TiO$_2$(110) surface. In order to probe the dynamics more efficiently, the temperature of the simulations was set to $T = 900$ K using the Car-Parrinello scheme to propagate the system consistently using the PBE+$U$ functional. The selected temperature is far above ambient yet sufficiently low so as to not decompose the surface. Thus, the phonon dynamics is accelerated and the sampling of the PES is enhanced on the picosecond AIMD time scale. As starting configurations for the AIMD simulations, we employed one structure in which the Au adatom is adsorbed on top of an O$_b$ atom (see Fig. 5(C) and Table IV) and a second structure where it is adsorbed in a bridge position between an O$_b$ atom and a Ti$_{5c}$ atom (see Fig. 5(B) and Table IV). After equilibrating the structures at 300 K for several picoseconds, the system was heated to the target temperature of 900 K for the present analysis.

Let us first consider the scenario with the Au adatom adsorbed on top of a surface O$_b$ atom, labeled as site O1 in Fig. 6 where the diffusion path of the Au adatom on the stoichiometric TiO$_2$(110) surface is visualized. During the simulation, the Au adatom diffuses in the [001] direction along the row of bridging oxygen atoms, O$_b$. Adatom diffusion is mediated by the Au atom hopping between nearest-neighbor oxygen atoms. As demonstrated in Fig. 6, the Au adatom is originally bonded to the surface bridging O1 atom with an Au–O1 bond length of $\sim 2$ Å (red line); it diffuses along the O$_b$ row and after $\sim 0.75$ ps reaches a configuration where it is equidistant between the O1 and O2 atoms. Then it jumps on top of the row’s next atom, the O2 site, where the Au–O2 bond length is $\sim 2$ Å (green line). The Au diffusion proceeds along the O$_b$ row and at about 2 ps the Au adatom is shared between O2 and the next site, O3 (blue line), until it jumps on top of O3 forming a bond of $\sim 2$ Å.

The charge localization and charge hopping dynamics along the adatom migration path is monitored by computing, as a function of time, the occupation matrix of each Ti $d$–$\alpha$ and $d$–$\beta$ spin orbital along the trajectory (same analysis as in94). As shown in Fig. 8 the excess charge donated by the Au atom to the substrate is initially localized on the second–layer Ti2 site but transfers from there to site Ti3 on the sub–picosecond time scale (at $t \sim 0.75$ ps). As seen by comparing Fig. 8 to Fig. 6 one observes that $t \sim 0.75$ ps corresponds exactly to the jump of Au from the O1 to the O2 site. A qualitatively similar scenario happens at about 2 ps which corresponds to the next hopping event of the Au atom from site O2 to O3. Thus, the motion of the surface gold adatom along the row of bridging oxygen atoms, O$_b$, appears to be fully correlated with the localization and hopping dynamics of the excess charge injected into the oxide support in the second layer of Ti atoms.

This dynamical scenario is distinctly different from what has been found recently for the excess charge induced by oxygen vacancies V$_O$ in the bridging row on the same substrate. In the presence of gold adatoms, the present simulations suggest a more localized configuration for the excess electron. This localized electron appears to preferentially populate sites in the vicinity of the Au atom and to closely follow the motion of the oxidized adatom. Another interesting phenomenon observed during the simulation is the absence of excess charge on the substrate at about 1.5 ps. Computing the spin density close to $t = 1.5$ ps we observe that the charge localized at second–layer Ti sites disappears from the substrate and goes to the Au adatom, where it sits for a fraction of a picosecond before returning to the substrate and occupying the Ti3 site. As observed in our previous work, the excess charge populating specific second–layer Ti sites and coming from the Au adatom adsorbed on top of O$_b$ atoms migrates easily by phonon–assisted (thermally activated) hopping to other Ti sites.

