

Adsorption of water on thin $V_2O_3(0001)$ films

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Abstract

$V_2O_3(0001)$ films have been grown epitaxially on Au(111) and W(110). Under typical UHV conditions these films are terminated by a layer of vanadyl groups as has been shown previously [A.-C. Dupuis, M. Abu Haija, B. Richter, H. Kuhlenbeck, H.-J. Freund, $V_2O_3(0001)$ on Au(111) and W(110): growth, termination and electronic structure, *Surf. Sci.* 539 (2003) 99]. Electron irradiation may remove the oxygen atoms of this layer. H_2O adsorption on the vanadyl terminated surface and on the reduced surface has been studied with thermal desorption spectroscopy (TDS), vibrational spectroscopy (IRAS) and electron spectroscopy (XPS) using light from the BESSY II electron storage ring in Berlin. It is shown that water molecules interact only weakly with the vanadyl terminated surface: water is adsorbed molecularly and desorbs below room temperature. On the reduced surface water partially dissociates and forms a layer of hydroxyl groups which may be detected on the surface up to $T \sim 600$ K. Below ~ 330 K also co-adsorbed molecular water is detected. The water dissociation products desorb as molecular water which means that they recombine before desorption. No sign of surface re-oxidation could be detected after desorption, indicating that the dissociation products desorb completely.
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1. Introduction

Vanadium oxides play an important role in catalysis where they act as part of catalysts for different reactions, most of them involving transfer of oxygen atoms [2]. Usually V_2O_5 is used together with other oxides to improve reactivity and selectivity [3,4]. It is often claimed that vanadyl groups are the reactive centers [2]. However, details of the nature of the active centers under reaction conditions, including the vanadium oxidation state and the reaction pathways are still under active discussion (see Ref. [5] and references therein).

In oxidation reactions such as propane oxy-dehydrogenation ($C_3H_8 + \frac{1}{2}O_2 \rightarrow C_3H_6 + H_2O$) and methanol oxidation ($CH_3OH + \frac{1}{2}O_2 \rightarrow H_2CO + H_2O$), which both occur on vanadium oxide catalysts, formation of H_2O plays an

important role. In the context of an investigation of these reactions on $V_2O_3(0001)$ it appeared to be desirable to also study the interaction of water.

Water is a frequently studied adsorbate [6]. It often dissociates upon contact with a surface, forming adsorbed hydroxyl groups which may play a role in catalytic processes occurring on these surfaces. Dissociation is especially likely on defect sites, but there are also reports of dissociation on regular surfaces [7,8]. A comprehensive overview of water adsorption of different surfaces has been published by Henderson [6].

As reported in Ref. [1], well ordered $V_2O_3(0001)$ layers can be grown on Au(111) and W(110). It was shown that these films are terminated by a layer of vanadyl groups under typical UHV conditions. Electron irradiation removes the oxygen atoms of the vanadyl groups, leading to a surface terminated by vanadium atoms (see Fig. 1). We have chosen to use these films for the adsorption studies described in this manuscript in order to learn about the interaction of water with vanadyl groups and, in the case of the

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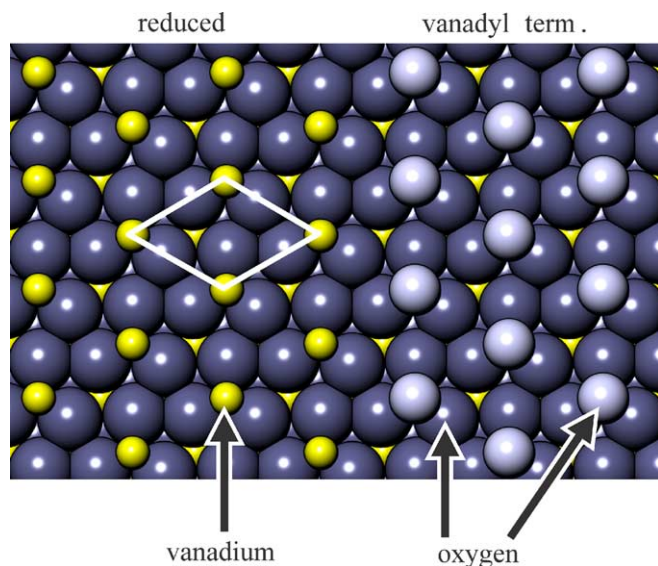


Fig. 1. Structure of the reduced and the vanadyl terminated surface. The surface unit cell is indicated. The structure of the vanadyl terminated surface has been established with STM by Schoiswohl et al. [9]. For the case of the reduced surface unpublished STM data [10] indicate that the surface is terminated by vanadium atoms as shown in the figure.

reduced surface, with co-ordinatively unsaturated and reduced vanadium atoms.

