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Chemisorption of H_2O on the surface of Ti_2O_3: Role of *d* electrons and ligand geometry

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The interaction of H_2O with both nearly perfect and defect Ti_2O_3 surfaces has been studied by ultraviolet photoemission spectroscopy. Perfect Ti_2O_3 (047) surfaces, which contain fivefold O-coordinated Ti^{3+} cations, rapidly chemisorb molecular H_2O, with an accompanying transfer of electrons from the Ti a_{1g} band to the molecule-surface complex. Saturation coverage of adsorbed H_2O is less than one-half monolayer. The extramolecular relaxation-polarization shift for molecularly adsorbed H_2O is 1.0 eV, and the O-lone-pair orbital is dominant in bonding to the surface. There is no evidence for dissociative chemisorption of H_2O on Ti_2O_3 (047). On Ti_2O_3 surfaces containing a high density of defects, dissociative adsorption of H_2O is observed; the chemisorbed species is believed to be OH^- radicals. Some molecular adsorption of H_2O may also occur for larger exposures. These results indicate that the presence of Ti^{3+} surface ions alone is *not* sufficient to catalyze the dissociation of H_2O, in contrast to previous interpretations of data on TiO_2 and $SrTiO_3$. Presumably other Ti valence states or the more complicated ligand structure of defect sites are required for dissociation of H_2O.

I. INTRODUCTION

The interaction of molecules with transition-metal-oxide surfaces is both interesting in its own right and of great practical importance in catalysis and photocatalysis.[1] We have previously investigated the surface electronic structure of single-crystal Ti_2O_3 and the interaction of oxygen with both nearly perfect and high-defect-density Ti_2O_3 surfaces.[2] Complex band-bending and charge transfer processes were found to occur in that system.

In this paper we present results on the interaction of water with single-crystal Ti_2O_3 surfaces. Water is a particularly important adsorbate on oxides (and perovskites) of Ti because of the activity of TiO_2 and $SrTiO_3$ in the photoelectrolytic production of hydrogen from water.[3] While TiO_2 has Ti^{4+} $3d^0$ cations in the bulk, the active surface sites for photocatalytic processes are believed to be Ti^{3+} $3d^1$ cations at surface defect sites.[1] Hence H_2O chemisorption on Ti_2O_3, whose bulk cations have a Ti^{3+} $3d^1$ configuration, constitutes an important model system.

Ti_2O_3 has been found to cleave well along an (047) plane, which contains all fivefold-coordinated surface cations in alternately tilted oxygen octahedra (see Fig. 1 in Ref. 2). The electronic structure of cleaved surfaces was found to be very similar to that of the bulk, with no bending of the bands at the surface. Exposure to O_2, however, removes electrons from surface Ti $3d$ orbitals and bends both cation and anion bands upward at the surface. The O $2p$ band moves about 4 times as far in energy as does the Ti $3d$ band, resulting in significant changes in surface electronic structure. The changes in surface band structure resulting from the formation of defects on the surface, and their interaction with O_2, have also been reported in Ref. 2.

In Sec. II the experimental techniques that are used will be discussed briefly. Section III summarizes the surface band structure of Ti_2O_3 (047), the previous measurements with 21.2-eV photons having been augmented with measurements at 40.8 eV. The interaction of H_2O with cleaved Ti_2O_3 (047) surfaces is described in Sec. IV, and the effects of H_2O exposure on high-defect-density Ti_2O_3 surfaces are examined in Sec. V. Section VI discusses the interpretation of the data in terms of possible chemisorption mechanisms.

II. EXPERIMENTAL METHODS

The methods of sample preparation and characterization and a description of the ultraviolet photoemission (UPS) measurements are given in Ref. 2.

