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MODELS FOR THE PHOTOELECTROLYTIC DECOMPOSITION OF WATER
AT SEMICONDUCTING OXIDE ANODES

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ABSTRACT

Surface states at semiconducting TiO_2 /electrolyte interfaces are believed to play an important role in charge transfer and thereby the efficiency of photoelectrochemical processes at such interfaces. Theoretical calculations were therefore performed using the SCF-X α -SW method to determine the position and character of surface states at various characteristic interfaces. At the TiO_2 /water interface, antibonding surface states were found which when occupied would explain the experimentally observed dissociation of water into hydroxyl groups at n-type semiconducting TiO_2 surfaces. Similarly, antibonding surface states were found at the TiO_2/OH^- interface which when occupied would tend to destabilize the OH bond. A likely mechanism for the dissociation of water and decomposition of certain photoanodes in photoelectrochemical cells based on the above results is presented. The effects of surface reconstruction at heavily reduced TiO_2 surfaces on the validity of our calculations are also discussed.

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INTRODUCTION

The present fuel shortage has stimulated much research concerning the production of hydrogen gas by the photoelectrolysis of water on semiconductor electrode surfaces. To date, only a few semiconducting oxides, including titanium dioxide and some perovskites, have been shown to remain inert in cell operation and decompose water. In all cases surface states at the electrode-electrolyte interface are believed to play an important role in the charge transfer process and thereby the overall efficiency of such cells.^(1,2) Little is known, however, concerning the source of these surface states and the manner in which they assist the photoelectrolytic process. In the following, SCF- $X\alpha$ -SW calculations are presented which serve to clarify some of these issues.

The catalytic behavior of a surface often depends on its ability to interact electronically with the adsorbate. The determination of the electronic structure of the surface perturbed by the chemisorbed species may, therefore, provide a basis for understanding charge transfer catalysis. In order to understand the electronic interaction between water and a TiO_2 surface, cluster molecular-orbital calculations were performed using the Self-Consistent-Field- $X\alpha$ -Scattered Wave (SCF- $X\alpha$ -SW) method⁽³⁾. The SCF- $X\alpha$ -SW method was chosen over the conventional Hartree-Fock Self-Consistent-Field Linear-Combination-of-Atomic-Orbitals (HF-SCF-LCAO) method since the former is less laborious and costly in computer time and leads to a more reliable description of electronic structure.⁽³⁾ Molecular orbital methods were chosen over band theory since it offers a more appropriate description of local interactions and chemical bonding.

Previous SCF- $X\alpha$ -SW studies⁽⁴⁾ have shown that the local electronic struc-

Key words: Photoelectrolysis, catalysis, titanium dioxide, perovskite titanates

ture of bulk TiO_2 (rutile) can be realistically modelled in terms of a $(\text{TiO}_6)^{8-}$ cluster, yielding results in good agreement with measured photoemission and optical absorption spectra. In the same manner, the chemisorption of H_2O on a titanium dioxide surface can be modelled by the combination of a TiO_2 surface cluster and an adsorbed H_2O molecule. In the remainder of this paper, results for the clean, water-chemisorbed, and OH^- -chemisorbed surfaces are presented and compared with recently measured photoemission spectra. With these results, a possible mechanism is suggested for the dissociation of water in the photoelectrochemical cell.

RESULTS OF CALCULATIONS

Figure 1a shows the schematic energy level diagram for "bulk" TiO_2 as calculated by the SCF- $\text{X}\alpha$ -SW method along with those for the free oxygen and titanium atoms. Only the $\text{Ti}3d$ and $\text{O}2p$ levels are shown since they are the only ones involved in bonding on this energy scale. One observes that the titanium $3d$ level splits into the antibonding e_g^* and t_{2g}^* levels which represent the conduction band of bulk TiO_2 . The valence band is composed mainly of oxygen bonding and nonbonding $2p$ character and lies approximately 3eV below the conduction band.

CLEAN SURFACES

The simplest model for the clean (110) titanium dioxide surface is the $(\text{TiO}_5)^{6-}$ cluster which consists of a slightly distorted and truncated octahedron in which a titanium atom is surrounded by five nearest-neighbor oxygen atoms. These slight distortions are ignored in our analysis to simplify calculations. Furthermore, since this is nearly the same local environment of a titanium

atom in the perovskite structure, this cluster also represents the (100) active surface site of SrTiO_3 . The charge on the cluster is chosen such that the valencies of the atoms sum to zero. This simulates charge transfer with neighboring titanium atoms in the solid.