Next we consider the situation where the Au adatom is initially adsorbed at a bridge position between an O$_b$ atom and a Ti$_{5c}$ atom (see Fig. 7). There it forms two bonds with the O1 and Ti1 atoms, with Au–O1 and Au–Ti1 bond lengths of $\sim 2.3$ Å (red line) and $\sim 2.8$ Å, respectively. Also in this case, the gold atom originally bonded to the O1 and Ti1 atoms is found to diffuse exclusively along the [001] direction. Now, however, the gold atom hops between pairs of nearest–neighbor O and Ti atoms. After $\sim 0.8$ ps, a configuration is reached in which the gold atom is equidistant between the O1 and O2 (and Ti1 and Ti2) sites before it jumps into another bridge position between the O2 (green line) and Ti2 sites. By performing static calculations, we show that Au adatoms adsorbed on bridge sites do not induce reduction of the substrate (see Fig. 8(B)), thus all the Ti ions of the substrate preserve their 4+ oxidation state and a very weak oxidation of the Au adatom is observed. This is fully confirmed by the dynamical simulations: along the trajectory, the Ti–3$d$ orbitals are found to be empty, which implies that no localization of charge on substrate Ti sites is observed.

Even at an elevated temperature of 900 K, we do not observe diffusion of the Au adatom in the [110] direction,
namely from the top of \( O_b \) atoms to bridge sites between \( Ti_{5c} \) and \( O_b \) atoms, on the timescale of picoseconds. This dynamics is consistent with previous findings\(^\text{265}^\) based on static or NEB\(^\text{112}^\) calculations which predict a relatively high energy barrier, \( \sim 0.35 \text{ eV} \), for this process to happen compared to others. In conclusion, dynamical PBE+U simulations demonstrate that Au adatoms diffuse highly directionally on the stoichiometric rutile (110) surface. They can easily migrate either along the top of the bridging oxygen rows of the clean \( TiO_2(110) \) surface or around the area between these rows from one bridging position to the next one along the [001] direction. We did not observe, on the picosecond timescale, translational motion perpendicular to this direction, e.g. from one \( O_b \) row to a neighboring row via suitable bridging positions.

**C. Au adatom adsorption on the reduced \( TiO_2(110) \) surface**

Starting with the reduced \( TiO_2(110) \) surface in the presence of an \( O_b \) surface oxygen vacancy the Au metal adatom is found to adsorb preferentially at the \( V_O \) vacancy. Such surface oxygen vacancies result in stable anchoring sites for Au adatoms, which bind at about 0.90 Å above the \( O \) vacancy site with two Ti nearest neighbors at 2.68 Å obtained from both PBE+U and PBE. The corresponding PBE+U (PBE) calculated adsorption energies of \(-1.54 \text{ eV} \) (\(-1.57 \text{ eV} \)) are much larger than the binding to the stoichiometric surface (see Table \( \text{IV} \)), which is consistent (\(-1.6 \text{ to } -1.8 \text{ eV} \)) with previous GGA calculations\(^\text{25}^\). The strong adsorption of an Au atom at the \( V_O \) site entails a strong charge rearrangement at the Au/oxide contact. In the presence of an isolated \( V_O \) vacancy, the charge neutrality of the system is maintained by the presence of two reduced \( Ti^{3+} \) ions. The bonding charge distribution (see Fig. \( \text{V(D)} \)) shows that, upon Au adsorption at the \( V_O \) vacancy site, the charge transfer occurs now from the reduced substrate to the supported metal atom, thus leaving a reduced surface with a single \( Ti^{3+} \) ion. This indicates that the charge transferred from the reduced substrate to the adsorbate comes from one of the two \( Ti^{3+} \) ions. As a result this process leads to the formation of a negatively charged \( Au^{9-} \) adspecies. The analysis of the DOS (see Fig. \( \text{V (D)} \)) now shows that the charge transferred from the substrate to the Au atom moves toward the latter’s half-filled 6s band, which turns out to be almost completely filled. In conclusion, these calculations not only suggest a greatly increased stability of Au adatoms adsorbed onto \( O \) vacancies when compared to the stoichiometric surface as a reference, but also a very different chemical reactivity with respect to admolecules in view of their different charge state. The resulting ramifications for CO activation will be discussed in Sec. \( \text{V(B)} \).

