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# Theoretical analysis of the electronic spectra of water adsorbed on the rutile $TiO_2$ (1 1 0) and MgO (1 0 0) surfaces

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**Abstract**

We present analysis of the molecular orbitals of an isolated water molecule physisorbed on the rutile $TiO_2$ (1 1 0) surface and MgO (1 0 0) surface. On the $TiO_2$ surface the $3a_1$ and $1b_1$ orbitals split due to the interactions with the surface atoms. This resembles the features of the experimental electronic spectra that were interpreted as an evidence for water dissociation. On MgO surface the water molecular orbitals exhibit some splitting for the $1b_1$ orbital, but not sufficient to produce a $\pi$ orbital-like peak in the electronic spectra. Perturbations of the $1b_2$ and $3a_1$ orbitals also contribute to broadening observed in the experimental electronic spectra.


## 1. Introduction

Experimental electronic spectra are widely used in studies of adsorption [1–4]. Methods such as UV photoelectron spectroscopy (UPS) and metastable impact electron spectroscopy (MIES) have been used to prove or reject the existence of molecular or atomic groups on a surface. For instance, recent MIES study of water adsorption on rutile $TiO_2$ (1 1 0) surface at a wide coverage range by Kempter and co-workers [5] suggested a possibility of water dissociation upon adsorption. It was based on the observation of an emission band that matches reasonably well the $\pi$ orbital of the hydroxyl ion. The same interpretation was also used in a more recent MIES experiment of water on MgO (1 0 0) surface by Goodman and coworkers [3]. Such a feature is accepted as an evidence for water dissociation on the surface. However, other features of the spectra are not well understood, for instance, the broadening of the $3a_1$ water orbital upon adsorption on $TiO_2$ (1 1 0) surface [5]. While these results provided extremely useful information about the state of adsorbates, many factors can affect the overall electronic spectra, thus making its interpretation sometimes difficult. Two main factors that contribute to the changes in the adsorbate spectrum upon adsorption are: (1) the shifts in the orbital energies due to electrostatic adsorbate–surface interactions and (2)

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the possibility of creation of new states due to the change of the symmetry and the coupling with the surface states. Furthermore, the broadening in the spectra is often thought of as result of the thermal fluctuation of the adsorbate position with respect to the surface. At high adsorbate coverage the lateral adsorbate–adsorbate interactions can contribute to changes in the electronic spectrum [6]. However, this phenomenon can also occur in the low coverage regime in case of adsorbate forming 2D or 3D clusters on the surface [7]. In order to unravel the origin of the changes in the observed spectra, we first need to deconvolute the effects of the substrate and of the co-adsorption on the electronic spectra. Therefore, in this study we focus mainly on the electronic spectrum of an isolated water molecule upon molecular adsorption on the surface. The effects of co-adsorption will be reported in a future study. In particular, we perform a theoretical analysis of the water molecular orbitals upon adsorption on the $TiO_2$ (1 1 0) and MgO (1 0 0) surfaces. Earlier experimental and theoretical studies [2,8,9] found that isolated water adsorbs in the molecular form predominantly on the $TiO_2$ (1 1 0) surface and exclusively on the MgO (1 0 0) surface, and thus we consider only the molecular adsorption in this study.

Two recent MIES experiments are used as the primary experimental references. One describes the measurements of the electronic spectra of water on rutile $TiO_2$ (1 1 0) surface done by Kempter and co-workers [5]. Electronic states attributed to $OH^-$ orbitals were observed at sub-monolayer coverages (mostly 0 to 0.5 Langmuir, where 2 Langmuir corresponded to 1 monolayer). The second experimental study was performed by Goodman and co-workers [3] on $D_2O$ adsorbed on MgO (1 0 0) in UHV conditions. This is the first experimental evidence of at least partial dissociation on a defect free MgO (1 0 0) surface in partial coverage regime. Two-dimensional cluster formation was invoked to explain such observation. Again, we will address the effects of co-adsorption on dissociative chemisorption of water on a clean MgO (1 0 0) surface in a future study.

