

# Analysis of Excited States in Photoactive Titania Nanostructures

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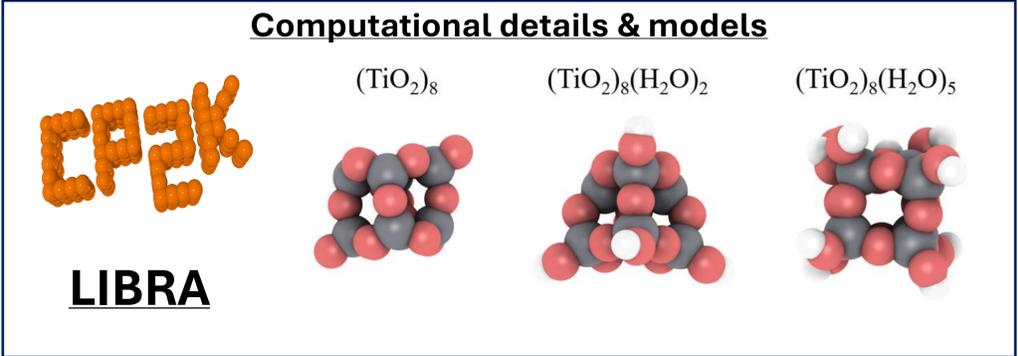
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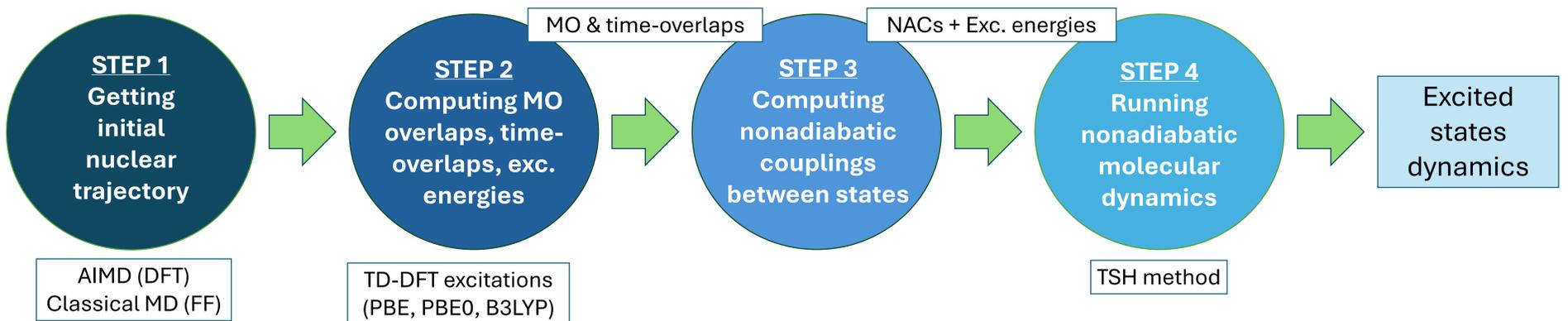
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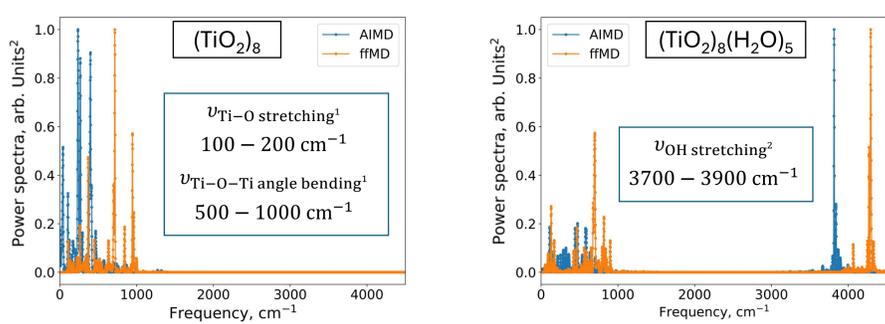
Processes heterogeneously photocatalyzed require computational strategies beyond the ground state analysis through the Density Functional Theory (DFT). A **new roadmap** calls for explicitly exploring the excited states for **modelling** efficient photoactive nanostructures. Here, we analyze the dynamics of excited states in **(TiO<sub>2</sub>)<sub>8</sub> clusters**. While we shed light on the **effect of water coverage** on the dynamics of various excited states, we perform an initial **methodological assessment** of nonadiabatic molecular dynamics (NA-MD) recipes for further use in larger and more realistic titania nanostructures.



