

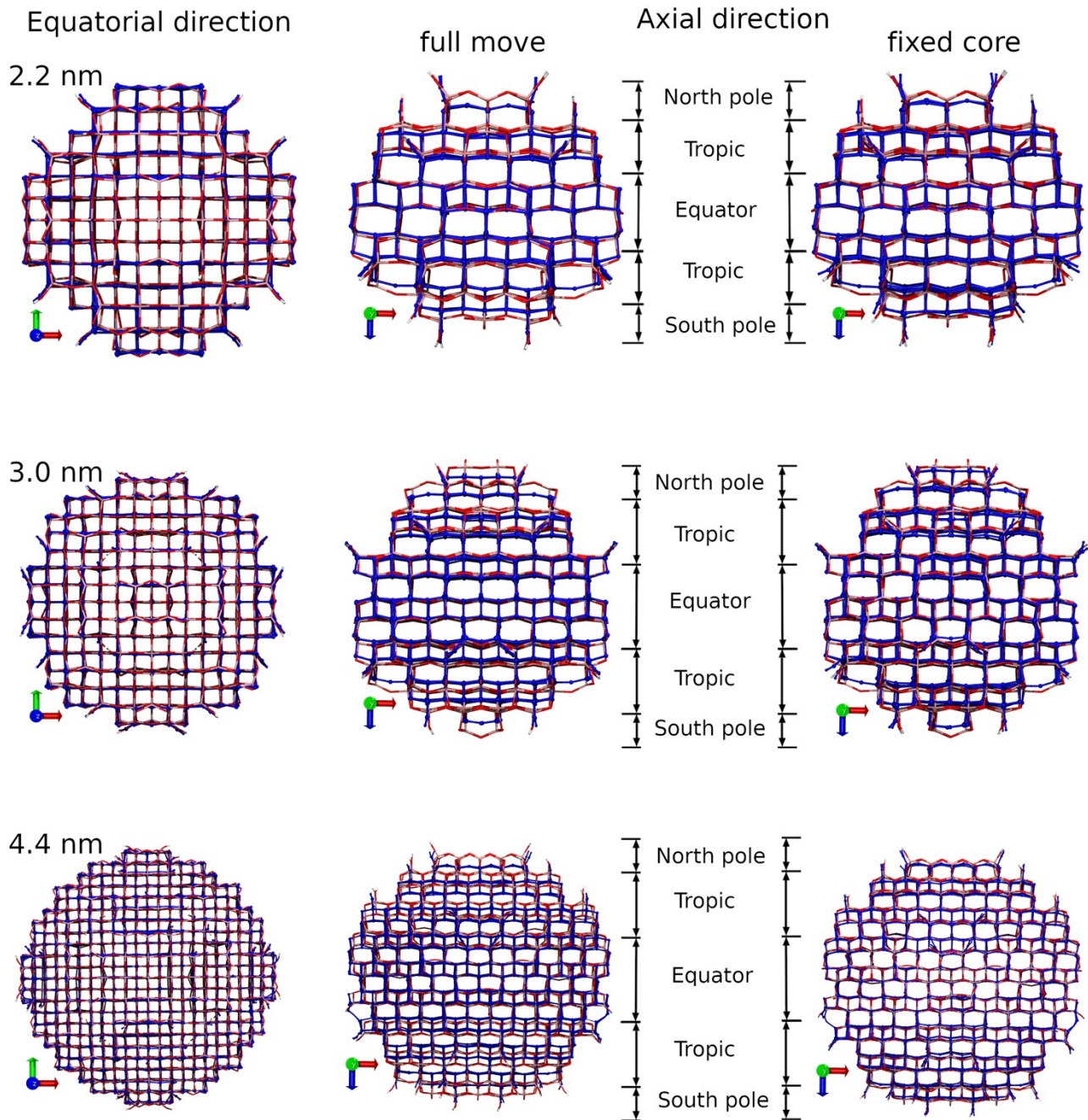
## Electronic Supplementary Information

### **Reactive Molecular Dynamics Simulations of the Hydration Shells Surrounding Spherical TiO<sub>2</sub> Nanoparticles: Implications for Proton-Transfer Reactions**

