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Structural study of adsorption of isonicotinic acid and related molecules on rutile TiO₂(1 1 0) II: XPS

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Abstract

The adsorption of monolayers of the pyridine-carboxylic acid monomers (isonicotinic acid, nicotinic acid, and picolinic acid) on rutile TiO₂(1 1 0) has been studied by means of X-ray photoemission spectroscopy. An investigation of the O 1s spectra shows that the molecular carboxylic groups are deprotonated and, hence, that the molecules bind to the surface in a bidentate mode. Moreover, the binding energy of those core levels that are related to the pyridine ring atoms shift as a function of molecule relative to the substrate O 1s and Ti 3p levels, while the position of the core levels related to emission from the carboxylic group are constant relative to the substrate levels. The molecule-dependent shifts are attributed to local intermolecular interactions that determine the proximity of adjacent molecular rings and thus the core-hole screening response of the neighbouring molecules. We propose a simple molecular arrangement for each case which satisfies the known constraints.
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1. Introduction

The three monomeric pyridine-carboxylic acid isomers (C₅H₄NCOOH, cf. Fig. 1) and benzoic acid (C₆H₅COOH) form a series of molecules that differ from each other by a change in one parameter only, i.e, the position of the nitrogen atom or the exchange of the nitrogen by a C–H group. This makes the series interesting for an investigation of the impact of these parameter changes on the characteristics of the molecular systems. This is especially true for environments in which the molecules interact with other components such as surfaces and other molecules, since an understanding of the mechanisms defining the

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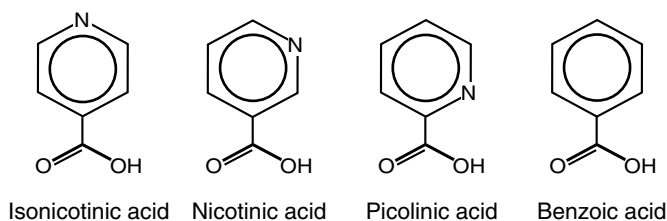
Fig. 1. Schematics of the pyridine-carboxylic acids and benzoic acid. Unspecified vertices represent either carbon atoms or carbon atoms with associated hydrogen atoms. For isonicotinic acid, the nitrogen atom is in the para, for nicotinic acid in the meta, and for picolinic acid in the ortho position.

characteristics help to facilitate the tailoring of molecular systems for particular applications.

The present paper is the second of two which are concerned with the structures of monolayers of the pyridine–carboxylic acid monomers and benzoic acid on rutile $TiO_2(1\,1\,0)$. The first paper [1], in the following referred to as "I", dealt with X-ray absorption spectroscopy (XAS) and scanning tunneling microscopy (STM) results. There it was found from XAS that the monolayer preparations of the pyridine-carboxylic acid monomers and of benzoic acid contained a minimum of two adsorbate species distinguished by the set of molecular angles which described them. While the exact number of different pyridine/phenyl ring orientations could not be determined, the measurements gave clear evidence that the orientations were not completely random. When assuming the existence of exactly two species, their polar angle—measured from the surface normal to the ring plane—did not exceed 40°. It could be inferred from the observed polar scan behaviour that this result should semiquantitatively also hold for a larger number (>2) of different species. The existence of at least two different species was attributed to adsorbate–adsorbate interactions that also could be identified from the STM measurements, and which for benzoic acid were previously discussed at some length based on STM and other data [2,3].

The presentation of the X-ray photoemission spectroscopy (XPS) data below is divided into two parts. First, the O 1s spectra are shown to provide evidence for a bidentate bonding mode of the molecules. Second, the N 1s, C 1s, and O 1s data are investigated for both mono- and multilayers of the pyridine-carboxylic acids. A comparison of these shows that the monolayer spectra are strongly influenced by adsorbate–adsorbate interactions, which manifest themselves in the spectra as chemical shifts. In order to reach this conclusion the total system screening response in the final state has to be considered. We argue that the excellent screening capability of the pyridine ring π-system leads to a redistribution of the positive charge caused by the core-ionisation, resulting in similar environmental responses for all three molecules. The observed trends are finally attributed to the variations in screening response of neighbouring molecules due to structural differences, which are intimately connected to the location of the nitrogen atom for each species.

2. Experimental

The XPS experiments were carried out at beamlines I511 and D1011 at MAX-Lab. The details of the experimental setup can be found in I. There the crystal and monolayer preparation procedures have also been described. In short, the crystals used in the experiments were initially made conducting by annealing in 1×10^{-6} Torr oxygen at 700 °C. During this they acquired a light blue colour, which was the same during all measurements as judged by eye. The surface was prepared by repeated cycles of Ar sputtering and annealing in 1×10^{-6} Torr oxygen. The outcome of this procedure was regularly checked by LEED, which exhibited a 1×1 pattern.

The molecules were sublimated from a thermal evaporator (for powder temperatures see part I). The monolayers were prepared by keeping the

samples at 200 °C, which in all cases prevented the formation of more than one molecular layer. The monolayers were ordered as could be observed from the angle dependence of the X-ray absorption spectra (part I). LEED patterns of the isonicotinic acid monolayer exhibited a (1×1) structure. From the STM results (part I) one would rather expect a (2×1) overlayer. We therefore suggest that the LEED experiment might have sampled the substrate instead of the molecular overlayer due to either insufficient long-range order of the molecular overlayer or due to electron beam damage induced by the electron flux from the LEED instrument. Multilayers were achieved by cooling the sample to temperatures between −95 and −110 °C during sublimation and experiment.