**D. Au substitutional defects on the \( TiO_2(110) \) surface: \( Au_xTi_{(1-x)}O_{2-\delta} \)**

Another reaction channel of gold interacting with titania surfaces is via the chemical exchange of Ti atoms. We studied the scenario where an Au atom substitutes a surface \( Ti_{5c} \) site, which we call “\( Au@V_{Ti5c} \)”. The presence of such an Au substitutional point defect induces a rearrangement of the neighboring atoms, leading to the formation of a distorted squared planar “\( AuO_2 \)” unit (see Fig. \( \text{V} \)). In this configuration, the Au atom relaxes outward by 0.62 Å and is found to be coordinated by four surface \( O \) atoms (at about 2.0 Å). The incorporation of an Au atom into the titania surface does not yield a change in the occupation of the \( Ti-3d \) states: all Ti ions preserve their formal oxidation state \( Ti^{4+} \). However, the adsorption of an Au adatom into a \( V_{Ti5c} \) vacancy site is strongly exothermic, releasing \(-6.38 \text{ eV} \) (or \(-6.21 \text{ eV} \) when using PBE), shown in Table \( \text{IV} \).

This particular defective surface is found to be extremely reactive. We have computed the energy required to remove one of the oxygen atoms \( O_n \) (\( n = 1, 2, 3 \)) in the surface layer (see Fig. \( \text{V} \) for site labeling). The atoms \( O1 \) and \( O3 \) are \( O_b \) atoms while the atom \( O2 \) is an in–plane oxygen. Our PBE+U values for the \( O1 \), \( O2 \), and \( O3 \) vacancy formation energies are \( 1.52, 2.20 \), and \( 1.36 \text{ eV} \) respectively, which is in accord with previous PBE calculations\(^\text{21}^\). For the stoichiometric, undoped \( TiO_2(110) \) surface, the corresponding PBE+U value of \( E_{V}^0 \) is \( 2.97 \text{ eV} \) for an oxygen vacancy, \( V_O \), in the bridging row, compared to \( O1 \) and \( O3 \) here. These values suggest that substituting a surface \( Ti_{5c} \) atom with an Au atom greatly weakens the binding of surface \( O \) atoms, as observed in the case of CeO\(_2\) surfaces\(^\text{109,111}^\).

In Fig. \( \text{V(E)} \), the total DOS and PDOS of the doped \( Au@V_{Ti5c} \) surface is depicted in the presence of an oxygen vacancy. Here, the missing oxygen is the bridging \( O3 \) atom, \( O_3 \) atom (see Fig. \( \text{V} \)), the vacancy formation energy of which is found to be lowest (\( 1.36 \text{ eV} \)) when Au substitutes a Ti atom at a \( Ti_{5c} \) site, which we call “\( Au@V_{Ti5c}, V_{O3} \)”. Concerning the electronic structure, the main difference between the two scenarios, i.e. one obtained by substituting a \( Ti_{5c} \) with an Au atom \( Au@V_{Ti5c} \) and the other generated by substituting a \( Ti_{5c} \) with an Au atom and by removing a surface \( O_b \) atom \( Au@V_{Ti5c}, V_{O3} \), is related to the reduction of the oxide substrate. As we can extract from Fig. \( \text{V(E)} \), in presence of a vacancy located in a neighboring bridging oxygen row, \( O3 \), the excess electron resulting from this vacancy transfers to the substrate and a filled state appears in the band gap. This gap state stems from a \( Ti-3d \) orbital, thus reducing one second–layer Ti ion to \( Ti^{3+} \).
FIG. 6: Side view (left panel) and top view (central panel) of the diffusion path of the Au adatom on the stoichiometric TiO$_2$(110) surface at 900 K. The Au atom, initially adsorbed on top of the bridging oxygen atom O1, diffuses along the O$_b$ bridging row by hopping from one oxygen to the next, O1 $\rightarrow$ O2 $\rightarrow$ O3, as visualized by the worm-like trajectory. The right panel shows the time evolution of the Au–O$_n$ ($n=1,2,3$) bond lengths; the dashed line at 2.00 Å refers to the optimized equilibrium Au–O bond length.

