



Molecular damage in bi-isonicotinic acid adsorbed on rutile TiO₂(1 1 0)

James N. O'Shea^{a,*}, J. Ben Taylor^a, Louise C. Mayor^a, Janine C. Swarbrick^a, Joachim Schnadt^b

^aSchool of Physics and Astronomy, University of Nottingham, NG7 2RD, UK

^bDepartment of Synchrotron Radiation Research, Lund University, Sweden

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ABSTRACT

Here we present the characteristic signatures in X-ray absorption and photoemission spectroscopy for molecular damage in adsorbed monolayers of bi-isonicotinic acid on a rutile TiO₂(1 1 0) surface. Bi-isonicotinic acid is the anchor ligand through which many important inorganic complexes are bound to the surface of TiO₂ in dye-sensitized solar cells. The nature of the damage caused by excessive heating of the adsorbed monolayer is consistent with splitting the molecule into two adsorbed isonicotinic acid molecular fragments. The effect on the lowest unoccupied molecular orbitals (involved in electron transfer in the molecule) can be understood in terms of the adsorption geometry of the reaction products and their nearest neighbor interactions.

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1. Introduction

Molecular damage of adsorbed molecules is one of the most important experimental considerations in synchrotron radiation experiments. This is particularly important when working with the very high photon flux densities of third generation synchrotron soft X-ray beamlines. Many organic molecules survive intact only on the order of seconds under this level of irradiation. Closely related to beam damage is that caused by heating. For the bi-isonicotinic acid (4,4'-dicarboxy-2,2'-bipyridine) molecule the spectroscopic results of both types of damage is the same. Bi-isonicotinic acid is a very important molecule with respect to dye-sensitized solar cells (DSSCs) since it is most often the ligand which anchors the most efficient inorganic sensitizer molecules to the surface of the TiO₂ substrate [1–5]. Previous work has shown that this ligand molecule provides a route for ultra-fast electron transfer from the molecule to the conduction band of the substrate on the low femtosecond timescale [6–8], and its integrity is therefore critical to the function of DSSCs based on this molecular anchor. Given the application of synchrotron radiation to study these and related systems, and a consideration of the stability of an operational DSSC, a systematic study of beam and thermal damage is an important part of our understanding of this important technology. At its most fundamental level molecular damage results from excessive

excitation of electrons. Bond instabilities result, for example, from the direct loss of electrons from the bond, or the excitation of unmaintainable vibrational modes. If these processes allow the molecule to access a stable state, either kinetic or thermodynamic then damage will proceed (we will return to this point in Section 3.2). Thermal and beam damage therefore cause problems when trying to compare spectra from different preparations of a molecule. Changes in spectral features cannot simply be assigned to the intended change in the sample composition unless damage can be ruled out as a contributing factor. The characteristic signatures of thermal or beam damage in specific molecules, while not routinely reported in the literature, are invaluable to those working with similar molecules and in some cases of crucial importance.

The specific example considered here is the case of the aforementioned bi-isonicotinic acid molecule (a member of the pyridine carboxylic acid family) adsorbed on a rutile TiO₂(1 1 0) surface. Recognizing the signatures of thermal and beam damage is particularly important for resonant photoemission (RPES) measurements of the charge transfer dynamics between the molecule and the substrate [6] where acquisition times are long and the integrity of the molecular orbitals is imperative. This is because, from a core-level spectroscopic perspective, molecular damage (generally) leads to a non-linear decrease in the intensity of the unoccupied molecular orbitals as measured by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. In a core-hole clock implementation of RPES, the intensities of the NEXAFS-derived unoccupied states

* Corresponding author. Tel.: +44 115 9515149.

