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Journal:	<i>Journal of Materials Chemistry A</i>
Manuscript ID	TA-ART-07-2024-004750.R1
Article Type:	Paper
Date Submitted by the Author:	19-Aug-2024
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# Enhancement of hole capture and water dissociation on rutile TiO<sub>2</sub>(110) by intermolecular hydrogen bonding: time-domain ab initio study

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**Abstract:** Photocatalytic water splitting has been a focal point of research to solve the energy and environmental issues. However, the understanding of photocatalytic water splitting and coupled dynamics of photogenerated charge carriers at molecule/semiconductor interfaces is still limited. We have combined ab initio molecular dynamics, real-time time-dependent density functional theory, and nonadiabatic molecular dynamics to study dissociation of water and capture of photogenerated holes on pristine rutile TiO<sub>2</sub>(110) surface. Our simulations indicate that intermolecular hydrogen bonding (IHB) between water molecules facilitates water dissociation. The dissociation energy of water molecules in pristine, non-dissociated structure is reduced by 15%, from 0.26 eV to 0.21 eV, due to IHB. In the semi-dissociated structure, the dissociation energy of water molecule is only 0.13 eV, owing to proton transfer induced by IHB. In the semi-dissociated structure, IHB between H<sub>2</sub>O and terminal hydroxyl (O<sub>t</sub>H) stabilizes the dissociated structure. Further, IHB promotes spatial isolation of O<sub>t</sub>H and bridging hydroxyl (O<sub>br</sub>H) and inhibits their recombination. The stabilized dissociated structure activates high-frequency vibrational modes that increase the nonadiabatic coupling and promote hole capture on a femtosecond timescale, accelerating the capture rate by 36%. The findings provide important insights into photo-dissociation of water on rutile TiO<sub>2</sub>(110), particularly shedding

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light on the impact of key intermediates on the photocatalytic process.

**Keywords:** Rutile  $\text{TiO}_2(110)$ , water splitting, semi-dissociation, time-dependent density functional theory, nonadiabatic molecular dynamics

## 1. Introduction

Hydrogen energy, as an efficient and clean energy source, holds tremendous potential for addressing the energy crisis and reducing carbon emissions. Photolysis of water, a crucial technique, harnesses solar energy to split water into hydrogen and oxygen, thereby enabling efficient hydrogen production.<sup>1-3</sup> Since the pioneering discovery of photocatalytic water splitting on TiO<sub>2</sub> electrodes under ultraviolet light by Fujishima and colleagues in 1972,<sup>4</sup> photocatalytic water splitting on TiO<sub>2</sub> has garnered significant attention and serves as a model system for studying water dissociation.<sup>5-12</sup> The dissociation of water on TiO<sub>2</sub> surface is influenced by various factors, such as surface defects, adsorption structures, surface water coverage, and charge distribution.<sup>13-24</sup> Many current efforts focus on photocatalytic reactivity mediated by defects. For example, numerous experiments and theoretical works suggest that the dissociation of water on rutile TiO<sub>2</sub>(110) occurs at surface bridging oxygen (O<sub>br</sub>) vacancies, but the dissociation of H<sub>2</sub>O on perfect rutile (*p*-rutile) TiO<sub>2</sub>(110) remains elusive.<sup>13, 25-30</sup>

Over the years, numerous experimental and theoretical studies have attempted to elucidate whether water molecules dissociate on the *p*-rutile TiO<sub>2</sub>(110) surface, but the current conclusions remain controversial. On the one hand, some experimental and theoretical studies suggest that water molecule dissociation occurs only on oxygen vacancies of TiO<sub>2</sub>(110) surface. For example, using scanning tunneling microscopy (STM), Brookes et al. observed that only bridging hydroxyl (O<sub>br</sub>H) is formed by the dissociation of water at oxygen vacancies on the rutile TiO<sub>2</sub>(110) surface.<sup>13, 25</sup> They did not observe terminal hydroxyl (O<sub>t</sub>H) adsorbed on five-coordinated Ti sites (Ti<sub>5c</sub>) formed by the dissociation of water at non-oxygen vacancies, therefore they suggested that water molecules cannot dissociate on the *p*-rutile TiO<sub>2</sub>(110) surface. Density functional theory (DFT) simulations conducted by Liu et al. indicated that water molecules do not dissociate on the *p*-rutile TiO<sub>2</sub>(110) surface at coverages of 0.5 mol/L and 1 mol/L.<sup>31</sup> On the other hand, some studies suggest that water molecules can dissociate on the *p*-rutile TiO<sub>2</sub>(110) surface. Walle et al. utilized synchrotron radiation photoelectron spectroscopy to find that water dissociation at oxygen vacancies competes with dissociation at defect-free regions.<sup>26, 29</sup> Using STM, Yang et al. observed the appearance of O<sub>t</sub>H on the Ti<sub>5c</sub> site of *p*-rutile TiO<sub>2</sub>(110) under ultraviolet light exposure.<sup>30, 32</sup> Their work provides direct

evidence for photoinduced water dissociation on the *p*-rutile  $\text{TiO}_2(110)$  surface. In addition to the experiments, quantum molecular dynamics (MD) simulations also revealed that the assistance of surface  $\text{O}_{\text{br}}$  contributes to the water dissociation on *p*-rutile  $\text{TiO}_2(110)$ .<sup>33</sup>

Although some studies suggest that water molecules can dissociate on the *p*-rutile  $\text{TiO}_2(110)$  surface, experimental results demonstrate that the efficiency of photocatalytic water decomposition on this surface is very low. Consequently, most studies conclude that surface-bridging oxygen vacancies are the key factor facilitating water dissociation. Du et al. observed through high-resolution STM that once  $\text{O}_{\text{br}}\text{H}$  and  $\text{O}_{\text{t}}\text{H}$  occupy adjacent positions, they immediately disappear due to the reformation of water.<sup>34</sup> This discovery provides a clue for explaining the low efficiency of photoinduced water molecule dissociation on *p*-rutile  $\text{TiO}_2(110)$ . It is hard for the  $\text{O}_{\text{t}}\text{H}$  species generated by the dissociation of water to desorb from  $\text{Ti}_{5\text{c}}$  and migrate along the surface, preventing separation of  $\text{O}_{\text{br}}\text{H}$  and  $\text{O}_{\text{t}}\text{H}$  and leading to formation of  $\text{O}_{\text{br}}\text{H}/\text{O}_{\text{t}}\text{H}$  pairs, referred to as “pseudo-dissociated” water.<sup>35</sup> Car-Parrinello MD simulations also indicated that  $\text{O}_{\text{br}}\text{H}/\text{O}_{\text{t}}\text{H}$  pairs undergo rapid recombination on *p*-rutile  $\text{TiO}_2(110)$ .<sup>36</sup> Thus, the rapid recombination of  $\text{O}_{\text{br}}\text{H}/\text{O}_{\text{t}}\text{H}$  pairs in the pseudo-dissociated state may be the key factor limiting effective photoinduced dissociation of water. It is noteworthy that both experiments and theoretical simulations indicate that the adsorption of water molecules on the rutile  $\text{TiO}_2(110)$  in the form of dimers or one-dimensional water chains is more favorable compared to monomer adsorption, with these molecules interconnected through hydrogen bonds.<sup>15, 37, 38</sup> Experiments show that water molecules adsorbed in the dimeric form exhibit a higher dissociation efficiency compared to monomer adsorption, which is attributed to cooperativity mediated by strong intermolecular hydrogen bonds (IHB).<sup>32</sup> Up to now, the detailed mechanism of water molecule dissociation on *p*-rutile  $\text{TiO}_2(110)$  remains unclear, particularly regarding how to overcome the recombination of the  $\text{O}_{\text{br}}\text{H}/\text{O}_{\text{t}}\text{H}$  pairs in the pseudo-dissociated state and effectively capture photogenerated holes. Further research is needed to address these questions.

