

Chapter 4

Adsorption structure of formic acid reaction products on $\text{TiO}_2(110)(1 \times 1)$

Titanium dioxide (TiO_2), also called titania, is one of the most widely used oxides in the chemical industry, in various applications ranging from its use in solar cells for the production of hydrogen and electric energy, as a gas sensor, as a support for metal clusters in catalysis, as white pigment in paints, in cosmetic products and even in ice creams, etc. In heterogeneous catalysis, TiO_2 is used to decontaminate polluted air in exhaust streams and waste water by means of the so called photocatalytic oxidation (PCO). Photocatalytic oxidation involves the mineralisation of harmful organic compounds (e.g. volatile organic compounds and bioaerosols) into harmless inorganic ones at the surface of a semiconductor irradiated with ultra-violet light. Notice that the term “photocatalysis” is not meant to imply catalysis by light. In photocatalytic oxidation, when the surface of the semiconductor used as catalyst is irradiated with light of energy high enough to overcome its band gap, an electron is transferred from the valence band to the conduction band of the semiconductor. Once photoexcitation occurs across the band gap, there is sufficient lifetime for the created electron-hole pair to undergo charge transfer to adsorbed species (e.g. O_2 , OH^-) on the semiconductor surface resulting from contact with the solution or the gas phase. The resulting ionised species (e.g. O_2^- , OH°) are very reactive, and they ‘attack’ organic contaminants adsorbed on the surface of the semiconductor, producing a progressive break-up of molecules to yield mainly to CO_2 and H_2O . Thus, the initial photoexcitation takes place in the catalyst substrate and the photoexcited catalyst then interacts with the adsorbed noxious molecules to transform them into nontoxic compounds. Fig. 4.1 shows schematically the PCO process¹.

Among all the semiconductors used so far in photocatalytic reactions, TiO_2 is currently considered the most promising catalyst for air and water photocatalytic decontamination². This is not only due to its proved ability to mineralise a wide range of organic compounds

¹For more detailed information about the PCO process see the reviews by J.T. Yates, Jr. [87] and by A. Mills [88], and references therein

²Although stoichiometric TiO_2 is considered to be an insulator, the presence of bulk oxygen vacancies makes it an n-type semiconductor.

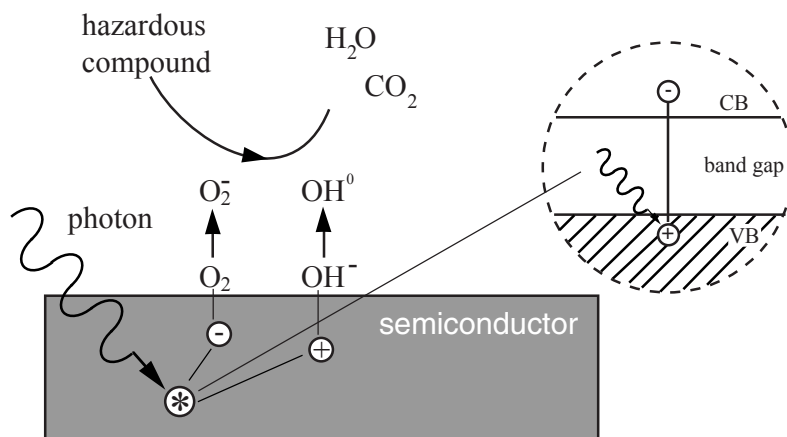


Figure 4.1: Schematic picture of the PCO process

(see [89] and [90], and references therein), but also because TiO_2 is cheap, non-toxic, an abundant product, and it has a high chemical stability. On the other hand, using TiO_2 as a photocatalyst implies that a large part of the solar spectra cannot be used because of the large TiO_2 band gap (3.1 eV). This is a serious disadvantage. As sunlight comprises only a few per cent of ultraviolet light, expensive light sources must often be employed to activate TiO_2 for photocatalysis to occur. In this regard the use of narrower band gap semiconductors would be more favorable from the point of view of effective utilization of solar energy. However, this situation can be improved, for instance, by using vanadium-doped TiO_2 [91], which extends the wavelength range of the TiO_2 catalyst into the visible region.

Normally PCO is carried out using colloidal or particulate TiO_2 suspensions. Although these catalysts have high photodegradation efficiency for organic compounds, separation of the catalysts from the system after the reaction is sometimes difficult. In this context, TiO_2 films have recently gained much attention as useful photocatalysts [92]. Another problem with oxide powders is that they are strong light scatterers, which creates dark regions in which photocatalytic oxidation cannot occur. Light-guiding materials (used to reduce the areas of shadow) coated with TiO_2 thin films have recently been shown to achieve high kill-rates of bacteria relevant to hygiene (such as *Escherichia coli* and some others) [93]. Such materials may therefore be interesting to disinfect surfaces in microbiological laboratories and areas in intensive medical use. Thus, the study of photodecomposition of organic compounds on TiO_2 surfaces is of real practical interest.

Moreover, even though the basic principles of photocatalytic oxidation are known, some important issues regarding the reactive sites, the reaction intermediate species, the role of these species in the PCO process, and the detailed mechanism remain unsettled. A thorough understanding of the photocatalytic process is necessary for the development and design of highly reactive photocatalysts. In this regard, single-crystal surfaces can provide the possibility to study a well-ordered structure with known surface area and controlled surface coverages of the reactant molecules and the surface reactive sites.

The reaction of formic³ acid (HCOOH), also called methanoic acid, over TiO₂ surfaces is a model system suitable for studying heterogeneous photocatalytic oxidation of harmful organic compounds. Although formic acid itself is not listed as a priority hazardous compound (nor by the European Environment Agency [94], neither by the U.S. Environmental Protection Agency [95]), it is often used as a test molecule for new photocatalysts, mainly because it is an intermediate product in the decomposition of more harmful organic compounds. Moreover, formic acid serves as a useful model compound for studies of photocatalytic efficiency because it has a simple molecular structure, it is readily susceptible to photodegradation, and there are very limited possibilities for the formation of intermediates during its decomposition. Besides all this, the possibility offered by titania surfaces to create surface defect point sites (which play an active role in the PCO process [96]) in a controlled way under UHV conditions, makes them good model systems for the study of photocatalytic oxidation processes.

Experimental and theoretical efforts have been undertaken to understand the chemistry of formic acid on TiO₂ surfaces [97–120], but there are still some important questions that remain unresolved. It is known that formic acid dissociates on the TiO₂(110) surface [99]. The dissociation products, formate (HCOO⁻) and a proton (H⁺) are adsorbed on the surface. The proton is thought to be bonded to an oxygen atom of the substrate to form a hydroxyl group. Nevertheless, there is only limited explicit experimental evidence of the presence of these OH species [102,111]. Moreover, there is a lack of consensus regarding the presence of various formate species differently bonded to the TiO₂(110) surface [109,115,118]. Furthermore, different reaction paths have been postulated for the decomposition of formic acid over the TiO₂(110) surface [99,102]. This could be related to differences in the initial adsorption stages of the various studies. An accurate determination of the adsorption structure of the formic acid dissociation products on the (110) titania surface might help to understand the fundamental mechanism which formic acid undergoes when it decomposes on the titania surface.

Our aim was to determine quantitatively the structural geometry of formic acid upon adsorption on a TiO₂(110)-(1x1) surface. We wanted also to see if more than one formate species adsorbs on the surface, and if possible to elucidate the location of the H⁺ unit from the carboxylic group of the formic acid. In order to do this, we have applied the photoelectron diffraction technique. We want to stress that compared with the large number of quantitative structural determinations of adsorbates on metals and non-oxide semiconductors, there are very few such studies of adsorbates on oxide surfaces. Usually it is more difficult to handle oxide surfaces than their metal counterparts. In many cases, the preparation of clean metal oxide surfaces in a reproducible and reliable way is an arduous task. Moreover, there is a lack of structural data for clean metal oxide surfaces, which is an impediment for the quantitative structural determination of adsorbates on these surfaces. One problem is the difficulty in applying many of the relevant experimental techniques. The insulating nature of most metal oxides hinders the application of experi-

³From the Latin word for ant, *formica*. Formic acid is a defense fluid of some ant species

mental techniques that involve the use of charged particles (due to charging problems). Furthermore, the use of X-ray diffraction techniques has not yet been widely exploited, due mainly to the weak scattering nature of the O atoms. An additional problem is the degradation of the oxide surfaces during measurement due to radiation damage, in particular for molecular adsorbate covered surfaces.

4.1 The rutile $\text{TiO}_2(110)$ surface

Two different crystal structures of TiO_2 are commonly used in photocatalysis: *rutile* and *anatase* (titania naturally occurs also in a third crystal structure named *brookite*). While rutile crystals are readily available, anatase crystals are more difficult to obtain. The reason is that anatase is a metastable phase; it transforms into rutile at temperatures between 780-1180 K, depending on the sample preparation conditions. Fig. 4.2.a shows the tetragonal bulk unit cell of rutile TiO_2 , which contains two molecules of titanium dioxide. Each Ti^{4+} cation is completely coordinated with six O^{2-} anions in an octahedral configuration. This octahedron is not regular, showing a slight orthorhombic distortion, with the distances of the titanium and the oxygen ions at the apexes of the octahedron (those labelled in the figure with the numbers 3 and 6) being slightly longer. All O^{2-} anions are three-fold coordinated.

