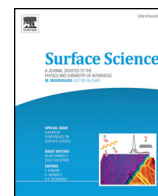




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## Interaction of carboxylic acids with rutile TiO<sub>2</sub>(110): IR-investigations of terephthalic and benzoic acid adsorbed on a single crystal substrate

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### ABSTRACT

The adsorption of two carboxylic acids, benzoic acid (BA) and terephthalic acid (TPA), on a single crystal rutile TiO<sub>2</sub>(110) substrate was studied using infrared reflection–absorption spectroscopy (IRRAS) in conjunction with DFT calculations. On the basis of the high-quality IR data (in particular for the OH bands), various adsorbate species with different geometries could be identified. The adsorption of both, BA and TPA, on TiO<sub>2</sub>(110) leads to deprotonation of carboxylic acids and protonation of substrate O-atoms. At low coverage, the deprotonated BA molecule adsorbs on TiO<sub>2</sub>(110) in an upright, bidentate configuration, while the TPA molecule adopts a flat-lying geometry with both carboxylates bound to the surface in a monodentate geometry. At higher coverages, a transition from flat-lying to upright-oriented TPA molecules occurs. At saturation coverage, both BA and TPA molecules undergo dimerization indicating the presence of pronounced attractive intermolecular interactions. We propose that the BA dimers are stabilized by the interaction between adjacent phenyl rings, while the TPA dimerization is attributed to the formation of double hydrogen bonds between adjacent apical carboxylic groups.

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### 1. Introduction

As a result of their catalytic, optical, and electronic properties, oxides are used in many application fields. A particular important example is titanium oxide which is used in catalysis and photocatalysis [1,2], as white pigment, in sun blockers, and also in solar technologies [3–5]. An important part of the Grätzel-cell, a dye-sensitized device for the conversion of sunlight into electrical energy (DSSC) first reported in 1991, is a mesoporous oxide layer (TiO<sub>2</sub>, SnO<sub>2</sub>, ZnO) [3]. Since the cross-section for photon absorption, the initial and crucial step in the conversion of light into electrical energy, is fairly small in bulk oxide materials, organic dye molecules are used in the Grätzel-cell as photon antennae. Photons absorbed by the organic molecule are converted into electron–hole (e–h) pairs. In the next step, the e–h pairs are transferred to the oxide where they are separated, and the conversion into electrical energy takes place. Typically, these dyes contain an aromatic core and are grafted to the TiO<sub>2</sub> surface via carboxylic acid groups reacting with

the surfaces of the TiO<sub>2</sub> particles yielding carboxylates bound to the substrate.

Titanium oxide exists in three different modifications: rutile, anatase, and brookite. Only the first two are used in technical applications. In the present work, we will focus on rutile, r-TiO<sub>2</sub>, and in particular on its most stable (and thus most abundant) (110) surface. The chemical properties of this best-studied oxide surface, r-TiO<sub>2</sub>(110), have been reviewed in quite some detail previously [6]. The surface chemistry of r-TiO<sub>2</sub>(110) substrates is rather complex. Different preparation conditions, over-annealing or sputtering, leads to defects like oxygen vacancies which strongly influence the surface chemical properties. Whereas the fully oxidized surface is rather inert, at oxygen vacancies, a number of reactions become possible, rendering a defective oxide surface rather reactive [7].

In order to elucidate the chemical interaction of carboxylic groups with the r-TiO<sub>2</sub> substrate, the crucial step for anchoring dye molecules within a DSSC, we have undertaken a detailed investigation on the interaction of two simplest aromatic carboxylic acids, benzoic acid (BA) and terephthalic acid (TPA, often also referred to as benzenedicarboxylic acid (BDC)) with the rutile TiO<sub>2</sub>(110) surface.

The adsorption of BA and TPA molecules on TiO<sub>2</sub> substrates has been extensively investigated in previous work. Guo et al. [8,9] studied the BA/TiO<sub>2</sub>(110) model system by using scanning tunneling microscopy

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(STM), electron stimulated desorption in ion angular distributions (ESDIAD), and low energy electron diffraction (LEED). They reported that BA adsorbs dissociatively on the  $\text{TiO}_2(110)$  surface forming benzoate species, which are bound via the bidentate carboxylate groups to the five-fold coordinated  $\text{Ti}_{5c}$  atoms in an upright adsorption geometry. They proposed that the attractive interaction between adjacent benzoates results in the formation of T-shaped dimers along the  $[1-10]$  direction. Further multiple investigations [10–12] using x-ray absorption spectroscopy (XAS), x-ray photoemission spectroscopy (XPS), and STM have confirmed these findings.

The adsorption of TPA molecules on  $\text{TiO}_2(110)$  has also been studied by means of near-edge x-ray absorption fine structure (NEXAFS) spectroscopy, STM, and noncontact atomic force microscopy (NC-AFM) [13–16]. On the basis of the experimental results, the occurrence of two different adsorbate species was reported: at low coverages (up to 0.30 ML), the TPA molecules were found to adopt a disordered and flat-lying adsorption geometry, while at full monolayer, a conversion from a flat-lying to an upright orientation was detected (Fig. 1). In addition, the combined experimental and theoretical studies revealed dimerization of TPA molecules at saturation coverage [14–16].

