

Short Hydrogen Bonds at the Water/TiO₂ (Anatase) Interface

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The nature of peculiar, short H bonds formed by water molecules in contact with the (101) anatase surface and their effects on the structural and vibrational properties of the first water layers adsorbed on the same surface have been investigated by performing density functional theory (DFT) total energy calculations and ab initio molecular dynamics (AIMD) simulations at different temperatures. Present results show that these short H bonds originate from a water/anatase interface effect related to an electronic charge transfer from surface Ti atoms to surface O atoms, mediated by water molecules. Further, AIMD simulations performed at low temperature indicate that such short H bonds are at the ground of both the atomic arrangements of the water layers and the peculiar features appearing in the corresponding vibrational spectra. The same interface effect significantly influences also the atomic arrangements and the vibrational properties of intermediates of the O₂ photoreduction reaction, which turn out to be involved in similar charge transfer processes as well as in the formation of short H bonds. AIMD simulations show that these short H bonds are still present at room temperature and give estimates of the vibrational frequencies of the same intermediates, which are in a quite good agreement with the experimental findings. Such an agreement supports the unifying theoretical picture proposed here for water molecules and O₂ photoreduction intermediates in contact with the anatase surface.

Introduction

Water molecules in contact with a catalyst surface can play a significant role in heterogeneous catalytic and photocatalytic processes.¹ In particular, this applies to the surfaces of metal oxides, which represent a relevant class of heterogeneous catalysts,² and to the surfaces of TiO₂ anatase and rutile polymorphs, likely the most used photocatalysts.^{3–5}

In a recent work,⁶ we have investigated the vibrational properties of intermediates of the oxygen photoreduction reaction occurring at the (101) anatase surface and compared our theoretical results with the vibrational frequencies measured by using a multiple internal reflection infrared technique (MIRIR), especially sensitive to solid/solution interfacial species.⁷ The O₂ photoreduction reaction plays a key role in the photocatalytic processes occurring at the TiO₂ surface. Oxygen molecules scavenge very efficiently photogenerated electrons and segregate them from oxidizing holes.⁷ Moreover, the intermediates of this reaction act themselves as further oxidizing media in photodegradation processes.^{3,5} In the above-mentioned study, we have reported the existence of a significant effect of the anatase surface on the properties of adsorbed water molecules as well as of intermediates of the O₂ photoreduction: short H bonds, that is, shorter than the usual distance of about 1.9 Å in liquid water, form between water molecules in contact with the surface, surface O atoms and reaction intermediates. Such an effect implies that (i) the first water layers adsorbed on the anatase surface (ad-layers) form a network stronger than that usually expected, and (ii) the above short H bonds can have considerable effects on the vibrational modes of intermediates

containing O and H atoms and embedded in that network of water molecules, as reported in detail in ref 6. In particular, only when calculations are performed by surrounding such intermediates with water molecules, the estimated vibrational frequencies match the measured ones.

The behavior of water layers adsorbed on the reduced and defect-free TiO₂ anatase (101) surfaces has been recently investigated by Tilocca and Selloni by performing ab initio molecular dynamics (AIMD) calculations at the temperature of 160 K.^{8,9} These studies were mainly focused on the phenomenon of H₂O dissociation on the TiO₂ surface as well as on the structure and energetics of the water overlayers. The temperature of 160 K was chosen because two monolayers of water adsorbed on the anatase surface are found to be thermodynamically stable in vacuum up to 190 K.¹⁰

In the present paper, we extend our previous study on the O₂ photoreduction intermediates by carefully investigating (i) the fine interplay between the anatase surface, the water molecules, and the intermediates, which is at the origin of the short H bonds, and (ii) the combined effects of temperature and short H bonds on the structural and vibrational properties of the water ad-layers and the intermediates. Thus, first the nature of the short H bonds has been investigated in water ad-layers in their stable configurations as given by geometry optimization procedures. Then, the effects of these H bonds and temperature on the properties of the water ad-layers have been investigated by performing AIMD calculations at different temperatures. Similar investigations have been performed in the case of the short H bonds formed by the O₂ photoreduction intermediates in contact with the anatase surface. The AIMD simulations have been performed by considering a water bilayer adsorbed on the (101) anatase surface and including thermal effects above 190 K and up to the room temperature (RT). In this way, present results complement the AIMD results mentioned above as well as our

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previous study, by permitting also to get new RT estimates of the vibrational properties of O_2 reduction intermediates which better simulate the experimental conditions. In particular, present results show that the short H bonds originate from a *water/anatase* interface effect inducing an electronic charge transfer from surface Ti atoms to surface O atoms, which is mediated by the water molecules. Such bonds persist at low temperature (e.g., 150 K) in the water bilayer by affecting its structural and vibrational properties and by giving it features of a somewhat rigid network which disappears at higher temperatures. The achieved results also indicate that the same interface effect is at the ground of the short H bonds formed by the O_2 photoreduction intermediates. Such H bonds persist at RT and heavily affect the vibrational frequencies of the same intermediates. More specifically, when the combined effects of the short H bonds and temperature are taken into account, a very good agreement is found between the calculated vibrational frequencies and the experimental results. Such an agreement supports the unifying theoretical picture proposed here for water molecules and intermediates of the O_2 photoreduction in contact with the anatase surface.

