Adsorption and stability of malonic acid on rutile TiO$_2$ (110), studied by near edge X-ray absorption fine structure and photoelectron spectroscopy

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Abstract

The adsorption of malonic acid on rutile TiO$_2$ (110) has been studied using photoelectron spectroscopy and C K-edge, near edge X-ray fine structure spectroscopy (NEXAFS). Analysis of the O 1s and Ti 2p spectra suggest that the molecule adsorbs dissociatively in a doubly-bidentate adsorption geometry as malonate. The data are unable to distinguish between a chelating bonding mode with the backbone of the molecule lying along the [001] azimuth or a bridging geometry along the direction. Work carried out on a wiggler beamline suggests that the molecule is unstable under irradiation by high-flux synchrotron radiation from this type of insertion device.

1. Introduction

The interaction between carboxylic acids and TiO$_2$ is important in many areas of research; for example, titanium is often used for biomedical implants where the TiO$_2$ surface of the implant is in contact with biological molecules [1–5]. The carboxylic acid-TiO$_2$ interface also has importance in technological applications such as the dye-sensitised solar cell (DSSC) or Grätzel cell [6]. Since its invention, many different dyes have been investigated; most of which have relied on bonding to the TiO$_2$ through carboxylic acid groups [7–10]. Aranyos et al. [11] have shown that the number of attaching carboxylates on the dye influences the photoelectrochemical properties of the dye-sensitised electrode. It is also thought that the ordering of the molecules and strength of the interaction are important in the charge transfer process. In addition to the photovoltaic and biomedical applications described above, TiO$_2$ is a well known photocatalyst and reactions at TiO$_2$ surfaces are of interest in solar energy driven reactions such as water splitting [12], production of fuels such as methanol [13] and cleaning wastewater containing organic pollutants [14].

Carboxylic acids are widely believed to attach to rutile TiO$_2$ (110) surfaces dissociatively via deprotonation, where the hydrogen atom is lost from the carboxylic acid group (leaving COO$^-$) [15,16]. The majority of molecules then bond to the surface through the two oxygen atoms of the carboxylic acid group in a bridging bidentate structure, to two adjacent five-fold-coordinated titanium atoms on the surface [17]. Malonic acid is a simple dicarboxylic acid as shown in Fig. 1. This molecule could potentially be used as an anchoring molecule to attach any organic molecule onto a TiO$_2$ surface via the central CH$_2$ group. Such molecules could be used to functionalise the TiO$_2$ surface for biomedical or photovoltaic applications. Clearly for such applications the mode of bonding and the stability of the adsorbed species have some importance.

Investigating the stability of organic molecules under a synchrotron radiation X-ray beam can be very challenging. Measurements recorded at synchrotrons may provide misleading results if the molecules being investigated are damaged or break up under the beam. This is particularly important if the data acquisition time is long when damage to the molecules or photocatalysed reactions can occur in a matter of seconds. In addition, if molecules that are potentially viable for use in photovoltaic cells are unstable under the X-ray beam they may also be susceptible to long-term degradation under sunlight. Since the carboxylic acid groups usually anchor the entire dye to the TiO$_2$, a loss in...
integrity of these bonds could lead to a loss of the charge transfer route from the dye into the TiO₂. It has been shown by O'Shea et al. [18] that the ligand used in the N₃ dye, bi-isonicotinic acid, is damaged under synchrotron radiation resulting in the bi-isonicotinic acid molecules splitting into two isonicotinic acid molecules. Similar results were found for glycine adsorbed on the rutile TiO₂ (110) surface [5,19]. These observations may raise questions about the design of new high flux beamlines on 3rd generation synchrotron sources for the study of these molecules and measures that may be required to reduce these problems.

This paper presents photoemission spectra and NEXAFS spectra to investigate the adsorption of malonic acid on the rutile TiO₂ (110) surface. The molecular adsorption is studied using NEXAFS and photoelectron spectroscopy in order to determine the bonding geometry and mode of bonding. In addition, a comparison of the stability of the adsorbed malonic acid is made by carrying out photoelectron spectroscopy measurements on a bending magnet beamline and comparing these to work carried out on an insertion device beamline.