The H_2O used for chemisorption was triply distilled, deionized water contained in a glass vial attached to a variable-leak valve on the ultrahigh-vacuum system. It was degassed by repeated freezing and thawing while under vacuum. Mass analysis of the vapor admitted to the vacuum system showed a maximum impurity level of about 500 ppm O_2. (The actual O_2 level may have been lower than that, but the cracking of H_2O in the ionizer of the mass spectrometer precluded more accurate measurements.) For this reason, exposures were limited to 10^3 L (1 L = 1 langmuir = 10^{-6} Torr sec) in order to eliminate any possible effects due to O_2, which interacts strongly with the Ti_2O_3 surface. Electron-stimulated spectroscopies were used only at the completion of the UPS measurements in order to avoid electron-stimulated desorption of the adsorbed species.

III. ELECTRONIC STRUCTURE OF CLEAN Ti_2O_3 (047)

In order to determine the chemisorbed state of molecules on a surface from UPS measurements, the clean-surface electronic structure must be known. The 21.2-eV UPS spectrum for vacuum-cleaved Ti_2O_3 (047) has been reported previously.[2] Those measurements have now been extended to 40.8-eV He II, since higher-energy spectra were necessary for the unambiguous identification of some peaks in the UPS difference spectra for H_2O chemisorbed on Ti_2O_3. The results of measurements at both photon energies are shown in Fig. 1. There are qualitative differences in the O $2p$ valence-band region of these two spectra, due primarily to the different final states involved. Unfortunately, band-structure calculations for the region of those final states do not exist.[4] However, some information can be obtained from a qualitative comparison of the band shapes.

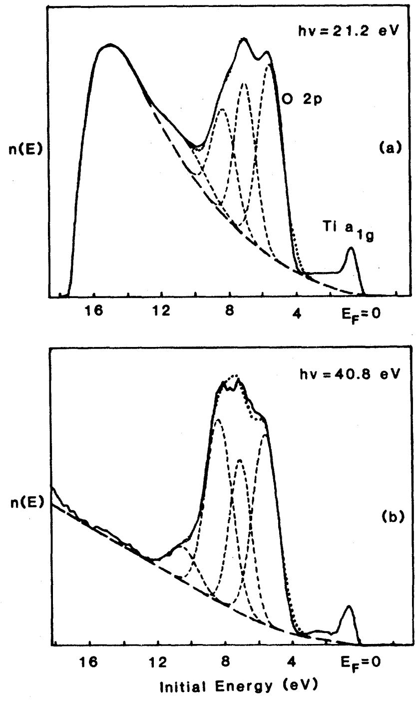

FIG. 1. UPS spectra for vacuum-cleaved Ti_2O_3 (047) taken using (a) 21.2-eV and (b) 40.8-eV photons. Solid lines are the experimental data, long dashed lines are assumed backgrounds, short dashed curves are Gaussians used to fit the O $2p$ band, and dotted lines are the resultant fits.

Photoemission spectra consist of primary, unscattered photoelectrons on a background of secondary electrons that have been produced by inelastic scattering of the primaries. In UPS this background spectrum is a complex function of the density of states at all energies attainable with the photon energy used.[5] It can be calculated if the band structure is known; the result is a relatively smooth curve, even when there is appreciable structure in the density of states.[6] If the band structure is not known, the background can be approximated and removed from the data without introducing significant distortion in the primary electron spectrum.[7] The long dashed lines in Fig. 1 show the background functions used.

Since we are interested in the qualitative changes in the UPS spectra produced by different photon energies, we have modeled the valence-band region with simple functions. Gaussians were chosen because they gave the best fit to the sharp edges of the band. The minimum number of Gaussians necessary to satisfactorily reproduce the valence-band shapes is four. In both spectra, the same energy positions relative to E_F were used for the Gaussians, while their amplitudes and widths were allowed to vary independently until the best fits were obtained. In Fig. 1 the individual Gaussians are given by the small dashed curves, and their sums, including the background function, are given by the dotted curve, which is visible only when it diverges from the data. The energy locations of the Gaussian lines, their full width at half maximums (FWHM's), and their integrated areas (normalized to the sum of the areas under the O $2p$ band) are presented in Table I; the relative amplitude of the Ti a_{1g} band is also included.

