Structure of clean and adsorbate covered single crystal rutile-TiO$_2$ surfaces

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1. Introduction

TiO$_2$ is exploited in a number of applications, including solar power, catalysis, gas sensing, and corrosion protection, where surface properties are central to operation. This commercial importance drives cutting-edge research into this material; activity extends from development of novel titania based structures exhibiting enhanced surface functionality to fundamental work aiming to gain mechanistic insight into surface processes. This latter effort is typically concerned with studies of model low Miller index single crystal TiO$_2$ surfaces, with the rutile polymorph being the focus of most effort. On this basis, these rutile-TiO$_2$ surfaces, particularly the (110) face, have become the most studied single crystal metal oxide substrates. In order to maximize nanoscale knowledge, studies are usually performed under ultra high vacuum (UHV) conditions. However, there is a growing trend of addressing such surfaces in ambient gaseous and liquid environments.

Partially, rutile-TiO$_2$ surfaces have attracted so much attention due to the ready availability of high-quality single crystals. Additionally, the necessary electrical conductivity to allow their study by charged particle methods is simply imparted by reducing the crystals in UHV. This approach has largely eliminated the need to grow highly-ordered ultrathin films of rutile-TiO$_2$ on conducting substrates, although some work has been published (see, for example refs 1-3); Kuhlenbeck et al.$^4$ cover work on various oxide films in another contribution to this volume.

In this review article, we concentrate on the geometric structure of single crystal rutile-TiO$_2$ surfaces, both clean and adsorbate covered. Such information is key to full mechanistic understanding of surface properties, including chemical reactivity. We begin
with clean surface structures, before addressing the adsorbed geometry of inorganic and organic molecules, as well as metal overlayers. Where available, fully quantitative surface structure determinations will be presented, which result in precise information about adsorbate and/or substrate atomic coordinates. Typically, such studies employ electron/photon scattering based surface probes, including quantitative low energy electron diffraction (LEED-IV), surface X-ray diffraction (SXRD), and photoelectron diffraction (PhD). The results of near edge X-ray absorption fine structure (NEXAFS) measurements will also be discussed, which facilitate the determination of the angular orientation of molecular adsorbates; illustrations suggesting adsorption sites on the basis of such NEXAFS data are to some extent speculative. Furthermore, as quantitative structural data are still quite rare, we also consider more qualitative work, in particular the application of scanning probe microscopy (SPM) to visualize adsorbate bonding sites and the growth mode of metals. Theoretical studies related to experiments are also discussed.

This review builds on the seminal *Surface Science Report* on the surface science of TiO$_2$ by Diebold,$^5$ as well as more recent review articles.$^6$-$^{12}$ It is hoped that both newcomers to this field and experienced practitioners will find this contribution useful to their research.

2. Clean Surfaces

2.1 TiO$_2$(110)

As indicated above, rutile-TiO$_2$(110) is the most studied low Miller index single crystal metal oxide surface. Figure 1 shows a pseudo-space-filling model of the ideal
bulk-terminated structure of this surface, complete with labelling of the topmost atoms, i.e. bridging oxygens (O_b), 5-fold coordinated titaniums (Ti_5c) and in-plane oxygens. According to Tasker’s rules for the stability of ionic crystal surfaces, this face should be stable without the need for substantial reconstruction. Indeed, this prediction is consistent with experimental findings, including the most complete fully quantitative structures determinations to date, undertaken with LEED-IV and SXRD. The optimized structures emerging from this work are detailed in Table 1, where atomic displacements away from the ideal bulk-terminated TiO_2(110)(1×1) surface are listed; the ball and stick model of the surface in Figure 2 facilitates identification of the atoms in Table 1. These LEED-IV and SXRD studies are impressively consistent, especially as many of the atomic displacements have been determined rather precisely. Most notably, the bridging oxygens (O(1)) are found to shift away from the bulk by 0.08 ± 0.05 Å (LEED-IV)/0.10 ± 0.04 Å (SXRD). Previously, the relaxation of these atoms had been the subject of some debate. The surface five fold titanium atoms (Ti(2)) relax inwards, i.e. -0.19 ± 0.03 Å (LEED-IV)/-0.11 ± 0.01 Å (SXRD).

Results from two other experimental structure determinations, employing medium energy ion scattering (MEIS) and PhD, are also listed in Table 1. Again, there is generally good agreement in terms of the values of atomic displacements, although the error bars associated with the MEIS and PhD optimized structures are typically somewhat larger. The only exception to this agreement is the -0.06 ± 0.06 Å displacement of Ti(4) in the optimized MEIS structure. In the other studies the displacement of this atom is in the opposite direction, e.g. 0.14 ± 0.03 Å from LEED-IV.

As regards ab initio calculations of the TiO_2(110)(1×1) surface geometry, more
recent calculations typically reproduce the most salient features of the experimental structure determinations. For example, Hameeuw et al.\textsuperscript{19} predict a displacement away from the bulk of 0.06 Å for O\textsubscript{b}, and a -0.15 displacement for Ti\textsubscript{5c} towards the bulk. However, there are technical issues with such calculations, and care has to be taken to ensure that the correct approach is adopted.\textsuperscript{20,21}

Many SPM images have been acquired from TiO\textsubscript{2}(110)(1×1), that are consistent with the structure illustrated in Figures 1 and 2. As regards scanning tunnelling microscopy (STM), contrast is such that bright rows running in the [001] direction are typically due to the Ti\textsubscript{5c} atoms (see Figure 3). This origin was established in early work that used chemical probes as well as by comparison with STM simulations.\textsuperscript{22,23} In contrast, non-contact atomic force microscopy (NC-AFM) typically images the O\textsubscript{b} rows as protrusions. However, a different tip termination can give rise to a reversal of contrast, with the Ti\textsubscript{5c} rows becoming brightest, as illustrated in Figure 4.\textsuperscript{24,25} Note that both STM and NC-AFM images of TiO\textsubscript{2}(110) can also have quite different appearances to those shown here.\textsuperscript{26-28}

As well as providing images of the long range ordered structure, the real power of these SPM techniques is to probe local discontinuities, including point defects. On TiO\textsubscript{2}(110)(1×1), the most commonly observed defect is a bridging oxygen vacancy (O\textsubscript{b}-vac), which usually appears in STM images as a bright spot on the dark O\textsubscript{b} row, as shown in Figure 3. In NC-AFM, these defects can appear as bright protrusions or dark depressions, depending on the tip condition (see Figure 4). Typically, standard surface preparation in UHV (cycles of Ar\textsuperscript{+} bombardment and thermal annealing) leads to a surface coverage of these O\textsubscript{b}-vacs of approximately 0.05 - 0.1 ML, where 1 ML is
defined as the number of surface unit cells. As discussed later, water easily dissociates in these vacancies to form two bridging hydroxyls (OH\textsubscript{b}).\textsuperscript{29,30} Indeed, this reactivity is such that surfaces probed in UHV are often decorated with these OH\textsubscript{b}’s unless special care is taken. In accord with ref 31, wherever necessary we will henceforth refer to the TiO\textsubscript{2}(110)(1\times1) surface with O\textsubscript{b}-vacs as r-TiO\textsubscript{2}(110), and the label h-TiO\textsubscript{2}(110) will be used for the same surface following water dissociation at the O\textsubscript{b}-vacs. Likewise oxidized TiO\textsubscript{2}(110) will be referred to as o-TiO\textsubscript{2}(110). Typically, o-TiO\textsubscript{2}(110) is prepared by exposing r-TiO\textsubscript{2}(110) to O\textsubscript{2}, although o-TiO\textsubscript{2}(110) will also denote samples which have been prepared by annealing in O\textsubscript{2} or those that have been allowed to cool in O\textsubscript{2} after UHV annealing. It should be noted that in many of the studies discussed in this review, the presence or absence of OH\textsubscript{b}’s has not been explicitly determined.

Besides their visibility in SPM, for many years it has been assumed that these O\textsubscript{b}-vacs give rise to the Ti 3\textit{d} band gap state (BGS), due to the formation of Ti\textsuperscript{3+} cations, which lies at ~ 1 eV binding energy (BE) in valence band photoemission spectra (see, for example, ref 32). Recently, however there has been some debate about this BGS feature, with Wendt et al.\textsuperscript{31,33} concluding that it originates almost entirely from Ti\textsuperscript{3+} interstitials (Ti\textsubscript{int}) present in the surface selvedge. However, further work has adduced evidence for an O\textsubscript{b}-vac origin.\textsuperscript{34-38} For example, as depicted in Figure 5, Yim et al.\textsuperscript{34} have shown that there is a linear dependence between BGS intensity and the O\textsubscript{b}-vac density, indicating that the latter is the primary origin of the former. It should be pointed out that the non-zero intercepts in the plots in Figure 5 arise from a small, unknown contribution to the BGS, possibly Ti\textsubscript{int}. More recent measurements by Mitsuhara et al.\textsuperscript{37} and Walle et al.\textsuperscript{38} suggest that both O\textsubscript{b}-vac and Ti\textsubscript{int} contribute to the BGS, with Mitsuhara et al.,\textsuperscript{37} showing
that the non-\(O_b\)-vac contribution increases with substrate reduction.

Concerning structural studies of these point defects, PhD measurements have been undertaken from the BGS feature. Simulations of the experimental data indicate that the charge associated with this state is delocalized over several lattice Ti atoms, with significant weight on a second layer Ti (Ti(3) in Figure 2). Notably, simulations that explicitly test for the presence of \(\text{Ti}_{\text{int}}\) in the top three layers of TiO\(_2\)(110)(1×1) do not fit the experimental data. This result suggests that any contribution to the BGS not attributed to the presence of \(O_b\)-vacs by Wendt et al., Yim et al., and Mitsuhara et al. may arise from deeper lying \(\text{Ti}_{\text{int}}\) as suggested by Papageorgiou et al., or may not be related to \(\text{Ti}_{\text{int}}\) at all. Other defects, for example, include sub-surface O-vacs. Currently, theoretical modelling of this BGS does not provide any further insight into its spatial distribution, as results are very much dependent on details of the approach adopted; further effort is required to determine the most appropriate theoretical methodology to produce reliable predictions in this area.

Beyond the (1×1) termination of TiO\(_2\)(110), several other surface phases appear when the substrate is further reduced, as discussed in a review by Bowker in 2006. There are two principal structures of concern, namely a (1×2) reconstruction, and one created by shear plane termination. For the (1×2) surface, two variants exist, namely simple and cross-linked phases. An STM image of the simple (1×2) reconstruction is shown in Figure 6. After a number of years of debate regarding the atomic anatomy of this phase (see, for example, ref 8), the geometry displayed in Figure 7 was determined from LEED-IV measurements. This structure, which is known as the Ti\(_2\)O\(_3\) added-row termination, was first proposed by Onishi and Iwasawa on the basis of STM
images.\textsuperscript{48,49} It is consistent with other experimental data,\textsuperscript{50,51} as well as \textit{ab-initio} calculations.\textsuperscript{52,53} STM data also evidence higher order 1xn structures.\textsuperscript{42,54}

An STM image of the more complex \textit{cross-linked} or \textit{x-linked} (1×2) reconstruction is displayed in Figure 8, which seems to be favored at higher degrees of substrate reduction.\textsuperscript{42-44} These \textit{x-link} rows are ordered to an extent, with a spacing of about twelve unit cells in the [001] direction. To date, no quantitative structure determination of this phase has been published. Nevertheless, a recent NC-AFM study concludes that the (1×2) added rows have a Ti$_3$O$_6$ stoichiometry,\textsuperscript{55} as was first suggested by Bennett et al.\textsuperscript{44} In other words, the suggestion is that these added rows have a different structure to those formed without \textit{x-links}.

A further feature of bulk rutile-TiO$_2$ is the formation of crystallographic shear planes, when it becomes sufficiently non-stoichiometric. An increase in the number of oxygen atoms shared by neighboring TiO$_6$ pseudo-octahedra is what characterizes the shear planes. Their importance for surface structure is that shear planes can terminate at the (110) surface, giving rise to step structures. These steps have a height of \(~1.6\) Å, half that of regular steps on the (110) surface, and they can form up-down step arrays, as well as staircase arrangements. Shear plane termination has been identified on surfaces of bulk TiO$_2$(110)\textsuperscript{42,56} as well as on ultrathin films of TiO$_2$ grown on Ni(110).\textsuperscript{3}

\subsection*{2.2 TiO$_2$(011)}

Given the tetragonal nature of the rutile-TiO$_2$ bulk unit cell, the (011) and (110) faces are not the same. Until relatively recently, little work had been undertaken on the (011) surface, but this was changed by studies suggesting it may have enhanced photo-
catalytic activity (see, for example, ref 57). Initially, the surface structure was probed through a combination of SPM and first principles total energy calculations. Employing this approach, Beck et al.\textsuperscript{58} concluded that titanyl (Ti=O) groups terminated the surface, which is reconstructed to a (2×1) unit cell, as illustrated in Figure 9a. They even suggested that the titanyls provided a possible explanation for the enhanced photoactivity. However, a NC-AFM study\textsuperscript{59} came up with a quite different structure, labelled as the micro-facetted missing-row model (Figure 9b). Given this apparent uncertainty about the TiO\textsubscript{2}(011)(2×1) geometry, SXRD\textsuperscript{60,61} and LEED-IV\textsuperscript{63} were applied to resolve the debate, demonstrating that neither of the previous SPM-based models were correct. Figure 9c shows the structure resulting from analysis of the SXRD and LEED-IV data, which has a topmost layer of zigzag rows of twofold coordinated oxygen atoms. Most importantly, there are no titanyl groups in this structure. Moreover, only local atomic displacements are required to form the reconstruction, i.e. the surface has the same stoichiometry as the underlying substrate, which is not the case for the SPM-based structures. \textit{Ab initio} calculations also favor this structure,\textsuperscript{60-61} and the latest STM simulations reproduce the appearance of STM images.\textsuperscript{62}

Oxygen vacancies are also observed on the (011) face in STM images. In contrast to images of the (110) surface, these appear as missing spots.\textsuperscript{64} This difference arises because Ti atoms are imaged on the (110) and O atoms are imaged on the (011). Another disparity is that pairs of vacancies are often observed for the (011) surface instead of isolated vacancies for the (110).\textsuperscript{64}

\subsection*{2.3 TiO\textsubscript{2}(100)}
Concerning, TiO$_2$(100), there has not been much progress in relation to its surface structure since Diebold’s review.$^5$ One reason for this stagnation is the rather complex set of possible terminations. As well as a (1×1) surface phase, three types of (1×3) termination have been imaged with SPM, as shown in Figure 10,$^{65}$ along with a (1×7) reconstruction.$^{66}$ Given that more than one of these terminations may coexist on the surface at any one time, typical diffraction/scattering approaches are problematic. Nevertheless, SXRD has previously been employed to probe the structure of a (1×3) reconstructed surface.$^{67}$

The latest analysis of the SXRD data,$^{68}$ employing direct methods, resulted in the structure shown in Figure 11b; a microfacet structure (see Figure 11a) was concluded from the original analysis.$^{67}$ In Figure 11b, TiO$_6$ pseudo-octahedra share additional edges to those in the bulk, which is similar to the situation where crystallographic shear planes form in the reduced Magnéli phase in the bulk.$^{69}$ Such a structure is associated with non-stoichiometry, i.e. the formation of TiO$_{2-x}$, which is consistent with photoemission spectra.$^{70}$ These latter data show that Ti$^{3+}$ species are formed on the (1×3) surface as evidenced by the presence of a BGS.

Lindan et al.$^{71}$ have employed density functional theory (DFT) calculations to predict likely (1×3) geometries. They propose two candidates, their so-called ‘flat’ and ‘microfacet’ structures, neither of which matches the SXRD structures.$^{67,68}$ However, they do comment that these terminations are apparently consistent with SPM data.$^{65}$ It is worth noting that current ideas regarding modelling of TiO$_2$ surfaces suggest that either hybrid functionals or the use of DFT+U is necessary to accurately model structures containing O vacancies,$^{72}$ as is the case here. Given that Lindan et al.$^{71}$ adopted another
approach, this is a modelling problem worth revisiting.

As indicated above, a (1×7) unit cell has also been imaged by STM on TiO$_2$(100). However, no attempt was made in that study to suggest its atomic scale geometry. Previously, both (1×7) and (1×5) phases have been reported on the basis of LEED patterns, although it has been argued that these apparent unit cells may have arisen from spot splitting due to the substrate exhibiting a vicinal (100) surface.

A further reconstruction of the (100) surface, namely c(2×2), has been identified on ion-beam thinned samples, through a combination of transmission electron diffraction, direct methods analysis, and DFT calculations. A (1×1) termination was also identified in this work after prolonged annealing in O$_2$, but no (1×3) reconstruction was found. This apparent discrepancy is almost certainly due to very different approaches to sample preparation between the UHV ‘surface science’ experiments described above and the transmission electron diffraction measurements in refs 75,76. For the latter, the sample was exposed to a 5 keV Ar$^+$ beam, which reduces the sample, and makes it transparent to electrons. Heating this reduced surface in an atmosphere of O$_2$ or Ar for 1023-1073 K creates the c(2×2) structure. Prolonged annealing in an atmosphere of O$_2$ leads to the disappearance of the c(2×2) structure, i.e. formation of the (1×1) surface. It should be noted that it is suggested in refs 75,76 that no (1×3) unit cell is apparent due to the high O$_2$ pressure used during annealing; even under the Ar atmosphere, the environment is likely to be much more oxygen-rich than when annealing in UHV.

The c(2×2) structure emerging from ref 76 is presented in Figure 12. More specifically, Figure 12a displays an in-plane map of atomic positions generated by application of direct methods to the transmission electron diffraction data. The optimum
DFT structure is shown in Figure 12b, which agrees well with the experimental data. The reconstruction comprises corner-sharing TiO$_4$ tetrahedra, and has two oxygen vacancies per surface unit cell.

2.4 TiO$_2$(001)

Diebold noted in her review$^5$ that the structure of TiO$_2$(001) remained to be determined with a high degree of reliability. At the time of writing, this statement is still largely true. Indeed, the only quantitative, experimental structure determination of TiO$_2$(001) is from 1991, where LEED-IV was employed to determine the structure of a cleaved (1×1) surface.$^{77}$ Limited data were obtained, although two possible surface structures were concluded to be more likely. One of these solutions is largely a bulk-like termination with only very minor atomic displacements (\(< 0.1 \text{ Å}\)), whereas the other involves greater distortions in the second layer. Morgan and Watson have recently performed DFT+U calculations indicating that such a (1×1) surface is energetically stable,$^{72}$ although the predicted atom relaxations are not in complete quantitative agreement with experiment.$^{77}$

Upon annealing, the (001) termination of rutile-TiO$_2$ becomes more complex. On the basis of LEED, two distinct structures have been identified, which are typically labelled as \{011\} and \{114\} micro-faceted phases;\textsuperscript{78} the \{114\} structure forms at higher substrate anneal temperatures. Concerning the \{114\} phase, which appears as a latticework-like structure in STM, several studies have attempted to deduce its geometry.$^{79-81}$ However, each study proposes a somewhat different surface structure, with the latest concluding a stoichiometric termination,$^{81}$ and so reliable structural information
remains a future goal.

2.5 TiO$_2$\((111)\)

To date, there is a single STM study dealing with clean TiO$_2$\((111)\), which evidences the formation of three different terminations depending on the UHV preparation recipe.$^{82}$ A surface prepared by annealing at 1024 K, without Ar$^+$ sputtering, has rectangular symmetry. The other two terminations were observed subsequent to cycles of Ar$^+$ sputtering and annealing at 976 K. One termination appears hexagonal [(1\(\times\)1) unit cell], whilst the other has a zigzag motif [(1\(\times\)2) unit cell].

2.6 Stepped surfaces

\(\text{TiO}_2\)(210)

\(\text{TiO}_2\)(210) is a vicinal surface, being a plane midway between the (100) and (110) faces. By analogy with metal surfaces, the (210) surface would be expected to form facets of these two low Miller index parent planes, because they should have significantly lower energy. Instead, atomistic simulations of TiO$_2$\((210)\) predict that it terminates in a saw-tooth structure containing only \{110\} nanofacets.$^{83}$ STM images of this surface are interpreted in light of these calculations.$^{83}$ Empty states imaging is employed so that Ti atoms are expected to form the basis of the images. Indeed, the position of defects in the images is most easily interpreted in this way, although as indicated in ref 83, further work is required to reliably elucidate the structure of rutile-TiO$_2$\((210)\).

\(\text{TiO}_2\)(771) & \(\text{TiO}_2\)(870)
Off-cut TiO$_2$(110) samples have been recently examined by STM, photoemission and DFT calculations.$^{84}$ The aim of this work was to investigate step structure formation driven by the creation of vicinal surfaces. Steps and kinks on surfaces of metal and other materials expose low coordination sites, which in a number of cases have been demonstrated to have enhanced reactivity.$^{85-88}$ The presence of such sites on rutile-TiO$_2$ surfaces may have a similar effect, as suggested by first principles calculations.$^{89}$

In ref 84, two different stepped TiO$_2$(110) surfaces were examined, namely TiO$_2$(771) and TiO$_2$(870), where the former displays a high density of $<1\bar{1}1>$ steps, and the latter predominantly $<001>$ steps. Most notably, strand-like structures are found to extend out from the $<1\bar{1}1>$ steps (see Figure 13). These appear to be formed by incorporating point defects to form non-stoichiometric added rows, a process that was modelled by DFT calculations. Material transport is thought to be the key factor in favoring the growth of strands at the step edge.

A further study probing steps on the TiO$_2$(110) surface has employed in situ surface modification to generate thermodynamically metastable steps, rather than examining off-cut samples,$^{90}$ Ar$^+$ ion sputtering at grazing incidence was used to fabricate $<[1\bar{1}0]>$ steps. STM images, in combination with DFT modelling, suggest that these steps locally reconstruct to form edges resembling the TiO$_2$(001)-{011} mirco-facetted surface.$^{75}$

3. Inorganic Non-Metallic Adsorbates

3.1 Oxygen

O$_2$ is often present in environments where TiO$_2$ might be used in technological applications. Added to this, the interaction of O$_2$ and TiO$_2$ is directly relevant to device
technology such as solar cells, gas sensors, and catalytic converters. Adsorption and reactions of $O_2$ on TiO$_2$(110) has been reviewed by Pang et al.\textsuperscript{8} and Dohnálek et al.\textsuperscript{9} The interaction of $O_2$ and OH in particular was also reviewed by Liu et al.\textsuperscript{91} In this section, we focus on recent developments concerning $O_2$ adsorption on $r$- and $h$-TiO$_2$(110) and the reoxidation of TiO$_2$(011).

\textit{r-TiO$_2$(110) at room temperature}

The dissociation of $O_2$ at $O_b$-vac was discussed in detail in our previous review.\textsuperscript{8} A number of techniques including temperature programmed desorption (TPD),\textsuperscript{92} STM,\textsuperscript{93-95} and DFT calculations\textsuperscript{96,97} indicate that $O_2$ dissociates in the $O_b$-vac: one O atom fills the vacancy and the other is deposited as an O adatom ($O_{ad}$) on a nearby Ti$_{5c}$ site:

\begin{equation}
O_b\text{-vac} + O_2(g) \rightarrow O_b + O_{ad}.
\end{equation}

After exposing $r$-TiO$_2$(110) to $O_2$, in addition to single $O_{ad}$ arising from equation 1, Wendt et al.\textsuperscript{31} observed pairs of $O_{ad}$ on nearby Ti$_{5c}$ sites along [001] and proposed a dissociation channel unrelated to $O_b$-vac whereby an $O_2$ molecule dissociates to form a pair of $O_{ad}$. As shown in Figure 14, Du et al.\textsuperscript{98} imaged the same area of the surface before and after exposure to $O_2$ and indeed find no statistical correlation of paired $O_{ad}$ and $O_b$-vacs in the image prior to $O_2$ exposure, thereby supporting the reaction proposed by Wendt et al.\textsuperscript{31}

\begin{equation}
O_2 \underset{Ti}{\xrightarrow{T_{1b}}} 2O_{ad}.
\end{equation}
However, DFT calculations from several groups indicate that dissociation on the perfect surface is not favored.\textsuperscript{31,96,99,100} By supplying electrons from Ti\textsubscript{int}, Wendt et al.\textsuperscript{31} suggest that the dissociation can be made exothermic by $\sim$4 eV. Calculations by Du et al.,\textsuperscript{98} on the other hand suggest that the major source of electrons is itinerant charge from O\textsubscript{b}-vac with a smaller contribution from Ti\textsubscript{int}. The charge withdrawn from O\textsubscript{b}-vac to facilitate dissociation of O\textsubscript{2} at Ti\textsubscript{5c} may be responsible for the observation that not all O\textsubscript{b}-vac can be healed by exposure to O\textsubscript{2}.

\textit{r-TiO\textsubscript{2}(110) at low temperature}

The two dissociation channels (equations 1 and 2) were investigated as a function of sample temperature and sample reduction.\textsuperscript{101} O\textsubscript{b}-vac mediated dissociation was found between 100 and 150 K. O\textsubscript{2} dissociation via equation 2 sets in at $\sim$180 K and $\sim$142-180 K for less- and more-reduced TiO\textsubscript{2}(110) samples, respectively. Very recently, Lira et al.\textsuperscript{102} also examined an even more reduced sample, finding an onset temperature of 120 K for dissociation via equation 2.

Despite plentiful evidence for the existence of molecularly adsorbed O\textsubscript{2} at low temperature, this species has not been imaged with STM until very recently, when Scheiber et al.,\textsuperscript{103} Wang et al.,\textsuperscript{104,105} and Tan et al.\textsuperscript{106} successfully imaged O\textsubscript{2} molecules at the surface. Figures 15b-f, show five sequential scans of the surface following an exposure of 0.02 L O\textsubscript{2} at 80 K. O\textsubscript{2} molecules chemisorb at O\textsubscript{b}-vacs, manifesting in either the annihilation of the O\textsubscript{b}-vac intensity or by its replacement with a very faint intensity (see for example the squares in Figure 15b). Imaging at typical literature values (1-2 V,
0.1-1.0 nA) for TiO$_2$(110) results in rapid tip-induced dissociation of O$_2$ at the O$_b$-vac (equation 1). As such, imaging of O$_2$ requires very ‘gentle’ tunneling parameters. As can be seen in Figure 15b-f, even scanning at 1.0 V and 10 pA leads to dissociation.

Wang et al.$^{104}$ show that there is a clear correlation between tip-induced dissociation and $I_t$, as shown in Figure 16. This correlation was not seen in earlier work due to the comparatively high tunnelling currents used ($I_t = 4$-50 pA).$^{103}$ Figure 16 shows that even as low as $I_t = 1$ pA, $V_t$ must be below 1.2 V to avoid dissociation. Wang et al. suggested both inelastic electron tunnelling and field effects as possible mechanisms for the tip-induced dissociation.

Tan et al.$^{106}$ modelled the chemisorbed O$_2$ with DFT, finding that the molecule binds with its axis parallel to [1$\overline{1}$0], in line with previous calculations.$^{94,96,107-109}$ The simulated STM image reproduces the experimental data, giving a faint intensity between the bright Ti$_{5c}$ rows.

Apart from O$_{ad}$ resulting from O$_2$ dissociation in O$_b$-vac, Scheiber et al.$^{103}$ also observed O$_{ad}$ paired along [1 $\overline{1}$ 0]. The pair has a contrast distinct from two O$_{ad}$ adventitiously adsorbed in such positions. Repeat scanning of the same area leads to the conversion of the pair into a single O$_{ad}$ with the same contrast as other O$_{ad}$. As such, Scheiber et al.$^{103}$ propose that an explosion occurs over the O$_b$-vac, leading to two O$_{ad}$ adjacent in [1 $\overline{1}$ 0] without annihilation of the O$_b$-vac. One of the O$_{ad}$ then migrates into the O$_b$-vac, perhaps assisted by the tip.

Tan et al.$^{106}$ provide an alternative explanation for the paired O$_{ad}$. Their modelling predicts a tilted geometry only $\sim$0.15 eV more unstable than the flat-lying configuration, with a barrier of 0.5 eV and a return barrier of 0.35 eV. As the molecule can be tilted left
or right, Tan et al.\textsuperscript{106} propose that the STM excites the O\textsubscript{2} molecule via inelastic tunnelling so that it switches between flat, left-, and right-tilt configurations. Some evidence for this switching behavior is provided by placing the tip over the O\textsubscript{b}-vac position and measuring \(I_t\) vs. time. \(I_t\) has two values: the high (low) value was interpreted as the O\textsubscript{2} molecule being under (tilted away) from the tip. At 1.4 V, the dwell time in each position is about an order of magnitude lower than at 1.2 V. At 1.6 V, no switching can be discerned due to the rate being too fast for the bandwidth of the STM preamplifier. At some point, for the 1.6 V \(I_t\) vs. t trace, \(I_t\) goes permanently into the low current state, which was taken as dissociation to O\textsubscript{ad}.

By using extremely gentle tunnelling parameters \((V_t = 0.3\ \text{V}; \ I_t = 1\ \text{pA})\), Wang et al.\textsuperscript{104} discovered that O\textsubscript{2} chemisorbs on the Ti\textsubscript{5c} sites as well as in O\textsubscript{b}-vacs, as shown in Figure 17. The STM images were acquired at \(~50\ \text{K}, \ O_2\) exposure being at \(~50\ \text{K}\) and \(~130\ \text{K}\). No difference was found. Annealing the latter to 180 K, led to dissociation of O\textsubscript{2} in the O\textsubscript{b}-vacs. Annealing further (to 260 K) results in the dissociation of O\textsubscript{2} at Ti\textsubscript{5c} sites via equation 2, identifiable by the pairing of O\textsubscript{ad} in the [001] direction. As such, it was concluded that O\textsubscript{2} chemisorbed at O\textsubscript{b}-vacs and Ti\textsubscript{5c} are the precursors to O\textsubscript{ad} formed by equations 1 and 2, respectively.

Given that the images displayed by Lira et al.\textsuperscript{101,102} were taken at \(~1.25\ \text{V}\) and \(~0.1\ \text{nA}\) and that the transition temperatures found by Lira et al.\textsuperscript{101,102} are significantly lower than those reported by Wang et al.,\textsuperscript{104} it seems reasonably likely that at least some of the O\textsubscript{2} dissociation thought to be thermally-induced is in fact tip-induced.

Following low temperature adsorption of O\textsubscript{2} on \(\text{r-TiO}_2(110)\), an O\textsubscript{2} TPD peak can be found near 410 K. This peak has proven extremely difficult to assign. As the
adsorption temperature is increased, the amount of O\textsubscript{2} desorbed in the ~410 K state is reduced until the state disappears at an adsorption temperature of 180 K.\textsuperscript{110} Furthermore, after annealing to ~435 K, the 410 K TPD peak is not revived. To account for these observations, Henderson et al.\textsuperscript{110} suggest that at 120 K, up to three O\textsubscript{2} molecules per O\textsubscript{b}-vac adsorb. As the surface is heated, one O\textsubscript{2} per O\textsubscript{b}-vac dissociates. The remaining O\textsubscript{2} molecules desorb molecularly at ~410 K.

In contrast to this, Kimmel and Petrik find that just over two O\textsubscript{2} adsorb per O\textsubscript{b}-vac.\textsuperscript{111} Their surface was exposed to O\textsubscript{2} at 25 K. Dohnalek et al.\textsuperscript{112} have already shown that O\textsubscript{2} physisorbs at similar temperatures on a stoichiometric surface: at low coverage (\(\leq\) 0.5 ML), a peak is found at 70 K that shifts to 60 K with coverage. At intermediate coverage (0.5-1 ML), there is a dramatic shift to low temperature (40 K). Above this coverage, a new peak develops at ~41 K that saturates at ~1.5 ML.

On the \(r\)-TiO\textsubscript{2}(110) surface in question here, no physisorption is seen in the TPD below an exposure of 2 O\textsubscript{2}/O\textsubscript{b}-vac, yet the O\textsubscript{2} electron stimulated desorption (ESD) indicates a linear increase of O\textsubscript{2} coverage with O\textsubscript{2} exposure. At exposures above 2 O\textsubscript{2}/O\textsubscript{b}-vac, the integrated O\textsubscript{2} desorption coverage increases linearly up until a total coverage of ~1.5 ML, as expected based on the results of Dohnalek et al.\textsuperscript{112}

TPD was also taken up to 800 K. Below an exposure of 2 O\textsubscript{2}/O\textsubscript{b}-vac (1.8 O\textsubscript{2}/O\textsubscript{b}-vac), a very small peak was found at ~440 K, slightly offset from the ~410 K peak observed by Henderson et al.\textsuperscript{110} (Note for ease of comparison, this peak will be referred to as the “410 K” peak). Exposure above 2 O\textsubscript{2}/O\textsubscript{b}-vac leads to an increase in the “410 K” peak with the coverage rapidly saturating (~0.025 ML for an sample with 0.08 ML O\textsubscript{b}-vac).
vacs). From these data, the coverage of chemisorbed O\textsubscript{2} was found to be \textasciitilde2.35 O\textsubscript{2}/O\textsubscript{b-vac}.\textsuperscript{111}

O\textsubscript{2} ESD measurements suggest some chemical change upon annealing O\textsubscript{2}/TiO\textsubscript{2}(110) above 100 K. Annealing an O\textsubscript{2}/TiO\textsubscript{2}(110) sample with coverages \textless1 O\textsubscript{2}/O\textsubscript{b-vac} or \textasciitilde2 O\textsubscript{2}/O\textsubscript{b-vac} at 100 K gives rise to samples with similar ESD kinetics. However, annealing to 400 K leads to radically divergent behavior. For coverages \textless1 O\textsubscript{2}/O\textsubscript{b-vac}, there is almost no ESD signal, as the O\textsubscript{2} dissociates according to equation 1. The ESD signal is comparable to clean TiO\textsubscript{2}(110) where there is no O\textsubscript{2} at all. At \textasciitilde2 O\textsubscript{2}/O\textsubscript{b-vac}, the initial ESD signal is low compared to O\textsubscript{2}/TiO\textsubscript{2}(110) annealed to only 100 K but high compared to clean TiO\textsubscript{2}(110). Furthermore, the decay of the signal is much slower, such that after 40 s, it is the largest signal.

This last point can be emphasized by plotting the O\textsubscript{2} ESD signal integrated over a later electron exposure period (i.e. 40-160 s) against the annealing temperature, as shown in Figure 18. The signal increases above 200 K, peaks at 390 K, then decreases above 400 K. It was concluded that a new chemisorption state occurs with an onset of \textasciitilde200 K and was attributed to a tetraoxygen configuration predicted from DFT calculations.\textsuperscript{113} The signal attributed to tetraoxygen decreases rapidly between 400-500 K, suggesting that it decomposes and is therefore responsible for the “410 K peak” observed in TPD. As outward diffusion of Ti\textsubscript{int} is active at this temperature,\textsuperscript{114} reaction with Ti\textsubscript{int} means that not all of the oxygen is detected in the TPD peak.