The calculated energy levels for the $(\text{TiO}_5)^{6-}$ surface cluster are shown in Figure 1b. Here the 3d levels split further due to the lower symmetry near the surface. Since the cluster method does not correctly treat the Madelung constant, the resultant energy levels are only on a relative scale and must be aligned with the absolute scale. This is usually done by choosing a nonbonding level and aligning it with that of the free atom, since nonbonding levels are not expected to shift much upon bonding. The diagrams are aligned using the 02p nonbonding level, which lies at the top of the valence band.

The splitting of the t_{2g}^* and e_g^* levels in the surface cluster results in the d_{yz}^* and d_{xz}^* states extending into the energy gap. These band gap surface states are simply due to the truncation of the lattice. In the intrinsic material, only levels to the top of the valence band are filled while these bandgap surface states are empty. If the material is made n-type, however, these surface states become occupied.

Similar calculations were performed for the $(\text{TiO}_4)^{4-}$ cluster, which represents the oxygen deficient (110) surface. The resultant energy level diagram shown in Figure 1c reveals that the d levels are further split by the reduced symmetry of this surface. A new characteristic surface state, designated by $d_{z^2}^*$, is generated at this surface.

SURFACE CLUSTERS WITH CHEMISORBED WATER

To study the interaction of water with a TiO_2 surface, calculations for both surface clusters were extended to include a chemisorbed water molecule.

The resultant energy diagrams for both surfaces are largely a superposition of those for the separated clean surfaces and H_2O molecule.

The electronic structure of the $(TiO_5)^{6-}H_2O$ cluster is shown in Figure 2, along with that for the clean surface and that for the H_2O molecule. The figures are aligned such that the oxygen 2p nonbonding levels coincide, which is the top of the valence band for the surface clusters and the b_1 level for the water molecule. The antibonding a_1^* and b_2^* water levels are normally empty and lie about 5eV above the filled b_1 level. In the $(TiO_5)^{6-}H_2O$ cluster, the water valence levels are still identifiable (mixing very little with the TiO_2 valence band) and are pulled down almost uniformly in energy. The a_1 level does, however, shift more to tighter binding energy and bonds more with titanium than the b_1 and b_2 levels. This suggests that water is chemisorbed onto the surface as an intact molecule and bonds to the surface through the a_1 orbital. The antibonding a_1^* and b_2^* water levels are also pulled down in energy but mix more strongly with the TiO_2 3d levels. These states, normally unoccupied in the intrinsic material could however become filled if the material were made n-type by reduction or doping.

Photoemission data of Henrich⁽⁵⁾ for water chemisorbed on annealed (110) TiO_2 and (100) $SrTiO_3$ surfaces show the H_2O levels displaced uniformly about 2eV below the top of the valence band with the a_1 orbital shifting more to tighter binding energies, in agreement with our calculations. This suggests non-dissociative water chemisorption on the annealed surface. Our calculations however predict a larger shift for the water levels of about 4eV. This discrepancy may be due to the short bonding distance between the surface and the H_2O molecule chosen for the calculation. The bonding distance between the surface titanium atom and the water oxygen atom may very well be greater than

the bulk Ti-O bond length of $1.94 \text{ \AA}$ chosen. A larger value would have the effect of lowering the attraction between the surface and the water molecule, thereby lessening the perturbation on the H_2O molecule.

Lo, Chung, and Somarjai⁽²⁾ likewise conclude on the basis of their photoemission studies that water molecules chemisorbed on stoichiometric TiO_2 surfaces remain undissociated. On the other hand, for surfaces reduced by heating to above 800°C or by argon bombardment, they obtained evidence for the existence of dissociated water in the form of hydroxyl groups. We later show that dissociation of water molecules on reduced surfaces of TiO_2 can be explained by considering the destabilizing effects that occupation of the $d_{yz}^* - b_2^*$ antibonding states have on the stability of the H_2O molecule.

SURFACE CLUSTERS WITH ADSORBED OH RADICALS

As a simple model for the TiO_2 -electrolyte interface in a photo-electrochemical cell, the $(\text{TiO}_5)^{6-}\text{OH}^-$ and $(\text{TiO}_4)^{4-}\text{OH}^-$ clusters were chosen to represent the local electronic interaction between the titanium dioxide surface and basic electrolyte. The resultant energy levels are a superposition of those for the clean surfaces and the OH^- ion, with some mixing. The results for the $(\text{TiO}_5)^{6-}\text{OH}^-$ cluster are shown in Figure (3) along with the energy levels of the OH radical and clean surface cluster. Again the diagrams are aligned at the nonbonding oxygen 2p level, which is the filled π level for the OH^- ion. The π and σ OH^- levels appear to remain relatively unperturbed upon chemisorption, but the antibonding σ^* and π^* levels are pulled far down in energy to interact with the TiO_2 d levels resulting in additional surface states within the band gap. In the next section these states will be shown to play a potentially important role in the photoelectrolytic decomposition of water.

