HREELS, TPD and XPS study of the interaction of water with the α -Cr₂O₃(001) surface

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Abstract

The interaction of water with the (001) surface of α -Cr₂O₃ was examined with temperature programmed desorption (TPD), high resolution electron energy-loss spectroscopy (HREELS) and X-ray photoelectron spectroscopy (XPS). Two α -Cr₂O₃(001) surfaces were examined, both of which were grown on α -Al₂O₃(001) substrates using oxygen plasma-assisted molecular beam epitaxy (MBE). The two surfaces differed in that one was grown with α -Fe₂O₃ interlayers whereas the other was grown directly on α -Al₂O₃(001). The in-plane lattice spacing of the α -Cr₂O₃(001) surface on α -Fe₂O₃/ α -Al₂O₃(001) was 2% expansively strained relative to the unstrained α -Cr₂O₃(001) surface grown directly on α -Al₂O₃(001). Both the strained and unstrained surfaces exhibited similar water TPD behavior, with the possible exception that the desorption states of water on the strained surface were shifted slightly to lower temperatures relative to those on the unstrained surface. Water adsorbs on α -Cr₂O₃(001) in both molecular and dissociative states, with the former desorbing in TPD at 295 K and the latter at 345 K. TPD uptake measurements and XPS data suggest that each surface Cr³⁺ atom has the capacity to bind two water molecules, one in a molecular state and one in a dissociative state. Water in the dissociative state is comprised of two distinct OH groups based on HREELS, one of which is a terminal group with a $\nu(\text{OH})$ mode at 3600 cm⁻¹ and the other of which is presumably a bridging group with a $\nu(\text{OH})$ mode at 2885 cm⁻¹. These losses shift to 2645 and 2120 cm⁻¹ with D₂O adsorption. The low loss energy for the bridging OH/OD group indicates its involvement in a very strong hydrogen-bonded interaction with another species, presumably the oxygen atom of the terminal OH group. This pairing behavior is likely responsible for the first-order desorption kinetics observed for the recombinative desorption state at 345 K. The hydrogen-bonding interaction is unusually strong, as exemplified by the very low $\nu(\text{OH})$ frequency for the bridging OH group. Studies on the oxygen pre-exposed surface indicate that oxygen atoms, formed by O₂ dissociation, block the H₂O dissociative channel but do not block the molecular adsorption channel. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The molecular-level interactions of water with oxide surfaces are of great fundamental importance

in understanding many chemical, geochemical and material science phenomena. Most oxide surfaces exposed to the ambient are decorated with a variety of molecularly and dissociatively adsorbed forms of water. These various species influence and alter the chemical reactivity of oxide surfaces in different ways. Yet the surface structural proper-

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ties of the oxide that influence water chemistry are not well understood. Studies on single crystals greatly facilitate the potential for understanding the relationship between surface structure and surface reactivity.

The basal plane [also referred to as the (001) or (0001) plane] of corundum materials, such as α - Al_2O_3 , α - Cr_2O_3 and α - Fe_2O_3 , offers the unique structural environment of highly coordinatively unsaturated cation sites at a reasonably high surface density and with a fairly well-understood surface structure. The outermost layer of these surfaces is comprised of a layer of cations residing on a sheet of oxygen anions [1–12]. The surface cation sites are three-fold coordinated, whereas cations in the bulk are six-fold coordinated. This undercoordination results in the surface cations relaxing inward toward the outermost sheet of oxygen anions in order to lower the surface free energy, whereas the relaxation is somewhat lifted by a chemisorbed layer. The surface coverage of these three-coordinated cations is one third of that of the anions in the underlying oxygen sheet, resulting in surface charge neutrality with the number of metal-derived dangling bonds being equivalent to the number of oxygen-derived dangling bonds. The ideal α - Cr_2O_3 (001) surface termination is illustrated in Fig. 1. Although this is the general structure adopted by many studies, at

least one study has recently proposed that the cations in the surface are disordered at room temperature, and that interstitials may exist between the first two anion sheets [12].

The interaction of water with the (001) plane of α - Cr_2O_3 has been examined in this study. Previous experimental work on the interaction of water with the α - Cr_2O_3 (001) surface has suggested that water dissociation occurs only at defect sites based on photoemission results [13]. This conclusion is partially corroborated by semi-empirical embedded cluster calculations by Bredow, which suggest that molecular adsorption is favored over dissociative adsorption on the Cr-terminated surface [1]. Results presented in this study, however, show that the three-fold coordinated Cr^{3+} sites on the α - Cr_2O_3 (001) surface not only dissociate water under ultrahigh vacuum (UHV) conditions, but also have the capacity to bind both a water molecule and a hydroxyl group, resulting in a total water monolayer coverage of twice the surface density of cation sites. The hydroxyl channel is blocked, however, by preadsorbed oxygen.

2. Experimental

The α - Cr_2O_3 (001) surfaces used in this study were grown on α - Al_2O_3 (001) substrates using molecular beam epitaxy (MBE). The films were grown at a substrate temperature of about 775 K using growth rates between 0.03 and 0.1 Å/s in an oxygen plasma (for additional details see Ref. [14]). Two different films are discussed in this study, both of which were characterized in the MBE system using low energy electron diffraction (LEED), reflection high-energy electron diffraction (RHEED), X-ray photoelectron spectroscopy (XPS) and X-ray photoelectron diffraction (XPD). RHEED [14] and XPD [15] results indicate that both films are corundum in structure (hence the ' α ' designation). The first film consisted of alternating layers of α - Cr_2O_3 and α - Fe_2O_3 of variable thickness terminated with about 200 Å of α - Cr_2O_3 . The α - Cr_2O_3 film on α - Fe_2O_3 maintains the in-plane lattice spacing of α - Fe_2O_3 (001), which is about 2% expanded relative to the spacing in the natural α - Cr_2O_3 (001) surface. The surface of

Fig. 1. Schematic model of the Cr-terminated α - Cr_2O_3 (001) surface. The small black circles are Cr^{3+} cations and the large white circles are O^{2-} anions.

this film will hereafter be referred to as the strained α -Cr₂O₃(001) surface. The second film consisted of about 500 Å of α -Cr₂O₃ grown directly on α -Al₂O₃(001). RHEED results indicate that the surface of this α -Cr₂O₃ film on α -Al₂O₃(001) adopts the bulk-like in-plane spacing of α -Cr₂O₃(001) [14]. The surface of this film will hereafter be referred to as the unstrained α -Cr₂O₃(001) surface. The LEED pattern of the strained α -Cr₂O₃(001) surface showed the typical hexagonal pattern observed in other studies [16–18]. The spots were very sharp, and the background was low. The LEED pattern from the unstrained surface possessed broader spots with a higher background. As will be discussed below, this was due to substantial charging of unstrained surface in the LEED beam. Charging in the X-ray source was alleviated by using a low energy electron flood gun.