2. Experimental

The experiments were carried out on beamline D1011 (40 eV ≤ hν ≤ 1500 eV) at MAX-lab, Sweden, and beamline MPW6.1 (30 eV ≤ hν ≤ 350 eV) at SRS Daresbury Laboratory, UK. Beamline D1011 [20] is a bending magnet beamline with a photon flux of 10¹²–10¹³ photons s⁻¹ and beamline MPW6.1 was a wiggler insertion device beamline [21] with a photon flux of 10¹²–10¹³ photons s⁻¹ over the photon energy range used in these measurements. The endstation of beamline D1011 is equipped with a Scienta SES200 hemispherical analyser with an angular acceptance angle of ±6°.

The rutile TiO₂ (110) crystal (Pi-kem Ltd.) was cut and epi-polished on one side to within 0.2° of the (110) plane. The crystal was prepared by repeated cycles of 1 keV Ar⁺ ion etching and annealing to 750 °C in vacuum until XPS spectra showed no contamination and a sharp (1 × 1) LEED pattern was obtained [22]. Malonic acid powder (>99%, Fluka) was degassed in an evaporating arm for 1 h by heating to ~100 °C. Malonic acid decomposes at 135 °C so care was taken not to heat the acid to temperatures higher than this. To dose the TiO₂ with malonic acid the temperature of the tantalum envelope containing the powder was reduced to 80–95 °C, whilst the TiO₂ crystal was held at room temperature (ca. 23 °C). For the measurements carried out on MPW6.1 of the SRS the rutile TiO₂ (110) surface was subjected to multiple exposures (ranging from 1 to 15 min, equivalent to ca. 0.6–100 L) of malonic acid but no evidence of multilayer formation was observed. In the measurements performed on beamline D1011 at MAX-Lab, the rutile TiO₂ (110) crystal was exposed to malonic acid for approximately 15 min (equivalent to ca. 100 L).

Photoemission and NEXAFS data were recorded from the rutile TiO₂ (110) surface before and after evaporation of malonic acid. Photoemission spectra were recorded at normal emission, with the incident beam at 40° to the surface normal. Clean and dosed spectra were aligned on the binding energy scale using Fermi edges recorded from the tantalum sample clips. Binding energies are quoted to ±0.1 eV. Peak fitting of the photoelectron spectroscopy data was performed using CasaXPS software. A Shirley background was subtracted from the photoemission data. Voigt curves (70% Gaussian: 30% Lorentzian) were used to fit the core level photoemission spectra. Photoemission spectra are normalised to the incident photon flux unless stated otherwise.