Kimmel and Petrik attribute the discrepancy of their work (chemisorption of \textasciitilde2 O\textsubscript{2}/O\textsubscript{b-vac}) with the work by Henderson et al.\textsuperscript{110} (chemisorption of \textasciitilde3 O\textsubscript{2}/O\textsubscript{b-vac}) to the different method of estimating the coverage in the “410 K peak”. In the earlier work,\textsuperscript{110}
the amount of desorbing $O_2$ was not calibrated. Instead, the oxygen coverage was estimated from the $O_2$ sticking coefficient that decreases rapidly with exposure. In the work by Kimmel and Petrik,\textsuperscript{111} the amount of $O_2$ desorbed was calibrated with respect to the saturation coverage for physisorbed $O_2$ at $\sim 25$ K which is 1.5 ML.

Lira et al.\textsuperscript{101} suggest an alternative explanation for the discrepancy above. They also revisited the $O_2$ TPD experiment and find that different amounts of $O_2$ desorb in the “410 K peak” depending on the history of the sample [the amount of $O_2$ desorbed was calibrated by $O_2$ desorption from Pt(111)-O(2×2)]. On one sample, under light reduction conditions ($\sim 0.029$ ML O$_{b}$-vacs), they found that the “410 K” peak had a saturation coverage of $\sim 0.07$ ML. For the same sample under medium reduction conditions ($\sim 0.061$ ML O$_{b}$-vacs), the saturation coverage of the “410 K” peak did not change, remaining at $\sim 0.07$ ML. Another sample which was subjected to higher anneal temperatures throughout its history had an O$_{b}$-vac density of 0.083 ML and the saturation coverage of the “410 K” peak was about 5 times higher at 0.4 ML. (Subsequent experiments show that the coverage of the “410 K” peak eventually decreases with even more reduced samples.\textsuperscript{102}

As the “410 K” TPD peak clearly does not scale with the O$_{b}$-vac density, Lira et al.\textsuperscript{101} reject previous explanations for this peak whereby the main charge donor to $O_2$ was attributed to O$_{b}$-vac. In their new model, they suggest that $O_2$ dissociates via equations 1 and 2 as the temperature is ramped towards 400 K. At $\sim 360$-400 K, outward diffusion of Ti$_{int}$ is activated according to Zhang et al.\textsuperscript{114} at which point O$_{ad}$ and possibly $O_2$ will react with Ti$_{int}$ thereby creating a depletion layer of Ti$_{int}$. The desorption of $O_2$ in the “410 K” peak is thus attributed to a lack of charge at the surface.
While this model can explain the large coverage variation observed in the “410 K” TPD peak, the O\textsubscript{b}-vac model nevertheless seems important in describing the chemisorption of O\textsubscript{2}. Adsorption of 1 O\textsubscript{2}/O\textsubscript{b}-vac followed by annealing to 400 K prevents any further O\textsubscript{2} chemisorption.\textsuperscript{111} This was attributed to O\textsubscript{2} dissociating in the O\textsubscript{b}-vacs according to equation 1 and therefore removing O\textsubscript{b}-vac related adsorption sites. Furthermore, the O\textsubscript{b}-vac density can be increased with electron bombardment without affecting the Ti\textsubscript{int} density. In this way, Kimmel and Petrik increased their O\textsubscript{b}-vac density to 0.145 ML (from 0.08 ML) and did see an increase in the quantity of O\textsubscript{2} chemisorbed. Note that these measurements are not directly connected to the “410 K” TPD peak as they were made by measuring the exposure interval before the onset of O\textsubscript{2} physisorption at low temperature.\textsuperscript{111}

Alongside thermal and electron stimulated desorption, photon stimulated desorption (PSD) can also provide valuable insight into chemisorption states.\textsuperscript{115-122} Previously,\textsuperscript{8} we discussed PSD results from Lu et al.\textsuperscript{115} and Perkins and Henderson.\textsuperscript{118}

Briefly, Lu et al.\textsuperscript{115} found that the total oxygen desorption rate increases significantly as an O\textsubscript{2}/TiO\textsubscript{2}(110) surface is heated from 105 to 350 K, whereas the CO\textsubscript{2} photooxidation yield almost completely attenuates over the same temperature range. As such, two chemisorption states for O\textsubscript{2} were proposed (\(\alpha\) and \(\beta\)) with the \(\alpha\) state dominating at ~105 K. Annealing above ~200 K converted the \(\alpha\) to the \(\beta\) state. Due to the complicated decay kinetics, the \(\alpha\) state was later proposed to consist of two states,\textsuperscript{116} \(\alpha_1\) and \(\alpha_2\), then to follow a fractal rate law.\textsuperscript{117} By irradiating the O\textsubscript{2}/TiO\textsubscript{2}(110) surface with UV light prior to TPD, Perkins and Henderson\textsuperscript{118} (and later Sporleder et al.\textsuperscript{119}) showed that the “410 K” peak depletes, and therefore assigned this peak to the \(\alpha_2\) state.
Recently, Sporleder et al.\textsuperscript{119} have measured the velocity distributions of photodesorbed O\textsubscript{2}. They found two fast components and a slow component, as shown in Figure 19. The average translational energy of the slow component varied almost proportionally with the sample temperature (100-260 K) and was assigned to photoexcited O\textsubscript{2} that are trapped by the surface before thermally desorbing.

Annealing the O\textsubscript{2}/TiO\textsubscript{2}(110) sample to 260 K, then cooling back to 100 K before taking the velocity measurements does not change the distributions, indicating that species which transform irreversibly do not contribute to the photodesorption yield. This rules out photodesorption from dissociated O\textsubscript{2} and it was therefore concluded that two separate chemisorbed O\textsubscript{2} states are responsible for the two fast components, for example O\textsubscript{2} at O\textsubscript{b}-vacs, O\textsubscript{2} adjacent to O\textsubscript{b}-vacs, or O\textsubscript{2} at Ti\textsubscript{5c} sites stabilized by Ti\textsubscript{int}. As the velocity distributions show no dependence on photon energy over the range studied (3.45-4.16 eV), this suggests a substrate-mediated, hole-capture desorption mechanism.\textsuperscript{7,115,120}

If the O\textsubscript{2} chemisorption changed state from $\alpha \rightarrow \beta$, then this should also be reflected in the velocity distribution of the pre-annealed (260 K) sample. As such, this thermal transformation was also ruled out. Nevertheless, in a separate experiment, Sporleder et al.\textsuperscript{119} also observed, qualitatively, the behavior reported by Lu et al.\textsuperscript{115} described above. To account for this, Sporleder et al.\textsuperscript{119} suggest that the desorption kinetics must change but not the initial binding states of the photoactive O\textsubscript{2}.

Petrik and Kimmel also investigated the PSD of O\textsubscript{2} on TiO\textsubscript{2}(110) at low temperature ($\sim$28 K).\textsuperscript{121,122} $^{18}$O\textsubscript{2} was adsorbed at 28 K and the sample was heated to 100 K, while measuring the $^{18}$O\textsubscript{2} yield. The sample was then irradiated for 30 s at 28 K to
obtain the integrated $^{18}\text{O}_2$ PSD. As can be seen in Figure 20, the PSD signal increases linearly up to a coverage of $1\, \text{O}_2/\text{O}_b$-vac, after which the PSD signal still increases linearly but with a much steeper slope, up to $2\, \text{O}_2/\text{O}_b$-vac after which the signal plateaus.

There are two simple explanations for the increased PSD yield above a coverage of $1\, \text{O}_2/\text{O}_b$-vac. The second $\text{O}_2$ may simply have a larger PSD yield. Alternatively, addition of a second molecule could also increase the PSD yield of the first molecule. Petrik and Kimmel showed that the latter case prevails. A small coverage of $^{18}\text{O}_2$ was chemisorbed and the integrated $^{18}\text{O}_2$ PSD was compared with the same amount of $^{18}\text{O}_2$ chemisorbed together with a larger amount of $^{16}\text{O}_2$: a much larger signal was obtained for $^{18}\text{O}_2$ with almost no $^{16}\text{O}^{18}\text{O}$ being detected. (Interestingly, physisorbed $^{16}\text{O}_2$ exchanges significantly with chemisorbed $^{18}\text{O}_2$.)

The measurements of Petrik and Kimmel also indicate that a maximum $\sim 40\%$ of chemisorbed $\text{O}_2$ desorbs during UV irradiation. Re-adsorbing $\text{O}_2$ onto this UV irradiated surface shows that there is a reduction of available sites, which was taken to mean that the $\text{O}_2$ that remained after irradiation is partitioned between photoblind $\text{O}_2$ and photodissociated $\text{O}_2$.

They propose that at a coverage of $1\, \text{O}_2/\text{O}_b$-vac, one $\text{O}_2^{2-}$ chemisorbs in the vacancy whereas at a coverage of $2\, \text{O}_2/\text{O}_b$-vac, two $\text{O}_2$ molecules chemisorb at or near the vacancy. Photo-induced holes reacting with $\text{O}_2^{2-}$ ($\text{O}_2$) lead to photodesorption with a low (high) probability. Additionally, Petrik and Kimmel propose that photoexcited electrons promoted into the conduction band by UV excitation react with $\text{O}_2^{2-}$ ($\text{O}_2$) leading to $\text{O}_2$ dissociation or creation of photoblind species with a high (low) probability.
As described above, Wang et al.\textsuperscript{104} used STM with gentle conditions to image molecular O\textsubscript{2} adsorbed at O\textsubscript{b}-vac and at Ti\textsubscript{5c} sites. As such, they were also able to examine the effect of UV irradiation on these O\textsubscript{2} species.\textsuperscript{105} They found that O\textsubscript{2} at O\textsubscript{b}-vacs were active for photodissociation and O\textsubscript{2} at Ti\textsubscript{5c} sites were active for photodesorption.

The coverage of photodissociated, photodesorbed, and undissociated O\textsubscript{2} were tracked as function of coverage, as shown in Figure 21. The amount of photodesorbed and photodissociated species both increase linearly at low coverages, with no unreacted O\textsubscript{2}. Above a critical coverage, photodissociation is nearly quenched and undissociated O\textsubscript{2} appears and thereafter also increases linearly with coverage. Wang et al.\textsuperscript{105} connect this undissociated O\textsubscript{2} with the photoblind species identified by Petrik and Kimmel.\textsuperscript{121,122} At a coverage near 1 O\textsubscript{2}/O\textsubscript{b}-vac, the partition of photo -desorbed, -dissociated, and -blind O\textsubscript{2} is quantitatively similar to the earlier measurement.\textsuperscript{121,122}

Wang et al.\textsuperscript{105} suggest that the arrest in the O\textsubscript{2} dissociation rate and the formation of photoblind O\textsubscript{2} both arise from the imbalance in the consumption of photo-induced electrons and holes. As the concentration of O\textsubscript{2} at O\textsubscript{b}-vacs is greater than that at Ti\textsubscript{5c}, a larger number of electrons are consumed in the dissociation compared with holes consumed in photodesorption. As a result there is an accumulation of holes, which beyond a critical coverage recombine effectively with electrons, thus inhibiting the photodissociation. Likewise, photoblind O\textsubscript{2} can result from reaction of O\textsubscript{2}\textsuperscript{2-} with excess holes to form O\textsubscript{2}\. In support of the creation of a ‘new’ O\textsubscript{2} species, Wang et al. found that deliberately scanning over these undissociated O\textsubscript{2} with ‘harsh’ tunnelling parameters (1.8 V, 150 pA) did not lead to their dissociation.
Whilst the work of Wang et al.\textsuperscript{105} indicates that O\textsubscript{2} adsorbed at Ti\textsubscript{5c} must be one of the photodesorbed species measured previously\textsuperscript{115,119} (and therefore may be one source of the “410 K” peak in TPD at coverages \( \leq 1 \) O\textsubscript{2}/O\textsubscript{b-vac}), the other species identified by Sporleder et al.\textsuperscript{119} is yet to be identified. As Sporleder et al.\textsuperscript{119} used high O\textsubscript{2} exposures, it is unknown whether both species exist at lower coverage.

The work of Kimmel and Petrik suggest that the new species should appear at coverages \( > 1 \) O\textsubscript{2}/O\textsubscript{b-vac}.\textsuperscript{121,122} This species could arise from charge sharing between O\textsubscript{2} adsorbed at Ti\textsubscript{5c} or may yet involve a second O\textsubscript{2} molecule adsorbed at the O\textsubscript{b-vac}.

In the work of Wang et al.,\textsuperscript{105} the coverage of O\textsubscript{2} at Ti\textsubscript{5c} sites increases linearly with coverage, accounting for \( \sim 10\% \) of the total coverage at \( \sim 1 \) O\textsubscript{2}/O\textsubscript{b-vac}. If the increase in coverage remains linear at higher coverage, then at the coverage of 2.35 O\textsubscript{2}/O\textsubscript{b-vac}, \( \sim 0.23 \) of the O\textsubscript{2} molecules would be at Ti\textsubscript{5c} sites. On the basis that \( \sim 2.35 \) O\textsubscript{2} chemisorb per O\textsubscript{b-vac},\textsuperscript{111} it may be that 2 O\textsubscript{2} do indeed adsorb at O\textsubscript{b-vac} with the excess adsorbing at Ti\textsubscript{5c} sites.

Tan et al.\textsuperscript{106} probed the evolution of O\textsubscript{2} chemisorption and dissociation as a function of O\textsubscript{2} exposure with STM. In Figures 15b-f, we saw five sequential scans of the surface following an exposure of 0.02 L O\textsubscript{2}. In Figure 15g, 0.12 L O\textsubscript{2} was added so that each O\textsubscript{b-vac} is filled with O\textsubscript{2} (a small number have already dissociated). Figure 15h shows the resulting image after another 0.2 L O\textsubscript{2} is added: it is almost identical to Figure 15g, except there are a small number of new O\textsubscript{ad} paired in [001] which arise from tip-induced dissociation of O\textsubscript{2} at Ti\textsubscript{5c} sites. Remarkably, the O\textsubscript{2} in the O\textsubscript{b-vacs} are now stable to repeated scanning at 1.0 V and even to high bias scanning up to 2.2 V. As the cumulative exposure to O\textsubscript{2} is 0.34 L for Figure 15h compared to 0.14 L in Figure 15g,
Tan et al.\textsuperscript{106} tentatively suggest that two O\textsubscript{2} may be adsorbed at each O\textsubscript{b}-vac in Figure 15h, which would support the interpretation of Kimmel and Petrik.\textsuperscript{121,122}

Significant progress has been made in our understanding of the adsorption of O\textsubscript{2} on \(\text{r-TiO}_2(110)\) since our previous review,\textsuperscript{8} although a number of key questions remain. At low temperature, two molecularly-adsorbed O\textsubscript{2} species were revealed in STM images: O\textsubscript{2} at O\textsubscript{b}-vac.\textsuperscript{103-106} O\textsubscript{2} at Ti\textsubscript{5c} sites.\textsuperscript{104,105} It is a reasonable assumption that these species are the precursors to the dissociated O\textsubscript{ad} found near O\textsubscript{b}-vacs,\textsuperscript{92-93} and the dissociated pairs of O\textsubscript{ad} not spatially-correlated with O\textsubscript{b}-vac, respectively.\textsuperscript{31,98} While O\textsubscript{2} dissociation in O\textsubscript{b}-vacs was in-line with most expectations, O\textsubscript{2} dissociation at Ti\textsubscript{5c} was not consistent with calculations.\textsuperscript{31,96,99,100} Some additional supply of electrons whether from Ti\textsubscript{int} (ref 31) or from O\textsubscript{b}-vac (ref 98) was required in order to make the reaction exothermic. Variable temperature STM revealed that O\textsubscript{2} dissociates at O\textsubscript{b}-vac by 180 K and O\textsubscript{2} dissociation at Ti\textsubscript{5c} occurs by 260 K.\textsuperscript{104}

As Wang et al.\textsuperscript{105} were able to image both molecularly adsorbed species, they were able to directly observe a differential response to UV irradiation: O\textsubscript{2} at O\textsubscript{b}-vac were active for photodissociation and O\textsubscript{2} at Ti\textsubscript{5c} were active for photodesorption. In ensemble-averaged, photodesorption experiments, the presence of two chemisorbed O\textsubscript{2} species have been identified from the velocity distributions,\textsuperscript{119} one of which must be O\textsubscript{2} at Ti\textsubscript{5c}.\textsuperscript{105} The other O\textsubscript{2} species active for photodesorption is yet to be identified but may be related to the increased PSD yield observed by Petrik and Kimmel with coverages above 1 O\textsubscript{2}/ O\textsubscript{b}-vac. Given that Sporleder et al.\textsuperscript{119} used saturation coverages of O\textsubscript{2}, it would be illuminating to revisit the experiment using coverages below 1 O\textsubscript{2}/ O\textsubscript{b}-vac: is only one
chemisorbed O\textsubscript{2} states detected? If so, is the additional chemical state due to the presence of a second O\textsubscript{2} molecule adsorbed at the O\textsubscript{b-}vacs, as tentatively suggested by Tan et al.\textsuperscript{106}

The origin of the “410 K” TPD peak is close to being understood. Lira et al.\textsuperscript{101,102} showed that the intensity depended on the sample history or level of reduction and was not correlated to O\textsubscript{b-vac} density. They propose that desorption of O\textsubscript{2} in this peak is due to a lack of charge at the surface as the Ti\textsubscript{int} is consumed as the temperature ramps towards 400 K.

Previously, Perkins and Henderson,\textsuperscript{118} and more recently Sporleder et al.\textsuperscript{119} have shown that the 410 K peak can be entirely depleted by UV illumination of the sample prior to the TPD measurement. As such, O\textsubscript{2} that can be photodesorbed was connected with the 410 K peak. It turns out that this, in itself, is not enough to connect these two species as the photodissociated species would also be rendered inactive for TPD because isotopic measurements indicate that the desorption is molecular.\textsuperscript{110} However, because Perkins and Henderson,\textsuperscript{118} were able to replenish the TPD peak by re-adsorbing O\textsubscript{2}, this rules out that O\textsubscript{2} adsorbed at O\textsubscript{b-vac} contribute to the “410 K” peak. This means that one or both of the O\textsubscript{2} states active for photodesorption must be the origin of the “410 K” peak.

\[ h\text{-TiO}_2(110) \]

The adsorption of O\textsubscript{2} on \textit{h-TiO}_2(110) has been intensively explored recently. From STM results, Wendt et al.\textsuperscript{31} suggested that for exposures up to \(~4\) L, O\textsubscript{2} removes the OH\textsubscript{b}, apparently without leaving any reaction products. This reaction was also studied
by Zhang et al.\textsuperscript{124} However, prior to adsorption of O\textsubscript{2}, they flashed the sample to \(\sim350\) K in order to remove any molecular water. This almost entirely supresses the mobility of OH\textsubscript{b} from frame to frame (\(\sim2\) mins/frame). Upon exposure to O\textsubscript{2}, the OH\textsubscript{b} were removed also with no apparent product (Figure 22), in line with the earlier work.\textsuperscript{31} However, the frame-to-frame mobility of the OH\textsubscript{b} increased dramatically, from 0 to \(\sim48\%\). As molecular water is known to facilitate the diffusion of water,\textsuperscript{8,9,125} this was taken as evidence that water is the reaction product. TPD and ESD support this conclusion. Note that the OH\textsubscript{b} cannot be entirely removed (\(\sim0.007\) ML OH\textsubscript{b} remain in the work of Zhang et al.\textsuperscript{124}).

The overall reaction mechanism proposed by Zhang et al.\textsuperscript{124} is as follows:

\[4\text{OH}_b + \text{O}_2 \rightarrow 4\text{O}_b + 2\text{H}_2\text{O}, \quad \text{.................................................................(3)}\]

which is the sum of four other reactions:

\[\text{OH}_b + \text{O}_2 \rightarrow \text{O}_b + \text{HO}_2 \quad \text{.................................................................(4)}\]
\[\text{OH}_b + \text{O}_{ad} \rightarrow \text{OH}_t + \text{O}_b \quad \text{.................................................................(5)}\]
\[\text{OH}_b + \text{HO}_2 \rightarrow \text{O}_b + \text{O}_{ad} + \text{H}_2\text{O} \quad \text{.................................................................(6)}\]
\[\text{OH}_b + \text{OH}_t \rightarrow \text{O}_b + \text{H}_2\text{O}. \quad \text{.................................................................(7)}\]

Rather than this cumulative reaction, on the basis of STM movies, Matthiesen et al.\textsuperscript{126} propose a reaction mechanism whereby O\textsubscript{2} reacts with successive OH\textsubscript{b}, until a pair of water molecules is formed, as shown in Figure 23.
Exposure of $O_2$ beyond that required to react off the $OH_b$ leads to the appearance of two types of bright spots in the STM image. The majority (~80%) were assigned to $OH_t$ by Zhang et al.\textsuperscript{124} with the minority species as yet unassigned. Similar results were obtained by Wendt et al.\textsuperscript{31} although no assignment of the species was made.

Exposure of a partially hydroxylated TiO$_2$(110) surface to $O_2$ has also been investigated recently. As one would expect, Du et al.\textsuperscript{127} and Zhang et al.\textsuperscript{124} observed all the reaction steps described above for $O_2$ on $r$-TiO$_2$(110) and $h$-TiO$_2$(110), i.e. equations 1, 2, 4-7. However, the overall evolution of these species reveals some interesting behavior.

The coverage of species identified in STM is plotted against the $O_2$ exposure in Figure 24. $O_b$-vacs and $OH_b$ are gradually consumed up to $5.6 \times 10^{15}$ $O_2$/cm$^2$ (~10 L). At the same time, $O_{ad}$ rises fairly quickly as there are two channels (equations 1 and 2). Further exposure to just a small amount of $O_2$ leads to complete attenuation of $O_b$-vac and $O_{ad}$. $OH_b$ reduces only slightly and ($HO_2$ + $OH_t$) rises slowly throughout the $O_2$ exposures examined. As can be seen in Figure 24, at the same dosing step as the $O_b$-vac/$O_{ad}$ annihilation, there is a massive increase in the mobility of the features. As such, the rapid annihilation was attributed to water catalysis of equations 5 and 7.

At much higher $O_2$ exposures (~90 L), Papageorgiou et al.\textsuperscript{40} found a different behavior. A number of small, bright spots can be seen on the Ti$_{5c}$ sites (bright rows) in the STM image recorded after the $O_2$ exposure (Figure 25). As the bright spots have a uniform appearance, it was concluded that they are due to one final product. Prior to reaction with $O_2$ there were about 72 $OH_b$ species and 38 $O_b$-vacs. Given that there are 118 bright spots after and only 72 H atoms prior to the $O_2$ exposure, this seems to rule out
the possibility that the new species are OH, (or indeed any H-containing product). The corollary is that the bright spots correspond to O, in line with the conclusions of Henderson et al. \(^\text{128}\)

On the basis that dissociation of each O requires two electrons per O, there is a discrepancy with the results of Henderson et al. \(^\text{128}\) O-vacs can supply two electrons (2Ti\(^{3+}\)) and OH one (1Ti\(^{3+}\)), so one would only expect 74 O to form from 38 O-vacs and 72 OH. As such, an additional supply of electrons is required to form the extra O, and Ti\(_{\text{int}}\) are suggested to donate extra charge to the O-vac and OH. \(^\text{40}\) When this extra charge is transferred to adsorbates, O is found to be by far the most stable O\(_x\)H\(_y\) (x = 1-2, y = 0-2) species. In the absence of extra charge, H\(_2\)O\(_2\) is the most stable. \(^\text{40,129}\) The idea of charged O-vac seems to be supported by current imaging tunneling spectroscopy (CITS) measurements where the current map at -2 V is not well described by calculations of the neutral O-vac. \(^\text{40}\) It should be noted that a (small) D ESD signal remains up to exposures well beyond 90 L, and therefore an explanation is still needed to account for the H-containing species left on the surface. \(^\text{124}\)

Reoxidation was explored in some detail in ref 8 for the (110) surface. \(^\text{130-132}\) Briefly, at high temperature O reacts with Ti\(_{\text{int}}\) that diffused to the surface at high temperature (at \(~500\) K or above). At the lower temperature range, a cyclic (1\(\times\)2)\(\rightarrow\)(1\(\times\)1)\(\rightarrow\)(1\(\times\)2) growth occurs (layer-by-layer) whereas at higher temperatures, the surface grows laterally (step-flow) at the expense of the layer-by-layer growth. \(^\text{130,132}\)

Tao et al. \(^\text{133}\) applied this reoxidation procedure to the TiO\(_2\)(011)(2\(\times\)1) surface. A 2D structure previously assigned to Ca-segregation was observed in STM, as shown in Figure 26. Ca segregation was ruled out by the lack of correlation between the
appearance of the new structure in STM with that of Ca in Auger electron spectroscopy (AES) spectra and by growing TiO$_2$ homoepitaxially by depositing Ti in a reactive oxygen environment at mild temperatures. In the latter case, this led to the same structure observed by reoxidation. Of particular interest to photocatalysis, this new structure was shown by valence band photoelectron spectroscopy (PES) and scanning tunneling spectroscopy (STS) to have a reduced band-gap, bringing it into the visible region for band-gap excitation.

3.2 Hydrogen adsorbates

TiO$_2$ photocatalyses the splitting of water, and it is this photoactivity which underpins the use of TiO$_2$ in numerous technologies such as self-cleaning surfaces, air/water purification devices, and novel solar cells. Moreover, water is present in the vast majority of technological applications of TiO$_2$. As such, the interaction of water with TiO$_2$ surfaces is a crucial area of research.

Water on rutile surfaces has has been extensively reviewed by Henderson in 2002 and summarized again in Diebold’s review. For TiO$_2$(110), the dissociation of water at O$_b$-vacs on TiO$_2$(110) has been described in detail recently, and we will focus on the most recent developments which include the dissociation on the perfect surface as well as devoting time to water layers and the structure under ambient and liquid environments. Water on the rutile (011) face will also be reviewed but for information on the other surfaces, the reader is referred to the earlier reviews.

3.2.1 Water
Water Dissociation

It is now well-established that water dissociates in the O$_b$-vacs on TiO$_2$(110) forming two OH$_b$ species according to the scheme shown in Figure 27 and this was discussed in detail in our previous review.$^8$

One of the outstanding questions from that review is the matter of water dissociation in the absence of O$_b$-vac. Theoretical calculations still do not give a clear picture and it has been a hotly debated topic.$^8$

One of the difficulties of obtaining definitive experimental data is that of finding a scheme to prepare perfect surfaces, free of O$_b$-vacs so that their effects do not have to be disentangled. One suggestion was to use an STM tip operated at high voltage to remove hydrogen from a full-hydroxylated surface. However, such a method can only be applicable to scanning probes. It turns out that exposing the hydroxylated surface to O$_2$ can create an almost perfect surface, s-TiO$_2$(110), as discussed in Section 3.1.$^{31,124}$ This must be carefully done, as over exposure to O$_2$ will create O$_x$H$_y$.

Walle et al.$^{138}$ create s-TiO$_2$(110) by exposing a hydroxylated surface to O$_2$ incrementally whilst monitoring the OH 3$\sigma$ peak in valence band PES.$^{138}$ A small fraction of OH cannot be removed (just over 0.01 ML). A monolayer was prepared on both r-TiO$_2$(110) and s-TiO$_2$(110) by annealing a multilayer to ~210 K. The O 1$s$ PES spectra are almost identical, having components from molecular water and OH. Figure 28 shows the effect of annealing the water multilayer on the s-TiO$_2$ sample from 160 K. The OH peak intensity stays the same up to 210 K and has desorbed by 295 K, which is consistent with previous experiments. This indicates that the OH is not in the same state as the OH$_b$ formed from dissociation in O$_b$-vac, which desorbs at a much higher
temperature (~490 K). Walle et al.\textsuperscript{138} suggest a mixed OH–H$_2$O phase similar to that predicted by Lindan et al.\textsuperscript{139} and more recently invoked by Wendt et al.\textsuperscript{125} to explain the water-assisted diffusion across [001] rows.

Duncan et al.\textsuperscript{140} exploited the chemical-state specificity of photoelectron diffraction (PhD) to demonstrate that at temperatures of ~190-200 K, exposure of TiO$_2$(110) to water does indeed lead to the formation of two types of OH species, terminal OH (OH$_t$) and OH$_b$ together with molecular water. The Ti–OH bond lengths found for these two species are 1.85 ± 0.08 Å for OH$_t$ and 1.94 ± 0.07 Å for OH$_b$. The bond length of OH$_b$ compares well with an earlier PhD measurement (1.97 Å), following exposure to atomic hydrogen (see Section 3.2.2 later).\textsuperscript{141} Furthermore, in calculations that model Ti–OH$_t$ coexisting with Ti–OH$_b$ on a perfect surface, bond lengths of 1.87 and 2.06\textsuperscript{142} and 1.63 and 1.87 Å,\textsuperscript{143} are reported, respectively, for OH$_t$ and OH$_b$. In both cases, the Ti–OH$_t$ bond is significantly shorter, in line with the PhD measurement.

These results indicate there is another pathway for water dissociation on TiO$_2$(110) that does not involve O$_b$-vacs. However, little is known about the newly identified pathway. On suggestion is that dissociation occurs on the perfect surface, perhaps at Ti$_{5c}$ sites. Even though Walle et al.\textsuperscript{138} do indeed use a nearly-perfect surface, their own valence band PES data show a BGS connected to this surface.\textsuperscript{38} On the other hand, the latest calculations that employ truly perfect surfaces, predict molecular adsorption of water.\textsuperscript{144}

\textit{Water Layers}
As described in our previous review, there is still some debate over the structure of water layers that form at low temperature. Briefly, work function measurements indicate that the first layer should adsorb with O facing down and H up, implying adsorption onto Ti$_5$ sites, later verified by STM and PhD. As no further work function changes are observed after the first layer, the implication is that the second layer lies parallel to the surface. High resolution electron energy loss spectroscopy (HREELS) indicated hydrogen bonding within the second layer but not to the first layer. However, by observing interlayer H-D mixing, evidence was found for H-bonding between the two layers.

These observations seem to have been reconciled by a very recent reflection-absorption infra-red spectroscopy (RAIRS) experiment that used s- and p-polarized light incident along [001] and [1 $\bar{1}$ 0] together with ab initio molecular dynamics simulations. Figures 29 and 30 show the proposed models for one and two layers of water, respectively, together with the RAIRS spectra, calculated vibrational densities of state (VDOS), and spectra simulated from the VDOS.

The IR peak at 2605 cm$^{-1}$ for D$_2$O corresponds to that seen at 3505 cm$^{-1}$ in HREELS. As this peak does not shift or attenuate in going from 1 ML to 2 ML, it was concluded that there was no H-bonding. A dangling OH bond (i.e. not H-bonded) would be expected to lie normal to the surface but that is not the observation in RAIRS: the peak is observed in s-polarized spectra and is a positive absorption in p-polarized spectra, indicative of a parallel geometry. Moreover, the bond responsible for this peak is similar in the first and second layers. Likewise, a recent calculation of the vibrational
frequency spectra showed that the peak that results from H-bonding does not shift in going from one to two water layers.\textsuperscript{144}

The monolayer structure proposed by Kimmel et al.\textsuperscript{149} can also be thought of as an array of 1D rows. Indeed, 1D rows have been observed in low temperature STM variously by Brookes et al.\textsuperscript{29} and Matthiesen et al.\textsuperscript{150} Most recently, these 1D layers have been investigated by Lee et al.\textsuperscript{151} Their STM measurements show that at 50 K, isolated water monomers adsorb on top of Ti$_{5c}$ atoms. However, as the coverage increases, water molecules start to form 1D chains along the [001] direction. Thermal annealing at 190 K leads to the formation of longer chains (up to \textasciitilde 24 molecules long) facilitated by the diffusion of water on the surface.\textsuperscript{150} (Note that in the earlier work by Matthiesen et al.\textsuperscript{150} water tetramers and higher multimers were found to be unstable, and it is not clear what the reason is for the discrepancy).

\textit{Water at ambient pressures}

Previously,\textsuperscript{8} we showed results from ambient pressure PES that indicate exposure of TiO$_2$(110) to water at relatively high pressures leads first to the formation of OH$_b$, which nucleate H$_2$O-OH$_b$ complexes, that themselves act as nucleation points for further water adsorption.

TiO$_2$(110), (100), and (001) surfaces were measured with polarization modulation IR external reflection spectroscopy in atmospheric conditions.\textsuperscript{152} The p- and s-polarizations are rapidly modulated and their difference measured in real time. The idea is that for 3D isotropic components, such as water vapour and bulk water, the signal will be cancelled out. For the (110) and (100) surfaces, a single peak is observed at 3279 cm$^{-1}$ that was assigned to an O–H stretch. This peak was significantly downshifted from the
UHV measurement of 3690 cm$^{-1}$ in HREELS, attributed to H-bonding with the surrounding water. This peak was absent in the (001) surface and the authors conclude that this is due to a lack of O$_b$ species on that surface. In other words, the OH only forms at O$_b$ sites present on the (110) and (100) faces but not the (001).

Takahashi and Yui used these samples to examine the mechanism for UV-induced hydrophilicity. One suggestion in the literature is that UV induces the formation of OH and that makes the surface more hydrophilic,$^{153}$ whereas other research points to photo-oxidation of adsorbed hydrocarbons.$^{154}$ Water contact angles indicated that each surface became more hydrophilic after UV irradiation. However, there is no significant change in the polarization modulation infrared external reflection spectroscopy (PM-IER) spectra (the peaks for (110) and (100) shift to 3277 cm$^{-1}$ under irradiation but revert to their original positions when the irradiation was stopped) indicating that another mechanism independent of the number of OH is responsible for the hydrophilicity. Note that there are no details of the initial sample preparation procedures.$^{152}$ These conclusions of Takahashi and Yui are in line with the conclusions of Zubkov et al.$^{154}$ who showed no change in the IR spectroscopy of TiO$_2$ powders upon UV irradiation.

**Liquid water**

There have been numerous studies of TiO$_2$(110) under liquid water, some of which are reviewed in 155 together with other water-mineral interfaces. Uetsuka et al.$^{156}$ prepared samples in UHV by sputtering/annealing, then transferred these samples in to a beaker of water for 5 mins. After re-entry into UHV, the sample was imaged with STM. The sample contained pits which were 1-3 layers deep in contrast to a previous contact
AFM measurement of polished TiO$_2$(110) in liquid water which saw no erosion.$^{157}$ More recent NC-AFM images recorded under water from sputter/annealed surfaces showed some evidence of erosion but not conclusively.$^{158}$ For example, even after 3 hrs immersion in liquid water, any erosion was not significant. An air-annealed sample (1273 K for 24 hrs) showed no evidence of erosion under water.