XPS of the strained film showed only Cr in the formal 3+ oxidation state with the expected multiplet splitting observed in the Cr 2p features [14]. The splitting does not change irrespective of whether grazing or normal angle detection is employed, suggesting that the Cr cations in the surface and bulk have the same oxidation state. This same behavior was observed by Dillmann et al. for thin Cr₂O₃(0001) films grown on Cr(110) [19]. Splitting in the Cr 2p_{3/2} spectrum of thin Cr₂O₃(0001) films grown on Cr(110) was originally assigned to the simultaneous presence of Cr²⁺ and Cr³⁺ at the surface by this group [16], but was later re-interpreted to multiplet splitting [19,20]. However, recently this group has used ab initio cluster calculations to suggest the surface Cr cations are in the 2+ oxidation state [21]. Although an assignment to Cr³⁺ is used here based on the similarity of the bulk-sensitive and surface-sensitive XPS measurements, this issue is not a focus of this paper and will not be discussed further.

The films were transferred through air to a second UHV system for studies with temperature programmed desorption (TPD), high resolution electron energy-loss spectroscopy (HREELS), Auger electron spectroscopy (AES) and static secondary ion mass spectrometry (SSIMS). The samples were mounted in the second UHV cham-

ber using a method described previously [22], that permits heating to 1000 K, and cooled to below 120 K. Briefly, this method involves sandwiching a thin Au foil between the back face of the crystal and the polished surface of a Ta plate, with the crystal held in place by mechanical force applied using W clips. After transfer and bakeout, the film surfaces were covered with a monolayer (or more) of carbonaceous deposits, along with some alkali ions and assorted other trace contaminants. These impurities were easily removed by mild sputtering with 500 V Ar⁺ and by annealing in UHV. The strained surface showed little or no effect of charging during sputtering at 300 K, but the unstrained surface required simultaneous exposure to 20 eV electrons from a flood gun in order for the sample not to charge during sputtering. Fig. 2 shows the AES spectrum (using a 3 keV electron beam) from the strained α -Cr₂O₃(001) surface after sputtering and annealing at 850 K in UHV. Aside from the small Ar AES feature at 214 eV, all other features

Fig. 2. AES spectrum of the clean strained α -Cr₂O₃(001) surface.

observed are from Cr or O. This AES spectrum resembled that published previously by Fukuda and Ignatiev from a polycrystalline α -Cr₂O₃ film on Cr metal [23]. AES of the unstrained surface was not possible due to sample charging.

The diffusion of Fe and/or Al from the underlying films and/or substrate during high temperature annealing was of concern, so the levels of Fe⁺ and Al⁺ were monitored over time using SSIMS. The SSIMS Fe⁺ and Al⁺ signals, compared with the total Cr⁺ yield from all its isotopes, were 1–2% and <1% (respectively) for the clean strained surface, and 0% and 6–7% (respectively) for the clean unstrained surface. These impurity levels are reasonable given that the strained film was grown on an α -Fe₂O₃ film, and the unstrained film was grown directly on α -Al₂O₃(001).

High purity H₂O and D₂O were obtained from Aldrich, and were further purified by several freeze–pump–thaw cycles. The gasline used in dosing water was acclimate to each gas prior to use. Water was dosed through a 1/4" OD stainless steel tube using a calibrated pinhole aperture doser. Typical exposures involved placing the crystal within 1 mm of the front of the tube followed by admitting approximately 100–200 mTorr of H₂O to the high pressure side of the pinhole. Exposures were then culminated by evacuating the high pressure side of the pinhole and waiting for about 60 s to capture residual water molecules emerging down the tube from the pinhole. The exact surface area of the sample exposed to the water beam is not accurately known. As discussed in the text, the profile of the dosed ‘spot’ on the sample is likely domed, extending beyond the surface area defined by the inner diameter of the dosing tube. Therefore, the actual exposures on the sample are smaller than those estimated using an exposed area based on the doser tube’s cross-sectional area, and may be somewhat non-uniform due to the doming effect. All TPD measurements were performed by dosing water with the sample at 120 K followed by heating at a rate of 2 K/s. Separate water experiments were conducted in the MBE system in order to measure the O 1s core-level spectra. Water doses of 300 s at a partial pressure of 5×10^{-8} Torr were applied to the strained surface at sample temperatures of 250 and 300 K.

The unstrained α -Cr₂O₃(001) film was susceptible to charging in the charged particle beams of LEED, HREELS, SSIMS and AES. As a result, HREELS experiments were performed only on the strained α -Cr₂O₃(001) surface, and only in the specular direction using a beam energy of 13.8 eV. Lower beam energies resulted in charging of this film, whereas higher beam energies were less sensitive to the dipole scattered losses of adsorbed water. The somewhat limited semiconducting behavior of the strained film was likely due to carrier states in the underlying α -Fe₂O₃(001) film, which was in contact with the W clips used to hold the substrate in place. Dosing and analysis temperatures for the HREELS experiments are mentioned in the text.

3. Results and discussion

3.1. Interaction of water with the 2% strained α -Cr₂O₃(001) surface

3.1.1. TPD results

Fig. 3 shows H₂O ($m/e=18$) TPD spectra as a function of exposure from H₂O adsorbed at 120 K on the strained α -Cr₂O₃(001) surface. At low exposures, a single H₂O TPD state is observed at 345 K that does not shift with increasing exposure. This peak saturates at an H₂O exposure between 0.9 and 1.0×10^{15} molecules/cm². A second H₂O TPD state grows in at about 295 K in this same exposure regime. This second H₂O TPD peak is not saturated for exposures below 1.4×10^{15} molecules/cm². Additional H₂O TPD states appear at 185 and 210 K for H₂O exposures between 1.4 and 2.0×10^{15} molecules/cm², whereas exposures above 2.0×10^{15} molecules/cm² result in multilayer formation at 165 K. The TPD states at 295 and 345 K can be assigned to chemisorbed forms of adsorbed water, presumably at Cr³⁺ cation sites, whereas the TPD states at 185 and 210 K can be assigned to physisorbed or hydrogen-bonded forms of adsorbed water. The amount of water adsorbed in the 185 and 210 K TPD states prior to multilayer formation is only about 30% of that adsorbed above 250 K, suggesting that the

Fig. 3. TPD spectra of H_2O ($m/e=18$) from various H_2O exposures at 120 K on the strained $\alpha\text{-Cr}_2\text{O}_3(001)$ surface. The dashed and solid line traces correspond to exposures above and below 1.3×10^{15} molecules/ cm^2 , respectively.

coverage of these physisorption/hydrogen bonding sites is limited by the chemisorbed layer.

The 345 K TPD peak was fit to coverage-independent first-order desorption kinetics for water exposures below that required for formation of the 295 K TPD peak. Adequate fits were obtained with an activation energy of 89 kJ/mol and a prefactor of $7 \times 10^{12} \text{ s}^{-1}$. The peak shapes and widths of the fits matched the data well for coverages between 3 and 7×10^{14} molecules/ cm^2 . However, slight coverage dependencies were necessary in order to fit the data at lower coverages.

Fig. 4 shows H_2O TPD peak area analysis of the data in Fig. 3 (with the inclusion of data that is not shown in Fig. 3 for the sake of clarity). The two lines in Fig. 4 are from the total H_2O TPD peak area (filled circles) and the H_2O TPD peak area above 250 K (hollow circles), both as a function of H_2O exposure on the clean strained

Fig. 4. Water TPD peak area data as a function of water exposure. The solid and hollow circles correspond to the total TPD peak area and the TPD peak area above 250 K, respectively. Data points include, but are not restricted to, data shown in Fig. 3. Lines drawn through the data are from least-squares fits.