3. Results

3.1. Characterisation of the adsorption mode of malonic acid on rutile TiO₂ (110)

We begin by discussing the spectra recorded on the bending-magnet beamline D1011 at MAX-lab. Fig. 2 shows the O 1s spectra for clean rutile TiO₂ (110) and for malonic-acid-dosed rutile TiO₂ (110) recorded at a photon energy of 700 eV. The O 1s spectrum recorded from the clean surface is fitted with a single peak at 530.4 eV. This is attributed to the oxygen atoms in the TiO₂ crystal [23]. Following adsorption of malonic acid on TiO₂, the O 1s spectrum can be fitted with three peaks at binding energies as shown in Table 1. The first peak is assigned to the oxygen atoms in the TiO₂ surface [23] and is at a similar binding energy to the corresponding peak in the clean spectrum. The second peak at 532.0 eV is assigned to carboxyl oxygen atoms in the molecule [24]. There are four oxygen atoms in each malonic acid molecule, which are not equivalent (two are carbonyl and two are hydroxyl oxygen species). If the molecule adsors on the surface in a twice-bidentate bridging structure (bonding through all 4 oxygen atoms following deprotonation of both acid groups) to form malonate shown in Fig. 2, then all of the oxygen atoms will be in the same chemical environment, resulting in one peak in the spectrum [25]. The O 1s spectrum recorded upon adsorption of the malonic acid strongly suggests that the molecule is indeed doubly deprotonated and adsors in a twice-bidentate geometry following deprotonation of the acid groups, as shown schematically in Fig. 2c. The third, rather weak peak, at a binding energy of 533.9 eV may arise from a small number of intact carboxyl group OH species, for example if some fraction of the molecules are adsorbed in a monodentate geometry [26] (Fig. 2d) and therefore adsorbed only through a single carboxylate group (Fig. 2e). It is also possible that this peak arises from a small number of molecules not bonded to the surface, for example forming the beginnings of a second layer of malonic acid. Table 1 shows the binding energies, percentage of total O 1s signal and summarises the assignment of peaks fitted to the O 1s spectra for clean rutile TiO₂ (110) and for malonic-acid-dosed rutile TiO₂ (110). What is clear from these data is that the majority of the malonic acid is adsorbed in a doubly bidentate mode following deprotonation of the carboxyl groups.

Fig. 3 shows the Ti 2p spectra recorded at a photon energy of 1000 eV for clean rutile TiO₂ (110) and following adsorption of malonic acid normalised to the intensity of the Ti 2p₃/₂ peak. Table 2 summarises the binding energies, percentage of total Ti 2p signal and origins of the peaks [27,28] fitted to the Ti 2p spectra for clean rutile TiO₂ (110) and
for malonic-acid-dosed rutile TiO$_2$ (110). The presence of the Ti$^{3+}$ derived peak is widely attributed to O-bridging oxygen vacancies on the surface [29]. The data show that there is no shift in the binding energy of the Ti 2p$_{3/2}$ peak suggesting that there is no malonic-acid-induced band-bending following adsorption in contrast to the adsorption of similar molecules such as dopamine [30] and catechol [31] on anatase and rutile TiO$_2$ surfaces. In addition, Table 2 shows that there is very little change in the intensity of the Ti$^{3+}$ derived peaks indicating that adsorption of the molecule does not lead to ‘healing’ of the O-bridging vacancies.

Table 1

| Binding energy (eV) | Clean rutile | Malonic-acid-dosed rutile | Origin of peak |
|---------------------|--------------|---------------------------|----------------|
| 530.4 (100%)        | 530.3 (69.0 ± 0.7%) | Oxygen atoms in TiO$_2$ surface [23] |
| 532.0 (28.1 ± 1.5%) | 532.0 (28.1 ± 1.5%) | Carboxyl oxygen atoms [24] |
| 533.9 (2.9 ± 2.1%)  | 533.9 (2.9 ± 2.1%) | Molecule hydroxyl groups [43] |

Table 2 also gives the intensities of the Ti 2p$_{3/2}$ peak before and after dosing with malonic acid. A rough approximation of the surface coverage can be obtained from these values using the equation,

$$I_d = I_c (1 - \phi_A + \phi_A \exp(-d/\lambda \cos \theta))^{[28]},$$

where, $I_d$ is the intensity of the Ti 2p$_{3/2}$ peak of the dosed surface and $I_c$ for the clean surface, $\phi_A$ is the surface coverage, $d$ is the ‘diameter’ of the molecule, $\lambda$ is the inelastic mean free path (IMFP) and $\theta$ is the angle of the incident X-ray beam relative to the surface normal (40°). Using the measured change in the intensity of the Ti 2p$_{3/2}$ peak ($I_d/I_c$) of 0.63, the IMFP of TiO$_2$ of 1.7 nm [32] and taking an approximate ‘diameter’ of the malonic acid molecule to be 10 Å, we obtain a coverage of 0.26. This would suggest that there is roughly one molecule for every four five-fold coordinated Ti atoms (Ti$_{5c}$) at the surface. This supports the doubly-bidentate adsorption geometry inferred by the O 1s spectrum following adsorption of malonate.