In this study, we employed the surface charge representation of external embedded potential (SCREEP) method [10] within the embedded cluster methodology to study the behavior of the water molecular orbitals upon adsorption on the $TiO_2$ (1 1 0) and MgO (1 0 0) surfaces. Similar analysis was done earlier on studying the nature of the excited state of water adsorbed on $TiO_2$ (1 1 0) surface [11]. In this study, clusters of $Ti_7O_{14}$ and $Mg_{17}O_{17}$ and the adsorbed water (see Fig. 1) were treated quantum mechanically at the MP2 level of theory with 6-31G(d,p) basis set [12]. In addition, the same systems were also treated at the Hartree–Fock level of theory using a smaller basis set. In particular, for water adsorbed on $TiO_2$ surface LANL1MB [13] basis and pseudopotentials were used for Ti atoms, and CEP-31G [14] for oxygen and hydrogen atoms while for water adsorbed on

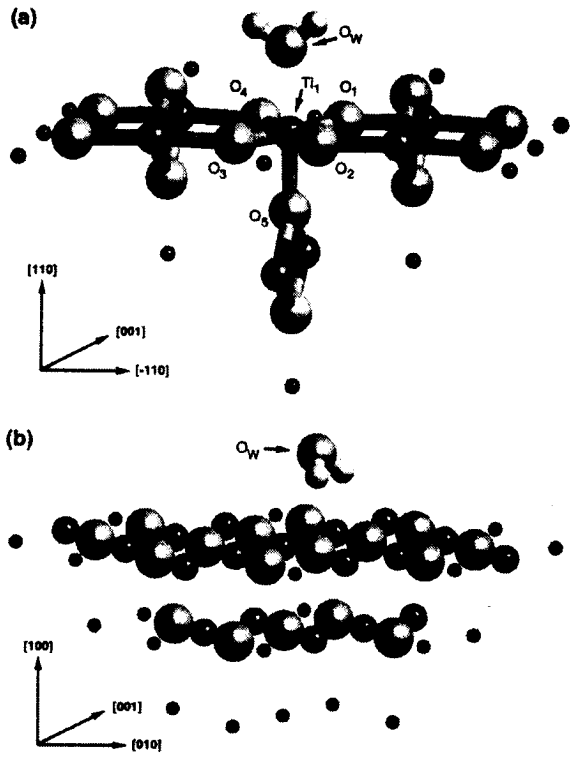


Fig. 1. (a) $TiO_2$ cluster representing the (1 1 0) rutile surface used in the present work. Large light spheres, O; small light spheres, H; large dark spheres, Ti; and small dark spheres, embedding whole ion pseudopotentials. (b) MgO cluster representing the (1 0 0) surface. Large light spheres, O; small light spheres, H; large dark spheres, Mg; and small dark spheres, embedding whole ion pseudopotentials. Labels referred to in the Letter are indicated. Direction of the axes is shown.

MgO surface 6-31G(d,p) basis set was used for the four Mg and O atoms closest to the water molecule and the water molecule, while the 3-21G(d) basis set was used for the remaining atoms. More details on the embedded cluster calculations can be found in our previous study [9]. We found that for equilibrium structures of the adsorbed water on $TiO_2$ and MgO surfaces, the differences in the water orbital energies calculated using the two levels of theory are less than 0.1 eV. Hence, due to the large number of calculations involved, we used the HF level with the smaller basis sets for the study of thermal fluctuation effects. All calculations were done using the GAUSSIAN 98 program [15]. To study the effects of water–surface interactions we plot the partial density of states (DOS) of the water molecule as a function of the O–surface distance and the tilt angle of the water plane with respect to the surface plane. The atomic composition of the molecular orbitals allows us to classify the electronic states of water according to their symmetry.