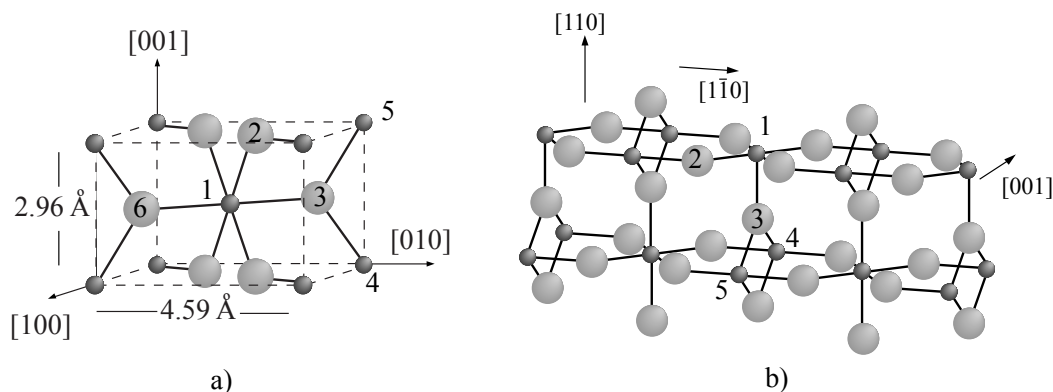


Figure 4.2: a) Unit cell of bulk rutile TiO_2 ; b) Bulk terminated rutile $\text{TiO}_2(110)-(1 \times 1)$ surface

Rutile TiO_2 surfaces have been widely studied in surface science because many of the problems commonly associated with oxides can be solved in this case. First, there are standard procedures to prepare the TiO_2 surfaces under UHV conditions in a reproducible way. Second, the charging problem can be overcome by increasing the electrical conductivity via reduction of the bulk through thermal treatment (i.e. creating bulk oxygen vacancies by annealing). Among the titania surfaces, the (110) surface is the most extensively investigated rutile surface. This is mainly because it is the most stable of the low-index faces. Other low index faces of rutile titania reconstruct upon heating to temperatures below 1000 K (the (001) and the (100) surface reconstruct through faceting at 750 K and 900 K respectively [121]), but the (110) rutile face is stable up to temperatures

around 1200 K. At this temperature the LEED pattern of the (110) surface changes from (1x1) to (1x2) (several models have been suggested for the (1x2) reconstruction, but we will not discuss them here⁴).

Imaginary cleaving⁵ of the TiO_2 rutile crystal along the (110) plane can result in three different surface terminations. In Fig. 4.2.b we show the only termination that complies the requirements of the Tasker's [123] and LaFemina's [124] approaches for the creation of a stable oxide surface. That is, the $\text{TiO}_2(110)$ -(1x1) surface shown in Fig. 4.2.b is non-polar [123] and fulfils the autocompensation criterion [124]. According to Tasker's concept, the dipole moment of a repeat unit perpendicular to the surface must be zero. If we take into account the unit consisting of the three outermost layers in Fig. 4.2.b, and consider that titanium and oxygen atoms have formal charges of 4+ and 2-, then the total dipole moment of this unit is zero. The termination of the $\text{TiO}_2(110)$ -(1x1) surface is also believed to be autocompensated by a charge transfer from the cation dangling bonds to the anion dangling bonds, both oriented perpendicular to the surface. As a result, the titanium dangling bonds will be completely empty, whereas the oxygen dangling bonds will be completely full. A striking characteristic of this surface is that it is not flat. Rows of 'bridging' O atoms, which are two-fold coordinated, lie above the main surface plane along the [001] direction. These bridging-O atoms can be removed by annealing in UHV. This creates surface oxygen vacancies that are very important for the reactivity of the surface. The main surface plane contains equal numbers of six- and five-fold coordinated Ti atoms arranged in alternating rows parallel to the [001] direction. The believe that the five-fold coordinated Ti atoms have one empty dangling bond perpendicular to the surface, makes them the most probable adsorption site in the absence of surface oxygen vacancies.

Experimental [125–129] and theoretical [131–136] studies indicate that the $\text{TiO}_2(110)$ -(1x1) surface is relaxed with respect to the bulk-truncated termination. Table 4.1 lists the results of some of these studies regarding the relaxations in atomic positions of the outermost layers (those that appear labelled in Fig. 4.3)

Although the actual values of the relaxations differ from one study to another, the majority of the studies are in agreement as to the direction in which these relaxations occur. Most of the atoms relax along the direction perpendicular to the surface. The bridging O atoms and the five-fold coordinated Ti atoms relax inwards, while the in-plane O atoms and the six-fold coordinated Ti atoms are displaced outwards. Only the oxygen atoms in the main plane move laterally towards the position occupied by the five-fold coordinated Ti atoms. According to the SXR D study the largest displacement is the one suffered by the bridging O atoms, which move inwards by 0.27 Å. This surprising result implies a reduction of the Ti(1)-O(1) bond length of almost 12% compared to the same bond length in the bulk-terminated surface (1.71 Å instead of 1.94 Å in the bulk). XPD [128] and ICISS (impact-collision ion-scattering spectroscopy) experiments [125, 127] found compa-

⁴For a description of the (1x2) different model structures see chapter 11 of reference [122] and references therein

⁵Although cleavage in the mineral form occurs preferentially along (110), it is not of high quality

Displacements	SXRD	FP-LAPW	LCAO	PW-PP-GGA	FP-LAPW
$\delta_{[110]}$ Ti(1)	0.12 ± 0.05	0.08	0.23	0.09	-0.05
$\delta_{[110]}$ Ti(2)	-0.16 ± 0.05	-0.23	-0.17	-0.12	-0.18
$\delta_{[110]}$ O(3)	-0.27 ± 0.08	-0.16	-0.02	-0.09	-0.16
$\delta_{[110]}$ O(4)	0.05 ± 0.05	0.09	0.03	0.11	-0.12
$\delta_{[1\bar{1}0]}$ O(4)	0.16 ± 0.08	0.06	0.05	0.05	0.07
$\delta_{[110]}$ O(5)	0.03 ± 0.08	-0.09	0.02	-0.05	-
$\delta_{[110]}$ O(6)	0.00 ± 0.08	-0.05	0.00	-	-

Table 4.1: Surface atomic relaxations (in Å) determined for the $\text{TiO}_2(110)-(1 \times 1)$ surface by SXRD (Surface X-ray Diffraction) [126], FP-LAPW (full-potential linear augmented plane wave) [131,134], LCAO(linear combination of atomic orbitals) [134]and PW-PP-GG(plane-wave pseudo potential generalised gradient approximation) [133]

rable values for the displacement of the bridging-O atoms relative to their position in the bulk-terminated (110) surface. Another ICISS experiment [129] gave a value for the layer spacing of the bridging-O atoms comparable to that of the bulk-truncated structure. A more recent LEED experiment (Lindsay et al., private communication [130]), gives a value for this particular relaxation which is closer to that given by the theoretical calculations. All the theoretical studies found a much smaller displacement for the bridging-O atoms. Notice that all the theoretical results correspond to zero temperature. Thus, strong anharmonic thermal vibrations of the titania surface atoms could account for the discrepancy between the theoretical simulations and many of the experimental results.

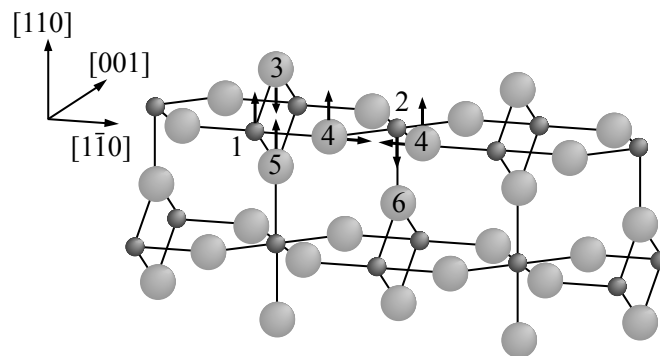


Figure 4.3: Direction of the surface atomic relaxations observed by SXRD [126]

4.1.1 Oxygen vacancies

The most important defects present in TiO_2 crystals are bulk and surface oxygen vacancies. Bulk oxygen vacancies can be created by annealing the titania crystals to temperatures above 880 K. These defects produce a remarkable modification of the colour and the conductivity of titania crystals. The colour changes from the initially pale yellow, transparent to light, to a blue colour, the darkness of which increases with the number of bulk oxygen vacancies created. This colour variation is due to the creation of the so called *colour centres*. When a negative ion vacancy is created in an ionic crystal, an electron may be localised in the vicinity of such a point defect. This electron can be considered to be bound to a positively charged centre, and therefore, it can have a series of quantified energy levels. Excitations between these levels produce optical absorption lines. Thus, the creation of colour centres in a crystal confers an intense colour to the otherwise transparent crystal. The presence of these oxygen vacancies also results in n-type doping. This lowers the resistivity of titania by more than one order of magnitude [137], leading to high conductivity. It is this characteristic that makes TiO_2 single crystals such a suitable system for surface science experimentalists, since it allows the application of surface sensitive techniques that involve the use of charged particles.

