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# Benzohydroxamic acid on rutile TiO<sub>2</sub>(110)-(1×1)– a comparison of ultrahigh-vacuum evaporation with deposition from solution<sup>\*</sup>

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ARTICLE INFO

Keywords: TiO<sub>2</sub>(110) Benzohydroxamic acid Density functional theory calculations X-ray photoelectron spectroscopy (XPS)

## ABSTRACT

Hydroxamic acids are an interesting anchor group for organic molecules on oxide surfaces, but very few studies exist on their adsorption on well-defined single-crystal surfaces under well-defined conditions. In the present paper, we use X-ray photoelectron spectroscopy to follow the adsorption of benzohydroxamic acid on a rutile  $TiO_2(110)-(1\times1)$  single-crystal surface. We compare evaporation in ultrahigh vacuum with deposition from ethanol and acetonitrile solutions. Furthermore, we carried out density functional theory calculations to support the assignment of adsorbates. Several species appear on the surface, which are most evident in the N 1s region. The low-coverage species can be explained as originating from a hydroxamate, and decomposed species related to oxygen vacancies or defects. Identification of the high-coverage species, however, remains elusive, and several possibilities are discussed.

### 1. Introduction

Anchoring organic molecules to oxide surfaces is important for many organic electronic, photovoltaic, and photocatalytic devices. The anchoring is done through specific functional groups, such as carboxylic acids, phosphonic acids, sulfonic acids, silanes, acetylacetonates, catechols, or hydroxamic acids [1–6]. Hydroxamic acids represent a particular class of anchoring groups. They are already applied in collection and accumulation processes, such as flotation [7], and they have been shown to possess extremely good electron-transfer properties [4,8–11]. Another interesting property is the stability of hydroxamic acid anchor groups, in particular under basic conditions, in contrast to other linker groups such as carboxylic acid [8,9].

While the adsorption of carboxylic acid on oxides has been studied in great detail [12–15], much less is known about the adsorption of hydroxamic acids under well-defined conditions. In the context of

flotation, their adsorption properties were experimentally studied on different mineral surfaces, and the results indicate a chelating hydroxamate, producing a five-membered ring [16–21]. To the best of our knowledge, there is only one experimental study covering the adsorption on well-defined single-crystal studies under ultrahigh-vacuum (UHV) conditions where the interaction of (di)hydroxamic acid on Au(111) and Ag(111) is reported [22]. In particular, there is no single-crystal investigation of hydroxamic acid deposition under UHV on anatase or rutile, while several studies focus on the adsorption on amorphous TiO<sub>2</sub> thin films [23], on native oxides [24], and on rutile and anatase nanoparticles [25].

Yang et al. [23] investigated the adsorption behavior of different solution-deposited hydroxamic acids on amorphous TiO<sub>2</sub> thin films by attenuated total reflection infrared spectroscopy (ATR-IR), supported with density functional theory (DFT) calculations, and the results indicated the adsorption as hydroxamates in a bidentate configuration [23].

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https://doi.org/10.1016/j.susc.2021.121955

Received 4 June 2021; Received in revised form 30 August 2021; Accepted 28 September 2021 Available online 29 September 2021 0039-6028/© 2021 Elsevier B.V. All rights reserved.

 $<sup>^{\</sup>star}\,$  This article is part of the Special Issue Functional Molecules on Oxide.

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Another study by Folkers et al. [24] used XPS to investigate the adsorption of long-chain hydroxamic acids from solution on the native oxides of several metals, and assigned the undissociated hydroxamic acid as the main species on the native oxide of titanium [24]. Furthermore, the binding mode and the protonation state of solution-deposited benzohydroxamic acid on anatase and rutile TiO<sub>2</sub> nanoparticles were addressed by Brennan et al. [25], applying infrared spectroscopy and DFT calculations. Their results indicate a mixture of different binding geometries, with the five-membered chelating mono-deprotonated species as the most stable [25]. The composition of the different binding ing motifs has, unfortunately, not been resolved yet.

Even though experiments of hydroxamic acids on TiO<sub>2</sub> single-crystal surfaces are scarce, several theoretical studies, in particular DFT calculations, were performed addressing the adsorption configuration of molecules with a hydroxamic acid linker group, mainly on anatase [9,11, 25–30]. For the hydroxamic acid linker group on rutile TiO<sub>2</sub>(110)-(1×1) to the best of our knowledge only one calculation was published by Ambrosio et al. [26], showing that the mono-dissociated bridging-bidentate binding mode is more stable than on anatase TiO<sub>2</sub>(101).

