Adsorption dynamics of water on the surface of TiO2 (110)

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Abstract. Rutile titanium dioxide TiO2 is used in a number of technological areas. Therefore, in surface science, it has become the most studied oxide surface. Water adsorption on rutile TiO2 (110) has been investigated using the X-ray photoelectron spectroscopy (XPS) and the work function study (WF): water adsorption induces formation of a dipole layer, which locally changes the work function. This can be experimentally observed as the onset shift of the secondary electron energy spectrum. While XPS seems to be insufficiently sensitive to monitor water adsorption on TiO2, there is a clear work function change undoubtedly attributed to the water adsorption. The measurements were done for different water vapour pressures, exposure times, sample temperatures and general surface conditions. Time evolutions of the work function change and the H2O partial pressure, enable us to successfully model the adsorption dynamics and help us understand the observed results. The analysis clearly shows existence of at least three different adsorption sites. Their interplay governs the work function time evolution, while the relative contributions depend on the surface temperature and, presumably, its topography. These results will be discussed in the light of several recent experimental and theoretical studies of this system done by other authors.

1. Introduction

TiO2 is one of the most studied metallic oxides due to the possible applications in photocatalysis, heterogeneous catalysis, as a gas sensor, solar cell, biocompatible material etc. Besides, it is investigated as a model metallic oxide surface. Rutile TiO2 (110) has attracted particular attention as the most stable TiO2 surface. The chemical activity of this surface is mainly governed by the bridging oxygen vacancies (BOV) which act as the adsorption sites for different molecules. Water adsorption on TiO2 (110) is thoroughly investigated using various surface sensitive experimental techniques among which STM particularly shed light to this very complex system [1, 2].

The vast majority of H2O/TiO2 (110) studies have been performed on the unreconstructed (1x1) surface, shown in Figure 1(a). It practically always contains small relative concentration of BOV $N_{BOV}$ (up to 10-12 %) [3]. Further increase of BOV concentration leads to the (2x1) surface reconstruction, the latter being able to sustain wide range of $N_{BOV} \leq 55$ % [4]. Although the question concerning the corresponding atomic arrangement is still open, it is generally accepted that (2x1) reconstruction is

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formed from the nonreconstructed surface by adding Ti$_2$O$_3$ rows on the top of every second Ti row of the (1x1) surface (see Figure 1b).

![Figure 1](image1.png)

**Figure 1** The most common structures of rutile TiO$_2$ (110) surfaces: a) bulk terminated TiO$_2$ (110)-(1x1) surface; b) reconstructed TiO$_2$ (110)-(2x1) surface, model proposed by Onishi et al. [2].

Concerning the water adsorption on rutile TiO$_2$ (110)-(1x1) surface, two adsorption sites have been mainly identified: BOV on which the dissociative adsorption takes place yielding in formation of two hydroxyls with hydrogen atoms facing the vacuum, and the non-dissociative adsorption on titanium rows with two hydrogen atoms facing the vacuum (it is accepted that the in plane oxygen atoms are not active adsorption sites). The latter is desorbed at 265 K while the recombination of the hydroxyl groups that lead to desorption from oxygen vacancies takes place at about 500 K [5]. It should be stressed that even at vacuum conditions of about $3 \times 10^{-10}$ mbar of residual gas surfaces with N$_{BOV}$ of about 5 % can be fully hydroxylated within a few minutes (the exposures of about 0.1 L!) [3] This peculiar result can be explained only by the high mobility of water molecules adsorbed at the surface which allows them to inspect more than one adsorption site: when adsorbed at Ti rows, water molecules travel along the rows until they find BOV on which the dissociative adsorption takes place [5]. There are only few works related to the water adsorption on (2x1) reconstructed rutile TiO$_2$ (110) surface [6, 7]. The main conclusion is that the adsorption takes place at BOV.

Adsorptions of water or hydroxyl molecules, which are both polar, make a dipole layer at the rutile surface reducing the work function. According to the well-known Topping model [8] the work function change is directly proportional to the dipole concentration as long as the concentration is not too high. The work function change i.e. the dipole concentration can be simply followed by monitoring change of the onset position of the secondary electron distribution. The corresponding experimental technique is known as Work Function Study (WF). To the best of our knowledge, WF has been employed to monitor the water adsorption dynamics of on rutile TiO$_2$ (110) [6, 7, 9] but not for the unreconstructed surface.