X-ray crystal truncation rods (CTR) have been measured for a TiO$_2$(110) sample immersed in water.$^{159}$ The sample was prepared in four steps: (1) ultrasonic cleaning successively in: deionized water, 1% HNO$_3$, high-purity methanol, deionized water, 10% H$_2$O$_2$ and again, deionized water; (2) annealing of the vacuum-dried crystals at 1373 K for 1 hr in an air furnace; (3) hydrothermal reaction in deionized water in a Teflon cup housed within a pressure vessel at 493 K for 12 hrs and (4) a final ultrasonic treatment in deionized water.

Both O$_b$ and terminal O (O$_t$, above Ti$_{5c}$ sites) are fully occupied. The Ti$_{5c}$–O$_t$ distance is 2.13 ± 0.03 Å. This is significantly longer than a typical Ti–O bond in the bulk (1.98 Å) but also shorter than the Ti$_{5c}$–OH$_2$ bond found in PhD measurements of molecularly adsorbed water (2.21 ± 0.02 Å).$^{146}$ DFT calculations at low coverage predict a short bond for Ti$_{5c}$–OH$_t$ as well, although those at 2 ML which have a mixture of dissociated and molecular water find bond lengths of 1.98 Å and 2.19 Å. As such, Zhang et al. propose that 30% of the water in the O$_t$ position is dissociated with the rest being molecular water. There are an additional three water adsorption locations around the A4, A3, and A1 sites at a similar height above the O$_t$ site, as shown in Figure 31.
At the rutile (110)-water interface, the Ti below O_b rows relax outwards and the Ti below the O_1 row relax inwards, with their relaxation amplitudes decreasing from 0.05 Å at the surface to ~0.01 Å four Ti layers down.

\textit{TiO}_2(011)

The adsorption of water on TiO$_2$(011)(2\times1) has been rather well studied recently. Valence band PES show that the 3\sigma state indicative of hydroxyl appears at low water exposures.$^{160,161}$ Thereafter, states arise from molecular water. Temperature dependent PES measurements indicate that molecular water desorbs around 200 K whereas hydroxyls remain up to \sim 310 K. On the basis of DFT calculations on the titanyl model (see Section 2.2), it was suggested that water dissociated at the mono-coordinated oxygen sites after which a mixed molecular-dissociated monolayer formed.$^{160,161}$

He et al.$^{162}$ have re-interpreted those data based on DFT calculations of the more recently-proposed model (see Section 2.2 for more details).$^{60-63}$ At the regular surface sites, only molecular adsorption occurs, dissociation being limited to O-vacs.

Figure 32 shows STM images of the clean surface and after exposure to water. In Figure 32b, water was dosed at room temperature whereas in c and d, low temperatures were used (\sim 130 and 115 K). At room temperature, bright spots appear on the zigzag rows and as they often appear in pairs (see the inset in Figure 32c as well), they were identified as OH formed from water dissociation. DFT calculations show that it is easier to remove top two-fold O atoms (O$_{2c}$) rather than side O$_{2c}$. Likewise, water dissociation is easier on the top O$_{2c}$, compared to side O$_{2c}$ and this is reflected in the relatively rare appearance of side OH in STM images.$^{162}$
At low temperature, clusters of bright spots appear which were assigned as water-containing and further exposure to water leads to 1D chains. The DFT calculations indicate that while water can only physisorb weakly to the perfect surface, it can form an H-bond with a top OH. A second water molecule can then form H-bonds with both the H$_2$O–OH complex and an adjacent side O$_{2c}$. At a coverage of ~0.22 ML at 170 K, the 1D clusters are ~100 Å in length. Increasing the sample temperature to 185 K leads to most of the chains disappearing, leaving just a few clusters, consistent with the earlier PES work.

Calculations suggest that in liquid water, the unreconstructed (1×1) TiO$_2$(011) structure is stabilized by a monolayer of water tightly bound to the under-coordinated Ti sites at the surface.\textsuperscript{163} It was posited that the (2×1) reconstructed surface could be ‘back’ constructed to the (1×1) surface in an aqueous environment. Although this is yet to be tested experimentally, some evidence has been given for adsorbate-induced restructuring of the (2×1) surface, including after exposure to water above 10$^{-3}$ Torr.\textsuperscript{164}

3.2.2 Atomic Hydrogen

Suzuki et al.\textsuperscript{165} deposited atomic hydrogen onto the TiO$_2$(110) surface by dosing H$_2$ (1 × 10$^{-8}$ mbar) with a hot filament (~1800 K) in front of the surface. In STM, they found bright spots between the bright Ti$_{5c}$ rows that increased with the exposure time. The coverage saturated at 0.23 ML with no ordering.

Using helium atom scattering (HAS), Kunat et al.\textsuperscript{166} find an ordered (1×1) hydrogen overlayer. Well-separated peaks in ancillary He-TPD suggested that there were two chemically distinct H species. As such, they tentatively proposed that at low
temperature (300 K), H adsorbs on the O\textsubscript{b} sites and the Ti\textsubscript{5c} sites. At higher temperature (500 K), only the OH\textsubscript{b} are present.

HREELS indicates a loss that could be assigned to O–H stretching (Figure 33),\textsuperscript{167} consistent with that found after water dissociation to OH\textsubscript{b}. In contrast to the earlier suggestion,\textsuperscript{166} Ti–H modes could not be found in HREELS. STM images show an ordered array of spots always with gaps so that the maximum coverage obtained was 0.7 ML. Yin et al.\textsuperscript{167} could only find these rows with exposure two orders of magnitude greater than that by Suzuki et al.\textsuperscript{165} and therefore speculate that the earlier work included OH\textsubscript{b} from water dissociation.

TPD taken from their H/TiO\textsubscript{2} surface surprisingly did not yield an H\textsubscript{2} peak or a significant water peak,\textsuperscript{167} although the HREELS clearly shows the depletion of the signal from O–H stretching. DFT calculations give an activation energy of only 1.11 eV to form subsurface OH, compared to 2.64 eV for recombinative desorption as H\textsubscript{2}. As such, it was concluded that annealing H/TiO\textsubscript{2} leads to subsurface migration of H.\textsuperscript{167} Interestingly, a surface covered with up to 0.5 ML OH\textsubscript{b} was created by UV-induced desorption of trimethylacetate from a TiO\textsubscript{2}(110) surface adsorbed with trimethylacetic acid. Quantitative analysis of the H\textsubscript{2}O TPD ruled out this subsurface migration.\textsuperscript{168} The reason for the discrepancy with the work of Yin et al.\textsuperscript{167} is not known, although it could be related to the reported (1×1) overlayer reported in the earlier work.\textsuperscript{167}

The simultaneous NC-AFM/STM images in Figure 34 show Ti\textsubscript{5c} rows bright in both the AFM and STM images.\textsuperscript{169} OH\textsubscript{b} can be seen as bright spots between these rows in both sets of images. However, a minority of the bright spots in the STM image have a very faint appearance and are absent entirely in the AFM image. Rescanning the same
area led to some of the OH\textsubscript{b} species converting into the minority defects. DFT calculations indicate that it is feasible that the surface H is pushed down into subsurface interstitial sites by the tip with an activation energy of \(~1.6\text{-}1.8\) eV\textsuperscript{170,171}

Unterberger et al.\textsuperscript{141} used PhD to study OH\textsubscript{b}. In order to obtain a high coverage, they dosed atomic hydrogen from a commercial tube cracker. Based on the proportion of hydroxyl and oxidic components of the O 1s peak, a coverage of 0.4\text{-}0.5 ML was found. The value was higher than the saturation coverage in the STM study by Suzuki et al.\textsuperscript{165} but lower than the 1 ML inferred from HAS.\textsuperscript{166} The H atoms were found to attach to the O\textsubscript{b}, forming OH\textsubscript{b}, as expected from the previous work. The Ti\text{–OH\textsubscript{b}} was found to be at 1.97 ± 0.05 Å, which is 0.10\text{-}0.15 Å longer than the Ti-O\textsubscript{b} bond in the clean surface. Despite this, there are no significant changes to the positions of the other atoms, as they remain essentially in the same place as in the clean surface.

Atomic hydrogen was also deposited onto a TiO\textsubscript{2}(011)-(2\times1) surface by cracking hydrogen at a hot filament.\textsuperscript{172} Bright spots appeared with a saturation coverage of 0.22 ML (1 ML is defined as the density of (1\times1) surface unit cells) which were assigned as hydroxyl, resulting from H adsorption. A TiO\textsubscript{2}(011)-(2\times1) surface previously covered with \(~0.12\) ML OH at room temperature was imaged at high temperature (500 K). At the high temperature, nearly all the OH was absent. Interestingly, after returning to room temperature, \(~0.10\) ML OH reappeared. It was concluded that hydrogen diffuses into the subsurface region at room temperature and diffuse back out as the temperature is reduces. The observation of a slightly lower coverage following cooling suggests that some of the H remains in the subsurface.
These observations differ from most of the literature on TiO\(_2\)(110), where annealing the hydroxyated surface leads to desorption of water.\(^8,145,147,168\) DFT calculations found that diffusion into the subsurface was favoured compared to desorption due to a combination of weak H adsorption at the surface, low kinetic barrier, and facile bulk-diffusion channels.

It should be noted that bright spots with the same appearance as the deposited H can also be observed on ‘clean’ surfaces and behave in the same way and it was surmized that these form by out-diffusion from the bulk.\(^{172}\)

### 3.3 Carbon Adsorbates

CO\(_2\) and CO are both used extensively in surface science as probe molecules to test the surface structure and reactivity. As a greenhouse gas, there is intense research into methods of CO\(_2\) capture as well as its conversion into useful fuel. Photocatalytic reforming of CO\(_2\) on TiO\(_2\) is a promising strategy for carbon recycling.\(^{173}\) Studies of CO on TiO\(_2\)(110) are driven partly by the CO oxidation reaction which on Au/TiO\(_2\)(110) is active even at low temperature.\(^{174}\)

Since its discovery,\(^{175}\) the novel properties of C\(_{60}\) (and C\(_{60}\) derivatives) have led to numerous adsorption studies. For instance, Cuberes et al.\(^{176}\) used C\(_{60}\) constrained in one-dimension on the step-edges of Cu(111) to create arrays of molecules which could be slided with the STM, like the beads on an abacus.

### 3.3.1 CO\(_2\)
TPD studies of CO$_2$ on r-TiO$_2$(110) show two peaks, at ~137 K and ~166 K. The peak at 166 K saturated with an exposure of ~9 × 10$^{13}$ molecules cm$^{-2}$, after which another peak grows in at ~137 K which saturated with an exposure of ~5 × 10$^{14}$ molecules cm$^{-2}$. (The TiO$_2$(110)(1×1) surface has 5 × 10$^{14}$ primitive unit cells per cm$^2$). As the sticking probability was measured to be near unity, the low temperature peak represents a coverage of ~0.85 ML (i.e. near to one CO$_2$ per Ti$_5$c site) while the high temperature peak represents a coverage of ~0.17 ML, near to the O$_b$-vac coverage of ~0.1 ML. As the 166 K peak was also absent in TPD curves employing a nearly-perfect sample, it was assigned to CO$_2$ adsorbed at O$_b$-vac, which we shall refer to as CO$_2$(O$_b$-vac).$^{177}$

Subsequent TPD measurements confirm this assignment.$^{178,179}$ Thompson et al.$^{178}$ created O$_b$-vac by annealing an o-TiO$_2$ sample to increasingly high temperatures in UHV, taking CO$_2$ TPD between each increment. The intensity of the high temperature peak grows with anneal temperature. Pre-adsorbed O$_2$ is known to heal O$_b$-vac and this also quenches this peak. None of these TPD experiments detected any dissociation to CO.

A loss at 2340 cm$^{-1}$ in HREELS could be assigned to CO$_2$ at normal lattice sites on the basis that this loss could be removed by annealing to ~130 K. This loss is almost unchanged from gas phase CO$_2$, indicating a near-linear geometry. No losses could be detected for CO$_2$(O$_b$-vac). This could either be because the coverage is below the detection limit or the bonding geometry is different and the peak is obscured in the phonon losses.$^{177}$ Sticking coefficient measurements indicate a precursor-mediated adsorption mechanism.$^{177,179}$
STM images have been taken at 55 K and 80 K following exposure to CO\textsubscript{2}. Sorescu et al.\textsuperscript{180} found CO\textsubscript{2} adsorbed at O\textsubscript{h}-vacs [CO\textsubscript{2}(O\textsubscript{h}-vac)] as well as on Ti\textsubscript{5c} sites. CO\textsubscript{2}(O\textsubscript{h}-vac) spots can be distinguished from OH\textsubscript{b} by their greater height. Similar results were obtained by Acharya et al.\textsuperscript{181} who found \textasciitilde80\% of the CO\textsubscript{2} adsorbs as CO\textsubscript{2}(O\textsubscript{h}-vac), with the remainder sitting on Ti\textsubscript{5c} sites. They further resolve CO\textsubscript{2}(O\textsubscript{h}-vac) into two configurations: about 65\% of them are elliptical, elongated along [1 \overline{1} 0], and symmetric across [001]. The other 35\% are also elongated in [1 \overline{1} 0] but with the intensity shifted to one side. By comparing with cluster calculations for the symmetric CO\textsubscript{2},\textsuperscript{182} Acharya et al.\textsuperscript{181} propose a bent configuration involving two Ti sites with four bonds between them and the CO\textsubscript{2}. For the asymmetric species, they propose a carbonate-like species with involves the C atom bonding to an adjacent in-plane O.

DFT calculation by Sorescu et al.\textsuperscript{180} suggest instead that a linear but inclined configuration is the most stable for CO\textsubscript{2}(O\textsubscript{h}-vac). Tan et al.\textsuperscript{183} also find this tilted geometry to be the most stable, but because the vertical configuration is only 0.16 eV higher in energy, they suggest that both could co-exist and therefore account for the two types of CO\textsubscript{2}(O\textsubscript{h}-vac) which they also observe. As for CO\textsubscript{2} at the Ti\textsubscript{5c} sites, Tan et al.\textsuperscript{183} suggest that these spots probably arise from contamination. Even at \textasciitilde15 K, they found that CO\textsubscript{2} cannot be imaged in a stable fashion at the Ti\textsubscript{5c} sites because of very fast diffusion.

Lee et al.\textsuperscript{184} and Tan et al.\textsuperscript{183} used individual electrical pulses from an STM tip to dissociate CO\textsubscript{2} while recording the \textit{I}–\textit{t} trace during each pulse, as shown in Figure 35. By varying the current used in the pulses, a log-log plot can be made of the dissociation rate, \( R_{\text{diss}} \) vs. \( I \), the slope, \( n \), being the exponent in the power law relationship, \( R_{\text{diss}} \propto I^n \).\textsuperscript{185} In
both sets of measurements, \( n = 1 \), indicating a one-electron process. Lee et al.\(^{184}\) plotted the dissociation probability as a function of bias voltage and found a threshold at 1.7 V. It was concluded that dissociation occurs via a transient CO\(_2^-\) species that then dissociates into CO and O\(^-\).

CO\(_2\) adsorption was also studied at higher coverages by Lin et al.\(^{186}\) using a combination of STM, RAIRS, TPD, and theoretical calculation. In line with the reports above, STM at 50 K indicates that the O\(_b\)-vac sites are the first to be populated. CO\(_2\)(O\(_b\)-vac) were associated with a TPD peak at 166 K in ref 177. However, quantitative analysis of this peak shows it corresponds to three times the coverage of O\(_b\)-vacs. RAIRS measurements show the presence of two types of CO\(_2\) when the coverage is \(~\)3 times greater than the O\(_b\)-vac coverage and only one type when the coverage is below the O\(_b\)-vac coverage. This was rationalized by DFT + U calculations that indicate that the presence of CO\(_2\)(O\(_b\)-vac) stabilize the binding of CO\(_2\) in adjacent Ti\(_{5c}\) sites.

Up to a coverage of \(~\)0.5 ML, STM indicates that CO\(_2\) adsorbs on the Ti\(_{5c}\) and are highly mobile at 50 K STM, consistent with the observation by Tan et al. at 15 K.\(^{183}\) An oxidized TiO\(_2\)(110) surface can be created by removal of CO\(_2\) (O\(_b\)-vac) by tip-induced dissociation. This oxidized sample is employed in the remaining STM experiments discussed here for CO\(_2\)/TiO\(_2\)(110). Re-exposure of this surface to CO\(_2\) enabled ‘tracks’ running in [001] to be imaged. This is a result of imaging CO\(_2\) molecules repeatedly during a scan. DFT calculations find that the most stable geometry has one O atom (denoted O\(_a\)) on top of a Ti\(_{5c}\) site with the O=C=O axis tilted by \(~45^\circ\) along the [1 \(\bar{1}\) 0] direction towards an adjacent O\(_b\) atom. Translation along the Ti\(_{5c}\) row and rotation about the Ti\(_{5c}\)-O\(_a\) axis is facile with barriers of 0.06 eV and 0.05 eV, respectively. This explains
both the rapid diffusion of CO\textsubscript{2} and the pairing of features in STM along [1 \bar{T} 0] which arises from time-averaged imaging of CO\textsubscript{2} in multiple configurations.

At 0.5 ML CO\textsubscript{2}, these paired features form a (1\times1) pattern. Given the coverage, this result indicates that CO\textsubscript{2} is still mobile with individual CO\textsubscript{2} being imaged repeatedly within an image. At 0.67 ML paired features can be observed with a coverage of 0.67 ML, indicating that CO\textsubscript{2} diffusion is hindered. The paired features are arranged in lines along the Ti\textsubscript{5c} sites separated by about 4.5 Å: a model is proposed whereby CO\textsubscript{2} adsorbs on Ti\textsubscript{5c} sites with every third site missing a CO\textsubscript{2} molecule. This creates pairs of CO\textsubscript{2} (along [001]) separated by two TiO\textsubscript{2} units with the CO\textsubscript{2} in the pairs pointing away from each other.

At 1 ML, paired features are no longer observable. Instead, an out-of-phase arrangement of the zigzag chains is imaged which creates a (2\times2) pattern. A model was proposed, consisting of a zigzag arrangement of tilted CO\textsubscript{2} molecules along the Ti\textsubscript{5c} rows. This structure is similar to that proposed for 1 ML N\textsubscript{2} in section 3.5.4. An additional 0.5 ML CO\textsubscript{2} could be adsorbed at O\textsubscript{b} sites according to TPD measurements and again similar to the situation for N\textsubscript{2} on TiO\textsubscript{2}(110).

Lin et al.\textsuperscript{187} also studied the adsorption of CO\textsubscript{2} on o-TiO\textsubscript{2}(110) using STM. At 50 K, CO\textsubscript{2} is found to adsorb preferentially on Ti\textsubscript{5c} sites next to O\textsubscript{ad} rather than on O\textsubscript{b}-vacs. However, after annealing to 100–160 K, O\textsubscript{b}-vacs are preferentially filled, indicating a kinetic barrier for CO\textsubscript{2} adsorption in these vacancy sites. The difference between the CO\textsubscript{2} binding energy on O\textsubscript{b}-vacs and Ti\textsubscript{5c} sites next to the O\textsubscript{ad} is found to be only 0.009–0.025 eV. The barrier for CO\textsubscript{2} diffusion away from O\textsubscript{ad} being is estimated to be ~0.17 eV.
3.3.2 CO

Linsebigler et al.\textsuperscript{188} performed TPD of C\textsuperscript{18}O on \textit{o}- and \textit{r}-TiO\textsubscript{2}(110). At the lowest exposure (7.1 \times 10^{12} \text{ molecules cm}^{-2}) CO desorbs from \textit{o}-TiO\textsubscript{2} at \textasciitilde 170 K. As the exposure is increased, the peak shifts to lower temperature and saturates at 2.1 \times 10^{15} \text{ molecules cm}^{-2} with the peak maximum at 135 K. This downshift is due to intermolecular repulsion and is also apparent from sticking measurements.\textsuperscript{189} 2.1 \times 10^{15} \text{ molecules cm}^{-2} corresponds to a coverage of only \textasciitilde 0.4 ML. A later TPD study used a lower base temperature (32 K compared to 105 K in the earlier work) to show that the 135 K peak actually saturates near 1 ML.\textsuperscript{112} Further exposure to CO leads to another even lower temperature peak at \textasciitilde 52 K.

TPD from \textit{r}-TiO\textsubscript{2} showed a similar profile to that from \textit{o}-TiO\textsubscript{2} except for a high temperature component that appears and scales with pre-annealing temperature. The high temperature component saturates at 2.1 \times 10^{15} \text{ molecules cm}^{-2}, which corresponds to about 0.04 ML, well within the range of typical O\textsubscript{b}-vac densities. The role of O\textsubscript{b}-vac was validated by exposing \textit{r}-TiO\textsubscript{2} to O\textsubscript{2}, thereby blocking the O\textsubscript{b}-vac sites and eliminating the high temperature feature.\textsuperscript{188} However, rather than adsorbing in the vacancy, it was proposed that CO simply adsorbs in the vicinity. This is because the overall CO yield does not change with O\textsubscript{b}-vac density. Adsorbing into O\textsubscript{b}-vacs should not affect the bonding at Ti\textsubscript{5c}, so it was reasoned that in such a case, the presence of vacancies should increase the overall yield.

No dissociation was detected by monitoring for any scrambling of \textsuperscript{18}O with \textsuperscript{16}O from the lattice nor by a TPD/CO exposure/TPD cycle where the two TPD curves were
identical. If CO dissociates in O\textsubscript{b}-vac, one would expect the vacancy to become inactive for further association with CO.

After exposing a TiO\textsubscript{2}(110) surface to CO (10\textsuperscript{-7} mbar range) at 110 K, Rohmann et al.\textsuperscript{190} found a peak at 2183 cm\textsuperscript{-1} in RAIRS. Upon evacuation to the 10\textsuperscript{-10} mbar range, there was a shift to 2190 cm\textsuperscript{-1} and a 25% loss of intensity, assigned to a CO ν\textsubscript{1} stretch on a Ti\textsubscript{5c} site. The result was confirmed by a loss seen in HREELS at 2200 ± 15 cm\textsuperscript{-1}.\textsuperscript{190}

Recently, STM at 80 K has been used to investigate CO on r-TiO\textsubscript{2}(110).\textsuperscript{191} In line with the idea that CO adsorbs in the vicinity of O\textsubscript{b}-vac but not in them,\textsuperscript{188} CO was found at the Ti\textsubscript{5c} sites near to O\textsubscript{b}-vac, as shown in Figure 36. Almost no CO adsorbs directly adjacent to the O\textsubscript{b}-vac, ~60% are one lattice spacing away and ~30% are two lattice spacings away. Recently, it has been found using STS, resonant PhD, and theoretical calculation that the electron density from O\textsubscript{b}-vac is spread around several sites around and beneath the vacancy.\textsuperscript{39,40,192} Zhao et al.\textsuperscript{191} suggest that this excess electronic charge could participate in back-bonding giving the CO a negative charge and thereby favoring sites slightly away from the O\textsubscript{b}-vac.

Zhao et al.\textsuperscript{191} used DFT calculations to test the stability of the O\textsubscript{b}-vac site and the Ti\textsubscript{5c} sites around it. As one would expect from the STM data, the most stable site is one lattice spacing away.

Wang et al.\textsuperscript{193} and Lee et al.\textsuperscript{194} both used STM to study the adsorption of CO on o-TiO\textsubscript{2}(110). At T ≤ 80 K, exposure of o-TiO\textsubscript{2} to CO leads to CO adsorbing near to the O\textsubscript{b}-vacs, as just discussed above.\textsuperscript{191} At 100-120 K, the CO molecules become diffusive (O\textsubscript{ad} are still almost immobile). When a CO molecule finds an O\textsubscript{ad}, a CO–O\textsubscript{ad} complex
forms along [001], and if another CO finds it, a CO-O$_{ad}$-CO complex forms along [001], as shown in Figure 37.

While individual CO molecules are quite easily made to diffuse or desorb away with positive electrical pulses of $\geq$2.5 V, Wang et al.$^{193}$ found the complexes to be stable to pulses up to $+4$ V and also to UV light. On the other hand, Lee et al.$^{194}$ found that negative pulses (-3.5 V) could remove the CO component in the complex.

Figure 38 shows O$_{ad}$/CO TPD and ESD. In comparison with CO on clean TiO$_2$(110), the TPD peak broadens and shifts to slightly higher temperature, indicative of a higher desorption activation energy. As for the ESD, while the O$^+$ yield from $^{18}$O$_{ad}$ on clean TiO$_2$(110) is more-or-less temperature independent, in the case of $^{18}$O$_{ad}$/CO, there is a dip in the yield between 100-120 K, around the temperature that the complex is found. This is probably due to neutralization of the O$^+$ ions by nearby CO. DFT calculations indicate a modest energy benefit in forming the complex that is mainly electrostatic in nature.

The photo-oxidation of CO to CO$_2$ has been a topic of considerable interest, with Lu et al.$^{115}$, as discussed in section 3.1, showing that O$_2$ can photodesorb or photo-oxidize CO upon UV irradiation. Recently, Zhang and Yates have proposed an electron attachment mechanism for the photo-oxidation of CO.$^{195}$ More recently, Petrik and Kimmel have instead proposed multiple non-thermal reaction steps.$^{196}$
C\textsubscript{60} was vapor-deposited onto TiO\textsubscript{2}(110)(1×1).\textsuperscript{197-200} STM and NC-AFM indicate that at submonolayer coverages, the molecules adsorb preferentially at step edges. Further deposition leads to ordered islands that grow from the decorated step edges. Figure 39 shows an NC-AFM image that resolves the O\textsubscript{b} rows of the substrate together with the C\textsubscript{60} islands. From this image a centered c(5×2) rectangular superstructure was proposed,\textsuperscript{198} with the molecules aligned over the troughs between the O\textsubscript{b} rows. Despite the TiO\textsubscript{2}(110) substrate being decorated with defects, the C\textsubscript{60} overlayer is highly ordered, suggesting that the intermolecular C\textsubscript{60}–C\textsubscript{60} interaction dominates over the C\textsubscript{60}–TiO\textsubscript{2} interactions.

More recent STM images supported by LEED and HAS indicate a p(5×2) overlayer.\textsuperscript{200} In fact, the proposed overlayer is the same as that in ref 198: it is the nomenclature in the earlier work that is incorrect. The weak molecule–surface interactions inferred by Loscke et al.\textsuperscript{198} were also confirmed by near-edge X-ray absorption fine structure (NEXAFS), HAS, and PhD.\textsuperscript{200} In C K-edge NEXAFS, almost no difference is seen between s- and p-polarized spectra at 0.8 or 1.7 ML. Furthermore, the spectra also match well with a multilayer of C\textsubscript{60} on Au, indicating that the unoccupied C\textsubscript{60} molecular orbitals have not been significantly altered upon surface deposition.

PhD patterns for C\textsubscript{60} molecules on various systems consist of strongly anisotropic and well-resolved forward scattering peaks along the main bond directions. However, for this C\textsubscript{60}/TiO\textsubscript{2} system, there is low anisotropy and an almost featureless pattern that suggests a poorly-defined molecular geometry in the forward focusing regime. Only a bright belt ranging from a polar angle of 10° to 45° and azimuthally extended over 120° is observed, as shown in Figure 40. This can be explained in two ways: (1) all molecules are
fixed on the surface with the same polar orientation but each one having a different azimuthal orientation along the surface normal or (2) all molecules are adsorbed in a specific polar geometry but with dynamic rotation along their surface normal.

The diffraction pattern was analysed by simulating the pattern from the five simplest high symmetry orientations of C_{60}: adsorption via a single C atom (atom566), a hexagon, a pentagon, a hexagon-hexagon dimer (dimer66) or a pentagon–hexagon dimer (dimer56). Both hexagon and dimer56 configurations have maxima almost completely within the belt seen in the experiment. Furthermore, their maxima are almost complementary, appearing at polar angles in such a way that a combination of both orientations almost entirely covers the observed emission belt. Two adsorption geometries is not unexpected given that the p(5×2) symmetry contains C_{60} in two adsorption positions.

The adsorption geometries were further tested with DFT calculations that include vDW interactions. Above a Ti_{5c} site, a dimer56 geometry is found and between two Ti_{5c} sites, a hexagon orientation is found, as shown in Figure 41.

C_{60} was also deposited on an x-linked TiO_{2}(110)(1×2) surface. STM shows that as with the 1×1 surface, the molecules lie on the Ti_{5c} rows, in this case between the added 1×2 rows. At low coverage, the C_{60} is located at neighboring sites to the x-links whereas at higher coverage, the C_{60} arranges into rows along the Ti_{5c} rows. The separation of C_{60} along [001] is 10 Å, consistent with that in a C_{60} crystal, whereas the separation of C_{60} along [1\bar{1}0] is alternately 11 Å, then 15 Å, so that the C_{60} rows are paired as shown in Figure 42 (the substrate periodicity in [1\bar{1}0] is 13 Å). That the C_{60} is restricted to Ti_{5c}
rows suggests an important role of C\textsubscript{60}-substrate bonds but also strong intermolecular bonds play a role in forming pairs across [1 \bar{1} 0].

On the TiO\textsubscript{2}(100)(1\times3) surface, C\textsubscript{60} adsorbs atop the ridges of the reconstruction at low coverage. Higher coverages show ordering on parts of the image along [001], while clusters can be seen elsewhere. In the ordered areas, alternate rows of C\textsubscript{60} vary in height along [1 \bar{1} 0] forming a highly corrugated structure. Annealing to 600 K, increases the surface order with the majority of the surface showing structures forming rows in the [001]. A model was proposed whereby rows of C\textsubscript{60} separated by \textasciitilde 10 Å align along [001] and are located both on the ridges and in the troughs.\textsuperscript{201}

### 3.4 Silicon

The interaction of Si or SiO\textsubscript{x} with oxides may be important in the development of nanoscale electronics. To this end, the growth of Si on TiO\textsubscript{2}(110)(1\times2) was studied by Abad et al.\textsuperscript{202} For Si coverage up to a monolayer, a heterogeneous layer is formed, consisting of a mixture of different suboxides SiO\textsubscript{x} (1 < x \leq 2) on top of a further reduced TiO\textsubscript{2} surface. Increasing the Si coverage led to the complete attenuation of the characteristic (1\times2) LEED pattern, indicating the absence of long-range order. Annealing the SiO\textsubscript{x} overlayer results in the recovery of the 1\times2 LEED pattern. LEED I-V curves from both substrate and overlayer indicate the formation of nanoscale SiO\textsubscript{x} clusters.

SiO\textsubscript{x} was also deposited onto TiO\textsubscript{2}(100) by annealing the crystal in air with the crystal enclosed in a quartz case. SiO\textsubscript{x} was deposited onto the surface from the quartz case. An ordered (3\times4) pattern was observed in LEED, consistent with NC-AFM images.
taken in pure water. A model based on rutile-like SiO$_2$ was proposed, with the surface layers consisting of Ti$_{1-x}$Si$_x$O$_2$.\textsuperscript{203}

### 3.5 Nitrogen Adsorbates

NO$_2$ and NO or NO$_x$ (\(x = 1\) or \(2\)) gases are some of the most harmful environmental pollutants. They arise from automotive engines and industrial combustion systems. One way to remove NO$_x$ is by oxidation over TiO$_2$ to form nitrate.\textsuperscript{204}

#### 3.5.1 NO$_2$

NO$_2$ chemistry on TiO$_2$(110) has recently been probed with ambient pressure core-level PES.\textsuperscript{205} There are two pressure regimes: low (<10$^{-5}$ Torr) and high (>10$^{-5}$ Torr) where water, presumably from the chamber walls, appears. From 10$^{-8}$-10$^{-5}$ Torr NO$_2$, the N 1s peak can be deconvolved into NO$_3$, NO$_2$, and atomic N components with areal ratios matching their counterpart signals in the O 1s region. The coverage of these species can then be plotted against coverage, as shown in Figure 43. In the low pressure regime, the two NO$_x$ components saturate at ~10$^{-6}$ Torr NO$_2$ with coverages of 0.1-0.2 ML each. The atomic N component saturated later (~10$^{-5}$ Torr NO$_2$) at ~0.2 ML.

These results are in line with an earlier UHV study of NO$_2$ adsorption on TiO$_2$(110) where, based on core-level PES, NEXAFS, and DFT calculation, it was proposed that NO$_2$ disproportionates: NO$_2$ (ads) $\rightarrow$ NO$_3$ (ads) and NO (g), with the NO desorbing.\textsuperscript{206}

An atomic N component was also observed in UHV, particularly when a heavily reduced surface that included Ti$^{3+}$ and Ti$^+$ (\(\delta < 3\)) was used. Rodriguez et al.\textsuperscript{206}
monitored the evolution of the Ti 2p peak as a function of NO₂ exposure. After 10 L, only Ti⁴⁺ components could be seen. Given that a small Ti³⁺ component is usually observed even for oxidized TiO₂ due to subsurface Ti³⁺, this implies that NO₂ decomposes not only at O₆-vac but also draws the subsurface defects (most likely Ti₃⁺) to the surface to react further.

The behavior at high pressure only deviates from the UHV scenario above ~10⁻³ Torr where the component assigned to NO₃ increases sharply due to reaction of physisorbed NO₂ with water forming HNO₃. Furthermore, the coverage of atomic N increases to 0.5 ML, far higher than the coverage of O₆-vac, giving more evidence for reaction with subsurface defects.²⁰⁵

3.5.2 NO

In TPD following ¹⁵NO adsorption on TiO₂(110), NO desorbs molecularly at ~120 K. In addition to this, N₂O is found to desorb at 169 K and 250 K. The lower temperature N₂O peak is absent for α-TiO₂ samples and an α-TiO₂ sample annealed in UHV to 400 K. The 169 K N₂O peak appears after UHV annealing to 500 K and scales with the UHV anneal temperature up to 800 K. Given that UHV annealing creates O₆-vac, it was concluded that the 169 K N₂O peak corresponds to an NO reaction with O₆-vac.²⁰⁷

On an α-TiO₂(110) surface, TPD shows that NO desorbs molecularly at ~127 K. At higher coverage, additional peaks occur at 169 and 250 K. These additional peaks arise from cracking of N₂O formed from interaction of pairs of NO. The NO yield at 127 K decreases with the appearance of these new peaks.²⁰⁸
Abad et al.\textsuperscript{209} also find reduced Ti species to be reactive with NO. Their conclusions are based on observations of PES at room temperature. Ar\textsuperscript{+} sputtered samples were used in order to introduce reduced Ti\textsuperscript{3+/2+} species. The low BE shoulder in the Ti 2p peak and the BGS were diminished upon exposure to NO, with no evidence of any nitrogen adsorption in PES or AES measurements. Unlike the observations for NO\textsubscript{2}, even at very high exposures (500 L), subsurface Ti\textsuperscript{3+/2+} could be detected. Similarly, for a TiO\textsubscript{2}(110)(1×2) surface, the same workers found that the Ti\textsuperscript{3+} sites in the added Ti\textsubscript{2}O\textsubscript{3} rows were healed upon exposure to NO\textsubscript{2}, with no nitride detected.\textsuperscript{210}

The adsorption of NO was recently probed on h-TiO\textsubscript{2}(110).\textsuperscript{211} After exposing to NO at room temperature, STM revealed the presence of new features with a bright-dark-bright (BDB) contrast as shown in Figure 44a and b. By analysing sequential areas of the surface under a background pressure of NO (2 × 10\textsuperscript{-9} mbar), it could be seen that the appearance or disappearance of BDB could be correlated with the disappearance or appearance of OH\textsubscript{b}, respectively, as shown in Figure 44c. This indicates that OH\textsubscript{b} is involved in the capture of NO but is not consumed; it is left behind when NO desorbs.