2. Experimental

The experiments were performed using two different UHV systems. One system is located at the BESSY II electron storage ring in Berlin. It is attached to the UE52-PGM plane grating monochromator which delivers photons in the energy range from 90 eV to 1500 eV. The system consists of two chambers which may be separated by a gate valve. The upper chamber contains facilities for ion sputtering, gas dosing, low energy electron diffraction (LEED) and metal deposition using an Omicron EFM4 evaporator. In the lower chamber XPS measurements may be performed using a Scienta SES200 electron energy analyzer. Photoelectrons are produced by synchrotron light from the BESSY II storage ring in Berlin. The spectra shown here have been recorded with linearly polarized synchrotron light. In order to optimize the surface sensitivity, the photon energy was chosen such that the kinetic energy of the detected electrons was around 100 eV. The overall energy resolution was better than 100 meV.

The second UHV system is used for vibrational spectroscopy and TDS. It also comprises two chambers with the upper one containing facilities for sputtering, LEED, thermal desorption spectroscopy, metal deposition with an Omicron triple EFM evaporator and infrared absorption spectroscopy using a modified Mattson RS-1 spectrometer. The incidence angle of the IR light relative to the sample normal is 85° and IR spectra were recorded by accumulating 500 scans with a resolution of 2 cm^{-1} . In the lower chamber HREELS studies may be performed

with a VSI Delta 05 spectrometer. TDS spectra were acquired with a HIDEN HAL RC 201 quadrupole mass spectrometer equipped with a pumped Feulner cup [11]. While TDS spectra were recorded, the nozzle entrance of the Feulner cup was located at a distance of a few 100 μm in front of the sample surface. The heating rate was controlled with a computer-controlled feedback system (manufactured by H. Schlichting, Germany).

Dosing of water gas was performed via a tube ($\phi \approx 1\text{ cm}$) directed towards the sample surface and positioned directly in front of it. With this setup the water pressure in the chamber during water dosing could be kept low, which is important since water sticks strongly to the chamber walls. For the adsorption experiments doubly de-ionized water was used. Several freeze-pump-thaw cycles were performed to remove gases dissolved in the liquid.

The samples were mounted using tantalum and tungsten wires attached to a hollow rod which could be filled with liquid nitrogen for cooling purposes. Temperatures of 88 K could be reached. In the case of the IRAS/HREELS/TDS system the sample was heated by passing an electrical current through the wires holding the sample whereas in the other system a tungsten filament mounted behind the backside of the sample was used for heating via electron irradiation or thermal radiation for not too high temperatures. During the experiments heating via electron irradiation was avoided to prevent unintentional surface reduction. A tungsten-rhenium (26%/5%) thermocouple spot-welded to the sample was used for temperature control in the case of the W(110) substrate. The temperature of the Au(111) crystal was measured with a chromel/alumel thermocouple inserted into a small hole drilled into the crystal's side.

Vanadium was evaporated with Omicron EFM4 and triple EFM electron beam evaporators from vanadium wires with 2 mm diameter. The evaporation rate was calibrated by evaporating some 10 min with constant metal vapor flux, measuring the thickness of the so-obtained vanadium film with a quartz micro-balance, and dividing the film thickness by the evaporation time. Typical evaporation rates were between 0.5 and 1 $\text{\AA}/\text{min}$.

Reduction of the oxide film was performed by electron irradiation using an external tungsten filament positioned in front of the sample. An electron current of 5 mA with a kinetic energy of 500 eV was incident onto the sample surface for 120 s. In order to avoid high sample temperatures this was done in four cycles of 30 s duration and a cool down period between the cycles.