2. Experimental

The experiments were performed in the multipurpose surface analysis apparatus described elsewhere [10]. The sample color is dark blue indicating O-deficient bulk reduced sample. It was cleaned using several sputtering/annealing cycles (3 keV Ar$^+$ at about 20° with respect to the surface plane, 773 K for 10 min) until only Ti and O peaks were present in X-ray Photoelectron Spectroscopy (XPS) survey spectra. Secondary electron emission was stimulated by non-monochromated X-rays emitted from the Mg anode of an X-ray source, routinely used for XPS. The sample was biased to -30 V to allow the detection of electrons with low kinetic energies. If the energy of secondary electrons with respect to the sample vacuum level is $E_k^S$ the measured energy will be $E_k^A = 30\,V + E_k^S + WF^S - WF^A$ where $WF^S$ and $WF^A$ are the work functions of the sample and the analyzer, respectively. Lowering $WF^S$ will shift the measured secondary electron energy spectrum towards the lower energies. Water used in the adsorption experiments has been purified using several freeze-pump-thaw cycles. Its partial pressure during the adsorption experiments has been followed using the pressure rise detected by the ionization gauge. The purity of the introduced gas has been checked by the residual gas analyzer.

3. Adsorption dynamics modeling

Before we present a simple model for the water adsorption dynamics on unreconstructed rutile TiO$_2$(110), let us clear out several points about the results one can get from WF measurements [11,
Energy distribution of the secondary electrons is generally a superposition of different contributions associated to the surface regions described by their local work functions. Let us recall that WF actually provides the information only about the parts of the surface having the smallest work function i.e. the highest dipole concentration in our case. As already stated, the dipoles can be formed on BOV (as pairs of hydroxyls) and on the Ti rows (molecular adsorption). The hydroxyl mobility is much smaller than that of the water molecules, which can readily diffuse along the Ti rows [5]. Hence, the highest dipole concentration should be in the regions close to the hydroxyl dipoles i.e. adsorption sites for the molecular adsorption of interest are the Ti atoms in the vicinity of the hydroxyl dipoles. Having that in mind and according to the Topping model for the low dipole concentration [8], the work function shift should be
\[ \Phi_{\text{WF}} = -\frac{e}{\epsilon_0} \left[ n_{\text{vac}} \cdot 2 \mu_{\text{OH}} \theta_{\text{vac}} + N_{\text{eff}} \cdot \mu_{\text{H2O}} \theta_{\text{H2O}} \right], \]
where \( n_{\text{vac}} \) and \( N_{\text{eff}} \) are the surface concentrations relative to \( n_{\text{Ti}} \) and the dipole moments are given in Deby. The adsorption dynamics is governed by the time evolution of \( \theta_i \). The adsorption rate should be equal to the product of the particle flux \( \Phi \) and the probability that the adsorption will take place (sometimes called the sticking coefficient): \( \frac{dn}{dt} = \Phi \cdot P_{\text{adsorption}} - \beta n \), where \( n \) is the concentration of adsorbed species and \( \beta \) is the desorption rate. Let us now assume that a molecule has a chance to be adsorbed only if it ‘falls’ on the adsorption site i.e. on a specific surface atom. This case corresponds to the water molecule adsorption on the Ti rows. The adsorption probability is then equal to the probability that the atom hits an empty adsorption site \( n_a(1-\theta_a)n_s \) is the surface concentration of all atoms and \( n_a (\theta_a) \) is the surface concentration (coverage) of potential adsorption sites) multiplied by the probability that the adsorption is actually going to happen. The latter can be related to the concentration of adsorbing molecules or the existence of adsorption energy, but it should be only temperature dependent. We shall describe these effects by a single coefficient \( \alpha(T) \):
\[ n_a \cdot \frac{d\theta_a}{dt} = \Phi \cdot \alpha \cdot n_a(1-\theta_a)n_s - \beta \cdot n_a \theta_a \text{ i.e.} \]
\[ \frac{d\theta_a}{dt} = \Phi \cdot \alpha \cdot \frac{(1-\theta_a)}{n_s} - \beta \cdot \theta_a. \]  

