

TiO₂(110) 표면에 흡착된 물분자의 결합 활성화에 관한 MO 연구

姜大福

경성대학교 화학과
(2002. 2. 14 접수)

Molecular Orbital Analysis of Water Activation on TiO₂(110) Surface

Dae-Bok Kang

Department of Chemistry, Kyungseung University, Pusan 608-736, Korea
(Received February 14, 2002)

요약. TiO₂(110) 표면에서 물의 OH 결합 활성화가 어떤 전자적 메커니즘에 의해 이루어지는지 extended Hückel 방법을 통해 알아보았다. 물분자는 3a₁ 오비탈의 시그마 상호작용 결과로 5배위 Ti^{IV} 원자 바로 위에 수직으로 흡착한다. 이 결합구조에서는 물분자의 H 원자가 TiO₂의 2배위 bridging O²⁻ (O_b) 원자와 너무 멀리 떨어져 있으므로 OH 결합 해리를 촉진시키는 수소결합 상호작용을 할 수 없으므로 물분자를 O_b 원자쪽으로 기울여 수소결합이 형성되도록 한다. 이 경우 O_b p 오비탈로부터 흡착 물분자의 LUMO 2b₁ 반결합성 오비탈로 전자밀도의 이동이 일어나고 또 물의 3a₁ 오비탈(약한 결합성)로부터 Ti^{IV} 3d₂ 오비탈로 전자밀도의 이동이 일어나므로써 물의 OH 결합이 상당히 약화됨을 확인할 수 있었고 그 결과 OH와 H로 해리할 것이라는 해석이 가능하다.

주제어: MO계산, TiO₂, 물

ABSTRACT. A molecular orbital analysis based on the extended Hückel calculations has been carried out to study the OH bond activation of water on the TiO₂(110) surface. H₂O binds with its axis perpendicular to the surface on top of the five-coordinate Ti^{IV} atom via its 3a₁ orbital. In this bonding situation, the two-coordinated bridging O²⁻ atom (O_b, basic site) on TiO₂(110) is too distant from an H atom of water to form hydrogen-bonding interactions with water that facilitate O-H bond cleavage. It has been elucidated that the O-H bond is appreciably weakened when the water molecule is tilted to give a hydrogen bond with the O_b atom. This mechanism includes mutual transfer of electron density from the 3a₁ orbital of the water molecule to the Ti^{IV} 3d₂ orbital and from the O_b p orbitals to the LUMO 2b₁ of the adsorbed water molecule. This should result in lengthening of the O-H bond in the surface complex and the subsequent dissociation into the fragments OH and H.

Keywords: Molecular Orbital Calculations, Titanium Oxide, Water

INTRODUCTION

Titanium dioxide is an important material with a wide range of applications in catalysis, photocatalysis,¹⁻³ and sensor technology.⁴ The discovery of the photocatalytic splitting of water on rutile TiO₂ surfaces⁵ has stimulated much effort to understand water adsorption on its surfaces. There has been a considerable amount of experi-

mental work on the adsorption of H₂O on TiO₂(110),⁶⁻⁹ although not all of it has given clear conclusions. The experimental indications are that water can be adsorbed both molecularly and dissociatively on the (110) surface. A unifying aspect of all these studies is that dissociation does occur only at low coverages. In contrast, theoreticians are unanimous in predicting dissociation at all coverages.¹⁰⁻¹⁷ Most of theoretical studies have been devoted

to determine whether the adsorption of water on the TiO_2 (110) surface is molecular or dissociative. Nothing is known about the electronic factors responsible for the water activation by the surface, despite a great deal of investigation.

The purpose of the present work is to explore orbital interactions associated with the transition from molecular to dissociative adsorption of water on the rutile TiO_2 (110) surface. The properties examined in this study include: (1) the molecular orbital energy level spectrum of the adsorption complex, (2) the analysis of charge transfer associated with the adsorbate-substrate bond, and (3) the identification of those states which are most likely to lead to the O-H bond weakening, followed by dissociation of H_2O . For these purposes we will make use of extended Hückel molecular orbital (EHMO) calculations and the two-dimensional character of the system via tight-binding approximation, implemented with the CAESAR and YACHMOP suites of programs.¹⁸

The conceptual tools we use are density of states (DOS), crystal orbital overlap populations (COOP), electron densities, and overlap populations (OP).¹⁸ The fragment molecular orbital analysis and simple perturbation theory are used to trace the adsorbate-substrate interaction which is critically affected by the energy levels of the interacting fragments. It allows us to understand the change of electronic structures between the bare surface, the adsorbate, and the composite chemisorbed system. Extended Hückel parameters used in the calculations are listed in Table 1.