E-mail address: james.oshea@nottingham.ac.uk (J.N. O'Shea).

define the total photoabsorption cross-section to which the relative abundance of electrons emitted via different autoionization channels (participator, spectator and Auger) is scaled [14]. Any loss of integrity in the unoccupied molecular orbitals during the experiment through beam damage could completely undermine the RPES observations. Our previous studies of the adsorption and charge transfer dynamics of bi-isonicotinic acid adsorbed on a variety of surfaces [6–8,10–12,15–17] successfully eliminated molecular damage through continuously scanning the incident beam across the surface to maintain the exposure below a well characterized limit. This technique is also used in the present study, in which we focus our attention on the *nature* of the damage to the adsorbed bi-isonicotinic acid molecule.

Thermal damage, while unlikely to occur *during* a measurement (notwithstanding localized heating due to soft X-ray irradiation), is particularly relevant to the preparation of monolayers of bi-isonicotinic acid on a TiO₂(110) surface. The molecule forms multilayers on the surface at room temperature and requires heating of the substrate close to the molecular sublimation temperature of ~230 °C in order to remove the physisorbed multilayers and leave a chemisorbed monolayer [7]. A closely related approach is to hold the surface at this temperature during the deposition such that the adsorption is limited to a single monolayer [6]. The alternative method for preparation of a monolayer of the molecule is to deposit, at room temperature, just enough molecules to form a coverage close to a monolayer. In this paper we present a comparison of these methods and highlight the molecular damage induced by excessive heating or prolonged exposure to soft X-rays.

2. Experimental methods

Experiments were carried out at the undulator beamline I511-1 at the Swedish synchrotron facility MAX-lab [18]. The beamline has a photon energy range of 50–1500 eV and the rotatable end station is equipped with a Scienta R4000 hemispherical analyzer. The base pressure in both the analysis chamber and preparation chambers was $\sim 1 \times 10^{-10}$ mbar.

The substrate was single crystal rutile TiO₂(110) of dimensions $10 \times 10 \times 1$ mm (Pi-Kem, UK). It was clamp mounted, using tantalum clips, on a silicon wafer of the same dimensions. The mounting was made so as to ensure good electrical and thermal contact. Heating of the crystal was performed by resistive heating of the silicon. A thermocouple was attached in close proximity to the crystal in order to monitor the temperature. Bulk defects were introduced into the crystal by cycles of 1 keV Ar⁺ sputtering followed by annealing at ~700 K, until the crystal turned blue. This dopes the crystal n-type [19] and avoids any appreciable sample charging.

Before adsorbate deposition the surface was cleaned by 1 keV Ar⁺ sputtering for 10–20 min, and checked by observing the disappearance of the C 1s core-level. To achieve extended flat domains of TiO₂(110) and to minimize the number of surface defects caused by sputtering, the crystal was annealed at ~700 K for 10–20 min [20]. Cooling in oxygen was not undertaken, due to the possibility of the formation of irregular networks of 6 Å pseudo-hexagonal rosettes known to occur on the TiO₂(110) surface [20]. The annealing process was checked by monitoring the shape of the Ti 2p peaks until a single dominant Ti⁴⁺ oxidation state was observed. LEED measurements showed a clear pattern consistent with a well defined (110) surface.

Bi-isonicotinic acid (Sigma–Aldrich, UK) was evaporated from a home built evaporator ~20 cm from the sample. The powder was outgassed thoroughly and evaporated at a temperature of ~230 °C. Multilayers were prepared by deposition onto the substrate at room temperature. Monolayers of bi-isonicotinic acid were prepared by two methods. In the first method, termed here

as *hot*, a multilayer was first formed and then gently heated off to leave the chemisorbed monolayer. This method has been used successfully in recent studies and is analogous to holding the crystal at an elevated temperature during the deposition [6,12,17]. The main advantage of the former method is that the absolute temperature of the crystal does not need to be known as it can be increased gradually until the desorption of the multilayer is observed by monitoring the shape of the O 1s peaks in the X-ray photoelectron spectra (XPS), which reflect the differing local environments experienced by the two carboxylic oxygen atoms in the two preparations (discussed in Section 3.1). In the second type of preparation, termed here as *cold*, a monolayer was formed by a short deposition of the molecule onto the surface at room temperature. Control over this technique is difficult and as such, only sub-monolayer coverage was achieved in this study.