Herein, we apply synchrotron-radiation X-ray photoelectron spectroscopy (XPS) and DFT calculations to improve our understanding of the adsorption of benzohydroxamic acid (BHA) on a single-crystal rutile  $TiO_2(110)$ - $(1 \times 1)$  surface. To help bridge the gap between well-defined model systems and more realistic conditions, we compare adsorption under UHV with deposition from solution.

# 2. Experimental section

Four different UHV setups were used to perform the measurements presented below. All photoemission measurements of the vacuumdeposited molecules were performed at the Materials Science beamline at the synchrotron facility Elettra in Trieste, Italy. The end-station of the Materials Science beamline has a base pressure of  $2{\times}10^{-10}\,\text{mbar}$  and is equipped with a SPECS PHOIBOS 150 hemispherical energy analyzer. Powder XP spectra were acquired in a PHI Quantera II Scanning XPS Microprobe equipped with a monochromatic Al Ka X-ray source and a dual-beam charge neutralization setup, allowing non-conductive powders to be measured. This chamber has a base pressure of  $1 \times 10^{-9}$  mbar. Measurements of benzohydroxamic acid deposited from ethanolic solutions were carried out at the Brazilian Synchrotron Light Source (LNLS), Campinas, Brazil, using the Planar Grating Monochromator (PGM) for soft X-ray spectroscopy (100-1500 eV) beamline with a base pressure of  $2 \times 10^{-10}$  mbar in the photoemission end station. Finally, benzohydroxamic acid deposition from acetonitrile solutions was carried out in an UHV setup equipped with a liquid-cell. This chamber has a base pressure of  $5 \times 10^{-10}$  mbar and is equipped with a monochromatic Al Ka X-ray source and a SPECS PHOIBOS 150 hemispherical energy analyzer. A more detailed description of this setup can be found in literature [31].

Rutile TiO<sub>2</sub>(110) single-crystals were purchased from CrysTec GmbH (Berlin, Germany). All crystals used in Trieste were pre-reduced by annealing in 1 bar hydrogen until their color turned blue to avoid timeconsuming annealing at the synchrotron. Each crystal was cleaned by several cycles of argon sputtering (1 kV,  $2 \times 10^{-6}$  mbar) and annealing to 850 K in UHV, producing the expected (1×1) LEED pattern. Upon removal from the vacuum chamber after the experiments, the crystal exhibited a slightly deeper blue color. After cleaning, minor amounts of nitrogen (less than 4% of the amount of nitrogen in 1 ML BHA) and almost no carbon (less than 2% of the amount of carbon in 1 ML BHA) were detected by XPS. We determine the BHA coverages from the ratio of the C 1s and Ti 2p signals assuming layers of uniform thickness and composition. Since carbon is present at multiple heights within the molecules, the C 1s signal is less affected by a change in adsorption geometry compared to nitrogen. We define 1 ML as the C 1s / Ti 2p ratio for the saturated layer of benzohydroxamic acid at room temperature (300 K). This procedure was already used previously, as described in the

methodology section in [32].

Benzohydroxamic acid (99%, CAS-number: 495–18–1) and potassium benzohydroxamate (purity not given, CAS-number 32,685–16–8) were purchased from Sigma-Aldrich Chemie GmbH and used as received. Benzohydroxamic acid was characterized by nuclear magnetic resonance spectroscopy (NMR), elemental analysis, and transmission infrared spectroscopy (TIR). Potassium benzohydroxamate was characterized by TIR. For TIR, the powders were grinded in KBr. Both powders showed the expected features when comparing with reported spectra [33,34], and no impurities were detected.

Benzohydroxamic acid was evaporated under UHV from a graphite crucible kept at 310-320 K (just above room temperature). The high vapor pressure of the hydroxamic acid at room temperature required water-cooled evaporators to keep the evaporators cold during bakeout and cryopumps in the main chamber to keep the background pressure of benzohydroxamic acid low. Evaporation directly into a mass spectrometer yielded the expected fragmentation pattern of pure BHA [34]. Multilayers of BHA were deposited on the  $TiO_2(110)$ -(1×1) surface by cooling the substrate to a temperature of 180 K. XP spectra of the evaporated multilayers (not shown) are also consistent with those of the as-purchased powders, further indicating evaporation of intact molecules. To correct for charging (most notably observed for the powder measurements) and/or for uncertainties of the photon energy (synchrotron), the binding energy axes were referenced to the C 1s peak of the phenyl ring forced to 284.7 eV (yielding a value of 530.1 eV for the O 1s peaks of the TiO<sub>2</sub> substrate), using spectra measured with a photon energies of 1486.6 eV (Al Ka in the lab) or 650 eV (synchrotron), if not denoted otherwise. Note that we used the C1s peak of the phenyl ring as reference, since the powder spectra did not contain Ti signals. In addition, all spectra measured at the synchrotrons were normalized to the incident photon flux as measured by a gold mesh. All experiments at the PHI Quantera II UHV chamber were performed with powders pressed onto double-sided copper tape. To compensate for charging dual electron and ion neutralization was used. Longer measurements caused beam damage on the powders, most likely caused by the dual neutralization. To avoid beam damage the measurement time was therefore reduced to 5 min, where no beam damage was observed. No beam damage was observed for the synchrotron measurements.