The spectra were calibrated in the following manner: for the monolayer preparations the spectra were aligned at the O 1s substrate peak at 530.05 eV relative to the conduction band (CB) edge of the TiO_2 substrate. This value was obtained from the O 1s ionisation potential for a monolayer of bi-isonicotinic acid on $TiO_2(1\,1\,0)$ [4] and an estimate for the position of the CB edge derived from a valence spectrum and the size of the optical bandgap as described in Ref. [5]. Alternatively, the spectra could be aligned at the Ti 3p substrate level and related to the CB edge in the same manner. Both calibrating procedures delivered results consistent within 0.05 eV for the pyridine-carboxylic acids and 0.1 eV for benzoic acid, respectively. For the thick films, the spectra were aligned at the C 1s carboxylic peak and then adjusted to the ionisation potential of bi-isonicotinic acid. Since only relative differences in ionisation potential will be considered in the following, these calibrations supply all necessary information for both the mono- and the multilayers.

3. Results and discussion

3.1. O 1s XPS: bidentate adsorption

In Fig. 2 the O 1s X-ray photoemission spectra obtained at 600 eV photon energy (benzoic acid and clean surface: 700 eV) are shown. We include data for bi-isonicotinic acid published previously [4] and for a clean TiO_2 surface for comparison. The spectral parameters are given in Table 1. For both the monolayer and the thick film case the results are similar for the different molecules. The thick film spectra contain two chemically shifted peaks due to the two different oxygen atoms of the protonated carboxylic group, in line with the findings for gaseous benzoic acid [6]. The spectra for the pyridine-carboxylic acid monomer multilayers do not contain any spectral signature of the substrate at 534.8 eV in contrast to the present case of bi-isonicotinic acid [4], and from the signal-to-noise ratio and the mean free path for electrons with a kinetic energy of approximately 70 eV we estimate the thickness of the monomer films to be at least 40 Å (bi-isonicotinic acid 20 Å).

The monolayer spectra consist of two peaks. The lower binding energy peak is—in accordance with the case of bi-isonicotinic acid and the observed angular intensity dependence—attributed to the substrate oxygen atom. The existence of only one molecular peak at 531.5 eV (benzoic acid), 531.6 eV (picolinic acid), and 531.7 eV (isonicotinic and nicotinic acids), respectively, indicates negligible differences in the local chemical environment of the oxygen atoms, and thus that the carboxylic group is deprotonated. Following the discussion for bi-isonicotinic acid [4,7] we propose a 2M-bidentate (bridge) bonding geometry (cf. Fig. 7(b)). This interpretation is supported by evidence for dissociative adsorption in a bridge geometry of formic acid [8–15] and acetic acid [2,3,16], the proposed geometry for benzoic acid [2,3] on $TiO_2(1\,1\,0)$, and the results of the STM investigation discussed in I.

The present results cannot clarify the position of the dissociated protons. There appear to be two principal possibilities, namely, (a) the adsorption of the protons on the bridging oxygen atoms, and (b) the desorption of water formed from the molecular protons and surface oxygen atoms. The latter process would, however, give rise to an increase in defect state intensity that can be observed at energies above the valence band edge. Since we have not observed such a spectral change we assume that the protons bind to the surface as proposed in possibility (a). This assumption is in agreement with theoretical results [17,18]. The
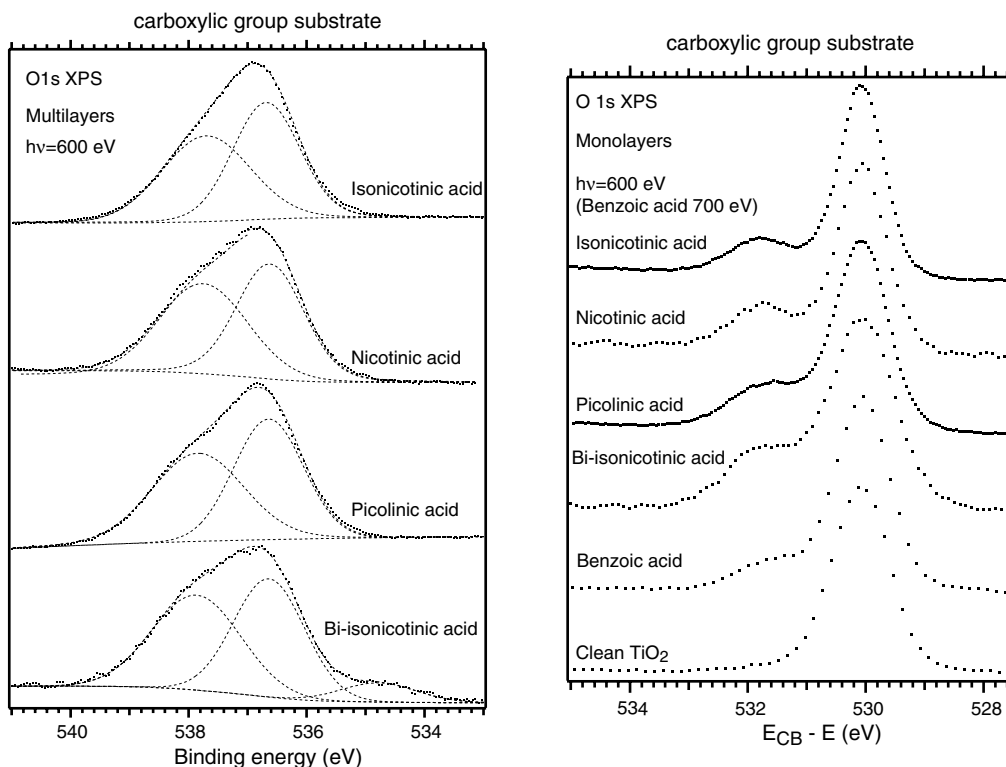
Fig. 2. O 1s photoemission spectra for the indicated preparations. The bi-isonicotinic acid data were taken from Ref. [4]. The energies of the monolayer spectra are referenced to the CB edge E_{CB}. For the monolayer spectra the splitting between the substrate and carboxylic peak ranges from 1.4 eV for benzoic acid to 1.5 eV for picolinic acid, and 1.6 eV for the isonicotinic, nicotinic, and bi-isonicotinic acids. For the thick film the splitting between the two molecular peaks is smallest for isonicotinic acid with 1.0 eV, while it amounts to 1.2 eV for nicotinic and picolinic acid, and 1.3 eV for bi-isonicotinic acid. The component at 534.8 eV for the bi-isonicotinic acid thick film spectrum is related to the substrate oxygen, indicating that the film is somewhat thinner (thickness ∼20 Å) than for the other molecules (thickness at least 40 Å). The overall instrumental resolution (photon energy and electron analyser) was approximately 250 meV except for the samples of benzoic acid, bi-isonicotinic acid, and the clean surface. For these it was ≈350 meV (benzoic acid and bi-isonicotinic acid) and ≈400 meV (clean surface).