Fig. 3. Ti 2p spectra of clean rutile TiO$_2$ (110) and malonic-acid-dosed rutile TiO$_2$ (110) recorded at a photon energy of 700 eV. The black dots are the experimental data, the red line is the total fit to the data and the dashed lines are the components fitted to the data. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
deviation from the expected stoichiometric ratio of the two C derived peaks for malonate is not clear. It may be due to photoelectron effects, since the carboxylate carbon is closer to the surface than the central alkyl carbon then the photoemitted electron wave is more likely to be diffracted due to backscattering from the underlying surface [33]. Previous work on using this analyser in a normal emission geometry has also shown deviations from stoichiometry for the atoms closest to the surface [34]. However in the absence angle-resolved or energy-resolved photoelectron diffraction measurements this is not certain for the current case. A comparison of a “survey” C 1s spectrum (recorded with a step size of 0.5 eV) and the spectrum shown in Fig. 4, which was recorded 30 min after the wide scan shows no significant change in the intensity or width of the two peaks (see Supplementary information Fig. S1). This suggests that the molecule is stable under synchrotron radiation on beamline D1011 for the duration of the measurements made on D1011 at MAXlab. The deviation from stoichiometry for the C 1s however does not rule out the possibility that some dissociation or reaction has occurred at the surface prior to exposure to the beam. The most obvious decomposition reaction for this molecule would be the formation of acetate and formate by scission at the CH₂ group as shown in Fig. 1. However this would not change the overall COO:CH₂ ratio. Loss of the CH₂ group would of course lead to an increase in the relative amount of COO, which is not consistent with the C 1s spectrum. Another possibility, which would be consistent with the data, would be adsorption through only one carboxylate and subsequent loss of the second carboxylate group as CO₂. The latter is a slow reaction at 90 °C in aqueous solution at low pH, and becomes even slower at pH > 4 [35] thus we expect it to be unlikely in vacuum. During deposition, great care was taken to keep the temperature low, and, in the absence of water, so we expect little decomposition to have occurred although of course this can never be completely ruled out.

Fig. 5a shows carbon K-edge NEXAFS spectra from a malonic acid-dosed rutile TiO₂ (110) surface, recorded with the electric vector of the incident synchrotron radiation (SR) beam along the [001] azimuth. The incident angle of the SR beam was varied from 20° to 90° relative to the sample surface. The spectrum with the SR beam at 90° to the surface (normal incidence) was recorded immediately following exposure of the surface to around 100 L of malonic acid. In all of the spectra, a sharp peak is observed at a photon energy of 288.8 ± 0.2 eV and a broad resonance centred around 301 eV is also clearly visible. The energies and line shapes of these features are all in good agreement with those recorded for NEXAFS spectra of formate, acetate and propionate adsorbed on rutile TiO₂ (110) recorded by Gutiérrez-Sosa et al. [17]. The sharp peak at 288.8 ± 0.2 eV is assigned to C 1s → π* excitations in the carboxylate groups. If both carboxylate groups bond to surface titanium atoms in a bidentate structure, as suggested by the O 1s photoelectron spectrum, the carboxyl carbon atoms should produce one main π* resonance as we observe here. The broad resonance at around 301 eV is attributed to C 1s → σ* transitions.