Monochromator exit slits were set to give a resolution of <100 meV for photons of energy $h\nu = 400$ eV. The monochromator was calibrated by taking the energy separation of core-level photoemission peaks excited by X-rays in 1st and 2nd order. The analyzer exit slit was set to a 0.3 mm curved aperture. For the recording of near-edge X-ray absorption fine structure (NEXAFS) spectra, a taper was applied to the undulator to reduce the intensity variation of the radiation over the photon energy range of interest. Analyzer pass energies and photon energies for different core-level spectra are given in the respective figure captions. Due to the susceptibility of the molecule to suffer beam damage under irradiation by soft X-rays, the sample was moved continuously so that no molecules on the surface were exposed to the beam for longer than 50 s (determined from fast photoemission to be below the exposure limit for detectable beam damage). All spectra shown in the paper are the raw data subject to the stated energy calibration. Where fitting is shown of the peaks and background these were performed in an IGOR Pro environment using Gaussian–Lorentzian functions and a Shirley function, respectively.

3. Results and discussion

3.1. Adsorption of bi-isonicotinic acid

Upon adsorption to rutile TiO₂(110), bi-isonicotinic acid is expected to adopt a 2M-bidentate bonding geometry [9–11,17], as

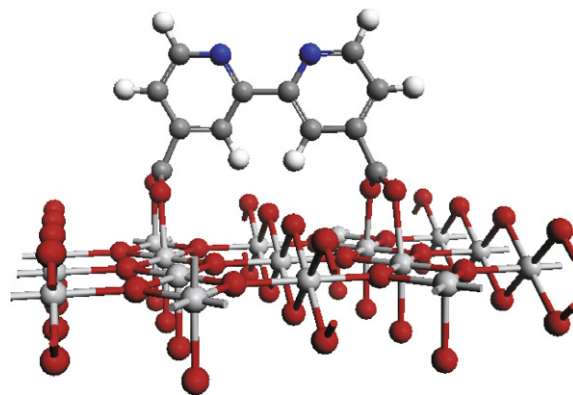


Fig. 1. The optimized 2M-bidentate bonding geometry of bi-isonicotinic acid adsorbed on rutile TiO₂(110) in agreement with previous studies [9–12]. The geometry was optimized using CASTEP code [13] at the DFT-GGA level with a plane wave basis set cut-off of 300 eV and the Perdew Burke Ernzerhof functional. Atoms in the oxide substrate were constrained to their bulk lattice positions. White spheres represent hydrogen, grey spheres carbon, red spheres oxygen, blue spheres nitrogen and light grey spheres represent titanium atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

shown in Fig. 1. A similar adsorption geometry has also been found on the anatase TiO_2 surface [15,21]. Bi-isonicotinic anchors to the surface through the deprotonated carboxylic groups, and as such all four oxygen atoms in the molecule are equivalent [9–11]. Attachment of the molecule via the deprotonated carboxylic group is a common feature of aromatic carboxylic acid molecules adsorbed on TiO_2 [15–17,22–24]. In the O 1s core-level spectrum we therefore expect to see just two features, one due to the molecule and the other due to the $\text{TiO}_2(110)$ surface. This is clearly observed for both the hot and the cold monolayers in the O 1s spectra shown in Fig. 2. These spectra have been calibrated to the substrate O 1s peak at 530 eV. In the case of the cold preparation, the intensity of the molecule peak at 531.47 eV binding energy is lower relative to the substrate peak than for the hot preparation (where it occurs at 531.63 eV) since it necessarily represents a sub-monolayer coverage as discussed in Section 2. It is noted that the change in peak separation between the hot and cold preparations is attributed to a shift in the substrate peak arising from the different surface coverage produced by the two preparation methods. The resulting 0.16 eV shift to lower binding energy in the full monolayer is most likely due to the quenching of surface defect states which continue to cause band-bending at the sub-monolayer coverage of the cold preparation. The spectra indicate that both preparation routes result in the same adsorption bond. Any intact (i.e. non-deprotonated) carboxylic groups would result in two oxygen features derived from the molecule, as shown in Fig. 3 for a multilayer of bi-isonicotinic acid. The peak at 533.2 eV in Fig. 3 is due to the hydroxyl component and the molecule peak at 531.9 eV is due to the carbonyl of the intact carboxylic group. The carbonyl oxygen