Federico Soria, Cristiana Di Valentin\*

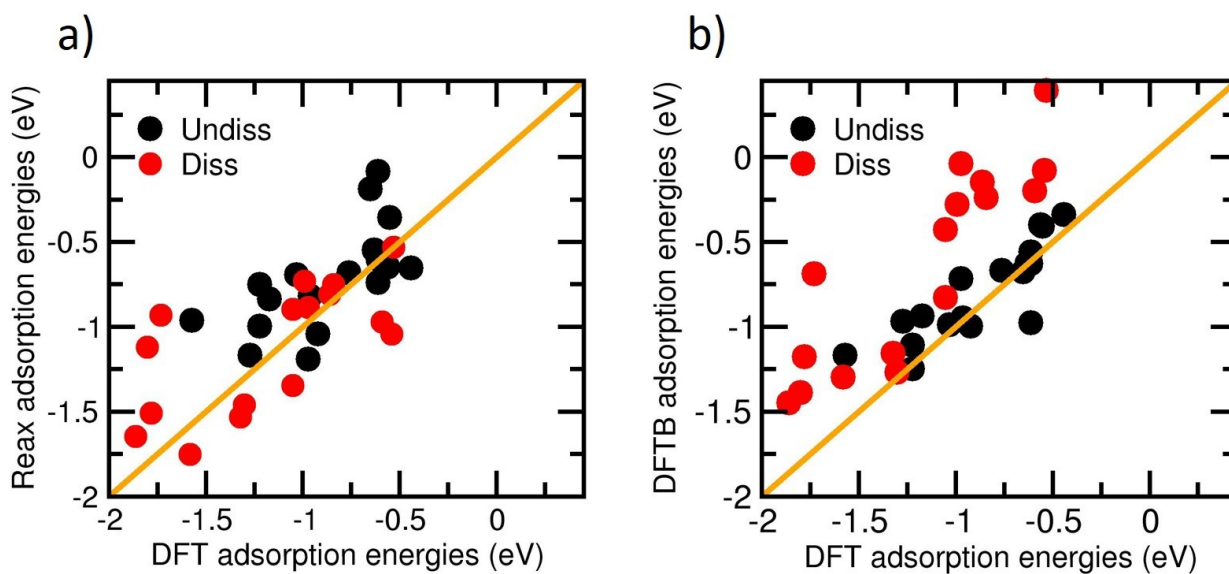
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\* Corresponding author: [cristiana.divalentin@unimib.it](mailto:cristiana.divalentin@unimib.it)