DISCUSSION

As a result of our calculations we have been able to predict the relative positions of surface states generated at TiO_2 -vacuum, $-\text{H}_2\text{O}$ and $-\text{OH}^-$ interfaces as well as the character of these states. It should be noted that the adsorbate itself has a strong influence on the position, character and number of surface states that exist at a given interface. In the following we consider the consequences that occupation of these surface states have on water dissociation and photoelectrolysis and compare these predictions with experimental evidence.

CLEAN SURFACES

A number of investigators have recently studied the surface electron structure of TiO_2 by ultraviolet photoemission spectroscopy (UPS), low-energy-electron diffraction (LEED) and Auger electron spectroscopy (AES). Henrich, et al.⁽⁶⁾ observed a UPS peak at about 2.5eV above the bottom of the valence band for annealed TiO_2 surfaces which they attributed to surface defect states. This peak increased by more than a factor of 10 under argon-ion bombardment which was shown to result in the formation of Ti^{3+} ions at the surface.⁽⁶⁾ Lo, et al.⁽²⁾ observed similar absorption peaks which were sensitive to annealing and Ar bombardment treatments. Both studies are consistent with our calculations which indicate the existence of normally empty surface states which become occupied upon reduction of the surface resulting in the formation of Ti^{3+} ions. Subsequent exposure of the surface to oxygen results in a sharp decrease in the emission peak indicating a reversible depopulation of the Ti-like surface states.

WATER DISSOCIATION

In investigating the chemisorption of water on variously treated TiO_2 surfaces by photoemission (UPS), Lo, et al. ⁽²⁾ discovered that whereas water is adsorbed as an intact molecule on oxidized TiO_2 surfaces, it appears to dissociate on reduced surfaces leaving behind $(\text{OH})^-$ molecules adsorbed on the surface. Henrich, et al. ⁽⁵⁾ observed similar results for argon bombarded (110) TiO_2 surfaces upon exposure of up to 10L H_2O .

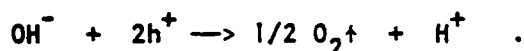
Since existence of Ti^{3+} ions at the surface appears to be critical in determining the manner in which water molecules adsorb on the surface we examine the consequences of surface state occupation on bonding between TiO_2 and adsorbed water molecules.

Reduction of the TiO_2 surface by argon bombardment or annealing in hydrogen should result in occupation of the $d_{yz}^* - b_2^*$ levels of the TiO_2 -OH interface (see Fig. 2). The contour diagrams for these orbitals are shown in Figure 4. The d_{yz}^* orbital is antibonding between the titanium 3d and oxygen 2p levels; this is revealed by opposite signs in the overlapping lobes between the titanium and oxygen. In the diagrams, the lobes are shrunken in size and are not shown as overlapping for clarity. The sign inside the lobes represents the phase of the wave-function: overlapping lobes of the same sign signify bonding. When the d_{yz}^* and b_2^* orbitals mix, the titanium d lobes and the oxygen 2p lobe (of H_2O) overlap in a bonding fashion as do the oxygen 2p lobes (of the lattice) and the hydrogen lobe. When the $d_{yz}^* - b_2^*$ orbital is occupied, as it is in the bombarded TiO_2 surface with chemisorbed water, bonding between the titanium d and oxygen 2p (of H_2O) and the surface oxygen 2p and hydrogen orbitals will be strengthened; the OH bonding within the water molecule will be weakened since the overlapping orbitals have opposite phase. Thus, a plausible mechanism

exists for the break-up of chemisorbed water into OH radicals on the surface if and only if the surface states with antibonding character are occupied as they are in reduced TiO_2 . Similar results are also obtained for the $(\text{TiO}_4)^{4-}\text{H}_2\text{O}$ cluster.

PHOTOELECTROLYTIC DECOMPOSITION OF WATER

When n-type photoanodes such as TiO_2 or SrTiO_3 are immersed in liquid electrolytes and are illuminated with band-gap light, oxygen gas (O_2) is known to be released.⁽⁷⁾ This process of oxygen evolution has been modeled assuming that a Schottky barrier is formed at the solid liquid interface at which electron-hole pairs are formed during illumination. The built-in space-charge field is then believed to cause the photo-generated holes to be swept towards the interface while the electrons are swept away from the interface towards the platinum counter-electrode. The OH^- ions adsorbed at the interface are now believed to lose their electrons to the semiconductor valence band via surface states⁽¹⁾ producing oxygen by the reaction



Because the energy of the electrons associated with the OH^- ions (commonly referred to as the OH^-/O_2 redox level) lie considerably above the semiconductor valence band in energy, direct charge transfer is highly unlikely. The existence of surface states nearly degenerate with the OH^-/O_2 level would, however, exhibit the high tunneling probabilities necessary for efficient charge transfer across the interface. Although such surface states are believed to play an important role in photoelectrolysis, little is now known concerning their identity.