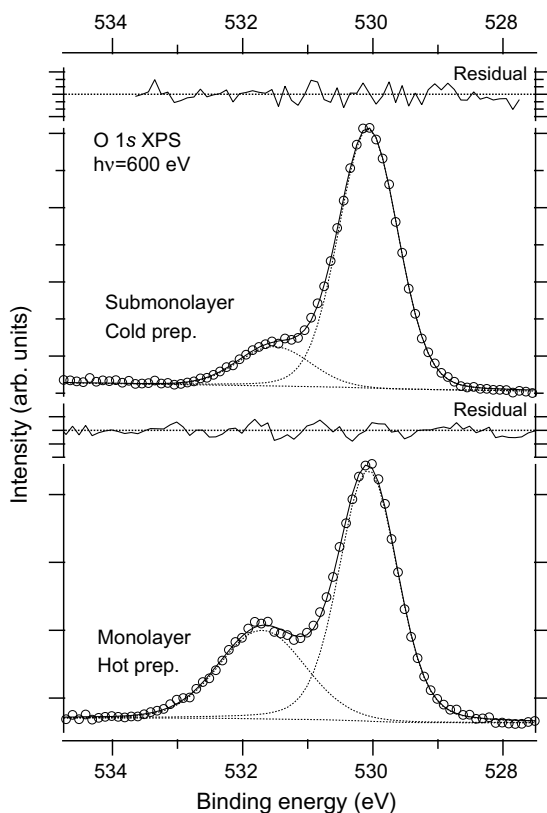


Fig. 2. O 1s core-level spectra for bi-isonicotinic acid monolayers and sub-monolayers, prepared by hot and cold methods (respectively) on $\text{TiO}_2(110)$. Spectra are calibrated to the substrate O 1s signal at 530 eV. The top residual has an amplitude 2% of the peak intensity above the background. The bottom residual has an amplitude of 5%. All spectra were taken in normal emission. Total instrumental resolution was <200 meV.

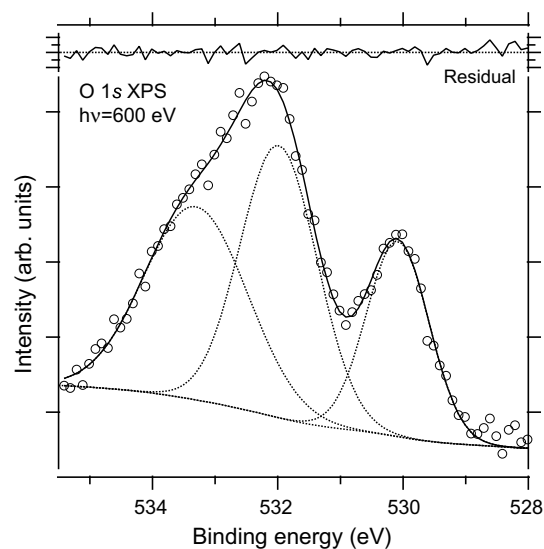


Fig. 3. O 1s core-level spectra for a bi-isonicotinic acid multilayer on $\text{TiO}_2(110)$. The multilayer was formed from further deposition on the sub-monolayer preparation presented in Fig. 2. Spectrum is calibrated to the substrate derived peak. The residual has an amplitude 10% of the peak intensity above the background.

peak appears at a higher energy (1.9 eV from substrate peak) as compared with the monolayers (1.63 eV from substrate peak). This is attributed to a reduction in charge screening from the substrate and/or a charging of the multilayer. Importantly the separation between the molecular oxygen components (1.3 eV) is in very good agreement with previous studies [10,17].