The $\text{V}_2\text{O}_3(0001)$ layers were prepared by deposition of 50 \AA vanadium onto the respective substrate in 1×10^{-7} mbar of oxygen at 600 K followed by annealing at 670 K at the same oxygen pressure for 15 min. Annealing at 850 K for 10 min in vacuum completed the procedure. After preparation the substrate was covered by a well ordered $\text{V}_2\text{O}_3(0001)$ film with a thickness of $\approx 100\text{ \AA}$. A LEED pattern of $\text{V}_2\text{O}_3/\text{Au}(111)$ is displayed in Fig. 2. As expected for a corundum(0001) surface the spots are arranged with a hexagonal symmetry. No

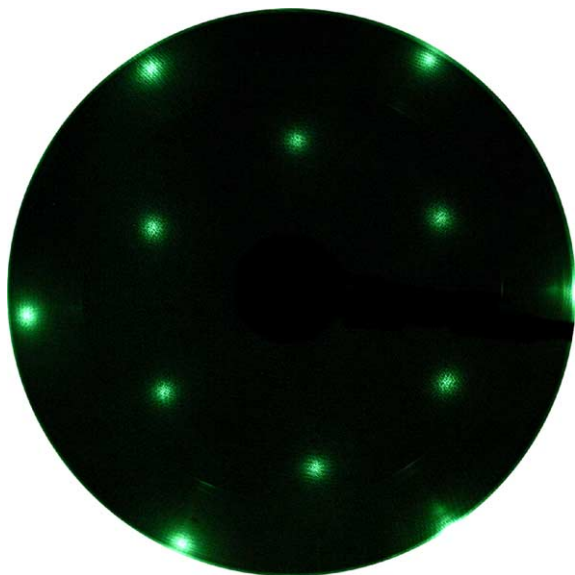


Fig. 2. LEED pattern of $V_2O_3(0001)/Au(111)$. $E_p = 50$ eV.

obvious differences could be found for the properties of $V_2O_3(0001)$ films on $Au(111)$ and $W(110)$ which may at least partially be due to the fact that the films are so thick that the influence of the oxide-substrate interface onto the surface should be small.

3. Results and discussion

Photoelectron spectra of the valence band and the O1s and V2p core level region of water on reduced and vanadyl terminated $V_2O_3(0001)$ are displayed in Fig. 3 for different annealing temperatures. At temperatures $T \leq 165$ K the typical levels of ice show up in the data. Further annealing leads to an O1s peak at around 533.5 eV in the case of the vanadyl terminated surface (Fig. 3(d)). This level may be attributed to molecular water (a list of O1s binding energies of water on different substrates may be found in Ref. [6, p. 16]). We note that this peak exhibits slightly different binding energies and intensities at different temperatures, and slight variations are observed in the corresponding valence band spectra (Fig. 3(c)). This may be due to co-adsorbed contaminations and to effects induced by the photon beam like desorption, defect formation and reaction. It may also play a role that electrons from somewhat different areas of the sample surface were detected in different spectra. The reason for the latter is that due to the low temperature required for the adsorption experiments the sample had to be cooled. This was done by filling the hollow rod holding the sample holder with liquid nitrogen. Due to thermal expansion effects the sample position could change by a few mm upon evaporation of the liquid nitrogen and refilling.

In the XPS core level data of the reduced surface (Fig. 3(b)) two water induced O1s levels at 531.3 eV and 533.2 eV get visible after removal of the ice layer ($T \geq 177$). The feature at higher binding energy may be assigned to molecular water and the level at 531.3 eV in

the spectra of the reduced surface is due to surface hydroxyl groups [12] which disappear from the surface at $T \leq 600$ K whereas the molecular water desorbs below 330 K. Using the O1s XPS intensities of the substrate, the hydroxyl groups and the adsorbed water molecules we have performed a rough estimate of the OH and H_2O coverages using an estimate of the inelastic mean free electron path length of 5 Å as obtained for similar compounds (for instance: Cr_2O_3 : 5.34 Å at 100 eV) using Sven Tougaard's Quases package (www.quases.com). A value of about 5 Å may also be obtained from the data of Seah and Dench ('universal curve') [13]. The result of the calculation is that at 188 K the hydroxyl coverage is ~ 1.6 (groups per surface unit cell) and that the water coverage is ~ 2.3 . At 363 K the calculated hydroxyl coverage drops to ~ 1.1 whereas the water molecules are essentially gone. Applying the same analysis to the O1s peak of water remaining on the vanadyl terminated surface after ice desorption (Fig. 3(d)) yields coverages between 0.5 and 1.1 molecules per surface unit cell for $200 \text{ K} \leq T \leq 256 \text{ K}$. The large spread of the data may be explained by contaminations, photon induced effects and differing sample positions as explained above. We note that the calculated coverages represent only rough estimates since the inelastic mean free electron path length is not known exactly and since electron diffraction effects which may have a significant influence at kinetic energies near 100 eV have not been considered.