In the case of the hydroxyl adsorption at bridging oxygen vacancies, the diffusion along the Ti rows plays an important role. The direct consequence is that a water molecule ‘probes’ \( M \) different adsorption sites in average. If the probability of finding an empty adsorption site in a single trial is \( P_i = n_a(1-\theta_a)n_s \) the probability that the molecule will find the adsorption sites by maximum \( M \) trials is \( 1-(1-P_i)^M \). If \( P_i << 1 \), which is certainly the case, it can be shown that
\[ \frac{d\theta_a}{dt} = \frac{\Phi}{n_s} \left[ 1 - \exp \left( -M \alpha \frac{n_a(1-\theta_a)}{n_s} \right) \right] - \beta \cdot \theta_a. \]

The equations (2) and (3) are used to model the adsorption dynamics of water on Ti rows and bridging oxygen vacancies, respectively.

3. Results
WF results clearly show two different behaviors in terms of water adsorption dynamics which reflect the surface structure. The difference is present in the XPS results as well. We denote the two surfaces non-reconstructed and partially reconstructed due to the reasons given below. In both cases the overall work function change never exceeds 0.2 eV, which is the reason why the results are quite noisy. Still,
by applying strict and careful experimental procedure they are reproducible and can be generally used (in correlation with XPS measurements and modeling) to yield considerable information about the water adsorption on rutile TiO$_2$ (110) surface.

3.1. Non-reconstructed surface

3.1.1. XPS measurements

The XPS measurements has been performed prior and after each water adsorption experiment. The main XPS lines of oxygen (O 1s) and titanium (Ti 2p) were recorded in order to monitor the surface composition and the peak shapes.

The measured O:Ti composition ratio in the case of the unreconstructed surface is 72:28, with the uncertainty of ±1. Water adsorption does not show any influence to the composition. The discrepancy from the expected 66:33 can be due to different reasons such as inadequate relative sensitivity factors used for the composition analysis (since they are not provided by the manufacturer the data from [13] are used). Additionally, small matrix effects [14] and material depth non-homogeneity could be also partly responsible for the discrepancy.

The peak shapes are also influenced by the surface structure. The Ti 2p peak (Figure 2a) clearly consists of two contributions modeled by pseudo-Voigt profiles. Assuming that the main peak corresponds to Ti from TiO$_2$ (so called Ti$^{4+}$) the other one is related to the bridging oxygen vacancies (the corresponding peak shifts are 1.7 eV for Ti 2p$_{3/2}$ and 2.4 eV for Ti 2p$_{1/2}$) [1]: it is generally assumed that by the creation of BOV two Ti atoms are left with unsaturated bonds which is seen in the XPS as the peak corresponding to Ti$_3$O$_3$ bond (Ti$^{3+}$ state). Since the surface concentration of Ti is the same as that of the bridging oxygen, relative magnitude of the Ti$^{3+}$ contribution is two times the relative concentration of oxygen vacancies. The strange feature concerning the Ti$^{3+}$ peak is that it does not disappear after the water adsorption (which should saturate the dangling bonds): the difference between the XPS spectra taken before and after the adsorption experiment is negligible. The same effect was also observed in [7] and [9]. The Ti$^{3+}$ contribution could be related to the concentration of the bridging oxygen vacancies on the freshly prepared surface i.e. before any adsorption, including that from the residual gas, takes place (cf. Section 4). The relative contributions of the Ti$^{3+}$ peak and the estimated BOV concentration are given in Table 1. However, one should have in mind that titanium atoms at interstitial sites can generally be in Ti$^{3+}$ and Ti$^{4+}$ states [1].

Figure 2a shows O1s peak, also modeled by 2 pseudo-Voigt profiles, the main one corresponding to TiO$_2$ and the other one, identified as TiO$_x$, (the peak shift is 1.6 eV) usually associated to the native oxides of Ti [15]. The peak shift for the Ti$_3$O$_3$ is only 0.1 eV so it could not be reliably resolved, while the oxygen from water (the peak shift should be about 3±1 eV [16]) was not observed. The relative contribution of the TiO$_x$ peak is about 11 % with the fluctuations less than 1 % (see Table 1).
3.1.2. Work function change measurements