3.2. Molecular damage in bi-isonicotinic acid

Having reviewed the routes to the successful adsorption of bi-isonicotinic acid on the $\text{TiO}_2(110)$ surface, we now turn our attention to the damage caused to the adsorbed molecules on the surface. The first results considered, presented in Fig. 4, are N 1s

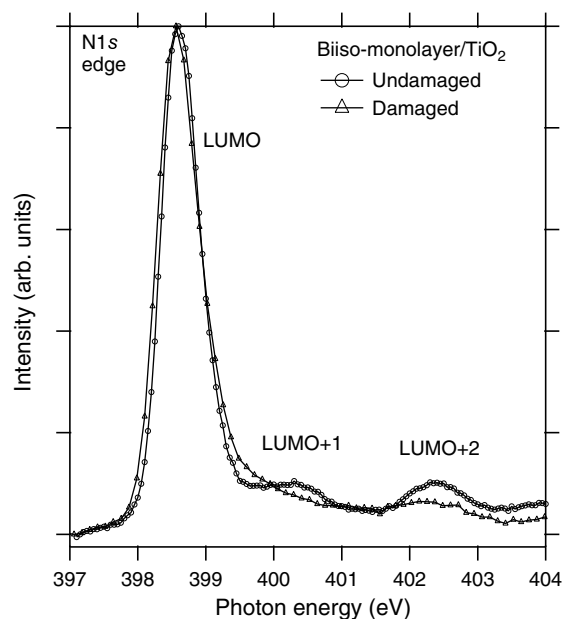


Fig. 4. N 1s NEXAFS for an undamaged and damaged monolayer of bi-isonicotinic acid on $\text{TiO}_2(110)$. Spectra have been corrected for the variation in background caused by the undulator. In the specific case shown, damaging was brought about by heating. Total instrumental resolution was ~ 180 meV.

NEXAFS spectra for an undamaged and a damaged monolayer of bi-isonicotinic acid. For the undamaged preparation, the NEXAFS spectrum compares very well (within experimental error) to previous studies [11,12]. The LUMO occurs at an energy of 398.6 eV, the LUMO + 1 at 400.3 eV and the LUMO + 2 at 402.4 eV photon energy. The specific spectrum presented here as the damaged molecule is that measured after heating a pristine monolayer to $\sim 250^\circ\text{C}$ for 5 min ($\sim 50^\circ\text{C}$ higher than the normal temperature for the hot preparation method). However, the same result is obtained after continuous irradiation of the sample with soft X-rays for periods of time greater than ~ 10 min.

Two main differences exist between the damaged and undamaged spectra. The first is the loss of definition (essentially a smearing out) of the LUMO + 2 (3rd lowest unoccupied molecular orbital) resonance. The second, and perhaps more significant, is the almost complete loss of the LUMO + 1 resonance. It is the LUMO + 1 peak that is particularly indicative of the substrate–molecule interaction in adsorbed bi-isonicotinic acid molecules. This is based on the reproduction of the LUMO + 1 by quantum mechanical calculations, showing that its states derive from a large degree of hybridization of adsorbate orbitals which are predominantly located around the carboxylic group, with the Ti 3d states that form the bottom of the substrate conduction band [11]. Loss of this peak might suggest a substantial change in the way the molecule and substrate interact through the carboxylic group (if not in the nature of the molecule itself). This is exemplified in the case of bi-isonicotinic acid molecules, effectively isolated from the substrate in a multilayer for which no feature at the energy of the LUMO + 1 is found, although a strong peak at the LUMO + 2 position still is observed [11].