It is currently not clear which type of adsorption sites the water molecules remaining on the vanadyl terminated surface occupy after ice desorption (Fig. 3(d)). According to currently ongoing STM investigations [10] it is not straightforward to prepare a vanadyl terminated surface with a low density of defects without controlling the surface with STM. This was not done in the experiments described here and therefore defect adsorption of water may be considered. However, a surface defect density which would easily explain a water coverage of about one as observed in the data was never observed in the STM images and therefore it may be assumed that the water molecules occupy regular surface sites.

In the case of the vanadium terminated surface molecular water remains on the surface after ice desorption, together with hydroxyl groups (Fig. 3(b)). In view of the high water coverage (~ 2.3 at 188 K) defect adsorption may be ruled out. It may be the case that mixed OH + H_2O overlayers form on the surface as observed on $Pt(111) + O$ (see Refs. [14,15] and references herein) and $TiO_2(111)-(2 \times 1)$ [16]. These layers are stabilized by OH– H_2O interactions. However, the IRAS data discussed below (Fig. 4) exhibit an O–H vibration of the hydroxyl groups which does not change its energy when the water molecules desorb (below 330 K, see Fig. 3(b)) which would probably indicate that OH– H_2O interactions do not play a significant role.

At the top of Fig. 3(a) and (b) the spectra of the reduced surface before H_2O adsorption and after thermal removal of the hydroxyl groups are compared. Apart from subtle