Numerous first-principles calculations and molecular dynamics simulations of the water-splitting process focused on its electronic and thermodynamic aspects. These simulations are based on the Born-Oppenheimer approximation, and thus, are conducted in the ground

electronic state. More advanced methods are needed for studying the dynamics of photogenerated hole capture at the surface, which is important for a comprehensive understanding of the mechanism of water splitting on surfaces. Time-domain ab initio nonadiabatic molecular dynamics (NAMD) simulations can investigate excited-state charge transfer, relaxation, and recombination processes at photocatalytic interfaces at the atomic level, providing new insights into the mechanisms of photocatalytic surface reactions.<sup>39</sup> Using NAMD simulations, Kaxiras, Meng et al., studied the photo-driven oxidation and dissociation of H<sub>2</sub>O and CH<sub>3</sub>OH on the rutile TiO<sub>2</sub>(110) surface.<sup>40, 41</sup> Their work revealed the reaction intermediates, adsorption structures, and timescales of photogenerated carrier capture. Zhao et al. discovered through ab initio NAMD simulations that the activation of the bending and asymmetric stretching vibrational modes of CO<sub>2</sub> molecules is key to capturing photogenerated electrons, a process that can be completed within 100 fs.<sup>42</sup> The capture of surface photogenerated charges has become an essential aspect of studying photocatalytic reaction mechanisms.

In this study, we employed DFT, time-dependent DFT (TD-DFT), and nonadiabatic (NA) MD methods to investigate the dynamics of water dissociation and capture of photogenerated holes on *p*-rutile TiO<sub>2</sub>(110). Ab initio MD (AIMD) simulations reveal that water monolayer undergoes spontaneous partial dissociation (semi-dissociation). Strong hydrogen bonds (HBs) between O<sub>br</sub>H and O<sub>t</sub>H in the semi-dissociated system stabilize the dissociated structure and inhibit recombination of O<sub>br</sub>H/O<sub>t</sub>H pairs. Moreover, the dissociation of water with a lowered reaction barrier, induced by HBs, leads to spatial isolation of the O<sub>br</sub>H and O<sub>t</sub>H species, further preventing their recombination. NAMD simulations show that capture of photogenerated holes in the semi-dissociated system is significantly accelerated compared to the monolayer system and occurs on a femtosecond timescale. This is primarily attributed to the enhanced nonadiabatic coupling between adjacent states. The electron-vibrational interaction analysis reveals that hole capture is mainly promoted by high-frequency vibration modes that are activated after the initial semi-dissociation. The stronger electron-phonon coupling and enhanced high-frequency vibrational modes accelerate energy relaxation leading to the photogenerated hole capture. Our study emphasizes the importance of intermediates during the

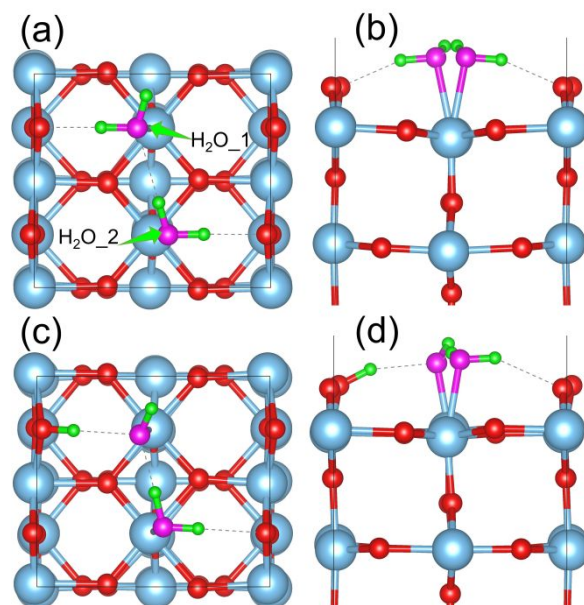
photocatalytic water dissociation process on metal oxide surfaces.

## 2. Computational methods

A  $2 \times 1$  supercell comprised by five layers of rutile  $\text{TiO}_2$  (O-Ti-O) is constructed as our model for the water splitting. To eliminate dangling bonds, pseudo-hydrogens were added to saturate the bottom Ti and O atoms, with assigned charges of +1.33e and +0.66e, respectively, based on the previous work.<sup>39, 43</sup> The calculated rutile  $\text{TiO}_2(110)$  surface model has lattice parameters of  $a = 5.93 \text{ \AA}$ ,  $b = 6.57 \text{ \AA}$ , and  $c = 30.70 \text{ \AA}$ . The model consists of 64 atoms, including 20 oxygen atoms, 40 titanium atoms, and 4 pseudo-hydrogens. A  $15 \text{ \AA}$  vacuum layer was added perpendicular to the surface to eliminate interactions introduced by the periodic arrangement.

The geometry optimization, electronic structure calculations, and adiabatic molecular dynamics simulations were performed using the Vienna Ab initio Simulation Package (VASP) software.<sup>44</sup> The Perdew-Burke-Ernzerhof (PBE)<sup>45</sup> functional was employed to handle the electronic correlation and exchange energy, and the interaction between valence electrons and atomic cores was described using the Projected Augmented Wave (PAW)<sup>46-48</sup> pseudopotentials. The energy cutoff for the plane wave basis was set to 500 eV. The DFT-D3 method<sup>49</sup> was employed to describe the weak van der Waals interactions. Geometry optimization and electronic structure calculations were performed using  $3 \times 3 \times 1$  and  $6 \times 6 \times 1$  Monkhorst-Pack k-point grids<sup>50</sup>, respectively. Search for the minimum energy paths and transition state optimizations for the dissociation of water molecules were performed using the Climbing Image Nudged Elastic Band (CI-NEB)<sup>51</sup> method. In all calculations, the energy convergence criterion for the electronic self-consistent field was  $10^{-5} \text{ eV}$ , and the structures were fully optimized until the ionic forces were less than  $0.02 \text{ eV/\AA}$ . After obtaining the optimized geometry at 0 K, the system was heated to 200 K using velocity rescaling. Subsequently, a 12 ps adiabatic molecular dynamics trajectory was obtained in the microcanonical ensemble with a time step of 1 fs. To simulate the quantum dynamics of capture of photogenerated holes by  $\text{H}_2\text{O}$ , 1000 structures were selected from the 12 ps trajectory as initial structures for the NAMD simulation. The NAMD simulation were carried out using fewest switches surface hopping

(FSSH) implemented with the time-dependent Kohn-Sham theory.<sup>52-54</sup> This method has been proven reliable in simulating the dynamics of photogenerated charge carriers in various condensed-phase materials and systems.<sup>55-70</sup>



**Fig. 1** Top and side views of water molecules adsorbed on the *p*-rutile  $\text{TiO}_2(110)$  surface in **(a, b)** monolayer and **(c, d)** semi-dissociated forms. The two water molecules are labeled as  $\text{H}_2\text{O\_1}$  and  $\text{H}_2\text{O\_2}$  in part a. The side views in **2b** and **2d** only show the top two O-Ti-O layers. **Fig. S1** presents  $2 \times 2$  supercells to demonstrate the adsorption structures more clearly. The light blue and red balls represent the Ti and O atoms in  $\text{TiO}_2$ , respectively, while the pink and green balls represent the O and H atoms in water molecules, respectively. The visualization is achieved with the VESTA software.<sup>71</sup>

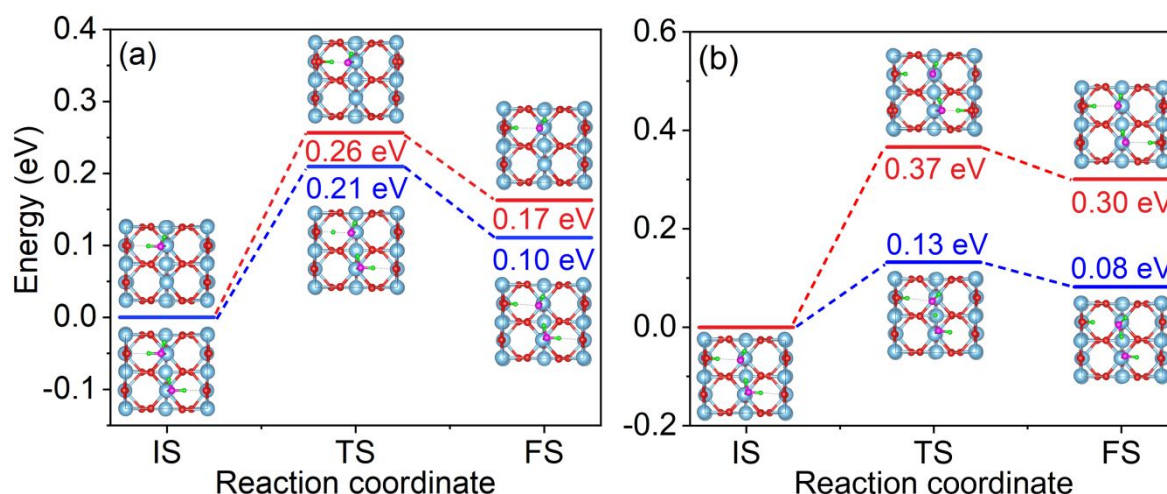
### 3. Results and discussion

#### 3.1 Geometric structure

The dissociation of water molecules on the  $\text{TiO}_2$  surface is an endothermic reaction. Water molecules are more likely to adsorb on the five coordinated Ti atoms ( $\text{Ti}_{5c}$ ) on the surface as intact molecules, forming a  $\text{Ti}_{5c}\text{-*OH}_2$  structure. The dissociated  $\text{*OH}$  and  $\text{*H}$  tend to recombine and regenerate water molecules, as observed in experiments.<sup>34</sup> We studied adsorption of a water monolayer on the *p*-rutile  $\text{TiO}_2(110)$  surface. Our model includes adsorption of one water molecule on each surface  $\text{Ti}_{5c}$  site, with an adjacent water molecule interacting with the first one by IHB and forming HB with the bridging oxygen atoms on the



