Water Multilayers on TiO$_2$ (101) Anatase Surface: Assessment of a DFTB-Based Method

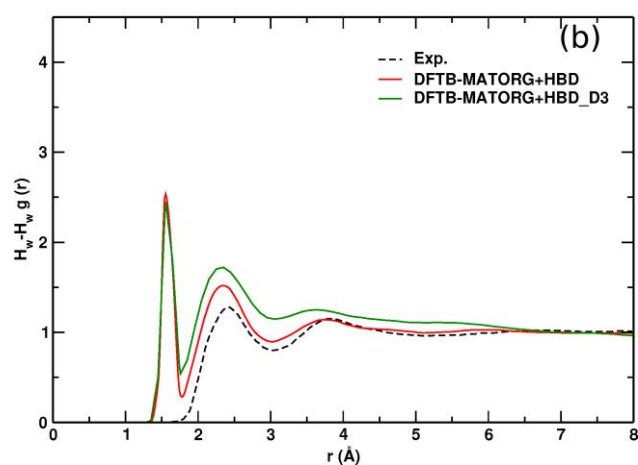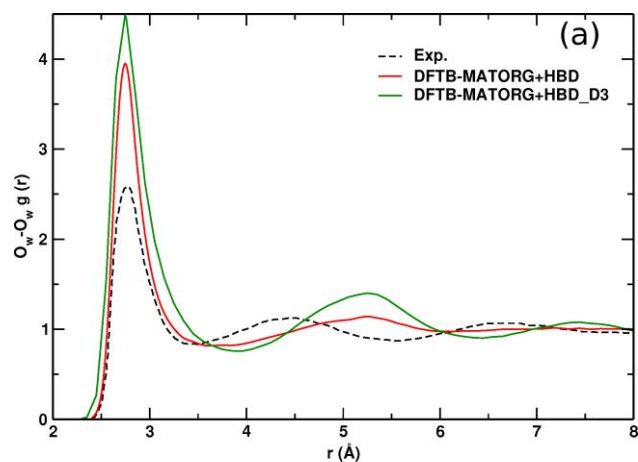Daniele Selli,[1] Gianluca Fazio,[1,2] Gotthard Seifert,[2] Cristiana Di Valentin[1*]

[1]Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Milano Italy
[2]Technische Universität Dresden, Institut für Theoretische Chemie, D-01062 Dresden, Germany

SUPPORTING INFORMATION

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[*] Corresponding author: cristiana.divalentin@mater.unimib.it