PES spectra of the Ti 2p and the band gap regions indicate that the intensity of the low BE shoulder and the BGS peak are diminished with exposure to NO. DFT calculations indicate that the OH\textsubscript{b} transfers charge to the NO molecule, consistent with the PES observation. This leads to negatively charged N, which can interact more strongly (0.64 eV compared with 0.40 eV) with the Ti\textsubscript{5c} sites than without the negative charge.

\subsection*{3.5.3 N\textsubscript{2}O}
Core-level PES, second harmonic generation (SHG) measurements, TPD, and DFT calculations have all pointed to the dissociation of N$_2$O at O$_b$-vac.$^{212-214}$ However, a more recent TPD study finds only molecular desorption.$^{215}$

For an r-TiO$_2$(110) surface with an O$_b$-vac density of 0.05 ML, at low coverage a small N$_2$O peak develops at ~175 K, saturating at ~2.7 × 10$^{13}$ molecules cm$^{-2}$, whereupon another N$_2$O peak develops at ~150 K. This latter peak continues to grow up to coverage of ~5.4 × 10$^{14}$ molecules cm$^{-2}$. As such, the 175 K peak can be assigned to molecular adsorption in O$_b$-vac with the ~150 K peak being due to adsorption at Ti$_{5c}$ sites. Desorption from higher coverages leads to a peak that maximizes at 110 K. This can be attributed to desorption from a second layer N$_2$O.

The 175 K peak was examined further by desorption from o-TiO$_2$, s-TiO$_2$, and h-TiO$_2$ as shown in Figure 45. For s-TiO$_2$ and h-TiO$_2$, the peak was completely eliminated whereas for o-TiO$_2$, a very small peak remained that was attributed to some reaction with O$_{ad}$. Note also that exposing r-TiO$_2$(110) to even very high amounts of O$_2$ does not entirely eliminate the O$_b$-vacs (as discussed in Section 3.1) and this might also contribute to the remaining small peak. The difference with the earlier TPD results was attributed to a greater contamination level in the earlier work.$^{213}$

3.5.4 N$_2$

The physisorption of N$_2$ on TiO$_2$(110) was studied with TPD.$^{112}$ The sample was prepared by cycles of Ne ion sputtering at 850 K in a background of 2.66 × 10$^{-7}$ mbar O$_2$ and annealing in UHV at 900 K. The absence of the water TPD peak at ~490 K indicated
that there were no O\textsubscript{b}-vac on this surface. The surface can probably be described as s-TiO\textsubscript{2}(110).

The N\textsubscript{2} TPD data indicated three coverage regimes. At low coverage (\(\leq 0.5\) ML), a peak is found at 105 K that shifts to 90 K with coverage. At intermediate coverage (0.5-1 ML), there is a dramatic shift to low temperature (90-40 K). Above this coverage, a new peak develops at \(~43\) K that saturates at \(~1.5\) ML. By also taking into account calculations on this system,\textsuperscript{216,217} Dohnálek et al.\textsuperscript{112} propose models for each of these regimes.

At low coverage, N\textsubscript{2} initially adsorbs end on over the Ti\textsubscript{5c} sites. At 0.5 ML, the N\textsubscript{2} form a c(2\times2) arrangement, based on the N\textsubscript{2}-N\textsubscript{2} repulsion evident by the low temperature shift of the TPD peak. At 1 ML, N\textsubscript{2} molecules adsorb end-on to each Ti\textsubscript{5c} site but are tilted alternately away and towards each other along [1\,\bar{1}\,0]. The extra repulsion is responsible for the dramatic shift of the TPD peak to lower temperature at this coverage. At 1.5 ML, the remaining 0.5 ML of N\textsubscript{2} adsorb over the O\textsubscript{b} sites. It is noteworthy that in the Kinetic Monte Carlo simulations,\textsuperscript{217} after the Ti\textsubscript{5c} sites were saturated at 77 K, an extra 0.5 ML N\textsubscript{2} was able to adsorb on top of these O\textsubscript{b} sites.

The TiO\textsubscript{2}(110) surface was imaged at room temperature under an atmospheric pressure of N\textsubscript{2} using NC-AFM.\textsuperscript{218} While the quality factor of the cantilever oscillation was heavily damped, surprisingly, it was still possible to obtain atomically resolved images of the surface, including individual point defects that were assigned to O\textsubscript{b}-vacs. As it has since been shown that OH\textsubscript{b} have a very similar appearance to O\textsubscript{b}-vac in STM as well as NC-AFM,\textsuperscript{24,25} it may also be that these point defects are OH\textsubscript{b} arising from
reaction of the \( O_b \)-vac with water in the residual vacuum created by \( N_2 \)-induced desorption from the chamber walls.

### 3.5.5 \( NH_3 \)

PES measurements by Román et al.,\(^{219}\) Diebold and Madey,\(^{220}\) and Farfan-Arribas and Madix\(^{221}\) show that ammonia adsorbs almost entirely molecularly on \( TiO_2(110) \). Diebold and Madey proposed a \( c(2 \times 2) \) overlayer as shown in Figure 46 with \( NH_3 \) bonded \( N \)-down onto \( Ti_{5c} \) sites.\(^{220}\)

This model is supported, to an extent, by STM experiments and DFT calculations.\(^{222,223}\) The STM study by Suzuki et al.\(^{222}\) showed \( NH_3 \) species adsorbed on the \( Ti_{5c} \) rows and the calculations show that the configuration with \( N \) down is the most stable. More recent STM images by Pang et al.\(^{224}\) show that at saturation \( NH_3 \) coverage (approaching 0.5 ML), the nearest \( NH_3-NH_3 \) distance in the [001] direction is ~6 Å but any interaction along [1 1 0] is not strong so that areas of local \( c(2 \times 2) \) and \( p(2 \times 2) \) can both be seen (Figure 47).

Saturation coverages of \( NH_3 \) were reported to reduce after creation of defects by annealing or electron bombardment, as monitored by a valence band PES feature,\(^{225}\) as well as TPD.\(^{221}\) This decrease in saturation coverage has been rationalized on the basis that \( NH_3 \) preferentially adsorbs into \( O_b \)-vacs, thereby blocking more than one regular \( Ti_{5c} \) site. However, STM images of the surface before and after exposure to \( NH_3 \) did not reveal any tendency to fill \( O_b \)-vacs, although the initial \( O_b \)-vac coverage was quite low.\(^{224}\) In line with this, Kim et al.\(^{226}\) used molecular beam dosing and TPD to show that the
surface charge and not the O₆-vac density is the controlling factor in determining the zero coverage binding energy.

3.6 Sulfur Adsorbates

Like, NOₓ, SO₂ is one of the major air pollutants, arising from combustion of coal and oil. As with de-NOₓ catalysts, many oxides are employed in de-SOₓ processes.\textsuperscript{227} Added to this, sulfur and sulfur-containing compounds act as poisons in catalytic reactions. These related issues motivate the work described in this section.

3.6.1 SO₂

There are apparently conflicting reports on the adsorption of SO₂ on TiO₂(110) which is discussed by Diebold together with SO₂ adsorption on TiO₂(100).\textsuperscript{5} For instance, while Smith et al.\textsuperscript{228} find no (or very little) interaction with SO₂ (up to exposures of 10⁶ L) on the basis of PES on a TiO₂(110) sample annealed in 1.33 × 10⁻⁷ mbar O₂, Onishi et al.\textsuperscript{229} give evidence for the adsorption of SO₃²⁻ on r-TiO₂(110) by comparing S 2p PES spectra with standard samples (Na₂S, Na₂SO₃, and Na₂SO₄).\textsuperscript{230} Onishi et al.\textsuperscript{229} also detected the presence of S²⁻ on a TiO₂(441) surface in addition to SO₃²⁻, the sulfide being attributed to oxidation of Ti³⁺ to Ti⁴⁺ at step edges. The difference between these results may be due to the absence of O₆-vacs in the earlier work.\textsuperscript{228}

At low temperature, NEXAFS experiments give evidence for chemisorbed SO₂ which transforms to SO₄²⁻ ≥ 135 K via an SO₃-like intermediate.\textsuperscript{231,232} Recently, S K-edge NEXAFS spectra were simulated for SO₂ and SO₃ adsorption based on the two structural models shown in Figure 48.\textsuperscript{233} These are the most stable configurations given
by previous DFT calculations.\textsuperscript{234,235} As can be seen in Figure 49, the calculated SO\textsubscript{2} spectrum matches very well with the experimental measurement of SO\textsubscript{2}/TiO\textsubscript{2}(110) but less well with the proposed SO\textsubscript{3} intermediate. The discrepancy could arise from the presence of more than one SO\textsubscript{x} species at 150 K or from the involvement of defects which was not considered in the calculation.

STM at low temperature (120 K) reveals the presence of a (2×1) ordered overlayer at saturation exposure,\textsuperscript{236} contradicting experiments by Sayago et al.\textsuperscript{237,238} who reported a disordered overlayer. Lower coverage STM reveals bright spots that sit approximately over the Ti\textsubscript{5c} bright rows in positions not correlated with the positions of O\textsubscript{b}-vac.

Following annealing to 300 K, only one type of SO\textsubscript{x} species could be detected in STM. Given the expectation of a sulfite and sulfate species, it was therefore surmised that the sulfate-like species is removed during imaging and the sulfite-like species migrates to O\textsubscript{b}-vacs (their density is comparable to the O\textsubscript{b}-vac density). Annealing further to 420 K apparently led to the formation of sulfate species at O\textsubscript{b}-vacs.\textsuperscript{236}

Hartmann et al.\textsuperscript{239} studied the adsorption of SO\textsubscript{2} on TiO\textsubscript{2}(110)(1×2) with STM and AES. Experiments were performed with a TiO\textsubscript{2}(110) sample that had an ordered x-linked (1×2) structure. As further experiments were carried out, the sample became re-oxidized at the surface, so that SO\textsubscript{2} exposure was also performed on surfaces terminated with a mixture of the (1×1) and simple (1×2) structure.

New species appear first on the (1×2) rows, with no ordering detected in STM or LEED. After prolonged SO\textsubscript{2} exposures the overall appearance of the surface becomes very irregular, with the (1×2) surface structure remaining weakly discernible.
Nevertheless, locally ordered linear structures can be seen in some areas along the (1×2) rows, with a repeat length two or three times larger than the substrate (Figure 50). There seems to be no difference in reactivity between areas with and without x-linked rows, although the x-links themselves seem less reactive than the rows. At very high SO$_2$ exposure (1500 L), an ordered (2×1) overlayer forms on the 1×1 surface.

Only one peak (at 151.3 eV) is detected in AES. Standard SO$_x$ compounds, such as Ag$_2$SO$_4$, Na$_2$SO$_4$, and Na$_2$SO$_3$ have two or three peaks spread between 120-145 eV whereas sulfides such as Ag$_2$S and CdS have only one peak at 151 eV. As such, Hartmann et al.$^{239}$ proposed that TiS$_x$ and TiO$_x$ species form at the surface. Although Hartmann et al.$^{239}$ note that it is possible that any SO$_x$ species are desorbed rapidly by electron stimulated desorption (during AES), their results seem to be in line with the early measurements of Smith et al.$^{28}$ The latter was from a sample reduced by Ar$^+$ bombardment where TiS$_2$ was detected.

3.6.2 S

The adsorption of elemental sulfur on r-TiO$_2$(110) was described by Diebold.$^5$ Briefly, when sulfur is deposited at room temperature, it dissociates [the electrochemical cells used to deposit S typically form S$_n$ ($n \geq 2$)] into individual S atoms which sit on the Ti$_{5c}$ sites according to STM.$^{240-242}$ The BGS state in PES is also quenched, indicating that S adsorbs at O$_b$-vacs.$^{242}$ Core level PES indicated the presence of SO$_x$ species as well as S at Ti$_{5c}$ and O$_b$-vac.$^{242,243}$ At low temperature, S$_2$ and S$_n$ species can also be detected.

Annealing S/TiO$_2$(110) or depositing S at high temperature (≥1203 K) results in STM images that show S over the O$_b$ rows, and the S 2$p$ core level peak shifts to lower
BE, contrary to the expectation for \( \text{SO}_x \) formation. The Ti 2\( p \) peak develops a shoulder and the BGS also appears.\(^{240,242,243}\) This all points to a replacement of \( \text{O}_b \) atoms rather than adsorption on them. Depending on the temperature and coverage, various ordered S overlayers can be formed: \( \text{S}(3\times1) \), \( \text{S}(3\times3) \), \( \text{S}(4\times1) \).\(^{240,241}\)

A model for the \( \text{S}(3\times1) \) structure was proposed by Hebenstreit et al.\(^{240}\) that involves the replacement of every third \( \text{O}_b \) and the removal of all other \( \text{O}_b \) atoms. Recently, this model was confirmed quantitatively using SXRD.\(^{244}\) Sulfur adsorption gives rise to significant restructuring of the substrate that has been detected as deep as the fourth layer of the selvedge. The replacement of \( \text{O}_b \) with S is thought to give rise to a significant motion of co-ordinated 6-fold titanium atoms away from the adsorbate, along with a concomitant rumpling of the second (oxygen) substrate layer.\(^{244}\)

### 3.7 Chlorine

The study of halogens is almost entirely limited to Cl\(_2\) on TiO\(_2\)(110) and was described by Diebold et al.\(^5\) The work was partly motivated by the fact that Cl is a common impurity in TiO\(_2\) catalysts and pigments. Briefly, at room temperature, Cl\(_2\) was found by STM to dissociate via a ballistic mechanism whereby part of the initial binding energy of the Cl\(_2\) is transformed to kinetic energy, so that distinct pairs of Cl were found adsorbed at the Ti\(_{5c}\) sites.\(^{245}\) About 10% of the Cl atoms could not be correlated with a partner, which was initially thought to be scattering into vacuum. Further study suggested instead that the other Cl atom adsorbed in the \( \text{O}_b\)-vac.\(^{246}\) At temperatures above 473 K, STM and PES suggest that Cl replaces \( \text{O}_b\)-vacs. Interestingly, on lightly reduced sample
(light blue), there was no evidence of Cl adsorption at 473 K, suggestive of a pivotal role for subsurface defects, such as Ti$_{\text{int}}$.

Subsurface, positively-charged impurities can be detected in empty states STM of TiO$_2$(110) as a bright region about 20-30 Å wide. At room temperature, the region around this charged defect does not contain Cl. This was attributed to the competition for electrons between the electronegative Cl atom and the positively charged impurity atom.\textsuperscript{247} On a related note, KPFM images of a TiO$_2$(110) surface decorated with Cl adatoms show an increase in the local workfunction over the Cl adatoms, consistent with electron accumulation at the Cl atoms.\textsuperscript{248,249}

4. Organic Adsorbates

Studies of the adsorption and chemistry of organic molecules on single crystal rutile-TiO$_2$ surfaces are motivated by technological applications such as heterogeneous catalysis, dental implants, and solar cells. On this basis, there is a considerable archive of literature on this topic, with work ranging from the adsorption of small prototypical molecules in UHV to deposition of large multi-functional species (e.g. dye molecules) from solution phase. However, as regards fully quantitative structure determinations, only a very few have been reported to date. More typically, details of adsorbate geometries are restricted to the angular orientation of species from NEXAFS measurements, or identification of the lateral location of an adsorbed molecule through SPM images.

Below, we review organic adsorbate structures. In each section, beginning with organic acids and other related –COOH containing molecules, we attempt to collate results for chemically similar molecules.
4.1 Organic acids

$TiO_2(110)$

It is well established that the simplest carboxylic acid, formic acid (HCOOH)\(^\text{250-253}\) adsorbs dissociatively (acidic hydrogen cleavage) at room temperature on $TiO_2(110)(1\times1)$, i.e.

$$HCOOH_{(g)} \rightarrow [HCOO]^{\text{-}}_{(ads)} + H^+_{(ads)}$$

In addition, it is known that formate ([HCOO]\(^\text{-}\)\(_{(ads)}\)) forms a (2\times1) overlayer on $TiO_2(110)(1\times1)$ at a saturation coverage of approximately 0.5 ML (where 1 ML corresponds to one formate per surface 5-fold Ti).\(^\text{250}\) The bonding geometry of this formate species has been quantitatively determined in great detail by means of both PhD\(\text{254}\) and LEED-IV.\(^\text{255}\) As illustrated in Figure 51, it is concluded that formate binds to the surface in a bridging-bidentate mode through both of its oxygens to two adjacent five-fold surface titanium atoms (Ti\(_{5c}\)'s), so that its molecular plane is aligned with the [001] azimuth, i.e. it lies parallel to the rows of bridging oxygens. The two optimum local adsorption geometries, determined from scanned-energy mode PhD and LEED-IV, are compared in Figure 52. Inspection of the values of the various structural parameters indicates that there is excellent agreement between the two independent experimental structure determinations. Even the greatest disparity, namely the separation of the two formate oxygen atoms (d(O-O)), is within experimental uncertainty ($\Delta = 0.11 \pm 0.24$ Å).
There is a similar excellent level of agreement between the PhD and LEED-IV studies in terms of the substrate relaxations induced by the adsorption of formate. Table 2 lists these substrate relaxations as atomic displacements away from an ideal bulk-terminated TiO$_2$(110)(2×1)-[HCOO]$^-$ surface, together with those determined for clean TiO$_2$(110)(1×1) in UHV. Typically, following formate adsorption the atomic displacements are lower in magnitude than on the clean surface. This result is unsurprising, as the coordination of surface 5-fold Ti atoms increases to bulk-like 6-fold upon formate adsorption.

Besides determining the structure of the adsorbed formate and related substrate relaxations, the PhD study concluded that the dissociated acidic hydrogen (H$_{\text{ads}}^+$) was attached to an O$_b$, forming OH$_b$ (see Figure 5). It should be noted that the presence of this hydroxyl’s hydrogen was not ascertained directly, due to weak electron scattering of H atoms, but from a requirement to include both formate and bridging oxygen atoms in the best-fit between experimental and theoretically simulated O 1s PhD data. In contrast, no evidence of this OH$_b$ emerged from the analysis of this LEED-IV data. However, this apparent discrepancy may simply arise from a lack of sensitivity of the LEED-IV measurements to this structural element, as the local environment of the OH$_b$ bridging oxygen is only marginally different to that of a naked O$_b$. Furthermore, such OH$_b$’s may not display long-range order, and so although detectable by PhD, which relies only on local order, may be invisible in the LEED-IV experiment.

The formate adsorption geometry on TiO$_2$(110)(1×1) deduced from PhD and LEED-IV is consistent with ab initio theoretical predictions, as well as other experimental work; we note that a much earlier PhD study found a very
similar adsorption site, even though a much more limited data set was acquired and analysis did not include any consideration of substrate relaxation. Additionally, some measurements\textsuperscript{252,253,263,264} have suggested the presence of a second formate species on TiO\textsubscript{2}(110)(1×1). From RAIRS\textsuperscript{252} and NEXAFS,\textsuperscript{263} it was concluded that this second formate comprizes \(\sim 30 - 40\%\) of a saturated (2×1) overlayer, and is oriented such that its molecular plane is aligned along the [1\overline{1}0] direction, i.e. it is azimuthally rotated by 90° with respect to the PhD/LEED-IV formate. On the basis of earlier \textit{ab initio} calculations,\textsuperscript{256} it has been suggested that this second formate species is associated with adsorption at bridging oxygen vacancies,\textsuperscript{252} where one O from [HCOO]\textsuperscript− fills the O\textsubscript{b}-vac and the other is bonded to a neighboring Ti\textsubscript{5c}.

No evidence for a second formate species was found in the PhD study, although it was explored during structure determination;\textsuperscript{254} only single formate geometries were considered in simulation of the LEED-IV data.\textsuperscript{255} Consequently, there appears to be a significant disparity between the PhD,\textsuperscript{254} and the RAIRS\textsuperscript{252} and NEXAFS\textsuperscript{263} studies. However, as indicated in ref 254, it may merely be that the population of the second formate species is minimal in the PhD study due to differences in experimental conditions. The results of two STM studies support this view,\textsuperscript{264,265} indicating that substrate temperature may be the crucial parameter. Bowker et al.,\textsuperscript{264} following formic acid dosing at room temperature, imaged a second azimuthally rotated formate species, but at a concentration of only \(\sim 1\%\) of the ordered (2×1)-[HCOO]\textsuperscript− overlayer. In contrast, STM images from a TiO\textsubscript{2}(110)(1×1) surface exposed to formic acid and then annealed to 350 K for 400 min\textsuperscript{265} suggest that under these conditions the coverage of the azimuthally rotated form, located at bridging oxygen vacancies, is much more a substantial (\(\sim 35\%\) of
the adsorbed formate moieties adopted this geometry). It should be noted that a monodentate formate, also adsorbed at an oxygen vacancy, is additionally proposed to form subsequent to this low temperature anneal (~ 15% of surface formate species).

Besides formic acid, the only other carboxyl containing molecule to be the subject of a fully quantitative structure determination on TiO$_2$(110)(1×1) is the simplest amino-acid glycine (NH$_2$CH$_2$COOH). Scanned-energy mode PhD from the O 1s core level has been employed for this purpose.$^{266}$ Mimicking the previously discussed PhD study of formic acid adsorption on this substrate,$^{254}$ it was found that a surface glycinate ([NH$_2$CH$_2$COO]$^-$) and OH$_b$ are required to adequately reproduce diffraction data, i.e. adsorption occurs through acidic hydrogen dissociation. Indeed, the optimized adsorption structure emerging from this work is in excellent agreement with that of formate on TiO$_2$(110)(1×1), as illustrated in Figure 53. This result agrees with the structure proposed on the basis of STM images,$^{267}$ which indicated local (2×1) adsorbate ordering. It also agrees with recent first principles calculations.$^{268}$ Additionally, this ab initio study concluded that the glycine’s nitrogen forms a hydrogen bond with the OH$_b$. The coordinates of the nitrogen were not elucidated in the PhD study.$^{266}$ An earlier theoretical prediction$^{269}$ that glycine bonds to TiO$_2$(110)(1×1) in its zwitterionic form (NH$_3^+$CH$_2$COO$^-$) has been invalidated by experimental results. Indeed, current evidence suggests that the zwitterion only exists in multilayer films of glycine,$^{266}$ a deduction supported by molecular dynamics simulations.$^{270}$

Turning to other organic molecules containing one carboxyl group, it is often presumed that their adsorbed state is similar to that of formic acid on TiO$_2$(110)(1×1), i.e. they undergo dissociative adsorption to form the carboxylate, which adopts a bonding
geometry analogous to that illustrated in Figure 51. Experimental evidence acquired to date is largely consistent with this hypothesis. For example, ESDIAD data indicate that the molecular plane of acetate ([H$_3$CCOO]$^-$) bound to TiO$_2$(110)(1×1) is oriented perpendicular to the surface plane.$^{271}$ A C K-edge NEXAFS study corroborates this result, and also concludes that propanoate ([H$_5$C$_2$COO]$^-$) exhibits a similar angular geometry.$^{266}$ As regards the lateral location of such species, STM images at low adsorbate coverages have been analysed to extract this information, e.g. ref 272, where it is concluded that the bonding site of trimethylacetate ((CH$_3$)$_3$C$^-$COO) matches that of formate on TiO$_2$(110)(1×1). Interestingly, more recently published STM images of this system$^{273}$ have been interpreted as indicating the presence of a second azimuthally rotated (90°) bonding configuration for trimethylacetate, involving adsorption at a bridging oxygen vacancy. Clearly, this result parallels the situation for formate, where several studies have concluded the presence of a similarly-bound second formate species.$^{252,263-265}$

NEXAFS has additionally been applied to probe the orientation of more complex carboxyl containing species on TiO$_2$(110)(1×1), including benzoic acid (C$_6$H$_5$COOH) and three pyridine-carboxylic acid (C$_5$NH$_5$COOH) isomers, namely isonicotinic acid, nicotinic acid, and picolinic acid$^{274}$ (see Figure 54 for a depiction of these molecules). In that particular study, the primary focus was the angular geometry of the aromatic ring (phenyl/pyridyl), which was found in each case to be oriented such that the ring plane lies close to the surface normal. This geometry is to be expected, if, as core level PES data suggest,$^{275}$ all of these molecules undergo dissociative adsorption and are bound to the surface by their –COO$^-$ group. More interestingly, it was found that for each adsorption
system the aromatic ring adopts more than one azimuthal orientation, suggesting that there are at least two inequivalent adsorbate geometries. Consistent with an earlier study of benzoic acid,\textsuperscript{276} complementary STM images suggest that these different ring orientations may result from dimer formation driven by edge-to-face ring (C-H/π-system) interaction. In a more recent STM study,\textsuperscript{277} no evidence for such benzoate dimer structures was found, with simply a highly ordered (2×1) overlayer being imaged at close to saturation coverage. As previously discussed for formate on TiO$_2$(110)(1×1), it may be that this apparent discrepancy arises from variations in experimental methodology.

The angular orientation of the phenyl ring in the amino acid phenylalanine (C$_6$H$_5$CH$_2$CH(NH$_2$)COOH) has also been probed by NEXAFS.\textsuperscript{278} Analogous to the simpler amino acid, glycine, chemisorption on TiO$_2$(110)(1×1) is reported to be achieved through loss of the carboxyl group’s acidic hydrogen, with the phenyl ring plane tilting away from the surface normal by ~25°. In contrast to the work on benzoic and pyridine-carboxylic acid isomers,\textsuperscript{274} the azimuthal attitude of the ring was not explicitly considered in this study.

Motivated by the technological promise of titania-based dye sensitized solar cells (DSSCs), the structure of an even larger molecule, namely 2-cyano-3-(4-N,N-diphenylaminiophenyl)-trans-acrylic acid (see Figure 55) has been the subject of another NEXAFS study.\textsuperscript{279} Orientational information has been extracted as a function of coverage up to 1 ML. It was found that as the adsorbate density rises the molecule adopts an increasingly upright geometry, suggesting that inter-molecular interactions significantly influence adsorption geometry.
As well as examining the structure of larger molecules containing a single carboxyl, there is increasing effort to determine the structure of molecules containing more than one of these functional groups on TiO$_2$(110)(1×1). For example, the adsorption of terephthalic acid (C$_6$H$_4$(COOH)$_2$), an aromatic dicarboxylic acid, has been studied by Rahe et al.$^{280}$ Similar to ref 279, NEXAFS data have been acquired as a function of surface coverage, accompanied by NC-AFM. An almost flat lying adsorption geometry was deduced at low coverage (∼ 0.07 ML), possibly associated with binding to surface defects. In contrast, at 1 ML, the adsorbed terephthalic acid species is much more upright (tilt angle of 20 ± 10° away from the surface normal). NC-AFM images indicate that a well-ordered (2×1) overlayer is formed for ∼ 0.3 ML ≤ θ ≤ ∼ 0.8 ML, with a (2×3) unit cell becoming increasingly dominant in the range ∼ 0.8 ML to 1 ML. It is argued that the (2×3) phase results from hydrogen bonding between the topmost carboxylic acid groups of two neighbouring terephthalic acid molecules. This suggestion is supported by ab initio calculations,$^{281}$ which find such inter-adsorbate binding to be energetically favorable. Additionally, also in accord with experimental results, this theoretical study predicts that at low coverage terephthalic acid adsorbs with its phenyl ring parallel to surface. It is further determined that surface bonding is achieved through both (deprotonated) carboxyl groups; each [–COO$^-$] binds in a monodentate fashion to a Ti$_{5c}$. A similar geometry is favored in calculations by Watkins et al.$^{282}$ NC-AFM and DFT calculations also suggest a comparable flat-lying geometry is likely for a related molecule, trimesic acid (C$_6$H$_3$(COOH)$_3$), which has a third carboxylic acid group.$^{283}$

The adsorbed geometry of another dicarboxylic acid, bi-isonicotinic acid (2,2’-bipyridine–4,4’–dicarboxylic acid),) has been probed,$^{284,285}$ due to its role as a surface
binding ligand for DSSC dye molecules. A combination of O 1s core level PES, N K-edge NEXAFS measurements, and theoretical modelling were applied for this purpose. It was concluded that this molecule binds as bi-isonicotinate to the surface through two [–COO]− groups, and is oriented such that the pyridine ring planes are close to upright (a tilt angle of ~25° away from the surface normal. Figure 56 depicts the proposed adsorption geometry. There have also been studies of the adsorption of a complete dye molecule, Ru(4,4’-dicarboxy-2,2’-bipyridine)2(NCS)2, which incorporates two bi-isonicotinic acid ligands. Onishi’s group have employed STM to elucidate the interaction of this species with TiO2(110)(1×1).286,287 Dye exposure was achieved by immersing the TiO2 substrate, with or without a pivalate capping layer, in an acetonitrile solution of the dye. From the height and shape of adsorbate related features, it was deduced, in combination with DFT results,288 that this dye binds to the surface through two carboxylate groups from the same bi-isonicotinate ligand.

In contrast to the significant effort to examine the geometry of –COOH containing species on the (1×1) phase of TiO2(110), structural studies of these entities on (1×2) reconstructed substrates is restricted to STM. Formic289 and benzoic acid,277,290 as well as glycine,267 have all been studied in this manner, although details of adsorbed geometries are limited. Bennett et al.289 imaged formic acid, presumably adsorbed as formate, on the x-linked (1×2) phase. They found a preference for binding to the x-links, forming a rather disordered overlayer. Qiu and Barteau also found no evidence of adsorbate ordering following glycine dosing.267 Turning to benzoic acid, recent STM images acquired from a x-linked (1×2) surface indicate that adsorption occurs in the troughs between the added rows, forming a (2×2) overlayer as coverage increases.277 It is further concluded that the
phenyl ring is rotated by 90° relative to the carboxylate group, which is proposed to be due to adsorbate-substrate hydrogen bonding, i.e. phenyl ring plane is aligned perpendicular to O₆ rows.

In contrast to the carboxylic acids, much less work has been done on other organic acids, such as the phosphonic acids. The adsorption of methyl phosphonic acid [CH₃P=O(OH)₂] on TiO₂(110)(1×1) was studied with STM, NC-AFM, LEED, and DFT calculations. The nature of the phosphonic acids is somewhat more complicated, in that bonds can be made from the P=O, as well as the two P—OH groups, both of which may be deprotonated. It turns out that the adsorption geometry is very similar to the carboxylic acids: bridging bidentate bonding to two Ti₅c sites, with a (2×1) overlayer at saturation coverage (~0.5 ML). The issue of whether one or two OH bonds are deprotonated could not be resolved with the methods used. Hydroxyl associated with the deprotonation could not be imaged with SPM and the calculations found the doubly-deprotonated phosphonate to be only 0.17 eV more stable than the singly-deprotonated phosphonate. Calculations for phosphonic acid adsorption on rutile (110) and anatase (101) also favored bridging, bidentate configurations.

**TiO₂(011)**

To date, the only experimental work examining the structure of carboxylic acid containing molecules on TiO₂(011) has been undertaken by Batzill and coworkers. These researchers have studied the adsorption of acetic acid (H₃CCOOH) on the reconstructed (2×1) phase with STM. In sharp contrast to TiO₂(110)(1×1), it is concluded that acetic acid initially only adsorbs at defects on TiO₂(011)(2×1), dissociating to form
surface bound acetate. These moieties then act as nuclei for the growth of 1D acetate ‘clusters’, running along the troughs of the reconstructed substrate in the [01\bar{T}] direction. On the basis of supporting DFT calculations, they interpret their results in terms of adsorbate-induced surface restructuring through breaking of selected substrate bonds. In addition, it is suggested that both mono- and bridging bidentate acetate bonding configurations may coexist within these 1D ‘clusters’.

More recent DFT calculations concerned with the adsorption of formic acid on TiO$_2$(001)(2x1) predict that adsorption is only weakly favourable on regular surface sites$^{294}$. This result is consistent with the STM data suggesting that initially acetic acid is preferentially adsorbed at defects on this surface$^{164,293}$.

$\text{TiO}_2(001)$

Barteau and coworkers have undertaken detailed studies to explore the chemistry of various carboxyl containing molecules, along with other organic species, on TiO$_2$(001) (see, for example, ref 295). Primarily, they have focused upon adsorption on two different terminations, namely the so-called ‘{011}-facetted’ and ‘{114}-facetted’ surfaces, contrasting their reactivity. Concerning atomic scale adsorption geometries, however, beyond concluding that similar to TiO$_2$(110) carboxylic acids adsorb dissociatively (acidic hydrogen cleavage), any deductions are by necessity largely speculative; Barteau et al. rely upon substrate surface structures suggested in an early qualitative LEED study.$^{78}$ For formate, some additional insight into its adsorption geometry on the ‘{114}-facetted’ phase has been gained through STM by Iwasawa’s group.$^{79}$ High-resolution images clearly indicate the presence of surface adsorbates,
suggested to be formate species located at 4-fold and 5-fold coordinated Ti atoms, although the substrate surface structure is still not completely certain (as discussed in Section 2.4).

\(\text{TiO}_2(111)\)

STM has been used to image the adsorption structure of formate on this little studied low Miller index surface.\(^{296}\) Prior to adsorption, the surface exhibited nanometer sized (1×1) and (1×2) phases. Both terminations facilitate dissociative adsorption of formic acid at room temperature. On the basis of long Ti-Ti distances at the surface, complementary HREELS data, and adsorbate number density and mobility, it is concluded that the resulting formate is bound to single surface Ti atoms through one (monodentate) and/or both (chelating bidentate) of its oxygen atoms.