FIG. 7: Side view (left panel) and top view (central panel) of the diffusion path of the Au adatom on the stoichiometric TiO$_2$(110) surface at 900 K. The Au atom, initially adsorbed on a bridge site between the O1 and Ti1 atoms, diffuses by hopping in between pairs of nearest-neighbor O$_b$ bridge and Ti$_{5c}$ atoms as visualized by the worm-like trajectory. The right panel shows the time evolution of the Au–O$_n$ and Au–Ti$_n$ ($n=1,2$) bond lengths; the dashed lines at 2.30 and 2.80 Å refer to the optimized equilibrium Au–O and Au–Ti bond lengths, respectively.

E. \textit{Ab initio} thermodynamics of defective Au/TiO$_2$(110) surfaces

The effects of temperature and pressure on the relative stability of Au/TiO$_2$ metal/oxide surfaces have been taken into account by employing the formalism of approximate \textit{ab initio} thermodynamics, as sketched in Sec. II. To this end, we compute the free energies of Au adsorption, $\Delta G_{\text{ads}}(T,p)$ as given by Eq. (6), and report them in Fig. 10 as a function of the O chemical potential including a conversion to oxygen partial pressures at several relevant temperatures. These free energies are measured relative to the stoichiometric surface and therefore include the free energy cost of creating whatever vacancy the gold atom may be associated with.

As highlighted by the colors in Fig. 10, it is possible to identify four thermodynamically stable phases. The first phase, which holds for values of $\mu_O > -1.35$ eV, corresponds to the scenario where a surface Ti$_{5c}$ atom has been replaced by an Au adatom, denoted \textquotedblright Au@V$_{Ti5c}$\textquotedblright. In oxidative environments, and at the reference conditions that are traditionally used in most computational studies, this structure becomes the thermodynamically most stable one. The second most stable structure thermodynamically is the one obtained by removing a surface O atom from a bridging row based on the Au@V$_{Ti5c}$ structure described above, which is called \textquotedblright Au@V$_{Ti5c}, V_{O3}$\textquotedblright, since the missing O$_b$ atom is the O3
atom (refer to Fig. 9). We have shown that the PBE+U energy required for removing the O3 oxygen atom, i.e. the vacancy formation energy $E_{O3}^{V}$, from the surface of the Au@V$_{Ti5c}$ structure amounts to 1.36 eV. This is significantly lower than the required energy of 2.97 eV to remove an O$_b$ atom from the ideal, stoichiometric TiO$_2$ surface. Therefore the TiO$_2$(110) oxide surface becomes a better oxidant when doped with gold.

As demonstrated in Fig. 10, the Au@V$_{Ti5c}$, V$_{O3}$ surface structure becomes thermodynamically stable for $-1.79 \text{ eV} < \mu_O < -1.35 \text{ eV}$. It turns out that these two defective surface structures, Au@V$_{Ti5c}$ and Au@V$_{Ti5c}$, V$_{O3}$, are thermodynamically stable in a wide range of temperatures $T$ and pressures $p$ that are relevant for applications in the realm of catalysis. In contrast, the adsorption of Au adatoms on the stoichiometric TiO$_2$(110) surface is thermodynamically stable only in a quite narrow range of values of the O chemical potential of $-2.05 \text{ eV} < \mu_O < -1.79 \text{ eV}$. Finally, the adsorption of Au adatoms on O vacancies becomes thermodynamically stable for values of $\mu_O < -2.05 \text{ eV}$. We therefore conclude that under O–rich conditions, the thermodynamically most stable structure is the defective surface structure Au@V$_{Ti5c}$ obtained by substituting a surface Ti$_{5c}$ atom with an Au adatom, while under Ti–rich conditions, the Au adatoms are preferentially adsorbed at O vacancies.
V. GOLD–PROMOTED TITANIA: INTERACTIONS WITH CO PROBE MOLECULES