Malonate would be expected to give rise to a similar shaped spectrum to acetate but the intensity of the σ* resonance relative to the π* resonances (broad higher energy features) should be twice as large given the same angle of incident light on the sample. This is because according to the building block principle, the NEXAFS spectrum of a molecule should be a linear combination of the individual spectra of its functional groups or bonds [36]. Although it seems that the relative intensity of the π*-derived peak to the σ* derived peak is larger in this work compared to the corresponding spectrum for acetate from ref. 15, a definitive comparison is not possible due to the variation in the intensity of the peaks with the incident photon angle. The angle-resolved NEXAFS data recorded with the electric vector of the incident X-ray beam along the [001] azimuth seem to show some angular dependence, as shown in Fig. 5b. Fitting of the Stohr equations [37] gives a tilt angle of the C=O groups of 56° ± 10°. However, the angle derived for the molecular tilt (i.e. the tilt of the carboxylate groups relative to the surface normal) of 56° is close to the ‘magic angle’ of 54.7° [37]. This means that we are unable to unambiguously determine whether the molecules are ordered on the surface. A lack of ordering may be due to decomposition of the molecule under the synchrotron radiation beam, although on the bending-magnet beamline we did not observe any changes to suggest decomposition of the molecule. The O 1s spectra suggest that a small number of the molecules may in fact be adsorbed in a singly bidentate geometry, which would leave the other carboxyl group free to rotate around the central C atom; sterically, and electrostatically one would perhaps expect the two carboxyl groups to be orthogonal to one another. The presence of some singly bidentate adsorbed species would give rise to a minority species with the π* vector at some other
angle relative to the bonded carboxylate groups. A third possibility for
the apparent lack of order is the bonding geometry of the carboxylate
groups with respect to the azimuthal geometry of the crystal. This latter
would occur if the molecules are oriented with the π* vector of the
bonded carboxylate groups along the 110 azimuth. In this situation
no angular variation would be observed in the NEXAFS spectra[37]
obtained by rotating the polar angle. Unfortunately, angle-resolved
NEXAFS spectra could not be recorded along the 110 azimuth due to
limitations of the sample manipulator.
The O 1s photoemission data suggest that the majority of the mole-
cules are adsorbed in a doubly bidentate mode following loss of the pro-
ton from both carboxylic acid groups. Fig. 6 shows a schematic of two
possible adsorption geometries, which are consistent with the data.
The molecule–surface (Tisurface – Omolecule) bond lengths used for the
bridging geometry shown in Fig. 6b is 2 Å. This is consistent with
bond length deduced from photoelectron diffraction measurements
for formate adsorption in a bidentate bridging mode on this surface
[38]. As discussed above it was not possible to obtain the azimuthal
angle from the NEXAFS data, thus it is not possible to determine
which of these structures is most likely from our data. However, most
studies of carboxylic acid adsorption on rutile TiO2 (110) surfaces in
ultra-high vacuum suggest a bridging bidentate geometry to be favoured[16] as shown in Fig. 6b. The figure suggests that the molecule
would in theory be able to bond across the bridging oxygen rows since
the central carbon atom is likely to coincide with the valley between
two neighbouring bridging oxygen atoms (Obr).
It is well known that O-vacancies can easily be produced at the rutile
TiO2 (110) surface by electron or ion bombardment. As mentioned
above on the rutile TiO2 (110) surface oxygen is thought to be lost
from the bridging oxygen rows. The intensity of the Ti 2p component
associated with Ti3+ allows us to estimate that the concentration of
oxygen vacancies at the TiO2 (110) surface is rather low, ca. 4 ± 3%
[39,40]. It is clear that our measurement characterises the adsorption
of malonic acid at a largely undefected surface. The Ti 2p spectra
discussed above do not show any change in the intensity of the Ti3+
derived peak upon adsorption of the malonic acid. It is possible that
the presence of O-vacancies in a more highly defected surface may
lead to a change in the adsorption mechanism at the vacancy sites.
Indeed DFT calculations for dopamine adsorbed on anatase surfaces
suggested the molecule adsorbed preferentially in a chelating mode
(i.e. both O atoms bonded to a single surface Ti) at O-vacancy sites
[41]. The absence of a change in the intensity of the Ti3+ derived peak in the Ti 2p spectra does not rule this possibility out for the current
study since it is well known from water adsorption studies that
although water adsorbs at O-vacancies, Ti3+ is not removed from the
surface [29]. With regard to the effect of O-vacancy concentration on
molecular adsorption at the rutile TiO2 (110) surface generally, there
is still some debate. It would therefore be interesting to probe the effect
of the surface O-vacancy concentration of TiO2 on the adsorption of
malonic acid.
3.2. Synchrotron radiation induced beam damage of malonic acid on rutile
TiO2 (110)
Fig. 7 shows the C 1s photoelectron spectra following a 15 minute
dose of malonic acid at 90 °C (can 100 L), recorded at a photon energy
of 350 eV on the insertion device beamline, MPW6, at the Daresbury
SRS. The spectra can be fitted with two peaks at binding energies of
285.9 eV and 289.7 eV, which again are assigned to CH2 and COO−
carbon atoms in the molecule [28]. A number of core level and valence
band spectra were recorded over a period of a few hours before the
beam was shut off for 12 h and the spectrum was recorded again, as
shown in Fig. 7 (curve b). This spectrum was recorded from a slightly different location on the crystal. The C 1s spectrum was then recorded again (c) 7 min and (d) 12 min after spectrum (b). The position of the beam on the crystal was then moved again and the C 1s spectrum recorded is shown in Fig. 7 (curve e). C 1s spectra were then recorded (f) 3 min, (g) 15 min, (h) 34 min and (i) 53 min after spectrum (e) with the sample constantly exposed to the soft X-ray beam. On the new location on the crystal, the peak at 289.7 eV is a similar height to the lower binding energy peak but slowly reduces in intensity with time spent under the X-ray beam. The change in the peak areas of the C 1s components is also shown in Fig. 7. It can be seen clearly that the higher binding energy peak area decreases, accompanied by an increase in the area of the lower energy peak, which might indicate the conversion of COO to CH2/CH3 groups at the surface. Over a period of 12 min ((c) and (d) in Fig. 7), following spectrum (b) there is very little change in the peak area of the CH-derived peak. The COO derived peak undergoes a further loss of intensity after 7 min but does not change between 7 and 12 min. When the beam position is moved on the sample surface, there is an increase in both peak areas (point (e)). However, Table 3 shows that moving to a new position on the crystal does not result in a return to the original 1:1.4 ratio of the alkyl:carboxyl peak intensity. Continued exposure of the surface (points (f)–(i)) to the high flux beam leads to a decrease in the areas of both peaks suggesting that the molecules are being desorbed from the surface. The ratio of the areas of the peaks at 285.9 eV and 289.7 eV binding energy remains roughly constant over this range, suggesting that both species are lost together. In addition to the change in intensity of the two peaks, we note that both peaks become broadened relative to the spectrum recorded in Fig. 7. This may be due to the formation of a mixture of molecules at the surface caused by decomposition of the malonate species. One may expect that there would be a slight downward shift in the binding energy of the alkyl carbon in acetate or formate relative to malonate, due to the extra carboxyl group in malonate. The decomposition of malonic acid seems to have occurred much more rapidly in