Computational Methods

Total energy calculations have been performed by using density functional theory (DFT) methods in the local spin density and generalized gradient approximation (LSD-GGA) approach.¹¹ Beyond LDA, LSD-GGA+U calculations^{12–14} have been also performed in order to circumvent the possibly too poor LSD-GGA electron correlation description (see the criticism reported in ref 15). We can anticipate that both approaches lead to very similar results for all of the system investigated in this work (see Supporting Information). Total energies have been calculated at the Γ point in a supercell approach by using ultrasoft pseudopotentials¹⁶ (see Supporting Information) and the PBE gradient corrected exchange–correlation functional.¹⁷ The Kohn–Sham orbitals were expanded in plane waves up to energy cutoffs of 25 and 150 Ry for the wave functions and the charge density, respectively. In detail, a (3×2) surface cell, formed by adding about 12 Å of vacuum space to three O–Ti–O layers (nine atomic planes) has been used. Geometry optimizations have been performed by fully relaxing the first and second topmost layers of the surface cell. The atoms of the third layer have been relaxed in a surfacelike configuration and then kept fixed in further geometry optimizations.¹⁸

Difference electron density (ρ_{diff}) maps have been analyzed to unravel the occurrence of charge transfer processes between surface and molecules. For example, $\rho_{\text{diff}}[\text{H}_2\text{O-anatase}]$ is given by $\rho[\text{H}_2\text{O-anatase}] - (\rho[\text{H}_2\text{O}] + \rho[\text{anatase}])$ where $\rho[\text{H}_2\text{O-anatase}]$ is the electron density of a supercell containing the molecule–semiconductor system, $\rho[\text{H}_2\text{O}]$ is the electron density of the same supercell with the molecule only, and the analogue for the $\rho[\text{anatase}]$ density. Thus, a $\rho_{\text{diff}}[\text{H}_2\text{O-anatase}]$ map can indicate the charge displacements induced by an interaction between the molecule and the surface.

AIMD calculations^{19,20} have been performed by using (2×2) surface cells obtained by adding about 8 Å of empty space to two O–Ti–O layers (six atomic planes).²¹ Such supercells have been used to investigate the properties of a bilayer of water molecules as well as of surface intermediates embedded in this bilayer. AIMD simulations have been performed by using a 3 au time step and a 300 K temperature controlled by Nosé thermostats for about 10 ps. Water bilayer simulations have been also performed at the temperatures of 50 and 150 K. The latter calculations permit a comparison of present results with the

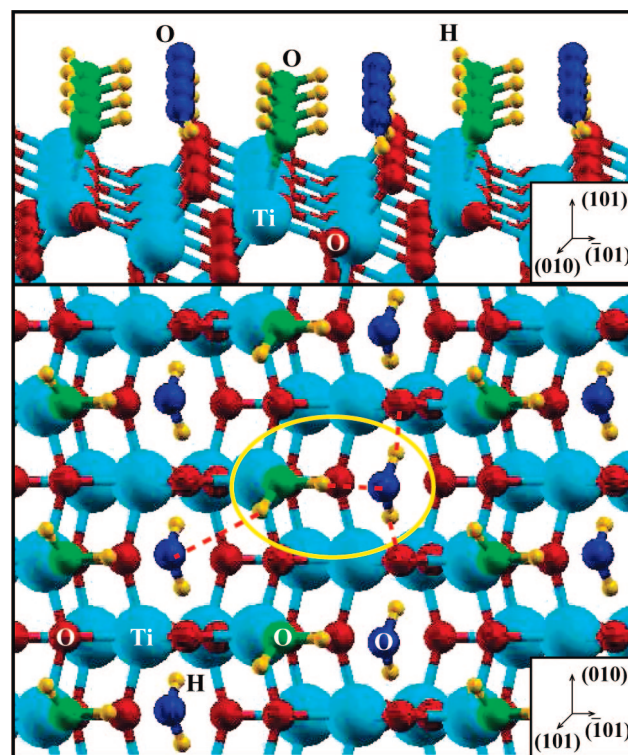


Figure 1. Optimized geometry of an ordered water bilayer adsorbed on the TiO_2 (101) anatase surface; side and top views are given in the upper and lower parts of the figure, respectively. O atoms belonging to a first and a second water monolayers are represented by green and dark blue spheres, respectively. The figure also shows the structure of the (101) anatase surface when the water molecules are ideally removed. Circled water molecules represent the structural ad-layer unit shown in detail in Figure 2.

experimental results achieved at low temperature surface/vacuum conditions. The vibrational frequencies of the investigated systems have been obtained by calculating power spectra from the velocity autocorrelation functions. Such a procedure permits an accurate sampling of the system configurations as well as a better simulation of the experimental conditions.

Results and Discussion

Water Molecules on the (101) Anatase Surface. Origin of Short H Bonds. Preliminarily, it should be recalled that the bulk of anatase is characterized by six-fold coordinated Ti atoms (Ti_{6c}) surrounded by three-fold coordinated O atoms (O_{3c}) located at the vertices of a distorted octahedron. The (101) anatase surface presents rows of five-fold (under-)coordinated Ti atoms (Ti_{5c}) and of two-fold (under-)coordinated O atoms (O_{2c}) also referred to as bridging O atoms; see Figure 1.

In agreement with previous studies,^{8,9} present geometry optimization calculations have found several, almost degenerate configurations for a bilayer of water molecules in contact with the (101) anatase surface. The most ordered among these configurations, shown in Figure 1, can be used to point up some interesting features of that water bilayer. When the molecules belonging to the second layer are ideally removed, Figure 1 shows the configuration of the first water monolayer, which is characterized by water molecules adsorbed on the Ti_{5c} surface atoms. The desorption energy per molecule estimated for this monolayer (0.69 eV, in excellent agreement with experimental findings, see ref 10) is close to the corresponding value estimated for a single water molecule adsorbed on a surface Ti_{5c} atom. This fact indicates that on the (101) anatase surface, the Ti_{5c}