A. CO molecular adsorption on Au/TiO$_2$(110) surfaces

We have shown that our calculations predict the two most stable adsorption sites of an Au adatom adsorbed on the stoichiometric TiO$_2$(110) surface, differing energetically by only $\pm$0.1 eV. The lowest energy configuration is that with the Au adatom adsorbed onto a bridge site between a surface O$_b$ atom and a first-layer Ti$_{5c}$ atom. A detailed analysis of the electronic structure of this configuration shows that all Ti ions belonging to the substrate preserve their formal oxidation state Ti$^{4+}$. The other stable structure consists of an Au adatom sitting on top of an O$_b$ atom of the (110) surface. The metal adsorption on an O$_b$ top site induces a strong charge rearrangement at the metal/oxygen contact and entails the reduction of a second-layer Ti ion which becomes formally Ti$^{3+}$.

Using these preferred structures, we now study their interaction with a CO admolecule. A CO molecule is placed end–on at 2.5 Å above the Au adatoms. The adsorption of the CO molecule on an Au adatom adsorbed at an O$_b$ site is found to be strongly exothermic, releasing $-2.66$ eV ($-2.33$ eV using PBE; see Table IV). This is in accord with earlier calculations. In this configuration, the CO molecule is aligned with the Au adatom and oriented normal to the surface (see Fig. 11F). The computed value of the C–O bond length is 1.15 Å compared to a value of 1.14 Å of an isolated CO molecule using the same approach. The PBE+U (PBE) value of the distance between the Au atom and the substrate O$_b$ atom to which it is bonded is 1.98 Å (1.97 Å), while the Au to C distance is 1.88 Å (1.88 Å). Analysis of the PDOS (see Fig. 11F) reveals that at this Au/TiO$_2$ contact, only one Ti$^{3+}$ ion is present before and after adsorption, and that the excess charge populating the substrate occupies the same second–layer Ti–3d orbital. Therefore, the charge redistribution due to adsorbing a CO molecule does not further reduce the oxide support. However, the bonding charge analysis (also displayed in Fig. 11F) shows that the Au adatom is involved in charge depletion (blue areas), while both the C and O atoms accumulate the resulting excess charge (red areas).

We now consider the interaction between a CO molecule and the Au atom adsorbed onto the bridge site. Again, the mechanism is exothermic by $-2.27$ eV (or $-2.17$ eV when using PBE instead of PBE+U). In this configuration, the CO molecule is bonded to the Au atom and the C–O bond length is 1.15 Å as in the previous case. Here, however, the CO–Au structure is found to be tilted with respect to the surface at an angle of about 60° (see Fig. 11G). The PBE+U (PBE) values of the distances between the Au adatom and the Ti$_{5c}$ atom before and after the adsorption of molecular CO are 2.79 (2.88) and 3.90 Å (3.88 Å), respectively, while the distances between the metal and the O bridging atom before and after CO adsorption are 2.30 (2.39) and 1.99 Å (2.01 Å), respectively. The analysis of the PDOS as depicted in Fig. 11G shows, in this case, that at the Au/TiO$_2$ contact, the charge redistribution reduces the oxide support, contrary to the previous scenario. We recall that when Au is adsorbed onto a bridge site, all the substrate Ti ions preserve their formal Ti$^{4+}$ oxidation state. Upon CO adsorption onto the Au atom occupying a bridge position, one Ti ion is reduced. The additionally reduced Ti$^{3+}$ ion, which belongs to the first TiO$_2$ layer, is precisely the ion that forms a bond with the Au in the bridge configuration before CO adsorption.