$\alpha\text{-Cr}_2\text{O}_3(001)$ surface. A first-order least-squares fit of the total TPD peak area data results in a line that intersects the origin. This indicates that within the detection limits of the system all adsorbed water molecules are recovered in TPD as water (that is, no irreversible decomposition occurs). The 250 K point was chosen as a delineation temperature between the high temperature and low temperature desorption states of H_2O . Water desorption above this temperature is primarily from species chemisorbed at cation sites. The intersection of the two lines occurs at an exposure of 1.2×10^{15} molecules/ cm^2 , and corresponds to the coverage at which all cation sites are saturated (assuming unity sticking at 120 K). The peak area data corresponding to monolayer saturation is not flat for exposures above 1.2×10^{15} molecules/ cm^2 , as one would have expected. This effect has been

observed in other water–oxide studies employing the collimated pinhole doser [22,24], and possibly indicates that the water beam emerging from the doser does not deposit a spot with a square-edged profile, but deposits a domed spot whose extremities exceed the inner diameter of the dosing tube (see experimental section). For this reason, the monolayer states on the fringes of the spot fill at a slower rate compared with those in the center of the spot. This effect has been discussed recently by Livingston et al. for the growth of water ice on Ru(001) [25]. As a consequence, the monolayer saturation coverage estimated by the intersection of the two least-squares traces in Fig. 4 represents a maximum because the surface area exposed to the beam is larger than the inside diameter of the tube (which is assumed to be the exposed surface area of the crystal).

The coverage of exposed Cr^{3+} cations on the ideal Cr-terminated $\alpha\text{-Cr}_2\text{O}_3(001)$ surface is $4.77 \times 10^{14} \text{ cm}^{-2}$. However, when $\alpha\text{-Cr}_2\text{O}_3$ is grown on an $\alpha\text{-Fe}_2\text{O}_3/\alpha\text{-Al}_2\text{O}_3(001)$ film [14] (as discussed in the experimental section) it is lattice matched to the $\alpha\text{-Fe}_2\text{O}_3$ basal plane structure resulting in a surface Cr^{3+} coverage of $4.55 \times 10^{14} \text{ cm}^{-2}$. Assuming the doming effect discussed above contributes a small error to the measured saturation water coverage from the data in Fig. 4, the saturation water coverage estimated in Fig. 4 ($1.2 \times 10^{15} \text{ molecules/cm}^2$) is roughly twice that of the surface Cr^{3+} cation site density, suggesting that two water molecules are adsorbed per surface Cr^{3+} cation site. In principle, multiple coordination should be possible since the exposed Cr^{3+} cations are lacking three ‘ligands’ in their coordination sphere. However, examples of coordination of multiple water molecules to a single metal cation have not, to our knowledge, been reported on a single crystal metal oxide surface.

Isotopic oxygen studies, such as those performed on $\text{TiO}_2(110)$ and $\text{TiO}_2(100)$ [26], and on $\alpha\text{-Fe}_2\text{O}_3(012)$ [24], were attempted on $\alpha\text{-Cr}_2\text{O}_3(001)$ in an effort to verify water dissociation. However, SSIMS results (not shown) indicate that the only ^{18}O incorporated into the surface while exposing $5 \times 10^{-7} \text{ Torr } ^{18}\text{O}_2$ at 600 to 800 K was that due to adsorbed oxygen adatoms that capped each exposed Cr^{3+} cation site [19]. The

TPD spectrum of water adsorbed on the oxygen exposed surface is noticeably different from that for the clean surface, and will be discussed below. Although in concept the opposite exchange process (H_2^{18}O adsorbed on the $\alpha\text{-Cr}_2^{16}\text{O}_3(001)$ surface) could also probe for dissociation, H_2^{18}O was not available for this experiment. Instead, HREELS was used to successfully address the issue of the adsorbed state of water on $\alpha\text{-Cr}_2\text{O}_3(001)$.

3.1.2. HREELS results

The adsorbed state of water, in terms of molecular or dissociative forms, can be determined using vibrational spectroscopy. HREELS has been successfully used to address the adsorbed state of water on single crystal $\text{TiO}_2(110)$ [22] and $\alpha\text{-Fe}_2\text{O}_3(012)$ [24]. Vibrational analysis of adsorbates on oxides using HREELS is made consider-

Fig. 5. HREELS spectra from the strained $\alpha\text{-Cr}_2\text{O}_3(001)$ surface with (dashed line) and without (solid line) Fourier deconvolution. All spectra were collected in specular direction at 300 K with a beam energy of 13.8 eV.

ably easier by removal of multiple phonon losses using Fourier deconvolution [22]. Fig. 5 shows HREELS data from the clean strained α -Cr₂O₃(001) surface, obtained at 300 K, before (solid traces) and after (dashed traces) Fourier deconvolution. Intense optical phonon losses are observed at 685 and 360 cm⁻¹, with weaker losses at 575, 455 and 160 cm⁻¹. The 685 and 360 cm⁻¹ losses are somewhat lower in frequency than the 708 and 416 cm⁻¹ losses observed by Freund's group for α -Cr₂O₃ thin films grown by oxidation of Cr(110) [27,28]. Their data also appear to contain evidence for a weak loss on the low energy loss side of the 708 cm⁻¹ feature, although this was not specifically discussed in their papers. The longitudinal optical phonon frequencies perpendicular to the *c*-axis of α -Cr₂O₃ have been calculated by two groups using infrared data. Renneke and Lynch [29] obtained frequencies of 766, 602, 446 and 420 cm⁻¹, while Serna et al. [30] obtained frequencies of 734, 593, 442 and 306 cm⁻¹. Serna et al. have assigned the lowest frequency feature to the displacement of the cations relative to the anion lattice, which as a result is unlikely to possess much oscillator strength. This phonon mode is not detected by HREELS. For the detected phonon modes, the frequencies measured by HREELS for the strained α -Cr₂O₃(001) surface are lower than either those calculated from IR data or those measured by HREELS for the α -Cr₂O₃(001) film on Cr(110) [27,28]. This may be the result of the 2% expansive strain in the in-plane structure of the α -Cr₂O₃(001) film when grown on α -Fe₂O₃(001). Unfortunately, this hypothesis could not be tested by performing HREELS on the unstrained α -Cr₂O₃(001) surface because of its charging limitations. The 160 cm⁻¹ loss cannot be assigned to an optical phonon mode, but may result from the soft surface phonon mode previously detected by Wolter et al. [31] on the α -Cr₂O₃(001) film on Cr(110). A recent theoretical study has proposed that soft surface phonon modes may exist on oxides such as TiO₂(110) [32]. Fourier deconvolution removed virtually all of the multiple loss intensity above 800 cm⁻¹, with the exception of the remnant of loss intensity at 1370 cm⁻¹ (see the 'x 25' spectrum in Fig. 5). This multiple phonon remnant is not removed by

Fourier deconvolution because it results from a combination of dipole and non-dipole scattering processes [33]. Note also the presence of a weak loss at about 915 cm⁻¹. This loss will be assigned in the following discussion.