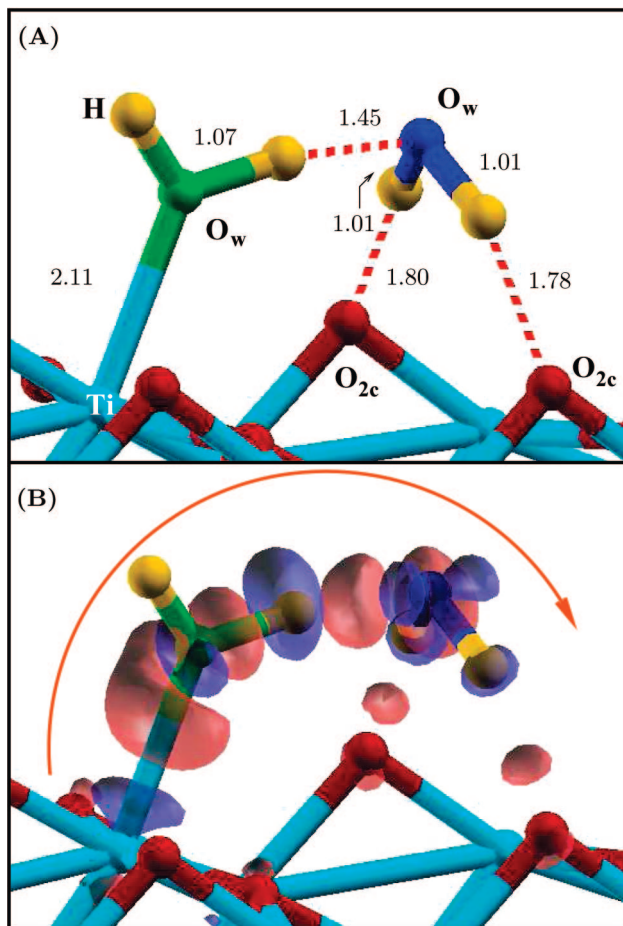


Figure 2. The structure and the difference density map $\rho[2\text{H}_2\text{O-anatase}] - (\rho[\text{H}_2\text{O}(\text{I})] + \rho[\text{H}_2\text{O}(\text{II})] + \rho[\text{anatase}])$ of a pair of water molecules adsorbed on the (101) anatase surface are given in the parts (A) and (B), respectively. Red (blue) zones of the difference map indicate an increase (decrease) of the charge density due to the surface-molecule interactions. The arrow indicates a charge transfer chain directed from the Ti_{5c} to the two O_{2c} surface atoms, passing through the water molecules.

absorption sites preferred by the water molecules are too far (3.81 Å) to permit the formation of an appreciable H-bond net. On the contrary, in the case of the (110) rutile surface the distance between two surface Ti atoms is considerably lower (2.99 Å) and the H-bond net plays an important role already at the monolayer coverage.^{22,23} Regarding the water bilayer, the molecules adsorbing over the first layer set up units of a two-molecules structure like that circled in the lower part of Figure 1. This structure is characterized by the formation of short H bonds (see Figure 2A), both between the two molecules ($\text{H}-\text{O}_w$) and between water molecules and bridging O_{2c} surface atoms ($\text{H}-\text{O}_{2c}$). It is worth noticing that such short bonds are not a special feature of an ordered water bilayer. They form indeed also in the case of geometry optimizations performed by starting with different initial configurations. Moreover, we can anticipate that the same bonds show a strong inertia to break during AIMD runs. We have carefully checked present results against possible artifacts due to the employed theoretical methods. As an example, geometry optimizations of bulk water (simulated by using 32 molecules) show the formation of H bonds having a typical length of about 1.9 Å in a quite good agreement with both experimental and theoretical findings.²⁴ Thus, the occurrence of short H bonds is peculiar of water molecules in contact with the (101) anatase surface. In agreement with the above

structural results, the desorption energy calculated for the two-molecules configuration of Figure 2A is 1.52 eV, that is, larger than twice the desorption energy estimated for an isolated molecule forming an $\text{O}_w-\text{Ti}_{5c}$ bond with a Ti_{5c} surface site (that is, 1.38 eV), thus indicating the formation of exceptionally strong H bonds. In fact, in the configuration of Figure 2A, only one of the two molecules forms an $\text{O}_w-\text{Ti}_{5c}$ bond, the second molecule being anchored to the surface only through two $\text{H}-\text{O}_{2c}$ and one $\text{H}-\text{O}_w$ hydrogen bonds, that is, roughly, these three H bonds are as strong as the $\text{O}_w-\text{Ti}_{5c}$ bond. The density difference map of this system, shown in Figure 2B, clarifies the special stability of this peculiar structure. As shown in Figure 2B, a charge transfer chain, indicated by the arrow, induces indeed a charge displacement from a Ti_{5c} to two O_{2c} surface atoms through the two water molecules, thus strengthening both the $\text{O}_w-\text{Ti}_{5c}$ bond, which is shorter than that formed by an isolated water molecule, and the three H bonds. We explain such a charge transfer in terms of an interface effect related to the ionic character of the O-Ti bonds in anatase and to the properties of the water molecules. In fact, it is generally assumed the formation of Ti_{6c}^{+4} and O_{3c}^{-2} pairs in the bulk of anatase. This implies that a fraction of two-thirds of electronic charge is transferred from a Ti atom to each of its six O neighbors. Thus, formally, undercoordinated Ti_{5c} and O_{2c} surface atoms carry an excess and a defect of electronic charge, respectively. We can assume therefore that in the charge transfer chain of Figure 2B, some excess of electronic charge on a surface Ti_{5c} atom is transferred to the O_{2c} surface atoms through the pair of water molecules. Moreover, as shown in the same figure, such a transfer is permitted by the peculiar properties of the water molecules, that is, by a rearrangement of the electronic charge around the O_w atoms and between the H and O atoms involved in the formation of the H bonds. The short H bonds forming at the water-anatase interface induce also peculiar features in the IR spectra of water molecules, as it will be discussed in a following section.

AIMD Simulations. The results of AIMD calculations confirm the picture given by the above geometry optimization results. AIMD runs have been started from disordered optimized configurations of a water bilayer adsorbed on the anatase surface. Further runs starting from the ordered configuration shown in Figure 1 provide similar results. In this investigation, the attention is focused on the structure of the H-bond network occurring at the water/anatase interface and on the variations of its properties on a wide range of temperature between 50 and 300 K. More specifically, an analysis has been performed of the radial distribution functions related to the formation of H bonds as well as of the vibrational frequencies of the water bilayer. Both quantities have been estimated by performing three different AIMD simulations at the temperature values of 50 K (T1), 150 K (T2), and 300 K (T3).