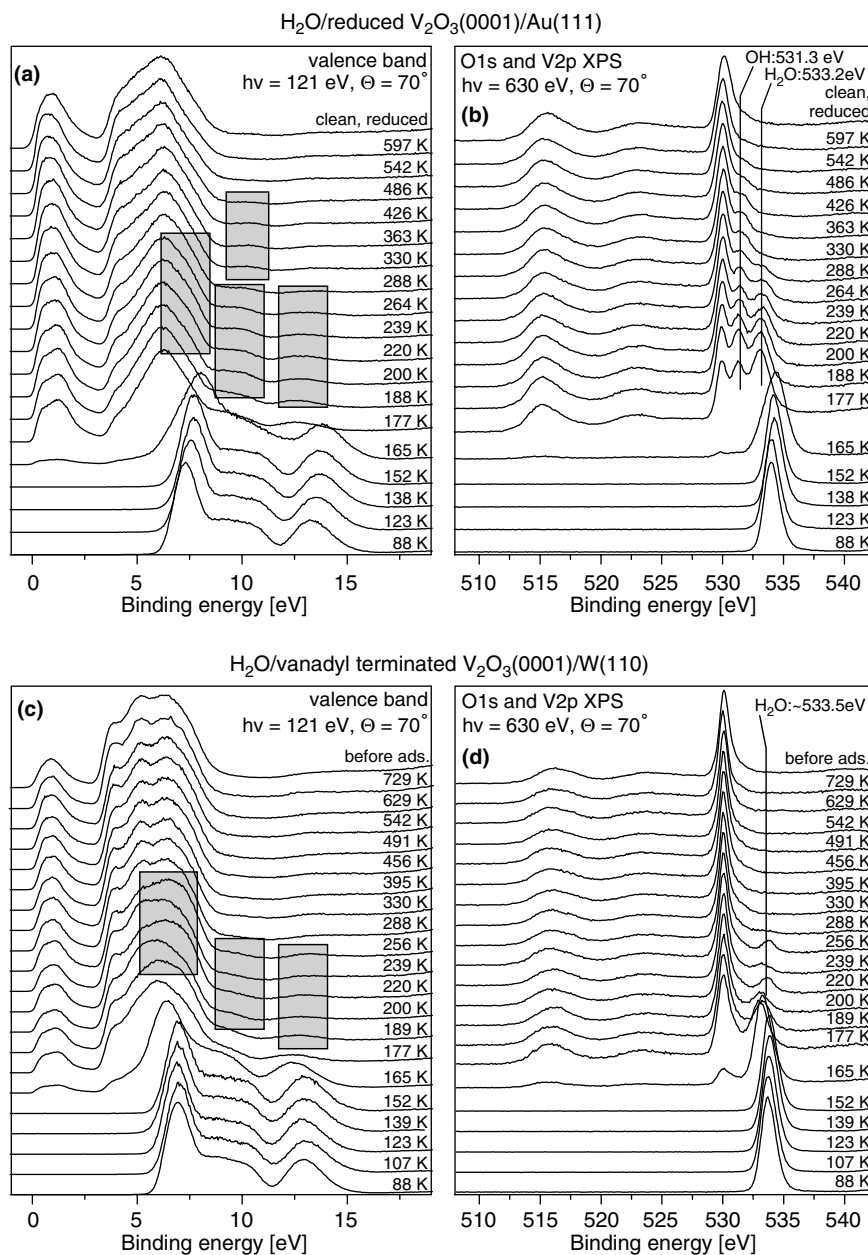


Fig. 3. Photoelectron spectra of the valence band (a,c) and the O1s + V2p region (b,d) of water on vanadyl terminated and reduced $V_2O_3(0001)$ as a function of the annealing temperature. Multilayers of water were adsorbed at 88 K. Before acquiring the spectra for a certain temperature the sample was shortly annealed at this temperature. After this the sample was cooled down and the spectra were recorded at low temperature.

changes the spectra are very similar which indicates that re-oxidation of the surface did not take place. This means that the water fragments are removed more or less completely from the surface after annealing at 597 K. We note that the shape of the valence band spectra is very sensitive to oxidation state changes (see Ref. [1]). A valence band spectrum of the vanadyl terminated surface is shown in Fig. 3(c), top spectrum.

In the valence band spectra (Fig. 3(a) and (c)) the water and hydroxyl induced levels are rather weak which may be a consequence of the low O2p cross section at the employed photon energy. Nevertheless, the spectroscopic signatures of water and OH are identifiable also in these spectra

(marked by shaded rectangles). According to Ref. [6, p. 12] the $1b_2$ level of adsorbed water may be expected at around 12–13 eV, the $3a_1$ level at around 8–10 eV, and the $1b_1$ state between 6 eV and 8 eV. All three levels are identifiable in the spectra. For hydroxyl groups emission at about 11 eV (1π) and 7.5 eV (3σ) may be expected [17,18]. Only the 1π level is weakly detectable in Fig. 3(a).

IRAS data are shown in Fig. 4. At low temperature the broad absorption feature of the O–H stretching vibration of ice is visible between 3000 cm^{-1} and 3600 cm^{-1} . A small structure at 3694 cm^{-1} is found in the spectra of the vanadyl terminated (panel (b)) and the reduced surface (panel (a)) which seems to disappear upon heating together with

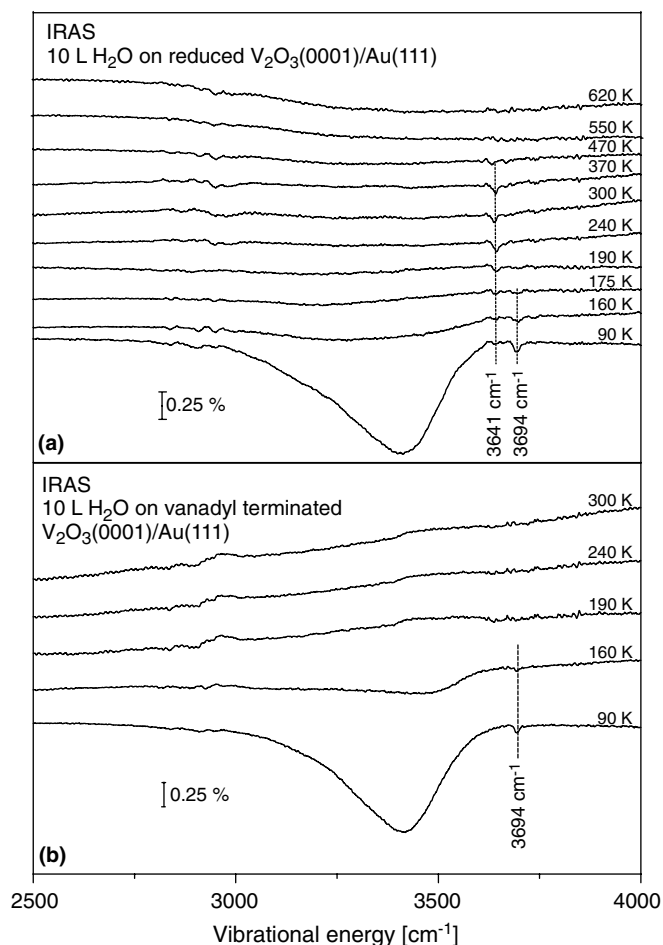


Fig. 4. IRAS spectra of water on reduced (a) and vanadyl terminated (b) $V_2O_3(0001)/Au(111)$ as a function of the annealing temperature. Water was dosed at 90 K and warmed up stepwise. After each annealing step the sample was cooled down again and a spectrum was recorded. We note that there are some features at around 2900 cm^{-1} and above 3600 cm^{-1} which are artifacts of the infrared spectrometer. All spectra are referenced to the spectra of the respective non-covered surface, i.e. the spectra shown in panel (a) result from a division of absorption spectra of a water-covered reduced surface by a spectrum of the non-covered reduced surface and the spectra shown in panel (b) result from a division of absorption spectra of a water-covered vanadyl terminated surface by a spectrum of the non-covered vanadyl terminated surface.