Table 1
Parameters for the O 1s spectra (Fig. 2)

	Isonicotinic acid	Nicotinic acid	Picolinic acid	Benzoic acid	Bi-isonicotinic acid
Peak separation Δ, multilayer	1.02	1.13	1.20		1.23
Position carboxylic peak (C), monolayer	531.70	531.71	531.58	531.54	531.70
Relative to the isonicotinic acid position	0	+0.01	−0.12	−0.16	0
Position substrate peak (S), monolayer	Adjusted to 530.05 eV				
Δ(C, S), monolayer	1.65	1.64	1.51	1.49	1.65

All values are in eV. The experimental uncertainty of the relative energies is estimated to be 0.02 eV for the monolayers and 0.1 eV for the multilayers.

adsorption of protons to the bridging oxygens could lead to a shift in the O 1s core level. Since we observe two peaks only, one of which we have

attributed to the substrate and the other to the molecular oxygen atoms, we speculate that this shift either is not very large or that it is comparable

to the shift between the substrate and adsorbate O 1s levels.

3.2. Core level binding energy shifts: evidence for neighbouring molecule interactions

The following discussion is primarily aimed at an understanding of the spectral behaviour of the pyridine-carboxylic acid monomers, while the benzoic acid and bi-isonicotinic acid spectra provide supporting information. In this discussion it will be crucial to distinguish between spectral features related to photoemission from the carboxylic group and from the pyridine ring. Peaks related to the latter are contained in the C 1s spectra in Fig. 3 (parameters in Table 2) and in the N 1s spectra in Fig. 4 (parameters in Table 3). The O 1s spectrum in Fig. 2, in contrast, is composed of contributions from the substrate and the carboxylic group, only.

3.2.1. Multilayer spectra: similarity of the pyridine ring responses

Concentrating on the multilayer spectra first, it is found that these are very similar to each other

for all three pyridine-carboxylic acids, in particular regarding the energies of all the peaks, but also with respect to the peak widths. The most notable difference is an additional peak in the N 1s spectrum of picolinic acid, which is related to bulk hydrogen bonding [19,20]. Tuning the preparation conditions can suppress the hydrogen bonding by the introduction of disorder in these films. From the intensity of the feature it is judged that the percentage of hydrogen bonded molecules is below 10%. For the following discussion it is important that the separation of the carboxylic C 1s peaks at around 294 eV and the C 1s pyridine ring peaks at around 290.5 eV is almost the same for all three molecules. This finding together with the overall similarity of all the spectra shows the equivalency of the molecules with regard to the photoemission process and, in particular, that the differing distance of the N atom from the carboxylic group does not have any major influence on the energies. This is the first major conclusion of this paper, and establishes that the molecules, and in particular the pyridine rings, act as a single unit. The primary assumption leading up to this conclusion is that disorder in the film prevents accidental
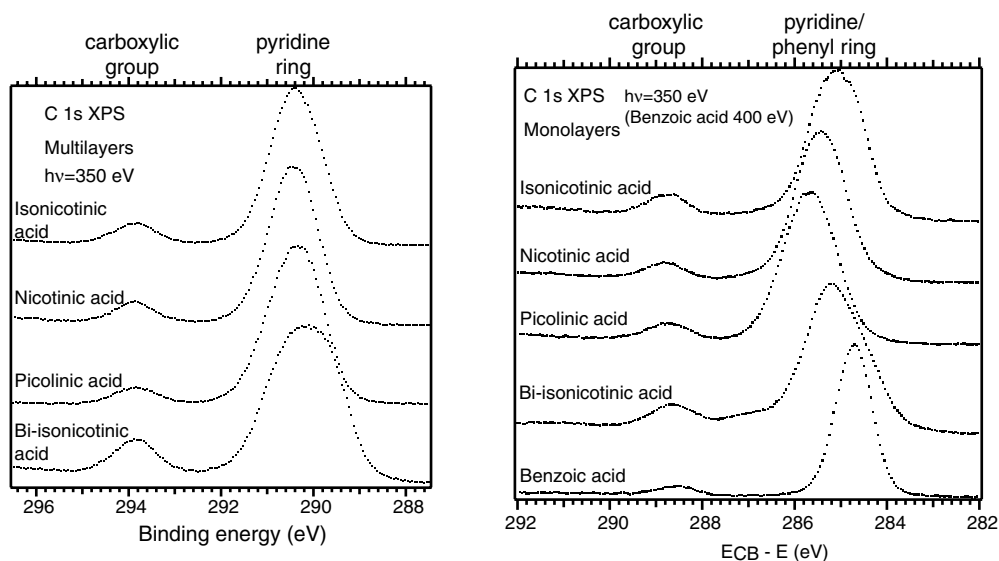