Table 1. Atomic parameters used in the calculations^a

| Atom | Orbital | H_a (eV) | ζ_1^b | ζ_2^b |
|------|---------|------------|---------------|---------------|
| Ti | 4s | -8.97 | 1.500 | |
| | 4p | -5.44 | 1.500 | |
| | 3d | -10.81 | 4.550(0.4391) | 1.600(0.7397) |
| O | 2s | -32.30 | 2.275 | |
| | 2p | -14.80 | 2.275 | |
| H | 1s | -13.60 | 1.300 | |

^aFrom ref 22.

^bExponents and coefficients (in parentheses) in a double- ζ expansion of the metal d orbital.

RUTILE TiO_2 (110) SURFACE AND H_2O MOLECULE

The rutile form of TiO_2 is a tetragonal system that can be described by two lattice parameters ($a=4.594\text{\AA}$, $c=2.958\text{\AA}$).¹⁹ Fig. 1 shows a $(\text{Ti}_{15}\text{O}_{36})^{12}$ cluster of the ideal (110) surface to be considered for the MO calculations. The x, y, and z axes correspond respectively to the $[\bar{1}10]$, $[001]$, and $[110]$ crystallographic directions. The surface is terminated with an outermost plane of oxygen (O_b) atoms which appear as rows in the $[001]$ direction and occupy bridging positions between the second layer sixfold-coordinated titanium ($\text{Ti}(6)$) atoms. The equatorial planes of the octahedra of oxygen atoms around the $\text{Ti}(6)$ atoms are perpendicular to the surface. Rows of threefold-coordinated oxygen (O_p) atoms lie in the plane of the Ti atoms connecting the chains of $\text{Ti}(6)$ and fivefold-coordinated titanium ($\text{Ti}(5)$) atoms. As a model for the band structure calculations we use a slab containing two O-Ti₂O₂-O plane units. The unit cell Ti_4O_8 is repeated along the $[\bar{1}10]$ and $[001]$ directions. The dimensions of this surface unit cell are $\sqrt{2} a c$ (along $[\bar{1}10]$ and $[001]$, respectively). No geometry relaxation of the surface was considered throughout our EH calculations.

For a free H_2O molecule the bond angle and the OH bond lengths are taken as 104.5° and 0.957\AA , respectively.²⁰ For adsorbed H_2O we set the bond angle and the OH bond lengths equal to those reported for free H_2O .

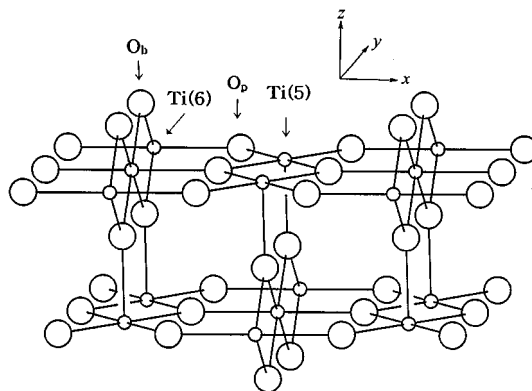
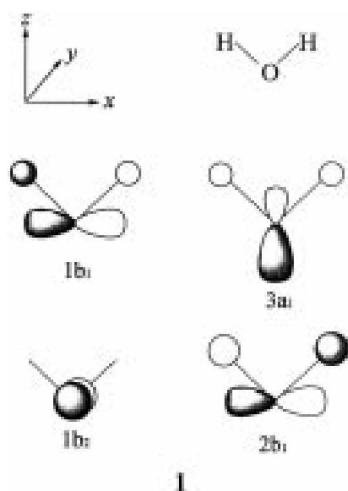


Fig. 1. The $(\text{Ti}_{15}\text{O}_{36})^{12}$ cluster used to study the H_2O adsorption on TiO_2 (110). O_b represents the bridging oxygens, O_p the in-plane oxygens, $\text{Ti}(5)$ the fivefold-coordinated titaniums, and $\text{Ti}(6)$ the sixfold-coordinated titaniums.



except when one OH bond is stretched. The four molecular orbitals of H₂O, those which are believed to be important in bonding with the surface, are presented in 1. These MO's are labeled in a way that is consistent with the coordinate system used in this work in which the z-axis is the C₂ axis of the water molecule, and the xz plane is the molecular plane.