the O–H vibration of ice. This feature has been identified previously as being due to the vibration of dangling OH groups on the ice surface [19] (for D_2O adsorption see also Refs. [20,21]). The vibration at 3641 cm^{-1} is only visible in the spectra of water on the reduced surface (panel (a)). It disappears between 470 and 550 K and is to be assigned to the surface hydroxyl groups. The intensity of this feature is small at low temperature and increases at $T \geq 175\text{ K}$, i.e. after desorption of the water multilayer. This may be viewed as an indication that the surface hydroxyl groups form after multilayer desorption or that the intensity of their O–H vibration is smeared out at low temperature due to hydrogen-bonds of the hydroxyl groups with the water molecules of the multilayer. Features due to the molecular water which remains on the surface after multi-

layer desorption (as visible in Fig. 3(b) and (d)) could not be detected in the IRAS data. The reason for this could be that the water molecules are lying flat on the surface as observed for the $H_2O/Pt(111) + O$ system. This would lead to a small IR absorption cross section due to the cancellation of the molecule's dipole moment by its image in the substrate. Another point to consider is that the infrared spectra always exhibited a certain level of noise induced by instabilities of the infrared spectrometer which could easily hide weak vibrations.

One may ask why H_2O does not dissociate on the vanadyl terminated surface, but on the reduced surface. There are two arguments: (1) in the case of the vanadyl terminated surface access of the water molecules to the vanadium atoms is hindered since these are capped by oxygen atoms, whereas on the reduced surface the vanadium atoms are freely accessible and (2) the oxidation state of the vanadium atoms on the reduced surface is lower than on the vanadyl terminated surface as has been shown by Dupuis et al. [1] which means that the surface vanadium atoms on the reduced surface have more 3d charge to interact with the water molecules. Part of this charge may, for instance, be transferred to the hydroxyl groups.

Henderson and Chambers studied the interaction of water with the structurally similar $Cr_2O_3(0001)$ surface [22]. For this surface two OH-induced vibrations at 3600 cm^{-1} and 2885 cm^{-1} were reported. The occurrence of two different vibrational levels was attributed to the existence of two chemically inequivalent hydroxyl groups on the surface. A hydrogen-bond interaction between the two groups in the unit cell was identified as the reason for the low energy of the second vibration. In the case of the $V_2O_3(0001)$ surface only one O–H vibration could be identified although the OH coverages appear to be similar (~ 1.6 as compared to two in the $Cr_2O_3(0001)$ case). This may indicate that the structures of the OH layers are different.

Fig. 5 shows IRAS data recorded after annealing the ice layer on the vanadyl terminated $V_2O_3(0001)$ surface at different temperatures near to the multilayer desorption temperature. Striking changes occur to the structure of the O–H vibration peak at $T \sim 160\text{ K}$ which is near to the multilayer desorption temperature. Such changes have been observed before by a number of authors and were attributed to a crystallization of the amorphous ice layer [20,21,23].

Fig. 6 displays thermal desorption spectra of H_2O on reduced and vanadyl terminated $V_2O_3(0001)/Au(111)$. Panels (a) and (b) show clearly that there are sharp desorption maxima (β_v and β_r) near to the multilayer desorption peaks (α_v and α_r). These peaks (β_v and β_r) may be attributed to desorption of double layer water [6,24,25].