Fig. 3. C 1s photoemission spectra for the indicated preparations. The high-binding energy peak at 294 eV (monolayers 288.5 eV) corresponds to the carboxylic group while the main peak is due to emission from the ring C 1s levels. The overall instrumental resolution (photon energy and electron analyser) was approximately 180 meV except for benzoic acid and bi-isonicotinic acid, for which it was 230 and 315 meV, respectively.

Table 2
Parameters for the C 1s spectra (all values in eV)

	Isonicotinic acid	Nicotinic acid	Picolinic acid	Benzoic acid	Bi-isonicotinic acid
Position carboxylic peak, monolayer	288.78	288.80	288.78	288.55	288.66
Relative to the isonicotinic acid position	0	0.02	0	−0.23	−0.12
Position main peak, monolayer	285.11	285.39	285.63	284.74	285.19
Relative to the isonicotinic acid position	0	0.28	0.52	−0.37	0.08
Peak separation Δ, monolayer	3.67	3.41	3.15	3.81	3.47
Peak separation Δ, multilayer	3.50	3.45	3.45		
FWHM carboxylic peak, monolayer	0.94	0.94	0.99	0.96	1.02
FWHM main peak, monolayer	1.35	1.30	1.37	0.90	1.5 (0.1)
FWHM carboxylic peak, multilayer	1.05	0.98	1.12		
FWHM main peak, multilayer	1.31	1.25	1.39		

The experimental uncertainty of the positions amounts to about 50 meV.
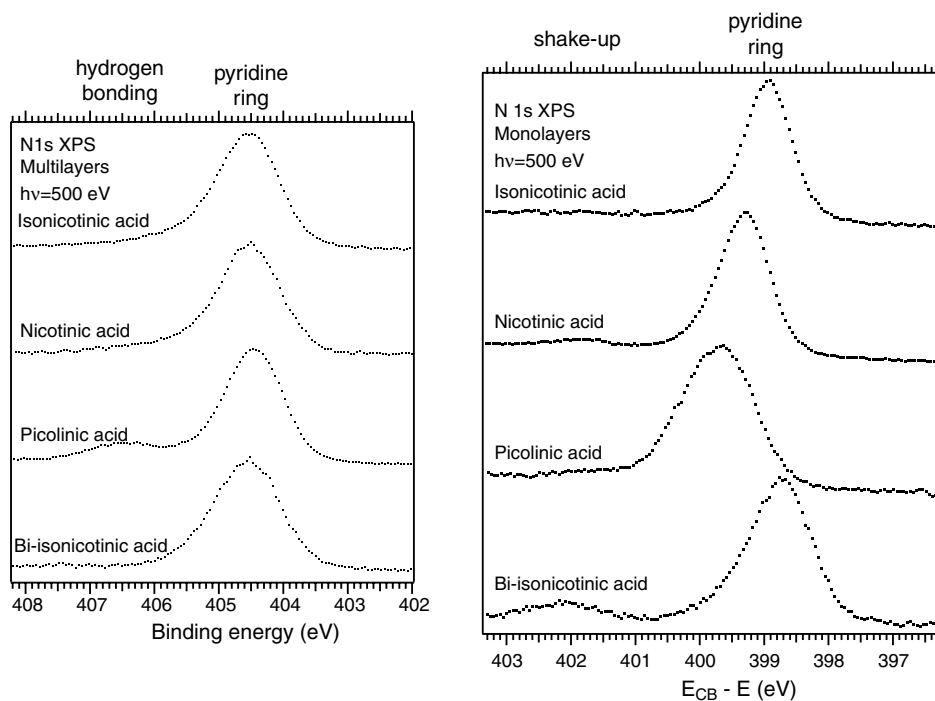

Fig. 4. N 1s photoemission spectra. The bulk molecules in the picolinic acid multilayer are partly hydrogen-bonded to adjacent moelcules [19,20] which gives rise to the structure at 406.5 eV, while the main peak at 404.5 eV is traced back to emission from non-hydrogen-bonded species. Besides the main peak an additional feature is observed at approximately 402 eV for the monolayers. For the monomers, it appears most clearly for nicotinic acid, but is also present in the isonicotinic acid and picolinic acid spectra. It is tentatively assigned to a shake-up as discussed in the text. The overall instrumental resolution (photon energy and electron analyser) was approximately 230 meV (350 meV for bi-isonicotinic acid).

cancellation of differing intramolecular screening terms by intermolecular terms, i.e., that the inter-molecular terms are averaged to the same result

for all three molecules. We attribute the equivalent response deduced from this observation to the ability of the molecular π-system to efficiently

screen a core-hole, which can be rationalised from the abilities of such systems to redistribute the valence electrons [21–23].