Examining again the energy levels for the $(\text{TiO}_5)^{6-}\text{OH}^-$ cluster we find that the states labeled d_{xy}^* , $d_{yz}^*-\pi^*$ and $d_{z^2}^*-\sigma^*$ lie within the band-gap. Since the TiO_2 anodes used for photoelectrolysis are n-type with a Fermi level near the bottom of the conduction band, these levels have a high probability of being occupied. Recent surface photocurrent spectroscopy data of Mavroides, et al.⁽¹⁾ for reduced SrTiO_3 operating in an electrolytic cell with basic electrolytic support the occupation of these bandgap surface states.

To explain the observed O_2 gas released from the semiconductor surface according to the proposed equation above, one must first show a mechanism for splitting the O-H bond in the OH radical. In general, bonds are broken by occupying antibonding orbitals or by depopulating bonding orbitals. The $(\text{TiO}_5)^{6-}\text{OH}^-$ results show the top valence level to be mainly of $\text{OH}^- \pi$ character. Under illumination in the electrochemical cell, this state would most probably be depopulated. However, since it is a nonbonding $\text{O}2p$ level, it does not bond with hydrogen so its depopulation would not be expected to destabilize the OH bond. On the other hand, the occupation of antibonding orbitals may lead to destabilization of the O-H bond.

If we consider the lowest antibonding orbital, d_{xy}^* , we observe that it does not mix with the OH^- orbital due to symmetry conservation and thus contains no OH^- character. Similarly, examination of the contour map of the $d_{yz}^*-\pi^*$ orbital in Figure 5A shows that no OH breakup is expected since the π^* orbital contains no H bonding.

Occupation of the $d_{z^2}^*-\sigma^*$ orbital would, however, tend to destabilize the O-H bond since the σ^* orbital is antibonding between the oxygen and hydrogen. Occupation of the $d_{z^2}^*-\sigma^*$ orbital would also tend to promote bonding between the Ti atom and the oxygen atom of the OH^- ion since their wavefunctions are in-phase.

Thus, occupation of the $d_{z^2}^* - \sigma^*$ orbital would provide a mechanism for breaking the O-H bond, while leaving the O of OH bonded to the surface.

Other antibonding states higher in energy on the $(TiO_5)^{6-}OH^-$ energy diagram also contain some σ^* character, though not as much as the $d_{z^2}^* - \sigma^*$ level (i.e., less mixing between the d^* and σ^* orbitals). For this reason, occupation of the $d_{z^2}^* - \sigma^*$ orbital is expected to be, in large part, responsible for splitting the O-H bond, although higher states may contribute to some extent.

The contour diagram of the $d_{z^2}^* - \sigma^*$ orbital (Figure 5B) shows the oxygen atom of the OH radical to be more strongly bonded to the Ti atom than the oxygen atoms of the lattice (which are antibonding with respect to the Ti atom). This suggests that the observed O_2 gas released from the oxide surface during photoelectrolysis may originate from the lattice. Oxygen atoms leaving the surface layer would thereby create vacancies which might then be occupied in turn by oxygen ions originating with the adsorbed OH^- ions.

The possibility suggested above that surface oxygen ions may be released preferentially from TiO_2 surfaces during illumination, might explain their relative stability to photodecomposition. For non-oxide electrodes, regeneration of the lost surface anions from the adsorbed OH^- ions would not be possible and might therefore explain their propensity to decompose under illumination.

EXTENSION OF CALCULATIONS

The above calculations have been performed using the simplest models possible to represent the ideal clean TiO_2 surface interacting with adsorbed species. A major simplification made in our calculations was to assume that the n-type TiO_2 and $SrTiO_3$ surfaces differed from the stoichiometric (annealed) surfaces by only the occupation of the bandgap states. Both Henrich, et al.⁽⁶⁾ and Lo, et

al.⁽²⁾ report, however, that Argon bombarded surfaces and highly reduced (oxygen deficient) surfaces become disordered and show a succession of different surface-defect phases depending on the degree of reduction. In fact, extensive bombardment on the TiO_2 surface results in the formation of a different compound, Ti_2O_3 , on the surface. Similar phenomena are known to occur in bulk TiO_2 upon reduction. A whole range of closely spaced intermediate compounds are formed related to the parent rutile structure by a series of "shear" transformations in which planes of oxygen ions are removed from the lattice resulting in modified Ti-Ti bond lengths and reduced symmetry.⁽⁸⁾

Such structural transformations are not believed to occur in TiO_2 or the Perovskite titanates made "n-type" by virtue of doping rather than by creation of oxygen deficiency. Consequently, our calculations should be more directly applicable to such surfaces. On the other hand, since similar photoelectrolytic response has been observed for both reduced and doped samples, the implication exists that models presented above are at least qualitatively correct in either case.