With the exception of the smallest peak at 10.3 eV below E_F, whose fit is most strongly dependent on the choice of background, the widths of the lines

TABLE I. Gaussian fits to the UPS spectra of Ti_2O_3 (047).

	$h\nu=21.2$ eV		$h\nu=40.8$ eV	
Center energy (eV)	Relative amplitude	FWHM (eV)	Relative amplitude	FWHM (eV)
O $2p$				
5.40	0.40	1.70	0.34	1.80
6.90	0.27	1.45	0.25	1.60
8.15	0.21	1.65	0.34	1.85
10.30	0.12	3.40	0.07	2.00
Ti a_{1g}	0.05	0.87	0.03	0.83

determined for the two photon energies are very similar. The main difference between the 21.2- and 40.8-eV spectra is an increase in the relative amplitude of the 8.15-eV peak in the He II spectrum. It has been suggested that the line at 8.15 eV in the 21.2-eV spectrum corresponds to the admixture of Ti $3d$ wave functions in the primarily O $2p$ valence band.[2] But the increase in amplitude of that peak in the 40.8-eV spectrum is accompanied by a decrease in the amplitude of the Ti a_{1g} band just below E_F. Since the initial states for both of these peaks should consist primarily of Ti $3d$ orbitals, the final states for the two transitions must be significantly different at the two photon energies. Unfortunately, no band calculations exist for the region of the final states for either spectrum, so it is not possible to verify this.[4] Since in most materials the structure in the density of states tends to decrease for energies farther above E_F, the relative amplitudes of the 8.15-eV peak (assuming that it is cation derived) and the a_{1g} band in the 40.8-eV spectrum should more nearly correspond to the initial density of states.

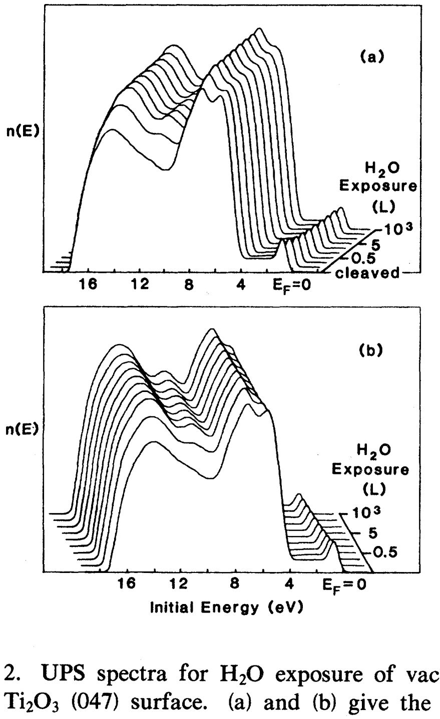

FIG. 2. UPS spectra for H_2O exposure of vacuum-cleaved Ti_2O_3 (047) surface. (a) and (b) give the same data viewed from different angles. $h\nu=21.2$ eV.

IV. INTERACTION OF H_2O WITH Ti_2O_3 (047) SURFACES

The 21.2-eV UPS spectra that are obtained when a cleaved Ti_2O_3 (047) surface is exposed to various amounts of H_2O are shown in Fig. 2; Figs. 2(a) and 2(b) present the same data viewed from different angles. The most striking changes in the spectra upon H_2O chemisorption are the appearance of a peak at about 10 eV below E_F and a slight reduction in amplitude of the Ti a_{1g} band; some changes in the region of the O $2p$ valence band can also be seen. The variation in the work function with H_2O exposure will be discussed below.

