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Nature of the excited states of the rutile TiO_2(1 1 0) surface with adsorbed water

Vladimir Shapovalov, Eugene V. Stefanovich, Thanh N. Truong *

Department of Chemistry, Henry Eyring Center for Theoretical Chemistry, University of Utah, 315 S. 1400 E., Room 2020, Salt Lake City, UT 84112, USA

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Abstract

We present an ab initio embedded cluster study of the ground and excited states for the rutile (1 1 0) surface with adsorbed water molecule. The calculated adsorption energies and geometries are compared with available experimental data. Upon photoexcitation, an electron–hole pair is created. We found that the electron is localized in the subsurface and thus cannot be directly involved in surface processes whereas the hole is localized on the surface oxygen atoms and enhances the radical character of the hydroxyl group. Our results support experimental suggestions that OH radical is the active species in photocatalysis on TiO_2 surface. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The nature of the electronically excited states on titanium dioxide surface is important for understanding the photocatalytic properties of TiO_2. Under radiation TiO_2 is capable of oxidizing organic impurities in aqueous solution and decomposing water molecules into hydrogen and oxygen [1]. This property was attributed to the band gap in titanium dioxide that slows down recombination of the electron–hole pair produced upon photoexcitation [1–4]. It is known that the electron–hole pair, after being generated, can diffuse and recombine in the volume of a titania particle. It was suggested that such a pair can also be localized at the surface. Surface-localized electron may result in the formation of an O^{2-} anion, and ultimately, in the formation of hydrogen peroxide [2]. Surface-localized hole can lead to the desorption of O^+ ion [5], the formation of radicals ($OH^\bullet$, $R^\bullet$), and cation (H^+) from the following reactions [2]:

$$H_2O + h^+ \rightarrow OH^\bullet + H^+ \qquad (1)$$

$$RH + h^+ \rightarrow R^\bullet + H^+ \qquad (2)$$

Since the surface-localized hole and electron produce different active species, they lead to totally different reaction pathways. Thus, information on the location of the electron–hole pair is crucial in for understanding the mechanisms of photo-catalytic processes on TiO_2 surfaces. Unfortunately, to

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* Corresponding author. Tel.: +1-801-581-7272; fax: +1-801-581-4353.

E-mail address: truong@chemistry.chem.utah.edu (T.N. Truong).

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the best of our knowledge, to date there has been no theoretical studies on the nature of such electron–hole pair. In this study, we investigated the nature of the electron–hole pair on the rutile TiO_2 (1 1 0) surface with adsorbed water using an ab initio embedded cluster methodology. We selected the (1 1 0) surface since it has a well-established structure and has been studied extensively [1,6–9]. In addition, this surface plane is the most stable thermodynamically and accounts for 60% of the massive rutile TiO_2 surface [10]. Though it is known that the chemical reactivity of the rutile TiO_2 surface is greatly affected by both structural and charge defects, the use of the ideal surface in this study allows us to focus on one aspect, namely the nature of the electron–hole pair on the rutile surface. It would also encourage surface scientists to confirm our predictions by experimental techniques.

2. Computational details

We employed an embedded cluster methodology in this study. It is perhaps the only viable approach for studying excited states in extended systems at the present time. In this methodology, a sufficiently large quantum cluster consisting of the adsorbate and a cluster representing the adsorption site and its surrounding are treated quantum mechanically, while the Madelung potential from the remaining part of the crystal is represented classically by a set of point charges. These point charges can be determined accurately using the surface charge representation of external embedding potential (SCREEP) method [11]. A stoichiometric cluster Ti_7O_{14} as shown in Fig. 1 is selected to represent the active region of the TiO_2(1 1 0) surface. This cluster is reasonably large for our purpose. We had performed a convergence study with respect to the cluster size earlier and showed that the adsorption energies can be trusted to within about 4 kcal/mol [12]. Hay–Wadt effective-core pseudopotential basis set [13] was used for Ti, CEP-31G [14] for oxygen, and 31G for hydrogen atoms. In addition, a set of d and p polarization functions was added to oxygen and hydrogen atoms of the adsorbed water molecule.

Three different systems were considered, specifically: (1) a clean surface, (2) surface with molecular adsorbed water, and (3) surface with dissociatively chemisorbed water. The experimental structure of the TiO_2(1 1 0) surface [15] was used to construct the embedded cluster models. Oxygen of the water molecule was assumed to be bound to the five-coordinated surface Ti_1 atom, and hydrogen of water in the dissociative case is bound to the nearest oxygen atoms O_1 or O_2 sticking out of the surface. In all geometry optimizations, only surface atoms bound to the adsorbed species (Ti_1, O_1, and O_2) along with the adsorbate atoms were allowed to relax.

