Orientation of acetic acid hydrogen bonded to acetate terminated TiO_2(110)

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Keywords: Model photocatalysis; rutile TiO_2(110); acetic acid; ambient pressure photoemission, NEXAFS

Abstract

Acetic acid is a common pollutant for which photocatalytic degradation over titania provides a mitigating strategy. Knowledge of the bonding of acetate/acetic acid to this substrate is needed to aid interpretation of the photocatalytic data. In this work we use ambient pressure near edge X-ray absorption fine structure to measure the coverage and geometry of acetate in the $TiO_2(110)$ contact layer as well as acetic acid in an additional layer. A saturation coverage of 0.5 monolayers in both layers is found up to an acetic acid pressure of 10^{-1} Torr at 266 K. The geometry of acetate appears to be unchanged by adsorption of an additional layer of acetic acid, which involves a majority species bidentate bonded to neighboring Ti_{5c} sites and a minority species bonded in a perpendicular geometry. Acetic acid has a similar geometry dictated by hydrogen bonding to the contact layer as well as the substrate.

1. Introduction

Acetic acid is an air pollutant that has been proposed to form part of an ordered overlayer on the surface of $TiO_2(110)$ when exposed to the atmosphere [1]. Moreover, acetic acid is reported to be photo-decomposed on TiO_2 [2]. In seeking an understanding of the photocatalytic mechanism(s) it is important to know the structure of the reactant interface. In Ultra High Vacuum (UHV) conditions, acetic acid is thought to deprotonate at the rutile $TiO_2(110)$ surface to form acetate species that bond in two configurations [3,4]. The presence of two configurations is based on Near Edge X-ray Absorption Fine Structure (NEXAFS) measurements, which indicate an apparent twist out of the molecular plane out of the [001] azimuth [3]. The same apparent twist in NEXAFS is observed for formate [3], where Reflection Absorption Infrared Spectroscopy (RAIRS) [5], Scanning Tunnelling Microscopy (STM) [6], and calculations [7] point to the presence of two or more formate configurations. An earlier High Resolution Electron Energy Loss Spectroscopy (HREELS) pointed to dissociative adsorption of formic acid on $TiO_2(110)$ to produce formate and hydroxyl species [8]. In the majority configuration of the carboxylates the oxygen atoms are bidentate bonded to adjacent Ti_{5c} sites in the [001] direction, which are accompanied by a nearby hydroxyl (see Figure 1). A key minority component lies perpendicular to this configuration. For acetate at room temperature saturation coverage, which is 0.5 ML (1 monolayer corresponds to the number of $TiO_2(110)$ surface unit cells), 2/3 of the adsorbed molecules are in the majority configuration [3]. If the NEXAFS data are analyzed as a single domain, the apparent twist arises from an average of the majority and minority geometries [3]. There are no reports of a similar minority component in room temperature STM results for acetate on $TiO_2(110)$ [9,10], which could arise from a contrast effect. Additional species are observed in low temperature STM, with a second-layer physisorbed acetic acid molecule being observed at 148 K [11].

It was proposed that the minority formate and acetate species involves one oxygen atom of the molecule being bonded to a bridging oxygen vacancy (O_{bvac}), the other bonding to a five-fold coordinated Ti atom (Ti_{5c}) [3-7]. It is now known that O_{bvac} are rapidly converted to bridging hydroxyl species (OH_b) by reaction with water in the residual vacuum [4]. Hence, it is likely that at least some of the minority species involve hydrogen bonding to OH_b. This is the bonding suggested for a minority formate species observed at the surface of an interface formed with TiO_2(110) and aqueous formic acid [12].

The adsorbed species associated with exposure of TiO_2(110) to aqueous solutions of acetic acid forms (2 × 1) domains [12] similar to that found for UHV adsorption [9,10]. The quantitative structure of the acetic acid interface with TiO_2(110) has also been measured with surface x-ray diffraction (SXRD), with the results pointing to bidentate bonding of acetate as in the case of the UHV prepared overlayer [13]. The lack of detection of minority acetate species by SXRD could arise from disorder. Long range ordering in the second layer was also not observed, preventing an assessment of its local geometry. In this study we explore the orientation of a layer of acetic acid adsorbed in addition to the acetate contact layer. This is achieved using NEXAFS, a technique that relies only on short-range order. The results point to an orientation of acetic acid molecules that mirrors that of the acetate.

2. Experimental

Experiments were carried out on beamline 11.0.2 at the Advanced Light Source (ALS) [14]. The beamline output is 99% linear or circular polarised light over the photon energy range $75 \leq h\nu \leq 2150$ eV, with the facility for rotation of the *E*-vector of linearly polarised X-rays [15]. The Ambient Pressure Photoemission Spectroscopy (APPES) end-station has a SPECS electron energy analyser that can operate in a background pressure of up to 10 Torr.

A rutile hydroxylated h-TiO_2(110) sample (*Pi-Kem*) was prepared by cycles of Ar^+ sputtering and annealing to 1000 K until a (1 × 1) low energy electron diffraction (LEED) pattern was observed. Exposure to the residual vacuum was used to hydroxylate the substrate. The sample was initially exposed to 100 L (1 Langmuir = 1 x 10^{-6} Torr.s) of glacial acetic acid vapor at room temperature. This was dosed from a vial of the acid via a leak valve at 1 × 10^{-6} Torr after several freeze/pump/thaw cycles to remove dissolved gases. At this exposure a saturated coverage of 0.5 ML acetate is achieved, with a (2 × 1) LEED pattern being observed. Synchrotron radiation photoemission was used to confirm the absence of contamination. APPES studies involved measurement at elevated pressures of the vapor at reduced temperatures. The photon energy was calibrated by reference to the C K-edge π^* resonance of acetate on TiO_2(110) at 288.8 eV [3], while the photoemission binding energy scale was calibrated using the O 1s binding energy of TiO_2(110) at 530.4 eV [16]. Ambient pressure NEXAFS monitored the C KLL Auger peak of acetate/acetic acid, centred at E_{KE} = 249 eV, as a measure of the surface X-ray absorption coefficient.