Fig. 6. Schematic ball and stick diagrams of two possible bonding modes of malonate on rutile TiO2 (110) which involves dissociation of both carboxylate groups upon adsorption. (a) Doubly bidentate chelating mode along the [001] 5-fold co-ordinated Ti atoms and (b) Doubly bidentate bridging adsorption along the [110] direction crossing the bridging oxygen rows. Red spheres represent oxygen atoms, blue is titanium, white is hydrogen and black is carbon. The Tisurface–Omolcules bond lengths are set to 2 Å in both cases.

Fig. 7. Left panels: (a)–(i) C 1s spectra of malonic-acid-dosed rutile TiO2 (110) recorded at a photon energy of 350 eV. The black dots are the experimental data, the red line is the total fit to the data and the dashed lines are the components fitted to the data. Right panel: Integrated peak areas of the C 1s peaks at 289.5 eV (red open circles) and 285.9 eV (blue filled squares). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
the work carried out on MPW6.1 of the SRS than on D1011 at MAX-lab. If one considers the power falling on the samples based on the flux and the fact the D1011 beam spot size is roughly 3 mm × 1 mm and that on MPW6.1 was roughly 0.6 mm × 0.3 mm then one has roughly between 20 and 2000 times the power incident on the sample on the MPW6.1 beamline.