Geometries of all species were optimized in the ground state at the Hartree–Fock (HF) level of theory. Single-point calculations at the Møller–Plesset second order perturbation theory (MP2) level using the same basis set were carried out to improve energetic and electronic density information. Excitation energies were estimated using the configuration interaction with all single excitations (CIS) method. All calculations were carried out using the GAUSSIAN98 computer program [16].

3. Results

3.1. Ground state (singlet)

For the ground state, from the partial optimization we found that the TiO_2 clean surface exhibits inward relaxation, particularly the five-coordinated Ti_1 atom by a distance $\delta_1 = -0.10$ Å, and the bridging O_1 and O_2 atoms by $\delta_2 = -0.22$. This compares well with the experimental values of $\delta_1 = -0.16 \pm 0.05$ Å and $\delta_2 = -0.27 \pm 0.08$ Å [15]. Both dissociative and molecular water adsorption complexes are found to be stable, though the molecular adsorption has a lower adsorption energy of -35.9 kcal/mol as compared to -13.4 kcal/mol for the dissociative adsorption. Inclusion of the basis set superposition error (BSSE) would raise these values by about 6.9 kcal/mol [12]. This brings the calculated adsorption energies in better agreement with the experimental range of -14 to -24 kcal/mol [7,17]. Our results are consistent with the experimental observation that water ad-

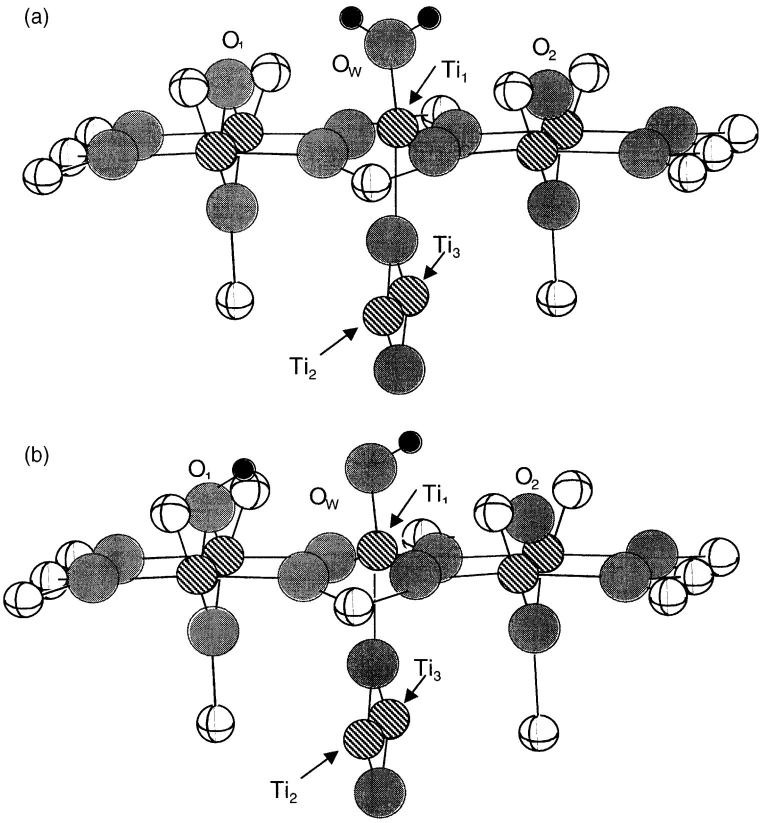

Fig. 1. Structures and atom labels of the TiO_2 quantum clusters in our embedded cluster models. Hatched atoms are Ti, solid gray atoms are O, and solid black atoms are H. White atoms are a part of the SCREEP embedding scheme and do not have basis functions. (a) molecularly adsorbed water, (b) dissociatively chemisorbed water.

sorbs on the $TiO_2(1\,1\,0)$ surface mostly in the physisorbed form [7,18,19].