3. Results and Discussion

Following saturation of TiO_2(110) with 0.5 ML of acetate at room temperature, C 1s and O 1s photoemission spectra were recorded at photon energies of 395 eV and 735 eV, respectively. The C 1s photoemission spectrum, presented in Figure 2(a), contains two peaks at 285.9 eV and 289.3 eV BE, which correspond to the methyl carbon (CH_3) and the carboxylate carbon (COO^-), respectively [17]. The difference in the peak intensities likely arises from an attenuation and/or a diffraction effect [17,18]. The corresponding O 1s spectrum (Figure 2(b)) also contains two peaks. One arises from the substrate at 530.4 eV, while the second one, at 532.1 eV, has contributions from the carboxylate group and bridging hydroxyls (OH_b) [19].

C 1s PES spectra recorded at 4 different partial pressures of acetic acid are presented in Figure 3 along with the 0.5 ML spectrum. When the pressure is increased to 10^{-5} Torr, two additional peaks are observed. It has been reported that acetic acid can be distinguished from acetate in PES by a shift to a higher binding energy because of the negative charge associated with the anion [20]. On this basis the second set of peaks are assigned to a more weakly bonded acetic acid layer. Their intensity increases with the partial pressure of acetic acid and another set of peaks are observed only at 10^{-2} Torr and above. C 1s spectra with the sample withdrawn from the path of the incident beam while the acetic acid pressure in the chamber was held at 10^{-1} Torr (not shown) confirmed that these peaks originate from gas-phase acetic acid. These peaks are significantly shifted relative to the two adsorbed species. This is due to the lack of screening of the core hole that is present in the condensed phase [21]. The energy separation observed between the methyl and carboxyl peaks of gas-phase acetic acid is 3.8 eV, which is in good agreement with previous studies [22,23].

A Gaussian/Lorentzian function fitted to both peaks of the saturated surface was used to quantify the coverage of the additional adsorbed layer. This also saturates at 0.5 ML, which is achieved at 10^{-2} Torr with the surface at 266 K. As for the acetate layer, the methyl C 1s peak is significantly larger than that for the carboxyl. This suggests that the molecule is oriented in a similar manner to the acetate layer, with the methyl carbon positioned further from the substrate and the carboxylate carbon closest to the surface. It is therefore proposed that the acetic acid has two hydrogen bonds to the surface, one from the carbonyl oxygen to a surface hydroxyl, the second between the OH of the molecule to a substrate bridging oxygen atom. A second species is also proposed where an acetic acid molecule forms a hydrogen bond with a bridging oxygen on the $TiO_2(110)$ surface and a methyl hydrogen atom of an adsorbed acetate molecule. Bonding of formate to the $TiO_2(110)$ surface involving surface OH groups has been evidenced with STM [12]. A model illustrating the notional bonding site of the second acetic acid layer is presented in Figure 4. In this arrangement, the additional layer will not significantly attenuate the photoemission signal from acetate, resulting in similar C 1s intensities from both adlayers.

NEXAFS was used initially to examine the bonding orientation of the 0.5 ML acetate overlayer on $TiO_2(110)$ for comparison with previous work [3]. The orientation of the molecule was determined by exploiting the dependence of the C 1s → π* NEXAFS intensity as a function of the alignment of the π* vector orbital $\vec{O}$ with the direction of the E-vector of the incident X-rays [3]. A maximum in the C 1s → π* intensity is observed when the E-vector of the incident beam is parallel to $\vec{O}$, which lies perpendicular to the carboxylate plane or carbonyl bond. A schematic of the associated coordinate systems of the photon beam and the sample is displayed in Figure 5. Polarized X-rays are incident on the sample at angle of θ to the sample surface. The orientation of $\vec{O}$ is described by the tilt away from the surface normal ($\vec{N}$), α, and the azimuthal twist out of the forward direction of the incident beam, ϕ.

Spectra representing the difference between C K-edge NEXAFS spectra with and without 0.5 ML of acetate on $TiO_2(110)$ are presented in Figure 6 aftter normalization to the absorption edge step. This subtraction serves to remove structure in the beamline output. Spectra were recorded as a function of the angle of polarization of the E-vector, β. The incident beam was held normal to the surface ($\theta = 90°$) so $\beta = 0°$ corresponds to the E-vector aligned with the $[1\bar{1}0]$ direction of the $TiO_2(110)$ surface. A peak at 288.8 eV in each spectrum that diminishes as β is rotated from the $[1\bar{1}0]$ azimuth of the surface to the [001] azimuth is the C 1s → π* resonance. A second set of data were recorded with the beam incident along the $[1\bar{1}0]$ azimuth of the substrate and at an angle of incidence of $\theta = 19°$ (not shown).

The π^* intensity polarization dependence was quantified by fitting the resonance to a mixed Gaussian (70%) / Lorentzian (30%) peak sitting on a step function. The latter represents the absorption-edge step. The equations of Stohr and Outka [24] describing the transition intensity, *I* were used to determine the orientation of the acetate molecules:

$$I = C[(\cos^2\beta)I^{\parallel} + (\sin^2\beta)\, I^{\perp}],$$

where $I_V^{\parallel} = \mathrm{A}(\cos^2\theta\cos^2\alpha + \sin^2\theta\sin^2\alpha\cos^2\phi)$ and $I_V^{\perp} = \mathrm{A}\sin^2\alpha\sin^2\phi$. $I^{\parallel}(I^{\perp})$ are the π^* resonance intensities that arise in response to illumination by the component of the *E*-vector that lies parallel (perpendicular) to the plane of incidence. A is a constant that depends on the geometry of the system [24].

Data from both azimuths were fitted simultaneously so as to define a unique set of parameters, the results of the fit being shown in Figure 7(a). This corresponds to a tilt angle of α = 70 ± 8° and its twist angle, ϕ = 32° ± 3° out of the $[1\bar{1}0]$ azimuth of the surface. In other words, the C-C axis of acetate is tilted by 20 ± 8° relative to the surface normal and the O-C-O plane is twisted 32° ± 3° out of the [001] direction of the substrate. The azimuthal angle is in reasonable agreement with a study by Gutiérrez-Sosa *et al* (26 ± 5°), which was interpreted as arising from an average of the 2/3 majority and 1/3 minority acetate orientations [3]. The slightly tilted configuration evidenced here is consistent with theoretical work [25], although it is slightly larger than the figure derived by Gutiérrez-Sosa et al of 0° ± 5° [3]. A similarity of results is expected since as noted above, it is very likely that the surface studied in the earlier work was actually h-TiO_2(110).