RESULTS AND DISCUSSION

Electronic properties of the bare TiO₂(110) surface

As shown in Fig. 1, there are two different Ti atoms on the ideal rutile (110) surface. One is surrounded by a slightly distorted octahedron of oxygen atoms and the other becomes fivefold-coordinated by the removal of an oxygen atom from an axial position of the octahedron. Our calculations indicate that the electronic structure of this surface is quite comparable to the one²¹ of bulk TiO₂. Reduction of the coordination of Ti(5) atoms is not in itself sufficient to alter surface electronic structure.

The total DOS and the projected density of states (PDOS) on bridging oxygen (O_b) calculated for the slab system are shown in Fig. 2. In addition to the expected O 2s, O 2p, and Ti d bands (the low-lying O 2s band is not shown), we note particularly the appearance of a sharp peak at the top of the O 2p band which is associated with the contribution of O_b states to the total DOS. These O_b states are higher than the in-plane O_p states and are closer to the Fermi level (E_f). The origin of this comes from a different coordination of the oxygen atoms. The coordination

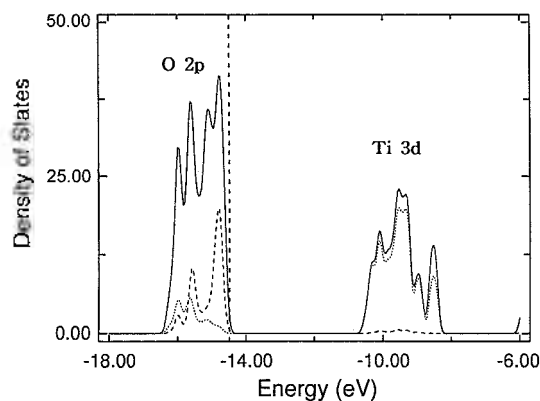


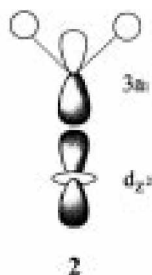
Fig. 2. Density of states of TiO₂(110). The dotted and dashed lines represent the PDOS on the Ti and O_b atoms, respectively. The vertical dashed line refers to the Fermi level.

of O_b and O_p atoms at the (110) surface is two and three, respectively. The levels of O_p are shifted to lower energies due to more oxygen-titanium bonding states; this is related to its reduced basic properties. The presence of the O_b 2p states just below E_f also contributes to explaining the greater reactivity of O_b, which is at the same time more basic. This means that acidic species such as a proton will interact with O_b rather than O_p. Thus the protonation of O_b leading to dissociative adsorption of water seems to be favorable. Both Ti(5) and Ti(6) atoms carry slightly different charges, -2.05 and +1.81, respectively. The charges of the oxygen atoms are between -0.90 and -1.20.

Chemisorption of H₂O

The coordinatively unsaturated surface Ti(5) ions provide strong Lewis acid (electron acceptor) sites for H₂O adsorption. We have considered only the case in which the water molecule bonds by its oxygen to the Ti(5) cation with the two hydrogens pointing upwards and symmetrically located, because first-principles calculations^{10,14} show that this is the preferred orientation mode. The atoms of the water molecule are in the (001) plane, viz., the xz plane of Fig. 1. A Ti-OH₂ distance of 2.07 Å was taken from literature values¹³ and held constant in our adsorption models.

We first consider the adsorption properties of one H₂O molecule adsorbed on a Ti(5) center of the (Ti₁₅O₃₆)¹² model cluster. The adsorption energy is calculated to be 1.63 eV, indicating a rather strong interaction. The bonding of H₂O to Ti⁴⁺ sites is largely dominated by the -donor



interaction of the H₂O 3a₁ orbital with the empty 3d_{z²} and 4p_z titanium ion orbitals (see **2** for a schematic illustration). The water molecule donates 0.32 electron to the surface; it can be expected that the positive charge on this surface Ti³⁺ site will decrease accordingly. As shown in *Table 2*, charge on the Ti⁴⁺ site was decreased by 0.25.

The DOS curves for H₂O at Ti(5) are displayed in *Fig. 3a*. The H₂O 3a₁ orbital interacts strongly to be stabilized by

Table 2. Electron densities and overlap populations for the bare TiO₂(110) surface and the TiO₂(110)H₂O surface