Two energy spectra of secondary electrons, one taken before and one during the water desorption at room temperature, are presented in Figure 3. While the onset shift is clearly visible, the rest of the energy spectra fully overlap clearly indicating the local character of the work function change. Concerning the time evolution of the work function change (Figure 4a), initial steep drop of the work function followed by the much slower decrease can be clearly observed. This behavior cannot be explained by the existence of a single adsorption site in the frame of the proposed model: if the fast adsorption takes place, the coverage increases quickly until it saturates into the equilibrium between the adsorption and desorption rates (cf. figure 4b). Therefore, the additional slow increase of the coverage can only be explained by the second contribution from another kind of adsorption sites having slower adsorption rate. The water partial pressure decrease contributes only to the work function recovering corresponding to the 2nd contribution. We denote the contributions and appropriate adsorption sites as primary (corresponding to the steep drop of the work function) and secondary (corresponding to the slower drop of the work function followed by the work function recovering). At room temperature, desorption readily takes place from the secondary adsorption sites, while the primary sites are not affected by it. Hence, the equilibrium coverage for the primary adsorption sites should be 1. Besides, the primary sites are occupied very quickly (for the exposure less than 1 L). According to the experimental and theoretical investigations done by different groups on unreconstructed rutile TiO$_2$ (110) (cf. Introduction) we identify the primary adsorption sites as the BOV and the secondary sites as the Ti atoms. Therefore we apply the approach presented in Section 3 to model the water adsorption dynamics.

![Figure 3](image-url) **Figure 3** Energy distribution of secondary electrons emitted from TiO$_2$ (110) before and after the water exposure of about 7 L

![Figure 4](image-url) **Figure 4** a) Time evolution of the work function change due to the water exposure at room temperature to the unreconstructed surface and the modelling result; b) calculated time evolution of the coverages and the H$_2$O partial pressure time evolution

From the comparisons to different experimental results it appears that the argument of the exponential term in equation (3) is much smaller than 1. Therefore, since $e^{-x} \approx 1 - x$, (3) can be approximated by $d\theta_p/dt = \Phi \cdot M \cdot \alpha (1 - \theta_p)/n_s - \beta \cdot \theta_p$. Consequently, we assume that the concentration of bridging oxygen vacancies (i.e. the primary adsorption sites) does not influence the adsorption rate but only the overall change of the work function. By ‘condensing’ the unknown parameters (i.e. by their multiplication) we come to the following set of equations used to model the experimental results:

$$\Delta WF(eV) = -1.96(I_1 \cdot 2\theta_1 + I_2\theta_2)$$

$$\frac{d\theta_1}{dt} = 1.7865 \cdot 10^5 \cdot \rho(mbar) \cdot A_1(1 - \theta_1)$$

$$\frac{d\theta_2}{dt} = 1.7865 \cdot 10^5 \cdot \rho(mbar) \cdot A_2(1 - \theta_2) - \beta_1 \cdot \theta_1 - \beta_2 \cdot \theta_2$$

where $\rho$ is the partial pressure of water, $I_1 = N_{vac} \cdot \mu_{O_{2H}}$, $I_2 = N_{Tieff} \cdot \beta_1 \cdot \theta_2$, $A_1 = \rho \cdot M_{vac} \cdot \alpha_{O_{2H}}$, $A_2 = \rho \cdot \theta_{Tieff}$ and $\beta_1 = 0$. Since the water partial pressure is time dependent, the differential equations can be solved only numerically. Obviously, parameters ($A_i$ and $\beta_i$) govern the water adsorption dynamics, while $I_i$ is the magnitude of the i-th contribution. The parameters $A_i$ and $\beta_i$ can be adjusted and kept constant to
provide the best fit to all measurements while $I_i$ change depending on the experimental conditions. Their magnitudes are given in Table 1. Water adsorption has been performed for the samples at room temperature, as well as at 336 K and 373 K. Very good match with the experiments is obtained in all cases, as it is illustrated in Figure 4a, keeping $A_i$ and $\beta_i$ unchanged.

3.2. Partially reconstructed surface

3.2.1. XPS analysis

Air exposure of the sample followed by the long term annealing at 600 K and residual gas pressure in the 10⁻⁷ mbar range (due to the baking of the vacuum system) contributes to the considerable changes in the XPS spectra even after the standard cleaning procedure described in Section 2. First of all, there is a considerable relative change of the surface composition – O:Ti composition ratio changed from 72:28 for nonreconstructed surface to 87:13 (the uncertainty is again ±1). The relative contribution of Ti³⁺ peak increased also to 20-30 % depending on the surface conditions. It should correspond to the BOV concentration of about 10-15 %, which sounds confusing knowing that the surface concentration of oxygen increased as well. The relative contribution of the TiOₓ bond of the O1s peak generally increased and it varied in the range 10-17 %.