The data were also fitted with contributions explicitly from two acetate geometries to represent the majority and minority configurations, with the O-C-O plane in the [001] or $[1\bar{1}0]$ azimuth, respectively. This results in the fits shown in Figure 7(b), which indicates a 73% contribution from the majority configuration in good agreement with the earlier study

[3]. The tilt angle of the C-C bond away from the surface normal is 20° ± 4° for this configuration, while that for the minority configuration is 15° ± 14°. Note that the fits in Figure 7(a) and (b) are the same, which is expected.

NEXAFS data were then recorded from the $TiO_2(110)$ surface while exposed to an acetic acid pressure of 10^{-2} Torr. Based on the analysis of the APPES results described above, the resulting overlayer contains 0.5 ML acetic acid in addition to the first 0.5 ML of acetate. As in the case of the 0.5 ML acetate experiment, two data sets were recorded at two angles of incidence ($\theta = 90°$ and $\theta = 19°$). The resulting difference spectra (with acetic acid – clean surface), normalized to the absorption step-edge are displayed in Figure 8. The π^* resonance again appears at 288.8 eV but now has three contributions: the first 0.5 ML of acetate, the second layer 0.5 ML of acetic acid and a contribution from acetic acid in the gas phase. The last of these can be assessed from the APPES results, which indicate that the relative contribution to the C 1s signal is ~3% at 10^{-2} Torr. This value has been used as the contribution to the X-ray absorption step edge. This makes the reasonable assumption that the relative C KLL Auger cross sections are the same and that the relative gas phase contribution is not significantly modified by the change in electron kinetic energy from about 110 eV for APPES to 249 eV for APNEXAFS. It also ignores the small difference in the gas-phase induced attenuation of the gas phase and surface photoemission intensity. There will be a 3% contribution to the π^* peak intensity at the magic angle intensity (β=54.7°) in the normal incidence data [24]. This is sufficiently small to be ignored.

The π^* intensities were obtained in the same manner as described for the 0.5 ML acetate data. Two equal contributions were assumed from acetate in the first layer and from acetic acid in the ‘second’ layer based on the APPES results, with only one configuration from each. To limit the number of variables, the acetate geometry is taken to be that found for 0.5 ML single domain acetate (a two domain description would produce the same result), with only the acetic acid geometry varied as a single domain. Analysis of the data along the lines described above indicates that at 10^{-2} Torr the C-C bond is apparently tilted 21° ± 4° away from the surface normal and the O-C-O plane twisted 50° ± 2° out of the [001] azimuth). This suggests a similar geometry to the acetate contact layer as shown in Figure 4.

The physisorbed species depicted on the left side of Figure 4 is the majority species, with the molecular plane lying along the [001] azimuth. This would give a feature in STM in the centre of a four-fold hollow of chemisorbed acetate molecules if it were positioned out-of-phase along [001]. This was the position determined for second layer physisorbed acetic acid at 148 K [11]. As for the minority species on the right hand side of Figure 4, this could give rise to an STM feature in a similar position, depending on the image contrast. Both bond geometries shown in Figure 4 differ from those suggested in Ref. 11, although this was on the basis of STM data alone.

4. Conclusions

A saturation coverage of acetate resulting from acetic acid adsorption on h-TiO_2(110) was examined with PES and NEXAFS under UHV conditions as well as with the sample held at pressures of 10^{-5}-10^{-1} Torr of acetic acid. PES analysis of the surface revealed an additional layer containing acetic acid that increased in coverage before saturation at 0.5 ML, which is the same coverage as the first layer of acetate. The intensity of the peak associated with the methyl carbon in PES is roughly twice that of that carboxyl(ate) carbon for both layers, which suggests that the second layer is composed of molecules with their methyl group oriented away from the surface, as is known to be the case for the first layer.

NEXAFS revealed a slight tilt out of the polar normal (20.1° ± 4.2°) in the $[1\bar{1}0]$ direction of the majority configuration in the UHV case, where only 0.5 ML of acetate is present. When the sample was examined at higher acetic acid pressure the additional layer was seen to orient with a polar angle close to that of the first layer, suggesting a similar orientation relative to the substrate.

Disclosure statement

The authors declare no conflict of interest for this work.

Acknowledgements

We are grateful to Jo Stöhr for useful discussions. This work was supported by the European Research Council Advanced Grant ENERGYSURF (G.T.), European Cooperation in Science and Technology Action CM1104, EPSRC (UK) through grants EP/G067384/1, EP/J008869/1, and the Alexander von Humboldt Stiftung (Germany). G.T. is also supported by the Royal Society through a Royal Society Wolfson Research Merit Award. HB and MS acknowledge support by the Director, Office of Science, Office of Basic Energy Sciences, and by the Division of Chemical Sciences, Geosciences and Biosciences (HB) of the U.S. Department of Energy at LBNL under Contract No. DE-AC02-05CH11231.