We carried out laboratory and synchrotron measurements depositing molecules from solution at room temperature. Laboratory measurements were carried out using a liquid reactor attached to the UHV chamber under an Argon atmosphere [31]. In short, the substrate surface was placed in contact with a 500 µm BHA acetonitrile solution forming a meniscus, for 15 min. When removing the sample from solution, typically a drop of liquid remains on the surface wetting the surface. This drop needs to be removed to prevent multilayer deposition and thus the sample is extensively rinsed with a 10 ml stream of acetonitrile from a syringe, dried with Argon and after pumping down moved back to UHV for measurement. At the synchrotron, the clean crystal was transferred outside UHV and immediately placed in a specifically designed Teflon cell where only the substrate surface contacts a 500 µM ethanolic BHA solution for 15 min. After removal from the solution, the sample was extensively rinsed in a 10 ml stream of ethanol from a syringe, dried using a N2 stream and moved back to the transfer chamber in a N2 atmosphere.

DFT calculations were performed using the Vienna Ab-Initio Simulation Package (VASP) which employs a plane-wave basis set and a periodic supercell method. Potentials within the projector augmented wave (PAW) method [35,36] and gradient-corrected functionals in the form of the generalized-gradient approximation (GGA) with Perdew Burke Ernzerhof (PBE) functional [37,38] were used. For bulk optimization, TiO<sub>2</sub> lattice parameters were determined by minimizing the total energy of the unit cell using a conjugated gradient algorithm to relax the ions. The optimization of structural parameters was performed considering a set of  $9 \times 9 \times 9$  Monkhorst–Pack k-points to sample the Brillouin Zone [39] with a cut condition of  $10^{-3}$  eV for the total energy between

two ionic relaxation steps. The electronic relaxation convergence criterion was set to 10<sup>-4</sup> eV and Van der Waals interaction between pairs was included by means of Grimme DFT-D2 method [40]. A kinetic energy cutoff of 600 eV was employed for all the calculations. The rutile TiO<sub>2</sub>(110)-(1×1) surface was modeled with a slab containing four Ti layers and 1×4 surface unit cells, resulting in a 0.66  $\times$  1.19  $\times$  1.11 nm supercell (see Fig. 4 below). Lattice parameters obtained from bulk optimization were used to build the slab. The first Ti layer including all its neighboring O ions was allowed to fully relax, while the bottom layers of the slab were fixed to their bulk positions. A vacuum gap of approximately 2.8 nm was employed to provide sufficient space for the adsorbates avoiding their interactions with neighboring slabs. During optimization, a set of 7×7×1 Monkhorst-Pack k-points was used. The adsorption of BHA was investigated calculating the adsorption energy (Eads) on different sites. Eads was computed by subtracting the energies of the gas-phase BHA and the clean surface E(slab) from the energy of the adsorbed system as follows:  $E_{ads} = E(BHA/slab) - E(BHA) - E(slab)$ . With this definition, negative adsorption energies indicate energetically favorable adsorption sites on the surface.

#### 3. Results and discussion

Fig. 1 (top) shows the O 1s XP spectra for three different coverages (0.20, 0.71 and 1.00 ML) of benzohydroxamic acid, deposited onto rutile  $\text{TiO}_2(110)$ - $(1 \times 1)$  held at room temperature, compared with reference spectra of benzohydroxamic acid powder and potassium benzohydroxamate powder (bottom). For both powders, the binding energies agree well with literature values [41]. After deposition of BHA, two O 1s peaks are clearly visible, which are assigned to the oxygen atoms of the titania substrate at 530.1 eV and the oxygen atoms of the molecule at 531.6 eV.