## Non-Adiabatic Molecular Dynamics Roadmap



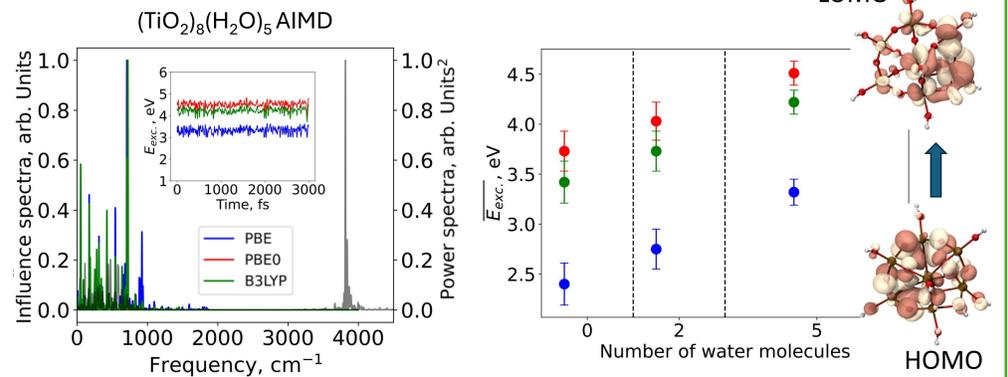
### STEP 1: NUCLEAR TRAJECTORY



AIMD introduces anharmonic effects -> lower frequency values but also busier vibrational densities  
Qualitatively the same -> tested FFs are accurate and computationally-efficient

<sup>1</sup>Ohsaka, T.; Izumi, F.; Fujiki, Y. *J. Raman Spectrosc.* 1978, 7, 321-324  
<sup>2</sup>Mino, L.; Morales-García, Á.; Bromley, S. T.; Illas, F. *Nanoscale* 2021, 13, 6577-6585

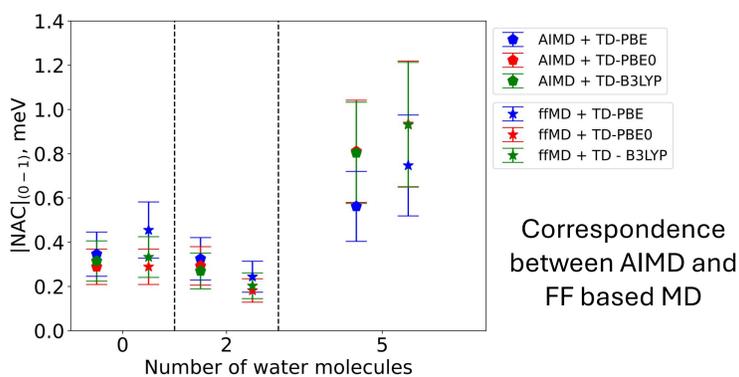
### STEP 2: TD-DFT EXCITATIONS



S<sub>1</sub>→S<sub>0</sub> transition is driven by the Ti-O bending and stretching modes  
OH stretching modes not coupled to the S<sub>1</sub>→S<sub>0</sub> transition

Hydration degree increases the excitation energies  
Hybrid functionals mitigate CT underestimation of PBE  
Larger densities located around the Ti-O bonds