Fig. 6 shows Fourier deconvoluted HREELS data from the clean strained α -Cr₂O₃(001) surface (a) and from the clean surface exposed to a saturation exposure of H₂O (b) and D₂O (c) at 300 K. The clean surface spectrum shows the phonon remnant at 1370 cm⁻¹ and the weak loss at 915 cm⁻¹. Exposure of this surface to H₂O at 300 K results in new losses at 3600 and 2885 cm⁻¹, and a more intense loss at 915 cm⁻¹ (Fig. 6b). The 3600 cm⁻¹ loss is reflective of an OH stretching mode [designated as $\nu(\text{OH})$] of an isolated OH group. The term 'isolated' is used in the infrared (IR) spectroscopy literature of oxide

Fig. 6. Fourier deconvoluted HREELS spectra from the clean strained α -Cr₂O₃(001) surface (a), from the clean surface exposed to saturation H₂O at 300 K (b), and from the clean surface exposed to saturation D₂O at 300 K (c). All spectra were collected in specular direction at 300 K with a beam energy of 13.8 eV.

powders in reference to an OH group whose proton is not involved in hydrogen-bonding [34]. (For these isolated OH groups, no distinction is usually made regarding whether or not the hydroxyl's oxygen atom is involved in hydrogen-bonding to other species.) The absence of hydrogen-bonding in an OH group is almost always reflected by a $\nu(\text{OH})$ mode above 3500 cm^{-1} . On the other hand, the broad loss at 2885 cm^{-1} is uncharacteristically low for typical hydrogen-bonded OH groups, and indicates an OH group involved in an unusually strong hydrogen-bonding interaction. (This is discussed in greater detail in Section 3.1.4.) Several IR studies on the interaction of water with $\alpha\text{-Cr}_2\text{O}_3$ powders have observed OH stretching features corresponding to isolated and hydrogen-bonded species [35–37]. These studies have detected sharp features between 3600 and 3650 cm^{-1} that have been assigned to terminal OH groups on $\{001\}$ planes. However, the stretching modes of hydrogen-bonded OH species are generally observed in the $3200\text{--}3400\text{ cm}^{-1}$ region, and these studies do not observe $\nu(\text{OH})$ features below 3000 cm^{-1} . This may be because the O–H oscillator strength of strongly hydrogen-bonded OH groups is often too weak to be detected by IR [34]. The 915 cm^{-1} loss is due to the bending mode $[\delta(\text{OH})]$ of an OH group, and may be from either the isolated or hydrogen-bonded species (or both). The H_2O HREELS spectrum in Fig. 6b also shows a broad and weak feature in the vicinity of 1600 cm^{-1} that can be assigned to the $\delta(\text{HOH})$ mode of chemisorbed water.

Losses are observed in HREELS at 2645 and 2120 cm^{-1} , with weaker intensity features at 3600 and 915 cm^{-1} , when the clean surface is exposed to D_2O (Fig. 6c). The latter set are presumably due to background H_2O adsorption and/or residual hydrogen-containing water dosed with the D_2O . The former set of losses is consistent with an H/D shift (both of 1.36) expected for the $\nu(\text{OD})$ counterparts to the $\nu(\text{OH})$ losses at 3600 and 2885 cm^{-1} (Fig. 6b). An isotope shift for the $\delta(\text{OH})$ mode at 915 cm^{-1} should result in a $\delta(\text{OD})$ mode at about 700 cm^{-1} , which unfortunately is obscured by the intense oxide phonon loss at 685 cm^{-1} . Note also that the feature at 1600 cm^{-1} has shifted. The $\delta(\text{DOD})$ mode should

be at about 1200 cm^{-1} , but is not readily apparent in the HREELS spectrum of Fig. 6c. Dosing the $\text{D}_2\text{O}/\text{OD}$ -covered surface with a large exposure of H_2O at 300 K results in HREELS intensity being shifted back to the 3600 and 2885 cm^{-1} losses as a result of H–D exchange (data not shown). The loss pairs at $3600/2885\text{ cm}^{-1}$ and $2645/2120\text{ cm}^{-1}$ can be toggled back and forth by consecutive exposures to H_2O and D_2O , indicating that water adsorption, H/D exchange and water desorption are facile at 300 K (as one might expect from inspection of the TPD data in Fig. 3). Based on these observations, the 2885 and 2120 cm^{-1} losses can be assigned to strongly hydrogen-bonded OH and OD species, respectively, as opposed to impurities that give rise to C–H and C–D stretches. A structural model for these species is presented below in Section 3.1.4.

The loss labeled ‘bkgd CO_2 ’ in Fig. 6 is at 1310 cm^{-1} , and is from background adsorption of CO_2 during the course of the HREELS data acquisition. The species responsible for this loss is presumably a carboxylate based on previously published work by Freund's group for CO_2 adsorbed on $\alpha\text{-Cr}_2\text{O}_3(001)$ films on $\text{Cr}(110)$ [28,38]. In separate work, we have found no evidence for a chemical reaction between CO_2 and water on $\alpha\text{-Cr}_2\text{O}_3(001)$, suggesting that (under UHV conditions) CO_2 only influences water surface chemistry by simple site blocking [39].

The HREELS analysis in Fig. 6 was performed at 300 K because the sample experienced charging if exposed to the HREELS electron beam at the sample base temperature obtained by LN2 cooling (120 K). However, HREELS analysis at 300 K did not permit characterization of the water species that desorbs in the 295 K TPD peak. Fortunately, only limited charging of the sample occurred at 230 K , which is a sample temperature that retains the majority of the 295 K water TPD state. This sample temperature could be maintained within $\pm 20\text{ K}$ by regulating the amount of LN2 in the manipulator. Fig. 7 shows the HREELS spectrum obtained from a saturation exposure of H_2O on the strained $\alpha\text{-Cr}_2\text{O}_3(001)$ surface at 230 K . It should be pointed out that the elastic peak count rate from the clean surface was considerably attenuated at 230 K and the resolution was slightly

Fig. 7. Fourier deconvoluted HREELS spectrum from the clean strained α -Cr₂O₃(001) surface exposed to saturation H₂O at 230 K. The spectrum was collected in specular direction at 300 K with a beam energy of 13.8 eV.

degraded compared with the 300 K spectrum. The signal-to-noise ratio was also lower at 230 K compared with at 300 K. These changes in the clean surface spectrum indicate that some charging occurs at 230 K. Nevertheless, the 230 K HREELS spectrum is similar to that obtained at 300 K with a few notable exceptions. First, the broad loss observed in Fig. 6 at 2885 cm⁻¹ for 300 K H₂O adsorption is split into two losses at 2925 and 2675 cm⁻¹ for 230 K H₂O adsorption. Second, the 915 cm⁻¹ loss is shifted to slightly higher loss energy at 955 cm⁻¹. Third, the δ (HOH) mode of molecular water is more intense after adsorption at 230 K compared with the 300 K spectrum. Finally, a weak loss is observed at 3470 cm⁻¹ as a shoulder on the intense 3600 cm⁻¹ loss. Although the 3470 cm⁻¹ loss is at the noise level, its presence was reproducibly observed in the HREELS spectrum over a series of six independent surface

measurements. In contrast to these changes, the 3600 cm⁻¹ loss is unaffected by the presence of the additional H₂O adsorbed in the 295 K TPD state.