After subtraction of the substrate oxygen peak (the peak was fitted with the shape identical to that of the clean surface and only the area was allowed to change), it is evident that the adsorbed molecules give rise to just one single O 1s peak (dashed vertical line), at a binding energy position very close to that of the potassium benzohydroxamate reference. We therefore tentatively suggest that benzohydroxamic acid deprotonates upon adsorption resulting in hydroxamate surface species. The deprotonation should be accompanied by the formation of hydroxyl groups on the surface. However, since hydroxyl groups are expected to show up at 531.2–531.7 eV in the O 1s spectra [42–44], they strongly overlap with the hydroxamate peak, and thus we are not able to resolve them.

Fig. 2 shows the C 1s and N 1s spectra corresponding to the depositions shown in Fig. 1. In the C 1s spectra (left panel) three peaks are visible, a dominating peak at 284.7 eV, which is assigned to the phenyl ring in BHA, and two smaller features at 287.6 and 289.4 eV.

At high coverage (green and red spectra), the feature at 287.6 eV dominates. Its binding energy is in almost perfect agreement with the amide carbon (N—C=O) of potassium benzohydroxamate [41,45]. In line with the conclusion derived from the O 1s spectra, we therefore conclude that the majority species at this coverage is a hydroxamate.

At low coverages (black spectrum), however, this species coexists with another species with a peak at 289.4 eV, with roughly a 1:1 ratio. This binding energy is consistent with a strongly oxidized carbon species such as an anhydride, lactone, orthoester, or carbonate [46–50]. Other options are carbamate, urea, imide or similar species [51–56]. The concentration of this species is low and not affected by coverage.

The N 1s spectra are also shown in Fig. 2 (right panel). At low coverage (black spectrum), two nitrogen species are visible at 400.1 and 398.3 eV, with a 1:1 ratio. A similar 1:1 ratio is seen for the two small C 1s features at this coverage (see above). The binding energy of 400.1 eV is consistent with the value observed for potassium benzohydroxamate, confirming the presence of hydroxamate on the surface. The other N 1s species at 398.3 eV is likely related to the strongly oxidized carbon species, which we attributed to species formed upon decomposition at oxygen vacancies or defects. The binding energy of 398.3 eV could



**Fig. 1.** O 1s XP spectra of different coverages of benzohydroxamic acid deposited on  $TiO_2(110)$ - $(1 \times 1)$  at room temperature (see Fig. 2 for the corresponding C 1s and N 1s spectra). For clarity, we show both the as-measured spectra and the spectra with the contribution from the  $TiO_2(110)$  substrate subtracted. Reference spectra of benzohydroxamic acid powder and potassium benzohydroxamate powder are shown for comparison (black lines: data, red lines: fit envelope; the colors of the fitted peaks refer to the colors of the corresponding atoms in the sketches).

indicate a nitride-like species even though it does not exactly fit the value of titanium nitride (TiN) at 397.1 eV [57]; atomic nitrogen as found previously by Diebold group would be another possibility [58]. As the coverage is increased (red and green spectra), the hydroxamate N 1s species shifts slightly down to a binding energy of 399.8 eV;



**Fig. 2.** C 1s and N 1s XP spectra for benzohydroxamic acid deposited on  $TiO_2(110)$ -(1×1) at room temperature (see Fig. 1 for the corresponding O 1s spectra). Reference spectra of benzohydroxamic acid powder and potassium benzohydroxamate powder are also included for comparison (black lines: data, red lines: fit envelope; the colors of the fitted peaks refer to the colors of the corresponding atoms in the sketches).

interestingly, this peak and also the O 1s peak at 531.6 eV in Fig. 1 do not further increase when increasing the coverage from 0.7 to 1.0 ML. We attribute this behavior to the attenuation of the anchor group signals by the phenyl group of more upright standing molecules at higher coverage (similar to the attenuation of the Ti substrate signal in Fig. 1). With increasing coverage also a new nitrogen species appears at 401.0 eV. This species cannot be distinguished from the hydroxamate signals in the O 1s and C 1s regions but is shifted by almost 1.2 eV in the N 1s region. The nature of the hydroxamate N 1s low-binding-energy species (399.8–400.1 eV) will be determined in the DFT calculations (see below), and the nature of the hydroxamate N 1s high-binding-energy configuration (401.0 eV) after presenting the effect of annealing.