Surface oxygen vacancies (see Fig. 4.4) are known to enhance the reactivity of the $\text{TiO}_2(110)$ surface (e.g. they are responsible for water dissociation into hydroxyl groups at room temperature [138]). Surface oxygen vacancies can be created in a controlled way under UHV conditions. Among the various techniques to produce surface defects in rutile titania (110) surfaces, thermal annealing in vacuum has been shown to produce the lowest amount of defects with very little structural damage to the surface. Moreover, surface defects created by UHV annealing are all of Ti^{3+} type, that is, their presence can be seen in the Ti $2p$ and Ti $3p$ core level photoemission spectra as a shoulder at lower binding energies than the main Ti^{4+} peak. It is assumed that these Ti^{3+} -like defects are due to the removal of oxygen atoms of the bridging rows. When a bridging O atom is removed, formally two electrons should remain in the vacancy site (in order to maintain charge neutrality). The first empty orbital on neighbouring O anions which is accessible for these electrons is the $3s$, which has an energy that is several eV higher than their original energy. However, the $3d$ orbitals on the two adjacent Ti atoms are empty, and the energy cost of placing one (or more) electrons in them is not high. Thus, surface oxygen vacancies are considered to be point defects that consists of two Ti^{3+} ions having a $3d^1$ electronic configuration. This is shown by the appearance in photoemission of a small peak at approximately 0.7-0.9 eV below the Fermi energy, which indicates the population of the $3d$ orbitals. Notice that the bulk oxygen vacancies have also a Ti^{3+} character. Therefore, in order to use XPS to quantify the percentage of oxygen vacancies present at the surface grazing emission geometries are needed. Surface point defects can be observed by other experimental techniques apart from photoemission. In electron energy loss spectroscopy they appear as a peak at 0.75 eV [139,140]. In LEED their presence can be seen as a slight broadening of the (1x1) spots along the [001] direction. AFM visualises surface oxygen

vacancies as black points on the bright lines associated with bridging oxygen rows [141]. In STM, contrast is dominated by electronic rather than geometric effects. Due to this, rows of five-fold coordinated Ti atoms are reported to be imaged as bright rows, while bridging-O rows (which protrude from the main surface plane) are considered to appear in the STM image as dark rows. Oxygen vacancies are believed to be imaged by STM as bright spots between five-fold coordinated Ti rows. Notice that hydroxyl groups are also visualised as bright spots between five-fold coordinated atoms, but their apparent height and their extent in the [001] direction are different from those associated with oxygen vacancies [138].

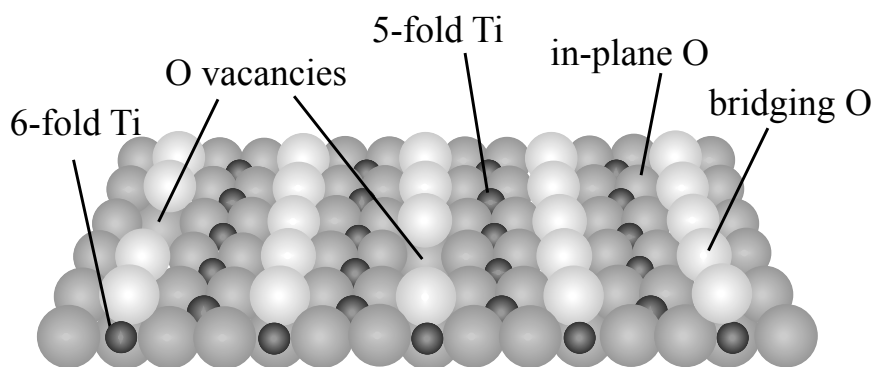


Figure 4.4: Schematic of the rutile $\text{TiO}_2(110)-(1 \times 1)$ surface including some bridging oxygen vacancies

Electron bombardment creates defects that are limited to the outermost TiO_2 surface layer. These defects are due to desorption of bridging-O atoms induced by electronic transitions. When electron-beam exposure creates a hole in the Ti $3p$ core level, one (or two) electrons from the O $2p$ band can decay to the Ti $3p$ level. If two of these electrons are involved in filling the Ti $3p$ hole through an interatomic Auger process, the original oxygen anion (O^{2-}) becomes an oxygen cation (O^+) which is subject to a high Coulomb repulsion force due to the neighbouring Ti^{4+} cations, and is ejected into vacuum. This is known as the *Knotek-Feibelman* mechanism [142]. Electron-stimulated defects also show exclusively Ti^{3+} character in photoemission [143]. However, they behave differently than those created by annealing [144]. This difference may be caused by more complicated structures associated with electron-stimulated defects [145].

Argon ion bombardment produces much higher quantities of defects with mixed Ti oxidation states (Ti^{+3} , Ti^{+2} , Ti^{+1} and even Ti^{+0}). Such sputter-damaged surfaces are topographically complex, involving much structural damage to the surface and the near-surface region.

4.1.2 Experimental recipe for the preparation of nearly defect-free TiO₂(110) surfaces

As discussed above, the two standard experimental methods to prepare clean and well-ordered surfaces under UHV conditions (i.e. annealing and sputtering) both cause defects on the TiO₂ surfaces. Since these defects have been proved to play a very important role in the reactivity of titania surfaces, one must proceed carefully in order to obtain nearly defect-free TiO₂(110)-(1x1) surfaces. For the TiO₂ surface to be conductive, it must be annealed at temperatures around 900 K for long periods (1 hour). In order to reduce surface damage during sputtering of the surface and to avoid Ar incorporation into it, it is preferable to use brief sputtering (~10 min) with low energetic Ar ions (~500 eV). Preferential sputtering has been reported for these surfaces; thus, the angle of the Ar⁺ beam with respect to the surface must be changed often. After brief sputtering, the restoration of the surface can be achieved by moderately long annealing (i.e. 30 min) at high temperatures around 1000 K. Several cycles of sputtering and annealing as described above are recommended to obtain a clean, well-ordered and nearly defect-free TiO₂(110)-(1x1) surface.

One commonly-used way to reduce the number of oxygen vacancies present in titania surfaces is to anneal in the presence of an oxygen atmosphere. However, during this procedure O₂ may dissociate at vacancies forming O radicals which are very reactive [146]. Moreover, if the O₂ gas is not entirely free of water, the later will readily adsorb on the surface. The use of dark blue crystals is not recommended, since their annealing in oxygen results in the formation of complex surface morphologies.

4.2 Previous studies on the HCOOH/TiO₂(110) system

Formic acid selectively decomposes on oxide surfaces. On acidic oxides it decomposes via dehydration to produce H₂O and CO, whereas on basic oxides it does so via dehydrogenation producing H₂ and CO₂. Indeed, the selectivity of its decomposition has been used to scale the acid-base character of oxides. However, in the case of the TiO₂(110) surface, Onishi and coworkers [98,99] have observed a switchover of reaction paths as a function of the substrate temperature. At temperatures below 650 K the dehydrogenation process dominates, while above this temperature dehydration is preferred. Nevertheless, a later study by Henderson [102] suggests that formic acid decomposition on a TiO₂ surface involves a more complex set of chemical reactions that cannot adequately be described in terms of simple dehydration or/and dehydrogenation mechanisms. These complex processes involve the creation of oxygen vacancies by the reaction of the acid proton with lattice oxygen atoms to form water and the creation of some minor intermediate products such as formaldehyde (HCHO). This controversy might be due to differences in the starting structure of titania, which can influence the adsorption process. Indeed, the question

regarding how many formate units bond at different adsorption sites on the $\text{TiO}_2(110)$ surface is still under debate.

It is well known that the adsorption at room temperature of formic acid on a stoichiometric $\text{TiO}_2(110)-(1\times 1)$ surface leads to a (2×1) overlayer [97] at an approximate saturation coverage of 0.5 ML [99]. UPS [99], HREELS [102, 107, 111] and RAIRS [109] measurements are all consistent with the formic acid molecule losing the H atom of its carboxylic group upon adsorption. Thus, at room temperature, HCOOH dissociates on $\text{TiO}_2(110)$ into formate (HCOO^-) and a proton (H^+). The proton is thought to remain at the surface after formic acid decomposition, possibly bonded to an O atom of the substrate, creating an hydroxyl group (OH^-). HREELS measurements by Henderson [102] showed a weak loss that could be due to an O-H stretching mode associated with the presence of a surface hydroxyl group, but its weak intensity precludes a definite assignment. Improved HREELS experiments [111] assigned a feature appearing in the 3000 cm^{-1} region to the presence of an hydroxyl group adsorbed on the surface. XPS does not distinguish between OH^- and HCOO^- , since the O 1s emission associated with a hydroxyl group adsorbed on $\text{TiO}_2(110)$ appears to lie at essentially the same energy as that of the formate (the energy shifts from the substrate oxygen are 1.6 eV for hydroxyl groups [144] and 1.7 eV for formate [104], both towards higher binding energy). No features attributable to the presence of hydroxyl groups have been observed by means of STM [100, 101, 118]. However, recent *ab initio* density functional calculations have shown that coadsorption of H stabilises the (2×1) geometry [112, 113].