4.2 Alcohols

\(\text{TiO}_2(110)\)

There is, as yet, no fully quantitative structure determination of even the simplest alcohols on \(\text{TiO}_2(110)(1\times1)\). Instead, to date, structural information has been derived primarily from STM images and \textit{ab initio} calculations, as well as inferred from non-structural probes (e.g. TPD). Analogous to \(\text{H}_2\text{O}\), it has been concluded for a range of aliphatic alcohols that dissociative adsorption occurs at \(\text{O}_b\)-vacs, i.e.

\[
\text{ROH}_{(g)} + \text{O}_b\text{-vac} + \text{O}_b \rightarrow \text{RO}^-_{(ads)} + \text{OH}_b,
\]
with the O from the alkoxide moiety filling the \(O_h\)-vac (see, for example, refs 297-303). Zhang et al. have employed STM to observe these reaction products subsequent to exposure to methanol, butan-2-ol, or octanol.\(^{300,302}\) Representative images are presented in Figure 57, which show the impact of dosing butan-2-ol at room temperature onto \(\text{TiO}_2(110)(1\times1)\).\(^{301}\) The clean substrate is displayed in Figure 57a, which is consistent with a \((1\times1)\) termination, decorated with a small concentration of \(O_h\)-vacs (bright spots on dark rows). Focussing on the three \(O_h\)-vacs highlighted by white arrows, subsequent to butan-2-ol exposure (Figure 57b) these features become much brighter, which was interpreted as binding of 2-butoxide at these sites. Clearly, no details of the adsorbate conformation can be gleaned from the image. The three crosses in Figure 57b are concluded to mark the locations of \(\text{OH}_b\)'s resulting from the dissociation of the three butan-2-ol molecules.

In addition to dissociative adsorption at \(O_h\)-vacs, alcohols can also bond to regular \(\text{Ti}_{5c}\) sites on \(\text{TiO}_2(110)(1\times1)\). Evidence for such species is provided in Figure 57b by the bright protusions labelled ROH, which are located atop \(\text{Ti}_{5c}\) rows. Further details of their adsorbed state remain uncertain, including whether adsorption is molecular or dissociative.\(^{297-299,301,303}\) Most recently, Hansen et al. have employed STM to deduce that ethanol can adsorb both intact and as ethoxide at \(\text{Ti}_{5c}\) sites.\(^{303}\) Variations in adsorbate heights, mobility from time-lapsed STM images, and reactivity, in conjunction with DFT calculations, were all used to reach this conclusion. Other \textit{ab initio} calculations of methanol on \(\text{TiO}_2(110)(1\times1)\) are consistent with this mixed molecular/dissociative adsorption scenario.\(^{304}\)
Besides work on monohydric alcohols (1× –OH), the adsorbed structures of polyhydric alcohols have also been examined. Diebold and coworkers have employed STM in conjunction with first principles calculations to probe the bonding geometry of catechol (benzene-1,2-diol) on TiO$_2$(110)(1×1).$^{305}$ Adsorption at Ti$_{5c}$ sites was concluded to occur, with an ordered (4×1) overlayer being observed at close to saturation coverage. At low coverage, as illustrated in Figure 58, *ab initio* modelling suggests that adsorption involves both –OH groups dissociating, with the resulting dialkoxide moiety forming a bridging-bidentate ligand attached to two neighbouring Ti$_{5c}$’s, similar to carboxylate binding to the same surface. Two OH$_b$’s are also formed. A more complex bonding arrangement emerges for the (4×1) phase, involving both bidentate and monodentate (single –OH dissociated) benzene-1,2-diol derived alkoxide species. It is concluded that two adsorbed phases coexist, one consisting of monodentate adsorbates alone, and the other involving mixed monodentate-bidentate bonding. These two configurations are apparently stabilized by inter-adsorbate hydrogen bonding, and can easily interconvert by means of proton transfer between the OH$_b$’s and mono/bi-dentate alkoxides. It should be noted that the (4x1) unit cell is concluded to result from alternate left/right tilting of the adsorbates’ phenyl rings to minimize inter-adsorbate repulsion; at lower coverage the molecular plane of the bidentate catecholate species is upright.

More recently, Zhang et al.$^{306}$ have employed STM to study the adsorption of another diol, namely 1,2-propanediol (HO(CH$_2$)$_3$OH), on TiO$_2$(110)(1x1). At the very low adsorbate coverages imaged in their measurements, adsorption was concluded to occur at O$_b$-vacs through cleavage of one of the O-H bonds, forming O$_b$(CH$_2$)$_3$OH. The
intact OH is reported to be located above a Ti$_{5c}$ site. This group can also undergo (reversible) dissociation, leading to an adsorbed dialkoxide, i.e. O$_b$(CH$_2$)$_3$O-Ti$_{5c}$.

A more complex molecule, 2,3,6,7,10,11-hexahydroxytriphenylene, containing six –OH groups has been deposited on TiO$_2$(110)(1×1), and probed with NEXAFS.$^{307}$ As is apparently quite typical of such planar molecules, regardless of functional group(s), it was found that the angular adsorption geometry is coverage dependent, i.e. the molecular plane lies closer to the surface normal with increasing coverage. More specifically, in the submonolayer regime the molecular plane of 2,3,240,710,11-hexahydroxytriphenylene displays a tilt angle of ~ 60° away from the surface normal in the [\(\bar{T}\)10] azimuth. At monolayer saturation coverage, this tilt angle decreases towards 0°, i.e. the adsorbates were concluded to be more or less upright and azimuthally oriented such that their molecular planes are parallel to the O$_b$ rows. However, as the author of ref 307 points out, data interpretation for the monolayer coverage was not entirely definitive.

*Other TiO$_2$ surfaces*

The adsorption of alcohols has been studied on other low Miller index rutile TiO$_2$ surfaces. To date, however, there has been no significant experimental insight into adsorbate geometries.

**4.3 Aldehydes, Ketones, and Acid anhydrides**

Despite interest in the surface chemistry of the aldehyde group on TiO$_2$, there has been little work directly probing adsorbed structures. For the simplest molecules possessing this functionality, namely formaldehyde (HCHO) and acetaldehyde
(CH$_3$CHO), only theoretical modelling has been used to predict adsorption sites.$^{308-310}$ On the contrary, some experimental effort has been applied to ascertaining the structure of benzaldehyde (C$_6$H$_5$CHO) on both TiO$_2$(110) and TiO$_2$(001).

STM has been employed to image isolated C$_6$H$_5$CHO molecules on TiO$_2$(110)(1×1). As with –COOH and –OH containing organic molecules, they were found to be located above the Ti$_{5c}$ rows.$^{311}$ On the basis of complementary DFT calculations, the bonding was suggested to be through the formation of an O-Ti$_{5c}$ bond ($\eta^1$-atop configuration), with the adsorbate’s molecular plane at an oblique angle to the O$_b$ rows (see Figure 59a). Interestingly, stronger binding at O$_b$-vacs was predicted from the DFT, but no such defect related adsorption was identified in STM images. Calculations were also conducted to investigate the impact of Ti interstitials on benzaldehyde adsorption. In addition to the monodentate $\eta^1$-atop bonding just outlined, the presence of an additional near-surface Ti also favored adsorption involving bidentate bonding through both the C and O in the aldehydic C=O group to O$_b$ and Ti$_{5c}$, respectively ($\eta^2$-dioxyalkylene configuration, see Figure 59b). Notably, the –CHO group’s C-H bond is cleaved to facilitate this bonding mode, and so the resulting local ensemble is essentially equivalent to that suggested to be the result of [HCOO]$^-$ adsorption at O$_b$-vacs on TiO$_2$(110)(1×1).$^{252,256}$ Beyond simply examining the chemisorbed benzaldehyde, images of the surface bound pinacolate ([C$_6$H$_5$CHOCHOC$_6$H$_5$]$^2^-$) product formed through coupling of two benzaldehyde molecules have also been reported in ref 312. This reaction product is again found to reside on Ti$_{5c}$ rows, with a Ti interstitial key to its formation.
On TiO$_2$(100), NEXAFS has been applied to probe the orientation of benzaldehyde.$^{314}$ Measurements were acquired from a reduced surface, prepared by Ar$^+$ sputtering, which was exposed to benzaldehyde at 160 K, and then flashed to 250 K. This thermal treatment was concluded to result in chemisorbed benzaldehyde and/or the pinacolate (see above). Interestingly, C-K edge NEXAFS spectra suggest adsorbate disorder, whereas O K-edge data indicate some preferred angular orientation. However, it is difficult to draw any definitive structural conclusions from the data, due to the ill-defined nature of the sputtered surface, as well as uncertainty over the precise nature of the adsorbed species.

Concerning ketones, the most pertinent publications are two STM studies of acetone (CH$_3$COCH$_3$) adsorption on TiO$_2$(110)(1×1) by Yasuo et al.$^{312}$ and Xia et al.$^{313}$ Yasuo et al.$^{312}$ found that adsorption onto a clean surface, exhibiting a small number of O$_b$-vacs, resulted in the appearance of new mobile features on the Ti$_{5c}$ rows. On the basis of DFT modelling,$^{315}$ it was concluded that an $\eta^1$-atop bonding mode was likely, i.e. acetone is located atop a Ti$_{5c}$, binding through O. In sharp contrast Xia et al.$^{313}$ report that acetone adsorbs at O$_b$.vacs rather than Ti$_{5c}$ sites. This disparity in adsorption site may be a result of the presence OH$_b$’s in one of the two studies. Yasuo et al.$^{312}$ acquired further STM images subsequent to acetone adsorption onto a TiO$_2$(110)(1×1) surface decorated with O$_{ad}$ atoms. A different adsorbed complex was reported to form, which was ascribed to bridge bonding $\eta^2$-2,2-propanediolate, bound to neighbouring Ti$_{5c}$’s, as depicted in Figure 60; the DFT calculations$^{315}$ found this species to be stable.

As regards acid anhydrides, which contain two C=O groups attached to the same O atom, relatively little effort has been directed towards studying the adsorption on single
crystal rutile TiO$_2$ substrates. Ashima et al. have studied the adsorption of acetic
anhydride ((CH$_3$CO)$_2$O) on TiO$_2$(110)(1×1), concluding dissociative adsorption from
vibrational spectra.$^{316}$ STM data acquired from the same system$^{317}$ support this result. It
is proposed that two types of surface acetate result from this dissociation, i.e.

$$(\text{CH}_3\text{CO})_2\text{O}_{(g)} + \text{O}_b \rightarrow \text{CH}_3\text{COO}^-_{(ads)} + \text{CH}_3\text{COO}^-_{(ads)}.$$  

STM images are analysed to suggest that CH$_3$COO$^-_{(ads)}$ is adsorbed in the typical
configuration for carboxylic acids on TiO$_2$(110)(1×1), i.e. bridging-bidentate to two
neighbouring Ti$_{5c}$’s. For CH$_3$COO$^-_{b(ads)}$, the adsorption geometry mimics that suggested
for formic acid at O$_b$-vacs.$^{252,256,265}$ The authors also argue that some of the CH$_3$COO$^-_{b(ads)}$
species convert to CH$_3$COO$^-_{(ads)}$ resulting in production of O$_b$-vacs.$^{317}$

A larger molecule, containing two acid anhydride groups, whose structure has
been probed on both the TiO$_2$(110)(1×1) and TiO$_2$(011)(2×1), is 3,4,9,10-perylene-
tetracarboxylic-dianhydride (PTCDA). Figure 61 shows the structure of this molecule,
which is widely studied due its potential as an organic semiconductor. NEXAFS has been
employed to determine the orientation of this molecule as a function of coverage on
TiO$_2$(110)(1×1).$^{318}$ At 1 ML coverage (as per definition in ref 318), NEXAFS data
suggest a disordered overlayer, whilst the majority of the PTCDA molecules are flat lying
in the multilayer regime. More interestingly, at 0.5 ML coverage, a tilted adsorption
geometry is determined, with the molecular plane being inclined away from the surface
normal by $50^\circ \pm 10^\circ$. It is proposed that this molecular orientation is a result of interfacial
bonding through one of the acid anhydride groups, perhaps involving ring-opening with
bonds to three Ti_{5c}'s and an O_{vb} as well as the perylene core to O_{vb} atoms. The latter interaction is suggested on the basis of the results of a combined NC-AFM and DFT study examining the adsorption of a similar molecule, N,N’-bis(1-hexylheptyl)-3,4,9,10-perylene-tetracarboxylic-diimine, on the same substrate.\cite{319} In that work, adsorbates appear to be centered on the O_{vb} rows with their long axis parallel to them. Theoretically, it is predicted that these molecules are not entirely flat-lying, but that they adopt a somewhat inclined geometry tilting over into the shallow trenches between O_{vb} rows. It should be noted that the authors further conclude from NC-AFM images that adsorption involves O_{vb}-vacs, but that these entities are apparently neglected in the \textit{ab initio} calculations.

Concerning PTCDA on TiO_{2}(011)(2\times1), STM has been applied to examine surface adsorbate structure.\cite{320,321} For low coverages, the adsorption mode is shown to change over a narrow range of substrate temperature. At 100°C, ordered 1D chains, extending in the [01\overline{1}] azimuth are formed. Within these structures, each PTCDA molecule is apparently flat-lying, located in the trough between the topmost zigzag rows of oxygen atoms, with its longer axis parallel to these rows. Decreasing the substrate temperature to 80°C during deposition leads to isolated PTCDA molecules decorating the terraces, with their longer molecular axis rotated by 90°. At 120°C, step-edge adsorption, and 2D/3D agglomeration is favored. Closer to monolayer saturation coverage, two types of 2D PTCDA islands are formed, exhibiting internal translational order, and disorder, respectively. We would like to point out that no consideration was given to PTCDA-induced substrate restructuring in this STM study, which was suggested to occur following acetic acid adsorption on TiO_{2}(011)(2\times1).\cite{164}
4.4 Amines, Azo and Pyridine Compounds

Structural data is again relatively scarce for organics with nitrogen-containing functional groups, although several such studies have already been mentioned in earlier sections, e.g. work on TiO$_2$(110)(1×1) concerned with the adsorption of glycine,$^{266-268}$ which possesses a primary amine (-NH$_2$) group. Another study of some interest involves STM imaging of both azobenzene ((C$_6$H$_5$)$_2$N$_2$) and aniline (C$_6$H$_5$NH$_2$) on TiO$_2$(110)(1×1).$^{322}$ Concerning azobenzene, it proved impossible to map the lateral position of this molecule on the substrate at low coverage, due to its high mobility under the measurement conditions, i.e. sample at room temperature. In contrast, a well-ordered c(2×2) overlayer was clearly visible at close to monolayer saturation, although identification of the adsorbate-substrate alignment is not possible at this coverage. However, through comparison with STM images of aniline covered TiO$_2$(110)(1×1), it is concluded that the azobenzene has dissociated in the c(2×2) overlayer to form two phenyl imide (C$_6$H$_5$N) moieties, as aniline also forms a very similar c(2×2) superstructure; the c(2×2) unit cells are also apparent in LEED. Support for this dissociation is provided by valence band photoemission data.$^{323}$ Ab initio modelling also suggests that such chemistry is more likely to occur for azobenzene adsorbed on TiO$_2$(110)(1×1) than in the gas phase, although molecular desorption is still favored over dissociation.$^{324}$ Additionally, these calculations predict that intact azobenzene is bound to the surface as the cis-isomer, with the two nitrogen atoms bonding to neighbouring Ti$_{5c}$’s; trans-azobenzene is more stable the gas phase.
More quantitative structural data have been acquired for a larger amine, (4,4’,4”-Tris)N-(1-naphthyl)-N-phenyl-amino-triphenylamine (see Figure 62), on TiO$_2$(110)(1×1), through the application of NEXAFS.$^{325}$ Data were collected from an adsorbed monolayer, bilayer, and multilayer of these molecules. It was found that molecular orientation did not vary greatly over this range of coverage. A geometry towards flat-lying was concluded, with the tilt angle between the molecular plane and the surface increasing somewhat with coverage, i.e. 35° at a monolayer to 47° for multilayer. As the authors indicate, adsorbed molecules may not be completely planar due to the potential for rotation about N-C bonds, which could complicate interpretation of the NEXAFS analysis.

Two other nitrogen containing organic molecules, pyridine (C$_5$H$_5$N) and 2,6-dimethylpyridine ((CH$_3$)$_2$C$_5$H$_3$N), have been the subject of STM measurements on TiO$_2$(110)(1×1).$^{326,327}$ Both molecules were concluded to adsorb on Ti$_5$c rows, but moved across the surface at the imaging temperature (room temperature); pyridine was found to be significantly more mobile than 2,6-dimethylpyridine. Further images of pyridine$^{327}$ suggest that these molecules preferentially diffuse to step sites.

### 4.5 Aromatic Hydrocarbons

The adsorbed structures of aromatic hydrocarbons on single crystal TiO$_2$ substrates have been primarily pursued with STM and/or NEXAFS. For example, Zhou et al. have acquired STM data from the prototypical aromatic molecule, benzene (C$_6$H$_6$), on TiO$_2$(110)(1×1).$^{328}$ To enable benzene related protrusions to be observed, they maintained the substrate at < 40 K to minimize adsorbate mobility. Under these conditions, discrete benzene molecules were imaged at monolayer coverage; at lower
adsorbate densities 1D chains running parallel to the O_b rows were observed, but individual molecules could not be resolved. No further structural details were obtained from the experimental data, but supporting first principles calculations suggest a flat-lying adsorption geometry for benzene with its center located above the midpoint between two Ti_{5c}'s. NEXAFS spectra acquired from benzene on TiO_2(110)(1×1) support this prediction,$^{329}$ showing that for coverages up to a monolayer benzene is close to flat-lying. Tilt angles were determined to be 24° ± 5° and 19° ± 8° for monolayer and submonolayer coverage, respectively.

Further to examining benzene, the adsorption on TiO_2(110)(1×1) of naphthalene (C_{10}H_8) and anthracene (C_{14}H_8), which consist of two and three fused benzene rings, respectively, was also discussed in ref 329. In the monolayer regime, NEXAFS data again indicate near flat-lying molecules on the substrate, with naphthalene being ordered azimuthally so that its long axis is parallel to the O_b rows. For all three molecules, the authors suggest that any deviation from a completely flat-lying geometry is likely due to adsorption at surface defects and/or vibrations.

Two other fused polycyclic aromatic molecules, perylene (C_{20}H_{12}) and pentacene (C_{22}H_{14}), have been studied on TiO_2(110)(1×1).$^{330,331}$ Experimental data again indicate similar adsorbate orientations to those of benzene, naphthalene, and anthracene.$^{329}$ NEXAFS was applied to determine a close to flat-lying geometry for perylene molecules at a coverage of ~ 1 ML (coverage was derived from quartz crystal microbalance data).$^{330}$ Both NEXAFS and STM were employed to probe the adsorption of pentacene.$^{331}$ For monolayer coverage and below, it was found that these molecules are azimuthally oriented such that their long axis is parallel to the O_b-rows (analogous to naphthalene$^{330}$),
and are tilted around this axis by 25° ± 2° away from the surface plane, i.e. they adsorb with their molecular plane close to parallel to the surface. Such a flat-lying geometry is maintained in the multilayer regime, at least up to 3 ML.

Motivated by potential importance as components in organic-based devices, the adsorbed geometry of a linear oligophenylene, para-sexiphenyl \((C_6H_5(C_6H_4)_4C_6H_5)\), on \(\text{TiO}_2(110)(1\times1)\) has also been examined.\(^{332,333}\) Grazing incidence XRD, AFM, and reflection difference spectroscopy (RDS) indicate that, within the first monolayer, the orientation of the para-sexiphenyl is dependent on substrate temperature during deposition. At 370 K, the molecules are near to up-right, forming a highly-ordered crystalline overlayer, whereas for room temperature deposition para-sexiphenyl lies down with its long axis parallel to the \(O_b\) rows.

Finally, STM has been employed to probe the interaction of so called ‘violet lander’ molecules with both \(\text{TiO}_2(110)(1\times1)^{334}\) and \(\text{TiO}_2(011)(2\times1)^{321}\). These entities, which are of interest to molecular electronics, consist of a central planar polyaromatic segment and four side 3,5-di-tert-butylphenyl groups (‘legs’), through which the molecule adheres to the surface. High resolution images acquired from \(\text{TiO}_2(110)(1\times1)\) indicate that the violet lander adsorbs with its legs located above the \(\text{Ti}_{5\text{c}}\) rows.\(^{334}\) As shown in Figure 63, two different azimuthal orientations are adopted, i.e. aligned such that its longer axis is parallel to the \(O_b\) rows, or rotated 30° away from this direction. On \(\text{TiO}_2(011)(2\times1)^{321}\), it is concluded that the long axis of this molecule is typically azimuthally rotated by about 41° away from the zigzag rows of topmost oxygen atoms, with the legs located over Ti atoms.
4.6 Organometallic Compounds

Work by Onishi’s group on the adsorption geometry of a DSSC dye molecule, Ru(4,4’-dicarboxy-2,2’-bipyridine)$_2$(NCS)$_2$, on TiO$_2$(110)(1×1) has been outlined in Section 4.1 This study is one of several to try to gain insight into the structure of relatively complex organometallic species on rutile TiO$_2$ surfaces.

Copper phthalocyanine (CuPc), in particular, has been the focus of significant attention. Wang et al. have used STM to elucidate its adsorption on both $x$-linked TiO$_2$(110)(1×2) and TiO$_2$(210). It is concluded that CuPc adsorbs on the $x$-linked (1×2) reconstructed (110) surface at step edges, $x$-links, and in the trough between the added rows. In the latter location, it is deduced that the plane of the molecule is typically tilted somewhat away from parallel to the (110) surface. A tilted geometry was also proposed for CuPc on defect free areas of TiO$_2$(210), with flat-lying adsorption occurring at defects. The adsorption of this organometallic species has also been probed on TiO$_2$(011)(2×1) with STM. Step edge adsorption is again observed, along with adsorption on the terraces. Apparently, molecules adsorbed in this latter region can have their Cu atom either centered above the zigzag oxygen rows, or in the troughs between them. Furthermore, two different azimuthal orientations are suggested to occur for terrace bound adsorbates.

Besides CuPc, the geometry of zinc phthalocyanine (ZnPc) adsorbed on TiO$_2$(110)(1×1) has been probed by NEXAFS. For the first layer of molecules, directly attached to the substrate, a tilt angle of the molecular plane relative to the surface of 30° is concluded. However, it is indicated that further work is required to determine the adsorbed configuration, as the molecule may be buckled, or otherwise distorted, due to
specific adsorbate-substrate interactions. In addition, it may be that there are multiple adsorption geometries as discussed above for CuPc on other rutile TiO$_2$ surfaces. NEXAFS spectra has also been recorded from another near-planar Zn containing organometallic, namely zinc-protoporphyrin, on TiO$_2$(110)(1×1). These data indicate that the adsorbed molecules are close to flat-lying at sub-monolayer coverages. However, they display a much more up-right orientation at a monolayer.

Copper hexafluoroacetylacetonate (Cu(hfac)$_2$) adsorption on TiO$_2$(110)(1×1) has also been studied using NEXAFS in conjunction with other surface probes; Figure 64 depicts Cu(hfac)$_2$. It is concluded that at room temperature this organometallic molecule adsorbs dissociatively, as follows:

$$\text{Cu(hfac)}_2(\text{g}) \rightarrow \text{Cu(hfac)}_{\text{ads}} + \text{hfac}_{\text{ads}}.$$ 

A (2×1) overlayer is formed, and NEXAFS spectra show that both adsorbed fragments are approximately upright, and aligned with the O$_b$ rows. On this basis, it is suggested that Cu(hfac)$_{\text{ads}}$ is bound via its Cu atom to two neighbouring O$_b$’s and that hfac$_{\text{ads}}$ bonds via its two oxygen atoms to two neighboring Ti$_{5c}$’s.

5. Metals

A thorough overview of metal growth on rutile TiO$_2$ can be found in the review by Diebold. A more recent review concerning metal interactions with oxides by Fu and Wagner focuses in particular on the electronic interaction and the chemical reaction at the metal/oxide interface, and various trends can be seen on TiO$_2$(110). Here, we will
examine the structure of metal films on rutile TiO$_2$, focusing especially on developments since the review of Diebold.$^5$ Structure is taken to include issues such as growth mode, nucleation points, and morphology changes upon annealing.

The growth mode under thermodynamic equilibrium conditions is determined as follows:$^{341}$

$$\Delta \gamma = \gamma_{\text{metal}} + \gamma_{\text{metal-substrate}} - \gamma_{\text{substrate}}$$

where $\gamma_{\text{metal}}$, $\gamma_{\text{metal-substrate}}$, and $\gamma_{\text{substrate}}$ are the free energies of the metal surface, the metal/substrate interface, and the substrate surfaces, respectively. For $\Delta \gamma > 0$, 3D island growth occurs [Volmer-Weber (VW)] otherwise, 2D layer growth occurs [Frank-van-der-Merwe (FM)]. At higher coverages, a 2D layer (or layers) can be followed by 3D clusters [Stranski-Krastanov growth (SK)]. As $\gamma_{\text{metal-substrate}}$ cannot be easily measured, it is often approximated by the heat of formation of the metal oxide ($-\Delta H^0_{\text{metal oxide}}$), although a better approximation can be made by also including the heat of formation of the metal ($-\Delta H^0_{\text{metal}}$) to account for metal-metal interactions.$^{342}$

Specifically for TiO$_2$(110), Hu et al.$^{341}$ have plotted $-\Delta H^0_{\text{metal}}$ vs. $-\Delta H^0_{\text{metal oxide}}$ both per mole of metal, as shown in Figure 65. The plot can be divided into three zones. In zone I, $-\Delta H^0_{\text{metal}}/\Delta H^0_0 > 1$ which means that metal-metal interactions are stronger than metal/TiO$_2$ interactions. As expected then, 3D clustering has been observed in this zone. The opposite is true in zone III where $-\Delta H^0_{\text{metal}}/\Delta H^0_0 < 1$ and 2D layer growth has been observed. In zone II, $-\Delta H^0_{\text{metal}}/\Delta H^0_0 = 1$ and other factors come into play, such as
interfacial stress and kinetic constraints so that both 3D and 2D layer growth has been
seen. Indeed, even though Cr displays VW growth, this is kinetically limited: 2D growth
occurs up to a critical submonolayer coverage of ~0.8 ML, after which 3D growth
prevails (see section 5.5). This 2D islanding (2DI) growth mode is discussed in detail by
Ernst et al.\textsuperscript{343} using Cu/ZnO(0001)-O as a case study. However, as will be seen, even
metals in zone I such as Pt and Au grow in this mode, albeit with a much lower critical
coverage (~0.01 and ~0.1 ML, respectively).

5.1 Group 1

The adsorption of alkali metals (AM) on metal oxides is a topic of technological
importance. These metals are used extensively as reaction promoters in catalysis. Li
interactions with TiO\textsubscript{2} are particularly important in connection with battery connections.

\textit{TiO\textsubscript{2}(110)}

Na and K are the most extensively studied alkali metals on TiO\textsubscript{2}(110). Onishi et
al.\textsuperscript{344} found that deposited Na was disordered until a critical coverage was reached after
which Na spontaneously orders into a c(4×2) superstructure detected by LEED. A model
was proposed which involves the formation of arrays of Na\textsubscript{2}O-dimers. In this model, each
of the Na atoms is adsorbed in between sites, as shown in Figure 66. Onishi and Iwasawa
revisited the system with STM,\textsuperscript{345} showing that Na adsorbs over the Ti\textsubscript{5c} rows. Hence the
adsorption site was reassigned to the atop Ti position (Figure 66).

In ion shadowing/blocking experiments, the adjacent position was favored
(Figure 66). However, this assignment is at odds with a number of theoretical studies as well as a more recent extended X-ray absorption fine structure (EXAFS) study that favor the between site.

The between site was also found for K adsorbed on TiO$_2$(110) in an EXAFS study, although it should be noted that the K/TiO$_2$(110) sample was annealed to 600 K following deposition. STM and NC-AFM images suggested that the K was arranged in rows either side of the O$_b$ rows. More recent NC-AFM images recorded at ~80 K but with K deposited at room temperature reveals individual K atoms that are adsorbed either side of the O$_b$ rows as shown in Figure 67. This is suggestive of either the between or the adjacent site and on the basis of additional DFT calculations, Yurtsever et al. also favor the between site.

Sasahara et al. use Kelvin probe force microscopy (KPFM) to show that the Na is almost completely ionized at low coverage with similar results being found by Yurtsever et al. for K on TiO$_2$(110). These KPFM results are consistent with earlier spectroscopic data which show that for Li, Na, K, and Cs, there is significant electron transfer from the alkali metals, leading to ionic bonding up to about 0.5 ML, after which further deposition gives metallic alkalis (For Li, see ref 353; for Na, see refs 345,354, 36; for K, see refs 354, 355; for Cs, see 354,356-358)

Evidence for the charge transfer comes, for example, from an increase of the BGS intensity in valence band PES with increasing AM coverage, from a decrease in the workfunction with increasing AM coverage, and from an extremely weak or even absent AM s peak in metastable impact electron spectroscopy (MIES): the AM s peak when present an be detected just below $E_F$. 94
For metallic behavior at higher coverage, the evidence comes from the evolution of an intense AM $s$ peak in MIES with increasing coverage, the presence of characteristic plasmon losses in electron energy loss spectroscopy (EELS) at high coverages, little or no further reduction of the workfunction with increasing coverage and shifts in the binding energy in PES. To illustrate this, valence band PES and MIES data are shown in Figure 68 for Cs on TiO$_2$(110).\textsuperscript{356}

At low temperature (130 K), the growth of Li follows the pattern described above. However, as the temperature increases to 300 K, the Li 2$s$ peak observed in MIES decreases in intensity and is difficult to detect above 260 K. At this temperature desorption is not expected (for instance, no desorption of K or Cs occurs at least up to 300 K). Similarly, reaction with species in the ambient vacuum can be excluded on the basis that no such reaction is observed for K or Cs. As such, Krischok et al.\textsuperscript{353} concluded that Li is either inserted into the TiO$_2$ surface or migrates into the bulk. Calculations show that although the tendency for Li to intercalate on anatase TiO$_2$ is much higher than for rutile,\textsuperscript{359} it is nevertheless possible at the observed temperatures.

Krüger et al.\textsuperscript{36} took advantage of the well-defined adsorption site of Na and its behavior as an electron donor on TiO$_2$(110) to address a recent hot topic: the source of the BGS.\textsuperscript{31,31,34-35,39,98,360,361} An electron excess was introduced onto TiO$_2$(110) by deposition of Na. Resonant PES (ResPES) tuned to enhance the BGS shows the increase in intensity that one would expect. PhD from this same peak reveals the same distribution of the BGS for Na/TiO$_2$(110) and $r$-TiO$_2$(110). Given that both diffraction patterns fit well with a model that explicitly places all Ti$^{3+}$ species at lattice sites, it was concluded that the BGS arises from O$_6$-vacs, with the distribution dictated by electrostatics.
Nevertheless, it remains feasible that the electrons donated by deeper lying Ti\textsubscript{int} would localize in the same way as those donated by Na, in line with the interpretation by Papageorgiou et al.\textsuperscript{40}

\textit{TiO\textsubscript{2}(100)}

Most work on the (100) surface focuses on the ordered c(2×2)-K surface which forms after annealing to \(~1000\) K. Charge transfer from K to near-surface Ti for the c(2×2)-K surface is widely reported. For instance, Purdie et al.\textsuperscript{362} show that the BGS at \(~0.9\) eV absent on the clean 1×1 surface becomes filled upon formation of the c(2×2) overlayer. However, more recent studies by Lindsay et al.\textsuperscript{363,364} show the situation to be much more complicated.

For an initially stoichiometric surface, upon deposition of K, the BGS does indeed increase, as it does for AM on TiO\textsubscript{2}(110) described above. However, after annealing, the BGS decreases in intensity until it vanishes at 1020 K; the temperature required to form a sharp c(2×2) LEED pattern. This behavior is replicated in Ti 2\textit{p} core level PES where a significant shoulder that appears at a lower binding energy when K is deposited vanishes upon annealing (the shoulder is indicative of reduced Ti\textsuperscript{3+} states). These results were rationalized by DFT calculations that suggest that the K is fully oxidized to K\textsuperscript{+} but the electron excess is located anywhere in the bulk.\textsuperscript{363} These conclusions seem reasonable on the basis of recent PhD experiments by Krüger et al.\textsuperscript{36} discussed above where it is shown that deposition of Na leads to localisation of donated electrons in a number of sub-surface sites even without annealing.
On a more reduced surface, Lindsay et al.\textsuperscript{363} observed a (1 -1 2 2) overlayer also seen by Moritz et al. as reported in ref 363. A small shoulder remained in the Ti 2p PES spectrum even after annealing. However, this is thought to arise not from charge transfer but from further reduction of the surface due to the thermal annealing required to form the c(2×2) overlayer.

As for the TiO$_2$(100)1×3 surface, Brause et al.\textsuperscript{365} have used MIES and valence band PES to study the adsorption of K and Cs. The situation is similar to that found for AM on TiO$_2$(110): up to ~0.5 ML, there is an electronic transfer from K and Cs. Further deposition of K or Cs lead to metallic behavior.

$\text{TiO}_2(441)$

The adsorption of Na on TiO$_2$(441) was studied by Onishi et al.\textsuperscript{345} They found almost the same behavior as on the (110) surface. The differences were that the workfunction reduction was ~1 eV less than on the (110) surface and that the c(4×2) superstructure was not obtained. A greater number of Ti$^{3+}$ species to begin with, due to the high step density, explains the smaller workfunction change and the narrow terrace width means a c(4×2) superstructure cannot form.

5.2 Group 2

Alkaline earth metals act as reaction modifiers on a number of substrates including metal oxides. The interactions of Ca and Ba with TiO$_2$ are particularly relevant. In the case of Ca, this is because of the role of Ca in Ti-containing bone implants\textsuperscript{366} and for Ba, this is due to the use of barium oxide in de-NO$_x$ catalysts.\textsuperscript{367}
Calcium adsorption was first reported following bulk segregation. For example, Zhang et al.\textsuperscript{368} studied an ordered layer of bulk segregated Ca on the (110) surface. A c(6×2) LEED pattern was observed, together with STM images that showed a row structure running in the [001] and [1\bar{1}0] directions. A calcium titanate structure was proposed based on core level PES data that showed Ca in the +2 state.

In contrast, Nörenberg and Harding reported a p(3×1) adlayer also formed by segregation on the basis of STM, LEED, reflection high energy electron diffraction (RHEED), and theoretical calculation.\textsuperscript{369-371} Their observed c(6×2) LEED pattern was rationalized by invoking the presence of antiphase boundaries.

Bikondoa et al.\textsuperscript{372} obtained overlayer structures by bulk segregation of Ca and by metal vapor deposition (MVD) of Ca, followed by post-annealing to 1100 K. With either adsorption method, the rows originally observed by Zhang et al. were seen in STM as shown in Figure 69a. 2D islands with a clear c(6×2) symmetry were also imaged with STM (Figure 69b). Surfaces dominated by rows or 2D islands both gave the same c(6×2) LEED pattern. Close inspection of Norenberg and Harding’s filled states STM image also reveals this c(6×2) symmetry.\textsuperscript{370}

Li et al.\textsuperscript{373} showed that submonolayer coverages of Ba vapor-deposited onto o-TiO\textsubscript{2}(110) led to oxidized Ba even without annealing. Above 1 ML, their results indicate that Ba is metallic, reminiscent of the AM metal behavior described above. Their conclusions were based on valence band and core-level PES as well as ResPES. For example, the Ti 3d defect state has zero intensity before deposition of Ba and maximizes
with ~1 ML Ba. Similarly the workfunction of the system goes down with Ba coverage with a plateau beyond 1 ML.