3.2.2. Monolayer spectra: molecule-dependent binding energy shifts

A different situation is encountered for the monolayer spectra. While the peaks related to the carboxylic groups in the O 1s (Fig. 2) and the C 1s spectra (Fig. 3) are located at the same energies for all three pyridine-carboxylic acid isomers as in the multilayers, the pyridine ring peaks in the N 1s (Fig. 4) and C 1s (Fig. 3) spectra have different energies with an ordering (from highest to lowest binding energy) picolinic acid–nicotinic acid–isonicotinic acid. [1,2] In contrast to the changes found for the energies, the peak widths, with the exception of the N 1s peak of picolinic acid, are found to be essentially unchanged from the multilayers. We ascribe the relatively large widths of the C 1s main lines of approximately 1.30 eV to

chemical shifts between the different carbon atoms in combination with vibrational broadening, an interpretation that is supported by the considerably narrower C 1s peak of benzoic acid with its chemically near-equivalent phenyl ring carbon atoms as well as the much broader C 1s peak of bi-isonicotinic acid, which contains a larger number of inequivalent carbon atoms.

3.2.3. Monolayer angular dependence: pyridine ring component assignment

To further elucidate the last point, we examine the angle dependence of the monolayer C 1s spectra. A sequence of XPS spectra measured at different electron detection angles is presented in Fig. 5 for isonicotinic acid, while Fig. 6 contains angle-resolved data for nicotinic acid, picolinic acid, and benzoic acid (observe the different normalisation procedures described in the figure captions). For isonicotinic acid the relative intensity of the low-binding energy side of the pyridine ring peak is reduced upon going to more grazing emission angles. Given the evidence for (at least) two molecular orientations with respect to the substrate in I, and the monotonic trends observed in the present angle dependencies, we rule out significant photoelectron diffraction effects in the present case. Since the sampling depth decreases for these angles, this means that the low-binding energy part of the peak (284–285 eV) is related to emission from pyridine ring carbon atoms that lie closer to the substrate than those that emit at somewhat higher binding energy (285–286 eV). [3] The near-upright geometry of the pyridine-carboxylic acid adsorbates in general and isonicotinic acid in particular (cf. I) suggests that the high-binding energy part can be attributed to emission from atoms 1 and 5, which are the direct neighbours of the nitrogen atom and equivalent by symmetry, and the low-binding energy part to

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[1] Note, however, that the calibration procedure does not result in absolute binding energies relative to the vacuum level. Properly expressed, this means that the core level peaks related to the carboxylic group do not shift relative to the substrate O 1s and Ti 3p features, which is in contrast to the behaviour of the pyridine ring components.

[2] As an exception from this general assignment, the additional weak structure at around 402 eV in the N 1s monolayer spectra is constant in energy. One plausible explanation is that this peak is related to a shake-up that involves the carboxylic group and that effectively results in a final state in which the additional positive charge from the photoionisation process has been moved to the carboxylic group/substrate complex in the shake-up process. A corresponding peak is found for bi-isonicotinic acid, although somewhat higher in energy and much larger in intensity. Also this structure is clearly related to the adsorption on the TiO_2 surfaces, since it is not found for the bi-isonicotinic acid multilayer. The difference between the monomer molecules and the bi-isonicotinic acid is probably related to the presence of the link to the second pyridine ring that modifies both the electronic structure which allows for the shake-up process as well as the possibility of different intramolecular screening channels. Taken together, these effects could explain the observed differences. The constant binding energy throughout the molecular series suggests in any case that the final state of this particular feature is more similar in character to the substrate/carboxylic group-related features of the O 1s and C 1s spectra than to the pure pyridine related main peaks of the C 1s and N 1s spectra (see the discussion of the distinctions between these peaks in the main text).

[3] In principal, photoelectron diffraction effects [24] could invalidate the sampling depth argument by substantially changing the observed intensities in certain geometries [25]. Since in the present case the shape modification is consistent over a large range of angles, we conclude that such effects play a minor role at most.

Table 3
Parameters extracted from the N 1s spectra

	Isonicotinic acid	Nicotinic acid	Picolinic acid	Bi-isonicotinic acid
Position, monolayer	398.94	399.33	399.72	398.80
Relative to the isonicotinic acid position	0	0.39	0.78	−0.14
FWHM, monolayer	0.87	0.93	1.30	1.14
Position, multilayer	404.54	404.54	404.45	
Relative to the isonicotinic acid position	0	0	−0.09	
FWHM, multilayer	1.09	1.15	1.04	1.22

All values given are in eV. The experimental uncertainty is about 50 meV. For bi-isonicotinic acid no reliably calibrated spectrum was available, so that the peak position was omitted here.
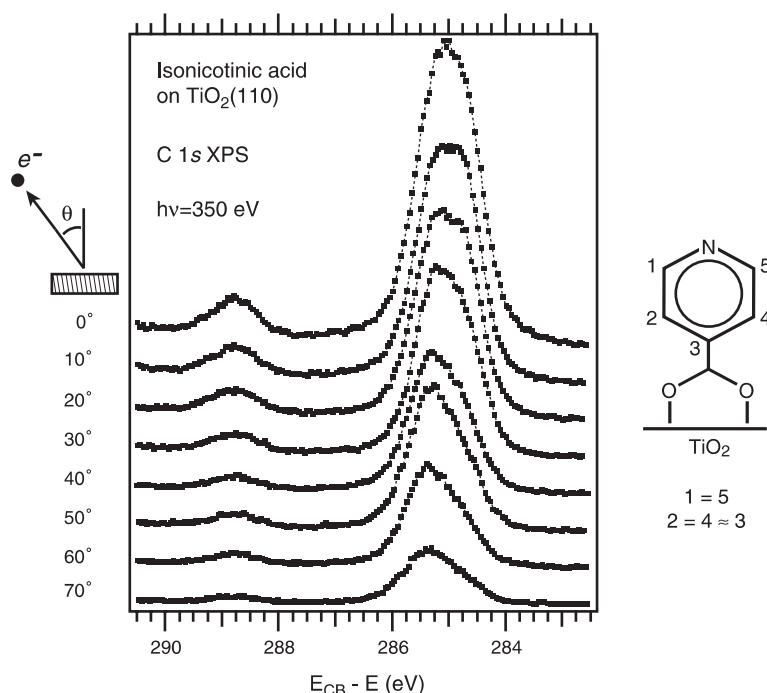