Recent studies by Subbarao, et al.⁽⁹⁾ on TiO_{2-x} and $\text{TiO}_{2-x}\text{F}_x$ showed that the fluorine doped TiO_2 exhibited a different spectral response than reduced TiO_2 . This difference was characterized by a greater sensitivity to longer wavelengths and generation of higher photocurrent with the fluorine doped material. Similar studies by Kowalski and Tuller⁽¹⁰⁾ on reduced and Nb doped BaTiO_3 showed the doped material to exhibit much enhanced photocurrents under similar conditions.

The above results are consistent with the expectation that the reduced surfaces will possess surface states with different character and at different energies than the surface states calculated here which are more characteristic of the doped materials. Further work is underway to determine whether surfaces with Ti_2O_3 character can explain the differences in photoresponse observed for the two types of surfaces.

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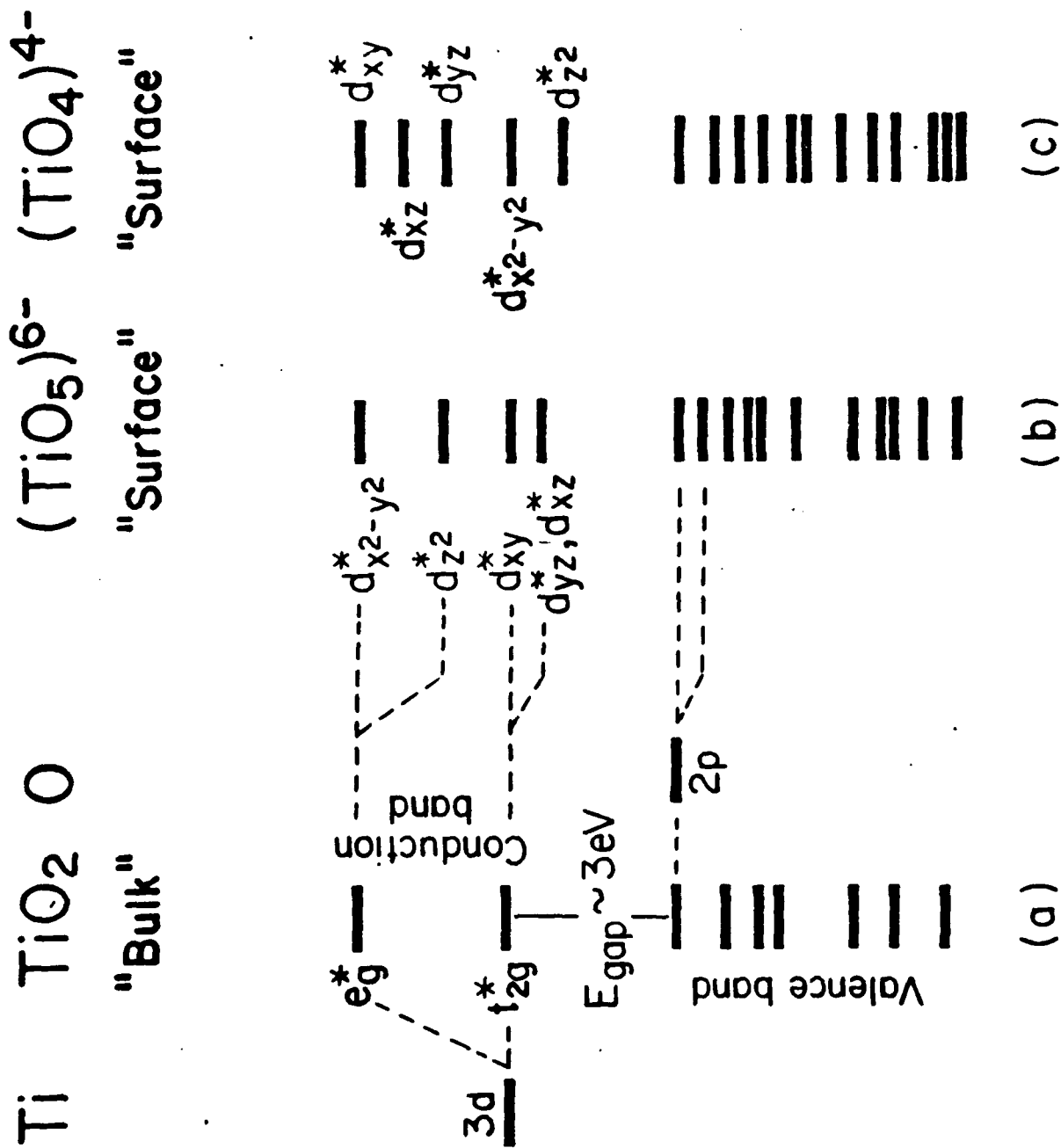
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FIGURE CAPTIONS