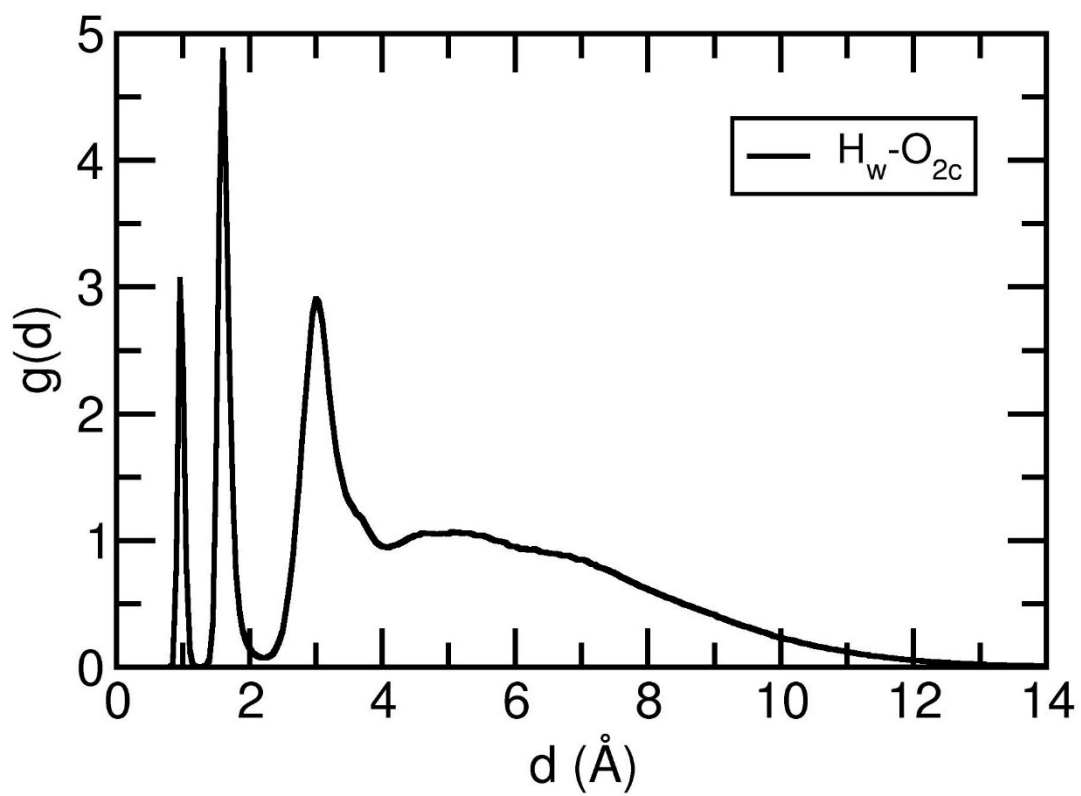


**Figure S1:** DFT and ReaxFF structures of the NSs overlapped. Red and brown stick represent the DFT, while blue stick represents the ReaxFF structures. As can be seen in the equatorial direction the overlapping is very good. In the axial direction, when a simulation leaving all atoms move is done the reduction of the size in the NSs is observed. The reduction of the size starts in the tropic regions and moves to the poles. However, when the core of the NS is kept fixed the description of the NS by

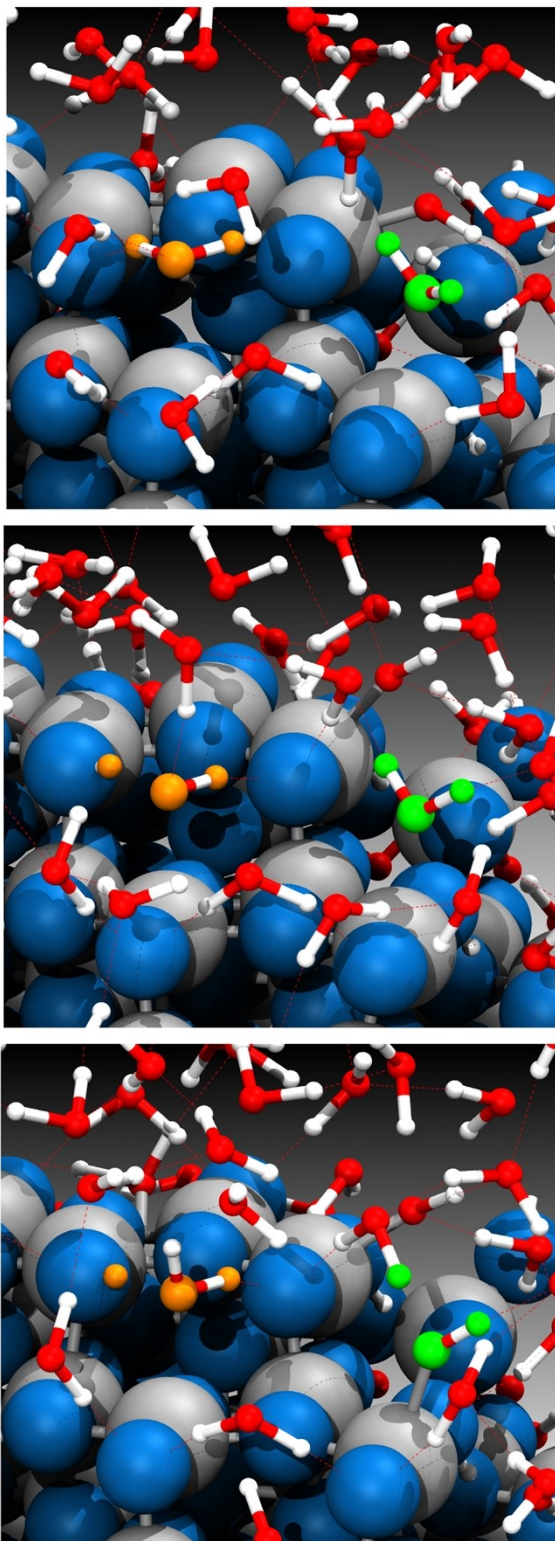
ReaxFF improves considerably. Now the overlapping in the axial direction is very good in the equator and tropics regions and a tiny disagree is seen towards the pole regions.