3.2.2. Work function change measurements

As in the case of the XPS results, sample treatment after the air exposure had substantial influence to the WF results as well i.e. to the water adsorption dynamics. A typical result is presented in Figure 5. Besides the two contributions present for the nonreconstructed surface, we observe the third one characterized by slow dynamics and the lack of desorption at room temperature. The relative magnitude of the third contribution depends on the surface preparation: it is more pronounced after the first cleaning right after the air exposure; afterwards, its relative magnitude generally decreases but still varies considerably depending on the sputtering/annealing time. The third contribution can be very efficiently described using the adopted model by introducing the third adsorption sites through the corresponding equation $d\theta_3/dt = 1.7865 \times 10^5 \cdot p(\text{mbar}) \cdot A_3(1 – \theta_3)$ and modifying the expression (1) which now becomes

$$\Delta WF(\text{eV}) = -1.96(\theta_1 \cdot 2\theta_1 + \theta_2 \cdot \theta_2 + \theta_3 \cdot 2\theta_3)$$

(5)

Since we observe increase of the BOV concentration, and knowing that the desorption from these sites is negligible at room temperature, we address the 3rd contribution to BOV showing different dynamical behavior in terms of water desorption as compared to the 1st contribution. More arguments that further justify this assumption will be given in Section 4. The parameter $A_3$ was tuned to properly describe the experimentally observed water adsorption dynamics keeping the parameters $A_2$ and $\beta_2$ the same as for the unreconstructed surface (while $A_1$ had to be changed as well, cf. Section 4). Finally, the magnitudes of the three contributions have been adjusted for every experimental result. The match (Figure 5a) with the experiment is excellent. The corresponding time evolution of $\theta_i$ (i = 1-3) as well as of the water partial pressure evolution is given in figure 5b.

At the end of the water adsorption experiment i.e. after the water molecules are desorbed from the Ti rows, only hydroxyl dipoles are present at the surface. For this surface, we measured the temperature dependence of the work function shift in the range from the room temperature to about 473 K and back (Figure 6). When increasing the temperature, the work function change decreases relatively slowly until it reaches about 373 K. Then the recovering becomes steeper until the sample temperature reaches about 393 K when a kind of saturation takes place i.e. the work function does not change with further temperature increase. The work function is now even higher than at the beginning of the experiment. If the hydroxyls were desorbed at elevated temperature one should expect that after cooling some of the BOV should be again occupied by the water from the residual gas so that the work function returns to about the same value as in the beginning of the experiment. However, when the same sample is cooled down to the room temperature, there is only slight decrease of the work function. This is expected since the hydroxyls from rutile TiO₂ (110) begin to desorb at temperatures...
of about 500 K [2]. The result can be explained by the surface diffusion of hydroxyls, which should decrease the work function change by decreasing the hydroxyl concentration. This is in accordance to the earlier conclusion that the observed WF change is due to the formation of areas with low work function at the sample surface.

![Graph](image)

**Figure 5** a) Time evolution of the work function change due to the water exposure at room temperature to the partially reconstructed surface and the modelling result; b) calculated time evolution of the coverages and of the H$_2$O partial pressure

![Graph](image)