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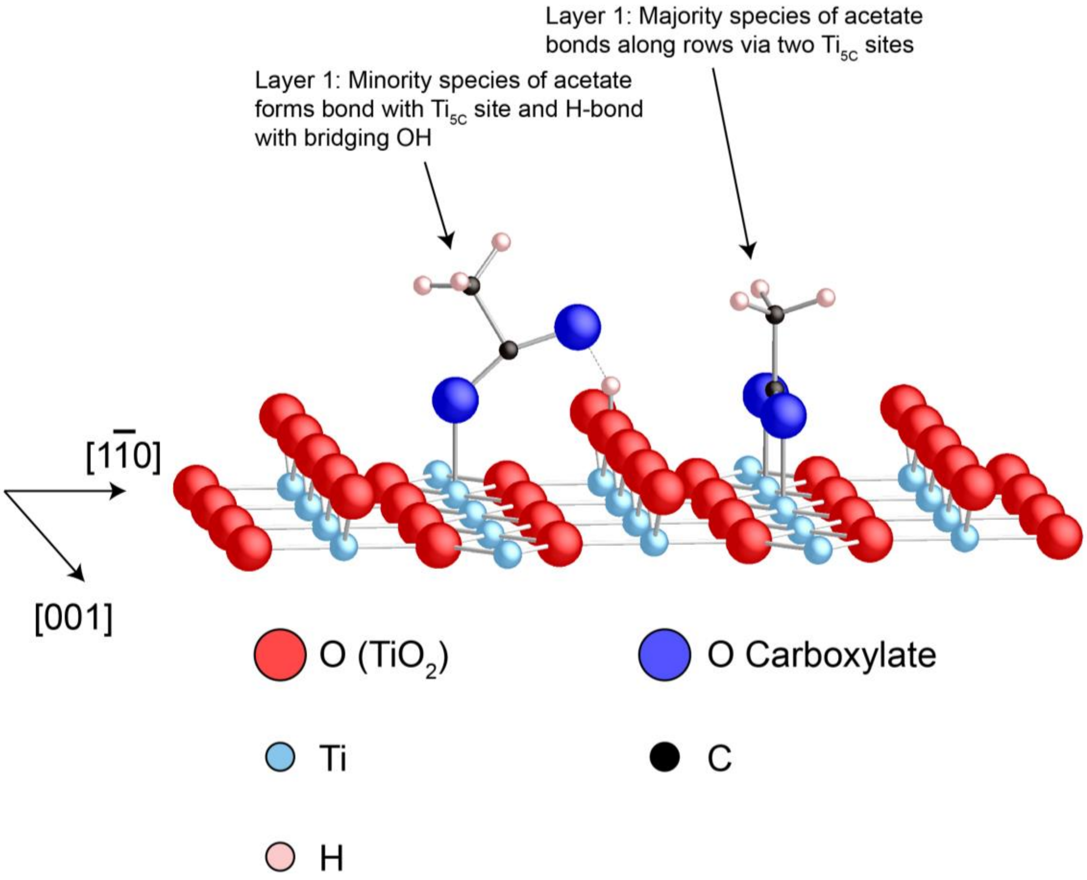

Fig. 1. Ball and stick model illustrating the orientation of 0.5 ML acetate on the TiO_2(110) surface as determined by NEXAFS. The configuration is formed following deprotonation of acetic acid at the metal oxide surface. Additional bridging hydroxyls are formed on the surface.

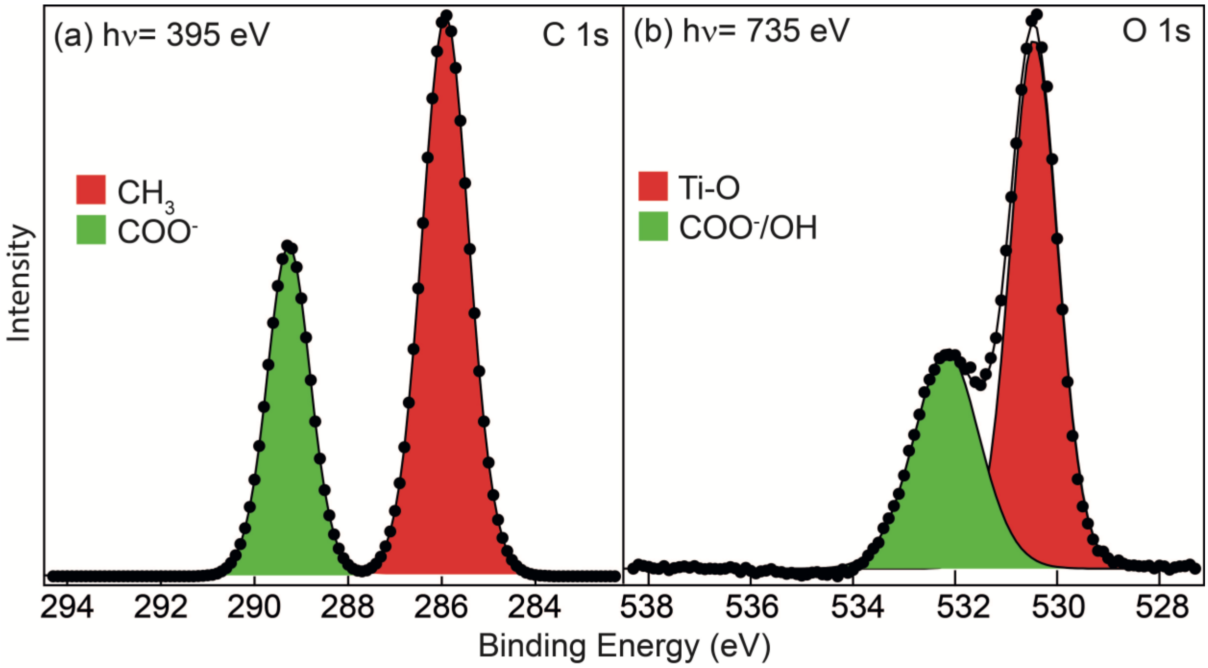

Fig. 2. (a) C 1s and (b) O 1s photoemission spectra from $CH_3COO^-/TiO_2(110)$ recorded at normal emission with incident photon energies of 395 eV and 735 eV, respectively. Circles are experimental data and numerical fits to the data are represented by a solid line. In (a), the peak at BE = 285.9 eV arises from C atoms from the carboxylate (COO) group of acetate (highlighted in red), while that observed at 289.3 eV arises from C atoms contained in the methyl (CH_3) group of the same ion (highlighted in green). In (b), apart from the O 1s peak originating from the substrate (BE = 530.4 eV, highlighted in red), an additional peak centred on BE = 532.1 eV (highlighted in green) arises from the two oxygen atoms in the carboxylate group of the acetate ion. This peak is convoluted with that associated with surface hydroxyls.