Radial Distribution Functions ($g(R)$) centered on water H atoms and related to the lengths of the $\text{H}-\text{O}_w$ water-water H bonds and the $\text{H}-\text{O}_{2c}$ water-surface H bonds are shown in Figure 3A,B, respectively. At the T1 temperature, the water bilayer is quite rigid. Further radial distribution functions (not shown here) indicate indeed that the O_w atoms of the first layer are tightly bound to the surface Ti_{5c} atoms with $\text{Ti}-\text{O}_w$ distances in a short-range of values between 2.1 Å and 2.4 Å. Moreover, the molecules of the second layer are involved in a quite complex balance between intermolecular (cohesive) and surface-molecule (adhesive) interactions. In the former case, they form two different types of short $\text{H}-\text{O}_w$ bonds with the first layer molecules: one very short bond ($g(R)$ peaked at 1.52 Å in Figure 3 (A)) is related to a configuration similar to that shown in

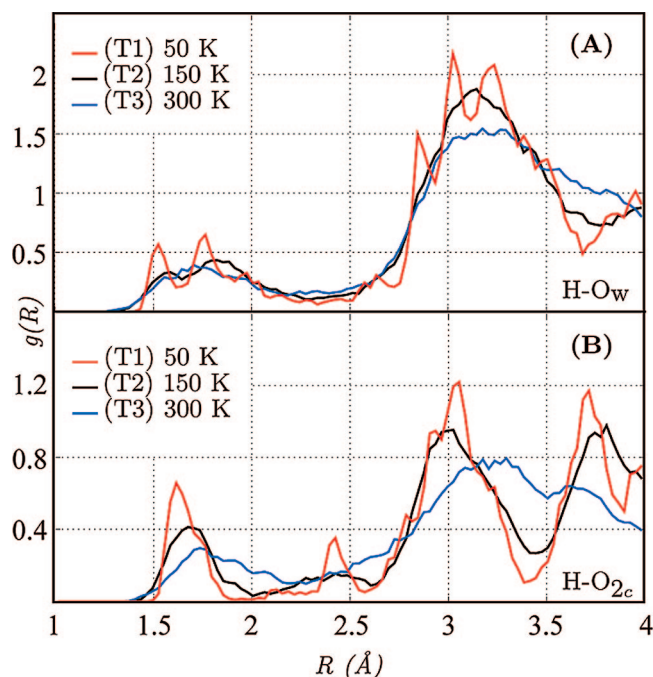


Figure 3. Radial distribution functions estimated for a water bilayer adsorbed on the anatase surface and centered on the water H atoms: (A) distances between these H atoms and water O_w atoms (covalent OH bonds are not shown), and (B) distances between these H atoms and surface O_{2c} atoms. The plots shown in the figure correspond to AIMD simulations performed at three different temperatures.

Figure 2 (A); a second short bond ($g(R)$ peaked at 1.76 Å in Figure 3 (A)) is related to a configuration slightly different from that shown in Figure 2 (A), where only one H atom points toward the O_{2c} surface atoms. Regarding the adhesive interactions, the second-layer molecules form short H– O_{2c} bonds ($g(R)$ peaked at 1.61 Å in Figure 3 (B)). The above adhesive and cohesive interactions give rise to a dense network of short H bonds (Figure 3 shows also several peaks, at the T1 temperature, in the range of 2.5 to 4.0 Å which do not correspond to H bonds, rather to distances between H atoms of a water molecule and O atoms of neighboring water molecules). At the T2 temperature, the structure of the water bilayer undergoes little changes with respect to the previous case. Intermolecular and surface-molecule H bonds become slightly longer ($g(R)$ peaked at 1.58 Å and 1.81 Å in Figure 3 (A), and at 1.68 Å in Figure 3 (B), respectively), and $g(R)$ features become larger, stating a greater mobility of the water layers. It may be worth noticing that even the radial distribution functions reported in ref 8 and corresponding to an AIMD run at 160 K show the occurrence of short H– O_{2c} and H– O_w bonds (1.6–1.7 Å), in agreement with the present T2 results. The above results also agree with experiments showing that both the first and second water layers are thermodynamically stable in ultra high vacuum (UHV) conditions up to the temperature of 190 K, when the second layer desorbs.¹⁰ At the T3 temperature, experimentally, both the water layers are unstable in UHV conditions. Notwithstanding, we have performed AIMD simulations also at this temperature for two reasons. First, IR features of molecular water adsorbed on the anatase surface in air flow²⁵ or mild vacuum²⁶ conditions are observed up to 423 K.^{25,26} Second, RT calculations may better simulate real photocatalytic processes. During the T3 AIMD run, the first layer of water molecules still maintains a symmetrical order, i.e., the O_w atoms are bound to the Ti_{5c} surface atoms, while the H bonds with the molecules of the second layer are weakened and elongated. Moreover, the

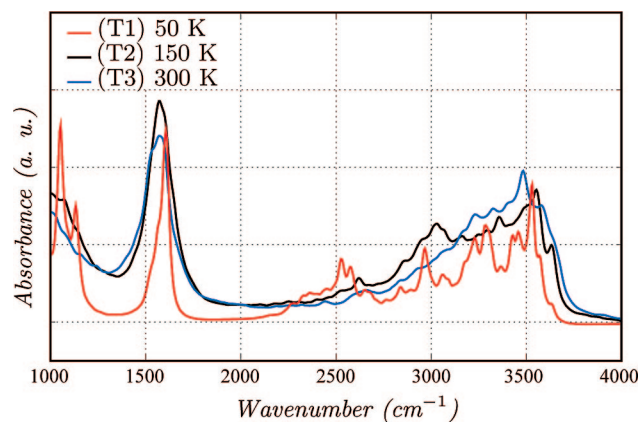


Figure 4. Vibrational spectra of a water bilayer adsorbed on the anatase surface, as obtained from AIMD simulations. The three plots shown in the figure are related to the three different temperatures considered in the simulations.

second layer has no more a definite structure and the molecules are free to move above the first layer.²⁷ Both the H– O_w and H– O_{2c} distribution functions reflect these structural changes: the H-bond peaks are indeed enlarged and shifted toward longer bonds, approaching the length of about 1.9 Å,²⁴ characteristic of bulk water H bonds. Finally, every kind of fine structure of the $g(R)$ s is completely lost.