The configuration in Fig. 11G, where the CO–Au structure is tilted by $\sim 60^\circ$ with respect to the substrate, is used as an initial condition for a short AIMD run at room temperature in order to probe dynamical instabilities. In less than 0.4 ps, the CO–Au complex bends and sits perpendicular to the surface, therefore recovering the structure obtained upon molecular CO adsorption on gold sitting on top of an O$_b$ atom. The difference in the binding energies for CO molecule adsorption on the top and bridge configurations described above can be attributed in part to the tilting of the Au–CO complex with respect to the surface plane. More important, however, is the position of the reduced Ti$^{3+}$ site. Previous studies on charge localization induced by O$_b$ vacancies on TiO$_2$ surfaces have shown that excess electrons, which are trapped at specific Ti sites, migrate easily by phonon–assisted hopping to other Ti atoms, thus exploring different electronic structure topologies. In particular, it was found that the most stable sites for charge localization belong to the second subsurface layer under Ti$_{5c}$ rows. The topologies where the excess charge is shared between surface Ti$_{5c}$ atoms and second or third subsurface layer sites below Ti$_{5c}$ rows were found to be about 0.2–0.3 and 0.3–0.4 eV higher in energy, respectively. It is therefore conceivable that we would observe a similar dynamics for excess charge de– and re–localization.

B. CO adsorption on Au$_1$/TiO$_2$$_{(2−x)}$(110) and Au$_2$/TiO$_2$$_{(2−x)}$(110) surfaces

The interaction between a CO molecule and a single Au adatom adsorbed at a bridging site or on top of an O$_b$ atom on the TiO$_2$(110) surface has been investigated above. We now concentrate on the interaction between CO molecule and Au adatom adsorbed at a bridging O vacancy. It has been shown that the metal adatom strongly interacts with this reduced oxide support. The resulting Au$^{δ−}$ adatom is highly stable, considering its binding energy of $-1.54$ eV. Our calculations predict a fairly weak interaction between molecular CO and the Au$^{δ−}$ adatom. The CO molecule initially located end–on at 2.5 Å above the Au$^{δ−}$ species is found to bind with about $-0.41$ eV. This binding energy is close to an order
FIG. 11: Electronic structure analyses (based on the PBE+U approach) of (F) a CO molecule adsorbed on a supported Au adatom (originally the Au atom was adsorbed at a bridging O atom) on the TiO$_2$(110) surface, (G) a CO molecule adsorbed on a supported Au adatom (originally the Au atom was adsorbed between a bridging O atom and a Ti$_{5c}$ atom) on the TiO$_2$(110) surface, (H) of the Au$_2$ dimer adsorbed onto surface and (I) a CO molecule bonded to an Au$_2$ dimer adsorbed onto a surface O vacancy on the TiO$_2$(110) surface. The left panel represents the bonding charge $\delta \rho (z)$ integrated over planes perpendicular to the surface and plotted as a function of the height from the surface. The central panel displays the bonding charge $\Delta \rho (\vec{r})$ at an isovalue of $\pm 0.06 \text{ e/Å}^3$ where electron accumulation and depletion are represented by red and blue areas, respectively. The right panel shows the total DOS and atom resolved projected DOS (PDOS), as indicated, where energies are with respect to the Fermi level, which is marked by a solid vertical line.
of magnitude lower than the binding energy of the positively charged Au adatom adsorbed on the stoichiometric TiO$_2$(110) surface, which binds with $-2.66$ eV.

Our calculations show that while positively charged Au$^{6+}$ ions supported on the TiO$_2$(110) surface are shown to activate molecular CO, negatively charged Au$^{5-}$ adspecies, which are incorporated into surface O vacancies, interact only weakly with CO adsorbates. This is in line with the scenario of Au adsorbed on the CeO$_2$ substrate$^{[103,118]}$, where it has been shown that the higher stability of Au adatoms adsorbed onto surface is the basis of the deactivation mechanism during CO oxidation. The oxidation mechanism proposed$^{[120]}$ involves three steps: the spillover of the CO molecule, the actual oxidation via a lattice oxygen atom leading to CO$_2$ desorption, and the diffusion of the Au adatom into the newly formed O vacancy, which results in negatively charged Au$^{5-}$ adspecies that prevents the adsorption of molecular CO.