Fig. 5. Angle-dependent C 1s measurement on a monolayer of isonicotinic acid on $TiO_2(1 1 0)$. The emission angle was varied as depicted in the geometry sketch. The spectra are normalised to the photon intensity. The geometrical, and hence binding energy, equivalence of the ring C atoms is indicated by the numbers under the sketch of the molecular structure. See the text for discussion.

emission from atoms 2, 3, and 4 (see Fig. 5 for the atom numbering).

The assumption that the C 1s peaks related to the atoms in direct proximity to the nitrogen atom have a higher binding energy than the remaining three C atoms explains the observed angle behaviour in the other compounds, as well. The upright geometry, in conjunction with the N atom not being "on top" of the molecule for nicotinic acid

and picolinic acid, leads to an inequivalency of atoms 1 and 5 on the one side and atoms 2, 3, and 4 on the other with regard to the mean free path. The effective rotation of the pyridine ring as the isomer is varied is thus expected to lead to a disappearance of the relative angle dependence, so that the peaks scale uniformly, as is in fact observed (Fig. 6). Similarly, the absence of any angle dependence for the C 1s spectrum of benzoic acid
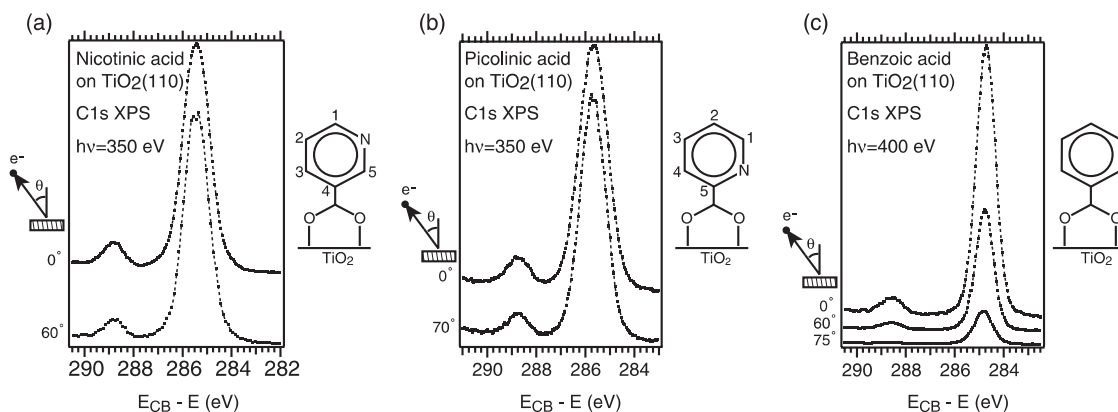
Fig. 6. Angle-dependent C 1s measurements on monolayers of nicotinic acid, picolinic acid, and benzoic acid on TiO$_2$(1 1 0). (a) Nicotinic acid and (b) Picolinic acid: The spectra were normalised to the main peak intensity as the experimental settings were slightly different in the different scans, which is why a photon intensity normalisation was not possible. (c) Benzoic acid: The spectra are normalised to the photon flux. The ring C 1s binding energies are deduced to follow the same trend as in Fig. 5, i.e., determined by the proximity to the N atom. See the text for discussion.

together with the lower width (see above) corroborates the notion of chemically (nearly) equivalent carbon atoms in the absence of a ring nitrogen atom.

3.2.4. Geometric model development

From the discussion above the following points can be established so far:

(1) The constant separation of the N 1s and C 1s peaks, the constant separations of the C 1s carboxylic and pyridine ring components, and the constant widths of these peaks in the (disordered) multilayer suggests that the screening effects are independent of the relative positions of the N atom and the carboxylic groups. This is taken as a sign for the efficient screening of the core-hole by the π-system of the molecule.
(2) In the (ordered) monolayers, the core level peaks related to the carboxylic group maintain a constant separation to the substrate O 1s and Ti 3p peaks.
(3) In contrast, the pyridine ring components in the N 1s and C 1s spectra of the monolayer shift similarly relative to the substrate peaks as a function of the molecule. The peak energies have an ordering, from highest to lowest

binding energy, picolinic acid–nicotinic acid–isonicotinic acid.
(4) The similarly excessive widths of the C 1s peaks related to the pyridine carbon atoms and the observed angle dependence are consistent with a model in which the different carbon atoms have characteristic binding energies depending on the distance from the nitrogen atom, which have roughly the same separations for all three molecules.
(5) The N 1s peak of the picolinic acid monolayer is considerably broader than the corresponding multilayer peak. In all other cases, the widths of the monolayer and multilayer peaks are comparable.

Points 1 and 3 indicate that interactions among *structurally ordered* molecules in the monolayer are responsible for the trend in binding energy shifts for the ring atoms. One can envision several possible interactions which could affect the binding energies of the molecular core electrons: (a) the covalent bond to the substrate, and (b) intermolecular interactions, which can take the form of van der Waals and/or Coulombic terms which vary with the particular arrangements of the molecules. We will argue in what follows for a model incorporating all of these terms, and which

appears to give a consistent description of all observed trends.