The water vibrational spectra obtained by a Fourier transform of the velocity autocorrelation functions given by the AIMD runs are shown in Figure 4. These spectra present peculiar features, related to the formation of short H bonds, which closely match the above radial distribution functions. They can be divided in three main zones: (i) a zone above 2000 cm^{-1} , which contains the ν_{OH} stretching modes of water molecules; (ii) a zone between 1300 and 2000 cm^{-1} , containing the δ_{OH} bending modes of water molecules; and (iii) a zone below 1300 cm^{-1} , containing the crystal phonons and the librational modes of water molecules.^{28,29}

The ν_{OH} stretching modes of the water molecules adsorbed on the anatase surface are greatly affected by the formation of the above strong H bonds which, generally, lower their frequency. In detail, the low temperature T1 spectrum shows a complex fine structure in which at least four different kinds of vibrational modes can be isolated, grouped around the 2530, 2970, 3290, and 3530 cm^{-1} frequencies. Among such four bands, the first three can be assigned to the three kind of short H bonds discussed in the $g(R)$ s analysis (i.e., the H bonds with lengths of 1.52, 1.61, and 1.76 Å in the order). The highest frequency band is related to modes of the second layer molecules having H atoms pointing upward and free from any bonding. The spectral features characterizing the T1 spectrum are still recognizable in the T2 spectrum, although they are shifted to higher frequencies, 2620, 3030, 3360, and 3560 cm^{-1} , due to a weakening of the H bonds. Finally, the T3 spectrum shows only an unresolved broadband centered at about 3400 cm^{-1} which relates with the disappearance of short H bonds. Such a spectral feature is very similar to that shown at RT by a TiO_2 /water interface⁷ or hydrated TiO_2 samples.²⁶

The δ_{OH} bending modes of water molecules adsorbed on the anatase surface do not show the complex structure found for the stretching modes. δ_{OH} modes are generally raised in frequency by the formation of H bonds. However, as discussed above, the H-bond network weakens at increasing temperatures. Thus, a very sharp band in the T1 spectrum, peaked at 1610 cm^{-1} , is broadened and slightly shifted to lower frequencies

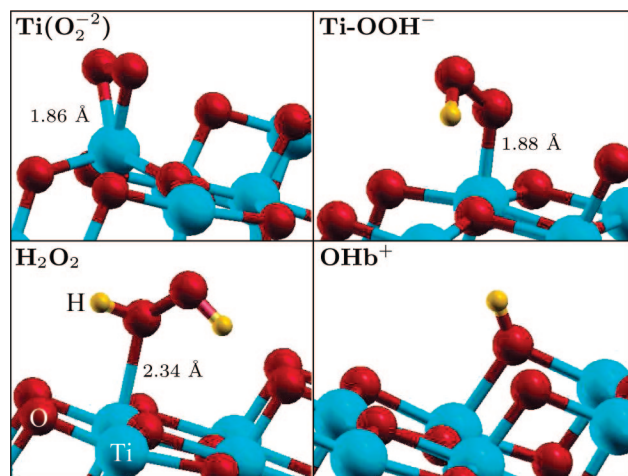
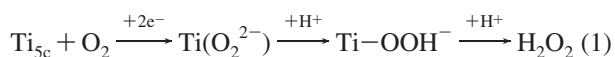


Figure 5. Structure of different intermediates of the O₂ photoreduction reaction forming close to or at the anatase surface.

moving to higher temperatures. At the T3 temperature, the δ_{OH} band is peaked at 1580 cm⁻¹, which is in quite good agreement with the experimental findings.^{7,26}

Regarding the low frequency modes, experimentally the tail of surface phonons is observed at frequencies lower than about 1200 cm⁻¹.²⁹ Such a tail is well represented in Figure 4 in the cases of the T2 and T3 spectra. T1 spectra is considerably different due to the occurrence of two clearly visible bands peaked at 1050 cm⁻¹ and 1130 cm⁻¹. These bands can be related to the bands estimated in the 500–800 cm⁻¹ range for the librational modes of water in ice.²⁸ Their appearance at higher frequencies in the T1 spectra support the occurrence of a rigid and H-bonded structure of water molecules as well as of special structures, as the one shown in Figure 2.

Oxygen Photoreduction Intermediates. In the O₂ photoreduction reaction, photogenerated electrons are trapped by oxygen molecules through surface-molecule charge transfer processes, as described in detail in refs 6, and 7. These processes lead to the formation of charged surface peroxy species, Ti(O₂²⁻) in Figure 5, which behave as very efficient traps for solvated H⁺ ions. Accordingly, the following reaction path was proposed^{6,7}



where a surface Ti(O₂²⁻) peroxy forms, by protonation, a charged Ti-OOH⁻ hydroperoxy intermediate and by further protonation a weakly adsorbed hydrogen peroxide molecule; see Figure 5. The reaction rate is massively enhanced when the TiO₂ surfaces are placed in contact with a low pH water solution.⁷ Moreover, such a low pH environment induces the titration of basic bridging O_{2c} sites, which leads to the formation of charged OHb⁺ surface bridging hydroxyls; see Figure 5.⁶

In our previous paper,⁶ the experimental vibrational lines reported in the MIRIR study⁷ have been assigned to intermediates of the O₂ photoreduction on the grounds of harmonic vibrational calculations performed upon equilibrium geometries. Such assignments are summarized in Table 1. Strong H bonds played a key role in such assignments. In particular, in the case of bending modes they induced a raising of the usual bending vibrations up to higher frequencies (δ_{OH} bending modes in Table 1) and the appearance of new vibrational modes (δ'_{OH} bending modes in Table 1) as detailed in ref 6. In the present study, we have considered these assignments at the light of the above

TABLE 1: Assignments of the Experimental MIRIR Vibrational Frequencies (Reference 7) to Intermediates of the O₂ Photoreduction As Reported in Reference 6^a

MIRIR study			theory		
lines	species	mode	lines	species	mode
943	Ti(O ₂)	ν_{OO}	958	Ti(O ₂ ²⁻)	ν_{OO}
			971	Ti-OOH ⁻	ν_{OO}
887	H ₂ O ₂	ν_{OO}	898	H ₂ O ₂	ν_{OO}
838	Ti-OOH	ν_{OO}		<i>b</i>	
1250–1120	H ₂ O ₂	δ_{OH}	1184	H ₂ O ₂	δ'_{OH}
	Ti-OOH		1151	Ti-OOH ⁻	δ'_{OH}
			(1075)	OH-b ⁺	δ_{OH}
1023	OOH	ν_{OO}	1014	OH-b ⁺	δ'_{OH}
			(1075)	OH-b ⁻	δ_{OH}