Fig. 3 shows the valence band (VB) and the Ti  $2p_{3/2}$  spectra of the initial TiO<sub>2</sub>(110)-(1×1) surface and after the deposition of 0.20, 0.71 and 1.00 ML of BHA molecules. Two features are clearly distinguished in the valence band spectra. The broad peak between 3.4 and 10.0 eV below the Fermi level corresponds to the O 2p band [59], whereas the minor peak observed in the band gap at around 0.9 eV below the Fermi level corresponds to ordefect states (for a detailed discussion see literature [14,60–64]). The Ti  $2p_{3/2}$  spectra show a main peak at 459.0 eV due to Ti<sup>4+</sup> with a shoulder at lower binding energy due to Ti<sup>3+</sup> [14,65]. When BHA molecules are deposited on the surface both the VB defect state signal and the Ti<sup>3+</sup> signal attenuate to a larger extent than the substrate O 2p and Ti<sup>4+</sup> signals. This indicates that BHA

adsorption removes oxygen vacancies from the surface, in line with the oxygen vacancy/defect-induced BHA decomposition proposed from the 398.3 eV N 1s and the 289.4 eV C 1s signals. Finally, we note that as the BHA coverage increases new peaks appear at around 3.0, 10.5, 14.0 and 17.5 eV below the Fermi level due to BHA electronic states.

The XPS data discussed above indicate that the -OH group in BHA deprotonates upon adsorption forming a hydroxamate species. Furthermore, different BHA surface species are suggested by the N 1s XPS data as a function of coverage: The species yielding the peak at 398.3 eV is associated with adsorption and decomposition at defect sites and is present for all coverages. At low coverages, there is only one hydroxamate surface species (400.1 eV), whereas at higher coverages two hydroxamate species (399.8 and 401.0 eV) are observed. Fig. 4 shows the most likely possible configurations for the hydroxamate binding mode [25]. Bearing in mind that hydroxamic acids are known to exist in the keto and enol tautomeric forms [8,66], the -N(H)-OH group could monodeprotonate and bind to a single Ti ion forming a monodeprotonated monodentate (mm) species or a chelating species (mc) or bind to two Ti ions forming a bidentate species (mb). BHA could also bind as a dianionic species giving rise to dideprotonated bidentate (db; also denoted as doubly deprotonated) or chelating (dc) forms.

Fig. 4 also shows the DFT-optimized structures of the bare  $TiO_2(110)$ - $(1\times1)$  surface and the different binding modes of one benzohydroxamic acid molecule on the surface. All calculations were



**Fig. 3.** Valence band and Ti  $2p_{3/2}$  XP spectra of benzohydroxamic acid on TiO<sub>2</sub>(110)-(1×1). These preparations are the same as for the hydroxamic acid deposition depicted in Figs. 1 and 2. The clean surface spectra were shown for comparison, and these were prepared with a lower annealing temperature (50 K lower). The valence band spectra were only divided by the mesh current (as for all spectra). To correct for attenuation with increasing coverage the Ti  $2p_{3/2}$  peaks were normalized to a height of one. The Ti  $2p_{3/2}$  peaks were aligned to a binding energy of 459.0 eV.

carried out by placing one BHA molecule in the  $1 \times 4$  supercell resulting in a molecular surface density equal to  $1.28 \text{ nm}^{-2}$ . A rough estimation from XPS comparing the C 1s to Ti 2p ratio of BHA with the ratio of CoTPP on TiO<sub>2</sub>(110) gives a molecular density of the saturated BHA layer of  $2.6 \pm 0.3$  molecules/nm<sup>2</sup>. Thus, the density of the structure used in DFT corresponds to 50 to 60% of the saturated monolayer (1 ML). Note that the molecule is adsorbed in its mono- or dideprotonated form and the resulting protons are included in the calculation as surface hydroxyl groups. Different surface sites for H adsorption after molecular deprotonation were analyzed resulting in energy differences lower than 0.02 eV. Adsorption energies and bond lengths of the DFToptimized binding modes are given in Table 1.

The interatomic distances are similar for all adsorbed species. In all cases, the N—O<sub>a</sub> distance decreases with deprotonation and formation of a Ti—O<sub>a</sub> bond. The N—C and the C—C interatomic distances decrease while the C—O<sub>b</sub> distance increases for bidentate and chelating species. Notably, the N—C distances are shorter for the dideprotonated species in line with cleavage of the N—H bond. The adsorption energies indicate that the monodeprotonated bidentate bridging (mb) binding configuration is the most favorable binding mode at this surface coverage. Our results are in agreement with previous DFT calculations [26] showing that the most stable configuration of hydroxamic acid on rutile TiO<sub>2</sub>(110)-(1×1) is the monodeprotonated bridging bidentate configuration as found here.