### STEP 3: NACs

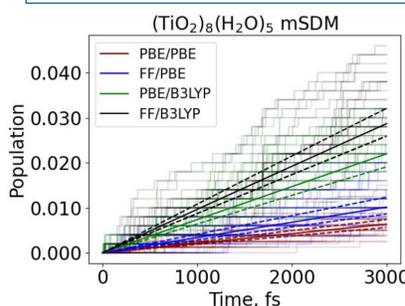
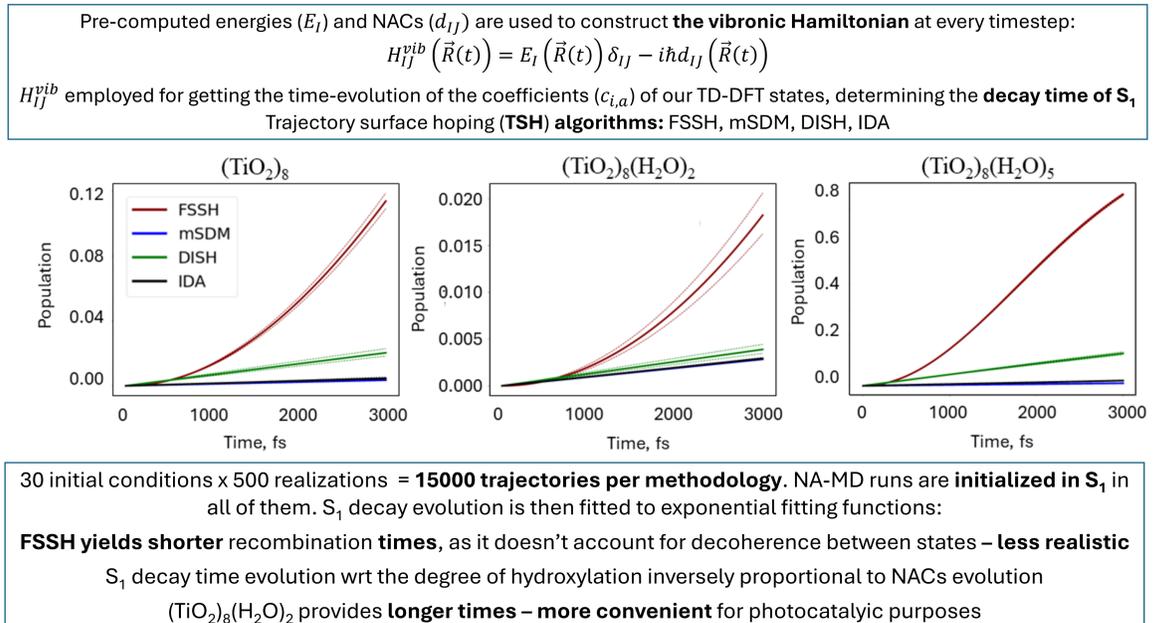


Correspondence between AIMD and FF based MD

(TiO<sub>2</sub>)<sub>8</sub>(H<sub>2</sub>O)<sub>2</sub> presents lower average NACs than bare case, as states become slightly more separated in energy

As more water molecules are added, the states acquire similar spatial distributions and symmetries: (TiO<sub>2</sub>)<sub>8</sub>(H<sub>2</sub>O)<sub>5</sub> possesses better electronic state mixing and thus larger NACs

### STEP 4: NA-MD



$\tau_{PBE/PBE} = 4.6 \pm 0.1$  ps  
 $\tau_{FF/PBE} = 2.5 \pm 0.0$  ps  
 $\tau_{PBE/B3LYP} = 135.0 \pm 20.7$  ps  
 $\tau_{FF/B3LYP} = 103.1 \pm 11.1$  ps

FF + TD-B3LYP + mSDM  
 $\tau_{(TiO_2)_8} = 1024.9$  ps  
 $\tau_{(TiO_2)_8(H_2O)_2} = 1033.5$  ps  
 $\tau_{(TiO_2)_8(H_2O)_5} = 103.1$  ps

mSDM method involves a complex description leading to the elimination of coherences and thus to larger decay  
Hybrid (B3LYP, PBE0) TD-DFT functionals give rise to faster S<sub>1</sub>-S<sub>0</sub> recombination (green, black)  
Good agreement in final results between ffMD and AIMD!!

## Acknowledgements