**Figure 6** Temperature evolution of the work function change of TiO$_2$ (110) surface

**Figure 7** Average time between two hopes of hydrogen atoms along bridging oxygen rows of TiO$_2$ (110) surface [19]

**Table 1** The coefficients obtained from the modelling of WF change in time and the XPS results

| Surface condition | Unreconstructed rutile TiO$_2$ (110) surface $T = 300$ K | Unreconstructed rutile TiO$_2$ (110) surface $T = 326$ K | Unreconstructed rutile TiO$_2$ (110) surface $T = 373$ K | Partially reconstructed rutile TiO$_2$(110) surface at room temperature |
|-------------------|--------------------------------------------------------|--------------------------------------------------------|--------------------------------------------------------|---------------------------------------------------------------------|
| $I_1$             | 0.037                                                  | 0.033                                                  | 0.022                                                  | 0.02 ± 0.01                                                         |
| $A_1$             | 13                                                     | 13                                                     | 13                                                     | 3-12                                                                |
| $I_2$             | 0.25                                                   | 0.25                                                   | 0.1                                                    | 0.06 ± 0.03                                                        |
| $A_2$             | 0.06                                                   | 0.06                                                   | 0.06                                                   | 0.06                                                                |
| $\beta_2$         | 0.003                                                  | 0.003                                                  | 0.003                                                  | 0.003                                                              |
| $I_3$             | 0                                                      | 0                                                      | 0                                                      | 0.07 ± 0.04                                                        |
| $A_3$             | 0                                                      | 0                                                      | 0                                                      | 0.05                                                               |
| $x_{max}$         | 0                                                      | 0                                                      | 0                                                      | 0.8 ± 0.1                                                          |
| $I_2/I_1$         | 6.7                                                    | 7.5                                                    | 4.5                                                    | 4 ± 2                                                               |
| $N_{Ti^{3+}}$ (%) | 8-11                                                   | 9.1                                                    | 7.4                                                    | 25 ± 5                                                             |
| $N_{BOV}$ (%)     | 4-5.5                                                  | 4.55                                                   | 3.7                                                    | 12.5 ± 2.5                                                          |
4. Discussion
Rutile with the (110) orientation is the most stable TiO$_2$ surface: it is usually not a problem to obtain it unreconstructed (i.e. with the reconstruction (1x1)). However, ion sputtering being the standard cleaning procedure introduces BOV. After the sample annealing, the surface again becomes with (1x1) reconstruction but creation of BOV in the bulk is the price one has to pay. Each cleaning cycle increases BOV bulk concentration. This crystal is sometimes denoted as 'reduced'. The direct consequence is that TiO$_2$ changes the electrical properties from a good insulator into N-type semiconductor (which is convenient for the surface characterization techniques that usually use charged particles as a probe). The optical properties change as well: initially transparent, with the increase of BOV TiO$_2$ becomes pale blue, then darker, and finally black. The color of the crystal is frequently used to describe the state of the sample [1].

Although Ti interstitials can be in Ti$^{3+}$ state, it is accepted that the concentration of BOV equals half of the Ti$^{3+}$ surface concentration. The relative change of oxygen concentration due to the water adsorption cannot be observed in XPS composition measurements since the technique is sensitive to first ten atomic layers. However, the fact that XPS profile of the Ti 2p peak does not change after the H$_2$O exposure is puzzling. Recent paper of the Aarhus group [17] reveals this paradox: the creation of BOV does not leave two Ti atoms with unsaturated bonds because these atoms do not stay on their original positions! They migrate into the bulk on interstitial sites instead. Latter, when BOV is filled-in with a hydroxyl, they do not return back right away due to the limited mobility. Having this in mind it seems reasonable to conclude that the contribution that we identify as Ti$^{3+}$ corresponds to Ti interstitials, still representing a measure of the BOV concentration. This also explains why the peak does not disappear after the adsorption takes place. Besides, one should be careful when estimating BOV concentration from Ti$^{3+}$ signal since Ti interstitials (i.e. BOV) are present in the bulk as well in spite of their limited mobility.

When the crystal becomes heavily reduced, it is not possible anymore to obtain (1x1) surface reconstruction. The surface becomes usually (2x1) reconstructed instead having strong influence to the water adsorption dynamics BOV (being the dominant water adsorption sites in this case [6, 7]) are farther from the Ti rows as compared to the nonreconstructed surface (cf. Figure 1). This could suppress H$_2$O molecules adsorbed on Ti rows to ‘reach’ BOV. Indeed, WF measurements done on TiO$_2$ (110)-(2x1) surface show very slow response to the water adsorption [7], qualitatively very much alike the third contribution identified in this work. Moreover, our earlier WF measurements on heavily reduced TiO$_2$ (110) [11] also show very similar behavior in terms of adsorption dynamics. The total WF change in these measurements was 0.4 eV or even more, strongly suggesting high BOV concentration and probably (2x1) reconstruction. At first site, the observed relative increase of Ti$^{3+}$ signal can be understood as the increase of BOV concentration (about 15 %) leading to the (2x1) reconstruction. If so, three questions are still open: 1. How did we abruptly introduce such a high quantity of BOV and provoked (2x1) reconstruction; 2. From WF measurements it seems that besides (2x1), (1x1) reconstructions are still present in spite of increased BOV concentration; 3. In the case of (2x1) reconstruction Ti$^{3+}$ signal partially corresponds to Ti atom in Ti$_2$O$_3$ (which is also in Ti$^{3+}$ state) so it cannot be used as a measure of BOV concentration.