The results discussed above are obtained after adsorption of BHA molecules in UHV. Thus, to gain further information, we deposited benzohydroxamic acid from ethanol and acetonitrile solutions onto

UHV-cleaned rutile TiO<sub>2</sub>(110)-(1×1) crystals. Fig. 5 shows the O 1s, N 1s and C 1s XP spectra of the solution-deposited BHA molecules compared to the spectra of the vacuum-deposited BHA monolayer. Given that the spectra were measured on three different experimental setups, they were all normalized to the same maximum height to facilitate the comparison. The binding energies of all spectra (except the C 1s peak for ethanol, where no reference spectrum with 650 eV was measured) were aligned to the O 1s peak of the substrate at 530.1 eV. This was done because the C 1s spectra of the solvent-deposited molecules were slightly broadened, possibly due to co-adsorption of unwanted species. Although the solvent influences the BHA tautomeric equilibrium position, BHA molecules are in the keto form in polar solvents like ethanol and acetonitrile [33]. We carried out experiments using acetonitrile and ethanol solutions as the adsorption behavior could be different using protic and aprotic solvents. However, the XPS data shown in Fig. 5 indicates that BHA molecules form similar layers when using both solvents.

Overall, the O 1s and C 1s XP spectra of the solution-deposited molecules show the same main features as the spectra obtained after deposition from UHV. The O 1s spectra indicate that the hydroxyl group in BHA molecules (N—OH) deprotonates and the C 1s spectra shows a signal at 287.6 eV due to the amide carbon in the adsorbate. The molecules deposited from ethanol (black spectra) exhibit an O 1s peak at the same binding energy of around 531.6 eV as the vacuum-deposited molecules (green). The larger ratio of this peak to the substrate peak at 530.1 eV suggests that deposition from solution results in a larger coverage than that of the saturated monolayer of the vacuum-deposited molecules. However, we should bear in mind that deposition from



**Fig. 4.** DFT-optimized geometry of the supercell employed in the calculations. The slabs (top left) contain four Ti layers and  $1 \times 4$  surface unit cells. Possible surface binding schemes (mono = monodeprotonated and di = dideprotonated) are shown together with the corresponding DFT-optimized geometries and adsorption energies. The coloring scheme is: O in the solid=red, O in BHA=orange, Ti=green, C=dark gray, N=blue and H=light gray.

| Table 1                                                                         |
|---------------------------------------------------------------------------------|
| Adsorption energies and bond lengths for the different binding modes of ben-    |
| zohydroxamic acid on $TiO_2(110)$ -(1×1). The labels of the different oxygen    |
| atoms in the hydroxamic acid functional group are given by $O_a$ -NH-C- $O_b$ . |

|                         | BHA  | mm    | mb    | mc    | db    | dc    |
|-------------------------|------|-------|-------|-------|-------|-------|
| E <sub>ads</sub> (eV)   |      | -1.29 | -2.20 | -1.04 | -2.04 | -0.98 |
| Ti – O <sub>a</sub> (Å) |      | 1.85  | 1.99  | 2.11  | 1.83  | 1.99  |
| Ti – O <sub>b</sub> (Å) |      |       | 1.99  | 2.12  | 1.89  | 2.00  |
| $N - O_a$ (Å)           | 1.40 | 1.33  | 1.34  | 1.34  | 1.35  | 1.36  |
| N – C (Å)               | 1.37 | 1.38  | 1.34  | 1.32  | 1.31  | 1.31  |
| $C - O_b$ (Å)           | 1.25 | 1.23  | 1.26  | 1.28  | 1.31  | 1.32  |
| C – C (Å)               | 1.48 | 1.51  | 1.48  | 1.45  | 1.47  | 1.46  |
| N – H (Å)               | 1.02 | 1.02  | 1.02  | 1.01  |       |       |

solution could result in the co-adsorption of unwanted species (solvent molecules or dissolved impurities) which would yield a larger apparent coverage. Thus, it is not possible to compare the molecular coverages obtained after depositing molecules from UHV and from solution.