| | TiO ₂ (110)+H ₂ O ^a | TiO ₂ (110)H ₂ O |
|-----------------------------|--|--|
| Electron density | | |
| Ti(5) ^b | | |
| 4s | 0.257 | 0.291 |
| 4p _x | 0.162 | 0.162 |
| 4p _y | 0.169 | 0.172 |
| 4p _z | 0.098 | 0.181 |
| 3d _{z²} | 0.275 | 0.367 |
| 3d _{xz} | 0.191 | 0.197 |
| 3d _{yz} | 0.209 | 0.238 |
| O (H ₂ O) | | |
| 2p _x | 1.330 | 1.322 |
| 2p _y | 2.000 | 1.950 |
| 2p _z | 1.852 | 1.558 |
| H ₂ O | | |
| 1b ₁ | 2.000 | 1.984 |
| 3a ₁ | 2.000 | 1.771 |
| 1b ₂ | 2.000 | 1.950 |
| 2b ₁ | 0.000 | 0.001 |
| 4a ₁ | 0.000 | 0.006 |
| Net charge | | |
| Ti(5) | 2.05 | 1.80 |
| H ₂ O | 0.00 | 0.32 |
| Overlap population | | |
| Ti(5)-OH ₂ | | 0.37 |
| O-H (H ₂ O) | 0.63 | 0.63 |

^aSeparated bare TiO₂(110) surface and a H₂O molecule.

^bTi(5)-Ti cation that is directly bonded to H₂O.

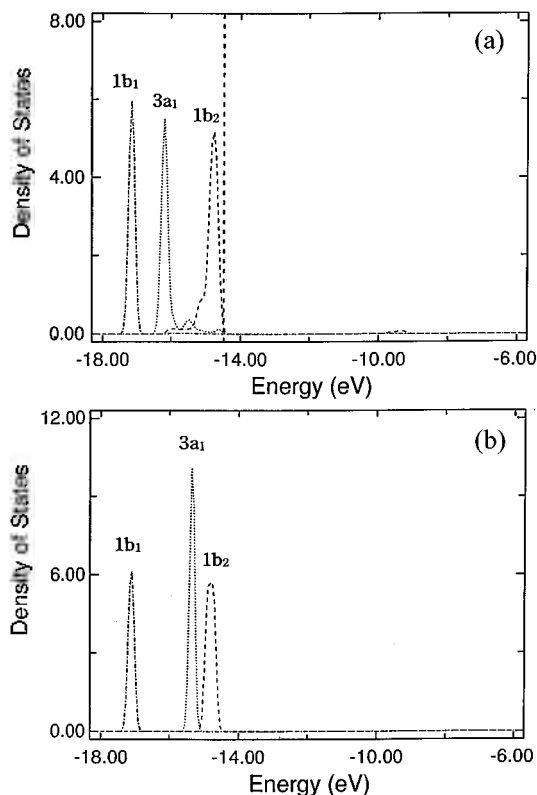


Fig. 3. (a) DOS of H₂O at Ti(5). (b) DOS of the isolated H₂O monolayer. The vertical dashed line refers to the Fermi level.

about 0.8 eV, while the 1b₁ and 1b₂ orbitals are only slightly stabilized. This relative shift is caused by the fact that the 3a₁ orbital overlaps much better with the adsorption site than the others. The overall bonding stabilization comes from the 3a₁ orbital of H₂O which strongly interacts with the 3d_{z²} and 4p_z orbitals of the titanium cation. As a result of the two-electron bonding interaction, the electron density shifts from the adsorbed water molecule to the surface, which results in a depopulation of 3a₁ by 0.23 electron. This can be confirmed from the electron densities of the Ti(5) and O (from H₂O) atomic orbitals calculated for the bare TiO₂(110) and the TiO₂(110)H₂O surfaces listed in *Table 2*. The most significant change in the electron density of the oxygen atom from H₂O upon H₂O adsorption clearly comes from its 2p_z orbital which points toward the Ti(5) site above which the water molecule sits: a loss of 0.29 electron is computed. Another 0.06 electron loss is from the oxy-

gen $2p_x$ and $2p_y$ π orbitals. Much of this electron loss results in a gain of 0.17 electron to the $3d_{z^2}$ and $4p_z$ orbitals of Ti(5). One should be aware, however, that the HII calculations tend to exaggerate electron flows. An overlap population of 0.37 is obtained between the Ti(5) and the oxygen atom from H₂O, indicating a rather strong surface-adsorbate bonding.

Dissociation of H₂O on TiO₂(110)

Let us now examine O-H bond breaking in water adsorbed to the (110) surface. Assuming that water is adsorbed dissociatively, the proton goes on a bridging oxygen (O_b) sticking out of the surface, whereas the remaining hydroxyl group binds perpendicularly to the fivefold-coordinated Ti(5) atom. It is also assumed that the protons are adsorbed on top of O_b atoms at a distance 0.957 Å, characteristic of the OII interatomic distance in OH⁻ and H₂O. The Ti(5)-OH bond length is set to 1.78 Å.¹³ The adsorption energy, 2.56 eV, is much larger than that for the molecular adsorption. Dissociative adsorption of the H₂O molecule is therefore energetically favored relative to molecular adsorption.