Since the present AIMD simulations have shown that Au adatoms diffuse rather easily on the stoichiometric surfaces, several theoretical and experimental studies suggest that V$_0$ vacancies in bridging oxygen rows, O$_b$, are active nucleation sites for Au$_n$ clusters on the TiO$_2$(110) surface$^{[7,113,114]}$. It is therefore expected that nucleation and growth of Au$_n$ clusters on the rutile surface is intimately related to the presence of surface oxygen vacancies. To get a glimpse, we next investigated the limiting case of a gold dimer, Au$_2$, adsorbed at an O$_b$ vacancy. The optimized structure of an Au$_2$ dimer adsorbed onto a surface bridging O vacancy is depicted in Fig. 12 (a). The computed value of the adsorption energy of Au$_2$ on the reduced TiO$_2$(110) surface, calculated with respect to the isolated Au$_2$ molecule, is $-1.17$ eV ($-1.19$ eV with PBE). The adsorption mechanism induces reduction of an additional Ti ion, leading to a gold dimer into an O vacancy and two second-layer Ti$^{3+}$ ions (see Fig. 11 (H)). The two gold atoms are located 1.20 Å above the O vacancy site, whereas the distances between the Au atoms and the nearest-neighbor Ti atoms are 2.80 Å and the Au–Au distance amounts to 2.51 Å compared to 2.53 Å of the isolated gold dimer using the same method.

Next, a CO molecule is positioned above the Au$_2$ dimer adsorbed onto the surface O vacancy. After relaxation, the CO molecule reaches the most stable configuration of Fig. 12(b). The computed binding energy is $-1.22$ eV ($-1.00$ eV using PBE), in good agreement with previous studies$^{[88]}$. This value is about half of that obtained for adsorption of CO on a single Au adatom adsorbed on the stoichiometric surface ($-2.66$ eV) but distinctly lower than the energy calculated on the Au/TiO$_2$(2−x) surface ($-0.40$ eV). We therefore find that a cluster as small as Au$_2$ nucleated at an O vacancy on the reduced TiO$_2$(110) surface favors the formation of stable CO adsorbates. Specifically, the CO molecule binds to the Au atom that is farthest from the O vacancy and the Au–Au distance elongates from 2.51 to 2.78 Å. The interaction between CO and the metal oxide does not induce further reduction of the substrate; before and after adsorption, two reduced Ti$^{3+}$ ions are present (see Fig. 11 (I)). In Fig. 12, we plot the spin density of the Au$_2$ dimer adsorbed on the reduced TiO$_2$ surface (a) and the spin density after adsorbing a CO molecule to this Au$_2$/TiO$_2$(2−x) metal/oxide substrate (b). In each panel, we can see that both Ti$^{3+}$ ions belong to subsurface layer sites below Ti$_{5c}$ rows.

It is clear from these calculations that a gold “cluster” as small as the Au$_2$ dimer adsorbed onto a bridging O vacancy leads to a promoted support that strongly binds to molecular CO. Furthermore, the step from one to two gold atoms greatly changes the electronic properties, thus lending support to the general view that the reactivity of gold nanoparticles nucleated at O vacancies is strongly size dependent.

**VI. CONCLUSIONS AND OUTLOOK**

We have performed periodic density functional based calculations that account for the on–site Coulomb interaction via a Hubbard correction (“GGA+U”) on stoichiometric, reduced, and gold–promoted rutile TiO$_2$(110) surfaces. Structure optimizations, ab initio thermodynamics calculations, and ab initio molecular dynamics simulations have been carried out both using PBE+U and plain PBE in order to provide a broad picture on the interactions of these surfaces with several catalytically important molecules.