On the other hand, the N 1s spectra of the solution-deposited films show marked differences with the N 1s spectra of the vacuum-deposited molecules. First, we should note that the N 1s spectra of both solutiondeposited films are almost identical. Importantly, both lack the lowbinding-energy 398.3 eV feature of the vacuum-deposited molecules, which we attributed to adsorption at oxygen vacancies/defects (see Fig. 3). Exposure to ambient air will fill up these vacancies/defects, as it results in a very fast adsorption of traces of carboxylic acids [67]. We therefore view the absence of the low-binding-energy nitrogen species in the solution-deposited molecules as a further evidence that this species is related to oxygen vacancies/defects in the  $TiO_2(110)$  surface. The binding energies of the two species in the N 1s spectra of the solution-deposited molecules at 400.8 and 399.2 eV are comparable to those observed for the vacuum-deposited saturated monolayer (401.0 and 399.8 eV). We therefore tentatively suggest that the same species are formed for all three deposition procedures. The main difference is the different ratio of the two nitrogen species for the solution-deposited



**Fig. 5.** O 1s, C 1s and N 1s XP spectra of solution-deposited benzohydroxamic acid on  $TiO_2(110)$ - $(1 \times 1)$  compared with the vacuum-deposited saturated monolayer from Fig. 1. The O 1s region of the molecules deposited from acetonitrile solution is not shown because the surface sensitivity at a photon energy of 1486.7 eV is insufficient to observe the molecules in the O 1s region next to the intense substrate peak.

molecules. This could be an effect of different coverages or, perhaps more likely, the absence of the low-binding-energy species at 398.3 eV, which we attribute to oxygen vacancies/defects. If the number of molecules in this low-binding-energy peak would instead adopt the high-coverage adsorption configuration one would roughly get the two-to-one ratio observed for the solution-deposited molecules. The solutions would also allow for proton exchange between the surface and the solution, whereas the abstracted protons remain on the surface in UHV. Noteworthy, the N 1s spectra of our solution-deposited benzohydroxamic acid show good agreement with the spectra of the solution-deposited long-chained alkanehydroxamic acid on the native oxide of titanium obtained by Folkers et al. [24]. Interestingly, these authors concluded that the main adsorption product is the intact acid and the monodeprotonated hydroxamate is the side product, while we exclude the presence of the intact acid from our O 1s spectra.

The effect of temperature was explored to gain further insight into the different binding modes. Fig. 6 shows the evolution of the O 1s, C 1s and N 1s spectra of 1 ML benzohydroxamic acid vacuum-deposited at RT, upon stepwise annealing to 600 K. The increase of the TiO<sub>2</sub> substrate O 1s signal at 530.1 eV and the simultaneous decrease of the adsorbate signal 531.6 eV indicate desorption starting at 380 K. Simultaneously, also the hydroxamate signal at ~287.6 eV starts to decrease. Desorption is also evident from the N 1s spectra, where a decrease in the 401.0 eV signal is observed in the 300–400 K range followed by a decrease in the 399.8 eV signal at higher temperatures. This could be caused by the high-coverage 401.0 eV surface species recombining with surface protons and desorbing as intact hydroxamic acid, or it could be caused by a decomposition on the surface and desorption of fragments.

Fig. 7 shows the O 1s, C 1s and N1 s XP spectra as a function of temperature for the molecule deposited from acetonitrile. In this case, the intensity of the O 1s spectra, which is dominated by the substrate signal due to the poor surface sensitivity when using Al-K<sub> $\alpha$ </sub> radiation  $(h\nu = 1486.7 \text{ eV})$ , increases with temperature as desorption takes place. This is accompanied by a decrease in the C 1s signal. Note that the C 1s spectra also shows that the hydroxamic acid group at 287.6 eV is still visible at 400 K, but disappears at 450 K, in line with the temperature behavior of the vacuum-deposited molecules (the remaining peak at ~289.2 eV likely is carbonate). The N 1s region again is compatible with a simple decrease in coverage: The high-coverage species (high N 1s binding energy species) has decreased by  $\sim$ 50% at 400 K, and has vanished at 450 K. The low-coverage species (low N 1s binding energy species) is stable up to 400 K and has vanished at 500 K. The most notable difference between the two annealing series is the large amount of carbon remaining on the surface for the acetonitrile-deposited molecules at 500 K. This indicates the presence of unwanted surface species that were co-deposited with BHA molecules from solution and are more thermally stable than hydroxamic acid.

The effect of temperature discussed above suggests that both the vacuum-deposited and the solution-deposited surface species have a similar behavior. The N 1s spectra as a function of temperature suggest that the high-coverage species (N 1s: 401.0 eV) has a weaker interaction with the surface than the low-coverage species (N 1s: 399.8 eV). Furthermore, the O 1s spectra demonstrates that in both binding modes the -N(H)-OH group in BHA is deprotonated resulting in surface hydroxamate. Whereas DFT calculations indicate that the low-coverage species (N 1s: 399.8 eV) is the monodeprotonated bidentate bridging



Fig. 6. O 1s, C 1s and N 1s X-ray photoelectron spectra for benzohydroxamic acid vacuum-deposited on TiO<sub>2</sub>(110)-(1×1) at room temperature and after subsequent annealing steps. For each step, the sample was annealed for 2 min and the measurements were performed at room temperature.