Pang et al.\textsuperscript{374} studied Ba on TiO\textsubscript{2}(110). Deposition of Ba was via MVD. With only brief annealing of the Ba/TiO\textsubscript{2}(110) system (3-6 min at 1000 K), STM images reveal a disordered, particulate film. STM together with NC-AFM images recorded after annealing for much longer led to an overlayer identical to that found in the earlier Ca work.\textsuperscript{372}

Theoretical studies have placed Ca and Ba atoms in high symmetry sites finding the \textit{between} site favored by Na and K also to be the most stable for Ca and Ba.\textsuperscript{375-377} However, since the ordered c(6\times2) Ca and Ba overlayers both require high temperature annealing to form, a model which includes some structural rearrangement of the TiO\textsubscript{2} surface may also need to be considered.

At higher coverage, various row structures develop for Ca and Ba that in either case are only partially ordered. The morphology of the surface changes significantly and it seems likely that Ti and O are supplied from the surface to grow some type of Ca- or Ba-Ti-O structure.\textsuperscript{371,372,374}

We are not aware of any studies of the other alkali earth metals on TiO\textsubscript{2}(110), although MgTiO\textsubscript{3} and SrTiO\textsubscript{3} films with thicknesses of about 100 nm have been grown.\textsuperscript{378}

\textit{TiO\textsubscript{2}(011)}

Low energy ion scattering (LEIS) indicates that Ca forms at the surface by bulk-segregation. Initially, the presence of Ca was associated with a new ordered structure.\textsuperscript{64}
However, subsequent work by Tao et al.\textsuperscript{133} indicates that this ordered structure is formed by reoxidation, as described in Section 3.1. The detection of this ordered structure with STM is not correlated with the Ca signal intensity in AES.

\textit{TiO}_2(100)

The growth of Mg was studied on the 1×3 surface using valence band PES and MIES.\textsuperscript{379} The PES and MIES results suggest that charge transfer occurs from Mg to the Ti 3\textit{d} states so that the Mg is non-metallic up to a coverage of 0.5 ML. Further deposition of Mg leads to metallic character. These results are similar to those found for AM on TiO\textsubscript{2}(110) and Ba on TiO\textsubscript{2}(110), except in the latter case the onset of metallic character occurs at 1 ML.\textsuperscript{373}

\textit{TiO}_2(001)

Kubo and Nozoye deposited Ba by MVD.\textsuperscript{380} They observed rows in STM that run in the [010] and [001] directions as shown in Figure 70. These rows were observed predominantly at step edges and around pits and it was inferred that Ti and O from the substrate was used to grow Ba-Ti-O rows, thus creating pits in the TiO\textsubscript{2} surface. Such rows may have a similar origin to those found for Ba and Ca on TiO\textsubscript{2}(110), discussed above.

\textbf{5.3 Group 4}
Deposition of Ti on TiO$_2$(110) has been shown to introduce oxygen deficiency to TiO$_2$(110)\textsuperscript{381} as discussed previously by Diebold.\textsuperscript{5} Tao et al.\textsuperscript{133} deposited Ti in an oxygen environment onto TiO$_2$(011)2×1 in order to differentiate the reoxidation-induced structure from a Ca segregation structure. Deposition of Ti led to the same structure as reoxidation.

No studies of Hf have been performed since the review by Diebold and further details can be found there.\textsuperscript{5} Briefly, deposition of Hf on TiO$_2$(110) leads to reduction of the TiO$_2$ and the formation of an HfO$_2$ layer. Further deposition leads to metallic clusters.

5.4 Group 5

The growth of V and Nb on rutile surfaces has not been studied further since the review by Diebold et al.\textsuperscript{5} Briefly, deposition of V on TiO$_2$(110) leads to oxidation of the overlayer with higher coverages being metallic. At about ~5 ML, islands form with the following epitaxy determined by angle-resolved PES (ARPES): bcc(100)[100]V||(110)[110] TiO$_2$. V was also studied on x-linked TiO$_2$(110)(1×2). Small V clusters decorate the (1×2) rows with no preference for step edge sites.

The growth of Nb on TiO$_2$(110) leads to oxidation of Nb and reduction of the substrate Ti.\textsuperscript{382} Nb-doped TiO$_2$(110) and TiO$_2$(100) substrates themselves form a substantial sub-field to the work described in this review. Nb with five valence electrons substitutes Ti which only has four, so that n-type semiconductivity is introduced without the need for further reduction.\textsuperscript{383,384} As this review is largely focused on TiO$_2$ surfaces made semiconducting by intrinsic defects, i.e. O\textsubscript{b}-vacs and Ti interstitials, readers are referred Diebold’s review for further information.\textsuperscript{5}
5.5 Group 6

CrO$_2$/TiO$_2$ is used in magnetic media and Cr-doped TiO$_2$ attracts interest as a p-type gas sensor. Co-doping with Sb on the other hand results in visible-light photoactivity.

MVD of Cr has been studied on $\alpha$-TiO$_2$(110) using LEIS as well as core-level and valence band PES.$^{385-388}$ LEIS indicates that Cr grows initially as quasi-2D islands,$^{386,387}$ 2D islands were also observed in subsequent STM images taken from $\gamma$-TiO$_2$(110), as shown in Figure 71.$^{389}$

In PES, the Ti 2$p$ peak develops a low BE shoulder and the BGS increased in intensity upon deposition of Cr, indicating reduction of Ti$^{4+}$ to Ti$^{3+}$ as well as oxidation of Cr. The position of the Cr 2$p$ peak is consistent with Cr$^{2+}$.$^{385-388}$ Such reduction was also observed in the appearance of the Ti3$d$ BGS in valence band PES taken from Cr/TiO$_2$(001).$^{390}$

Calculations point to the between site (Figure 66) as the most stable for Cr atom adsorption on TiO$_2$(110),$^{385}$ which is similar to many other reactive metals (alkali, alkaline earth metals and Ce). For thicker overlayers, STM shows the presence of 3D particles with no apparent step edge preference.$^{389}$ LEED and medium energy electron diffraction (MEED) indicate that Cr grows as Cr bcc(100)[100]||(110)[110]TiO$_2$.$^{388}$

Cr has also been doped into TiO$_2$(110) crystals by calcining with Cr$_2$O$_3$ powder, the upper few µm being on the order of 2-3 atom %. After performing standard UHV preparation of the Cr-TiO$_2$ sample,$^{391}$ NC-AFM images gave a typical $h$-TiO$_2$(110)(1×1) appearance except for the appearance of added rows which were assigned to Cr$_2$O$_3$. The
number of hydroxyls present on the surface is 0.5 ML, which we know forms from 0.25 ML O_b-vacs (Sections 2.1 and 3.2.1).\textsuperscript{8,9} This is far higher than would be expected from an undoped sample prepared in the same manner (~0.05 ML).

Charge neutrality in Cr-doped TiO\textsubscript{2} can be maintained by substituting three Ti\textsuperscript{4+} species with one Cr\textsuperscript{6+} and two Cr\textsuperscript{3+} atoms. However, even though the charge is balanced, there may be instability due to lattice mismatch. Ti\textsuperscript{4+} has an ionic radius of 60.5, Cr\textsuperscript{3+} 61.5 and Cr\textsuperscript{6+} 44.0 pm. The weighted average of one Cr\textsuperscript{6+} and two Cr\textsuperscript{3+} radii is 55.7 pm, so that there is an 8\% mismatch with that of Ti\textsuperscript{4+}. By adding Ti\textsuperscript{3+}, which has an ionic radius of 67.0 pm, the lattice mismatch can be reduced. Ti\textsuperscript{3+} can be created by the creation of O_b-vacs, thereby explaining the high concentration observed in NC-AFM. Furthermore, to maintain charge neutrality, Cr\textsuperscript{3+} can be removed from the crystal by segregation as Cr\textsubscript{2}O\textsubscript{3}, accounting for their presence at the surface. It is worth noting that doping with equal quantities of Cr:Sb does not lead to an increase in O_b-vacs where charge neutrality can be maintained by formation of Cr\textsuperscript{3+} and Sb\textsuperscript{5+} and where the average ionic radius (60.8 pm) almost matches that for Ti\textsuperscript{4+}.\textsuperscript{392}

Cr was also doped into TiO\textsubscript{2}(110) by ion implantation.\textsuperscript{393} Cr was distributed uniformly to the depth of about 300 nm with an average concentration of ~1 atom %. The samples were found to be ferromagnetic at room temperature with the magnetic field oriented parallel to the sample surface. NEXAFS showed spectra similar to Cr\textsubscript{2}O\textsubscript{3} and quite different to Cr metal or CrO\textsubscript{2}.

The growth of Mo on TiO\textsubscript{2}(110) has been studied in some detail.\textsuperscript{394-404} Pétigny et al.\textsuperscript{404} and Domenichini et al.\textsuperscript{403} deposited Mo by MVD onto TiO\textsubscript{2}(110) samples prepared in a number of ways such as by annealing in O\textsubscript{2} (10\textsuperscript{-5} mbar), Ar\textsuperscript{+} bombardment, and O\textsubscript{2}+.
bombardment. In each case, they found the same growth behavior on the basis of breaks in the plots of AES vs. deposition time: Mo grows in the SK mode with three layers of amorphous MoO_x followed by 3D islanding.

In contrast to these AES results, STM images taken after deposition of Mo on the simple TiO_2(110)(1×2)\textsuperscript{401} and onto a TiO_2(110) surface decorated with some (1×2) patches\textsuperscript{394} reveal the presence of nanoparticles. In the latter case, small 2D islands initially form on the 1×1 terraces with no preference for step edges, similar to the situation discussed above for Cr.

PES indicates that Mo is initially oxidized with the surface Ti being reduced to Ti\textsuperscript{3+} and Ti\textsuperscript{2+}.\textsuperscript{396,398-400,403,404} As the O 1s to Mo 3d peak intensity ratio is nearly identical at near-normal and grazing emission angles, it was suggested that the oxygen is uniformly distributed throughout the Mo film. This implies that oxygen diffuses from the TiO_2 substrate into the Mo. Such a mechanism is supported by the AES data from Berkó et al.\textsuperscript{394} which reveals an increase in the O/Ti peak intensity ratio in AES with Mo deposition time.

Although no ordering of the overlayer was found even after annealing, crystalline, rectangular particles were observed in STM. On the other hand, because PhD can probe shorter range order, it was shown that Mo grows epitaxially even without annealing: bcc Mo(100)[001]||(110)[001]TiO_2.\textsuperscript{400} Annealing to 673 K improves the order of the particles and correlates with a loss of oxygen, i.e. reduction of Mo.

Note that the growth and annealing behavior of Mo on TiO_2(110) depends also on the dose rate and the bulk stoichiometry.\textsuperscript{398,399} For instance, deposition of Mo at high flux leads to a metallic film\textsuperscript{399} and annealing a Mo/TiO_2(110) sample that is bulk
stoichiometric leads to the formation of MoO\(_x\) (x > 2) rather than metallic Mo in the case described above.\(^{398}\)

W has been grown on TiO\(_2\)(110) by atomic layer deposition (ALD)\(^{405}\) and by MVD.\(^{406}\) The sample was annealed in air, then exposed to UV light for the ALD which employed cycles of exposure to Si\(_2\)H\(_6\) and then WF\(_6\) (both at 13 mbar). Core level PES indicated that most of the W is in the W\(^{6+}\) state with about 10% of the signal corresponding to W\(^{4+}\). Intermittent-contact AFM revealed the W film morphology to be similar to the air-annealed TiO\(_2\). A 3D map of the W atoms relative to the rutile lattice was generated from X-ray standing waves (XSW) data and shows surface tungsten atoms equally occupying the two nonequivalent Ti sites with a slight outward displacement.

The MVD experiments were performed on \(\sigma\)-TiO\(_2\)(110). As one would expect, the \(\sigma\)-TiO\(_2\) surface does not exhibit a BGS peak in valence band PES. The BGS peak appears upon deposition of W and increases in intensity with W coverage. Beyond 0.16 ML, the BGS shifts towards the \(E_F\) indicating an increase in metallic character. Post-annealing of W/TiO\(_2\) at 975 K induces complete oxidation of submonolayer W, whereas reduction to metallic tungsten occurs for higher coverage (1.6 ML).

5.6 Group 7

Deposition of submonolayer coverages of Mn on TiO\(_2\)(110) leads to reduction of Ti\(^{4+}\), as shown by the appearance of a shoulder on the low BE side in the core level PES Ti 3\(p\) peak. The peak position of Mn 3\(p\) is consistent with Mn\(^{2+}\). Deposition of a much thicker Mn film leads to a BE shift to lower energy indicative of metallic character.
Annealing to ~923 K desorbs metallic Mn, leaving behind about the same amount of Mn$^{2+}$ as the initial submonolayer deposition.$^{407}$

5.7 Group 8

Deposition of submonolayer coverages of Fe on $\alpha$-TiO$_2$(110) leads to reduction of Ti. This is evidenced by the appearance of BGS in valence band PES and also by the appearance of a feature ~3.5 eV above $E_F$ in inverse photoemission spectroscopy,$^{408}$ which is indicative of reduced Ti species. The interpretation of the BGS is complicated by overlap with the Fe 3$d$ band. Contributions from Ti 3$d$ and Fe 3$d$ were disentangled by monitoring their intensity following exposure to O$_2$ and their intensity vs. the photon energy in ResPES.$^{409,410}$ Electron transfer from Fe to TiO$_2$(001) was also suggested on the basis of work-function measurements.$^{411}$

FM growth was first proposed from AES break points,$^{412}$ then a LEIS study suggested VW growth.$^{413}$ Most recently, the SK growth mode was proposed from the observation of a break point in the intensity vs. coverage plot of the gap state in the PES.$^{409}$

Break points determined by PES and AES tend not to be as reliable as LEIS measurements, as the latter method is sensitive to just the top layer,$^{414}$ so VW growth is the most likely. Indeed, STM of $h$-TiO$_2$(110) indicates that Fe initially grows as individual atoms and 2D islands up to 0.15 ML, then as 3D islands with increasing coverage, as shown in Figure 72.$^{389}$ LEED and MEED at high coverage indicate that Fe grows as Fe bcc(100)[100]||(110)[110]TiO$_2$.$^{388}$
LEIS in combination with core level PES also shows that, following annealing above 773 K, Fe becomes encapsulated by a TiO$_x$ layer. The Fe peak in LEIS is almost completely attenuated and the Fe 2$p$ peak is significantly less intense. The Ti 2$p$ spectrum develops a more intense shoulder on the lower BE, indicating an increase in Ti$^{3+}$ as well as Ti$^{2+}$ states. The Fe peak in LEIS was recovered by gentle sputtering with Ne$^+$ ions.$^{415}$

Fe has been implanted into TiO$_2$(110) and (001) by ion implantation at room temperature and 900 K. Mössbauer measurements indicated ferromagnetism due to α-Fe for both room temperature implanted samples and ferromagnetism due to Fe$_3$O$_4$ for the high temperature (001) implanted sample.$^{416}$

Ru has been deposited onto an ultrathin film of rutile TiO$_2$(110) surfaces via metallo-organic chemical vapour deposition (MOCVD) of Ru$_3$(CO)$_{12}$. On an ultrathin rutile (110)-like film supported on Mo(110), RAIRS indicates that a disordered film forms upon deposition at low temperature (90 K). Decomposition begins at 250 K and the complex become invisible to RAIRS at 295 K. TPD indicates that decomposition is complete at 600 K. STM measurements from a surface annealed to 600 K show the presence of clusters that are distributed on the terraces and step edges. Linear rows were visible as well as clusters and attributed to adatoms, although they may also correspond to (1×2) strings.$^{417}$

Stone et al.$^{418}$ deposited Ru$_3$(CO)$_{12}$ onto a surface with both (1×1) and (1×2) regions. The complex tends to adsorb on the (1×2) rows rather than the (1×1) areas, as detected by STM. The sample was then annealed to 373 K, 673 K, then 773 K.

At 673 K, the complex should have decomposed into just Ru. The particle concentration is much reduced and their size increased at 673 K and more so at 773 K.
Interestingly, small (1×1) terraces have grown over the (1×2) areas at 673 K and above. It is evident in the 773 K image that these (1×1) patches either surround the Ru particles or are connected to them. Two possible explanations were suggested for this. Oxygen from the decomposed complex either reacts with Ti_{int} to grow TiO_2(110) or with Ru to form RuO_2(110): a number of studies indicate that RuO_2(110) grows isostructurally on TiO_2(110).^{419,420}

### 5.8 Group 9

TiO_2-supported Ir and Rh catalyze a number of reactions. For instance, Rh/TiO_2 is a catalyst for CO and arene hydrogenation^{421,422} and the partial oxidation of methane to syngas^{423} and Ir/TiO_2 is a low temperature catalyst for CO and H_2 oxidation.^{424}

Since the discovery of room temperature ferromagnetism in Co-doped anatase TiO_2, Co-doped TiO_2 has become a topic of interest. Co-doped rutile TiO_2 has also demonstrated room temperature ferromagnetism for the (110), (100), and (001) faces. The weight of evidence suggests that the ferromagnetism originates from Co^{2+} substituted into Ti^{4+} sites in the crystal rather than from Co nanoclusters at the surface.^{425-428}

Rh was grown on TiO_2(110) by MVD. Core level PES indicates a decrease in the lower BE shoulder of the Ti 2p peak and this was attributed to electron transfer from reduced Ti^{3+} sites.^{429} Although the integrated intensity of the Rh 3d peak was suggestive of layer-by-layer growth for the first few layers, subsequent STM images^{430} and LEIS measurement^{431} show instead that Rh grows as 3D particles, even at 160 K according to the LEIS. The low temperature islands were found to be smaller than those at room
temperature. STM also shows that Rh grows as 3D islands on TiO$_2$(110)(1×2) and TiO$_2$(001).\textsuperscript{432-434}

Very large 3D crystallites on TiO$_2$(110) could be grown by depositing less than 1\% ML Rh onto the TiO$_2$(110) surface. Annealing to 1100 K creates Rh seeds which consist of larger crystallites. Further deposition of Rh at 1100 K then led to the growth of the existing seeds.

This seeded growth method relies on the much greater mobility of Rh adatoms and small clusters compared with larger clusters. The method was first developed for Rh on TiO$_2$(110)(1×2).\textsuperscript{433,435} The separation of particles using the seeding method can be tuned by adjusting the coverage in the seeding step and the final crystallite size can likewise be tuned by the coverage in the growth step. This seeded growth was also applied to Ir on TiO$_2$(110)(1×2) where, as with Rh, as-deposited Ir forms 3D islands. For Ir, the annealing steps were at 1200 K.\textsuperscript{436} In all cases, the final crystallites had two shapes: regular hexagons and particles elongated in the [001] direction. As the (111) and (100) faces are the most stable, the hexagonal particles were assumed to have a (111) top facet and (100) side facets whereas the elongated particles a (100) top facet with (111) side facets.\textsuperscript{430,433,435,436}

Ir was also deposited from its vapor onto an $x$-linked (1×2) surface held at 1073 K. Islands formed that are slightly elongated in [001].\textsuperscript{437} Further Ir was deposited at room temperature then post-annealed to 1073 K: this created further islands also elongated in [001]. Due to the rectangular shape, and because the heights of the particles seem to be quantized with a spacing of 3 Å, Maeda et al.\textsuperscript{437} suggest that they have grown IrO$_2$(110) (interlayer spacing of 3.2 Å) rather than Ir(111), which has an interlayer
spacing of 2.2 Å). The source of oxygen was attributed to a pressure rise to the 10^{-9} mbar range during annealing or from oxygen diffusing from the bulk. It should be noted that Berkó et al.\textsuperscript{436} annealed their Ir/TiO\textsubscript{2}(110) system to a higher temperature apparently without forming IrO\textsubscript{2}. STM-local barrier height (LBH) measurements indicate little or no charge transfer between the proposed IrO\textsubscript{2} particles and the TiO\textsubscript{2}.\textsuperscript{437}

For Rh particles, annealing can lead to encapsulation by a TiO\textsubscript{x} layer. This seems to depend on the reduction state of the TiO\textsubscript{2} substrate. A core level PES study by Berkó et al.\textsuperscript{430} revealed no encapsulation of Rh on a (1×1) surface. However, encapsulation occurs for Rh on a (1×1) surface that had been pre-sputtered as well as for Rh on (1×2) surfaces. Encapsulation of Rh on the (1×1) surface can also be induced by annealing in H\textsubscript{2}. More recent studies that also use LEIS do detect encapsulation even after UHV annealing of Rh on the (1×1) surface.\textsuperscript{438}

A very recent STM study of the encapsulation of Rh on TiO\textsubscript{2}(110)(1×2) reveals a worm-like structure, which is probably a precursor to a wheel-like structure (Figure 73).\textsuperscript{439} This is strikingly similar to the pinwheel phase found for encapsulated Pd on TiO\textsubscript{2}(110)(1×2). The latter will be discussed together with similar TiO\textsubscript{x} encapsulating layers formed on Pd and Pt supported on TiO\textsubscript{2}(110) and also for TiO\textsubscript{2} ultrathin films formed onto Pt(111) in Section 5.9.

Rh and Ir have also been deposited onto TiO\textsubscript{2} surfaces by MOCVD. For example, Ir(CH\textsubscript{3}COCH\textsubscript{2}COCH\textsubscript{3})\textsubscript{3} has been deposited onto a TiO\textsubscript{2}(110)(1×1) surface with (1×2) strings,\textsuperscript{440} tris(allyl)Rh has been deposited on TiO\textsubscript{2}(001),\textsuperscript{441,442} and Rh[Rh(CO)\textsubscript{2}Cl]\textsubscript{2} has been deposited on TiO\textsubscript{2}(110)\textsuperscript{429} and a crystallographically sheared TiO\textsubscript{2}(110) surface (cs-TiO\textsubscript{2}).\textsuperscript{443}
After annealing the Ir complex to 890 K, Ir or IrO$_2$ particles were found at the (1×2) strings and the step edges and after annealing to 1220 K, the particles were mainly at the step edges.$^{440}$ For the Rh complex on cs-TiO$_2$, annealing to 473 K seems to decompose and desorb the organic part of the complex leaving clusters that decorate the upper half-steps. Annealing to 573 K did not give rise to any notable change in the morphology.$^{443}$

5.9 Group 10

Group 10 metal supported on TiO$_2$ are important catalytic and photocatalytic systems being active for reactions such as CO oxidation and water cleavage.$^{444}$

*Nucleation and Growth*

For Ni, early studies suggest SK growth based on EXAFS and breakpoints in AES.$^{445-447}$ Since then, SPM, RHEED, and LEIS measurements have shown clearly that Ni,$^{448-450}$ as well as Pd$^{451}$ and Pt,$^{452-456}$ grows either as 3D islands or with the 2DI mechanism on TiO$_2$(110). The latter is a kinetically limited 3D growth mode described by Ernst et al.$^{343}$ There is evidence that Ni,$^{249,450}$ Pd,$^{451}$ and Pt grow initially as one or two layer high quasi-2D islands.$^{453,454}$ For Pd, the transition to 3D islanding occurs at a coverage of 0.012 ML whereas for Ni the transition coverage is about five times higher. For Pt, the coverage for transition to 3D growth has not been measured. Pd clusters have also been observed with STM on the TiO$_2$(100)(1×3) and (001) surfaces, although the coverages were too high to test for the presence of 2D islands.$^{457,458}$
For Ni, STM images from Tanner et al.\textsuperscript{448} and Zhou et al.\textsuperscript{449} reveal preferential nucleation of particles at step edges. On the other hand, Fujikawa et al.\textsuperscript{450} found small uniformly-sized particles distributed uniformly over the surface with no step edge preference. While the other two studies involved deposition of Ni at room temperature, Tanner et al. deposited Ni onto the sample held at 375 K, so that particles are more likely to find the most thermodynamically stable sites. Fujikawa et al.\textsuperscript{450} used a dose rate about an order of magnitude greater than that of Zhou et al.\textsuperscript{449} They suggest that this, together with the larger separation between step edges in their work means that there is a greater chance of Ni-Ni collisions at the surface which leads to nucleation at the terraces.

In the case of Pd, all STM studies except for one\textsuperscript{459} find preferential nucleation at the steps. The reason for the discrepancy is not obvious: Howard et al.\textsuperscript{459} use a similar doser to other workers\textsuperscript{460,461} and a similar dose rate to Xu et al.\textsuperscript{451} One possibility (which could also be a consideration for Ni) may be the exact nature of the surface, for example, the vacancy density and the degree of hydroxylation. Such effects seem to be important for Au on TiO$_2$(110) and will be discussed in Section 5.10.

No preferential step edge decoration has been reported to date for Pt on TiO$_2$(110) at room temperature. This includes both as-prepared surfaces\textsuperscript{452-454,456} and a TiO$_2$ surface prepared by oxygen plasma treatment.\textsuperscript{455}

Pd and Pt have also been studied extensively on various TiO$_2$(110)(1×2) surfaces. For a (1×1) surface decorated with (1×2) strands, STM images by Jak et al.\textsuperscript{460,462} show the strands and particularly the ends of the strands, as well as the step edges, are the preferential nucleation points. This preference for the end of (1×2) strands was also observed for Pt.\textsuperscript{463} This was exemplified by an STM study by Gan et al.\textsuperscript{455} that employed
a vicinal surface with ~65 Å wide (1×2) terraces alternating with ~5 Å wide (1×1) terraces: Pt has a strong preference for decoration of the 1×2 ends, as shown in Figure 74.

On a slightly x-linked (1×2) surface, STM images by Gan et al.\textsuperscript{455} show that at low coverage (0.2 ML), Pt clusters grow at the center of the (1×2) rows. The x-links do not appear to be nucleation sites. For Pd, on an ordered, densely, x-linked surface, Pd was arranged in lines running along [1 1 0]. It was inferred from this, together with a correlation analysis of the clean and Pd covered surface, that Pd is adsorbed on the x-links.\textsuperscript{443}

\textit{Size selection}

Ni\textsubscript{n}\textsuperscript{+} (n = 1, 2, 5, 10, 15),\textsuperscript{464} Pd\textsubscript{n}\textsuperscript{+} (n = 1, 2, 4, 7, 10, 16, 20, 25),\textsuperscript{465} and Pt\textsubscript{n}\textsuperscript{+} (n = 4, 7-10,15)\textsuperscript{466,467} have been deposited on TiO\textsubscript{2}(110). LEIS indicates that Ni\textsubscript{n} and Pd\textsubscript{n} adsorb intact with the clusters lying flat on the surface until about n = 10 after which they begin to form a second layer. Similar conclusions were made based on STM images for Pt\textsubscript{n}, where second layer growth began at n = 8, but with Pt\textsubscript{8} and Pt\textsubscript{9} having both planar and 3D configurations. In the STM images of Pt\textsubscript{n}, there is no preference for step edge nucleation.\textsuperscript{466}

Small Pt particles were also formed on this surface by dosing an organometallic precursor, (methylcyclopentadienyl) trimethyl platinum or MeCpPtMe3, and annealing at 450 K. Two types of particles were formed: slightly larger particles and size-limited particles probably bound into a Pt-TiO\textsubscript{x} complex.\textsuperscript{468,469}

Micelle encapsulated Pt nanoparticles have also been used in order to control the Pt particle size. The encapsulating polymer was removed by exposure to an oxygen
plasma, after which no C 1s could be detected in core-level PES. After annealing to 575 K, STM images reveal a very narrow size distribution. Although the surface reconstructs to (1x2) upon annealing to 1273 K, little change in nanoparticle morphology is seen until annealing to 1333 K, where it was apparent that Pt was desorbing.\textsuperscript{470} As will be seen below, such stability under annealing is quite different for nanoparticles formed by MVD.

\textit{Charge Transfer}

For Ni, an early study using shifts of the core-level PES suggest a transfer of electrons from the TiO\textsubscript{2}(110) to Ni.\textsuperscript{471} Later, Onishi et al.\textsuperscript{445} found a decrease in the workfunction as Ni is deposited which reaches a minimum of 4.6 eV from its initial position at 5.3 eV. From this, a charge transfer of 0.1 e\textsuperscript{-} per Ni atom to the substrate was proposed. KPFM measurements also indicate some electron transfer from Ni clusters to TiO\textsubscript{2}(110).\textsuperscript{249}

There is also some agreement from core-level PES measurements of the Ni 2p peak by Tao et al.\textsuperscript{472} who find a 0.06 eV transfer to TiO\textsubscript{2}(001) and a 0.1 eV transfer to TiO\textsubscript{2}(110). However, an Auger parameter analysis (using L\textsubscript{3}M\textsubscript{4,5}M\textsubscript{4,5}) was used in order to separate initial and final state effects, which according to Bagus et al.\textsuperscript{473} is invalid when the Auger transitions involve states with high lying d-holes.

Using r-TiO\textsubscript{2}(110), Aizawa et al.\textsuperscript{464} found no oxidation of Ni after deposition of Ni\textsubscript{n+} (n = 1, 2, 5, 10, 15) when the deposition energy was 1 eV/atom. This was based on core level PES measurements of the Ni 2p peak. However, at higher impact energies,
oxidation to Ni$^{3+}$ can be observed. In contrast, for $o$-TiO$_2$(110) (TiO$_{2-2}$), a Ni$^{3+}$ peak is present even with an impact energy of 1 eV/atom as shown in Figure 75.

For Pd on $o$-TiO$_2$(110), Negra et al.$^{474}$ used PES to monitor the Pd 3$d$ and Ti 3$p$ peaks. While the Pd 3$d_{5/2}$ peak shows a shift to lower BE with Pd coverage, the Ti 3$p$ peak does not change within the experimental limit. As such the Pd BE shift was attributed to a size effect only and it was concluded that there is no charge transfer. The effect of Pd on the O 2$p$ band was also probed using ResPES. The band was deconvoluted into four components and after depositing three different coverages of Pd, each component varied with photon excitation energy in the same way as for the clean surface, indicating little interaction between Pd and TiO$_2$.

In the case of Pt, both core level and valence band PES measurements, including work function measurements indicate no charge transfer with Pt deposition.$^{475}$ For a pre-sputtered TiO$_2$(110) sample,$^{476, 477}$ core level and valence band PES indicates electron transfer from the surface to the Pt particles on the basis of a quenching of the low BE Ti 2$p$ shoulder and the BGS, respectively.

Pt atoms and clusters were deposited on $r$-TiO$_2$(110).$^{453, 478}$ Both atoms and clusters showed small decreases in the local work function, indicative of charge transfer from Pt to the surface. The work-function decrease over a single atom is ~0.25 eV,$^{478}$ whereas for the clusters,$^{453}$ the amount of charge per Pt atom was calculated as $\leq 0.1$ e$^-$ per Pt atom. The discrepancy with the earlier work probably arises from the more sensitive detection available with KPFM.

*Epitaxy*
A number of geometries have been proposed for Ni clusters. (100) and (111) top facets were proposed on the basis of PhD, whereas a LEED study indicated (111) facets parallel to the surface or tilted to form a Ni(131) interface with the TiO$_2$(110). A more recent STM and RHEED study suggests that Ni grows as Ni fcc(110)[$\bar{1}$10]||(110)[001]TiO$_2$. This was rationalized on the basis that the average lattice misfit is minimized. This (110) configuration was validated by polarization-dependent total-reflection fluorescence XAFS (PTRF-XAFS) measurements.

As the coverage is increased, STM images indicate that the clusters become elongated along [001] and develop facets so they become ‘hut-like’. RHEED indicates that the long facets are of (111) character and the short facets probably (100). The tendency to elongate along [001] is apparent in the oval shape of Ni particles seen in STM even when they are very small.

At low coverage (<3 ML), RAIRS using CO as a probe indicates that Pd(100) and Pd(110) faces are predominantly exposed. At higher coverage (10 ML), features in the RAIRS spectrum consistent with Pd(111) develop and a diffuse (111) pattern is also observed in LEED. On the basis of coaxial impact-collision ion scattering spectroscopy and RHEED, Pd grows as Pd fcc (111)[1 $\bar{2}$ 1]||(110)[001] TiO$_2$ for coverages above ~2 ML.

For Pt, LEED and ARPES find the following epitaxy: Pt fcc (111)[1 $\bar{1}$ 0]||(110)[001]TiO$_2$.452

Annealing
Ni, Pd, and Pt clusters on TiO$_2$(110) increase in size when annealed. For Pd on TiO$_2$(110)(1×1) and (1×2), particle growth was monitored \textit{in-situ} using high temperature STM.\textsuperscript{459,482} For the (1×1) surface, the particles were relatively static which is suggestive of Ostwald ripening. However, Howard et al.\textsuperscript{459} note that their initial coverage is quite high and that at lower coverage, smaller clusters may be more mobile so that coalescence is more important in the earlier work of Jak et al.\textsuperscript{462} The situation is also complex for the (1×2) surface. While coalescence is observed, there seem to be many more events where clusters decay rapidly, yet the overall growth rate is slow.\textsuperscript{482}

Deposition of Pd onto a hot TiO$_2$(110)(1×1)\textsuperscript{483} or (1×2)\textsuperscript{484} surface leads to some hexagonal particles as well as the elongation of other particles. This was also observed for Pt on a TiO$_2$(110) (1×n) surface.\textsuperscript{485} For Pd on the (1×1) surface, this elongation was particularly marked, extending at least up to 1 µm. These Pd ‘nanowires’ were examined with energy-filtered X-ray photoemission electron microscopy (XPEEM) which indicated that the wires and the hexagonal particles have the same metallic composition according to the shape of the extracted Pd 3$d$ peak (Figure 76).\textsuperscript{483}

Annealing Fe, Co, Rh, Ir, Ni, Pd, and Pt on TiO$_2$ in a reducing environment is known to lead to the strong metal support interaction (SMSI) whereby the ability of the metal to adsorb molecules such as CO is lost.\textsuperscript{5} One mechanism for SMSI is the physical encapsulation of the metal with the substrate metal oxide.

Recently, Fu et al.\textsuperscript{486} have suggested four requirements for encapsulation to occur: (1) $E_F$ (oxide) > $E_F$ (metal), (2) the substrates are reduced or $n$-type doped oxides with small surface energies, such as TiO$_2$ and CeO$_2$, (3) the supported metals have large work functions and large surface energies, and (4) the anneal temperature is sufficiently high
for mass transport. Figure 77 shows a plot of the surface energies and work functions of a number of metals. All the metals for which TiO₅ encapsulation has been reported fall in the top right-hand side of the plot as would be expected, except for Fe and Co. The cause of these anomalies is not yet known.