After the molecular adsorption to the Ti(5) cation, the study of dissociation process starts by tilting the water molecule towards a nearby surface O_b atom. After one OH bond of the water molecule is broken, the proton binds to the O_b atom and the OH group tilts back until O atom is again perpendicular above the Ti(5) atom. Bredow and Jug¹³ calculated a somewhat high barrier (1.0 eV) for this process and the barrier drastically decreased as hydrogen bonding and local surface relaxation were included. A tilting of the water molecule as a precursor to dissociation might be accompanied by a weak interaction of the OH bond with the O_b atom. In order to see the change in the electronic properties of water as the molecule is tilted, the overlap populations are calculated as a function of tilt angle of the H₂O-Ti(5) bond with respect to the surface normal. Throughout tilting, the Ti(5)-OII₂ bond distance is kept at 2.07 Å. The overlap populations at different tilt angles are shown in Fig. 4. The decrease in the O-II overlap population during tilting is accompanied by an increase in the overlap population between an H atom of water and its nearest-neighbor O_b atom. As a result of tilting the water molecule at 35° to have the OH bond nearly parallel to the surface, the hydrogen atom is located very close to the O_b atom, allowing rather strong

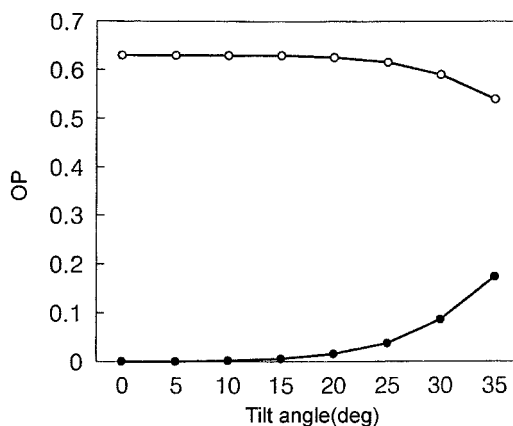
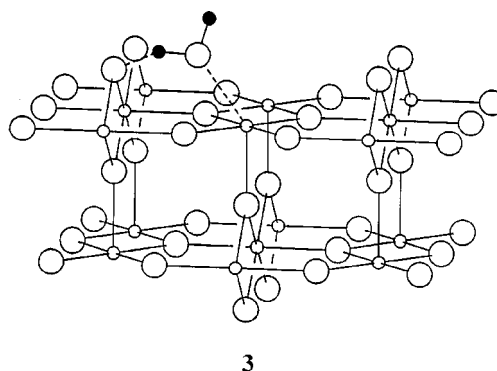


Fig. 4. The overlap populations of O-II (○) and O_b -H (●) as a function of tilt angle of the H₂O-Ti(5) bond from the surface normal for H₂O chemisorption at the Ti(5) site on TiO₂(110).



3

H-bond formation ($OH \cdots O_b$, 1.20 Å, see 3). This new $OH \cdots O_b$ bonding ($OP=0.17$) is accomplished at the expense of the O-H bonding within the water molecule. Such a weakening of the OH bond can be closely related to a relatively low barrier to water dissociation.

Important electron densities and overlap populations are compared in Table 3 for the bare TiO₂(110) and the TiO₂(110) H₂O(t) surfaces, where H₂O(t) is a label for the water molecule tilted 35° towards a O_b atom from the surface normal. As expected, the H₂O $3a_1$ orbital interacts strongly with the Ti(5) $3d_{z^2}$, $3d_{xz}$, and $4p_z$ states. A loss of 0.22 electron from the $3a_1$ orbital is computed due to the interactions.

The $2b_1$ orbital of H₂O is the lowest unoccupied molecular orbital (LUMO) and antibonding between the $2p_x$ orbital of oxygen and the $1s$ orbitals of two hydrogen atoms.

Table 3. Electron densities and overlap populations for the bare $\text{TiO}_2(110)$ surface and the $\text{TiO}_2(110)/\text{H}_2\text{O}(t)$ surface

