



Ab initio study of water adsorption on $\text{TiO}_2(110)$: molecular adsorption versus dissociative chemisorption

Eugene V. Stefanovich, Thanh N. Truong *

Henry Eyring Center for Theoretical Chemistry, Department of Chemistry, University of Utah, Salt Lake City, UT 84112, USA

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Abstract

Ab initio embedded cluster calculations of water interaction with the $\text{TiO}_2(110)$ surface predict that molecular adsorption is more favorable than dissociative chemisorption. Unlike all previous calculations, this result is in agreement with recent temperature-programmed desorption and modulated beams experiments. Calculated surface relaxation, water adsorption energy and the densities of electronic states are also in good agreement with available experimental data. This agreement suggests that the embedded cluster model developed in this work is an accurate predictive tool that can be useful for theoretical studies of photocatalytic reactions on titanium dioxide surfaces. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Photochemistry on TiO_2 –water interfaces has become an active research area since discovery of photoelectrolysis of water on TiO_2 electrodes [1] and photocatalytic mineralization of water pollutants in the presence of TiO_2 colloids (for review see, e.g., Ref. [2]). These discoveries had important implications for solar energy conversion and environmental cleanup. Many efforts have been devoted to improvement of the performance of the titanium dioxide photocatalyst to make it suitable for widespread industrial applications.

Despite numerous experimental studies, the mechanism of TiO_2 photocatalysis is still unclear. Incident light generates electron–hole pairs in TiO_2 particles. Some of the electrons and holes migrate to the surface where they can be trapped, or interact with water molecules, surface hydroxyls and adsorbates. Most of suggested mechanisms postulate that the primary step in photocatalysis is the formation of OH radicals due to the interaction of valence band holes either with adsorbed water molecules or with surface hydroxyls. Which one of these routes is actually occurring depends on the mode of H_2O adsorption on the TiO_2 surface and at the aqueous interface. Thus, one of the most fundamental questions is whether water adsorbs in molecular or in dissociated form on the TiO_2 surface. This remains a subject of controversy even for the most studied rutile (110) surface. Recent experimental studies on

* Corresponding author. Fax: +1 801 581 8433; E-mail: truong@mercury.chem.utah.edu

single-crystal $\text{TiO}_2(110)$ surfaces indicate that water is adsorbed in molecular form even at low coverages [3–7]. The small amount of dissociated water observed in these studies may be linked to structural and/or point defects such as steps or kinks [6]. Experimentally, the adsorption energy of H_2O on TiO_2 was deduced from fitting TPD spectra and from analysis of modulated beam experiments (see Table 1).

In contrast to these experimental findings, all existing theoretical studies predict complete dissociation of H_2O on the $\text{TiO}_2(110)$ surface [8–14] (see Table 1). Non-empirical studies [11–14] have been performed on periodic models formally corresponding to 1 and 0.5 ML coverages. From these results it is not easy to make conclusions about adsorption properties of a single water molecule. The most elaborate periodic DFT calculations predict the adsorption energy for the dissociated state of 24.9 kcal/mol at the monolayer coverage [12]; the molecularly adsorbed water was about 6 kcal/mol higher in energy. At half-coverage the adsorption energy increases to 31.1 kcal/mol [13], and at zero coverage limit this value can be extrapolated to about 37.3

kcal/mol. The dissociative chemisorption was always found to be more stable than molecular adsorption.

This disagreement has stimulated experimental groups to return again and again to the issue of molecular versus dissociative adsorption of water on $\text{TiO}_2(110)$. However, no solid evidence was found for dissociative adsorption of a single water molecule on the defect-free surface. In this study we reconsider water adsorption on $\text{TiO}_2(110)$ from a theoretical point of view. We use a non-empirical embedded cluster model which has not been applied to the $\text{H}_2\text{O}/\text{TiO}_2$ case before. The essence of this model is representation of the adsorption site by a quantum cluster embedded in the Madelung potential from the rest of the crystal and in the short-range pseudopotentials from nearest cations. This model and similar approaches, e.g., with electrostatic embedding only, have demonstrated their accuracy and applicability in numerous studies of bulk and surface defects and adsorption on highly ionic oxides like MgO and CaO. Recently the embedded cluster model has been successfully applied for studies of water interaction with Al_2O_3 surfaces [15,16]. In addition, a thorough comparison with periodic HF calculations on $\text{CO}/\text{TiO}_2(110)$ adsorption has confirmed the applicability of the embedded cluster model for TiO_2 surface studies [17].