surface, as shown in **Fig. 1a** and **1b**. **Fig. 1c** and **1d** demonstrate that dissociation of the water molecule in the monolayer system leads to formation of a semi-dissociated structure with surface adsorbed  $\text{H}_2\text{O}-\text{O}_\text{t}\text{H}$  species. After the water molecule dissociation, the length of the IHB in semi-dissociated structure decreases from 2.11 Å to 1.71 Å, indicating that the IHB strength increases. The IHB facilitates the dissociation of  $\text{H}_2\text{O}$ , making the adsorption of water on  $\text{TiO}_2$  stronger. Compared to the non-dissociated monolayer system, the length of the bonds between Ti and  $\text{O}_\text{w}$  (oxygen atoms in water) are significantly reduced in the semi-dissociated system. In particular, the  $\text{Ti}-\text{O}_{\text{w}1}$  bond length is reduced by 0.33 Å. This indicates that the dissociation of a water molecule in the monolayer system enhances stability of the water adsorption on the  $\text{TiO}_2$  surface. The IHBs between  $\text{H}_2\text{O}$  and  $\text{O}_\text{t}\text{H}$  in the semi-dissociated system plays a crucial role in stabilizing the  $\text{O}_{\text{br}}\text{H}$  and  $\text{O}_\text{t}\text{H}$  pairs, and facilitates the dissociation of  $\text{H}_2\text{O}$  further.



**Fig. 2** (a) Minimum energy pathways for water dissociation on  $p$ -rutile  $\text{TiO}_2(110)$  for non-hydrogen bonded system (monomer adsorption system) (red line) and monolayer water molecule adsorption (blue line). (b) Two pathways for the  $\text{H}_2\text{O}_2$  molecule dissociation in the semi-dissociated system. One pathway is the dissociation of  $\text{H}_2\text{O}_2$  to form  $\text{O}_\text{t}\text{H}$  and  $\text{O}_{\text{br}}\text{H}$ , and the other pathway is induced by IHB between  $\text{O}_\text{t}\text{H}$  and  $\text{H}_2\text{O}_2$ . **Fig. S2** shows enlarged views of the initial state (IS), transition state (TS), and final state (FS) structures.

In practical  $\text{TiO}_2$  photocatalytic water splitting systems, the  $\text{TiO}_2$  surface typically has multiple layers of adsorbed water molecules, forming a more complex HB network. In such cases, the monolayer adsorption structure on the  $\text{TiO}_2$  surface is augmented by additional IHBs.

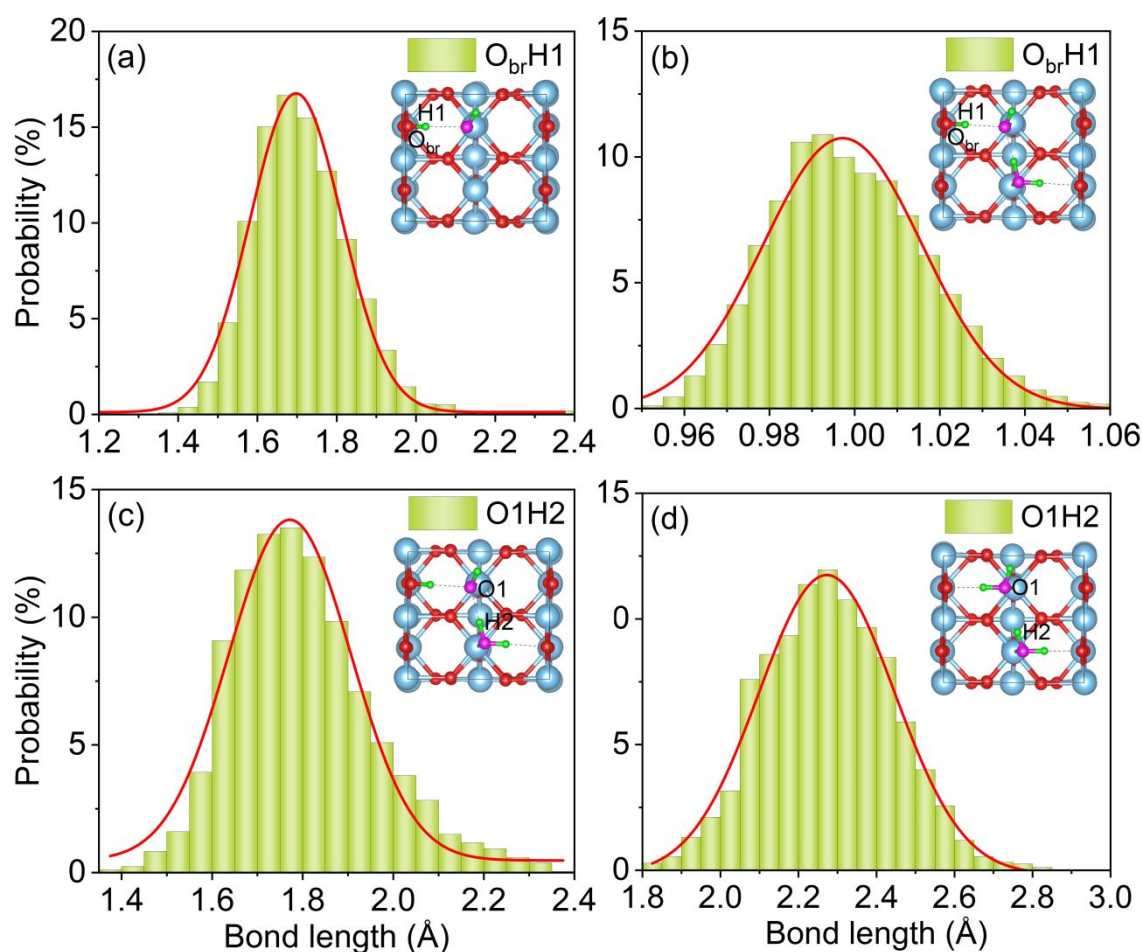
We chose the monolayer water adsorption on the  $\text{TiO}_2$  surface as our study model for the following reasons. First, stable monolayer water adsorption structures have been observed experimentally on both rutile and anatase  $\text{TiO}_2$  surfaces.<sup>72, 73</sup> This provides a direct connection between our work and experiment. Second, the monolayer water adsorption model provides a simple and efficient model to study the effect of IHBs on dissociation of water molecules and hole capture on  $\text{TiO}_2$ .

### 3.2 Dissociation of $\text{H}_2\text{O}$ on rutile $\text{TiO}_2(110)$

The dissociation barrier is a critical factor in assessing the dissociation efficiency of water. To evaluate the effect of hydrogen bonding on water dissociation, we calculated the dissociation barriers for water molecule in both the non-hydrogen bonded (monomer adsorption) system and the monolayer system, as shown in **Fig. 2a**. The dissociation barrier of water molecule in monomer adsorption system is 0.26 eV, in agreement with the previous reports of  $\sim 0.3$  eV.<sup>19, 74</sup> It is noteworthy that the reverse dissociation barrier is only 0.09 eV, and the low barrier implies that the  $\text{O}_{\text{br}}\text{H}/\text{O}_{\text{t}}\text{H}$  pairs tend to recombine to regenerate water molecules. This phenomenon, known as “pseudo-dissociation” in previous literature, is a crucial factor limiting the efficiency of water dissociation on the *p*-rutile  $\text{TiO}_2(110)$  surface.<sup>34, 35</sup> Compared to the dissociation of water molecule in monomer adsorption system, the dissociation barrier of a water molecule in the monolayer system is reduced to 0.21 eV, indicating that the IHBs make the dissociation more favorable. The reverse barrier for the  $\text{O}_{\text{br}}\text{H}/\text{O}_{\text{t}}\text{H}$  pairs to recombine is 0.11 eV, slightly increased compared to the monomer adsorption system. This suggests that the HB between  $\text{H}_2\text{O}$  and  $\text{O}_{\text{t}}\text{H}$  can inhibit to some extent the recombination of  $\text{O}_{\text{br}}\text{H}/\text{O}_{\text{t}}\text{H}$  pairs.