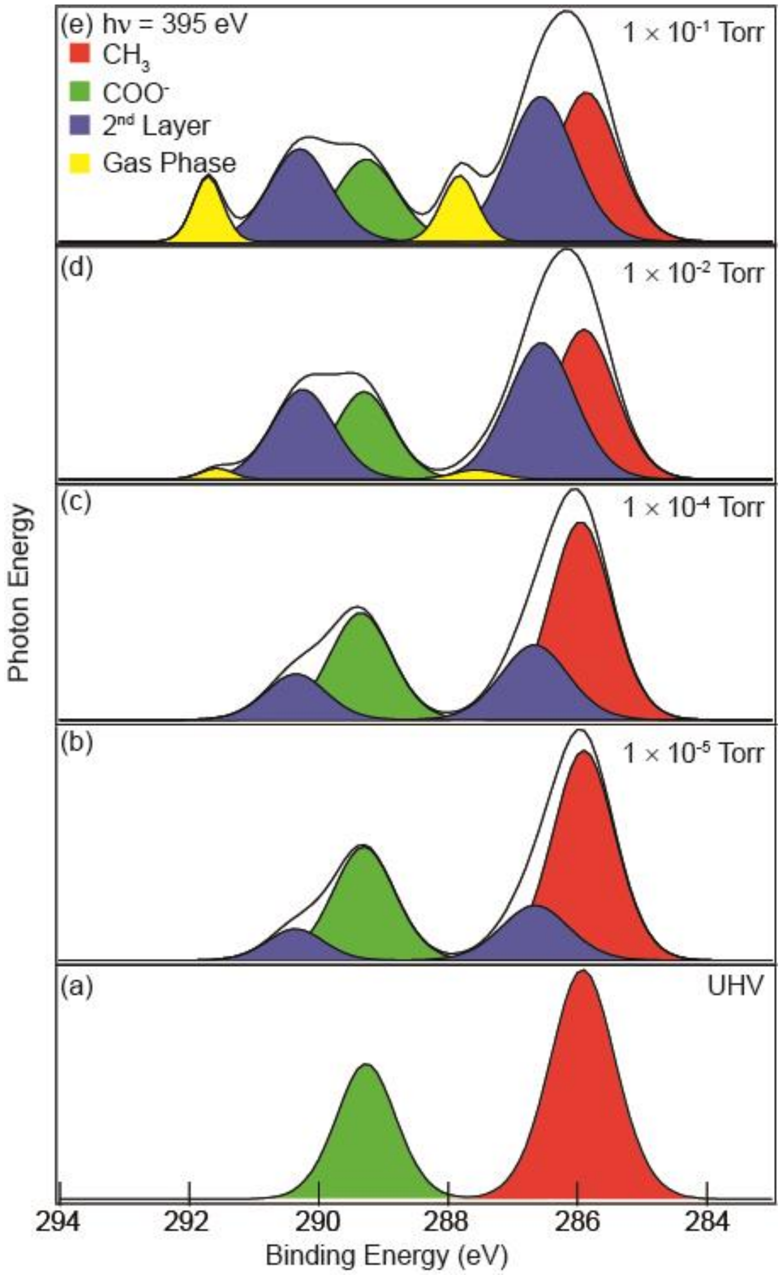

Fig. 3. C 1s normal emission photoemission spectra (hν = 395 eV) obtained from; (a) the TiO_2(110) surface following saturation with 0.5 ML of acetate and the TiO_2(110) surface held under (b) 10^{-5}, (c) 10^{-4}, (d) 10^{-2} and (e) 10^{-1} Torr of acetic acid pressure. Data were recorded between 273 K and 266 K as the pressure of acetic acid increased. The spectra have been normalized to the highest peak, at about 286 eV binding energy. This is attenuated at higher pressures, for example by about 10% at 10^{-2} Torr.

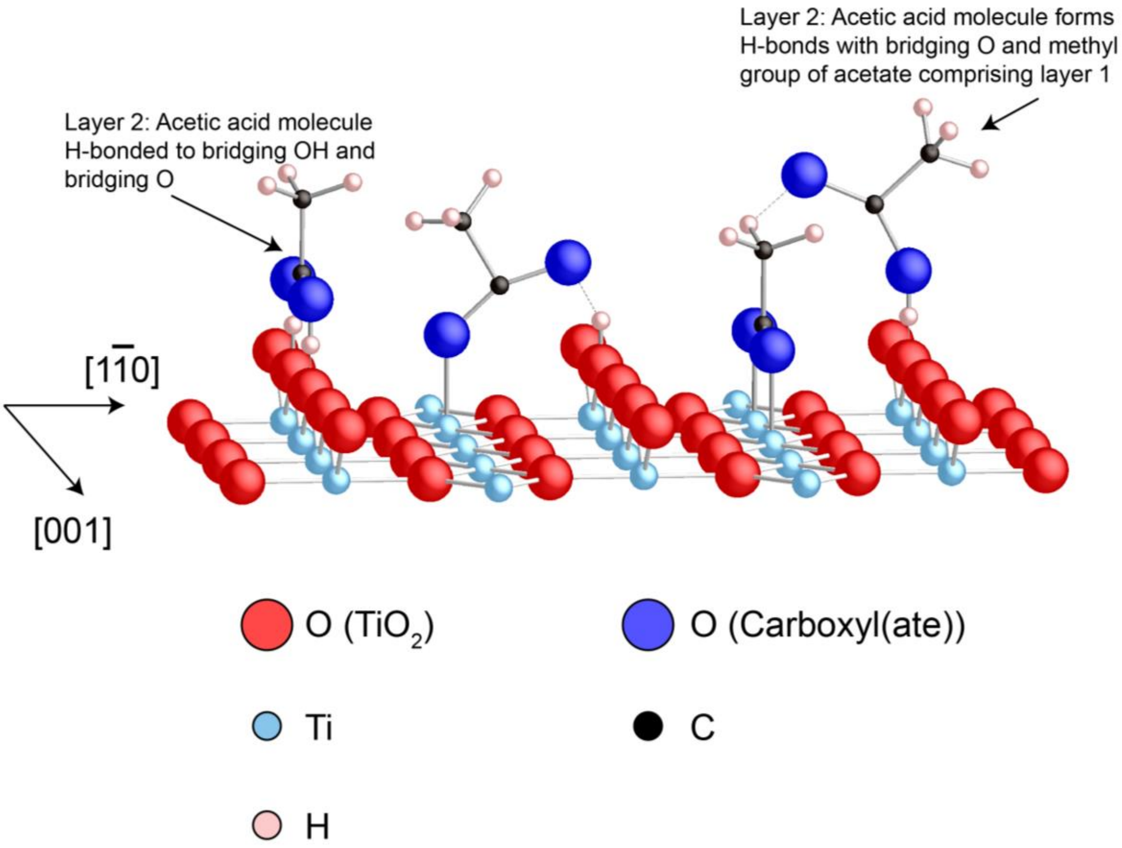

Fig. 4. Ball and stick model showing the geometries proposed for second layer acetic acid on the basis of the APPES and APNEXAFS results. The second layer appears when the system is held under higher partial pressures of acetic acid ($\geq 10^{-2}$ Torr).