Encapsulation of Pt and Rh supported on TiO₂(110) by TiOₓ upon annealing in UHV (>675 K) was observed as far back as the 1980s on the basis of, for example, depth profiling core-level PES: the top layer has peaks shifted to a lower BE, suggestive of Ti³⁺ or Ti²⁺ states and as the sputtering time is increased, the peaks shift back to higher BE as the substrate TiO₂ is uncovered.⁴⁸⁷,⁴⁸⁸ Since then, evidence from ion scattering measurements clearly demonstrates that encapsulation occurs for Ni,⁴⁸⁹ Pd,⁴⁹¹ and Pt,⁴⁹⁰,⁴⁹¹ as well as Fe and Rh described previously in Section 5.7 and 5.8.⁴¹⁵,⁴³⁸ Figure 78 shows the LEIS data obtained by Dulub et al.⁴⁹¹ for clean TiO₂, as-deposited Pt, and Pt/TiO₂ after annealing.

Atomically resolved STM images have been obtained on top of similarly-prepared Pt,⁴⁹¹ Pd,⁴⁹²,⁴⁹³ and Rh islands.⁴³⁹ These images are characterized by a pinwheel and two types of zigzag motifs. The STM image of the pinwheel structure for the Rh and Pd structures are shown in Figures 73 and 79, respectively, whereas the two zigzag structures are shown in Figure 80. The appearance of the pinwheel can be simulated by superimposing an expanded, rotated hexagonal lattice over the Pd(111) substrate lattice, as shown in Figure 79b. By reproducing these LEED patterns in a separate chamber with PES facilities, an additional component in the 2p peak was found that was attributed to either Ti³⁺ or Ti²⁺, and which was enhanced at a grazing emission angle.⁴⁹²
A series of systematic experiments focused instead on MVD of Ti on Pt(111) in a background of O₂, followed by further annealing in oxygen. Six different types of ultrathin film were formed. While the \( w \) and \( w' \) phases are somewhat similar to the pinwheel structures observed by Bennett et al. for Pd and Majzik et al. for Rh, the relationship is not as clear as for the zigzag structures. \( z' \) and \( z \) correspond directly to the zigzag encapsulation layers found by Dulub et al. for Pt and Bennett et al. for Pd, respectively, as shown in Figure 80.

In the single crystal Pt(111) work, each phase could be individually probed free from convolution with any underlying TiO₂(110) substrate. It turns out that the \( z \) and \( w \) phases are indistinguishable on the basis of their Ti 2p core level peaks, each having a peak at lower BE compared to Ti⁴⁺. Sedona et al. point out that because of size effects, it is difficult to determine formal oxidation states. In angle-scanned PhD, oscillations of the intensity can be observed when an ordered array of scatterers lies between an emitter and detector. This means that if the emitter is located at the outermost layer of the ultrathin film, there will be no intensity modulation of the corresponding PES signal. As the Ti 2p scans have intensity oscillations and the O 1s scans do not, this is indicative of Pt-Ti-O stacking. A Ti₆O₈ model was proposed for the \( z \) phase as shown in Figure 81. Due to the prevalence of defects in the \( z' \) phase, three models were proposed which account for the slightly different STM images obtained, as shown in Figure 82. They range from TiO₁.₂₅-TiO₁.₂₀ and are virtually isoenergetic.

Although large particles have been grown in order that the encapsulation of the top facets can be imaged with STM, this is not a necessity for encapsulation. This was exemplified recently by testing the CO oxidation reaction on Pd/TiO₂(110)(1×1) After
annealing to 1100 K, the particles were made unreactive. Sputtering the Pd/TiO$_2$(110) sample recovered the reactivity and interestingly, even subsequent re-annealing did not lead to further encapsulation. The rationale is that sputtering depletes oxygen on TiO$_2$ and stoichiometry is restored by inward diffusion of Ti cations, that is, in the opposite direction required for encapsulation.$^{499}$

5.10 Group 11

Cu, Ag, and Au nanoparticles dispersed on metal oxide surfaces have been extensively studied due their use or potential use in a number of catalytic systems. Specifically for TiO$_2$, Ag may be a cheaper alternative to, say, Au or Pt, for metal/titania-based photocatalysts. Au nanoparticles supported on TiO$_2$ have been extensively studied ever since the seminal work by Haruta et al.$^{174}$ that demonstrated that such systems catalyze oxidation and hydrogenation reactions. It was found that catalytic activity was dependent on the presence of small Au particles so that much research has focused on size effects. Au-based model catalysts, including Au supported on TiO$_2$(110) and other oxides was reviewed recently by Gong.$^{500}$

Nucleation and Growth

At room temperature, Au grows with the 2DI mechanism on TiO$_2$(110). At low coverage, one or two layer (quasi-2D) high islands are formed up to a critical submonolayer coverage of $\sim$0.1 ML, after which 3D islands appear. Evidence comes from a range of measurements, including for example STM$^{501,502}$ and LEIS.$^{503}$ Recent
GISAX measurements find two layer high particles at 0.05 ML and three layer high particles at 0.1 ML.\textsuperscript{504}

For Cu, at very low coverages (\textasciitilde 0.03 ML) 2D islands were found with STM but already at this coverage, 3D islands co-exist.\textsuperscript{505} This is in agreement with LEIS measurements that find 3D growth, even at low coverage and low temperature (160 K).\textsuperscript{506} Earlier work that relied on AES break-points suggested SK growth.\textsuperscript{507} A more recent study using break-points in PES also proposed SK growth,\textsuperscript{508} although this is in clear conflict with direct evidence provided by the earlier STM data.\textsuperscript{505}

For Ag, there is evidence for the formation of 2D clusters from surface differential reflectance (SDR) and LEIS\textsuperscript{509,510} but to date, such clusters have not been imaged with STM, despite thorough attempts.\textsuperscript{511,512} At low temperature (110 K), recent STM images add real-space evidence for 2D clusters\textsuperscript{513} to that obtained, for example from LEIS and workfunction measurements.\textsuperscript{514,515}

Chen et al.\textsuperscript{505,511} showed that both Cu and Ag tend to display self-limiting growth. Below \textasciitilde 0.5 ML, all islands tend to have the same size, nearly independent of the coverage. On the other hand, island density increases dramatically with coverage. Above \textasciitilde 0.5 ML, the island size increases but the diameters remain more-or-less the same: the growth is in height. Kolmakov and Goodman deposited and imaged Au sequentially onto the same part of the surface.\textsuperscript{502} Curves showing width, height, and number density vs.

coverage (Figure 83) exemplify the self-limiting behavior found by Chen et al.\textsuperscript{505,511} Furthermore, because they measure the same area of the surface, the increase in size of the width distribution with coverage was unambiguously attributed to the newer clusters.
All three metals have been reported to decorate the step edges although recent work shows that the situation is rather complex. Besenbacher et al.\textsuperscript{513,516} have shown that the nucleation and growth of Ag and Au depends critically on the exact nature of the TiO\textsubscript{2}(110) surface. \(r\)-TiO\textsubscript{2}(110), \(h\)-TiO\textsubscript{2}(110), and \(o\)-TiO\textsubscript{2}(110) all give rise to different behavior. For \(r\)- and \(h\)-TiO\textsubscript{2}(110), relatively large Ag clusters are shown to decorate the step edges. This implies that neither O\textsubscript{b}-vac nor OH\textsubscript{b} are nucleation sites. On \(h\)-TiO\textsubscript{2}(110), Au behaves as Ag. However, on \(r\)-TiO\textsubscript{2}(110), small homogenously distributed nanoparticles were observed with no step decoration. This was taken as evidence for nucleation at O\textsubscript{b}-vac. For the \(o\)-TiO\textsubscript{2} surface, both Ag and Au deposition led to small nanoparticles homogeneously distributed on the surface with no step decoration (Figure 84). For Au,\textsuperscript{516} the clusters were estimated to range between 1-7 atoms in size (from supporting DFT calculations) whereas for Ag,\textsuperscript{513} it was thought that most Ag clusters were monomers.

A more recent KPFM study by Chung et al.\textsuperscript{517} on \(h\)-TiO\textsubscript{2}(110) shows Au clusters homogeneously distributed on the surface without step decoration. The discrepancy is attributed to either the dose rate or the degree of surface hydroxylation. While Matthey et al.\textsuperscript{516} use e-beam deposition, and Chung et al.\textsuperscript{517} resistive heating (of a Mo crucible), this does not seem to be the reason for the discrepancy. Maeda et al.\textsuperscript{518,519} also deposit Au by resistive heating (of wire) yet also find step edge decoration. On the other hand, deposition of Au\textsuperscript{+} monomers led to large clusters also with no preferential step edge nucleation.\textsuperscript{520}

On surfaces more reduced than \(r\)-TiO\textsubscript{2}(110), TiO\textsubscript{x} species (\(x < 2\)) are present. Such species are precursors to the (1\(\times\)2) reconstruction. By imaging the same area of the
surface before and after deposition of Au, Park et al.\textsuperscript{521} show that these TiO\textsubscript{x} species nucleate the growth of Au.

For Cu on the simple (1\times2) surface, Reddic et al.\textsuperscript{522} found the same self-limiting behavior as for the (1\times1) surface, except that the Cu cluster density was higher for equivalent doses. The steps edges are also not decorated in contrast to the 1\times1 surface. Both these observations are attributed to the (1\times2) surface being defective, with a high density of nucleation points on the terraces. This also decreases the Cu mobility, so that step edges are not reached. Instead, the ends of the (1\times2) rows tend to act as preferential nucleation points due presumably to undercoordination of the Ti. Annealing the Cu particles had the same effect as on the (1\times1) surface: their size increases while their density decreases and there is still a narrow size distribution consistent with the self-limiting size.

Luo et al.\textsuperscript{512} also found that Ag disperses more completely on the (1\times2) surface compared to the (1\times1) surface. Tong et al.\textsuperscript{523} report on Ag deposited on a partially formed (1\times2) surface. However, close inspection of the STM image suggests that the ‘(1\times2)’ areas appear to be Ca rows as judged from characteristic rows running in [1\overline{1}0] as well as [001]. The same applies to another study of Cu on TiO\textsubscript{2}(110).\textsuperscript{524}

Kitchin et al.\textsuperscript{401} have studied the growth of Au on the simple (1\times2) surface. They report that Au clusters preferentially nucleate at the end of rows and at step edges although they also report significant nucleation at terrace sites. While many of the observable defects have indeed nucleated Au clusters, it is difficult to see any preference for step edges. A similar picture was found by Maeda et al.\textsuperscript{518} for \textit{x-linked} TiO\textsubscript{2}(110)(1\times2). 3D particles could be found on the added rows, \textit{x-links}, and step edges.
As with Cu and Ag on the simple (1×2), Au disperses more completely on the (1×2) surface.

3D islands were observed in STM images of Cu on a TiO$_2$(001) sample faceted to (011).$^{525}$ Similarly, 3D Au islands were observed on a TiO$_2$(001) ultrathin film supported on Mo(100).$^{1,526}$

Size selection

Buratto et al.$^{520,527}$ deposited size-selected Ag$_n^+$ and Au$_n^+$ onto TiO$_2$(110). Ag$_1^+$ is highly mobile at the surface, resulting in large clusters that preferentially nucleate at step edges. Dimers are less mobile but are still able to form relatively large clusters that nucleate at step edges and terrace sites. Trimers have limited mobility on the surface, remaining as trimers predominantly on the terraces.$^{527}$

A similar trend was seen for Au$_n^+$ ($n = 1$-8).$^{520}$ Deposition of the monomer led to large clusters, indicating their mobility. Au$_2^+$-Au$_4^+$ were found to lie flat while Au$_5^+$-Au$_8^+$ consisted of two layers.

Organometallic complexes and micelles have also been used to control particle sizes.$^{528-533}$ For instance, Tanizawa et al.$^{533}$ deposited Cu(DPM)$_2$ (DPM = dipivaloylmethanate, 2,2,6,6,7,7,5-heptadione) as a precursor onto an air-annealed TiO$_2$(110) surface which was then inserted into a UHV chamber. Reduction of the Cu species with H$_2$ at 363 K led to a trimer with (111) orientation but tilted by ~30º from the TiO$_2$(110) normal, according to PTRF-XAFS measurements.

Charge Transfer
Charge transfer either to or from small Au particles to the oxide substrate has long been thought to be one of the possible causes of the enhanced catalytic activity of such nanoparticles.  

Minato et al. used valence band PES to study this issue. The BGS peak area decreased with increasing Au coverage, suggesting that electron density associated with O\textsubscript{b}-vac is donated to the Au nanoparticles. Okazawa at al. present similar data but make the opposite interpretation. They suggest that the O\textsubscript{b}-vacs are characterized by electron deficiency and that the BGS signature is therefore reduced by electron donation into the O\textsubscript{b}-vacs from Au. This interpretation of the electronic structure of O\textsubscript{b}-vacs is at odds with most of the literature which shows an electron excess associated with O\textsubscript{b}-vacs.

Recent KPFM results (Figure 85) from Chung et al. show an increase in the local contact potential difference (LCPD) over the Au particles. The increase in the LCPD can be attributed to the presence of negatively charged Au particles that form dipoles at the surface, indicative of electron transfer from TiO\textsubscript{2} to the Au. Interestingly, the direction of charge transfer is reversed for Au atoms deposited on an o-TiO\textsubscript{2} surface according to photostimulated desorption measurements by Zhang et al.

For Ag on r- and h-TiO\textsubscript{2}, the BGS was attenuated with Ag coverage as observed by Minato et al. for Au. However, the interpretation was that the Ag layer attenuates the BGS peak. For o-TiO\textsubscript{2}, the results are the same as for Au: the BGS grows with deposition of Ag, indicative of electron transfer from Ag to TiO\textsubscript{2}, as shown in Figure 86.
An early study of Cu on TiO$_2$ suggested a charge transfer from Cu to TiO$_2$ based on shifts in Cu 3$d$ BE in PES.$^{541}$ Shifts in Cu 2$p$ BE were also observed by Diebold et al.$^{506}$ and attributed to finite cluster size effects. Instead, because there were no changes in oxidation state of Ti$^{4+}$ and O$^{2-}$, it was concluded that no charge transfer occurred.$^{506}$

On the basis of the appearance of a BGS peak in valence band PES after deposition of Cu on $o$-TiO$_2$(110), Nakajima et al.$^{508}$ concluded that electron transfer occurs from Cu to TiO$_2$, which is in line with observations from Ag and Au.$^{513,540}$

Electron transfer from the $x$-linked TiO$_2$(110)(1×2) to small Au particles was inferred from local barrier height measurements with the transfer direction reversed for larger Au particles.$^{519}$

Epitaxy

CO was used as a probe molecule for a RAIRS study of the surface morphology of Cu on TiO$_2$(110).$^{542}$ At low coverage (~1.7 ML) a band appears at ~2100 cm$^{-1}$ which is consistent with a number of high index faces: (211), (311) and (755). At higher coverage (~6 ML), (111), (110), and (100) were identified, more-or-less in line with an earlier RAIRS study where (111) and (110) faces were identified for a 4-7 layer film.$^{543}$

LEED, RHEED, and high resolution transmission electron microscopy (HRTEM) indicate that such thicker films have a (111) termination: fcc(111)[1 $\bar{1}$ 0]Cu||(110)[001]TiO$_2$. Similar films of Ag and Au can have a (112) as well as (111) termination: fcc(112)[ $\bar{1}$ 10]metal||(110)[001]TiO$_2$.$^{544,545}$

Annealing
In general, annealing Cu, Ag, and Au in UHV or depositing with the sample hot leads to an increase in the cluster size with a concomitant decrease in the cluster density. Interestingly, for Cu and Ag\textsuperscript{505,511} the self-limiting behavior still seems to hold at each anneal temperature.

By STM imaging of the same area before and after annealing (950 K) Au particles on TiO\textsubscript{2}(110), Ostwald ripening (whereby large clusters grow at the expense of small ones) could be ruled out in favor of cluster migration and coalescence.\textsuperscript{502} In the former case, annealed clusters should remain more-or-less stationary. However, as shown in Figure 87, annealed clusters move a significant distance (up to 5 nm) from their original positions.

When Ag and Au on \textit{o}-TiO\textsubscript{2}(110) are annealed to \textasciitilde340 K,\textsuperscript{516} there is almost no change in the height distributions, which backs up the proposal of enhanced bonding of these metals on \textit{o}-TiO\textsubscript{2}(110) compared to \textit{r}- and \textit{h}-TiO\textsubscript{2}(110) (the same experiment for Au on \textit{r}-TiO\textsubscript{2} led to sintering).

Annealing Au on the \textit{x}-linked (1\times2) surface to 460 K greatly reduced the density of particles on the added rows. After annealing to 860 K, Au at \textit{x}-links were also greatly reduced, so that nearly all particles were at step edges.\textsuperscript{518}

\textbf{5.11 Group 13}

Submonolayer Al is completely oxidized at the TiO\textsubscript{2}(110) surface, as evidenced by the appearance of a lower BE Ti 2p shoulder that increases with Al coverage.\textsuperscript{546} A BGS peak also appears which is consistent with electron transfer from Al to TiO\textsubscript{2}. STM images indicate the growth of small particles that are distributed homogeneously with no
step edge preference.\(^5\) (A net structure that appeared in STM images with Al deposition can now be attributed simply to the appearance of either O\(_b\)-vacs or OH\(_b\).)\(^8\) Above 1 ML, oxidized and metallic Al are both evident from AES. However, the metallic component is oxidized within minutes even at room temperature. For thicker films (6 ML), metallic Al persists for hours but can be oxidized rapidly by annealing.

### 5.12 Group 14

SnO\(_2\) was deposited by pulsed laser deposition (PLD) at room temperature on \(o\)-TiO\(_2\)\((110)\) and TiO\(_2\)\((1\times2)\).\(^5\) In both cases, just after deposition, Sn was found to be in an oxidized state. Irradiation with an electron beam led to reduction of SnO\(_2\) into a metallic state, with the reduction rate on the \((1\times2)\) surface being at least 3 times higher than that on \((1\times1)\). STM of SnO\(_2\) on the \((1\times2)\) surface, measured before and after electron beam irradiation, suggest that the TiO\(_2\) substrate is simultaneously reoxidized: decomposing the \((1\times2)\) reconstruction. To rule out that the presence of Sn simply destabilizes the \((1\times2)\) rows, metallic Sn was deposited on the clean \((1\times2)\) surface. Sn atoms were found homogeneously over the surface without disrupting the \((1\times2)\) rows.\(^5\)

### 5.13 Group 15

Sb was doped into the near-surface region of TiO\(_2\)\((110)\) by ion implantation. Valence band PES shows that the dopant quenches the BGS. Replacing the BGS is a well-defined shoulder that overlaps with the top of the O 2\(p\) valence band. The shoulder was attributed to a 5\(s\)-5\(p\) hybrid orbital localized on surface Sb.\(^5\)
5.14 Lanthanoid series

STM images of 0.1 ML Ce vapor-deposited onto TiO$_2$(110) reveal individual atoms homogeneously distributed at the surface with no preference for step edges, as shown in Figure 88. Core level and valence band PES indicates reduction from Ti$^{4+}$ to Ti$^{3+}$ and that Ce is present as Ce$^{3+}$. Accompanying DFT calculations favor the Ce$^{3+}$ state in the between site (Figure 66) also proposed for alkali and alkaline earth metal atoms. Deposition in a pressure of O$_2$ leads to a series of CeO$_x$ particles still in the +3 state. Deposition of Cu, Pt, and Au nanoparticles onto the CeO$_x$/TiO$_2$(110) led to very active water-gas shift catalysis. Further details can also be found in the review of model Au catalysts by Gong et al.\textsuperscript{500}

6. Outlook

There has been considerable progress in the understanding of both clean surface structure and adsorbate geometries since previous reviews of this area. Nevertheless, there remain areas of considerable controversy and debate. The cause celebre is H$_2$O adsorption on TiO$_2$(110). Recent calculations point to molecular adsorption on the perfect surface.\textsuperscript{144} Such a surface is only achievable in-silico. In the (UHV) real world, the reaction of H$_2$O with as-prepared TiO$_2$(110) is dominated by the interaction with O-vacancies. It is possible to create the (110) surface with a very low density of point defects by exposing the partially hydroxylated surface to O$_2$. This has been described as a stoichiometric surface.\textsuperscript{31,38,98,138} Water is found to dissociate on such a surface.\textsuperscript{138} At first sight this suggests a discrepancy with theory.\textsuperscript{144} However, the ‘stoichiometric surface’ has a significant density of band gap states, which are not present on the perfect surface.
They may contribute to the reactivity. In fact, there is strong evidence that this is the case in reactions of O\textsubscript{2} with TiO\textsubscript{2}(110). Additional theoretical work would help in clarifying this picture.

Another area that warrants particular attention is the quantification of surface structures for organic overlayers. Much structural work relies on NEXAFS. Although this allows the angular orientation of molecular adsorbates to be determined, it does provide a full structure determination.

The vast majority of work continues to focus on surfaces under UHV conditions. Although there is still much work to do in this area, there is an essentially unexplored range of experiments at ambient pressure and liquid interfaces that is now technically feasible. The appropriate techniques include surface X-ray diffraction, SPM, ambient pressure photoemission and X-ray absorption spectroscopy. Measurements of this type will be vital to explore the fundamental physics and chemistry associated with photocatalysis under more realistic conditions and coupled to UV illumination.

One obstacle to ambient pressure/liquid interface studies concerns sample preparation. There seem to be two broad approaches that one can take. The first involves sample preparation in UHV, followed by introduction into the liquid/ambient pressure environment. This has the advantage that the surface structure is well-established but does not remove the necessity of employing a vacuum chamber. The other approach is to prepare samples outside of vacuum. This approach has a clear practical advantage in the simplicity of the sample preparation. However, a surface science approach would dictate that such samples are well-characterized, even if there is no special reason why the surface has to have the same structure as vacuum-prepared surfaces.
Time resolved experiments over a range of timescales will also be hugely important. Since it can reasonably be assumed that the energy imperative is not going to fade, the burgeoning field of TiO$_2$ surface science seems set to continue.

**Acknowledgements**

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**Figure Captions**

**Figure 1** Pseudo-space filling model of ideal bulk-terminated TiO$_2$(110)(1×1). Blue (red) spheres are oxygen (titanium) atoms. Red rectangle indicates (1x1) surface unit cell.

**Figure 2** Ball and stick model of TiO$_2$(110)(1×1). Blue (red) spheres are oxygen (titanium) atoms. The numerical labelling of the atoms is to allow identification (see Table 1). Symmetry paired atoms are denoted by *.

**Figure 3** STM images of TiO$_2$(110)(1×1) (135 Å)$^2$. Bright rows correspond to Ti$_{5c}$ sites. O$_b$-vacs appear as bright protrusions on the dark O$_b$ rows.

**Figure 4** 115 × 185 Å$^2$ NC-AFM images of TiO$_2$(110)(1×1) recorded with Δƒ = ~-45 Hz and applied voltage, 1.4 V. (a) Recorded before a tip change with O$_b$ bright, and (b) recorded after a tip change with O$_b$ dark. Blue arrowheads indicate coincident defects. The yellow line is in the same position in both images. In (a) it lies on a bright O$_b$ row going over a dark defect, whereas in (b) it lies on a dark O$_b$ row and goes over a bright defect. Adapted from ref 25 with permission. Copyright 2006 American Physical Society. http://link.aps.org/doi/10.1103/PhysRevB.74.073411

**Figure 5** Normalized integrated intensities of the BGS peak in PES as a function of O$_b$-vac density on the TiO$_2$(110)(1×1) surface determined from STM. (a) Data taken from experiments on r-TiO$_2$(110). The red marker is from an as-prepared sample and the light-blue, green, and black markers are for the same sample after 5, 10, and 20 s of electron bombardment, respectively. The dark-blue marker is from another sample, judged to be
more bulk-reduced than the other sample by its color. (b) Data taken from experiments on an initially \( h \)-TiO\(_2\)(110) surface (in this case, the O\(_{\text{vac}}\) density plotted is that before hydroxylation). The data points are from the initially hydroxylated surface (filled square), after exposure to 10 L O\(_2\) (filled circle), and from the O\(_2\)-exposed surface following electron bombardment for 2 s (open square), 5 s (open circle) and 10 s (open triangle). The black lines in both graphs represent the best linear fit. Reprinted with permission from ref 34. Copyright 2010 American Physical Society. http://link.aps.org/doi/10.1103/PhysRevLett.104.036806

**Figure 6** STM images of *simple* (1×2) reconstruction of TiO\(_2\)(110). (a) (500 Å\(^2\)) area, and (b) (30 Å\(^2\)) area. Adapted with permission from ref 46. Copyright 2006 American Physical Society. http://link.aps.org/doi/10.1103/PhysRevLett.96.055502

**Figure 7** Ball and stick model of the *simple* TiO\(_2\)(110)(1×2) reconstruction with Ti\(_2\)O\(_3\) added-rows. Blue spheres are oxygen and red spheres are Ti ions.

**Figure 8** (1060 Å\(^2\)) STM image of *x-linked* TiO\(_2\)(110)(1×2). Some *x-links* are marked with red rectangles. The separation between a pair of *x-links* is indicated. The inset shows an 80 × 30 Å\(^2\) STM image of a similar surface, highlighting the cross shapes of the links.

**Figure 9** Ball and stick models of TiO\(_2\)(011). Blue (red) spheres are oxygen (titanium) atoms. (a) and (b) illustrate the structures proposed in ref. 58 and ref. 59, respectively, for the (2×1) reconstruction. (c) depicts the (2×1) geometry deduced from SXRD\(^{60,61}\) and LEED-IV\(^{63}\). (d) shows bulk-terminated TiO\(_2\)(011)(1×1). The green [red] shaded area
indicates the atoms lost from (1×1) surface during formation of (2×1) structure displayed in (a) [(b)]. Reprinted with permission from ref 60. Copyright 2008 American Physical Society. http://link.aps.org/doi/10.1103/PhysRevLett.101.185501

**Figure 10** (a) 80 × 100 Å² NC-AFM image of (1×3)-α (top right) and ‘microfacet’-(1×3) (bottom left) terminations of TiO₂(100). The inset shows a line profile. (b) 50 Å × 70 Å STM image of TiO₂(100)(1×1) which lies on the lower terrace, and (1×3)-β. The inset shows an STM profile along the line shown. Adapted with permission from ref 65. Copyright 1999 American Physical Society.

**Figure 11** Octahedra model representations of (a) the microfacet model proposed in ref 67, and (b) the model concluded by Landree et al.68 At the center of each octahedron is a titanium atom and oxygen atoms are positioned at the corners. The darker shade is used to highlight the major differences between (a) and (b). Adapted with permission from ref 68 “Structure of the TiO₂₋ₓ(100)-1x3 surface by direct methods.” Copyright (1999), with permission from Elsevier

**Figure 12** Structure proposed for the TiO₂(100)c(2×2) reconstruction.76 (a) Direct methods scattering map revealing the in-plane positions of Ti and O atoms in the surface. (b) Top- and side-view of the DFT-relaxed structure with large and small spheres corresponding to O and Ti, respectively. Surface TiO₄ tetrahedra are colored blue. Reprinted with permission from ref 76. Copyright 2008 American Physical Society. http://link.aps.org/doi/10.1103/PhysRevLett.100.086102
Figure 13 (a) 600 x 190 Å² and (b) (180 Å)² STM images of rutile-TiO₂(771). Ti₅c rows and O₅-vacs [one is marked with hexagon in (b)] appear bright. A step edge strand is marked with a rectangle in (b). Adapted with permission from ref 84. Copyright 2012 American Physical Society. [link](http://link.aps.org/doi/10.1103/PhysRevLett.108.236103)

Figure 14 83 x 73 Å² STM images of the same area of the r-TiO₂(110) (a) before and (b) after O₂ exposure at 300 K. (c),(d) are duplicates of (a),(b) respectively, with features being marked according to the legend. Insets show ball models of the rectangular region marked in (c) and (d). Reproduced from ref 98 with permission of the PCCP Owner Societies. [link](http://dx.doi.org/10.1039/C000250J)

Figure 15 STM images (57 x 97 Å²; 1.0 V; 10 pA; 80 K) obtained from stepwise exposure of O₂ on r-TiO₂(110) within the same area. (a) Before O₂ dosing. (b)-(f) Sequentially acquired images after 0.02 L of O₂ showing the dissociation of the adsorbed O₂ during scanning (step I). The green arrows show the slow scan directions. (g) Image showing the fully filled O₅-vac after an additional 0.12 L O₂ dose (step II). (h) Image acquired after another additional 0.20 L O₂ (step III). Dashed squares mark the faint features that correspond to O₂ adsorbed at O₅-vac, dashed rectangles mark the intermediate state of the adsorbed molecular O₂ at O₅-vac, and white arrows mark the paired O₅d dissociated at Ti₅c sites. (i),(j) Line profiles corresponding to crossed lines 1 and 2 in (g) and lines 1’ and 2’ in (h). The red arrow denotes the crosspoint of the two lines. Reprinted with permission from ref 106. Copyright 2011 American Chemical Society.
Figure 16 Probability of O₂ dissociation by the STM tip at Ti₅c (red symbols) and O₅-vac sites (blue symbols), as a function of sample bias voltage in the constant tunneling current mode. (Curves for O₂ at Ti₅c were not obtained for Iₜ > 1 pA due to the large tip instabilities at bias < 0.3 V. The lines are shown to guide the eye. Reprinted with permission from ref 104. Copyright 2010 American Chemical Society.

Figure 17 STM images after exposure of 3 × 10¹⁴ O₂ cm⁻² (a) at 130 K, followed by annealing at (b) 180 K and (c) 260 K for 10 min, showing the onset of thermally induced O₂ dissociation at O₅-vac sites (equation 1 in the main text) above 150 K and at Ti₅c sites (equation 2 in the main text) above 230 K. All images were acquired at 50 K, and at Vₜ = 0.3 V, Iₜ = 1 pA. Reprinted with permission from ref 104. Copyright 2010 American Chemical Society.

Figure 18 Integrated O₂ ESD vs. annealing temperature for coverages of 0.27 ML (circles) and 0.03 ML (triangles). The total O₂ ESD yield (solid circles) decreases as the film is heated above ~200 K, but the integrated signal at later times (open circles) maximizes at ~390 K. The inset shows the O₂ ESD vs. time for a an O₂ coverage <1 O₂/O₅-vac annealed to 100 K (ii) and 400 K (iii) and for a coverage of 2 O₂/O₅-vac annealed to 100 K (i) and 400 K (iv). For 2 O₂/O₅-vac, the stimulated desorption kinetics changes. Reprinted with permission from ref 111. Copyright 2008 American Physical Society. http://link.aps.org/doi/10.1103/PhysRevLett.100.196102
Figure 19 Velocity distributions of photodesorbed O$_2$ from r-TiO$_2$(110) pre-exposed to 80 L of oxygen at 100 K for different substrate temperatures: (a), (b) 100, (c) 200, and (d) 260 K. The pump excitation energy was 4.16 eV (298 nm). Solid lines correspond to the flux and depletion corrected experimental data, and dashed lines are calculated Boltzmann distributions at the corresponding surface temperature. The inset shows a plot of the mean translational energies of the “slow” velocity component as a function of substrate temperature. The sample in (b) was annealed to 260 K then cooled to 100 K to take the measurement. Reprinted with permission from ref 119. Copyright 2009 American Chemical Society.

Figure 20 Integrated $^{18}$O$_2$ PSD (blue triangles) and TPD (orange squares) vs. $^{18}$O$_2$ coverage. While no thermal desorption is observed for coverages < 0.19 ML (or ~2 O$_2$/O$_b$-vac), PSD is readily observed, and the signal increases linearly over two different coverage ranges. Reprinted with permission from ref 122. Copyright 2011 American Chemical Society.

Figure 21 Concentration of photodesorbed O$_2$ at Ti$_{5c}$ sites, photodissociated O$_2$ at O$_b$-vacs, and nondissociated O$_2$ at O$_b$-vacs after UV irradiation for 15 min, as a function of the initial O$_2$ coverage. The dashed lines are linear regressions. Reprinted with permission from ref 105. Copyright 2011 American Chemical Society.

Figure 22 STM images of the same area (150 Å)$^2$ on h-TiO$_2$(110) with 0.126 ML OH$_b$. (a) Before and (b)-(d) after cumulative O$_2$ exposure of $2.4 \times 10^{15}$, $9.6 \times 10^{15}$, and $3.4 \times$
$10^{16}$ O$_2$ cm$^2$, respectively. Reprinted with permission from ref 124. Copyright 2009 American Chemical Society.

**Figure 23** (a) DFT-based potential energy diagram. Large, red circles correspond to calculated local potential energy minima, whereas small, red circles indicate values deduced using the climbing NEB procedure. The initial configuration is $r$-TiO$_2$(110) with two O$_b$-vacs and two H$_2$O gas phase molecules. The first step is dissociation of the H$_2$O molecules in the O$_b$-vacs to form $h$-TiO$_2$(110) with four OH$_b$ (the number of O$_b$-vacs or OH$_b$ on the TiO$_2$(110) surface is denoted on the bottom axis). The second step is the adsorption of an O$_2$ molecule on $h$-TiO$_2$(110). The pathway in which O$_2$ becomes HO$_2$ before dissociation into OH-O is shown as a thick black line, whereas the thin red line accounts for a pathway in which O$_2$ dissociates ($E_a = 0.51$ eV) before the reduction. The former pathway is kinetically preferred. Desorption of the (H$_2$O)$_2$ leads to a clean TiO$_2$(110) surface, $s$-TiO$_2$(110), with no point defects in the uppermost surface layer. (b)-(h) Ball models (top views) of selected reaction intermediates. O$_{ad}$ (yellow balls) indicates the O atoms of the adsorbates. Reprinted from from ref 126 with permission. Copyright 2009 American Chemical Society.

**Figure 24** (a) Coverage of O$_b$-vacs, OH$_b$, O$_{ad}$, and (OH$_t$ + HO$_2$) species vs. cumulative O$_2$ exposure on the partially hydroxylated TiO$_2$(110) surface, obtained from analysis of a (30 Å)$^2$ area. (b) The percentage of features that moved between subsequent STM images (∼2 min/image) after various O$_2$ exposures. Reprinted with permission from ref 124. Copyright 2009 American Chemical Society.
Figure 25 Reaction of O\textsubscript{2} with TiO\textsubscript{2}(110). (a) 130×170 Å\textsuperscript{2} STM image of a partially hydroxylated TiO\textsubscript{2}(110) surface that contains O\textsubscript{b}-vac and OH\textsubscript{b}. An O\textsubscript{b}-vac, an OH\textsubscript{b}, and an OH\textsubscript{b} pair are indicated. (b) The surface in (a) after exposure to ~90 L O\textsubscript{2} at 300 K. One of the bright spots assigned to O\textsubscript{ad} is circled. (d) A histogram showing the height distribution of 276 bright spots found on the Ti\textsubscript{5c} rows fitted to two Gaussian curves. The data are taken from an unsmoothed, larger version of the image in (c). The histogram indicates that the reaction products are almost entirely from one species. Reprinted with permission from ref 40. Copyright 2010 National Academy of Sciences, U.S.A.