Figure S1. Comparison of the oxygen-oxygen (O_w-O_w, **a**) and hydrogen-hydrogen (H_w-H_w, **b**) radial distribution functions (RDF): dashed black line, experimental measurement; red line, DFTB-MATORG+HBD with the modified γ function for the H-bond; green line, DFTB-MATORG+HBD with the inclusion of the Grimme's D3 dispersion correction.
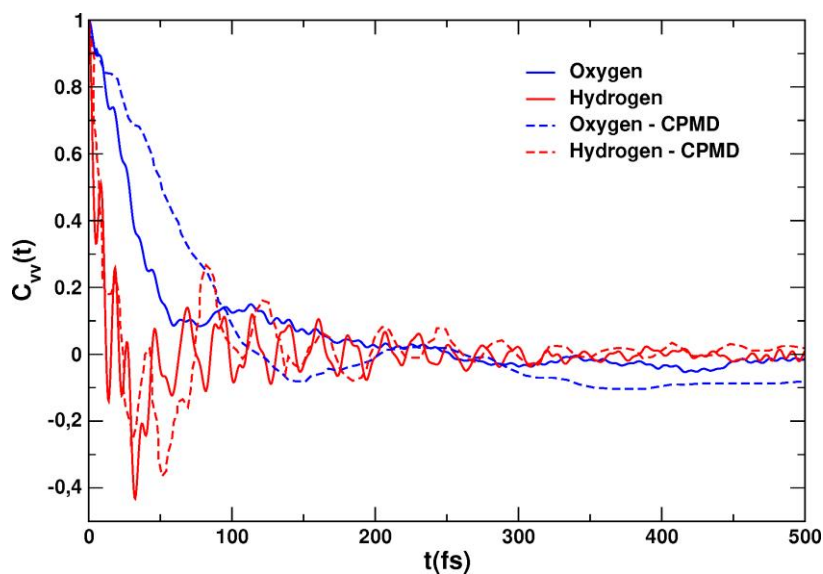
Figure S2. Comparison of the oxygen (blue, solid line) and hydrogen (red, solid line) velocity autocorrelation function (C_{vv}) calculated with DFTB-MATORG+HBD, with the oxygen (blue, dashed line) and hydrogen (red, dashed line) ones calculated with CPMD from Ref. 1.
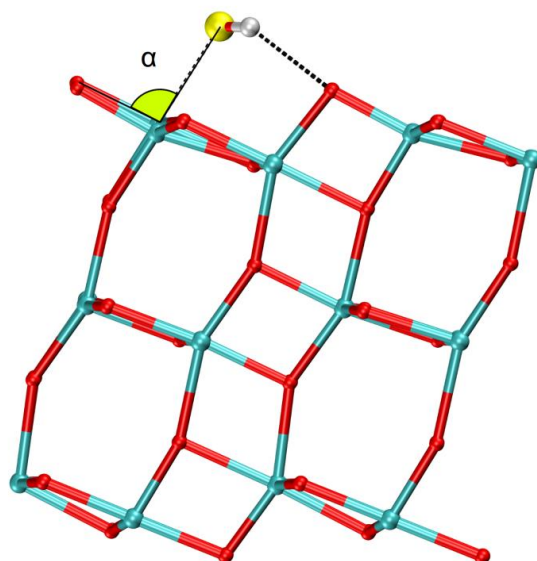
Figure S3. Definition of the bond angle α between the water molecule and the (101) anatase slab.
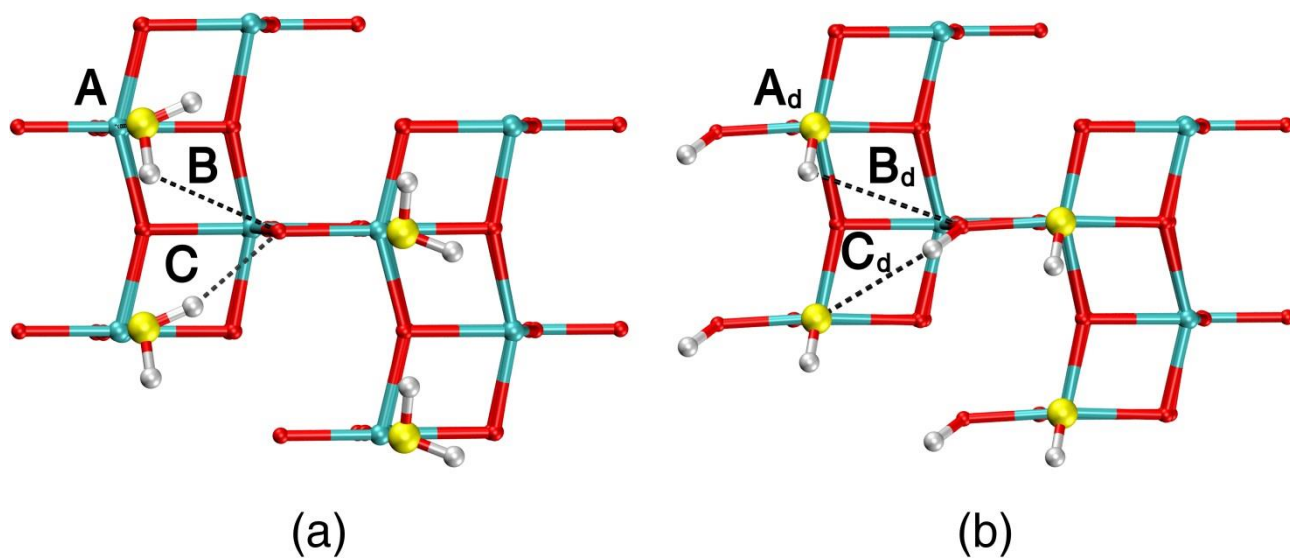
**Figure S4.** Molecular, H_2O (a) and dissociated, OH, H (b) equilibrium structure in the full water coverage regime, $\theta = 1$. Values of bond distances are reported in the **Table S1**.

Table S1. Relevant interatomic distances (in Å) of the equilibrium structures of H$_2$O (*Molecular Adsorption*, top panel) and OH, H (*Dissociative Adsorption*, bottom panel) on the (101) TiO$_2$ anatase slab, in the *full coverage regime* (θ = 1) as obtained with DFTB and DFT methods. H is the hydrogen atom of the OH group bound to the Ti atom, whereas H* is the hydrogen atom bound to the bridging O$_{2c}$ atom. These geometrical parameters are graphically defined in **Figure S3** and **Figure S4**. The absolute error reported in parenthesis for DFTB data is calculated with respect to the PBE value.