As shown in **Fig. 2b**, there are two possible water dissociation pathways in the semi-dissociated system. One pathway leads to formation of  $\text{O}_{\text{br}}\text{H}$  on the  $\text{O}_{\text{br}}\text{H}$ , with the dissociation barrier as high as 0.37 eV (red line). The other pathway involves dissociation of the  $\text{H}_2\text{O}_2$  molecule induced by HB between  $\text{O}_{\text{t}}\text{H}$  and  $\text{H}_2\text{O}_2$ . The dissociation barrier for the second pathway is much lower, 0.13 eV (blue line), making the dissociation of water molecules much more likely. Importantly, the dissociation of  $\text{H}_2\text{O}_2$  induced by the IHB leads to spatial

isolation of  $O_{br}H$  and  $O_tH$ , effectively preventing their recombination.



**Fig. 3** Probability distributions of  $O_{br}H$  bond lengths in (a) single water molecule and (b) monolayer systems, and IHB lengths (c) after and (d) before water dissociation in the monolayer system.

### 3.3 Dynamic structure induced by water dissociation on rutile $TiO_2(110)$

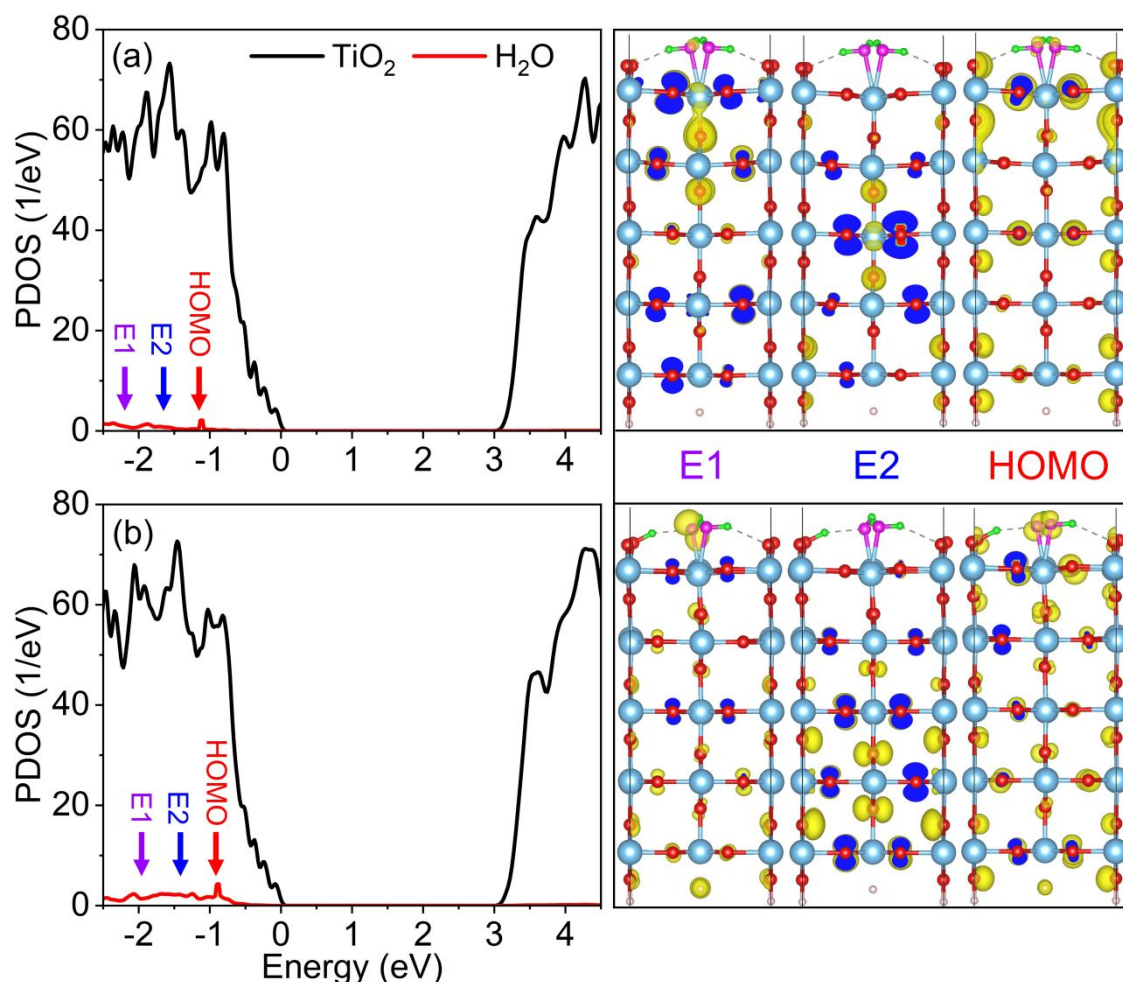
Fluctuations in bond lengths in AIMD simulations characterize motion of H atoms and revealing stability of the dissociated structure after water molecule dissociation. As shown in **Fig. 3** presents distributions of lengths of the  $O_{br}H$  bond and the IHB in the monolayer and semi-dissociated systems over the 12 ps MD trajectory. **Fig. 3a** shows that the  $O_{br}H$  bond lengths in the monomer adsorption system range from 1.4 Å to 2.1 Å, with the peak around 1.7 Å. The typical bond length of a hydroxyl group is in the 0.96 Å to 1.02 Å range. The calculated values are significantly larger, indicating that the  $O_{br}H$  bond is highly unstable and that the hydrogen atom in  $O_{br}H$  returns to the oxygen atom in  $O_tH$ . The AIMD trajectory reveals that

the  $O_{br}H/O_tH$  pair undergoes fast recombination within 0.2 ps, **Fig. S3**. This is consistent with the experiments showing that  $O_{br}H/O_tH$  pairs rapidly disappear in the pseudo-dissociated state.<sup>34</sup>

In contrast, the distribution of the  $O_{br}H$  bond lengths in the semi-dissociated structure, **Fig. 3b**, formed after dissociation of a water molecule in the monolayer system, ranges from 0.96 Å to 1.04 Å, which is typical for the hydroxyl bond length. Thus, the H atom produced after the water dissociation can be stably adsorbed on  $O_{br}$ . The evolutions of the  $O_{br}H$  and  $O_tH$  bond lengths during the AIMD trajectory are shown in **Fig. S4**, indicating that the dissociated water molecule in the monolayer system did not undergo recombination. The lengths of the IHBs reflect the bond strength: as the IHB length decreases, the IHB strength increases. Compared to the monolayer system, **Fig. 3d**, the IHB in the semi-dissociated system is significantly shorter, primarily distributed around 1.75 Å, **Fig. 3c**. This indicates a significant enhancement in the IHB strength between  $O_tH$  and  $H_2O\_2$ . Although the strengthening of the IHB between  $O_tH$  and  $H_2O\_2$  in the semi-dissociated system did not induce a permanent intermolecular proton transfer, the increased HB strength stabilized the  $O_{br}H/O_tH$  pairs and suppressed the  $O_{br}H/O_tH$  pair recombination in the pseudo-dissociated state.

As shown in **Fig. 3c** and **3d**, the dissociation of  $H_2O$  enhances the strength of IHB, which in turn promotes the dissociation of  $H_2O\_2$ . The dissociation energy barrier induced by IHB is only 0.13 eV. **Fig. S5** shows the evolution of the H-O bond length in  $H_2O\_2$  in both the monolayer and semi-dissociated systems during the MD process. It can be observed that the H-O bond length increases in the semi-dissociated system due to the enhanced IHB. An increase in the bond length indicates a weakening of the bond, making the H-O bond more prone to dissociation, rationalizing the significantly reduced energy barrier for dissociation of  $H_2O\_2$  induced by IHB. Additionally, **Fig. 3** demonstrates that the O-H bond length fluctuates more in the semi-dissociated system compared to the monolayer system. The enhanced movement of H atoms is accompanied by a stronger electron-vibrational coupling in the system, accelerating relaxation and capture of holes by  $H_2O\_2$ . Chu et al. discovered through both theoretical and experimental studies that methanol molecules adsorbed on the  $TiO_2$  surface significantly enhance the ability to capture excited state holes due to the quantized motion of

protons, thereby improving the efficiency of the photochemical reaction.<sup>75</sup> Overall, the increased IHB strength in the semi-dissociated system leads to higher efficiency of water dissociation, according to our thermodynamic analysis, and accelerated capture of photogenerated hole, according to our kinetic analysis.