Benzohydroxamic Acid on TiO<sub>2</sub>(110) - Annealing Series - Acetonitrile Deposition

Fig. 7. O 1s, C 1s and N 1s X-ray photoelectron spectra for benzohydroxamic acid deposited from acetonitrile solution on TiO<sub>2</sub>(110)-(1×1) at room temperature and after subsequent annealing steps. For each step, the sample was annealed for 5 min and the measurements were performed at room temperature.

configuration, identifying the high-coverage species (N 1s: 401.0 eV) is not straightforward. Its weaker surface bond suggests that it could be a monodentate species. However, this alone does not account for its higher N 1s binding energy (1.2 eV). We initially considered the possibility of N deprotonation, but this would result in an N 1s BE shift in the opposite direction [41]. On the contrary, N protonation is expected to increase the N 1s binding energy by around 2 eV [68-71]. Strong hydrogen bonds have a similar effect and have been known to increase

the BE of a core level by up to 1.2 eV depending on bond length [72]. As the coverage of hydroxamate is increased, more protons are formed on the surface, and they are compressed into an increasingly smaller area. This effectively decreases the pH on the surface and could lead to a protonation of the aminic (C-NH-OH) nitrogen atoms forming secondary ammonium ions (C—NH<sub>2</sub><sup>+</sup>—OH). However, in bulk hydroxamic acids and hydroxamates, mainly two types of hydrogen bonding are known, namely (1) strong hydrogen bonding between the protons of the hydroxyl at the nitrogen atoms (N-OH) and the oxygen at the carbonyl group (C=O) [53], and (2) weaker hydrogen bonds between the protons of the aminic nitrogen (N-H) and the carbonyl oxygen group (C=O) [33,45,73,74]. Thus, any protonation or hydrogen bonding of the molecule would therefore be expected to happen to the oxygen atoms rather than to the nitrogen atoms itself [41,75]. Although, a protonation or strong hydrogen bond to the nitrogen atom would explain our experimental observations, it would therefore not be the expected behavior. To conclude, the nature of the high-coverage nitrogen species remains elusive and further experiments and theoretical calculations are necessary to sort through the different possibilities. This is, however, out of the scope of our present study.

#### 4. Conclusion

We have investigated the adsorption of benzohydroxamic acid on rutile TiO<sub>2</sub>(110)-(1×1) both in UHV and from solution using X-ray photoelectron spectroscopy and density functional theory calculations. Molecules are adsorbed as hydroxamate species after the -N(H)-OH group in BHA deprotonates. Solution-deposited molecules show two binding modes, whereas molecules deposited from UHV result in an extra species. The analysis of the evolution of surface oxygen vacancies/ defects as a function of BHA coverage suggests that this later mode is associated with decomposition at oxygen vacancies/defects and therefore is not present when adsorbing molecules from solution. N 1s spectra as a function of coverage shows that one binding mode is present at low coverages (399.8 - 400.1 eV) and a second mode appears at larger coverage (401.0 eV). DFT calculations indicate that the most favorable low-coverage binding mode is a monodeprotonated bidentate bridging configuration. UHV-deposited and solution-deposited BHA molecules show a similar temperature evolution and suggest that the highcoverage binding mode has a weaker surface interaction than the lowcoverage binding mode. Furthermore, there is a shift in the N 1s binding energy of 1.2 eV between both species. This suggests that the highcoverage binding mode could be a monodentate hydroxamate species with hydrogen bonds to the N atom. However, it is not possible to provide a conclusive identification of the high-coverage surface species with the available data and further experiments and theoretical calculations are required.

### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgments

This project was financially supported by the Deutsche For schungsgemeinschaft (DFG) within the Research Unit FOR 1878 fun-COS – Functional Molecular Structures on Complex Oxide Surfaces, by the Agencia Nacional de Promoción de la Investigación, el Desarrollo Tecnológico y la Innovación (PICT-2018–03276) and by the Universidad de Buenos Aires (20020190100028BA). CERIC-ERIC consortium and Czech Ministry of Education, Youth and Sports (project LM2018116) are acknowledged for financial support. C.C.F. thanks CONICET for a scholarship. The authors thank Corinna Stumm for helping us to reduce the TiO<sub>2</sub> crystals, Simon Schötz for measuring reference TIR spectra, Alexander Graßruck for putting effort into titanyl-benzohydroxamate complex extraction and David Reger for providing reference NMR spectra.

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