It is widely accepted that the formate units are bonded in a bidentate fashion to two 5-fold coordinated Ti atoms on the surface, with the molecular axis perpendicular to the surface (formate A in Fig. 4.5). STM [100, 118] experiments and a number of theoretical studies [106, 112, 113] are consistent with this view. XPD data from the O 1s and C 1s core levels [104] showed that the axis of the molecule is aligned along the [001] azimuth and that is perpendicular to the surface, with an estimated OCO bond angle of $126 \pm 4^\circ$, a value close to that of the formic acid molecule in the gas phase. Bearing this result in mind, the O atoms of the formate should be offset from the true atop sites above the five-fold coordinated Ti atoms along the [001] azimuth, since the Ti-Ti distance along the [001] Ti rows (2.96 \AA) is larger than the O-O distance by approximately 0.68 \AA . A PhD experiment [105] led to the claim that the molecule is indeed bidentate with the two O atoms slightly off-top two five-fold coordinated Ti atoms and with a layer spacing between oxygen atoms of the formate species and the surface Ti cations of $2.1 \pm 0.1\text{ \AA}$. However, this study has serious deficiencies. First, it is based in a single PhD spectrum. We have discussed already in this thesis (see section 3.1, page 37) the problem of the appearance of multiple local minima in fitting experimental PhD spectra. We concluded that in order to avoid the possibility of fitting to an incorrect local minimum, a large data set of PhD spectra recorded at different emission geometries is necessary. Second, it has to be stressed that the raw data of this study are extremely noisy with no clear modulation. The authors needed to apply a four-point smoothing of the data to obtain the modulation function used in the analysis. Moreover, the analysis of this single smoothed

modulation function involved only a refinement of a structure obtained using Hartree-Fock calculations. In this optimisation the only structural parameter which seems to have been varied is the distance along the $[110]$ direction from the molecule to the main Ti-O plane of the $\text{TiO}_2(110)$ surface. Moreover, the amplitude of the theoretical modulations is bigger than the experimental one by more than a factor of five. Finally, this PhD study is based on the wrong assumption that the signal that appears in the O 1s photoemission spectrum at around 1.7 eV relative to the oxide component upon exposure to formic acid is uniquely due to the presence of formate species. As already mentioned, the O 1s chemical shift of formate on $\text{TiO}_2(110)$ is essentially identical to that of OH on this surface [144], so if the surface has coexisting formate and hydroxyl species, the O 1s PhD data will comprise an incoherent sum of the signals from these two species and must be analysed accordingly.

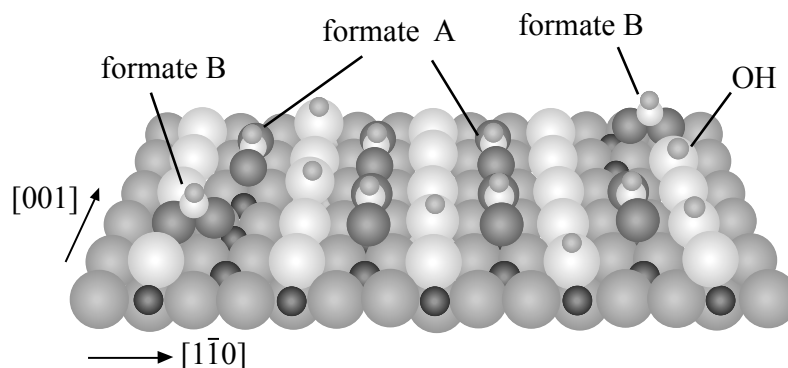


Figure 4.5: Possible products of the reaction of HCOOH over a $\text{TiO}_2(110)$ - (1×1) surface

A RAIRS study by Hayden et al. [109] is consistent with the presence of a majority species having this same azimuthal orientation, but it also indicates the existence of a second formate species (suggested to be formate B in Fig. 4.5), which is aligned perpendicular to the $[001]$ direction. The formation of this minority species (around 33% of the total coverage) appears to be connected with the density of surface O vacancies, which may be created in part by the dissociative adsorption of formic acid. C K-edge NEXAFS data [115] are also in agreement with the presence of a second formate species with this perpendicular azimuthal alignment formate species in the same relative proportion as in Hayden's work. However, Bowker et al. [118] have recently questioned these conclusions. In an STM study, they observed some features that they suggest could be ascribed to the presence of a formate species adsorbed in a different site than the majority species. Although this may be the second species implicated by the RAIRS and NEXAFS studies, Bowker et al. showed that this feature can account for only a 1% of the total number of formate species adsorbed on the surface. The large difference between Bowker's finding and the much higher coverage of a second formate species proposed by the RAIRS and NEXAFS measurements may be related to differences between the initial titania surfaces used in these studies. We should also note the larger formic acid exposures used in the RAIRS (650 L) and NEXAFS (100 L) experiments in comparison to the lower exposures we (and others, e.g. [99,118]) needed to obtain the (2×1) LEED pattern that corresponded

to the saturated phase. Bowker et al. suggest that these large dosages could possibly lead to higher coverages of formate through some lower rate adsorption process.

The main goal of the present study was to determine the adsorption structure geometry of formate adsorbed on a nearly defect-free $\text{TiO}_2(110)-(1 \times 1)$ surface, and see if we could detect any evidence for the presence of a second formate species adsorbed on the surface. Since the proton is believed to be bonded to an O atom of the substrate, and the emission from the O 1s core level of OH on $\text{TiO}_2(110)-(1 \times 1)$ appears at a binding energy in the same energy region of that of the formate, we also wanted to see if it would be possible to determine the exact adsorption site for the H atom by studying the PhD modulations of the O 1s core level peak.

4.3 Description of the experiment

The $\text{TiO}_2(110)$ crystals were provided by the firma PI-KEM. The crystal was first annealed in UHV at a temperature of 1000 K for 1 hour. This yielded a crystal with a light blue colour, which provides an indication of the concentration of bulk oxygen vacancies and the associated colour centres and defines the sample conductivity. The surface was then cleaned by several cycles of gentle Ar^+ ion bombardment (500 eV, 15 mins) followed by annealing of the substrate at temperatures between 900-1000 K for periods of 30 minutes. After this preparation, LEED showed a sharp (1×1) pattern and the Ti 2p photoemission spectrum (see Fig. 4.6) was essentially without any trace of the high kinetic energy shoulder which is believed to be associated with the presence of surface oxygen vacancies.

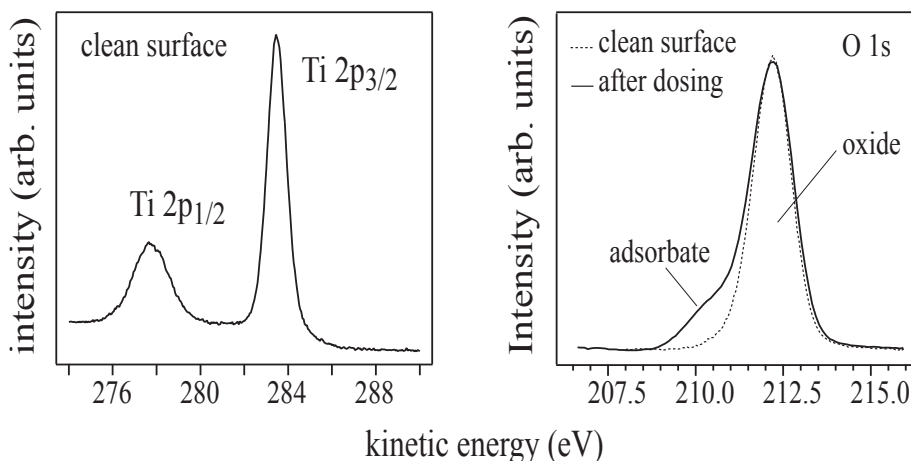


Figure 4.6: Ti 2p core level photoemission spectrum from a clean nearly defect-free $\text{TiO}_2(110)-(1 \times 1)$ surface; O 1s photoemission spectrum before and after HCOOH exposure. Both spectra are measured at a photon energy of 750 eV

These two fingerprints have been associated with the obtention of a nearly defect-free $\text{TiO}_2(110)-(1\times 1)$ surface. Formic acid from the firm Aldrich-Sigma of purity 98% was further purified by several freeze-pump-thaw cycles before exposure. Afterwards, the purity of the formic acid gas was checked using a mass spectrometer. The $\text{TiO}_2(110)-(1\times 1)$ surface was then exposed to typically $10\text{-}50 \times 10^{-6}$ mbar s of formic acid at a substrate temperature of 300 K. This led to the formation of the expected (2×1) LEED pattern. A characteristic O 1s photoemission spectrum after exposure to 10×10^{-6} mbar s of HCOOH at room temperature is shown in the right panel of Fig. 4.6 and compared with the O 1s photoemission spectrum from the clean surface. The O 1s spectra are normalised to the intensity value of the oxide component.

PhD measurements were performed at the undulator beam line UE56/2 at BESSY II. These measurements were made in a partial pressure of formic acid of 3×10^{-9} mbar to minimise the effect of photon-induced desorption.

4.4 Adsorption structure

Fig. 4.7 shows the O 1s and C 1s PhD spectra measured from the (2×1) surface phase created after the room temperature exposure of the $\text{TiO}_2(110)-(1\times 1)$ surface to formic acid. Bearing in mind that the formate ion is generally supposed to bond through the O atoms, the weak modulation amplitudes (mainly $\pm 20\%$ or even less) observed in our data for the O 1s PhD spectra would imply a lack of a single high-symmetry adsorption site. The C 1s PhD spectra show very weak modulations ($\pm 10\%$ or less) in most emission geometries. The strongest modulations, with a very long period, are observed at high off-normal geometries in $[001]$, in particular at 60° polar emission angle. Long period modulations are characteristic of backscattering from scatterers close to the emitter, which in this case are probably the two oxygen atoms within the formate species. This is in agreement with the widely accepted adsorption geometry in which the formate molecular plane is oriented perpendicular to the surface along $[001]$. The weaker, shorter period modulations that appear at close to normal emission are probably due to scattering from the more distant substrate atoms. The absence of significant modulations along the orthogonal azimuth suggests that the great majority of the adsorbed formate species are aligned in the $[001]$ azimuth.