1. a) Energy level diagrams of bulk TiO_2 and the free titanium and oxygen atoms
b) Energy levels for the clean (110) TiO_2 and (100) SrTiO_3 surface modeled by the $(\text{TiO}_5)^{6-}$ cluster or
c) the $(\text{TiO}_4)^{4-}$ cluster.
2. Calculated energy levels for the $(\text{TiO}_5)^{6-}$, H_2O , and $(\text{TiO}_5)^{6-}\text{H}_2\text{O}$ clusters representing the clean TiO_2 surface, the water molecule, and the water chemisorbed surface.
3. Calculated energy levels for the clean TiO_2 surface, the OH^- ion, and the OH^- chemisorbed surface.
4. Contour diagrams of the d_{yz}^* and b_2^* antibonding orbitals before mixing in the $(\text{TiO}_5)^{6-}\text{H}_2\text{O}$ cluster.
5. a) Contour diagram of the antibonding d_{yz}^* and π^* orbitals for the $(\text{TiO}_5)^{6-}\text{OH}^-$ cluster.
b) Contour diagram of the antibonding $d_{z^2}^*$ and σ^* orbitals for the $(\text{TiO}_5)^{6-}\text{OH}^-$ cluster.



$(\text{TiO}_5)^{6-}$

"Surface"

— $d_{x^2-y^2}^*$
— $d_{z^2}^*$
— d_{xy}^*
— d_{yz}^*, d_{xz}^*

— — — — —

H_2O

— b_2^*
— a_1^*

— b_1

— a_1

— b_2

$(\text{TiO}_5)^{6-} \cdot \text{H}_2\text{O}$

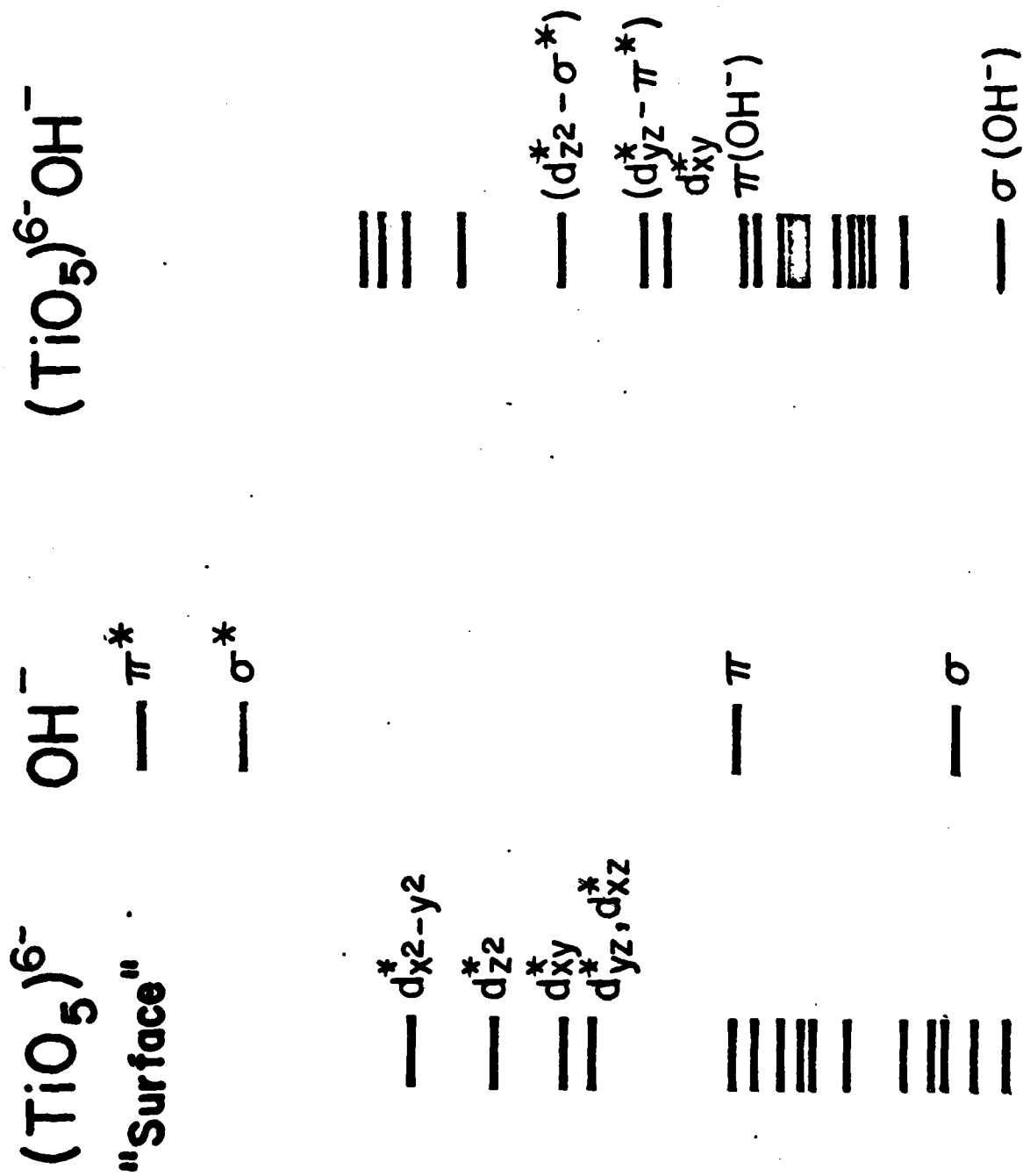
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— —
— — $(d_{yz}^* - b_2^*)$