That the nature of the damage in bi-isonicotinic acid might be centered on the carboxylate link (as suggested by the NEXAFS) is in some respects consistent with changes observed in the O 1s spectra shown in Fig. 5 due to excessive heating of the hot monolayer. The separation between the molecular and substrate peaks remains unchanged (within the experimental resolution), but the intensity of the molecular peak is significantly weaker. This implies a loss of oxygen atoms associated with the molecules, which in bi-isonicotinic acid can come about through only two routes: either

by breaking the bond between the pyridine ring and the carboxylic group or by breaking the bonds between the oxygen atoms and the carboxylic carbon atom. It is worth noting that the first option requires the subsequent desorption of the carboxylic group, otherwise we would observe a peak in the O 1s photoemission corresponding to adsorbed CO_2 . In the second option, breaking the bond between the oxygen atoms and the rest of the molecule would leave the oxygen adsorbed only to titanium atoms in the surface. While not in an identical chemical environment to the bridging oxygens on the surface, we would not expect the binding energy of these additional oxide atoms to have a significantly different binding energy and would therefore be incorporated into the substrate O 1s peak rather than that of the molecule. It is fair to say that neither hypothesis is particularly likely due to the large number of strongly covalent bonds that would need to be broken, nor are they compatible with changes observed in the C 1s spectra.

Two effects are most noticeable in the C 1s data, shown in Fig. 6, upon excessive heating. The first is that when the spectra are calibrated to the substrate O 1s peak (consistent with all other data presented in this study), the binding energy of the carboxylic group remains constant at 298.8 eV whereas the C 1s peak associated with the pyridine ring structure of the molecule shifts to lower binding energy, from 285.5 eV to 285.2 eV. Moreover, the intensity of the carboxylic group relative to the ring carbon remains the same, contrary to what we would expect for either the loss or decomposition of the carboxylic groups. This C 1s data implies that the damage is instead localized in the ring structure of the molecule. The decrease in the intensity of the molecule peak observed in the O 1s spectrum in Fig. 5 is therefore more likely to be due to the desorption or total decomposition of a fraction of the adsorbed molecules. It is worth noting at this point that the separation between the main ring peak and the carboxylic group in the C 1s region is well known for a range of pyridine carboxylic acids relating to bi-isonicotinic acid [17]. Most notable is that for bi-isonicotinic acid the separation has been found in this previous study to be 3.47 eV in agreement with the undamaged monolayer shown in Fig. 6, while for isonicotinic acid (the single pyridine ring version of bi-isonicotinic acid) the separation is 0.2 eV larger at 3.67 eV, consistent with the damaged monolayer in Fig. 6.

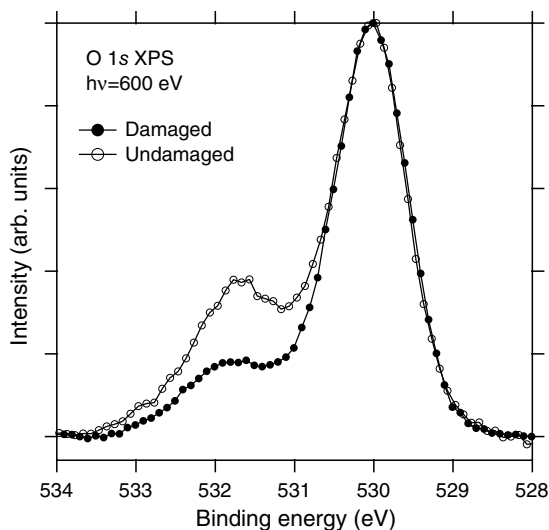


Fig. 5. O 1s core-level spectra for bi-isonicotinic acid monolayers on $\text{TiO}_2(110)$, prepared by the hot method. Damaging was brought about by excessive heating of the monolayer. Spectra were taken at normal emission and calibrated to the O 1s substrate core-level. The spectra have been subject to a background subtraction and subsequently normalized so that they have an equal area. Total instrument resolution was <200 meV.