Our standard ‘projection method’ to obtain a semi-quantitative estimate of the adsorption site is designed to be applicable only to elemental substrates, for which all scatterers are assumed to have the same scattering phase shifts. Moreover, the method has shown to be less successful in situations with low symmetry adsorption sites or multiple site occupations, as may be the case here. Therefore, the present analysis is entirely based on the use of trial-and-error modelling, simulating the experimental data with multiple scattering calculations for different trial structures.

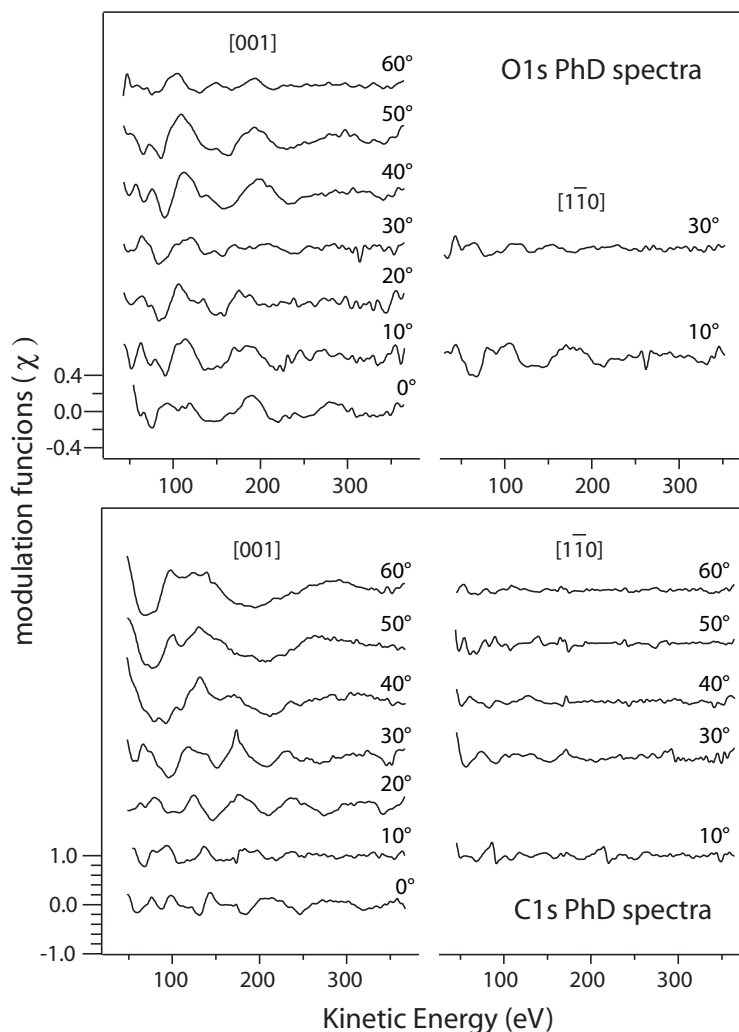


Figure 4.7: O 1s and C 1s PhD spectra measured from the (2x1) surface phase created after the room temperature exposure of the $\text{TiO}_2(110)-(1 \times 1)$ surface to formic acid

A key starting point in the analysis of the PhD data is, of course, the structure of the $\text{TiO}_2(110)$ surface on which the adsorption occurs. As discussed in section 4.1, for the (1x1) clean surface there is a clear consensus that the surface is terminated as shown in Fig. 4.2 in such a way as to be both non-polar and ‘auto-compensated’ in the dangling bond charges. As already mentioned, the most detailed experimental structure determination of this surface, using surface X-ray diffraction (SXRD) [126], reveals some local relaxations of the positions of the atoms in the outermost layers, mainly perpendicular to the surface, as do the several theoretical total energy calculations for this structure. However, we may expect these relaxations to be modified by the presence of the adsorbate and we have therefore conducted some optimisation of these parameters in our structure determination. Nevertheless, since the PhD technique is most sensitive to the location of near neighbours to the emitter atoms, the initial stages of the structure determination concentrated on adjusting the position of the adsorbate atoms on a rigid substrate chosen

either to be an ideal bulk termination or the clean surface structure given by the SXRD study. Because the formate species is expected to be bonded to the surface through the O atom(s), which will therefore be closer to the substrate atoms and capable of showing a stronger dependence of their PhD modulations on the adsorption geometry, the initial stages of structure determination focussed on the O 1s PhD spectra alone.

The first model we explored was based on the assumption that the adsorbate O 1s PhD arises entirely from the O atoms in the single adsorbed formate species A shown in Fig. 4.5. This is the geometry favoured by the earlier PhD work and the theoretical studies, and it corresponds to the model widely accepted in the related literature. We explored not only the species A geometry of Fig. 4.5, but also the possibility that the molecule is not symmetrically bonded to two adjacent Ti atoms, but may have one of the O atoms more nearly atop one Ti atom. We also tested a model with the formate placed atop a 5-fold coordinated surface Ti atom in a bidentate fashion. These initial explorations clearly shows a preference for the species A geometry. Notice that the Ti-Ti distance along [001] (2.96 Å) is significantly larger than the O-O distance in an undistorted formate ion (2.21 Å), so some offset of the O atoms from truly atop the Ti atoms is inevitable.

The results of this optimisation of the species A adsorption geometry alone are shown in Fig. 4.8 in which the experimental PhD modulation spectra are compared with these best-fit theoretical simulations. The primary structural parameters for this place the O atom 2.02 Å above the Ti atoms and offset from a true atop site by 0.34 Å (along the [001]), with the C atom 0.52 Å further above the surface than the O atoms. Clearly this geometry is very similar to that found in the earlier, far more limited, PhD study. However, unlike this earlier investigation, our simulations reproduce quite well the amplitude of the PhD modulations using reasonable mean-square vibrational amplitudes (0.0049 Å² for the substrate atoms, 0.0066 Å² for the O emitters perpendicular to the surface and along [001], but an enhanced value of 0.066 Å² along [110]). However, as can be clearly seen from Fig. 4.8, the overall fit is not very good. This disagreement between experimental and simulated PhD spectra is also reflected in the R-factor value of 0.47. For systems showing strong PhD modulations R-factor values in the range 0.1-0.2 can generally be achieved, while even in the case of the relatively weak modulations seen here, a value of around 0.3 or less would be expectable for a correct structure. Although the fits are reasonably good near normal emission, they are poor at larger polar angles. A near-top adsorption geometry for the O emitter atoms, such as the one associated with the formate species A, is expected to give dominant modulations due to the nearest-neighbour backscattering at near-normal emission angles. However, the experimental data show even larger modulations around 40-50° in the [001] azimuth which are not expected, or found, for this near-atop scattering geometry. This indicates the presence of a second surface species having an O emitter with a different local geometry from that of formate A. Notice that the bridging O atoms of the TiO₂(110) surface have nearest-neighbour Ti atoms in the layer below that are in the directions expected to give strong backscattering at approximately this geometry. This observation suggests that the second adsorbed species may have a chemically-shifted O emitter atom occupying O bridging sites.

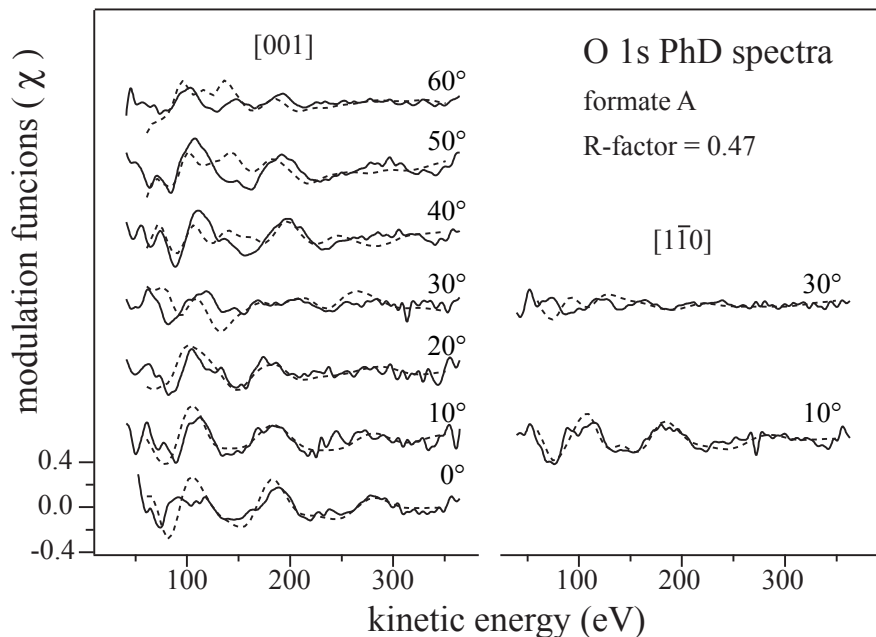


Figure 4.8: Comparison of the experimental O 1s PhD modulation spectra (full lines) from the formate-covered $\text{TiO}_2(110)-(2 \times 1)$ surface with the results of the best-fit theoretical calculations (dashed lines) for a model assuming the formate A geometry only

One possibility is that one O atom of a different formate species (species B in Fig. 4.5) occupies an oxygen vacancy in this bridging site. Notice that this second formate species is azimuthally rotated by 90° relative to species A, and so could account for the RAIRS and NEXAFS results mentioned earlier. The other possibility is that this additional O emitter is a bridging oxygen atom which has become part of a hydroxyl species as a result of the reaction with a H atom from the formic acid dissociation.