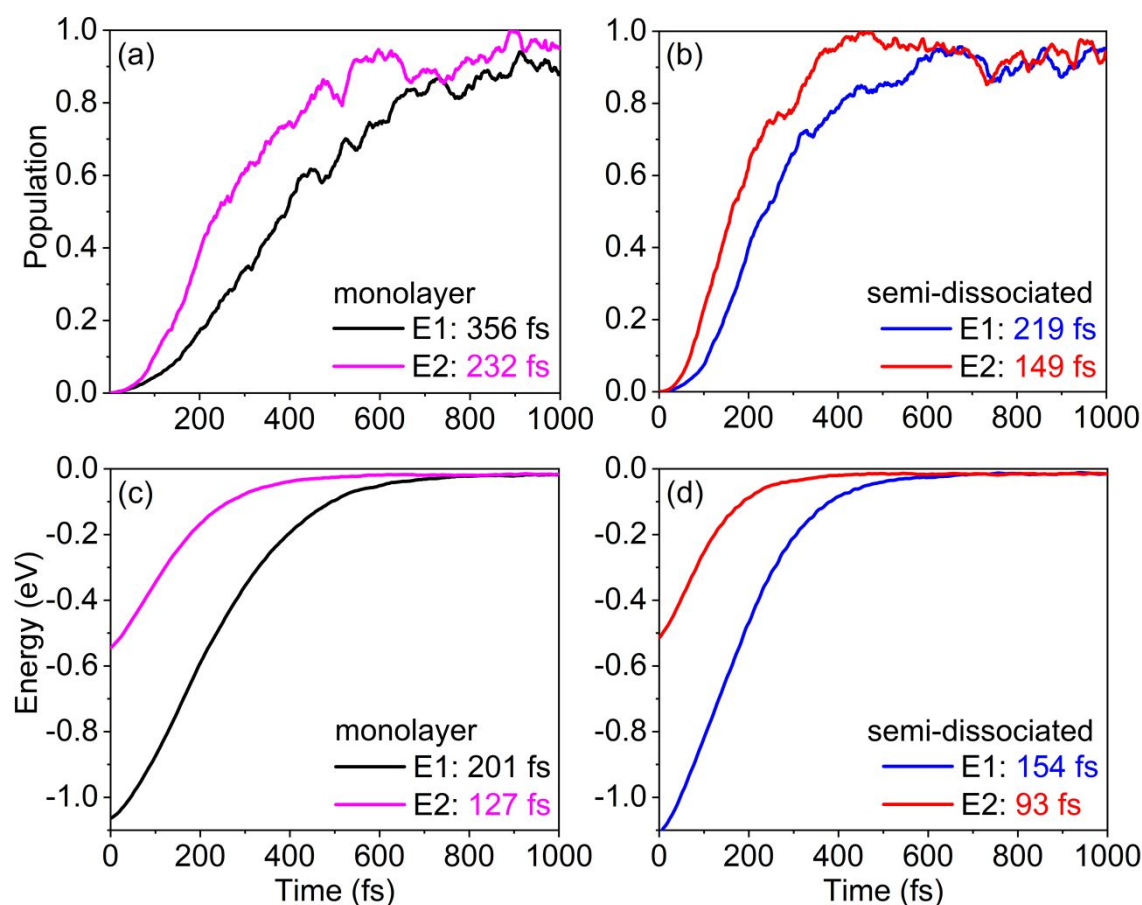


**Fig. 4** PDOSs for (a) monolayer and (b) semi-dissociated systems. The PDOS of water is doubled for clarity. The purple, blue, and red arrows indicate the high (E1) and low energy (E2) photogenerated hole states, and the HOMO energy level. The charge densities are visualized with the VASPKIT and VESTA software.<sup>71, 76</sup>

### 3.4 Electronic structure

**Fig. 4a** and **4b** display the projected density of states (PDOS) for the monolayer and semi-dissociated systems, respectively. Although computationally efficient, the PBE DFT functional mistreats electron-electron interactions among *d* electrons in strongly correlated systems, and as a result, underestimates the TiO<sub>2</sub> band gap. To correct the band gap, we refer to prior

experimental and theoretical works and introduce a "scissor operator" expanding the gap to match the experimental value.<sup>77-79</sup> We determined the locations of the highest occupied molecular orbital (HOMO) of water in the monolayer and semi-dissociated systems by studying charge density distributions of the electronic states. The positions of the HOMO energy levels are presented by red arrows in **Fig. 4a** and **4b**, and the corresponding charge densities are presented on the right side of the figure, in particular, depicting the  $O_p$  orbital features of the water HOMOs. The water molecule dissociation has an impact on the position of the HOMO energy level. Compared to the monolayer system, **Fig. 4a**, the water HOMO energy level shifts by 0.3 eV towards the valence band maximum in the semi-dissociated system, **Fig. 4b**, and the  $H_2O$  contribution to the DOS increases in this energy range. More advanced electronic structure methods, e.g., hybrids functionals, should exhibit qualitatively similar results. The charge density plots also show higher charge (hole) density on the adsorbed waters in the semi-dissociated system, which facilitates trapping of photogenerated holes and subsequent dissociation of water molecules.



**Fig. 5 (a, b)** Dynamics of hole capture by the water HOMO in the monolayer and semi-



dissociated systems, respectively. E1 and E2 represent high- and low-energy photogenerated hole donor states. **(c, d)** Energy relaxation processes in the monolayer and semi-dissociated systems, with E1 and E2 as the initial states.

### 3.5 Hole capture and energy relaxation dynamics

The capture of photogenerated holes is a key factor in driving the dissociation of surface water molecules.<sup>30, 80-83</sup> The rate of hole capture determines the efficiency of water molecule dissociation on the rutile TiO<sub>2</sub>(110) surface. With the HOMO energy level of water as the hole acceptor, we study hole capture dynamics starting with the hole at higher and lower energies in TiO<sub>2</sub>, 1.0 eV and 0.5 eV above the water HOMO level, E1 and E2, respectively. **Fig. 5a** and **5b** present the dynamics of hole capture by the HOMO of water in the monolayer and semi-dissociated systems, respectively. We employed a Gaussian function,  $P(t) = 1 - \exp[-0.5 * (-t/\tau)^2]$ , to fit the curves and obtain time scales of the photogenerated hole capture. The data shown in **Fig. 5a** and **5b** demonstrate that if the hole starts at a lower energy, its capture is faster, and importantly, that the hole capture is notably faster in the semi-dissociated than monolayer system, compare 219 fs vs. 356 fs for the higher energy initial condition, and 149 fs vs. 232 fs for the lower initial energy. This implies that the semi-dissociated system not only effectively suppresses the recombination of O<sub>br</sub>H and O<sub>t</sub>H pairs, but also accelerates hole capture, thereby promoting the subsequent rapid dissociation of H<sub>2</sub>O. During the relaxation of the hole from a TiO<sub>2</sub> donor state to the water HOMO level, the photogenerated hole loses energy through coupling with phonons. As shown in **Fig. 5c** and **5d**, the relaxation of energy in the monolayer and semi-dissociated systems occurs within 100-200 fs, faster than the corresponding hole capture. Thus, holes lose significant amounts of energy before transferring to H<sub>2</sub>O, forming holes that are not “sufficiently hot”. The insufficiently hot holes may not have enough energy for oxidation of water molecules, which can be another factor restricting the oxidation of water on rutile TiO<sub>2</sub>(110).