Unlike the case of O_2 adsorption on this surface,[2] H_2O adsorption does not bend the bands significantly. The upper edge of the O $2p$ valence band only rises by about 0.2 eV after 10^3-L exposure; the bottom edge of the Ti a_{1g} band rises by about 0.1 eV. This relative stability of the band structure upon adsorption permits meaningful UPS difference spectra to be taken for this system, provided that the spectra are aligned in the proper manner. The difference spectra that result when the 100-L and the clean-surface spectra are aligned at either the bottom edge of the a_{1g} band or at the upper edge of the valence band are shown in Fig. 3; the shifts of the clean-surface spectra differ by 75 meV between the two cases. Alignment of the spectra at the a_{1g} band gives an accurate representation of the depopulation of that band upon H_2O exposure, but

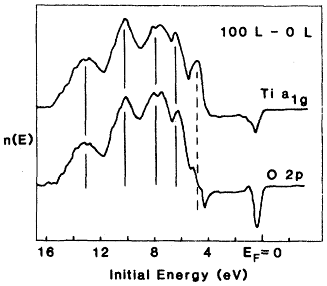

FIG. 3. UPS difference spectra for cleaved Ti_2O_3 (047) exposed to 100-L H_2O. See text for additional discussion.

it introduces a spurious peak on the upper edge of the O $2p$ band, indicated by the dashed line in Fig. 3; that peak is simply due to the difference in energy of the O $2p$ bands in the clean and H_2O-covered spectra. It is greatly reduced in amplitude when the upper edge of the O $2p$ band is used for alignment. That alignment does distort the region of the Ti a_{1g} band, however. The remaining peaks in the difference spectra, whose positions are indicated by solid vertical lines in Fig. 3, are essentially unaffected by the choice of band bending. Since the molecular orbitals of the chemisorbed species all fall on or below the O $2p$ band, we have aligned the upper edge of that band when taking differences.

The difference spectra thus obtained are shown in Fig. 4. (The spurious peak at about 8 eV is slightly larger here than in Fig. 3 since the data were taken on different cleaves.) A single phase, consisting of four peaks between 11 and 17 eV below E_F, is seen to adsorb rapidly at low exposures. (Since the highest-binding-energy peak is rather close to the vacuum-level cutoff in the 21.2-eV spectra, its existence and location were confirmed by 40.8-eV spectra, where the background was smaller and smooth in the vicinity of that peak.) The manner in which this phase chemisorbs can be seen more clearly in Fig. 5, where sequential differences for the data in Fig. 4 are plotted. Chemisorption is rapid up to 0.3 L, with virtually no adsorption from 0.3 to 10^3 L. The depopulation of the Ti a_{1g} band occurs primarily during the first 0.3-L exposure; however, there is a slight decrease in a_{1g} emission at higher exposures.

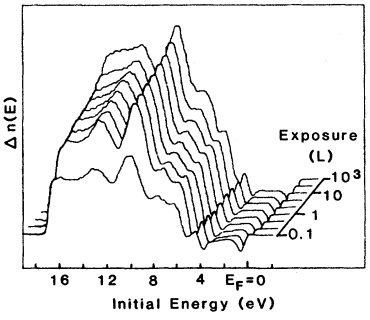

FIG. 4. UPS difference spectra for H_2O exposure of cleaved Ti_2O_3 (047), aligned at the top edge of the O $2p$ band.

The behavior of the work function ϕ for the exposure of four cleaved Ti_2O_3 (047) surfaces to H_2O is shown in Fig. 6. The ordinate $\Delta\phi$ is the change in ϕ from the value for the cleaved surface. (The values of ϕ for different cleaves varied by as much as 0.3 eV.) The abscissa used in Fig. 6 is the area under the peak at 10 eV in the difference spectra, normalized to its average value for exposures greater than 2 L; this was done since essentially no changes are observed in the UPS spectra above 2 L. It is thus a measure of the number of molecules adsorbed on the surface. The lines connect the points in order of increasing exposure.

There are large quantitative differences between the data for different cleaves in Fig. 6, which is characteristic of the behavior of ϕ on cleaved Ti_2O_3 (047) surfaces. Two trends in the data are common to all of the spectra, however. First, ϕ changes by 100 meV or less for all spectra between 0 and 0.8 on the abscissa; the detailed manner in which ϕ changes in this region varies from cleave to cleave, however. Second, ϕ increases with additional H_2O exposure after the UPS difference spectra have ceased to change measurably; this is the vertical rise about an abscissa of 1.0 in Fig. 6. We will return to a discussion of this behavior in Sec. VI below.