We concentrated first on the possibility that the chemically-shift O 1s signal arises from formate species alone. We have optimised a model based on a mixture of A and B formate species only, assuming an occupancy ratio of 2:1, as preferred by the RAIRS and NEXAFS results. The results of the full optimisation of this model (including surface atomic relaxations) are shown in Fig. 4.9.a. Clearly the resulting fit is much improved, particularly for the larger polar emission angles in $[001]$, consistent with our expectation. This visual improvement is also reflected in a much reduced R-factor value of 0.24. However, this optimisation involves a very significant distortion of the conformation of the B formate species (see Fig. 4.9.b), with unphysical values for the C-O distance ($d_{\text{C-O}_I} = 2.5 \text{ \AA}$), which casts doubt on the validity of this solution. Of course, the B geometry implies that the two C-O bonds are now inequivalent, since the formate is bonded to the surface via only one of the O atoms. Nevertheless, the distortion is several tenths of an Ångstrom larger than might be expected for such geometry. If we constrain the geometry of the formate B species to reasonable interatomic distances, the fit to the experimental data is significantly worse.

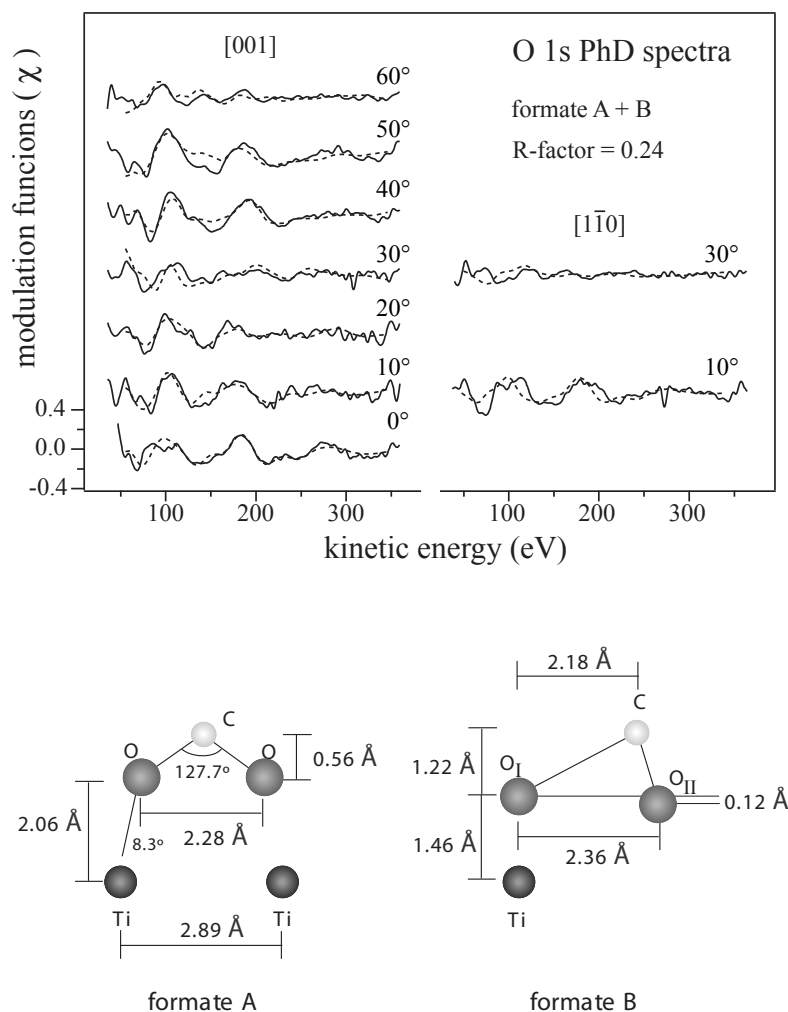


Figure 4.9: a) Comparison of the experimental O 1s PhD spectra from the formate-covered $\text{TiO}_2(110)(2 \times 1)$ surface (full lines) with the results of the best-fit theoretical calculations for a model with co-occupation of the formate A and formate B geometries in a 2:1 ratio (dashed lines). b) Schematic diagrams showing the local structural geometries of formate A and formate B species corresponding to this optimisation

The simulations for the alternative structural model in which one assumes that the chemically-shifted O 1s PhD arises from a mixture of coexistent A formate species and OH species (with the O in the bridging sites) leads to an even lower R-factor of 0.20 and a further improvement in the visual appearance of the fit, as can be seen in Fig. 4.10. Notice that in this model we have assumed that there is one OH species per formate species, thus consistent with the stoichiometry of the original formic acid with both dissociation products remaining on the surface.

The results regarding the photoelectron diffraction modulations shown by the O 1s core level therefore favour the role of a coexistent OH species over a large component of a second formate species. The superiority of this model over that formerly explored in which two differently adsorbed formate species are present on the surface may be presumably

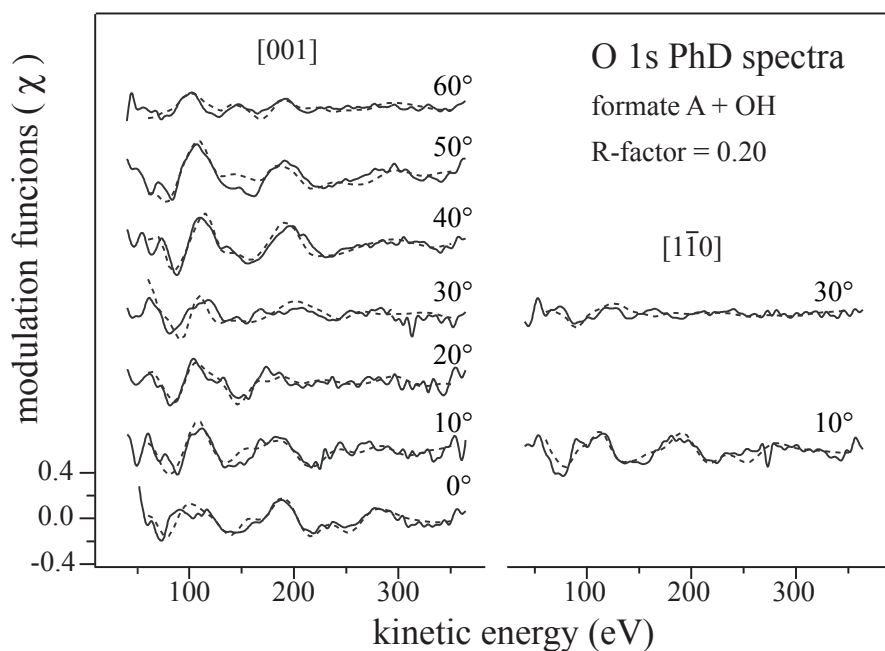


Figure 4.10: Comparison of the experimental O 1s PhD modulation spectra (full lines) from the formate-covered $\text{TiO}_2(110)(2 \times 1)$ surface with the results of the best-fit theoretical calculations (dashed lines) for a model assuming co-occupation of the formate A and OH in the ratio 1:1

related with the fact that the second O atom in the formate B species does not occupy either of the favoured geometries. We have not considered, however, the possibility of including both formate B and OH species in addition to the formate A geometry. In this case, the non-bonding O atom of the formate B species corresponds to a substantially smaller fraction of the O emitters than in the model comprising only formate A and formate B. Taking a model including 2/3 of the formate species on the A site with an equal number of OH species, together with 1/3 of the formate in B sites but with no corresponding OH, we obtained a fit which is only slightly worse than that obtained for the formate A plus OH model, with a lowest R-factor of 0.21 (data not shown). In this model, the formate B species is far less significantly distorted than in the case shown in Fig. 4.9.b. Notice that in this simulation we have not included OH species associated with the adsorption of the formate B species. Indeed, it is not really clear what associated OH species occupation is to be expected with this second formate species. If we assume that formate B results from interaction with an oxygen surface vacancy, it would be reasonable to think that each formate B should also generate a bridging OH. However, the higher occupation proposed in the literature for this species (slightly more than 30%) is far higher than that typical of the oxygen surface vacancy occupation of a (1×1) clean surface (which is generally thought to be only of a few per cent). Therefore, such a large concentration would imply the existence of a mechanism for creating oxygen vacancies, for example by interaction of formic acid with a surface hydroxyl to create a formate B on the surface while desorbing as H_2O molecule. This mechanism would imply that formation of the

formate B species ‘removes’ OH species created via the formation of formate A species. This may rationalise the different results of the RAIRS and NEXAFS studies. The formic acid dosages used in these experiments (650 L and 100 L, respectively) were much higher than that necessary to obtain a (2x1) saturated layer. For these large exposures, once the (2x1)-formate A overlayer is formed (with the coadsorption of H⁺ at the bridging O atoms to form OH), the further incoming HCOOH cannot any longer accommodate on top of the 5-fold coordinated Ti atoms of the surface. This may force it to react with the OH groups according to the reaction mechanism described above.

Bearing in mind this uncertainty, the specific model we have tested for coexisting formate A and B species plus OH, is actually midway between the two extremes, and we can anticipate that an increasing number of OH species will lead to a better R-factor. Therefore, using only the O 1s PhD data we cannot exclude possible co-occupation of the formate B geometry along with formate A and OH.