## 2. Results and discussion

### 2.1. $H_2O$ on $TiO_2$ (1 1 0) surface

#### 2.1.1. Spectra of the equilibrium structure

For the present analysis we used an optimized structure for water molecularly adsorbed on the rutile (1 1 0) surface from our earlier study [9]. The cluster orbital analysis shows that the water forms four occupied orbitals on the $TiO_2$ surface, as opposed to three in vacuum (Fig. 2). The partial density of states of the water oxygen reveals that the fourth state is the result of the interaction of the water $1b_1$ orbital with the surface. Such interaction results in the split of the original $1b_1$ orbital into two orbitals designated as $1b_1$ and $2b_1$, with the deeper $1b_1$ having a little higher share of $O_W$ $2p_y$ atomic orbital than the more shallow $2b_1$. The gap between $1b_1$ and $2b_1$ is 1.40 eV at the MP2 level of theory. The $1b_1$ orbital is mostly due to interaction between the adsorbed water with the $2p_y$ atomic orbital of the $O_5$ atom lying below the adsorbing $Ti_1$ atom; whereas $2b_1$ is mostly due to interaction with the

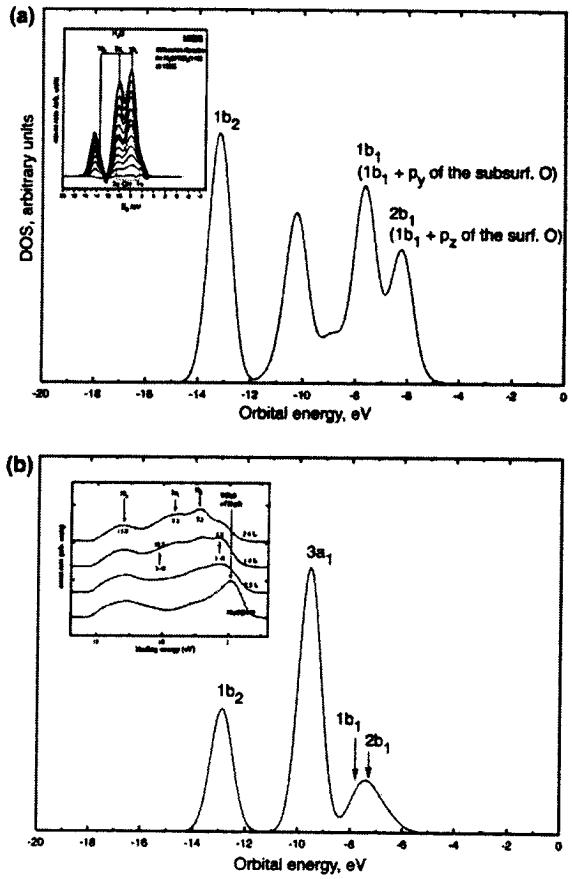


Fig. 2. Partial density of states of the water molecule in the equilibrium geometry. (a) Water adsorbed on the $TiO_2$ (1 1 0) surface. In the inset: difference of the experimental MIES spectra of the $TiO_2$ (1 1 0) surface with adsorbed water and the bare $TiO_2$ (1 1 0) surface [5]. (b) Water adsorbed on the MgO (1 0 0) surface. In the insert: an experimental MIES spectra of the MgO (1 0 0) surface with adsorbed water [3].

$2p_z$ orbitals of the nearest surface oxygen atoms: $O_1$, $O_2$, $O_3$, and $O_4$. The isodensity plots of the water orbitals of $1b_1$ and $2b_1$ are shown in Figs. 3a and b, respectively.

The positions of the electronic states of the water molecule are given in Table 1 along with the experimental values [5]. It is interesting to note that the location of the $2b_1$ peak is located in the region where the $1\pi$ orbital of hydroxyl is suggested in the MIES spectra on Fig. 2. In other words, the molecularly adsorbed water produces a peak close to that of the hydroxyl making experimental verification of the dissociative process