^a ν_{OO} and δ_{OH} indicate O–O stretching and O–H bending frequencies, respectively. δ'_{OH} modes are peculiar bending modes induced by short H bonds formed by the intermediates with surrounding water molecules. Alternative assignments are in parentheses. ^b Further theoretical results (not reported in ref 6) assign this line to an intermediate of the water photooxidation process.³⁴

discussion on the short H bonds forming at the water-anatase interface. Thus, we have investigated first the equilibrium configurations of the Ti-OOH⁻, H₂O₂, and OHb⁺ intermediates embedded in a bilayer of water molecules as well as the origin of the relative short H bonds. Then, we have investigated the structural and vibrational properties of the same intermediates by performing AIMD simulations at the temperature of 300 K in order to evaluate the combined effects of the H bonds and temperature on the assignments of the above vibrational lines.

Short H Bonds. Among the above intermediates, the OHb⁺ species and the H₂O₂ molecules give rise to short H bonds similar in nature to those forming between water molecules in contact with the anatase surface. On the contrary, the Ti-OOH⁻ do not. In detail, Figure 6A shows the stable configuration and the short H bonds formed by an OHb⁺ and two neighboring water molecules, as given by geometry optimization procedures applied to this surface group embedded in a bilayer of water molecules. In Figure 6B, a density difference map of the same system shows a charge displacement, indicated by the arrow, from a Ti_{5c} surface atom to the OHb⁺ and a surface O_{2c} atom, which is mediated by the two water molecules in a way quite similar to that shown in Figure 2B. Such a result can be explained by taking into account that the defect of electronic charge assumed above for an O_{2c} bridging atom is not nullified by its bonding with a H⁺ ion. Thus, the O_{2c} bridging atoms and the OHb⁺ surface species play the same role in the charge transfer process involving the water molecules and the Ti_{5c} surface atoms.

In the case of a H₂O₂ molecule embedded in a water bilayer, the stable configuration given by the geometry optimization procedures shows that this molecule forms a weak bond with a Ti surface atom and a short H bond with a surrounding water molecule. The corresponding density difference map (not shown here) indicates that the H₂O₂ molecule is involved in a charge transfer from a Ti_{5c} surface atom to an O bridging atom similar to that shown in Figure 2B, where the H₂O₂ molecule plays the same role of a water molecule.

Finally, in the case of the Ti-OOH⁻ intermediate, the results of the geometry optimization procedure applied to this species embedded in a water bilayer correct the results reported in our previous study.⁶ In fact, the formation of short H bonds between

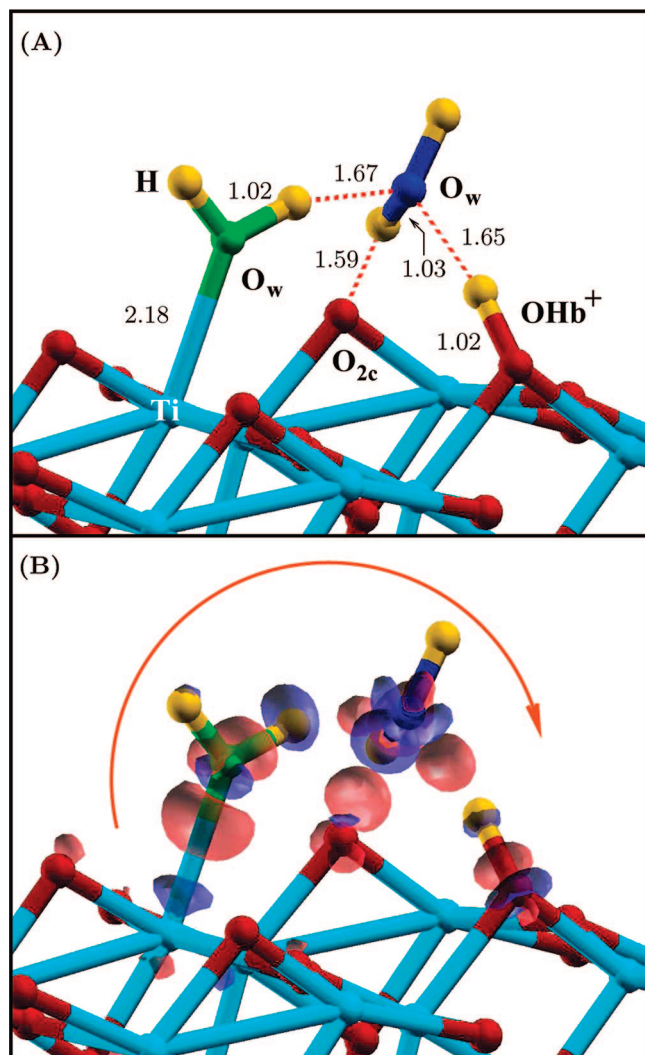


Figure 6. The structure and the difference density map $\rho[2\text{H}_2\text{O}-\text{OHb}^+-\text{anatase}] - (\rho[\text{H}_2\text{O}(\text{I})] + \rho[\text{H}_2\text{O}(\text{II})] + \rho[\text{OHb}^+\text{ anatase}])$ of an OHb^+ group and two water molecules adsorbed on the (101) anatase surface are given in parts (A) and (B), respectively. Red (blue) zones of the difference map indicate an increase (decrease) of the charge density due to the surface-molecule interactions. The arrow indicates a charge transfer chain directed from the Ti_{5c} to the OHb^+ group and a surface O_{2c} , passing through the water molecules.

the $\text{Ti}-\text{OOH}^-$ and a water molecule, indicated by our previous results, occurs only when this intermediate is surrounded by a small number of water molecules. On the contrary, when embedded in a water bilayer, the $\text{Ti}-\text{OOH}^-$ species does not mediate a charge transfer between Ti_{5c} and O_{2c} surface atoms, likely because such a mediating role is played more efficiently by the network of the water molecules. As a matter of fact, the $\text{Ti}-\text{OOH}^-$ forms a typical H bond (1.95 Å) with one of the surrounding water molecules.