Some further information on the role of a second formate species may be obtained from the C 1s PhD spectra, which we have so far not considered. Fig. 4.11 shows the comparison of the experimental C 1s PhD spectra with the results of the simulations for two different structural models. The upper panel shows the optimisation of a model based on the presence of the formate A species only. The lower panel correspond to optimisation of a model of 2/3 of formate A species with 1/3 of the formate B species. Notice, of course, that these spectra are independent of the OH coverage, as this species does not contribute to the C 1s emission. The C 1s PhD spectra show very weak modulations ($\pm 10\%$ or less) in most emission geometries, so we do not expect very good agreement even for a correct structure. Such low modulation amplitudes render experimental noise more significant and are more likely to expose any weaknesses of the theoretical modelling. This problem is reflected in the relatively large R-factors of 0.36 and 0.48 found for the two structural models, although visual inspection of the data corresponding with a single formate A species shows that all the main modulations of the data are actually simulated relatively well. We have already mentioned that the strongest modulations, of very long periodicity, seen at 60° polar emission angle in [001] can probably be attributed to intramolecular backscattering from the O atoms (the weaker, shorter period modulations are attributable to scattering from the more distant substrate atoms). Therefore, the absence of such modulations in the orthogonal azimuth may suggest that the great majority of the adsorbed formate species are aligned in the [001] azimuth. The simulations for the model involving both A and B formate species in the ratio 2:1 favoured by RAIRS and NEXAFS show a reduction in the theoretical modulation amplitudes of the intramolecular PhD effects in [001].

The striking feature of the results for this model is the absence of strong modulations at higher off normal geometries along the [1 $\bar{1}$ 0], which would correspond to intramolecular scattering within the formate B species. It seems that the $\sim 33\%$ contribution of the B species is not sufficient to produce these particular strong modulations. The overall fit is significantly worse, as reflected in a larger R-factor of 0.46.

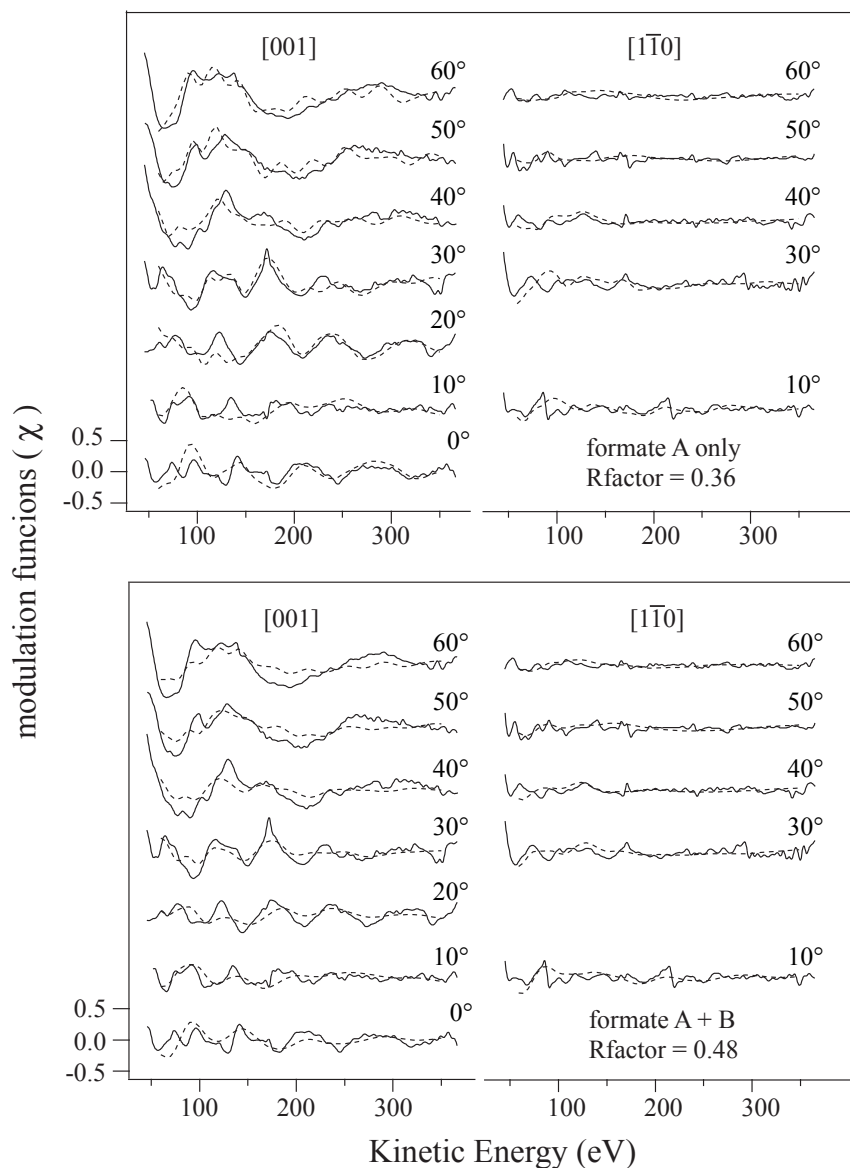


Figure 4.11: Comparison of the experimental C 1s PhD modulation spectra (full lines) from the formate-covered $\text{TiO}_2(110)(2 \times 1)$ surface with the results of the best-fit theoretical calculations (dashed lines) for: (a) a model assuming occupation of the formate A species only and (b) a model assuming co-occupation of the formate A and formate B species in the ratio 2:1

In view of these results, we therefore conclude that we can exclude the model based in the coexistence of formate A and B species in a ratio of 2:1. Of course, a much smaller fractional occupation of this second formate species cannot be ruled out on the basis of our PhD results.

Fig. 4.12 shows the detailed local structural parameter values around the adsorbate species for the best-fit formate A + OH structural model. Notice that the value of the interlayer spacing between the O atoms of the formate A species and the Ti atoms below them ($2.06 \pm 0.03 \text{ \AA}$) is slightly larger than the spacing found in the model in which a single formate A species was considered to be adsorbed on the surface, without coadsorption of the OH species. Actually, theoretical calculations that favour the coadsorption of both dissociation products of formic acid, found similar lengthening in the Ti-O bond length for the formate A depending on the presence of the co-adsorbed OH [112].

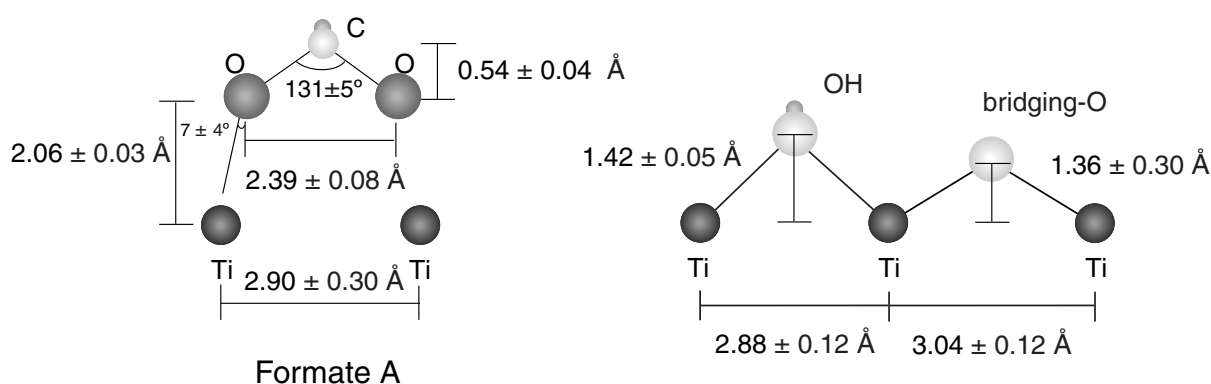


Figure 4.12: Schematic diagram of the best-fit local structure for the formate A and OH bridging species

Notice that, incidentally, the value found in the restricted earlier PhD study for the Ti-O bond length is similar to that found in the present work. The O-O distance within the formate A molecule is found to have a value of $2.39 \pm 0.08 \text{ \AA}$, which is considerably larger than that of the undistorted formate ion (2.21 \AA). As commented previously, some increase in the O-O distance is to be expected due to the mis-match with the Ti-Ti distance. Actually, similar O-O distances have been found for adsorbed formate on different Cu surfaces [147,148]. Unlike in the formic acid molecule, the C-O bonding is now symmetric, with a value of $1.31 \pm 0.08 \text{ \AA}$. The O-C-O angle is found to be $131 \pm 5^\circ$, slightly larger than that found in the XPD study [104], but similar to that obtained for formate adsorbed on Cu(100) [149].

As commented before, the structural optimisation also involved adjustments to the location of the near-surface Ti and O atoms in the substrate. Fig. 4.13.a shows a perspective view of the $\text{TiO}_2(110)-(1 \times 1)$ surface with numbers attached to the inequivalent near-surface atoms whose location has been optimised. The arrows indicate the direction in which the displacements along the direction normal to the surface of these atoms with respect to the positions they occupied in an ideally bulk-terminated structure occur.

Fig. 4.13.b shows a plan view of the surface including the formate A and OH species, the lateral displacements of the surface Ti and O atoms being indicated by dashed circles at the bulk-terminated locations. These displacements are summarised in table 4.2 together with the displacements determined by SXRD [126] of the same atoms in the clean $\text{TiO}_2(110)-(1 \times 1)$ surface relative to the ideal bulk-terminated surface. Table 4.3 reviews the Ti-O bond lengths at the $\text{TiO}_2(110)-(1 \times 1)$ surface in an ideal bulk-terminated structure, for the (1×1) clean surface as found by SXRD and at the formic acid-reacted surface as found in this study.