In order to understand the obtained results we refer to the investigation of the TiO$_2$ (110)-(1x1) exposure to oxygen (p$_{O_2}$ in 10$^{-6}$-10$^{-5}$ mbar range) at elevated temperatures (600-800 K) (cf. [1] and references therein). The main conclusion is that at elevated temperatures Ti interstitials come to the surface and react with oxygen from the atmosphere building TiO$_2$ (110)-(2x1) reconstructed islands on the top of the unreconstructed TiO$_2$ (110) surface. We assume that similar process took place during the baking process: the sample was at about 600 K for few days exposed to the residual gas in the 10$^{-7}$ mbar range consisting mainly of water. This would explain the three open questions above mentioned: 1. The surface concentration of BOV was actually not increased; 2. The sample surface is nonreconstructed on which (2x1) reconstructed islands are grown the latter being responsible for the 3rd contribution in the model; besides, the lowest work function regions are larger than the grown islands; 3. Ti$^{3+}$ signal growth is mainly due to the Ti$_2$O$_3$ rows in (2x1) reconstructed islands.
If the (2x1) is made by adding Ti$_2$O$_3$ rows above the nonreconstructed surface, one should expect increase of the Ti surface composition being in contrast to our measurements. Besides, if the atomic arrangement of the (2x1) reconstructed surface is valid we should expect stronger suppression of the 1$^\text{st}$ contribution than of the 2$^\text{nd}$ one (in the frame of the (2x1) islands there should still be some Ti rows), which is again in contrast to our observations (see below). Impact collision ion scattering spectroscopy measurements of rutile TiO$_2$ (110)-(2x1) did not detect Ti rows in the first layer [18]. The authors suggest that the rest of the Ti rows (those not covered by the Ti$_2$O$_3$ rows) are actually covered by some kind of oxygen structure. Here discussed results including the increase of the TiO$_x$ contribution of the O 1s peak for the partially reconstructed surface strongly support their conclusions.

Let us now focus to the results of modeling. In the case of the unreconstructed surface, it is easy to decouple the contributions due to the lack of desorption for the 1$^\text{st}$ and intense desorption for the 2$^\text{nd}$ one. Moreover, this enables to get reliable determination of the coefficients $I_1$ and $A_1$ (the first defining the magnitude and the second the dynamics of the primary contribution) in contrast to the those describing the secondary contribution: the existence of the desorption makes possible to get a good fit for different sets of parameters. Additionally, the determined magnitudes of the coefficients $A_1$ and $\beta_1$ are not reliable due to the questionable precision of the water partial pressure measurement (the appropriate system was not calibrated for H$_2$O). Nevertheless, the obtained values confirm the basic assumptions on which the model is based: $A_1>1$ i.e. $M_1>1$ (since $\alpha_1$, being a probability, has to be in the interval $[0, 1]$, confirming the idea that due to the surface diffusion several surface atoms are inspected in the search for the adsorption site. In contrast, $A_2$ and $A_3$ are both less than 1 implying the lack of the surface diffusion. Parameters that define the water dynamics of the 2$^\text{nd}$ and 3$^\text{rd}$ contribution should not depend on the surface structure since the interaction between the H$_2$O molecule and the adsorption site is mainly ‘local’. This is the main reason why we kept them constant. On the other hand, change from (1x1) reconstruction to the partially reconstructed surface reduces the length of Ti rows and thus decreases $A_1$, which is exactly what we observe (cf. Table 1).