Table 1
Calculated (without BSSE) and experimental adsorption energies for $\text{H}_2\text{O}/\text{TiO}_2(110)$

Method	Adsorption energy, kcal/mol		References
	Molecular adsorption	Dissociative adsorption	
Theory			
SINDO1	29.9	41.9	[9]
Periodic DFT	31.3 ^a	37.3 ^a	[12,13]
Embedded cluster (HF) ^b	34.5 (32.7)	7.9 (7.5)	this study
Embedded cluster (B3LYP) ^b	34.9	22.6	this study
Embedded cluster (MP2) ^b	34.4 (37.1)	18.0 (23.3)	this study
Experiment			
TPD	17–19	n/o	[3–5]
Modulated beams	14–24	n/o	[4]

^aExtrapolated to zero coverage limit.

^bTaking into account basis set superposition effects lowers adsorption energies by less than 7 kcal/mol.

In parentheses results with double-zeta basis set on central Ti atom of the cluster.

2. Method

We represented the surface adsorption site by the cluster $[\text{Ti}_7\text{O}_{14}]$ shown in Fig. 1 with adsorbed dissociated water molecule. Our use of the neutral cluster obeying the stoichiometry of the crystal is important for better representation of the electronic structure of the crystal surface. We have studied adsorption of a single water molecule in both molecular and dissociative geometries. Calculations were carried out using Hartree–Fock, MP2, and B3LYP methods. The MP2 and non-local density functional B3LYP methods are known to be rather accurate in representing reaction energetics, while the Hartree–Fock (HF) approximation is useful for studying electronic spectra via Koopmans theorem. The electronic structure of the cluster was treated in the valence

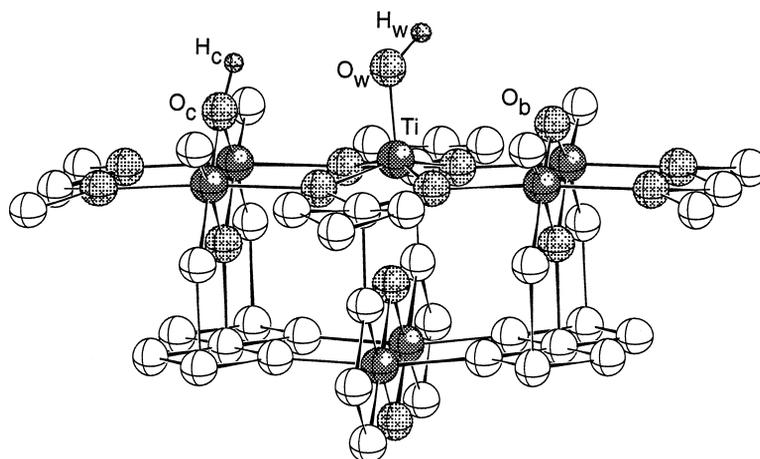


Fig. 1. Embedded cluster model for $\text{H}_2\text{O}/\text{TiO}_2(110)$ adsorption used in this study. Atoms belonging to the quantum cluster $[\text{Ti}_7\text{O}_{14}] + \text{H}_2\text{O}$ are shown as shaded circles. Empty circles indicate some atoms in the crystal environment. The optimized geometry in the dissociative adsorption local minimum is shown.

approximation. Core electrons of the cluster and adsorbed water were substituted by effective core pseudopotentials (ECP). Two basis sets (I and II) were explored in our calculations. In the set I we used LANL ECP and the minimum basis set for titanium atoms [18]. Oxygen atoms were treated using the SBK pseudopotential [19]. The CEP-31G basis was placed on oxygens in TiO_2 crystal, and a polarization d-function with the exponent of 0.85 was added to the oxygen basis set on the water molecule. The standard 31G basis was placed on hydrogens. The set II differs from the set I only by using the double-zeta basis [18] on the central Ti atom in the cluster. With this selection of basis sets, calculated dissociation energy of water (113.6 kcal/mol in B3LYP, 108.4 kcal/mol in MP2) underestimates the experimental value of 119 kcal/mol [20]. Dissociation energy of 81.3 kcal/mol calculated with the HF method is even lower. From this we can conclude that our calculations would be biased toward dissociative form of water adsorption on the TiO_2 surface. Note that a similar bias is characteristic for the periodic DFT method which underestimates water dissociation energy by about 12 kcal/mol [12].