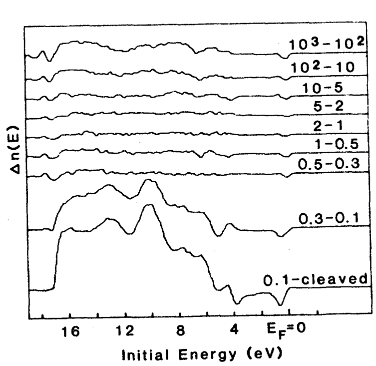

FIG. 5. Sequential UPS difference spectra for data in Fig. 4.

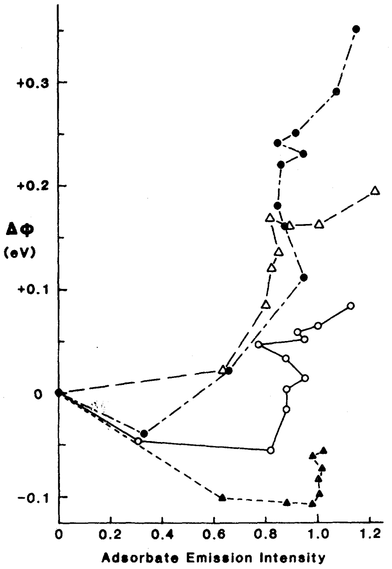

FIG. 6. Change in work function, $\Delta\phi$, for H_2O exposure of cleaved Ti_2O_3 (047) surfaces. See text for discussion of abscissa. Data for four cleaved surfaces are shown.

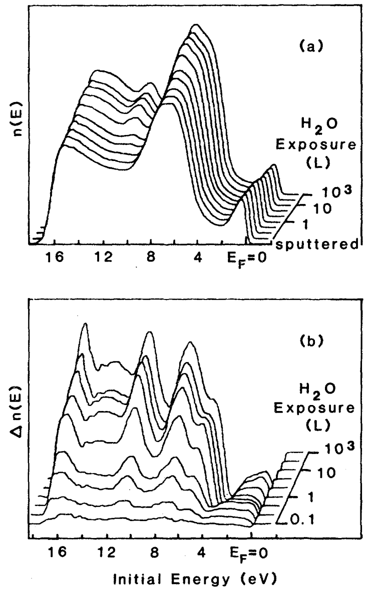

FIG. 7. (a) UPS spectra for H_2O exposure of high-defect-density Ti_2O_3 surface. (b) UPS difference spectra for data in (a), aligned at the upper edge of the O 2*p* band.

V. INTERACTION OF H_2O WITH HIGH-DEFECT-DENSITY Ti_2O_3 SURFACES

When defects are created on a nearly perfect Ti_2O_3 surface by inert-gas-ion bombardment,[2] the surface loses oxygen, with electrons being transferred from the O^{2-} ions to the surface Ti 3*d* band; this is shown in Fig. 4 of Ref. 2. In addition, the structure in the O 2*p* valence band becomes less well defined, and defect surface states are created in the bulk band gap between the O 2*p* and the a_{1g} bands. Low-energy electron diffraction patterns completely disappear, and the composition of the top few planes of the surface becomes more nearly that of TiO than Ti_2O_3. The electronic and geometric structure of defects on the Ti_2O_3 (047) surface has been discussed previously.[2]