The carboxylic groups of all three molecules are linked to the substrate by two highly oriented [26] substrate bonds, which place the oxygen atoms into locations which essentially continue the bulk structure. It can thus be expected that the screening properties are largely defined by the highly polarisable TiO_2 substrate, which is supported by point 2 above. A large degree of hybridisation of adsorbate states involving the carboxylic groups with substrate states has been found in calculations [18,27], which corroborates this assumption.

This suggests that the shifts of the pyridine ring atom core lines are due to relatively local effects. Such local effects in the form of van der Waals and Coulombic terms (point (b) above) are very sensitive to the exact geometrical arrangement of the molecules. The Coulombic contributions are particularly sensitive to the location of the nitrogen atom, and the van der Waals forces to the relative ring orientations [28]. The results of part I already suggest a T-like nearest-neighbour ring orientation, which can largely be attributed to the optimisation of the van der Waals interactions. We propose that an interaction between the nitrogen with its lone-pair orbital and a hydrogen atom on a neighbouring molecule is responsible for the Coulombic interaction, and that this N–H interaction modifies the geometry of the neighbouring molecules from that induced by the van der Waals interaction alone. In particular, the molecules involved can optimise this interaction by bending towards each other, bringing them into closer proximity. This will enhance the dielectric screening contributions from molecules adjacent to the core-excited one. The near-rigid shift of the different C 1s (pyridine ring) components (point 4 above) lends support to this picture.

The possibility of such an arrangement, in which a nitrogen atom interacts with a hydrogen atom on a neighbouring molecule, should have a clear dependence on the position of the nitrogen atom. It is easiest to evaluate the situation for the two extreme cases, isonicotinic acid and picolinic acid. While isonicotinic acid easily can interact with neighbouring molecules via their N and H atoms by bending towards each other, this possibility is ex-

cluded for picolinic acid due to the unfavourable position of the N atom. The lack of such a relatively strong interaction and the resulting dominance of the van der Waals and dipole–dipole interactions could lead to a larger number of realised geometries (see below) and thus a broadening of the N 1s line as observed (point 5). Nicotinic acid is an intermediate case. While it is amenable to geometries which favour N–H interactions, these geometries are less optimal with respect to a close proximity of the neighbouring molecules than in the isonicotinic acid case. Thus the trend of point 3 above is accounted for, assuming that the optimisation of the intermolecular geometries simultaneously optimises the intermolecular screening.

The assumption of a local effect between a nitrogen and a hydrogen atom is supported by the finding that the observed shift within the molecular series is larger for the N 1s core levels than for the C 1s levels. That both core levels shift in a similar way is due to the core-hole screening efficiency of the π-system [21,23], and the somewhat larger response of the N 1s levels than that of the C 1s levels can be seen as a first-order correction to this picture. It is further supported by the observation of an intermolecular resonance in the N 1s XAS of isonicotinic acid (see I).

In Figs. 7(a), 8, and 9 structures are proposed for the pyridine-carboxylic acid adsorbates on TiO_2-(1 1 0) which we feel to be the simplest that fulfill the points discussed above. In addition, the full first substrate layer is shown in Fig. 7(b) in order to illustrate the bidentate substrate binding for one of the molecules. The bonds of the other molecules to the substrate are very similar to the one shown and have therefore been omitted in the figures.

Common to the proposed structures is that the unit cell contains four molecules. The equivalency of the nitrogen atoms with respect to a N 1s excitation makes it necessary to include four molecules in the models for isonicotinic acid and nicotinic acid, since a dimer structure with a T-like configuration would produce inequivalent sites, and likely two distinguishable binding energies. In both the isonicotinic acid and nicotinic acid cases the N atoms interact with a hydrogen atom of a neighbouring molecule. As discussed above and apparent in the figures, the steric hindrances are
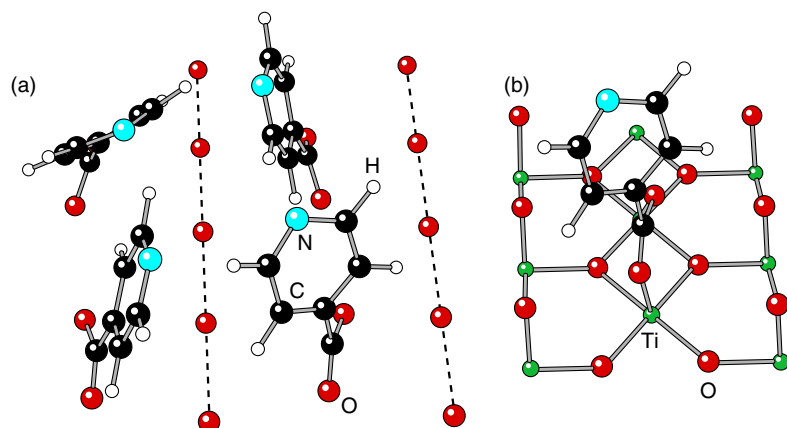
Fig. 7. (a) Proposal for the adsorption geometry of isonicotinic acid on TiO$_2$(1 1 0). The TiO$_2$ substrate atoms have been left out with the exception of the bridging oxygen atoms along the [0 1] surface direction ([0 0 1] in bulk notation). These have been indicated by the dashed lines. (b) The lower righthand isonicotinic acid molecule has been redrawn together with the full first layer of the substrate in order to illustrate the bidentate bond of the molecule to the substrate. The carboxylic group is deprotonated and the molecular oxygen atoms bind to two adjacent Ti substrate atoms. The other molecules with different pyridine ring, but similar carboxylic group orientations bind to the substrate in an equivalent way. The here seen apparent angle between the molecular oxygen atoms and the substrate atomic rows is a byproduct of the visualisation, and is not meant to represent a physical measurement. However, we cannot rule out such distortions. (a) and (b) Please refer to the following atom colour scheme (colour version/grey scale version): white/white spheres hydrogen, light blue/light grey spheres nitrogen, green/medium grey small spheres titanium, red/dark grey spheres oxygen, black/black spheres carbon.
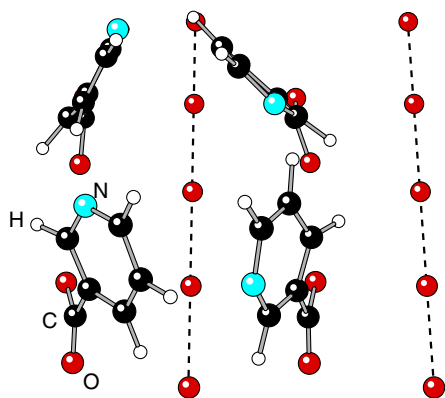