**Figure S2:** Correlation between the adsorption energy of undissociated and dissociated water molecules on different sites of the NS as obtained with (a) ReaxFF and DFT and (b) DFTB and DFT.

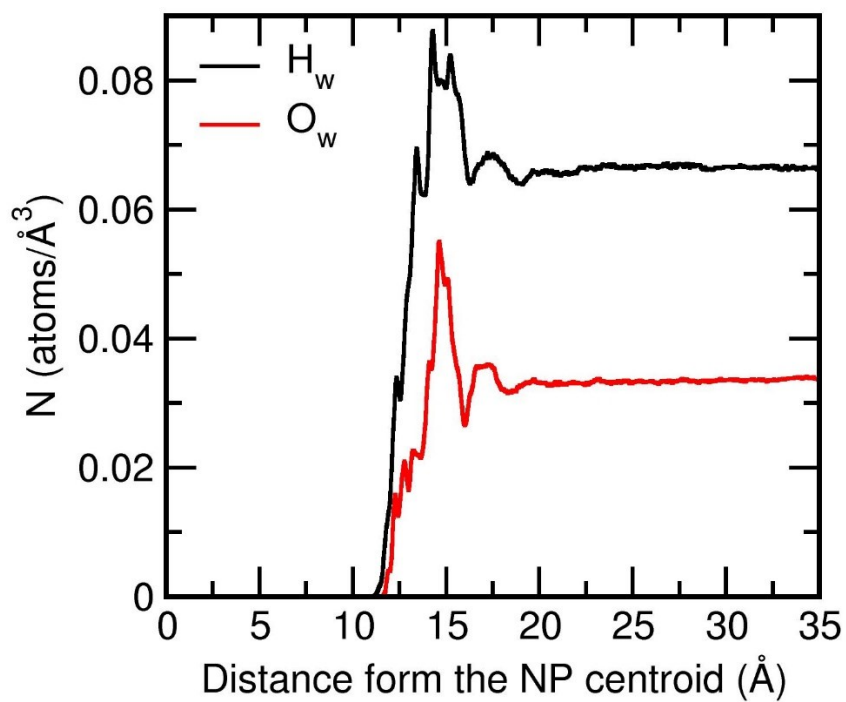


**Figure S3:** Distribution function  $g(d)$  between the H atoms of the water molecules and  $O_{2c}$  on the NS.



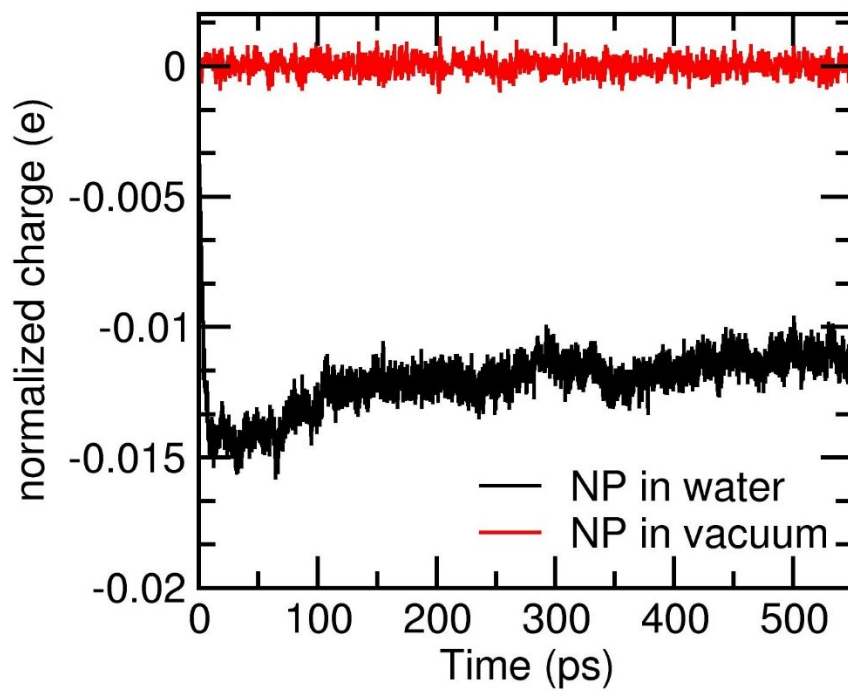
**Figure S4:** reaction mechanism observed for water reaction on the NS at high coverages regimen involving four water molecules at 300 K. First, two