When such a high-defect-density Ti_2O_3 (047) surface is exposed to H_2O, the UPS spectra change as shown in Fig. 7(a). A new peak appears at about 11 eV below E_F, and the intensity in the region of the valence band increases. There is a corresponding depopulation of the Ti a_{1g} band and of the defect surface states between the Ti 3*d* and O 2*p* bands. The UPS difference spectra, taken by aligning the upper edge of the O 2*p* valence band, are shown in Fig. 7(b). They exhibit strikingly different structure than that seen for the cleaved surface. The high-defect-density Ti_2O_3 surface interacts with water to produce a two-peaked difference spectrum at low exposures, with the peaks separated by 3.5 eV. The peaks continue to grow with exposure up to about 5 L, indicating a sticking coefficient less than unity. Above 2 L a smaller peak, about 14 eV below E_F, also becomes visible in the difference spectra. [This peak was *not* observed on a bisectrix Ti_2O_3 surface that had been ion-bombarded; the other two peaks were identical to those on the sputtered (047) surface.]

The behavior of the work function when defect Ti_2O_3 surfaces are exposed to H_2O is also completely different than that for cleaved surfaces; results for three different runs are shown in Fig. 8. The ordinate is the same as that in Fig. 6, and the abscissa is the sum of the areas under the two main peaks in the difference spectra, normalized to the average value for exposures greater than 2 L. ϕ decreases linearly with adsorbate coverage in this case, and the data are much more reproducible than they are for cleaved surfaces.

VI. DISCUSSION

When the nearly perfect Ti_2O_3 (047) surface is exposed to H_2O up to 10^3 L, the UPS spectra in Figs. 4 and 5 show that only one phase adsorbs. The fact that the adsorption is essentially complete by 0.3 L indicates a sticking coefficient close to unity and a coverage at saturation of less than one molecule per surface cation. Comparison of the UPS difference

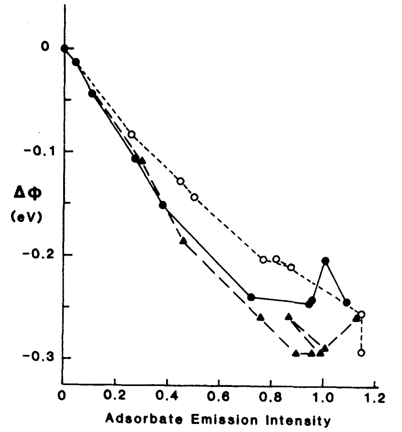

FIG. 8. Change in the work function, $\Delta\phi$, for H_2O exposure of high-defect-density Ti_2O_3 surfaces. See text for discussion of abscissa. Data for three sputtered surfaces are shown.

spectra for four different cleaved Ti_2O_3 (047) surfaces exposed to 100-L H_2O with the UPS spectrum for molecular H_2O, shown in Fig. 9, strongly suggests that the adsorbed species is molecular water.[8] If H_2O were to dissociatively chemisorb as OH^- radicals, the difference spectra should exhibit two peaks[9,10] such as those seen for H_2O chemisorption on ion-bombarded Ti_2O_3. The best alignment of the gas-phase H_2O orbitals with the difference spectra is that shown in Fig. 9; it gives an extramolecular relaxation-polarization (ERPS) shift of 1.0 eV. The spacing between the b_1 and b_2 orbitals is the same as in the gas phase,[8] and the a_1 or O-lone-pair orbital is stabilized by 0.45 eV relative to the b_1 and b_2 upon adsorption.

The UPS and work-function data suggest a probable model for the manner in which H_2O molecules chemisorb on the Ti_2O_3 (047) surface. The fact that the separation between the b_1 and b_2 orbitals for adsorbed H_2O is the same as in gas-phase water, while the O-lone-pair orbital is shifted 0.45 eV to larger binding energy, indicates that bonding to the surface is primarily via the O atom, with the H atoms away from the surface. That the O atom bonds to the fivefold-coordinated surface cations, completing the octahedral O coordination that they have in the bulk, is inferred from the partial depopulation of the a_{1g} band. The reduction in intensity of that band is roughly proportional to the increase in amplitude of the three H_2O molecular orbitals up to 0.3-L exposure; the additional depopulation of the a_{1g} band for higher exposures will be discussed below.