Fig. 8. Proposal for the adsorption geometry of nicotinic acid on TiO$_2$(1 1 0). The substrate bond via the carboxylic group is equivalent to that of isonicotinic acid (cf. Fig. 7(b)). The colour scheme is described in the caption of Fig. 7.

smaller for isonicotinic acid than for nicotinic acid, so that a closer proximity can be achieved. As a result, a core hole on the pyridine ring is assumed to be better screened for isonicotinic acid than for nicotinic acid. In contrast, such a N–H interaction is suppressed sterically for picolinic acid. The ad-

sorbate will still try to optimise the dipole–dipole and van der Waals energies. Since such a geometry is not dictated by the orientation of the N atom to the same extent as for the other isomers, we therefore speculate that a number of different geometries will be realised, resulting in a distribution of binding energies, and therefore explaining the larger width of the N 1s core level. Panels (a) and (b) of Fig. 9 illustrate two such different orientations of the pyridine rings that are conceivable, in particular when considering that more neighbours than those displayed influence the molecular orientation and intermolecular screening.

That the unit cell contains four molecules in the proposed structures is not in conflict with the suggested dimer formation in I. With respect to the twofold substrate symmetry, only two molecular species can be distinguished in the models and the same XAS angle dependence is retrieved as for a model in which only half of the unit cell suggested here is employed in a given case. Thus the XAS, STM, and XPS data for these systems can be reconciled within a single picture, based on a few guiding principles.
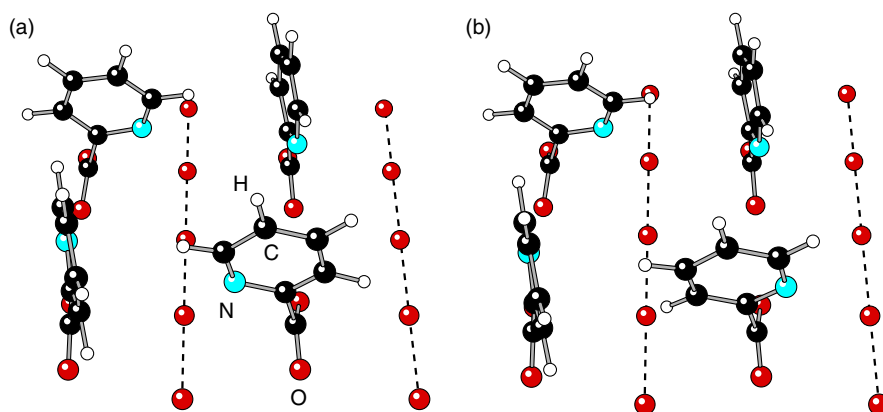
Fig. 9. Proposals for approximately equivalent geometries of picolinic acid on $TiO_2(1\,1\,0)$. The lower right hand molecule has been rotated 180° between (a) and (b). The substrate bond via the carboxylic group is equivalent to that of isonicotinic acid (cf. Fig. 7(b)). Please, refer to the colour scheme in the caption of Fig. 7.

4. Conclusions

The pyridine-carboxylic acid monomers have been investigated by XPS in both multilayers and monolayers adsorbed on rutile $TiO_2(1\,1\,0)$. It has been demonstrated that those spectral monolayer features of a particular isomer which are related to emission from the pyridine ring atoms display a near-rigid shift relative to the same component of the other isomers, while the peaks related to the carboxylic groups have the same energies in all three isomers. This differing behaviour has been related to differences in the ground state geometries of the molecules. Isonicotinic acid and to a smaller degree nicotinic acid are able to optimise their geometry via an interaction between the nitrogen atom and a hydrogen atom on a neighbouring molecule, which leads to a closer proximity of the pyridine rings. This in turn enhances the intermolecular screening ability for a core hole, which explains the binding energy shifts observed for excitations located on the pyridine rings. Such an N–H interaction is sterically hindered for picolinic acid, which results in a larger intermolecular distance for the picolinic acid monolayer than for those of isonicotinic acid and nicotinic acid. A core hole on the pyridine ring of picolinic acid is thus least efficiently screened within the investigated molecular series. In contrast, this local interaction between the pyridine rings is not reflected in the carboxylic groups, which are characterised by the strong bond to the highly polarisable substrate.

Based on these findings we have proposed models for the molecular arrangements of the monolayers, in which a unit cell contains four molecules. These models fulfill the structural demands implied by the results presented here and in I. Testing of these models awaits further experiments, such as photoelectron diffraction.

Acknowledgements

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