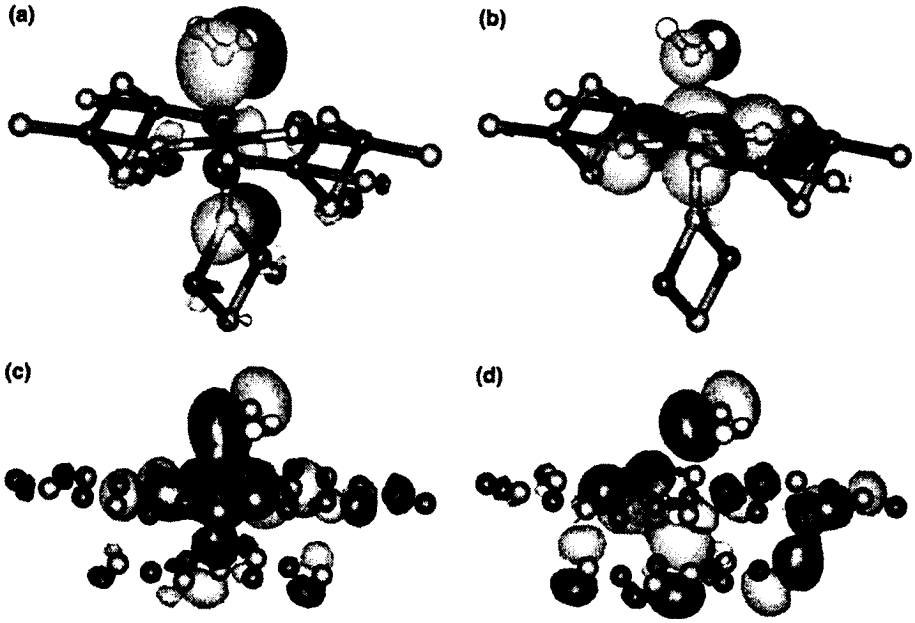


Fig. 3. Isodensity plots of the orbitals of the $b_1$ symmetry of the water molecule adsorbed on the $TiO_2$ and MgO surfaces: (a) $TiO_2$, $1b_1$ orbital; (b) $TiO_2$, $2b_1$ orbital; (c) MgO, $1b_1$ orbital; and (d) MgO, $2b_1$ orbital.

Table 1
Positions of the molecular orbitals of water (MOs) on $TiO_2$ rutile (1 1 0) surface, eV (MP2/6-31G(d,p))

| $H_2O$ on rutile (1 1 0) surface | | | | $H_2O$ on MgO (1 0 0) surface | | | |
|---|---|---|---|---|---|---|---|
| MO | Theory | MO | Expt. [5] (eV) | MO | Theory | MO | Expt. [3] (eV) |
| $1b_2$ | −13.2 | $1b_2$ | −13.2 | $1b_2$ | −12.9 | $1b_2$ | −13.0 |
| $3a_1$ | −10.3 | $3a_1$ | −10.0 | $3a_1$ | −9.6 | $3a_1$ | −9.4 |
| $1b_1$ | −7.6 | $1b_1$ | −7.8 | $1b_1$ | −7.8 | $1b_1$ | −7.3 |
| $2b_1$ | −6.2 | $1\pi$ | −6.3 | $2b_1$ | −7.2 | $1\pi$ | −5.8 |

more difficult. This result has a very important implication that the existence of a peak about −6.3 eV is a necessary but not sufficient evidence for water dissociation on the surface. Furthermore, there is no clear indication of the $3\sigma$ orbital in these spectra. This would make the analysis of experimental spectra more difficult. The $3a_1$ orbital is also perturbed by the surface oxygen atoms, and exhibits a shoulder at about −9 eV. It is caused by the interaction with the $p_z$ orbital of $O_5$ atom of the crystal surface. This feature can contribute to the widening of the $3a_1$ peak in the experimental spectra, more so in the UPS spectra than the MIES, since MIES is less sensitive than UPS to the states below the crystal surface.

*2.1.2. Effects of the thermal local motion of the adsorbed water*

First, we examine the effects of stretching along the water $O_W$–$Ti_1$ bond. Increasing the distance between the water molecule and the surface results in the increase of the energy of all orbitals. Such perturbation induce large changes to the $3a_1$, $1b_1$, and $2b_1$ orbitals while leaving the $1b_2$ orbital as a relatively well defined band (see Fig. 4). When the distance between $H_2O$ and the surface is increased by 0.3 Å from its equilibrium value, the $3a_1$ orbital has a significant increase in the contribution of the $O_W$ $2p_y$ orbital. The $O_W$ $2p_y$ orbital belongs to the $1b_1$ symmetry, and the whole combination no longer conforms to the point group of the water

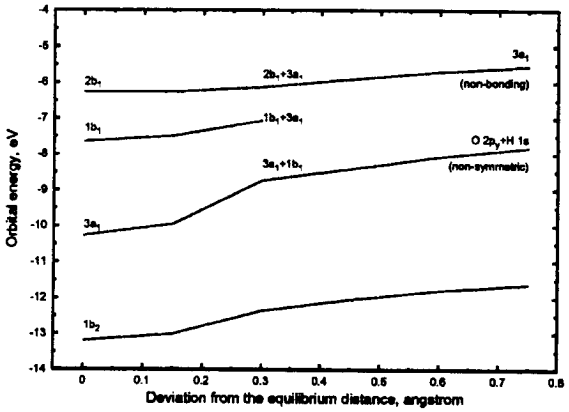


Fig. 4. Changes in the water orbital energies upon increasing the Ti–$O_W$ bond distance.