In the case of the partially reconstructed surface determining coefficients $I_3$ and $A_3$ also looks very reliable. In conclusion, we can try to yield some physical parameters starting from the coefficients $I_1$ and $I_3$. But before that, the coefficients $I_1$ have to be redefined in order to incorporate the assumptions of the existence of (1x1) and (2x1) regions. We introduce parameters $x$ and $y$ in the range $[0, 1]$ as abundance of (2x1) islands and the abundance of Ti rows, respectively. Then, $I_1 = N_1 \mu_{\text{OH}}(1-x)$, $I_2 = N_2 \mu_{\text{H}_2\text{O}}y$ and $I_3 = N_3 \mu_{\text{OH}}x$. Depending on the structure of the (2x1) islands, $y$ can be equal to $1-x$ (no Ti rows on (2x1) islands), or to $(1-x)/x$ (with Ti rows on (2x1) islands). Since the parameters $A_2$ and $\beta_2$ are fixed, the ratio $I_1/I_2$ for different structures should help us to estimate if the (2x1) islands contain Ti rows. From the data given in Table 1 it seems that $I_1/I_2$ does not depend too much on the surface structure (i.e. $y \approx 1-x$) which further supports our assumption about the structure of (2x1) islands. Assuming that relative concentration of BOV at (2x1) islands is the same as for the nonreconstructed surface ($N_1 = N_3$) we can estimate parameter $x$ from the ratio $I_3/I_1 = (x/(1-x))$. This equality does not hold: the adsorption of water from the residual gas on BOV is going to take place mainly on the nonreconstructed regions because $A_1 >> A_3$. Therefore, $x=I_3/(I_1+I_1-N_3/N_1)$ and since $N_1 < N_3$ the approximate expression will give overestimated value for $x$. From the data in Table 1 we estimate that $x$ should be smaller than 0.8.

To the best of our knowledge, there is no experimental or theoretical data of the dipole moment of hydroxyl adsorbed on rutile TiO$_2$ (110). Assuming that the Ti$^{3+}$ signal corresponds mainly to BOV in the case of the nonreconstructed surface its estimation might look straightforward: the parameter $I_1$ (which we address to the hydroxyl adsorption at BOV) for unreconstructed surface should be divided by the estimated relative BOV concentration obtained from the XPS measurements. By doing that we get the value of 0.95 D at room temperature which seems to be too high: H$_2$O adsorption on Ti rows of this system reduces the dipole moment of the molecule from 1.84 D to 0.47 D and the dipole moment of the OH bond is 1.51 D. One of the problems arises from the fact that not all BOV contribute to the measured work function change, since some of them are occupied by the water from the residual gas before the measurement actually began. Knowing that the base pressure is in the low $10^{-10}$ range, this
effect can be significant [3]. However, its direct consequence would be underestimating the dipole moment. The main problem is actually related to the fact that the measured BOV concentration is averaged to the whole surface while the WF signal is related to the low work function areas where the concentration is certainly higher. An elegant way to resolve this problem is to heat the sample and increase the mobility of hydrogen atoms. After some time, depending on the temperature, the dipole distribution should become homogeneous. Indeed, this is what we observe: the calculated dipole moment drops to 0.8 D for 336 K and 0.6 D for 373 K (we did not observe any evidence of hydroxyl desorption for these temperatures). From the work function dependence on the sample temperature it seems that the convenient temperature would be about 423 K. Additional advantages of the sample heating would be strong suppression of the surface contamination as well as of the 2nd contribution.

In order to better understand the temperature dependence of the work function (Figure 6), we refer to the work of the Austin group concerning the hydrogen migration along the bridging oxygen rows of rutile TiO$_2$ (110)-(1x1) surface [19]. Based on their measurements and modeling the temperature dependence of the average hopping time can be calculated, which is presented in Figure 7. At the temperature of about 400 K the average hopping time drops to few tens of seconds, which probably provides enough mobility to obtain homogeneous surface distribution of hydroxyls in several minutes. Having in mind that this is the typical time scale in our experiments, the steep work function increase at 390 K (cf. Figure 6) quantitatively agrees very well with the results of the Austin group.

5. Summary
Water adsorption dynamics on rutile TiO$_2$ (110) surface has been monitored using the time evolution of the work function change for different sample temperatures. A model is presented which successfully describes the obtained data. XPS sample analysis provided estimation of the bridging oxygen vacancy concentration. Using the proposed model, three adsorption sites are identified: bridging oxygen vacancies in (1x1) and (2x1) reconstructed regions and the Ti rows. The upper limit of the abundance of (1x1) islands was estimated as well. The temperature dependence of the work function change can be very well explained by the investigations of the hydrogen mobility along bridging oxygen rows, done by the Austin group. Finally, on the basis of this investigation we propose a novel method to estimate the dipole moment of hydroxyls formed on the bridging oxygen rows.

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