| | $\text{TiO}_2(110)/\text{H}_2\text{O}$ | $\text{TiO}_2(110)/\text{H}_2\text{O}(t)^a$ |
|-----------------------------|--|---|
| Electron density | | |
| Ti(5) | | |
| 4s | 0.257 | 0.278 |
| 4p _x | 0.162 | 0.162 |
| 4p _y | 0.169 | 0.169 |
| 4p _z | 0.098 | 0.149 |
| 3d _{z²} | 0.275 | 0.329 |
| 3d _{xz} | 0.191 | 0.238 |
| 3d _{yz} | 0.209 | 0.217 |
| O _b | | |
| 2p _x | 1.852 | 1.787 |
| 2p _z | 1.843 | 1.805 |
| O (H ₂ O) | | |
| 2p _x | 1.330 | 1.595 |
| 2p _y | 2.000 | 1.973 |
| 2p _z | 1.852 | 1.496 |
| H ₂ O(t) | | |
| 1b ₁ | 2.000 | 1.971 |
| 3a ₁ | 2.000 | 1.777 |
| 1b ₂ | 2.000 | 1.973 |
| 2b ₁ | 0.000 | 0.126 |
| 4a ₁ | 0.000 | 0.049 |
| Net charge | | |
| Ti(5) | 2.05 | 1.86 |
| O _b | -1.20 | -1.07 |
| H ₂ O | 0.00 | 0.13 |
| Overlap population | | |
| HOH...O _b | | 0.17 |
| O-H (H ₂ O) | 0.63 | 0.53 |

^aH₂O(t)-H₂O tilted to O_b at 35° with respect to the surface normal.

This orbital allows the interaction with the 2p_x-2p_z orbital of the surface O_b atom resulting in a gain of 0.13 electron to the 2b₁ orbital when the water molecule is tilted 35° off the normal to the surface. The σ-backdonation interaction of the O_b orbital into the empty H₂O 2b₁ is indicated schematically in 4. First we mix 1b₁ with O_b p_x-p_z orbitals. The 1b₁ orbital is lower in energy than the O_b p orbitals. The bonding component of the interaction will be composed mainly of 1b₁ with some O_b p character mixed into it. We could trace its involvement via PDOS and COOP curves in Fig. 5. It is found at -17.3 eV. The antibonding counterpart will consist of O_b p orbitals with 1b₁ mixed in out-of-phase. We now mix 2b₁ into the

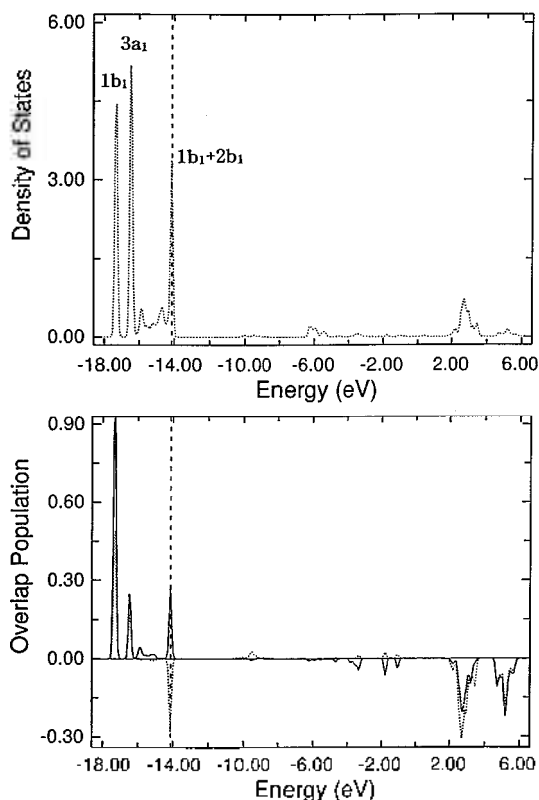
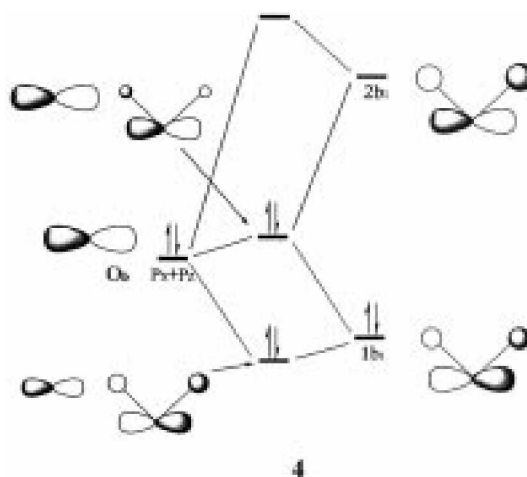
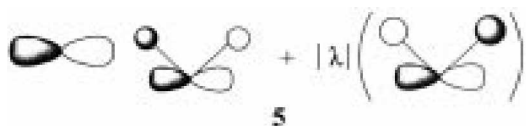


Fig. 5. PDOS, and O-H (solid line) and O_b-H (dotted line) COOP curves for the H₂O adsorbed in a tilted conformation (θ=35°). The dashed line refers to the Fermi level.