Within the data sets shown in Fig. 6, panel (c) compares spectra of 2 L of water on the two differently terminated surfaces. The spectrum of water on the vanadyl terminated surface essentially only exhibits a broad desorption peak with a maximum at $T \sim 227\text{ K}$ which may be attributed to molecular (sub)monolayer water as was also observed

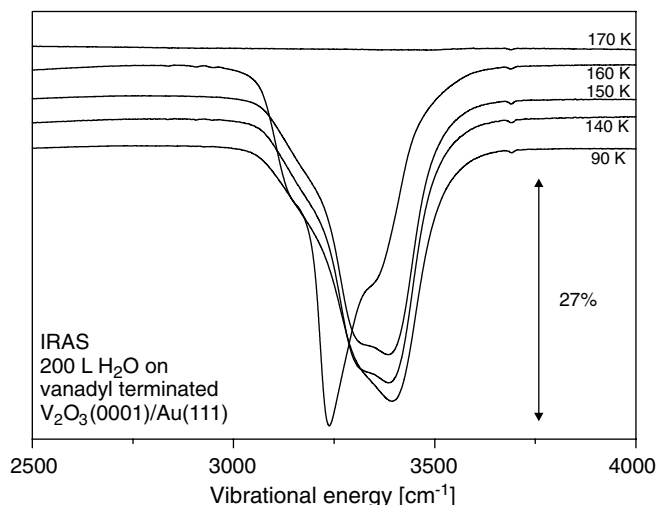


Fig. 5. IRAS data of water on vanadyl terminated V₂O₃(0001)/Au(111). Similar to the data shown in Fig. 4(b), but with finer temperature steps near to the multilayer desorption temperature.

in the O1s XPS data shown in Fig. 3(d). The intensity smoothly levels off towards higher temperature and no additional structure appears (except for a weak shoulder at 291 K). It is obvious that the intensity at 700 K is still significantly higher than the intensity at temperatures below the first desorption peak. Since the photoemission data (see Fig. 3) show that the water induced features are essentially gone at $T \geq 600$ K for the reduced surface and at $T \geq 300$ K for the vanadyl terminated surface this is likely due to water sticking to the inner walls of the Feulner cup and its pumping system.

In the case of the reduced surface the desorption peak of molecular water in Fig. 6(c) is shifted towards higher temperature with its maximum now appearing at 266 K which points towards a slightly stronger bond to the surface and/or within the layer. Additional broad structures are visible up to a temperature of about 600 K. Since this is approximately the temperature at which the hydroxyl induced signals in the XPS data (Fig. 3(b)) and the IRAS data

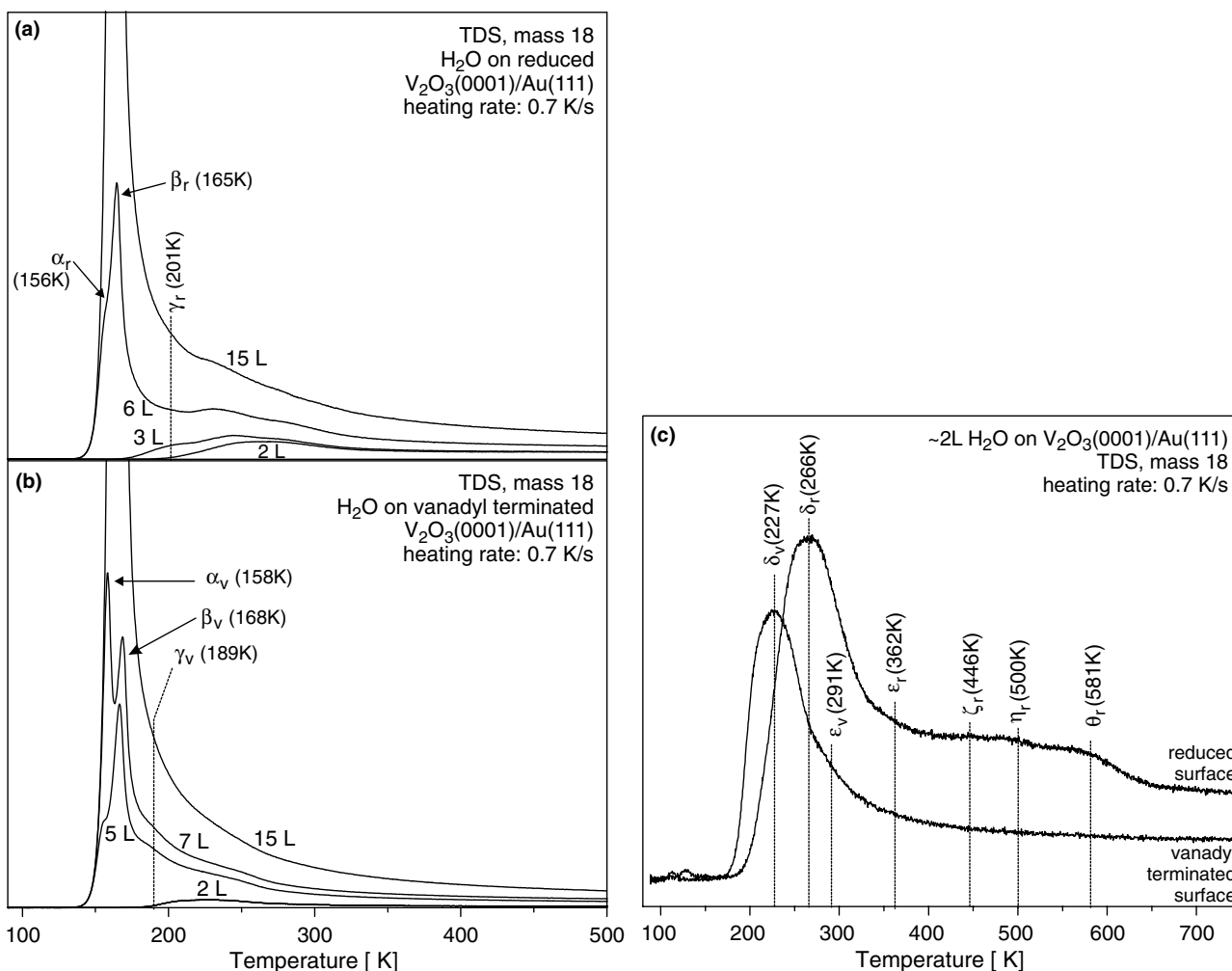
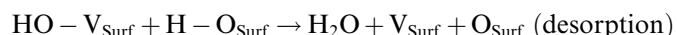