Fig. 2 shows the plot of the density of states (DOS) of the molecular absorbed complex. Using the same procedure as done in a previous study [20], this plot was obtained by smoothing the MP2 cluster orbital energy levels with gaussian functions having a half-width of 1 eV. Zero of energy was placed at the top of the valence band. Classified according to the isolated water point symmetry group C_{2v}, the $1b_2$, $3a_1$, and $1b_1$ molecular orbitals of the adsorbed water molecule are found at −8.7, −5.5, and −1.9 eV, respectively. Our results agree quite well with the experimental data [19] shown in Table 1. Since the energy splitting between these orbitals is sensitive to the orientation of water with respect to the surface, such agreement supports the calculated adsorption structure and also validates our theoretical model.

3.2. Excited state (triplet)

In the case of molecularly adsorbed water, the adsorption energy is −40.7 kcal/mol relative to the TiO_2 surface in the excited state and a water molecule at infinity. We used population analysis to determine localization of the electron–hole pair. Contour plots of the electron density difference between the excited and the reference ground state are shown on Fig. 3a and b. We found that the electron is mostly localized on the third layer Ti_2 and Ti_3 atoms (see Fig. 1). Because this electron is inaccessible from the surface it is unlikely to participate in the surface reactions. The hole is found

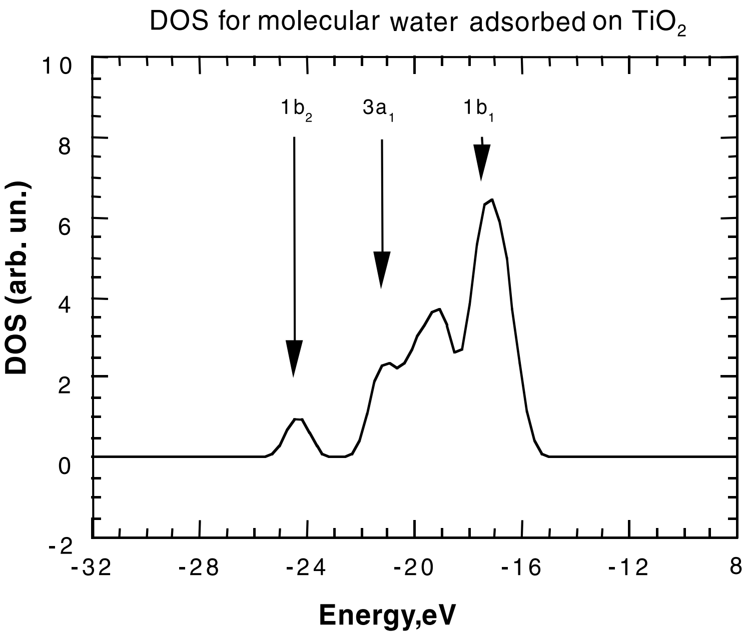

Fig. 2. Density of states (arbitrary units) of water molecularly adsorbed on TiO_2(1 1 0) surface.

Table 1
Positions of water induced peaks on the rutile TiO_2(1 1 0) surface relative to the top of the valence band (in eV)

Peak label	UPS experiment[a]	Theory
$1b_2$	−9.2	−8.7
$3a_1$	−6.3	−5.5
$1b_1$	−1 to −5	−1.9

[a] Ref. [19].

mostly localized on the oxygen atom below the five-coordinated Ti_1 atom (Fig. 3a).

In the case of dissociatively adsorbed water, the adsorption energy relative to the TiO_2 surface excited state and water at infinity is −22.9 kcal/mol. Similar plots of electron density difference are shown in Fig. 3c and d. The electron is localized on the same Ti atoms in the sub-surface as in the case of molecular dissociation. Most of the hole states are localized on the oxygen O_W of the hydroxyl group and some on the oxygen atom below the five-coordinated Ti_1 (see Fig. 3c). Because of this reduced amount of electronic charge on the hydroxyl it acquires a significant hydroxyl radical character. The evolution of this state can result in either hydroxyl radical desorbing from the surface, or in charge transfer to other adsorbed species, or radical reactions at the surface, such as

$$HO^\bullet + RH \rightarrow R^\bullet + H_2O \tag{3}$$

4. Discussion

It is interesting to relate our findings with the current knowledge on the system. It has been well accepted that after the band gap excitation the electron is trapped by Ti^{4+} ions [3,21]. Our results not only support this but also further point out the specific Ti^{4+} ions in the sub-surface that trap the electron, thus suggesting that the trapped electron is not directly accessible for surface reactions. So far not much has been known about the state of the hole. Several models have been proposed including $OH^\bullet$ or $OOH^\bullet$ radicals, and V-center having a hole trapped at an oxide ion, O^-, adjacent to the cation vacancy, V_{Ti}, O_2^-, O_2^{3-}, or O_3^- [22]. Mechanisms involving direct transfer of the hole to the solute particles were also proposed [23]. Several experimental studies reported observing Ti(IV)–O–Ti^{4+}–$O^\bullet$ radicals [24] or vacancy and/or