The hole capture process involves transitions between adiabatic electronic states, induced by nonadiabatic coupling (NAC). NAC induces energy exchange between the electronic and vibrational subsystems, and the rate of electron-vibrational energy exchange leading to hole

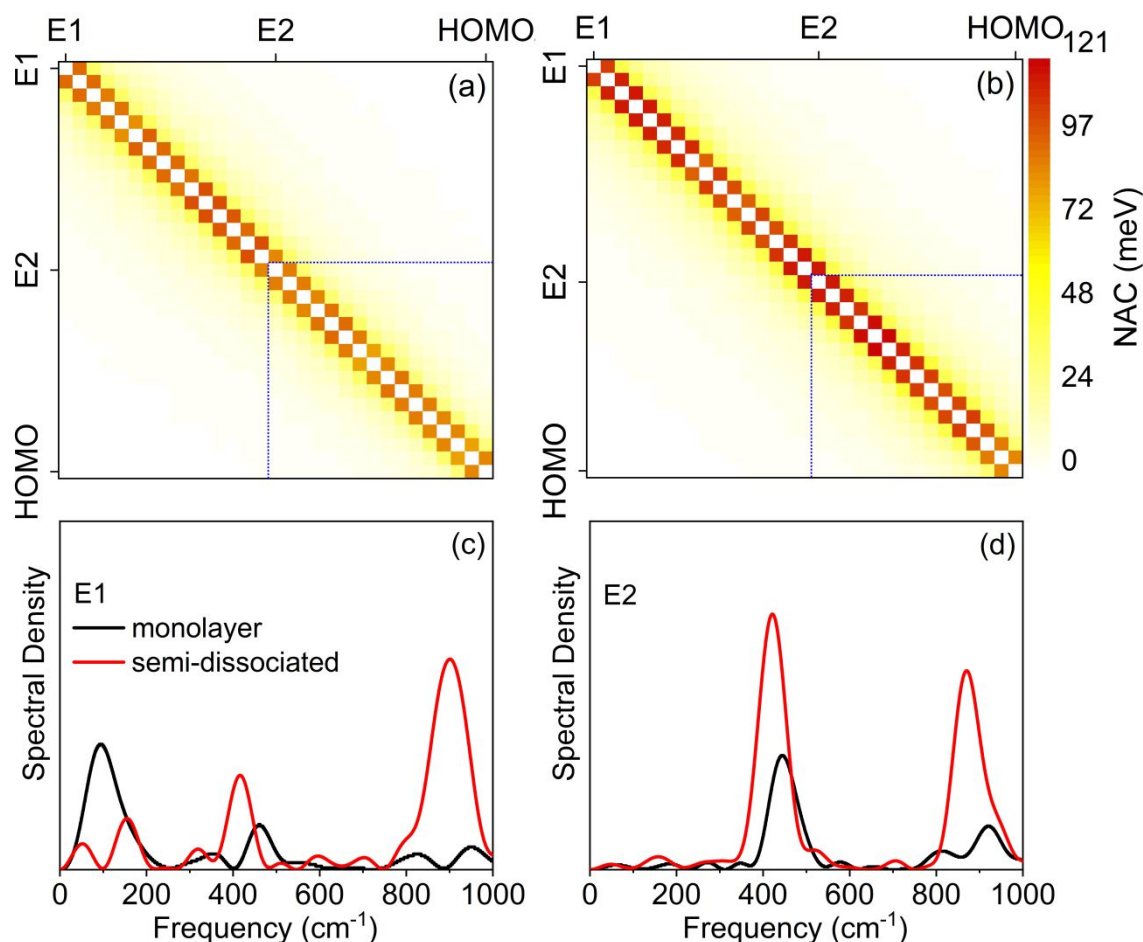
capture is determined by NAC magnitude. The NAC is defined as,  $d_{ij} = -i\hbar \langle \varphi_i | \nabla_R | \varphi_j \rangle \cdot \dot{\mathbf{R}}$ , and it is a scalar product of the electronic matrix element of the atomic gradient vector operator,  $\langle \varphi_i | \nabla_R | \varphi_j \rangle$ , and the atomic velocity,  $\dot{\mathbf{R}}$ . Therefore, the magnitude of NAC depends on the overlap of wave functions between orbitals and the extend of atomic motion. **Fig. S5** demonstrates that H atoms fluctuate much more in the semi-dissociated than monolayer system, rationalizing the larger NAC and faster hole capture.

**Fig. 6a** and **6b** presents two-dimensional heat maps of the average absolute NAC between electronic states involved in the hole capture process for the monolayer and semi-dissociated systems, respectively. The deeper the color, the stronger the NAC. The NAC is the strongest between adjacent states, followed by the next nearest states. The stronger NAC between adjacent states implies that the hole relaxation and capture is a sequential process, i.e., the hole hops down in energy through the manifold of  $\text{TiO}_2$  states before being captured by the water HOMO. The NAC is stronger in the semi-dissociated than monolayer system. This is due to the vigorous movement of H atoms in the semi-dissociated system generates larger NAC. (as shown in **Fig. S5**). **Table 1** summarizes the energy ranges and the averaged absolute NACs for the hole capture processes starting from the higher, E1 and lower, E2 energies in  $\text{TiO}_2$  to the water HOMO. The larger NAC in the semi-dissociated system explains the faster hole transfer (E1 to HOME0: 14.19 meV vs 16.75 meV, E2 to HOMO: 23.06 meV vs 30.13 meV), quantitatively rationalizing why water molecules in the semi-dissociated system can capture photogenerated holes more quickly, **Fig. 5**.

**Table 1** Energy Range and Average Absolute NACs for Hole Transfer from E1, E2 in  $\text{TiO}_2$  to Water HOMO in the Monolayer and Semi-Dissociated Systems.

System	E1-HOMO		E2-HOMO	
	Energy range (eV)	NAC (meV)	Energy range (eV)	NAC (meV)
monolayer	1.06	14.19	0.54	23.06
semi-dissociated	1.11	16.75	0.51	30.13





**Fig. 6 (a, b)** Average absolute NACs between pairs of electronic states involved in hole relaxation in the monolayer and semi-dissociated systems, respectively. **(c, d)** Spectral densities obtained from FTs of unnormalized autocorrelation functions for the fluctuation of energy gaps between the donor states (E1 and E2) and the acceptor state (water HOMO).

Spectral density plots, **Fig. 6c** and **6d**, identify vibrational modes that couple to the electronic subsystem, accommodate the excess energy released during hole relaxation and facilitate hole transfer. The spectral densities corresponding to hole transfer process are obtained by Fourier transforms (FTs) of the unnormalized autocorrelation functions of the energy gap fluctuations between the hole donor and acceptor states. The locations of the peaks in the spectral densities identify frequencies of the active vibrations, while the intensities of the peaks represent the strength of the electron-phonon coupling to the vibration at the corresponding frequency. At a given temperature, higher frequency vibrational modes generate faster atomic velocities, creating larger NAC, and larger NAC accelerates electron-vibrational energy

exchange and hole capture. The spectral densities demonstrate that the hole transfer is primarily coupled with high-frequency vibrations, and that low-frequency vibration have relatively small contributions to the hole transfer. The peak around  $150\text{ cm}^{-1}$  corresponds to the  $B_{1g}$  vibration of  $\text{TiO}_2$  and the vibration of  $\text{H}_{\text{br}}$ ,<sup>84</sup> while the peak around  $400\text{ cm}^{-1}$  represents the  $E_g$  mode arising from the stretching vibration of  $\text{O-Ti-O}$ .<sup>85, 86</sup> The peak near  $900\text{ cm}^{-1}$  corresponds to the bending motion of water molecules.<sup>87</sup> As shown in **Fig. 6c** for the higher energy initial  $\text{TiO}_2$  state E1, the semi-dissociated system exhibits a stronger high-frequency electron-phonon coupling, especially near  $900\text{ cm}^{-1}$ , enhancing the NAC between E1 and the acceptor state. For the lower energy initial state E2, **Fig. 6d**, the hole transfer is driven only by the high-frequency vibrations near  $400\text{ cm}^{-1}$  and  $900\text{ cm}^{-1}$ . Low-frequency contributions are insignificant in this case. The signals at both  $400\text{ cm}^{-1}$  and  $900\text{ cm}^{-1}$  are stronger for the semi-dissociated than monolayer system. The stronger signals seen in the spectral densities correspond to the larger NAC, and rationalize faster hole relaxation and capture in the semi-dissociated system. Overall, for the relaxation of high energy (E1) and low energy (E2) initial excited state holes, the stronger high-frequency vibrational modes coupled to the hole relaxation process in the semi-dissociated system generate larger NAC. This accelerates the capture of photogenerated holes by water molecules, thereby improving the oxidation efficiency of water.