Fig. 6. Left panel: thermal desorption spectra obtained after adsorption of different amounts of water onto reduced (a) and vanadyl terminated (b) V₂O₃(0001)/Au(111). Right panel: comparison of the spectra obtained after dosing of 2 L of water on reduced and vanadyl terminated V₂O₃(0001) (c). The identified desorption maxima are marked and enumerated by greek letters in the spectra and the desorption temperatures are indicated. The indices 'r' and 'v' refer to the reduced and the vanadyl terminated surface, respectively.

(Fig. 4(a)) disappear it is near at hand to assume that these desorption states are related to the disappearance of the hydroxyl groups. Since this process obviously leads to water desorption, the water fragments must recombine on the surface before desorption. This leads to the following scheme for dissociative adsorption and recombinative desorption of H_2O on $\text{V}_2\text{O}_3(0001)$:



Such a recombination upon annealing is not uncommon for oxide surfaces [6]. However, one would expect to see two different absorption peaks in the infrared data (Fig. 4(a) and (b)) due to two (likely) different surface hydroxyl groups which is not the case. Such a negative result has also been obtained in studies of water adsorption on other surfaces. In the case of water on $\text{Fe}_2\text{O}_3(012)$ it was assumed that two types of hydroxyl groups form, i.e. terminal and bridge-bonded groups [26], with the second type being invisible or giving only a weak signal in vibrational spectra due to a small dynamic dipole moment. An explanation of this type was also put forward by Yu et al. to explain the absence of a second O–H stretching vibration in the case of hydroxyl groups on $\text{MgO}(100)$ [27]. The possibility that the dynamic dipole moment of one type of OH groups is weak and the possibility that two chemically equivalent OH groups form were named by Henderson to explain the observation of only one O–H stretching vibration for hydroxyl groups on $\text{TiO}_2(110)$ [6,24]. One of these explanations may also hold for the case of hydroxyl groups on $\text{V}_2\text{O}_3(0001)$.

4. Summary

We have shown that water interacts only weakly with the vanadyl terminated $\text{V}_2\text{O}_3(0001)$ surface. Only molecular water adsorption is observed and the water molecules desorb below 300 K, whereas on the vanadium terminated reduced surface water dissociates to form hydroxyl groups with a surface coverage of about 1.6 molecules per unit cell. The hydroxyl groups are removed completely from the surface upon annealing at $T \geq 600$ K. Reasons for the different reactivities of the two surfaces may be (1) the capping of the vanadium atoms by oxygen atoms on the vanadyl terminated surface which hinders access to the vanadium atoms in contrast to the situation on the reduced surface and (2) the enhanced reactivity of the vanadium atoms on the reduced surface due to their lower oxidation state. For the vanadyl terminated surface as well as for the vanadium terminated surface molecular water is observed at low temperature with coverages of ~ 0.5 – 1.1 on the vanadyl terminated surface and ~ 2.3 on the vanadium terminated surface.

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