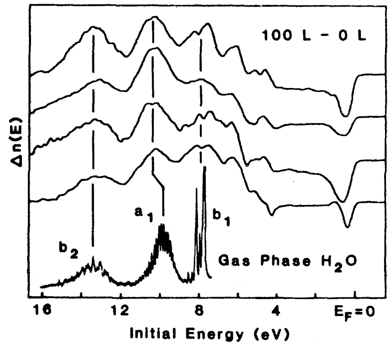

FIG. 9. Comparison of UPS difference spectra for four cleaved Ti_2O_3 (047) surfaces exposed to 100-L H_2O with UPS spectra for molecular H_2O.

The relatively small change in ϕ (Fig. 6) for low H_2O exposures indicates that no more than a small-surface dipole layer is created by the adsorbed molecules. Free H_2O molecules have a permanent dipole moment of 1.87 debye,[11] which would decrease ϕ by about 1.4 eV for one-fourth monolayer coverage if the twofold axis were normal to the local Ti-O_4 surface plane[2] and the molecule did not distort upon adsorption. Thus, the charge that is transferred out of the a_{1g} band must go into the H_2O-surface complex above the surface plane in order to compensate the molecular dipole. A charge of one electron per adsorbed H_2O molecule placed 0.3 Å above the surface cation plane would be sufficient to counter the effect of such a dipole. The fourth peak in the UPS difference spectra, at 6.4 eV below E_F, could correspond to that charge. (The 6.4-eV peak could also arise from changes in the shape of the O $2p$ valence band, however.) The actual situation is more complex, of course, due to distortion of the H_2O molecule, hybridization of molecular and surface orbitals,[12] etc., but our data are not sufficient to refine the model further.

The increase in ϕ by as much as 250 meV after the UPS spectra indicate that H_2O adsorption is essentially complete could arise from two different effects. Since the UPS difference spectra in Fig. 5 do show some additional reduction in a_{1g} band intensity above 0.3 L, a disproportionately large amount of charge may be transferred to the adsorbed molecular layer as the last few molecules squeeze onto the surface at saturation. An alternative possibility is that the molecules change their orientation near saturation coverage so that the permanent dipole of the H_2O molecules tips further away from the surface normal. A rotation of only 13° for a free H_2O molecule at one-quarter monolayer coverage would change the surface dipole contribution to ϕ by 250 meV. The present data cannot distinguish between these two possibilities.

The fact that H_2O adsorbs molecularly on nearly perfect Ti_2O_3 (047) surfaces for low exposures is significant when compared with results on TiO_2.[1,13–15] On vacuum-fractured TiO_2 (110) surfaces, very little adsorption of any type is seen for low H_2O exposures.[14] On both TiO_2 (110) surfaces that had been ion-bombarded and annealed and on ion-bombarded surfaces containing a high density of surface defects, dissociative chemisorption has been reported for low H_2O exposures.[13,15] At higher exposures, water chemisorbs molecularly on all types of TiO_2 surfaces.[1,13] (The ERPS shift seen for H_2O on TiO_2 is larger than that for Ti_2O_3, however: 2.5 eV compared to 1.0 eV, respectively.) Based on the TiO_2 data it has been suggested that Ti^{3+} ions (or perhaps some type of surface reconstruction on annealed surfaces) are necessary for dissociative adsorption of H_2O.[1,13,15] On a perfect Ti_2O_3 (047) surface all of the surface cations are presumably Ti^{3+}, indicating that the presence of a single d electron on a fivefold-coordinated Ti cation is *not* sufficient to cause dissociation of H_2O.

When defects are produced on Ti_2O_3 by Ar^+-ion bombardment, the surface becomes oxygen deficient, with an attendant charge transfer to the Ti a_{1g} band and to defect surface states in the Ti $a_{1g}-O\,2p$ bandgap.[2] The enhanced metallic nature of the surface is evidenced by the increase in the density of states at the Fermi level. Exposure of this surface to H_2O results in a two-peaked difference spectrum for low exposures (Fig. 7); there is an accompanying transfer of charge out of the a_{1g} band and the band-gap surface states. We assign the two peaks to adsorbed OH^- radicals resulting from the dissociative adsorption of H_2O. Such a two-peaked structure in the UPS spectra has been seen both for gaseous OH radicals[9] where the two peaks are separated by 2.2 eV, and OH^- in solid NaOH,[10] where the peaks are separated by 4.2 eV.