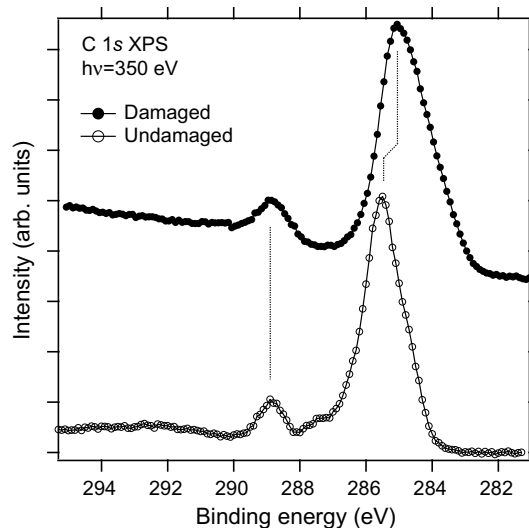


Fig. 6. C 1s core-level spectra for bi-isonicotinic acid monolayers on $\text{TiO}_2(110)$. Damaging was brought about by excessive heating of the monolayer. The undamaged C 1s spectrum was prepared by the cold method. Spectra are calibrated to the substrate O 1s signal. All spectra were taken at normal emission and have been normalized to the height of the main peak. Total instrument resolution was <160 meV.

The second important observation in the C 1s spectrum is the loss of the shake-up feature, which before damaging, can be seen at 287.5 eV. This has also previously been observed for bi-isonicotinic acid, and is conspicuously absent in the C 1s spectrum of isonicotinic acid [17].

If the product of molecular damage in bi-isonicotinic acid is isonicotinic acid (strictly and at least initially isonicotinic acid radicals), as discussed above, some of the molecules must either desorb or decompose in order to account for the decrease in the molecule O 1s intensity relative to that of the substrate. The width of the main peak in the C 1s spectrum of damaged bi-isonicotinic acid is significantly greater than both the undamaged molecule or what we would expect for isonicotinic acid. However, the asymmetry to the low binding energy side of the main peak is consistent with an increase in atomic carbon, which would be expected to occur at around 284 eV. The additional width of the main peak is plausibly attributed to the fraction of molecules that underwent complete dissociation on the surface.

The photoemission data thus suggests that the product of damage to adsorbed bi-isonicotinic acid molecules can be tentatively identified as isonicotinic acid. The DFT (CASTEP) optimized geometry of the damaged monolayer is shown in Fig. 7. The radical state as shown is thermodynamically higher in energy than the intact structure shown in Fig. 1 by 3.17 eV. However, the split structure represents a kinetically stable local minimum with a large energy barrier to reforming the initial molecule due to the spatial separation of the two fragments. We can visualize the mechanism of the damage as the excessive excitation of the central bond which joins the two rings. At some critical separation the rings become free to rotate around the axis formed by the bond to the carboxylic group which anchors it to the surface. Moreover, it is likely that the radical state will bond to residual hydrogen atoms on the surface (from the original deprotonation of the adsorbed bi-isonicotinic acid) to form intact isonicotinic acid molecules. CASTEP calculations place this structure much closer in energy (0.68 eV) to the intact molecule and two protons adsorbed on the surface.

A closer inspection of the N 1s NEXAFS spectrum shown in Fig. 4 is therefore required, in particular a comparison with the NEXAFS of related pyridine carboxylic acids including isonicotinic acid. The N 1s NEXAFS for a monolayer of isonicotinic acid adsorbed on the TiO₂(110) surface has been shown in previous work [12,25] to be very similar to that of bi-isonicotinic acid with two notable exceptions. The first is the separation between the LUMO (lowest unoccupied molecular orbital) and the LUMO + 2, which for the bi-isonicotinic acid monolayer is 3.8 eV while for the isonicotinic acid monolayer is 3.4 eV. In this respect the conversion of bi-isonicotinic acid to isonicotinic acid is consistent with the N

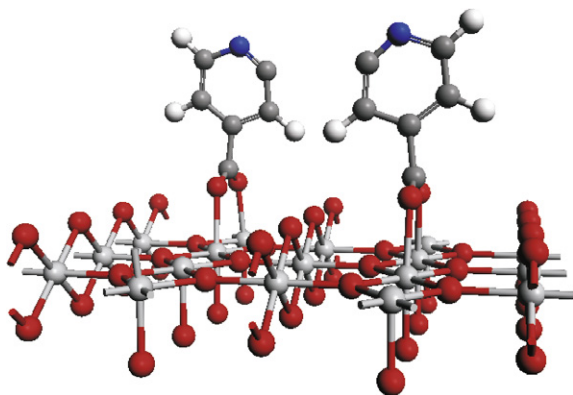


Fig. 7. The optimized geometry (calculated using the same conditions as Fig. 1) of two isonicotinic acid fragments adsorbed on rutile TiO₂(110) resulting from the molecular damage of adsorbed bi-isonicotinic acid as discussed in the text.