Molecular Adsorption

Method	Ti$_{5c}$ − OH$_2$ A (Å)	H …O$_{2c}$ B (Å)	H …O$_{2c}$ C (Å)	α (°)
DFTB-MATSCI	2.46 (+0.08)	2.11 (−0.89)	2.11 (−0.23)	104.8°
DFTB-MATORG+HBD	2.41 (+0.03)	2.14 (−0.86)	2.15 (−0.19)	105.2°
DFT-PBE	2.38	3.00	2.34	93.0°

Dissociative Adsorption

| Method	Ti$_{5c}$ − OH A$_d$ (Å)	H …O$_{2c}$ B$_d$ (Å)	H* …OH C$_d$ (Å)
DFTB-MATSCI	1.91 (+0.05)	3.48 (+0.18)	2.65 (−0.06)
DFTB-MATORG+HBD	1.92 (+0.06)	3.94 (+0.64)	3.10 (+0.39)
DFT-PBE	1.86	3.30	2.71
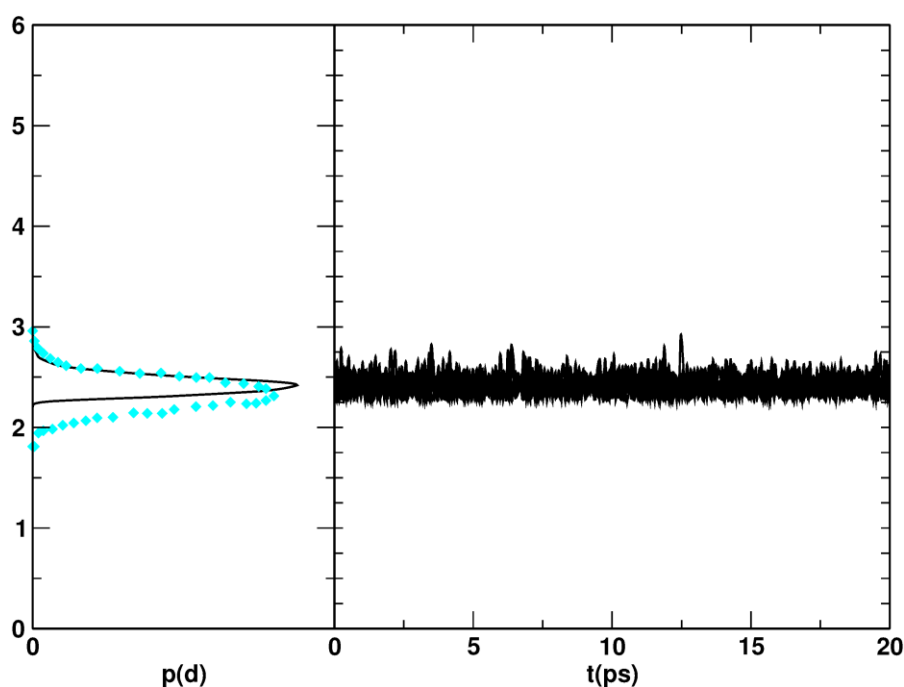
Figure S5. MATORG+HBD and DFT/PBE distribution *p(d)* and time evolution *d(t)* of the Ti − O Euclidean distances between the water molecule (O atoms) of the monolayer and the titania surface (Ti$_{5c}$ atoms). The DFT Car-Parrinello corresponding distribution *p(d)* in cyan diamonds is obtained adapting the data from ref. 2 with trigonometric transformations, assuming that the α angle, as defined in **Figure S1**, is on average that of the static PBE calculations.