water (marked as orange and green) are molecularly adsorbed on undercoordinated Ti atoms. Second, the orange water loses a proton atom who migrate to O<sub>2c</sub> site (forming a bridging OH). Third, after three proton transfer reactions the

orange water accept a proton while the green water loses one giving rise to the formation of a new terminal OH.

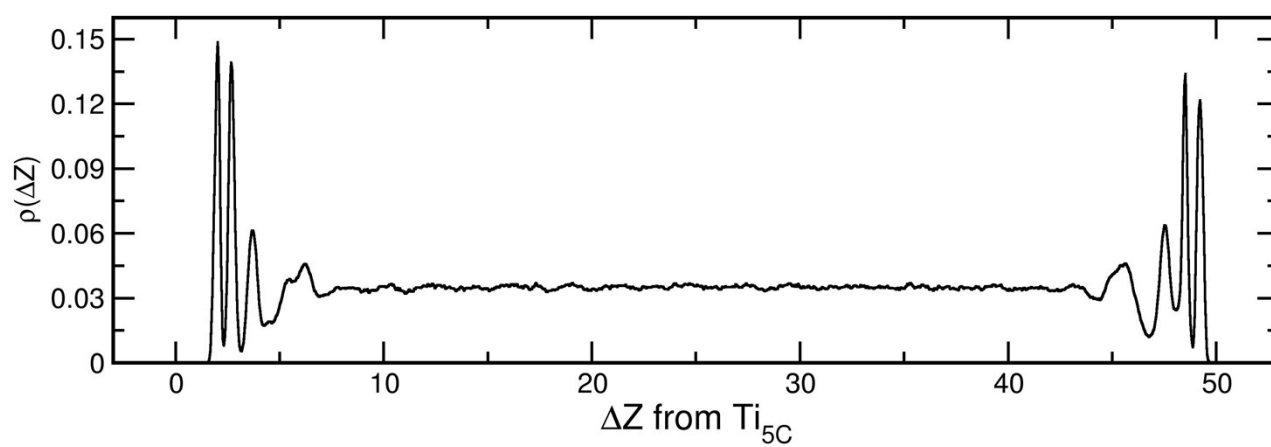


**Figure S5:** Number density distribution of O and H atoms of water molecules around the 2.2 nm NP. The distance is measured from the NP center.