The presence of a more intense 1615 cm⁻¹ loss in Fig. 7 strongly suggests that the 295 K TPD state is due to molecular adsorbed water. This molecularly adsorbed water appears to perturb the hydrogen-bonded OH groups in that their ν (OH) loss is altered. Since the ν (OH) loss for the isolated OH is unaffected by the presence of molecular water, the δ (OH) mode observed at 955 cm⁻¹, which is shifted with coadsorbed H₂O, is probably from the hydrogen-bonded OH group and not from the isolated OH group.

3.1.3. XPS results

Based on the HREELS results discussed in the previous section, the 345 K TPD peak can be assigned to desorption of water from recombination of two distinctively different OH groups. HREELS results also suggest that the 295 K TPD peak is due to desorption of molecularly adsorbed water. In order to confirm these assignments, XPS analysis was performed on the strained α -Cr₂O₃(001) surface. Fig. 8 shows O 1s photoemission spectra for the clean surface detected at normal (a) and glancing (b) angle of detection. (In order to compensate for the varying degrees of charging encountered in these measurements, the O 1s spectrum was shifted by aligning the Cr 2p_{3/2} binding energy to that observed in the literature [40].) Although the spectral resolution is slightly degraded at glancing angle detection due to focal length variations, both clean surface spectra yield a sharp O 1s feature at about 531.5 eV. The glancing angle spectrum appears to possess slightly more intensity on the high binding energy side of the O 1s peak. Exposure of the clean surface to 15 L of H₂O at 300 K broadens the O 1s feature but also results in increased intensity in the high binding energy shoulder (Fig. 8c). Exposure of the clean surface to 15 L of H₂O at 250 K further alters the O 1s spectrum in that the peak is considerably broadened, and a new feature appears at about 534 eV (Fig. 8d). The O 1s feature obtained at normal emission after 250 K adsorption of water (not shown) is essentially identical to that obtained from the clean

Fig. 8. O 1s XPS spectra for the clean strained α -Cr₂O₃(001) surface at (a) normal (90°) and (b) glancing (10°) angle of detection, and for the clean strained α -Cr₂O₃(001) surface exposed to 15 L H₂O at 300 K (c) and at 250 K (d), both at the glancing angle. The center of each peak was referenced to a binding energy of about 531.5 eV.

surface (Fig. 8a) with the exception that a very weak feature is detected at about 535 eV. Since normal incidence detection is mainly sensitive to the bulk, the width of the O 1s spectrum at glancing angle in Fig. 8d must be associated with the oxygen-containing species in the outermost surface layer(s). The broadness of the peak may result from inhomogeneous lifting or partial lifting of the surface relaxation by the water/hydroxyl adlayer.

The high binding energy shoulder in the O 1s spectrum after H₂O adsorption at 300 K can be assigned to the O 1s feature from a surface OH group based on other studies that have detected OH groups on surfaces using XPS [41]. The feature at 534 eV after H₂O adsorption at 250 K is consistent with molecularly adsorbed water [41]. The intensity of the OH feature is weak in the 300 K

spectrum (Fig. 8c) because the rate of desorption of water in the 345 K H₂O TPD peak is non-zero at 300 K for a fully hydroxylated surface. This tends to restrict the sustainable coverage of dissociated water at 300 K under UHV conditions to a subsaturation level. This problem is not significant for the case of XPS analysis of the 298 K TPD peak at 250 K (see Fig. 3). Since a 250 K adsorption temperature precludes the presence of physisorbed states of water (detected in TPD below 250 K), the 295 K TPD state can be assigned to desorption of molecularly adsorbed water, in agreement with the assignment arrived at from HREELS data. The coverage of H₂O and OH at 250 K can be estimated using the XPS data in Fig. 8d. The spectrum was curve fit using three gaussians. The coverages of H₂O and OH on the surface at 250 K can be determined from the attenuation of the O 1s signal from the lattice. The escape length was estimated by comparing the O 1s intensity of the oxygen exposed surface relative to that of the clean surface. Previous infrared studies suggest that oxygen exposure to the α -Cr₂O₃(001)/Cr(110) surface results in each surface Cr cation being 'capped' with an atomic O species via dissociative oxygen chemisorption [19]. Assuming this is the case and the surface atomic oxygen coverage is equal to the cation density in terminal layer, then the O 1s signal from the atomic O species (at 532.4 eV) can be used to estimate the escape length of O 1s photoelectrons originating from the oxide (at 531.5 eV). Using the methodology of Tanuma et al. [42], a value of 18 Å is obtained for the escape length of the O 1s photoelectrons. This is consistent with the 14–17 Å value estimated by Tanuma for the isostructural α -Al₂O₃. Based on this value for the O 1s escape length, the coverages of OH and H₂O at 250 K are both approximately equivalent to the surface coverage of three-coordinate Cr³⁺ sites (about $4.6 \times 10^{14} \text{ cm}^{-2}$), in agreement with the TPD data.

3.1.4. Model for adsorbed water on α -Cr₂O₃(001)

Based on the TPD, HREELS and XPS results presented above, we propose the following model for how H₂O interacts with the Cr-terminated α -Cr₂O₃(001) surface. TPD results suggest that

the monolayer saturation coverage of water obtained by exposure at 120 K in UHV is twice that of the surface density of exposed Cr^{3+} cations. Water in the chemisorbed monolayer desorbs in two TPD states of approximately equal proportions at 345 and 295 K (Fig. 3). HREELS has identified two $\nu(\text{OH})$ modes at 3600 and 2885 cm^{-1} for water adsorbed in the 345 K H_2O TPD state (Fig. 6b). These features shift to 2645 and 2120 cm^{-1} with D_2O adsorption. The two $\nu(\text{OH})$ modes are in strong contrast to each other, one representing an isolated O—H bond and one representing an O—H bond that is involved in an unusually strong hydrogen-bonding interaction. (For the relationship between the $\nu(\text{OH})$ frequency and the strength of the hydrogen-bonding interaction, see Novak [43], as discussed by Thiel and Madey [41].) These HREELS features can be interpreted in two ways. In the first case, the 3600 and 2885 cm^{-1} losses can be assigned to two different $\nu(\text{OH})$ modes of a molecularly adsorbed water molecule in which one O—H bond is strongly hydrogen-bonded to either a surface anion site or to another H_2O molecule and the second O—H bond is free of hydrogen-bonding interactions. This situation exists for ice surfaces where dangling O—H bonds have been observed by vibrational spectroscopy [41]. For the second case, the two losses can be assigned to two different OH groups, one of which is involved in hydrogen-bonding and the other of which is not. Given that the loss intensity in the vicinity of 1600 cm^{-1} (region in which the $\delta(\text{HOH})$ mode of molecular H_2O is observed) is weak, whereas an intense loss is observed at 915 cm^{-1} (region in which the $\delta(\text{OH})$ mode of OH is observed), water in the 345 K TPD peak can be assigned to recombinative desorption of dissociated water molecules. This assignment is consistent with the XPS results of Fig. 8. However, this does not mean that molecular water is not present on the surface at 300 K. Some intensity is detected in the $\delta(\text{HOH})$ region, possibly indicating that a small steady-state population of molecular water may exist on the surface at 300 K, as has been proposed for water on $\alpha\text{-Fe}_2\text{O}_3(012)$ [24].