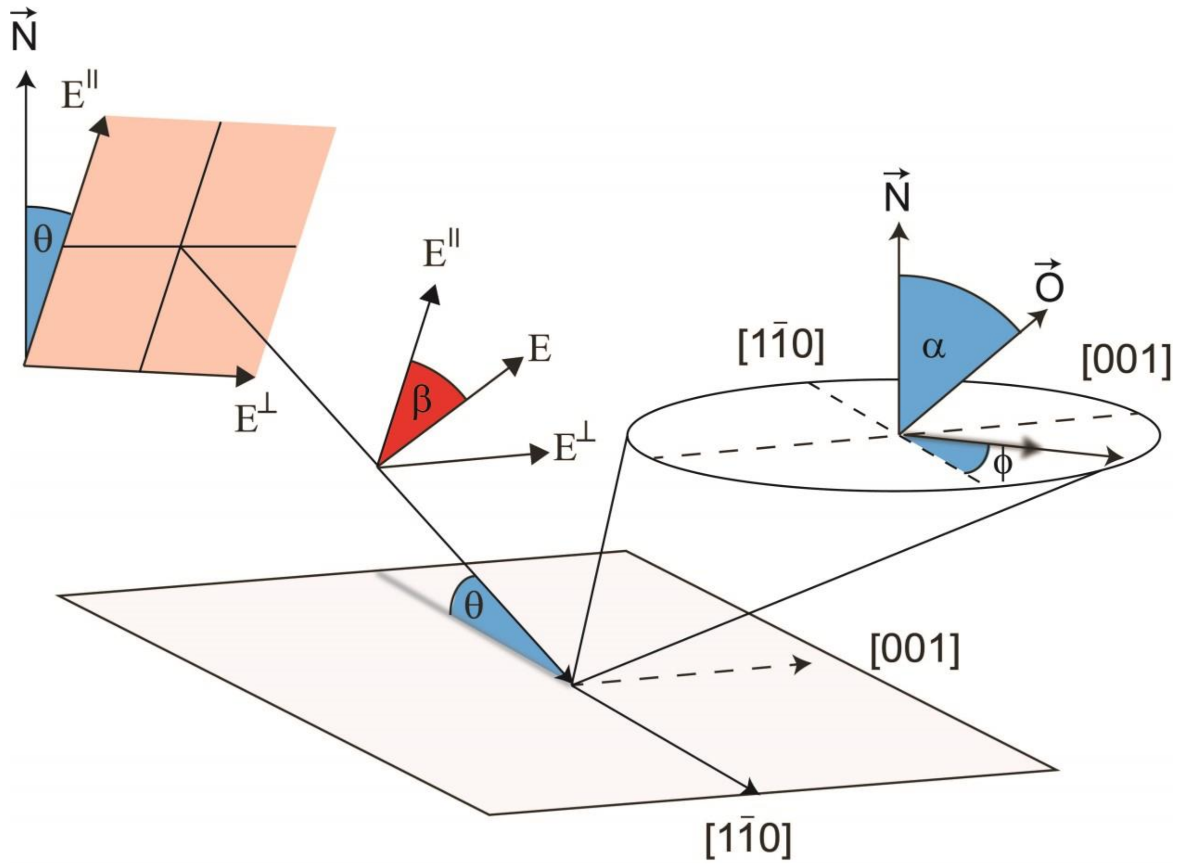

Fig. 5. Schematic describing the coordinate systems of the incident photon beam, the $TiO_2(110)$ surface and the vector $\vec{O}$, which describes the orientation of the molecular orbital under examination. The orientation of this vector is defined by its polar angular separation from the surface normal, α, and the azimuthal angular separation from the incident beam direction, ϕ. $E^{||}$ ($E^{\perp}$) is the component of the *E*-vector parallel (perpendicular) to the plane of incidence. β is the angle between $E^{||}$ and the *E*-vector.