It is important to have a proper representation of the embedding potential in the quantum zone from the rest of the crystal. To minimize the effect of bond truncation at the periphery of the quantum

cluster and to prevent electron leakage from the cluster to the environment, Ti ions nearest neighbors to the quantum cluster were represented by the LANL pseudopotentials [18]. The rest of the infinite crystal lattice (a 12-layer slab parallel to the (110) surface) was modeled as an array of point charges. The Madelung potential in the cluster from the nearest 492 ions was calculated explicitly, while the potential from the rest of the infinite lattice was represented by additional 296 point charges located on a surface enclosing the cluster region using the SCREEP (surface charge representation of the electrostatic embedding potential) model [21]. The SCREEP approximation resulted in a very small r.m.s. deviation of 0.7 mhartree from the exact Madelung potential inside the quantum cluster.

For ions outside the quantum cluster we use charges corresponding to formal ionicities $q_{\text{Ti}} = +4$; $q_{\text{O}} = -2$. The use of formal charges as opposed to fractional charges in the cluster environment yielded better agreement with results of periodic calculations on CO/TiO_2 system [17].

It is known from previous X-ray diffraction experiments [22] that 5-coordinate Ti (labelled 'Ti' in Fig. 1) and bridging surface oxygens (O_c and O_b in Fig. 1) exhibit the largest deviation from the bulk termination positions on the $\text{TiO}_2(110)$ surface. Moreover, these atoms have the strongest interaction with adsorbed water and its dissociation products. Therefore

their inclusion in the geometry optimization is crucial for obtaining correct adsorption structure and energetics. Thus, in addition to optimizing positions of water atoms, 5-coordinate Ti and bridging surface oxygens were also fully relaxed. Positions of all other atoms in the slab were taken from experiment [22].

Interactions of O^{2-} ions in the environment with H^+ nuclei of hydrogens and O^{6+} cores of oxygens in the quantum cluster were represented as a Coulomb term plus repulsion. The $O^{2-}-O^{6+}$ repulsive potential was taken from the OPLS force field [23], and the $O^{2-}-H^+$ repulsion was defined as the difference between the point-charge interaction $-2/r$ and the energy of the OH^- ion computed with CEP-4G basis on oxygen. This potential was fitted to the expression Ae^{-br} , with $A = 16.355$ hartree and $b = 2.6085$ bohr $^{-1}$. $O^{2-}-O^{6+}$ and $O^{2-}-H^+$ repulsive potentials had a very small effect on geometry and energetics of adsorption. For example, their contributions to the molecular and dissociative adsorption minima differ by only 0.11 kcal/mol.

Convergence of our results with respect to the cluster size was tested in calculations of H_2O adsorbed on smaller $[Ti_3O_6]$ and $[Ti_5O_{10}]$ clusters. Test calculations with a $[Ti_3O_6] + H_2O$ cluster using all-electron basis set (3-21 basis on Ti; 6-31G basis on crystal oxygens and hydrogen; 6-31G* basis on water oxygen) showed that adsorption energies obtained in the valence approximation can be trusted to within about 4 kcal/mol. We found that optimized HF and B3LYP geometries are close to each other. Therefore, geometry optimizations in the $[Ti_7O_{14}]$ cluster have been done with the HF method using basis set I. Then MP2 and B3LYP single point calculations were performed at these optimized structures to get more reliable energetic information.

For analysis of the electronic structure of adsorption and for comparison with ultraviolet photoelectron spectroscopy (UPS) experiments it is convenient to plot electronic densities of states (DOS) for different adsorption geometries (see Fig. 2). These DOS curves were obtained by broadening HF one-electron energy levels (obtained using basis set I) with a Gaussian function having the width of 1.0 eV at the half-maximum. In Table 3 we compare positions of water-induced peaks with those from UPS spectra [24]. Calculated values were obtained by

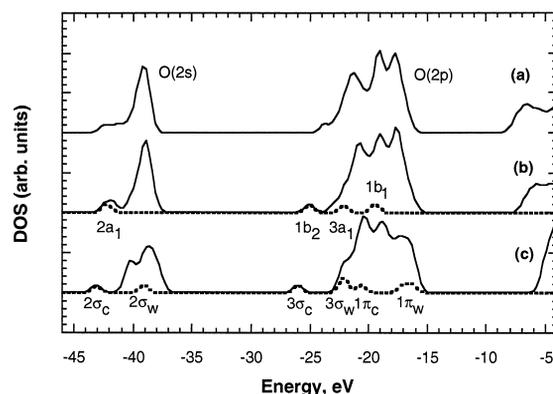


Fig. 2. Calculated DOS spectra for bare TiO_2 surface (a), molecularly adsorbed water (b), and dissociatively adsorbed water (c). Broken curves show schematically DOS peaks induced by adsorption.

adding 0.5 eV (half-width of the Gaussian exponent used for level broadening) to the energy difference between the one-electron levels of interest and the top level of the valence band. Experimental values were obtained by assuming that the top of the valence band is located at 4.25 eV below the Fermi level [24].