MATORG+HBD

1.73   1.70

E_{H-bond} = -0.27 eV

DFT/PBE

1.94   1.64

E_{H-bond} = -0.19 eV
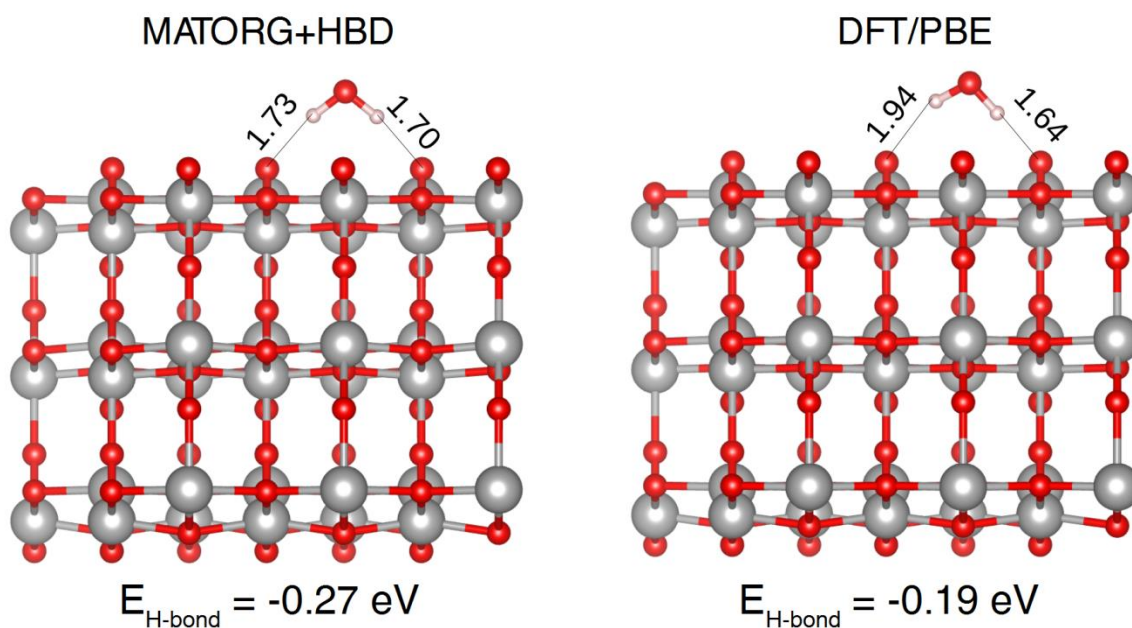
Figure S6. MATORG+HBD and DFT/PBE (101) anatase slab with a single water molecule in the same position as the second layer water molecules of the BL2 bilayer. Relevant H-bond distances are also given. The strength of the H-bond has been estimated with single-point calculations of these structure and the isolated systems.
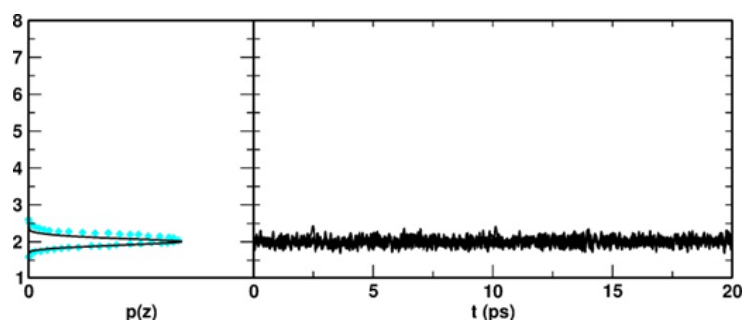