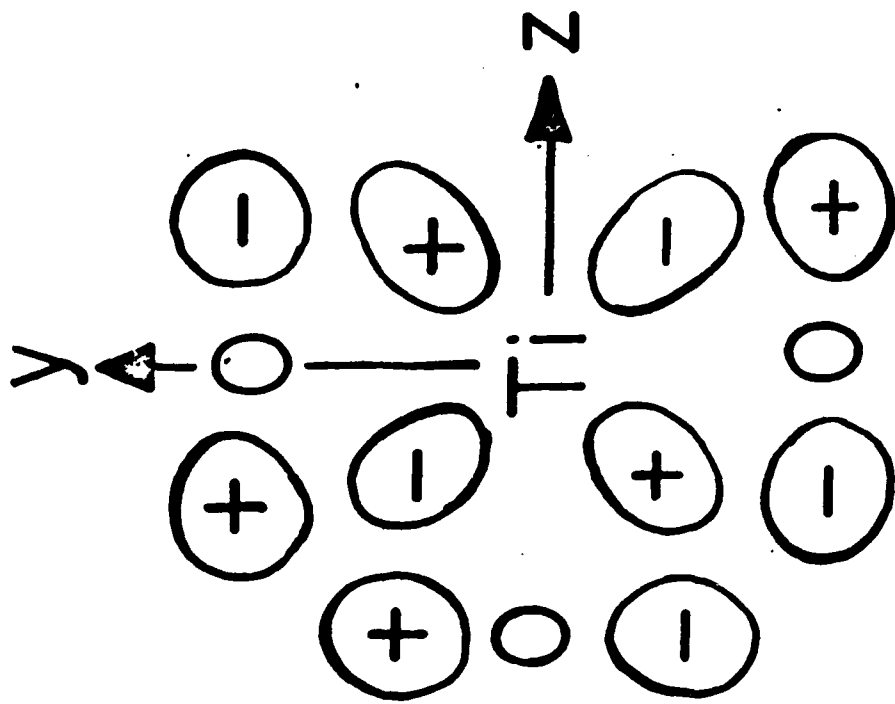
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— $b_1(\text{H}_2\text{O})$