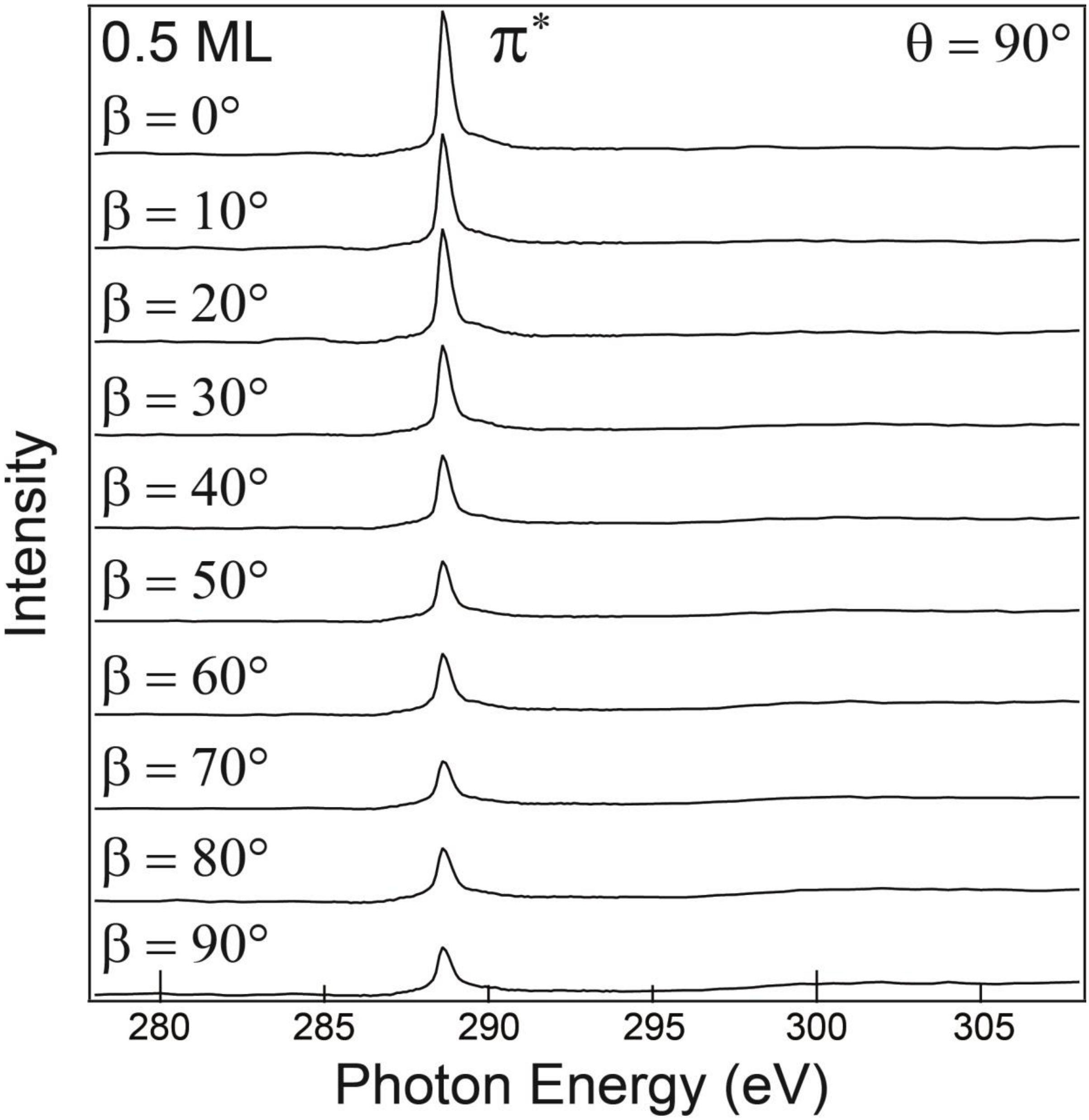

Fig. 6. C K-edge NEXAFS difference spectra of the h-TiO_2(110) surface following saturation with 0.5 ML of CH_3COO^-, recorded at normal incidence. Spectra were recorded as the *E*-vector of the incident photon beam was rotated from the $[1\bar{1}0]$ azimuth (β=0°) to the [001] azimuth (β=90°). Spectra are normalized to the X-ray absorption step-edge.

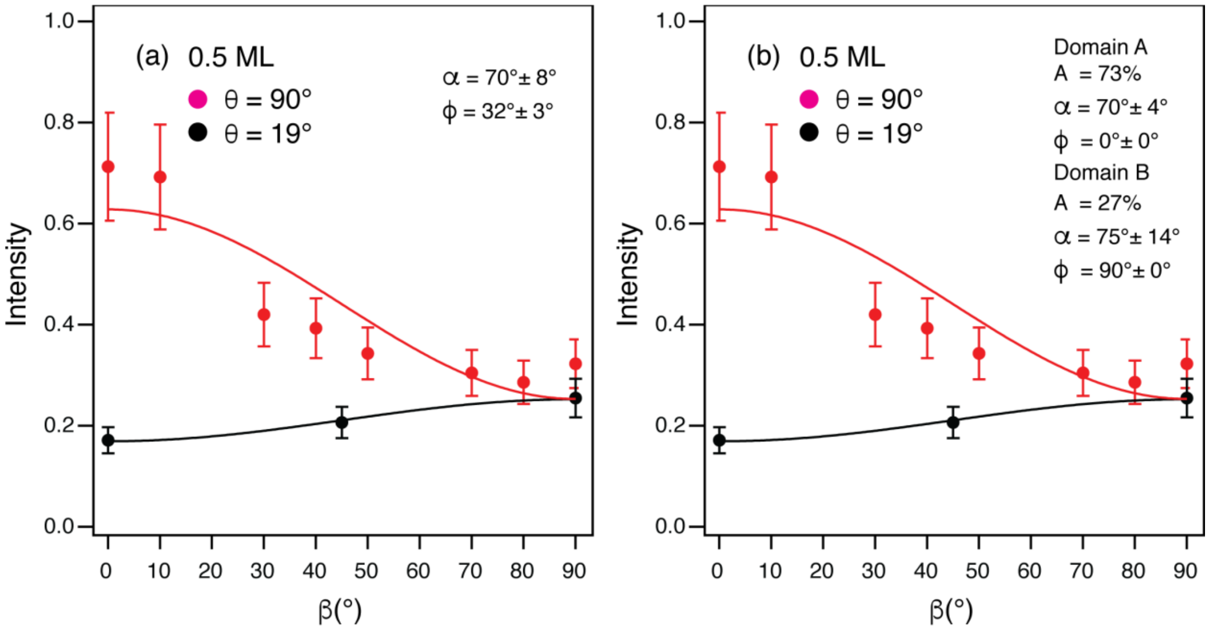

Fig. 7. Best fit to the 0.5 ML acetate on TiO_2(110) NEXAFS data shown in part in Figure 6. (a) Normalized integrated intensity of the C 1s → π* transition as a function of angle of polarization of the E-vector, □, determined at two different incident angles: □=90° (upper, red) and 19° (lower, black). Error bars represent experimentally acquired data and solid lines represent numerical fits to the data using the appropriate equations adapted from ref. 22. Both sets of data (θ = 90˚, 19˚) were fit simultaneously with optimization of the tilt (α) and twist angles (ϕ). (b) As for (a) but with two domains of CH_3COO^- co-occupying the substrate. The best fit has 73% of the molecules in domain A, in which the carboxylate plane is orientated along [001] and tilted 20±4° out of the surface normal. The remaining 27% of molecules are orientated along [1$\bar{1}$0]. The molecules comprising this minority species are tilted 15±14.0° away from the surface normal.