1s X-ray absorption spectra shown in Fig. 4. The loss of definition of the LUMO + 2 resonance in this spectrum can be interpreted as the emergence of a second component between 0.3 and 0.4 eV to lower photon energy.

The second difference between the NEXAFS of bi-isonicotinic acid and isonicotinic acid monolayers concerns the LUMO + 1 resonance. Since both exhibit a LUMO + 1 feature we would therefore reasonably expect to observe such a resonance for damaged bi-isonicotinic acid if the product is isonicotinic acid, which is not the case. However, while the LUMO + 1 is present in both molecules the energy and origin of the resonance is quite different in each case. As mentioned at the beginning of the discussion, the LUMO + 1 feature in bi-isonicotinic acid (at a separation of 1.7 eV from the LUMO) is attributed to the interaction of the molecule with the substrate through the carboxylic groups and is successfully reproduced as such in quantum mechanical calculations [11]. In contrast, the LUMO + 1 feature in isonicotinic acid (at a slightly higher separation of 1.9 eV from the LUMO) has been attributed to a N–H interaction induced by nearest neighbor molecule interactions, exhibiting a σ^* -like angular dependence [17]. This identification is supported by the fact that the LUMO + 1 resonance is much weaker in monolayers of *nicotinic acid* (where the nitrogen atom is one ring position closer to the carboxylic anchor group), and is all but absent in *picolinic acid* (where the nitrogen atom is adjacent to the carboxylic group). The assumption in these cases is that steric hindrance arising from the molecular geometry makes it increasingly difficult to support a N–H intermolecular interaction between the chemisorbed molecules.

The absence of the LUMO + 1 in the damaged bi-isonicotinic acid monolayer may therefore lie in an inability of the product molecules to form intermolecular interactions with their nearest neighbors. This is entirely reasonable based on the initial adsorption geometry of the intact bi-isonicotinic acid molecule shown in Fig. 1. The positions of any isonicotinic acid-like products on the surface following the damage are therefore fixed in the positions dictated by the staggered 2M-bidentate adsorption geometry of the parent molecule, rather than the optimum adsorption geometry of isonicotinic acid. The intermolecular N–H interaction is therefore unlikely, resulting in the loss of the corresponding LUMO + 1 feature in the NEXAFS. It is also worth remembering that since the product of splitting bi-isonicotinic acid molecules is actually (at least initially) two isonicotinic acid radicals, they will inevitably interact somewhat differently with their nearest neighbors than isonicotinic acid molecules possessing a full complement of hydrogens.

4. Conclusions

The molecular products resulting from thermal and soft X-ray beam damage of bi-isonicotinic acid molecules chemisorbed to a rutile TiO₂(110) surface has been investigated using core-level photoemission and X-ray absorption spectroscopy. The O 1s and C 1s photoemission spectra are consistent with the proposed scenario that the bi-isonicotinic acid molecule splits into two isonicotinic acid molecules. The smearing out of the LUMO + 2 resonance in the N 1s NEXAFS is also consistent with this model, resulting from the reduced separation of this resonance in iso- compared to bi-isonicotinic acid monolayers. The loss of the LUMO + 1 resonance is attributed to the constrained geometry of the chemisorbed products determined by the adsorption of the parent molecule. The inevitably increased molecular separation on the surface leads to a reduction in nearest neighbor interactions (proposed to be the origin of the LUMO + 1 in adsorbed isonicotinic acid). In addition to elucidating the nature of the damage in bi-isonicotinic acid, this data highlights the observable signatures of

molecular damage which it is hoped will be a valuable insight for those working with this and closely related molecules.

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