The behavior of the work function is consistent with the above interpretation. OH^- radicals would be expected to chemisorb at surface cation sites via their negative O atoms, giving rise to a surface dipole layer that would reduce ϕ. The measured work function decreases linearly as the two-peaked difference spectrum increases in amplitude (Fig. 8), dropping by 0.3 eV by 10-L exposure, in striking contrast to the behavior of H_2O on cleaved surfaces.

Chemisorption of H_2O on high-defect-density Ti_2O_3 surfaces is qualitatively similar to that on ion-bombarded TiO_2,[13] where dissociative adsorption was observed for exposures below about 30 L; for larger exposures molecular H_2O was found to chemisorb on TiO_2. Molecular adsorption of H_2O may also occur on ion-bombarded Ti_2O_3 surfaces, since the peak seen at about 14 eV in the difference spectra (Fig. 7) is in the location that would be expected for the b_1 orbital of H_2O.[8] Adsorption on metallic defect Ti_2O_3 surfaces can also be compared to recent measurements of H_2O chemisorption on Ti metal,[16] where dissociative adsorption has been found for exposures of up to 10 L at room temperature on stepped Ti (0001). The additional peaks that appear in the UPS spectrum for H_2O on Ti (0001) have nearly the same separation as those reported here; the ERPS shifts are also nearly the same for the two materials. The results on metallic Ti are thus consistent with our results on the high-defect-density Ti_2O_3 surface with its enhanced d-electron concentration and metallic conductivity.

The measurements of H_2O chemisorption on both nearly perfect and defect Ti_2O_3 surfaces reported here provide valuable information on the interaction of H_2O with transition-metal-oxide surfaces. The fivefold-coordinated surface cations on Ti_2O_3 (047) have a strong affinity for molecular H_2O, but they do not result in dissociative adsorption. This shows that the presence of Ti^{3+} surface ions alone is not sufficient to catalyze the dissociation of H_2O. It has been pointed out by Heiland and Lüth,[17] in fact, that none of the experiments performed on either TiO_2 or $SrTiO_3$ surfaces proved conclusively that Ti^{3+} ions were responsible for the dissociative chemisorption of H_2O. Similar fivefold Ti sites on TiO_2 (110), which have a $Ti^{4+}\,3d^0$ configuration,[18] are relatively inert for even molecular H_2O adsorption.[14]

Defect sites on both TiO_2 and Ti_2O_3, which presumably contain Ti ions having several different valence states, do catalyze H_2O dissociation.[1,13,15] The defect sites on TiO_2 surfaces have generally been characterized in terms of "$Ti^{3+}-O$-vacancy complexes."[1,19,20] Such a complex is the simplest type of surface defect, and it is presumably responsible for the band-gap surface states seen in photoemission and energy-loss spectra of TiO_2 and $SrTiO_3$ surfaces.[1,18,19] The electronic structure of an O-vacancy defect on TiO_2 has been discussed previously in terms of covalent sharing of d electrons by unscreened cation pairs.[18] This pairing does *not* exist on the Ti_2O_3 (047) surface, even though all of the cations have partially filled d orbitals.[2] The cation-cation screening is greatly reduced in the vicinity of an O vacancy on Ti_2O_3 (047), however (see Fig. 1 in Ref. 2), and there is presumably a greater degree of covalent cation-cation interaction. It is thus possible that cation pairs catalyze H_2O dissociation on both TiO_2 and Ti_2O_3. This is again the simplest interpretation of the experimental data, however, and it does not at all rule out the possibility that other cation valence states or more complex defect geometries are required.

ACKNOWLEDGMENT

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