In agreement with plain PBE calculations and experimental results, we find that H atoms preferentially adsorb on surface O$_b$ atoms of the stoichiometric surface. Adsorption of hydrogen results in its reduction and transfer.
of close to one electron per H atom to the substrate. Using PBE+U, however, the electron transferred by a single H atom into the substrate localizes preferentially at second–layer Ti sites (whereas plain PBE yields a delocalized state). Both PBE+U and PBE calculations show a decrease in the adsorption energy as a function of coverage and a maximum coverage of about 60–70%. Oxygen vacancies are the preferred adsorption sites for H2O dissociation and similar values for the adsorption energies of water are obtained with and without the Hubbard correction. Our PBE+U calculations predict the presence of two reduced Ti3+ ions before and after the adsorption of water, indicating that the adsorption of water does not further reduce the support (whereas plain PBE again yields delocalized excess electrons).

Akin to plain PBE calculations, PBE+U predicts a weak interaction between CO molecules and the reduced TiO2 substrate. The data indicate that CO adsorbs at both oxygen vacancies in the bridging surface rows, O5c, and fivefold coordinated titania sites in the first layer, Ti5c. While PBE calculations give similar energy values for CO at oxygen vacancies and at Ti5c, PBE+U calculations show that the adsorption of CO at those Ti5c sites which are nearest neighbors of the oxygen vacancies is energetically disfavored. Upon CO adsorption on the reduced oxide, the resulting charge redistribution does not reduce further the titania substrate.

Addressing next the interaction of titania with gold, both PBE+U and PBE calculations predict two most stable adsorption sites for Au adatom adsorption on the stoichiometric TiO2 surface. On the one hand, once an Au adatom is adsorbed at a bridge site between a surface O5b atom and a first–layer Ti5c atom, PBE+U suggests that all the Ti ions belonging to the substrate preserve their formal oxidation state Ti4+, indicating a very weak oxidation of Au. On the other hand, if the Au adatom is adsorbed on top of an O5b atom, a net charge transfer from the metal to surface, leading to a positively charged Auδ+, is observed. In this case, the metal adsorption entails the reduction of a second–layer Ti ion, which formally becomes Ti3+. Ab initio molecular dynamics reveals that gold adatoms on stoichiometric TiO2(110) are very mobile. They are found to migrate easily along the [001] direction, either along the top of bridging oxygen rows or around the area between such rows. In the former case, we observe an interesting subsurface charge delocalization and relocation dynamics of the excess charge.

Promotion of the (110) rutile surface via adsorption of gold atoms or substitution of Ti by Au results in a system with greatly changed electronic properties and thus modified reactivities in the realm of heterogeneous catalysis. This is traced back to the oxidation state of the gold adatoms, which is determined by the site at which the Au atom is adsorbed as well as by the stoichiometry of the substrate. Isolated Au atoms supported by the stoichiometric TiO2 surfaces are shown to induce a significant charge redistribution at the metal/oxide contact. The calculations, both PBE+U and PBE, show positively charged Auδ+ adspecies supported on the stoichiometric surface which activate CO admolecules. In stark contrast, the negatively charged Auδ− adspecies, which are incorporated into surface O5b vacancies, interact only weakly with the same CO molecules. We have shown that structures obtained by substituting a first–layer Ti5c ion with an Au atom weakens the bond of surface O atoms, akin to recent observations with ceria. Ab initio thermodynamics mappings of the surface phase diagram predict that the “Au@V5c” and “Au@V3c, V3o” of temperatures and pressures relevant for catalytic applications. Finally, we have shown that although a single Au adatom bound to a surface O vacancy weakly binds CO, a second gold atom adsorbed simultaneously into the O vacancy leads to the formation of a gold dimer, Au2, featuring distinctly different electronic and binding properties.

We expect that these insights will be of great help in understanding the catalytic activity of gold-promoted titania interfaces with liquid water as used in selective oxidation reactions of more complex molecules.

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