#### 4. Conclusion

In summary, the quantum dynamics of water dissociation and capture of photogenerated holes by a water monolayer and an isolated water molecule adsorbed on the rutile  $\text{TiO}_2(110)$  surface were studied using the DFT, real-time TD-DFT, and NAMD methods. DFT calculations indicate that IHBs between waters lower the barrier of water molecule dissociation, facilitating the process. AIMD results demonstrate that strengthening of IHBs in the semi-dissociated system stabilizes the dissociated structure, and inhibits recombination of  $\text{O}_{\text{br}}\text{H}/\text{O}_{\text{t}}\text{H}$  pairs. Further, IHBs facilitate spatial isolation of  $\text{O}_{\text{br}}\text{H}/\text{O}_{\text{t}}\text{H}$  pairs, breaking the “pseudo-dissociated” state.

NAMD simulations reveal that the capture of photogenerated holes is significantly accelerated in the semi-dissociated system compared to the pristine system. The hole capture

time is reduced by 36%, primarily due to the enhanced NAC between neighboring electronic states. The fast hole capture implies a higher dissociation efficiency for subsequent water splitting, which is a key factor in improving the yield of photocatalyzed splitting of water on  $\text{TiO}_2$ . Stronger coupling of holes to high-frequency vibrations and additional active high-frequency vibrational modes in the semi-dissociated structure contribute to the accelerated capture of photogenerated holes as well. None of these effects are observed for isolated water molecules on  $\text{TiO}_2$ .

The findings reported in this work are expected to apply to other metal oxide surfaces, such as  $\text{RuO}_2$  and  $\text{SrTiO}_3$ , especially in recognizing the importance of IHB in the hole capture and water dissociation processes. Water adsorption structures on other classes of materials, such as metal nitrides and carbon nitrides, are likely to differ from those in metal oxides. Still, IHB should play a key role there as well. Related phenomena can take place in other cases, such as the photocatalytic oxidation of  $\text{CH}_3\text{OH}$  on  $\text{TiO}_2$  surfaces. Capture of photogenerated holes depends on the properties of the  $\text{CH}_3\text{O}^\cdot$  intermediate formed after  $\text{CH}_3\text{OH}$  dissociation, and the HB hydrogen bonding should also be a significant factor influencing the capture of photogenerated holes in  $\text{CH}_3\text{OH}$ . Future theoretical studies can focus on modeling ultrafast chemical reactions induced by photogenerated holes. For this purpose, one can employ the impulsive two-state method.<sup>39, 42</sup> Additional modeling studies on other classes of material systems and with other molecules are required in order to establish the generality of the conclusions reported in this work, and to formulate common theoretical principles underlying atomistic dynamics of photocatalytic reactions. Experimental studies combining spatial and temporal resolutions, e.g., using scanning tunneling microscopy and time-resolved spectroscopy, can provide important data to test and verify theoretical work and create new insights for constructing a detailed and comprehensive picture of water photolysis and related photocatalytic reactions.

Our work offers a detailed investigation of surface reaction kinetics and photogenerated hole capture dynamics during the dissociation of water adsorbed on *p*-rutile  $\text{TiO}_2(110)$  surfaces. By exploring the role of special intermediates in the photocatalyzed water splitting, our work deepens understanding of the complex reactions occurring on metal oxide surfaces.

**Conflicts of interest**

The authors declare no competing financial interest.

**Acknowledgements**

This work was supported by the National Science Foundation of China, grant No. 92372121. R.L. acknowledges the Fundamental Research Funds for the Central Universities. C.C. acknowledges financial support by the Guangdong Basic and Applied Basic Research Foundation (No. 2023A1515110101). O. V. P. acknowledges support of the US National Science Foundation (grant CHE-2154367).

## References

1. J. O. Abe, A. Popoola, E. Ajenifuja and O. M. Popoola, *Int. J. Hydrogen Energy*, 2019, **44**, 15072-15086.
2. S. Nandy, T. Hisatomi, T. Takata, T. Setoyama and K. Domen, *J. Mater. Chem. A*, 2023, **11**, 20470-20479.
3. F. Xu and B. Weng, *J. Mater. Chem. A*, 2023, **11**, 4473-4486.
4. A. Fujishima and K. Honda, *Nature*, 1972, **238**, 37-38.
5. J. S. Schubert, J. Popovic, G. M. Haselmann, S. P. Nandan, J. Wang, A. Giesriegl, A. S. Cherevan and D. Eder, *J. Mater. Chem. A*, 2019, **7**, 18568-18579.
6. X. Ma, Y. Shi, J. Liu, X. Li, X. Cui, S. Tan, J. Zhao and B. Wang, *J. Am. Chem. Soc.*, 2022, **144**, 13565-13573.
7. X. Zhang, C. Bo, S. Cao, Z. Cheng, Z. Xiao, X. Liu, T. Tan and L. Piao, *J. Mater. Chem. A*, 2022, **10**, 24381-24387.
8. J. Tang, J. R. Durrant and D. R. Klug, *J. Am. Chem. Soc.*, 2008, **130**, 13885-13891.
9. J.-Q. Li, Y. Sun and J. Cheng, *J. Mater. Chem. A*, 2023, **11**, 943-952.
10. J. Lian, K. Shibata, Y. Xiao, S. Du, T. Tanaka, Y. Qi, O. Ishitani, K. Maeda, Z. Feng and F. Zhang, *J. Mater. Chem. A*, 2023, **11**, 141-148.
11. Q. Guo, Z. Ma, C. Zhou, Z. Ren and X. Yang, *Chem. Rev.*, 2019, **119**, 11020-11041.
12. J. Yan, Y. Zhang, S. Liu, G. Wu, L. Li and N. Guan, *J. Mater. Chem. A*, 2015, **3**, 21434-21438.
13. R. Schaub, P. Thstrup, N. Lopez, E. Lægsgaard, I. Stensgaard, J. K. Nørskov and F. Besenbacher, *Phys. Rev. Lett.*, 2001, **87**, 266104.
14. O. Bikondoa, C. L. Pang, R. Ithnin, C. A. Muryn, H. Onishi and G. Thornton, *Nat. Mater.*, 2006, **5**, 189-192.
15. J. Lee, D. C. Sorescu, X. Deng and K. D. Jordan, *J. Phys. Chem. Lett.*, 2013, **4**, 53-57.
16. H. Hussain, G. Tocci, T. Woolcot, X. Torrelles, C. Pang, D. Humphrey, C. Yim, D. Grinter, G. Cabailh and O. Bikondoa, *Nat. Mater.*, 2017, **16**, 461-466.
17. P. J. Lindan, N. Harrison and M. Gillan, *Phys. Rev. Lett.*, 1998, **80**, 762-765.
18. C. Zhang and P. J. Lindan, *J. Chem. Phys.*, 2003, **118**, 4620-4630.
19. P. J. Lindan and C. Zhang, *Phys. Rev. B*, 2005, **72**, 075439.
20. R. Schaub, E. Wahlstrom, A. Rønnau, E. Lægsgaard, I. Stensgaard and F. Besenbacher, *Science*, 2003, **299**, 377-379.
21. L. A. Harris and A. A. Quong, *Phys. Rev. Lett.*, 2004, **93**, 086105.
22. Y. Ji, B. Wang and Y. Luo, *J. Phys. Chem. C*, 2012, **116**, 7863-7866.
23. J. Chen, C. Penschke, A. Alavi and A. Michaelides, *Phys. Rev. B*, 2020, **101**, 115402.
24. S. Selcuk and A. Selloni, *Nat. Mater.*, 2016, **15**, 1107-1112.
25. I. Brookes, C. Muryn and G. Thornton, *Phys. Rev. Lett.*, 2001, **87**, 266103.
26. L. Walle, D. Ragazzon, A. Borg, P. Uvdal and A. Sandell, *Surf. Sci.*, 2014, **621**, 77-81.
27. M. A. Henderson, *Surf. Sci.*, 1996, **355**, 151-166.
28. L. Walle, A. Borg, P. Uvdal and A. Sandell, *Phys. Rev. B*, 2009, **80**, 235436.
29. R. L. Kurtz, R. Stock-Bauer, T. E. Msdey, E. Román and J. De Segovia, *Surf. Sci.*, 1989, **218**, 178-200.
30. S. Tan, H. Feng, Y. Ji, Y. Wang, J. Zhao, A. Zhao, B. Wang, Y. Luo, J. Yang and J. Hou,

*J. Am. Chem. Soc.*, 2012, **134**, 9978-9985.