Despite these efforts, more detailed information on the nature of the chemical anchoring of BA and TPA molecules to the  $r\text{-TiO}_2(110)$  substrate is still lacking. This is mainly due to the fact that the experimental methods used so far (see above) are rather insensitive both to the deprotonation of BA and TPA molecules and also to the different configurations of carboxylate groups (e.g. mono- vs. bidentates). Further experimental and theoretical studies on BA/ $\text{TiO}_2$  and TPA/ $\text{TiO}_2$  systems are thus required to clarify the following points: 1) molecular vs. dissociative adsorption; 2) coverage-dependent adsorption structures; 3) origin of the dimer formation.

Here, we investigate the adsorption of BA and TPA molecules on  $\text{TiO}_2(110)$  at different coverages by using infrared reflection-absorption spectroscopy (IRRAS). Determining the frequencies of the hydroxyl and carboxylate stretching bands with high resolution should allow for unambiguous conclusions on the question whether carboxylic acid groups are still intact or are deprotonated upon interaction with the substrate. If the acid is deprotonated, a substrate hydroxyl species should be formed, exhibiting a characteristic vibrational frequency clearly different from vibrations of a carboxylic acid group. In addition, a close analysis of the IR data allows us to gain deeper insight into the adsorption configuration (i.e. the occurrence of mono- and bidentate species) and into the question whether dimers of BA and TPA adsorbate species are present on  $\text{TiO}_2(110)$ . This question is particularly interesting in case of TPA, since for an upright species (as proposed in previous works [13–16]), one would assume the occurrence of both protonated and deprotonated carboxylic acid groups.

In the past, the acquisition of high-resolution IRRAS data recorded at grazing incidence for dielectric single crystals has only very rarely been reported due to technical difficulties. In this work, high-quality IRRAS data (showing, in particular, well-resolved substrate hydroxyl bands) are reported which provide direct spectroscopic evidence for the formation of different coverage-dependent adsorption species after exposure of the  $\text{TiO}_2(110)$  surface to BA and TPA molecules. The assignment of the experimentally observed vibrational bands is supported by DFT calculations.

## 2. Experimental

### 2.1. IRRAS experiments

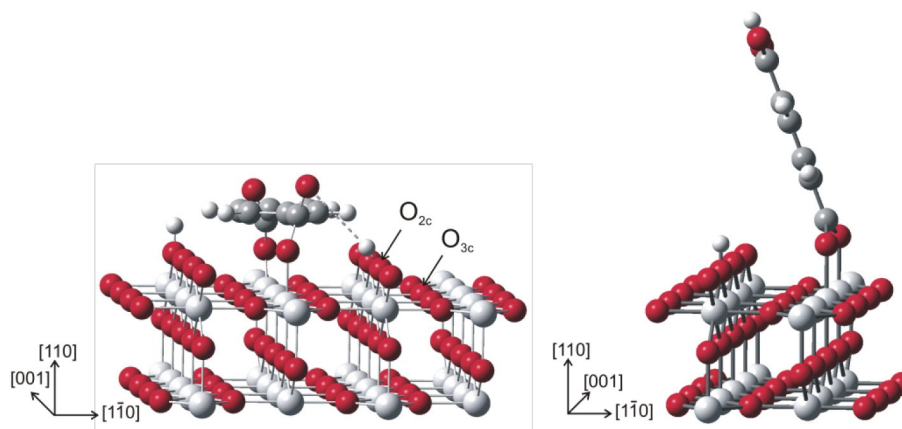
All IRRAS spectra presented here were recorded using a novel UHV-FTIR apparatus (Prevac, Rógow, Poland) [17] equipped with a state-of-the-art FTIR spectrometer (Bruker Vertex 80v, Bruker Optics, Ettlingen, Germany). The  $r\text{-TiO}_2(110)$  single crystal ( $10 \times 5$  mm, MaTeck, Jülich, Germany) was prepared by a sequence of sputtering and annealing cycles as described in Ref. [7]. The BA and TPA molecules (purchased from Merck and Aldrich and used without further processing) were deposited on the substrate by employing a Knudsen cell evaporator in a dedicated preparation chamber, which is connected via a distribution chamber to the infrared chamber of the apparatus. The vapor pressure of benzoic acid was sufficiently high to also obtain deposition for a room temperature Knudsen cell. The thick layer was prepared by exposing the cold substrate (140 K) to the molecular beam originating from the Knudsen cell. In case of TPA, the vapor pressure is so small that with a room temperature Knudsen cell only submonolayers could be prepared. For higher coverages, the Knudsen cell containing TPA molecules had to be heated to 433 K to obtain a flux sufficiently intense for the preparation of TPA mono- and multilayers.

The high-resolution IR spectra reported here were taken with a base pressure in the IR chamber of  $1 \cdot 10^{-10}$  mbar. A grazing angle of incidence angle of  $80^\circ$  was used. For each set of data, 2048 scans with a resolution of  $4 \text{ cm}^{-1}$  were accumulated. Background correction was carried out by subtracting a reference spectrum recorded using the same parameters for the clean substrate immediately before deposition of the molecular adsorbates.

IR-reflectivity and -absorbance calculations were performed by using the equations derived by Hansen et al. [18,19] and by Mielczarski et al. [20], as described in detail in Ref. [21].

### 2.2. DFT calculations

All quantum chemical calculations have been performed with the plane wave code VASP [22,23]. The  $\text{TiO}_2(110)$  surface was treated in



**Fig. 1.** Ball-stick model for the adsorption of terephthalic acid on rutile  $\text{TiO}_2(110)$ . Left panel: flat-lying configuration, right panel: upright configuration [13,16]. Color code: oxygen (TPA) = red, carbon = grey, hydrogen = white, oxygen ( $\text{TiO}_2$ ) = red, titanium = light grey.

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