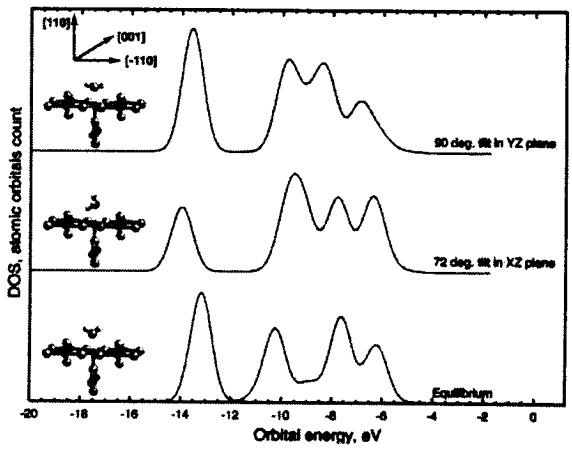


Fig. 5. Changes in the water spectrum at different orientations of the water molecule on the rutile $TiO_2$ (1 1 0) surface.

molecule. As the distance increases further, the orbital becomes a combination of the $O_W$ $2p_y$ and H 1s atomic orbitals (with no $O_W$ $2p_z$ contribution). This orbital also does not possess the symmetry of the water molecule, and it probably is only possible due to the interactions with the surface states. Similarly, in the $1b_1$ and $2b_1$ orbitals the share of $O_W$ $2p_y$ decreases, and $O_W$ $2p_z$ contribution appears at 0.3 Å stretch, and increases from then on. They also converge to form only one peak. At 0.75 Å deviation from the equilibrium the orbital consists of almost pure $O_W$ $2p_z$, with no $O_W$ $2p_y$ or H 1s contribution. Consequently, it should be classified as non-bonding $3a_1$.

Second, we investigated the effects of the changes in the relative orientation of the adsorbed water with respect to the surface plane. In particular, we examined two possible rotations. One is rotation of water about the [−1 1 0] direction (perpendicular to the bridging oxygen rows) passing through the water oxygen atom. This change can also be visualized as tilting of the water molecule plane from the equilibrium upright position to position parallel to the rutile surface. As the deviation from the equilibrium orientation of the water molecule increases, the biggest changes are observed for the bonding $1b_2$ and $3a_1$ orbitals (Fig. 5).

The energy of the $1b_2$ orbital monotonously decreases by 0.79 eV over the angle change from the equilibrium value to 72° deviation from the equilibrium. Its intensity also decreases. The energy of the $3a_1$ orbital monotonously increases by 0.5 eV over the same angle range. At the maximum deviation of 72° from the equilibrium position the $3a_1$ splits into two parts, with the new state appearing 0.45 eV above the original $3a_1$ state. The intensity of the new peak is about 50% of the original $3a_1$. Due to the proximity, these two peaks are not resolved in Fig. 5. The energy of both $1b_1$ and $2b_1$ orbitals does not change significantly during this kind of rotation: the overall change was −0.15 eV for $1b_1$, and −0.14 eV for $2b_1$.