31. L.-M. Liu, C. Zhang, G. Thornton and A. Michaelides, *Phys. Rev. B*, 2010, **82**, 161415.
32. W. Yang, D. Wei, X. Jin, C. Xu, Z. Geng, Q. Guo, Z. Ma, D. Dai, H. Fan and X. Yang, *J. Phys. Chem. Lett.*, 2016, **7**, 603-608.
33. W. Zhang, J. Yang, Y. Luo, S. Monti and V. Carravetta, *J. Chem. Phys.*, 2008, **129**, 064703.
34. Y. Du, N. A. Deskins, Z. Zhang, Z. Dohnálek, M. Dupuis and I. Lyubinetsky, *J. Phys. Chem. C*, 2009, **113**, 666-671.
35. S. Wendt, J. Matthiesen, R. Schaub, E. K. Vestergaard, E. Lægsgaard, F. Besenbacher and B. Hammer, *Phys. Rev. Lett.*, 2006, **96**, 066107.
36. W. Langel, *Surf. Sci.*, 2002, **496**, 141-150.
37. J. Matthiesen, J. Hansen, S. Wendt, E. Lira, R. Schaub, E. Lægsgaard, F. Besenbacher and B. Hammer, *Phys. Rev. Lett.*, 2009, **102**, 226101.
38. B. Hammer, S. Wendt and F. Besenbacher, *Top. Catal.*, 2010, **53**, 423-430.
39. C. Cheng, O. V. Prezhdo, R. Long and W.-H. Fang, *J. Am. Chem. Soc.*, 2022, **145**, 476-486.
40. G. Kolesov, D. Vinichenko, G. A. Tritsarlis, C. M. Friend and E. Kaxiras, *J. Phys. Chem. Lett.*, 2015, **6**, 1624-1627.
41. P. You, D. Chen, X. Liu, C. Zhang, A. Selloni and S. Meng, *Nat. Mater.*, 2024, **23**, 1100-1106.
42. W. Chu, Q. Zheng, O. V. Prezhdo and J. Zhao, *J. Am. Chem. Soc.*, 2020, **142**, 3214-3221.
43. W. Chu, W. A. Saidi, Q. Zheng, Y. Xie, Z. Lan, O. V. Prezhdo, H. Petek and J. Zhao, *J. Am. Chem. Soc.*, 2016, **138**, 13740-13749.
44. G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169-11186.
45. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
46. P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953-17979.
47. W. Chu, Q. Zheng, A. V. Akimov, J. Zhao, W. A. Saidi and O. V. Prezhdo, *J. Phys. Chem. Lett.*, 2020, **11**, 10073-10080.
48. W. Chu and O. V. Prezhdo, *J. Phys. Chem. Lett.*, 2021, **12**, 3082-3089.
49. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
50. H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188-5192.
51. G. Henkelman, B. P. Uberuaga and H. Jónsson, *J. Chem. Phys.*, 2000, **113**, 9901-9904.
52. J. C. Tully, *J. Chem. Phys.*, 1990, **93**, 1061-1071.
53. S. A. Fischer, B. F. Habenicht, A. B. Madrid, W. R. Duncan and O. V. Prezhdo, *J. Chem. Phys.*, 2011, **134**, 024102.
54. C. F. Craig, W. R. Duncan and O. V. Prezhdo, *Phys. Rev. Lett.*, 2005, **95**, 163001.
55. Y. Wei, W.-H. Fang, Q. Fang and R. Long, *J. Phys. Chem. C*, 2018, **122**, 7041-7050.
56. X. Wang and R. Long, *J. Phys. Chem. Lett.*, 2021, **12**, 7553-7559.
57. X. Wang and R. Long, *J. Phys. Chem. Lett.*, 2021, **12**, 2763-2769.
58. Y. Wei, L. Li, W. Fang, R. Long and O. V. Prezhdo, *Nano Lett.*, 2017, **17**, 4038-4046.
59. D. Liu, Y. Wu, A. S. Vasenko and O. V. Prezhdo, *Nanoscale*, 2023, **15**, 285-293.
60. X. Zhao, A. S. Vasenko, O. V. Prezhdo and R. Long, *J. Phys. Chem. Lett.*, 2022, **13**, 11375-11382.
61. D. Liu, Y. Wu, M. R. Samatov, A. S. Vasenko, E. V. Chulkov and O. V. Prezhdo, *Chem. Mater.*, 2024, **36**, 2898-2906.

62. K. Hyeon-Deuk and O. V. Prezhdo, *ACS nano*, 2012, **6**, 1239-1250.
63. V. V. Chaban, V. V. Prezhdo and O. V. Prezhdo, *J. Phys. Chem. Lett.*, 2013, **4**, 1-6.
64. L. Zhang, A. S. Vasenko, J. Zhao and O. V. Prezhdo, *J. Phys. Chem. Lett.*, 2019, **10**, 1083-1091.
65. L. Qiao, W. H. Fang, R. Long and O. V. Prezhdo, *Angew. Chem.*, 2020, **132**, 4714-4720.
66. R. Long, O. V. Prezhdo and W. Fang, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2017, **7**, 1-29.
67. Z. Zhang, L. Liu, W.-H. Fang, R. Long, M. V. Tokina and O. V. Prezhdo, *Chem*, 2018, **4**, 1112-1127.
68. C. Cheng, W.-H. Fang, R. Long and O. V. Prezhdo, *JACS Au*, 2021, **1**, 550-559.
69. S. Agrawal, B. Wang, Y. Wu, D. Casanova and O. V. Prezhdo, *Nanoscale*, 2024, **16**, 8986-8995.
70. X. Ma, W.-H. Fang, R. Long and O. V. Prezhdo, *J. Am. Chem. Soc.*, 2024, **146**, 16314-16323.
71. K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2011, **44**, 1272-1276.
72. G. A. Kimmel, M. Baer, N. G. Petrik, J. VandeVondele, R. Rousseau and C. J. Mundy, *J. Phys. Chem. Lett.*, 2012, **3**, 778-784.
73. C. Dette, M. A. Pérez-Osorio, S. Mangel, F. Giustino, S. J. Jung and K. Kern, *J. Phys. Chem. C*, 2018, **122**, 11954-11960.
74. Q. Guo, C. Xu, Z. Ren, W. Yang, Z. Ma, D. Dai, H. Fan, T. K. Minton and X. Yang, *J. Am. Chem. Soc.*, 2012, **134**, 13366-13373.
75. W. Chu, S. Tan, Q. Zheng, W. Fang, Y. Feng, O. V. Prezhdo, B. Wang, X.-Z. Li and J. Zhao, *Sci. Adv.*, 2022, **8**, eabo2675.
76. V. Wang, N. Xu, J.-C. Liu, G. Tang and W.-T. Geng, *Comput. Phys. Commun.*, 2021, **267**, 108033.
77. D. C. Cronmeyer, *Phys. Rev.*, 1952, **87**, 876-886.
78. L. Lin, S. Mo and D. Lin, *J. Phys. Chem. Solids*, 1993, **54**, 907-912.
79. C. Cheng, Y. Zhu, W.-H. Fang, R. Long and O. V. Prezhdo, *JACS Au*, 2021, **2**, 234-245.
80. H. Zhou, X. Zhang, J. Zhang, H. Ma, F. Jin and Y. Ma, *J. Mater. Chem. A*, 2021, **9**, 7650-7655.
81. G. A. Tritsarlis, D. Vinichenko, G. Kolesov, C. M. Friend and E. Kaxiras, *J. Phys. Chem. C*, 2014, **118**, 27393-27401.
82. H. Sun, D. J. Mowbray, A. Migani, J. Zhao, H. Petek and A. Rubio, *ACS Catal.*, 2015, **5**, 4242-4254.
83. J. Chen, Y.-F. Li, P. Sit and A. Selloni, *J. Am. Chem. Soc.*, 2013, **135**, 18774-18777.
84. G. C. Vásquez, D. Maestre, A. Cremades and J. Piqueras, *J. Raman Spectrosc.*, 2017, **48**, 847-854.
85. O. Frank, M. Zukalova, B. Laskova, J. Kürti, J. Koltai and L. Kavan, *Phys. Chem. Chem. Phys.*, 2012, **14**, 14567-14572.
86. E. Shojaei and M. Mohammadizadeh, *J. Phys.: Condens. Matter*, 2009, **22**, 015401.
87. S. A. Fischer, W. R. Duncan and O. V. Prezhdo, *J. Am. Chem. Soc.*, 2009, **131**, 15483-15491.

The data that support the findings of this study are available from the corresponding author, RL , upon reasonable request.