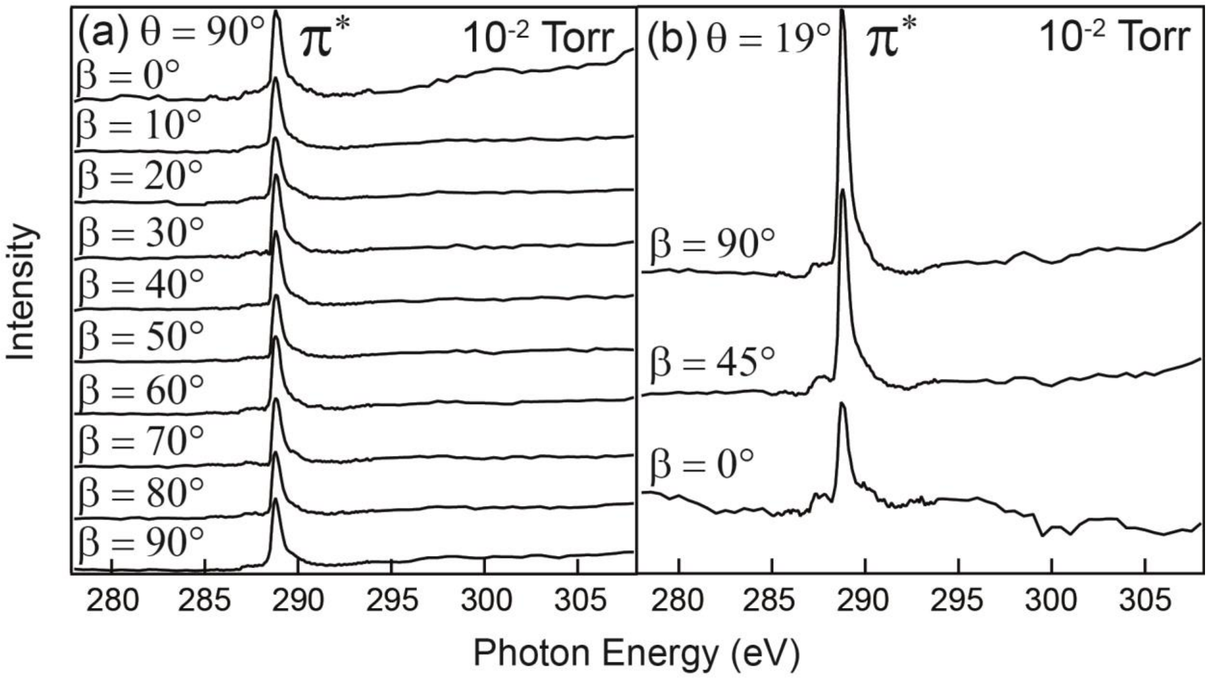

Fig. 8. C K-edge difference spectra recorded from h-TiO_2(110) at 268.5 K at an acetic acid pressure of 10^{-2} Torr and incidence angles of (a) θ = 90° and (b) θ = 19°. Spectra were recorded as the *E*-vector of the incident photon beam was rotated from the $[1\bar{1}0]$ azimuth (β=0°) to the [001] azimuth (β=90°). Spectra are normalized to the X-ray absorption step-edge.

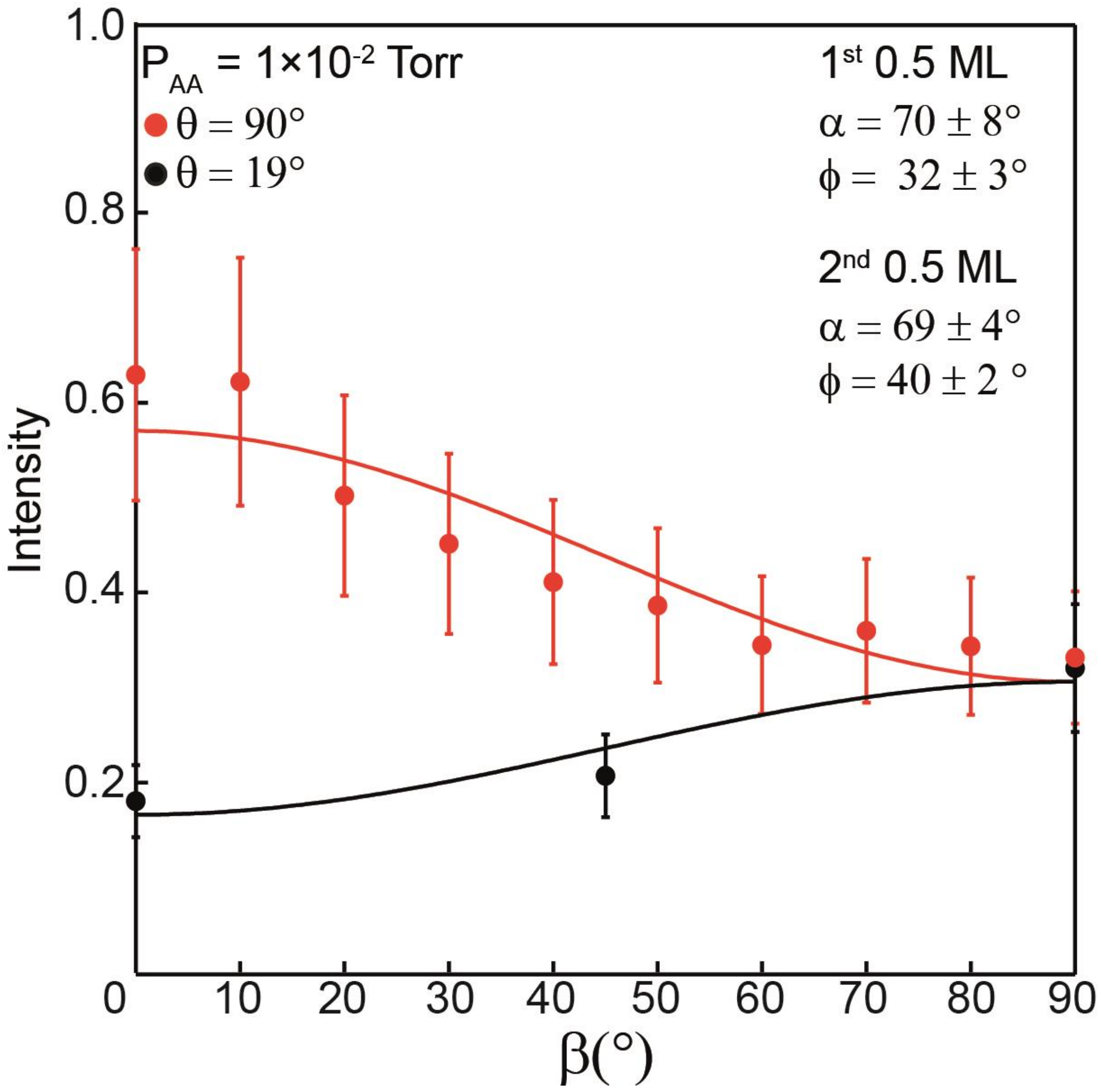

Fig. 9. As for Figure 7(a) but with data from Figure 8. The geometry of the first layer acetate was taken to be unchanged from that at 0.5 ML coverage. On this basis the second layer geometry closely resembles that of the first layer.