Figure 26 STM images of the TiO\textsubscript{2}(011) surface. (a),(b) The (2×1) reconstructed surface. (c),(d) The new TiO\textsubscript{2} phase formed after annealing in 1.33×10\textsuperscript{-6} mbar O\textsubscript{2}. Image size (a),(c) (500 Å)\textsuperscript{2}. The surface unit cell for the rectangular (2×1) reconstruction is indicated in (b) and the quasi-hexagonal symmetry of the new TiO\textsubscript{2} phase is shown in (d). A line defect in the new TiO\textsubscript{2} phase can also be seen in (d). This defect is an anti-phase boundary due to the registry of the new phase with the TiO\textsubscript{2}(011) substrate. (e) Line profiles indicating the corrugation along the lines indicated in (b) and (d). Reprinted from ref 133. Copyright 2011 Nature Publishing Group.

Figure 27 Schematic depictions of water dissociation on TiO\textsubscript{2}(110). Blue and red spheres denote lattice O and Ti, respectively. The light blue spheres are O\textsubscript{b} atoms, which lie in the [001] azimuth of the substrate. Parallel Ti rows that lie between the O\textsubscript{b} rows are Ti\textsubscript{5c}.
atoms. The green sphere and pink spheres indicate the O atom and H atoms that originate from water.

Figure 28 (a) O 1s spectra for water adsorption on s-TiO$_2$(110) free from O$_b$-vacs. The spectra show the results after progressive heating of a multilayer of water and each spectrum has been deconvolved into individual contributions from the substrate, OH and H$_2$O. (b) Estimates of the OH and H$_2$O coverages. Reprinted with permission from ref 138. Copyright 2009 American Physical Society. http://link.aps.org/doi/10.1103/PhysRevB.80.235436

Figure 29 Structure and dynamics for 1 ML D$_2$O on r-TiO$_2$(110). (a) Top and (b) side views of the calculated structure. (c) Calculated VDOS (solid lines) and d($\omega$) parameters (dashed lines) versus frequency. The same colors are used for each direction for both the VDOS and d parameters. (d) RAIRS spectra for s- and p-polarized light along both azimuths (solid lines) and simulated spectra (dashed lines) using the d($\omega$) shown in (c). Reprinted with permission from ref 149. Copyright 2012 American Chemical Society.

Figure 30 Structure and dynamics for 2 ML D$_2$O on TiO$_2$(110). (a) Top and (b) side views of the calculated structure. (c) Calculated VDOS (solid lines) and d($\omega$) parameters (dashed lines) versus frequency. The same colors are used for each direction for both the VDOS and d parameters. (d) RAIRS spectra for s- and p-polarized light along both azimuths (solid lines) and simulated spectra (dashed lines) using the d($\omega$) shown in (c). Reprinted with permission from ref 149. Copyright 2012 American Chemical Society.
Figure 31 (a) Ball and stick model of TiO$_2$(110). Atoms and adsorption sites are labeled as O1–O12, Ti1–Ti8, and A1–A6 for oxygen, titanium, and the adsorbates, respectively. Note that the O2 and O1 sites also referred to as the BO and TO sites, as indicated. The surface non-primitive unit cell and the coordinate axes are also shown. Ti–O tri-layers are labeled as Layer 1–4, starting from the surface. 30% of the water in the O$_t$ position is dissociated with the rest being molecular water. There are an additional three water adsorption locations around the A4, A3, and A1 sites at a similar height above the O$_t$ site. (b) Top view of the TiO$_2$(110) surface with the lateral locations of the potential adsorption sites. Adapted with permission from ref 159 "Structure of rutile TiO$_2$ (110) in water and 1 molal Rb+ at pH 12: Inter-relationship among surface charge, interfacial hydration structure, and substrate structural displacements". Copyright (2007), with permission from Elsevier.

Figure 32 STM images of TiO$_2$(011)(2×1). (a) Clean surface with an O vacancy circled in the inset. (b) After exposure to 10 L of water at room temperature. (c) After dosing 0.4 L water at ~130 K. The inset shows pairs of OH groups. (d) After exposure to 0.8 L water at ~115 K. Reprinted with permission from ref 162. Copyright 2009 American Chemical Society.

Figure 33 HREELS and TPD on TiO$_2$(110). (a) HREELS spectra recorded for the clean TiO$_2$(110) surface (curves A and B) and after exposure to 2000 L of atomic hydrogen at room temperature and subsequent annealing to 400 K and 550 K (curves D and E). Curve
A is the raw spectrum, and Fourier-deconvoluted spectra are shown in curves B–E. (b) TPD recorded after exposing the clean TiO$_2$(110) surface to 2000 L of atomic hydrogen at 300 K (curve B is H$_2$ and curve C is H$_2$O) and after exposing the surface hydrogenated at room temperature to 50 L CO at 95 K (curve A: CO). Reprinted with permission from ref 167. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

**Figure 34** (100 Å)$^2$ NC-AFM and STM current maps (average $I_t$) of TiO$_2$(110). $\Delta f = 46.9$ Hz, bias voltage = 0.97 V, and peak-to-peak amplitude is 250 Å. (a),(b) then (c),(d) were recorded simultaneously with a time-lapse of 4 min between the two pair of images. Circles highlight OH$_b$ and squares highlight subsurface OH. (e) Line profiles showing the AFM and STM corrugation before (blue) and after (red) an H atom was moved to the subsurface site. Reprinted with permission from ref 169. Copyright 2009 American Physical Society. http://link.aps.org/doi/10.1103/PhysRevLett.102.136103

**Figure 35** STM images (85 × 119 Å; 1.0 V; 10 pA) of (a) r-TiO$_2$(110), (b) after CO$_2$ adsorption in situ at 80 K, and (c) after tip-induced CO$_2$ dissociation. (d) A typical $I_t$-t curve during the voltage pulse. (e) Schematic representation of the tip-induced CO$_2$ dissociation, leading to healing of the O$_b$-vac and either desorbed CO or adsorbed CO at Ti$_{5c}$ site. (f) Plots of CO$_2$ dissociation rate as a function of $I_t$ at different bias voltages. Reprinted with permission from ref 183. Copyright 2011 American Physical Society. http://link.aps.org/doi/10.1103/PhysRevB.84.155418
**Figure 36** (85 Å$^2$) STM images acquired at 80 K in the same area of r-TiO$_2$(110) (a) before and (b) after CO exposure. (c),(d) 44 × 30 Å$^2$ images expanded from (a),(b) as indicated by the rectangles. The TiO$_2$(110) surface structure is superimposed. Green squares denote O$_b$-vac and blue dots the CO at Ti$_{5c}$. Reprinted with permission from ref 191. Copyright 2009 American Chemical Society.

**Figure 37** (a) (50 Å$^2$) STM image of CO/O/TiO$_2$(110) after annealing to 110 K. The pear-shaped feature in the ellipse is a CO-O complex formed upon annealing. A line profile along the red line is shown in (d). (b) (35 Å$^2$) STM image of an area with CO-O, O$_{ad}$, and three O$_b$-vacs with a lattice superimposed. Two small black dots mark the positions of CO and O in the CO-O complex. (c) (80 Å$^2$) STM image of CO/O/TiO$_2$(110) at a higher coverage of CO. The peanut-shaped feature in the ellipse is a CO-O-CO complex. A line profile along the blue line is shown in (d). Two panels in the inset show an electrical pulsing experiment. A negative pulse (-3.5 V, 30 ms) is applied to the upper CO molecule while scanning the area where the CO-O-CO complex is located (left panel). A CO-O complex is shown after a CO molecule is displaced from the CO-O-CO complex by the pulse (right panel). (d) Line profiles along CO-O and CO-O-CO complexes along the red and blue lines in (a) and (c), respectively. Arrows indicate the positions of CO and O. Reprinted with permission from ref 194. Copyright 2011 American Chemical Society.

**Figure 38** (a) CO TPD from clean (black) and o-TiO$_2$(110) (red). The exposure of CO was the same for both experiments (9.6 × 10$^{12}$ molecules cm$^{-2}$). The TPD curve
maximum shift from 133 to 139 K can be clearly observed (marked by two dotted lines).

(b) $^{18}$O$_2$ ESD yield from $^{18}$O-covered TiO$_2$(110) surface with (red circles) and without
(blue squares) CO as a function of annealing temperature. The ESD yields were measured
at 81 K after annealing to the temperature indicated. Three $^{18}$O$_2$ ESDIAD patterns at 80,
120, and 160 K are also shown above the yield curves. The ESDIAD patterns are all
circular, indicating normal O$^+$ ejection and therefore Ti$_{5c}$—O$_{ad}$ bonds approximately
normal to the surface. Reprinted with permission from ref 194. Copyright 2011 American
Chemical Society.

Figure 39 (a) (250 Å)$^2$ NC-AFM ($\Delta f$) image of C$_{60}$ on TiO$_2$(110) showing single C$_{60}$
molecules and islands. Single C$_{60}$ molecules (dashed circle) and OH$_b$ (one is indicated by
an arrow) can be seen on the terrace while a C$_{60}$ island is attached to a step edge. (b)
Model of the C$_{60}$ island structure. The C$_{60}$ molecules are drawn with their vdW radii (~10
Å). The molecules are centered in the troughs formed by the O$_b$ rows. The exact lattice
site within the troughs, however, cannot be determined and is arbitrary in the model.
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http://dx.doi.org/10.1088/0957-4484/20/6/065606

Figure 40 Experimental and simulated PhD patterns. C 1s photoemitted intensity for
different polar and azimuthal angles. Kinetic energy is 580 eV. The five main
orientations for C$_{60}$ have been simulated. The shaded rectangle drawn across all the
pattern acts as a guide for the eye, highlighting the experimental emission belt. Reprinted
Figure 41 DFT-vdW optimized atomic models for C$_{60}$ on TiO$_2$(110). (a) Top view. The superstructure unit cell is represented. Two different orientations are observed depending on the adsorption site: hexagon (in between two Ti$_{5c}$ atoms) and dimer$_{56}$ (atop a Ti$_{5c}$ atom). (b) Side view along the [1̅10]. Both molecules have a very similar adsorption height, approximately 3.2 Å, consistent with a weakly interacting system. Reprinted with permission from ref 200. Copyright 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Figure 42 (a) (149 Å)$^2$ STM image of a C$_{60}$ monolayer on x-linked TiO$_2$(110)(1×2). (b) Proposed model. The dotted circle represents the vdW sphere of a C$_{60}$ molecule (10.5 Å). Reprinted with permission from ref 197. Copyright 2006 American Chemical Society.

Figure 43 Estimated coverages of various species based on the (a) N 1s and (b) O 1s components for high-pressure exposures of NO$_2$ on TiO$_2$(110) at room temperature. Filled circles correspond to chemisorbed NO$_3$ (sometimes referred to as ‘nitrates’), empty circles to NO$_2$ (‘nitrites’), empty squares to atomic nitrogen, and filled squares to adsorbed H$_2$O. Reprinted with permission from ref 205. Copyright 2010 American Chemical Society.
**Figure 44** Adsorption/desorption of NO in vicinity of OH\textsubscript{b} on TiO\textsubscript{2}(110). (a),(b) Two consecutive (60 Å\textsuperscript{2}) STM images ($V_{t}$ = +1.6 V and $I_{t}$ = 0.2 nA) of the same part of an $h$-TiO\textsubscript{2}(110) surface with ~0.05ML of NO. The images were collected in an NO background pressure of ~2 × 10\textsuperscript{-9} mbar. In the area marked with a white circle, an NO-related feature disappears, and OH\textsubscript{b} appears at a neighboring O site. The black circle marks the reverse process. (c) Fluctuations in coverage of adsorbed OH\textsubscript{b} and NO features vs. time in the same NO background pressure. (d) Density of OH\textsubscript{b} and NO-related adsorbates vs. NO exposure, normalized to the initial density of OH\textsubscript{b}. The lines are plotted to guide the eye. These data indicate that OH\textsubscript{b} is involved in the capture of NO, but is not consumed in the process. Reprinted with permission from ref 211. Copyright 2012 American Chemical Society.

**Figure 45** N\textsubscript{2}O TPD (m/e = 44) spectra from N\textsubscript{2}O dosed on differently prepared TiO\textsubscript{2}(110) surfaces. The correlation between the N\textsubscript{2}O peak (labelled N\textsubscript{2}O\textsubscript{v}) at 175 K and O\textsubscript{h}-vacs can be established on the basis of its depletion on hydroxylated, stoichiometric, and oxidized TiO\textsubscript{2}(110) surfaces [$h$-, $s$-, and $o$-TiO\textsubscript{2}(110)]. Reprinted with permission from ref 215. Copyright 2012 American Chemical Society.

**Figure 46** Ball model of TiO\textsubscript{2}(110). In the lattice, small, black spheres represent Ti atoms and large, gray spheres represent O. O atoms at the surface are shaded lighter. The ammonia is arranged with c(2\times2) symmetry as proposed by Diebold and Madey\textsuperscript{220} and also in a (2\times1) region on top of 5-fold coordinated Ti atoms. The c(2 \times 2) unit cell is indicated with a solid white rectangle and the dashed white rectangle marks the (2 \times 1).
Adapted with permission from ref 224. Copyright 2007 Institute of Physics. http://dx.doi.org/10.1088/0957-4484/18/4/044003

Figure 47 230 × 100 Å STM image of TiO$_2$(110) exposed to 100 L NH$_3$ near room temperature. The black parallelograms indicate the unit cells of NH$_3$ which are arranged with c(2×2) periodicity and the white rectangles are drawn over unit cells with (2×1) order. Reprinted with permission from ref 224. Copyright 2007 Institute of Physics. http://dx.doi.org/10.1088/0957-4484/18/4/044003

Figure 48 Adsorption models considered in the S K-edge NEXAFS spectra simulations of SO$_2$/TiO$_2$(110). Adapted from ref 233 with permission of the PCCP Owner Societies. http://dx.doi.org/10.1039/b811925b

Figure 49 Time-dependent DFT S 1s excitation spectra for the adsorption models shown in Figure 48 compared with the experimental spectra.$^{231}$ The dashed lines in (a) and (b) are the experimental spectra recorded at 100 K and 150 K, respectively. Adapted from ref 233 with permission of the PCCP Owner Societies. http://dx.doi.org/10.1039/b811925b

Figure 50 Sequential STM images obtained during SO$_2$ exposure at 6.66 × 10$^{-7}$ mbar and 300 K, starting with a freshly prepared $x$-linked TiO$_2$(110)(1×2) surface prior to the first SO$_2$ exposure. The tunneling parameters were 2.6 V and 0.2 nA. Each image is identified by a number and the time at which it was taken. The scale and the orientation of the crystallographic directions are shown in the upper right and lower left corner of the first
frame, respectively. An area displaying ordered assemblies is marked by a white circle in frame #4. Reprinted with permission from ref 239 “Monitoring the interaction of sulfur dioxide with a TiO2(110) surface at 300 K by scanning tunneling microscopy.” Copyright (2002), with permission from Elsevier.

Figure 51 Schematic ball and stick diagram of the adsorption geometry of [HCOO]- on TiO2(110)(1×1), as determined from PhD254 and LEED-IV.255 The location of the dissociated acidic hydrogen, deduced from PhD data, is also indicated. The numerical labelling of atoms is employed in Table 2 for identification purposes. Symmetry pair atoms are denoted by *.

Figure 52 Schematic diagrams of the local formate adsorption geometry, indicating various best-fit structural parameters derived from PhD254 (top) and LEED-IV255 (bottom).

Figure 53 Schematic diagram of the adsorption geometry of glycinate on TiO2(110)(1×1), as determined from PhD.266 The positions of the C, N, and H atoms were not explicitly determined.

Figure 54 Structures of each of the three pyridine-carboxylic acid isomers studied in ref 274.

Figure 55 Structure of 2-cyano-3-(4-N,N-diphenylaminiophenyl)-trans-acrylic acid studied in ref 279.
**Figure 56** Ball and stick model of the most likely adsorption geometry for bisonicotinate on TiO$_2$(110)(1×1) emerging from refs 284,285. In the adsorbate, the light spheres in the rings are nitrogens, the dark spheres are carbons, the smallest spheres are hydrogens, and the largest are oxygen atoms.

**Figure 57** STM images of TiO$_2$(110)(1×1) before (a) and after (b) butan-2-ol exposure. (a) Arrows indicate the location of O$_b$-vacs. (b) Arrows indicate 2-butoxides bound to O$_b$-vacs. Crosses mark the locations of OH’s. Also labelled are butan-2-ol species adsorbed at regular Ti$_{5c}$ sites. Adapted with permission from ref 301. Copyright 2007 American Chemical Society.

**Figure 58** Ball and stick model of the bridging-bidentate bonding geometry of catecholate.$^{305}$ Also depicted are the two OH’s resulting from the predicted catechol dissociation upon adsorption.

**Figure 59** Adsorption geometries of benzaldehyde on TiO$_2$(110)(1×1).$^{311}$ (a) $\eta^1$-atop configuration, and (b) $\eta^2$-dioxyalkylene configuration.

**Figure 60** Schematic diagram of bridge-bonding $\eta^2$-2,2-propanedioilate species on TiO$_2$(110)(1×1), which is proposed to form following acetone exposure to a surface decorated with O$_{ad}$ atoms.$^{312,315}$

**Figure 61** Structure of 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) studied in ref 317.

**Figure 62** Structure of (4,4’,4”-Tris)$N$-(1-napthyl)-N-phenyl-amino-triphenylamine studied in ref 325.
**Figure 63** (a) STM image of TiO$_2$(110)(1×1) subsequent to deposition of violet lander molecules. (b) High resolution image showing two different adsorption geometries, and corresponding illustration of the likely structures. Reprinted with permission from ref 334. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

**Figure 64** Structure of copper hexafluoroacetylacetonate (Cu(hfac)$_2$) studied in ref. 339.

**Figure 65** Thermodynamic factors and the growth mode of metals on TiO$_2$(110). The graph plots $-\Delta H^0_{\text{oxide}}$ and $-\Delta H^0_{\text{metal}}$ both per mole of metal on TiO$_2$(110). Filled circles and open squares represent experimentally observed 3D island and 2D layer growth modes, respectively and crosses represents the positions of metals whose growth modes have not been determined. $-\Delta H^0_{\text{metal}}$ oxide of Au and Pt are approximated as zero. Adapted with permission from ref 341 “A new insight into the growth mode of metals on TiO2(1 1 0)”. Copyright (2001), with permission from Elsevier.

**Figure 66** Schematic of TiO$_2$(110) showing the: between site (green, open triangle), adjacent site (yellow, open triangle), bridging site across two O$_b$ (pink line), atop O$_b$ site (red, filled square), and atop Ti$_{5c}$ site (blue cross).

**Figure 67** (68 Å)$^2$ NC-AFM image of K adatoms on h-TiO$_2$(110). Reprinted with permission from ref 351. Copyright 2011 American Physical Society.
**Figure 68** MIES and valence band PES near $E_F$ for Cs 6s and Ti 3d, respectively, as a function of coverage. Reprinted from ref 356 “Study of the electronic structure of TiO$_2$(110) and Cs/TiO$_2$(110) with metastable impact electron spectroscopy and ultraviolet photoemission spectroscopy (HeI)”. Copyright (2000), with permission from Elsevier.

**Figure 69** STM images of Ca vapor deposited on TiO$_2$(110). (a) Image showing Ca-induced row structure ($500 \times 400 \ \text{Å}^2$). (b) Image showing Ca-induced 2D layer, ($94 \ \text{Å}^2$). The white arrows are along the [001] direction. Modified with permission from ref 372. Copyright 2004 American Chemical Society.

**Figure 70** STM images ($3000 \ \text{Å}^2$) of the Ba-Ti-O nanocrystals formed on TiO$_2$(001). (a) Ba atoms were deposited at room temperature and subsequently heated at 1273 K in UHV. (b) After two cycles of the deposition/anneal procedures of (a). Reprinted from ref 380. Copyright 2002 American Chemical Society.

**Figure 71** $240 \times 130 \ \text{Å}^2$ STM image of Cr on TiO$_2$(110). The surface is decorated with 2D islands (squares) together with a much smaller species (circles), possibly individual Cr atoms. Adapted from ref 389. Copyright 2002 A. J. Limb.

**Figure 72** ($800 \ \text{Å}^2$) STM image of Fe on TiO$_2$(110). The substrate is covered mainly with 2D islands together with some 3D clusters. Adapted from ref 389. Copyright 2002 A. J. Limb.
**Figure 73** (50 Å)$^2$ constant height STM images from a hexagonal Rh particle formed at 1050 K. The lattice parameters are indicated. Reprinted from ref 439. Copyright 2011 American Chemical Society.

**Figure 74** STM images of vicinal TiO$_2$(110)(1×2). (a) (320 Å)$^2$ image of the clean surface. (b) (1000 Å)$^2$ image following deposition of 0.1 ML Pt. The inset is (340 Å)$^2$. Reprinted from ref 455 “Effects of titania surface structure on the nucleation and growth of Pt nanoclusters on rutile TiO$_2$(110)”. Copyright (2001), with permission from Elsevier.

**Figure 75** The Ni 2$p$ PES spectra of the Ni clusters on (a) $r$-TiO$_2$(110), (b) TiO$_{2.22}$(110), and (c) TiO$_{2.35}$(110). The cluster impact energies are stated to the right of the spectra. Reprinted with permission from ref 464. Copyright 2002 American Institute of Physics.

**Figure 76** XPEEM images and PES of TiO$_2$(110) after depositing 0.4 ML Pd at 900 K. XPEEM images recorded at ~13 µm field of view and 420 eV photon energy. Spectral-XPEEM images (a-d) correspond to binding energies of 342.1 eV (off core level), 340.1 eV (on core level), 337.1 eV (off core level), and 334.7 eV (on core level), respectively. Image (e) (corresponding to the same area as panels (a)-(d) is an XPEEM secondary electron image recorded above the Pd M4,5 edge at $h\nu = 420$ eV and shows all of the Pd-related features. In (f), the Pd 3$d$ $\mu$XPS signal acquired at $h\nu = 640$ eV from a 20 µm field of view is displayed as a red curve (from a different region to the movie).
The line shape was fitted using a Doniac-Sunjic function (gray line). Spectra from 10 Pd dotlike nanoparticles are displayed in blue and from 2 nanowires in green. Blue and green circled areas display the regions sampled to generate the nanoparticle and nanowire spectra, respectively. Light gray lines in the spectra correspond to the image energies of (a)-(d). The oval shape of the field of view is due to a contrast aperture in the imaging optics. Reprinted with permission from ref 483. Copyright 2009 American Chemical Society.

**Figure 77** Surface energy, $\gamma_M$, and work function, $\phi$, of different transition metals. In region I, encapsulation is expected ($\phi > 5.3$ eV and $\gamma_M > 2$ Jm$^{-2}$) and in region II ($\phi < 4.7$ eV), oxidation of metals on TiO$_2$ is possible. Apart from for Fe and Co, all the metals for which TiO$_x$ encapsulation has been reported fall in the top right-hand side of the plot as would be expected. The cause of these anomalies is as yet unknown. Reprinted with permission from ref 486. Copyright 2005 American Chemical Society.

**Figure 78** Low-energy He$^+$ ion scattering (LEIS) spectra of the clean TiO$_2$(110) surface (bottom), after evaporation of 25 ML Pt at room temperature (center), and after the high-temperature treatment causing encapsulation (top). Reprinted with permission from ref 491. Copyright 2000 American Physical Society. http://link.aps.org/doi/10.1103/PhysRevLett.84.3646

**Figure 79** (a) (105 Å)$^2$ STM image of the pinwheel structure formed by annealing Pd/TiO$_2$(110)(1×2) in UHV up to 970 K. The circle highlights a pinwheel and the three
triangles mark out part of the ideal pinwheel structure. (b) A hexagonal lattice of 3.25 Å periodicity is rotated by 3º and superimposed on a lattice of 2.75 Å periodicity giving rise to the superstructure drawn in bold. This pattern reproduces the pinwheel motif seen in (a). Adapted with permission from ref 492. Copyright 2002 American Chemical Society.

**Figure 80** (a) 101 × 50 Å² STM image of the z structure formed by annealing Pd/TiO₂(110)(1×2) under UHV in steps reaching 970 K. (b) STM image of the z’ structure formed by annealing 25 ML of Pt on TiO₂(110)(1×1). (c) (170 Å)² STM image of z-TiOₓ prepared by MVD of Ti on Pt(111) in 10⁻⁶ mbar O₂ then post-annealing to 823 K in 10⁻⁷ mbar O₂. (d) 150 × 110 Å² STM image of the z’ structure formed by MVD of Ti on Pt(111) in under 10⁻⁶ mbar O₂ then annealing to 673 K for 110 mins <10⁻¹⁰ mbar O₂. The images are adapted with permission from ref 492 (copyright 2002 American Chemical Society) in (a) ref 491 (copyright 2000 American Physical Society, http://link.aps.org/doi/10.1103/PhysRevLett.84.3646) in (b) ref 496 (copyright 2007 American Chemical Society) in (c) and ref 498 (copyright 2008 American Physical Society, http://link.aps.org/doi/10.1103/PhysRevB.77.115417) in (d).

**Figure 81** Model proposed for z-TiOₓ on the basis of DFT calculations (right) and the corresponding simulated STM image at +1.00 V (left). The STM image is obtained by using four Pt layers to describe the metal support. The brighter four-coordinated Ti atoms (denoted as Ti₄ in the figure) are responsible for the zigzag-like motif (underlined) along the [1̅10] direction of the support, whereas the three-coordinated Ti atoms (denoted as Ti₃ in the figure) are hardly visible. Only the outermost Pt layer is shown in the figure for
clarity. Ti, O and Pt are shown as blue, red and gray balls, respectively. Reprinted with permission from ref 496. Copyright 2007 American Chemical Society.

Figure 82 Comparison between the simulated and experimental STM images for the z’-TiOₓ structure for different models that account for slightly different structures seen in STM. (a) and (b) have TiO₁.₂₅ stoichiometry whereas (c) has TiO₁.₂₀ stoichiometry. In the ball and stick models, O is red and Ti is blue. Reprinted with permission from ref 498. Copyright 2008 American Physical Society.


Figure 83 Au cluster growth on TiO₂(110) measured with STM from the same area during the dosing sequence. The apparent diameters, d, and apparent heights, h (×10), are shown as a function of coverage. The right-hand scale corresponds to the evolution of the number density (N) of Au clusters. The atomic step height (aS) is shown (×2) in order to demonstrate the stability of the tip (the step height hardly changes). Reprinted with permission from ref 502. Copyright 2002 The Japan Chemical Journal Forum and Wiley Periodicals, Inc.

Figure 84 (130 Å)² STM images of (a) r-, (b) h-, and (c) o-TiO₂(110) before Au exposure. Some Oₐ-vacs, OHₐ, and O_ad are highlighted with squares, hexagons, and circle, respectively. The insets (30 Å)² show the point defects in detail. (d)-(i) STM images after 0.03 ML Au exposure. (d)-(f) are (130 Å)² and (g)-(i) are (350 Å)². In (d)-
(f), the heights of the Au clusters above the terraces are given by contour lines at 1.2, 3.2, and 5.2 Å. From ref 516. Reprinted with permission from AAAS.

Figure 85 (25 Å)² images showing (a) the NC-AFM topography and (b) the simultaneously obtained LCPD image of Au adsorbed on h-TiO₂(110). (c) The height and (d) the LCPD profile taken along the lines indicated in (a) and (b), respectively. The circle indicates one of the Au clusters. Reprinted with permission from ref 517. Copyright 2011 American Institute of Physics.

Figure 86 Valence band PES spectra acquired on (a) r-TiO₂(110) and (b) o-TiO₂(110) before (black line) and after Ag exposure at 100 K (red, blue, and green lines). In both plots, a BE of 5.7 eV [most intense O 2p feature on r-TiO₂(110)] is marked by a dashed line. (c) Magnification of the BGS region in (b). Note that (c) also shows the spectrum corresponding to ~0.67 ML Ag (light blue) that was omitted in (b). Reprinted with permission from ref 513. Copyright 2010 American Chemical Society.

Figure 87 STM images of the Au/TiO₂(110). (a) as deposited and (b) the same area after annealing at 950 K for 30 mins. Changes in the location of the clusters in (b) with respect to their precursors from (a) are marked with small white dots. Solid circles in (a) denote groups of clusters that were presumed to coalesce upon annealing. Dashed areas mark TiO₂ terraces that undergo partial decay. Reprinted with permission from ref 502. Copyright 2002 The Japan Chemical Journal Forum and Wiley Periodicals, Inc.
Figure 88 (a) STM image of Ce atoms vapor-deposited on a clean TiO$_2$(110) surface at 298 K in UHV. (b) Lowest energy structure obtained in DFT calculations for the adsorption of a Ce atom on TiO$_2$(110). Reprinted with permission from ref 551. Copyright 2010 American Chemical Society.
Figure 3
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Figure 86
Table 1 Atomic displacements away from bulk-terminated TiO$_2$(110)(1×1) obtained from analysis of LEED-IV, SXRD, MEIS, and PhD studies. Figure 2 shows the identity of the atoms. A negative value indicates that the atom moves towards the bulk for a displacement perpendicular to the surface plane, and in the [1 T 0] direction for a lateral displacement.

<table>
<thead>
<tr>
<th>Atom</th>
<th>LEED-IV$^{16}$</th>
<th>SXRD$^{16}$</th>
<th>MEIS$^{17}$</th>
<th>PhD$^{18}$</th>
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<td>O(1)</td>
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<td>0.10 ± 0.04</td>
<td>0.13 ± 0.16</td>
<td>0.17 ± 0.15</td>
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<td></td>
<td>0.19 ± 0.08</td>
<td>0.17 ± 0.03</td>
<td>0.05$^a$</td>
<td>0.00 +0.15/-</td>
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<td>O(2) [110]</td>
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<td>0.19 +0.10/-</td>
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<td>Ti(2)</td>
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<td>-0.11 ± 0.01</td>
<td>-0.09± 0.09</td>
<td>-0.26 ± 0.08</td>
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<td>O(3)</td>
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<td>0.07 ± 0.04</td>
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<td>O(4)</td>
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$^a$No error estimates are given in 16 for these parameters, due to their strong coupling.
Table 2  Substrate atom displacements away from the bulk-terminated TiO$_2$(110)(2×1)-[HCOO]$^-$ structure, resulting from analysis of PhD$^{254}$ and LEED-IV$^{255}$ data. Also listed are the atomic displacements of clean TiO$_2$(110)(1×1) derived from LEED-IV.$^{16}$ Figure 1 provides a key to the identity of the atoms. A negative value indicates that the atom moves towards the bulk for a displacement perpendicular to the surface plane, and in the [1$\bar{1}$0] and [001] directions for lateral displacements. NC indicates that a quantitative comparison is inappropriate, due to different symmetry considerations in the LEED-IV and PhD studies. ‘-’ denotes that no optimisation of the coordinates of the atoms was undertaken. SF signifies that the displacement is symmetry forbidden on the clean (1×1) surface.

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<tr>
<th>Atom</th>
<th>PhD (254)</th>
<th>LEED-IV (255)</th>
<th>LEED-IV (1×1) (16)</th>
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<td>-0.10 ± 0.03</td>
<td>-0.19 ± 0.03</td>
</tr>
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<td>Ti (1) [001]</td>
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<td>-0.01 ± 0.13</td>
<td>SF</td>
</tr>
<tr>
<td>Ti (2) [110]</td>
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<td>0.25 ± 0.03</td>
</tr>
<tr>
<td>Ti (3) [110]</td>
<td>NC</td>
<td>0.05 ± 0.04</td>
<td>0.25 ± 0.03</td>
</tr>
<tr>
<td>Ti (4) [110]</td>
<td>-</td>
<td>-0.02 ± 0.12</td>
<td>-0.09 ± 0.07</td>
</tr>
<tr>
<td>Ti (5) [110]</td>
<td>-</td>
<td>0.00 ± 0.08</td>
<td>-0.09 ± 0.07</td>
</tr>
<tr>
<td>Ti (6) [110]</td>
<td>-</td>
<td>-0.03 ± 0.05</td>
<td>0.14 ± 0.05</td>
</tr>
<tr>
<td>Ti (6) [001]</td>
<td>-</td>
<td>0.05 ± 0.24</td>
<td>SF</td>
</tr>
<tr>
<td>O (1) [110]</td>
<td>0.02 ± 0.30</td>
<td>0.02 ± 0.04</td>
<td>0.10 ± 0.05</td>
</tr>
<tr>
<td>O (1) [001]</td>
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<td>0.02 ± 0.19</td>
<td>SF</td>
</tr>
<tr>
<td>O (2) [110]</td>
<td>NC</td>
<td>0.13 ± 0.09</td>
<td>0.27 ± 0.08</td>
</tr>
<tr>
<td>O (2) [1$\bar{1}$0]</td>
<td>NC</td>
<td>-0.04 ± 0.18</td>
<td>-0.17 ± 0.15</td>
</tr>
<tr>
<td>O (3) [110]</td>
<td>NC</td>
<td>0.05 ± 0.13</td>
<td>0.27 ± 0.08</td>
</tr>
<tr>
<td>O (3) [1$\bar{1}$0]</td>
<td>NC</td>
<td>-0.22 ± 0.25</td>
<td>-0.17 ± 0.15</td>
</tr>
<tr>
<td>O (4) [110]</td>
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<td>-0.02 ± 0.06</td>
<td>0.06 ± 0.10</td>
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<td>O (4) [001]</td>
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</tr>
<tr>
<td>O (5) [110]</td>
<td>0.02 ± 0.22</td>
<td>-0.02 ± 0.07</td>
<td>0.00 ± 0.08</td>
</tr>
<tr>
<td>O (5) [001]</td>
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<td>-0.04 ± 0.22</td>
<td>SF</td>
</tr>
<tr>
<td>O (6) [110]</td>
<td>-</td>
<td>0.04 ± 0.15</td>
<td>0.06 ± 0.12</td>
</tr>
<tr>
<td>O (6) [1$\bar{1}$0]</td>
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<td>-0.07 ± 0.18</td>
</tr>
<tr>
<td>O(7) [110]</td>
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<td>0.06 ± 0.12</td>
</tr>
<tr>
<td>O(7) [1$\bar{1}$0]</td>
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<td>-0.01 ± 0.32</td>
<td>-0.07 ± 0.18</td>
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<tr>
<td>O (8) [110]</td>
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<td>0.00 ± 0.17</td>
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<td>O (8) [001]</td>
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<td>O (9) [110]</td>
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<td>O (9) [001]</td>
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<td>-0.09 ± 0.52</td>
<td>SF</td>
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