Recent molecular dynamics calculations by Hass et al. [9] predict that H_2O dissociates on the

isostructural $\alpha\text{-Al}_2\text{O}_3(001)$ surface by proton transfer from a H_2O molecule (adsorbed at a cation site) to a neighboring surface anion site. The most favorable water dissociation mechanism appears to involve proton transfer to the next-to-nearest neighbor anion site away from the cation site (what Hass et al. refer to as a ‘1–4 transfer’). This corresponds to the first anion site that is found in moving along the [100] direction away from a surface cation site (see Figs. 1 and 9). This is as opposed to proton transfer to a lattice oxygen atom in the same coordination sphere of the Cr^{3+} cation (a ‘1–2 transfer’), which Hass et al. predict is less favorable. Bredow, in calculating the minimum energy for the dissociation of a single water molecule on the Cr-terminated $\alpha\text{-Cr}_2\text{O}_3(001)$ surface, examined only the 1–2 transfer process and found it to be slightly less stable than molecular adsorption [1]. Bredow also found that the fully hydrated surface was considerably more stable than the fully hydroxylated surface. The case of both molecular and dissociated water on a single cation site was not considered by either Bredow or Hass et al.

Fig. 9 shows a schematic model for the OH

Fig. 9. Schematic model for the structure of OH groups on the Cr-terminated $\alpha\text{-Cr}_2\text{O}_3(001)$ surface.

groups generated from water dissociation on the α -Cr₂O₃(001) based on our experimental results and partially on the model proposed by Hass et al. [9]. Our results suggest that water dissociates on α -Cr₂O₃(001), forming a terminal OH group bound at the cation site and a bridging OH group at a first layer lattice anion site. The '1–4' model of Hass et al. has been modified by inclusion of hydrogen-bonding between the two types of OH group in an effort to rationalize the HREELS data (Figs. 6 and 7) that shows evidence for hydrogen-bonding between the two types of hydroxyl. By tilting the terminal OH group from its atop position by about 45° toward the bridging OH group, an O–O distance of about 2.8 Å can be obtained between the two hydroxyl groups with the proton on the bridging OH group pointing at the terminal OH. This geometry, although purely speculative and somewhat arbitrarily chosen, provides a hydrogen-bonded pair of hydroxyls whose structure is consistent with the HREELS data, and provides a pairing of OH groups that is consistent with the first-order desorption kinetics of the 345 K TPD state (that is, first-order in the coverage of paired, hydrogen-bonded OH groups). The latter is consistent with what is observed for the recombinative desorption of water on the (1 × 1) surface of α -Fe₂O₃(012) [24]. Also, the tilting of the terminal OH group towards the bridging OH group opens a potential coordination site on the Cr³⁺ cation in which a second water molecule can adsorb, in accordance with TPD, HREELS and XPS data. Notice that a molecularly adsorbed water in this site will 'hang' over the bridging OH group potentially altering the structure and fundamental vibrational mode frequencies of that hydroxyl. This may explain the small changes observed in the ν (OH) and δ (OH) modes of the hydrogen-bonded OH group upon coadsorption of molecular water.

3.2. Interaction of water with the unstrained α -Cr₂O₃(001) surface

As mentioned in the experimental section, the α -Cr₂O₃ film grown on α -Fe₂O₃/ α -Al₂O₃(001) is 2% expanded in-plane relative to the bulk-terminated α -Cr₂O₃(001) surface. However, the

α -Cr₂O₃ film grown on α -Al₂O₃(001) yields an α -Cr₂O₃(001) surface with a bulk-terminated α -Cr₂O₃(001) surface structure [14]. Since the presence of strain may influence the surface chemistry of adsorbates, the TPD of water from the unstrained α -Cr₂O₃(001) surface is compared in Fig. 10 with that observed for the strained α -Cr₂O₃(001) surface (data taken from Fig. 3). In general, the two TPD spectra are very similar to each other, each showing the same number of desorption states with approximately the same relative peak intensities and desorption temperatures. The two low temperature features at 185 and 210 K from both surfaces overlay each other almost exactly. The pair of high temperature features, however, are slightly shifted from each other, with the peak temperatures from the unstrained α -Cr₂O₃(001) surface approximately 10 to 15 K higher than those from strained α -Cr₂O₃(001). These peak temperature differences likely arise

Fig. 10. Comparison of the H₂O TPD spectra ($m/e=18$) from about 2×10^{15} molecules/cm² exposure of H₂O to the strained (dashed line) and unstrained (solid line) α -Cr₂O₃(001) surfaces.

from a slight difference in the temperature measured at the two samples. Although not attempted, a compilation of TPD spectra from several sample mountings would likely yield a small spread in the H₂O TPD peak temperatures centered about the peak temperatures for both surfaces. Yet such temperature variations have not been observed in the water TPD peak temperature in the course of our studies on TiO₂(110) using the same crystal mounting method (see experimental section) on numerous different crystal mountings [22,26]. Given that the thermal conductivity of TiO₂ rutile is about a factor of 4 less than that of α -Al₂O₃ sapphire [44], which is the substrate for both α -Cr₂O₃ films, one might expect larger thermal incongruities in TiO₂ substrates. Therefore, it is possible that the small H₂O TPD peak differences observed for the two α -Cr₂O₃(001) surfaces could in fact be due to the 2% in-plane structural difference between the two surfaces. In any event, it is clear that a small expansive strain does not significantly alter the desorption properties of water from the α -Cr₂O₃(001) surface, and that both surfaces exhibit the same kinds of water chemistry discussed in previous sections.

3.3. Effect of preadsorbed oxygen on water TPD

Since oxygen is a prevalent molecule in both humid and aqueous environments, and since many oxide surface preparation schemes utilize O₂, the effect of preadsorbed oxygen on the TPD properties of water has been examined. Dillmann et al. have previously observed that oxygen binds very strongly to Cr³⁺ sites on α -Cr₂O₃(001) films grown on Cr(110) [19]. These authors detected both molecular and dissociative forms of adsorbed oxygen using TPD, IR and ELS. The molecular channel gives rise to an O₂ TPD feature at 320 K, whereas the disappearance of the dissociative species (oxygen adatoms) is not observed in TPD. However, Dillmann et al. have observed the attenuation of a $\nu(\text{Cr}=\text{O})$ mode at 1005 cm⁻¹ between 700 and 850 K due to desorption of these oxygen adatoms.