The data above seem to suggest the decomposition of the malonic acid under the high flux MPW6.1 beamline, most probably to form acetate on the surface by spitting of the malonate as shown in Fig. 1. The relative intensity of the COO$^-$ to CH$_2$ peaks of around 0.8 is similar to that obtained by Quah et al. for acetic acid adsorption on this surface [28]. The formation of acetate from malonic acid is at odds with the fact obtained by Quah et al. for acetic acid adsorption on this surface [28]. The formation of acetate from malonic acid is at odds with the fact obtained by Quah et al. for acetic acid adsorption on this surface [28]. The formation of acetate from malonic acid is at odds with the fact obtained by Quah et al. for acetic acid adsorption on this surface [28]. The formation of acetate from malonic acid is at odds with the fact obtained by Quah et al. for acetic acid adsorption on this surface [28]. The formation of acetate from malonic acid is at odds with the fact obtained by Quah et al. for acetic acid adsorption on this surface [28]. The formation of acetate from malonic acid is at odds with the fact obtained by Quah et al. for acetic acid adsorption on this surface [28]. The formation of acetate from malonic acid is at odds with the fact obtained by Quah et al. for acetic acid adsorption on this surface [28]. The formation of acetate from malonic acid is at odds with the fact obtained by Quah et al. for acetic acid adsorption on this surface [28]. The formation of acetate from malonic acid is at odds with the fact obtained by Quah et al. for acetic acid adsorption on this surface [28]. The formation of acetate from malonic acid is at odds with the fact obtained by Quah et al. for acetic acid adsorption on this surface [28]. The formation of acetate from malonic acid is at odds with the fact obtained by Quah et al. for acetic acid adsorption on this surface [28]. The formation of acetate from malonic acid is at odds with the fact obtained by Quah et al. for acetic acid adsorption on this surface [28]. The formation of acetate from malonic acid is at odds with the fact obtained by Quah et al. for acetic acid adsorption on this surface [28]. The formation of acetate from malonic acid is at odds with the fact obtained by Quah et al. for acetic acid adsorption on this surface [28]. The formation of acetate from malonic acid is at odds with the fact obtained by Quah et al. for acetic acid adsorption on this surface [28]. The formation of acetate from malonic acid is at odds with the fact obtained by Quah et al. for acetic acid adsorption on this surface [28]. The formation of acetate from malonic acid is at odds with the fact obtained by Quah et al. for acetic acid adsorption on this surface [28]. The formation of acetate from malonic acid is at odds with the fact obtained by Quah et al. for acetic acid adsorption on this surface [28].

4. Conclusions

Photoelectron and NEXAFS spectroscopies have been used to study the interaction of malonic acid with a relatively defect-free rutile TiO$_2$ (110) surface. O 1s core-level photoelectron spectra recorded from a freshly deposited monolayer of malonic acid suggest that the majority of the molecules adsorb in a doubly-bidentate geometry to four Ti$_5c$ atoms, i.e. both carboxyl groups appear to bond via deprotonation. Angle-resolved NEXAFS spectra suggest the C=O groups are tilted 56° ± 10° from the surface normal and that the molecule remains intact upon adsorption. Unfortunately the azimuthal orientation of the molecule could not be determined from the NEXAFS data. It is also found that the adsorbed molecule is unstable under soft X-ray radiation on an insertion device beamline. The XPS spectra recorded over several hours suggest decomposition to form acetate, although there may also be other species such as formate and intact malonic acid on the surface.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.susc.2014.03.015.

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Table 3

| Fig. 7 | (a) | (b) | (c) | (d) | (e) | (f) | (g) | (h) | (i) |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Ratio of peak areas at 285.9/289.7 eV binding energy | 1.07 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |

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