The embedded cluster approach described above was implemented in our locally modified GAUSSIAN-92/DFT computer program [25].

3. Results and discussion

3.1. Surface structure

We present in Table 2 results of our calculations for the surface relaxation in comparison to experimental observations and theoretical data. Comparison of our results to those from periodic DFT calculations [26] is of special interest because the calculation method used in this work was essentially the same as that employed for studying water adsorption on TiO_2 by Gillan and co-workers [12–14]. Both methods yield the shift of Ti atoms on the edge of experimental interval. However, our result for the relaxation of bridging O atoms (-0.22 Å) is in better agreement with experiment (-0.27 Å) than periodic DFT (-0.02 Å).

Table 2

Calculated and experimental shifts (perpendicular to the surface plane; in Å) of atoms on the TiO₂(110) surface with respect to bulk termination

Method	5-Coordinate Ti	Bridging O	Reference
Theory			
Pair-potentials	−0.25	−0.08	[34]
FLAPW	−0.18	−0.16	[31]
Periodic DFT (LDA)	−0.17	−0.07	[35]
Periodic DFT (GGA)	−0.11	−0.02	[26]
Embedded cluster ^a	−0.10	−0.22	this work
Experiment			
X-Ray diffraction	−0.16 ± 0.05	−0.27 ± 0.08	[22]

^aAll other atoms in the slab were fixed at their experimentally determined positions [22].

Our calculated averaged Mulliken ionic charges of −1.2 on oxygens are consistent with existing estimates of the ionicity of TiO₂ [27–30]. In Fig. 2a we present calculated DOS for the bare TiO₂(110) surface. As expected, DOS consists of three major bands: the lower energy band composed mainly of O(2s) orbitals, the upper valence band with the main contribution from O(2p) states, and the empty conduction band whose lower energy states are formed primarily by Ti(3d) orbitals. The calculated energy separation between O(2s) and O(2p) bands (14.9 eV) and the width of the O(2p) band (7.1 eV) are close to those obtained in previous theoretical [28,31] and experimental [32] studies. It is well known that the energy gap between valence and conduction band appears overestimated if calculated as the LUMO–HOMO difference in the HF method. A better estimate for the band gap can be obtained as the difference between *total* energies of the excited triplet state of the cluster (unrelaxed triplet exciton) and the ground singlet state. In our calculations this difference amounts to 2.7 eV in HF and 4.8 eV in MP2 which can be compared to the experimental band gap of TiO₂ (3.0 eV). Note that the B3LYP method yields the triplet–singlet energy difference of only 0.3 eV. This is clearly an indication of the fact that although density functional approach is rather accurate for the ground state, its predictions for excited states are unreliable.

Results reported above indicate that geometric and electronic structures of the TiO₂(110) crystal surface are reproduced rather well by our embedded

cluster model. Thus we can turn to discussion of water adsorption on this surface.

3.2. Molecular adsorption of H₂O on TiO₂(110)

Our calculations show that in its lowest energy configuration, water is adsorbed in the molecular form. The molecule is oriented perpendicular to the surface with O atom pointing toward 5-coordinate Ti atom. Ti–O_w distance is 2.25 Å, and the geometry of adsorbed H₂O differs only slightly from that in the gas phase. The binding energy with basis set I was found to be 34.4 kcal/mol by HF geometry optimization. Single-point B3LYP and MP2 calculations give 34.9 and 34.4 kcal/mol, respectively. The basis set superposition error (BSSE) of 6.9 kcal/mol was evaluated by the counterpoise method. This large BSSE suggests that results may be sensitive to the choice of the basis set. For checking this we have performed additional calculations using the basis set II. As seen from Table 1, this results in increase of the MP2 adsorption energy by 3–5 kcal/mol. Thus our best estimate for the adsorption energy of molecular water is about 30 kcal/mol in good agreement with previous calculations.