Fig. 11a shows TPD spectra from a 1.1×10^{15} molecules/cm² exposure of H₂O adsorbed on the unstrained α -Cr₂O₃(001) surface

Fig. 11. H₂O ($m/e=18$) and O₂ ($m/e=32$) TPD spectra from 1.0×10^{15} molecules/cm² H₂O adsorbed to the O₂-presaturated, strained α -Cr₂O₃(001) surface at 120 K (a), and for the same H₂O exposure adsorbed at 120 K after heating the O₂-presaturated surface to: (b) 600, (c) 692, (d) 750, (e) 800, (f) 857 and (g) 950 K.

presaturated with O₂ at 120 K. Oxygen was dosed by backfilling the chamber with a 20 L exposure. The O₂ ($m/e=32$) TPD trace is shown as a dashed line, and the H₂O ($m/e=18$) TPD trace is shown as a solid line. The main O₂ TPD features are at 145, 180 and 285 K. The lower temperature features are from physisorbed states on the α -Cr₂O₃(001) surface (or possibly from the sample holder [45]), whereas the 285 K TPD state has been assigned to molecularly bound O₂ at a Cr³⁺ site [19]. The O₂ TPD peak temperature observed from the strained α -Cr₂O₃(001) surface is about 35 K lower than that observed by Dillmann et al. This could be due, in part, to the higher ramp rate used by those authors (4 K/s), but may also be due to differences in temperature measurements. The water TPD spectrum from H₂O dosed on the O₂-presaturated surface (Fig. 11a) is significantly

different from that observed on the clean surface (Figs. 10 and 11g). The TPD peaks at 210 and 310 K, assigned to physisorbed and chemisorbed H_2O molecules (respectively), were present. However, the intense H_2O TPD peak at 355 K was absent and was replaced with a broader and weaker feature centered at about 380 K. Additionally, the total amount of H_2O adsorbed above 250 K decreased by 45% for the O_2 -presaturated surface. The adsorbed state of the H_2O molecules desorbing in the 380 K TPD state is not known since HREELS experiments were not performed on this system. However, it is not unreasonable to assign the 380 K TPD state to recombinative desorption of hydroxyl groups given that the peak temperature is above that for the hydroxyl recombinative process observed on the clean surface (Figs. 10 and 11g). Kinetics for the OH recombination process in the 380 K TPD peak are clearly different from those for the 355 K TPD state on clean surface based on differences in peak shapes and temperatures.

The remaining TPD spectra shown in Fig. 11 probe, using water, the annealing temperature required to regenerate the clean surface after oxygen exposure. For each of these experiments, the O_2 -saturated surface was heated to progressively higher temperatures and then probed with H_2O TPD. Preheating the O_2 -saturated surface up to 600 K did not significantly alter the subsequent H_2O TPD (Fig. 11b), except that more surface sites were available for H_2O adsorption in the TPD states above 240 K after desorption of O_2 in the 285 K TPD state (Fig. 11a). After heating the O_2 -saturated surface to 690 K, a small H_2O TPD peak appears at 355 K (Fig. 11c). This H_2O TPD peak increases in intensity and the 380 K H_2O TPD state attenuates as the O_2 -saturated surface is preheated to progressively higher temperatures. However, the H_2O TPD spectrum does not fully resemble the clean unstrained $\alpha\text{-Cr}_2\text{O}_3(001)$ surface H_2O TPD spectrum even after heating to 860 K (Fig. 11f), indicating that some Cr^{3+} sites still remain 'capped' with O adatoms. Annealing at 950 K was sufficient to remove all atomic oxygen species from the unstrained $\alpha\text{-Cr}_2\text{O}_3(001)$ film. This is consistent with the findings of Dillmann et al. [19] discussed above. This series of TPD

experiments clearly shows that atomic oxygen influences the adsorption properties of water on the $\alpha\text{-Cr}_2\text{O}_3(001)$ surface.

The $\text{O}_2\text{-H}_2\text{O}$ experiment in Fig. 11 was repeated on the strained surface with similar results. However, a variation of this experiment is shown in Fig. 12 that probes the effect of high temperature $^{18}\text{O}_2$ treatment on the TPD of H_2^{16}O on the strained $\alpha\text{-Cr}_2\text{O}_3(001)$ surface. For this experiment, the surface was exposed to 150 L of $^{18}\text{O}_2$ at 700 K and cooled in $^{18}\text{O}_2$ to below 640 K before evacuating the chamber of $^{18}\text{O}_2$. This surface treatment presumably yields an $\alpha\text{-Cr}_2\text{O}_3(001)$ surface in which most, if not all, of the surface Cr^{3+} sites are capped with atomic ^{18}O . Water TPD ($m/e=18$) from this surface gives a peak at 295 K with a tailing feature at higher temperature (Fig. 12a). The total H_2O TPD peak area above 250 K from

Fig. 12. H_2^{16}O ($m/e=18$) and H_2^{18}O ($m/e=20$) TPD spectra from about 5×10^{15} molecules/ cm^2 H_2^{16}O exposure adsorbed on the strained $\alpha\text{-Cr}_2\text{O}_3(001)$ surface at 120 K after exposure of the surface to 150 L $^{18}\text{O}_2$ at 700 K (a). The H_2^{16}O ($m/e=18$) TPD spectrum from the clean surface (b) is included for comparison.

this surface was nearly 50% less than that observed from the clean surface (Fig. 12b). (For the purposes of this comparison, the $m/e=18$ and 20 signals in Fig. 12a were combined.) This 50% decrease in the $\alpha\text{-Cr}_2\text{O}_3(001)$ surface's ability to bind water arises primarily from the absence of the high temperature H_2O TPD state (at 345 K) attributed to OH recombination on the clean surface, whereas the majority of the observed water desorption is found at the same temperature as the molecular desorption state on the clean surface (at 295 K). It therefore seems logical to conclude that oxygen adatoms on the Cr^{3+} sites block the dissociation of water but do not block H_2O adsorption into the molecular state. The $m/e=20$ TPD trace in Fig. 12a shows that little or no oxygen atom scrambling occurs between the coadsorbed H_2^{16}O and ^{18}O atoms, which is further evidence for the absence of water dissociation on the oxygen capped Cr^{3+} sites. (The $m/e=20$ signal tracks the $m/e=18$ signal, indicating that it arises primarily from exchange in the mass spectrometer, which unavoidably is exposed to $^{18}\text{O}_2$ during the surface oxidation process.) There is, however, a slight enhancement in the relative amount of H_2^{18}O desorbing above 330 K, suggesting that the high temperature tail is due to recombinative desorption of water. Based on these findings, the Cr^{3+} cation sites appear to bind both a water molecule and an oxygen adatom, but proton transfer between the water and the oxygen atom to form two geminal dihydroxyl species does not occur (under UHV conditions). Instead, oxygen can be viewed as a poison of H_2O dissociation sites on $\alpha\text{-Cr}_2\text{O}_3(001)$. This is the complete opposite of what Epling et al. observed for the interaction of oxygen adatoms and water molecules on $\text{TiO}_2(110)$ [46]. This difference between the coadsorption behavior of water and atomic oxygen on $\alpha\text{-Cr}_2\text{O}_3(001)$ and on $\text{TiO}_2(110)$ suggests that water dissociation is very sensitive to the nature of the oxide surface.

4. Conclusions

The $\alpha\text{-Cr}_2\text{O}_3(001)$ surface is very active for dissociation of water under UHV conditions.