AIMD Simulations at 300 K. The combined effects of H bonds and temperature on the structural and vibrational properties of the above intermediates have been investigated by performing two distinct AIMD simulations lasting for about 12 ps. The first one regards a system containing one H_2O_2 molecule embedded in a water bilayer at the anatase surface. The second one regards a system containing both a $\text{Ti}-\text{OOH}^-$ group and an OHb^+ group, not directly interacting each other and both embedded in a water bilayer. Such an arrangement permits to include in a same, neutral supercell two oppositely charged species resulting from a donor-acceptor $\text{OHb}-\text{Ti}-\text{OOH}$ compensation.⁶

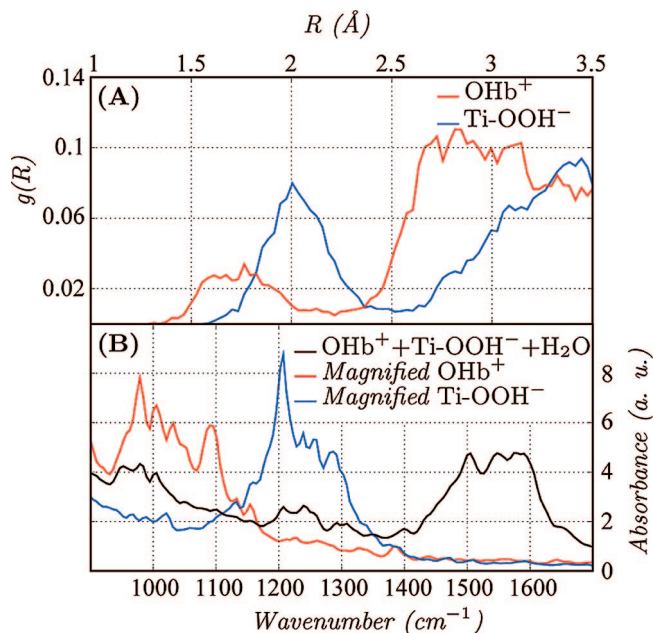


Figure 7. Radial distribution functions (A) and vibrational spectra (B) of the $\text{Ti}-\text{OOH}^-$ and OHb^+ intermediates of oxygen photoreduction, adsorbed on the anatase surface and embedded into a water bilayer, as given by AIMD simulations at 300 K. The distribution functions are centered on the H atoms of the surface species and related to the distances between these H atoms and the water O atoms. Magnified spectra are related to the autocorrelation functions of a subset of atoms, including only those of the adsorbed intermediates.

Radial distribution functions centered on the H atoms of the $\text{Ti}-\text{OOH}^-$ and OHb^+ surface species and related to the H bonds formed by these species with the O_w atoms of the surrounding water molecules are shown in Figure 7A. In the case of the OHb^+ group, the corresponding distribution function shows a broad feature approximately centered around 1.6–1.7 Å, thus indicating that this group forms a short H bond with a neighboring water molecule even at RT. On the contrary, the H bonds formed by the $\text{Ti}-\text{OOH}^-$ group with the surrounding water molecules are particularly loose, the corresponding $g(R)$ being peaked at 2.01 Å. These RT results confirm the picture given by the geometry optimization procedures.

The vibrational spectra corresponding to the $\text{Ti}-\text{OOH}^-$ and OHb^+ species match with the different features of their $g(R)$; see the magnified spectra shown in Figure 7B. In detail, the magnified OHb^+ plot shown in the figure represents the contribution of the δ_{OH} bending frequencies of the very OHb^+ species to the vibrational spectrum, as extracted from the AIMD trajectories, and the analogue for the $\text{Ti}-\text{OOH}^-$ group. The OHb^+ contribution corresponds to an irregular band approximately ranging between 1000 and 1100 cm^{-1} which nicely agrees with the measured band peaked at 1023 cm^{-1} ; see Table 1. This result also agrees with a hardening of the δ_{OH} bending frequencies due to the formation of short H bonds already suggested in our previous study.⁶ In that study, we reported indeed that a frequency value of 820 cm^{-1} calculated for the isolated OHb^+ group is raised and split to the values of 1014 and 1075 cm^{-1} when the group forms short H bonds with few surrounding water molecules.⁶

At variance with the case of the OHb^+ group, the weaker H bonds formed by the $\text{Ti}-\text{OOH}^-$ group with the surrounding water molecules scarcely affect the value of the corresponding δ_{OH} bending frequency. The magnified spectrum corresponding to the $\text{Ti}-\text{OOH}^-$ group contains a broadband peaked at 1210

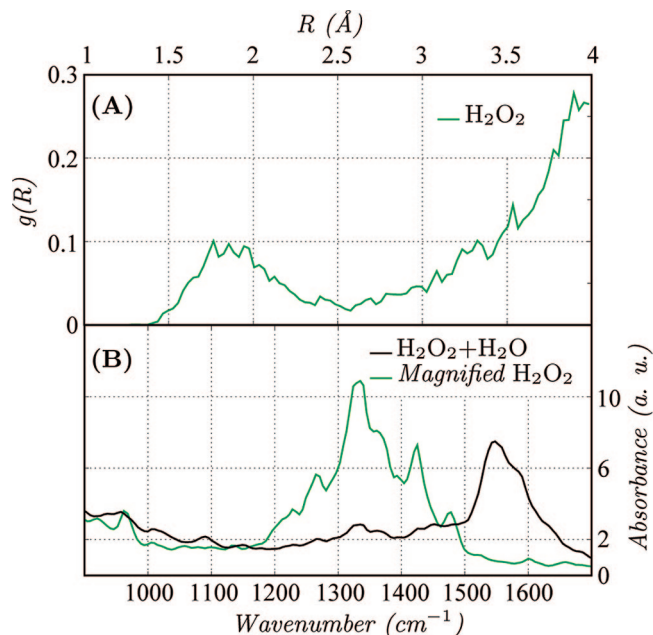


Figure 8. Radial distribution functions (A) and vibrational spectra (B) of an H₂O₂ molecule embedded into a water bilayer and adsorbed on the anatase surface, as given by AIMD simulations at 300 K. The distribution function is centered on the hydrogen peroxide H atoms and related to the distance between these H atoms and the water O atoms. The magnified spectrum is related to the autocorrelation functions of a subset of atoms, including only those of the H₂O₂ molecule.

cm⁻¹ and related to the δ_{OH} vibrational mode. This band very nicely agrees with the experimental band ranging between 1120 and 1250 cm⁻¹; see Table 1. On the other hand, this result rules out the assignment proposed in our previous study.⁶ In that case, the experimental frequencies were related to δ'_{OH} hindered modes induced by short H bonds pertaining to a Ti–OOH⁻ group surrounded by a few water molecules.