— $a_1(\text{H}_2\text{O})$

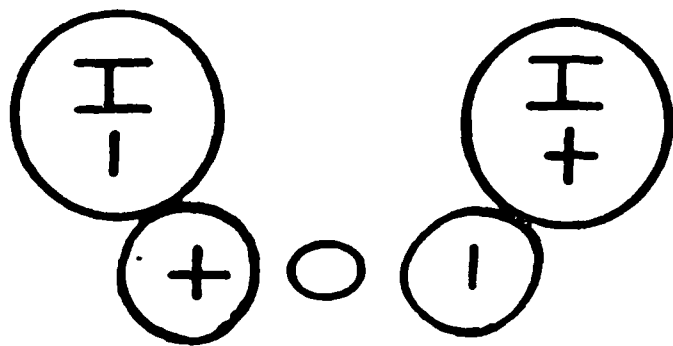
— $b_2(\text{H}_2\text{O})$





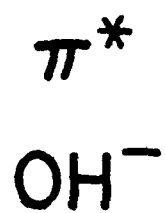
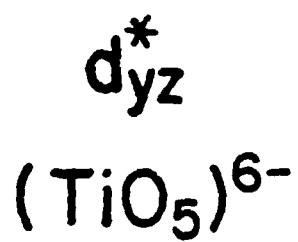
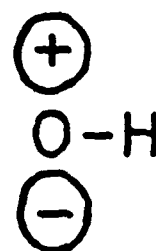
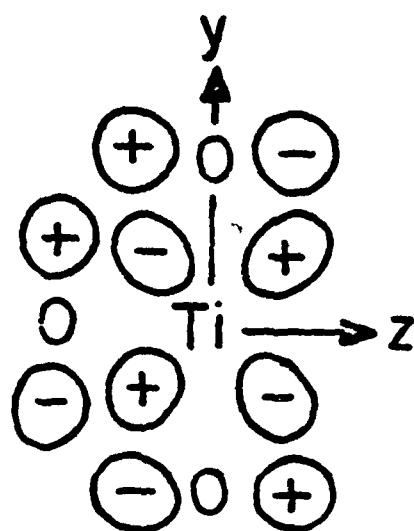
d_{yz}^*

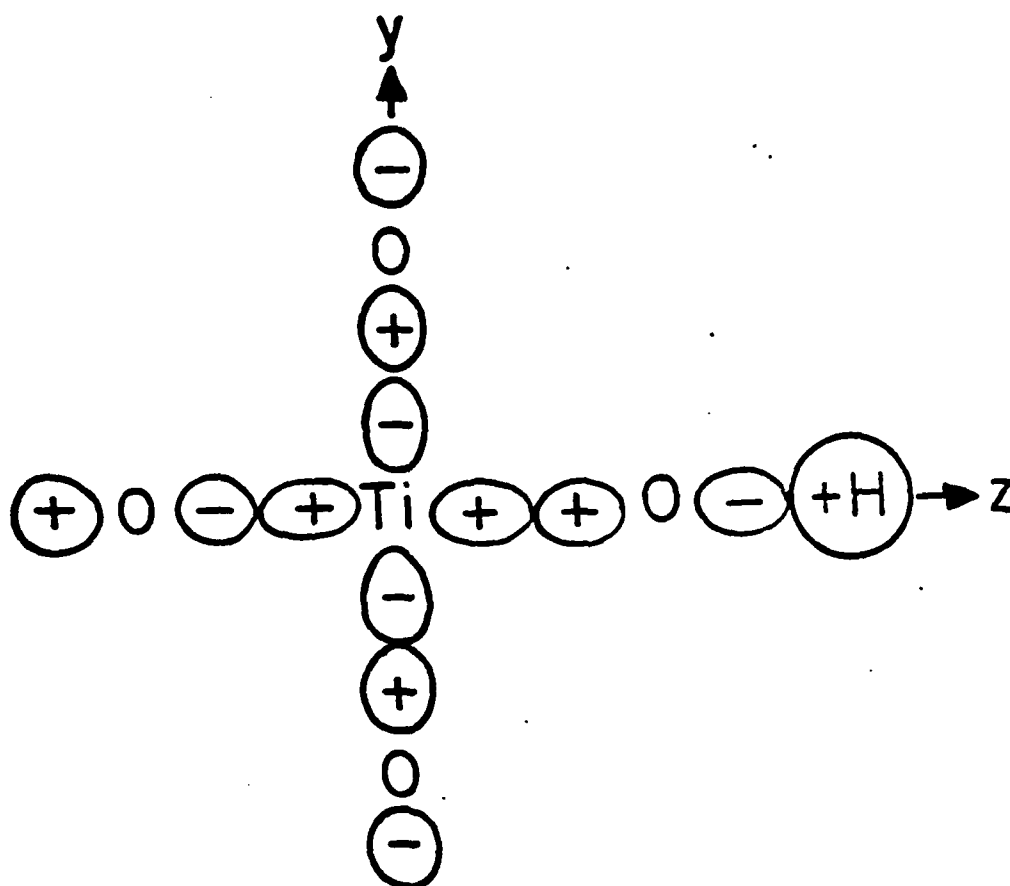
$(TiO_5)^{6-}$



$b_2(\pi^*)$

H_2O





$(d_{z^2}^* - \sigma^*)$

$(\text{TiO}_5)^{6-} \text{OH}^-$