Water adsorption results in formation of paired OH groups comprised of a terminal OH group (containing the water molecule's oxygen atom) and a bridging OH group (containing a surface oxygen atom) in which the proton of the latter is hydrogen-bonded to the oxygen of the former. The hydrogen-bonding interaction is unusually strong, resulting in a very low $\nu(\text{OH})$ stretch at 2885 cm^{-1} for the bridging OH group. These paired hydroxyls recombine with first-order desorption kinetics to evolve water in TPD at 345 K. The three-coordinate Cr^{3+} cation that is the site for the terminal OH group also has the capacity to bind another water molecule in a non-dissociative form. To our knowledge, this is the first observation of multiple water species bound to a single cation site on a single crystal oxide surface. Preadsorbed oxygen, however, blocks the dissociative channel, but does not block the molecular adsorption site.

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References

- [1] T. Bredow, Surf. Sci. 401 (1998) 82.
- [2] C. Rehbein, N.M. Harrison, A. Wander, Phys. Rev. B 54 (1996) 14066.
- [3] F. Rohr, M. Baeumer, H.-J. Freund, J.A. Mejias, V. Staemmler, S. Mueller, L. Hammer, K. Heinz, Surf. Sci. 372 (1997) L291.
- [4] S. Thevuthasan, Y.J. Kim, S.I. Yi, S.A. Chambers,

- J. Morais, R. Denecke, C.S. Fadley, P. Liu, T. Kendelewicz, G.E. Brown Jr., Surf. Sci. 425 (1999) 276.
- [5] E. Wasserman, J.R. Rustad, A.R. Felmy, B.P. Hay, J.W. Halley, Surf. Sci. 385 (1997) 217.
- [6] V.E. Puchin, J.D. Gale, A.L. Shluger, E.A. Kotomin, J. Guenster, M. Brause, V. Kempter, Surf. Sci. 370 (1997) 190.
- [7] S. Blonski, S.H. Garofalini, Surf. Sci. 295 (1993) 263.
- [8] T.J. Godin, J.P. LaFemina, Phys. Rev. B 49 (1994) 7691.
- [9] K.C. Hass, W.F. Schneider, A. Curioni, W. Andreoni, Science 282 (1998) 265.
- [10] I. Manassidis, A. De Vita, M.J. Gillan, Surf. Sci. 285 (1993) L517.
- [11] C. Rehbein, F. Michel, N.M. Harrison, A. Wander, Surf. Rev. Lett. 5 (1998) 337.
- [12] T. Gloege, H.L. Meyerheim, W. Moritz, D. Wolf, Surf. Sci. 441 (1999) L917.
- [13] D. Cappus, C. Xu, D. Ehrlich, B. Dillmann, C.A. Ventrice Jr., K. Al Shamery, H. Kuhlnebeck, H.-J. Freund, Chem. Phys. 177 (1993) 533.
- [14] S.A. Chambers, Y. Liang, Phys. Rev. B (2000) in press.
- [15] S.A. Chambers, unpublished results.
- [16] C. Xu, M. Hassel, H. Kuhlnebeck, H.-J. Freund, Surf. Sci. 258 (1991) 23.
- [17] M. Bender, D. Ehrlich, I.N. Yakovkin, F. Rohr, M. Bauemer, H. Kuhlnebeck, H.-J. Freund, V. Staemmler, J. Phys. C: Condens. Matter 7 (1995) 5289.
- [18] Q. Guo, L. Gui, P.J. Möller, K. Binau, Appl. Surf. Sci. 92 (1996) 513.
- [19] B. Dillmann, F. Rohr, O. Seiferth, G. Klivenyi, M. Bender, K. Homann, I.N. Yakovkin, D. Ehrlich, M. Bäumer, H. Kuhlnebeck, H.-J. Freund, Faraday Discuss. 105 (1996) 295.
- [20] I. Hemmerich, F. Rohr, O. Seiferth, B. Dillmann, H.-J. Freund, Z. Phys. Chem. 202 (1997) 31.
- [21] J.A. Mejias, V. Staemmler, H.-J. Freund, J. Phys. C: Condens. Matter 11 (1999) 7881.
- [22] M.A. Henderson, Surf. Sci. 355 (1996) 151.
- [23] Y. Fukuda, A. Ignatiev, Solid State Commun. 41 (1982) 597.
- [24] M.A. Henderson, S.A. Joyce, J.R. Rustad, Surf. Sci. 417 (1998) 66.
- [25] F.E. Livingston, J.A. Smith, S.M. George, Surf. Sci. 423 (1999) 145.
- [26] M.A. Henderson, Langmuir 12 (1996) 5093.
- [27] C.A. Ventrice Jr., D. Ehrlich, E.L. Garfunkel, B. Dillmann, D. Heskett, H.J. Freund, Phys. Rev. B: Condens. Matter 46 (1992) 12892.
- [28] H. Kuhlnebeck, C. Xu, B. Dillmann, M. Hassel, B. Adam, D. Ehrlich, S. Wohlrab, H.-J. Freund, U.A. Ditzinger, H. Neddermeyer, M. Neuber, M. Neumann, Ber. Bunsenges. Phys. Chem. 96 (1992) 15.
- [29] D.R. Renneke, D.W. Lynch, Phys. Rev. A 138 (1965) 530.
- [30] C.J. Serna, J.L. Rendon, J.E. Iglesias, Spectrochim. Acta 38A (1982) 797.
- [31] K. Wolter, D. Scarano, J. Fritsch, H. Kuhlnebeck, U. Schröder, A. Zecchina, H.-J. Freund, discussion comments, Discuss. Faraday Soc 114 (1999) 90 and personal communication.
- [32] N.M. Harrison, X.-G. Wang, J. Muscat, M. Scheffler, Faraday Discuss. 114 (1999) 305.
- [33] K.W. Wulser, M.A. Langell, Phys. Rev. B 48 (1993) 9006.
- [34] A.A. Davydov, Infrared Spectroscopy of Adsorbed Species on the Surface of Transition Metal Oxides, Wiley, New York, 1984.
- [35] A. Zecchina, S. Coluccia, E. Guglielminotti, G. Ghiotti, J. Phys. Chem. 75 (1971) 2774.
- [36] S. Kittaka, T. Sasaki, N. Fukuhara, H. Kato, Surf. Sci. 282 (1993) 255.
- [37] G. Busca, V. Lorenzelli, G. Ramis, R.J. Willey, Langmuir 9 (1993) 1492.
- [38] O. Seiferth, K. Wolter, B. Dillmann, G. Klivenyi, H.-J. Freund, D. Scarano, A. Zecchina, Surf. Sci. 421 (1999) 176.
- [39] M.A. Henderson, unpublished work.
- [40] X. Li, V.E. Henrich, Surf. Sci. Spectra 5 (1998) 165.
- [41] P.A. Thiel, T.E. Madey, Surf. Sci. Rep. 7 (1987) 211.
- [42] S. Tanuma, C.J. Powell, D.R. Penn, Surf. Interface Anal. 11 (1988) 577.
- [43] A. Novak, Struct. Bond. (Berlin) 18 (1974) 177.
- [44] R.C. Weast (Ed.), Handbook of Chemistry and Physics, fifty seventh ed., CRC Press, Cleveland, OH, 1977.
- [45] M.A. Henderson, W.S. Epling, C.L. Perkins, C.H.F. Peden, U. Diebold, J. Phys. Chem. B 103 (1999) 5328.
- [46] W.S. Epling, C.H.F. Peden, M.A. Henderson, U. Diebold, Surf. Sci. 412/413 (1998) 333.