The second type of rotation occurs about the [0 0 1] direction (parallel to the bridging oxygen rows on the $TiO_2$ surface) passing through the water oxygen atom. The water molecule was rotated over the angle of 90° with a step of 18°. The orbital energies of the $1b_2$, $1b_1$, and $2b_1$ orbitals monotonously decreased, and the energy of $3a_1$ orbital increased. The shifts in the orbital energies between the equilibrium orientation and the 90° deviation from equilibrium are −0.40 eV for $1b_2$, 0.42 eV for $3a_1$, −0.61 eV for $1b_1$, and −0.76 eV for $2b_1$. At the deviation angle of 72° or more the $3a_1$ orbital splits, with the new state appearing about 1 eV above the main $3a_1$ state (not resolved on Fig. 5). The intensity of the new peak is about 22% that of the main $3a_1$ at 72° deviation, and 40% at 90° deviation. We believe this new state contributes to the broadening of the $3a_1$ peak observed in

the experimental spectra [5]. The $2b_1$ gradually attenuates, as $1b_1$ grows stronger.

### 2.2. $H_2O$ on MgO (1 0 0) surface

We found that the effects of the MgO crystal surface on the molecular orbitals of adsorbed water are more simple compared to that in the rutile–water system. The calculated MP2 orbital energies are listed in the Table 1 along with the experimental values [3]. Only the water $1b_1$ orbital exhibits splitting into $1b_1$ and $2b_1$ due to the interaction with the surface states, but this doublet cannot be resolved in out DOS plot (Fig. 2). The isodensity plots of the two $b_1$ orbitals are shown in Figs. 3c–d. At the equilibrium geometry this splitting is 0.48 eV, compared to 1.4 eV between the experimental $1b_1$ and $1\pi$ peaks [3]. The largest splitting between $1b_1$ and $2b_1$ orbitals is 0.74 eV, corresponding to the water molecule rotated about the [1 0 0] direction by 180°. The energy of this configuration is 20.1 kJ/mol higher than the energy of the equilibrium geometry. Increasing the angle between the plane of the water molecule and the MgO surface from the equilibrium angle of 64–200° results in the two $b_1$ orbitals converging at −8.0 eV. The energy of both $3a_1$ and $1b_2$ orbitals monotonously decrease by about 0.7 eV over this angle range. During rotation about the [1 0 0] direction, the orbital energies gradually decrease by 0.4 eV for the $1b_2$ and $3a_1$ orbitals, 0.3 eV for the $1b_1$ orbital, and less than 0.1 eV for the $2b_1$ orbital. Increasing the distance between the surface and the water molecule from 2.5 to 4.1 Å results in monotonous decrease of the $b_2$ orbital by 0.5 eV, and of the $3a_1$ orbital by 0.3 eV. $1b_1$ and $1b_2$ orbitals first converge at around 7.5 eV for 3.3 Å separation between the surface and the water oxygen atom, and then the energy of the converged $1b_1$ orbital gradually decreases by 0.3 eV.

In summary, the changes in the water molecular orbital energies due to thermal fluctuations and interactions with the surface states cannot explain for the observed separation between the $1b_1$ peak and the new peak in the experimental MIES spectrum [3] assigned to the hydroxyl $\pi$ orbital. Our results support the experimental interpretation of water dissociation on MgO (1 0 0) surface in the recent MIES experiment.

## 3. Conclusions

We presented an analysis of the molecular orbitals of an isolated water molecule adsorbed on rutile $TiO_2$ (1 1 0) and MgO (1 0 0) surfaces. Particular attention is given to the effects of the thermal geometry fluctuations and interactions with the surface states on the observed electronic spectra. We found that for water absorbed on $TiO_2$ (1 1 0) surface, interactions with the surface states result in a splitting of the water $1b_1$ peak. The new peak is located very close to the peak that was identified as the $1\pi$ peak of the hydroxyl in the recent MIES experiment. This indicates that while the existence of the new peak is necessary, it is not a sufficient evidence for the dissociation of water on the surface. In addition, thermal geometric fluctuations can explain the broadening of the $3a_1$ peak. For water adsorbed on MgO (1 0 0) surface, the effects of the interactions with the surface states and of the thermal fluctuations are smaller and cannot explain the existence of the new peak in the MIES spectra. Thus, our results support the interpretation that the new peak is due to the hydroxyl group that resulted from the water dissociation. It should be noted that the role of 2D and 3D cluster formation on the surface in stabilizing the hydroxyl groups was not considered in this study. Such cluster formation can also affect the orbital energies as suggested in the experimental studies [3,5,7] [6]. This study solves the first part of the puzzle. Further study is certainly needed, with particular attention to the effects of co-adsorption.

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