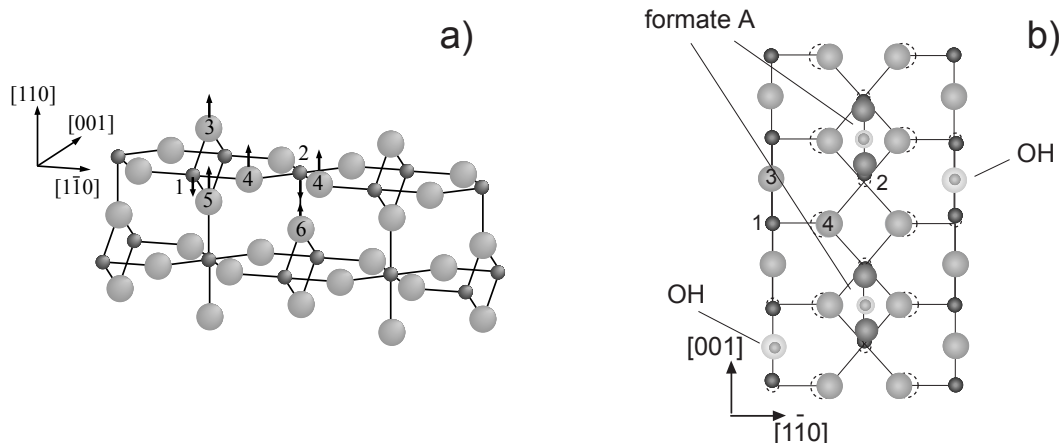


Figure 4.13: Perspective view of the $\text{TiO}_2(110)$ surface and defining near-surface atom numbers. The direction of the displacements of these atoms are shown by arrows. (b) plan view of the surface including the formate (A) and OH species, the lateral displacements of the surface Ti and O atoms being indicated by dashed circles at the bulk-terminated locations.

We have to stress that the PhD technique is intrinsically a local structural technique, most sensitive to the location of near neighbours to the emitter atoms, so this optimisation of the substrate structure is a second-order effect. This is actually reflected in the large error bars found for these parameters. Notice that unlike the relaxations observed by SXRD for the $\text{TiO}_2(110)-(1 \times 1)$ clean surface, the presence of a (2×1) -overlayer structure allows now the displacement of the Ti atoms bonded either to the formate A or to the bridging OH species along $[001]$, as is indeed found in our simulations. The Ti-O bond length for the bridging oxygen atoms in the presence of the formate and the hydroxyl species is significantly longer than that found for the clean surface, so the adsorbate bonding has an influence beyond the nearest neighbour substrate atoms. A striking result is the large displacement found for the ‘in plane’ O atoms along $[1\bar{1}0]$ towards the Ti atom bonded to the O atom of the formate A species, although the large error estimated for this parameter confirms that our calculations are not very sensitive to the exact location of these atoms.

We want to point out that the optimisation of the local adsorption structure of the final model comprising co-adsorbed formate A and bridging OH species was carried out from two distinct initial $\text{TiO}_2(110)-(1 \times 1)$ structures corresponding to the bulk-terminated one

Displacements	Clean (SXR)	HCOOH induced
$\delta_{[110]}$ Ti(1)	$+0.12 \pm 0.05$	-0.08 ± 0.06
$\delta_{[001]}$ Ti(1)	-	$+0.04 \pm 0.06$
$\delta_{[110]}$ Ti(2)	-0.16 ± 0.05	-0.07 ± 0.08
$\delta_{[001]}$ Ti(2)	-	$+0.03 \pm 0.15$
$\delta_{[110]}$ O(3)	-0.27 ± 0.08	$+0.10 \pm 0.30$
$\delta_{[110]}$ O(4)	$+0.05 \pm 0.05$	-0.06 ± 0.30
$\delta_{[1\bar{1}0]}$ O(4)	$\pm 0.16 \pm 0.08$	$+0.41 \pm 0.34$
$\delta_{[110]}$ O(5)	$+0.05 \pm 0.08$	-0.04 ± 0.30
$\delta_{[110]}$ O(6)	0.00 ± 0.08	$+0.02 \pm 0.22$

Table 4.2: Displacements (in Å) of the near-surface Ti and O atoms in TiO₂(110) relative to an ideal bulk-terminated structure for the clean surface (values taken from the SXR study [126]) and for the formic acid-reacted surface of this study. Notice that displacements along the direction [001] and [1 $\bar{1}$ 0] are symmetry forbidden for the (1x1) clean surface but not for the (2x1) formate phase

Bondlength	bulk-terminated	(1x1) clean surf. SXR	(2x1) HCOOH-reacted surf.
Ti ₁ -O ₃	1.94	1.71 ± 0.07	2.04 ± 0.25
Ti ₁ -O ₄	1.99	2.15 ± 0.09	2.40 ± 0.35
Ti ₁ -O ₅	1.94	1.99 ± 0.09	1.88 ± 0.20^a 1.94 ± 0.20^b
Ti ₂ -O ₄	1.94	1.84 ± 0.05	1.73 ± 0.20 1.68 ± 0.20
Ti ₂ -O ₆	1.99	1.84 ± 0.13	1.90 ± 0.22
formate O	-	-	2.08 ± 0.03
OH	-	-	2.02 ± 0.05

Table 4.3: Ti-O bond lengths (in Å) at the TiO₂(110) surface in an ideal bulk-terminated structure, for the (1x1) clean surface as found by SXR [34], and for the formic acid-reacted surface studied here; ^abelow OH, ^bbelow bridging-O

and that found in the SXR experiment by Thornton et al. The results obtained in these two independent simulations for all the structural parameters included in the optimisation were in very good agreement with each other, all falling well within the variance of the minimum value of the R-factor. The final values that are given in this thesis are the result of optimising an structure that was obtained by averaging these two previously optimised structures. The final value obtained for the inner potential was 9 ± 6 eV, comparable to the value obtained for the clean surface [128]

4.5 General discussion and conclusions

We have studied, by means of photoelectron diffraction, the structural geometry of the surface species produced on the rutile $\text{TiO}_2(110)-(1\times 1)$ surface after room temperature exposure to formic acid. The results of this study allow us to resolve two hitherto unanswered questions regarding this system. Firstly, our results prove that exposure to formic acid of a nearly-free of defects $\text{TiO}_2(110)-(1\times 1)$ lead to the adsorption of a single formate species, that is aligned along [001] bridging two adjacent 5-fold coordinated Ti surface atoms with the O atoms in off-atop sites; this is the geometry which has generally been supposed to be correct, being favoured by STM images, the results of several total energy calculations, and the original PhD study, despite its several limitations. The Ti-O bond length is $2.08 \pm 0.03 \text{ \AA}$, and the O-O distance has a value of $2.39 \pm 0.30 \text{ \AA}$. Our results exclude the possibility of a large ($\sim 33\%$) fractional occupation by the formate species of a second site azimuthally rotated by 90° and bonded to a surface oxygen vacancy site, as proposed in some earlier infrared and X-ray absorption spectroscopic experiments. Of course, as indicated by the Ti $2p$ photoemission spectrum from the clean surface, one would expect the oxygen vacancy concentration of the clean surface to be only of a few per cent, much less than the value required to account for this level of co-occupation. Indeed a recent STM study provided some evidence for possible partial occupation (less than 1%) of this second site. One possibility which has been suggested is that reaction with formic acid may actually create surface oxygen vacancies through water desorption due to disproportionation of surface hydroxyl groups which can occur at 350 K [?]. In this regard we have already discussed a possible mechanism for the reaction of formic acid over (2x1)-formate saturated TiO_2 surface, that is consistent with the large exposures used in the RAIRS and NEXAFS experiments in which these second formate species were observed and with the observation of H_2O as the main desorption product at temperatures slightly higher than room temperature. Indeed, it is also possible that the exact sample temperature ('room temperature') is an important factor influencing the presence of this species in view of the low disproportionation temperature.

Secondly, we have found clear evidence for the coexistence of this formate species and hydroxyl. The hydroxyl species are formed by H attachment to the surface bridging O atoms and have a Ti-O bond length of $2.02 \pm 0.05 \text{ \AA}$ compared with the value of 1.94 \AA for the non-hydrated ideally-terminated solid and 1.71 \AA found for the clean surface by SXRD. The coverage of this hydroxyl species is assumed equivalent to that of the formate species, consistent with the stoichiometry of the reaction.

Notice (see table 4.3) that the Ti-O distances associated with both adsorbed species are significantly longer than the Ti-O distances in bulk TiO_2 . This may be related to the fact that the nature of the bonding to the surface of HCOO^- and OH^- is expected to differ from the bonding nature in TiO_2 which is commonly regarded as purely ionic.

One particularly interesting aspect of the results of our study is the identification of the geometry associated with the hydrogen adsorption. In general, most spectroscopies

and surface structural probes are ‘blind’ to surface hydrogen, and strictly this is also true here; certainly PhD cannot determine H atoms sites directly as hydrogen has no core electronic state which is localised on adsorption, and it is also difficult to obtain any precision in locating H atoms through electron scattering because their cross-section is so low. Nevertheless, our results have established the direct consequence of the adsorbed hydrogen by locating the exact local geometry of the O atoms of the OH species which is formed by the hydrogen adsorption.