In the case of the H₂O₂ molecule, the radial distribution function shown in Figure 8A corresponds to the sum of the radial functions centered on each of the two H atoms and related to the H bonds formed with the O_w atoms of the surrounding water molecules. The $g(R)$ plot shows a broad feature, approximately centered around 1.7 Å. However, an analysis of the AIMD trajectories shows that such a result is related to the occurrence of a complex balance between short and long H bonds: when one side of the molecule is tightly joining a water molecule, the other side experiments indeed a loose H bond. Thus, the above value of 1.7 Å represents a mean length of the H bonds formed by this molecule. The peculiar character of the H₂O₂ molecule affects also the corresponding vibrational spectrum, shown in Figure 8B. Once more, the contribution corresponding to the δ_{OH} bending frequencies of the H₂O₂ molecule is represented by a magnified plot. Such a contribution, characterized by a very broadband ranging from 1200 to 1500 cm⁻¹, corresponds to all of the different δ_{OH} bending modes of the hydrated H₂O₂ molecule.

Experimentally, values of 1266 and 1315 cm⁻¹ have been reported for the δ_{OH} bending frequencies of gaseous hydrogen peroxide, which are raised to 1385 and 1407 cm⁻¹ in a crystalline phase, where they are also accompanied by the appearance of hindered modes with frequency values of 650 and 808 cm⁻¹.³¹ Thus, the AIMD spectrum shown in Figure 8 seems to reflect the properties of H₂O₂ molecules forming both strong and weak H bonds. However, in the MIRIR spectrum

only weak and not assigned traces can be found in the frequency range where the AIMD results locate the H₂O₂ δ_{OH} bending modes. Some different effects may concur to explain such an apparent disagreement: (i) H₂O₂ molecules formed in the oxygen photoreduction are oxidized more easily than water molecules by surface trapped photogenerated holes.^{32–34} They can be readily subtracted from the spectral investigation; (ii) the MIRIR technique employed to acquire the vibrational spectrum is an especially interface-sensitive one. Thus, it detects quite efficiently the Ti(O₂⁻²) and Ti–OOH⁻ intermediates, which are strongly chemisorbed species (we have calculated adsorption energy values of 2.37 and 2.17 eV for these species, respectively). On the contrary, the H₂O₂ molecule is weakly adsorbed on the anatase surface, the adsorption energy value being 0.55 eV. Thus, it can easily desorb from the surface and pass into the solution bulk, by escaping from the IR measure; (iii) in our previous study,⁶ we calculated the relative intensities of all the intermediates of the above reaction path. The achieved results show that the more an adsorbed species is close to the surface, the higher spectral intensity is estimated. For example, being 1.0 the arbitrary intensity of the stretching band of a HF molecule (such a molecule has been inserted in the vacuum zone of every supercell as a common reference), the relative intensity values estimated for the ν_{OO} stretching modes of Ti(O₂⁻²), Ti–OOH⁻ and H₂O₂ species are equal to 20.0, 10.9 and 0.9, respectively. A similar trend has been found for the δ_{OH} bending modes of the Ti–OOH⁻, H₂O₂, and OHb⁺ species. Thus, we suggest that no experimental band can match the weak δ_{OH} contributions of the H₂O₂ molecule. Accordingly, the experimental band peaked at 887 cm⁻¹ and assigned to the ν_{OO} stretching mode of H₂O₂ (see Table 1) is appreciable only as a shoulder very close to the strong band peaked at 943 cm⁻¹ in the MIRIR spectra.

Conclusions

The nature of short H bonds formed by water molecules in contact with the (101) anatase surface and their effects on the structural and vibrational properties of a water bilayer adsorbed on the same surface have been investigated by performing total energy calculations and AIMD simulations at different temperatures. Present results show that these peculiar H bonds, stronger than the H bonds usually formed in bulk water, originate from a water/anatase interface effect, which induces an electronic charge transfer from surface Ti_{5c} atoms to surface O_{2c} atoms, mediated by the water molecules. AIMD simulations performed at low temperature predict a structure of the water bilayer characterized by short H bonds which also induce the appearance of peculiar features in the corresponding vibrational spectra. Such features persist at a temperature of 150 K. At room temperature, instead the properties of adsorbed water start to resemble those of bulk water. These results reveal therefore the existence of peculiar properties of a water bilayer in contact with the anatase surface, which should stimulate experimental investigations. Moreover, present results show that the same interface effect can significantly influence the atomic arrangement and the vibrational properties of intermediates of the oxygen photoreduction reaction. When embedded in a water bilayer, some of these intermediates take part indeed in the same charge transfer processes involving the water molecules, as well as in the formation of short H bonds. AIMD simulations show that these short H bonds are still present at room temperature. Moreover, they give estimates of the vibrational frequencies for the same intermediates which are in a quite good agreement with the experimental findings. Such an agreement supports the

unifying theoretical picture proposed here for water molecules and intermediates in contact with the anatase surface.

Finally, present results indicate that it is mandatory to take into account the combined effects of the water/anatase interface and temperature both for a better understanding of heterogeneous catalysis processes and to achieve estimates of measurable quantities, as vibrational frequencies, reliable and close to experimental data.

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Supporting Information Available: Details on the theoretical methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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