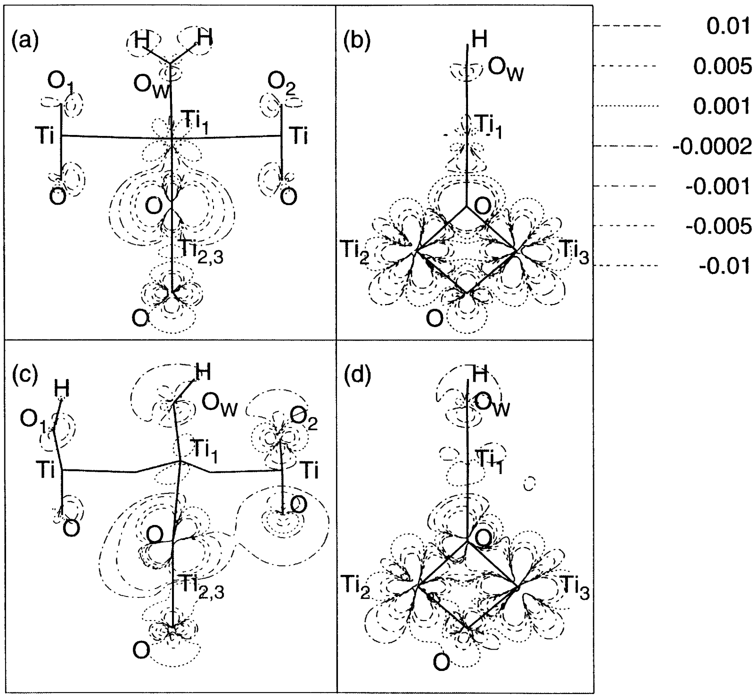

Fig. 3. Contour plots of the electron density difference between the excited state and the reference ground state. Negative values correspond to the hole and positive values to the excess electron in the excited state. Cross-sections (a) and (c) pass through the O_1, O_2, and O_w atoms, and cross-sections (b) and (d) pass through the Ti_1, Ti_2, and Ti_3 atoms. The isovalues were chosen to produce readable plots while preserving important features.

impurity stabilized delocalized holes [22], such as V_{Ti}–O^-–Ti(IV)–OH^- or V_{Ti}–O^-–Ti(IV)–O^{2-}–M^{n+}, where V_{Ti} is a cation vacancy, and M^{n+} is an impurity. The absence of the hyperfine structure in the EPR spectra in the above works was an argument against formation of hydroxyl radicals on the surface. Nevertheless, hydroxyl radicals on the TiO_2 surface were detected in both direct observations of the ESR spectra [25,26] and indirectly through dynamics studies of the electron transfer [27], and observation that intermediates in the photocatalysis process are typically hydroxylated structures [21,28,29].

Our results suggest that the hole is delocalized over at least two surface oxygen atoms, and both – O^-–Ti(IV)–OH^- and $OH^\bullet$ species can be formed. The concentrations of these species, however, will depend on the surrounding. For example, hydroxyl radical scavengers would shift the equilibrium towards formation of $OH^\bullet$, which would be consistent with the results based on the observation of the intermediates and reaction products [25,29]. On the other hand, strong acids and bases as in Ref. [24] could shift the equilibrium away from generation of the hydroxyl radicals.

Our present study did not include the solvent effects. Since the electron is trapped in the subsurface it is expected to have small solvent effects. Similarly, the hole yields radical character on the surface species and therefore, is also expected to have small solvent effects. We are currently carrying out similar study at the solid–water interface to confirm our above speculation.

5. Conclusion

We performed ab initio embedded cluster calculations of the ground and excited states of the rutile $TiO_2(1\,1\,0)$ surface, and of molecularly and dissociatively adsorbed water on this surface. We found that the electronic excitations in this system in vacuum result in hole states localized on the atoms exposed on the surface. In the case of molecularly adsorbed water the most probable evolution path is transfer of the hole from the surface oxygen to other adsorbed species. In the case of dissociatively adsorbed water this path is also possible, but there is a possibility of a hydroxyl radical forming and desorbing from the surface. The excess electron is localized on the sub-surface Ti atoms and is not accessible for surface reactions. Work is underway to study solvent effects on this system, and the possibility of desorption and charge transfer from the active sites to other adsorbed species.

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