Fig. 2b shows DOS curves for molecularly adsorbed water. Three adsorption-induced peaks in the region of the O(2p) valence band can be traced back to molecular orbitals of the water molecule 1b₁, 3a₁, and 1b₂. In Table 3 we compare their energetic positions with those obtained from UPS spectra taken at 130 K [24]. Calculations and experiment are in excellent agreement with each other. It is worth

Table 3

Binding energies (in eV, relative to the top of the valence band) of DOS peaks induced by water adsorption on the TiO₂(110) surface

Peak label	This work	Experiment ^a
Molecular adsorption		
1b ₂	9.3	9.0
3a ₁	6.4	6.1
1b ₁	3.8	3.8
Dissociative adsorption		
3σ _c	10.5	n/o
1π _c	5.1; 6.8	n/o
3σ _w	6.6	6.8
1π _w	0.8; 1.6	0.3...4.3

^a Ref. [24].

noting that upon adsorption the $3a_1$ feature shifted by about 0.8–1.4 eV to higher binding energies with respect to $1b_1$ and $1b_2$ peaks. A similar shift (by 0.7–1.0 eV depending on the sample preparation) has been found in experimental spectra [24,33]. As discussed by Henrich [33], this shift is characteristic for the water molecule adsorbed with its axis perpendicular to the surface on top of the Ti atom in agreement with our results.

3.3. Dissociative chemisorption of H_2O on $TiO_2(110)$

Geometry optimization in the dissociative minimum yields structure shown in Fig. 1. One OH bond of the water molecule is broken and the proton binds to a nearby bridging surface oxygen. Thus two hydroxyl groups are formed; one having oxygen from crystal ($O_cH_c^-$) and another with oxygen originally belonging to the water molecule ($O_wH_w^-$). We observed also that 5-coordinate Ti atom is pulled up by 0.4 Å with respect to its position in bulk-terminated surface. This large shift is consistent with periodic DFT calculation which predicts that Ti atom raises by 0.5 Å above the surface [13]. However, other aspects of the geometry relaxation are rather different in these two methods. For instance, we have not observed large shifts of O_c and O_w oxygen atoms (in DFT calculation their separation reduces to 2.77 Å [12]). Moreover, the O_w-H_c distance in our calculations is 3.1 Å, while in DFT study [12] it is much shorter: about 2.3 Å. Thus, residual attraction between O_w and H_c could be one reason for stabilization of the dissociated water in DFT calculations. In our calculations taking into account correlation effects (MP2 and B3LYP) the dissociative minimum is 12–16 kcal/mol higher in energy than the minimum corresponding to molecular adsorption. This agrees with the experimental finding discussed in Section 1 that molecular adsorption is preferable on this surface. The difference is even larger (25–27 kcal/mol) when the HF method is used. This discrepancy suggests that correlation effects are important for understanding water adsorption and dissociation on TiO_2 .

DOS for the dissociated state is shown in Fig. 2c. Our calculated positions of DOS features due to $O_cH_c^-$ and $O_wH_w^-$ hydroxyls are compared with experimental results in Table 3. From this comparison it follows that peaks observed in experiment are most likely due to the $O_wH_w^-$ hydroxyl.

4. Conclusions

From our calculations we conclude that isolated water adsorbs on the $TiO_2(110)$ surface preferentially in the molecular form above 5-coordinate Ti ion perpendicular to the surface with oxygen pointing toward Ti. Adsorption energy is estimated to be about 30 kcal/mol. The energy minimum corresponding to the dissociative chemisorption is 12–16 kcal/mol higher. It is difficult to say why previous theoretical studies (in particular Refs. [12–14]) predicted the opposite situation: dissociative adsorption was found to be more stable than molecular. Most likely this was due to their use of periodic boundary conditions with high adsorbate coverages. This practice may result in distorted adsorbate geometries and several kcal/mol errors in adsorption energies.

To our knowledge this is the first theoretical study predicting, in agreement with experiment, that single water molecule adsorbs in molecular form on the $TiO_2(110)$ surface. Our results are also in good agreement with measured surface relaxation, water adsorption energies and electronic spectra. Therefore the computational model suggested here seems to be suitable for further theoretical exploration of chemistry and photo-chemistry on the surface of TiO_2 particles. In our future studies we plan to investigate the excited state for water adsorbed on TiO_2 surface and TiO_2 –water interface with the aim to clarify the mechanism of photo-generation of OH radicals.

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