Figure S7. MATSCI ML Distribution $p(z)$ and time evolution $z(t)$ of the perpendicular distances between the water molecule (O atoms) of the water monolayer and the titania surface (Ti_{5c} atoms). The DFT Car-Parrinello corresponding distribution $p(z)$ is reported in cyan diamonds.[2]
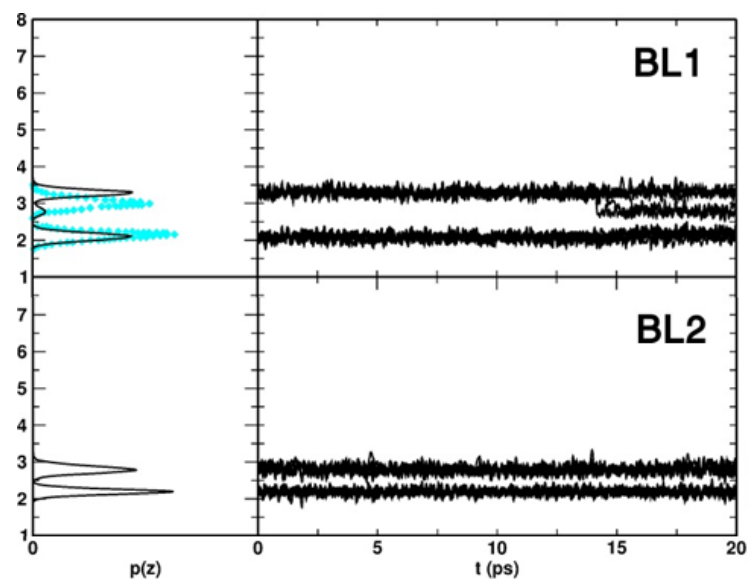
Figure S8. MATSCI BL1 and BL2 distribution $p(z)$ and time evolution $z(t)$ of the perpendicular distances between the water molecule (O atoms) and the titania surface (Ti_{5c} atoms). The DFT (PBE) Car-Parrinello corresponding distribution $p(z)$ is reported in cyan diamonds.[2]
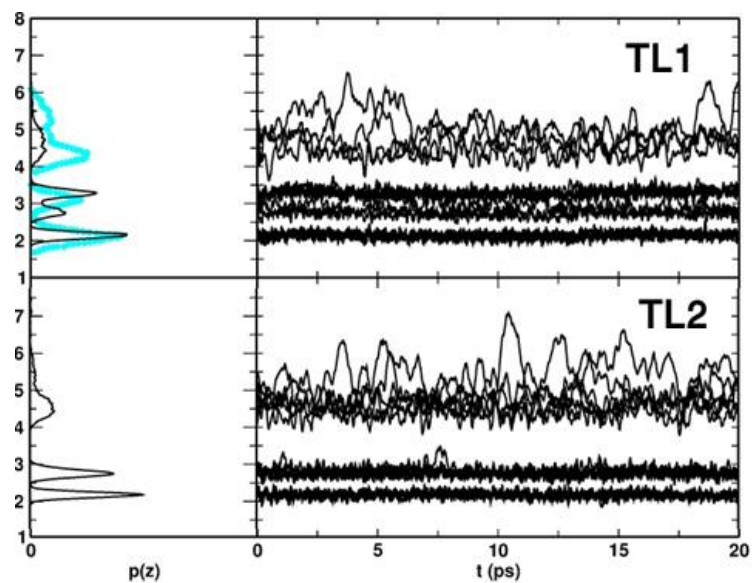
Figure S9. MATSCI TL1 and TL2 Distribution $p(z)$ and time evolution $z(t)$ of the perpendicular distances between the water molecule (O atoms) and the titania surface (Ti_{5c} atoms). The DFT Car-Parrinello corresponding distribution $p(z)$ is reported in cyan diamonds.[2]
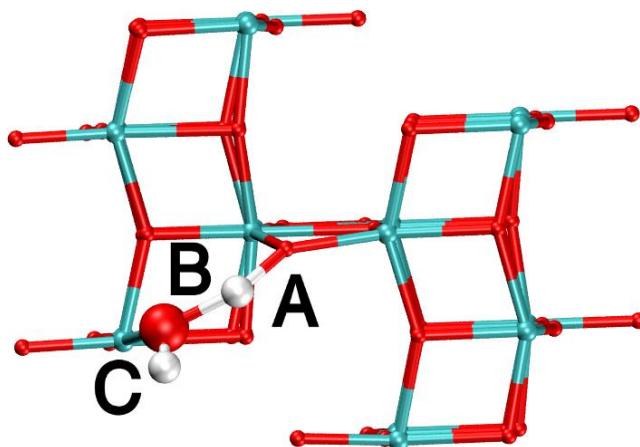
Figure S10. DFTB optimized structure of the transition state for the process of water dissociation (coverage θ = 0.25). Values of bond distances are reported in the **Table S2**.

Table S2. Geometrical parameters, as defined graphically in **Figure S10**, for the transition state structure of water dissociation on the (101) anatase slab model with the DFTB methods and in the DFT reference.[3,4]

	A	B	C
MATSCI	1.34	1.44	2.27
MATORG+HBD	1.15	1.48	2.25
DFT-B3LYP-D*	1.18	1.35	2.06

[1] Kühne, T. D.; Krack, M.; Parrinello M. Static and Dynamical Properties of Liquid Water from First Principles by a Novel Car-Parrinello-like Approach *J. Chem. Theory Comput.* **2009**, *5*, 235–241.

[2] Tilocca, A.; Selloni, A. *J. Phys. Chem. C* **2012**, 116, 9114−9121.

[3] Ferrighi, L.; Datteo, M.; Fazio, G.; Di Valentin, C. *J. Am. Chem. Soc.* **2016**, *138*, 7365 – 7376.

[4] These values have been calculated using the methods and the procedures employed in Ref. 3 to determine the transition structure of a similar reaction barrier.