antibonding combination. The phase with which 2b₁ mixes in will be controlled by the p(O_b)-2b₁ interaction, because the O_b p_x+p_z orbitals are the major contributors to the



orbital in question. The O_b p orbitals are located lower in energy than $2b_1$; hence $2b_1$ will mix in an O_b -H bonding way: the phase is as shown in **5** (λ is an MO mixing coefficient). The net result is drawn at the top left of **4**. Note that the primarily O_b p-type orbital is rendered nearly nonbonding by the participation of the higher-lying $2b_1$ orbital in it, with the result that the $1s$ contribution centered on the proton is nearly canceled. In *Fig. 5* the DOS for this orbital is projected out in the Fermi level region. But in this region, the extent of the $2b_1$ orbital mixing is not enough to cancel out any s orbital contribution from the water hydrogens, because the mixing is small due to its poor energy match. It does pick up density in the range of interest at the Fermi level. About 0.13 electron is donated from the surface (primarily O_b) to $2b_1$. As a consequence of population of the $2b_1$, the O-H bond of water becomes weakened.

Returning to *Table 3*, we see that the electron density of $2p_x$ of the oxygen atom from H_2O increases from 1.330 in a free water molecule to 1.595 in the surface complex, whereas that of $2p_x$ ($2p_z$) of the O_b atom decreases from 1.852 (1.843) in the bare surface to 1.787 (1.805) in the surface complex. This is attributed to the transfer of electrons from the O_b into the empty H_2O $2b_1$. These changes in electron distribution are favorable for the dissociation of water molecules into fragments OH and H followed by the formation of monodentate and bidentate hydroxyl groups adsorbed on the $TiO_2(110)$ surface. *Table 3* shows that the net charge transfer from H_2O molecule to the surface is small, only 0.13. Despite a small charge transfer, a significant redistribution of the electron density between the water molecule and the surface occurs. The transfer of the electron density from the $3a_1$ to the $Ti(5)$ $3d_{z^2}$, $3d_{xz}$ and $4p_z$ orbitals is in part compensated by the reverse transfer of the electron density from the O_b $2p_x$ - $2p_z$ orbitals to the LUMO $2b_1$ of the water molecule. The latter process is accompanied by the weakening of the O-H bonds in an adsorbed water molecule due to an increase in the population of the antibonding molecular orbital. This is the key factor in the

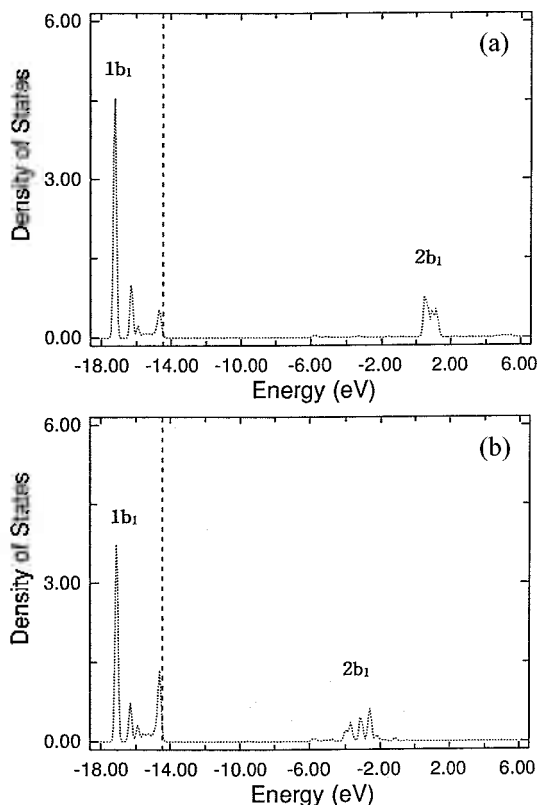


Fig. 6. Evolution of $2b_1$ orbital at two selected O-H distances of one O-H bond. (a) 0.957 and (b) 1.157 Å for the H_2O molecule adsorbed in a tilted conformation ($\theta=25^\circ$). The dashed line refers to the Fermi level.

dissociative adsorption of water on rutile $TiO_2(110)$. As the $2b_1$ becomes occupied by electrons, the O-H bond is stretched towards O_b . Simultaneously, the $2b_1$ level comes down in energy, resulting in better energy match and interactions with O_b bands.