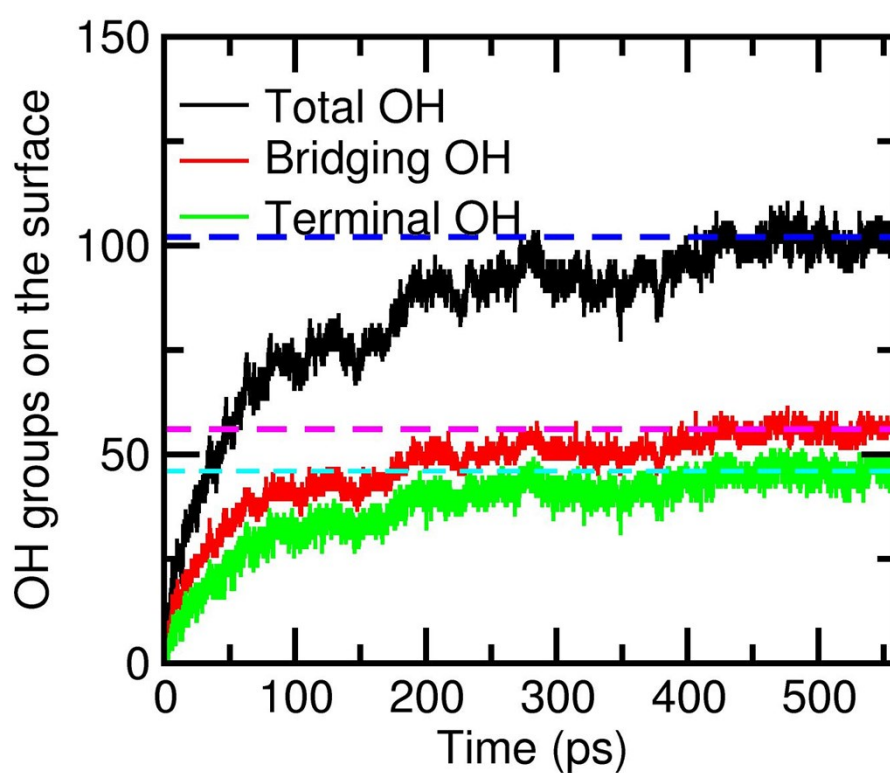


**Figure S6:** Total charge of the 2.2 nm NP normalized by the total number of atoms as a function of the simulation time in water environment and in vacuum.



**Figure S7:** Vertical distribution of the distances between the water molecules (O atoms) and the surface ( $Ti_{5C}$ ) on both side of the anatase (101) slab.





**Figure S8:** Evolution of the OH groups on the anatase (101) surface as a function of time at 300.0 K. It can be seen that after 400 ps the plots become constant. The horizontal dashed lines indicate an average of final number of total, bridging and terminal OH groups on the surface.

**Table S1** – Adsorption energy (in eV) of a single water molecule on anatase (101) calculated by ReaxFF comparing with previous DFT values. Both molecular and dissociated adsorption modes are considered.

coverage	Method	E <sub>ads</sub>		ΔE <sub>ads</sub>	Reference
		molecular	dissociated		
0.25	Reax	-1.01	-0.84	0.23	
0.25	PW-PBE	-0.74	-0.30	0.44	Ref. 1
0.25	LCAO-PBE	-0.71	-0.38	0.33	Ref. 2
0.25	LCAO-HSE	-0.84	-0.54	0.30	Ref. 2
0.25	LCAO-PBE0	-0.78	-0.47	0.31	Ref. 3
0.25	LCAO-PBE0-D3	-1.03	-0.62	0.41	Ref. 3
0.25	LCAO-HSE6	-0.77	-0.46	0.31	Ref. 3

- 1) Vittadini, A.; Selloni, A.; Rotzinger, F. P.; Grätzel, M., Structure and Energetics of Water Adsorbed at TiO<sub>2</sub> Anatase (101) and (001) Surfaces. *Physical Review Letters* **1998**, *81* (14), 2954-2957.
- 2) Martinez-Casado, R.; Mallia, G.; Harrison, N. M.; Pérez, R., First-Principles Study of the Water Adsorption on Anatase (101) as a Function of the Coverage. *The Journal of Physical Chemistry C* **2018**, *122* (36), 20736-20744.
- 3) Thorben, P.; Thorsten, K., Water Adsorption on Ideal Anatase-TiO<sub>2</sub>(101) – An Embedded Cluster Model for Accurate Adsorption Energetics and Excited State Properties. *Zeitschrift für Physikalische Chemie* **2020**, *234* (5), 813-834.