Fig. 6 shows the evolution of the $2b_1$ orbitals at two selected O-H distances of one O-H bond, 0.957 and 1.157 Å, for the H_2O adsorption geometry tilted 25° off the normal to the surface. The $2b_1$ peaks at 1.157 Å are broader than those at 0.957 Å, an indication of more interaction with the surface. The electron density of the $2b_1$ orbitals is compared here in the O-H bond stretching from 0.957 to 1.157 Å: 0.03 and 0.12, respectively. There are more electrons occupying the $2b_1$ at the increased O-H separation. This is caused by the fact that the bigger DOS peak at the Fermi level results from more mixing of $2b_1$ into the band (see *Fig. 6*).

CONCLUSION

In this study, we presented the MO explanation for binding of water to the $\text{TiO}_2(110)$ and hydrogen transfer to surface oxygen atom. The $\text{TiO}_2(110)$ surface can be made active for water dissociation by tilting an adsorbed water molecule towards a two-coordinated bridging O^{2-} site. The close proximity of an H atom from the water molecule and the O_b site should facilitate the OH bond cleavage. This might be a result of occupation of the LUMO $2b_1$ through the mixing of $2b_1$ in an O_b -H bonding way into the antibonding combination between the $1b_1$ and O_b p orbitals as discussed above. The filling of the $2b_1$ orbital is responsible for most, but not all, of the water bond activation. The rest is mainly due to depopulation of $3a_1$ orbital (slightly bonding between oxygen and hydrogen) upon adsorption.

Acknowledgment. This work was supported by Kyung-sung University Research Grants in 2001.

REFERENCES

1. Fox, M. A.; Dulay, M. T. *Chem. Rev.* **1993**, *93*, 341.
2. Henrich, V. E.; Cox, P. A. *The Surface Science of Metal Oxides*; Cambridge University Press: England, 1993.
3. Linsebigler, A. L.; Lu, G.; Yates, J. T., Jr. *Chem. Rev.* **1995**, *95*, 735.
4. Huusko, J.; Lantto, V.; Torvela, H. *Sensors Actuators* **1993**, *B15-16*, 245.
5. Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37.
6. Henderson, M. A. *Surf. Sci.* **1996**, *355*, 151.
7. Henderson, M. A. *Langmuir* **1996**, *12*, 5093.
8. Hugenschmidt, M. B.; Gamble, L.; Campbell, C. T. *Surf. Sci.* **1994**, *302*, 329.
9. Kurtz, R. L.; Stockbauer, R.; Madey, T. E.; Roman, E.; de Segovia, J. L. *Surf. Sci.* **1989**, *218*, 178.
10. Goniakowski, J.; Gillan, M. J. *Surf. Sci.* **1996**, *350*, 145.
11. Goniakowski, J.; Bouetto-Russo, S.; Noguera, C. *Surf. Sci.* **1993**, *284*, 315.
12. Goniakowski, J.; Noguera, C. *Surf. Sci.* **1995**, *330*, 337.
13. Bredow, T.; Jug, K. *Surf. Sci.* **1995**, *327*, 398.
14. Fahmi, A.; Minot, C. *Surf. Sci.* **1994**, *304*, 343.
15. Lindan, P. J. D.; Harrison, N. M.; Holender, J. M.; Gillan, M. J. *Chem. Phys. Lett.* **1996**, *261*, 246.
16. Lindan, P. J. D.; Muscat, J.; Bates, S. P.; Harrison, N. M.; Gillan, M. J. *Faraday Discuss.* **1997**, *106*, 135.
17. Lindan, P. J. D.; Harrison, N. M.; Gillan, M. J. *Phys. Rev. Lett.* **1998**, *80*, 762.
18. (a) For a description of the methodology and orbital interactions, see Hoffmann, R. In *Solids and Surfaces: A Chemists View in Bonding in Extended Structures*; VCH: New York, 1988. (b) Ren, J.; Liang, W.; Whangbo, M.-H. *C.AESAR: Crystal and Electronic Structure Analyzer*; <http://www.PrimeC.com>, 1998. (c) Landrum, G. A. *YAcHMOP: Yet Another extended H ckel Molecular Orbital Package*; <http://yaehmop.sourceforge.net>, 1997.
19. Wyckoff, R. W. G. *Crystal Structures*, 2nd. ed.; Wiley Interscience: New York, 1964; Vol. 1.
20. Eisenberg, D.; Kauzmann, W. *The structure and Properties of Water*; Oxford University Press: New York, 1969.
21. For a theoretical study of nifite, see: (a) Grunes, L. A.; Leapman, R. D.; Wilker, C. N.; Hoffmann, R. *Phys. Rev.* **1982**, *B25*, 7157. (b) Burdett, J. K. *Inorg. Chem.* **1985**, *24*, 2244.
22. Hallet, J.-F.; Hoffmann, R. *J. Am. Chem. Soc.* **1989**, *111*, 3548.